Networking a hollow cage *via* guest coordination†

Yasuhiro Kobayashi, Masaki Kawano* and Makoto Fujita*

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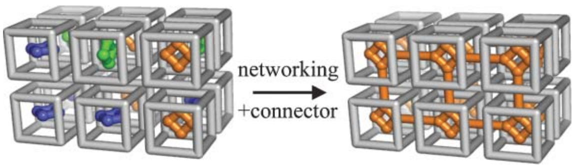
A hollow coordination cage with a highly symmetric cavity was successfully self-assembled to form a 2D-network having a less symmetric cavity *via* networking of disordered guests with a metal connector.

The hollow of self-assembled cages and capsules provides an isolated micro environment where new properties of molecules are often exhibited through host–guest complexation.[1] Crystallization of the host–guest complexes prepared in solution is an important issue for not only the detailed crystallographic structure analysis but also the induction of new physical properties through the anisotropic orientation of the guest molecules in a crystalline state. When a host compound has a highly symmetric structure, however, it is often inevitable to observe disordered guests in the crystal structure because there are no strong intermolecular interactions between the guests in the void of the host. The site disorder problem hampers the accurate structure analysis of the guests as well as the potential applications of the complexes to highly anisotropic solid materials. Here we report the ordering of the guest orientation in a highly symmetrical host *via* guest networking. When a guest molecule possesses appropriate coordination sites, a guest network is generated by simply adding a connector (typically a metal ion) on crystallization, preventing the guest disorder problem (Scheme 1).

Self-assembled M_6L_4 hollow cage **1** has T_d symmetry. The guest disorder problem is often encountered in the crystallographic analysis of its host–guest complexes. To prevent the guest disorder, we examined the guest networking according to the strategy of Scheme 1. We chose 2,4,6-tris(4-pyridyl)triazine (**2**) as a coordinative guest on the basis of the knowledge that large planar aromatic compounds such as pyrene and perylene provide crystalline host–guest complexes with **1**.[2] The advantage of **2** as the coordinative guest is that this planar guest efficiently stacks on one of the ligands of **1**, still leaving a void capable of binding the second guest.[3] In this study, Cp′Mn(CO)$_3$ (**3**, Cp′ = methylcyclopentadienyl) was used as the second guest because of our interest in its photo-reactivity in the cavity.[4] Noteworthy is that the non-coordinative second guest **3** is located at a fixed position of the cavity thanks to ordering the first guest (**2**) *via* its networking. The pairwise selective recognition of **2** and **3** in the cavity of **1** was effectively carried out in an aqueous solution. Suspending **2** (0.06 mmol) and **3** (0.05 mmol) in a D_2O solution of **1** (0.03 mmol, 2 mL) at 373 K for 1.5 h resulted in the formation of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ in a 58% NMR yield. Homo-recognized complex $\mathbf{1}\supset(\mathbf{3})_4$ was also formed in a 5% NMR yield, while another homo-recognized complex, $\mathbf{1}\supset(\mathbf{2})_n$, was not detected (Fig. 1).[5] For $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ complex, eight signals were displayed in the NMR for the triazine ligand involved in the framework of **1**. This observation indicates C_{3v} symmetry for the $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ complex. Namely, guest **2** is stacked on one of the four triazine ligands of **1** and the remaining void is occupied by **3**.



Scheme 1 Guest ordering by networking of a hollow cage *via* guest coordination.

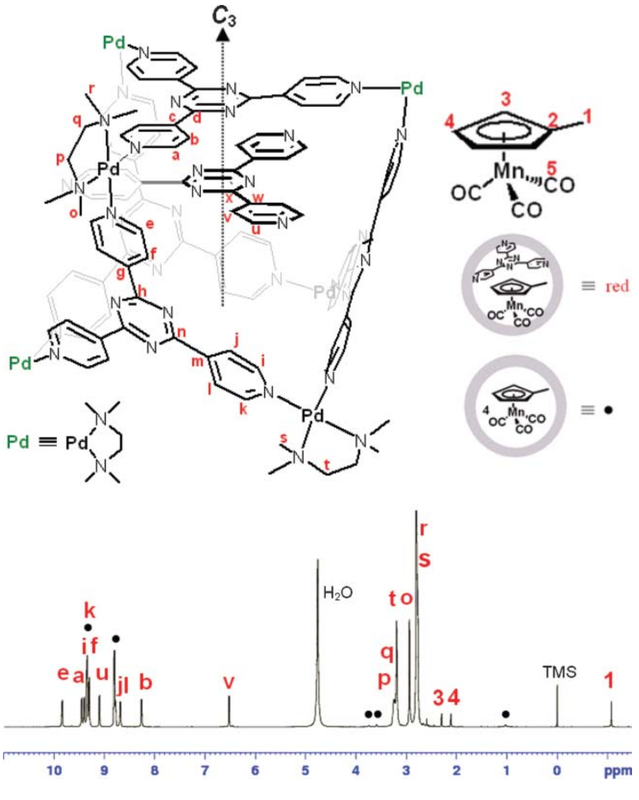


Fig. 1 NMR spectrum of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ in D_2O.

Department of Applied Chemistry, School of Engineering, The University of Tokyo and CREST, Japan Science and Technology Corporation (JST), 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.
E-mail: mkawano@appchem.t.u-tokyo.ac.jp; mfujita@appchem.t.u-tokyo.ac.jp; Fax: (+81) 3 5841 7257; Tel: (+81) 3 5841 7204

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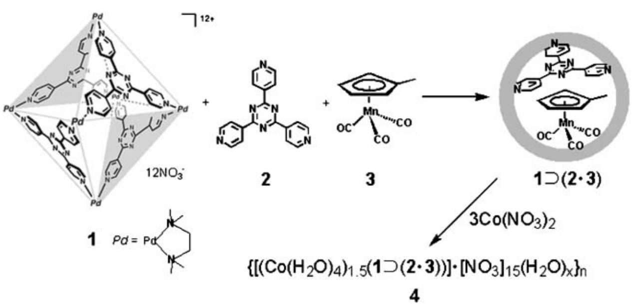

Single crystals of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ were obtained by the slow evaporation of the solvent. The molecular structure of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ was obtained by X-ray analysis.‡ However, most of the crystal structures revealed guest-disordering where guest **3** was randomly stacked on the four equivalent triazine ligands of **1**.

To prevent the guest disorder, we carried out the crystallization of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ in the presence of a metal ion connector ($Co(NO_3)_2$). When an aqueous solution (0.5 mL) of $Co(NO_3)_2$ (100 mmol) was slowly layered onto an aqueous solution of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ (0.005 mmol, 0.5 mL) and kept at 296 K over 4 weeks, we successfully obtained a hexagonal single crystal of $\{[(Co(H_2O)_4)_{1.5}(\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3}))]\cdot[NO_3]_{15}\cdot x(H_2O)\}_n$ (**4**), whose crystal structure is shown in Fig. 2. The coordinative ligands **2** encapsulated in the cavity of **1** form 2D-honeycombed layers (Fig. 2a) which are stacked along the *c*-axis to constitute a 1D-channel containing a number of water and nitrate ions.[6] The co-enclathrated guest **3** is located only at one corner of the cage because three other corners are occupied by ligand **2**. Although guest **3** is still disordered at two positions in the corner (Fig. 3), site disorder at the four corners of the tetrahedral cage is prevented by our guest-networking strategy.[7]

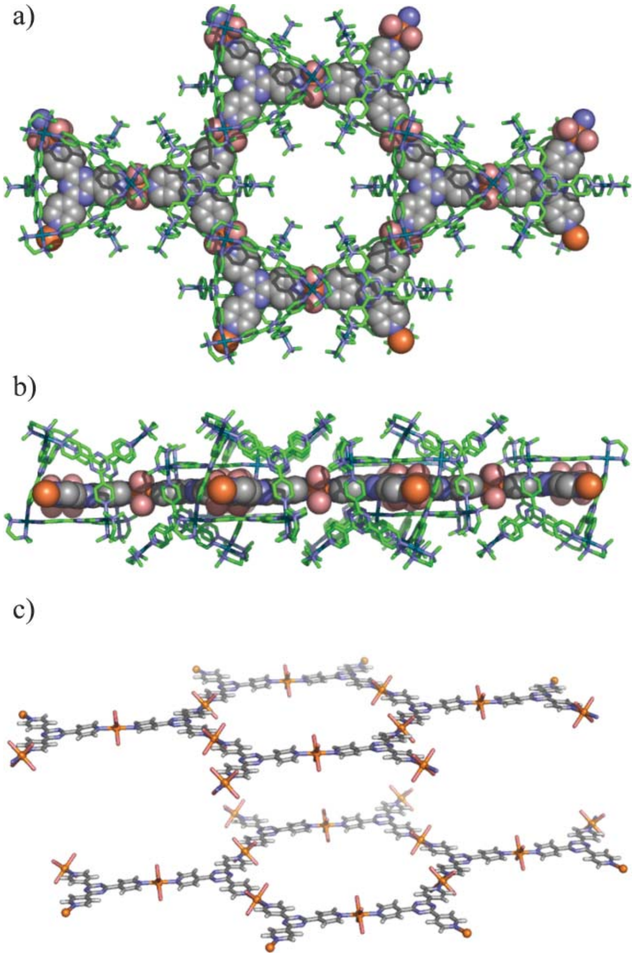

Fig. 2 Molecular structure composed of $[(Co(H_2O)_4)_{1.5}(\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3}))]^{15+}$: a) top view, b) side view, c) 2D-network structure consisting of **2** and $Co(H_2O)_4$ in **4**.

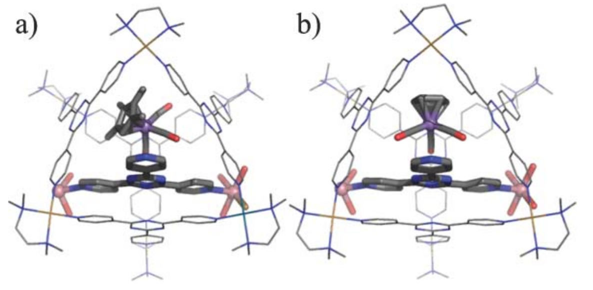

Fig. 3 Disordered guest structure in the cage component of $[(Co(H_2O)_4)_{1.5}(\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3}))]^{15+}$. Occupancy factors: a) 46%, b) 34%.

We investigated several combinations of transition metal carbonyl complexes with planar aromatic guests such as triphenyltriazine (**5**) and triphenylene (**6**) for selective bimolecular encapsulation. Each combination of **1** with **5** and **6** resulted in bimolecular encapsulation. As expected, the crystallographic analyses of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{5})$ and $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{6})$ showed severely disordered structures of the guests (Figs. S9 and S10), emphasizing that, if a guest in the cage is hardly influenced by the external environment, the guest orientation can be hardly controlled in the cage in the solid state.

In summary, we have demonstrated that guest disorder in $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ along the four equivalent C_{3v} axes of hollow cage **1** is prevented by the networking coordinative guest **2** *via* complexation with $Co(NO_3)_2$ connectors. The crystallographic observation of the second guest **3** is made easier and more accurate by the networking. Accordingly, the solution host–guest chemistry of the highly symmetric cage is easily translated into a solid state chemistry which can be directly subjected to crystallographic analysis. An *in situ* crystallographic study on the photo-reactivity of **3** in the cavity of **1** is under way.

Notes and references

‡ Crystallographic analyses of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$, $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{5})$, $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{6})$, and $\{[(Co(H_2O)_4)_{1.5}(\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3}))]\cdot[NO_3]_{15}\cdot x(H_2O)\}_n$ (**4**): Crystal data for $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$: monoclinic, *C*2/*c*, $a = 46.536(2)$, $b = 27.0972(2)$, $c = 37.781(2)$ Å, $\beta = 101.487(1)^\circ$, $V = 46687(4)$ Å^3, $Z = 8$, $T = 90(2)$ K, $D_{calcd} = 1.155$ g cm^{-3}, $\mu = 0.561$ mm^{-1}, Final R_1 ($I > 2\sigma(I)$) = 0.1374, wR_2 (all data) = 0.3803, GOF = 1.154.

Crystal data for $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{5})$: triclinic, $P\bar{1}$, $a = 24.817(7)$, $b = 24.85(1)$, $c = 24.835(6)$ Å, $\alpha = 64.50(2)$, $\beta = 65.16(2)$, $\gamma = 60.19(2)^\circ$, $V = 11617(6)$ Å^3, $Z = 2$, $T = 90(2)$ K, $D_{calcd} = 1.019$ g cm^{-3}, $\mu = 0.564$ mm^{-1}, Final R_1 ($I > 2\sigma(I)$) = 0.1712, wR_2 (all data) = 0.4301, GOF = 1.026.

Crystal data for $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{6})$: tetragonal, $I4_1/a$, $a = 26.084(2)$, $b = 26.084(2)$, $c = 31.490(3)$ Å, $V = 21426(3)$ Å^3, $Z = 4$, $T = 90(2)$ K, $D_{calcd} = 1.398$ g cm^{-3}, $\mu = 0.645$ mm^{-1}, Final R_1 ($I > 2\sigma(I)$) = 0.0643, wR_2 (all data) = 0.1784, GOF = 1.080.

Crystal data for **4**: monoclinic, *C*2/*c*, $a = 46.512(12)$, $b = 27.256(7)$, $c = 37.602(10)$ Å, $\beta = 101.57(2)^\circ$, $V = 46701(21)$ Å^3, $Z = 8$, $T = 90(2)$ K, $D_{calcd} = 1.195$ g cm^{-3}, $\mu = 0.617$ mm^{-1}, Final R_1 ($I > 2\sigma(I)$) = 0.1647, wR_2 (all data) = 0.3933, GOF = 1.212.

All the diffraction data were measured on a Siemens SMART/CCD diffractometer (MoK$_\alpha$ radiation, λ = 0.71073 Å). CCDC 618992–618995 ($\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$, (**4**), $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{5})$, and $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{6})$) contain the supplementary crystallographic data. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612562j

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5 Temperature-dependent NMR indicates the presence of two types of encapsulated compounds, $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ and $\mathbf{1}\supset(\mathbf{3})_4$ (Fig. S6).

6 Interestingly, the single crystal of **4** is considerably more stable than those of $\mathbf{1}\supset(\mathbf{2}\cdot\mathbf{3})$ and $\mathbf{1}\supset(\mathbf{3})_4$, because of the networking of the cages. Therefore, the single crystal is more suitable for *in situ* observation of photoreaction by X-ray analysis.

7 One is tilted over **2** while another is perpendicular to **2** (Fig. 3).