

Supporting Information

**Tiara[5]arenes: Synthesis, Solid-State Conformational Studies, Host-Guest Properties, and Application as Nonporous Adaptive Crystals**

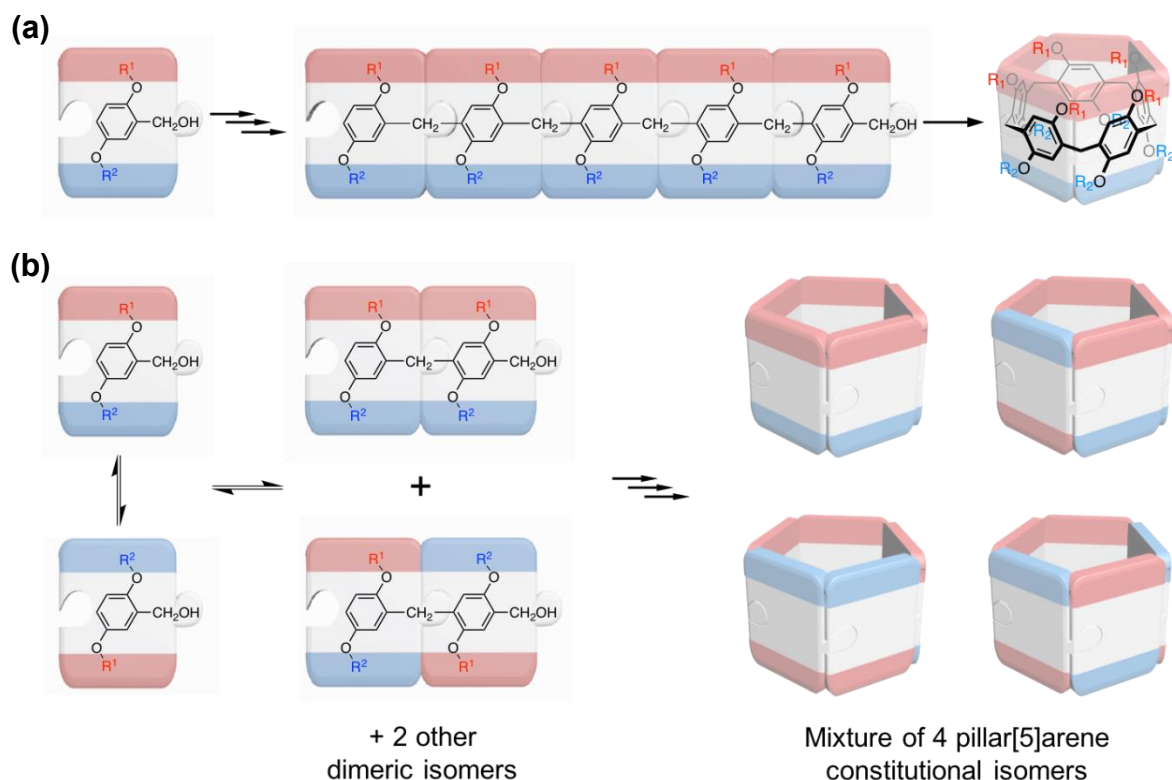
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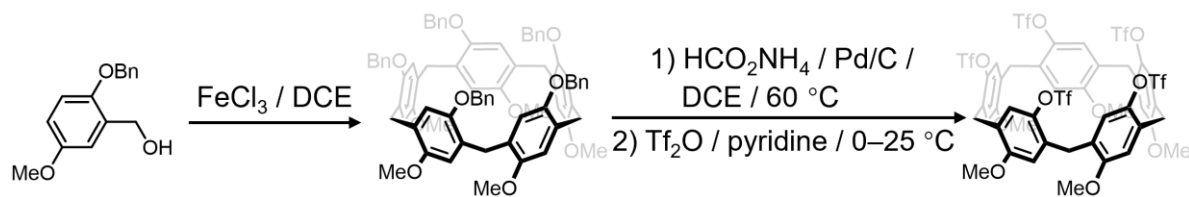
## 1. General Methods

Starting materials, reagents, and solvents were purchased from commercial vendors and used as received, unless otherwise noted. All reactions were performed under an argon atmosphere and in dry solvents, unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel GF254. Flash column chromatography was performed over silica gel (200–300 mesh or 300–400 mesh).  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on Bruker Advance 400 MHz and 600 MHz spectrometers at ambient temperature, unless otherwise noted. The chemical shifts are listed in ppm on the  $\delta$  scale and coupling constants were recorded in Hz. Chemical shifts are calibrated relative to the signals of the non-deuterated solvents ( $\text{CHCl}_3$ :  $\delta$  7.26 ppm,  $\text{CH}_3\text{OH}$ :  $\delta$  3.31 ppm,  $(\text{CD}_3)_2\text{CO}$ ,  $\delta$  2.05 ppm). High-resolution mass spectra (HRMS) were measured on a Q-Exactive™ HF/UltiMate™ 3000 RSLCnano using a Nano ProFlow meter with ProFlow technology in positive mode.

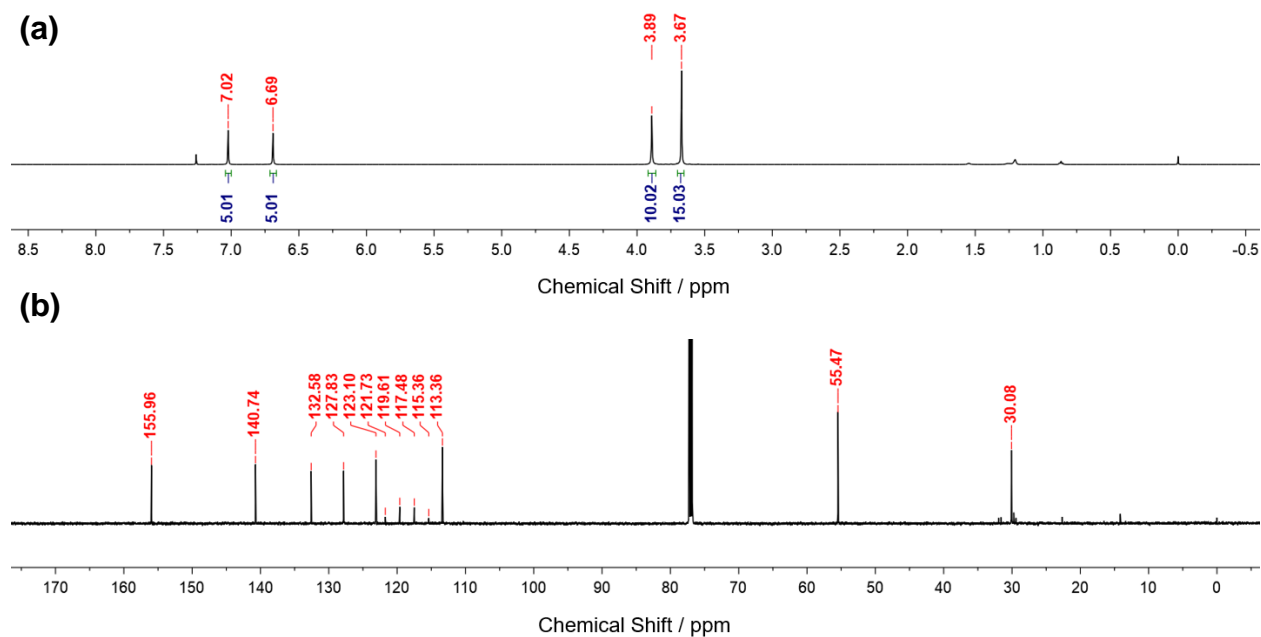
## 2. Synthetic Procedures



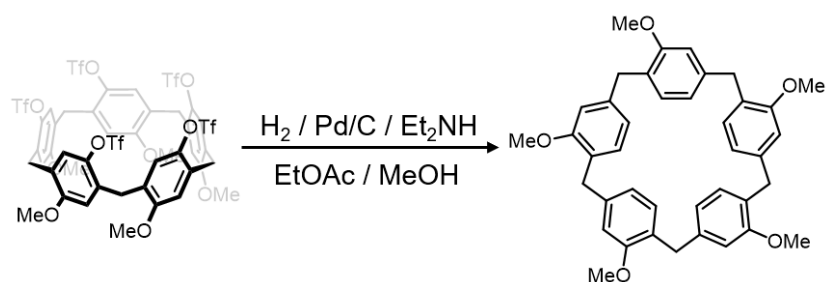
**Scheme S1.** Schematic representations of the preoriented synthesis of  $C_5$ -symmetric rim-differentiated pillar[5]arene (**RD-P[5]**). (a) Without retro-Friedel-Crafts reaction, the oligomerization in the presence of a Lewis acid proceeds in a “head-to-tail” fashion and leads to the exclusive formation of the regioregular linear pentamer, which eventually cyclizes into **RD-P[5]**. (b) The presence of water introduces retro-Friedel-Crafts reactions and results in a mixture of **RD-P[5]** and 3 other undesired constitutional isomers.



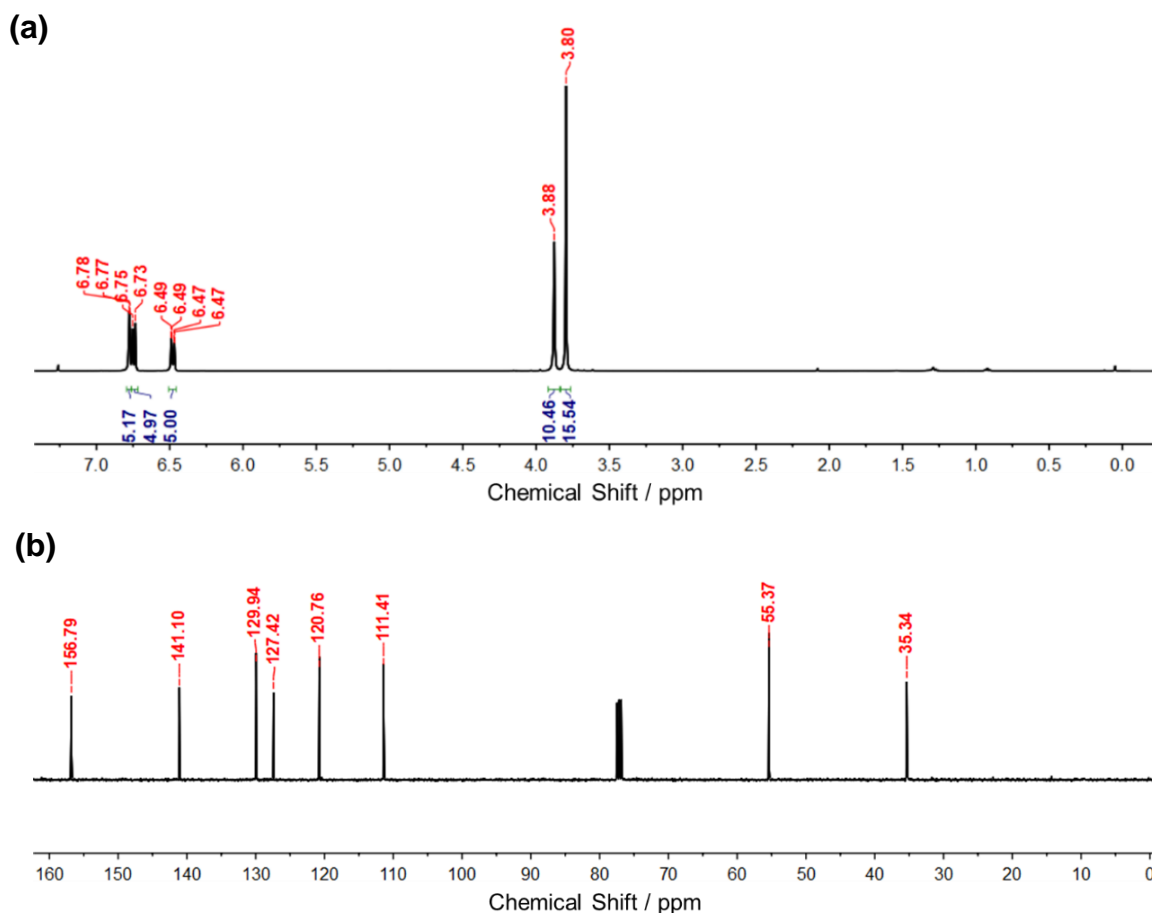
**(OTf)<sub>5</sub>-P[5]**:<sup>[1]</sup> (2-(benzyloxy)-5-methoxyphenyl)methanol<sup>[1]</sup> (1.7 g, 7 mmol, 1.0 eq.) was dissolved in anhydrous 1,2-dichloroethane (DCE) (700 mL), and anhydrous FeCl<sub>3</sub> (114 mg, 0.7 mmol, 0.1 eq.) was added. Reaction mixture was stirred at 25 °C for 4 h, filtered and quenched with MeOH (100 mL) then solution concentrated to dryness. Column chromatography (silica, EtOAc/*n*-hexane, 1/4) followed by recrystallization from EA and Hexane afforded **(OBn)<sub>5</sub>-RD-P[5]** as a white solid (378 mg, 0.33 mmol, 25%). Multiple reactions were set up in parallel for gram-scale synthesis. To a solution of **(OBn)<sub>5</sub>-RD-P[5]** (1.0 g, 0.88 mmol, 1.0 eq.) in DCE (50 mL) was added Pd/C (10% wt, wetted with 55% H<sub>2</sub>O, 1.0 g) and HCO<sub>2</sub>NH<sub>4</sub> (1.1 g, 17.6 mmol, 20 eq.). Solution was heated to 60 °C and stirred for 4 h, filtered over a pad of celite and concentrated to dryness to afford **(OH)<sub>5</sub>-RD-P[5]** as a white solid (600 mg, 0.88 mmol, quant.). Then a solution of **(OH)<sub>5</sub>-RD-P[5]** (freshly obtained from 1.0 g **(OBn)<sub>5</sub>-RD-P[5]**, 0.88 mmol, 1.0 eq.) in dry pyridine (20 mL) was added Tf<sub>2</sub>O (1.11 mL, 6.6 mmol, 7.5 eq.) at 0 °C (ice bath). The resulting solution was allowed to warm to 25 °C for 12 h. Water was added, and the precipitate was filtered and dried. Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane, 1/4) afforded **(OTf)<sub>5</sub>-RD-P[5]** as a white solid (1.027 g, 0.76 mmol, 87%).



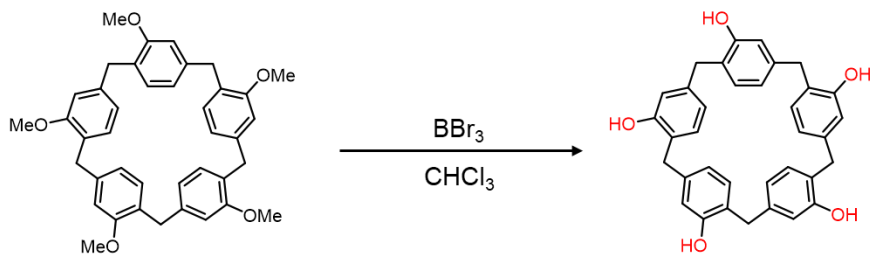
**Figure S1.** (a) <sup>1</sup>H NMR (600 MHz) and (b) <sup>13</sup>C NMR (150 MHz) spectra of **(OTf)<sub>5</sub>-RD-P[5]** (CDCl<sub>3</sub>, 298 K).



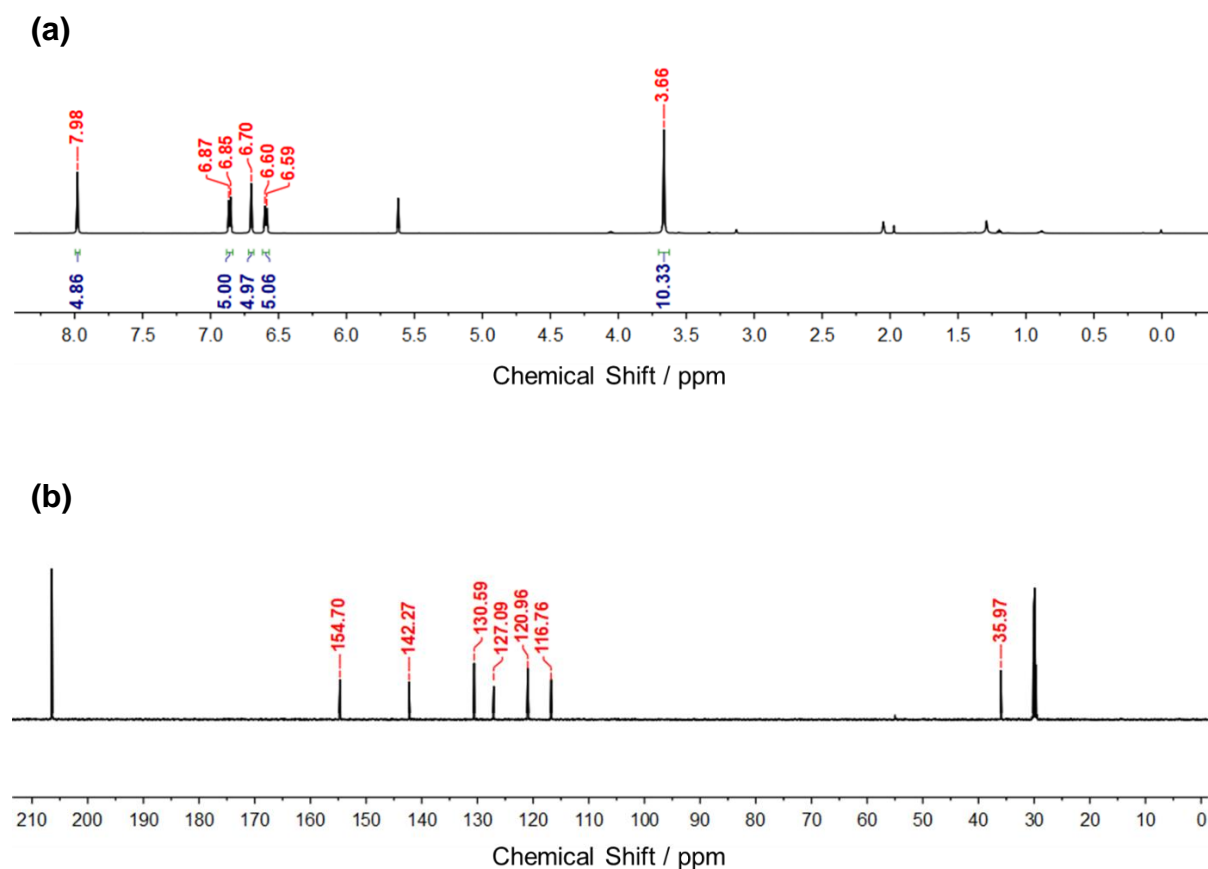
**T[5]-(OMe)<sub>5</sub>**: To a solution of **(OTf)<sub>5</sub>-RD-P[5]**<sup>[1]</sup> (320 mg, 0.24 mmol, 1.0 eq.) in 1:1 MeOH:EtOAc (10 mL) was added diethylamine (0.15 mL, 1.43 mmol, 6 eq.) followed by Pd/C (10% wt, wetted with 55% H<sub>2</sub>O, 250 mg). The resulting mixture was stirred under H<sub>2</sub> atmosphere at 25 °C for 24 h, filtered over a pad of celite and concentrated to dryness. Column chromatography (EtOAc/*n*-hexane, 1/9) afforded product (138 mg, 0.23 mmol, 96%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.73 (d, *J* = 1.6 Hz, 5H), 6.69 (d, *J* = 7.7 Hz, 5H), 6.43 (dd, *J* = 7.7 Hz, 1.6 Hz 5H), 3.83 (s, 10 H), 3.75 (s, 15 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 156.7, 141.0, 129.9, 127.3, 120.7, 111.3, 55.3, 35.3. HRMS (ESI) *m/z* [*M* + Na]<sup>+</sup> Calcd. for C<sub>35</sub>H<sub>30</sub>O<sub>5</sub>Na 553.1991, found 553.2017.



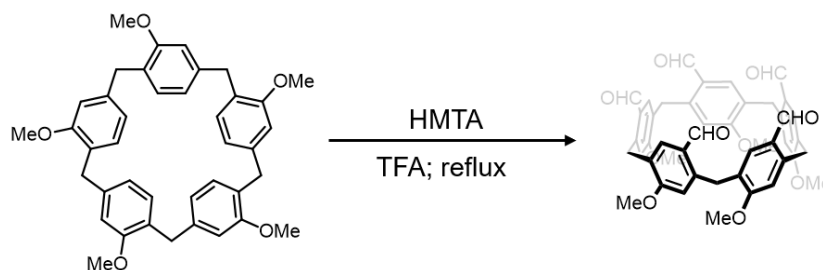
**Figure S2.** (a) <sup>1</sup>H NMR (400 MHz) and (b) <sup>13</sup>C NMR (101 MHz) spectra of **T[5]-(OMe)<sub>5</sub>** (CDCl<sub>3</sub>, 298 K).



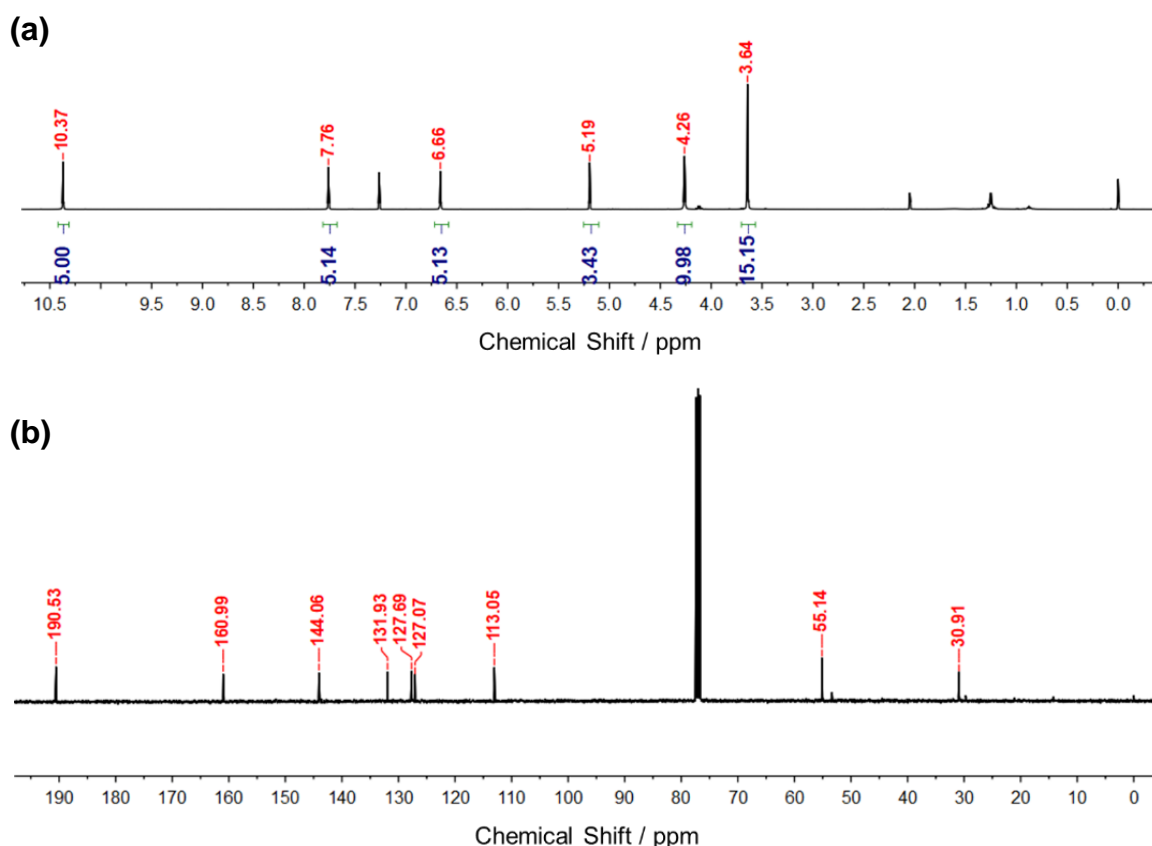
**T[5]:** To a solution of **T[5]-(OMe)<sub>5</sub>** (50 mg, 0.083 mmol, 1.0 eq.) in dry  $\text{CHCl}_3$  (3 mL) was added  $\text{BBr}_3$  (0.15 mL, 1.6 mmol, 19 eq.). The resulting mixture was stirred at 25 °C for 24 h. Water (10 mL) was added and the mixture was washed with copious amounts of water, brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated to dryness. Column chromatography ( $\text{MeOH}/\text{CH}_2\text{Cl}_2$ , 0/100 to 4/96) to afford product as a white solid (43 mg, 0.082 mmol, quant.).  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  7.97 (s, 5H), 6.85 (d,  $J = 7.7$  Hz, 5H), 6.7 (d,  $J = 1.7$  Hz, 5H), 6.58 (dd,  $J = 7.7$  Hz, 1.7 Hz, 5H), 3.66 (s, 10H).  $^{13}\text{C}$  NMR (101 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  154.7, 142.3, 130.6, 127.1, 120.9, 116.7, 35.9. HRMS (ESI)  $m/z$  [ $M + \text{H}$ ]<sup>+</sup> Calcd. for  $\text{C}_{40}\text{H}_{41}\text{O}_5$  601.2954, found 601.2944.



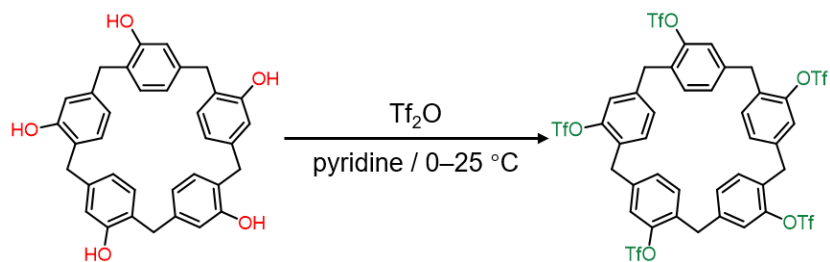
**Figure S3.** (a)  $^1\text{H}$  NMR (400 MHz) and (b)  $^{13}\text{C}$  NMR (101 MHz) spectra of **T[5]** ( $(\text{CD}_3)_2\text{CO}$ , 298 K).



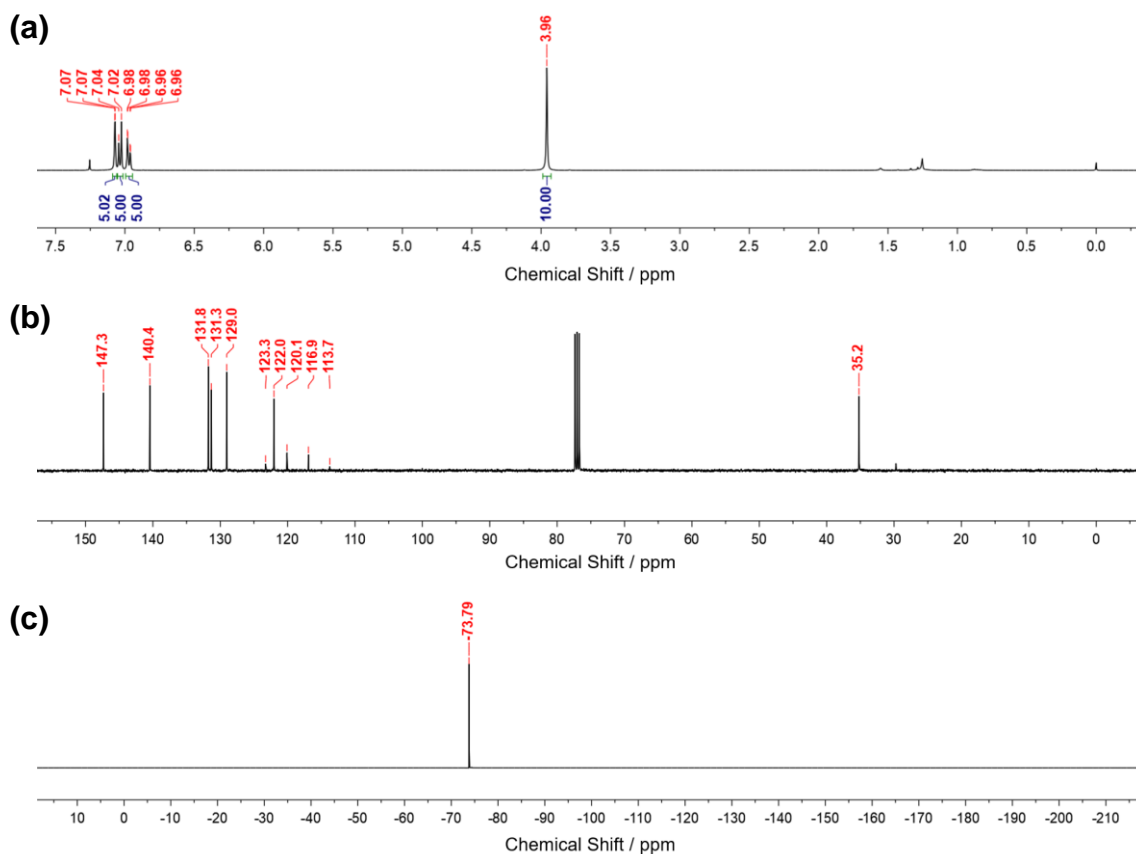
***p*-Formyl-T[5]-(OMe)<sub>5</sub>:** To a solution of T[5]-(OMe)<sub>5</sub> (50 mg, 0.083 mmol, 1.0 eq.) in trifluoroacetic acid (10 mL) was added hexamethylenetetramine (HMTA) (0.29 mg, 2.1 mmol, 25 eq.). The resulting mixture was vigorously refluxed for 6 h under inert atmosphere, then cooled to RT, diluted with ice-cold 1 M HCl (20 mL) and dichloromethane (20 mL), and vigorously stirred at RT for 3 h. The organic layer was separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic layer was washed with satd. NaHCO<sub>3</sub> (2 × 25 mL), brine (2 × 25 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification by column chromatography (EtOAc/*n*-hexane, 6/4) afforded ***p*-formyl-T[5]-(OMe)<sub>5</sub>** (38 mg, 0.051 mmol, 61%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.37 (s, 5H, -CHO), 7.76 (s, 5H), 6.66 (s, 5H), 4.26 (s, 10H), 3.64 (s, 15H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.5, 160.9, 144.1, 131.9, 127.7, 127.1, 113, 55.1, 30.9. HRMS (ESI) *m/z* [*M* + Na]<sup>+</sup> Calcd for C<sub>45</sub>H<sub>41</sub>O<sub>10</sub> 741.2694, found 741.2671.



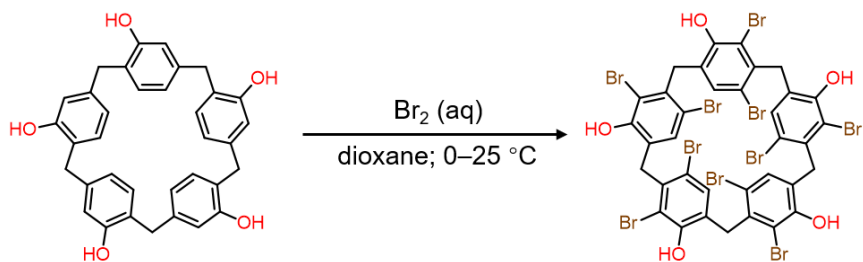
**Figure S4.** (a) <sup>1</sup>H (400 MHz) and (b) <sup>13</sup>C NMR (101 MHz) spectra of ***p*-formyl-T[5]-(OMe)<sub>5</sub>** (CDCl<sub>3</sub>, 298 K).



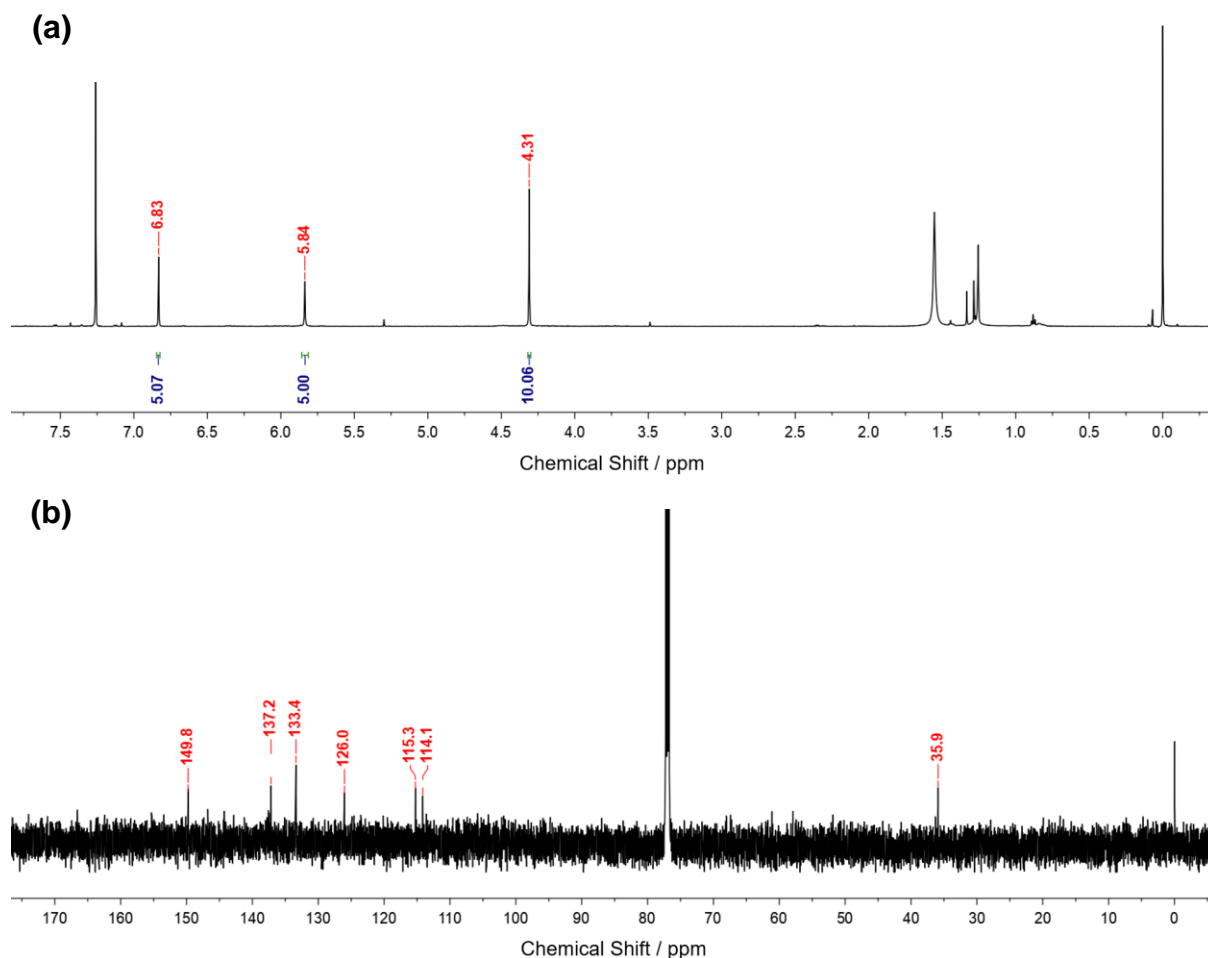
**T[5]-(OTf)<sub>5</sub>**: To a solution of **T[5]** (90 mg, 0.17 mmol, 1.0 eq.) in dry pyridine (2.5 mL) was added Tf<sub>2</sub>O (222 μL, 1.36 mmol, 8.0 eq.) at 0 °C (ice bath). The resulting solution was allowed to warm to 25 °C for 24 h. Water (10 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. Column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub>, 1/19) afforded the product as a white solid (161.8 mg, 0.136 mmol, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.07 (s, 5H), 7.03 (d, *J* = 8.0 Hz, 5H), 6.97 (dd, *J* = 8.0, 1.2 Hz, 5H), 3.96 (s, 10H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.3, 140.4, 131.8, 131.3, 129.0, 122.0, 118.5 (q, *J* = 320.2 Hz), 35.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -73.79. HRMS (ESI) *m/z* [*M* + *K*]<sup>+</sup> Calcd for C<sub>40</sub>H<sub>25</sub>F<sub>15</sub>O<sub>15</sub>S<sub>5</sub>K 1228.9195, found 1228.9188.



**Figure S5.** (a) <sup>1</sup>H (400 MHz), (b) <sup>13</sup>C (101 MHz), and (c) <sup>19</sup>F (376 MHz) NMR spectra of **T[5]-(OTf)<sub>5</sub>** (CDCl<sub>3</sub>, 298 K).

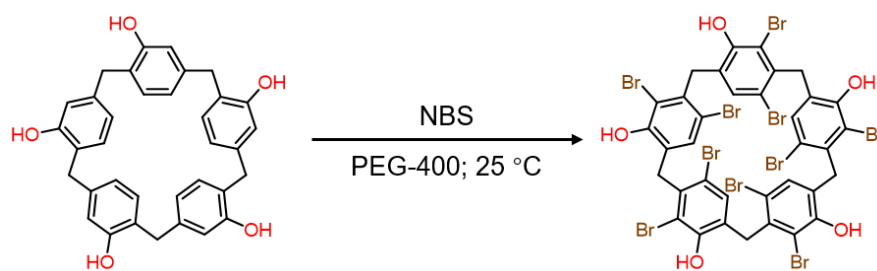


***o,p*-Dibromo-T[5]:** To a solution of **T[5]** (10.3 mg, 0.02 mmol, 1.0 eq.) in dioxane (1.0 mL) was added bromine water dropwise (3.0 mL) at 0 °C (ice bath). The resulting solution was allowed to warm to 25 °C for 24 h and concentrated to dryness. Water (10 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. Column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub>, 1/99) afforded the product as a pale yellow solid (10.0 mg, 0.008 mmol, 41%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.83 (s, 5H), 5.84 (s, 5H), 4.31 (s, 10H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 149.8, 137.2, 133.4, 126.0, 115.3, 114.1, 35.9. HRMS (ESI) *m/z* [*M* + Na]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>20</sub>Br<sub>10</sub>O<sub>5</sub>Na 1342.2934, found 1342.2992.

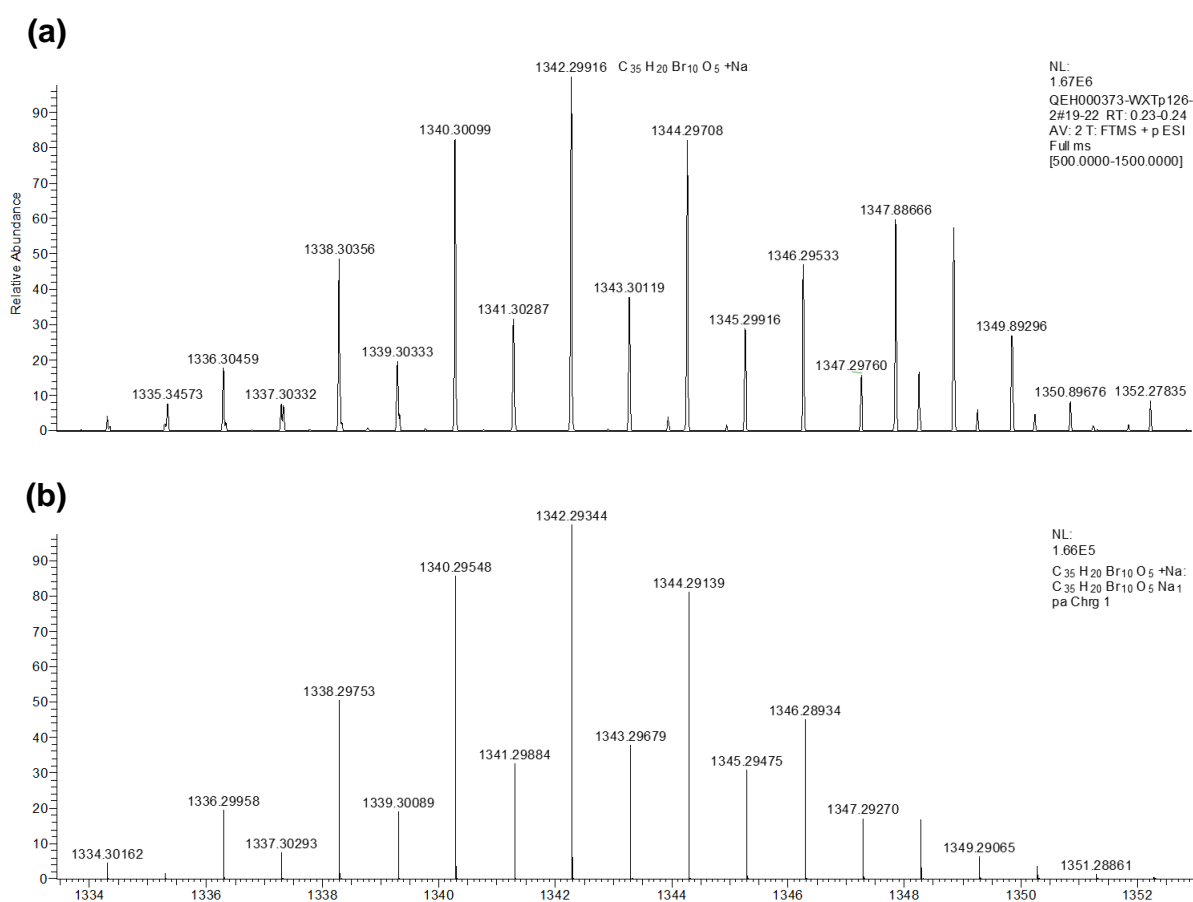


**Figure S6.** (a) <sup>1</sup>H (600 MHz) and (b) <sup>13</sup>C (151 MHz) NMR spectra of *o,p*-dibromo-T[5] (CDCl<sub>3</sub>, 298 K).

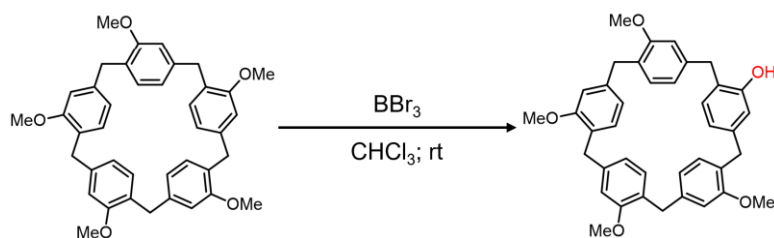




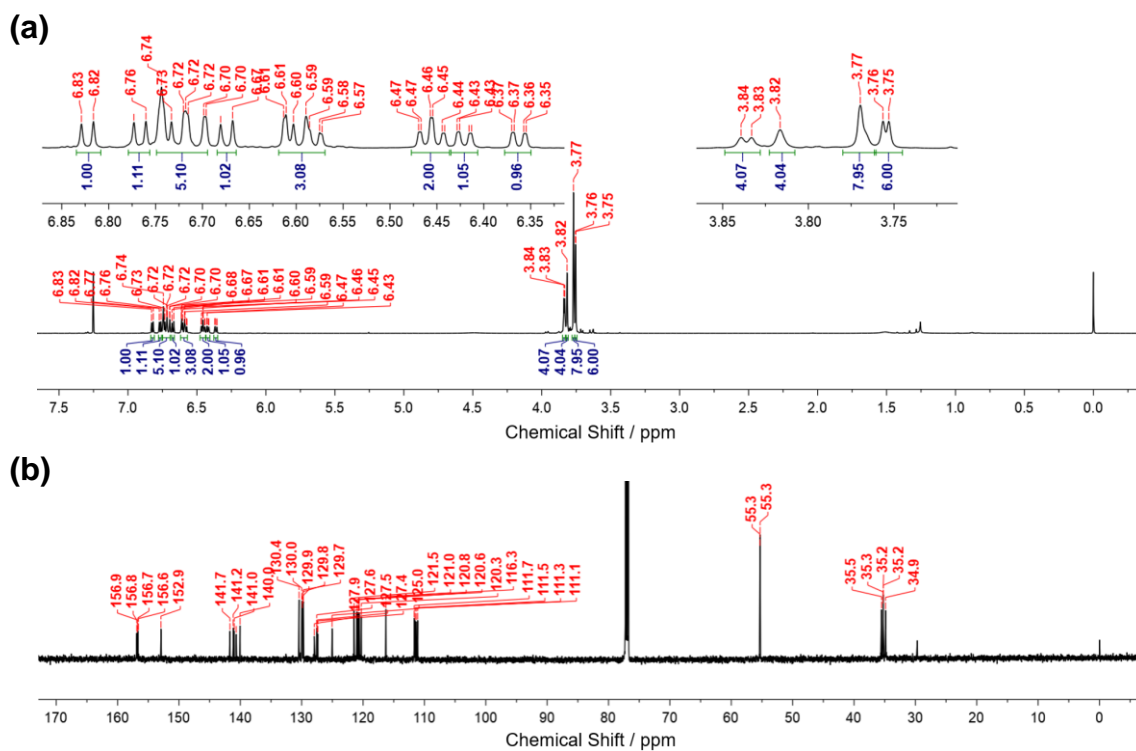
***o,p*-Dibromo-T[5]:** To a solution of **T[5]** (10.3 mg, 0.02 mmol, 1.0 eq.) in PEG-400 (1.0 mL) was added NBS (35.6 mg, 0.2 mmol, 10.0 eq.) in 5 min at 25 °C for 1 h. Water (10 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. Column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub>, 1/99) afforded the product as a pale yellow solid (2.1 mg, 1.6 μmol, 8%).



**Figure S7.** (a) ESI mass spectrum of *o,p*-dibromo-T[5] and (b) simulated isotopic distribution for molecular formula C<sub>35</sub>H<sub>20</sub>Br<sub>10</sub>O<sub>5</sub>Na [*M* + Na].



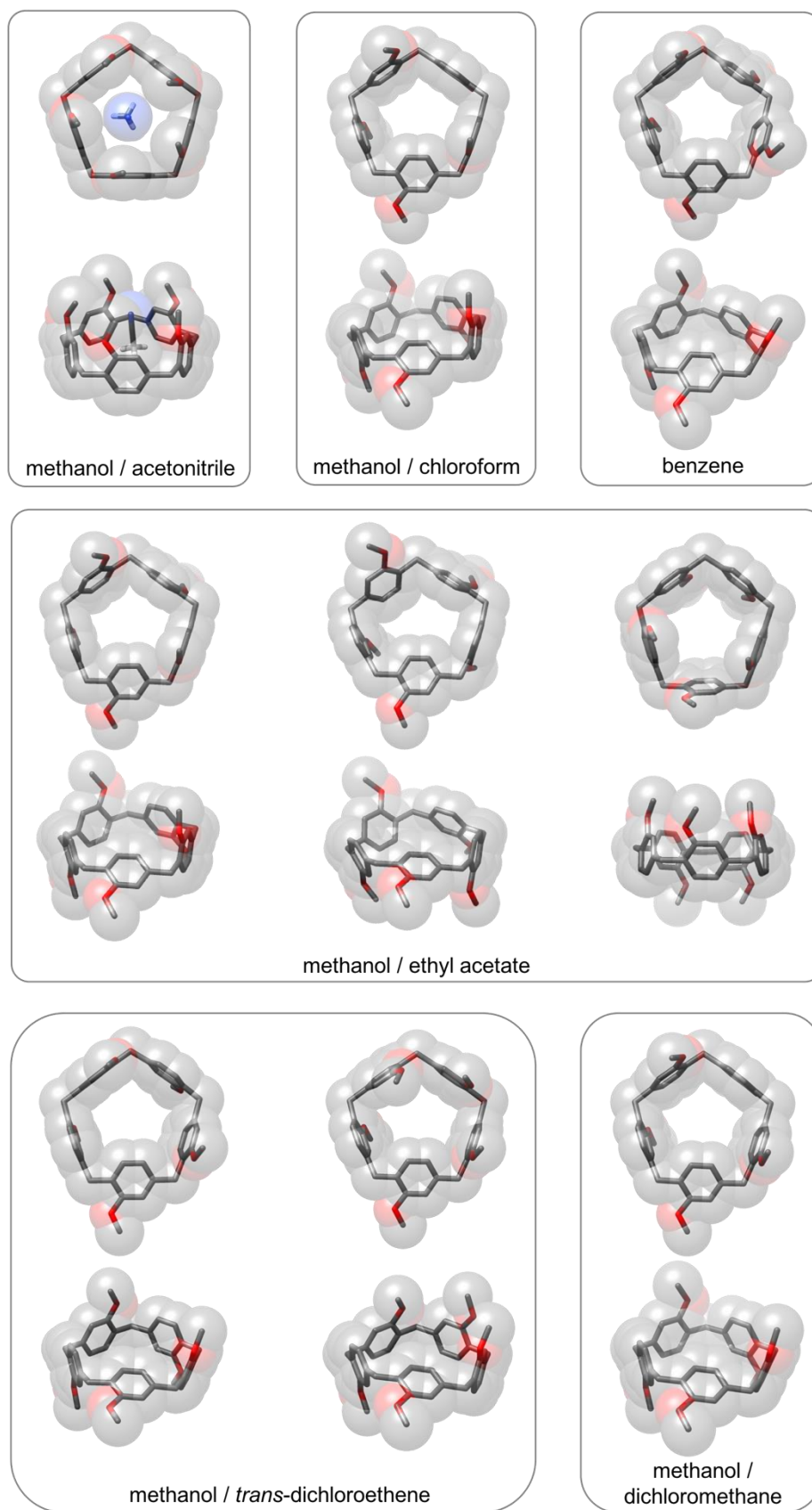
**T[5]-2,3,4,5-(OMe)<sub>4</sub>**: To a solution of **T[5]-(OMe)<sub>5</sub>** (353.6 mg, 0.59 mmol, 1.0 eq.) in dry CHCl<sub>3</sub> (15 mL) was added BBr<sub>3</sub> (225.9 mg, 0.89 mmol, 1.5 eq.) at room temperature for 24 h. Water (30 mL) was added to quench the reaction and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 45 mL). The combined organic extract was dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuum, and purified by column chromatography (EtOAc/*n*-hexane, 1/9) afforded the product as white solid. (110.6 mg, 0.19 mmol, 32%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.82 (d, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.75–6.69 (m, 5H), 6.67 (d, *J* = 7.7 Hz, 1H), 6.62–6.57 (m, 3H), 6.46 (td, *J* = 7.6, 1.6 Hz, 2H), 6.42 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.36 (dd, *J* = 7.7, 1.6 Hz, 1H), 3.84 (s, 2H), 3.83 (s, 2H), 3.82 (s, 4H), 3.77 (s, 6H), 3.76 (s, 3H), 3.75 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 156.9, 156.8, 156.7, 156.6, 152.9, 141.7, 141.2, 141.0, 140.7, 140.0, 130.4, 130.0, 129.9, 129.8, 129.7, 127.9, 127.6, 127.5, 127.4, 125.1, 121.5, 121.0, 120.8, 120.6, 120.3, 116.3, 111.7, 111.6, 111.3, 111.1, 55.3, 55.3, 35.5, 35.3, 35.2, 35.2, 34.9. HRMS (ESI) *m/z* [*M* + H]<sup>+</sup> Calcd for C<sub>39</sub>H<sub>38</sub>O<sub>5</sub>H 585.2647, found 585.2660.



**Figure S8.** (a) <sup>1</sup>H NMR (600 MHz), (b) <sup>13</sup>C NMR (151 MHz) NMR spectra of **T[5]-2,3,4,5-(OMe)<sub>4</sub>** (CDCl<sub>3</sub>, 298 K).

### 3. X-Ray Crystallography

Single crystals suitable for X-ray diffraction were selected and mounted in inert oil in cold gas stream and their X-ray diffraction intensity data was collected on a Rigaku XtaLAB FRX diffractometer equipped with a Hypix6000HE detector, using Cu  $K\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Crystals were kept at the temperature listed in **Table S1-S7** during data collection. By the use of Olex2,<sup>[2]</sup> the structure was solved either (i) with the ShelXS<sup>[3]</sup> structure solution program using Direct Methods or (ii) with the ShelXT<sup>[4]</sup> structure solution program using Direct Methods or Intrinsic Phasing. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Some guest molecules were refined isotropically due to disorder that could not be modeled precisely. Distance restraints were also imposed on some disordered guest hexane molecules. Selected details of the data collection and structural refinement of each compound can be found within **Table S1-S7** and full details are available in the corresponding CIF files. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre and may be obtained free of charge via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure S9.** Top and side views of assorted T[5]-(OMe)<sub>5</sub> conformers found in crystal structures obtained under different crystallization conditions.

**Table S1.** Crystal data and structure refinement for **T[5]-(OMe)<sub>5</sub>**

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Empirical formula	C <sub>40</sub> H <sub>40</sub> O <sub>5</sub>
Formula weight / g mol <sup>-1</sup>	600.72
Temperature / K	160.00(10)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	11.30470(10)
<i>b</i> / Å	12.60500(10)
<i>c</i> / Å	12.78350(10)
$\alpha$ / °	76.1580(10)
$\beta$ / °	88.8410(10)
$\gamma$ / °	66.9490(10)
Volume/ Å <sup>3</sup>	1621.97(3)
<i>Z</i>	2
$\rho_{\text{calc}}$ / g cm <sup>-3</sup>	1.230
$\mu$ / mm <sup>-1</sup>	0.634
<i>F</i> / 000	640.0
2 $\theta$ range for data collection / °	7.164 to 149.378
Crystal size / mm <sup>3</sup>	0.2 × 0.02 × 0.02
Index ranges	-14 ≤ <i>h</i> ≤ 13, -15 ≤ <i>k</i> ≤ 15, -15 ≤ <i>l</i> ≤ 15
Reflections collected	45791
Independent reflections	6363 [ <i>R</i> <sub>int</sub> = 0.0375, <i>R</i> <sub>sigma</sub> = 0.0193]
Data/restraints/parameters	6363/0/411
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.079
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub><i>I</i></sub> = 0.0513, <i>wR</i> <sub>2</sub> = 0.1435
Final <i>R</i> indices [all data]	<i>R</i> <sub><i>I</i></sub> = 0.0554, <i>wR</i> <sub>2</sub> = 0.1472
Largest diff. peak / hole / e Å <sup>3</sup>	0.53/-0.25
CCDC No.	1957868
Crystallization solvents	methanol/chloroform

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**Table S2.** Crystal data and structure refinement for CH<sub>3</sub>CN<sup>-</sup>T[5]-(OMe)<sub>5</sub>

Empirical formula	C <sub>42</sub> H <sub>43</sub> NO <sub>5</sub>
Formula weight / g mol <sup>-1</sup>	641.77
Temperature / K	159.99(10)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	12.0935(2)
<i>b</i> / Å	17.8479(3)
<i>c</i> / Å	17.9763(2)
$\alpha$ / °	95.1170(10)
$\beta$ / °	106.5750(10)
$\gamma$ / °	105.9900(10)
Volume / Å <sup>3</sup>	3515.19(9)
<i>Z</i>	4
$\rho_{\text{calc}}$ / g cm <sup>-3</sup>	1.213
$\mu$ / mm <sup>-1</sup>	0.626
<i>F</i> / 000	1368.0
2 $\theta$ range for data collection / °	5.216 to 149.272
Crystal size / mm <sup>3</sup>	0.2 × 0.2 × 0.2
Index ranges	-14 ≤ <i>h</i> ≤ 15, -21 ≤ <i>k</i> ≤ 22, -18 ≤ <i>l</i> ≤ 22
Reflections collected	34158
Independent reflections	12350 [ <i>R</i> <sub>int</sub> = 0.0208, <i>R</i> <sub>sigma</sub> = 0.0283]
Data/restraints/parameters	12350/1/1069
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.140
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub><i>I</i></sub> = 0.0701, <i>wR</i> <sub>2</sub> = 0.1651
Final <i>R</i> indices [all data]	<i>R</i> <sub><i>I</i></sub> = 0.0727, <i>wR</i> <sub>2</sub> = 0.1681
Largest diff. peak / hole / e Å <sup>3</sup>	0.28/-0.28
CCDC No.	1896025
Crystallization solvents	methanol/acetonitrile

**Table S3.** Crystal data and structure refinement for PhMe@T[5]

Empirical formula	C <sub>42</sub> H <sub>40</sub> O <sub>6</sub>
Formula weight / g mol <sup>-1</sup>	640.74
Temperature / K	301.60(10)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	10.1845(2)
<i>b</i> / Å	12.1980(2)
<i>c</i> / Å	15.5764(2)
$\alpha$ / °	98.7530(10)
$\beta$ / °	102.834(2)
$\gamma$ / °	107.544(2)
Volume/ Å <sup>3</sup>	1748.27(3)
<i>Z</i>	2
$\rho_{\text{calc}}$ / g cm <sup>-3</sup>	1.217
$\mu$ / mm <sup>-1</sup>	0.644
<i>F</i> / 000	680.0
2 $\theta$ range for data collection / °	5.988 to 149.204
Crystal size / mm <sup>3</sup>	0.2 × 0.2 × 0.2
Index ranges	-12 ≤ <i>h</i> ≤ 12, -15 ≤ <i>k</i> ≤ 15, -19 ≤ <i>l</i> ≤ 19
Reflections collected	33007
Independent reflections	6919 [ <i>R</i> <sub>int</sub> = 0.0218, <i>R</i> <sub>sigma</sub> = 0.0147]
Data/restraints/parameters	6919/577/604
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.075
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0531, <i>wR</i> <sub>2</sub> = 0.1520
Final <i>R</i> indices [all data]	<i>R</i> <sub>1</sub> = 0.0604, <i>wR</i> <sub>2</sub> = 0.1600
Largest diff. peak / hole / e Å <sup>3</sup>	0.41/-0.35
CCDC No.	1957871
Crystallization solvent	toluene

**Table S4.** Crystal data and structure refinement for C<sub>6</sub>H<sub>6</sub>@T[5]-(OMe)<sub>5</sub>

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Empirical formula	C <sub>52</sub> H <sub>52</sub> O <sub>5</sub>
Formula weight / g mol <sup>-1</sup>	756.93
Temperature / K	159.99 (10)
Crystal system	monoclinic
Space group	<i>P2<sub>1</sub>/c</i>
<i>a</i> / Å	13.07000(10)
<i>b</i> / Å	25.2860(2)
<i>c</i> / Å	13.24560(10)
$\alpha$ / °	90
$\beta$ / °	106.9020(10)
$\gamma$ / °	90
Volume/ Å <sup>3</sup>	4188.42(6)
<i>Z</i>	4
$\rho_{\text{calc}}$ / g cm <sup>-3</sup>	1.200
$\mu$ / mm <sup>-1</sup>	0.595
<i>F</i> / 000	1611.0
2 $\theta$ range for data collection / °	6.992 to 149.61
Crystal size / mm <sup>3</sup>	0.15 × 0.1 × 0.1
Index ranges	-16 ≤ <i>h</i> ≤ 16, -31 ≤ <i>k</i> ≤ 31, -15 ≤ <i>l</i> ≤ 16
Reflections collected	78807
Independent reflections	8439 [ <i>R</i> <sub>int</sub> = 0.0320, <i>R</i> <sub>sigma</sub> = 0.0158]
Data/restraints/parameters	8439/0/550
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.020
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub><i>I</i></sub> = 0.0409, <i>wR</i> <sub>2</sub> = 0.0984
Final <i>R</i> indices [all data]	<i>R</i> <sub><i>I</i></sub> = 0.0441, <i>wR</i> <sub>2</sub> = 0.1006
Largest diff. peak / hole / e Å <sup>3</sup>	0.15/-0.21
CCDC No.	1957867
Crystallization solvent	benzene

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**Table S5.** Crystal data and structure refinement for *trans*-ClCH=CHCl@T[5]-(OMe)<sub>5</sub>

Empirical formula	C <sub>82</sub> H <sub>82</sub> Cl <sub>2</sub> O <sub>10</sub>
Formula weight / g mol <sup>-1</sup>	1298.37
Temperature / K	159.99(10)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	13.2135(10)
<i>b</i> / Å	16.4229(3)
<i>c</i> / Å	16.6046(3)
$\alpha$ / °	71.707(2)
$\beta$ / °	82.4130(10)
$\gamma$ / °	86.2830(10)
Volume / Å <sup>3</sup>	6462.83(18)
<i>Z</i>	2
$\rho_{\text{calc}}$ / g cm <sup>-3</sup>	1.272
$\mu$ / mm <sup>-1</sup>	1.354
<i>F</i> / 000	1376.0
2 $\theta$ range for data collection / °	5.646 to 149.864
Crystal size / mm <sup>3</sup>	0.2 × 0.2 × 0.2
Index ranges	-15 ≤ <i>h</i> ≤ 16, -20 ≤ <i>k</i> ≤ 20, -19 ≤ <i>l</i> ≤ 20
Reflections collected	42039
Independent reflections	13437 [ <i>R</i> <sub>int</sub> = 0.0373, <i>R</i> <sub>sigma</sub> = 0.0371]
Data/restraints/parameters	13437/1/857
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.068
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub><i>I</i></sub> = 0.0499, <i>wR</i> <sub>2</sub> = 0.1379
Final <i>R</i> indices [all data]	<i>R</i> <sub><i>I</i></sub> = 0.0586, <i>wR</i> <sub>2</sub> = 0.1461
Largest diff. peak / hole / e Å <sup>3</sup>	0.59/-0.61
CCDC No.	1957869
Crystallization solvents	methanol/ <i>trans</i> -dichloroethene

**Table S6.** Crystal data and structure refinement for **T[5]-(OMe)<sub>5</sub>**

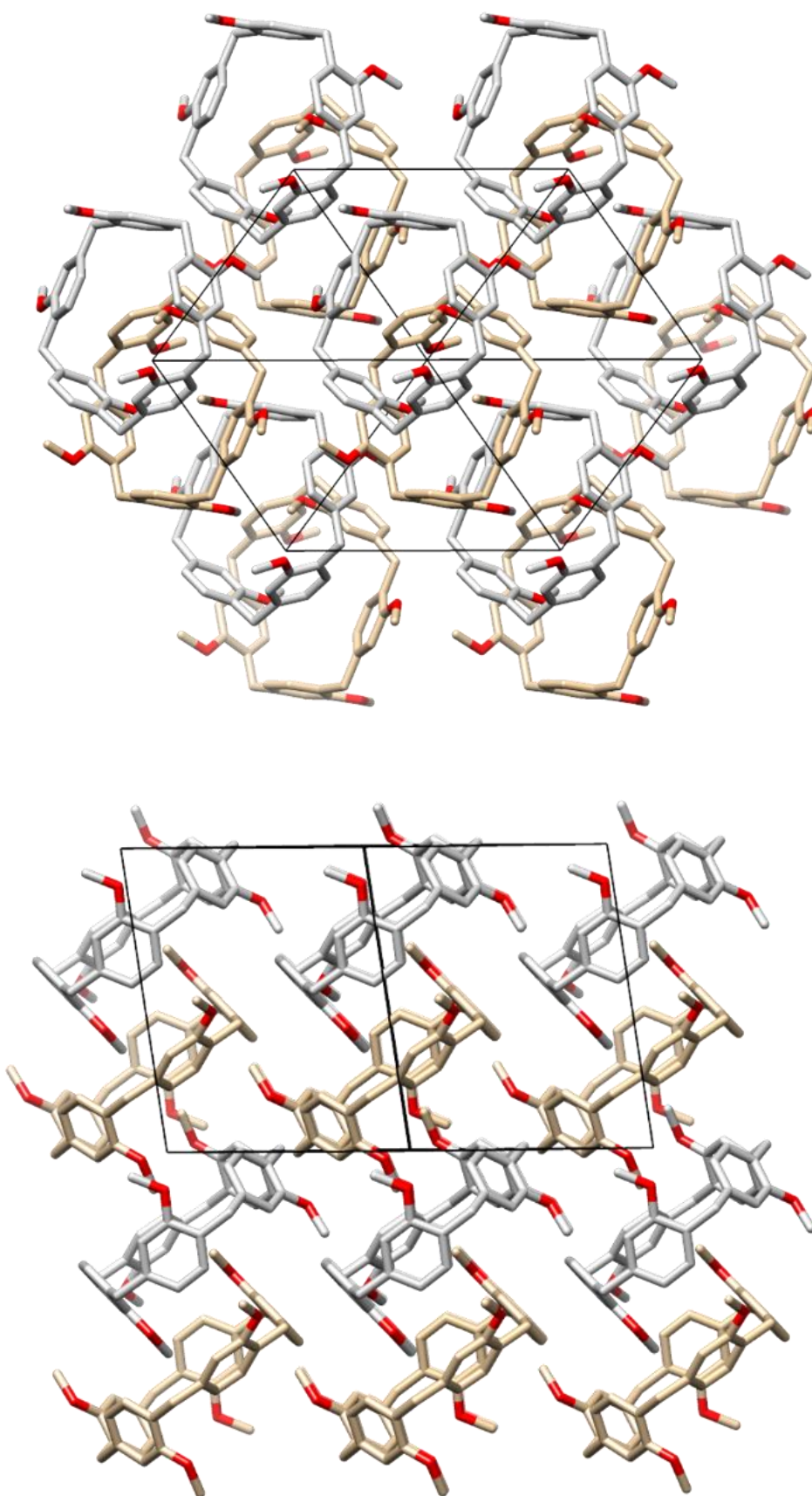
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Empirical formula	C <sub>40</sub> H <sub>40</sub> O <sub>5</sub>
Formula weight / g mol <sup>-1</sup>	600.72
Temperature / K	159.99(10)
Crystal system	monoclinic
Space group	<i>P2<sub>1</sub></i>
<i>a</i> / Å	12.1727(2)
<i>b</i> / Å	42.9634(6)
<i>c</i> / Å	12.7404(2)
$\alpha$ / °	90
$\beta$ / °	104.079(2)
$\gamma$ / °	90
Volume / Å <sup>3</sup>	6462.83(18)
<i>Z</i>	2
$\rho_{\text{calc}}$ / g cm <sup>-3</sup>	1.238
$\mu$ / mm <sup>-1</sup>	0.637
<i>F</i> / 000	2574.0
2 $\theta$ range for data collection / °	4.114 to 104.49
Crystal size / mm <sup>3</sup>	0.1 × 0.05 × 0.05
Index ranges	-12 ≤ <i>h</i> ≤ 12, -43 ≤ <i>k</i> ≤ 43, -13 ≤ <i>l</i> ≤ 12
Reflections collected	68727
Independent reflections	14411 [ <i>R</i> <sub>int</sub> = 0.0558, <i>R</i> <sub>sigma</sub> = 0.0417]
Data/restraints/parameters	14411/1/1641
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.073
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub><i>I</i></sub> = 0.0857, <i>wR</i> <sub>2</sub> = 0.2265
Final <i>R</i> indices [all data]	<i>R</i> <sub><i>I</i></sub> = 0.0917, <i>wR</i> <sub>2</sub> = 0.2319
Largest diff. peak / hole / e Å <sup>3</sup>	0.58/-0.38
CCDC No.	1957870
Crystallization Solvents	methanol/ethyl acetate

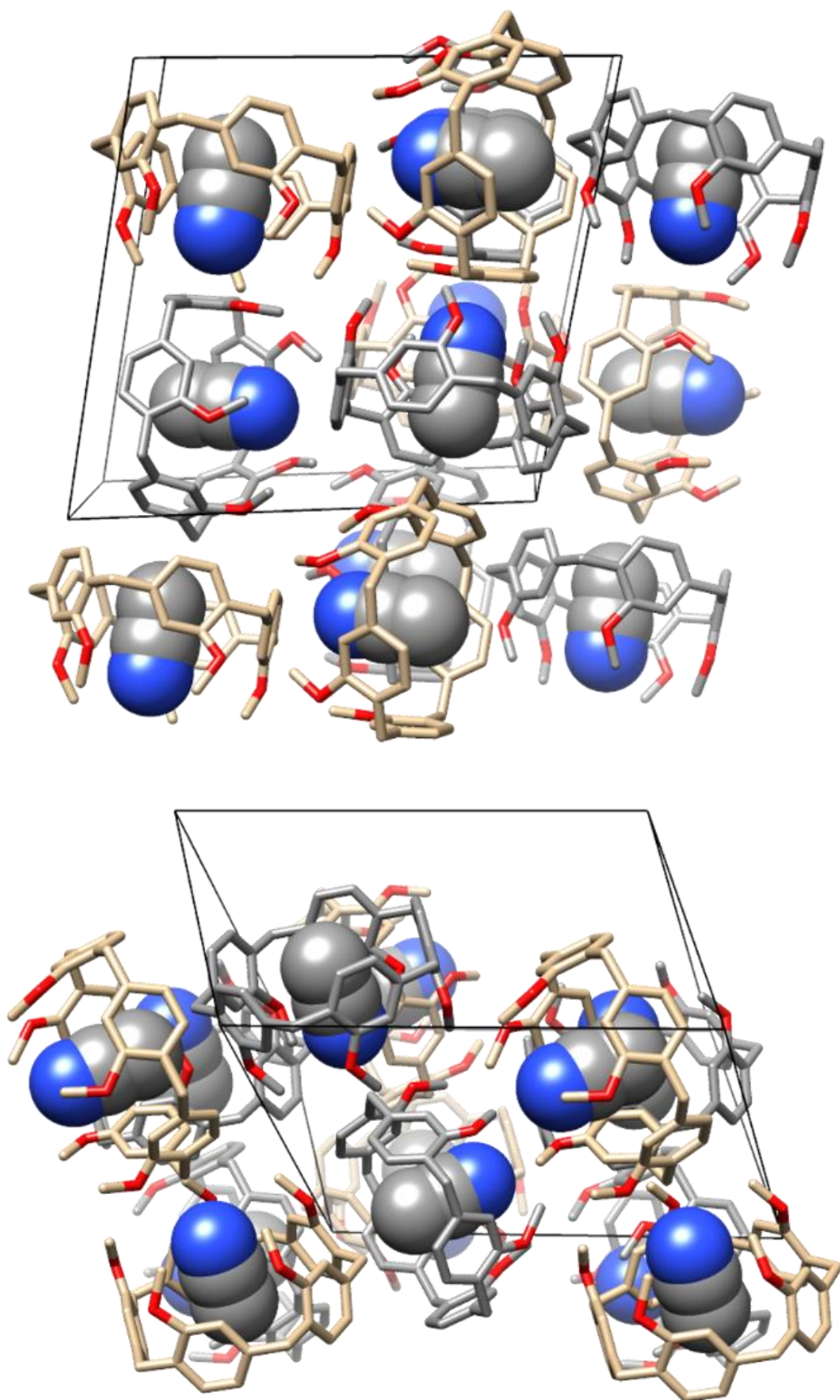
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**Table S7.** Crystal data and structure refinement for CH<sub>2</sub>Cl<sub>2</sub>@T[5]-(OMe)<sub>5</sub>

Empirical formula	C <sub>81</sub> H <sub>82</sub> Cl <sub>12</sub> O <sub>10</sub>
Formula weight / g mol <sup>-1</sup>	1286.36
Temperature / K	159.99(10)
Crystal system	monoclinic
Space group	C2/c
<i>a</i> / Å	20.3292(5)
<i>b</i> / Å	15.6783(4)
<i>c</i> / Å	22.5018(6)
<i>α</i> / °	90
<i>β</i> / °	106.973(3)
<i>γ</i> / °	90
Volume/ Å <sup>3</sup>	6859.5(3)
<i>Z</i>	4
$\rho_{\text{calc}}$ / g cm <sup>-3</sup>	1.246
$\mu$ / mm <sup>-1</sup>	1.333
<i>F</i> / 000	2728.0
2 $\theta$ range for data collection / °	7.244–149.952
Crystal size / mm <sup>3</sup>	0.5 × 0.2 × 0.03
Index ranges	-25 ≤ <i>h</i> ≤ 25, -19 ≤ <i>k</i> ≤ 19, -28 ≤ <i>l</i> ≤ 27
Reflections collected	61508
Independent reflections	6836 [ <i>R</i> <sub>int</sub> = 0.0813, <i>R</i> <sub>sigma</sub> = 0.0269]
Data/restraints/parameters	6836/0/435
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.067
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.1292, <i>wR</i> <sub>2</sub> = 0.3170
Final <i>R</i> indices [all data]	<i>R</i> <sub>1</sub> = 0.1343, <i>wR</i> <sub>2</sub> = 0.3201
Largest diff. peak / hole / e Å <sup>3</sup>	0.94/-0.32
CCDC No.	1896024
Crystallization solvents	methanol/dichloromethane

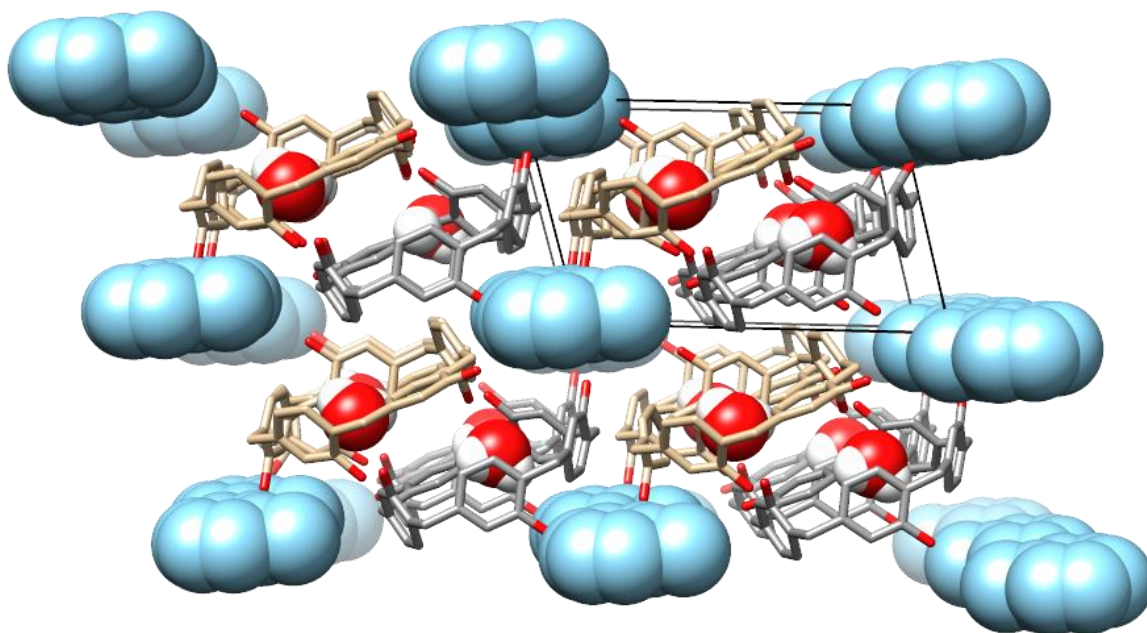
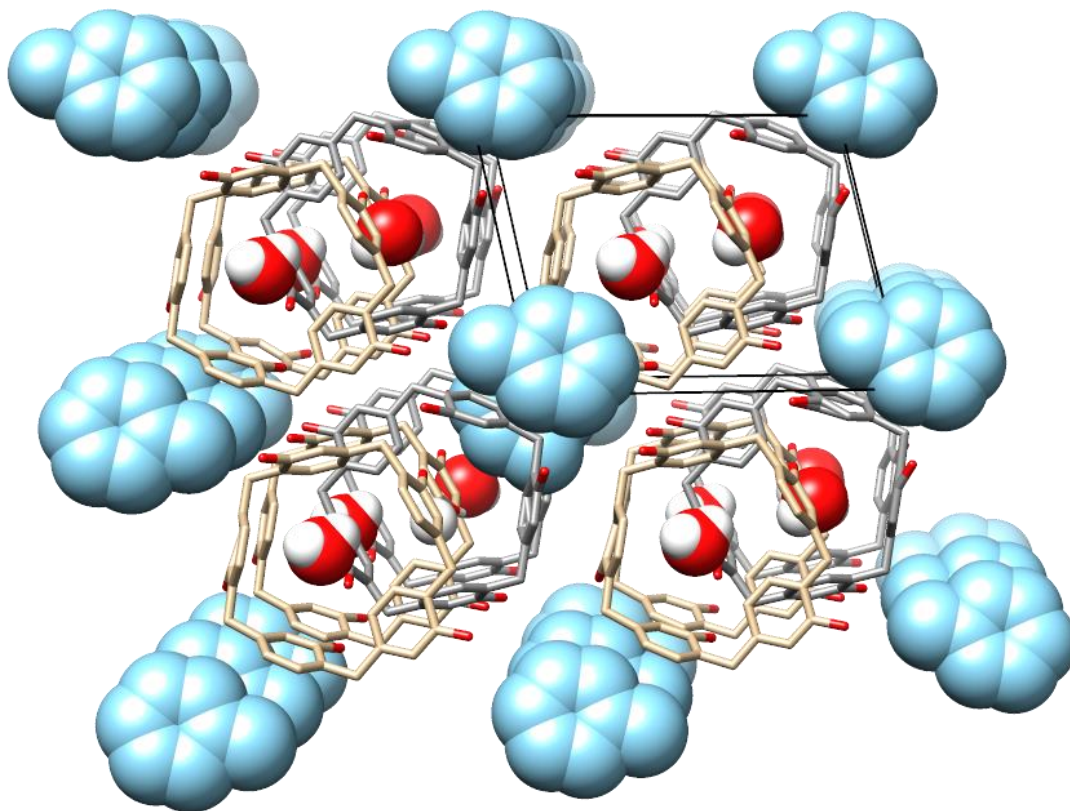


**Figure S10.** Unit cell of **T[5]-(OMe)<sub>5</sub>** (crystallized by vapor diffusion of MeOH into CHCl<sub>3</sub>) viewing from [111] (top) and [1-10] (bottom) directions.

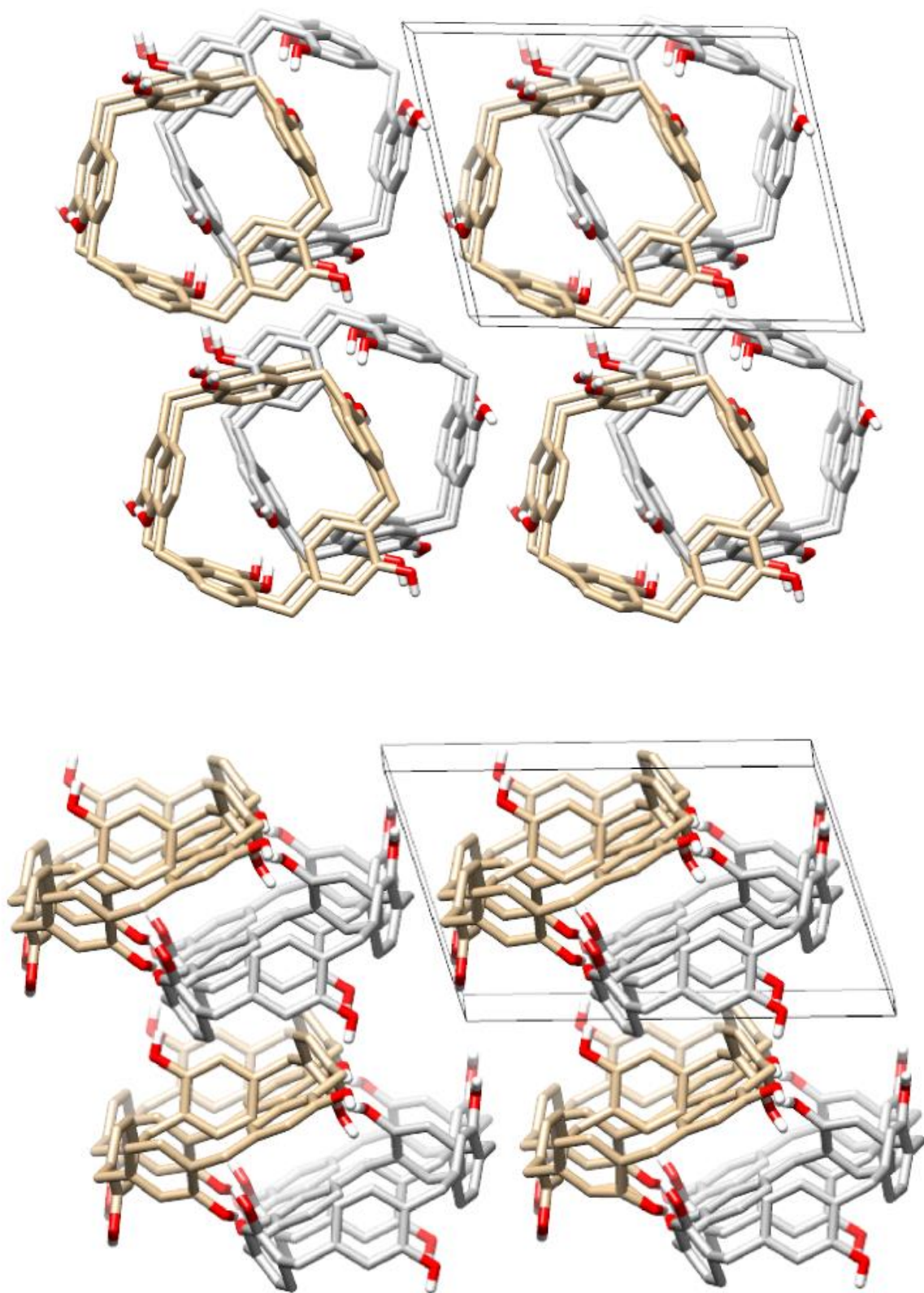


**Figure S11.** Unit cell of  $\text{CH}_3\text{CNCT}[5]\text{-(OMe)}_5$  viewing from  $[100]$  (top) and  $[101]$  (bottom) directions.



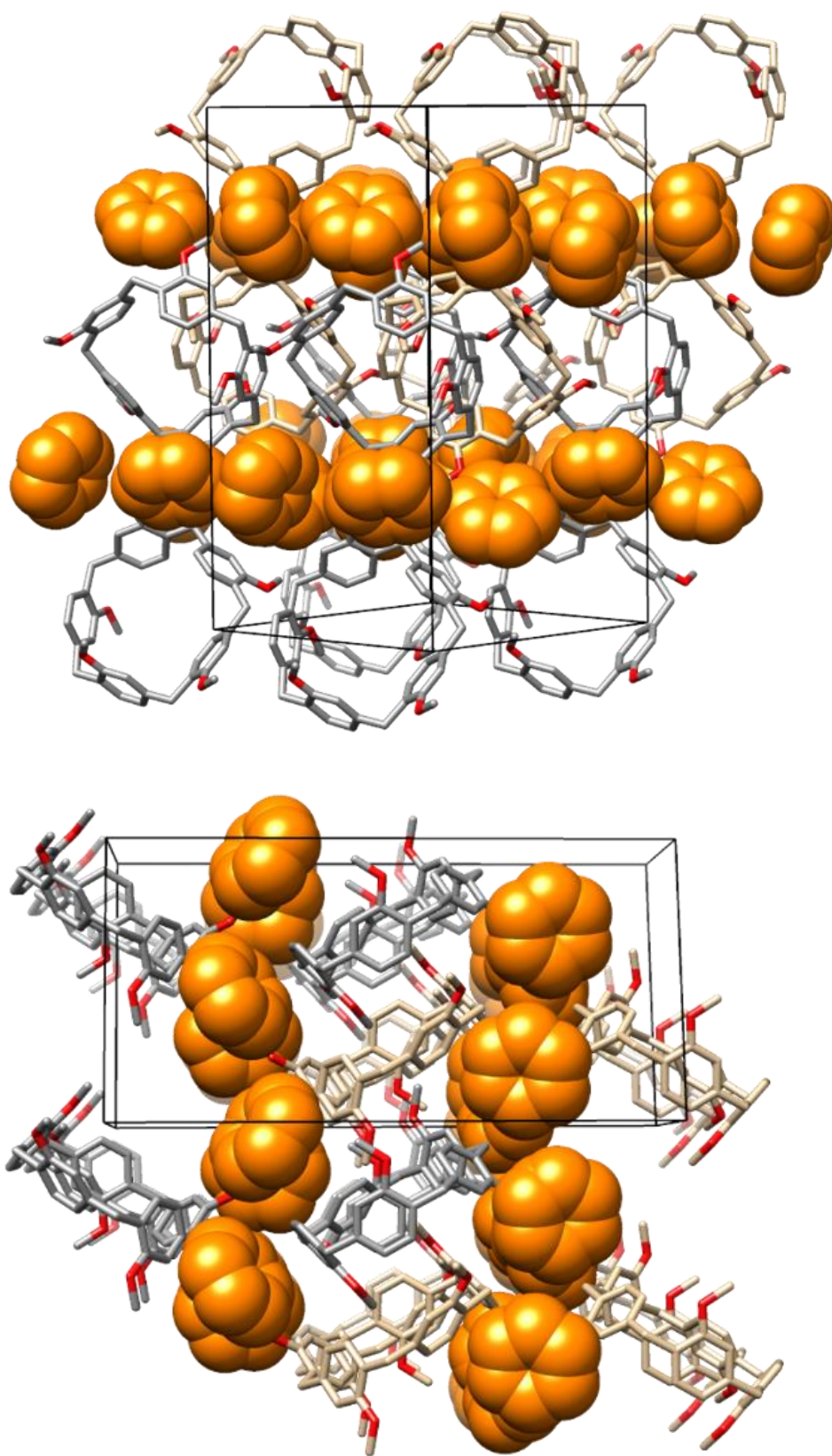


**Figure S12.** Unit cell of PhMe@T[5] viewing from [100] (top) and [010] (bottom) directions. Color code: PhMe, sky blue.



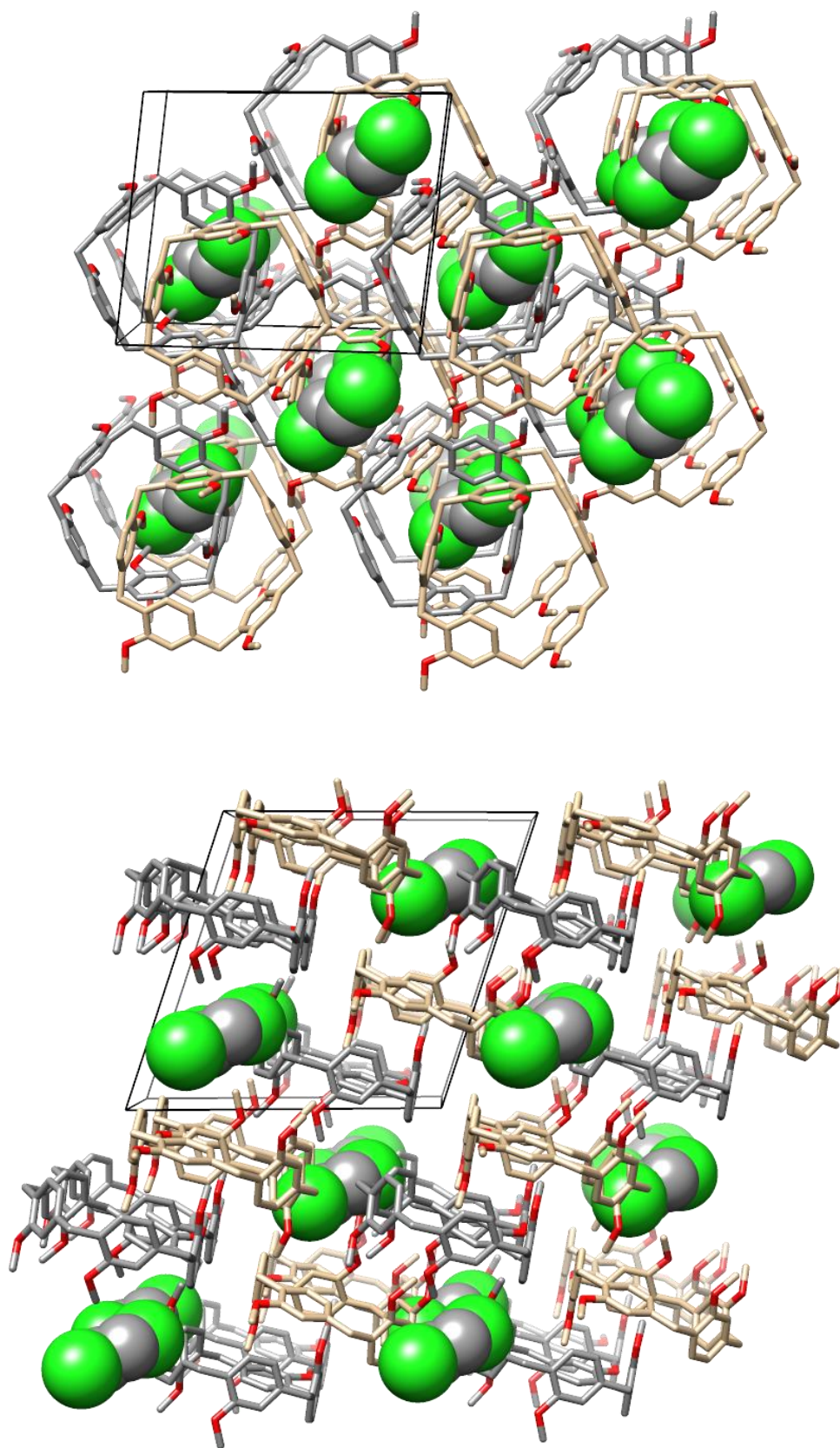
**Figure S13.** Unit cell of PhMe@T[5] viewing from [100] (top) and [010] (bottom) directions. All solvent molecules are omitted for clarity.



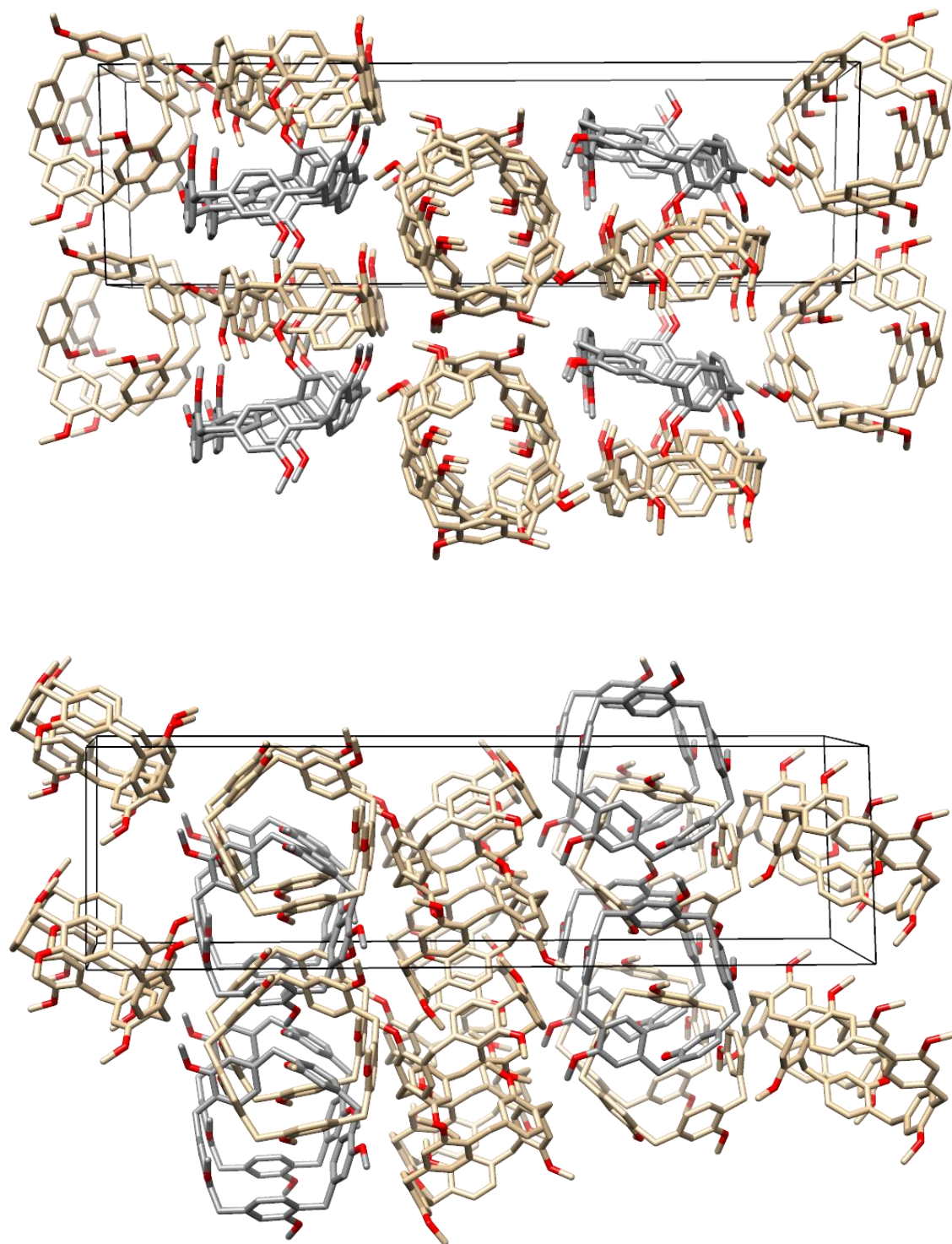


**Figure S14.** Unit cell of  $C_6H_6@T[5]-(OMe)_5$  viewing from [101] (top) and [100] (bottom) directions. Color code:  $C_6H_6$ , orange.

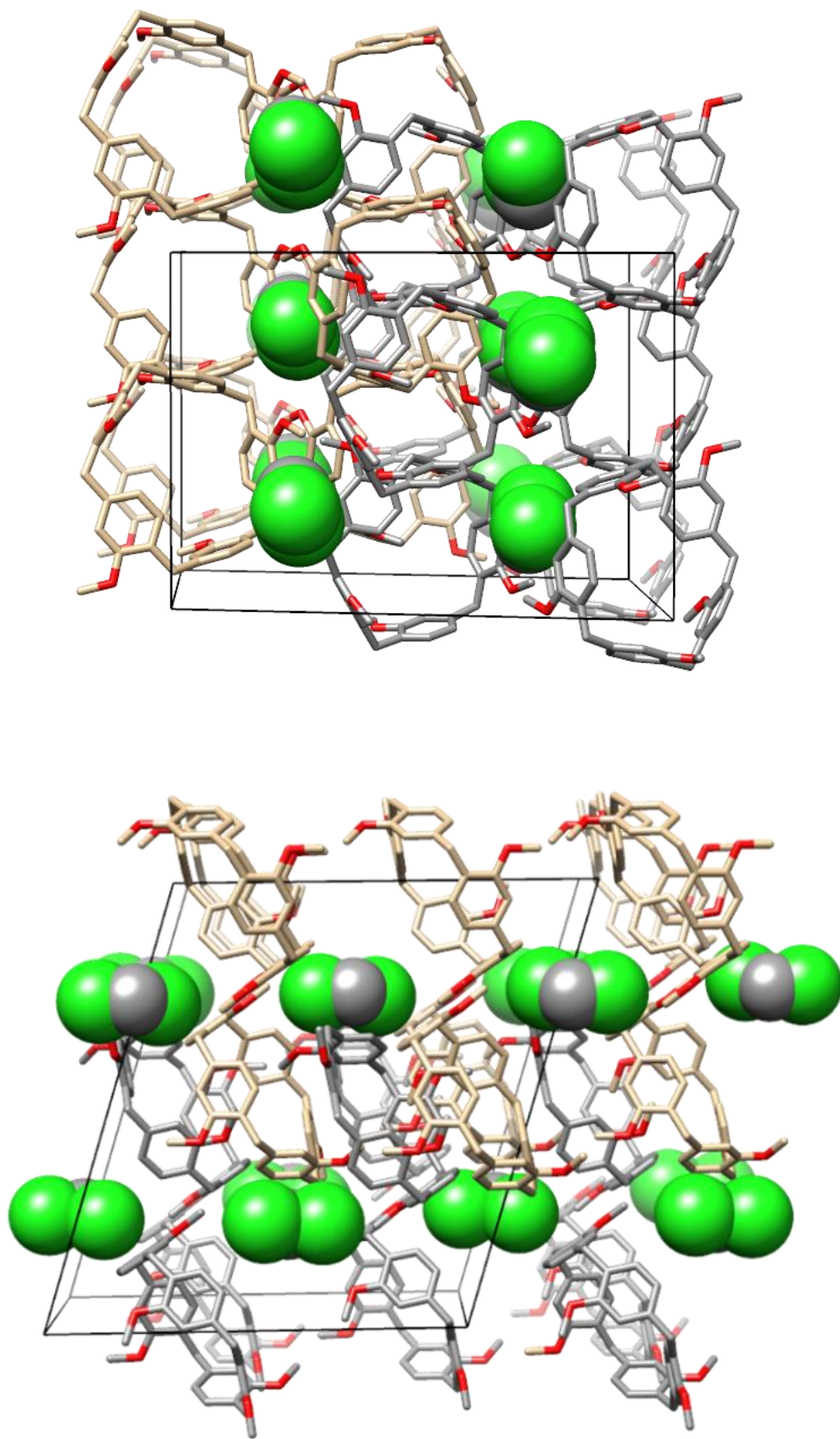




**Figure S15.** Unit cell of *trans*-ClCH=CHCl@T[5]-(OMe)<sub>5</sub> viewing from [010] (top) and [100] (bottom) directions



**Figure S16.** Unit cell of T[5]-(OMe)<sub>5</sub> (crystallized by vapor diffusion of MeOH into EtOAc) viewing from [100] (top) and [001] (bottom) directions.



**Figure S17.** Unit cell of  $\text{CH}_2\text{Cl}_2@T[5]-(\text{OMe})_5$  viewing from  $[100]$  (top) and  $[010]$  (bottom) directions.



#### 4. Host-Guest Binding Studies

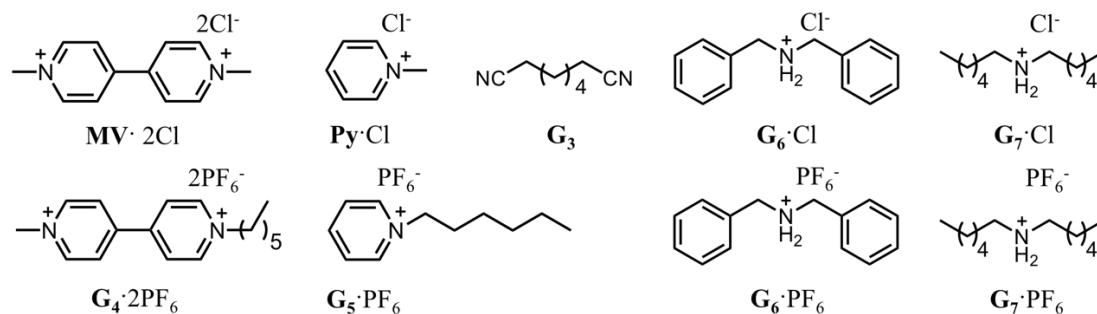
$^1\text{H}$  NMR titrations were performed in  $\text{CD}_3\text{OD}$  or  $(\text{CD}_3)_2\text{CO}$  procured commercially from Cambridge Isotope Laboratories at ambient temperature (298 K) by adding incremental amount of guest solution (1 M) into **T[5]** host solution (5 mM). For each titration experiment 20 equivalent of guest were added unless otherwise noted. Changes in chemical shift ( $\Delta\delta$ ) of  $^1\text{H}$  NMR signals of **T[5]** aromatic protons ( $\text{H}_p$ ,  $\text{H}_o$ , and  $\text{H}_m$ ) were recorded. Titration curve-fitting and association constant values (listed in Table S8) were calculated by employing the *BindFit* program developed by Prof. Pall Thordarson of UNSW.<sup>[5]</sup> This program employs a nonlinear least-squares regression analysis and is available free of cost online through the following link: <http://supramolecular.org/>.

**Table S8.** Association constants ( $K_a$ ) between **T[5]** and various guests

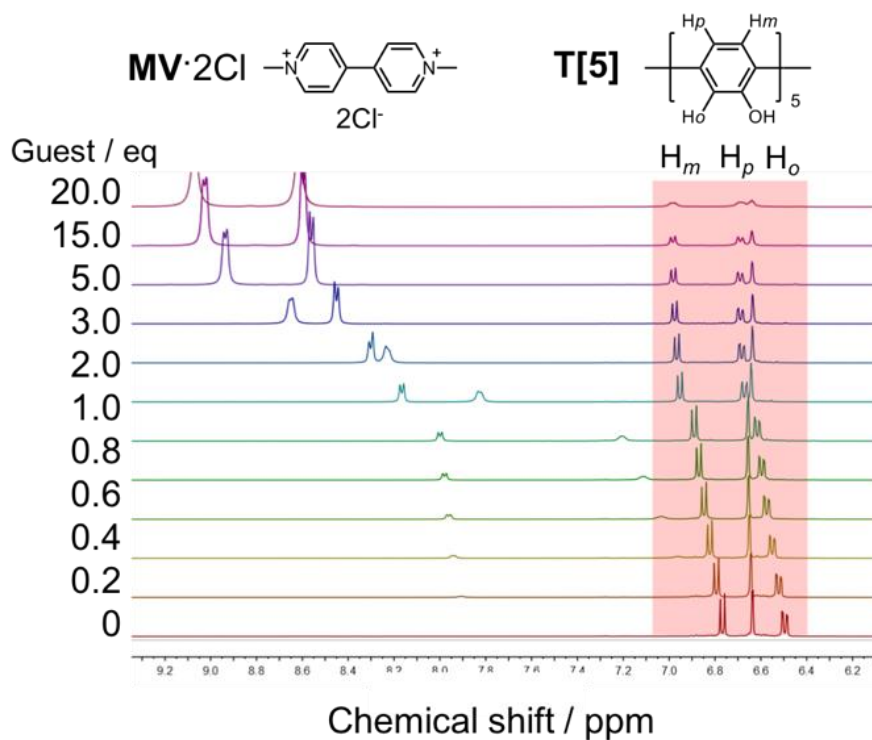
Guests	Solvents	$K_a / \text{M}^{-1}$	Binding Stoichiometry <sup>b</sup>
<b>MV</b> ·2Cl		$(1.0 \pm 0.2) \times 10^3$	
<b>Py</b> ·Cl		$(1.2 \pm 0.2) \times 10^3$	
<b>G<sub>3</sub></b>	Methanol- $d_4$	$57 \pm 1.5$	1:1
<b>G<sub>6</sub></b> ·Cl		N/A <sup>a</sup>	
<b>G<sub>7</sub></b> ·Cl		N/A <sup>a</sup>	
<b>G<sub>4</sub></b> ·2PF <sub>6</sub>		$70 \pm 3.1$	
<b>G<sub>5</sub></b> ·PF <sub>6</sub>		$55 \pm 3.6$	
<b>G<sub>3</sub></b>	Acetone- $d_6$	N/A <sup>a</sup>	1:1
<b>G<sub>6</sub></b> ·PF <sub>6</sub>		N/A <sup>a</sup>	
<b>G<sub>7</sub></b> ·PF <sub>6</sub>		N/A <sup>a</sup>	

<sup>a</sup> Changes of chemical shift observed were negligible for curve-fitting.

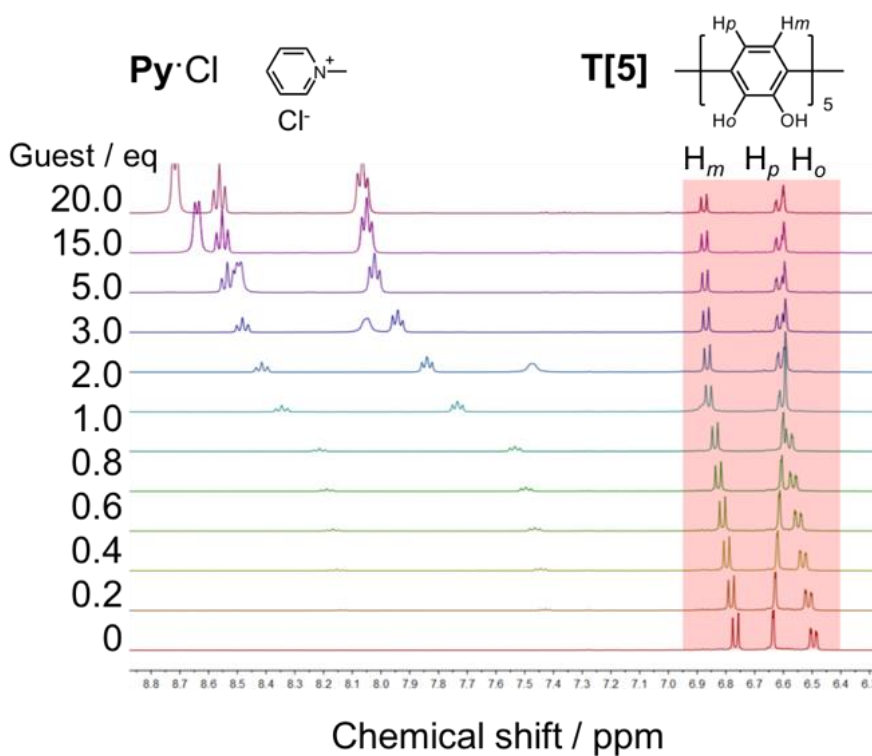
<sup>b</sup> 1:1 Binding stoichiometry was chosen in the *BindFit* program.<sup>[6,7]</sup>



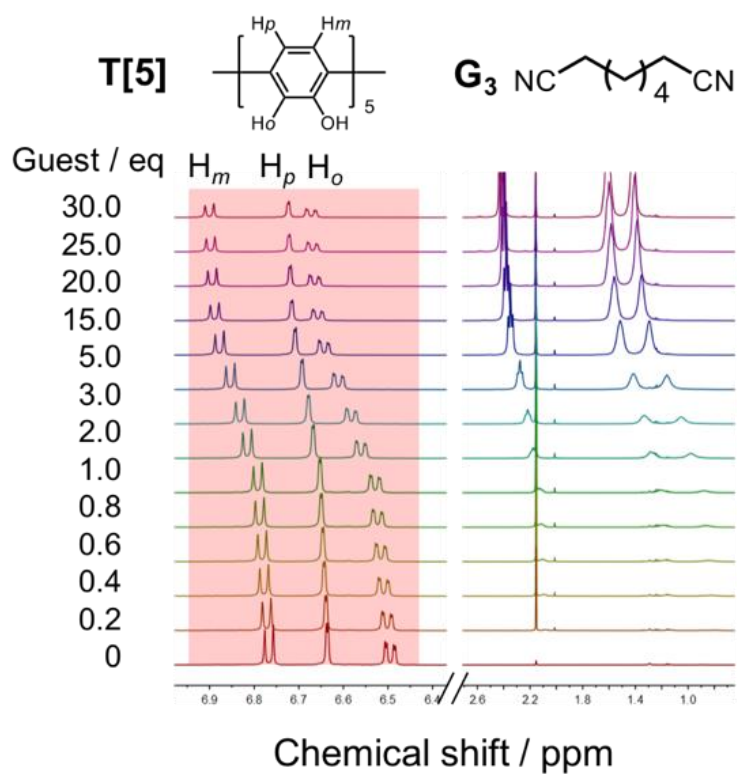
**Scheme S2.** Various guest molecules employed in the host-guest binding studies.



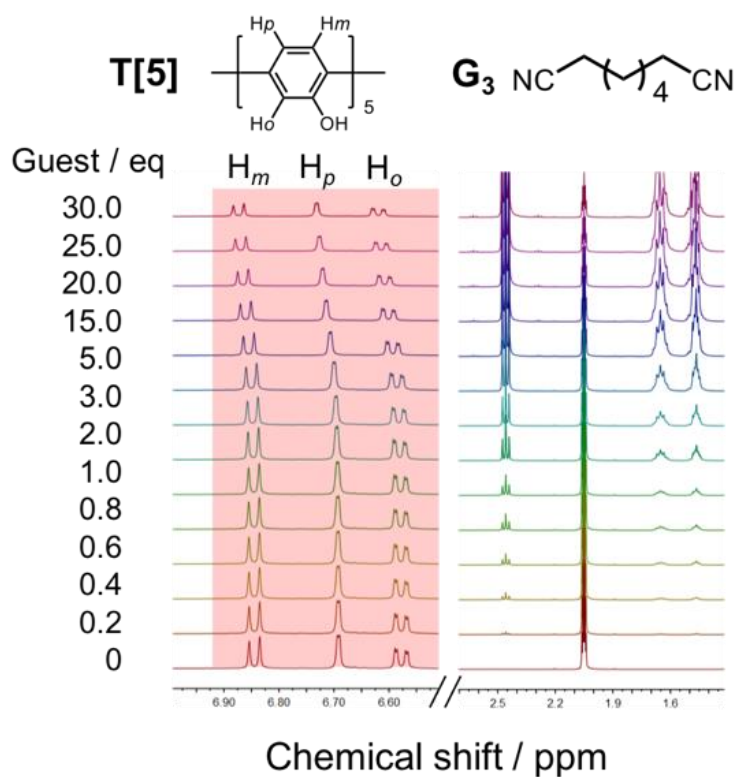
**Figure S18.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_3\text{OD}$ , 298 K) of **T[5]** at a concentration of 5.00 mM upon titration of **MV·2Cl** and **(b) Py·Cl**.



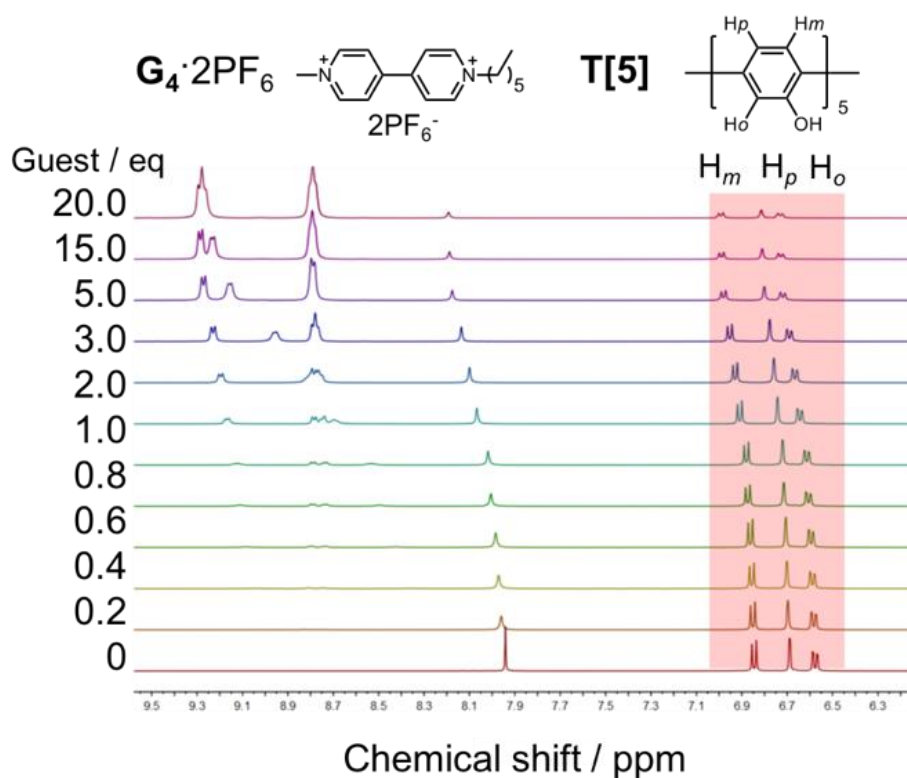
**Figure S19.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_3\text{OD}$ , 298 K) of **T[5]** at a concentration of 5.00 mM upon titration of **Py·Cl**.



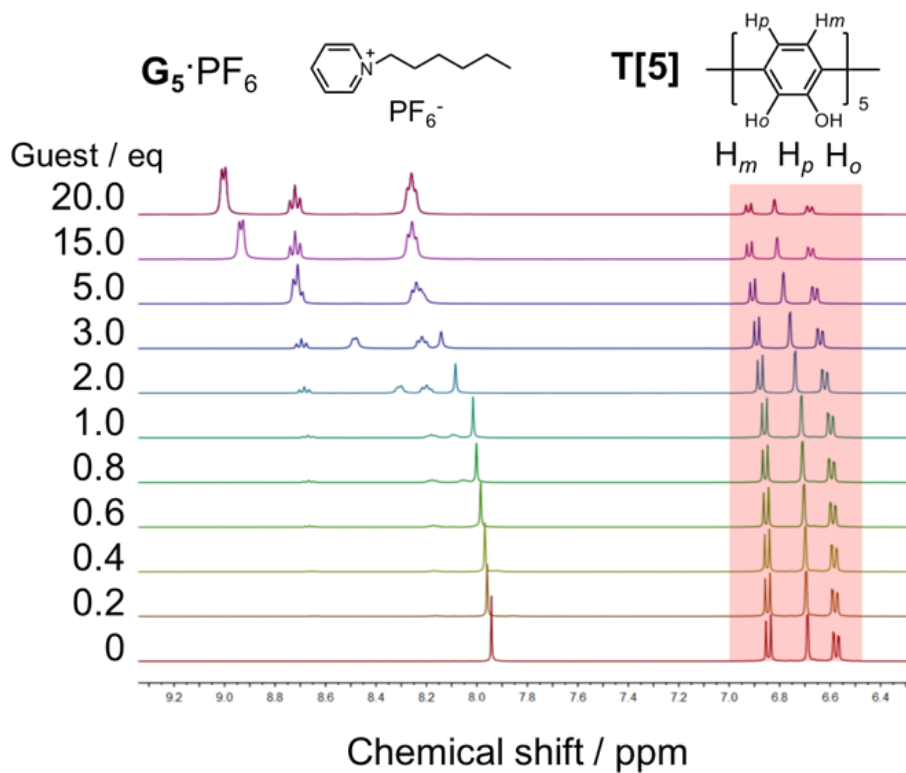
**Figure S20.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_3\text{OD}$ , 298 K) of  $\mathbf{T[5]}$  at a concentration of 5.00 mM upon titration of  $\mathbf{G}_3$ .



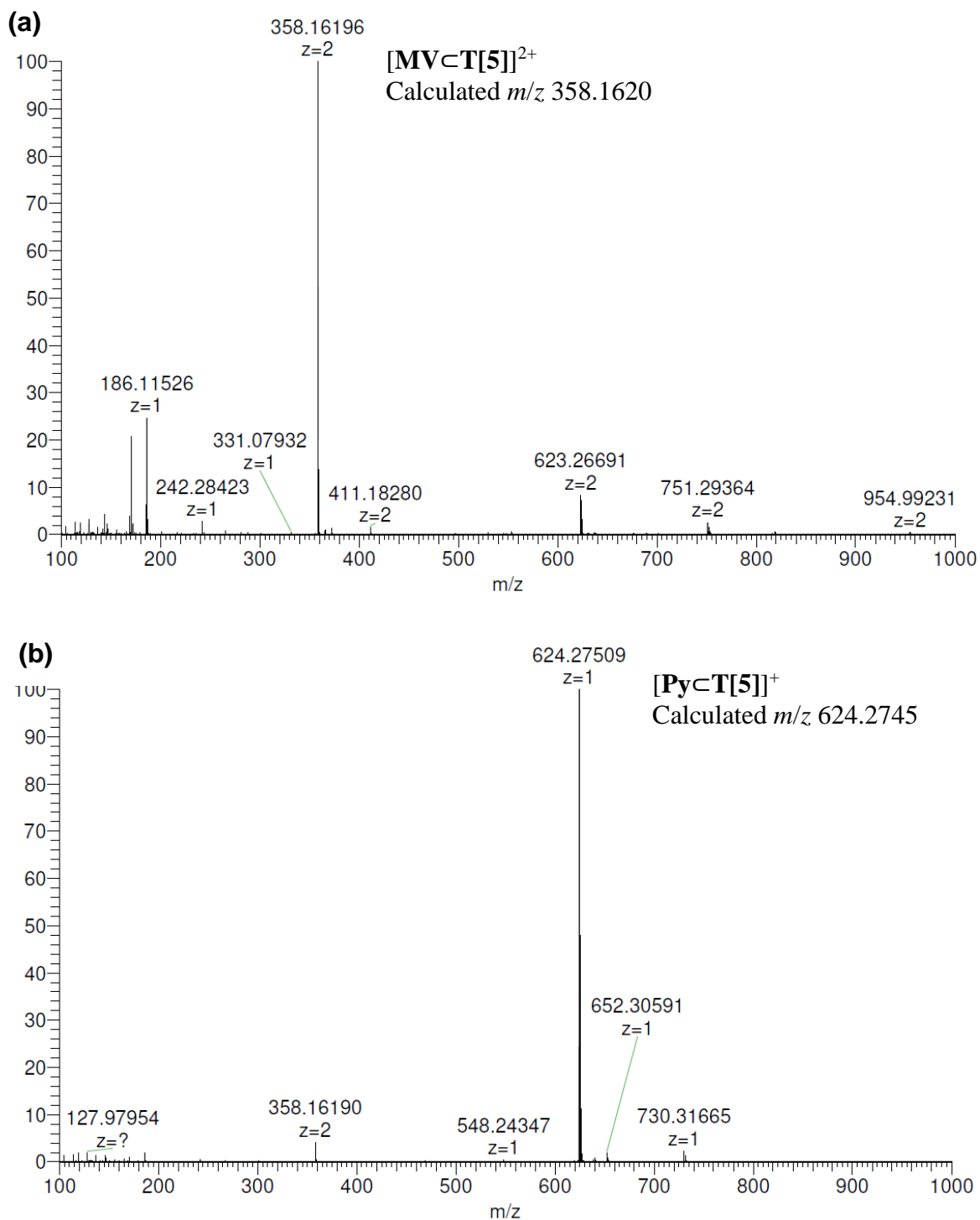
**Figure S21.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_3\text{COCD}_3$ , 298 K) of  $\mathbf{T[5]}$  at a concentration of 5.00 mM upon titration of  $\mathbf{G}_3$ .



**Figure S22.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $(\text{CD}_3)_2\text{CO}$ , 298 K) of **T[5]** at a concentration of 5.00 mM upon titration of **G<sub>4</sub>·2Cl**.



**Figure S23.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $(\text{CD}_3)_2\text{CO}$ , 298 K) of **T[5]** at a concentration of 5.00 mM upon titration of **G<sub>5</sub>·Cl**.



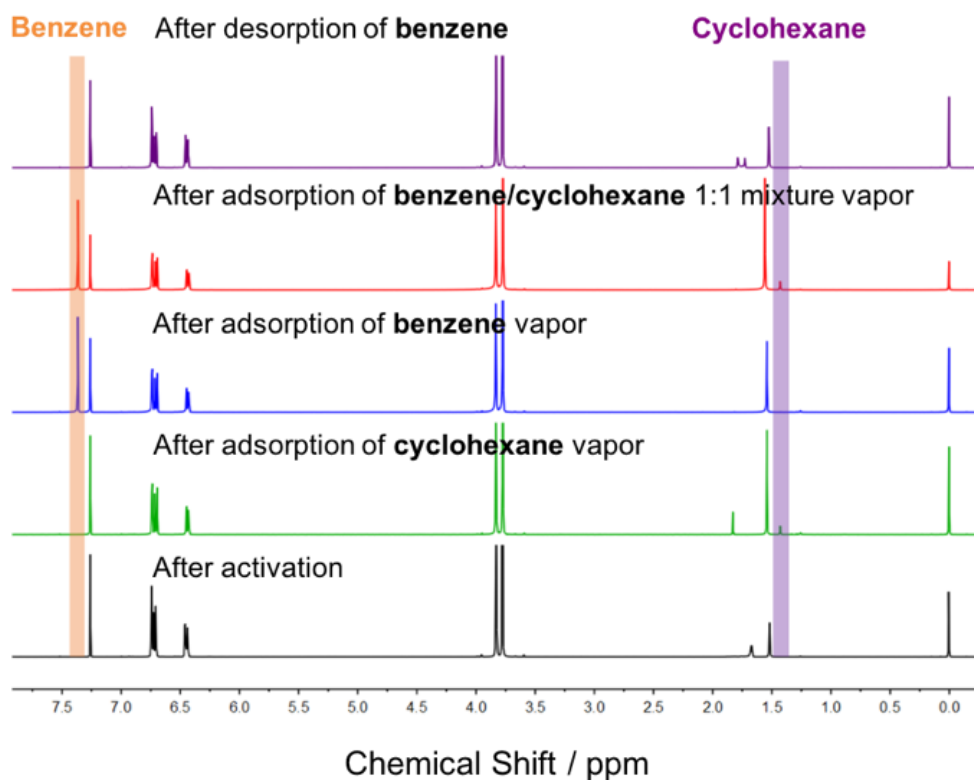
**Figure S24.** ESI mass spectra of (a) [MVcT[5]]·2Cl and (b) [PycT[5]]·Cl. Samples were prepared by dissolving T[5] in MeOH (0.5 mg/mL) with 5 eq. of MV·2Cl and Py·Cl guests, respectively, before further dilution for analysis.



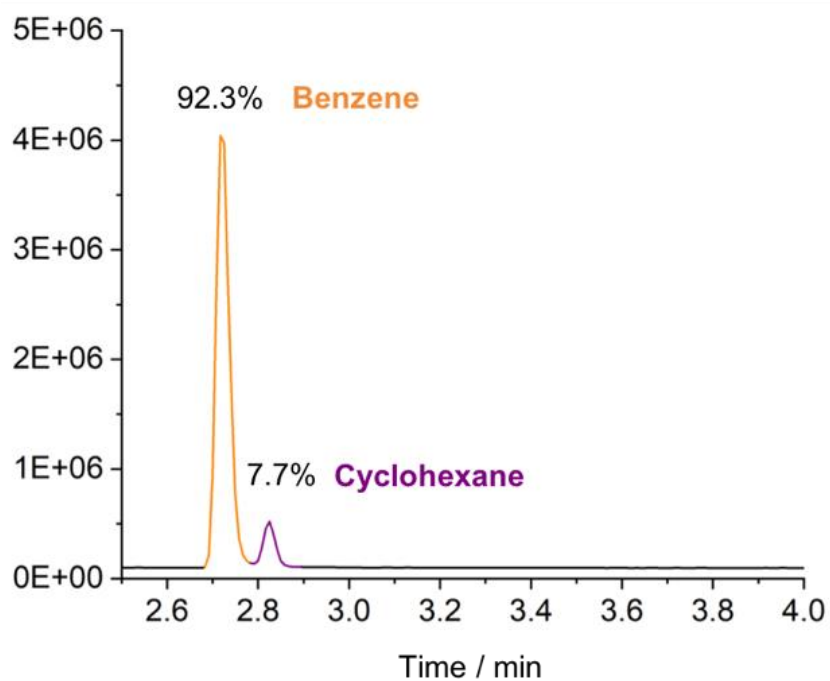
## 5. Vapor-Solid Sorption and Fractionation Experiments

For each solid-vapor sorption and fractionation experiment, an open 2 mL vial containing 2.0 mg of activated **T[5]-(OMe)<sub>5</sub>** adsorbent was placed in a sealed 20 mL vial containing 1 mL of solvent or solvent mixture (50:50 v/v). Relative uptake amount in the **T[5]-(OMe)<sub>5</sub>** crystals was determined by <sup>1</sup>H NMR integrals of corresponding proton signals of completely dissolved material in CDCl<sub>3</sub>. Gas chromatography characterizations were also performed in order to determine the relative uptake amounts of mixed solvents in **T[5]-(OMe)<sub>5</sub>** crystals more accurately. Desorption experiments after saturation were carried out by thermogravimetric analysis.

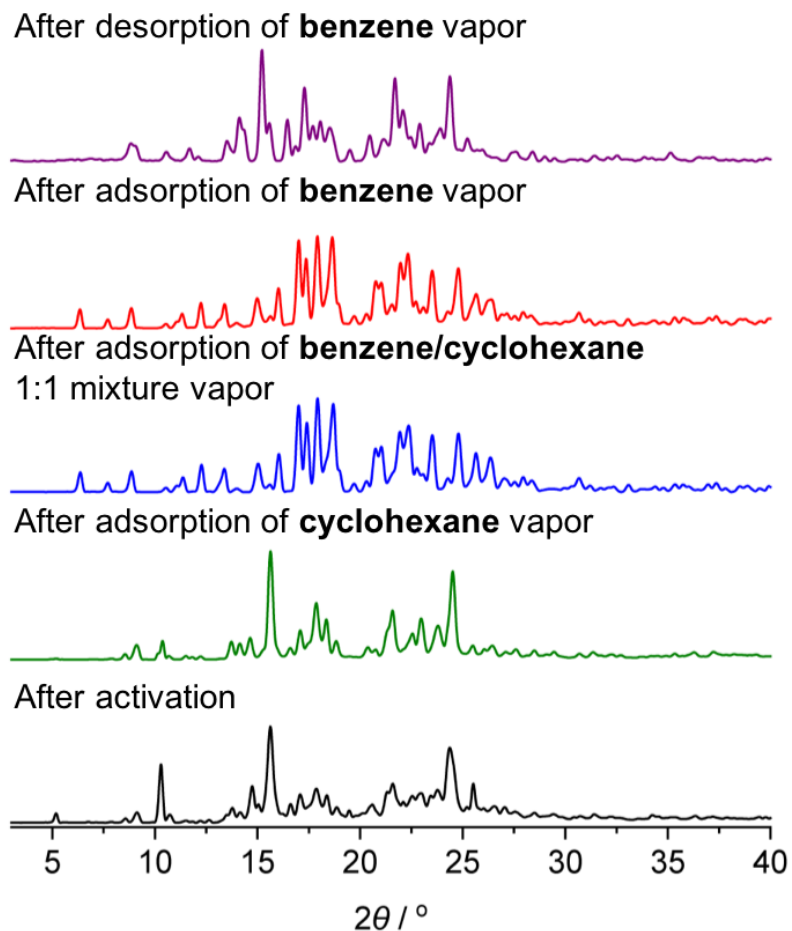
Thermogravimetric analysis (TGA) was conducted on a METTLER TOLEDO TGA 2 operated at 10 K min<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/Max-2500 X-ray diffractometer. Data were collected over the range of 3–40° at a scan rate of 5°·min<sup>-1</sup>. Gas chromatography (GC) measurements were carried out on a Shimadzu GCMS-QP2010 Plus with an FID detector. The following GC method was used: the oven was programmed from 30 °C, ramped at 5 °C·min<sup>-1</sup> increments to 300 °C within 15 min hold; injection temperature 300 °C; detection temperature 300 °C; helium (carrier gas) flow-rate 3.0 mL·min<sup>-1</sup>; samples were analyzed using headspace injections and were performed by incubating the sample at 50 °C for 5 min followed by sampling 1 mL of the headspace.



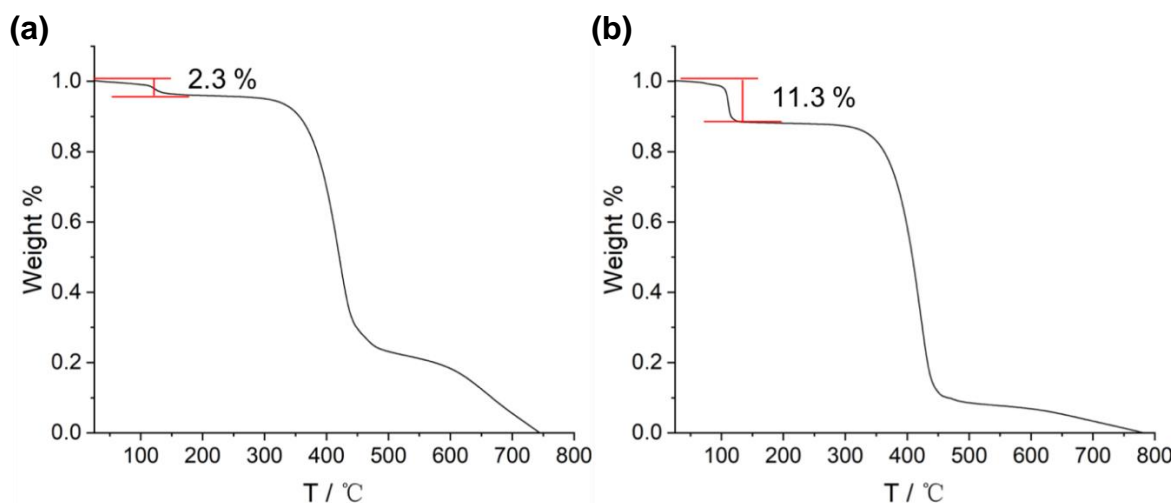
**Figure S25.** <sup>1</sup>H NMR spectra (400 MHz, 298 K, CDCl<sub>3</sub>) of T[5]-(OMe)<sub>5</sub> after benzene/cyclohexane vapor adsorption/desorption.



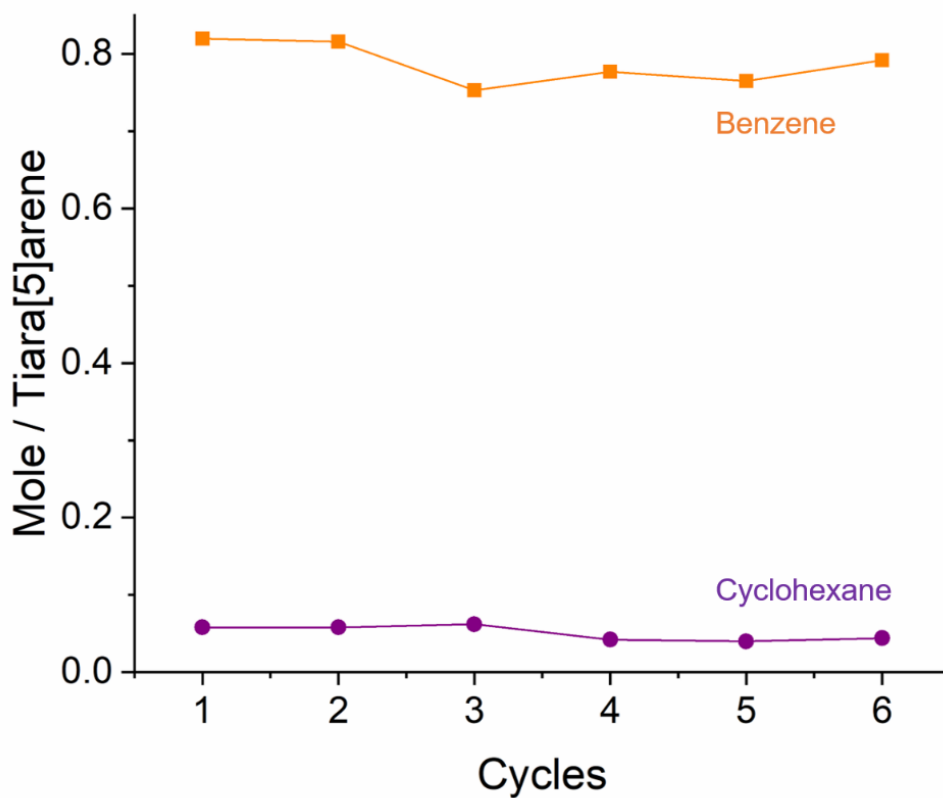
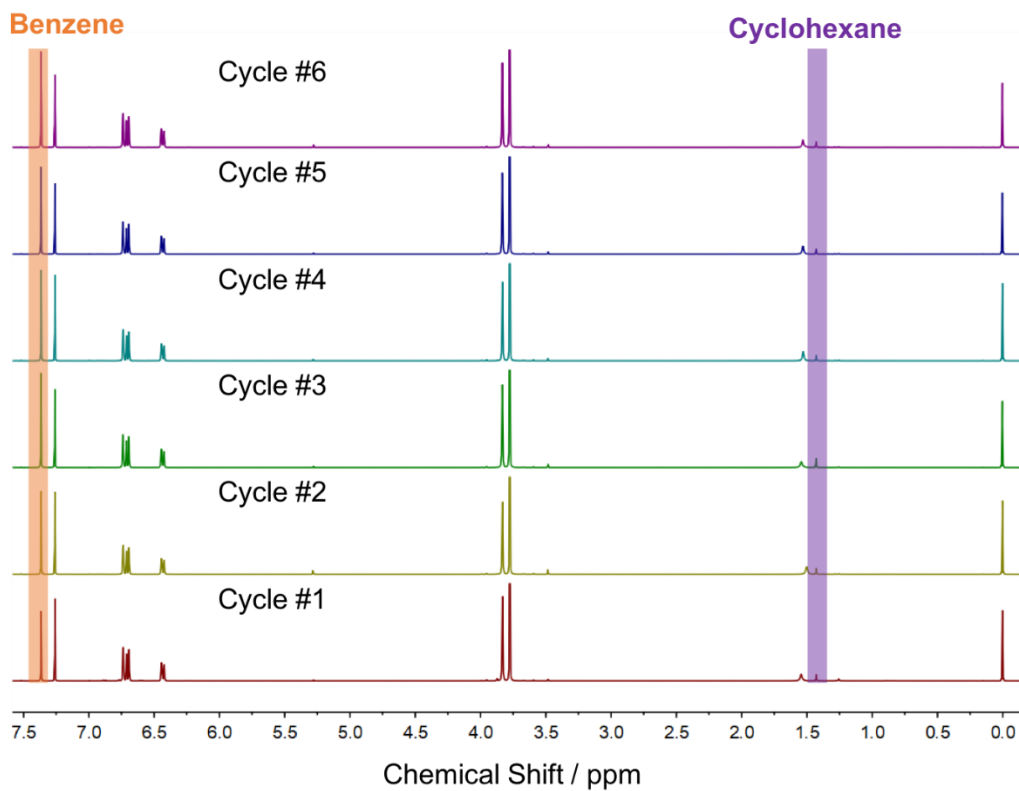
**Figure S26.** Relative uptakes of benzene/cyclohexane (adsorption time 7 h) in activated T[5]-(OMe)<sub>5</sub> determined by gas chromatography.



**Figure S27.** Powder X-ray diffraction (PXRD) patterns of activated  $\text{T[5]-(OMe)}_5$  and  $\text{T[5]-(Me)}_5$  after benzene/cyclohexane vapor adsorption/desorption experiments.



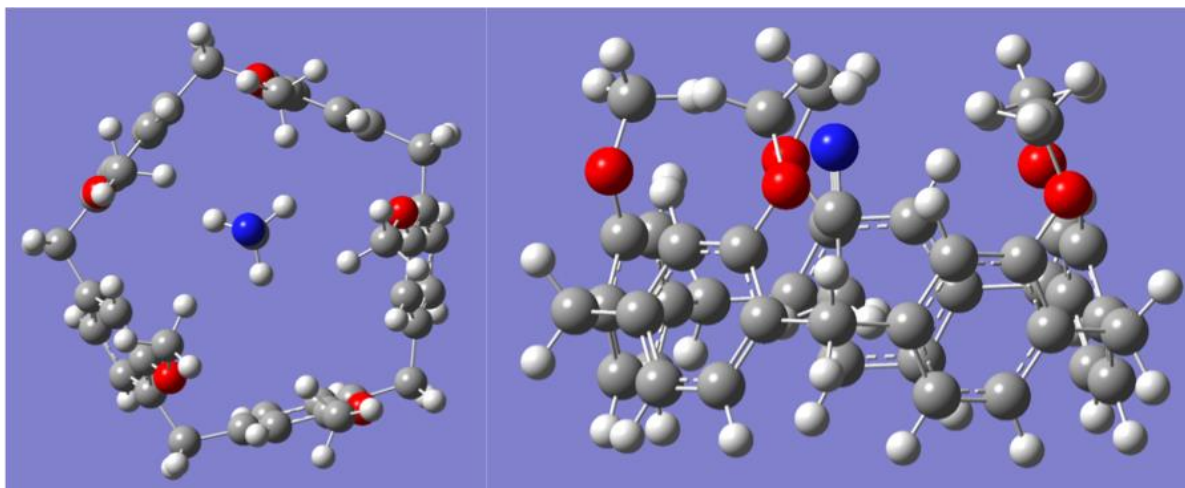
**Figure S28.** Thermogravimetric analysis of (a) activated  $\text{T[5]-(OMe)}_5$ . The 2.3% weight loss observed can be attributed to the loss of water in the sample; (b)  $\text{T[5]-(OMe)}_5$  after adsorption of benzene. The 11.3% weight loss can be attributed to the loss of water and benzene combined. The net weight loss of benzene correspond to 0.8 benzene per  $\text{T[5]-(OMe)}_5$  (mol/mol).



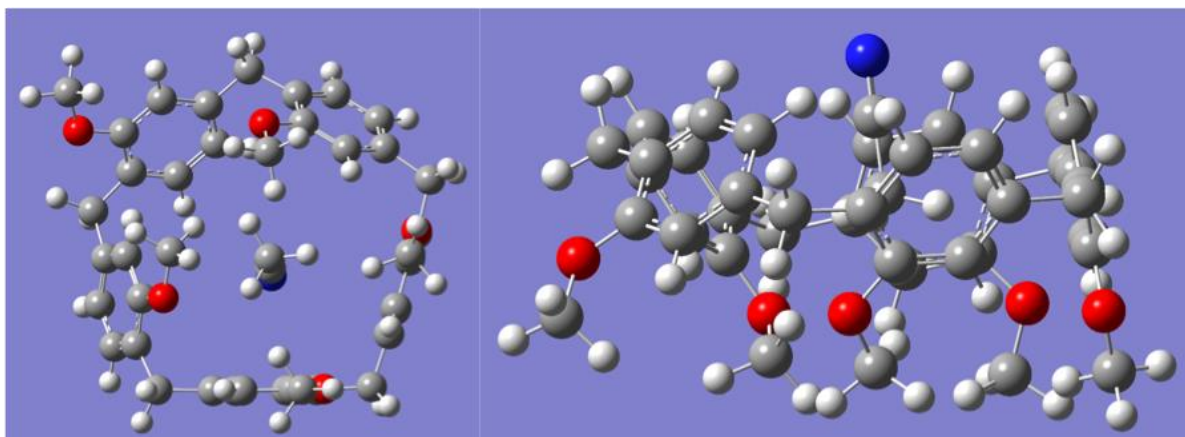
**Figure S29.** Relative uptake mole ratio of benzene and cyclohexane in  $\text{T}[5]-(\text{OMe})_5$  crystalline materials through six cycles of activation/adsorption determined by  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K).

## 6. Computational Details

All quantum-chemical computations were performed using the Gaussian16 suite of programs (version B.1), with the wB97XD functional and basis sets referred to as implemented in there.<sup>[8]</sup> Input files were made via Chem3D, and the results were visualized using Gaussview 6.



**Figure S30.** Optimized geometry of MeCN@T[5]-(OMe)<sub>5</sub> with the MeCN guest molecule in the experimentally observed orientation.



**Figure S31.** Optimized geometry of MeCN@T[5]-(OMe)<sub>5</sub> with the MeCN guest in the cavity antiparallel to the experimentally observed orientation.

The experimentally observed ‘ordered’ structure of CH<sub>3</sub>CN@T[5]-(OMe)<sub>5</sub> is illustrated in Figure S30. The ‘rather chaotic’ structure of CH<sub>3</sub>CN@T[5]-(OMe)<sub>5</sub> with the MeCN sitting in the cavity in the antiparallel orientation (Figure S31) is calculated to be 6.2 kcal/mol higher in energy and therefore not observed experimentally.

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## 8. Author Contributions

W.Y., K.S., X.W, T.U.T., Y.C., S.L. and K.D. synthesized all compounds in this study. W.Y., K.D. and J.X. collected and processed X-ray crystallographic data. W.Y. and K.S. conducted host-guest binding studies. W.Y. carried out adsorption and fractionation experiments. Y.G. performed mass spectrometry characterizations. H.Z. performed quantum-chemical calculations. H.Z. and A.C.-H.S. conceived the project and designed the experiments. W.Y., K.S., X.W., H.Z. and A.C.-H.S. analyzed the data and wrote the manuscript. All authors discussed the results and commented on the manuscript.