Electronic Supplementary Information

Self-assembly of Water-soluble TPPS in Organic Solvents: From Nanofibers to Mirror Imaged Chiral Nanorods

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1. Experimental details

Materials

(1R,2R)-(-)-1,2-Diaminocyclohexane (R-DAC, >98%, TCI), (1S,2S)-(+)-1,2-Diaminocyclohexane (S-DAC, >98%, TCI), 5,10,15,20-Tetrakis(4-sulfophenyl)porphyrin Hydrate (TPPS, >98%, TCI) were used as received without further purification or treatment.

Assembly of TPPS nanostructures in organic solvents

Experimentally, the TPPS supramolecular nanostructures were assembled by injecting chloroform (5 mL) into a TPPS methanol solution (0.5 mL, $2 \times 10^{-3} \text{ M}$) under vigorous stirring at ambient conditions. It was found that green floccules were formed immediately after the mixing. On the other hand, for the DAC-assisted assembly, almost similar operations were carried out except that a chloroform solution of DAC molecules (5 mL) was injected into a TPPS methanol solution (0.5 mL, $2 \times 10^{-3} \text{ M}$). The concentration of the DAC molecules dissolved in chloroform was tuned to an appropriate value such that the molar ratio between TPPS and DAC (TPPS/DAC) molecules in the assembly systems is 2/1, 1/1, 1/2 and 1/4, respectively.

Measurements of circular dichroism (CD), linear dichroism (LD), and FT-IR spectra

After the above-mentioned operations, the obtained dispersions were subjected to circular dichroism (CD) spectral investigations. In practice, the measurements of the CD spectra were carried out at arbitrary times using the samples fabricated in the same or different batches. For the samples fabricated without the assistance of DAC molecules, ambiguous CD spectra with or without Cotton effect are observed stochastically, namely, sometimes positive, sometimes negative or even zero Cotton effects were detected from the same sample. On the other hand, for those samples fabricated with the assistance of DAC, their CD spectra were measured in the similar manner except that the obtained CD results displayed an evident dependence on the chirality of the involved DAC molecules. Besides, the linear dichroism (LD) spectra of the samples were also recorded. To estimate the contamination of CD spectra by the LD artifacts, the measured CD and LD spectra were unified as the same unit (delta OD), after which the contribution of LD to the CD spectra were estimated according to the semi-empirical equation reported previously.^{S1}

For the measurements of the FT-IR spectra, the nanostructures, pure TPPS, or pure DAC species were deposited on the single face polished silicon (111) wafers, respectively. The as-obtained samples were kept in a high vacuum chamber for 24 hours, after which they were subjected to FT-IR spectral investigations. The measurements were carried out in terms of transmission FT-IR spectra.

Apparatus and measurements

JASCO UV-550 and JASCO J-815 CD spectropolarimeters were employed for the UV-vis, CD and LD spectral measurements, respectively. JASCO IR-660 spectrometer was used for the measurements of the FT-IR spectra. The SEM measurements were carried out by using a Hitachi S-4800 system (Japan). In order to make a clear contrast, the samples employed for the SEM investigations were covered with 30~40 nm platinum by vacuum deposition. TEM and HRTEM images of the nanostructures were obtained with a FEI Tecnai G² F20 U-TWIN, which was operated with an accelerating voltage of 80 kV. The accelerating voltage was set as 80 kV, because during the measurements of the HRTEM images, our supramolecular nanostructures suffer a fast amorphization under a stronger electron beam (acceleration voltage of 200 kV).

2. Supporting Figures



Fig. S1. The CD (black curve) and LD (red curve) spectra of the TPPS assemblies formulated without the existence of DAC species. The spectra were unified as the same unit (Δ OD) and made comparable by using a semiempirical equation.^{S1} The contribution of LD effect to the Cotton effect was thus estimated to be less than 50%. This confirms that our nanofiber formulated without the presence of DAC was really chiral.



Fig. S2. The CD (black and red curves) and LD (blue and green curves) spectra of the TPPS assemblies formulated with a TPPS/DAC of 2/1 (A), 1/1 (B) and 1/2 (C). The spectra were unified as the same unit (Δ OD) and made comparable by using a semiempirical equation.^{S1} The contribution of the LD effect to the Cotton effect was thus estimated to be negligible in these cases. The black and blue curves are the results of the assemblies formulated with assistance of R-DAC, and the red and green curves are those formulated with the assistance of S-DAC.



Fig. S3. Large area SEM images of the TPPS nanostructures assembled with the assistance of R-DAC. The TPPS/R-DAC is 1/4.



Fig. S4. Large area SEM images of the TPPS nanostructures assembled with the assistance of S-DAC. The TPPS/S-DAC is 1/4.



Fig. S5. The CD (black and red curves) and LD (blue and green curves) spectra of the TPPS assemblies formulated with a TPPS/DAC of 1/4. The spectra were unified as the same unit (Δ OD) and made comparable by using a semiempirical equation.^{S1} The contribution of the LD effect to the Cotton effect was thus estimated to be negligible in these cases. The black and blue curves are the results of the assemblies formulated with assistance of R-DAC, and the red and green curves are those formulated with the assistance of S-DAC.



Fig. S6. FT-IR spectra of R-DAC (black curve), TPPS powders (red curve), and the TPPS assemblies (blue curve) formulated with assistance of R-DAC at a TPPS/R-DAC of 1/4.

As shown in **Figure S6**, strong vibrations at *ca*. 3340, 3298, 1634 and 1573 cm⁻¹, ascribing to the N-H vibrations, could be detected from the FT-IR spectrum of DAC. In the FT-IR spectrum of TPPS, SO3⁻ vibrations appeared at *ca*. 1230 and 1170 cm⁻¹. In contrast, for the FTIR spectrum of the TPPS/DAC assemblies, the SO3⁻ vibrations of TPPS shifted to 1216 and 1177 cm⁻¹ accompanied by a substantial weakness of the N-H vibrations of DAC. These experimental facts indicated that the formation of the TPPS/DAC complex could be partially ascribed to the hydrogen bond between the SO3⁻ group of TPPS and the –NH₂ group of DAC.

On the other hand, the $-NH_3^+$ vibrations generally exhibit featureless peaks in the FT-IR spectra, making it difficult to be well assigned. However, TPPS generally manifests itself as zwitterionic species, in which the strong acidity of its sulfonic acid groups could lead to a mono- or diprotonation of its central nitrogen atoms. This could be evidenced from its UV-vis spectra, where three or two Q-bands could be detected when TPPS/DAC is 1/0, 2/1 and 1/1, as shown in **Figure 1D**, **2A** and **2B**, respectively. Four Q-bands were observed for TPPS/DAC 1/2 complex (**Figure 2C**). In the case of a TPPS/DAC of 1/4 (**Figure 3C**), where the amount of the involved DAC species is further increased, the Q-bands become indiscernible. This could be owing to the occurrence of aggregation. In addition, these facts indicate that the original self-diprotonated zwitterionic TPPS species are gradually deprotonated with the increase of the amount of the DAC molecules, leading to the formation of $-NH_3^+$ groups in DAC, namely the protonated DAC. This is reasonable since TPPS and DAC are generally strong acidic and alkaline species, respectively. Thus, the complex was formed through both electrostatic interaction and H-bond between TPPS and DAC.

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