

論文の内容の要旨

Supramolecular Metal Complexes of Tetrakis(bipyridyl)porphyrin Ligand

(テトラキス (ビピリジル) ポルフィリン配位子からなる超分子金属錯体)

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[Introduction]

Coordination-driven self-assembly of organic ligands and metal ions is a powerful method for construction of large and well-defined molecular architectures. In particular, supramolecular metallohosts possess unique functions reflecting geometrical characteristics of their isolated inner space. When organic ligands with one kind of multiple metal binding sites are mixed with a certain metal ion, resulting structures are usually highly symmetric with chemically equivalent metal centers (Figure 1a). This is because synthesis conditions such as types of counter anions, solvents, and temperature tend to define the metal coordination geometry into one species. In this context, a new methodology to generate unsymmetrical structures with more than one kind of metal centers from a simple and symmetric organic ligand would open a new direction towards more elaborate

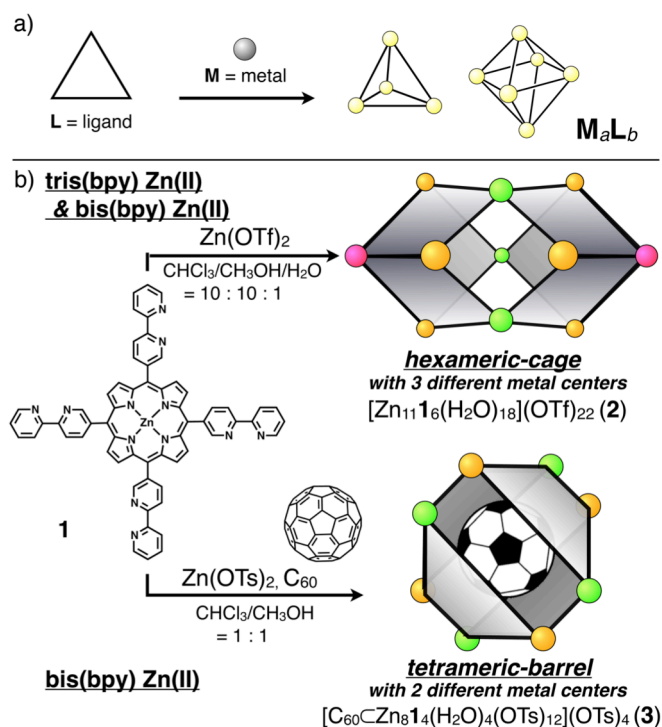


Figure 1. a) Metal-mediated self-assembly providing uniform polyhedral complexes comprised of chemically equivalent metal centers. b) Zn(II)-mediated self-assembly generating two supramolecular metal complexes, *hexameric-cage* (**2**) and *tetrameric-barrel* (**3**), through different modes of Zn(II) center formation from a C_4 -symmetric tetrakis(bipyridyl) Zn-porphyrin ligand **1**. A ligand bound to the axial position of five-coordinate Zn center of **1** is omitted from the chemical structure.

supramolecular functions.

In this study, I designed a Zn-porphyrin ligand **1** with four (2,2'-bipyridin)-5-yl (= bpy) groups directly attached to the central Zn-porphyrin. Porphyrins have fascinating photochemical and redox properties, and featured by its rigid C_4 -symmetric aromatic framework. Via coordination-driven self-assembly of the ligand **1**, various multiporphyrin architectures have been constructed. In particular, two supramolecular metal complexes, *hexameric-cage* $[\text{Zn}_{11}\mathbf{1}_6(\text{H}_2\text{O})_{18}](\text{OTf})_{22}$ (**2**) ($\text{OTf}^- = \text{CF}_3\text{SO}_3^-$) and *tetrameric-barrel* $[\text{C}_{60}\text{CZn}_8\mathbf{1}_4(\text{H}_2\text{O})_4(\text{OTs})_{12}](\text{OTs})_4$ (**3**) ($\text{OTs}^- = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$), have been constructed through different modes of Zn(II) center formation (Figure 1b). Two important factors that lead to unsymmetrical yet well-defined self-assembled structures are; 1) well-balanced complexation conditions that induce different types of homo- and heteroleptic metal centers; and 2) rigidity of the tetrakis(bipyridyl)porphyrin ligand **1** that determines relative positions of different kinds of metal centers.

[Hexameric-cage **2** through the formation of three different Zn(II) centers]

Hexameric-cage (**2**) was constructed by complexation of ligand **1** and $\text{Zn}(\text{OTf})_2$ in $\text{CHCl}_3/\text{CH}_3\text{OH}/\text{H}_2\text{O} = 10:10:1$. This well-balanced aqueous complexation condition allows the simultaneous formation of both tris(bpy) and hydrated bis(bpy) Zn(II) units. The unsymmetrical structure of *hexameric-cage* (**2**) was fully characterized by NMR measurements, ESI-MS, and X-ray crystal analysis. The ^1H NMR spectrum of the ligand **1** showed that **1** has a time-averaged C_4 -symmetry in solution, that is, four bpy groups are chemically equivalent on the NMR timescale (Figure 2a). In contrast, as many as 36 different aromatic ^1H signals were observed for the ^1H NMR spectrum of **2**, indicating that the desymmetrized **1** exhibits a C_1 symmetry in the complex **2** (Figure 2b–d). Its X-ray analysis revealed a cage framework of $[\text{Zn}_{11}\mathbf{1}_6(\text{H}_2\text{O})_{18}]^{22+}$, featuring six Zn-porphyrin rings and eleven

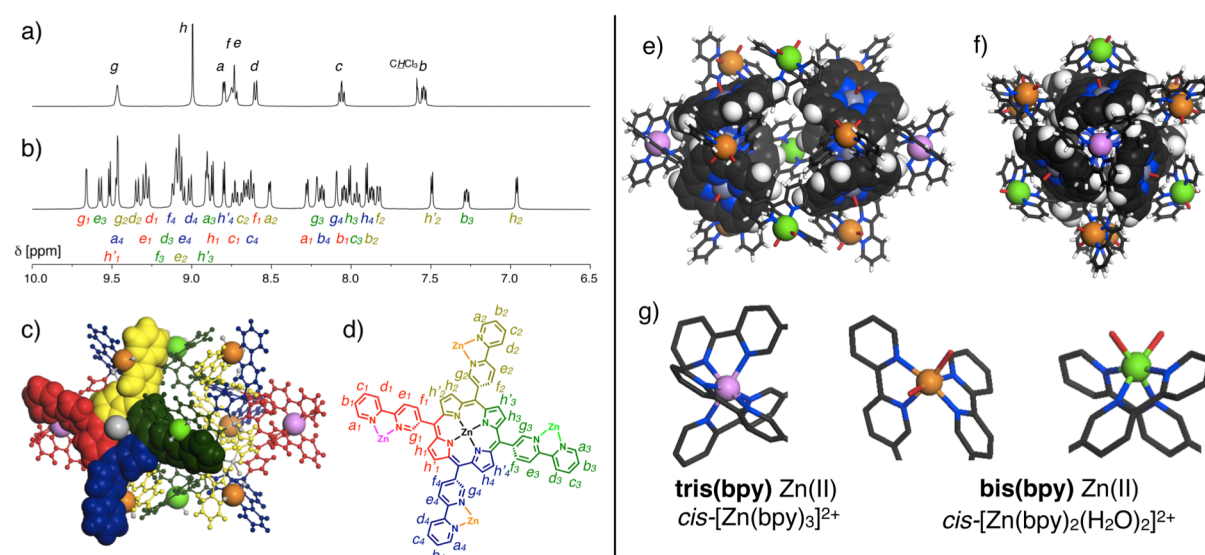


Figure 2. Characterization of *hexameric-cage* $[\text{Zn}_{11}\mathbf{1}_6(\text{H}_2\text{O})_{18}](\text{OTf})_{22}$ (**2**). a–d) ^1H NMR spectra of **1** and **2** (500 MHz, 300 K). a) **1** in $\text{CDCl}_3/\text{CD}_3\text{OD} = 1:1$ (v/v%). b) **2** in CD_3CN . c) Structure of **2** in which one Zn-porphyrin **1** is highlighted. d) Labeling of hydrogen atoms of **1** in **2**. e)–g) X-ray crystal structure of **2**. e) A view from the C_2 -symmetry axis. f) A view from the C_3 -symmetry axis. OTf^- anions, free solvents, and hydrogen atoms of H_2O coordinating to Zn(II) are omitted for clarity. g) Coordination geometries of three different bpy-Zn(II) units.

bpy-Zn(II) units (Figure 2e–g). There existed three different hexacoordinate Zn(II) centers in **2**, one kind of tris(bpy) Zn(II) units and two kinds of doubly-hydrated bis(bpy) Zn(II) units. Thus, H₂O molecules play a vital role in constituting the framework of [Zn₁₁1₆(H₂O)₁₈]²²⁺.

[Unsymmetrical guest encapsulation inside hexameric-cage **2**]

The [Zn₁₁1₆(H₂O)₁₈]²²⁺ framework of **2** has a triangular bipyramidal shaped inner space ($V \sim 730 \text{ \AA}^3$, $d \sim 9 \times 18 \text{ \AA}$) surrounded by six Zn-porphyrin rings (Figure 3a). The cage **2** unsymmetrically encapsulated up to two π -electron deficient aromatic guests, 2,7-dinitro-9-fluorenone (**4**), through π - π interactions with Zn-porphyrin rings on its inner wall (Figure 3b). The formation of a host-guest complex [4₂C2] encapsulating two molecules of **4** was confirmed by ¹H NMR measurements at 250 K (Figure 3c). The signals for one side of **4** ((i, j, k) = (-0.66, -1.36, -0.33 ppm)) in [4₂C2] were remarkably upfield shifted ($\Delta\delta = -8.41 \sim -9.90 \text{ ppm}$) from those in the absence of cage **2**. This indicates that only one side of **4** lay deep at the edge of the triangular bipyramidal shaped cavity of **2**, being considerably affected by the shielding-effect from Zn-porphyrin rings. The unsymmetrical encapsulation by a self-assembled supramolecular host composed of simple components is a meaningful step towards artificial enzyme-mimic chemical systems that can exhibit high regioselectivity in host-mediated molecular recognition and reactions.

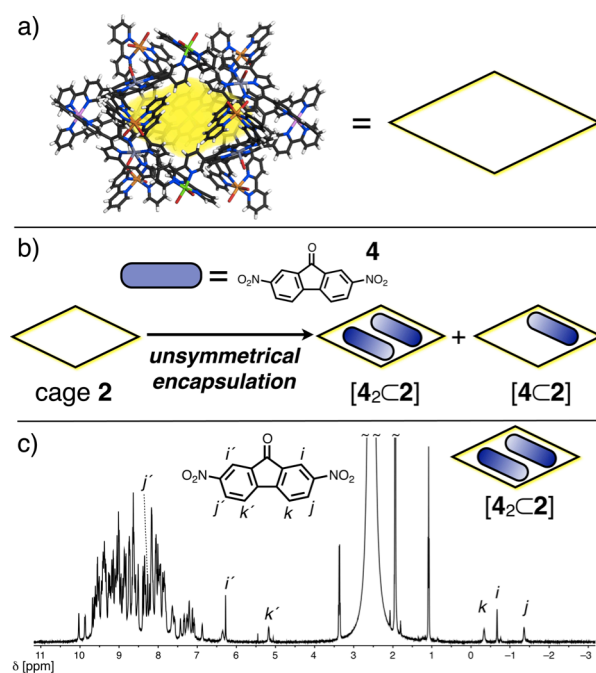


Figure 3. a) Visualization of the triangular bipyramidal shaped inner space of **2**. b) Unsymmetrical encapsulation of 2,7-dinitro-9-fluorenone (**4**) inside the cavity of **2**. c) ¹H NMR spectrum of guest-inclusion complexes [4₂C2] and [4C2] ([4₂C2]:[4C2] = 3.5:1) (500 MHz, 250 K, CD₃CN). ¹H NMR signals of one side of **4** encapsulated in [4₂C2] at the edge of the cavity and those of the other side are denoted with (i, j, k) and (i', j', k'), respectively.

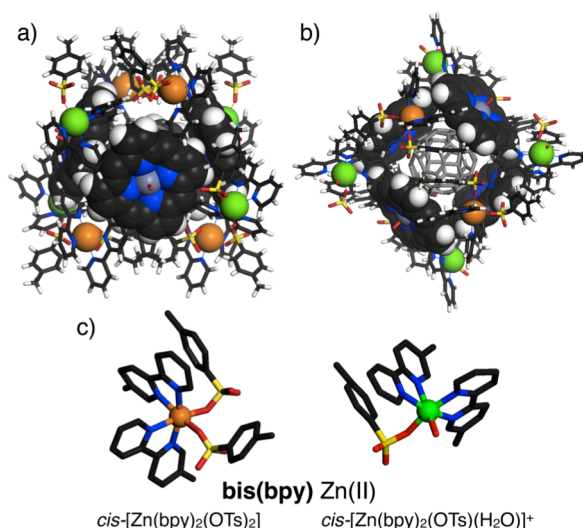


Figure 4. A preliminary result of X-ray analysis for **3**. Positions of the non-hydrogen atoms were determined experimentally. a) A view perpendicular to the S₄-symmetry axis. b) A view from the S₄-symmetry axis. c) Coordination geometries of two different kinds of bis(bpy) Zn(II) units.

[*Tetrameric-barrel 3* with two kinds of bis(bpy) Zn(II) centers]

An inclusion complex, *tetrameric-barrel* $[C_{60}CZn_8\mathbf{1}_4(H_2O)_4(OTs)_{12}](OTs)_4$ (**3**), was constructed by complexation of ligand **1** and $Zn(OTs)_2$ in a mixed solvent $CHCl_3/CH_3OH = 1:1$ in the presence of C_{60} fullerene as a template (Figure 1b). The *tetrameric-barrel 3*, in which one C_{60} fullerene was surrounded by four Zn-porphyrins, was characterized by 1H and ^{13}C NMR, ESI-MS, and X-ray crystal analysis (Figure 4). In the framework of **3**, there existed two different bis(bpy) Zn(II) units coordinated by TsO^- anions. Thus, it was demonstrated that, by employing TsO^- anions as stopper ligands with an adequate coordinating ability, another unsymmetrical supramolecular metal complex was achieved by effective control of coordination geometries of bpy-Zn(II) units.

[*Dimeric-sandwich 5* via Ag(I)-mediated self-assembly]

Zn-porphyrin has a large π -electron rich aromatic surface, which interacts with other molecules via π - π interaction. Complexation of ligand **1** and AgX (X^- = non-coordinating anion) resulted in *dimeric-sandwich* $[Ag_4\mathbf{1}_2]X_4$ ($5 \cdot X_4$) possessing bis(bpy) Ag(I) units (Figure 5). The distance between two parallel Zn-porphyrins (*ca.* 6.5 Å) of *dimeric-sandwich 5*⁴⁺ was ideal for intercalation of aromatic molecules, and indeed **5**⁴⁺ served as a good receptor for π -electron deficient guests such as acenaphthenequinone (**6**).

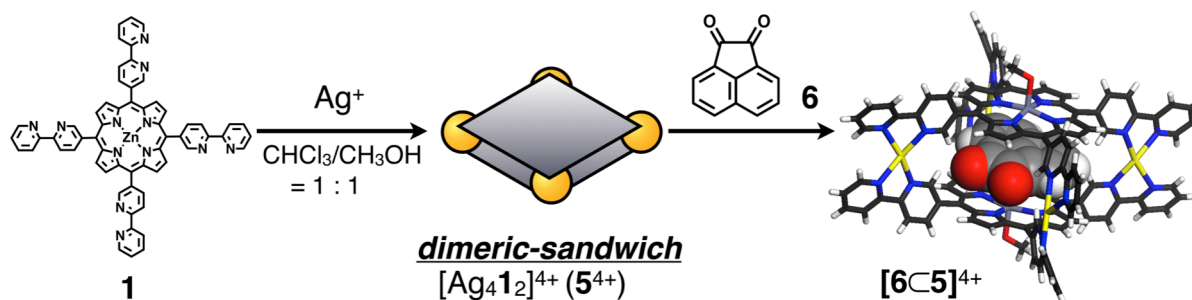


Figure 5. Ag(I)-mediated self-assembly generating *dimeric-sandwich 5*⁴⁺ and its guest intercalation.

[Conclusion]

Various supramolecular metal complexes composed of the C_4 -symmetric tetrakis(bipyridyl) Zn-porphyrin ligand **1** have been constructed utilizing coordination characteristics of metal ions. Each multiporphyrin structure exhibits a unique guest inclusion property reflecting size, shape, and environment of its inner space. For Zn(II)-mediated self-assembly, the use of coordinating solvents and counter anions as stopper ligands with moderate coordination abilities has proven to be an important factor to induce unsymmetrical yet well-defined supramolecular structures.