Manipulation and control of a single molecular rotor on Au (111) surface*

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Three different methods are used to manipulate and control phthalocyanine based single molecular rotors on Au (111) surface: (1) changing the molecular structure to alter the rotation potential; (2) using the tunnelling current of the scanning tunnelling microscope (STM) to change the thermal equilibrium of the molecular rotor; (3) artificial manipulation of the molecular rotor to switch the rotation on or off by an STM tip. Furthermore, a molecular 'gear wheel' is successfully achieved with two neighbouring molecules.

Keywords: single molecular rotor, scanning tunnelling microscope, single-molecule manipulation
PACC: 8116D, 6116P, 8116T

Low-dimensional molecular systems with intriguing physical properties have potential applications in fabricating nanodevices and nanomachines.[1−4] Mimicking biological design by synthesizing artificial molecular machines and putting them to work, in particular, harnessing the motion of single molecules, is believed to be one of main routes to the emerging field of nanoscale engineering.[5,6] So far, attempts at design, synthesis, and controllable operation of molecular machines have yielded analogues of rotors,[7−9] gears,[10] switches,[11] shuttles,[12,13] turnstiles,[14] ratchets,[15] wheels,[16] even complex wheelbarrows,[17,18] nanocars,[19] elevators,[20] and refrigerators.[21] The essential part of these machines, the motor, which is utilized to convert the energy into controllable molecular motion, is one of the most challenging components for the device fabrication. Compared with motors in solids and solutions, surface-mounted rotors present the best potential, and mastering the properties of molecular rotors bound on a surface is a logical step towards their practical utilities. Only after the development of surface science as well as nanoscience can the rotation of single molecules be probed on the surface with STM, which has become of particular interest and benefit for such an advance.

Over the last decade, the rotation of porphyrin or sulfide based organic molecules on surface has been often observed and analysed. Individual porphyrins have been first observed to spin very fast in vacancies of an ordered network and be reversibly locked back into position in the network.[22] Rotation of copper phthalocyanine on Si (110) surface and even on C_{60} film has been explored by STM images.[23] The bond between sulfur and substrate atoms is found to serve as the rotation centre for sulfide molecules.[24−26] In our recent studies, regular arrays of anchored molecular rotors have been successfully constructed on Au (111) surface.[27] The single $(t\text{-Bu})_4$-ZnPc molecule thermally rotates around the nitrogen–gold adatom bond and then around the fixed point on the surface after the lateral motion has been blocked by the gold adatom. The molecular rotor shows variable rotating configurations at different positions on the reconstructed Au (111) surface.

However, further application of the molecular motors has a prerequisite of a higher level of control over the configurational conversion. In the present paper, we demonstrate that for such thermally induced molecular rotors, changing the molecular structure and also the tunnelling current during STM probing can effectively change the rotation configuration. Furthermore, the manipulation of a single molecular rotor by an STM tip and artificial 'gear wheel' structures by two coupled molecular rotors can be success-

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fully achieved

The three selected molecules in our experiment were tetra-tert-butyl zinc phthalocyanine ((*t*-Bu)$_4$-ZnPc), zinc phthalocyanine (ZnPc) and iron phthalocyanine (FePc). The experiment was performed by an Omicron low temperature scanning tunnelling microscope (LT-STM) system with a base pressure well below 2.0×10^{-8} Pa. An atomically clean Au (111) surface was prepared by repeating cycles of Ar^+ sputtering and subsequent annealing, and then it was dosed with a minute quantity of (*t*-Bu)$_4$-ZnPc, ZnPc or FePc (Aldrich, 98%) by thermal evaporation at 540 K, respectively. Afterwards, the sample was transferred into the STM chamber and cooled down to 78 K by liquid nitrogen or 5 K by liquid helium. The STM measurements were performed with an electrochemically etched tungsten tip in a constant current mode. All the bias voltages are referred to the potentials of the sample with respect to the tip.

Figure 1 shows the topographic configurations of (*t*-Bu)$_4$-ZnPc molecules at different temperatures on Au(111) surface. Fig. 1(a) gives the STM image of single molecules and molecular clusters at a temperature of 5 K. Here all molecules are frozen and each single (*t*-Bu)$_4$-ZnPc molecule is imaged as four bright lobes. Intermolecular interaction bonds molecules into clusters in such a way that one lobe of one molecule attaches to two lobes of the neighbouring molecule to form a dimer or trimer. By contrast, when the temperature is raised to 78 K (Fig. 1(b)), elliptical or circular features start to appear in the STM images, which have been confirmed to be due to the rotation of single molecules. These molecular rotors can even self-assemble into regular arrays on the herringbone reconstructed Au (111) surface under appropriate experimental conditions.[27]

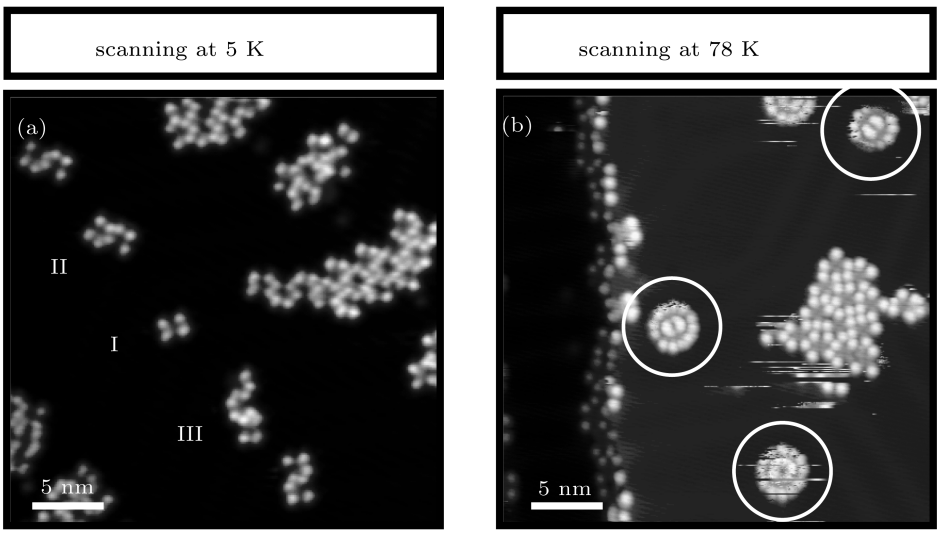


Fig. 1. STM images of molecular structure, showing thermally induced rotation of (*t*-Bu)$_4$-ZnPc molecules. (a) All the molecules are frozen on the surface, appearing as four lobes at 5 K. The numbers I, II and III indicate molecular monomer, dimer and trimer, respectively. Parameters: 30 nm×30 nm, $U = -1.8$ V, $I = 0.05$ nA. (b) At 78 K individual molecules are rotating on the Au (111) surface, resulting in a circular shape, as labelled in the dotted circles. Parameters: 30 nm×30 nm, $U = -1.4$ V, $I = 0.1$ nA.

The thermally induced rotation of a molecule is actually random and thus can be viewed as a type of Brownian motion. Generally, Brownian rotation is described by the following Langevin equation:[28]

$$I\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} = \frac{-\partial V_{\mathrm{net}}}{\partial\theta} - \eta\frac{\mathrm{d}\theta}{\mathrm{d}t} + \xi(T,t), \tag{1}$$

where I is the moment of inertia of the rotor about the rotational axis, V_{net} is the potential in which the rotor moves, η is the friction constant, ξ is stochastic torque representing thermal fluctuation in the system, T is the temperature, and t is the time. In what follows, we show that the rotation of a single molecule can be manipulated by changing the three items on the right-hand side of Eq. (1).

For the system of interest here, V_{net} and η can be tuned by changing the molecular structure, thereby changing the molecule-substrate interaction. As shown in Fig. 2, a row of phthalocyanine-based molecules

rotate at 78 K, and they are stable at 5 K at the elbow position of the herringbone structure of Au (111) surface. All of them rotate around the nitrogen atom which is bonded to a gold adatom (two arrows label the 'spokes' of the rotation in the images). The upper panel is corresponding to the (t-Bu)$_4$-ZnPc molecular rotor. Each bright dot in the outer ring of the rotation configuration represents the tert butyl (t-Bu) group. We choose another molecule ZnPc (shown in the middle panel) which is the core structure of the molecule (t-Bu)$_4$-ZnPc but without t-Bu groups. In this case, the bright dots in the outer ring of the molecular rotor represent only the phenyls rather than t-Bu groups. Thus both the potential and the friction for rotation will increase because in the (t-Bu)$_4$-ZnPc case the butyl groups can lift the molecule phthalocyanine and this may reduce the potential for a facile rotation. Such an effect can be seen from the number of dots on the outer ring. The typical number of dots for the (t-Bu)$_4$-ZnPc rotor is 7 while for ZnPc it is 5. The higher the dot number is, the greater the number of probable positions that the butyl can reach, which means a more facile rotation at the same temperature.

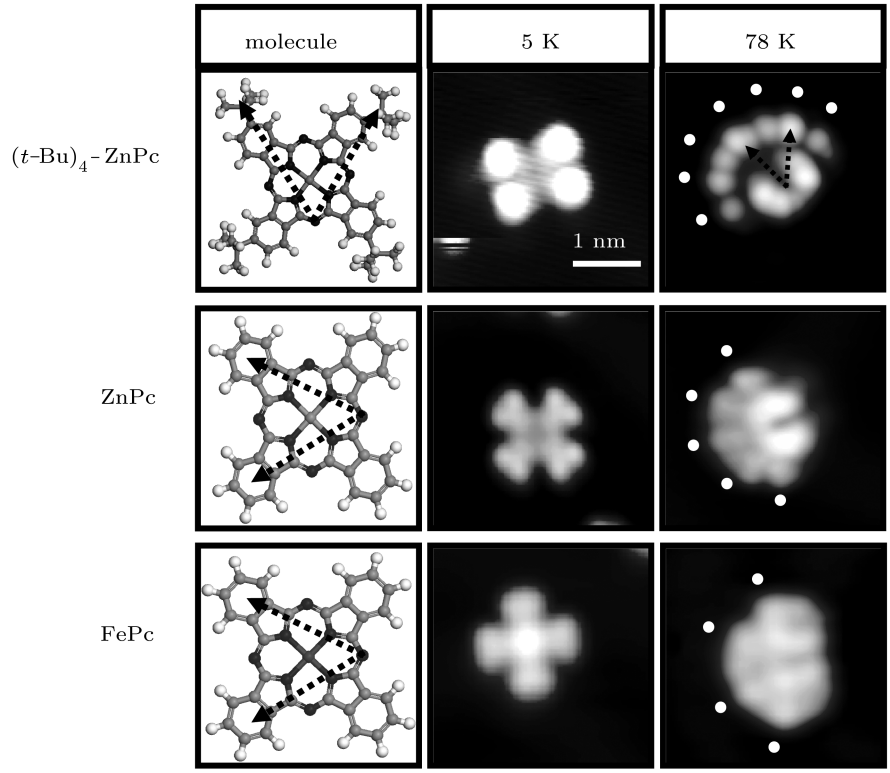


Fig. 2. STM images showing manipulation on the rotation behaviour with modified molecular structure. Upper panel: (t-Bu)$_4$-ZnPc molecular rotor; middle panel: zinc phthalocyanine (ZnPc); bottom panel: iron phthalocyanine (FePc). All these rotors are observed at the elbow position of the Au(111). In panels, left: molecular structures; middle: frozen at 5 K; right: rotating at 78 K. The dot arrows in each image indicate the rotation 'spokes' of the molecules. The circular dots in the 78 K images indicate the most probable stable positions of the molecules.

In order to increase the interaction between molecule and substrate and thus the friction constant, we change the central metal zinc atom of the ZnPc molecule into iron as shown in the bottom panel of Fig. 2. The STM image at temperature 5 K shows that the FePc molecules are adsorbed dispersively on the Au (111) surface because the charge transferred from the substrate to the molecule forms a repulsive dipole between molecules.[29] Owing to the stronger interaction between the substrate and the iron in the core, the molecule FePc rotates with more difficulty than the molecule ZnPc, which can be used to interpret the difference in the STM image between ZnPc and FePc qualitatively. We can see only 4 dots outside ring in the rotating image and two separated parts inside the circle ring for FePc rotors. This means the FePc molecules only prefer to sit at two stable positions and the rotating configuration looks like two adjacent molecules. The strong interaction with substrate makes FePc molecule have a large friction constant and thus lower rotating speed. Note that,

by changing the core into a magnetic atom, a prototype electronic generator is actually manufactured on the surface if a vertical magnetic field is added.

Considering that the molecular rotor is intrinsically a thermally stable system, the tunnelling current from the STM tip will locally disturb the thermal equilibrium of a single molecular rotor. So it is possible for the tunnelling current to affect the stochastic torque ξ.

Figure 3 shows the current dependence of the (t-Bu)$_4$-ZnPc molecular rotor. As shown in Fig. 3(a), when a small tunnelling current (0.1 nA) is applied, only a semicircle rotation pattern can be observed, which is due to the limited rotation of the (t-Bu)$_4$-ZnPc at a particular position of the herringbone reconstructured surface. When the tunnelling current is increased to 0.2 nA, the molecule rotates more actively so that the degree of circular arc of the rotation pattern becomes larger (Fig. 3(b)). When the current is increased to 0.9 nA, a full circle of rotation pattern can be clearly observed (Fig. 3(d)). This gradual increase in the degree of the circular arc means that the molecule becomes more active and can gradually override the barrier formed by the Au (111) reconstruction and covers the whole circle eventually. The above result shows a gradual activation process while increasing the current. Since the molecular rotation is driven by thermal energy, the STM current provides a certain amount of energy to locally heat the rotating molecules.

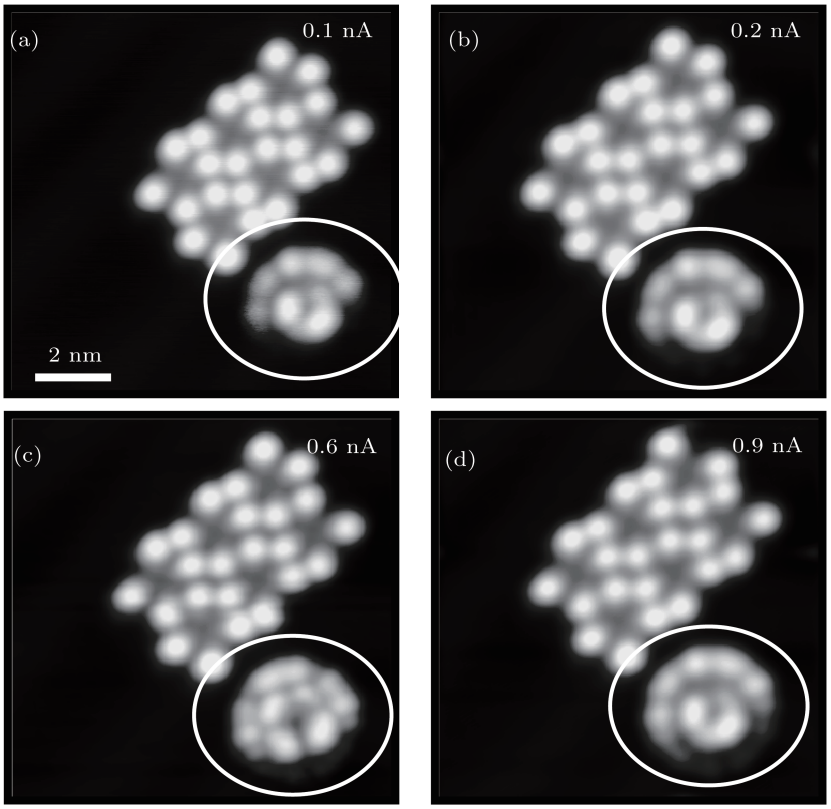


Fig. 3. A sequence of STM images (10 nm×10 nm, $U = -1.3$ V) showing manipulation on the rotation behaviour of the (t-Bu)$_4$-ZnPc molecular rotor by changing the tunnelling current. (a) $I = 0.1$ nA, (b) $I = 0.2$ nA, (c) $I = 0.6$ nA and (d) $I = 0.9$ nA. The molecular rotor can sweep faster and with more degrees as the tunnelling current increases. The circles represent the same rotating molecule.

In order to artificially manipulate the molecular rotor, we employ the method of tip manipulation of a 'brake' or 'clutch' molecule to control the rotating molecules. As shown in Fig. 4, one molecule acts as a brake manipulated by the STM tip in order to mechanically control the molecular rotor. Initially, a (t-Bu)$_4$-ZnPc molecule rotates near one trimer cluster in the fcc region of the gold surface (Fig. 4(a)). When one of the neighbouring molecules (labelled by an arrow) is slowly pushed by the STM tip to get close to this sixfold rotor, the rotation can be totally blocked and two molecular dimers are left on the scanning area (Fig. 4(b)). Curiously, the original rotor can be recovered into rotating mode as before once the blocking molecule is taken away (Fig. 4(c)). The same process can be achieved repeatedly as shown in (Fig. 4(d)). This experiment

demonstrates definitely that the circular pattern at 78 K originates from the rotation of a single molecule and suggests that our rotors seem tireless.

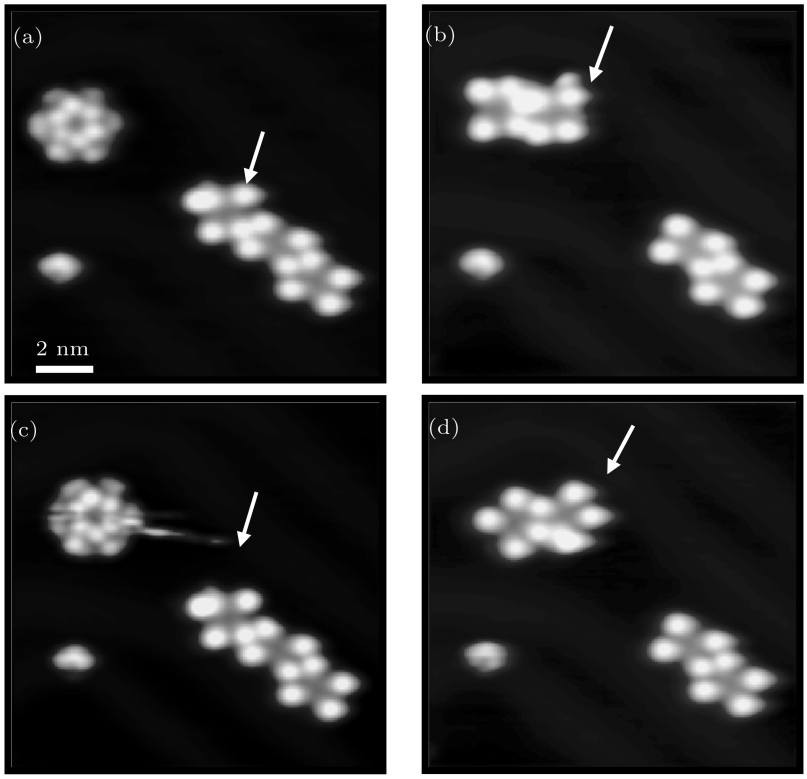


Fig. 4. A sequence of STM images showing the artificial manipulation of the (t-Bu)$_4$-ZnPc molecular rotor by the STM tip. (a) A (t-Bu)$_4$-ZnPc molecule rotates near one trimer cluster on Au(111) surface; (b) The 'brake' molecule marked by the arrow, coming from the trimer cluster, is pushed closely to block the rotating molecule and then (c) drawn back to unblock the molecular rotor. This process of the tip manipulating the molecular rotor is highly reversible and repeatable (d). Scanning parameters: 12.8nm×12.8 nm, $U = -1.4$ V, $I = 0.1$ nA.

Based on the prototype molecular rotor, more complex systems are expected to be architected. As shown in Fig. 5, a molecular 'gear wheel' structure is formed by two adjacent molecular rotors coupling together.

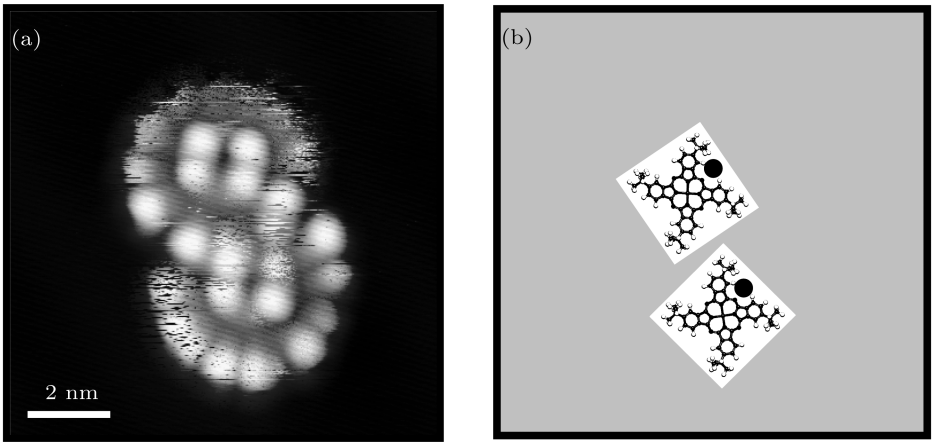


Fig. 5. (a) STM image showing the formation of a molecular 'gear wheel' like system using two adjacent (t-Bu)$_4$-ZnPc molecular rotors. (b) A schematic illustration showing one of the possible configurations of the two 'dancing' molecules during rotation. The solid dots indicate the gold adatoms as the rotation centres of the molecules. Scanning pararemeters: 5 nm×5 nm, $U = -2.0$ V, $I = 0.1$ nA.

Normally the molecule (t-Bu)$_4$-ZnPc in fcc regions of gold surface forms circular rotors; however, two circular rotors block each other and form two semicircular rotors like a gear wheel (Fig. 5(a)). Disturbed by each other,

these double molecular rotors usually turn out to be unstable and irregular. Figure 5(b) gives a schematic illustration for the double rotor, from which we can see how the two rotating molecules are coupled together. Each rotor has a gold adatom underneath marked as a small solid dot. This observation suggests a possible way to form a more complex rotating system by molecular self-assembly.

In summary, we investigate phthalocyanine based molecular rotors anchored onto a gold surface. The molecular rotating behaviour can be manipulated by changing the molecular structure and the STM tunnelling current. An STM tip is also used to manipulate a 'brake' molecule to block a nearby single molecular rotor, and an artificial 'gear wheel' structure has been successfully achieved by using two coupled rotating molecules. The work on surface mounted molecular rotors provides both a fundamental understanding of molecular devices and also a type of nano-machine.

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