ChemPubSoc Europe

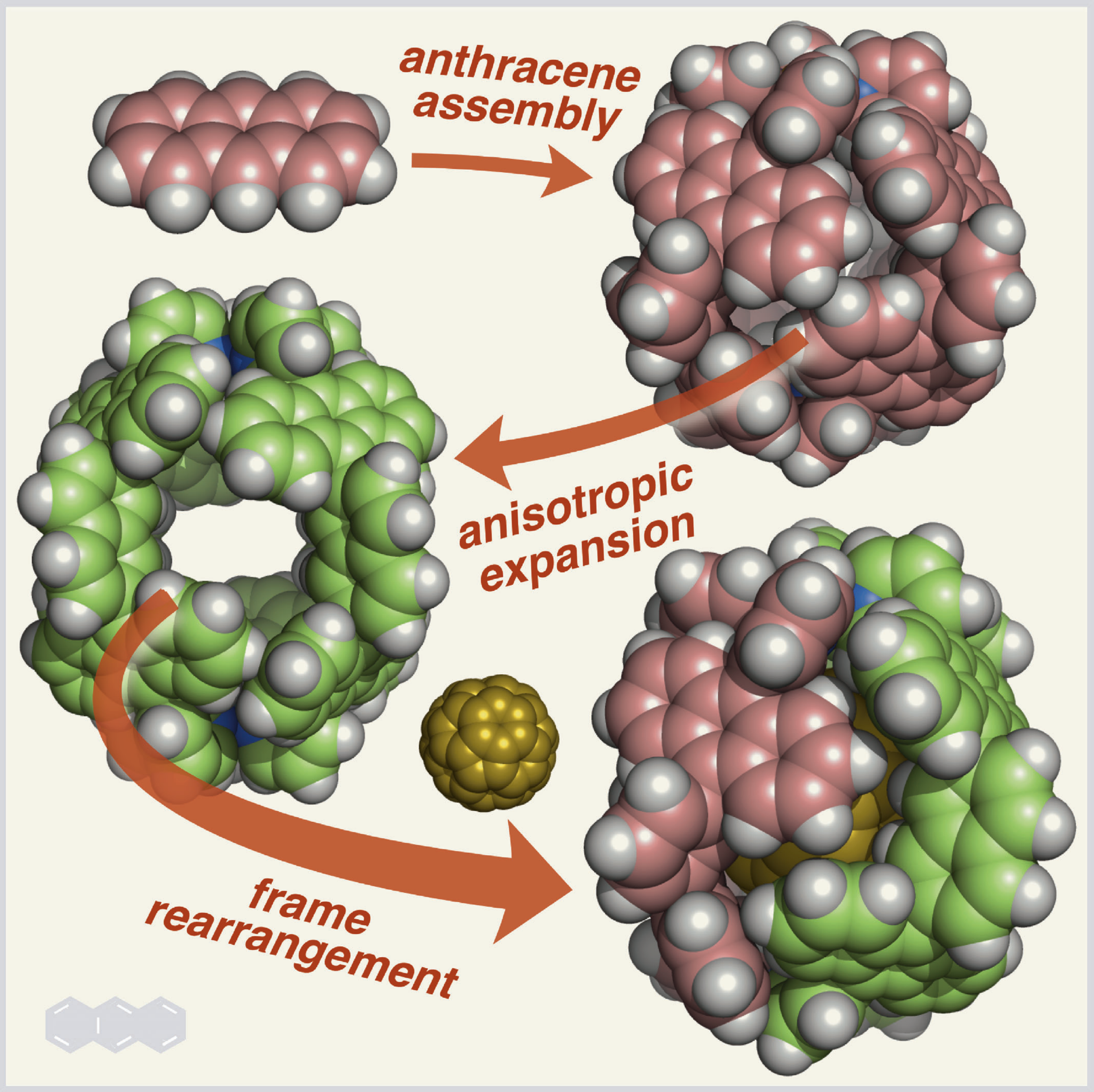
DOI: 10.1002/chem.201406445

CHEMISTRY
A European Journal
Communication

Host–Guest Systems

Anisotropic Expansion of an M_2L_4 Coordination Capsule: Host Capability and Frame Rearrangement

Masahiro Yamashina, Tsubasa Yuki, Yoshihisa Sei, Munetaka Akita, and Michito Yoshizawa*[a]



Abstract: Anisotropic expansion of a spherical M_2L_4 coordination capsule through the elongation of the ligand led to a new $M_2L'_4$ capsule. The expanded capsule provides an elliptical cavity encircled by polyaromatic frameworks with large openings and thereby can encapsulate elliptical fullerene C_{70} and monofunctionalized fullerene C_{60} in high yields. In addition, selective formation of a new $M_2L_2L'_2$ capsule occurs by mixing the original M_2L_4 and expanded $M_2L'_4$ capsules in a 1:1 ratio upon addition of C_{60} or monofunctionalized C_{60} as a template molecule.

Coordination-driven self-assembly has proven to be useful for preparing three-dimensional molecular architectures with designed functions.[1,2] Simple elongation of organic ligands enables polyhedral coordination cages to enlarge their inner space.[3] The host capability of the expanded cavities has been intensively investigated, whereas the selective incorporation of the original and elongated ligands into a single-cage framework remains uncommon, but would be expected to exhibit unknown host–guest behavior in the new cavity. M_2L_4 coordination cages and capsules are accessible molecular hosts providing a simple composition and highly symmetric framework, so that copious amounts of the derivatives have been prepared.[4] However, the “anisotropic” expansion of the cage frameworks, as well as the elucidation of the host properties of the expanded structures, has not been reported.[5–7] Herein, we describe: 1) the anisotropic expansion of an M_2L_4 coordination capsule by using an elongated organic ligand (L′) (Figure 1 a); and 2) the encapsulation of fullerene C_{70} and monofunctionalized fullerene C_{60} by the expanded $M_2L'_4$ capsule in high yields. Furthermore, we report 3) the selective formation of a new $M_2L_2L'_2$ capsule from a 1:1 mixture of the original M_2L_4 and expanded $M_2L'_4$ capsules upon addition of C_{60} or monofunctionalized C_{60} as a template (Figure 1 b).

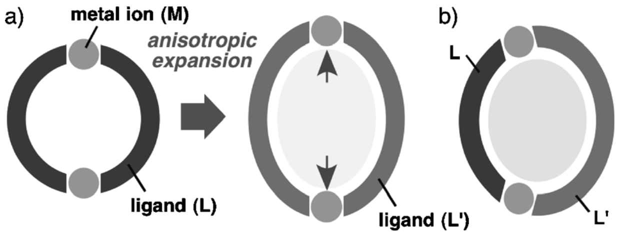


Figure 1. Cartoon representation of a) the anisotropic expansion of a coordination capsule through the elongation of the ligand and b) a coordination capsule with mixed ligands.

Bispyridine ligand **1** with two embedded anthracene panels (Figure 2 a) acts as a building block for the construction of spherical M_2L_4 coordination capsules with various metal ions (M = Zn, Pd, Pt, Ni, Co, Cu, and Mn).[8] Of them, Pd^{II}-linked M_2L_4 capsule **2** shows the quantitative encapsulation of large guest molecules up to fullerene C_{60} (ca. 1 nm) in the spherical cavity.[9] Herein, we designed new bent shaped bispyridine ligand **3** by the replacement of the phenylene spacer in ligand **1** with a naphthylene spacer (Figure 2 b, c). In a manner similar to ligand **1**, the elongated ligand **3** forms $M_2L'_4$ coordination capsule **4** upon treatment with Pd^{II} ions. As a result, small elongation of the length of ligand **1** by 2.5 Å leads to *large anisotropic expansion of the cavity volume* of **2** by approximately 90 Å^3, which imports new capsule **4** to enhanced host capability.

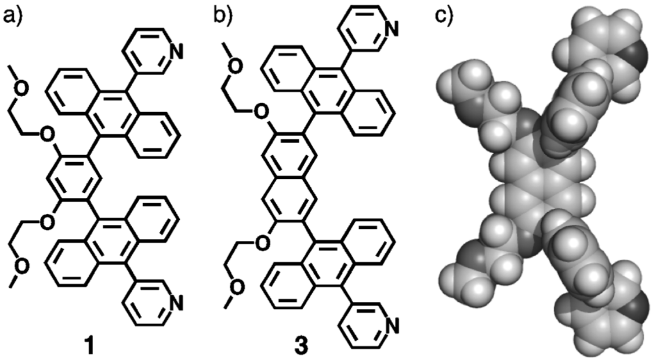


Figure 2. a) Previous bispyridine ligand **1** and b) elongated bispyridine ligand **3** reported herein. c) The optimized structure of **3** (DFT calculation, B3LYP/6-31G* level, a side view).

Elongated bispyridine ligand **3** was synthesized starting from 2,7-dihydroxynaphthalene in 30 % overall yield (six steps; Scheme S1 in the Supporting Information).[10] When a mixture of **3** (12.8 μmol), $[Pd_2Cl_2(DMSO)_2]$ (6.5 μmol), and $AgNO_3$ (16 μmol) in [D$_6$]DMSO (0.5 mL) was stirred at 100 °C for three hours, Pd^{II}-linked $M_2L'_4$ capsule **4** was formed quantitatively, as confirmed by NMR spectroscopy and MS (Figure 3). In the NMR spectrum, the apparent shifts of the pyridyl signals $H_{g\text{-}j}$ are characteristic of Pd^{II}–pyridine coordination, and the large upfield shift of the naphthylene signal H_b (7.17 ppm, $\Delta\delta_{max} = -0.69$ ppm) is indicative of the formation of a capsular assembly (Figure 3 b, c). The ^{1}H DOSY NMR spectrum showed the presence of a single product with a diffusion coefficient (*D*) of 1.32×10^{-10} m^2 s^{-1} ($\log D = -9.88$).[10] The $M_2L'_4$ composition of **4** was established by ESI-TOF MS analysis: observed prominent signals at *m/z* 1734.0, 1135.4, and 836.0 were assigned to the $[\mathbf{4}-n\cdot NO_3^-]^{n+}$ species (*n* = 2, 3, and 4, respectively; Figure S16 in the Supporting Information). An isostructural Pt^{II}-linked capsule was also formed under the similar conditions (Figures S17–22 in the Supporting Information).

The formation of an $M_2L'_4$ coordination capsule and the success in anisotropic cavity expansion were unambiguously evidenced by the X-ray crystallographic analysis of capsule **4**. The pale yellow single crystals were obtained by slow concentra-

---

[a] M. Yamashina, T. Yuki, Dr. Y. Sei, Prof. Dr. M. Akita, Dr. M. Yoshizawa
Chemical Resources Laboratory, Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 226-8503 (Japan)
Fax: (+81) 45-924-5230
E-mail: yoshizawa.m.ac@m.titech.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201406445.

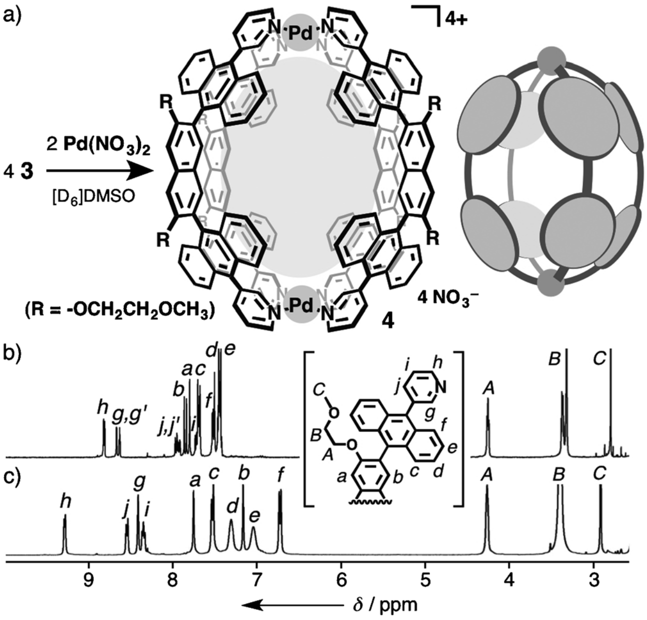


Figure 3. a) Schematic representation of the formation of expanded molecular capsule **4** and its cartoon representation. ^{1}H NMR spectra (400 MHz, [D$_6$]DMSO, RT) of b) ligand **3** and c) capsule **4**.

tion of a CH_3CN/H_2O (2:1) solution of **4** over one week. The crystal structure shows that four molecules of ligand **3** are bound to two Pd^{II} ions in a square-planer manner to form an elliptical capsular structure with a virtual D_{4h} symmetry (Figure 4a–c). The capsule framework provides four openings with diameters of 0.74–1.07 nm at the equatorial positions, which is a sharp contrast to the closed-shell framework of previous capsule **2** (Figure 4d).[8a] The Pd–Pd distance of capsule **4** (1.61 nm) is longer than that of **2** (1.36 nm), whereas the widths of their capsule cavities are quite similar (**4**: 1.14 nm and **2**: 1.12 nm).[11] The cavity volume of capsule **4** was calculated to be approximately 670 Å^3.[12] Therefore, we emphasize that the cavity volume of capsule **2** could be anisotropically expanded ($\Delta V \approx 90$ Å^3) through the small elongation ($\Delta d = 2.5$ Å) of ligand **1**.

Molecular capsule **4** has a large elliptical cavity encircled by polyaromatic frameworks with large openings and thereby encapsulated one molecule of elliptical fullerene C_{70} and monofunctionalized fullerene C_{60} in high yields (Figure 5a). When a suspended acetonitrile solution (0.5 mL) of **4** (1.4 μmol) and **C$_{70}$** (2.3 μmol) was stirred at 80 °C for three hours, a clear dark brown solution of **4⊃C$_{70}$** was obtained after filtration of suspended **C$_{70}$**. The structure of **4⊃C$_{70}$** was unambiguously confirmed by NMR and MS analyses. In the ^{1}H NMR spectrum, the proton signals derived from the anthracene moieties of **4** were significantly broadened owing to the restricted motion by efficient aromatic–aromatic interactions between the multiple polyaromatic panels and the encapsulated **C$_{70}$** (Figure 5b). Thus, the host–guest structure is stable enough even under MS conditions: ESI-TOF MS analysis of the product exclusively showed the prominent peaks assignable to the $[\mathbf{4}\supset\mathbf{C_{70}}-n\cdot NO_3^-]^{n+}$ ($n = 4$–2) species (Figure S28 in the Supporting Information). In addition, although **C$_{70}$** is insoluble in acetonitrile, the dark brown acetonitrile solution of **4⊃C$_{70}$** exhibited broad UV/Vis absorption bands at 450–700 nm, arising from **C$_{70}$** encapsulated in the cavity of **4** (Figure 5d).[13]

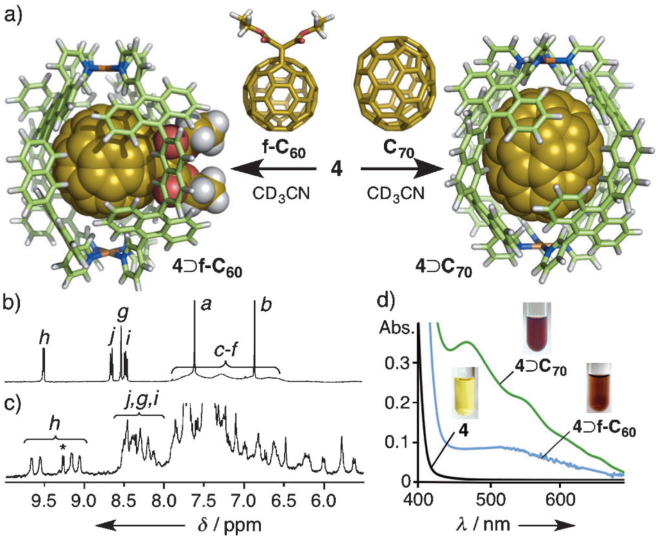


Figure 5. a) Schematic representation of the encapsulation of fullerene derivatives within capsule **4** and the optimized structures of **4⊃C$_{70}$** and **4⊃f-C$_{60}$** (R=H) by force-field calculations without counterions. ^{1}H NMR spectra (400 MHz, CD_3CN, RT) of b) **4⊃C$_{70}$** and c) **4⊃f-C$_{60}$** (*: free host). d) UV/Vis spectra (CH_3CN, RT, 0.6 mM) of **4**, **4⊃C$_{70}$**, and **4⊃f-C$_{60}$**.

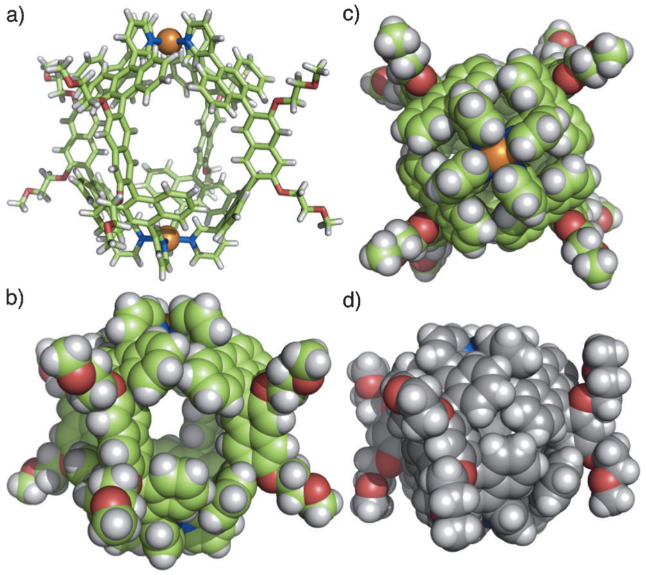


Figure 4. X-ray crystal structures of coordination capsules **4** and **2**. a) Ball-and-stick and b,c) space-filling representations (side and top views) of **4**. d) Space-filling representation of **2** (side view). The counteranions and solvent molecules are omitted for clarity.

Similar to the formation of **4⊃C$_{70}$**, capsule **4** accommodated diethyl malonate-derivatized fullerene C_{60} (**f-C$_{60}$**) to afford a dark brown solution of **4⊃f-C$_{60}$** in 86% yield (Figure 5a,d). Expectedly, the ^{1}H NMR spectrum of **4⊃f-C$_{60}$** revealed desymmetrization of the capsule framework due to the encapsulation of the guest with a bulky substituent, which penetrated one of the four openings (Figure 5 c). The pyridyl signal H_h of the capsule split into four signals from 9.07 to 9.68 ppm after binding **f-C$_{60}$**. The formation of 1:1 host–guest complex **4$\supset$f-C$_{60}$** was clearly elucidated by the ESI-TOF MS spectrum, in which prominent signals were observed at *m/z* 2173.6, 1427.8, and 1055.6, assigned to the [**4$\supset$f-C$_{60}$**$-n\cdot NO_3^-$]$^{n+}$ species ($n=2$, 3, and 4, respectively; Figure S30 in the Supporting Information). The three-dimensional host–guest structures of **4$\supset$C$_{70}$** and **4$\supset$f-C$_{60}$** obtained by force-field calculations are in good agreement with the NMR and MS data (Figures 5 a and S44 in the Supporting Information).[12] In contrast, the encapsulation of **C$_{70}$** and **f-C$_{60}$** by capsule **2** was not observed under various conditions.[14]

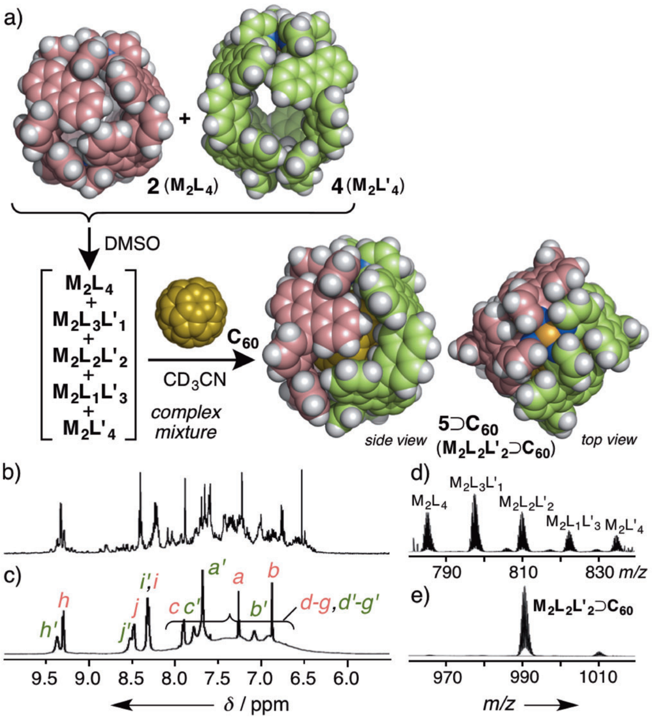


Figure 6. a) Schematic representation of the C$_{60}$-induced reorganization of capsules **2** and **4** ($R=H$). ^{1}H NMR spectra (500 MHz, CD$_3$CN) of b) a complex mixture of $M_2L_nL'_{4-n}$ ($n=0$–4; RT); and c) **5$\supset$C$_{60}$** (50 °C). ESI-TOF MS spectra (CH$_3$CN, RT) of d) the complex mixture and e) **5$\supset$C$_{60}$**.

Unexpectedly, we found the guest-induced reorganization[15] of expanded capsule **4** and original capsule **2** in the presence of fullerene C$_{60}$, leading to the sole formation of new capsule **5** (Figure 6 a). When capsules **4** and **2** (in a 1:1 ratio) were combined in DMSO at 100 °C for 3 h, the complicated ^{1}H NMR and ESI-TOF MS spectra of products were obtained (Figure 6 b, d), which indicates the generation of a mixture of M$_2$L$_4$, M$_2$L$_3$L'$_1$, M$_2$L$_2$L'$_2$, M$_2$L$_1$L'$_3$, and M$_2$L'$_4$ capsules. On the other hand, addition of fullerene C$_{60}$ to the complex mixture in acetonitrile followed by stirring the mixture at 80 °C for three hours resulted in the quantitative formation of the **5$\supset$C$_{60}$** complex with the composition of Pd$_2$·**1**$_2$·**3**$_2$$\supset$**C$_{60}$**.[16] The ESI-TOF MS analysis of the resultant solution showed a simple spectrum, in which prominent signals were observed at *m/z* 2044.0, 1342.0, and 991.0, assigned to the [**5$\supset$C$_{60}$**$-n\cdot NO_3^-$]$^{n+}$ species ($n=2$, 3, and 4, respectively; Figures 6 e and S36 in the Supporting Information). Peaks derived from other host–guest complexes and the empty capsules were not observed. In the ^{1}H NMR spectrum, two sets of the pyridyl signals ($H_{\text{h-j}}$ and $H_{\text{h'-j'}}$) and the pendant methoxyethoxy signals ($H_{\text{A-C}}$ and $H_{\text{A'-C'}}$) of **5$\supset$C$_{60}$** were clearly observed (Figures 6 c and S31 in the Supporting Information). Because each of capsules **2** and **4** can quantitatively encapsulate one molecule of **C$_{60}$**, the **5$\supset$C$_{60}$** structure is a thermodynamically favored product over the other possible $M_2L_nL'_{4-n}$$\supset$**C$_{60}$** structures ($n=0$, 1, 3, and 4). The **5$\supset$C$_{60}$** complex, in principle, is able to generate two geometrical isomers, *cis*- and *trans*-isomers, based on the coordination geometry of the square-planar Pd^{II} center. Force-field calculations indicated that the structure of the *cis*-isomer, which is an unusual "Janus"-like capsule, is much more favorable than that of the *trans*-isomer ($\Delta E=-22.2$ kcal mol^{-1}; Table S2 in the Supporting Information).[10,12] In addition, the combination of a 1:1 mixture of capsules **2** and **4** with the monofunctionalized C$_{60}$ (**f-C$_{60}$**) led to the selective formation of a **5$\supset$f-C$_{60}$** complex (Figures S48 and 49 in the Supporting Information).

The strong encapsulation of the fullerene derivatives and the selective rearrangement of the host frameworks most probably stem from efficient host–guest aromatic–aromatic interactions. Thus, neither host–guest interaction, nor frame rearrangement was observed by the treatment of the capsules with aliphatic and small aromatic guests (e.g., 1-acetyladamantane and [2.2]paracyclophane) as well as anionic guests (e.g., sodium tetraphenylborate) under the same conditions.

In summary, we presented the anisotropic expansion of a spherical M$_2$L$_4$ coordination capsule with a polyaromatic anthracene shell through the simple elongation of the organic ligand. The expanded M$_2$L'$_4$ capsule provides a large elliptical cavity surrounded by polyaromatic frameworks with four openings and thereby encapsulates elliptical fullerene C$_{70}$ as well as monosubstituted fullerene C$_{60}$. More importantly, the guest-induced reorganization of the expanded M$_2$L'$_4$ capsule and the original M$_2$L$_4$ capsule occurs in the presence of C$_{60}$ or monosubstituted C$_{60}$, which exclusively gives multicomponent M$_2$L$_2$L'$_2$ capsule. The preparation of new expanded M'$_2$L'$_4$ capsules by using a variety of metal ions (M') and the guest-induced frame rearrangement of the M'$_2$L'$_4$ capsule and previously reported M'$_2$L$_4$ capsules[8] are currently under investigation.

Acknowledgements

This work was supported by the Japan Society for the Promotion of Science (JSPS) through a "Funding Program for Next-Generation World-Leading Researchers (NEXT Program)" and by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) through Grants-in-Aid for Scientific Research on Innovative Areas "Soft Molecular Systems". We thank Dr. Norifumi Kishi (RIKEN) and Dr. Ken-ichi Sano (Nippon Inst. of Tech.) for helpful discussions and generous support of this work.

Keywords: anthracene · coordination capsules · fullerenes · guest-induced reorganization · host–guest systems

[1] J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, 2nd ed., Wiley, Chichester, **2009**.

[2] a) F. Hof, S. L. Craig, C. Nuckolls, J. Rebek, Jr., *Angew. Chem. Int. Ed.* **2002**, *41*, 1488 – 1508; *Angew. Chem.* **2002**, *114*, 1556 – 1578; b) D. M. Vriezema, M. C. Aragonès, J. Elemans, J. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* **2005**, *105*, 1445 – 1489; c) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem. Int. Ed.* **2009**, *48*, 3418 – 3438; *Angew. Chem.* **2009**, *121*, 3470 – 3490; d) H. Amouri, C. Desmarets, J. Moussa, *Chem. Rev.* **2012**, *112*, 2015 – 2041; e) T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* **2013**, *113*, 734 – 777; f) K. Harris, D. Fujita, M. Fujita, *Chem. Commun.* **2013**, *49*, 6703 – 6712; g) M. M. J. Smulders, I. A. Riddell, C. Browne, J. R. Nitschke, *Chem. Soc. Rev.* **2013**, *42*, 1728 – 1754; h) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848 – 1860; i) L. Xu, L.-J. Chen, H.-B. Yang, *Chem. Commun.* **2014**, *50*, 5156 – 5170.

[3] Expansion of polyhedral coordination cages (representative examples): a) R. W. Saalfrank, B. Hörner, D. Stalke, J. Salbeck, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1179 – 1182; *Angew. Chem.* **1993**, *105*, 1223 – 1225; b) B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield, P. J. Stang, *J. Am. Chem. Soc.* **1999**, *121*, 10434 – 10435; c) M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, T. Ozeki, S. Sakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem. Int. Ed.* **2004**, *43*, 5621 – 5625; *Angew. Chem.* **2004**, *116*, 5739 – 5743; d) R. A. Bilbeisi, J. K. Clegg, N. Elgrishi, X. d. Hatten, M. Devillard, B. Breiner, P. Mal, J. R. Nitschke, *J. Am. Chem. Soc.* **2012**, *134*, 5110 – 5119; e) D. Fujita, K. Suzuki, S. Sato, M. Yagi-Utsumi, Y. Yamaguchi, N. Mizuno, T. Kumasaka, M. Takata, M. Noda, S. Uchiyama, K. Kato, M. Fujita, *Nat. Commun.* **2012**, *3*, 1093; f) N. Ousaka, S. Grunder, A. M. Castilla, A. C. Whalley, J. F. Stoddart, J. R. Nitschke, *J. Am. Chem. Soc.* **2012**, *134*, 15528 – 15537.

[4] a) D. A. McMorran, P. J. Steel, *Angew. Chem. Int. Ed.* **1998**, *37*, 3295 – 3297; *Angew. Chem.* **1998**, *110*, 3495 – 3497; b) N. B. Debata, D. Tripathy, D. K. Chand, *Coord. Chem. Rev.* **2012**, *256*, 1831 – 1945.

[5] Anisotropic expansion of coordination cages without host capability for neutral guest molecules: a) D. L. Caulder, K. N. Raymond, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1440 – 1442; *Angew. Chem.* **1997**, *109*, 1508 – 1510; b) C. J. Kuehl, Y. K. Kryschenko, U. Radhakrishnan, S. R. Seidel, S. D. Huang, P. J. Stang, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4932 – 4936; c) J. R. Shakirova, E. V. Grachova, A. J. Karttunen, V. V. Gurzhiy, S. P. Tunik, I. O. Koshevoy, *Dalton Trans.* **2014**, *43*, 6236 – 6243.

[6] Anisotropic expansion of coordination boxes by the use of template molecules: a) M. Yoshizawa, J. Nakagawa, K. Kumazawa, M. Nagao, M. Kawano, T. Ozeki, M. Fujita, *Angew. Chem. Int. Ed.* **2005**, *44*, 1810 – 1813; *Angew. Chem.* **2005**, *117*, 1844 – 1847; b) Y. Yamauchi, M. Yoshizawa, M. Akita, M. Fujita, *J. Am. Chem. Soc.* **2010**, *132*, 960 – 966.

[7] Anisotropic expansion of hydrogen-bonding capsules by the use of template molecules: D. Ajami, J. Rebek, Jr., *Angew. Chem. Int. Ed.* **2007**, *46*, 9283 – 9286; *Angew. Chem.* **2007**, *119*, 9443 – 9446.

[8] a) Z. Li, N. Kishi, K. Hasegawa, M. Akita, M. Yoshizawa, *Chem. Commun.* **2011**, *47*, 8605 – 8607; b) Z. Li, N. Kishi, K. Yoza, M. Akita, M. Yoshizawa, *Chem. Eur. J.* **2012**, *18*, 8358 – 8365; c) M. Yoshizawa, J. K. Klosterman, *Chem. Soc. Rev.* **2014**, *43*, 1885 – 1898.

[9] a) N. Kishi, Z. Li, K. Yoza, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 11438 – 11441; b) N. Kishi, Z. Li, Y. Sei, M. Akita, K. Yoza, J. S. Siegel, M. Yoshizawa, *Chem. Eur. J.* **2013**, *19*, 6313 – 6320; c) M. Yamashina, Y. Sei, M. Akita, M. Yoshizawa, *Nat. Commun.* **2014**, *5*, 4662.

[10] See the Supporting Information.

[11] We measured the diagonal distances between the opposing naphthylene hydrogen atoms (H_b) of capsule **4** and between the opposing phenylene hydrogen atoms (H_b) of capsule **2**.

[12] Crystal structure of **4** was used to generate the optimized structures. The calculations were carried out by using Materials Studio (version 5.0, Accelrys Software Inc., San Diego, CA).

[13] Although the previous capsule **2** binds only $\mathbf{C_{60}}$ from a mixture of $\mathbf{C_{60}}$ and $\mathbf{C_{70}}$, the present capsule **4** bound $\mathbf{C_{60}}$ and $\mathbf{C_{70}}$ in a 1:1 ratio under similar conditions (Figure S45 in the Supporting Information).

[14] Optimized structures of the host–guest complexes (Figure 5 a) revealed that the distances between the anthracene panels and $\mathbf{C_{70}}$ or $\mathbf{f\text{-}C_{60}}$ are approximately 3.7 Å, which indicated the existence of aromatic–aromatic π-stacking interactions.

[15] Guest-induced reorganization of molecular cages by using small guest molecules: a) M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649 – 1650; b) S. Hiraoka, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 10239 – 10240; c) M. C. Calama, P. Timmerman, D. N. Reinhoudt, *Angew. Chem. Int. Ed.* **2000**, *39*, 755 – 758; *Angew. Chem.* **2000**, *112*, 771 – 774; d) F. Hof, C. Nuckolls, J. Rebek, Jr., *J. Am. Chem. Soc.* **2000**, *122*, 4251 – 4252; e) M. Ziegler, J. J. Miranda, U. K. Andersen, D. W. Johnson, J. A. Leary, K. N. Raymond, *Angew. Chem. Int. Ed.* **2001**, *40*, 733 – 736; *Angew. Chem.* **2001**, *113*, 755 – 758; f) 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.

[16] The combination of a mixture of capsules **2** and **4** with $\mathbf{C_{70}}$ gave $\mathbf{4}\supset\mathbf{C_{70}}$, **2**, and oligomers (Figures S46 and 47 in the Supporting Information). The molecular-modeling studies on the $M_2L_nL'_{4-n}\supset\mathbf{C_{60}}$ complexes indicated that the $M_2L_2L'_2$ framework of capsule **5** encapsulates $\mathbf{C_{60}}$ more efficiently due to the complementary size and shape (Table S2 in the Supporting Information).

Received: December 11, 2014