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Mechanics of Molecule-Gears with Six Long Teeth

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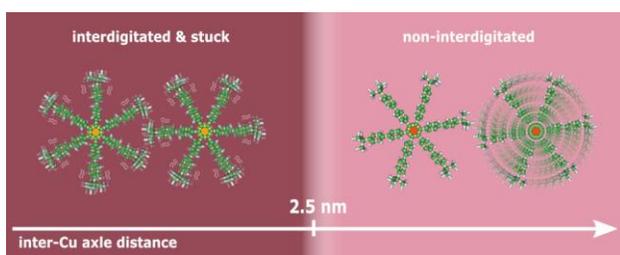
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KEYWORDS: large molecule-gear, molecule-machinery, LT-UHV STM, molecule manipulation, mono-atomic step edge.

ABSTRACT: On a Pb(111) surface in its superconducting state, the construction of a train of two and three hexa-tert-butylbiphenylbenzene molecule-gears (HB-BPB) is presented using a single Cu ad-atom rotation axle per molecule-gear for the two first ones. The new presented HB-BPB gears have been designed and synthesized with very long biphenyl teeth to minimize the number of Cu rotation axles for a long train construction when engaged at larger inter-axle distances. It leads to a strong mechanical entanglement between the gears and renders a transmission of rotation along the train difficult. To minimize this classical entanglement, a practical solution is presented by using a native Pb(111) surface mono-atomic step and by positioning each molecule-gear of the train at different mono-atomic step heights on the supporting surface. This allows the construction of functioning long molecule-gear trains.

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INTRODUCTION

Gears are essential elementary devices for constructing mechanical machinery like clocks,¹ for transmitting and converting the motive power of a motor² and for building calculators able to work in hostile environments like in nuclear power plants or in space.³ Minimizing the energy for those machineries to function and reducing their weight for portability require miniaturizing the gears as much as possible. Depending on the available technology of the period, cogwheels of decreasing size have been successively fabricated by hand, machine tools, 3D-printing and molding,⁴ optical micro-lithography,⁵ field-ion beam lithography,^{6,7} e-beam lithography⁸, supramolecular assemblies (Ref. 9, Ref. 10) and more recently using scanning tunneling microscopy (STM) single molecule manipulation protocols⁹ applied to molecule-cogwheels obtained by chemical synthesis.¹⁰

To date, the smallest known functioning short molecule-gear train was constructed on Au(111) using star-shaped pentaphenylcyclopentadiene molecules (PPCP) with one phenyl tooth per molecule ending with a tert-butyl group in the para position, that acts as a steric tag and also like a molecular handle (Figure 1, left).¹¹ Small PF₃ molecules have been advocated long ago for gearing effects depending on the metal surface used,¹² but they are not rigid enough for such functioning while isolated on a metal surface.^{13,14} A little larger in diameter than PPCP, the step by step rotation of a single hexa-tert-butylpyrimidopentaphenylbenzene (HB-NBP) molecule (Figure 1, center) mounted on a native atomic scale impurity on Au(111) had been explored experimentally¹⁰. Very recently the same molecule was successfully arranged in a train of single-molecule gears on Pb(111), leading to correlated motion of the interlocked cogwheels.¹⁵ Larger in diameter, tin-phthalocyanine molecules (SnCl₂Pc) have also been used for exploring a molecular domino effect based on a 35° jittering of each SnCl₂Pc along the molecular train.¹⁶

There are plenty of possibilities to optimize the functioning of a train of molecule-gears from (1) the supporting surface of the train, (2) the rotation axle of each molecule-gear, (3) the central molecular core of the gear, (4) the structure and length of their teeth and finally (5) the ground state potential energy surface (PES) for rotations along the train while mounted each on a rotation axle. For (1) and also (5), normal metal,¹⁰ superconductor¹⁵ and semi-conductor¹⁷ surfaces have been explored to tune the PES molecule-gear rotation barrier and moderate the surface friction effects. For (2) and in relation to the choice of a supporting surface, different types of atomic scale axles have been explored, with an initial attempt to exploit native atomic scale defects at the Au(111) herringbone kink reconstruction.¹⁰ Those native herringbone kinks on Au(111) are arranged with about 8 nm periods on large Au(111) atomically flat terraces.^{10,11} This separation is too large as compared to the current known molecule-gear lateral size (smaller than 2 nm) to engage two of them together in a mechanical interaction. As a consequence, alternative and more modular approaches have been pursued, ranging from the use of specific single metallic atoms on purpose evaporated on the supporting surface¹⁵ to direct chemical bonding to the surface.¹¹ Also multistep chemical synthesis now allows chemists to prepare a wide range of tailor-made molecule-gears with various shapes and structures.¹⁸ In particular, it is possible to synthesize metallo-organic structures to be deposited on surface, incorporating a top rotor linked to a central single metal atom rotation axle, itself supported by an additional ligand. The latter thus holds the rotor and the rotation axle away from the surface and acts as anchor on surface, with structures ranging from tripodal hydrotris(indazolyl)borate¹⁹ to penta(bromophenyl)cyclopentadiene for which its propeller shape can mimic deposition on a chiral surface.²⁰ For (3), the central core was up to now a small circular shape molecular group such as a cyclopentadiene or a phenyl core.^{10,11,15} Larger in diameter, a central molecular

chemical core like hexabenzocoronene²¹ generally leads to a non-stable rotation around an atomic axle. This is because such a nanographene like molecular core does not offer a lateral diffusion barrier height in the centre of this core that would be large enough to ensure a stable rotation around a single centred ad-atom. For (4), the debate about the teeth relies on the mechanical rigidity of short teeth relative to long ones as compared with the necessity to use long teeth to be able to construct a long train of molecule-gears with a moderate number of STM molecular manipulation steps.^{22,23} Finally, for (5), the resulting ground state PES topology must be such that a collective rotation from the first to the last molecule-gear within a long molecule-gear train should be possible without having the trajectory on this PES to end up in a deep local minimum, *de facto* blocking the transmission of rotation along this train.¹¹

We present here the construction of a train of two and three hexa-*tert*-butylbiphenylbenzene molecule-gears (HB-BPB) using a single Cu ad-atom axle per molecule-gear for the two first ones. For (1): the supporting surface, a lead sample was selected to minimize the on-surface electronic friction during the motion of the molecule. The Pb(111) superconducting surface efficiently cancels the surface image charge (electron-hole quantum coupling) contribution to the electronic friction of the molecule.²⁴ For (2): the rotation axle, we have selected a single Cu ad-atom per gear on the Pb(111) surface because the Cu ad-atom apparent height is here equal to the impurity height on the herringbone-kink of Au(111) surface.¹⁵ For (3): the central core of the molecule-gear, we have kept a phenyl core because it has been shown to be well adapted to the Cu/Pb(111) single atom rotation axle.¹⁵ For (4): the teeth structure, starting from PPCP molecule carrying phenyl teeth and one *tert*-butylphenyl group as steric tag and handle (Figure 1, left) and from HB-NBP molecule with *tert*-butylphenyl teeth and one *tert*-butylpyrimidyl group as chemical tag (Figure 1, center), an interesting possible length extension of the teeth is to go from

a phenyl to a biphenyl spacer between the central phenyl core and the peripheral *tert*-butyl groups, leading to the HB-BPB molecule presented in Fig. 1 (right). No chemical tag was inserted at this stage because of its inefficiency on the Pb(111) surface.¹⁵ For (5): the ground state PES, it is still out of the scope of the new field of molecule-gear mechanics optimization because of the large lateral size of the supporting surface required for the calculations of the large number of mechanical degrees of freedom involved per molecule-gear. One can expect to calculate a minimum energy path for rotation transmission along a long train of gears but not the complete ground state PES as a function of a few characteristic angles per molecule-gear.^{15,23}

We first present the HB-BPB 2D islands formation and its LT-UHV-STM images on the superconducting Pb(111) surface and how to isolated single HB-BPB molecules when extracted one by one from a 2D island edge. Next, the challenges and results related to transmission of rotation from one molecule-gear to the next along a molecular train are presented. After analyzing those results, a first practical solution is described and tested using a native Pb(111) surface mono-atomic step with one HB-BPB on the upper and the second one on the lower terraces.

Sub-monolayer compact deposition of long teeth HB-BPB molecule-gears (a few mg of HB-BPB molecular powder in a quartz crucible at 320 °C during 10 min in UHV) was performed on a Pb(111) surface (cleaned by cycles of argon ion sputtering and annealing) maintained at room temperature. The Cu ad-atoms were then evaporated on the Pb(111) surface through a small shutter of our cryostat after mounting the Pb(111) sample on the sample stage of our LT-UHV 4-STM maintained at liquid He (LHe) temperature.²⁵ Cu ad-atoms are adsorbed on the fcc(111) hollow sites of the lead having 60 pm of apparent height using the standard STM imaging condition. Molecular imaging and manipulation were performed indistinctively on any of the

four STM in a vertical tip configuration.²⁵ The chemical synthesis of the HB-BPB molecule is described in the Supporting Information.

RESULTS AND DISCUSSION

STM molecule manipulation and gear construction with Cu ad-atom. Sub-monolayer deposition of the Fig. 1 (right) HB-BPB molecule leads to the formation of large 2D islands on the Pb(111) surface as shown in Fig. 2a. Those 2D islands have a hexagonal close-packed structure with a nearest neighbour distance of 2.2 nm (± 0.01 nm) (Fig. 2b). Extended by one phenyl group per tooth as compared to HB-NBP molecule-gears,¹⁰ the 2.6 nm in diameter (core-to-core distance between the outermost end hydrogens of 2 opposite teeth) of those long teeth molecule-gears is larger than the observed 2.2 nm nearest neighbour distance on the Pb(111) surface. As a consequence, the tert-butyl groups of a given HB-BPB molecule-gear are now intertwined with the tert-butyls of neighbouring gears (Fig. 2b). Then, the degree of molecular entanglement in those 2D islands is higher than in a 2D molecular cluster of HB-NBP molecules only congregated by van der Waals interactions. Using STM single molecule manipulation protocols, this renders the extraction of a single molecule from its 2D island difficult.

The only way we have found to extract one HB-BPB molecule from its 2D island is to target and then STM manipulate a molecule located at the vertex of a given 2D molecular island. The molecular manipulation conditions are quite hard with a very small 1 M Ω STM junction tunnelling resistance in a pushing mode (see Fig. 3). We have already been confronted with such extreme molecular manipulation conditions while extracting bis-binaphthylidurene (BBD) molecules assembled by pair in small 2D molecular islands on an Au(111) surface²⁶ or PPCP molecules also on Au(111) [11]. In the latter case, it was even necessary to gently indent the

STM tip apex in a given PPCP molecules 2D island to separate the PPCP molecules on the surface.

Once extracted, a long teeth HB-BPB molecule-gear is extremely mobile even at LHe temperature on the Pb(111) surface. To be stabilized on a Pb(111) terrace, each HB-BPB molecule must be directly brought to a Cu ad-atom without any STM manipulation interruption between the 2D island edge and its targeted Cu ad-atom or to an already stabilized molecule (for example by a surface atomic scale defect). To construct a two molecule-gears train, extracted molecules were manipulated in a pushing mode close to a pair of Cu ad-atoms having an interatomic distance between 2.4 nm and 2.6 nm, i.e. slightly shorter than HB-BPB molecular diameter. We first use several Cu ad-atom stations before reaching the definitive pair of Cu axles. Then, the HB-BPB were mounted one by one on the pair axles at the end of the STM molecular manipulations. Notice that even if the HB-BPB molecule diameter has now increased as compared with HB-NBP, it is still possible to mount it centred atop Cu ad-atom by STM mechanical manipulation because in both cases the core is a phenyl ring (Fig. 3 inset).

Train of two molecule-gears with a handle. Two HB-BPB molecule-gears were mounted each on a single Cu ad-atom and positioned to propagate a rotation along a train of two HB-BPB molecule-gears with the help of a third HB-BPB molecule not mounted on a Cu ad-atom, thus acting as a handle.¹⁵ Different Cu-Cu inter-atomic distances were tried on the Pb(111) surface: 2.6 nm as shown in Fig. 4 and 2.4 nm in Fig. 5, compared to the 1.9 nm inter-axle distance used in the case of the HB-NBP molecules also on Pb(111).¹⁵ Other intermediate Cu-Cu inter-atomic distances were also explored. The results were generally the same for all Cu-Cu distances smaller than 2.6 nm leading to a mechanical interaction between interdigitated teeth of two

consecutive HB-BPB molecule-gears. Unfortunately, no propagation of rotation was observed along the train of molecules even when stabilized by the handle HB-BPB molecule.

For the 2.6 nm Cu-Cu distance case and as presented in Fig. 4b, the teeth extremities in gear 1 (G1) and gear 2 (G2) are too far away to allow correlated motion when G1 is STM tip manipulated. This can be explained by the STM contrast of each tooth which is mainly coming from the corresponding *tert*-butyl chemical end group. Its lateral STM corrugation extension is normally about 40 % larger than the van der Waals equivalent diameter of a *tert*-butyl moiety¹⁰ (see also Fig. 2c). On Fig. 4b, the *tert*-butyl remaining in between the two *tert*-butyls of the other molecule is therefore not even in van der Waals contact.

After completely engaging a handle molecule (H) with the G1 gear (Fig. 4c), the *tert*-butyl extremity of the handle H is well positioned in between the two *tert*-butyls of the two G1 teeth, and H and G1 are thus properly interdigitated. This is possible because H is not mounted on a Cu ad-atom and can be pushed and then interdigitated with G1 by STM molecular manipulations. In this case, the STM tip can rotate H and G1 together because they consequently form a robust supramolecular assembly rotating around the G1 Cu ad-atom rotation axle. As a consequence, G1 is step by step rotating from Fig. 4(d1) to Fig. 4(d7) as already observed in the case of the short teeth HB-NBP molecule-gears.¹⁵ But G2 remains immobile, as expected from the absence of interdigitation between G1 and G2.

Between this 2.6 nm and the small 2.4 nm Cu-Cu distance range, no intermediate distance was found for a handle H rotation to be transmitted from G1 to G2. Notice that within such a 200 pm intermediate distance interval, it may formally exist a Cu-Cu distance giving rise to a transmission of rotation between the two molecule-gears while considering a continuous Cu-Cu interatomic distance tuning.²³ However, on a Pb(111) surface, surface crystallography limits this

tuning to a small series of Cu-Cu distances. Below 2.5 nm, none of them were adapted to a gear train mechanical functioning. In this range of Cu-Cu interatomic distances, gear G1 is no more rotating while rotating the handle H. In Fig. 5, the example of a 2.4 nm Cu-Cu interatomic distance is shown, where the handle H is only rotating around gear G1 like in a rack and pinion mechanical motion (Fig. 5(d1) to Fig. 5(d4)).²⁷

We interpret this blocking of the transmission of rotation by invoking the mechanical flexibility of the biphenyl in a given tooth. One can expect that the *tert*-butyl at the end of each tooth will be able to avoid this flexibility, but the six *tert*-butyls are only physisorbed on the Pb(111) surface. As a consequence, any potential energy increase coming from an STM molecular manipulation will be first transferred on the *tert*-butyl (leading to a lateral end shift per tooth) and on a phenyl to phenyl relative rotation angle, since the terminal *tert*-butyls maintain the biphenyls groups away from the surface in a weak van der Waals interaction regime. In the case of the molecule-gears train presented in Fig. 5 and while STM manipulating the handle H for a rotation, the first main energy minima encountered on the ground state PES are the teeth mechanical deformation and not the collective rotation of G1 around its Cu ad-atom axle, normally followed by a collective G2 rotation. Such transmission of rotation along the Fig. 5 (and Fig. 4) molecular train is a very difficult minimum energy path trajectory to build up on the ground state PES following an STM manipulation of the H molecule.

Gear train across an atomic step surface. One possibility to lower the rotation potential barrier on the molecule-gear train PES in a way to favor a collective rotation propagation along the train is to reduce the mechanical interactions between the entangled teeth of the consecutive G1 and G2 gears. As presented in Fig. 6, a mono-atomic step edge can be used for this purpose on the Pb(111) surface. As illustrated in Fig. 6a, the 285 pm height difference between the upper and

lower terraces permits to position one molecule-gear on the upper terrace and the second one on the lower terrace to reduce the intermolecular mechanical interactions. This was possible after having located the required single Cu-adatoms for the respective rotation axle on the upper and the lower terraces with the required interatomic distances. In this configuration, the rotation of the first gear of the train, located on the upper terrace, propagates to the second one, still with the help of a non-Cu mounted handle molecule (Fig. 6e). On the ground state PES of this molecular train, the potential energy barrier in the direction of the rotation transmission is now lower than the barrier height corresponding to the deformation of the two phenyl per tooth.

CONCLUSION

The strong mechanical entanglement between the HB-BPB molecules renders a transmission of rotation along a molecular train difficult. The potential energy increase caused by the STM tip apex manipulation triggers a minimum energy trajectory on the multidimensional electronic ground state PES of the molecular train which stops in a potential energy valley associated with the mechanical deformation of the long biphenyl teeth. This valley is not corresponding to a correlated gears rotations direction. The potential energy barrier along this expected collective rotation path on the PES is certainly larger than along the multiple possible mechanical coordinates for relaxation of the first gear in the trains of molecule-gears presented in Fig. 4 and Fig. 5. It remains to design new long and rigid molecular teeth able to transmit rotation without provoking a blocking of trajectory on the corresponding ground state potential energy surface. One possibility is to decrease the interaction between the rotating elements and the surface for example by raising up the cogwheels on an anchoring unit. Molecules have been synthesized^{28,29}

and work is underway to study trains of gears with the goal to improve the transmission of rotation.

ASSOCIATED CONTENT

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

(I) Materials and methods for the synthesis and characterization of the molecules, (II) synthetic procedures and (III) ^1H and ^{13}C NMR spectra of the compounds. (PDF)

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Notes

The authors declare no competing financial interest.

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Figure 1

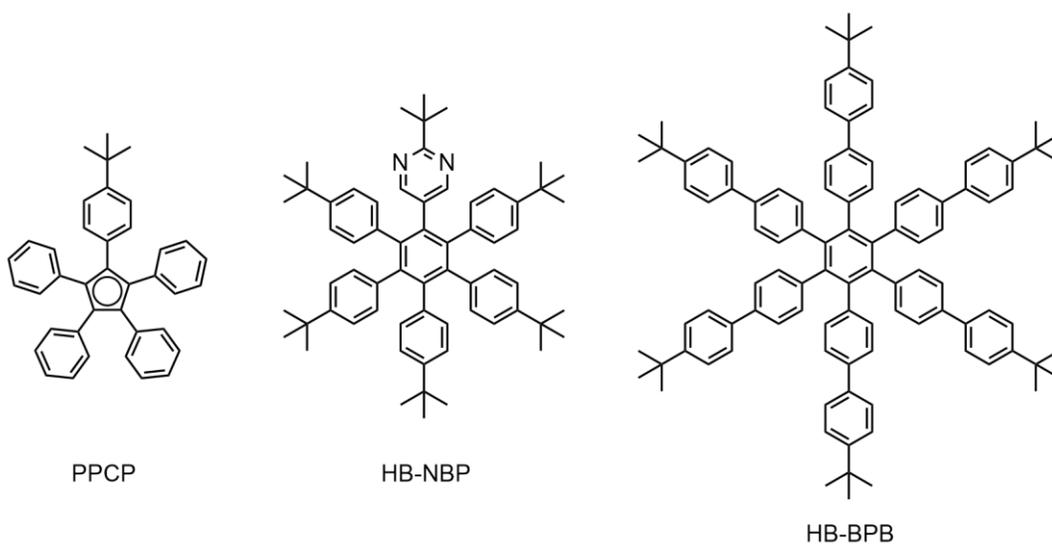


Figure 1. The chemical structure of the molecule-gears used in former studies: pentaphenylcyclopentadiene (PPCP, depicted as a radical on surface) (left), hexa-*tert*-butylpyrimidopentaphenylbenzene (HB-NBP) (center) and the one of our new hexa-*tert*-butylbiphenylbenzene molecule-gear with its elongated teeth and without a chemical tag for this work (HB-BPB) (right).

Figure 2

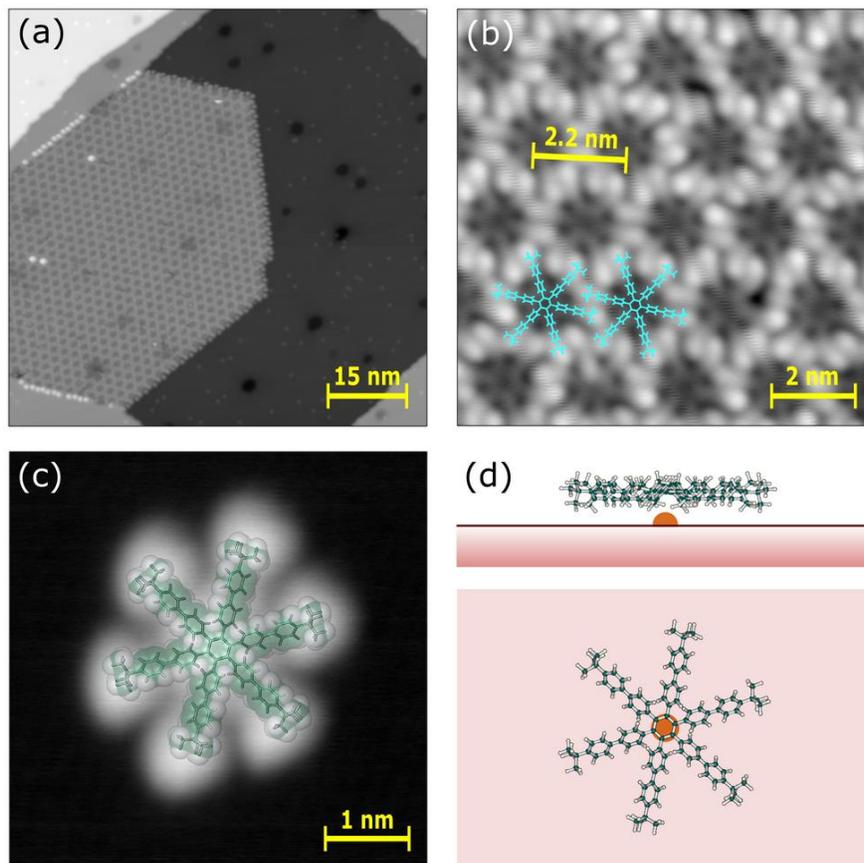


Figure 2. (a) Constant current STM image recorded on one STM of our LT-UHV 4-STM of a 2D molecular cluster of the HB-BPB molecules, (b) a detailed inner STM image of the hexagonal close-packed structure of the HB-BPB molecule-gears and (c) the HB-BPB molecular skeleton with its van der Waals radius superimposed on the experimental STM image of a single molecule mounted on a single Cu ad-atom using the manipulation procedure presented in Fig. 3, and (d) its artistic lateral and top views surface conformation. LT-UHV 4-STM imaging conditions: 100 mV, 10 pA.

Figure 3

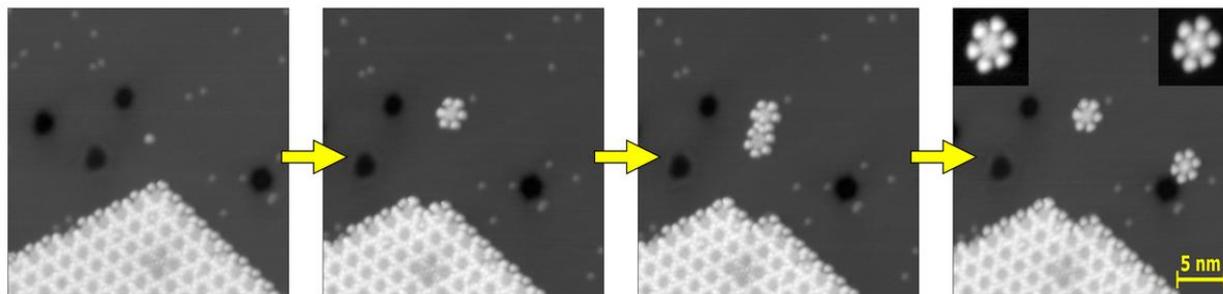


Figure 3. Illustration of a HB-BPB molecule sitting at the vertex of a 2D molecular island and STM tip extracted by lateral manipulations. During this manipulation, a small droplet coming from the tip and consisting of a few metal atoms was trapped by the molecule. The second extracted molecule was stabilized by first attaching it to the first extracted molecule, and then directly STM manipulated and mounted on its Cu ad-atom. The two black insets of the right STM image are showing height difference of the molecule centre between an off-centred (left) and a centred (right) Cu axle. LT-UHV 4-STM imaging conditions: 100 mV, 10 pA. STM molecular manipulation conditions with a vertical STM tip configuration: 1 M Ω STM tunneling junction resistance in a pushing mode.

Figure 4

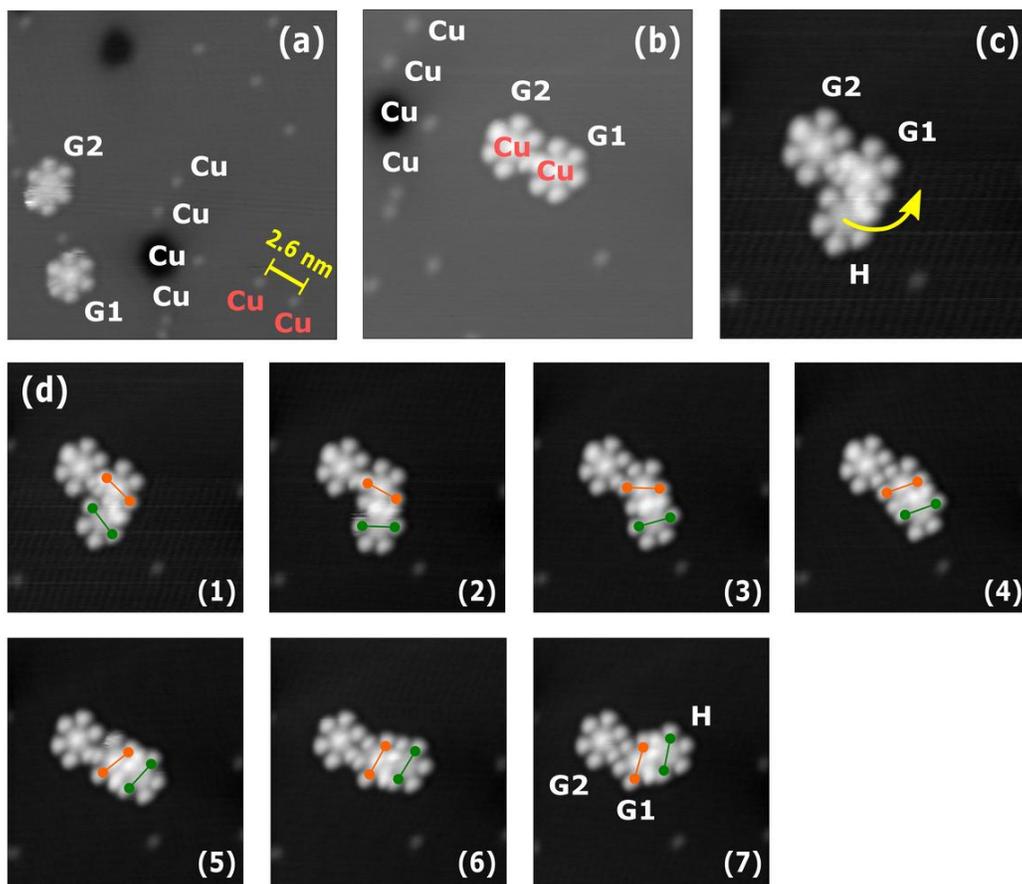


Figure 4. The LT-UHV 4-STM construction sequence and the attempt to trigger a transmission of rotation along a train of two HB-BPB molecule-gears (G1, G2) using a handle molecule (H) not mounted on a single Cu ad-atom on the Pb(111) surface for a 2.6 nm Cu-Cu distance. (a) The LT-UHV 4-STM image of the two HB-BPB molecules and some isolated Cu ad-atoms before the molecule-gears mounting by LT-UHV 4-STM manipulation. (b) After the mounting and (c) after the assembly of the H handle molecule. The series (d1) to (d7) demonstrates that under STM manipulation the H molecule (depicted in green) is leading to the G1 molecule-gear (depicted in orange) rotation with no transmission to G2. LT-UHV 4-STM imaging conditions: 1 V, 10 pA, LT-UHV 4-STM handle manipulation conditions: 4 M Ω for the tunnelling junction resistance in a vertical STM tip configuration. White small dots are single Cu-Adatoms.

Figure 5

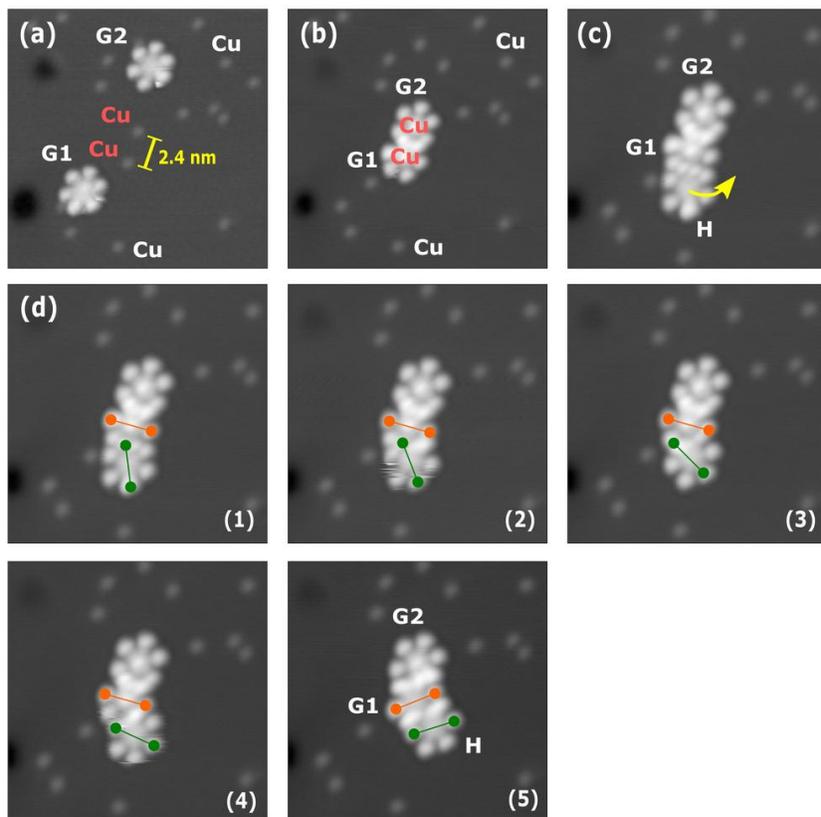


Figure 5. The LT-UHV 4-STM construction sequence and the attempt to trigger a transmission of rotation along a train of two HB-BPB molecule-gears (G1, G2) using a handle molecule (H) not mounted on a single Cu ad-atom on the Pb(111) surface for a 2.4 nm Cu-Cu distance. (a) The LT-UHV 4-STM image of the two HB-BPB molecules and some isolated Cu ad-atoms before the molecule-gears mounting by LT-UHV 4-STM manipulation. (b) After the mounting and (c) after the assembly of the H handle molecule. The series (d1) to (d4) demonstrates that under STM manipulation only the H molecule (depicted in green) is rotating basically around the G1 molecule-gear (depicted in orange) but no rotation at all is observed for G2. G1 was then dismantled from its Cu axle by a manipulation step from (d4) to (d5). LT-UHV 4-STM imaging conditions: 1 V, 10 pA, LT-UHV 4-STM handle manipulation conditions: 4 M Ω for tunnelling junction resistance in a vertical STM tip configuration.

Figure 6

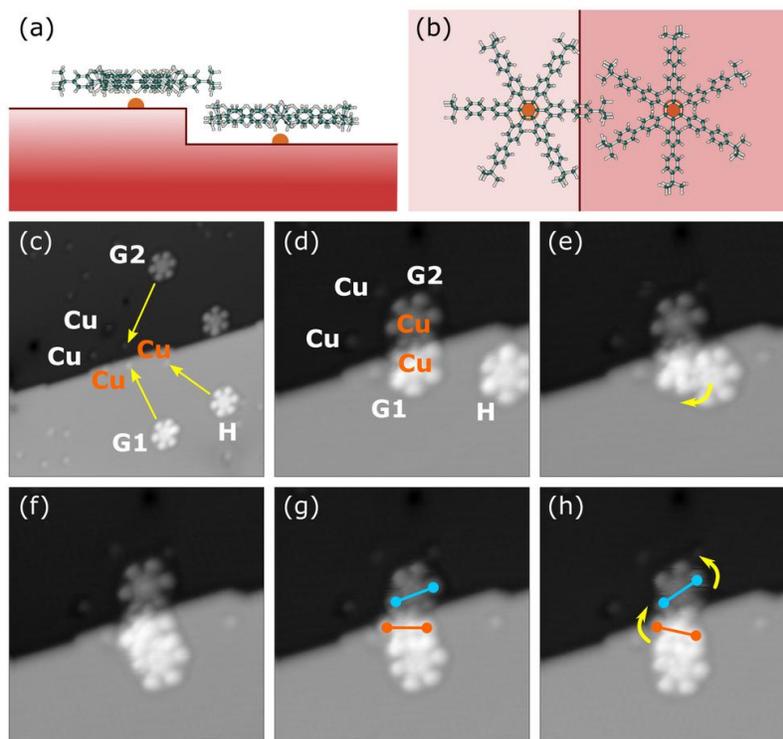


Figure 6. (a) A lateral artistic view of the constructed molecular machinery exploiting a Pb(111) monoatomic step surface configuration and (b) the top view of this machinery. (c) to (d) The LT-UHV 4-STM construction sequence using a mono-atomic step edge on the Pb(111) surface in order to lower the potential energy barrier along the transmission of rotation trajectory on the multidimensional ground state PES. Along a Pb(111) monoatomic step edge, the machinery was constructed by first identifying two Cu ad-atoms with the adapted Cu-Cu interatomic distance relative to the step edge location. (e) to (f) Only the first molecule (on upper terrace near the step edge and previously on a Cu rotation axle) rotates and is then dismounted from its Cu axle. (f) to (g) The second molecule (on lower terrace) is also dismounted from its Cu axle by the constraint of the first molecule rotation. (g) to (h) The first gear rotation is transmitted to second gear, whose angle of rotation is around 15 degrees. LT-UHV 4-STM imaging conditions: 100 mV, 10 pA. STM Manipulation conditions identical to Fig. 4 and 5.