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Reversible Chiral Switching of Bis(phthalocyaninato) Terbium(III) on a Metal Surface

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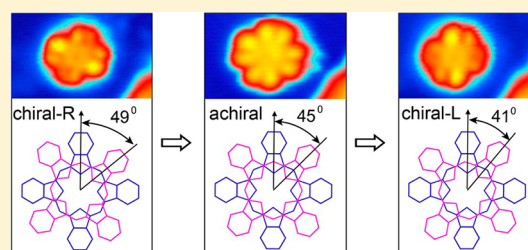
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S Supporting Information

ABSTRACT: We demonstrate a reversible chiral switching of bis(phthalocyaninato) terbium(III) molecules on an Ir(111) surface by low temperature scanning tunneling microscopy. With an azimuthal rotation of its upper phthalocyanine ligand, the molecule can be switched between a chiral and an achiral configuration actuated by respective inelastic electron tunneling and local current heating. Moreover, the molecular chiral configuration can be interchanged between left and right handedness during the switching manipulations, thereby opening up potential nanotechnological applications.

KEYWORDS: Molecule chirality, molecule switch, scanning tunneling microscopy, molecule manipulation, TbPc₂



Molecular switches interconvert between bistable states and could function as potential storage bits for building molecule-based devices.¹ With scanning tunneling microscopy (STM), various molecular switches supported on surfaces can be studied at the single molecule level.^{2–15} Most molecular switches operate by changing conformation^{2–11} although other forms of operations like electron charging^{11–14} or bond formation¹⁵ have also been demonstrated recently. Chirality, on the other hand, is of fundamental importance in biological systems and also has technological significance for asymmetric heterogeneous catalysis. If one could control the chirality within a single molecule, its physical properties (e.g., photophysics) as well as functionalities (e.g., catalytic activities) could also be controlled. STM offers a unique tool to investigate molecular chirality, ranging from supramolecular organization^{16,17} to chirality manipulation of single adsorbates.^{18,19} Here we demonstrate a molecular switch using bis(phthalocyaninato) terbium(III) (TbPc₂) molecules adsorbed on Ir(111), where a chirality change is explicitly manifested.

TbPc₂ is composed of two organic phthalocyanine (Pc) ligands with a terbium(III) metal ion sandwiched in between (Figure 1a). As a free molecule, its two Pc ligands have a relative staggering angle of 45°. Due to its single molecule magnet behavior originating from the lanthanide ion, the double-decker class molecule has attracted intense research interest.^{21–27} It was shown recently that the spin state of TbPc₂ on Au(111) can be modified with molecular switching,²⁵ where the molecules studied were however embedded in a self-assembled monolayer film and a chirality switching of an individual molecule was not resolved.

The experiments were performed with a homemade low temperature STM²⁸ at 6 K in ultrahigh vacuum. The Ir(111) substrate was cleaned by Ar⁺ ion sputtering at 800 V and then flashing to 1200 °C for 2 min. Then the sample was annealed under an oxygen pressure of 8.0 × 10^{−7} mbar followed by flashing cycles to remove carbon impurities. TbPc₂ molecules were thermally sublimed in situ onto the Ir(111) substrate from a home-built ceramic cell evaporator held at ~700 K. During deposition, the substrate was kept either at room temperature or at ~100 K. An electron beam heated tungsten tip was used as the STM probe. The dI/dV-V scanning tunneling spectroscopy (STS) data were acquired by a lock-in detection of the tunneling current with a modulation voltage of 1777 Hz superimposed to the sample voltage.

STM images show a random distribution of individual TbPc₂ molecules on the Ir(111) surface deposited at room temperature (Figure S1 of the Supporting Information (SI)). All molecules adopt a face-on configuration, that is, with one Pc ligand facing the surface. When the STM images are taken with a bias voltage of ~1.7 V, the molecules appear with *asymmetric* shapes (Figure 1b and Figure S1b, SI) with distinctive intensity contrast between their two pairs of opposite pyrrole rings. However, they appear as very similar four-lobed structures (Figure 1c and Figure S1a, SI) when imaged with lower voltages. In previous studies of TbPc₂ molecules on metal surfaces, a mirror *symmetric*, thereby *achiral*, eight-lobed

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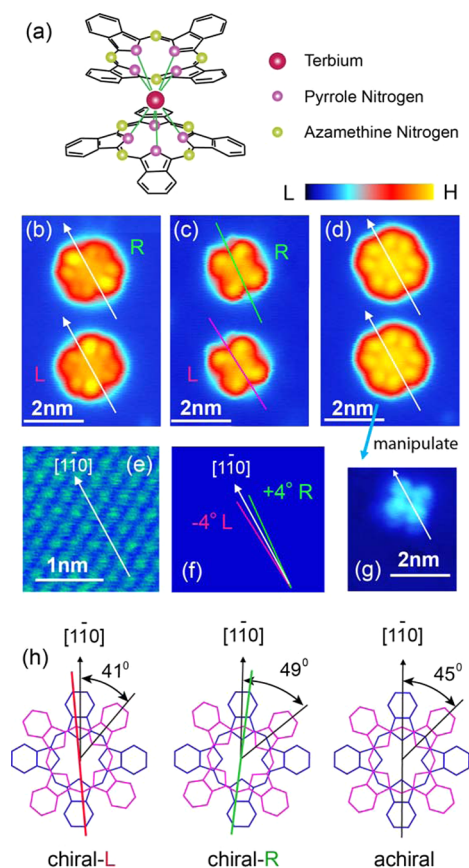


Figure 1. Chirality of TbPc₂ on Ir(111). (a) Molecular structure of TbPc₂. (b–d) STM images show two TbPc₂ molecules which are initially chiral (b, c) and become achiral in an eight-lobed state (d) after switching. Imaging conditions: $V = -1.0$ V, $I = 0.1$ nA for c; $V = 1.7$ V, $I = 0.1$ nA for b and d. The principal axis of the L/R chiral TbPc₂ (red/green line) indicates a misalignment of $\pm 4^\circ$ with respect to the $[1-10]$ direction (white arrow) of Ir(111), as is depicted in f. The principal axis of the eight-lobed TbPc₂ in d aligns with $[1-10]$. (e) Atomic resolution of Ir(111) (-1.0 V, 0.2 nA) with $[1-10]$ direction labeled. (g) STM image (-1.0 V, 0.2 nA) of a single-decker decomposed from an identically oriented TbPc₂ as in d with a lateral tip manipulation (0.3 V, 50 nA) along the light blue arrow direction. (h) Structural models of TbPc₂ with different chirality properties corresponding to their adsorption configurations in b–d. The lower Pc (colored in blue) has two opposite lobes along $[1-10]$. The principal axis of the upper Pc (colored in purple) is marked with a red/green line for the left/right-handed TbPc₂. The staggering angles between the two Pc's are indicated.

structure is commonly observed where the top and bottom Pc ligands are staggered 45° to each other.^{22,23} Indeed, we are able to switch the asymmetric molecules in Figure 1b to the achiral eight-lobed structure (Figure 1d and h) using an STM manipulation scheme. The two molecules in Figure 1b that we denote as “L” and “R” type, respectively, cannot be superposed on their own mirror images but are mirror images of each other. Thus they are *chiral* and represent two enantiomers with $[1-10]$ surface direction (Figure 1e) as their mirror-symmetry axis. Careful analysis reveals that the two molecules in Figure 1c are slightly misaligned with respect to $[1-10]$. The marked principal axes of the molecules indicate a misalignment angle of $+4^\circ$ for the top molecule (R) and -4° for the lower one (L) (Figure 1f and h). We define the molecule possessing the $-(+)$ 4° misalignment, that is, L (R)

type, as left (right)-handed. After the switching the misalignment disappears, and the molecular principal axes are then aligned with the substrate $[1-10]$ direction (Figure 1d and h).

There are two possible rotational scenarios to account for the 4° misalignment and the observed chirality: a whole-rotational configuration, where the molecule keeps the 45° staggering angle between its two Pc's and rotates by 4° with respect to the crystallographic direction of Ir(111) as a whole; or a relative-rotational configuration, in which the lower Pc stays aligned with the substrate leaving the upper Pc rotated by 4° . To differentiate these two scenarios, we performed STM lateral manipulations to the molecule. The upper Pc ligand is removed from the molecule, leaving the lower single-decker at the original place. The remaining single-decker²⁹ aligns with the substrate crystallographic direction and is staggered 45° relative to the upper one (Figure 1g). This demonstrates that the lower Pc binds tightly to the substrate and the relative-rotational configuration is adopted by the chiral molecule. Moreover, the azimuthal rotational motion of the double-decker complex has been explored in several studies,^{25,30,31} which support the above arguments. It can thus be concluded that the molecular switching event is associated with a relative azimuthal rotation between the upper Pc and the surface-immobilized lower Pc (Figure 1h).^{32,33} Due to the three-dimensional structure of TbPc₂, the relative-rotation lifts its mirror symmetry, rendering it a chiral motif.

To switch a molecule, a voltage pulse is applied to the center of its top Pc ligand with opened feedback loop. During this process, the tunneling current is recorded as a function of time. An abrupt change in the tunneling current is associated with a switching event. A sequence of STM induced molecular switching events is presented in Figure 2. When a $+2$ V voltage pulse is applied to the right molecule in Figure 2a, it switches from the chiral four-lobed to the achiral eight-lobed state (Figure 2b). The corresponding tunneling current signal shows an abrupt change in magnitude upon the switching (Figure 2e).^{8,34} The molecule can be switched with negative voltage pulses as well. A -2 V pulse (Figure 2e) switches the left molecule in Figure 2b to the achiral eight-lobed structure (Figure 2c). For the reverse switching from the achiral eight-lobed to the chiral four-lobed state, a different STM manipulation scheme is used: With a fixed bias voltage of 50 mV, the tip is approached to the center of the right molecule in Figure 2c and then retracted to its original position after 0.1 s.³⁵ During the tip approach, the tunneling current increases exponentially (Figure 2f). At ~ 700 nA, a sudden drop of the current occurs (marked with a red arrow), denoting the switching of the molecule. The reverse switching of the left molecule is confirmed by STM imaging in Figure 2d, where it now shows the restored chiral four-lobed structure. The success rate of this process is $\sim 5\%$, as the molecule often decomposes due to the high current. Note that, with the tip approaching laterally as in our decomplexation experiment, a much lower current of about 5 nA is sufficient to decompose the molecule.

To understand the mechanisms of switching, STS measurements are performed by positioning the STM tip above the center of a chiral molecule. As shown in Figure 3a, when the sample bias is ramped from -1.5 V to $+2.5$ V, the dI/dV signal is featureless until it reaches $+1.5$ V where its intensity rapidly increases. Thus, we assign $+1.5$ V as the onset of the lowest unoccupied molecular orbital (LUMO) of the chiral state. Before reaching a peak maximum, the conductance abruptly drops at $\sim +2$ V due to the molecular switching to the achiral

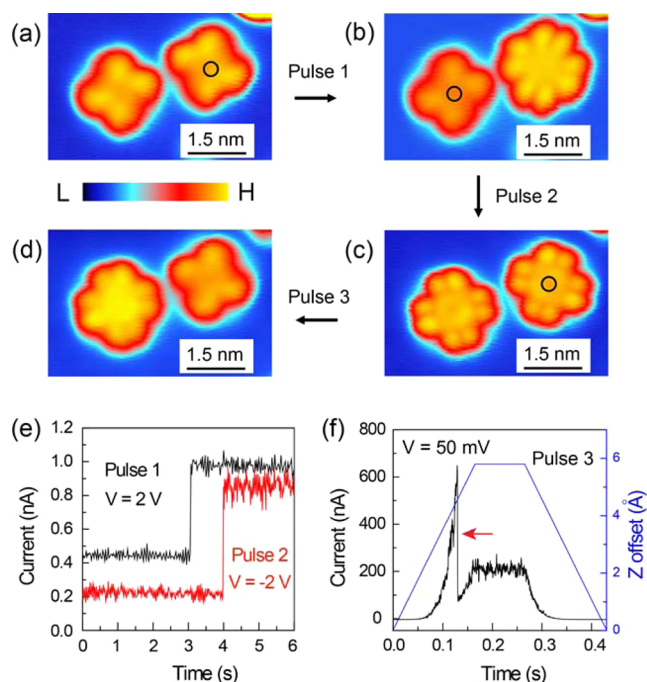


Figure 2. Reversible switching of TbPc₂ on Ir(111). (a–d) A sequence of STM images showing the controlled switching of TbPc₂ molecules between a chiral four-lobed state and an achiral eight-lobed state on Ir(111). Each consecutive image shows the outcome of the STM tip manipulations whose position is marked in the previous image with a circle. Imaging conditions: -1.0 V, 0.1 nA. (e, f) Tunneling current recorded over time during the switching manipulations with the tip positioned above the center of the molecule. The feedback loop was stabilized at 1.0 V, 0.1 nA (-1.0 V, 0.1 nA) prior to and opened during manipulations with a voltage pulse of 2 V (-2 V) for Pulse 1 (2). In f, the feedback loop was stabilized at -1.0 V, 0.1 nA prior to and opened during the manipulation which was performed with controlled tip movement and a constant applied voltage of 50 mV. A red arrow marks an abrupt current change associated with the molecule switching from the achiral to the chiral state.

state. When the bias voltage is ramped back, the dI/dV curve follows a distinctly different trajectory of the newly switched achiral state. Now two prominent peaks appear at $+1.2$ V and -1.1 V, which are ascribed to the LUMO and the highest occupied molecular orbital (HOMO) of the achiral state, respectively. Similarly, to switch the chiral molecule using a negative bias voltage, the bias is ramped from $+1.5$ V to -2.5 V. The recorded dI/dV curve is also featureless until -1.8 V where an increase in conductance occurs, which is assigned as the HOMO of the chiral state. At ~ -2 V, the molecule switches to the achiral state, and when the bias is ramped back, the previously observed HOMO and LUMO peaks of the achiral state show up again (Figure 3a).

In light of the explicit overlap between the manifested conductance jump and a molecular state, we attribute the switching event from the chiral to achiral state to be induced by inelastic electron tunneling (IET).^{2,6} In an IET process, the energy of tunneling electrons is transferred to the molecule via a temporary electron attachment to the molecule and the subsequent vibrational relaxations.^{8,34} When the transferred energy is large enough to overcome the energy barrier of an azimuthal rotation of the molecule's upper Pc, the switching event occurs. An IET-induced switching process does not necessarily require a resonant tunneling condition. However, in

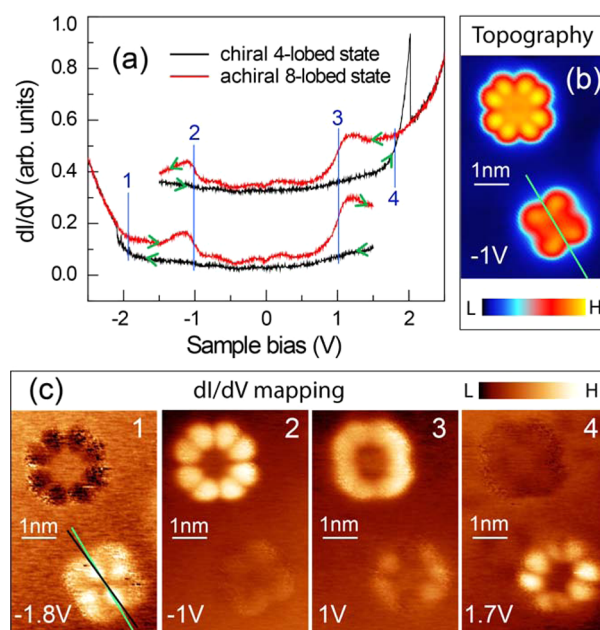


Figure 3. Electronic structure of TbPc₂ on Ir(111). (a) Differential conductance spectra measured above the center of TbPc₂. The bias ramping directions are marked with green arrows. The molecules were originally in the chiral four-lobed state, and the abrupt conductance changes indicate the switching transitions to the achiral eight-lobed state. (Tunneling gap: -1.0 V, 0.1 nA. Modulation voltage: 20 mV.) The numbers labeled in a correspond to the numbering in c. (b) Topographic image (-1.0 V) of two TbPc₂ molecules in different states. (c) Conductance mapping of the two molecules in b taken at as indicated bias voltages, showing the spatial distributions of their frontier orbitals both in the chiral state (mapping 1 and 4) and in the achiral state (mapping 2 and 3). The principal axis of the chiral molecule's upper/lower Pc is marked with a green/black line in b and mapping 1 of c. The STM images and mappings were obtained in constant current mode at 0.1 nA with a modulation of 30 mV.

the case of off-resonance tunneling, the tunneling electron's residing time on the molecule exponentially decreases with reduced electron energy to the resonance ion state, thereby dramatically diminishing the probability of switching.^{3,6} To rule out other possible switching mechanisms, we investigated the tip-sample distance dependence of the threshold switching bias, which gives an almost constant value (Figure S2, SI). This observation demonstrates that the switching process is not driven by the electrical field or a thermal process, because it is independent of the electric field² and the power of tunneling electrons.

We found that TbPc₂ molecules deposited at a low substrate temperature of ~ 100 K all show the achiral eight-lobed configuration (Figure S3, SI). After annealing the sample to room temperature, all of the molecules appear in the chiral configuration indicating that a thermally assisted process can switch the molecules from the achiral to the chiral state. Therefore, for the reverse switching shown in Figure 2f, the process is very likely triggered by tunneling-electron-generated local heating,³⁶ similar to the thermal switching process because of the high current (~ 700 nA).³⁷ It is noted that a low bias voltage (50 mV) was used in Figure 2f to ensure the tunneling electrons are of low energy, preventing the molecule from switching back to the achiral state via IET. A low negative bias voltage of -50 mV has also been successfully employed to switch the molecule from an achiral to a chiral state,

substantiating that the reversal switching may be caused merely by a local heating effect as it is insensitive to bias polarity.

Next, we directly visualize the spatial distribution of the molecule's frontier orbitals via dI/dV spectroscopic mapping. Figure 3b shows two TbPc₂ molecules of different states. Their dI/dV maps are presented in Figure 3c: At -1.0 V ($+1.0$ V) where the HOMO (LUMO) of the achiral molecule is located, an intense molecular orbital with eight well (less) separated lobes is resolved on the ligand. This is in agreement with previous reports of the same molecule adsorbed on Cu(111)²² and can be correspondingly attributed to the π orbital of the upper Pc. The intensity of the chiral molecule is low in accordance with its off-resonance tunneling condition. While at -1.8 V ($+1.7$ V) where the tail of the chiral molecule's HOMO (LUMO) resides, an intense molecule orbital is observed, the electronic signature of the achiral molecule fades out. Remarkably, the LUMO of the chiral molecule exhibits a distortion away from its square shape, with prominent intensity contrast between its two pairs of opposite lobes. This evidences that the structural chirality is transformed into a chiral electronic structure, which is responsible for the clear chirality expression from the topographic images taken at $+1.7$ V in Figure 1b. The HOMO of the chiral molecule shows four bright lobes³⁸ staggered on top of a square-shaped state, which may originate from its lower and upper Pc ligand respectively, as judged from their orientations relative to the molecule. Interestingly, the mirror axis of the four bright lobes (marked with a black line) aligns with the substrate crystallographic direction and rotates by about 4° relative to the molecule's principal axis (marked with a green line), substantiating the proposed relative-rotational configuration of the chiral molecule.

It is computationally challenging to accurately model the adsorption configuration and electronic structure of TbPc₂ adsorbed on the Ir(111) substrate due to its large size. Nevertheless, recently reported density functional theory calculations performed for a free molecule could give some insight into our spectroscopic features. The conductance mapping of the eight-lobed molecule's ligand frontier orbitals matches those of an isolated [TbPc₂]⁻ as calculated in ref 22. An azimuthal rotation between the two Pc rings changes their mutual coupling strength and consequently shifts the frontier orbitals of TbPc₂.²⁵ According to ref 20, the HOMO–LUMO gap of [TbPc₂]⁻ becomes wider with a small azimuthal rotational angle between the two Pc's. This qualitatively reproduces the trend of our observation: The HOMO–LUMO gap changes from ~ 2 V of the achiral eight-lobed state to ~ 4 V of the chiral four-lobed state.

We further demonstrate that the chiral TbPc₂ can be switched between its two enantiomer states by STM. Because the azimuthal rotation of the molecule's upper Pc can be either clockwise or counter-clockwise when switching, this provides the feasibility of changing the handedness of the chiral molecule with switching manipulations. Figure 4a shows a molecule with right-handedness as revealed from the STM imaging at 1.7 V. When imaging at a sample bias of -2.5 V, the molecule is switched to the achiral state during scanning, leaving an abrupt change in the scanning line (Figure 4b). In this way, the chiral molecules within the scanning range can be switched with certainty to the achiral state in a more efficient manner. After switching back to the chiral state, the molecule now possesses left-handedness (Figure 4c).

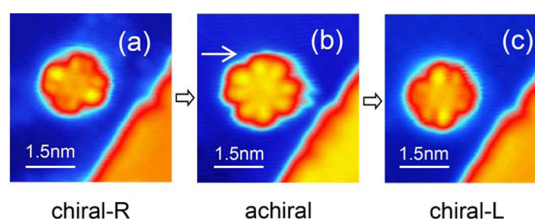


Figure 4. Chirality manipulation of TbPc₂ on Ir(111). STM topographic images of a TbPc₂ molecule switched from the chiral state (a) to the achiral state (b) and further switched back (c). A white arrow in b marks the switching during scanning, where the slow scanning direction is from top to bottom. Chirality properties of the respective switching states are indicated below the corresponding STM images. Imaging parameters: $V = 1.7$ V, $I = 0.1$ nA for a and c; $V = -2.5$ V, $I = 0.1$ nA for b.

In summary, we have demonstrated a molecular switch based on a process of reversible chirality change. By means of respective inelastic electron tunneling and local current heating, the TbPc₂ molecule can be switched among left and right-handed configurations and that of an achiral configuration. In view of the intricate correlation between magnetism and structure, the chiral switching of the molecule paves the way for future studies on how the magnetic behavior of molecular magnets evolves with molecular switching at a single molecule level by spin-polarized STM.³⁹ Additionally, the double-decker single molecule magnet can be prepared macroscopically in one of the bistable states simply by deposition at different substrate temperatures, which allows using ensemble-averaged techniques like X-ray magnetic circular dichroism^{24,26} for the characterization of magnetic properties.

■ ASSOCIATED CONTENT

Supporting Information

Additional STM images show the chirality of four-lobed TbPc₂ molecules on the Ir(111) surface with different orientations, the threshold switching bias of TbPc₂ against tip–sample separations from the chiral to the achiral state, and TbPc₂ molecules all exhibiting eight-lobed structures after a low temperature molecule deposition. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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