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Ex Situ SFM Study of 2-D Aggregate Geometry of Azobenzene Containing Bolaform Amphiphiles after Adsorption at the Mica/Aqueous Solution Interface

Bo Zou, Liyan Wang, Tao Wu, Xiaoyong Zhao, Lixin Wu, and Xi Zhang*

Key Lab of Supramolecular Structure and Spectroscopy, Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China

Song Gao, Michael Gleiche, Lifeng Chi,* and Harald Fuchs

Physikalisches Institut, Westfälische Wilhelms-Universität, D-48149, Münster, Germany

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Self-assembled nanometer-sized stripes are obtained spontaneously by electrostatic adsorption of bolaform amphiphiles bearing hydrophilic pyridinium headgroups and rigid hydrophobic azobenzene onto mica sheets. The ordered stripes have a repeat spacing of 10 nm, and the ordered region can extend over macroscopic areas. The formation of such nanostructures mainly depends on the concentration of the bolaform amphiphiles. The template effect of the mica sheet also plays a crucial role in the molecular organization at the liquid–solid interface. The degree of order of the stripes is influenced by adding electrolyte into the aqueous solution or upon irradiating the solution for physical adsorption under UV light.

Introduction

Amphiphiles at interfaces are a traditional but challenging topic in colloid chemistry and now especially in supramolecular science.¹ The aggregation behavior of amphiphiles is usually complex and depends strongly on their structure and solution conditions. Bolaform amphiphiles are molecules containing two hydrophilic moieties connected by a hydrophobic chain.² They can also be viewed as two conventional amphiphiles covalently linked via their hydrophobic chain ends. In diluted solutions, they may form elongated, threadlike and platelike micelles. Lamellar lyotropic mesophases are usually found in more concentrated systems. Bolaform amphiphiles bearing rigid mesogenic parts are amphotropic; that is, they display lyotropic as well as thermotropic phase behavior.^{3,4} Membranes consisting of a mixture of bolaform lipids and conventional lipids show higher stability against chemical and thermal degradation.⁵ It has also been shown that cationic bolaform amphiphiles can form self-assembled monolayers on negatively charged substrates and be used widely to assemble multilayer nanoarchitectures by sequentially alternating adsorption.⁶

Surface patterning with microscopically defined structures is another rapidly developing topic. It can be used

to control various physical properties locally. Many techniques have been used to provide laterally structured surfaces, such as microphase separation of block copolymers⁷ and the well-established concept of soft lithography.⁸ Mesoscopic two-dimensional (2-D) ordering of inorganic/organic hybrid structures can be also formed by simple cast films.⁹ However, building up of regular arrays of nanostructures through molecular self-assembly has been less frequently addressed. Because molecular assemblies are normally in the size range of 1–100 nm, surface patterning based on molecular self-assembly may provide an alternative way that could overcome the lithographic limit. Recently, some interesting results have been reported concerning the regular packing of two-dimensional aggregates formed by amphiphilic molecules at the air–water interface and transferred onto solid substrates.¹⁰ Zhang et al. have demonstrated that the self-assembled monolayer of polyether dendron can lead to the formation of a patterned surface with nanometer-sized

* To whom correspondence should be addressed. Fax: +86-431-8923907. E-mail: Xi@mail.jlu.edu.cn.

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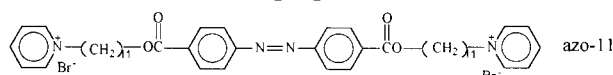
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Chart 1. Chemical Structures of Bolaform Amphiphiles

features and the nanostructure can be controlled by the size of the dendron.¹¹

Since Manne et al. observed the existence of surface micelles using the scanning force microscope (SFM) in 1994,¹² the surface aggregations of ionic, nonionic, and zwitterionic surfactants have been widely studied.¹³ Direct images of surfactant aggregates at solid/liquid interface are obtained with precontact repulsive forces in fluid. The shapes of aggregates are thought to result from a compromise between free curvature as defined by the dimensionless packing parameter and the specific constraints imposed by molecule–substrate interaction. However, the surface micelles of conventional surfactants are stable only in solution, so the ordered structure cannot be observed after the substrate has left the solution environment. We have occasionally found that a kind of bolaform amphiphile containing hydrophilic pyridinium headgroups and rigid hydrophobic azobenzene can be physically adsorbed onto mica sheets to form stable nanostripes at ambient conditions.¹⁴ We herein report further studies on the self-assembly of bolaform amphiphiles at the liquid/solid interface, focusing on the formation of patterned surface structures on solid substrates. Our main interest is to understand how the experimental conditions and chemical structures of the bolaform amphiphiles influence the molecular packing in the self-assembled nanostructures.

Experimental Section

The bolaform amphiphile used in this work, azobenzene-4,4'-dicarboxylic acid bis(pyridinium undecyl ester) dibromide (**azo-11**) (Chart 1), is provided by Professor H. Ringsdorf and Dr. V. Hessel, Institute of Organic Chemistry, University of Mainz, Germany. The synthesis of the substances is described elsewhere.⁶

We selected muscovite mica (purchased from PLANO W. Plannet GmbH, Germany) as the substrate to adsorb the bolaform amphiphiles. A freshly cleaved mica sheet was immersed into an aqueous solution of the bolaform amphiphile **azo-11**. The concentration of **azo-11** used for adsorption was chosen to be 1.0×10^{-4} M, above the critical micelle concentration (cmc). After adsorption for 30 min, the mica sheet was taken out, washed with Milli-Q, and dried for about 30 min in a desiccator (with P_2O_5). Except for the kinetics study, adsorption time was fixed at 30 min.

SFM observation of the self-assembled nanostructures was carried out at room temperature with commercial instruments (Digital Instruments, Nanoscope IIIA, Dimension 3000 and Multimode) using Si cantilevers purchased from DI and Nanosensor. E and J scanners were selected for Multimode. The SFM images were taken with instruments operating in tapping

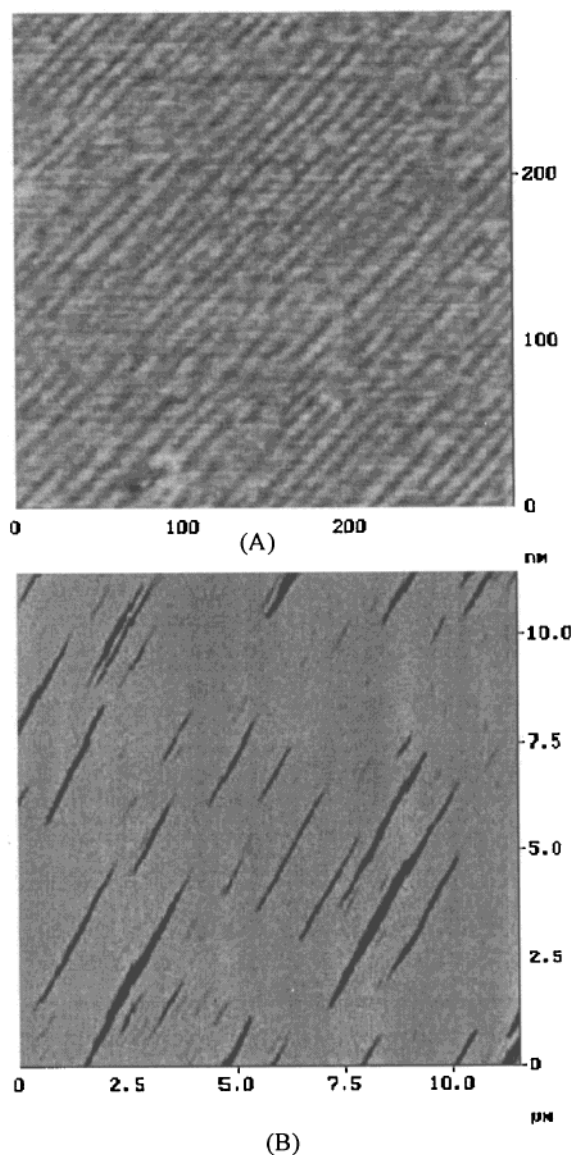


Figure 1. SFM images of bolaform amphiphile **azo-11** on a mica sheet. Self-assembled nanosized stripes are formed by immersion of the mica sheet into an aqueous solution of **azo-11** with a concentration of 1.0×10^{-4} M, as shown (A) in small areas and (B) in large areas.

mode (height and phase) for air. We used section analysis to analyze the width of stripes and the depth of the monomer. We used bearing analysis to analyze the coverage of the sample.

UV/vis spectra were recorded on a Shimadzu UV spectrometer for the aqueous solution of **azo-11**. Fluorescence spectra were recorded on a Shimadzu RF spectrometer to measure the cmc of the aqueous solution of **azo-11**.

Results and Discussion

1. Surface Adsorption. SFM observation reveals that **azo-11** forms well-ordered stripes on a freshly cleaved mica sheet (Figure 1A). On the basis of section analysis, the mean spacing of ordered stripes is approximately 10 nm. The dark areas seen here are uncovered regions. The defects also show a preferred orientation (Figure 1B). The stripes are packed parallel to the elongated defects. The ordered regions with the same orientation extend to lengths on the order of a centimeter. The width of the ordered stripes indicates that such an ordered structure is formed by regular packing of molecular assemblies rather than by just single molecules. Control experiments

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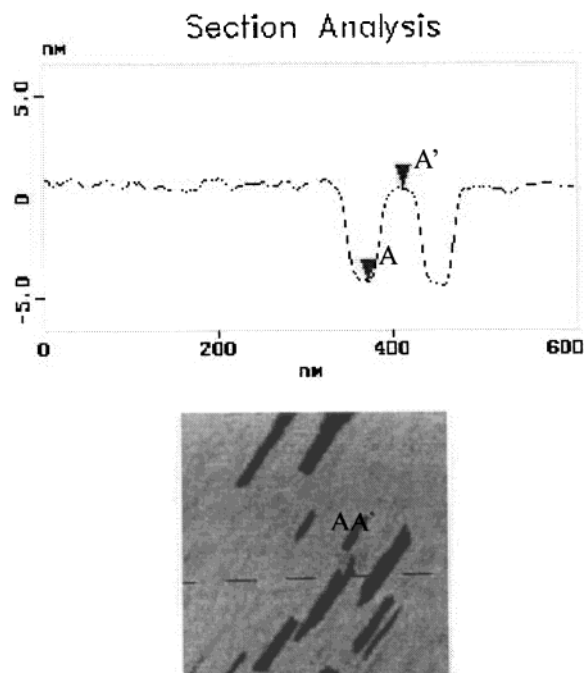


Figure 2. Section analysis of the thickness of the assemblies of **azo-11**.

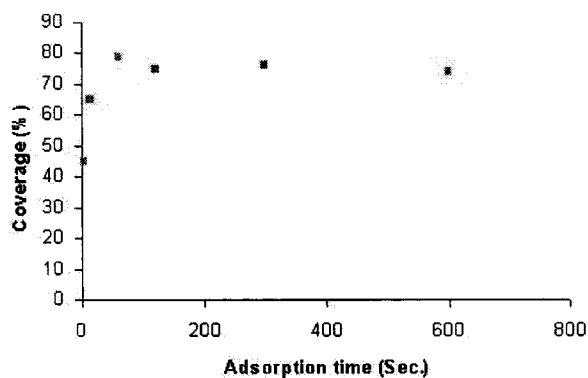


Figure 3. Relationship between film coverage (%) and adsorption time (s). The concentration of bolaform amphiphile **azo-11** used for adsorption is 1.0×10^{-4} M.

were performed by observing a blank, freshly cleaved mica sheet under the same conditions. These experiments revealed that the surface of the blank mica sheets was homogeneous and without any unique structures, because of the resolution limit of the tapping mode.

Figure 2 shows a section analysis of the thickness of self-assemblies of **azo-11** on a mica sheet. The cross-sectional profile along the line A–A' of this image shows that the depth of the step between A and A' is approximately 4.6 nm. This result is in good agreement with the layer spacing, 4.2 nm, of the cast film, which is deposited on a silicon slide and determined by X-ray diffraction. From a molecular modeling calculation, the molecular length of **azo-11**, in its fully stretched form, is estimated to be 4.3 nm. Therefore, it is concluded that the **azo-11** molecules are deposited monomolecularly onto the mica sheets.

The kinetics of the adsorption process was studied by analyzing the film coverage from SFM images with bearing analysis. The coverage was found to reach its maximum value within 2 min and keep almost constant thereafter (Figure 3). We have elongated the adsorption time up to 24 h; there is no difference regarding the maximum adsorption. The maximum coverage is about 75%, indi-

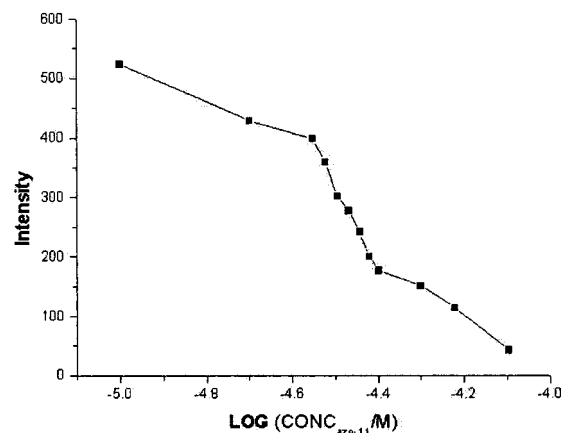


Figure 4. Measurement of cmc by using the fluorescence quench blanking method.

cating the existence of many defects. The very fast adsorption process would be in conjunction with the fact that electrostatic attraction may occur between the mica surface and surfactant aggregates. However, the driving force for the surface adsorption should be based on collective interaction of different intermolecular forces as well as an entropy effect.

2. Concentration Effect. The micellar behavior of **azo-11** was characterized by the fluorescence quench blanking method. The exciting wavelength (λ_{ex}) was chosen to be 290 nm, and the fluorescence spectrum showed two emission band peaks at 325 nm and 360 nm, respectively. With the increasing of concentration, the fluorescence intensity gradually decreases. The concentration at which fluorescence intensity demonstrates acute change is usually considered to be the cmc. Figure 4 shows the change of fluorescence intensity (325 nm as indicator) plotted against the concentration of **azo-11**. From this figure, we obtain a cmc of 3.4×10^{-5} M for **azo-11**.

We and other groups have previously used similar bolaform amphiphiles in fabricating layer-by-layer assemblies, but no such nanosized ordered structures have been found. A possible reason could be that the concentrations of bolaform amphiphile used for adsorption are often lower than the cmc of amphiphiles to avoid the possibility that micelles instead of isotropically dissolved monomers might adsorb on mica.⁶

Considering concentrations used for adsorption are above the cmc, we could speculate that the formation of the ordered structure may be related to the micelle in the solution. To investigate possible concentration dependence, **azo-11** concentration was varied systematically. We found that stripe structures are formed for a concentration of 5.0×10^{-5} M and above. The ordered structures show little change even when the concentration is as high as 1.0×10^{-3} M. However, there is a critical concentration, 3.3×10^{-5} M, at which ordered structures and irregular aggregates coexist (Figure 5A). It is in good agreement with the cmc. Below this concentration, for example at 2.5×10^{-5} M, stripe structures are completely lost. Instead, only irregular aggregates exist on the mica sheet (Figure 5B).

3. Template Effect. We believe the cooperative effect of electrostatic interactions, π – π stacking, and van der Waals forces plays an important role in molecular organization in solution and at the liquid–solid interface. It is found that the ordered packing of stripes could not form without a crystalline template, that is, a mica sheet. When depositing two layers of polyelectrolytes of diazoresin and poly(sodium styrene sulfonate) alternatively

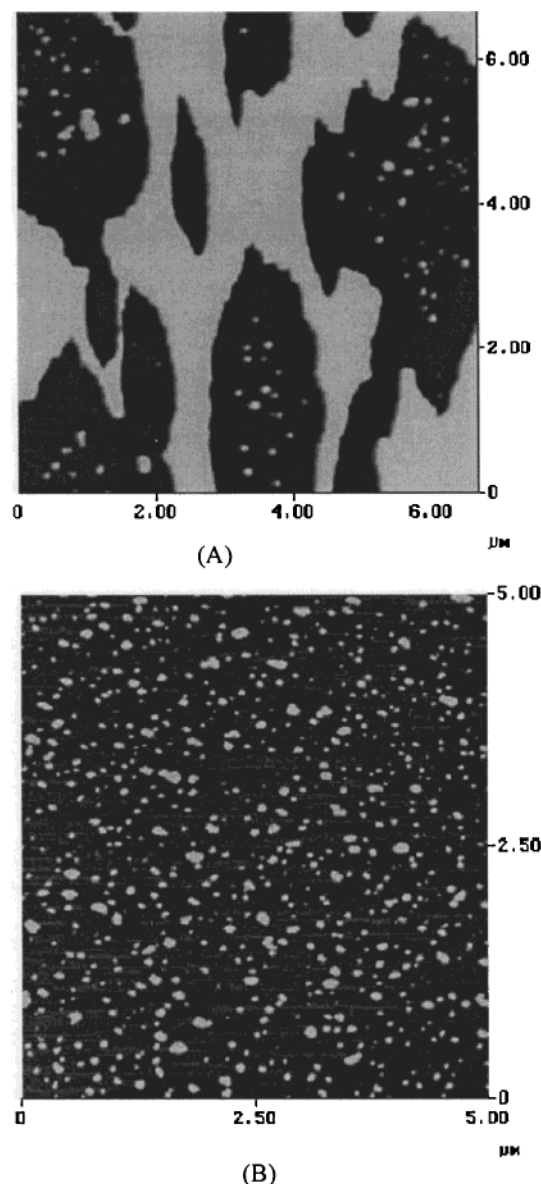


Figure 5. Ordered structures and irregular aggregates coexist when the concentration of **azo-11** reaches a critical value, 3.3×10^{-5} M, as shown in (A). Only irregular aggregates exist on the mica sheet when the concentration of **azo-11** is diluted to as low as 2.5×10^{-5} M, as shown in (B).

onto the mica sheet,¹⁵ a resulting mica sheet with negative charge but amorphous surface was obtained. With such a mica sheet, we repeated the previous experiments. It is found that the bolaform amphiphile **azo-11** can adsorb onto the negatively charged surface, but it cannot form any regular supramolecular structures on an amorphous surface. Furthermore, by replacing the mica sheet by a silicon or glass slide, **azo-11** can spread well onto the silicon and glass slide, but it cannot form any ordered structures in a long-range order (Figure 6A). Instead, roughly round aggregates are distributed irregularly onto the silicon slides.

To further demonstrate the template effect, we used a kind of modified mica sheet with rhombus holes as substrates.¹⁶ To realize mica with rhombus holes, the mica was bombarded with heavy ions and then treated with

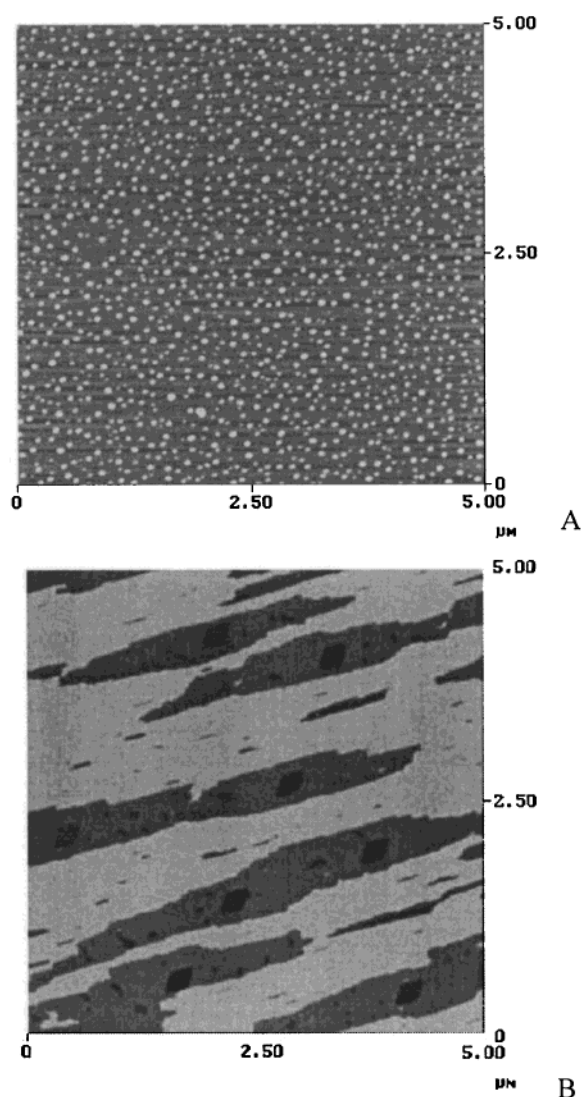


Figure 6. SFM image of **azo-11** adsorbing on substrates: (A) silicon and (B) mica which is modified with rhombus holes.

HF. It is found that the nice nanostripes of **azo-11** can form well in this modified mica without adsorption around the holes (Figure 6B). An interesting finding is that the nanostripes expectedly orient along the edge of the rhombus holes. Yang et al. reported the existence of energetically preferred attachment sites along a particular orientation relative to the mica crystal.¹⁷ In our case, it is believed that the order of **azo-11** stripes is correlated to the orientation of the substrate.

4. Photoinduced Variation of Surface Structure.

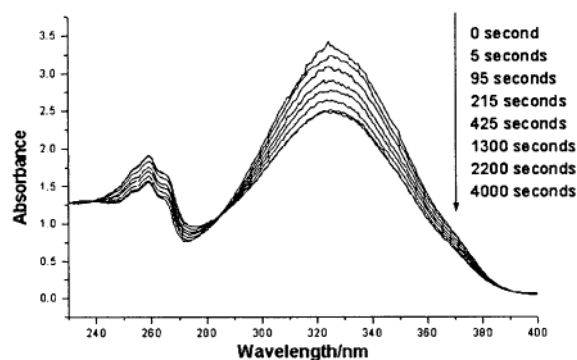
The photoinduced trans–cis isomerization of azobenzene is a well-known photochemical phenomenon, and many derivatives bearing azobenzene have received attention because of the potential applications in the area of optical storage devices.¹⁸ Figure 7A shows the change in UV/vis adsorption of **azo-11** in water upon irradiation with light at 324 nm. The adsorption peak around 259 nm is attributed to the $\pi-\pi^*$ transition of *cis*-azobenzene, and the peak around 324 nm is attributed to *trans*-azobenzene.¹⁹ The isosbestic points indicate that only one photoprocess occurs simultaneously. After 40 min of UV

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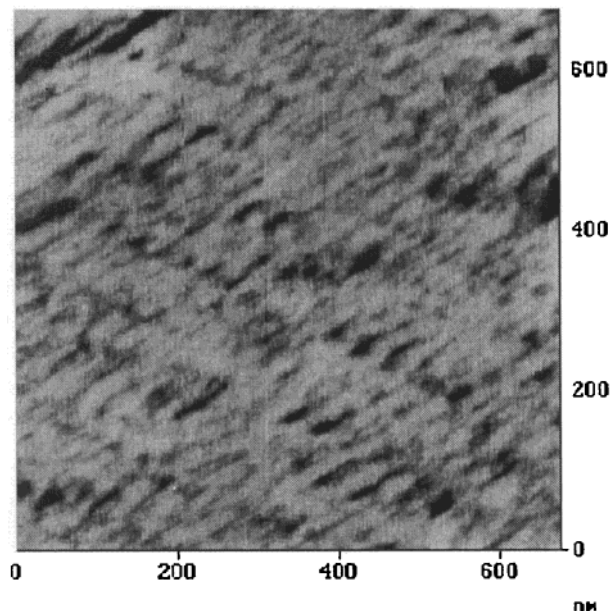
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(A)



(B)

Figure 7. (A) UV-vis absorption spectra of **azo-11** with different irradiation time under UV-vis light. (B) SFM image of **azo-11** adsorbing on a mica sheet. The **azo-11** aqueous solution used for adsorption is irradiated for about 40 min before immersion of the mica sheet and during the adsorption process.

irradiation, trans-cis isomerization reaches its equilibrium. It is seen that the trans-cis isomerization cannot be complete in this case. In other words, trans and cis isomers can coexist even after UV irradiation in this condition.

After the **azo-11** solution was exposed under UV irradiation for up to 40 min, a clean mica sheet was immersed into the **azo-11** solution for 30 min while irradiating with the UV source. The condition for the surface adsorption was kept the same as mentioned above. We found a coexistence of irregular regions and ordered ones, although some places hold the ordered structures as shown in Figure 7B. One possible reason is that the trans-cis isomerization of azobenzene between the bolaform amphiphile could partially influence the aggregation behavior of bolaform amphiphile in solution and subsequently influence the interfacial aggregation. *trans*-Azobenzene can form lamellar structures easily, whereas it is difficult for *cis*-azobenzene to do so. This observation fits well into the above data that the trans-cis isomerization cannot be completed for the system, as revealed

by UV/vis absorption spectra. At room temperature and after UV irradiation, the trans-cis isomers coexist. Therefore, under these conditions, we cannot get perfect stripes. Furthermore, a post-UV irradiation upon the self-assembled nanostripes on mica sheets does not induce any obvious change.

5. Effect of Electrolyte Additives on the Surface Structure. The interfacial aggregation through electrostatic adsorption can be influenced by adding electrolytes into the solution.²⁰ We kept the concentration of **azo-11** constant at 1.0×10^{-4} M while changing the concentration of electrolytes in the solution systematically in order to study the effect of electrolyte. With the increase of the electrolyte concentration, the coverage of the self-assemblies on mica is changing, from low to high and from high to low. Above a critical concentration, a patterned structure could be extended over large areas almost without defect. The concentration is fixed the same for comparison of the effect of different electrolytes. Different electrolytes have different defect-free concentrations. Keeping the same cation Na^+ , the order of defect-free concentration for electrolytes is sodium chloride (no critical concentration) > sodium iodide (9×10^{-4} M) > sodium salicylate (5×10^{-4} M) > sodium perchlorate (1×10^{-4} M).

Figure 8 show SFM images of the self-assembled bolaform amphiphiles on the freshly cleaved mica sheets at different sodium perchlorate concentrations. The concentration of this electrolyte is changed from 1.0×10^{-4} M to 0.1 M. When a small amount of electrolyte is added ($C = 1.0 \times 10^{-4}$ M), the coverage can be as high as 99.8% in the range $6 \times 6 \mu\text{m}^2$ (Figure 8A). If zoomed in small scale, we can find that only a slight change is induced for the nanostripes (Figure 8B). When we increase the electrolyte concentration to 5×10^{-4} M, we can observe that the nanostripes no longer keep the same orientation (Figure 8C) and the coverage decreases to 85.5%. With the increase of the electrolyte concentration, the ions should take up some of the adsorption sites, resulting in a lower coverage. When the concentration of the electrolyte is as high as 0.1 M, the long-range ordered structure disappears completely (Figure 8D).

Because sodium salicylate has a strong attraction for bolaform amphiphiles with hydrophilic pyridinium headgroups,²¹ exchange of halide ions with the strongly associating salicylate ions reduces electrostatic repulsion between headgroups and favors the self-assembly and close-packing of bolaform amphiphiles. In this case, because of the banding of salicylate with pyridinium headgroup, the width of the ordered stripes is extended to be about 16 nm (Figure 9). So, we can adjust the width, coverage, and orientation of the stripes from changing the kind of electrolyte and its concentration.

Conclusion

In summary, we have done successfully the ex situ SFM study of the 2-D aggregate geometry of azobenzene containing bolaform amphiphiles after adsorption at the mica/aqueous solution interface. The features of the bolaform amphiphiles enrich some unique properties of the ordered structure like stability, in nanometer scale and over larger areas. It was reported that the bolaform amphiphile bearing mesogenic groups inclines to form a lamellar structure in aqueous solution. So, the formation of nanostripes should be incurred by a fusion of lamellar micelles on a planar mica sheet. We assume that the outer

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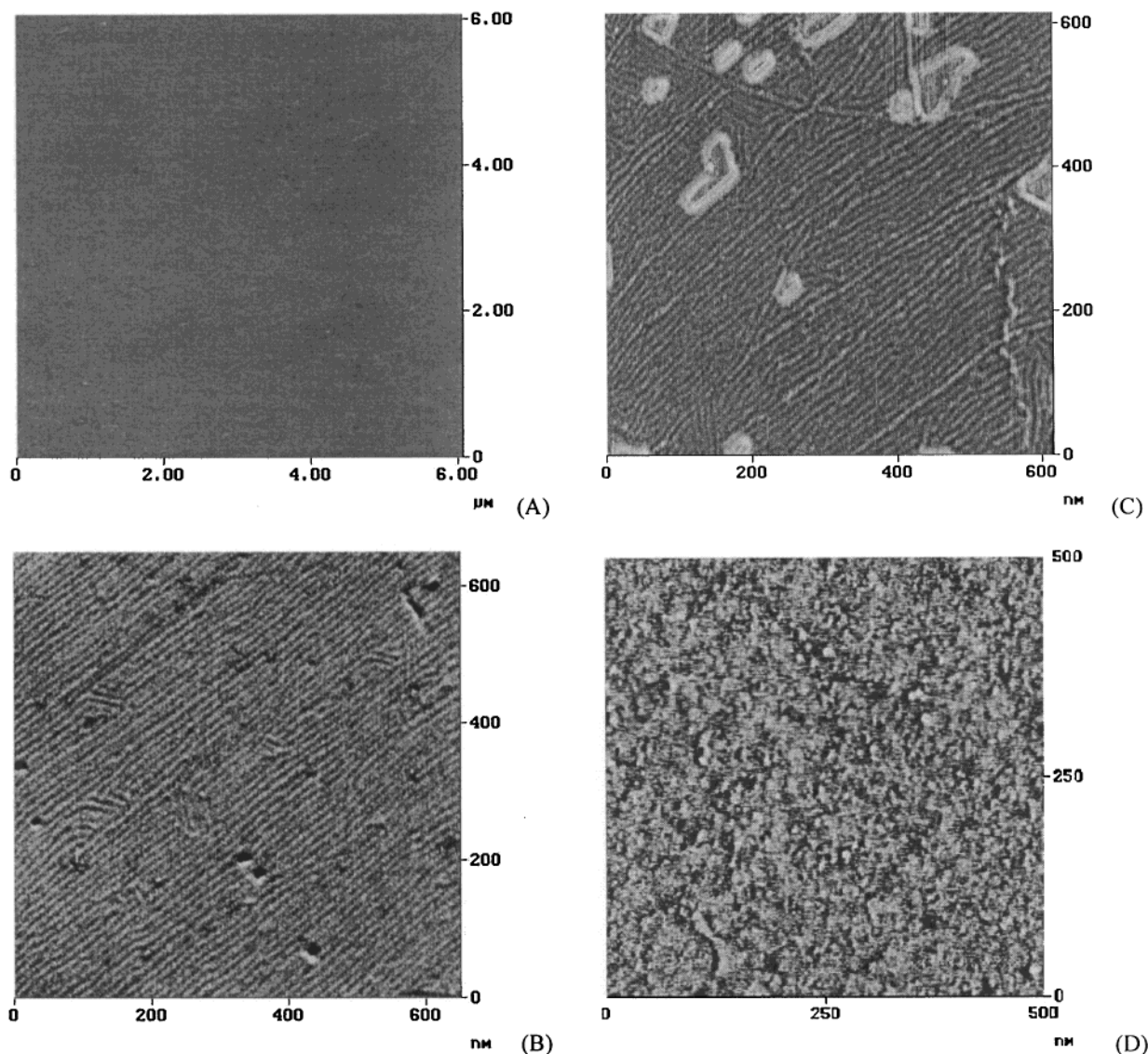


Figure 8. SFM images of **azo-11** adsorbing on a mica sheet. The image in large scale resulted from **azo-11** solutions with sodium perchlorate, $c = 1.0 \times 10^{-4}$ M, as shown in (A). Also shown are images resulting from **azo-11** solutions with different sodium perchlorate concentrations: (B) $c = 1.0 \times 10^{-4}$ M, (C) $c = 5.0 \times 10^{-4}$ M, and (D) $c = 1.0 \times 10^{-1}$ M.

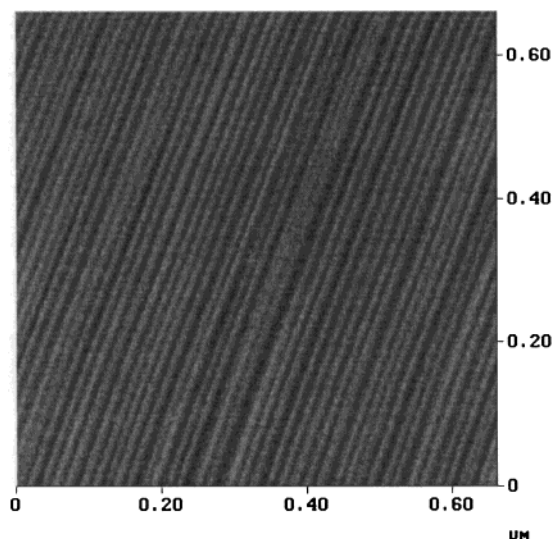


Figure 9. SFM image of **azo-11** adsorbing on a mica sheet, resulting from **azo-11** solutions with sodium salicylate.

surface of a lamellar micelle should be different from the inner surface that interacted with the negatively charged

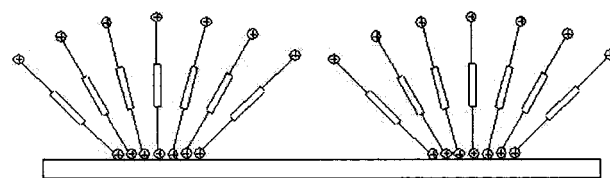


Figure 10. Model for the structure of **azo-11** adsorbed on the mica sheet.

surface of mica because of electrostatic interaction between the adjacent layers. This could be responsible for the formation of curvature of the ordered surface structures (Figure 10). Such an electrostatic mismatch can alter the energy balance in the aggregate with the change in electrostatic interactions also affected by hydration/counterion effects along with van der Waals and hydrophobic interactions (and possibly the π -stacking interactions in this case), the balance of which may certainly result in a change in aggregation state. The mechanism for the long-range order is not very clear, but the template effect of the substrate should play an important role in surface organization.

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