

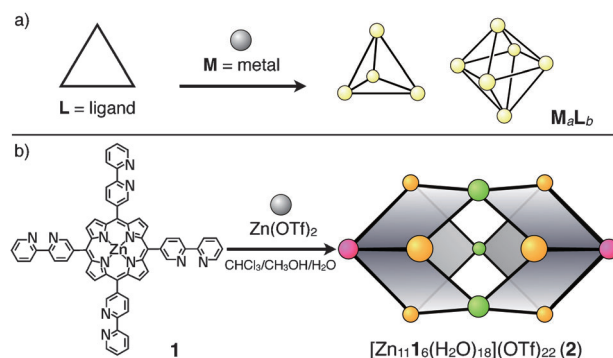
# A Self-Assembled Multiporphyrin Cage Complex through Three Different Zinc(II) Center Formation under Well-Balanced Aqueous Conditions\*\*

Takashi Nakamura, Hitoshi Ube, Motoo Shiro, and Mitsuhiro Shionoya\*

Coordination-driven self-assembly of organic ligands and metal ions is a powerful method for construction of large and well-defined molecular architectures.<sup>[1]</sup> A large number of excellent examples for supramolecular coordination structures have been reported,<sup>[2]</sup> such as squares, tetrahedra, octahedra, and cuboctahedra. In particular, supramolecular hosts with an isolated inner space possess unique functions such as molecular recognition,<sup>[3]</sup> catalytic reactions,<sup>[4]</sup> control of guest motion,<sup>[5]</sup> and stabilization of unstable species,<sup>[6]</sup> reflecting geometrical characteristics of each inner space.

It is well understood that both precise design of organic ligands with multiple binding sites and deliberate choice of metal species are important in setting up an initial condition for their spontaneous supramolecular assembly. For instance, upon addition of a certain metal ion to organic ligands possessing multiple metal binding sites of the same type, resultant self-assembled structures become highly symmetric with chemically equivalent metal centers under a given condition (Figure 1a). For more intricate self-assembled structures, now-common procedures are differentiation of binding sites and/or use of more than one kind of metal ion.<sup>[7]</sup> Moreover, several polynuclear complexes with different metal centers constructed from one kind of metal ions and bridging ligands possessing two chemically equivalent bidentate units have been reported.<sup>[8]</sup> These examples have proven that combination of even simple ligands and metal ions can lead to intricate structures. In most cases, however, the binding stoichiometry of ligands to metal centers stays constant in each complex. Thus, a method to generate unsymmetrical structures with more than one kind of metal center from a simple organic ligand would open a new direction towards more elaborate supramolecular functions.

In this regard, we envisioned that simultaneous formation of several different metal centers under well-balanced com-



**Figure 1.** Metal-mediated self-assembly leading to well-defined supramolecular complexes. a) Metal-mediated self-assembly providing uniform polyhedral complexes (a tetrahedron and an octahedron are shown) comprised of chemically equivalent metal centers. b) Zn<sup>II</sup>-mediated self-assembly forming a supramolecular cage complex  $[Zn_{11} 1_6(H_2O)_{18}](OTf)_{22}$  (**2**) through the formation of three different kinds of Zn<sup>II</sup> centers from a  $C_4$ -symmetric Zn-porphyrin ligand **1**. A  $H_2O$  ligand bound to the axial position of Zn-porphyrin **1** is omitted from the chemical structure for clarity and for ambiguity of the axial ligand in solution. The Zn<sup>II</sup> centers depicted in the same color (purple, orange, and green) are equivalent with each other.

plexation conditions with coordinating co-solvents would have great potential as a strategy to construct intricate self-assembled structures. Herein we report a supramolecular cage complex,  $[Zn_{11} 1_6(H_2O)_{18}](OTf)_{22}$  (**2**) ( $OTf = CF_3SO_3$ ), formed from  $Zn(OTf)_2$  and a  $C_4$ -symmetric Zn-porphyrin ligand **1** in an aqueous–organic mixed solvent (Figure 1b). Although the ligand **1** has four chemically equivalent (2,2'-bipyridin)-5-yl (bpy) groups attached to a central Zn-porphyrin, the resulting cage complex **2** possesses three different kinds of Zn<sup>II</sup> centers with bpy ligands. Notably, two different kinds of hydrated bis(bpy) Zn<sup>II</sup> units were formed in addition to a tris(bpy) unit under a well-balanced aqueous condition, leading to complex **2** with an unsymmetrical yet well-defined structure. Its triangular bipyramidal inner space surrounded by six Zn-porphyrin rings allowed unsymmetrical inclusion of up to two  $\pi$ -acceptor guest molecules, 2,7-dinitro-9-fluorenone (**3**),<sup>[9]</sup> through  $\pi$ – $\pi$  interactions with Zn-porphyrin rings on the inner wall.

Metalloporphyrins have metal- and/or ligand-centered photochemical and redox properties, and so far many studies have been conducted to develop functional self-assembled molecular systems.<sup>[10,11]</sup> Molecular design has often been done making the most of  $C_4$ -symmetry of porphyrin ring. For instance, Nitschke et al. have recently reported a self-assembled  $M_8L_6$  cubic cage complex formed from  $C_4$ -symmetric

[\*] T. Nakamura, Dr. H. Ube, Prof. Dr. M. Shionoya  
Department of Chemistry, Graduate School of Science  
The University of Tokyo  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)  
E-mail: shionoya@chem.s.u-tokyo.ac.jp  
Dr. M. Shiro  
Rigaku Corporation  
3-9-12 Matsubaracho, Akishima, Tokyo 196-8666 (Japan)

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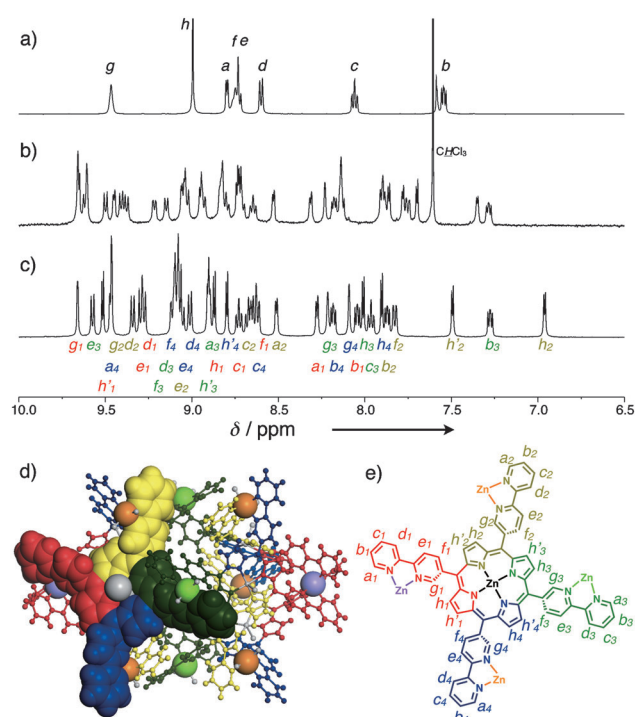
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tetrakis(pyridylimine) ligands and  $\text{Fe}(\text{OTf})_2$ .<sup>[12]</sup> A Zn-porphyrin ligand **1** used in our study possesses four bpy groups directly attached to the *meso* positions of the central Zn-porphyrin ring. X-ray crystallographic analysis of **1** revealed its rigid structure (Supporting Information, Figure S9). Owing to the steric repulsion between the  $\beta$  hydrogen of the porphyrin ring and the hydrogen at the 4-position of bpy, the bpy groups do not take coplanar conformation with the central porphyrin ring. The dihedral angles between the bpy groups and the porphyrin ring were in the range from 61 to 87° in the crystal structure.

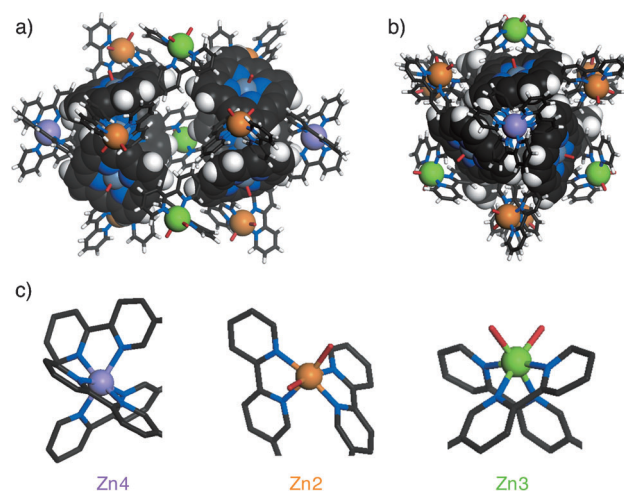
$\text{Zn}^{\text{II}}$  was selected for coordination-driven self-assembled structures, because  $\text{Zn}^{\text{II}}$  is coordinatively labile and thus adaptable in coordination behaviors. It is known that  $\text{Zn}^{\text{II}}$  and 2,2'-bipyridine form mono(bpy), bis(bpy), and tris(bpy)  $\text{Zn}^{\text{II}}$  complexes, depending on synthesis conditions for counteranions and solvents.<sup>[13]</sup> In this work, well-balanced complexation conditions were developed for the formation of a well-defined anisotropic supramolecular cage structure with both bis(bpy) and tris(bpy)  $\text{Zn}^{\text{II}}$  units. We envisioned that such synthesis conditions could be realized by controlling the amount of coordinating solvent. Moreover, the rigidity of the tetrakis bidentate ligand **1** was considered a key factor to determine the relative positions of different kinds of metal centers leading to an unsymmetrical yet finite structure.

Complexation of ligand **1** and  $\text{Zn}(\text{OTf})_2$  was examined by  $^1\text{H}$  NMR spectroscopy in an aqueous–organic mixed solvent  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O} = 10:10:1$  (Figure 2). Under these conditions, 2,2'-bipyridine and  $\text{Zn}(\text{OTf})_2$  were expected to form either hydrated bis(bpy) complex,  $[\text{Zn}(\text{bpy})_2(\text{D}_2\text{O})_2]^{2+}$ , or tris(bpy) complex,  $[\text{Zn}(\text{bpy})_3]^{2+}$ . The  $^1\text{H}$  NMR spectrum of the ligand **1** showed that **1** had a  $C_4$  symmetry in solution; that is, four bpy groups were chemically equivalent on the NMR timescale (Figure 2a). Upon addition of  $\text{Zn}(\text{OTf})_2$  and heating the reaction mixture at 60°C for 3 h, a set of sharp signals assignable to a supramolecular cage complex **2** appeared (Figure 2b). As many as 36 different aromatic  $^1\text{H}$  signals were observed, indicating that desymmetrized **1** exhibited a  $C_1$  symmetry in the complex **2**. In a synthetic scale experiment, ligand **1** and  $\text{Zn}(\text{OTf})_2$  underwent complexation in  $\text{CHCl}_3/\text{CH}_3\text{OH}/\text{H}_2\text{O} = 10:10:1$ , and the complex **2** was isolated in 76% yield after recrystallization from  $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{Et}_2\text{O}$ . ESI-MS analysis of this product in a  $\text{CH}_3\text{CN}$  solution clearly found a set of signals assignable to complex **2** with the composition  $[\text{Zn}_{11}\text{L}_6](\text{OTf})_{22}$  (Supporting Information, Figure S11). A UV/Vis absorption spectrum of **2** showed Soret and Q bands characteristic to Zn-porphyrin, while they were broadened and red-shifted compared with those of ligand **1** (Supporting Information, Figure S39).

Crystals suitable for X-ray analysis were obtained by slow vapor diffusion of  $\text{CH}_2\text{Cl}_2$  into  $\text{CH}_3\text{OH}$  solution of **2**. The X-ray analysis unambiguously revealed a cage framework of  $[\text{Zn}_{11}\text{L}_6(\text{H}_2\text{O})_{18}]^{22+}$ , featuring six Zn-porphyrin rings and eleven bpy- $\text{Zn}^{\text{II}}$  units (Figure 3).<sup>[14]</sup> The shape of complex **2** can be perceived as an enneahedron with all of its faces being quadrilaterals (Figure 1b). There exist three different kinds of six-coordinate  $\text{Zn}^{\text{II}}$  centers in **2** apart from Zn1 of porphyrin **1** (Figure 3c). Two Zn4 centers at the both ends of **2** (depicted in purple in Figure 3) were bound by three bpy groups, which



**Figure 2.** Characterization of ligand **1** and  $\text{Zn}^{\text{II}}$  complex. a)–c)  $^1\text{H}$  NMR spectra of **1** and **2** (500 MHz, 300 K). a) **1** in  $\text{CDCl}_3/\text{CD}_3\text{OD} = 1:1$  (v/v). b) **1** and  $\text{Zn}(\text{OTf})_2$  (11:6  $\text{Zn}(\text{OTf})_2/\mathbf{1}$ ) after heating at 60°C for 3 h in  $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O} = 10:10:1$ . c) Crystals of **2** dissolved in  $\text{CD}_3\text{CN}$ . d) X-ray crystal structure of  $[\text{Zn}_{11}\text{L}_6(\text{H}_2\text{O})_{18}]^{22+}$  in which one Zn-porphyrin **1** is highlighted and color-coded in red, yellow, green, and blue, to present its  $C_1$  symmetry in **2**. See also Figure 3 for the structure of **2**. e) Chemical structure and labeling of hydrogen atoms of **1**. Colors are coded according to the structure in (d).



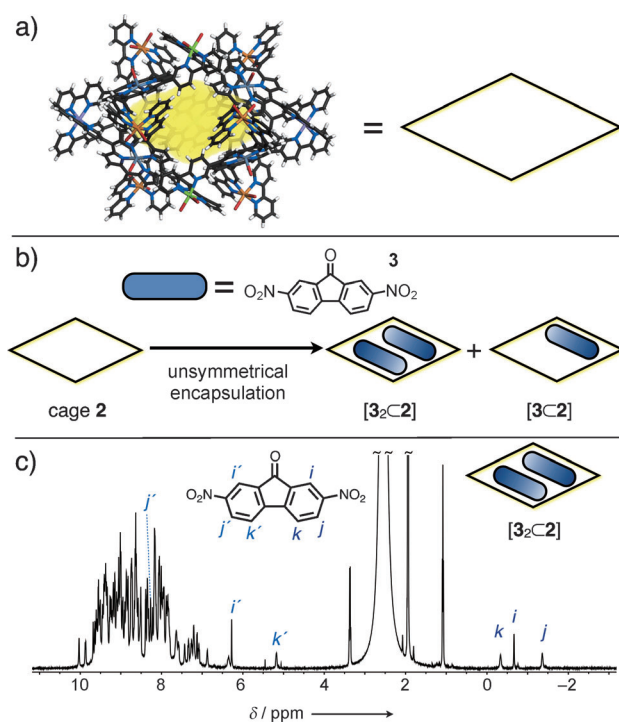
**Figure 3.** The X-ray crystal structure of **2**.  $\text{TfO}^-$  anions, free solvents, and hydrogen atoms of  $\text{H}_2\text{O}$  coordinating to  $\text{Zn}^{\text{II}}$  are omitted for clarity. Three different kinds of  $\text{Zn}^{\text{II}}$  centers bound by bpy groups are colored in purple (Zn4), orange (Zn2), and green (Zn3). Zn1 centers in the porphyrin rings are colored in gray; colors of the other atoms are based on CPK coloring. a) and b) Views from a  $C_2$  symmetry axis (a) and from a  $C_3$  symmetry axis (b).  $\text{Zn}^{\text{II}}$  atoms and porphyrin rings are shown as a space-filling model. The others are shown as a stick model. c) Coordination geometries of three different kinds of bpy- $\text{Zn}^{\text{II}}$  units. Hydrogen atoms are omitted for clarity.

is denoted as *cis*-{Zn4(bpy)<sub>3</sub>}. Six Zn<sup>II</sup> centers positioned in the shoulder of **2** (orange) were coordinated by two bpy and two H<sub>2</sub>O molecules, which is denoted as *cis*-{Zn2(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>}. Three Zn<sup>II</sup> ions in the middle (green) also formed hydrated *cis*-{Zn3(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>}, but relative positions of pyridine rings at the edge of ligand **1** were in the *trans* geometry around the Zn<sup>II</sup> centers, while those of Zn<sup>II</sup> units were in the *cis* geometry. Each Zn<sup>II</sup> of the porphyrin part of **1** was coordinated by one axial H<sub>2</sub>O ligand from outside of the cage complex to form a square-pyramidal geometry in which Zn<sup>II</sup> was displaced by 0.14(2) Å from the N<sub>4</sub> plane. When taken together, the stoichiometry of the cationic framework of **2** is [Zn<sub>11</sub>1<sub>6</sub>(H<sub>2</sub>O)<sub>18</sub>]<sup>22+</sup>. In terms of Δ-Λ configuration of the metal centers in **2**, *cis*-{Zn4(bpy)<sub>3</sub>} (purple) and *cis*-{Zn2(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>} (orange) have the same optical isomerism, while *cis*-{Zn3(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>} (green) has the opposite isomerism.

The <sup>1</sup>H NMR spectrum of **2** was fully analyzed by <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>1</sup>H NOESY NMR spectroscopy, which indicated that complex **2** is stable in solution and its basic structure is the same as that obtained by X-ray analysis (Figure 2c; Supporting Information, Figures S13–S16, Table S1). In the NOESY measurement, several strong diagnostic interligand NOE signals were observed for bis(bpy) Zn<sup>II</sup> units ((a<sub>2</sub>, a<sub>4</sub>), (g<sub>2</sub>, g<sub>4</sub>), (a<sub>3</sub>, g<sub>3</sub>)) and for several β protons of porphyrin rings ((h<sub>2</sub>, g<sub>4</sub>), (h'<sub>2</sub>, h'<sub>1</sub>), (h'<sub>3</sub>, d<sub>3</sub>)). Furthermore, proton signals with characteristic chemical shifts (h<sub>2</sub>, f<sub>2</sub>, h'<sub>1</sub>, etc.) were well-explained by the shielding and deshielding effects from aromatic rings of the neighboring ligands.

H<sub>2</sub>O molecules play a vital role in constituting the framework of [Zn<sub>11</sub>1<sub>6</sub>(H<sub>2</sub>O)<sub>18</sub>]<sup>22+</sup> in light of the fact that 24 H<sub>2</sub>O molecules coordinate to 15 Zn<sup>II</sup> centers in the crystal state. Actually, a mixed solvent containing about 5 % of H<sub>2</sub>O facilitated the generation of complex **2**, whereas the complexation in non-aqueous CDCl<sub>3</sub>/CD<sub>3</sub>OD = 1:1 did not efficiently proceed the formation of **2** (Supporting Information, Figure S37). This result suggests that H<sub>2</sub>O molecules act as important stopper ligands in the Zn<sup>II</sup>-mediated self-assembly process. The presence of H<sub>2</sub>O was also important for stabilization of hydrated structures of complex **2** in the solution. In hot CH<sub>3</sub>CN, complex **2** was converted into a structural isomer in which Δ-Λ isomerism of three bis(bpy) Zn<sup>II</sup> units (depicted in green) in the middle of the cage were reversed from that of **2**, whereas in the presence of solvent amount of H<sub>2</sub>O (CH<sub>3</sub>CN/H<sub>2</sub>O = 20:1 (v/v)), this conversion was not observed and complex **2** remained stable (Supporting Information, Figures S17–S29, Tables S2–S3). In summary, the moderate coordination ability of H<sub>2</sub>O towards Zn<sup>II</sup> centers allowed the formation of both tris(bpy) and hydrated bis(bpy) Zn<sup>II</sup> units, leading to the unsymmetrical yet well-defined self-assembled complex **2**.

The [Zn<sub>11</sub>1<sub>6</sub>(H<sub>2</sub>O)<sub>18</sub>]<sup>22+</sup> framework of **2** (Figure 3a,b) has a triangular bipyramidal shaped inner space as revealed by X-ray analysis. Its cavity (ca. 9 × 18 Å) is surrounded by six Zn-porphyrin rings, and its volume was calculated to be about 730 Å<sup>3</sup> (Figure 4a). The cavity has three windows (d ≈ 4 Å) in the middle of **2**. With these features, this cavity could be used for multiporphyrin-based functions.



**Figure 4.** Unsymmetrical encapsulation of 2,7-dinitro-9-fluorenone (**3**) inside triangular bipyramidal shaped cavity of the cage complex **2**. a) Visualization of the triangular bipyramidal shaped inner space of **2** surrounded by six Zn-porphyrin rings. The volume was calculated to be 730 Å<sup>3</sup> (Connolly surface, probe radius: 4.0 Å). b) Unsymmetrical encapsulation of 2,7-dinitro-9-fluorenone (**3**) inside the cavity of **2**. Up to two π-acceptor guest molecules **3** were captured on the Zn-porphyrin ring of the inner wall by π-π interactions. c) <sup>1</sup>H NMR spectrum of guest-inclusion complexes [3<sub>2</sub>C<sub>2</sub>] and [3C<sub>2</sub>] (500 MHz, 250 K, CD<sub>3</sub>CN). The ratio of [3<sub>2</sub>C<sub>2</sub>]:[3C<sub>2</sub>] was 3.5:1. <sup>1</sup>H NMR signals of one side of **3** encapsulated in [3<sub>2</sub>C<sub>2</sub>] at the edge of the cavity and those of the other side are denoted with (i, j, k) and (i', j', k'), respectively.

To confirm characteristic guest inclusion ability of cage **2**, encapsulation of 2,7-dinitro-9-fluorenone (**3**), a symmetrical π-acceptor molecule exhibiting charge-transfer properties,<sup>[9a]</sup> was examined. This guest molecule was captured unsymmetrically within the triangular bipyramidal shaped cavity of **2**, by π-π interactions with π-donor Zn-porphyrin on the cavity wall (Figure 4b). Upon mixing guest **3** with cage **2** in CD<sub>3</sub>CN, a host-guest complex [3<sub>2</sub>C<sub>2</sub>] that encapsulates two molecules of **3** was formed as a major species, as confirmed by 1D and 2D <sup>1</sup>H NMR measurements at 250 K (Figure 4c; Supporting Information, Figures S30–S36). <sup>1</sup>H NMR signals of encapsulated **3** of [3<sub>2</sub>C<sub>2</sub>] appeared at δ = 8.27, 6.28, 5.17, –0.33, –0.66, and –1.36 ppm (2H value each), respectively. The signals for one side of **3** ((i, j, k) = (–0.66, –1.36, –0.33 ppm)) were greatly shifted upfield (Δδ = –8.41 ≈ –9.90 ppm) from those in the absence of cage **2**, which indicates that only one side of **3** lay deep at the edge of the cavity of **2** and was considerably affected by the shielding-effect from Zn-porphyrin rings. In the NOESY measurement, diagnostic NOE signals were observed between protons of one side of encapsulated **3** and those of cage **2** at the edge of inner cavity ((j, g<sub>1</sub>), (j, h'<sub>2</sub>), (k, h<sub>2</sub>)), which supports the



unsymmetrical encapsulation of **3** inside **2** (Supporting Information, Figure S34). These results also mean that the flipping of guest **3** within the cavity was slower than the  $^1\text{H}$  NMR timescale at 250 K. It should be noted that the unsymmetrical guest encapsulation of **3** was achieved by triangular bipyramidal shaped cavity of the supramolecular host **2**, which was self-assembled from the simple  $C_4$  symmetric building block **1** and  $\text{Zn}^{\text{II}}$  ions under the well-balanced aqueous condition. Such unsymmetrical encapsulation by a self-assembled supramolecular host is a meaningful step towards artificial enzyme-mimicking chemical systems that can exhibit impressive levels of regioselectivity in host-mediated reactions.

In conclusion, we have constructed a supramolecular metal complex  $[\text{Zn}_{11}\text{1}_6(\text{H}_2\text{O})_{18}](\text{OTf})_{22}$  (**2**) composed of a combination of  $\text{Zn}(\text{OTf})_2$  and a  $C_4$ -symmetric, tetrakis(bipyridyl) Zn-porphyrin ligand **1**. Three different kinds of bpy- $\text{Zn}^{\text{II}}$  units, one kind of tris(bpy), and two kinds of hydrated bis(bpy)  $\text{Zn}^{\text{II}}$  units, are formed stably to result in a discrete cage complex with a well-defined shape and size. In this self-assembly process,  $\text{H}_2\text{O}$  molecules, which possess a moderate coordination ability for  $\text{Zn}^{\text{II}}$ , play vital roles in the formation and stabilization of **2**. Furthermore, the Zn-porphyrin hexameric cage **2** captures up to two symmetrical  $\pi$ -acceptor molecules **3** unsymmetrically within its triangular bipyramidal shaped cavity. Thus, metal-organic self-assembly in a solution containing a moderate amount of coordinating molecules has been proven to be an excellent way to create unsymmetrical supramolecular architectures. This conceptual advance would add a fresh dimension to construction of elaborate and intricate self-assembled molecular systems.

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- [14] Crystal data for **2**:  $\text{C}_{394}\text{H}_{304}\text{Cl}_{12}\text{F}_{66}\text{N}_{72}\text{O}_{122}\text{S}_{22}\text{Zn}_{17}$ , FW = 11495.26, red blocks,  $0.29 \times 0.22 \times 0.16 \text{ mm}^3$ , trigonal, space group  $R\bar{3}2$  (no. 155),  $a = 24.812(1)$ ,  $c = 79.373(3) \text{ \AA}$ ,  $V = 42320(3) \text{ \AA}^3$ ,  $Z = 3$ ,  $T = 93 \text{ K}$ ,  $\lambda(\text{MoK}\alpha) = 0.71075 \text{ \AA}$ ,  $2\theta_{\text{max}} = 37.68^\circ$ , Friedel pairs 3302,  $R_1 = 0.0875$ ,  $wR_2 = 0.2418$  (after SQUEEZE), GOF = 1.062, Flack Parameter 0.50(3), largest diff. peak and hole  $0.74/-0.40 \text{ e \AA}^{-3}$ . See the Supporting Information for details. CCDC 881253 (**1**) and 881254 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).