

O 89: Poster Session VII: Organic molecules on inorganic substrates: electronic, optical and other properties III

Time: Thursday 10:30–12:30

Location: P

O 89.1 Thu 10:30 P

Single-molecule rotation and translation — ●GRANT J. SIMPSON¹, SAMUEL HAJEK¹, VÍCTOR GARCÍA-LÓPEZ², A. DANIEL BOESE¹, JAMES TOUR², and LEONHARD GRILL¹ — ¹University of Graz, Graz, Austria — ²Rice University, Houston, TX, USA

Control of the orientation and the rotation direction of a single molecule is crucial to the understanding of molecular machines. In turn, the rotational orientation of a molecule can affect the efficiency of translation in a particular direction. Here, we report how single dipolar nanocar-type molecules adsorbed on a Ag(111) surface can be rotated with 100% directionality using the electric field of a scanning tunnelling microscope [1]. This high control relies on a specific interaction of the molecule with a silver surface atom and can be disrupted either by introducing a further adatom or by changing the chemical structure of the molecule. The influence of chemical modification on the nanocar-surface interaction is also explored on different noble metal surfaces in view of the upcoming nanocar race in early 2022.

[1] Simpson, G.J., García-López, V., Boese, A.D., Tour, J., Grill, L., Nat. Commun., 10, 4631 (2019)

O 89.2 Thu 10:30 P

Molecular orientation and phase transitions of DHTAP on Cu(110) — ●CLAUDIA LÓPEZ-POSADAS¹, MICHAEL GYÖRÖK¹, ANTONY THOMAS², THOMAS LEONI², OLIVIER SIRI², CONRAD BECKER², and PETER ZEPPENFELD¹ — ¹Institute of Experimental Physics, Johannes Kepler University Linz, Altenberger Str. 69, A-4040 Linz, Austria — ²Aix-Marseille University, CNRS, CINaM, UMR 7325, F-13288 Marseille, France

The structure and orientation of 5,14-dihydro-5,7,12,14-tetraazapentacene (DHTAP) layers deposited on Cu(110) was studied using reflectance difference spectroscopy (RDS), Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED). The evolution of the RDS signal allows to identify the sequential formation of up to three monolayers as well as a phase transition upon completion of the first one. DHTAP molecules in the first monolayer are always lying flat with their long molecular axis aligned parallel to the [-110]-direction of the Cu(110) surface. However, for subsequent layers the orientation critically depends on the deposition temperature T. At T=240K the DHTAP molecules are mostly aligned parallel to the ones in the first layer, whereas at room temperature and above their preferential orientation is along the [001]-direction, i.e., orthogonal to the molecules in the first layer. Finally, the main optical transitions and the orientation of the transition dipole moments of the DHTAP layers were extracted from the RDS spectra and compared with recent theoretical investigations on individual DHTAP molecules.

O 89.3 Thu 10:30 P

Exciton-trion dynamics of a single molecule probed by Radio-frequency STM-induced luminescence — JIŘÍ DOLEŽAL^{1,2}, SOFIA CANOLA¹, ●PABLO MERINO^{3,4}, and MARTIN ŠVEC^{1,5} — ¹Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10/112, CZ16200 Praha 6, Czech Republic — ²Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, CZ12116 Praha 2, Czech Republic — ³Instituto de Ciencia de Materiales de Madrid, CSIC, Sor Juana Inés de la Cruz 3, E28049 Madrid, Spain — ⁴Instituto de Física Fundamental, CSIC, Serrano 121, E28006 Madrid, Spain — ⁵Regional Centre of Advanced Technologies and Materials, Šlechtitelů 27, CZ78371 Olomouc, Czech Republic

Combination of radio-frequency (RF) modulated bias and photon detection overcomes the microsecond time resolution limit of transimpedance amplifiers in conventional STM. Here, we report two novel tip-enhanced optical methods: for calibration of RF transmission by detecting the energy of the plasmon edge and for measuring time evolution of fluorescent systems by phase shift of the RF signal. The RF phase-shift method corrected for amplitude transmission is applied to Zinc Phthalocyanine (ZnPc) molecules on NaCl/Ag(111). We generate excitons and trions in ZnPc, determine their dynamics and trace the evolution of the system in the picosecond range. In addition, we explore dependence of effective lifetimes on bias voltage, propose a conversion mechanism from neutral excitons to trions via charge capture and perform a stochastic simulation to corroborate the experimental

results.

O 89.4 Thu 10:30 P

Excited state dynamics of terrylene — ●BOUBACAR TANDA BONKANO^{1,2}, SAMUEL PALATO^{1,2}, SERGEY KOVALENKO¹, LUKAS GIERSTER^{1,2}, BJOERN KOBIN¹, STEFAN HECHT^{1,3}, and JULIA STAEHLER^{1,2} — ¹Institut für Chemie, Humboldt-Universität zu Berlin — ²Fritz-Haber-Institut der MPG, Berlin — ³Leibniz-Institut für Interaktive Materialien, RWTH Aachen

In hybrid solar cells, the separation of the electron-hole pairs after photogeneration is a key aspect of the light harvesting functionality. This requires, in hybrid inorganic/organic systems, the use of molecules that have excited states with sufficiently long lifetime to allow charge separation. In order to investigate terrylene molecules, we performed two types of time-resolved spectroscopy, time-correlated single photon counting (TCSPC) and broadband transient absorption (TA) using a white light continuum probe. The steady state absorption and emission spectra of terrylene monomers in solution show mirrored lineshapes. Both the TCSPC and TA consistently show a decay of 3.7 ns for the excited state S_1 . Thin terrylene film shows absorption bands strongly (> 0.5 eV) blue-shifted due to H-aggregation. Photoexcitation of the H-aggregate leads to the formation of an induced absorption band at 2.3 eV, indicating the presence of transient terrylene monomers. A phenomenological fit model allows for the disentanglement of the participating elementary processes. The determination of the relaxation pathways is challenging but yet necessary for a better understanding and control of terrylene-based systems, beneficial for applications.

O 89.5 Thu 10:30 P

On-surface synthesis of porphyrin tetramers — ●EDUARDO CORRAL-RASCON¹, ALEXANDER RISS¹, PINGO MUTOMBO², ADAM MATEJ², YANG BAO¹, PAVEL JELINEK², and WILLI AUWÄRTER¹ — ¹Physics Department E20, Technical University Munich, Germany — ²Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

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 Ag(100)-supported porphyrin tetramers that possess a cyclooctatetraene (COT) moiety at their center. Bond-resolved atomic force microscopy (AFM) and scanning tunneling microscopy (STM) supported by density functional theory (DFT) calculations were used to characterize the coupling and the emerging electronic properties. In particular we compared the apparent bond lengths and electronic states of Zn-metalated and different tautomers of base-free tetramers.

[1] Wiengarten, A. et al. J. Am. Chem. Soc. 2014, 136, 26, 934.

[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 89.6 Thu 10:30 P

Nuts and bolts of core-hole constraint based ab-initio simulations for K-shell x-ray photoemission and absorption spectra — ●BENEDIKT P. KLEIN^{1,2}, SAMUEL J. HALL¹, and REINHARD J. MAURER¹ — ¹Department of Chemistry, University of Warwick, Coventry, United Kingdom — ²Diamond Light Source, Didcot, United Kingdom

X-ray Photoemission (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy are important tools used to study the electronic structure of materials and surfaces. Here, ab-initio simulations can help with the interpretation of complex spectra consisting of overlapping signatures. Approximate core-hole constraint based simulation methods using Density Functional Theory (DFT) such as the Delta-Self-Consistent-Field (Δ SCF) method or the transition potential (TP) method are widely employed to predict the K-shell XPS and NEXAFS spectra for a wide range of systems at reliable accuracy and affordable computational cost. We present our variants of both the Δ SCF and the TP method (coined Δ IP-TP) by applying

them to exemplary molecules in the gas-phase, in molecular crystals, and at metal-organic interfaces. Thereby we systematically assess how practical simulation choices affect the stability and accuracy of the calculated transitions, which we compare to experimental data. The investigated choices include the exchange-correlation functional, the basis set, the method of core-hole localization, and the use of periodic boundary conditions. For the benefit of practitioners in the field, we discuss sensible default choices and limitations of the methods.

O 89.7 Thu 10:30 P

Atomic band structure of occupied and unoccupied states of C₆₀ multilayer films — •RALF HEMM, FLORIAN HAAG, NORMAN HAAG, MARTIN MITKOV, SEBASTIAN EMMERICH, MARTIN AESCHLIMANN, and BENJAMIN STADTMÜLLER — University of Kaiserslautern (TUK) and research center OPTIMAS, Erwin-Schroedinger-Str. 46, 67663 Kaiserslautern, Germany

The implementation of molecular materials in everyday technology is

hindered by their poor charge carrier mobility that is rooted in the strong localization of the molecular valence states on single molecular sites. Only in rare cases, strongly dispersive bands have been observed in these materials. Here, we focus on such an exceptional case and study the band structure of C₆₀ multilayers on Ag(111) and Cu(111). Using momentum microscopy, we find strongly dispersive valence bands with complex momentum-dependent photoemission patterns that point to the formation of an atomic crystal-like band structure in C₆₀ thin films [1]. Interestingly, these strongly dispersing states in C₆₀ are not limited to the valence band structure, but also extend to the unoccupied band structure above the vacuum level [2]. These states above the vacuum energy are of particular interest since they are typical final states of the photoemission processes. Hence, their momentum distribution has to be taken into account when extracting the band dispersion of occupied and excited states in a (inverse) photoemission experiment of molecular films on surfaces.

[1] N. Haag et al. Phys. Rev. B 101, 165422 (2020)

[2] J. H. Weaver et al., Phys. Rev. Lett. 66, 1741 (1991)