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Ab Initio Investigation of the Switching Behavior of the Dithiole-Benzene Nano-Molecular Wire

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We report a first-principle study of electrical transport and switching behavior in a single molecular conductor consisting of a dithiole-benzene (DTB) sandwiched between two Au(100) electrodes. *Ab initio* total energy calculations reveal DTB molecules on a gold surface, contacted by a monoatomic gold scanning tunneling microscope (STM) tip to have two classes of low energy conformations with differing symmetries. Lateral motion of the tip or excitation of the molecule cause it to change from one conformation class to the other and to switch between a strongly and a weakly conducting state. Thus, surprisingly, despite their apparent simplicity, these Au-DTB-Au nanowires are shown to be electrically bi-stable switches, the smallest two-terminal molecular switches to date. The projected density of states (PDOS) and transmission coefficients are analyzed, and it suggests that the variation of the coupling between the molecule and the electrodes with external bias leads to switching behavior.

Keywords: Molecular electronics, Density Functional Theory, Electron transport, Non-Equilibrium Green's function, Molecular switch, Dithiol-benzene

INTRODUCTION

Electronic devices that switch between high and low resistance states are at the heart of the modern information technology. As miniaturization of this technology continues to progress the long-standing fundamental problem of identifying and understanding the smallest physical systems that are capable of switching behavior is attracting growing interest [1-9]. Recently, it has been discovered experimentally and theoretically that some molecular wires (*i.e.*, single molecules carrying an electric current between a pair of metal nano-electrodes) can exhibit electrical bistability and switch between strongly and weakly conducting states, either spontaneously or in response to a change in the applied bias voltage [1-4]. It has been suggested that this intriguing behavior may be due to charging of the molecule and/or changes of the molecular geometry (conformation) [1-5]; however, the complexity of the experimental systems has so far prevented the development of a quantitative explanation. On the theoretical side, the possibility of making molecular wire switches by introducing a third (gate) electrode into the system has been explored [6-8], as has the possibility of designing two-terminal molecular wires that switch due to electric field-induced conformational changes [4,9]. In this work, we demonstrate theoretically that a much smaller and simpler two-terminal molecular wire can exhibit bi-stability and switching than has been thought possible until now, and present a realistic theory of its behavior *via* the most expensive computational method, *i.e.*, Density Functional Non-Equilibrium Green's Function, DFT-NEGF, method. We

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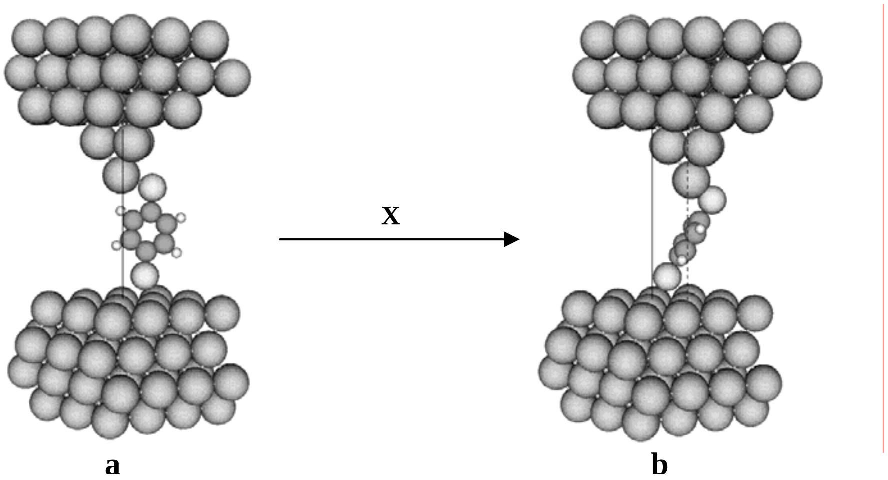

Fig. 1. A schematic of a 1,4-dithiole-benzene STM between Au(100) electrodes. (a) Edge conformation for STM tip over hollow substrate bonding site. (b) Face conformation. (Vertical lines indicate on the initial position of the STM tip, while, the dashed line demonstrate the position of the tip after its movment).

consider a 1,4-dithiole-benzene (DTB) molecular wire with one sulfur end group bonded to a gold substrate and the other to a monoatomic gold scanning tunneling microscope (STM) tip as depicted in Fig. 1. Our *ab initio* total energy calculations demonstrate that this system has low energy conformations of two distinct types that have different symmetries. We employed the SIESTA [10] code which replaces core electrons by pseudo potentials and describes valence electrons by an atomic-like basis set. We use a double-ζ + polarization basis set for the organic and a single-ζ polarized basis set for the gold *s, p and d* channels. The exchange and correlation potential is calculated using the local density approximation (LDA).

Flipping between these conformations is predicted to occur in response to lateral motion of the STM tip, and also, for some positions of the STM tip, in response to excitation of the wire by a current pulse or spontaneously at finite temperatures. The symmetry change when the molecular wire flips results in a large change in its current-voltage characteristic. Thus, its electrical conductance exhibits bi-stability and switching.

Theoretical work [11-16] stimulated by a pioneering molecular wire experiment [17] has elucidated various aspects of electron transport through Au-DTB-Au wires. However the possibility that wires of this type may be bi-stable or capable of switching is, to our knowledge, the first calculation with a full atomistics *ab initio* description of both the gold electrodes and DTB molecular wire [4,18]. Thus, as well as identifying the smallest two-terminal molecular switch to date, the present work sheds a new light on the mechanisms of molecular bistability and switching of Au-DTB-Au molecular wires, one of the most important paradigms of molecular electronics. The molecular switch that we describe should be amenable to experimental study with presently available techniques. Thus, our findings also raise the prospect of bridging the gap that has persisted in this field between theory and experiment since molecular switching was first observed.

The organization of the papers is as follows. We start with a brief description of the Density Functional based Non-Equilibrium Green's Function method, and then we present calculations of the *(I-V)* spectrum of a DTB molecule, together with an analysis of the molecular levels important for electron transmission. Finally, the results will be summarized.

Computational Details

The calculations have been performed using a recently developed first-principles package SMEAGOL [19,20], which is based on the combination of DFT (as implemented in the well-tested SIESTA method [10]) with the NEGF technique [21,22]. SMEAGOL is capable of fully self consistently modeling the electrical properties of nano-scale devices that consist of an atomic scale system coupling with two semi-infinite electrodes. Such nano-scale devices are referred to as two-probe systems and they are divided into three parts for theoretical calculations: left and right electrodes, and a central scattering region. The scattering region actually includes a portion of the semi-infinite electrodes. The simulation procedure of such two-probe systems can be described briefly as follows.

Firstly, the electronic structure of two electrodes is calculated only once by SMEAGOL to get a self-consistent potential. This potential will be shifted rigidly relative to each other by the external potential bias and provides natural real space boundary conditions for the Kohn-Sham (K-S) effective potential of the central scattering region. Then, from the Green's function of the central scattering region, it can obtain the density matrix and thereby the electron density. Once the electron density is known, the DFT Hamiltonian matrix, which is used to evaluate the Green's function, can be computed using the above boundary conditions by means of standard methods.

$$\hat{G} = \lim_{\delta \to 0}[(E + i\delta)\hat{S} - \hat{H}_{S[\rho]} - \hat{\Sigma}_L - \hat{\Sigma}_R]^{-1} \tag{1}$$

where $\hat{H}_{S[\rho]}$ is DFT Hamiltonian and $\hat{\Sigma}_L$ and $\hat{\Sigma}_R$ are the self-energies, respectively for the left and right lead. This procedure is iterated until self-consistency is achieved. Moreover, the current through the atomic scale system can be calculated from the corresponding Green's function and self-energies using Landauer-Buttiker formula [23].

$$I(V) = \frac{2e}{h}\int_{-\infty}^{+\infty} dE[f_l(E - \mu_l) - f_r(E - \mu_r)]T(E,V) \tag{2}$$

where μ_l and μ_l are the electrochemical potentials of the left and right electrodes, respectively, *i.e.*,

$$\mu_L - \mu_R = eV_b \tag{3}$$

and f_r, f_l are the corresponding electron distribution of the two electrodes. *T(E,V)* is the transmission coefficient at energy *E* and bias voltage *V*, which is given by

$$T(E,V) = Tr[\mathrm{Im}\Sigma_l(E)G^R(E)\mathrm{Im}\Sigma_r(E)G^A(E)] \tag{4}$$

where $G^R(E)$ and $G^A(E)$ are the retarded and advanced Green's function of the central region. Based on the eigenchannel decomposition of the conductance, this total transmission *T(E)* can be decomposed into nonmixing eigenchannels $T_n(E)$ [24] as:

$$T(E) = \sum_n T_n(E) \tag{5}$$

In our DFT calculation, the local-density approximation (LDA) to the exchange-correlation potential [25] is used. Only valence electrons are considered in the calculation, and the wave functions are expanded by localized numerical (pseudo)atom orbitals (PAO's) [26]. The atomic cores are described by norm-conserving pseudo potentials [27].

In the *ab initio* calculations of the energetics of Au-DTB-Au wires, the STM tip was represented by a tetrahedron of Au atoms and the Au(100) substrate by an electrode consisting of three layers of Au atoms as shown in Fig. 1. We searched for low-energy molecular wire conformations holding the positions of the Au atoms fixed and keeping one of the S atoms of the DTB over the hollow site between the three Au substrate atoms since it is believed that organic thiol molecules bond to Au(100) surfaces *via* a sulfur atom at this location [28]. All other coordinates of the atoms of the wire were allowed to vary freely.

The lowest energy conformation of the molecular wire when the Au tip atom is directly over the hollow bonding site of the substrate and 9.9 Å from the substrate is depicted in Fig. 1a. The molecule orients itself so that the Au tip atom is approximately coplanar with the benzene ring. We will refer to this as an edge conformation of the wire since the Au tip atom faces the edge of the benzene ring. If the Au tip is moved further from the substrate, so that it becomes geometrically possible for the molecule to stand perpendicularly to the substrate with the terminal Au atom of the STM tip directly over the upper S atom, we find this upright geometry to be unstable energetically: As long the tip atom is close enough to the molecule for a chemical bond to form between the Au and S atoms, the molecule relaxes to a tilted position. We note that such non-linear bonding geometries of Au, S and C atoms have also been found in recent *ab initio* simulations of monoatomic Au wires bonded to other organic thiolate molecules [29].

When the Au tip is moved laterally away from the position over the hollow substrate bonding site, we find the molecular wire's ground state conformation to change dramatically. This is illustrated in Fig. 1b where the tip has been displaced laterally in the x direction from its (x = 0) position in Fig. 1a. Interestingly, the molecule adopts an orientation in which it tilts as far from the normal to the substrate as it can while maintaining the chemical bond between the Au tip atom and the upper S atom of the molecule. Most importantly, however, as the lateral tip displacement increases the molecule rotates about its S-S axis from its edge conformation through an angle of л/2 to an orientation in which the Au tip atom is over the flat face of the benzene ring, as in Fig. 1b. (For example, we find the highly conducting excited face conformation obtained by rotating the molecule from the (weakly conducting) ground state edge conformation in Fig. 1a through л/2 about the S-S axis corresponds to an energy saddle point *kT* room above the ground state; thus this excited state will be populated significantly at room temperature). We shall refer to this as a face conformation. Thus, the ground state conformation of the molecular wire switches from edge to face as the STM tip moves laterally away from the location where the molecule bonds to the substrate.

RESULTS AND DISCUSSION

We now examine the implications of the conformational switching and bi-stability described above for electrical current through the molecular wire. In recent years, much progress has been made developing theories of electron transport through molecules [11-16,30-33]. An important conclusion has been that the current at low bias is carried by molecular orbitals. The overlap between the orbitals and the states of the contacts is sensitive to the orientation of the molecule relative to the contacts, which implies a strong orientation-dependence of the molecular wire's conductance [15]. Such overlap effects have been found in semi-empirical [11,16)] and density functional [13] transport calculations.

Thus, it is reasonable to expect them to result in a significant change in conductance when an Au-DTB-Au wire switches between an edge and a face conformation, and our calculations show this to be the case. Since DFT calculations have been successful in explaining the experimental current-voltage characteristics of a variety molecular wires consisting of organic thiol molecules bonded to gold electrodes [16,30,32], we adopted this approach here. In Fig. 2, we show the calculated current of the molecular wire in its ground state conformation for a sequence of positions of the STM tip along a linear trajectory over the molecule that passes through the locations that the tip occupies in Fig. 1. When the tip is farthest from the center where the molecule bonds to the substrate the molecule in its ground state is in the face conformation and is highly conducting at a source-drain bias around 1.5 V. When the tip moves towards the center, the molecule's ground state switches to the edge configuration, which is seen to be much less conducting in the same range of bias. Thus, whenever the molecule is made to flip from a face conformation to an edge conformation, either by displacing the STM tip laterally or by exciting the molecule thermally or by a current pulse, the molecule is predicted to switch from a highly conducting to a weakly conducting state, and vice versa. This large difference in conductance between the edge and face conformations can be understood within Landauer theory [23] by considering the transmission probabilities, *T*, for electrons to scatter through the molecular wire, taking account of orientational effects [15]. The Fermi energy of gold in our DFT model is near -5.32 eV.

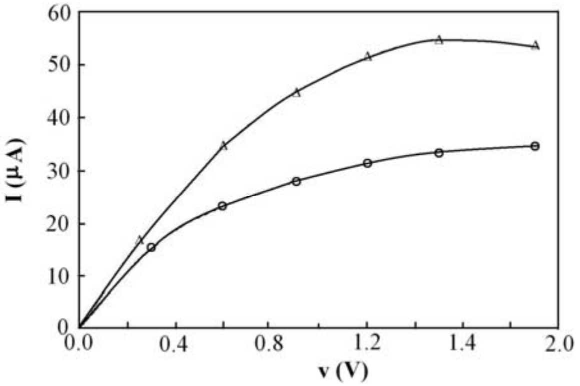

Fig. 2. Calculated current for DTB conformations at two STM tip positions. At 1.5 V the molecule is in the ''*ON*'' state when the tip is at the *face* condition and ''*OFF*'' at the *edge* state: (Δ) face, (○) edge.

A possible controlling factor in understanding molecular wires is the nature of the coupling of the continuum of energy states in the lead to the discrete energy levels of the molecular system. We believe it to be important to study how the energy levels of the molecule change when placed in contact with the metallic leads. The nature of these changes will be discussed below for configuration of the contacts and the DTB molecule. We calculated the energy levels for the DTB molecule using Density Functional Theory method. Results show that HOMO is at -5.11 eV with a LUMO of -4.74 eV. Both of these levels describe π bonds on the C ring. The character of the HOMO is that of Cπ around the ring with some Sπ content. The other levels in the DTB spectrum between the DTB HOMO-LUMO also have S character, and also contain Cπ and Cσ bonding states. The σ states are due to the two states in the DTB's spectrum that occur within the traditional HOMO-LUMO gap of DTB.

An isolated DTB molecule has 40 valance electrons, thus orbital 20 is the HOMO and orbital 21 the LUMO. When DTB is coupled to the Au electrodes both orbitals have energies below the Au Fermi level (-5.32 eV), and are therefore occupied.

Figure 3 shows the zero bias transmission spectra of the system in the face conformation. It has a region of strong transmission above the Fermi energy, and a peak of weaker strength below, where electrons incident from one of the electrodes can transmit across the molecule to the other electrode significantly. The transmission peaks immediately below the Fermi energy can be attributed to the highest occupied molecular orbital (HOMO) of the DTB and those above to the lowest unoccupied molecular orbital (LUMO). The Fermi energy lies nearest the LUMO, so the onset of conductance is due to electron transmission through the LUMO. In these conformations, there is a strong overlap between the first LUMO molecular orbital and the atomic orbitals on the Au tip atom. This results in the strong transmission due to the first LUMO above the Fermi energy in Fig. 3 and in the strong current peak seen for the face conformations in Fig. 2. To understand why incident states in these two energy regions can transmit across the molecule significantly, we calculated the projection of the density of states (PDOS) of the combined system onto all the DTB basis orbitals. The PDOS is calculated by:

$$P(E) = \left\langle \psi^{m}(E) \middle| \Psi(E) \right\rangle = \left\langle \sum_{i}^{mol} c_i(E)\phi_i(\vec{r}) \middle| \sum_{j}^{all} c_j(E)\phi_j(\vec{r}) \right\rangle, \tag{6}$$

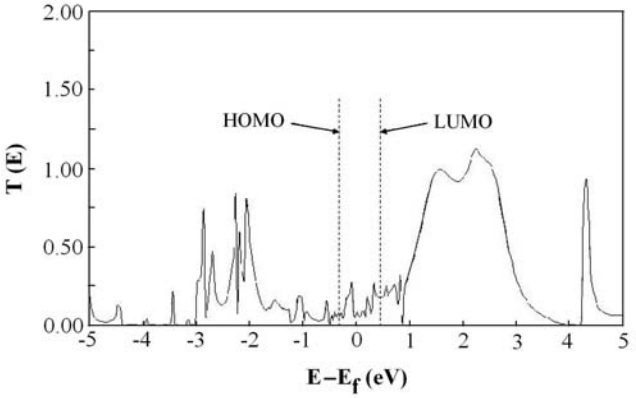

Fig. 3. Transmission function under zero bias as function of the injection energy of electron of the DTB molecule coupled to Au(100) electrodes (*face* conformation). All energies are relative to the Fermi energy of the open system (The HOMO/LUMO energy levels of the isolated DTB molecule is specified by vertical dashed lines).

where $\Psi(E)$ is the eigenstate of the whole system and $\psi^{m}(E)$ is the contribution of the basis orbitals of the molecule to $\Psi(E)$, $\{\phi\}$ are the nonorthogonal basis set of the system, and c_i and c_j are expanding coefficients. The sum over i only runs over the basis orbitals of the molecule, and the sum over j runs over all the basis orbitals of the whole system.

The PDOS will give us information on how much the basis orbitals in the molecule contribute to the eigenstate of the whole open system and how strongly the molecule couples with the electrodes at certain energy, E. The PDOS is shown in Fig. 4. We note that, corresponding to the *T-E* curve, there is also an energy region where the PDOS takes a comparatively large value. A strong coupling makes incident electrons at certain energy easily transmit across the molecule, and this will give rise to a large transmission coefficient at this energy. This is clearly shown by comparison of the transmission spectra and PDOS spectra shown in Figs. 3 and 4.

As a consequence, a large transmission coefficient indicates a strong coupling between the electrodes and the molecule, and the evolution of transmission curves with external biases can help us understand how the changes of the coupling between the electrodes and molecule determines the

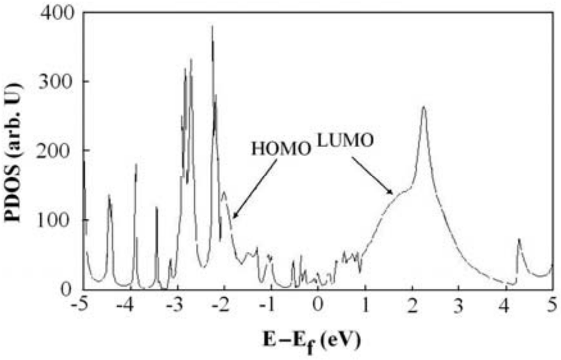

Fig. 4. The projection of the density of states (PDOS) of the combined system onto all the DTB basis orbitals, (*face* conformation). All energies are relative to the Fermi energy of the open system (The arrows demonstrate the HOMO/LUMO energy levels of the DTB after coupling with the electrodes).

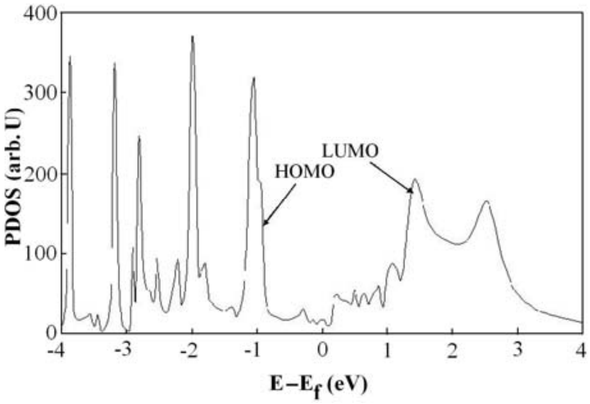

Fig. 6. The projection of the density of states (PDOS) of the combined system onto all the DTB basis orbitals, (*edge* conformation). All energies are relative to the Fermi energy of the open system.

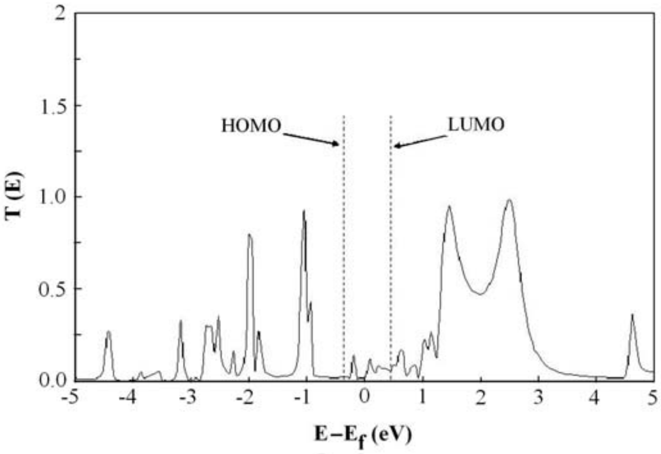

Fig. 5. Transmission function under zero bias as function of the injection energy of electron of the DTB molecule coupled to Au(100) electrodes (*edge* conformation). All energies are relative to the Fermi energy of the open system.

I-V characteristics in the system.

Regarding the edge conformation, the molecular orbitals are oriented differently and their overlap with the orbitals on the Au tip atom is weaker. As shown in Fig. 5, the Fermi energy lies nearest the HOMO, in contrast with the face conformation, so the onset of conductance is due to electron transmission through the HOMO. There is a weak overlap between the first HOMO molecular orbital and the atomic orbitals on the Au tip atom. This results in the weak transmission due to the first HOMO below the Fermi energy in Fig. 5 and in the weak current peak seen for the edge conformations in Fig. 2. Figure 6 shows the PDOS calculated for the edge conformation, and similar to the face conformation it corresponds to the *T-E* curve, that is, there is also an energy region where the PDOS takes a comparatively small value. A weak coupling makes incident electrons at certain energy hardly transmit across the molecule, and this will give rise to a small transmission coefficient at this energy. Thus, we arrive at the unexpected prediction that a molecule as simple as DTB can be made to switch through its interaction with a suitable STM tip. The *ON* state corresponds to the molecule oriented in such a way that its ring faces the tip, whereas in the *OFF* state the edge of the ring faces the tip. The switching can be induced by passing the tip over the molecule (the transition between Fig. 1a and Fig. 1b).

We predict an unusual and striking experimental signature of switching induced by the motion of the tip: The conductance should be low at the center of the STM image of the molecule where the edge conformation is stable and high when the tip moves away from the center of the image and the face conformation becomes stable. Experimental observation of switching induced by passing the tip over the molecule may be facilitated at low temperatures where thermal excitation of the higher energy conformations is minimal. For example, we find the highly conducting excited face conformation obtained by rotating the molecule from the (weakly conducting) ground state edge conformation in Fig. 1a through $\pi/2$ about the S-S axis corresponds to an energy saddle point (kT_{room}) above the ground state; thus this excited state will be populated significantly at room temperature.

CONCLUSIONS

In conclusion, we demonstrate theoretically by Density Functional Non-Equilibrium Green's Function, method that a much smaller and simpler two-terminal molecular wire can exhibit switching, and we present a realistic theory of its behavior. We consider a 1,4-dithiole-benzene molecular wire with one sulfur end group bonded to an Au(100) substrate and the other to a monatomic Au scanning tunneling microscope (STM) tip as depicted in Fig. 1. We investigated two conformations of the DTB molecule linked to Au(100) electrodes; *edge* and *face* conformations (Fig. 1a, b, respectively).

We found that the *face* conformations of the molecular wire showed highly conducting, *ON* condition, at the first conductance peak near 1.5 V while the *edge* conformation are weakly conducting, *OFF* condition, there (Fig. 2). Thus, whenever the molecule is made to flip from a *face* conformation to an *edge* conformation, the molecule is predicted to switch from a highly conducting to a weakly conducting state.

The switching mechanism that we have introduced here relies on the coupling between the molecule and contacts and thus should be broadly applicable. We have proposed experiments with a conventional or novel self-assembled STM to test that, and hope that the ideas put forward here will facilitate bridging the gap between theory and molecular switching experiments.

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