Electronic supplementary information

Charge-transfer Inclusion Complex Formation of Tropylium Cation with Pillar[6]arenes

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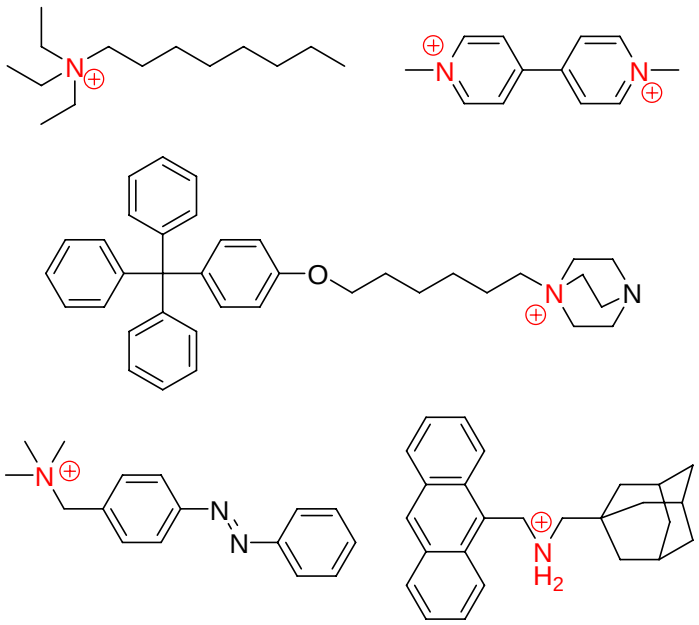
Contents

Materials and methods.

per-Ethylated pillar[5,6,7]arenes (EtP5A, EtP6A and EtP7A) and *per*-hydroxylated pillar[6]arene (OHP6A) were prepared according to literature procedures.[S1] Tropylium tetrafluoroborate and halogenated hydrocarbons were commercially available and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV500 instrument. Electrospray ionization mass spectra (ESI-MS) were recorded on a Bruker Daltonics, Inc. APEXIII7.0 TESLA FTMS instrument. Ultraviolet-visible (UV-vis) spectra were measured employing a Shimadzu UV-2401PC using a conventional 1 cm path (1 × 0.25 cm) quartz cell in a thermostated compartment, which was kept at 25 ^{o}C through a Shimadzu TB-85 Thermo Bath unit.



Scheme S1. Some organic nitrogen-containing cation guests for P6As.

Copies of ^{1}H NMR and ^{13}C NMR spectra of pillararene hosts.

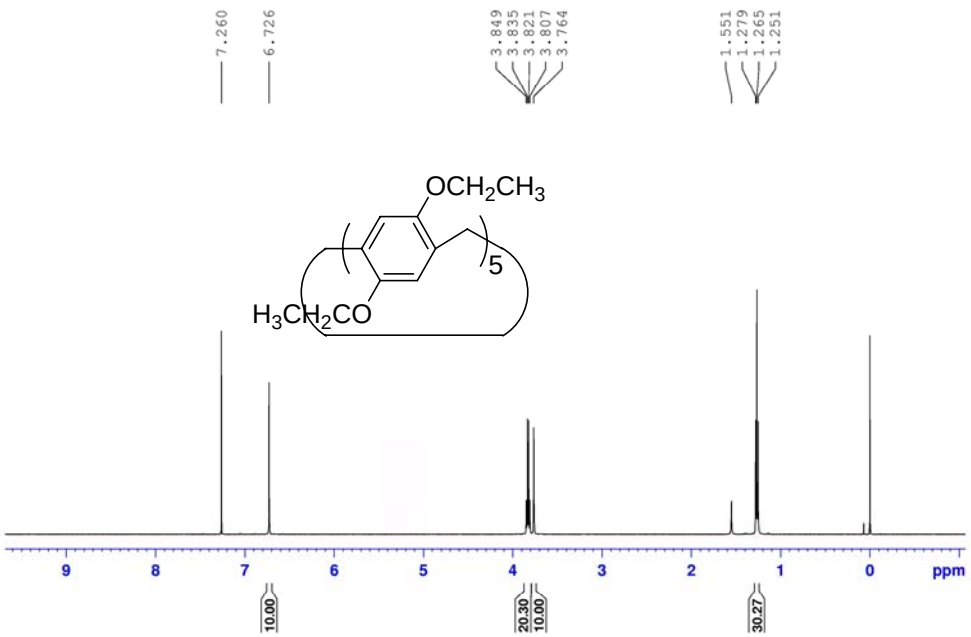


Figure S1. ^{1}H NMR spectrum (500 MHz) of EtP5A in $CDCl_3$.

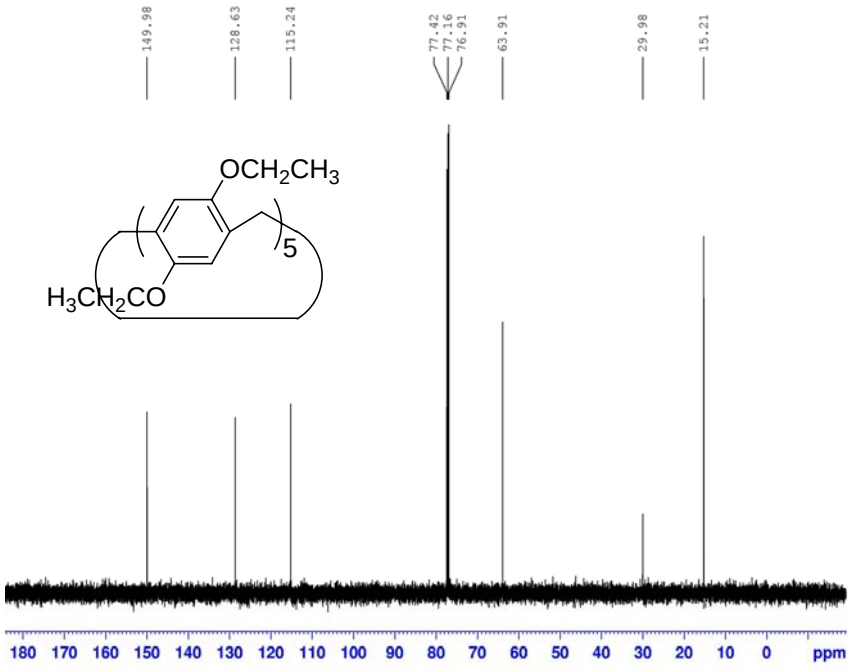


Figure S2. ^{13}C NMR spectrum (125 MHz) of EtP5A in $CDCl_3$.

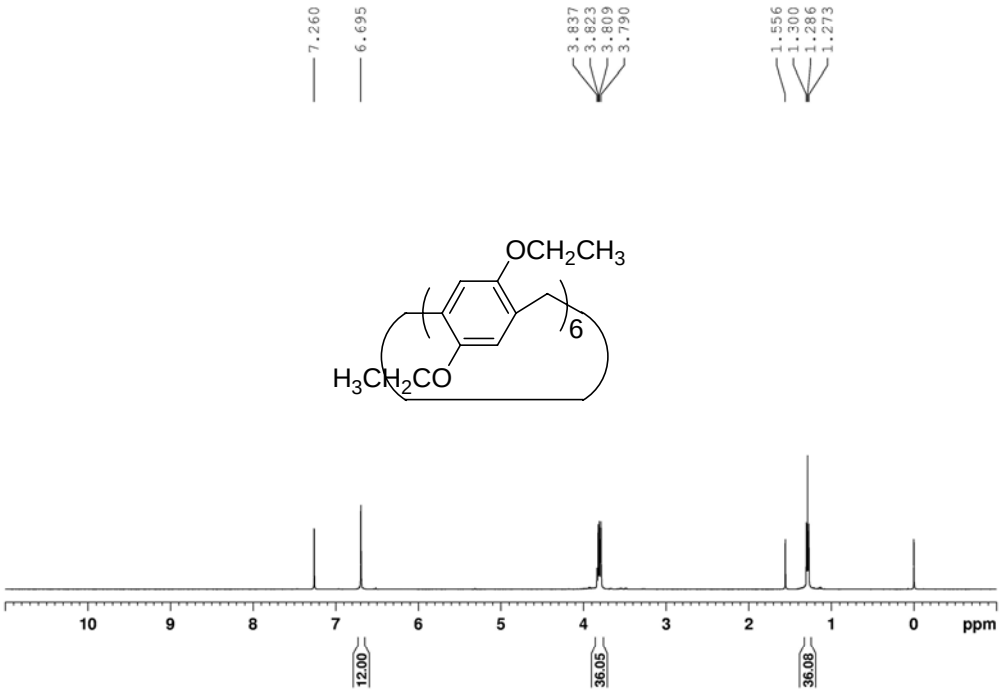


Figure S3. ^{1}H NMR spectrum (500 MHz) of EtP6A in $CDCl_3$.

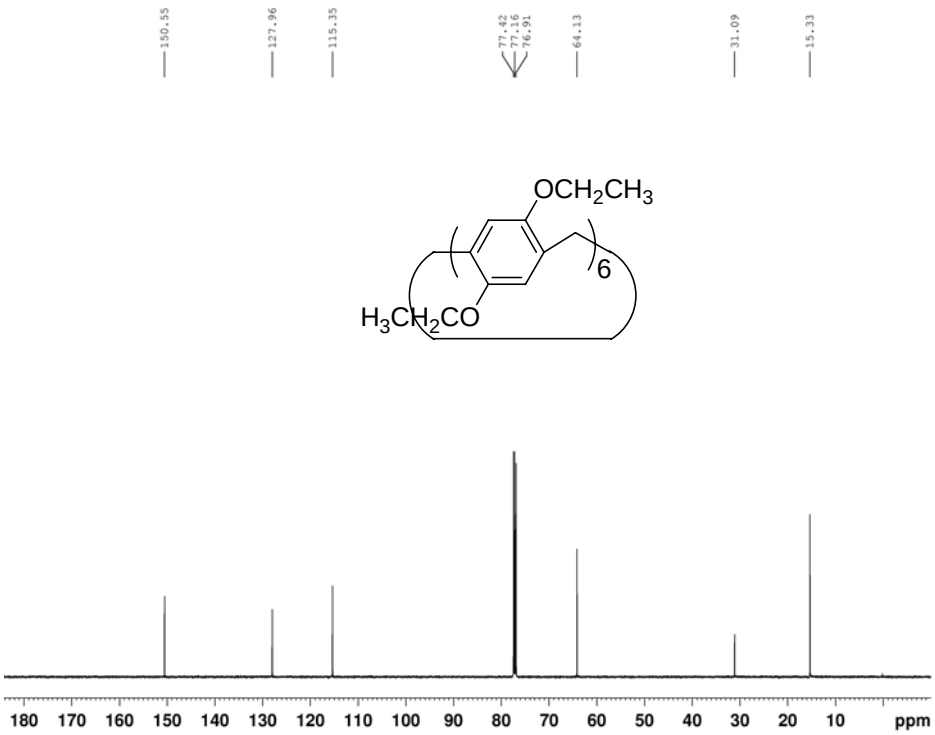


Figure S4. ^{13}C NMR spectrum (125 MHz) of EtP6A in $CDCl_3$.

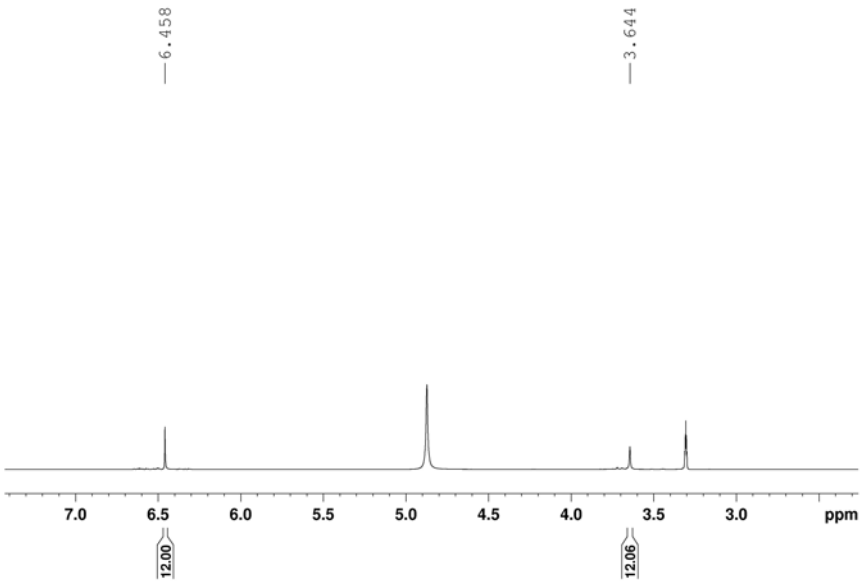


Figure S5. ^{1}H NMR spectrum (500 MHz) of OHP6A in methanol-d_4.

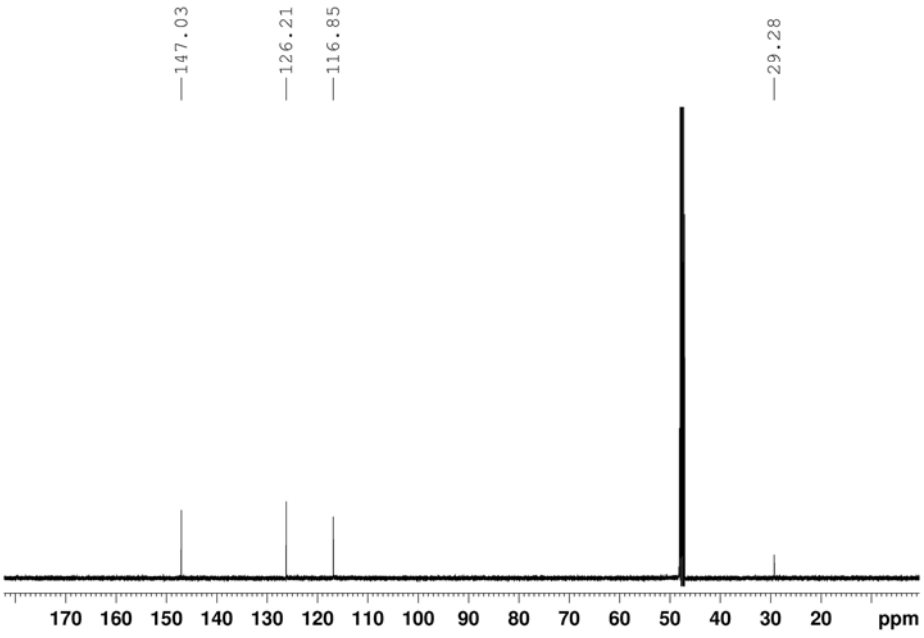


Figure S6. ^{13}C NMR spectrum (125 MHz) of OHP6A in methanol-d_4.

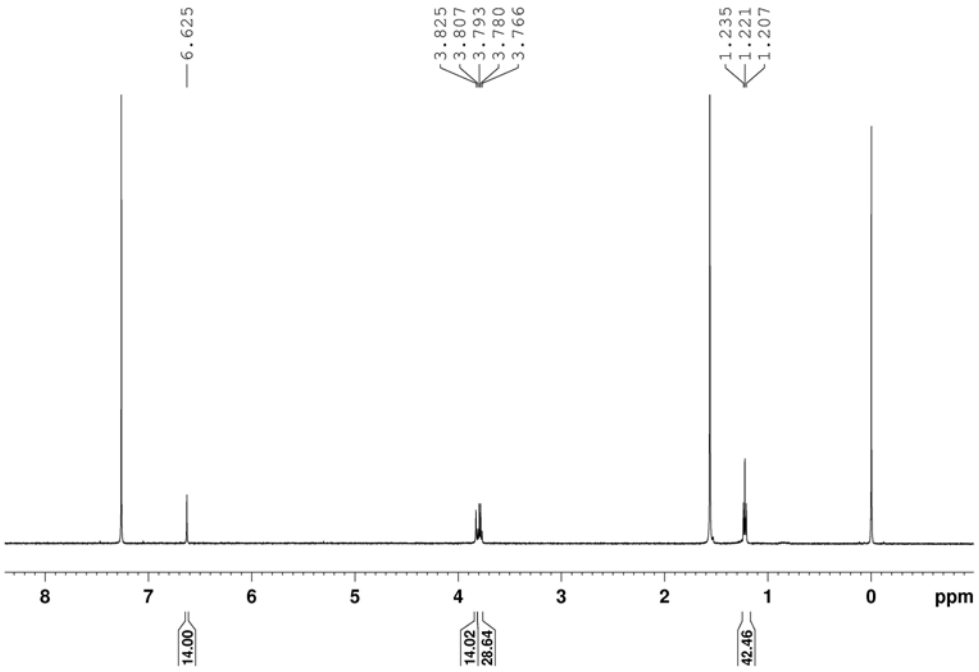


Figure S7. ^{1}H NMR spectrum (500 MHz) of EtP7A in $CDCl_3$.

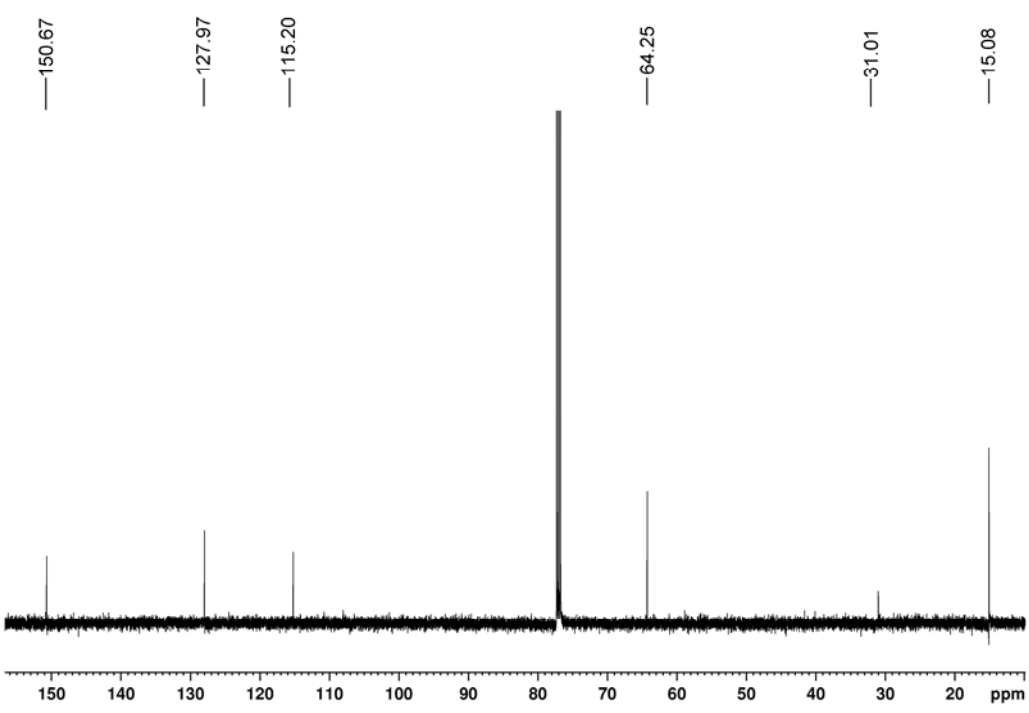


Figure S8. ^{13}C NMR spectrum (125 MHz) of EtP7A in $CDCl_3$.

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^{1}H NMR spectra.

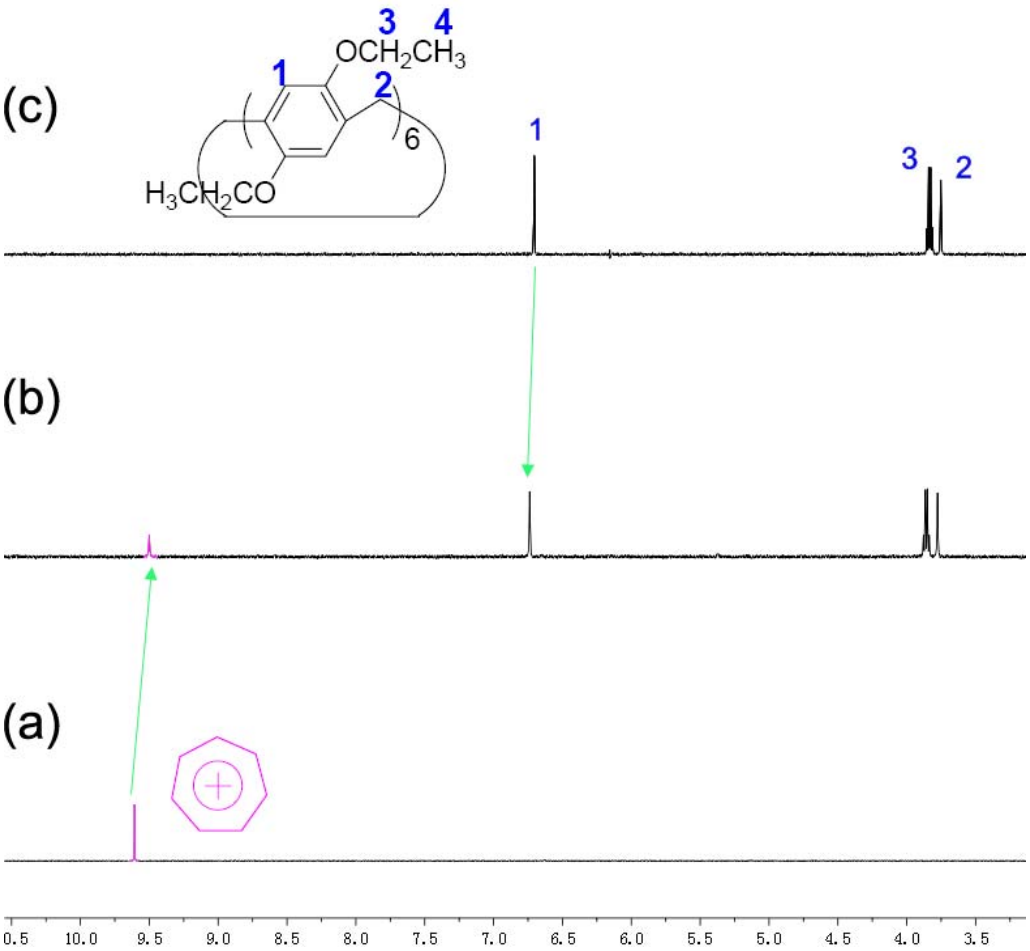


Figure S9. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **T**·BF_4, (b) **T**·BF_4 + EtP6A, and (c) EtP6A in acetone-d_6 at 2.0–2.3 mM.

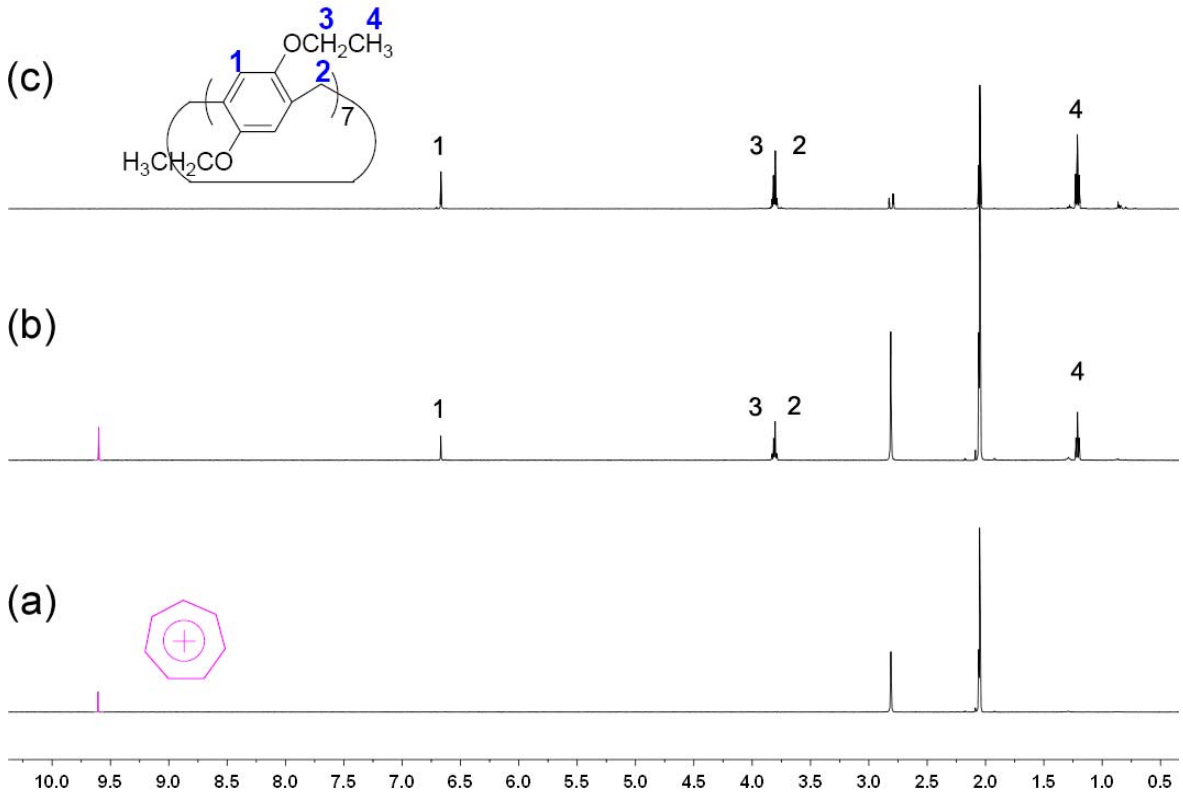


Figure S10. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **T**·BF_4, (b) **T**·BF_4 + EtP7A, and (c) EtP7A in acetone-d_6 at 1.9–2.0 mM.

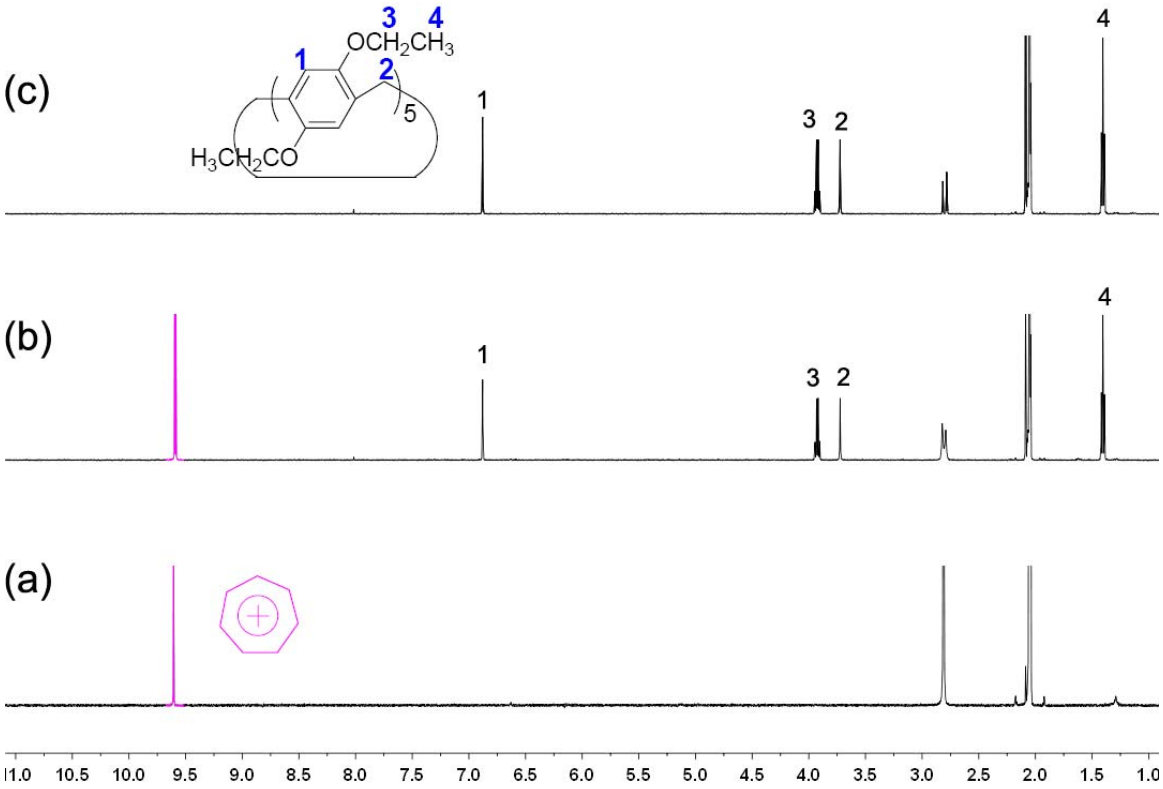


Figure S11. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **T**·BF_4, (b) **T**·BF_4 + EtP5A, and (c) EtP5A in acetone-d_6 at 1.7–2.0 mM.

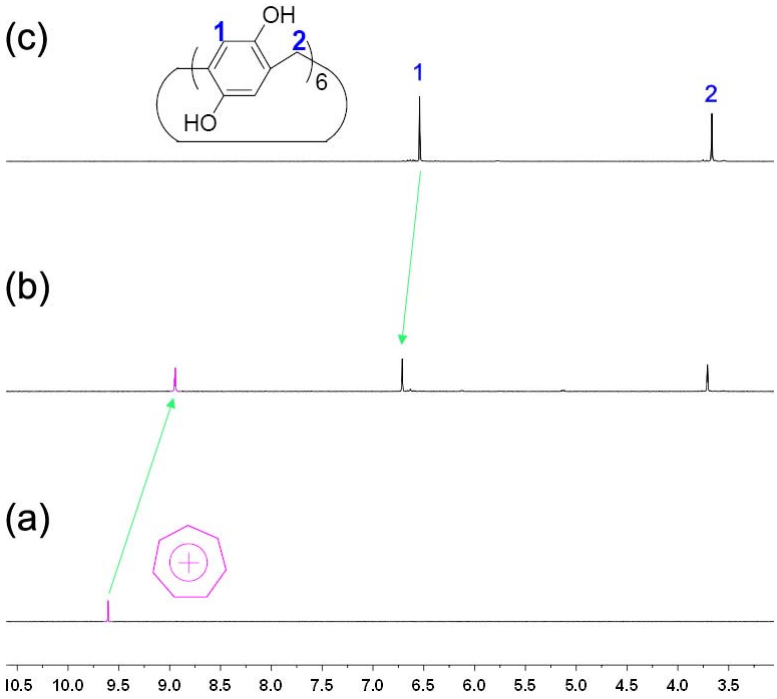


Figure S12. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **T**·BF_4, (b) **T**·BF_4 + OHP6A, and (c) OHP6A in acetone-d_6 at 1.9–2.1 mM.

UV-vis spectra.

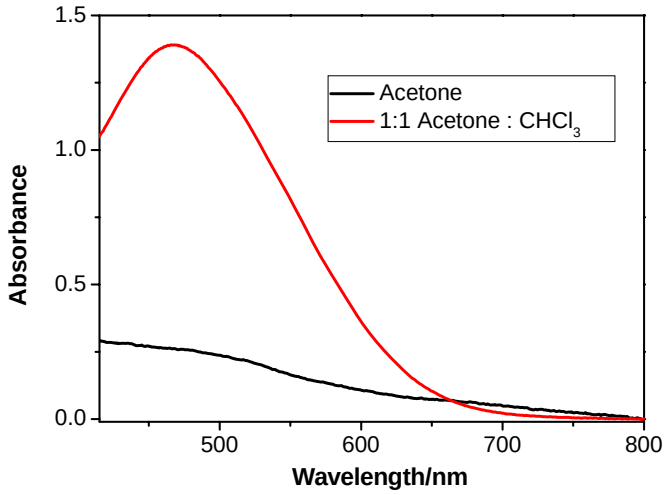


Figure S13. UV-vis spectra of an equimolar mixture of **T**·BF_4 and EtP6A (2.8 mM) in 1 : 1 acetone−$CHCl_3$ and pure acetone solutions at 298 K.

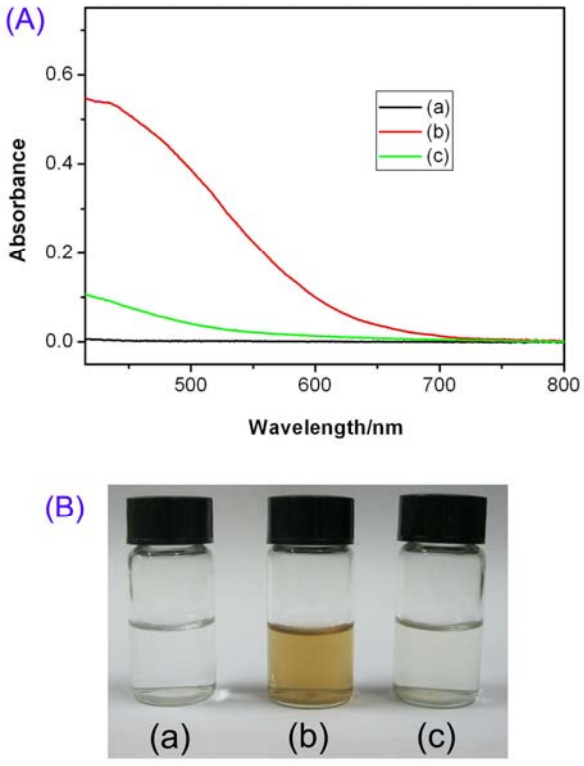


Figure S14. UV−vis spectra (A) and color changes (B) of **T**·BF_4 (2.8 mM) upon complexation with 1.0 eq. of OHP6A in acetone solution at 298 K. (a) **T**·BF_4, (b) **T**·BF_4 + OHP6A, and (c) OHP6A.

ESI mass spectrum of an equimolar mixture of T·BF_4 and OHP6A.

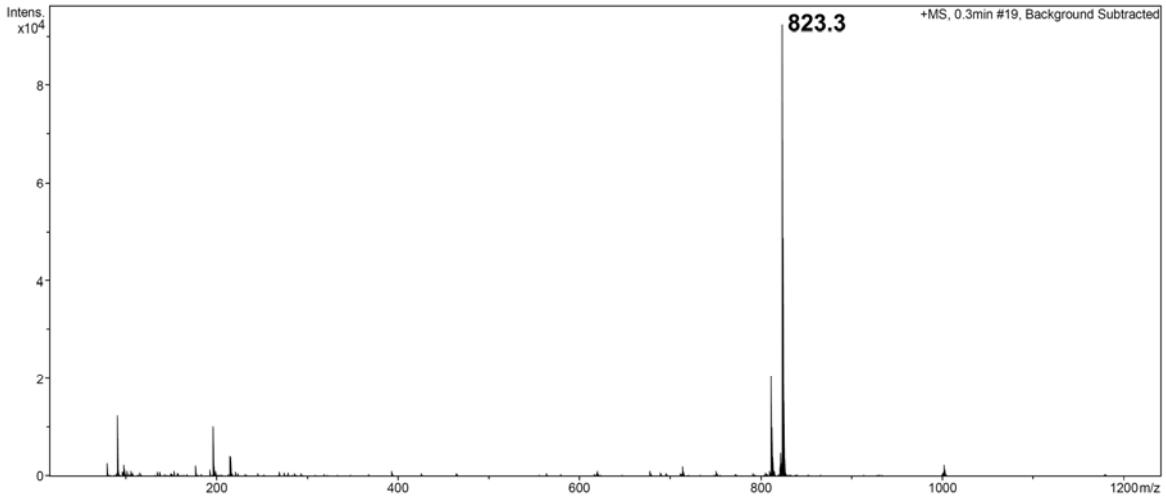
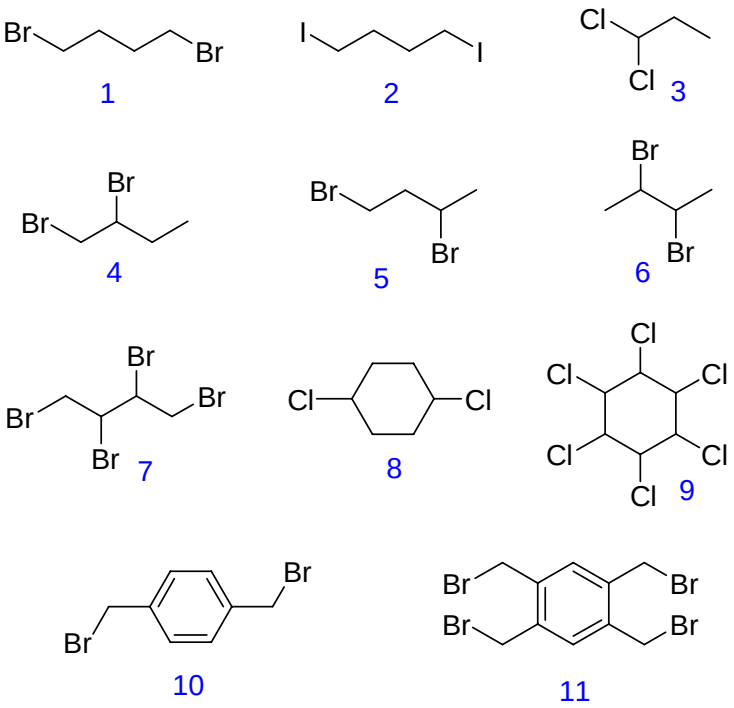


Figure S15. ESI mass spectrum of an equimolar mixture of **T**·BF_4 and OHP6A in methanol solution. The concentration of host/guest is about 0.5 μmol/L.

In the ESI mass spectrum of an equimolar mixture of **T**·BF_4 and OHP6A (Figure S15), only one intense peak for the 1 : 1 complex $[\mathbf{T}\subset\text{EtP6A}]^+$ (m/z 823.3) was observed.

Binding behavior of neutral halogenated hydrocarbons by EtP6A.

Considering that our previous works have reported the strong binding strength between P5As with α, ω-dihaloalkanes, some halogenated hydrocarbons (Scheme S2) are expected to fit P6A hosts. The complexation of 1,4-dibromobutane (**1**) and 1,4-diiodobutane (**2**) by *per*-ethylated pillar[6]arene (EtP6A) host was first investigated by ^{1}H NMR experiments. As can be seen from Figure S16 and S17, no obvious signal changes were observed for the guests upon addition of about one equivalent EtP6A in the ^{1}H NMR spectra, indicating no complexation between EtP6A and these two guests. These results are reasonable since that the methylene chain, which fit the cavity size of P5As, is relatively small compared with P6A's cavity. Then several other halogenated hydrocarbons (**3**−**7**) bearing halogen atoms in their middle positions were chosen as the guest molecules. The introduction of halogen atoms can enlarge the guests' sizes, and there may exist additional halogen···π interations. Unfortunately, no NMR changes were found either. (Figure S18−S22) For halogenated hydrocarbons containing cyclohexane rings and benzene rings (**8**−**11**), similar results were obtained. (Figure S23−S26)



Scheme S2. Structures of neutral halogenated hydrocarbons.

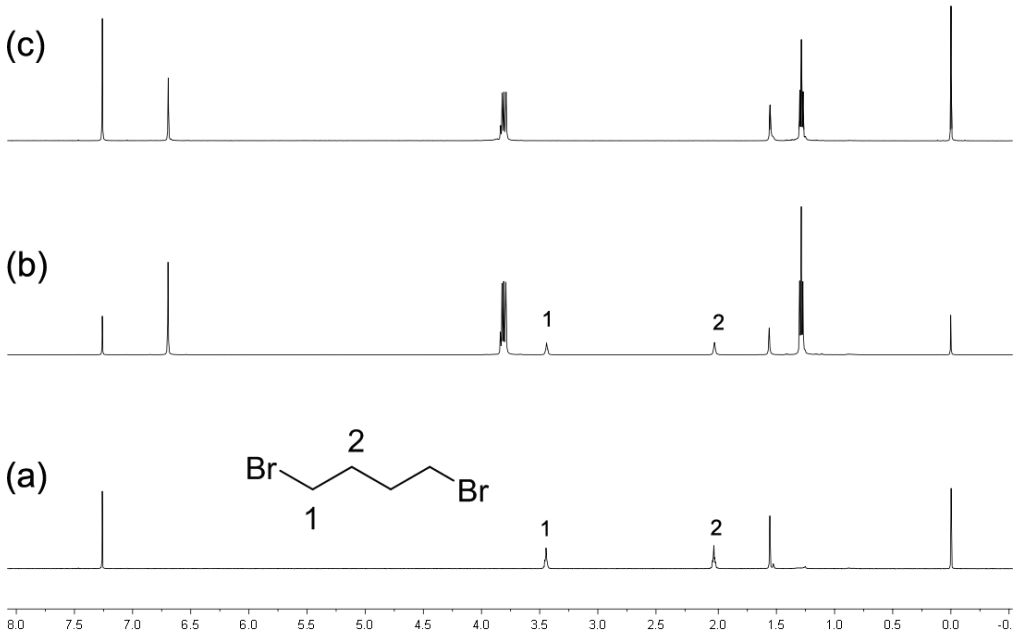


Figure S16. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **1**, (b) **1** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.9–4.2 mM.

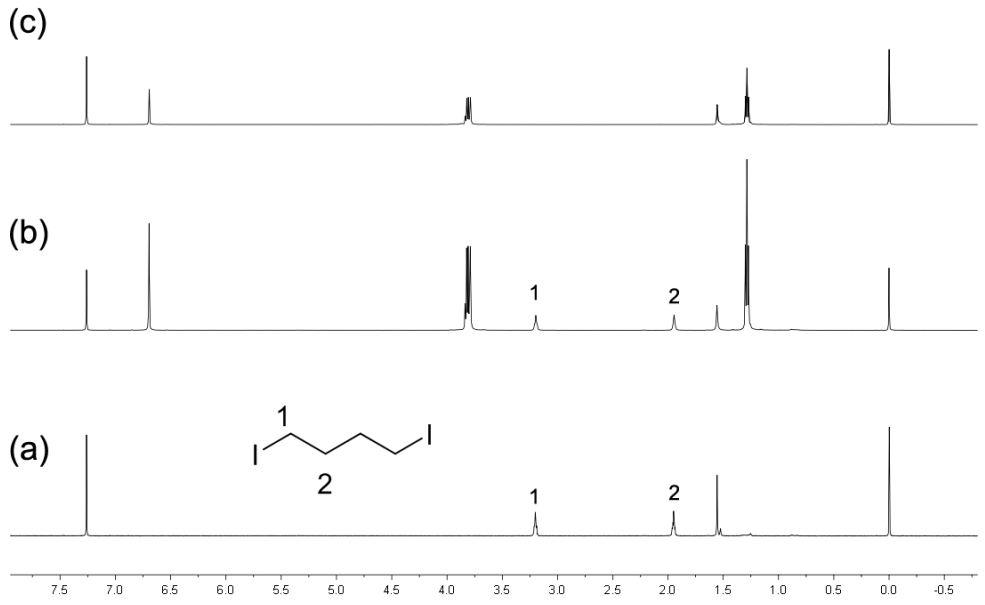


Figure S17. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **2**, (b) **2** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.8–4.2 mM.

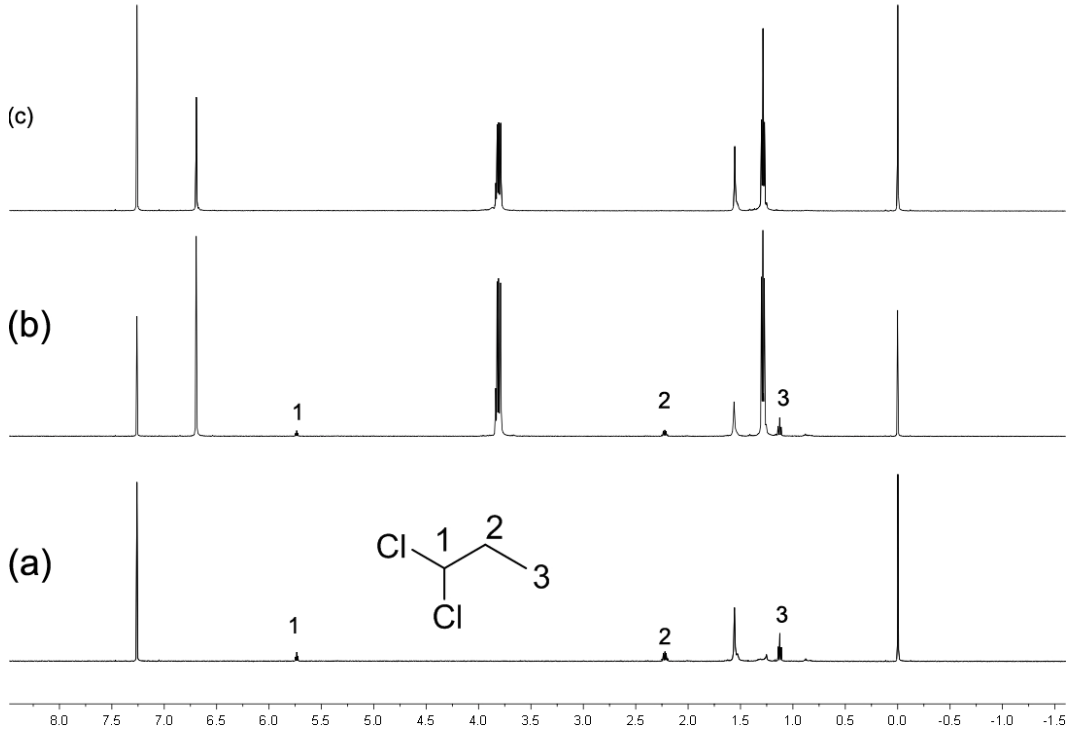


Figure S18. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **3**, (b) **3** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.4–4.0 mM.

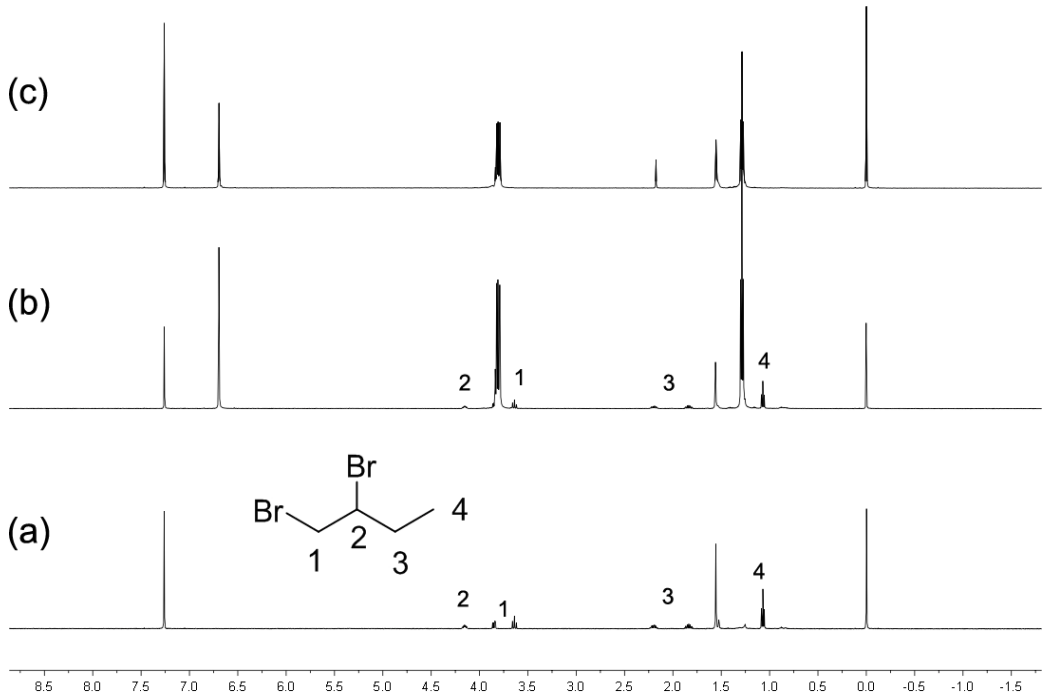


Figure S19. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **4**, (b) **4** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.4–4.0 mM.

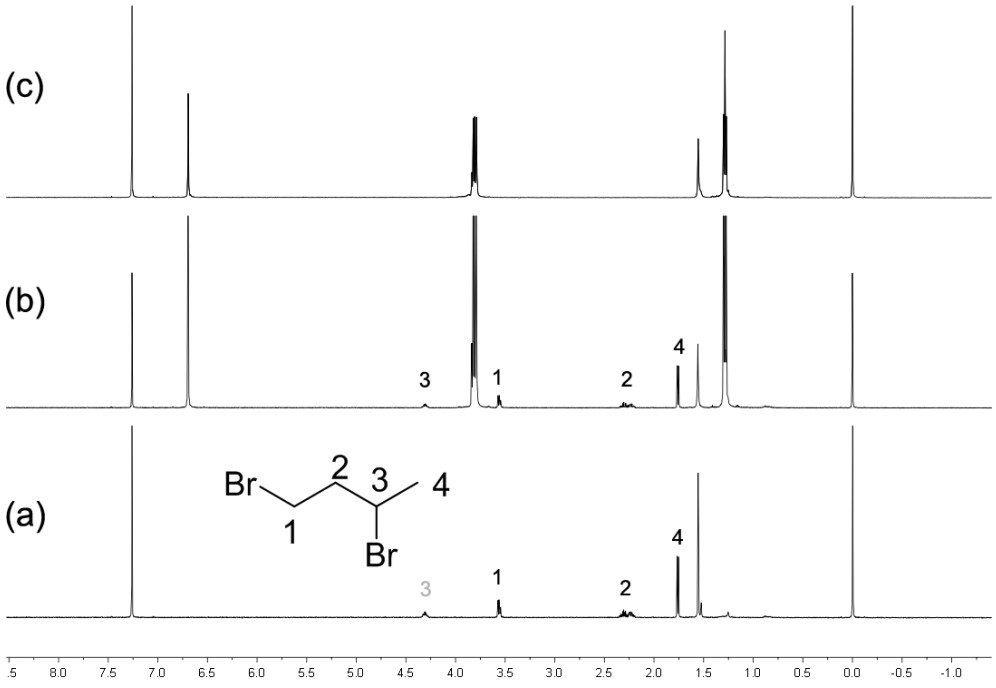


Figure S20. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **5**, (b) **5** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.5–4.0 mM.

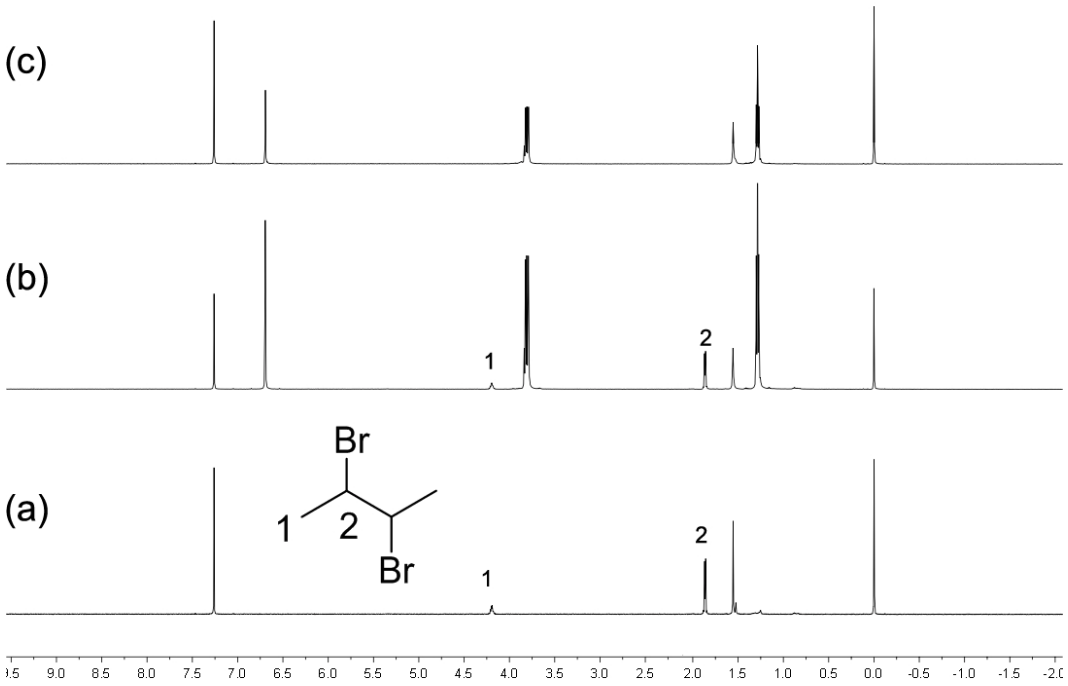


Figure S21. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **6**, (b) **6** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.6–4.0 mM.

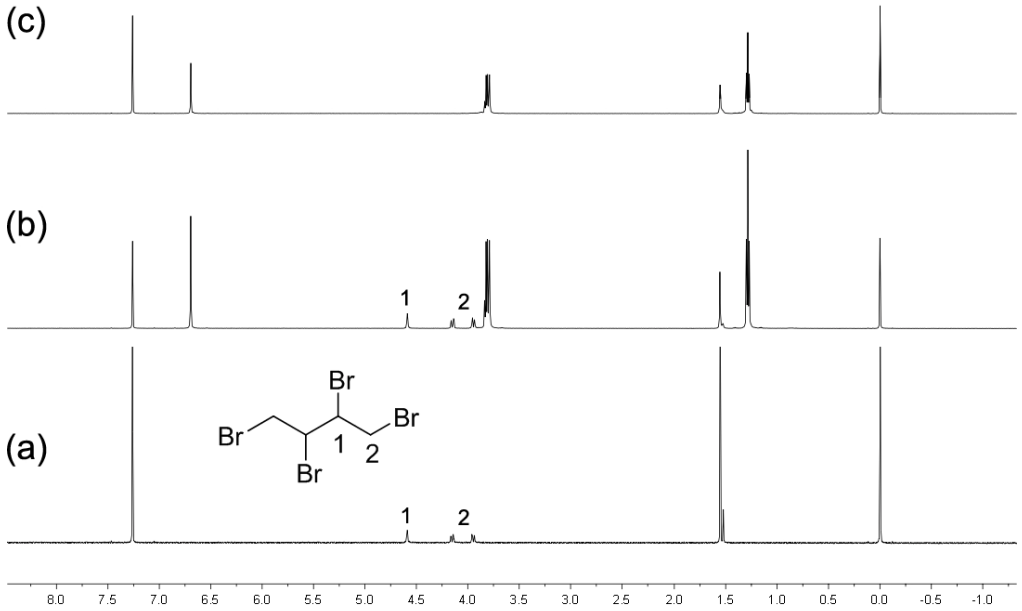


Figure S22. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **7**, (b) **7** + EtP6A, and (c) EtP6A in $CDCl_3$ at 4.0–4.3 mM.

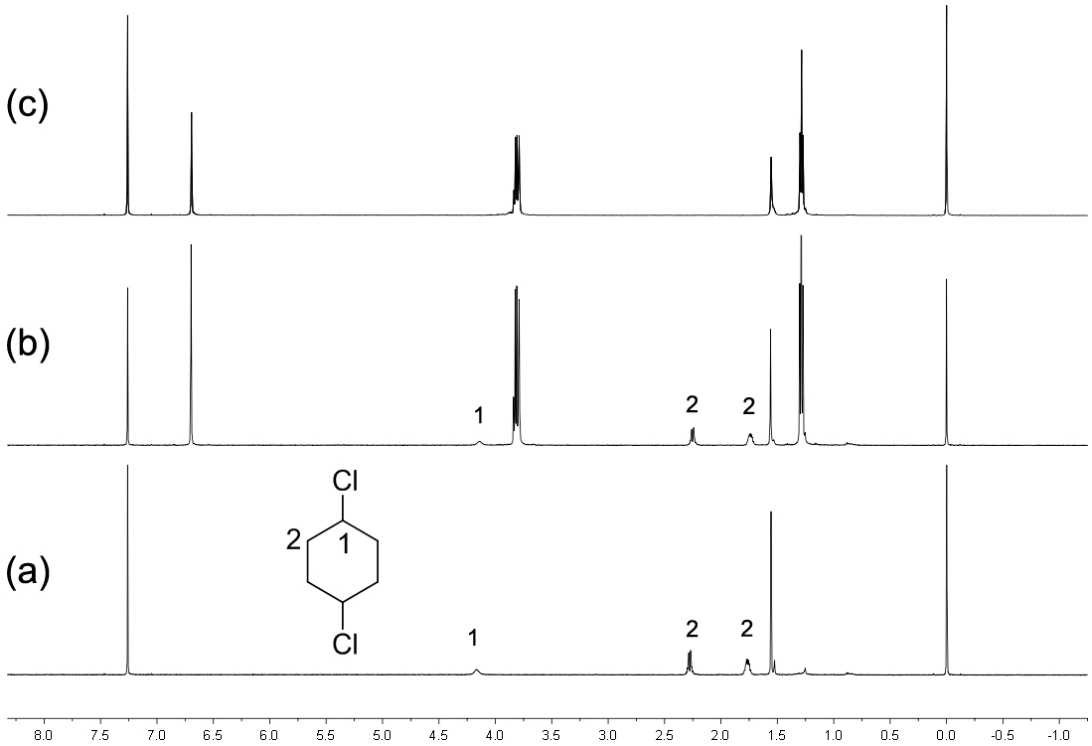


Figure S23. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **8**, (b) **8** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.5–4.1 mM.

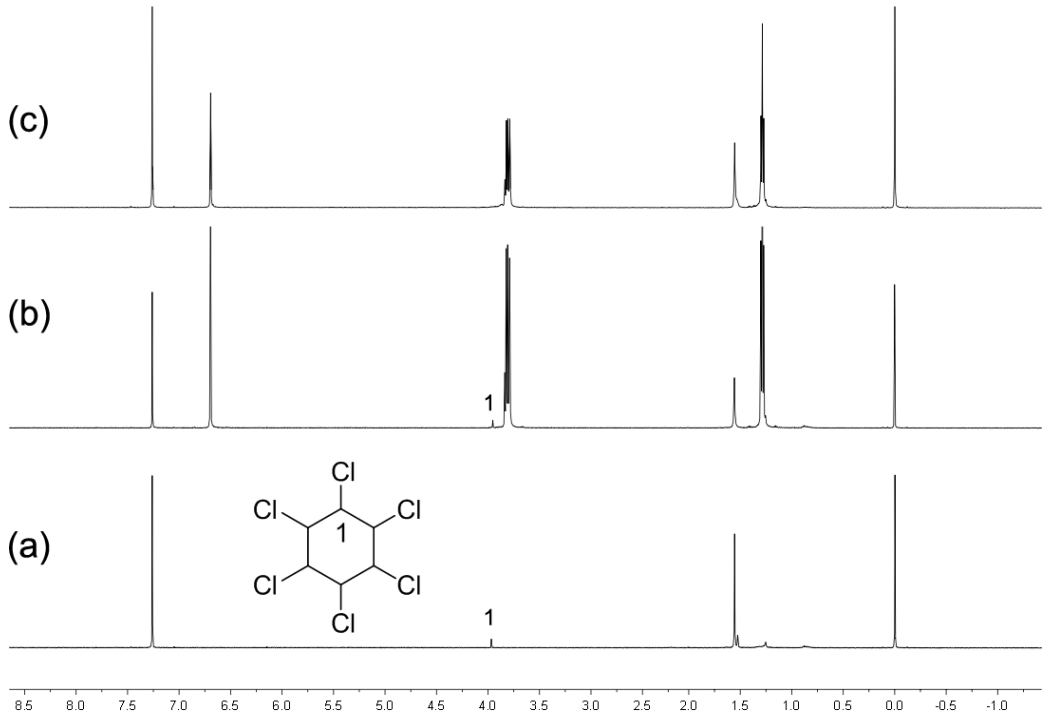


Figure S24. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **9**, (b) **9** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.3–4.0 mM.

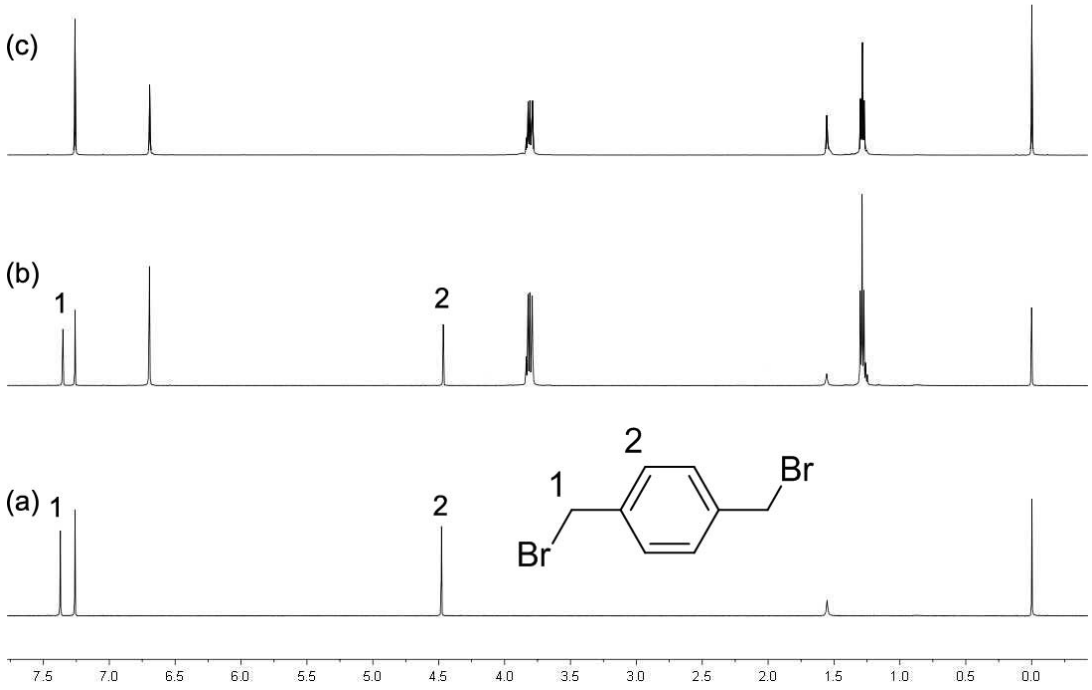


Figure S25. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **10**, (b) **10** + EtP6A, and (c) EtP6A in $CDCl_3$ at 4.0–4.6 mM.

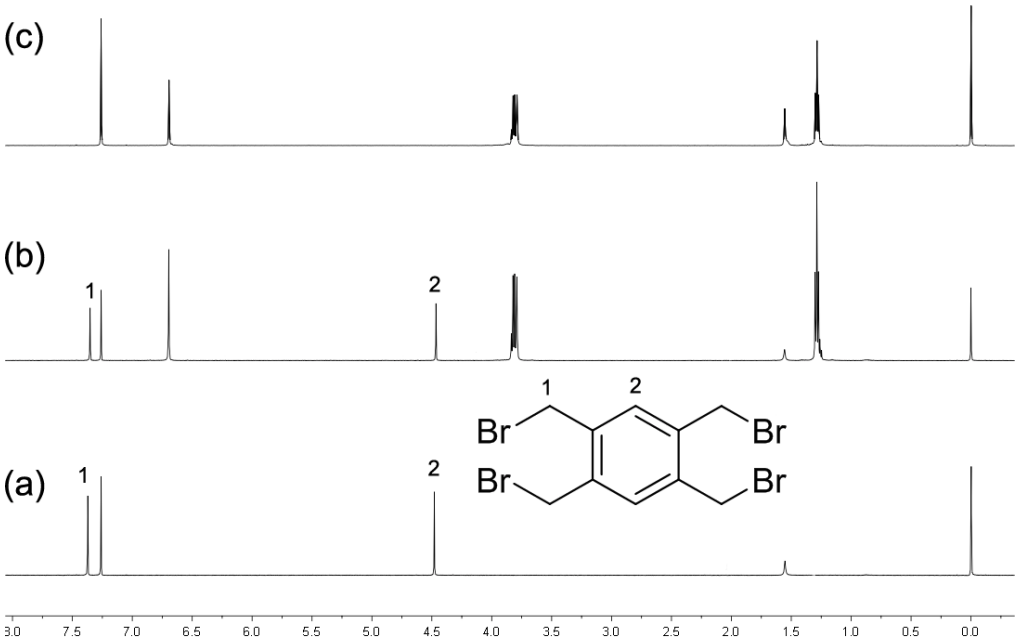


Figure S26. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **11**, (b) **11** + EtP6A, and (c) EtP6A in $CDCl_3$ at 3.9–4.6 mM.

Determination of the association constants.

For the present host-guest system, chemical exchange is fast on the NMR time scale. To determine the association constant, NMR titrations were done with solutions which had a constant concentration of pillararene host and varying concentrations of **T**·BF_4 guest. Using the nonlinear curve-fitting method, the association constant was obtained for each host-guest combination from the following equation[S2]:

$$A = (A_\infty/[\mathrm{P6A}]_0)\ (0.5[\mathrm{G}]_0 + 0.5([\mathrm{P6A}]_0+1/K_a) - (0.5\ ([\mathrm{G}]_0^2+(2[\mathrm{G}]_0(1/K_a - [\mathrm{P6A}]_0)) + (1/K_a + [\mathrm{P6A}]_0)^2)^{0.5}))$$

Where A is the chemical shift change of H_1 on EtP6A (or OHP6A) host at $[G]_0$, A_∞ is the chemical shift change of H_1 when the host is completely complexed, $[P6A]_0$ is the fixed initial concentration of the EtP6A (or OHP6A) host, and $[G]_0$ is the initial concentration of guest.

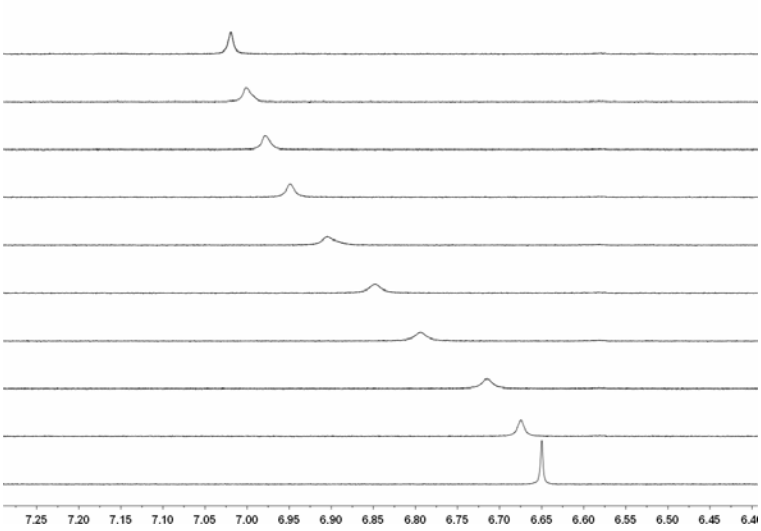


Figure S27. Partial ^{1}H NMR spectra (500 MHz, in acetone-d_6–$CDCl_3$ (1 : 1, v : v), 298 K) of EtP6A at a concentration of 0.50 mM upon addition of tropylium tetrafluoroborate. From bottom to top, the concentration of tropylium tetrafluoroborate was 0, 0.040, 0.23, 0.44, 0.60, 0.82, 1.1, 1.5, 1.9, and 2.5 mM.

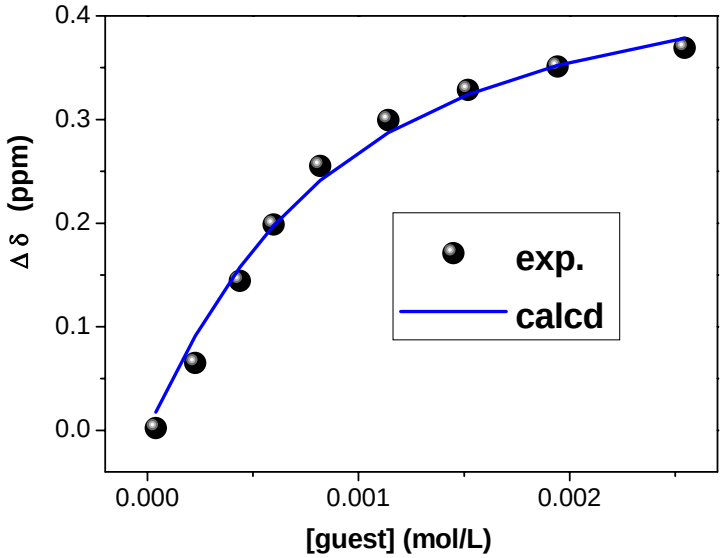


Figure S28. The non-linear curve-fitting (NMR titrations) for the complexation of EtP6A host (0.50 mM) with tropylium tetrafluoroborate in 1 : 1 acetone-d_6–$CDCl_3$ at 298 K. The concentration of tropylium tetrafluoroborate was 0.040, 0.23, 0.44, 0.60, 0.82, 1.1, 1.5, 1.9, and 2.5 mM.

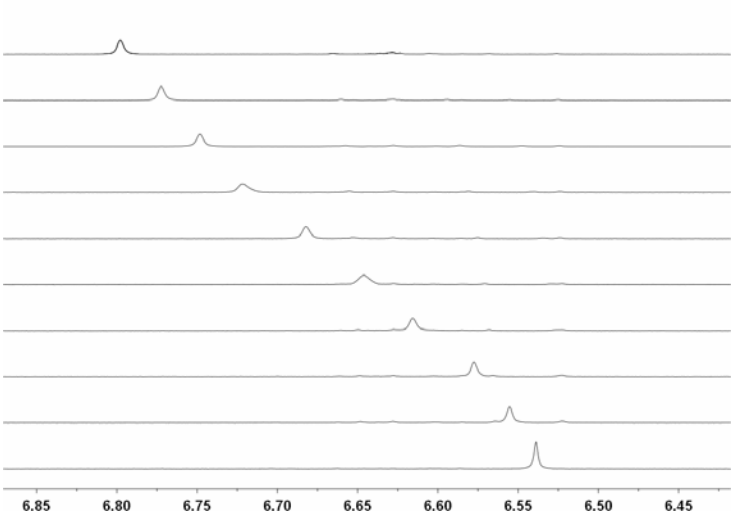


Figure S29. Partial ^{1}H NMR spectra (500 MHz, in acetone-d_6, 298 K) of OHP6A at a concentration of 1.0 mM upon addition of tropylium tetrafluoroborate. From bottom to top, the concentration of tropylium tetrafluoroborate was 0, 0.28, 0.66, 1.5, 2.2, 3.4, 5.2, 7.2, 9.2, and 12 mM.

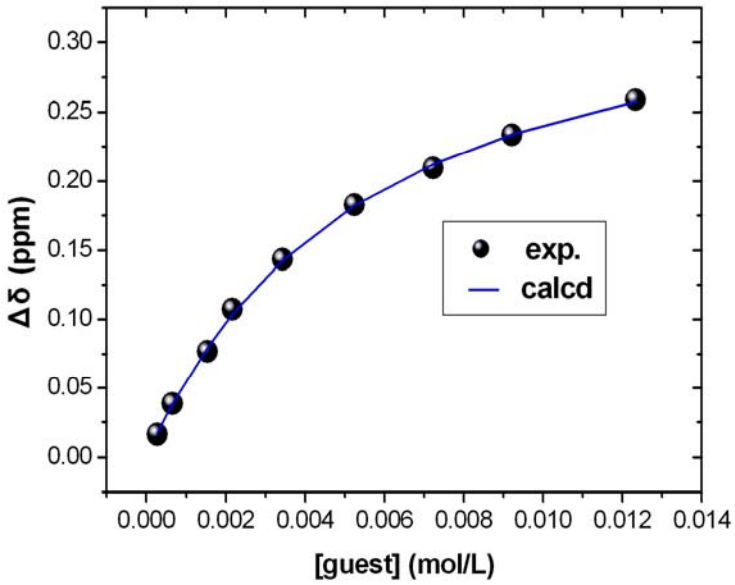


Figure S30. The non-linear curve-fitting (NMR titrations) for the complexation of OHP6A host (1.0 mM) with tropylium tetrafluoroborate in acetone-d_6 at 298 K. The concentration of tropylium tetrafluoroborate was 0.28, 0.66, 1.5, 2.2, 3.4, 5.2, 7.2, 9.2, and 12 mM.

References

[S1] (a) D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem., Int. Ed.*, **2009**, *48*, 9721; (b) T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* **2008**, *130*, 5022; (c) X.-B. Hu, Z. Chen, L. Chen, L. Zhang, J.-L. Hou and Z.-T. Li *Chem. Commun.*, **2012**, *48*, 10999; (d) Y. Ma, X. Chi, X. Yan, J. Liu, Y. Yao, W. Chen, F. Huang, and J.-L. Hou, *Org. Lett.*, **2012**, *14*, 1532.

[S2] (a) K. A. Connors, Binding Constants; Wiley: New York, **1987**. Corbin, P. S. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; (b) R. P. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi , D. J. Williams, *J. Am. Chem. Soc.*, **1996**, *118*, 4931; (c) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang, H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1807.