

O 12: Organic-Inorganic Hybrid Systems and Organic Films II

Time: Monday 15:00–16:45

Location: WIL A317

O 12.1 Mon 15:00 WIL A317

Promoted exchange reaction between alkanethiolate self-assembled monolayers and an azide-bearing substituent — RUI YAN¹, LOÏC LE PLEUX², MARCEL MAYOR², and MICHAEL ZHARNIKOV¹ — ¹Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — ²University of Basel, Department of Chemistry, St. Johannisring 19, CH-4056 Basel, Switzerland

The possibility of ultraviolet (UV) light promoted exchange reaction (UUPER) between the primary alkanethiolate (AT) self-assembled monolayers (SAM) and an azide-functionalized substituent (12-Azido-1-dodecanethiol, C12N3), capable of click reaction with ethynyl-bearing species, is demonstrated. This reaction resulted in the mixed AT/C12N3 films, with the portion of C12N3 precisely controlled by selection of a suitable UV dose. As the primary matrix, either non-substituted or oligo(ethylene glycole) (OEG) substituted AT SAMs were used, targeting mixed SAMs of chemical and biological significance. To demonstrate the flexibility of the approach, UV light with two different wavelengths (254 and 375 nm) was used, applied to the non-substituted and OEG-substituted AT SAMs, respectively. The surface density of the chemically active azide groups embedded in the non-reactive primary matrix could be varied according to the composition of the mixed SAMs. For the OEG-AT/C12N3 films, this resulted in the preparation of templates for specific protein adsorption, comprising biotin-bearing moieties embedded in the protein-repelling OEG-AT matrix.

O 12.2 Mon 15:15 WIL A317

The effect of different anchoring groups on immobilized Ruthenium (II) Bipyridine complexes for dye sensitized solar cells: A computational study — ANIK SEN and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

There is a currently a growing interest in the development of dye sensitized solar cells (DSSC) based on the p-type inorganic semiconductors such as NiO. The working principle is based on hole injection into the valence band of the p-type semiconductor from the photo excited semiconductor. We have performed density functional theory (DFT) calculations in order to understand the influence of different anchoring groups and spacer molecules attached to a photoactive Ruthenium polypyridine dye molecule on the physical and chemical properties of the DSSCs. The conversion efficiency of the dye molecules is assessed using time-dependent DFT. The NiO substrate is modeled within the cluster approach, and implicit solvent model calculations are performed to take the influence of the liquid environment into account.

The immobilized photo-active complexes bind to the NiO-substrate through the anchoring groups in mono-, bi- and tri-dentate forms. In our discussion of the computational results, we will in particular discuss the correlation between the adsorption geometry and the electronic structure of the complexes which is critical for the overall performance of the DSSC.

O 12.3 Mon 15:30 WIL A317

Spin-dependent dispersion of the hybrid band structure of the Alq3/Co interface — JOHANNES STÖCKL¹, ANATOL JURENKOW¹, NICOLAS GROSSMANN¹, BENJAMIN STADMÜLLER¹, MIRKO CINCHETTI², and MARTIN AESCHLIMANN¹ — ¹Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrödinger-Straße 46, 67663 Kaiserslautern, Germany — ²Experimentelle Physik VI, Technische Universität Dortmund, 44221 Dortmund, Germany

Extensive studies in the last decade revealed that the spin polarization of ferromagnetic surfaces can be strongly altered by the adsorption of organic molecules. This effect is usually attributed to the formation of hybrid interface states across the metal-organic interface. Here we use spin- and angle-resolved photoemission (SR-ARPES) performed with VUV radiation to reveal changes in the spin dependent surface band structure of a thin cobalt film upon adsorption of the prototypical molecule Alq3. For the bare Co(100) surface, we find clearly dispersing d-bands along Γ -X in the vicinity of the Fermi energy, leading to an overall negative spin polarization at EF. The dispersion of the d-bands, and hence the corresponding spin polarization, change upon adsorption of Alq3. In particular, the effective mass of the Co

d-bands increases significantly for both majority- and minority bands leading to an almost flat band dispersion and a uniform spin polarization for electron momenta at the Alq3/Co interface. Our findings will be discussed in the framework of a final state diffraction effect at the metal-organic interface and the formation of hybrid interface states.

O 12.4 Mon 15:45 WIL A317

Competition of surface-assisted organometallic and dehydrogenation reactions of non-functionalized porphyrin on Cu (111) — FEIFEI XIANG, ANJA GEMEINHARDT, and M. ALEXANDER SCHNEIDER — Solid State Physics, Friedrich-Alexander-University Erlangen-Nürnberg, 91058, Erlangen, Germany

The adsorption properties, self-assembly and surface assisted reactions of 5,15-diphenylporphyrin (2H-DPP) on Cu(111) are studied by low-temperature scanning tunneling microscopy in ultra-high vacuum. When deposited at room temperature and imaged at 80 K, well-ordered chain-like 2H-DPP structures along Cu [11-2] and equivalent directions are found that are stabilized by a weak interaction between the phenyl and pyrrole rings of neighboring molecules. At elevated annealing temperatures, an intramolecular dehydrogenation reaction is first triggered along with the Cu metalation of the DPP core producing a new planar Cu-DPP species on the surface. After that, two types of oligomer reaction products are formed, one of which consists of the planar Cu-DPP species linked by C-Cu-C bonds and the other by C-C covalent bonds. The latter product is the dominant species on the surface. We argue that is due to much faster reaction rates of the covalent bonded species than of the Cu linked species on Cu (111).

O 12.5 Mon 16:00 WIL A317

Structural, electronic and optical properties of K-doped PTCDA monolayer domains on Ag(111) — M. GRUENEWALD¹, C. ZWICK¹, F. OTTO¹, A. BABY^{2,3}, E. VERWÜSTER², O. T. HOFFMANN², R. FORKER¹, B. STADTMÜLLER⁴, G. P. BRIVIO³, G. FRATESI^{3,5}, C. KUMPF⁶, E. ZOJER², and T. FRITZ¹ — ¹Institute of Solid State Physics, Friedrich Schiller University Jena — ²Institute of Solid State Physics, Graz University of Technology — ³Department of Materials Science, University of Milano-Bicocca — ⁴Fachbereich Physik and Research Center OPTIMAS, University of Kaiserslautern — ⁵Dipartimento di Fisica, Università degli Studi di Milano — ⁶Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich

Here we report the influence of potassium doping on highly ordered ultrathin layers of the dye molecule 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) on Ag(111). The doped thin films have been characterized by LEED, STM, PES, x-ray standing wave (XSW), and differential reflectance spectroscopy (DRS). The experimental results are consistently interpreted with the help of density functional theory (DFT) calculations. We find that potassium doping induces a structural reordering of the commensurate PTCDA herringbone phase into point-on-line structures comprising charge-transfer complexes. Their stoichiometries are determined to K₂PTCDA and K₄PTCDA with potassium adsorption sites nearby the anhydride groups. PTCDA appears doubly negatively charged in both complex geometries; metal-organic hybridization becomes weaker with increasing potassium concentration.

O 12.6 Mon 16:15 WIL A317

Self-assembly and metal coordination of surface-adsorbed Porphyrin molecules — JINGYI LI¹, CHRISTIAN WÄCKERLIN¹, STEPHAN SCHNIDRIG², EVELYNE JOLIAT², ROGER ALBERTO², and KARL-HEINZ ERNST^{1,2} — ¹Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland — ²Institut für Chemie, Universität Zürich, CH-8057 Zürich, Switzerland

The porphyrin molecule, which in contrast to porphyrin consists of four fused pyridine groups instead of pyrrole groups in its macrocycle, has been predicted to be a potential molecular catalyst. Using thermal desorption and X-ray photoelectron spectroscopy, we demonstrate that in monolayer coverage on Cu(111), the core of porphyrin is metalated with Cu adatoms at 377 K. Scanning tunneling microscopy reveals different self-assembly patterns before and after metalation. 2D honeycomb and 1D linear arrangements of porphyrin molecules are formed by linking the cyano groups of porphyrin to Cu adatoms. Dehy-

drogenation at the periphery of the molecule after annealing at 520 K leads to the disappearance of self-assembled layers.

O 12.7 Mon 16:30 WIL A317

Comparison of various approaches to van der Waals interactions for anthracene and pentacene on Ag(111) — •JULIANA MORBEC and PETER KRATZER — Faculty of Physics, University of Duisburg-Essen, Germany

Anthracene and pentacene molecules have great potential for optoelectronic applications due to their high carrier mobility and excellent electroluminescence and photoluminescence. In this work we performed density-functional theory calculations to investigate the effects of the van der Waals (vdW) interactions on the structural and electronic properties of anthracene and pentacene adsorbed on the Ag(111) sur-

face [1]. Our results show that vdW interactions strongly affect the stability and structural properties of both anthracene/Ag(111) and pentacene/Ag(111), but have little effect on the electronic properties of these systems. In particular, we found that the inclusion of vdW corrections is crucial to correctly describe the flat adsorption geometry of anthracene/Ag(111) observed in experiments. Moreover, we found that the adsorption of anthracene induces a larger reduction in the work function of the Ag(111) surface than pentacene, which is consistent with the stronger physisorption character observed in anthracene/Ag(111). The vdW interactions were treated using both the pairwise density-dependent vdW^{surf} approach [2] and many-body dispersion (MBD) method [3].

[1] Juliana M. Morbec and Peter Kratzer, submitted (2016). [2] V. G. Ruiz et al., Phys. Rev. Lett. 108, 146103 (2012). [3] A. Ambrosetti et al., J. Chem. Phys. 140, 18A508 (2014).