

## Stabilizing interfacial micellar aggregates by enhanced supramolecular interaction or surface polymerization\*

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*Abstract:* This presentation describes the surface micelles formed by self-organization of amphiphilic molecules at the solid/liquid interface, and reviews the methods of stabilizing the surface micelles by enhancing the intermolecular interaction or introducing covalent bonds in self-assemblies. This type of work may provide new avenues for fabricating organic nanostructure materials, as well as possible applications arising from the mimicry of biomineralization processes.

*Keywords:* scanning transmittometry; sampling; particle synthesis.

### INTRODUCTION

Amphiphiles can self-organize into micellar structures with defined size and shape in bulk solutions [1,2], and these structures can adsorb onto a solid/liquid interface forming ordered surface micelles. Although the existence of the surface micelles was proposed in 1955 [3], it was not confirmed for a long time because of the limit of characterization methods. In 1994, Manne and Gaub employed a scanning force microscope to observe the interfacial organization of surfactant and for the first time provided the direct evidence of surface micelles [4]. From then on, the interfacial organization of surfactant was widely studied, and it was found that the conventional surfactants such as hexadecyltrimethylammonium bromide (CTAB) can form adsorbed spherical, cylindrical, or hemicylindrical micelles, and bilayer structures at a solid/liquid interface [4–6]. Because the forces that hold the amphiphilic molecules together are not caused by strong covalent or ionic bonds but arise from weak forces such as van der Waals, hydrophobic interaction [7], these structures can only be visualized at the solid/liquid interface; when the substrate is taken out from the solution, these well-defined structures will fall apart. Engineering the robustness of the interfacial structures may lead to applications such as templates for making nanostructured materials and mimicking biomineralization processes. We adopted two ways to stabilize the interfacial aggregates: enhancing the intermolecular interaction and introducing a covalent-bond link in the organization.

In the past few years, we have focused on the design and synthesis of self-organizing units for surface micelles at solid/liquid interfaces, as shown in Fig. 1. On the one hand, we have proposed a method for stabilizing surface micelles by enhancing intermolecular interactions [8–13]. On the other hand, we have employed physically initiated polymerization to stabilize surface micelles made of polymerizable surfactants [14]. Owing to the environment-reliable property of the self-assemblies, tapping

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in fluid atomic force microscope (in situ AFM) is employed to observe the structure of the surface micelles at the solid/liquid interface. By this technique, the morphology of a surface micelle can be visualized without being destroyed, because the scanning probe only gently taps but does not scratch the sample surface. To confirm if the surface micelles are stable against the drying process, ex situ AFM observation is also carried out in air. Herein, we introduce several possibilities of fabricating stable surface micelles based mainly on our own work, and discuss the factors that govern the morphology and robustness of the resulting surface aggregates.

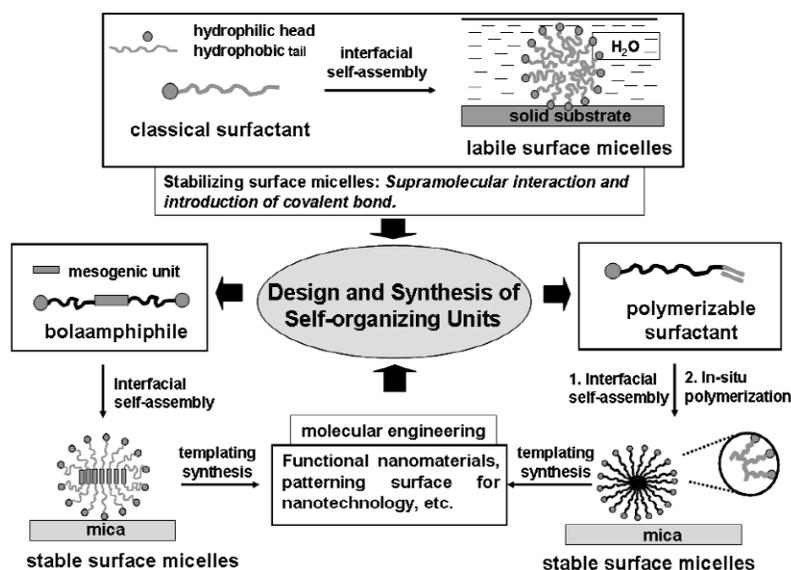
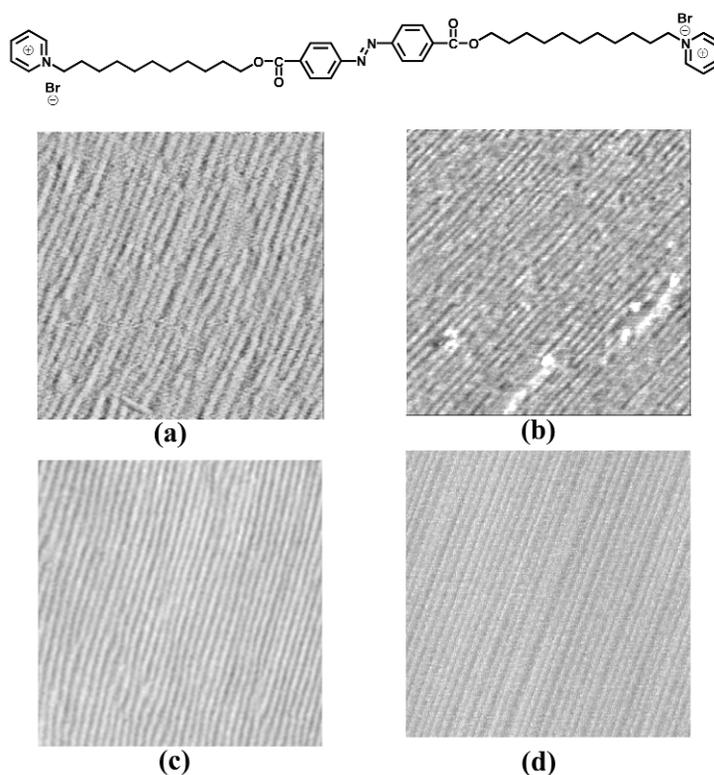


Fig. 1 Schematic illustration of ways to stabilize surface micelles.

## INTRODUCTION OF MESOGENIC GROUPS INTO BOLAAMPHIPHILE

Bolaamphiphiles are molecules containing two hydrophilic heads connected by hydrophobic chains [15]. It is known that the bolaamphiphiles have special aggregation behavior compared with the conventional surfactants [15,16], and cationic bolaamphiphiles can form a self-assembled monolayer on negatively charged substrates [17,18]. The introduction of mesogenic group into the bolaamphiphiles may enhance the intermolecular interaction of the bolaamphiphiles and result in robust supramolecular self-assemblies.

Based on this idea, we designed and synthesized a bolaamphiphile bearing an azobenzene mesogenic group and two hydrophilic pyridinium heads, **azo-11**, as shown in Fig. 2 [8–10]. In situ AFM observation reveals that **azo-11** forms well-ordered stripes on a freshly cleaved mica sheet (Fig. 2a). The stripes show a preferred orientation with a mean distance about 10 nm. 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. In testing the stability of the molecular assemblies, the substrate is taken out from the solution, dried in air, and observed by ex situ AFM. As shown in Fig. 2b, the stripes still exist and the stripe width keeps the same as that obtained by in situ AFM observation, which shows that the supramolecular aggregates formed by self-organization of **azo-11** are stable enough against the drying process.



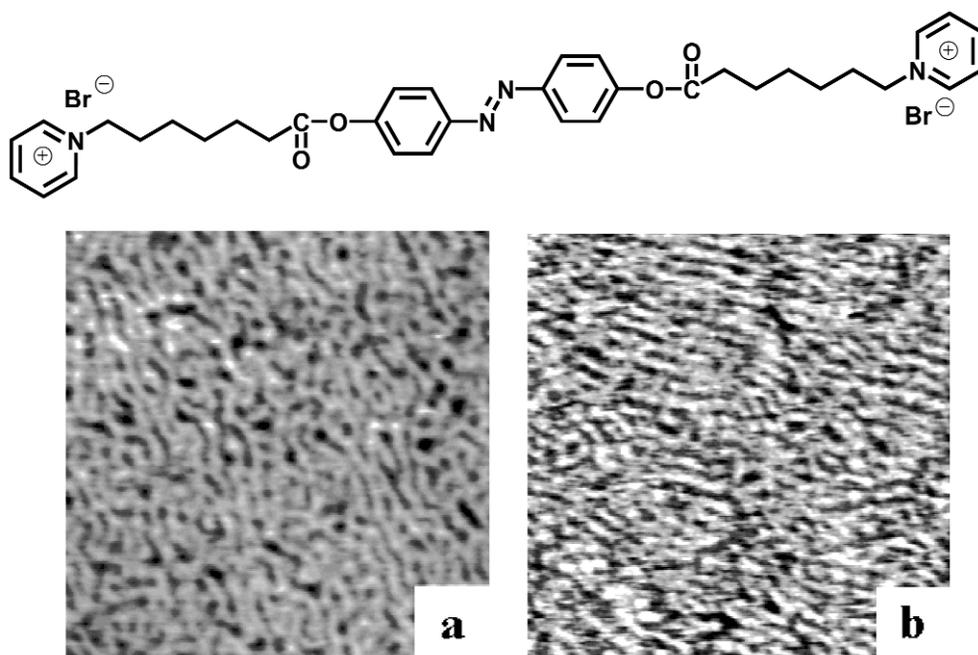
**Fig. 2** (a) In situ and (b) ex situ AFM images of **azo-11** adsorbed on a mica sheet, data scale 370 × 370 nm. Counterion effect: (c) in situ; (d) ex situ, data scale 530 × 530 nm. Reproduced from refs. [13,14] with permission from the Royal Society of Chemistry and the American Chemical Society.

### Counterion effect

The micellar aggregates are supramolecular assemblies based on noncovalent bonds, so their morphologies can be adjusted by changing the external conditions [10]. For example, adding sodium salicylate leads to the increase of the stripe width from 10 to 16 nm, because sodium salicylate has a strong attraction for bolaamphiphiles with hydrophilic pyridinium head groups and exchange of halide ions with the strongly associating salicylate ions can reduce electrostatic repulsion between head groups, which are responsible for the formation of larger self-assemblies. As shown in Figs. 2c and 2d, these self-assembled structures are also stable, because ex situ observation has shown similar results as in situ observation.

### Spacer effect

Besides counterions, the length of hydrophobic spacer in the bolaamphiphile can also affect the self-organization of the surface micelles [11]. **Azo-6**, a similar bolaamphiphile to **azo-11** but with a shorter spacer, exhibits distinctly different self-organization behavior at the solid/liquid interface, forming diversified self-assembled interfacial geometries with change of conditions [16]. As shown in Fig. 3, in situ AFM reveals that **azo-6** forms wormlike micelles at low concentrations and short-range ordered cylindrical surface micelles at high concentrations. When observed by ex situ AFM, none of the aggregation geometries of **azo-6** can be retained when the substrate is taken out from the solution, indicating that the surface micelles of **azo-6** cannot withstand the drying process because of its short spacer.



**Fig. 3** In situ AFM images ( $600 \times 600$  nm) of **azo-6** adsorbed at the solution/mica interface: (a)  $1.0 \times 10^{-4}$  M; (b)  $2.0 \times 10^{-4}$  M. Reproduced from ref. [15] with permission from the American Chemical Society.

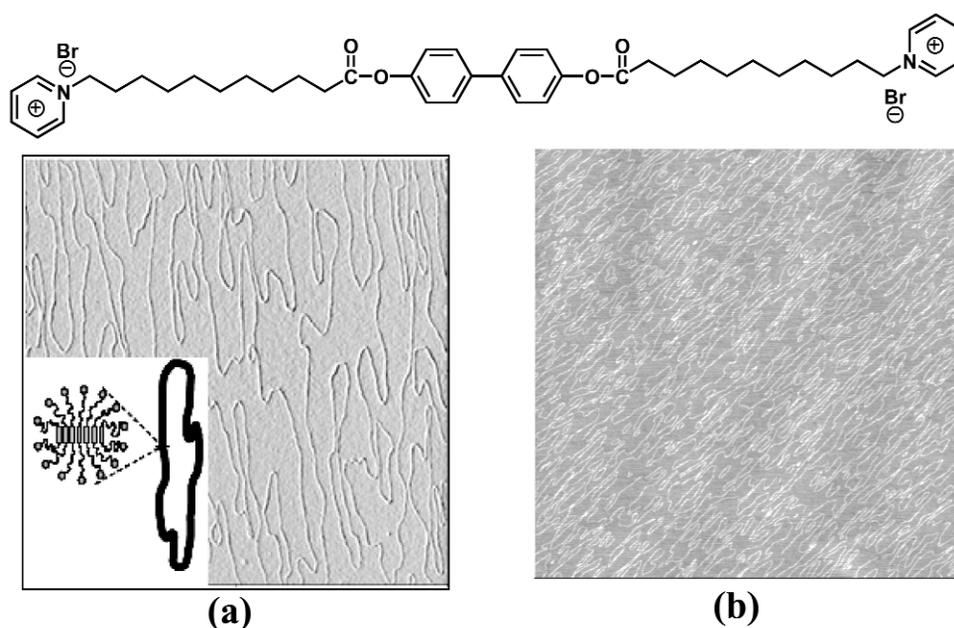
Therefore, the spacer length also plays an important role in enhancing the robustness of the surface micelles.

### Substrate effect

The interfacial organization is a compromise of the substrate-templating effect and the intermolecular interactions, such as electrostatic interactions,  $\pi$ - $\pi$  stacking, and van der Waals forces. So, the substrate should play an important role in the interfacial organization, and the substrate effect can become a dominating factor in determining the surface morphology when the intermolecular interactions among the surfactants are not strong enough. Taking **azo-11**, for example, the ordered packing of stripes cannot be obtained without a crystalline template. Through alternatively depositing two layers of polyelectrolytes, diazoresin and poly(sodium styrene sulfonate), onto the mica sheet, the surface is still negatively charged but becomes amorphous [10]. With such a modified mica sheet, 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 structure in a long-range order. Instead, irregularly distributed spherical aggregates are formed on the silicon substrate.

### Different mesogen

**BP-10** is another bolaamphiphile-bearing biphenyl mesogenic group [9,12]. In situ AFM observation shows that the bolaform amphiphile **BP-10** forms cylindrical micelles, with a “spaghetti” shape at the mica/liquid interface, as shown in Fig. 4a. The width of the spaghetti is about 40 nm and some spaghettis can extend over micrometers. The ex situ AFM image (Fig. 4b) appears to be the same structure as



**Fig. 4** Cylindrical micelles of BP-10 on a mica sheet. (a) In situ AFM observation with a possible model picture; (b) ex situ AFM observation. Scan size is  $5 \times 5 \mu\text{m}$ . Reproduced from ref. [13] with permission from the Royal Society of Chemistry.

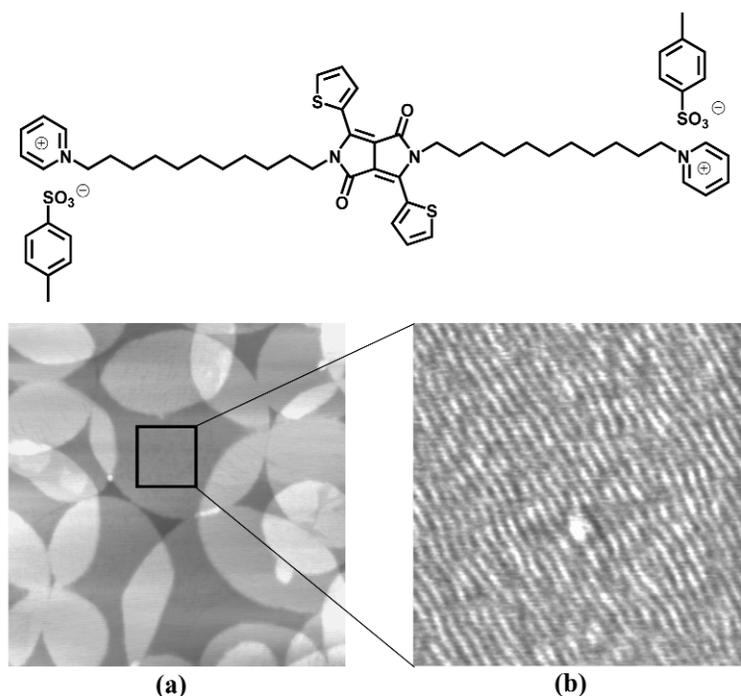
that of the in situ AFM image, suggesting that **BP-10** can retain its structure formed in the solution. So, changing the chemical structure of bolaamphiphile can lead to the formation of self-assemblies with different morphologies.

The stability of the dry-state surface micelles can be investigated by heating the substrate and monitored by temperature-dependent AFM [12]. Taking **BP-10**, for example, no obvious change can be observed until the substrate is heated to  $50^\circ\text{C}$ . With gradual increase of the substrate temperature from  $50^\circ\text{C}$ , the width of the cylindrical micelles increases. When the substrate is heated to  $70^\circ\text{C}$  and held at this temperature for 1 h, the single cylindrical micelle becomes as wide as  $70\text{--}80\text{ nm}$ . These changes are the result of the lateral diffusion of the cylindrical micelles on mica, which is caused by the enhanced mobility on heating the substrate. Therefore, the noncovalent bonded self-assemblies cannot only be stable against drying, but also can withstand thermal treatment up to  $70^\circ\text{C}$ .

### INTRODUCTION OF STRONG $\pi$ - $\pi$ STACKING MOIETIES INTO BOLAAMPHIPHILE

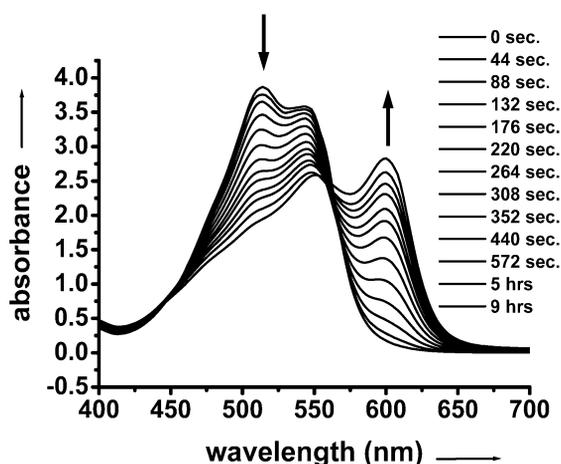
We are wondering if a similar idea can be also applied to bolaamphiphile-bearing  $\pi$ - $\pi$  stacking moiety. In order to answer this question, we have introduced strong  $\pi$ - $\pi$  stacking moiety of diaryldiketopyrrolopyrrole (DPP) dye into bolaamphiphiles, and have found that such a bolaamphiphile with appropriate spacer length gives a stable micellar nanostructure [13]. As shown in Fig. 5, **DPP-11** forms disk-like micelles with diameters ranging from several hundreds of nanometers to one micrometer. The section analysis of Fig. 5a shows that the disk-like micelles have an average thickness of about  $3.7\text{ nm}$ . This value agrees well with the length of a single **DPP-11** molecule, suggesting that the disks are a monolayer structure with the thickness of a single molecule. Although the self-organization of the amphiphiles is mainly driven by the hydrophobic effect, once the disk-like micelle forms, the  $\pi$ - $\pi$  stacking interaction becomes another dominating factor that enhances the stability of the micelles. Detailed study on the disk-like aggregate reveals that there are uniform stripes of about  $10\text{ nm}$  in width within

the disk (Fig. 5b). Thus, the disk-like micelle is a combination of micro- and nanostructures, which can be explained in terms of a compromise between the different intermolecular interactions. The intermolecular  $\pi$ - $\pi$  stacking in the middle part of the aggregate forces the molecules to pack densely, while the repulsive interaction of the positively charged head groups has the reverse effect. A compromise between these two types of interaction could lead to the crystallization of the amphiphiles, which should be responsible for the formation of the observed stripe-like structure.



**Fig. 5** Ex situ AFM observation of DPP-11 micellar structures adsorbed on a mica sheet: (a) large area image,  $2 \times 2 \mu\text{m}$ ; (b) small area image,  $400 \times 400 \text{ nm}$ .

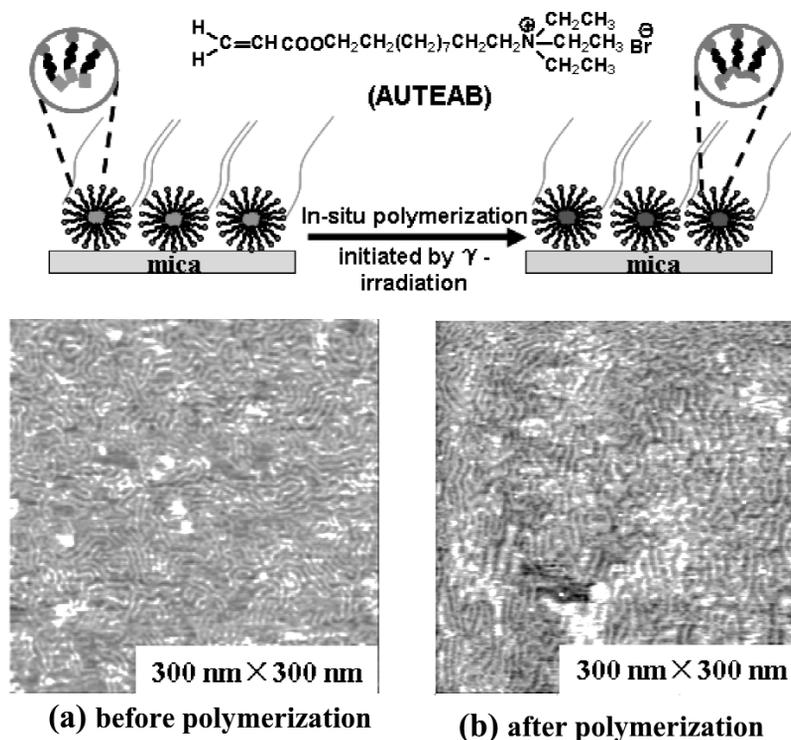
Interestingly, in contrast to the normal formation of micelles that reaches equilibrium in a very short time, DPP-11 requires a relatively long period to self-organize, allowing the dynamic process to be monitored. As shown in Fig. 6, absorption bands at around 514 and 540 nm corresponding to the monomer absorption appear at the beginning. With the decrease of the monomer absorption band, the absorption around 601 nm increases gradually with time, which is assigned to the aggregation in the formation of micelles. The absorption change of DPP-11 almost reaches a plateau in 10 min, thus suggesting an equilibrium situation.



**Fig. 6** Time-resolved absorbance of DPP-11 in an aqueous solution. 504 nm: monomer absorption; 601 nm: aggregate absorption.

### INTRODUCTION OF POLYMERIZABLE GROUPS

Introducing polymerizable groups into amphiphiles to retain the surface micelle by polymerization is another effective method to stabilize surface micelles [14]. However, usual polymerization needs heating or adding initiator into the reaction system, which will risk destroying the micellar structure. Because  $\gamma$ -ray-initiated polymerization can be carried out at low or room temperature without additional initiator, it is possible to be used to retain the micelle structure during the polymerization process. Taking 11-acryloyloxyundecyltriethylammonium bromide (AUTEAB), for example, it forms wormlike micelles with a mean width about 6 nm at the interface, as revealed by in situ AFM in Fig. 7a. Owing to a lack of strong binding interaction among the amphiphiles, these wormlike surface micelles will fall apart in the dry state. In order to elongate the lifetime of the micellar structures, a cryogenic treatment is used to freeze the surface micellar conformation, and then  $\gamma$ -irradiation is employed to initiate the polymerization. As shown in Fig. 7b, the preformed wormlike micellar structures at the mica/water interface are preserved after polymerization.



**Fig. 7** Schematic illustration of  $\gamma$ -ray-initiated polymerization for stabilizing surface micelles (top) and AFM images of surface micelles formed by AUTEAB before (a) and after (b) the polymerization. Reproduced from ref. [18] with permission from the American Chemical Society.

## CONCLUSIONS AND OUTLOOKS

Although the surface micellar aggregates of amphiphilic molecules are inherently dynamic and fluid, we have proposed different methods to stabilize the micellar aggregates through enhancement of supramolecular interactions or introduction of covalent bonds. To introduce mesogen or  $\pi$ - $\pi$  stacking groups into bolaamphiphiles can certainly increase intermolecular interaction and therefore result in the formation of stable surface assemblies. If the intermolecular interaction is not strong enough in the micellar aggregate such as **azo-6**, it can form surface structures with different morphologies in terms of the nature of the substrate. For **DPP-11** micellar aggregates with strong intermolecular interaction, it can form stable structures in solution, and the resulting surface micellar aggregates are independent of its substrate. We have also suggested a simple method to stabilize surface micelles by  $\gamma$ -ray-initiated polymerization. It is anticipated that stable surface micelles could be used to fabricate organic nanostructure materials, leading to applications arising from templating synthesis and mimicry of biomineralization process.

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## REFERENCES

1. (a) H. Ringsdorf, B. Schlarb, J. Venzmer. *Angew. Chem., Int. Ed. Engl.* **27**, 113 (1988); (b) M. Ahlers, W. Mueller, A. Reichert, H. Ringsdorf, J. Venzmer. *Angew. Chem., Int. Ed. Engl.* **29**, 1269 (1990); (c) T. Kunitake. *Angew. Chem., Int. Ed. Engl.* **31**, 709 (1992); (d) J.-M. Lehn. *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim (1995).
2. S. J. Candau, E. Hirsch, R. Zana, M. Adam. *J. Colloid Interface Sci.* **122**, 430 (1988).
3. A. M. Gaudin, D. W. Fuerstenau. *Trans. AIME* **202**, 958 (1955).
4. (a) S. Manne, J. P. Cleveland, H. E. Gaub, G. D. Stucky, P. K. Hansma. *Langmuir* **10**, 4409 (1994); (b) S. Manne, H. E. Gaub. *Science* **270**, 1480 (1995).
5. (a) I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger, S. M. Gruner. *Science* **273**, 892 (1996); (b) S. Manne, T. E. Schaeffer, Q. Huo, P. K. Hansma, D. E. Morse, G. D. Stucky, I. A. Aksay. *Langmuir* **13**, 6382 (1997); (c) M. Jaschke, H. J. Butt, H. E. Gaub, S. Manne. *Langmuir* **13**, 1381 (1997); (d) H. N. Patrick, G. G. Warr, S. Manne, I. A. Aksay. *Langmuir* **15**, 1685 (1999).
6. (a) R. E. Lamont, W. A. Ducker. *J. Am. Chem. Soc.* **120**, 7602 (1998); (b) W. A. Ducker, E. J. Wanless. *Langmuir* **15**, 160 (1999).
7. Y. L. Chen, S. Chen, C. Frank, J. Israelachvili. *J. Colloid Interface Sci.* **153**, 244 (1992).
8. S. Gao, B. Zou, L. F. Chi, H. Fuchs, J. Q. Sun, X. Zhang, J. C. Shen. *Chem. Commun.* 1273 (2000).
9. B. Zou, M. F. Wang, D. L. Qiu, X. Zhang, L. F. Chi, H. Fuchs. *Chem. Commun.* 1008 (2002).
10. B. Zou, L. Y. Wang, T. Wu, X. Y. Zhao, L. X. Wu, X. Zhang, S. Gao, M. Gleiche, L. F. Chi, H. Fuchs. *Langmuir* **17**, 3682 (2001).
11. D. L. Qiu, B. Song, A. L. Lin, C. Y. Wang, X. Zhang. *Langmuir* **19**, 8122 (2003).
12. M. F. Wang, D. L. Qiu, B. Zou, T. Wu, X. Zhang. *Chem. Eur. J.* **9**, 1876 (2003).
13. B. Song, Z. Q. Wang, S. L. Chen, X. Zhang, Y. Fu, M. Smet, W. Dehaen. *Angew. Chem., Int. Ed.* **44**, 4731 (2005).
14. X. Zhang, M. F. Wang, T. Wu, S. C. Jiang, Z. Q. Wang. *J. Am. Chem. Soc.* **126**, 6572 (2004).
15. (a) J.-H. Fuhrhop, J. Mathieu. *J. Chem. Soc., Chem. Commun.* 144 (1983); (b) J.-H. Fuhrhop, J. Mathieu. *Angew. Chem., Int. Ed. Engl.* **23**, 100 (1984); (c) J.-H. Fuhrhop, T. Wang. *Chem. Rev.* **104**, 2901 (2004).
16. A. Gulik, V. Luzzati, M. D. Rosa, A. Gambacorta. *J. Mol. Biol.* **182**, 131 (1985).
17. (a) Y. Okahata, T. Kunitake. *J. Am. Chem. Soc.* **101**, 5231 (1979); (b) M. Shimomura, R. Ando, T. Kunitake. *Ber. Bunsen-Ges. Phys. Chem.* **87**, 1134 (1983); (c) T. Kunitake. *Angew. Chem., Int. Ed. Engl.* **31**, 709 (1992).
18. G. Z. Mao, Y. H. Taso, M. Tirrell, H. T. Davis, V. Hessel, H. Ringsdorf. *Langmuir* **9**, 3461 (1993).