

O 97: Organic/bio Molecules on Metal Surfaces IV

Time: Friday 10:30–13:00

Location: TRE Phy

O 97.1 Fri 10:30 TRE Phy

Dispersion Corrected DFT Calculations for the Adsorption of Phthalocyanines on Au(111) — ●JOHANN LÜDER, OLLE ERIKSSON, BIPLAB SANYAL, and BARBARA BRENA — Uppsala University, Box-516, 75120 Uppsala, Sweden

An accurate description of physisorbed systems including dispersion, e.g. van der Waals, forces is still a challenge in density functional theory (DFT). We have investigated the adsorption of the technological relevant metal-free Phthalocyanine (H₂Pc) and Copper-Phthalocyanine (CuPc) on Au(111). We compared several available methods including pair-potentials and sparse-matter functionals for a monolayer of H₂Pc on Au(111). The calculations of H₂Pc on Au(111) showed that accurate results were obtained with optB86b-DF1 and the Tkatchenko-Scheffler (TS) method. The adsorption of CuPc on the same surface was studied with the TS method, and the accuracy of the obtained results was confirmed by recent experimental X-ray standing wave measurements.

O 97.2 Fri 10:45 TRE Phy

From terpyridine species to metal organic coordination networks — ●THOMAS DIENEL¹, ROLAND WIDMER¹, RALPH KOITZ², MARCELLA IANNUZZI², A. DIETER SCHLÜTER³, JÜRIG HUTTER², and OLIVER GRÖNING¹ — ¹nanotech@surfaces Lab, Empa, Überlandstrasse 129, CH-8600 Dübendorf, Schweiz — ²Department of Chemistry, University of Zurich, CH-8057 Zurich, Schweiz — ³Department of Materials, Institute of Polymers, ETH Zurich, CH-8093 Zurich, Schweiz

Substrate-supported metal organic coordination networks offer the possibility to adjust electronic and magnetic properties on the nanometer scale and represent a step towards the realization of two-dimensional polymers [1]. Here, we report on the adsorption behavior of trifunctional terpyridine monomers on coinage metals by means of low-temperature scanning tunneling microscopy. On copper (Cu(111)), the orientation of the terpyridine molecules exhibits a pronounced anisotropy, while a similar behavior was not observed for silver and gold. This is analyzed by density functional theory, revealing specific registries between the monomers and the corresponding substrates. We discuss the impact of this registry on the formation of self-assembled metal organic coordination networks by copper or iron adatoms.

[1] T. Bauer, Z. Zheng, A. Renn, R. Enning, A. Stemmer, J. Sakamoto, A.D. Schlüter, *Angewandte Chemie International Edition*, 50, 7879-7884 (2011).

O 97.3 Fri 11:00 TRE Phy

Surface-assisted synthesis of large hydrocarbon macrocycles: Honeycombenes and their organometallic intermediates — QITANG FAN¹, CICI WANG¹, YONG HAN¹, JUNFA ZHU¹, MIN CHEN², HANS-JÖRG DRESCHER², MALTE ZUGERMEIER², HAN ZHOU², JULIAN KUTTNER², GERHARD HILT², WOLFGANG HIERINGER³, and ●J. MICHAEL GOTTFRIED² — ¹National Synchrotron Radiation Laboratory, University of Science and Technology of China — ²Fachbereich Chemie, Philipps-Universität Marburg, Germany — ³Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Germany

Honeycombenes constitute a novel class of hexagonal hydrocarbon macrocycles, which are made by surface-assisted synthesis. The basic representative is [18]-honeycombene or hyperbenzene, a hexagon consisting of 18 phenyl rings.[1] The macrocycle was synthesized by surface-assisted Ullmann coupling of six 4,4"-dibromo-m-terphenyl (DBTP) precursor molecules on Cu(111). Hyperbenzene assembles to form close-packed islands with hexagonal symmetry. As intermediates of the surface Ullmann reaction, stable cyclic and linear organometallic species with C-Cu-C bonds have been observed. Their large diameters (2 nm for [18]-honeycombene) make the honeycombenes promising candidates for nanotroughs that could host metal and semiconductor particles or large organic molecules. [1] Q. Fan, C. Wang, Y. Han, J. Zhu, W. Hieringer, J. Kuttner, G. Hilt, J. M. Gottfried, *Angew. Chem. Int. Ed.* 52 (2013) 4668.

O 97.4 Fri 11:15 TRE Phy

Hydrogen-bonded networks of triarylamine molecules on noble metal surfaces — ●CHRISTIAN STEINER¹, DAVID GESSNER¹,

UTE MEINHARDT², BETTINA GLIEMANN², MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, University of Erlangen-Nürnberg, Germany — ²Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Germany

Hydrogen bonding is a highly directional interaction that has successfully been applied towards the construction of complex supramolecular architectures both in bulk and on surfaces. Here, we present a low temperature scanning tunneling microscopy study of hydrogen-bonded networks on noble metal surfaces using triarylamine derivatives functionalized with diaminotriazine and carboxylic moieties as molecular building blocks. While on Au(111) extended hexagonal hydrogen-bonded networks with different pore-sizes are formed, the strong surface-molecule interaction leads to different hydrogen-bonded assemblies on Cu(111). In addition, we performed comparative STM measurements of the same triarylamine networks formed from solution on HOPG in ambient conditions and discuss their structure and stability. Such self-assembled organic nanostructures formed at room temperature and atmospheric pressure are highly appealing with respect to applications.

O 97.5 Fri 11:30 TRE Phy

Steering on-surface polymerization of dibromopyrene on metal substrates — ●FEI SONG¹, TUAN ANH PHAM¹, JONAS BJORK², and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, the Netherlands — ²Department of Physics Chemistry and Biology, Linköping University, Sweden

Self-assembly of functional molecular building blocks into supramolecular structures has attracted a wealth of attention in the past due to its potential usage in molecular devices [1]. However, a drawback of such regular nanostructures is, due to their comparably weak intermolecular interactions, poor thermal and chemical stability. Consequently, robust structures with covalently bonded architectures have attracted much attention as a new alternative route towards the design of nanostructures [2]. Herein, we discuss the formation of stable molecular networks on different metal substrates through on-surface polymerization of the molecular precursor dibromopyrene. The investigations were carried out by using a combination of scanning tunneling microscopy, x-ray photoemission spectroscopy, and density functional theory. We demonstrate that the surface-confined polymerization can be steered by the chosen substrate. [1] Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* 2005, 26, 3245. [2] Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M.; Peters, M. V.; Hecht, S. *Nature Nanotech.* 2007, 2, 687.

O 97.6 Fri 11:45 TRE Phy

Predicting the mechanochemical behavior of multivalent thiol ligands on gold surfaces from free energy relationships — ●MARTIN ZOLOFF MICHOFF, JORDI RIBAS-ARINO, and DOMINIK MARX — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780, Bochum, Germany

Free energy relationships have been widely used in physical organic chemistry in the past 50 years to predict the reactivity of molecules in solution. Recently, it has been shown that this kind of analysis can also be applied to molecular systems adsorbed on transition metal surfaces [1]. In the last 10 years, we have been interested in our group in the mechanochemical properties of thiols adsorbed on metallic surfaces such as Au or Cu [2]. We will present a significant amount of data that shows that the binding strength and the mechanical behavior of the thiol – gold bond can be predicted in terms of the electronic properties of the molecular systems and making use of free energy relationships. On one side, we have focused on monothiols, because they provide a straightforward way of tuning their electronic structure properties by means of changing a substituent in the molecule. On the other, we have also investigated multivalent thiolated molecules, which are more interesting from the point of view of their potential applications, such as providing the anchoring for biocompatible polymers used to coat gold nanoparticles in medical applications [3].

[1]R. A. van Santen *et al. Chem. Rev.* 2010, 110, 2005–2048. [2] J. Ribas-Arino, D. Marx *Chem. Rev.* 2012, 112, 5412–5487. [3] J. V. Jokerst *et al. Nanomedicine* 2011, 6, 715–728.

O 97.7 Fri 12:00 TRE Phy

Subphthalocyanine based nanocrystals — ●MARTA TRELKA^{1,2}, ANAÍS MEDINA³, DAVID ÉCJA², CHRISTIAN URBAN², OLIVER GRÖNING⁴, ROMAN FASEL⁴, JOSÉ GALLEGOS⁵, CHRISTIAN CLAESSENS³, ROBERTO OTERO^{2,6}, TOMÁS TORRES^{3,6}, and RODOLFO MIRANDA^{2,6} — ¹University of Bielefeld, 33615 Bielefeld, Germany — ²Universidad Autónoma de Madrid, 28049 Madrid, Spain — ³Universidad Autónoma de Madrid, 28049 Madrid, Spain — ⁴Empa Swiss Federal Laboratories for Materials Testing and Research, 3602 Thun, 8600 Dübendorf, Switzerland — ⁵Instituto de Ciencia de Materiales de Madrid, 28049 Madrid, Spain — ⁶Instituto Madrileño de Estudios Avanzados en Nanociencia, 28049 Madrid, Spain

We will present Scanning Tunneling Microscopy studies on Subphthalocyanine (SubPc) molecules that lead to the formation of 3D nanocrystals on a Cu(111) surface. Subphthalocyanine molecules are significantly large macrocycle aromatic structures with a boron atom in the center. Strong molecule-molecule interactions can be expected due to the high dipole moment along the boron-ligand axis. For molecules with a chlorine atom linked to the boron axis, the formation of the organic nanocrystals is found to increase the coverage of sublimated molecules on the surface. The nanocrystals grow up to third layer creating trimers imaged as a bright protrusion. In the studies, the importance of the dipole moment for the growth process is presented. Taking into account the obtained data it is concluded that organic molecules can lead to growth at a metal surface into nanocrystals.[1]

[1] SubPc based nanocrystals Chem. Comm. (2011) 47,9986-9988

O 97.8 Fri 12:15 TRE Phy

Fabrication of ssDNA/oligo(ethylene glycol) monolayers and complex nanostructures and brushes by promoted exchange reaction — M. NURUZZAMAN KHAN and ●MICHAEL ZHARNIKOV — Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

Using a representative test system, we present here a versatile approach to prepare mixed monolayers of thiolate-bound single stranded DNA (ssDNA) and oligo(ethylene glycol) substituted alkanethiols (OEG-AT) in a broad range of compositions as well as ssDNA/OEG-AT patterns of desired shape imbedded into biorepulsive background. The procedure involves two steps. First, primary, well-defined OEG-AT monolayer on a solid support is exposed to electrons or UV light in either homogeneous or lithographic fashion. Second, the promoted (by the irradiation in the first step) exchange reaction between the damaged OEG-AT species in the film and ssDNA substituents in solution occurs, resulting in formation of ssDNA/OEG-AT monolayer or pattern. The composition of the mixed films or ssDNA/OEG-AT spots (lithography) can be precisely adjusted by electron or UV dose in almost entire composition range. The above procedure relies on commercially available compounds and is applicable to both thiolate substituted and disulfide type ssDNA, both symmetric and asymmetric. The fabricated OEG-AT/ssDNA templates and patterns can be, if necessary, extended into the z-dimension by surface-initiated enzymatic polymerization, which may result in formation of highly ordered ssDNA brushes and in sculpturing complex ssDNA brush patterns.

O 97.9 Fri 12:30 TRE Phy

Conformation Selection by Charge State Dependent Deposition of Unfolded Proteins — ●GORDON RINKE¹, STEPHAN RAUSCHENBACH¹, LUDGER HARNAU^{2,3}, ALYAZAN ALBARGHASH¹, MATHIAS PAULY¹, and KLAUS KERN^{1,4} — ¹Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, Stuttgart — ²Max-Planck-Institute for Intelligent Systems, Heisenbergstr. 3, Stuttgart — ³IV. Institute for Theoretical Physics, University Stuttgart, Pfaffenwaldring 57, Stuttgart — ⁴Institut de Physique de la Matière Condensée, Ecole Polytechnique Federale de Lausanne, Switzerland

The conformation of polymers or proteins often define the electronic and mechanical properties of the single molecule just as well as the meso- and macro scale material properties. It is determined by the chemical interaction with itself and the environment in thermal equilibrium, which means that typically it cannot be addressed actively. Here we show that the conformation of unfolded Cytochrome proteins on a surface can be steered actively between fully extended and completely compact by electrospray ion beam deposition. The charge state and the deposition energy are free parameters in this approach, which can be used independently to control the molecules mechanical stiffness and the intensity of the collision. A quantitative analysis of the obtained conformations with scanning tunneling microscopy and molecular dynamics simulations show that, in addition to the initial gas phase conformation, the mechanical deformation during the ion surface-collision contributes significantly to the final conformation. Thus our methodology adds a new dimension to vacuum processing of molecules.

O 97.10 Fri 12:45 TRE Phy

Planarized Cyano-Functionalized Triarylamines on Coinage Metal Surfaces: Intermolecular vs. Molecule/Substrate Interactions — ●KATHRIN MÜLLER¹, STEFANO GOTTARDI¹, JUAN CARLOS MORENO LOPEZ¹, HANDAN YILDIRIM², UTE MEINHARDT³, ABDELKADER KARA², MILAN KIVALA³, and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, Netherlands — ²Department of Physics, University of Central Florida, Orlando, USA — ³Department of Chemistry and Pharmacy, University Erlangen-Nürnberg, Germany

The formation of well-ordered molecular networks on surfaces has gained increasing attention over the last decades due to their application in devices for molecular electronics. However, the intermolecular as well as the molecule/substrate interactions, which govern the self-assembly process, are often not well understood. We conducted a detailed study of a cyano-functionalized triarylamine molecule on different coinage metal surfaces. By using scanning tunneling microscopy and density functional theory studies we found that the substrates play a crucial role in the self-assembly process. While on Au(111) two different well-ordered phases with micrometer sized domains were found, on Cu(111) only small patches of close packed molecules were observed next to a disordered phase. In contrast only one close-packed phase with micrometer sized islands was found on Ag(111). This study shows that although coinage metal surfaces are considered to be passive they can strongly influence the molecular self-assembly, due to their different electronic and structural corrugation.