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# A facile and efficient preparation of prism[6]arene and its dual responsive complexation with 1-adamantane ammonium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate

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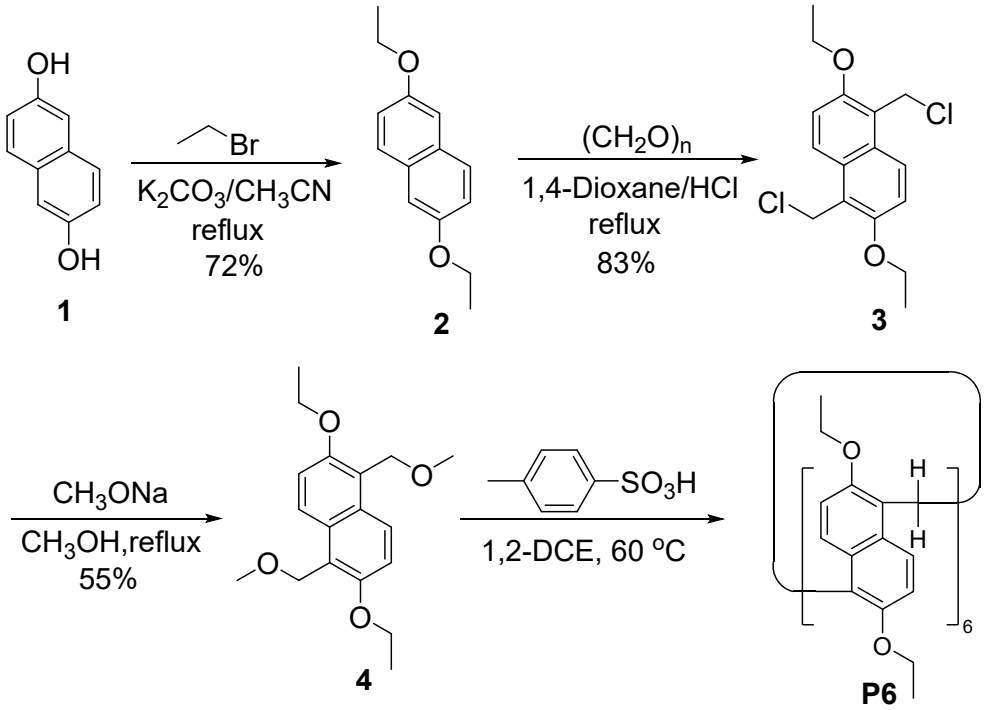
## Supporting Information


| | | |
|---|---|---|
| 1. | *Materials and methods* | S2 |
| 2. | *Synthetic route for prism[6]arene (**P6**)* | S2 |
| 3. | *Synthesis of **2*** | S2 |
| 4. | *Synthesis of **3*** | S4 |
| 5. | *Synthesis of **4*** | S6 |
| 6. | *Synthesis of prism[6]arene (**P6**)* | S8 |
| 7. | *The product of the reaction when using chlorobenzene as the solvent* | S10 |
| 8. | *Calculations of the diameter for **P6*** | S11 |
| 9. | *Synthesis of 1-adamantane ammonium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (**G**)* | S12 |
| 10. | *Fluorescence titration experiments of **P6** and **G** in $CHCl_3$* | S13 |
| 11. | *Complexation of **P6** and **G** with pH control* | S15 |
| 12. | *Electrospray ionization mass spectrum of a solution of **P6** and **G*** | S17 |
| 13 | *$^1$H NMR spectrum of 1 mM of **P6** and **G*** | S17 |
| 14. | *X-ray crystallographic data* | S18 |

*1. Materials and methods*

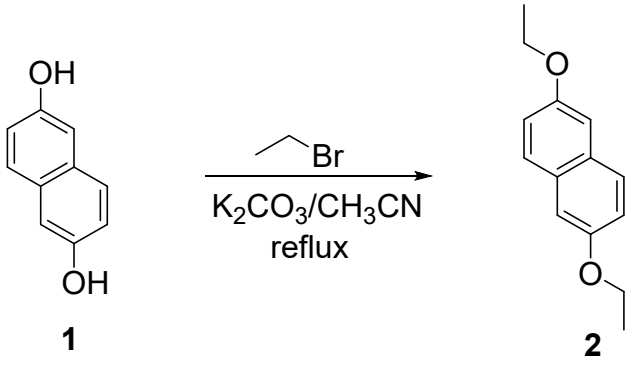
All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. All the NMR spectra were collected on a Bruker Ascend™ 400 MHz spectrometer. The melting points were collected on a SGW®X-4A micro melting point apparatus. The fluorescence experiments were conducted on a F-7000 spectrofluorophotometer (Japan Hitachi Nake high-tech enterprise)

*2. Synthetic route for prism[6]arene (**P6**)*




***Scheme S1***. Synthesis of prism[6]arene (**P6**).

*3. Synthesis of **2**[S1]*



In a 250 mL three-neck flask, 2,6-naphthalenediol (6.40 g, 0.040 mol), $K_2CO_3$ (5.53 g, 0.040mol), bromoethane (34.0 g, 0.310 mol) and $CH_3CN$ (100 mL) were added. The reaction mixture was stirred at reflux for 24 h. After the solid was filtered off, the solvent was removed. The residue was partitioned between water (100 mL) and dichloromethane (100 mL). The water layer was extracted with dichloromethane (50 mL × 3). The combined organic phase was washed with water (100 mL) and saturated NaCl solution (100 mL), and dried over anhydrous $Na_2SO_4$. After filtration, evaporation, and recrystallization in methanol, **2** was obtained as a white solid (6.22 g, 72%), M.p. 157.5–158.2 °C. $^1$H NMR (400 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): 7.62 (d, $J$ = 8.8 Hz, 2H), 7.13 (dd, $J$ = 8.8, 2.4 Hz, 2H), 7.09 (d, $J$ = 2.4 Hz, 2H), 4.12 (q, $J$ = 7.0 Hz, 4H), 1.47 (t, $J$ = 7.0 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): δ 155.48, 129.84, 128.20, 119.30, 107.04, 63.59, 15.02.

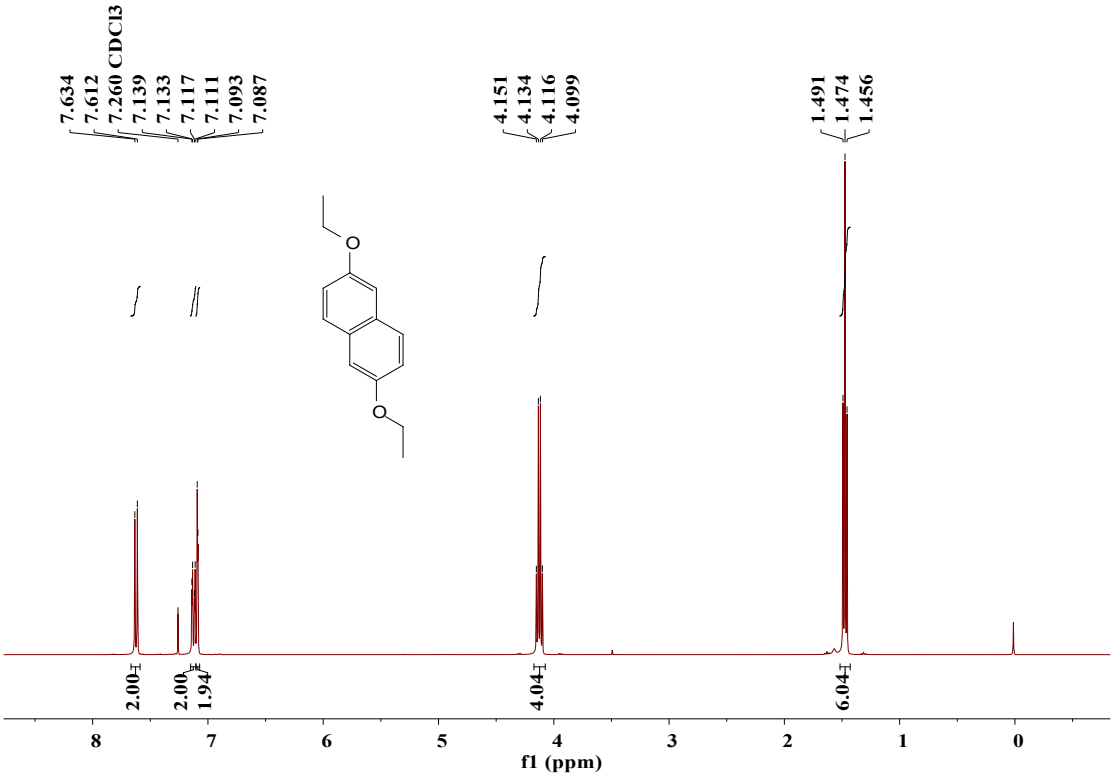



***Figure S1***. $^1$H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **2**.

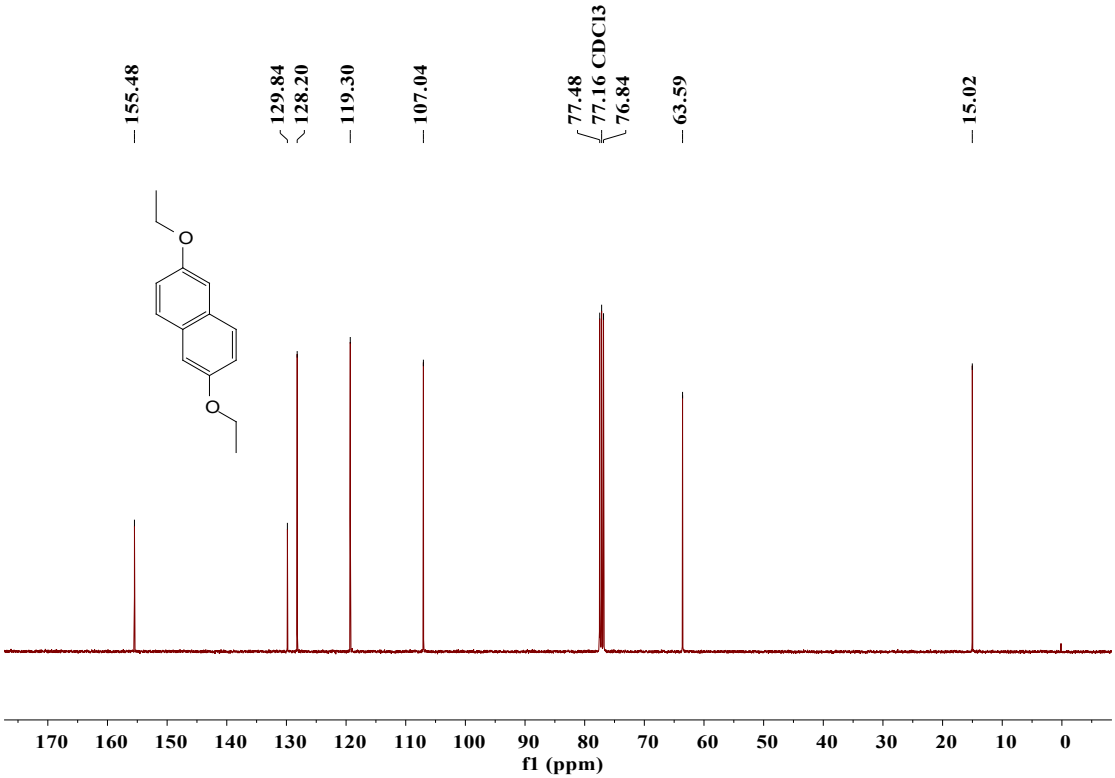
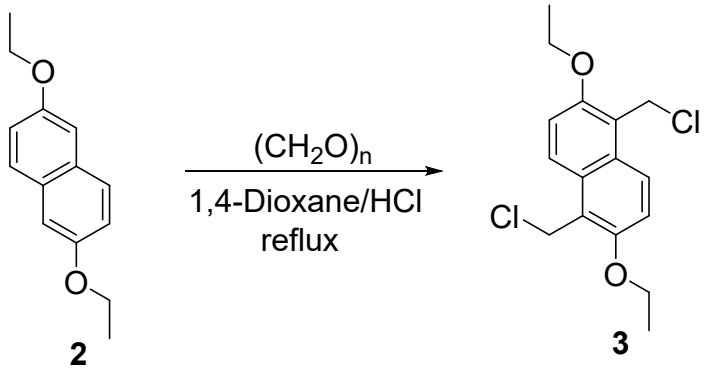



***Figure S2***. $^{13}$C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **2**.

*4. Synthesis of **3***




Compound **2** (2.20 g, 10.2 mmol), $(CH_2O)_n$ (0.916 g, 30.5 mmol), 1,4-dioxane 50 ml, and 10 ml 36%-38% HCl solution were added to an 150 ml three-necked flask, and the mixture was stirred at reflux temperature for 12 h. After the reaction solution cooled, the occurring precipitation were filtered and washed several times with distilled water to obtain a white solid of 2.65 g. Yield: 83%, M.p. (decomposition at 132 °C). $^1$H NMR (400 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): 8.05 (d, $J$ = 8.0 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 5.16 (s, 4H), 4.25 (q, $J$ = 8.0 Hz, 4H), 1.49 (t, $J$ = 8.0 Hz, 6H). $^{13}$C NMR

(100 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): δ 153.30, 128.25, 125.85, 119.34, 116.11, 65.57, 37.40, 15.31.

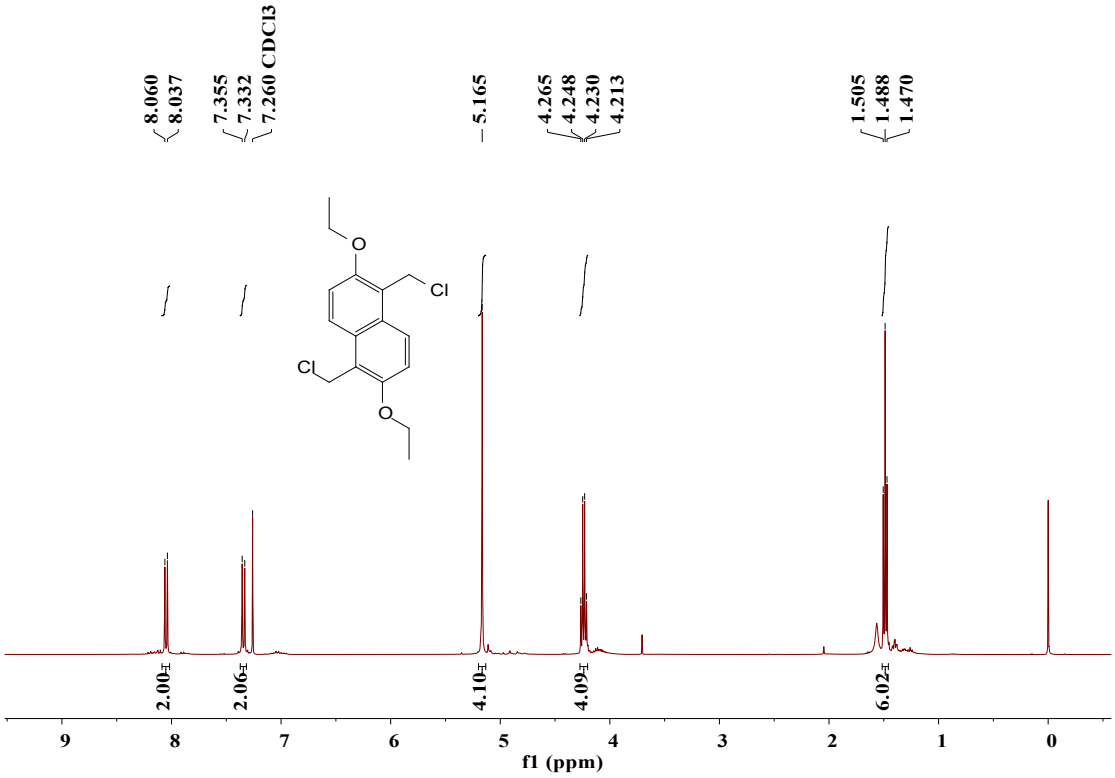



***Figure S3***. $^1$H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **3**.

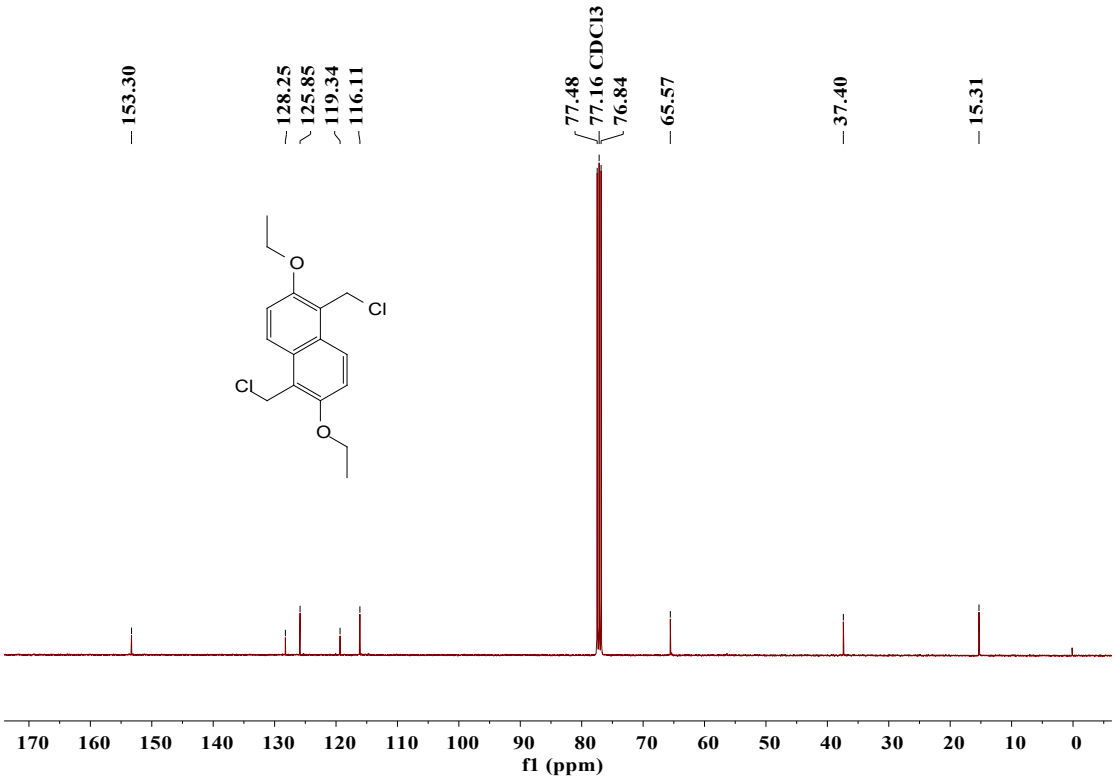
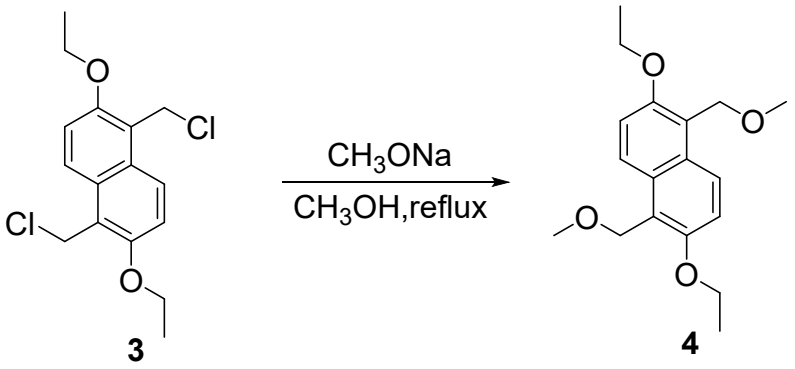



***Figure S4***. $^{13}$C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **3**.

*5. Synthesis of **4***




In a 150 ml round-bottom flask, compound **3** (0.460 g, 1.47 mmol), methanol (50 ml), $CH_3ONa$ (0.796 g, 14.7 mmol), were added and the mixture was under reflux for 8 h. After the reaction solution was concentrated, it was poured into ice water, and the precipitate was collected and filtered to obtain a white solid. After it was purified by chromatography on silica gel (chromatography), 0.247 g of **4** was obtained as a white solid (yield: 55%), M.p. 149–151 °C. $^1$H NMR (400 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): 8.08 (d, $J$ = 8.0 Hz, 2H), 7.29 (d, $J$ = 8.0 Hz, 2H), 4.97 (s, 4H), 4.18 (q, $J$ = 6.0 Hz, 4H), 3.40 (s, 6H), 1.45 (t, $J$ = 6.0 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): δ 153.56, 129.65, 126.21, 119.37, 116.05, 65.64, 64.68, 57.87, 15.34. HREI-MS: $m/z$ 327.1567 $[M + Na]^+$ (100%). $C_{18}H_{24}O_4$, 304.1675, found 304.1675, error 0 ppm.

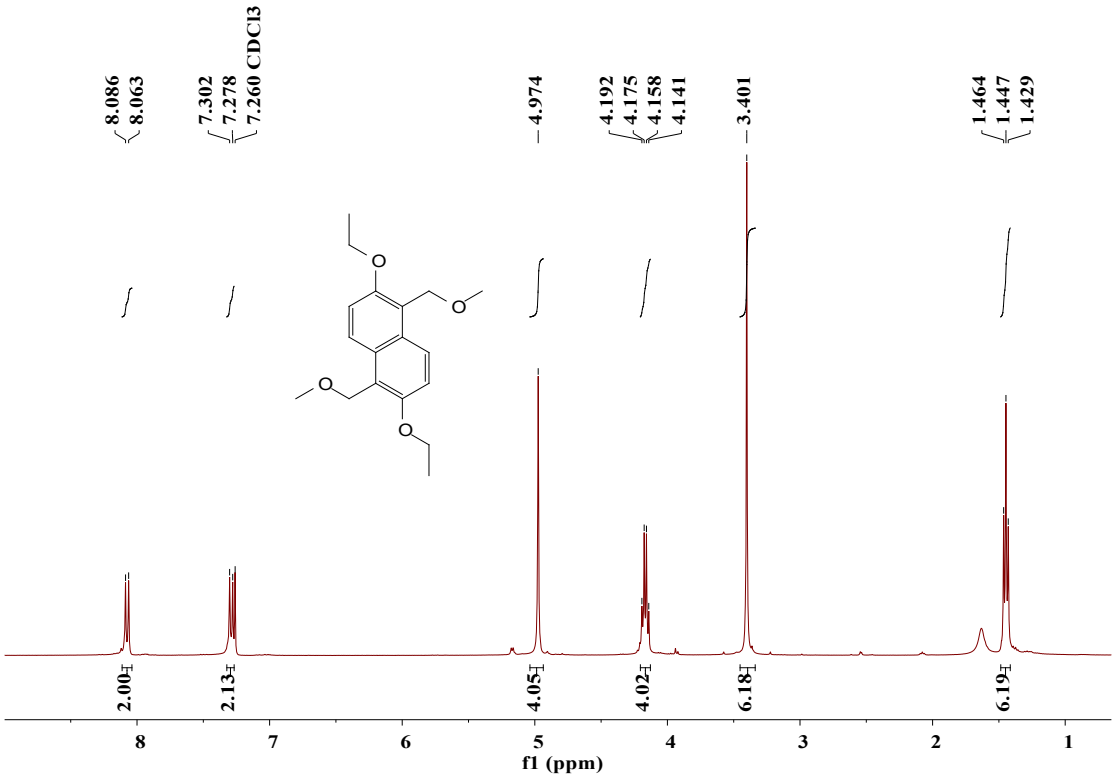



***Figure S5***. $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **4**.

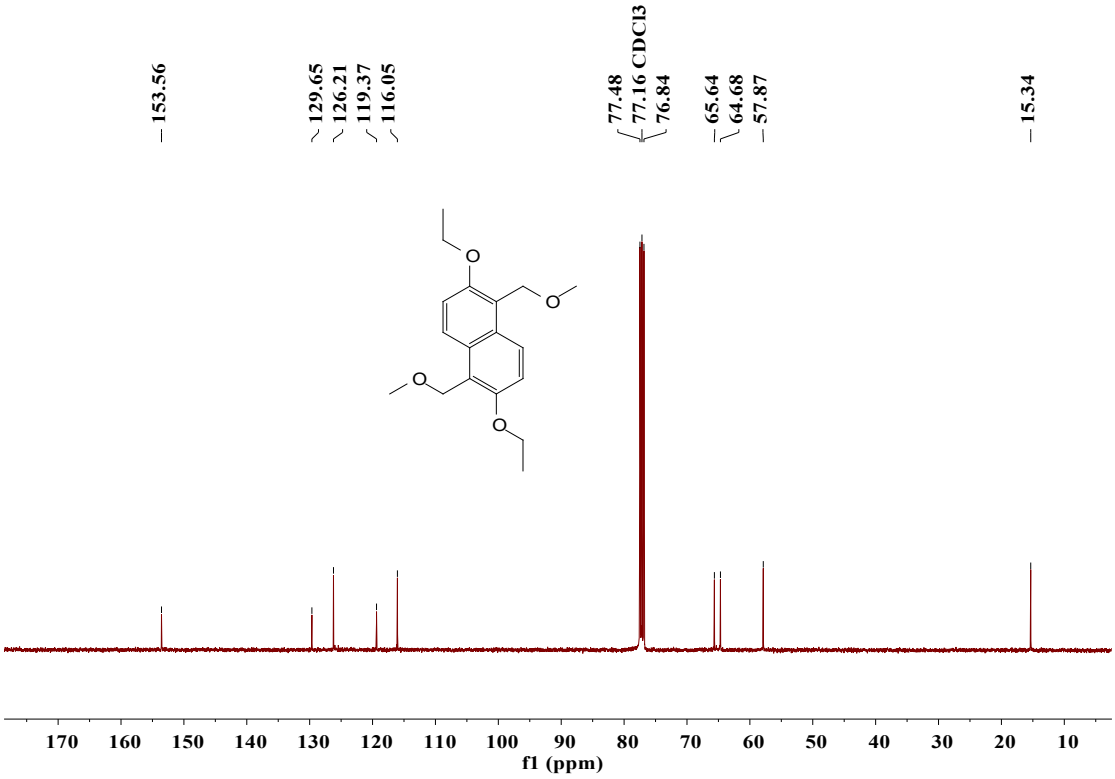
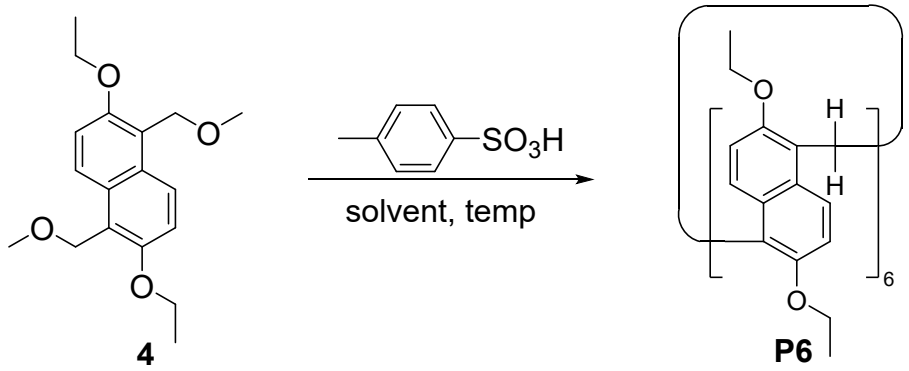



***Figure S6***. $^{13}$C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **4**.

*6. Synthesis of prism[6]arene (**P6**)*




Method 1: To a 100 mL round bottom flask **4** (153 mg, 0.503 mmol), 4-methylbenzenesulfonic acid monohydrate (95.7 mg, 0.503 mmol) and 1,2-dichloroethane (40 mL) were added. The mixture was heated at 60 ºC for 20 min. Then dichloromethane (20 mL) was added and the solution was washed with water (30 mL × 3). The solvent was removed and the residue was purified by chromatography on silica gel (petroleum ether/dichloroethane, *v*/*v* 2:1 → 1:2) to obtain prism[6]arene (P6) as a white solid (76.0 mg, 66%). The reactions in $CH_2Cl_2$ and $CHCl_3$ were conducted in the same process, and the results were shown in Table S1.

Method 2: To a 100 mL round bottom flask, **4** (198 mg, 0.651 mmol), 4-methylbenzenesulfonic acid monohydrate (124 mg, 0.651 mmol) and chlorobenzene (30 mL) were added. The mixture was heated at 60 ºC for 35 min. Then the reaction solution was added to 100 ml of methanol, a white solid appeared, which was filtered and dried to give **P6** (134 mg, 90%) as a white solid. The reaction in 1,1,2,2-tetrachloroethane was conducted in the same process, and the results were shown in Table S1. M.p. >340°C. $^1$H NMR (400 MHz, $CDCl_3$, room temperature) $\delta$(ppm): 8.23 (s, 4H), 7.80 (s, 4H), 7.47 (s, 4H), 7.40 (s, 4H), 6.91 (s, 4H), 6.29 (s, 4H), 4.90 (s, 8H), 4.36 (m, 20H), 3.07 (s, 4H), 1.45-1.68 (m, 28H), -0.87 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$, room temperature) $\delta$(ppm): δ 155.26, 154.90, 154.21, 132.85, 129.76, 128.16, 127.27, 126.86, 119.60, 118.11, 117.30, 69.38, 68.71, 68.37, 26.76, 24.63, 18.82, 16.81. HREI-MS: m/z calcd for $C_{90}H_{97}O_{12}$ $[M + H]^+$ (100%), 1369.6975, found 1369.6989, error 1 ppm.

Table S1 Solvent effects in the synthesis of **P6**

| Entry | Solvents | Temp(°C) | Time(min) | Yield(%) |
|---|---|---|---|---|
| 1 | 1,2-DCE | 60 | 20 | 66 |
| 2 | 1,2-DCE | 25 | 60 | trace |
| 3 | $CH_2Cl_2$ | 39.8 | 20 | 75 |
| 4 | $C_2H_2Cl_4$ | 25 | 40 | 60 |
| 5 | $C_2H_2Cl_4$ | 60 | 13 | 52 |
| 6 | $CHCl_3$ | 60 | 20 | 93 |
| 7 | $C_6H_5Cl$ | 60 | 35 | 90 |

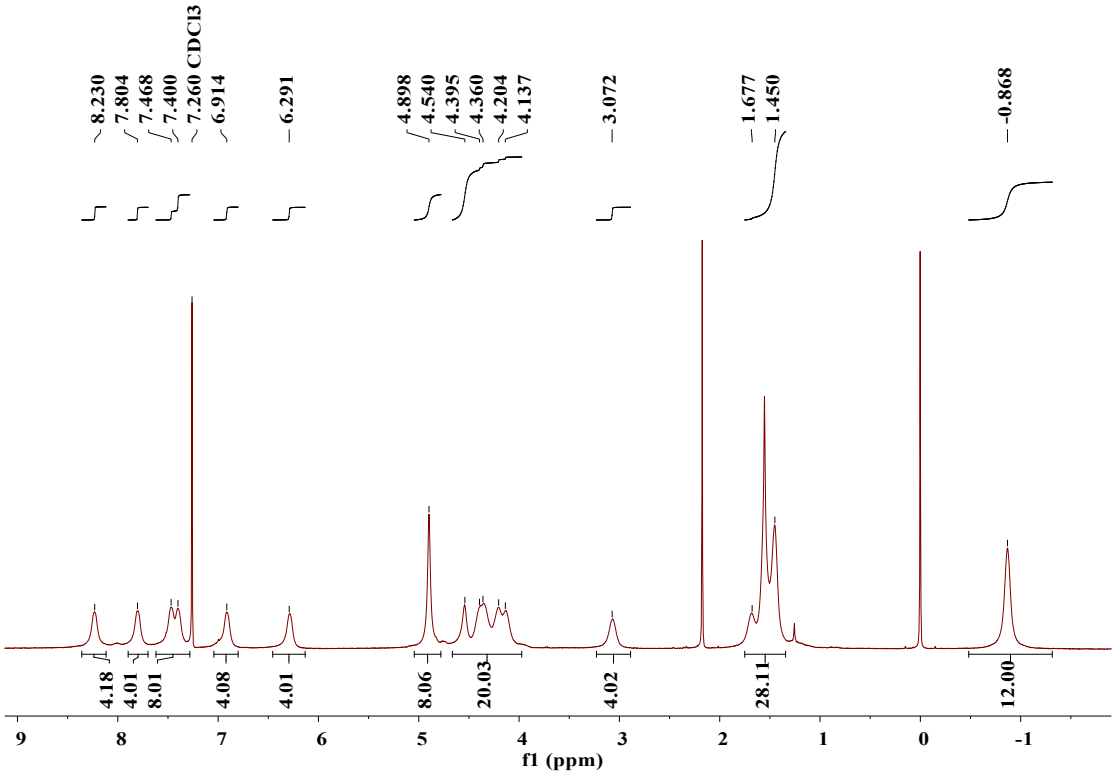



***Figure S7***. $^1$H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **P6**.

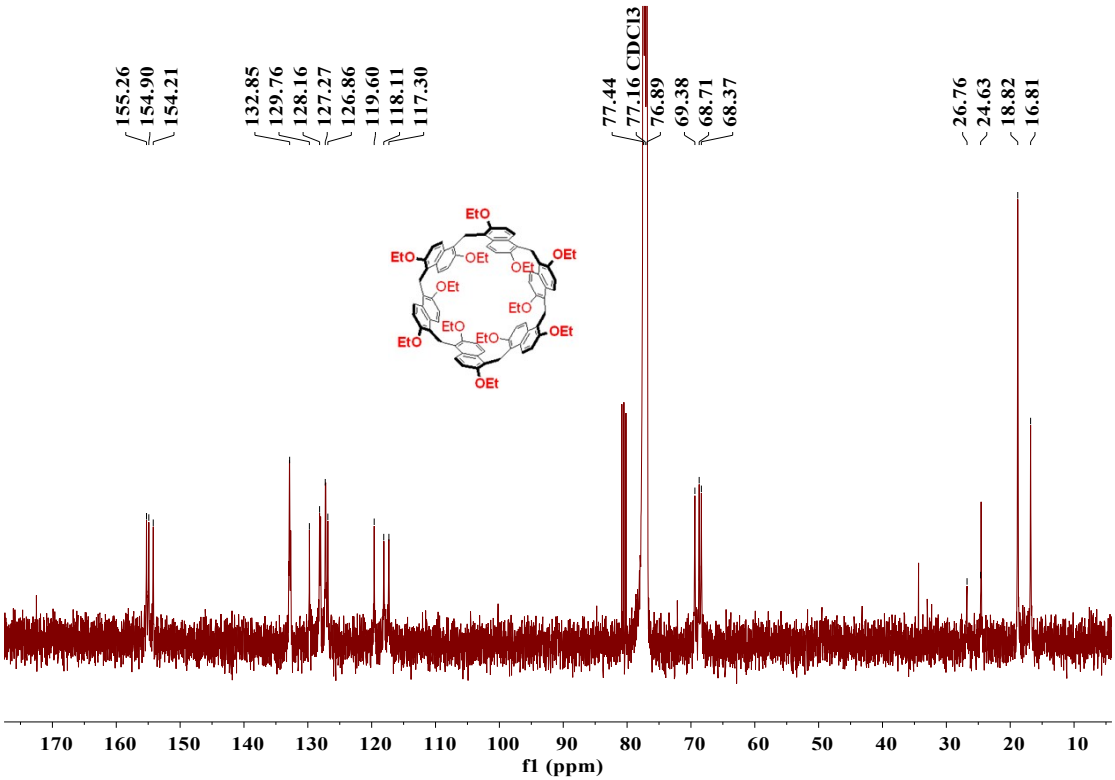



***Figure S8***. $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **P6**.

*7. The product of the reaction when using chlorobenzene as the solvent*

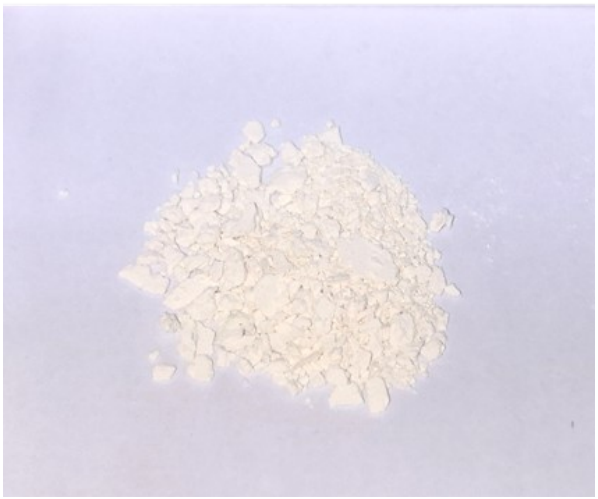


***Figure S9***. The white product of the reaction when using chlorobenzene as the solvent.

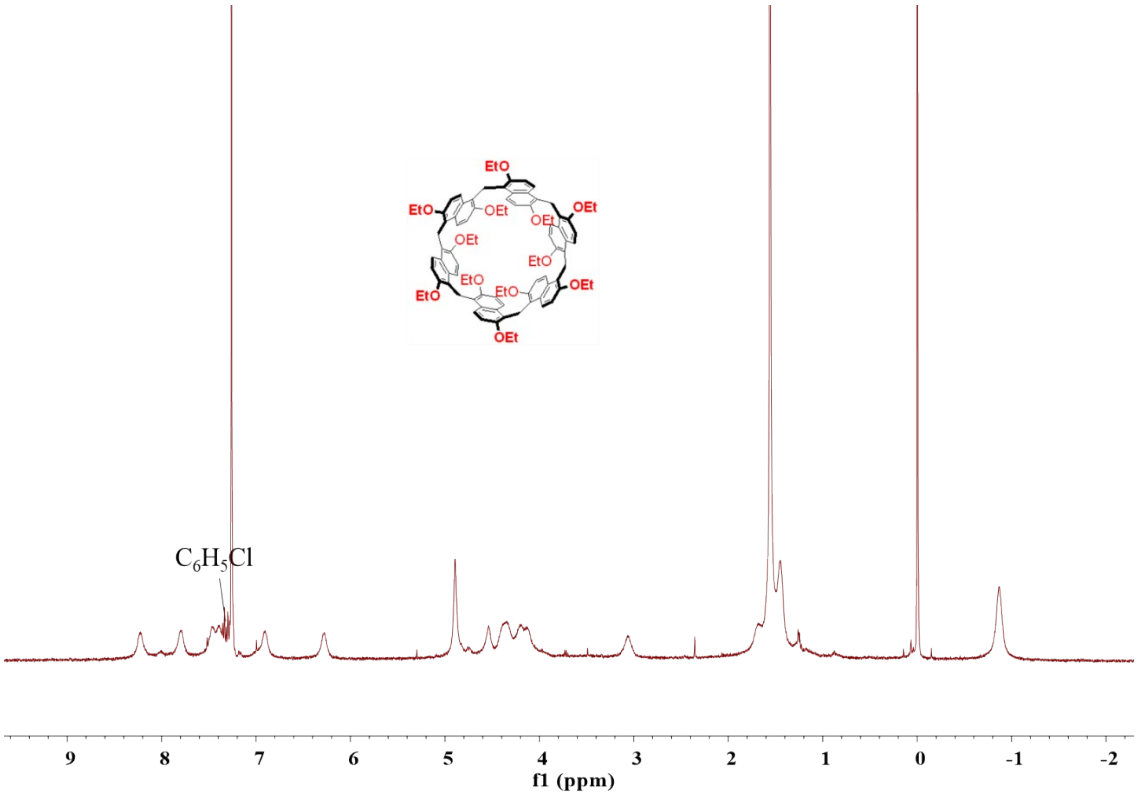
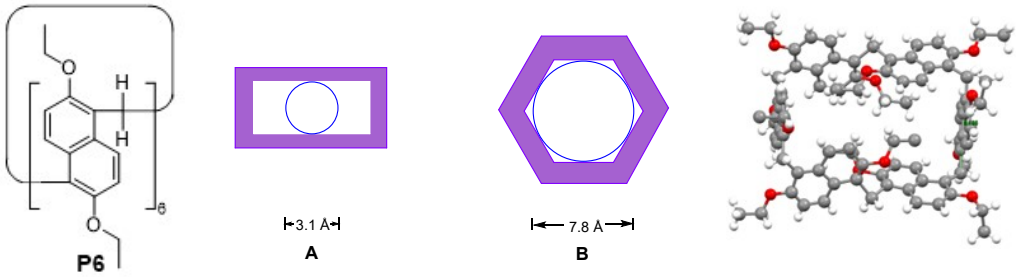



***Figure S10***. $^{1}H$ NMR spectrum (400 MHz, $CDCl_3$, room temperature) of white product.

*8. Calculations of the diameter for **P6***

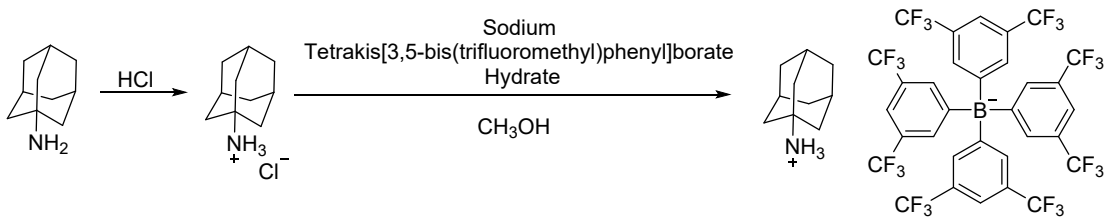



By treatment of the closed and open structures of the macrocycles as a nearly square cuboid-shape and a regular hexagonal prism, respectively, ignoring the substituents on the oxygen atoms of the repeating units, we can calculate the internal cavity diameter for the two states of the host molecule. The mean side length of the hexagon is $d_{c\text{-}c}$=6.46 Å. The van der waals radius of carbon atom is $r_{vdWc}$=1.70 Å.

The diameter **A** of the closed structure of the macrocycle is diameter of tangent circle in the cuboid. **A**= $d_{c\text{-}c}$-2* $r_{vdWc}$

The diameter **B** of the open structure of the macrocycle is diameter of hexagon inscribed circle. **B**= $d_{c\text{-}c}$/tan 30°-2* $r_{vdWc}$

*9. Synthesis of 1-adamantane ammonium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (**G**)*




**5** **6** **G**

To a round bottom flask was added **5** (200 mg, 1.32 mmol) and 36% HCl (30 mL), and the mixture was stirred at room temperature for 12 h. The solvent was then evaporated off. After drying under reduced pressure, the desired product **6** was obtained quantitatively. The solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate hydrate (285 mg, 0.32 mmol) in 20 ml dry methanol was added **6** (50 mg, 0.27 mmol). The resulting solution was stirred at room temperature for 12 hours. Then the solvent was removed in vacuo. The residue was suspended in $H_2O$ (15 mL), extracted with $CH_2Cl_2$ (15 mL × 3). The organic layer was collected, washed with $H_2O$ (15 mL), dried ($Na_2SO_4$), and concentrated to give **G** (230 mg, 85%). $^1$H NMR (400 MHz, $CDCl_3$, room temperature) $\delta$ (ppm): 7.71 (s, 8H), 7.56 (s, 4H), 5.88 (t, $J$ = 52.0 Hz, 3H), 2.20 (s, 3H), 2.00 (s, 6H), 1.75 (d, $J$ = 12.0 Hz, 3H), 1.56 (d, $J$ = 12.0 Hz, 3H).

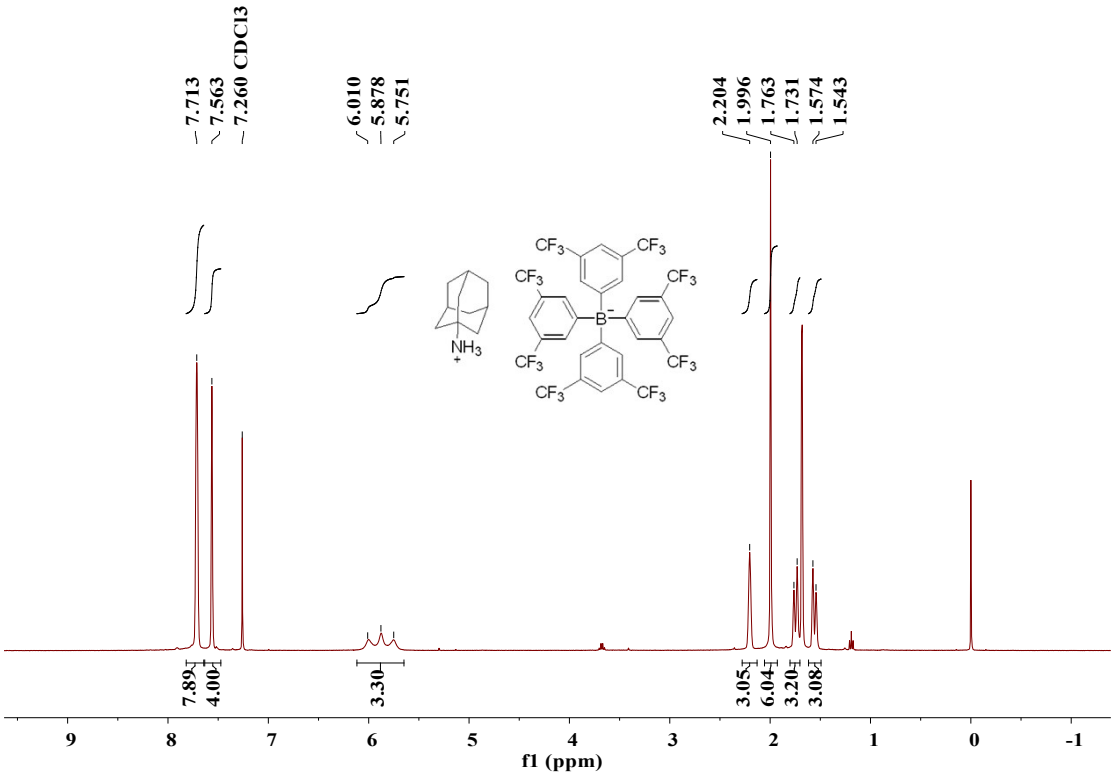



***Figure S11***. $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **G**.

*10. Fluorescence titration experiments of **P6** and **G** in $CHCl_3$*

To determine the stoichiometry and association constant for the complexation between **P6** and **G**, the binding constants were determined by fluorescence titration in an 1 cm quartz cuvette in $CHCl_3$ at 298 K. After excitation at 375 nm, a decrease in fluorescence intensity of **P6** at 418.2 nm was recorded. The host concentration remained constant (0.01 mM), while **G** varied between 0.0 and 0.052 mM. The binding constant ($K_a$) was determined by fitting the experimental data. By a non-linear curve-fitting method, the association constant ($K_a$) of **P6⊃G** was estimated to be about 3.71 (± 0.45) × $10^5$ $M^{-1}$ . By a mole ratio plot, 1:1 stoichiometry was obtained for the complexation between **P6** and **G**.

The non-linear curve-fitting was based on the equation:[S2]

$\Delta F = (\Delta F_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5\ ([G]_0^2 + (2[G]_0(1/Ka - [H]_0)) + (1/Ka + [H]_0)^2)^{0.5}))$ Where $\Delta F$ is the fluorescence intensity change at 418.2 nm at $H_0$, $\Delta F_\infty$ is the fluorescence intensity change at 418.2 nm when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of **G**.

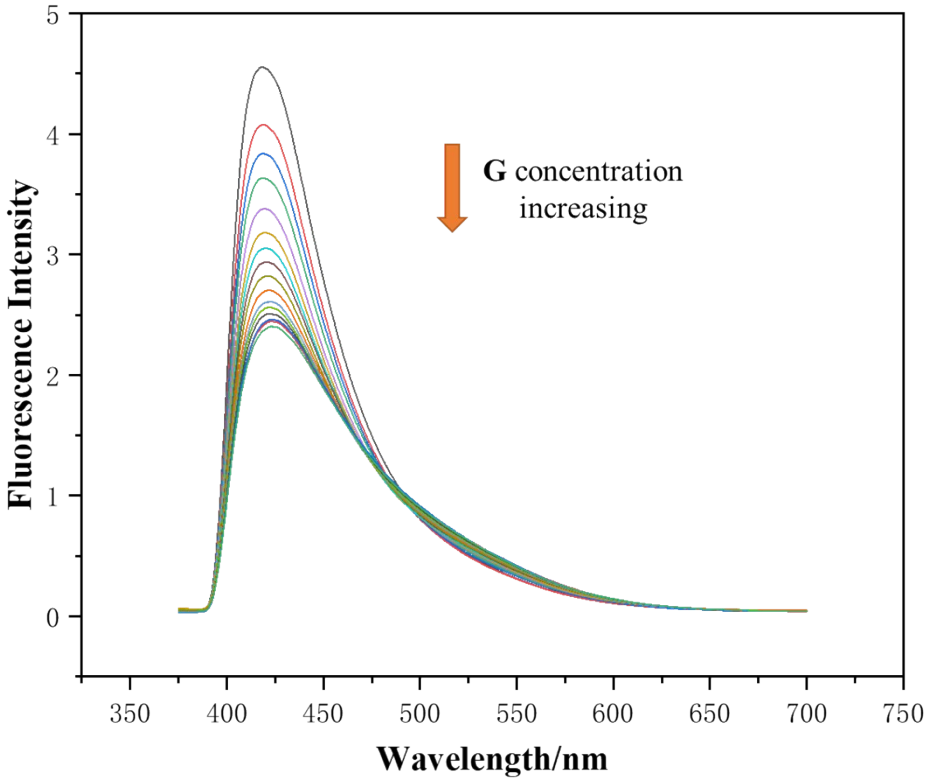



***Figure S12***. Fluorescence spectra of **P6** at a concentration of 0.01 mM upon gradual addition of **G** (0.052 mM).

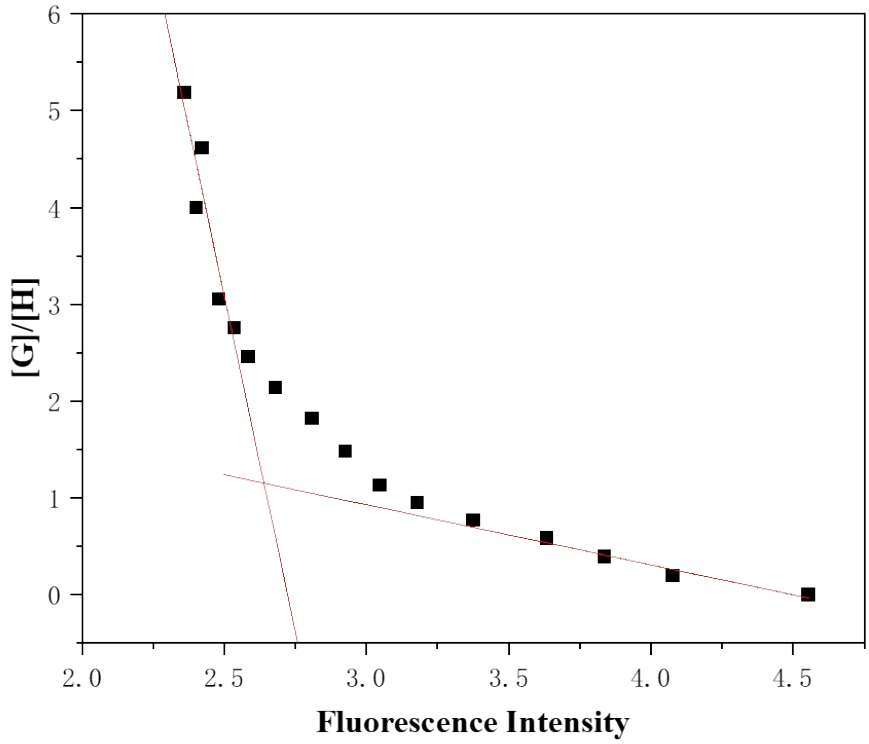



***Figure S13***. Mole ratio plot for **P6** and **G**, indicating a 1:1 stoichiometry.

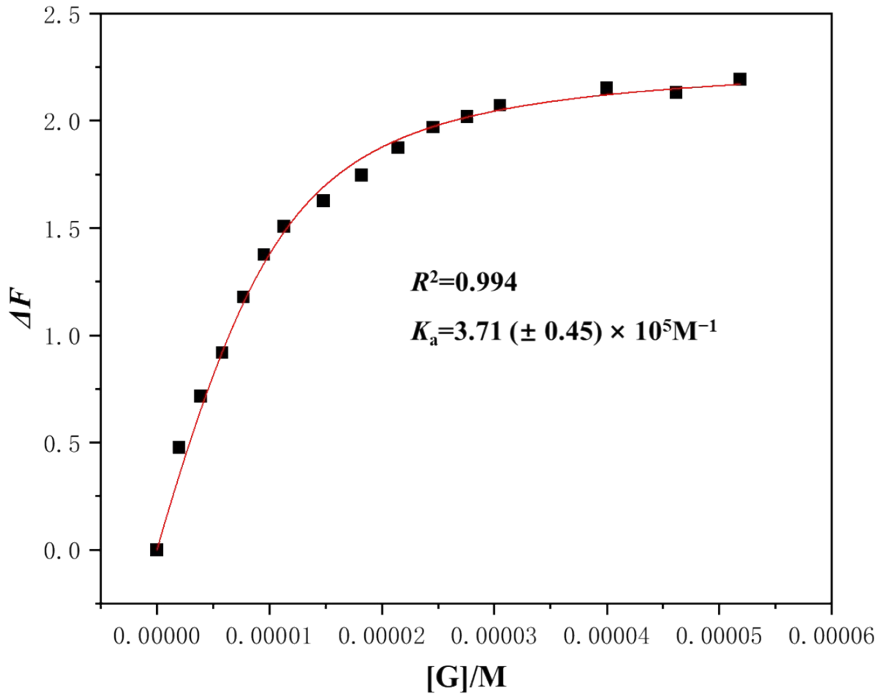



***Figure S14***. The fluorescence intensity changes of **P6** upon addition of **G**. The red solid line was obtained from the non-linear curve-fitting based on the above equation.

*11. Complexation of **P6** and **G** with pH control*

The pH control does work according to Figure S15. When excess triethylamine (TEA) was added to the equimolar solution of P6 and G, the guest G changed from a cation to a neutral molecule. The adamantaneamine molecule cannot complex with P6 or has weak complexation compared with that of the cation. Correspondingly, the two peaks corresponding to protons on naphthalene ring changed to multiple peaks and the signals below 0 ppm appeared, indicating a disassembly process between P6⊃G (spectra b and c in Figure S15). After excess $CF_3COOH$ (TFA) was added to neutralize the triethylamine while the adamantaneamine is acidified again to a cation. P6 was able to bind the adamantaneamine cation again. Correspondingly, aromatic protons on P6 converge to two peaks, indicating the formation of P6⊃G (spectrum d in Figure S15). The chemical shift of the protons below 0 ppm changed back at the chemical shifts could not recover fully may be the result of the ionic strength changes of the solution after the addition of TEA and TFA.

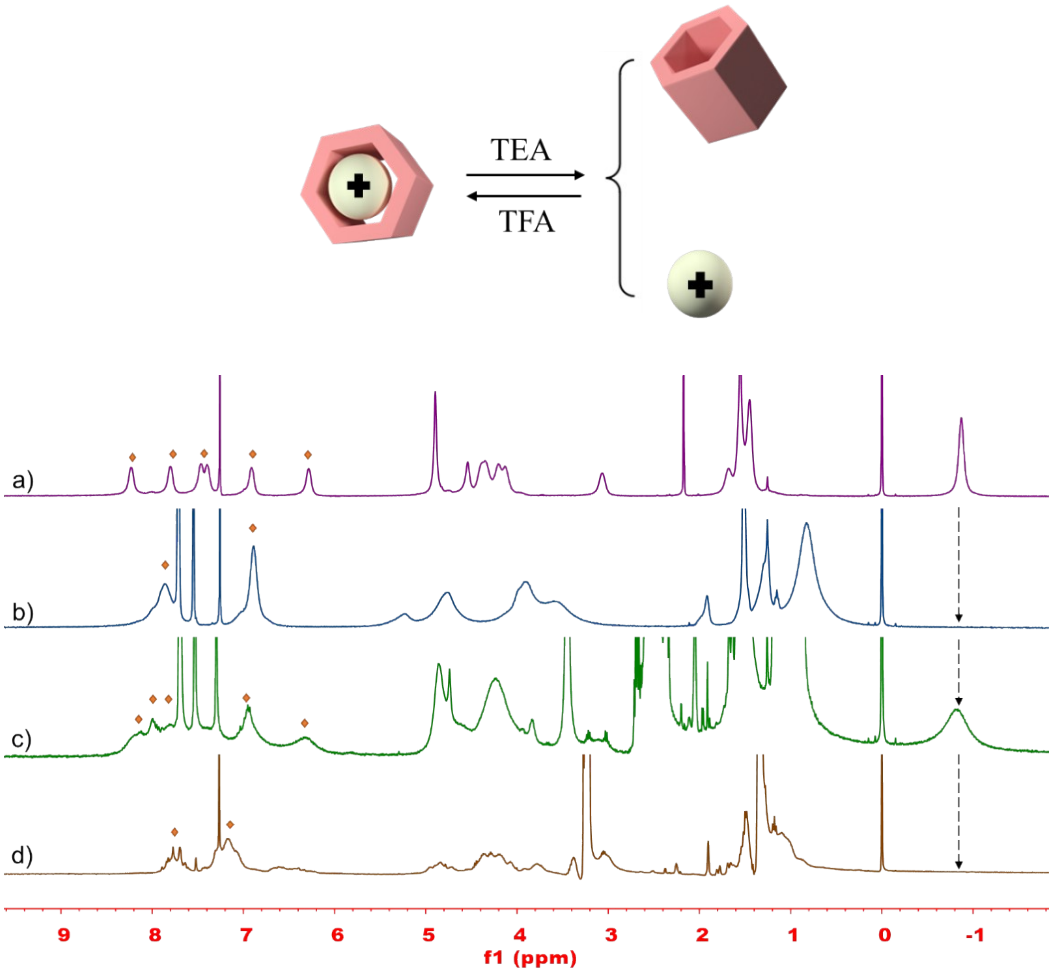



***Figure S15***. $^{1}$H NMR spectra (400 MHz, $CDCl_3$, room temperature) of (a) 3.6 mM **P6** (b) 3.6 mM **P6** and **G**, (c) 3.6 mM **P6** and **G** + excess triethylamine, (d) 3.6 mM **P6** and **G** + excess triethylamine + excess $CF_3COOH$.

*12. Electrospray ionization mass spectrum of a solution of **P6** and **G***

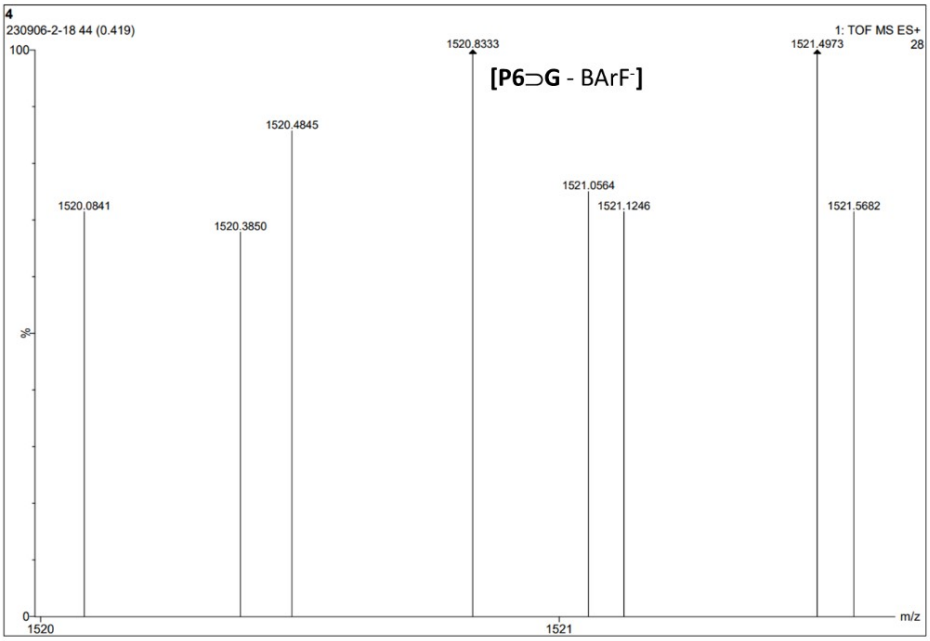



***Figure S16.*** Electrospray ionization mass spectrum of a solution of **P6** and **G**. Assignment of main peaks: m/z 1520.8333 [**P6⊃G** – $BArF^-$] (100%).

*13. $^1H$ NMR spectrum of 1 mM of **P6** and **G***

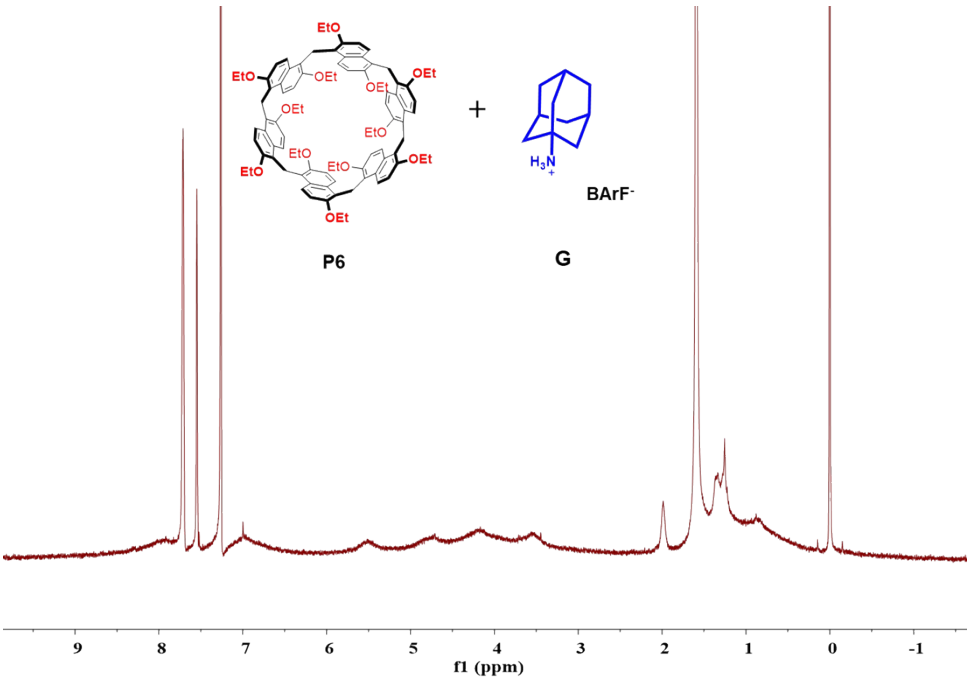



***Figure S17.*** $^1H$ NMR spectra (400 MHz, $CDCl_3$, 22 °C) of 1 mM **P6** and **G**.

*14. X-ray crystallographic data*

The X-ray intensity data of prism[6]arene were collect on Bruker D8 VENTURE Metaljet PHOTON II equipped with Ga Kα radiation (λ = 1.34139 Å) at 225 K. The structure was solved with SHELXD structure solution program and refined with the SHELXL 2019/3.

*References:*

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