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Two-Step Template Method for Synthesis of Axis-Length-Controlled Porphyrin-Containing Hollow Structures

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π–Conjugated porphyrin-containing hollow structures with defined axis-length were successfully synthesized by a two-step template method, i.e., template-assisted cyclization and oligomerization. During the oligomerization, templates played important roles in controlling the reaction rates and the axis lengths. The hollow structures exhibited an extended effective π–conjugation because of the high coplanarity between porphyrins.

Host molecules with one dimentional (1D) hollow structures have attracted attention for use in channels and achievement of unique molecular arrangement in host–guest chemistry because of their one-dimensional cavity.[1] The functions of the host–guest complexes can be manipulated by the molecular structures and components. In particular, porphyrin-containing hollow structures are expected to provide 1D functional cavities, because porphyrins show unique optical properties and catalytic abilities.[2] For example, molecular tubes consisting of porphyrins (porphyrin tubes) can align fullerenes[3] in one dimension using the π planes of porphyrins; this characteristic is exhibited by photovoltaic materials.[4] Such functions of the porphyrin-containing hollow structures depend on the cavity sizes and axis lengths. To realize defined functions of the hollow structures, it is necessary to develop synthetic methods for structure-controlled porphyrin-containing hollow structures.

Previous porphyrin-containing hollow structures were constructed by one-dimensional alignment of ring structures composed of multiple porphyrins, named porphyrin rings. The binding modes among the porphyrin rings are categorized into two types. One is non-covalent bonding: Aida and Tani successfully constructed porphyrin tubes by intermolecular hydrogen bonds and π–π interactions among the porphyrin rings, providing hollow structures.[4,5] The other binding mode is covalent bonding. Covalently linked porphyrins show efficient charge transport[6a] and non-linear optical properties[6b] due to the π electron delocalization among porphyrins. Therefore, porphyrin-containing hollow structures in which porphyrin rings are linked by covalent bonding are promising

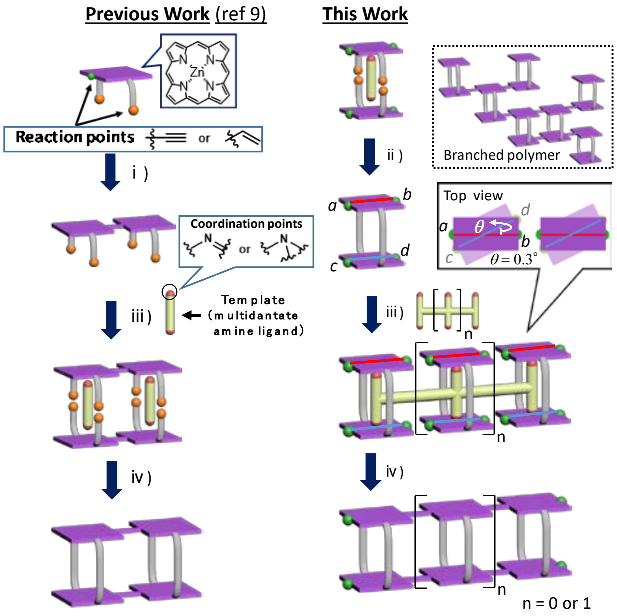

Figure 1. Template synthesis of porphyrin-containing hollow structures (left: previous method, right: this method); (i) dimerization, (ii) template-assisted cyclization, (iii) complexation, and (iv) template-assisted oligomerization. θ means the angle between directions **ab** (red line) and **cd** (blue line), and DFT calculations showed that the angle of the porphyrin ring is 0.3° (Figure S12, ESI†).

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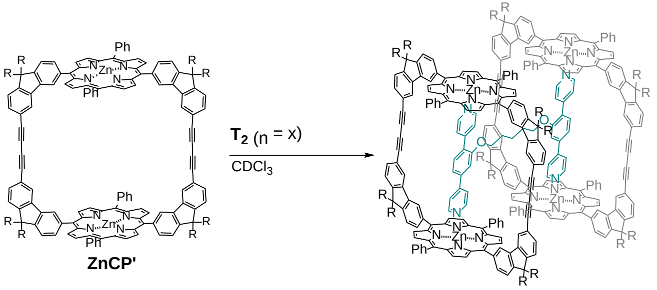
for a unit of electronic/optical materials and host molecules that align guest molecules. However, to construct the 1D cavity with porphyrin rings needs the formations of the multiple covalent bondings between the porphyrin rings. These ladder polymerization is required to suppress the production of byproducts, including branched polymers (Figure 1, upper right).

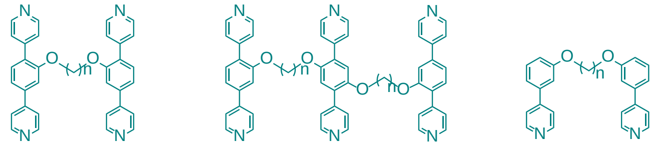
Template methods that employ coordination bonding between zinc porphyrins and amines have been used to prepare challenging structures, such as length-defined porphyrin oligomers[7] and cavity size-defined porphyrin rings.[8] Chujo, Hupp, and Anderson reported the template-assisted synthesis of porphyrin-containing hollow structures from linear porphyrin dimers (trimers) via sequential dimerization (trimerization), complexation, and template-assisted cyclic oligomerization (Figure 1, left).[9] In the template synthesis, the numbers of coordination points in the templates and shapes, control the cavity sizes of the hollow structures. Furthermore, Anderson reported a synthetic method for porphyrin tubes via cyclization, π-elongation, and cyclic oligomerization.[9d] However, these methods require precursors with predefined lengths. A template method for the selective synthesis of porphyrin-containing hollow structures with defined-axis length from a single porphyrin ring is required.

We envisage that the oligomerization of cyclic porphyrins using templates has the potential to be applied in preparing structure-controlled porphyrin-containing hollow structures with high efficiency. The method comprises two stepwise template-assisted processes: template-assisted cyclization complexation, and template-assisted oligomerization (Figure 1, right). The axis lengths of the hollow structures can be controlled by the numbers of coordination points and shapes of the templates. We anticipated that oligomerization would occur among porphyrin rings on the templates to prohibit excess reactions under a high dilution condition. Herein, we describe a two-step template method to prepare structure-controlled porphyrin-containing hollow structures.

The molecular design is described below. A key prerequisite for the oligomerization of the precursor is that two opposite porphyrins in directions **ab** and **cd** (Figure 1, right center) are horizontally aligned to increase the proximity of the reaction points. To realize the alignment, it is important to design a strain-free porphyrin ring. A previous porphyrin ring, which comprised of nickel porphyrins and *m*-phenylenes was designed, and the angle, θ, between directions **ab** and **cd** was determined to be 25.2° in the crystal structure.[4b] The torsion is assumed to arise from the saddle-shaped porphyrins and curved diynes. In this study, we designed a square porphyrin dimer, **ZnCP',** comprised of planar zinc porphyrin and rectangular fluorene units (Scheme 1). DFT calculations showed that the optimized structure had a torsion-less square structure; the angle, θ, was 0.3° (Figure S12, ESI†). Generally, extended π–conjugated molecules have low solubilities in organic solvents due to weak intermolecular interactions, such as π–π and CH–π.[10] To increase the solubility, eight esters were introduced to the fluorene units, outside of the square porphyrin dimer.

Scheme 1. Complexation between **ZnCP'** and **T$_2$** (n = x).





T$_2$ (n = 4, 6, 8, 12) **T$_3$** (n = 8) **T$_2$'** (n = 6)

Figure 2. Templates for the oligomerization.

Recently, we reported the selective synthesis of a square porphyrin dimer derivative, **ZnCP'** (Scheme 1), via template-assisted cyclization (Figure 1, right ii).[11] In this study, we investigated the complexation abilities of **ZnCP'** and the templates (Figure 1, right iii). We designed templates, **T$_2$** (n = 4, 6, 8, and 12), with two 1,4-di(pyridin-4-yl)benzene units linked by alkyl chains for dimerization (Figure 2). Different lengths of alkyl chains were introduced to the templates to evaluate the effect of the length on the oligomerization. **T$_2$'** (n = 6) is employed as a reference molecule to **T$_2$** (n = 6) in investigating the relationship between the association constant and the reaction. The ratio of **ZnCP**s to the templates **T$_2$** (n = 4, 8, and 12) in the complexes was 2:1, as confirmed by ^{1}H NMR titration experiments in $CDCl_3$ (Figures S1-S5, ESI†). These results confirmed that the proximity of the two **ZnCP**s increased via the complexation.

As the template-assisted oligomerization, we selected the Glaser reaction. The transition state of the Glaser reaction goes through horizontal arrays of two copper acetylides; therefore, the reaction is expected to be suitable for the synthesis of porphyrin-containing hollow structures with coplanar and linear porphyrins.[12] In fact, the Glaser reaction incorporating a copper catalyst is known to be effective for molecules with high linearity.[13] In this study, we prepared a Zn-square porphyrin dimer, **ZnCP,** with alkynes on porphyrins (see ESI†). Template-assisted synthesis of **ZnCP$_2$** was carried out by oligomerization of **ZnCP**. The Glaser reaction of **ZnCP** with **T$_2$** (n = 6) under a highly diluted condition (7.6×10^{-6} M) selectively afforded **ZnCP$_2$,** whereas the reaction hardly proceeded in the absence of **T$_2$** (n = 6) (Figures 3a and 3b). The templates were removed by filtration using silica gel (CH_2Cl_2/EtOAc/pyridine = 100/10/1, v/v/v). Subsequently, **ZnCP$_2$** was isolated in 25% yield by size exclusion chromatography (toluene/pyridine = 100/1, v/v) of the obtained mixture. **ZnCP$_2$** was characterized by ^{1}H NMR and high-resolution matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry. Consequently, it was clarified that the template with two 1,4-di(pyridin-4-yl)benzene units can accelerate the oligomerization of the square porphyrin dimers via selective dimerization.

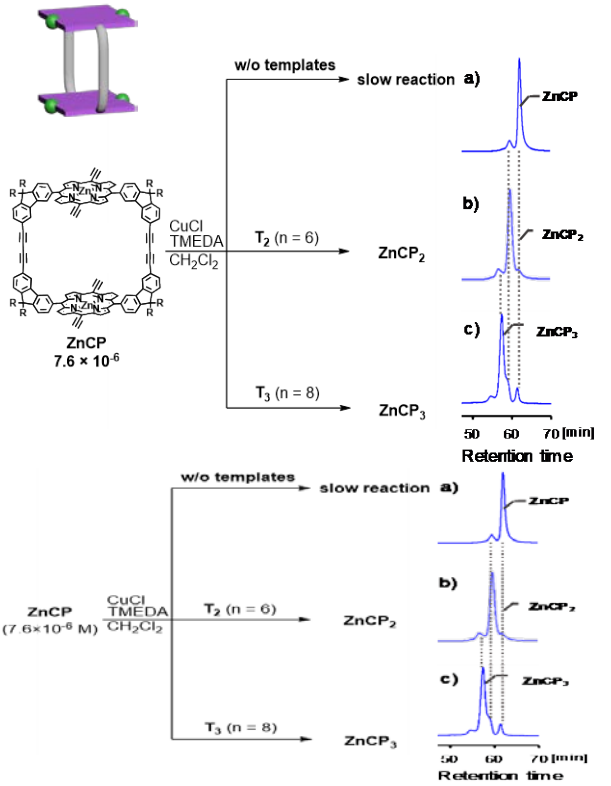
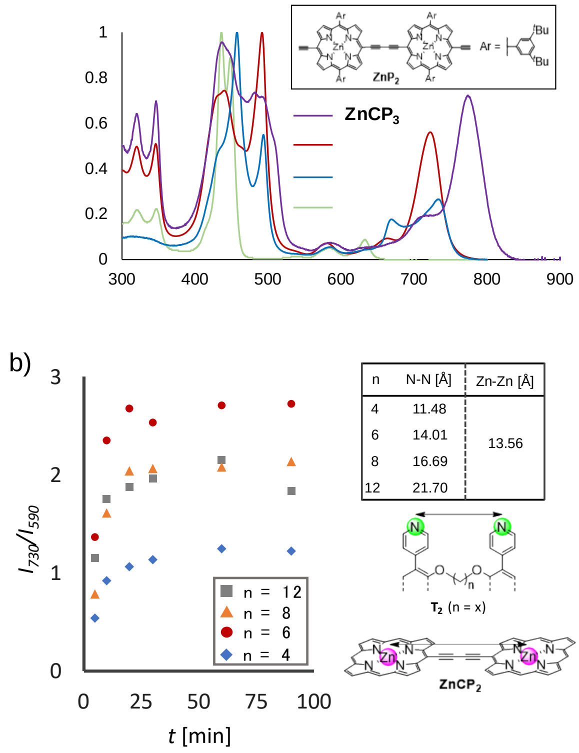


Figure 3. Size exclusion chromatography traces for the template-assisted synthesis of porphyrin-containing hollow structures (eluent: THF, UV: 420 nm); (a) without a template, (b) with $\mathbf{T_2}$ (n = 6), and (c) with $\mathbf{T_3}$ (n = 8).

We investigated the relation between linker lengths of the templates and oligomerization rate by UV-Vis spectroscopy. $\mathbf{ZnCP_2}$ and **ZnCP** exhibit different absorption properties (Figure 4a); I_{590} (**ZnCP**) is much larger than I_{730} (**ZnCP**), whereas I_{590} ($\mathbf{ZnCP_2}$) is much smaller than I_{730} ($\mathbf{ZnCP_2}$) (Figure 4a). Therefore, I_{730}/I_{590} can be used as an indicator of the extent of dimerization. The change of I_{730}/I_{590} in the oligomerization using $\mathbf{T_2}$ (n = 6) led to the largest initial rate among $\mathbf{T_2}$ (n = 4, 6, 8, and 12), whereas the change in oligomerization using $\mathbf{T_2}$ (n = 4) led to the smallest one (Figure 4b). The differences in the reaction rates are probably owing to the linker lengths of the templates. DFT calculations suggested the distance between two zinc atoms of $\mathbf{ZnCP_2}$**,** and between two nitrogen atoms of $\mathbf{T_2}$ (n = 4, 6, 8, and 12). As shown in Figure 4c, $\mathbf{T_2}$ (n = 6) has a proper axis length of $\mathbf{ZnCP_2}$, which provided efficient proximity of the reaction points. Next, we compared the association constants and oligomerization rates. The oligomerization of **ZnCP** with $\mathbf{T_2'}$ (n = 6), comprised of two pyridine units, did not proceed well in contrast with that **ZnCP** with $\mathbf{T_2}$ (n = 6) (Figure S8, ESI†). UV-Vis titration experiments afforded the association constant between **ZnCP'** and $\mathbf{T_1}$ with 1.7×10^8 M^{-1}, which is much higher than the association constant, K_a, between zinc tetraphenylporphyrin (**ZnTPP**) and pyridine (K_a ~ 10^3 M^{-1}), based on the chelate effect.[15] The high affinity between **ZnCP** and $\mathbf{T_2}$ (n = 6) enabled the efficient oligomerization via selective dimerization even under highly diluted conditions.

The template method was applied to the synthesis of $\mathbf{ZnCP_3}$ via selective trimerization of **ZnCP**s. Although the use of six methylenes as a linker was conventional in oligomerization, $\mathbf{T_3}$ (n = 6) exhibited low solubility in organic solvents. Instead of $\mathbf{T_3}$ (n = 6), $\mathbf{T_3}$ (n = 8) with a longer alkyl linker was designed. Before the oligomerization, it was required that the template penetrate three **ZnCP**s. ^{1}H NMR titration experiments (Figures S6 and S7, ESI†) confirmed a 3:1 complexation ratio between **ZnCP'** and $\mathbf{T_3}$ (n = 8). The complexation proceeded within several



n	N-N [Å]	Zn-Zn [Å]
4	11.48	13.56
6	14.01	
8	16.69	
12	21.70	

Figure 4. (a) Absorption spectrum of $\mathbf{ZnCP_3}$, $\mathbf{ZnCP_2}$, $\mathbf{ZnP_2}$, and **ZnCP** ($CHCl_3$/pyridine = 100/1; temperature: r.t.), (b) Progress of the oligomerization at different templates, $\mathbf{T_2}$ (n = x), based on I_{730}/I_{590}, where I_{590} and I_{730} denote the absorbances at 590 nm and 730 nm, respectively. I_{730}/I_{590} is the ratio of I_{730} to I_{590}. (c) Comparison between the distances of nitrogen–nitrogen of templates, $\mathbf{T_2}$ (n = x), and zinc–zinc of a porphyrin-containing hollow structure $\mathbf{ZnCP_2}$, arrows indicate interatomic distances, nitrogen–nitrogen or zinc–zinc.

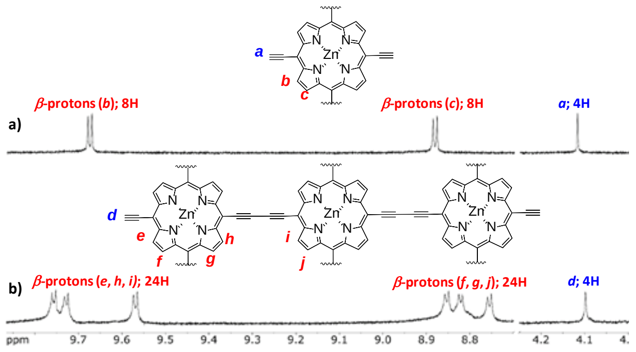


Figure 5. ^{1}H NMR spectra of a) **ZnCP** and b) $\mathbf{ZnCP_3}$ in $CDCl_3$ (+1% pyridine-d_5) at 298 K. Color: β-proton signals, red; alkyne proton, blue.

minutes at room temperature, probably due to the small activation Gibbs energy, $\Delta G^{\ddagger}_{298\mathrm{K}}$, of the dissociation process between **ZnCP** and **T_3** (n = 8) ($\Delta G^{\ddagger}_{298\mathrm{K}}$ between **ZnCP'** and 1,4-di(pyridin-4-yl)benzene was found to be 61.7 kJ·mol^{-1}, Figure S11, ESI†). Consequently, it is assumed that the proximity of the three **ZnCP**s to each other increased via the penetration process. As expected, the Glaser reaction of **ZnCP** with **T_3** (n = 8) selectively afforded the trimer, **$ZnCP_3$** (Figure 3c). **$ZnCP_3$** was isolated in 10% yield, by silica gel filtration and GPC. Molecular ion peaks of **$ZnCP_3$** were detected by high-resolution MALDI-TOF MS spectrometry (m/z = 7844.83). In the ^{1}H NMR spectrum of **$ZnCP_3$**, six different doublet peaks corresponding to the β protons of porphyrins, and one singlet peak corresponding to alkyne protons were confirmed (Figure 5). The integral ratio of all β protons to alkyne protons was 12:1. Consequently, it was revealed that the numbers of coordination points in the templates could control the axis lengths of the porphyrin-containing hollow structures.

The high coplanarity between porphyrins led to efficient elongation of π–conjugation. UV-Vis absorption spectroscopy revealed that the Q band of porphyrins in **$ZnCP_2$** exhibited one major peak around 720 nm, while that in linear porphyrin dimer **ZnP_2** was split into two peaks around 670 nm and 730 nm (Figure 4a). Generally, the dihedral angle of two porphyrins linked by a diyne varied with the rotation of the diyne. Conversely, the dihedral angle of two porphyrins in **$ZnCP_2$** or **$ZnCP_3$** were assumed to be almost 0° due to the hollow structure, which resulted in one Q band,[14] although two Q bands assigned to rotation isomers were observed in the spectrum of **ZnP_2**.[15] Due to the π-conjugated hollow structure, **$ZnCP_3$** exhibited absorbance almost in the near-infrared region.

In conclusion, we developed a two-step template method for the selective synthesis of axis-length- and cavity-size-controlled porphyrin-containing hollow structures with long effective π-conjugations. During the oligomerization, the numbers of 1,4-di(pyridin-4-yl)benzene units could control the axis lengths of the porphyrin-containing hollow structures due to the high affinity to square porphyrin dimers. The linker lengths of the templates and the association constant between square porphyrin dimers and templates affected the reaction rate. The template method is expected to be applied to longer π-conjugated porphyrin-containing hollow structures.

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Conflicts of interest

There are no conflicts to declare.

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