

## Supporting Information

# Aqueous-phase tunable multi-color luminescent supramolecular assemblies based on cucurbit[10]uril-enhanced intermolecular charge-transfer interactions

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## General Experimental Section.

Cucurbit[10]uril (CB[10]) was prepared according to the published procedures.<sup>1</sup> The compounds and the reagents purchased from commercial suppliers were used without further purification. NMR spectra (<sup>1</sup>H, <sup>13</sup>C) were measured on Agilent 600 MHz DD2. Mass spectrometry were acquired on a Bruker FT-ICR Apex IV qQ equipped 12T super conducting magnet. UV/Vis experiments were carried out with a SHIMADZU UV-3600 instrument with 1 cm pathlength cells at 298 K. Fluorescence spectra were recorded on a PerkinElmer LS-55 machine. Fluorescence lifetime and quantum yield were obtained with an Spectrofluorometer FS5 and FLS920. Dynamic light scattering (DLS) was measure by Nicomp 380 Z3000 at room temperature.

Fluorescence Quantum Yields (QY) measurements were carried out using FLS920 spectrometer and the Integrating Sphere accessory at 25 °C. The Fluorescence Quantum Yield of the samples were calculated based on the absolute method. The performance of the integrating sphere was verified by using the sample rhodamine 101 as test sample, we obtained the rhodamine 101 sample in ethanol QY is 95.45%, which is consistent with the literature. We set both excitation wavelength and emission wavelength to the chosen excitation wavelength ( $\lambda_{exc}$ ). Use a wide band width in the excitation path ( $\Delta \lambda_{exc} = 12$  nm) and a narrow band width in the emission path ( $\Delta \lambda_{em} = 0.1$  nm). Run an emission spectrum that extends from 25 nm below the wavelength of excitation right up to the longest end of the expected emission spectrum. Use a wavelength step size of 1nm and an integration time of 1s (= 0.2 s dwell time x 5 repeats). Use the same method to measure the spectrum of blank and sample respectively, and calculate the fluorescence quantum yield ( $\varphi_F$ ) according to Formula (1).<sup>2</sup>

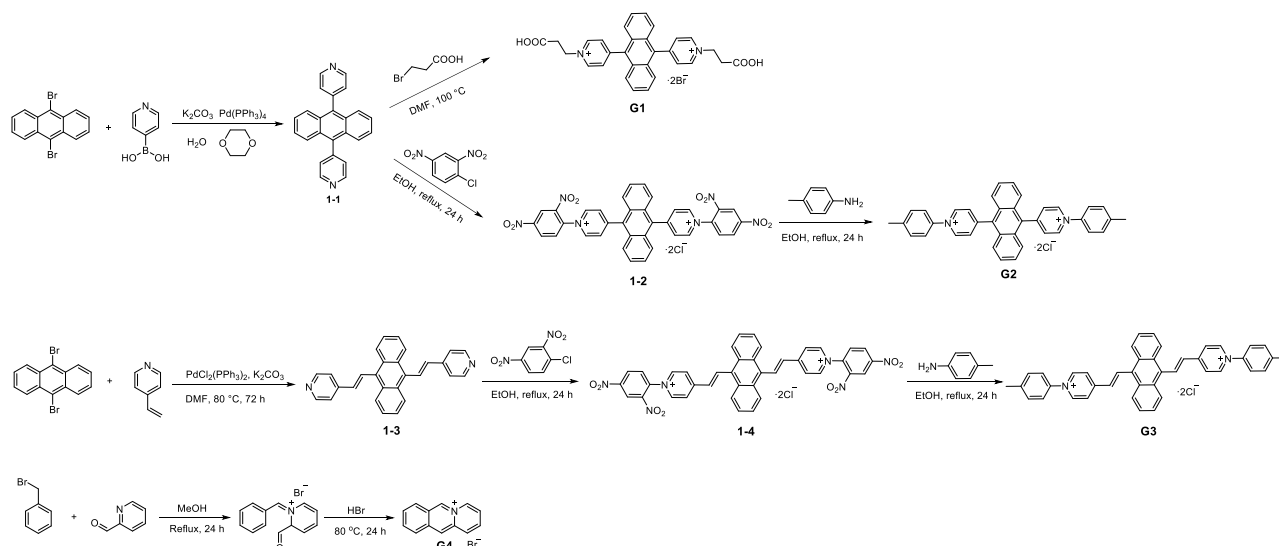
$$\varphi_F = \frac{\int I_{Emission}}{\int I_{Solvent} - \int I_{Emission}} \quad (1)$$

$I_{emission}$  : The emission spectrum of sample;

$I_{solvent}$  : the spectrum of light used to excite only (water);

$I_{sample}$  : the spectrum of light used for exciting sample in solvent.

## Synthesis and characterization.



**Scheme S1.** Synthesis route of compounds **G1**, **G2**, **G3**, and **G4**.

Synthesis of **G2** and **G4** were adapted and modified from previously reported procedures.<sup>3-5</sup>

### 4,4'-(anthracene-9,10-diyl) bis (1-(propanoic acid) pyridin-1-ium) bromide (**G1**)

Compound 1-1 (100 mg, 0.3 mmol) and 3-bromopropionic acid (138 mg, 0.9 mmol) were added in DMF (10 ml) and was heated to 100 °C for 24 h. Then the reaction mixture was cooled and collected the solid by centrifugal, the solid was washed three times with ethanol. Drying in vacuum oven obtained a yellow solid **G1** (160 mg, 80 %). <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O) δ 9.08 (d, *J* = 5.9 Hz, 1H), 8.15 (d, *J* = 6.1 Hz, 1H), 7.46 (s, 1H), 4.95 (s, 1H), 3.19 (s, 1H). <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>) δ 171.76, 155.05, 145.74, 132.85, 129.99, 127.89, 127.26, 125.69, 57.22, 35.92. HRMS (ESI): *m/z* [M-2Br]<sup>2+</sup> calcd. for C<sub>32</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub><sup>2+</sup>: 239.0950, found: 239.0943.

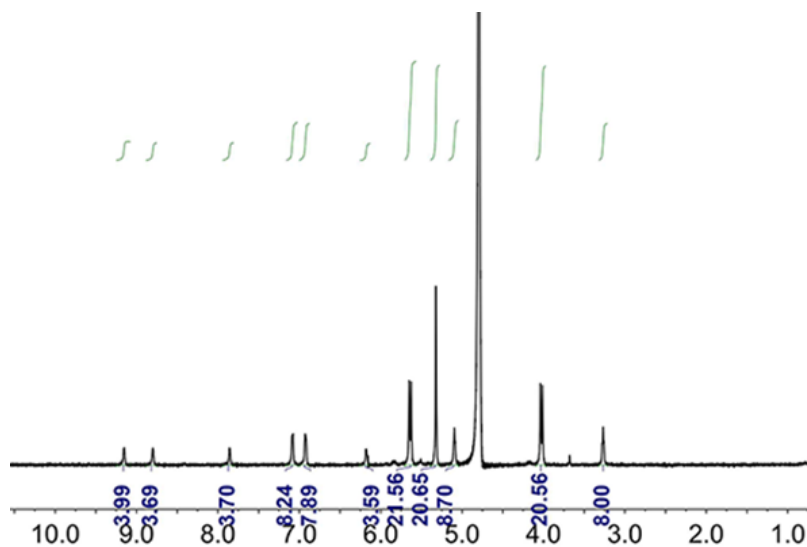
### Pyridinium, 4,4'-(9,10-anthracenediyl)di-2,1-ethenediyl) bis [2,4-dinitrobenzen-(9Cl)] (**1-4**)

Compound 1-3 (200 mg, 0.52 mmol) and 1-chloro-2,4-dinitrobenzene (527 mg, 2.6 mmol) were added in EtOH (20 ml) and was heated to refluxed for 24 h. Then the reaction mixture was cooled and collected the solid by centrifugal, the solid was washed three times with ethanol. Drying in vacuum oven obtained a red solid **1-4** (340 mg, 83 %). <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O) δ 9.42 (s, 1H), 9.06 (d, *J* = 6.3 Hz, 3H), 8.98 (d, *J* = 8.7 Hz, 1H), 8.79 (d, *J* = 16.5 Hz, 1H), 8.47 (d, *J* = 6.4 Hz, 3H), 8.33 (d, *J* = 18.4 Hz, 4H), 7.67 (d, *J* = 7.8 Hz, 3H), 7.26 (d, *J* = 16.4 Hz, 1H). <sup>13</sup>C NMR (151 MHz, D<sub>2</sub>O and DMSO-*d*<sub>6</sub>) δ 157.21, 151.08, 146.48, 144.65, 142.15, 140.16, 134.07, 133.54, 132.82, 132.14, 130.64, 128.94, 127.49, 126.07, 124.21. HRMS (ESI): *m/z* [M-2Cl]<sup>2+</sup> calcd. for C<sub>40</sub>H<sub>26</sub>N<sub>6</sub>O<sub>8</sub><sup>2+</sup>: 359.0900, found: 359.0903.

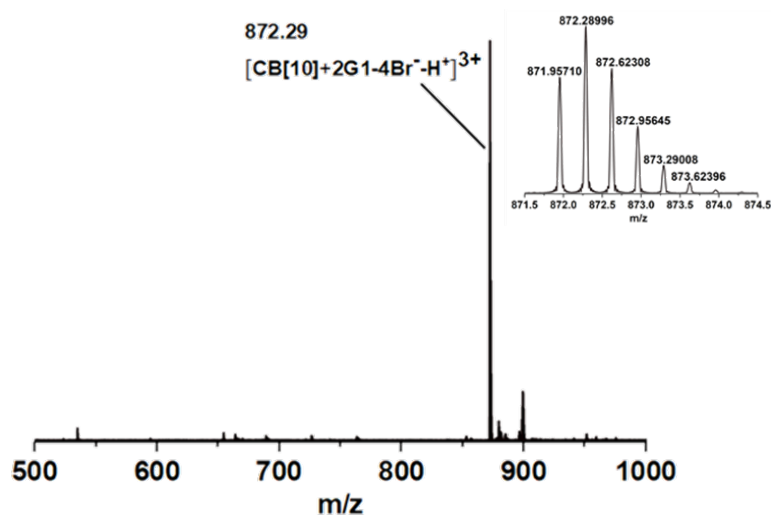
### Pyridinium, 4,4'-(9,10-anthracenediyl)di-2,1-ethenediyl) bis [p-tolyl-(9Cl)] (**G3**)

Compound 1-4 (205 mg, 0.26 mmol) and 4-Methylaniline (139 mg, 1.3 mmol) were added in EtOH (20 ml) and was heated to 80 °C for 24 h. Then the reaction mixture was cooled and collected the solid by centrifugal, the solid was washed three times with EtOH and ethyl ether. Drying in vacuum oven obtained a yellow solid **G3** (160 mg, 80 %). <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O) δ 8.59 (d, *J* = 6.2 Hz, 1H), 8.38 (d, *J* = 15.9 Hz, 0H), 8.21 (s, 1H), 7.68 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.45 (s, 0H), 7.36 (s, 1H), 6.97 (d, *J*

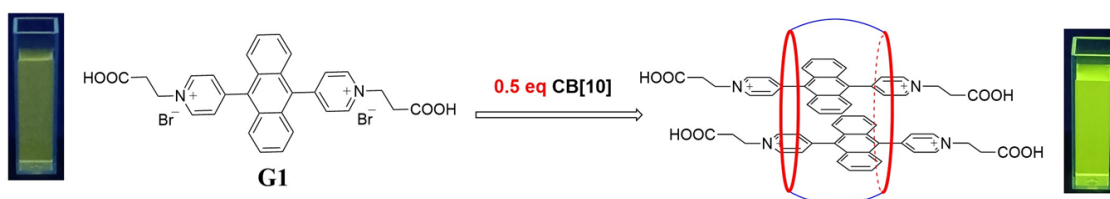
= 16.4 Hz, 1H), 2.22 (s, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{D}_2\text{O}$  and  $\text{DMSO-d}_6$ )  $\delta$  144.80, 143.82, 141.36, 133.90, 133.30, 132.65, 130.46, 128.71, 127.36, 125.78, 124.98, 21.97. HRMS (ESI):  $m/z$   $[\text{M}-2\text{Cl}]^{2+}$  calcd. for  $\text{C}_{42}\text{H}_{34}\text{N}_2^{2+}$ : 283.1350, found: 283.1357.



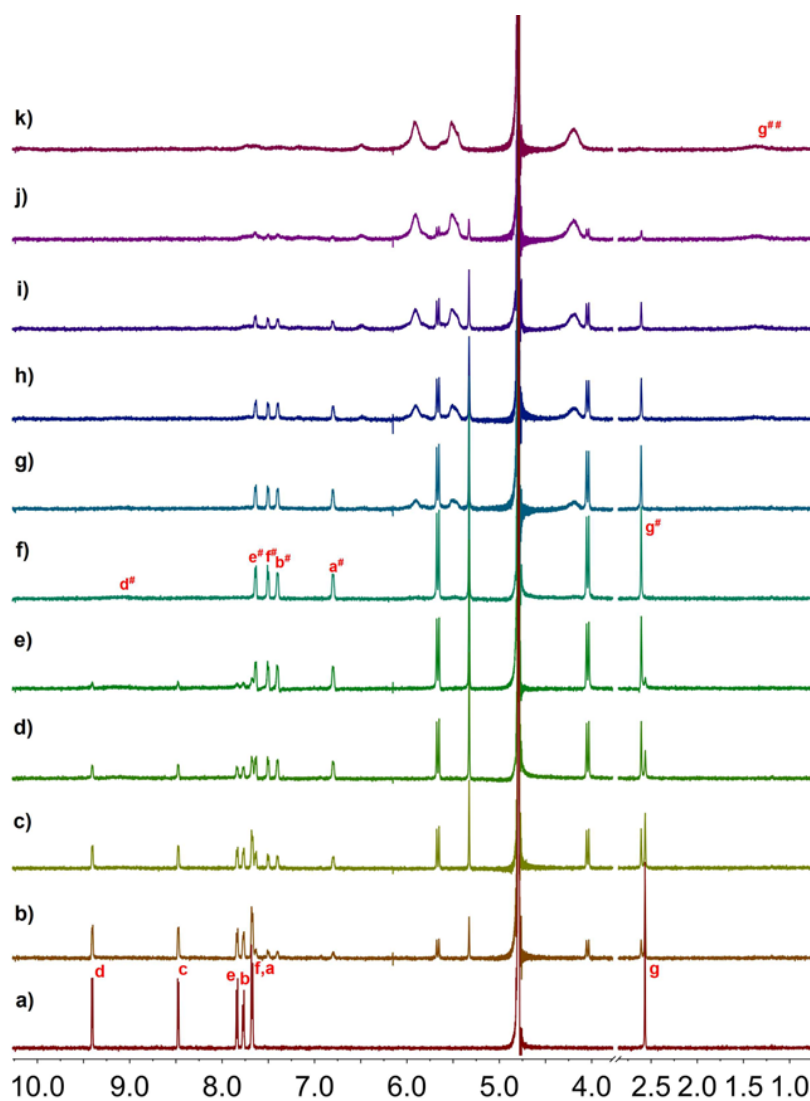
**Figure S1**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of **G1** (0.5 mM) in the presence of 0.5 equiv. of CB[10].



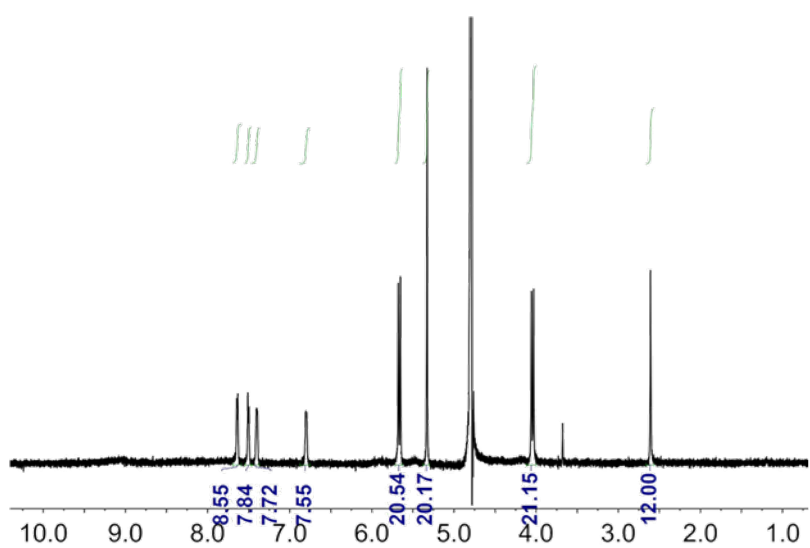
**Figure S2** ESI-MS spectrum of **G1** with 0.5 equiv. of CB[10].



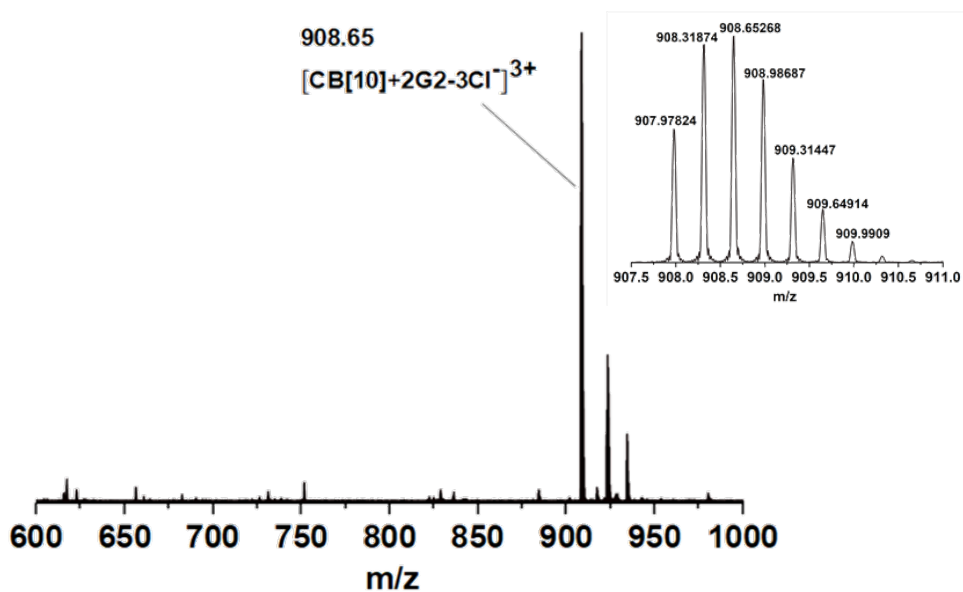
**Figure S3** Schematic illustration of the host-guest binding mode of **G1** in the presence of 0.5 equiv. of CB[10].



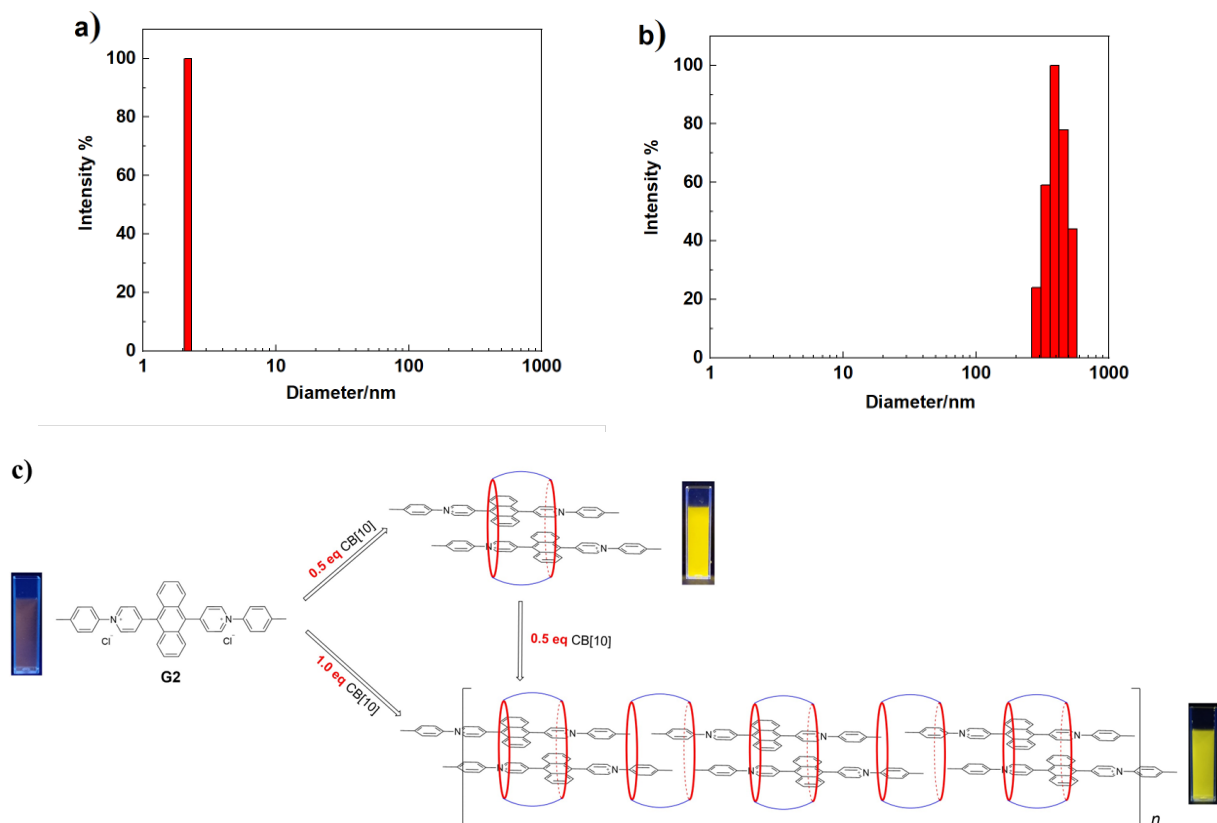
**Figure S4**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of **G2** (0.5 mM) in the presence of different amount of CB[10] (a : 0, b : 0.1, c : 0.2, d : 0.3, e : 0.4, f : 0.5, g : 0.6, h : 0.7, i : 0.8, j : 0.9, k : 1.0 equiv.).



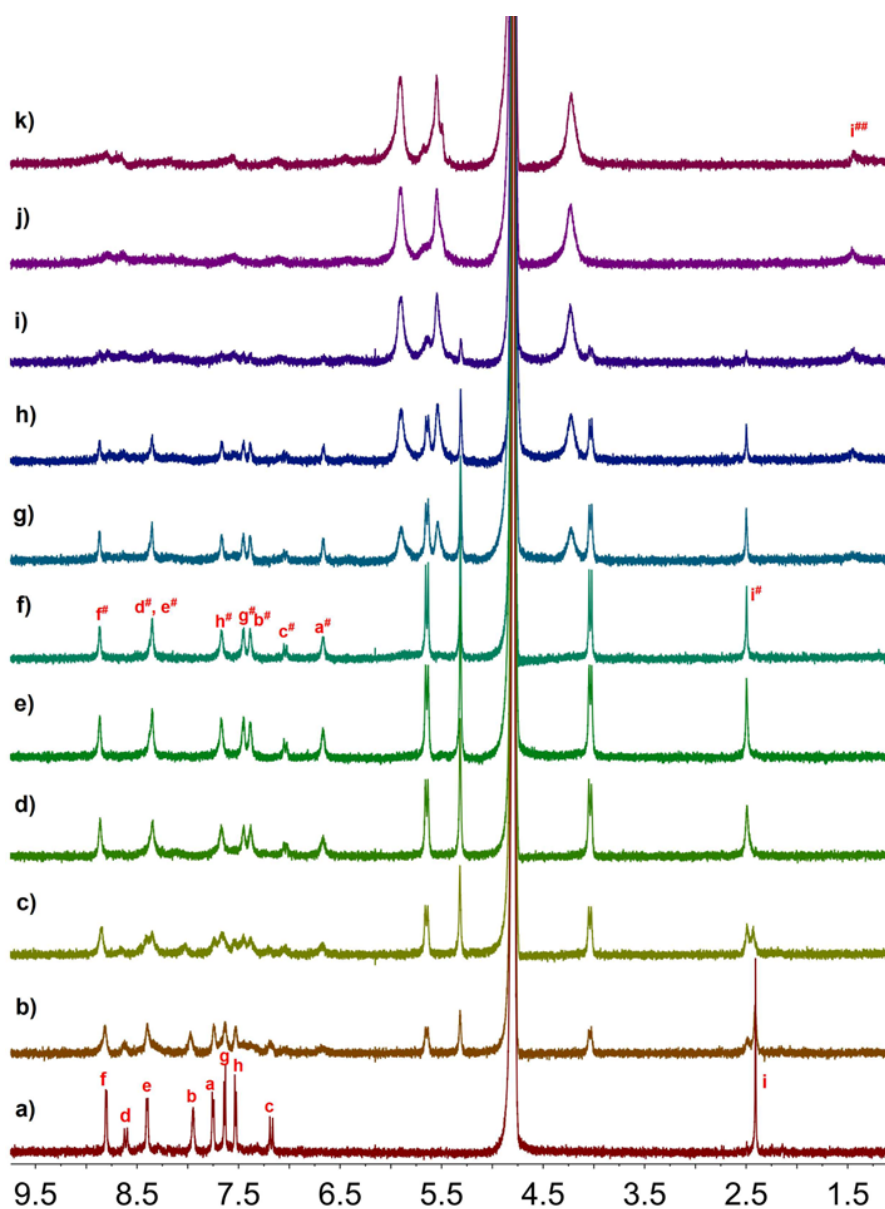
**Figure S5**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of **G2** (0.5 mM) in the presence of 0.5 equiv. of CB[10].



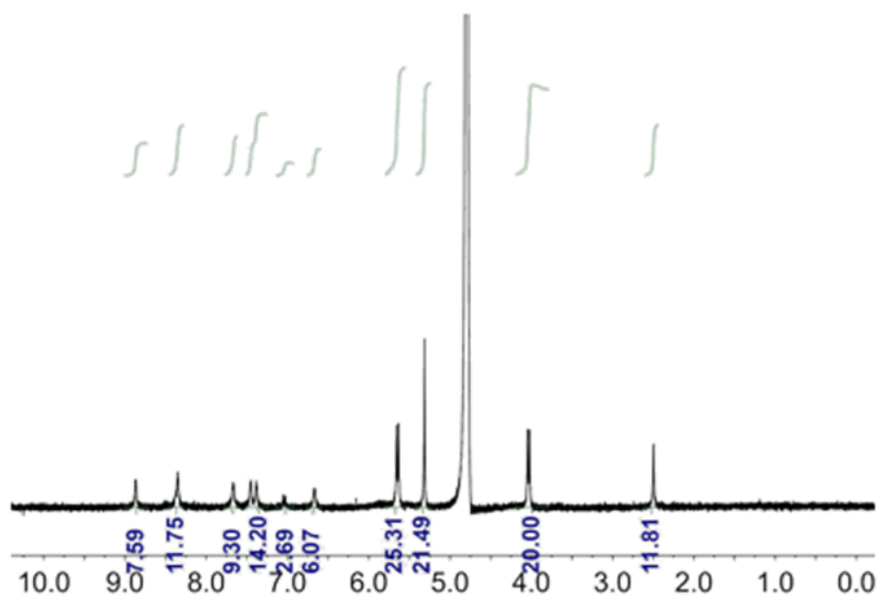
**Figure S6** ESI-MS spectrum of **G2** with 0.5 equiv. of CB[10].



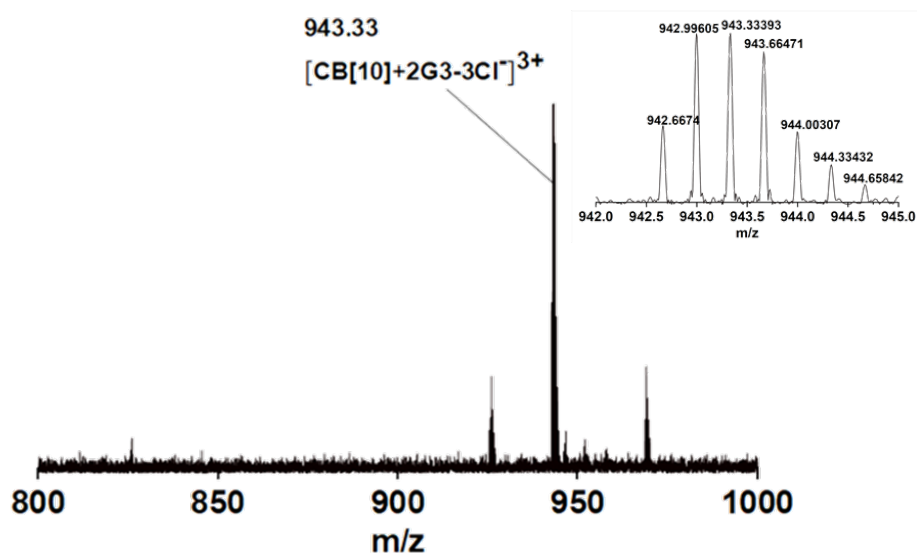
**Figure S7** (a) The DLS of **G2** (0.015 mM) in the presence of 0.5 equiv. of CB[10], (b) 1.0 equiv. of CB[10]. (c) Schematic illustration of the host-guest binding mode of **G2** in the presence of 0 - 1.0 equiv. of CB[10].



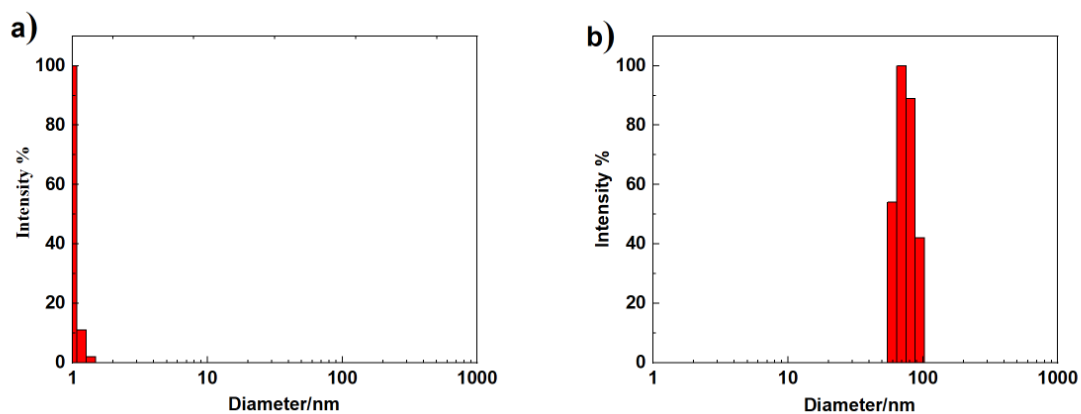
**Figure S8**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of **G3** (0.5 mM) in the presence of different amount of CB[10] (a : 0, b : 0.1, c : 0.2, d : 0.3, e : 0.4, f : 0.5, g : 0.6, h : 0.7, i : 0.8, j : 0.9, k : 1.0 equiv.).



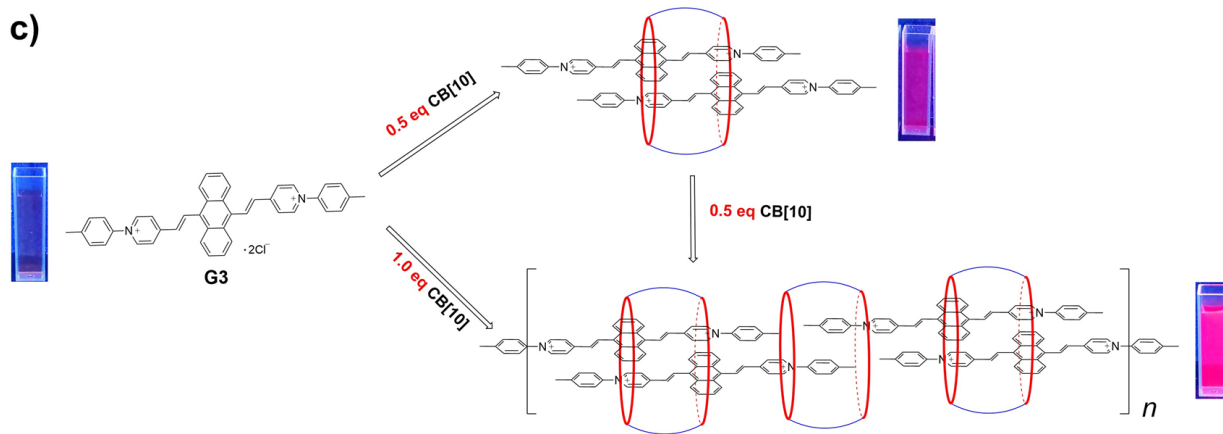
**Figure S9**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of **G3** (0.5 mM) in the presence of 0.5 equiv. of CB[10].



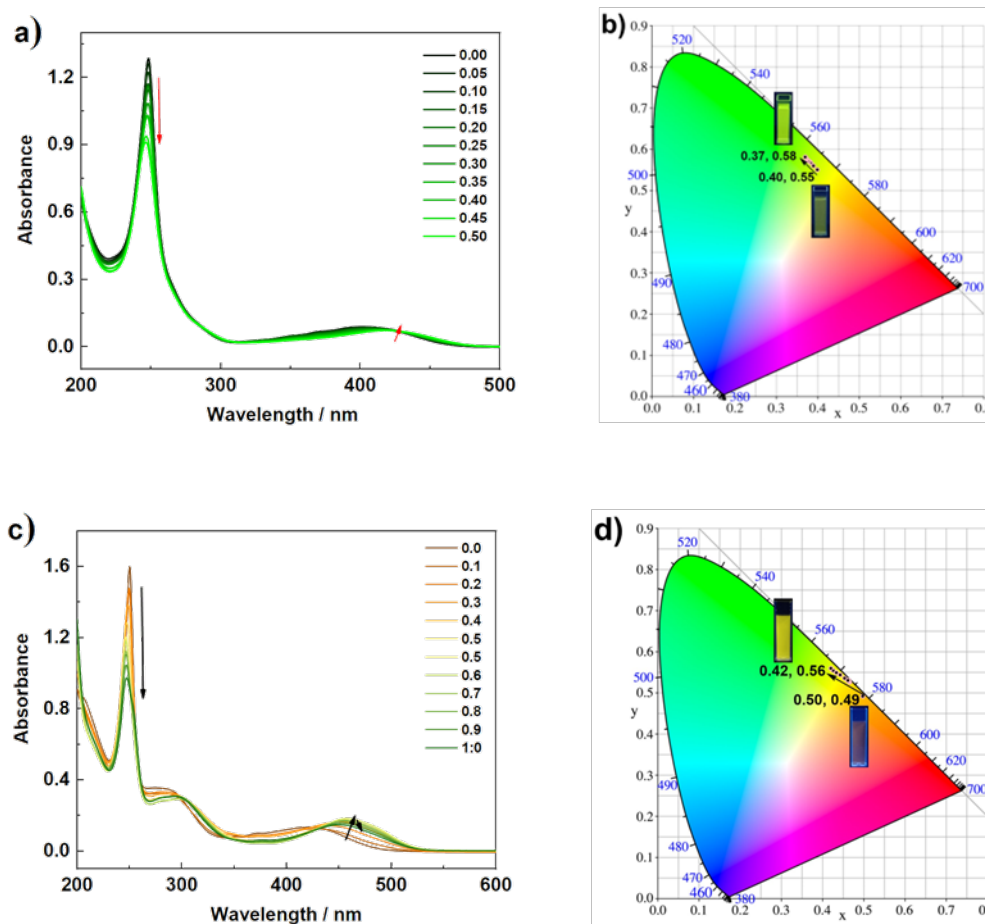
**Figure S10** ESI-MS spectrum of **G3** with 0.5 equiv. of CB[10].

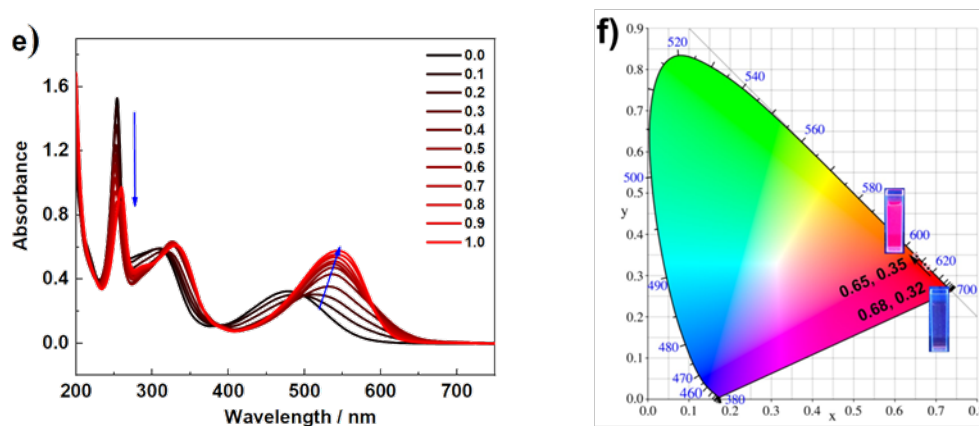




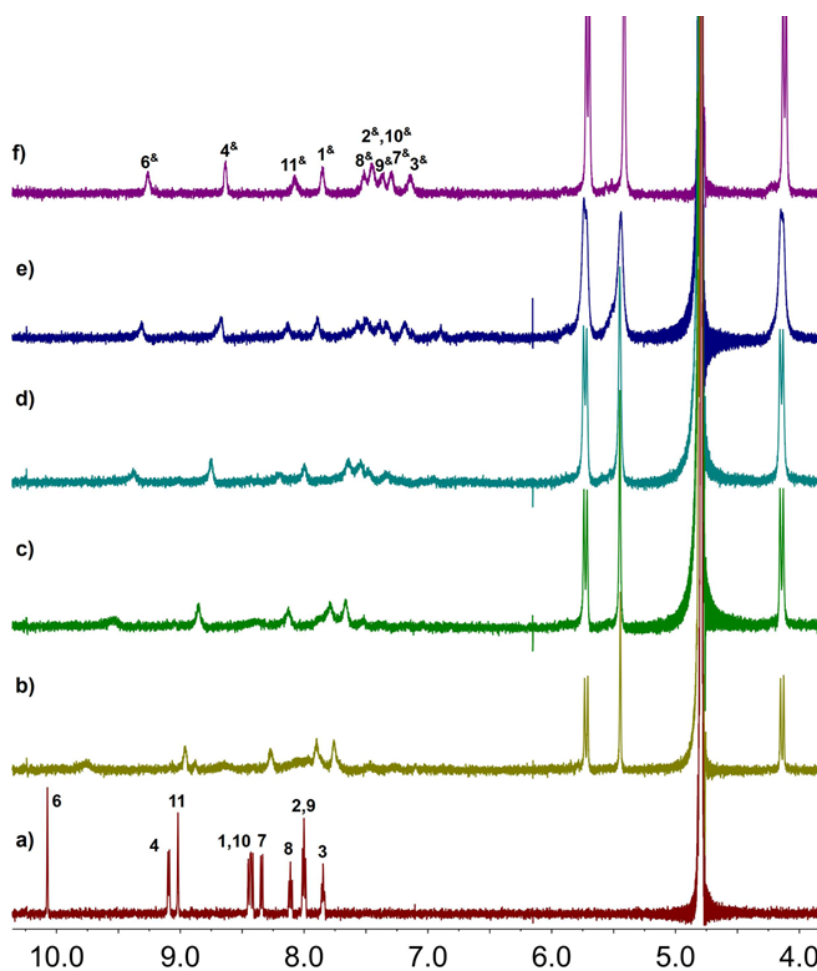


**Figure S11** (a) The DLS of **G3** (0.025 mM) in the presence of 0.5 equiv. of CB[10], (b) 1.0 equiv. of CB[10]. (c) Schematic illustration of the host-guest binding mode of **G3** in the presence of 0 - 1.0 equiv. of CB[10].

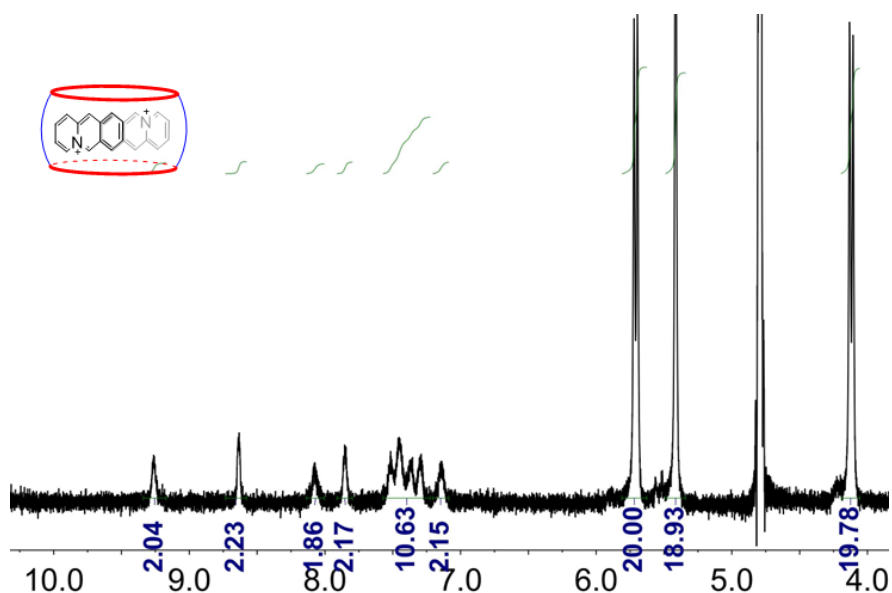




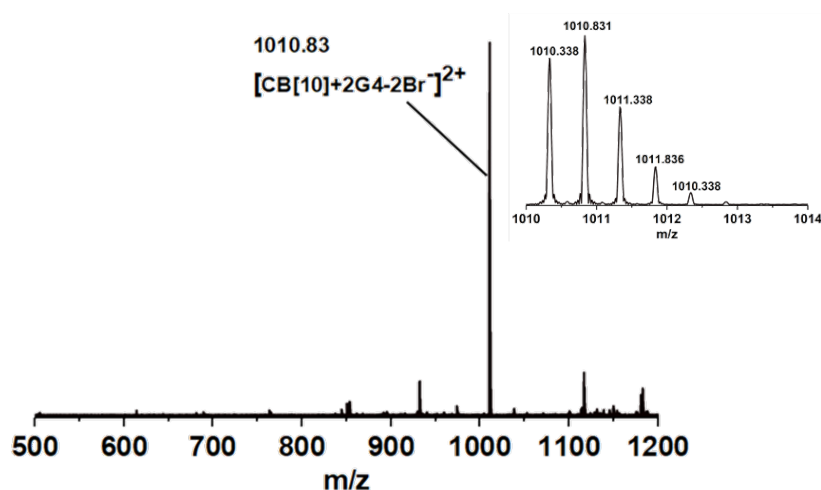
**Figure S12** The UV-Vis absorption spectra (a, c, e) and CIE coordinate diagrams (b, d, f) of **G1** (0.015 mM), **G2** (0.015 mM), **G3** (0.025 mM) in the presence of different amount of CB[10] (0 - 0.5/1.0 equiv.).



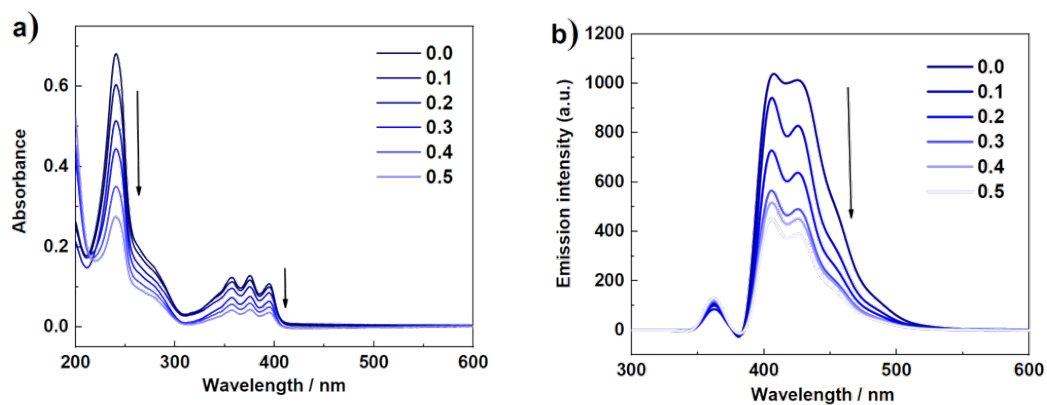
**Figure S13**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of **G4** (0.5 mM) in the presence of different amount of CB[10] (a : 0, b : 0.1, c : 0.2, d : 0.3, e : 0.4, f : 0.5 equiv.).



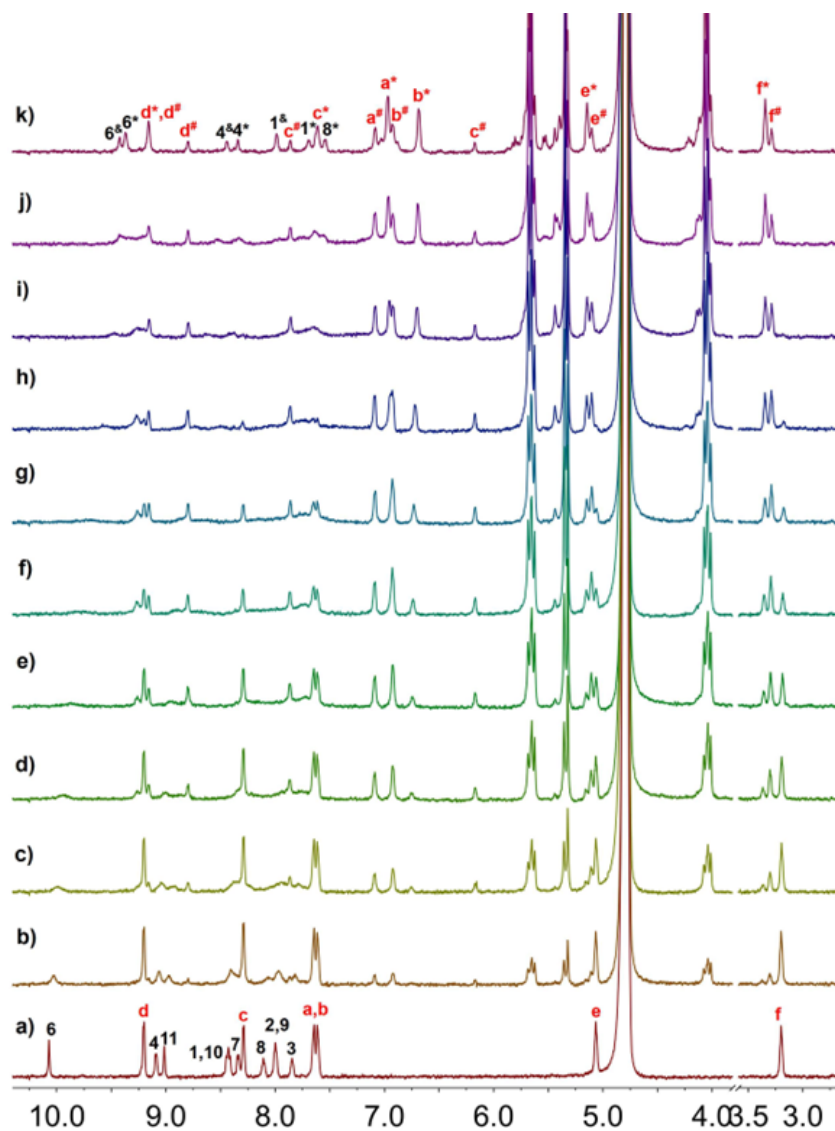
**Figure S14**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of **G4** (0.5 mM) in the presence of 0.5 equiv. of CB[10].



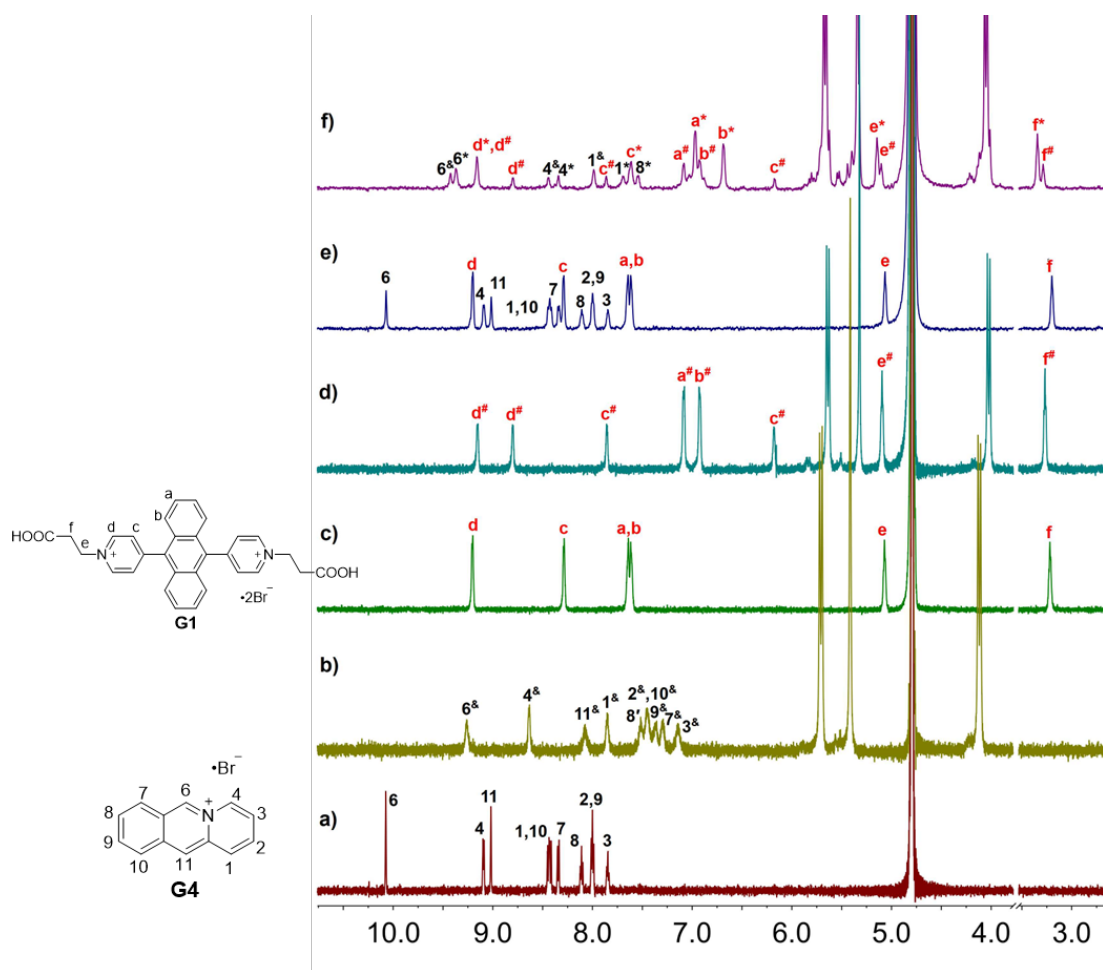
**Figure S15** ESI-MS spectrum of **G4** with 0.5 equiv. of CB[10].



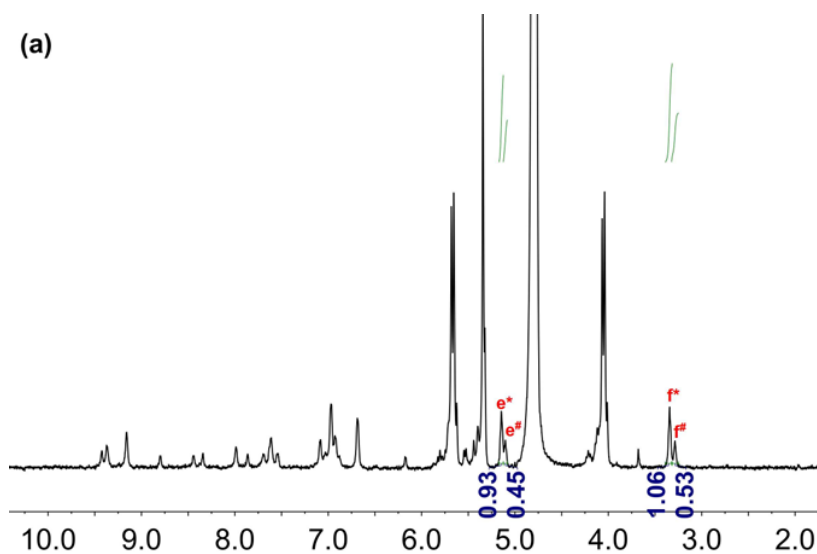
**Figure S16** (a) The UV-Vis absorption spectra, (b) the fluorescence spectra of **G4** (0.015 mM) in the presence of different equiv. of CB[10] (0 - 0.5 equiv.,  $\lambda_{\text{ex}} = 360 \text{ nm}$ ; slit width: Ex = 12 nm, Em = 3 nm).

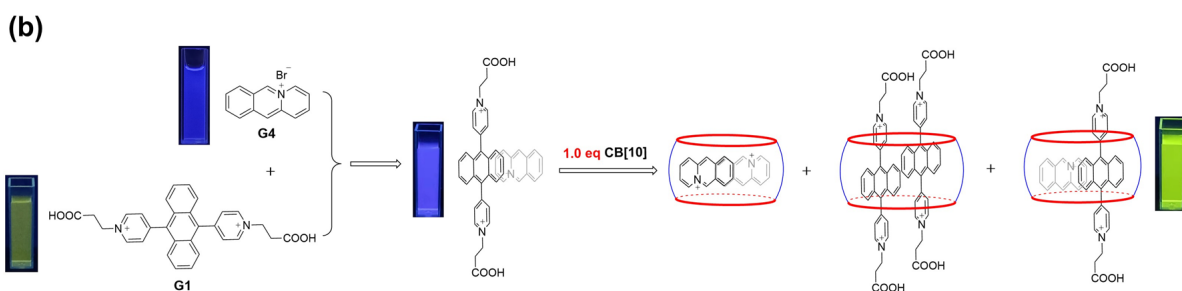


**Figure S17**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of equal amounts of **G1** and **G4** (0.5 mM) with addition of different amounts of CB[10] (a : 0, b : 0.1, c : 0.2, d : 0.3, e : 0.4, f : 0.5, g : 0.6, h : 0.7, i : 0.8, j : 0.9, k : 1.0 equiv.) (resonances of CB[10]·**G1**·**G4** are marked with ‘\*’, resonances of CB[10]·**G1**<sub>2</sub> are marked with ‘#’, and resonances of CB[10]·**G4**<sub>2</sub> are marked with ‘&’ ).

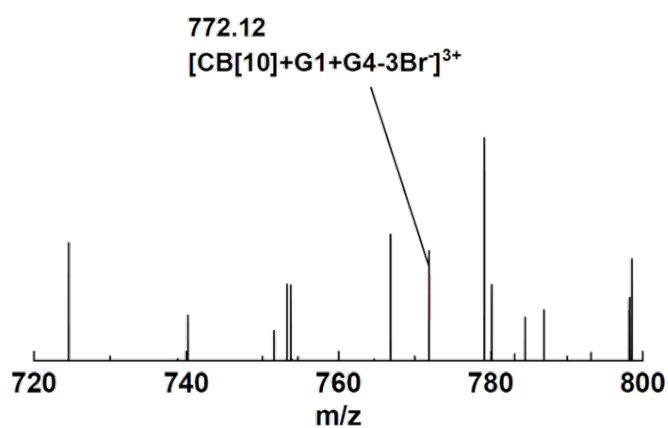


**Figure S18**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ ) of (a) free **G4**, (b)  $\text{CB}[10]\cdot\text{G4}_2$ , (c) free **G1**, (d)  $\text{CB}[10]\cdot\text{G1}_2$ , (e) a 1:1 mixture of **G1** and **G4**, (f) a 1:1:1 mixture of **G1**, **G4** and  $\text{CB}[10]$  (resonances of  $\text{CB}[10]\cdot\text{G1}\cdot\text{G4}$  are marked with '\*', resonances of  $\text{CB}[10]\cdot\text{G1}_2$  are marked with '#', and resonances of  $\text{CB}[10]\cdot\text{G4}_2$  are marked with '&')

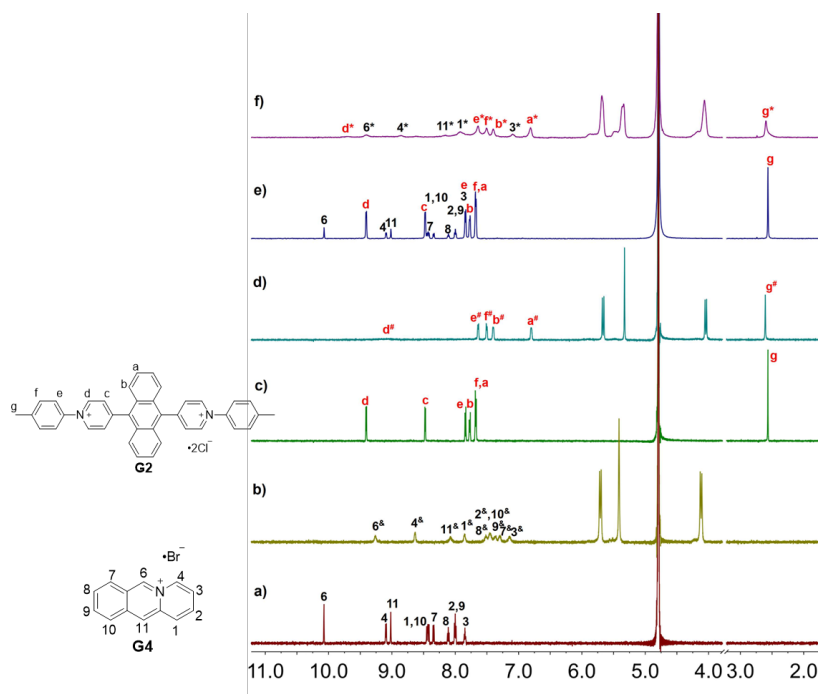




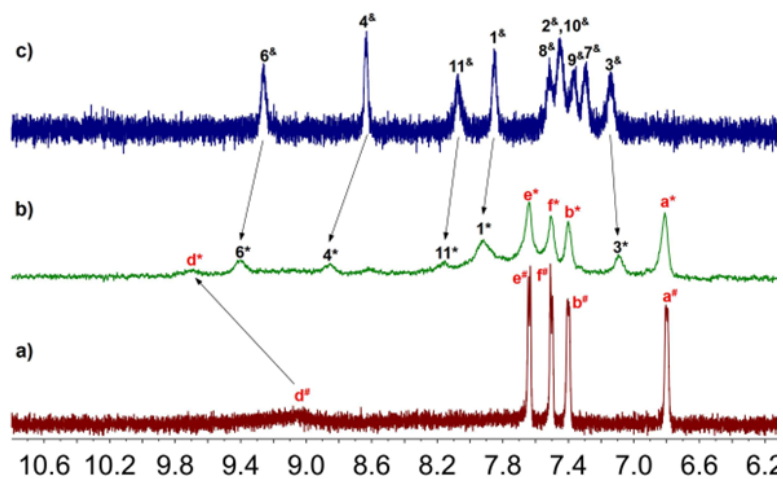
**Figure S19** (a)  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{D}_2\text{O}$ ), (b) Schematic illustration of host-guest binding mode of equal amounts of **G1** and **G4** (0.5 mM) in the presence of 1.0 equiv. of CB[10].



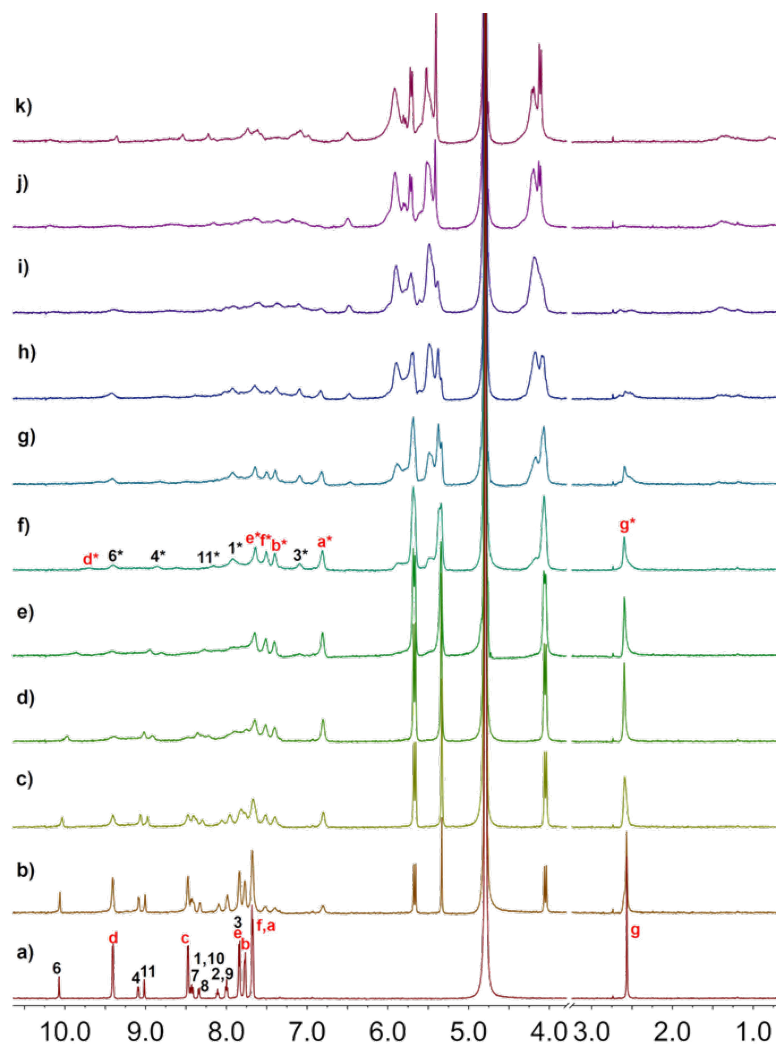
**Figure S20** The ESI-MS spectrum of equal amounts of **G1** and **G4** with 1.0 equiv. of CB[10].



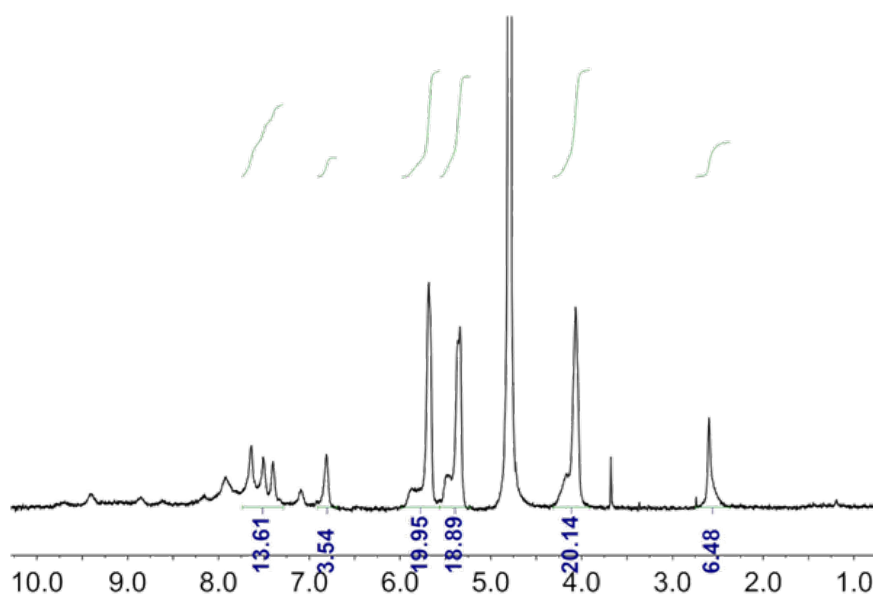
**Figure S21**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ ) of (a) free **G4**, (b) CB[10]·**G4**<sub>2</sub>, (c) free **G2**, (d) CB[10]·**G2**, (e) a 1:1 mixture of **G2** and **G4**, (f) a 1:1:1 mixture of **G2**, **G4** and CB[10].



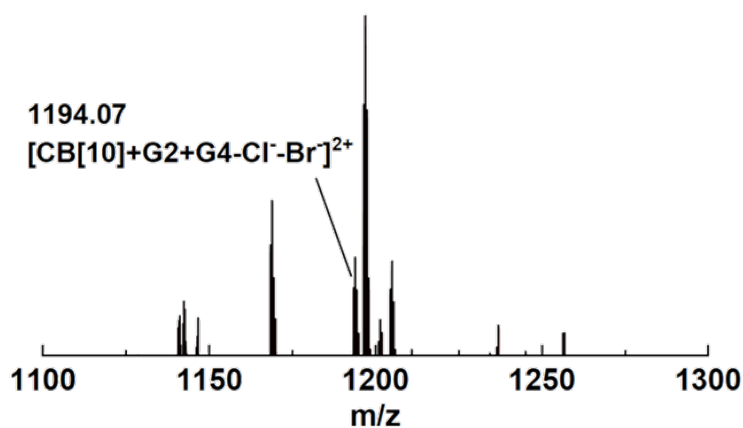
**Figure S22**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ ) of (a)  $\text{CB}[10]\cdot\text{G}_2$ , (b) a 1:1:1 mixture of  $\text{G}_2$ ,  $\text{G}_4$  and  $\text{CB}[10]$ , (c)  $\text{CB}[10]\cdot\text{G}_4$  (0.5 mM).



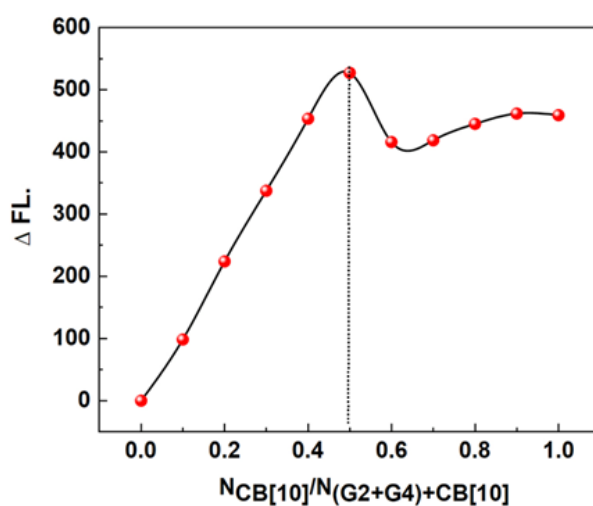
**Figure S23**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ ) of equal amounts  $\text{G}_2$  and  $\text{G}_4$  (0.5 mM) in the presence of different amount of  $\text{CB}[10]$  (a : 0, b : 0.2, c : 0.4, d : 0.6, e : 0.8, f : 1.0, g : 1.2, h : 1.4, i : 1.6, j : 1.8, k : 2.0 equiv.).



**Figure S24** <sup>1</sup>H NMR spectrum (600 MHz, D<sub>2</sub>O) of equal amounts of **G2** and **G4** (0.5 mM) in the presence of 1.0 equiv. of CB[10].

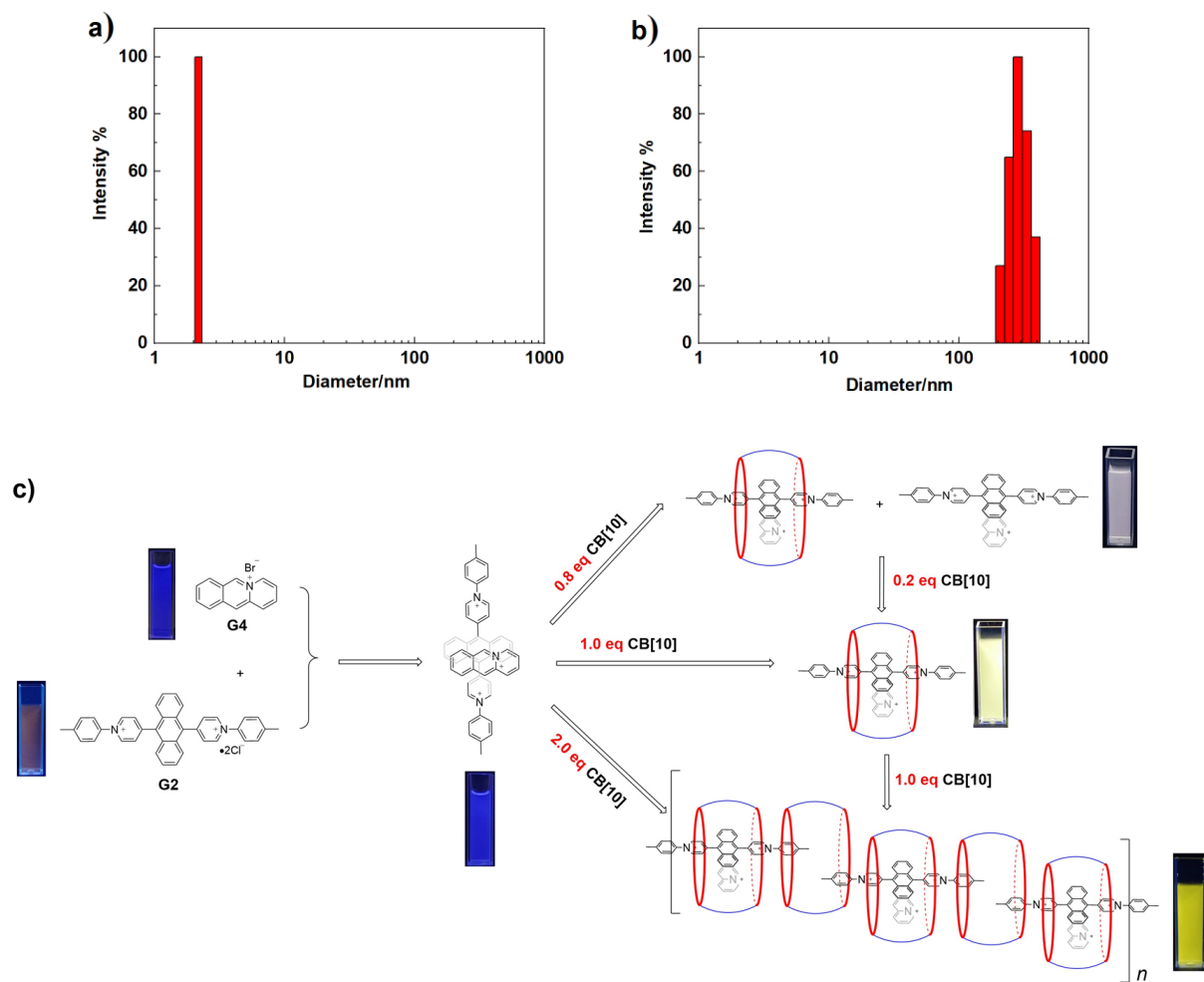


**Figure S25** The ESI-MS spectrum of equal amounts of **G2** and **G4** with 1.0 equiv. of CB[10].

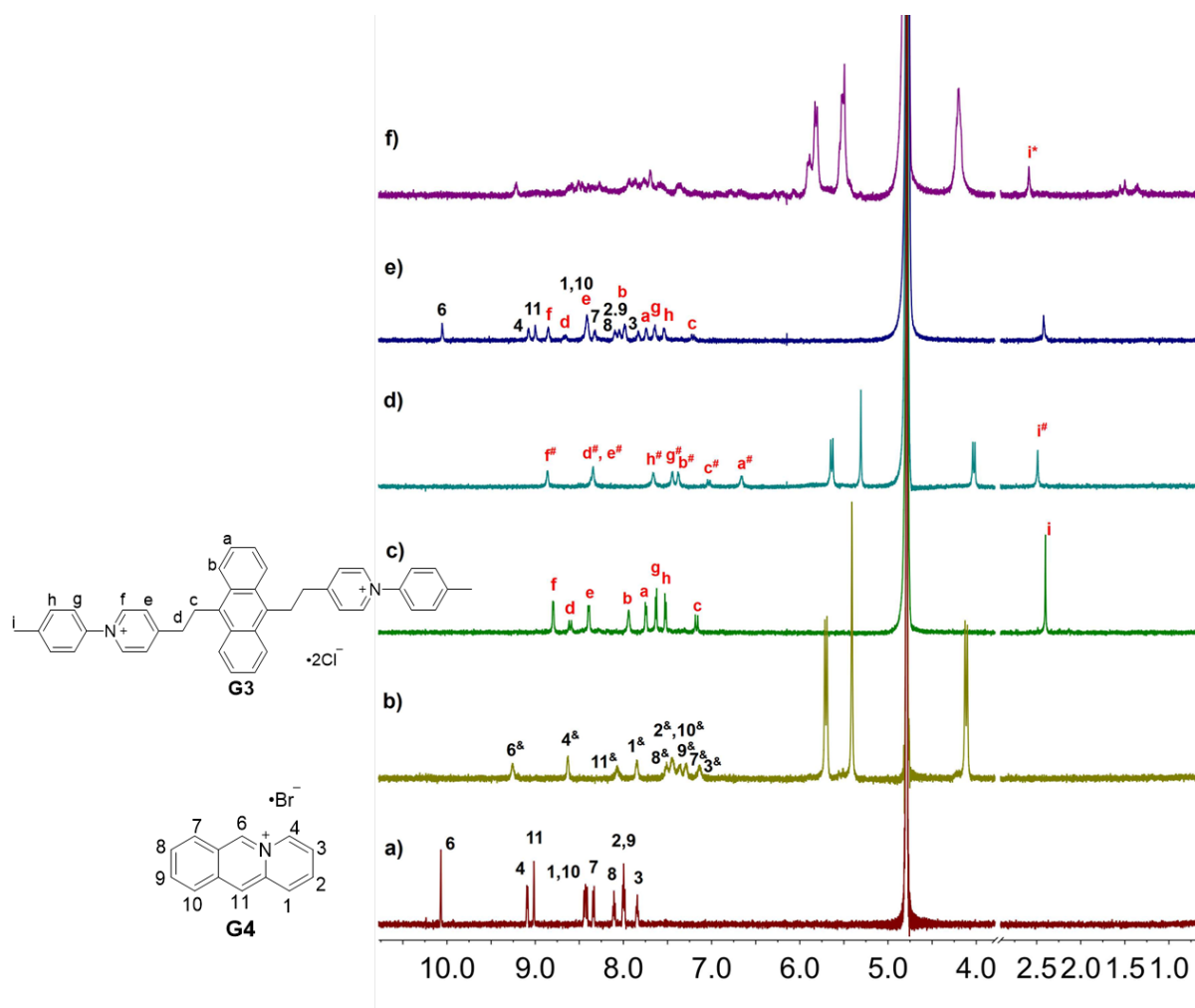


**Figure S26** The Job's plot obtained from fluorescence titration<sup>6</sup> (supporting the 1:1:1 stoichiometry of the complex formed by equal amounts of **G2** and **G4** with 1.0 equiv. of CB[10]).

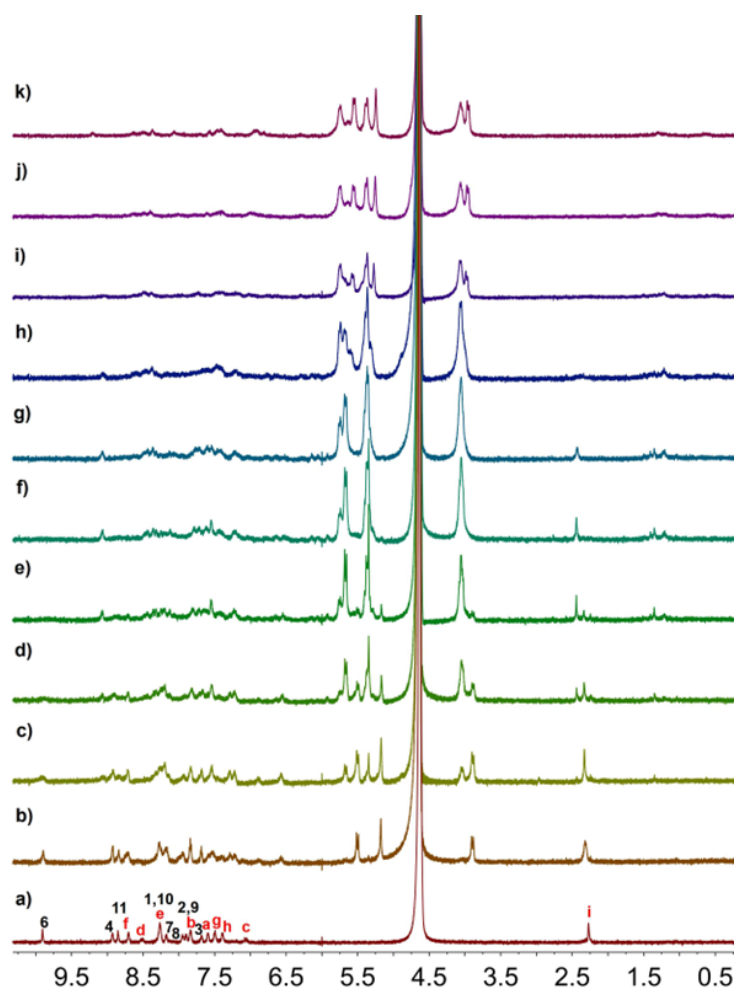




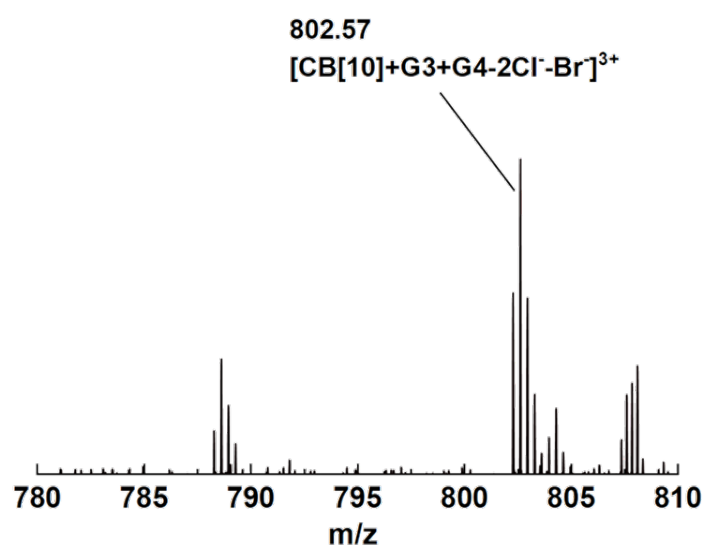
**Figure S27** (a) DLS of equal amounts of **G2** and **G4** (0.015 mM) in the presence of 1.0 equiv. of CB[10], and (b) 2.0 equiv. of CB[10]. (c) Schematic illustration of host-guest binding mode of equal amounts **G2** and **G4** with CB[10] (0 - 2.0 equiv.) in aqueous solutions.



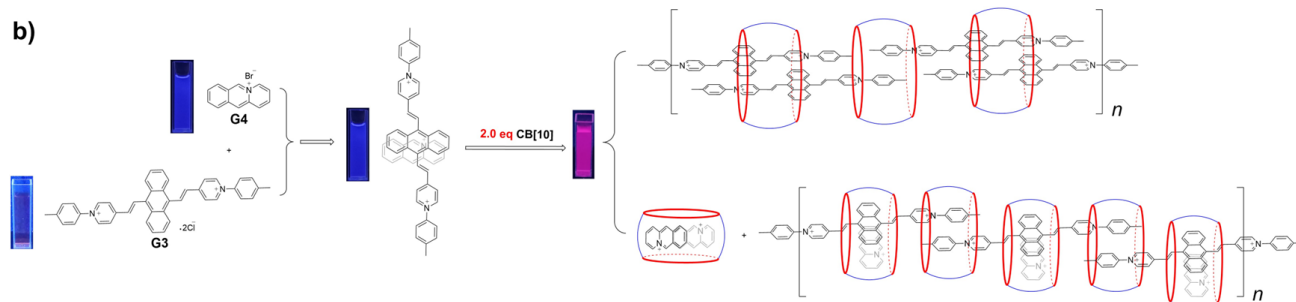
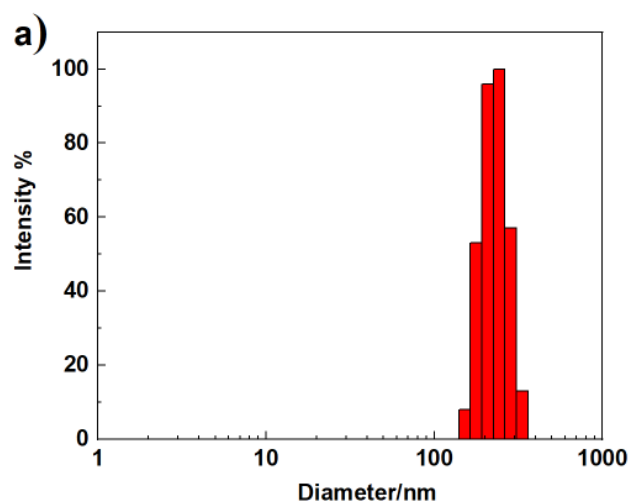
**Figure S28**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ ) of (a) free **G4**, (b)  $\text{CB}[10]\cdot\text{G4}_2$ , (c) free **G3**, (d)  $\text{CB}[10]\cdot\text{G3}_2$ , (e) a 1:1 mixture of **G3** and **G4**, (f) a 1:1:1 mixture of **G3**, **G4** and  $\text{CB}[10]$ .



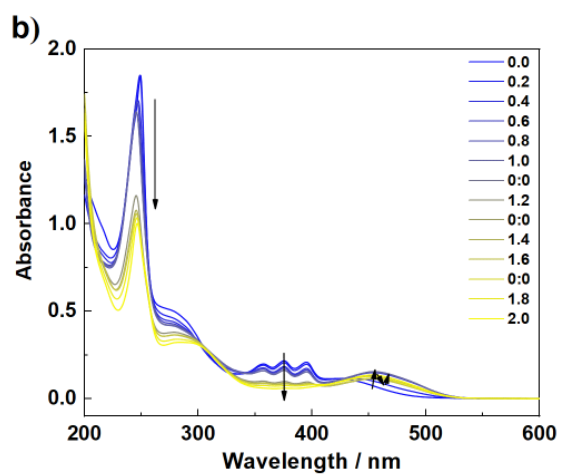
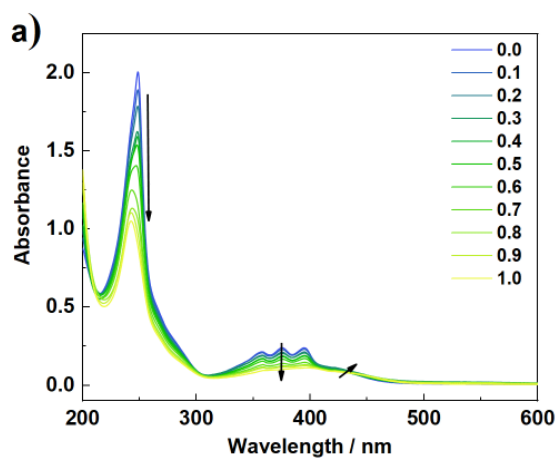
**Figure S29**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{D}_2\text{O}$ ) of equal amounts of **G3** and **G4** (0.5 mM) in the presence of different amount of CB[10] (a : 0, b : 0.2, c : 0.4, d : 0.6, e : 0.8, f : 1.0, g : 1.2, h : 1.4, i : 1.6, j : 1.8, k : 2.0 equiv.)

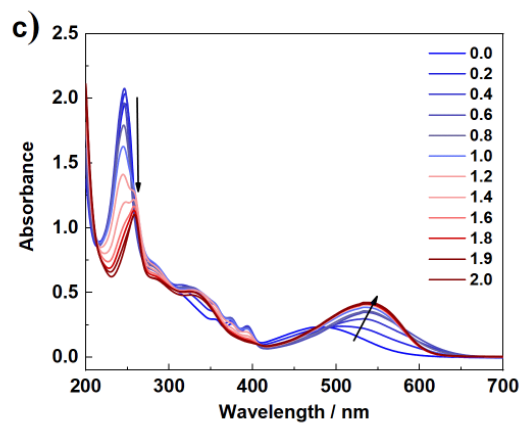


**Figure S30** The ESI-MS spectrum of equal amounts of **G3** and **G4** with 1.0 equiv. of CB[10].

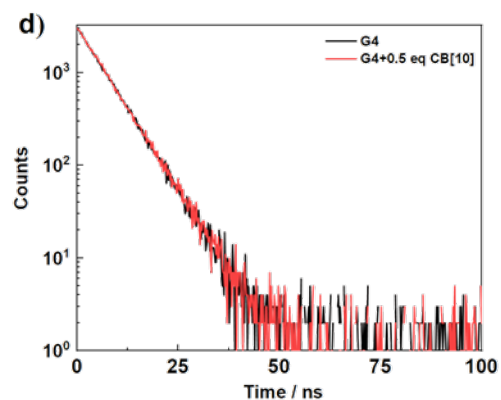
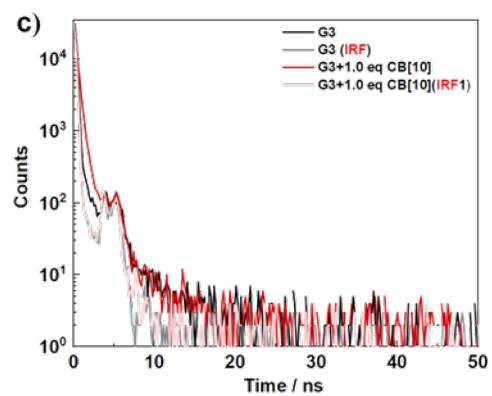
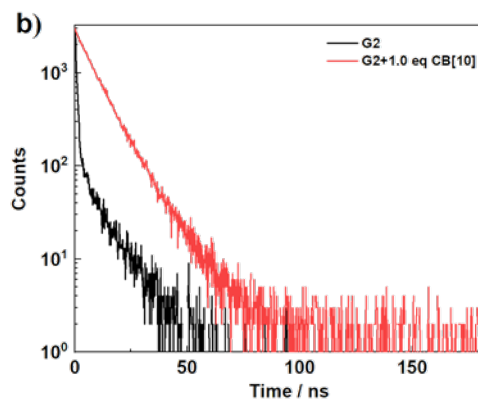
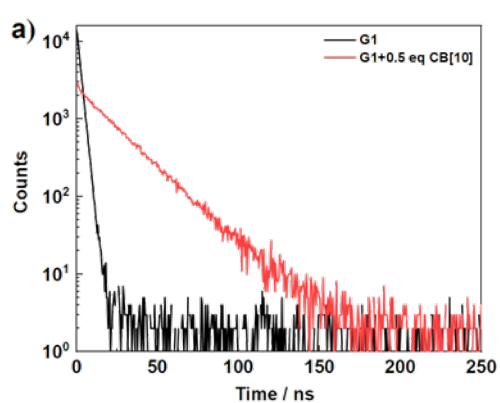


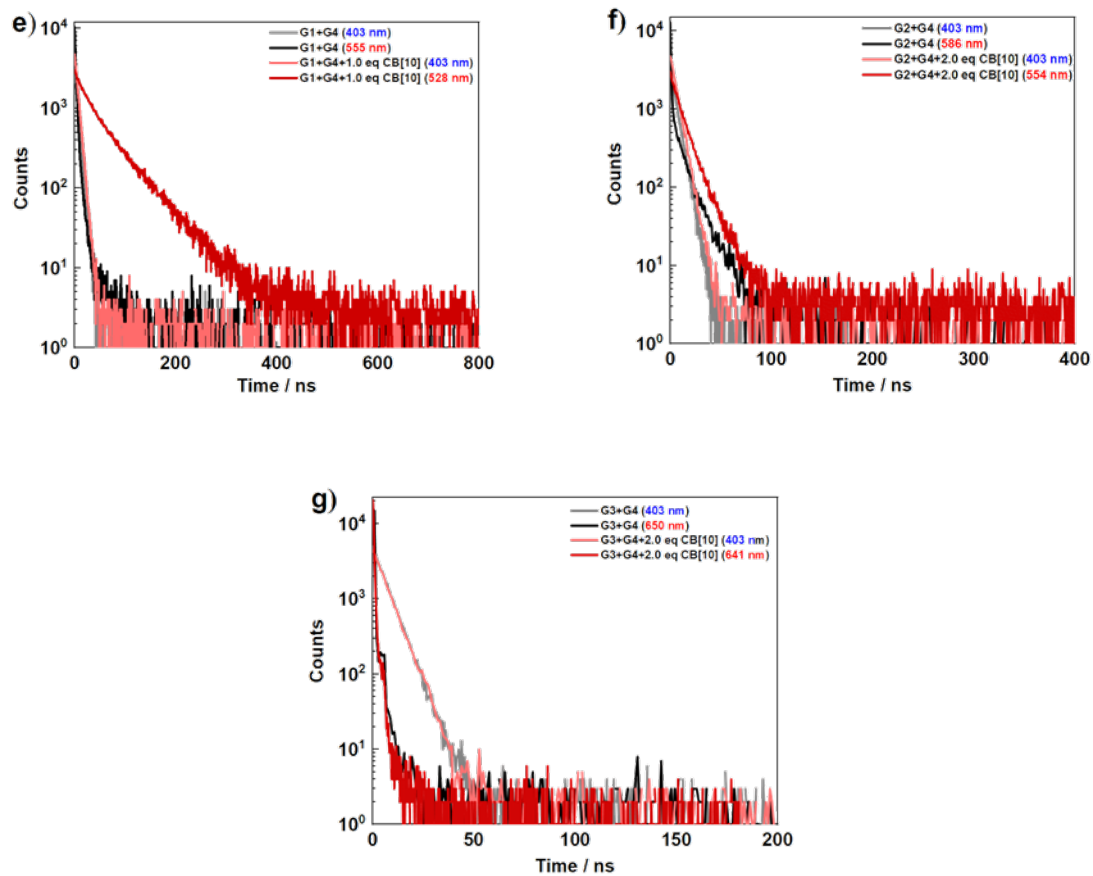
**Figure S31** (a) DLS of equal amounts of **G3** and **G4** (0.025 mM) in the presence of 2.0 equiv. of CB[10]. (b) Schematic illustration of host-guest binding mode of equal amounts **G3** and **G4** with 2.0 equiv. of CB[10].





**Figure S32** The UV-Vis absorption spectra of equal amounts **G1** and **G4** (0.015 mM) (a), **G2** and **G4** (0.015 mM) (b), **G3** and **G4** (0.025 mM) (c), in the presence of different amount of CB[10] (0 - 1.0 / 2.0 equiv.)

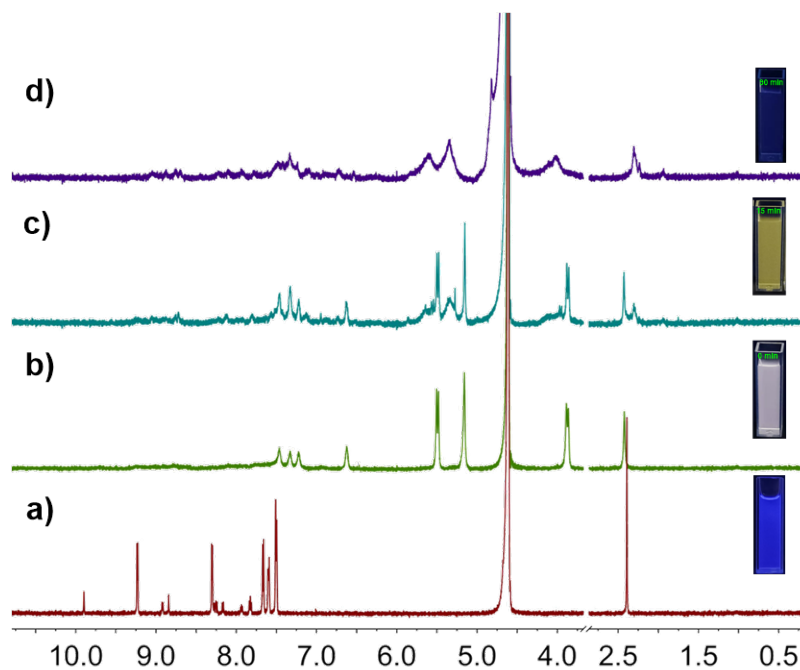




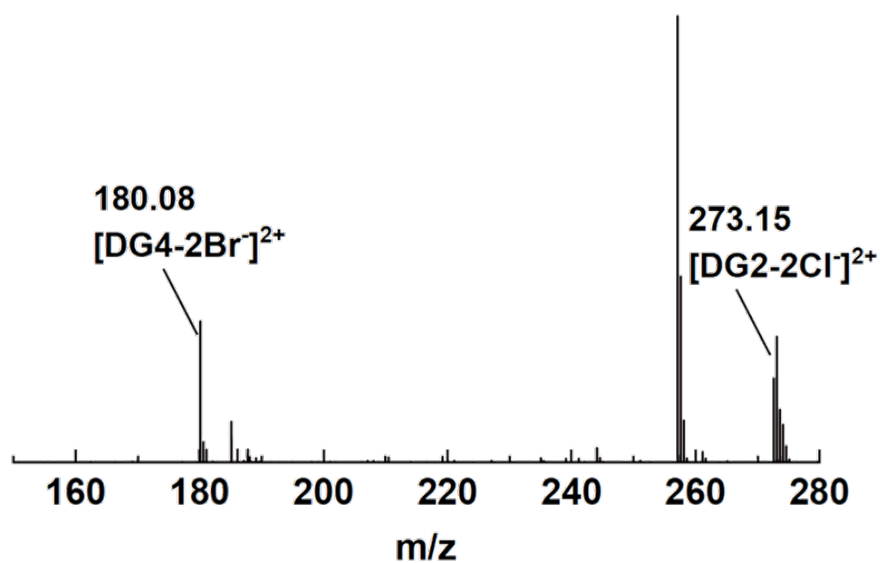
**Figure S33** Time-correlated single photon counting decay profiles for **G1** (a), **G2** (b), **G3** (c), **G4** (d), equal amounts of **G1** and **G4** (e), equal amounts of **G2** and **G4** (f), equal amounts of **G3** and **G4** (g) with CB[10].

**Table S1** Steady-state spectral data of **G1-G4** in aqueous solution.

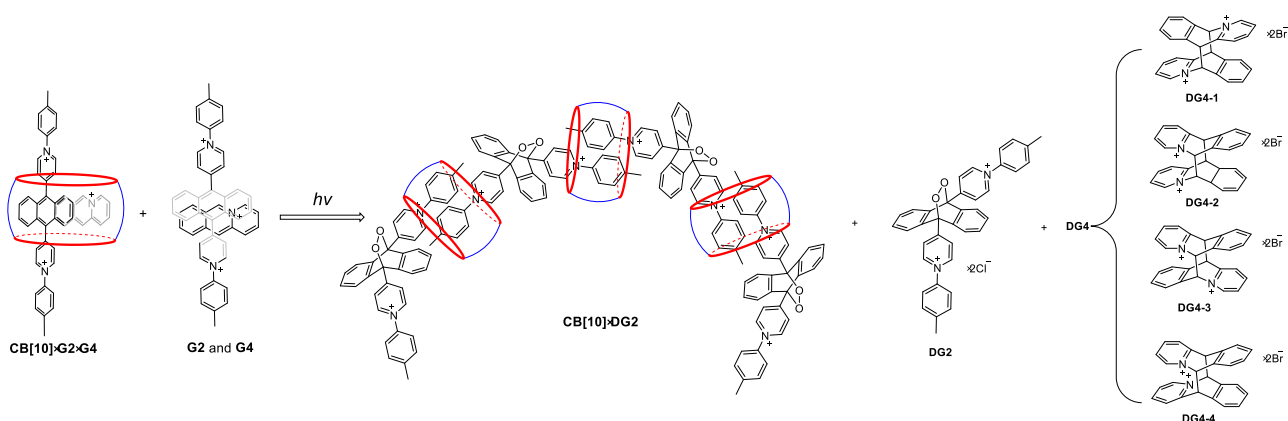
	$\lambda_{em}/nm$	$\tau/ns$	$\phi_F/\%$
G1	555	2.16	2.60
G1+0.5 eq CB[10]	543	21.19	35.93
G2	586	3.48	0.03
G2+1.0 eq CB[10]	555	9.20	45.37
G3	650	0.34	0.01
G3+1.0 eq CB[10]	645	0.56	2.30
G4	403	6.14	29.32
G4+0.5 eq CB[10]	403	6.16	21.12
G1+G4	403/555	6.03/3.18	13.53
G1+G4+1.0 eq CB[10]	403/528	6.19/48.16	27.67
G2+G4	403/586	6.07/3.38	12.71
G2+G4+2.0 eq CB[10]	403/554	6.20/11.26	60.70
G3+G4	403/650	6.12/0.36	7.14
G3+G4+2.0 eq CB[10]	403/641	6.12/0.60	2.14

**Figure S34**  $^1H$  NMR spectra (600 M,  $D_2O$ , 298 K) of equal amounts of free **G2** and **G4** (a), the equal amounts **G2** and **G4** in the presence of 0.8 equiv. of CB[10] (b), sample b after UV irradiation in air for 15

min (c), 90 min (d).

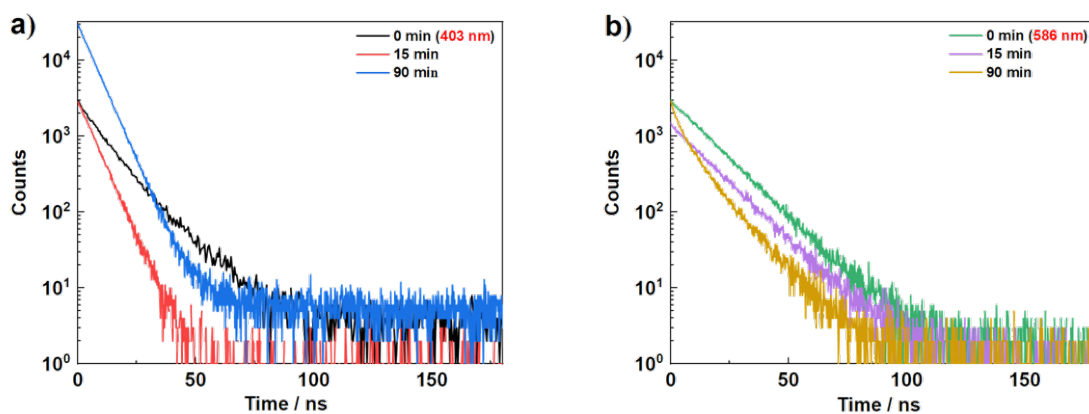


**Figure S35** The ESI-MS spectrum of the white-light solution (the equal amounts **G2** and **G4** in the presence of 0.8 equiv. of CB[10]) after UV irradiation in air for 90 min).



**Figure S36** The schematic diagram of photoreaction products structure of the white-light solution after UV irradiation in air for 90 min.

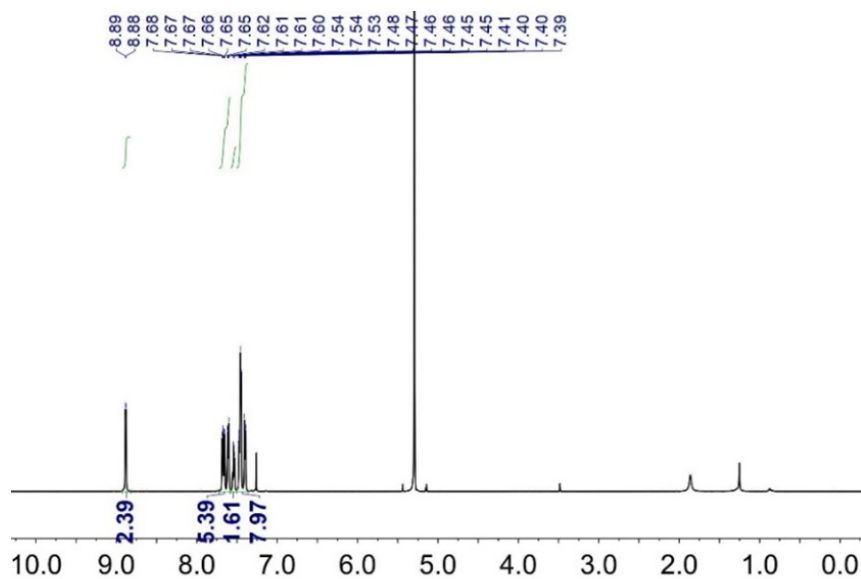




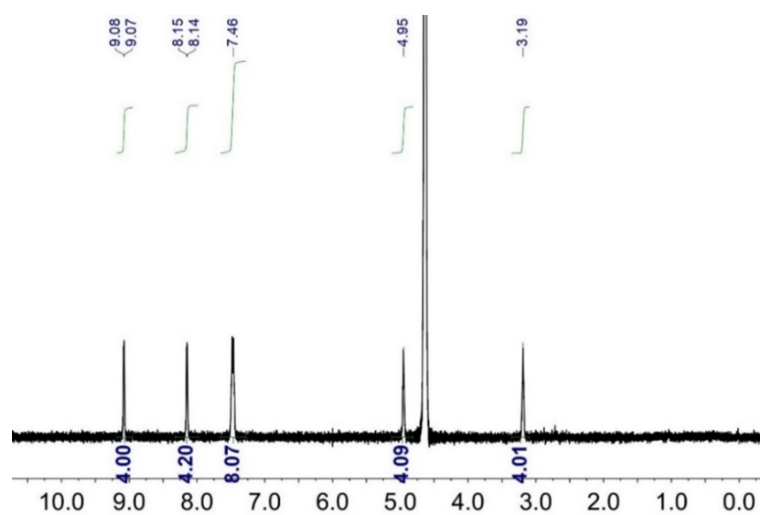
**Figure S37** Time-correlated single photon counting decay profiles for white-light solution under UV irradiation for 0 min, 15 min and 90 min.

**Table S2** Steady-state spectral data of white-light solution under UV irradiation for 0 min, 15 min and 90 min in aqueous solution.

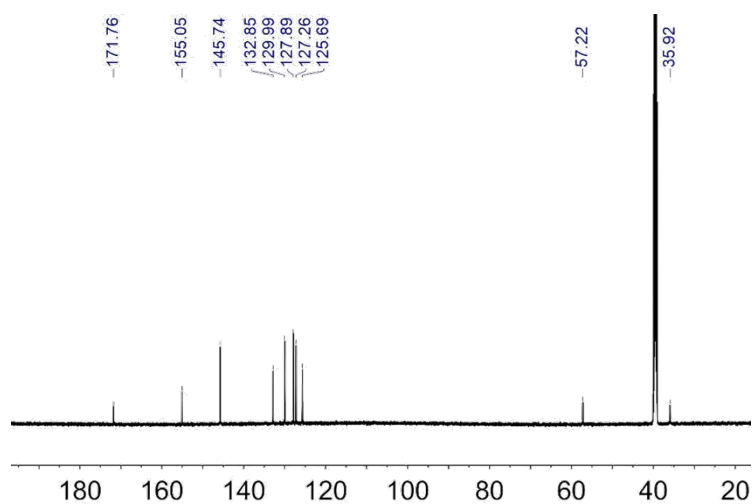
0.8 eq CB[10] and G2-G4	$\lambda_{em}/nm$	$\tau/ns$	$\phi_F/\%$
0 min	403/586	6.08/14.26	42.48
15 min	403/586	6.09/14.31	30.42
90min	403/586	6.08/9.28	6.97



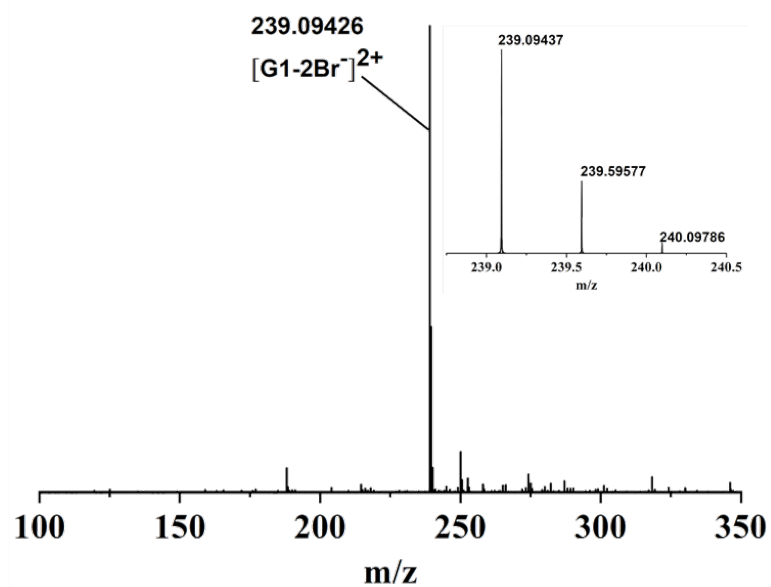
**Figure S38** The  $^1H$  NMR spectrum of compound **1-1** (600 MHz,  $CDCl_3$ , 298 K).



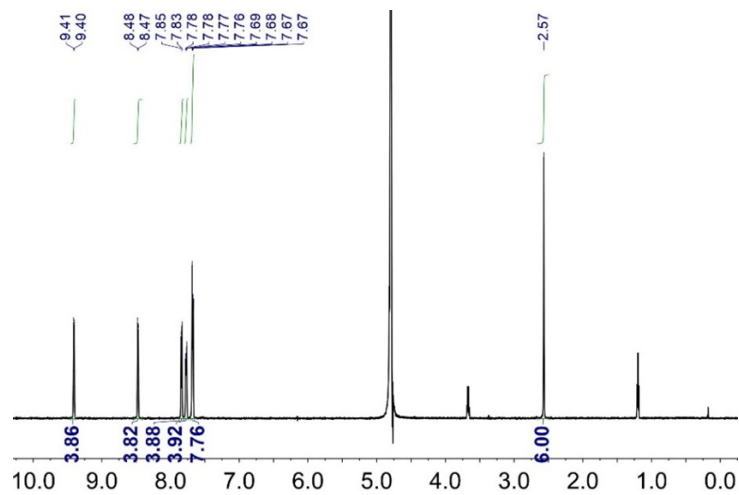
**Figure S39** The  $^1\text{H}$  NMR spectrum of compound **G1** (600 MHz,  $\text{D}_2\text{O}$ , 298 K).



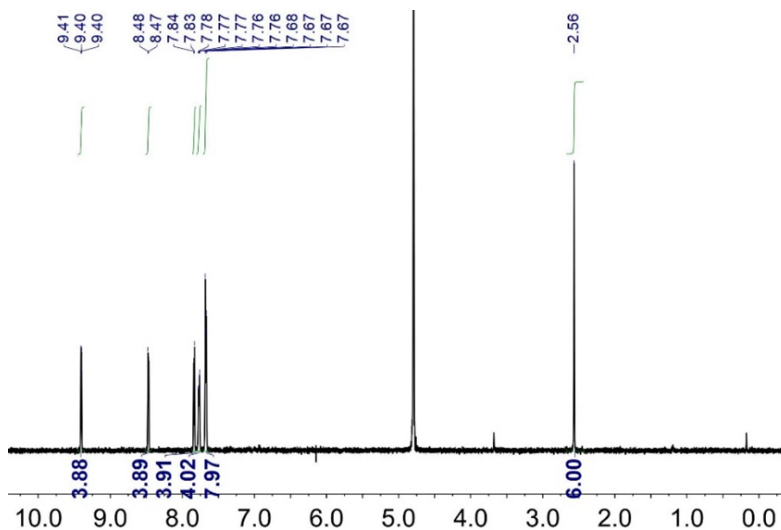
**Figure S40** The  $^{13}\text{C}$  NMR spectrum of compound **G1** (600 MHz,  $\text{DMSO-d}_6$ , 298 K).



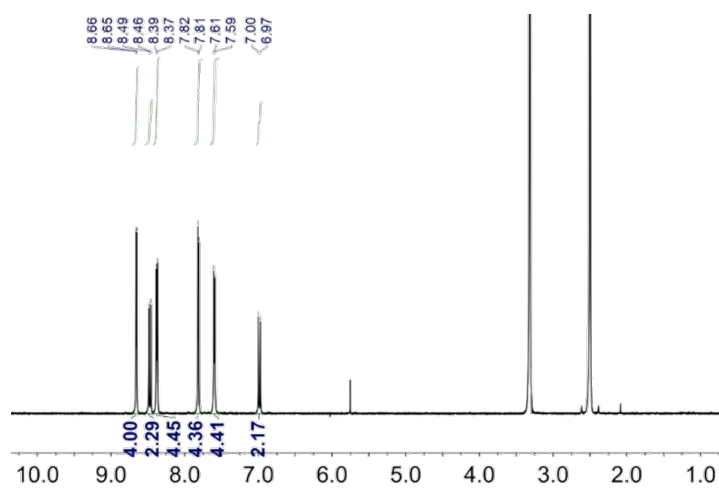
**Figure S41** HRMS (ESI) spectra of compound **G1**.



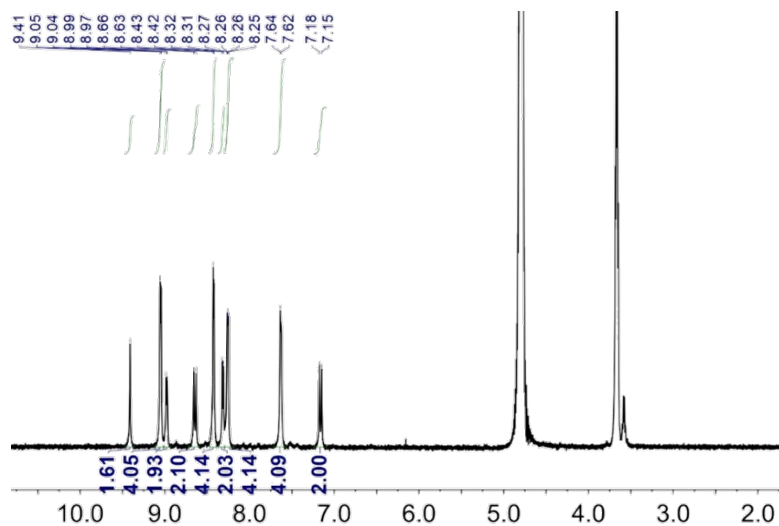
**Figure S42** The  $^1\text{H}$  NMR spectrum of compound **1-2** (600 MHz,  $\text{D}_2\text{O}$ , 298 k).



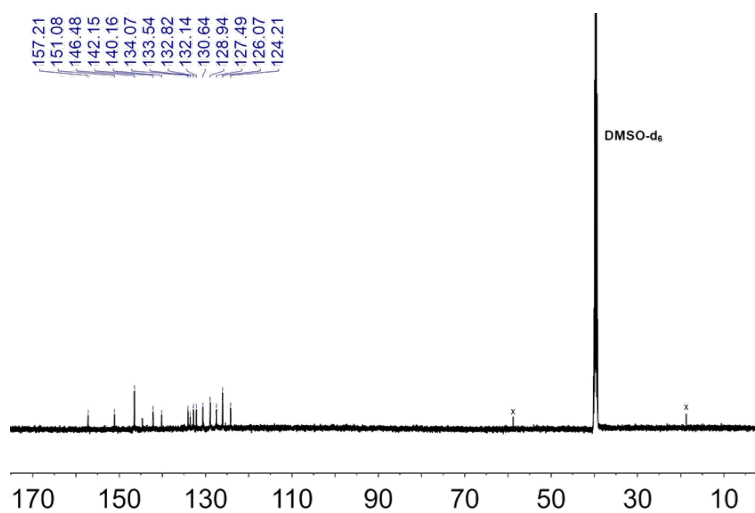
**Figure S43** The  $^1\text{H}$  NMR spectrum of compound **G2** (600 MHz,  $\text{D}_2\text{O}$ , 298 k).



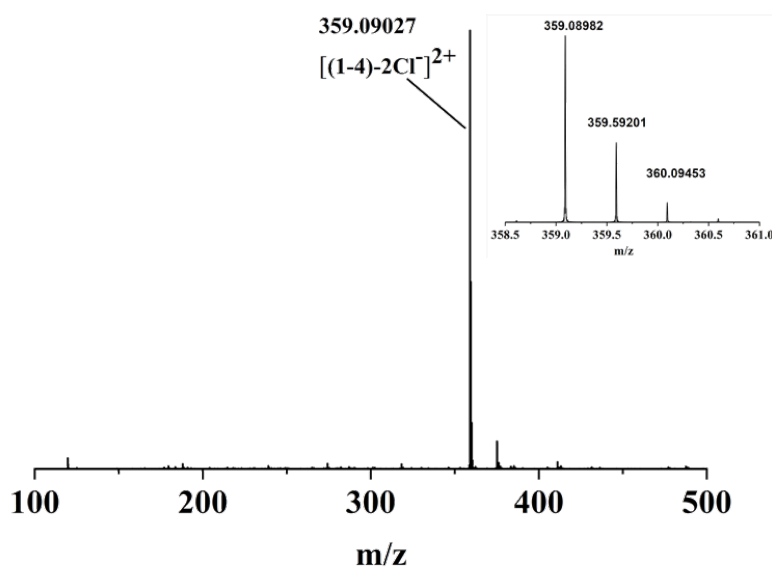
**Figure S44** The  $^1\text{H}$  NMR spectrum of compound **1-3** (600 MHz,  $\text{DMSO-d}_6$ , 298 k)



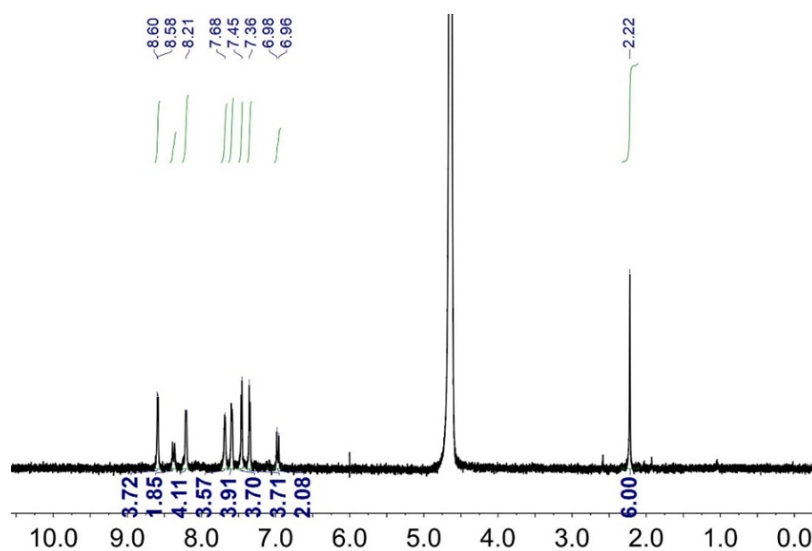
**Figure S45** The  $^1\text{H}$  NMR spectrum of compound **1-4** (600 MHz,  $\text{D}_2\text{O}$ , 298 k).



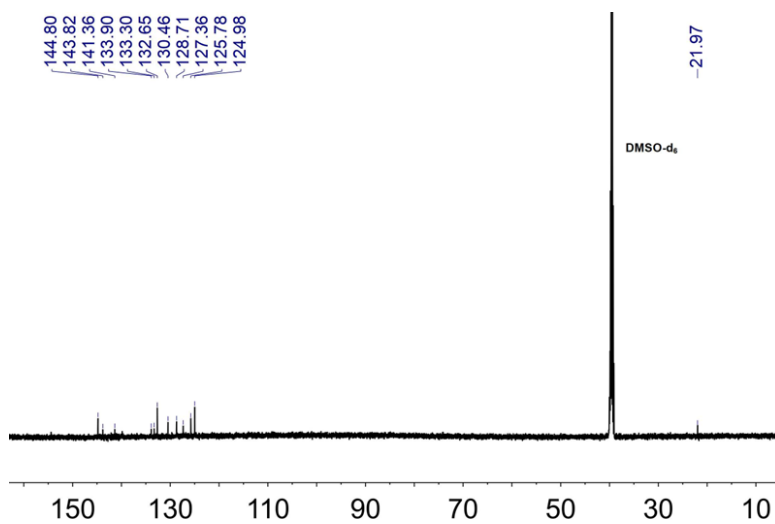
**Figure S46** The  $^{13}\text{C}$  NMR spectrum of compound **1-4** (600 MHz,  $\text{D}_2\text{O}$  and  $\text{DMSO-d}_6$ , 298 k).



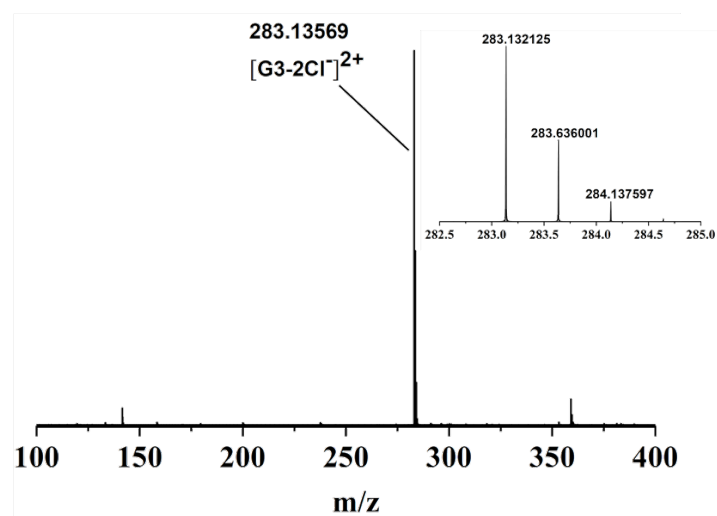
**Figure S47** HRMS (ESI) spectra of compound **1-4**.



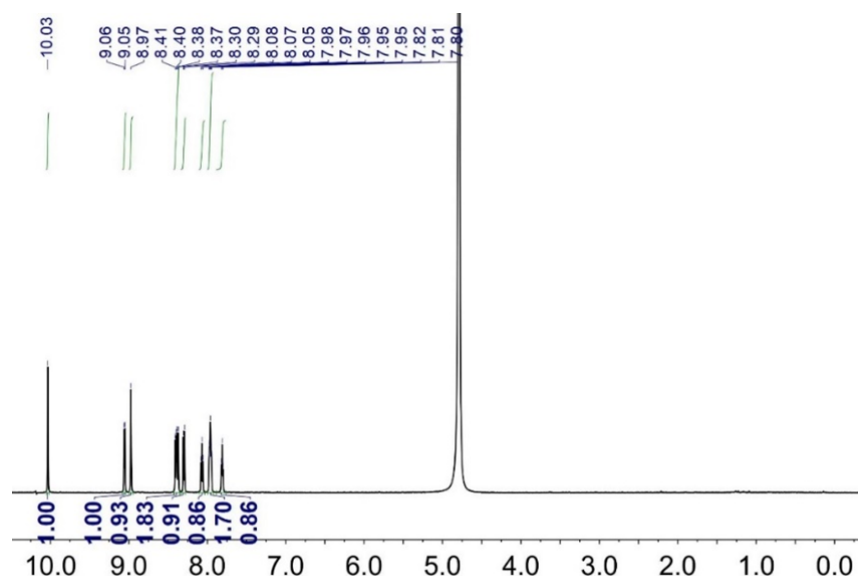
**Figure S48** The  $^1\text{H}$  NMR spectrum of compound **G3** (600 MHz,  $\text{D}_2\text{O}$ , 298 k).



**Figure S49** The  $^{13}\text{C}$  NMR spectrum of compound **G3** (600 MHz,  $\text{D}_2\text{O}$  and  $\text{DMSO-d}_6$ , 298 k).



**Figure S50** HRMS (ESI) spectra of compound **G3**.



**Figure S51** The  $^1\text{H}$  NMR spectrum of compound **G4** (600 MHz,  $\text{D}_2\text{O}$ , 298 k).

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- 5 C. K. Bradsher, L. E. Beavers, Aromatic Cyclodehydration. XXX. Acridizinium Salts<sup>1</sup>, *J. Am. Chem. Soc.*, 1955, **77**, 4812-4813.
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