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A C_{60}-Templated Tetrameric Porphyrin Barrel Complex via Zinc-Mediated Self-Assembly Utilizing Labile Capping Ligands

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Supporting Information

ABSTRACT: Coordination-driven self-assembly utilizing labile capping ligands has been exploited as a novel strategy for metallo-cage containers. Herein, we report a tetrameric porphyrin barrel complex $[C_{60}\subset Zn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}](OTs)_4$ (**2**) (OTs = *p*-$CH_3C_6H_4SO_3$) formed from a tetrakis(bipyridyl)porphyrin ligand **1**, $Zn(OTs)_2$, and a template guest, C_{60} fullerene. The tetrameric-barrel **2** contains two kinds of bis(bpy) Zn^{II} centers coordinated by TsO^- anions which serve as labile capping ligands in the formation of the finite structure of **2**.

Metallo-cage containers have been widely studied for their versatility in design[1−3] and for excellent functions utilizing isolated inner spaces.[4] In general, as metal coordination geometries are usually symmetrical (square-planar, tetrahedral, octahedral, etc.), the combination of metal ions with simple bridging ligands tends to result in infinite 1D, 2D, or 3D coordination networks. Such metal-assembled complexes with pores are called porous coordination polymers (PCP) or metal organic frameworks (MOF) and have been extensively investigated for their ability for gas absorption and sensors.[5] On the other hand, for finite, discrete metallo-cage complexes, one has to consider a certain way to "close" the coordination network. One useful strategy is to "cap" some of the metal coordination sites by chelating ligands to prevent polymerization.[6] In this study, we found that labile capping ligands, i.e., counteranions and solvents, are key factors determining the final metal-assembled structures.

Porphyrins have multiple functions regarding molecular recognition, redox and photochemical reactions, and molecular transport.[7] In particular, self-assembled porphyrins exhibit interesting functions based on their cooperative behavior,[8] where the relative positions of porphyrins are well controlled.

We have recently reported that a hexameric porphyrin cage complex $[Zn_{11}\mathbf{1}_6(H_2O)_{18}](CF_3SO_3)_{22}$ (**3**) is formed under well-balanced aqueous conditions from $Zn(CF_3SO_3)_2$ and a C_4-symmetric Zn-porphyrin ligand **1** with four 2,2′-bipyridin-5-yl (= bpy) groups (see Figure S30 and ref 9 for the details). In the formation of the discrete hexameric-cage **3**, coordinating water molecules as cosolvent act as stopper ligands on the Zn^{II} centers to form both tris(bpy) Zn^{II} and bis(bpy) Zn^{II} units.

This finding further encouraged us to use counteranions and solvents as labile capping ligands to obtain new self-assembled products from the tetrakis(bipyridyl)porphyrin ligand **1**,[9,10] which include heteroleptic Zn^{II} centers consisting of both bpy of **1** and additional counteranions and/or coordinating solvents (i.e., $[Zn(bpy)_nX_m]$ (X = anion or solvent)). So far, the formation and conversion between different self-assembled complexes have been achieved by changing metal-to-ligand ratios,[11] acid−base control in solution,[12] or employing suitable templating molecules.[13] However, it is rather difficult to use counteranions and solvents for controlling the final metal-assembled frameworks.

Herein, we report the synthesis and characterization of a novel tetrameric porphyrin barrel complex $[C_{60}\subset Zn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}](OTs)_4$ (**2**) (OTs = *p*-$CH_3C_6H_4SO_3$) formed from a tetrakis(bipyridyl)porphyrin ligand **1**, $Zn(OTs)_2$, and a template guest, C_{60} fullerene (Figure 1). The tetrameric-barrel **2** contained two kinds of bis(bpy) Zn^{II} centers bound by TsO^- anions. We found that it is important to control coordination geometries around Zn^{II} centers by

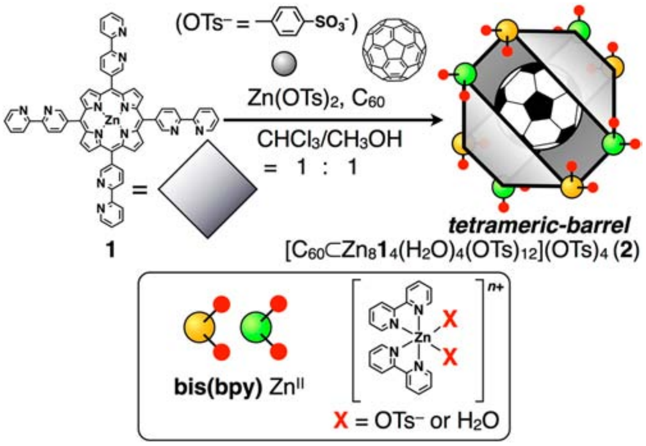

Figure 1. Tetrameric porphyrin barrel complex $[C_{60}\subset Zn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}](OTs)_4$ (**2**) constructed by Zn^{II}-mediated self-assembly utilizing labile capping ligands. A ligand bound to the axial position of Zn-porphyrin **1** is omitted from the chemical structure for clarity and due to the ambiguity of the axial ligand in solution. The Zn^{II} centers depicted in the same color (orange and green) are in an equivalent chemical environment with each other (see also Figure 4 for their coordination geometries).

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counteranions to construct the finite structure of **2** as well as to use C_{60} fullerene as the template.

In a preliminary research stage, we examined the effects of counteranions on the formation of complexes of 2,2′-bipyridine (bpy) and various Zn^{II} salts by ^1H NMR spectroscopy (see Table S2 and Figures S10−S23 for the details). Major species generated in solution were clearly dependent on the coordination abilities of anions to Zn^{II} centers.[14] Zn^{II} salts with weakly coordinating anions (e.g., $CF_3SO_3^-$) formed tris(bpy) Zn^{II} complexes $[Zn(bpy)_3]^{2+}$. In contrast, moderately coordinating anions (e.g., TsO^-) generated bis(bpy) Zn^{II} complexes $[Zn(bpy)_2X_x]^{n+}$ (X = anion or solvent), and strongly coordinating anions (e.g., $CH_3CO_2^-$) provided mono(bpy) Zn^{II} complexes $[Zn(bpy)X_x]^{n+}$.

In view of these findings, the effects of counteranions and solvents were investigated on the Zn^{II}-mediated self-assembly of tetrakis(bipyridyl)porphyrin ligand **1** by ^1H NMR spectroscopy and ESI-TOF mass spectrometry (Table S3 and Figures S24−S28). A mixed solvent, $CDCl_3/CD_3OD$ = 1:1 (v/v) or $CDCl_3/CD_3OD/D_2O$ = 10:10:1 (v/v/v), was used to investigate the effect of coordination of D_2O together with those of anions on the self-assembly process. The results of Zn^{II}-mediated self-assembly of ligand **1** with various counteranions are summarized in Figure 2. To summarize: (1) with weakly coordinating anions, tris(bpy) Zn^{II} $[Zn(bpy)_3]^{2+}$ is formed, which resulted in only a mixture of unidentified oligomeric complexes of ligand **1** and Zn^{II} that are mainly composed of $[Zn(bpy)_3]^{2+}$units; (2) slightly coordinating anions and solvents generated a hexameric complex $[Zn_{11}\mathbf{1}_6X_{18}]^{n+}$ with partial structures based on both tris(bpy) and bis(bpy) Zn^{II} $[Zn(bpy)_2X_2]^{n+}$; and (3) moderately coordinating anions provided a tetrameric complex $[Zn_8\mathbf{1}_4X_{16}]^{n+}$ and/or a trimeric complex $[Zn_6\mathbf{1}_3X_{12}]^{n+}$, with partial structures based on bis(bpy) Zn^{II} units.[15] Thus, different self-assembled complexes of **1** were established by the effective geometry control of bpy-Zn^{II} units based on the coordination abilities of counteranions and solvents.

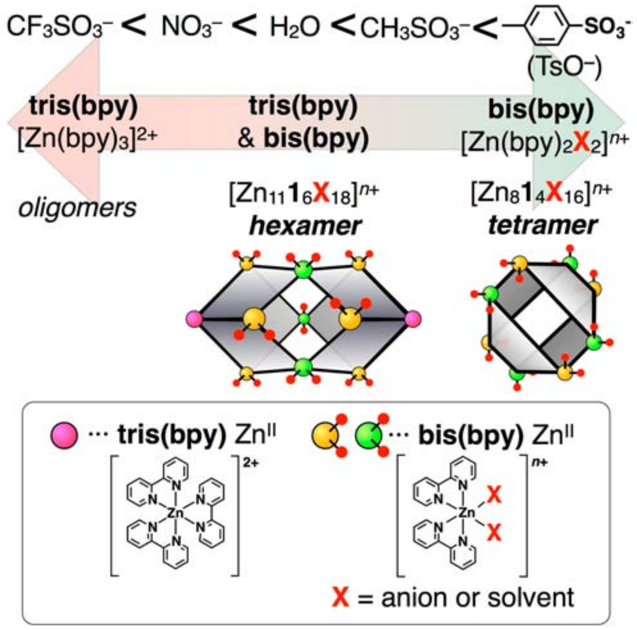

Figure 2. Zn^{II}-mediated self-assembly of tetrakis(bipyridyl)porphyrin ligand **1** controlled by the coordination abilities of counteranions and solvents. Major coordination modes of bpy-Zn^{II} units are summarized together with the corresponding supramolecular Zn^{II} complexes of **1** in a $CDCl_3/CD_3OD$ = 1:1 (v/v) mixed solvent (300 K). Relative strength of coordination of H_2O to Zn^{II} centers is that of the case when D_2O was used as a cosolvent in a $CDCl_3/CD_3OD/D_2O$ = 10:10:1 (v/v/v) ratio.

With a view to a novel discrete supramolecular complex based on the anion-coordinating strategy, complexation of $Zn(OTs)_2$ and ligand **1** was investigated by ^1H NMR spectroscopy in $CDCl_3/CD_3OD$ = 1:1 (v/v) (Figure 3b). Under this condition, Zn^{II} and bpy groups were expected to form bis(bpy) Zn^{II} units coordinated by TsO^- anions. Several sets of sharp signals appeared in the ^1H NMR spectrum after equilibrium was reached, indicating that some discrete supramolecular complexes were generated. ESI-TOF mass measurement of the sample suggested that a tetramer $[Zn_8\mathbf{1}_4X_{16}]^{n+}$ (X = TsO^- or solvent) was formed as a major species, together with a trimer $[Zn_6\mathbf{1}_3X_{12}]^{n+}$ (Figure S28).[15] From the metal-to-ligand ratios of these complexes, it was speculated that they have partial structures based on bis(bpy) Zn^{II} units $[Zn(bpy)_2X_2]^{n+}$.

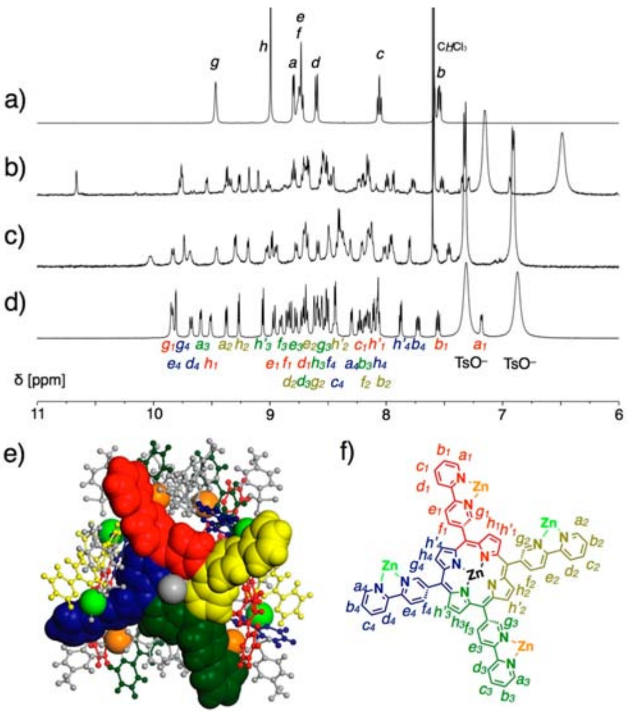

Figure 3. Formation of the tetrameric porphyrin barrel complex **2**. (a−d) ^1H NMR spectra (500 MHz, 300 K): (a) **1** in $CDCl_3/CD_3OD$ = 1:1 (v/v); (b) **1** and $Zn(OTs)_2$ (2 eq [/**1**]) after heating at 60 °C for 14 h in $CDCl_3/CD_3OD$ = 1:1; (c) (b) + C_{60}, after heating at 65 °C for 24 h; (d) isolated tetrameric barrel complex **2** dissolved in CD_3OD. (e) The structure of $[C_{60}\subset Zn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}]^{4+}$ in which one Zn-porphyrin **1** is highlighted and color-coded in red, yellow, green, and blue, to bring out its C_1 symmetry in **2**. See also Figure 4 for the structure of **2**. (f) Chemical structure and labeling of hydrogen atoms of **1**. Colors are coded according to the structure in (e).

Next, the equilibrium shift between tetramer and trimer was investigated by encapsulating a suitable template guest. Here, fullerene C_{60} was chosen as a template guest, because it was known to strongly interact with porphyrin via π−π interactions.[16] By adding fullerene C_{60} to the complexes of ligand **1** and $Zn(OTs)_2$ (2 eq [/**1**]) in $CDCl_3/CD_3OD$ = 1:1, followed by heating at 65 °C for 24 h, a new set of sharp signals assignable to a single species appeared in the ^1H NMR spectrum (Figure 3c). As many as 36 different aromatic ^1H signals were observed and indicated that desymmetrized **1** exhibited a C_1 symmetry in the complex. ESI-TOF mass analysis found a set of signals assignable to a tetrameric complex with the composition of $[Zn_8\mathbf{1}_4X_{16}]$ (X = anion or solvent) encapsulating one C_{60} molecule (Figure S6). In a synthetic scale experiment, the tetrameric-barrel complex $[C_{60}\subset Zn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}](OTs)_4$ (**2**) was isolated in 75% yield after recrystallization (Figure 3d). The ^{13}C NMR spectrum of **2** gave a distinguishing signal assigned to C_{60} at δ = 138.0 ppm (for comparison, a signal of C_{60} in $CDCl_3$ was observed at δ = 141.1 ppm),[17] which suggested the inclusion of C_{60} (Figure S2). A UV−vis absorption spectrum of tetrameric-barrel **2** showed that Zn-porphyrin's Soret band of **2** was broadened and red-shifted compared with that of the previously reported hexameric-cage complex **3** (λ_{max} from 433.0 nm (**3**) to 441.5 nm (**2**)) (Figure S7). Similar spectral changes in the Soret band were reported for other multiporphyrin hosts encapsulating C_{60}, which suggest electronic interactions between Zn-porphyrin and C_{60}.[16a,c,f]

Single crystal X-ray diffraction analysis of the inclusion complex unambiguously revealed a framework of $[C_{60}\subset Zn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}]^{4+}$, in which four Zn-porphyrin ligands **1** wrapping around fullerene C_{60} were in the shape of a barrel (Figure 4).[18] There existed eight bis(bpy) Zn^{II} units in **2**. Four of them are denoted as $[Zn(bpy)_2(OTs)_2]$, in which each Zn^{II} was coordinated by two TsO^- anions (depicted in orange in Figure 4). While the other four are denoted as $[Zn(bpy)_2(H_2O)(OTs)]^+$, in which each Zn^{II} was coordinated by one H_2O and one TsO^- anion (depicted in green in Figure 4). In the crystal, there existed four unbound TsO^- ions per one molecule of **2**. Although the ligand **1** has four chemically equivalent metal binding sites in its metal-free state, **1** adopted a C_1 symmetry in the complex. This was consistent with the observation in ^1H NMR measurement (Figure 3d). The overall framework of $[C_{60}\subset Zn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}]^{4+}$ has a pseudo S_4 point group symmetry.[19] Therefore, the complex **2** is achiral.

For more detail, four TsO^- anions coordinated to $[Zn(bpy)_2(OTs)_2]$ (orange) cap the top and bottom of the porphyrin tetrameric-barrel through $\pi-\pi$ stacking with bipyridyl groups (Figures 4c and S9). It is thus confirmed that TsO^- anions work as capping ligands to Zn^{II} and constitute important parts of the self-assembled complex. The inner cavity encapsulating a fullerene C_{60} has a ball shape with a volume of 810 $Å^3$ (Connolly surface, probe radius: 1.0 Å) (Figure 4d). Included C_{60} strongly interacts with Zn-porphyrin rings via $\pi-\pi$ stacking (~3.0 Å), which verifies the role of C_{60} as a template guest to stabilize the structure of **2**.

The ^1H NMR spectrum of **2** was fully analyzed by $^1H-^1H$ COSY and $^1H-^1H$ NOESY NMR spectroscopy. This supports that complex **2** is stable in solution and its basic structure is the same as the one determined by X-ray analysis (Figures S3−S5 and Table S1). In the NOESY measurement, several strong diagnostic interligand NOE signals were observed for bis(bpy) Zn^{II} units ((a_1, a_3), (a_2, a_4), (g_2, g_4)) and several β protons of porphyrin rings ((h_2, h_4), (g_1, h'_2), (h_1, d_4)). Furthermore, proton signals with characteristic chemical shifts (a_1, d_4, h'_4, etc.) are well explained by the shielding and deshielding effects from the neighboring ligands, which support the solution structure of **2**.

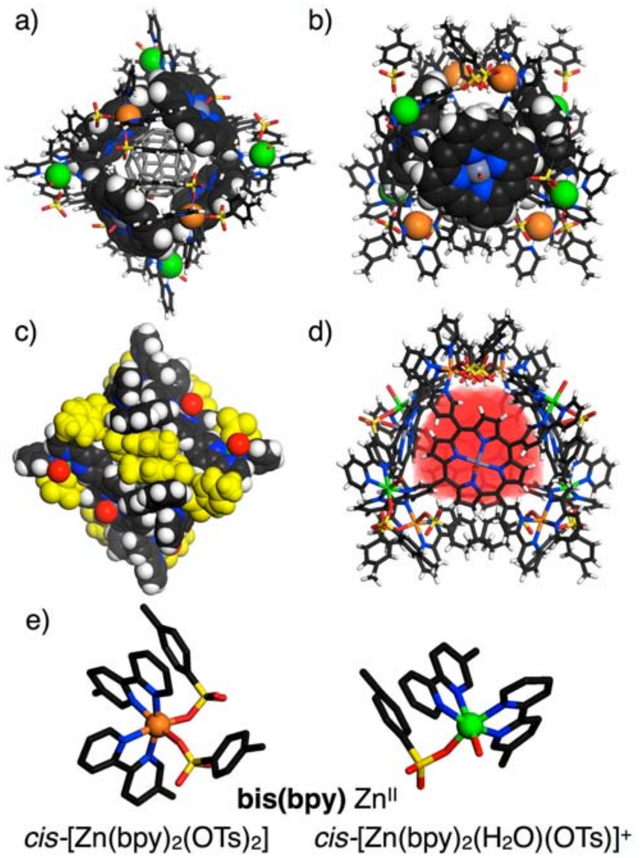

Figure 4. X-ray crystal structure of the tetrameric-barrel complex **2**. Unbound TsO^- anions, solvents, and hydrogen atoms of H_2O coordinating to Zn^{II} are omitted for clarity. Two different Zn^{II} centers bound by bpy groups are colored in orange and green. Zn^{II} centers in the porphyrin rings are colored in gray; colors of the other atoms are based on CPK coloring. (a) Top view (from an S_4 axis) and (b) side view (perpendicular to an S_4 axis). (c) Positions of TsO^- anions capping the tetrameric barrel. TsO^- anions are colored in yellow. (d) Visualization of the ball-shaped inner space of **2** encapsulating one C_{60} molecule. (e) Coordination geometries of two kinds of bis(bpy) Zn^{II} units. Hydrogen atoms are omitted for clarity.

To compare the effect of a template guest C_{60} with that of coordination control via counteranions and solvents in the formation of tetrameric-barrel **2**, the TsO^- anion was replaced by weakly coordinating $CF_3SO_3^-$, and the complexation with ligand **1** was examined in the presence of C_{60} (Figure S29). Under this condition where tris(bpy) Zn^{II} unit formation is dominant, the complexation behavior was not affected by C_{60}, and therefore tetrameric-barrel **2** was not formed. This result demonstrates that the TsO^- anion plays an important role in generating the complex **2** composed of bis(bpy) Zn^{II} units and that the template effect of C_{60} was not so strong as to induce a tetrameric-barrel structure by changing the dominant coordination geometry of Zn^{II}.

In conclusion, proper selection of coordinating counteranions and solvents allowed the construction of the tetrameric-barrel porphyrin complex $[C_{60}\subset Zn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}](OTs)_4$ (**2**) (OTs = p-$CH_3C_6H_4SO_3$) from tetrakis(bipyridyl)porphyrin ligand **1**, $Zn(OTs)_2$, and a template guest C_{60} fullerene. TsO^- anion plays an important role as capping ligands on the two different kinds of bis(bpy) Zn^{II} units and produces the framework of tetrameric-barrel **2**. Thus, a finite self-assembled complex with heteroleptic metal centers can be constructed from the combination of labile coordinating capping ligands (counter-anions and solvents) and multidentate rigid chelating linker ligands, utilizing the effective control of coordination geometries around metal centers. This method would offer a new tool for the construction of coordination-driven self-assembled systems in a controlled manner. The tetrameric-barrel **2** has a unique structure, in which C_{60} is tightly surrounded by four Zn^{II}-porphyrin rings and isolated from the outside environment, so that its photophysical behaviors may lead to electron transfer-based catalytic functions.[20] Furthermore, this study would also contribute to the developments of shape-shifting metallo-cage container systems that change their functions in response to external solution environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and 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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(18) Crystal data for **2**: $C_{412}H_{228}N_{48}O_{56}S_{16}Zn_{12}$, $Fw = 8076.26$, red, block, $0.32 \times 0.27 \times 0.18$ mm^3, orthorhombic, space group *Pccn* (no. 56), $a = 30.152(9)$ Å, $b = 30.764(9)$ Å, $c = 44.449(13)$ Å, $V = 41231(21)$ Å^3, $Z = 4$, $T = 93$ K, $\lambda(\mathrm{MoK}\alpha) = 0.71073$ Å, $\theta_{\max} = 21.14°$, $R_1 = 0.1887$, $wR_2 = 0.4982$, GOF = 1.767, largest diff. peak and hole 2.52/−0.82 e^-/Å^3. See the SI for experimental and refinement details. CCDC 942782 contains the crystallographic data for this paper and can be obtained free of charge from the CCDC (http://www.ccdc.cam.ac.uk/data_request/cif).

(19) The construction of *O*-symmetric $\mathbf{M}_8\mathbf{L}_6$ cubic complexes, and D_4 and D_{2h} symmetric $\mathbf{M}_8\mathbf{L}_4$ tube-like complexes, from metal ions **M** and tetrakis(pyridylimine) ligands **L**, was reported: (a) Meng, W.; Breiner, B.; Rissanen, K.; Thoburn, J. D.; Clegg, J. K.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 3479. (b) Meng, W.; Clegg, J. K.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 1881.

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