



Molecular adlayer and photo-induced structural transformation of a diarylethene derivative on Au(1 1 1) investigated with scanning tunneling microscopy

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ABSTRACT

The self-assembly and photo-induced structural transformation of a diarylethene derivative 1,2-bis(3,5-dimethyl dithioene [3,2-*b*:2',3'-*d*]thiophene-2-yl) perfluorocyclopentene (BDDTP) have been investigated by cyclic voltammetry and electrochemical scanning tunneling microscopy (EC-STM) on a Au(1 1 1) substrate. BDDTP was found to form two ordered adlayer structures on Au(1 1 1) surface. STM observation revealed that the original ordered structures transformed into disordered adlayers after ex situ and in situ ultraviolet (UV) irradiation. Such a dramatic difference in the self-assembly behavior of BDDTP before and after UV irradiation results from the conformational transformation induced by photo-irradiation and the associated molecule–substrate interaction change. The result provides useful information to understand the self-assembly behavior and photochromic reaction of diarylethenes compounds on solid supports.

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1. Introduction

Construction of two-dimensional (2D) molecular nanostructures on solid surfaces is recognized as an important step for the development of functional nanomaterials and nanodevices [1–5]. Various kinds of functional organic molecules with unique structures and properties have been synthesized and their 2D assemblies have been investigated [6–12]. Among them, photochromic compounds such as azobenzenes and diarylethenes are of great interests due to their potential use in the miniaturized devices including optical data storage units, photoswitches, photoresponsive sensors, etc. [13–16]. To fabricate a device based on photoactive molecules, it is significant to know molecular isomerization/reaction and structural transformation occurred at surfaces under photo-irradiation [16–18]. Along with many techniques such as X-ray diffraction and surface-enhanced Raman spectroscopy available to examine photoreaction at surfaces [19,20], scanning tunneling microscopy (STM) has been proved to be a powerful tool to study the photoresponsive systems owing to its ability to provide direct real space evidence at molecular level [21–31]. By using STM, the photochemical process and structural transformation of photoactive molecules can be scrutinized before and after photo-irradiation with submolecular resolution.

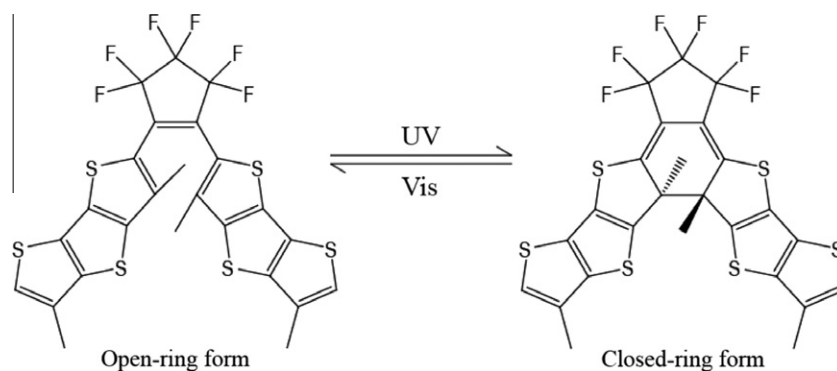
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Diarylethene derivatives represent a large family of photochromic compounds, which undergo reversible photochemical isomerization between open-ring form and closed-ring form under ultraviolet (UV) light irradiation and visible light irradiation [14,32–34]. Unlike the photo-induced cis–trans isomerization of azobenzene, both isomers of diarylethene are thermodynamically stable. The photoisomerization process of diarylethene involves the chemical bond formation and breaking. The featured cyclization photoisomerization leads to significant changes in many chemical and physical properties, such as luminescence [35], optical rotation [36], magnetic properties [37], electrochemical behavior [38], and electronic characteristic modulation [39]. More recently, the potential of diarylethene compounds to be used as molecular optoelectronic devices has been demonstrated [40,41]. For example, Katsonis et al. studied the reversible conductance switching of diarylethenes bonded on a gold surface through a Au–S linker [40]. Compared to the well-documented azobenzene system, there are few reports on the self-assembly and photoisomerization of diarylethene derivatives on a solid substrate [30,31], which is important to build up molecular optoelectronic devices based on diarylethene.

Dithieno [3,2-*b*:2',3'-*d*]thiophene (DTT) is a thiophene oligomer with interesting electric and optical properties and is widely used as a building block in organic semiconductor materials [42,43]. By linking two DTT units with a cyclopentane bridge, a new diarylethene derivative 1,2-bis(3,5-dimethyl dithioene [3,2-*b*:2',3'-*d*]thiophene-2-yl) perfluorocyclopentene (BDDTP) was synthesized recently (Scheme 1) [34]. It was found that BDDTP exhibits inter-



Scheme 1. The chemical structure and photochromic reaction of BDDTP.

esting photochromic behavior and conductivity modulation in solution and in Langmuir–Blodgett (LB) films. In the present research, BDDTP was employed as a model compound to understand the orientation and assembly structure of diarylethene on a Au(1 1 1) surface in aqueous solution before and after photo-irradiation. The photoisomerization of BDDTP on Au(1 1 1) was studied by cyclic voltammetry and electrochemical STM (EC-STM). STM revealed that the open-ring isomer of BDDTP could form two ordered structures on Au(1 1 1) surface. However, the original ordered structures could no longer be found after ex situ and in situ UV irradiation. Instead, disordered adlayers could be observed with STM. The dramatic difference of the self-assembly behavior between the open-ring and closed-ring isomers results from the molecular conformational change and the associated molecule–substrate interaction change. The result provides useful information to understand the self-assembly behavior and photochromic reaction of diarylethenes compounds on solid supports.

2. Experimental section

BDDTP was synthesized by using the method described in the literature [34], and was dissolved in acetonitrile (analytic grade) with a concentration of 1×10^{-5} M. Electrolyte solution was prepared by diluting ultrapure HClO₄ (Kanto Chemical Co., Inc., 99.999%) with Milli-Q water.

Cyclic voltammogram (CV) measurements were carried out with an EG&G PAR (Princeton Applied Research) 2273 Electrochemical System. The Au(1 1 1) electrode was mechanically polished with successively finer grades of Al₂O₃ and annealed at ca. 900 °C to remove mechanical damages. Before each measurement, the Au(1 1 1) electrode was further annealed in a H₂ flame and quenched in Milli-Q water saturated with hydrogen. The experiments were performed in a three-compartment electrochemical cell in N₂ atmosphere [44,45]. The solution was deaerated with high purity N₂ before measurements. All electrode potentials were referred to the reversible hydrogen electrode (RHE) in 0.1 M HClO₄.

EC-STM measurements were performed with Nanoscope E (Veeco Inc., Santa Barbara, CA). The Au(1 1 1) electrode was prepared by the Clavilier method [46]. The adlayers of BDDTP were obtained by immersing Au(1 1 1) into BDDTP solution for 1 min. The Au(1 1 1) electrode was then rinsed with Milli-Q water to remove the remnant molecules and was mounted quickly onto a STM electrochemical cell. The tunneling tips were prepared from electrochemically etched tungsten wire (0.25 mm in diameter) in 0.6 M KOH, and were coated with transparent nail polish to minimize Faradic current. STM images were recorded in the constant-current mode. Molecular models were built in Materials Studio 3.0. The ultraviolet–visible (UV–Vis) absorption spectra were recorded on an ultraviolet spectrophotometer (Unico Co., UV 4802).

3. Results and discussion

3.1. Cyclic voltammograms

The electrochemical behavior of BDDTP on a Au(1 1 1) electrode was measured by using cyclic voltammetry in 0.1 M HClO₄ at a scan rate of 50 mV/s. Fig. 1 shows the CVs of the bare, BDDTP, and irradiated BDDTP modified Au(1 1 1) electrodes. The CV of the bare Au(1 1 1) electrode (line a) in the double-layer potential region is in agreement with the result reported previously [47,48]. A pair of redox peak around 0.60 V is related to the lift of the $(22 \times \sqrt{3})$ reconstruction of Au(1 1 1) surface. It demonstrates that a well-defined and clean Au(1 1 1) surface is exposed to the electrolyte solution. Line b is the CV obtained from BDDTP modified Au(1 1 1) electrode. The adsorption of BDDTP results in the disappearance of the reconstruction peak and the decrease of the electric charge in the double-layer. Since no peaks could be seen in line b, it could be concluded that BDDTP is inert to be oxidized or reduced in the investigated potential region. After measuring the CV of unirradiated BDDTP modified Au(1 1 1) electrodes, the electrode is taken out from the electrochemical cell, directly irradiated by UV light with a wavelength of 365 nm for 10 min, and then put into the electrochemical cell for further measurement. The CV is shown as line c in Fig. 1, which exhibits a similar shape to the line b. It indicates that the photo-irradiation with UV light does not result in the change of the electrochemical

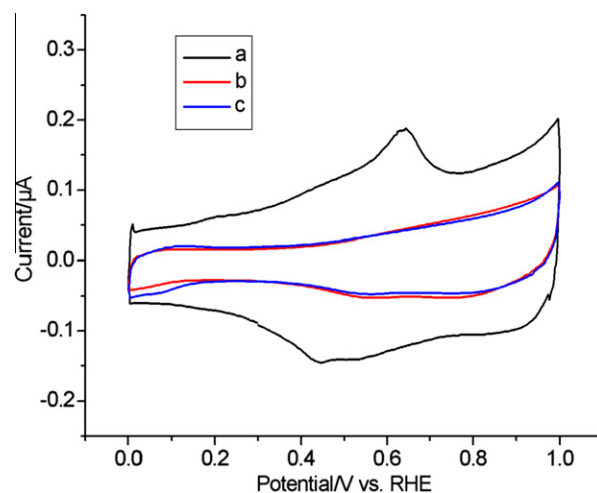


Fig. 1. Typical CVs measured in 0.1 M HClO₄ in the potential region between 0 and 1.0 V at a scan rate of 50 mV/s: (a) bare Au(1 1 1); (b) BDDTP modified Au(1 1 1) before UV irradiation; (c) BDDTP modified Au(1 1 1) after 10 min UV irradiation.

behavior of BDDTP. The result is in agreement with that obtained in the acetonitrile solution [34].

3.2. STM of BDDTP adlayers before UV irradiation

3.2.1. Structure I

EC-STM study reveals that BDDTP is able to self-assemble into two ordered structures on reconstructed Au(111) surface in aqueous solution. Fig. 2 shows typical large-scale STM images of structure I formed by BDDTP, which was recorded at 0.55 V. Such a structure was found independent of the potential from 0.35 V to 0.7 V in the experiment. Bright spots can be distinguished in the image in Fig. 2A, which arrange into high ordered molecular rows and extend over the flat terrace of the substrate surface. The detailed information of structure I is revealed by a higher resolution STM image in Fig. 2B. Careful observation illustrates that the bright spots display a “V” shape in Fig. 2B. The average size of the spots is measured to be about 1.4 nm. Both shape and size of the spots are in agreement with the BDDTP molecules in open-ring form. The results from STM image and the chemical structure of BDDTP suggest that the “V” shaped molecules take flat-lying configuration on the substrate. A molecular pair is

formed by two reversely adsorbed molecules, which form a building unit for the adlayer. The molecular pairs arrange into 2D molecular array to form the ordered structure I. A schematically illustration for such a molecular arrangement is overlaid in Fig. 2B with four BDDTP molecule pairs.

It has been reported that one of the DTT groups in BDDTP resonate on two positions in the solid state, with occupancies of 50.4% and 49.6% respectively [34]. The structural resonance in crystal suggests that the open-ring isomer is faintly flexible, and may tune its conformation to adsorb on Au(111) surface. Nevertheless, considering the similarity between the two resonance structures and possible substrate effect on the BDDTP conformation, it is difficult to distinguish the exact conformation of the open-ring isomer in the STM image. To simplify, one resonance structure is employed to build up the structural model for structure I, as proposed in Fig. 2C. A unit cell is also determined and shown in Fig. 2B and C. The constants measured from the STM image are $a = 2.20 \pm 0.15$ nm, $b = 3.10 \pm 0.15$ nm, and $\alpha = 77 \pm 3^\circ$. The coverage of structure I is calculated to be $0.30 \text{ molecules nm}^{-2}$. Every two “V” shaped molecules arrange reversely to decrease steric repulsion, and extend on Au(111) to form the stable structure I.

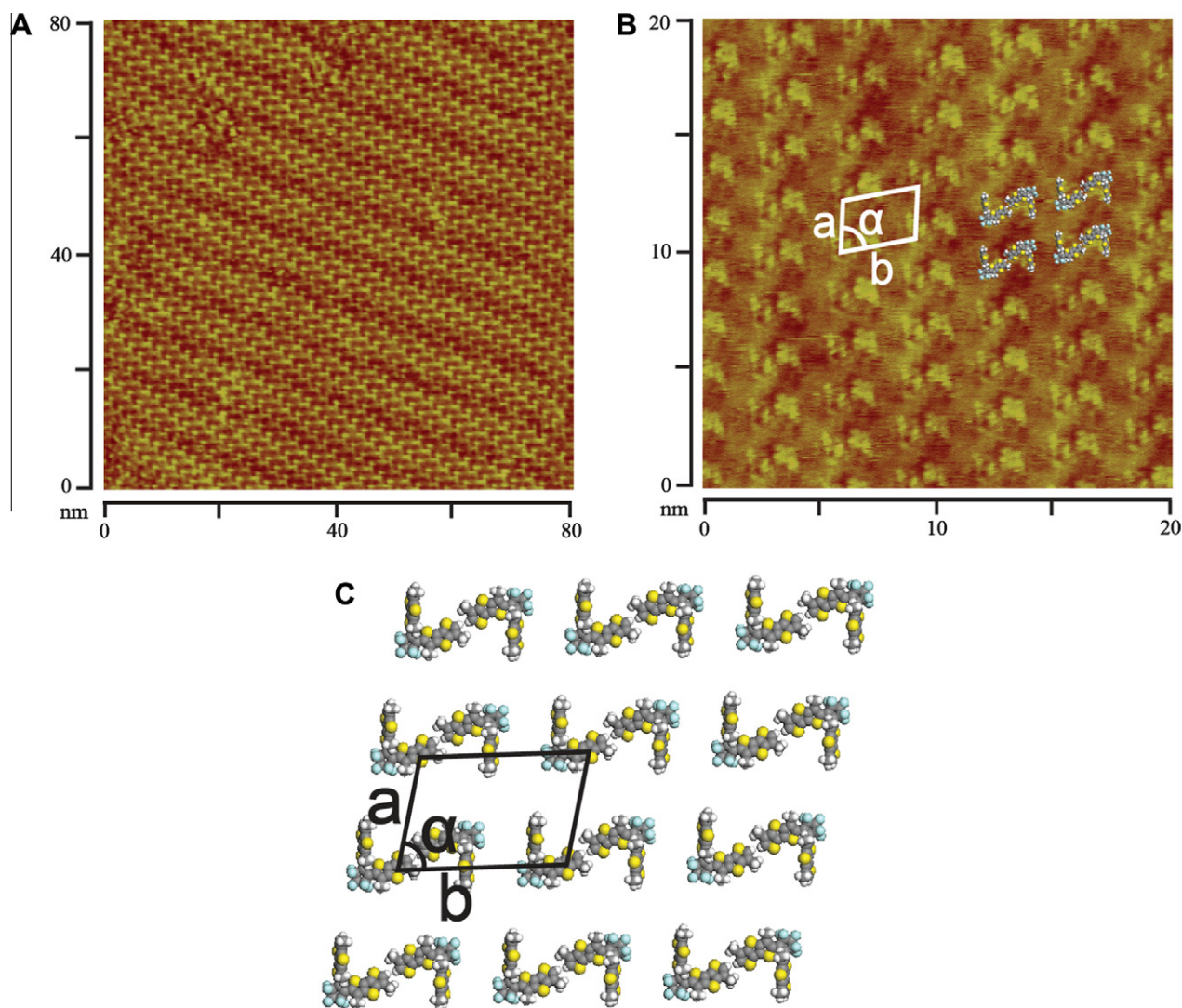


Fig. 2. (A) Large-scale and (B) high resolution STM images of BDDTP structure I on Au(111) before UV irradiation. The imaging conditions in A and B are $E_{\text{bias}} = -293$ mV, $I_{\text{set}} = 1.25$ nA. (C) Proposed structural model for BDDTP structure I on Au(111).

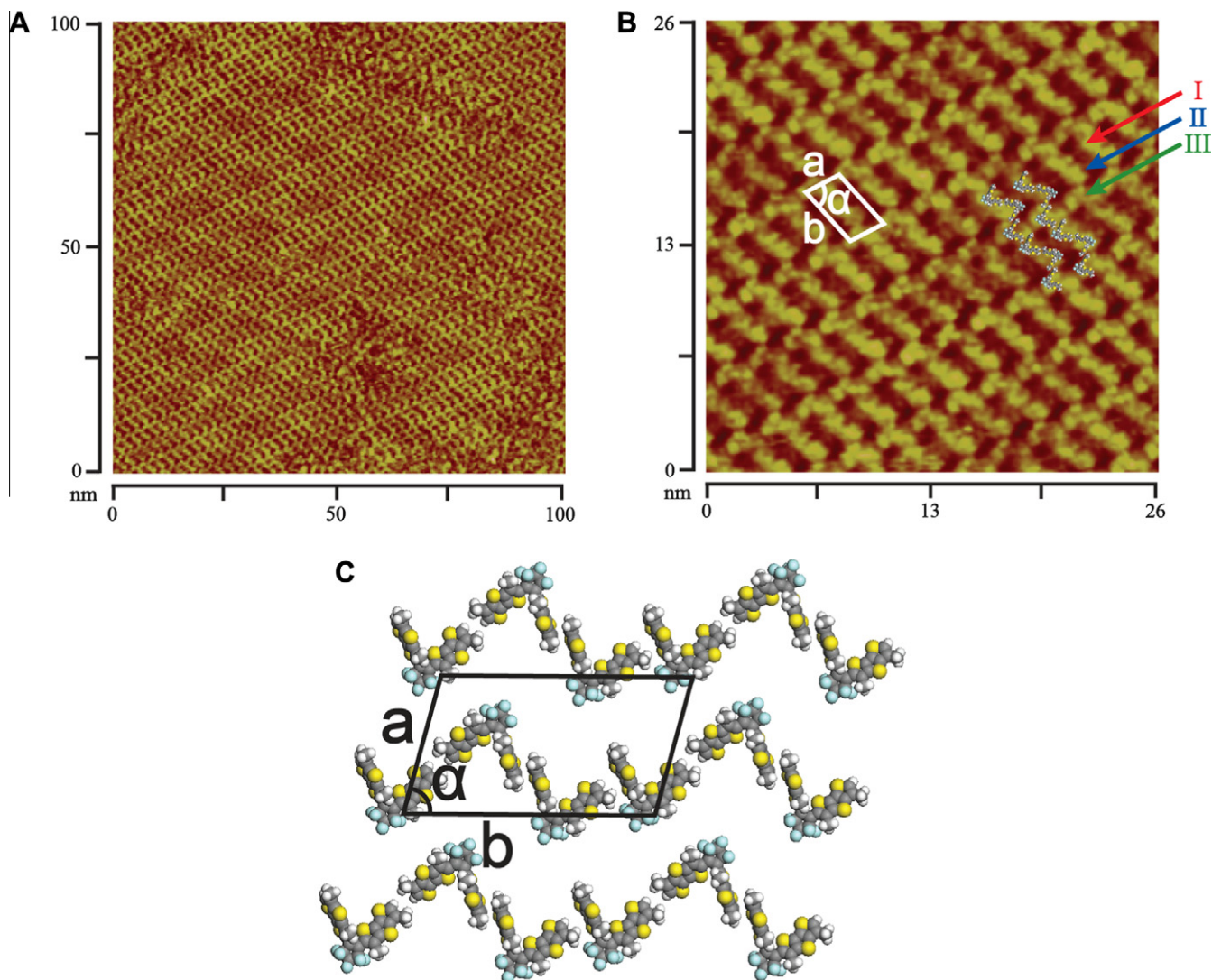


Fig. 3. (A) Large-scale and (B) high resolution STM images of BDDTP structure II on Au(111) before UV irradiation. The imaging conditions in A: $E_{\text{bias}} = -414$ mV, $I_{\text{set}} = 1.63$ nA; and in B: $E_{\text{bias}} = -372$ mV, $I_{\text{set}} = 1.63$ nA. (C) Proposed structural model for BDDTP structure II on Au(111).

3.2.2. Structure II

A second self-assembled structure of BDDTP can also be observed with STM. Fig. 3A is a typical large-scale STM image of the structure II, which display a ladder like feature. Similar to structure I, structure II is stable at a potential from 0.35 V to 0.7 V. The high resolution STM image of structure II shown in Fig. 3B reveals more detailed structural information. V-shaped bright spots with an average size of about 1.4 nm can be distinguished in the image. The bright spots are ascribed to the open-ring isomer of BDDTP. Similar to the case in structure I, the adsorbed conformation of BDDTP in structure II is flat-lying on the substrate. A building unit could also be determined, which is composed of three molecules. Two molecules adsorb reversely to form a BDDTP pair. The molecular pairs are packed side by side to form molecular rows I and II as shown in Fig. 3B, acting as parallel steps of the molecular ladders. The third molecule in each building block adsorbs beside the molecular pair with a little offset, and arranges to form molecular row III as a side pillar of the molecular ladder, which is also outlined in Fig. 3B. A schematically illustration for such a molecular arrangement is overlaid in Fig. 3B by four BDDTP building units.

On the basis of the STM analysis, a structural model for the BDDTP structure II is proposed as shown in Fig. 3C. Similar to the case in structure I, only one resonance structure of the open-ring

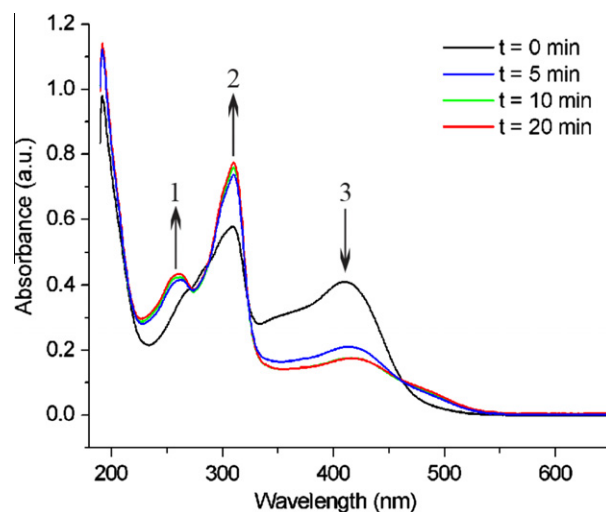


Fig. 4. UV-Vis absorption spectra of BDDTP in acetonitrile with a concentration of 1×10^{-5} M under UV irradiation. The samples were irradiated by UV light with a wave length of 365 nm for 0 min, 5 min, 10 min, and 20 min and then examined, respectively.

isomer is employed to build up the structural model. Every two BDDTP molecules arrange reversely. The third molecule is interposed between neighboring molecular rows. A unit cell is determined and shown in Fig. 3B and C. The constants measured from the STM image are $a = 2.20 \pm 0.15$ nm, $b = 3.95 \pm 0.15$ nm, and $\alpha = 78 \pm 3^\circ$. The molecular coverage of structure II is calculated to be 0.35 molecules nm^{-2} . Compared with structure I, the molecular coverage of structure II is higher.

3.3. STM of BDDTP adlayer after ex situ UV irradiation

The photochromic reaction in the BDDTP crystal is inhibited due to the unsuitable distances between the reactive carbon atoms. However, when in solution or in LB films, BDDTP undergoes cyclizative photochromic reaction by forming a covalent bond to close the molecule under UV light irradiation [34]. The resulted closed-ring isomer of BDDTP is more rigid than the open-ring isomer.

The photoisomerization of BDDTP in acetonitrile was followed by UV–Vis absorption spectra as shown in Fig. 4. Before photo-irradiation, two absorption peaks could be observed at 308 nm and 410 nm. After irradiation with a UV light of 365 nm for 5 min, a new absorption peak appeared at 260 nm and is earmarked by arrow 1. The peak at 308 nm (arrow 2) increases and become sharper, whereas the intensity of the peak at 410 (arrow 3) decreases significantly. Since the spectra recorded after irradiation 10 min and 20 min are overlaid, it can be concluded that the photoisomerization of BDDTP in solution is accomplished in 10 min.

We used STM to study the photoisomerization of BDDTP on Au(1 1 1) surface. The adlayer is prepared by the sample irradiated for 10 min. Fig. 5A is a typical large-scale STM image of the adlayer formed by using the irradiated solution. Bright spots spread disorderly all over the surface, demonstrating that the photo-irradiated BDDTP has a dramatically different assembly behavior on Au(1 1 1) substrate. The underlying Au(1 1 1) reconstruction lines are still visible from the STM image. Such a disordered adlayer is stable and could hardly be disturbed by potential change throughout

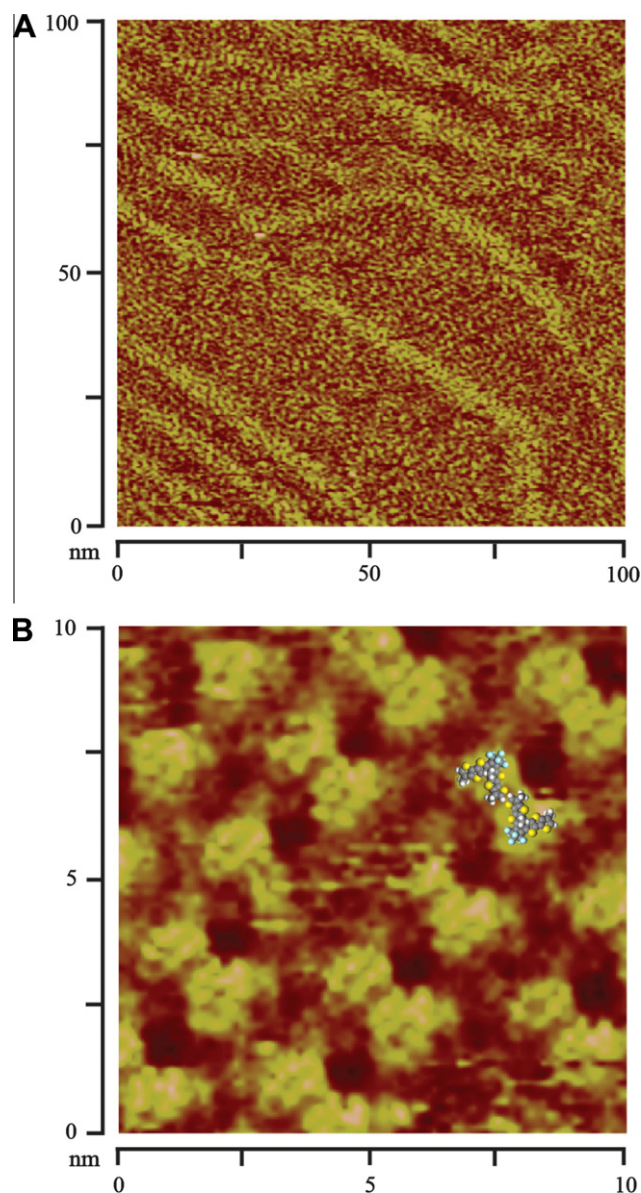


Fig. 5. (A) Large-scale and (B) high resolution STM images of BDDTP adlayers on Au(1 1 1) after ex situ UV irradiation. The imaging conditions in A: $E_{\text{bias}} = -190$ mV, $I_{\text{set}} = 1.01$ nA; and in B: $E_{\text{bias}} = -215$ mV, $I_{\text{set}} = 1.06$ nA.

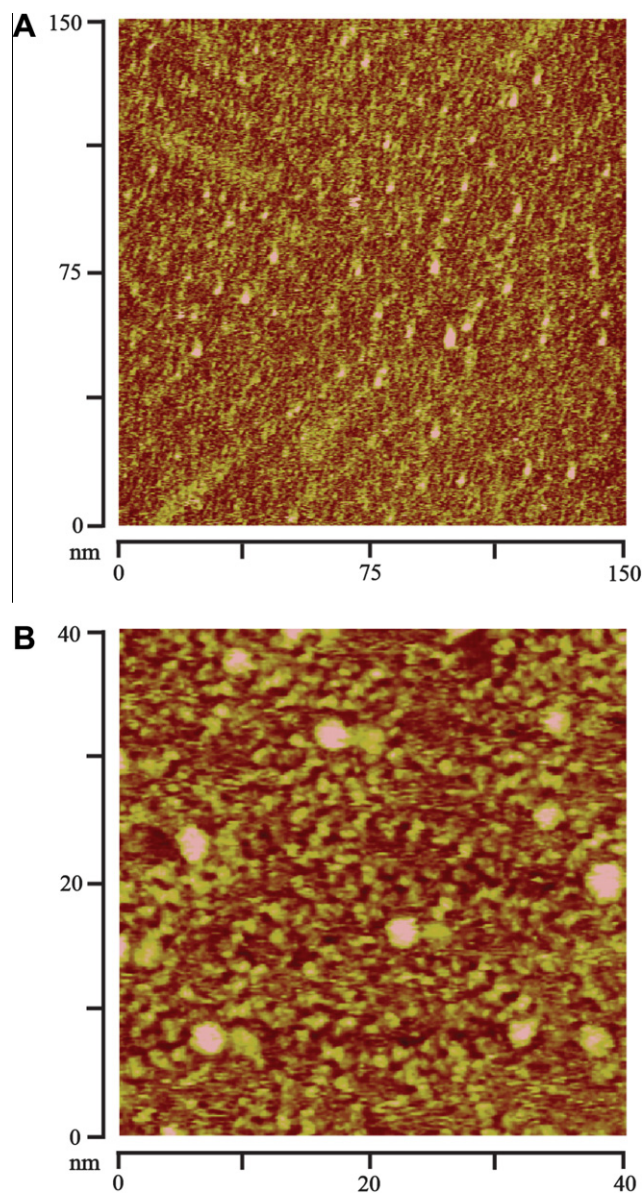


Fig. 6. (A) Large-scale and (B) high resolution STM images of BDDTP adlayers on Au(1 1 1) after in situ UV irradiation. The imaging conditions in A: $E_{\text{bias}} = -266$ mV, $I_{\text{set}} = 1.15$ nA; and in B: $E_{\text{bias}} = -337$ mV, $I_{\text{set}} = 1.31$ nA.

the experiments. Individual molecules could be distinguished by STM, especially in small regions with locally ordered adlayer. Fig. 5B shows a high resolution STM image of the locally ordered structure. Round spots with an average size of 1.5 nm could be clearly seen in the image, which display different shapes and sizes as compared to the V-shaped open-ring BDDTP isomers, and are ascribed to the closed-ring isomer of BDDTP. Every two molecules adsorb closely to form a molecular pair. However, the distances between neighboring molecular pairs are varied, which is different from the case in structure I formed by the open-ring isomer. The coverage of the closed-ring isomer of BDDTP is estimated to be 0.32 ± 0.04 molecules nm^{-2} by counting the number of molecules in several high resolution STM images obtained at different area. The coverage is close to that of the ordered adlayers of open-ring BDDTP molecules. The disordered adlayers formed by the closed-ring isomers of BDDTP can be attributed to the conformational change of molecules after irradiation. The photoreaction and its effects on the self-assembly of BDDTP were successfully disclosed by STM at a molecular level.

3.4. STM of BDDTP adlayer after in situ UV irradiation

In order to better understand the photoisomerization of BDDTP on solid surface, the self-assembled adlayers were also studied with STM upon in situ irradiation. Ordered structures of the open-ring form of BDDTP were first prepared on Au(1 1 1) surface. After the structures were examined by STM, the electrolyte was removed from the electrochemical cell. The BDDTP modified Au(1 1 1) electrode was directly irradiated by UV light with a wave length of 365 nm for 10 min. Then the cell was refilled with the electrolyte for STM imaging.

Fig. 6A is a typical STM image obtained after in situ UV irradiation. The original ordered structures I and II could no longer be found. Instead, a disordered adlayer is formed on Au(1 1 1), which is similar to the adlayer obtained after ex situ irradiation. The high resolution STM image in Fig. 6B clearly shows that bright spots spread all over the image. The typical size of the spots is measured to be 1.5 nm, in agreement with the size of the closed-ring isomer. Similar to the case in the adlayer structure with ex situ irradiation,

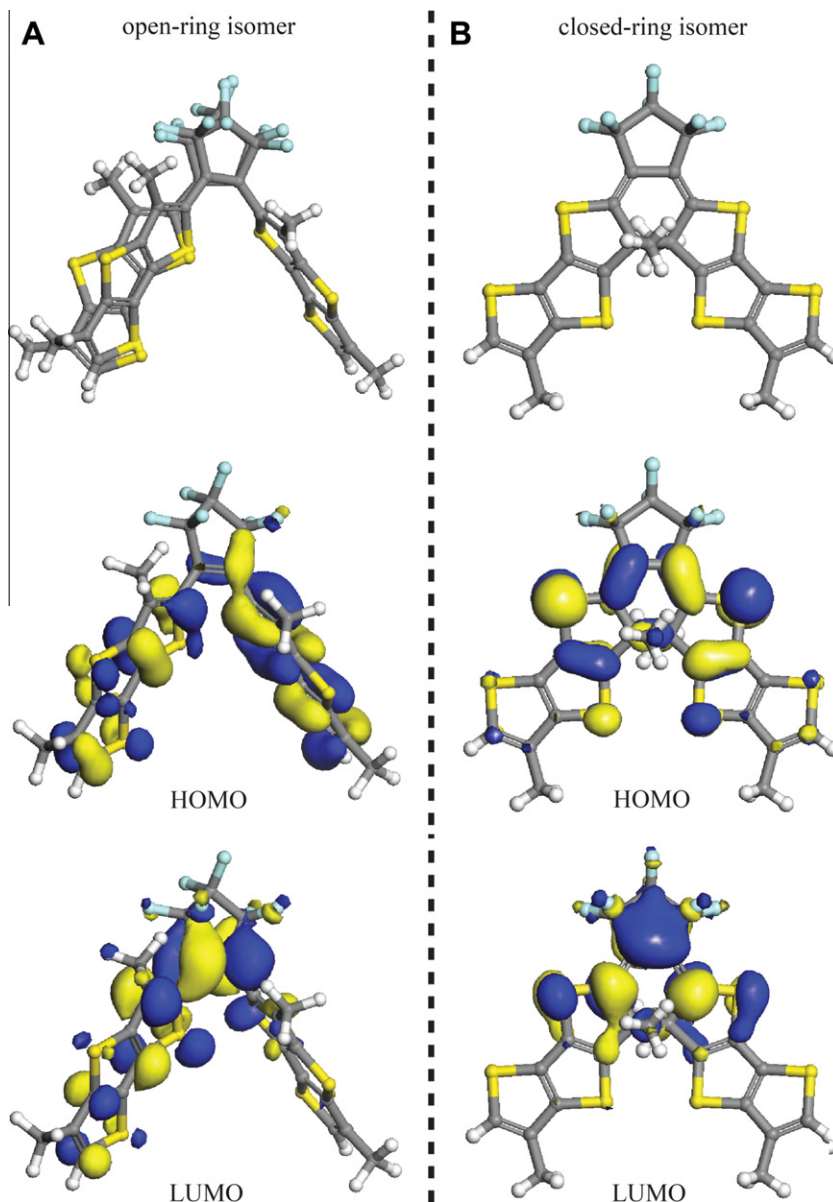


Fig. 7. The calculated molecular conformations and the HOMO–LUMO orbitals of the open-ring form (A) and closed-ring form (B) of BDDTP. For the open-ring isomer, the structural resonance is presented, while the HOMO–LUMO orbitals were calculated by the structure used in structural models.

the spots in STM images are attributed to the closed-ring form of BDDTP molecules. It demonstrates that the BDDTP molecules can be transformed into the closed-ring form when irradiated by UV light on the surface as well as in solution, resulting in the structural transformation from ordered structures to disordered adlayers accordingly. The result is in agreement with the photoisomerization of BDDTP in LB films [34]. Moreover, compared with the adlayers obtained under ex situ irradiation, it is notable that many bright clusters could be seen in Fig. 6A and B. Similar phenomenon was reported for other photosensitive systems [27]. Such clusters may arise from the aggregation of the closed-ring isomers during the in situ UV irradiation.

3.5. Discussion

A photo-induced structural transformation of BDDTP on Au(111) from ordered to disordered structures has been investigated by EC-STM. The open-ring and the closed-ring form of BDDTP display dramatically different self-assembly behavior, which results from different structural conformations and the associated molecule–substrate interaction change. Fig. 7 shows the molecular conformations as well as the HOMO–LUMO orbitals of the open-ring isomer and the closed-ring isomer of BDDTP. It could be seen in Fig. 7A that the open-ring isomer displays “V” shaped resonance structures. Both of the resonance structures are not planar, but with dihedral angles of 80.38° and 73.45° between the two DTT planes [34]. The structural resonance of the open-ring isomer in Fig. 7A indicates that the open-ring isomer is flexible, and could tune its conformation to adsorb stably on Au(111) substrate. The molecule–substrate interaction is moderate to stabilize the two ordered structures on surface. The calculated HOMO and LUMO orbitals are in good agreement with the “V” shaped spots in the STM images. On the contrary, owing to the formation of a covalent bond between the active carbon atoms under UV light irradiation, the closed-ring isomer possesses a more planar and rigid structure as shown in Fig. 7B. The calculated HOMO and LUMO orbitals are also in agreement with the round shape feature as shown in the STM images. It is well known that different molecule/substrate interactions can modulate the self-assembled structures [49–52]. Excessive molecule/substrate interaction can drive the molecules to form random structures on surface [50–52]. It is speculated that the molecule/substrate interaction for closed-ring isomer is significantly higher than the open-ring isomer due to the rigid planar molecular structure and the related favorable π -substrate interactions. As a result, disordered structures of the closed-ring isomer are formed on surface. The dramatic difference in the self-assembly behavior of the two isomers of BDDTP demonstrates that the conformational transformation induced by photo-irradiation plays a key role in the molecular self-assembly of BDDTP.

4. Conclusions

In summary, the photo-induced transformation of the self-assembled structures of the photochromic molecule BDDTP on Au(111) surface has been studied by EC-STM and other techniques. Before UV light irradiation, the open-ring isomer of BDDTP was found to form two ordered structures on Au(111) surface. However, after ex situ and in situ UV irradiation, the ordered structures were transformed into disordered adlayers with small regions of locally ordered structures. The molecular configurations of the adsorbed open-ring and closed-ring form of BDDTP were determined by STM. It indicates that the conformational transformation induced by photo-irradiation as well as molecule–substrate interaction leads to the dramatically different self-assembly

behavior of the two isomers of BDDTP. The result presents direct evidence on the photoisomerization of BDDTP at molecular level, which helps to understand the self-assembly and photochromic reaction of diarylethene derivatives on surfaces.

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