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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds \textbf{BrP5, 1I, 1PF6} and \textbf{2I} were synthesized according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer. The crystal data were collected on an Oxford Diffraction Xcalibur Atlas Gemini Ultra instrument.
2. A 2D NMR NOESY spectrum of \(1I\) and \(BrP5\)

![Fig. S1 NOESY spectrum (500 MHz, chloroform-\(d\), rt) of a solution of 2.00 mM BrP5 and 2.00 mM 1I.](image)

3. Stoichiometry and association constant determination for the complexation between \(BrP5\) and \(1I\)

To determine the stoichiometry and association constant between \(BrP5\) and \(1I\), \(^1\)H NMR titration was done with solutions which had a constant concentration of \(1I\) (0.50 mM) and varying concentrations of \(BrP5\). By a non-linear curve-fitting method, the association constant between guest \(1I\) and host \(BrP5\) was calculated. The non-linear curve-fitting was based on the equation: \(^5\)

\[
\Delta \delta = (\Delta \delta_\infty / [G]_0) \left( 0.5[H]_0 + 0.5([G]_0 + 1/K_a) - (0.5([H]_0^2 + (2[H]_0(1/K_a - [G]_0)) + (1/K_a + [G]_0^2)^{0.5}) \right)
\]  
(Eq. S1)

where \(\Delta \delta\) is the chemical shift change of \(H_b\) on \(1I\) at \([H]_0\), \(\Delta \delta_\infty\) is the chemical shift change of \(H_b\) when the guest is completely complexed, \([G]_0\) is the fixed initial concentration of the guest, and \([H]_0\) is the varying concentration of \(BrP5\).
Fig. S2 $^1$H NMR spectra (500 MHz, chloroform-$d$ and methanol-$d_4$ (3:2, v/v), rt) of 1I at a concentration of 0.500 mM with different concentrations of BrP5: (a) 0.00 mM, (b) $8.50 \times 10^{-3}$ mM, (c) $2.10 \times 10^{-2}$ mM, (d) $3.70 \times 10^{-2}$ mM, (e) $6.70 \times 10^{-2}$ mM, (f) $8.00 \times 10^{-2}$ mM, (g) 0.143 mM, (h) 0.196 mM, (i) 0.419 mM, (j) 0.560 mM, (k) 0.856 mM, (l) 1.02 mM, (m) 1.53 mM, and (n) 2.52 mM.
3.1 Stoichiometry determination for the complexation between BrP5 and 1I

![Molar ratio plot](image)

Fig. S3 Molar ratio plot for the complexation between BrP5 and 1I in a mixed solvent of chloroform-d and methanol-d4 (3:2, v/v), indicating a 1:1 binding stoichiometry.

3.2 Association constant determination for the complexation between BrP5 and 1I

![Chemical shift changes](image)

Fig. S4 The chemical shift changes of Hb on 1I upon addition of BrP5 in a mixed solvent of chloroform-d and methanol-d4 (3:2, v/v). The black solid line was obtained from the non-linear curve-fitting using Eq. S1.
4. Stoichiometry and association constant determination for the complexation between BrP5 and 1PF6

**Fig. S5** The chemical structure of 1PF6.

**Fig. S6** $^1$H NMR spectra (500 MHz, chloroform-$d$ and methanol-$d_4$ (3:2, v/v), rt) of 1PF6 at a concentration of 0.500 mM with different concentrations of BrP5: (a) 0.00 mM, (b) $5.00 \times 10^{-2}$ mM, (c) $9.10 \times 10^{-2}$ mM, (d) 0.162 mM, (e) 0.219 mM, (f) 0.387 mM, (g) 0.526 mM, (h) 1.02 mM, (i) 1.57 mM, (j) 2.03 mM, (k) 2.26 mM, and (l) 2.93 mM.
**Fig. S7** Molar ratio plot for the complexation between BrP5 and 1PF6 in a mixed solvent of chloroform-d and methanol-d₄ (3:2, v/v), indicating a 1:1 binding stoichiometry.

**Fig. S8** The chemical shift changes of H₃⁺ on 1PF6 upon addition of BrP5 in a mixed solvent of chloroform-d and methanol-d₄ (3:2, v/v). The black solid line was obtained from the non-linear curve-fitting using Eq. S1.
5. A 2D NMR NOESY spectrum of 2I and BrP5

Fig. S9 NOESY spectrum (500 MHz, chloroform-d and methanol-d₄ (3:2, v/v), rt) of a solution of 4.00 mM BrP5 and 2.00 mM 2I.

6. Stoichiometry and association constant determination for the complexation between BrP5 and 2I

To determine the stoichiometry and association constant for the complexation between BrP5 and 2I, ¹H NMR titration experiments were done with solutions which had a constant concentration of 2I (5.00 × 10⁻⁴ M) and varying concentrations of BrP5. The non-linear curve-fitting was based on the equation:⁵³

\[
\Delta \delta = \frac{(\Delta \delta_{HG1} [H] + \Delta \delta_{HG2} K_1 K_2 [H]^2)}{(1 + K_1 [H] + K_1 K_2 [H]^2} \quad \text{Eq. S2}
\]

where \( \Delta \delta \) is the chemical shift change of Hₐ' on 2I at [H], \( \Delta \delta_{HG} \) is the chemical shift change of Hₐ' when 2I is completely complexed by the first pillar[5]arene, \( \Delta \delta_{HG2} \) is the chemical shift change of Hₐ' when 2I is completely complexed by the second pillar[5]arene. [G] is the fixed initial concentration of 2I. [H] is the varying concentration of BrP5.
**Fig. S10** $^1$H NMR spectra (500 MHz, chloroform-$d$ and methanol-$d_4$ (3:2, v/v), rt) of 2I at a concentration of 0.500 mM with different concentrations of BrP5: (a) 0.00 mM, (b) $1.75 \times 10^{-2}$ mM, (c) $4.70 \times 10^{-2}$ mM, (d) $9.25 \times 10^{-2}$ mM, (e) 0.124 mM, (f) 0.186 mM, (g) 0.232 mM, (h) 0.371 mM, (i) 0.695 mM, (j) 1.50 mM, (k) 2.15 mM, (l) 3.05 mM, and (m) 4.77 mM.
6.1 Stoichiometry determination for the complexation between BrP5 and 2I

![Molar ratio plot](image1)

**Fig. S11** Molar ratio plot for the complexation between BrP5 and 2I in a mixed solvent of chloroform-d and methanol-d₄ (3:2, v/v), indicating a 2:1 binding stoichiometry.

6.2 Association constant determination for the complexation between BrP5 and 2I

![Chemical shift changes](image2)

**Fig. S12** The chemical shift changes of H₆' on 2I upon addition of BrP5 in a mixed solvent of chloroform-d and methanol-d₄ (3:2, v/v). The black solid line was obtained from the non-linear curve-fitting using Eq. S2.

S10
7. X-ray crystal data of BrP5≥II and BrP5≥2I

<table>
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<tr>
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<th>BrP5≥II</th>
<th>BrP5≥2I</th>
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</thead>
<tbody>
<tr>
<td>Crystallization Solvent</td>
<td>chloroform</td>
<td>THF/methanol</td>
</tr>
<tr>
<td>Collection Temperature</td>
<td>170.0 K</td>
<td>296.15 K</td>
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<tr>
<td>Sum Formula</td>
<td>C_{62}H_{70}Br_{10}NO_{10}</td>
<td>C_{125}H_{140}Br_{20}I_{2}N_{2}O_{20}</td>
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<tr>
<td>Mr</td>
<td>1915.19</td>
<td>3842.18</td>
</tr>
<tr>
<td>Crystal System</td>
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</tr>
<tr>
<td>Space Group</td>
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<td>P -1</td>
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<tr>
<td>a [Å]</td>
<td>12.9329(4)</td>
<td>12.5317(9)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>25.2167(8)</td>
<td>15.7091(12)</td>
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<tr>
<td>c [Å]</td>
<td>21.2593(7)</td>
<td>18.2229(15)</td>
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<td>α [°]</td>
<td>90</td>
<td>81.626(2)</td>
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<td>β [°]</td>
<td>96.527(2)</td>
<td>80.866(2)</td>
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<tr>
<td>γ [°]</td>
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<td>75.600(2)</td>
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<tr>
<td>V [Å³]</td>
<td>6888.3(4)</td>
<td>3409.4(5)</td>
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<tr>
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<td>Final R1 values (I &gt;2σ(I))</td>
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<td>Final R1 values (all data)</td>
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<td>Final wR(F2) values (all data)</td>
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<td>Largest difference peak and hole [e.A-3]</td>
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<td>CCDC</td>
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<td>1900475</td>
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Illustration of the disorder of BrP5:2I crystals:

In the crystal structure, two iodine anions, a 2I molecule and five -CH2-CH2-Br groups on BrP5 were disordered over two positions with a 55:45, 50:50 and 50:50 site occupancy split, respectively. The guest molecule 2I was disordered in the void made by two centrosymmetric BrP5 molecules (Fig. S13).

![Fig. S13 Illustration of the disorder of a guest 2I molecule in the void between two host BrP5 molecules. The hydrogen atoms are omitted for clarity.](image)

8. The packing structure of the crystal formed by BrP5 and 2I

![Fig. S14 The packing structure of the crystal formed by BrP5 and 2I.](image)
If the two iodide ions were distributed in the both ends, the electrostatic interactions will hinder the packing of the [3]pseudorotaxanes.

9. References:

