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Template-Directed Synthesis of Flexible Porphyrin Nanocage and Nanorings via One-Step Olefin Metathesis

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Supporting Information

ABSTRACT: We describe the fabrication of a suite of flexible porphyrin cages and nanorings from a simple tetraalkene-derived zinc porphyrin monomer via a highly efficient template-directed strategy. The zinc porphyrin monomers were preorganized together by coordination with N atoms of multidentate ligands. Subsequent one-step olefin metathesis furnished a bisporphyrin cage, a triporphyrin nanoring, and a hexaporphyrin nanoring. In the case of the hexaporphyrin nanoring, 24 terminal olefins from six porphyrin monomers reacted with each other to form 12 new double bonds, delivering the final product. The triporphyrin and hexaporphyrin nanorings were further employed as hosts to encapsulate C_{60} and C_{70}.

Molecular cages and nanorings have attracted great attention over the past two decades because of their potential applications in guest encapsulation, catalysis, artificial light-harvesting antennae, molecular devices and machines, and drug delivery.[1] This has led to the development of synthetic strategies and subsequent studies of either covalent[2] or noncovalent[3] cages and nanorings. Compared with non-covalently linked structures, covalent nanocages and nanorings generally present high structural stability, which is particularly important for high turnover in catalysis and for medical or material applications.[2] However, the controllable synthesis of covalent nanocages and nanorings is a great challenge because of the possibility of forming other linear or cyclic oligomers.[2,4] The template-directed strategy is a powerful method for constructing nanoscopic architectures with high complexity. In this approach, precursor molecules self-organize via intermolecular interactions with the assistance of templates and then react each other to deliver a final complex structure.[5a] Metalloporphyrins incorporated into a cage or nanoring can stabilize guest molecules via coordination bonds or $\pi-\pi$-stacking interactions, which can also be lent to form the preorganization of the hollow architecture in a templated reaction.[4,5a] A diverse range of porphyrin cages and nanorings have been elegantly synthesized by employing carefully selected nitrogen-containing templates and porphyrin precursors.[2a,4a,5−7,8a,9] Nevertheless, almost all of the reported multiporphyrin nanorings, apart from the bisporphyrin cages, were rigid and singly linked via Sonogashira or Glaser coupling reactions of trans-disubstituted porphyrin monomers. Examples of flexible and doubly linked multiporphyrin nanorings remain rare, although flexible bisporphyrin cages have been well-established.[6,9a,g−i] Although entirely rigid structures possess some distinctive advantages, such as persistent configurations and excellent electrochemical and photophysical properties,[2a,8a−d] flexibility or the combination of flexibility with rigidity is also important in natural and unnatural self-assemblies, especially for the construction of variable or tunable supramolecular systems.[8e,f]

Herein we present a highly efficient strategy of template-directed synthesis of a suite of flexible porphyrin cages and nanorings from an easily prepared *meso*-tetraalkene-derived porphyrin monomer via one-step olefin metathesis, which has been well-known as a kind of dynamic covalent chemistry (DCC).[10] The products depend on the templates used. A porphyrin cage was fabricated when a bidentate ligand, 1,4-diazabicyclo[2.2.2]octane (DABCO, **2**), was used as the template, while a triporphyrin nanoring and a hexaporphyrin nanoring were obtained from the same monomer when a tripyridyl and hexapyridyl templates, respectively, were used. The triporphyrin and hexaporphyrin nanorings were composed of three or six doubly linked porphyrins, forming three-dimentional (3D) and deeper cylindrical cavities, which could be further applied as hosts for fullerenes.

The synthetic route for the porphyrin cage and nanorings is illustrated in Scheme 1. The tetraalkene-derived zinc porphyrin **1** was easily prepared from the reaction of 4-(but-3-en-1-yloxy)benzaldehyde and pyrrole according to a procedure similar to that described by Adler et al.[11] followed by coordination with zinc acetate. The zinc porphyrin derivative **1** was subsequently utilized as a monomer for the synthesis of the porphyrin cage and nanorings. With DABCO as a ligand, two molecules of **1** were preorganized together to form the sandwich-type dimer $\mathbf{1}_2\cdot\mathbf{2}$, from which bisporphyrin cage **3a** was obtained in 47% yield via a one-pot olefin metathesis reaction. The alkenes of **3a** were then reduced with H_2 catalyzed by Pd/C to afford cage **3b** in 78% yield. The DABCO template was highly stabilized in the cavities of both **3a** and **3b** as a result of the well-fit sizes of the cages for DABCO and the strongly cooperative coordination interactions between the two zinc porphyrins and DABCO.

When 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine (TPT, **4**) was used as the template, three zinc porphyrin monomers **1** coordinated with one TPT molecule to form $\mathbf{1}_3\cdot\mathbf{4}$ with a triangular-prism shape. Grubbs' II catalyst was then added to trigger olefin metathesis, by which 12 terminal alkenes on three porphyrin monomers exchanged successively to produce cyclic porphyrin trimer **5a**. At the same time, six ethylenes were released. The alkenes on **5a** were then hydrogenated to provide nanoring **5b**, during which the TPT template was simultaneously lost.

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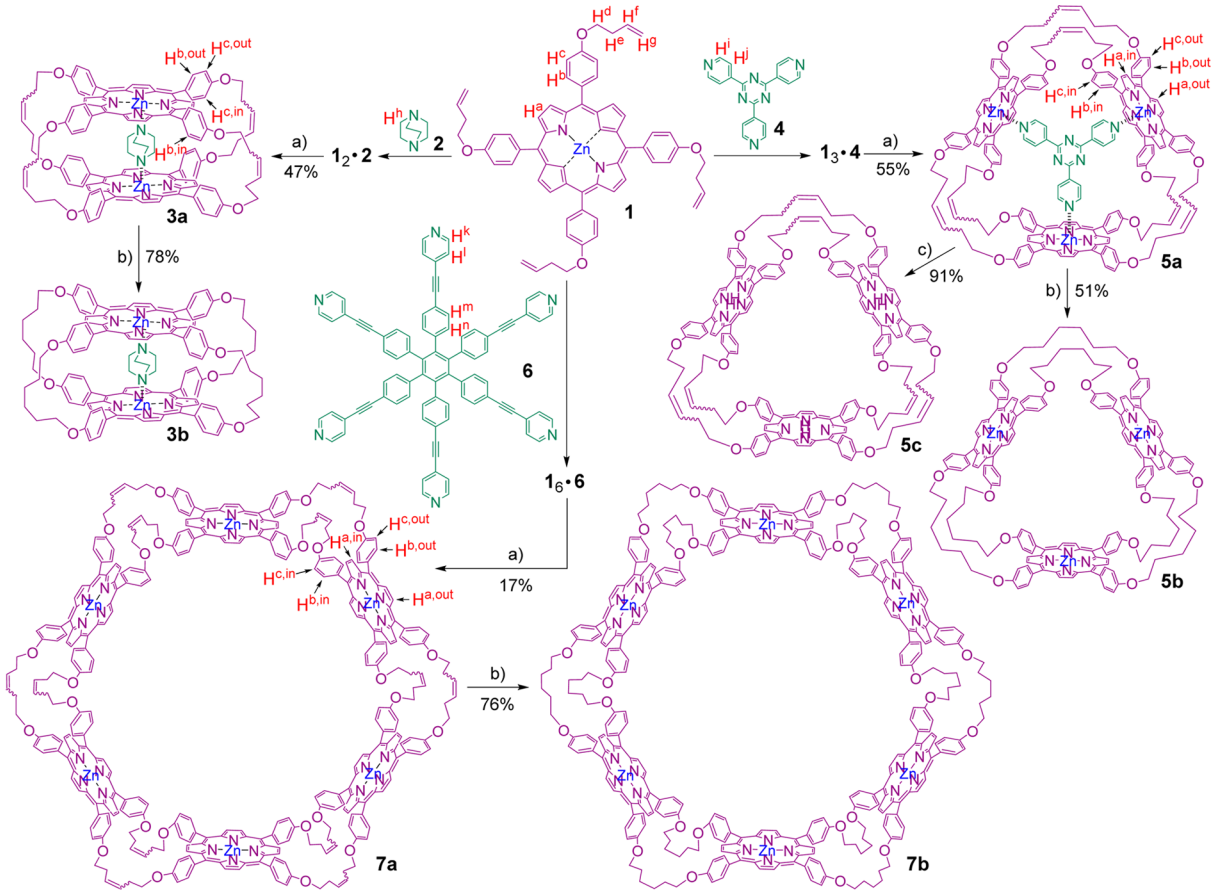
Scheme 1. Template-Directed Synthesis of Bisporphyrin Cages 3, Triporphyrin Nanorings 5, and Hexaporphyrin Nanorings 7[a]



[a]Reaction conditions: (a) Grubbs' II catalyst, CH_2Cl_2, r.t.; (b) 10% Pd/C, H_2, 0.2 MPa, THF, r.t.; (c) trifluoroacetic acid, CH_2Cl_2.

Introducing trifluoroacetic acid into a solution of **5a** removed both the TPT template and zinc atoms to yield **5c**. This template-directed protocol was then extended to a six-porphyrin system. Hexaporphyrin nanoring **7a** was synthesized via in situ olefin metathesis from a preorganized hexaporphyrin supramolecule $\mathbf{1}_6$·**6**, which was previously formed from six molecules of monomer **1** and one molecule of hexadentate template **6**. In this case, 24 terminal olefins from six porphyrin monomers reacted each other to form 12 new double bonds in one pot. The resulting product **7a** was separated with no template attached, probably because of the weak binding interaction and loose fit between the sizes of **7a** and **6**. The alkenes on **7a** were also then saturated to furnish nanoring **7b**.

The templating behavior of **1** toward the multidentate ligands was first investigated by ^{1}H NMR spectroscopy (Figure 1b,d,f). After **1** coordinated with the ligands **2**, **4**, and **6**, the chemical shifts of the pyrrole protons H^a and the phenyl protons H^b and H^c of **1** moved upfield, indicative of the formation of $\mathbf{1}_2$·**2**, $\mathbf{1}_3$·**4**, and $\mathbf{1}_6$·**6**. As displayed by the values of the chemical shift changes, the templating effect decreased as the number of participating porphyrin monomers increased, the trend of which was almost consistent with the trend of synthetic yields of **3a**, **5a**, and **7a**. After the olefin metathesis reaction, the terminal olefinic signals (H^g) observed in the ^{1}H NMR spectra of $\mathbf{1}_2$·**2** (Figure 1b), $\mathbf{1}_3$·**4** (Figure 1d), and $\mathbf{1}_6$·**6** (Figure 1f) disappeared, and only nonterminal olefinic signals (H^f) were detected for **3a** (Figure 1c), **5a** (Figure 1e), and **7a** (Figure 1g). The simultaneous existence of *cis*- and *trans*-olefin isomers was observed in all of the

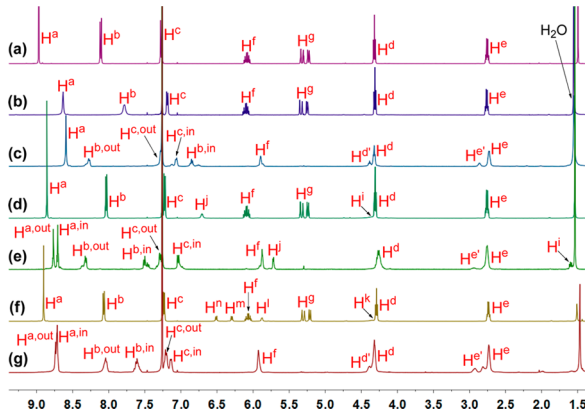


Figure 1. Partial ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectra of (a) **1**, (b) $\mathbf{1}_2$·**2**, (c) **3a**, (d) $\mathbf{1}_3$·**4**, (e) **5a**, (f) $\mathbf{1}_6$·**6**, and (g) **7a**.

^{1}H NMR spectra of **3a**, **5a**, and **7a** (Figure 1c,e,g), while the ^{1}H NMR spectra of the hydrogenated products (Figures S6, S15, and S24 in the Supporting Information) indicated formation of three highly symmetric species, as expected for the structures of **3b**, **5b**, and **7b** (Scheme 1). After the porphyrin cage and nanorings were generated, the chemical shifts of H^b and H^c split into two sets of peaks ($H^{b,in}$, $H^{b,out}$ and $H^{c,in}$, $H^{c,out}$, respectively; Figure 1c,e,g), clearly showing the different chemical environments of the phenyl protons pointing inside and outside. The signals of $H^{b,in}$ and $H^{c,in}$ shifted to higher field, which was influenced by the shielding effect of the porphyrin cage or

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nanorings. Similarly, the shielding effect was observed against the templates in **3a**, **3b** and **5a**, resulting in obvious upfield shifts of H^h on DABCO (Figures S3 and S6) and H^i and H^j on TPT (Figure S11). In the ^{1}H NMR spectra of nanorings **5a** and **7a**, the pyrrole protons H^a also split into two sets of peaks $H^{a,in}$ and $H^{a,out}$ (Figure 1e,g) because of their different chemical environments, as $H^{a,in}$ is located in the "wall" of the nanoring while $H^{a,out}$ points outside of the "edge".

The structures of the porphyrin cages and nanorings were further supported by ^{13}C NMR, ^{1}H−^{1}H correlation spectroscopy (COSY), and heteronuclear single-quantum coherence (HSQC) spectra. In the ^{1}H−^{1}H COSY spectra of **3a** (Figure S4), **5a** (Figure S13), and **7a** (Figure S22), correlations were found between $H^{b,in}$ and $H^{c,in}$, $H^{b,out}$ and $H^{c,out}$, and H^d and H^e. In the ^{1}H−^{1}H COSY spectrum of **5a** (Figure S13), one set of peaks from H^i located at 1.63 ppm had a correlation with protons H^j at 6.10 ppm, confirming the existence of the TPT template. Nevertheless, no peaks corresponding to template **6** were observed in the NMR spectra of **7a** and **7b**.

MALDI-TOF MS studies provided further evidence for the formation of the porphyrin cages and nanorings. The MALDI-TOF mass spectrum of **3a** showed a peak at m/z 1804.50 (Figure S27) attributed to $[M - DABCO + H]^+$, while a similar peak was observed for **3b** at m/z 1812.58 (Figure 2a) attributed to $[M - DABCO + H]^+$. For nanoring **5a**, one related peak was found at m/z 2706.79 (Figure S29) attributed to $[M - TPT + H]^+$. For **5b** and **5c**, related peaks were found at m/z 2718.87 (Figure 2b) and m/z 2517.11 (Figure 2c), respectively, attributed to $[M + H]^+$. Nanorings **7a** and **7b** exhibited related peaks at m/z 5414.4 (Figure S32) and m/z 5439.0 (Figure 2d), respectively, corresponding to $[M + H]^+$. All of these peaks were isotopically resolved and agreed very well with their theoretical distributions.

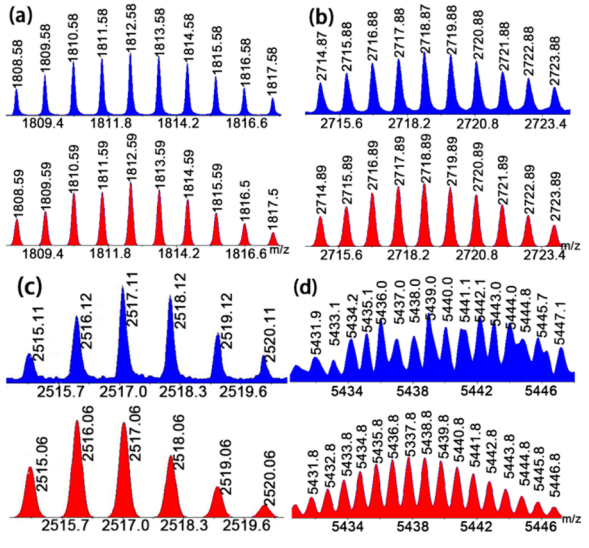

Figure 2. Experimental (blue) and calculated (red) MALDI-TOF MS spectra (positive reflection mode) of (a) $[\mathbf{3b} - DABCO + H]^+$, (b) $[\mathbf{5b} + H]^+$, (c) $[\mathbf{5c} + H]^+$, and (d) $[\mathbf{7b} + H]^+$.

Transmission electron microscopy (TEM) was used to directly visualize the triporphyrin and hexaporphyrin nanorings. Dark-gray spherical structures formed from 1×10^{-8} M solutions of **5a** and **7a** in CH_2Cl_2 were observed. The diameters of **5a** ranged from 1.3 to 1.8 nm with an average of ∼1.5 nm (Figure 3b,c); the diameters of **7a** ranged from 2.0 to 3.7 nm with an average of ∼3.4 nm (Figure 3d). Dynamic light scattering (DLS)

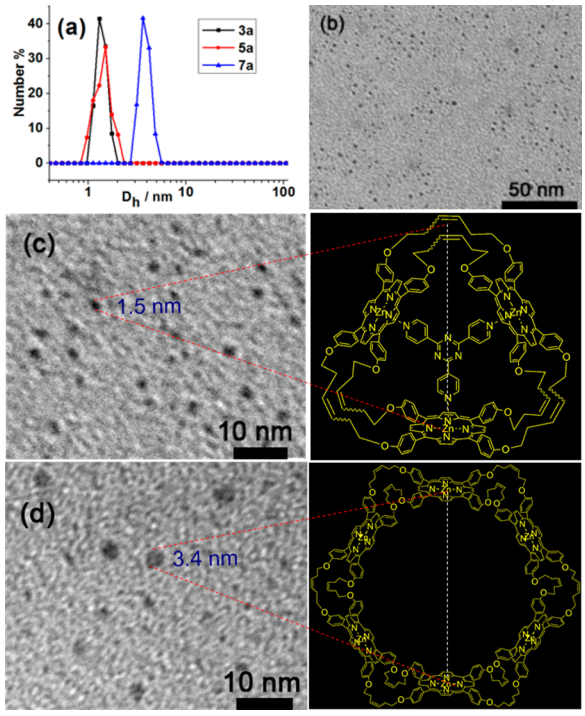

Figure 3. (a) DLS data for **3a**, **5a**, and **7a** in CH_2Cl_2 (1×10^{-8} M). (b) Low-magnification TEM image of **5a**. (c) High-magnification TEM image of **5a**. (d) High-magnification TEM image of **7a**.

experiments using 1×10^{-5} M solutions of the porphyrin cage and nanorings in CH_2Cl_2 showed narrow distributions (Figure 3a). The average hydrodynamic diameters (D_h) of **3a** (Figure 3a, black), **5a** (Figure 3a, red), and **7a** (Figure 3a, blue), were measured to be ∼1.3, ∼1.5, and ∼3.6 nm, respectively, in accordance with the sizes observed in the TEM images.

Furthermore, the encapsulation of fullerenes by triporphyrin nanoring **5c** and hexaporphyrin nanoring **7a** was investigated via absorption spectroscopy, emission spectroscopy, and isothermal titration calorimetry (ITC). The UV−vis spectra of **5c** and **7a** in CH_2Cl_2 displayed a typical porphyrin Soret band at 400−450 nm (Figure 4a). After **5c** and **7a** complexed with excess C_{60} or C_{70}, the absorbance of the porphyrin units decreased, accompanied by a bathochromic red shift (∼449 cm^{-1}), as a result of host−guest electronic interactions.[8a] Emission spectroscopy further supported the encapsulation of C_{60} and C_{70} into **5c** and **7a**. Excitation of a solution of **5c** in CH_2Cl_2 at 450 nm gave two strong emission bands at λ_{max} = 658 and 728 nm (Figure 4b), whereas almost no emission at 658 nm and sharply reduced emission at 728 nm were found for both C_{60}@**5c** and C_{70}@**5c** because of the strong interactions and efficient energy transfer

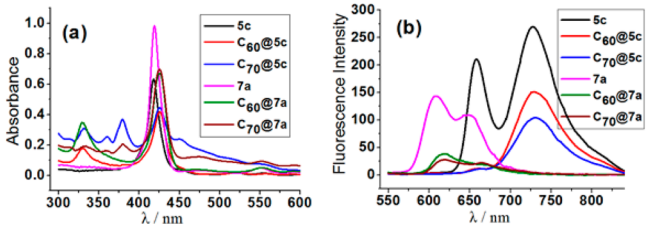

Figure 4. (a) UV−vis and (b) fluorescence (λ_{ex} = 450 nm, CH_2Cl_2/benzene = 100:1, 1×10^{-6} M, room temperature) spectra of **5c**, C_{60}@**5c**, C_{70}@**5c**, **7a**, C_{60}@**7a**, and C_{60}@**7a**.

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between the host and guests. Similar fluorescence quenching phenomena were also observed in the emission spectra of C_{60}@**7a** and C_{70}@**7a**. The binding stoichiometries for all of the complexes C_{60}@**5c**, C_{70}@**5c**, C_{60}@**7a**, and C_{70}@**7a** were determined to be 1:1 by ITC experiments. The association constants (K_a) of C_{60}@**5c** and C_{70}@**5c** in benzene were estimated to be 3.3×10^6 and 2.3×10^6 M^{-1}, respectively (Figures S33 and S34), while $K_a = 3.4 \times 10^5$ and 1.4×10^5 M^{-1} for C_{60}@**7a** and C_{70}@**7a**, respectively (Figures S35 and S36). The weaker binding of **7a** to C_{60} and C_{70} is probably due to the fact that the cavity of **7a** is too large for C_{60} and C_{70}. It is reasonable that these porphyrin nanorings containing flexible alkoxyl chains could adjust their sizes according to different guests, so high association constants were obtained for both the triporphyrin and hexaporphyrin nanorings and no obvious selectivities were obtained for C_{60}/C_{70}.

In conclusion, we have described the template-directed synthesis of a bisporphyrin cage and two cylindrical porphyrin nanorings from an easily accessible *meso*-tetraalkene-derived porphyrin monomer via one-step olefin metathesis. The alkenes on the products were then hydrogenated to afford alkane-linked and highly symmetric porphyrin cage and nanorings. These flexible cages and nanorings were characterized by a range of analytical methods. The triporphyrin and hexaporphyrin nanorings were further employed as hosts to bind C_{60} and C_{70} with high association constants (up to 3.3×10^6 M^{-1}). The controllable, template-directed construction of topologically complex architectures from a simple precursor provides pathways toward new nanoscopic designs with interesting structures and functions, thus avoiding the lengthy procedures associated with traditional synthetic routes.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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