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Atomic force microscopy study of self-organization of chiral azobenzene derived from amino acid

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Abstract

A kind of chiral azobenzene amphiphile, *N*-[4-(4-dodecyloxyphenylazo)benzoyl]-L-glutamic acid (C₁₂-Azo-L-Glu; as shown in Fig. 1), was synthesized and the self-organization properties on solid substrates were investigated. C₁₂-Azo-L-Glu underwent a reversible *trans*–*cis* photoisomerization in dilute solution. While the photoisomerization was suppressed on solid substrate because of the H-aggregation, indicating the formation of compact film. When C₁₂-Azo-L-Glu was cast from ethanol solution onto the hydrophilic surface of mica, a stable flat-layered structure formed spontaneously in large scale. High-resolution images allowed the identification of the relative orientation of molecular rows in the ordered thin film and the crystal lattice of mica. A molecular packing model of the layered structure was proposed. There was a template effect of mica to the self-organization process. Hydrogen bonding, π – π interaction and the chiral center in the molecule played the important roles in the self-organization process. The cooperative competitive effect between them led to the highly ordered structure.

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1. Introduction

The self-organization of molecules on the surface of solid substrates offers a strategy for constructing nanostructures with chemical functionalities and physical properties that are potential useful as active components in electronic devices [1–3]. One of the most important

things for applications is to construct a stable ordered thin film in large scale. Among the properties that influence the electrical and optical behavior of physisorbed thin films are the orientation of the molecules relative to the substrate and the formation of domain structures [4]. The design and synthesis of molecules that contain all the necessary information to organize themselves spontaneously into well-defined supramolecular entities provides one of the most important challenges in supramolecular chemistry [5,6]. Whitten and co-workers [7,9] and Whitesides et al. [8] had reported that the incorporation of an aromatic group into hydrocarbon chain of an amphiphile resulted in an

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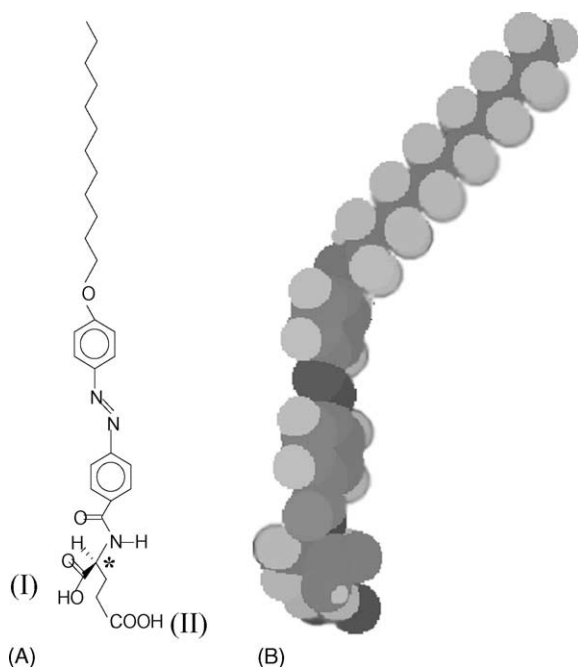


Fig. 1. (A) Chemical structure of C_{12} -Azo-L-Glu. (B) The energy-minimized configuration of C_{12} -Azo-L-Glu (the length of this molecule is about 30.5 Å).

enhanced self-assembly process in aqueous solution and at air–water interface, as a consequence of strong non-covalent attraction between the aromatic chromophores.

To construct a stable ordered structure on solid substrate spontaneously, we designed a chiral azobenzene amphiphile, *N*-[4-(4-dodecyloxyphenylazo)benzoyl]-L-glutamic acid (C_{12} -Azo-L-Glu; as shown in Fig. 1), which containing a chiral center and two carboxyl groups. Multiple interactions between molecules were presented in the self-organization system. Lateral hydrogen-bonding network, π – π stacking and hydrogen bonding between molecules and substrate occurred at the same time. The cooperative competitive effect between them led to the stable ordered structure in a long-range order.

2. Experimental

2.1. Synthesis

4-(4-Dodecyloxyphenylazo)benzoic acid [10] was dissolved in SOCl_2 and refluxed for 8 h to obtain 4-(4-

dodecyloxyphenylazo)benzoyl chloride. L-Glutamic acid reacted with 4-(4-dodecyloxyphenylazo)benzoyl chloride in a mixture of THF and water at basic condition to get C_{12} -Azo-L-Glu. The structure of the compound was tested by FT-IR and ^1H NMR. FT-IR (cm^{-1}): 3411 (N–H), 2922 and 2853 ($-\text{CH}_3$, $-\text{CH}_2-$), 1706 (carboxyl group), 1643 (amide I), 1538 (amide II), 1603 and 1503 (benzene rings), 1588 and 1470 (N=N). ^1H NMR was carried out on Bruker DMX-400 instrument operating at 400 MHz. ^1H NMR (CD_3SOCD_3 , δ , ppm): 0.87 (t, 3H, $-\text{CH}_3$), 1.35 (m, 16H, $-\text{CH}_2-$), 1.43 (t, 2H, $-\text{CH}_2-$), 1.75 (m, 2H, $-\text{CH}_2-$), 2.09 (2H, $-\text{CH}_2-$), 2.23 (m, 2H, $-\text{CH}_2-$, linked to the carboxyl group), 4.09 (t, 2H, $-\text{CH}_2-$, linked to oxygen atom), 4.46 (m, $-\text{CH}-$, chiral center), 7.15 (2H, CH, benzene ring), 7.92 (4H, CH, benzene ring), 8.06 (2H, CH, benzene ring).

2.2. Photochromism

Dilute solution of C_{12} -Azo-L-Glu in ethanol and cast film on CaF_2 substrate was used for UV-Vis spectra and photochromism measurements. The sample was irradiated by a 100 W mercury arc lamp through a filter in the range of 300–400 nm. The UV-Vis spectra were recorded by a Shimadzu 1600 spectrometer.

2.3. AFM investigations

C_{12} -Azo-L-Glu was dissolved in ethanol to form a solution with the concentration of 2×10^{-3} M. The atomic force microscopy (AFM) investigations were conducted using a commercial system (SPA300HV, Seiko Instruments Inc., Japan) with a 20 μm scanner. A triangular-shaped Si_3N_4 cantilever with spring constant of 0.02 N m^{-1} was used to acquire images in contact mode. All images were recorded under ambient conditions at 22 °C. Substrates were freshly cleaved planes of mica (10 mm \times 10 mm). After the atoms of substrates were resolved, a drop of C_{12} -Azo-L-Glu solution was applied to the substrates and studied by AFM after solvent had evaporated slowly. The scan directions in all images maintained uniform. Each of the images presented here was the representation of several images taken at different times to ensure reproducibility.

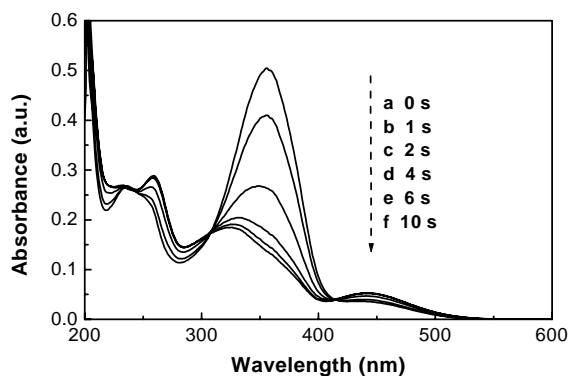


Fig. 2. UV-Vis spectra of C_{12} -Azo-L-Glu in ethanol solution with the concentration of 1×10^{-6} M: (a) before UV irradiation; (b–f) UV irradiation at 365 nm for different times.

3. Results and discussion

Photoisomerization of C_{12} -Azo-L-Glu in dilute ethanol solution is shown in Fig. 2. Typical of azobenzene derivatives, the *trans* form is more stable and is the dominant isomer before irradiation by UV light. The characteristics of the *trans* form are a strong $\pi-\pi^*$ transition at 357 nm and a weak $n-\pi^*$ transition at 444 nm [11]. The absorption at 240 nm is attributed to a $\pi-\pi^*$ transition whose moment is generally parallel to the short axis of *trans* isomer [12,13]. Upon UV irradiation, the $\pi-\pi^*$ band shifts to shorter wavelength and the $n-\pi^*$ band become more intense, indicating that the *trans* form is converted to the *cis* form in solution [14]. After the irradiation for 10 s, the photo-stationary state is reached. The *trans-cis* isomerization in solution is nearly quantitative and is reversible. The *cis* form is short-lived that most of *cis* isomers can revert to *trans* form when treated with visible irradiation for a few minutes.

UV-Vis spectra of C_{12} -Azo-L-Glu cast on CaF_2 substrate is shown in Fig. 3a. The absorption maximum (λ_{max}) of C_{12} -Azo-L-Glu on CaF_2 substrate is blue shifted by 7 nm (350 nm) in comparison to that in dilute solution (357 nm). The blue shift is correlated with the parallel-type aggregation (H-aggregation) of the azobenzene chromophores [15]. The intensity of $\pi-\pi^*$ transition is much lower than the absorption at 240 nm, which is inverted compared with that in dilute solution. There is no obvious difference between the UV-Vis spectra before and after UV irradiation, indi-

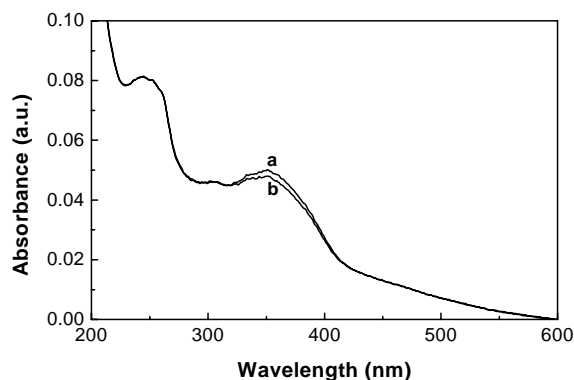


Fig. 3. UV-Vis spectra of C_{12} -Azo-L-Glu cast on CaF_2 : (a) before UV irradiation; (b) after UV irradiation at 365 nm for 3 min.

cating the photoisomerization is suppressed on CaF_2 substrate. Since the cross-sectional area of *cis* isomer is larger than that of the *trans* isomer, free volume is considered to be necessary for the molecule to photoisomerize [16]. It can be concluded from the UV-Vis spectra that C_{12} -Azo-L-Glu forms compact film on solid substrate.

Large-scale image obtained on the dried C_{12} -Azo-L-Glu adsorbate on newly cleaved mica surface is shown in Fig. 4A. The chiral molecules assembled to a flat-layered structure in a very long-range order. The layers with irregular boundary and smooth surface can be observed clearly. Cross-sectional analysis along the line marked *ab* (Fig. 4B) shows a step with the height of about 5.8 nm. This value is corresponding to the thickness of the bilayer if we take the estimation that the fully extending of molecules C_{12} -Azo-L-Glu is about 3.05 nm from the energy-minimized configuration. The corrugation over the surface of each layer is less than 0.1 nm.

At atomic scale, the lattice structure of mica surface can be recognized in air and the inset shows the Fourier pattern that indicates a hexagonal crystal lattice (Fig. 5A). The molecular resolution image obtained from the layered structure is shown in Fig. 5B. The inset shows its Fourier pattern that indicates an oblique crystal lattice, which can accommodate only pure enantiomers [17,18]. This image also shows two-dimensional periodic structure at the molecular level. Rows of the chain ends are aligned at approximately 82° . From the zoomed-in image

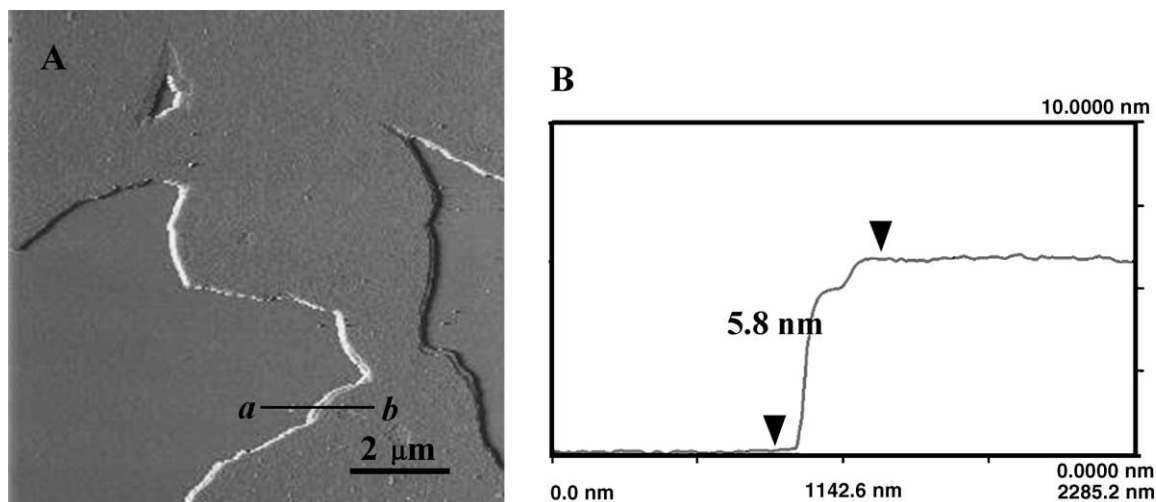


Fig. 4. (A) A large-scale AFM image ($10\ \mu\text{m} \times 10\ \mu\text{m}$) of the flat-layered structure of $\text{C}_{12}\text{-Azo-L-Glu}$ adsorbate on mica surface. (B) Cross-section analysis along the line drew in the direction of ab in (A).

(Fig. 5C) one can see the crystal lattice more clearly. The unit cell dimensions a_0 and b_0 , and the intermolecular spacings X and Y ($X = Y$) are labeled. The angle between a_0 and b_0 is 90° . Moreover, the directions of the rows of the chain ends in the upper layer are the same as the layer below it. Compared with the molecular resolution image of mica surface and the layered structure, a template effect of mica to the self-organization process can be observed clearly. The direction of a_0 is identical to the $(2\ \bar{1}\ 0)$ direction of $(0\ 0\ 1)$ face of mica. Fig. 5D is a proposed molecular packing model of the layered structure based on the analysis of the AFM images.

The above results suggest that the interactions between the molecules in the first layer and the mica surface play a key role in the self-organization process. It is generally agreed that assembly of chiral molecules is determined by the competition between two factors: the presence of chiral centers often induces helicity; while directional attractive interactions such as hydrogen bonding and face-to-face π - π aromatic stacking help generate linear arrays of molecules [19,20]. Based on Nandi and Bagchi's effective pair potential (EPP) approach [21,22], the EPP for chiral molecules depends on the size of the groups attached to the chiral center, their separation distance, and their relative orientation. The minimal energy conformation of a D-D or L-L pair shows double

energy-minimum states, with one minimum at a twist angle between adjacent two molecules and at a short distance (twist state), while the second, at nearly 0° but at large separation (linear state). Under normal condition, the former will be effective forming helical aggregates. In our previous work, it has been demonstrated that the cooperative competitive process of the two energy-minimum states led to special interfacial properties, and they can coexist in the same layer under a certain condition [23]. Here, the tendency to form twist state is suppressed by the directional interactions between molecules. The process of assembly of chiral molecules can be controlled to form flat-layered structure with the linear alignment of molecules.

As shown in Fig. 1A, two carboxyl groups in the molecule $\text{C}_{12}\text{-Azo-L-Glu}$ are at different steric position. One of them (carboxyl I) is attached to the chiral center directly and another (carboxyl II) is separated by two $-\text{CH}_2-$ groups from the chiral center. Carboxyl II can move more freely than carboxyl I and can adjust the location of molecule to match the crystal lattice of mica well. When molecules $\text{C}_{12}\text{-Azo-L-Glu}$ were applied to the hydrophilic surface of mica, carboxyl II in the molecules interact with the domains of oxygen ions by hydrogen bonding and the hydrophobic hydrocarbon chains extend upwards. Since amide functional groups possess the Z-configuration

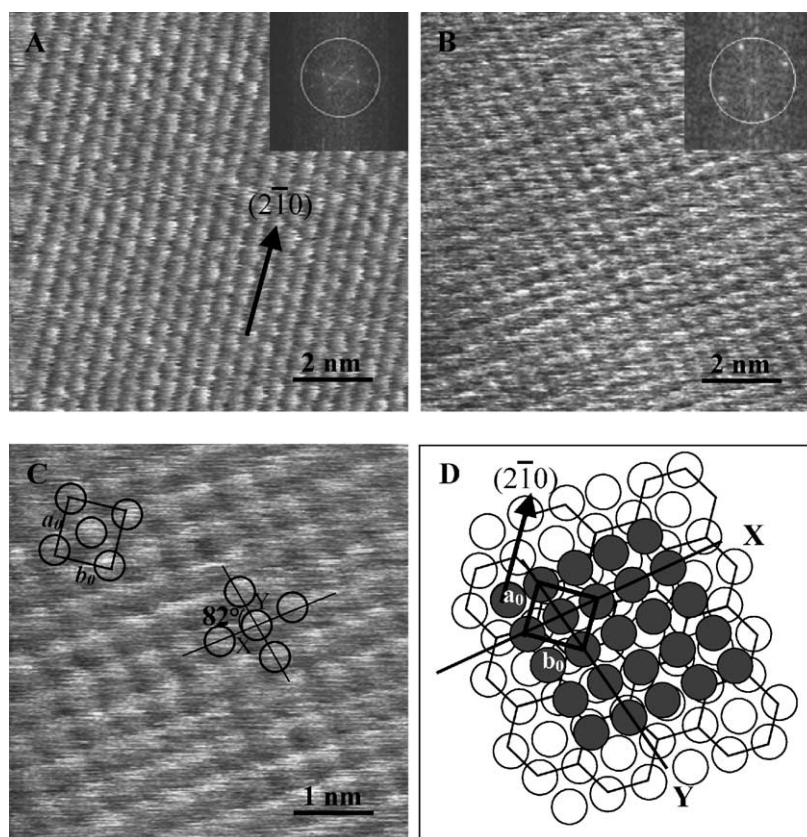


Fig. 5. (A) AFM image at the atomic scale of mica in the air obtained before dropping the solution on it (the inset shows the Fourier pattern that indicates a hexagonal crystal lattice). (B) High-resolution AFM image obtained from the surface of this flat-layered structure (the inset shows the Fourier pattern that indicates an oblique crystal lattice). (C) Zoomed-in image of (B), the crystal lattice can be observed more clearly. (D) Proposed molecular packing model of the layered structure.

structure for long-chain molecule [24], chiral molecules assemble regularly and match with each other to form an intermolecular hydrogen-bonding network shown in Fig. 6A. At the same time, the face-to-face π - π interactions of azo groups occur. The direction of π - π interactions is almost perpendicular to the hydrogen-bond network in two-dimensional plane.

After the first layer had grown on mica surface, the surface become hydrophobic with hydrocarbon chains extended upward, and there is an angle of 82° between the rows of chain ends (shown in Fig. 5C). As for the second layer, the molecules aligned along the hydrophobic lines formed by the first layer through Van der Waals interactions. The molecules in the second layer interact with another molecule by interlayer hydrogen bond to give a smooth hydrophobic surface and the

bilayer structure formed. On the third layer, it can grow the bilayer repetitively like that on the first layer. The multilayer is very stable since there are strong lateral interactions in two perpendicular directions in each layer accompany by the interactions between the substrate and the molecules. Fig. 6B is an illustration of the non-covalent interaction networks in this system, viewed from the top.

4. Summary

A kind of chiral azobenzene amphiphile was designed and the self-organization properties on solid substrates were investigated. UV-Vis spectra showed that photoisomerization was suppressed on solid

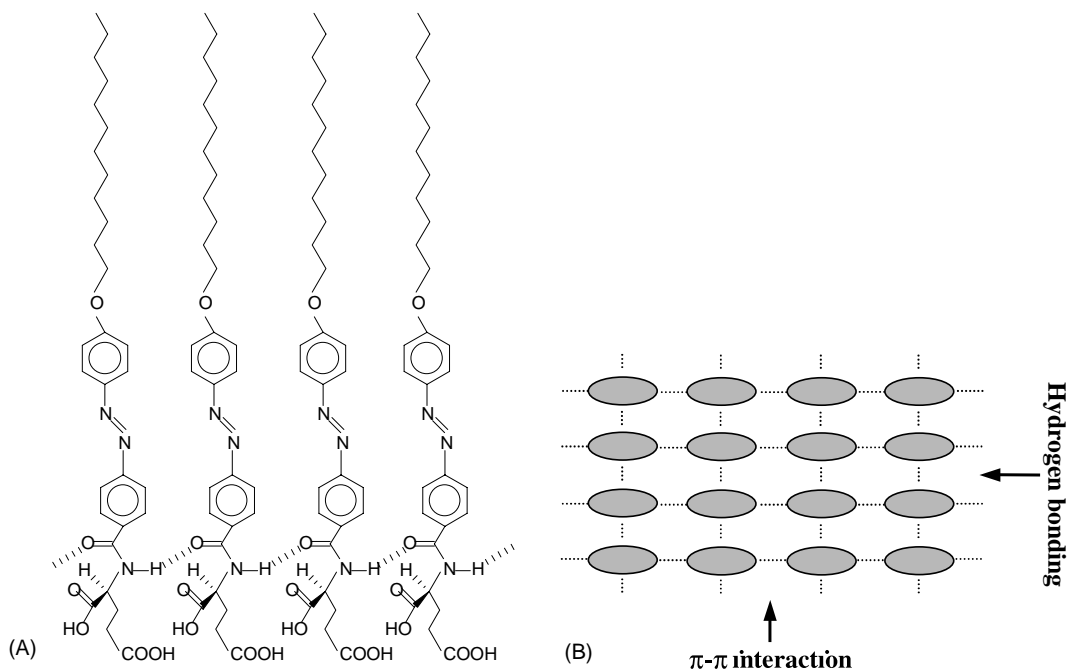


Fig. 6. (A) Schematic representation of hydrogen-bonding network of the aggregation of C₁₂-Azo-L-Glu within each layer. (B) An illustration of the non-covalent interaction networks in this system, viewed from the top.

substrate because of the formation of H-aggregation. AFM studies indicated that C₁₂-Azo-L-Glu self-organized into stable flat-layered structure in a long-range order spontaneously. The results presented here suggested that to design lateral interactions networks and strong interactions between molecules and substrate at the same time will be a new strategy to organize molecules into stable highly ordered ensembles on solid surfaces spontaneously. This will be of great significance to incorporation of organic functional molecules into electronic devices.

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