

STM Investigation of the Photoisomerization of an Azobis-(benzo-15-crown-5) Molecule and Its Self-assembly on Au(111)

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Scanning tunneling microscopy (STM) has been employed to investigate the photoisomerization of azobis-(benzo-15-crown-5) on Au(111). A self-assembled monolayer of azobis-(benzo-15-crown-5) with a (3×7) symmetry was observed on Au(111). After ex-situ UV-light irradiation, a new adlayer structure with a different molecular arrangement could be seen on Au(111), although the domain size of the ordered packing is small. On the basis of a high-resolution STM image and photochemical reaction result, schematic models have been proposed for the original and ex-situ irradiated adlayers. After in-situ UV-light irradiation, the ordered arrays disappeared and many bright clusters emerged at domain boundaries. The results presented here provide direct evidence at the molecular level for a photochemical reaction.

Introduction

Photochemical reaction, as one of the important chemical reactions, plays a key role in many fields, such as optical data storage,¹ photoelectronics,² sensors,³ and photocatalytic systems.⁴ Nature has also made use of photoresponsive systems to control biological systems. Trans/cis photoisomerization of rhodopsin in the retina is employed to convert light energy into chemical energy and send an electrical signal to the nervous system.⁵ To fabricate a molecular device based on photoactive compounds, it is important to know what changes may take place in the photoreaction. Many techniques such as UV–vis absorption spectroscopy, X-ray diffraction, and surface-enhanced Raman spectroscopy are employed to study photoresponsive systems,^{6,7} providing average structural information. However, scanning tunnel microscopy (STM) is also a powerful method to analyze a photochemical reaction with structural evidence at the molecular level.⁸

Azobenzene, a typical photochromic compound, experiences photochemical isomerization, which is often accompanied by dramatic changes in molecular geometry. Owing to their attractive photosensitive properties, the azobenzene derivatives have been utilized as photoswitching units to control the structure and the function of supramolecular systems.^{9–11} With STM, the photoisomerization of some alkyl-derivated azobenzenes on highly oriented pyrolytic graphite (HOPG) has been studied by imaging the starting material and the reaction product, directly providing the structural evidence for the photoisomerization.^{12–14} Although the photoisomerization of an azobenzene-derivated thiol on an Au substrate was investigated,^{15,16} only information about film thickness was obtained. Until now, no direct information at the molecular level for the photoisomerization of azobenzene on a metal substrate was reported, which is important for the development of photosensitive electric nanodevices.

Crown ethers and their derivatives have attracted much attention due to their application in ionic conduction.¹⁷ On the

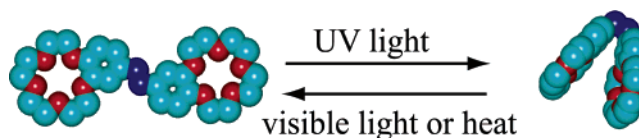


Figure 1. Structural change of switchable trans and cis forms of azobis-(benzo-15-crown-5).

other hand, crowned azobenzene experiences more drastic changes in molecular geometry than alkyl-derivated azobenzene after isomerization. In the present research, a home-synthesized crowned azobenzene, azobis-(benzo-15-crown-5), was employed to prepare adlayers on an Au(111) surface. The chemical structure and the structural change in the photoisomerization of the molecule are optimized by Hyperchem 6.0 and shown in Figure 1. The photoisomerization of the azobis-(benzo-15-crown-5) molecules on Au(111) was studied by cyclic voltammetry (CV) and electrochemical STM.

Experimental Section

Azobis-(benzo-15-crown-5) was synthesized according to the previous literature.¹⁸ The preparation for the Au(111) sample and electrolyte solution is in the same procedure as reported in the literature.¹⁹ A well-defined Au(111) electrode was prepared by the crystallization of a molten ball formed at the end of an Au wire (99.999%) in a hydrogen–oxygen flame. For CV measurements, one of the (111) facets was mechanically polished with successively finer grades of Al_2O_3 and annealed at 900 °C for 24 h to remove damages on the surface. Before each measurement, the Au(111) electrode was further annealed in a hydrogen–oxygen flame and quenched in pure water saturated with hydrogen. The self-assembled monolayer (SAM) of azobis-(benzo-15-crown-5) was obtained by immersing Au(111) into an ethanol solution containing 0.1 mM azobis-(benzo-15-crown-5) for 1 min. Then, the Au(111) electrode was rinsed with Milli-Q water to remove the remnant molecules and was transferred into the STM electrochemical cell. The aqueous HClO_4 was prepared by diluting HClO_4 (Cica-Merck, Japan, Ultrapure grade) with Milli-Q water.

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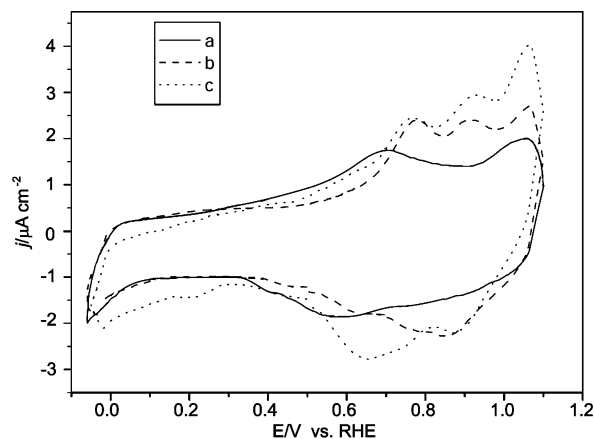


Figure 2. Steady-state cyclic voltammograms of bare Au(111) (line a), azobis-(benzo-15-crown-5)-modified Au(111) (line b), and azobis-(benzo-15-crown-5)-modified Au(111) after 10 min irradiation (line c) measured in 0.1 M HClO₄ in the potential region between -0.05 and 1.1 V at a scan rate of 50 mV/s.

CV measurements were carried out with the hanging meniscus method in a three-compartment electrochemical cell under N₂ atmosphere.²⁰ Electrochemical STM measurements were carried out with a Nanoscope E microscope (Digital Instrument Inc.). The STM tips used were made from electrochemically etched tungsten wire (0.25 mm in diameter) in 0.6 M KOH. To minimize faradic currents, the sidewalls of the tips were sealed with clear nail polish. All STM images were acquired in the constant-current mode, and raw data were shown here without any other processing such as low or high pass. The electrode potentials were reported with respect to the reversible hydrogen electrode (RHE) in 0.1 M HClO₄.

All molecular models were optimized with the Hyperchem software package (version 6.0).

Results and Discussion

Cyclic Voltammograms. The electrochemical behavior of the azobis-(benzo-15-crown-5)-modified Au(111) electrode was investigated by CV. CVs were recorded in 0.1 M HClO₄ using the hanging meniscus method. Figure 2 shows the CVs of bare, unirradiated, and irradiated azobis-(benzo-15-crown-5)-modified Au(111) electrodes in 0.1 M HClO₄. The CVs were recorded at a scan rate of 50 mV s⁻¹. It can be seen from the CV curve of the bare Au(111) (line a) that the double-layer potential region is extended from -0.05 to 1.1 V identical to the results reported previously,²⁰ demonstrating that a well-defined Au(111) surface is exposed to HClO₄ solution and free from contamination. Line b is the CV curve obtained from the azobis-(benzo-15-crown-5)-modified Au(111) electrode. The adsorption of azobis-(benzo-15-crown-5) has resulted in the disappearance of the reconstruction peaks. Two anodic peaks at 0.77 and 0.91 V can be seen in the CV. A broad cathodic peak is observed at 0.86 V. The CV shown by line c was recorded on an irradiated azobis-(benzo-15-crown-5)-modified Au electrode. The electrode was prepared by directly irradiating an azobis-(benzo-15-crown-5) adlayer on Au with a high-pressure Hg lamp for ca. 10 min. After the irradiation, the *trans* film has been converted to a mixture film of *trans* and *cis* species. Although the anodic peaks in the CV are almost in the same overall shape as that in line b, two separated cathodic peaks are observed at 0.65 and 0.86 V. The electrochemical measurements demonstrate the existence of the azobis-(benzo-15-crown-5) adlayer on Au(111).

The electrochemical behavior of azobenzene derivatives was reported in previous literature.^{21–23} On a *cis*-azobenzene-

derivative modified-SnO₂ glass electrode, a pair of redox peaks was observed in its CV in a KClO₄ solution buffered with Britton–Robinson buffer. The peaks were attributed to the oxidation and reduction of the molecules. However, on the *trans*-azobenzene-derivative modified-SnO₂ glass electrode, no clear reduction peak was seen within the electroinactive potential window of the SnO₂ glass electrode. On the other hand, two pairs of peaks were observed in the CVs of the thiol-functionalized *trans*- and *cis*-azobenzene-derivative modified poly-gold electrodes in 0.1 M NaClO₄ (pH 5.0, buffered with Britton–Robinson buffer). The two separated peaks correspond to two steps of reversible one-electron, one-proton reduction/oxidation in the *cis*-isomer-modified electrode. In the present study, for the crown ether part of the molecules, no electrochemical reaction in this potential range can be detected.²⁴ Therefore, the electrochemical process may be similar to that on a thiol-functionalized *trans*- and *cis*-azobenzene-derivative modified poly-gold electrode.²³ However, if the experiment is carried out in a strong acidic solution, then a side reaction would take place.²² And, after the irradiation, the *trans*-azobis-(benzo-15-crown-5) could not be transferred to the *cis* isomer completely, which makes the electrochemical process of the azobis-(benzo-15-crown-5) molecules complicated. A detailed study is now in progress.

STM of Azobis-(benzo-15-crown-5) Adlayer. Figure 3a is a typical large-scale STM image of azobis-(benzo-15-crown-5) on Au(111) obtained at 0.55 V with a bias voltage of -107 mV and a set-point current of 1.1 nA. A highly ordered azobis-(benzo-15-crown-5) array extends over the flat terrace of Au(111). Two domains can be seen crossing each other with an angle of 120° . The structural details are revealed by the higher resolution STM image (Figure 3b). Each molecule appears as a dumbbell shape with two dark depressions. The distance between these two depressions is about 1.05 nm, consistent with the distance between the centers of the crown ether ring in an azobis-(benzo-15-crown-5) molecule. The results from STM observation and the chemical structure of azobis-(benzo-15-crown-5) suggest that the molecules are flat-lying on the Au(111). The conformation with a dark depression can be assigned to the crown ring and that bright part connecting the two dark depressions is the azobenzene part. This feature can be more clearly seen in the height-shaded surface plot shown in Figure 3c. A *trans* isomer of azobis-(benzo-15-crown-5) molecules can be defined from the image. The molecular rows indicated by **A** and **B** in Figure 3b, cross each other at an angle of 120° within an experimental error of $\pm 2^\circ$. Both the **A** and **B** directions are along the $\langle 110 \rangle$ direction by comparison of Au(111)–(1×1). The repeating distances along the **A** and **B** directions are 0.86 ± 0.1 and 2.01 ± 0.1 nm, respectively. On the basis of the above analysis, a tentative model can be constructed for the ordered array of azobis-(benzo-15-crown-5) (Figure 3d). Compared with the atom image of Au(111), the unit cell with a (3×7) symmetry is outlined.

After recording the STM image at 0.55 V, the electrode potential was scanned in an increment of 10 mV in both the negative and positive directions. Almost the same images as shown in Figure 3 are observed in the potential range from 0 to 0.75 V. The results indicate that azobis-(benzo-15-crown-5) can form a stable adlayer on the Au(111) surface consistent with the results in electrochemical measurement.

STM of Azobis-(benzo-15-crown-5) Adlayer after Ex-Situ Irradiation. As a typical photosensitive compound, azobis-(benzo-15-crown-5) will isomerize from the *trans* to *cis* form after being irradiated by UV light. After the images of the

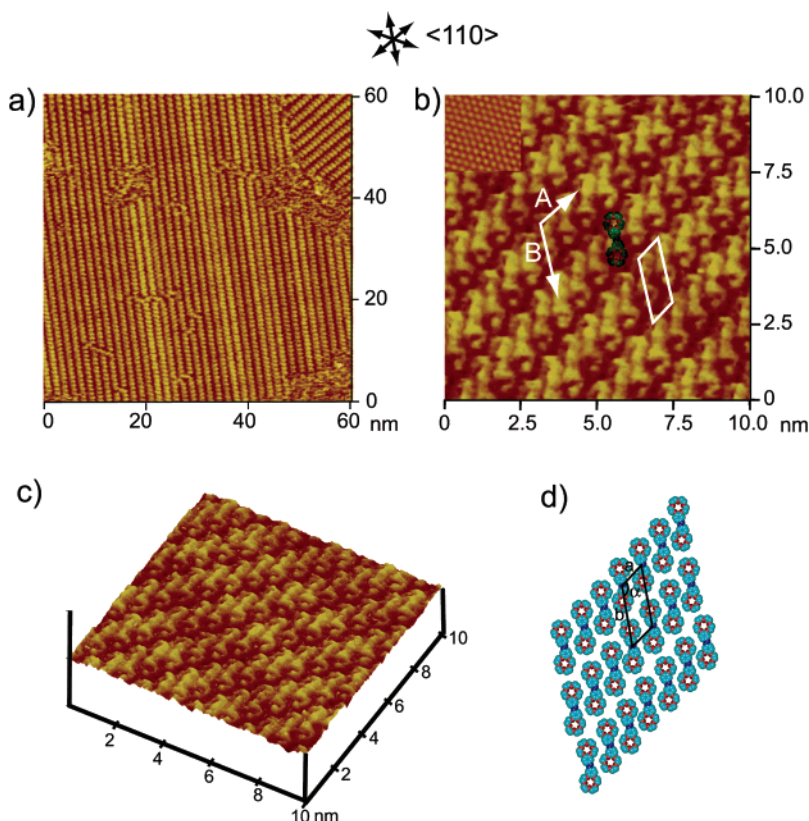


Figure 3. (a) Typical large-scale STM image, (b) high-resolution STM image, and (c) height-shaded surface plot of an azobis-(benzo-15-crown-5) adlayer on Au(111). An inserted STM image in (b) shows the Au(111) substrate. (d) Proposed structural model for the azobis-(benzo-15-crown-5) adlayer.

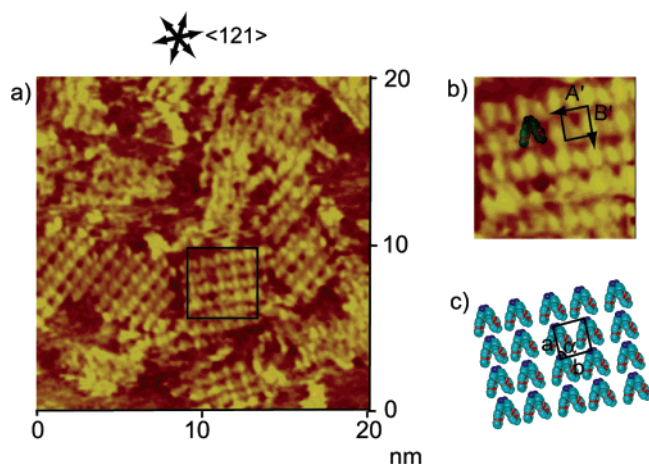


Figure 4. (a) Typical STM image of azobis-(benzo-15-crown-5) adlayer prepared in an irradiated solution showing the cis-isomer adlayer, recorded with a bias voltage of -107 mV and a set-point current of 1.1 nA. (b) Enlarged image of the indicated area in (a). (c) Proposed structural model for (b).

azobis-(benzo-15-crown-5) adlayer were obtained, the photoisomerization was studied with STM. The ethanol solution containing azobis-(benzo-15-crown-5) was irradiated by a high-pressure Hg lamp for 10 min. The UV-vis absorption spectrum was employed to confirm the photochemical reaction and the existence of the cis isomer (the results are not shown here). A bare Au(111) electrode was immersed into the irradiated solution for 1 min to form a SAM on the surface and then transferred to an STM electrochemical cell. Figure 4a shows the typical STM images of the SAM formed in the irradiated azobis-(benzo-15-crown-5) solution. The image was recorded at 0.55 V. It is clearly seen that the SAM consists of several domains. As shown

in the image of Figure 4a, STM reveals a new packing pattern in the adlayer after UV-light irradiation. The adlayer symmetry is changed. The molecular rows of **A'** and **B'** are along the $\langle 121 \rangle$ and $\langle 110 \rangle$ directions, respectively, and cross each other at an angle of $90^\circ \pm 2^\circ$. Moreover, the molecular appearance shows a quite different conformation from that in Figure 3. Figure 4b is an enlarged image of Figure 4a in the outlined part. Each molecule now appears as a "V" shape with two elongated dots. When the STM image is compared with the chemical structure, the elongated dot corresponds to the crown ether of an azobis-(benzo-15-crown-5) molecule. The molecular row in the **A'** direction is along the $\langle 121 \rangle$ direction by comparison of Au(111)-(1 \times 1), while **B'** is along the $\langle 110 \rangle$. The repeated distances along **A'** and **B'** are measured to be 0.99 ± 0.1 and 0.86 ± 0.1 nm, respectively. On the basis of the STM results, a tentative model for the cis-isomer adlayer is proposed in Figure 4c in which a $(2\sqrt{3} \times 3)$ unit cell is outlined. Another obvious feature of the monolayer after irradiation is the numerous defects. The size of ordered domains is small, resulting from the symmetry of the cis isomer and its complicated arrangement in the monolayer. The direct evidence for the photoisomerization of azobis-(benzo-15-crown-5) at a molecular level was obtained.

STM of Azobis-(benzo-15-crown-5) Adlayer after In-Situ Irradiation. To better understand the photoisomerization, in-situ irradiation was also studied. After the trans-isomer monolayer was imaged, the electrolyte was removed from the electrochemical cell. The azobis-(benzo-15-crown-5)-modified Au electrode was directly irradiated with a high-pressure Hg lamp to induce a photochemical reaction. After irradiation, the cell was refilled with the electrolyte. Figure 5 is a typical STM image after the electrode was irradiated for 30 s. As shown in the image, many bright clusters emerge on the SAM. Some ordered arrays disappeared, especially for those in the domain

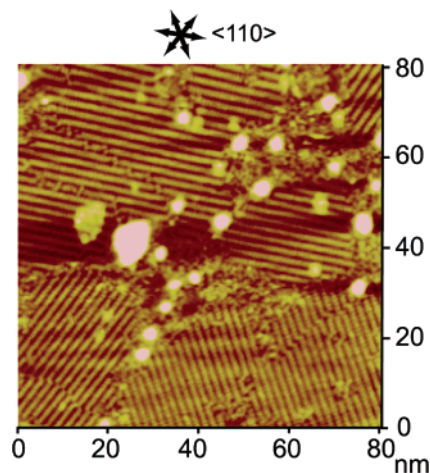


Figure 5. Typical STM image of the azobis-(benzo-15-crown-5) adlayer on Au(111) after being in-situ irradiated for 30 s.

boundary, which indicates that photoisomerization starts at the domain boundary. Due to the strong spatial restriction in the SAM of the trans isomer, only a few percent of the trans species isomerized to the cis form. At the loosely packed boundary, the isomerization occurs easily. With the increase of irradiation time, the domain of the ordered array became smaller and more bright clusters appeared. From the photoreaction mechanism, the trans-form molecules could be isomerized to the cis form after UV irradiation. Although the single *cis*-azobis-(benzo-15-crown-5) molecule was not discerned in the STM image, the aggregation of the cis isomer was observed. In previous studies, ordered adlayers of alkyl-derived azobenzenes on HOPG were found after in-situ irradiation,^{12–14} different from the present results. The following factors are believed to contribute to the difference. First, according to the chemical structure, the *cis* isomer appears as two wings of a butterfly as shown in Figures 1 and 4. For the spatial conformation, the *cis* isomer is not planar. On the other hand, the *cis* isomers of those alkyl-derived azobenzenes are near planar. The special conformation may be responsible for the disordered structure. Second, the long alkyl chains in the alkyl-derived azobenzenes will substantially enhance the adsorption stability on the solid surface. Moreover, the photoisomerization of those previous systems occurred in the solid–liquid interface with the existence of molecules in solution.^{12–14} Irradiating the system will lead to the increase of the *cis*-isomer concentration in solution and the desorption of trans-isomer molecules from the solid surface, thus enhancing the adsorption of *cis*-form molecules. The dynamic exchange of the molecules on the surface and in solution will promote the recovering of the defects in the self-assembled adlayers. However, in our experiment, the electrolyte was removed during irradiation. The SAM is a lack of molecular exchange between the Au(111) surface and electrolyte solution.

Conclusions

In summary, STM and electrochemical methods have been used to investigate the adsorption of azobis-(benzo-15-crown-5) on Au(111) in 0.1 M HClO₄ solution. Azobis-(benzo-15-

crown-5) molecules are adsorbed on the Au(111) surface and form well-ordered adlayers. Immersing Au(111) into a UV-light-irradiated azobis-(benzo-15-crown-5) solution results in a new SAM on Au(111) with a different molecular arrangement. A ($2\sqrt{3} \times 3$) structure is defined. On the basis of high-resolution STM images and photoreaction results, schematic models have been proposed for the unirradiated and ex-situ irradiated SAMs. The direct evidence about photoisomerization of azobenzene on a metal substrate at the molecular level is obtained. After in-situ irradiation, some ordered arrays disappeared and many bright clusters emerged. The results show that the photochemical reaction started at the domain boundary of the SAM, which will be important for the fabrication of the nanostructure and the development of photoresponsive electric nanodevices.

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