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Confined supramolecular nanostructures of mesogen-bearing amphiphiles†

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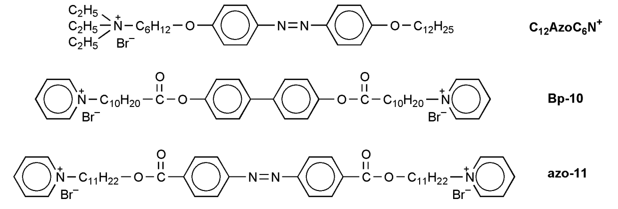
Stable surface nanostructures with different morphology have been successfully constructed by modifying the chemical structure of synthetic amphiphiles; by introducing mesogenic groups into bolaform amphiphiles, stable spaghetti-like or stripe-like nanostructures can be obtained; it is believed that such a kind of surface structure could be used for templating synthesis and assembly.

Amphiphiles at interfaces are a traditional but challenging topic in colloid chemistry and now especially in supramolecular science.[1] The existence of clusters of surfactant molecules at the solid–liquid interface was first observed long ago.[2] However, strong direct evidence that surfactants form micelle-like structures at the liquid–solid interface was provided more recently by Manne and Gaub using *in-situ* atomic force microscopy (soft contact-in-fluid AFM).[3] The surface aggregations of cationic surfactants, anionic surfactants, nonionic and zwitterionic surfactants have been widely studied.[3,4] The roles of substrates, concentration, electrolyte type, pH value, alcohol and temperature in determining the shape of the surface aggregates have been examined systematically by Ducker *et al.*[4]

We have been interested in the surface aggregations of amphiphiles bearing mesogenic groups (Scheme 1), because the mesogenic groups may enhance the intermolecular interactions among amphiphiles. By monitoring the interfacial self-organization, using *ex-situ* AFM (tapping-in-air), we have shown that self-assembled nanometer-sized stripes are formed spontaneously by electrostatic adsorption of bolaform amphiphiles bearing hydrophilic pyridinium headgroups and rigid hydrophobic azobenzenes onto a mica surface.[5] In this work, we compare the surface aggregation of single-chain and bolaform amphiphiles bearing mesogenic groups. The goal of this research is to understand whether we can obtain surface nanostructures with controlled morphology by modifying the chemical structure of synthetic amphiphiles. Using *ex-situ* AFM and *in-situ* (tapping in fluid), we also focus on whether we can obtain stable self-assembled nanostructures by incorporation of mesogenic groups into the amphiphiles.

The three compounds we have targeted to address these questions are a single-chain ammonium surfactant containing azobenzene (denoted as **$C_{12}AzoC_6N^+$**), a bolaform amphiphile bearing a biphenyl group (denoted as **BP-10**), and a bolaform amphiphile bearing azobenzene (denoted as **azo-11**).[6] The critical micelle concentration (cmc) was measured either by conductivity or fluorescence quench blanking methods: 4.2×10^{-5} M for **$C_{12}AzoC_6N^+$**, 1.2×10^{-3} M for **BP-10**, 3.4×10^{-5} M for **azo-11**.



Scheme 1 Chemical structures of amphiphiles bearing mesogenic groups.

In-situ AFM observation reveals that **$C_{12}AzoC_6N^+$** forms globular micelles at the mica–liquid interface (Fig. 1A). The inset is a magnified image. It is seen that surface micelles are formed when the concentration is 1.0×10^{-4} M, above its cmc. The diameter of the aggregates is about 14 nm. To investigate the possibility of a concentration dependence, the concentration of **$C_{12}AzoC_6N^+$** was varied systematically from 1.0×10^{-4} M to 1.0×10^{-6} M. We observed almost the same AFM images with surface micelles for a concentration of 1.0×10^{-5} M and above. It means the surface critical micelle concentration (s-cmc) at the mica–liquid interface is 1.0×10^{-5} M, lower than that of the bulk aqueous solution (4.2×10^{-5} M). This is probably due to the larger attraction between surfactant molecules and the solid substrate than between the surfactant molecules and the solution. Provided that the concentration of **$C_{12}AzoC_6N^+$** is below its s-cmc, *e.g.* 1.0×10^{-6} M, *in-situ* AFM observation only shows a homogeneous surface without any organized structures. This indicates that the micelles cannot form at the solid–liquid interface if the concentration of the surfactant is below the s-cmc.

A mica surface with **$C_{12}AzoC_6N^+$** surface micelles at the solid–liquid interface was taken out and put into a dessicator (P_2O_5) for drying, and then imaged by *ex-situ* AFM. It was found that **$C_{12}AzoC_6N^+$** forms branch-like stripes on the mica surface under ambient conditions, as shown in Fig. 1B. The difference between the observations provided by *in-situ* and *ex-situ* AFM can be explained by the instability of the micelles. In other words, the surface micelles formed by the interfacial adsorption of **$C_{12}AzoC_6N^+$** at the mica surface are destroyed upon drying.

Comparatively, *in-situ* and *ex-situ* AFM were used to study the surface aggregation of the bolaform amphiphile **BP-10**. *In-situ* AFM observation has shown that the bolaform amphiphile **BP-10** forms the spaghetti-like micelles at the mica–liquid interface, as shown in Fig. 2A. The width of the spaghetti is about 40 nm and some spaghetti can extend over micrometers, and it is seen that the s-cmc is close to the cmc in the bulk for

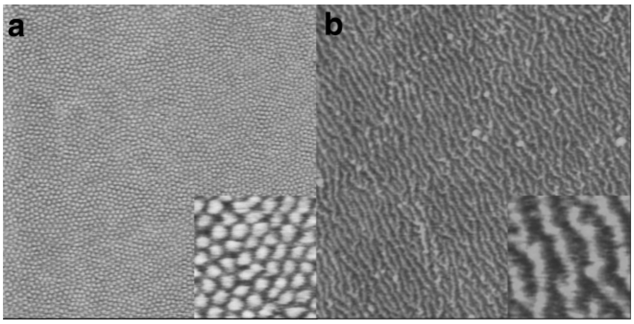


Fig. 1 AFM image of **$C_{12}AzoC_6N^+$** adsorbed at the mica–water interface when the concentration is 1.0×10^{-4} M (2.5 × cmc). Both images are 1.3 µm × 1.3 µm. Inset images are 144 nm × 144 nm. a) *In-situ* AFM image. The diameters of the globule-like aggregates are about 14 nm. b) *Ex-situ* AFM image. The width of branch-like stripes is about 16 nm.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b201444k/

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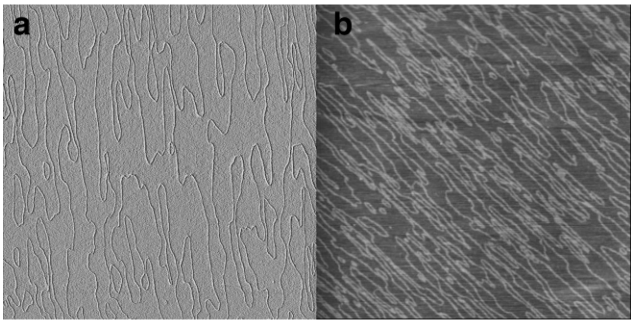

Fig. 2 AFM image of **BP-10** adsorbed at the mica–water interface when the concentration is 4.0×10^{-3} M (~ 3 × cmc). Both images are 5 μm × 5 μm. a) *In-situ* AFM image. The width of spaghetti-like micelles is about 40 nm. b) *Ex-situ* AFM image. The width of spaghetti-like micelles is about 40 nm.

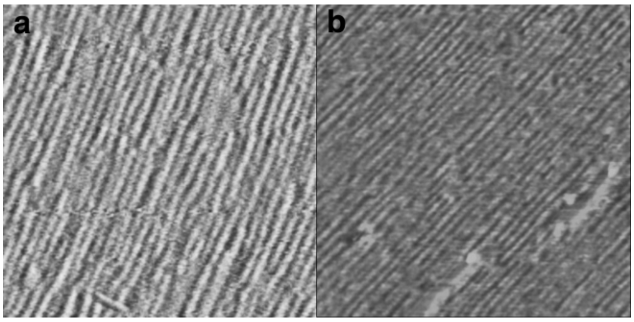

Fig. 3 AFM image of **azo-11** adsorbed at the mica–water interface when the concentration is 1.0×10^{-4} M (3 × cmc). Both images are 370 nm × 370 nm. a) *In-situ* AFM image. The width of stripes is about 10 nm. b) *Ex-situ* AFM image. The width of stripes is about 10 nm.

this bolaform amphiphile. *Ex-situ* AFM observation also clearly revealed that spaghetti-like micelles are formed at the mica surface, as shown in Fig. 2B. When the concentration of the **BP-10** solution was diluted to 2.0×10^{-3} M, the spaghetti-like structure is still seen as indicated by *ex-situ* AFM, but it shows many defects. However, when the concentration of the **BP-10** solution was as low as 5.0×10^{-4} M, only globule-like aggregates with different sizes exist on the mica surface as observed by *ex-situ* AFM. The most interesting result is that the *ex-situ* AFM images appear the same as that of the *in-situ* AFM images. This demonstrates that the organized structure formed by spontaneous adsorption of bolaform amphiphiles **BP-10** is much less sensitive to drying than the single chain surfactants.

The bolaform amphiphile **azo-11** can form well ordered stripes separated by about 10 nm on the mica surface (Fig. 3B). Such a stable ordered structure could be influenced by many factors such as substrates, buffer of electrolytes and so on as reported in our previous publications.[5] However, *in-situ* AFM observation allows us to exclude the effect of water evaporation and drying processes on the observed molecular organization. In this work, we carried out the *in-situ* AFM observation of bolaform amphiphile **azo-11** adsorbed on the mica surface, as shown in Fig. 3A. Comparing the two modes of AFM observation, it is seen clearly that *in-situ* and *ex-situ* AFM both demonstrate similar results, although it seems that the *in-situ* AFM image is better-resolved, thus giving more details, *e.g.* structural defects. This further demonstrates that the bolaform amphiphile bearing mesogenic groups can form stable of self-assembled nanostructures. In addition, it strongly supports our assumption that the ordered stripes are formed by physical adsorption of cylindrical micelles at the mica surface.

In summary, we have successfully carried out an *in-situ* and *ex-situ* AFM study of the 2-D aggregate geometry of mesogen-bearing amphiphiles after adsorption at the mica–aqueous solution interface. $\mathbf{C_{12}AzoC_6N^+}$ tends to form globule-like micelles in aqueous solution due to the hydrophobic effect. When adsorbed onto a mica surface, it can form globule-like surface micelles. Although this single chain amphiphile bears a mesogenic group, the interaction among the amphiphiles in the micelles is still not strong enough to keep the micelle stable by drying. However, for the bolaform amphiphiles bearing mesogenic groups, both **BP-10** and **azo-11** can form stable surface aggregates. These should be related to the unique chemical structure of bolaform amphiphiles, which are molecules containing two hydrophilic moieties connected by a hydrophobic chain. These compounds incline to form lamellar or cylindrical micelles in solution. The surface self-assembled nanostructures of **BP-10** and **azo-11** are believed to be caused by a fusion of the cylindrical micelles on a planar mica surface as indicated by AFM. However, the template effect of mica for **BP-10** is not so strong as that of the **azo-11**; therefore **BP-10** forms spaghetti-like surface aggregates and looks like random supramolecular polymers, whereas **azo-11** forms nanometer stripes with preferred orientation. It is well known that macromolecular science was brewed from its contradiction with colloid science,[1a] but it seems that at the level of supramolecular science there exists to some extent unity between macromolecular and colloid science.

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