Construction of a [2]pseudorotaxane and a [3]pseudorotaxane based on perbromoethylated pillar[5]arene/pyridinium iodide ion-pair recognition

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Electronic Supplementary Information (13 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **BrP5, 1I, 1PF6** and **2I** were synthesized according to literature procedures.[S1] 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***

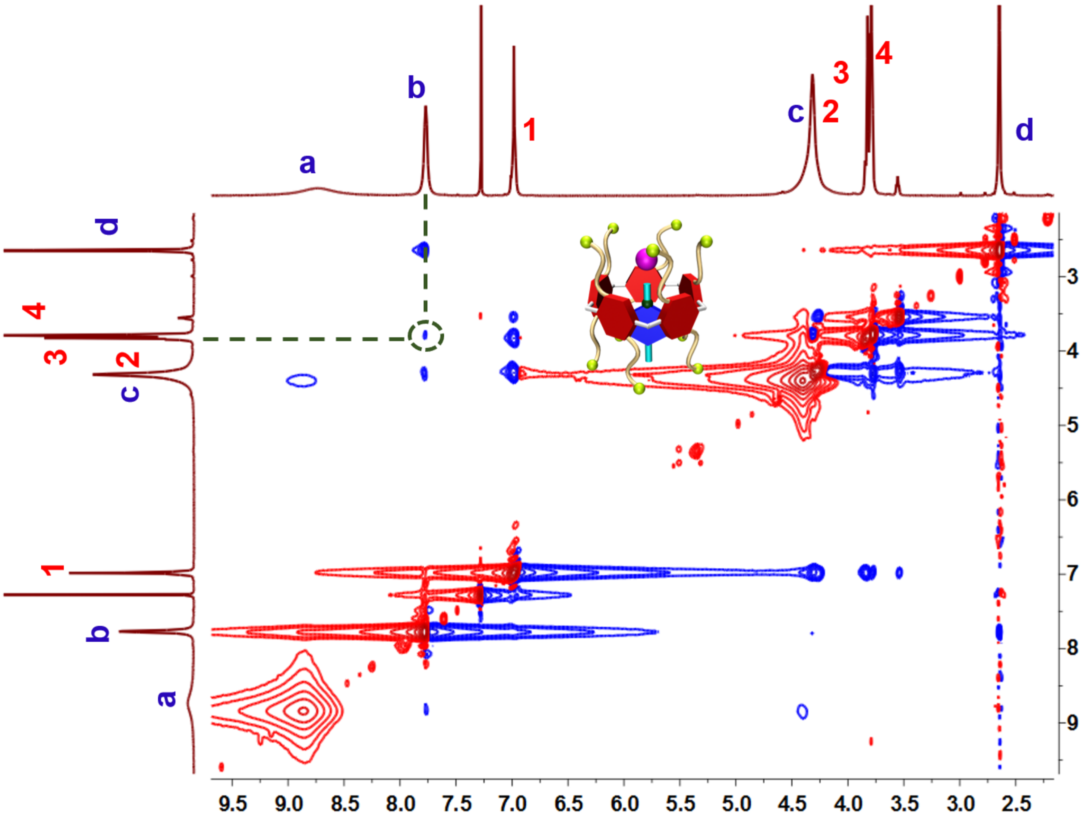

Fig. S1 NOESY spectrum (500 MHz, chloroform-*d*, rt) of a solution of 2.00 mM **BrP5** and 2.00 mM **1I**.

*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:[S2]

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

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**.

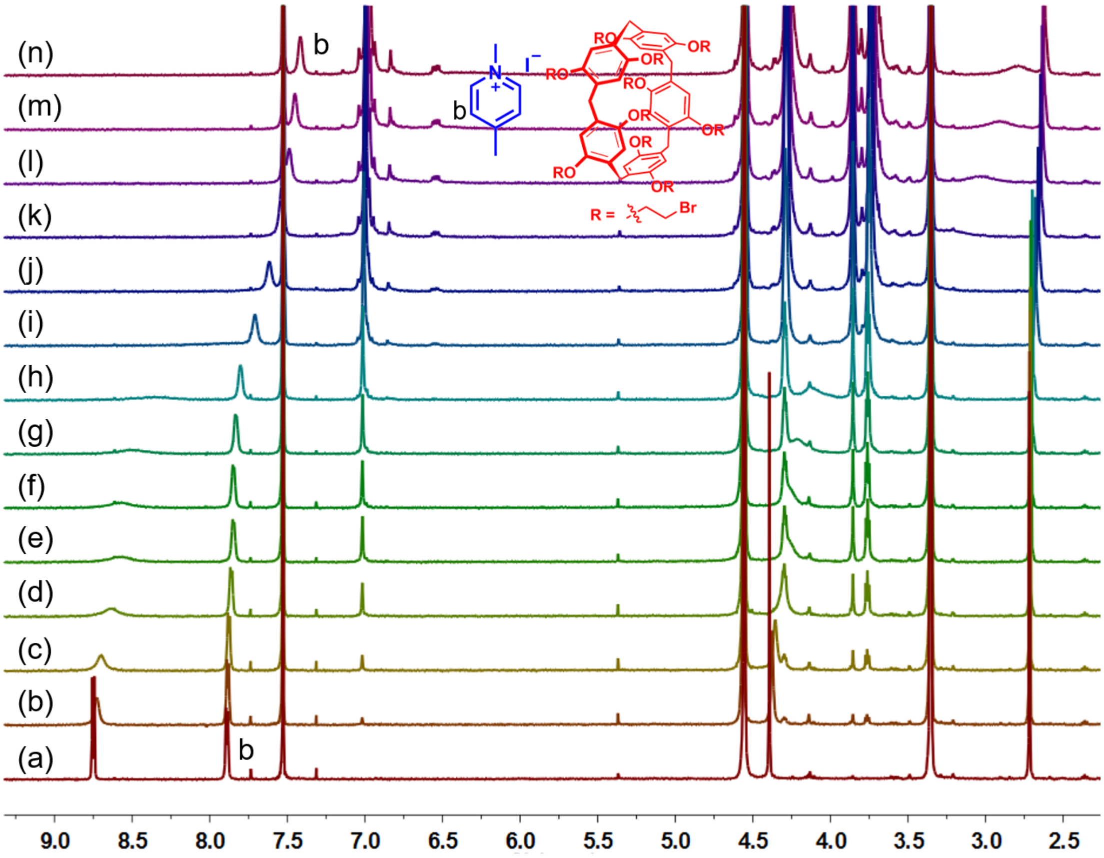

Fig. S2 ^{1}H NMR spectra (500 MHz, chloroform-*d* and methanol-d_4 (3:2, *v*/*v*), rt) of **1I** at a concentration of 0.500 mM with different concentrations of **BrP5**: (a) 0.00 mM, (b) 8.50 × 10^{-3} mM, (c) 2.10 × 10^{-2} mM, (d) 3.70 × 10^{-2} mM, (e) 6.70 × 10^{-2} mM, (f) 8.00 × 10^{-2} mM, (g) 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***

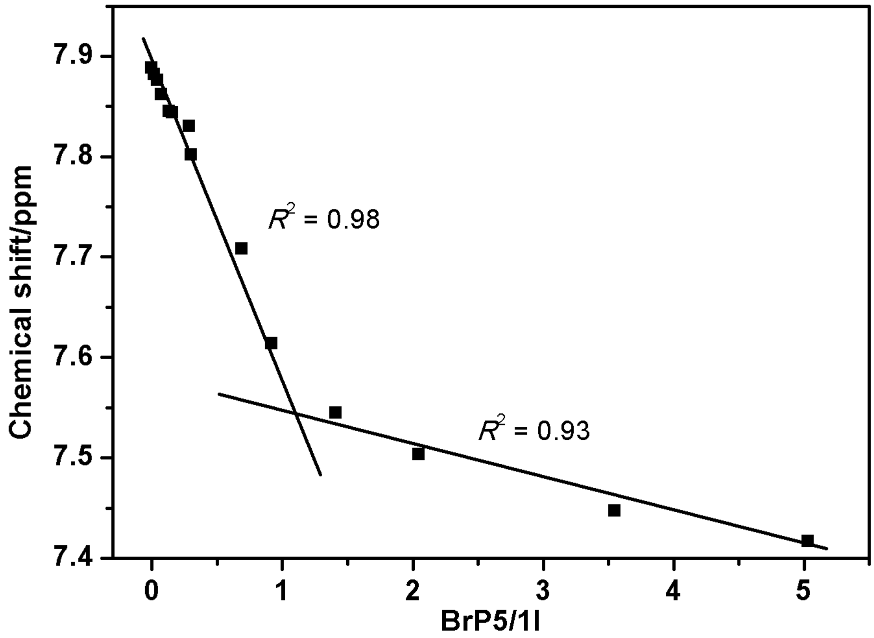

Fig. S3 Molar ratio plot for the complexation between **BrP5** and **1I** in a mixed solvent of chloroform-*d* and methanol-d_4 (3:2, *v*/*v*), indicating a 1:1 binding stoichiometry.

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

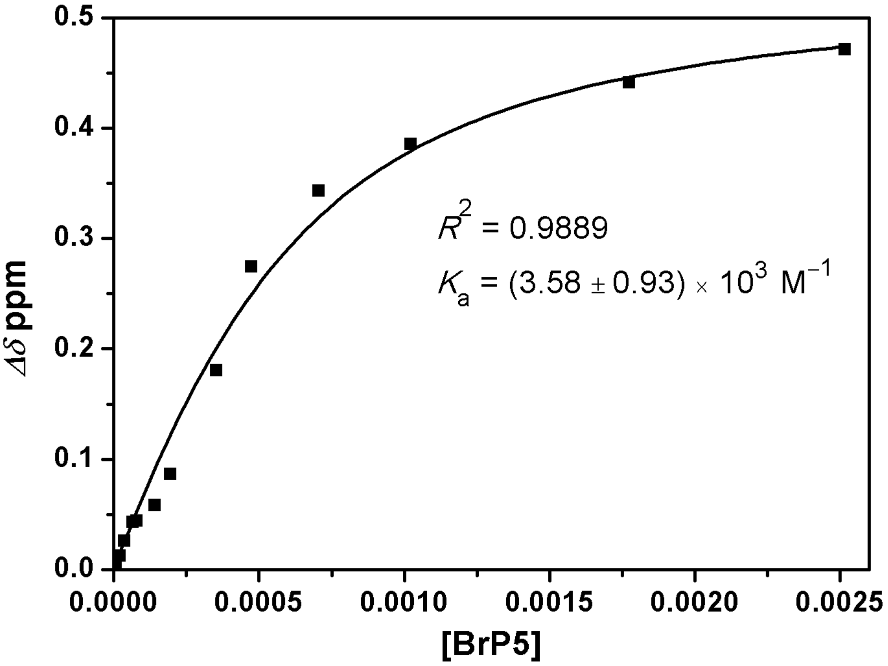

Fig. S4 The chemical shift changes of H_b on **1I** upon addition of **BrP5** in a mixed solvent of chloroform-*d* and methanol-d_4 (3:2, *v*/*v*). The black solid line was obtained from the non-linear curve-fitting using Eq. S1.

4. *Stoichiometry and association constant determination for the complexation between **BrP5** and **1PF6***

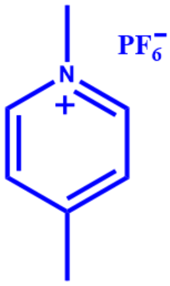

Fig. S5 The chemical structure of **1PF6**.

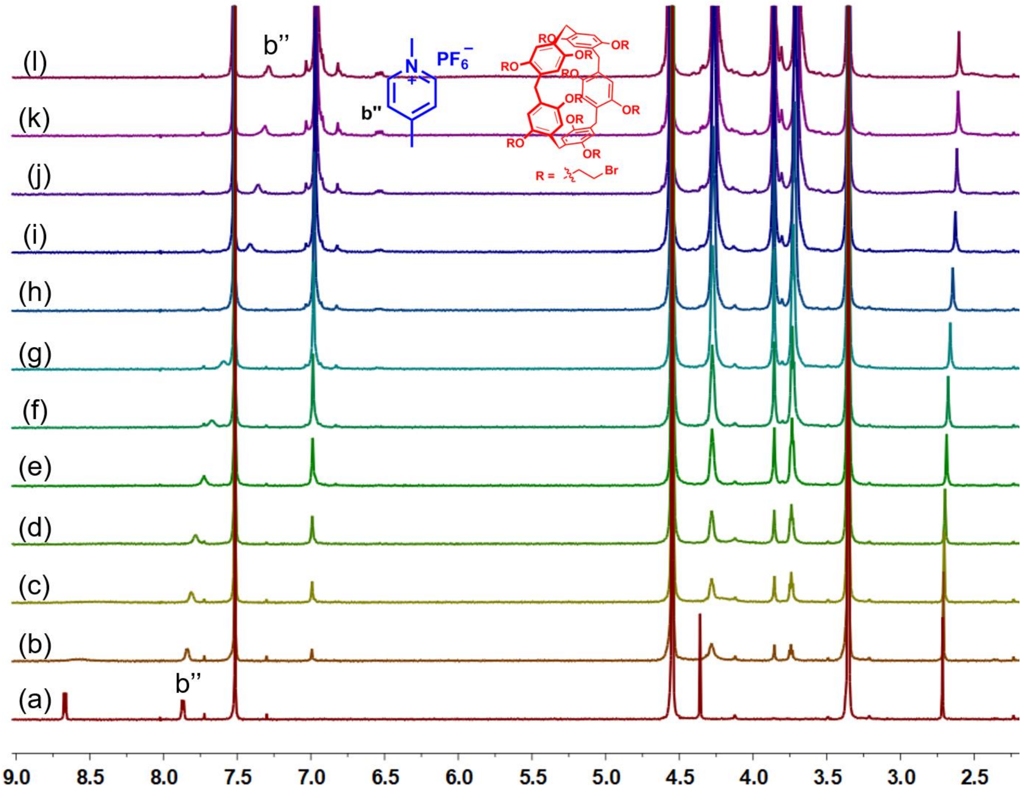

Fig. S6 ^{1}H NMR spectra (500 MHz, chloroform-*d* and methanol-d_4 (3:2, *v*/*v*), rt) of **1PF6** at a concentration of 0.500 mM with different concentrations of **BrP5**: (a) 0.00 mM, (b) 5.00 × 10^{-2} mM, (c) 9.10 × 10^{-2} mM, (d) 0.162 mM, (e) 0.219 mM, (f) 0.387 mM, (g) 0.526 mM, (h) 1.02 mM, (i) 1.57 mM, (j) 2.03 mM, (k) 2.26 mM, and (l) 2.93 mM.

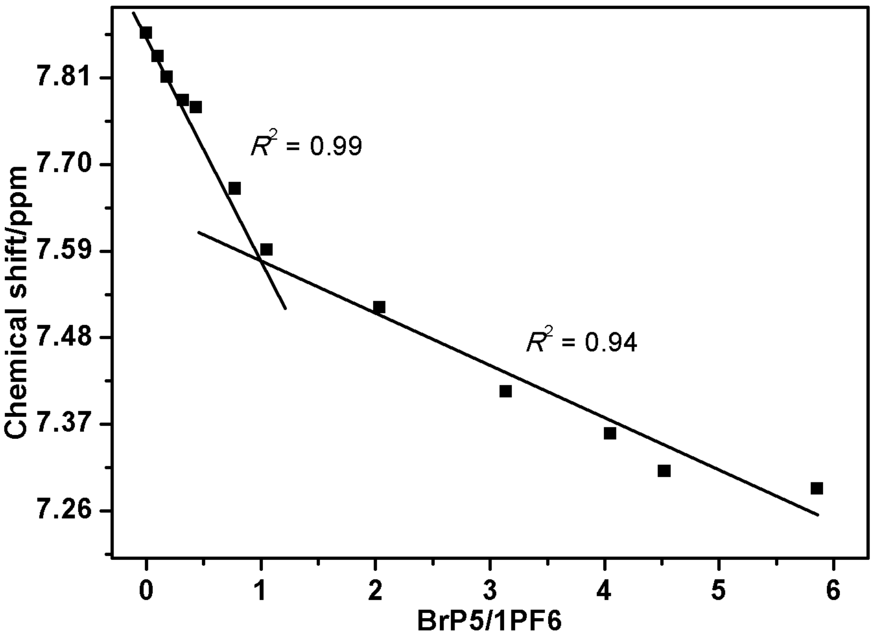

Fig. S7 Molar ratio plot for the complexation between **BrP5** and **1PF6** in a mixed solvent of chloroform-*d* and methanol-d_4 (3:2, *v*/*v*), indicating a 1:1 binding stoichiometry.

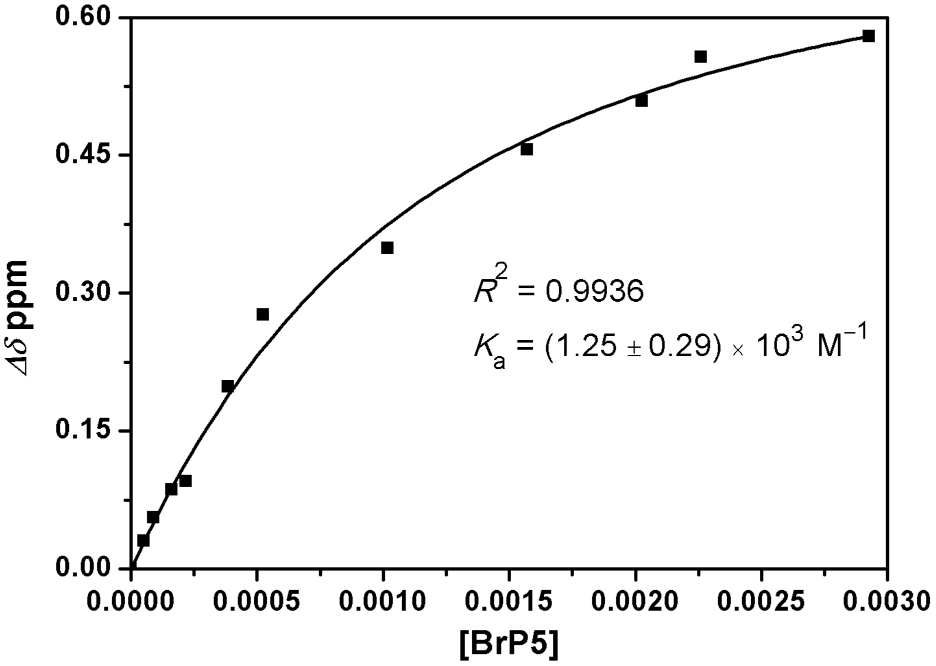

Fig. S8 The chemical shift changes of $H_{b''}$ on **1PF6** upon addition of **BrP5** in a mixed solvent of chloroform-*d* and methanol-d_4 (3:2, *v*/*v*). The black solid line was obtained from the non-linear curve-fitting using Eq. S1.

5. *A 2D NMR NOESY spectrum of **2I** and **BrP5***

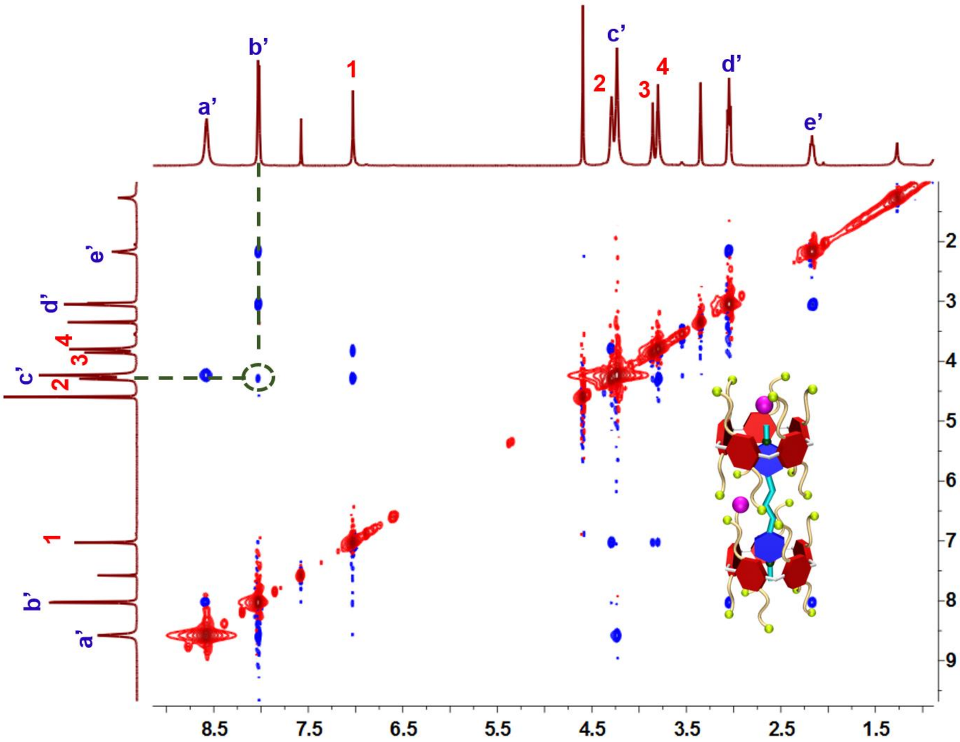

Fig. S9 NOESY spectrum (500 MHz, chloroform-*d* and methanol-d_4 (3:2, *v*/*v*), rt) of a solution of 4.00 mM **BrP5** and 2.00 mM **2I**.

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**, ^{1}H 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:[S3]

$$\Delta\delta = (\Delta\delta_{HG}K_1[H] + \Delta\delta_{HG2}K_1K_2[H]^2) / (1 + K_1[H] + K_1K_2[H]^2) \qquad \text{Eq. S2}$$

where $\Delta\delta$ is the chemical shift change of $H_{a'}$ on **2I** at [H], $\Delta\delta_{HG}$ is the chemical shift change of $H_{a'}$ when **2I** is completely complexed by the first pillar[5]arene, $\Delta\delta_{HG2}$ is the chemical shift change of $H_{a'}$ 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**.

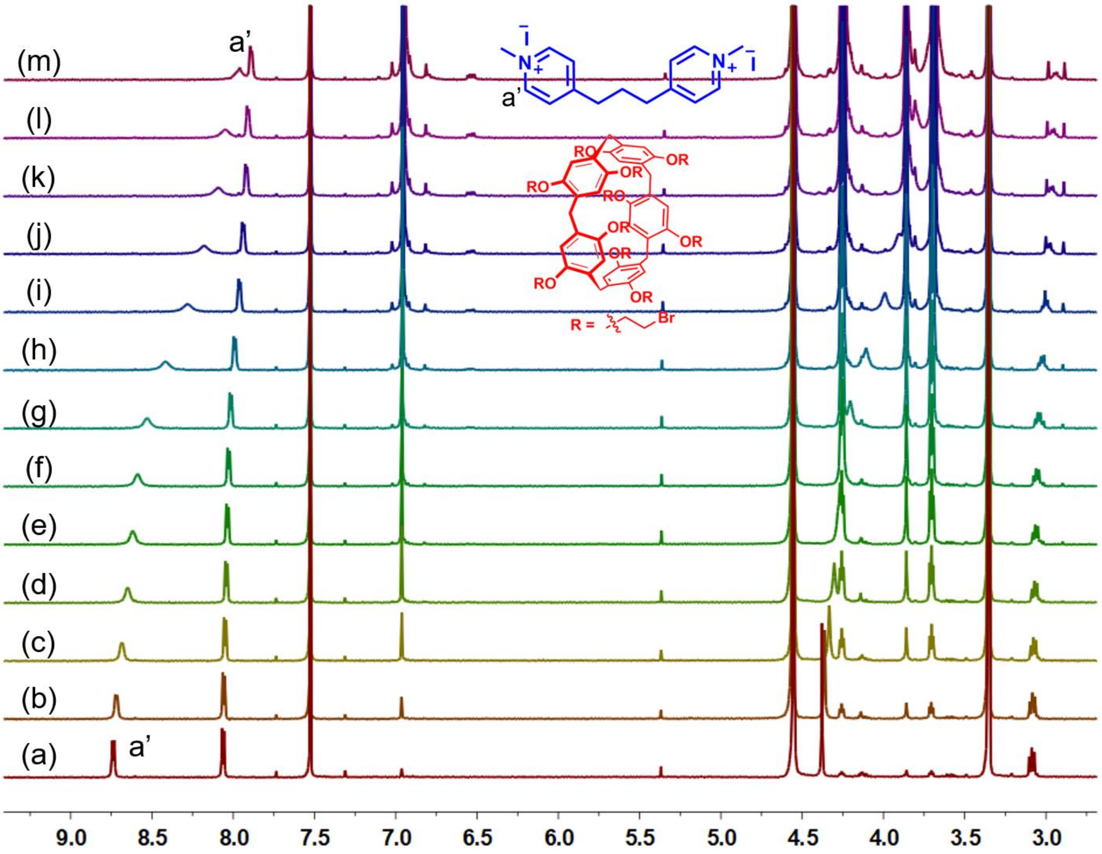

Fig. S10 ^{1}H NMR spectra (500 MHz, chloroform-*d* and methanol-d_4 (3:2, *v*/*v*), rt) of **2I** at a concentration of 0.500 mM with different concentrations of **BrP5**: (a) 0.00 mM, (b) 1.75 × 10^{-2} mM, (c) 4.70 × 10^{-2} mM, (d) 9.25 × 10^{-2} mM, (e) 0.124 mM, (f) 0.186 mM, (g) 0.232 mM, (h) 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***

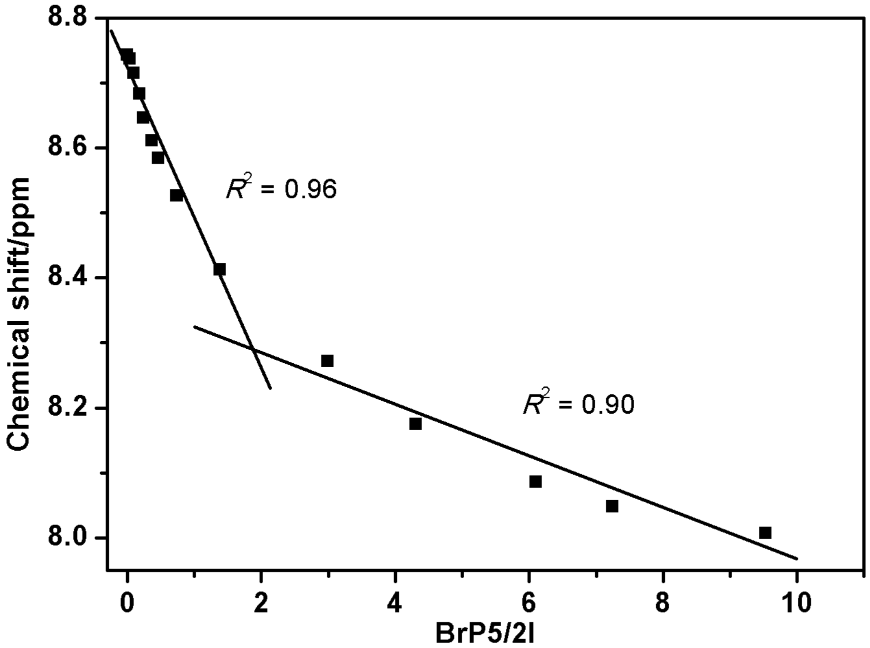

Fig. S11 Molar ratio plot for the complexation between **BrP5** and **2I** in a mixed solvent of chloroform-*d* and methanol-d_4 (3:2, *v*/*v*), indicating a 2:1 binding stoichiometry.

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

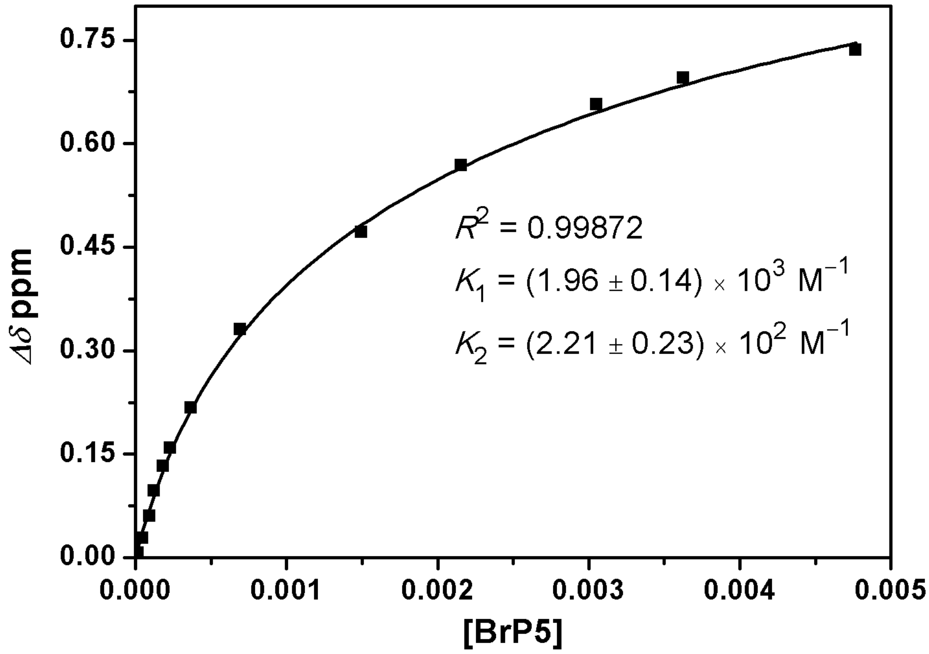

Fig. S12 The chemical shift changes of $H_{a'}$ on **2I** upon addition of **BrP5** in a mixed solvent of chloroform-*d* and methanol-d_4 (3:2, *v*/*v*). The black solid line was obtained from the non-linear curve-fitting using Eq. S2.

7. X-ray crystal data of ***BrP5⊃1I*** *and* ***BrP5$_2$⊃2I***

	BrP5⊃1I	**BrP5$_2$⊃2I**
Crystallization Solvent	chloroform	THF/methanol
Collection Temperature	170.0 K	296.15 K
Sum Formula	$C_{62}H_{70}Br_{10}INO_{10}$	$C_{125}H_{140}Br_{20}I_2N_2O_{20}$
Mr	1915.19	3842.18
Crystal System	Monoclinic	Triclinic
Space Group	$P2_1/c$	P -1
a [Å]	12.9329(4)	12.5317(9)
b [Å]	25.2167(8)	15.7091(12)
c [Å]	21.2593(7)	18.2229(15)
α [°]	90	81.626(2)
β [°]	96.527(2)	80.866(2)
γ [°]	90	75.600(2)
V [Å3]	6888.3(4)	3409.4(5)
Z	4	1
D*calcd* [g cm-3]	1.847	1.871
μ[mm-1]	6.320	6.384
F(000)	3728.0	1870.0
2*θ* range [°]	4.526 – 52.798	4.786 – 52.99
Reflections collected	137005	56647
Independent reflections, *Rint*	14115, 0.1333	13929, 0.0460
Data /restraints /parameters	14115/12/808	13929/688/917
Final *R*1 values ($I > 2\sigma(I)$)	0.0892	0.0703
Final *R*1 values (all data)	0.1641	0.0894
Final $wR(F_2)$ values (all data)	0.2511	0.2208
Goodness-of-fit on F^2	1.025	1.089
Largest difference peak and hole [e.A-3]	2.03/-1.22	3.06/-3.43
CCDC	1900476	1900475

Illustration of the disorder of **BrP5**$_2$**⊃2I** crystals:

In the crystal structure, two iodine anions, a **2I** molecule and five -CH$_2$-CH$_2$-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).

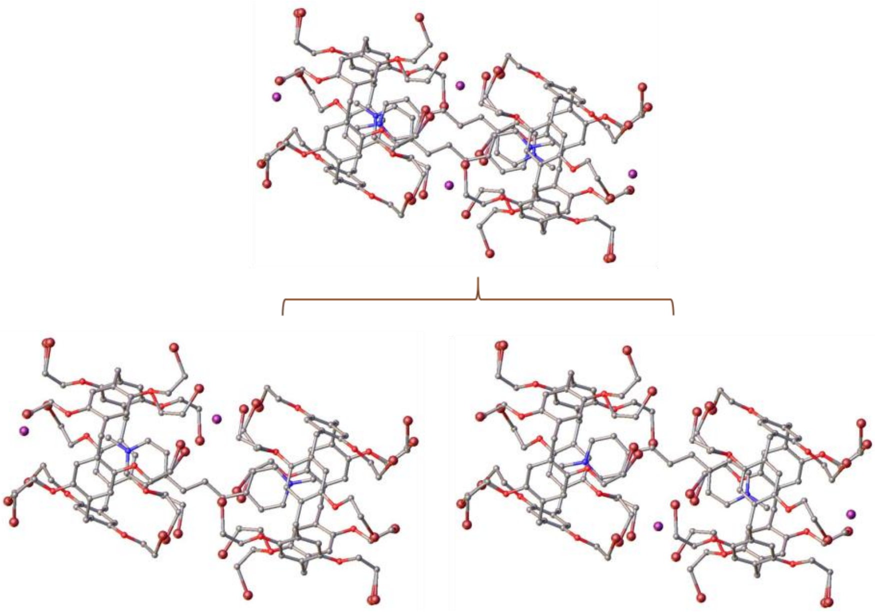

Fig. S13 Illustration of the disorder of a guest **2I** molecule in the void between two host **BrP5** molecules. The hydrogen atoms are omitted for clarity.

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

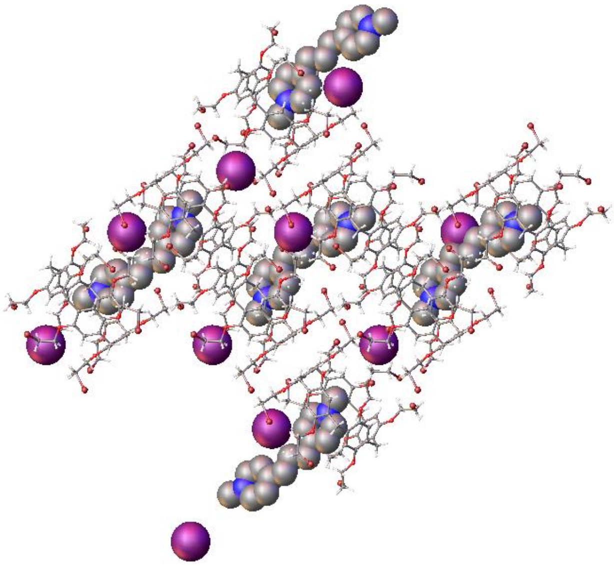

Fig. S14 The packing structure of the crystal formed by **BrP5** and **2I**.

If the two iodide ions were distributed in the both ends, the electrostatic interactions will hinder the packing of the [3]pseudorotaxanes.

9. References:

S1. (a) T. Muramatsu, A. Toyota, M. Kudou, Y. Ikegami and M. Watanabe, *J. Org. Chem.*, 1999, **64**, 7249; (b) Y. Ma, X. Ji, F. Xiang, X. Chi, C. Han, J. He, Z. Abliz, W. Chen and F. Huang, *Chem. Commun.*, 2011, **47**, 12340.

S2. K. A. Connors, *Binding Constants*; Wiley: New York, 1987; P. S. Corbin, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999.

S3. P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305.