

O 28: Organic Molecules on Inorganic Substrates I: Switching and Manipulation

Time: Tuesday 10:30–13:00

Location: H24

O 28.1 Tue 10:30 H24

Controllable three-terminal molecular switch based on adsorption site jiggling — ●ANJA BAUER¹, MARKUS MAIER², JOSEFINE DIEGEL¹, WERNER SCHOSSER¹, FABIAN PASCHKE¹, YURIY DEDKOV^{1,3}, FABIAN PAULY¹, RAINER WINTER², and MIKHAIL FONIN¹ — ¹Department of Physics, University Konstanz, D-78457 Konstanz — ²Department of Chemistry, University Konstanz, D-78457 Konstanz — ³Department of Physics, Shanghai University, 200444 Shanghai, China

Realization schemes for tuning the electronic and magnetic properties as well as for the control of molecular motion on surfaces are of crucial importance for the fabrication of molecule-based functional devices. One possibility to controllably tune the properties of individual molecules relies on the atomically precise manipulation of the environment.

Here, we investigate the switching behavior of single triazatruxene (TAT) molecules on Ag(111) by low temperature STM. Time-dependent current measurements reveal a current-induced telegraph noise, which is characteristic for switching between well-defined states. The pristine TAT molecule switches between three states of different adsorption geometry and orbital population. The switching rate can be efficiently controlled by the tunneling parameters. We further show the possibility to controllably initiate or suppress the switching process by detaching or attaching hydrogen to the nitrogen atoms of TAT as well as to manipulate the switching rates by modification of the molecule's environment.

O 28.2 Tue 10:45 H24

Electrochemistry of single molecules by atom manipulation — ●SHADI FATAYER, FLORIAN ALBRECHT, NIKOLAJ MOLL, GERHARD MEYER, and LEO GROSS — IBM Research - Zurich

The charge state of an adsorbed molecule significantly affects its physical as well as its chemical properties, for example, adsorption position, molecular conformation and aromaticity. The proven capabilities of single-electron sensitivity [1,2] and atomic-resolution [3] of atomic force microscopy (AFM) make it an ideal tool to perform charge-state manipulation experiments while atomically resolving the induced changes within the molecule. Here, we present AFM-based results that demonstrate both the control in charge-state and the capability of resolving the atomic structure of a single molecule for different molecules.

[1] L. Gross, et al. *Science* 324, 5933 (2009) [2] S. Fatayer, et al. *Nature Nanotechnology* 13, 376 (2018) [3] L. Gross, et al. *Science* 325, 5944 (2009)

O 28.3 Tue 11:00 H24

Effect of deprotonation on the electronic structure of phthalocyanine molecules on molybdenum disulfide — ●GAEL REECHT, NILS KRANE, CHRISTIAN LOTZE, and KATHARINA J FRANKE — Freie Universität Berlin, Berlin, Germany

Scanning probe techniques (SPM) enable the modification of the chemical structure of single molecules with atomic precision. The formation of radicals is one of the capabilities of this single-molecule chemistry but their stabilization is generally inhibited for molecule directly adsorbed on a metal substrate. Here we study by scanning tunneling microscopy and spectroscopy free-base phthalocyanines on MoS₂/Au(111). We observe that under the influence of the tip, the molecule can be modified with major changes of its electronic structure. By investigating the tautomerization properties of the phthalocyanine and with DFT simulations in gas phase, we determine that the modification of the molecule is due to a deprotonation, from H₂Pc to HPc. With the MoS₂ acting as decoupling layer, the deprotonated molecule keep its radical character, with the HOMO being singly occupied.

O 28.4 Tue 11:15 H24

Influence of the spatial extent of molecules on their properties as detectors in MONA applications — ●TIM ZENGER¹, JENS KÜGEL¹, MARKUS LEISEGANG¹, and MATTHIAS BODE^{1,2} — ¹Physikalisches Institut, Experimentelle Physik II, *Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Wilhelm Conrad Röntgen Center of Complex Material Systems (RCCM), *Universität Würzburg, Am Hubland, 97074 Würzburg

The Molecular Nanoprobe (MONA) technique [1] takes advantage of dynamic processes in molecules to enable the measurement of electron

transport on a nanometer scale via STM. In this technique charge carriers injected from the STM tip propagate through the sample until they are detected by a molecule, usually phthalocyanine, via a reversible proton transfer reaction, called tautomerization. In contrast to a STM probe, however, these macromolecules possess a significant spatial extent that could have an effect on their properties as detectors of electronic transport. Here we present studies of phthalocyanine molecules to investigate the influence of its cross-like arms on the switching properties in MONA measurements. In detail, we show both angular and distance-dependent measurements of the switching probabilities. These results are compared to naphthalocyanine molecules, which are characterized by larger arms.

[1] M. Leisegang *et al.*, *Nano Lett.* **18**, 3, 2165-2171 (2018)

O 28.5 Tue 11:30 H24

Controlled consecutive charging of self-assembled clusters of molecules — ●PHILIPP SCHEUERER and JASCHA REPP — University of Regensburg, Regensburg, Germany

Molecular self-assembly on insulating films [1] or insulators is a promising approach to create functional molecular structures as building blocks for future electronics. Controlled manipulation of single electrons in such structures as recently demonstrated for individual weakly coupled molecules on insulating films [2], represents an important step to understanding intermolecular electronic interactions.

Here, we investigate the charge transfer in self-assembled molecular structures of Perylenetetracarboxylic dianhydride (PTCDA) molecules on thick insulating films. By applying a bias voltage between the tip of a non-contact atomic force microscope and the underlying conductive sample we inject charges into small molecular clusters with single-electron control. Making use of the sensitivity of AFM to detect single electrons we locate the position of charges within clusters. Depending on the number of injected charges either stable charge configurations or tip-induced motion of charges within the island is observed. The latter leads to a damping signal with a pronounced spatial signature.

[1] S. Burke *et al.*, *Nature Communications* 6, 8312 (2015)

[2] W. Steurer *et al.*, *Nature Communications* 6, 8353 (2015)

O 28.6 Tue 11:45 H24

Discriminating and counting the possible molecular conformations in a prototypical molecular wire junction — ●MARVIN KNOL^{1,2}, ALEXANDER DIENER^{1,2}, PHILIPP LEINEN^{1,2}, F. STEFAN TAUTZ^{1,2}, and CHRISTIAN WAGNER^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ²JARA-Fundamentals of Future Information Technology

Mechanical manipulation of molecules with a scanning probe microscope (SPM) is a versatile technique to study molecular properties and to create new single-molecular devices [1,2,3]. One example is the exciting research field of quantum transport through molecules, which is often hampered by the lack of precise control over the molecular junction conformation. Here we report molecular manipulation experiments in which a single PTCDA (perylene-tetracarboxylic dianhydride) molecule is suspended between two metal electrodes; a Ag(111) surface and a non-contact AFM/STM tip in a variety of discrete junction conformations. We record frequency shift and conductance fingerprints in a tip-space volume of only 0.1 Å³ and perform a statistical analysis thereof to discriminate and count the possible tip-molecule-surface conformations. Our work is a step towards the complete identification of the so-far unobservable atomic structure of molecular junctions and could be the key to fully reproducible quantum transport studies.

[1] C. Wagner *et al.* *Phys. Rev. Lett.* 115, 026101 (2015)

[2] T. Esat *et al.* *Nature* 558, 573 (2018)

[3] R. Temirov *et al.* *Phys. Rev. Lett.* 120, 206801 (2018)

O 28.7 Tue 12:00 H24

Molecular motors studied on surfaces by scanning tunneling microscopy — ●MONIKA SCHIED¹, PETER JACOBSON¹, DONGDONG LIU², JAMES M. TOUR², and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, University of Graz, Austria — ²Department of Chemistry, Rice University, USA

Artificial molecular motors that convert an external energy input 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. Molecules on surfaces have the advantage of a fixed point of reference and confinement in two dimensions making it easier to study the directionality of their motion.

The uni-directional rotation of the motors investigated in this study is based on a combination of double bond isomerisation and helix inversion. This so-called Feringa motor has already been implemented into molecular structures to enable or enhance their lateral translation on metal surfaces [2, 3].

Here, we image single motor molecules on metallic surfaces by low-temperature scanning tunnelling microscopy (STM). To obtain insight into the underlying processes, the same molecule is imaged before and after applying an external stimulus, using either light or voltage pulses from the STM tip, and changes in the molecular adsorption are studied.

[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 28.8 Tue 12:15 H24

Imprinting Directionality into Proton Transfer Reactions of an Achiral Molecule — ●MARKUS LEISEGANG¹, JENS KÜGEL¹, and MATTHIAS BODE^{1,2} — ¹Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Wilhelm Conrad Röntgen Center of Complex Material Systems (RCCM), Universität Würzburg, Am Hubland, 97074 Würzburg

Molecular motors play a mayor role in biological processes. This has inspired scientists in the past to design molecular machines with controlled functionality on the nanoscale [1]. One key feature of any motor is directional motion. In molecules directional motion is usually induced by structural chirality which on one hand restricts the motion to a fixed direction, but on the other hand can't easily be changed [2]. Here we present a scanning tunneling microscopy study of achiral H₂Pc and HPc molecules that acquire chirality by adsorption onto a Ag(100) surface. The induced chirality is caused by a -29° ($+29^\circ$) rotation of H₂Pc with respect to the [011] substrate direction, resulting in tautomerization that preferentially occurs in a clockwise (counterclockwise) direction. The directionality is found to be independent of energy and location of charge carrier injection. We show that—in contrast to unalterable structural chiralities determined by the molecular structure—the direction of proton motion in HPc on Ag(100) can be inverted by a rotation of the molecule.

[1] M. van den Heuvel *et al.*, *Science* **317**, 333-336 (2007)

[2] J. Berna *et al.*, *Nat. Mater.* **4**, 704 (2005)

[3] J. Kügel *et al.*, *ACS nano* **12**, 8733-8738 (2018)

O 28.9 Tue 12:30 H24

High-Resolution Vibronic Spectra of Molecules on Molybdenum Disulfide Allow for Rotamer Identification — NILS KRANE¹, ●CHRISTIAN LOTZE¹, GAËL REECHT¹, LEI ZHANG², ALE-

JANDRO L. BRISEÑO², and KATHARINA J. FRANKE¹ — ¹Fachbereich Physik, Freie Universität Berlin — ²Department of Polymer Science and Engineering, University of Massachusetts, USA

Scanning tunneling spectroscopy (STS) is a tool that allows to address individual molecules in a precisely known surrounding. However, it bears the drawback that it requires a conductive substrate. Deposition of organic molecules on a metal substrate leads to strong hybridization of the electronic states. Preservation of the molecular character requires the inclusion of thin band-gapped materials.

Here, we present STS experiments performed on 2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene (BTTT) molecules adsorbed on a single layer molybdenum disulfide (MoS₂) on Au(111). We show that it acts as an effective electronic decoupling layer that exhibits a small electron-phonon coupling strength. Differential conductance spectra of the molecules exhibit a multitude of sharp characteristic peaks, originating from vibronic states of BTTT. These vibronic fingerprints of different molecules allow for an identification of different rotamers. DFT calculations of the molecule in gas phase provide all details for an accurate simulation of the vibronic spectra of both investigated rotamers [1].

[1] Krane, *et al.*, *ACS Nano*, 2018, 12, 11, 11698-11703

O 28.10 Tue 12:45 H24

Machine learning for single molecule manipulation — PHILIPP LEINEN^{1,2}, MALTE ESDERS³, KRISTOF SCHÜTT³, KLAUS-ROBERT MÜLLER³, F. STEFAN TAUTZ^{1,2}, and ●CHRISTIAN WAGNER^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ²JARA Fundamentals of Future Information Technology, Jülich, Germany — ³Institut für Softwaretechnik und Theoretische Informatik, Technische Universität Berlin, Germany

The controlled mechanical manipulation of individual molecules with a scanning probe microscope (SPM) allows the fabrication of single-molecule devices [1,2] and metastable supramolecular assemblies [3]. Machine learning can reduce the tedious work of finding a successful manipulation protocol for a certain manipulation tasks. We use reinforcement learning (RL) to automatically solve the prototypical task of removing a single PTCDA (perylene-tetracarboxylic dianhydride) molecule from a hydrogen-bonded assembly [3]. Since our RL application is not fully in-silico but receives its feedback from an actual experiment, it needs a training efficiency on par with a human to be useful. We achieve this by teaching the machine some “intuition” about the Cartesian space in which the manipulation takes place by, e.g., spawning a series of weak learners along all tried trajectories and training on unseen state-action pairs. Our method could be a blueprint for solving various manipulation tasks posed in a Cartesian space.

[1] C. Wagner *et al.* *Phys. Rev. Lett.* **115**, 026101 (2015)

[2] T. Esat *et al.* *Nature* **558**, 573 (2018)

[3] M. F. B. Green *et al.* *Beilstein J. Nanotechnol.* **5**, 1926 (2014)