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A Train of Single Molecule-Gears

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KEYWORDS: Molecule-gear train, Molecule-machinery, LT-UHV STM, molecule manipulation, Single Atom Axle.

ABSTRACT: Two molecule-gears, 1.2 nm in diameter with 6 teeth, are mounted each on a single copper ad-atom separated exactly by 1.9 nm on a lead surface using a low temperature scanning tunneling microscope (LT-STM). A functioning train of 2 molecule-gears is constructed completed with a molecule-handle. Not mounted on a Cu ad-atom axle, this ancillary molecule-gear is mechanically engaged with the first molecule-gear of the train to stabilize its step by step rotation. Centered on its Cu ad-atom axle, the rotation of the first gear of the train step by step rotates the second similar to a train of macroscopic gears. From the handle to the first and to this second molecule-gear, the exact positioning of the two Cu ad-atom axles on the lead surface ensures that the molecular teeth to teeth mechanics is fully reversible.

Sacrificial layer based SiO₂ micro-gears technology and their rotational mechanics have shown a rapid development since 30 years.¹ This was recently pushed forwards down to the mesoscale with the nanofabrication of solid state nano-gears having a 30 nm diameter and using the nanolithography resist itself for the gear material.² The demonstration that a designed molecule can do more than a random rotation on a surface³ was accompanied by the study of a series of single molecule mechanical machinery like the non-reversible CO Domino effect molecular cascade,⁴ the molecular rack and pinion,⁵ the molecule wheelbarrow,⁶ the switchable molecule-motors⁷ and molecule-vehicles⁸⁻¹⁰ able to function alone on a surface and not in average among billion and in solution.¹¹

The stabilization of a stable atomic scale rotation axle is the bottleneck for constructing single molecule rotating machinery. For long, native not well identified atomic scale impurities found at the kinks of the Au(111) herringbone reconstructed surface have been used as a rotation axle.^{3,12} Chemical bonding was also used either directly on the surface¹³ or supported by a molecular tripod.⁷ Here we present a molecule-gear train constructed at 5 K with three HB-NBP (C₆₄N₂H₇₆) molecules (Fig. 1f) by a series of single atoms and molecules STM manipulations performed on a Pb(111) surface. For the atomic scale rotation axle and among the Ag, Cu and Co possible isolated ad-atoms on the Pb(111) surface, we have selected Cu because of its apparent height equal to atomic scale impurity height on the Au(111) surface. This selection results from DFT calculations to determine the adsorption surface distance and adsorption site of Ag, Cu and Co on the Pb(111) surface and if there is a possible exchange between those atoms and the Pb(111) surface atoms. This also leads to determine that the Cu atoms must be evaporated while the Pb(111) surface is already at LHe temperature. Mounted and stabilized by van der Waals interactions on a Cu ad-atom axle on Pb(111) (Fig. 1), a single molecule-gear is stable with no thermal activated random

rotation up to a surface temperature of 20 K. The chirality of the HB-NBP molecule on the surface cannot be used for a one-way rotation due to the micro-reversibility principle³. The Pb(111) surface was selected in a way to minimize the electronic friction between the molecule-gears in rotation and the Pb(111) surface.¹⁴ This lowering of the electronic friction is coming from the fact that the contributions to the surface image charge of the small weight electron-hole quantum state configurations entering in the ground state of this molecule (while adsorbed on a metal surface) is cancelled when the metallic surface is in its superconducting state.

Lateral translations and step by step rotations of a single molecule equipped with lateral tooth chemical groups have been well studied with the STM.³ The energy to trigger a rotation can come from the surface thermal energy,^{12,15} from a short time duration of the STM bias voltage pulse^{7,13,16-18} or from a mechanical interaction (pushing, pulling) between the molecule and the end atom of the STM tip apex.^{3,19} This last protocol is used here because it is in general more reliable than a bias voltage pulse actuation whose resulting inelastic ro-vibronic excitations has a large tendency to be equi-distributed among all the mechanical degrees of freedom with no bottleneck effects. The functioning of our molecule-gear train is also based on a fine tuning of the Cu ad-atom axle inter-atomic distance on the Pb(111) surface. When meshing with the tooth of another molecule-gear, the relaxed conformation of the molecular tooth and their relative flexibility complete the gear-train molecular design. The 5 K surface temperature ensures that each molecule-gear is in its electronic and mechanical ground states. Using the tip apex end atom mechanical interactions with the molecule, the potential energy increase of the ancillary handle molecule-gear during a manipulation step for rotation beneficiates mainly to the collective rotation angles of the two others molecule-gears along the train. Mechanical decoherence and dissipation towards the many others

mechanical degrees of freedom of the train is not perturbing this transmission of rotation triggered by single STM molecule manipulation in a pushing mode.

Thermally sublimated HB-NBP molecules are forming 2D islands on the small terraces available on our Pb(111) surface (Suppl. Info. S1). They are also imaged adsorbed a few together around atomic scale impurities on this surface (Fig. 1a). They are not stable alone on a terrace (Suppl. Info. S1) even when intentionally STM manipulated from the border of a 2D molecular island. This confirms the reduced Pb(111) surface electronic friction during surface molecule diffusion when the lead sample is cooled down below its critical superconducting temperature. In the LT-UHV STM images with, for instance, 500 mV of bias voltage and 10 pA of tunneling current, the Cu ad-atom apparent height is 60 pm. It is the same apparent height than the atomic-sized defects found at the herringbone kinks of the reconstructed Au(111) surface (Suppl. Info. S2). They were previously employed as uncontrolled surface native rotation axle.^{3,12} On the Pb(111) surface and unlike on Au(111) and Cu(111),^{3,5} the pyrimidine chemical tag introduced to follow the step by step rotation of a molecule-gear cannot be discriminated at low bias voltage in the molecule-gear STM image. Our interpretation is that the HB-NBP molecules are physisorbed at larger surface distances on Pb(111) than for example on Au(111). As a consequence, the width of the positive tunnelling resonance carrying the tag signature is smaller on Pb(111) than on Au(111) and this molecular orbital signature cannot be observed at low bias voltage on Pb(111). In absence of this chemical tag effect, the tooth height difference was used on the Pb(111) surface to follow the molecule rotation with one tooth over 6 teeth having always a lower apparent height as compared to the 5 others in this HB-NBP ground state physisorbed conformation (Fig. 1d).

To be mounted on a Cu ad-atom axle, one molecule-gear was first selected at a mono-atomic step edge. Then, the STM junction resistance was reduced to 5 M Ω with the STM tip apex generally positioned in the center of this molecule. The tip apex trajectory is determined for the molecule-gear to be directly positioned atop the targeted Cu ad-atom. During a molecule manipulation sequence, the Cu ad-atom can also be displaced from its hollow site to the next requiring in this case a complete re-alignment of the gear train after construction. While mounted and centered on-top its Cu axle, a protrusion is imaged at the molecule-gear center as shown in Fig. 1d. Elastic Scattering Quantum Chemistry (ESQC) constant current low bias voltage image calculations²⁰ were performed to extract the corresponding molecule-gear conformation. They confirm that the molecular adsorption geometry is modified as compared with the gas phase conformation. One tert-butyl tooth directs its two methyl groups slightly downward in contrast with the 5 other teeth with only one of their methyl groups downward regardless the mounting on a Cu ad-atom (Figs. 1e and 1f). The step by step rotation sequences reported below were analyzed using this surface conformation characteristics in the STM images after a given series of molecule manipulations.

After its mounting and centring on a Cu ad-atom and to step by step rotate the molecule-gear, both constant current and constant height STM mechanical manipulation for a rotation were attempted unsuccessfully. Typical junction resistance were from 20 M Ω to 100 M Ω searching the best STM tip location and trajectory over the molecule-gear.³ In many cases, the molecule-gear was dismounted from its Cu axle and moved laterally alone because a small rotation can give access to a minimum energy path lateral motion on this Pb(111) surface (Suppl. Info S3, Fig. 3.2). In rare cases, both the molecule and the Cu ad-atom were displaced laterally (Suppl. Info. S4) illustrating how a centred atop Cu molecular configuration is a metastable conformation for a

molecule-gear alone on Pb(111). During a manipulation sequence and even at constant current (to minimize the tip apex molecule interactions strength), this repulsive interaction is mechanically destabilizing this atop configuration. According to semi-empirical molecular mechanics calculations,²¹ a total of 15 stable stations are potentially existing for a stand-alone molecule-gear on its Cu ad-atom axle (Suppl. Info. S3). This corresponds to the fcc(111) C_{3v} symmetry Pb(111) surface around a hollow-site (i.e., the Cu ad-atom axle of rotation position).). Here, the number of stations can be 3, 6, 9, 12 or 15 depending on the chemical structure of mounted molecule. For our HB-NBP molecule-gear, the 15 stable conformations are in competition with the lateral surface shift of the HB-NBP centre relative to its Cu ad-atom axle (Suppl. Info. S3). Furthermore, and according to the Suppl. Info. S3, stations 1 & 2, 3 & 4, 6 & 7, 8 & 9, 11 & 12 and 13 & 14 are very close in energy with a conformational barrier height change below 50 meV between each two. This leads only to 9 possible stable stations on the Pb(111) surface. Therefore, the step by step exploration of those 15 stations by STM mechanical manipulations is rather unstable as observed experimentally (Suppl. Info. S4).

Ramping up the bias voltage was also performed, positioning for example the tip apex at a tooth location or at the centre of molecule. Permutation of the teeth conformation between the two methyl group's downward one (which induces lower apparent height than others) and one of one methyl group downward teeth occurred above 2.5 V. This leads generally to a random rotation (in direction and angle) of the molecule-gear while remaining centred on its Cu ad-atom (Suppl. Info. S5). Here and on the excited states potential energy surface, the resulting inelastic tunnelling current excitations is not very efficient in opening a collective conformation change trajectory which will lead the molecule-gear to turn in only one direction. This energy is used first by the molecule-gear to permute the conformation of 2 teeth, a conformation change path which is

energetically less demanding on the molecule-gear excited state potential energy surface than activating the complete rotation of the molecule-gear. When a complete rotation is occurring, it is 50% in one direction and 50% in the other direction because the little chirality resulting from the physisorption on Pb(111) is not reflected on the excited states potential energy surface because dispatched in too many direction on those surfaces. Notice also that an inelastic tunnelling excitation process is a quantum process which is not allowing a full occupation of those excited states. This is lowering the amount of energy transferred to the mechanical degrees of freedom as compared to a vertical optical excitation.

To stabilize the Cu atop molecule-gear configuration, a second molecule-gear with one of its tert-butyl groups absent was meshed laterally by its remaining teeth to the atop Cu one as presented in Figs. 2a and 2b. One teeth missing molecule-gears can always be found on the Pb(111) surface. They are certainly produced during the molecular sublimation process. No need here to mount this second molecule-gear (here after the handle) on a Cu ad-atom axle. Once mechanically entangled with the handle by STM molecule manipulation in a pushing mode, the atop centred Cu molecule-gear rotates gently, step-by-step and clockwise when STM manipulated clockwise (and anticlockwise, the reverse). We have observed 9 stable stations for this handle-gear mechanical machinery while rotating the handle (Fig. 2c). Here, the STM tip apex end atom must be centred on the handle molecule as presented in Fig. 2c (see also Suppl. Info. S6). The un-toothed phenyl part on the handle and the apparent lower height tooth of the molecule-gear are always adsorbed on same site during a one-step rotation event. Stabilized by its handle, the number of stations of the handle-gear mechanism must be reduced as compared to the previous unstable 15 stations because the handle works at different angles for rotation ($\pm 12^\circ$ if it was a rigid body mechanism) relative to the Cu ad-atom of its molecule-gear partner. It is down to 9 stations due to $3\sigma_v$ specular

symmetry in C_{3v} system. We have also observed 2 meta-stables stations whose occurrence is depending on the detail tip end atom apex interactions with the handle and of its conformation changes during the rotations. Consequently, and for the rotation sequence presented in Fig. 2c, stations ix & x are similar and also stations xi & xii. The major molecular mechanical effect of the handle is to stabilize the tendency of the Cu centred molecule-gear to escape from its Cu single ad-atom axis when STM manipulated even in a constant current soft mode of manipulation because of the ground state escape ways well identified by calculations (Supp. Inf. S4). Then, the teeth on the handle are transmitting the rotation by a simple teeth to teeth repulsive effect in view of the relatively low 0.2 eV rotation potential energy barrier between the 9 stations (Supp. Inf. S4).

To construct a train of gears, two molecule-gears were also mounted one after the other and centered each on a single Cu ad-atom separated by an interatomic distance of 1.9 nm on the Pb(111) surface. This distance is determined for the teeth of each molecule-gear to be interdigitated enough to ensure a transmission of rotation by inter-teeth repulsion effect as observed above between the handle and the gear. This Cu-Cu distance must not be too close to avoid the attraction between the two molecule-gears which may destabilize their respective atop position on the Cu ad-atom by forming an independent $C_{64}N_2H_{76}$ molecules entangled dimer. This 1.9 nm distance was determined by testing different Cu interatomic distance, rotating one molecule-gear and imaging the molecule-gear dimer. A long time ago, the construction of the first mechanical astronomical clock had also required such an optimization for transmitting a rotation motion from one bronze gear to the next.²² Since the Pb(111) surface nearest-neighbour hollow site interatomic distance is 0.20 nm, we have explored different Cu ad-atom surface configurations to reach this 1.9 nm interatomic distance. But manipulating a single Cu ad-atom alone by the STM tip was difficult on the Pb(111) surface because the Pb atomic radius is one of the largest in its category

leading to a large Pb(111) corrugation. Here, we have used the known $C_{64}N_2H_{76}$ molecule property to be able to lower a single Cu ad-atom lateral diffusion barrier on Cu(111)²². This works also on Pb(111) with different STM manipulation conditions than for rotating the handle. (Suppl. Info. S4).

For our molecular machinery to function, the handle molecule was added to our train of 2 molecule-gears following the STM molecule manipulation procedure presented above. Without this handle, the rotation of the first molecule-gear is not transmitted to the second one because of a progressive de-centring of the 2 molecule-gears relative to their Cu single ad-atom axle. It causes the teeth in interaction to avoid each other by a lateral conformation change leading to a ripping effect well reproduced by semi-empirical molecular mechanics calculations (Suppl. Info S7). Smaller Cu-Cu distances have been also tried. But in those case, the two molecule-gears were interacting too strongly. To construct a functioning molecule-gear train, this demonstrates the delicate competition between teeth conformation changes (especially their respective tert-butyls terminal group and their rotation around their respective phenyl) and the centring of each molecule-gear on its Cu axle. As a result and with smaller Cu-Cu distance, the two molecule-gears were stuck and only the handle was able to rotate around its molecule-gear.

Once constructed, the first molecule-gear of the train is step by step rotated by STM manipulating the handle. As presented in Fig. 3, the step by step rotation of the first molecule-gear of the train is transmitted to the second one (See also Suppl. Info. S6). In this now rather complex molecular machinery, it is of prime importance to have the two molecule-gear well atop and centred on their respective Cu ad-atom as commented above. This centring avoids the lateral motion of those 2 molecule-gears which are now self-stabilized by their entangled teeth and by the handle. As a result, the rotation motion is transmitted by steps of about 30 degrees. This angle

cannot be exactly 30 degrees because of the repulsive interactions between the entangled teeth during a given rotation step (see Fig. 3 caption determined values). Those interactions are creating intramolecular conformation changes along the gear train which must accommodate at each rotation step the quite rigid Pb(111) surface atomic lattice order to reach the ground state of this $C_{64}N_2H_{76}$ constructed molecular trimer. As a consequence, the transmission of rotation along the molecular gear train is the result of a more complex mechanics than its rigid macroscopic¹ or solid state mesoscopic counter parts².

CONCLUSION

Along a train of molecule-gears and as demonstrated here, the transmission of a rotation motion from the first molecule-gear to the next requires a precise optimization of the atomic axle per gear and of the relative positioning of each molecule-gear along the train to be compatible with the molecular teeth flexure in between the molecule-gears. Then, this transmission is reproducible and reversible. Such rotation transmission is important for the future construction of a molecular scale *Pascaline* mechanical calculator, to measure the motive power of a single molecule motor using different molecule-gear train length (or molecule-gears of different diameters and teeth) and to input data on an atomic scale quantum circuit by mechanically toggling single molecule switch per input digit. All those applications are pointing the importance of on-surface semi-classical molecular mechanics performed with an atomic scale precision and molecule per molecule.

MATERIALS AND METHODS

The $C_{64}N_2H_{76}$ molecule-gears were sublimated on the Pb(111) surface in UHV and at room temperature just after the UHV Pb(111) surface cleaning using cycles of Ar⁺ sputtering and heat

treatment. After the Pb(111) surface sample transfer inside the low temperature STM chamber and its 5K thermalization, the Cu atoms were deposited on this surface through a small window with a shutter installed on the LT-shield in this chamber. Our microscope is the new ScientaOmicron instrument equipped with four STM scanners able to take images and to perform spectroscopic measurements independently from each other on the same surface.²⁴ Cu ad-atoms are adsorbed on the Pb(111) hollow sites of this close-packed structure surface with an extremely low 0.001 ML coverage to ease the molecule-gears train construction.

The ESQC technique²⁰ was used to determine the molecule conformation on the lead surface and to calculate the corresponding STM image of the molecule-gear. The ASED+ semi-empirical method²¹ was employed to optimize the molecule conformation.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Molecule-gears on a Pb(111) surface, atomic scale axle height, direct STM mechanical manipulation of a single molecule-gear, molecular mechanics calculations of the handle effect, rotational manipulation of a molecule-gear by voltage pulse, and movies (PDF)

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Notes

The authors declare no competing financial interest.

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Figure 1

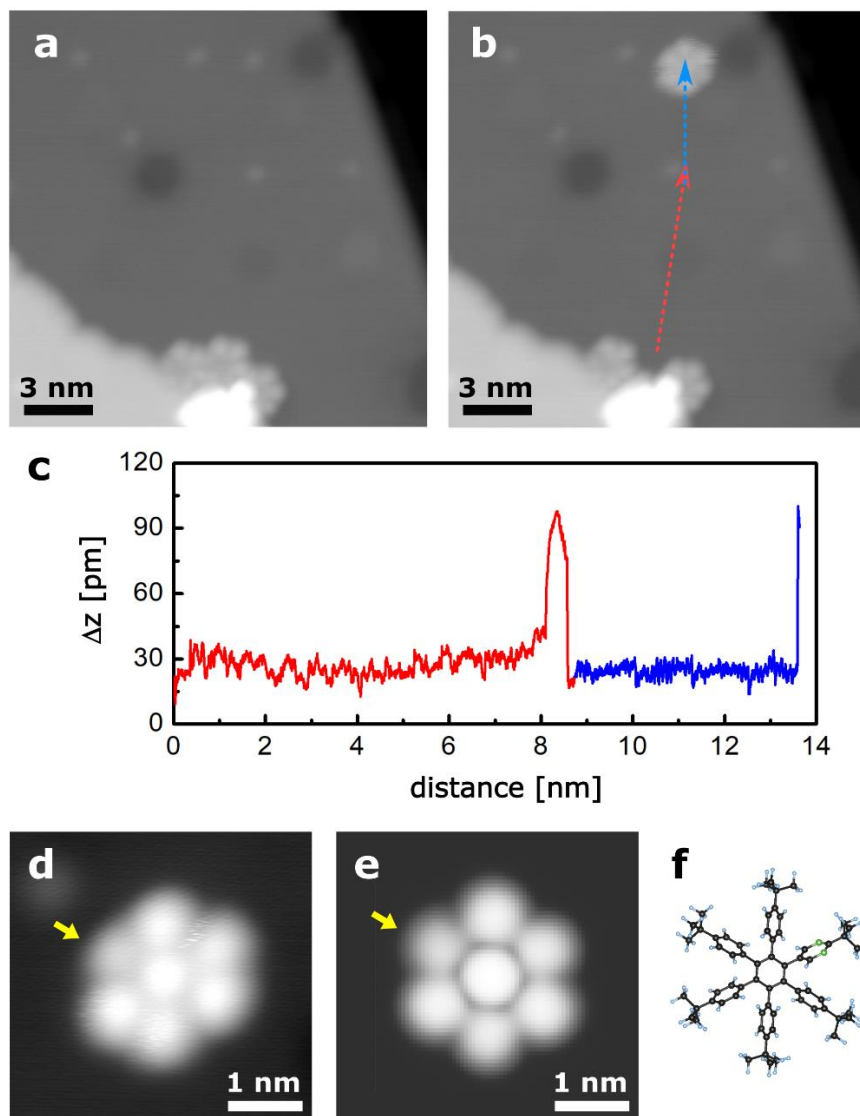


Figure 1. An HB-NBP ($C_{64}N_2H_{76}$) molecule-gear mounted on its single Cu ad-atom axle on Pb(111) surface. (a) Molecule-gears sublimated on a lead surface at room temperature are stabilized when attached to an impurity. The Cu atoms deposited on cryogenic sample can be identified together with hexagonal Ar-bubbles on Pb(111). (b) A molecule-gear was mechanically manipulated by STM tip and mounted on a single Cu atom axle. The first attempt of fixing on its

axle (red arrow displays the tip trajectory during manipulation and is corresponding to the tip height profile presented in (c) by red line) was not successful because of an over manipulation, which brought the Cu atom to also move when the molecule was detached from it. Molecule was mounted successfully during the second attempt (blue coloured in both (b) and (c)). Here the tip height is jumping up exactly 60 pm when the molecule is mounted atop the Cu ad-atom. (d) the STM experimental image of this molecule-gear on its Cu axle with the central protrusion coming from this Cu ad-atom with a tooth having a lower apparent height than other five (indicated by an arrow). (e) ESQC calculated STM image showing also the difference between these teeth contrast resulting from different tertiary butyl group angles. (f) the on-surface optimized molecular conformation used in those calculations. All STM images were taken under the conditions of $V = 100$ mV and $I = 10$ pA.

Figure 2

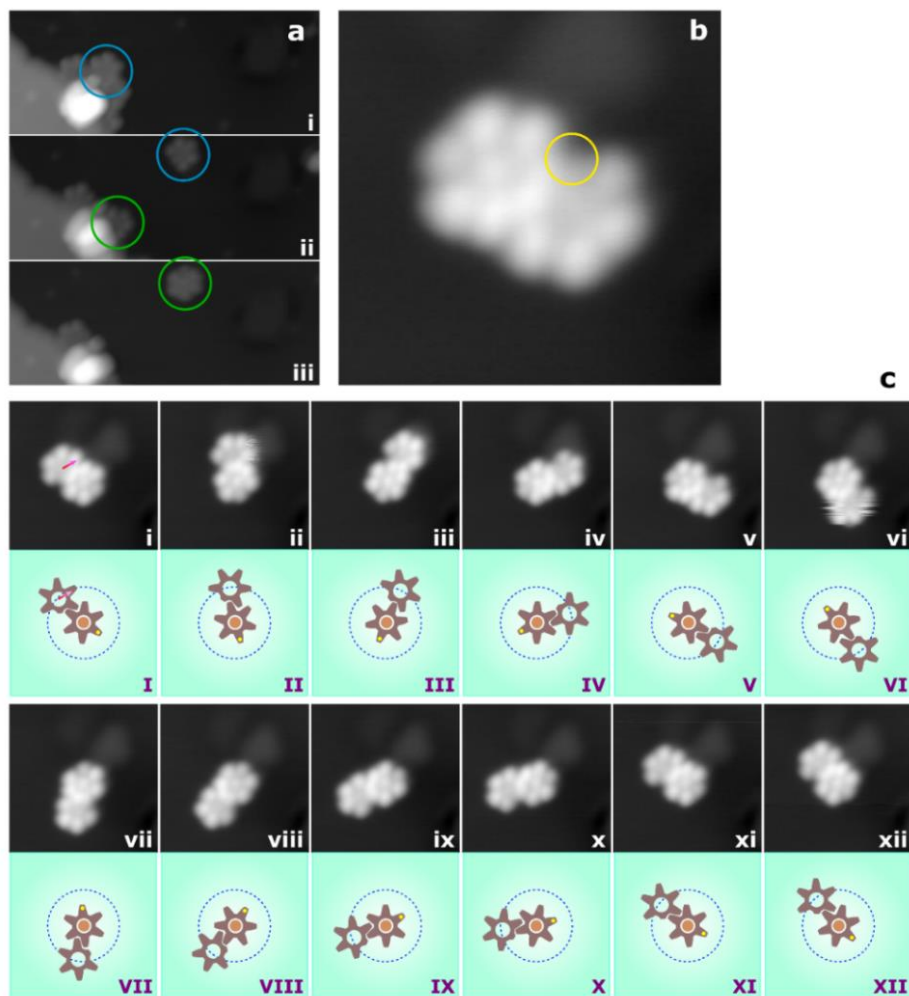


Figure 2. A single Molecule-gear rotation sequence using an ancillary molecule handle. (a) The molecule-gears were dragged away from the impurity. The molecule in the blue circle in i and ii (before and after manipulation) had lost a tert-butyl tooth and the one in the green circle (in ii and iii) is a complete one. (b) The single molecule-gear with its molecule-handle was constructed starting from the two molecules in a. The intact molecule-gear was mounted first on Cu axle and the one with a missing tooth was manipulated in mechanical contact after. The arm of the missing tooth was positioned close to main gear molecule (marked by yellow circle). The lower in height tooth is facing the far side of the handle molecule. (c) i-vii: a sequence of experimental STM

images recorded during a step-by-step full rotation sequence with the corresponding I-XII schematic diagram using a classical mechanical gear model. The arrow in i indicates the STM tip trajectory for the rotation from i to ii. The same manipulation condition, i.e. the initial and the end points for the manipulation at each step were carefully set at the same location of the handle-molecule. Notice that during a rotation, the handle molecule does not rotate around the molecule-gear like in a rack-and-pinion machinery. The missing tooth position of the handle and of the lower height tooth site of the gear keep the same conformation. 11 stations were observed in this experiment. All STM images (8 nm x 8 nm) were taken under the conditions of $V = 500$ mV and $I = 10$ pA.

Figure 3

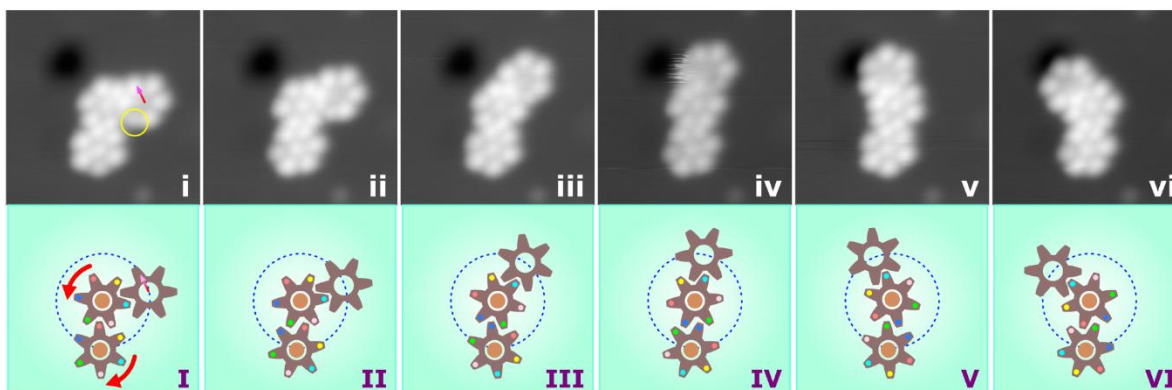
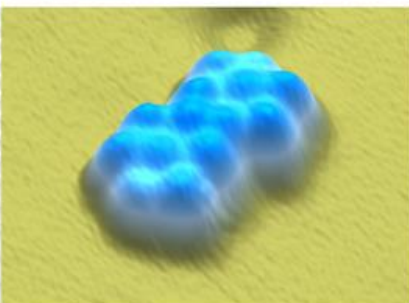
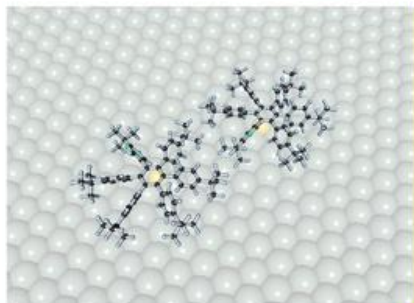


Figure 3. The transmission of rotation along a molecule-gear train. i-vi, a sequence of experimental STM images during the step-by-step rotation and transmission along a molecule-gears train and in I-VI, the corresponding schematic diagram using a classical mechanical gear model. The train rotation is performed with the first molecule-gear (in the middle of the train) using its handle molecule with no central protrusion (no Cu axle). The rotation is transferred to the second bottom molecule-gear. Step by step, the rotation angle of the first molecule-gear is between 20 to 35 degrees. In contrast, the second gear rotation alternates between 27 and 33 degree due to the stabilization from the handle molecule. The handle and molecule-gear are better coupled than the two molecule-gears. The handle molecule reaches its own stable position after reaching the end point of manipulation on the Pb(111) surface. Noticed that the teeth height difference on the first molecule-gear is difficult to discriminate. The lower height tooth of the handle molecule (yellow circle in i) stops precisely at the same location each step after manipulation, it is a proof of the first gear rotation. On the other hand, the lower height tooth of the second gear molecule changes its site during rotation. It is due to the alignment of the tert-butyl group angles of the teeth when they are meshing at the connecting point of the two molecule-gears during the transmission of rotation. All STM images (8 nm x 8 nm) were taken under the conditions of $V = 500$ mV and $I = 10$ pA.

Table of content graphics

Molecule-gears



Macroscopic gears

