

Nano-size stripes of self-assembled bolaform amphiphiles

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Self-assembled nano-sized stripes are obtained spontaneously by electrostatic adsorption of bolaform amphiphiles onto mica sheets. The ordered stripes are separated from each other by about 10 nm, and the ordered region can extend over macroscopic areas.

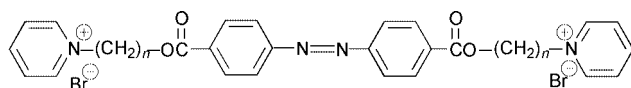
Amphiphiles at interfaces are a traditional but challenging topic in colloid chemistry, and now especially in supramolecular science.^{1,2} Bolaform amphiphiles are molecules containing two hydrophilic moieties connected by a hydrophobic chain.³ It is shown that bolaform amphiphiles have different aggregation behaviors,⁴ and cationic bolaform amphiphiles can form a self-assembled monolayer on negatively charged substrates.^{5,6} Surface patterning with microscopically defined structures is another rapidly developing topic.⁷ Some interesting results have recently been reported concerning the regular packing of two-dimensional aggregates formed by amphiphilic molecules at the air–water interface and transferred onto solid substrates.^{8,9} The self-assembled monolayer of the polyether dendron can lead to the formation of a patterned surface with nanometer-sized features and the nanostructure can be controlled by the size of the dendron.^{10,11}

Combining the above two fields, we herein report not only the interfacial self-assembly of bolaform amphiphiles, but also an approach for creating ordered nano-sized surface structures. They are obtained spontaneously by electrostatic adsorption of bolaform amphiphiles containing rigid hydrophobic azobenzene groups and hydrophilic pyridinium head groups onto mica slides. The size of the structure is in the nanometer region and it is formed by molecular self-assembly at the liquid–solid interface. Our main interest is to establish a method for surface patterning and to understand how the experimental conditions or chemical structure influence the molecular packing in the self-assembled nano-structures.

The bolaform amphiphiles included in this work are azobenzene-4,4'-dicarboxylic acid bis(pyridiniohexyl ester) dibromide (**azo-11**), and azobenzene-4,4'-dicarboxylic acid bis(pyridinioundecyl ester) dibromide (**azo-6**) (Scheme 1). The syntheses of the substances are described elsewhere.⁴ Scanning force microscopy (SFM) observation of the self-assembled nano-structures was carried with commercial instruments (Digital Instrument, Nanoscope III, Dimension 3000TM and MultimodeTM), operating in tapping mode.

To construct nano-sized stripes on mica a clean mica sheet was immersed into aqueous solution of **azo-11** (*c.* = 1.0×10^{-4} M, unless given otherwise). After adsorption for a certain time, the mica sheet was taken out and dried for about 30 min in a desiccator (P₂O₅). Except for the kinetics study, adsorbing time was 30 min for **azo-11** and **azo-6**.

Confocal Raman of the mica sheet after immersion in **azo-11** solution for 30 min confirmed that dicationic **azo-11** was



n = 6, **azo-6**; *n* = 11, **azo-11**

Scheme 1 Chemical structures of bolaform amphiphiles.

successfully adsorbed. We observed four peaks at 1403, 1457, 1497 and 1602 cm⁻¹, where the former two peaks corresponded to azo Fermi, and the latter two peaks were attributed to benzene.

The adsorption kinetics were studied by analyzing the film coverage from SFM images. This increases rapidly for **azo-11** with adsorption time initially. From SFM, within about 2 min, the film coverage reaches equilibrium and remains almost constant thereafter. It is conjectured that electrostatic attraction between the substrate and adsorbing molecules is the driving force for adsorption of cationic molecules onto the negatively charged surface.

SFM observation reveals that **azo-11** forms well-ordered stripes on a freshly cleaved mica sheet (Fig. 1A). The mean distance of ordered stripes is about 10 nm. They show a preferred orientation (Fig. 1B). The dark areas seen here are uncovered regions. The stripes are packed parallel to the elongated defects. The ordered regions with the same orientation can extend to large areas, up to centimeters. The nanometer size of the ordered stripes indicates that such an ordered structure is not formed by regular packing of single molecules but rather by molecular assemblies. Considering the fact that the **azo-11** concentration used for adsorption is above the critical micelle concentration (cmc), we speculate that the formation of the structure should be related to the micelle in the solution.

In order to confirm the above speculation, we varied the **azo-11** concentration systematically. We found that stripe structures are formed for concentrations of 5.0×10^{-5} M and above, even at 1.0×10^{-3} M, although the ordered structure shows a slight change at this concentration compared with the normal one. However, there is a critical concentration, 3.3×10^{-5} M, at which ordered structures and irregular aggregates co-exist (Fig. 1C). Below this, *e.g.* at 2.5×10^{-5} M, stripe structures may be completely lost. Instead, only irregular aggregates exist on the mica sheet (Fig. 1D). The cmc of **azo-11** was measured to be 3.4×10^{-5} M by the dramatic change of fluorescence with concentration.

Ourselves and others have used similar bolaform amphiphiles to fabricate the layer-by-layer assemblies previously, but no such nano-sized structure has been found. The reason could be that the concentration of bolaform amphiphile used for assemblies is often chosen to be lower than the critical concentration in order to avoid micelles and to ensure isotropic monomer deposition for multilayer construction.^{5,6} Further evidence to support the above argument is given by UV/Vis irradiation experiments. After the **azo-11** solution was exposed to UV/Vis irradiation for up to 30 min, the film was prepared under the same conditions as above. Although mostly ordered regions were observed, we found that there are also some irregular regions. One possible reason is the *trans*–*cis* isomerization of azobenzene in between the bolaform amphiphile, which could partially destroy the structure of elongated micelles in solution. The UV/Vis absorption spectra support our assumption that the *trans*–*cis* isomerization can not be complete for the system, and some *cis*–*trans* mixture exists even after UV/Vis irradiation for 30 min.

For a similar bolaform amphiphile but with a shorter spacer, **azo-6**, we cannot find any similar structures even when we vary

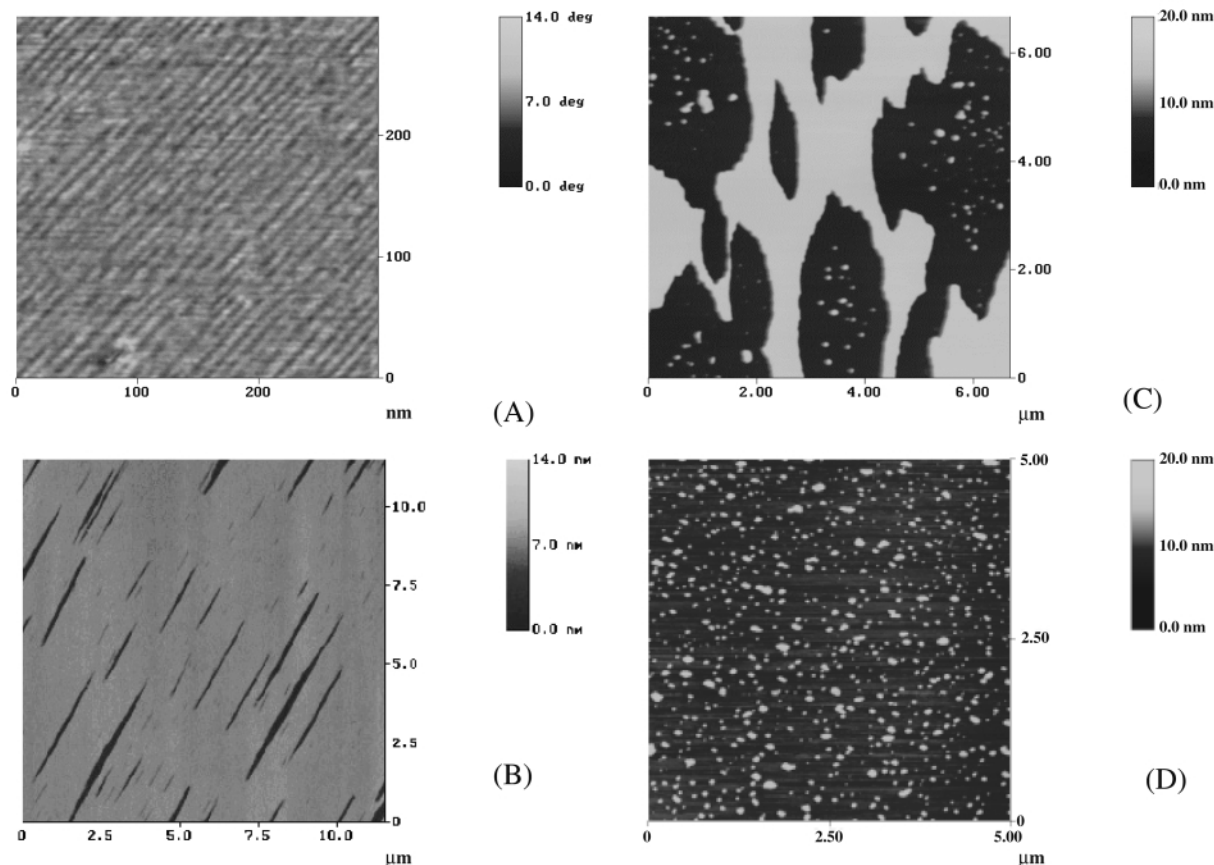


Fig. 1 SFM images of **azo-11** on a mica sheet. Self-assembled nano-sized stripes are formed by immersion of mica sheet into an aqueous solution of **azo-11** ($c. 1.0 \times 10^{-4}$ M), as shown in (A) in small areas and (B) in large areas. Ordered structures and irregular aggregates co-exist when the concentration of **azo-11** reaches a critical value, 3.3×10^{-5} M (C). Only irregular aggregates exist on mica sheet when the concentration of **azo-11** is as low as 2.5×10^{-5} M (D).

the concentration and prolong adsorbing time. It is inferred that the compromise between aggregation behavior of the compounds in solution, electrostatic interaction and van der Waals forces *etc.* plays an important role in molecular organization at the liquid–solid interface.

It is also found that the ordered packing of stripes could not form without a crystalline template *i.e.* a mica sheet. By depositing two layers of polyelectrolytes of diazo-resin and poly(sodium styrene sulfonate) alternately onto the mica sheet, a modified mica sheet with a negative charge but an amorphous surface was obtained. With this modified mica sheet, we repeated the previous experiments and found that the bolaform amphiphile **azo-11** can adsorb onto the negative charged surface. Unfortunately, no regular supramolecular structures were formed. Furthermore, by replacing the mica sheet by a glass slide, **azo-11** spread well onto the glass slide, but did not form any ordered structures.

In conclusion, we have demonstrated a very simple way to create ordered surface structures, based on the self-assembly of bolaform amphiphiles at the liquid–solid interface. As a result, it enhances many of the unique features of the ordered structure, like stability on a nanometer scale and over very large areas. Considering the great diversity of bolaform amphiphiles, we anticipate that this type of pattern fabricating method might open up other possibilities for surface modification.

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Notes and references

- 1 J. M. Lehn, *Supramolecular Chemistry—Concepts and Perspectives*, VCH, Weinheim, 1995.
- 2 H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem., Int. Ed. Engl.*, 1988, **23**, 113.
- 3 J. H. Fuhrhop, U. Liman and H. H. David, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 339.
- 4 V. Hessel, H. Ringsdorf, R. Laversanne and F. Nallet, *Recl. Trav. Chim. Pays-Bas*, 1993, **112**, 339.
- 5 G. Decher, in *Comprehensive Supramolecular Chemistry*, vol. 9, ed. J. P. Sauvage and M. W. Hosseini, Pergamon, Oxford, 1996, pp. 507–528.
- 6 X. Zhang and J. C. Shen, *Adv. Mater.*, 1999, **11**, 1139.
- 7 Y. Xia, J. A. Rogers, K. E. Paul and G. M. Whitesides, *Chem. Rev.*, 1999, **99**, 1823.
- 8 S. Manne and H. E. Gaub, *Science*, 1995, **270**, 1480.
- 9 T. Kato, M. Kameyama, M. Ehara and K. I. Imura, *Langmuir*, 1998, **14**, 1786.
- 10 Z. S. Bo, L. Zhang, X. Zhang, J. C. Shen, S. Höppener, L. F. Chi and H. Fuchs, *Chem. Lett.*, 1998, 1197.
- 11 L. Zhang, F. W. Huo, Z. Q. Wang, L. X. Wu, X. Zhang, S. Höppener, L. F. Chi, H. Fuchs, J. W. Zhao, L. Niu and S. J. Dong, *Langmuir*, 2000, **16**, 3813.