

Supramolecular Chirality of Achiral TPPS Complexed with Chiral Molecular Films

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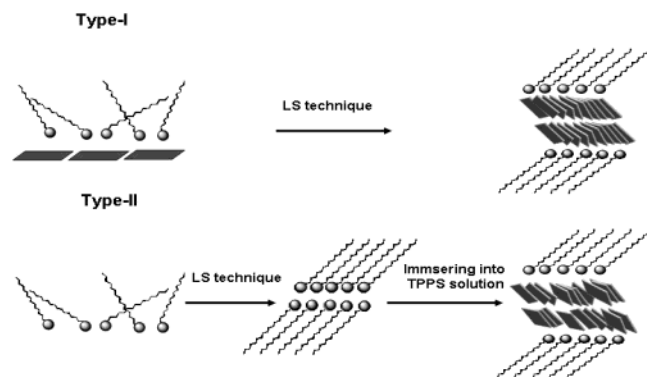
The fabrication and supramolecular chirality of complex multilayer films of tetrakis(4-sulfonato-phenyl)-porphine (TPPS) and long-chain enantiomers of tryptophan derivatives (D-Trp or L-Trp) were investigated. Two methods were employed to assemble the supramolecular films of Trp with TPPS. In one method, Trp was spread on the aqueous subphase containing TPPS at pH 3.1, and the complex monolayer was formed in situ through the adsorption. The subsequent deposition of the thus-formed monolayer onto solid substrates provided type I complex films. In the other method, a preformed multilayer film of Trp on a solid substrate was immersed into the TPPS solution, and ex situ adsorption afford the formation of the type II complex films. A series of techniques such as UV-vis spectroscopy, circular dichroism (CD) spectroscopy, and atomic force microscopy (AFM) were used to characterize these complex multilayer films. It has been found that TPPS can form J aggregates and show chirality in both types of multilayer films. It was interesting that the sign of the Cotton effect in type I multilayer films appeared to be undetermined no matter what kind of Trp enantiomer was used. However, the supramolecular chirality of the TPPS J aggregate in type II multilayer films was determined by the chirality of Trp. AFM measurement on the films revealed that TPPS formed larger nanorod structures in type I films and produced small granular aggregates in type II film. A possible mechanism was proposed on the difference of the chiral monolayer and multilayer film in controlling the chirality of achiral dye molecules.

Introduction

Recently, supramolecular chirality has been receiving increasing interest.^{1,2} Supramolecular chirality is usually achieved by noncovalent interactions between asymmetric molecules. Besides chiral components, achiral components also play an important role in the construction of chiral molecular assemblies. Some achiral molecules are reported to form chiral supramolecular assemblies induced by certain chiral substrates.^{3–6} In some cases, even those achiral molecules can also form chiral supramolecular assemblies without any chiral template.^{7,8} The appearance of such chirality could be due to chiral symmetry breakage,^{9–11} especially when the helicity in different spatial manifestations is a predominant driving force. In this context, helical organizations have been described for supramolecular systems based on metal coordination,¹² H-bonding interactions,¹³ and the generation of enantiomerically enriched J aggregates from achiral monomers.¹⁴ Furthermore, an interfacial interaction can also afford the formation of chiral assemblies from achiral molecules. Previously, we have found that through interfacial interactions such as coordination¹⁵ and photopolymerization¹⁶ some achiral amphiphiles can form chiral assemblies. In addition, through an interfacial electrostatic interaction, achiral positively charged amphiphiles and meso-tetrakis-(4-sulfonato-phenyl) porphyrin (an anionic porphyrin, abbreviated TPPS) were found to form chiral assemblies also.¹⁷ TPPS is a well-investigated dye, which can form a stable J aggregate in an appropriate pH range. Although a 10- μ M TPPS solution showed no aggregation at pH 3.1, when it is adsorbed onto positively charged amphiphilic monolayers, it can form the J aggregate in the interfacial films and the complex film show chirality. It

could be true that a helical arrangement of TPPS through the π - π stacking underneath the monolayer is responsible for such chirality. However, in that case, the chirality of TPPS was uncontrollable (i.e., the chirality can be different in sign in different batches). It is well known that in some chiral environments the chirality of achiral molecules can be induced through the interaction with the chiral environment. In this case, the chirality of achiral molecules usually follows the chirality of the environment. On the basis of this consideration, in this paper we tried to control the supramolecular chirality of TPPS by assembling them on chiral organized molecular films. Generally, charged dyes could be incorporated into oppositely charged multilayer films through electrostatic adsorption either in situ in the monolayer^{18–22} or ex situ in multilayer films.²³ We selected the long-chain enantiomers of an aromatic amino-tryptophan as the chiral amphiphiles and fabricated the complex films of Trp and TPPS in situ in the monolayer (type I) and ex situ in the multilayer films (type II). The aromatic amino derivative was selected because it has a free amino group that can interact with TPPS. In addition, it showed a CD signal in the UV region, which could be used as an indicative parameter of the chirality. In this paper, we found that both types of multilayer films showed supramolecular chirality. However, the sign of the CD signals of the type I film appeared to be random, which is independent of the chirality of the chiral monolayers. The chirality of TPPS in type II multilayer films, however, followed the chirality of the Trp film, showing the effectiveness of the latter method in controlling the supramolecular chirality of TPPS. The complex monolayer formation and the supramolecular chirality of the complex films were characterized by

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SCHEME 1: Schematic Illustration of the Preparation Process of the Two Types of Multilayer Films

π -A isotherms, circular dichroism (CD) spectroscopy, UV-vis spectroscopy, and atomic force microscopy (AFM) measurements.

Experimental Section

Materials. Tetrakis(4-sulfonatophenyl)porphine (TPPS) was purchased from Dojindo Laboratories as a sodium salt and was used without further purification. Enantiomers of the long-chain aromatic amino derivatives, L-tryptophan hexadecyl ester (L-Trp) and D-tryptophan octadecyl ester (D-Trp), were synthesized as reported previously.²⁴

Assembling of the Complex Multilayer Films. The multilayer films were assembled in two ways, defined as type I and type II, as illustrated in Scheme 1. For the type I multilayer, L-Trp or D-Trp was spread on the subphase containing 1×10^{-5} M TPPS (pH 3.1), and a complex film was formed in situ in the monolayer. Subsequent deposition of the in situ formed complex monolayer between L- (or D-) Trp and TPPS provided the type I multilayer film. For the type II multilayer film, an L- (or D-) Trp monolayer on water was first deposited on a quartz substrate. Then the film was immersed into an aqueous solution containing TPPS (pH 3.1), and the type II multilayer film was formed.

Procedures. Measurements of surface pressure-area (π -A) isotherms and the deposition of multilayer films were carried out using a computer-controlled KSV-1100 film balance system (KSV instruments, Helsinki, Finland). After spreading an L-Trp or D-Trp chloroform solution for 20 min, a monolayer was compressed, and the π -A isotherms were measured with a compressing speed of 5 mm/min. The complex monolayer was transferred onto quartz substrates using a horizontal lifting method for UV-vis and CD measurements. For type II multilayer films, the L-Trp or D-Trp films on quartz plates were immersed into a 10- μ M TPPS solution (pH 3.1), and the plates were taken off at different time intervals, washed, and dried for characterization. A JASCO UV-530 spectrophotometer was used for the UV-vis absorption measurements, and CD spectra were recorded on a JASCO J-810 CD spectrometer. In the process of measuring CD spectra, the multilayer film was placed perpendicular to the light path and rotated within the film plane to avoid polarization-dependent reflections and eliminate the possible angle dependence of the CD signals.^{17,25} An in situ formed monolayer was transferred onto freshly cleaved mica, and AFM images were recorded on a Digital Instruments Nanoscope III multimode system (Santa Barbara, CA) with a silicon cantilever using tapping mode. In the case of type II multilayer films, the AFM images were measured at different

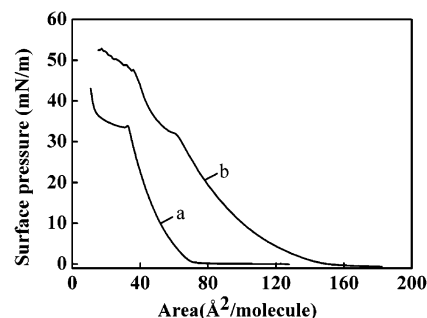


Figure 1. π -A isotherms of L-Trp on (a) pure water and (b) the subphase containing TPPS at pH 3.1.

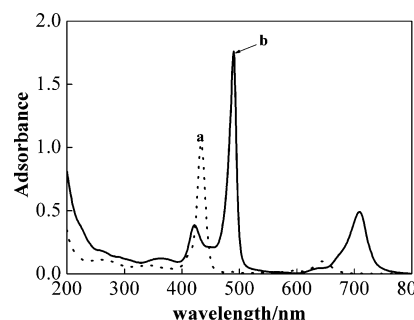


Figure 2. UV-vis adsorption spectra of (a) the TPPS solution (10 μ M, pH 3.1) and (b) the type I complex film of L-Trp/TPPS transferred at 30 mN/m.

immersion times. AFM images are shown in the height mode without any image processing except flattening.

Results

Fabrication of Type I Complex Multilayer Film. When an L- (or D-) Trp chloroform solution was spread on a subphase containing TPPS, a complex monolayer could be formed, as shown in Figure 1. In comparison with the amphiphiles on water, the isotherm of the monolayer spread on the TPPS subphase showed an increase in molecular area. Such a complex monolayer could be deposited onto solid substrates using a horizontal lifting method. Figure 2 shows the UV-vis spectra of the transferred multilayer film on a quartz plate in comparison with the spectrum of the TPPS solution. In the aqueous solution (pH 3.1), TPPS showed two adsorption bands at 432 nm and 640 nm, which are attributed to the Soret band and Q band of the protonated monomer porphyrin.²⁶ In the multilayer film, Soret and Q bands showed a larger red shift and appeared at 490 and 709 nm, respectively. Such large shifts of the absorption band can be ascribed to the J-aggregate formation of TPPS in the complex multilayer film.²⁷⁻³⁰ In addition, a relative weak absorption band could be observed in the multilayer at 422 nm, which could be attributed to H aggregation.³¹ This indicated that upon complex formation between Trp and TPPS at the air/water interface TPPS could be incorporated into the film as the J aggregate and the H aggregate. This is essentially the same as those reported for the other amphiphiles on the TPPS subphase.¹⁷

Fabrication of Type II Multilayer Films. The type II multilayer film could be fabricated by immersing a preformed L- or D-Trp multilayer film into aqueous TPPS solution. Figure 3 shows the UV-vis spectral changes of the L-Trp multilayer film in TPPS solution at different time intervals. Three bands were observed at 421, 487, and 705 nm, which can be ascribed to the H aggregate and the Soret and Q bands of the J aggregate, respectively. This indicated that by immersing the multilayer

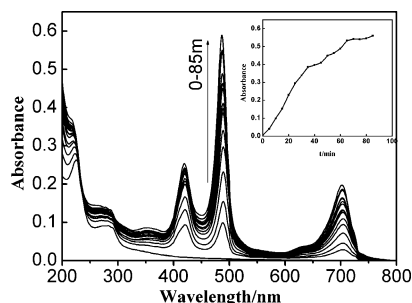


Figure 3. UV-vis spectral changes of a 20-layer L-Trp multilayer film immersed in an aqueous solution of 10 μ M TPPS (pH 3.1) at various immersion times. The inset presents the plot of the absorption intensity at 487 nm for the film as a function of immersion time.

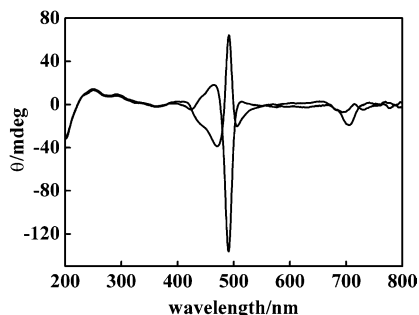


Figure 4. CD spectra of the type I complex film of L-Trp/TPPS transferred at 30 mN/m for different fabrication batches.

film into the aqueous solution TPPS can also be incorporated into the film as both J and H aggregates. However, by increasing the immersion time, the absorption intensity at the band 487 nm increased also. By plotting the intensity of the band at 487 nm as a function of immersion time, the absorption kinetic curve could be obtained. It revealed that the absorption of the Soret band increased linearly at the beginning, and after about 60 min, equilibrium was achieved.

CD Spectra of Type I and Type II Multilayer Films. Figure 4 shows the CD spectra of the type I multilayer films. In the UV region, a Cotton effect was observed, which can be assigned to Trp aromatics.³² Remarkably, a bisignate (with both positive and negative sign) CD signal centered at the absorption wavelength of the J band at 490 nm was observed. After the experiment was repeated many times, it was found that although we always got the same signal in the Trp region, the sign of the CD signal in the Soret and Q bands was undetermined (i.e., the sign could be positive or negative in different fabrication batches). Using the D-Trp enantiomer, the situation was similar. We got the same signal (just opposite to that of L-Trp) in the UV region, but the sign of the CD signals in the TPPS absorption was undetermined. That is to say, no matter what kind of enantiomer we used, the CD signals of TPPS in the complex multilayer films always appeared randomly. These results resembled those of complex multilayer films fabricated from achiral amphiphiles and TPPS, indicating that the chiral monolayers of Trp could not induce the chirality of TPPS in the complex multilayer films.

In the case of the type II multilayer film, the situation was different. Figure 5 shows CD spectral changes of a Trp multilayer transferred onto the solid substrate at a surface pressure of 30 mN/m immersed in the TPPS solution at different time intervals. Remarkable bisignate (with both positive and negative sign) CD signals centered at the absorption wavelength of the J band at 487 nm and the Cotton effect signals centered at 705 nm were observed in the Soret band and the Q band of

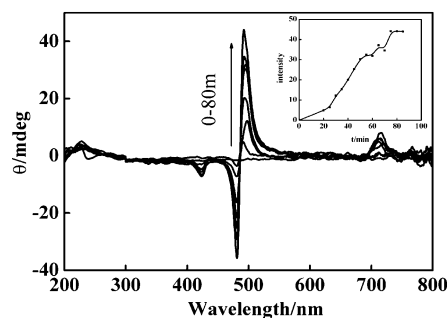


Figure 5. CD spectra of the 10- μ M TPPS-adsorbed 20-layer L-Trp multilayer film for various immersion times at pH 3.1. The inset presents the intensity of band at 491 nm versus immersion time.

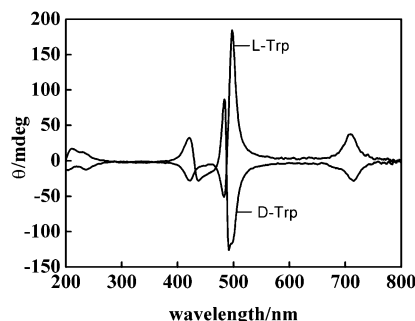


Figure 6. CD spectra of the type II multilayer films of L- (D-)Trp. The concentration of TPPS is 100 μ M at pH 3.1.

TPPS after being immersed for 20 min. With increasing time, the intensity of the split CD band increased also. Importantly, the sign of the CD signal always increased in the same direction. Repeated experiments showed that for the type II multilayer film the CD signals could always be repeated. When we use another enantiomer of Trp, opposite CD signals were observed, as shown in Figure 6. It followed the chirality of the enantiomer amphiphiles.

AFM Studies on the Surface Structure of the Complex Multilayer Film. AFM has been used to characterize the surface structure of the transferred type I and type II multilayer films. Figure 7 demonstrates the AFM images of the L-Trp film before and after TPPS adsorption. L-Trp on mica forms a flat surface with some dots that might be due to the aggregation of L-Trp. Upon immersing the film in TPPS solution for only 1 min, a granular structure was observed. With increasing immersion time, these granular structures became densely packed, and their sizes became larger. These results showed that the TPPS molecule can aggregate in the L-Trp film and form short-range-ordered aggregates. Such adsorption of TPPS into Trp films could also be seen from the height profile of the AFM picture. The film thickness increased with immersion time, showing the incorporation of TPPS into the Trp multilayer film. In addition, X-ray diffraction of the Trp multilayer film before and after immersion revealed an increase in the layer distance from 3.76 to 5.80 nm, suggesting that the J aggregate of TPPS in the multilayer film was 2D. However, for the type I film fabricated through the in situ complex in a monolayer, nanorod or nanofiber structure were observed at low or high pressure by AFM, as seen in Figure 8. At low pressure, a long threadlike structure was observed over the whole scale of 1 μ m. The thread is several tens of nanometers in width and extends to several hundreds of nanometers. At a higher surface pressure, these nanorods gathered together. These images meant that a long-range-ordered aggregate was formed in the type I film.

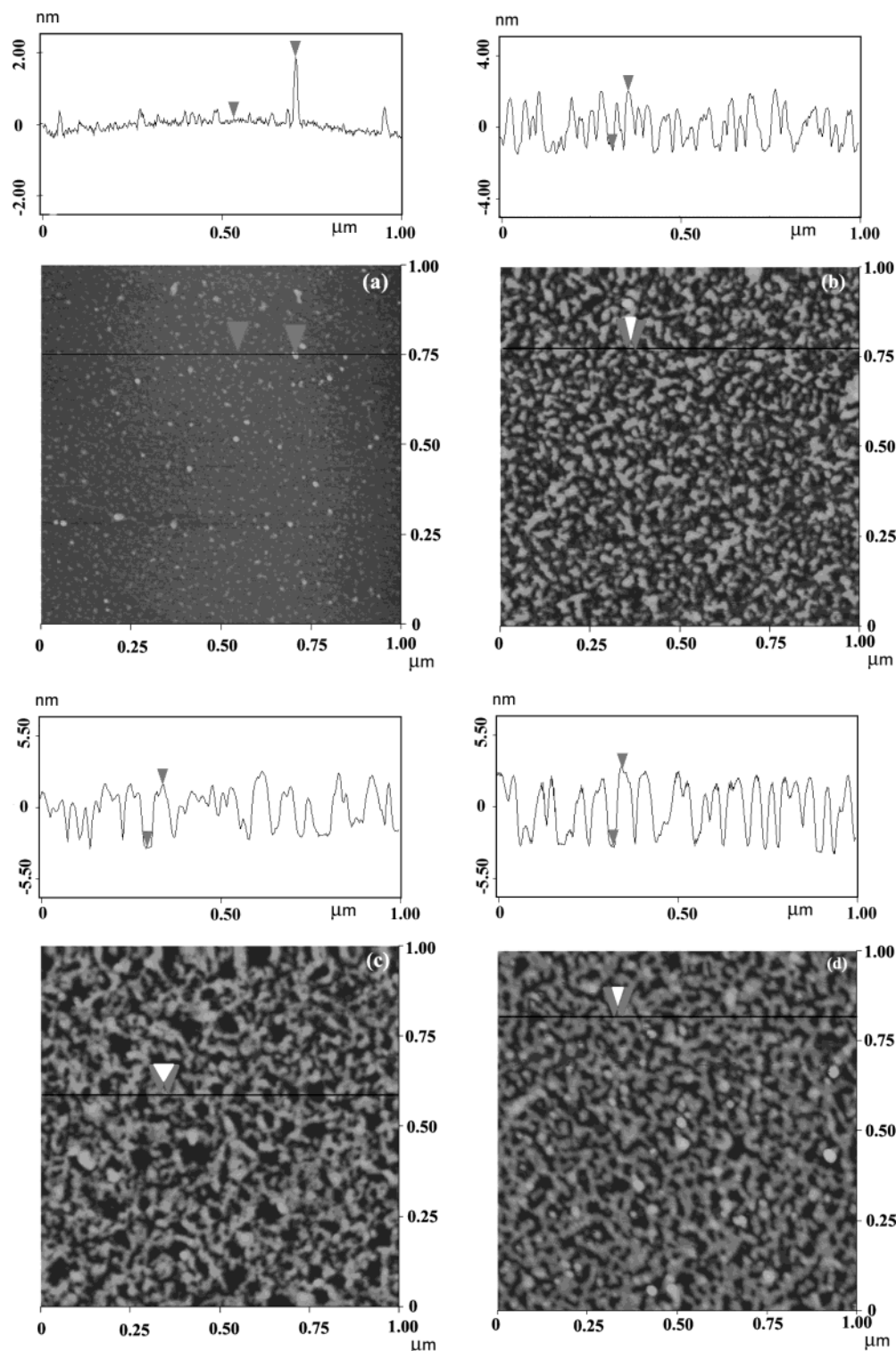


Figure 7. AFM picture of the type II complex multilayer film at (a) 0 min, (b) 1 min, (c) 2 min, and (d) 10 min.

Discussion

Aggregation of TPPS in Type I and Type II Multilayer Films. At the air/water interface, TPPS can form a complex monolayer with Trp monolayer in situ through the interfacial electrostatic interaction due to the protonation of Trp. This is similar to the case of other achiral amphiphiles we reported before.¹⁷ By immersing the Trp multilayer film in the TPPS solution, a complex multilayer film also formed because of the penetration of TPPS into the preformed film. There existed equilibrium in such ex situ adsorption. It took about 60 min to obtain a saturated complex film. Soret and Q bands are observed

at 487 and 705 nm, respectively. In comparison with the J aggregate formed in type I multilayer films, the J aggregate in type II films showed a slight blue shift of the J band. It was reported that the size or the aggregation number of the J aggregate is related to the UV-vis absorption spectra. The red shift of the J band in comparison with the monomer band in the type I film, which is larger than that of the type II film, indicated that the type I film formed a J aggregate with more TPPS molecules. This conclusion was supported by analyzing the J bands of the two spectra using the full width at half-height (fwhh). The fwhh values of the Soret band of the J aggregate

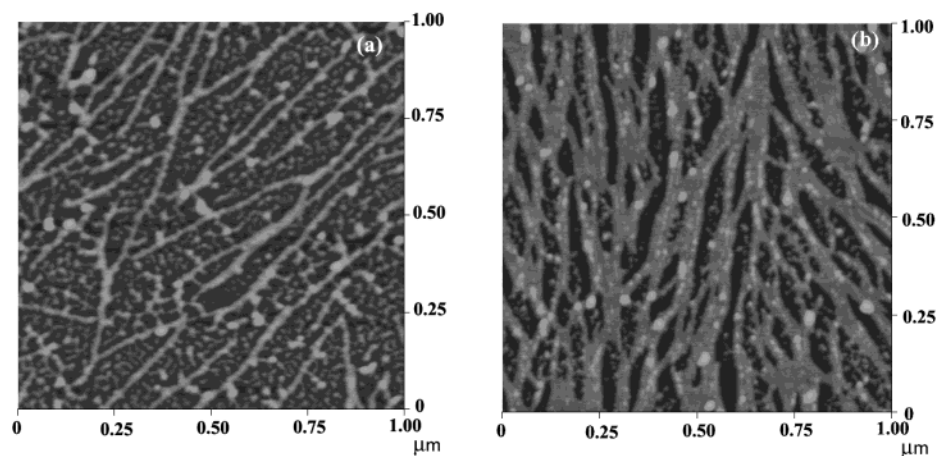


Figure 8. AFM picture of the type I complex film at different surface pressures: (a) 15 mN/m and (b) 30 mN/m.

in type I and type II multilayer films were 565 and 826 cm^{-1} , respectively. Knap et al. theoretically predicted that the adsorption spectral width of the aggregate is narrower than that of the monomer by a factor of \sqrt{N} , where N represents the spectroscopic aggregation number.³³ On the basis of their work, it can be suggested that the spectroscopic aggregation number in the type I film is twice that of the type II film. However, the physical sizes of the J aggregates were also different. Although larger and nanorodlike morphologies were observed for the type I film, only small granular particles were observed for the type II multilayer film because in the case of the type I method TPPS can grow freely into larger size aggregates. In the case of the type II film, the growth of the J aggregate was confined into the local positions of the preformed multilayer films. Such different aggregation behavior is supposed to affect the chirality of the complex films.

Supramolecular Chirality of the TPPS Complex Films.

In our previous work, we found that the supramolecular chirality of TPPS could be obtained even through achiral molecules. Our previous work showed that the simple air/water interface could afford the symmetry breakage of the achiral molecules to form a chiral assembly. In that case, the sign of the chirality was formed by chance. Therefore, we can get the CD signals only without a determined sign. To realize control of the chirality of the TPPS assemblies in the complex multilayer film, we used a chiral amphiphile instead in this paper. However, in the case of the type I multilayer film, the chirality of TPPS is still uncontrollable (i.e., the sign of the CD signals appeared randomly, regardless of the chirality of the amphiphiles). It is well known that the J aggregate of TPPS can exhibit chirality, which appears randomly because of the achiral nature of the molecule.¹⁴ Therefore, the supramolecular chirality of the TPPS J aggregate in the complex film of the chiral amphiphile with TPPS can be affected by two factors: the chirality of the J aggregate of TPPS and the chirality of the amphiphiles. In the case of the type I multilayer film, the chirality was uncontrollable because in the type I multilayer film the complex between Trp and TPPS was formed first in the monolayer. Upon spreading Trp on the aqueous subphase of TPPS, the complex between Trp and TPPS was formed immediately. Because of the flexibility of the complex Langmuir monolayer, TPPS could form J aggregates easily and grow very large. In this case, the aggregation tendency of TPPS was far greater than that of Trp. Therefore, we got the complex film in which the chirality of TPPS was independent of the chiral monolayer template. In the case of the type II multilayer film, the situation is different. Once the L- or D-Trp multilayer film is formed, the Trp

molecules will form chiral domains or a chiral nucleus. When TPPS aggregated in the spaces of the films, they grew along the Trp domains and could follow the chirality of only the template itself. In addition, the J aggregate could not grow large enough because of the confinement of the multilayer film. Therefore, in this case, we get the Trp/TPPS multilayer films where the supramolecular chirality of TPPS can be controlled by the chirality of enantiomeric amphiphile. We also constructed the complex multilayer film with the type II method using an achiral octadecylamine and TPPS. The results showed that the sign of the CD signal was random and uncontrollable. Therefore, it can be concluded that the supramolecular chirality of TPPS can be controlled only by using a chiral multilayer film as a template.

Conclusions

Complex multilayer films of TPPS and chiral Trp amphiphiles can be formed by in situ or ex situ adsorption. In both cases, TPPS can be incorporated as a J aggregate. Although larger J aggregate are formed through in situ complex formation in monolayers, small aggregates were obtained in the ex situ method. Both of the complex multilayer films showed supramolecular chirality, and strong CD signals were observed in the corresponding Soret and Q bands of the TPPS aggregate. Although the supramolecular chirality of TPPS was uncontrollable through in situ complex formation between the enantiomeric amphiphile monolayer and TPPS, it could be controlled via ex situ complex formation with the preformed enantiomeric multilayer films. The chirality of TPPS in the latter case followed the chirality of the chiral films. It was suggested that in the case of ex situ complex formation the growth of the TPPS J aggregate on the chiral domains of Trp multilayer films plays an important role in controlling the supramolecular chirality of TPPS. These results gave an important clue to the control of the chirality of TPPS in solid films.

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