# Conformational Changes of Single Molecules Induced by Scanning Tunneling Microscopy Manipulation: A Route to Molecular Switching

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A detailed experimental and theoretical investigation of the processes involved in the manipulation of individual specially designed porphyrin-based molecules by scanning tunneling microscopy at low temperature is presented. On a stepped Cu(211) surface, the interaction between tip and molecule was used to locally modify in a reversible way the internal configuration of a single molecule, thus drastically changing the tunneling current passing through it. Model calculations confirm that this manipulation realizes the principle of a conformational molecular switch.

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The development of nanoelectronic devices has focused research attention onto the possibilities offered by single molecules [1]. Electronic properties and the interaction of some promising molecules with metallic surfaces have been investigated with the scanning tunneling microscope (STM) [2] and the synthesis of dedicated molecules has made possible new nanoscale experiments [3,4]. Besides, the ability of STM to manipulate atoms and small molecules [5–8] has been extended to position single large molecules [9] with the prospect to build molecular nanostructures.

In order to fabricate a nanoscale device with a molecule, this molecule must exhibit electronic effects such as rectification [10], switching [11], or amplification [12]; it must be arranged and positioned in a controlled way; and finally it must be interconnected to other molecules and/or to a preformed electrical circuit.

A possibility of realizing a molecular switch is offered by the manipulation of special molecules performed with the STM tip. As one can see in the sketch of Fig. 1a, the idea is to control the tunneling current by intramolecular conformation changes of a molecule, ensuring either a high or a low resistance $R$ through the junction. As shown by calculations performed using the elastic scattering quantum chemistry (ESQC) technique, in the case of Cu-TBPP molecules, $R$ varies by many orders of magnitude by a simple 90° rotation of one leg of the molecule (Fig. 1c). In this Letter, we report on the successful implementation of this device under the tip of an STM (Fig. 1b). By means of a combined theoretical and experimental work, we demonstrate the ability of the STM tip to reversibly modify the internal conformation of a molecule, thus modifying its electronic properties.

Low temperature (LT) STM [6] was used to investigate the intramolecular conformations of Cu-tetra-3,5 *di-ter-butyl-phenyl porphyrin* (Cu-TBPP) molecules (Fig. 1d) deposited on Cu(211). For clarity of the chemical constitution, the four TBP legs are plotted parallel to the porphyrin ring ($\Theta = 0$). In the gas phase, however, the legs are oriented perpendicular to the porphyrin ($\Theta = 90°$). To implement the molecular switch of Fig. 1b, STM vertical and lateral manipulation modes were used to select and change the orientation of one Cu-TBPP leg in a controlled manner. The variation of current through this leg was

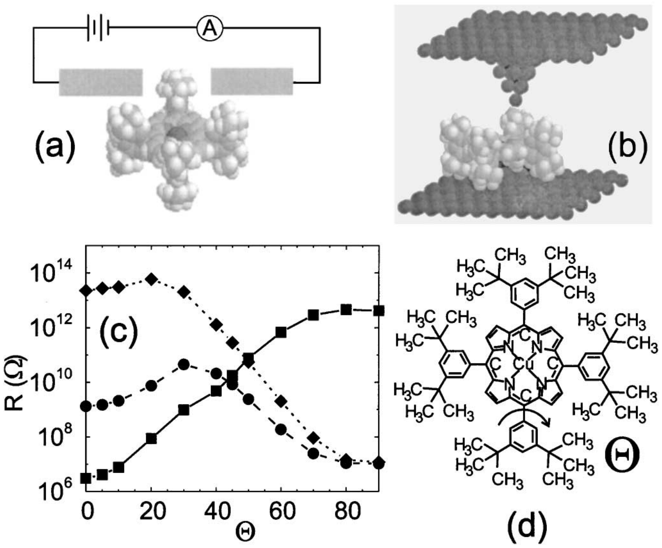

FIG. 1. (a) Planar tunneling junction equipped with a single Cu TBPP molecule modeling a molecular switch. The tunneling current is passing through only one leg, and the resistance $R$ of the junction depends on the leg conformation. (b) Experimentally realized STM junction implementation of this molecular switch. (c) Calculated variation of $R$ in the case (a) (squares) and (b) vs the rotational angle $\Theta$ of one leg using the elastic scattering quantum chemistry (ESQC) method. In the planar implementation the interelectrode distance is 9 Å, while in the STM two tip apex to surface distances are represented: $z_0 = 7$ Å (circles) and $z_0 = 9$ Å (diamonds). (d) Chemical structure of Cu TBP porphyrin.

quantitatively investigated as a function of the distance between tip and molecule. We show that the current passing through a single leg is strongly dependent on its orientation, which can be switched mechanically by the STM tip apex.

The experiments were performed in ultrahigh vacuum with a self-built LT-STM described elsewhere [13]. All measurements were performed at 15 K. The Cu(211) sample, which consists of (111) nanofacets and (100) intrinsic steps, was prepared by several cycles of sputtering with Ne ions and annealing to 700 K. Cu-TBPP molecules were evaporated at 300 °C for 10 sec on Cu(211) while keeping the crystal at room temperature. The STM images show large (211) terraces where the molecules are isolated and uniformly distributed. All the images presented were recorded at a sample voltage of about 30 mV and at a current of about 400 pA. No significant changes in the images were observed by varying the value and the polarity of the voltage. As a tip we used electrochemically etched tungsten wire, formed by controlled contact between the tip and the Cu sample. Therefore we expect the tip to be covered with copper.

STM images of Cu-TBPP/Cu(211) are presented in Fig. 2. In their preferential orientations (Fig. 2a) the molecules show eight bright lobes, with an apparent height of about 2 Å, while the porphyrin ring is hardly visible. The intrinsic edges of the stepped substrate are visible in the STM image with a very small corrugation [7]. In a few cases, as shown in Fig. 2b, a brighter single lobe appears among the double lobes with an apparent height of about 4 Å.

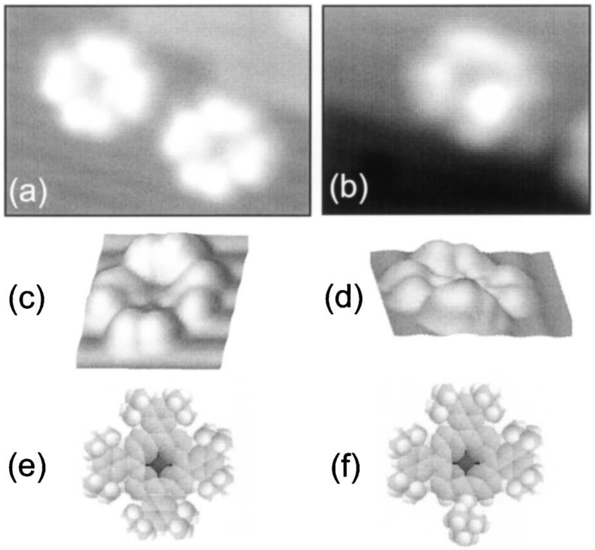

FIG. 2. (a) STM image of a Cu-TBPP molecule on Cu(211) lying flat on the surface and oriented parallel to the intrinsic step edges. (b) STM image of a Cu-TBPP molecule on Cu(211) showing one leg rotated out of the porphyrin plane. (c) and (d), calculated full STM images of a Cu-TBPP on Cu(211) for (a) and (b) using ESQC. The molecule orientation and its intramolecular conformation have been optimized to minimize both the potential energy of the molecule and the numerical distance between the experimental and calculated images. (e) and (f): Sketch of the approximate molecular conformation for (a) and (b).

On Cu(100), the central Cu-TBPP part was also not imaged and only the four legs provided the contrast with one lobe per leg [9]. This was interpreted as an electronic decoupling of the porphyrin's delocalized $\pi$-orbital system from the metallic surface, and the conformation of the four TBP legs was found perpendicular to the surface by calculating the full STM image of the molecule [9]. On Cu(100), the apparent height of the legs is 5 Å, while the value estimated from the molecular dimensions is about 11 Å [9]. On the Cu(211) surface, the (111) facets impose another conformation to the legs as compared to the Cu(100) case. The legs are now largely tilted and the two end butyl groups of a given leg are interacting with the surface, giving two lobes instead of one per leg (Fig. 2a) and showing that the legs are practically flat on the surface. In the case of the single bright spot of Fig. 2b, on the contrary, one leg seems rotated out of the porphyrin plane. To evaluate the tilt angle of the legs for both configurations, we have calculated the full STM image of a Cu-TBPP molecule on the Cu(211) surface using the ESQC technique for different leg conformations. A total of 770 molecular orbitals were taken into account in the calculation, including the exact Cu(211) surface atomic structure and a tip apex of 27 atoms. A tilt angle of 10° relative to the surface was found in the case of flat legs, in agreement with the experimental data (Fig. 2a). In the case of Fig. 2b, the calculations demonstrate that one leg is rotated around its $\sigma$ bond of 55° out of the plane of the porphyrin. The calculated STM images are reported in Figs. 2c and 2d, respectively, while the molecular models (Figs. 2e and 2f) roughly visualize the two different conformations of the molecule. It is important to note (see Fig. 1c) that the calculated tunneling resistance through a leg decreases more than 1 order of magnitude by passing from the flat case of Fig. 2a to the rotated case of Fig. 2b. Therefore the flat leg case can be called the "OFF state" of the switch, while the rotated leg can be considered the "ON state."

A further step in the implementation of the molecular switch is now to use manipulation techniques to reversibly modify the molecular conformation. First of all, we have performed lateral manipulation of the Cu-TBPP molecules. Although at room temperature a Cu-TBPP molecule can be easily manipulated on different Cu surfaces [9], at low temperature on Cu(211) only a strong repulsive force can move it along the intrinsic steps. However, passing with the tip over the molecule in lateral manipulation condition, i.e., at a tunneling resistance of $6 \times 10^4\ \Omega$, induces a rotation of legs out and/or in the porphyrin plane. In Figs. 3a–3c, the manipulation was performed in the direction of the Cu(211) step edges through the legs. As shown in this manipulation sequence, under these conditions a single leg can be rotated in both directions (55° or 10°).

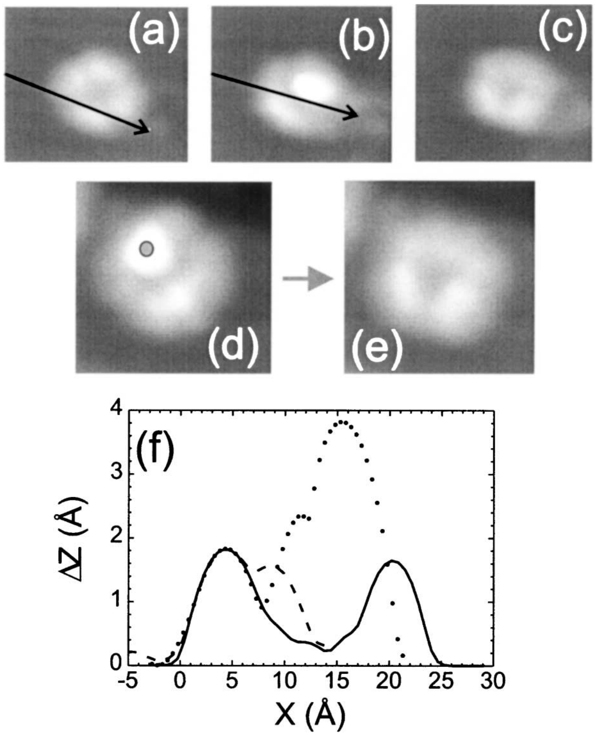

FIG. 3. STM images showing the rotation of a leg induced by (a)–(c) lateral and (d)–(e) vertical manipulation. The lateral manipulation was performed in the direction indicated by the arrows in (a) and (b) at a tunneling resistance of $6 \times 10^4\ \Omega$; (b) shows the result of the manipulation in (a), and (c) shows the result of the manipulation in (b). (e) Result of the vertical manipulation performed by positioning the tip on the point indicated with a circle on image (d). (f) Calculated STM scans of the Cu-TBPP molecule across an ON leg (dotted line), an OFF leg (dashed line), and across two opposite OFF legs (continuous line).

The rotation of a single leg around the porphyrin-leg-$\sigma$ bond from the rotated to the flat conformation, i.e., from the ON to the OFF state of the switch, is possible also by vertical manipulation. The vertical manipulation was performed at $V = 30$ mV by positioning the tip on the bright spot (Figs. 3d–3e) and reducing the tip apex-surface distance by 4 Å, thus pushing the leg downwards. After this manipulation sequence, the leg adopts the 10° conformation angle showing its characteristic two lobes. A series of calculated STM scans across the Cu-TBPP molecule, presented also in Fig. 3, confirms this interpretation of the control of the leg tilt angle by the STM tip apex.

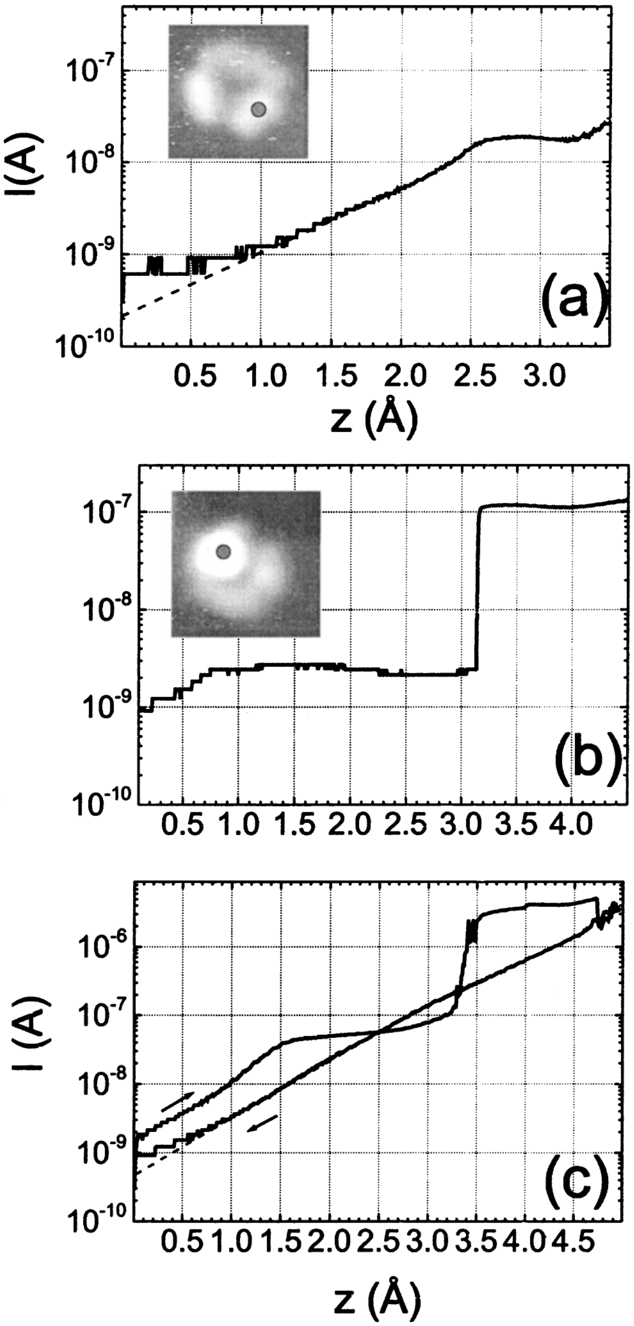

FIG. 4. $I(z)$ curves recorded (a) on an OFF leg and (b) on an ON leg. The exact position of the tip is shown in the insets. The starting tip-surface distance $z_0$ is, respectively, (a) 5.5 Å and (b) 7.5 Å, relative to the electrical contact point between tip and surface (12.7 kΩ STM junction resistance). (c) $I(z)$ curve recorded during the controlled rotation of a leg from the ON leg to the OFF leg states with $z_0 = 7$ Å. A sample voltage of 1 V has been applied during this $I(z)$ cycle. The dotted lines in (a) and (c) show the prolongation of the $I(z)$ behavior at low $z$, not visible in the experimental curves because of the limited sensitivity of the preamplifier.

To experimentally demonstrate the principle of the molecular switch, we have quantitatively investigated the interaction between tip apex and leg during a vertical manipulation sequence by recording the tunneling current $I = I(z_0 - z)$ vs the height of the tip on the surface. On a flat leg (switch OFF), for $V = 30$ mV and starting at $z_0 = 5.5$ Å, the measured $I(z)$ curve is shown in Fig. 4a. Initially the current grows exponentially, as observed up to the electrical contact point on a clean surface or on a $C_{60}$ molecule up to the van der Waals contact point [14]. At $z = 2.5$ Å, a plateau occurs because the tip apex reaches the van der Waals contact point with the flat leg. At this point and contrary to the large current increase in the

$C_{60}$ case, the leg continues to be tilted towards a full planar conformation. Here, model calculations show that there is a competition between the molecular orbital hybridization of the phenyl of the leg with the central porphyrin which favors an increase of $I$ and the deformation of the molecule which lowers $I$. The process is perfectly reversible. Beyond $z = 3.3$ Å, the through space tunneling current starts to be larger than the through leg one, and an exponential regime is recovered.

When the same procedure is applied on a rotated leg (switch ON) with the bias voltage still at 30 mV, the corresponding $I(z)$ curve is reported in Fig. 4b. In this case, the initial $z_0 = 7.5$ Å was kept large enough to avoid the rotation of the leg already at the start of the $I(z)$ measurement. The curve shows two well-defined plateaus, at $3 \times 10^{-9}$ Å and $1 \times 10^{-7}$ Å, respectively, with a sudden change between them at $z = 3$ Å. The lower plateau corresponds to the competition described for the plateau of Fig. 4a when the tip apex starts to tilt the leg. This plateau has a length of more than 2 Å because a full rotation of the leg is required to reach the OFF conformation. Then, the conductance through the leg changes reversibly by about 2 orders of magnitude, demonstrating that the leg has reached its OFF conformation.

We take now benefit of this mechanical control to demonstrate experimentally the principle of the switch proposed in Fig. 1b. Figure 4c shows the $I(z)$ curve recorded during a complete ON-OFF cycle of the molecular switch. The ON state of the switch is chosen at $z_0 = 7$ Å, with a large (1 V) bias voltage to initially avoid the tip-leg interaction. The STM junction resistance is 670 M$\Omega$ in this case. The ON-OFF switching is performed by a large $z$ reduction down to $z = 4$ Å, and then back to $z_0 = 7$ Å. In the OFF conformation and for $z_0 = 7$ Å the STM junction resistance reaches the value of 2.1 G$\Omega$. As one can see from Fig. 4c, 1 order of magnitude difference in resistance is present between the ON and OFF states, quantitatively demonstrating the principle of the switch, and in perfect agreement with the theoretical predictions reported in Fig. 1c. As calculated (Fig. 1c), $z_0 = 9$ Å would provide a better difference between the ON and OFF state, but the tunneling current in the OFF state is at this distance too low to be measured, proving the validity of the calculated switch.

The OFF-ON back switching process results from the lateral manipulation already described (Figs. 3a–3b), consisting of a $z$ reduction, a small lateral shift of the tip apex position to return permanently at $z_0 = 7$ Å. After this process the junction resistance is again 670 M$\Omega$ and the leg is back to its ON conformation.

In conclusion, we have presented a LT-STM study of individual Cu-TBPP molecules on Cu(211) and we have shown that by means of vertical and lateral manipulation it is possible to rotate single legs around their $\sigma$ bond, in and out of the porphyrin plane. The interaction between tip and molecules has been quantitatively investigated by recording $I(z)$ curves on different positions. We have finally demonstrated that the controlled rotation of the legs induced by the STM tip realizes the principle of a conformational molecular switch.

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