

Supporting Information

Color-tunable Luminescent Materials via a CB[8]-based Supramolecular Assembly Strategy

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1. General Information

^1H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were acquired on an LCT Premier XE mass spectrometer. UV-Vis absorption spectra and fluorescence spectra were recorded on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1 cm, quartz cells), respectively. Chemicals were used as received from Adamas, Acros, Aldrich. All solvents were used as received, without further processing.

2. Synthesis

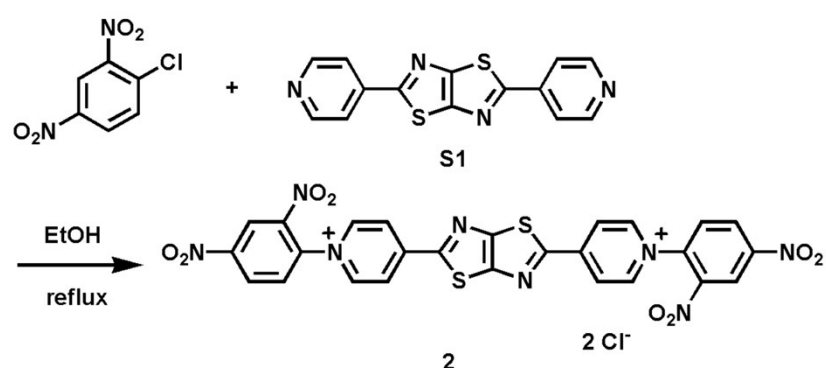


Figure S1. Synthesis of **2**.

Compound S1 is synthesized according to references^[1].

2: Compound S1 (0.350 g, 1.18 mmol) and 2,4-dinitrochlorobenzene (3.590 g, 17.72 mmol) was added to 150 mL EtOH. The mixture was stirred and under reflux for 14 days. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. 5 mL EtOH was added to the mixture and stirred under reflux for another 3 days. The mixture was then cooled to room temperature and 10 mL Me₂CO was added. The solid was obtained by centrifugation. The crude product was washed by Me₂CO (30 mL × 3). The residual solvent was evaporated in vacuum to afford the **2** (0.761 g, 92.0 %) as a brown solid. ^1H NMR (400 MHz, D₂O) δ : 9.42 (d, $J = 2.4$ Hz, 2H, Ar H), 9.30 (d, $J = 7.2$ Hz, 4H, Ar H), 8.96 (dd, $J = 2.4$ Hz, $J = 8.4$ Hz, 2H, Ar H), 8.95 (d, $J = 7.2$ Hz, 4H, Ar H), 8.32 (d, $J = 8.4$ Hz, 2H, Ar H). ^{13}C NMR (100 MHz, DMSO- d_6) δ : 165.3, 156.4, 149.3, 148.2, 147.4, 143.1, 138.5, 132.0, 130.3, 124.0, 121.5. LRMS (ESI) (m/z): $[\text{M}-2\text{Cl}]^{2+}$ calcd for $[\text{C}_{26}\text{H}_{14}\text{N}_8\text{O}_8\text{S}_2]^{2+}$: 315.0, found: 315.0.

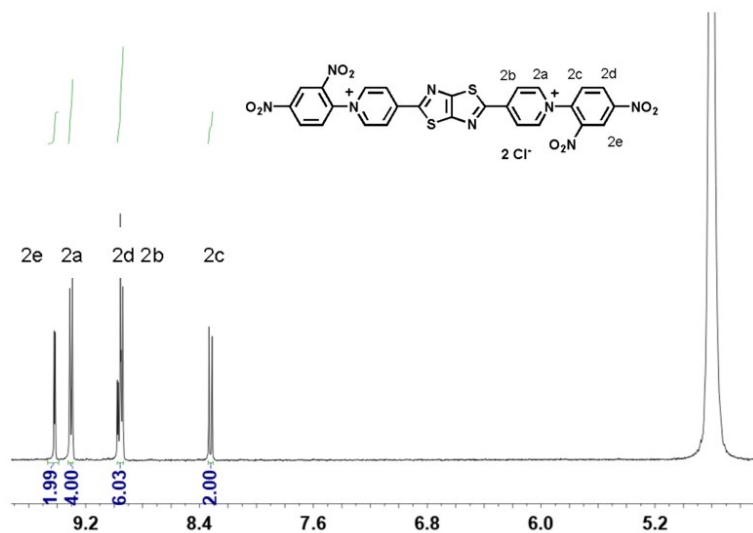


Figure S2. 2, ¹H NMR (400 MHz, 1.1 mM, D₂O).

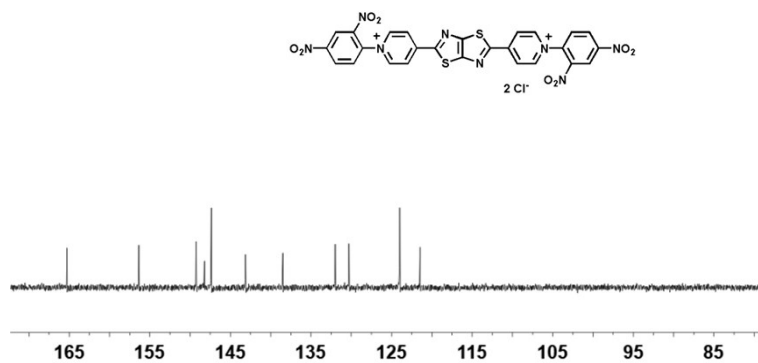


Figure S3. 2, ¹³C NMR (100 MHz, DMSO-d₆).

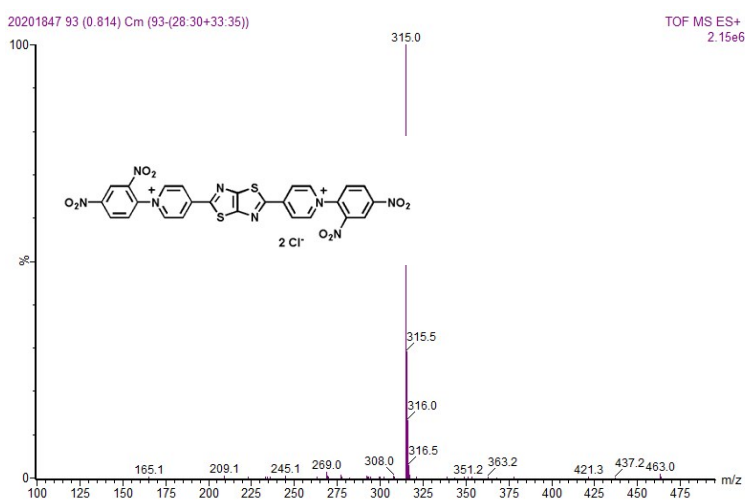


Figure S4. 2, ESI-MS.

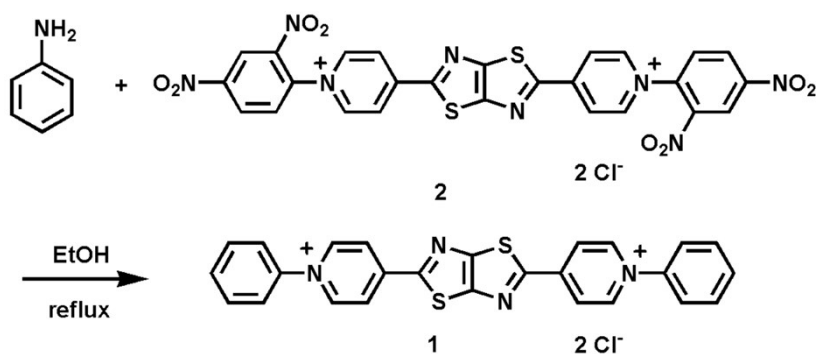


Figure S5. Synthesis of **1**.

1: Compound **2** (0.130 g, 0.185mmol) and aniline (0.060 g, 0.644 mmol) was added to 100mL EtOH. The mixture was stirred under reflux for 18 hours. The mixture was then cool to room temperature and the solvent was evaporated under reduced pressure to 5mL. The concentrated reaction mixture was mixed with 30mL Me₂CO, centrifugated, decanted and a solid was collected. The crude product was washed by Me₂CO (25mL×4). The residual solvent was evaporated in vacuum to afford the **1** (0.086g, 89.1 %) as a yellow solid. ¹H NMR (400 MHz, D₂O) δ): 9.25 (d, J = 6.4 Hz, 4H, Ar H), 8.80 (d, J= 7.2 Hz, 4H, Ar H), 7.70-7.80. (m, 10H, Ar H) ¹³C NMR (100 MHz, DMSO-d₆) δ): 165.2, 155.8, 146.5, 146.0, 142.4, 131.5, 130.3, 124.7, 124.1. LRMS (ESI) (m/z): [M-2Cl]²⁺ calcd for [C₂₆H₁₈N₄S₂]²⁺: 225.0, found: 225.0.

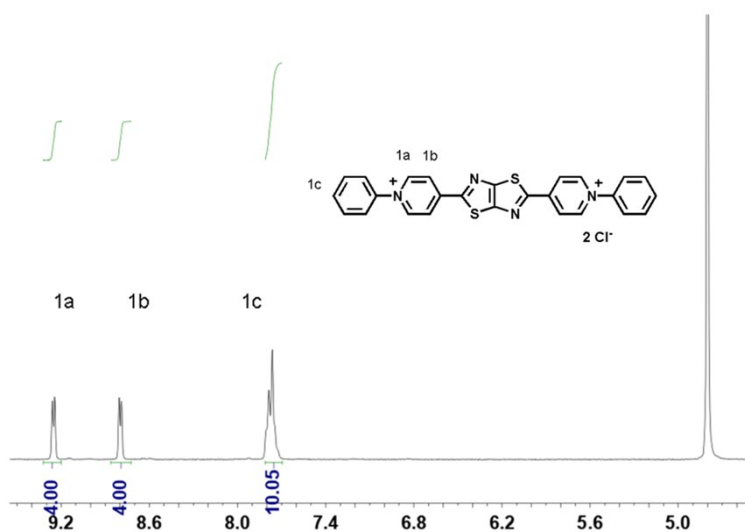


Figure S6. 1, ¹H NMR (400 MHz, 1.3 mM, D₂O).

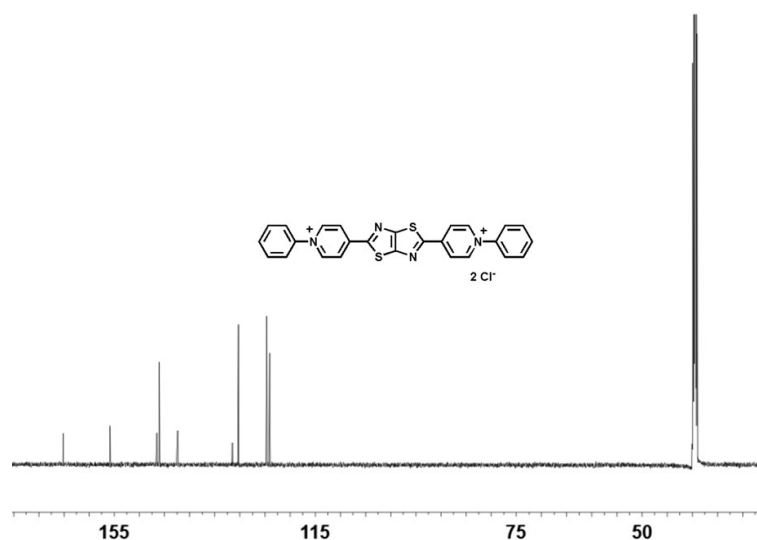


Figure S7. 1, ^{13}C NMR (100 MHz, DMSO-d_6).

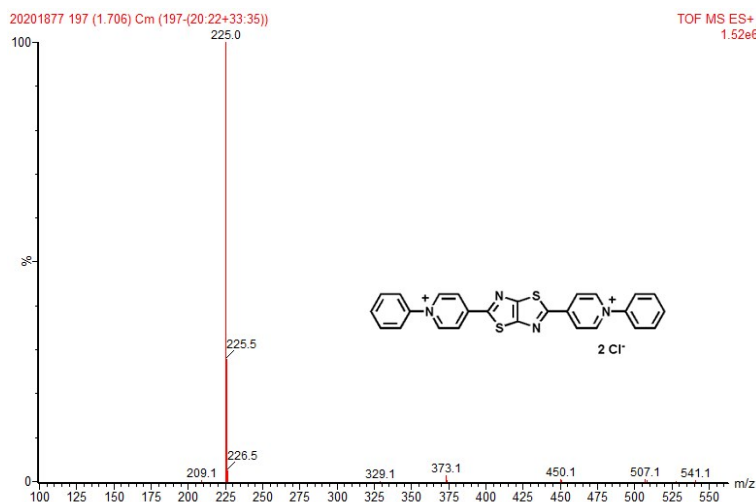


Figure S8. 1, ESI-MS.

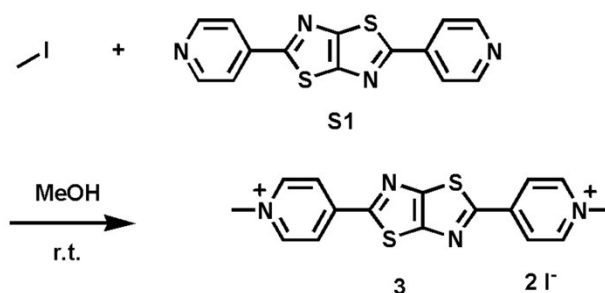


Figure S9. Synthesis of **3**.

3: Compound S1 (0.193 g, 0.65mmol) and iodomethane (5.0 ml, 80.31 mmol) was added to 5mL MeOH. The mixture was stirred at room time for 5 days. The mixture was then mixed with 20mL Me_2CO , centrifuged, decated and a solid was collected. The crude product was washed by Me_2CO (25mL \times 5). The residual solvent was evaporated in vacuum to afford the **3** (0.304g, 89.0 %) as a orange solid. ^1H NMR (400 MHz, D_2O) δ : 8.93 (d, $J = 6.4$ Hz, 4H, Ar H), 8.62 (d, $J = 6.4$ Hz, 4H, Ar H),

4.43 (s, 6H, CH₃) ¹³C NMR (100 MHz, DMSO-d₆) δ: 165.2, 155.0, 146.8, 145.5, 123.8, 47.9. LRMS (ESI) (m/z): [M-2I]²⁺ calcd for [C₁₆H₁₄N₄S₂]²⁺: 163.0, found: 163.0.

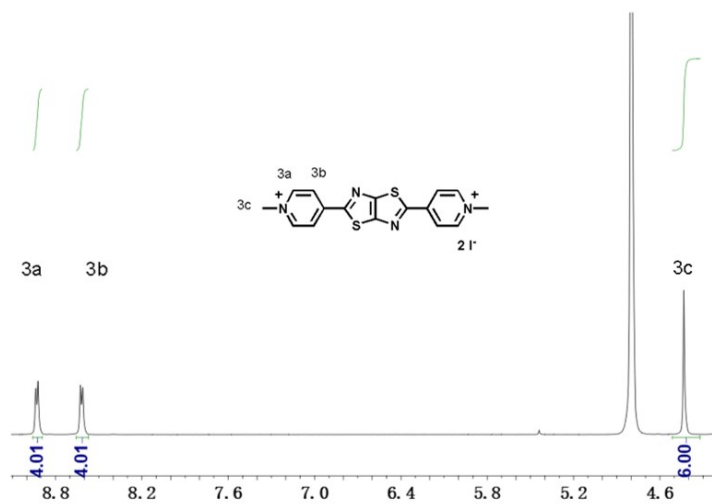


Figure S10. 3, ¹H NMR (400 MHz, 1.5 mM, D₂O).

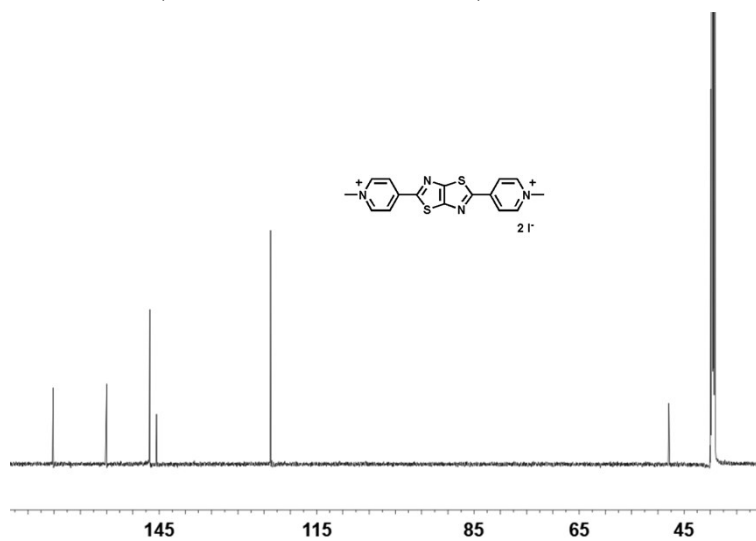


Figure S11. 3, ¹³C NMR (100 MHz, DMSO-d₆).

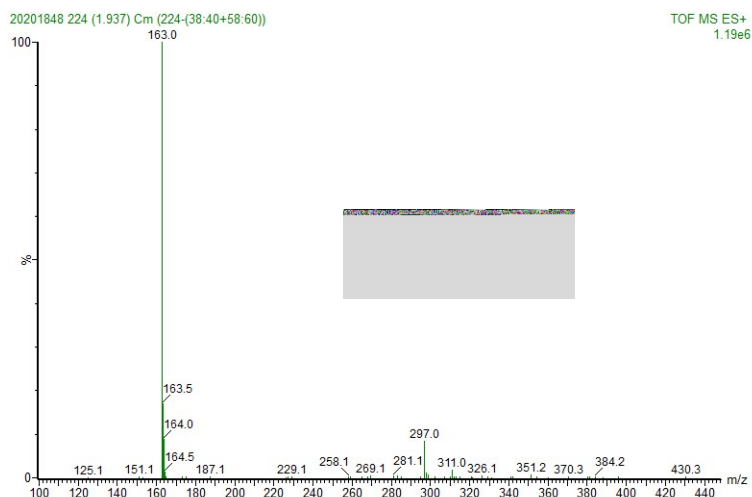


Figure S12. 3, ESI-MS.

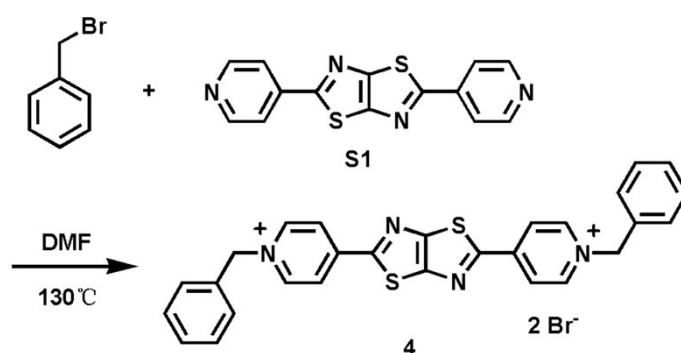


Figure S13. Synthesis of **4**.

4: Compound **S1** (0.500 g, 1.69mmol) and benzyl bromide (3.0 ml, 2.53 mmol) was added to 3mL DMF. The mixture was stirred at 130°C for 26 hours. The mixture was then cool to room temperature and mixed with 10mL MeOH, centrifugated, decanted and a solid was collected. The crude product was washed by MePh (20mL×5). The residual solvent was evaporated in vacuum to afford the **4** (0.896g, 83.0 %) as a yellow solid. ^1H NMR (400 MHz, D_2O) δ : 9.04 (d, $J = 6.8$ Hz, 4H, Ar H), 8.63 (d, $J = 6.8$ Hz, 4H, Ar H), 7.53 (s, 10H, Ar H), 5.87 (s, 4H, CH_2) ^{13}C NMR (100 MHz, DMSO-d_6) δ : 165.2, 155.2, 146.3, 146.0, 134.2, 129.5, 129.3, 128.9, 124.7, 63.2. LRMS (ESI) (m/z): $[\text{M}-2\text{Br}]^{2+}$ calcd for $[\text{C}_{28}\text{H}_{22}\text{N}_4\text{S}_2]^{2+}$: 239.1, found: 239.1.

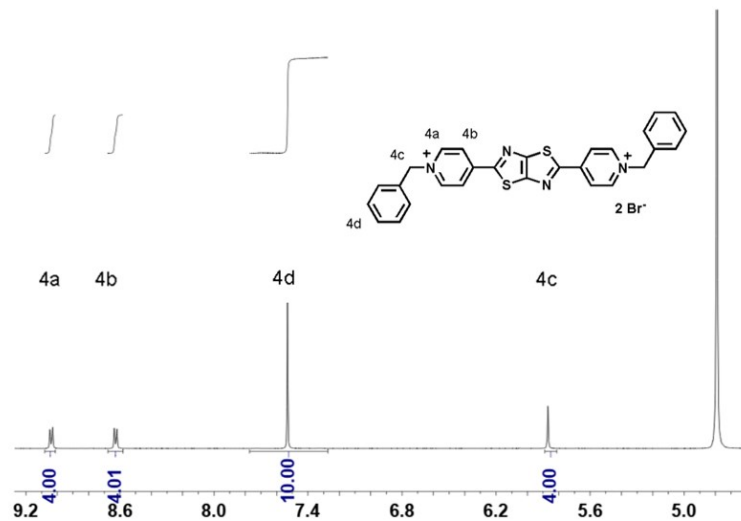


Figure S14. 4, ^1H NMR (400 MHz, 1.2 mM, D_2O).

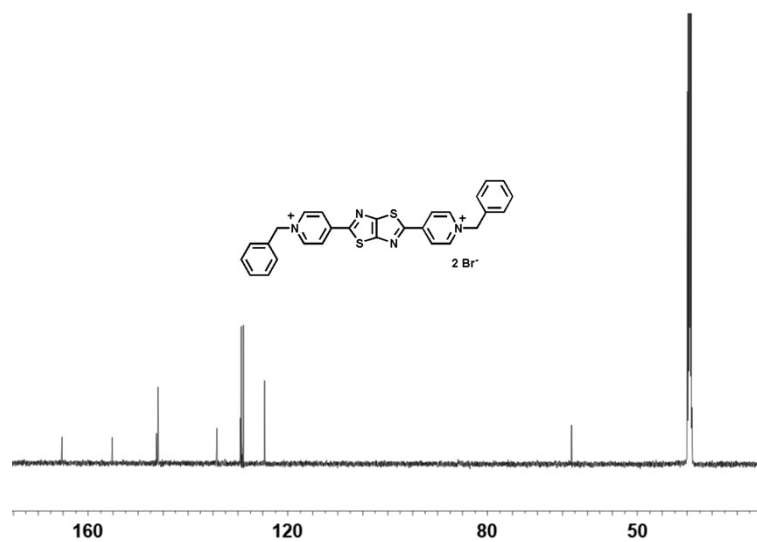


Figure S15. 4, ^{13}C NMR (100 MHz, DMSO-d_6).

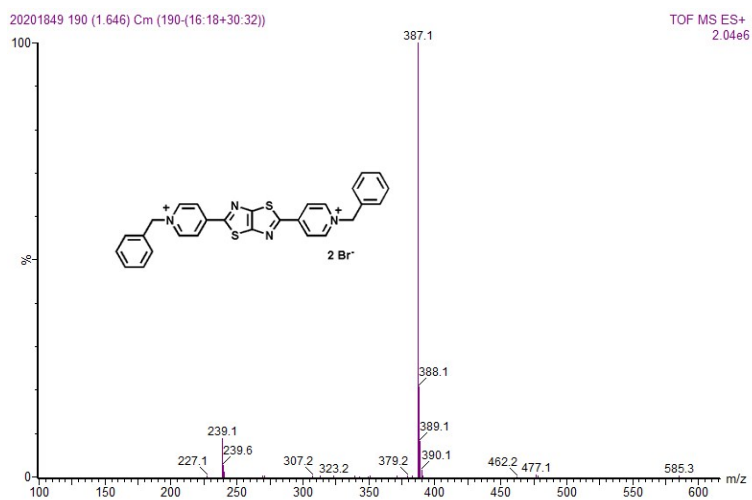


Figure S16. 4, ESI-MS.

3. ITC data, ^1H NMR spectra, UV-vis absorption spectra and fluorescence emission spectra.

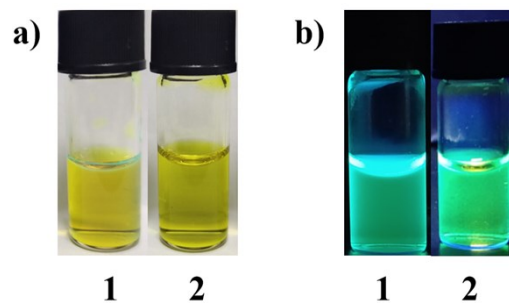


Figure S17. (a) Images of **1** and **2** solution (>1 mM). (b) Images of **1** and **2** solution (>1 mM) under UV light at 365 nm.

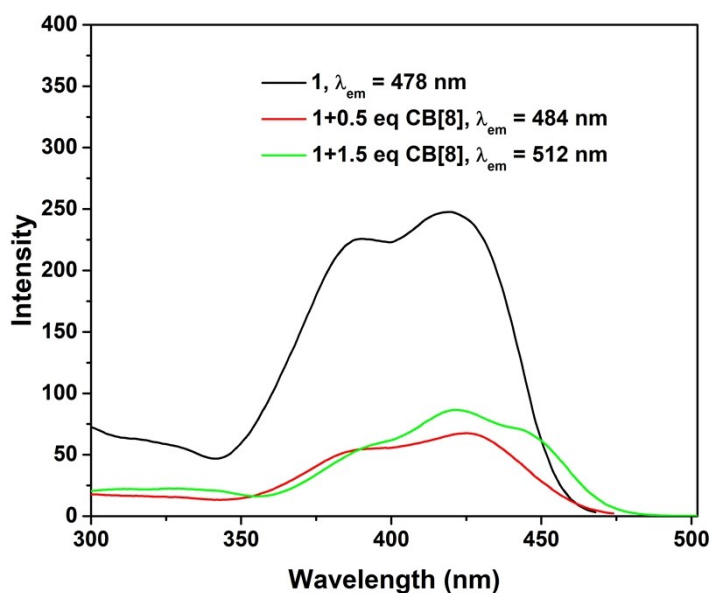


Figure S18. The excitation spectra of **1** (10 μM), **1**₂@CB[8] (10 μM , 0.5eq CB[8]) and **1**₂@CB[8]₃ (10 μM , 1.5eq CB[8]).

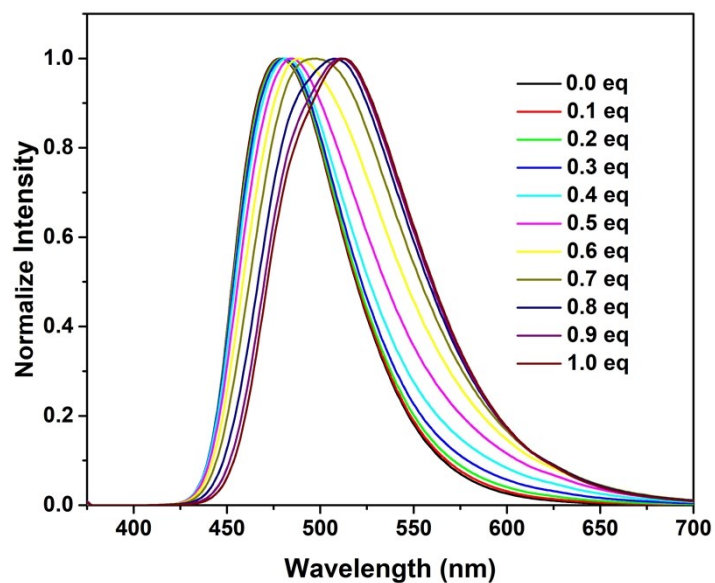


Figure S19. Normalized fluorescence emission spectra of **1** (10 μM) solutions with an increasing concentration of CB[8] (excitation wavelength: 365 nm). The fluorescent peak of **1** at 478 nm shift to 512 nm after more than 0.5 equivalent of CB[8] solution was added.

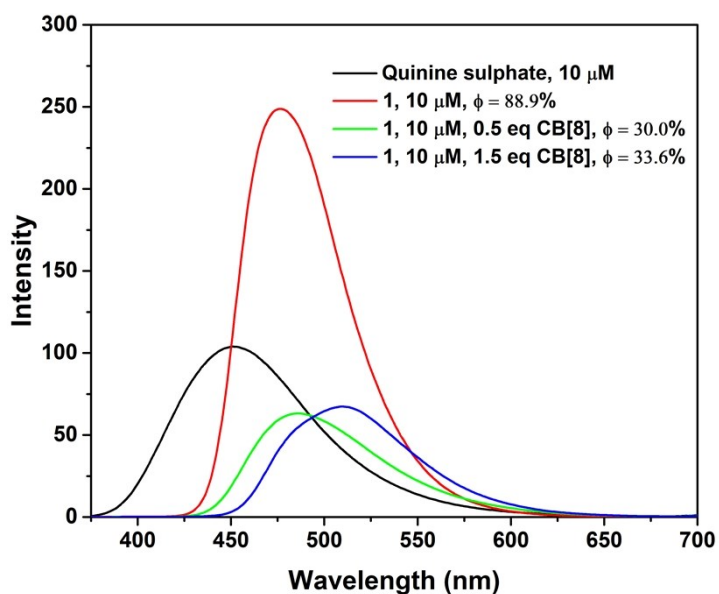


Figure S20. The fluorescence quantum yield spectra of **1**. Excitation wavelength was 350 nm. The fluorescence quantum yield of quinine sulphate as reference is 54.6% (Reported value)^[2].

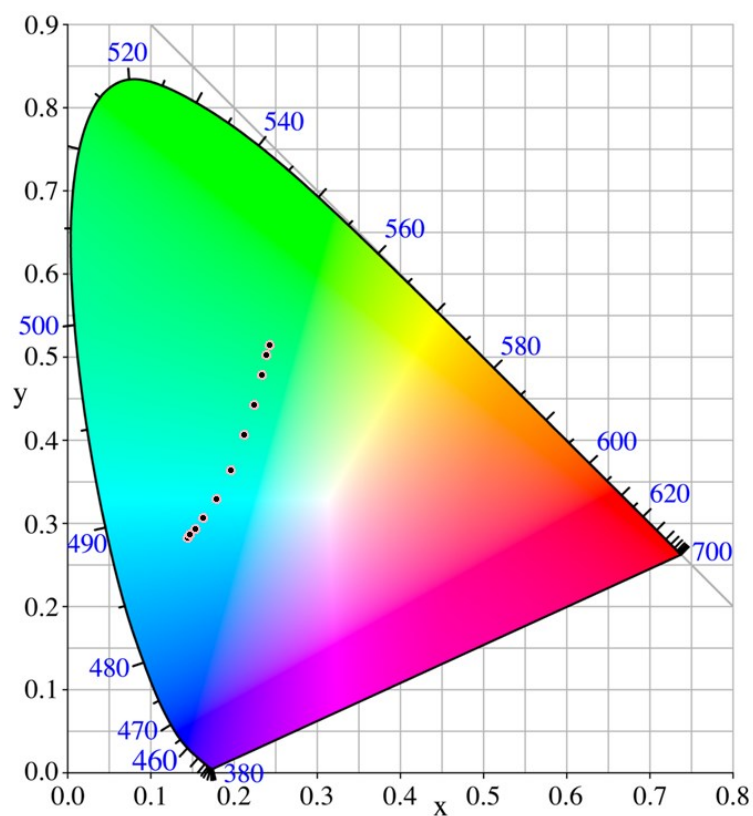


Figure S21. CIE of solution (**4**, 10 μM) with increasing concentrations of CB[8] (excitation wavelength: 365 nm). The colors changes from blue to green.

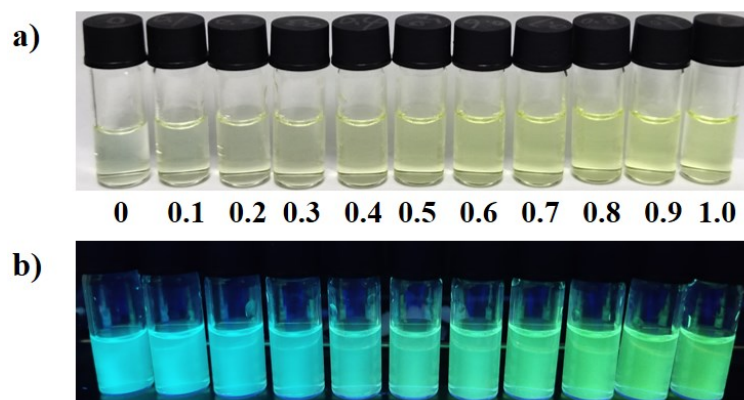


Figure S22. (a) Images of solution of **1** (10 μM) upon addition of CB[8] with increasing concentrations (0-1.0 equiv). (b) Images of solution of **1** (10 μM) upon addition of CB[8] with increasing concentrations (0-1.0 equiv) under UV light at 365 nm.

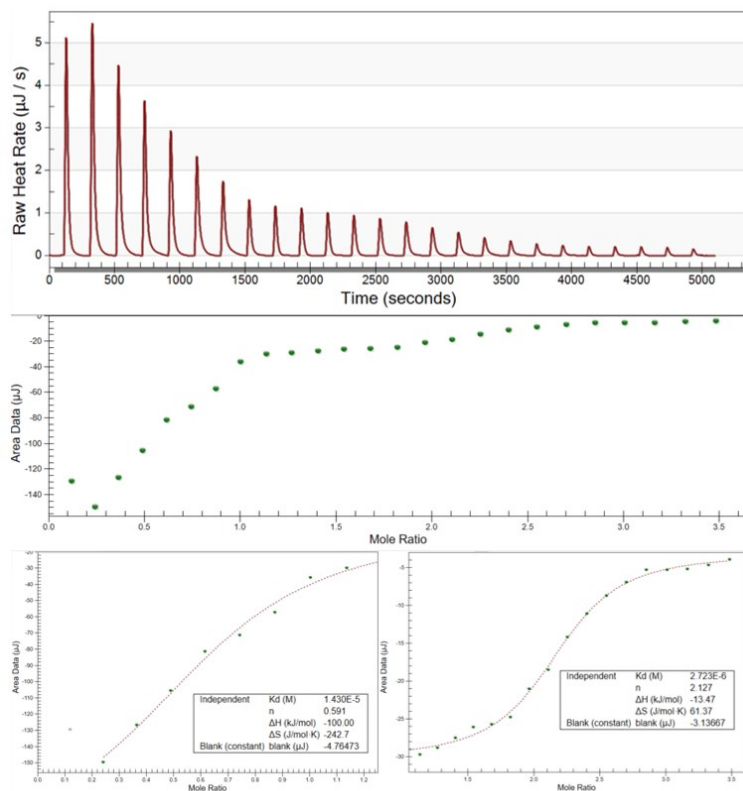


Figure S23. ITC data for compound **1** with CB[8]. Buffer solution: H₂O, cell: c(CB[8]) = 0.1 mM, syringe: c(**1**) = 1.0 mM.

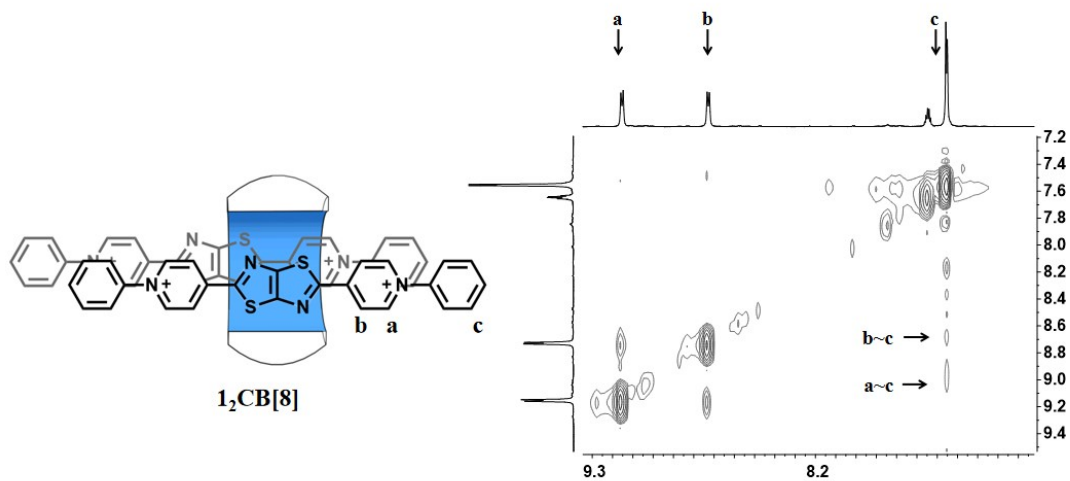


Figure S24. The binding mode of the host–guest complexes (**1**₂@CB[8]) and NOSEY spectrum of compound **1** (4.2 mM) with 0.5 equiv CB[8] in D₂O.

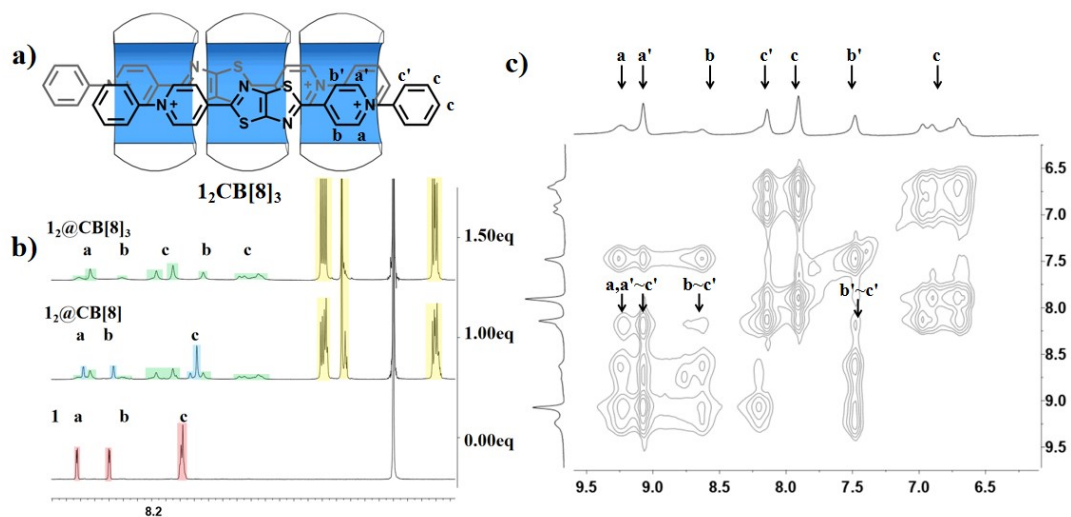


Figure S25. The possible binding mode of the host-guest complexes ($1_2@CB[8]_3$) (a), spectra of **1** solution with an increasing concentration of CB[8](b) and NOSEY spectrum of compound **1** (3.8 mM) with 1.5 equiv CB[8] in D_2O (c).

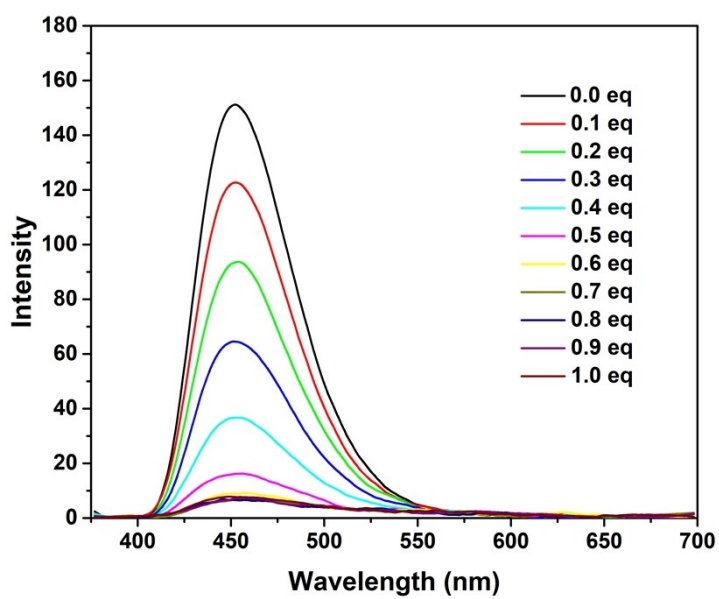


Figure S26. Fluorescence emission spectra of **3** (10 μ M) solution with increasing concentrations of CB[8].

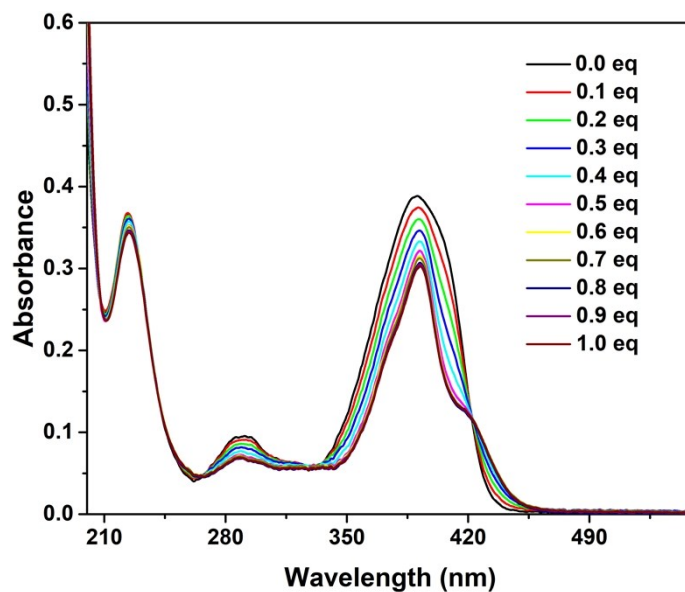


Figure S27. UV-vis absorption spectra of **3** (10 μM) solution with increasing concentrations of CB[8].

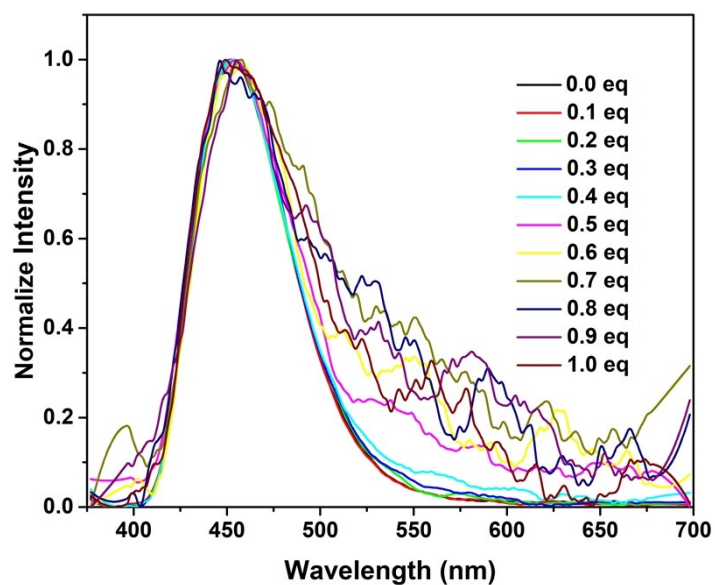


Figure S28. Normalized fluorescence emission spectra of **3** (10 μM) solution with increasing concentrations of CB[8] (excitation wavelength: 365 nm). The fluorescent peak of **3** at 452 nm changed less while the emission was decreased.

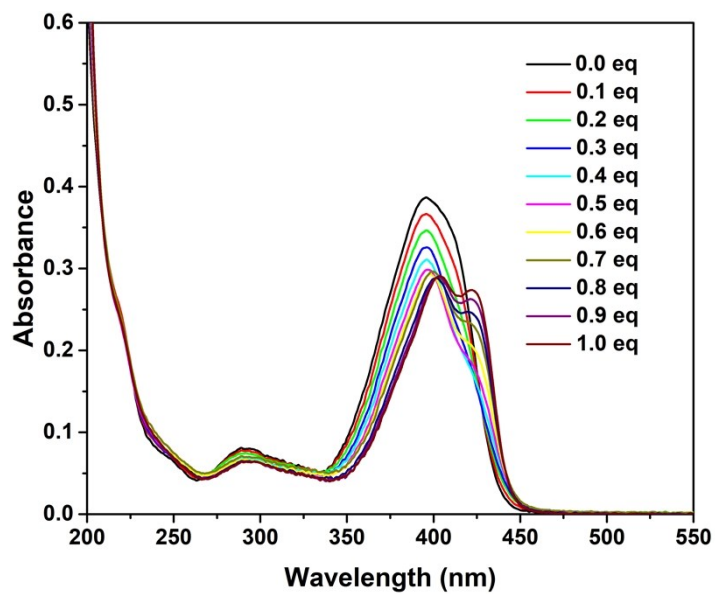


Figure S29. UV-vis absorption spectra of **4** (10 μM) solution with increasing concentrations of CB[8].

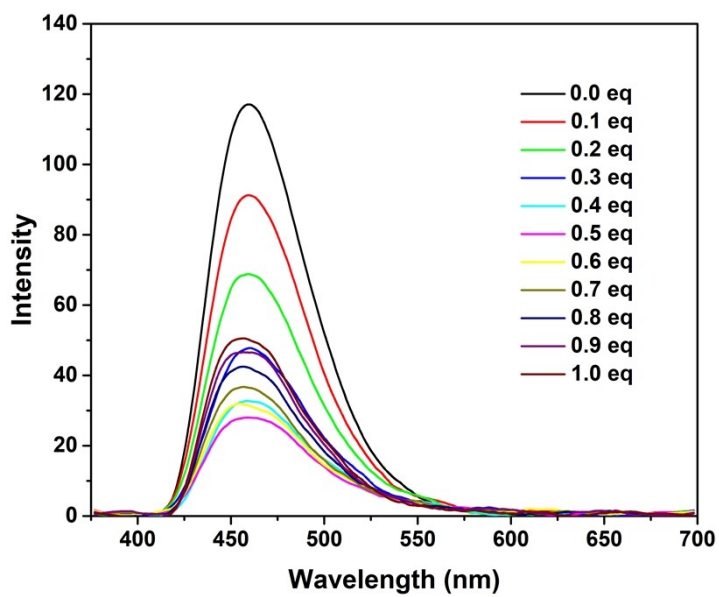


Figure S30. Fluorescence emission spectra of **4** (10 μM) solution with increasing concentrations of CB[8].

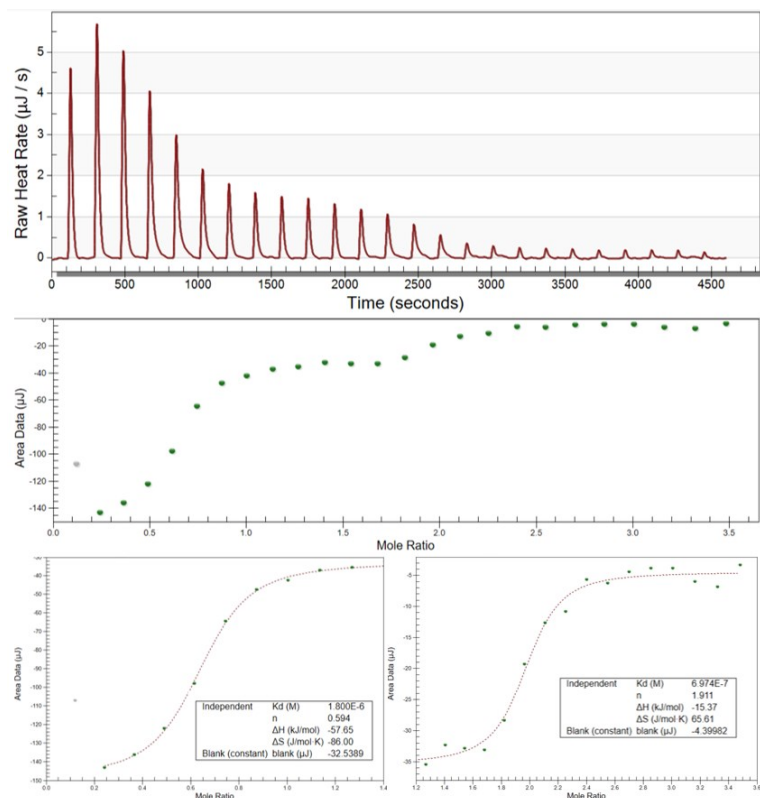


Figure S31. ITC data for compound **4** with CB[8]. Buffer solution: H₂O, cell: c(CB[8]) = 0.1 mM, syringe: c(**4**) = 1.0 mM.

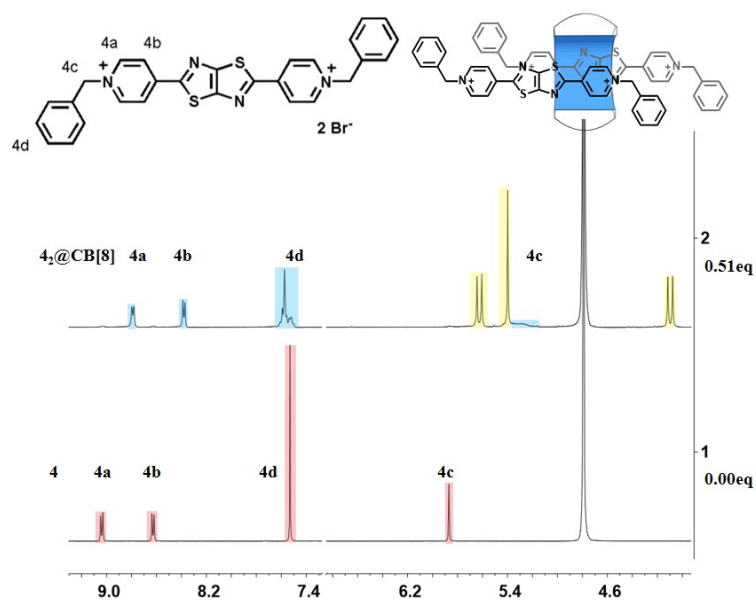


Figure S32. ¹H NMR spectra of **4** (1.1 mM) with increasing concentrations of CB[8].



Figure S33. (a) Images of **3**, **4**, **2** and **1** (from left to right) solution (10 μM).

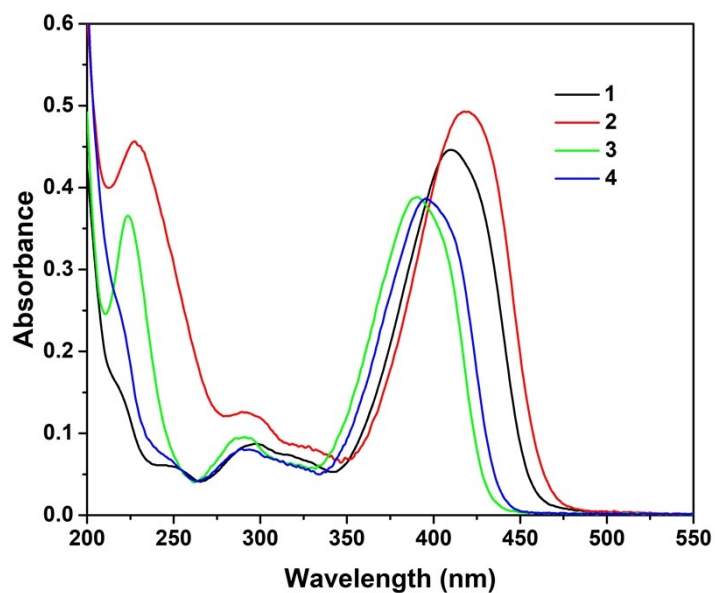


Figure S34. UV-vis absorption spectra of **1**, **2**, **3** and **4** (10 μM) solution. Compound **2** have the largest molar extinction coefficient.

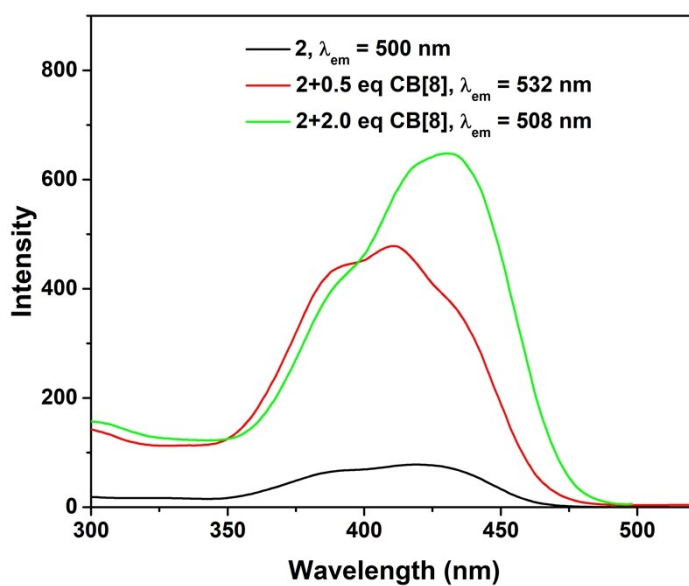


Figure S35. The excitation spectra of **2** (10 μM), **2**₂@CB[8] (10 μM , 0.5eq CB[8]) and **2**@CB[8]₂ (10 μM , 2.0eq CB[8]).

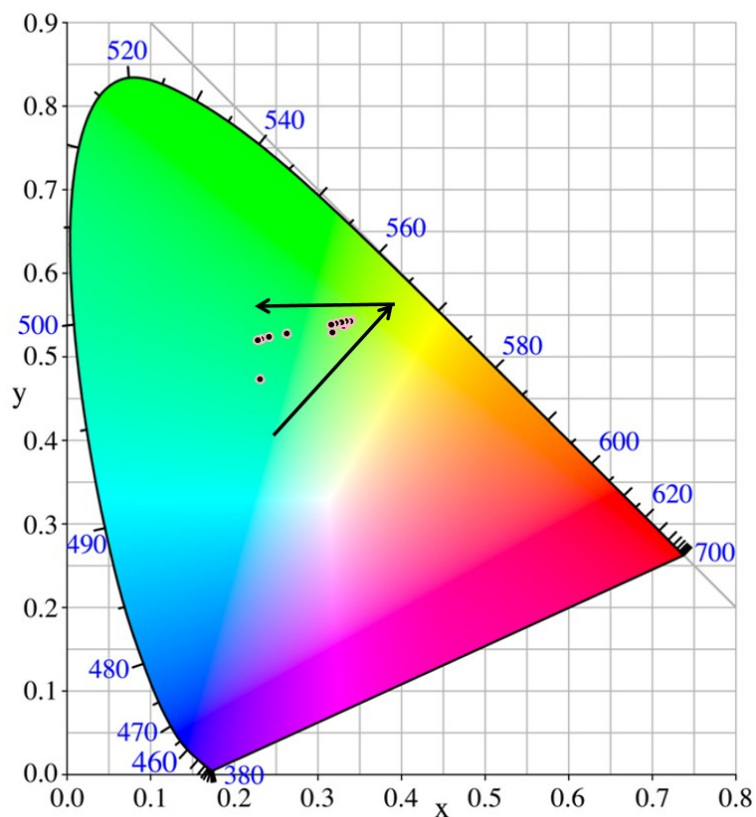


Figure S36. CIE of solution (**2**, 10 μM) at increasing concentrations of CB[8] (excitation wavelength: 365 nm).

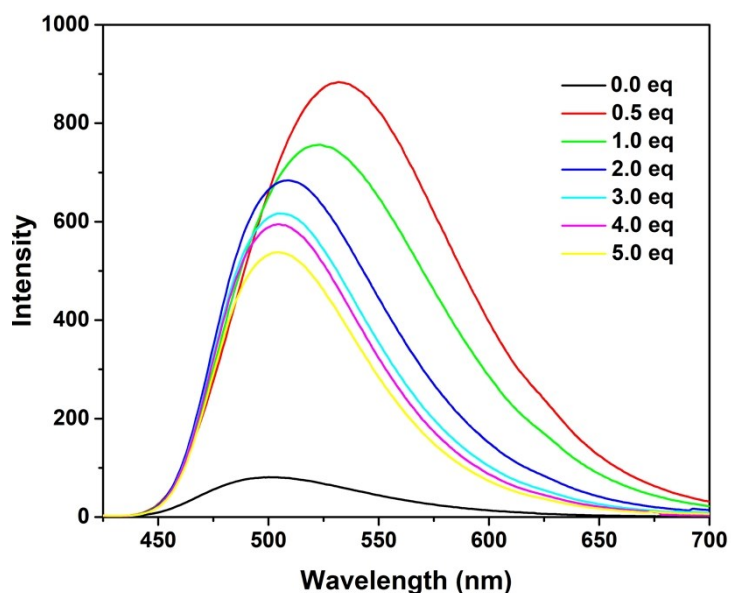


Figure S37. Fluorescence emission spectra of **2** (10 μM) solution with increasing concentrations of CB[8] (excitation wavelength: 365 nm). The fluorescent peak of **2** at 500 nm shift to 532nm while 0.5 equivalent of CB[8] solution was added, adding more CB[8] solution, the emission wavelength had a blue-shift to 504 nm.

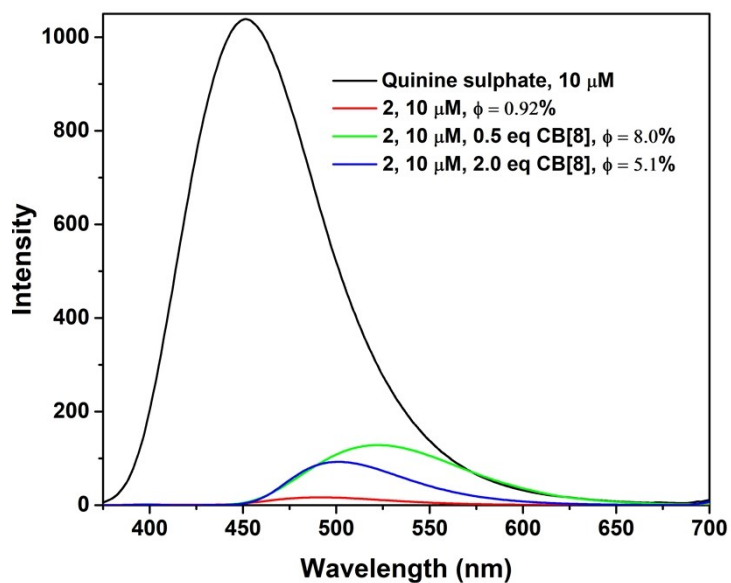


Figure S38. The fluorescence quantum yield spectra of **2**. Excitation wavelength was 350 nm. The fluorescence quantum yield of quinine sulphate as the reference is 54.6% (Reported value)^[2]. Remarkable changes were observed in quantum yield of **2** upon the titration of the CB[8].

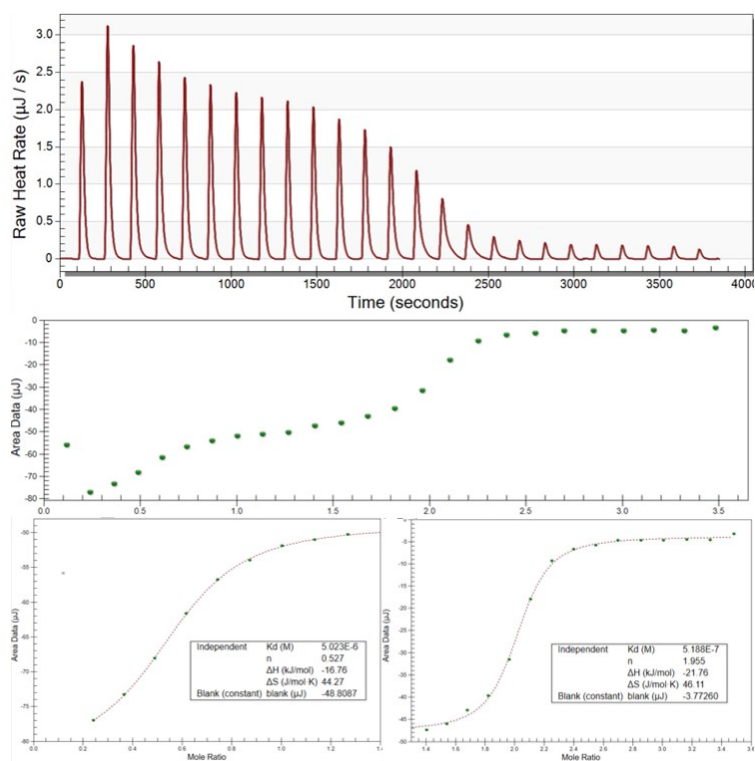


Figure S39. ITC data for compound **2** with CB[8]. Buffer solution: H₂O, cell: c(CB[8]) = 0.1 mM, syringe: c(**2**) = 1.0 mM.

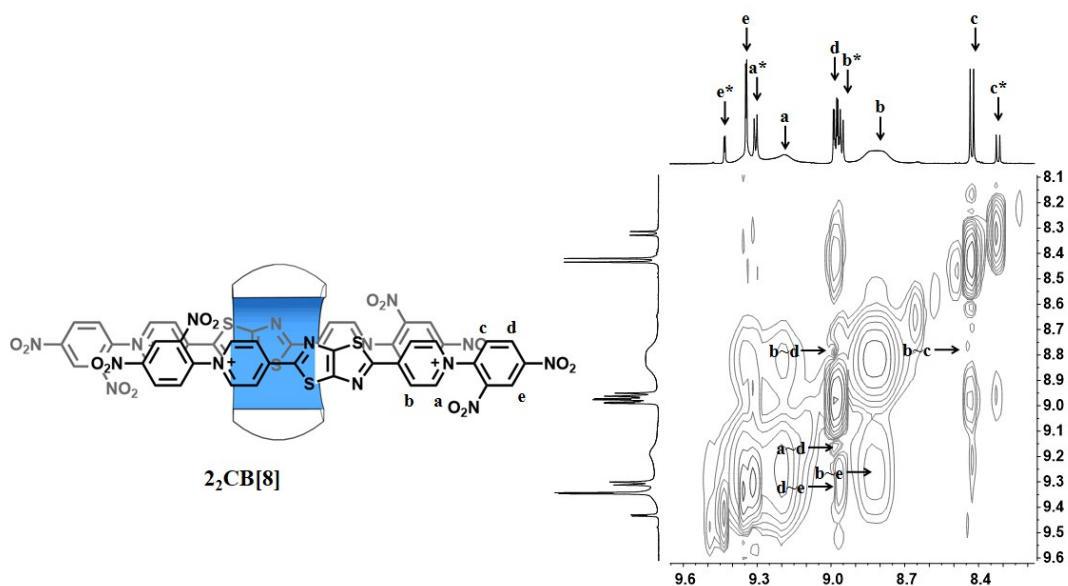


Figure S40. A schematic presentation for the chemical structures of **2** and the host–guest complex of CB[8] with **2** (left). NOSEY spectrum of compound **2** (2.6 mM) with 0.5 equiv CB[8] in D₂O (right).

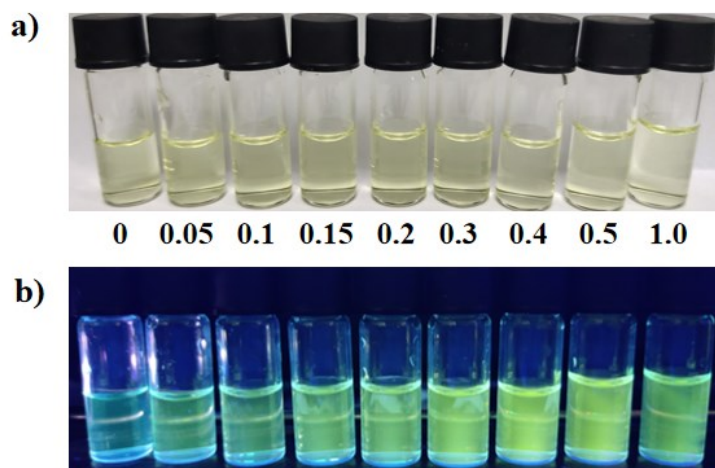


Figure S41. (a) Images of solution of **2** (10 μM) upon addition of CB[8] solutions with increasing concentrations (0-1.0 equiv). (b) Images of solution of **2** (10 μM) upon addition of CB[8] solutions with increasing concentrations (0-1.0 equiv) under UV light at 365 nm.

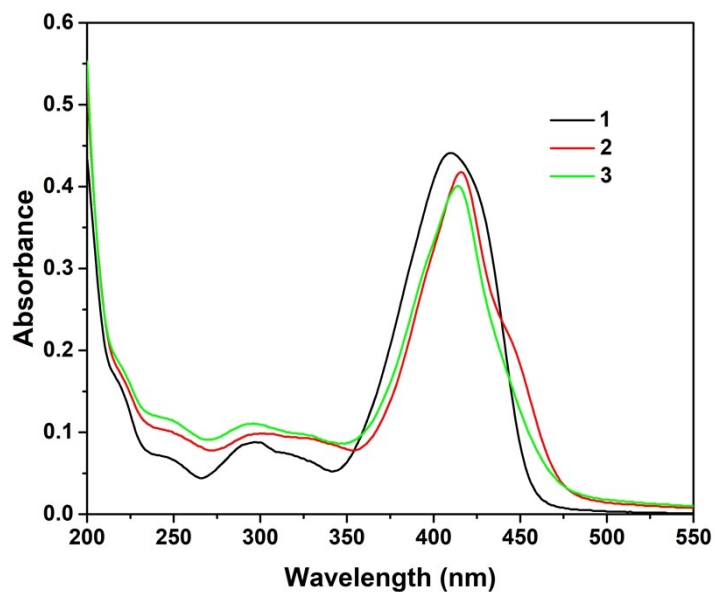


Figure S42. UV-vis absorption spectra of **1** (10 μ M) solution with increasing concentrations of CB[8] and ADA. 1 (**1**, 10 μ M), 2 (**1**, 10 μ M, CB[8], 10 μ M), 3 (**1**, 10 μ M, CB[8], 10 μ M, ADA, 1 mM).

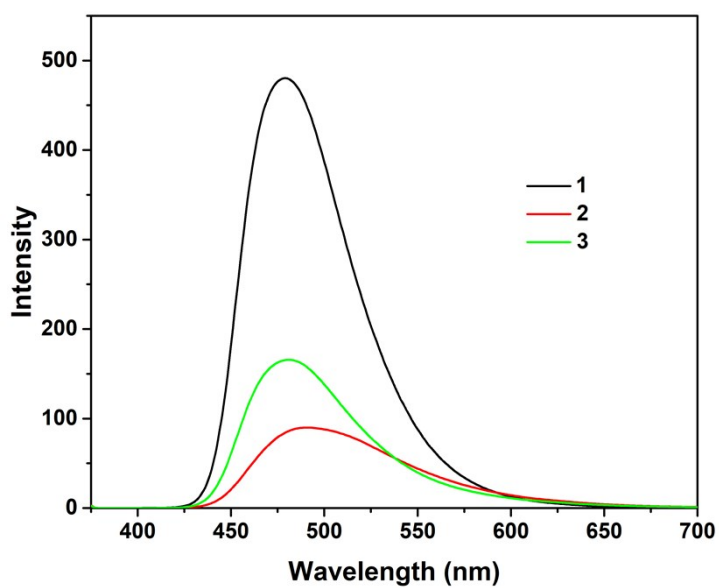


Figure S43. fluorescence emission spectra of **1** (10 μ M) solution with increasing concentrations of CB[8] and ADA. 1 (**1**, 10 μ M), 2 (**1**, 10 μ M, CB[8], 10 μ M), 3 (**1**, 10 μ M, CB[8], 10 μ M, ADA, 1 mM).

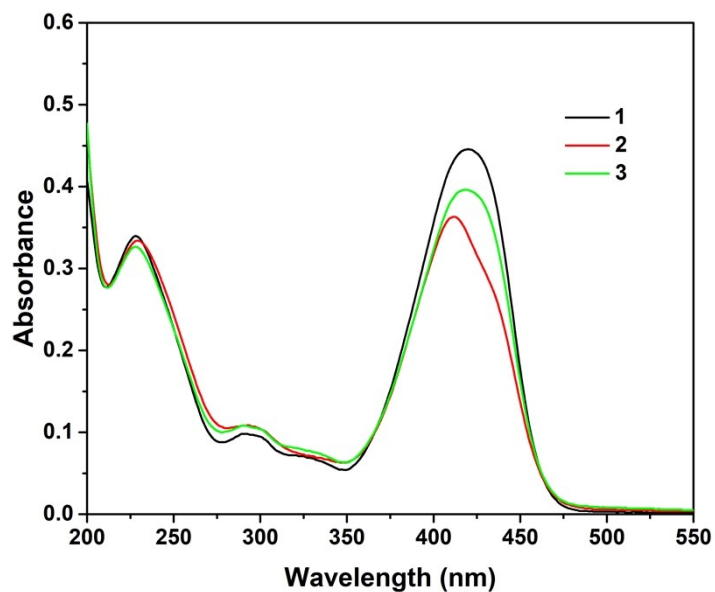


Figure S44. UV-vis absorption spectra of **2** (10 μM) solution with increasing concentrations of CB[8] and ADA. 1 (**2**, 10 μM), 2 (**2**, 10 μM , CB[8], 5 μM), 3 (**2**, 10 μM , CB[8], 5 μM , ADA, 1 mM).

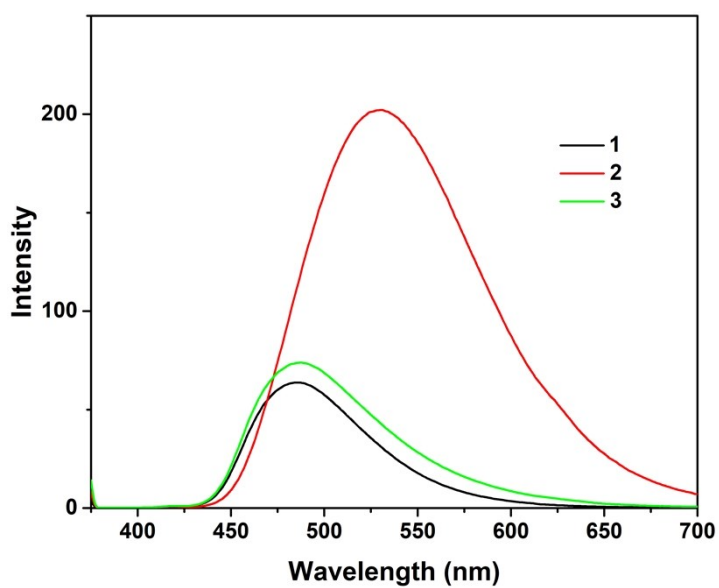


Figure S45. fluorescence emission spectra of **2** (10 μM) solution with increasing concentrations of CB[8] and ADA. 1 (**2**, 10 μM), 2 (**2**, 10 μM , CB[8], 10 μM), 3 (**2**, 10 μM , CB[8], 10 μM , ADA, 1 mM).

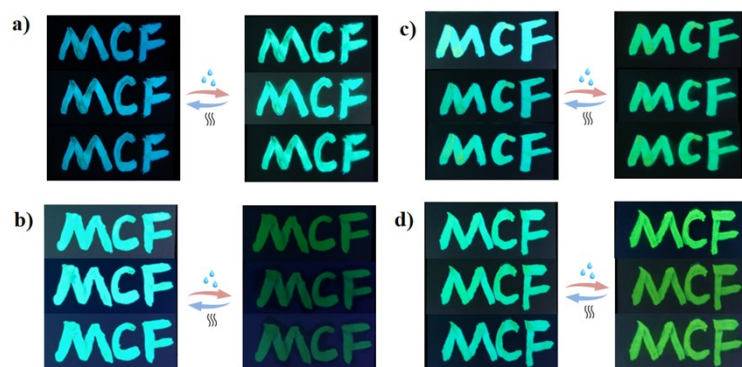


Figure S46. Images of **1**(a), **2**(b), **1** with CB[8](c) and **2** with CB[8](d) supported on silica gel under UV light at 365 nm. Each sample had three replications. The results shown the good reversibility and repeatability of the materials.

4. Reference:

- [1] A. N. Woodward, J. M. Kolesar, S. R. Hall, N. Saleh, D. S. Jones and M. G. Walter, *J. Am. Chem. Soc.*, 2017, **139**, 8467-8473
- [2] W. H. Melhuish, *J. Phys. Chem.*, 1961, **65** (2), 229-235.