

Self-Assembled Hybrids Composed of Block Copolymer/Porphyrin Metal Complex via Hydrogen Bonding

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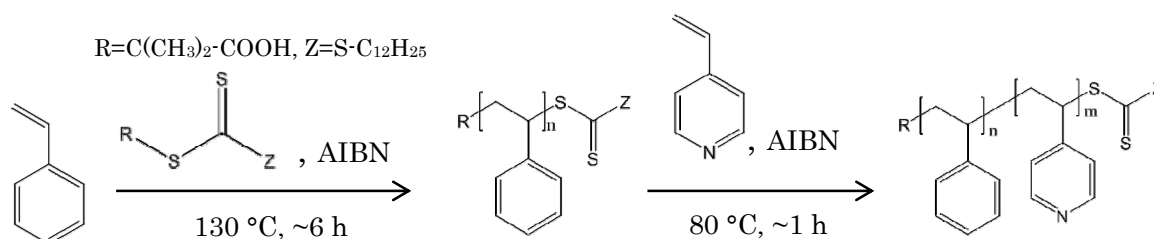
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Synthesis of polystyrene-*b*-poly(4-vinylpyridine) (SP).

SP was synthesized via RAFT polymerization by using the monofunctional chain transfer agent (S-1-dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate) (Scheme 1). Both styrene and 4-vinylpyridine monomers were purified by passing through an aluminum oxide column before use. Styrene (20.0g, 0.192 mol) was polymerized with a monofunctional RAFT agent (0.146 g, 0.4 mmol) in bulk at 130 °C for approximately 6 h. After deactivation of the macro-RAFT agent with liquid nitrogen, S macro-RAFT agent was purified with reprecipitation into methanol three times ($M_n = 28000$, $D = 1.08$). Then, 4-vinylpyridine (8.36 g, 79.6 mmol) was polymerized with AIBN (2.64 mg, 0.016 mmol) from the S macro-RAFT agent (1.5 g, 0.0535 mmol) at 80 °C in bulk for approximately 60 min. After deactivation with liquid nitrogen, SP was purified with multiple reprecipitation into hexane.

Scheme S1. Synthesis of SP



Gel permeation chromatography (GPC) for S precursor and SP diblock copolymers.

GPC was performed to measure dispersity of the S precursor and three SP block copolymers by using three TSK-GEL G4000H_{HR} columns combined with a DP-8020 dual pump and a UV detector (Tosoh Corp.), as shown in Figure S1. The wavelength of the irradiated UV for measurements is 220 nm. The eluent was dimethylformamide (DMF) and the flow rate was 1 ml/min. A calibration curve by polystyrene standards was basically used for all the measurements to estimate the dispersity index .

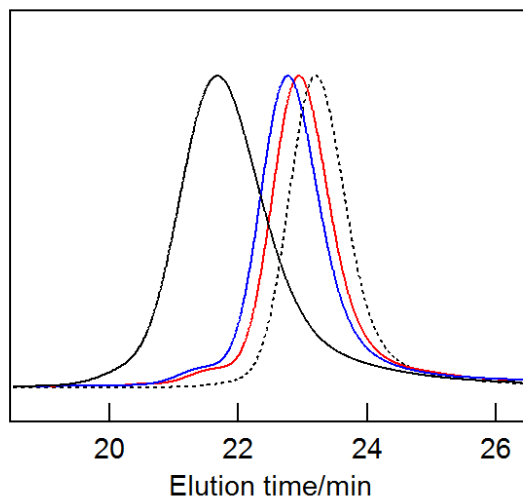


Figure S1. GPC chromatograms of an S homopolymer (dashed black line) and three SP block copolymers, where red, blue, and black solid lines represent SP1, SP2, and SP3, respectively.

¹H NMR for S precursor and SP diblock copolymers.

The molecular weight of the S precursor was determined by ¹H NMR spectroscopy (Varian), by comparing the integral of peaks at 3.2 ppm from two protons at the end of the polymer adjacent to the RAFT agent residue (S-C(=S)-S) with the integral of the proton peaks of benzene ring on the side chain of polystyrene (Figure S2). ¹H NMR was also used to measure the mole ratio of SP (Figure S3). The solvent used for these experiments was deuterated chloroform (CDCl₃).

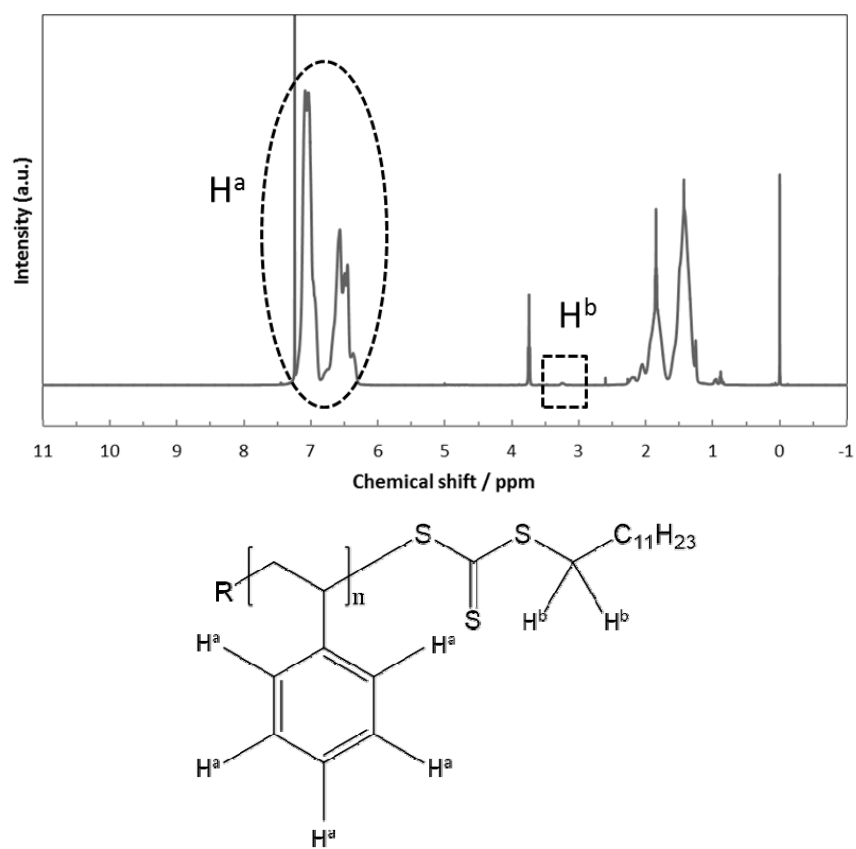
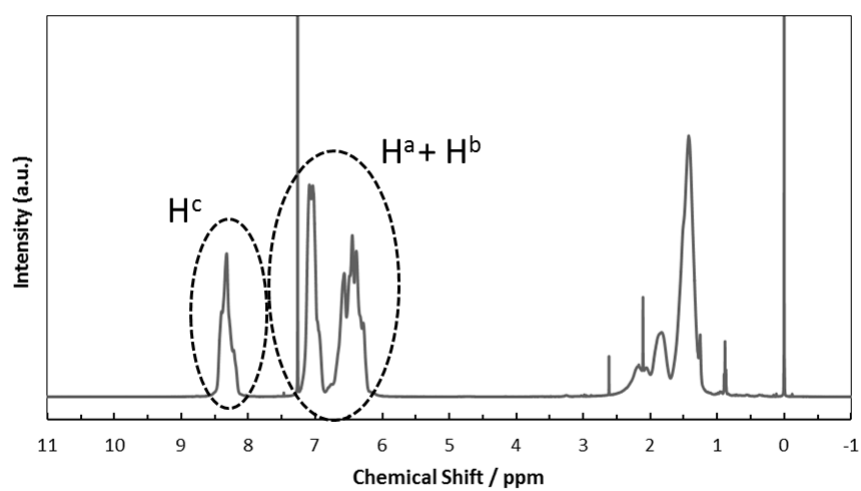


Figure S2. ^1H NMR spectrum and chemical structure of the precursor S.



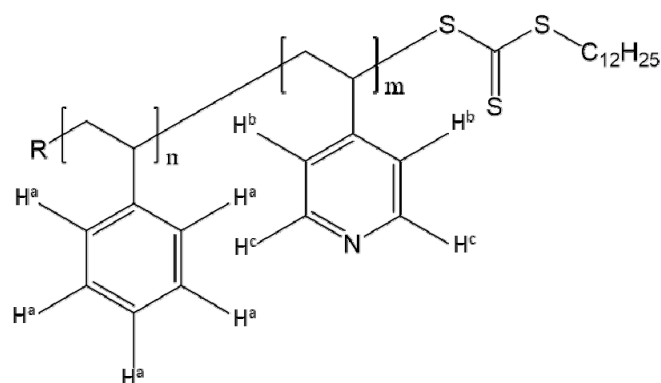


Figure S3. ^1H NMR spectrum and chemical structure of SP.

Synthesis of zinctetrakis(4-carboxyphenyl)porphyrin (ZCP). (Scheme S2)

Firstly, tetrakis(4-carboxyphenyl)porphyrin (TCP, 100 mg) was dissolved in 50 ml of DMF. Then, 150 mg of zinc acetate dihydrate $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$ was dissolved in 5 g of methanol, and this solution was mixed with the TCP solution in DMF. The mixed solution was stirred and heated at 70°C for 3 h. After the reaction, the DMF was evaporated, and the residue was dissolved in 300 g of acetic acid and the solution was passed through the aluminum column to remove the unreacted $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$ and TCP. Then, acetic acid was evaporated from the solution after column purification; finally, 85.3 mg of crude ZCP was collected. This crude product was further recrystallized with NMP and diethyl ether, yielding purple solid of purified ZCP (68.1 mg, Figure S4).

Scheme S2. Synthesis of ZCP

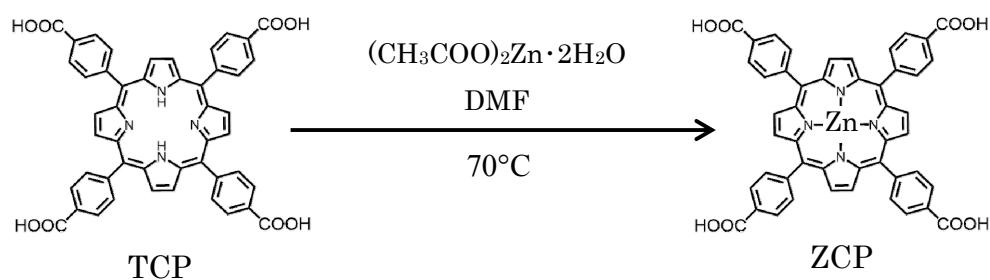


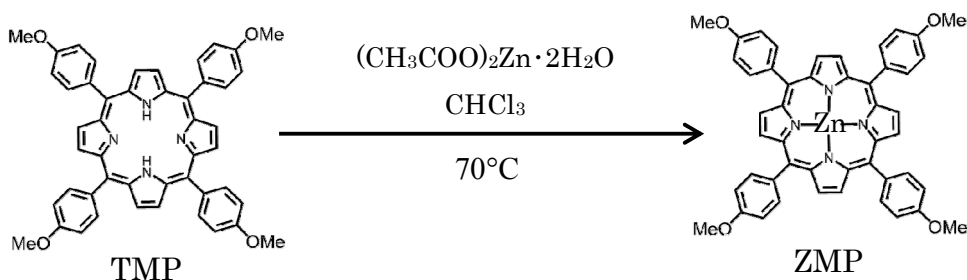


Figure S4. Photograph of ZCP powder.

Synthesis of zinctetrakis(4-methoxyphenyl)porphyrin (ZMP) (Scheme S3).

Firstly, tetrakis(4-methoxyphenyl)porphyrin (TMP, 100 mg) was dissolved in 50 ml of chloroform. Then, 150 mg of zinc acetate dihydrate $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$ was dissolved in 5 g of methanol, and this solution was mixed with the TMP solution in chloroform. The mixed solution was stirred and heated at 70°C for 3 h. After the reaction, the reaction solution was passed through the aluminum column to remove the unreacted $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$ and TMP. Then, chloroform was evaporated from the solution after column purification; finally, 84.7 mg of crude ZMP was collected. This crude product was further recrystallized with THF and diethyl ether, yielding purple solid of purified ZMP (59.1 mg, Figure S5).

Scheme S3. Synthesis of ZMP



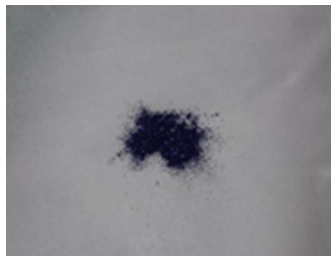


Figure S5. Photograph of ZMP powder.

Macroscopic appearance of SP1/ZCP and SP1/ZMP hybrids.

A hybrid film prepared by mixing SP1 and ZCP with a weight ratio of 1:0.1 showed a glossy purple color with smoothness (Figure S6), whereas a hybrid film prepared by mixing SP1 and ZMP with a weight ratio of 1:0.1 showed a non-glossy bluish color without smoothness.

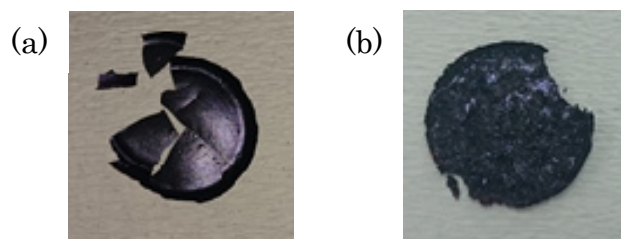


Figure S6. Macroscopic appearance of (a) SP1/ZCP(0.1) and (b) SP1/ZMP(0.1) hybrid films.

FT-IR spectra of neat SP2 and SP2/ZCP hybrids. (Figure S7)

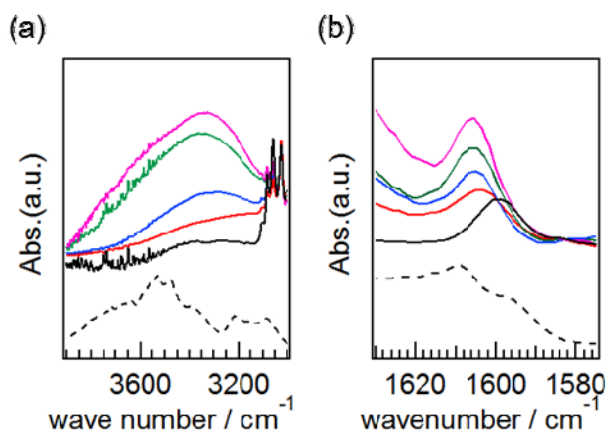


Figure S7. FT-IR spectra of neat SP2, their hybrids, and neat ZCP. (a) A region between 3000 and 3900 cm^{-1} . (b) A region between 1575 and 1630 cm^{-1} . The black dashed line represents neat ZCP, whereas the black, red, blue, green, and pinky purple lines represent neat SP2, SP2/ZCP(0.1), SP2/ZCP(0.3), SP2/ZCP(0.5), and SP2/ZCP(0.7), respectively.

DSC thermograms of neat SP2 and SP2/ZCP hybrids. (Figure S8)

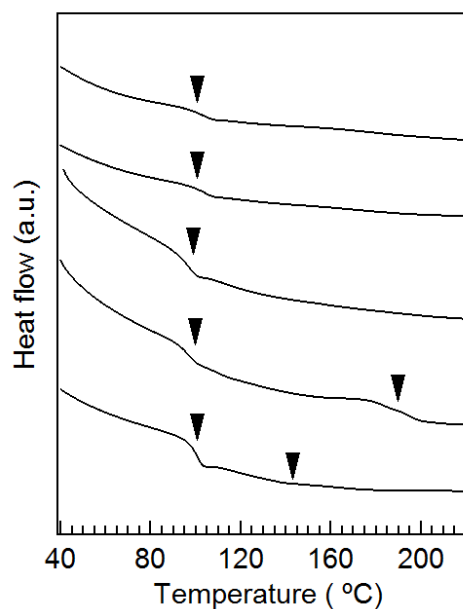


Figure S8. DSC thermograms of SP/ZCP hybrids. Thermograms are displayed in the order of the amount of ZCP added from bottom to top: neat SP, SP2/ZCP(0.1), SP2/ZCP(0.3), SP2/ZCP(0.5), and SP2/ZCP(0.7).

TEM images of SP/ZCP hybrids.

TEM images of the hybrids that are listed in Table 2 but are not shown in Figure 4 are shown in Figure S9.

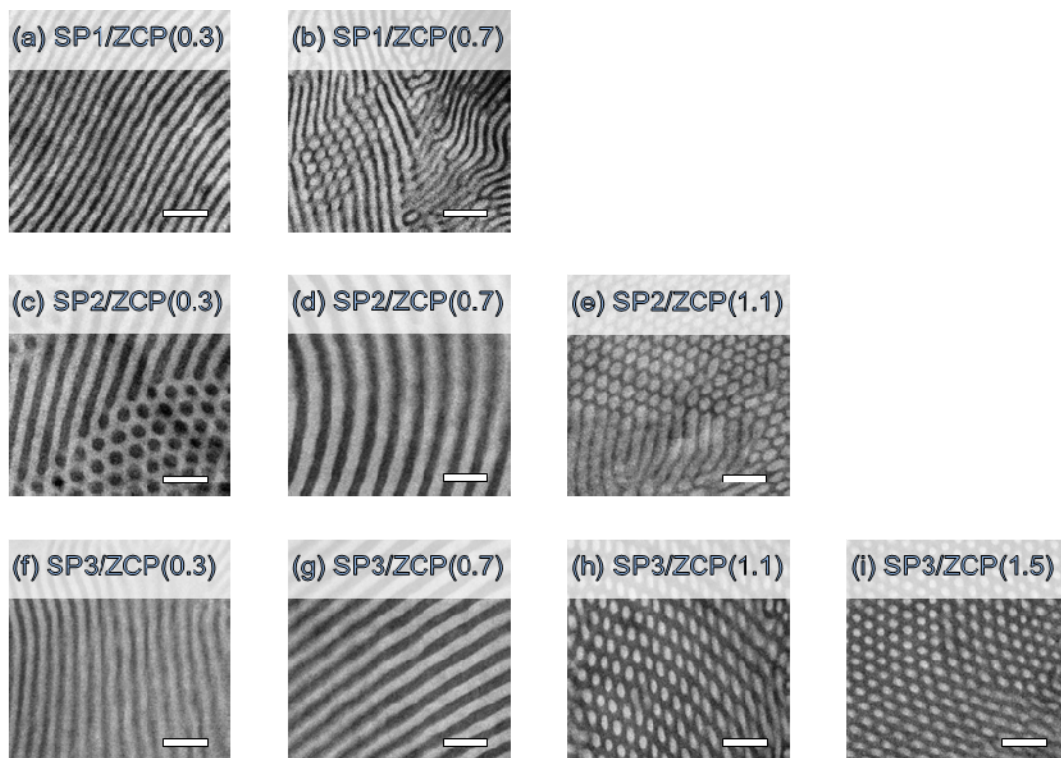


Figure S9. TEM images of SP1/ZCP (a,b), SP2/ZCP (c-e), SP3/ZCP (f-i) hybrids. Scale bars represent 100 nm.

EDX spectrum of neat SP2.

EDX was used to perform an elemental analysis for the STEM observation area of the specimen of neat SP2 subjected to iodine vapor. The elements detected in the specimen were identified (Figure S10) as C, N, Si (from contamination of silicon grease), I (from iodine vapor staining), Mo (from the Mo grid), and Fe (from the electron microscope lens tube). The peak derived from Zn was not confirmed on the spectrum of neat SP2

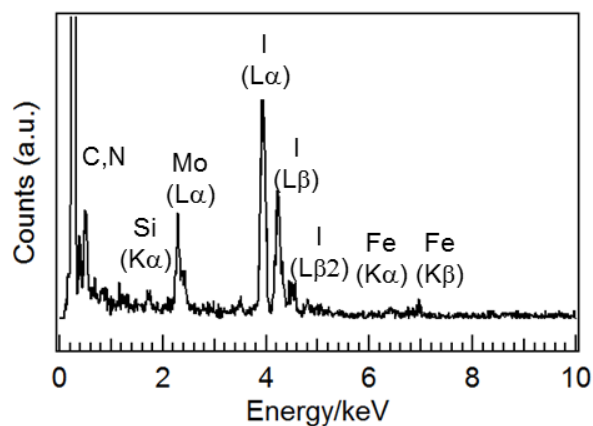


Figure S10. EDX spectrum of neat SP2.

Domain spacing determined by SAXS profiles.

Domain spacing (D) in Table 2 was estimated by using SAXS profiles and the following equations.

For lamellar structures,

$$D = \frac{2\pi}{q_1}$$

was used, where q_1 is the primary peak in the profile.

For cylindrical structures,

$$D = \sqrt{\frac{4}{3}} \cdot \frac{2\pi}{q_1}$$

was used.

For spherical structures,

$$D = \sqrt{\frac{3}{4}} \cdot \frac{2\pi}{q_1}$$

was used.