O 83: Organic molecules on inorganic substrates: electronic, optical and other properties III

Time: Thursday 15:00–17:30 Location: HSZ/0201

O 83.1 Thu 15:00 HSZ/0201

Spin-Crossover and Structural Correlation in Surface Confined Indigo-Based Fe-Coordination Polymers — •Mohammad Salehi[1], Aliki Soufla[2], Hongxiang Xu[1,5], Fulden Eratam[3], David A. Duncan[3,4], Tien-Lin Lee[3], Joachim Reichert[1], Johannes V. Barth[1], and Anthoula C. Papageorgiou[2] — [1]Technical University of Munich, DE — [2]National and Kapodistrian University of Athens, GR — [3]Diamond Light Source, UK — [4]University of Nottingham, UK — [5]Peking University, CN

Surface confined coordination polymers (CPs) exhibiting spin-crossover (SCO) behavior hold promise for molecular spintronics. By harnessing the natural dye indigo as a molecular building block, we investigated [Fe-indigo]$_n$ CPs on Ag(111). Sub-molecular resolution scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) confirmed well-defined CPs. We employed Fe L-edge X-ray absorption near-edge spectroscopy and high-resolution Fe $2p$ soft X-ray photoelectron spectroscopy to probe the spin states of Fe-indigo CPs at different temperatures. The data analysis supports thermally activated spin-crossover behavior, as predicted by density functional theory calculations. Normal incidence X-ray standing wave analysis yielded varying adsorption heights of Fe centers. We correlate the spin state with structural variations, revealing the interplay between ligand fields and magnetic properties.

O 83.2 Thu 15:15 HSZ/0201

Probing pi-conjugation in functionalized pentacene via photoemission orbital tomography — Felix Otto[1], Andrei Matestskii[2], Maximilian Schaal[1], Elise Fürch[1], Jonas Brandhoff[1], Roman Forker[1], François C. Bocquet[2], Michael G. Ramsey[3], Serguei Soubatch[2], •Peter Puschnig[3], Frank Stefan Tautz[2], and Torsten Fritz[1] — [1]Institute of Solid State Physics, Friedrich Schiller University Jena, Germany — [2]PGI-3, FZ Jülich & RWTH Aachen University, Germany — [3]Institute of Phyics, University of Graz, Austria

Tuning the electronic structure of polycyclic aromatic hydrocarbons is an effective route to control their physical and chemical properties. Here, we present an experimental approach that enables direct assessment of how chemical functionalization modifies the conjugation length of adsorbed molecules. We demonstrate the method using pentacenequinone (P2O), a functionalized pentacene derivative that forms a self-assembled monolayer on Ag(110), as confirmed by low-energy electron diffraction and scanning tunneling microscopy. Employing photoemission orbital tomography, we combine experimental photoelectron momentum maps with density-functional-theory simulations to elucidate the character of the frontier molecular orbitals. Our results provide direct experimental evidence that the functional group in P2O disrupts the conjugation of the parent pentacene backbone, causing the electronic structure of P2O to resemble two electronically decoupled naphthalene units. This interpretation is further supported by the observed increase in the band gap upon functionalization.

O 83.3 Thu 15:30 HSZ/0201

Stochastic spin-state transitions in an Fe(II) spin-crossover complex on Cu(111) — •Jasmeen Jasmeen[1], Sujoy Karan[1], Karl Ridier[2], Reecht Gaël[1], and Manuel Gruber[1] — [1]Faculty of Physics and CENIDE, University of Duisburg-Essen, 47057 Duisburg, Germany — [2]2LCC, CNRS and Université de Toulouse, UPS, INP, 31077 Toulouse, France

Spin-crossover molecules can be switched between a low- ($S = 0$) and a high-spin ($S = 1$) state using external stimuli. Although the switching properties of crystalline powder were shown to strongly depend on the molecules environment, a full microscopic description is lacking. The switching of individual molecules in contact with a surface, evidenced in recent years, open new routes to further understand the impact of the local environment in the switching properties.

Using scanning tunneling microscopy at 4.5 K, we investigated the [Fe(HB(1,2,4-triazolyl)3)2] complex in direct contact with Cu(111) surface, focusing on the dynamics of its spin-state switching and the factors controlling switching behavior. The switching is triggered by injecting current at voltages above 0.5 V and monitored by the induced change in conductance.

We observe a drastic change of the switching yield with the local molecular environment, showing a clear dependence on both the number and the spin-state of neighboring molecules. These observations suggest that intermolecular interactions influence the switching efficiency.

Funding from the CRC 1242 is gratefully acknowledged.

O 83.4 Thu 15:45 HSZ/0201

Coordination and Molecular Band Dispersion of a 2D Metal-Organic Network — •Martin Anstett[1], Lu Lyu[2], Jannis Lessmeister[1], Alexander Schmid[2], Ralf Hemm[1], Vitaliy Feyer[3], Yan Yan Grisan Qiu[3], Simone Mearini[3], Martin Aeschlimann[1], and Benjamin Stadtmüller[2] — [1]Department of Physics and Research Center OPTIMAS, RPTU University Kaiserslautern-Landau, 67663 Kaiserslautern, Germany — [2]Experimentalphysik II, Institute of Physics, University of Augsburg, 86135 Augsburg, Germany — [3]Peter Grünberg Institute (PGI-6), Jülich Research Centre, 52428 Jülich, Germany

Two-dimensional metal-organic porous networks (2D-MOPNs) provide a versatile platform exploring emergent electronic and magnetic phenomena at designed surface nanoarchitectures. Here, we prepare a cobalt-coordinated hexaaza-triphenylene-hexacarbonitrile (HATCN) network on Ag(111) to fingerprint the role of metal centers in mediating electronic behaviour. Scanning tunnelling microscopy (STM) reveals an ordered network structure. Photoelectron momentum microscopy identifies a distinct hybrid interface state arising from the Co-mediated coupling with the molecules. These results reveal the microscopic mechanism underlying the role of metal centers in tailoring the electronic structures of 2D-MOPN systems.

O 83.5 Thu 16:00 HSZ/0201

Phthalocyanine-based bipartite lattices: Towards a molecular Lieb lattice — •Tzu-Chao Hung[1], Luis M. Mateo[2], Leo Gross[3], Diego Peña[2], and Jascha Repp[1] — [1]University of Regensburg, Germany. — [2]Universidade de Santiago de Compostela, Spain. — [3]IBM Research Europe - Zurich, Switzerland.

The Lieb lattice is a text-book example of topology governing material properties: Its sublattice imbalance gives rise to extended degenerate states resulting in a flat band. Here, we realize several different covalently bonded phthalocyanine (Pc)-based Lieb-lattice prototypical structures by means of on-surface synthesis. Bond-resolved atomic force microscopy images reveal planar structures with extended π-conjugation. Differential conductance maps, combined with density-functional theory calculations and tight-binding models, confirm strong inter-site electronic coupling and quantum states with symmetry-enforced nodes and symmetry-protected degeneracy. Structures of increasing complexity allow exploring the evolu-tion of these symmetry-derived features.

O 83.6 Thu 16:15 HSZ/0201

Correlation-driven d-band modifications promote chemical bonding at 3d-ferromagnetic surfaces — •David Janas[1], Andreas Windischbacher[2], Alessandro Sala[3], Manuel Gruber[4], Mehdi Bouatou[4], Vitaliy Feyer[5], Iulia Cojocariu[5], Andrea Droghetti[6], Peter Puschnig[1,2], Giovanni Zamborlini[1], and Mirko Cinchetti[1] — [1]TU Dortmund University — [2]Karl-Franzens-University Graz — [3]CNR-Istituto Officina dei Materiali (IOM), Trieste — [4]University of Duisburg-Essen — [5]Elettra Sincrotrone Trieste — [6]Ca' Foscari University of Venice

Many-body effects at adsorbate-metal interfaces play a crucial but often overlooked role in designing spintronic and electrocatalytic materials. We recently showed that a chemisorbed oxygen layer on ferromagnetic (FM) Fe enhances electron correlation, causing narrowing of the Fe d-bands near the Fermi level, and a reduced exchange splitting, with direct implications for surface reactivity [1]. Here, we study a pentacene monolayer on oxygen-passivated Fe using momentum-resolved photoemission, scanning tunneling microscopy/spectroscopy, and Hubbard-corrected density functional theory (DFT+U) guided by dynamical mean-field theory (DMFT). Non-standard U values reproduce unexpectedly strong molecule-substrate interactions on a nominally passivated surface, highlighting the decisive role of electron correlation at organic/FM interfaces [2].

[1] Janas, D.M., et al. Adv. Mater., 35, 2205698 (2023).

[2] Janas, D.M., et al. accepted in Small.

O 83.7 Thu 16:30 HSZ/0201

A quantum dot-functionalized scanning tunnelling microscope tip: Sensing through electron-vibron coupling — •Stefan Schulte[1,2,3], Emilio Scontrino[1,4], Taner Esat[1,3], F. Stefan Tautz[1,3,4], and Ruslan Temirov[1,2,3] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — [2]II. Physikalisches Institut, Universität zu Köln, Germany — [3]Fundamentals of Future Information Technology, Jülich Aachen Research Alliance (JARA), Germany — [4]RWTH Aachen University, Germany

Scanning tunnelling microscope (STM) tips functionalized with a single-molecule quantum dot (QD) have been used for quantitative measurements of electrostatic surface potentials through a technique known as scanning quantum dot microscopy (SQDM) [1]. The functionalization of STM tips with large organic molecules has further enabled measurements of electrostatic and magnetic fields at the atomic scale [2, 3]. Here, we attach a naphthalene tetracarboxylic dianhydride (NTCDA) molecule, acting as a QD, to the tip of an STM and investigate charge transport through the resulting junction. In the resonant regime, the transport through the NTCDA QD exhibits signatures of electron-vibron coupling. We propose that this electron-vibron coupling can be leveraged to map surface polarizability with sub-nanometre resolution.

[1] C. Wagner *et al.*, Phys. Rev. Lett. **115**, 026101 (2015).
[2] B. Verlhac *et al.*, Science **366**, 623 (2019).
[3] T. Esat *et al.*, Nat. Nanotechnol. **19**, 1466 (2024).

O 83.8 Thu 16:45 HSZ/0201

Spatial Mapping of Vibronic Excitations in a Single Organometallic Complex — Xiangzhi Meng[1], Kai Uwe Clausen[2], Marie-Laure Bocquet[3], •Alexander Weismann[1], Niklas Ide[1], Felix Tuczek[2], and Richard Berndt[1] — [1]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — [2]Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany — [3]Laboratoire de Physique de l'École normale supérieure, ENS, Université PSL, CNRS, Sorbonne Université, Université Paris Cité, 75005 Paris, France

Vibronic excitations in single molecules at nanoscale interfaces are central to molecular electronics and are usually modeled with a double-barrier tunneling junction that assumes a homogeneous electric field and ignores atomic details of the contacts. Using STM measurements of a nonplanar organometallic complex on Ag(111), we obtain spatially resolved vibronic maps that reveal shifts in excitation energies caused by reordering of occupied molecular orbitals under the rapidly decaying tip potential. These shifts vary strongly with tip position. Combined with modeling, our results show that tip-induced, atomically varying electric fields can actively control molecular orbitals and must be considered in studies of nonplanar molecules.

O 83.9 Thu 17:00 HSZ/0201

Exciton Dynamics and Charge Transfer at Prototype Organic/Organic Interfaces Studied with LEEM and 2P-PEEM — Franz Niklas Knoop, •Klaus Stallberg, and Winfried Daum — Institute of Energy Research and Physical Technologies, TU Clausthal, Germany

Organic semiconductor (OSC) films deposited on weakly interacting substrates, such as natively oxidized silicon, often suffer from poor structural order. Using low-energy electron microscopy (LEEM), we show that para-sexiphenyl (p-6P) molecules on SiO_2 serve as a wetting layer, promoting the growth of microcrystalline phthalocyanine (Pc) thin films, which renders Pc/p-6P/SiO_2 a structurally well-defined model for an organic heterojunction. Using two-photon photoemission (2PPE), we study the exciton dynamics in both CuPc and F_{16}CuPc films on p-6P/SiO_2. For F_{16}CuPc/SiO_2, i.e., in absence of p-6P, the S_1 exciton is observed with a lifetime of 50 ps, indicating negligible influence of the substrate on the exciton dynamics. In contrast, for F_{16}CuPc/p-6P/SiO_2, the S_1 exciton is quenched. Moreover, laser-induced changes in electron reflectivity reveal a surface potential shift for F_{16}CuPc/p-6P/SiO_2, which points to the formation of surface dipoles upon optical excitation of F_{16}CuPc. Accordingly, we attribute the S_1 exciton quenching to formation of charge transfer (CT) excitons, which is compatible with the type II energy level alignment at the F_{16}CuPc / p-6P interface. In contrast, at the CuPc/p-6P type I heterojunction no charge transfer takes place. Accordingly, neither exciton quenching nor significant surface potential shifts are observed.

O 83.10 Thu 17:15 HSZ/0201

Magnetic Excitations in on-surface metallacrown complexes — •Robert Ranecki[1,2], Stefan Lach[2], Anne Lüpke[3], Angeliki Athanasopoulou[3], Eva Rentschler[3], and Christiane Ziegler[2] — [1]QNS, Seoul, Korea — [2]RPTU Kaiserslautern-Landau and OPTIMAS, Kaiserslautern, Germany — [3]Inst. of Inorganic and Analytical Chemistry, JGU Mainz

The implementation of quantum information processing demands achieving electrical control over spin-qubits that can be integrated into scalable architectures. Addressing this challenge, multi-spin-carrying molecules on surfaces offer a route to surface-integrable qubits: chemically diverse with tunable spin properties. However, the interaction with the supporting substrate can dramatically modify the electronic and magnetic properties of such complexes. Here, we present spin-flip inelastic tunneling spectroscopy studies of pentanuclear metallacrown complexes, CuCu4 and CuFe4, under adsorption onto Au(111) surface. By comparing the experimental results with perturbative electron transport model simulations[1], we extract quantitative values of the exchange coupling constants and determine the ground spin states of the metallacrown complexes[2]. These findings advance our understanding of the spin interactions in complex molecular systems adsorbed on surfaces, paving the way towards future quantum technologies.

[1] Ternes, M. New J. Phys. 17, 063016 [2] Ranecki, R. et al., J. Phys. Chem. C 127, 13186; Ranecki, R. et al., J. Phys. Chem. C 126, 15907