

O 69: Poster Wednesday: Organic Molecules on Inorganic Surfaces

Time: Wednesday 17:45–20:00

Location: Poster B2

O 69.1 Wed 17:45 Poster B2

Reactions of Tetrapyrroles with Lead on Metal Surfaces — ●MARK HUTTER¹, MALTE ZUGERMEIER¹, GUOQING LYU², MARTIN SCHMID¹, STEFAN RENATO KACHEL¹, NIAN LIN², and J. MICHAEL GOTTFRIED¹ — ¹Fachbereich Chemie, Philipps-Universität Marburg, Germany — ²Department of Physics, The Hong Kong University of Science and Technology, Hongkong, China

Metal complexes of tetrapyrroles such as porphyrins and phthalocyanines play important roles in living organisms and for various technological applications. While most studies focus on transition metal complexes, we report here the interaction of tetrapyrrole monolayers with Pb as a typical main group metal. STM shows that tetrapyrrolylporphyrin (2HTPyP) on Au(111) reacts with metallic Pb, as evidenced by increased apparent heights in the molecular centers. Corresponding XPS studies with tetraphenylporphyrin (2HTPP) show the presence of Pb(II), indicating the formation of a Pb(II)TPP complex. Interestingly, annealing to 520 K leads to a reduction of the apparent height and the Pb(II) related XPS signal decreases. These findings are consistent with two possible mechanisms. In the first one, Pb(II)TPP is initially formed in a Pb-up geometry, such that the Pb(II) ion is detached from the Au substrate and thus retains its nominal oxidation state. Annealing transforms the complex to Pb-down geometry, in which the Pb(II) center receives electron density from the substrate and is reduced to Pb(0). In the second one, the Pb(II) center is replaced by a substrate Au atom upon annealing. For further clarification, TPD/AES studies were performed.

O 69.2 Wed 17:45 Poster B2

Rotation of a Single-Molecule Dipole — ●GRANT J SIMPSON¹, VÍCTOR GARCÍA-LÓPEZ², A. DANIEL BOESE¹, JAMES M TOUR², and LEONHARD GRILL¹ — ¹University of Graz, Graz, Austria — ²Rice University, Texas, USA

Control of the orientation and the direction of rotation of a single molecule is crucial to the understanding of molecular machines. Directed rotation is also necessary to transfer mechanical work from one molecule to another in a controlled way. Here, we report how single dipolar molecules adsorbed on a Ag(111) surface can be oriented with maximum precision using the electric field in the junction of a scanning tunneling microscope. Rotation is found to occur around a fixed pivot point and both directions of rotation are realised with 100% directionality. The pivot point arises as result of the interaction of an oxygen atom in the molecule and a silver atom of the surface. By introducing a further Ag adatom underneath the molecule, this interaction can be disrupted and the rotation of the molecule can be modified.

O 69.3 Wed 17:45 Poster B2

Investigation of side chain substituted quaterthiophenes on pristine and C₆₀-covered Ag(111) — ●JARI DOMKE, FALKO SOJKA, MARCO GRUENEWALD, CHRISTIAN ZWICK, ROMAN FORKER, and TORSTEN FRITZ — Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany

Side chain substituted dicyanovinyl quaterthiophenes (DCV4T-Et2) have been of interest for their application as absorber molecules in small molecule organic solar cells [1]. We investigate thin films of DCV4T-Et2 on Ag(111) as well as on C₆₀ monolayers on Ag(111). Structural characterization of the films is carried out by means of distortion corrected low-energy electron diffraction (MCP-LEED) [2] and low-temperature scanning tunneling microscopy (LT-STM), optical characterization by differential reflectance spectroscopy (DRS) [3] and Photoluminescence (PL). We find that DCV4T-Et2 forms highly ordered structures on Ag(111). The optical properties depend on the layer thickness, most likely due to formation of aggregates.

[1] O. Guskova *et al.*, J. Phys. Chem. C **117** (33), 17285–17293 (2013).

[2] F. Sojka *et al.*, Rev. Sci. Instrum. **84**, 015111 (2013).

[3] R. Forker *et al.*, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. **108**, 34–68 (2012).

O 69.4 Wed 17:45 Poster B2

Spectroscopic studies of thin hemin and cytochrome-c films using a PEEM with fs-laser and He-I excitations — ●FRANZ NIKLAS KNOOP¹, JONAS DARIUS FORTMANN¹, ANSGAR PAUSCH¹, KLAUS STALLBERG², GERHARD LILIENKAMP¹, UWE SCHRÖDER³, and

WINFRIED DAUM¹ — ¹IEPT, TU Clausthal — ²Surface Physics, Uni Marburg — ³IÖNC, TU Braunschweig

Microbial fuel cells (MFC) offer the potential to convert chemical energy of organics in waste water to electricity. Besides questions of technical realization, the electron transfer process in the bacterial biofilms is topic of current research. Previous studies suggest that redox-active, membrane-associated cytochromes play a crucial role in the transfer processes for *Geobacter sulfurreducens*, a promising candidate for MFCs. Aiming at a spectromicroscopic characterization of bacteria films, we studied thin films of the protein cytochrome c and the porphyrin hemin b, the latter being similar to the redox-active center heme c of the protein, using photoelectron emission microscopy (PEEM) with fs-laser excitation. For cytochrome c and hemin b we observe in our laser excitation spectra a pronounced Soret band at 415 nm and 400 nm, respectively, with very strong spectral broadening in the case of condensed hemin. While for cytochrome c laser-induced changes of the Soret band spectra were observed, hemin b spectra are not affected by laser irradiation. As a second route, we evaluate the possibilities of PEEM with excitation from a He-I UV light source and present first spectroscopic results for these films. We acknowledge financial support of the research group ElektroBak by the State of Lower Saxony.

O 69.5 Wed 17:45 Poster B2

Reorganization energy and polaronic effects in pentacene adsorbed on NaCl(001) surfaces — ●JAKOB SCHLÖR, DANIEL HERNANGÓMEZ-PÉREZ, DAVID A. EGGER, and FERDINAND EVERS — Universität Regensburg, Germany

Combined atomic-force and scanning-tunneling experiments allow to control single-electron transfer to and from organic molecules immobilized on electrically insulating NaCl surfaces [1]. By ramping the bias voltage, V_{bias} electrons tunnel in (out) of the molecule occupying the LUMO (HOMO) molecular orbital. V_{bias} at the onset of tunneling depends on the bias sweep direction, giving rise to a hysteresis that is closely related to the polaronic reorganization energy. Here, we employ electronic structure calculations based on the density functional theory to study the interplay of charging with ionic relaxations in the NaCl support. We calculate reorganization energies of different charge transitions for pentacene adsorbed on a NaCl(001)-surface and compare them to experimental findings.

[1] Fatayer *et al.*, Nature Nanotechnology, 13, p.376–380 (2018)

O 69.6 Wed 17:45 Poster B2

Electronic Structure and Interaction between Organic Charge-Transfer Molecules on Single-Layer MoS₂/Ag(111) — ●ASIEH YOUSOFNEJAD, GAËL REECHT, CHRISTIAN LOTZE, and KATHARINA J. FRANKE — Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Organic electronic devices such as organic solar cells and organic light emission diodes are highly promising devices for future technologies. Organic solar cells constitute electron donor (D) and electron acceptor (A) molecules for efficient charge separation upon photon absorption. At the interface between donor and acceptor, charge transfer may occur even without illumination. Using scanning tunneling microscopy and scanning tunneling spectroscopy, we study the structure and electronic properties of DCV5T-Me₂ (D) and C₆₀ (A) on single-layer Molybdenum disulfide (SL-MoS₂) on Ag(111). SL-MoS₂ acts here as a decoupling semiconducting layer, which inhibits strong hybridization with the substrate. First, we investigate isolated islands formed by either C₆₀ or DCV5T-Me₂. Co-depositing both molecules on MoS₂ also leads to homo-molecular islands. At the interface of C₆₀ and DCV5T-Me₂ islands, we find a modified electronic structure, suggesting a charge transfer between C₆₀ and DCV5T-Me₂.

O 69.7 Wed 17:45 Poster B2

Functionalization of Si(553)-Au surface with small organic molecules — ●SANDHYA CHANDOLA¹, JULIAN PLAICKNER¹, EUGEN SPEISER¹, CONOR HOGAN², and NORBERT ESSER¹ — ¹Leibniz-Institut für Analytische Wissenschaften-ISAS e.V. Schwarzschildstrasse 8, 12489 Berlin, Germany — ²Istituto di Struttura della Materia-CNR (ISM-CNR), via Fosso del Cavaliere 100, 00133 Rome, Italy

The adsorption of small organic molecules on vicinal Au- Si(111) surfaces is shown to be a versatile route towards controlled growth of ordered organic-metal hybrid 1D nanostructures. We investigate molecular adsorption by establishing a direct connection between optical spectra and surface structure via ab-initio calculations. Optical spectra and their theoretical interpretation gives us information on structural and electronic properties of the system. We use a surface-sensitive and polarization-sensitive optical technique, Raman Spectroscopy (RS), to investigate the adsorption of toluene-3,4-dithiol (TDT) molecules on Si(553)-Au surfaces. As a first step, we use RS to investigate TDT adsorption on a SERS (surface enhanced Raman scattering) substrate which is known to produce significant surface enhancement when adsorbed with molecules. Distinctive vibrational modes have been identified and correlate well with the vibrational frequencies of the TDT molecule. RS of TDT adsorption on Si(553)-Au shows very weak vibrational modes which appear to be related to the molecular vibrations. In order to increase the detection sensitivity of the molecules on the Si(553)-Au surface, silver islands were deposited on the surface to increase the density of hot spots and thus enhance the Raman signal.

O 69.8 Wed 17:45 Poster B2

Formation of Highly Ordered Porous 2D Networks from Cyano-Functionalized Porphyrins on Cu(111) — ●RAJAN ADHIKARI, MICHAEL LEPPER, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

We investigated Cu-5, 10, 15, 20-tetrakis-(p-cyano)phenylporphyrin (CuTCNPP) on Cu(111) using Scanning Tunneling Microscopy in ultra-high vacuum at room temperature. While the adsorption behavior on Cu(111) in terms of intramolecular conformation and supramolecular arrangement of the free-base analogue 2HTCNPP and the corresponding porphyrin without cyano functionalization, i.e., CuTPP was previously reported, [1, 2] CuTCNPP behaves significantly different. It forms a peculiar hexagonal honeycomb-type pattern with triangular pores, initially coexisting with parallel arranged 1D molecular chains. Annealing to 400 K yields a complete transformation to the hexagonal honeycomb-type pattern. The hexagonal honeycomb pattern is formed by three Cu-TCNPP molecules linked by interstitial Cu-adatoms on the substrate. In summary, we report on a novel porous supramolecular structure, which might be well suited as a nanoscaled template. References: [1] M. Lepper, et al., Chem. Commun. 53 (2017) 8207 [2] K. Diller, et al., J. Chem. Phys. 136 (2012) 014705

O 69.9 Wed 17:45 Poster B2

Surface characterization of en-APTAS monolayers on n-GaN(0001) — ●NURHALIS MAJID^{1,3}, GERHARD LILIENKAMP¹, NURSIDIK YULIANTO^{2,3}, HUTOMO S. WASISTO², and WINFRIED DAUM¹ — ¹IEPT, TU Clausthal, Clausthal-Zellerfeld, Germany — ²IHT, TU Braunschweig, Braunschweig, Germany — ³Research Centre for Physics, LIPI, Tangerang Selatan, Indonesia

Surface functionalization of metal oxide semiconductors with N-[3-(trimetoxysilyl)propyl]ethylenediamine (en-APTAS) self assembled monolayers provides a viable route for the development of selective NO₂ gas sensors. A similar functionalization of GaN surfaces could allow for the development of nanoscale NO₂ gas sensors. Here, we investigate properties of en-APTAS monolayers, prepared by dip coating on n-GaN(0001), by AFM, AES and XPS. The adsorption of en-APTAS is characterized by the SiLVV and SiKLL Auger lines and N 1s photoemission with binding energies of 398.8 eV, 400 eV, and 401.6 eV associated to primary, secondary and protonated amine groups, respectively. We observe an anomaly of the SiLVV/SiKLL Auger intensity ratio for the en-APTAS monolayer which suggests that the Si atoms are located close to the top of the layer. Implications for the suitability of this organic/inorganic hybrid system for NO₂ gas sensing applications are discussed.

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O 69.10 Wed 17:45 Poster B2

Motorized molecules studied by scanning tunneling microscopy — ●PETER JACOBSON¹, JAMES TOUR², and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, University of Graz, 8010 Graz, Austria — ²Department of Chemistry, Rice University, Houston, Texas 77005, USA

Motorized molecules are envisioned as cargo carriers at the nanoscale. Critical to their success is the controlled activation of motion using external stimuli. In Feringa type motors, UV light triggers a sequence of isomerization and helical inversion steps leading to the unidirectional rotation of the motor. When incorporated into larger molecules, these motors are a potential source of unidirectional translation at surfaces. Scanning probe microscopy is an ideal tool to investigate the single molecule dynamics of these molecular machines, but commonly used metal substrates have drawbacks, such as the quenching of excited states by conduction electrons. An alternate approach is to deposit them on semiconducting substrates, thereby reducing the adsorption strength of the molecule on the surface and removing a potential path for quenching. Here, I will present initial results on motorized molecules containing a Feringa motor on semiconducting surfaces.

O 69.11 Wed 17:45 Poster B2

Superhydrophilic/hydrophobic double-sided polycaprolactone-based scaffolds produced via DC plasma treatment — ●KSENIA STANKEVICH¹, VALERIYA KUDRYAVTSEVA¹, YURI ZHUKOV², ALEXANDRA PERSHINA³, VICTOR FILIMONOV¹, EVGENY BOLBASOV¹, and SERGEI TVERDOKHLEBOV¹ — ¹National Research Tomsk Polytechnic University, Tomsk, Russian Federation — ²Saint-Petersburg State University, Saint-Petersburg, Russian Federation — ³Siberian State Medical University, Tomsk, Russian Federation

Polymer biodegradable scaffolds treated with plasma possess the essential properties of biocompatible materials. However, hydrophobic recovery occurring after the plasma treatment limits the application of the method. Here, we create thin porous polycaprolactone- (PCL-) based scaffolds with a thin Ti coating by direct-current plasma treatment. The plasma activated surface allows for the subsequent linker-free immobilisation of hyaluronic acid (HA) that helps to retain improved wettability. As HA is attached only to the plasma treated area of the material, a scaffold with a hydrophobic side and a superhydrophilic side can be created. Appropriate modification did not affect the morphology or mechanical properties of the scaffold, while improving scaffold wettability. The immobilised HA not only conferred high biocompatibility, but also stabilised the superhydrophilic surface against hydrophobic recovery. Cell proliferation assay demonstrated better cell adhesion to hydrophilic side modified with HA rather than hydrophobic. The proposed approach can potentially realise biomaterials with gradual wettability from biodegradable polymers.

O 69.12 Wed 17:45 Poster B2

Interfacial reactivity and adhesive properties of ternary transition metal nitride hard coatings in contact with polymers — ●MARTIN WIESING — Universität Paderborn, Paderborn, Germany

The surface oxidation behaviour of the prototypical nitric hard coating Ti_{0.5}Al_{0.5}N and its adhesive interactions with polycarbonate were investigated and related to its surface chemical and defect structure. The joint ion and electron spectroscopic analysis of the thermal and electrochemical surface oxidation allowed to develop a microscopic model of oxidation spanning the range from the early stages of oxidation to the formation of thick oxidation layers. The results corroborate the high significance of the surface electronic and defect structure for the reactivity of the metal-like and oxidic surfaces of Ti_{0.5}Al_{0.5}N.

UHV based Dynamic Force Spectroscopy (DFS) was performed to reveal the nature of the force interactions between Ti_{0.5}Al_{0.5}N and polycarbonate and their intimate relation to the surface oxide structure.

A novel experimental approach for the analysis of van der Waals forces based on Lifshitz theory combined with Reflection Electron Energy Loss Spectroscopy (REELS) was introduced to complement the force analysis. The method allows for the first time to determine highly accurate Hamaker coefficients of thin surface layers (>1 nm).

The here presented results are highly significant for understanding the corrosion and oxidation behaviour of hard coatings and to control their adhesive behaviour in contact with polymers.

O 69.13 Wed 17:45 Poster B2

Hybrid Zipper-Like Biopolymer Sorbents with Tunable Anion Sorption Properties — ●INIMFON UDOETOK¹, LEE WILSON¹, and JOHN HEADLEY² — ¹Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan, S7N 5C9 — ²Water Science and Technology Directorate, Environment and Climate Change Canada, 11 Innovation Boulevard, Saskatoon, Saskatchewan, S7N 3H5

Quaternary composite (CGCFe) and ternary composite (CCFe) materials with variable morphology were prepared from carboxymethyl cellulose (CMC), chitosan, glutaraldehyde as the cross-linker, while iron III species acted as Lewis acid sites to impart unique anion binding properties. Characterization results provided evidence of cross-linking between the amine groups of chitosan and glutaraldehyde, variable iron doping and morphology for the composites. Equilibrium uptake results indicate that CGCFe surpassed the sorption capacity of CCFe, where greater uptake was noted at lower temperature. The monolayer sorption capacity of CGCFe for 2-naphthoxy acetic acid (S6) was 263 mg/g and 484 mg/g at alkaline and acidic pH conditions, respectively, with limited discrimination of OSPW naphthenate components, according to variable DBE or molecular weight range. Regeneration studies showed that CGCFe retained 95% of its sorption capacity after 5 cycles through a saline responsive zipper-like structural transition. This study provides insight on the role of Fe (III) species, cross-linking, and biopolymer structure that relate to anion binding properties in aqueous solution.

O 69.14 Wed 17:45 Poster B2

AFM as a unique tool for biological surface science: from collagen nanobiomaterials and cell guidance to cancer biomark-

ers and beyond — ●ANDREAS STYLIANOU — Cancer Biophysics Laboratory, University of Cyprus, Nicosia, Cyprus

Atomic Force Microscopy (AFM) belongs to the scanning probe microscopy family and is one of the most popular techniques in surface science, including biological surface science and biomaterials. As the majority of biological interactions/reactions occur on surfaces or interfaces, it is of crucial importance to investigate the involved phenomena at the nanoscale level. In my talk, I will present the use of AFM as a unique tool in biological surface science based on my previous and ongoing research results. I will demonstrate the use of a number of AFM techniques in order to study (i) collagen thin film nanoscale formation and (ii) laser/optical radiation-collagen interactions [e.g., second harmonic generation (SHG), low level laser-(LLL) and ultraviolet-(UV)]. Furthermore, I will show how AFM can be used in order to investigate the effects of surface nanocharacteristics (nanotopography, nanomechanical properties) on cell-collagen interactions and how these characteristics guide cells, including their shape, orientation, mechanical properties and their migration/invasion properties. Finally, I will discuss recent and ongoing work aimed at using AFM techniques as a diagnostic tool for assessing cancer biomarkers for cancer cell identification, cancer diagnosis and therapeutic response prediction.