

A cationic water-soluble pillar[5]arene: synthesis and host – guest complexation with sodium 1-octanesulfonate

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Electronic Supplementary Information (13 pages)

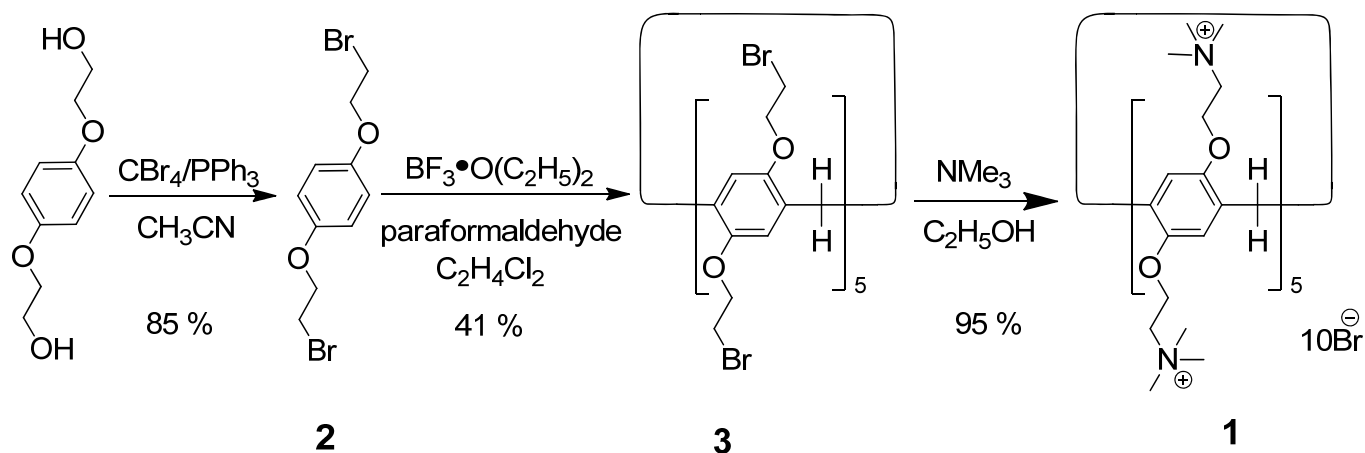
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|---|-----|
| 1. <i>Materials and methods</i> | S2 |
| 2. <i>Syntheses of compounds 1, 2 and 3</i> | S3 |
| 3. <i>Stoichiometry and association constant determination for the complexation between 1 and G</i> | S10 |
| 4. <i>Electrospray ionization mass spectrum of an equimolar water solution of 1 and G</i> | S12 |

1. Materials and methods

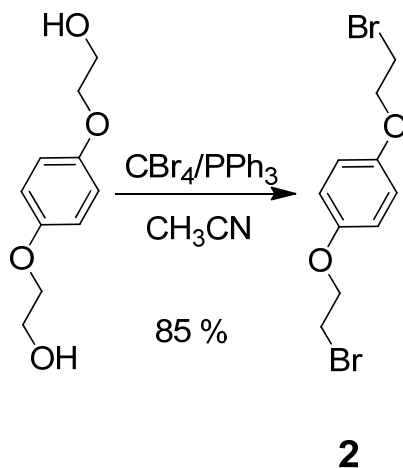
All reagents were commercially available and used as supplied without further purification. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. High resolution mass spectra were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

2. Synthesis of **1**

Scheme S1. Synthesis of **1**.



2.1. Synthesis of compound **2**^{S1}



Carbon tetrabromide (39.8 g, 120 mmol) was slowly added in small portions to a solution of 1,4-bis(2-hydroxyethoxy)benzene (10.0 g, 50.4 mmol) and triphenylphosphine (31.5 g, 120 mmol) in 300 mL of dry acetonitrile at 0 °C with stirring. The reaction mixture was allowed to warm to room temperature, and the resulting clear solution was stirred for another 4 h under N₂. Then 200 mL of cold water was added to the reaction mixture, where product **2** precipitated as a white solid. The product was collected by vacuum filtration, thoroughly washed with methanol/water 60:40, and then recrystallized from methanol. The white flake-like crystals were dried under high vacuum (13.8 g, 85 %). The ¹H NMR spectrum of **2** is shown in Figure S1. ¹H NMR (400 MHz, chloroform-*d*, room temperature) δ (ppm): 6.89 (s, 4H), 4.27 (t, *J* = 6.3 Hz, 4H), 3.64 (t, *J* = 6.3 Hz, 4H).

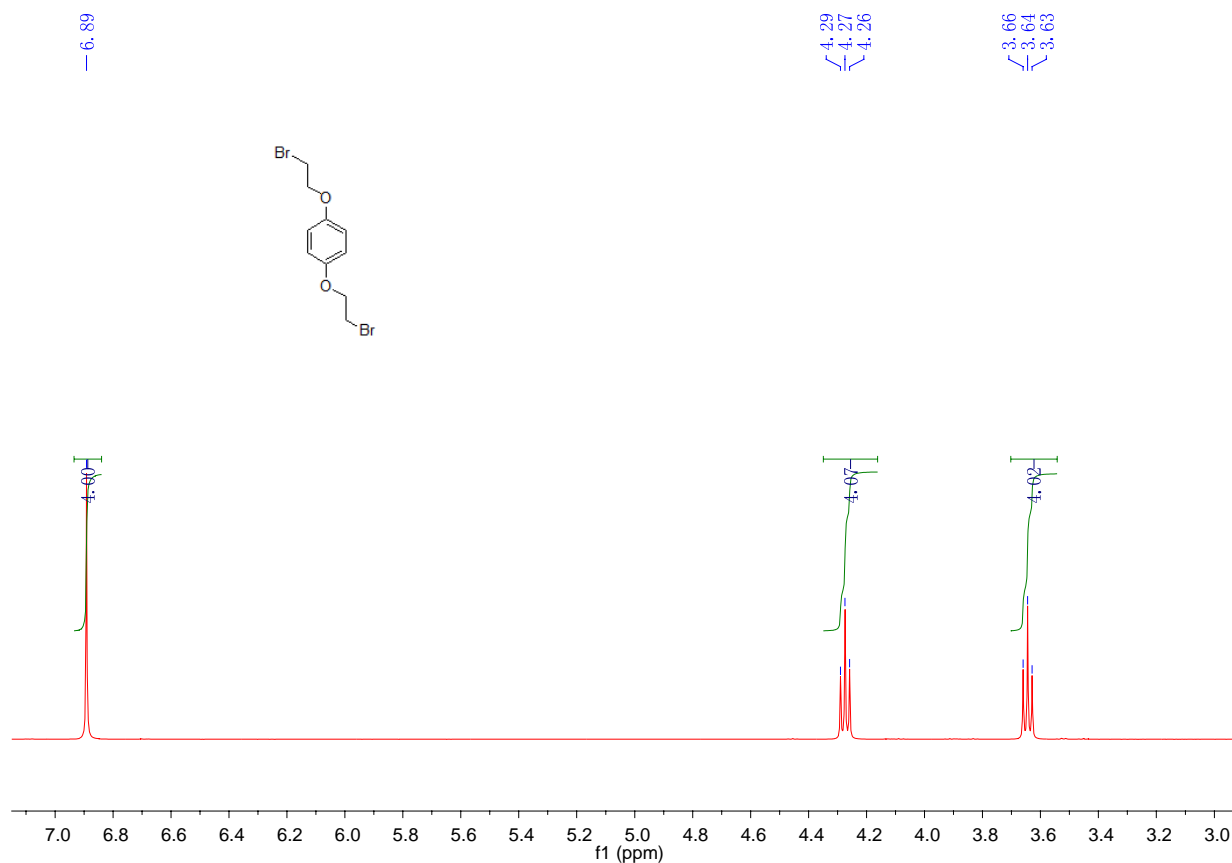
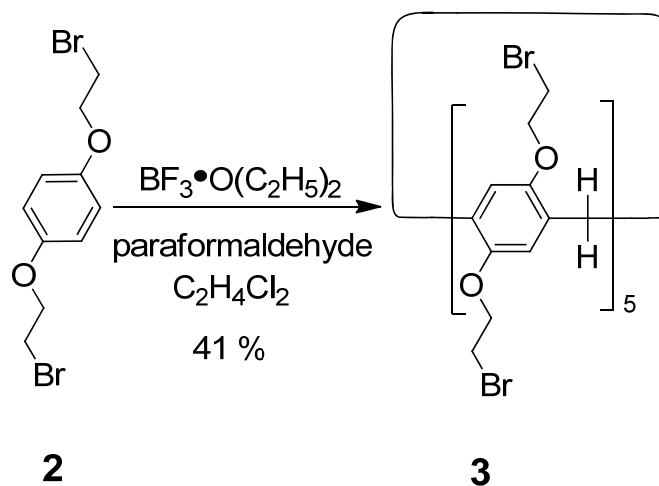


Fig. S1. ¹H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **2**.

2.2. Synthesis of compound **3**^{S2}



To a solution of **2** (3.37 g, 11.5 mmol) in 1, 2-dichloroethane (200 mL), paraformaldehyde (0.349 g, 11.5 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (BF₃·(OC₂H₅)₂, 1.63 g, 11.5 mmol) was added to the solution and the mixture was stirred at room temperature for 3 h. A green solution was got. After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:2 v/v) as the eluent to get a white powder (1.6 g, 41 %). Mp: 95.0–97.0 °C. The ¹H NMR spectrum of **3** is shown in Figure S2. ¹H NMR (400 MHz, chloroform-*d*, room temperature) δ (ppm): 6.93 (s, 10H),

4.25 (t, $J = 5.7$ Hz, 20H), 3.86 (s, 10H), 3.65 (t, $J = 5.7$ Hz, 20H). The ^{13}C NMR spectrum of **3** is shown in Figure S3. ^{13}C NMR (125 MHz, chloroform- d , room temperature) δ (ppm): 149.58, 128.97, 116.00, 68.88, 30.65, and 29.32. LRESIMS is shown in Figure S4: m/z 1702.5 $[\text{M} + \text{Na}]^{1+}$ (100%). HRESIMS is shown in Figure S5: m/z calcd for $[\text{M} + \text{Na}]^+ \text{C}_{55}\text{H}_{60}\text{Br}_{10}\text{O}_{10}$, 1702.5938; found 1702.58.

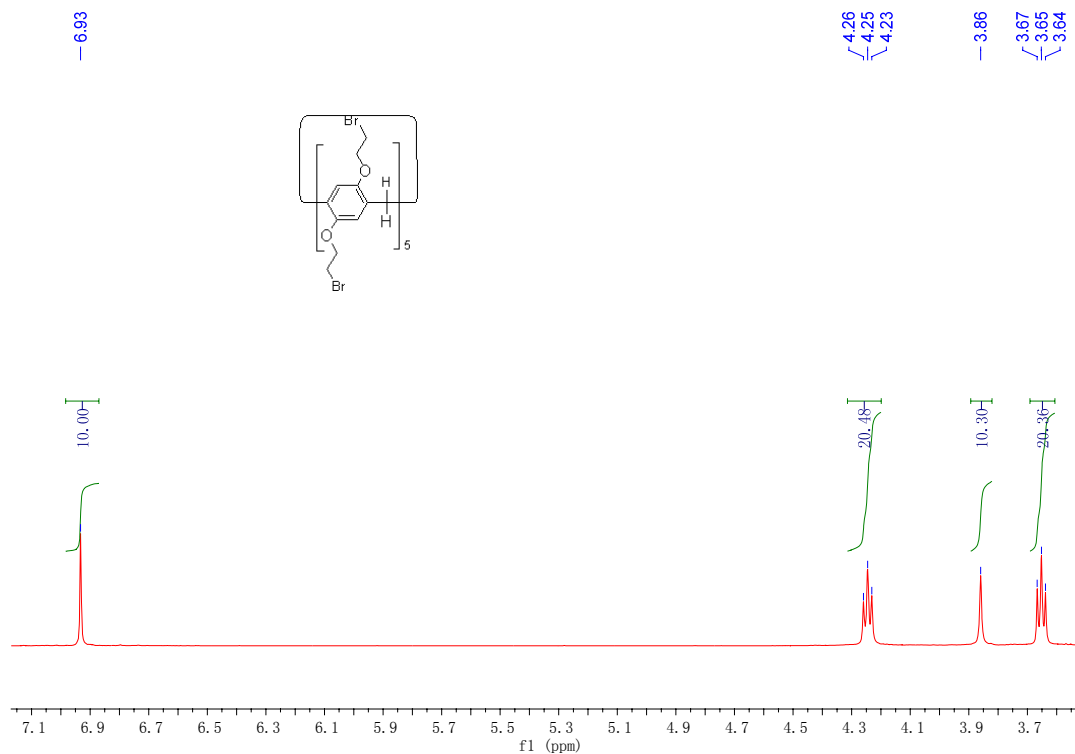


Fig. S2. ^1H NMR spectrum (400 MHz, chloroform- d , room temperature) of **3**.

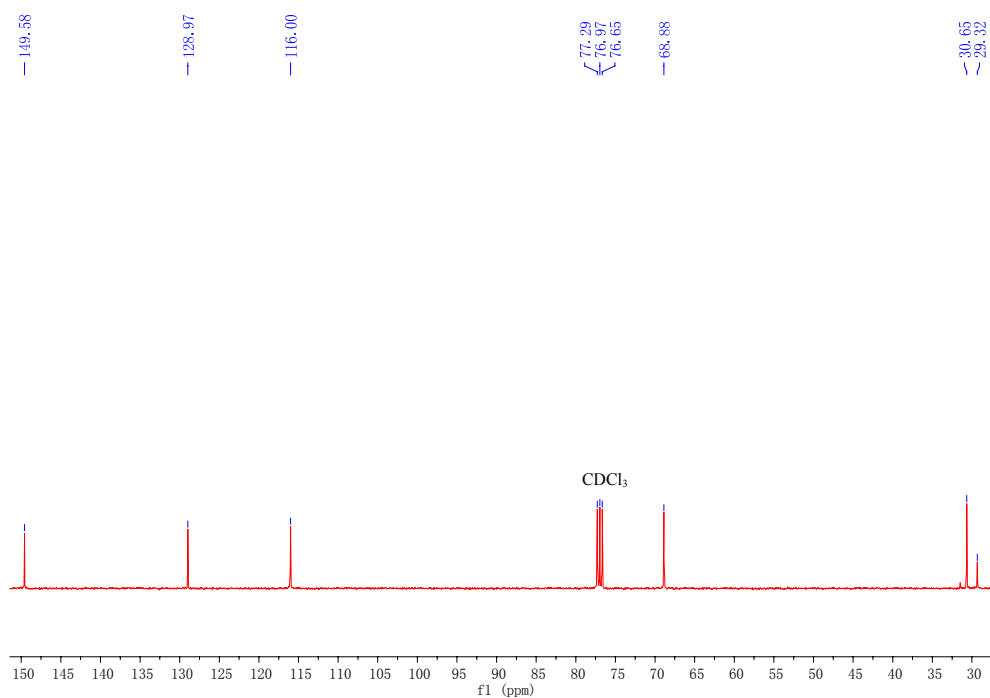


Fig. S3. ^{13}C NMR spectrum (125 MHz, chloroform- d , room temperature) of **3**.

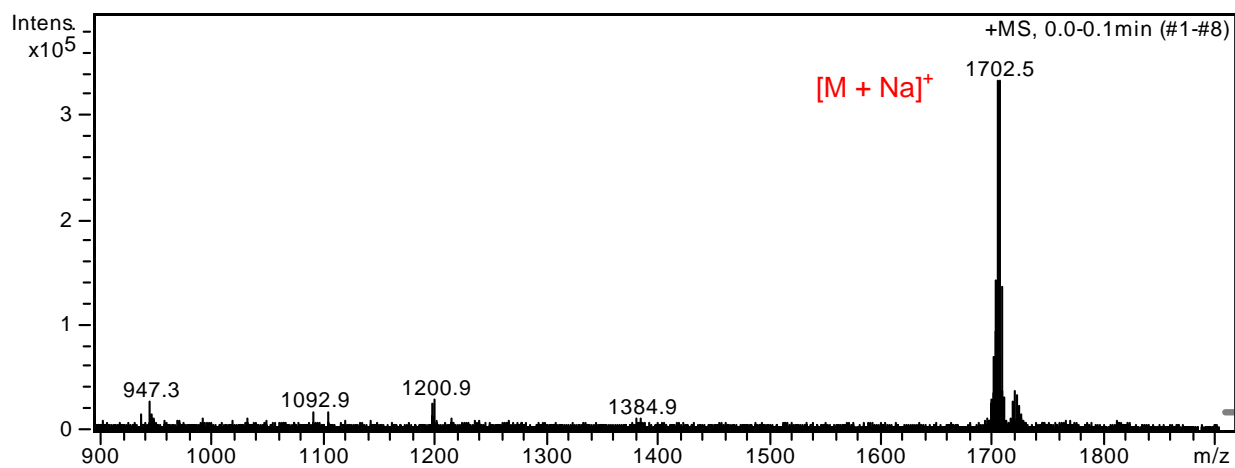


Fig. S4. Electrospray ionization mass spectrum of **3**.

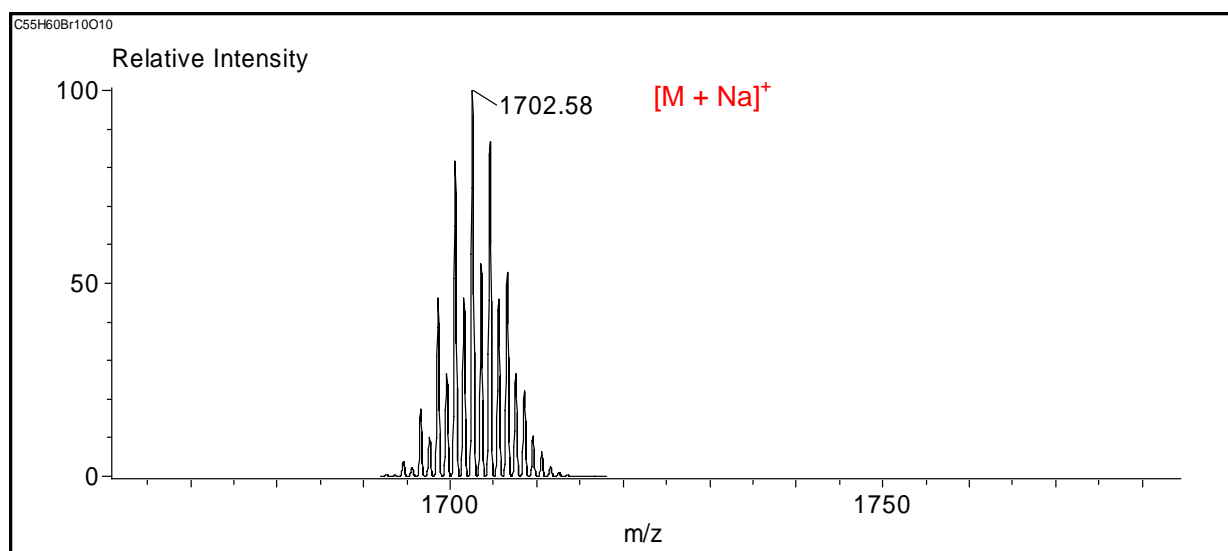
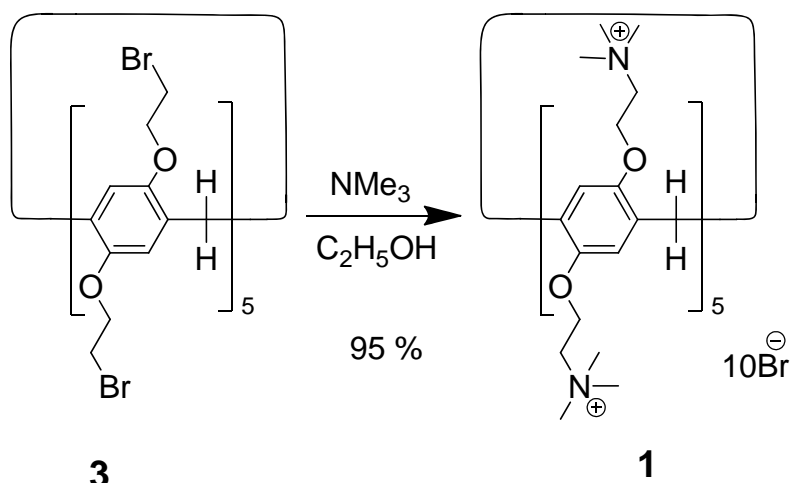


Fig. S5. High resolution electrospray ionization mass spectrum of **3**.

2.2. Synthesis of compound **1**



Compound **3** (1.00 g, 0.595 mmol) and trimethylamine (33 % in ethanol, 6.43 mL, 23.8 mmol) were added to ethanol (50 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation, deionized water (20 mL) was added. After filtration, a clear solution was got. Then the water was removed by evaporation to obtain **1** as a colorless solid (1.28 g, 95 %). Mp: 101.0–103.0 °C. The ¹H NMR spectrum of **1** is shown in Figure S6. ¹H NMR (400 MHz, D₂O, room temperature) δ (ppm): 6.98 (s, 10H), 4.48 (s, 20H), 3.94 (s, 10H), 3.84 (s, 20H), 3.24 (s, 90H). The ¹³C NMR spectrum of **1** is shown in Figure S7. ¹³C NMR (125 MHz, D₂O, room temperature) δ (ppm): 149.30, 129.89, 116.55, 64.91, 63.49, 54.13, and 29.57. LRESIMS is shown in Figure S8: *m/z* 1055.12 [M – 2Br]²⁺, 677.11 [M – 3Br]³⁺, 487.66 [M – 4Br]⁴⁺, 374.31 [M – 5Br]⁵⁺, 298.46 [M – 6Br]⁶⁺. HRESIMS is shown in Figure S9: *m/z* of C₈₅H₁₅₀Br₁₀N₁₀O₁₀ 1055.25 [M – 2Br]²⁺, 677.19 [M – 3Br]³⁺, 487.66 [M – 4Br]⁴⁺, 374.35 [M – 5Br]⁵⁺, 298.47 [M – 6Br]⁶⁺.

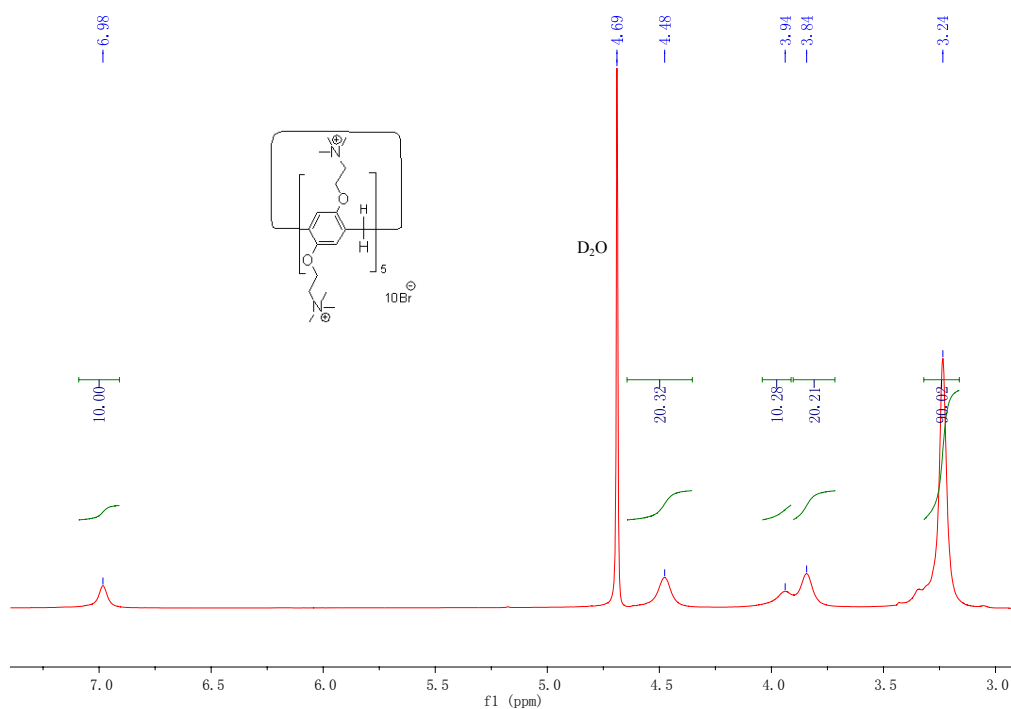


Figure S6. ¹H NMR spectrum (400 MHz, D₂O, room temperature) of **1**.

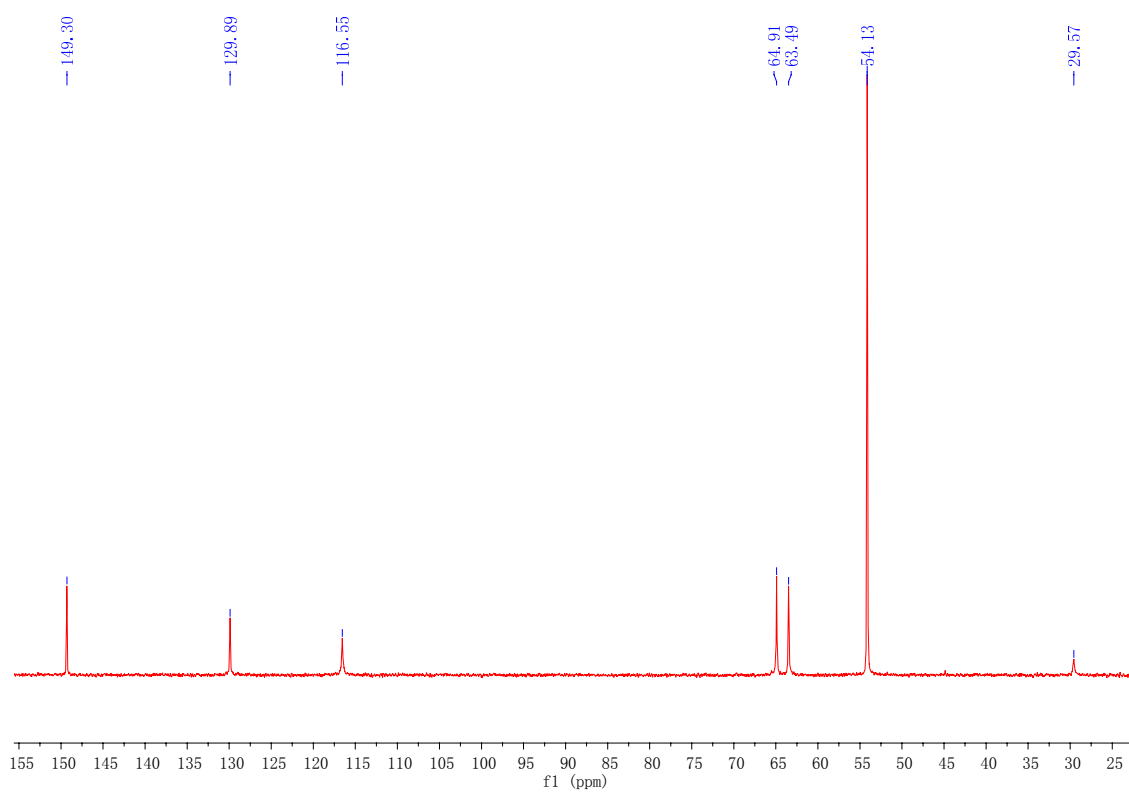


Figure S7. ^{13}C NMR spectrum (125 MHz, D_2O , room temperature) of **1**.

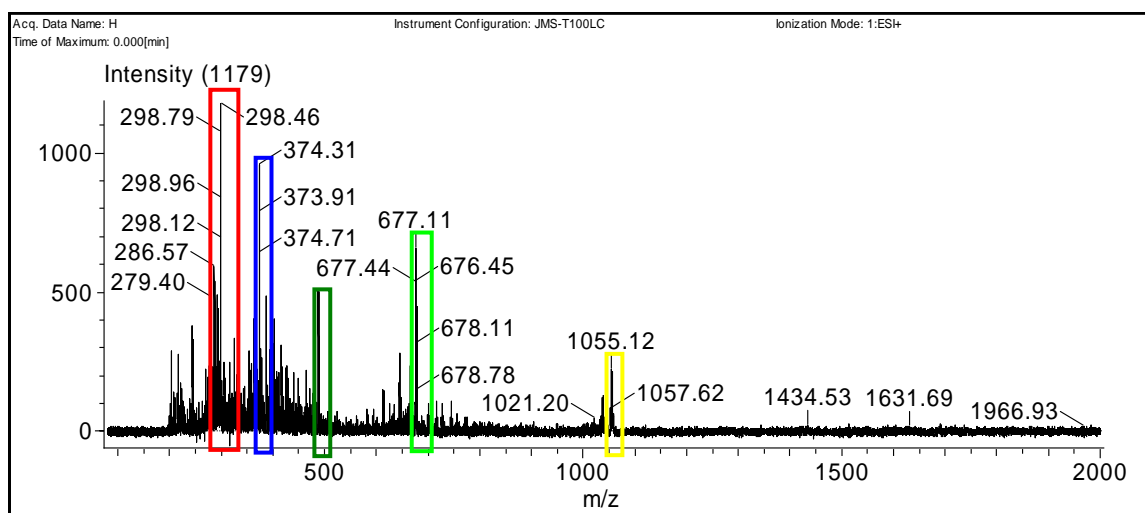
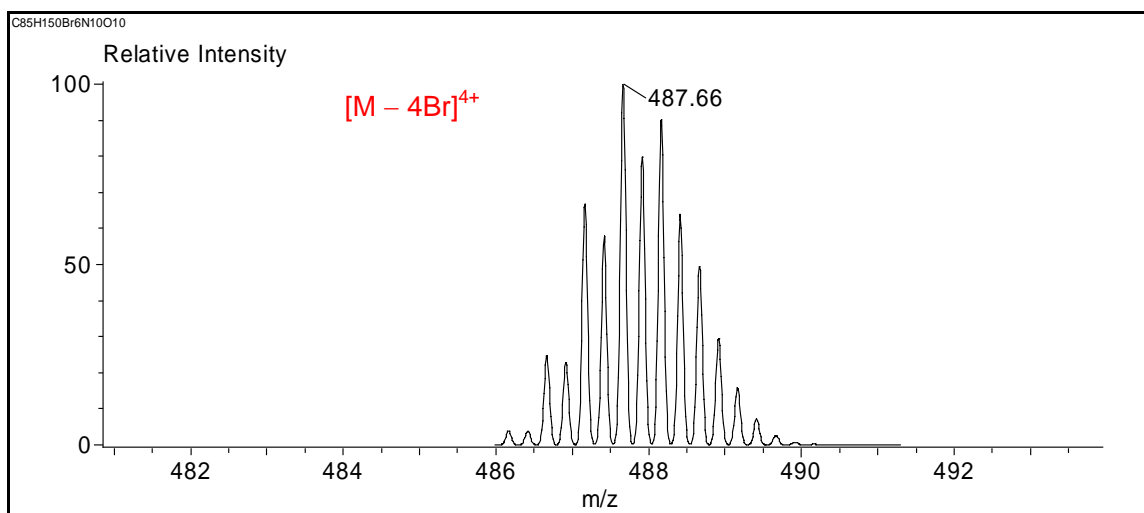
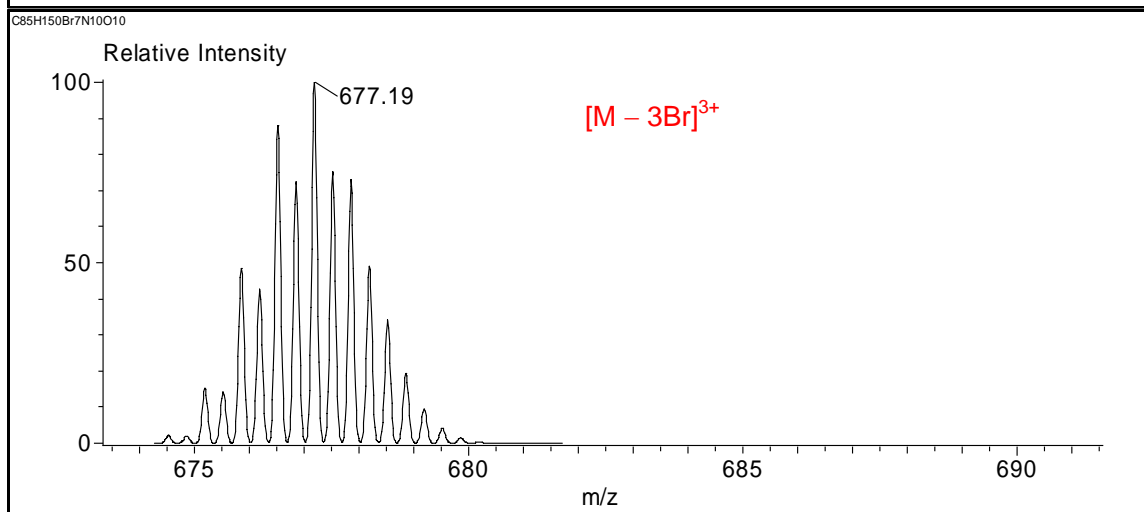
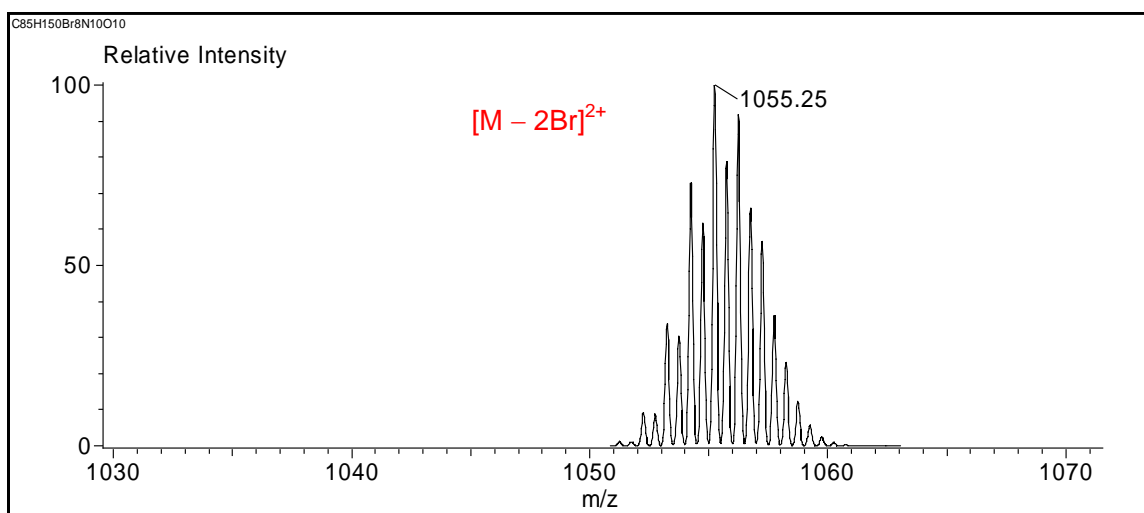


Figure S8. Electrospray ionization mass spectrum of **1**.



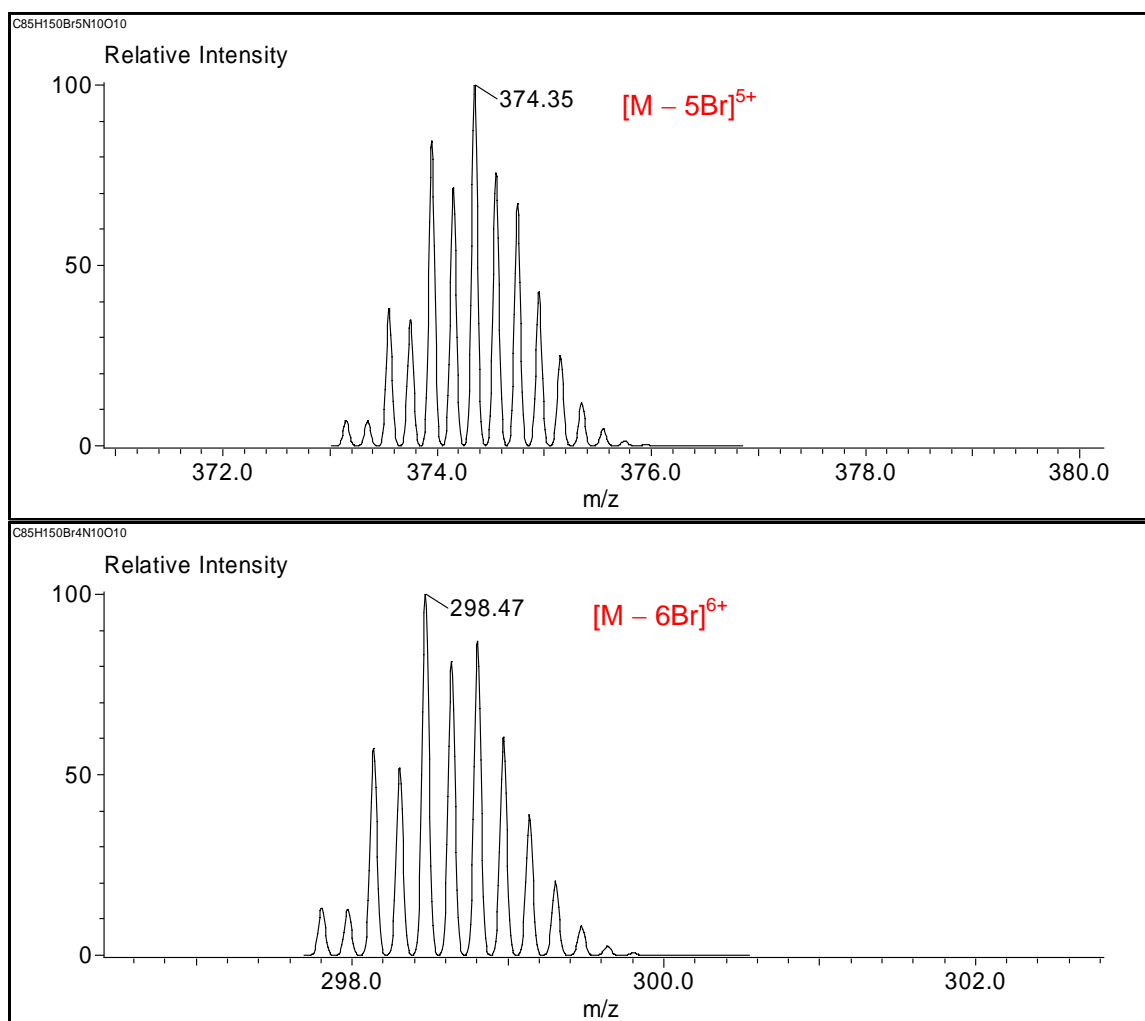


Figure S9. High resolution electrospray ionization mass spectra of **1**.

3. Stoichiometry and association constant determination for the complexation between **1** and **G**

To determine the stoichiometry and association constant between **1** and octyl sodium sulfonate (**G**), ^1H NMR titrations were done with solutions which had a constant concentration of **G** (16 mM) and varying concentrations of **1**. By a non-linear curve-fitting method, the association constant between the guest and **1** was calculated. By a mole ratio plot, a 1:1 stoichiometry was obtained; the guest was shown to form a 1:1 complex with **1**.

The non-linear curve-fitting was based on the equation:^{S3}

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

Where $\Delta\delta$ is the chemical shift change of H_1 on **G** at $[\text{H}]_0$, $\Delta\delta_{\infty}$ is the chemical shift change of H_1 when the guest is completely complexed, $[\text{G}]_0$ is the fixed initial concentration of the guest, and $[\text{H}]_0$ is the varying concentrations of **1**.

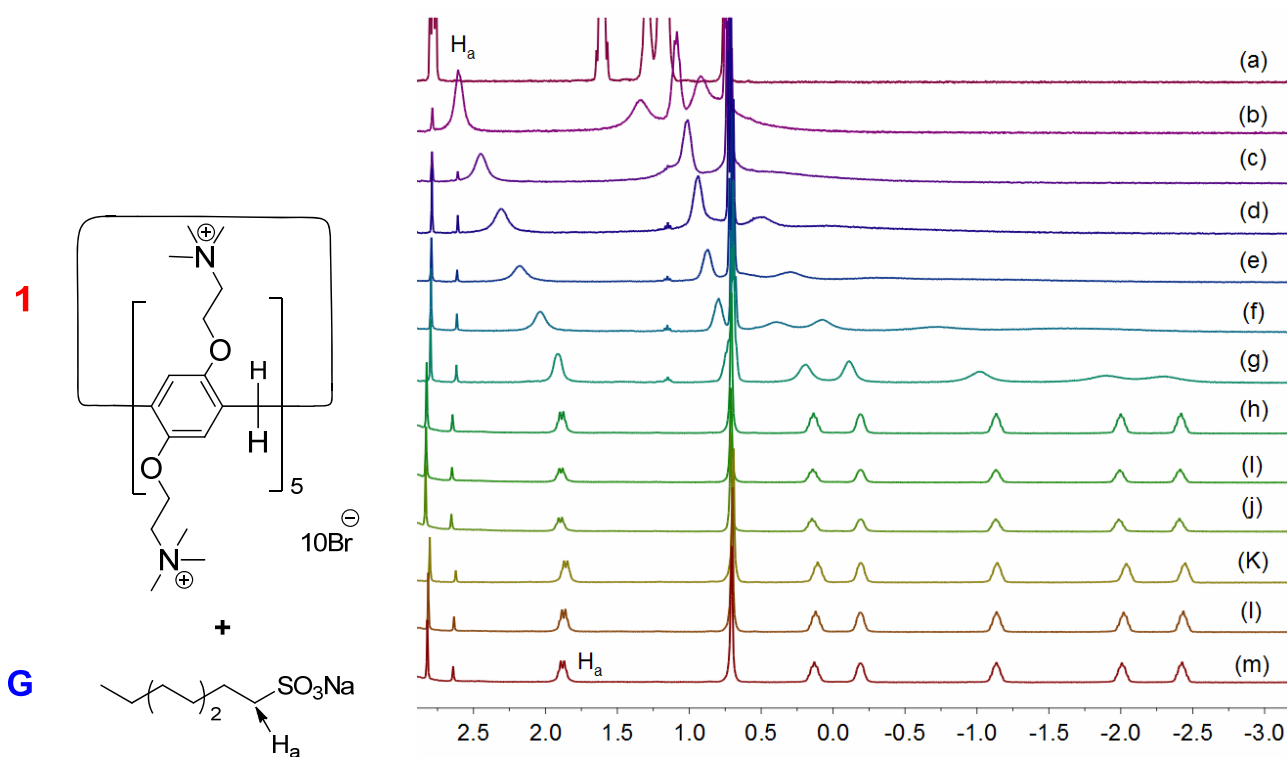


Figure S10. ^1H NMR spectra (D_2O , 293 K, 400 MHz) of **G** at a concentration of 16 mM upon different concentrations of **1**: (a) 0.00 mM, (b) 3.07 mM, (c) 5.92 mM, (d) 8.57mM, (e) 11.03 mM, (f) 13.89 mM, (g) 16.51 mM, (h) 21.18 mM, (i) 25.21 mM, (j) 31.81 mM, (k) 36.99 mM, (l) 44.60 mM, (m) 49.92 mM.

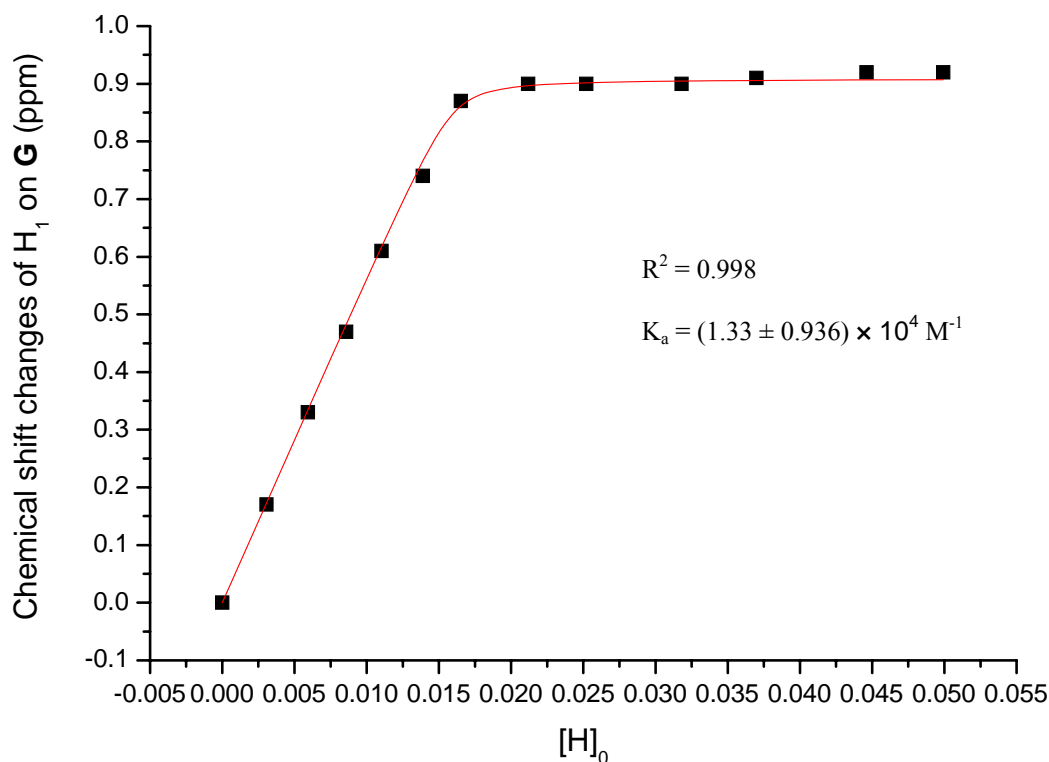


Figure S11. The chemical shift changes of H_1 on **G** upon addition of **1**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

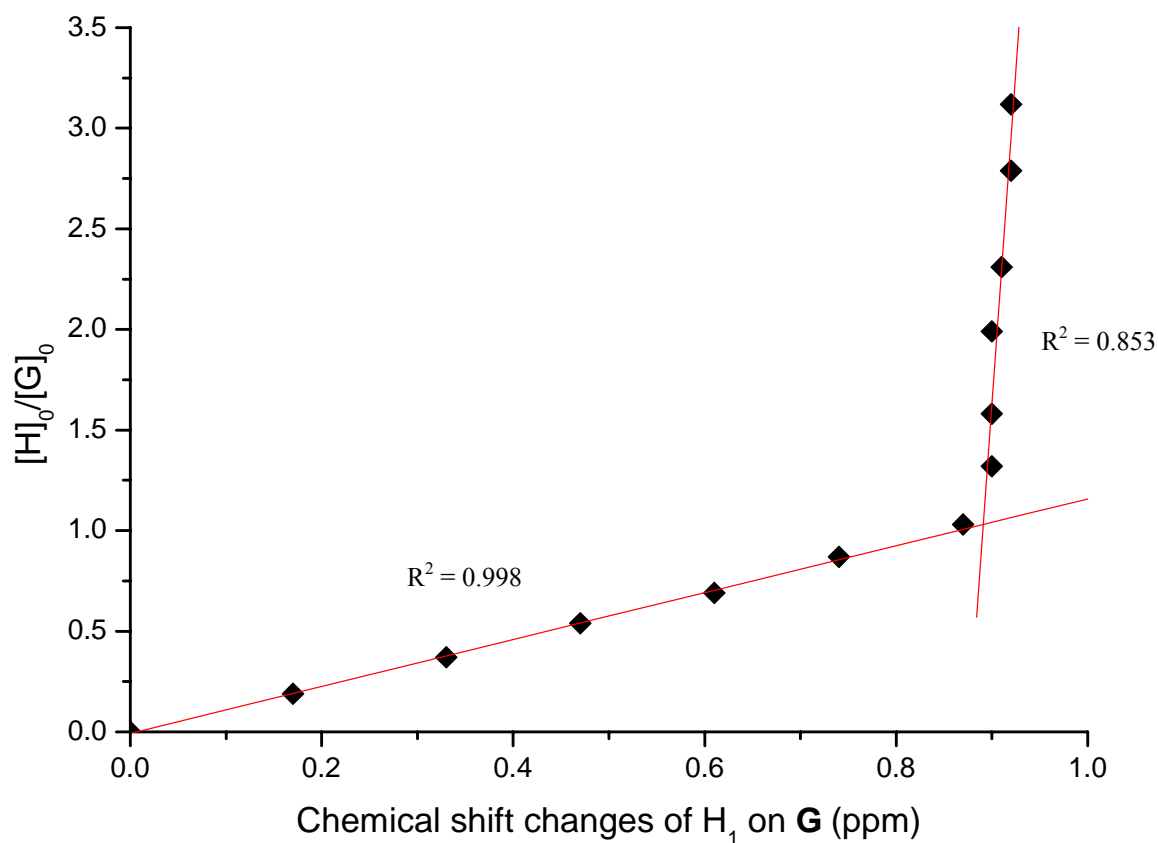
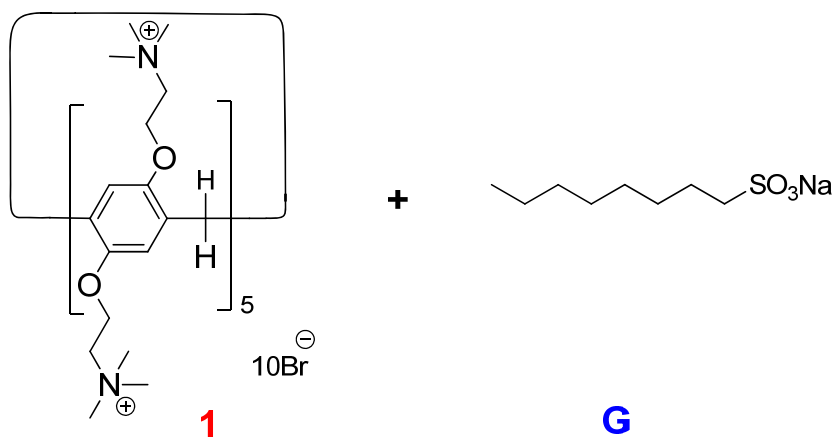


Figure S12. Mole ratio plot for the complexation between **1** and **G**, indicating a 1:1 stoichiometry.

4. Electrospray ionization mass spectrum of an equimolar water solution of **1** with **G**.



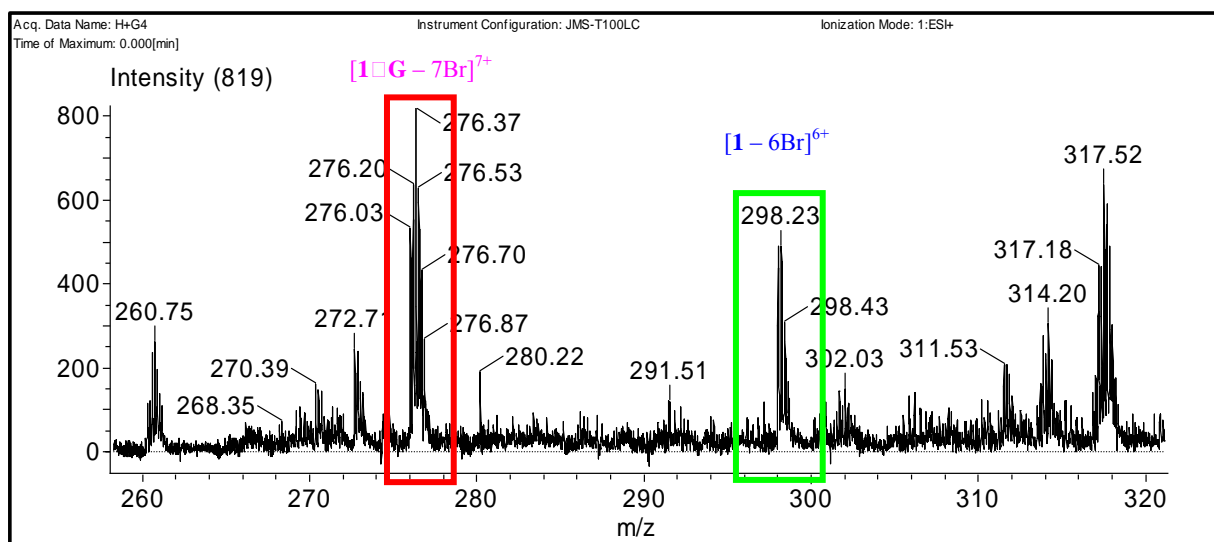


Figure S13. Electrospray ionization mass spectrum of an equimolar water solution of **1** with **G**. Assignment of main peaks: m/z 276.37 $[1 \supset G - 7Br]^{7+}$, 298.23 $[1 - 6Br]^{6+}$.

References:

- S1. M.R. Pinto, B.M. Kristal and K.S. Schanze, *Langmuir*, 2003, **19**, 6523–6533.
- S2. T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022–5023.
- S3. P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931–4951.