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# Exploring the Interatomic Forces between Tip and Single Molecules during STM Manipulation

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**ABSTRACT**

**The interaction between a single molecule and the STM tip during intramolecular manipulation is investigated in detail. We show that the conformational change of complex organic molecules can be induced reversibly and very reliably by using exclusively attractive forces. By studying the dependence of this process on the bias voltage and the tip position, the driving forces are characterized. Different regimes of tip–molecule interactions are observed as a function of the distance.**

Many large organic molecules have enough internal degrees of freedom to present different stable conformations when adsorbed on a surface.[1] A challenging task with regard to device miniaturization down to the molecular scale is to control the conformations of a single molecule with picometer-scale precision. A molecular switch was realized by rotating only one single leg of a tetra-di-*tert*-butyl-phenyl porphyrin with the tip of the scanning tunneling microscope (STM).[2] Intramolecular mechanics have also been performed by switching a porphyrin macrocycle between a planar and a nonplanar conformation.[3] Very recently, inelastic tunneling[4] was used to trigger a biphenyl molecule between two adsorption sites on Si(100).[5]

In this work, we have explored the full range of interaction between the tip apex of an STM and a molecule equipped with legs causing one and the same conformational change of this molecule. Our manipulation experiment is based on the intramolecular bistability of the di-tert-butyl-phenyl groups (legs) of a Lander molecule when adsorbed on a Cu(110) surface. By selecting tip−molecule geometries where exclusively attractive forces are active, we reversibly switch the legs between two stable conformational states. The high reliability of this method allows us to characterize in detail different regimes of tip apex−molecule interactions.

Experiments have been performed in an ultrahigh vacuum chamber with a base pressure of $10^{-10}$ mbar. The molecules are deposited onto the clean Cu(110) sample as described previously.[6] Images were taken with a home-built[7] low-temperature STM (LT-STM), running at 7 K, in constant-current mode using a tunneling current of 0.1 nA and a bias voltage of 1 V (with respect to the tip). The corresponding tip height of about 7 Å (determined from $I(z)$ curves) is the starting point for vertical feeds $\Delta z$. Although a tungsten tip is used, it is presumably covered with copper because of many controlled tip crashes performed to improve its quality.

A detailed investigation of the molecule−tip interaction during manipulation requires a molecule that can be reliably switched between two stable conformations. A suitable candidate is the Reactive Lander (RL) molecule (Figure 1a) adsorbed on Cu(110). This molecule[8] consists of a polyaromatic central board and four lateral 3,5-di-*tert*-butyl-phenyl groups, which are known to adopt two different well-identified conformations on a surface.[6] After deposition onto Cu(110) at room temperature, annealing at 370 K and subsequent cooling to 7 K, all RL molecules are adsorbed at step edges and act (equivalently to Single Lander molecules[9,10]) as templates for the formation of a double row of copper atoms underneath them.[6] The RL central board is lifted up by this nanostructure while the four molecular legs exceed it laterally (Figure 1b). This configuration prevents the molecule from translation or rotation and points to more freedom of rotation of the legs than in any common adsorption site on the surface, making repeated conformational changes of the legs possible. For our manipulation experiment, the molecule has to be moved along the nanostructure by at least one lattice constant of Cu(110) (2.55

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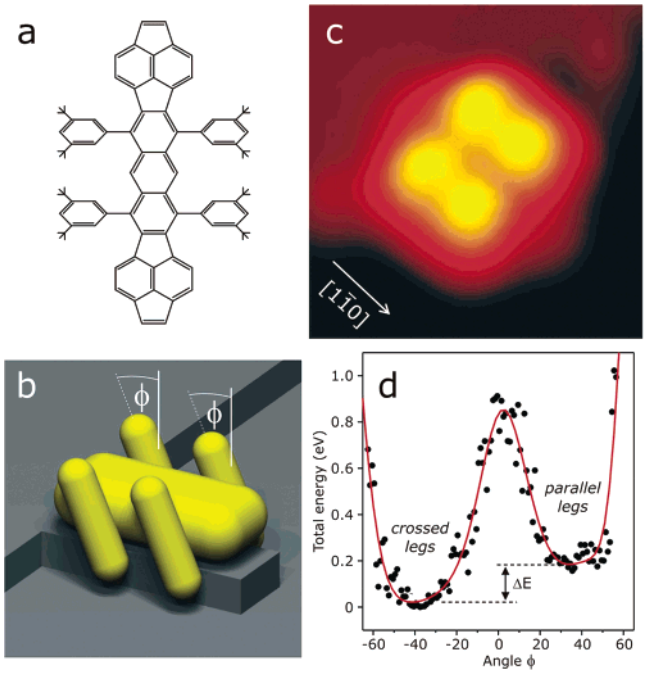


**Figure 1.** (a) Chemical structure and (c) STM image (35 × 35 Å$^2$; $I = 0.2$ nA and $U = 1$ V) of a Reactive Lander (RL) molecule adsorbed on a Cu(110) nanostructure (always oriented in [1−10] direction). (b) Adsorption geometry of RL molecules on the Cu nanostructure (in the parallel legs conformation) with the rotation angle $\phi$ of one pair of molecular legs indicated. (d) Total energy of the molecule−nanostructure−copper surface system as a function of the rotation angle $\phi$ of one pair of legs (the solid line is plotted to guide the eye). The two minima correspond to the crossed legs ($\phi = -37°$) and parallel legs ($\phi = +37°$) conformations with an energy difference of $\Delta E$. The curve is obtained by rotating only one pair of legs (on the same side of the central board) and leaving the other pair in the initial position.

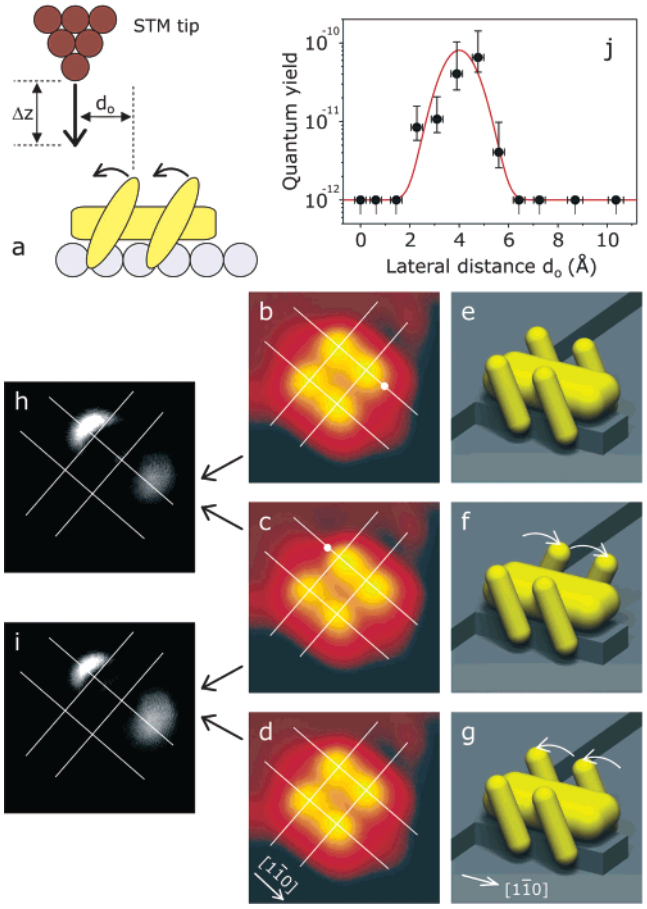


**Figure 2.** (a) Scheme of the manipulation process: One pair of molecular legs rotates upon approaching the STM tip. (b−d) Series of STM images (all 35 × 35 Å$^2$; $I = 0.2$ nA and $U = 1$ V), switching one and the same RL molecule from the parallel legs to the crossed legs conformation and back (white lines connect the position of the four legs of the initial image (b) to emphasize the conformational changes). (e−g) Schemes of the corresponding conformations. The lateral tip position of the subsequent manipulation is marked in the STM images by a white dot and the achieved conformational changes are indicated in the schemes by arrows. The differences between the STM images are plotted in images h and i (black areas indicate no difference) for b and c and c and d, respectively. (j) Quantum yield (events per electron) vs lateral tip distance $d_o$ (from the intensity maximum of the nearest leg) along the [1−10] direction (constant tip height and bias voltage). The error is determined from the deviation from the average time.

Å) toward the lower terrace in order to minimize the leg interaction with the nearby mono-atomic Cu step edge. In STM images the molecule appears as four bright lobes, corresponding to the lateral molecular legs (Figure 1c). The legs positioned on the same side of the central molecular wire always rotate together, resulting in the so-called parallel legs (PL) and crossed legs (CL) conformations, where both pairs are oriented in the same or opposite directions, respectively. As confirmed by calculations of the conformational energy,[10] the two observed conformations are energetically stable (Figure 1d).

The principle of the manipulation is shown in Figure 2a. At constant bias voltage and while maintaining the lateral tip position fixed, the STM tip is approached vertically toward the molecule until one pair of legs rotates, changing the molecular conformation. A successful manipulation shows up as an abrupt increase in the tunneling current during the tip approach. Imaging the molecule afterward confirms the successful manipulation as presented in Figure 2b−i, where one molecule is manipulated from the parallel to the crossed legs conformation and back. As can be seen in the STM images and the subtraction plots (h−i), only one pair of legs rotates (while the entire molecule remains fixed) and the process is completely reversible as the initial conformation is precisely restored in image d. This manipulation mode is nondestructive for the tip and the molecule, because only attractive forces are used. The resulting high reliability leads to a very high rate of successful events of more than 99% and thus enables us to repeat the same conformational change on the same single molecule many (>100) times (see the Supporting Information). Notice that in a repulsive mode (as for the molecular switch[2]), pushing on a leg holds the risk of damaging the STM tip and/or the molecule because repulsive forces become very large at small distances. The tip height, at which the manipulation process occurs during the approach, turns out to be characteristic for the conformational change. By analyzing many equivalent manipulation processes (of the conformational change PL to CL in Figure 2b and c) a threshold value of $\Delta z$ of 0.8 ± 0.2 Å is determined, below which (i.e., at larger tip heights) no

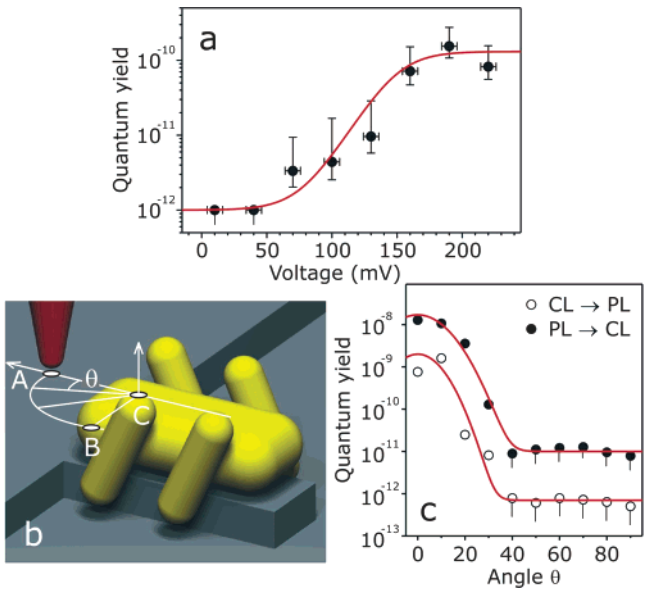


**Figure 3.** (a) Quantum yield (events per electron) of the manipulation (from crossed to parallel legs) vs the bias voltage at a fixed tip height ($\Delta z = 3$ Å). (b) Experimental setup for the determination of the quantum yield as a function of the lateral tip position with respect to the RL molecule, i.e., the azimuthal angle $\theta$. Position A ($\theta = 0°$) refers to the tip in front of the molecular leg; B and C correspond to tip positions sideways ($\theta = 90°$) and above, respectively. The results are plotted in diagram c for two opposite conformational changes (crossed legs to parallel legs and vice versa). Bias voltage (1 V), tip height (about 4.7 Å for CL to PL and 6.3 Å for PL to CL), and lateral distance (4 Å) of the STM tip are kept constant. Each series in diagrams a and c is obtained for one and the same molecule. The reason for the difference of the maximum quantum yield between diagrams a and c is that the two series are taken with two different molecules, thus exhibiting different potential barrier heights due to the local atomic environment. The solid lines are drawn to guide the eye.

conformational change can be induced. Note that the potential barrier height and thus the required threshold tip height can change from one molecule to the other because of the local atomic environment at the step edge. It is therefore important to study the dependence of the process on the manipulation parameters always for one and the same molecule within one series.

Quantum yields (the number of events per tunneling electron) have been determined from the current and the waiting time needed for a successful manipulation event.[11] The dependence of the quantum yield on the lateral distance, $d_o$, between tip and leg in the [1−10] direction (defined in Figure 2a) shows a maximum at about 4 Å (Figure 2j). This value is therefore used in all manipulation series. The dependence of the quantum yield on the bias voltage is plotted in Figure 3a for one and the same conformational change of a single molecule (while the tip height is fixed). While no conformational change can be induced at small voltages up to 50 mV, quantum yields up to more than $10^{-10}$ events/electron are achieved at voltages above. A threshold voltage of 110 ± 30 mV is visible, showing that the manipulation process depends not only on the tip apex−molecule distance, but also on the bias voltage.

The fact that the tip has to be approached in front of the molecule (at $d_o > 2$ Å in Figure 2j) points to a directional force driving the manipulation. This observation is confirmed by Figure 3b and c, where the STM tip was positioned at various angles $\theta$ off the [1−10] direction, always at the same height and lateral distance from the molecular leg to be manipulated, leaving the tunneling current constant. While at large $\theta$ no conformational change can be induced, the quantum yield rises by several orders of magnitude when going below $\theta = 35°$ (Figure 3c), revealing a maximum in the quantum yield of the process when the tip apex is positioned in front of the molecule (position A). Note that the quantum yield is smaller (the current is larger as the tip must be closer to the surface) for conformational changes from crossed to parallel legs than for the opposite direction (PL to CL) because of the higher barrier for this conformational change (see Figure 1d) and therefore in need of larger forces.

Because the driving force of the manipulation is directional and depends on both the tip height and bias voltage, the process is likely driven by the electric field in the junction. It is known that electric-field-induced forces come into play when working with an STM:[12] Electric-field-induced diffusion requires permanently charged atoms or molecules[13] while interaction between the electric field and a dipole occurs when a local dipole moment is induced in the adsorbate, as proved recently for the first time for molecules.[3] The studied molecules exhibit no permanent dipole moment. We thus interpret our experimental results by the electric field that induces a dipole moment in the molecular legs. The conformational change is achieved by the electrostatic force acting on them in the presence of the electric field in the STM junction.

To confirm this interpretation, the threshold voltage was determined as a function of the tip height (Figure 4). Each data point corresponds to one single manipulation process, where (at a given $\Delta z$) the bias voltage is raised slowly ($\Delta U/\Delta t \approx 5$ mV/s) until the conformational change occurs. Notice that the same result is obtained for the inverse measurement, that is, when measuring the threshold tip height as a function of the bias voltage. For a PL to CL change, the result in Figure 4a shows that the conformational change can be successfully induced over a tip height range of 3 Å. The necessary bias voltage changes in this range and reveals an approximately linear relationship between the tip−molecule distance and the applied voltage if $\Delta z$ is below 3.7 Å (for both polarities). This dependence demonstrates the dipole−electric field interaction character. Ideally, the relationship between $U$ and $z$ should be linear, with a deviation at small tip heights.

Notice that above $\Delta z = 3.8$ Å no bias voltage has to be applied for a successful PL to CL conformation change. The rotation of the legs is induced simply by positioning the tip at a sufficiently small tip height between the leg and the tip apex. The potential barrier between the two leg orientations drops upon the tip approach and $\Delta E_{PL}$ goes to zero (Figure 4b), similar to the manipulation of single Co atoms on Cu(111).[14]

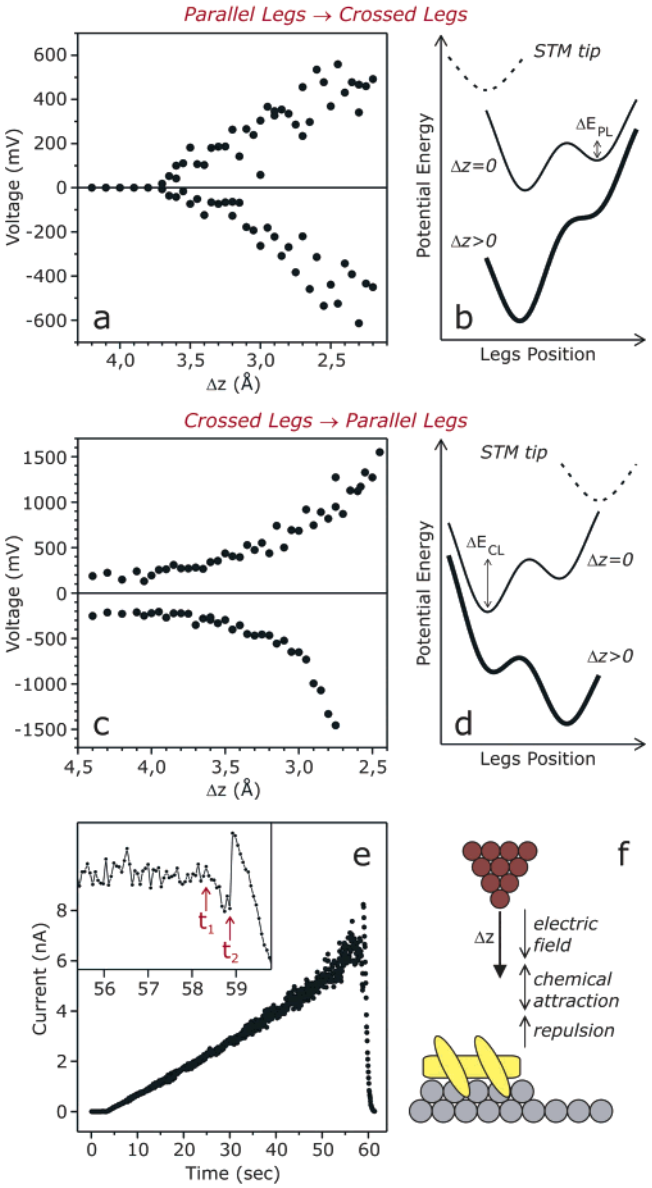


**Figure 4.** (a and c) Threshold voltages as a function of the vertical tip feed Δz of the manipulation process (for one and the same molecule). Corresponding schematic potential energy curves are plotted in diagrams b (manipulation from PL to CL) and d (from CL to PL). Dashed curve: tip-induced potential well. Solid line: molecular legs without tip. Bold solid line: molecular legs in the presence of the STM tip (Δz > 0; meaning the tip is approaching the surface), i.e., the sum of the tip-induced potential well and the double well potential of the molecule without a tip influence (Δz = 0). (e) Current signal during a conformational change from CL to PL at Δz = 4.5 Å (the bias voltage is changed from 0 to −300 mV). The inset shows an enlarged region with the important moments of tip retracting ($t_1$) and successful manipulation ($t_2$), visible as an abrupt current increase, marked by arrows. Lines are drawn to guide the eye. (f) Scheme of the three observed regimes of interatomic forces (at different tip heights).

When inducing the opposite conformational change (from CL to PL), the threshold voltage does not go to zero but decreases to minimum values of ±200 mV. This behavior could be due to the asymmetry of the double potential well profile (Figure 1d). A schematic model of a double potential well (Figure 4b and d) shows that this asymmetry can cause an important difference in the shape of a potential barrier when the tip is approached: While $\Delta E_{PL}$ (PL to CL) goes to zero upon a sufficient tip approach (Figure 4b), the potential barrier for the opposite change (CL to PL) is always present and $E_{CL}$ reaches a constant (finite) value at very small tip heights (Figure 4d). It was not possible to determine a CL to PL threshold voltage for Δz larger than 4.4 Å because no rotation of the legs can be induced as long as the tip is very close. At Δz = 4.5 Å the current signal increases linearly (Figure 4e) because the bias voltage is raised from 0 to −300 mV and exhibits no jump until the tip is retracted (at time $t_1$). However, an abrupt increase in the current signal is observed immediately afterward (at time $t_2$). This shows that the small distance between tip and molecular leg inhibits the conformational change by hindering the leg to rotate, but as soon as the tip apex is out of this repulsive force range the conformational change of the molecule occurs. Finally, at large tip−molecule distances (with a Δz below 2.2 or 2.5 Å in Figure 4a and b, respectively) no successful manipulation can be induced. This is likely due to the small horizontal force component as the lateral tip position is kept constant.

An additional observation that points against inelastic tunneling processes, which could induce the conformational changes together with a deformation of the potential landscape upon the tip approach, was made at high tunneling voltages: We have checked if larger bias voltages can induce the conformational change when the tip is not positioned in front of the molecular leg. It turned out that no conformational change can be induced at all (at tip heights in the Δz range of −2 to +3 Å and resulting currents up to 25 nA) if the tip is positioned sideways (position B in Figure 3b) or above the molecular leg (position C), even at voltages up to 3 V. Instead, the tip apex is modified or the molecule slightly changes its lateral position (retaining its conformation) or even dissociates. This points against inelastic tunneling effects as the driving process (although they also exhibit spatial sensitivity on the lateral tip position), especially for the case of a smaller potential barrier, that is, from PL to CL (Figure 4a), where the manipulation is done at bias voltages between 0 and 0.6 V under the usual conditions (i.e., tip in front of the leg). The applied voltages up to 3 V (and large tunneling currents) should therefore be by far sufficient if the tip is not in front of the molecular leg (the lowering of the potential barrier is abandoned).

In conclusion, we present the controlled and reversible intramolecular manipulation of the legs of a Reactive Lander molecule by vertically approaching the tip nearby one leg. This new manipulation mode is very reliable and nondestructive for a molecule because only attractive forces are active. All possible conformations of the molecule can be obtained repeatedly with a very high rate of success. We show how three different regimes of interatomic interactions can be explored on a single molecule by varying the distance between the tip and the molecule as shown schematically in Figure 4f: At large tip heights, electrostatic forces on the dipole moment induced in a molecular leg are invoked while chemical forces are observed when approaching the tip (no

bias voltage necessary). In addition to these attractive forces, the regime of repulsive forces is reached at very small tip heights.

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**Supporting Information Available:** Movie of 112 subsequent manipulations between two conformations of one and the same molecule with a success rate of 100%. The molecule does not move while one pair of legs is switched reversibly. This material is available free of charge via the Internet at http://pubs.acs.org.

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