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Submolecular Observation of Photosensitive Macrocycles and Their Isomerization Effects on Host−Guest Network

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Abstract: The macrocyclic compounds consisting of photosensitive units as parts of the frame have been extensively studied to mimic photoregulated functions in nature. In this paper, controlled assembly of well-ordered arrays of photosensitive macrocyclic rectangles is demonstrated by using a host−guest molecular template. 4NN-Macrocycle molecules are observed to photoisomerize from trans−trans−trans−trans (t,t,t,t) to a range of isomers including trans−trans−trans−cis (t,t,t,c) and trans−cis−trans−cis (t,c,t,c) isomers after irradiation of UV light. The photoisomers are also observed to affect the guest−host network characteristic appreciably. In the STM observations we can distinguish three (t,t,t,t) conformational isomers, three (t,t,t,c) conformational isomers, and one (t,c,t,c) isomer, which self-assemble into different adlayers with TCDB on a HOPG surface. This study provides a facile approach to study the photoisomerization processes of the azobenzene groups and the conformational photoisomers.

Introduction

The construction of 2D hydrogen-bonded porous networks, which can accommodate guest molecules, has been the subject of intense investigations due to potential applications in the fabrication of molecular scale devices. Organic molecular porous networks, the analogue of inorganic nanomeshes,[1−5] are ordered structures held together by noncovalent interactions such as hydrogen bonds, van der Waals force, and metal−organic coordination and can act as hosts for immobilization of guest molecules on the surface. By changing the building blocks the size of pores can be tuned to accommodate molecules of different size such as coronene, phthalocyanine, fullerenes, and so on.[6−10]

The macrocycles with alkyl side groups are a kind of promising building blocks in the porous networks.[11−18] They can form adlayers when adsorbed onto the surfaces, and their side groups are important to tune the self-assembling processes. A macrocycle with azobenzene groups is one of the typical photosensitive compounds whose reversible cis−trans isomerization causes drastic changes in structures and chemical properties. Previous studies have demonstrated that introduction of azobenzene groups could lead to light irradiation effects on organized molecular systems such as host molecules,[19] optical storage of information,[20,21] and so on.

Azobenzenes have been extensively studied for their unique photoisomerization properties. The transition from the thermodynamically stable trans to cis conformation can be induced by irradiation with UV light and reversed upon heating or irradiation with visible light. Photoisomerization of molecules containing a single azobenzene has been studied by scanning tunneling microscopy (STM).[22−34] Switching of azobenzene derivatives at the liquid−solid interface has been demonstrated.[26] Most

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studies were preformed in ultra high vacuum (UHV) conditions.[27−34] In this paper we synthesized a kind of macrocycle which has four azobenzene groups.[35] The macrocyclic compounds which are consisted of photosensitive units as parts of the frame have been extensively studied to mimic photoregurated functions in nature.[36−38] The light-induced conformational change of photosensitive units is efficiently conveyed to other parts of the molecules in such cyclic systems. Consequently, chemical and physical functions of these compounds could be changed in response to light irradiation. It has been observed that, when stabilized in the host molecular nanotemplate in ambient conditions, the macrocycles can form several different conformational isomers stabilized in different assembly structures. And we observed the transition of the assembly from the trans−trans−trans−trans (t,t,t,t) to the isomerized one, i.e., trans−cis−trans−cis (t,c,t,c), or trans-trans-trans−cis (t,t,t,c) isomers after irradiation with UV light. In addition, due to existence of the four $-CH_2-CH_2-$ groups of the 4NN-Macrocycle we can observe three (t,t,t,t) isomers, three (t,t,t,c) isomers, and one (t,c,t,c) isomer.

Experimental Section

1,2,17,18,33,34,48,49-Octaaza-[2 $_8$](4,4′)cyclophane-1,17,33,48-tetraene (4NN-Macrocycle)[35] and 1,3,5-tris(10-carboxydecyloxy)-benzene (TCDB)[6] were synthesized according to the reported procedures. A droplet of a heptanoic acid (>98%) (Acros Organics) solution containing TCDB ($<10^{-4}$ M), 4NN-Macrocycle ($<10^{-4}$ M), and a TCDB/4NN-Macrocycle mixture (4:1), (2:1), (1:1) was deposited respectively onto freshly cleaved, atomically flat HOPG surfaces. STM measurements were acquired under ambient conditions with a Nanoscope III A (Veeco Metrology). All STM images presented were recorded in constant current mode. The solution was kept in dark for one day before the photoisomerization experiment. After deposition on graphite surface, the sample was subjected to sufficient irradiation of 366 nm light with a high-pressure mercury lamp and glass filter (UVREF, Beijing Trusttech Co. Ltd.) for 15 min. The temperature of the sample was kept between 22 and 25 °C during the irradiation process. The lamp was at a distance of 25 cm from the sample. The STM experiments were performed in dark immediately after irradiation by UV light.

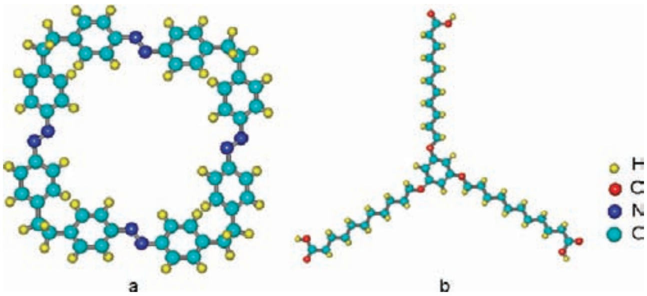

Figure 1. Chemical structures of (a) 4NN-Macrocycle and (b) TCDB.

Results and Discussion

1,3,5-tris(10-Carboxydecyloxy)-benzene (TCDB, Figure 1a), as a molecular template, can form two-dimensional networks on HOPG with well-defined nanoscale pores. The size of the unoccupied pore is about 2.4 nm × 1.3 nm.[6] The coadsorption of organic molecules such as the coronene and phthalocyanine into these pores has been previously reported.[7,8] 4NN-Macrocycle (Figure 1b) is a kind of azobenzenophane consisting of four azobenzene groups. We can not observe the 4NN-Macrocycle on surface solely, as shown in Figure S1.

A large-scale STM image of the molecular adlayer is shown in Figure 2a with the TCDB/4NN-Macrocycle mixing ratio of 4:1. Several domains, indicated by dashed lines, can be seen in the image. The appearance of the adlayer is different from that of the pure TCDB adlayer. An important feature is the appearance of monomer-entrapped architecture which shows one rectangle-shaped 4NN-Macrocycle molecule in a nearly hexagonal cavity, as shown in Figures 2b and S2. Some domains of TCDB are unfilled. Because of the confinement effect of TCDB, 4NN-Macrocycle molecules are observed as rectangular features. A high-resolution STM image is shown in Figures 2b and S2, and the details of the entrapped molecules are clearly visible. The bright rectangles are measured to be 2.4 nm × 1.6 nm, which is consistent with the expected size of the macrocyclic rectangles. Therefore, each bright hollow rectangle corresponds to a 4NN-Macrocycle molecule, indicated as a hollow red rectangle in Figure 2b. Six small bright features marked by green circles can also be observed around each rectangle, which correspond to the benzene cores of TCDB. On the basis of observed symmetry and intermolecular distance, a unit cell is superimposed on the image in Figure 2b with $a = 6.1 \pm 0.2$ nm, $b = 4.8 \pm 0.2$ nm, and $\alpha = 84.5° \pm 2.1°$. From the proposed model for the 4NN-Macrocycle molecule entrapped in TCDB networks, it could be noted that each TCDB molecule forms two pairs of hydrogen bonds with the adjacent TCDB molecule. Another carboxylic group extends the benzene core of adjacent TCDB molecule, which is different from the results previously reported.[6−9] All TCDB molecules are Y-shaped in this assembly configuration. The black hollow and the red hollow rectangles (as shown in Figure 2c) point out the hydrogen bonds and the six benzene cores of TCDB around one 4NN-Macrocycle molecule, respectively. A structural model for the adlayer is proposed (Figures 2c and S2) and in good agreement with the STM results. We name this kind of isomers as $(t,t,t,t)_1$.

An STM image of the well-ordered adlayer is shown in Figure 3a for TCDB/4NN-Macrocycle mixing ratio of 1:1. Another type of assembly can be identified. The characteristics of the adlayer are different from both those of the pure TCDB adlayer and those

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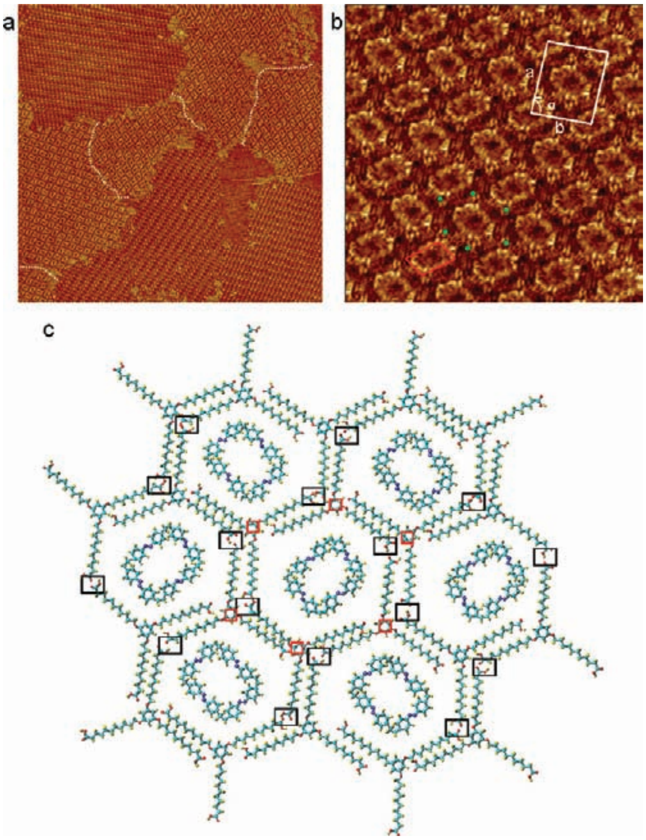

Figure 2. (a) Large-area STM image (153 nm × 153 nm, $I = 317$ pA, $V = 600$ mV) of entrapped monomer architecture on HOPG. (b) A high-resolution STM image (22 nm × 22 nm, $I = 189$ pA, $V = 735$ mV) of entrapped monomer architecture. (c) Molecular model for entrapped monomer architecture.

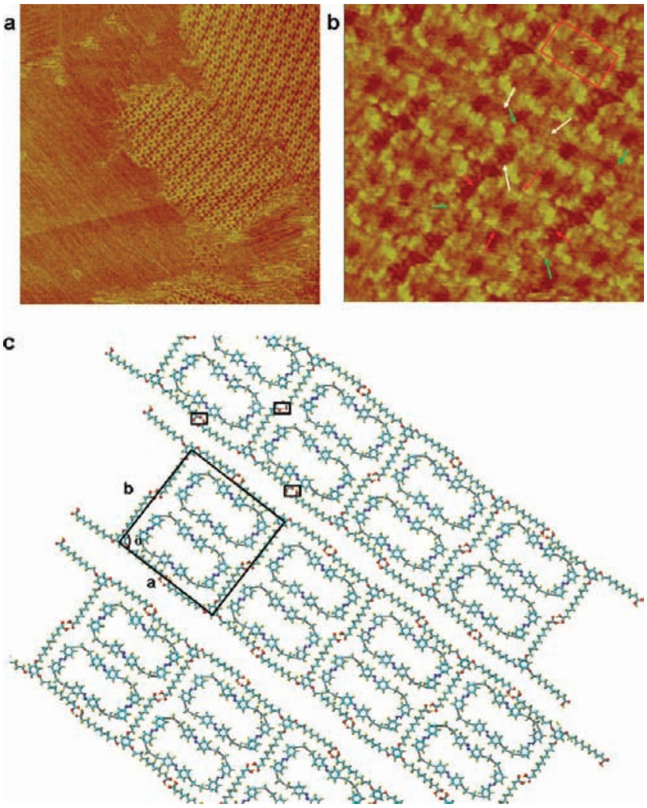

Figure 3. (a) Large-area STM image (124 nm × 124 nm, $I = 476$ pA, $V = 670$ mV) of entrapped dimer architecture on HOPG surface. (b) A high-resolution STM image (11 nm × 11 nm, $I = 483$ pA, $V = 1021$ mV) of entrapped dimer architecture. (c) Molecular model for entrapped dimer architecture.

of the adlayer as mentioned above in Figure 2. High-resolution STM images in Figures 3b and Figure S3 reveal the details of the entrapped molecules. The bright rectangles are measured to be 2.7 nm × 1.3 nm. Each hollow bright rectangle corresponds to a macrocyclic rectangle, indicated as a hollow red rectangle in Figure 3b. Four bright features directed by green arrows can also be observed around the rectangle dimer, which correspond to the benzene cores of TCDB molecules. Three white arrows direct the "arms" of the TCDB molecule. Four red arrows direct the azobenzene groups. A unit cell is superimposed on the image in Figure 3c with $a = 3.9 \pm 0.2$ nm, $b = 3.8 \pm 0.2$ nm, and $\alpha = 90.1° \pm 2.1°$. It is important to note that each TCDB molecule forms three pairs of hydrogen bonds with the three neighboring TCDB molecules (marked by three black hollow rectangles as shown in Figure 3c), which are also different from the previously reported networks.[6−9] The TCDB molecule is T-shaped instead of Y-shaped in this instance. We can also observe misalignments of relative positions between neighboring columns as shown in Figure S4. Such misalignments in relative positions between adjacent columns may suggest that there are no definitive hydrogen bonds between the columns, which are consistent with the molecular model in Figure 3c. We name these conformational isomers as $(t,t,t,t)_2$.

As a typical photosensitive compound, macrocycle will isomerize from the trans to cis conformation after irradiation with UV light. Kinetic measurements for thermal isomerization of macrocycle were reported.[35] The maximum absorbance is at 328 nm (λ_{max} of $\pi-\pi^*$ transition). The TCDB adlayers were not changed after UV-light irradiation, as shown in Figure S5.

Figure 4 shows the STM images of the assemblies prepared from the irradiated TCDB/4NN-Macrocycle adlayers on HOPG surface when the molecular ratio is about 2:1. Significantly different characteristics in the adlayer can be identified after UV-light irradiation, marked by type B in Figure 4a. The adlayer symmetry and the conformation of molecules entrapped in the cavities are both changed. We observe that the new molecular structure is appreciably longer than the unexcited macrocycles. The measured length is 3.0 ± 0.2 nm, and the width is 1.0 ± 0.1 nm. Moreover, the geometry of the macrocycles is different from that without UV irradiation. Such observed differences illustrate that the photoisomerization could occur in two opposite azobenzene groups and the other two azobenzene groups are unchanged. In Figure 4a, domain A is the unfilled TCDB network, while column B is the macrocycles of (t,c,t,c) isomer in the TCDB network. The inset of the Figure 4a is a high-resolution STM image of the (t,c,t,c) isomers in the TCDB network, and the details of the entrapped molecules are clearly visible. Two green spots correspond to two benzene cores of two TCDB molecules. Several features directed by the green and red arrows correspond to four azobenzene groups of the 4NN-Macrocycle molecule. The green arrows direct the cis forms, and the red ones direct the trans forms. Figure 4b is the molecular model for the photoisomers.

In addition, the monolayer after irradiation could be observed as the "disordered" domain (Figure 4c). In this type of adlayer, some molecules are photoexcited which we name as $(t,t,t,c)_1$

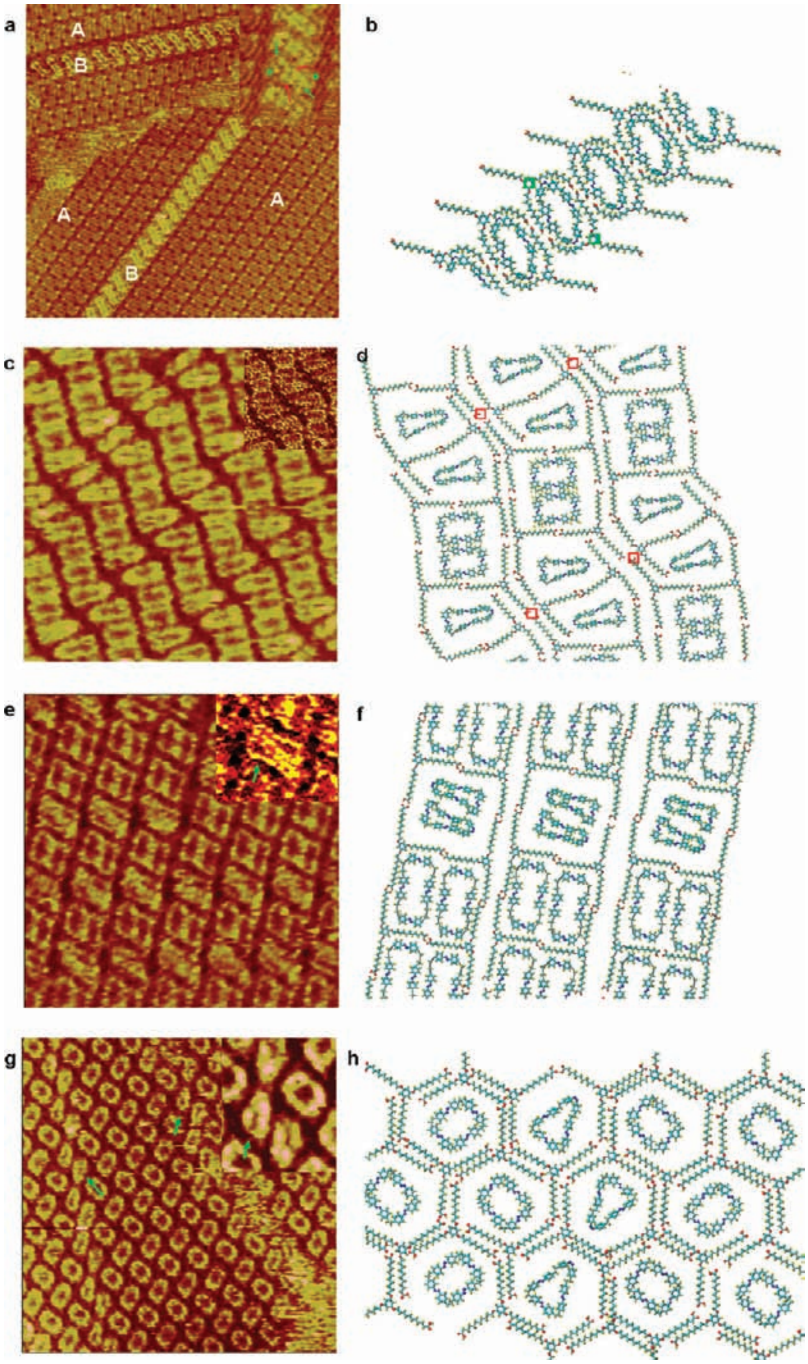

Figure 4. (a) High-resolution STM image (42 nm × 42 nm, I = 282 pA, V = 739 mV) of a self-assembly monolayer of irradiated TCDB/4NN-Macrocycle adlayers on HOPG surface. Domain A is the unfilled TCDB networks. Domain B is the (t,c,t,c) photoisomers in the TCDB networks. (b) Molecular model for Figure 4a. (c) An STM image (33 nm × 33 nm, I = 247 pA, V = 703 mV) of a "disordered" monolayer of irradiated TCDB/4NN-Macrocycle. The domain contains coexisting the (t,t,t,t)$_3$ and (t,t,t,c)$_1$ isomers. (d) Molecular model for Figure 4c. (e) An STM image (32 nm × 32 nm, I = 247 pA, V = 703 mV) of a "disordered" monolayer of irradiated TCDB/4NN-Macrocycle. The domain contains coexisting the (t,t,t,t)$_2$ and (t,t,t,c)$_2$ isomers. (f) Molecular model for Figure 4e. (g) An STM image (48 nm × 48 nm, I = 253 pA, V = 700 mV) of a "disordered" adlayer of (t,t,t,c)$_3$ and (t,t,t,t)$_1$. (h) Molecular model for Figure 4f.

and the others are not photoexcited which we name as (t,t,t,t)$_3$. The excited ones appear as extending triangles. The top of the triangle represents the cis azobenzene group, while three edges of the triangle represent the trans azobenzene group. Two (t,t,t,c)$_1$ photoisomers arrange antiparallelly in the adjacent cavities. The (t,t,t,t)$_3$ dimers and (t,t,t,c)$_1$s appear alternatively in the same column with zigzag characteristics which can be attributed to the steric hindrance and asymmetry of the photoisomers. The inset of Figure 4c is a high-resolution STM image of the (t,t,t,c) isomers in the TCDB networks. Figure 4d is the molecular model for the "disordered" domain. Because of the two pairs of hydrogen bonds (marked by red squares in Figure 4d) there is no misalignment phenomenon between the adjacent columns. It is therefore suggested that the two adlayers mentioned above are different from the adlayers shown in Figures 2 and 3.

There is another "disordered" molecular adlayer as shown in Figure 4e. In this adlayer the new (t,t,t,c)$_2$ conformational

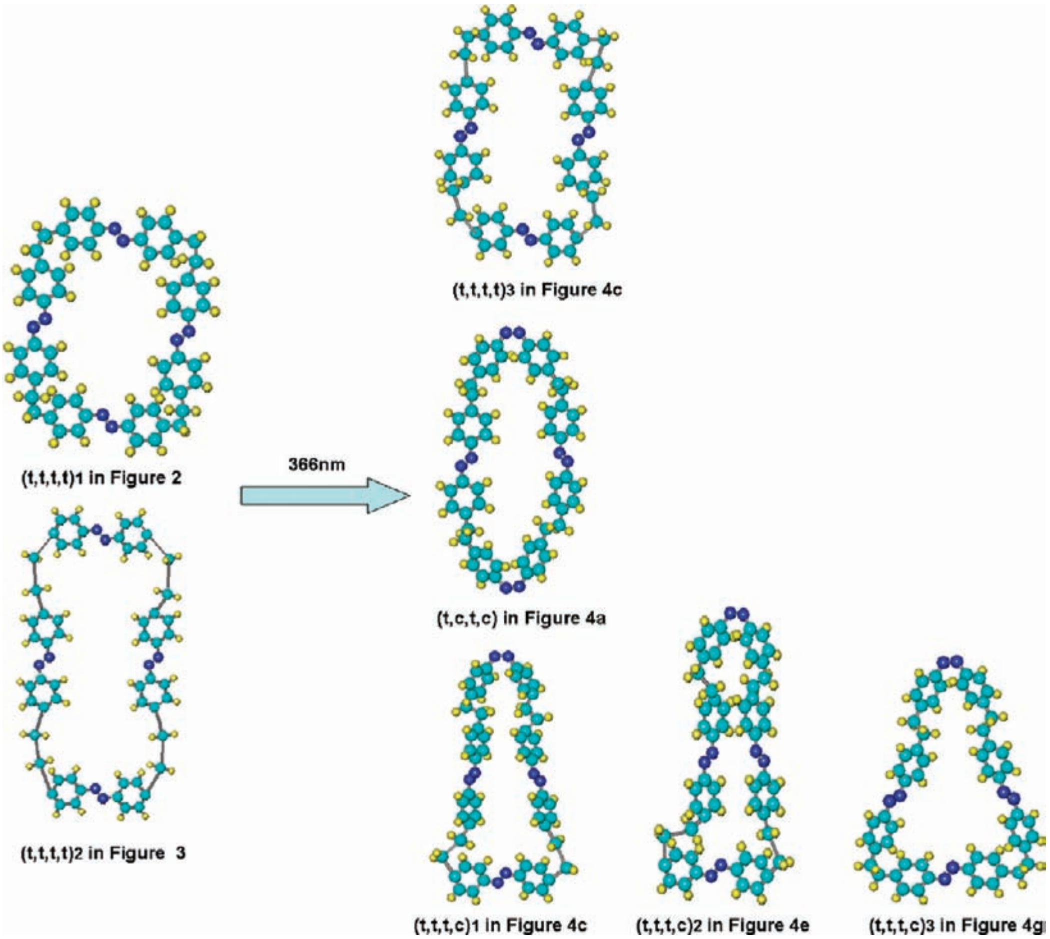

Figure 5. Molecular models of the conformational and photoisomers in the photoisomerization. $(t,t,t,t)_1$ and $(t,t,t,t)_2$ are observed on unirradiated surface as shown in Figures 2 and 3. The new $(t,t,t,t)_3$ isomer is obtained to coexist with $(t,t,t,c)_1$ photoisomer on irradiated surface as shown in Figure 4c. The photoisomers $(t,t,t,c)_2$ with $(t,t,t,t)_2$ and $(t,t,t,c)_3$ with $(t,t,t,t)_1$ are obtained on surfaces, respectively, as shown in Figure 4e−h. Three (t,t,t,c) photoisomers are not observed alone. The (t,c,t,c) photoisomer is entraped in the pore of TCDB.

isomers coexist with the $(t,t,t,t)_2$ isomers which are the same as the isomers in Figure 3. We can observe that the conformational isomers arrange antiparallelly in one cavity as shown in the insert of Figure 4e. The skew triangle is slimmer than the conformational isomer $(t,t,t,c)_1$ in Figure 4c due to the confinement effect by the pores of the TCDB network. The observation can illustrate that the four $-CH_2-CH_2-$ groups of the 4NN-Macrocycle are important to tune the molecular conformations. Although the adlayers are fabricated by (t,t,t,t) and (t,t,t,c) isomers too, the column does not have zigzag characteristics compared with Figure 4c. The (t,t,t,t) isomer and the self-assembly of the TCDB in this adlayer are the same as that in Figure 3.

Another new molecular packing structure is shown in Figure 4g. This one is seldomly observed on the surface. We can observe another $(t,t,t,c)_3$ conformational isomer mixed with the $(t,t,t,t)_1$ isomers. Two green arrows direct two column of $(t,t,t,c)_3$ as shown in Figure 4g. We can observe some distorted $(t,t,t,c)_3$ which is not an isoceles triangle (directed by the green arrow in the inset of Figure 4g).

In the STM observations we can distinguish up to seven conformational photoisomers as shown in Figures 4, 5, and S6 on the same surface when the sample is irradiated by UV light. Two conformational isomers $(t,t,t,t)_1$ and $(t,t,t,t)_2$, which form monomers or dimers, respectively, are entrapped in the pores of the TCDB adlayers as shown in Figures 2 and 3 under visible light conditions. When the sample is irradiated by UV light, new conformational isomers $(t,t,t,t)_3$ can be observed and form a different kind of adlayer as shown in Figure 4c in the presence of photoisomer $(t,t,t,c)_1$. The three (t,t,t,t) conformational isomers are distinguished by their aspect ratio between length versus width of the rectangle, $(t,t,t,t)_1/(t,t,t,t)_2/(t,t,t,t)_3 = 1.5{:}2.1{:}1.9$. The three (t,t,t,c) conformational photoisomers form dimers and self-assemble antiparallely in the adlayers, as shown in panels c, e, and g of Figure 4, respectively. $(t,t,t,c)_1$ or $(t,t,t,c)_3$ are entrapped in two adjacent cavities. The $(t,t,t,c)_2$ dimers are compactly entrapped in one cavity. Another significant characteristic is that the photoexcited dimers coexist in adjacent columns. The four (t,t,t,c) and (t,c,t,c) conformational photoisomers can be observed by STM with the aid of the host−guest self-assembling structures on surface.

In our study, the solvent molecules are not photosensitive and are not expected to contribute to the isomerization of the 4NN-Macrocycle. The solvent effect is mainly associated with the stability of the assembly structures as shown in the Supporting Information, Figure S7.

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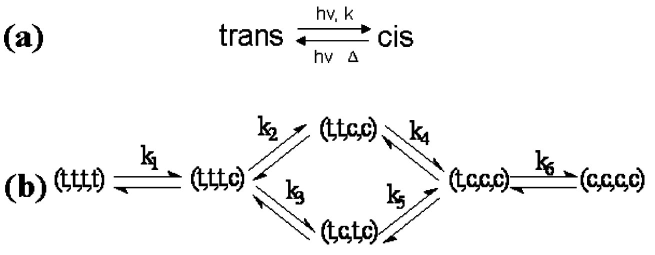

Figure 6. (a) Photochemical and thermal isomerization of the azobenzene. (b) Photochemical Isomerization of the 4NN-Macrocycle. The trans isomer is represented as t. The cis isomer is represented as c.

Table 1. Ratio of the Photoisomers[a]

	$(t,t,t,t)_1$	$(t,t,t,t)_2$	$(t,t,t,t)_3$	$(t,t,t,c)_1$	$(t,t,t,c)_2$	$(t,t,t,c)_3$	(t,c,t,c)
unirradiated	1	1.17	_	_	_	_	_
after irradiation	1.85	3.14	1	0.94	0.13	0.06	0.54

[a] The isomer in Figure 2 is regarded as $(t,t,t,t)_1$. The isomer in Figure 3 as $(t,t,t,t)_2$. The isomers in Figure 4c as $(t,t,t,t)_3$ and $(t,t,t,c)_1$. The isomer in Figure 4e as $(t,t,t,c)_2$. The isomer in Figure 4a as (t,c,t,c). The photoisomer dimer as $(t,t,t,c)_2$ $(t,t,t,c)_3$ in Figure 4e and g. $(t,t,t,c)_1$, $(t,t,t,c)_2$, $(t,t,t,c)_3$, and (t,c,t,c) are the photoisomers. $(t,t,t,t)_1$, $(t,t,t,t)_2$, and $(t,t,t,t)_3$ are conformational isomers. The relative ratio number of isomer "un-irradiation" versus that of $(t,t,t,t)_1$ is provided in the "un-irradiated" row. The relative ratio number of isomers after irradiation versus that of $(t,t,t,t)_3$ is also provided in the "after irradiation" row.

The parameter of the lifetime of the azobenzene photoexcited state is $\tau = 1/k$. The k value is the first-order rate constants, as shown Figure 6a. In general, the k value of the same photoreaction is different when measured in different solvents.[41] Some previous studies have discussed the lifetime of the photoexcited state of azobenzene on Au surface.[22−24] The compounds in these studies have only one azobenzene group and are covalently immobilized on surface. There are no azobenzene molecular exchanges between the surface and the solution. So when they measure the trans−cis ratio by deconvolution of the absorption spectra of the photostationary state, the only two isomers could be readily distinguished. They concluded that the value of the kinetic constant calculated for the thermal back cis−trans reaction on a metal surface is more than seven times lower than that in solution.[22] The rigidity of the aromatic backbone is responsible for the cooperative switch and the interchain interactions are fundamental for the long lifetime of the cis isomers on Au surfaces.

In this work, we can observe that the (t,t,t,c) has three conformational isomers as mentioned above. Because the pores of TCDB adlayers and the molecular ratio of the three (t,t,t,c) isomers are different, as shown in Figure 4 and Table 1, k should be different in the pores of TCDB on a HOPG surface. In other words there could be three different k values that correspond to one photoisomer (t,t,t,c) on the surface. In solution (t,t,t,c) could also have conformational isomers. The general methods could obtain the statistically averaged states of the isomers. The photochemistry studies could only measure the k values of the azobenzenophanes with two or three azobenzene groups successfully in solutions.[42−45] In this study we can identify the individual conformational isomers on the surface due to the immobilization effect of TCDB networks. The detailed proportion of the different structures on the surface is shown in Table 1 by counting the observed molecules after UV irradiation. It is presumed that adsorption−desorption process could accompany the assembly structures at liquid−solid interface. The conformational isomers are expected to have different adsorption−desorption behavior. So we can not quantitatively determine the k values due to the coexistence of several conformational isomers.

It would be interesting to compare the difference in ratio in solution and on the surface by indirect methods. The ratio of (t,t,c,c) is always twice as many as that of (t,c,t,c) in solution because the photoisomerization from (t,t,t,c) takes place with a ratio of probability of 2:1 for (t,t,c,c) and (t,c,t,c) in similar macrocycles.[46] When a trans azobenzene group in (t,t,t,c) photoisomerizes to cis, there are three possible sites to photoexcite. One of the two trans azobenzene units, which are adjacent to the cis azobenzene unit in (t,t,t,c), photoisomerizes from trans to cis and results in the (t,t,c,c) isomers. Nevertheless, (t,c,t,c) is isomerizated from (t,t,t,c), which is on the opposite side of the cis azobenzene in (t,t,t,c). Thus, the ratio of the concentration of (t,t,c,c) and (t,c,t,c) is always 2:1 in solution, which presume that the probability of the isomerization does not depend on the position.[46] However, we cannot observe (t,t,c,c) on the surface because it is not structurally favorable to fit in the cavities of TCDB, possibly due to the steric hindrance. In this paper the ratio of photoisomers is dependent on the cavity geometry of the TCDB adlayers on the surface.

The photoreaction process of the 4NN-Macrocycle is schematically shown in Figure 6b. We can not observe the (t,t,c,c), (t,c,c,c), and (c,c,c,c) photoisomers, possibly because they are structurally unfavorable to fit in the cavities of TCDB. Figure 5 is the molecular model for the photoisomers of 4NN-Macrocycle that we can observe.

As is known from the photoreaction mechanism, the trans form could isomerize to the cis form after UV irradiation. In the previous studies, ordered adlayers of single azobenzene moiety molecules on HOPG were also found after irradiation.[39,40] In this study, the photosensitive macrocycles are immobilized with the aid of molecular templates. Their isomerzation characteristics and several conformational isomers can be directly visualized and also dramatically affect the structural characteristics of the host networks.

Conclusions

In summary, the photosensitive macrocycles are immobilized in the TCDB network. STM images reveal the details of the well-ordered adlayers. The stoichiometry of TCDB/4NN-Macrocycle affects the structure of TCDB/4NN-Macrocycle. 4NN-Macrocycle molecules are observed to photoisomerizes from (t,t,t,t) to (t,t,t,c) and (t,c,t,c) photoisomers after irradiation with UV light. The direct observation about photoisomerization of macrocycles on HOPG at the single molecular level is obtained. Additionally we can distinguish three kinds of (t,t,t,c) or (t,t,t,t) conformational photoisomers at the same time on surface This method provides a facile approach to study the photoisomerizations of the macrocycles containing azobenzene groups. It could

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be beneficial for the fabrication of the nanostructure and the development of photosensitive nanodevices.

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Supporting Information Available: STM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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