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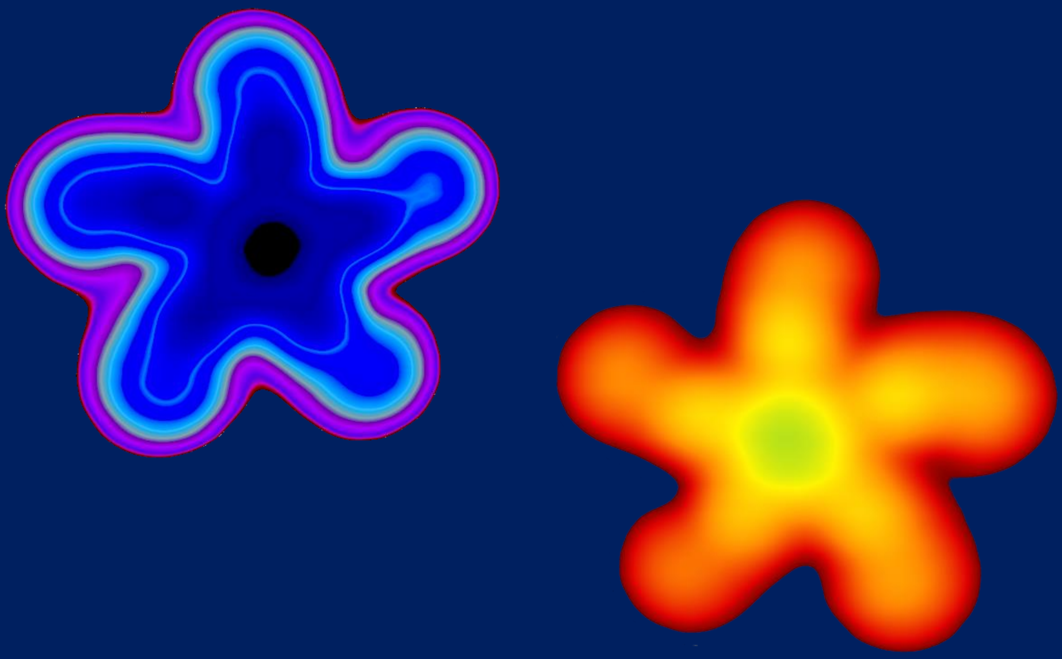

Single Molecule Machines on a Surface
Gears, Train of Gears, Motors, and Cars

November 24-25, 2021
P. Baudis Congress Center, Toulouse

"Diamant" Room

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24th November 2021

9:00	R. Berndt (Kiel) (Invited) Molecular spin switches and rotors on surfaces	p. 4
9:45	K.H. Au-Yeung (TU Dresden)* Voltage-pulse manipulation of azulene-based single molecules and dimers: the role of the dipole moment	p. 5
10:15	Coffee	
10:45	W.H Soe (CEMES Toulouse) Single molecule-gear Mechanics and train on a surface	p. 6
11:15	R. Gutierrez. (TU Dresden) Atomistic Modelling of Nanoscale Molecular and Solid-State Gears	p. 7
12:00	L. Grill (Uni Graz)* How to move single molecules: From the nanocar race to molecular telegraphy	p. 8
12:45	Lunch at P. Baudis	
14:00	Henri Pierre (Strasbourg)* Trypticene, sub-phthlocyanine and Ir(III) complexes acting as Molecular Wheels	p. 9
14:30	Y. Gisbert (CEMES Toulouse)* Synthesis of organometallic molecular winch prototype	p. 10
15:00	Break	
15:30	F. Lissel (Dresden)* DMBI - from molecular rotors to nanocars	p. 11
16:00	E. Masson (Ohio)* Visio Self-assembling molecular Lego: showcasing the Cucurbituril kit	p. 12
16:30	Open to one contribution	
17:00		
20:00	C'Nano Dinner at P. Baudis	

* Nanocar Race team

25th November 2021

9:00

H. Fuchs (Munster) (Invited)
From chemical bonds to molecular assemblers
p. 13

9:45

G. Simpson (Uni Graz)* Controlling the rotation and translation of a single molecule?
p. 14

10:30

R. Robles (DIPC San Sebastian)* Assembly, diffusion and rotation of organic molecules on a gold surface
p. 15

11:00

Break

11:30

T. Wang (DIPC San Sebastian)* Synthesis, manipulation and theoretical modeling of corannulene-based molecules on surfaces
p. 16

12:00

R. Widmer (EMPA) (Invited)
Molecular motor at the frontier of classical motion and quantum tunneling
p. 17

12.45

Lunch at P. Baudis

13:45

M. Van Hove (Hong Kong Baptist Uni.) Visio
Mechanisms of molecular machines
p. 18

14:15

X. Li (Liege) Probing the motion of a molecular rotor by single-molecule force spectroscopy
p. 19

14:45

Coffee

15:15

K. Houtsam (Gröningen) (Invited)
Towards 2D molecular templates on coinage metals and graphene for single molecule mechanics
p. 20

15:45

S. Hla (Ohio)* Visio Quantum Molecular Machines
p. 21

16:30

Workshop conclusions

* Nanocar Race team

Molecular spin switches and rotors on surfaces

Richard Berndt

Institut für Experimentelle und Angewandte Physik
Christian-Albrechts-Universität zu Kiel
Olshausenstr. 40,
D-24098 Kiel

http://www.ieap.uni-kiel.de/surface/ag-berndt/

Using low-temperature scanning tunneling microscopy (STM) and synchrotron radiation methods we explore the electron transport through molecules and their spin states at single crystal surfaces. The talk will address the switching of spin-crossover compounds and more unconventional ways of rendering molecules paramagnetic. In addition, analyses of simple molecular rotors and switching effects in molecular clusters will be presented.

Voltage-pulse manipulation of azulene-based single molecules and dimers: the role of the dipole moment

Kwan Ho Au-Yeung,[1] Tim Kühne,[1] Oumaima Aiboudi,[2] Franziska Lissel,[2]
Dmitry A. Ryndyk,[1] and Francesca Moresco[1]

[1]TU Dresden, 01062 Dresden, Germany
[2]Leibniz Institut für Polymerforschung, 01069 Dresden, Germany

Among the different mechanisms that can be used to drive a molecule laterally on a surface by the tip of a scanning tunneling microscope at low temperature (5 K), we used voltage pulses to manipulate azulene-based single molecules and nanostructures on Au(111). Upon thermal deposition, the molecules partially cleave and form metal-organic complexes while single molecules are very scarce, as confirmed by simulations. By applying voltage pulses to the different structures under similar conditions, we observe that only one type of the complexes can be controllably driven on the surface, which has the lowest dipole moment within all the investigated structures. In addition, experiments under different bias and tip height conditions reveal that the electric field plays the key role for the controlled motion. We discuss the different observed structures and their movement properties with respect to their dipole moment and charge distribution on the surface.

Single molecule-gear mechanics and train of on a surface

We-Hyo SOE

Centre d’Elaboration de Matériaux et d’Études Structurales (CEMES),
Centre National de la Recherche Scientifique (CNRS), 31055 Toulouse Cedex, France

International Center for Materials Nanoarchitectonics (WPI-MANA),
National Institute for Material Sciences (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

The functioning of a train of molecule-gears having 6 teeth each and a 1.2 nm molecular structure diameter was demonstrated. By means of atom/molecule manipulation technique using a *Scanning Tunnelling Microscope* (STM), the two central molecule-gears of the train are arranged exactly at a 1.9 nm separation from centre to centre using a single Cu ad-atom axle per molecule-gear. A given Cu is working as a pinning centre for the rotation of its mounted molecule-gear. A third molecule-gear playing the role of a handle is engaged with the first molecule-gear of the train to create the required rotation torque. [1]

How molecule size is an essential factor to design molecular machine parts was also demonstrated experimentally using the molecule-gear having a 2.6 nm of molecular structure diameter, which is about twice the size of the first molecule-gear functioning for the transmission of rotation from molecule to molecule. The distances between two molecule-gears of the train were explored in the 2.4 – 2.6 nm separation range of engagement from centre to centre using a single Cu ad-atom axle.

Extending by one phenyl the length of each tooth leads to a strong mechanical entanglement between the gears and renders difficult a transmission of the rotation along the train. To reduce this entanglement, the gear train constructed using well located Cu individual adatom axles one on upper terrace edge of a native mono-atomic step of Pb(111) surface and the other one on lower terrace edge was tested. [2]

Our Experimental attempts with gearing of carry over, which is essential for mechanical calculators, will also be reported.

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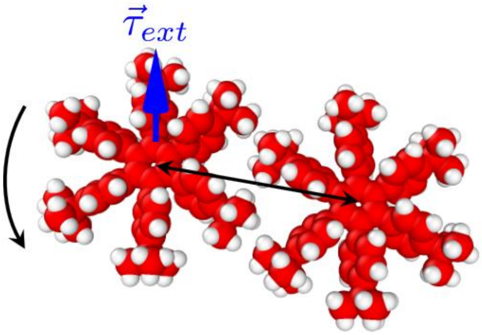
Atomistic Modelling of Nanoscale Molecular and Solid-State Gears

Rafael Gutierrez

Institute for Materials Science
Dresden University of Technology
Dresden, Germany

One fascinating perspective opened by the increasing control gained over nanoscale matter is the design of gears and gear trains involving molecular scale units or nanometer scale solid state gears. Implementing such nanoscale mechanical machines can be of potential interest in various fields such as nanorobotics and in the construction of devices immune to radiation. In addition to fabrication technologies based on bottom-up approaches, the production of solid-state gears using top-down methods may yield a viable path towards miniaturization. To guide ongoing experiments, it is, however, of crucial interest to shed light on the microscopic mechanisms that govern the mechanics of molecule and solid-state gears: how to trigger single gear rotation, how efficient is the transmission of rotational motion across gear trains, how to characterize frictional properties during gear rotation on substrates, to mention few of them. In this presentation we will address some of these issues from a computational point of view using large scale atomistic classical Molecular Dynamics simulations.



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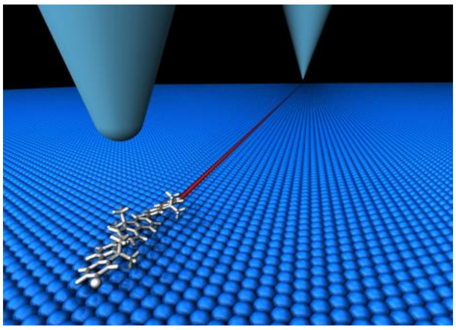
How to move single molecules:
From the nanocar race to molecular telegraphy

Leonhard Grill
Single-Molecule Chemistry group
University of Graz, Austria
www.nanograz.com

The motion of molecules at solid surfaces is not only of fundamental chemical interest, but also important for heterogeneous catalysis or growth processes. Spatial control over molecular movement is typically limited because motion at the atomic scale follows stochastic processes. In this presentation, various examples of controlled molecular motion at surfaces, studied by scanning tunneling microscopy (STM), will be discussed. The chemical structure of the molecule defines preferential orientations and directions of motion. Weak adsorption is advantageous for efficient motion, which could be achieved by specific molecular side groups and special STM manipulation protocols [1]. The same molecules can also be rotated with 100% directionality [2], allowing to map the electric dipole of the molecule via the molecular response to the applied field. For azobenzene switching units in a tetrahedral arrangement not only reversible photo-isomerization for the upright standing unit is found, due to decoupling, but also isomer-dependent diffusion on the surface is observed [3].

Isomerization is also a key process in molecular 'Feringa' motors [4]. In contrast to STM manipulation of such molecules [5], we used light in combination with heat to induce their (wavelength-dependent) translation on a metal surface [6]. Importantly, the light does not change the *number* of moving molecules, but their lateral *displacement*. While the STM induced motion of molecules at surfaces is typically restricted to displacements of few nm or less, we have observed single-molecule motion over distances of 150 nm – at the same time with a very high lateral precision of about 10 pm [7]. This allowed not only to directly measure the speed of a molecule in real space, but also to realize a sender-receiver experiment where a single molecule is controllably transferred between two separate STM tips (as sketched in the figure).



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Trypticene, sub-phthlocyanine and Ir(III) complexes acting as Molecular Wheels

Anna Roslawska,[a] Hassan Denawi,[b] Guillaume Schull,[a] Xavier Bouju,[b] Gwénaël Rapenne,[b] Valérie Heitz[c]
and Henri-Pierre Jacquot de Rouville[c]

[a] Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France
[b] CEMES-CNRS, Université de Toulouse, 31055 Toulouse, France;
[c] LSAMM, Institut de Chimie de Strasbourg, CNRS/UMR 7177, 4, rue Blaise Pascal, 67000 Strasbourg, France.
Email: hpjacquot@unistra.fr

The emergence of near-field microscopy techniques, such as the Scanning Tunneling Microscope (STM), has allowed to image single molecule on conductive surface with an atomic scale resolution. The STM tip can also manipulate elaborated single molecule in a controlled and reliable manner and has become a well-established technique to study their mechanical properties. However, the control of complex mechanical functions at the molecular scale still remains challenging. [1] In the last two decades, an increasing number of mechanical machines have been reported among molecular gears, motors and wheels can be cited. [2]

On a surface, two kinds of molecular motions can be distinguished, namely azimuthal (parallel to the surface) and altitudinal motion (perpendicular to the surface). An altitudinal rotational motion can be achieved by designing mechanical machines incorporating wheels. We reported a wheel dimer based on subphthalocyanine fragments incorporating an electronic tag[3] and a family of nano-vehicles incorporating trypticene wheels (Figure 1).[4] Surprisingly, STM studies of both systems demonstrated the controlled rotation of their wheels. Finally, in the context of the second edition Nanocar Race, we developed a new molecular wheel based on Ir(III) complexes. Our Ir(III)-wheel-dimer has an important dipole moment. It is expected to be competitive with other Nanocars of the contest.

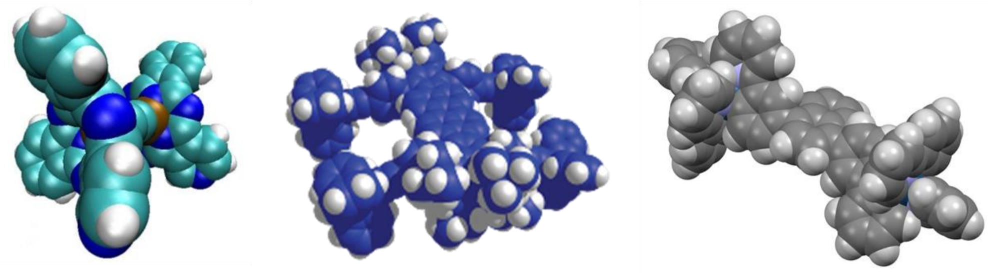

Figure 1. Structure of molecular vehicles incorporating two subphthalocyanine wheels, four triptycene wheels and two Ir(III) complexes respectively.

Acknowledgments

Financial Supports from the CNRS and the University Paul Sabatier are gratefully acknowledged.

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SYNTHESIS OF ORGANOMETALLIC MOLECULAR WINCH PROTOTYPES

Yohan Gisbert,[1] Claire Kammerer,[1] and Gwénaël Rapenne[1,2]

[1]*CEMES, Université de Toulouse, CNRS, Toulouse, France*
[2]*Division of Materials Science, NAIST, Nara, Japan*
yohan.gisbert@cemes.fr, http://www.cemes.fr/gns

In 2013, our group reported the synthesis of an electron-fueled ruthenium-based molecular motor able to provide unidirectional rotation when stimulated by the tip of a Scanning Tunneling Microscope. [1] This motor has been designed to be studied at the single molecule scale on surface, following a bottom-up building approach. [2]

To estimate the motive power of this motor, two strategies are currently being investigated, both involving the functionalization of the motor with a single polyethylene glycol (PEG) chain, attached thanks to a linker (L). This PEG tether is either directly allowing for AFM-based Single Molecule Force Spectroscopy experiments [3] in solution and at room temperature (a) or further functionalization with a molecular load, to be dragged on surface upon STM stimulation of the motor, acting as a molecular winch at low temperature (b).

To obtain the target molecular winches, two synthetic strategies were explored (c): a statistical approach involving the desymmetrization of the penta(bromophenyl)cyclopentadienyl ruthenium complex path (1) and a directed approach which discriminates one position of the cyclopentadienyl precursor path (2).[4] The design of these molecular machines will be presented, as well as both synthetic routes.

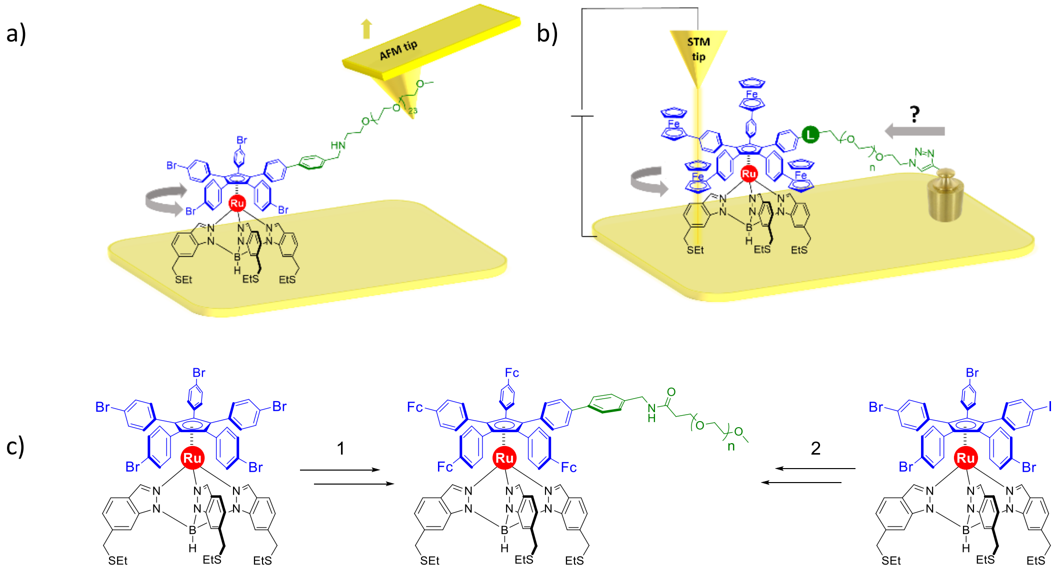

Fig. 1 a) Principle of the RT-AFM Single Molecule Force Experiments, b) Principle of the LT-STM experiments, c) Synthesis of a PEG-functionalized derivative of the ruthenium complex (Fc = ferrocene).

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DMBI - from molecular rotors to nanocars

Franziska Lissel

Leibniz Institute for Polymer Research Dresden, Germany.

2-(2-Methoxyphenyl)-1,3-dimethyl-1H-benzoimidazol-3-ium (o-MeO-DMBI) is used in organic electronics as an n-type dopant after iodine dissociation and formation of the organic radical [1]. Also, o-MeO-DMBI was studied as a molecular rotor in STM experiments, and the binding to the gold surface was initially described as radical [2]. Yet the molecule can also undergo an alternative reaction: the cleavage of the O–Me bond leads to an elimination of methyl iodide (MeI), resulting in the formation of 2-(1,3-dimethyl-1H-benzo[d]imidazol-3-ium-2-yl)-phenolate (DMBI-P) [3]. As the cleavage is thermally induced and takes place at 490 K under UHV conditions, the binding to the gold was recently described via charge back-donation using the oxygen, resulting in vertical DMBI-P rotors that at 5K rotate unidirectionally through six defined stations induced by tunneling electrons [4].

To investigate this system further, we synthesized an elongated derivative containing a naphthalene. This molecule can be evaporated onto a gold surface, but interestingly, does not bind to it. Instead, controlled lateral movement upon stimulation via the STM tip is observed.

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Self-assembling molecular Lego: showcasing the Cucurbituril kit

Eric Masson

Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, USA;
masson@ohio.edu

We will present the design and driving performance of the Ohio Bobcat Nanowagon, a [5]pseudorotaxane with an H-shaped chassis and 4 Cucurbit[7]uril (CB[7]) wheels, on a Au(111) track. A voltage bias applied to the tip of a scanning tunneling microscope was used to drive the assembly on the surface. The Nanowagon's adventures at the first Nanocar Race in Toulouse will also be presented. We will then discuss new recognition motifs of the CB[n] family that we identified recently, namely (1) the interaction, in aqueous solution, between guests and the outside wall of CB[n], a convex area void of any well-defined binding site,[1] (2) the formation of 2:2 head-to-head, 2:2 head-to-tail and 2:1 "stacked" complexes with CB[8] and pairs of Platinum acetylide and thiolate complexes[2-4], and (3) some counterintuitive encapsulations of hydrophilic guests inside CB[n] macrocycles.

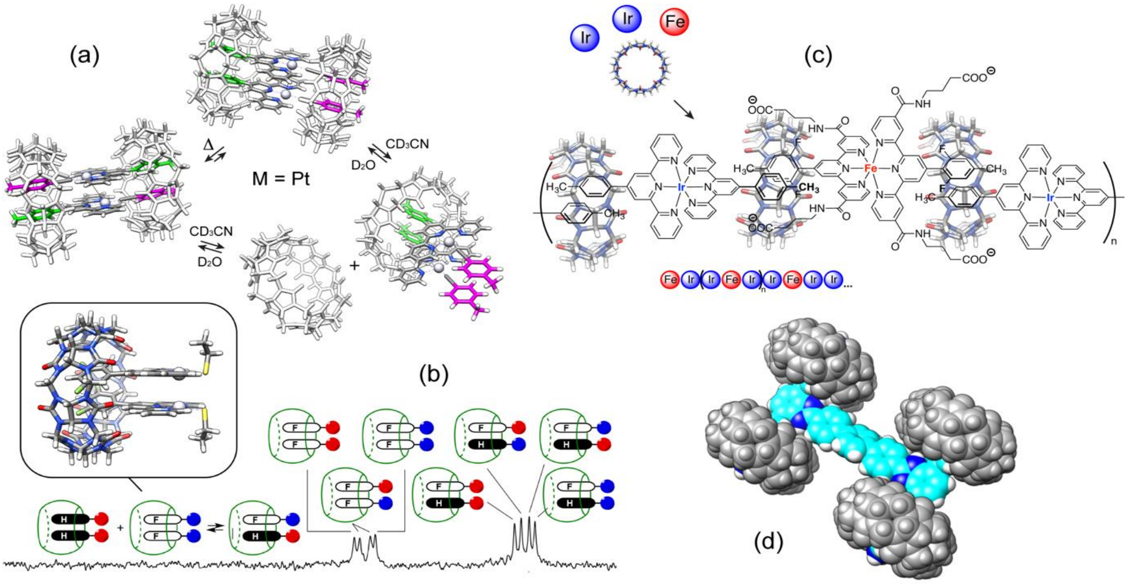

Figure. (a) Orientation-specific self-assembly of Pt(II) acetylides with CB[8] controlled by solvent and temperature. (b) "Dual layer" self-sorting between Pt thiolates and CB[8]. (c) Sequence-specific self-assembly of negative and positive metal-ligand complexes into dynamic oligomers in the presence of CB[8]. (d) The Ohio Bobcat Nanowagon!

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From chemical bonds to molecular assemblers

Harald Fuchs
Physikalisches Institut and Center for Nanotechnology (CeNTech)
Westfälische Wilhelms-Universität Münster
Heisenberg Str. 11
48149 Münster, Germany

Surfaces and interfaces represent low-dimensional spatial confinements opening unique pathways towards chemical reaction schemes with regio-selective and kinetic control that is not available in conventional liquid- or gas-phase chemistry [1]. Using N-heterocyclic carbenes (NHCs) on noble metal surfaces we identified a number of unique functional properties of this class of molecules which, depending on the chemical variation of their N-ligands, can get either immobilized to a single surface metal atom, or become able to pull a single atom out of the surface, then travelling, bound to this this ad-atom in the so-called 'ballbot'- motion type across the surface, eventually forming densely packed islands [2]. On the other hand, immobilized NHC-types, when modified with special asymmetric ligands introducing a ratchet like potential on the surface become uniaxial rotors [3]. We discovered a third fascinating property of ballbot-type NHCs on a reconstructed Au(1x2) surface: Here, an assembly of NHCs-ballbots is able to autonomously re-organize that surface atom by atom in a well-controlled and 'swarm-like' manor [4]. No external tools are required such as STM and AFM probes to start the process. Rather, the cooperative restructuring occurs in a zipper-mode by the NHC-machinery which is re-arranging Au-atoms with atomic precision, and in a massively parallel scheme. As a result, the Au(1x2) surface is transferred into an Au(1x3)-'Added Row (AR)' structure at room temperature. This observation may open a pathway for the generation of relatively simple 'programmed' and autonomously acting molecular species allowing to optimize surfaces in a cooperative way on selected surface areas.

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Controlling the rotation and translation of a single molecule

Grant J. Simpson[1], Samuel Hajek[1], Víctor García-López[2],
A. Daniel Boese[1] James Tour[2], Leonhard Grill[1]

1 University of Graz, Graz, Austria
2 Rice University, Texas, USA
grant.simpson@uni-graz.at

Control of the orientation and the direction of rotation of a single molecule is crucial to the understanding of molecular machines. In turn, the rotational orientation of a molecule can affect the efficiency of translation in a particular direction. Here, we report how single dipolar nanocar-type molecules adsorbed on a Ag(111) surface can be rotated with 100% directionality using the electric field of a scanning tunnelling microscope [1]. This high control relies on a specific interaction of the molecule with a silver surface atom. By overcoming this interaction, translations of the molecule are also possible. Such translations were utilised in winning the world's first nanocar race in 2017 [2]. The influence of chemical modification on the nanocar-surface interaction is also explored on different noble metal surfaces in view of the upcoming nanocar race in 2022.

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Assembly, diffusion and rotation of organic molecules on a gold surface

Roberto Robles[1], Vladimír Zobač[1], Nicolás Lorente[1,2]

[1]Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU).
20018 Donostia-San Sebastián, Spain.
[2]Donostia International Physics Center (DIPC).
20018 Donostia-San Sebastián, Spain.

The interplay between molecules and surfaces has become a rich playground to study a wide variety of phenomena. Advances in deposition procedures, scanning probe techniques, and theoretical simulation and modeling have allowed us to explore different many-body effects, the on-surface synthesis of new molecules, or the motion of molecules on the surface, among many other things.

Here we deposit two different organic molecules on a gold (111) surface. For the first one, acetylbiphenyl (ABP), we show how it diffuses along the main directions of the Au(111) surface, revealing the directionality of the molecule-surface interactions driven just by van der Waals forces [1]. This diffusion leads the molecules to form robust supramolecular assemblies stabilized by gold adatoms [2].

For the second molecule, DMBI-P, we show how the molecule is dissociated after deposition, getting anchored to the surface and forming a molecule-rotor that presents a unidirectional motion at 5 K [3].

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Synthesis, manipulation, and theoretical modeling of corannulene-based molecules on surfaces

Tao Wang[1,2], Jan Patrick Calupitan[2], Roberto Robles[2], Nicolas Lorente[1,2],
Diego Pena[3], Martina Corso[1,2], Dimas G.de Oteyza[1,2]

1 Donostia International Physics Center, San Sebastian, 20018, Spain.
2 Centro de Fisica de Materiales, CSIC-UPV/EHU, San Sebastian, 20018, Spain
3 Centro Singular de Investigacio´n en Quı´mica Bioloxica e Materiais Moleculares (CiQUS)
Departamento de Quımica Organica, Universidade de Santiago de Compostela,
Santiago de Compostela, 15782, Spain.

We present herein the synthesis, characterization, manipulation, and theoretical modeling of two prototypes of corannulene-based nanovehicles. Corranulene was chosen as the basis of our molecular scaffold because of its curve-to-flat transition having low kinetic barrier [1]. One state is expected to be mobile on the surface while the other is not; these two states simultaneously afford motion and stable on-surface characterization. For the first prototype, we used an on-surface route toward the synthesis of the nanocar. Precursors were first synthesized by aryne-based chemistry and Diels-Alder reaction and then deposited on the Au(111) surface. However, these precursors did not produce the target product, because the competing pathways for the formation of quasi-planar products have lower energy barrier, as confirmed by both STM experiment and DFT calculations [2]. Therefore, for the second prototype, we used a coranulene-based nanovehicle synthesized in solution. Two products were observed upon deposition on the surface. One product was found to be stationary and stable on the surface while the other was found to be mobile due to the three-dimensionality and the polarity afforded by the twisting around aromatic rings. In the last part, we give perspectives for possible future prototypes.

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Molecular motor at the frontier of classical motion and quantum tunneling

Samuel Stolz[1,2], Oliver Gröning[1], Jan Prinz[1,2], Harald Brune[2], Roland Widmer[1]

[1] *Empa, Swiss Federal Laboratories for Materials Science and Technology,*
8600 Dübendorf, Switzerland
[2] *Institute of Condensed Matter Physics, Station 3, EPFL, 1015 Lausanne, Switzerland*
(e-mail: roland.widmer@empa.ch)

In his seminal 1959 lecture "There's Plenty of Room at the Bottom", Richard Feynman envisioned the downscaling of information storage and machines to atomic dimensions[1]. Both challenges were eventually met, first by writing information by positioning single atoms on a nickel surface in 1990[2], then by the realization of the first artificial, light-driven molecular machine in 1999[3]. To this day, however, most synthetic molecular machines, while driven by quantum processes such as light absorption and bond reconfiguration, exhibit classical motion only[4,5].

We have realized and investigated a molecular motor, which converts non-directional, stochastic input stimuli into highly directional rotation and operates at the frontier between classical motion and quantum mechanical tunnelling. It consists of a single acetylene (C_2H_2) rotor anchored to a chiral atomic cluster that acts as stator and is provided by a PdGa(111) surface. By breaking spatial inversion symmetry, the stator defines the unique sense of rotation. We have studied the electronically and thermally activated (5-25 K) motion of this motor by scanning tunnelling microscopy (STM). While the thermally activated motion is non-directed, as dictated by the 2nd law of thermodynamics, inelastic electron tunnelling (IET) through C_2H_2 is able to trigger a rotation with a directionality exceeding 97%.

The acetylene on PdGa(111) motor therefore pushes molecular machines to their extreme limits, not just in terms of size, but also regarding structural precision, degree of directionality, and crossover from classical motion to quantum tunnelling. This ultra-small motor thus opens the possibility to investigate in-operando effects and origins of energy dissipation during tunnelling events, and ultimately energy harvesting at atomic scales.

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Mechanisms of molecular machines

Michel A. Van Hove

Department of Physics, and Institute of Computational and Theoretical Studies,
Hong Kong Baptist University, Hong Kong, China.

Central issues in molecular machines are energy intake, conversion, output and transmission. This talk will discuss basic issues of the operation of molecular motors, including energy conversion steps, continuous energy supply, the role of thermal energy, intentional start and stop of motion, unidirectionality of motion and transmission of rotation among gear-like molecules. Without intentional control of these aspects, motors create random motion and are largely useless. Some molecular machines cause reciprocal motion, as in muscles and switches, while others cause rotational motion, as in flagellae: we discuss mechanisms and theoretical models of both.

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Probing the motion of a molecular rotor by single-molecule force spectroscopy

Xun Li (1), Damien Sluysmans (1), Yohan Gisbert (2), Claire Kammerer (2),
Gwenael Rapenne (2), Anne-Sophie Duwez (1)

1) UR Molecular Systems, University of Liege, Sart-Tilman 4000, Belgium
2) CEMES, Universite de Toulouse, CNRS, Toulouse, France

Controlling internal motions of artificial molecular machines has become highly important for the design of functional devices with unprecedented properties. In this regard, different types of rotary molecular motors have been synthesized. For instance, a series of electron-fueled organometallic rotors was presented, consisting of (i) a five-armed rotary component and (ii) a tripodal stator made of a scorpionate ligand[1]. Both components are connected by a ruthenium atom allowing the rotation of the rotor with respect to the stator. Various molecular rotors of this type were already synthesized with the possibility of selectively modifying the rotor arm end-groups[2].

Using scanning tunneling microscopy (STM), Hla and co-workers[3] showed the rotational switching of individual rotary molecular motors adsorbed on a gold substrate. They evidenced the unidirectional motion of the rotor in both clockwise and anticlockwise directions when excited by an STM tip in an ultrahigh-vacuum environment and at low temperature.

Here we have probed the motion of single rotary motors in solution and at room temperature using atomic force microscopy (AFM)-based single-molecule force spectroscopy (SMFS). The stator component was modified to facilitate its anchoring on a gold substrate using Au-S interactions, and one arm of the rotor was chemically linked to a poly(ethylene oxide) (PEO) chain used as a tether for the attachment to the tip during force-spectroscopy experiments. SMFS experiments consist in approaching an AFM tip towards the surface where the motors are grafted to establish interactions with the PEO tether, and then retracting it away from the surface and observe the mechanical response of the probed molecule. Here, we show that we can successfully detect the rotation, both autonomously and when mechanically loaded, of the five-arm rotor around the single ruthenium atom and report on the direct measurement of the work generated by the rotation. We demonstrate how the intensity of the load influences the rotational speed and show that the nature of the arms influences the energy barrier, causing differences in the forces that the motor can develop.

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Towards 2D molecular templates on coinage metals and graphene for single molecule mechanics

R.S.K. Houtsma, A.J. Watson, B. D. Baker Cortes, N.D.R. Schmidt,
J. Li, S. Gottardi, J.C. Moreno Lopez, M. Enache, M. Stöhr

Zernike Institute for Advanced Materials, University of Groningen,
Nijenborgh 4, Groningen, The Netherlands
r.s.k.houtsma@rug.nl

For studying single molecule mechanics, both 2D molecular networks and metal-organic coordination networks (MOCNs) adsorbed on solid substrates can act as excellent templates. For instance, porous networks may be created with tuneable pore size dependent on the choice of the building blocks. The network pores are then used for trapping individual molecules so that their properties can be studied individually and in detail. On the other hand, networks with 1D topologies may be used for looking at the interaction of a controlled number of molecules. A huge variety of networks can nowadays be created thanks to the large tool box of available molecules and substrates.

Here, we will present examples for such (porous) molecular networks and discuss their properties. Porous networks were on the one side formed from porphyrin derivatives and Co adatoms on Au(111) based on metal-ligand interactions [1]. On the other side, a H-bonded porous network was obtained from 1,3,5-benzenetribenzoic acid on graphene [2]. Using graphene as substrate has the advantage to effectively decouple the 2D adsorbate structures from the underlying metallic substrate. Lastly, a close-packed porphyrin derivative-based network was formed on both Au(111) and graphene, permitting a comparison of the two substrates. A difference in diffusion was observed between the two substrates. In addition, measurements on the electronic properties of the networks on graphene show a significant decoupling of the networks once adsorbed on the graphene.

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Quantum Molecular Machines

Saw Wai Hla
Ohio University, USA

Synthetic molecular machines designed to operate on materials surfaces can convert energy into motion and they may be useful to incorporate into solid state devices. This talk will present molecular motors and molecular linear transport devices operating in the quantum regime on materials surfaces. Individual and self-assembled molecular machines on materials surfaces are imaged using low temperature scanning tunneling microscopy. By utilizing electric field or inelastic tunneling electrons from a scanning tunneling microscope tip, or by using tip-molecule force, operations of molecular motors, molecular propellers, and molecular transport devices are investigated on a one machine-at-a-time basis in an atomically clean environment [1-3]. These investigations reveal how charge and energy transfer are taken place within single molecule machines and molecular networks. By exploiting the chirality of the molecular structure, unidirectional rotation of the molecular propellers can be realized. Moreover, by introducing dipole active components in the rotor arms of the molecular motors, communication among the motors can be introduced [2]. Synchronization of the motors can be achieved depending on the symmetry of the molecular assemblies and the strength of the electric field.

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