

Selective Host–Guest Interactions of a Transformable Coordination Capsule/Tube with Fullerenes**

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Abstract: An M_2L_4 coordination capsule or an M_2L_2 coordination tube was selectively formed by the combination of Hg^{II} hinges and bent bispyridine ligands. The two structures reversibly interconvert at room temperature in response to modulation of the metal-to-ligand ratio and exhibit different host–guest interaction behavior. The capsule alone encapsulates large spherical molecules, fullerenes C_{60} and C_{70} , and the bound guests are released upon capsule-to-tube transformation by the simple addition of metal ions.

Covalently bonded assemblies and nearly all noncovalent assemblies formed by hydrophobic, hydrogen-bonding, and aromatic–aromatic interactions typically adopt a single molecular structure. Coordination-driven supramolecular structures, on the other hand, can change their conformation, geometry, and even molecular structure, often in a reversible fashion, depending on the solvent, the counterion, the template molecule, and the metal-to-ligand ratio.^[1–4] Detailed structural analyses and mechanistic studies of structural interconversions in various coordination cages containing metal hinges, such as Fe^{II} , Ni^{II} , Co^{II} , Zn^{II} , Pd^{II} , Hg^{II} , and Ag^I ions, have been reported. However, with the exception of guest-templated assemblies, reports on the host–guest behavior of interconvertible coordination cages are scarce.^[4b] A combination of dynamic structural changes and host behavior of supramolecular nanostructures is essential for the development of multistimuli-responsive functional molecules and materials.^[5] Herein we describe the preparation of M_2L_4 coordination capsule **2** and M_2L_2 coordination tube **3**, which reversibly interconvert at room temperature in response to changes in the metal-to-ligand ratio of Hg^{II} ion and bent bidentate ligand **1** (Figure 1).^[6] The two molecular assemblies both possess well-defined cavities with diameters of approximately 1 nm, but show different host–guest behavior. The capsule was found to effectively bind large spherical mole-

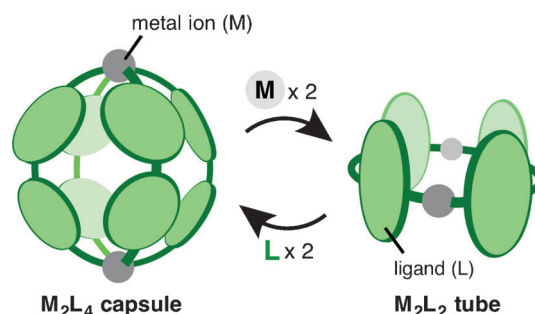


Figure 1. Schematic representation of the structural interconversion between M_2L_4 capsule **2** and M_2L_2 tube **3** ($M = Hg^{II}$).

cules, such as fullerenes C_{60} and C_{70} , whereas the tube displayed no binding affinity for these molecules.^[7,8] Furthermore, captured C_{60} and C_{70} guests were quantitatively released by a capsule-to-tube transformation upon the simple addition of Hg^{II} ions at room temperature.

We previously reported the quantitative formation of M_2L_4 coordination capsules from bent bispyridine ligand **1**, which contains two embedded anthracene units, and metal (M) ions ($M = Mn^{II}$, Co^{II} , Ni^{II} , Pd^{II} , Pt^{II} , Zn^{II} , and Cu^{II}).^[9] An M_2L_2 coordination tube was also obtained from the same ligand and Ag^I ions only in the presence of fullerene C_{60} .^[10] These reported capsular and tubular structures were the exclusive products, and their formation was insensitive to the ratio of the metal ion to the ligand. In sharp contrast, we can selectively generate the M_2L_4 capsule **2** or M_2L_2 tube **3** by varying the M/L ratio of the Hg^{II} ion^[11] and ligand **1** (Figure 1).

Mercury(II)-linked molecular capsule **2** and tube **3** were first prepared individually, and the structures were confirmed by NMR spectroscopic and ESI-TOF MS analysis (Figure 2).^[12] When a mixture of $Hg(OTf)_2$ (6.2 μ mol) and ligand **1** (12.3 μ mol) in CD_3CN (0.5 mL) was stirred at room temperature for 5 min, capsule **2** was formed quantitatively. The aromatic region of the 1H NMR spectrum of **2** showed nine signals derived from the anthracene ($H_{b,c,d,e}$), pyridine ($H_{f,g,h,i}$), and *meta*-phenylene (H_a) moieties (Figure 2c). The large upfield shifts of the two inner hydrogen atoms H_a and H_f ($\Delta\delta = -1.01$ and -0.84 ppm, respectively) are indicative aromatic shielding effects by the anthracene frameworks as a result of the formation of a capsular structure. The slight downfield shifts of the signals for the pyridyl hydrogen atoms $H_{g,h,i}$ are characteristic of metal–ligand coordination. ESI-TOF MS confirmed an M_2L_4 stoichiometry on the basis of a series of prominent peaks for $[2-nTfO^-]^{n+}$ ($n = 2, 3$, and 4) at m/z 907.1, 1259.4, and 1963.6 (see Figure S6 in the

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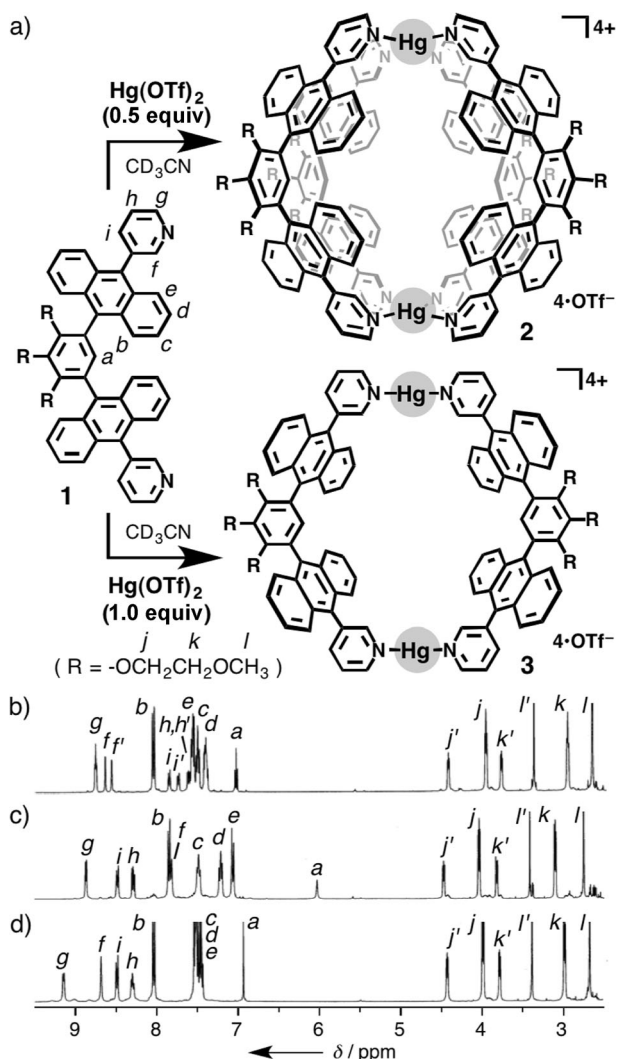


Figure 2. a) Selective formation of M_2L_4 capsule **2** and M_2L_2 tube **3** upon mixing of $\text{Hg}(\text{OTf})_2$ and ligand **1** in CD_3CN at room temperature. b–d) ^1H NMR spectra (400 MHz, CD_3CN , room temperature) of ligand **1** (b), capsule **2** (c), and tube **3** (d). Tf = trifluoromethanesulfonyl.

Supporting Information). NMR diffusion-ordered spectroscopy (DOSY) also revealed the formation of a single assembly: All proton signals of **2** showed the same diffusion coefficient of $7.87 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, thus indicating the formation of a structure with a diameter of 1.6 nm (see Figure S5).^[12,13] Molecular tube **3** was quantitatively obtained from a 1:1 molar mixture of $\text{Hg}(\text{OTf})_2$ and ligand **1** in acetonitrile under similar conditions. In the ^1H NMR spectrum of **3**, a new set of nine signals appeared in the aromatic region (Figure 2d). The observed downfield shifts of the signals for hydrogen atoms H_a and H_f ($\Delta\delta = +0.91$ and $+0.87$ ppm relative to **2**) are consistent with an open-ended tubular structure. An M_2L_2 composition of the product was elucidated by ESI-TOF MS analysis, with signals at m/z 534.4, 748.5, and 1156.3, which are assignable to the respective $[\mathbf{3} - n \cdot \text{TfO}^- + m \cdot \text{CH}_3\text{CN}]^{n+}$ ($n = 2-4$, $m = 0-3$) ions (see Figure S12).

X-ray crystallographic analysis provided verification of the M_2L_2 tubular structure of **3'** ($\text{R} = \text{OCH}_3$).^[12] Pale-yellow

single crystals were obtained by the slow evaporation of a solution of **3'** in acetonitrile at room temperature for 3 days. The crystal structure unambiguously revealed that two bent ligands of **1** are connected by two Hg atoms and thereby generate the expected molecular tube structure. The anti-podal Hg–Hg and the H_a – H_a (the opposing *meta*-phenylene hydrogen atoms) distances define the diagonals of the large tubular cavity as 15.0 and 10.8 Å, respectively (Figure 3a,b).

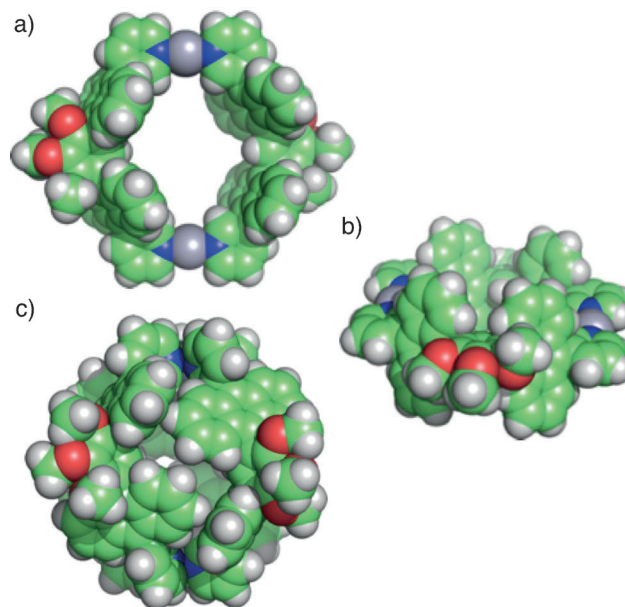


Figure 3. a) Front and b) side views of the X-ray crystal structure of molecular tube **3'** ($\text{R} = \text{OCH}_3$). The counterions and solvent molecules are omitted for clarity. c) Optimized structure of molecular capsule **2'** ($\text{R} = \text{OCH}_3$).

Each Hg atom adopts an octahedral geometry in which the two pyridyl rings of the ligands occupy opposing sites to establish a linear linkage ($\angle \text{N-Hg-N} \approx 180^\circ$). The remaining four coordination sites of each Hg atom are filled by two oxygen atoms (CF_3SO_3^- ion and H_2O) and two nitrogen atoms (CH_3CN ; see Figure S25). Crystals of capsule **2** of sufficient quality for X-ray crystallographic analysis were not yet obtained; however, the previous crystal structures of similar spherical M_2L_4 coordination capsules (in which $\text{M} = \text{Pd}^{\text{II}}$, Cu^{II} , and Zn^{II}) were used to generate an optimized model structure (Figure 3c).^[9,14]

Rapid interconversion between molecular capsule **2** and tube **3** was demonstrated by altering the metal-to-ligand ratio by the addition of further equivalents of the metal ion or the ligand and was observed by ^1H NMR spectroscopy. When $\text{Hg}(\text{OTf})_2$ (2 equiv) was added to a solution of M_2L_4 capsule **2** in acetonitrile, the capsule was quantitatively converted into M_2L_2 tube **3** within 15 min at room temperature. Similarly, the addition of ligand **1** (2 equiv) to tube **3** generated capsule **2** in quantitative yield.

Although both molecular capsule **2** and tube **3** possess large cavities of similar diameter (approximately 1 nm) surrounded by multiple anthracene units, their binding affinities for large spherical guests were different. The

treatment of a colorless solution of capsule **2** (2.1 μmol) in acetonitrile (0.4 mL) with fullerene C_{60} (6.3 μmol) for 15 min under ambient conditions provided host–guest complex $2\supset\text{C}_{60}$ in quantitative yield as a blue-violet solution (Figure 4a).^[12] Capsule **2** also encapsulated fullerene C_{70} under

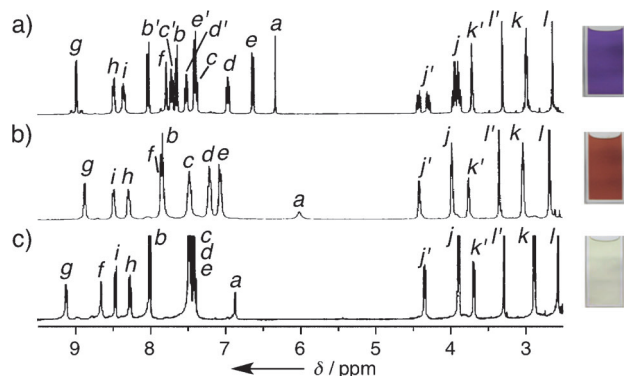


Figure 4. ^1H NMR spectra (400 MHz, CD_3CN , room temperature) and photographs of the solutions of a) complex $2\supset\text{C}_{60}$, b) complex $2\supset\text{C}_{70}$, and c) **3** formed upon the addition of $\text{Hg}(\text{OTf})_2$ (2 equiv) to the $2\supset\text{C}_{60}$ complex.

the same conditions to give a brown solution (Figure 4b). Both 1:1 host–guest complexes $2\supset\text{C}_{60}$ and $2\supset\text{C}_{70}$ were confirmed by ^1H NMR spectroscopic and ESI-TOF MS analysis.^[12,15] In contrast, tube **3** showed no affinity for C_{60} or C_{70} despite having an equally large cavity of similar chemical identity. The strong binding of capsule **2** can be ascribed to a greater number of polyaromatic panels interacting with the guest molecule and full enclathration in all directions.^[16]

The better fit of fullerene C_{60} in the cavity of capsule **2** results in a stronger binding affinity of capsule **2** for C_{60} than for C_{70} . The addition of C_{60} (1 equiv) to a solution of the $2\supset\text{C}_{70}$ complex in acetonitrile resulted in smooth guest exchange of fullerene C_{70} for C_{60} ; the $2\supset\text{C}_{60}$ complex quantitatively formed within 30 min at room temperature. Furthermore, all encapsulated fullerene guests were released upon the structural conversion of capsule **2** into tube **3** (Figure 5). When $\text{Hg}(\text{OTf})_2$ (2 equiv) was added to a clear solution of $2\supset\text{C}_{60}$ in acetonitrile, a suspension of C_{60} formed upon guest expulsion. The suspended C_{60} precipitate was readily separated from the pale-yellow solution of newly formed tube **3** by centrifuge (Figure 4c). Encapsulated C_{70} guests were also released from the $2\supset\text{C}_{70}$ complex in a similar manner upon structural transformation.

The UV/Vis spectra of molecular capsule **2** and tube **3** in CH_3CN displayed ligand-based absorption bands in the range of 320–430 nm typical of the $\pi\text{--}\pi^*$ transitions of the anthracene moieties (Figure 6a). Host–guest complexes $2\supset\text{C}_{60}$ (blue-violet) and $2\supset\text{C}_{70}$ (brown) exhibited broadened absorption bands of the fullerenes between 400 and 750 nm (Figures 4a,b and 6a). The anthracene-based emissions of the host assemblies were sensitive to the host structure and the trapped guest molecule. The excitation at 375 nm of capsule **2** in CH_3CN gave blue emission at $\lambda_{\text{max}} = 431$ nm with

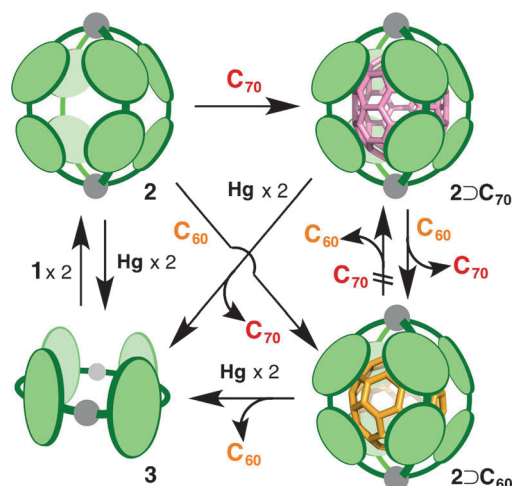


Figure 5. Schematic representation of the host–guest interactions of capsule **2** and tube **3** with fullerene guests through structural transformation.

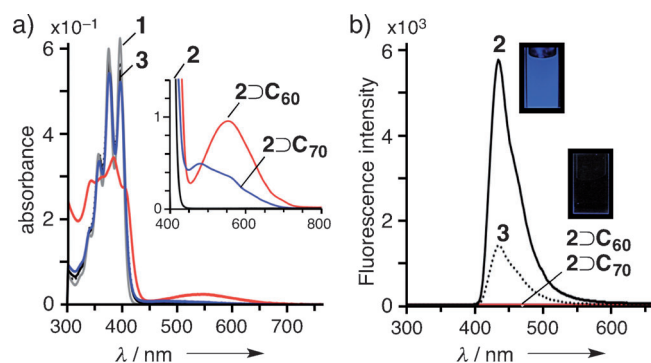


Figure 6. a) UV/Vis spectra (CH_3CN , room temperature) of **1** (0.24 mM), **2**, $2\supset\text{C}_{60}$, and $2\supset\text{C}_{70}$ (0.06 mM), and **3** (0.12 mM). b) Fluorescence spectra (degassed CH_3CN , $\lambda_{\text{ex}} = 375$ nm, room temperature) of **2**, $2\supset\text{C}_{60}$, $2\supset\text{C}_{70}$, and **3** with photographs of the solutions of **2** and $2\supset\text{C}_{60}$ ($\lambda_{\text{ex}} = 365$ nm).

an absolute quantum yield of $\Phi = 16\%$ (Figure 6b). In contrast, tube **3** was only weakly emissive ($\Phi = 4\%$). Complexes $2\supset\text{C}_{60}$ and $2\supset\text{C}_{70}$ were both non-emissive owing to strong host–guest interactions and efficient energy transfer from the host framework to the fullerene guest. Thus, structural transformation and guest encapsulation can be readily detected by the naked eye on the basis of the color and emission changes.

In summary, we successfully prepared a coordination-driven supramolecular capsule and tube in a selective fashion by using Hg^{2+} ions and bispyridyl dianthracene ligands. The two assemblies reversibly interconverted in response to changes in the metal-to-ligand ratio. Furthermore, the capsule and tube showed different host–guest behavior; only the capsule encapsulated fullerenes C_{60} and C_{70} . A subsequent capsule-to-tube transformation released the bound guest in response to an external stimulus (Hg^{2+} ions). The development of new functions of such supramolecular cavities encircled by multiple polyaromatic panels is currently a major interest of our research group.^[17]

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- [1] a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; b) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, 2nd ed., Wiley, Chichester, UK, **2009**; c) D. L. Caulder, K. N. Raymond, *Dalton Trans.* **1999**, 1185–1200; d) T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* **2013**, *113*, 734–777; e) M. M. J. Smulders, I. A. Riddell, C. Browne, J. R. Nitschke, *Chem. Soc. Rev.* **2013**, *42*, 1728–1754.
- [2] For counterion- or template-driven coordination cages, see: a) M. Scherer, D. L. Caulder, D. W. Johnson, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 1689–1694; *Angew. Chem. Int. Ed.* **1999**, *38*, 1587–1592; b) K. Umemoto, K. Yamaguchi, M. Fujita, *J. Am. Chem. Soc.* **2000**, *122*, 7150–7151; c) D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Chem. Asian. J.* **2006**, *1*, 82–90; d) I. A. Riddell, M. M. J. Smulders, J. K. Clegg, Y. R. Hristova, B. Breiner, J. D. Thoburn, J. R. Nitschke, *Nat. Chem.* **2012**, *4*, 751–756; e) I. A. Riddell, Y. R. Hristova, J. K. Clegg, C. S. Wood, B. Breiner, J. R. Nitschke, *J. Am. Chem. Soc.* **2013**, *135*, 2723–2733.
- [3] For solvent-dependent coordination cages, see: a) K. Suzuki, M. Kawano, M. Fujita, *Angew. Chem.* **2007**, *119*, 2877–2880; *Angew. Chem. Int. Ed.* **2007**, *46*, 2819–2822; b) S. Zarra, J. K. Clegg, J. R. Nitschke, *Angew. Chem.* **2013**, *125*, 4937–4940; *Angew. Chem. Int. Ed.* **2013**, *52*, 4837–4840.
- [4] For coordination cages and capsules that depend on the metal-to-ligand ratio, see: a) S. Hiraoka, T. Yi, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2002**, *124*, 14510–14511; b) S. Hiraoka, K. Harano, M. Shiro, M. Shionoya, *Angew. Chem.* **2005**, *117*, 2787–2791; *Angew. Chem. Int. Ed.* **2005**, *44*, 2727–2731; c) K. Harano, S. Hiraoka, M. Shionoya, *J. Am. Chem. Soc.* **2007**, *129*, 5300–5301.
- [5] V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines: Concepts and Perspectives for the Nanoworld*, Wiley-VCH, Weinheim, **2008**.
- [6] For mercury(II)-linked coordination cages and capsules, see: a) C.-Y. Su, M. D. Smith, H.-C. zur Loye, *Angew. Chem.* **2003**, *115*, 4219–4223; *Angew. Chem. Int. Ed.* **2003**, *42*, 4085–4089; b) S. Hiraoka, K. Harano, M. Shiro, Y. Ozawa, N. Yasuda, K. Toriumi, M. Shionoya, *Angew. Chem.* **2006**, *118*, 8838–8841; *Angew. Chem. Int. Ed.* **2006**, *45*, 6488–6491; c) S. P. Argent, H. Adams, T. Riis-Johannessen, J. C. Jeffery, L. P. Harding, W. Clegg, R. W. Harrington, M. D. Ward, *Dalton Trans.* **2006**, 4996–5013.
- [7] N. Martin, J.-F. Nierengarten, *Supramolecular Chemistry of Fullerenes and Carbon Nanotubes*, Wiley-VCH, Weinheim, **2012**.
- [8] For the encapsulation of fullerene C₇₀ by coordination cages, see: a) D. Sun, F. S. Tham, C. A. Reed, L. Chaker, M. Burgess, P. D. W. Boyd, *J. Am. Chem. Soc.* **2000**, *122*, 10704–10705; b) D. Sun, F. S. Tham, C. A. Reed, L. Chaker, P. D. W. Boyd, *J. Am. Chem. Soc.* **2002**, *124*, 6604–6612; c) E. Huerta, G. A. Metselaar, A. Frago, E. Santos, C. Bo, J. de Mendoza, *Angew. Chem. Int. Ed.* **2007**, *46*, 202–205; d) Y. Inokuma, T. Arai, M. Fujita, *Nat. Chem.* **2010**, *2*, 780–783; e) A. R. Stefankiewicz, E. Tamanini, G. D. Pantoş, J. K. M. Sanders, *Angew. Chem.* **2011**, *123*, 5843–5846; *Angew. Chem. Int. Ed.* **2011**, *50*, 5725–5728; f) W. Meng, B. Breiner, K. Rissanen, J. D. Thoburn, J. K. Clegg, J. R. Nitschke, *Angew. Chem.* **2011**, *123*, 3541–3545; *Angew. Chem. Int. Ed.* **2011**, *50*, 3479–3483.
- [9] a) N. Kishi, Z. Li, K. Yoza, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 11438–11441; b) Z. Li, N. Kishi, K. Hasegawa, M. Akita, M. Yoshizawa, *Chem. Commun.* **2011**, 47, 8605–8607; c) Z. Li, N. Kishi, K. Yoza, M. Akita, M. Yoshizawa, *Chem. Eur. J.* **2012**, *18*, 8358–8365.
- [10] N. Kishi, M. Akita, M. Kamiya, S. Hayashi, H.-F. Hsu, M. Yoshizawa, *J. Am. Chem. Soc.* **2013**, *135*, 12976–12979.
- [11] Hg^{II} ion is a readily accessible, diamagnetic metal ion capable of adopting various coordination geometries: a) E. C. Constable, *Coord. Chem. Rev.* **1985**, *62*, 37–83; b) D. K. Breiter, *Cadmium and Mercury in Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*, Vol. 6 (Eds.: J. A. McCleverty, T. B. Meyer), Elsevier, Oxford, **2004**, pp. 1253–1292.
- [12] See the Supporting Information. In the crystal structure, the coordination tubes are lined up in the same direction with infinite one-dimensional channels (see Figure S26). The solubility of C₆₀ and C₇₀ in CH₃CN is extremely low.
- [13] The hydrodynamic diameter was estimated by using the Stokes–Einstein equation (globular model).
- [14] Force-field calculations were carried out by the use of Materials Studio version 5.0 (Accelrys Software Inc., San Diego, CA).
- [15] To the best of our knowledge, there have been no previous reports of mercury(II)-linked coordination cages and capsules capable of binding neutral organic molecules.
- [16] A similar M₂L₂ coordination tube with Ag^I ions can bind fullerene C₆₀^[10] probably as a result of additional Ag^I–π interactions: a) M. Munakata, L. P. Wu, G. L. Ning, *Coord. Chem. Rev.* **2000**, *198*, 171–203; b) J. Burgess, P. J. Steel, *Coord. Chem. Rev.* **2011**, *255*, 2094–2103.
- [17] M. Yoshizawa, J. K. Klosterman, *Chem. Soc. Rev.* **2014**, DOI: 10.1039/C3CS60315F.