Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Pillar[5]arene-Based Ion-Pair Recognition for Constructing a [2]Pseudorotaxane with Supramolecular Interaction Induced LCST Behavior

Ming Li,[a] Bin Hua*[a,b] and Feihe Huang*[a,b,c]

a. *State Key Laboratory of Chemical Engineering, Key Laboratory of Excited-State Materials of Zhejiang Province, Stoddart Institute of Molecular Science, Department of Chemistry, Zhejiang University, Hangzhou 310027, China; Fax and Tel: +86-571-8795-3189. Email addresses: huabin@zju.edu.cn; fhuang@zju.edu.cn*

b. *ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou, 311215, China*

c. *Green Catalysis Center and College of Chemistry, Zhengzhou University, Zhengzhou 450001, China*

Electronic Supplementary Information (17 pages)

1. Materials and methods

Materials

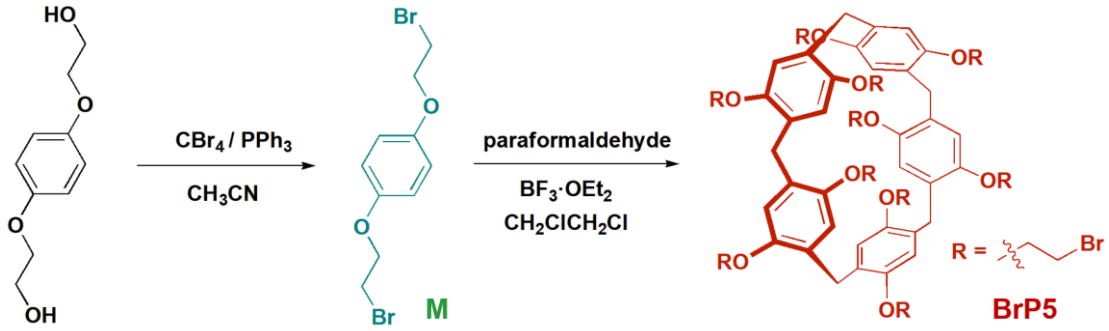
All reagents including guest compounds **G1**, **G2** and **G3** were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Compounds **M** and **BrP5** were prepared according to published literature procedures.[S1,S2]

Methods

NMR spectra were recorded with a Bruker Avance DMX 600 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra (LRESI-MS) were obtained on a Bruker Esquire 3000 Plus spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Dynamic light scattering (DLS) measurements were carried out on a Malvern Nanosizer S instrument at different temperatures. UV-vis absorption spectra were taken on a Cary Series UV-Vis spectrophotometer with a Cary Temperature Controller. 2D NOESY NMR spectra were collected on a Bruker Avance DMX-500 spectrometer with internal standard TMS.

Turbidity measurements. In this study, for temperature-variable UV-Vis measurements, 1 cm quartz cuvettes were used. The cloud points were determined by monitoring the transmission changes (at 500 nm) of the solutions heated at 1 °C min^{-1}; The values of the cloud points were defined as the temperature at which the transmission decreases by 50 %.[S3]

*2. Synthesis of the host **BrP5***



Scheme S1. Synthetic route to **BrP5**.

For the synthesis of **BrP5**: **M** and **BrP5** were successfully synthesized according to the previously reported literature procedures.[S1,S2] Briefly, **M** (3.37 g, 11.5 mmol) and an equivalent of paraformaldehyde (0.349 g, 11.5 mmol) were first dissolved in 1,2-dichloroethane (150 mL) at room temperature and allowed to stir for 15 min to crush the large paraformaldehyde particles. Then boron trifluoride etherate (3.26 g, 23.0 mmol) was added to the above solution and the mixture was stirred at constant temperature until the solution turned deep green. The resulting mixture was washed with water and dried with anhydrous Na_2SO_4 and concentrated under vacuum. Later, the crude product was purified by column chromatography on silica gel running with petroleum ether/dichloromethane (1:2 *v*/*v*) as the eluent to give the desired product as a white powder (1.8 g, 46%). ^{1}H NMR (600 MHz, $CDCl_3$, room temperature) δ (ppm): 6.91 (s, 10H), 4.22 (t, J = 5.6 Hz, 20H), 3.84 (s, 10H), 3.63 (t, J = 5.7 Hz, 20H).

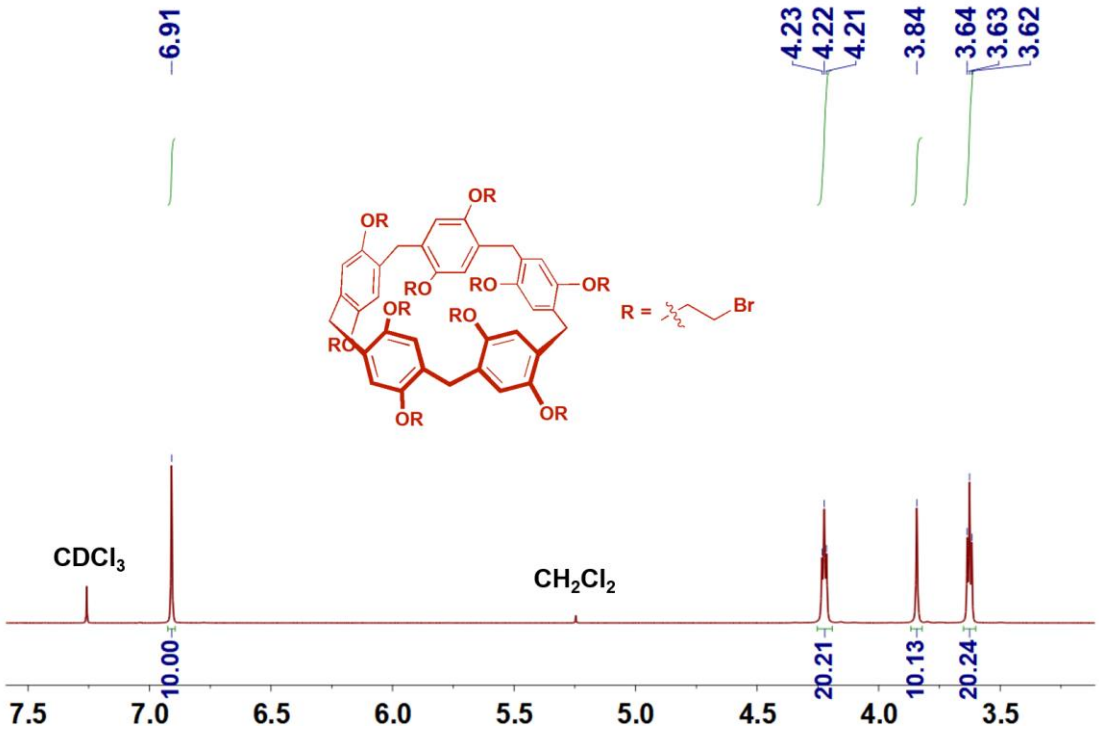


Fig. S1 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, room temperature) of **BrP5**.

*3. Studies of the host–guest interactions between **BrP5** and **G1***

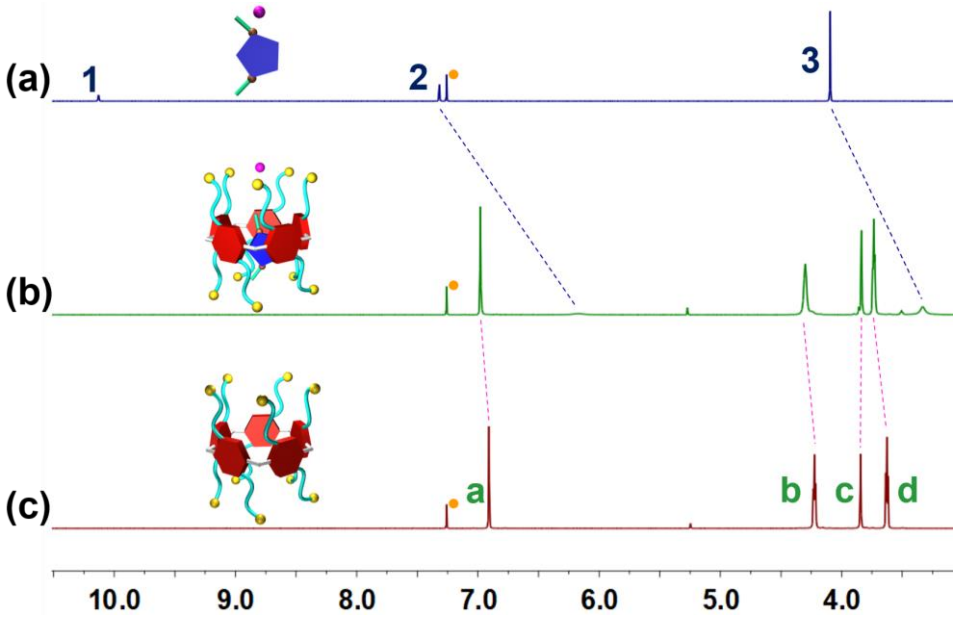


Fig. S2 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature): (a) **G1** (10.0 mM); (b) **BrP5** (10.0 mM) and **G1** (10.0 mM); (c) **BrP5** (10.0 mM). Peaks marked with orange dots are ascribed to chloroform-*d*.

4. Determination of stoichiometries and association constants for the complexation of ***BrP5*** *with* ***G1***, ***G2*** *and* ***G3***

To determine the stoichiometries and association constants for the complexations of **BrP5** with **G1**, **G2** and **G3**, NMR titrations were conducted with solutions which had a constant concentration of **BrP5** (2.00 mM) and varying concentrations of **G1**, **G2** and **G3**.

By a mole ratio plot, the stoichiometry was calculated to be 1:1. By a non-linear curve-fitting method, the association constant (K_a) of **BrP5⊃G1** was estimated to be (967 ± 72) M^{-1}.

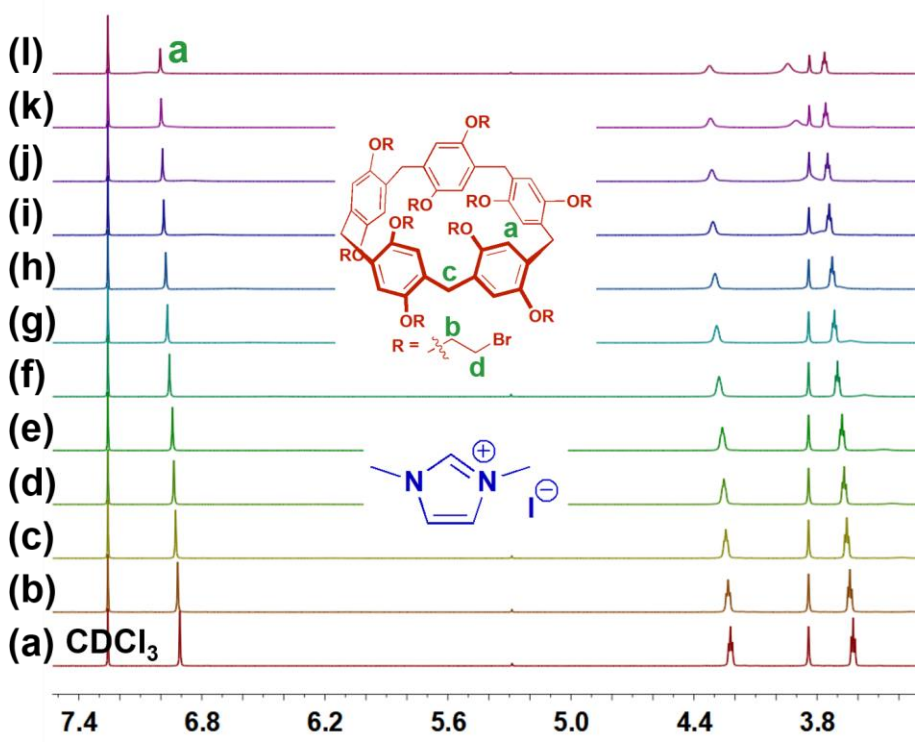


Fig. S3 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature) of **BrP5** at a constant concentration of 2.0 mM upon gradually addition of **G1** (15.0 mM): (a) 0.00 μL, (b) 10.0 μL, (c) 20.0 μL, (d) 30.0 μL, (e) 40.0 μL, (f) 65.0 μL, (g) 90.0 μL, (h) 115 μL, (i) 165 μL, (j) 215 μL, (k) 315 μL, and (l) 415 μL.

The non-linear curve-fitting was based on the equation:

$\Delta\delta = (\Delta\delta_\infty/[\mathbf{BrP5}]_0)\ (0.5[\mathbf{G1}]_0 + 0.5([\mathbf{BrP5}]_0 + 1/K_a) - (0.5\ ([\mathbf{G1}]_0^2 + (2[\mathbf{G1}]_0(1/K_a - [\mathbf{BrP5}]_0)) + (1/K_a + [\mathbf{BrP5}]_0)^2)^{0.5}))$ (Eq. S1)

where $\Delta\delta$ is the chemical shift change of H_a on **BrP5** at $[\mathbf{G1}]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_a when the host is completely complexed, $[\mathbf{BrP5}]_0$ is the fixed initial concentration of the host, and $[\mathbf{G1}]_0$ is the initial concentration of **G1**.

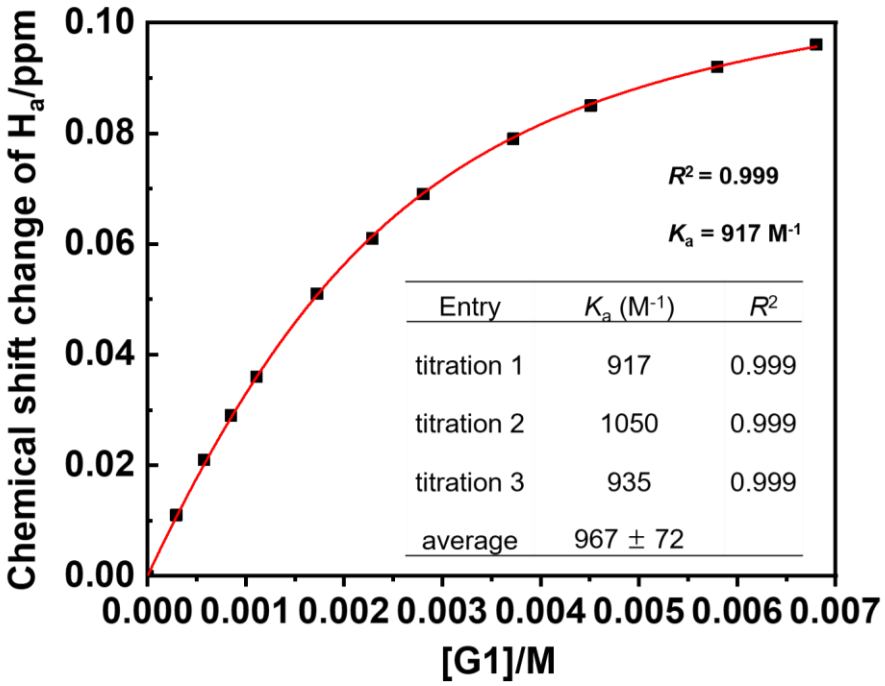


Fig. S4 The chemical shift changes of H_a on **BrP5** upon addition of **G1**. The red solid line was obtained from the non-linear curve-fitting using the above equation.

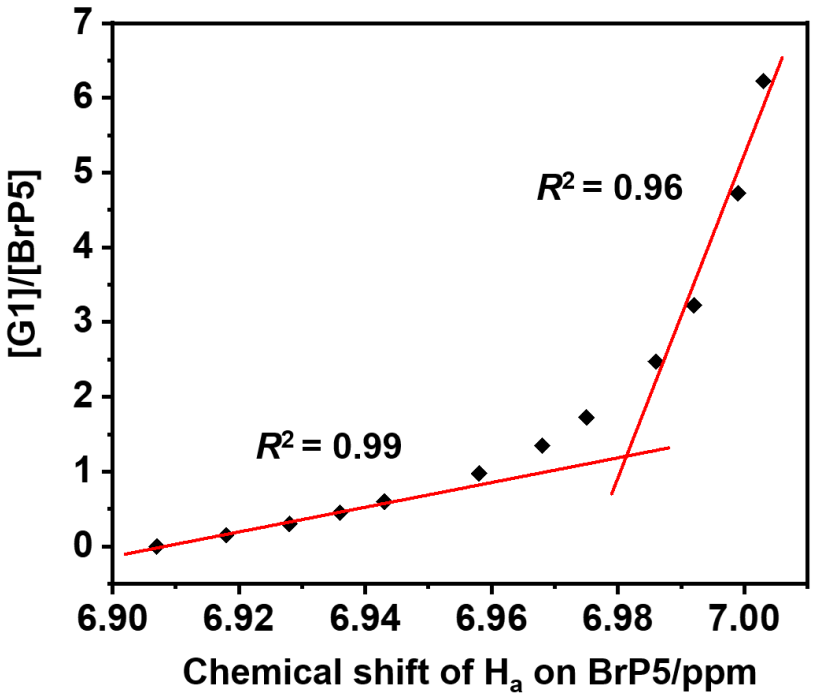


Fig. S5 Molar ratio plot for the complexation between **BrP5** and **G1** in chloroform-*d*, indicating a 1:1 binding stoichiometry.

By a non-linear curve-fitting method, the association constant of **BrP5⊃G2** was estimated to be (89 ± 20) M^{-1}. By a mole ratio plot, a 1:1 stoichiometry was also obtained.

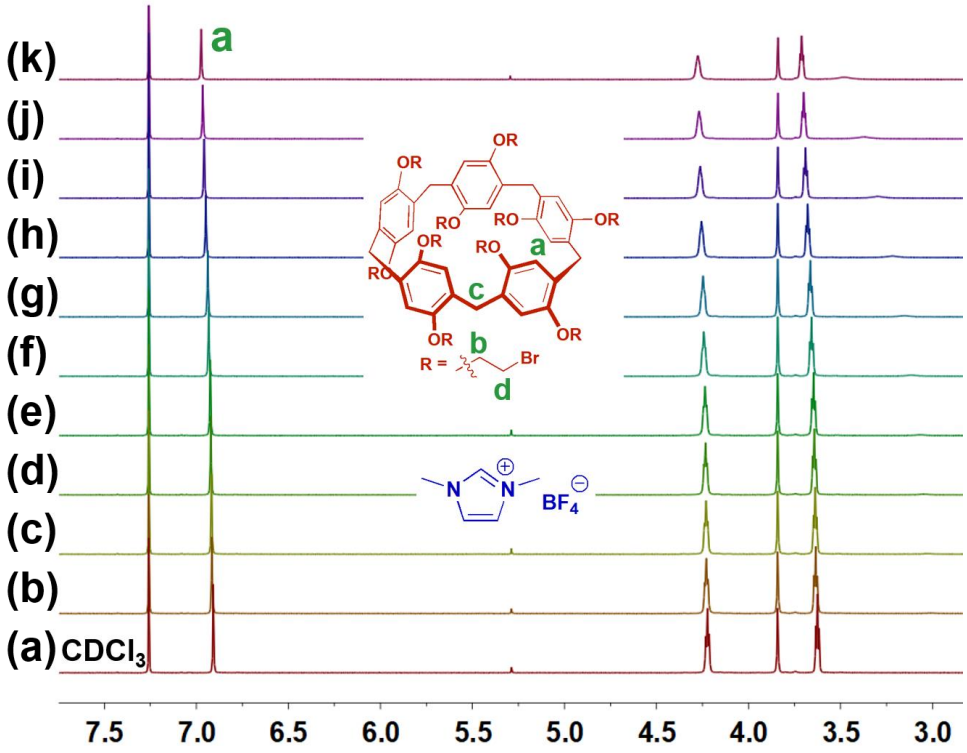


Fig. S6 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature) of **BrP5** at a constant concentration of 2.0 mM upon gradually addition of **G2** (15.0 mM): (a) 0.00 μL, (b) 10.0 μL, (c) 20.0 μL, (d) 30.0 μL, (e) 40.0 μL, (f) 65.0 μL, (g) 90.0 μL, (h) 115 μL, (i) 165 μL, (j) 215 μL, and (k) 315 μL.

The non-linear curve-fitting was based on the equation:

$\Delta\delta = (\Delta\delta_\infty/[\mathbf{BrP5}]_0)\ (0.5[\mathbf{G2}]_0 + 0.5([\mathbf{BrP5}]_0 + 1/K_a) - (0.5\ ([\mathbf{G2}]_0^2 + (2[\mathbf{G2}]_0(1/K_a - [\mathbf{BrP5}]_0)) + (1/K_a + [\mathbf{BrP5}]_0)^2)^{0.5}))$ (Eq. S2)

where $\Delta\delta$ is the chemical shift change of H_a on **BrP5** at $[\mathbf{G2}]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_a when the host is completely complexed, $[\mathbf{BrP5}]_0$ is the fixed initial concentration of the host, and $[\mathbf{G2}]_0$ is the initial concentration of **G2**.

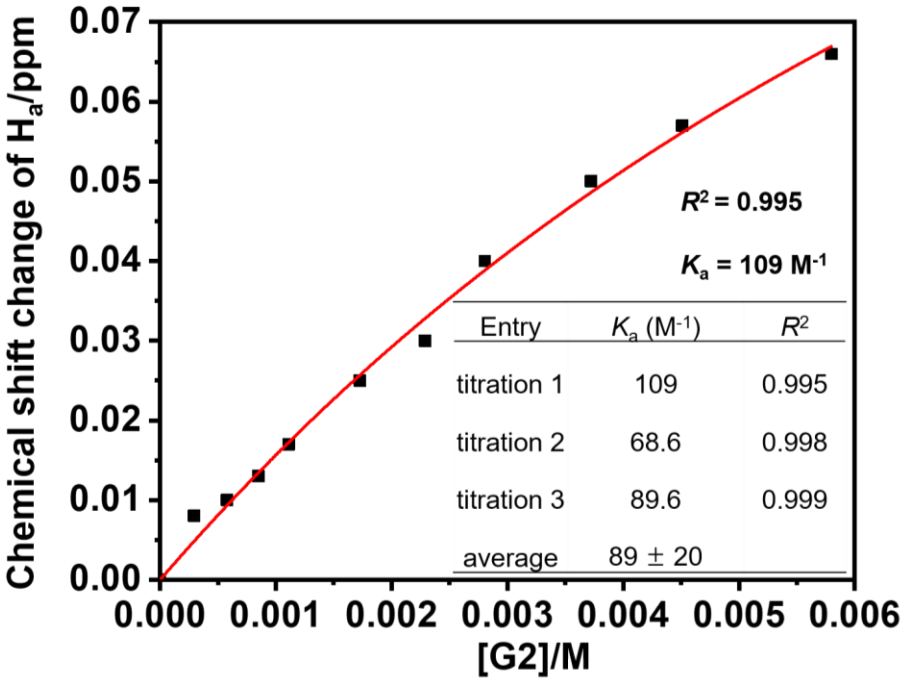


Fig. S7 The chemical shift changes of H_a on **BrP5** upon addition of **G2**. The red solid line was obtained from the non-linear curve-fitting using the above equation.

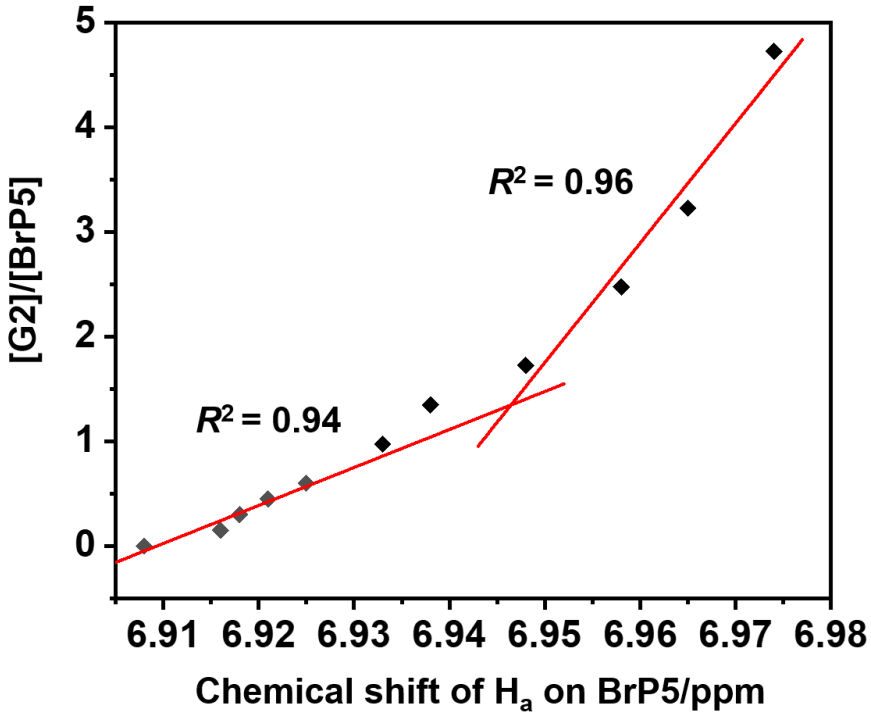


Fig. S8 Molar ratio plot for the complexation between **BrP5** and **G2** in chloroform-*d*, indicating a 1:1 binding stoichiometry.

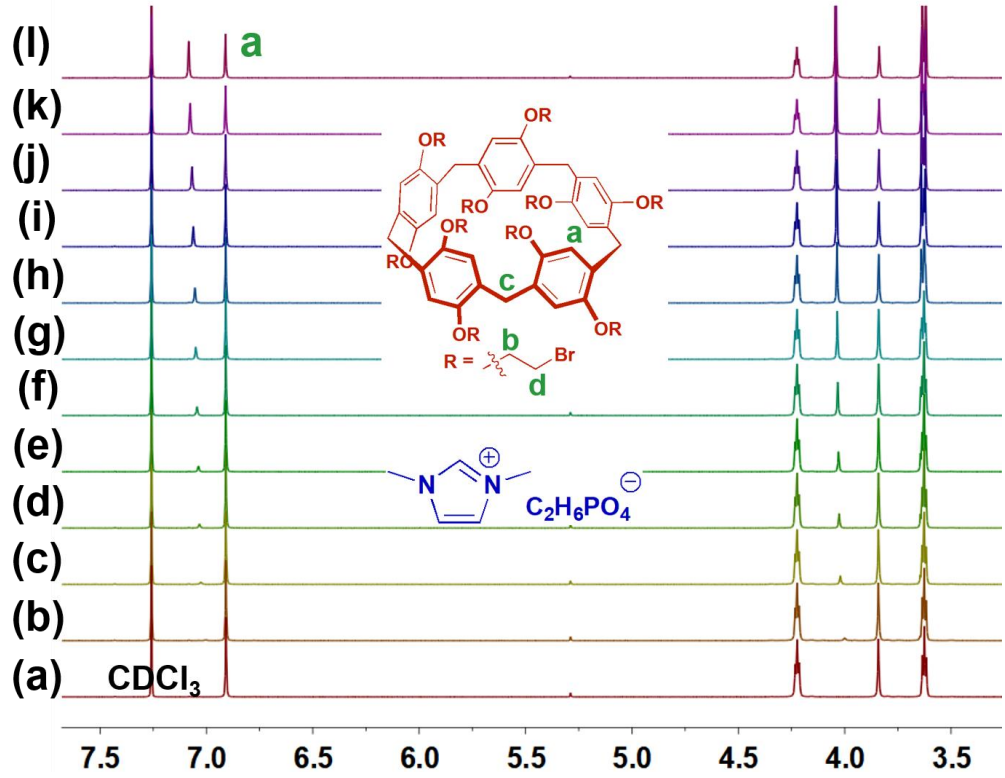


Fig. S9 Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, room temperature) of **BrP5** at a constant concentration of 2.0 mM upon gradually addition of **G3** (15.0 mM): (a) 0.00 μL, (b) 10.0 μL, (c) 20.0 μL, (d) 30.0 μL, (e) 40.0 μL, (f) 65.0 μL, (g) 90.00 μL, (h) 115 μL, (i) 165 μL, (j) 215 μL, (k) 315 μL, and (l) 415 μL.

Only very small shifts were observed for the H_a protons of the host **BrP5** even after the addition of 6.0 equiv. of **G3**. This observation suggests very weak host–guest binding of **G3** inside the inner cavity of the host **BrP5**. Therefore, the association constant was too small to be calculated for this complex.[S4]

*5. Electrospray ionization mass spectrum of a chloroform solution of **BrP5** and **G1***

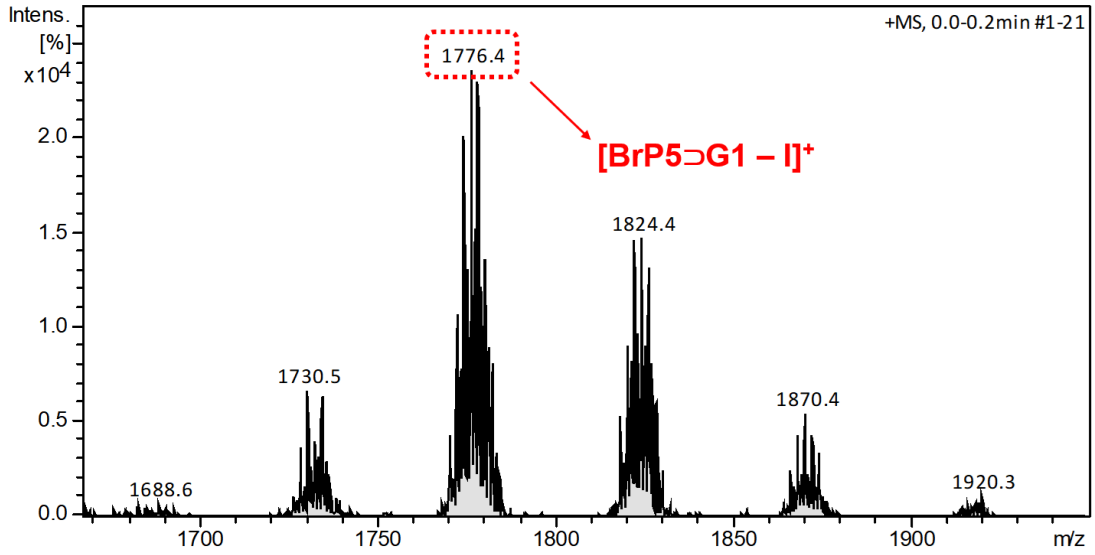


Fig. S10 The positive electrospray ionization mass spectrum of the [2]pseudorotaxane **BrP5⊃G1**. Assignment of the peak: *m/z* 1776.4 [**BrP5⊃G1** – I]$^+$, confirming the 1:1 complexation stoichiometry between **BrP5** and **G1**.

*6. Lower critical solution temperature studies of **G1** in the presence of **BrP5***

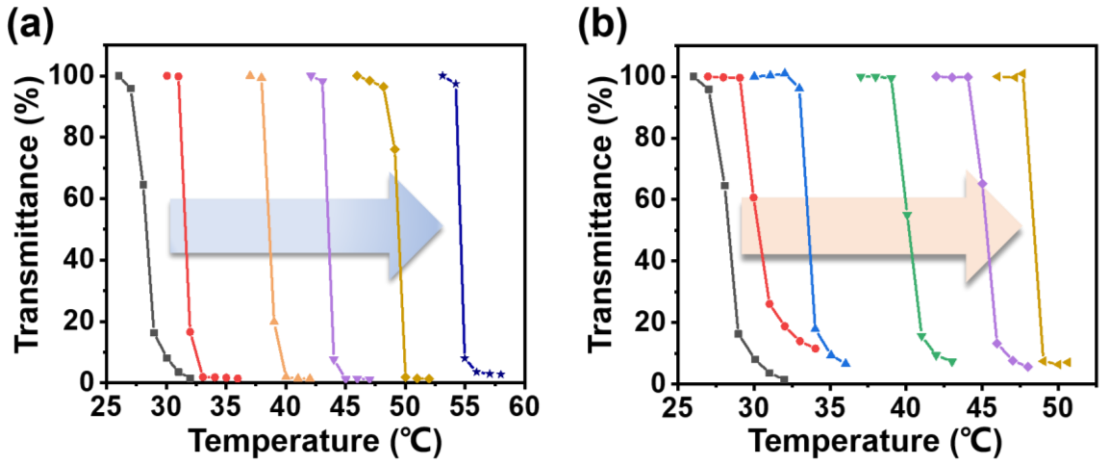


Fig. S11 (a) Temperature-dependence of light transmittance of the mixtures of **BrP5** and **G1** with different initial concentrations of **G1** (0.25 M, 0.30 M, 0.35 M, 0.45 M, 0.55 M and 0.75 M, from left to right, respectively), and the molar ratio of **BrP5** to **G1** was kept as a constant at 0.10. (b) The light transmittance as a function of temperature upon changing the molar ratio of **BrP5** to **G1** (0.10, 0.11, 0.12, 0.13, 0.14 and 0.15, from left to right, respectively), while the concentration of **G1** was kept at a constant concentration of 0.25 M.

*7. DLS studies of **G1** in the presence of **BrP5***

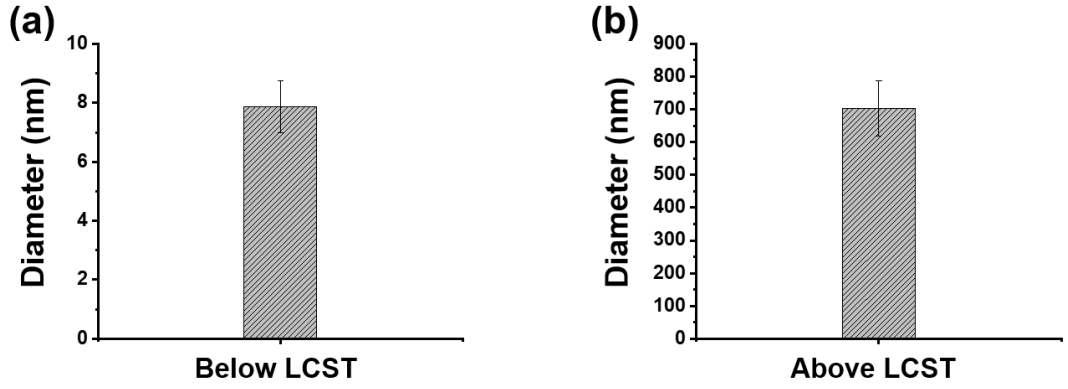


Fig. S12 The average size of **G1** in the presence of **BrP5** below (a) and above its LCST (b). [**G1**] = 0.25 M and the molar ratio of **BrP5** to **G1** was kept as a constant at 0.10.

*8. X-ray crystal data of the [2]pseudorotaxane **BrP5⊃G1***

Colorless and transparent crystals were obtained by *i*-Pr_2O vapor diffusion into a 1 mL chloroform solution containing equimolar **BrP5** and **G1**. Suitable crystals were isolated for single crystal X-ray diffraction. The molar ratio of **BrP5** and **G1** in the resulting [2]pseudorotaxane crystal structure was 1 : 1. CCDC number: 2065029.

Table S1. Experimental crystallographic data for the crystal of **BrP5⊃G1**.

Parameters	**BrP5⊃G1**
Formula	$C_{60}H_{69}Br_{10}IN_2O_{10}$
FW	1904.17
Temp. (K)	170.01
Crystal system	Triclinic
Space group	*P*-1
a (Å)	12.398(4)
b (Å)	15.694(6)
c (Å)	18.199(7)
α (°)	82.11(2)
β (°)	81.111(16)
γ (°)	75.804(16)
Volume (Å^3)	3373(2)
Z	2
ρ_{calc} (g cm^{-3})	1.875
F (000)	1852.0
Independent reflections	13742 [R_{int} = 0.0632, R_{sigma} = 0.0795]
Goodness-of-fit on F^2	0.899
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.1184,

	wR_2 = 0.2811
Final *R* indexes	R_1 = 0.1476,
[all data]	wR_2 = 0.2997
Largest diff. peak/hole (e Å^{-3})	3.63/-3.22

9. References:

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S2. Y. Ma, X. Ji, F. Xiang, X. Chi, C. Han, J. He, Z. Abliz, W. Chen and F. Huang, A Cationic Water-Soluble Pillar[5]arene: Synthesis and Host–Guest Complexation with Sodium 1-Octanesulfonate, *Chem. Commun.*, 2011, **47**, 12340–12342.

S3. T. Ogoshi, R. Shiga and T.-a. Yamagishi, Reversibly Tunable Lower Critical Solution Temperature Utilizing Host–Guest Complexation of Pillar[5]arene with Triethylene Oxide Substituents, *J. Am. Chem. Soc.*, 2012, **134**, 4577–4580.

S4. N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, Monofunctionalized Pillar[5]arene as a Host for Alkanediamines, *J. Am. Chem. Soc.*, 2011, **133**, 5668–5671.