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Formation of Supramolecular Polymers from Porphyrin Tripods

Hosoowi Lee, Dajung Lee, Inhye Kim, Eunji Lee,* and Woo-Dong Jang*

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ABSTRACT: A porphyrin tripod $(P_{Zn}T)$ composed of three zinc porphyrin wings connected via triazole bridges was prepared as a monomeric building block for a supramolecular polymer. $P_{Zn}T$ formed long fibrous supramolecular polymers with a diameter of 7 nm through the axial coordination of triazole nitrogen atoms to zinc porphyrins. The molecular packing structure of a $P_{Zn}T$ -based supramolecular polymer was assigned as a hexagonal columnar phase. $P_{Zn}T$ formed a stable 1:1 host-guest complex with 1,3,5tris(4-pyridyl)benzene (Py_3B) through axial coordination of pyridyl groups to zinc porphyrins. The host-guest complex between $P_{Zn}T$ and Py_3B adopts a cone-shaped geometry. After the addition of Py_3B , the host-guest complex exhibited a



characteristic X-ray diffraction pattern of rectangular columnar ordering. Furthermore, the formation of supercoiled helical fibrous assemblies was observed by transmission electron microscopy (TEM).

INTRODUCTION

Porphyrin derivatives are a group of aromatic macrocycles composed of four pyrrole subunits interconnected through methine bridges.^{1,2} Porphyrin derivatives are associated with a variety of biological functions such as oxygen transport, catalysis, and photosynthesis.³⁻⁵ Owing to their unique chemical and physical properties, porphyrin derivatives offer very attractive research topics to chemists. Particularly, bioinspired applications of porphyrin derivatives are attracting considerable attention.⁶⁻¹¹ Biomolecules adopt hierarchically assembled three-dimensional (3D) structures through various noncovalent interactions, such as hydrogen-bonding, $\pi-\pi$, electrostatic, and coordination interactions, to achieve specific bioactive functions.^{12,13} Porphyrin derivatives have also often been used as building blocks for hierarchical supramolecular assemblies.^{14–17} Among various self-assembled materials, supramolecular polymers, in which the monomer units are held together via noncovalent interactions, have been attracting attention.^{16,18–22} The chemical and physical properties of supramolecular polymers can be easily tuned by introducing specific functional groups into the monomeric building blocks. To construct a supramolecular polymer, tripodal structures with hydrogen-bonding moieties are often adopted as a building block for assembled structures.²³⁻²⁶ Nolte et al. reported the self-assembly of a columnar-stacked porphyrin tripod with the core of benzene tricarboxamide.^{27–29} Even though Fukuzumi et al. reported a triazolyl appended porphyrin tripod, they showed only electron transfer phenomena upon the formation of a complex with fullerene.³⁰ Osuka and other groups reported the self-assembly of triazolyl bearing porphyrin through coordination interaction between

triazole and zinc porphyrin.³¹⁻³⁴ In this study, a porphyrin tripod ($P_{Z_n}T$, Scheme 1) having three zinc porphyrin units connected through triazole bridging units was designed as a building block for a supramolecular polymer. Microscopic observations revealed that P_{Zn}T forms a hierarchically assembled supramolecular polymer through the axial coordination interaction between triazole nitrogen and zinc porphyrin units. Furthermore, we suggest guest-induced morphological change in the supramolecular polymer upon the addition of 1,3,5-tris(4-pyridyl)benznene (Py₃B; Scheme 1). Due to the strong binding affinity of a pyridyl group to zinc porphyrin, the pyridyl guest generally induces the dissociation of the supramolecular polymer. Surprisingly, in our system, the addition of Py_3B induced dissociation of self-assembled $P_{Zn}T$ upon the formation of a host-guest complex and the resultant host-guest complex was further assembled to helical superstructures, which is similar to the quaternary structure of proteins in nature.

EXPERIMENTAL SECTION

Materials and Measurements. All commercially available reagents were of reagent grade and were used without further purification. Dichloromethane (CH_2Cl_2), *n*-hexane, acetonitrile, tetrahydrofuran (THF), and toluene were freshly distilled before

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Scheme 1. Structures and Synthetic Procedures of Porphyrin Tripods and Its Structural Fragments^a



^aReagents and conditions: (i) trifluoroacetic acid (TFA), 60 °C, 30 min, (ii) [1] trifluoroacetic acid, CH₂Cl₂, 25 °C, 1.5 h, [2] *p*-chloranil, (iii) *N*-bromosuccinimide, CH₂Cl₂, 0 °C, 15 min, (iv) CuI, Pd(PPh₃)₂Cl₂, triethylamine (TEA), trimethylsilylacetylene, tetrahydrofuran (THF), 70 °C, 12 h, (v) CuSO₄:5H₂O, sodium ascorbate, KF, THF/H₂O (1:1), 70 °C, 2 days, (vi) NaN₃, 1,3,5-tris(bromomethyl)benzene acetone/H₂O (3:1), 25 °C, 1 h, (vii) [1,1'-bis(diphenylphosphino)ferrocene]dichloro-palladium(II), Na₂CO₃, 1,4-dioxane/H₂O (1:1), reflux, 2 days.

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each use. ¹H NMR spectra were recorded at 25 °C using a Bruker Avance DPX 250 or DPX 400 spectrometer. ¹³C NMR spectra were recorded at 25 °C using a Bruker DPX 400 spectrometer. Matrixassisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed using a Bruker Daltonics LRF20 with dithranol (1,8,9-trihydroxyanthracene) as the matrix. Recycling size-exclusion chromatography (SEC) was performed using a JAI model LC9201 equipped with JAIGEL-1H, JAIGEL-2H, and JAIGEL-3H columns using THF (DUKSAN pure chemicals) as the eluent. UV/vis absorption spectra were measured using a JASCO V-660 spectrometer with a thermostatic cell holder coupled with a controller (ETCS-761, JASCO), and fluorescence spectra were recorded using a JASCO FP-6300 spectrometer with a temperature controller (ETC-273T, JASCO), respectively. All spectral measure-

ments were carried out using a quartz cuvette with a path length of 1 cm. Transmission electron microscopy (TEM) images were obtained using a JEM-1400 operating at 120 kV (JEOL, Tokyo, Japan). For the TEM measurements, a drop of each sample in a mixed solvent of toluene/n-hexane was placed on a carbon-coated copper grid and allowed to evaporate under ambient conditions. The sample was stained by placing a drop of uranyl acetate solution (2 wt %) onto the surface of the sample-loaded grid. The deposited sample was allowed to rest for at least 1 min, after which the excess solution was wicked off using a filter paper. Atomic force microscopy (AFM) images were obtained using a Park Systems NX10 instrument. Each sample used for AFM measurements was dropped and spin-coated onto a freshly cleaved mica surface. The nematic phases of the as-cast films were observed using a Nikon Eclipse LV100 (Nikon, Tokyo, Japan). FT-IR measurement was conducted using JASCO FT/IR-4700. A frequencydoubled laser beam (repetition rate: 200 kHz, pulse duration: ~250 fs) from a collinear optical parametric amplifier (COPA, Light Conversion), which is pumped by a femtosecond regenerative amplifier (PHAROS, Light Conversion), was used as a light source for time-correlated single-photon counting (TCSPC) measurements. Fluorescence from the sample after photoexcitation was spectrally dispersed by a monochromator and then detected with a hybrid photodetector (PMA Hybrid 50, PicoQuant). The TCSPC module with picosecond event timer (PicoHarp 300, PicoQuant) was used to record picosecond time-resolved fluorescence traces of the samples.

1. 3,5-Bis(decyloxy)benzaldehyde (7.03 g, 16.8 mmol) was dissolved in pyrrole (500 mL), and trifluoroacetic acid (TFA, 0.5 mL, 6.53 mmol) was added to the solution. The reaction mixture was stirred for 30 min at 60 °C. After the reaction, triethylamine (TEA, 0.5 mL, 3.58 mmol) was added to neutralize the solution. The reaction mixture was chromatographed on silica gel using *n*-hexane and CH₂Cl₂ to obtain 1 (6.5 g) as a yellow liquid in 72% yield. ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (s, 2 H; -NH), 6.69 (m, 2 H; C₆H₃), 6.37 (m, 2 H; H in a pyrrole ring), 6.36 (q, 1 H; C₆H₃), 6.34 (t, 2 H; H in a pyrrole ring), 5.96 (m, 2H; H in a pyrrole ring), 5.39 (s, 1 H; a-H of pyrrole), 3.88–3.84 (t, 4 H; -OCH₂-), 1.76–1.69 (m, 4 H; -OCH₂CH₂-), 1.43–0.90 (m, 34 H; -(CH₂)₇CH₃).

2. To a solution of 1 (1.62 g, 3.03 mmol), benzaldehyde (643 mg, 6.06 mmol), and dipyrromethane (443 mg, 3.03 mmol) in CH₂Cl₂ (900 mL), TFA (0.5 mL, 6.53 mmol) was added and stirred for 1.5 h at 25 °C. p-Chloranil (4.47 g, 18.2 mmol) and TEA (0.5 mL, 3.59 mmol) were then added, and the reaction mixture was stirred for a further 3 h. The reaction mixture was concentrated to a volume of 200 mL and then chromatographed on silica gel with n-hexane and CH₂Cl₂. Without further purification, the mixture was dissolved in 10% MeOH/CH₂Cl₂ containing Zn(CH₃CO₂)₂·2H₂O (2 g, 9.11 mmol) and then stirred for 2 h at 25 °C. The reaction mixture was purified by column chromatography with 3% ethyl acetate/n-hexane; the second fraction was collected and evaporated to dryness. 2 (366 mg) was then obtained as a reddish-purple powder in 14% yield. ¹H NMR (400 MHz, CDCl₃): δ = 10.24 (s, 1 H; meso-H in P_{Zn}), 9.39– 8.98 (m, 8 H; pyrrole-β-H in P_{Zn}), 8.24-7.77 (m, 10 H; P_{Zn}-C₆H₅), 7.39 (d, 2 H; o-H in P_{Zn}-C₆H₃), 6.88 (t, 1 H; p-H in P_{Zn}-C₆H₃), 4.1 (t, 4 H; -OCH₂-), 1.85 (m, 4 H, -OCH₂CH₂-), 1.49-0.82 (m, 34 H; $-(CH_2)_7 CH_3$). MALDI-TOF-MS for $C_{58}H_{64}N_4O_2Zn m/z$: calcd 912.43, [M⁺]; found: 912.17.

3. *N*-Bromosuccinimide (122 mg, 0.685 mmol) was added to a solution of **2** (619 mg, 0.677 mmol) in dry CH_2Cl_2 (60 mL), and the solution was stirred under N₂ for 15 min at 0 °C. The reaction mixture was quenched with acetone (20 mL) and evaporated. The mixture was chromatographed on silica gel using CH_2Cl_2 as the eluent to obtain **3** (653.5 mg) as a purple solid in 97% yield. ¹H NMR (400 MHz, CDCl₃): δ = 9.69–8.88 (m, 8 H; pyrrole- β -H P_{Zn}), 8.19–7.76 (m, 10 H, P_{Zn}-C₆H₃), 7.30 (d, 2 H; *o*-H in P_{Zn}-C₆H₃), 6.82 (t, 1 H; *p*-H in P_{Zn}-C₆H₃), 4.04 (t, 4 H; -OCH₂-), 1.81 (m, 4 H; -OCH₂CH₂-), 1.46–0.84 (m, 34 H, -(CH₂)₇CH₃). MALDI-TOF-MS for C₅₈H₆₃BrN₄O₂Zn *m*/*z*: calcd 990.34, [M⁺]; found: 992.30.

4. 3 (502 mg, 0.505 mmol), CuI (1.92 mg, 0.01 mmol), and Pd(PPh₃)₂Cl₂ (7.09 mg, 0.01 mmol) were placed in a Schlenk flask. The flask was degassed under high vacuum and back-filled with N_2 .

Dried THF (2 mL), TEA (3 mL), and trimethylsilylacetylene (0.18 mL, 1.27 mmol) were added. The reaction mixture was stirred for 12 h at 70 °C and then extracted with CH₂Cl₂ and distilled water. The combined extract was concentrated and then purified by column chromatography with CH₂Cl₂ and *n*-hexane to obtain 4 (260 mg) as a reddish-purple solid in 50% yield. ¹H NMR (400 MHz, CDCl₃): $\delta = 9.76-8.85$ (m, 8 H; pyrrole- β -H in P_{Zn}), 8.21–7.76 (m, 10 H; P_{Zn}-C₆H₃), 7.4 (d, 2 H; *o*-H in P_{Zn}-C₆H₃), 6.84 (t, 1 H; *p*-H in P_{Zn}-C₆H₃), 4.08 (t, 4 H; $-OCH_2-$), 1.82 (m, 4 H; $-OCH_2CH_2-$), 1.45–0.82 (m, 34 H, $-(CH_2)_7CH_3$), 0.08 (s, 9 H, TMS-acetylene H). MALDI-TOF-MS for C₆₃H₇₂N₄O₂SiZn *m*/*z*: calcd 1008.47, [M⁺]; found: 1008.25.

5. NaN₃ (1.093 mg, 16.81 mmol) was added to a solution of 1,3,5-tris(bromomethyl)benzene (1.0 g, 1.8 mmol) in 15 mL of an acetone/H₂O mixture (3:1, v/v). The resulting suspension was stirred for 1 h at 25 °C, and the reaction mixture was extracted with CH₂Cl₂ and distilled water. The combined extract was evaporated to dryness. 5 (648 mg) was then obtained as a colorless liquid in 99% yield. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (s, 3 H; C₆H₃), 4.40 (s, 6 H; benzyl-H).

P_{Zn}T. CuSO₄·5H₂O (73.4 mg, 0.294 mmol), sodium ascorbate (58 mg, 0.29 mmol), KF (31 mg, 0.53 mmol), and 18-crown-6-ether (0.50 g, 1.9 mmol) were added to a mixture of 4 (175 mg, 0.176 mmol) and 5 (7.15 mg, 0.03 mmol) in 4.0 mL of THF/H₂O (1:1, v/v). The reaction mixture was stirred for 2 days at 70 °C and then extracted with CH2Cl2 and distilled water. The combined extract was evaporated and then purified by column chromatography with 30% THF/n-hexane. Further purification was performed using recycling SEC. The first fraction was collected from recycling SEC and then recrystallized with THF and $\mathit{n}\text{-}\text{hexane}$ to obtain $P_{Zn}T$ (21 mg) as a purple solid in 23% yield. ¹H NMR (400 MHz, THF-d₈): $\delta = 9.29-$ 8.75 (m, 27 H; pyrrole- β -H in P_{Zn} and triazole-H), 8.09 (m, 12 H; P_{Zn}-C₆H₅), 8.00 (s, 3 H; P_{Zn}-C₆H₃), 7.62-7.58 (m, 18 H; m- and p-H in P_{Zn}-C₆H₅), 7.74–7.73 (d, 6 H; o-H in P_{Zn}-C₆H₃), 6.88 (s, 3 H; p-H in P_{Zn} -C₆H₃), 6.23 (6 H; benzyl-H), 4.10 (t, 12 H; $-OCH_2-$), 1.90– 0.83 (m, 114 H, $-O(CH_2)_8CH_3$); ¹³C NMR (100 MHz, THF-d₈) $\delta =$ 159.46, 151.76, 151.20, 151.13, 150.71, 150.36, 146.14, 144.64, 139.88, 135.47, 132.72, 132.43, 132.37, 132.06, 129.2, 128.53, 128.13, 127.24, 122.36, 121.59, 115.42, 101.38, 68.97, 54.49, 33.00, 30.76, 30.69, 30.58, 30.43, 27.27, 23.69, 14.58. MALDI-TOF-MS for $C_{189}H_{201}N_{21}O_6Zn_3 m/z$: calcd 3052.39, [M⁺]; found: 3055.83.

P_{FB}**T**. **P**_{Zn}**T** was dissolved in CH₂Cl₂, and an excess of TFA was then added to the solution. The mixture was stirred for 3 h at room temperature. Ethylenediaminetetraacetic acid was added to remove the zinc ions, and the reaction mixture was then extracted using CH₂Cl₂ and aqueous sodium bicarbonate. The extract was purified by column chromatography with CH₂Cl₂. **P**_{FB}**T** was obtained in quantitative yield. ¹H NMR (400 MHz, CDCl₃): $\delta = 9.05-8.69$ (m, 24 H; pyrrole-β-H in P_{Zn}), 8.47 (s, 3 H; triazol-H), 7.92–7.35 (m, 39 H; overlapped peaks of P_{Zn}-C₆H₅ and *o*-H in P_{Zn}-C₆H₃), 6.87 (s, 3H; *p*-H in P_{Zn}-C₆H₃), 6.11 (s, 6 H; benzyl-H), 4.09 (t, 12 H; $-OCH_2-$), 2.02–0.83 (m, 114 H; $-O(CH_2)_8CH_3$), -2.85 (s, 6H; P_{FB}-NH). MALDI-TOF-MS for C₁₈₉H₂₀₇N₂₁O₆ *m*/*z*: calcd 2866.65, [M⁺]; found: 2869.65

TB. Azidomethyl benzene (406 mg, 3.05 mmol), 1-pentyne (208 mg, 3.05 mmol), $CuSO_4$ ·SH₂O (973 mg, 3.90 mmol), and sodium ascorbate (1.21 g, 6.10 mmol) were dissolved in 25 mL of THF/H₂O (4:1, v/v). The reaction mixture was stirred overnight at room temperature and then extracted with CH₂Cl₂ and distilled water. The extract was purified by column chromatography with ethyl acetate and *n*-hexane. **TB** (580 mg) was obtained in 94% yield. ¹H NMR (400 MHz, MeOD): δ = 7.70 (s, 1H; triazole-H), 7.37–7.29 (m, SH; C₆H₅), 5.54 (s, 2H; benzyl-H), 2.67–2.63 (t, 2H; -CH₂CH₂CH₃), 1.71–1.62 (m, 2H; -CH₂CH₂CH₃), 0.96–0.92 (t, 3H; -(CH₃)₂CH₃).

 Py_3B . [1,1'-Bis(diphenylphosphino)ferrocene]dichloro-palladium-(II) (80 mg, 1.1 mmol) and Na₂CO₃ (1.60 g, 15.1 mmol) were added to a solution of 1,3,5-tribromobenzene (157 mg, 0.5 mmol) and 4-pyridineboronic acid (250 mg, 2.03 mmol) in 40 mL of 1,4dioxane/H₂O (1:1, v/v). The mixture was degassed by bubbling a N₂ pubs.acs.org/Macromolecules

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Figure 1. Normalized absorption spectra of (a) $P_{Zn}T$, (b) $P_{FB}T$ in various solvent conditions, and (c) UV/vis spectral change upon the addition of TB (0–10 000 equiv) to ZnTPP (3.0 μ M) with (d) binding isotherm monitored at 429 nm.



Figure 2. (a) AFM image of a spin-coated $P_{Zn}T$ solution (10 μ M) in toluene onto mica, and TEM images obtained from the $P_{Zn}T$ specimen prepared form solutions (10 μ M) in (b) toluene and (c) 15% *n*-hexane containing toluene (inset of (c) indicates the diameter of the fiber).

flow through the solution for 10 min and then refluxed for 2 days. The solution was extracted with CH_2Cl_2 and distilled water. The organic phase was separated and then purified by column chromatography with 4% MeOH/CH₂Cl₂. The residue was recrystallized with chloroform and *n*-hexane. **Py₃B** (50 mg) was then obtained as a white solid in 50% yield. ¹H NMR (400 MHz, CDCl₃): δ = 8.76 (d, 6 H; pyridyl-H), 7.92 (s, 3 H; C₆H₃-H), 7.61 (dd, 6 H; pyridyl-H).

RESULTS AND DISCUSSION

The synthesis of $P_{Zn}T$ is illustrated in Scheme 1. Briefly, 1 was prepared by acid-catalyzed condensation between 3,5-decaneoxybenzaldehyde and pyrrole. Then, benzaldehyde was reacted with 1 and dipyrromethene under acid conditions and successively oxidized using chloranil to afford porphyrin 2. Subsequently, trimethylsilylacetylene was introduced at the meso position of 2 by bromination and the successive Sonogashira coupling reaction. Finally, $P_{Zn}T$ was prepared using a Cu(I)-catalyzed click reaction between 4 and 1,3,5-triazidomethylbenzene (5), where the deprotection of the trimethylsilyl group in 4 was conducted in a one-pot fashion due to the poor chemical stability of the ethynyl-bearing porphyrin. $P_{FB}T$ was prepared as a control compound via the demetallization of $P_{Zn}T$ by acid treatment.

UV/vis absorption of $P_{Zn}T$ and $P_{FB}T$ was measured under various solvent conditions to obtain information on molecular interaction (Figure 1a,b). $P_{Zn}T$ and $P_{FB}T$ exhibited completely different absorption patterns. $P_{Zn}T$ exhibited great expansion of the Soret band absorption to both shorter and longer wavelength regions, whereas $P_{FB}T$ exhibited relatively sharp Soret absorption. When a small amount of MeOH (1% by volume) was added to the toluene solutions, the Soret absorption band of $P_{Zn}T$ changed to a simple sharp pattern with slightly red-shifted absorption maximum. On the other hand, the absorption spectrum of $P_{FB}T$ did not change at all by the addition of MeOH. The sharpening and red-shifted absorption of P_{Zn}T by the addition of MeOH to zinc porphyrin units. In other words, the coordination of MeOH onto the zinc porphyrin interferes with the formation of supramolecular assemblies.

To the toluene solution of $P_{Zn}T$, *n*-hexane (15% by volume) was added to reinforce molecular interaction. As a result, $P_{Zn}T$ exhibited meaningful spectral changes by the addition of *n*-hexane, where the Soret absorption band of $P_{Zn}T$ was split to 416 and 437 nm. On the other hand, the absorption spectrum of $P_{FB}T$ did not change at all by the addition of *n*-hexane. Because the absorption spectrum of $P_{FB}T$ was not affected by the addition of both *n*-hexane and MeOH, we can conclude that $P_{FB}T$ does not form a molecular assembly in the toluene conditions. In general, the absorption of zinc porphyrin can be red-shifted by the binding of an axial ligand.³⁵ Consequently, the binding of a triazole unit to zinc porphyrin possibly contributes to the splitting of the Soret absorption of $P_{Zn}T$. To



Figure 3. V-T absorption spectral changes of $P_{zn}T$ (2.0 μ M) in toluene during (a) heating and (b) cooling between 368 and 278 K. (c) Overlaid cooling and heating curves obtained from the absorption at a wavelength of 435 nm.

clarify whether the triazole unit binds to zinc porphyrin or not, a structural fragment of $P_{Zn}T$ (TB; Scheme 1) was synthesized and titrated to zinc tetraphenylporphyrin (ZnTPP). Upon the titration of TB, the absorption of ZnTPP in toluene was gradually changed with clear isosbestic points at 426 and 556 nm, indicating the binding of TB to ZnTPP (Figure 1c,d). The association constant between TB and ZnTPP obtained by a nonlinear curve fitting using commercially available Hypspec software was 82 M^{-1} . Therefore, the broadening of $P_{Zn}T$ absorption can be interpreted as caused by the axial ligation of a triazole group to zinc porphyrin and the $\pi-\pi$ interaction between porphyrins.

When a toluene solution of $P_{Zn}T$ was spin-coated onto a mica substrate and subjected to atomic force microscopy (AFM), the formation of long fibrous assemblies was observed (Figure 2a). The fibrous assembly formed from $P_{Zn}T$ was further confirmed by transmission electron microscopy (TEM). The TEM observation of the $P_{Zn}T$ specimen prepared from a toluene solution exhibited irregular-shaped networks (Figure 2b). However, clear fibrous assemblies have been observed by the addition of *n*-hexane to the toluene solution (Figure 2c). Due to the solvophobic effect, the intermolecular interaction between $P_{Zn}T$ would be reinforced. Therefore, the formation of a secondary aggregate between the fibrous structures would be minimized, making it possible to confirm clear elementary fibrils with a diameter of about 7 nm on TEM images.

Variable-temperature (V-T) absorption measurements of $P_{Z_n}T$ in toluene were performed from 368 to 278 K to provide further understanding of self-assembling dynamics. As the temperature increases, the Soret absorption band of $P_{Zn}T$ becomes narrow, indicating the dissociation of the selfassembled structure (Figure 3a). In contrast, the absorption of $P_{Zn}T$ exhibited broadening of the Soret band during the cooling process, indicating that $P_{Zn}T$ changed from the monomeric state to the self-assembled state (Figure 3b). These temperature-dependent spectral changes were fully reversible without any hysteresis (Figure 3c). Moreover, when the absorption spectra of $P_{Zn}T$ in toluene (5.0 μ M) were monitored at different cooling rates, all cooling curves fully overlapped each other. Because the reversible spectral changes were found to be independent of the cooling rate, the self-assembling process of $P_{Zn}T$ would be a thermodynamic but not a kinetic process (Figure S1). Temperature-dependent fluorescent spectral changes of $P_{Zn}T$ and $P_{FB}T$ also showed different aspects. The fluorescence emission intensity of $P_{FB}T$ gradually decreased upon heating due to increasing nonradiative thermal relaxation of the excited state (Figure S2b). However, $P_{Zn}T$ exhibited gradual increment of the emission

intensity as increasing temperature, indicating the dissociation of the self-assembled $P_{Zn}T$ with increasing temperature (Figure S2a). As the only difference between $P_{Zn}T$ and $P_{FB}T$ is the presence of zinc atoms in the porphyrin units of $P_{Zn}T$, the different temperature-dependent behaviors clearly supported the involvement of axial coordination of the triazole nitrogen to the zinc atom in the formation of the supramolecular fibrous assemblies of $P_{Zn}T$.

Because $P_{Zn}T$ exhibited thermodynamically controlled reversible spectral changes, its degree of aggregation (α) , number-average degree of polymerization (DP), and aggregation constant (K_a) could be plotted as a function of temperature based on the changes in its V-T absorption spectra (Figure S3). 36,37 The absorption changes at a wavelength of 435 nm of $P_{Zn}T$ showed a sigmoidal curve, which was well fitted by an isodesmic model, indicating all of the processes are governed by the same K_a value. From the absorption change of $P_{Zn}T$, we derived the van't Hoff plot to estimate ΔH and ΔS during the supramolecular polymerization process, where the estimated ΔH and ΔS were $-73.7 \pm$ 2.7 kJ mol⁻¹ and -127 ± 8.4 J mol⁻¹ K⁻¹, respectively. From the result of van't Hoff analysis, the estimated K_a value of $P_{Zn}T$ in toluene at 330 K was about 1.37×10^5 M⁻¹, which is high enough to form a continuous supramolecular polymer. Because the K_a value of $\mathbf{P}_{\mathbf{Z}\mathbf{n}}\mathbf{T}$ is significantly greater than the binding constant of TB to ZnTPP, the addition of substoichiometric TB to $P_{Zn}T$ may not affect the morphology of the supramolecular polymer. In fact, the fibrous structure of P_{7n} T-based supramolecular polymer was also confirmed by AFM measurement even after the addition of 1.0 equivalent **TB** to $P_{Zn}T$ (Figure S4).

Wide-angle X-ray scattering (WAXS) measurement was conducted to elucidate the self-assembled structure of $P_{7n}T$. The WAXS spectrum of the spin-cast $P_{Zn}T$ film exhibited a hexagonal columnar structure with d-spacings of 21.3, 12.3, and 10.6 Å, which are assignable to the reflection peaks of the 100, 110, and 200 lattices, respectively (Figure 4a). The characteristic peak of the liquid-like packing of the long alkyl chains in the mesophase was also observed at $q = 1.5 \text{ Å}^{-1}$, corresponding to a d-spacing of 4.2 Å. The 21.3 Å spacing of the hexagonal lattice is too small to explain the 7 nm diameter of the fibrous structure by TEM observation (Figure 2c). We carried out a molecular modeling study using the Accelrys Materials Studio 7.0 software. Based on the modeling study, if $P_{Zn}T$ could form a fully extended geometry, the diameter of $P_{Zn}T$, the center-to the triazole unit, and center-to the porphyrin unit would be about 3.0, 0.6, and 1.1 nm, respectively (Figure 4b). Considering the molecular dimension, we speculated that the three triazole groups in a single



Figure 4. (a) WAXS spectrum of a spin-cast film of $P_{Zn}T$, (b) molecular model of $P_{Zn}T$ with a fully extended geometry, and (c) top view and (d) side view of the expected self-assembly structure of $P_{Zn}T$.

 $P_{Zn}T$ molecule cannot simultaneously bind to a neighboring $P_{Zn}T$ molecule. The results of FT-IR measurement also supported the existence of a coordination-free triazole moiety (Figure S5).³⁸ Two different stretching bands of triazole C-Hat 3121 and 3055 cm^{-1} appeared from $P_{Zn}T$, which can originate from coordinated and noncoordinated forms of a triazole group onto zinc porphyrin, respectively. Similarly, the mixture solution of ZnTPP and excess TB showed triazole C-H stretching bands at 3053 and 3130 cm⁻¹ due to the coexistence of coordinated and noncoordinated forms. By the addition of pyridine, the C-H stretching band at 3130 cm⁻¹, originated from the coordinated form of the triazole group, disappeared by the release of the triazole group from axial coordination onto zinc porphyrin. When Py_3B (Scheme 1) was added to $P_{Zn}T$, the stretching band around 3121 cm⁻¹ disappeared, indicating the release of triazole groups from axial coordination. In this context, a dimeric form of two zinc

porphyrin wings was assigned as the primitive unit for the molecular packing structure of the supramolecular polymer. Of the three triazole units in a single $P_{Zn}T$ molecule, one was coordinated to a porphyrin unit of the upper $P_{Zn}T$, another was coordinated to a porphyrin unit in the lower $P_{Zn}T$, and the other existed as a coordination-free form. As a result, $P_{Zn}T$ formed continuous coordination complexes with the porphyrin arrays in a hexagonal arrangement, in which the distance between the porphyrin building blocks was consistent with the hexagonal lattice observed by WAXS measurement (Figure 4c,d).

As observed in the FT-IR experiment, Py₃B addition exhibited replacement of an axial ligand from triazole to a pyridyl group. Therefore, we expected the formation of hostguest complexes between $P_{Zn}T$ and Py_3B . As expected, the spectra of P_{Zn}T upon titration to Py₃B exhibited clear isosbestic points at 421, 436, 559, 583, and 618 nm (Figure S6). The Job's plot analysis indicated the formation of a 1:1 host-guest complex between $P_{Zn}T$ and Py_3B ($P_{Zn}T$. Py_3B).³⁹⁻⁴¹ Because $P_{Zn}T$ formed a stoichiometric hostguest complex with Py_3B , we expected that the addition of Py3B would result in the dissociation of a coordination-based supramolecular polymer of $P_{Zn}T$ through competitive binding of Py_3B and a triazole unit to the zinc porphyrin unit. However, the TEM images of the host-guest complex $P_{Zn}T$. Py3B still showed a clear nanofibrous morphology, and the fibrous structure become clearer with increasing *n*-hexane content (Figure 5a-c). Very interestingly, supercoiled helical architectures were observed in 35% n-hexane-containing toluene (Figure 5c). The energy-minimized molecular structure of $P_{Z_n}T \cdot Py_3B$ showed a cone-shaped geometry (Figure 5d). To avoid unfavorable contact between the solvent molecules and the exposed porphyrin in the cone-shaped geometry, $P_{Zn}T{\boldsymbol{\cdot}}Py_3B$ might have associated with elemental fibrils, which then further associated to form supercoiled helical bundles.

Because $P_{Zn}T \cdot Py_3B$ also formed a fibrous supramolecular polymer, V-T-absorption spectra were measured to estimate thermodynamic parameters. As a result, $P_{Zn}T \cdot Py_3B$ also showed reversible spectral changes. Therefore, the degree of aggregation (α), number-average degree of polymerization



Figure 5. TEM images of $P_{Zn}T \cdot Py_3B$ obtained from (a) toluene, (b) 15% *n*-hexane, and (c) 35% *n*-hexane containing toluene solutions, (d) energy-minimized molecular structures, (e) WAXS spectrum of a spin-cast film, and (f) top view and (g) perspective view of the expected self-assembly structure of $P_{Zn}T \cdot Py_3B$.

(DP), and aggregation constant (K_a) could be plotted as a function of temperature based on the changes in its V-T absorption spectra (Figure S7). The absorption changes at 424 nm of $P_{Zn}T \cdot Py_3B$ showed a sigmoidal curve, which was well fitted by an isodesmic model. From the van't Hoff analysis, the estimated ΔH and ΔS were -121 ± 5 kJ mol⁻¹ and -258 ± 16 J mol⁻¹ K⁻¹, respectively. The ΔH and ΔS values of $P_{Zn}T \cdot Py_3B$ were greater than those of $P_{Zn}T$, indicating that the $P_{Zn}T \cdot Py_3B$ -based supramolecular polymer is thermodynamically more stable than $P_{Zn}T$. The estimated K_a value of $P_{Zn}T \cdot Py_3B$ in toluene at 330 K was about 5.05 × 10⁵ M⁻¹.

Time-correlated single-photon counting (TCSPC) measurement for both $P_{Zn}T$ and $P_{Zn}T \cdot Py_3B$ was conducted (Figure S8 and Table S1). Considering the isosbestic point observed on the absorption titration, excitation wavelength was fixed at 420 nm. The fluorescence emission decay profiles of both $P_{Zn}T$ and $P_{Zn}T \cdot Py_3B$ were fitted into double-exponential decay. The fluorescence lifetime of $P_{Zn}T$ was fitted into 1.2 and 0.3 ns. On the other hand, $P_{Zn}T \cdot Py_3B$ showed 1.0 and 0.3 ns of the fluorescence lifetime. The short-lived component would be ascribed due to the $\pi - \pi$ interaction.⁴² When comparing $P_{Zn}T$ and $P_{Zn}T \cdot Py_3B$, the population of a short-lived component of $P_{Zn}T \cdot Py_3B$ was significantly increased. Therefore, we can conclude an increased $\pi - \pi$ interaction after the formation of a host–guest complex between $P_{Zn}T$ and Py_3B .

To confirm the molecular packing structure, WAXS measurements were conducted using as-cast films of $P_{Zn}T$ · Py_3B (Figure 5e). The WAXS spectrum of as-cast $P_{Zn}T$ · Py_3B exhibited reflection peaks at d-spacings of 23.6, 20.1, 11.7, and 10.5 Å, which were assigned to the reflection peaks of the 100, 010, 200, and 020 lattices, respectively, and were indicative of rectangular columnar ordering (Figure 5f,g). The polarized optical microscopy (POM) image also showed birefringence with a nematic schlieren texture, further confirming the rectangular columnar ordering of $P_{Zn}T$ · Py_3B (Figure S9). The $P_{Zn}T$ · Py_3B film also exhibited a scattering peak at q = 1.7Å⁻¹ corresponding to a d-spacing of 3.7 Å, which was consistent with enhanced intermolecular $\pi - \pi$ interaction due to the cone-shaped packing geometry of $P_{Zn}T$ · Py_3B .

CONCLUSIONS

We designed a porphyrin tripod composed of three zinc porphyrin wings connected via triazole bridges as a monomer building block for a supramolecular polymer. Through the axial coordination of triazole nitrogen atoms to zinc porphyrins, $P_{Zn}T$ formed a long fibrous supramolecular polymer, which was confirmed by AFM and TEM observations. The association constant and number-average degree of polymerization were estimated from temperature-dependent absorption measurements. From the results of WAXS measurement, a molecular packing structure of a P_{Zn}T-based supramolecular polymer was assigned as a hexagonal columnar phase. P_{Zn}T formed a stable host-guest complex with Py3B with a coneshaped geometry. After the formation of the host-guest complexes, P_{Zn}T exhibited great morphological changes, where the linear fibrous assembly of $P_{Zn}T$ was transformed into a supercoiled helical architecture. Because the guest binding into P_{Zn}T strongly affected the self-assembled structure of supramolecular polymers, this system would pave the way for mimicking biological systems in which microscopic changes of biomolecules in response to stimuli lead to macroscopic changes of self-propagating hierarchical assemblies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c01446.

Additional absorption, emission, and FT-IR spectra, the V-T experiment, TCSPC measurement, and the POM image (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Eunji Lee School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Republic of Korea; o orcid.org/0000-0001-7494-1776; Email: eunjilee@gist.ac.kr
- Woo-Dong Jang Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea; orcid.org/0000-0002-1281-6037; Email: wdjang@yonsei.ac.kr

Authors

- Hosoowi Lee Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea
- **Dajung Lee** Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea
- Inhye Kim School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.0c01446

Notes

The authors declare no competing financial interest.

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