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Supramolecular Chirality and Chiral Inversion of Tetraphenylsulfonato Porphyrin Assemblies on Optically Active Polylysine

Li Zhang and Minghua Liu*

Beijing National Laboratory for Molecular Science (BNLMS), CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, People's Republic of China

The self-assembly and induced supramolecular chirality of a dianionic *meso*-tetraphenylsulfonato porphyrin (TPPS) on the optically active polylysine has been investigated. Our research has confirmed that in the presence of poly(L-lysine) (PLL) or poly(D-lysine) (PDL), TPPS could form both H and J aggregates and the exciton type Cotton effect was induced in the corresponding absorption bands of H and J-aggregates. We have further revealed that the induced chirality of the H-band always followed the chirality of PLL or PDL, while the sign of the exciton couplet in the J-band could be the same as or opposite to that of the H-band depending on the mixing sequence and the ratio of PLL or PDL to TPPS (*P/T* ratio). At a *P/T* ratio less than 4, both the J and H aggregates showed the same symbolic CD signal. At a *P/T* ratio larger than 4, the opposite sign of the exciton couplet was observed for H and J-bands when TPPS was added into PLL, while the same sign was obtained when PLL was added into TPPS. Interestingly, the J-band with the same sign as that of the H-band can be inverted into the opposite sign under heating. A mechanism relating to the dynamic and thermodynamic formation of the chiral aggregates in the presence of PLL or PDL was proposed.

Introduction

Porphyrin is an important class of functional materials. Among various porphyrins, the water-soluble *meso*-tetraphenylsulfonato porphyrin (TPPS) has attracted considerable interest due to its unique aggregation behavior in solutions. TPPS can assemble into various molecular aggregates and shows characteristic optical properties such as intense narrow absorption bands (J- and H-bands),[1−9] strong nonlinear optical response,[10] and fast energy transfer within the aggregates.[11−13] Besides these properties, the chirality of the TPPS aggregates have also been received great interest. Since TPPS itself is achiral, the chirality of the TPPS aggregates can be obtained only in a supramolecular level, that is, through the noncovalent interaction with itself or other substances. It is unique that TPPS can assemble into chiral aggregates by itself without introducing any chiral substances. For example, it has been reported that under vortex stirring, TPPS can assemble into chiral assemblies in aqueous solutions.[3,14] We have also revealed that TPPS could form chiral assemblies when assembled through the air/water interface.[15] In these cases, the handedness of the TPPS can be determined by the stirring direction or by a chance, which was due to the spontaneous symmetry breaking in the system. When interacted with other chiral substances, TPPS can form aggregates and their chirality can also be induced.[16−22] Since TPPS is negatively charged, cationic chiral polymer such as poly(L-lysine) (PLL) or poly(D-lysine) (PDL) was proved to be efficient in inducing the aggregation and chirality of TPPS.[19b,20−22] Not only the α-helical polylysine but also random coil polylysine was found to serve as a good template to induce the formation of J-aggregate and H-aggregate of TPPS and the chirality.[20,21] J-aggregates and H-aggregates of TPPS were chiral and the chirality of them was suggested to be related to the chirality of the polylysine.

However, on survey of the researches on the supramolecular chirality or induced chirality in the binary system of TPPS and PLL in acidic environment, it was found that the induced CD signal of the J-band and H-band could be different. For example, Periasamy and Nezu reported that the CD signal for both the J-aggregate and H-aggregate were negative under the templated poly(L-lysine).[20,21] Whereas Fukushima reported that the J-aggregates of TPPS on the polypeptide exhibited the opposite CD sign to that of H-aggregates in the presence of high amount of NaCl, although the polypeptide conformation was almost independence of NaCl concentration.[22] The theoretical and experimental research by Ohno et al. indicated that both J and H-band have the same sign of the exciton couplet.[3] This seemingly contradictory phenomenon inspires us to explore why and when the sign of the exciton couplet of H and J-band is the same or opposite and their relationship to the chirality of the template. Can this couplet with the different or same sign be inverted at a certain condition? In this paper, we have made a detailed investigation on the supramolecular chirality in the TPPS and polylysine (PLL or PDL) system. We have clearly shown that the induced chirality of H band always followed the chirality of the template, while the J-band could be the same as or opposite to the chirality of H band depending on the *P/T* ratio and the mixing sequence of TPPS and polylysine. Interestingly, upon heating or keeping the mixture at room temperature for a long time, the chirality of J-band was finally inverted into the aggregates showing the opposite Cotton effect to that of the H-band, revealing the difference in the dynamical controlled and thermodynamically controlled chirality of J-band. The aggregation and the supramolecular chirality of TPPS on the polymer were investigated through the UV−vis and CD spectra under various conditions.

* To whom correspondence should be addressed. E-mail: liumh@iccas.ac.cn.

Experimental Methods

Water-soluble porphyrin, *meso*-tetraphenylsulfonato porphyrin, was purchased from Dojindo Laboratories and used without further purification. Poly(L-lysine) (PLL) and poly(D-lysine) (PDL) were obtained from Sigma in hydrobromide salt and used without additional purification. The molecular weights of PLL and PDL are 22 100 and 27 200, respectively.

In all experiments, the concentration of TPPS was kept at 10 μM. The pH value of the TPPS solution was adjusted to 3.1 by hydrochloric acid to avoid the aggregation of TPPS and simultaneously to enable TPPS as zwitterionic species.[23] The stock solutions of PLL or PDL were prepared by dissolving a certain amount of sample directly into water. The stock solution of PLL or PDL was mixed with TPPS to form certain mixtures with different molar ratio of polymer to TPPS (P/T = molar concentration of lysine residue to TPPS).

To investigate the assembly of TPPS with polylysine, TPPS was mixed with PLL or PDL in different sequence. One is to prepare the mixture by adding a certain amount of the PLL or PDL solution dropwisely into ~5 mL of vigorously stirred solution to reach a final 5 mL 10 μM TPPS (pH = 3.1), which is defined as process I. Another is to add the nearly 5 mL TPPS (10 μM, pH = 3.1) solution to a slight amount of PDL or PLL solution with stirring, which is defined as process II. The temperature was kept at 20 °C during the whole process. The sample solutions were kept at 20 °C for 2 h before measurements in order to attain equilibrium.

The absorption and circular dichroism (CD) were obtained from a JASCO UV-530 spectrophotometer and a JASCO J-810 spectrophotometer, respectively. During the measurement of the absorption and CD spectra, 0.2 and 1 cm quartz cells were used, respectively. A droplet of the TPPS/PLL mixtures with various P/T ratios was added onto a mice surface. After drying, the sample was measured by the atomic force microscope (AFM). The AFM height images without any image processing except flattening were recorded on a Digital Instrument Nanoscope IIIa Multimode system (Santa Barbara, CA) with a silicon cantilever using the tapping mode.

Results

1. Aggregation and Supramolecular Chirality of TPPS on Polylysine: Effect of Mixing Sequence. Although individual TPPS does not form any aggregates in an aqueous solution of 10 μM at pH = 3.1, it forms the ordered aggregates when mixed with polylysine and an obvious color change can be seen. In addition, the mixtures show induced or supramolecular chirality in the corresponding absorption bands of TPPS. Interestingly, it is found that the mixing sequence, that is, whether TPPS was added into PLL solution or the PLL was added into TPPS solution, can affect the aggregation as well as the chirality of the resulted TPPS/PLL complex. In a typical experiment, the ratio of PLL to TPPS was kept at 8 and the assemblies were monitored by UV−vis and CD spectra. Figure 1 shows the UV−vis spectral changes upon mixing of TPPS with PLL in water.

In a 10 μM aqueous solution (pH = 3.1), TPPS exhibits two absorption bands at 432 and 640 nm, which can be assigned to the Soret band and Q-band, respectively. In the PLL/TPPS mixture, four adsorption bands are observed, as shown in Figure 1b,c. When TPPS was added into PLL (process II), as shown in Figure 1c, Soret and Q-bands show red-shifts to 490 and 709 nm, respectively, indicating the formation of J-aggregate of TPPS on the PLL template.[3,21] A relative weak absorption band is observed at 420 nm, which is blue shifted in comparisons
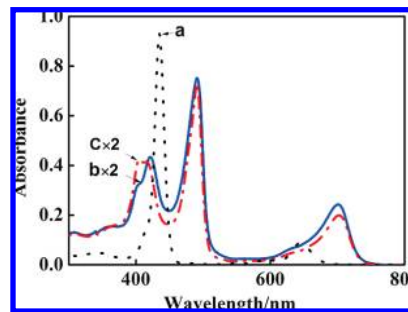

Figure 1. UV−vis spectra of (a, dotted line) the solution of TPPS (10 μM, pH = 3.1) and PLL/TPPS mixtures prepared by process I (b, solid line) and process II (c, dash dotted line) at P/T = 8.
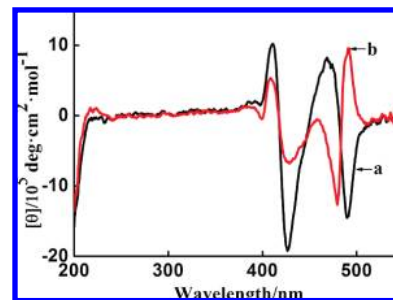

Figure 2. CD spectra of PLL/TPPS mixture in different mixing sequence (a) PLL was added to TPPS (process I); (b) TPPS was added to PLL solution (process II).

with the TPPS monomer in solution. This band has been attributed to the formation of H-aggregate.[4,24] In addition, an absorption band appears around 400 nm, which is ascribed to the H-dimer of TPPS on the PLL templates.[16,20] When PLL was added into TPPS solution (process I), the relative intensity of the three bands changed. The band at 400 nm shows an obvious decrease in this case. These spectral differences imply that the mixing sequence may affect the subtle aggregation of TPPS with PLL.

A larger difference comes from their corresponding CD spectra. It is well-known that when some achiral dyes are assembled on chiral polymers, the assemblies will show induced or supramolecular chirality;[18−22,25−27] so is the present case. Figure 2 shows the CD spectra of PLL/TPPS mixture with a mixed ratio of P/T = 8. Strong CD signals in the Soret band are observed. Interestingly, the shape of Cotton effect is different by the mixing sequence. The CD spectra can be regarded as a combination of two exciton couplet. One couplet is due to the TPPS H-aggregate, where negative and positive Cotton effects appear at 426 and 410 nm, respectively, with a crossover at 420 nm. The other can be assigned to the J-aggregates of TPPS, where negative and positive Cotton effects appear at 492 and 475 nm, respectively, with a crossover at 485 nm. When TPPS assembled with PLL, negative exciton chirality (long wavelength negative, short wavelength positive for the CD couplet corresponding to the Soret band)[28,29] is always detected for the H-band. However, the J-band shows a change depending on their mixing sequence. When PLL was added into TPPS, or in the process I, a negative couplet is observed for the J-band, which has the same sign with that of the H-band. In the process II, in which TPPS was added into PLL solution, a positive couplet is observed, which has the opposite sign to that of the H-band.

If PDL was used as the template, a similar phenomenon is observed. In the case of P/T = 8, a positive couplet is always observed for the H-band, while the J-band could be either
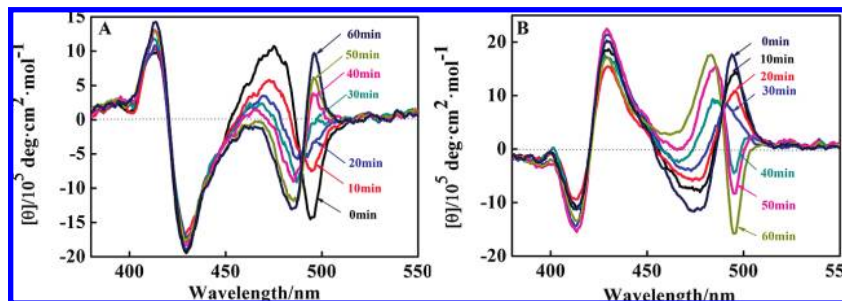
Figure 3. Time-dependence of CD spectra of (A) PLL/TPPS mixture and (B) PDL/TPPS mixture during assembling process I at 35 °C.
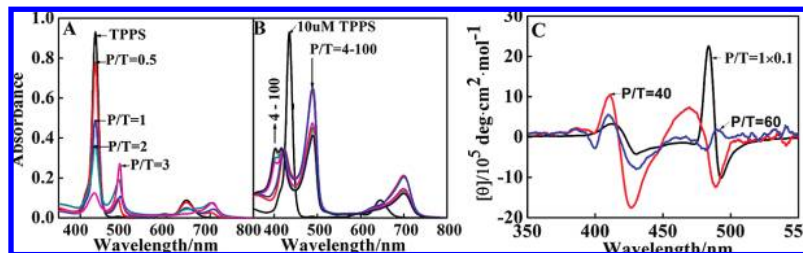

Figure 4. UV−vis spectra of 10 μM (pH = 3.1) TPPS assembled on PLL by adding PLL to TPPS with various *P/T* ratios. (A) *P/T* ratio at 0.5−3; (B) *P/T* ratio at 4−100; and (C) the corresponding representative CD spectra.

positive or negative depending on their mixing sequence. When TPPS was added into PDL, the negative exciton couplet is observed for the J-band, while it is positive when PDL was added into TPPS solution.

2. Inversion of Supramolecular Chirality in the Solution. From the spectral data above, it is seen that the chirality of H band followed the chirality of polylysine. However, the J-band showed a dependence on the mixing sequence of the two components. In order to further disclose the relationship between the sign of exciton couplet in the J-band and H band, the solution was kept at an elevated temperature of 35 °C and their CD spectral changes were monitored as a function of time. For the mixture obtained by the process II, there is no significant change in the CD spectra. However, for the mixture by process I, an interesting inversion of the J-band as a function of time is observed, as shown in Figure 3.

When PLL was added into TPPS solution, as shown in Figure 3a, the negative chirality is detected at the H- and J-band at the initial mixing at room temperature. When the mixture was heated to 35 °C and kept for a certain time, a significant change in the CD spectra is observed. Both negative Cotton effect at 492 nm and positive Cotton effect at 478 nm of the J-band decrease with the time until 30 min. After 30 min, the bisignate CD signal became a single band centered on 485 nm. With the time further increasing, a positive couplet is observed and the intensity of the couplet increases until 40 min. No significant change was detected for keeping the solution for an even longer time. During the whole inversion of the exciton chirality of the J-band, the CD signal of H-band shows only a slight change. When cooled down to room temperature, the CD spectra do not change anymore. When we did the parallel experiments on the PLL/TPPS mixture obtained by the process II, there was no change in the CD spectra. This means that the J-band showing the opposite exciton chirality with the H-band is more stable.

When PDL was used, similar phenomenon was observed, as shown in Figure 3b. In this case, the H-band always shows positive couplet. When PDL was added into TPPS, a positive couplet is observed in the initial for the J-band. Upon heating at 35 °C for 1 h, the band converts into a negative couplet.

There is no change for the mixture obtained by adding TPPS into PDL solution in which the J-band shows the negative couplet.

3. Dependence of Spectral Properties of the TPPS/PL Mixture on *P/T* Ratios. We have further investigated the UV−vis and CD spectra of TPPS assemblies on PL template at various *P/T* values since it has been reported that the *P/T* value affect the aggregation as well as the induced chirality.[20,30−32]

Figure 4 shows the UV−vis spectra of TPPS upon titration with PLL at various *P/T* ratios from 0.5 to 100. When less amount of PLL was added into the TPPS solution, that is to say, *P/T* = 0.5−3, the absorption bands at 434 and 644 nm undergo hypochromism and new bands appear at 489 and 702 nm. With the ratio of *P/T* increased to 4, a new adsorption band at 420 nm appears instead of the band at 434 nm, which can be ascribed to the formation of H aggregates induced by PLL templates. With a further increase of the *P/T* ratio, another absorption band appears at 401 nm. It is found that the intensity of this band increases with the *P/T* ratio, which indicates that the H-dimer of TPPS is formed when there is more PLL in the solution. During these UV−vis spectral changes, the CD spectra show a similar change. Both J- and H-bands show the same sign exciton couplet until the *P/T* ratio is extended to ca. 40. When the ratio was increased to 60, the J-band switches to positive and a weak negative Cotton effect is observed at around 400 nm. This indicates that the H-dimer of TPPS is also chiral.

For another assembling process in which TPPS was added into PLL, a slight different tendency was observed. In the UV−vis spectra, a strong band at 401 nm is observed when *P/T* is over 40. In the corresponding CD spectra, the J-band shows an opposite sign to that of the H-band. When the ratio of *P/T* is at 40, a new band appears at 401 nm. With the further increase of *P/T* ratio to 60, the CD signals of the J-band disappear while the band at 401 nm becomes strong. Upon further increasing the ratio of *P/T*, the CD spectra keep their shape and change a little with the *P/T* ratio.

Table 1 summarizes the sign of the CD spectra as a function of *P/T* ratios and the comparison of the two assembling sequences. It is clear that the CD spectra can be divided into three regions depending on the *P/T* values. When *P/T* is less
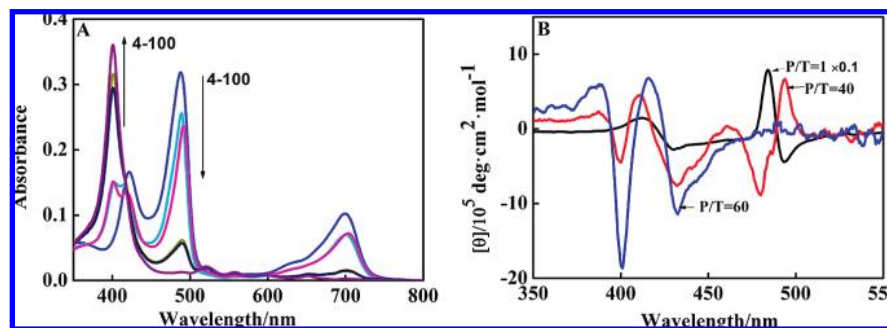
Figure 5. (A) UV−vis and CD (B) spectra of 10 μM at pH = 3.1 in the presence of PLL at different *P/T* ratios. The assemblies were formed by process II.

TABLE 1: Dependence of CD Signal of TPPS Chiral Assemblies on the *P/T* Ratio

Ratio of PLL to TPPS		H band (420 nm)	J band (485 nm)	H-dimer
P/T < 4	Process I	negative	negative[a]	nd
	Process II	negative	negative[a]	nd
4 ≤ *P/T* ≤ 40	Process I	negative	negative[b]	nd
	Process II	negative	positive	negative
P/T > 40	Process I	negative	positive	negative
	Process II	negative	nd	negative

[a] The negative couplet cannot be changed into positive one under heating at 35 °C and kept at room temperature for a long time. [b] The negative couplet can be changed into positive one under heating at 35 °C and kept at room temperature for a long time. nd: not detected.

Figure 6. An illustration on the formation of TPPS aggregate on polymer. The green block represents TPPS and its charges were omitted. (a) Pending type aggregate, in which one site of TPPS binds on the PLL, while the other unit stacked on the first in a head-to tail manner as J-aggregate. When less PLL presented in the solution or PLL was added into TPPS, such type of aggregates was predominantly formed and the process is a dynamical one. (b) Wrapping type aggregation, in which every TPPS unit is wrapping on the polymer chain, while these units formed a head-to-tails stacking as J-aggregate.

than 4, both of the mixing sequences give the same CD signal and the negative exciton is observed for both the J- and H-band. In addition, even upon heating to a higher temperature, the negative J-couplet will not convert into positive one.

In the *P/T* range of 4−40, we have found that process II always gives the opposite H- and J-couplet in the CD spectra, while process I gives the same negative couplet in their CD spectra. However, upon heating at 35 °C for a certain time, the negative J-couplet will change into a positive one. Moreover, the time to realize the inversion of the chirality was strongly dependent on the ratio of *P/T*. At a *P/T* ratio of 4, the time to inverse CD signal was 60 min, and the time was shortened to 30 min at *P/T* = 8. In the case of *P/T* at 40, only 10 min was enough to realize such inversion. The CD change was further analyzed by kinetic equation and a linear fit was obtained (Figure S1 in the Supporting Information). The slope of the line indicated that larger *P/T* ratio is more favorable for realizing the chiral inversion.

The third region is *P/T* > 40. Upon addition of PLL into TPPS (process I), the J-band and H-band show the opposite signal in the CD spectra, which is different from that of *P/T* < 40. While in the case of the addition of TPPS into PLL solution (process II), no CD signal can be detected for the J-band.

In addition, when the *P/T* was higher a new Cotton effect, which is the same sign the as H-band, appeared at around 400 nm. This band appeared at around a *P/T* of 40 for process II, while it appeared at 60 for process I. The process II showed a stronger CD signal.

Discussion

It has been well reported that optically active polylysine in the solution can induce the aggregation and supramolecular chirality of TPPS. Our results have confirmed this and further revealed several new features. First, depending on the mixing
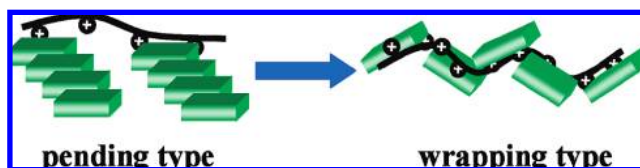
sequence, either the aggregation or the induced chirality could be different. Second, while the H-band always follows the chirality of polylysine, that of the J-band could be opposite or the same as the H-band depending on the mixing sequence as well as the *P/T* ratio. Third and the most important, we have further made it clear whether and when the chirality of the J-band with the same sign as H-band can be converted into the opposite one.

When mixing the TPPS with PLL or PDL, we used dilute TPPS solution in order to avoid the aggregation of TPPS itself. During such mixing, a dynamic assembly of TPPS on the concentrated PLL occurred. When PLL was added into TPPS in which TPPS formed a locally overconcentrated condition, TPPS tends to assemble on several limited binding sites of PLL dynamically. When TPPS was added into PLL solution, in which PLL was in a large excess, TPPS prefers to bind many sites on the PLL chain.

The *P/T* ratio can affect the binding of TPPS on PLL both dynamically and thermodynamically. When there is large number of positive charge centers in PLL than TPPS (high *P/T* ratio), TPPS will finally attach on many sites thermodynamically as a divalent anion. When *P/T* ratio is low, only limited sites can be occupied by TPPS. Figure 6 illustrated such interaction between TPPS and PLL as well as their resulted chirality.

When TPPS was mixed with PLL, due to the electrostatic interaction, TPPS can easily attach on PLL. Although TPPS have two net negative charges in pH = 3.1,[23] it seems that only one active site can attach on the PLL when *P/T* ratio is less than 4. It is interesting to question why this ratio is 4 but not 2 since TPPS is a divalent anion. This is because the distance between the two active sites of TPPS is 1.8 nm,[33] while the distance of the neighboring positive charge center in PLL is about 0.62 nm according to CPK model. Because of the steric hindrance, it seemed to be reasonable that one site but not two sites bind to PLL. In this case, the aggregates just pending are
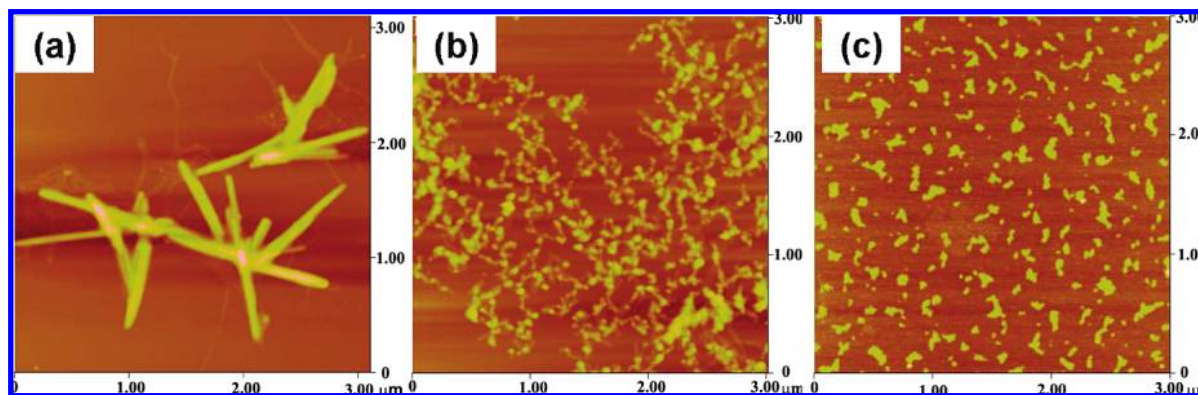
TPPS Assemblies on Optically Active Polylysine

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Figure 7. AFM images of TPPS/PLL complex with various *P/T* ratios cast on a mica surface. (a) *P/T* = 1; (b) *P/T* = 8; (c) *P/T* = 80.

on the polymer chain with the first TPPS attached on it. This aggregate is the same as those reported in many papers, in which H-band and J-band showed the same CD signals. Although the binding of TPPS to the different chain is possible, the aggregation of TPPS is stronger than that prohibited such interchain aggregation.

When *P/T* ratio is larger than 4, two sites of TPPS can possibly bind to PLL, which is thermodynamically more stable. In this case, the TPPS tended to form the aggregates along the polymer chain. In such case, while the H-aggregate followed the chirality of the polymer chain, the J-band showed an opposite signal due to their transition moment that was in different direction.

The effect of the mixing sequence can be explained as follows. When TPPS was added into PLL in which PLL was in large excess, TPPS predominantly formed the wrapped aggregates and the opposite H- and J-band was observed. When PLL was added into TPPS, the pending type aggregates were formed first dynamically. Upon heating, TPPS will prefer to bind more strongly on PLL using two sites and will transform from the pending type to the wrapping type. Thus, we observed the inversion of the chirality in the J-band.

When only a small amount of PLL existed in the mixture, neither method could lead to the wrapping of TPPS on PLL and thus only the Cotton effect with the same sign could be obtained. When a large number of PLL existed in the solution, no aggregation could be formed because TPPS tends to bind to PLL in separate binding sites. However, when PLL was added into TPPS in which a locally concentrated TPPS presented, the aggregate can still form on the template PLL. Once such TPPS aggregate was formed with PLL or PDL, it seemed that such aggregate itself was very stable. This explained why we still obtained J-aggregate at *P/T* ratio of 100 when PLL was added into TPPS.

The above model is further supported by the AFM observation. We cast the mixture with a different *P/T* ratio on a mica surface and measured their AFM pictures, as shown in Figure 7. Nanorod structures with a diameter of 60−100 nm were obtained when *P/T* = 1. This nanorod is supposed to be stacked by TPPS unit via the pending type aggregation. Such rigid nanorod structure is stable and can hardly be destroyed by heating the solution. Thus, we could not realize the chiral inversion in the lower *P/T* ratio region. When *P/T* ratio is 8, the rigid rod disappeared. Some necklace-like structures appeared. When *P/T* ratio is 80, a discrete heap was observed. This indicated that TPPS and PLL formed a "soft" structure. Such structure is possible for realizing the chiral inversion. Therefore, we observed chiral inversion in the TPPS/PLL mixture with higher *P/T* ratio.

Conclusions

We have demonstrated that a dianionic *meso*-tetraphenylsulfonato porphyrin could form chiral H-aggregates and J-aggregates on template poly(L-lysine) or poly(D-lysine). During such assembling process, both the mixing sequence and the relative ratio of polymer residue to the TPPS played important roles in determining the aggregations as well as the chirality. It was found that the local concentration of the PLL or TPPS determines the dynamic assembly of the TPPS on the polymer chain, while the final chirality and the aggregation were determined by the relative ratio of the PLL to TPPS thermodynamically. When the *P/T* ratio is less than 4, a pending type aggregate is essentially formed in which the H-band follows the chirality of polymer, while the J-band has the same sign of the chirality as that of the H-band. When the *P/T* ratio is larger than 4, the wrapping type aggregate is suggested in which the H-band follows the chirality of polymer, which the J-band shows as the opposite sign. In an appropriate *P/T* range (from 4 to 40), a pending type aggregate formed in the initial mixing when PLL was added into TPPS can be converted into wrapping one upon heating. The work provided the dynamical and thermodynamical assembly process of TPPS aggregates with the optically active polylysine. The CD spectral measurements have not only proved the induced chirality of the TPPS aggregates, but also provided a useful way in sensing the subtle difference of the aggregates, which cannot be obtained by UV−vis spectra.

Supporting Information Available: Dynamic change of CD spectra on incubation time at 35 °C and corresponding linear fitting curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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