Supplementary Information for

Synthesis of Per(5-N-carboxyamide-5-dehydroxylmethyl)-β-cyclodextrins and Their Selective Recognition Ability Utilizing Multiple Hydrogen Bonds

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1. Materials and methods

Unless otherwise noted, solvents and reagents were purchased from TCI Co., Ltd., Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., Nacalai Tesque, Inc. or Sigma-Aldrich Co., and used without further purification. Dry THF was purified by Glass Contour Ultimate Solvent System. Silica gel for column chromatography was purchased from Kanto Chemical Co. Inc. (Silica Gel 60 N (spherical, neutral, 40–50 μm or 63–210 μm)). GPC purification was performed on a JAI LC-9210 II NEXT system with JAIGEL-1HH/2HH columns using CHCl₃ as an eluent.

Measurements were performed at 298 K unless otherwise noted. ¹H, ¹³C, ³¹P NMR, and other 2D NMR spectra were recorded on a Bruker AVANCE III-400 and 600 spectrometers. Negative values were depicted in red in the spectra. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) for ¹H and ¹³C NMR measurements when CDCl₃ was used as a solvent. Solvent residual signals were used as a standard for ¹H and ¹³C NMR measurements when solvents other than CDCl₃ were used. Triphenylphosphineoxide in CDCl₃ (1 wt%) was used as an external standard (δ 30.0 ppm) for ³¹P NMR measurements.

Single-crystal X-ray crystallographic measurements were performed using Bruker APEX II ULTRA with MoKα radiation. Obtained data were processed using Bruker APEX2 and Yadokari-XG crystallographic software package. The initial structures were solved using SIR2014 (2, 1b) or SHELXT-2014 ((PhPO₃H⁻)·1b), and refined using SHELXL-2016. CCDC 1858034–1858036 contain the data for the structures. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

MALDI-TOF mass data were recorded on an AB SCIEX TOF/TOF 5800 system. IR spectra were recorded on a JASCO FT/IR-480 Fourier transform infrared spectrometer. Elemental analysis was performed on a Yanaco MT-6 analyzer with tin boats purchased from Elementar. We appreciate Mr. Ikuo Iida and Mr. Masao Sasaki for the measurements.
2. Synthesis of amide cyclodextrin derivatives

Synthesis of 1a

Under an argon atmosphere, 2\[^{[87]}\] (455 mg, 0.302 mmol, 1 eq), dicyclohexylcarbodiimide (1.11 g, 5.38 mmol, 18 eq), and 1-hydroxy-7-azabenzotriazole (371 mg, 2.72 mmol, 9 eq) were added to a 50 mL eggplant flask, and dissolved in dry THF (20 mL). The mixture was stirred at 60 °C for 30 min. Then, 2 M THF solution of methylamine (7.5 mL, 15.0 mmol, 50 eq) was added, and the mixture was stirred at 60 °C for 5 h. The mixture was concentrated in vacuo. 0.5 M HCl aq (40 mL) was added to the residue, and the mixture was stirred at r.t. for 30 min. The remaining colorless solid was removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (eluent: AcOEt/MeOH/H\_2O = 99/1/0–80/20/1) and gel permeation chromatography to give 1a (235 mg, 0.155 mmol, 51%).

Colorless solid; m.p. 171.0–174.0 °C;
\[^{1}\text{H} \text{NMR (acetone-}d_6, 600 \text{MHz)}: \delta 2.78 (d, J = 4.7 \text{ Hz, 21H}), 3.21 (dd, J = 3.2 \text{ Hz, 8.4 Hz, 7H}), 3.51 (s, 21H), 3.54 (dd, J = 8.4 \text{ Hz, 7H}), 3.56 (s, 21H), 3.95 (dd, J = 8.4 \text{ Hz, 7H}), 4.34 (d, J = 8.4 \text{ Hz, 7H}), 5.20 (d, J = 3.2 \text{ Hz, 7H}), 7.76 (br, 7H);
\[^{13}\text{C} \text{NMR (acetone-}d_6, 151 \text{ MHz)}: \delta 26.3, 58.7, 60.7, 72.6, 79.2, 81.7, 81.9, 98.6, 170.4;
\text{MALDI-TOF MS: } m/z [M+K]^+ \text{ calcd. for C}_{63}\text{H}_{105}\text{N}_{7}\text{O}_{35}\text{K} 1558.6; \text{ found 1558.5;}
\text{IR (KBr) } \nu_{\text{max}}: 1670 (s, C=O), 3318 (br, N-H) \text{ cm}^{-1};
\text{Elemental analysis: calcd. for C}_{63}\text{H}_{119}\text{N}_{7}\text{O}_{42} (1a·7H}_2\text{O): C, 45.95; H, 7.28; N, 5.95. found: C, 45.99; H, 7.20; N, 5.94.}
Synthesis of 1b

Under an argon atmosphere, 2[7] (151 mg, 0.104 mmol), dicyclohexylcarbodiimide (371 mg, 1.80 mmol, 18 eq), and 1-hydroxy-7-azabenzotriazole (111 mg, 0.82 mmol, 8 eq) were added to a 50 mL eggplant flask, and dissolved in dry THF (5 mL). The mixture was stirred at 60 °C for 30 min. Then, THF solution (5 mL) of p-toluidine (540 mg, 5.03 mmol, 50 eq) was added, and the mixture was stirred at 60 °C for 5 h. The mixture was concentrated in vacuo. 0.5 M HCl aq (40 mL) was added to the residue, and transferred to a separating funnel. The organic layer was separated, washed with sat. NaHCO₃ aq. (40 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. Acetonitrile (6 mL) was added to the residue, and undissolved solids were removed by filtration. The filtrate was purified by silica gel column chromatography (eluent: Hexane/AcOEt = 100/0–20/80), and reprecipitation with MeOH/H₂O to give 1b·5H₂O (121 mg, 0.059 mmol, 57%).

Colorless solid; m.p. 196.9–200.1 °C;

¹H NMR (CDCl₃, 600 MHz): δ 2.06 (s, 21H), 3.28 (dd, J = 2.9 Hz, 8.5 Hz, 7H), 3.56 (s, 21H), 3.67 (s, 21H), 3.74 (dd, J = 8.5 Hz, 7H), 4.00 (dd, J = 8.5 Hz, 7H), 4.59 (d, J = 8.5 Hz, 7H), 5.33 (d, J = 2.9 Hz, 7H), 6.53 (d, J = 8.0 Hz, 14H), 6.83 (d, J = 8.0 Hz, 14H), 8.76 (br, 7H);

¹³C NMR (CDCl₃, 151 MHz): δ 20.7, 58.7, 60.9, 72.4, 80.6, 80.9, 81.1, 98.7, 121.4, 128.9, 133.6, 134.3, 167.5;

MALDI-TOF MS: m/z [M+K]⁺ calcd. for C₁₀₅H₁₄₃N₇O₄₅K 2091.9; found 2091.7.

IR (KBr) ν_max: 1679 (s, C=O), 3315 (br, N-H) cm⁻¹;

Elemental analysis: calcd. for C₁₀₅H₁₄₃N₇O₄₅ (1b·5H₂O): C, 58.84; H, 6.73; N, 4.57. found: C, 59.10; H, 6.70; N, 4.49.
3. NMR and IR spectra of amide cyclodextrin derivatives

Figure S1. $^1$H NMR spectrum of 1a (acetone-$d_6$, 600 MHz)

Figure S2. $^{13}$C NMR spectrum of 1a (acetone-$d_6$, 151 MHz)
Figure S3. $^1$H NMR spectrum of 1b (CDCl$_3$, 600 MHz)

Figure S4. $^{13}$C NMR spectrum of 1b (CDCl$_3$, 151 MHz)
Figure S5. A MALDI TOF mass spectrum of the reaction mixture of amide condensation to synthesize 1b.
Figure S6. $^1$H NMR spectra of 1b at various temperatures ((a–d); CD$_2$Cl$_2$, (e–g); 1,1,2,2-tetrachloroethane-$d_2$, 600 MHz). (a) 217 K. (b) 223 K. (c) 233 K. (d, e) 298 K. (f) 373 K. (g) 393 K.
Figure S7. $^1$H NMR spectra of 1b in various solvents (600 MHz). (a) Acetone-$d_6$/D$_2$O = 3/2 (v/v). (b) CD$_3$CN / D$_2$O = 9/1 (v/v). (c) C$_6$D$_5$CD$_3$. (d) CDCl$_3$. (e) DMSO-$d_6$. (f) C$_6$D$_6$. (g) CD$_3$OD. (h) Acetone-$d_6$. (i) CD$_3$CN.
Table S1. Ratio of conformational isomers of 1b (1b_{in}/1b_{out}) in various solvents (1H NMR, 298 K).

<table>
<thead>
<tr>
<th>Solvents</th>
<th>1b_{in} [%]</th>
<th>1b_{out} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$CN</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>CD$_3$COCD$_3$</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>CD$_3$OD</td>
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<td>80</td>
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<tr>
<td>C$_6$D$_6$</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>CD$_3$SOCD$_3$</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane-$d_2$</td>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>C$_6$D$_5$CD$_3$</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>CD$_3$CN / D$_2$O = 9 / 1 (v/v)</td>
<td>3</td>
<td>97</td>
</tr>
<tr>
<td>CD$_3$COCD$_3$ / D$_2$O = 3 / 2 (v/v)</td>
<td>&lt; 2</td>
<td>&gt; 98</td>
</tr>
</tbody>
</table>
Figure S8. $^{13}$C NMR spectrum of 1b (CD$_3$CN, 151 MHz). See Table S3 for the assignment.
Figure S8. (Continued) $^{13}$C NMR spectrum of 1b (CD$_3$CN, 151 MHz). See Table S3 for the assignment.
Figure S8. (Continued) $^{13}$C NMR spectrum of 1b (CD$_3$CN, 151 MHz). See Table S3 for the assignment.
### Table S2. Chemical shifts [ppm] of $^1$H NMR signals of 1b in CD$_3$CN (600 MHz).

<table>
<thead>
<tr>
<th>Unit</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
<th>$e$</th>
<th>$f$</th>
<th>$g$</th>
<th>$h$</th>
<th>$i$</th>
<th>$j$</th>
<th>$k$</th>
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</thead>
<tbody>
<tr>
<td>Unit 1</td>
<td>4.98</td>
<td>3.13</td>
<td>3.26</td>
<td>3.81</td>
<td>4.50</td>
<td>3.34</td>
<td>3.56</td>
<td>10.51</td>
<td>7.68</td>
<td>7.73</td>
<td>2.70</td>
</tr>
<tr>
<td>Unit 2</td>
<td>5.11</td>
<td>3.11</td>
<td>3.20</td>
<td>3.90</td>
<td>4.14</td>
<td>3.43</td>
<td>3.57</td>
<td>8.73</td>
<td>7.35</td>
<td>7.10</td>
<td>2.29</td>
</tr>
<tr>
<td>Unit 3</td>
<td>5.34</td>
<td>3.29</td>
<td>3.76</td>
<td>3.93</td>
<td>4.69</td>
<td>3.46</td>
<td>3.65</td>
<td>8.34</td>
<td>6.73</td>
<td>6.65</td>
<td>2.18</td>
</tr>
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<td>Unit 4</td>
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<td>3.59</td>
<td>3.91</td>
<td>4.53</td>
<td>3.46</td>
<td>3.63</td>
<td>8.73</td>
<td>6.75</td>
<td>6.50</td>
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<td>Unit 5</td>
<td>4.88</td>
<td>3.17</td>
<td>3.14</td>
<td>3.53</td>
<td>3.47</td>
<td>3.37</td>
<td>3.42</td>
<td>8.25</td>
<td>7.09</td>
<td>6.56</td>
<td>2.07</td>
</tr>
<tr>
<td>Unit 6</td>
<td>5.33</td>
<td>3.29</td>
<td>3.38</td>
<td>3.64</td>
<td>4.31</td>
<td>3.51</td>
<td>3.67</td>
<td>8.16</td>
<td>6.79</td>
<td>6.51</td>
<td>2.03</td>
</tr>
<tr>
<td>Unit 7</td>
<td>5.44</td>
<td>3.18</td>
<td>3.48</td>
<td>4.12</td>
<td>4.01</td>
<td>3.51</td>
<td>3.74</td>
<td>9.66</td>
<td>7.25</td>
<td>6.67</td>
<td>2.06</td>
</tr>
<tr>
<td>1b$_{out}$ isomer</td>
<td>5.25</td>
<td>3.26</td>
<td>3.63</td>
<td>3.95</td>
<td>4.45</td>
<td>3.51</td>
<td>3.62</td>
<td>8.77</td>
<td>6.89</td>
<td>6.63</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Comparing the chemical shifts of each repeating unit, $^1$H signals of pyranose rings ($a$–$e$) of the unit 5 are notably shifted upfield due to the shielding effect of the included $p$-tolyl group. Considering the pattern of ROE signals and the degree of shielding/deshielding, the unit 5 is positioned on top of the included aromatic ring while the units 2,3,4,6,7 are positioned at its side. We presume that the self-included $p$-tolylamide group takes a cis conformation in the amide bond.
Table S3. Chemical shifts [ppm] of $^{13}$C NMR signals of 1b in CD$_3$CN (151 MHz).

<table>
<thead>
<tr>
<th>Unit</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$D$</th>
<th>$E$</th>
<th>$F$</th>
<th>$G$</th>
<th>$H$</th>
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</thead>
<tbody>
<tr>
<td>Unit 1</td>
<td>96.8</td>
<td>83.7</td>
<td>82.5</td>
<td>76.1</td>
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<td>58.7</td>
<td>62.0</td>
<td>172.3</td>
</tr>
<tr>
<td>Unit 2</td>
<td>99.6</td>
<td>80.8</td>
<td>81.9</td>
<td>80.1</td>
<td>74.4</td>
<td>58.8</td>
<td>59.6</td>
<td>167.5</td>
</tr>
<tr>
<td>Unit 3</td>
<td>100.2–100.3</td>
<td>83.8</td>
<td>83.0</td>
<td>81.9</td>
<td>73.5</td>
<td>61.1</td>
<td>61.7</td>
<td>168.6</td>
</tr>
<tr>
<td>Unit 4</td>
<td>100.2–100.3</td>
<td>82.4</td>
<td>82.2</td>
<td>82.2</td>
<td>73.1</td>
<td>59.1</td>
<td>61.2</td>
<td>169.4</td>
</tr>
<tr>
<td>Unit 5</td>
<td>101.6</td>
<td>81.4</td>
<td>81.5</td>
<td>82.6</td>
<td>73.7</td>
<td>60.8</td>
<td>58.3</td>
<td>168.0</td>
</tr>
<tr>
<td>Unit 6</td>
<td>98.2</td>
<td>81.8</td>
<td>82.3</td>
<td>85.6</td>
<td>75.6</td>
<td>58.0</td>
<td>61.4</td>
<td>169.7</td>
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<tr>
<td>Unit 7</td>
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<td>82.5</td>
<td>81.4</td>
<td>73.3</td>
<td>60.3</td>
<td>62.1</td>
<td>166.3</td>
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<td>1b$_{out}$ isomer</td>
<td>99.1</td>
<td>82.0</td>
<td>82.2</td>
<td>80.9</td>
<td>73.7</td>
<td>59.1</td>
<td>61.3</td>
<td>168.6</td>
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</table>

<table>
<thead>
<tr>
<th>Unit</th>
<th>$I$</th>
<th>$J$</th>
<th>$K$</th>
<th>$L$</th>
<th>$M$</th>
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</thead>
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<td>Unit 1</td>
<td>128.6</td>
<td>131.5</td>
<td>21.8</td>
<td>135.0</td>
<td>139.2</td>
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<tr>
<td>Unit 2</td>
<td>122.8</td>
<td>130.2</td>
<td>20.9–21.0</td>
<td>135.9–136.0</td>
<td>135.1–135.3</td>
</tr>
<tr>
<td>Unit 3</td>
<td>123.7</td>
<td>129.6</td>
<td>20.9–21.0</td>
<td>135.0</td>
<td>135.1–135.3</td>
</tr>
<tr>
<td>Unit 4</td>
<td>121.8–121.9</td>
<td>129.7–130.1</td>
<td>20.9–21.0</td>
<td>135.9–136.0</td>
<td>134.3–134.7</td>
</tr>
<tr>
<td>Unit 5</td>
<td>121.8–121.9</td>
<td>129.7–130.1</td>
<td>20.9–21.0</td>
<td>135.1–135.3</td>
<td>134.3–134.7</td>
</tr>
<tr>
<td>Unit 6</td>
<td>122.2</td>
<td>129.7–130.1</td>
<td>20.9–21.0</td>
<td>134.9</td>
<td>134.3–134.7</td>
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<tr>
<td>Unit 7</td>
<td>119.8</td>
<td>129.7–130.1</td>
<td>20.9–21.0</td>
<td>137.1</td>
<td>133.7</td>
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<tr>
<td>1b$_{out}$ isomer</td>
<td>122.3</td>
<td>129.9</td>
<td>20.9</td>
<td>135.6</td>
<td>134.7</td>
</tr>
</tbody>
</table>

![Diagram](image.png)
Figure S9. $^1$H–$^1$H COSY spectrum of 1b (CD$_3$CN, 600 MHz)

Figure S10. $^1$H–$^1$H TOCSY spectrum of 1b (CD$_3$CN, 600 MHz)
Figure S11. $^1$H–$^1$H ROESY spectrum of 1b (CD$_3$CN, 600 MHz)

Figure S11. (continued) $^1$H–$^1$H ROESY spectrum of 1b (CD$_3$CN, 600 MHz)
Figure S12. $^1$H–$^{13}$C HSQC spectrum of 1b (CD$_3$CN, 600 MHz)

Figure S13. $^1$H–$^{13}$C HMBC spectrum of 1b (CD$_3$CN, 600 MHz)
Figure S14. $^1$H DOSY spectrum of 1b (CD$_2$CN, 600 MHz)
Figure S15. IR spectra of amide cyclodextrin derivatives (KBr). (a) 1a. (b) 1b. (c–f) Values of C=O stretching vibrations for comparison.[88]–[S11]

The vibration of carbonyl C=O was observed at 1670 cm$^{-1}$ for 1a and 1679 cm$^{-1}$ for 1b. For comparison, the hydrogen-bonded amides of similar partial structures vibrate at lower frequencies (around 1650 cm$^{-1}$) in the solid state. Thus, only a part of the seven amide groups are considered to be participated as a hydrogen bond acceptor in the structures of 1a and 1b, which agrees with the crystal structure of 1b·$\text{5H}_2\text{O (Fig. 2)}$. 

S21 / S54
4. **1H NMR experiments to investigate guest binding**

4-1. **Encapsulation of \((n\text{-Bu}_4\text{N})(\text{PhPO}_3\text{H})\) by **1b**.**

**Preparation of \((n\text{-Bu}_4\text{N})(\text{PhPO}_3\text{H})\)**

\(n\)-tetrabutylammonium hydrogen phenylphosphonate \((n\text{-Bu}_4\text{N})(\text{PhPO}_3\text{H})\) was prepared by adding an aqueous solution of \(n\text{-Bu}_4\text{NOH}\) (10 wt%) to phenylphosphonic acid (76.4 mg, 0.484 mmol) in a 50 mL vial until the pH of the solution reached the first stoichiometric point (pH ~ 4.5). Removal of the solvent in vacuo gave 193 mg of \((n\text{-Bu}_4\text{N})(\text{PhPO}_3\text{H})\) as colorless solid. \(^1\text{H}\) NMR measurement confirmed the ratio of \(n\text{-Bu}_4\text{N}^+\) and \(\text{PhPO}_3\text{H}^-\) to be 1:1. The content of water in the sample was determined by a \(^1\text{H}\) NMR titration experiment of a \(\text{CDCl}_3\) solution of \((n\text{-Bu}_4\text{N})(\text{PhPO}_3\text{H})\). The sample contained 10 \(\text{H}_2\text{O}\) per one \(\text{PhPO}_3\text{H}^-\) (i.e., \((n\text{-Bu}_4\text{N})(\text{PhPO}_3\text{H})\cdot10\text{H}_2\text{O})\).

**Preparation of \((n\text{-Bu}_4\text{N})[\text{PhPO}_3\text{H}]=\textbf{1b}\)**

\textbf{1b} (16.9 mg, 7.9 µmol) and \(\text{CDCl}_3\) solution (400 µL) of \((n\text{-Bu}_4\text{N})(\text{PhPO}_3\text{H})\) (6.43 mg, 11.3 µmol, 1.5 eq) were added to an NMR tube. The sample was used for various NMR experiments.

\(^1\text{H}\) NMR (\(\text{CDCl}_3\), 600 MHz): \(\delta\) 0.90 (t, \(J = 7.2\) Hz, 12H), 1.26 (qt, \(J_q = 7.2\) Hz, \(J_t = 14.4\) Hz, 8H), 1.39 (tt, \(J_{t1} = 14.4\) Hz, \(J_{t2} = 9.2\) Hz, 8H), 1.94 (s, 21H), 2.92 (t, \(J = 9.2\) Hz, 8H), 3.15 (brd, \(J = 8.8\) Hz, 7H), 3.50 (s, 21H), 3.57 (dd, \(J = 8.8,8.8\) Hz, 7H), 3.60 (s, 21H), 3.94 (dd, \(J = 8.8\) Hz, 7H), 4.65 (d, \(J = 8.8\) Hz, 7H), 5.18 (br, 7H), 6.40 (d, \(J = 6.8\) Hz, 14H), 6.93 (d, \(J = 6.8\) Hz, 14H), 7.46 (t, \(J = 7.5\) Hz, 1H), 7.66 (dd, \(J = 7.5,7.5\) Hz, 2H), 8.36 (d, \(J = 7.5\) Hz, 2H), 8.56 (br, 1H), 10.03 (br, 7H).

\(^3\text{P}\) NMR (\(\text{CDCl}_3\), 243 MHz): \(\delta\) 9.3.
Figure S16. Encapsulation of (n-Bu₄N)(PhPO₃H) by 1b (¹H NMR, CDCl₃, 600 MHz). (a) 1b (16 mM). (b) 1b + (n-Bu₄N)(PhPO₃H) (1.5 eq.) Letters with dashes denote proton signals of (PhPO₃H)⊂1b, and the ones without dashes denote those of guest-free 1b and (n-Bu₄N)(PhPO₃H).

Figure S17. ³¹P NMR spectrum of a mixture of 1b (16 mM) and (n-Bu₄N)(PhPO₃H) (1.5 eq.) (CDCl₃, 243 MHz).
Figure S18. $^1$H–$^1$H ROESY spectrum of (n-Bu$_4$N)[(PhPO$_3$H)$_2$]] (CDCl$_3$, 600 MHz).

Figure S18. (continued) $^1$H–$^1$H ROESY spectrum of (n-Bu$_4$N)[(PhPO$_3$H)$_2$]] (CDCl$_3$, 600 MHz).
Figure S19. A titration experiment of (n-Bu₄N)(PhPO₃H) against 1b (0.5 mM) (¹H NMR, CD₃CN, 600 MHz). (a) 1b. (b–g) 1b + (n-Bu₄N)(PhPO₃H). (b) (n-Bu₄N)(PhPO₃H) 0.3 eq. (c) 0.5 eq. (d) 0.8 eq. (e) 0.9 eq. (f) 1.0 eq. (g) 1.1 eq.

Figure S20. Encapsulation of (n-Bu₄N)(PhPO₃H) by 1b in CD₂Cl₂ (¹H NMR, 600 MHz). (a) 1b (0.5 mM). (b) (a) + (n-Bu₄N)(PhPO₃H) (1.4 eq).
4-2. Binding of anions by methylamide derivative 1a in CDCl₃

Preparation of tetraalkylammonium salts

(n-Bu₄N)X (X = Cl, Br, I), (n-Bu₄N)(MeCO₂), and (Et₄N)(p-TolSO₃) were used as received. The other n-tetraalkylammonium salts were synthesized by the addition of n-tetraalkylammonium hydroxide (10% in aqueous solution) to an equimolar amount of the corresponding free acid, followed by concentration in vacuo and drying at 0.1 mmHg for over 3 h at room temperature. In the preparation of (n-Bu₄N)(PhPO₃), 2 equivalents of (n-Bu₄N)(OH) was used. The ratio of n-Bu₄N⁺ and anions were confirmed by ¹H NMR measurements prior to use.

A representative procedure ((n-Bu₄N)(MeCO₂) and 1a)

A stock solution of host 1a was prepared by dissolving 0.54 mg of 1a in 710 µL of CDCl₃ (0.46 mM). A stock solution of the guest (n-Bu₄N)(MeCO₂) was prepared by dissolving 6.13 mg of (n-Bu₄N)(MeCO₂) in 170 µL of the prepared stock solution of 1a ([MeCO₂⁻] = 120 mM). To an NMR tube was added 500 µL of the stock solution of 1a, and 4–5 µL each of the guest solution was titrated into the sample solution at the constant concentration of 1a. ¹H NMR measurements were carried out during the titration.

For the host-guest complexes whose guest exchanges are slower than the ¹H NMR timescale, the binding constant is determined from the integral values of the host-guest complex (Figs S25, S27, S28, S30, S31, S34, S35, S37–S40, S42, S45–S47, S50, S51, S53, and S54). For the host-guest complexes with faster exchanges (Figs S21, S23, and S48), the binding constant is determined from the least square fitting of 1:1 binding model using the TitrationFit software.⁵¹²

A general note (sections (4-2)–(4-5))

Letters with dashes denote proton signals of a host-guest complex, and the ones without dashes denote those of guest-free 1a/1b and a free guest.
Figure S21. A titration experiment of \((n\text{-}Bu_4N)(\text{MeCO}_2)\) against \(1\text{a} \ (0.5 \text{ mM})\) \((^1\text{H NMR, CDCl}_3, 600 \text{ MHz})\) (Table 1, entry 1a-1). (a) \(1\text{a}\). (b–k) \(1\text{a} + (n\text{-}Bu_4N)(\text{MeCO}_2)\). (b) \((n\text{-}Bu_4N)(\text{MeCO}_2)\) 2.5 eq. (c) 4.9 eq. (d) 7.3 eq. (e) 9.7 eq. (f) 12.1 eq. (g) 14.6 eq. (h) 17.0 eq. (i) 19.4 eq. (j) 21.8 eq. (k) 24.3 eq.

Figure S22. A least squares fitting to determine the binding constant \(K_a\) of MeCO\text{2}^- and \(1\text{a}\) in CDCl\text{3} (data of \(^1\text{H NMR signal g}).
Figure S23. A titration experiment of \((n\text{-Bu}_4\text{N})(\text{H}_2\text{PO}_4)\) against 1a (0.5 mM) (\(^1\)H NMR, CDCl\(_3\), 600 MHz) (Table 1, entry 1a-2). (a) 1a. (b–k) 1a + \((n\text{-Bu}_4\text{N})(\text{H}_2\text{PO}_4)\). (b) \((n\text{-Bu}_4\text{N})(\text{H}_2\text{PO}_4)\) 0.6 eq. (c) 1.1 eq. (d) 2.2 eq. (e) 3.2 eq. (f) 4.3 eq. (g) 5.4 eq. (h) 6.5 eq. (i) 7.5 eq. (j) 8.6 eq. (k) 10.8 eq.

Figure S24. A least squares fitting to determine the binding constant \(K_a\) of \(\text{H}_2\text{PO}_4^-\) and 1a in CDCl\(_3\) (data of \(^1\)H NMR signal \(i\)).
Figure S25. Investigation of interactions between (n-Bu4N)(MePO3H) and 1a (0.4 mM) (1H NMR, CDCl3, 600 MHz) (Table 1, entries 1a-3). (a) 1a. (b) 1a + (n-Bu4N)(MePO3H) 1.6 eq.

Figure S26. A titration experiment of (n-Bu4N)(PhCO2) against 1a (0.9 mM) (1H NMR, CDCl3, 600 MHz) (Table 1, entry 1a-4). (a) 1a. (b–k) 1a + (n-Bu4N)(PhCO2). (b) (n-Bu4N)(PhCO2) 1.1 eq. (c) 2.2 eq. (d) 3.3 eq. (e) 4.4 eq. (f) 5.5 eq. (g) 6.5 eq. (h) 7.6 eq. (i) 8.7 eq. (j) 9.8 eq. (k) 10.9 eq.
Figure S27. A titration experiment of (n-Bu₄N)(PhPO₃H) against 1a (0.9 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1a-5). (a) 1a. (b–k) 1a + (n-Bu₄N)(PhPO₃H). (b) (n-Bu₄N)(PhPO₃H) 0.2 eq. (c) 0.5 eq. (d) 0.8 eq. (e) 1.0 eq. (f) 1.1 eq. (g) 1.2 eq. (h) 1.6 eq. (i) 2.2 eq. (j) 4.3 eq. (k) 8.7 eq.

Figure S28. A titration experiment of (n-Bu₄N)(PhOPO₃H) against 1a (0.4 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1a-6). (a) 1a. (b–k) 1a + (n-Bu₄N)(PhOPO₃H). (b) (n-Bu₄N)(PhOPO₃H) 0.3 eq. (c) 0.7 eq. (d) 0.9 eq. (e) 1.1 eq. (f) 1.4 eq. (g) 1.6 eq. (h) 1.8 eq. (i) 2.0 eq. (j) 2.3 eq. (k) 4.5 eq.
Figure S29. A titration experiment of (Et₄N)(p-TolSO₃) against 1a (0.9 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1a-7). (a) 1a. (b–k) 1a + (Et₄N)(p-TolSO₃). (b) (Et₄N)(p-TolSO₃) 0.2 eq. (c) 0.5 eq. (d) 0.7 eq. (e) 0.9 eq. (f) 1.0 eq. (g) 1.1 eq. (h) 1.5 eq. (i) 2.0 eq. (j) 4.0 eq. (k) 8.0 eq.

Figure S30. Investigation of interactions between (n-Bu₄N)₂(PhPO₃) and 1a (0.4 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1a–8). (a) 1a. (b) 1a + (n-Bu₄N)₂(PhPO₃) 2.7 eq.
Figure S31. Investigation of interactions between (n-Bu₄N)(PhCH₂PO₃H) and 1a (0.4 mM) (^1H NMR, CDCl₃, 600 MHz) (Table 1, entry 1a-9). (a) 1a. (b) 1a + (n-Bu₄N)(PhCH₂PO₃H) 2.7 eq.

Figure S32. Investigation of interactions between (n-Bu₄N)X (X = Cl, Br, I) and 1a (0.5 mM) (^1H NMR, CDCl₃, 600 MHz). (a) 1a. (b-d) 1a + (n-Bu₄N)X. (b) X = Cl, 2.2 eq. (c) X = Br, 2.1 eq. (d) X = I, 2.0 eq.
4-3. Binding of anions by \( p \)-tolylamide derivative 1b in CDCl\(_3\)

![Figure S33](image1)

**Figure S33.** A titration experiment of (\( n \)-Bu\(_4\)N)(MeCO\(_2\)) against 1b (0.5 mM) (\( ^{1}H\) NMR, CDCl\(_3\), 600 MHz) (Table 1, entry 1b(CDCl\(_3\))-1). (a) 1b. (b–k) 1b + (\( n \)-Bu\(_4\)N)(MeCO\(_2\)). (b) (\( n \)-Bu\(_4\)N)(MeCO\(_2\)) 0.6 eq. (c) 1.0 eq. (d) 2.1 eq. (e) 3.1 eq. (f) 4.2 eq. (g) 5.2 eq. (h) 6.3 eq. (i) 7.3 eq. (j) 8.3 eq. (k) 10.4 eq. (l) (\( n \)-Bu\(_4\)N)(MeCO\(_2\)).

![Figure S34](image2)

**Figure S34.** A titration experiment of (\( n \)-Bu\(_4\)N)(H\(_2\)PO\(_4\)) against 1b (0.9 mM) (\( ^{1}H\) NMR, CDCl\(_3\), 600 MHz) (Table 1, entry 1b(CDCl\(_3\))-2). (a) 1b. (b–k) 1b + (\( n \)-Bu\(_4\)N)(H\(_2\)PO\(_4\)). (b) (\( n \)-Bu\(_4\)N)(H\(_2\)PO\(_4\)) 0.3 eq. (c) 0.6 eq. (d) 0.8 eq. (e) 1.0 eq. (f) 1.2 eq. (g) 1.4 eq. (h) 1.6 eq. (i) 1.8 eq. (j) 2.0 eq. (k) 4.1 eq.
Figure S35. A titration experiment of (n-BuN)(MePO₃H) against 1b (0.9 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1b(CDCl₃)-3). (a) 1b. (b−k) 1b + (n-BuN)(MePO₃H). (b) (n-BuN)(MePO₃H) 0.2 eq. (c) 0.5 eq. (d) 0.8 eq. (e) 1.1 eq. (f) 1.3 eq. (g) 1.6 eq. (h) 2.1 eq. (i) 5.3 eq. (j) 10.5 eq. (k) 21.1 eq. (l) (n-BuN)(MePO₃H).

Figure S36. A titration experiment of (n-BuN)(PhCO₂) against 1b (1.0 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1b(CDCl₃)-4). (a) 1b. (b−k) 1b + (n-BuN)(PhCO₂). (b) (n-BuN)(PhCO₂) 0.16 eq. (c) 0.24 eq. (d) 0.33 eq. (e) 0.36 eq. (f) 0.40 eq. (g) 0.56 eq. (h) 0.76 eq. (i) 2.36 eq. (j) 4.98 eq. (k) 10.23 eq.
Figure S37. A titration experiment of (n-Bu₄N)(PhPO₃H) against 1b (1.0 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1b(CDCl₃)-5). (a) 1b. (b–k) 1b + (n-Bu₄N)(PhPO₃H). (b) (n-Bu₄N)(PhPO₃H) 0.2 eq. (c) 0.4 eq. (d) 0.6 eq. (e) 0.7 eq. (f) 0.8 eq. (g) 1.0 eq. (h) 1.2 eq. (i) 1.5 eq. (j) 3.7 eq. (k) 7.3 eq. (l) (n-Bu₄N)(PhPO₃H).

Figure S38. A titration experiment of (n-Bu₄N)(PhPO₃H) against 1b (1.0 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1b(CDCl₃)-6). (a) 1b. (b–k) 1b + (n-Bu₄N)(PhPO₃H). (b) (n-Bu₄N)(PhPO₃H) 0.5 eq. (c) 0.8 eq. (d) 1.0 eq. (e) 1.2 eq. (f) 1.5 eq. (g) 2.0 eq. (h) 5.1 eq. (i) 7.2 eq. (j) 10.3 eq. (k) 20.6 eq. (l) (n-Bu₄N)(PhPO₃H).
Figure S39. A titration experiment of (Et₄N)(p-MeC₆H₄SO₃) against 1b (1.0 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1b(CDCl₃)-7). (a) 1b. (b–k) 1b + (Et₄N)(p-MeC₆H₄SO₃). (b) (Et₄N)(p-MeC₆H₄SO₃) 1.0 eq. (c) 2.0 eq. (d) 5.2 eq. (e) 7.3 eq. (f) 10.4 eq. (g) 14.5 eq. (h) 20.9 eq. (i) 26.1 eq. (j) 31.3 eq. (k) 46.3 eq. (l) (Et₄N)(p-MeC₆H₄SO₃).

Figure S40. A titration experiment of (n-Bu₄N)₂(PhPO₃) against 1b (1.0 mM) (¹H NMR, CDCl₃, 600 MHz) (Table 1, entry 1b(CDCl₃)-8). (a) 1b. (b–k) 1b + (n-Bu₄N)₂(PhPO₃). (b) (n-Bu₄N)₂(PhPO₃) 0.3 eq. (c) 0.6 eq. (d) 1.0 eq. (e) 1.3 eq. (f) 1.5 eq. (g) 1.8 eq. (h) 2.1 eq. (i) 6.2 eq. (j) 12.6 eq. (k) 25.3 eq. (l) (n-Bu₄N)₂(PhPO₃).
Figure S41. $^1$H NMR spectrum the sample of 1b with (n-Bu$_4$N)$_2$(PhPO$_3$) 25.3 eq (see Fig. S38k), which indicates that PhPO$_3^{2-}$ is encapsulated by 1b as PhPO$_3$H$^-$.  

Figure S42. A titration experiment of (n-Bu$_4$N)(PhCH$_2$PO$_3$H) against 1b (1.0 mM) ($^1$H NMR, CDCl$_3$, 600 MHz) (Table 1, entries 1b(CDC$_3$)-9). (a) 1b. (b–k) 1b + (n-Bu$_4$N)(PhCH$_2$PO$_3$H). (b) (n-Bu$_4$N)(PhCH$_2$PO$_3$H) 0.3 eq. (c) 0.5 eq. (d) 0.8 eq. (e) 1.0 eq. (f) 1.2 eq. (g) 1.5 eq. (h) 1.8 eq. (i) 2.0 eq. (j) 5.0 eq. (k) 10.0 eq. (l) (n-Bu$_4$N)(PhCH$_2$PO$_3$H).
Figure S43. Investigation of interactions between (n-Bu₄N)X (X = Cl, Br, I) and 1b (1.0 mM) (¹H NMR, CDCl₃, 600 MHz). (a) 1b. (b–d) 1b + (n-Bu₄N)X. (b) X = Cl, 10 eq. (c) X = Br, 11 eq. (d) X = I, 10 eq.

Figure S44. A titration experiment of (n-Bu₄N)((PhO)₂PO₂) against 1b (1.0 mM) (¹H NMR, CDCl₃, 600 MHz). (a) 1b. (b–k) 1b + (n-Bu₄N)((PhO)₂PO₂). (b) (n-Bu₄N)((PhO)₂PO₂) 0.6 eq. (c) 1.1 eq. (d) 1.7 eq. (e) 2.2 eq. (f) 2.8 eq. (g) 3.4 eq. (h) 3.9 eq. (i) 4.5 eq. (j) 5.0 eq. (k) 5.6 eq.
4-4. Binding of anions by p-tolylamide derivative 1b in DMSO-d$_6$

Figure S45. A titration experiment of (n-Bu$_4$N)(MeCO$_2$) against 1b (0.5 mM) ($^1$H NMR, DMSO-d$_6$, 600 MHz) (Table 1, entry 1b(DMSO-d$_6$)-1). (a) 1b. (b-k) 1b + (n-Bu$_4$N)(MeCO$_2$). (b) (n-Bu$_4$N)(MeCO$_2$) 0.6 eq. (c) 1.0 eq. (d) 1.4 eq. (e) 1.9 eq. (f) 2.4 eq. (g) 2.9 eq. (h) 3.4 eq. (i) 3.9 eq. (j) 4.9 eq.

Figure S46. Investigation of interactions between (n-Bu$_4$N)(H$_2$PO$_4$) and 1b (0.5 mM) ($^1$H NMR, DMSO-d$_6$, 600 MHz) (Table 1, entry 1b(DMSO-d$_6$)-2). (a) 1b. (b) 1b + (n-Bu$_4$N)(H$_2$PO$_4$) 1.5 eq.
Figure S47. Investigation of interactions between \( (n\text{-Bu}_4\text{N})(\text{MePO}_3\text{H}) \) and \( 1\text{b} \) (0.5 mM) \((^1\text{H NMR, DMSO-}d_6, 600 \text{ MHz}) \) (Table 1, entry \( 1\text{b}(\text{DMSO-}d_6-3). \) (a) \( 1\text{b} \). (b) \( 1\text{b} + (n\text{-Bu}_4\text{N})(\text{MePO}_3\text{H}) \) 1.2 eq.

Figure S48. A titration experiment of \( (n\text{-Bu}_4\text{N})(\text{PhCO}_2) \) against \( 1\text{b} \) (0.5 mM) \((^1\text{H NMR, DMSO-}d_6, 600 \text{ MHz}) \) (Table 1, entry \( 1\text{b}(\text{DMSO-}d_6-4). \) (a) \( 1\text{b} \). (b-k) \( 1\text{b} + (n\text{-Bu}_4\text{N})(\text{PhCO}_2). \) (b) \( (n\text{-Bu}_4\text{N})(\text{PhCO}_2) \) 0.3 eq. (c) 0.6 eq. (d) 0.9 eq. (e) 1.3 eq. (f) 1.8 eq. (g) 2.2 eq. (h) 2.8 eq. (i) 3.1 eq. (j) 3.7 eq. (k) 5.6 eq.
**Figure S49.** A least squares fitting to determine the binding constant $K_a$ of $\text{PhCO}_2^-$ and $1b$ in DMSO-$d_6$ (data of $^1$H NMR signal $f$).

**Figure S50.** A titration experiment of ($n$-Bu$_4$N)(PhPO$_3$H) against $1b$ (1.0 mM) ($^1$H NMR, DMSO-$d_6$, 600 MHz) (Table 1, entry 1b(DMSO-$d_6$)-5). (a) $1b$. (b–k) $1b$ + ($n$-Bu$_4$N)(PhPO$_3$H). (b) ($n$-Bu$_4$N)(PhPO$_3$H) 0.3 eq. c) 0.5 eq. (d) 0.9 eq. (e) 1.0 eq. (f) 1.1 eq. (g) 1.4 eq. (h) 1.7 eq. (i) 2.0 eq. (j) 5.0 eq. (k) 10.0 eq. (l) ($n$-Bu$_4$N)(PhPO$_3$H).
Figure S51. Investigation of interactions between \((n\text{-Bu}_4\text{N})(\text{PhOPO}_3\text{H})\) and 1b (0.5 mM) \((^1\text{H} \text{NMR, DMSO-}d_6, 600 \text{ MHz})\) (Table 1, entry 1b(DMSO-\(d_6\)-6). (a) 1b. (b) 1b + \((n\text{-Bu}_4\text{N})(\text{PhOPO}_3\text{H})\) 1.4 eq.

Figure S52. Investigation of interactions between \((\text{Et}_4\text{N})(p\text{-MeC}_6\text{H}_4\text{SO}_3)\) and 1b (0.5 mM) \((^1\text{H} \text{NMR, DMSO-}d_6, 600 \text{ MHz})\) (Table 1, entries 1b(DMSO-\(d_6\)-7). (a) 1b. (b) 1b + \((\text{Et}_4\text{N})(p\text{-MeC}_6\text{H}_4\text{SO}_3)\) 1.5 eq.
Figure S53. Investigation of interactions between \((n{-}Bu_4N)_2(PhPO_3)\) and \(1b\) (0.5 mM) \(^1\text{H}\) NMR, DMSO-\(d_6\), 600 MHz) (Table 1, entry \(1b(DMSO-d_6)-8\)). (a) \(1b\). (b) \(1b + (n{-}Bu_4N)_2(PhPO_3)\) 1.3 eq.

Figure S54. Investigation of interactions between \((n{-}Bu_4N)(PhCH_2PO_3)\) and \(1b\) (1.9 mM) \(^1\text{H}\) NMR, DMSO-\(d_6\), 600 MHz) (Table 1, entry \(1b(DMSO-d_6)-9\)). (a) \(1b\). (b) \(1b + (n{-}Bu_4N)(PhCH_2PO_3)\) 1.4 eq.
Figure S55. Investigation of interactions between (n-Bu₄N)X (X = Cl, Br, I) and 1b (0.5 mM) (^1H NMR, DMSO-d₆, 600 MHz). (a) 1b. (b−d) 1b + (n-Bu₄N)X. (b) X = Cl, 2.3 eq. (c) X = Br, 2.2 eq. (d) X = I, 2.2 eq.
4-5. Other $^1$H NMR experiments to investigate anion bindings

Figure S56. Investigation of interactions between ($n$-Bu$_4$N)(PhPO$_3$H) and per-O-methyl-$\beta$-cyclodextrin 7 (1.0 mM) ($^1$H NMR, CDCl$_3$, 600 MHz). (a) 7. (b) 7 + ($n$-Bu$_4$N)(PhPO$_3$H) 5.0 eq.

Figure S57. Release of ($n$-Bu$_4$N)(PhPO$_3$H) from 1b upon the addition of D$_2$O solvent (16 mM) ($^1$H NMR, 600 MHz). Letters with dashes denote proton signals of the host-guest complex (PhPO$_3$H$^-$)$\cdot$1b, and the ones without dashes denote those of free 1b and PhPO$_3$H$^-$. (a) 1b + ($n$-Bu$_4$N)(PhPO$_3$H) (1.3 eq) in CD$_3$CN. (b) 1b + ($n$-Bu$_4$N)(PhPO$_3$H) (1.3 eq) in CD$_3$CN/D$_2$O = 9/1 (v/v).

S45 / S54
Thermodynamic analysis of the guest inclusion in CDCl$_3$ and DMSO-$d_6$.

$^1$H NMR measurements to determine binding constants $K_a$ [M$^{-1}$] of PhCH$_2$PO$_3$H$^-$ by 1b at various temperatures.

1b·5H$_2$O (2.14 mg, 0.99 µmol, 1.0 eq) and (n-Bu$_4$N)(PhCH$_2$PO$_3$H) (1.36 µmol, 1.4 eq) are dissolved in CDCl$_3$ (520 µL) or DMSO-$d_6$ (500 µL). $^1$H NMR spectra of the sample were measured at various temperatures. Temperatures were calibrated by 4% MeOH in CD$_3$OD (in the experiments of CDCl$_3$ (255 – 323 K) and DMSO-$d_6$ (290 – 307 K)) or 80% ethylene glycol in DMSO-$d_6$ (in the experiment of DMSO-$d_6$ (307 – 385 K)).

Van’t Hoff plot analyses

The van’t Hoff plots (ln $K_a$ v.s. 1/T) of the conducted experiments did not give a linear relationship. Thus, a first-order approximation expressed as equations (S1–S3) was utilized to analyze the data.$^{[S13]}

\[
\ln K_a = a + \frac{b}{T} + \frac{c}{T^2} \quad \cdots \ (S1)
\]

\[
\Delta H = -R \left( b + \frac{2c}{T} \right) \quad \cdots \ (S2)
\]

\[
\Delta S = R \left( a - \frac{c}{T^2} \right) \quad \cdots \ (S3)
\]

Figure S58. $^1$H NMR spectra of 1b with PhCH$_2$PO$_3$H$^-$ (1.4 eq) at various temperatures (CDCl$_3$, 600 MHz). (a) 255.5 K. (b) 265.3 K. (c) 274.4 K. (d) 294.6 K. (e) 303.6 K. (f) 312.4 K. (g) 322.1 K.
Figure S59. A van’t Hoff plot of the binding constant $K_a$ in the inclusion experiment of PhCH$_2$PO$_3$H$^-$ by 1b in CDCl$_3$ (Fig. S56).

The dotted line in Fig. S59 represents the regression curve expressed as the equation (S1), where $a = -31.9$, $b = 2.16 \times 10^4$, and $c = -3.00 \times 10^7$.

Figure S60. Temperature dependence of thermodynamic parameters for the inclusion of PhCH$_2$PO$_3$H$^-$ by 1b in CDCl$_3$. (a) $\Delta H$ [kJ·mol$^{-1}$]. (b) $\Delta S$ [J·mol$^{-1}$·K$^{-1}$].
Figure S61. $^1$H NMR spectra of 1b with PhCH$_2$PO$_3$H$^-$ (1.4 eq) at various temperatures (DMSO-$d_6$, 600 MHz). (a) 291.4 K. (b) 305.9 K. (c) 309.3 K. (d) 319.5 K. (e) 331.2 K. (f) 341.7 K. (g) 351.8 K. (h) 362.7 K. (i) 372.5 K.
**Figure S62.** A van’t Hoff plot of the binding constant $K_a$ in the inclusion experiment of PhCH$_2$PO$_3$H$^-$ by 1b in DMSO-$d_6$ (Fig. S61).

The dotted line in Fig. S62 represents the regression curve expressed as the equation (S1), where $a = -21.4$, $b = 1.66 \times 10^4$, and $c = -2.30 \times 10^7$.

**Figure S63.** Temperature dependence of thermodynamic parameters for the inclusion of PhCH$_2$PO$_3$H$^-$ by 1b in DMSO-$d_6$. (a) $\Delta H$ [kJ⋅mol$^{-1}$]. (b) $\Delta S$ [J⋅mol$^{-1}$⋅K$^{-1}$].
5. X-ray crystallographic analysis

$2\cdot12.5\text{CH}_3\text{CN}\cdot2\text{C}_4\text{H}_8\text{O}_2\cdot3\text{H}_2\text{O}$

A single crystal of $2\cdot12.5\text{CH}_3\text{CN}\cdot2\text{C}_4\text{H}_8\text{O}_2\cdot3\text{H}_2\text{O}$ suitable for an X-ray diffraction analysis was obtained by the diffusion of CH$_3$CN vapor into a 1,4-dioxane solution of 2.

Crystal data: $\text{C}_{145}\text{H}_{227.5}\text{N}_{12.5}\text{O}_9$, $F_w = 3601.88$, colorless block, $0.28 \times 0.17 \times 0.15$ mm$^3$, monoclinic, space group $P2_1$ (No. 4), $a = 17.1191(11)$ Å, $b = 29.2535(18)$ Å, $c = 19.9019(13)$ Å, $\beta = 91.676(4)^\circ$, $V = 9962.5(11)$ Å$^3$, $Z = 2$, $T = 120$ K, $\lambda$(MoK$\alpha$) = 0.71073 Å, $\theta_{\text{max}} = 21.49^\circ$, $R_1 = 0.1111$, $wR_2 = 0.2905$, GOF = 2.323, Flack parameter 0.4(3). CCDC No. 1858034.

Refinements were performed using reflection data of 0.97 Å resolution, since the values of $R$-merge and mean $F_0^2/\sigma(F_0^2)$ in the resolution shell between 1.01 and 0.97 Å were 36.9% and 7.69, respectively. Solvent molecules were disordered thus refined isotropically. Some solvents were refined with DFIX and SIMU restraints. Some molecules of the crystallization solvents were so heavily disordered that they could not be located on a $d$-Fourier map after successive trials. The hydrogen atoms of waters, carboxylic acids, and acetonitriles could not be located on a $d$-Fourier map.
Figure S64. The molecular structure of $2_2 \cdot 12.5\text{CH}_3\text{CN} \cdot 2\text{C}_4\text{H}_8\text{O}_2 \cdot 3\text{H}_2\text{O}$ determined by X-ray diffraction analysis. C, light green; H, white; N, blue; O, red. (a) An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. (b) Packing in the crystal (stick model). (c,d) A space-filling model. Solvents were omitted for clarity. Side view (c) and top view (d).
**1b·5H₂O**

A single crystal of 1b·5H₂O suitable for an X-ray diffraction analysis was obtained by the slow evaporation of a MeOH/H₂O solution of 1b.

Crystal data:  C\textsubscript{105}H\textsubscript{143}N\textsubscript{7}O\textsubscript{40}, \textit{F}\textsubscript{w} = 2143.26, colorless block, 0.31 × 0.22 × 0.22 mm\textsuperscript{3}, orthorhombic, space group \textit{P}2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} (No. 19), \textit{a} = 14.988(2) Å, \textit{b} = 26.707(4) Å, \textit{c} = 27.946(4) Å, \textit{V} = 11186(3) Å\textsuperscript{3}, \textit{Z} = 4, \textit{T} = 120 K, \textit{\lambda}(MoK\alpha) = 0.71073 Å, \theta_{\text{max}} = 23.257°, \textit{R}\textsubscript{1} = 0.0619, \textit{wR}	extsubscript{2} = 0.1745, GOF = 1.144, Flack parameter 0.3(3). CCDC No. 1858035.

**Figure S65.** The molecular structure of 1b·5H₂O determined by X-ray diffraction analysis. C, light green; N, blue; O, red. (a) An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. (b) Internal cavity of 1b (probe radius, 1.0 Å; 1b, a stick model).
**1b·PhPO₃H·(n-Bu₄N)·C₆H₆**

A single crystal of 1b·PhPO₃H·(n-Bu₄N)·C₆H₆ suitable for an X-ray diffraction analysis was obtained by the slow diffusion of cyclohexane vapor into a benzene solution of (n-Bu₄N)[(PhPO₃H)·1b]

Crystal data: C₁₃₃H₁₈₁N₈O₃₈P, Fw = 2530.82, colorless block, 0.16 × 0.15 × 0.08 mm³, monoclinic, space group P2₁ (No. 4), a = 15.096(4) Å, b = 26.233(7) Å, c = 17.403(5) Å, β = 108.050(3)°, V = 6552(3) Å³, Z = 2, T = 120 K, λ(MoKα) = 0.71073 Å, θ max = 23.257°, R₁ = 0.0613, wR₂ = 0.1772, GOF = 1.136, Flack parameter 0.00(7). CCDC No. 1858036.

A disordered benzene molecules and n-butyl groups of a n-Bu₄N⁺ cation were refined isotropically with DFIX restraints.

**Figure S66.** The molecular structure of 1b·PhPO₃H·(n-Bu₄N)·C₆H₆ determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). C, light green; N, blue; O, red; P, orange. Hydrogen atoms were omitted for clarity.
6. References for the Supplementary Information

12. K. Akine, Titration, ver 1.1.0, For analysis of titration data in host-guest chemistry, 2013.