O 6: Organic/bio Molecules on Metal Surfaces I

Time: Monday 10:30–13:15 Location: TRE Phy

O 6.1 Mon 10:30 TRE Phy

Deposition and Characterization of Large Magnetic Molecules on Surfaces — •Judith Niedenführ[1], Bastian Feldscher[2], Jan-Philipp Broschinski[2], Thorsten Glaser[2], Andrei Postnikov[3], and Daniel Wegner[1] — [1]Westfälische Wilhelms-Universität, Münster, Germany — [2]Universität Bielefeld, Bielefeld, Germany — [3]Université de Lorraine, Metz, France

A key to building functional devices on the basis of single molecule magnets (SMMs), be it for potential high-density memory storage or molecular-electronics applications, is the ability to deposit and manipulate these nanomagnets on surfaces in a controllable and reproducible way. The typical evaporation process is not applicable, because it would lead to dissociation of these large organic molecules. We used two different unconventional preparation techniques, namely pulse injection and rapid heating, for in-situ deposition of the Cu_3-triplesalen complex onto a Au(111) surface. These complexes are the building blocks for a new generation of promising SMMs, which combine a high-spin ground state with a large magnetic anisotropy. The comparison of both techniques allows us to evaluate their advantages and drawbacks. The Cu_3-triplesalen molecules have been studied using a combination of scanning tunneling microscopy (STM) and spectroscopy (STS). We discuss details of the electronic structure and its consequences on the internal spin coupling and compare these with first-principle calculations within the framework of the density-functional theory. The comparison is also done for the slightly modified Cu_3-triplesalalen complex which is designed to exhibit an enhanced ferromagnetic coupling.

O 6.2 Mon 10:45 TRE Phy

Addressing the metal centers in multi-spin-center macromolecule on Au(111) — •Maciej Bazarnik[1], Bernhard Bugenhagen[2], Annika Frank[2], Jens Brede[1], Marc H. Prosenc[2], and Roland Wiesedanger[1] — [1]Institute of Applied Physics, University of Hamburg, D-20355 Hamburg, Germany — [2]Institute of Inorganic Chemistry, University of Hamburg, D-20146 University of Hamburg, Germany

The use of magnetic molecules opens a gateway to a flexible design of novel spintronic devices to store, manipulate, and read spin information at the nanoscale. Crucial is the precise knowledge of molecular properties at the interface towards an electrode. Progress in this field relies on resolving and understanding the physics at the relevant interfaces. In particular the role of individual molecular constituents and the impact of the atomic environment on molecular properties determine device relevant parameters, such as conductance and spin polarization.

Here, we applied scanning tunneling microscopy to address individual metallic centers of multi-spin-center macromolecules. The analysis focuses on different triplesalophene molecules which have been deposited in vacuo on a Au(111) substrate by either using thermal sublimation or electrospray deposition. The triplesalophene constitutes of three organic salene-like ligands and can be functionalized with various metal ions in order to modify, e.g. the molecular spin state, and/or termination groups to manage the molecule-molecule interactions. We will discuss the influence of terminal groups on the physicochemical properties of the molecules.

O 6.3 Mon 11:00 TRE Phy

Tuning the electronic structure of metal-organic complexes at the molecule-substrate interface — •Pascal Raphael Ewen[1], Jan Sanning[1], Nikos Doltsinis[2], Cristian Alejandro Strassert[1], and Daniel Wegner[1] — [1]Physikalisches Institut, Westfälische-Wilhelms Universität Münster, Deutschland — [2]Institut für Festkörpertheorie, Westfälische-Wilhelms Universität Münster, Deutschland

The coupling of molecules at surfaces ranging from the weak (physisorption) to the strong interaction regime (chemisorption) plays a crucial role both in the physical and chemical behavior. Fundamental processes such as conformal changes, dissociation and charge transfer have been observed upon adsorption. A systematic investigation of the adsorption and the electronic structure of slightly differing phosphorescent Pt(II) complexes offers information about the influence of ligands and substituents on their interactions with neighbors and the substrate. We have studied the impact of molecule-surface and intermolecular interactions on the self-assembly and electronic structure of Pt-complex monolayers on Au(111) using scanning tunneling microscopy (STM) and spectroscopy (STS) at low temperature. By determining energies and spatial distributions of several frontier orbitals, we are able to evaluate the impact of coupling and hybridization on the molecular electronic states.

O 6.4 Mon 11:15 TRE Phy

Electronic structure and relaxation behavior of a thin Fe(II) spin-crossover film — •Eric B. Ludwig[1], Holger Naggert[2], Matthias Kalläne[1], Sebastian Rohlf[1], Erik Kröger[1], Alexander Bannwarth[2], Arndt Quer[1], Kai Rossnagel[1], Lutz Kipp[1], and Felix Tuczek[2] — [1]Institut für Experimentelle und Angewandte Physik, Universität Kiel, D-24098 Kiel — [2]Institut für anorganische Chemie, Universität Kiel, D-24098 Kiel

Coordinative Fe(II) complexes are model systems for organic molecules, whose optical, electronic and magnetic properties can be manipulated by external stimuli. Moreover, the temperature- and irradiation-dependent spin transitions observed in a number of these materials may provide a suitable testbed toward the development of future spintronic devices.

Here, we present a ultraviolet photoelectron spectroscopy study on a vacuum-deposited thin film of $Fe(H_2bpz)_2(phen)$ on Au(111). Spectral features sensitive to the spin transition can be identified via comparison of the results of density functional calculations with the results of valence band measurements at different temperatures and varying irradiation conditions.

Our results provide evidence for a VUV-induced spin-state trapping effect at low temperatures. Furthermore, a high optical photon flux seems to stabilize the metastable high-spin state far above the LIESST transition temperature. The overall high- to low-spin relaxation behavior, however, shows similarities to amorphous samples of a related system.

O 6.5 Mon 11:30 TRE Phy

Fe on metalloporphyrin arrays: Site-selective adsorption, atomic switching and modification of magnetic moments — Saranyan Vijayaraghavan[1], •Willi Auwärter[1], David Ecija[1], Knud Seufert[1], Uta Schlickum[2,3], Markus Etzkorn[2,3], Stefano Rusponi[3], Pardeep K. Thakur[4], Sebastian Stepanov[2], Torsten Houwaart[5], Philippe Sautet[5], Marie-Laure Bocquet[5], Harald Brune[3], and Johannes V. Barth[1] — [1]Technische Universität München, Department of Physics, E20, Garching, Germany — [2]Max Planck Insitut für Festkörperforschung, Stuttgart, Germany — [3]Ecole Polytechnique Fédérale de Lausanne, Institut de Physique de la Matière Condensée, Lausanne, Switzerland — [4]European Synchrotron Radiation Facility, Grenoble, France — [5]Ecole Normale Supérieure de Lyon, Laboratoire de Chimie, Lyon, France

The confinement and ordering of nanoscale objects as individual atoms or molecules on substrates has gained widespread attention in recent years leading to the realization of individually addressable quantum arrays. Here, we use highly regular metalloporphyrin (Co-TPP) arrays on a Ag(111) support as template for the site-specific adsorption of Fe. Our multi-technique approach combining scanning tunneling microscopy, X-ray magnetic circular dichroism and complementary density functional theory calculations reveals an interaction between the Fe and the Co center of the porphyrin, reviving the magnetic moment of the latter, which was quenched upon adsorption. Furthermore, individual Fe atoms can be switched between four equivalent positions on the porphyrin macrocycle, reflecting the molecular saddle-shape.

O 6.6 Mon 11:45 TRE Phy

On the role of Entropy in conformational molecular switching of porphyrins on Cu(111) — Stefanie Ditze[4], Michael Stark[4], Florian Buchner[4], Andre Aichert[1], Norbert Jux[2], Nicola Luckas[3], Andreas Görling[3], Wolfgang Hieringer[3], Joachim Hornegger[1], Hans-Peter Steinrück[4], and •Hubertus Marbach[4] — [1]Lehrstuhl für Mustererkennung — [2]Lehrstuhl für Organische Chemie II — [3]Lehrstuhl für Theoretische Chemie — [4]Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

We observe and induce conformational switching of individual molecules via scanning tunneling microscopy (STM) at and close to room temperature. 2H-5,10,15,20-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin (2HTTBPP) adsorbed on Cu(111) forms a peculiar supramolecular ordered phase: the molecules arrange in alternating rows, with two distinct appearances in STM, which are assigned to concave and convex intramolecular conformations. Around room temperature, frequent bidirectional conformational switching of individual molecules from concave to convex and vice versa is observed. From the temperature dependence, detailed insights into the energy barriers and entropic contributions of the switching processes are deduced. With this contribution, we demonstrate that entropic effects can be a decisive factor for the self-assembly and the conformational switching behaviour of molecules at these temperatures.

O 6.7 Mon 12:00 TRE Phy

Switching and charging of a ruthenium dye — •Nadine Hauptmann[1], Christian Hamann[1], Hao Tang[2], and Richard Berndt[1] — [1]Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany — [2]CEMES/CNRS 29, rue Jeanne Marvig, B.P. 94347, 31055 Toulouse Cedex, France/ Université de Toulouse, UPS, 31055 Toulouse, France

The ruthenium dye N3 (cis-bis(isothiocyanato)bis-(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)), is deposited on metal surfaces by ultrahigh vacuum electrospray ionization and is investigated using low-temperature scanning tunneling microscopy. Scanning tunneling spectroscopy of single molecules reveals vibronic excitations that are related to the lowest unoccupied molecular orbital. Switching of N3 molecules attached to Ag(111) step edges may be induced and modifies the energy of the negative ion resonance as well as the vibrational progression. Moreover, charging of the molecule is induced at reversed bias. This data suggests a surprisingly weak electronic coupling of N3 to the Ag substrate. A double-barrier model reproduces the essential spectral features.

O 6.8 Mon 12:15 TRE Phy

Charge switching in a self-assembled acceptor-donor complex — •Paul Stoll[1], Janina N. Ladenthin[1], Tobias R Umbach[1], Christian Lotze[1], Isabel Fernandez Torrente[1], Nacho Pascual[2], and Katharina J. Franke[1] — [1]Fachbereich Physik, Freie Universität Berlin — [2]CIC NanoGUNE, San Sebastian

The switching mechanisms between metastable states in molecules is based on fundamental quantum physics and is potentially valuable for future applications in molecular electronics. We investigate the charge-transfer complex tetracyanoethylene (TCNE) and tetrathiafulvalene (TTF) on a Au(111) surface using low temperature scanning tunneling microscopy and spectroscopy. The molecules self-assemble in highly ordered islands with different stoichiometries. The TCNE molecules are found in two different charge states that are identified by the presence or abscence of a Kondo resonance. The rates of the random switching between these states are controlled by the tunneling current and the applied bias.

O 6.9 Mon 12:30 TRE Phy

Diarylethene molecules on a Ag(111) surface: stability and electric field-induced switching of single molecules — •Nino Hatter[1], Jonas Wirth[2], Robert Drost[1], Tobias R. Umbach[1], Sara Barja[1], Marc Zastrow[3], Karola Rück-Braun[3], Jose I. Pascual[4], Peter Saalfrank[2], and Katharina J. Franke[1] — [1]Institut für Experimentalphysik, Freie Universität Berlin, Germany — [2]Institut für Chemie, Universität Potsdam, Germany — [3]Institut für Chemie, Technische Universität Berlin, Germany — [4]CIC nanoGUNE, Dondostia-San Sebastian, Spain

Diarylethene derivatives are photochromic molecular switches, existing in two different forms, a ring-closed one with a conjugated π electron system and a ring-opened, where the conjugation is broken. Light irradiation can induce a reversible ring-opening/closing reaction, as has been shown for molecules in solution and bulk crystals. However, little is known about their switching behaviour when adsorbed on surfaces.

We present a combined approach of scanning tunneling microscopy/spectroscopy (STM/STS) and density functional theory (DFT) calculations of 4,4'-(4,4'-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl)dipyridine (PDTE) adsorbed on a Ag(111) surface. The STM measurements show only one isomer present on the surface after evaporation of PDTE which can be switched by controlled manipulation with the STM tip. Comparison to the DFT calculations suggests that the manipulation with the tip induces the ring-closure reaction.

O 6.10 Mon 12:45 TRE Phy

STM Induced Light Emission from Organic Molecules on Surfaces — •Maren C. Cottin, Ebru Özen, Tobias Roos, Doris Steeger, Detlef Utzat, Willy Platz, Rolf Möller, and Christian A. Bobisch — Faculty of Physics, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany

Most STM techniques rely on the elastic part of the tunneling current. In contrast, STM induced light emission (STM-LE) experiments analyze the excitation mechanisms in the tip sample junction due to inelastic tunneling processes. Laterally resolved photon maps reveal the specific sites of excitation [1,2], while spectra of the overall light intensity as a function of bias voltage as well as energy resolved spectra of the emitted light can be used to characterize and identify the involved radiative decay channels [3]. Here, we use STM-LE to characterize various organic/metal interfaces. E.g., we present intermolecularly resolved photon maps of the archetype molecule C_{60} on different substrates. From energy resolved spectra of the emitted light we try to identify the involved decay channels.

[1] R. Berndt et al., Science **262**, 1425 (1993).
[2] C. Chen et al., Phys. Rev. Lett. **105**, 217402 (2010).
[3] R. Berndt et al., Ultramicroscopy **42 − 44**, 355 (1992).

O 6.11 Mon 13:00 TRE Phy

Investigation of novel partial charge-transfer compounds based on triangulene derivatives by ultraviolet photoelectron spectroscopy (UPS) and near-edge X-ray adsorption fine structure (NEXAFS) — •Alisa Chernenkaya[1,2], K. Medjanik[2], M. Kivala[3], P. Nagel[4], M. Merz[4], S. Schuppler[4], T. Shubina[5], M. Baumgarten[3], K. Müllen[3], and G. Schönhense[2] — [1]Graduate School Materials Science in Mainz, 55128, Mainz, Germany — [2]Inst. für Physik, JGU, 55128, Mainz, Germany — [3]MPIP, 55021 Mainz, Germany — [4]KIT, Inst. für Festkörperphys., 76021 Karlsruhe, Germany — [5]Comp.-Chem.-Cent., 91052 Erlangen, Germany

A new class of donors and acceptors is represented by derivatives of the (4,4,8,8,12,12-hexamethyl-4*H*,8*H*,12*H*-benzo[1,9]quinolizino[3,4,5,6,7-defg]acridine) [1], so-called triangulene. We present UPS and NEXAFS results for molecular beam deposited thin films of triangulene and its trimethoxy derivative donors in complexes with the strong F4-TCNQ acceptor in comparison with density functional theory (DFT) calculations. The whole information about density of states (occupied valence states and unoccupied ones as well) in these charge-transfer systems is provided by these techniques as previously shown for pyrene derivatives [2]. We also compared CT complexes formation and film growth mechanisms in two systems that differ in three methoxy groups only.

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[1] M. Kivala et. al., Chem. Eur. J., 19, 8117-8128 (2013).
[2] K. Medjanik et. al., JACS 134, 4694-4699 (2012).