

## O 5: Organic Molecules at Surfaces 1: Substrate Effects

Time: Monday 10:30–13:00

Location: S051

**Topical Talk**

O 5.1 Mon 10:30 S051

**Molecular nanostructures on metals vs. graphene** — ●MEIKE STÖHR — Zernike Institute for Advanced Materials, University of Groningen, Netherlands

To preserve the (functional) properties of either individual adsorbates or well-ordered molecular assemblies upon adsorption on solid surfaces, the molecule substrate interactions have to be generally relatively weak. This can be achieved by introducing a decoupling layer between (metallic) surface and molecules. Among others, graphene has been shown to be a good choice towards this end due to its low density of states around the Fermi level [1]. For two different organic molecules, the similarities and changes will be discussed when adsorbed on metals and graphene, respectively [2]. In the second part, the formation of chevron-like graphene nanoribbons (GNRs) using Ullmann-type coupling will be presented in dependence of the substrate used. [3] While for Cu(111) and Ag(110) 1D metal-coordinated polymers were obtained GNR formation was successful on Au(111). The electronic properties of the GNRs were observed to display both a length and symmetry dependence. References: [1] S. Maier et al., Beilstein J. Nanotechnol. 12 (2021) 950. [2] J. Li et al., J. Phys. Chem. C 123 (2019) 12730; J. de la Rie et al., J. Phys. Chem. C accepted. [3] T.A. Pham et al., Small 13 (2017) 1603675; R.S.K. Houtsmä et al., submitted.

O 5.2 Mon 11:00 S051

**Emergence of a singly-occupied state of *p*-terphenyl-based thiols bound to sulphur defects on MoS<sub>2</sub>/Au(111)** — ●J. RIKA SIMON<sup>1</sup>, DMITRII MAKSIMOV<sup>2</sup>, JUAN PABLO GUERRERO FELIPE<sup>1</sup>, PAUL WIECHERS<sup>1</sup>, CHRISTIAN LOTZE<sup>1</sup>, ANA M. VALENCIA<sup>3,4</sup>, CATERINA COCCHI<sup>3,4</sup>, BJÖRN KOBIN<sup>4</sup>, STEFAN HECHT<sup>4</sup>, MARIANA ROSSI<sup>2</sup>, and KATHARINA J. FRANKE<sup>1</sup> — <sup>1</sup>Freie Universität Berlin, Germany — <sup>2</sup>MPI for the Structure and Dynamics of Matter, Hamburg, Germany — <sup>3</sup>Carl von Ossietzky Universität Oldenburg, Germany — <sup>4</sup>Humboldt-Universität zu Berlin, Germany

The combination of transition-metal dichalcogenides (TMDCs) and organic molecules into hybrid inorganic-organic systems is a field gathering much interest in recent years. The use of submonolayers of the TMDC MoS<sub>2</sub> as a decoupling layer in an STM junction is already well established and allows highly resolved *dI/dV* spectra. But 2D materials also have drawbacks: Their properties are highly dependent on their local structure, because defects influence their properties severely. Here we utilise these defects by anchoring the thiol-based molecule CF<sub>3</sub>-3P-SH (trifluoromethyl-*p*-terphenyl-thiol) into purposely created top-layer sulphur point defects in MoS<sub>2</sub> on Au(111). One end-group of the anchored molecule is bound to the defect, allowing it to rotate around the anchoring point. On such molecules we observe a Kondo resonance. *Ab initio* molecular dynamics simulations show the emergence of a singly-occupied molecular state near  $E_F$  depending on the configuration of the molecule with respect to the surface, which in turn gives rise to the observed Kondo resonance.

O 5.3 Mon 11:15 S051

**Electron spin resonance of iron-phthalocyanine molecules on a surface** — ●CHRISTOPH WOLF<sup>1,2</sup>, XUE ZHANG<sup>2,3</sup>, YU WANG<sup>1,2</sup>, PHILIP WILKE<sup>4</sup>, ANDREAS J. HEINRICH<sup>1,5</sup>, and TAEYOUNG CHOI<sup>5</sup> — <sup>1</sup>Center for Quantum Nanoscience, Institute for Basic Science (IBS), Seoul, Republic of Korea — <sup>2</sup>Ewha Womans University, Seoul, Republic of Korea — <sup>3</sup>Institute of Spin Science and Technology, South China University of Technology Guangzhou, China — <sup>4</sup>Physikalisches Institut, Karlsruhe Institute of Technology, Karlsruhe, Germany — <sup>5</sup>Department of Physics, Ewha Womans University, Seoul, Republic of Korea.

The combination of the high energy resolution of electron spin resonance (ESR) and high spatial resolution of the scanning tunneling microscope (STM) resulted in a novel probe with unparalleled capabilities for the study of surface physics.

In this work, we present the first application of this tool to molecules by ESR-STM spectroscopy of iron-phthalocyanine (FePc) molecules on thin layers of the insulator magnesium-oxide deposited on silver. Here, I will focus on the insight gained by combining density functional theory (DFT) and ESR-STM experiment. I will highlight successes and shortcomings of DFT by discussing electronic states of single FePc

molecules as well as the interaction between FePc dimers at the neV energy scale.

Finally, I will give an outlook on quantum coherent properties of FePc based on pulsed ESR measurements and a non-equilibrium Green's function model.

O 5.4 Mon 11:30 S051

**Mapping of resonant excitation channels of C<sub>60</sub>/Cu(111) sample system through multiphoton polychromatic momentum microscopy** — ●MARTIN MITKOV<sup>1</sup>, RALF HEMM<sup>1</sup>, TOBIAS FEUERBACH<sup>1</sup>, AARON GEBERT<sup>1</sup>, FLORIAN HAAG<sup>1</sup>, KA MAN YU<sup>1</sup>, MARTIN AESCHLIMANN<sup>1</sup>, and BENJAMIN STADTMÜLLER<sup>1,2</sup> — <sup>1</sup>TU Kaiserslautern and Research Center OPTIMAS, Erwin-Schrödinger Str. 46, 67663 Kaiserslautern, Germany — <sup>2</sup>Institut für Physik, Johannes-Gutenberg-Universität Mainz, Mainz 55128, Germany

Mapping the excited states of organic molecular thin films is of crucial importance for understanding the optical and transport properties of organic materials. Here, we present a multiphoton photoemission study of the excited states of the C<sub>60</sub>/Cu(111) interface for photon energies between 1.80 eV and 3.35 eV. Characteristic changes in the photoemission spectra for different photon energies allow us to determine the energetic positions of the excited states. In addition, we focus on the momentum-dependent photoemission pattern of the excited molecular states. The latter reveals distinct periodicities and symmetries based on the molecular orbitals involved in the optical excitation process. Altogether, this information will allow us to disentangle resonant intramolecular excitations from the Cu surface state. This allows us to uncover the photon energy-dependent excitation pathways of charge carriers at the C<sub>60</sub>/Cu(111) interface.

O 5.5 Mon 11:45 S051

**Disentangling the Complex Electronic Structure of an Adsorbed Nanographene: Cycloarene C108** — ●JOSE MARTINEZ-CASTRO<sup>1</sup>, RUSTEM BOLAT<sup>1</sup>, QITANG FAN<sup>2</sup>, SIMON WERNER<sup>2</sup>, HADI AREFI<sup>1</sup>, TANER ESAT<sup>1</sup>, JÖRG SUNDERMEYER<sup>2</sup>, CHRISTIAN WAGNER<sup>1</sup>, J. MICHAEL GOTTFRIED<sup>2</sup>, RUSLAN TEMIROV<sup>1,3</sup>, MARKUS TERNES<sup>1,4</sup>, and F. STEFAN TAUTZ<sup>1</sup> — <sup>1</sup>Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — <sup>2</sup>Department of Chemistry, Philipps-Universität Marburg, 35032 Marburg, Germany — <sup>3</sup>II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany — <sup>4</sup>II. Institute of Physics, RWTH Aachen University, D-52074 Aachen, Germany.

We combine low-temperature scanning tunneling spectroscopy, CO functionalized tips and algorithmic data analysis to investigate the electronic structure of the molecular cycloarene C108 (graphene nanoring) adsorbed on a Au(111) surface. We demonstrate that CO functionalized tips enhance the visibility of molecular resonances, both in differential conductance spectra and in real-space topographic images. Comparing our experimental data with *ab-initio* density functional theory reveals a remarkably precise agreement of the molecular orbitals and enables us to disentangle close-lying molecular states only separated by 50 meV at an energy of 2 eV below the Fermi level. We propose this combination of techniques as a promising new route for a precise characterization of complex molecules and other physical entities which have electronic resonances in the tip-sample junction.

O 5.6 Mon 12:00 S051

**Tuning of structure of cyano-porphyrin self-assemblies on surfaces: from metals to bulk insulators** — MAXIMILIAN AMMON<sup>1</sup>, MIRUNALINI DEVARAJULU<sup>1</sup>, YI LIU<sup>1</sup>, MARTIN GURRATH<sup>2</sup>, DOMINIK LUNGERICH<sup>3</sup>, ●BINBIN DA<sup>1</sup>, NORBERT JUX<sup>3</sup>, BERND MEYER<sup>2</sup>, and SABINE MAIER<sup>1</sup> — <sup>1</sup>Department of Physics, FAU Erlangen-Nürnberg, Erlangen, Germany. — <sup>2</sup>Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg, Erlangen, Germany. — <sup>3</sup>Lehrstuhl für Organische Chemie II, FAU Erlangen-Nürnberg, Erlangen, Germany.

We discuss the adsorption and binding motifs in self-assembled Zn-pCNTPP networks on Au(111), KBr(001), and MgO(001) using low-temperature STM and nc-AFM combined with DFT. Zn-CNTPPs adopt a planar adsorption geometry with the macrocycle parallel to the surface on all three surfaces and assemble in well-ordered islands. While a global minimum structure is found on KBr due to a strong

CN $\cdots$ K interaction, multiple and energetically nearly equivalent adsorption sites occur on MgO and Au. Therefore, commensurate adsorption is suggested on KBr, while optimizing the molecule-molecule interactions over molecule-surface interactions is more important on MgO and Au, which the STM and nc-AFM data experimentally evidence.[1] However, since the interaction of porphyrins with Au(111) is stronger than on MgO(001), the phenyl rings are more inclined toward the surface, resulting in larger unit cells on Au(111) and also the binding motif of the cyanophenyl groups changes.

[1] Ammon, M. et al., *Surface Science*, 723, 122097, 2022.

O 5.7 Mon 12:15 S051

**Comparing adsorption of triphenylene derivatives: metallic vs. graphitic surfaces** — ●JORIS DE LA RIE<sup>1</sup>, MIHAELA ENACHE<sup>1</sup>, QIANKUN WANG<sup>1</sup>, WENBO LU<sup>1</sup>, NICO SCHMIDT<sup>1</sup>, MILAN KIVALA<sup>2</sup>, and MEIKE STÖHR<sup>1</sup> — <sup>1</sup>Zernike Institute for Advanced Materials, University of Groningen — <sup>2</sup>Institute of Organic Chemistry, University of Heidelberg

Thin films of organic molecules show great promise for applications in future (nano)electronic devices, such as solar cells, light emitting diodes and transistors. A major factor in the performance of these films is the interface between substrate and molecular film. The interfacial properties depend on the balance between intermolecular and molecule-substrate interactions. Herein, we present a comparative study on self-assembled monolayers (SAMs) of a triphenylene-based donor molecule (HAT) on three substrates: Ag(111), graphene/Ir(111) and graphene/Ni(111). We studied the structure of the SAMs by means of scanning tunneling microscopy and low-energy electron diffraction, and their interaction with the substrates by X-ray and ultraviolet photoelectron spectroscopy. On each substrate, HAT formed a close-packed hexagonal network that is commensurate with the substrate. From the photoelectron spectroscopy measurements we only found a weak (physisorptive) interaction between molecules and substrates. This goes against the established belief for SAMs on metal surfaces, where commensurate networks are principally formed on strongly interacting surfaces where the molecules chemisorb.

O 5.8 Mon 12:30 S051

**The Number of KCl layers counts:**

**Thickness dependent Growth of Quinacridone on KCl on the Ag(100) surface** — ●NIKLAS HUMBERG<sup>1</sup>, RÉMI BRETTEL<sup>2</sup>, and MORITZ SOKOLOWSKI<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie der Universität Bonn, Germany — <sup>2</sup>University of Paris-Saclay, Institut des Sciences Moléculaires D'Orsay, France

The epitaxial growth of the prochiral molecule quinacridone (QA) on a

insulating KCl layer on the Ag(100) surface was investigated by STM. If QA is deposited onto a complete KCl layer, then the growth of QA structures is strongly dependent on the thickness of the KCl layer. For small amounts of QA on thin KCl layers small domains of parallel molecular chains were observed. The structure of these chains is identical to the chains that were previously observed on the Ag(100) surface. However, the repulsive substrate mediated interaction between neighboring chains that was observed on the Ag(100) surface cannot be observed on such KCl layers. Interestingly, depositing larger amounts of QA on such KCl layers leads to the formation of three-dimensional chain-like structures that show some similarities with the bulk crystal structures of QA.

Contrary to this, on thick KCl layers on the Ag(100) surface that are five or more monolayers high dewetting of the molecules and a formation of three-dimensional QA clusters was already observed for very small amounts of QA. These effects are explained by the interaction between the QA molecules and the silver substrate which still plays a role for thin layers but is suppressed by thick KCl layers.

O 5.9 Mon 12:45 S051

**Growth of chiral heptahelicene molecules on ferromagnetic Co and Fe thin-film substrates** — ●MOHAMMAD REZA SAFARI, FRANK MATTHES, DANIEL E. BÜRGLER, and CLAUS M. SCHNEIDER — Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich, 52425 Jülich, Germany

The discovery of chirality-induced spin selectivity effects [1,2], which result from an interaction between the electron spin and the handedness of chiral molecules, has sparked interest in surface-adsorbed chiral molecules due to potential applications in spintronics, enantioseparation, and chemical sensing. Here, we report growth studies of chiral heptahelicene molecules on two monolayers Fe on W(110), Co bilayer nano-islands on Cu(111), and for comparison on Cu(111) by low-temperature spin-polarized scanning tunneling microscopy. In all cases, the molecules remain intact, adsorb in a flat configuration, and exhibit specific in-plane orientations that reflect the symmetry of the substrate lattices. The Co and Fe layers remain out-of-plane magnetized after molecular adsorption. In addition, we are able to determine the helicity of individual molecules adsorbed on the highly reactive Fe and Co surfaces in a similar manner as previously reported for the less reactive Cu(111) surface [3]. These observations pave the way for further investigations of CISS effects in well-defined molecule-substrate systems on the single-molecule scale as a basis for theoretical modeling.

[1] B. Göhler *et al.*, *Science* **331**, 894 (2011). [2] K. Banerjee-Ghosh *et al.*, *Science* **360**, 1331 (2018). [3] K.-H. Ernst *et al.*, *Nano Lett.* **15**, 5388 (2015).