

O 2: Organic Molecules on Inorganic Substrates I: Electronic, Optical and Other Properties I

Time: Monday 10:30–13:00

Location: CHE 89

O 2.1 Mon 10:30 CHE 89

Hooke's law in a molecular spring: An nc-AFM and STM study of nonahelicene on Ag(110) — ●MAX HALBAUER¹, TAKASHI KUMAGAI², MARTIN WOLF¹, and AKITOSHI SHIOTARI¹ — ¹Fritz-Haber-Institute of the Max-Planck-Society, Faradayweg 4-6, 14195 Berlin, Germany — ²Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, 444-8585 Okazaki, Japan

Helicenes are a class of conjugated aromatic molecules representing macroscopic springs on the molecular scale. However, experimental insights on their mechanical properties remain scarce. This contribution employs scanning tunneling microscopy (STM) and noncontact atomic force microscopy (nc-AFM) measurements (UHV, liq. He) in order to address this issue. Frequency shift-distance traces were acquired on individual nonahelicene molecules and a planar reference molecule (coronene) and converted subsequently to force-distance curves. Model-functions accounting for the elasticity of the molecule were fitted to the data, which yielded the spring-constant - k - for elongation of nonahelicene. This work shows therefore that Hooke's law can be verified on the single-molecule scale by nc-AFM.

O 2.2 Mon 10:45 CHE 89

Complex rotational behavior of ground and excited molecular states — ●ANDREAS CHRIST, MARKUS LEISEGANG, PATRICK HÄRTL, and MATTHIAS BODE — Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

The high sensitivity of molecular rotors to the intricate molecule-substrate interaction leads to a large variety of their rotational behavior [1]. In some cases this interaction can even change for different rotational positions on a molecule's rotation path. We have studied these dependencies for copper-phthalocyanine (CuPc) on Cu(111) by means of low-temperature scanning tunneling microscopy. In agreement with previous results [2,3], we find one ground state oriented along the high-symmetry axes of the substrate and two excited states tilted by $\approx \pm 7^\circ$. A more detailed analysis reveals an exceptionally low threshold of ≈ 20 meV for rotations between these three stable states. Interestingly, the interaction of the molecule with the substrate and therefore the rotation rate varies significantly between the ground and the excited states due to their different molecular bending. Additionally, we find two adsorption positions, which slightly lift the degeneracy between the two excited states.

[1] D. Lensen *et al.*, *Soft Matter* **8**, 9053 (2012)[2] J. Schaffert *et al.*, *Phys. Rev. B* **88**, 075410 (2013)[3] S. Fremy-Koch *et al.*, *Phys. Rev. B* **100**, 155427 (2019)

O 2.3 Mon 11:00 CHE 89

Current Driven Unidirectional Rotation of Geländer Molecule — ●ŠTĚPÁN MAREK¹, JAN WILHELM², RICHARD KORYTÁR¹, and FERDINAND EVERS² — ¹Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Czech Republic — ²Condensed Matter Theory Group, Institute of Physics, Faculty of Theoretical Physics, University of Regensburg, Bavaria, Germany

Rotations of molecules driven by current are possible basis for construction of molecular motors. In "Geländer" molecules, the chiral structure was thought to drive the momentum transfer from travelling electrons to the molecule. We construct a simple model, motivated by our DFT based study, to explore the structure of the current density in such a molecule and identify the regions of the molecule that contribute majority of the angular momentum of the electron current. We also discuss the particularities of our results, especially the conservation of rotation direction under the exchange of electric bias direction. The results are compared with experimental observations.

O 2.4 Mon 11:15 CHE 89

SPM Tip-induced Cleavage of Bridging Groups to Generate Carbon Nanomaterials — ●ZILIN RUAN¹, TIM NAUMANN¹, JOHN B. BAUER², LUKAS HEUPLICK¹, HOLGER F. BETTINGER², and J. MICHAEL GOTTFRIED¹ — ¹Department of Chemistry, Philipps University Marburg, Hans-Meerwein-Straße 4, 35037 Marburg (Germany) — ²Institut für Organische Chemie, Auf der Morgenstelle 18, 72076

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The on-surface synthesis of carbon nanomaterials is usually carried out on a metal surface by thermal activation, wherein the reaction selectivity and outcome are influenced by various factors. By contrast, manipulations with a scanning probe microscope (SPM) avoid these obstacles by electrically triggering the chemical transformation of individual molecules via the SPM tip due to electronic excitation or inelastic energy transfer. Here, using tip manipulation, we explore the suitability of the removal of etheno- and diastereomeric 1,2-diol moieties to generate acenes. Compared to other previously used leaving groups such as monoketone, diketone and oxo bridges, the here used bridges have certain advantages in the precursor synthesis, but are more challenging regarding their on-surface removal. Investigation of the various main and side reactions offer a deeper understanding of complex elimination and rearrangement reactions induced by SPM manipulation.

O 2.5 Mon 11:30 CHE 89

Illuminating an individual non-fluorescent molecule — ●TZU-CHAO HUNG^{1,2}, YOKARI GODINEZ LOYOLA³, MANUEL STEINBRECHER¹, BRIAN KIRALY¹, ALEXANDER A. KHAJETOORIANS¹, NIKOS L. DOLTSINIS³, CRISTIAN A. STRASSERT³, and DANIEL WEGNER¹ — ¹Institute for Molecules and Materials, Radboud University, 6525 AJ Nijmegen, The Netherlands — ²Department of Physics, University of Regensburg, Regensburg, 93040, Germany — ³Physikalisches Institut and Center for Nanotechnology (CeNTech), Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

Combining scanning tunneling microscopy, spectroscopy and STM-induced luminescence (STML) allows us to study the optoelectronic properties down to the atomic scale. Generalizing the atomic control and imaging capabilities of STML to phosphorescent or even non-fluorescent molecules can provide a new route to fundamentally understand the photophysical properties of an individual molecule. Nickel phthalocyanine (NiPc) is a non-fluorescent molecule. Light emission from the ligand-centered excited state known as Q-band is quenched due to fast relaxation into the nonradiative metal-centered excited state. Hence, the transition energy of the Q-band can only be determined by absorption spectroscopy. Here, we propose an alternative approach to activate radiative decay of the Q-band of NiPc by utilizing STML in combination with control of the local environment and discuss the involved excitation and relaxation pathways. We compare our results with optical spectroscopy and ab initio calculations and discuss the involved excitation and relaxation pathways.

O 2.6 Mon 11:45 CHE 89

STM-induced luminescence from single graphene nanoribbons — ●SONG JIANG^{1,2}, TOMÁŠ NEUMAN^{1,2}, ALEX BOEGLIN¹, FABRICE SCHEURER¹, and GUILLAUME SCHULL¹ — ¹Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France — ²Institut des Sciences Moléculaires d'Orsay (ISMO), UMR 8214, CNRS, Université Paris-Saclay, 91405 Orsay Cedex, France

Graphene nanoribbons (GNRs) have emerged as promising candidates for high-performance nanoelectronic devices due to their tunable energy band gaps resulting from lateral quantum confinement and edge effects. The recent development of on-surface synthesis has achieved various types of atomically precise GNRs, revealing fascinating electronic, magnetic, and mechanical properties. Their optical properties, on the other hand, remain largely unexplored. The intrinsic luminescence properties of atomically precise GNR remain to be addressed at single molecule level. Here, excitonic emission from atomically precise GNRs synthesized on a metal surface is probed using a scanning tunneling microscopy (STM) approach. A STM-based strategy to transfer the GNRs to a partially insulating surface is used to prevent light emission quenching of the ribbons by the metal substrate. Sub-nanometer resolved STM-induced fluorescence spectra reveal emission from localized dark excitons build upon the topological end states of the GNRs accompanying with a series of vibronic peaks. Our study provides a novel path to investigate the interplay between excitons, vibrons and topology in atomically precise graphene nanostructures.

O 2.7 Mon 12:00 CHE 89

Substrate induced magnetic alignment and magnetization dynamics of dimetallofullerene single-molecule magnets —

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Since several years, lanthanide based single-molecule magnets (SMMs) are in focus of a broad research community due to their record high blocking temperatures above 77 K [1]. However, surface supported SMMs lag behind in terms of blocking temperatures and relaxation times due to molecule-substrate interactions. Yet, for the surface-supported lanthanide dimetallofullerene SMMs blocking temperatures of up to 28 K and long relaxation times were reported [2]. Here, we study the effect of coupling to a metallic substrate on the electronic and magnetic properties of Dy₂@C₈₀CH₂Ph and compare those to our results for the graphene substrate [3,4]. A combination of scanning tunneling microscopy, spectroscopy and X-ray absorption spectroscopy provides a detailed insight into the local electronic properties as well as magnetization dynamics of the studied SMMs.

[1] F.S. Guo *et al.* Science 362, 6421. [2] F. Liu *et al.* Nat. Commun. 10, 571 (2019). [3] F. Paschke *et al.* Adv. Mater. 2102844 (2021). [4] F. Paschke *et al.* Small 2105667 (2022)

O 2.8 Mon 12:15 CHE 89

Enantiospecific adsorption on a ferromagnetic surface at the single-molecule scale — •M.R. SAFARI¹, F. MATTHES¹, K-H. ERNST², D.E. BÜRGLER¹, and C.M. SCHNEIDER¹ — ¹Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich, 52425 Jülich, Germany — ²Molecular Surface Science Group, Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600, Dübendorf, Switzerland

The recently discovered effect of chirality-induced spin selectivity (CISS) not only enables spin-selective electron transport in organic molecules [1], but also offers a novel approach to chiral separation by exploiting the CISS-induced enantiospecific interaction of chiral molecules with perpendicularly magnetized substrates [2]. Using low-temperature spin-polarized scanning tunneling microscopy, we have investigated the enantiospecific adsorption of heptahelicene molecules on ferromagnetic Co bilayer islands [3,4]. High-resolution and spin-polarized STM images enable direct determination of the enantiomeric adsorption ratio R on oppositely magnetized Co islands. Statistical analysis of 748 molecules on 110 islands yields $R = 0.69 \pm 0.05$, which we attribute to different enantiospecific adsorption energies. The well-defined structural, electronic, and magnetic properties of the molecule-substrate systems make our results readily amenable to theoretical

modeling that will hopefully shed light on the microscopic origin of enantiospecific adsorption on ferromagnetic surfaces. [1] R. Naaman *et al.*, J. Phys. Chem. Lett. **3**, 2178 (2012); [2] K. Banerjee-Ghosh *et al.*, Science **360**, 1331 (2018); [3] M.R. Safari *et al.*, Nanomaterials **12**, 3281 (2022); [4] M.R. Safari *et al.*, arXiv:2211.12976 (2022)

O 2.9 Mon 12:30 CHE 89

Clars goblet based J1 & J2 alternative heisenberg spin half chain — •LIN YANG — TU Dresden, Dresden, Germany

Spin-1/2 alternating-exchange Heisenberg chain has been intensively pursued for decades not only for understanding its underlying many-body physics but also for its great potential of realizing quantum computing and information. The existing candidates are limited in effective spin arrays embedded in three dimensional crystals, where the quasi-one dimensional spin system is inevitably affected by the cross talk between arrays and the spin-phonon coupling. Here, paradigmatic alternating-exchanging Heisenberg chains with spin-1/2 are realized in a designer graphene system using on-surface synthesis. The couplings: $J_1 = 38$ meV, $J_2 = 23$ meV are determined by inelastic tunneling spectra, which is strong enough to support practical quantum operation.

O 2.10 Mon 12:45 CHE 89

CoPc on Ag(100): getting the most out of PEEM images —

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We use photoelectron emission microscopy (PEEM) and the Anderson method to study in situ the thin-film growth of cobalt-phthalocyanine (CoPc) on Ag(100) surfaces. Based on the Fowler-DuBridge theory, we were able to correlate the evolution of the mean electron yield acquired with PEEM for coverages up to two molecular layers of CoPc to the global work function changes measured with the Anderson method. For coverages above two monolayers, the transients measured with the Anderson method and those obtained with PEEM show different trends allowing us to determine the inelastic mean free path of the low-energy electrons while passing through the third layer of CoPc.[1] Already before (and during) the condensation of solid phases (2D islands or 3D crystallites), there is a dilute 2D gas phase consisting of individual molecules diffusing across the surface or clusters, which can not be resolved with PEEM. Therefore, we discuss, how image features below and above the resolution limit of a PEEM affect the mean electron yield and the (normalized) standard deviation.[2]

[1] Th. Wagner *et al.*, ACS Appl. Mater. Interfaces **12** (2022), 23983–23989 [2] Th. Wagner *et al.*, Ultramicroscopy **233** (2022), 113427