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Controllable Synthesis of Covalent Porphyrinic Cages with Varying Sizes via Template-Directed Imine Condensation Reactions

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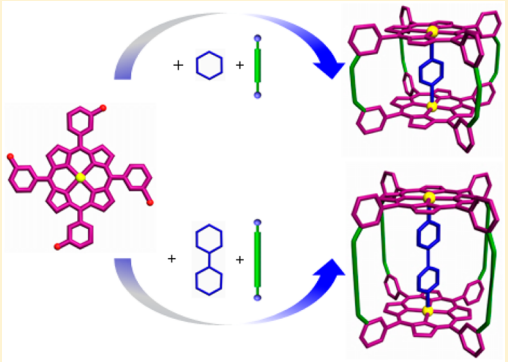
Supporting Information

ABSTRACT: Covalent porphyrinic cages (CPCs) have been a target of interest for years. In this paper, we report the design and synthesis of two CPCs in which the cofacial porphyrins have a distance of 7.66 and 11.96 Å via template-directed imine condensation reactions and through the selective choice of templating linker and diamine length.



Organic molecular cages have attracted considerable attention over the past few decades[1] due to their promising applications in host–guest chemistry,[2] nanoreactors,[3] gas absorption and separation,[4] and so forth. As the functionalization of cages can benefit the resulting compounds with new functions inside the cavity, the incorporation of functional groups into the cage framework is of significant interest.[5] Covalent porphyrinic cages (CPCs), tailored to combine the unique[6] photophysical and redox properties of porphyrins, have been a target of interest for years.[7] To date, several CPCs have been synthesized and have shown interesting applications in host–guest chemistry. For example, Zhang et al. reported a shape-persistent CPC that shows high selectivity in binding of C_{70} over C_{60}.[8] Li et al. developed a CPC that is able to recognize azide anions.[9] However, for these reported CPCs synthesized via a step-by-step approach, the reaction yields are generally not very high (10∼56%) and some of the synthesis steps are quite complicated. Considering the interesting properties of CPCs, other approaches to synthesize CPCs in a more efficient way need to be explored.

Template-directed synthesis, which can preorganize the reaction sites of the reactants around a molecular linking aid, has emerged as the method of choice for the construction of complex molecular architectures, e.g., mechanically interlocked molecules.[10] This strategy has also been used to construct CPCs. For example, Heitz and co-workers described the synthesis of a large and flexible CPC via a 1,4-diazabicyclo [2.2.2.] octane (DABCO) templated olefin metathesis reaction,[11] a method also adopted by Li et al. for the synthesis of a suite of flexible CPCs.[12] We should mention here that the yields of CPCs achieved via this strategy are reasonable but are still far from satisfying (40∼77%). In addition, side products are commonly formed, and chromatographic workup usually needs to be performed. Therefore, for CPCs to be synthesized more efficiently, this synthetic strategy needs to be further improved.

Imine bond formation, a reversible reaction that can possess the ability of "error-checking" or "proof-reading", provides a valuable opportunity to synthesize the targeted molecules under a thermodynamic control.[13] The marriage of template-directed synthesis and imine reaction has proven to be a most powerful synthetic tool in, for example, the construction of molecular Borromean rings.[14] Recently, for the first time, we have successfully utilized this approach to synthesize CPCs.[15] By using DABCO-templated imine condensation reactions, two CPCs (cage-**1** and cage-**2**) were constructed with quantitative yields starting from different diamine precursors. However, even though this strategy is very promising, there are still several challenges that need to be further explored: can we use other templates[16] to synthesize CPCs? Can we use longer templates to synthesize CPCs with larger size?[17] Herein, we report (Figure 1) the design and synthesis of two CPCs (cage-**3** and cage-**4**) in which the cofacial porphyrins have distances of 7.66 and 11.96 Å, respectively. Our results clearly demonstrate that, by selectively choosing the template (pyrazine and 4,4-

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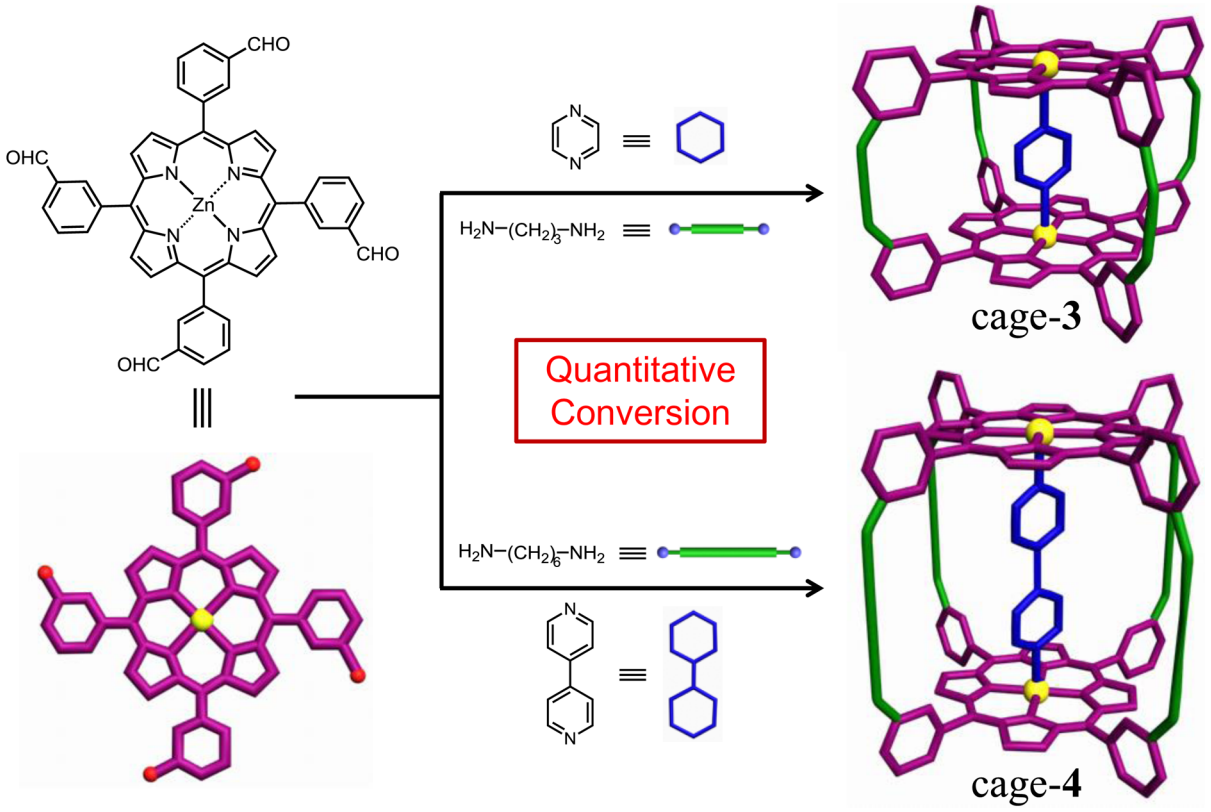

Figure 1. Graphical representations and structural formulas illustrating the formation of cage-**3** and cage-**4**.

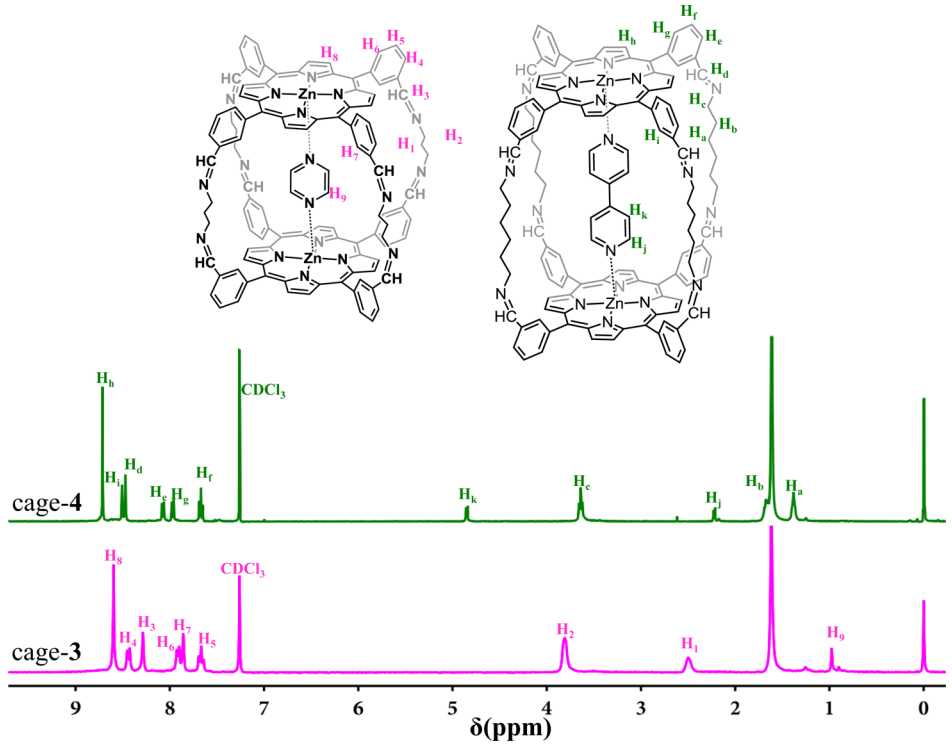

Figure 2. ^{1}H NMR spectra of cage-**3** (pink curve) and cage-**4** (green curve).

bypyridine) and adjusting the length of diamine spacers, cage-**3** and cage-**4** could be formed in one-step with quantitative conversion.

The precursor zinc(II) 5,10,15,20-tetrakis(3-benzaldhyde)-porphyrin (*m*-CHO-ZnP) was prepared according to our reported method.[15] The self-assembly behavior of *m*-CHO-ZnP with pyrazine and 4,4′-bipyridine was investigated by ^{1}H NMR spectroscopy (Figure S1 and Figure S2). *m*-CHO-ZnP can form stable face-to-face porphyrinic dimers with both ligands, which aids in cage formation. As such, we first designed and

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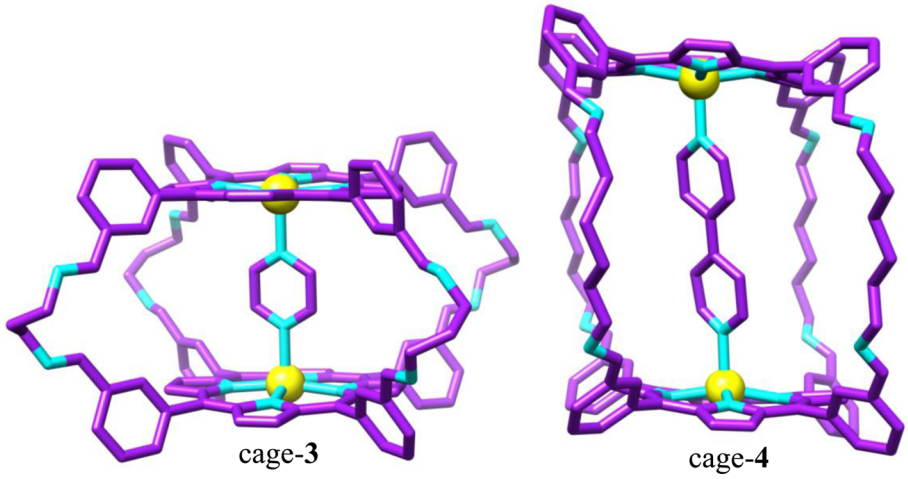

Figure 3. Crystal structures of cage-**3** and cage-**4**. Hydrogen atoms are omitted for clarity. C, purple; N, cyan; Zn, gold.

synthesized cage-**3** via pyrazine-templated imine condensation reactions. By mixing *m*-CHO-ZnP, pyrazine, and 1,3-propanediamine in $CHCl_3$ and then keeping the mixture at room temperature without stirring, thermodynamic equilibrium was reached within 24 h, and the desired cage-**3** can be formed in a quantitative conversion according to ^{1}H NMR spectroscopy (Figure S3 and Figure S4).

Cage-**3** was characterized by NMR spectroscopy, high resolution MALDI-TOF mass spectrometry (HR-MALDI-TOF-MS), and single crystal X-ray diffraction. The formation of cage-**3** is evident in the ^{1}H NMR spectrum (Figure 2, pink curve) from the appearance of a singlet (δ = 8.43 ppm) for the imine protons and the complete disappearance of the singlet (δ = 10.30 ppm) corresponding to the aldehyde. In addition, because of the formation of cage-**3**, the signal of the coordinated pyrazine protons was shifted upfield to 0.98 ppm compared to the initial face-to-face complex. Besides, the signals of the porphyrin protons (δ = 8.60 ppm) and aromatic protons are slightly shifted upfield compared to *m*-CHO-ZnP. HR-MALDI-TOF-MS of cage-**3** (Figure S6) confirms the constitutional identity of cage-**3** with a peak at m/z = 1729.53987, corresponding to $[M\text{-pyrazine} + H]^+$ (calcd: 1729.54130).

Single red crystals of cage-**3** were obtained by slow diffusion of acetone into a $CHCl_3$ solution, and its solid-state structure was determined by single-crystal X-ray crystallography. Cage-**3** crystallizes in the triclinic system with the $P\bar{1}$ space group. As shown in Figure 3, the distance of cofacial porphyrins in cage-**3** is 7.66 Å, and the pyrazine is complexed between the porphyrinic units through regular N−Zn bonds (2.18 Å), indicating no strain in the complex. Therefore, by choosing 1,3-propanediamine as the spacers, cage-**3** could be obtained through pyrazine-templated imine condensation reactions.

We then designed cage-**4** (Figure 1) with a larger size compared to cage-**3**, by choosing 4,4′-bypridine as the template. Because the length of 4,4′-bipyridine is longer than that of pyrazine, longer diamine spacers are expected, and 1,6-diaminohexane was used. Following the same synthetic procedure as for cage-**3**, desired molecular cage-**4** was also formed in quantitative conversion according to ^{1}H NMR spectroscopy (Figure S7and Figure S8). The structure of cage-**4** was also confirmed by several different techniques. As shown in Figure 2 (green curve), because of the formation of cage-**4**, a singlet (δ = 8.47 ppm) for the imine protons appeared, and the signals of the coordinated bipyridine protons were shifted upfield to 4.85 and 2.22 ppm compared to the initially formed face-to-face complex. Besides, only one set of signals for the porphyrin protons (δ = 8.71 ppm) was observed, and aromatic protons are slightly shifted upfield compared to *m*-CHO-ZnP. Furthermore, HR-ESI-MS (Figure S12) also supports the formation of cage-**4** by the presence of a peak at m/z = 1897.72800, which can be ascribed to the molecular ion peak of $[M - \text{bypridine} + H]^+$ (calcd: 1897.72911).

Slow diffusion of acetone into a $CHCl_3$ solution of cage-**4** also produced single red crystals suitable for X-ray crystallography. Cage-**4** crystallizes as well in the $P\bar{1}$ space group, and the crystal structure is shown in Figure 3. The 4,4′-bipyridine is coordinated to the zinc atoms of the porphyrins through regular N−Zn bonds (2.13 Å), again indicating strain-free and confirming that the 1,4-diaminohexane spacers are suitable to bridge between the two porphyrins coordinated to bipyridine. In addition, the zinc−zinc distance of cage-**4** is 11.96 Å, which is larger than that of cage-**3**. Therefore, by using a longer template molecule, a larger CPC can also be obtained in a one-step procedure and with quantitative conversion.

In summary, through careful choosing of template linker and length of the diamine, we were able to selectively form two CPCs with varying cavity sizes in a one-step procedure with quantitative conversion. As further confirmed by X-ray structures, the distance between the cofacial porphyrins of cage-**3** is 7.66 Å, whereas that of cage-**4** is 11.96 Å. From these reported CPCs (cage-**1** to cage-**4**), we believe that the template-directed imine condensation reaction can be used generally to synthesize CPCs of varying sizes. We should mention here that the existing templates have limited further applications as a host. Once the template was removed, we may obtain porous CPCs with varying cavity sizes, which may enable us to further investigate their applications for encapsulating different guest molecules.

■ EXPERIMENTAL SECTION

General Methods. Pyrazine, 4,4′-bipyridine, 1,3-propanediamine, 1,6-diaminohexane, and $CDCl_3$ were purchased from commercial sources and used without further purification. *m*-CHO-ZnP was prepared according to our previous method.[15] NMR spectra were measured on a 300 and 400 M nuclear magnetic resonance spectrometer. Chemical shifts are quoted as parts per million (ppm) relative to residual $CHCl_3$ at δ = 7.26 ppm. HRMS spectra were

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recorded on MALDI−TOF and ESI-MS. Melting point data were performed on a digital melting point meter with a microscopic detector. For cage-**3**, the single crystal X-ray data were collected at 298 K using a synchrotron radiation facility (λ = 0.720 Å). For cage-**4**, the X-ray crystal data were collected at 173 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

*Synthesis of Cage-**3**.* *m*-CHO-ZnP (30 mg, 0.038 mmol), excessive amounts of pyrazine (18.3 mg, 0.228 mmol), and 1,3-propanediamine (5.9 mg, 0.080 mmol) were dissolved in $CHCl_3$ (30 mL). The resulting mixture was left at room temperature for 24 h without stirring. Then, the solution was added dropwise to cool ether (100 mL), and purple solids precipitated out. Cage-**3** was filtered and isolated as a purple solid (30.6 mg, yield: 89%). Mp 189−190 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ 8.59 (s, 16H), 8.44 (d, J = 8.1 Hz, 8H), 8.29 (s, 8H), 7.91 (d, J = 7.2 Hz, 8H), 7.86 (s, 8H), 7.66 (t, J = 7.7 Hz, 8H), 3.81 (s, 16H), 2.51 (s, 8H), 0.98 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 162.0, 150.0, 143.4, 136.9, 135.1, 134.4, 131.9, 127.5, 125.4, 120.1, 57.6, 29.8. HR-MALDI-TOF MS calcd for $C_{108}H_{81}N_{16}Zn_2$ m/z: 1729.54130 [M − pyrazine + H]$^+$; found: 1729.53987. X-ray crystallographic data: $C_{117.72}H_{89.72}Cl_{17.16}N_{18}Zn_2$, M_r = 2495.54, triclinic, space group $P\bar{1}$, a = 14.171(3) Å, b = 14.945(3) Å, c = 17.378 Å, α = 93.35(3)°, β = 111.87(3)°, γ = 115.30(3)°, T = 293(2) K, Z = 1, V = 2982.2(13) Å^3, ρ_{calc} = 1.390 g cm^{-3}, μ = 0. 867 mm^{-1}, radiation wavelength (λ = 0.720 Å), θ_{max} = 27.093, no. of meas. reflns: 55803, no. of indep. reflns: 8934, R_{int} = 0.0711, R_1 = 0.0819, wR_2 = 0.2381. CCDC 1414483.

*Synthesis of Cage-**4**.* *m*-CHO-ZnP (100 mg, 0.127 mmol), excessive amounts of 4,4′-bipyridine (89 mg, 0.571 mmol), and 1,6-diaminohexane (31 mg, 0.267 mmol) were dissolved in $CHCl_3$ (50 mL). The resulting mixture was left at room temperature for 24 h without stirring. Then, the solution was added dropwise to cool ether (100 mL), and purple solids precipitated out. Cage-**4** was filtered and isolated as a purple solid (120 mg, yield: 92%). Mp 190−191 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 8.71 (s, 16H), 8.51 (s, 8H), 8.47 (s, 8H), 8.07 (d, J = 7.6 Hz, 8H), 7.96 (d, J = 7.9 Hz, 8H), 7.66 (t, J = 7.6 Hz, 8 H), 4.85 (d, J = 6.9 Hz, 4H), 3.75−3.57 (m, 16H), 2.22 (d, J = 6.9 Hz, 4H), 1.67 (m, 16H), 1.47−1.29 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 161.7, 150.2, 144.1, 143.6, 137.3, 134.6, 133.4, 131.9, 127.9, 126.9, 120.2, 62.6, 30.6, 27.3. HR-ESI MS calcd for $C_{120}H_{105}N_{16}Zn_2$ m/z: 1897.72911 [M − bipyridine + H]$^+$; found: 1897.72800. X-ray crystallographic data: $C_{145.43}H_{137.07}Cl_{17.36}N_{18}O_{3.21}Zn_2$, M_r = 2934.48, triclinic, space group $P\bar{1}$, a = 14.360(3) Å, b = 14.521(3) Å, c = 18.490(4) Å, α = 96.865(6)°, β = 102.787(6)°, γ = 103.857(5)°, T = 173(2) K, Z = 1, V = 3589.4(14) Å^3, ρ_{calc} = 1.358 g cm^{-3}, μ = 0. 716 mm^{-1}, radiation wavelength (λ = 0.71073 Å), θ_{max} = 25.027, no. of meas. reflns: 23745, no. of indep. reflns: 12530, R_{int} = 0.1201, R_1 = 0.0990, wR_2 = 0.1919. CCDC 1414588.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01781.

Details of the synthesis, NMR spectroscopy, high resolution mass spectrometry, and crystallographic data (PDF)

Cage-3 crystallographic data (CIF)

Cage-4 cyrstallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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(17) Once we use a longer template, a longer diamine spacer should be used, which may increase the chance of forming cyclic and oligomeric reaction products.

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