

## Electronic supplementary information

# Complexation of Neutral 1,4-Dihalobutanes with Simple Pillar[5]arenes That is Dominated by Dispersion Forces

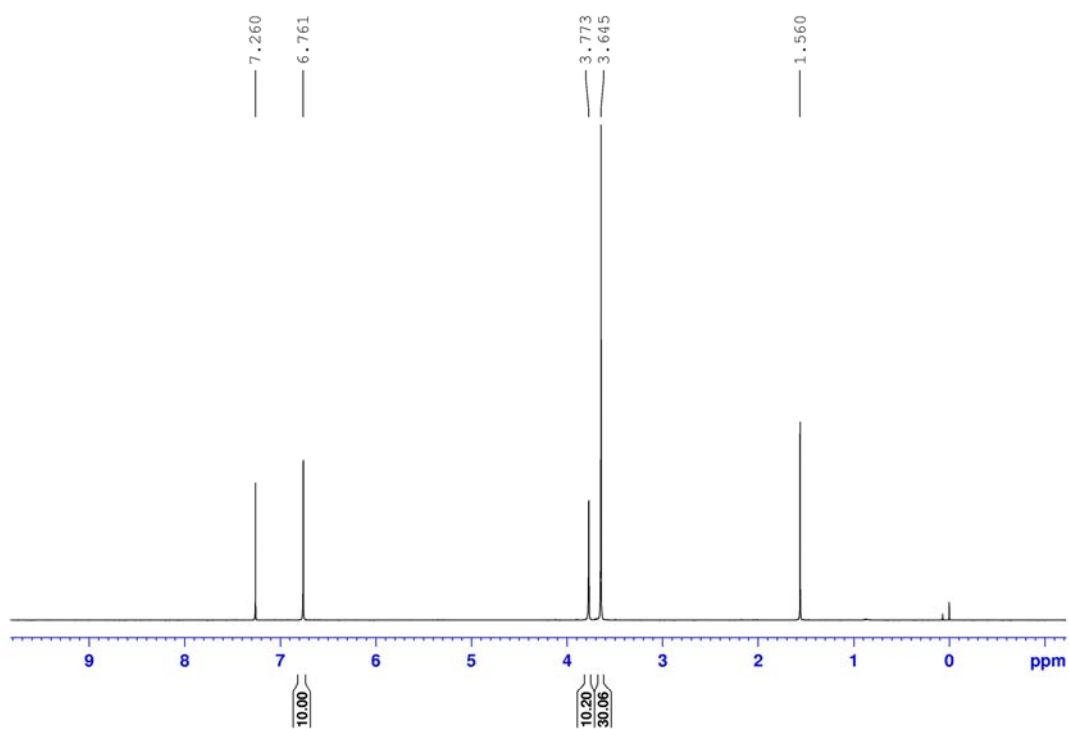
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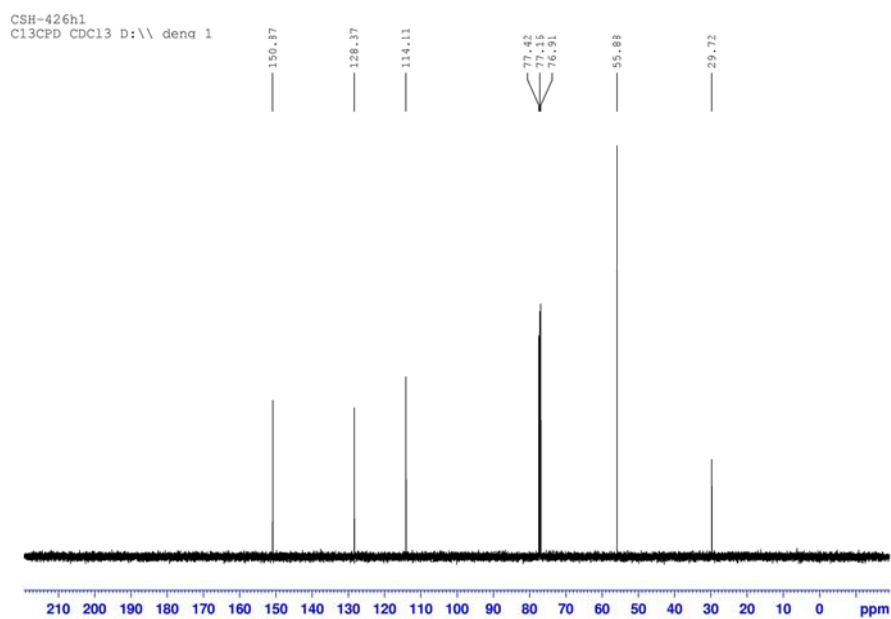
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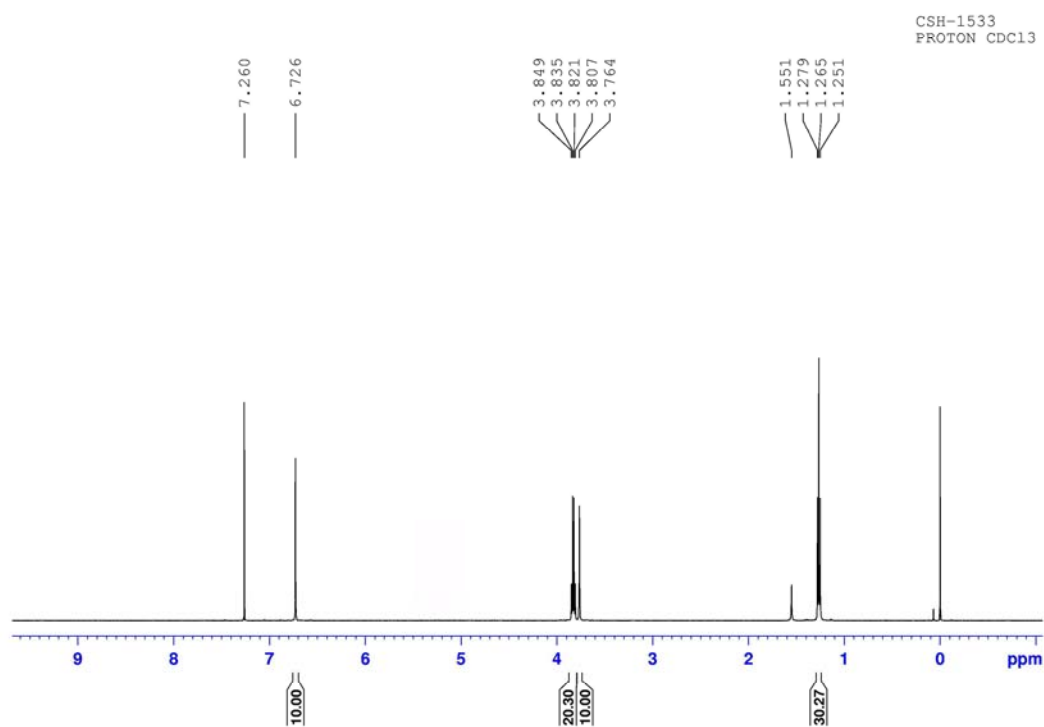
Copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of hosts.



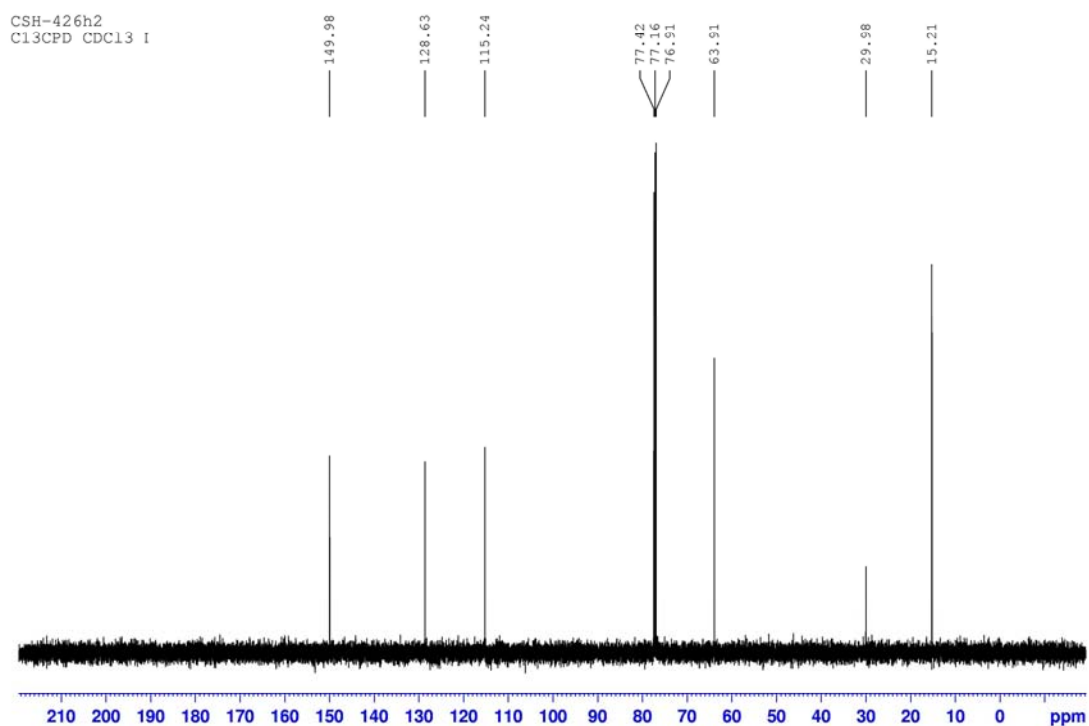
**Figure S1.**  $^1\text{H}$  NMR spectrum (500 MHz) of MeP5A in  $\text{CDCl}_3$ .



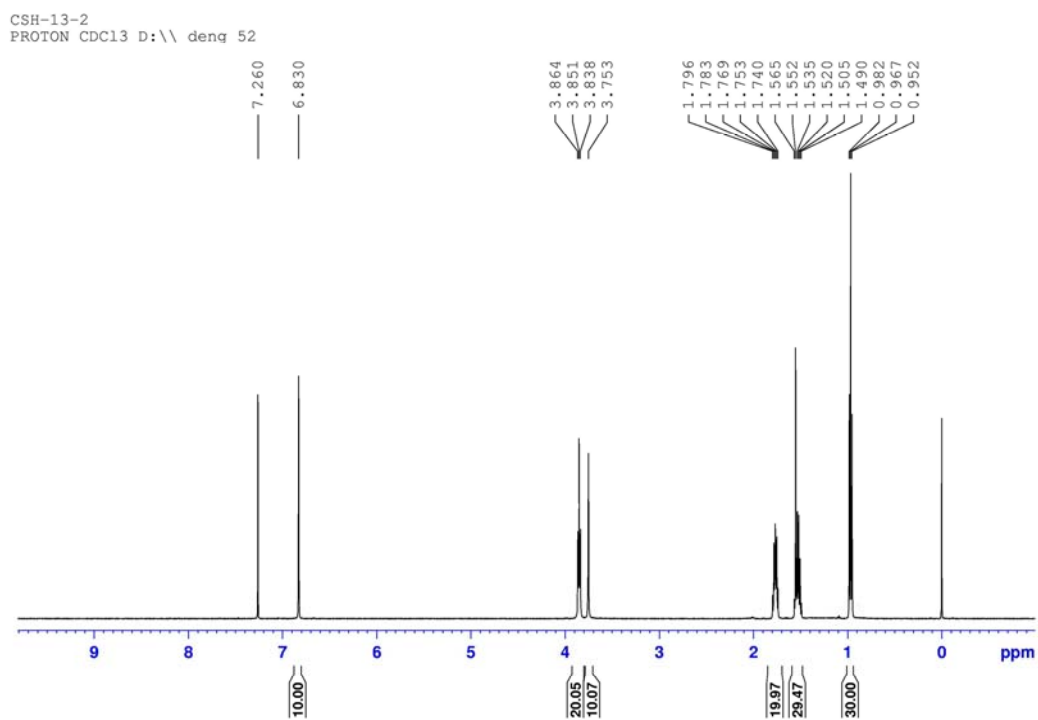
**Figure S2.**  $^{13}\text{C}$  NMR spectrum (125 MHz) of MeP5A in  $\text{CDCl}_3$ .



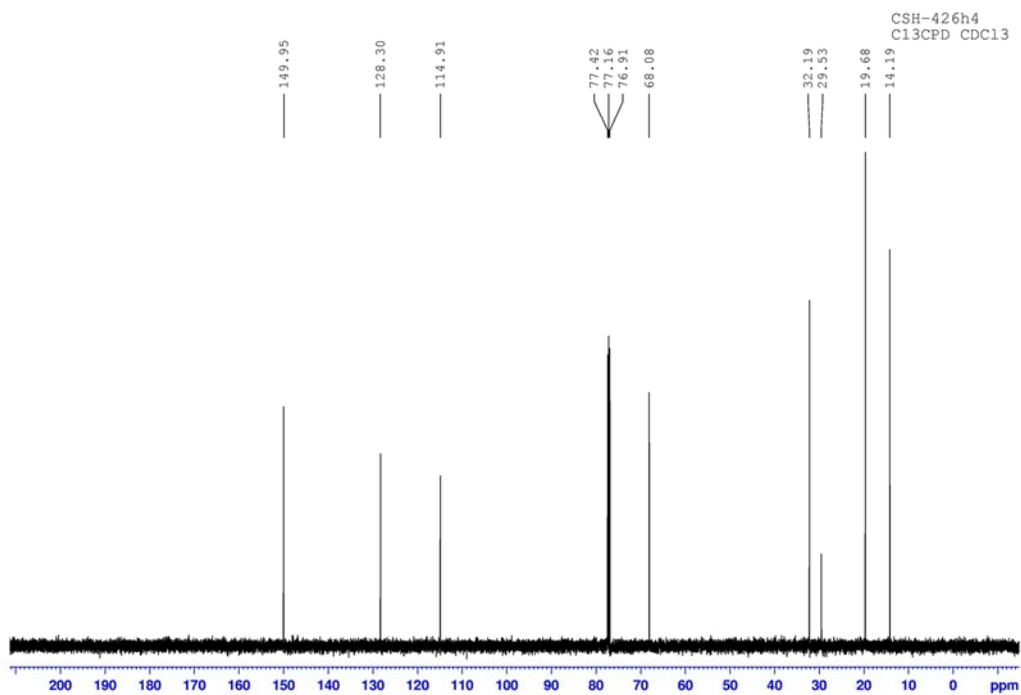
**Figure S3.** <sup>1</sup>H NMR spectrum (500 MHz) of EtP5A in CDCl<sub>3</sub>.



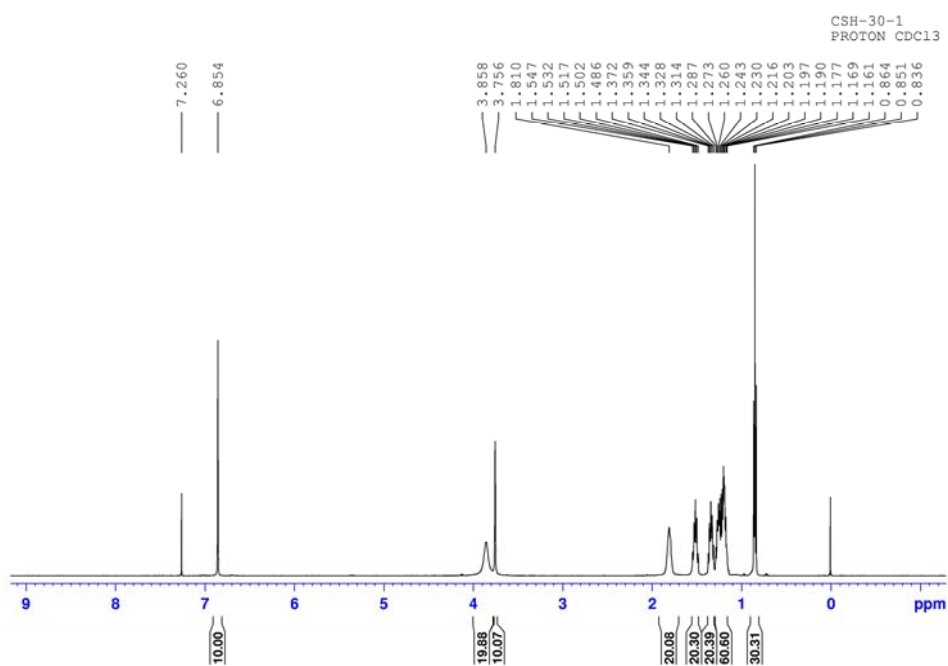
**Figure S4.** <sup>13</sup>C NMR spectrum (125 MHz) of EtP5A in CDCl<sub>3</sub>.



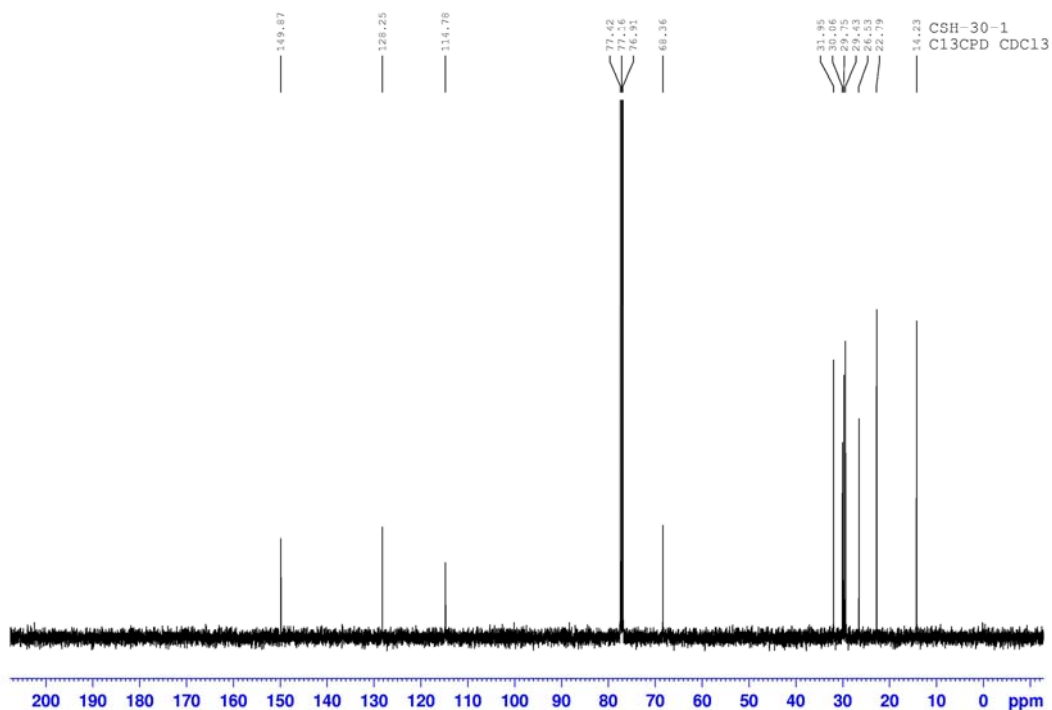
**Figure S5.**  $^1\text{H}$  NMR spectrum (500 MHz) of BuP5A in  $\text{CDCl}_3$ .



**Figure S6.**  $^{13}\text{C}$  NMR spectrum (125 MHz) of BuP5A in  $\text{CDCl}_3$ .

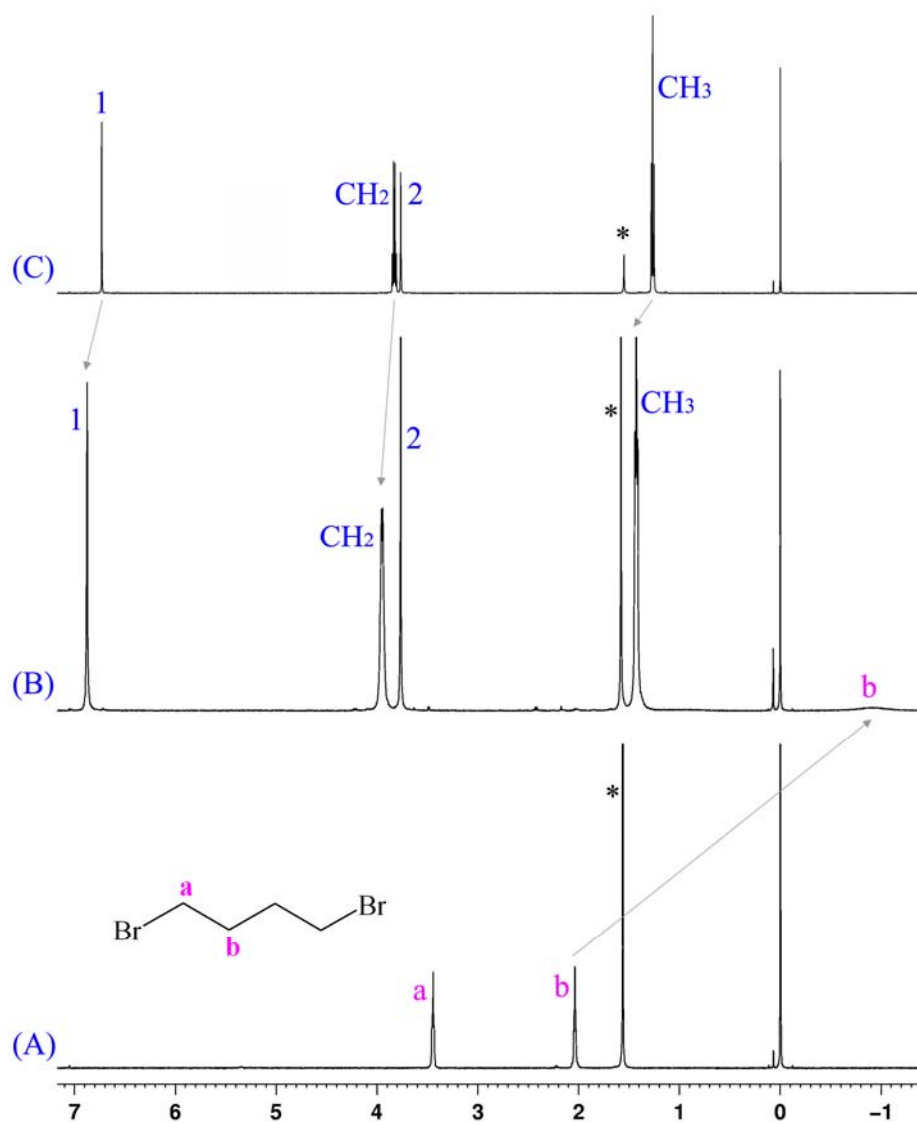


**Figure S7.**  $^1\text{H}$  NMR spectrum (500 MHz) of OctP5A in  $\text{CDCl}_3$ .

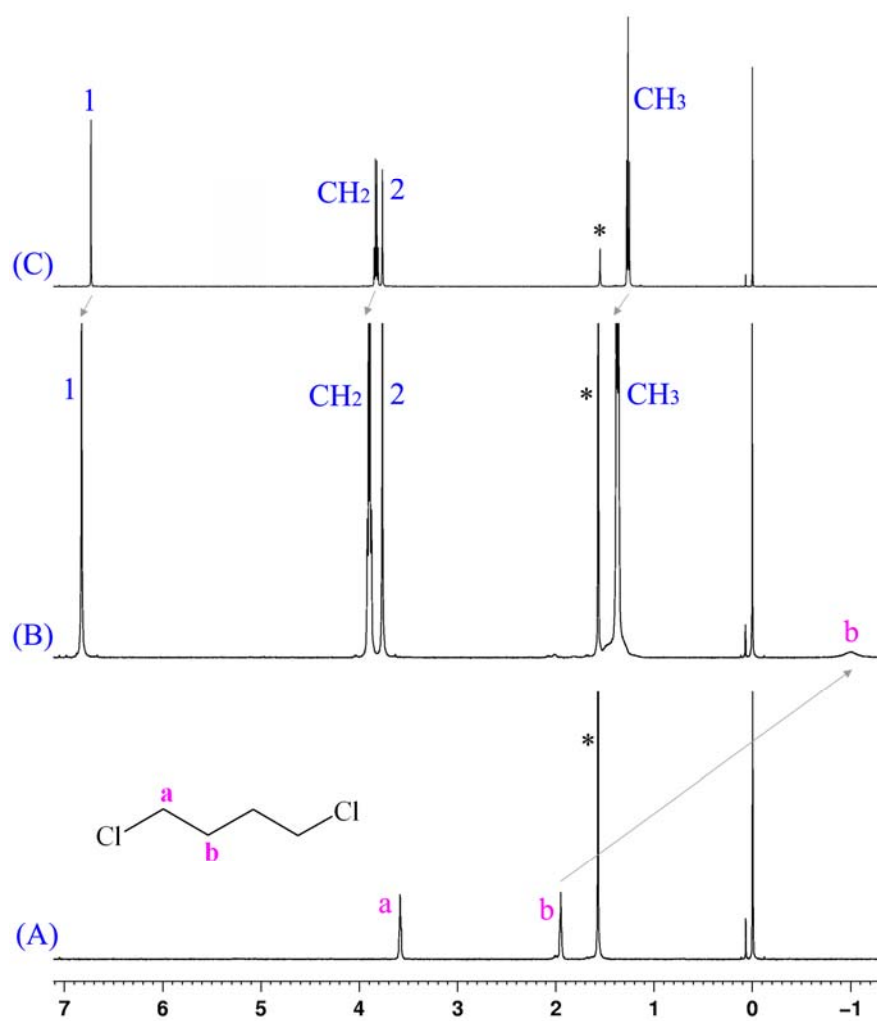


**Figure S8.**  $^{13}\text{C}$  NMR spectrum (125 MHz) of OctP5A in  $\text{CDCl}_3$ .

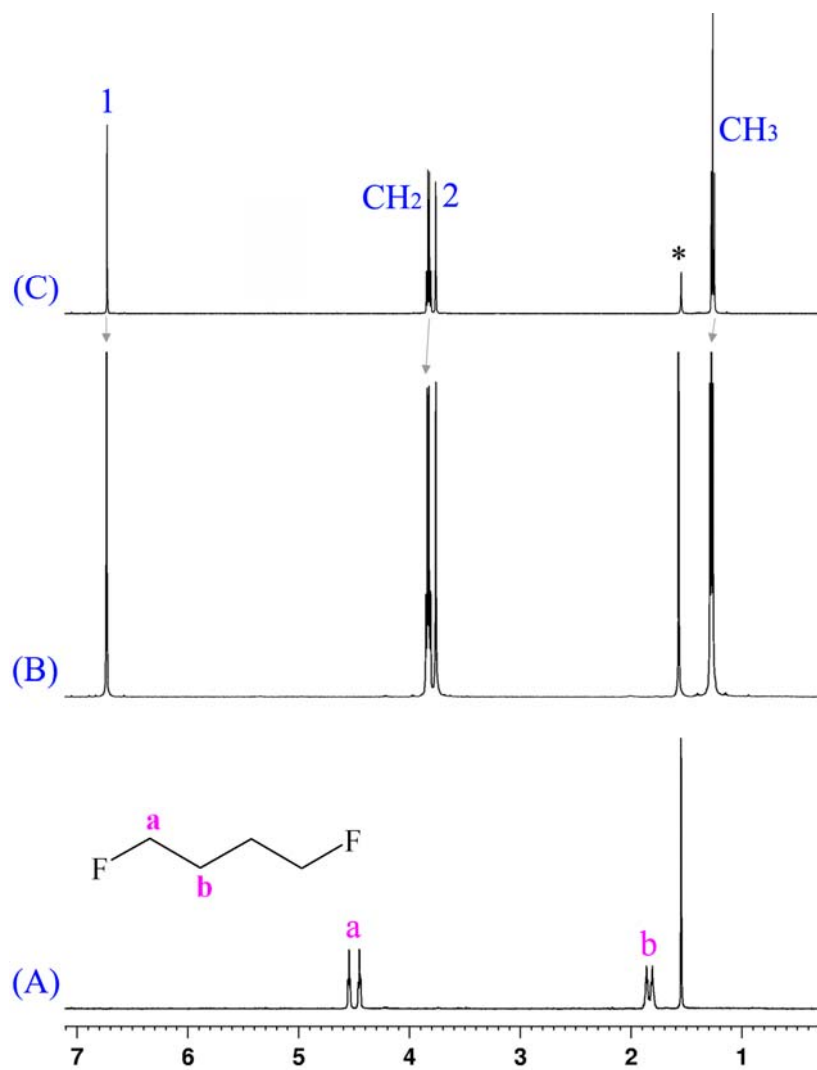
### $^1\text{H}$ NMR spectra of guests in the absence and presence of AIP5As.



**Figure S9.**  $^1\text{H}$  NMR spectra (500 MHz) of (a) DBrBu, (b) DBrBu + EtP5A, and (c) EtP5A in  $\text{CD}_3\text{Cl}$  at 4.2–5.0 mM. The peaks marked with an asterisk are due to water.

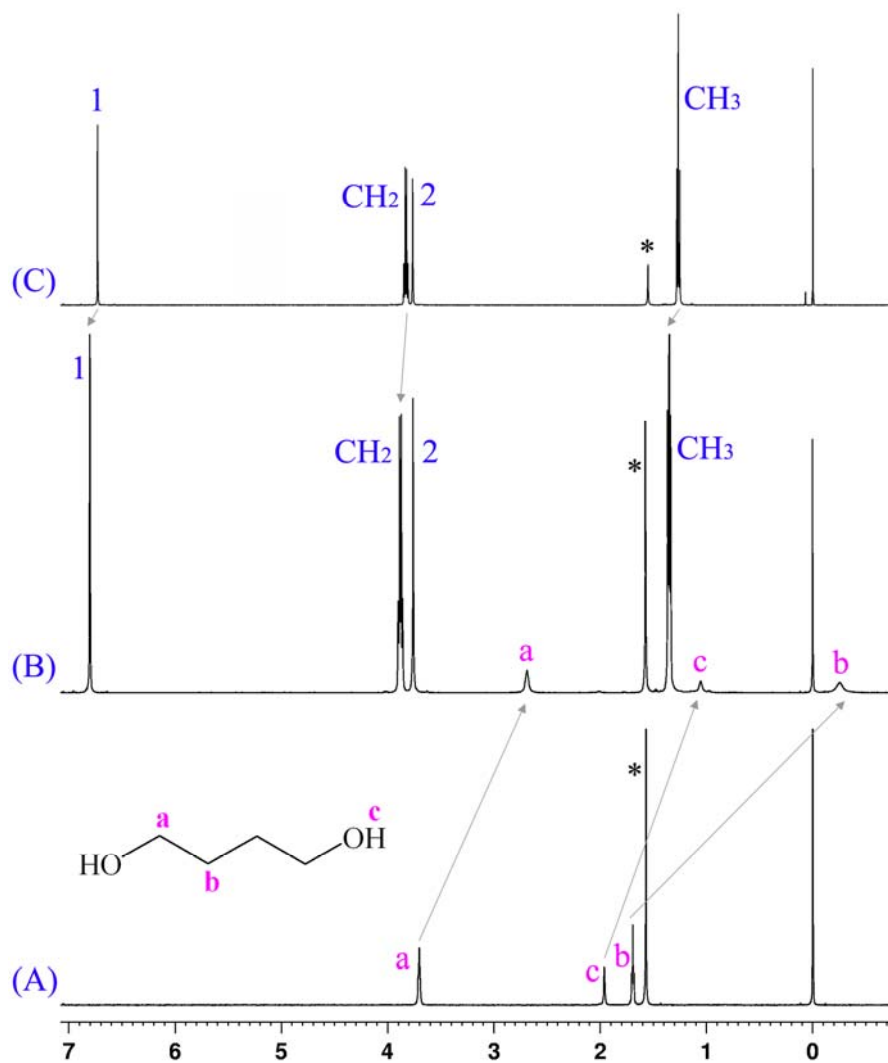


**Figure S10.** <sup>1</sup>H NMR spectra (500 MHz) of (a) DCIBu, (b) DCIBu + EtP5A, and (c) EtP5A in CD<sub>3</sub>Cl at 4.4–5.2 mM. The peaks marked with an asterisk are due to water.

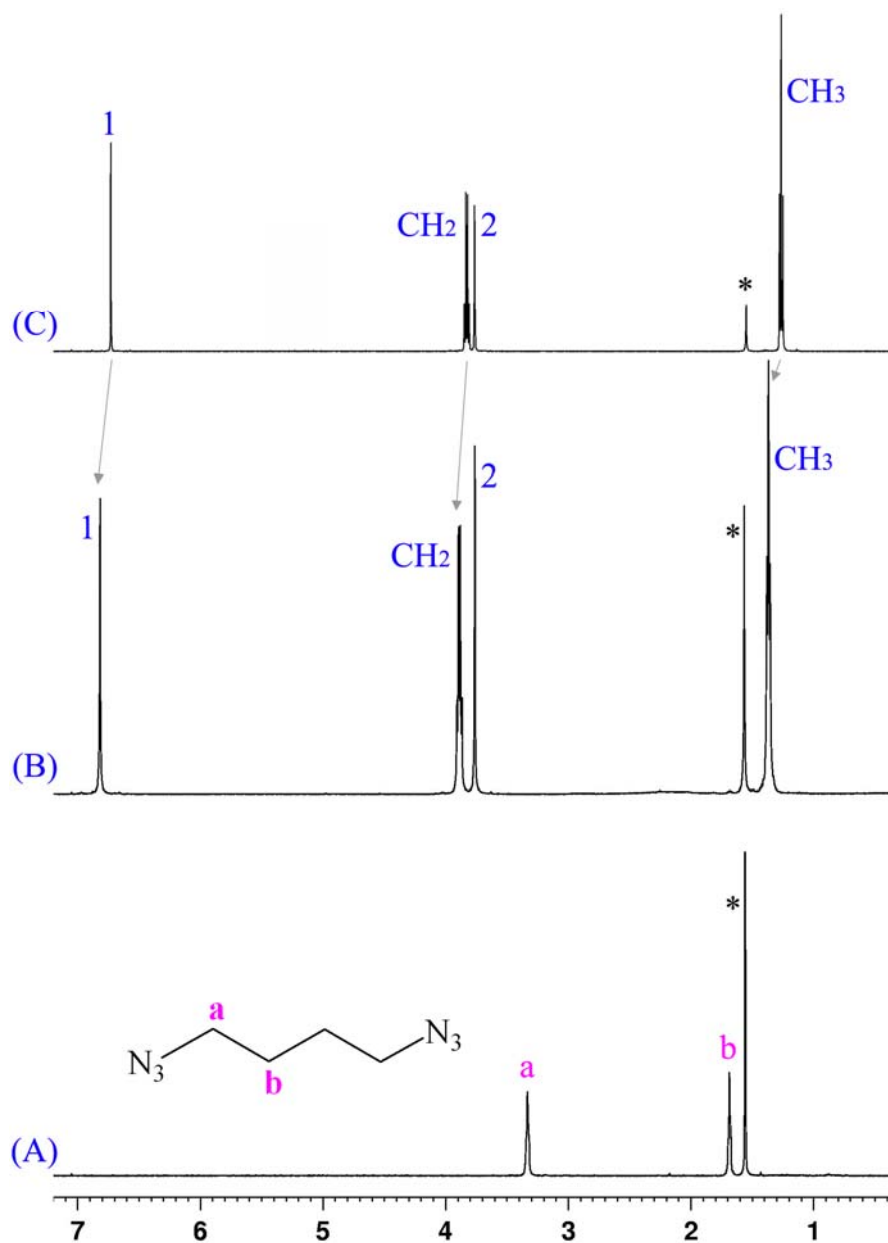


**Figure S11.**  $^1\text{H}$  NMR spectra (500 MHz) of (a) DFBu, (b) DFBu + EtP5A, and (c) EtP5A in  $\text{CD}_3\text{Cl}$  at 4.3–5.2 mM. The peaks marked with an asterisk are due to water.

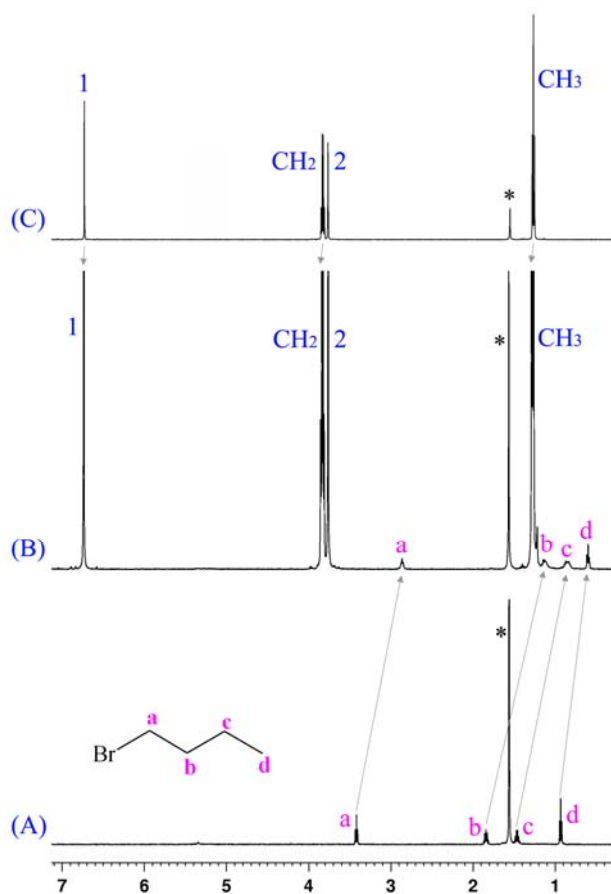




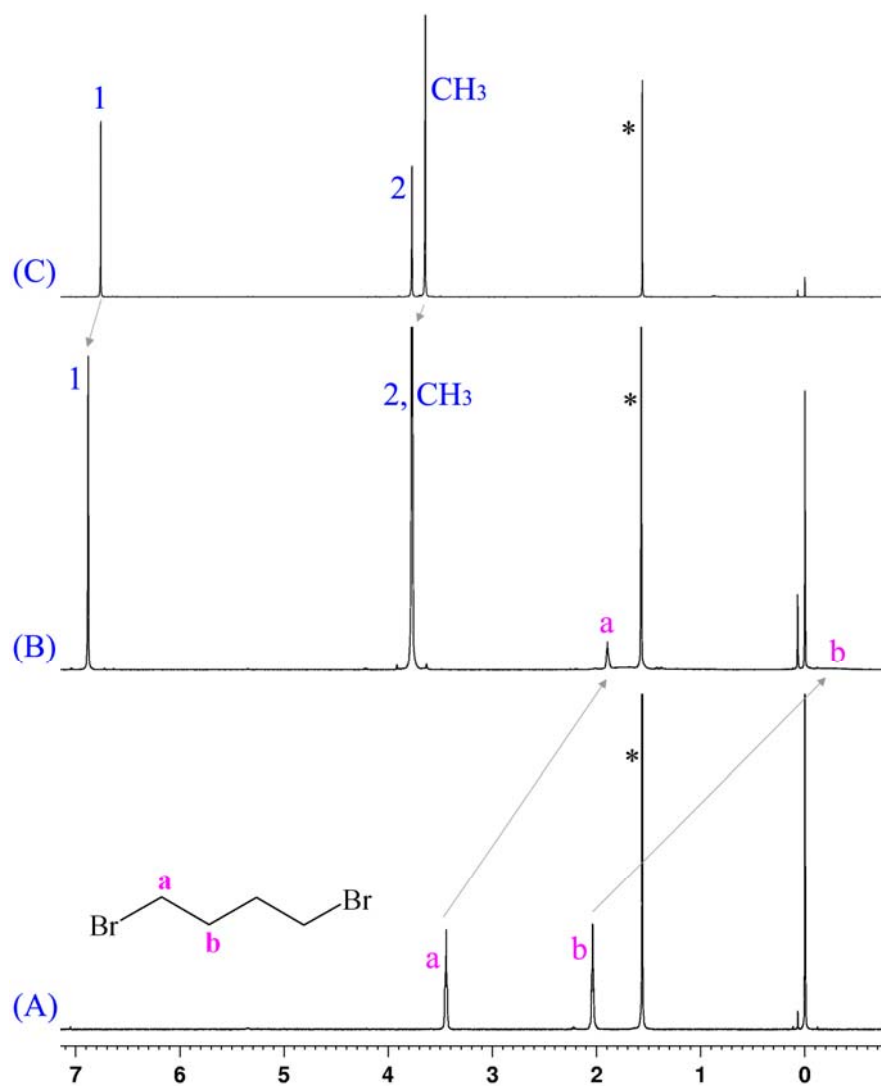
**Figure S12.** <sup>1</sup>H NMR spectra (500 MHz) of (a) DOHBU, (b) DOHBU + EtP5A, and (c) EtP5A in CD<sub>3</sub>Cl at 4.1–4.7 mM. The peaks marked with an asterisk are due to water.



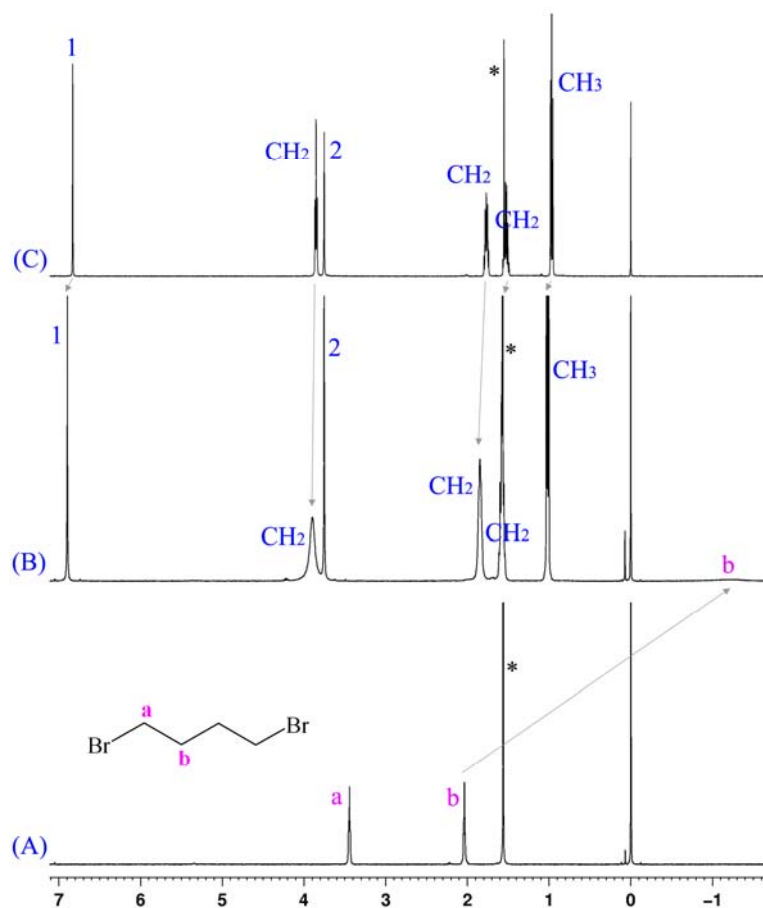
**Figure S13.** <sup>1</sup>H NMR spectra (500 MHz) of (a) DN<sub>3</sub>Bu, (b) DN<sub>3</sub>Bu + EtP5A, and (c) EtP5A in CD<sub>3</sub>Cl at 4.0–4.6 mM. The peaks marked with an asterisk are due to water.



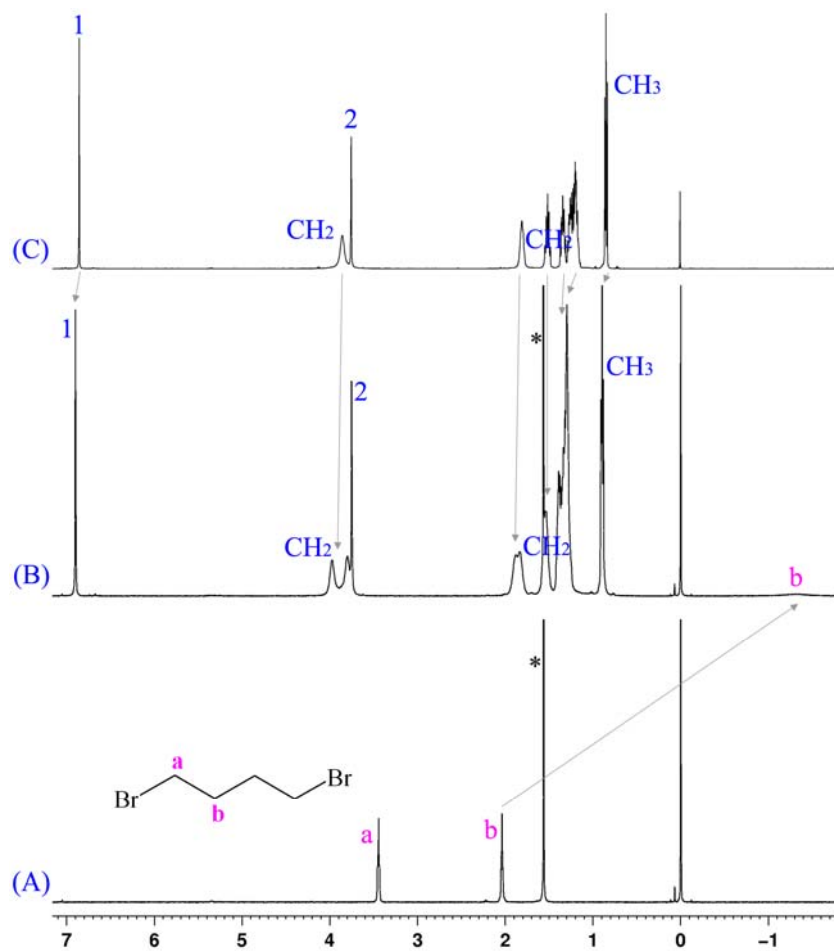
**Figure S14.**  $^1\text{H}$  NMR spectra (500 MHz) of (a) BrBu, (b) BrBu + EtP5A, and (c) EtP5A in  $\text{CD}_3\text{Cl}$  at 4.0–4.6 mM. The peaks marked with an asterisk are due to water.



**Figure S15.** <sup>1</sup>H NMR spectra (500 MHz) of (a) DBrBu, (b) DBrBu + MeP5A, and (c) MeP5A in CD<sub>3</sub>Cl at 4.2–4.8 mM. The peaks marked with an asterisk are due to water.

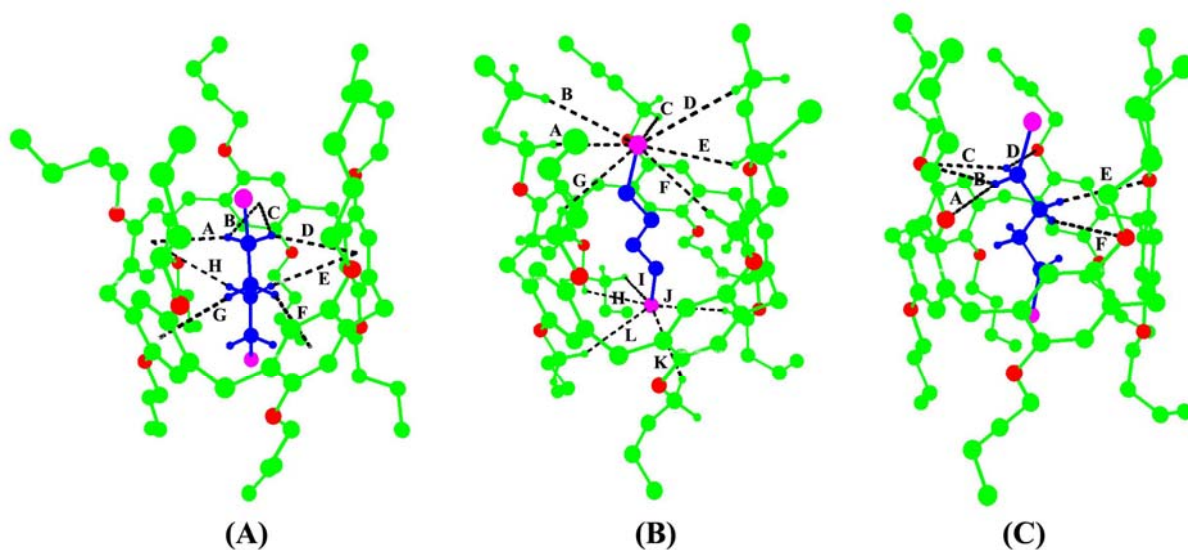


**Figure S16.** <sup>1</sup>H NMR spectra (500 MHz) of (a) DBrBu, (b) DBrBu + BuP5A, and (c) BuP5A in CD<sub>3</sub>Cl at 4.2–5.0 mM. The peaks marked with an asterisk are due to water.



**Figure S17.**  $^1\text{H}$  NMR spectra (500 MHz) of (a) DBrBu, (b) DBrBu + OctP5A, and (c) OctP5A in  $\text{CD}_3\text{Cl}$  at 4.2–5.1 mM. The peaks marked with an asterisk are due to water.

**Crystal structures of DIBu $\subset$ BuP5A, DFBu $\subset$ BuP5A and DCIBu $\subset$ OctP5A complexes.**

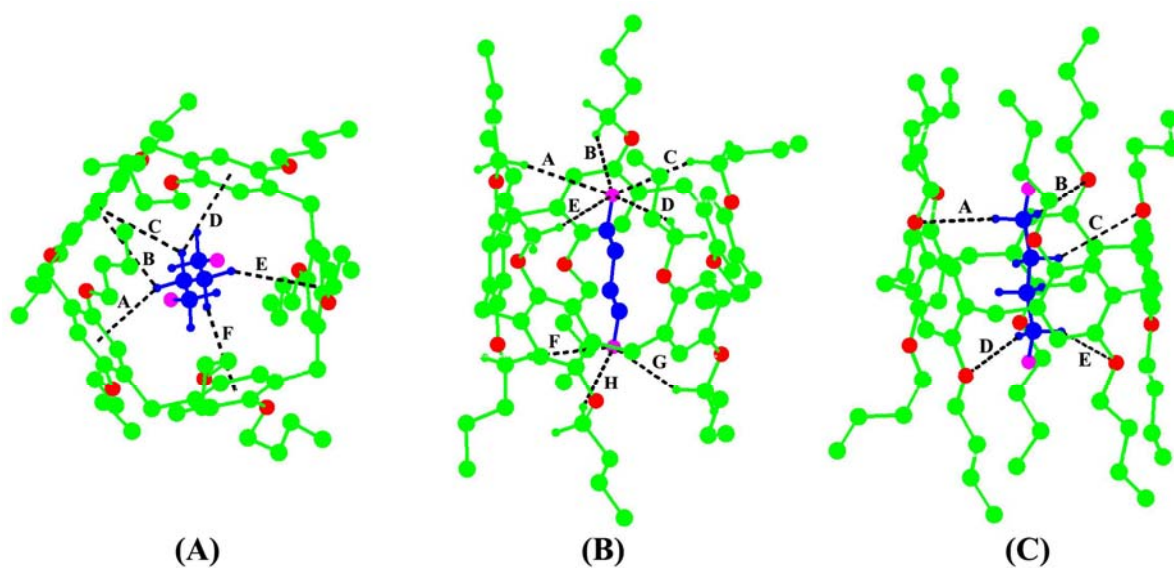


**Figure S18.** Crystal structure of the interpenetrated complex DIBu $\subset$ BuP5A. Hydrogens of the host have been omitted for clarity. BuP5A is green, DIBu is blue, oxygens are red, and iodines are magenta. Dashes represent C–H $\cdots$  $\pi$  interactions or C–H $\cdots$ I/O hydrogen bonds.

(A) C–H $\cdots$  $\pi$  parameters: H $\cdots$ ring centre distances (Å), C–H $\cdots$ ring angles (deg) A, 3.15, 156; B, 3.44, 111; C, 3.33, 118; D, 3.18, 144; E, 3.45, 135; F, 2.75, 144; G, 2.81, 176; H, 3.40, 150.

(B) C–H $\cdots$ I hydrogen-bond parameters: H $\cdots$ I distances (Å), C–H $\cdots$ I angles (deg) A, 3.25, 162; B, 3.19, 167; C, 3.47, 135; D, 3.44, 135; E, 3.41, 138; F, 3.34, 168; G, 3.33, 139; H, 3.25, 130; I, 3.43, 123; J, 3.21, 142; K, 3.35, 138; L, 3.29, 154.

(C) C–H $\cdots$ O hydrogen-bond parameters: H $\cdots$ O distances (Å), C–H $\cdots$ O angles (deg) A, 3.09, 155; B, 3.49, 102; C, 3.19, 133; D, 3.30, 135; E, 3.32, 144; F, 3.47, 162.



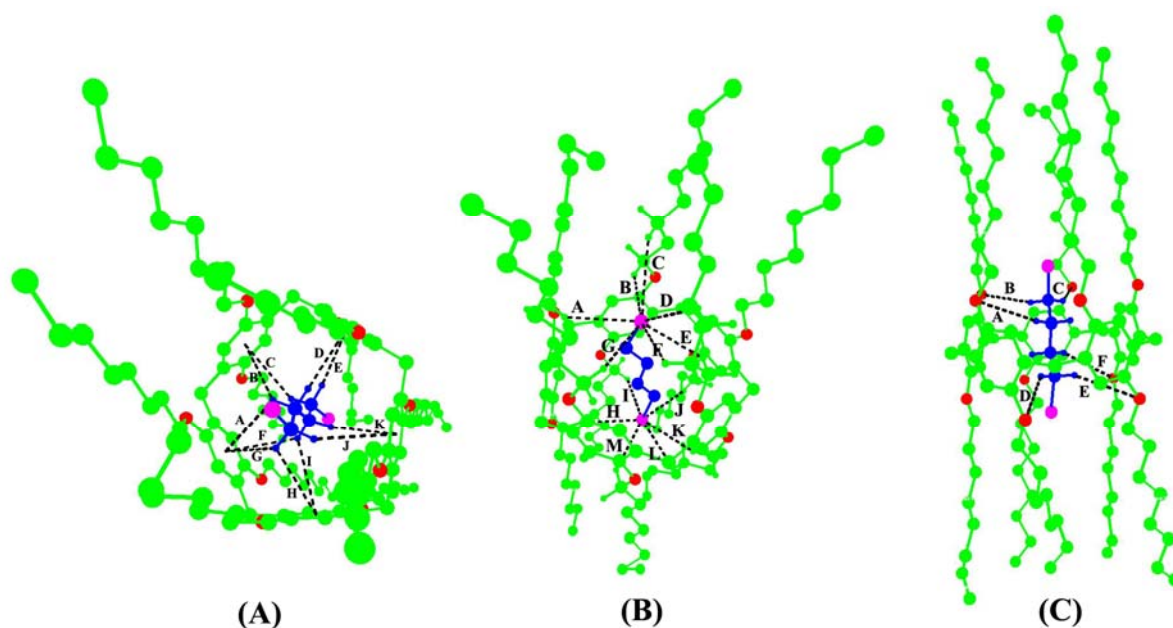
**Figure S19.** Crystal structure of the interpenetrated complex  $\text{DFBu} \subset \text{BuP5A}$ . Hydrogens of the host have been omitted for clarity. BuP5A is green, DFBu is blue, oxygens are red, and fluorines are magenta. Dashes represent  $\text{C-H} \cdots \pi$  interactions or  $\text{C-H} \cdots \text{F/O}$  hydrogen bonds.

(A)  $\text{C-H} \cdots \pi$  parameters:  $\text{H} \cdots \text{ring}$  centre distances ( $\text{\AA}$ ),  $\text{C-H} \cdots \text{ring}$  angles (deg) A, 3.17, 150; B, 3.44, 112; C, 3.42, 114; D, 3.14, 144; E, 3.07, 153; F, 2.98, 160.

(B)  $\text{C-H} \cdots \text{F}$  hydrogen-bond parameters:  $\text{H} \cdots \text{F}$  distances ( $\text{\AA}$ ),  $\text{C-H} \cdots \text{F}$  angles (deg) A, 3.21, 164; B, 2.90, 145; C, 2.87, 153; D, 3.39, 151; E, 3.48, 138; F, 2.92, 141; G, 3.02, 135; H, 3.11, 159.

(C)  $\text{C-H} \cdots \text{O}$  hydrogen-bond parameters:  $\text{H} \cdots \text{O}$  distances ( $\text{\AA}$ ),  $\text{C-H} \cdots \text{O}$  angles (deg) A, 3.39, 128; B, 3.19, 168; C, 3.38, 151; D, 3.35, 167; E, 3.11, 140.





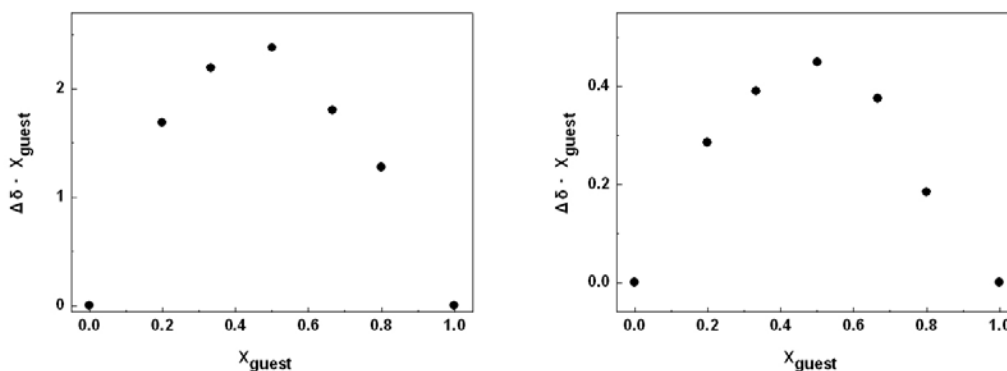
**Figure S20.** Crystal structure of the interpenetrated complex DCIBu ⊂ OctP5A. Hydrogens of the host have been omitted for clarity. OctP5A is green, DCIBu is blue, oxygens are red, and chlorines are magenta. Dashes represent C-H... $\pi$  interactions or C-H...Cl/O hydrogen bonds.

(A) C-H... $\pi$  parameters: H...ring centre distances (Å), C-H...ring angles (deg) A, 3.42, 116; B, 3.38, 137; C, 3.13, 138; D, 3.28, 144; E, 2.89, 166; F, 3.17, 132; G, 3.45, 130; H, 3.42, 115; I, 3.40, 122; J, 3.42, 142; K, 2.91, 160.

(B) C-H...Cl hydrogen-bond parameters: H...I distances (Å), C-H...Cl angles (deg) A, 3.23, 137; B, 2.84, 147; C, 3.45, 135; D, 3.30, 129; E, 3.03, 132; F, 3.26, 116; G, 3.02, 161; H, 3.11, 163; I, 2.94, 149; J, 3.22, 165; K, 3.05, 160; L, 3.49, 117; M, 3.02, 138.

(C) C-H...O hydrogen-bond parameters: H...O distances (Å), C-H...O angles (deg) A, 3.17, 164; B, 2.89, 165; C, 2.86, 140; D, 3.32, 139; E, 3.23, 159; F, 3.37, 155.

### Job plots.



**Figure S21.** Left: Job plot showing the 1 : 1 stoichiometry of the complex between DOHBU and EtP5A in  $\text{CDCl}_3$  by plotting the  $\Delta\delta$  in chemical shift of the guest's methylene proton  $\text{H}_b$  observed by  $^1\text{H}$  NMR spectroscopy against the mole fraction of guest ( $X_{\text{guest}}$ ). ( $[\text{host}] + [\text{guest}] = 12.0 \text{ mM}$ ). Right: Job plot showing the 1 : 1 stoichiometry of the complex between BrBu and EtP5A in  $\text{CDCl}_3$  by plotting the  $\Delta\delta$  in chemical shift of the guest's methyl proton observed by  $^1\text{H}$  NMR spectroscopy against the mole fraction of guest ( $X_{\text{guest}}$ ). ( $[\text{host}] + [\text{guest}] = 16.0 \text{ mM}$ ).