cis-trans Driven organized reorientation of an azobenzene derivative monolayer at the liquid/graphite interface†

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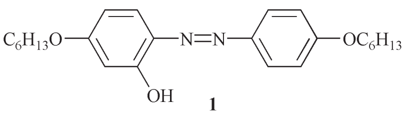
An azobenzene derivative, 2-hydroxy-4,4′-dihexyloxyazobenzene, in which a hydroxy group is introduced at the 2-position of the phenyl ring, forms an ordered monolayer at the liquid/graphite interface. Upon light irradiation, this monolayer can undergo a reversible *cis-trans* driven cooperative reorientation as observed by scanning tunneling microscopy.

Introduction

Self-assembled monolayers physisorbed at liquid/solid interfaces have aroused growing interest due to their potential applications in adhesion, wetting and as functional elements in nanotechnology.[1–5] A wide variety of molecules, such as alkanes, alcohols, fatty acids, *etc.*, have been found to form two-dimensional molecular lattices at the liquid/solid interface.[6–10] Among them, azobenzene derivatives have received special attention due to their interesting photoresponsive behavior.[11–13] It has been shown that suitably designed azobenzene derivatives can form long-range ordered arrangements of two-dimensional molecular lattices at the liquid/solid interface. Generally, due to the lack of lateral interconnection between molecules, the ordered arrangement of molecules will be destroyed by a local *cis-trans* isomerization process upon light irradiation.[11,12] From a technological viewpoint, it would be very useful to design a system that can undergo a reversible organized transition under irradiation.

In this work, we report the observation of a *cis-trans* driven cooperative organized sliding motion of an azobenzene derivative monolayer at a liquid/solid interface by scanning tunneling microscopy (STM). The azobenzene derivative used here is 2-hydroxy-4,4′-dihexyloxyazobenzene (**1**). In this molecule, a hydroxyl group is introduced in the 2-position of the phenyl ring. It is expected that the molecules can be held together by a hydrogen bond network to form a two-dimensional molecular architecture and that the intermolecular hydrogen bonds will endow the monolayer with new transition behavior upon irradiation.



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Experimental

The STM measurements were performed with a mechanically sharpened Pt/Ir tip operating under ambient conditions with a SPA 3700 STM/AFM system (Seiko Instruments, Japan). Prior to imaging, the compound was dissolved in 1-undecanol at a concentration of approximately 1 mg ml^{-1}. One drop of this solution was then applied to the basal plane of a piece of HOPG. The tip was immersed in the solution and brought close to the liquid/solid interface. Imaging was performed in the current imaging mode with bias voltages of 252 mV (sample positive) and an average tunneling current of 0.14 nA. STM images of the graphite surface, obtained at low tunneling voltages, were used for calibrations. Immediately after the sample image a calibration image of the graphite surface was acquired at exactly the same position. Acquisition time for a one-image frame (256 lines and 256 pixels per line) was approximately 30 s (limits set by the STM instrument). For the *trans-cis* isomerization experiment, the tip was first retracted. Then the graphite, its surface still coated with solution, was irradiated by putting a 30 W UV lamp (wavelength 365 nm) approximately 5 cm above the sample surface. After illumination for 20 min, the tip was immediately approached and the image scanned continuously as before irradiation.

Results and discussion

After **1** was dissolved in 1-undecanol, a small droplet of the solution was applied to the basal plane of newly cleaved highly orientated pyrolytic graphite (HOPG). In this case, a physisorbed monolayer formed spontaneously at the liquid/graphite interface. Fig. 1 shows the STM image of a **1** adlayer deposited from solution on the HOPG surface and the proposed molecular packing pattern of the adlayer. The ordered row-like structure with alternating bright and dark stripes can be clearly observed. The periodicity of every row is 2.9 ± 0.1 nm, corresponding well to the length of one extended molecule of **1** in the *trans* form. The brighter stripes with a width of 0.9 ± 0.1 nm in the STM image originate from the

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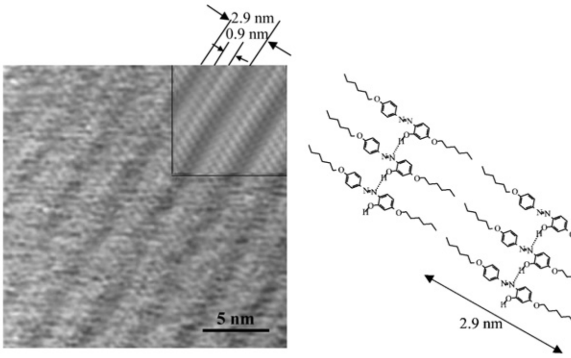

Fig. 1 STM image of an ordered monolayer of **1** formed by physisorption at the liquid/graphite interface from 1-undecanol solution. Image size: 20 × 20 nm^2. The image was obtained with a 252 mV bias and a 0.14 nA current setpoint in constant current mode. The inset is a cut of Fig. 1 after 2-D fast Fourier transform. In every row, the protrusion part can be clearly seen with a spacing of 9 Å, corresponding well to the intermolecular spacing of the azobenzene moiety of one molecule **1**. Next to the STM image is the proposed molecular packing pattern of **1** derived from this image.

azobenzene moieties and correspond to a higher tunneling current. The darker stripes in the image originate from the alkyl chains and correspond to a lower tunneling current.[14] The distance between neighboring molecules in a row was measured to be about 2.6 Å.

The formation of a physisorbed monolayer at the liquid/graphite interface results from the interactions between the molecules and the graphite surface. The positions of the molecules need to match with the graphite lattice to maximize the binding energy between the molecules and the graphite surface. Fig. 2 is a model for the molecular arrangement of *trans* **1** on a graphite surface based on STM observations. It shows that the molecules in adjacent rows are oriented along the $[21]_{HOPG}$ direction and that there is an inclination angle of 5° between the row direction and the $[12]_{HOPG}$ direction. This is supposed to be the energetically most favorable position of *trans* **1** on a graphite surface.

In **1**, the introduction of a hydroxyl group allows the formation of two types of *trans* configurations when taking the position of the hydroxyl group into account. As shown in Fig. 3, configuration I is prone to form intermolecular hydrogen bonds while in configuration II it is easy to form an intramolecular hydrogen bond. Hartree–Fock calculations were used to compare the ground state energies of configurations I and II. For configuration I, HF = −866.8526889, and for configuration II, HF = −866.8240217. The difference of their energies is 75.2 kJ mol^{-1}, indicating that configuration I is more stable than II. So in our system, molecule **1** tends to adopt the more stable configuration I and form lateral intermolecular hydrogen bonds between neighboring molecules. That is to say all molecules in one row are assumed to be connected by an intermolecular hydrogen bond network.

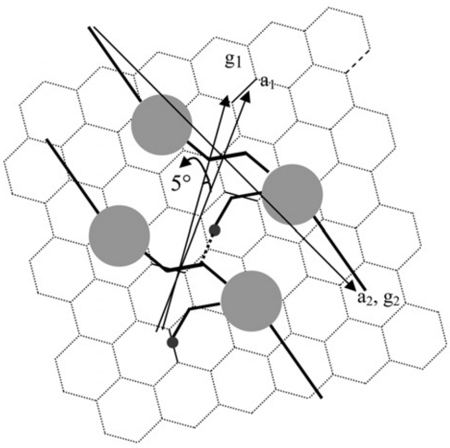

Fig. 2 Proposed orientation of *trans* **1** on a graphite surface with 2D packing vectors a_1 and a_2. a_1 is the direction of one row and a_2 is the direction of molecules in the adjacent row. $g_1$and g_2 are the lattice vectors of graphite along the $[12]_{HOPG}$ and $[21]_{HOPG}$ directions.

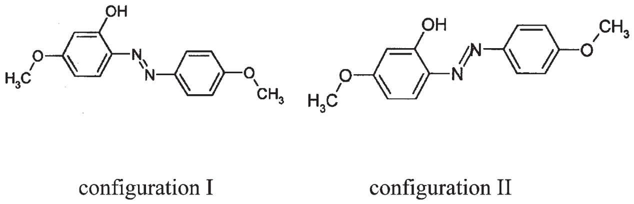

Fig. 3 The two types of *trans* configurations for molecule **1** used for the Hartree–Fock calculation. To simplify the calculation, a methyl group is used to replace the hexyl group.

After irradiation of the solution on the HOPG surface with UV light (365 nm) for 20 min, the graphite surface was re-examined immediately as before (Fig. 4). Owing to the *trans-cis* isomerization, the image exhibits a different orientation of the row-like structure. An ordered structure is also obtained but rotated by 60° compared with that before irradiation [Fig. 4(a)]. Continuing the image scanning, the row-like structure slowly rotates clockwise [Figs. 4(b) and 4(c)]. Within 3 min [Fig. 4(d)] the orientation of the row-like structure returns to that observed in Fig. 1. During the process of reorientation and recover, the width of every row hardly changes and the two-dimensional architecture exhibits a cooperative reorientation of all molecules on the nanoscale.[15] The sliding motion proceeds with a steady speed of about 1° s^{-1}.

For the realization of the cooperative sliding motion of the monolayer, the formation of a two-dimensional hydrogen bond network among neighboring molecules plays a key role in the whole process. Commonly, for a conjugated planar

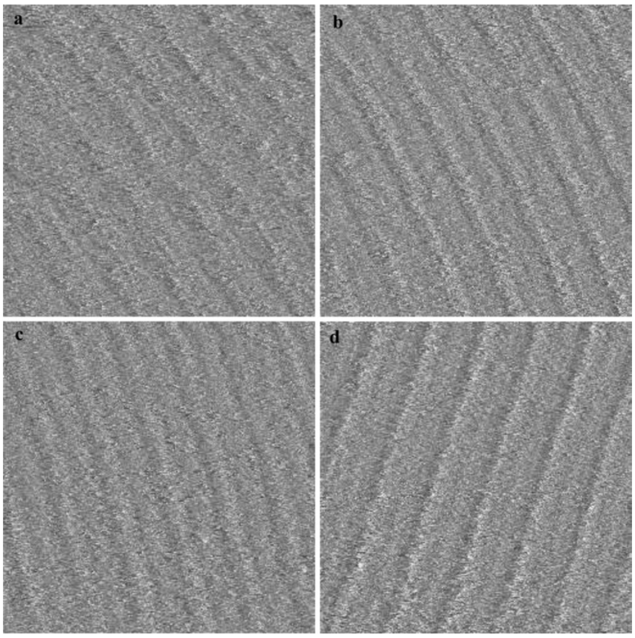

Fig. 4 STM images of **1** adsorbed from 1-undecanol solution after UV light irradiation. The image size is also 20 × 20 nm^2, corresponding to the same position as in Fig. 1. The bias and current parameters are the same as those in Fig. 1. (a) Image obtained immediately after UV irradiation; (b) and (c) continuously scanning images obtained after (a), every image scanning is finished within 10 s; (d) image obtained after 3 min.

molecule such as benzene, theoretical results showed that the energetically most favorable position of a benzene ring is on top of a C atom of the graphite lattice to form a planar-to-planar interaction with the graphite surface.[16,17] Under UV light irradiation, a part of the azobenzene molecules will be excited and undergo a *trans-cis* transition. After excitation, the N=N double bond will be converted to a N–N single bond and the conjugated planar structure of the molecules will be destroyed. This will cause a decrease of the binding energy between the molecules and the graphite surface. As a result, the excited molecules can depart from the graphite surface and the *trans-cis* transition can be completed through rotation of the N–N single bond; it is unnecessary to destroy the hydrogen bonds. Due to the presence of intermolecular hydrogen bonds, if one molecule in a row undergoes the *trans-cis* transition, the neighboring molecules in this row need to adjust their relative positions to provide enough space for the *cis* isomer. This will result in an alteration of the orientation of the row. The *cis* isomer is a thermodynamically unstable species and prone to convert back to the thermodynamically more stable *trans* isomer. In this experiment, the 20 min UV light irradiation time is so long that every molecule has a chance to complete one or several cycles of *trans-cis* or *cis-trans* transitions. During this time, the orientation of the rows is greatly altered on the graphite surface [Fig. 4(a)]. The experimental result shows that the deviation of the row orientation angle between Fig. 1 and Fig. 4(a) is about 60°. Limited by the experimental conditions (several tens of seconds are necessary to acquire a STM image), it is difficult to determine the original orientation of the rows just after UV light irradiation. After UV light irradiation, the *cis* isomers continue to undergo the *cis-trans* transition and release energy to the system. It is known that energy transfer is an essential intrinsic feature of hydrogen bonds.[18,19] Therefore, it can be expected that the released energy can be transferred efficiently among the molecules connected by the hydrogen bond network. The transferred energy can provide the driving force for the sliding motion of the monolayer on the graphite surface. To satisfy the demand for a position-matched orientation to obtain the maximum binding energy between the molecules and graphite surface, the molecules tend to reposition themselves in their original position. The released energy can compensate the loss of energy to overcome the energy barrier during the sliding motion. For azobenzene derivatives without hydrogen bonds, the lack of lateral interconnection between molecules will cause the ordered arrangement of molecules to be destroyed by such *cis-trans* or *trans-cis* transitions.[11,12] In our work, all molecules in one row are connected together by hydrogen bonds and thus the ordered arrangement of the row can be maintained during the transition process.

Conclusion

In summary, we report here the observation of a *cis-trans* driven sliding motion of an azobenzene monolayer at a liquid/graphite interface. In this cooperative system, the lateral hydrogen bonds restrict the behavior of every individual molecule and allow energy to be transferred efficiently among molecules. The position-matched orientation of **1** on the graphite surface determines where the *cis-trans* driven sliding motion stops. Such a reversible and organized manipulation of a monolayer at a liquid/graphite interface is of great technical interest in surface and interface phenomena.

Acknowledgements

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