

# Supramolecular Assemblies between a New Series of Gemini-Type Amphiphiles and TPPS at the Air/Water Interface: Aggregation, Chirality, and Spacer Effect

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Received: November 11, 2003; In Final Form: February 2, 2004

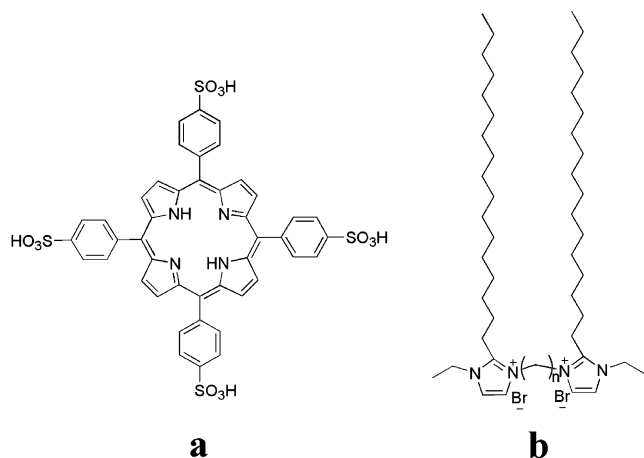
Supramolecular assemblies between a series of novel gemini amphiphiles (BisImC17Cn) and TPPS (tetrakis-(4-sulfonatophenyl)porphine) at the air/water interface were investigated. It was found that the gemini amphiphiles could form stable complex monolayers at the air/water interface with TPPS through electrostatic interaction and  $\pi$ - $\pi$  stacking. There is an inflection point in each of the surface pressure–area isotherms of the complex monolayers. At a certain pH value of the subphase, TPPS could complex with the gemini amphiphiles as a J-aggregate. AFM measurements revealed that nanofibers were formed in the transferred films onto solid substrates by a horizontal lifting method. Interestingly, all the complex films containing the J-aggregate of TPPS showed CD signals in the J-band although both of the amphiphiles and TPPS were achiral. Helical stacking of the TPPS underneath the gemini monolayers was suggested to be responsible for the supramolecular chirality of the multilayer films. The spacers in the gemini amphiphiles have great influence on the chirality of the system. For the film transferred at a surface pressure below the inflection point, the CD signals showed splitting only when the spacer length is larger than four methylene units. The films transferred at the surface pressure above the inflection points showed splitting CD signals of the Soret band of J-aggregates, which could be ascribed to the interaction between the J-aggregates. Moreover, for the film transferred above the inflection points, the CD intensity of the films decreased when the spacer length of the gemini amphiphile increased. It is further observed that many properties such as the width and thickness of the formed nanofibers showed a turning point at a spacer length of six methylene units. A mechanism including the convex of the spacers when they were larger than six methylenes was proposed.

## Introduction

The air/water interface provides a good environment to assemble a supramolecular structure where molecules can be orderly arranged and packed.<sup>1</sup> It is well-known that typical amphiphiles can be used as a monolayer-forming material to construct the assemblies at the air/water interface, while in situ complex formation between different species provides a complementary path for the assembly of the system. The latter way is sometimes more important to regulate the properties and functions of surface assemblies. For example, by adding metal salts in the subphase, stable monolayers could be formed.<sup>2–4</sup> In addition, using the in situ coordination, some organic ligands are reported to form stable monolayers.<sup>5</sup> For those charged amphiphiles, a good way to fabricate stable monolayers is to utilize the electrostatic interaction between two oppositely charged species.<sup>6–11</sup> Dye molecules are abundant in optical properties and are widely used as functional materials.<sup>12–19</sup> By taking advantage of the electrostatic interaction between the oppositely charged species, soluble dyes in water could be incorporated into the organized molecular films.<sup>10–19</sup> Previously, we have found that a porphyrin dye, TPPS, could form a complex monolayer with a series of typical amphiphiles through an interfacial electrostatic interaction.<sup>20</sup> It was found that TPPS could form J-aggregate in the complex multilayers and showed supramolecular chirality although both the amphiphiles and TPPS were achiral. The supramolecular chirality was suggested to be due to a helical stacking of the porphyrin macrocyclic rings, in which the sign of the film CD signals appeared

randomly although the films always showed the CD signals. Through using enantiomeric amphiphiles, we found that the chirality of the supramolecular system could be controlled in the organized films on solid substrate.<sup>21</sup> In this work, we designed a series of cationic gemini-type amphiphiles and investigated the aggregation and the supramolecular chirality of the TPPS/gemini amphiphile systems.

Gemini amphiphiles, consisting of two amphiphiles covalently related by a spacer between the two headgroups, have been received with increasing interest owing to their tunable molecular geometry, unusual physical properties of aggregation in aqueous solution, and superior performance in gene delivery.<sup>22–25</sup> In comparison with the conventional cationic amphiphiles, gemini amphiphiles are abundant in structural diversities such as the length of hydrophobic chains, spacers, headgroups, and counterions. Due to these structural features, gemini amphiphiles showed some interesting properties such as relative lower cmc, and good properties for gene therapy and others.<sup>26–31</sup> Among these, the length of the spacer is the most interesting, particularly in the interfacial monolayers. Previously, we have found that the length of the spacer could have a significant effect on the interfacial properties of a series of gemini surfactants. In this paper, we have designed a new series of gemini-type amphiphiles with various lengths of spacers to clarify the effect of the spacer of the gemini amphiphile on the aggregation and further the supramolecular chirality of the TPPS/gemini amphiphile systems. The water-insoluble gemini amphiphiles were



**Figure 1.** The chemical structure of TPPS and the gemini type amphiphiles: (a) TPPS (tetrakis(4-sulfonatophenyl)porphine) and (b) BisImC17C $n$ ,  $n = 2, 4, 6, 8, 10$ .

designed to eliminate the dissolutions of the monolayer materials in the subphase.

Similar to the case of conventional amphiphiles, these gemini-type amphiphiles could form stable complex monolayers with TPPS at the air/water interface. TPPS could be incorporated into the gemini monolayers as J-aggregates at a certain pH value. In addition, the J-aggregated TPPS in the complex films showed chirality. However, the intensity in the circular dichroism (CD) spectra changed significantly, depending on the spacer length of the gemini amphiphiles. The results gave a clear vision of the effect of the spacers on the supramolecular chirality.

The J-aggregation of TPPS into the gemini amphiphile monolayers and the chirality of the transferred multilayer films were characterized by the  $\pi$ - $A$  isotherms, CD spectra, UV-vis spectroscopy, and atomic force microscopy (AFM) measurements.

## Experimental Section

**Materials.** Anionic porphyrin, tetrakis(4-sulfonatophenyl)porphine (TPPS), was purchased from Tokyo Kasei and used without further purification. Synthesis of the gemini amphiphiles was carried out from the starting material of 2-heptadecyl-1H-imidazole (Tokyo Kasei) in two steps.<sup>32,33</sup> The intermediate 1-ethyl-2-heptadecyl-1H-imidazole was synthesized by nucleophilic reaction of 2-heptadecyl-1H-imidazole with bromoethane. Then the compound was reacted with dibromoalkane with different alkane lengths. The final products were purified by recrystallization and the structures were confirmed by the <sup>1</sup>H

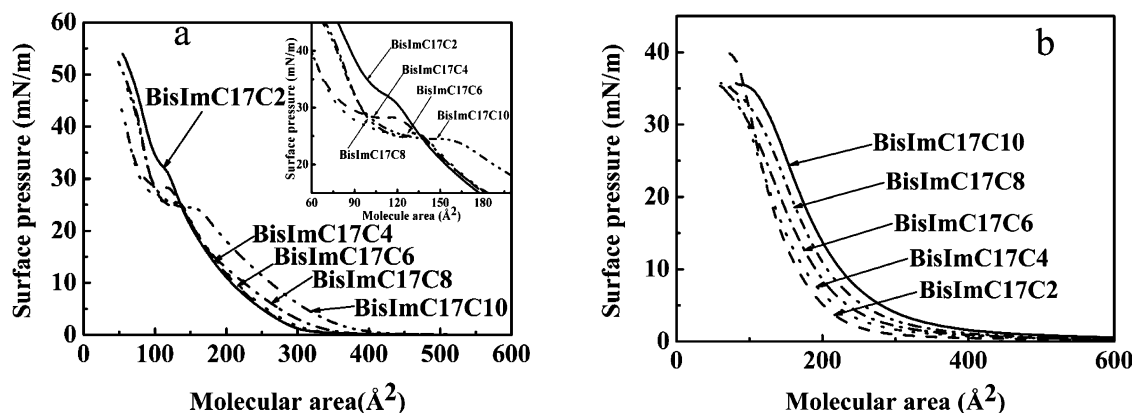
NMR and elemental analysis. The details of the synthesis will be reported elsewhere. The gemini-type amphiphiles are abbreviated as BisImC17C $n$  (bis(2'-heptadecyl-3'-ethylimidazolium)-1, $n$ -alkane dibromide), where  $n$  denotes the length of the spacer. Their chemical structures are shown in Figure 1.

**Procedures.** The surface pressure ( $\pi$ )-molecular area ( $A$ ) isotherms were measured on a KSV minitrough (KSV 1100, Helsinki, Finland). To fabricate the complex monolayer between the amphiphiles and TPPS, a chloroform solution of the gemini amphiphile (ca. 0.1 mM) was spread on an aqueous solution containing  $7.5 \times 10^{-6}$  M TPPS. The pH of the subphase was adjusted to 3.0 with hydrochloric acid to avoid the aggregation of TPPS. After 20 min for evaporating the solvent, surface pressure-area isotherms were obtained by compressing the barrier at a constant speed of 5 mm/min.

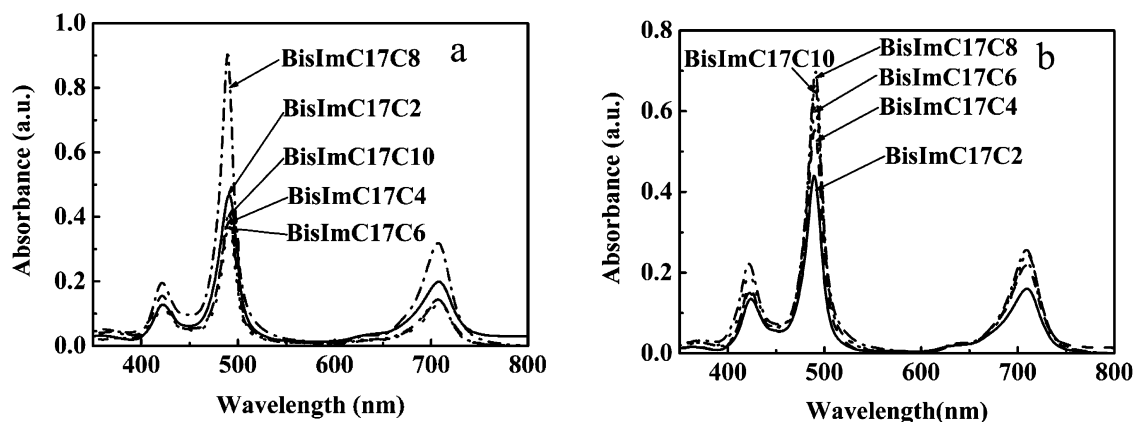
The complex monolayers were transferred onto quartz substrates by using a horizontal lifting method for UV-vis and CD measurements. CD spectra were recorded on a JASCO J-810 CD spectrometer. In the process of measuring CD spectra, the multilayer film on the quartz plate was placed perpendicular to the light path and continuously rotated within the film plane, using a homemade attachment to avoid the possible linear dichroism (LD) in the films.<sup>20,21,34</sup> It was verified that the CD spectra measured with this continuous rotation method were the same as those obtained by averaging 36 spectra which were measured by rotating the sample in a 10-deg step. UV-vis spectra were recorded on a JASCO V-530 UV-vis spectrometer. The AFM of the transferred films was measured on freshly cleaved mica by applying a Digital Instruments Nanoscope IIIa (Santa, Barbara, CA) with a silicon cantilever, using the tapping mode. AFM images are shown in the height mode without any image processing except flattening.

## Results and Discussion

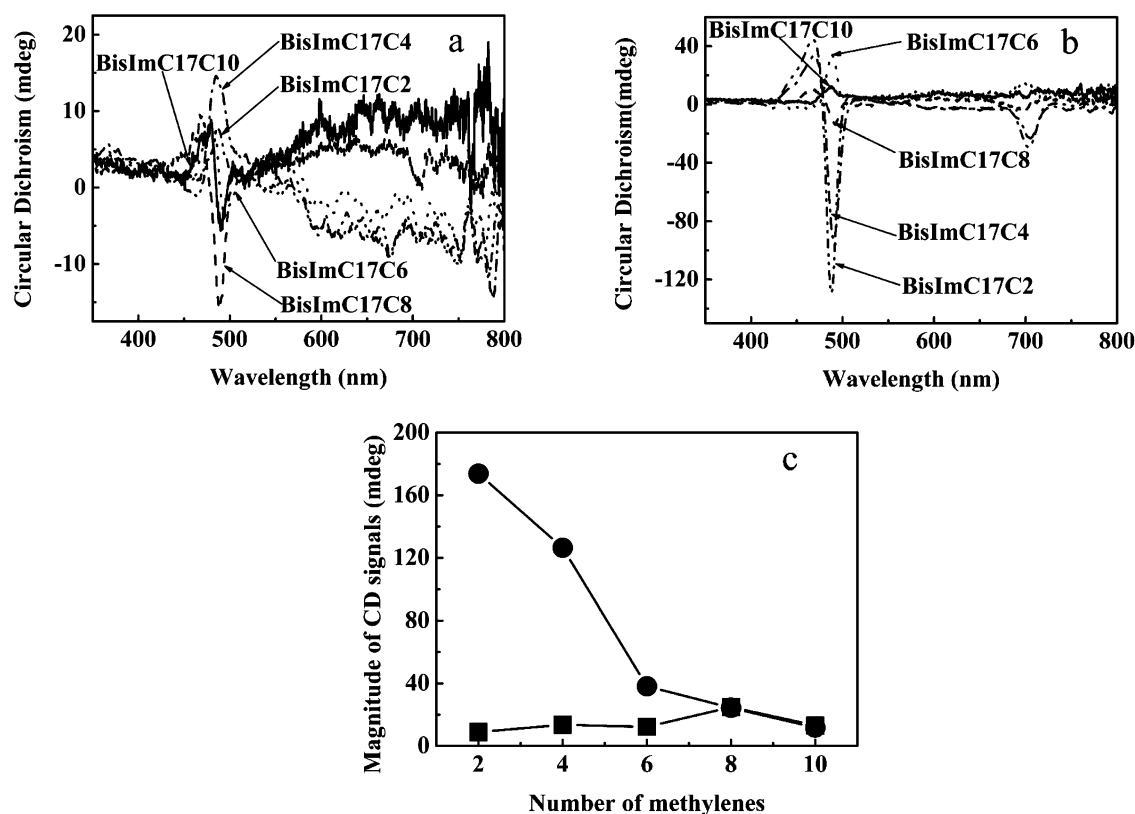
**Monolayer formation at the Air-Water Interface With TPPS.** Figure 2 shows the surface pressure-area ( $\pi$ - $A$ ) isotherms of the gemini amphiphile monolayers on the aqueous subphase containing  $7.5 \times 10^{-6}$  M TPPS at pH 3.0 and 10 °C. Gemini amphiphiles themselves could form stable monolayers on the water surface with a limiting molecular area of around 1.7–2.5 nm<sup>2</sup>/molecule, depending on the spacer length, as shown in Figure 2b. On the subphase of TPPS aqueous solution, the molecular areas increased in comparison with the corresponding gemini amphiphiles on the water surface, indicating the complex monolayer formation between TPPS and the gemini amphiphiles. There is an inflection point in the  $\pi$ - $A$  isotherm of each gemini amphiphile on the TPPS subphase that was not



**Figure 2.** The surface pressure-area isotherms of the gemini amphiphiles (a) on the subphase of TPPS aqueous solution at pH 3.0 at 10 °C and (b) on the subphase of pure water. The inset of the panel a is the expansion of the  $\pi$ - $A$  around the inflection point.



**Figure 3.** UV-vis spectra of TPPS/gemini amphiphile multilayer films (a) before the inflection points and (b) after the inflection points.



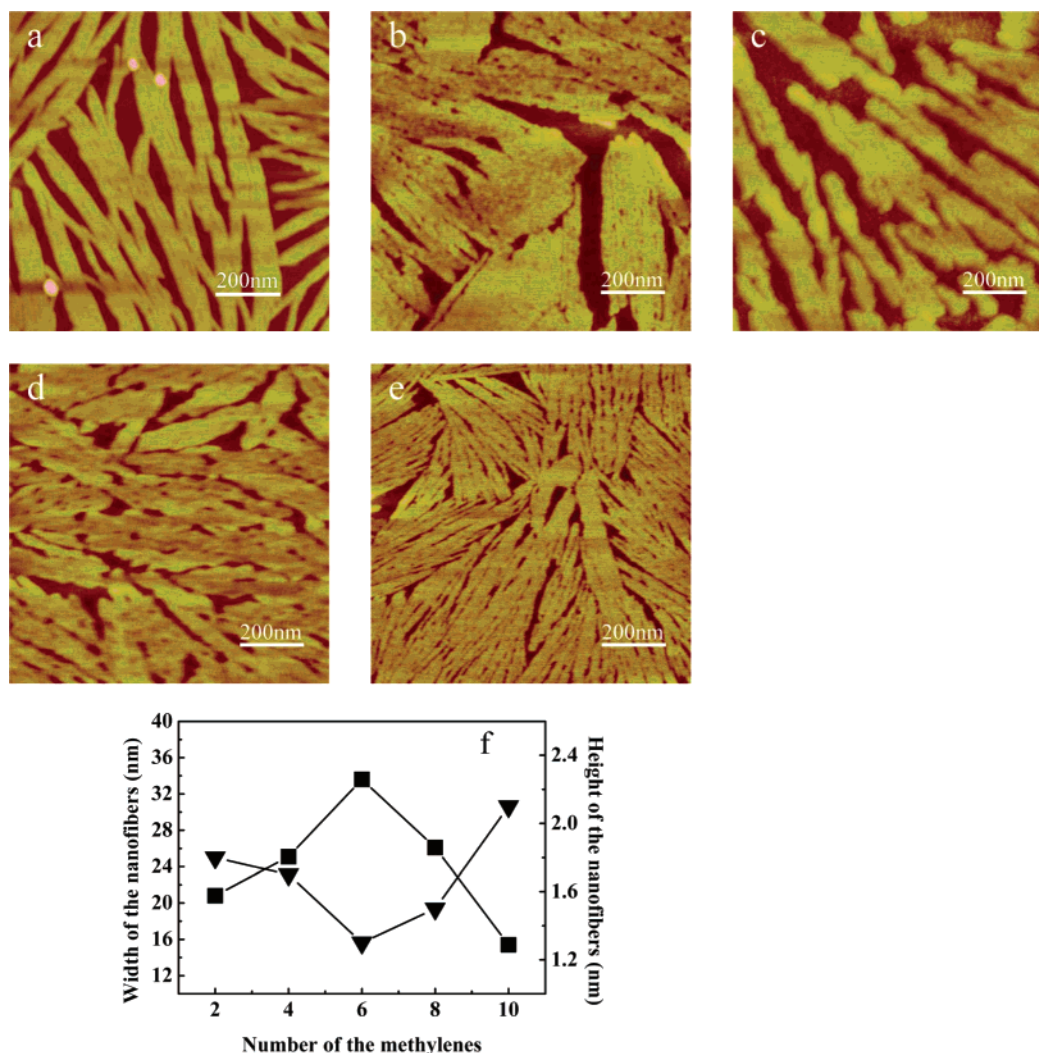
**Figure 4.** CD spectra of 12-layer multilayer films of gemini amphiphiles with TPPS: (a) transferred at 15 mN/m, which is before the inflection points, and (b) transferred at 33 mN/m for gemini C2, 27 mN/m for the others, which are after the inflection points. (c) Plot of the magnitude of CD signals against the spacer length: (■) before the inflection points and (●) after the inflection points. The magnitude of the CD was calibrated by dividing the absorption intensity of the J band at 490 nm.

observed for the monolayer of gemini amphiphile alone. It is further noted that the surface pressure of the inflection point showed a dependence on the spacer length of the gemini amphiphiles. The surface pressure at the inflection point of the monolayer of BisImC17C2 on TPPS is the highest. When the spacer length became larger such as for BisImC17C6, BisImC17C8, and BisImC17C10, the surface pressure at the inflection point remained the same. These changes in the isotherms of the amphiphile/TPPS monolayers suggested that the gemini amphiphiles have an obvious interaction with TPPS and the spacer length of the gemini may affect the packing of the TPPS.

#### Characterization of the Transferred Multilayer Films.

**UV-Vis Spectra of the Transferred Films.** The complex monolayers of gemini amphiphiles and TPPS could be transferred onto solid substrates by a horizontal lifting or Langmuir-Schaefer method. Figure 3 shows the UV-vis spectra of the

multilayer films transferred at 15 (below the inflection points) and 27 mN/m (above the inflection points), respectively. For the BisC17C2/TPPS multilayer film, it was transferred at 33 mN/m due to its higher inflection point. To avoid the aggregation of TPPS in aqueous solution before it interacts with amphiphiles, we used the aqueous TPPS subphase with a pH value of 3.0, where no aggregate of TPPS was observed. The UV-vis spectrum has verified that the aqueous TPPS solution exhibited two absorption bands at 432 and 640 nm, which could be attributed to the Soret band and Q-band in the monomer state, respectively. Because all the gemini amphiphiles showed no absorption in the visible region, the strong absorptions observed in the visible region indicated the formation of the complexed multilayer films of TPPS and gemini. Furthermore, in the multilayer films transferred both below and above the inflection points, Soret and Q-bands of TPPS appeared at about



**Figure 5.** The AFM images of one-layer complex LB films of gemini amphiphiles and TPPS transferred at 15 mN/m (a) BisImC17C2, (b) BisImC17C4, (c) BisImC17C6, (d) BisImC17C8, and (e) BisImC17C10. (f) Plot of the width and height of the nanofibers against the spacer length: (■) the width of the nanofibers and (▼) the height of the nanofibers.

490 and 709 nm, respectively. Such large shifts in comparison with the corresponding TPPS solution can be ascribed to the J-aggregate formation of TPPS in the complex multilayer films. In addition, a relatively weaker absorption band could be observed at 422 nm, which could be attributed to the face-to-face oriented H-aggregation.<sup>35,36</sup> These spectral data indicated that the monomeric TPPS could aggregate underneath the gemini amphiphile monolayers to predominantly form J-aggregates in the monolayers.

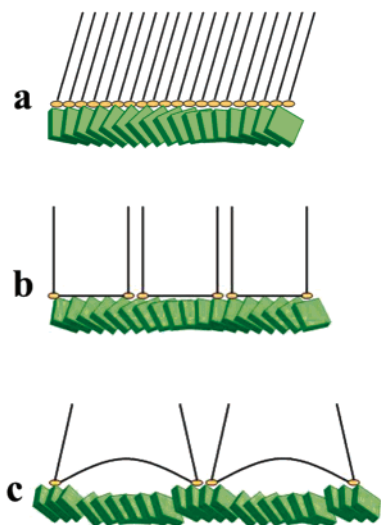
**CD Spectra of the Transferred Films.** Previously we have found that the complex multilayers formed by the TPPS and some conventional amphiphiles such as octadecylamine, *n*-hexadecyltrimethylammonium bromide (CTAB), etc. showed supramolecular chirality.<sup>21</sup> To see if the complex multilayer films of TPPS/gemini amphiphiles have chirality, we have measured the CD spectra of the transferred multilayer films. The films were transferred both before and after the inflection points. Figure 4 shows the CD spectra of the multilayer films. Similar to the case of conventional amphiphiles, all the complex films showed the supramolecular chirality. However, there are two distinct features of the CD spectra in the case of the gemini amphiphiles. First, the films transferred before the inflection point showed either exciton couplet or noncouplet CD signals, while those after the inflection points all showed exciton couplet CD signals. Besides, whether the film showed exciton couplet

or not was spacer length dependent. For the TPPS/gemini amphiphile multilayer films with a spacer of two and four methylenes, they showed basically a positive CD signal at around 487 nm without any couplet. From BisImC17C6, splitting of the Soret bands was observed. Second, the magnitudes of CD signals are also spacer length dependent, as shown in Figure 4c. There were some differences in the absorption intensity in the J-band of the multilayer films. To compare, the magnitude of CD signals in Figure 4c was calibrated by dividing the absorption intensity of the J-band in each multilayer film.

While there are no large fluctuations in the CD intensity for the films deposited before the inflection points, the magnitudes of the CD signals decreased significantly with the increase of spacer length after the inflection points. The intensity leveled off after the length of six methylenes. It was also noticed that the sign of the CD spectra appeared random, which was similar to the case of conventional amphiphiles.

**AFM Measurements.** To get further insight into the supramolecular chirality and the effect of the spacer length of the gemini amphiphile, the complex monolayer was transferred onto the newly cleaved mica and their surface morphologies were measured with AFM. The fiber-like structure appeared in every AFM image. These images are essentially the same as those of the conventional amphiphiles. However, the width of each fiber, averaged by measuring 20 fibers, showed a dependence on the





**Figure 6.** Illustration of the possible structures of the complex film of TPPS with (a) conventional amphiphiles, (b) gemini amphiphiles with shorter spacers (BisImC17C2 and BisImC17C4), and (c) those with longer spacers (BisImC17C6, BisImC17C8, and BisImC17C10)

spacer length (Figure 5 f). The widths of the fibers were 20.8, 25.1, 33.6, 26.1, and 15.4 nm for BisImC17C2, -C4, -C6, -C8, and -C10, respectively. The heights of the fibers were 1.8, 1.7, 1.3, 1.5, and 2.1 nm for BisImC17C2, -C4, -C6, -C8 and -C10, respectively. The two sets of data have the same trend that BisImC17C6 stands at the extrema in both parabolas.

## Discussion

The series of novel gemini amphiphiles showed some similar monolayer behaviors as those of the conventional amphiphiles. However, some distinct features are observed in the case of the gemini amphiphiles. Particularly, a clear spacer effect of the gemini amphiphiles was observed on the interfacial film properties such as the thickness and height of the nanofibers and intensity of the CD signals. All of these distinct features of the gemini amphiphiles and their spacer effect can be explained by the following model, as illustrated in Figure 6.

In the case of gemini amphiphiles, the two positively charged headgroups anchored on the water surface and the spacer of the gemini could lie flat or parallel to the water surface. When the spacer increased, these polymethylene groups could curve out from the water surface due to the increasing hydrophobic nature of the spacers. Due to the positive charge of the headgroup, TPPS could aggregate from the headgroup in the monolayer. During the aggregation, TPPS could form an aggregate in a helical sense and showed supramolecular chirality, which was observed also for conventional amphiphiles (Figure 6a). For the gemini amphiphiles, however, the aggregation could start from the two ends of the gemini. The TPPS molecules stacked between the two ends just like a number of packed bricks in the two walls. The packing between these bricks could be different depending on the length of the spacer. When the spacer is short (Figure 6b), the spacer is parallel to the water and it behaved like a side rigid support to the aggregate of the TPPS bricks. Such rigid support will strengthen the interaction between the bricks. When the spacer increased, the spacer will curve and behave like a rope above the side of the bricks (Figure 6c). This leads to the loose packing of the TPPS molecules between the two charged centers. Therefore, a decrease of the CD magnitude was observed upon increasing the spacer length. It was suggested that the spacer began to curve from

BisImC17C6. Therefore, we observed the turning point at BisImC17C6.

On the other hand, the excitation couplet of the J-band was related to the interaction between the aggregates. Such interaction was slightly different for the film transferred before and after the inflection points. When the film was compressed after the inflection points, the aggregates were packed closely and the excitation couplet was observed in all the films. However, when the J-aggregates were formed before the inflection points, the interaction between the J-aggregates could be different. When the spacer length is very short, there was no interaction between the J-aggregates because there was not much space for the J-aggregates to interact with each other. When the spacer length increased, such interaction became possible due to the increase in space. Therefore, the excitation couplet was only observed when the spacer was longer than four methylenes.

It was interesting to note that the turning point of the magnitude of CD signals occurred at the spacer length of six methylenes, where we suggested that the hexamethylene group began to curve. A similar phenomenon was observed in our previous results and those of other reports.<sup>37</sup> Our AFM measurements have further verified such a deduction. It was found that both the thickness and the width of the fibers showed an extrema at the hexamethylene spacer. When the spacer was curved, the two long alkyl chains will also tilt due to the hydrophobic interaction between the long alkyl chain and the spacer. In the case of BisImC17C6, the spacer curved only slightly, while the alkyl chains will tilt greatly. When the spacer became longer, it curved more and the alkyl chains tilted a little. In the case of a short chain, the spacer was parallel to the water surface and the alkyl chains need not be tilted much. Therefore, we have observed the thickest fiber with the lowest height in the nanofibers in the AFM for the BisImC17C6/TPPS monolayer.

## Conclusion

Complex monolayers between TPPS and a series of newly synthesized gemini amphiphiles can be formed at the air/water interface through the electrostatic interaction and  $\pi$ - $\pi$  stacking. There is one inflection point for every complex monolayer. TPPS could form predominantly J-aggregates in the transferred multilayer films both before and after the inflection points. Furthermore, they showed supramolecular chirality, which was suggested to be due to the helical stacking of the TPPS in the complex multilayers. The subtle conformational change of the spacer in the gemini amphiphile monolayer could greatly influence the supramolecular chirality of the multilayer films. It was suggested that the spacer could curve from hexamethylene as a spacer. When the spacer is shorter than six methylene groups, it is parallel to the film plane and can strengthen the aggregation of the TPPS and thus the supramolecular chirality of the TPPS/gemini amphiphiles. When the spacer length was larger than six methylene groups, the spacer behaved like a rope and will diminish the interaction between TPPS and thus decrease the chirality of the complex multilayer films. AFM measurements have given support to the proposed mechanism.

**Acknowledgment.** This work was supported by the Outstanding Youth Fund (No. 20025312), National Natural Science Foundation of China (No. 20273078), the Major State Basic Research Development Program (No. G2000078103, 2002CCA-03100) and the Fund of the Chinese Academy of Sciences.

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