



## Supporting Information

for

### Dicarboxylate recognition based on ultracycle hosts through cooperative hydrogen bonding and anion– $\pi$ interactions

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**Experimental details and characterization data (including  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and HRMS of precursor compounds and ultracycles, X-ray data for B4aH, theoretical calculations, and NMR titration data)**

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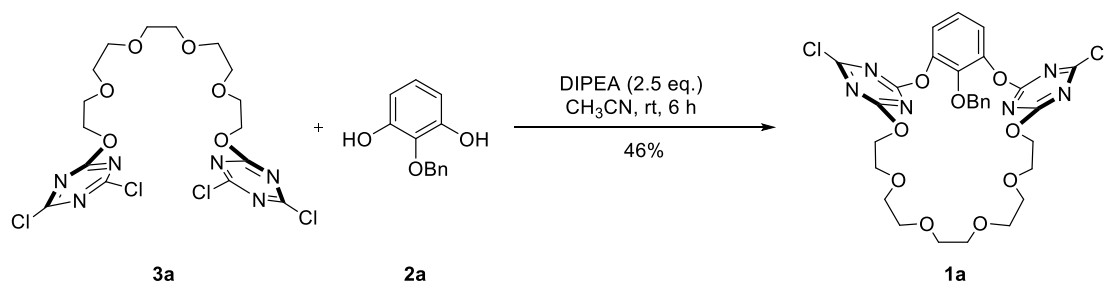
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## 1. General information

All chemicals were obtained from commercial sources and used without further purification unless stated otherwise. NMR spectra were recorded on Bruker 400 and 500 MHz NMR spectrometers at room temperature. Chemical shifts are reported in ppm and referenced to tetramethylsilane or the residual solvent resonance. Mass spectra were measured on a Thermo Fisher Exactive Mass Spectrometer. Infrared spectra were recorded using a Nicolet-6700 FT-IR spectrometer with KBr pellets in the 4000–400  $\text{cm}^{-1}$  region. Elemental analysis was recorded on Carlo Erba 1106. Melting points were determined on Melting Point Instrument SGWX-4 using a microscopic hot plate method and are uncorrected. X-ray diffraction was performed on a Rigaku R-Axis RAPID IP.

## 2. Synthesis and characterization

### 2.1 Synthesis and characterization of macrocyclic precursors

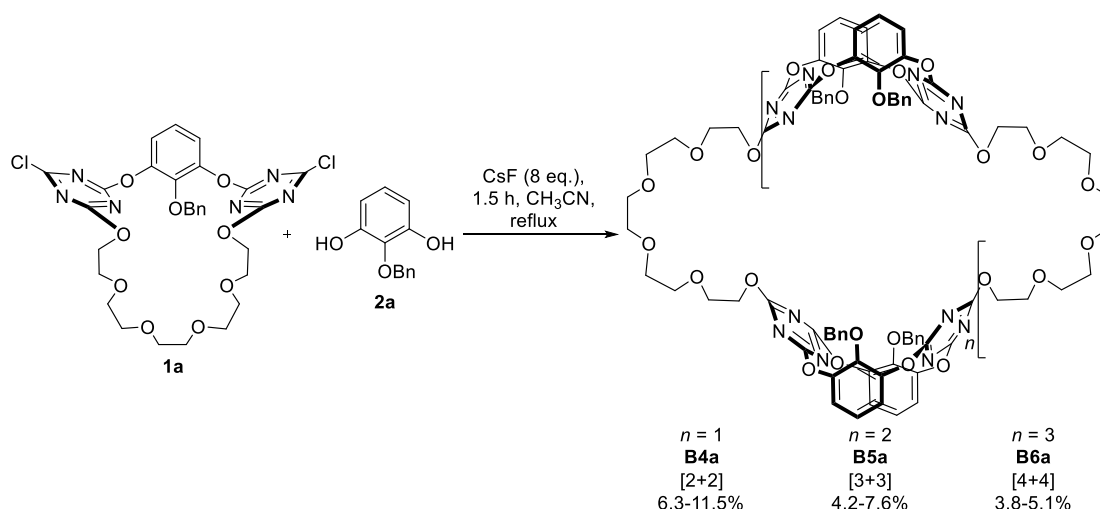


**Scheme S1.** Synthesis of macrocyclic precursor **1a**.

Synthesis of **1a** (in a manner similar to our previously reported procedure<sup>[S1]</sup>). Compound **3a**<sup>[S2]</sup> (1.07 g, 2.00 mmol) and 2-(benzyloxy)benzene-1,3-diol (**2a**<sup>[S3]</sup>, 0.44 g, 2.00 mmol) were dissolved in 200 mL acetonitrile. To this solution was added dropwise DIPEA (0.65 g, 5.00 mmol) in 60 mL acetonitrile during a period of 0.5 h, and then kept stirring for 5.5 h, and then solvent was removed under vacuum by a rotary evaporator. The residue was chromatographed on silica gel (100–200 mesh) with a mixture of ethyl acetate and petroleum ether 1:1 (v/v) as eluent to yield **1a** (0.63 g, 46%) as white solid.

**1a**: mp 38–41 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$  (ppm) 7.37–7.21 (m, 6H), 7.12 (s, 2H), 4.92 (s, 2H), 4.38 (t, *J* = 4.4 Hz, 4H), 3.67 (t, *J* = 4.6 Hz, 4H), 3.46 (m, 12H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz)  $\delta$  (ppm) 172.4, 172.2, 171.8, 145.2, 142.4, 136.6, 128.6, 128.5, 127.8, 124.5, 121.6, 75.5, 70.3, 68.9, 68.2; IR (KBr)  $\nu$  3201, 3059, 2877, 2803, 1700, 1455, 1397, 1094, 1060, 545 cm<sup>-1</sup>; HR-ESI-MS (positive ion mode) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>9</sub>: 677.1524, found: 677.1518; Anal. calcd (%) for C<sub>29</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>9</sub> + H<sub>2</sub>O: C, 48.82; H, 4.80; N, 11.78, found: C, 48.89; H, 4.96; N, 11.73.

## 2.2 Synthesis and characterization of ultracyclic precursors



**Scheme S2.** Synthesis of ultracyclic precursors **B4a**, **B5a** and **B6a**.

Synthesis of ultracycles **B4a**, **B5a**, and **B6a**. Compound **1a** (1.88 g, 3.00 mmol), 2-(benzyloxy)benzene-1,3-diol (**2a**, 0.65 g, 3.00 mmol) and cesium fluoride (3.65 g, 24.00 mmol) were added into 300 mL dry acetonitrile. Then, the mixture was allowed to reflux for 1.5 h under argon atmosphere. After cooling to room temperature, the mixture was filtered, and the filtrate was concentrated under vacuum by a rotary evaporator and then chromatographed on silica gel (100–200 mesh) with a mixture of dichloromethane/acetone 6:1–4:1 as eluent to yield **B4a** (155 mg, 6.3%), **B5a** (125 mg, 5.1%), and **B6a** (105 mg, 4.3%) as white solids.

**B4a**: mp 51–53 °C; <sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO, 500 MHz)  $\delta$  (ppm) 7.07–6.99 (m, 24H), 6.91 (d, *J* = 7.2 Hz, 8H), 4.72 (s, 8H), 4.39 (t, *J* = 4.5 Hz, 8H), 3.70 (t, *J* = 4.5 Hz, 8H), 3.57–3.53 (m, 24H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz)  $\delta$  (ppm) 174.0, 173.1, 145.3, 142.7, 136.6, 128.3, 128.0, 127.2, 124.2, 121.1, 74.9, 70.4, 70.3, 70.3, 68.4, 68.2; IR (KBr)  $\nu$  2876, 1577, 1557, 1486, 1382, 1335, 1281, 1238, 1119, 814, 750 cm<sup>−1</sup>; HR-ESI-MS (positive ion mode) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>84</sub>H<sub>80</sub>N<sub>12</sub>O<sub>24</sub>Na: 1663.5301, found: 1663.5314; Anal. Calcd (%) for C<sub>84</sub>H<sub>80</sub>N<sub>12</sub>O<sub>24</sub>: C, 61.46; H, 4.91; N, 10.24, found: C, 61.19; H, 4.90; N, 10.09.

**B5a:** mp 47–52 °C;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 500 MHz)  $\delta$  (ppm) 7.12–7.06 (m, 18H), 6.97–6.93 (m, 18H), 6.89 (d,  $J = 7.8$  Hz, 12H), 4.76 (s, 12H), 4.42 (t,  $J = 4.7$  Hz, 12H), 3.74 (t,  $J = 4.7$  Hz, 12H), 3.67–3.54 (m, 39H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ , 125 MHz)  $\delta$  (ppm) 173.6, 145.9, 143.2, 137.1, 128.6, 128.4, 127.9, 124.0, 75.3, 70.8, 70.8, 70.7, 68.9, 68.5; IR (KBr)  $\nu$  2922, 1577, 1557, 1486, 1382, 1334, 1281, 1119, 815  $\text{cm}^{-1}$ ; HR-ESI-MS (positive ion mode)  $m/z$ :  $[\text{M} + 2\text{Na}]^{2+}$  calcd for  $\text{C}_{126}\text{H}_{120}\text{N}_{18}\text{O}_{36}\text{Na}_2$ : 1253.8965, found: 1253.8983; Anal. Calcd (%) for  $\text{C}_{126}\text{H}_{120}\text{N}_{18}\text{O}_{36}$ : C, 61.46; H, 4.91; N, 10.24, found: C, 61.63; H, 5.22; N, 9.57

**B6a:** mp 51–53 °C;  $^1\text{H}$  NMR ( $d_6$ -DMSO, 500 MHz)  $\delta$  (ppm) 7.02–6.99 (m, 48H), 6.91 (d,  $J = 7.3$  Hz, 14H), 4.74 (s, 16H), 4.41 (t,  $J = 4.7$  Hz, 16H), 3.71 (t,  $J = 4.3$  Hz, 16H), 3.56–3.52 (m, 48H);  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 125 MHz)  $\delta$  (ppm) 172.9, 171.9, 144.2, 141.6, 135.6, 127.3, 127.0, 126.2, 123.0, 120.0, 73.8, 69.25, 69.20, 67.4, 67.2 ; IR (KBr)  $\nu$  2878, 1577, 1557, 1486, 1383, 1335, 1281, 1238, 1119, 814, 750  $\text{cm}^{-1}$ ; HR-ESI-MS (positive ion mode)  $m/z$ :  $[\text{M} + 3\text{Na}]^{3+}$  calcd for  $\text{C}_{168}\text{H}_{160}\text{N}_{24}\text{O}_{48}\text{Na}_3$ : 1117.3520, found: 1117.3538; Anal. Calcd (%) for  $\text{C}_{168}\text{H}_{160}\text{N}_{24}\text{O}_{48}$ : C, 61.46; H, 4.91; N, 10.24, found: C, 61.77; H, 5.08; N, 9.71.

## 2.3 HRESIMS studies of ultracyclic precursors.

The high-resolution ESI–MS studies were carried out.

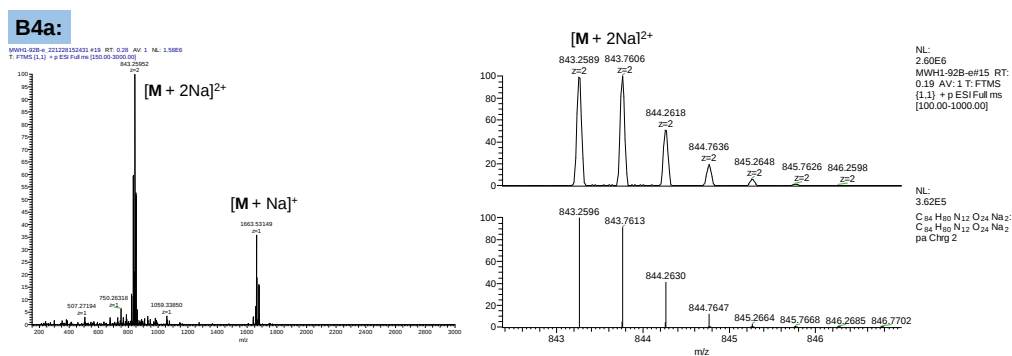


Figure S1. HRESIMS spectra of B4a.

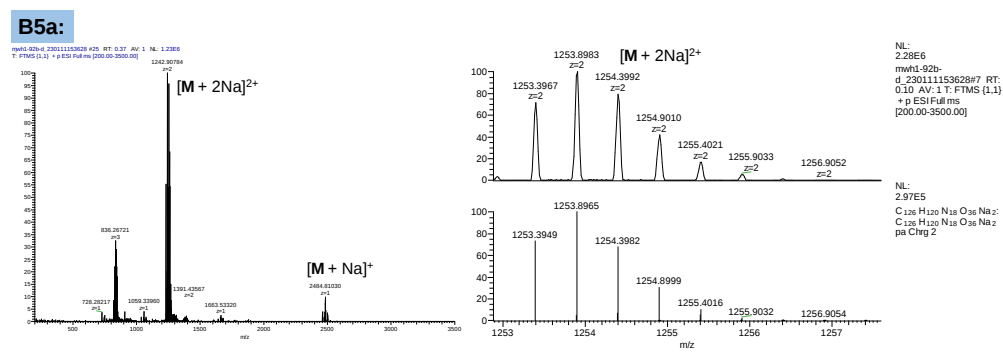


Figure S2. HRESIMS spectra of B5a.

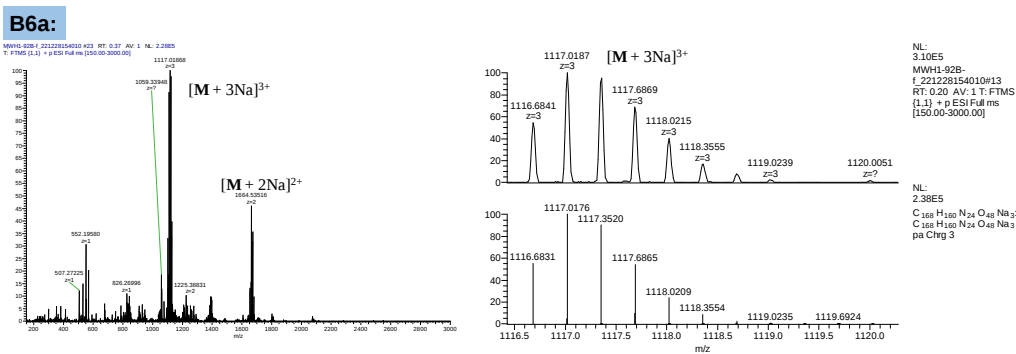
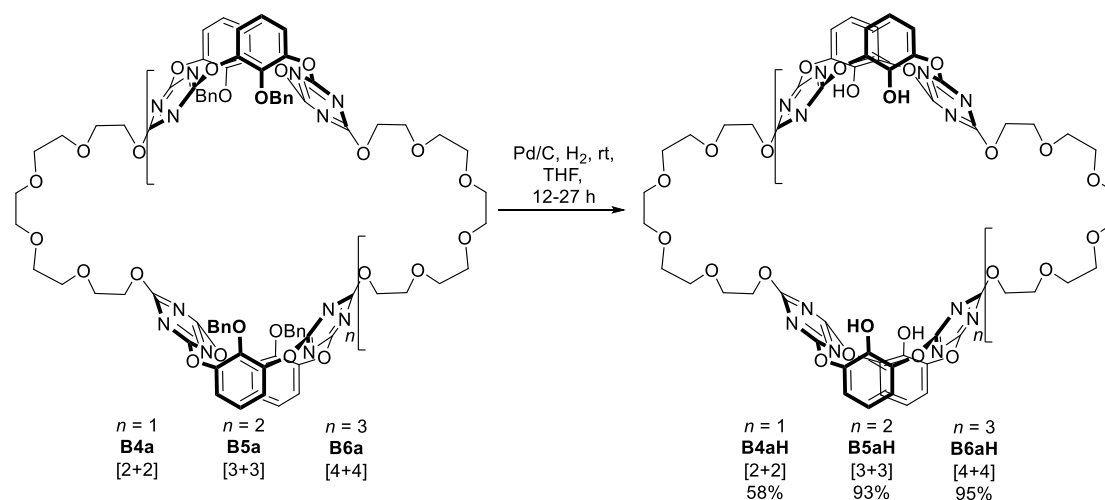


Figure S3. HRESIMS spectra of B6a.

## 2.4 Debenzylation of ultracycles.



**Scheme S3.** Debenzylation of ultracycles.

Synthesis of **B4aH** (taking **B4a** as an example, similarly for other compounds). At room temperature, **B4a** (100 mg, 0.0609 mmol), Pd/C (40 mg) and THF (20 mL) were mixed in a two-necked flask. The mixture was stirred for 24 h under a H<sub>2</sub> balloon. After filtration over diatomaceous earth, the filtrate was concentrated under vacuum by a rotary evaporator. The residue was recrystallized from methanol, dichloromethane, acetonitrile and ethyl ether to give purified compound **B4aH** (45 mg, 58%) as white solid.

**Table S1.** Construction of ultracycles.

| Entry | Compound   | Amount              | Pd/C   | Time | Yield |
|-------|------------|---------------------|--------|------|-------|
| 1     | <b>B4a</b> | 0.0609mmol, 100 mg  | 40 mg  | 24 h | 58%   |
| 2     | <b>B5a</b> | 0.0812 mmol, 200 mg | 120 mg | 27 h | 93%   |
| 3     | <b>B6a</b> | 0.0609 mmol, 200 mg | 150 mg | 12 h | 95%   |

**B4aH**: mp 42–44 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$  (ppm) 9.38 (s, 4H), 6.85 (d, *J* = 8.0 Hz, 8H), 6.63 (t, *J* = 8.4 Hz, 4H), 4.59 (t, *J* = 4.7 Hz, 8H), 3.83–3.76 (t, *J* = 4.0 Hz, 8H), 3.62–3.60 (m, 8H), 3.57–3.55 (m, 16H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz)  $\delta$  (ppm) 173.9, 173.2, 142.1, 141.2, 120.4, 118.6, 70.3, 70.3, 70.3, 68.65, 67.9; IR (KBr)

$\nu$  2876, 1577, 1500, 1394, 1335, 1259, 1119, 815  $\text{cm}^{-1}$ ; HR-ESI-MS (negative ion mode)  $m/z$ :  $[\text{M} - \text{H}]^-$  calcd for  $\text{C}_{56}\text{H}_{55}\text{N}_{12}\text{O}_{24}$ : 1279.3447, found: 1279.3468; Anal. calcd (%) for  $\text{C}_{56}\text{H}_{56}\text{N}_{12}\text{O}_{24}$ : C, 52.50; H, 4.41; N, 13.12, found: C, 52.05; H, 4.44; N, 12.73.

**B5aH**: mp 47–49  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz)  $\delta$  (ppm) 9.44 (s, 6H), 6.83 (d,  $J = 8.1$  Hz, 12H), 6.62 (t,  $J = 7.8$  Hz, 8H), 4.55 (s, 12H), 3.79 (s, 12H), 3.64–3.52 (m, 36H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 125 MHz)  $\delta$  (ppm) 173.3, 172.5, 141.5, 140.4, 119.8, 117.9, 69.7, 69.7, 69.6, 68.1, 67.4; IR (KBr)  $\nu$  2875, 1578, 1499, 1392, 1336, 1259, 1215, 1120, 845, 816  $\text{cm}^{-1}$ ; HR-ESI-MS (negative ion mode)  $m/z$ :  $[\text{M} - \text{H}]^-$  calcd for  $\text{C}_{84}\text{H}_{83}\text{N}_{18}\text{O}_{36}$ : 1919.5212, found: 1919.5216; Anal. Calcd (%) for  $\text{C}_{84}\text{H}_{84}\text{N}_{18}\text{O}_{36} + \text{H}_2\text{O}$ : C, 50.38; H, 4.68; N, 12.59, found: C, 50.82; H, 4.46; N, 12.30.

**B6aH**: mp 46–48  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz)  $\delta$  (ppm) 9.45 (s, 8H), 6.83 (d,  $J = 7.4$  Hz, 16H), 6.63 (t,  $J = 7.7$  Hz, 8H), 4.55 (s, 16H), 3.79 (s, 16H), 3.66–3.50 (m, 48H);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 125 MHz)  $\delta$  (ppm) 173.9, 173.1, 142.1, 141.0, 120.4, 118.5, 70.3, 70.3, 68.6, 67.9; IR (KBr)  $\nu$  2875, 1578, 1500, 1394, 1336, 1120, 947, 845, 816  $\text{cm}^{-1}$ ; HR-ESI-MS (positive ion mode)  $m/z$ :  $[\text{M} + 2\text{Na}]^{2+}$  calcd for  $\text{C}_{112}\text{H}_{112}\text{N}_{24}\text{O}_{48}\text{Na}_2$ : 1304.3456, found: 1304.3411; Anal. calcd (%) for  $\text{C}_{112}\text{H}_{112}\text{N}_{24}\text{O}_{48} + \text{H}_2\text{O}$ : C, 50.89; H, 4.61; N, 12.72; found: C, 51.27; H, 4.78; N, 12.03.

### 3. $^1\text{H}$ NMR titrations

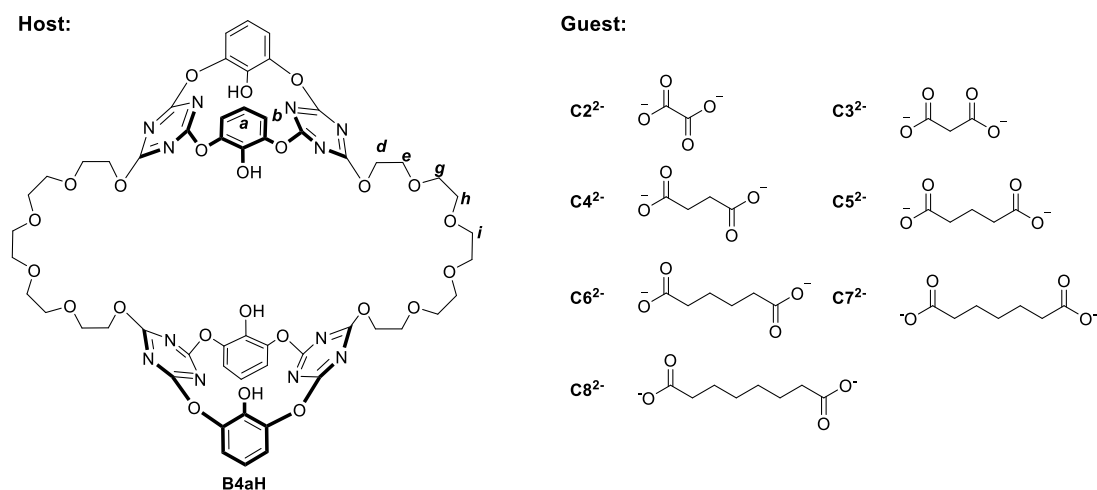
#### 3.1 Titration method and analysis

A stock solution of the host (1 mM in  $\text{CD}_3\text{CN}$ ) was prepared. The guest solutions were prepared by dissolving the dicarboxylates into the host stock solution, which resulted in a final concentration of 50 mM. 500  $\mu\text{L}$  of the host stock solution was added to an NMR tube to record an original spectrum, then titration spectra were obtained after the addition of aliquots of guest solutions.

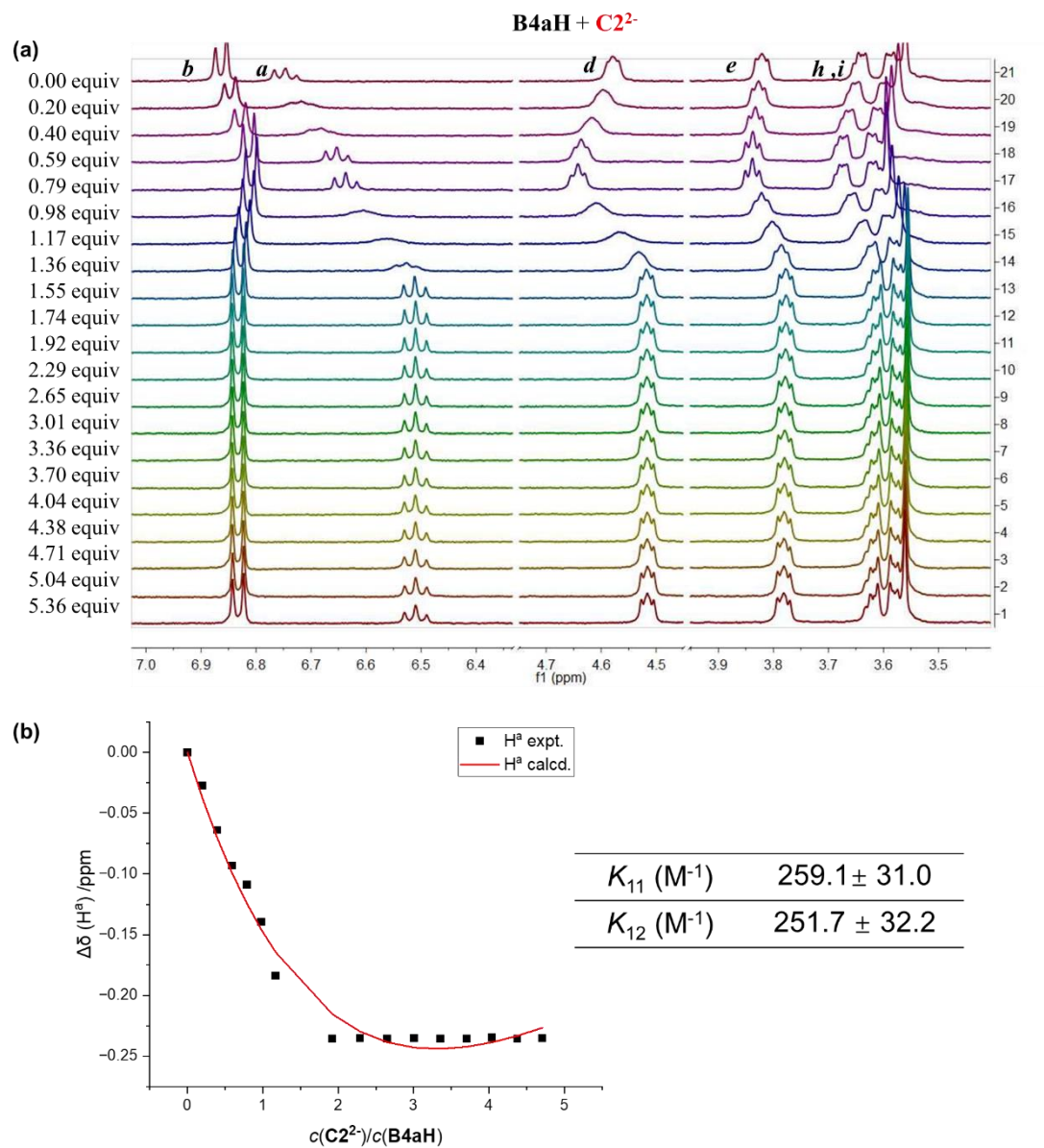
The aromatic proton  $\text{H}^a$  exhibited continuous upfield shifts, while  $\text{H}^b$  initially shifted upfield and then downfield. These chemical shift changes indicated the hydrogen bonding and anion– $\pi$  interactions between the carboxylate heads and the submacrocycles. The titration curves ( $\text{H}^a$ ) were analyzed using the Bindfit v0.5 program<sup>[S4–S6]</sup> to determine the binding stoichiometry (1:1 or 1:2) and binding constants.

#### 3.2 Titration data

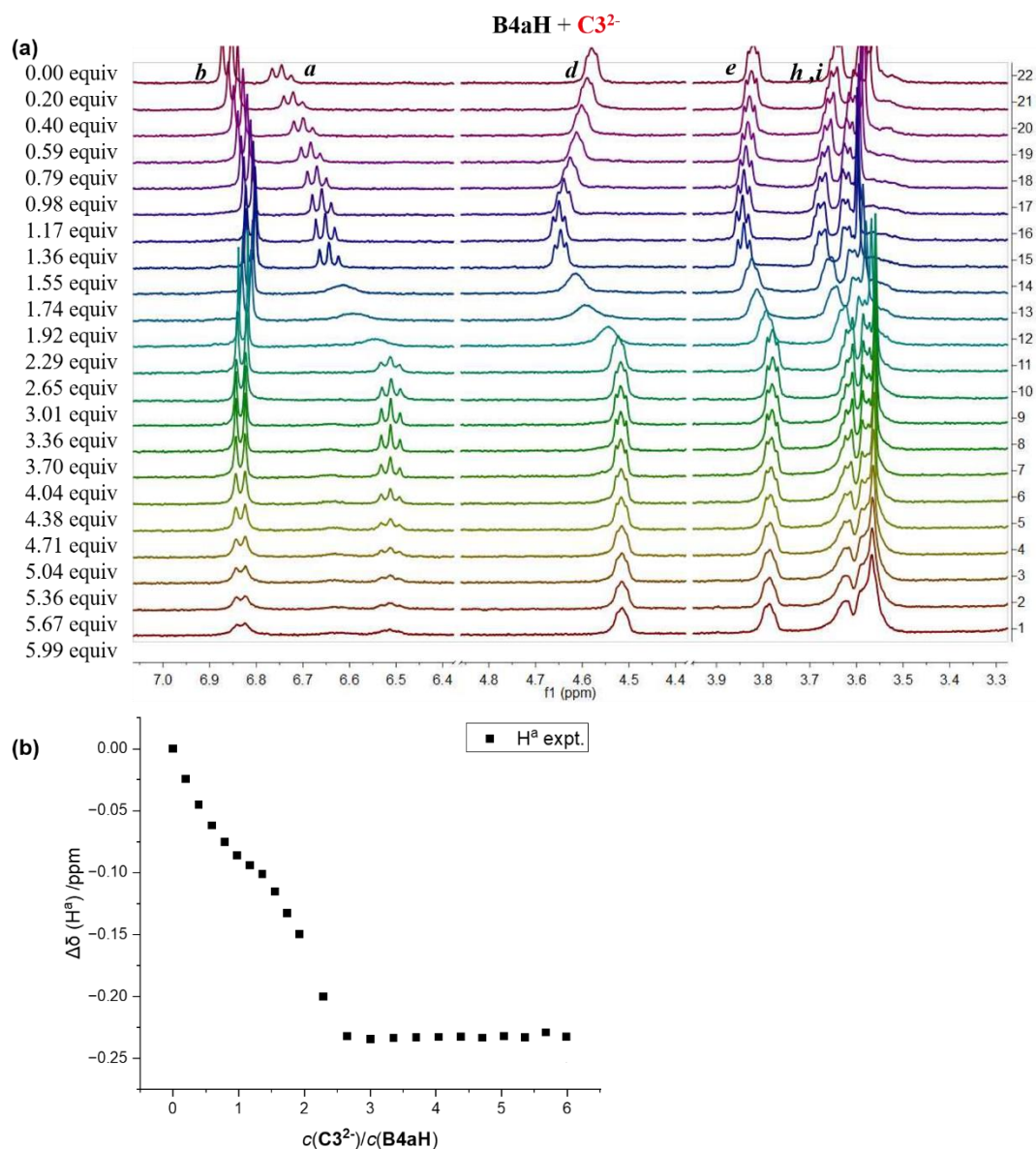
##### 3.2.1 Titration between **B4aH** and dicarboxylates



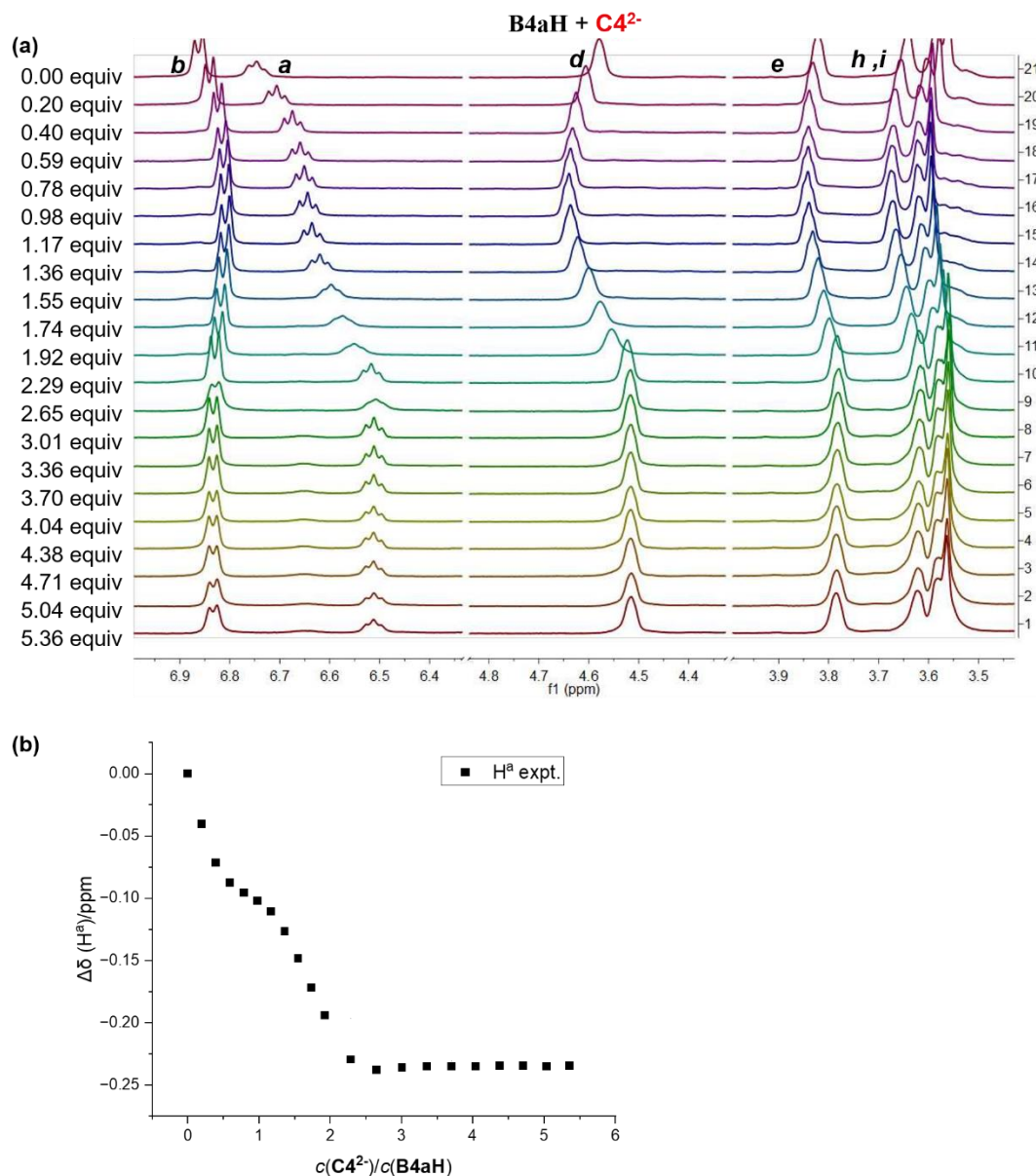
**Scheme S4.** The structure of **B4aH** and guests.



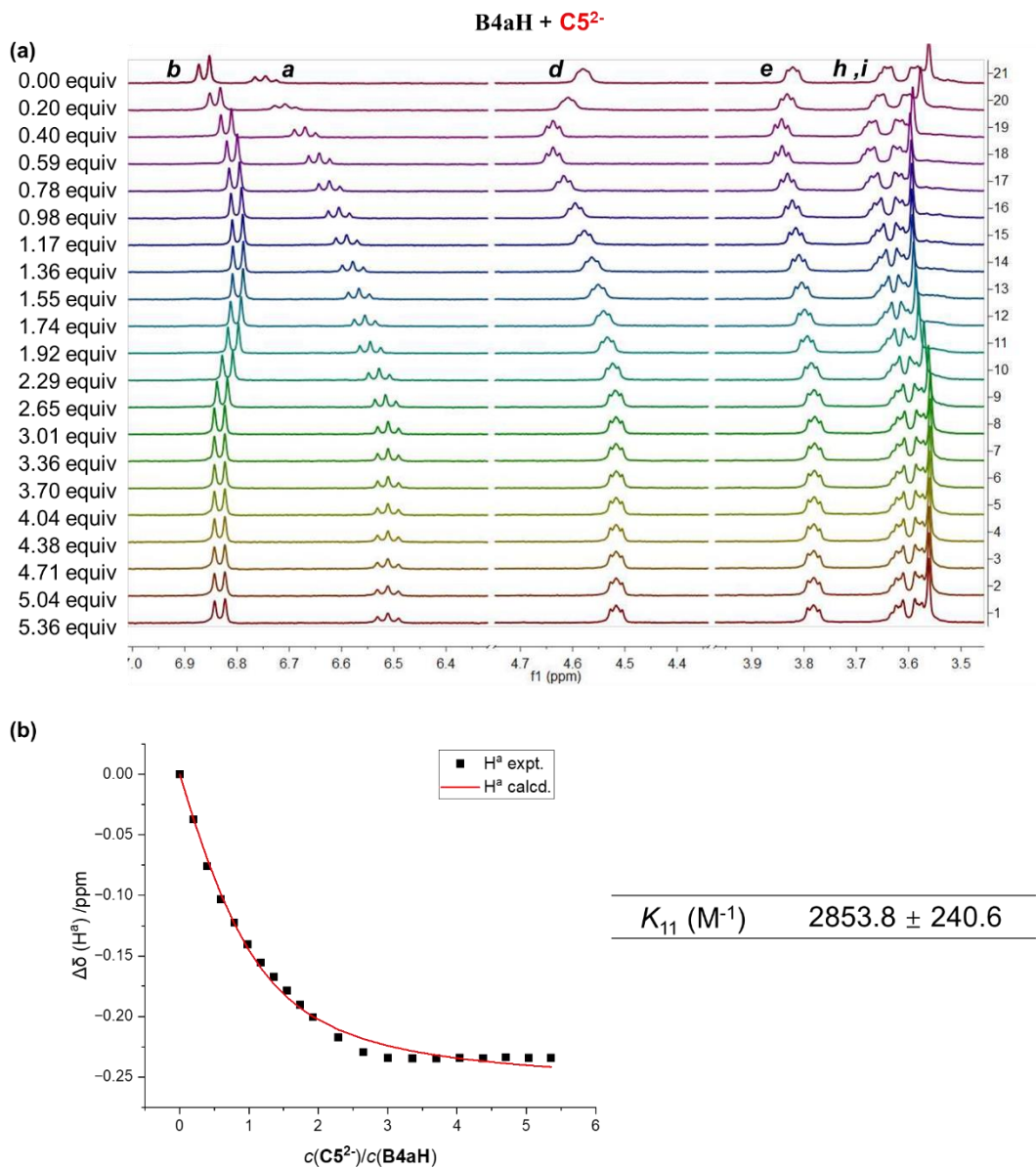
**Figure S4.** (a) <sup>1</sup>H NMR titration between **B4aH** and **C2<sup>2-</sup>** ( $c(\text{B4aH}) = 1 \text{ mM}$ ,  $c((\text{TBA}^+)_2\text{C2}^{2-}) = 50 \text{ mM}$ , 298 K, 400 MHz, CD<sub>3</sub>CN); (b) Fitting results of the titration.



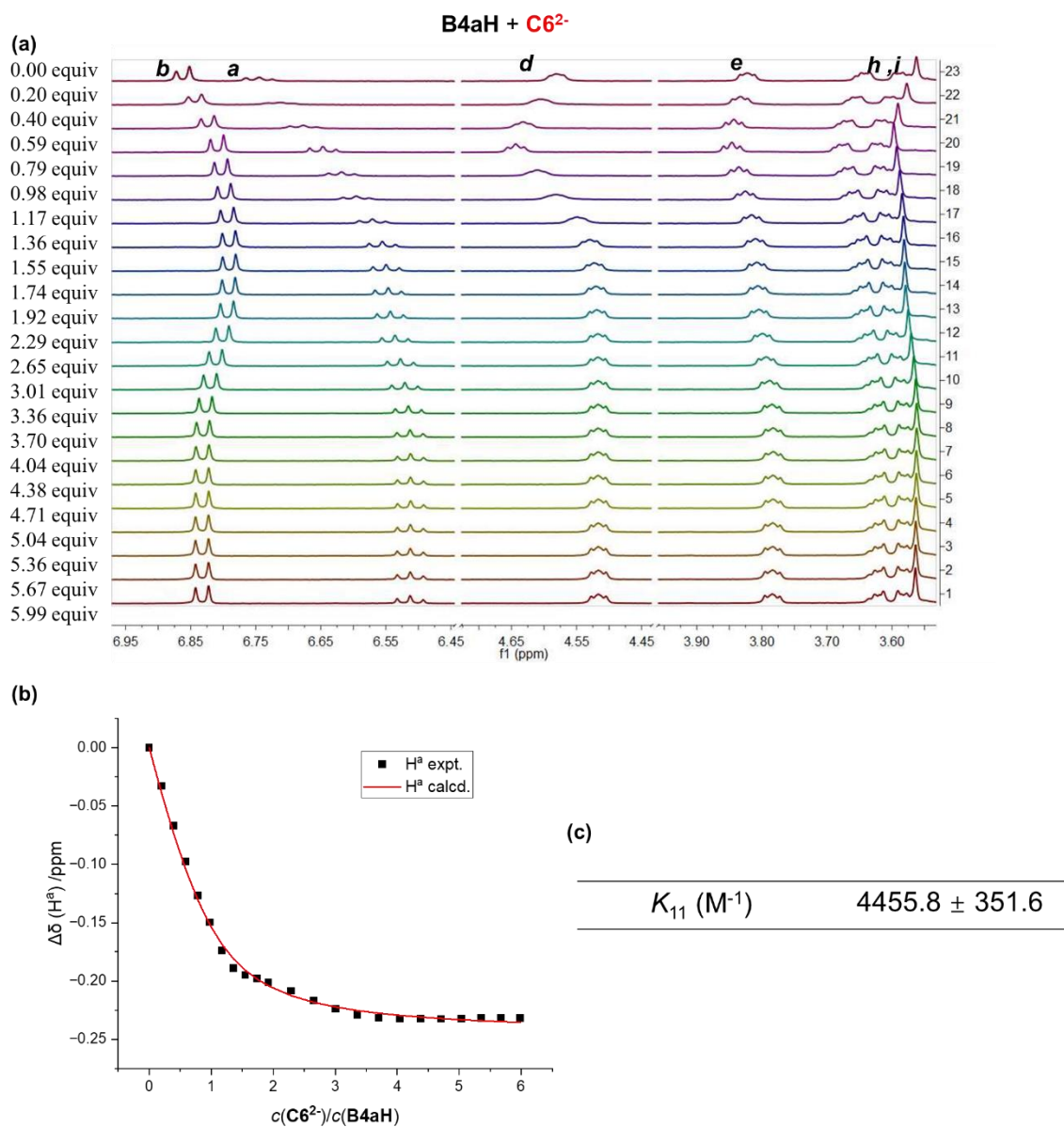
**Figure S5.** (a) <sup>1</sup>H NMR titration between **B4aH** and **C3<sup>2-</sup>** ( $c(\text{B4aH}) = 1 \text{ mM}$ ,  $c((\text{TBA}^+)_2\text{C3}^{2-}) = 50 \text{ mM}$ , 298 K, 400 MHz, CD<sub>3</sub>CN); (b) the chemical shift change curve. The irregular curve may arise from that the short chain length of the anion prevent synergistic recognition of the two subcavities, and it was also hard for the host to accommodate two anions to reach stable 1:2 complexation. In addition, the host conformation may change upon binding. As a result, no reliable binding constants could be obtained using either 1:1 or 1:2 binding models.



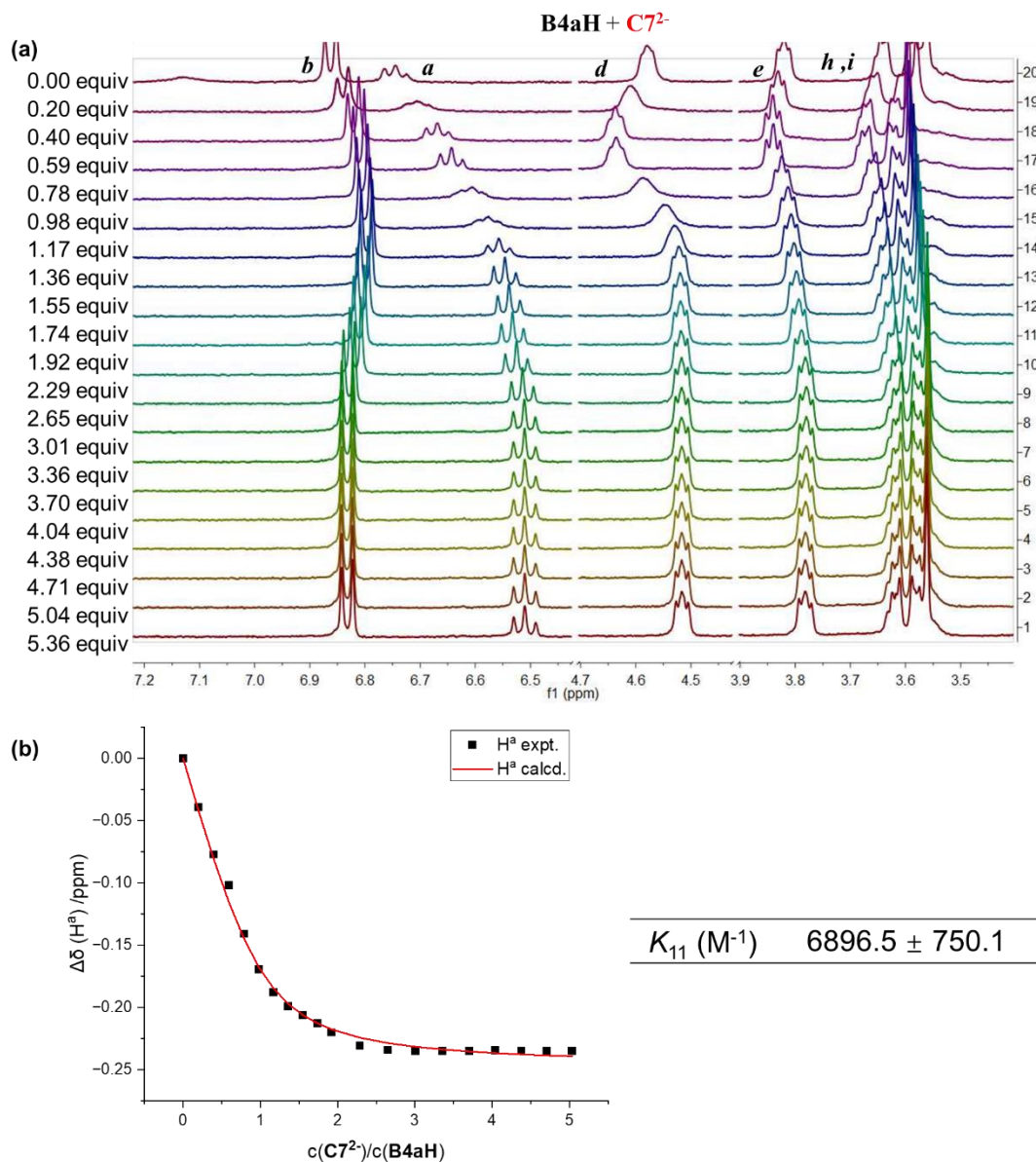
**Figure S6.** (a) <sup>1</sup>H NMR titration between **B4aH** and **C4<sup>2-</sup>** ( $c(\text{B4aH}) = 1 \text{ mM}$ ,  $c((\text{TBA}^+)_2\text{C4}^{2-}) = 50 \text{ mM}$ , 298 K, 400 MHz, CD<sub>3</sub>CN); (b) the chemical shift change curve. The irregular curve may arise from that the short chain length of the anion prevent synergistic recognition of the two subcavities, and it was also hard for the host to accommodate two anions to reach stable 1:2 complexation. In addition, the host conformation may change upon binding. As a result, no reliable binding constants could be obtained using either 1:1 or 1:2 binding models.



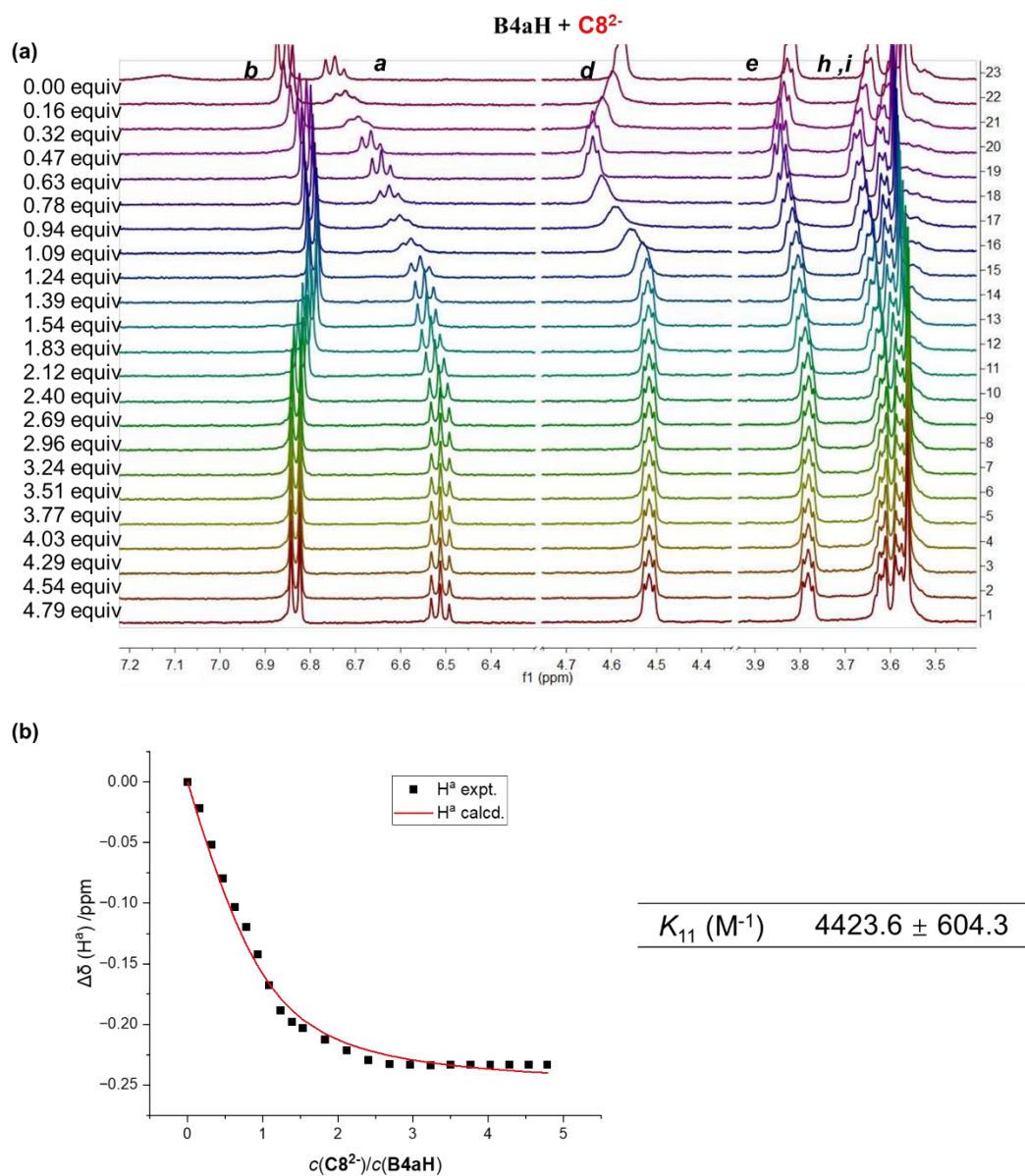
**Figure S7.** (a)  $^1\text{H}$  NMR titration between **B4aH** and **C5<sup>2-</sup>** ( $c(\text{B4aH}) = 1 \text{ mM}$ ,  $c((\text{TBA}^+)_2\text{C5}^{2-}) = 50 \text{ mM}$ , 298 K, 400 MHz,  $\text{CD}_3\text{CN}$ ); (b) Fitting results of the titration.



**Figure S8.** (a)  $^1\text{H}$  NMR titration between **B4aH** and **C6<sup>2-</sup>** ( $c(\text{B4aH}) = 1 \text{ mM}$ ,  $c((\text{TBA}^+)_2\text{C6}^{2-}) = 50 \text{ mM}$ , 298 K, 400 MHz,  $\text{CD}_3\text{CN}$ ); (b) Fitting results of the titration.

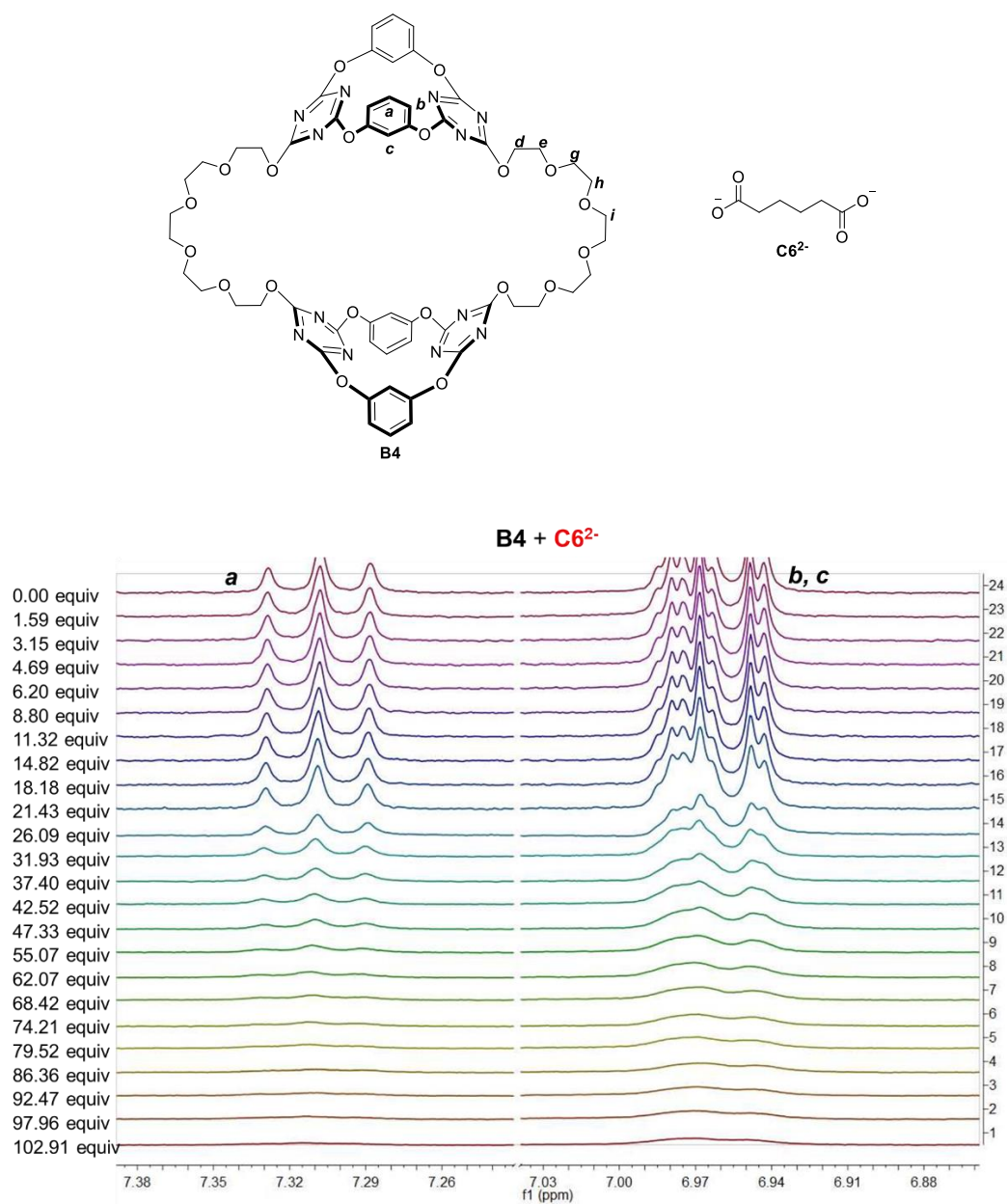


**Figure S9.** (a) <sup>1</sup>H NMR titration between **B4aH** and **C7<sup>2-</sup>** ( $c(\text{B4aH}) = 1 \text{ mM}$ ,  $c((\text{TBA}^+)_2\text{C7}^{2-}) = 50 \text{ mM}$ , 298 K, 400 MHz, CD<sub>3</sub>CN); (b) Fitting results of the titration.



**Figure S10.** (a)  $^1\text{H}$  NMR titration between **B4aH** and **C8<sup>2-</sup>** ( $c(\text{B4aH}) = 1 \text{ mM}$ ,  $c((\text{TBA}^+)_2\text{C8}^{2-}) = 50 \text{ mM}$ , 298 K, 400 MHz,  $\text{CD}_3\text{CN}$ ); (b) Fitting results of the titration.

### 3.2.2 Titration between **B4** and dicarboxylates.



**Figure S11.** <sup>1</sup>H NMR titration between **B4** and **C6<sup>2-</sup>** ( $c(\mathbf{B4}) = 1 \text{ mM}$ ,  $c((\text{TBA}^+)_2\text{C6}^{2-}) = 200 \text{ mM}$ , 298 K, 400 MHz, CD<sub>3</sub>CN).

#### **4. X-ray diffraction data**

Single crystal X-ray diffraction data was collected on a MM007HF Saturn724+ diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) at a temperature of 173 K. The intensity data were collected by the omega scans techniques, scaled, and reduced with CrystalClear (Rigaku Inc., 2007). X-ray were provided by a fine-focus sealed X-ray tube operated at 50 kV and 24 mA.

Integrated reflection intensities were produced and correction of collected intensities for absorption was done using the CrystalClear (Rigaku Inc., 2007) program. The structure was solved by direct methods using SHELXT (Sheldrick, 2014/2015). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms attached to carbon atoms were fixed at their ideal positions.

**Table S2.** Crystal data and structure refinement for **B4aH**.

| Identification code                          | <b>B4aH</b>                                                                                                                                        |
|----------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|
| CCDC number                                  | 2427464                                                                                                                                            |
| Empirical formula                            | C <sub>56</sub> H <sub>56</sub> N <sub>12</sub> O <sub>24</sub>                                                                                    |
| Formula weight                               | 1281.12                                                                                                                                            |
| Temperature                                  | 172.99(10) K                                                                                                                                       |
| Wavelength                                   | 1.54184 Å                                                                                                                                          |
| Crystal system                               | Triclinic                                                                                                                                          |
| Space group                                  | <i>P</i> −1                                                                                                                                        |
| Unit cell dimensions                         | <i>a</i> = 13.0092(4) Å, <i>α</i> = 65.878(3)°<br><i>b</i> = 15.5860(6) Å, <i>β</i> = 81.112(2)°<br><i>c</i> = 16.2685(4) Å, <i>γ</i> = 69.986(3)° |
| Volume                                       | 2828.36(17) Å <sup>3</sup>                                                                                                                         |
| Z                                            | 2                                                                                                                                                  |
| Density (calculated)                         | 1.504 Mg/m <sup>3</sup>                                                                                                                            |
| Absorption coefficient                       | 1.021 mm <sup>−1</sup>                                                                                                                             |
| F(000)                                       | 1336                                                                                                                                               |
| Crystal size                                 | 0.150 × 0.070 × 0.020 mm <sup>3</sup>                                                                                                              |
| Theta range for data collection              | 2.977 to 76.771°.                                                                                                                                  |
| Index ranges                                 | −15 ≤ <i>h</i> ≤ 16, −16 ≤ <i>k</i> ≤ 19, −20 ≤ <i>l</i> ≤ 20                                                                                      |
| Reflections collected                        | 38656                                                                                                                                              |
| Independent reflections                      | 11378 [ <i>R</i> <sub>int</sub> = 0.0715]                                                                                                          |
| Completeness to theta = 67.684°              | 99.70%                                                                                                                                             |
| Absorption correction                        | Semi-empirical from equivalents                                                                                                                    |
| Max. and min. transmission                   | 1.00000 and 0.60597                                                                                                                                |
| Refinement method                            | Full-matrix least-squares on F <sup>2</sup>                                                                                                        |
| Data / restraints / parameters               | 11378 / 0 / 833                                                                                                                                    |
| Goodness-of-fit on F <sup>2</sup>            | 1.023                                                                                                                                              |
| Final R indices [ <i>I</i> > 2σ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0526, <i>wR</i> <sub>2</sub> = 0.1436                                                                                    |
| R indices (all data)                         | <i>R</i> <sub>1</sub> = 0.0764, <i>wR</i> <sub>2</sub> = 0.1525                                                                                    |
| Extinction coefficient                       | n/a                                                                                                                                                |
| Largest diff. peak and hole                  | 0.708    d −0.438 e·Å <sup>−3</sup>                                                                                                                |

## 5. DFT calculation

Geometrical optimization was carried out with the Gaussian 16 suites<sup>[S7]</sup> using M06-2X<sup>[S8]</sup> density functional. 6-31G(d)<sup>[S9]</sup> basis set was used for all atoms for structure optimization. Frequency analyses were run to confirm that there is no imaginary frequencies and the structure obtained is local minima.

Electronic Energy: -5201.9214

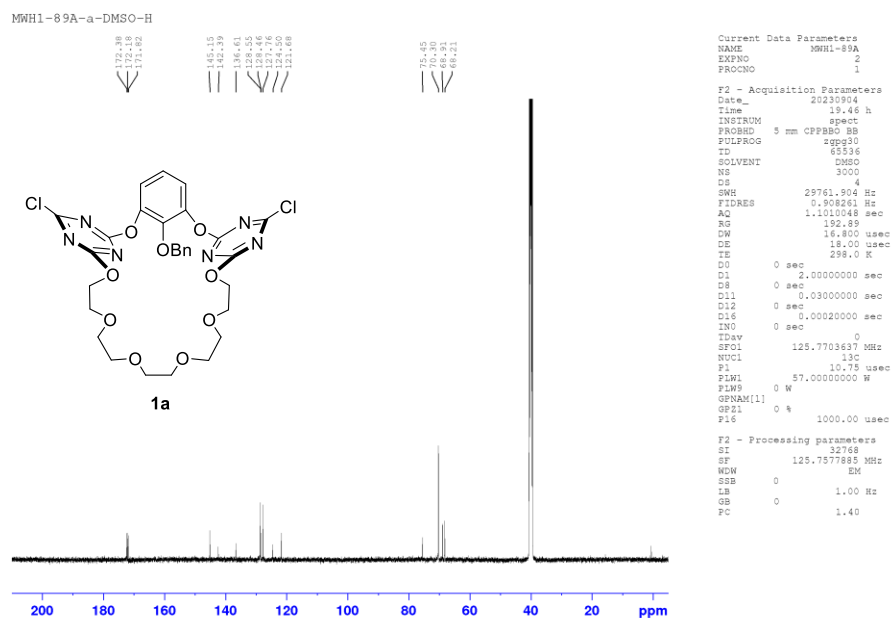
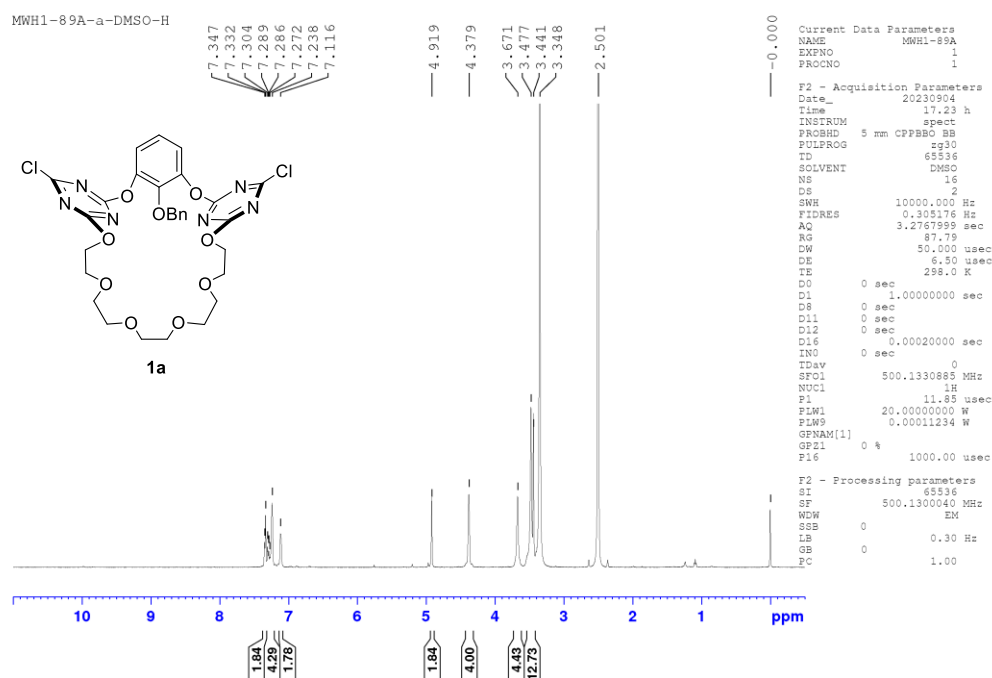
Cartesian coordinates:

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| C | -5.93109600 | -1.69187600 | 2.85470700  | H | -7.42496700 | -2.03562200 | 4.32953300  |
| O | -6.19763900 | -0.33062100 | 2.85180200  | H | -7.55124600 | -5.63804200 | -2.12441100 |
| N | -7.11672800 | -0.52628900 | 0.75622900  | H | -4.84911300 | -5.36288000 | 3.33374900  |
| C | -6.25171700 | -3.81644300 | 3.93872500  | H | -9.98725300 | -2.19729700 | -1.16146200 |
| C | -6.62107700 | -2.48899100 | 3.75937900  | H | 0.48939100  | -3.16429300 | -0.63858100 |
| C | -6.68927400 | 0.25072100  | 1.74781400  | H | -0.56508200 | -1.74701500 | -0.68342900 |
| N | -6.69820800 | 1.57037600  | 1.80383900  | H | 1.42361700  | -0.98025800 | -1.73676100 |
| C | -7.12924200 | 2.12251600  | 0.67352200  | H | 0.30754700  | -1.34318700 | -3.08157000 |
| N | -7.63041800 | 1.49201700  | -0.38140400 | H | -6.35256400 | 3.00622600  | -1.96054300 |
| C | -7.56891500 | 0.16782300  | -0.27787100 | H | -7.12973600 | 4.49490000  | -2.55846300 |
| C | -2.11609100 | -3.58272900 | -1.48925000 | H | -8.49547500 | 3.73910300  | -0.78549900 |
| N | -3.14235800 | -3.85507900 | -2.30195100 | H | -7.60086500 | 5.17509500  | -0.19501400 |
| C | -4.27351900 | -4.04832400 | -1.65023900 | C | 2.49202400  | -0.79836900 | 1.80794100  |
| N | -2.13202400 | -3.62820000 | -0.15631100 | C | 6.13337500  | -2.92510700 | 0.30660000  |
| C | -4.87923800 | -2.19223200 | 2.08261200  | O | 7.14420500  | -2.60222400 | -0.59010400 |
| C | -7.67672500 | -4.58036700 | -1.91810900 | N | 7.80103200  | -0.86938100 | 0.75697700  |
| N | -4.45078200 | -4.08676900 | -0.33193000 | C | 5.12261300  | -4.54252000 | 1.75920700  |
| O | -8.06093700 | -0.47955800 | -1.34083300 | C | 6.20688300  | -4.12264000 | 0.99033600  |
| O | -5.35735700 | -4.27438200 | -2.42461000 | C | 7.72155700  | -1.39353800 | -0.46238600 |
| O | -3.37456000 | -3.99285600 | 1.68735200  | N | 8.17655400  | -0.87782900 | -1.59281300 |
| C | -4.51675800 | -3.53026800 | 2.30883400  | C | 8.68657100  | 0.34217600  | -1.42850900 |
| C | -5.18359900 | -4.33855900 | 3.21135400  | N | 8.89900900  | 0.96178000  | -0.26934700 |
| C | -8.92400000 | -4.03129400 | -1.61797700 | C | 8.40914500  | 0.30422000  | 0.77399300  |
| C | -9.03352500 | -2.66512200 | -1.38326800 | C | 1.04317200  | 0.69188100  | 2.59790400  |
| C | -6.56457600 | -3.76177200 | -1.97794000 | N | 1.99389100  | 1.38404200  | 3.22923300  |
| C | -7.90423200 | -1.86044800 | -1.43985000 | C | 3.20079600  | 0.87628400  | 3.06300800  |
| C | -6.63518000 | -2.37625300 | -1.73074500 | N | 1.22415300  | -0.40057400 | 1.85333500  |
| C | -0.04003000 | -2.47855600 | -1.30675000 | C | 5.00733200  | -2.07639100 | 0.35542900  |
| C | 0.89883700  | -1.78400300 | -2.27210400 | C | 5.84979100  | 0.59066700  | 5.00508200  |
| C | -6.58614000 | 4.04984700  | -1.70570800 | N | 3.53026800  | -0.23491000 | 2.40528500  |
| C | -7.51312000 | 4.13307300  | -0.51127200 | O | 8.60985100  | 0.91422800  | 1.95328800  |

|   |             |             |             |   |             |             |             |
|---|-------------|-------------|-------------|---|-------------|-------------|-------------|
| O | 4.17456700  | 1.58092700  | 3.65525500  | C | 7.85578100  | 3.14863700  | -1.96137800 |
| O | 2.69091100  | -1.90413000 | 1.07469000  | O | 6.71233400  | 2.84304000  | -2.71041700 |
| C | 3.92576400  | -2.54758600 | 1.11573300  | C | 5.83325300  | 1.89242400  | -2.11332300 |
| C | 3.98226100  | -3.75134000 | 1.80845200  | C | 5.27702900  | 0.99211400  | -3.19046600 |
| C | 7.15929900  | 0.18698500  | 5.22945800  | O | 6.38250600  | 0.39615100  | -3.84022800 |
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| C | 5.45222400  | 1.04618400  | 3.75340700  | C | 5.79481100  | -1.96913800 | -4.04810300 |
| C | 7.66119600  | 0.71001800  | 2.94498900  | O | 4.48396000  | -1.96797400 | -3.53826800 |
| C | 6.33626200  | 1.10343700  | 2.66700300  | C | 4.17254600  | -3.15129000 | -2.84781900 |
| O | -5.40867700 | 4.78318100  | -1.44687800 | C | 2.93128700  | -2.91335400 | -2.02310200 |
| C | -4.69305600 | 5.00876100  | -2.63997200 | O | 1.83175100  | -2.65939500 | -2.86791100 |
| C | -3.28019600 | 5.44783800  | -2.33308200 | H | 9.28309400  | 2.70256100  | -3.51272100 |
| O | -3.28411600 | 6.75552700  | -1.78713000 | H | 9.96277200  | 2.68042300  | -1.85612800 |
| C | -2.45247500 | 6.91773900  | -0.66216800 | H | 8.06498700  | 4.22217600  | -2.07618200 |
| C | -3.10189300 | 6.44498000  | 0.62410500  | H | 7.70227100  | 2.95276200  | -0.89513900 |
| O | -3.09699300 | 5.04430600  | 0.69286200  | H | 5.02134600  | 2.41055400  | -1.58672500 |
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| C | -1.26145100 | 0.50699400  | 2.10025700  | H | 5.20566100  | -0.37727300 | -5.36226100 |
| O | -0.17917300 | 1.16975400  | 2.76894400  | H | 5.91398000  | -2.78824600 | -4.78215100 |
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| H | -4.65612400 | 4.08921000  | -3.24224900 | O | -1.00446600 | -3.20279800 | -2.09668600 |
| H | -2.70073300 | 5.44678400  | -3.26951800 | H | -6.78648800 | -4.44020000 | 4.64715700  |
| H | -2.82602800 | 4.73684400  | -1.63903700 | H | -9.80268700 | -4.66569000 | -1.57040300 |
| H | -2.25469500 | 7.99268400  | -0.57971500 | H | 5.16302700  | -5.48108100 | 2.30102900  |
| H | -1.49078700 | 6.40144900  | -0.79686700 | H | 7.46555400  | -0.16965500 | 6.20692800  |
| H | -4.13536300 | 6.82801200  | 0.65302600  | O | 5.05020900  | -0.96582000 | -0.36320500 |
| H | -2.55491000 | 6.86914200  | 1.48547200  | H | 4.21919400  | -0.33981000 | -0.32853200 |
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| H | -4.38808100 | 2.81811500  | 2.81228800  | O | -5.51783600 | -1.67552000 | -1.79169900 |
| H | -4.36085400 | 2.69401700  | 1.05298500  | H | -5.59846100 | -0.64806500 | -1.94642300 |
| H | -3.36236800 | 0.66369400  | 1.97722700  | O | -4.12082500 | -1.49216500 | 1.23319100  |
| H | -2.69332200 | 1.21678900  | 3.53708800  | H | -4.56168500 | -0.77551500 | 0.69146900  |
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| H | -1.31304500 | -0.54061700 | 2.41356300  | C | -0.83633500 | 2.29633100  | -1.05403300 |
| O | 8.96264100  | 0.99367900  | -2.55079900 | C | 0.51697800  | 1.58619300  | -0.98185600 |
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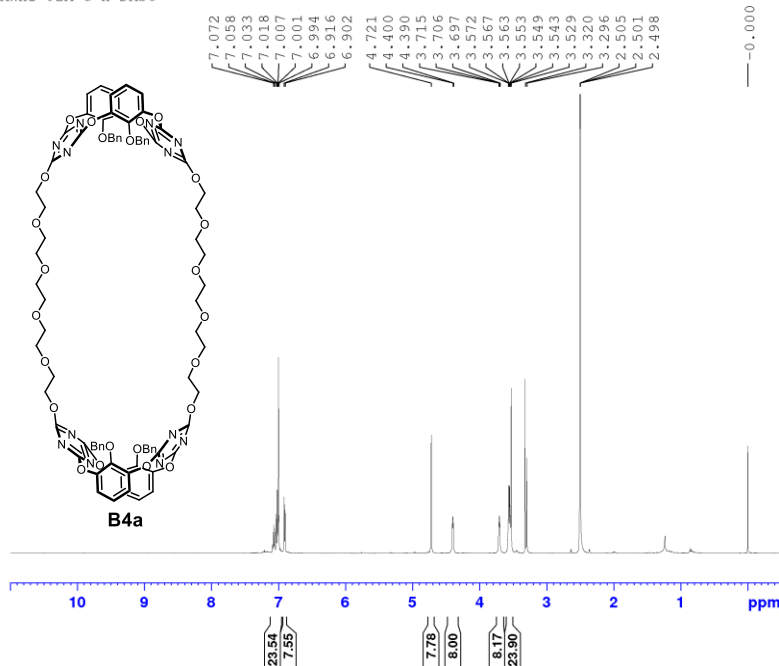
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| O | -5.23837200 | 0.75832100 | -2.23031300 | H | -3.44140700 | 2.47979700 | -2.57552600 |
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| H | -0.78200900 | 3.12600400 | -1.77603600 | O | 3.74730100  | 2.24663900 | 0.69267800  |
| H | -1.08353200 | 2.74593200 | -0.08174800 | O | 3.05363100  | 0.53097200 | -0.58496200 |
| H | 0.40847700  | 0.63526000 | -0.44301800 |   |             |            |             |

## 6. Copies and $^1\text{H}$ and $^{13}\text{C}$ NMR spectra



$^1\text{H}$  and  $^{13}\text{C}$  NMR of **1a** in  $\text{DMSO}-d_6$

MWH1-92A-e-H-DMSO

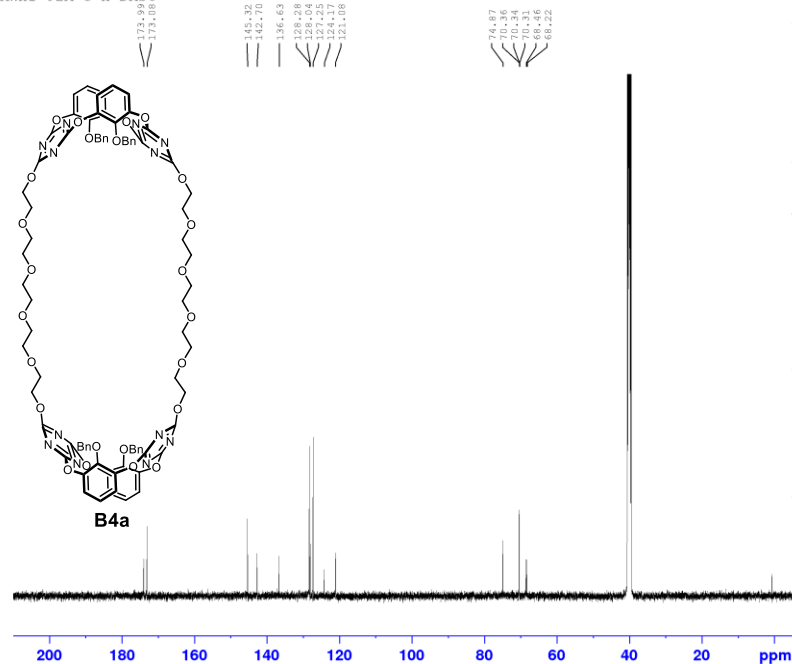


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PROCNO 1

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PULPROG zg30  
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SOLVENT DMSO  
NS 16  
DS 2  
SWH 10000.000 Hz  
FIDRES 0.305176 Hz  
AQ 3.2767999 sec  
RG 99.69  
DW 50.000 usec  
DE 6.50 usec  
TE 298.0 K  
D0 0 sec  
D1 1.00000000 sec  
D8 0 sec  
D11 0 sec  
D12 0 sec  
D16 0.00020000 sec  
IN0 0 sec  
TDav 0  
SFO1 500.1330885 MHz  
NUC1 1H  
P1 11.85 usec  
PLW1 20.00000000 W  
PLW9 0.0001234 W  
GPNAM[1]  
GP21 0 %  
P16 1000.00 usec

F2 - Processing parameters  
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GB 0  
PC 1.00

MWH1-92A-e-H-DMSO



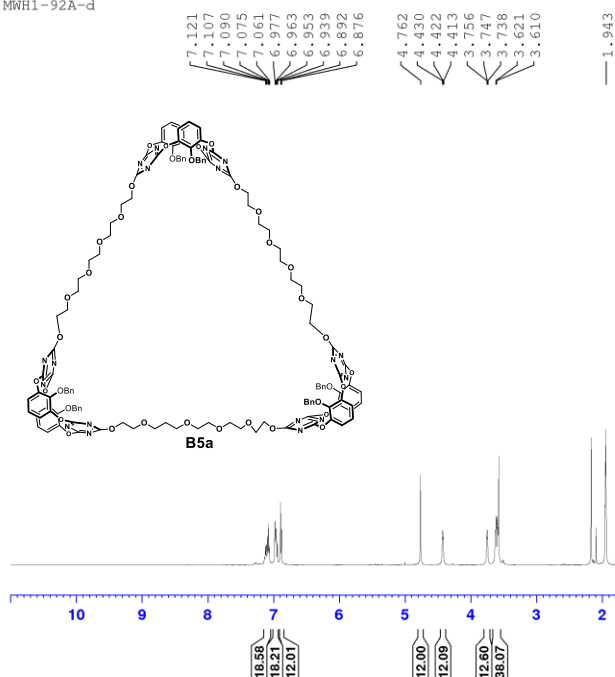
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DS 4  
SWH 29761.904 Hz  
FIDRES 0.808261 Hz  
AQ 1.1010048 sec  
RG 192.89  
DW 16.800 usec  
DE 18.00 usec  
TE 298.0 K  
D0 0 sec  
D1 2.00000000 sec  
D8 0 sec  
D11 0.03000000 sec  
D12 0 sec  
D16 0.00020000 sec  
IN0 0 sec  
TDav 0  
SFO1 125.7703637 MHz  
WUC1 13C  
P1 10.75 usec  
PLW1 57.00000000 W  
PLW9 0 W  
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P16 1000.00 usec

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LB 1.00 Hz  
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$^1\text{H}$  and  $^{13}\text{C}$  NMR of **B4a** in  $\text{DMSO}-d_6$

MWH1-92A-d

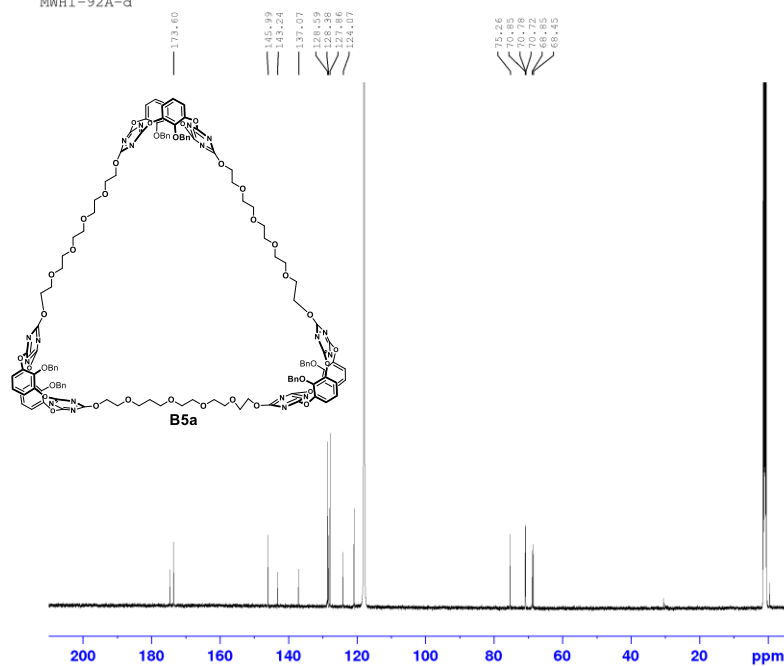


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FIDRES 0.305176 Hz  
AQ 3.2767999 sec  
RG 69.95  
DW 50.000 usec  
DE 6.50 usec  
TE 288.7 K  
D0 0 sec  
D1 1.00000000 sec  
D8 0 sec  
D11 0 sec  
D12 0 sec  
D16 0.00020000 sec  
INVO 0 sec  
TDav 0  
SF01 500.1330885 MHz  
NUC1 1H  
P1 11.25 usec  
PLW1 20.00000000 W  
PLW9 0.00010125 W  
GPNAM[1] 0 %  
GP21 0 %  
P16 1000.00 usec

F2 - Processing parameters  
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MWH1-92A-d

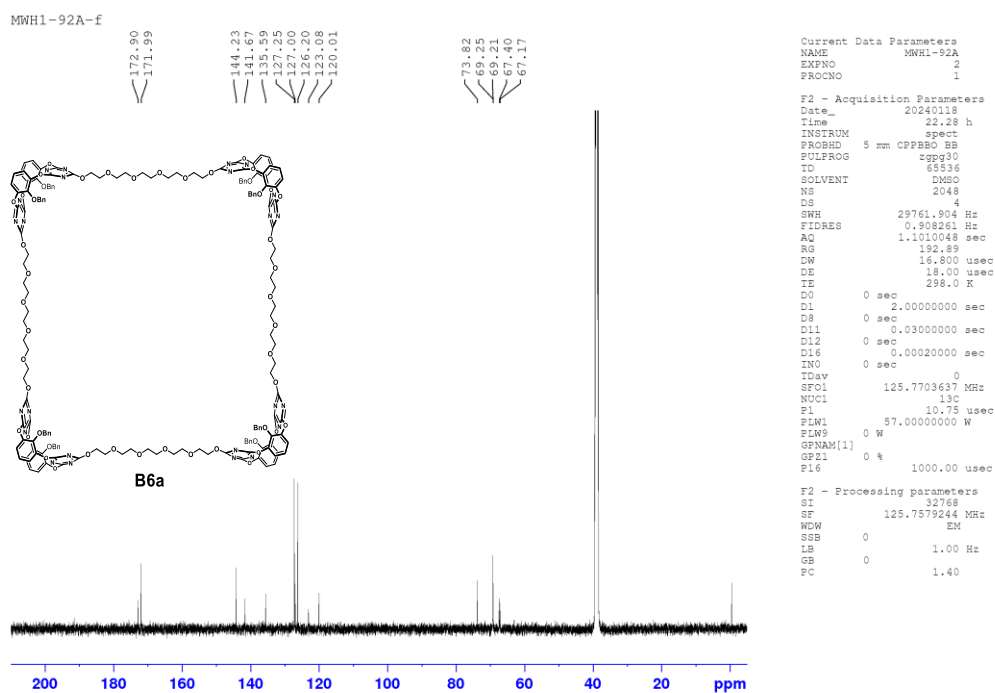
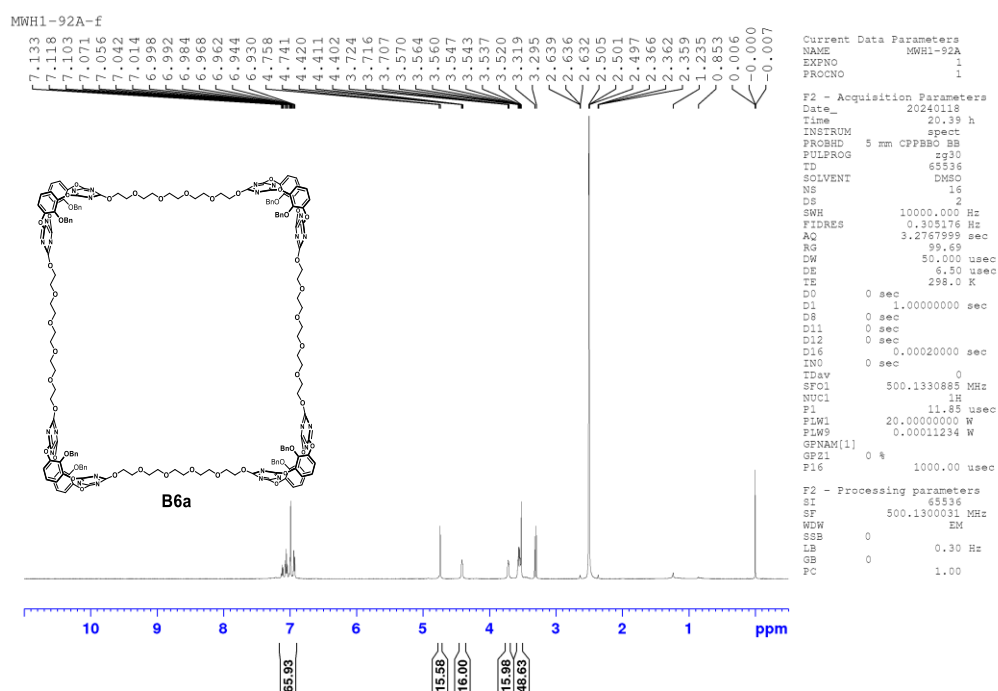


Current Data Parameters  
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EXPNO 14  
PROCNO 1

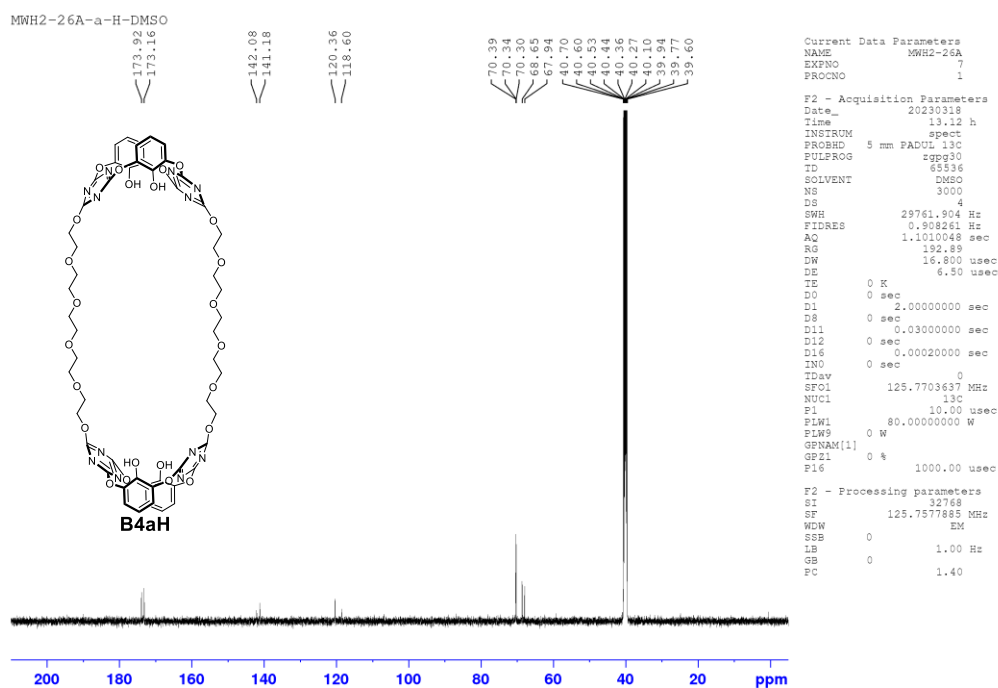
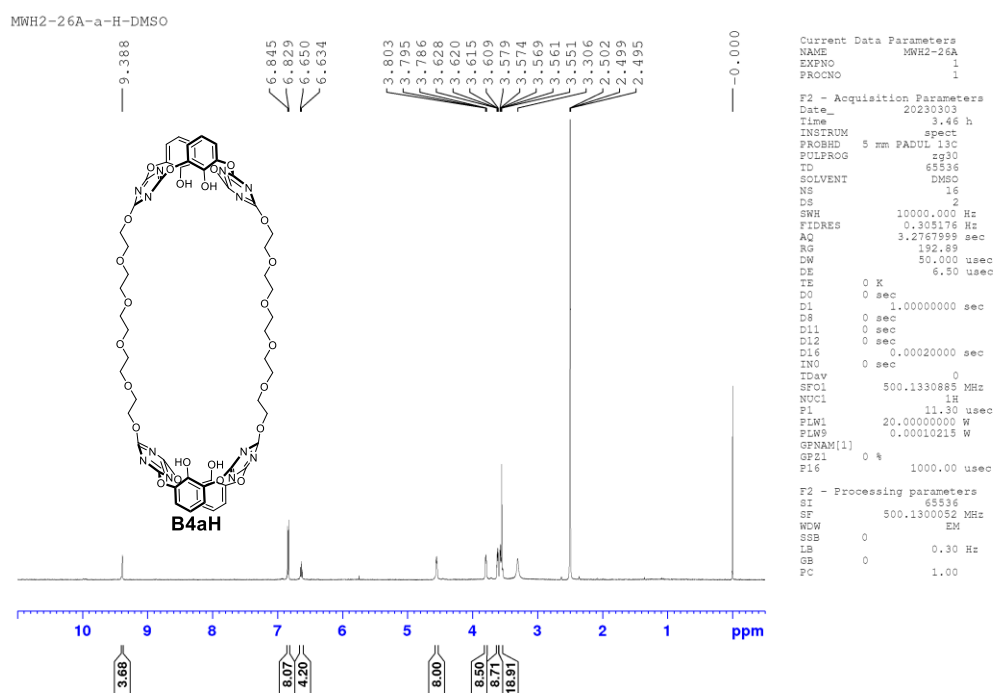
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DS 4  
SWH 29761.904 Hz  
FIDRES 0.908261 Hz  
AQ 1.1010048 sec  
RG 192.89  
DW 16.800 usec  
DE 18.00 usec  
TE 288.7 K  
D0 0 sec  
D1 2.00000000 sec  
D8 0 sec  
D11 0.03000000 sec  
D12 0 sec  
D16 0.00020000 sec  
INVO 0 sec  
TDav 0  
SF01 125.7703637 MHz  
NUC1 13C  
P1 10.50 usec  
PLW1 57.00000000 W  
PLW9 0 W  
GPNAM[1] 0 %  
GP21 0 %  
P16 1000.00 usec

F2 - Processing parameters  
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GB 0  
FC 1.40

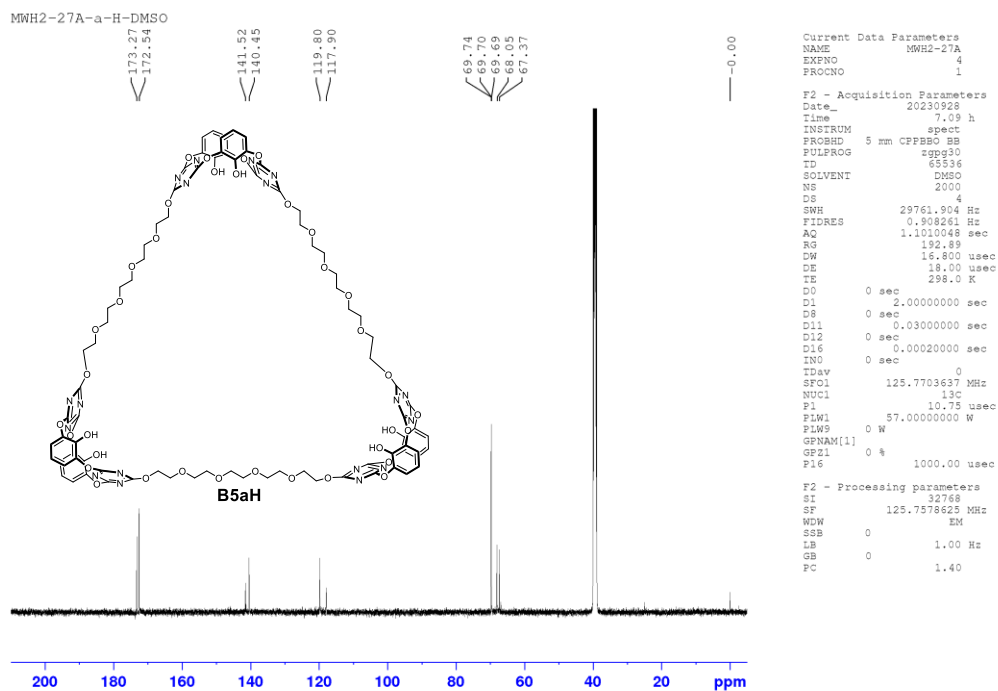
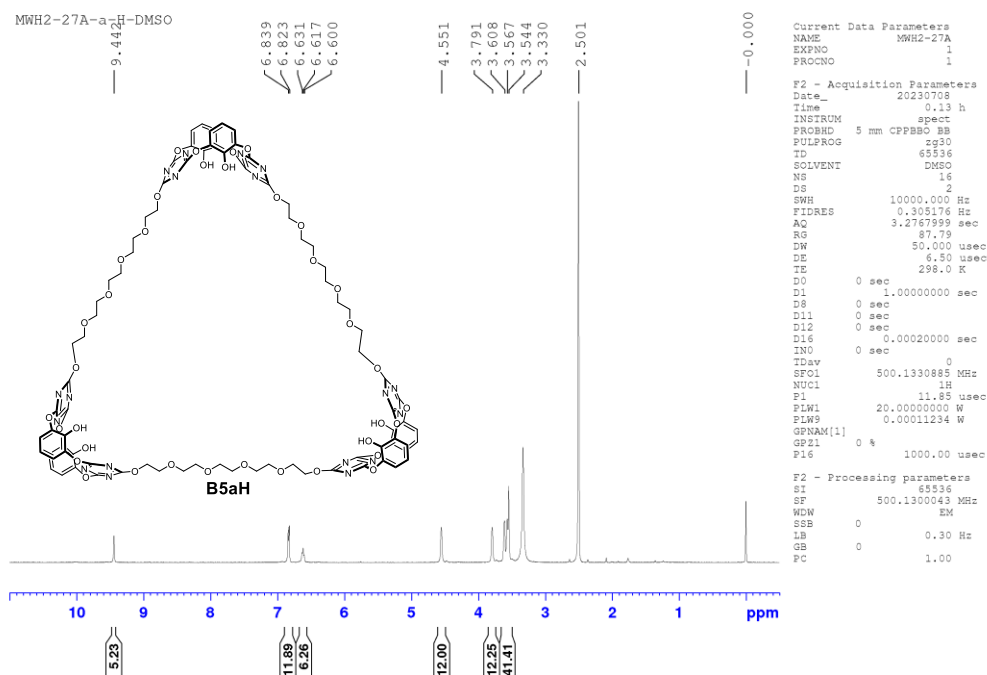
$^1\text{H}$  and  $^{13}\text{C}$  NMR of **B5a** in  $\text{CD}_3\text{CN}$



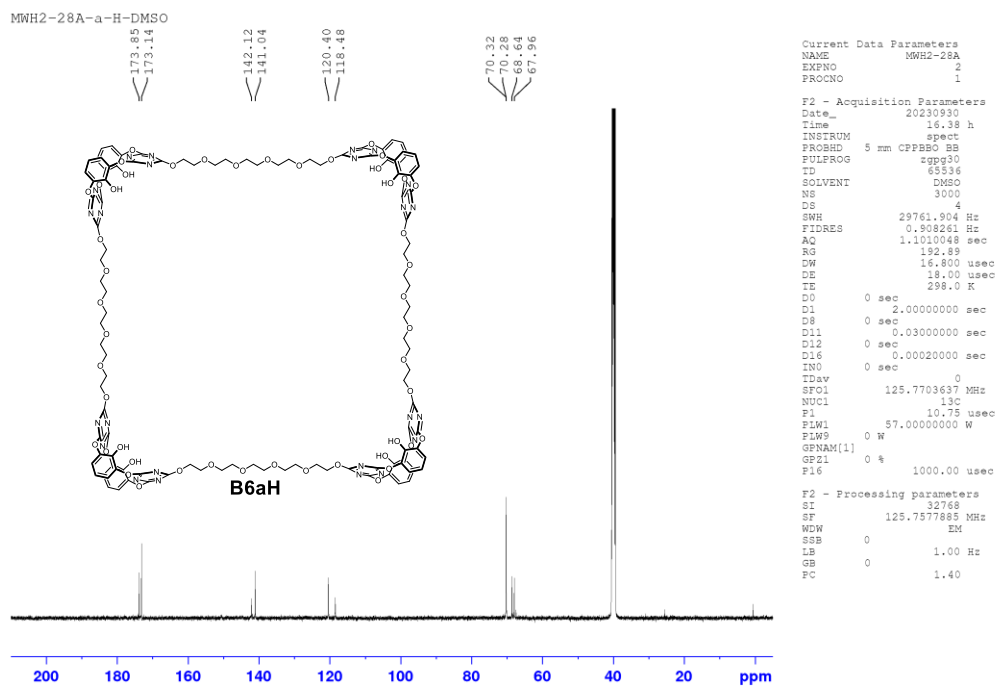
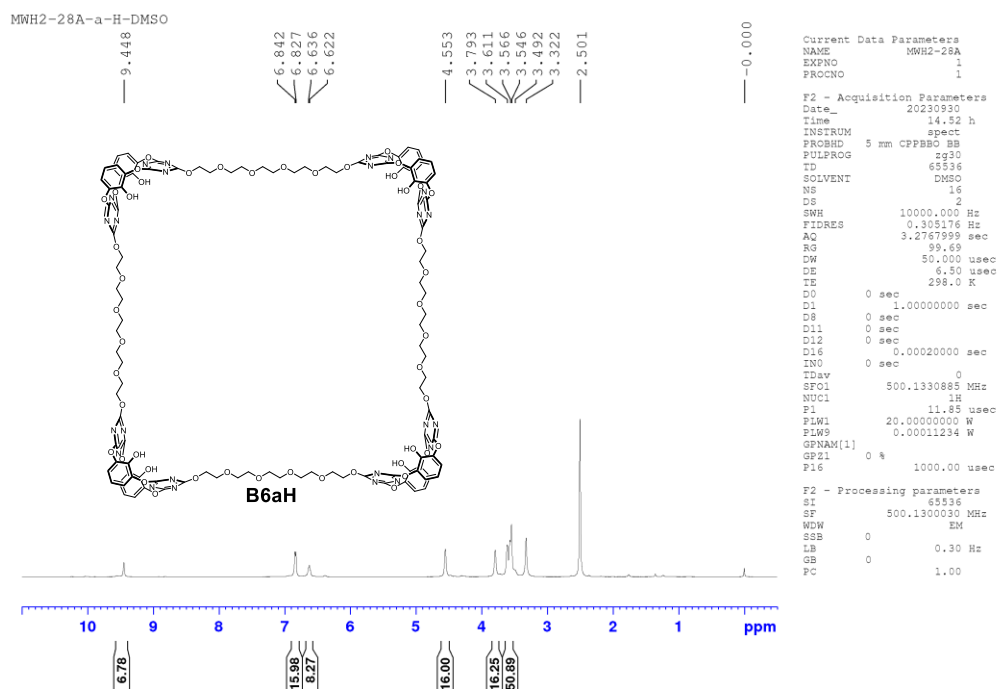
<sup>1</sup>H and <sup>13</sup>C NMR of **B6a** in DMSO-*d*<sub>6</sub>



$^1\text{H}$  and  $^{13}\text{C}$  NMR of **B4aH** in  $\text{DMSO-}d_6$



$^1\text{H}$  and  $^{13}\text{C}$  NMR of **B5aH** in  $\text{DMSO-}d_6$



<sup>1</sup>H and <sup>13</sup>C NMR of **B6aH** in DMSO-*d*<sub>6</sub>

## 7. References

- [S1] Luo, J.; Ao, Y.-F.; Malm, C.; Hunger, C.; Wang, Q.-Q.; Wang, D.-X. *Dalton Trans.* **2018**, 47, 7883-7887. doi: 10.1039/C8DT01727A.
- [S2] Luo, J.; Ao, Y.-F.; Wang, Q.-Q.; Wang, D.-X. *Angew. Chem. Int. Ed.* **2018**, 57, 15827–15831. DOI: 10.1002/ange.201810836.
- [S3] Michuhata, N.; Kaneko, Y.; Kasai, Y.; Tanigawa, K.; Hirokane, T.; Higasa, S.; Yamada, H. *J. Org. Chem.* **2013**, 78, 4319–4328. DOI: 10.1021/jo4003135.
- [S4] *Bindfit v0.5*: Supramolecular.org. <http://supramolecular.org>.
- [S5] Thordarson, P. *Chem. Soc. Rev.* **2011**, 40, 1305-1323. DOI: 10.1039/c0cs00062k.
- [S6] Hibberta, D. B.; Thordarson, P. *Chem. Commun.* **2016**, 52, 12792-1280. DOI: 10.1039/c6cc03888c.
- [S7] Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; et al.; Gaussian 16, Revision A. 03; Gaussian, Inc.: Wallingford, CT, 2016.
- [S8] Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.*, **1988**, 89, 2193–2218. DOI: 10.1063/1.455064 .
- [S9] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.*, **2008**, 120, 215–241. DOI: 10.1007/s00214-007-0310-x.