Supporting information

New Water-soluble Organic Capsules Are Effective in Controlling Excited State Processes of Guest Molecules

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Table of Contents

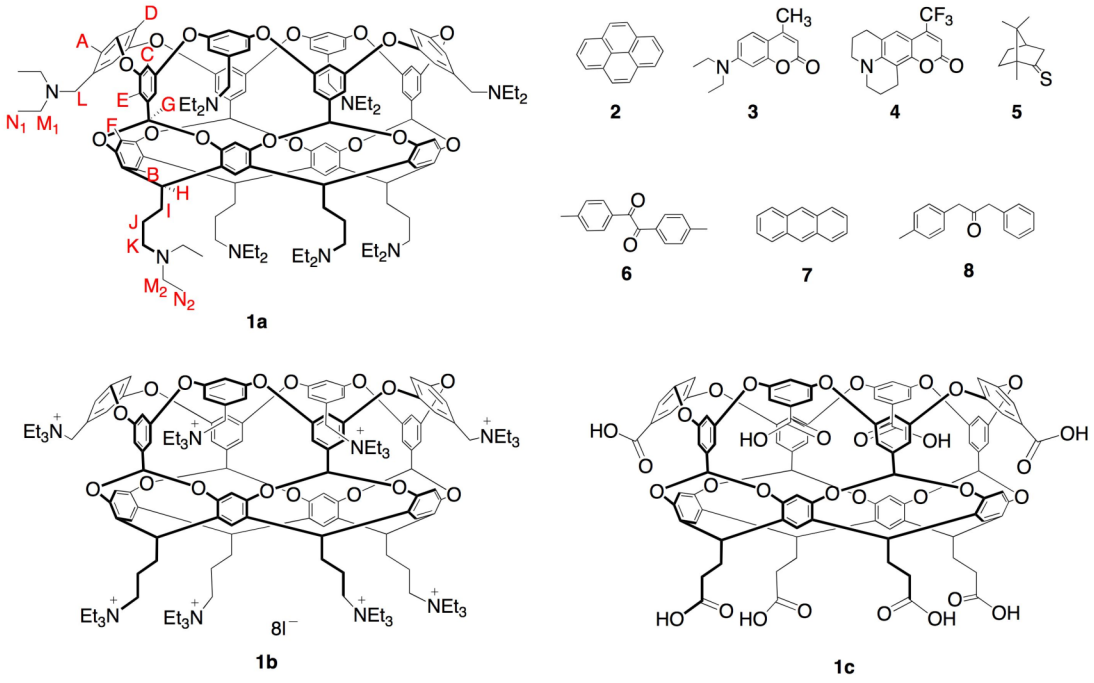
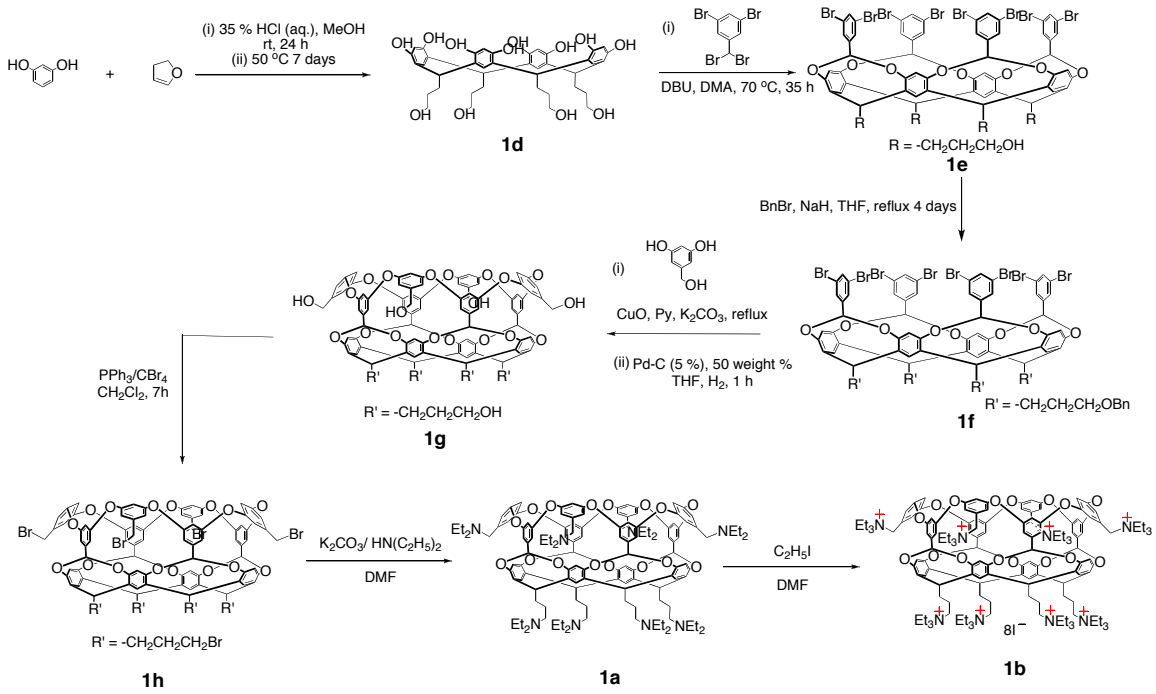


Chart S1. Structures of host and guests used for the study.

Experimental section

Synthesis of host **1a** and **1b**



Precursors **1d-1g** were synthesized by following the procedure reported earlier.[1]

Synthesis of **1h:**

To **1h (**0.3 g, 0.19 mmol) suspended in dichloromethane (25 mL) added triphenyl phosphine (0.89 g, 3.4 mmol) and carbon tetrabromide (1.26 g, 3.8 mmol). The reaction mixture was stirred in N_2 atmosphere for 7h. The reaction mixture was concentrated and purified by column chromatography using chloroform.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.9 (s, 8H), (s, 3H), 1.54 (q, 2H, J = 7.5 Hz), 7.40 (t, 3H, 8 Hz), 7.64 (d, 2H, J = 3Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.4, 23.5, 37.0, 49.5, 127.3, 127.8, 132.2 139.8 and 210.1.

MS (ESI): [$C_{96}H_{72}O_{16}Br_8$] Calcd.: 2136.8159, found: 2136.8292.

Synthesis of OAM (**1a**):

[1] Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2004**, *126*, 11408.

To **1i (**130 mg, 0.024 mmol) added DMF (5 mL) and potassium carbonate (0.1 g), stirred for half hour. To the above reaction mixture added 50 eq of diethyl amine. The reaction was stirred at 55 °C for two days. The reaction mixture was cooled and diluted with dichloromethane and washed with water (4x30 mL). The organic layer was dried over sodium sulphate and evaporated to yield **1a**. The obtained final product was dried over vacuum at 120 °C for 2 days.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 0.98 (t, 48H), 1.45 (m, 8H), 2.25 (t, 8H), 2.5 (m, 40H), 3.68 (s, 8H), 4.5 (s, 4H), 4.75 (t, 4H), 5.95 (s, 4H), 6.48 (s, 4H), 6.51 (s, 8H), 6.95 (s, 4H), 7.2 (s, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 11.5, 12.08, 24.92, 28.27, 29.72, 36.30, 46.68, 47.17, 52.32, 57.25, 105.58, 107.38, 109.65, 113.65, 114.95, 120.58, 136.76, 139.23, 144.958, 156.27, 161.146.

MS (ESI): [$C_{128}H_{152}O_{16}N_8$] Calculated: 2058.1399, found: 2058.1374.

Synthesis of OTEAM (**1b**):

1a (0.120 g) was dissolved in 2 mL of DMF, treated with excess of iodoethane and stirred for 2 days at RT. The reaction mixture was diluted with diethyl ether for the formation of precipitate. The precipitate was filtered and washed with excess of diethyl ether to remove unreacted iodoethane. The obtained yellow solid was dried over vacuum at 120 °C to remove any DMF present.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 1.23 (t, 72H), 1..54 (m, 8H), 4.47 (s, 4H), 4.529 (s, 4H), 4.59 (t, 4H) , 5.83 (s, 4H), 6.46 (s, 8H), 6.83 (s, 4H), 7.22 (s, 4H), 7.57 (s, 8H), 7.87 (s, 4H).

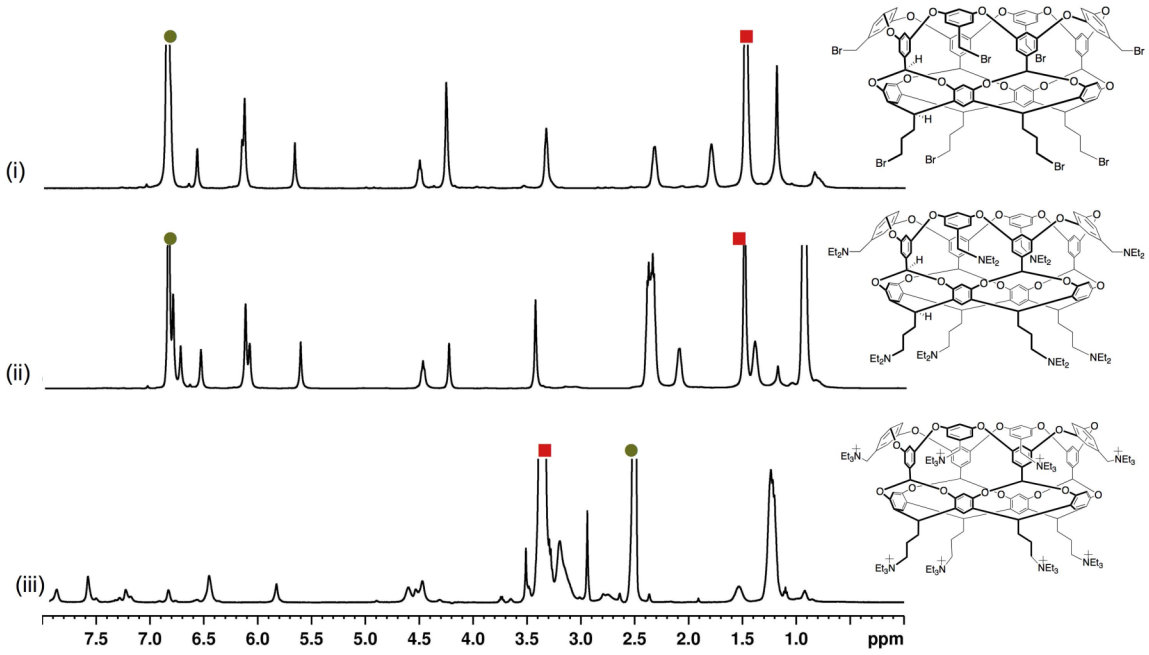


Figure S1. ^{1}H NMR (500 MHz) spectra (i) **1h** (in $CDCl_3$), (ii) **1a** (in $CDCl_3$) and (iii) **1b** (in DMSO-D_6) ■ indicates residual water signal ● indicates respective residual solvent.

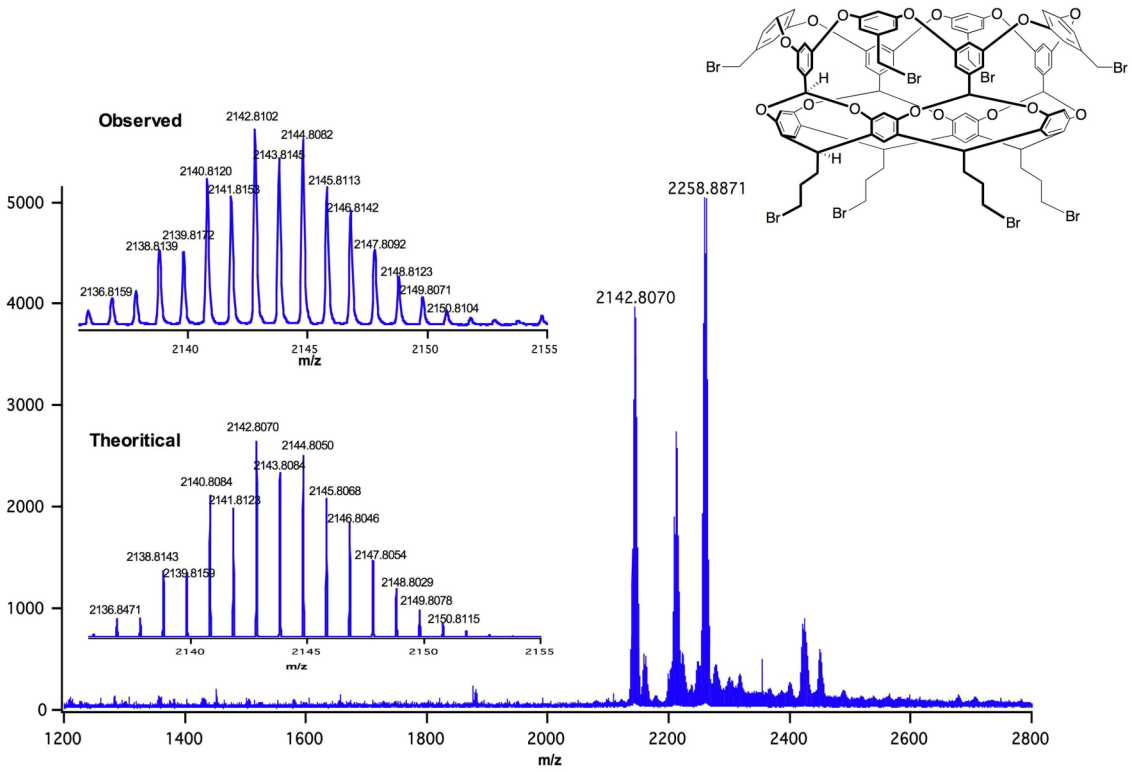


Figure S2. ESI-MS (Bruker microOTOF-Q II) of solution of **1h** in chloroform: acetone: acetonitrile (25:25:50) + 0.1% formic acid.

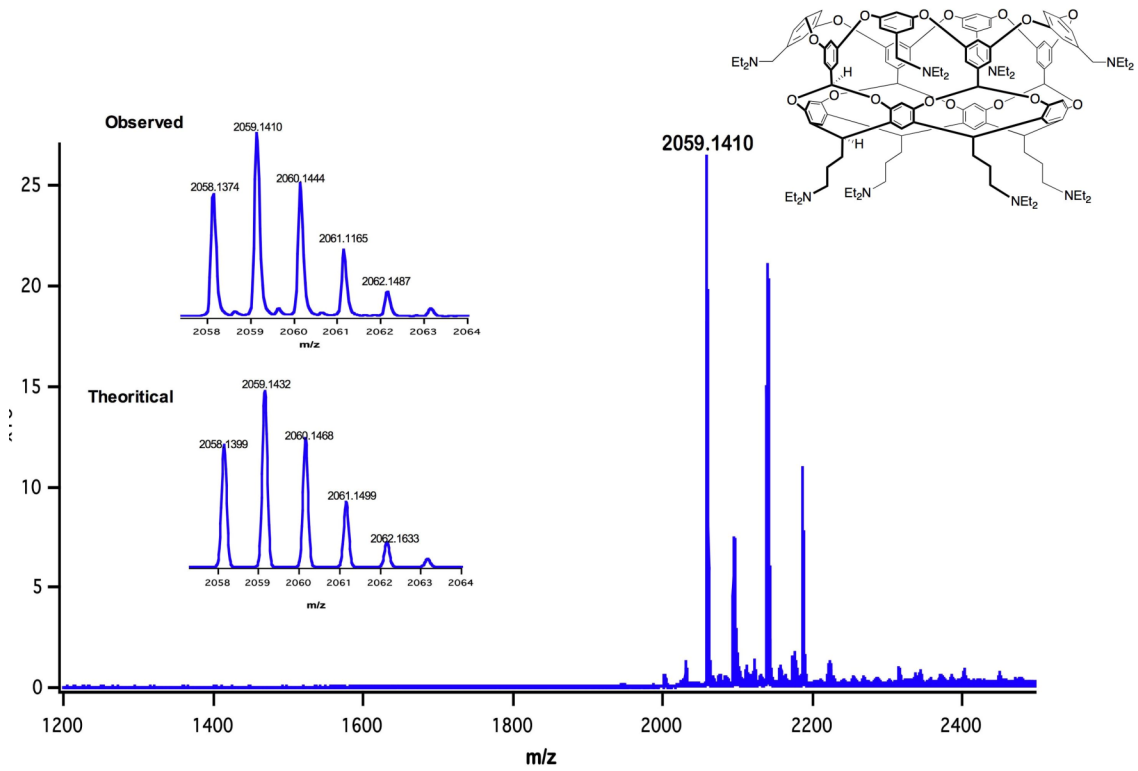


Figure S3. ESI-MS (Bruker microOTOF-Q II) of solution of **1a** in chloroform: acetone: acetonitrile (25:25:50) + 0.1% formic acid.

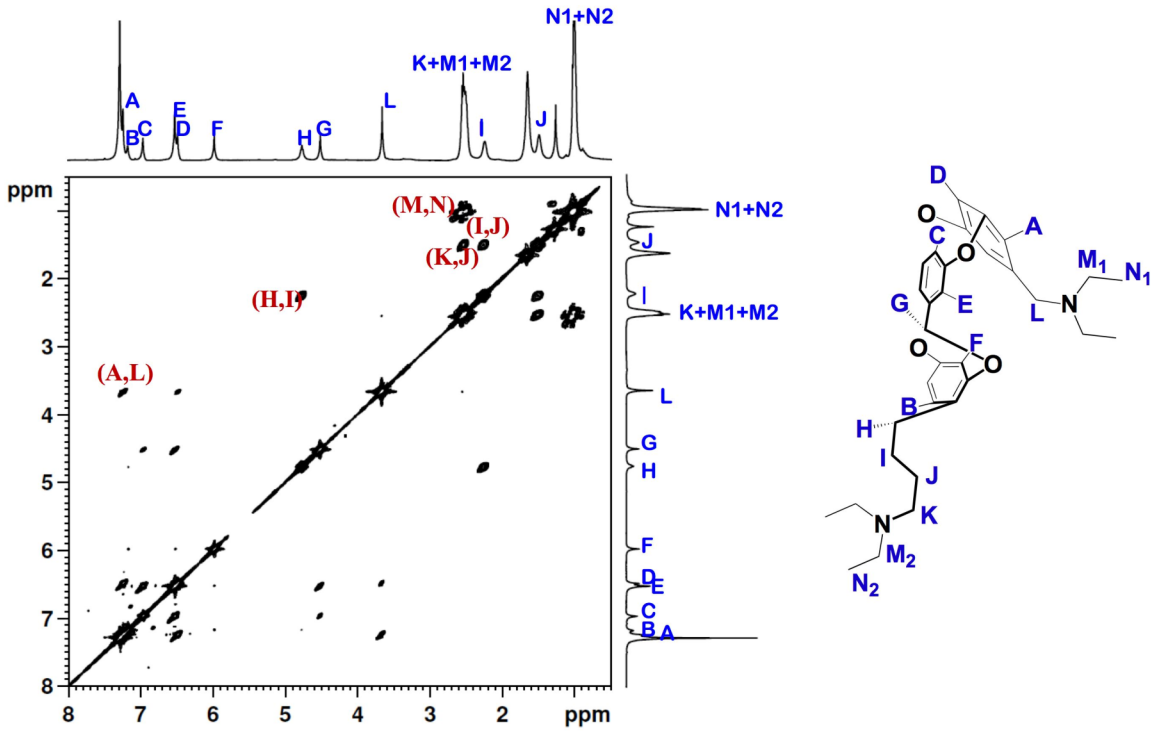


Figure S4. COSY Spectrum of 5mM solution of **1a** in $CDCl_3$.

*Preparation of stock solution of OAM (**1a**) in D_2O/DCl*

10.29 mg of host **1a** was taken in 10 mL round bottomed flask. Added 5mL methanol, sonicated well cloudy suspension was formed, to this added 3-4 drops of deuterium chloride in 35% weight in D_2O to get a clear transparent solution. Methanol was removed by rotary evaporator dried in high vacuum for 2-3 hr. Then added 5mL of D_2O to form 1mM stock solution.

Sample Preparation for Luminescence measurements:

Capsular assemblies of OAM (1 mM) were made separately by adding 5 μL of 60 mM solution of guest (in DMSO) to 600 μL of 1 mM OAM in D_2O/DCl (pH=1) for 2:1 (H:G) capsular assembly (for (2:2 capsular assembly 10 μL of 60 mM solution guest in DMSO was added to 600 μL solution of 1mM OAM). All emission experiment were performed using NMR tubes.

NMR Measurements

1D and 2D COSY NMR studies were carried out on a Bruker 500 MHz NMR spectrometer at 25 °C.

Emission (Fluorescence and Phosphorescence) experiments:

Steady–state Luminescence spectra were recorded using a FS920CDT fluorometer (Edinburgh Analytical Instrumnent). In some experiments a 406 nm Long-pass (cut-off) filter was placed in the emission light path to eliminate scattered excitation light.

Fluroescence lifetimes were measured by time-correlated single photon counting using nF920 fluorometer (Edinburgh Analytical Instruments). Phosphorescence lifetimes were measured on an OB920 fluorometer (Edinburgh Analytical Instruments) using a pulsed microsecond xenon lamp as excitation source and multi-channel scaling for data acquisition.

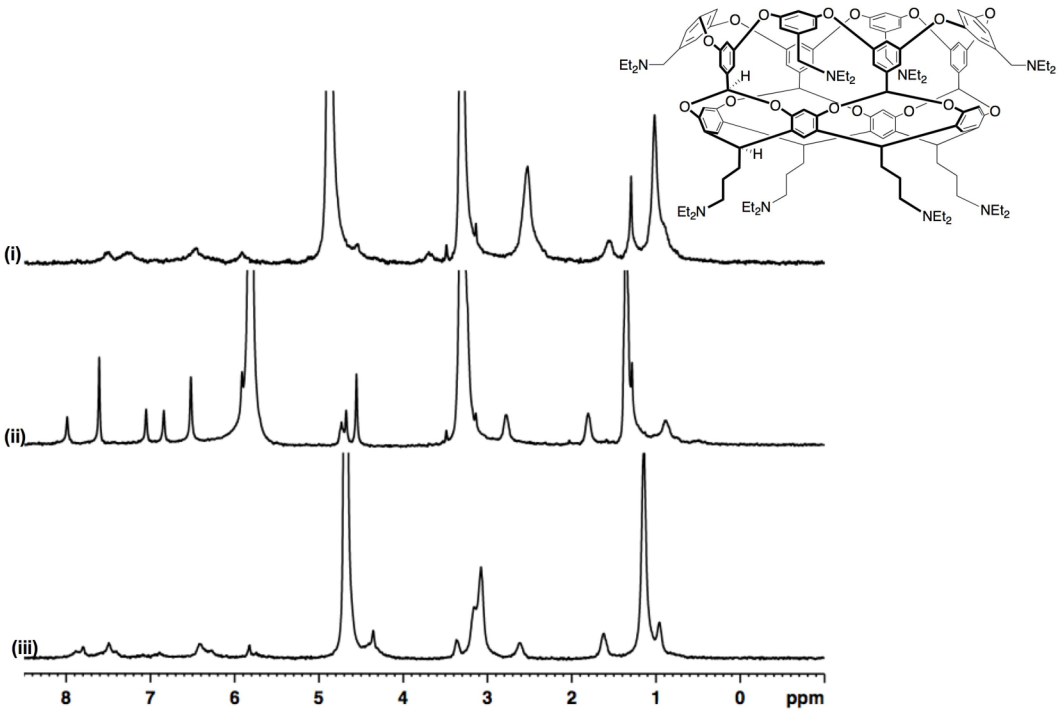


Figure S5. ^{1}H NMR spectra (500 MHz) (i) **1a** (1mM in CD_3OD), (ii) **1a** (1mM in CD_3OD/DCl) and (iii) **1a** (1mM in D_2O/DCl).

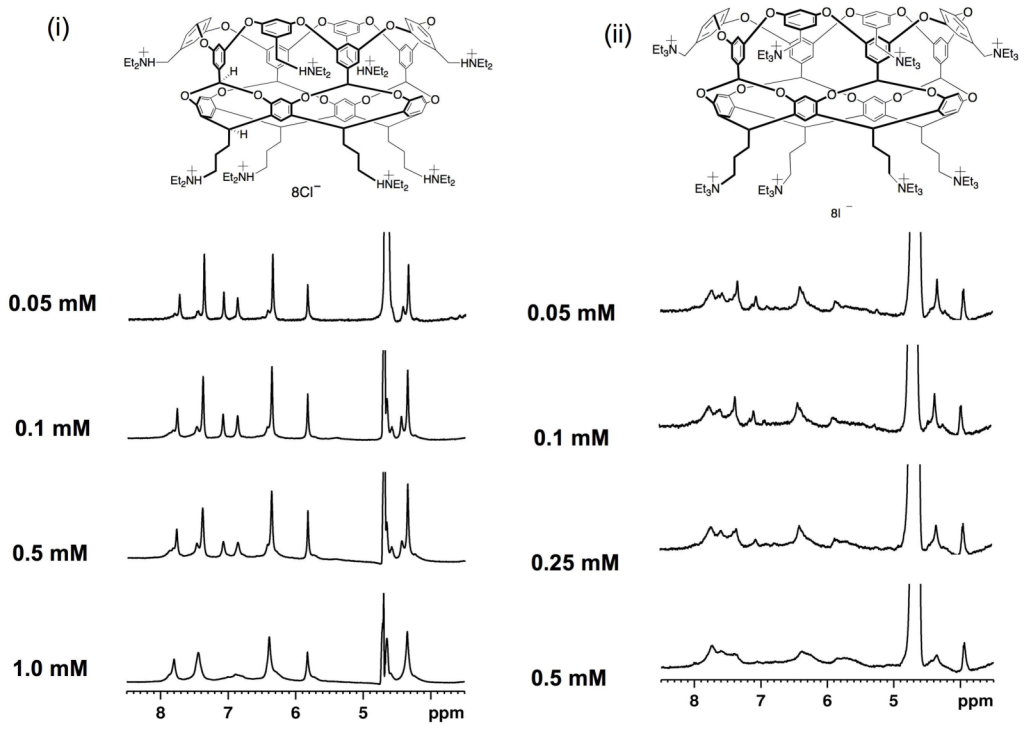


Figure S6. ^{1}H NMR spectra (500 MHz) of host (a) **1a** in D_2O/DCl (pH≈1), (b) **1b** at in D_2O (pH≈7) at various concentrations.

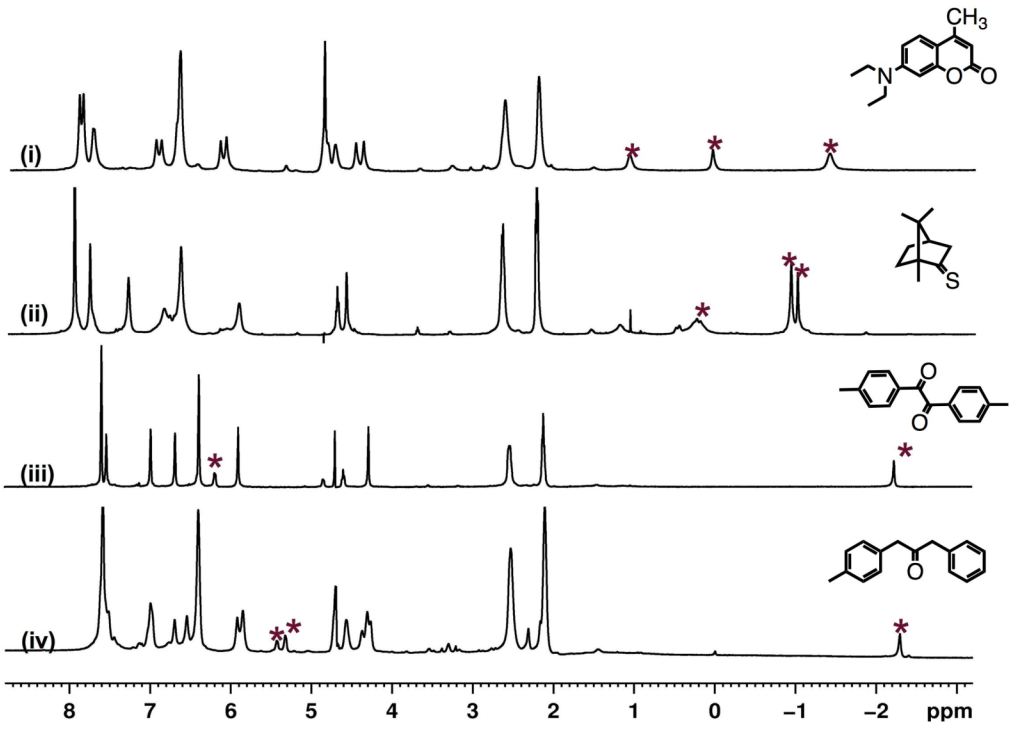


Figure S7. ^{1}H NMR spectra (500MHz) (i) **3**@**1c**$_2$ ([**1c**] = 1 mM; [**3**] = 0.5 mM), (ii) **5**$_2$@**1c**$_2$([**1c**] = 1 mM; [**5**] = 1 mM), (iii) **6**@**1c**$_2$([**1c**] = 1 mM; [**6**] = 0.5 mM) and (iv) **8**@**1c**$_2$([**1c**] = 1 mM; [**8**] = 0.5 mM) sodium borate buffer (pH≈9). Upfield resonances of bound guest protons are marked as *.

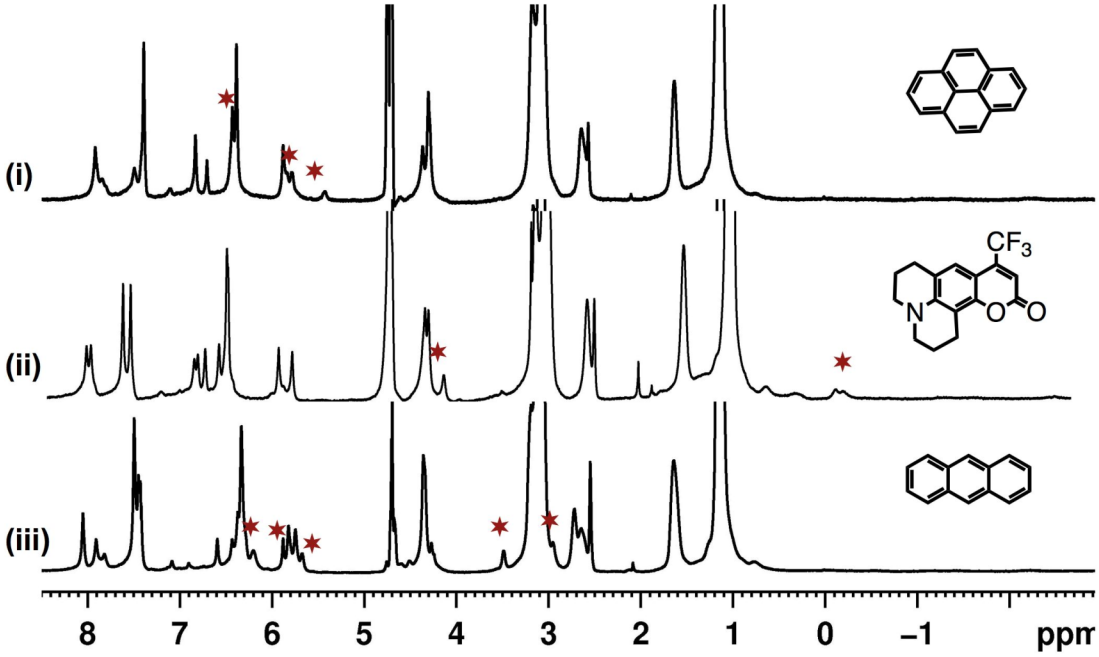


Figure S8a. ^{1}H NMR spectra (500MHz) (i) **2**@**1a**$_2$ ([**1a**] = 1 mM; [**2**] = 0.5 mM), (ii) **4**@**1a**$_2$([**1a**] = 1 mM; [**4**] = 0.5 mM) and (iii) **7**$_2$@**1a**$_2$([**1a**] = 1 mM; [**7**] = 1 mM) in D_2O/DCl (pH≈1). Upfield resonances of bound guest protons are marked as *.

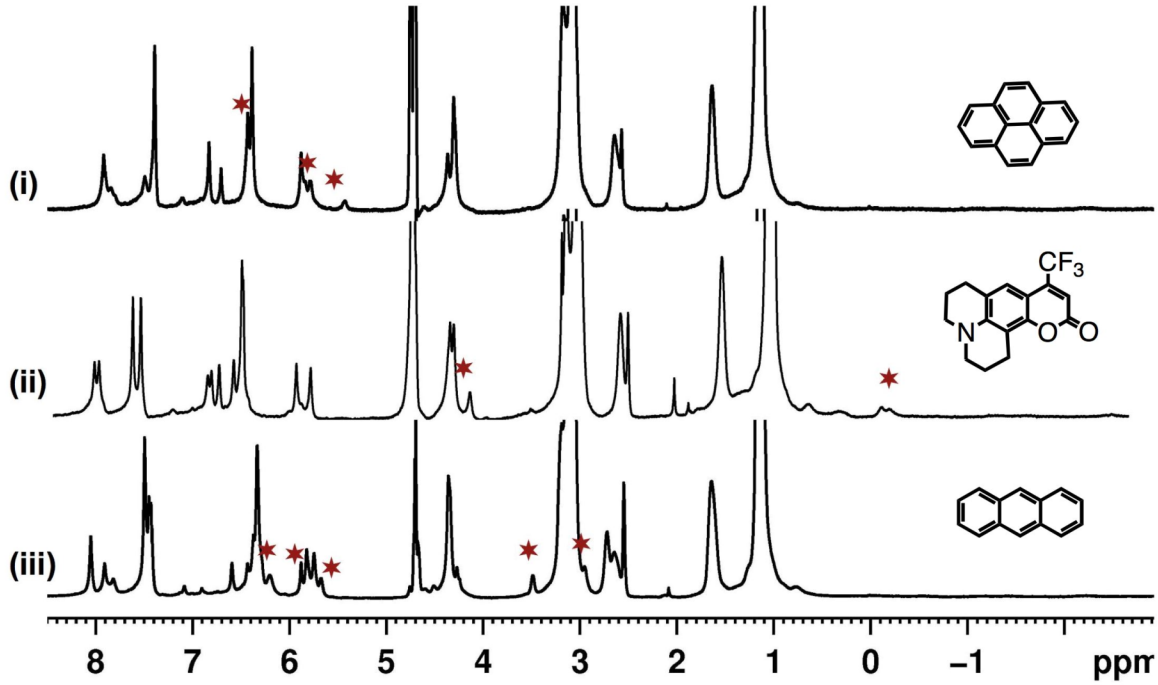


Figure S8b. ^{1}H NMR spectra (500MHz) (i) **2**@**1c**$_2$ ([**1c**] = 1 mM; [**2**] = 0.5 mM), (ii) **4**@**1c**$_2$([**1c**] = 1 mM; [**4**] = 0.5 mM) and (iii) **7**$_2$@**1c**$_2$([**1c**] = 1 mM; [**7**] = 1 mM) sodium borate buffer (pH≈9). Upfield resonances of bound guest protons are marked as *.

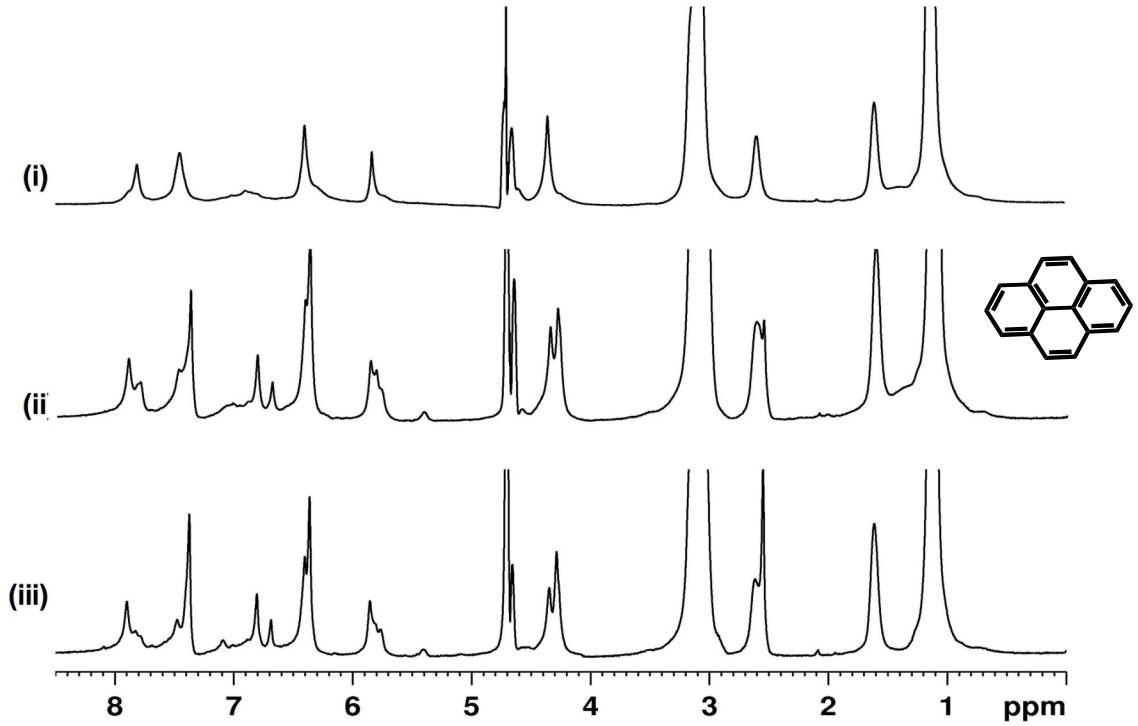


Figure S9. ^{1}H NMR titration spectra (500 MHz) of **2** with **1a** (i) **1a** (1mM in D_2O/DCl) (pH≈1) (ii) **1a**:**2** (1:0.25), (iii) **1a**:**2** (1:0.5) in D_2O/DCl (pH≈1).

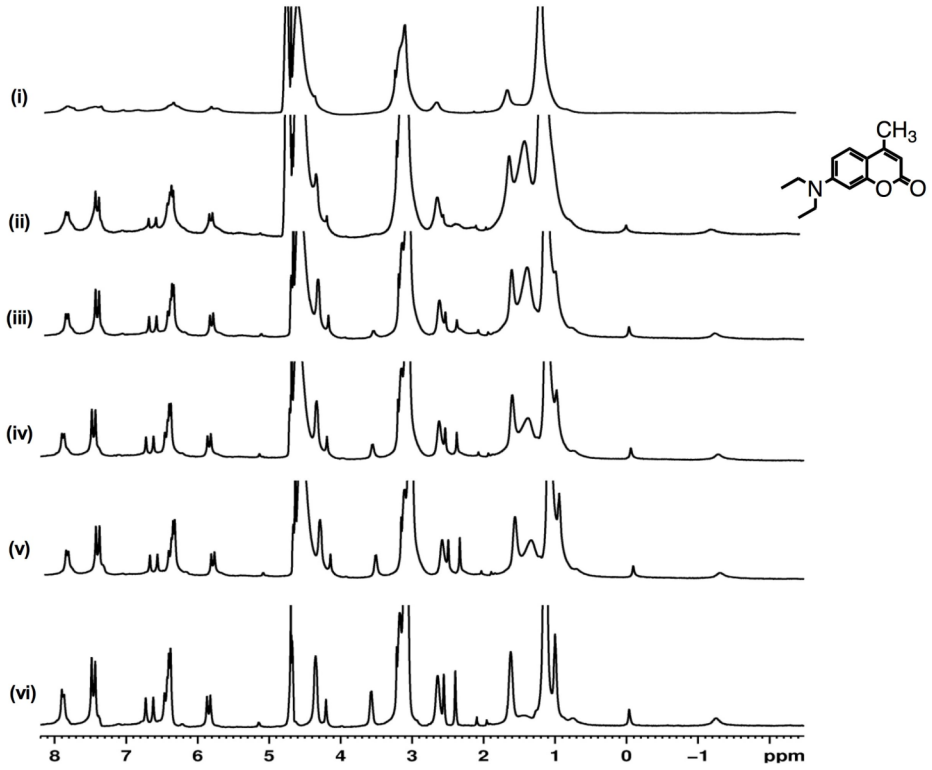


Figure S10. ^{1}H NMR titration spectra (500 MHz) of **3** with **1a** (i) **1a** (1mM in D_2O/DCl) (ii) **1a**:**3** (1:0.1), (iii) **1a**:**3**(1:0.2**)**, (iv) **1a**:**3**(1:0.3), (v) **1a**:**3** (1:0.4) and (vi) **1a**:**3** (1:0.5) in D_2O/DCl (pH≈1).

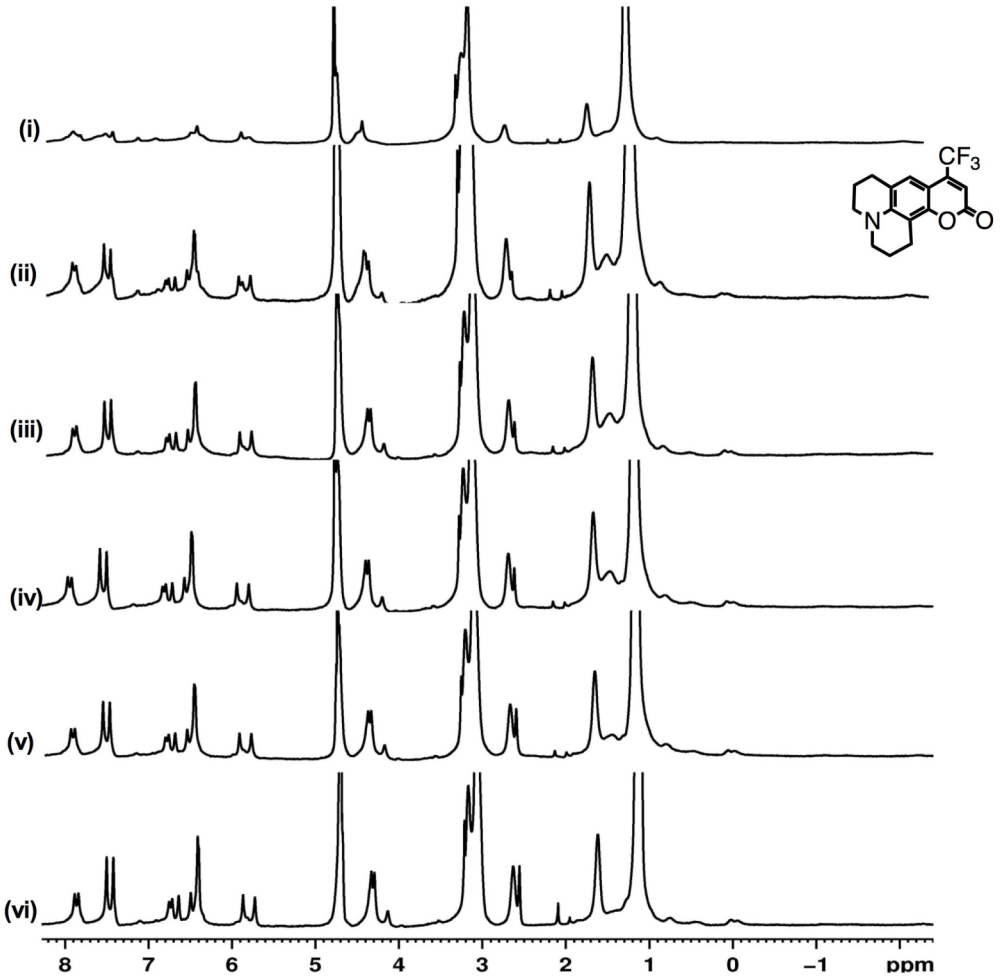


Figure S11. ^{1}H NMR titration spectra (500 MHz) of **4** with **1a** (i) **1a** (1mM in D_2O/DCl) (ii) **1a**:**4** (1:0.1), (iii) **1a**:**4**(1:0.2**)**, (iv) **1a**:**4**(1:0.3), (v) **1a**:**4** (1:0.4) and (vi) **1a**:**4** (1:0.5) in D_2O/DCl (pH≈1).

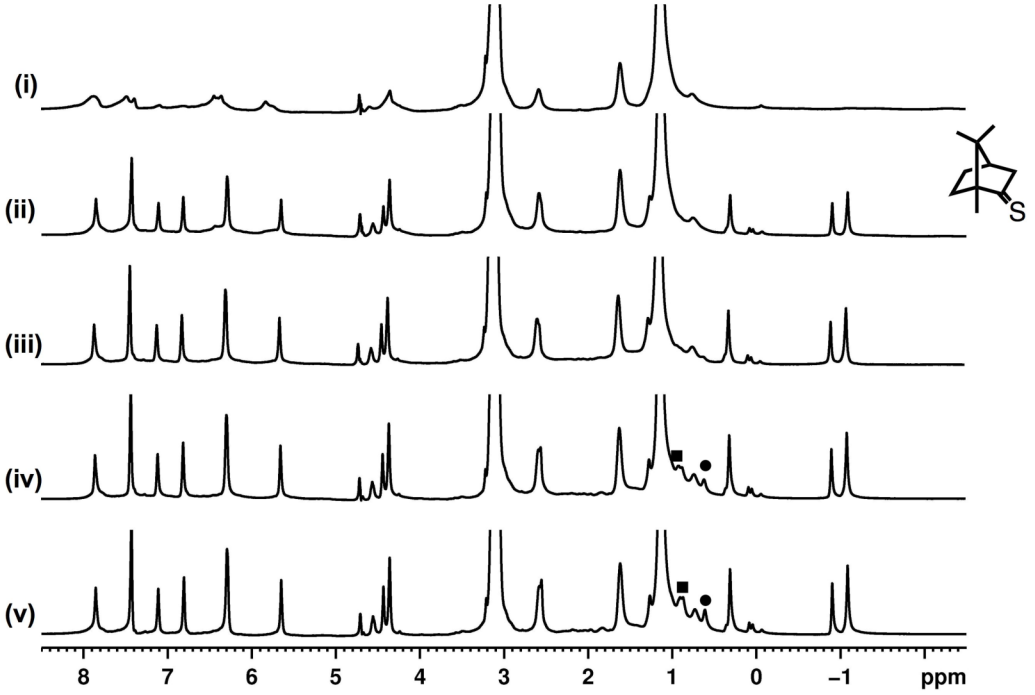


Figure S12. ^{1}H NMR titration spectra (500 MHz) of **5** with **1a** (i) **1a** (1mM in D_2O/DCl) (ii) **1a**:**5** (1:0.5), (iv) **1a**:**5** (1:1.25) and (v) **1a**:**5** (1:1.5) in D_2O/DCl (pH≈1). ● and ■ indicates excess uncomplexed guest proton resonances.

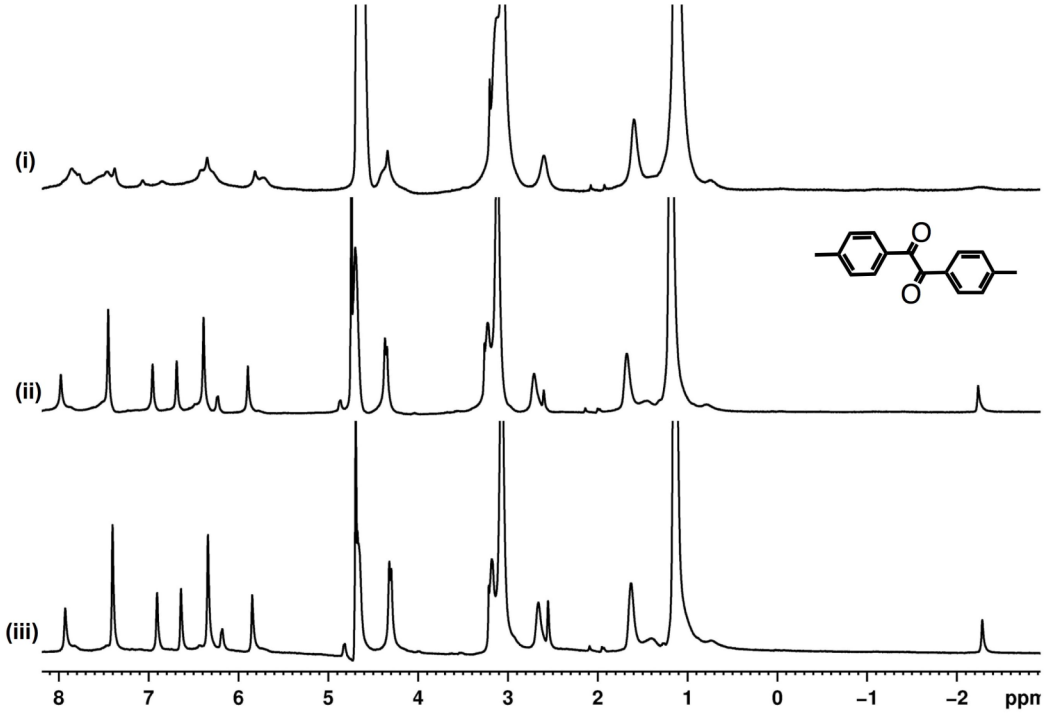


Figure S13. ^{1}H NMR titration spectra (500 MHz, D_2O) of **6** with **1a** (i) **1a** (1mM in D_2O/DCl) (ii) **1a**:**6** (1:0.25) and (iii) **1a**:**6** (1:0.5) in D_2O/DCl (pH≈1).

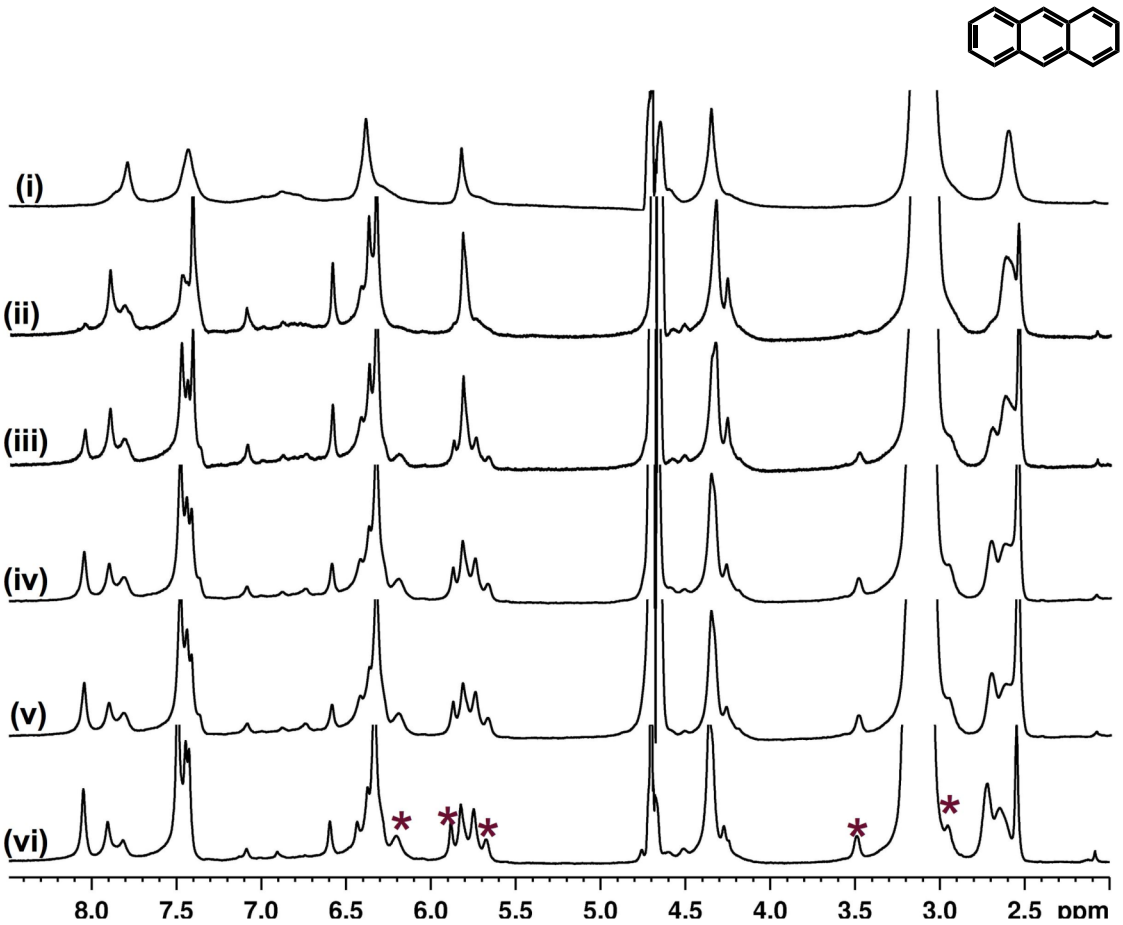


Figure S14. ^{1}H NMR titration spectra (500 MHz) of **7** with **1a** (i) **1a** (1mM in D_2O/DCl) (ii) **1a**:**7**(1:0.25), (iii) **1a**:**7** (1:0.5**)**, (iv) **1a:7** (1:0.75) and (v) **1a**:**7** (1:1) in D_2O/DCl (pH≈1).

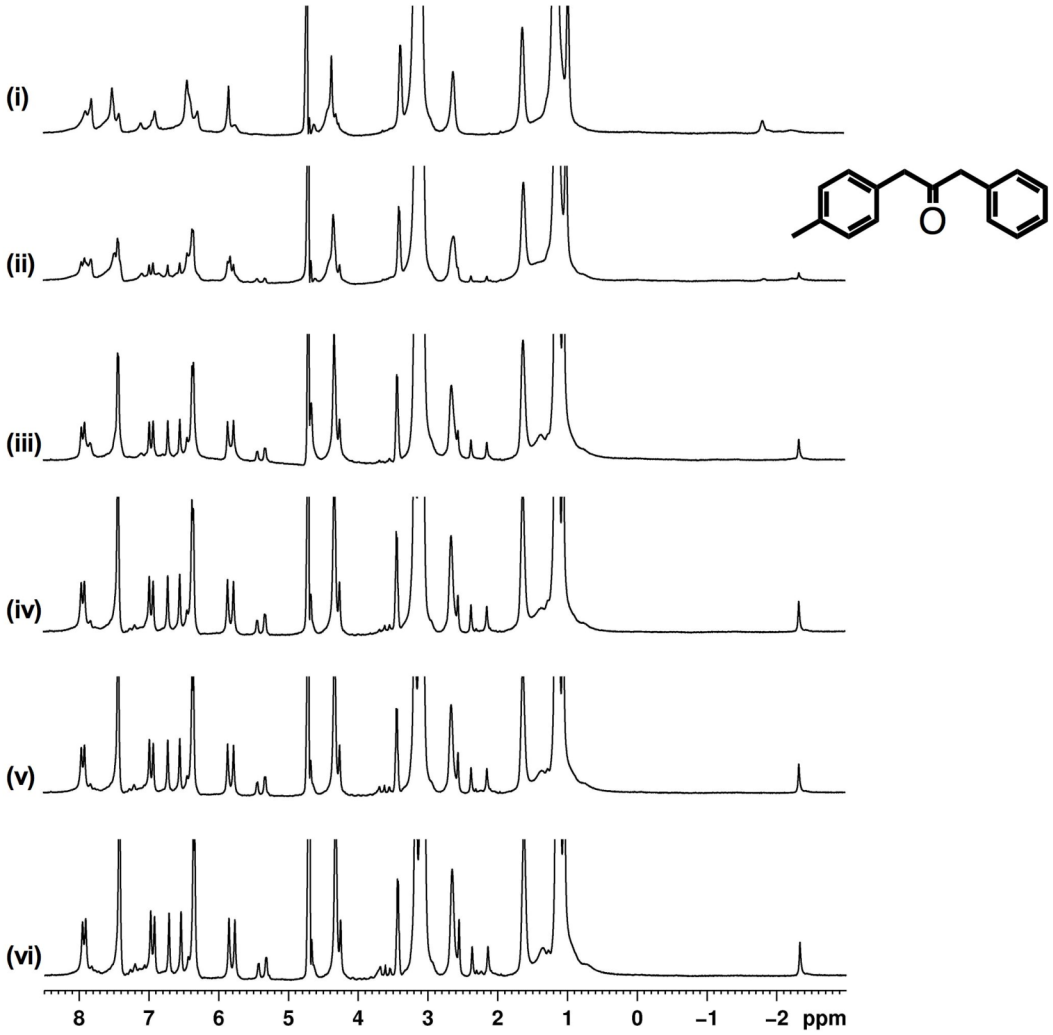


Figure S15. ^{1}H NMR titration spectra (500 MHz) of **8** with **1a** (i) **1a** (1mM in D_2O/DCl) (ii) **1a**:**8**(1:0.1), (iii) **1a**:**8** (1:0.2**)**, (iv) **1a:8**(1:0.3), (v) **1a**:**8**(1:0.4), and (vi) **1a**:**8** (1:0.5) in D_2O/DCl (pH≈1).

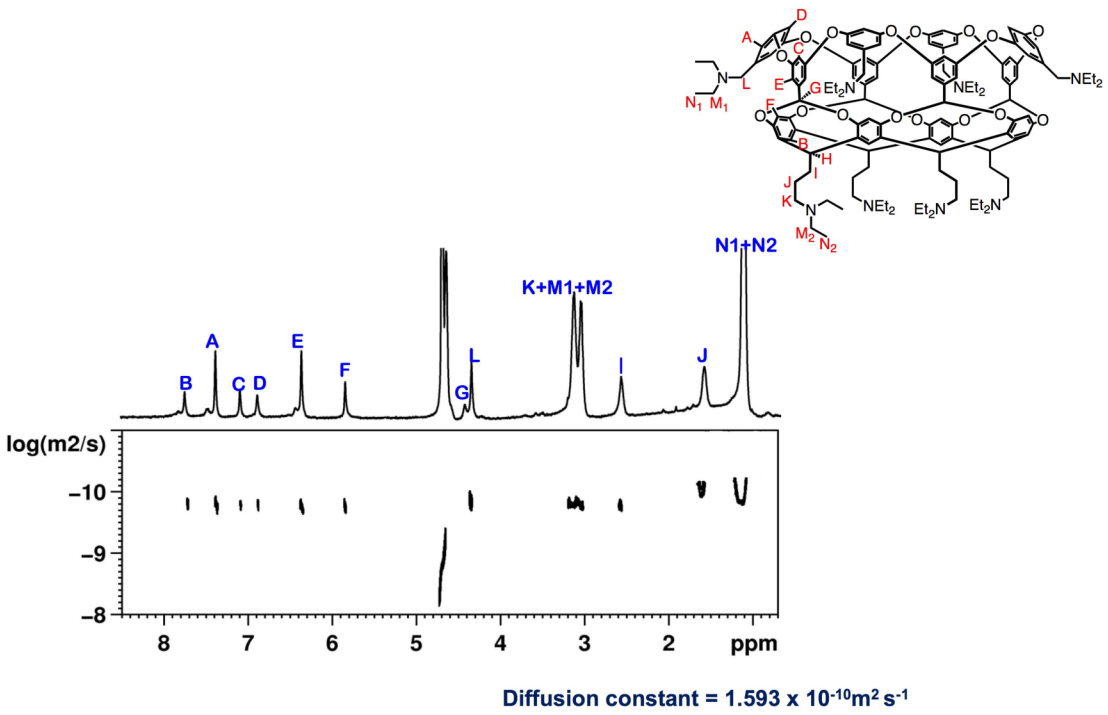


Figure S16. DOSY NMR spectrum of host **1a** in D_2O/DCl ([**1a**] = 0.1mM).

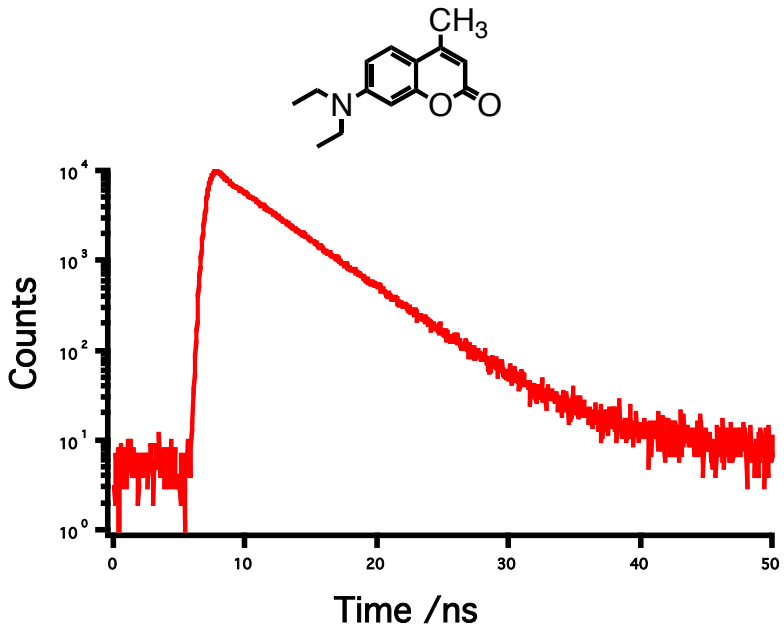


Figure S17. Fluorescence decay trace of **3**@**1a**$_2$ in D_2O/DCl (pH ≈ 1) [**1a**] = 1 mM; [**3**] = 0.5 mM (Lifetime = 4.14±0.2 ns). λ_{ex} = 350 nm and λ_{em} (monitoring) = 411 nm.

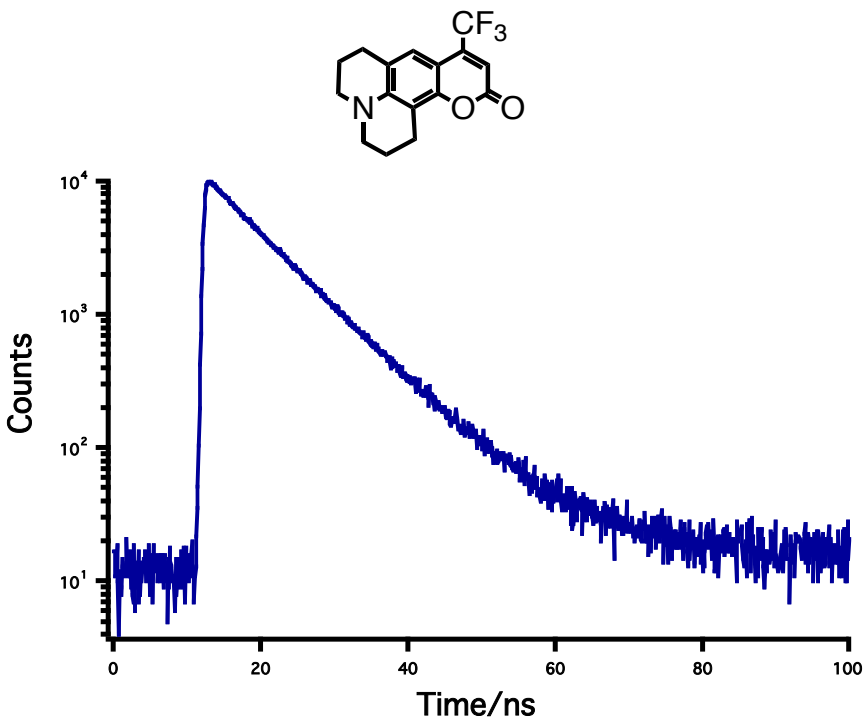


Figure S18. Fluorescence decay trace of **4**@**1a**$_2$ in D_2O/DCl (pH ≈ 1) [**1a**] = 1 mM; [**4**] = 0.5 mM (Lifetime = 7.92±0.4 ns). λ_{ex} = 400 nm and λ_{em} (monitoring) = 480 nm.

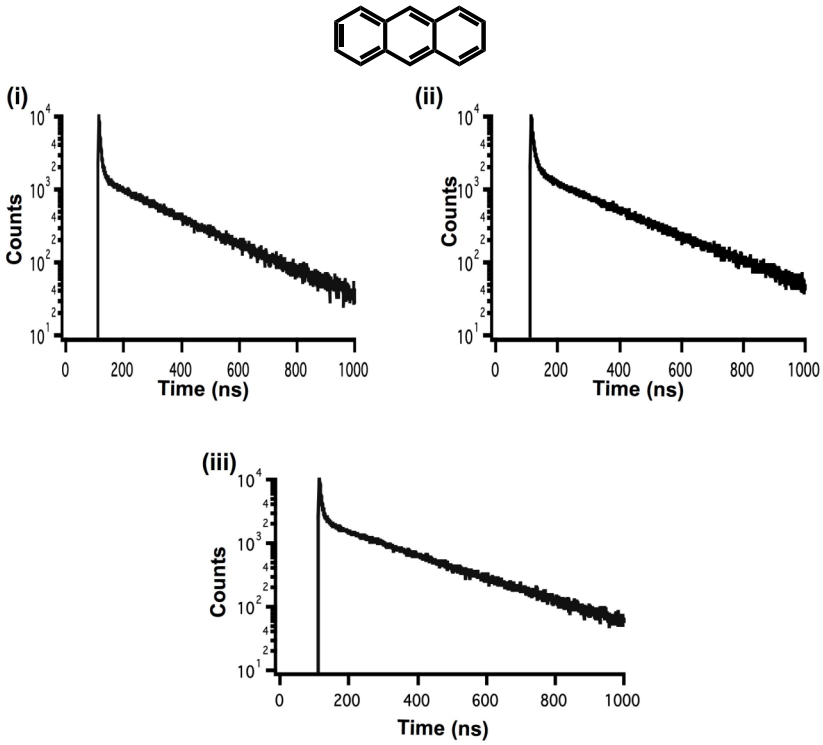


Figure S19. Fluorescence decay trace of $\mathbf{7}_2$@$\mathbf{1a}_2$ in D_2O/DCl (pH ≈ 1) [**1**] = 1 mM; [**7**] = 1 mM. λ_{ex} = 350 nm and λ_{em} (monitoring) (i) = 510 nm (τ_1(94%) = 224±12 ns, τ_2(6%) = 8.15 ns), (τ_1(95%) = 233±14 ns, τ_2(5%) = 12 ns)and (iii) (τ_1(97%) = 234±14 ns, τ_2(3%) = 13 ns).

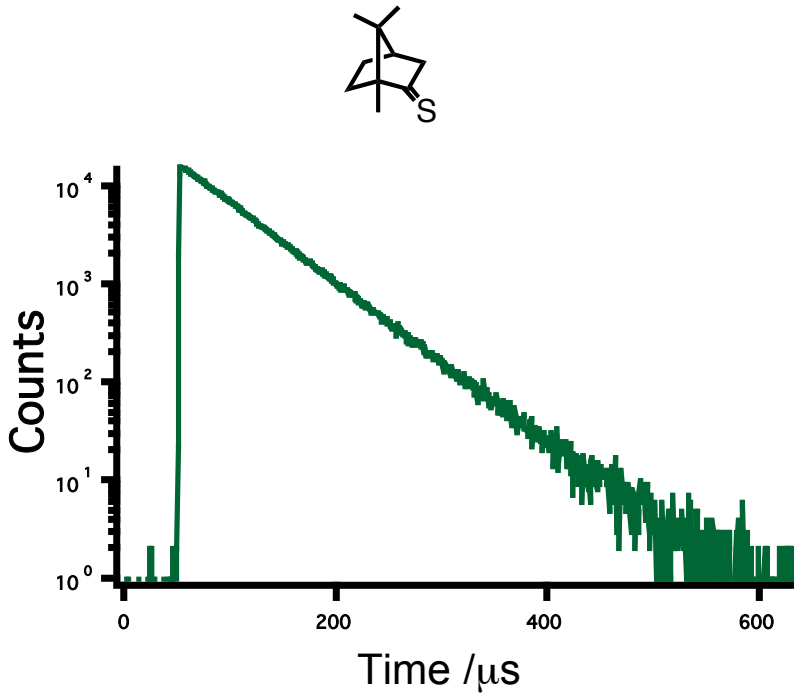


Figure S20. Phosphorescence decay trace of $\mathbf{5}_2$@$\mathbf{1a}_2$ in D_2O/DCl (pH ≈ 1) [**1a**] = 0.5 mM; [**5**] = 0.5 mM (Lifetime = 53±2.6 μs).). λ_{ex} = 254 nm and λ_{em} (monitoring) = 565 nm.

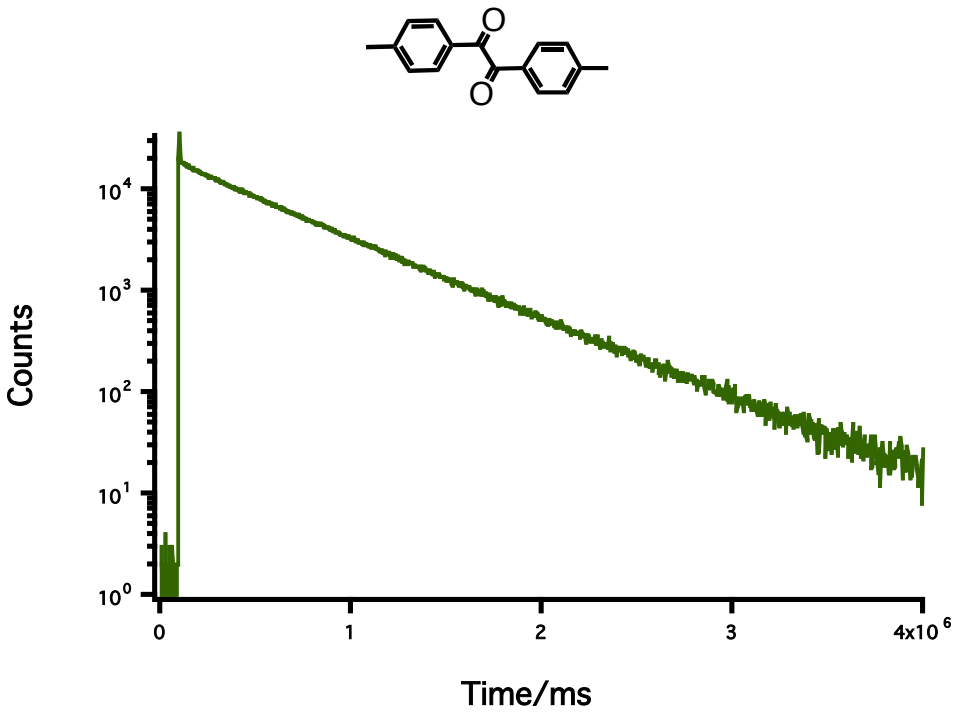


Figure S21. Phosphorescence decay trace of **6**@**1a**$_2$ in D_2O/DCl (pH ≈ 1) [**1a**] = 1 mM; [**6**] = 0.5 mM (Lifetime = 542±27 μs).). λ_{ex} = 310 nm, λ_{em} (monitoring) = 560 nm.

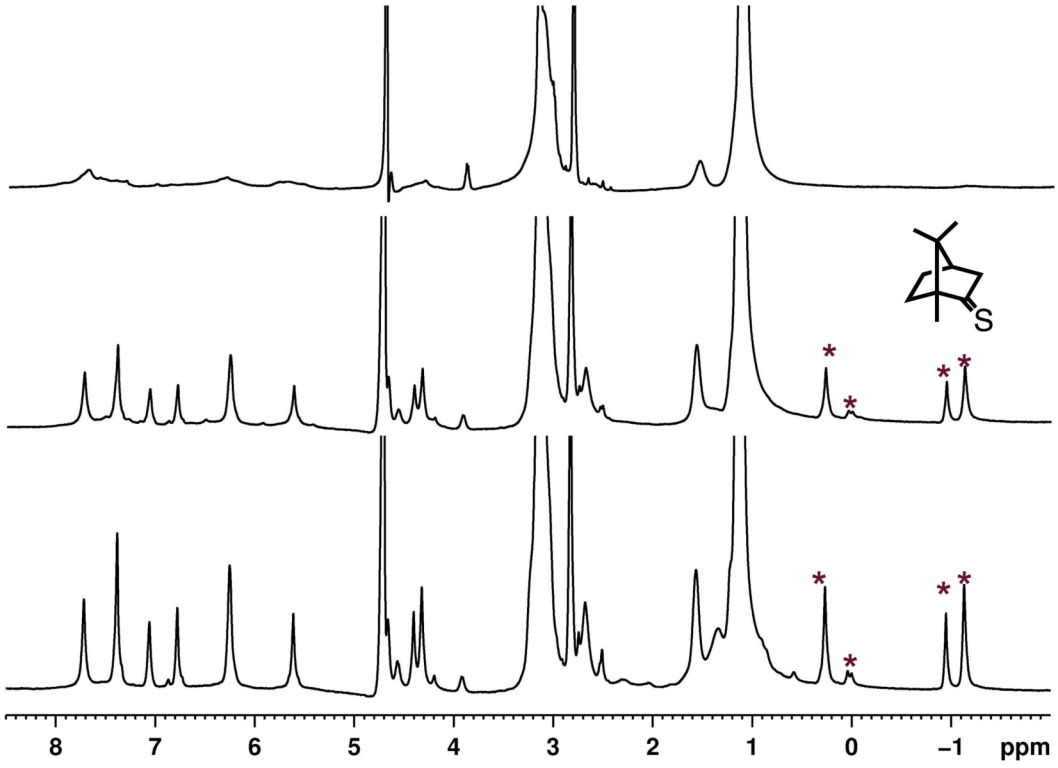


Figure S22. ^{1}H NMR titration spectra (500 MHz) of **5** with **1b** (i) **1b** (1mM in D_2O (ii) **1b**:**5**(1:0.5) and (iii) **1b**:**5** (1:1) in D_2O (pH≈7).

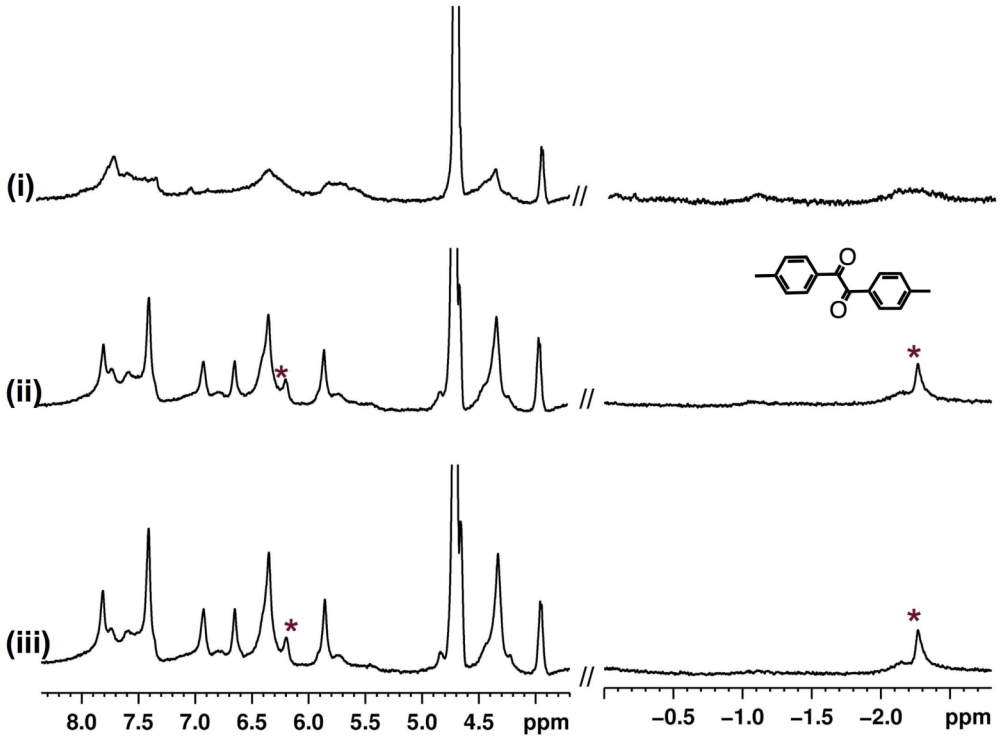


Figure S23. ^{1}H NMR titration spectra (500 MHz) of **6** with **1b** (i) **1b** (1mM in D_2O) (ii) **1b**:**6** (1:0.5) and (iii) **1b**:**6** (1:1 in D_2O (pH≈7).

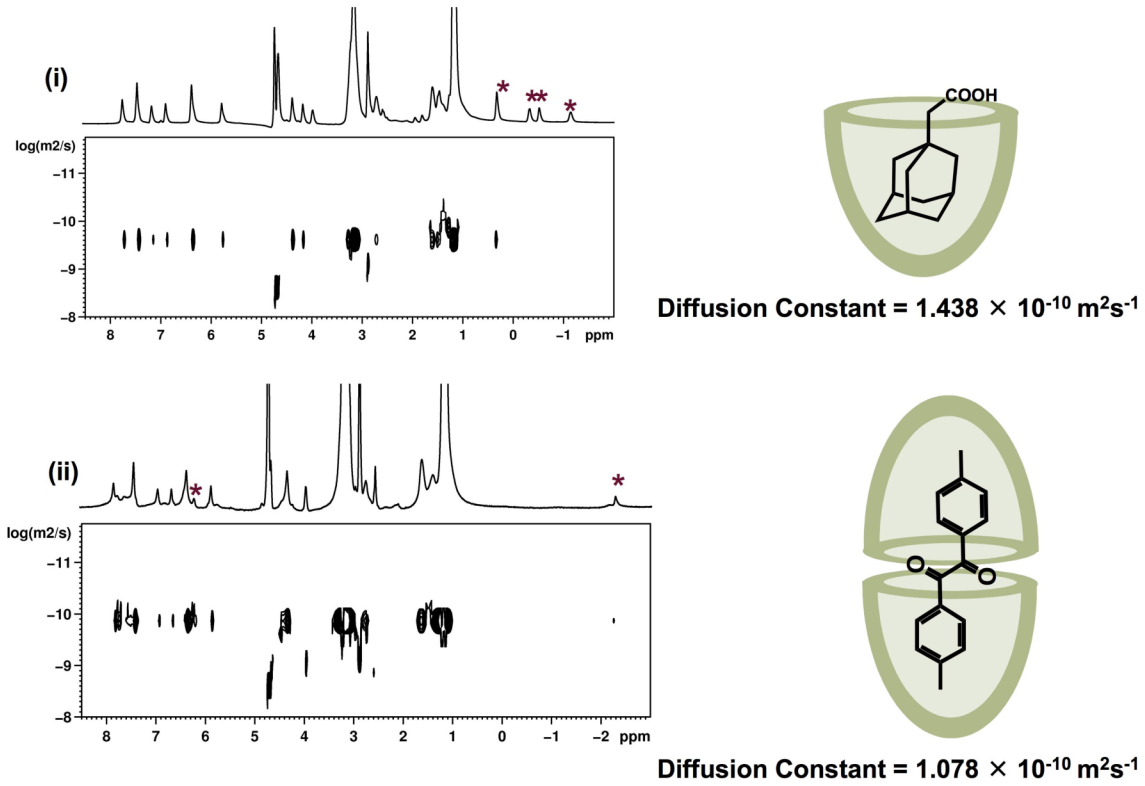


Figure S24. DOSY NMR spectra of complexes (i) 1-adamantylacetic acid@**1b** in D_2O ([**1b**] = 0.5mM, [1-adamantylacetic acid] = 0.5 mM), (ii) **6**@**1b**$_2$ in D_2O ([**1b**] = 0.5mM, [**6**] = 0.25 mM) in D_2O (pH≈7).

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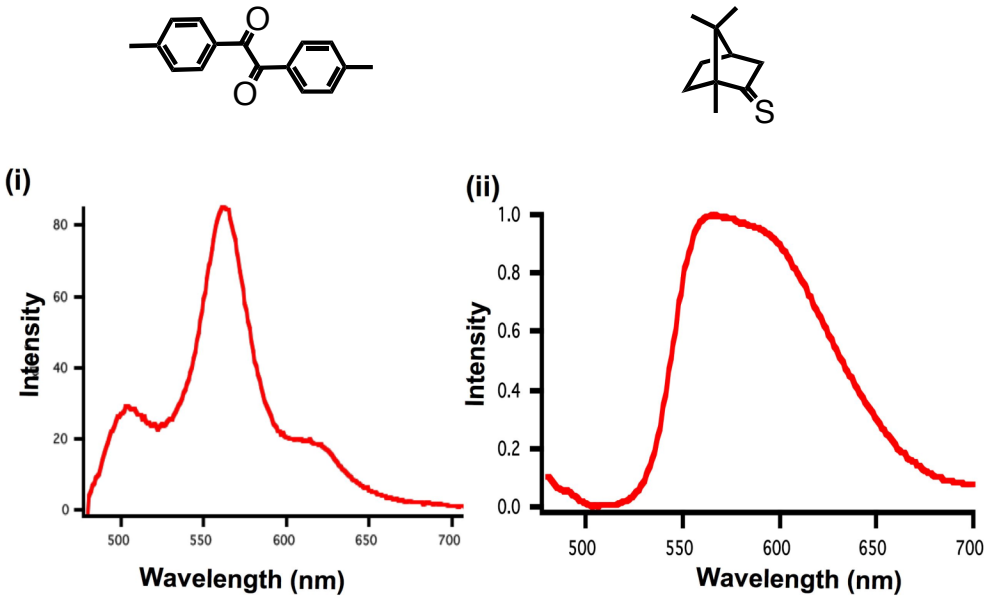

Figure S25. Emission spectra of (i) **6**@**1b**$_2$ (excitation wavelength = 310 nm, [**1b**] = 0.5 mM; [**6**] = 0.25 mM), (ii) **5**$_2$@**1b**$_2$ (excitation wavelength = 254 nm, [**1**] = 0.5 mM; [**5**] = 0.5 mM) in D_2O (pH≈7).