

## O 15: Organic Molecules on Inorganic Substrates II: Mainly Porphyrins

Time: Monday 15:00–18:00

Location: REC C 213

## Invited Talk

O 15.1 Mon 15:00 REC C 213

**Molecular nanostructures on metals vs. graphene: towards preserving functional properties** — ●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, thin insulating layers of either NaCl or hBN have been shown to be very useful to this end. The chemical inertness and the low density of states near the Fermi level also make graphene a good choice as a buffer layer to decouple adsorbed molecules from the underlying (metallic) substrate. For two different organic molecules, the changes in both structural and electronic properties will be discussed [1]. On the other hand, instead of turning off the molecule substrate interactions, enhancing the intermolecular interactions is another possibility for preserving the adsorbates' properties. This could be shown on the basis of charge-transfer interactions [2] as well as utilizing molecular coverage [3].

[1] J. Li et al., *J. Phys. Chem. C* 120 (2016) 18093; N. Schmidt et al., *Chem. Eur. J.* 25 (2019) 5065; J. Li et al., *J. Phys. Chem. C* 123 (2019) 12730. [2] K. Müller et al., *Small* 15 (2019) 190174. [3] B.D. Baker et al., *J. Phys. Chem. C* 123 (2019) 19681.

O 15.2 Mon 15:30 REC C 213

**On-surface synthesis of porphyrin tetramers** — ●EDUARDO CORRAL-RASCON, ALEXANDER RISS, YANG BAO, and WILLI AUWÄRTER — Physics Department E20, Technical University Munich, Germany

Covalently coupled porphyrins [1,2,3] hold great promise for molecular electronics, optoelectronics, gas sensing and light-harvesting. Furthermore, the electronic conjugation [4] might lead to antiaromatic behavior [3] and additionally offers ways to fabricate spin-coupled nanoarchitectures via introduction of metal centers into the porphyrin cores. Here we present the synthesis of porphyrin tetramers possessing a cyclooctatetraene (COT) moiety at the center of the molecules adsorbed on a Ag(100) surface. Bond-resolved atomic force microscopy (AFM) and scanning tunneling microscopy (STM) were used to characterize the coupling and the emerging electronic properties. In particular, we have investigated how the chemical structure affects the electronic conjugation throughout the molecule.

[1] Wiengarten, A. et al. *J. Am. Chem. Soc.* **2014**, 136, 26, 9346  
 [2] Bischoff, A. et al. *Angew. Chem.* **2018**, 130, 16262  
 [3] Nakamura, Y. et al. *J. Am. Chem. Soc.* **2006**, 128, 4119  
 [4] Fatayer, S. et al. *Science*. **2019**, 6449, 365, 142

O 15.3 Mon 15:45 REC C 213

**Electronic Fingerprint of a Tetraphenylporphyrin on MgO** — ●SILVIYA NINOVA<sup>1</sup> and MICHEL BOCKSTEDTE<sup>1,2,3</sup> — <sup>1</sup>Paris-Lodron-Universität Salzburg, Austria — <sup>2</sup>Friedrich-Alexander-Universität Erlangen-Nürnberg — <sup>3</sup>Johannes-Kepler Universität Linz, Austria

Porphyrin-substrate hybrid systems are the building blocks in a series of materials, such as the organic light-emitting diodes, chemical sensors, dye-sensitized solar cells and solar-energy conversions. Understanding and correctly describing the way molecules interact with the substrate upon adsorption hold the key to the prediction and improvement of the present-day devices.

Recently, distinct features were observed in the photoemission spectra of Co(II)-tetraphenylporphyrin on MgO/Ag(100) related to the molecular monolayer and film[1]. Here we investigate the structural and electronic changes the molecule undergoes upon deposition on the substrate in the framework of hybrid density-functional theory and beyond it. Our simulations of adsorption at different terrace and low-coordinated surface sites give an insight into the underlying distinct interactions and electronic features.

[1] Franke et al., *Physical Chemistry Chemical Physics*, 2017, 19, 11549-11553

O 15.4 Mon 16:00 REC C 213

**Oxidation-State Tuning and Supramolecular Mixed-Valence Phases: Nickel(II) Porphyrin on Ag(111)** — ●JAN HERRITSCH, QITANG FAN, MARIE ALBUS, and J. MICHAEL GOTTFRIED — Fach-

bereich Chemie, Philipps-Universität Marburg, Germany

Porphyrin complexes are of exceptional importance in the field of surface functionalization. The reactivity and selectivity towards gas molecules depends crucially on the active central atom. Here, we report on the influence of the adsorbate interaction on the electronic structure of a nickel porphyrin (NiOEP) monolayer on coinage metal surfaces studied by XPS and STM. Due to the size mismatch between the small low-spin d8 nickel(II) cation and the larger central cavity of the porphyrin macrocycle, the metal center shows a labile oxidation state which depends on the interaction with the metal surface. On the reactive Cu(111) surface, NiOEP forms a long-range ordered structure in which nickel centers are uniformly reduced, according to XPS. On less reactive Ag(111), NiOEP forms a mixed-valent adsorbate phase in which the Ni centers occur in two different oxidation states. The two separate peaks in the Ni 2p XP spectrum indicate that about 40 % of the Ni centers are reduced. STM shows a superstructure with an ordered arrangement of the metal centers in different oxidation states. Analysis of misaligned metastable domains reveals that the registry with the substrate is critical for obtaining the mixed-valence superstructure. On the most inert Au(111) surface, the oxidation state of the Ni centers remains unaffected by adsorbate interactions.

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**Exciton control in single-molecule fluorochromes** — ●JIRÍ DOLEŽAL<sup>1,2</sup>, PABLO MERINO<sup>3,4</sup>, PINGO MUTOMBO<sup>1</sup>, PAVEL JELÍNEK<sup>1</sup> und MARTIN ŠVEC<sup>1</sup> — <sup>1</sup>Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic — <sup>2</sup>Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic — <sup>3</sup>Instituto de Ciencia de Materiales de Madrid, CSIC, Sor Juana Inés de la Cruz 3, E28049, Madrid, Spain — <sup>4</sup>Instituto de Física Fundamental, CSIC, Serrano 121, E28006, Madrid, Spain

Plasmonic picocavities in highly defined environment of ultrahigh vacuum and cryogenic temperatures represent ideal testbeds for investigation of the photophysical properties of single-molecule photon emitters and to explore fundamental aspects of their luminescence. In this work, we studied two structural analogs with distinct electronic properties using a photon-scanning probe microscope: CuPc and ZnPc molecules adsorbed on NaCl / Ag(111) substrates. For the CuPc, we determine how its exact adsorption configuration and coupling to the substrate affect the S1 exciton energy and lifetime. For the ZnPc molecule, two competing excitons [1] are mapped in the real-space with submolecular resolution. Both phenomena are discussed in a broader context of ab-initio simulations and additional experimental evidence available from the atomic force and electron tunneling channels of the microscope.

[1] Doppagne B, Chong MC, Bulou H, Boeglin A, Scheurer F, Schull G. Electrofluorochromism at the single-molecule level. *Science* 2018;361:251-5.

O 15.6 Mon 16:30 REC C 213

**Thermal stability and conformational changes of a catalytically active metal/organic interface** — ●H. STURMEIT<sup>1</sup>, I. COJOCARIU<sup>2,6</sup>, A. COSSARO<sup>3</sup>, A. VERDINI<sup>3</sup>, L. FLOREANO<sup>3</sup>, C. AFRICH<sup>3</sup>, A. SALA<sup>3,4</sup>, G. COMELLI<sup>3,4</sup>, S. MORO<sup>4</sup>, M. STREDANSKY<sup>3,4</sup>, M. CORVA<sup>3,4</sup>, E. VESSELLI<sup>3,4</sup>, M. JUGOVAC<sup>2</sup>, P. PUSCHNIG<sup>5</sup>, C. M. SCHNEIDER<sup>2,6</sup>, V. FEYER<sup>2,6</sup>, G. ZAMBORLINI<sup>1</sup>, and M. CINCHETTI<sup>1</sup> — <sup>1</sup>TU Dortmund, Germany — <sup>2</sup>Forschungszentrum Jülich, Germany — <sup>3</sup>CNR-IOM, Lab. TASC, Italy — <sup>4</sup>Physics Department, University of Trieste, Italy — <sup>5</sup>Institut für Physik, Karl-Franzens-Universität Graz, Austria — <sup>6</sup>Fakultät für Physik and CENIDE, Universität Duisburg-Essen, Germany

Porphyrin molecules are widely employed as building blocks in photovoltaics, heterogeneous catalysis, gas sensing and the emerging field of on-surface magnetochemistry. When deposited on metal electrodes, they can undergo surface-induced chemical changes, such as partial dehydrogenation, dehydrocyclization or intramolecular structural modifications of their macrocycle. These changes alter their electronic structure and thus their reaction properties essentially. We demonstrate the high thermal stability of catalytically active Ni(I)TPP up to 350°C on a Cu electrode. Photoelectron tomography supported by photoemission and vibronic spectroscopy, and STM measurements prove that, below the fragmentation temperature, the adsorbed porphyrins do not experience any chemical modification, but undergo a conformational

modification, while preserving the stability of the reactive Ni(I) ion. This is crucial for the re-activation of saturated catalytical sites.

O 15.7 Mon 16:45 REC C 213

**CoTPP molecules deposited on passivated Fe-(100)-p(1x1)O: a molecular orbital tomography study** — ●DAVID JANAS<sup>1</sup>, HENNING STURMEIT<sup>1</sup>, IULIA COJOCARIU<sup>2</sup>, VITALIY FEYER<sup>2</sup>, STEFANO PONZONI<sup>1</sup>, GIOVANNI ZAMBORLINI<sup>1</sup>, and MIRKO CINCHETTI<sup>1</sup> — <sup>1</sup>Experimentelle Physik VI, TU Dortmund, 44227 Dortmund, Germany — <sup>2</sup>Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich, 52425 Jülich, Germany

In order to enhance the performances of molecular spintronic devices, a detailed knowledge of the physical properties at the interface is fundamental [1]. In this context molecular orbital tomography (MOT), which combines ab-initio calculations and angle-resolved photoelectron spectroscopy (ARPES), stands out as a powerful and reliable tool to unravel the orbital structure of molecular thin films at metal/organic interfaces [2]. In our work we apply MOT to investigate the interaction of paramagnetic molecules, namely CoTPP, on the passivated Fe-(100)-p(1x1)O surface. Recently, it was shown that the interactions at this interface lead to an emergent magnetic ordering of the molecular layer. Here, we use MOT to further characterize this intriguing system. In particular, we precisely determine the energy level alignment at the interface, the nature of the frontier orbitals, and the azimuthal orientation of the CoTPP molecules with respect to the substrate.

[1] Cinchetti, M., Dediu, V. & Hueso, L. Activating the molecular spinterface. *Nature Mater* 16, 507-515 (2017) doi:10.1038/nmat4902

[2] Puschig, P. et al. Reconstruction of molecular orbital densities from photoemission data. *Science* 326, 702-706 (2009)

O 15.8 Mon 17:00 REC C 213

**Electronic and magnetic properties of phthalocyanine molecules on rare-earth noble-metal surfaces** — ●LAURA FERNANDEZ<sup>1</sup>, RODRIGO CASTRILLO<sup>2</sup>, KHADIZA ALI<sup>2</sup>, MAXIM ILYN<sup>2</sup>, MICHELE GASTALDO<sup>3</sup>, MIGUEL ANGEL VALBUENA<sup>4</sup>, MARCOS PARADINAS<sup>3</sup>, AITOR MUGARZA<sup>3</sup>, and FREDERIK SCHILLER<sup>2,5</sup> — <sup>1</sup>Universidad del País Vasco, San Sebastian, Spain — <sup>2</sup>Centro de Física de Materiales and Material Physics Center, San Sebastian, Spain — <sup>3</sup>Catalan Institute of Nanoscience and Nanotechnology, Bellaterra, Spain — <sup>4</sup>IMDEA Nanociencia, Cantoblanco, Spain — <sup>5</sup>Donostia International Physics Center, San Sebastian, Spain

Here we explore new spin textured interfaces by using as a substrate non-conventional magnetic surface-confined alloys, which contains rare earths (RE) atoms and Au. The broad number of possible RE atoms used for the preparation of such alloys provides an attractive platform to optimize and tune magnetic metal-organic interfaces with many different spin textures. We focus on the growth of CuPc on different 2D surface compounds like GdAu<sub>2</sub>, HoAu<sub>2</sub>, and the paramagnetic YbAu<sub>2</sub>. For the study of the electronic properties we use X-ray and angle resolved photoemission spectroscopy, while the magnetic properties of the systems were investigated by X-ray magnetic circular dichroism. We observe similar electronic interaction of CuPc on these surfaces, with variation depending on the valence of the RE atom. From the magnetic point the different RE atom of the substrate induce different magnetic interactions with the CuPc molecule.

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**Real-space engineering the optoelectronic properties of single molecules** — ●TZU-CHAO HUNG, BRIAN KIRALY, JULIAN STRIK, ALEXANDER KHAJETOORIANS, and DANIEL WEGNER — Institute for Molecules and Materials, Radboud University, 6525 AJ Nijmegen, The Netherlands

While optical properties of light-emitting molecules are mostly studied via luminescence spectroscopy, several recent studies revealed a fundamental lack of understanding luminescence on the single-molecule level. Intermolecular and environmental interactions can have a significant

impact on the optoelectronic properties but are hardly controllable in ensemble measurement. We combine STM/STS and atomic manipulation to study the STM-induced light emission of single molecules and molecular assemblies. Using zinc-phthalocyanine (ZnPc) molecules on ultrathin NaCl films, we demonstrate how the emission yield, energy shift and resolution of luminescence spectra change by anchoring ZnPc to a step edge or by assembling molecules into chains. This not only allows us to understand and disentangle the impact of intermolecular and molecule-substrate coupling on exciton lifetimes, but ultimately permits high-resolution vibronic spectroscopy providing a chemical fingerprint of single molecules. Furthermore, utilizing the tautomerism of H<sub>2</sub>Pc, which can be manipulated by the tunneling current, we study how to fine-tune dipole-dipole coupling, toward sub-molecular design of the spectroscopic response.

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**Vibrational excitation mechanisms in tunneling spectroscopy beyond the Franck-Condon model.** — ●GAËL REECHT, NILS KRANE, CHRISTIAN LOTZE, and KATHARINA J. FRANKE — Freie Universität, Berlin, Germany

Since two decades, scanning tunneling spectroscopy (STS) is used to study vibrations of individual molecules on surface, either via inelastic tunneling spectroscopy (IETS) or vibronic spectroscopy. In the latter cases, experimental results were generally explained within the Franck-Condon picture, which treats vibronic excitations within the Born-Oppenheimer approximation and derives the excitation probabilities from an overlap integral of initial and final state. However this model cannot justify any spatial dependence of vibronic excitations. Here we study with low temperature STM, large organic molecules (thiophene derivative and phthalocyanine) on single layer MoS<sub>2</sub> on Au(111). The van der Waals layer acts as an efficient decoupling layer from the metal substrate and provides exceptional energy resolution of a few meV, which gives access to the rich vibronic signature of the investigated molecules. To explain the complete excitation model, spatially and energetically, we show that the Franck-Condon picture has to be combined with a vibration-assisted process, which perturbs the molecular wave functions, and therefore its overlap with the tip wave function. Using DFT calculations of the molecule in gas phase, our simple model reproduces the experimental spectra at arbitrary position of the STM tip over the molecule in great detail.

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**Direct observation of long-range surface-mediated molecule-molecule hybridization** — MARINA CASTELLI<sup>1</sup>, ●JACK HELLERSTEDT<sup>1</sup>, CORNELIUS KRULL<sup>1</sup>, SPIRO GICEV<sup>2</sup>, LLOYD CL HOLLENBERG<sup>2</sup>, MUHAMMAD USMAN<sup>2</sup>, and AGUSTIN SCHIFFRIN<sup>1</sup> — <sup>1</sup>School of Physics and Astronomy, Monash University, Clayton VIC 3800 Australia — <sup>2</sup>Centre for Quantum Computation and Communication Technology, Faculty of Science, University of Melbourne, VIC 3010, Australia

Metallated phthalocyanines are robust and versatile molecular complexes, whose properties can be tuned by changing its functional groups and central metal atom. Magnesium phthalocyanine (MgPc) is structurally close to the chlorophyll molecule responsible for photosynthesis in bio-organisms. Here we studied the electronic structure of MgPc on Ag(100) via low-temperature scanning probe microscopy (STM/STS/ncAFM) and density functional theory (DFT). Our ncAFM and STS data show that a single isolated MgPc molecule exhibits a flat four-fold symmetric morphology with doubly degenerate, partially populated lowest unoccupied molecular orbitals (LUMOs). Adjacent MgPc's (3 nm or less) show a lift of LUMO degeneracy and symmetry reduction. We explain this interaction by a two-step hybridization process: MgPc orbitals hybridize with Ag(100), forming molecule-surface orbitals with enhanced spatial extension that hybridize in turn with neighboring molecules. Distance-dependent analysis of the resulting symmetry reduction allows us to quantitatively describe the nature of this long-range surface-mediated interaction.