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Phase Switching of a Single Isomeric Molecule and Associated Characteristic Rectification

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Abstract: Variations in molecular electronic structures related to conformational change are exceedingly attractive because of their key role in the understanding and development of functional processes in molecular electronics and biology. We observed, for the first time, the novel phase switching of a photoactive isomeric molecule, *N*-(2-mercaptoethyl)-4-phenylazobenzamide (Azo molecule) at a single-molecule level, which exhibits a distinctive change in the conductive characteristic under scanning tunneling microscope (STM) measurement. In comparison with the results obtained by the measurement of photoactive isomerization of the isolated Azo molecule, which was performed also for the first time, the observed characteristics are attributed to the results of the trans and cis phase transformation of the Azo molecule, under the condition of an external electric field and current flow. A specific point is that the potential landscape of the system is controllable by the electric field and provides a conformational stability with asymmetric bias dependence resulting in rectification.

Introduction

The understanding and control of molecular functions at a single-molecule level is extremely important in nanoscale science and technology from both fundamental and practical points of view.[1−14] Recent intensive studies are leading to the clarification of the characteristics of novel molecular electronic properties, such as asymmetric charge transport through individual molecules. On the other hand, for example, the Azo molecule (Figure 1a) is a typical photoactive isomer and has been widely studied because of its simple structure and reversible cis−trans isomerization under photoillumination. Irradiation with ultraviolet (UV) (∼350 nm) and blue (vis) (∼440 nm) lights induces isomerization to metastable "cis" and stable "trans" conformations, respectively.[15] The absorption characteristic is easily controllable by the addition of polar groups on the Azo molecule. From these characteristics, the Azo molecule is promising for not only photoswitching and storage materials,[16−23] but also for photoactive biomaterials that, for example, control DNA hybridization.[24]

In consideration of these characteristics, it is of extreme interest to examine the coupling of the photoactive isomeric materials and its electronic characteristics. In particular, the controllability of the photoactive isomeric material by electronic processes is highly attractive for application to nanoscale molecular devices. In this study, the effect of the external excitation exerted by STM on the isolated Azo molecules

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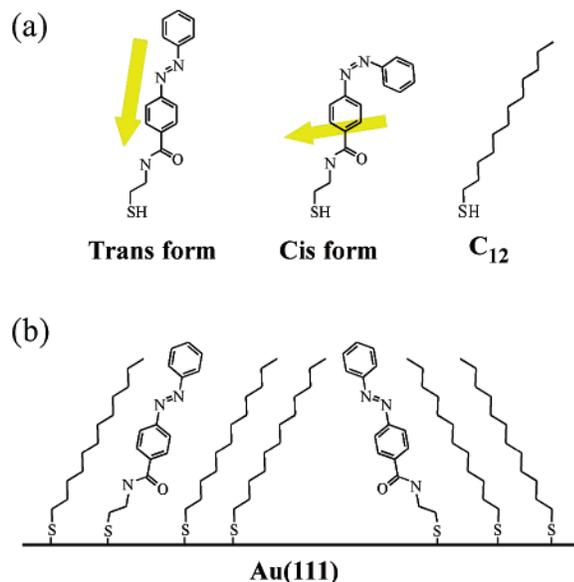(24) Asanuma, H.; Ito, T.; Yoshida, T.; Liang, X.; Komiyama. *Angew. Chem., Int. Ed.* **1999**, *38*, 2393−2395.

Figure 1. Schematic structures of (a) trans and cis isomerization of *N*-(2-mercaptoethyl)-4-phenylazobenzamide (Azo) and *n*-dodecanethiol (C$_{12}$) used in this study and (b) isolated Azo molecules embedded in *n*-dodecanethiol (C$_{12}$) self-assembled monolayer (SAM) films formed on a Au(111) substrate.

embedded in *n*-dodecanethiol (C$_{12}$) self-assembled monolayer (SAM) films formed on Au(111) substrates (Figure 1b) was investigated at a single-molecule level. Azo molecules were modified with a polar amide group to have a dipole, and the conformation-related novel transition in their electronic structure was observed for the first time. Photoisomerization of isolated Azo molecules is also presented for the first time.

Methods

Au(111) substrates were prepared by vapor deposition of 50−75-nm thick gold films onto freshly cleaved mica surfaces. During Au deposition, the temperature of the mica substrates was kept at 400 °C. The deposition rate was 0.08−0.1 nm/s, and the vacuum pressure was 1.0×10^{-6} Torr. Following the deposition, they were annealed at 400 °C for 1 h. With this Au(111) substrate, we made samples by two methods: (1) exchange reaction and (2) coadsorption reaction methods. Detailed procedures of the two methods are as follows. (1) C$_{12}$ SAM films were formed by dipping the Au(111) substrate into toluene solution with 1 mM C$_{12}$ molecules for 18−24 h. After being rinsed to remove the physisorbed molecules, the C$_{12}$/Au system was immersed in toluene solution containing 0.5−5 μM Azo molecules for 0.5−2 h, resulting in the formation of C$_{12}$ SAM including isolated Azo molecules (exchange reaction procedure). (2) Au(111) substrates were immersed into a toluene solution with a 99:1 (v/v) mixture of 1 mM C$_{12}$ and 1 mM Azo molecules for 10−15 h at room temperature (coadsorption reaction process). The samples were rinsed and heated at 80 °C for 3−6 h in a vaporized C$_{12}$ molecule atmosphere to improve the quality of films. After this procedure, they were rinsed with toluene again. Molecular density was controllable.[25] The difference in the structure between the samples prepared by the two methods is that Azo molecules are inserted only at the boundary and pit sites in the case of the exchange reaction method (see the Supporting Information). In the case of the coadsorption reaction method, Azo molecules were inserted into the C$_{12}$ domains in addition to the boundary and pit sites.

All STM images were obtained in N$_2$ atmosphere at room temperature using a Pt/Ir tip. The measurements and preparations were performed under dark conditions to avoid the effect of illumination on Azo molecule isomerization.
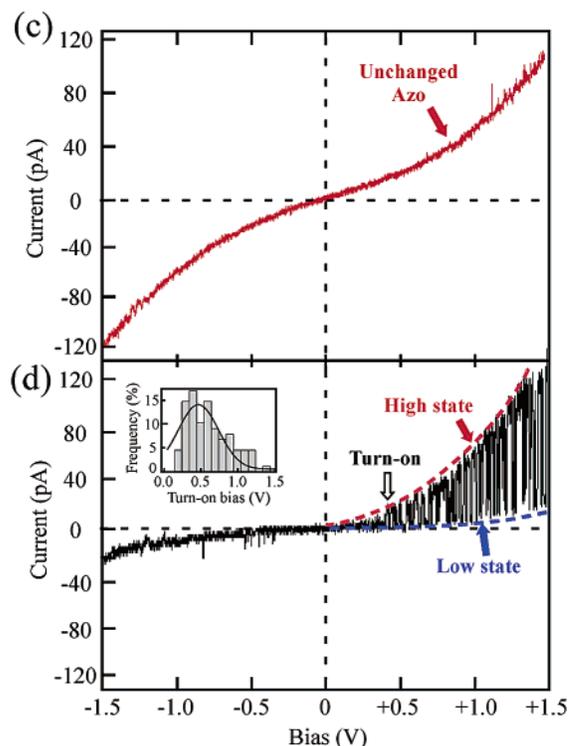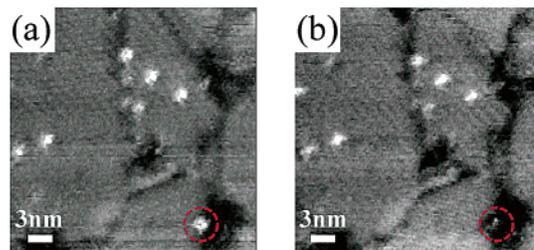
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Figure 2. Typical STM images of Azo-embedded C$_{12}$ SAM film obtained at (a) $V_s = +1.0$ V, $I_t = 10$ pA and (b) $V_s = -1.0$ V, $I_t = 10$ pA. (c) *I*−*V* curve obtained over an Azo molecule. (d) *I*−*V* curve measured over an Azo molecule which changed in brightness in (b). Histogram of the turn-on voltage for the flip-flop motion is shown in the inset.

As shown in Figure 1a, an Azo molecule modified with a polar amide group has a dipole in the direction of the long molecular axis in the trans form and tilted from the axis in the cis form. Therefore, the electric field applied between the substrate and the STM tip is expected to influence the molecular conformation, as predicted in a recent work by Troisi and Ratner.[26] Under the assumption of the molecular dipole strength and the tip−substrate distance of ∼3 D and ∼2 nm, respectively, the molecular dipole electric field interaction energy at room temperature for the trans form becomes about 1.2−3.6 k_BT for the applied voltages of 0.5−1.5 V.

Results

Figure 2a shows a typical STM image of an Azo molecule-embedded C$_{12}$ film at the sample bias voltage of +1.0 V. Bright protrusions are Azo molecules, and they are embedded in an area of densely packed C$_{12}$, at phase boundaries of the C$_{12}$ domains and in etch pits. On the other hand, Figure 2b shows an STM image of the same area with a sample bias of −1.0 V. As shown in Figure 2, parts a and b, the Azo molecules surrounded by densely packed C$_{12}$ molecules exhibit negligible

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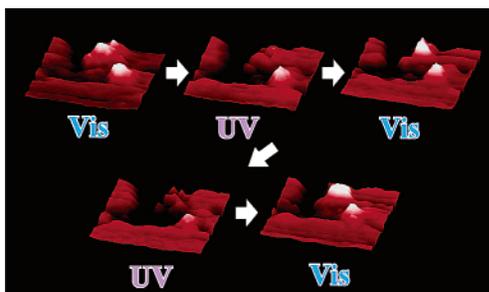
Figure 3. A series of STM images representing the cis–trans change in an isolated Azo molecule controlled by alternating UV (450 nm) and vis (325 nm) photoillumination (15 × 15 nm, V_s = +1.0 V, I_t = 10 pA).

change of brightness; however, those adsorbed in etch pits or at phase boundaries became darker at negative sample bias voltage (an example is marked by a red circle). This result suggests a conformational change of the loosely packed molecules instead of a homogeneous charge transfer without any conformational changes.[25,27]

Figure 2c shows I–V curves obtained over an unchanged Azo molecule. It shows a symmetric characteristic for positive and negative voltages. On the other hand, a typical I–V curve measured over an Azo molecule which changed in brightness is shown in Figure 2d. In contrast to the symmetric characteristic of I–V curves in Figure 2c, a drastic change was observed. Namely, tunneling current was almost flat between −1.0 V and +0.5 V, and rapid switching in the tunneling current between two I–V curves (high- and low-current states indicated by red and blue envelope curves) was observed in the high-positive voltage region.

The high-current state I–V curve shows a characteristic similar to that obtained for the unchanged Azo molecule shown in Figure 2c. The low-current state I–V curve has a shape similar to that obtained for negative voltage. The flip-flop motion rarely appears at negative bias voltage, but the observed cases are also between the two states. The inverse decay lengths obtained by I–Z measurement for the Azo molecules with the high- and low-current structures in a sample were 8.5 ± 1.6 nm^{-1} and 5.2 ± 1.3 nm^{-1}, respectively. The difference is attributed to the change in the characteristic electronic structure of the molecule. These results indicate that Azo molecules loosely surrounded by C_{12} molecules change their conformation between two distinct (high and low current) states during I–V measurement.

The high- and low-current states might be attributed to the trans and cis conformations, respectively. To examine the structures, photoisomerization of the isolated Azo molecules was investigated by illuminating the samples with ultraviolet (UV) (325 nm) and visual (vis) (440 nm) light using a He−Cd laser during STM measurements. Figure 3 shows an example of a series of STM images representing the structural change in isolated Azo molecules induced by alternating UV and vis photoillumination. Optically stimulated conformational change of Azo-SAM has been confirmed macroscopically in pioneer works.[16−22] This is the first direct observation of photoactive isomerization of the isolated azobenzene molecules controlled by photoillumination.
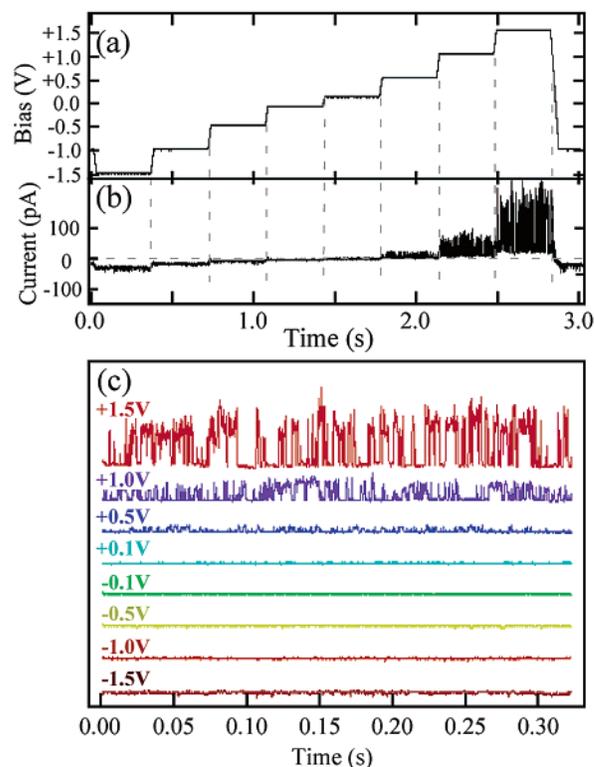
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Figure 4. Flip-flop motion analyzed by the newly developed stepwise I–V measurement technique. The applied voltage was changed stepwise to be −1.5, −1.0, −0.5, −0.1, +0.1, +0.5, +1.0, and +1.5 V, as shown in (a). (b) Change in the tunneling current due to the stepwise change in the applied bias voltage, observed for an Azo molecule, the detail of which is shown in (c).

The brightness of the STM image of Azo molecules changes with photoillumination. Some molecules changed less due to tight packing, as was pointed out in the previous macroscopic work,[21] and the optimal voltage for the measurement depends on the packing condition. However, loosely packed Azo molecules showed cis and trans structures, as expected, under UV and vis photoillumination, respectively. The observed change in the STM image of the isolated Azo molecules between trans and cis structures is similar to the change in the image observed at positive and negative bias voltages (Figure 2), namely, in the high- and low-current states.

In consideration of the experimental results, the structures observed during the STM measurement, i.e., the high- and low-current states, are attributed to the trans and cis conformational structures of an Azo molecule. This is the first observation of the conformational change of a photoactive isomer through an electronic process at the single-molecule level.

To examine the effect of the external excitation in more detail, we analyzed the bias voltage dependence of the flip-flop process using a newly developed stepwise I–V measurement technique. Namely, the applied voltage was changed stepwise as −1.5, −1.0, −0.5, −0.1, +0.1, +0.5, +1.0, and +1.5 V, as shown in Figure 4a, and the change in the corresponding current was measured. Figure 4b shows the change in the tunneling current, due to the stepwise change in the applied bias voltage, observed for an Azo molecule, the detail of which is shown in Figure 4c. Switching between two definite structures at each bias voltage is clearly shown. By the exponential fitting of the histogram of the residence time of the flip-flop motion, the lifetimes of the Azo molecule in the two states were acquired
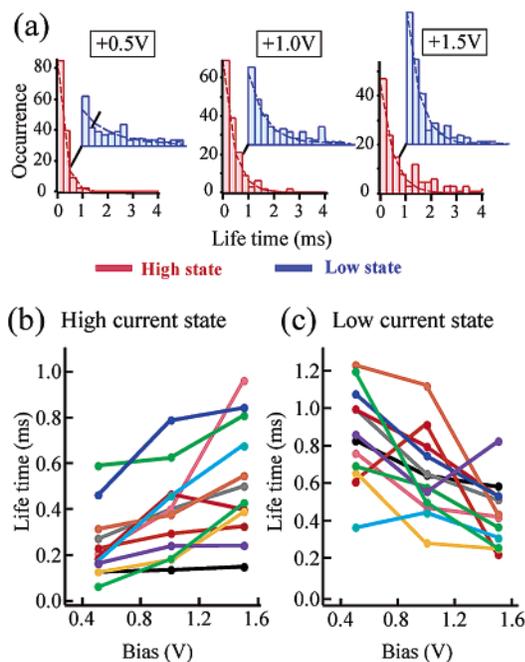
Figure 5. (a) Example of the bias-dependence of lifetime obtained for a sample. (b, c) Lifetimes of the Azo molecule in the two states acquired for each voltage, obtained by the exponential fitting of the residence time of the flip-flop motion in each of the two states.

for each set voltage. An example of the bias dependence of lifetime is shown in Figure 5a. The obtained lifetimes for the high- and low-current states (τ_H and τ_L) of several samples are summarized in Figure 5, parts b and c. The obtained values are scattered due to the effect of the packing condition of the surrounding C_{12} molecules. Since the voltage range is limited because of the damage to the molecules at higher voltage, it is difficult at this stage to obtain the precise voltage dependence of the lifetime. However, the lifetimes of the two states clearly change in opposite directions. There is the tendency that the lifetime of the high-current state becomes longer with an increase in the applied positive voltage. The results strongly indicate that the conformation of the Azo molecule is influenced by the external electric field and tends to be transformed to that of the high-current state as the positive sample voltage increases.

The change in the flip-flop rate between the two states, $\sim 1/(\tau_H + \tau_L)$, remains in the order of 10^3/s against the change of the tunneling current from the order of 10^7 (at +0.5 V) to 10^9 (at +1.5 V) electrons per second. Therefore, $10^4 - 10^6$ electrons are related to the excitation of each event, if the electronic process is included. The change in the number of electrons in the order of 10^2 does not seem to strongly influence the frequency of the flip-flop motion, and the residence ratio between the two states seems to change with the applied voltage, which is in good agreement with the process considered above.

It is difficult to evaluate the absolute potential barrier height. However, in consideration of the Boltzmann factor for a typical change in the ratio of the lifetime, $\tau_L = 4\tau_H$ at 0.5 V and $\tau_L = \tau_H$ at 1.5 V, the change in the difference of the potential energy is about $1-2\ k_BT$ (k_B is the Boltzmann constant, and T is the absolute temperature). These values are consistent with those estimated for the molecular dipole electric field interaction energy ($1.2-3.6\ k_BT$ for the applied voltages of $0.5-1.5$ V). The direction of the dipole moment is also consistent with the observed results under the assignment of the two states.

Since the low-current state is stable in the low bias voltage region, there exists a barrier height for the flip-flop motion which is sufficiently high compared to the thermal energy at room temperature. To explain the fact, inelastic tunneling may be a possible mechanism.[28-30] The stretching vibration modes of benzene—N and N=N in the Azo molecule are 1140 cm^{-1} (0.14 eV) and 1410 cm^{-1} (0.17 eV), respectively,[31] which are comparable to the rising edge of the histogram of the turn-on voltage (0.15−0.2 V). The value of $\sim$0.2 eV ($\sim$7 k_BT) is sufficient to explain the stability of the low-current state for the measurement of the low negative bias voltage region. The considerable point is that the low-current state, which was attributed to the cis phase, is apparently the ground state under the measurement condition not only for the negative bias voltage but also for the positive bias voltage. In previous work, the trans form was thought to be the ground state even for the Azo molecular films.[16] The tightly packed Azo molecules in the C_{12} film domains seem to retain the trans phase, as shown in Figure 2. According to the recent theoretical study, for example, the asymmetry of the system prepared to realize rectification is reduced by the charge transport itself, which is considered to be a reason for the rarity of the molecular rectification process.[32] The essential point is that the measurement condition influences the fundamental process itself, namely, changes in the functions themselves on undergoing the essential operating procedures. Although it is difficult to characterize the details at this stage, the understanding of this effect is important not only for the fundamental understanding of molecular characteristics but also for the development of functional materials.

In conclusion, we observed, for the first time, the novel phase switching of an photoactive isomeric molecule, *N*-(2-mercaptoethyl)-4-phenylazobenzamide (Azo molecule), which exhibits a distinctive change in the conductive characteristic under STM measurement. In comparison with the results obtained by the measurement of photoactive isomerization of the isolated Azo molecule, which was performed also for the first time, the observed characteristics are attributed to the results of the trans and cis phase switching of the Azo molecule, under the condition of an external electric field and current flow. A specific point is that the potential landscape of the system is controllable by the electric field and provides a conformational stability with asymmetric bias dependence, resulting in rectification.

Supporting Information Available: Synthesis of the Azo molecule and sample preparation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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