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A Chiral M_6L_4 Cage Complex Assembled from a D_{2h}-Symmetric Ligand: Self-Assembly, Structure, and Chirality Observation

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Chiral M_6L_4 cage structures were self-assembled by mixing a D_{2h}-symmetric ligand with a cis end-capped (diamine)Pd(NO_3)$_2$ complex [diamine = ethylenediamine (en), 2,2′-bipyridine (2,2′-bpy), or 1,2-cyclohexanediamine (cxn)]. This self-assembly was achieved by exploiting the template effect of an aromatic guest molecule. The structures were confirmed by CSI-MS, NMR observations, and X-ray crystallographic analysis. Having C_2 molecular chirality, two diastereomers were differentiated by attaching a chiral auxiliary on Pd(II).

Recent remarkable progress in non-covalent syntheses made possible the highly efficient construction of molecular containers and chambers with large hollow frameworks.[1] In particular, metal-mediated self-assembly of cage compounds, initiated by Saalfrank's M_4L_6-type cage[2] and Lehn's cylindrical cage,[3] have been to date extensively studied by several groups.[4] Recently, we showed the quantitative self-assembly of M_6L_4-type cage complex **3** from D_{3h}-symmetric, planer ligand **1**.[5] The cage **3** possesses the highest class of symmetry (T_d) among common organic/inorganic molecular assemblies and can accommodate as many as four large molecules (e.g., adamantanes and carboranes) along the C_3 axes of the cage.[6] Related D_{3h} symmetric ligands have been also shown to unequivocally provide highly symmetric structures like an open square pyramid[7] and a trigonal bipyramid.[8]

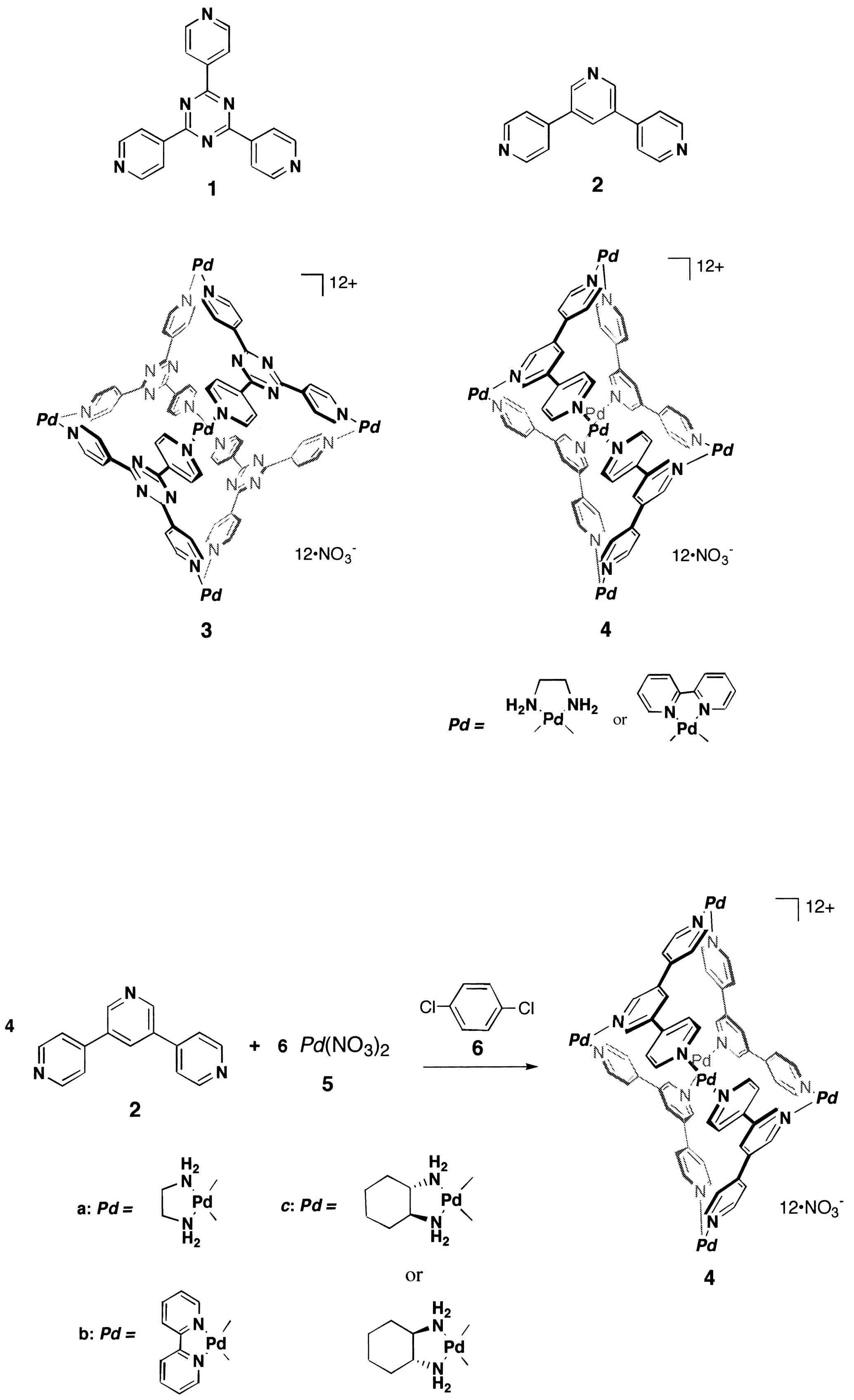
The organic ligands employed thus far for the self-assembly process are in general highly symmetric, avoiding the formation of structural isomers that arise from the different orientations of the same ligands in the assembly process. Hence, there are few reports on the successful assembly of unique cage structures from less symmetrical ligands.[9] Desymmetrization of the ligand structures is therefore an attractive task to explore the assembly of less symmetric cages that lead to site-specific functionalization of the cavities. Another intriguing aspect in the ligand desymmetrization is that the cage assemblies will have an opportunity to be chiral. In fact, we have previously reported the guest-induced assembly of a chiral cage from an AB_2-type D_{2h}-symmetric ligand.[10] Reymond also reported the assembly of a C_{3h}-symmetric ligand into a chiral cage framework with T-symmetry.[11] Similar assembly of a chiral cage from achiral components by hydrogen bonding has been widely studied by Rebek.[12]

In the present work, we have designed D_{2h}-symmetric ligand **2** by eliminating one pyridine ring from **1**. We have found that, upon complexation with cis end-capped Pd(II) units **5**, ligand **2** is assembled into a unique M_6L_4 type cage **4**. Accordingly, we discuss in the following sections the self-assembly, structure analysis, binding properties of cage **4** as well as its chiral derivation (Scheme 1).

Results and Discussion

Self-Assemby of 4a and 4b. The self-assembly of **4** was in fact achieved by exploiting the template effect of a guest molecule.[13] In the absence of a template, the assembly of **4a** from ligand **2** and Pd(II) unit **5a** in D_2O was concomitant with the formation of considerable amount of an oligomeric mixture (Fig. 1a). With an excess amount of an aromatic guest, *p*-dichlorobenzene (**6**), however, the ^1H NMR spectrum showed the conversion of the mixture to a sole product (Fig. 1b). The structure of the product was suggested as **4a** by CSI-MS[14] and 2D NMR observations. From CSI-MS, an M_6L_4 composition was indicated: e.g., *m*/*z* 830.3 for [**4a**-$(NO_3)_3$]$^{3+}$, 643.5 for [**4a**-$(NO_3)_4$·(dmf)$_2$]$^{4+}$, and 546.3 for [**4a**-$(NO_3)_5$·(dmf)$_5$]$^{5+}$. ^1H–^1H relay COSY and NOESY experiments showed the presence of two ligand environments (**A** and **B**) where each ligand is desymmetrized. All aromatic protons (*a*–*n*) involved in ligands **A** and **B** were unequivocally assigned through intra- and inter-ring correlation by relay-COSY and NOESY, respectively. These observations are in good accordance with the proposed structure of **4** that possesses a C_2-axis with two different environments for the four ligands. The signal of **6** was significantly upfield shifted ($\Delta\delta = -1.1$ ppm), indicating the enclathration of **6** within the cavity of **4a**. The host-guest ratio was estimated to be 1 : 1 by NMR integration. Similarly, the reaction of ligand **2** with 2,2′-bpy capped Pd(II) (**5b**) in the presence of **6** gave the same M_6L_4 framework (**4b**). The NMR of **4b** is however much more complicated, due to the restricted free rotation of 4-pyridyl groups by the steric demand of 3,3′-proton of the ancillary 2,2′-bpy ligand. Thus, pyridine α/α' or β/β' protons (e.g., *a*/*a*′ protons in Fig. 1c) appear unequivalently. Other aromatic guests such as *p*-xylene and *p*-diethylbenzene were also encapsulated by **4b**.

[#] CREST, Japan Science and Technology Corporation (JST).



Scheme 1.

Crystal Structure of 4b·6. The structure of **4** was finally confirmed by X-ray crystallographic analysis of clathrate complex **4b·6**. Single crystals of **4b·6** were obtained in 62% yield by standing the reaction solution at ambient temperature for 7

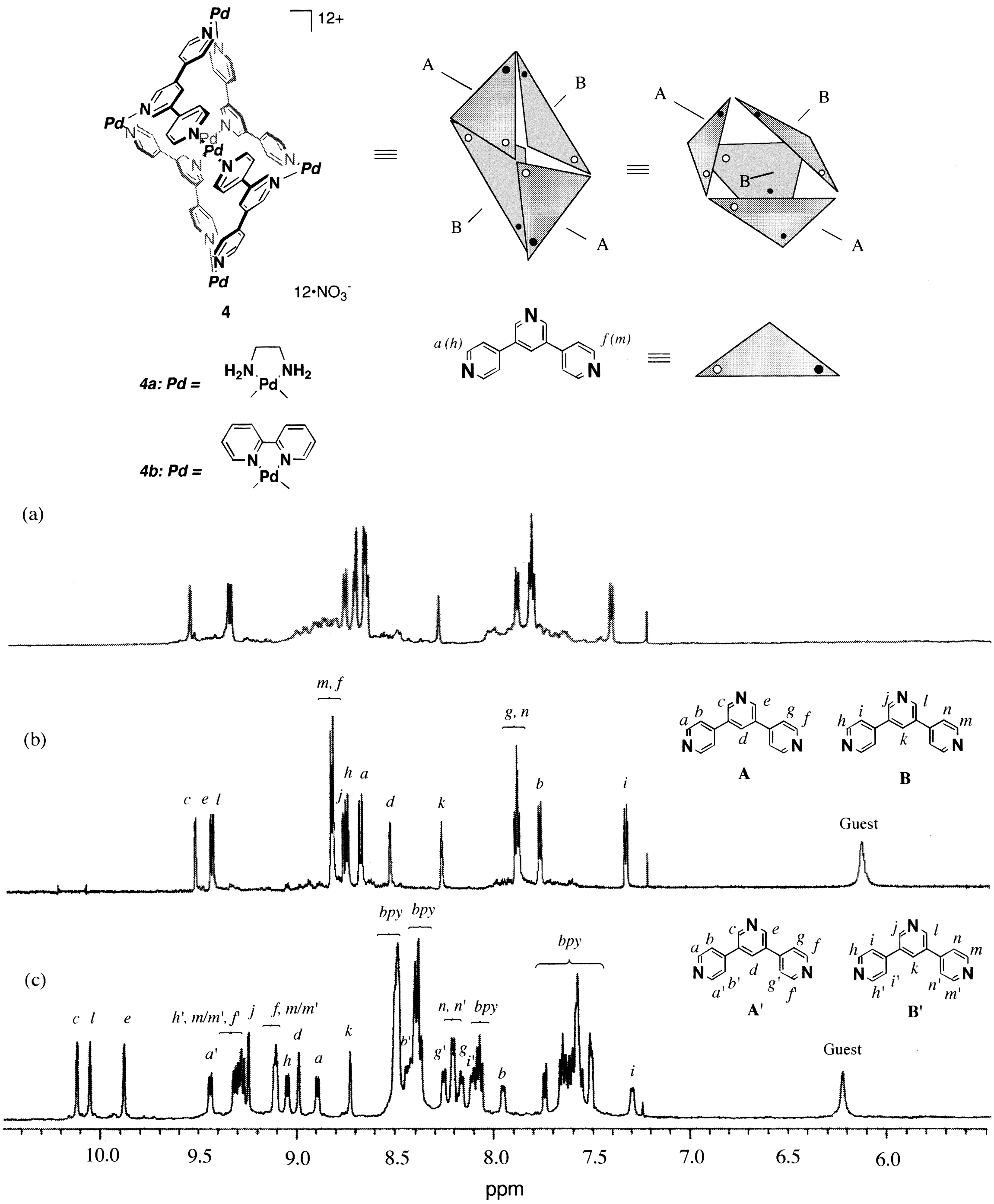


Fig. 1. Schematic representation of **4** and ^{1}H NMR of the reaction solutions (500 MHz, D_2O, 25 °C, TMS as an external standard). In the cartoonic representation, Pd(II) ions linking the corners of the ligands are omitted for clarity. Note that two corners of the triangle marked by black and white circles are inequivalent in the complex. (a) Oligomeric mixture ([**2**] = 3.3 mM, [**5a**] = 5.0 mM); (b) **4a•6** complex assembled upon the addition of an excess amount of **5** (suspended) ([**2**] = 3.3 mM, [**5a**] = 5.0 mM); (c) **4b•6** complex assembled upon the addition of an excess amount of **5** (suspended) ([**2**] = 9.9 mM, [**5b**] = 15.0 mM).

days. As expected, the crystal structure of **4b•6** displayed the proposed cage structure assembled from four ligands and six metals. In this structure, two ligands (in the front in Fig. 2a) are linked together between the terminal pyridine ring, making an *S*-shaped helical motif, while the other two are linked together in a mesomeric *X*-shaped motif. As a result, the cage possesses windows of two different types. The Pd–Pd distances are 13.6, 13.1, and 9.7 Å in the larger windows, while they are 9.7, 9.7, and 9.6 Å in the smaller one (Fig. 2c). Dimensions of the cage itself are approximately 2.5 × 2.1 × 2.2 nm, and the diagonal Pd–Pd distances are 17.8, 13.2, and 14.3 Å. In the solid structure, one molecule of **6** and one NO_3^- ion were encapsulated within the cage (Figs. 2b, c). Also 47 water molecules were found for a cage, these are hydrogen bonded

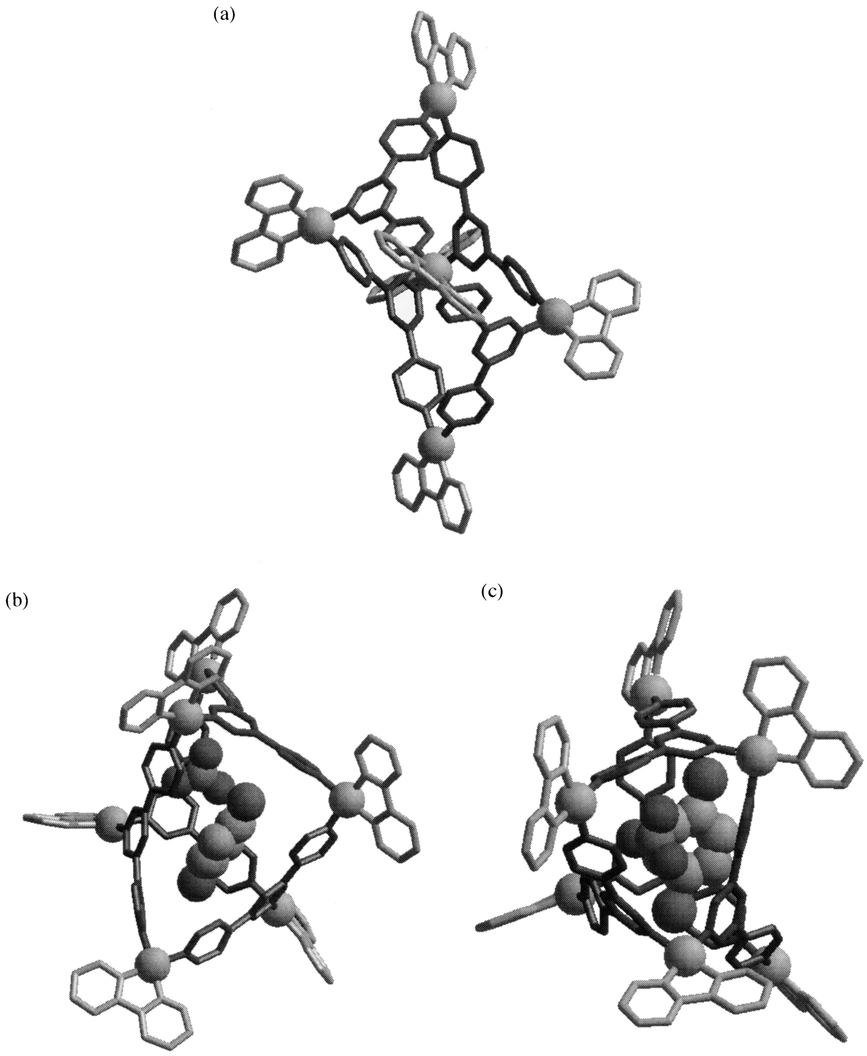


Fig. 2. Crystal structure of **4b·6**. For clarity, guest molecules are omitted. (a) A front view. (b) The view of the larger window. (c) The view of the smaller window.

with nitrate anions.

Observation of Molecular Chirality in Solution. The structure of **4b** has C_2 chirality, though the crystal consists of racemic **4b** with triclinic *P*-1 space group. To observe the molecular chirality, we attached a chiral auxiliary on Pd(II).[15] Thus, chiral Pd(II) block (*R*,*R*)-**5c** derived from (*R*,*R*)-1,2-diaminocyclohexane was subjected to the complexation with ligand **2** in the presence of template **6** (Scheme 1). ^{1}H-NMR spectrum again showed the quantitative formation of **4c·6** clathrate complex and, as expected, two diastereomers were observed. The diastereomer ratio was estimated by integration to be 1.3:1 (Fig. 3). Though the diastereoselectivity is low, it is worthy of note that a molecular chirality arises from achiral components. Indeed, while **5c** is silent in CD spectrum, **4c·6** shows the obvious Cotton effect, which is ascribed to the chiral orientation of the ligand frameworks in **4c·6**.[16] Indeed, enantiomeric Pd(II) block (*S*,*S*)-**5c** derived from (*S*,*S*)-1,2-diaminocyclohexane induced the opposite Cotton effect (Fig. 4). The absolute configuration of the major isomer of **4c·6** is not easy to determine because ΔG is estimated to be only 0.16 kcal mol^{-1}.

Conclusion

We have described the assembly of C_2 chiral M_6L_4 cages that are formed from an achiral D_{2h}-symmetric ligand with the help of aromatic template molecules. The results shown here emphasize the following merits of developing less symmetrical molecular assemblies. First, by introducing a chiral source in the environment (e.g., guest molecules, ancillary and bridging ligands, counter ions, etc.), the assemblies will have a chance to be optically active. Second, by the rational design of the ligands, they will be oriented in a unique fashion leading to a sole assembly. Third, the desymmetrized assemblies thus obtained will have site-specific functionality. The ultimate goal in the desymmetrized molecular assembly may be an artificial mimic of biological cages like protein pockets that assemble from prefunctionalized non-symmetric subunits in a unique way.

Experimental

General: ^{1}H NMR, ^{13}C NMR, H–H relay COSY, NOESY, and CH-COSY spectra were recorded on a Bruker DRX-500 (500

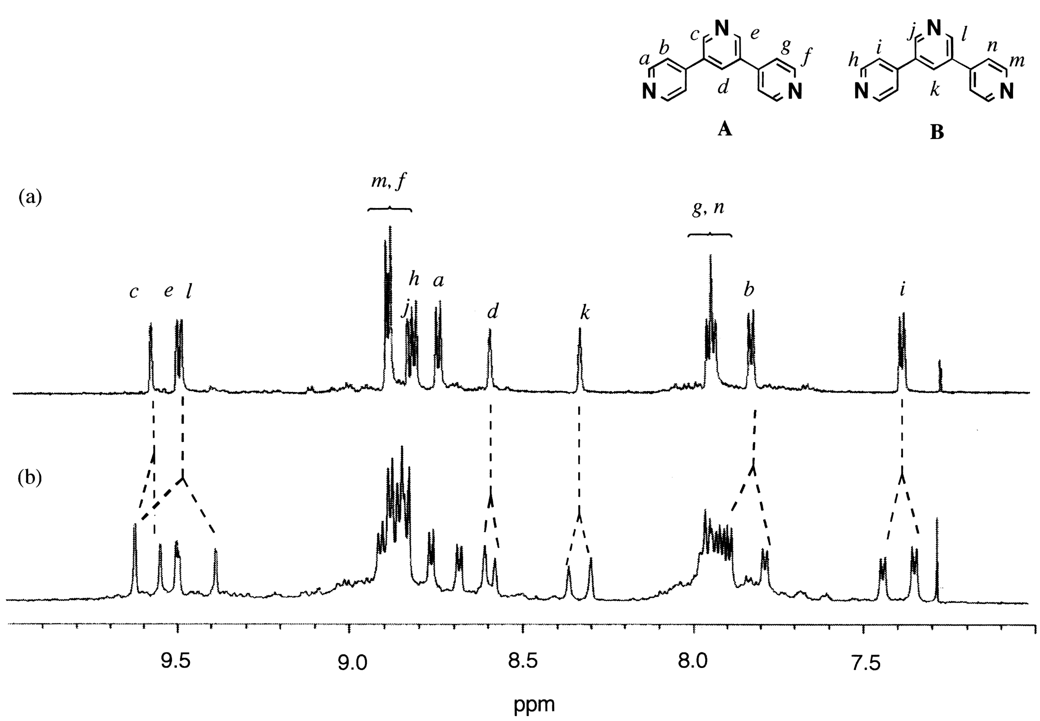


Fig. 3. ^{1}H NMR of the reaction solution (500 MHz, D_2O, 25 °C, TMS as an external standard). (a) **4a·6** complex assembled upon the addition of an excess amount of **6** (suspended) ([**2**] = 3.3 mM, [**5a**] = 5.0 mM); (b) **4c·6** complex assembled upon the addition of an excess amount of **6** (suspended) ([**2**] = 3.3 mM, [**5c**] = 5.0 mM).

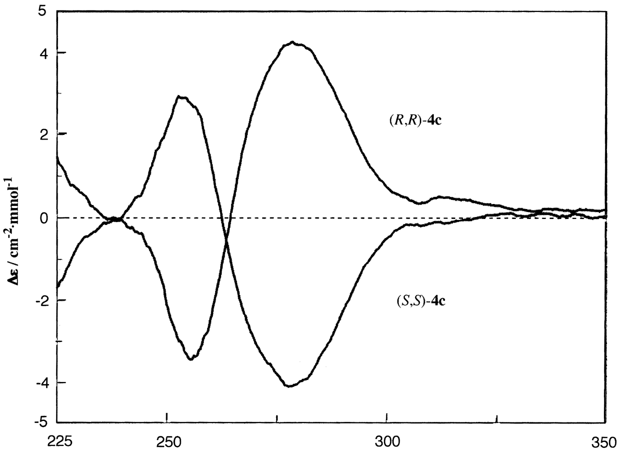


Fig. 4. Circular dichrogram of (*R*,*R*)- **4c·6** (0.5 mM) and (*S*,*S*)-**4c·6** (0.5 mM) in D_2O.

MHz) spectrometer and a Varian INOVA-500 (500 MHz) spectrometer. FTIR spectra were obtained on a SHIMADZU FTIR-8300 spectrometer as KBr pellets. CD spectra were recorded on a JASCO type J-820 spectropolarimeter. FAB-MS spectra were recorded with JEOL JMS-AX-550HA with *m*-nitrobenzyl alchohol (NBA) as a matrix. Melting points were determined on a YANACO MP-500V .

Materials: 4-Pyridylboronic acid pinacol ester,[17] **5a**,[18a] **5b**,[18b] **5c**,[18c] and **5d**[18c] were prepared according to the reported procedure.

Preparation of Ligand 2: 3,5-Dibromopyridyne(8.25 mmol, 1.94 g), 4-pyridylboronic acid pinacol ester (44.2 mmol, 9.03 g), [Pd(PPh_3)$_4$] (10 mol%, 0.883 mmol, 1.02 g), and K_3PO_4 (38.17 mmol, 8.10 g) were added to dioxane (200 mL), and the mixture was heated under reflux for 4 d. The reaction solution was quenched by H_2O and extracted with $CHCl_3$. After the organic layer was dried over K_2CO_3, filtered, and condensed in vacuo, the purification of the crude mixture by silica-gel column chromatography (AcOEt:hexane = 1:1) gave ligand **2** as a colorless solid (6.66 mmol, 1.56 g) in 82% yield. mp 178–179 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS as external standard) δ 8.96 (2H, d, *J* = 2.0 Hz, Py$H_{\alpha'}$), 8.77 (4H, d-like, *J* = 4.5 Hz, PyH_{α}), 8.13 (1H, t, *J* = 2.0 Hz, PyH_{γ}), 7.80 (4H, d-like, *J* = 4.5 Hz, PyH_{β}); ^{13}C NMR (125 MHz, $CDCl_3$, TMS as external standard) δ 150.7 (CH_{α}), 148.4 ($CH_{\alpha'}$), 144.6 (*C*q), 134.2 (*C*q), 132.7 (CH_{γ}), 121.6 (CH_{β}); IR (KBr) 3026.6, 1592.6, 1403.1, 1343.3, 1223.7, 1025.6, 990.9, 813.9, 709.8, 624.4, 552.6 cm^{-1}; FAB MS (matrix: *m*NBA) *m*/*z* 234 [(M + H$^+$)]$^+$; Anal. Calcd for $C_{15}H_{11}N_3$·$0.1H_2O$: C 76.64, H 4.80, N 17.88%. Found: C 76.65, H 4.69, N 17.87%.

Self-Assembly and Isolation of 4b·6 Complex: Ligand **2** (0.133 mmol, 31.0 mg) was suspended in D_2O solution (1.5 mL) of **5b** (0.20 mmol, 77.4 mg) and the mixture was heated at 80 °C for 15 min. Then, **6** (0.42 mmol, 61.0 mg) was added and the solution was stirred for 9 h at room temperature. After excess **6** was filtered, ^{1}H NMR showed almost the quantitative formation of **4b·6** complex. Single crystals which formed by standing the aqueous solution at ambient temperature for 7 d were collected by filtration, washed with water, and dried in vacuo to give pure **4b·6** (20.62 mmol, 69.9 mg) in 62% yield. mp 248–249 °C (dec.); ^{1}H NMR (500 MHz, D_2O, $SiMe_4$–$CDCl_3$ in a capillary), δ 10.13 (s, 2H, PyH_c), 10.06 (s, 2H, PyH_l), 9.89 (s, 2H, PyH_e), 9.45 (d, *J* = 6.0 Hz, 2H, Py$H_{a'}$), 9.33 (d, *J* = 6.0 Hz, 2H, Py$H_{h'}$), 9.30 (d, *J* = 6.0 Hz, 2H, Py$H_{m/m'}$), 9.29 (d, *J* = 6.0 Hz, 2H, Py$H_{f'}$), 9.26 (s, 2H, PyH_j), 9.14–9.12 (m, 4H, PyH_f, $H_{m/m'}$), 9.07 (d, *J* = 6.0 Hz, 2H, PyH_h), 9.00 (s, 2H, PyH_d), 8.91 (d, $J = 6.0$ Hz, 2H, PyH_a), 8.75 (s, 2H, PyH_k), 8.52–8.50 (m, 12H, bpy), 8.46 (d, $J = 8.0$ Hz, 2H, Py$H_{b'}$), 8.44–8.39 (m, 12H, bpy), 8.27 (d-like, $J = 6.0$ Hz, 2H, Py$H_{g'}$), 8.23–8.22 (m, 4H, PyH_n, $H_{n'}$), 8.18 (d-like, $J = 6.0$ Hz, 2H, PyH_g), 8.13 (d, $J = 4.4$ Hz, 2H, Py$H_{i'}$), 8.11–8.01 (m, 4H, bpy), 7.97 (d, $J = 4.6$ Hz, 2H, PyH_b), 7.76 (d, $J = 5.3$ Hz, 2H, bpy), 7.69–7.58 (m, 14H, bpy), 7.54–7.53 (m, 4H, bpy) , 7.32 (d, $J = 4.4$ Hz, 2H, PyH_i) 6.36 (bs, 4H, guest); ^{13}C NMR (125 MHz, D_2O), δ 156.88 (*C*q), 156.80 (*C*q), 156.76 (*C*q), 156.71 (*C*q), 156.66 (*C*q), 152.67 (*C*H$_a$), 152.53 (*C*H$_{a'}$), 152.15 (*C*H$_f$, H$_{f'}$, H$_m$, H$_{m'}$), 151.80 (*C*H$_{h'}$, H$_j$), 151.48 (*C*H$_e$), 151.25 (*C*H$_h$), 150.81 (*C*H$_{\mathrm{bpy}}$), 150.73 (*C*H$_l$), 150.69 (*C*H$_{\mathrm{bpy}}$), 150.23 (*C*H$_{\mathrm{bpy}}$), 150.06 (*C*H$_c$), 150.01 (*C*H$_{\mathrm{bpy}}$), 149.96 (*C*H$_{\mathrm{bpy}}$), 149.90 (*C*H$_{\mathrm{bpy}}$), 146.15 (*C*q), 145.40 (*C*q), 145.33 (*C*q), 145.26 (*C*q), 142.98 (*C*H$_{\mathrm{bpy}}$), 142.83 (*C*H$_{\mathrm{bpy}}$), 138.58 (*C*H$_k$), 137.21 (*C*H$_d$), 135.54 (*C*q), 135.05 (*C*q), 134.84 (*C*q), 131.18 (*C*q), 129.39 (*C*H$_{\mathrm{guest}}$), 128.13 (*C*H$_{\mathrm{bpy}}$), 126.42 (*C*H$_{i'}$), 125.50 (*C*H$_i$), 125.39 (*C*H$_{b'}$), 125.00 (*C*H$_{g'}$), 124.86 (*C*H$_n$, H$_{n'}$), 124.66 (*C*H$_b$, H$_g$), 124.52 (*C*H$_{\mathrm{bpy}}$), 124.37 (*C*H$_{\mathrm{bpy}}$). The assignments were confirmed by ^{1}H–^{1}H-relay COSY, NOESY, and CH-COSY. IR (KBr) 3412.8, 3072.9, 2321.6, 1611.9, 1446.5, 1388.7, 1161.1, 1018.3, 1018.3, 826.4, 764.2, 665.9, 545.3 cm^{-1}. Anal. Calcd for **4b**·12(NO_2)·(**6**)·22.5H_2O: C, 39.77; H, 3.73; N, 13.25%. Found: C, 39.51; H, 3.38; N, 13.05%.

Self-Assembly of 4a·6: Ligand **2** (0.015 mmol, 3.5 mg) was suspended in D_2O solution (4.5 mL) of **5a** (0.0225 mmol, 6.5 mg) and the mixture was heated at 80 °C for 15 min. Then, **6** (0.14 mmol, 20.0 mg) was added and the solution was stirred for 9 h at room temperature. After excess **6** was filtered, ^{1}H NMR showed almost the quantitative formation of **4a·6** complex: ^{1}H NMR (500 MHz, D_2O, $SiMe_4$–$CDCl_3$ in a capillary) δ 9.58 (s, 2H, PyH_c), 9.50 (s, 2H, PyH_e), 9.49 (s, 2H, PyH_l), 8.88 (d, $J = 6.5$ Hz, 8H, PyH_m, PyH_f), 8.82 (s, 2H, PyH_j), 8.80 (d, $J = 6.5$ Hz, 4H, PyH_h), 8.73 (d, $J = 6.5$ Hz, 4H, PyH_a), 8.58 (s, 2H, PyH_d), 8.32 (s, 2H, PyH_k), 7.94 (d, $J = 7.0$ Hz, 4H, PyH_g), 7.92 (d, $J = 6.0$ Hz, 4H, PyH_n), 7.81 (d, $J = 6.5$ Hz, 4H, PyH_b), 7.36 (d, $J = 6.5$ Hz, 4H, PyH_i), 6.07 (bs, 4H, guest), 2.99 (bs, 8H, en), 2.97 (bs, 4H, en), 2.94 (bs, 12H, en); ^{13}C NMR (125 MHz, D_2O) δ 152.11 (*C*H), 151.93 (*C*H), 151.86 (*C*H), 151.28 (*C*H), 151.15 (*C*H), 150.84 (*C*H), 150.76 (*C*H), 150.38 (*C*H), 145.42 (*C*q), 145.22 (*C*q), 144.84 (*C*q), 137.09 (*C*H), 136.25 (*C*H), 134.64 (*C*q), 134.25 (*C*q), 133.98 (*C*q), 133.83 (*C*q), 131.05 (*C*q), 129.08 (*C*H), 124.69 (*C*H), 124.16 (*C*H), 124.00 (*C*H), 123.89 (*C*H), 47.08(*C*H$_2$), 46.90 (*C*H$_2$). The assignments were confirmed by ^{1}H–^{1}H-relay COSY, and NOESY. CSI-MS (H_20 + DMF) *m/z* 830.3 [**4a**-$(NO_3)_3$]$^{3+}$, 680.0 [**4a**-$(NO_3)_4$·$(\mathrm{dmf})_4$]$^{4+}$, 661.7 [**4a**-$(NO_3)_4$·$(\mathrm{dmf})_3$]$^{4+}$, 643.5 [**4a**-$(NO_3)_4$·$(\mathrm{dmf})_2$]$^{4+}$, and 546.3 [**4a**-$(NO_3)_5$·$(\mathrm{dmf})_5$]$^{5+}$. While **4b·6** complex was successfully isolated by crystallization, all the attempts to isolate pure **4a·6** complex were unsuccessful because the addition of organic solvents did not cause crystallization or precipitation of the complex but the decomplexation of **4a·6** that led to further conversion of **4a** into oligomeric components.

Self-Assembly of (*R*,*R*)-4c·6: Ligand **2** (0.015 mmol, 3.5 mg) was suspended in D_2O solution (4.5 mL) of **5c** (0.0225 mmol, 7.9 mg) and the mixture was heated at 80 °C for 15 min. Then, **6** (0.14 mmol, 20.0 mg) was added and the solution was stirred for 9 h at room temperature. After excess **6** was filtered, ^{1}H NMR showed almost the formation of (*R*,*R*)-**4c·6** as a 1 : 1.3 diastereomer mixture: ^{1}H NMR (500 MHz, D_2O, $SiMe_4$–$CDCl_3$ in a capillary) **major isomer**: δ 9.54 (s, 2H, PyH_c), 9.50 (s, 2H, PyH_e), 9.38 (s, 2H, PyH_l), 8.90–8.82 (m, 14H, PyH_a, H_f, H_j, H_m), 8.75 (d, $J = 6.5$ Hz, 4H, PyH_h), 8.58 (s, 2H, PyH_d), 8.28 (s, 2H, PyH_k), 7.96–7.89 (m, 8H, PyH_g, H_n), 7.86 (d, $J = 7.0$ Hz, 4H, PyH_b), 7.32 (d, $J = 6.5$ Hz, 4H, PyH_i), 6.06 (bs, 4H, guest), 2.76, 2.08, 1.71, 1.38, 1.21 (bs, 60H, cyclohexane). **minor isomer**: δ 9.62 (bs, 4H, Py$H_{c'}$, $H_{l'}$), 9.49 (s, 2H, Py$H_{e'}$), 8.90–8.82 (m, 14H, Py$H_{f'}$, $H_{j'}$, $H_{h'}$, $H_{m'}$), 8.66 (d, $J = 7.0$ Hz, 4H, Py$H_{a'}$), 8.55 (s, 2H, Py$H_{d'}$), 8.34 (s, 2H, Py$H_{k'}$), 7.96–7.89 (m, 8H, Py$H_{g'}$, $H_{n'}$), 7.76 (d, $J = 6.5$ Hz, 4H, Py$H_{b'}$), 7.41 (d, $J = 6.5$ Hz, 4H, Py$H_{i'}$), 6.06 (bs, 4H, guest), 2.76, 2.08, 1.71, 1.38, 1.21 (bs, 60H, cyclohexane). The assignments were confirmed by ^{1}H–^{1}H-relay COSY, NOESY. ^{13}C NMR was unassignable due to the overlap of many signals from two diastereomers. CSI-MS (H_20 + DMSO) *m/z* 938.0 [**4c**-$(NO_3)_3$]$^{3+}$, 765.8 [**4c**-$(NO_3)_4$·$(\mathrm{dmso})_4$]$^{4+}$, 746.0 [**4c**-$(NO_3)_4$·$(\mathrm{dmso})_3$]$^{4+}$, 727.8 [**4c**-$(NO_3)_4$·$(\mathrm{dmso})_2$]$^{4+}$, 708.0 [**4c**-$(NO_3)_4$·(dmso)]$^{4+}$, and 600.4 [**4c**-$(NO_3)_5$·$(\mathrm{dmso})_4$]$^{5+}$.

Self-Assembly of (*S*,*S*)-4c·6: This complex was obtained in a similar way by the reaction of ligand **2** and (*S*,*S*)-**5c** in D_2O.

X-ray Crystal Structure Determination of 4b·6: [21] The diffraction was collected on a Siemens SMART/CCD diffractometer. Diffracted data were corrected for absorption using the SADABS[19] program. SHELXTL[20] was used for the structure solution and refinement was based on F^2, Goodness-of fit on $F^2 = 0.981$. All non-hydrogen atoms except a few atoms of water and nitrate ions, which have high thermal parameters, were refined anisotropically. Hydrogen atoms were fixed in calculated positions and refined isotropically with thermal parameters based upon the corresponding C-atoms [U(H) = 1.2 Ueq (C)]. Fractional coordinates, bond lengths and angles and anisotropic displacement parameters have been deposited as supporting information. Crystal data are as follows: triclinic, space group P-1; $a = 18.487(4)$ Å, $b = 22.325(5)$ Å, $c = 23.825(6)$ Å; $a = 110.435(4)°$, $b = 93.316(5)°$, $g = 99.761(5)°$; $V = 9007(4)$ Å^3; $D_c = 1.566$ Mg/m^3; $Z = 2$; $F(000) = 4344$; 31286 unique reflections out of 47921 with $I > 2\sigma(I)$; final R-factor $R_1 = 0.1304$ [$R_1 = 0.2919$ (all data)]; w$R_2 = 0.3067$ [w$R_2 = 0.3529$ (all data)]. The R-factor is high though all anions and 47 water molecules per cage were found and refined. The high R-factor could be due to the small size and weak diffraction of the crystal. However the crystal structure provides reliable evidence for the proposed structure of **4b·6**.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 176954.

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