

O 74: Organic Molecules at Surfaces 5: Molecular Switches

Time: Thursday 15:00–18:00

Location: S054

O 74.1 Thu 15:00 S054

Reprogrammable molecular memory array based on chemical switching — •TOBIAS BIRK¹, ANJA BAUER¹, FABIAN PASCHKE¹, RAINER WINTER², and MIKHAIL FONIN¹ — ¹Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany — ²Fachbereich Chemie, Universität Konstanz, 78457 Konstanz, Germany

Technology on a molecular base promises highly interesting innovations for ultra-dense information storage devices and molecular electronics. Recently, a molecular three-state switch based on triazatruxene (TAT) on Ag(111) has been shown to have a great potential as data storage unit [1].

Here, we demonstrate the precise manipulation of the switching characteristics of individual TAT molecules within a 2D array using a low temperature scanning tunneling microscope (STM). By using the tip of the STM and the field applied within the contact, a successive pinning of the molecule via alkyl groups is achieved, leading to a gradual suppression of the current induced molecular switching. The possibility to reversibly switch between differently pinned molecules in combination with the three-level switching of the unpinned molecule offers the possibility to realize 9 states on a single molecule. We also demonstrate that the intermolecular interaction between the switches within the 2D array leads to a strong increase of the number of states, which can be detected on a single TAT unit, yielding up to 24 distinguishable states.

[1] A. Bauer et al., *Adv. Mater* 32, 1907390 (2020)

O 74.2 Thu 15:15 S054

Uni-directional rotation of molecular motors on Cu(111) — •MONIKA SCHIED^{1,2}, DEBORAH PREZZI³, DONGDONG LIU⁴, PETER JACOBSON^{1,5}, ELISA MOLINARI³, JAMES M. TOUR⁴, and LEONHARD GRILL¹ — ¹University of Graz, Austria — ²Elettra Sincrotrone Trieste, Italy — ³Nanoscience Institute of CNR, Italy — ⁴Rice University, USA — ⁵The University of Queensland, Australia

Artificial molecular motors that convert external energy into controlled motion have seen great developments in the last decades [1]. While many studies exist in solution, little is known how such functional molecules behave on a surface. However, such a solid support can be advantageous as it offers fixed points of reference as well as confinement in two dimensions, making it easier to study the directionality of their motion.

We have used low-temperature scanning tunnelling microscopy (STM) to study single molecules with a so-called Feringa motor [2,3] on a Cu(111) surface. It was found that rotations of individual molecules can be induced over rather long distances by voltage pulses with the STM tip. Importantly, these rotations show high directionality (clockwise or anticlockwise), which will be discussed in view of their specific chemical structure and adsorption.

[1] W. R. Browne and B. L. Feringa, *Nat. Nanotech.* 1, 25 (2006)

[2] T. Kudernac et al., *Nature* 479, 208 (2011)

[3] A. Saywell et al., *ACS Nano* 10, 10945 (2016)

O 74.3 Thu 15:30 S054

Precise control of single-molecule motion on Ag(111) — •DONATO CIVITA, GRANT SIMPSON, and LEONHARD GRILL — Department of Physical Chemistry, University of Graz, Austria

The motion of molecules adsorbed on metal single crystal surfaces is of fundamental importance in various fields such as heterogeneous catalysis, and on-surface polymerization. During diffusion, however, the motion of adsorbed molecules is characterised by random direction changes and thus control is limited. Moreover, adsorbates in the surroundings as well as substrate defects can strongly influence molecular motion.

With the use of a scanning tunnelling microscope (STM) at low temperature, we can control the motion of single di-bromo-ter-fluorene (DBTF) molecules on a Ag(111) surface over distances of more than 100 nm with picometric precision [1]. We find that a single molecule can move strictly along one atomic row across the surface. The molecule can be repelled or attracted by the STM tip, driven by an interplay of van der Waals and electrostatic interactions. The large spatial extension of the motion, and its unidimensional confinement

allow the direct measurement of the molecular velocity. Ultimately, this system demonstrates the possibility of studying the influence of surrounding adsorbates, crystal defects, and STM tip on the molecular motion and velocity.

[1] D. Civita, M. Kolmer, G. J. Simpson, A.-P. Li, S. Hecht, L. Grill, *Control of long-distance motion of single molecules on a surface*, *Science*, Vol. 370, Issue 6519, pp. 957-960 (2020).

O 74.4 Thu 15:45 S054

Dynamics of a chiral molecular rotor under a scanning-tunneling microscope — •RICHARD KORYTÁR¹ and FERDINAND EVERS² — ¹Charles University, Prague — ²Universität Regensburg

Motivated by an experimentally realized chiral molecular switch, we devise a classical theory of the switching process, relevant for molecular electronics. The system of interest is a chiral molecular rotor in a scanning-tunneling setup, i.e. the switching occurs under the electric current. The molecule is modeled by a path in three dimensions. The path is massive and can rotate around a fixed axis. The incident electron traverses the path, inducing a torque on the path. We represent this two-body dynamics in a Lagrangian formalism. Switching mechanism and switching rates are discussed.

O 74.5 Thu 16:00 S054

Bipolar single-molecule electrofluorochromism — •TZU-CHAO HUNG¹, ROBERTO ROBLES², BRIAN KIRALY¹, JULIAN H. STRIK¹, BRAM A. RUTTEN¹, ALEXANDER A. KHAJETOORIANS¹, NICOLAS LORENTE², and DANIEL WEGNER¹ — ¹Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands — ²Centro de Física de Materiales, CFM/MPC (CSIC-UPV/EHU), Paseo de Manuel de Lardizabal 5, 20018 Donostia-San Sebastián, Spain

The interplay between the charge state and the fluorescence of a molecule is not only important for the spectroscopic analysis of chemical reactions, but electrofluorochromic molecules can also be utilized in displays, sensors, and switches. To understand the fundamental mechanisms on the single-molecule level, we studied the transient charged state of zinc phthalocyanine (ZnPc) adsorbed on ultrathin NaCl films on Ag(111) by combining scanning tunneling microscopy (STM) and spectroscopy (STS) with STM-induced luminescence (STML). We found evidence for both cationic ([ZnPc]⁺) and anionic ([ZnPc]⁻) fluorescence, depending on the polarity of the tip-sample bias. By carefully mapping the molecular frontier orbitals over a wide energy range, correlating them with onset energies for light emission and comparing with results from DFT calculations, we propose an alternative charging and electroluminescence mechanism. Our study provides new insights into the tunability of molecular optical response, as well as novel aspects toward utilization of bipolar electrofluorochromism in devices.

O 74.6 Thu 16:15 S054

Electronic Motor Based on Single Tripodal Chiral Molecule — •JULIAN SKOLAUT¹, LUKAS GERHARD¹, NICO BALZER², MICHAL VALASEK², JAN WILHELM⁴, PHILIPP MARKUS⁵, MARCEL MAYOR^{2,3}, FERDINAND EVERS⁴, and WULF WULFHEKEL^{1,5} — ¹Institute for Quantum Materials and Technologies, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany — ²Institute of Nanotechnology, KIT, Eggenstein-Leopoldshafen, Germany — ³Department of Chemistry, University Basel, Basel, Switzerland — ⁴Institute of Theoretical Physics, University of Regensburg, Regensburg, Germany — ⁵Physikalisches Institut, KIT, Karlsruhe, Germany

We present our results concerning a single molecular motor driven by the current in an STM. Three anchoring groups fix the molecules to a Au(111) surface. In specific ordered structures, the molecules adsorb such, that the protruding head group is free to rotate. This chiral group is supposed to perform a rotation in a preferred direction, proposed to be driven based on the chiral-induced spin selectivity (CISS) effect. At fixed tip positions above the molecules, three distinguishable current levels can be observed. These are interpreted as metastable rotational states. That way, two rotation directions can be defined. Via binomial tests, we verify that the surplus of rotational switches in one direction compared to the other is statistically significant. In voltage and current dependent measurements, two interesting trends are observed. Firstly, the rate of events decreases with increasing current. Secondly, the asymmetry in the switching events shows non-monotonic

behavior, depending on the voltage.

O 74.7 Thu 16:30 S054

Proton Transfer in Single Asymmetric Porphycene Molecules

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Studying single molecular switches is of interest for a better understanding of fundamental physical and chemical processes, but also in view of their possible use in smart materials and nanoscale applications. It has been shown that switches based on tautomerization, i.e. hydrogen transfer, are especially suited for scanning tunneling microscopy (STM) studies, because the electronic states near the Fermi level are very sensitive to the position of the hydrogen atoms. Experiments on symmetric molecules such as naphthalocyanine [1], tetraphenyl-porphyrin [2], and porphycene [3] showed that the energies of the tautomers are degenerate, barring environmental modulation. Thus, if one is interested in switching processes with preferential switching directions between multiple states, structurally asymmetric molecules are of particular interest.

Here, we report STM results of the tautomerization properties of 22-Oxahemiporphycene, a derivative of porphycene with an asymmetric macrocycle, on a metal surface.

- [1] Liljeroth et al. *Science*, 317 (2007), 1203-1206
- [2] Auwärter et al. *Nature Nanotechnology*, 7 (2011), 41-46
- [3] Kumagai et al. *Physical Review Letters* 111 (2013), 246101

O 74.8 Thu 16:45 S054

Tuning the chirality change of a single molecule by van der Waals interactions

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The chiral induction and control of molecules by non-covalent intermolecular interactions, like hydrogen bonding and van der Waals interactions, is crucial to understand the origin of homochirality in nature. However, it remains challenging to address these subtle intermolecular interactions at a single-molecular level, especially the weakest of them, the van der Waals interactions. Here, by adsorbing a specifically designed carbene molecule on a copper surface, we examine the influence of the van der Waals interactions on the chirality induction by scanning tunneling microscopy. While the strongly binding carbene center of this molecule suppresses any side-reactions upon excitation, its two low-interacting phenyl rings facilitate a chirality change induced by inelastically tunneling electrons. The potential energy of the chirality change is modified by the van der Waals interactions in the presence of a tip. A marginal change induces an asymmetric distribution of the carbene molecule between its two enantiomers during this chirality change. Our study shows how the weak van der Waals interactions alter the dynamics of chirality changes at the molecular level, enabling an in-depth understanding of the origin of homochirality in nature and providing new insights into the construction of homochiral supramolecular assemblies in solutions and on solid surfaces.

O 74.9 Thu 17:00 S054

Lateral Force Microscopy Reveals the Energy Barrier of a Molecular Switch

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Copper phthalocyanine (CuPc) is a small molecule often used in organic light emitting diodes where it is deposited on a conducting electrode. Previous scanning tunneling microscopy (STM) studies of CuPc on Cu(111) have shown that inelastic tunneling events can cause CuPc to switch between a ground state and two symmetrically equivalent metastable states in which the molecule is rotated. We investigated CuPc on Cu(111) and Ag(111) with STM and lateral force microscopy (LFM). Even without inelastic events, the presence of the tip can induce rotations and upon closer approach, causes the rotated states to be favored. Combining STM measurements at various temperatures and LFM measurements, we show that the long-range attraction of the tip changes the potential energy landscape of this molecular switch. We can also determine the geometry of the rotated and ground states. We compare our observations of CuPc on Cu(111) to CuPc on Ag(111). On Ag(111), CuPc appears flat and does not rotate. Stronger bonding typically involves shorter bond lengths, larger shifts of energy levels, and structural stability. Although the binding of CuPc to Cu(111) is stronger than that on Ag(111), the nonplanar geometry of CuPc

on Cu(111) is accompanied by two metastable states which are not present on the Ag(111) surface.

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O 74.10 Thu 17:15 S054

Evidence of trion-libron coupling in chirally adsorbed single molecules

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Interplay between the motion of nuclei and excited electrons in molecules plays a key role both in biological and artificial nanomachines. Here we provide a detailed analysis of coupling between quantized librational modes (librons) and charged excited states (trions) on single phthalocyanine dyes adsorbed on a surface. By means of tunnelling electron-induced electroluminescence, we identify librionic progressions on a μeV energy range in spectra of chirally adsorbed phthalocyanines, which are otherwise absent from spectra of symmetrically adsorbed species. Experimentally measured librionic spectra match very well the theoretically calculated libron eigenenergies and peak intensities (Franck-Condon factors) and reveal an unexpected depopulation channel for the zero libron of the excited state that can be effectively controlled by tuning the size of the nanocavity. Our results showcase the possibility of characterizing the dynamics of molecules by their low-energy molecular modes using μeV -resolved tip-enhanced spectroscopy.

O 74.11 Thu 17:30 S054

Design Principles for Metastable Standing Molecules

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Molecular nanofabrication with a scanning probe microscope is a promising route towards the prototyping of metastable functional molecular structures and devices which do not form spontaneously. The aspect of mechanical stability is crucial for such structures especially if they extend into the third dimension vertical to the surface. A prominent example are freestanding molecules on a metal which can function as field emitters or electric field sensors[1,2]. Improving the stability of such molecular configurations is an optimization task involving many degrees of freedom. Here, we present a combination of scanning probe experiments with ab initio potential energy calculations to investigate the stability of a prototypical standing molecule. We cast our results into a simple set of universal design principles for such metastable structures, the validity of which we demonstrate in two computational case studies. This offers the intuition needed to fabricate new devices without tedious trial and error.

[1] T. Esat, N. Friedrich, F. S. Tautz, R. Temirov, *Nature* **558**, 573 (2018)

[2] C. Wagner, M. F. B. Green, P. Leinen, T. Deilmann, P. Krüger, M. Rohlfing, R. Temirov, F. S. Tautz, *PRL* **115**, 026101 (2015)

O 74.12 Thu 17:45 S054

Improving the Switching Efficiency in Azobenzene Derivative Film on Graphite-Air Interface

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The trans isomer of azobenzene (AB) and its derivatives is the most abundant under equilibrium-thermodynamical conditions and is known to switch between its trans and cis states when triggered by light and electrons/holes on graphite.[1] In this work, we show that AB derivatives are switching between two cis states (cis, cis') when electrons/holes induced switching is performed on a cis dominant non-equilibrium initial condition at HOPG-air interface. The switching efficiency in the cis adlayer is several folds higher than that in the trans adlayer. This is related to the low switching barrier for cis-cis'

switching compared to that of trans-cis switching as revealed by density functional theory (DFT) calculations.

1) K. Yadav, S. Mahapatra, T. Halbritter, A. Heckel, T. G. Gopakumar, *J. Phys. Chem. Lett.*, 2018, 9, 6326-6333.