Electronic Supplementary Information (ESI)

Synthesis, Conformational and Host-Guest Properties of Water-Soluble Pillar[5]arene

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Experimental

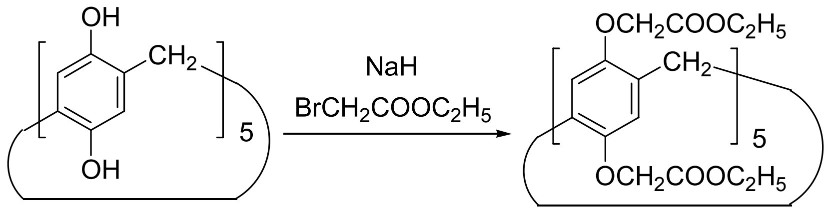
Materials. All solvents and reagents were used as supplied.

Measurements. The ^{1}H NMR spectra were recorded at 400 MHz and 500 MHz and ^{13}C NMR spectra were recorded at 100 MHz and 125 MHz with a JEOL-JNM EL400 and ECA500 spectrometers, respectively. Fluorescence spectra were recorded on a Hitachi F-2500 fluorescence spectrometer at room temperature. UV-Vis absorption spectra were recorded with a JASCO V-670 spectrophotometer at room temperature. For fluorescence and UV-Vis measurements, one centimeter quartz cuvets were used.

Pillar[5]arene (1) was synthesized according to the previous paper.[1]

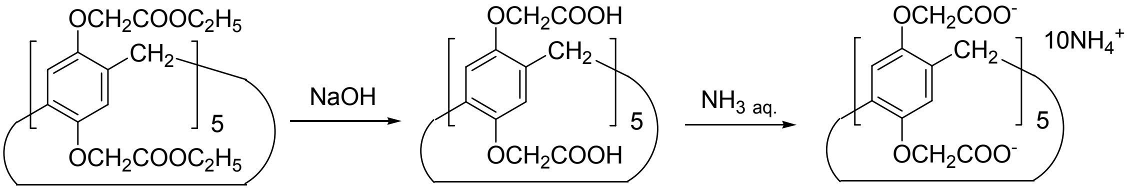
Ethoxycarbonylmethoxy-substituted pillar[5]arene (2). Under a nitrogen atmosphere Pillar[5]arene (**1**, 2.40 g, 3.93 mmol) was dissolved in DMF (30 mL) and THF (30 mL). Sodium hydride (3.00 g, 125 mmol) was added and the reaction mixture was stirred for 0.5 h. Then, excess of ethyl bromoacetate (9.00 mL, 81.0 mmol) was added and the reaction mixture was heated at 60 °C for 48 h. After removal of the solvent, the resulting solid was dissolved in CH_2Cl_2 and water. The organic layer was dried over anhydrous Na_2SO_4. After filtration, solvents were evaporated to give a solid. The remained solid was subjected to column chromatography (silica gel; CH_2Cl_2:acetone = 100:0 to 95:5). The first fraction containing product was concentrated and crystallized from acetone. (**2**, 0.620 g, 0.420 mmol, Yield: 10.7%.) ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.04 (s, 10H, phenyl protons), 4.55 (dd, 20H, methylene protons at both rims), 4.09 (m, 20H, ethyl protons), 3.86 (s, 10H, protons from methylene bridge), 0.96 (m, 30H, ethyl protons).

^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 196.3 (C of C=O), 148.9, 128.7, 114.4 (C of phenyl), 65.7 (C of methylene at both rims), 60.8 (C of ethyl) 29.2 (C of methylene bridge), 13.8 (C of ethyl). Anal. Calcd for C75H90O30: C, 61.22; H, 6.16. Found: C, 61.00; H, 6.13. MS(FAB) Calcd for C75H90O30 $[M]^+$: 1471, found 1471. Melting point (T_m): 196.7 °C.



Pillar[5]arene (**1**) **2**

Carboxylic Acid Groups-Substituted Pillar[5]arene (3). Compound **2** (0.150 g, 0.102 mmol), NaOH (0.300 g), ethanol (15 mL), water (15 mL) and THF (15 mL) were refluxed for 24 h. To the solution, diluted aqueous HCl was added. The precipitated solid was collected by filtration. The solid was washed with water several times and dried under reduced pressure. (**3**, 0.175 g, 0.147 mmol, yield: 72.0%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 12.96 (br, 10H, protons from COOH moieties), 7.11 (s, 10H, phenyl protons), 4.71 (d, 10H, inner methylene protons at both rims), 4.42 (d, 10H, outer methylene protons at both rims), 3.74 (s, 10H, protons from methylene bridge). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 170.5 (C of C=O), 148.4, 128.0, 114.2 (C of phenyl), 65.0 (C of methylene at both rims), 28.6 (C of methylene bridge). HRMS (FAB) Calcd for C55H51O30 $[M]^+$: 1191.2465, found 1191.2465. Melting point (T_m): 297.3 °C. To the suspension of compound **3** (200 mg, 0.168 mol) in aqueous solution (50 mL), aqueous ammonia solution (0.30 mL) was added. The heterogeneous suspension became a homogeneous solution by adding aqueous ammonia solution. The resulting solution was evaporated to give the salt (**4**), quantitatively. ^{1}H NMR (D_2O, 400 MHz, ppm): δ 6.61 (s, 10H, phenyl protons), 4.21 (s, 20H, methylene protons at both rims), 3.72 (br, 10H, protons from methylene bridge). ^{13}C NMR (D_2O, 125 MHz, ppm): δ177.8 (C of C=O), 151.2, 130.9, 117.7 (C of phenyl), 69.1 (C of methylene at both rims), 30.9 (C of methylene bridge).



2 **3** **4**

^{1}H and ^{13}C NMR Spectra of 2

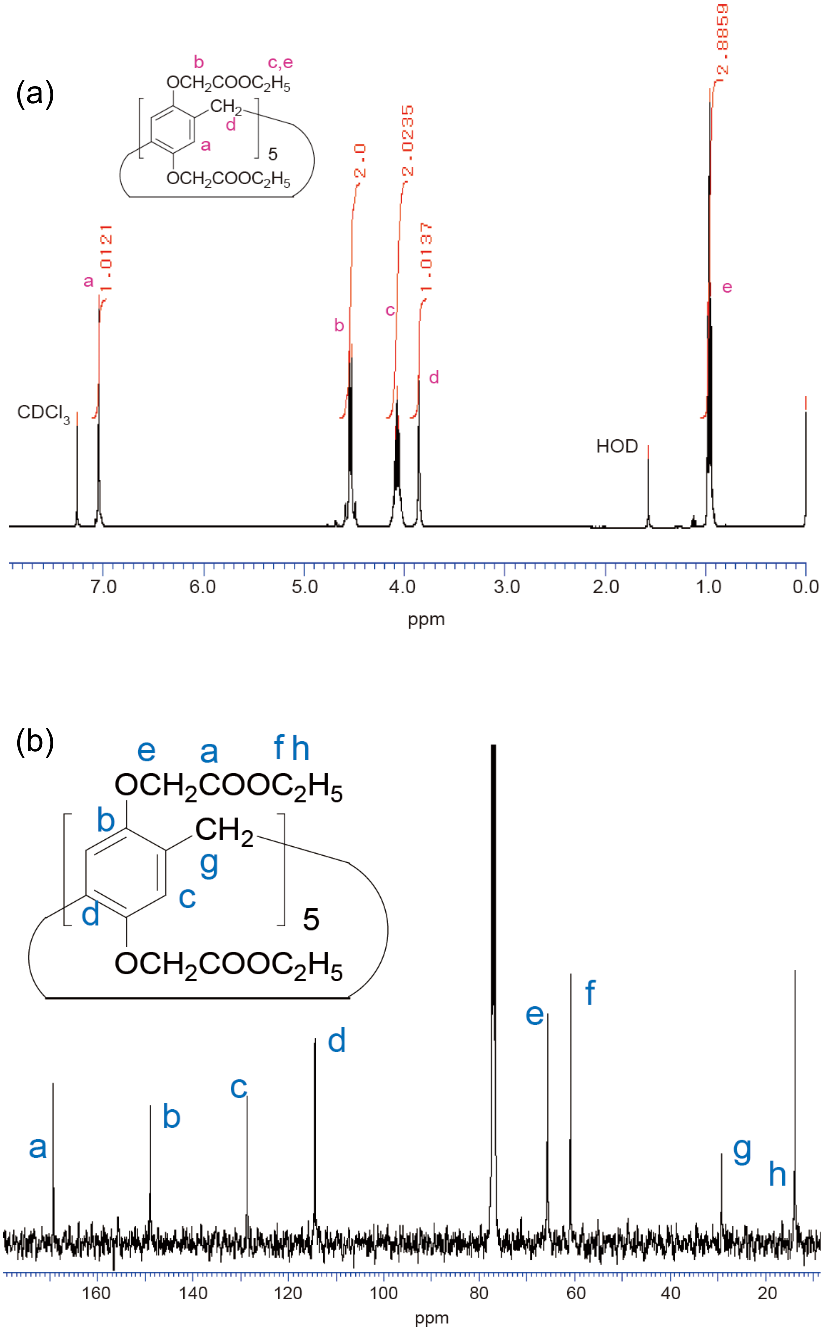


Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of **2** in $CDCl_3$.

^{1}H and ^{13}C NMR Spectra of 3

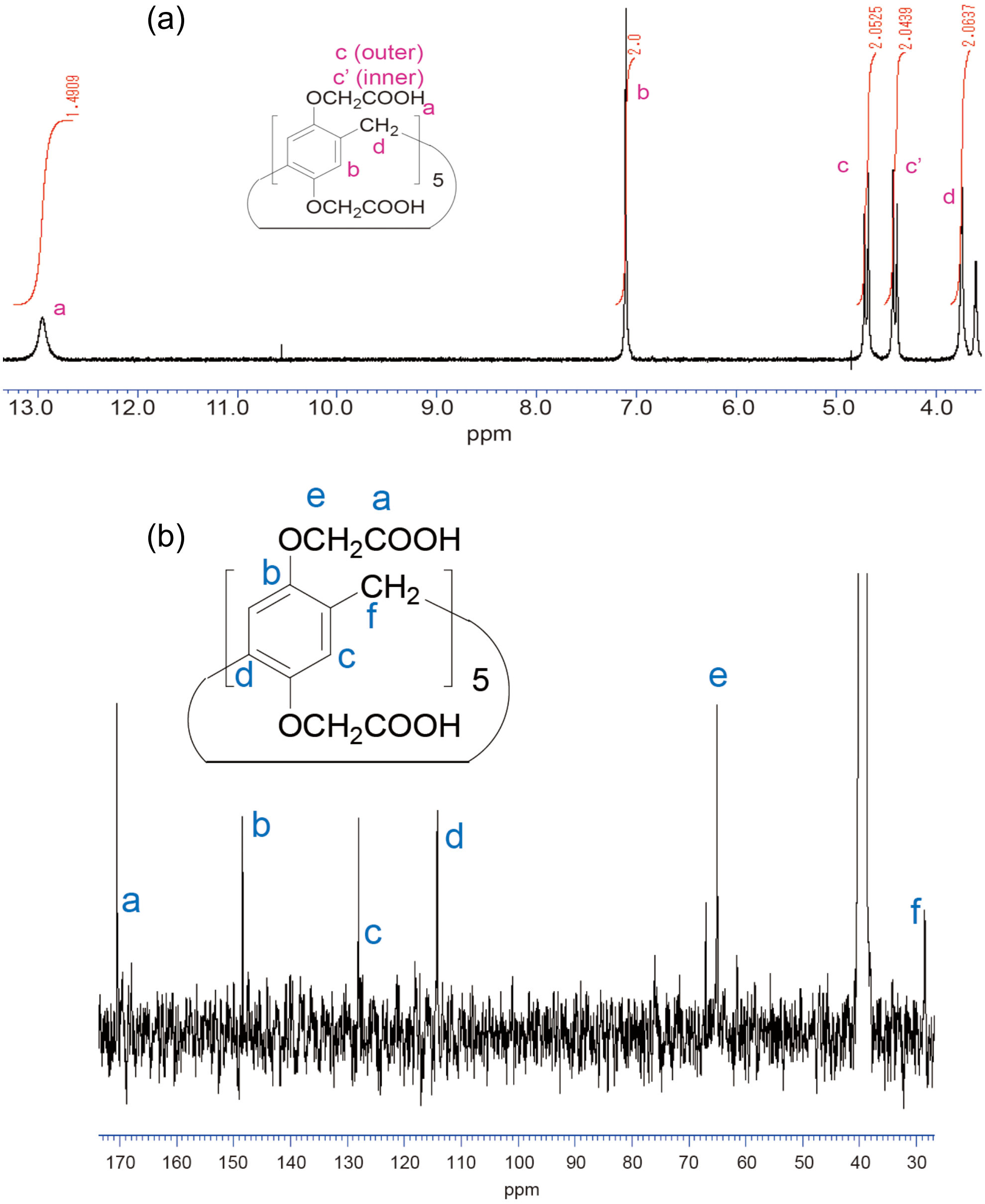


Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra of **3** in DMSO-d_6.

^{1}H and ^{13}C NMR Spectra of 4

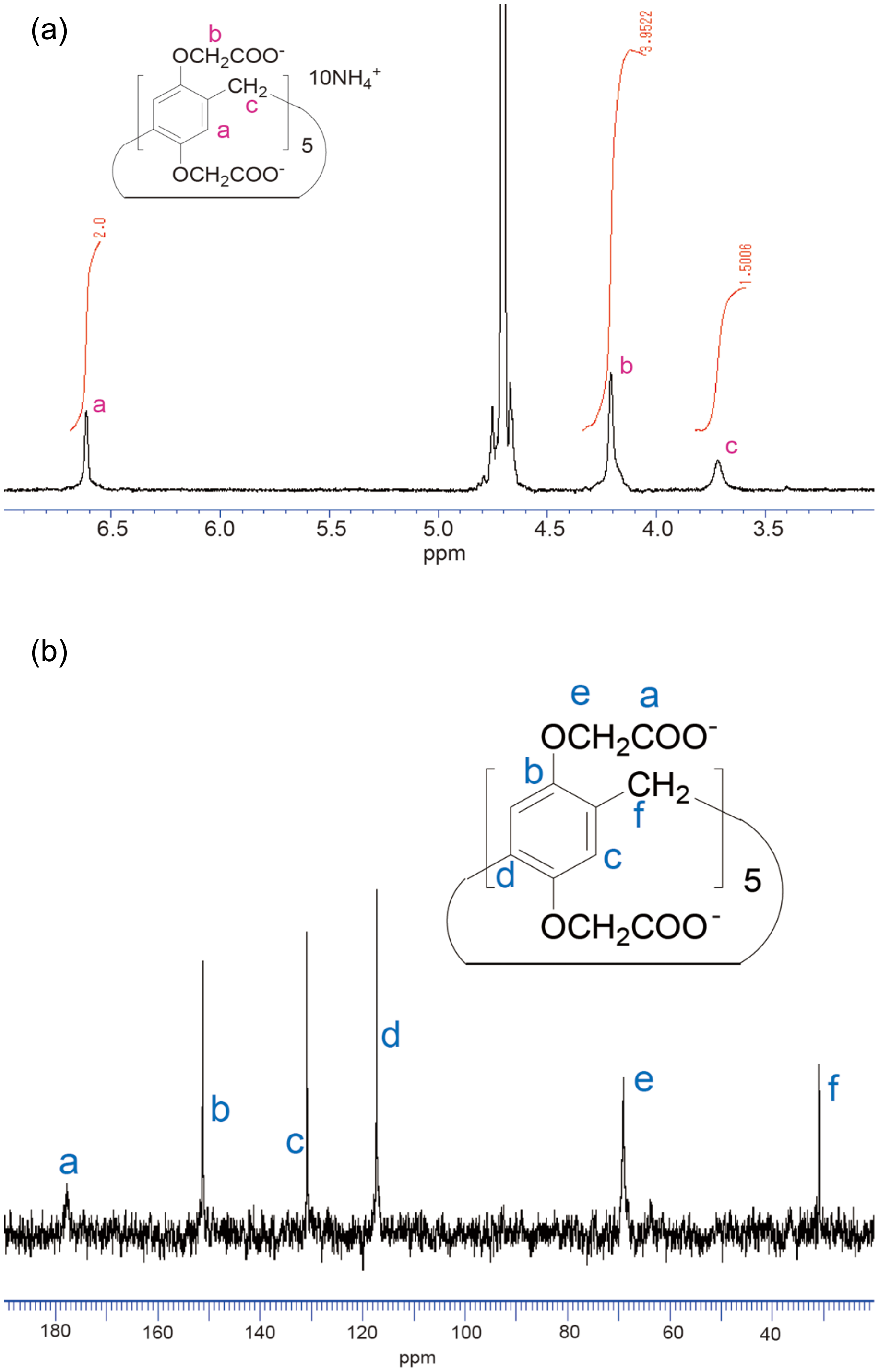


Figure S3. (a) ^{1}H and (b) ^{13}C NMR spectra of **4** in D_2O.

^{1}H NMR Spectra of 2 after Etherification (before Isolation of Conformers)

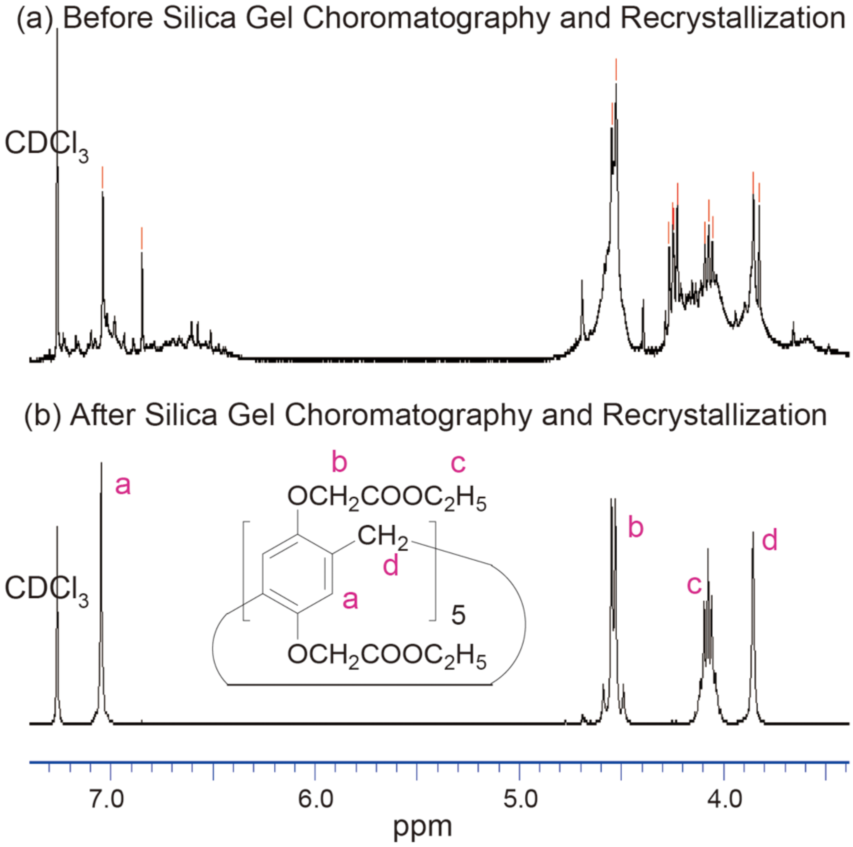


Figure 4S. ^{1}H NMR spectra of **2** (a) before and (b) after silica gel and recrystallization in $CDCl_3$. Complex split peaks from the phenyl (protons a) and methylene bridge (protons d) indicate formation of various conformers.

Variable-Temperature ^{1}H NMR Spectra of 2

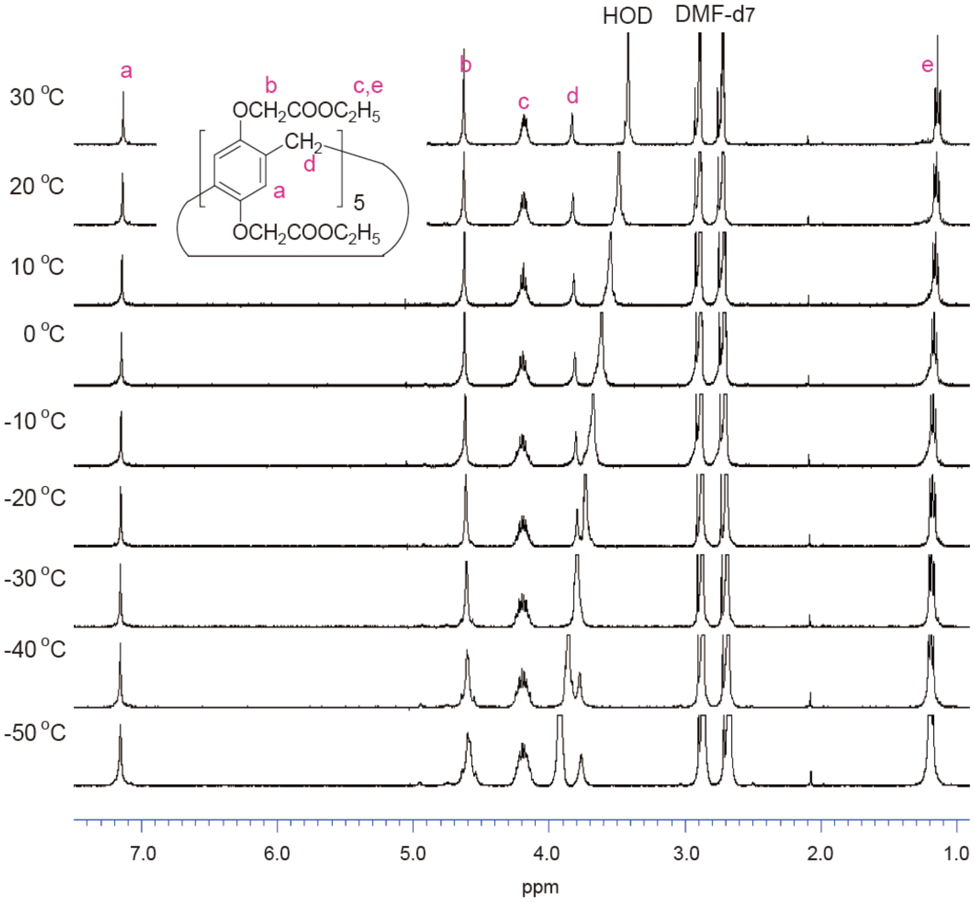


Figure 5S. Variable-temperature ^{1}H NMR spectra of **2** in DMF-d_7. Proton peaks of **2** were not split even at the low temperatures.

Variable-Temperature ^{1}H NMR Spectra of 3

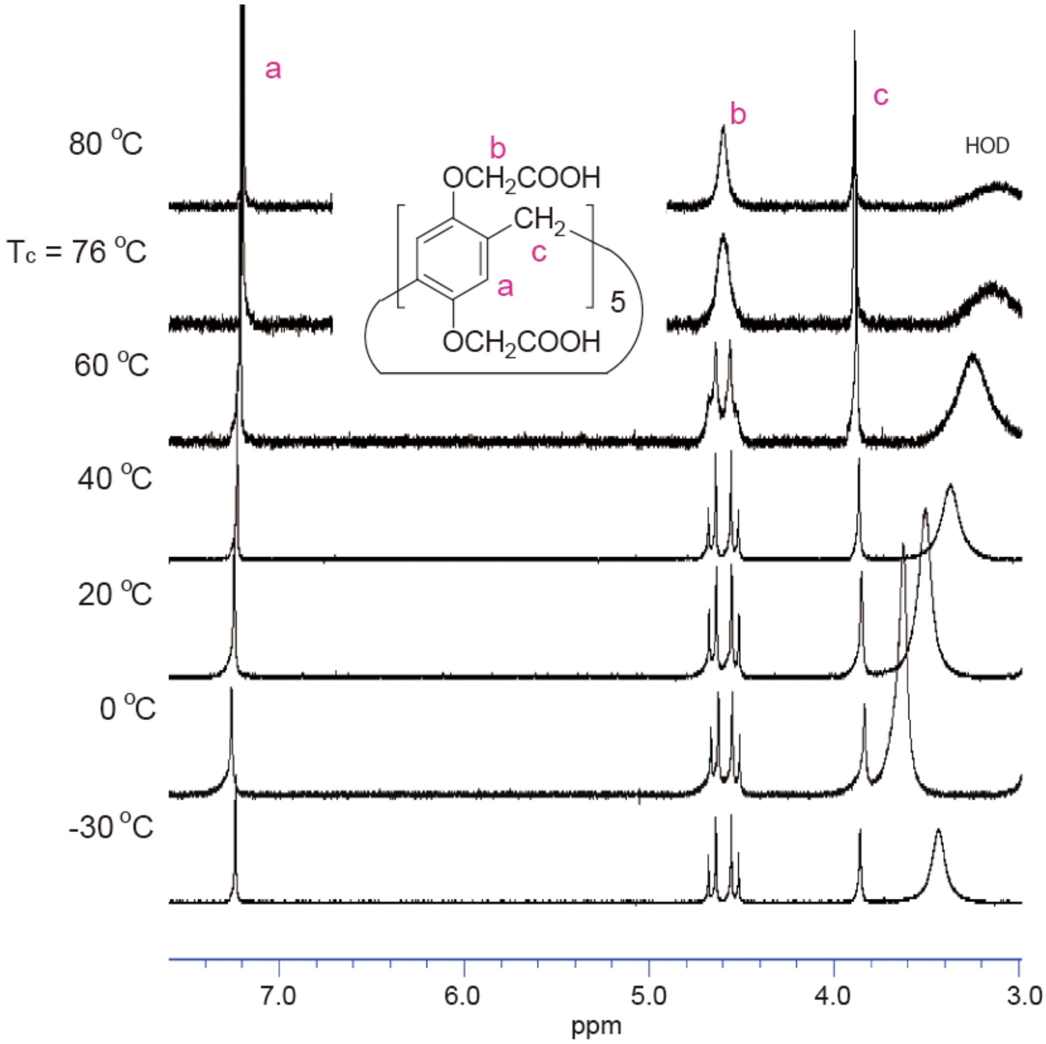


Figure 6S. Variable-temperature ^{1}H NMR spectra of **3** in DMF-d_7. The coalescence of the peak from the methylene protons at both the rims (peak b) was observed at 76 °C.

Variable-Temperature ^{1}H NMR Spectra of Water-Soluble Pillar[5]arene (4) with DMeBpy

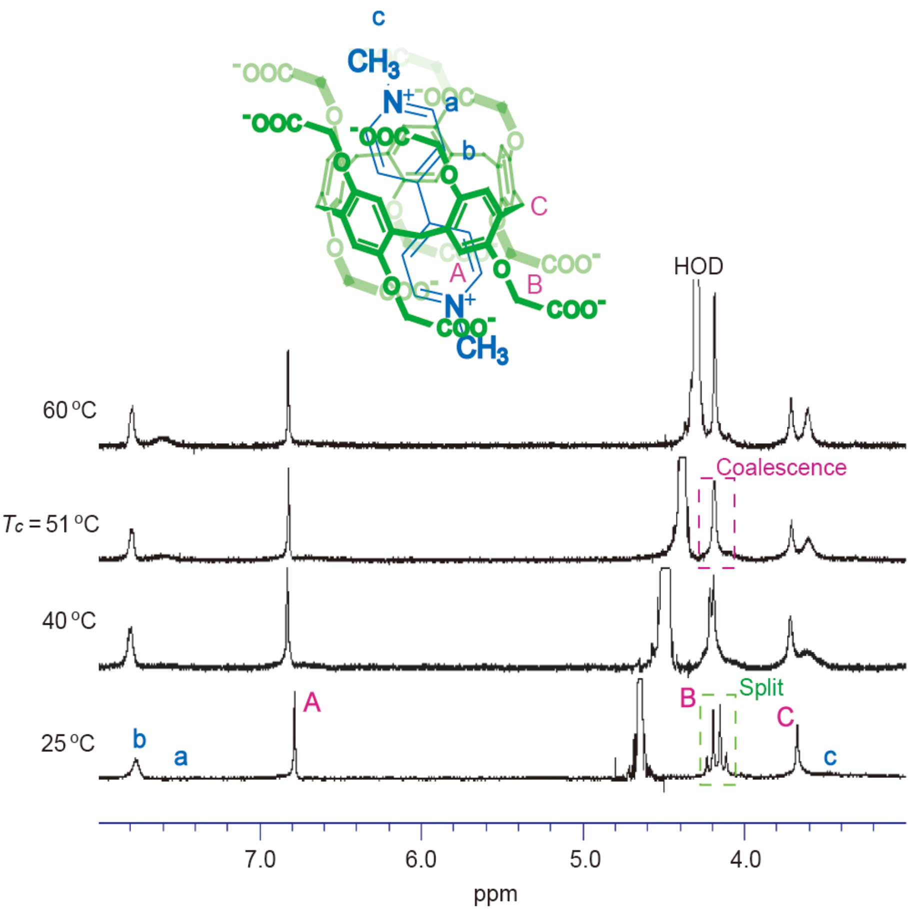


Figure 7S. Variable-temperature ^{1}H NMR spectra of the mixture of **4** (1.5 mM) and **DMeBpy** (2.0 mM) in D_2O. The coalescence of the peak from the methylene protons at both the rims (peak B) was observed at 51 °C.

Fluorescence Spectra of Water-Soluble Pillar[5]arene (4) with DMeBpy

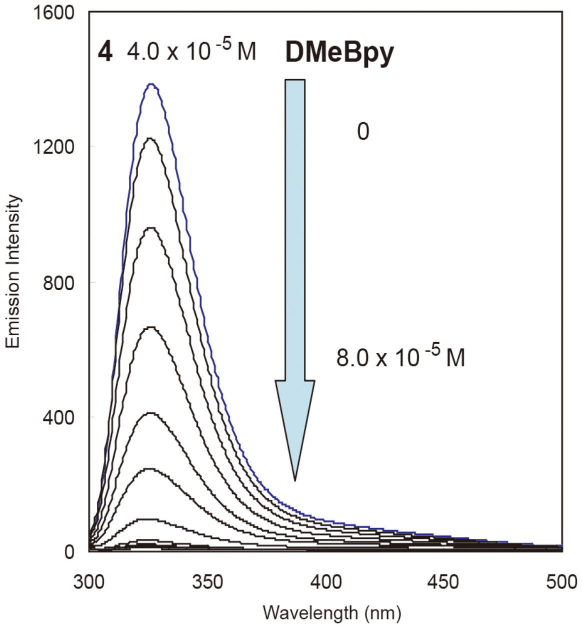
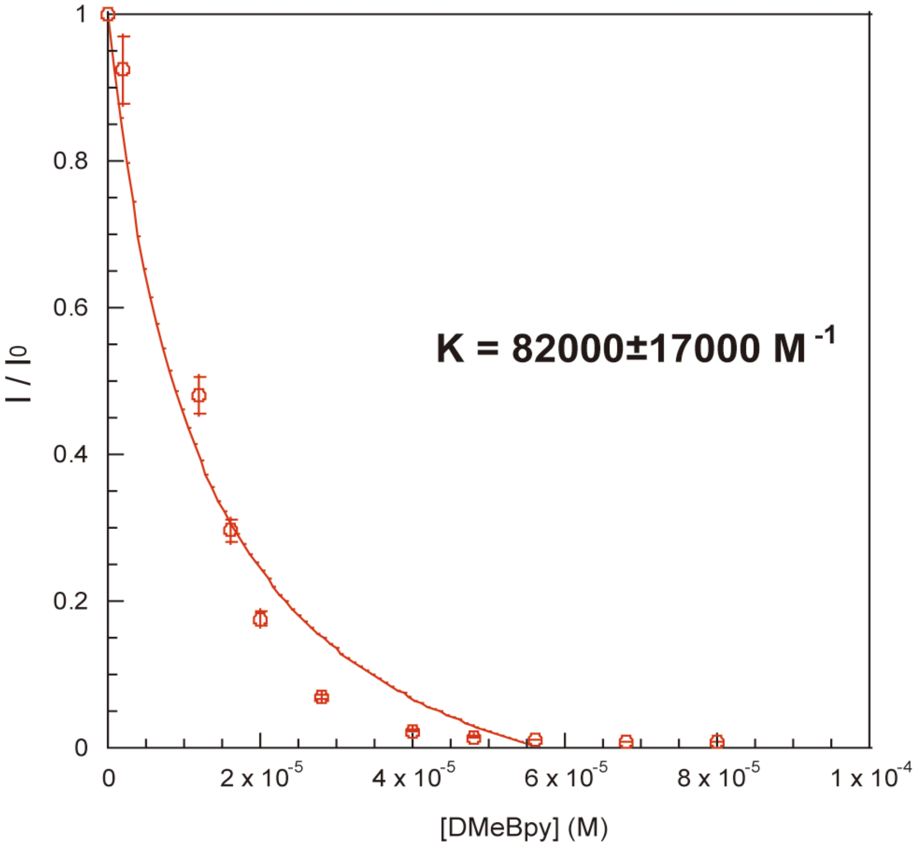


Figure 8S. Emission spectra of **4** (4.0 x 10^{-5} M) upon addition of **DMeBpy** (0-8.0 x 10^{-5} M) in aqueous media (excited at 291 nm). Upon addition of **DMeBpy**, emission from **4** was quenched, indicating the formation of the **4-DMeBpy** complex.

Determination of the Association Constants from Fluorescence Measurements



$$I/I_0 = \frac{(1+\alpha KC_{guest})}{(1+KC_{guest})} \qquad \text{(Eq. 1)}$$

Figure 9S. To determine the association constant (K) for the **4-DMeBpy** complex, steady-state fluorescence spectra were recorded at varying guest concentrations (C_{guest}). Changes in the ratios (I/I_0) of the fluorescence intensities at 333 nm from **4** upon addition of guest were calculated and plotted. The K value was determined to be 8.2 ± 1.7 x 10^4 M^{-1} for the **4-DMeBpy** complex by fitting data with Eq. 1, where α is a constant.[2]

References

1) T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.* 2008, **130**, 5022-5023.

2) K. A. Connors, In *Cyclodextrins, Comprehensive Supramolecular Chemistry*, ed. J. Szejtli and T. Osa, Pergamon, Oxford, UK, 1996, vol 3, p. 205.