Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Investigation of the binding modes of a positive charged pillar[5]arene: internal and external guest complexation.

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Supporting Information Section

1. NMR titration of H by G1

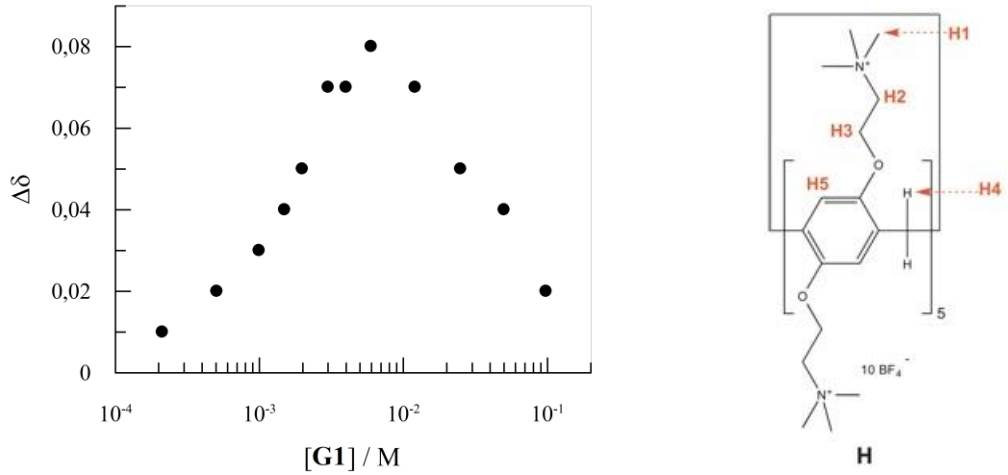


Figure S1. Complexation induced chemical shift (Δδ) for hydrogen atoms H1 of the host for complexation of **G1** by **H** in D_2O at 25 ^{O}C. [**H**]=1.5mM.

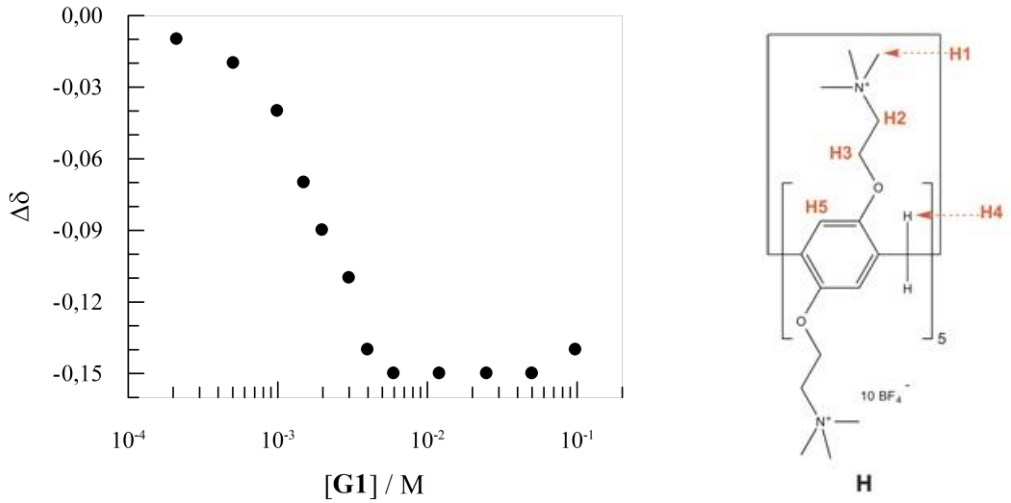


Figure S2. Complexation induced chemical shift (Δδ) for hydrogen atoms H5 of the host for complexation of **G1** by **H** in D_2O at 25 ^{O}C. [**H**]=1.5mM.

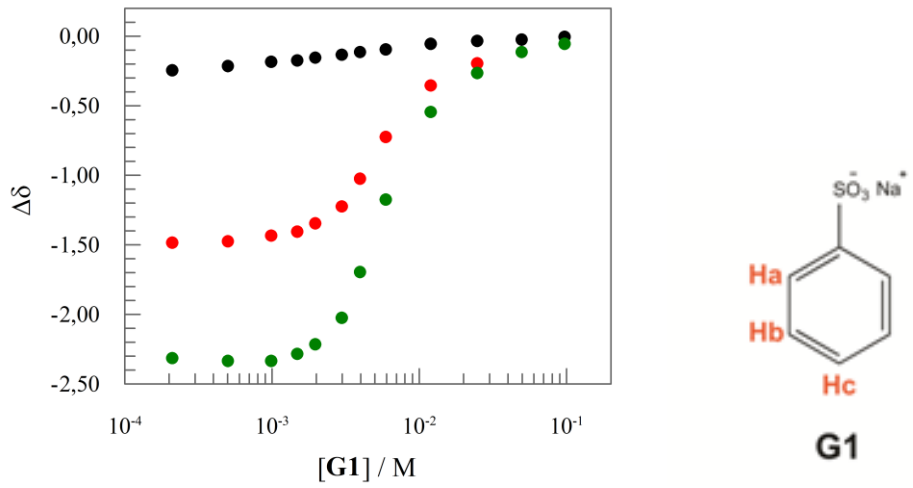


Figure S3. Complexation induced chemical shift (Δδ) for hydrogen of the guest for complexation of **G1** by **H** in D_2O at 25 ^{O}C. [**H**]=1.5mM. (●) Ha; (●) Hb and (●)Hc.

2. NMR titration of H by G2

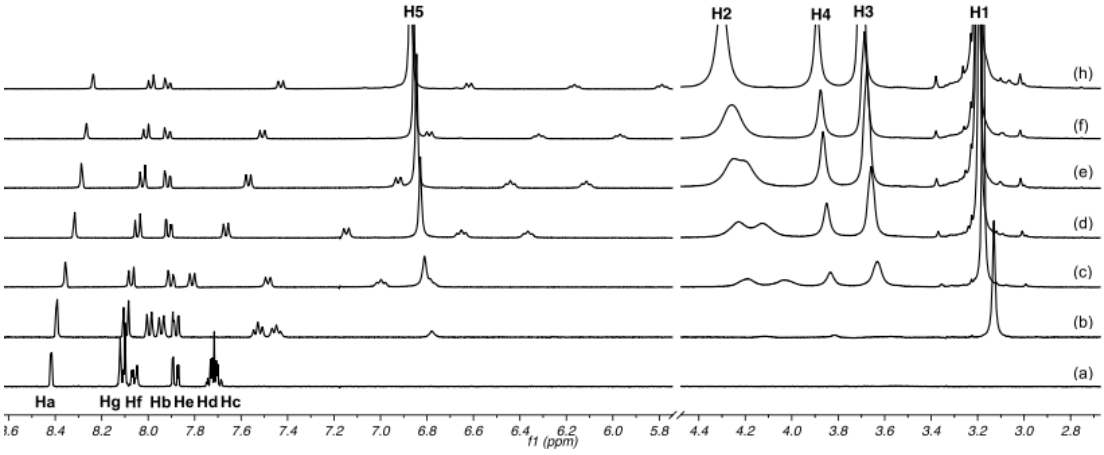


Figure S4. ^{1}H NMR spectra of **G2** (1.5 mM) in the presence of increasing amounts of **H** in D_2O. at 25 ^{O}C: (a) 0 mM, (b) 0.1 mM, (c) 0.5 mM, (d) 1.0 mM, (e) 1.5 mM, (f) 2.0 mM, (g) 3.5 mM. The spectrum (h) is free H (3.5mM).

3. Calorimetric titration of H by G2 and G3

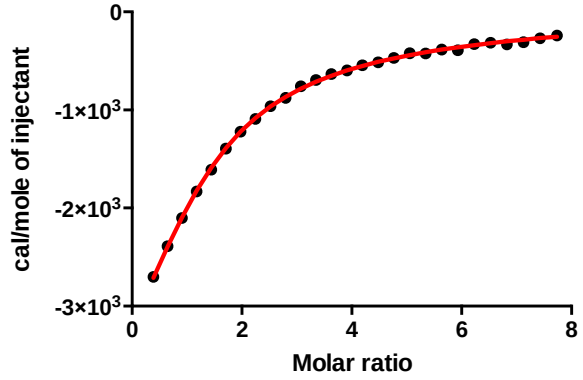


Figure S5. "Net" heat effect of complexation of **H** with **G2** for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using "two sets of binding sites" model.

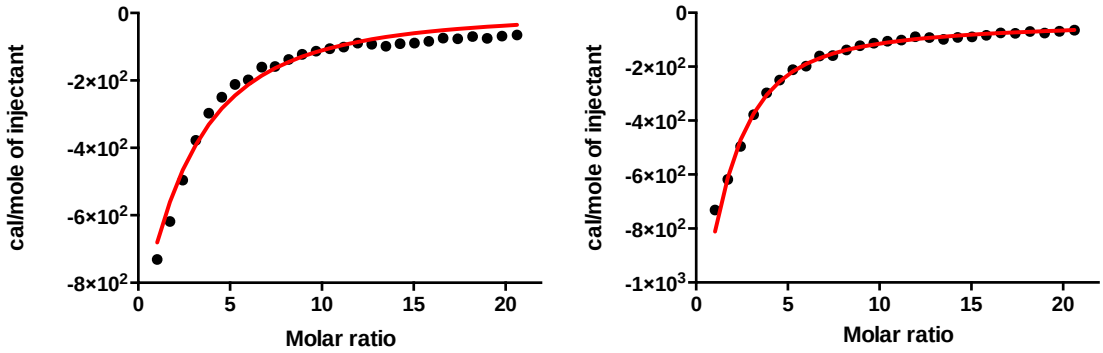
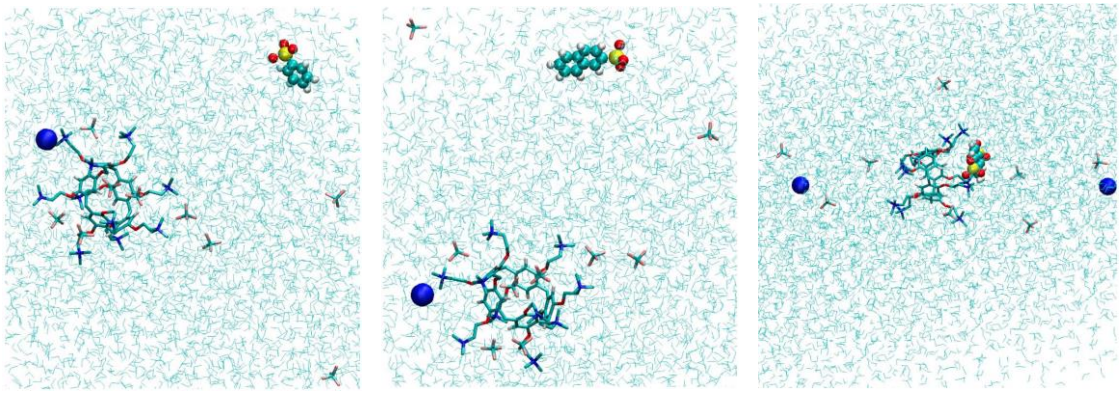


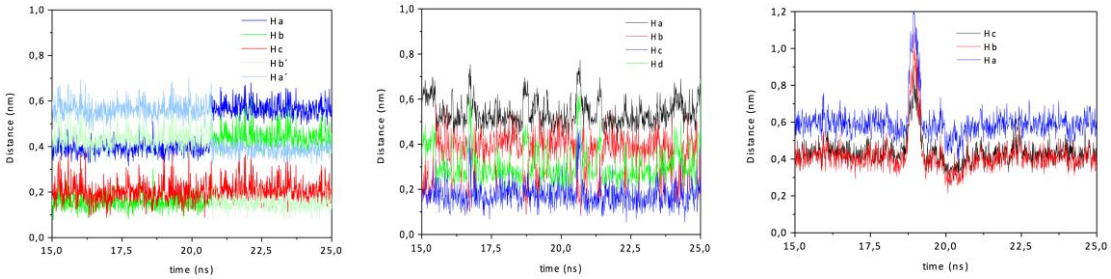
Figure S6. "Net" heat effect of complexation of **H** with **G3** for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation using "one set of binding sites" model (left) or "two sets of binding sites" model (right).

4. MD simulations



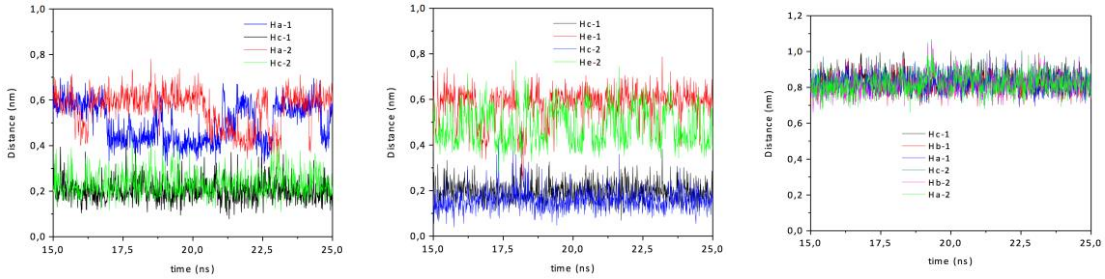
H:G1 **H:G2** **H:G3**

Figure S7. Starting points for the MD simulations, with **G1**, **G2** and **G3** in CPK representation and the **H** in stick representation. Color scheme: carbon = cyan, hydrogen = white, nitrogen = blue, sulfurs = yellow, oxygen = red (except for oxygen from water). Tetrafluoroborate is in stick representation and sodium in VDW representation. Borons, fluors and sodium are cyan, pink and blue, respectively. For simplicity, water molecules are light blue in line representation.



H:G1 **H:G2** **H:G3**

Figure S8. Plots of the distance between the center of the host cavity and selected hydrogens of **G1**, **G2** and **G3** for the 1:1 host-guest complex, as a function of calculation time (15-25 ns).



H:G1 **H:G2** **H:G3**

Figure S9. Plots of the distance between the center of the host cavity and selected hydrogens of **G1**, **G2** and **G3** for 1:2 host-guest complex, as a function of calculated time (15-25 ns).