

Supporting Information

Acid/base responsive pseudo[3]rotaxanes from amine naphthotubes and bis-pyridinium/isoquinolinium guests

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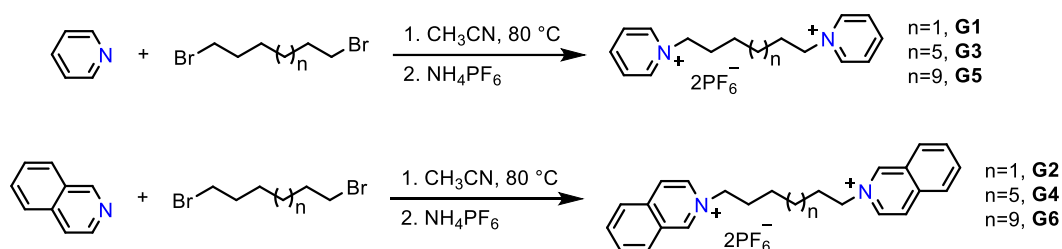
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1. Experimental section

1.1 Materials and methods. All reagents were commercially available and used without further purification. Solvents were either employed as purchased or dried prior to use by standard laboratory procedures. ^1H , ^{13}C NMR, 2D NMR spectra were recorded on a Bruker Avance-400, 500, or 600 NMR spectrometer. Chemical shifts are reported in ppm with residual solvents or TMS (tetramethylsilane) as the internal standards. High-resolution electrospray-ionization mass spectra (HR-ESI-MS) were recorded on an applied Q EXACTIVE mass spectrometry system. UV-vis absorption spectra were obtained on a Hitachi U-2600 UV-vis spectrophotometer. Compounds **H1**¹ and **G2**² were synthesized according to literature procedures.

1.2 Synthetic procedures of G1-G6



Scheme S1. Synthesis of guests **G1-G6**.

General synthetic procedure: Dibromoalkane (1.0 eq.) in MeCN was dropwise added into the solution of pyridine or isoquinoline (2.5 eq.) in MeCN at 80 °C. The resulting mixture was stirred vigorously overnight. After cooling to room temperature, the solution was concentrated in vacuum. The residue was washed with ether to give corresponding bromide salts. Saturated aqueous NH_4PF_6 was dropwise added into the solution of bromide salts in deionized water. After stirring for 6 h at room temperature, the white precipitate was collected through filtration and washed several times with deionized water. The filter cake was dried to afford corresponding products. The characterization data are shown below:

G1: white solid, yield: 76%. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 298 K): δ [ppm] = 9.04 – 8.97 (m, 4H), 8.63 – 8.53 (m, 2H), 8.17 – 8.08 (m, 4H), 4.55 (t, $J = 7.4$ Hz, 4H), 1.91 – 1.87 (t, $J = 7.3$ Hz, 4H), 1.34 – 1.25 (m, 4H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, 298 K):

δ [ppm] = 145.73, 144.79, 128.30, 60.94, 30.53, 24.98. ESI-TOF-HRMS: m/z calcd for $[M-PF_6]^+ C_{16}H_{22}F_6N_2P^+$, 387.1419; found 387.1413 (error = -1.5 ppm).

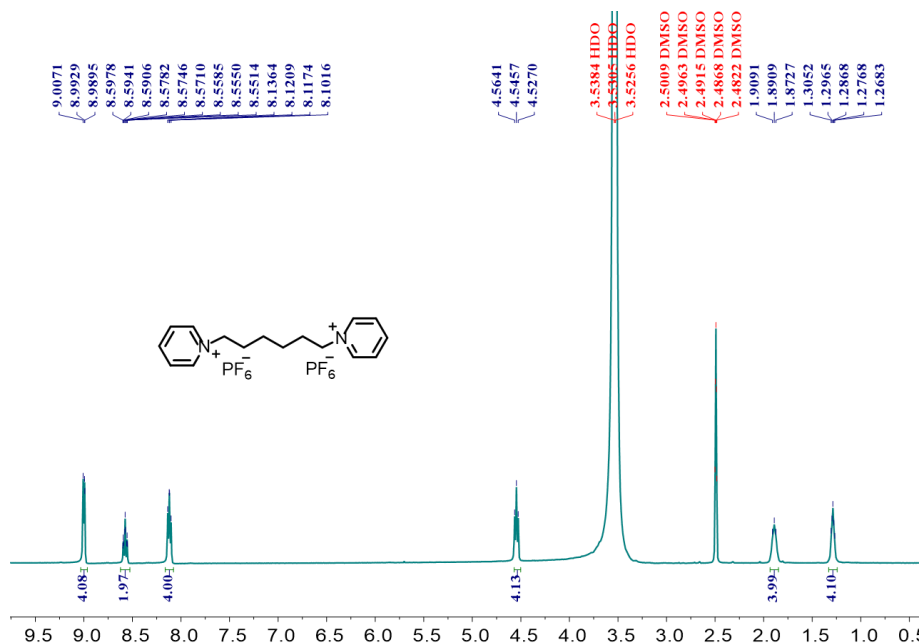


Figure S1. 1H NMR spectrum (400 MHz, DMSO- d_6 , 298 K) of compound G1.

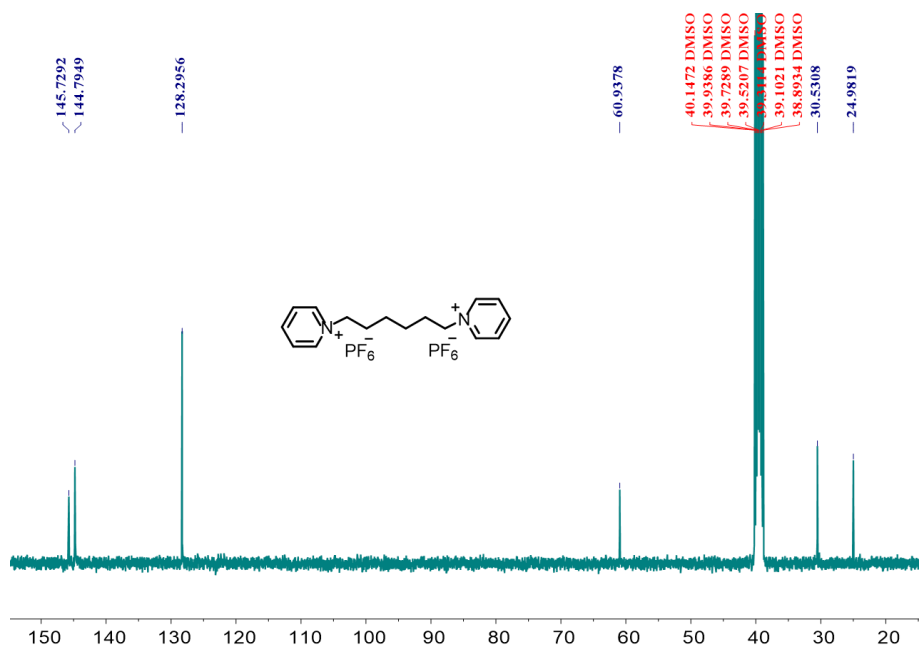


Figure S2. ^{13}C NMR spectrum (101 MHz, DMSO- d_6 , 298 K) of compound G1.

G3: white solid, yield: 48%. 1H NMR (600 MHz, DMSO- d_6 , 298 K): δ [ppm] = 9.06 (d, J = 5.7 Hz, 4H), 8.60 (t, J = 7.7 Hz, 2H), 8.17 – 8.14 (m, 4H), 4.58 (t, J = 7.5 Hz, 4H), 1.93 – 1.87 (m, 4H), 1.32 – 1.22 (m, 12H). ^{13}C NMR (151 MHz, DMSO- d_6 , 298 K): δ [ppm] = 145.46, 144.67, 128.07, 60.81, 30.66, 28.66, 28.34, 25.40. ESI-TOF-

HRMS: m/z calcd for $[M-PF_6]^+ C_{20}H_{30}F_6N_2P^+$, 443.2045; found 443.2035 (error = -2.3 ppm).

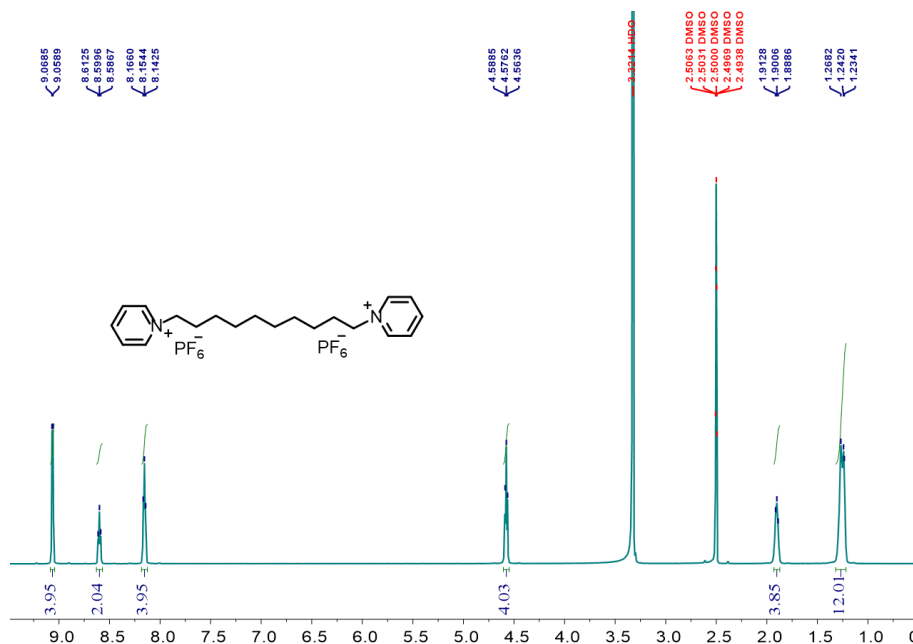


Figure S3. 1H NMR spectrum (600 MHz, $DMSO-d_6$, 298 K) of compound **G3**.

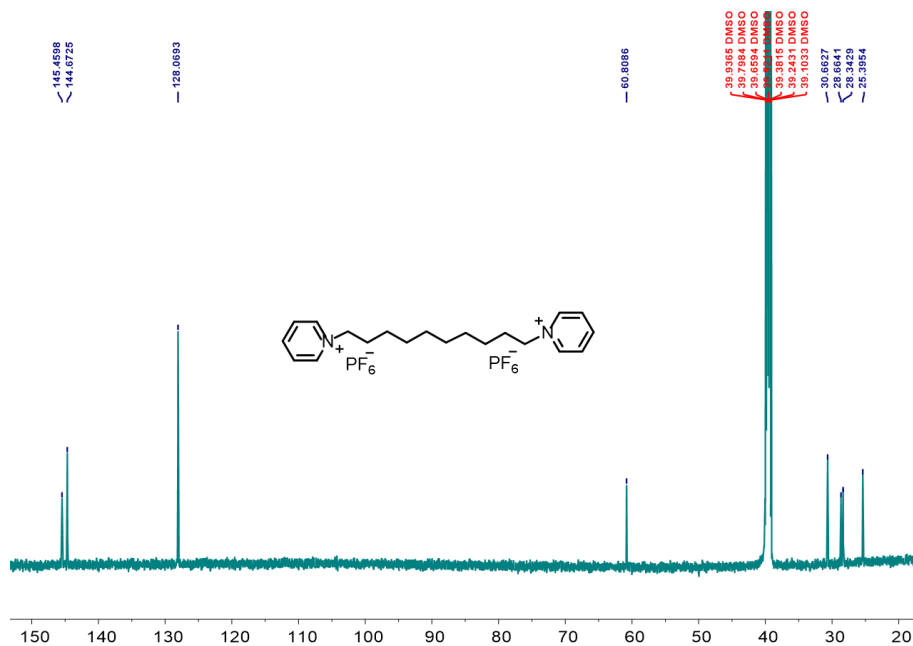


Figure S4. ^{13}C NMR spectrum (151 MHz, $DMSO-d_6$, 298 K) of compound **G3**.

G4: white solid, yield: 71%. 1H NMR (600 MHz, $DMSO-d_6$, 298 K): δ [ppm] = 10.05 (s, 2H), 8.78 (d, J = 6.8 Hz, 2H), 8.59 (d, J = 6.7 Hz, 2H), 8.47 (d, J = 8.3 Hz, 2H), 8.35 (d, J = 8.3 Hz, 2H), 8.28 – 8.25 (m, 2H), 8.10 – 8.06 (m, 2H), 4.72 – 4.66 (m, 4H), 2.01 – 1.98 (m, 4H), 1.31 – 1.29 (m, 8H), 1.25 – 1.23 (m, 4H). ^{13}C NMR (151 MHz, $DMSO-$

d_6 , 298 K): δ [ppm] = 149.88, 136.90, 136.85, 134.86, 131.20, 130.32, 127.25, 127.22, 125.86, 60.80, 30.44, 28.70, 28.42, 25.52. ESI-TOF-HRMS: m/z calcd for $[M-PF_6]^+$ $C_{28}H_{34}F_6N_2P^+$, 543.2358; found 543.2360 (error = 0.4 ppm).

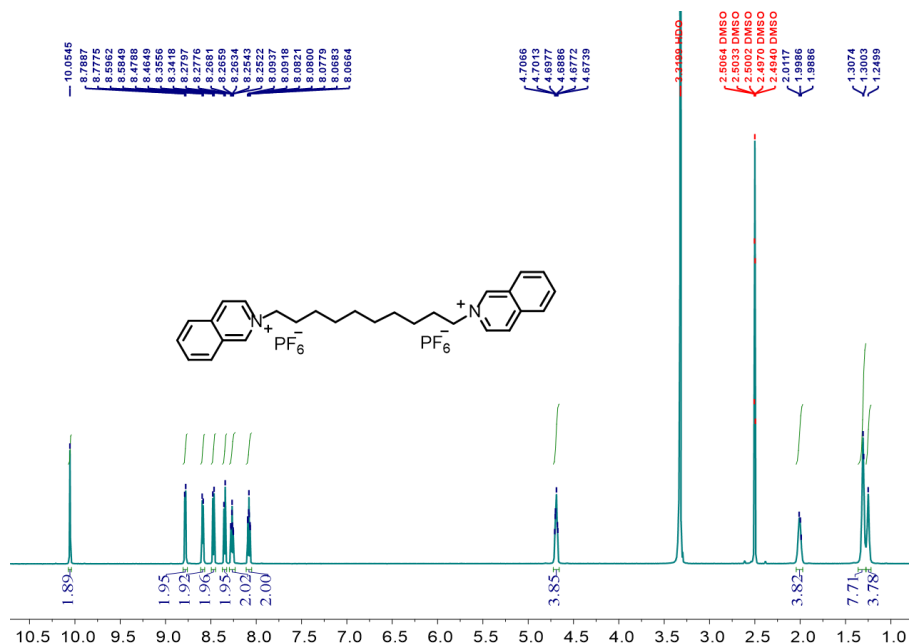


Figure S5. 1H NMR spectrum (600 MHz, DMSO- d_6 , 298 K) of compound G4.

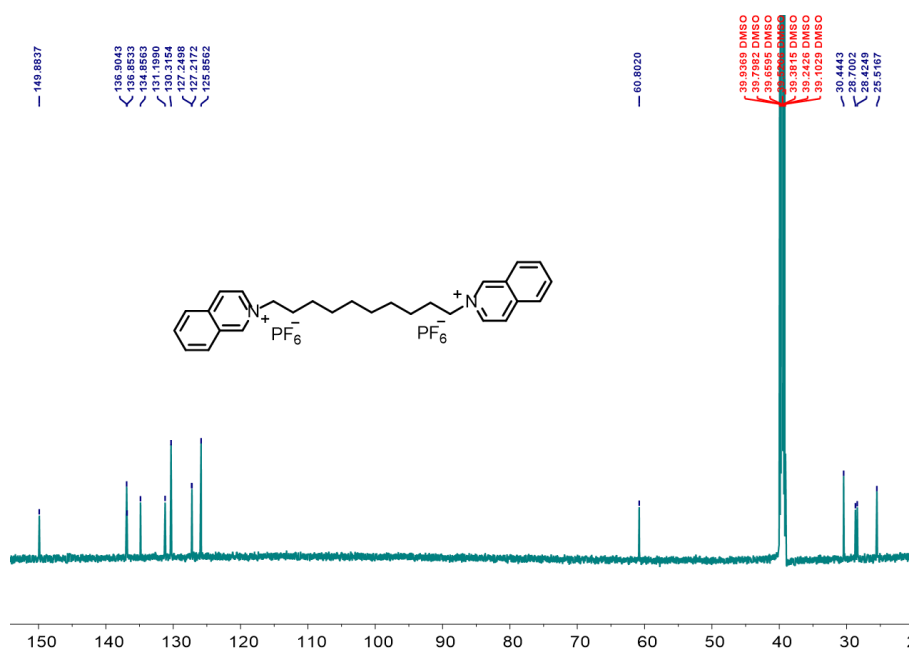


Figure S6. ^{13}C NMR spectrum (151 MHz, DMSO- d_6 , 298 K) of compound G4.

G5: white solid, yield: 90%. 1H NMR (400 MHz, DMSO- d_6 , 298 K): δ [ppm] = 9.09 – 9.02 (m, 4H), 8.61 – 8.59 (m, 2H), 8.19 – 8.10 (m, 4H), 4.57 (t, J = 7.5 Hz, 4H), 1.94 – 1.86 (m, 4H), 1.29 – 1.22 (m, 20H). ^{13}C NMR (101 MHz, DMSO- d_6 , 298 K): δ [ppm]

= 145.51, 144.72, 128.13, 60.91, 30.74, 29.27, 29.08, 29.01, 28.86, 28.45, 25.47. ESI-TOF-HRMS: m/z calcd for $[M-PF_6]^+ C_{24}H_{38}F_6N_2P^+$, 499.2671; found 499.2657 (error = -2.8 ppm).

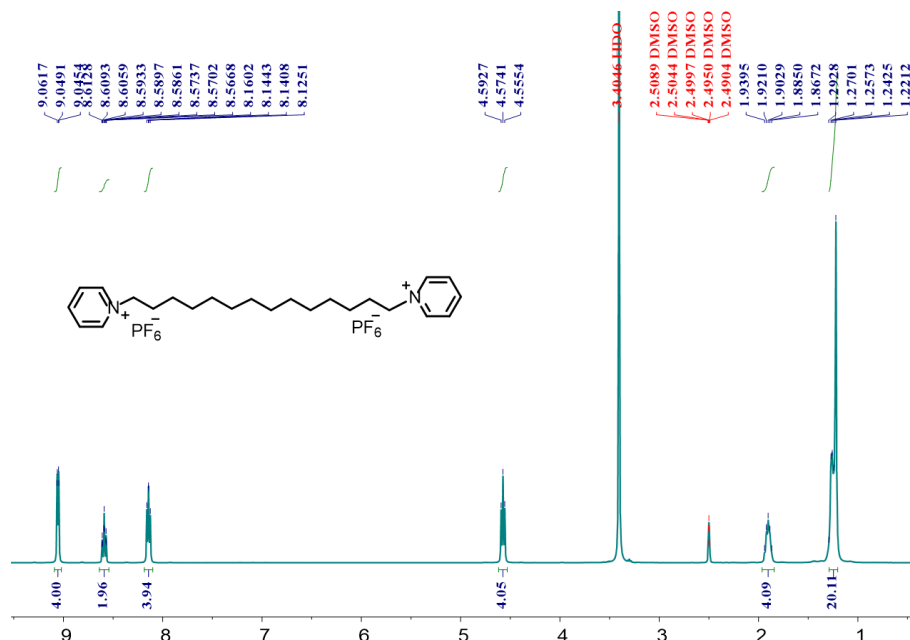


Figure S7. 1H NMR spectrum (400 MHz, DMSO- d_6 , 298 K) of compound G5.

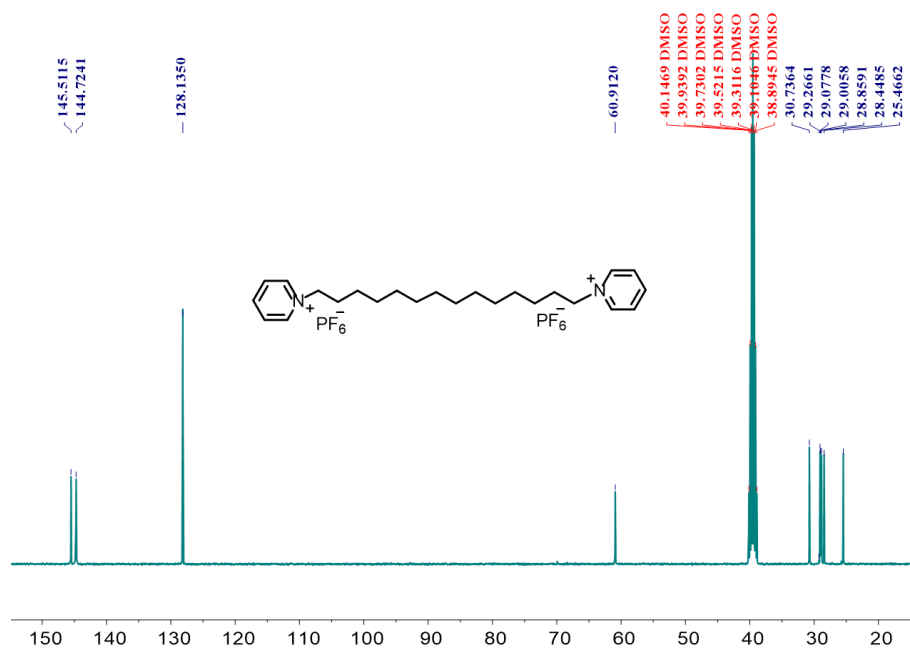


Figure S8. ^{13}C NMR spectrum (101 MHz, DMSO- d_6 , 298 K) of compound G5.

G6: white solid, yield: 30%. 1H NMR (400 MHz, DMSO- d_6 , 298 K): δ [ppm] = 10.06 (s, 2H), 8.80 – 8.78 (m, 2H), 8.59 (d, J = 6.8 Hz, 2H), 8.47 (d, J = 8.3 Hz, 2H), 8.35 (d, J = 8.4 Hz, 2H), 8.27 – 8.25 (m, 2H), 8.09 – 8.07 (m, 2H), 4.69 (t, J = 7.4 Hz, 4H), 2.02

– 1.99 (m, 4H), 1.33 – 1.20 (m, 20H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$, 298 K): δ [ppm] = 149.93, 136.92, 136.87, 134.90, 131.22, 130.35, 127.28, 127.24, 125.87, 60.82, 30.46, 29.04, 28.97, 28.82, 28.47, 25.53. ESI-TOF-HRMS: m/z calcd for $[\text{M-PF}_6]^+$ $\text{C}_{23}\text{H}_{42}\text{F}_6\text{N}_2\text{P}^+$, 599.2984; found 599.2980 (error = -0.7 ppm).

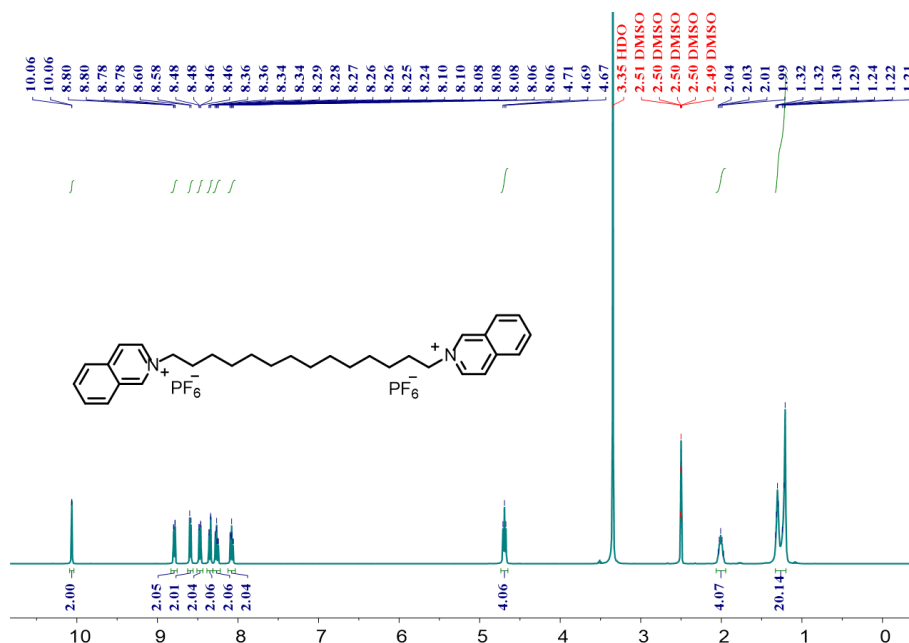


Figure S9. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 298 K) of compound G6.

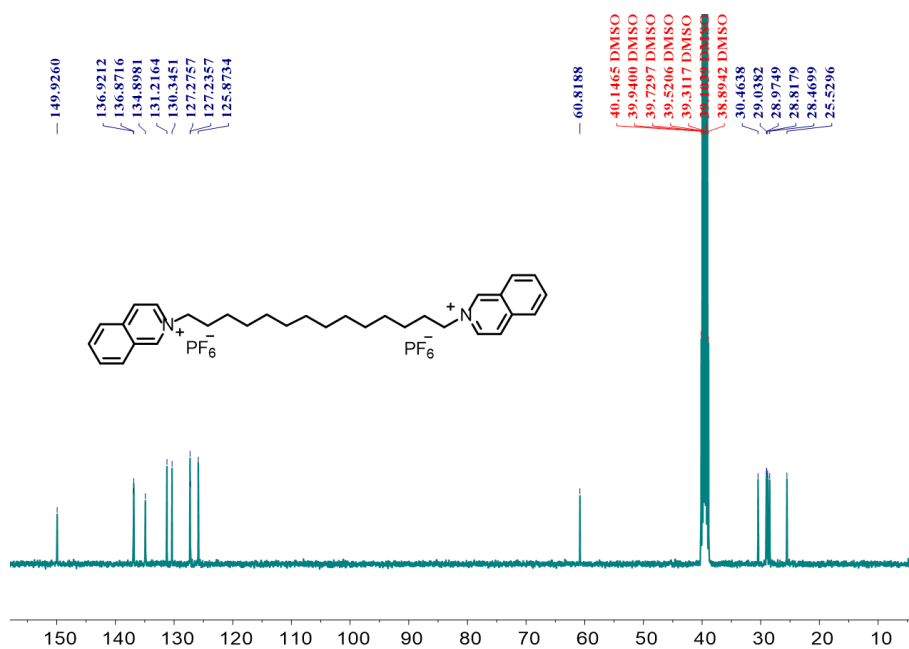


Figure S10. ^{13}C NMR spectrum (101 MHz, $\text{DMSO-}d_6$, 298 K) of compound G6.

2. Characterization data of pseudo[2]rotaxanes

2.1 ^1H NMR spectra of H1 and G1-G2

Determination of the association constants of the 1:1 complexes

The stoichiometries and association constants between **H1** and **G1-G2** were determined by ^1H NMR titrations. For a typical ^1H NMR titration, a 0.5 mM solution of **H1** was prepared in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ (1:1, v/v). This solution (0.5 mL) was placed in an NMR tube and then titrated with a solution of guest. Nonlinear curve-fitting method was then used to obtain the binding constants through the following equation:³

$$\delta = \delta_0 + \Delta\delta \left(\frac{0.5}{[\text{H}]_0} \left([\text{G}] + [\text{H}]_0 + 1/K_a - \left(([\text{G}] + [\text{H}]_0 + 1/K_a)^2 - 4[\text{H}]_0[\text{G}] \right)^{0.5} \right) \right) \quad (\text{Eq. S1})$$

where δ is the chemical shift of proton 2 on **H1** at $[\text{G}]$, δ_0 is the chemical shift of proton 2 on **H1** without guest, $\Delta\delta$ is the chemical shift change of proton 2 when the **H1** is completely complexed, $[\text{H}]_0$ is the fixed initial concentration of the **H1** and $[\text{G}]$ is the varying concentration of guest.

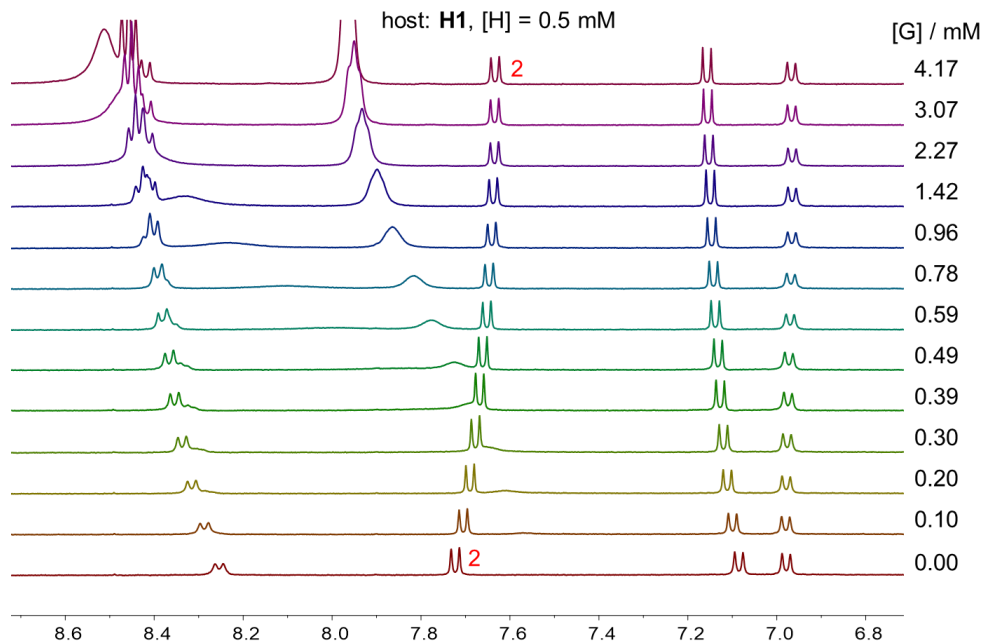


Figure S11. Partial ^1H NMR spectra (500 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of **H1** (0.5 mM) with different concentrations of **G1** (0~4.17 mM).

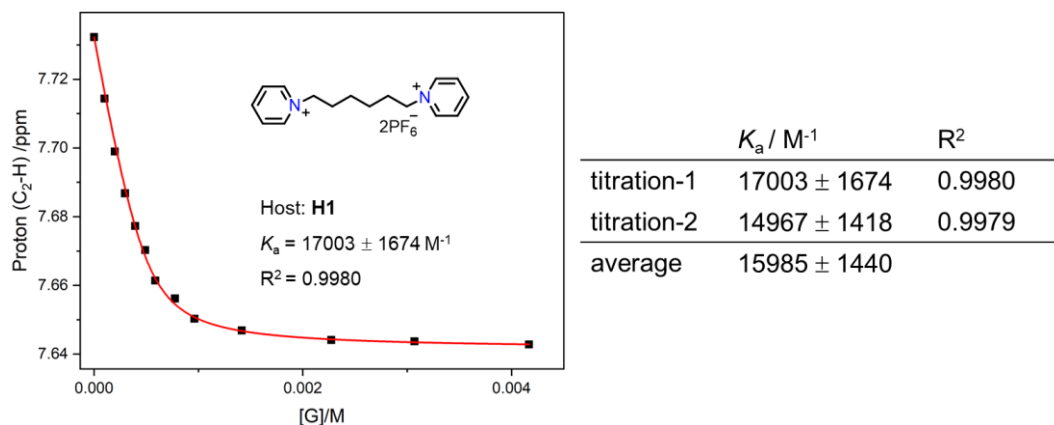


Figure S12. The chemical shift of H₂ on **H1** upon addition of **G1** in the 1:1 mixture of CD₂Cl₂ and CD₃CN at 298 K. The red solid line was obtained from the non-linear curve-fitting using Eq. S1. The titration was repeated twice.

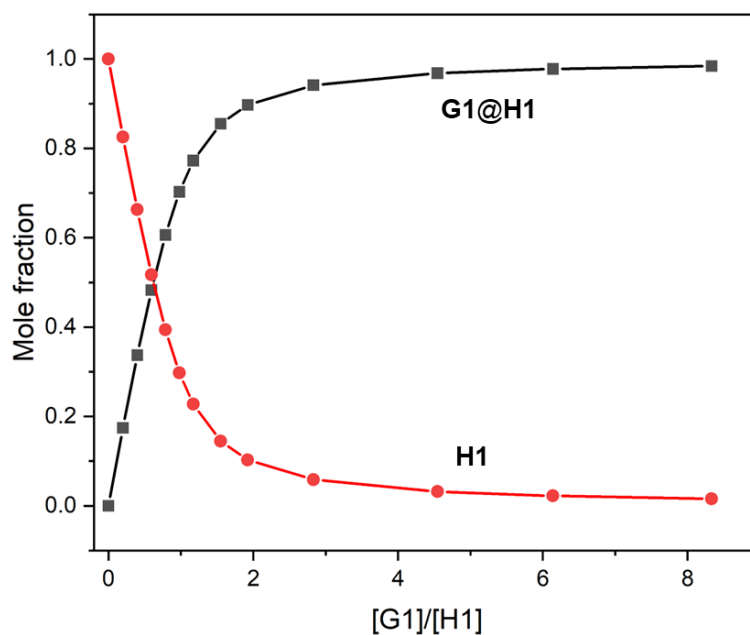


Figure S13. Plots of mole fractions of **H1** (red) and **G1@H1** (black) when titrating **G1** into a solution of **H1**. The concentration of [**G1@H1**] was calculated by $[HG] = 0.5([H]_0 + [G]_0 + 1/K_a) - 0.5((([H]_0 + [G]_0 + 1/K_a)^2 - 4[H]_0[G]_0)^{0.5})$.³ The concentration of [**H1**] was calculated by $[H] = [H]_0 - [HG]$.

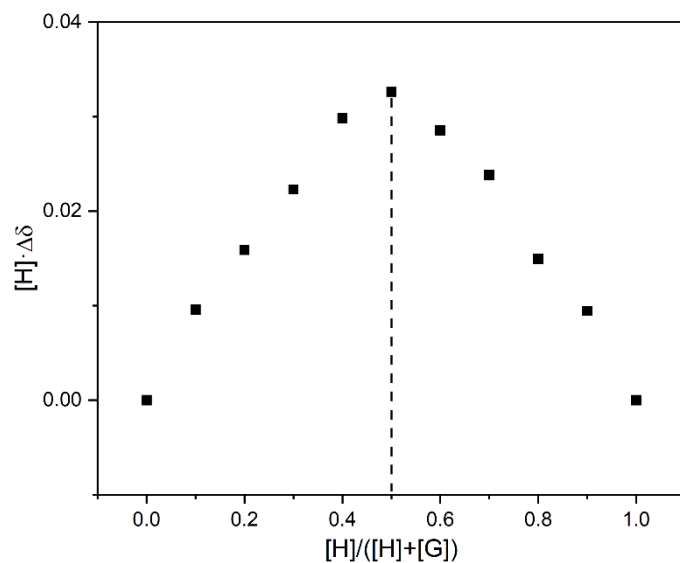


Figure S14. Job plot obtained by plotting the chemical shift change ($\Delta\delta$) of the host's proton 2 in ^1H NMR spectra by varying the ratio of host and guest against the mole fraction of host **H1**. This experiment supports the 1:1 binding stoichiometry between **H1** and **G1** in the 1:1 mixture of CD_2Cl_2 and CD_3CN .

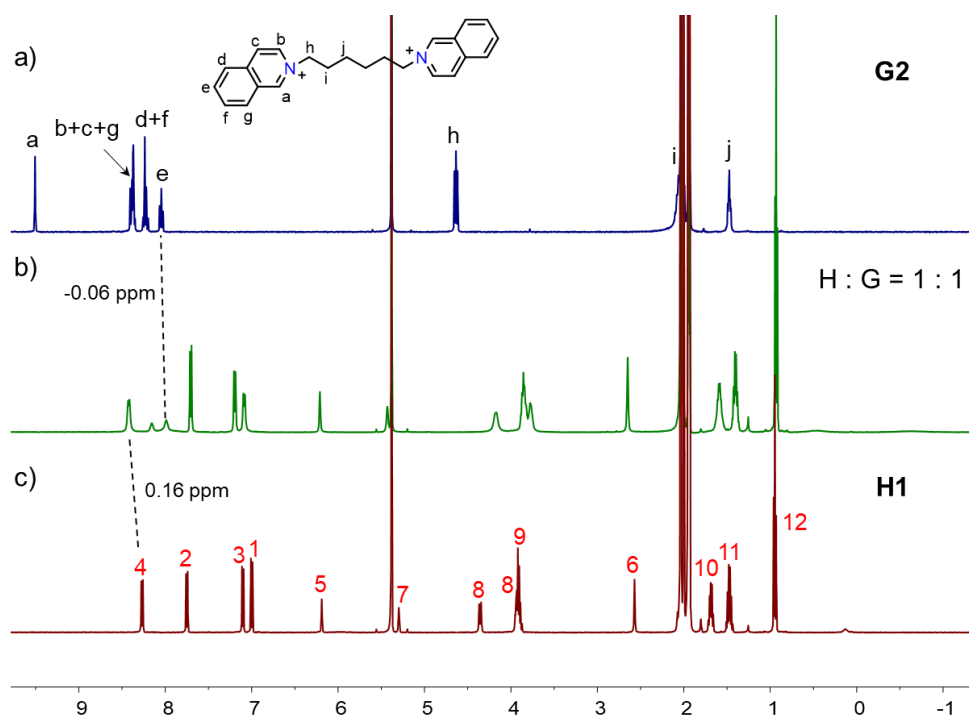


Figure S15. ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 1.0 mM, 298 K) of (a) **G2**, (c) **H1**, and (b) their equimolar mixture. In the host-guest mixture, the protons of the guest undergo significant shifts, accompanied with peak broadening or disappearing into the baseline, suggesting a binding event.

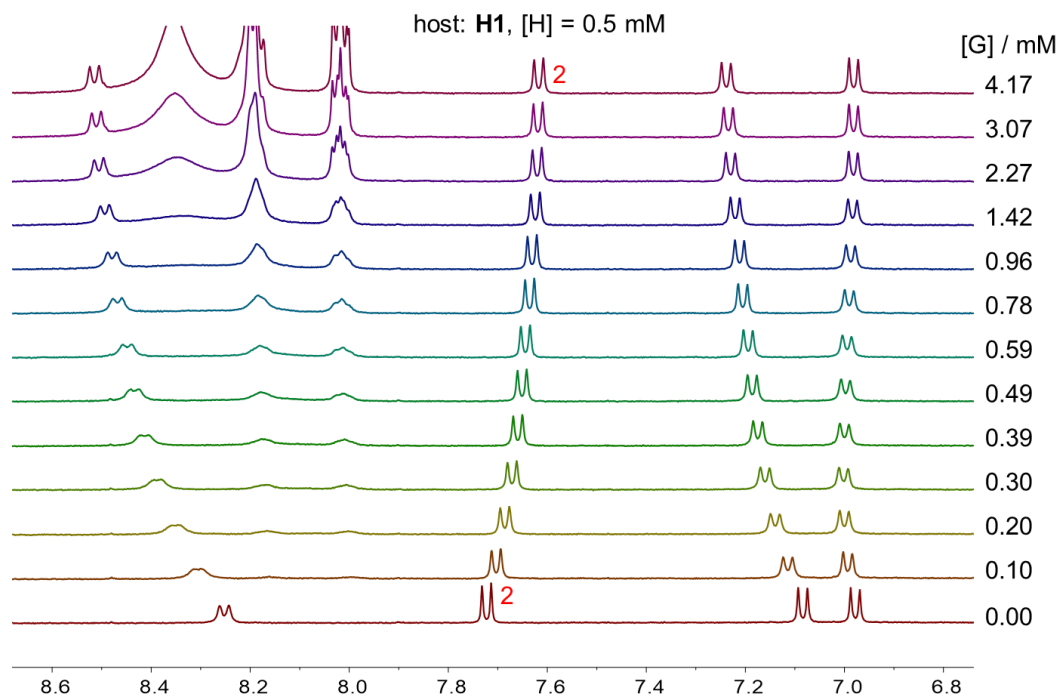


Figure S16. Partial ^1H NMR spectra (500 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of **H1** (0.5 mM) with different concentrations of **G2** (0~4.17 mM).

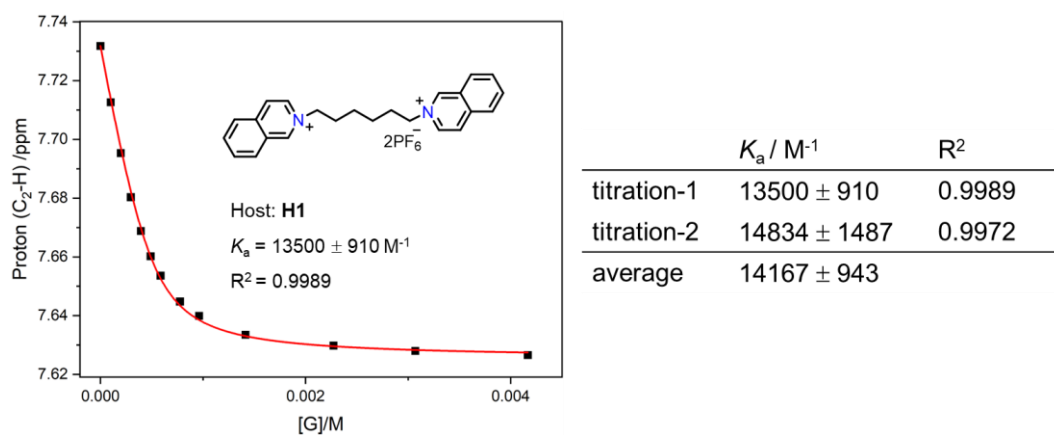


Figure S17. The chemical shift of H_2 on **H1** upon addition of **G2** in the 1:1 mixture of CD_2Cl_2 and CD_3CN at 298 K. The red solid line was obtained from the non-linear curve-fitting using Eq. S1. The titration was repeated twice.

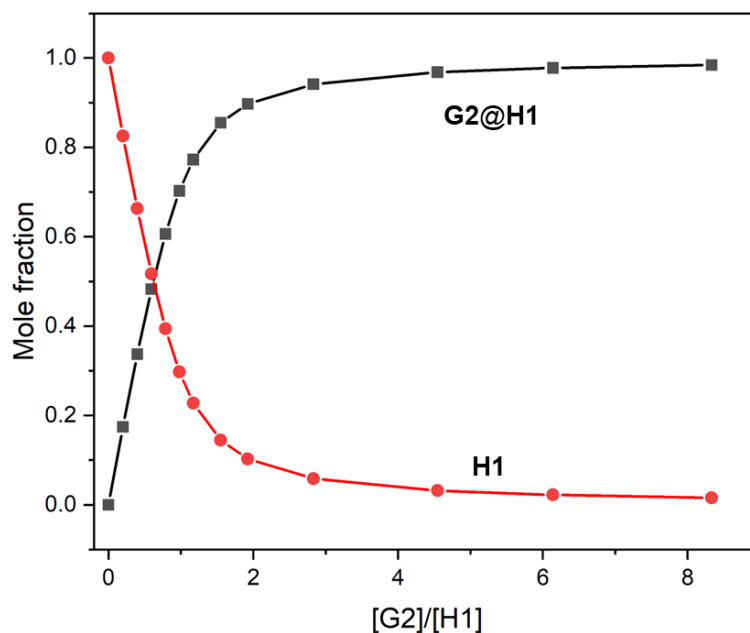


Figure S18. Plots of mole fractions of **H1** (red) and **G2@H1** (black) when titrating **G2** into a solution of **H1**. The concentration of [**G2@H1**] was calculated by $[HG] = 0.5([H]_0 + [G]_0 + 1/K_a) - 0.5(([H]_0 + [G]_0 + 1/K_a)^2 - 4[H]_0[G]_0)^{0.5}$.³ The concentration of [**H1**] was calculated by $[H] = [H]_0 - [HG]$.

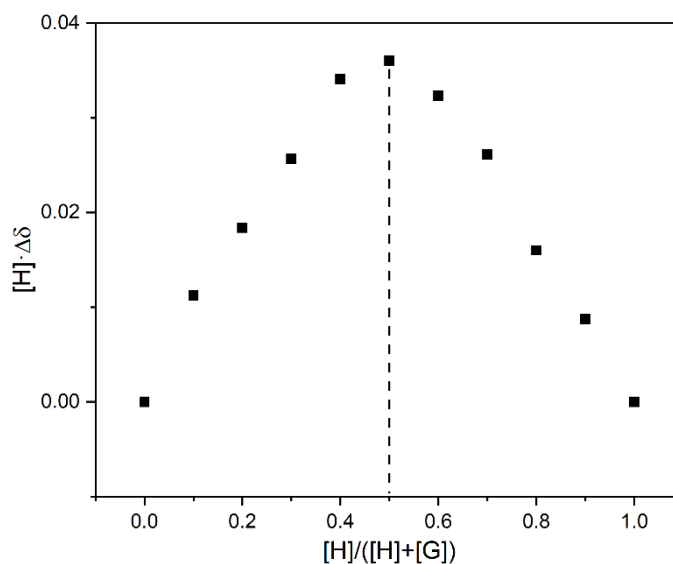


Figure S19. Job plot obtained by plotting the chemical shift change ($\Delta\delta$) of the host's proton 2 in ^1H NMR spectra by varying the ratio of host and guest against the mole fraction of host **H1**. This experiment supports the 1:1 binding stoichiometry between **H1** and **G2** in the 1:1 mixture of CD_2Cl_2 and CD_3CN .

2.2 ESI-MS of the 1:1 complexes

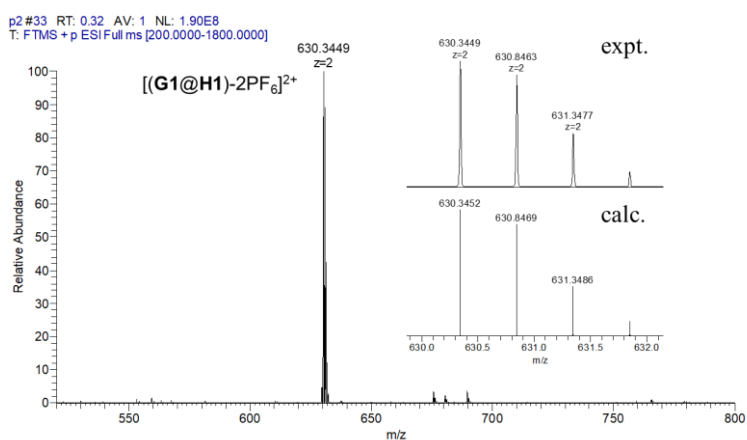


Figure S20. ESI-MS of G1@H1.

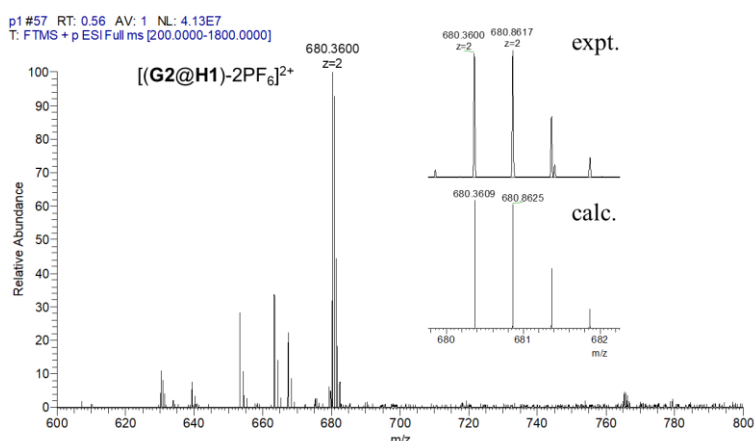


Figure S21. ESI-MS of G2@H1.

3. Characterization data of pseudo[3]rotaxanes

Determination of the association constants of the 2:1 complexes: The stoichiometries and association constants between **H1** and **G3-G6** were determined by 1H NMR titrations. For a typical 1H NMR titration, a 0.5 mM solution of guest was prepared in CD_2Cl_2/CD_3CN (1:1, v/v). This solution (0.5 mL) was placed in an NMR tube and then titrated with a solution of **H1**. Nonlinear curve-fitting method was then used to obtain the binding constants through the following equation:³

$$\delta = \delta_0 + (\Delta\delta_{HG}K_{a1}[H] + \Delta\delta_{H2G}K_{a1}K_{a2}[H]^2) / (1 + K_{a1}[H] + K_{a1}K_{a2}[H]^2) \quad (\text{Eq. S2})$$

where δ is the chemical shift of proton on guest (proton b on **G3**, **G5**; proton e on **G4**, **G6**) at $[H]$, δ_0 is the chemical shift of proton on guest without **H1**, $\Delta\delta_{HG}$ is the chemical

shift change of proton on guest when guest is completely complexed by the first **H1**, $\Delta\delta_{H_2G}$ is the chemical shift change of proton on guest when guest is completely complexed by the second **H1**. $[H]$ is the varying concentration of **H1**.

The concentration of $[G]$ can be calculated by $[G] = [G]_0 / (1 + K_{a1}[H] + K_{a1}K_{a2}[H]^2)$.³
 The concentration of $[HG]$ and $[H_2G]$ can be calculated by $[HG] = K_{a1}[H][G]$ and $[H_2G] = K_{a2}[HG][G]$, respectively. $[G]_0$ is the fixed initial concentration of the guest.

3.1 ¹H and 2D NMR spectra of H1 and G3-G4

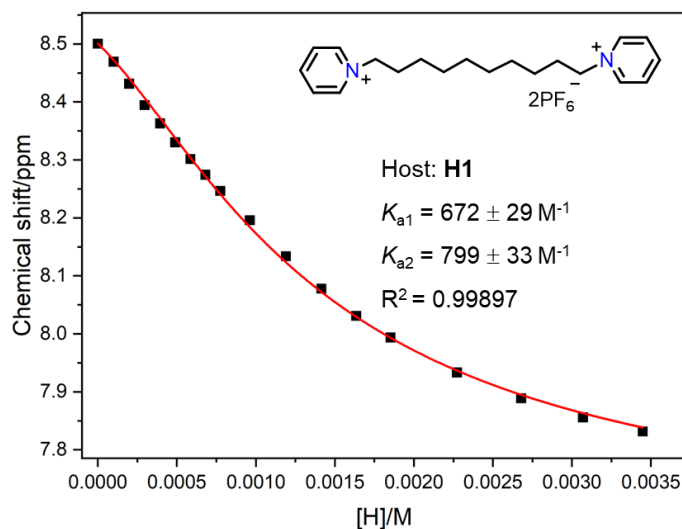


Figure S22. The chemical shift of H_b on **G3** upon addition of **H1** in the 1:1 mixture of CD_2Cl_2 and CD_3CN at 298 K. The red solid line was obtained from the non-linear curve-fitting using Eq. S2.

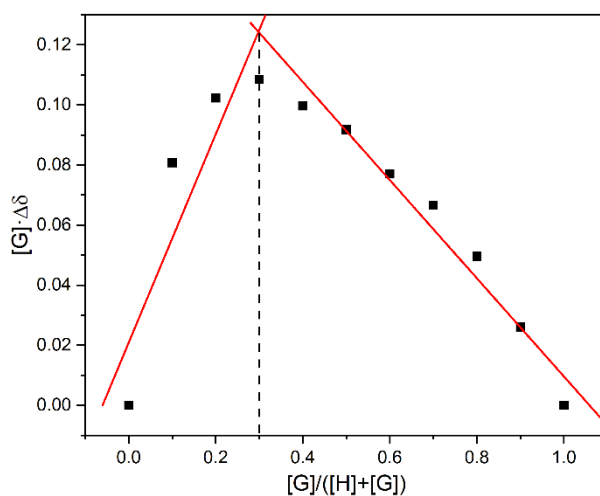


Figure S23. Job plot obtained by plotting the chemical shift change ($\Delta\delta$) of the guest's proton b in ¹H NMR spectra by varying the ratio of host and guest against the mole

fraction of guest **G3**. This experiment supports the 2:1 binding stoichiometry between **H1** and **G3** in the 1:1 mixture of CD₂Cl₂ and CD₃CN.

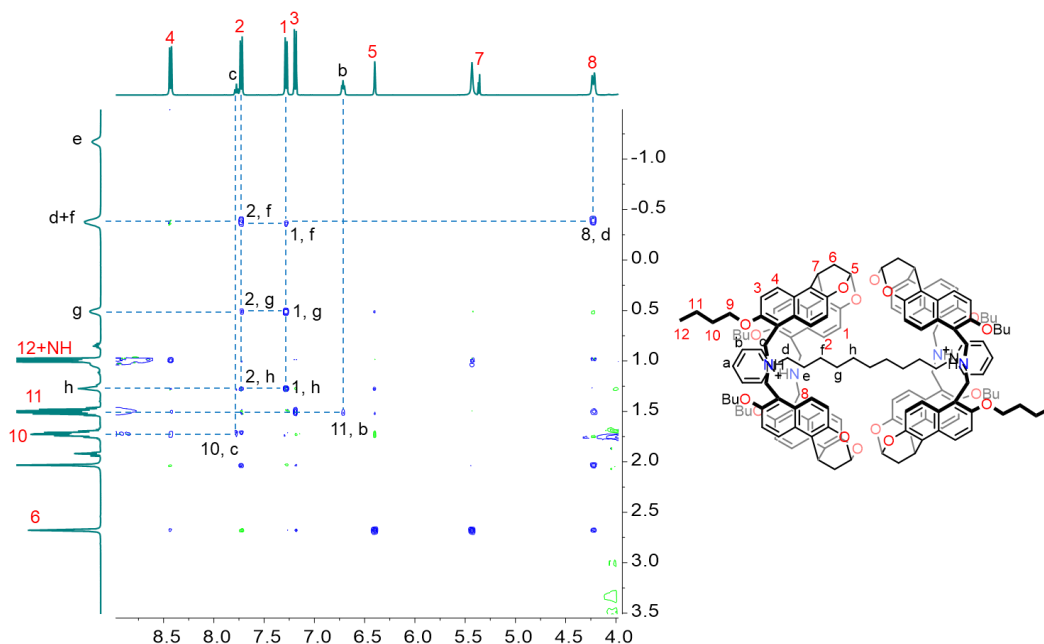


Figure S24. Partial ¹H,¹H-ROESY NMR spectrum (500 MHz, CD₂Cl₂:CD₃CN=1:1, 298 K) of **G3@H1₂** ([**H1**] = 16 mM). The peak attributed to protons H_a of the pyridinium rings on **G3** disappears into the baseline, and we can't discriminate it clearly in the NMR spectrum.

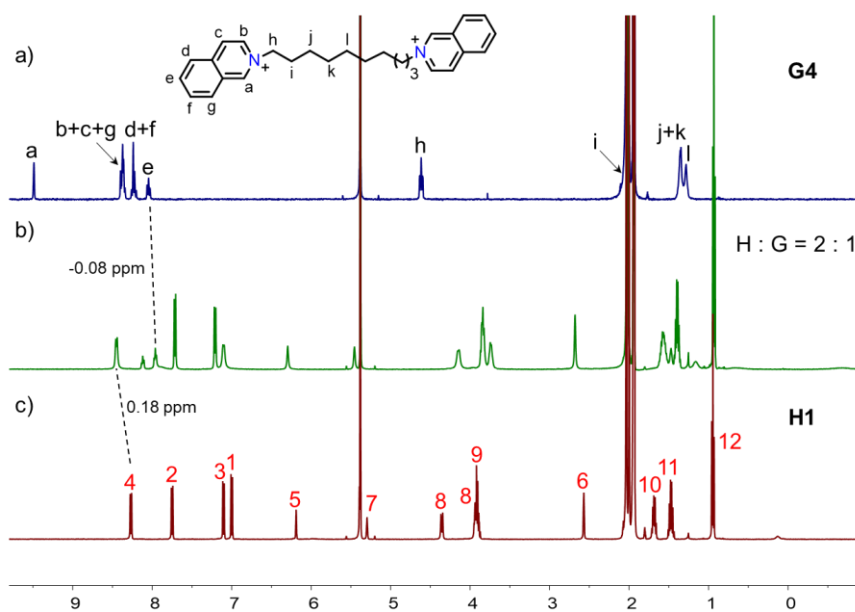


Figure S25. ¹H NMR spectra (400 MHz, CD₂Cl₂:CD₃CN=1:1, 1.0 mM, 298 K) of (a) **G4**, (c) **H1**, and (b) their 2:1 (H:G) mixture. In the host-guest mixture, the protons of

the guest undergo significant shifts, accompanied with peak broadening or disappearing into the baseline, suggesting a binding event.

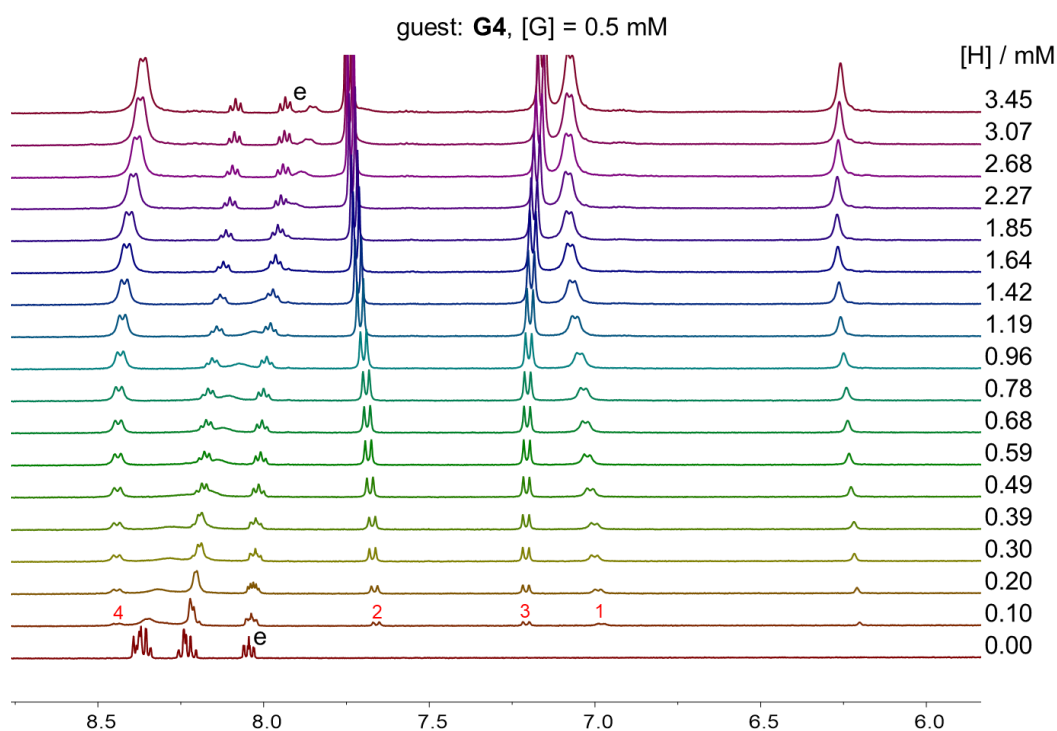


Figure S26. Partial ¹H NMR spectra (500 MHz, CD₂Cl₂:CD₃CN=1:1, 298 K) of **G4** (0.5 mM) with different concentrations of **H1** (0~3.45 mM).

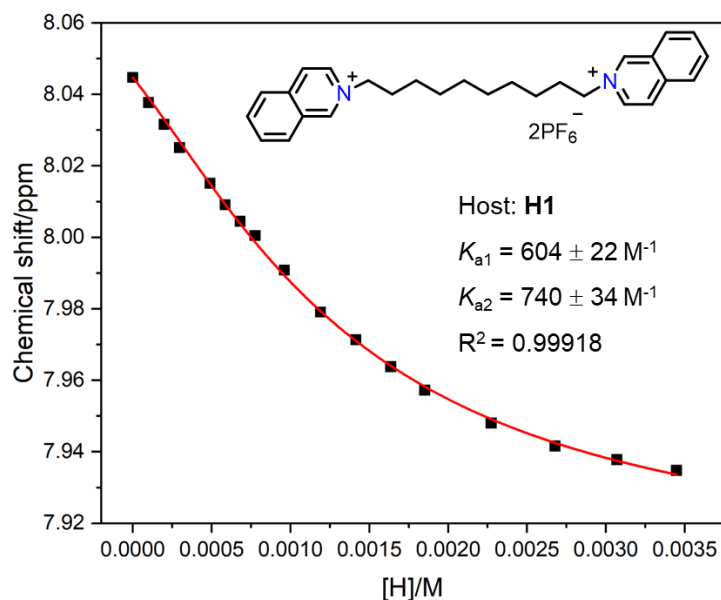


Figure S27. The chemical shift of H_e on **G4** upon addition of **H1** in the 1:1 mixture of CD₂Cl₂ and CD₃CN at 298 K. The red solid line was obtained from the non-linear curve-fitting using Eq. S2.

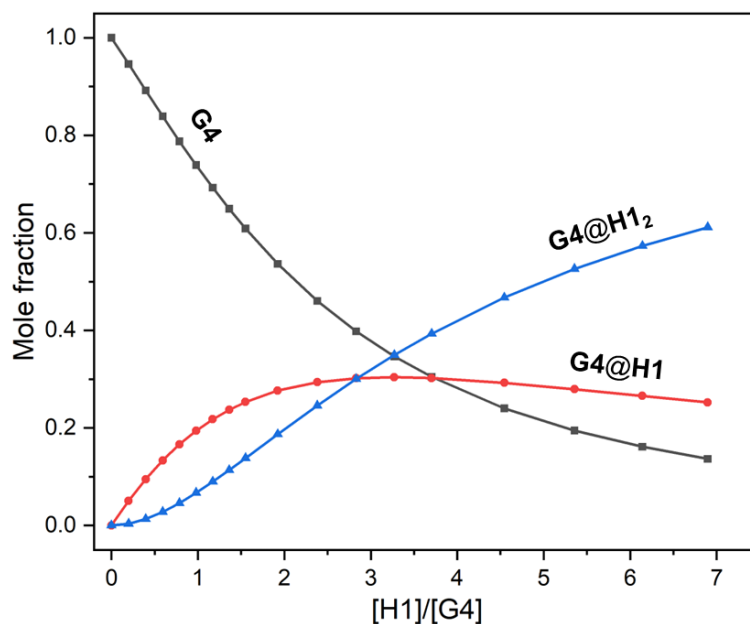


Figure S28. Plots of mole fractions of **G4** (black), **G4@H1** (red) and **G4@H1₂** (blue) when titrating **H1** into a solution of **G4**. The concentration of **[G4]** was calculated by $[G] = [G]_0 / (1 + K_{a1}[H] + K_{a1}K_{a2}[H]^2)$.³ The concentration of **[G4@H1]** and **[G4@H1₂]** were calculated by $[HG] = K_{a1}[H][G]$ and $[H_2G] = K_{a2}[HG][G]$, respectively. $[G]_0$ is the fixed initial concentration of the **G4**.

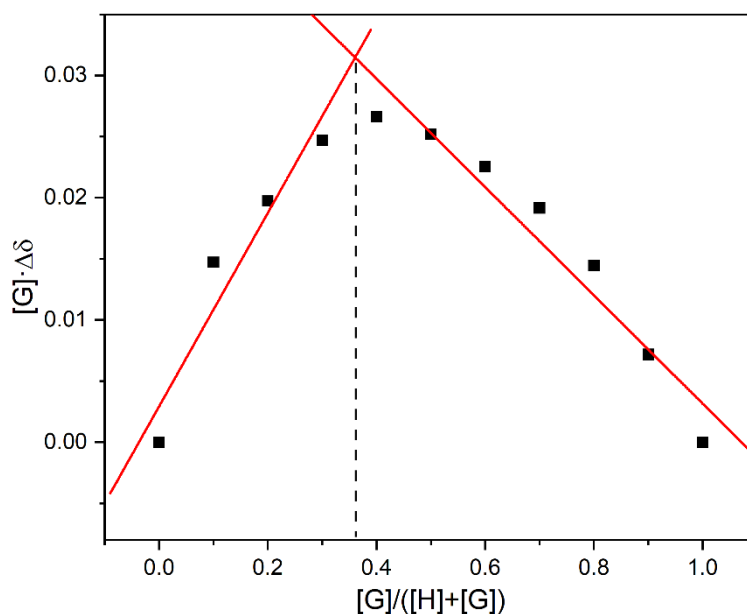


Figure S29. Job plot obtained by plotting the chemical shift change ($\Delta\delta$) of the guest's proton e in ^1H NMR spectra by varying the ratio of host and guest against the mole fraction of guest **G4**. This experiment supports the 2:1 binding stoichiometry between **H1** and **G4** in the 1:1 mixture of CD_2Cl_2 and CD_3CN .

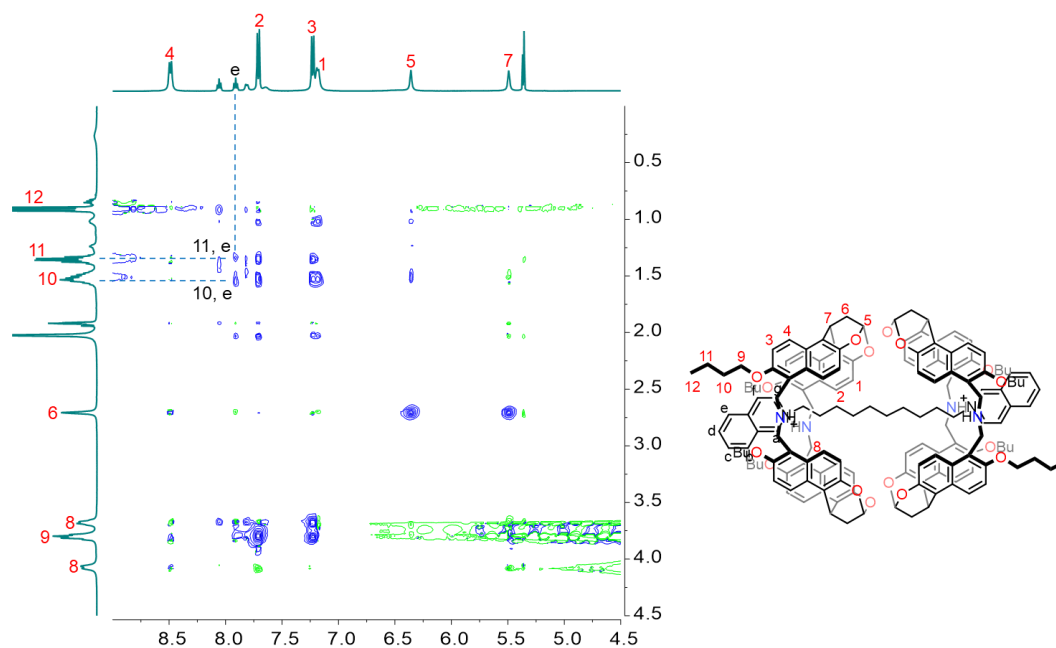


Figure S30. Partial ^1H , ^1H -ROESY NMR spectrum (500 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of G4@H1_2 ($[\text{H1}] = 16 \text{ mM}$). The peak attributed to H_e on G4 was assigned according the ^1H NMR titrations spectra. Other peaks attributed to protons on G4 exhibit significant broadening effects or disappear into the baseline, and we can't discriminate them clearly in the NMR spectrum.

3.2 ESI-MS of the 2:1 complexes

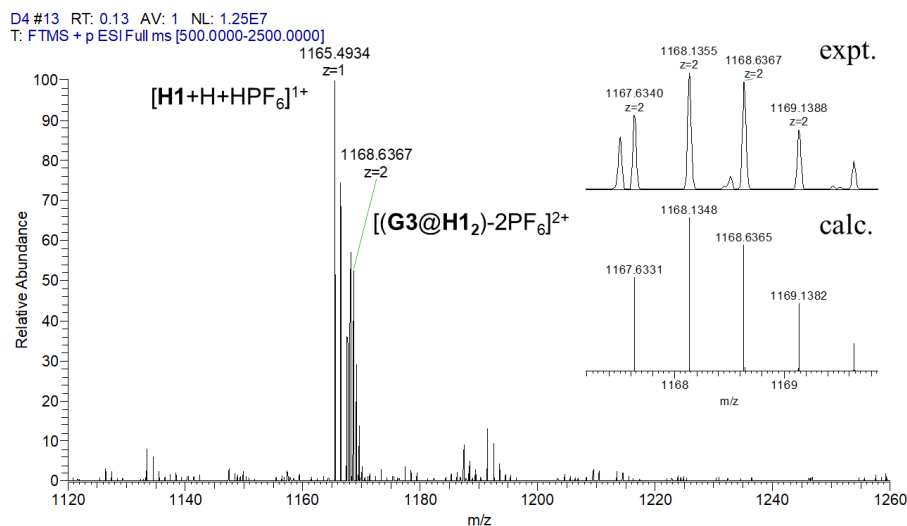


Figure S31. ESI-MS of G3@H1_2 .

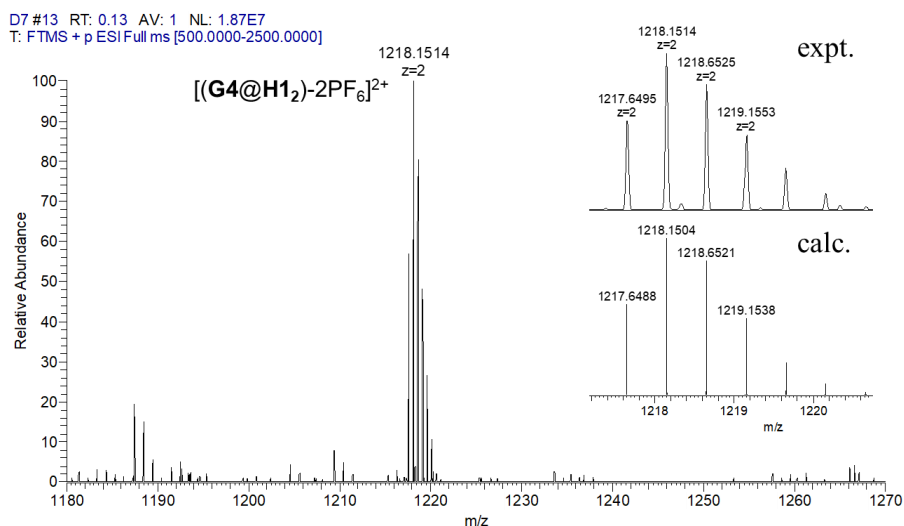


Figure S32. ESI-MS of G4@H12.

3.3 ^1H NMR spectra of H1 and G5-G6

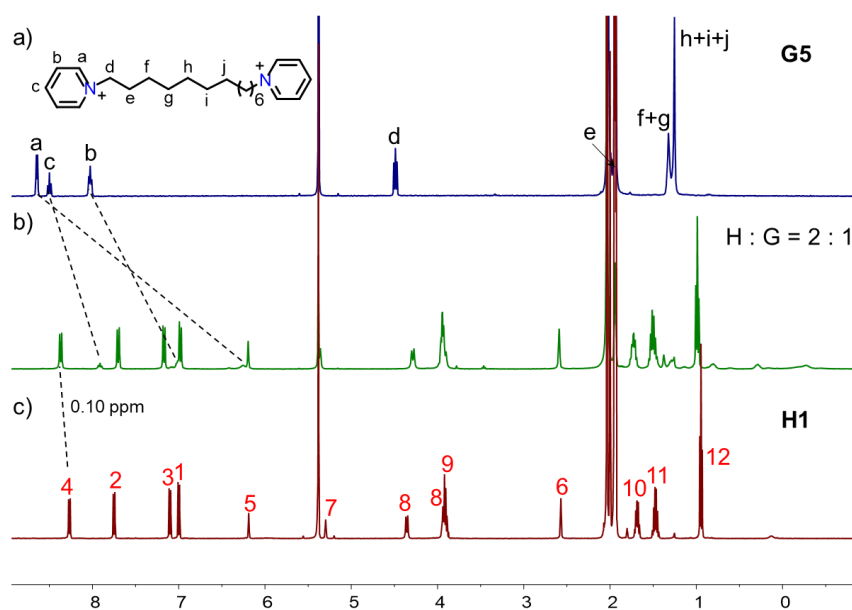


Figure S33. ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 1.0 mM, 298 K) of (a) **G5**, (c) **H1**, and (b) their 2:1 (H:G) mixture. In the host-guest mixture, the protons of the guest undergo significant shifts, accompanied with peak broadening or disappearing into the baseline, suggesting a binding event.

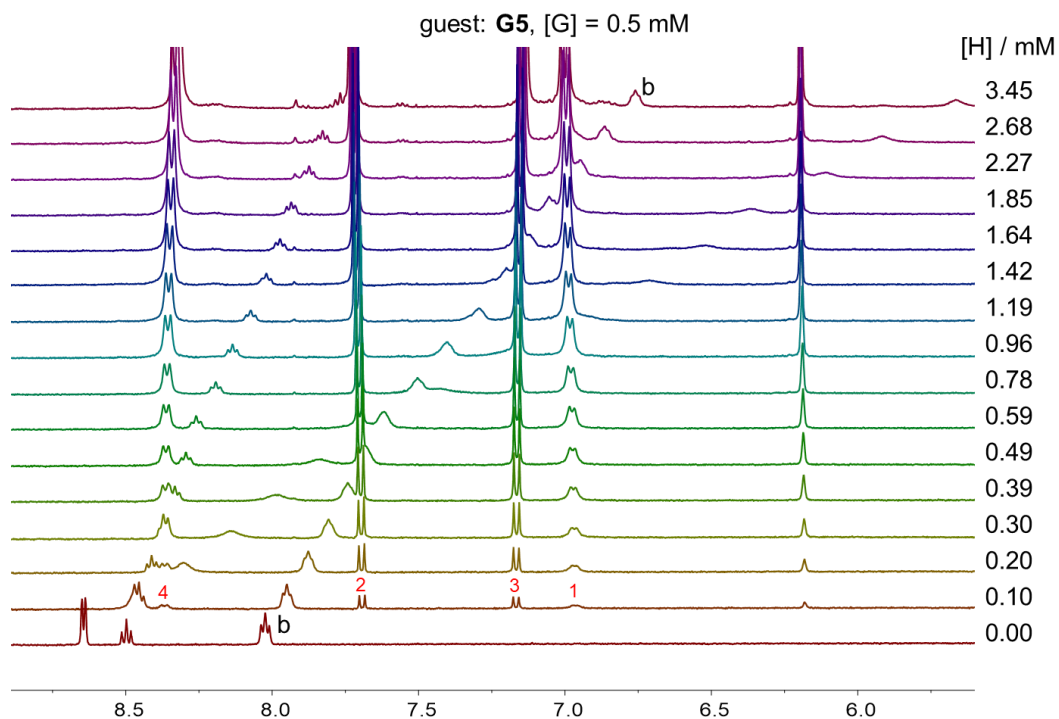


Figure S34. Partial ^1H NMR spectra (500 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of **G5** (0.5 mM) with different concentrations of **H1** (0~3.45 mM).

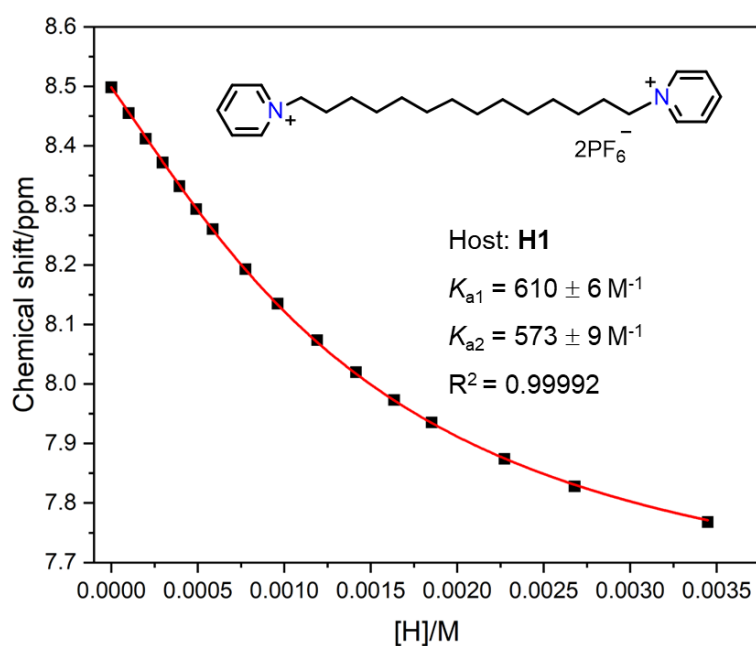


Figure S35. The chemical shift of H_b on **G5** upon addition of **H1** in the 1:1 mixture of CD_2Cl_2 and CD_3CN at 298 K. The red solid line was obtained from the non-linear curve-fitting using Eq. S2.

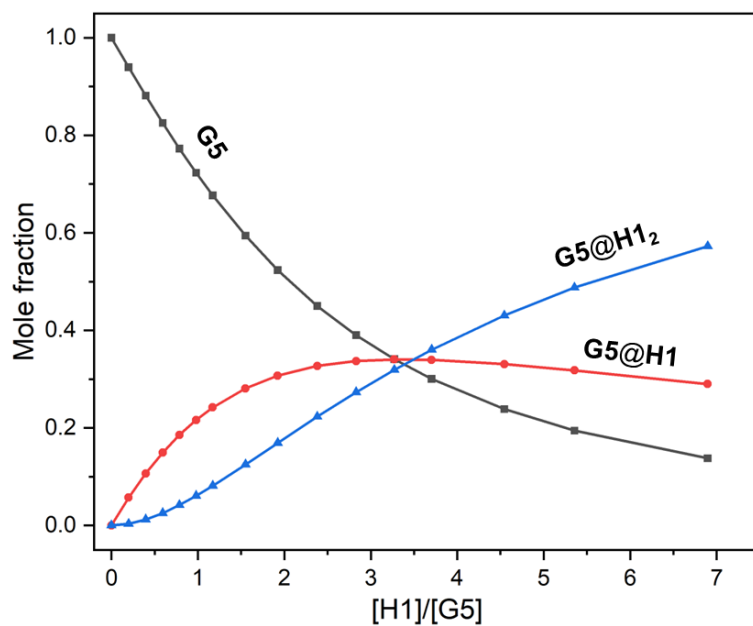


Figure S36. Plots of mole fractions of **G5** (black), **G5@H1** (red) and **G5@H1₂** (blue) when titrating **H1** into a solution of **G5**.

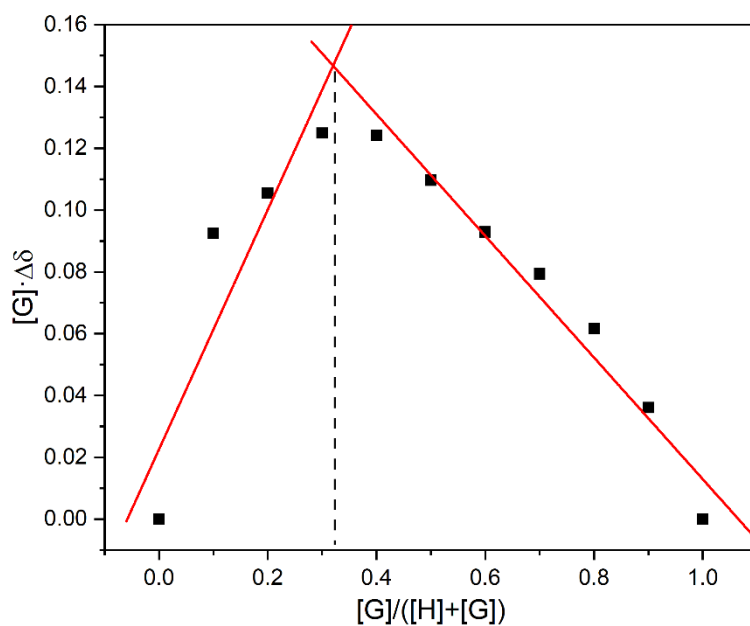


Figure S37. Job plot obtained by plotting the chemical shift change ($\Delta\delta$) of the guest's proton b in ^1H NMR spectra by varying the ratio of host and guest against the mole fraction of guest **G5**. This experiment supports the 2:1 binding stoichiometry between **H1** and **G5** in the 1:1 mixture of CD_2Cl_2 and CD_3CN .

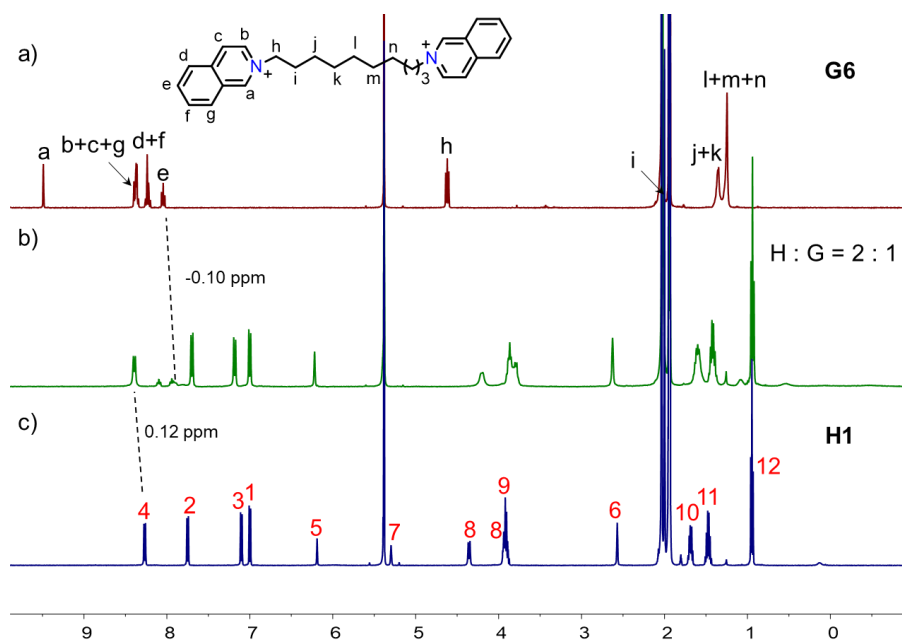


Figure S38. ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 1.0 mM, 298 K) of (a) **G6**, (c) **H1**, and (b) their 2:1 (H:G) mixture. In the host-guest mixture, the protons of the guest undergo significant shifts, accompanied with peak broadening or disappearing into the baseline, suggesting a binding event.

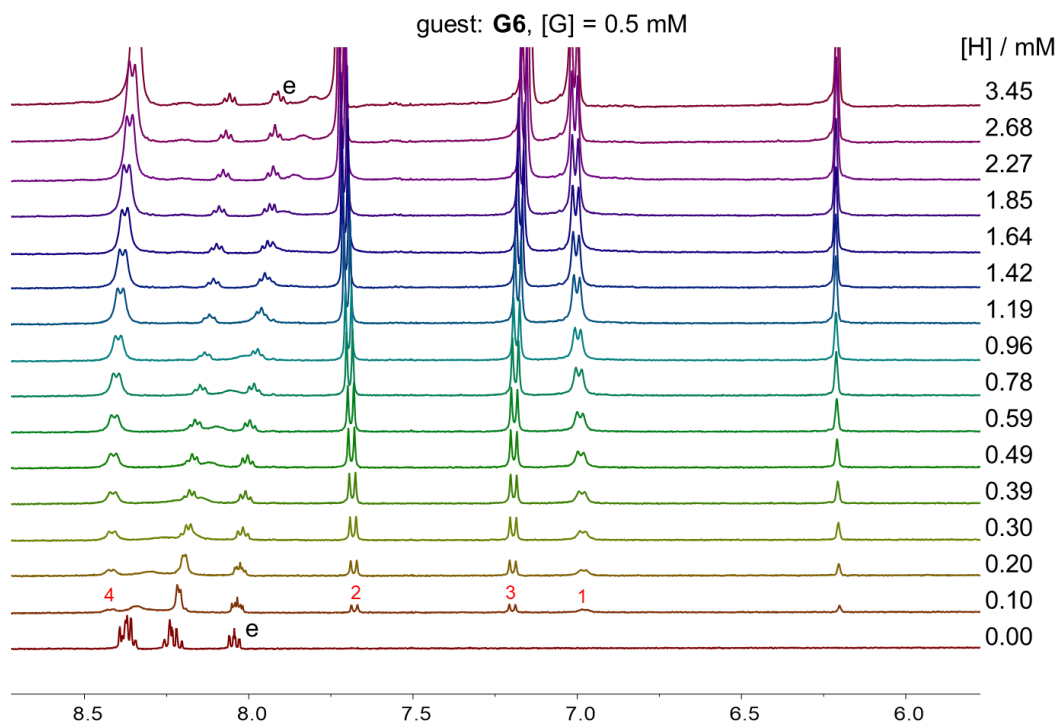


Figure S39. Partial ^1H NMR spectra (500 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of **G6** (0.5 mM) with different concentrations of **H1** (0~3.45 mM).

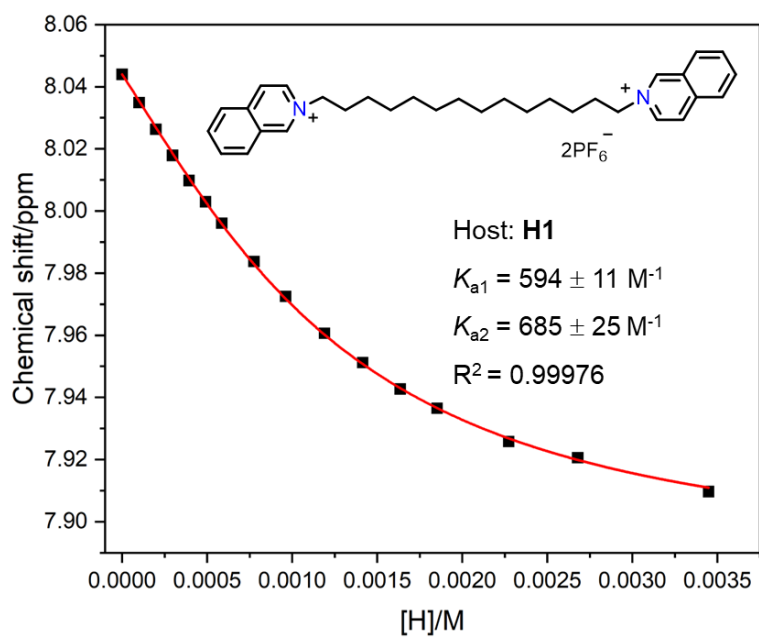


Figure S40. The chemical shift of H_c on **G6** upon addition of **H1** in the 1:1 mixture of CD_2Cl_2 and CD_3CN at 298 K. The red solid line was obtained from the non-linear curve-fitting using Eq. S2.

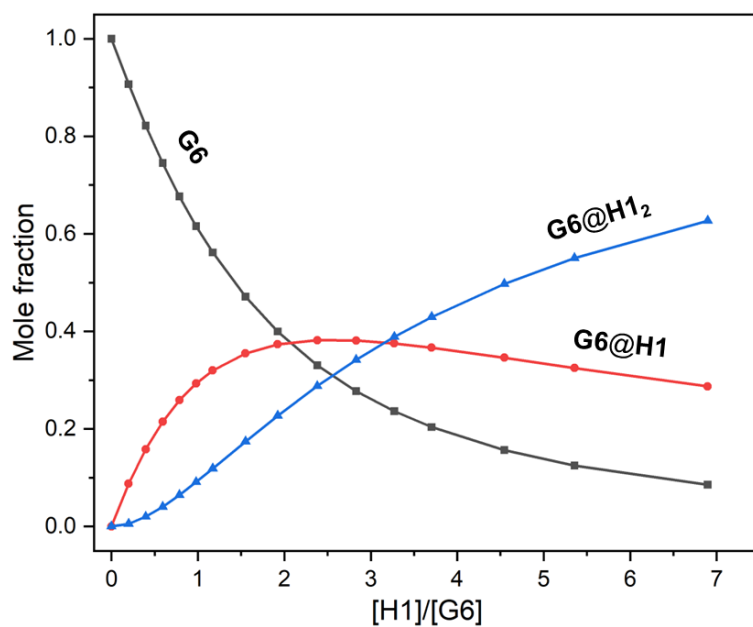


Figure S41. Plots of mole fractions of **G6** (black), **G6@H1** (red) and **G6@H1₂** (blue) when titrating **H1** into a solution of **G6**.

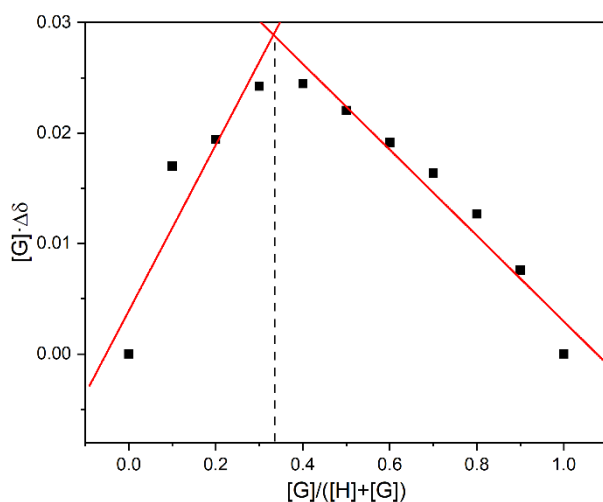


Figure S42. Job plot obtained by plotting the chemical shift change ($\Delta\delta$) of the guest's proton e in ^1H NMR spectra by varying the ratio of host and guest against the mole fraction of guest **G6**. This experiment supports the 2:1 binding stoichiometry between **H1** and **G6** in the 1:1 mixture of CD_2Cl_2 and CD_3CN .

3.4 ESI-MS of the 2:1 complexes

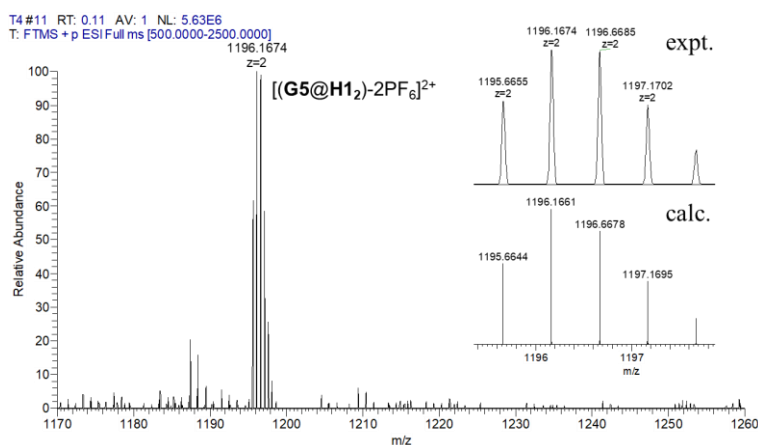


Figure S43. ESI-MS of **G5@H12**.

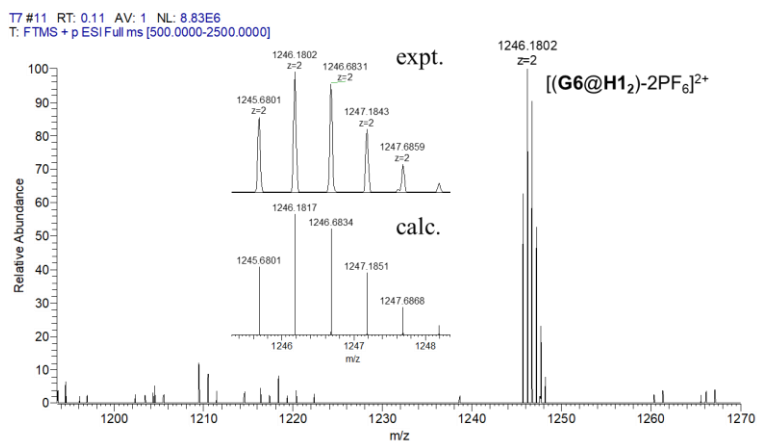


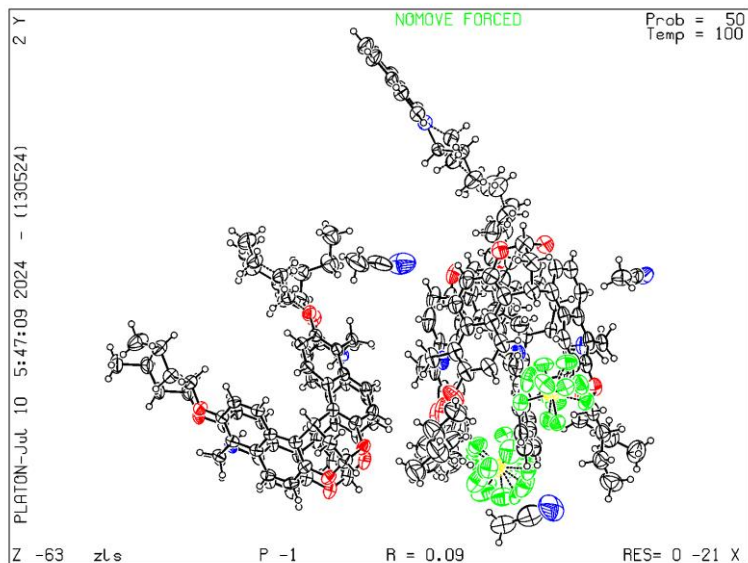
Figure S44. ESI-MS of **G6@H12**.

4. X-ray single crystallography

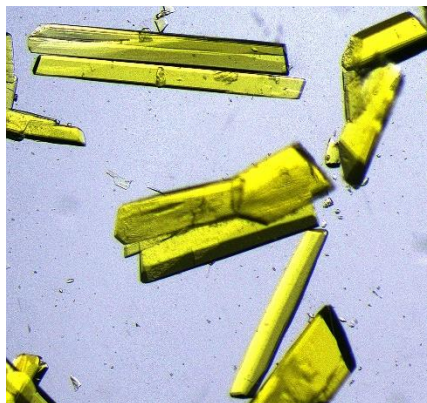
Suitable single crystals of **G4@H12•3CH₃CN** were successfully obtained by slow evaporation of their saturated solutions in 1, 2-dichloroethane and acetonitrile (1:1, v/v). Single crystal X-ray data were collected on a Bruker D8 VENTURE with Ga K α radiation ($\lambda = 1.34139 \text{ \AA}$) at 100 K. The structure was solved by intrinsic phasing methods (SHELXT) and refined by full-matrix least-squares F^2 using SHELXL⁴ in the OLEX2 program package.⁵ All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were fixed at calculated positions and refined by a riding mode.

Crystal data and structure refinement for **G4@H12•3CH₃CN**

entry	G4@H12•3CH₃CN
Moiety formula	2(C ₆₆ H ₇₀ N ₂ O ₈), C ₂₈ H ₃₄ N ₂ , 3(C ₂ H ₃ N) 2(F ₆ P),
Empirical formula	C ₁₆₆ H ₁₈₃ F ₁₂ N ₉ O ₁₆ P ₂
Formula weight	2850.14
Temperature/K	100
Crystal system	triclinic
Space group	<i>P</i> -1
a/Å	15.6160(7)
b/Å	22.8099(10)
c/Å	24.2217(10)
α /°	65.842(2)
β /°	74.382(2)
γ /°	77.047(2)
Volume/Å ³	7517.4(6)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.259
μ/mm^{-1}	0.601
F(000)	3016
Reflections collected	194297
Independent reflections	26565 [R _{int} = 0.0708, R _{sigma} = 0.0446]
Data/restraints/parameters	26565/2814/2289
Goodness-of-fit on F ²	1.077
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0918, wR ₂ = 0.2653
Final R indexes [all data]	R ₁ = 0.1070, wR ₂ = 0.2831
CCDC number	2370291



Crystal structure of **G4@H12•3CH₃CN**.



Optical microscopic pictures of **G4@H12** single crystals.

5. UV-Vis spectra of the complexes



Figure S45. Optical images show the solution color change because of the charge transfer between **H1** (2.0 mM or 4.0 mM) and **G1-G6** (2.0 mM) in 1:1 (v/v) $\text{CHCl}_3/\text{CH}_3\text{CN}$ solution.

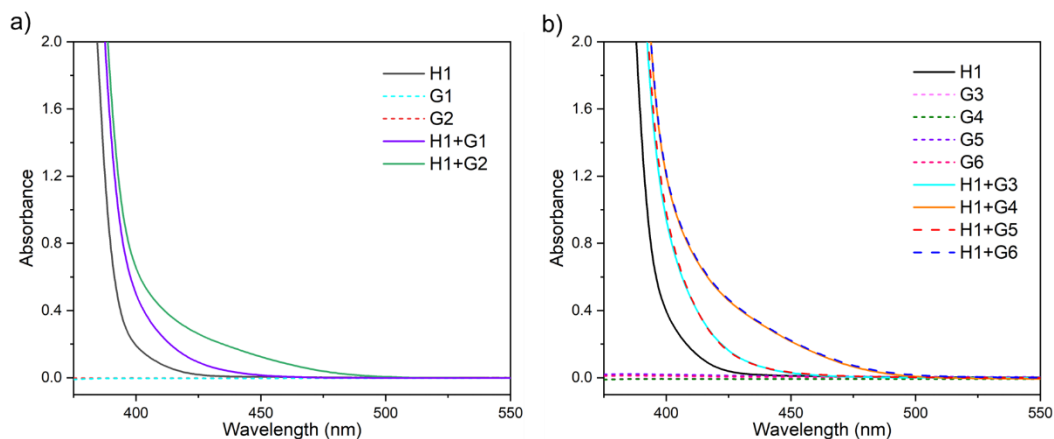


Figure S46. UV-vis spectra in 1:1 (v/v) $\text{CHCl}_3/\text{CH}_3\text{CN}$ solution at 298 K of (a) **H1** (2.0 mM) upon complexation with 1.0 equiv. of **G1-G2** and (b) **H1** (4.0 mM) upon complexation with **G3-G6** (2.0 mM).

6. Acid/base stimuli-responsive complexation

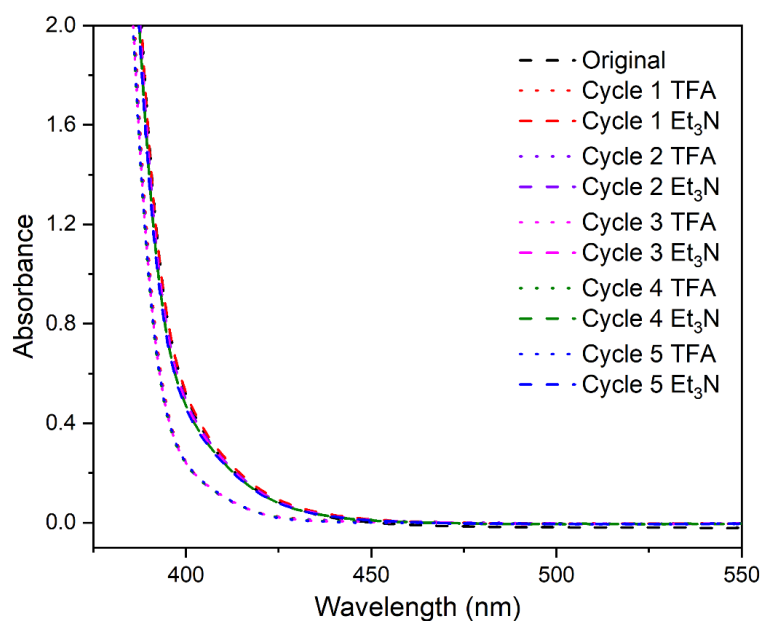


Figure S47. UV-vis spectra of **G1@H1** ($[\text{G1}]=[\text{H1}]=2.00$ mM, 298 K) in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1:1, v/v) in the acid/base stimuli-responsive cycles.

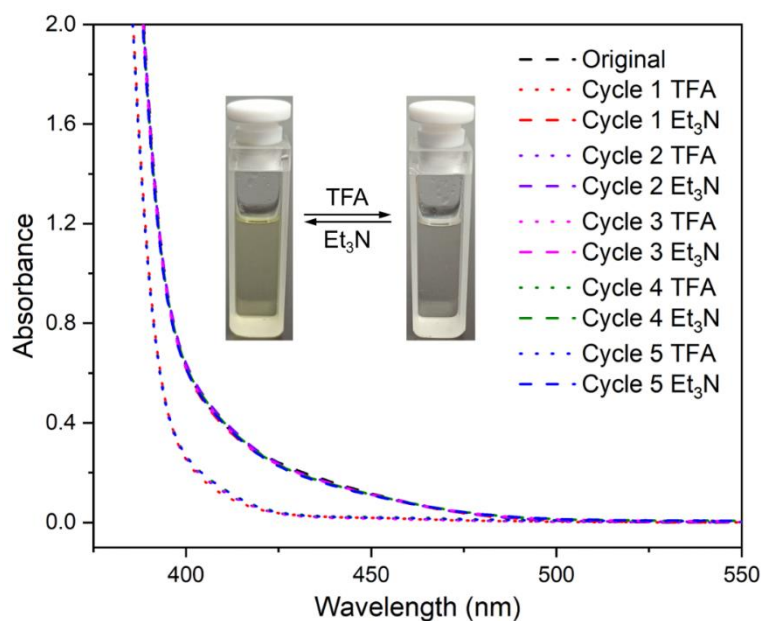


Figure S48. UV-vis spectra of **G2@H1** ($[G2]=[H1]=2.00$ mM, 298 K) in $CHCl_3/CH_3CN$ (1:1, v/v) in the acid/base stimuli-responsive cycles. Inset: acid/base stimuli-responsive color changes of **G2@H1**.

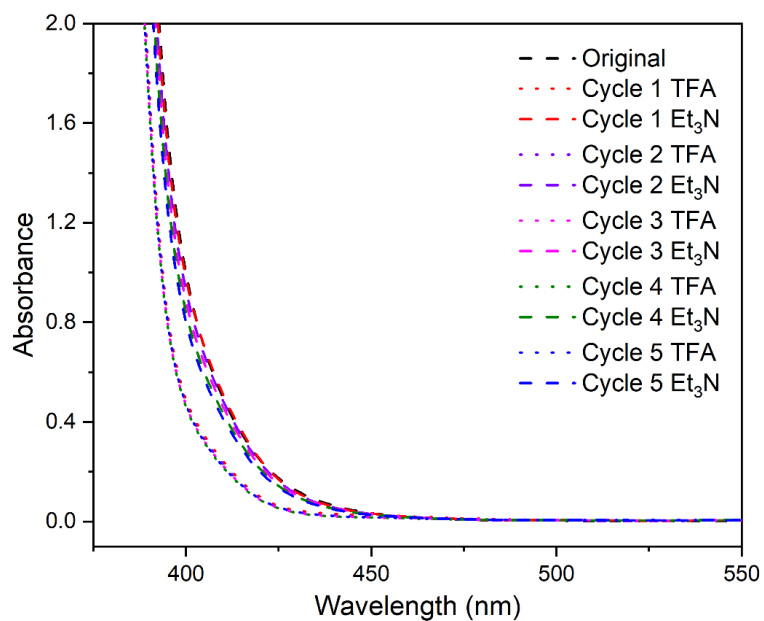


Figure S49. UV-vis spectra of **G3@H1₂** ($[G3]=2.00$ mM, $[H1]=4.00$ mM, 298 K) in $CHCl_3/CH_3CN$ (1:1, v/v) in the acid/base stimuli-responsive cycles.

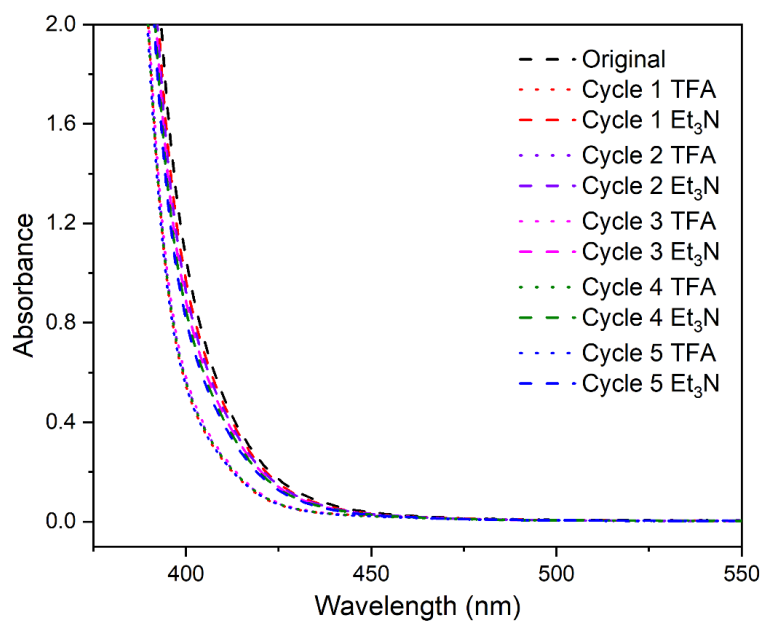


Figure S50. UV-vis spectra of **G5@H1₂** ($[G5]=2.00$ mM, $[H1]=4.00$ mM, 298 K) in $CHCl_3/CH_3CN$ (1:1, v/v) in the acid/base stimuli-responsive cycles.

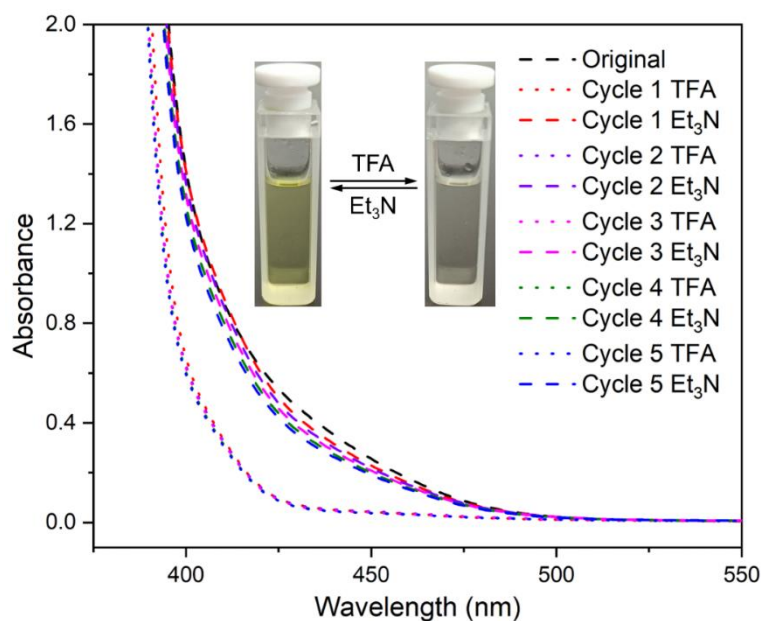


Figure S51. UV-vis spectra of **G6@H1₂** ($[G6]=2.00$ mM, $[H1]=4.00$ mM, 298 K) in $CHCl_3/CH_3CN$ (1:1, v/v) in the acid/base stimuli-responsive cycles. Inset: acid/base stimuli-responsive color changes of **G6@H1₂**.

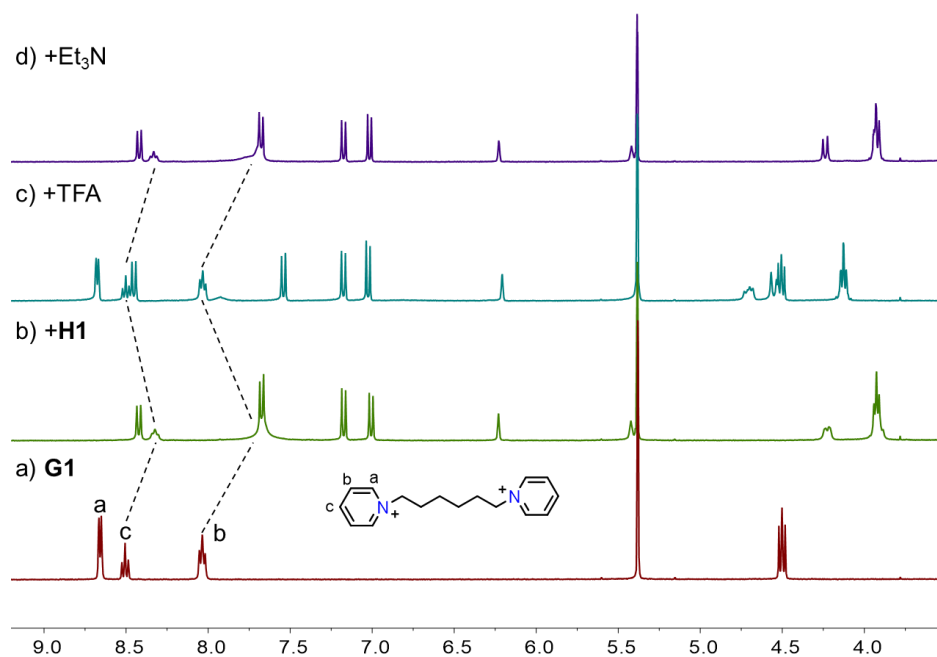


Figure S52. Partial ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of a) 1.0 mM free guest **G1**, b) after addition of 1 equiv. of **H1** (1.00 mM) to a), c) after addition of 3 equiv. of TFA to b), d) after addition of 3 equiv. of Et_3N to c).

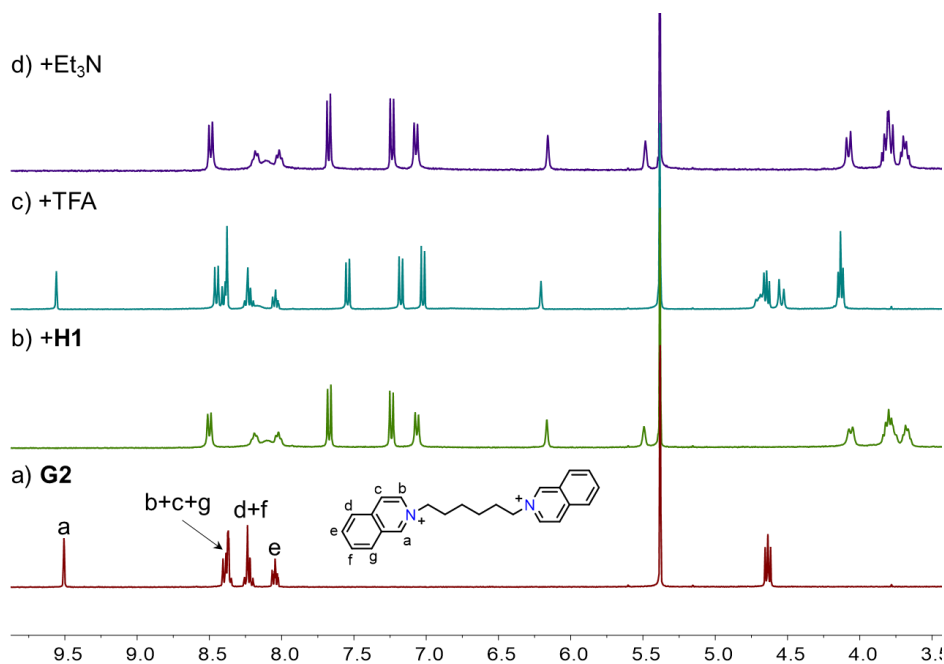


Figure S53. Partial ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of a) 1.0 mM free guest **G2**, b) after addition of 1 equiv. of **H1** (1.00 mM) to a), c) after addition of 3 equiv. of TFA to b), d) after addition of 3 equiv. of Et_3N to c).

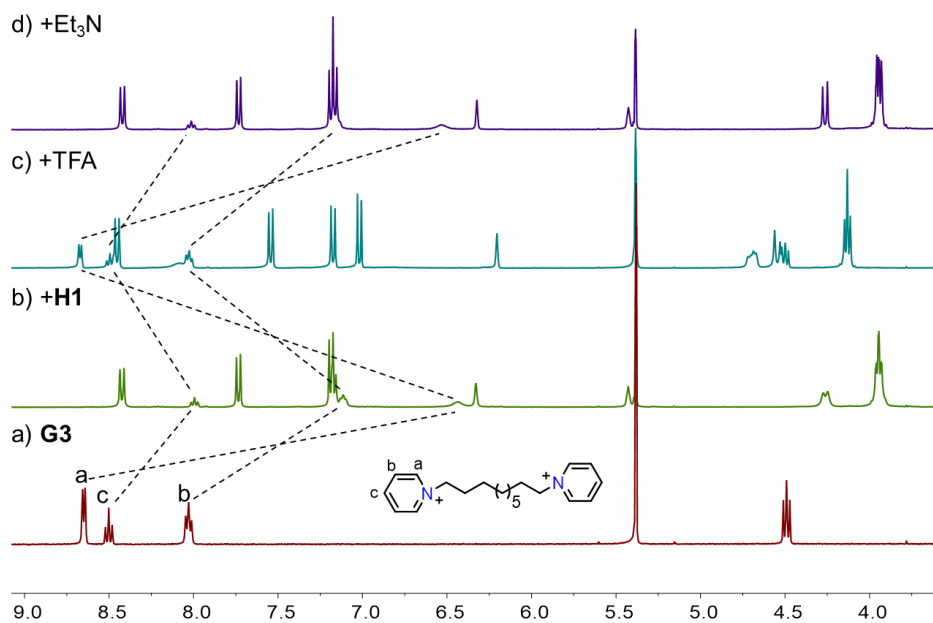


Figure S54. Partial ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of a) 1.0 mM free guest **G3**, b) after addition of 2 equiv. of **H1** (2.00 mM) to a), c) after addition of 6 equiv. of TFA to b), d) after addition of 6 equiv. of Et_3N to c).

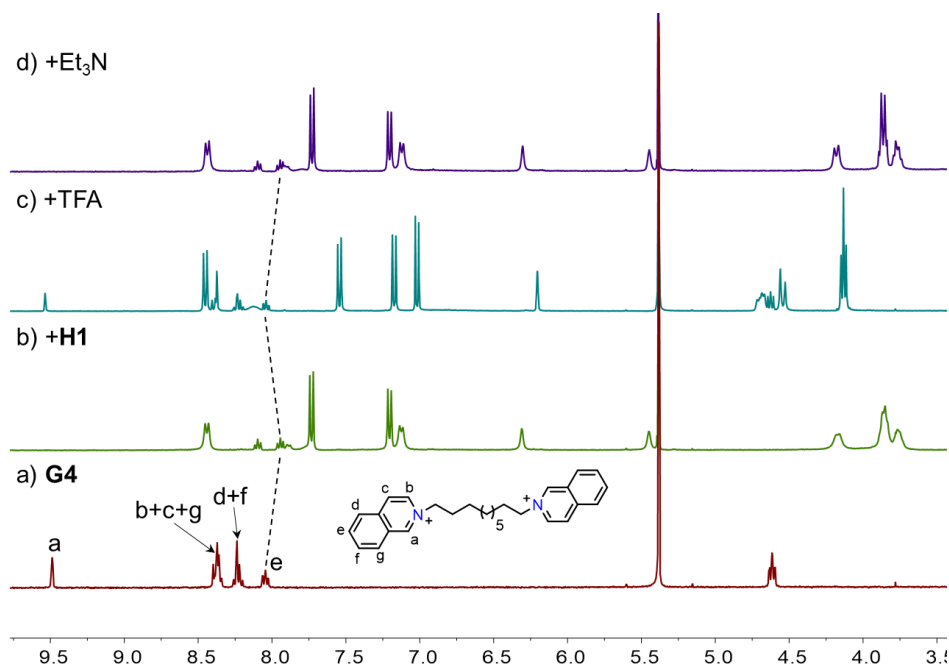


Figure S55. Partial ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of a) 1.0 mM free guest **G4**, b) after addition of 2 equiv. of **H1** (2.00 mM) to a), c) after addition of 6 equiv. of TFA to b), d) after addition of 6 equiv. of Et_3N to c).

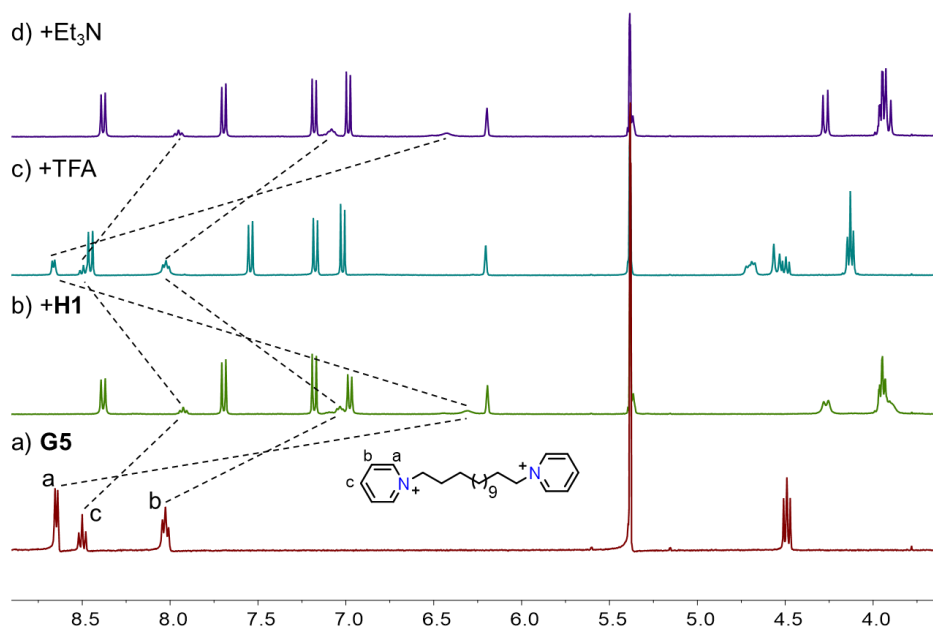


Figure S56. Partial ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of a) 1.0 mM free guest **G5**, b) after addition of 2 equiv. of **H1** (2.00 mM) to a), c) after addition of 6 equiv. of TFA to b), d) after addition of 6 equiv. of Et_3N to c).

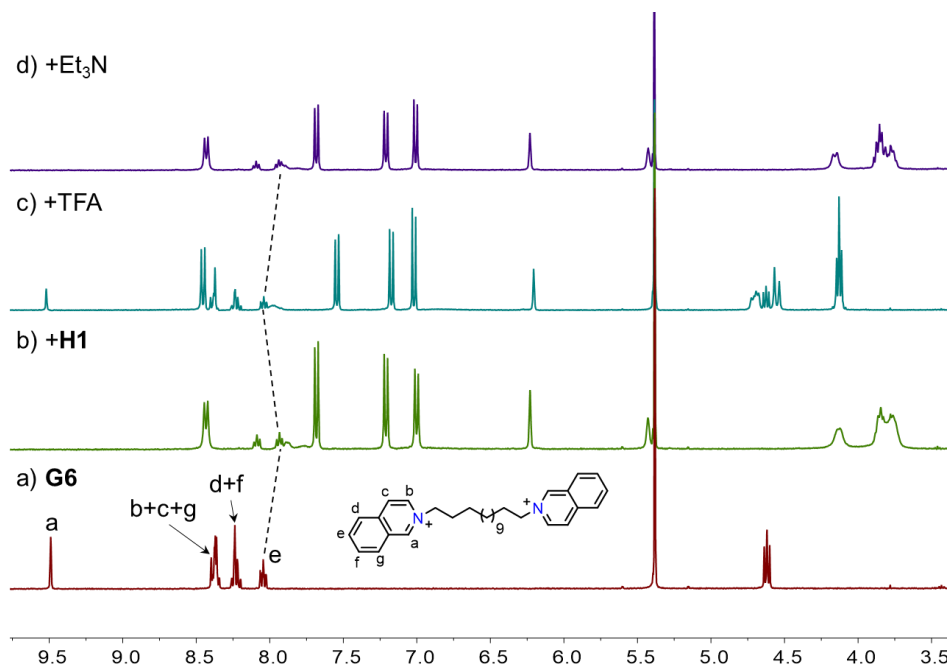
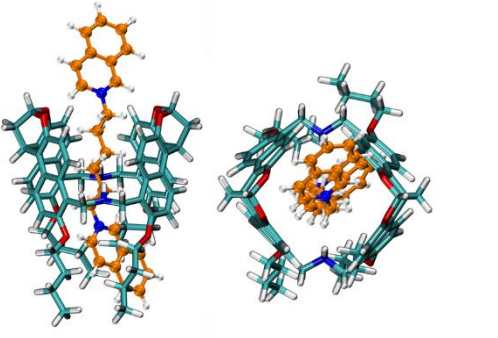
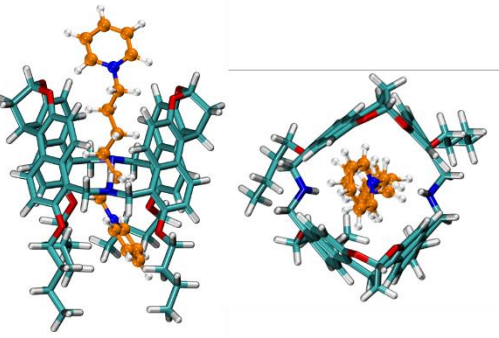


Figure S57. Partial ^1H NMR spectra (400 MHz, $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{CN}=1:1$, 298 K) of a) 1.0 mM free guest **G6**, b) after addition of 2 equiv. of **H1** (2.00 mM) to a), c) after addition of 6 equiv. of TFA to b), d) after addition of 6 equiv. of Et_3N to c).

7. Computational data

Computational Methods. Geometry optimizations were performed with Gaussian 16 software package,⁶ using the (B3LYP-D3(BJ)) method⁷ with 6-31G* basis set⁸ in vacuum without applying any geometry constraints (C1 symmetry). Frequency calculations were then conducted at the same computational level to confirm the nature of all located stationary points. Single point energy was calculated with Gaussian 16 software package using the (B3LYP-D3(BJ)) method with 6-311+G** basis set in vacuum. Non-covalent interaction (Independent gradient model based on Hirshfeld partition, IGMH) analysis⁹ was carried out with Multiwfn 3.8 (dev) program¹⁰ and visualized by the VMD 1.9.3 program.¹¹ (set isovalue = 0.005)

Energy-minimized structures of G1@H1 :	Energy-minimized structures of G2@H1 :
	
Cartesian coordinates of G1@H1 :	Cartesian coordinates of G2@H1 :
<pre>C 2.9805992 -1.6613262 -3.5946312 C 0.1967830 -1.2460181 -3.7236753 C 2.4683802 -0.4093861 -3.9983113 C 2.1497851 -2.7179322 -3.2752012 C 0.7359790 -2.5423812 -3.4102152 C 1.1126441 -0.1988760 -4.0286463 C -0.1866871 -3.6073482 -3.2611942 C -1.5449532 -3.3963872 -3.2332292 C -2.0610352 -2.0883241 -3.3897492 C -1.2142451 -1.0373220 -3.7244323 O 4.3608903 -1.7277522 -3.5259772 C 5.0007853 -2.9706013 -3.2102452 C 4.1260962 -4.1688734 -3.5129382 C 2.8248121 -3.9717923 -2.7280002</pre>	<pre>C -3.0979952 -3.7318013 -1.8694391 C -0.5176780 -4.1222883 -0.8159501 C -2.9331242 -4.2374853 -0.5608380 C -2.0189681 -3.4545572 -2.6889702 C -0.7016821 -3.6846183 -2.1732252 C -1.6759071 -4.4075113 -0.0408840 C 0.4597220 -3.4731682 -2.9588222 C 1.7186501 -3.5893663 -2.4230072 C 1.8861021 -3.9400333 -1.0663051 C 0.7989461 -4.2483903 -0.2691810 O -4.4141323 -3.5337003 -2.2396942 C -4.6577863 -2.8431112 -3.4613363 C -3.6814753 -3.2803552 -4.5334553 C -2.2900302 -2.8394372 -4.0653563</pre>

C	3.1611481	-3.7552693	-1.2511851	C	-2.3035692	-1.3187001	-3.9561103
O	5.3829123	-2.9424843	-1.8472831	O	-4.6198703	-1.4431421	-3.2163342
C	4.3877602	-3.2102783	-0.9206561	C	-3.4616472	-0.7372931	-3.4798852
C	2.2063781	-3.9580583	-0.2032180	C	-1.1805071	-0.4777680	-4.2345263
C	2.4778011	-3.4951183	1.1266101	C	-1.1958871	0.9004521	-3.8308833
C	3.7658292	-2.9563283	1.3972841	C	-2.4202312	1.4321951	-3.3310932
C	4.7068673	-2.8463703	0.4061720	C	-3.5358663	0.6449180	-3.1996622
C	1.4513370	-3.5371113	2.1213112	C	-0.0115410	1.6898791	-3.9263163
C	0.1917489	-4.0029453	1.7761621	C	1.1366051	1.1345721	-4.4809323
C	-0.0370561	-4.5903073	0.5115210	C	1.0924041	-0.1577640	-5.0584364
C	0.9533440	-4.5771813	-0.4378120	C	-0.0329090	-0.9353851	-4.9265644
O	-3.3827673	-1.7853730	-3.2428662	O	3.1518252	-3.9030773	-0.5178740
O	-0.8431592	-3.7722642	2.6525522	O	2.2714132	1.8853801	-4.4455093
C	3.3709123	3.4055592	2.0227822	C	-3.3631742	2.5005772	2.3640232
C	1.6819002	1.6455671	3.4156493	C	-1.1362331	3.5247873	0.9870631
C	3.8920863	2.2267081	2.6002452	C	-3.4824333	2.8867282	1.0120011
C	2.0385232	3.7565252	2.1465532	C	-2.1644592	2.5906322	3.0487262
C	1.1739761	2.8770302	2.8797592	C	-1.0455691	3.1860292	2.3820562
C	3.0640882	1.3568111	3.2584512	C	-2.3840852	3.3453672	0.3301110
C	-0.2030589	3.1606083	3.0743262	C	0.1600520	3.5057022	3.0618772
C	-1.0468960	2.2526682	3.6664133	C	1.2239591	4.0718963	2.4044752
C	-0.5491940	1.0134241	4.1208123	C	1.1493101	4.3273723	1.0187781
C	0.8013261	0.7209311	4.0597243	C	-0.0032510	4.0681553	0.3012480
O	4.3007564	4.1475972	1.3148391	O	-4.5350383	2.0357221	2.9309022
C	3.8050154	5.2173583	0.5175570	C	-4.5156003	1.5512071	4.2785173
C	2.7174203	5.9776474	1.2476041	C	-3.4791853	2.2664682	5.1189534
C	1.5408632	5.0091364	1.4186961	C	-2.1187252	2.0090911	4.4604473
C	1.0522572	4.6323383	0.0248080	C	-1.8940731	0.4983340	4.3898963
O	3.3666673	4.6878743	-0.7299670	O	-4.3082343	0.1541270	4.2533833
C	2.0240392	4.4429453	-0.9401801	C	-3.0044752	-0.3132400	4.2523353
C	-0.3139529	4.3985234	-0.3263030	C	-0.5992620	-0.1172710	4.3942793
C	-0.6279970	3.7702343	-1.5780831	C	-0.4756170	-1.5200191	4.1086563
C	0.4240001	3.5782823	-2.5162842	C	-1.6626591	-2.2879952	3.9560693
C	1.7118412	3.9535723	-2.2254921	C	-2.8987972	-1.7085871	4.0697813
C	-1.9757571	3.3812253	-1.8683441	C	0.8152981	-2.1241082	4.0146453
C	-2.9798931	3.7124844	-0.9775201	C	1.9358251	-1.3779661	4.3298513
C	-2.6952811	4.4635814	0.1869660	C	1.8175811	-0.0194140	4.6955313
C	-1.4001460	4.7875184	0.5041420	C	0.5887950	0.5959720	4.7030213
O	-1.4473081	0.0494421	4.5394523	O	2.2729842	4.8080603	0.3765520
O	-4.2672402	3.2817844	-1.2050701	O	3.1652262	-1.9835191	4.3809773
C	1.6359470	-2.8805022	3.4653453	C	0.0334030	3.0759002	-3.3328442
C	1.2863601	-0.6420210	4.4859353	C	-0.0271630	4.2796753	-1.1925811
C	-1.8081871	0.3136091	-4.0293773	C	1.0117411	-4.5767093	1.1889291
C	-2.2732911	2.5273523	-3.0734872	C	0.9822171	-3.4997872	3.4210002

C	-4.3336104	-2.8401191	-3.0498472	C	4.0432723	-4.9614674	-0.9316101
C	-5.6907075	-2.1962290	-2.8247072	C	5.3812964	-4.7333333	-0.2540840
C	-1.8147142	-4.8109043	2.9079692	C	3.4752393	1.3556111	-5.0134654
C	-3.2201783	-4.2898022	2.6443092	C	4.6244483	2.2659512	-4.6203973
C	-1.8744321	0.1253591	5.9168064	C	2.3977022	6.2504634	0.3580790
C	-2.7367572	-1.0916000	6.2035864	C	3.6038793	6.6169375	-0.4880720
C	-5.2162743	4.3110995	-1.5590051	C	4.0679063	-1.7529501	3.2901832
C	-6.5804114	3.6619744	-1.7071031	C	5.3664704	-2.4537112	3.6605123
H	3.1674712	0.3739260	-4.2739353	H	-3.8206513	-4.4819793	0.0143830
H	0.7403651	0.7792421	-4.3102643	H	-1.5699251	-4.7751353	0.9731901
H	0.1741179	-4.6249313	-3.1966032	H	0.3638240	-3.2040992	-3.9970093
H	-2.2121833	-4.2401592	-3.1090632	H	2.5961682	-3.4006552	-3.0342832
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H	4.6545072	-5.0734394	-3.1991292	H	-3.9400653	-2.8100262	-5.4860704
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H	0.7558109	-5.0407134	-1.3898551	H	-0.0466990	-1.9048971	-5.4086584
H	4.9524044	2.0215371	2.4951162	H	-4.4520053	2.8109682	0.5302900
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H	-0.6116050	4.0967903	2.7333212	H	0.2361300	3.3455632	4.1271933
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H	4.6817865	5.8198974	0.2848140	H	-5.5361044	1.6834041	4.6355143
H	3.1088864	6.3134334	2.2119462	H	-3.7071013	3.3354752	5.1538424
H	2.4205293	6.8541675	0.6653041	H	-3.5097073	1.8676791	6.1367235
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H	-1.2143290	5.3885764	1.3856371	H	0.5304510	1.6294061	5.0102574
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C	-4.7197503	0.6009172	0.0539620	H	-5.8855164	0.9001961	1.7175731
C	-4.2579073	0.0901771	2.3629202	H	-7.9175846	-1.8882231	-1.8002001
H	-2.3350462	-0.8563460	2.6837152	H	-5.6919214	-2.3953942	-0.8002291
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	H	-4.3642623	-2.1639932	1.1965631
	H	-4.3290963	-0.5925620	2.0046361

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