

## O 98: Organic Molecules on Inorganic Substrates VII

Time: Friday 10:30–12:15

Location: H17

O 98.1 Fri 10:30 H17

**An Electro Spray Ion Beam Deposition Device Employing Novel Ion Guide Concepts** — ●ANDREAS WALZ, PETER KNECHT, KAROLINA STOIBER, HARTMUT SCHLICHTING, and JOHANNES BARTH — Physics Department E20, Technical University of Munich, Germany

The world of nanostructures requires precise control and growth of atomically clean films of clusters or molecules on well-defined surfaces. Most state of the art techniques like organic molecular beam epitaxy are limited to small and sublimable clusters or molecules. Electro Spray Controlled Ion Beam Deposition (ES-CIBD) gives access to reactive, larger and thermolabile species including many biomolecules. However, near ambient conditions for the generation of ions via electro spray ionization conflict with the ultra-high vacuum routinely required for the deposition via soft-landing and subsequent investigations. The challenge is to overcome pressure differences of 13 orders of magnitude while preserving high ion flux for appropriate preparation times as well as precise control of the deposited species.

Here we introduce advanced radio frequency ion optics combining highly efficient ion transmission with extremely low neutral gas leakage. We present a modified stacked ring ion guide combined with a novel high order multipole - the Small Wire Ion Guide (SWIG) - and a blade ion guide. The mass of the deposited species is determined by a digital quadrupole mass spectrometer with adjustable frequency and nearly unlimited mass range. Simulations using the software package SIMION have assisted the design. The deposited layers have been investigated with scanning tunneling microscopy.

O 98.2 Fri 10:45 H17

**Physical decoupling of tetrapyrrolic metal-organic complexes on metal surfaces via self-assembled monolayers** — PETER S. DEIMEL, PETER FEULNER, JOHANNES V. BARTH, and ●FRANCESCO ALLEGRETTI — Physik Department E20, Technische Universität München, Deutschland

Tuning the electronic properties of metal-organic complexes such as metalloporphyrins (MPs) and metallophthalocyanines (MPcs) holds promise for their targeted application in, e.g., photocatalysis and molecular sensors. In such cases, the complexes will be “immobilized” on solid supports, and for such reason numerous studies have focused on their adsorption on model metal surfaces in vacuo. As MPs and MPcs typically adsorb with their tetrapyrrole macrocycle almost parallel to the metal surface, the interaction between the latter and the central metal ion can decisively alter the chemical and functional properties of the adsorbed complex and even quench its reactivity. Herein we explore a simple strategy to decouple, both spatially and electronically, two prototypical Fe-phthalocyanine and Ru-porphyrin monolayers from a Ag(111) surface, by preventing direct physical contact with the Ag support via insertion of a self-assembled monolayer (SAM) of fluorothiophenol. By combining photoelectron spectroscopy, temperature programmed desorption and low-energy electron diffraction, we show that at low temperatures the thiolate SAM indeed acts as molecular spacer layer. However, already below 300 K, the decoupling breaks down, resulting in an inverted layer stacking followed by complete removal of the SAM molecules at elevated temperatures.

O 98.3 Fri 11:00 H17

**Tuning TCNQ adsorption on Ag(100): A joint DFT and experimental study of the role of alkali coadsorption** — ●BILLAL SOHAIL<sup>1</sup>, LUKE ROCHFORD<sup>2</sup>, PHIL BLOWEY<sup>1</sup>, PHIL WOODRUFF<sup>3</sup>, GIOVANNI COSTANTINI<sup>1</sup>, and REINHARD J. MAURER<sup>1</sup> — <sup>1</sup>Department of Chemistry, University of Warwick, UK — <sup>2</sup>School of Chemistry, University of Birmingham, UK — <sup>3</sup>Department of Physics, University of Warwick, UK

TCNQ (7,7,8,8-tetracyanoquinodimethane) is a well established electron acceptor with an innate ability to form conductive organic salts. Interest in the multidisciplinary field of molecular electronics has piqued due to the variety of applications such as, organic photovoltaics (OPVs), organic field effect transistors (OFETs). Adsorbed on coinage metal surfaces, computational efforts find TCNQ adopts a specific geometry with the peripheral cyano groups bent toward the metal surface, which is lifted upon coadsorption with potassium. We present joint computational and experimental efforts to examine the intricate coupling of structure and electronic structure for TCNQ coadsorbed

with potassium atoms on Ag(100) surfaces. By combining many-body-dispersion-inclusive Density-Functional Theory [1] and x-ray standing wave (XSW) and STM measurements, we arrive at a comprehensive picture of structure and stability as determined by the balance of molecule-metal and molecule-molecule charge-transfer and dispersion interactions. [1] Maurer et al., *J. Chem. Phys.*, **143**, 102808 (2015);

O 98.4 Fri 11:15 H17

**Understanding Charge Transfer of TCNE on Cu(111) using Structure Search** — ●ALEXANDER T. EGGER<sup>1</sup>, LUKAS HÖRMANN<sup>1</sup>, ANDREAS JEINDL<sup>1</sup>, MILICA TODOROVIĆ<sup>2</sup>, PATRICK RINKE<sup>2</sup>, and OLIVER T. HOFMANN<sup>1</sup> — <sup>1</sup>Institute of Solid State Physics, TU Graz, Austria — <sup>2</sup>Department of Applied Physics, Aalto University, Finland

TCNE (tetracyanoethene) is known as a strong electron acceptor that forms charge-transfer complexes upon adsorption on metals. On Cu(111), it has been claimed [1] that this charge transfer includes the second layer, whereby molecules of this second layer are singly charged.

To understand these charge-transfer complexes, knowing the atomic structure of the adlayers is mandatory. However, the number of possible geometries is immense and an accurate description of charge transfer requires dispersion-corrected density functional theory (DFT), which – due to its computational costs – inhibits a brute-force search. Using two complimentary machine-learning-based approaches [2,3] allows us to predict the adsorption energies of an exhaustive set of coarse-grained candidate structures at reasonable computational cost while preserving the numerical accuracy of the electronic structure calculations.

Our studies reveal that for TCNE on Cu(111) charge transfer to the second layer is in fact negligible. Instead, a phase transition occurs in the first layer: At high coverage adsorbate molecules flip from face-on to edge-on orientation explaining the observed singly-charged species.

[1] Erley et al., *J. Phys. Chem.*, 91.11

[2] Hörmann et al., arXiv:1811.11702

[3] Todorović et al., arXiv:1708.09274

O 98.5 Fri 11:30 H17

**Surface polymorph formation explained: Acenequinones on Ag (111)** — ●ANDREAS JEINDL, LUKAS HÖRMANN, ALEXANDER T. EGGER, and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

Understanding (and modifying) the formation of surface polymorphs is still not straightforward, as it is hardly known why specific structures form. Experimental studies are hindered by the huge thermodynamic search space and kinetic trapping. Computational studies, on the other hand, are hampered by the so-called ‘configurational explosion’.

In this contribution, we computationally investigate the formation of surface polymorphs for a homologous series of acenequinones on Ag (111). We perform a comprehensive structure search utilizing the SAMPLE[1,2] approach, which combines a physically-motivated coarse graining of the potential energy surface with machine learning to overcome the configurational explosion.

Contrary to most machine learning methods, which rely on mere statistical correlation, our approach gives valuable physical insight into the systems of interest. We investigate the interactions of low-energy polymorphs, distinguishing between inter-molecular and molecule-surface interactions. For further insight, we map the interactions onto different parts of the molecules, which allows us to identify the main contributors of polymorph formation. This could serve as a first step towards establishing rules for a systematic design of surface layers.

[1] Hörmann et al., arXiv:1811.11702

[2] Scherbela et al., *Phys. Rev. Materials* 2, 043803

O 98.6 Fri 11:45 H17

**Hybrid nanoassemblies of ordered nanoparticles and perylene** — ●NATALIA ALYABYEVA, AIMERIC OUVRRARD, and BERNARD BOURGUIGNON — Institut des Sciences Moléculaires d’Orsay (ISMO), CNRS, Université Paris-Saclay, 91405 Orsay, France

We demonstrate ordering of hybrid assemblies of Pd nanoparticles (NPs) and perylene on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111). Multi-scale surface science techniques provide a complete description of this system. Scanning tunnelling microscopy (STM) probe topography, adsorption sites and local density of states, while differential reflectance spectroscopy

(DRS) and sum frequency generation (SFG) give access to molecular orientation, coverage and thickness. Different adsorption phases of perylene on alumina depending on coverage and the presence of NPs have been observed. Perylene organizations on bare alumina are in registry with the substrate, evidencing the balanced interplays of molecule-substrate and intermolecular interactions. Molecules are flat-laying at low coverage and up-standing when the layer densifies as well as in the multilayer regime. Ordered hybrid assemblies can be formed where perylene is flat-laying in between NPs smaller than 1 nm. For larger coverage and NP size, perylene is up-standing and also adsorbing on NPs. Disorder progressively appears, showing that NPs hinders long-range intermolecular interactions. Adsorption on NPs leads to a larger SFG signal and a different electronic structure as observed by DRS and STM. Ordered NPs and molecules offer a way to tune electronic, chemical, and optical properties to build optimal architectures for future nanoelectronic devices.

O 98.7 Fri 12:00 H17

**Injection-tuning at metal-semiconductor interfaces to boost organic electronics** — •FLORIAN VON WROCHEM<sup>1</sup> and MARIA ANITA RAMPI<sup>2</sup> — <sup>1</sup>Materials Science Laboratory, Sony Europe, Stuttgart (Germany) — <sup>2</sup>Universita di Ferrara, Ferrara (Italy)

The driving force in molecular electronics within the past decades has been to shift organic-based thin-film devices from basic research to the application level. In this talk, a few strategies toward the realization of organic electronic devices on the basis of ultrathin functional organic layers are outlined, specifically by leveraging on the self-assembly process at interfaces. In the first place, we show how large area molecular junctions of outstanding robustness can be realized using densely packed molecular metal-terpyridine complex oligomers, which might enable a versatile platform for functional optoelectronic layers. In the second part, a new class of self-assembled monolayers exhibiting a pronounced intrinsic dipole moment is presented, by which the injection properties in organic semiconductors can be tuned in view of in solar cell and organic memory applications.