Porphyrin tripod as a monomeric building block for guest-induced reversible supramolecular polymerisation

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Abstract

Reversible supramolecular polymerisation and depolymerisation of biomacromolecules are common and fundamental phenomena in biological systems, which can be controlled by the selective modification of biomacromolecules through molecular recognition. Herein, a porphyrin tripod (**DP_{Zn}T**) connected through a triazole bridge was prepared as a monomeric building block for guest-induced supramolecular polymerisation. Although the lone pair electrons in triazolic nitrogen potentially bind to the zinc porphyrin units through axial ligation, the intrinsic steric hindrance suppressed the coordination of the triazole bridge to the porphyrin unit in **DP_{Zn}T**. Therefore, **DP_{Zn}T** formed spherical nanoparticles through π - π interactions. The addition of 1,3,5-tris(pyridine-4-yl)benzene (**Py₃B**) caused the guest-induced fibrous supramolecular polymerisation of **DP_{Zn}T** by forming a 1:1 host-guest complex, which was further assembled into a fibrous polymer. Furthermore, addition of Cl^- to **DP_{Zn}T** induced the transformation of spherical nanoparticles to fibrous supramolecular polymers. The fibrous supramolecular polymers of **DP_{Zn}T** obtained by adding **Py₃B** or Cl^- were depolymerised to their original spherical particles after adding $\text{Cu}(\text{ClO}_4)_2$ or AgNO_3 , respectively.

Introduction

Reversible supramolecular polymerisation and depolymerisation, controlled by the selective modification of biomacromolecules through molecular recognition processes, are common and fundamental phenomena in biological systems^{1–7}. These guest-induced supramolecular polymerisations are of great interest because of their important roles in the biological systems. The growth of microtubules and actin filaments is a representative example of guest-induced fibrous supramolecular polymerisation^{3,5,7}. The growth and degradation of microtubules are initiated by the binding of GTP and hydrolysis of phosphate, respectively. Similarly, the binding of ATP to G-actin initiates the polymerisation of actin to form microfilaments, which are F-actin. Supramolecular polymerisations with significantly more complicated structural transformations compared with fibrous assemblies are also often found in nature. For example, clathrin with a triskelion structure is polymerised into a networked structure by recognising adaptor proteins to form clathrin-coated membranes.⁸ Although several examples of controlled supramolecular assembly growth and guest-induced supramolecular polymerisation have been reported,^{9–19} the reversible transition of self-assembled structures during supramolecular polymerisation has not yet been actively studied. Therefore, it is still challenging to develop artificial self-assembled structures that mimic both multivalency and morphological transitions observed in natural systems. From this perspective, we demonstrate the guest-induced supramolecular polymerisation and depolymerisation accompanied by morphological changes from spherical particles to fibrous nanostructured polymers. Morphological changes were realised through various noncovalent interactions such as π - π interaction, metal–ligand coordination, and hydrogen bonding. In this study, we prepared a porphyrin tripod (**DP_{Zn}T**; Figure 1) that formed spherical nanoparticles owing to intrinsic structural restriction. The triazole group in **DP_{Zn}T** did not form an axial coordination complex with the zinc porphyrin units in the neighbouring **DP_{Zn}T**. The

spherical nanoparticles of **DP_{Zn}T** transformed into fibrous or networked supramolecular polymers upon adding guest molecules, depending on the guest species. Furthermore, the supramolecular polymers dissociated into spherical nanoparticles after removing the guest species. This rationally designed porphyrin tripod enabled us to mimic the supramolecular polymerisation and depolymerisation occurring in natural biomolecules.

Results And Discussion

Spherical nanoparticle formation of **DP_{Zn}T**

The synthesis of porphyrin tripods was conducted by a copper-catalysed click reaction between 1,3,5-tris(azidomethyl)benzene and ethynyl-bearing porphyrin derivatives. As control compounds for **DP_{Zn}T**, the freebase and copper-coordinated forms of porphyrin tripods (**DP_{FB}T** and **DP_{Cu}T**, respectively; Fig. 1) were prepared to investigate the effect of axial coordination. Several structural fragments of **DP_{Zn}T**, **DPP_{Zn}**, **TB**, **m-TB**, and **TC** were also prepared for control experiments. The details of the synthetic procedures and characterisation of porphyrin tripods and compounds used in this study are summarised in the Supplementary Information (Supplementary Scheme 1).

The Lewis acidic zinc porphyrins generally show a strong binding affinity to the lone pair electrons in triazolic nitrogen to form axial coordination complexes.²⁰ The binding of axial ligands causes a bathochromic absorption shift of zinc porphyrins; however, the Soret absorption band of **DP_{Zn}T** appeared at approximately 412 nm, which is consistent with that of **DPP_{Zn}** (Fig. 2A). Therefore, the UV/vis absorption spectroscopic observation of **DP_{Zn}T** indicated the absence of axial coordination interactions between the triazole and porphyrin units. UV/vis titrations of **TB** and **m-TB** to **DPP_{Zn}** in toluene were performed to elucidate the absence of coordination interactions between the triazole and zinc porphyrin units in **DP_{Zn}T**. When **TB** was added to **DPP_{Zn}**, the absorption did not change even after the addition of 13,000 equivalents of **TB** (Supplementary Fig. 1A). In contrast, upon the successive addition of **m-TB** (0–9,600 eq.), the Soret absorption band of **DPP_{Zn}** exhibited a significant bathochromic shift with the existence of clear isosbestic points at 414.5, 543.5, and 575.0 nm (Supplementary Fig. 1B-C). The computer aided modeling of **TB** showed coplanar geometry between the triazole and the neighbouring phenyl group (Fig. 2B). These observations indicate that the triazole moiety with the neighbouring phenyl group cannot be coordinated to zinc porphyrin because of steric hindrance. Although **DP_{Zn}T** did not show a bathochromic absorption shift, a relatively large shoulder at approximately 400 nm was observed owing to the π - π stacking of the porphyrin units.^{21, 22} However, the intensity of the shoulder near 400 nm increased when a small amount of *n*-hexane (15%) was added to the solution of **DP_{Zn}T** in toluene, which could be attributed to the enhanced molecular interaction in **DP_{Zn}T** (Fig. 2A). The solution of **DP_{Zn}T** in toluene was spin-coated onto a freshly cleaved mica surface, and atomic force microscopy (AFM) was performed to observe the morphological aspects of **DP_{Zn}T**. The AFM image showed spherical nanoparticles with a height of approximately 3 nm (Fig. 2C). The formation of nanoparticles was also

observed when **DP_{Zn}T** was spin-coated onto highly oriented pyrolytic graphite (HOPG) (Supplementary Fig. 2). However, the average height of the nanoparticles was slightly shorter than that observed in the AFM specimen prepared on the mica substrate. The flattening of nanoparticles can explain the decreased average height of the nanoparticles on HOPG because of the high affinity of the alkyl chains to HOPG.^{23, 24} Grazing-incidence wide-angle X-ray scattering (GIWAXS) was conducted on the drop-cast films of **DP_{Zn}T**. Thus, the in-plane and out-of-plane diffraction of **DP_{Zn}T** overlapped well (Fig. 2D), indicating the absence of angular dependency in the wide-angle region owing to the formation of spherical nanoparticles.

Because **DP_{Zn}T** formed spherical nanoparticles, the morphological aspects of **DP_{FB}T** and **DP_{Cu}T**, non-coordinatable derivatives of **DP_{Zn}T**, were again measured by AFM. The AFM images of both **DP_{FB}T** and **DP_{Cu}T** also showed the formation of spherical nanoparticles (Supplementary Fig. 3), indicating that the coordination interaction does not contribute to the formation of spherical nanoparticles. Similar to **DP_{Zn}T**, the UV/vis absorption spectra of both **DP_{FB}T** and **DP_{Cu}T** exhibited a shoulder in the blue-shifted region of the Soret absorption of **DPP_{FB}** and **DPP_{Cu}**, respectively, indicating that the driving force for the spherical particle formation of porphyrin tripods is π - π interactions among the porphyrin units.

Guest-induced supramolecular polymerisation of **DP_{Zn}T**

The guest-induced supramolecular polymerisation of **DP_{Zn}T** was investigated (Fig. 3A). Considering the three zinc porphyrin units in **DP_{Zn}T**, we envisaged that **DP_{Zn}T** could also form a host-guest complex with 1,3,5-tris(4-pyridylbenzene) (**Py₃B**; Fig. 1) through axial coordination interactions.²⁵⁻²⁷ The UV/vis titration of **DP_{Zn}T** on the addition of **Py₃B** showed distinct spectral shifts with isosbestic points at 412, 541, and 575 nm (Fig. 3B). The binding isotherm recorded at 417 nm showed that the absorption reached saturation upon adding 1 equiv. of **Py₃B**, indicating a strong binding affinity of **Py₃B** toward **DP_{Zn}T** (Fig. 3C). Although it is difficult to estimate the binding constant between **Py₃B** and **DP_{Zn}T** because pristine **DP_{Zn}T** forms spherical nanoparticles, the apparent binding constant exceeds the upper limit ($K > 10^8$), which can be measured by the absorption changes.²⁸ Analysis using the continuous variation method (modified Job's plot analysis) suggested the formation of a 1:1 host-guest complex between **DP_{Zn}T** and **Py₃B** (**DP_{Zn}T**·**Py₃B**) (Supplementary Fig. 4).²⁹⁻³¹ Energy-minimised molecular modelling indicates that **DP_{Zn}T**·**Py₃B** adopts a cone-shaped geometry, wherein the porphyrin units of **DP_{Zn}T** are exposed to the outer environment. Therefore, the host-guest complex could undergo further aggregation to avoid unfavourable exposure to the exterior solvent molecules, similar to our previous study.³² Transmission electron microscopy (TEM) images showed the formation of fibrous supramolecular polymers of ca. 4.0 nm width (Fig. 4D). In addition, AFM images of **DP_{Zn}T** with 1 equiv. of **Py₃B** demonstrated fibrous supramolecular polymer formation (Supplementary Fig. 5). **DP_{Zn}T**, non-coordinatable **DP_{FB}T**, and **DP_{Cu}T** exhibited no absorption spectral changes upon adding **Py₃B** (Supplementary Fig. 6). Therefore, the binding of **Py₃B** to **DP_{Zn}T** plays a critical role in the formation of fibrous supramolecular polymers. The formation of supramolecular polymers of **DP_{Zn}T**·**Py₃B** was further

confirmed by ^1H diffusion-ordered spectroscopy (^1H DOSY) NMR experiments. **DP_{Zn}T·Py₃B** showed concentration-dependent changes in the diffusion coefficient (D) value (Supplementary Fig. 7A), indicating the concentration-dependent elongation of the supramolecular polymers.

In contrast, **DP_{Zn}T** formed networked supramolecular polymers on adding Cl^- . **DP_{Zn}T** has two types of anion-binding sites. The first type is the triazole groups generated by the click reaction, and the second type are Lewis acidic zinc atoms in the porphyrin wings. Anionic species can bind to triazolic C-H and zinc atoms in porphyrin wings through $\text{C-H}\cdots\text{X}^-$ hydrogen bonding and axial ligation, respectively.^{33, 34} The binding of anionic species to triazolic C-H and zinc porphyrin can be monitored by ^1H NMR spectroscopy. However, the ^1H NMR measurements of **DP_{Zn}T** are not eligible because **DP_{Zn}T** forms spherical nanoparticles. Therefore, the ^1H NMR spectral change of **TC**, a structural fragment of **DP_{Zn}T**, was monitored upon adding Cl^- to confirm the binding of halide ions to the triazole C-H group (Supplementary Fig. 8). Thus, the triazole C-H peak (H_a) of **TC** was downfield shifted from 7.23 to 7.38 ppm when Cl^- was added in the form of tetrabutylammonium salt, indicating the binding of Cl^- to **TC** through the $\text{C-H}\cdots\text{Cl}^-$ hydrogen bonding. The UV/vis absorption of **DPP_{Zn}** also showed a bathochromic shift upon adding Cl^- through axial coordination complex formation (Supplementary Fig. 9). The absorption spectra exhibited a similar bathochromic shift with clear isosbestic points at 417.5, 547.0, and 580.0 nm when Cl^- was added to **DP_{Zn}T** (Fig. 3E). The binding isotherm obtained from the absorption changes at 413 nm suggested that the absorption reached saturation after adding 20 equiv. of Cl^- (Fig. 3F). A toluene solution of **DP_{Zn}T** with 10 equiv. of Cl^- (**DP_{Zn}T·Cl**) was subjected to AFM after spin-coating onto a freshly cleaved mica surface to observe the morphological aspects. Therefore, we observed the formation of a fibrous network structure (Fig. 3G). Unlike pristine **DP_{Zn}T**, the in-plane and out-of-plane diffractions of the GIWAXS signals did not overlap with each other (Supplementary Fig. 10). The angular dependency on WAXS indicates that the packing structure of the mixture system of **DP_{Zn}T** with Cl^- differs from that of the spherical particles of pristine **DP_{Zn}T**. The D values obtained from ^1H DOSY NMR of **DP_{Zn}T** with 10 equiv. of Cl^- in toluene- d_8 confirmed the concentration-dependent elongation of the network structure. The D values gradually decreased with increasing concentration, indicating the elongation of the supramolecular polymer and formation of a fibrous network (Supplementary Fig. 7B).³⁵

The importance of Cl^- coordination on zinc porphyrin in **DP_{Zn}T** was supported by control experiments using **DP_{FB}T** and **DP_{Cu}T**. Unlike **DP_{Zn}T**, **DP_{FB}T** and **DP_{Cu}T** did not exhibit a bathochromic shift in the absorption spectra (Supplementary Fig. 11), indicating the absence of axial coordination of Cl^- to porphyrin units in both **DP_{FB}T** and **DP_{Cu}T**. However, ^1H NMR spectral studies showed that triazole units in **DP_{FB}T** interact with Cl^- through $\text{C-H}\cdots\text{Cl}^-$ hydrogen bonds; the triazolic C-H (H_a) signal was downfield shifted from 8.17 to 8.33 ($\Delta\delta = -0.16$ ppm) (Supplementary Fig. 12). The morphological aspects of **DP_{FB}T** and **DP_{Cu}T** were observed by AFM after adding 10 equiv. of Cl^- . AFM images showed that the shape of the spherical particles did not change; however, the size of the particles significantly increased.

Therefore, we concluded that both C-H...Cl⁻ hydrogen bonding and axial coordination interactions simultaneously contribute to the formation of networked supramolecular polymers.

Reversible supramolecular depolymerisation

Because the binding of **Py₃B** or Cl⁻ to **DP_{Zn}T** induced supramolecular polymer formation, the removal of **Py₃B** or Cl⁻ could lead to the dissociation of the supramolecular polymers. First, we attempted to remove **Py₃B** from the fibrous supramolecular polymers. Pyridyl group could be removed by adding copper ions as they form stable metal-coordination complexes with pyridyl ligands.³⁶ As aforementioned, **DP_{Zn}T** showed a bathochromic absorption shift during the formation of a 1:1 host-guest complex with **Py₃B**. The absorption spectrum almost recovered to that of pristine **DP_{Zn}T** (Fig. 4A) when Cu(ClO₄)₂ was added to **DP_{Zn}T**·**Py₃B**. After the solution was filtered to remove the insoluble precipitates, morphological aspects were observed by AFM. The AFM results indicated the formation of spherical nanoparticles in pristine **DP_{Zn}T** (Fig. 4B). For the networked supramolecular polymers, Cl⁻ was removed by AgNO₃ treatment.³⁷ With the addition of AgNO₃ to **DP_{Zn}T**·Cl⁻ solution in toluene, the Soret absorption band at 423.5 nm completely recovered to the absorption of the pristine **DP_{Zn}T** (Fig. 4C). After adding AgNO₃, the insoluble salt was removed by filtration, and the filtrate solution was spin-coated onto the mica surface for AFM measurements. The AFM results also indicated the recovery of the original spherical nanoparticles formed by pristine **DP_{Zn}T** (Fig. 4D). The UV/vis absorption spectral changes were monitored upon the addition of Cl⁻ and AgNO₃ (Fig. 4E) observe the reversibility of this process. The absorption changes at both 413 and 423.5 nm upon the successive treatment of Cl⁻ and AgNO₃ supported the reversible changes in supramolecular polymerisation and depolymerisation (Fig. 4F).

In summary, we prepared a triazole-bearing tripodal porphyrin, **DP_{Zn}T**, that formed spherical nanoparticles. UV/Vis titration with structural fragments of **DP_{Zn}T** and molecular modelling revealed that axial coordination of the triazole groups to the zinc porphyrin units was prevented owing to steric hindrance. The addition of **Py₃B** resulted in the formation of a 1:1 host-guest complex between **Py₃B** and **DP_{Zn}T**, and this host-guest complex was further aggregated to form a linear fibrous supramolecular polymer. The removal of **Py₃B** from the host-guest complex resulted in the formation of spherical nanoparticles by the reversible depolymerisation of linear fibrous supramolecular polymers. In contrast, the spherical nanoparticles of **DP_{Zn}T** were transformed into networked supramolecular polymers through the binding of Cl⁻. The original spherical nanoparticles of **DP_{Zn}T** were recovered by the reversible depolymerisation of networked supramolecular polymers when AgNO₃ was added to remove Cl⁻. Because **DP_{Zn}T** has successfully undergone supramolecular polymerisation and depolymerisation upon the treatment with **Py₃B**/Cl⁻ and Cu²⁺/Ag⁺, respectively, the results provide insight into a better understanding of molecular-level association processes in natural systems that exhibit structural transformation.

Methods

Reagents and synthesis

All commercially available chemicals were of reagent grade and used without further purification. Dichloromethane (CH_2Cl_2), *n*-hexane, acetonitrile, tetrahydrofuran (THF), and toluene were distilled before use. The ^1H NMR spectra were recorded at 25°C on a Bruker Avance DPX 250 and DPX 400 spectrometer. The ^{13}C NMR spectra were recorded at 25°C using a Bruker DPX 400 spectrometer. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), and integration. 2D-DOSY NMR spectra were recorded at 25°C using a Bruker Avance 600 spectrometer. Matrix-assisted laser desorption ionisation-time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Daltonics LRF 20 mass spectrometer with dithranol (1,8,9-trihydroxyanthracene) as the matrix. Recycling size exclusion chromatography was performed on a JAI LC-9201 chromatograph equipped with JAIGEL-1H, JAIGEL-2H, and JAIGEL-3H columns using THF (DUCKSAN Pure Chemicals, Republic of Korea) as the eluent.

Measurements and sample preparation

UV/Vis absorption spectra were recorded on a JASCO V-760 spectrometer equipped with a thermostatic cell holder coupled with a controller (ETCS-761, JASCO, Japan). The absorption spectral measurements were performed using a quartz cuvette with a path length of 1 cm. AFM images were obtained using a Park Systems NX10 instrument. For the AFM measurements, a drop of each solution was spin-coated onto freshly cleaved mica or HOPG substrates (3000 rpm, 60 s). TEM images were obtained using a JEM-1400 instrument operating at 120 kV (JEOL, Japan). For the TEM measurements, a drop of each sample in the solvent was placed on a carbon-coated copper grid and allowed to evaporate under ambient conditions. The sample was then allowed to rest for at least 1 min, after which the excess solution was wicked off using filter paper. The thin films for WAXS measurements were cast from each solution in toluene on a silicon substrate. WAXS measurements were performed on the PLS-II 9A beamline in the Pohang Accelerator (PAL, Pohang, Republic of Korea). The X-rays generated from the in-vacuum undulator were monochromated by Si(111) double crystals and focused on the detector position using the K_β -type mirror system. X-rays with a wavelength of 11.065 Å were used.

Modelling studies

The structural optimisation of the ground state of **TB** was obtained using the semi-empirical PM6 method in the Gaussian 09 software. A molecular modelling study for the complex of **DP_{Zn}T** with **Py₃B** was conducted using Accelrys Materials Studio 7.0.

Data availability

All data needed to evaluate the conclusions of this study are available in the main text or Supplementary Information. The data that support the findings of this study are available from the corresponding

authors upon reasonable request.

Declarations

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Author contributions

W.-D.J. and E L, directed this project; H.L. and D.L synthesised the compounds used in this study; H.L performed the spectroscopy and AFM measurements; I.K performed TEM measurement and computational modelling study; J.H.H. performed WAXS measurement; H.L. and W.-D.J. wrote the manuscript; all authors discussed the results and commented on the manuscript.

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Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Molecular structures of porphyrin tripods (DP_MT; M = Zn, 2H, Cu), structural fragments (DPP_M, TB, m-TB, and TC), and 1,3,5-tris(4-pyridyl)benzene (Py₃B).

Figure 2

Spherical nanoparticle formation of DP_{Zn}T.

A. Normalised absorption spectra of DP_{Zn}T (20 mM) in toluene (blue) and 15% *n*-hexane-containing toluene (red), and DPP_{Zn} (20 mM) in toluene (black), with TB (pink) and m-TB (green). **B.** Computer-aided molecular modelling TB with a schematic illustration of coordination and steric repulsion between TB

and DPP_{Zn} . **C.** An AFM image with height profiles of DP_{ZnT} in toluene (20 mM) spin-coated onto HOPG. **D.** GIWAXS images of DP_{ZnT} with in-plane (black line) and out-of-plane (red line) diffraction.

Figure 3

Guest-induced supramolecular polymerisation of DP_{ZnT} .

A. Schematic illustration of guest-induced supramolecular polymerisation of **DP_{Zn}T**. **B.** Absorption spectral changes of **DP_{Zn}T** (4.0 μ M) upon successive addition of **Py₃B** in toluene at 293 K. **C.** Binding isotherm observed at 417 nm upon successive addition of **Py₃B** to **DP_{Zn}T**. **D.** TEM image of **DP_{Zn}T** with 1 equiv. of **Py₃B**. **E.** Absorption spectral changes of **DP_{Zn}T** (4.0 μ M) upon successive addition of Cl⁻. **F.** Binding isotherm observed at 413 nm upon successive addition of Cl⁻ to **DP_{Zn}T**. **G.** AFM height image of **DP_{Zn}T** with 10 equiv. Cl⁻.

Figure 4

Reversible transformation from supramolecular polymer to nanoparticles of $DP_{Zn}T$.

A. Absorption spectral change of $DP_{Zn}T$ by adding Py_3B and successive treatment of $Cu(ClO_4)_2$. **B.** AFM height image of $DP_{Zn}T$ after removal of Py_3B using $Cu(ClO_4)_2$ treatment. **C.** Absorption spectral changes of $DP_{Zn}T$ by adding Cl^- and successive treatment of $AgNO_3$. **D.** AFM height image of $DP_{Zn}T$ after

removing Cl^- using AgNO_3 treatment. **E.** Reversible absorption changes of **DP_{Zn}T** by alternative treatment of Cl^- and Ag^+ . **F.** Absorption changes of **DP_{Zn}T** monitored at 413.5 nm (red line) and 423 nm (black line) upon alternative treatment of Cl^- and Ag^+ .

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