

## O 41: Focus Session: Functional Molecules at Surfaces II

Time: Tuesday 10:30–13:00

Location: TRE Ma

O 41.1 Tue 10:30 TRE Ma

**Tip-induced inversion of the chirality of a molecule's adsorption potential probed by the switching directionality** —

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The switching behaviour of surface-supported molecular units is determined by the shape of the adsorption potential. Here, by means of scanning tunneling microscopy, we study a triazatruxene (TAT) molecule on Ag(111), which shows a switching behavior characterized by transitions of the molecule between three states, and which we attribute to three energetically degenerate bonding configurations. Upon tunneling current injection the system can be excited, showing a pronounced switching directionality. Two surface enantiomers of TAT show opposite switching directions pointing at the chirality of the energy landscape of the adsorption potential as a key ingredient for directional switching. Further we show that by modifying the tunneling parameters, the symmetry of the adsorption potential can be controlled, leading to a suppression of the directionality or an inversion of the switching direction.

**Invited Talk**

O 41.2 Tue 10:45 TRE Ma

**Molecular switches at surfaces** — ●PETRA RUDOLF — Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

Molecular motors and switches form the basis of many important biological processes. In contrast to these solutions chosen by Nature for achieving complex tasks, mankind's present day technologies function exclusively through their static or equilibrium properties. One can therefore easily anticipate that the controlled movement of molecules or parts of molecules offers unprecedented technological possibilities for the future. In this presentation I shall show how to build molecular engines that allow movements at the molecular level to be coupled to the macroscopic world, e.g. to transport macroscopic objects like drops of liquid over a surface. I shall also discuss self-assembled monolayers of switches that can be addressed with light and charge transfer and demonstrate how such systems can be employed for \*read and write\* functions.

O 41.3 Tue 11:15 TRE Ma

**The role of double bond isomerization in the design of functioning metal-adsorbed molecular switches** — ●MARTIN LEA<sup>1</sup>, VASILIOS G. STAVROS<sup>1</sup>, DAVID A. DUNCAN<sup>2</sup>, and REINHARD J. MAURER<sup>1</sup> — <sup>1</sup>Department of Chemistry, University of Warwick, Coventry, United Kingdom, CV4 7AL — <sup>2</sup>Diamond Light Source, Didcot, United Kingdom, OX11 0DE.

Photoswitches are a class of organic molecules which have the ability to reversibly interconvert between two geometric states as a response to light absorption. Integration of such organic molecules in electronic devices requires adsorption upon a metal surface, which most often leads to the loss of switching function. In the case of the well-studied photoswitch Azobenzene, this loss of function upon surface adsorption has been previously identified computationally as a loss of bistability in the ground state, which is caused by strong coupling of the central nitrogen double bond with the metal substrate. [Angew. Chem. Int. Ed. 51, 12009 (2012)] However, it is unclear if this effect is common to all switches based on double bond isomerization or unique to the case of Azobenzene. In this study, we perform dispersion-inclusive Density Functional Theory calculations on a set of similar metal-adsorbed molecular switches which differ in the chemical composition of the photochromic moiety. By comparing the structure, stability, and electronic properties of metal-adsorbed molecular conformers, we establish mechanistic trends, which will potentially guide the design and synthesis of molecular switches in the future.

O 41.4 Tue 11:30 TRE Ma

**STM-induced tautomerization of phthalocyanines on BiAg<sub>2</sub>/Ag(111)** — ●MARKUS BÖHME<sup>1</sup>, MARKUS LEISEGANG<sup>1</sup>, DAVID MAIBERGER<sup>1</sup>, and MATTHIAS BODE<sup>1,2</sup> — <sup>1</sup>Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Wilhelm Conrad Röntgen Center for Complex Material Systems (RCCM), Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Organic molecules such as deprotonated phthalocyanines can show a tautomerization process in which the inner hydrogen atom changes its position. This electron-induced process cannot only be triggered when the STM tip is positioned directly above the molecule, but also by injecting charge carriers into the substrate a few nm away from the molecules [1,2]. Whereas experiments have mostly been performed on noble metals with a relatively simple electronic structure, such as Ag(111) with its electron-like quasi-free surface state, we will focus in this talk on a surface with a more complex band structure, i.e., the BiAg<sub>2</sub> surface alloy on Ag(111) which exhibits a giant Rashba effect [3]. We will present voltage- and current-dependent data of the tautomerization rate of HPc on BiAg<sub>2</sub>/Ag(111) and discuss the angular dependency of the switching rate of the molecule.

[1] P. Liljeroth *et al.*, *Science* **317**, 1203-1206 (2007).[2] M. Leisegang *et al.*, *Nano. Lett.* **18**, 2165 (2018).[3] C. Ast *et al.*, *Phys. Rev. Lett.* **98**, 186807 (2007).**Invited Talk**

O 41.5 Tue 11:45 TRE Ma

**Molecular Nanoprobe - utilizing a single molecule as detector** — ●MARKUS LEISEGANG — Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The transport properties of electrically conducting materials are determined by charge carriers scattering at electrons, phonons, and defects. A fundamental understanding of the underlying processes will require experiments on the level of single defects, bringing along the necessity of resolving transport properties down to the nanometer or even atomic scale. One approach towards this goal has been the development of multi-probe STMs, but their minimal tip-tip distance is usually limited to > 30 nm [1]. To circumvent this limitation, we invented the molecular nanoprobe (MONA) technique [2]. In MONA we utilize a charge-induced switching between discrete states of a single surface-adsorbed molecule, e.g. a tautomerization process, to detect the current injected remotely by the STM tip. Due to the local, near-field charge injection mechanism and the small size of the detector molecule, MONA allows for transport measurements in atomically controlled environments and over distances of a few nanometers. Our investigations on Ag(111) with its electron-like surface state show how scattering and interference processes affect the atomic-scale transport. Furthermore, we reveal the influence of the atomic lattice on transport properties in anisotropic surfaces.

[1] S. Yoshimoto *et al.*, *Nano Lett.* **7**, 956-959 (2007).  
[2] M. Leisegang *et al.*, *Nano Lett.* **18**, 2165-2171 (2018).

O 41.6 Tue 12:15 TRE Ma

**Quantum Tunneling in Intramolecular Hydrogen Transfer: The Case of Porphycene on Metal Surfaces** — ●YAIR LITMAN<sup>1</sup> and MARIANA ROSSI<sup>1,2</sup> — <sup>1</sup>Fritz Haber Institute of the Max Planck Society, Berlin, Germany. — <sup>2</sup>MPI for Structure and Dynamics of Matter, Hamburg, Germany

The intramolecular hydrogen transfer (IHT) of porphycene represents a paradigmatic process where nuclear quantum effects and anharmonicity result in unconventional hydrogen dynamics[1]. Here, we study the IHT of porphycene adsorbed on Cu and Ag surfaces at different temperatures. We couple density functional theory calculations including dispersion corrections with the ring-polymer instanton method[2]. This combination gives us access to unprecedented full-dimensional quantum mechanical reaction rates for porphycene on Cu(110) and Ag(110) in the deep tunneling regime. We predict rates in excellent agreement with experiments [3,4] and show the importance of heavy-atom tunneling in the reaction. We address the thus-far unexplained temperature dependence of the IHT and reveal that the observed activation energy is related to the energy difference between reactant and product, rather than reactant and transition state. Finally, we unequivocally identify

the IHT mechanism as stepwise for Cu(110) and show the existence of a sharp transition between concerted and stepwise mechanisms on Ag(110) surface. [1] Y. Litman, et al., J. Am. Chem. Soc. 141, 2526 (2019); [2] J. O. Richardson and S. Althorpe, J. Chem. Phys. 131, 214106 (2009); [3] T. Kumagai, et al., Phys. Rev. Lett. 111, 246101 (2013); [4] M. Koch, et al., J. Am. Chem. Soc. 139, 12681 (2017).

O 41.7 Tue 12:30 TRE Ma

**Controlled switching of a single CuPc molecule on Cu(111)** — •THILO GLATZEL<sup>1</sup>, SWEETLANA FREMY-KOCH<sup>1</sup>, ALI SADEGHI<sup>2</sup>, RÉMY PAWLAK<sup>1</sup>, SHIGEKI KAWAI<sup>3</sup>, ALEXIS BARATOFF<sup>1</sup>, STEFAN GOEDECKER<sup>1</sup>, and ERNST MEYER<sup>1</sup> — <sup>1</sup>Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland — <sup>2</sup>Department of Physics, Shahid Beheshti University, G.C., Evin, 19839-63113 Tehran, Iran — <sup>3</sup>International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki Tsukuba, Ibaraki 305-0044, Japan

Low temperature measurements of the tunneling current as a function of the applied bias voltage have been performed above individual copper phthalocyanine molecules adsorbed on Cu(111). By tuning of the applied bias, the molecule can be reversibly switched between two configurations. The underlying conformations are revealed by density functional calculations including van der Waals interactions, a  $C_{2v}$  symmetric ground state and two energetically equivalent states, in which the molecule is twisted and rotated around its center by  $\pm 7^\circ$ . For tip biases above 200mV position-dependent current switching is observed, as in previous measurements of telegraph noise [Schaffert et al., Nat. Mater. 12, 223 (2013)]. In a small voltage interval around zero the measured current becomes bistable. Switching to a particular state can be initiated by sweeping the voltage past well-defined pos-

itive and negative thresholds at certain positions above the molecule or by scanning at constant current and a reduced reverse bias.

O 41.8 Tue 12:45 TRE Ma

**Electronic Structure of a prototypical organic-inorganic interface: CuPc on In<sub>2</sub>O<sub>3</sub>(111)** — •MATTHIAS A. BLATNIK<sup>1</sup>, PETER JACOBSON<sup>2</sup>, MICHAEL SCHMID<sup>1</sup>, JAN ČEČAL<sup>3</sup>, ULRIKE DIEBOLD<sup>1</sup>, and MARGARETA WAGNER<sup>1,3</sup> — <sup>1</sup>Institute of Applied Physics, TU Wien, Wien, Austria — <sup>2</sup>School of Mathematics and Physics, University of Queensland, St. Lucia, Australia — <sup>3</sup>CEITEC, Brno University of Technology, Brno, Czech Republic

Indium oxide (In<sub>2</sub>O<sub>3</sub>) is a ubiquitous material in OLEDs and photovoltaics due to an ideally matched optical transmission window and metallic conduction at room temperature. When In<sub>2</sub>O<sub>3</sub> is paired with organic materials, a nearly universal fabrication step is the introduction of a thin organic buffer layer to improve the charge injection efficiency from In<sub>2</sub>O<sub>3</sub> to the organic active layers. Using a combination of STM, AFM and local spectroscopy (STS), we probe the adsorption structure and density of states at the prototypical copper phthalocyanine (CuPc) - In<sub>2</sub>O<sub>3</sub> interface. Two surface terminations were examined, the  $1 \times 1$  oxidized surface and the  $1 \times 1$  hydroxylated surface. Differential conductance ( $dI/dV$ ) measurements reveal the energetic positions of the HOMO and LUMO states which are critical for improving charge injection. STM/AFM imaging reveals single molecules adsorb in a flat, slightly tilted geometry in three symmetry-equivalent orientations. Increasing the coverage leads to a (densely packed) 1D chains oriented along the  $\langle 1\bar{1}0 \rangle$  directions. Finally, a  $(2 \times 2)$  superstructure with a building block consisting of three CuPc molecules is formed.