Supporting Information

CB[10]-Driven Self-Assembly of Homotrimer from Symmetric Organic Dye: Tunable Multicolor Fluorescence and Higher Solid-State Stability Than CB[8]-Included Homodimer

Le-Ping Zhang [a], Chuan-Zhi Liu [b], Ming Liu [c], Shuai Lu [d], Shang-Bo Yu [e], Qiao-Yan Qi [e], Guan-Yu Yang [a], Xiaopeng Li [d], Bo Yang [a]*, Zhan-Ting Li [e,f]*

[a] College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

[b] School of Chemistry and Chemical Engineering, Henan Engineering Laboratory of Green Synthesis for Pharmaceuticals, Shangqiu Normal University, Shangqiu 476000, China

[c] School of Chemistry and Chemical Engineering, Guizhou University, Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Department of Chemistry, Guiyang 550025, China

[d] College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518055, China

[e] Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

[f] Department of Chemistry, Fudan University, 2205 Songhu Road, Shanghai 200438, China

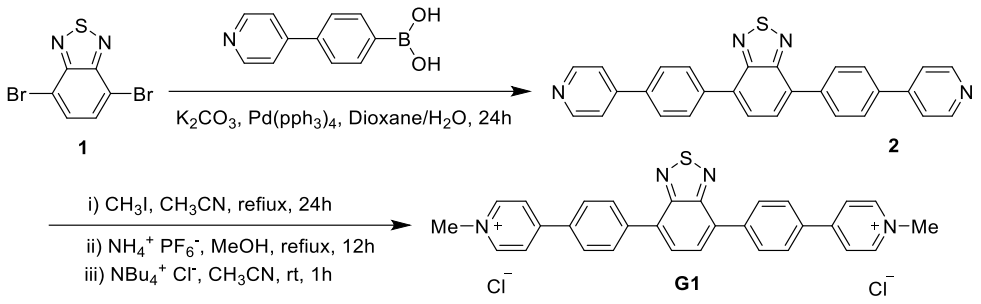
Experimental Methods

Materials and methods. All reagents were purchased from supplier and used without further purification. Column chromatography was performed on silica gel (200-300 mesh), and thin-layer chromatography (TLC) was performed on precoated silica gel plates (0.2 ± 0.03 mm thick). The molecular structures were confirmed using ^{1}H NMR, ^{13}C NMR and high-resolution ESI mass spectroscopy. ^{1}H, ^{13}C NMR, 2D NOESY and COSY spectra were recorded on 400 MHz spectrometers. 2D DOSY spectra were measured on 600 MHz spectrometer. The experiments were performed in the indicated solvents at room temperature (298 K). UV-Vis absorption spectra were performed on a UV-2600i (1 cm quartz cell was used). Fluorescence spectra were recorded on a RF-6000 (Excitation slit = 5 nm, Emission slit = 5 nm). Lifetime were recorded on a FLS980 (Excitation slit = 5 nm; Emission slit = 5 nm; Delay time = 0.0 ms; Gate time = 4 ms). Confocal luminescence imaging was carried out on a Leica SP8 confocal microscope.

Density functional theory (DFT). DFT calculations were using DMol3 code in Materials Studio software 7.0 (Accelrys Inc.). The exchange-correlation energy was calculated within the generalized gradient approximation (GGA) using PBE functional. As the PBE energy functional cannot describe the van der Waals dispersion interactions, a Grimme custom method for DFT-D correction was employed for the calculation of molecular adsorption. The valence electron functions were expanded into a set of numerical atomic orbitals by a double numerical basis with polarization functions (DNP), All-electron core treatment. The convergence criteria of energy, displacement and gradient were 1×10^{-5} Ha, 5×10^{-3} Å and 2×10^{-3} Ha/Å. The effect of the bulk solvent was investigated using the conductor-like screening model (COSMO) as implemented in Dmol3. This is a dielectric continuum solvation model in which the mutual polarization of the solute and solvent is represented by screening charges on the surface of the solute cavity. These charges are derived under the simplified boundary condition that the electrostatic potential vanishes for a conductor ($\varepsilon = 0$), and the charges are scaled to account for the finite dielectric permittivity of a real solvent. In this case, bulk water solvent is represented by a dielectric permittivity $\varepsilon = 78.54$.

Cell imaging. B16 cells were cultured in RPMI-1640 medium containing 10% FBS and 1% penicillin/streptomycin at 37°C, in 5% CO_2. The B16 cells were incubated with the **G1** (20 μM), **G1**⊂(CB[7])$_2$ ([**G1**] = 20 μM), (**G1**)$_2$⊂(CB[8])$_2$ ([**G1**] = 20 μM), and (**G1**)$_2$⊂(CB[10])$_3$ ([**G1**] = 20 μM) for 24 h at 37 ºC. Then the cells were washed with PBS (phosphate buffer saline) for three times, cells were fixed with 4% paraformaldehyde for 20min and transferred into Cell Imaging System (Leica SP8) for confocal luminescence imaging.

Synthesis Procedures



Synthesis of compound 2. A mixture of compound **1** (100 mg, 0.34 mmol), K_2CO_3 (242 mg, 1.75 mmol), $Pd(PPh_3)_4$ (40 mg), and 4-(4-Pyridyl)phenylboronic Acid (203 mg, 1.02 mmol) in the mixed solution of 1,4-dioxane/water (12 mL, 2:1), was heated to 100 °C under nitrogen for 24h. After falling to room temperature, 1,4-dioxane and water were removed by rotary evaporation. The solid is dissolved in dichloromethane. it was purified by column (dichloromethane/methanol = 100:1) to obtain yellow solid compound **2** (yield 40%). M.p. > 285 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, 4H), 8.14 (d, 4H), 7.90 (s, 2H), 7.86 (d, 4H), 7.63 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.02, 150.28, 147.85, 138.10, 138.07, 132.85, 130.00, 128.20, 127.33, 121.61. $[M+H]^+$ calcd for $C_{18}H_{18}N_4S$, 443.1317; found, 443.1340

synthesis of compound G1. A mixture of Compound 2 (330mg) and Methyl iodide (2ml) in CH_3CN (8ml) was stirred at 100 ° C for 24 hours. After falling to room temperature, acetonitrile were removed by rotary evaporation to obtain a yellowish solid. To the mixture was added MeOH (20ml) and a saturated aqueous solution of ammonium hexafluorophosphate was stirred at 80 ° C for 12 hours. The precipitate was filtrated and then dissolved in CH_3CN. To the solution was added dropwise saturated aqueous solution of tetrabutylammonium chloride. The precipitate was filtrated, washed with CH_3CN, and dried under vacuum to afford a yellowish solid compound **G1** (yield 65%). M.p. > 278 °C (decomp).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, 4H), 8.03 (d, 4H), 7.69 (d, 4H), 7.52 (m, 6H), 4.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.04, 153.69, 146.17, 140.53, 133.79, 132.12, 130.76, 129.47, 128.84, 124.55. $[M+H]^+$ calcd for $[C_{30}H_{24}N_4S]^{2+}$, 236.0855. Found, 236.0878.

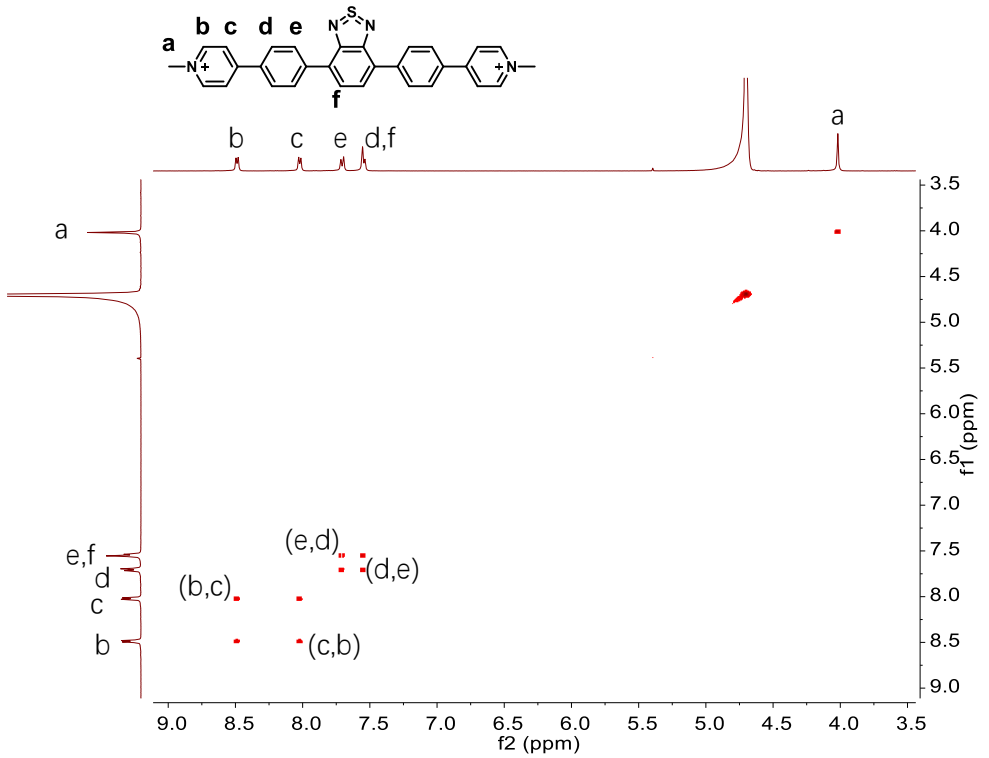


Figure S1. 2D ^{1}H–^{1}H COSY NMR spectrum (400 MHz, D_2O, 298 K) of **G1**.

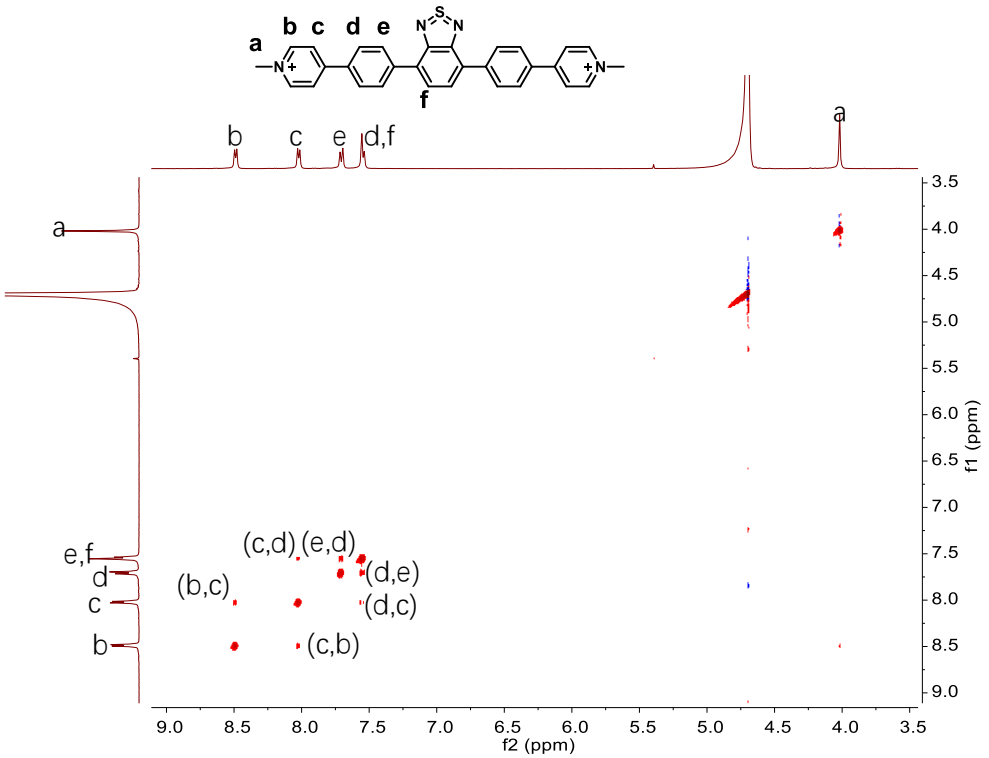


Figure S2. 2D ^{1}H–^{1}H NOESY NMR spectrum (400 MHz, D_2O, 298 K) of **G1**.

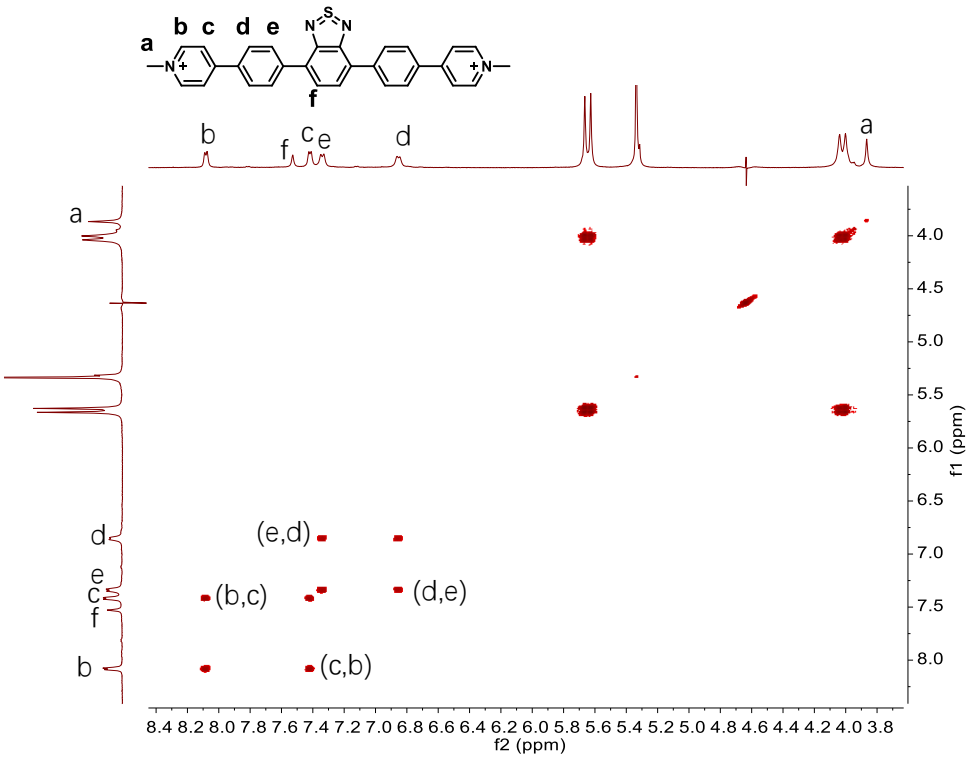


Figure S3. 2D ^{1}H–^{1}H COSY NMR spectrum (400 MHz, D_2O, 298 K) of (**G1**)$_3$⊂(CB[10])$_2$.

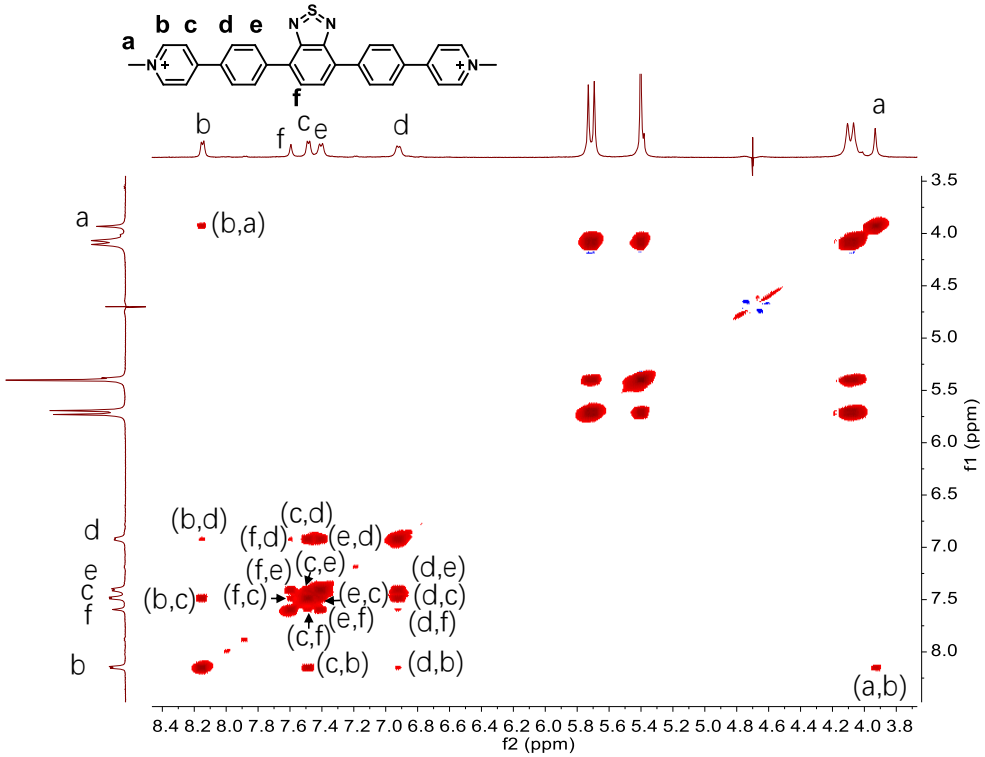


Figure S4. Annotated 2D ^{1}H–^{1}H NOESY NMR spectrum (400 MHz, D_2O, 298 K) of (**G1**)$_3$⊂(CB[10])$_2$.

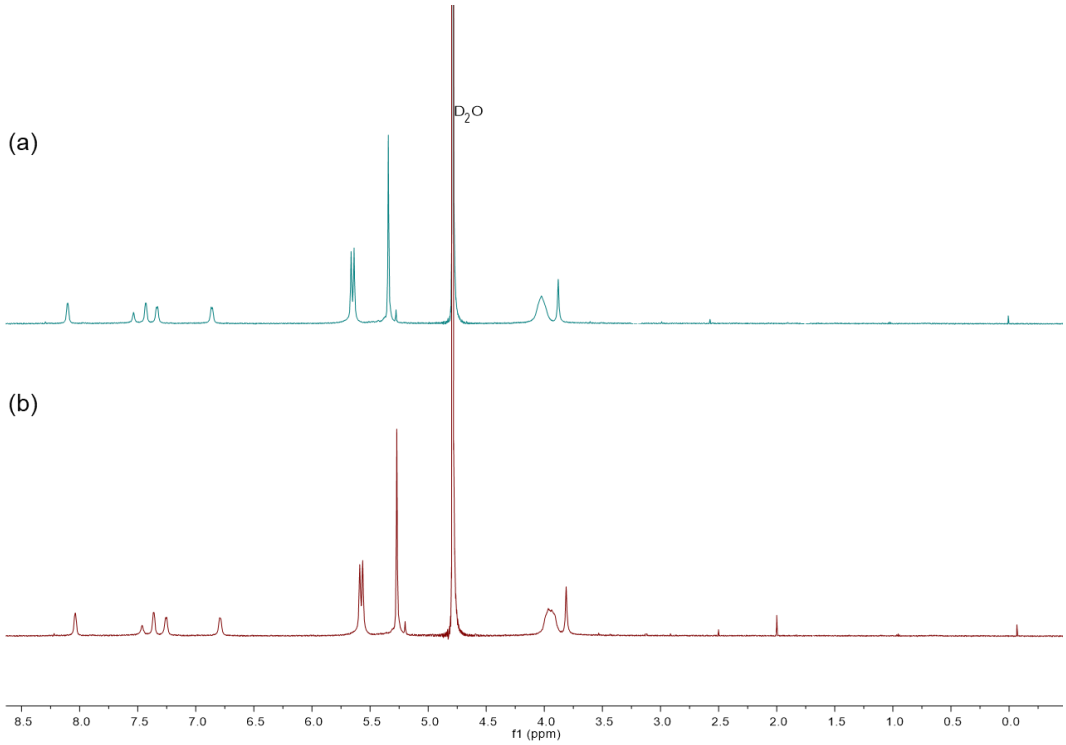


Figure S5. ^{1}H NMR spectra (600 MHz) of the mixture of **G1** (1.0 mM) and CB[10] (0.67 mM) in D_2O at 10 °C (a) and 4 °C (b).

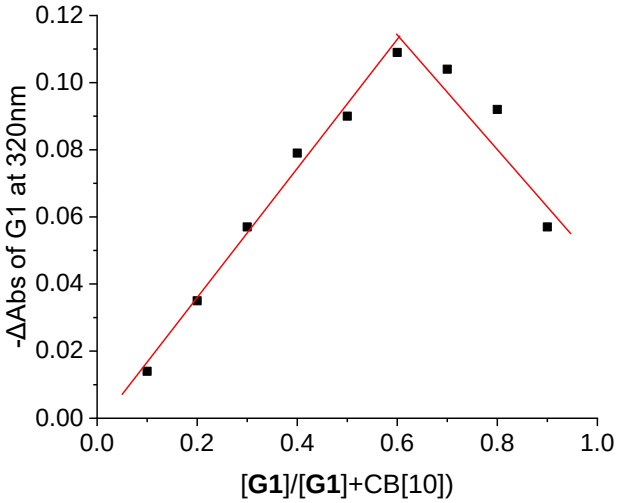


Figure S6. Job's plot obtained from UV-vis absorption spectroscopy (25 °C), which support the 3:2 stoichiometry of the complex formed by **G1** and CB[10]. [**G1**] + [CB[10]] = 0.01 mM.

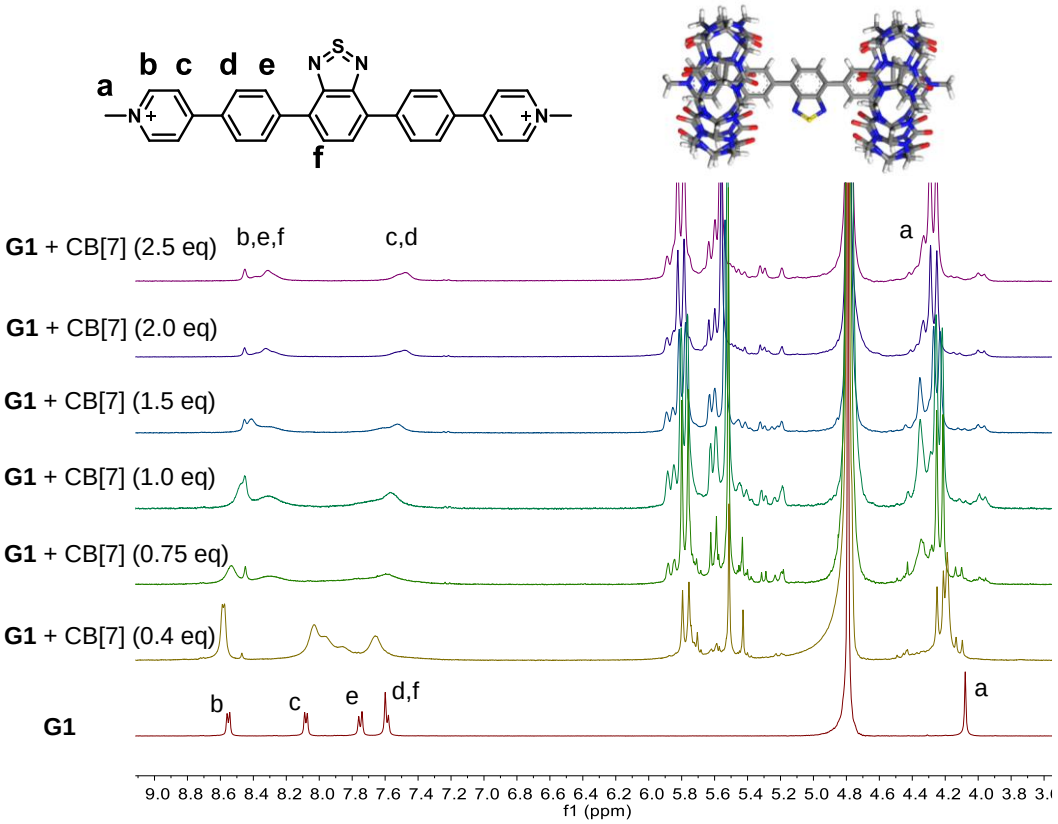


Figure S7. [1]H NMR spectra (400 MHz) of the mixture of **G1** (1.0 mM) and CB[7] (0 to 2.5 equiv.).

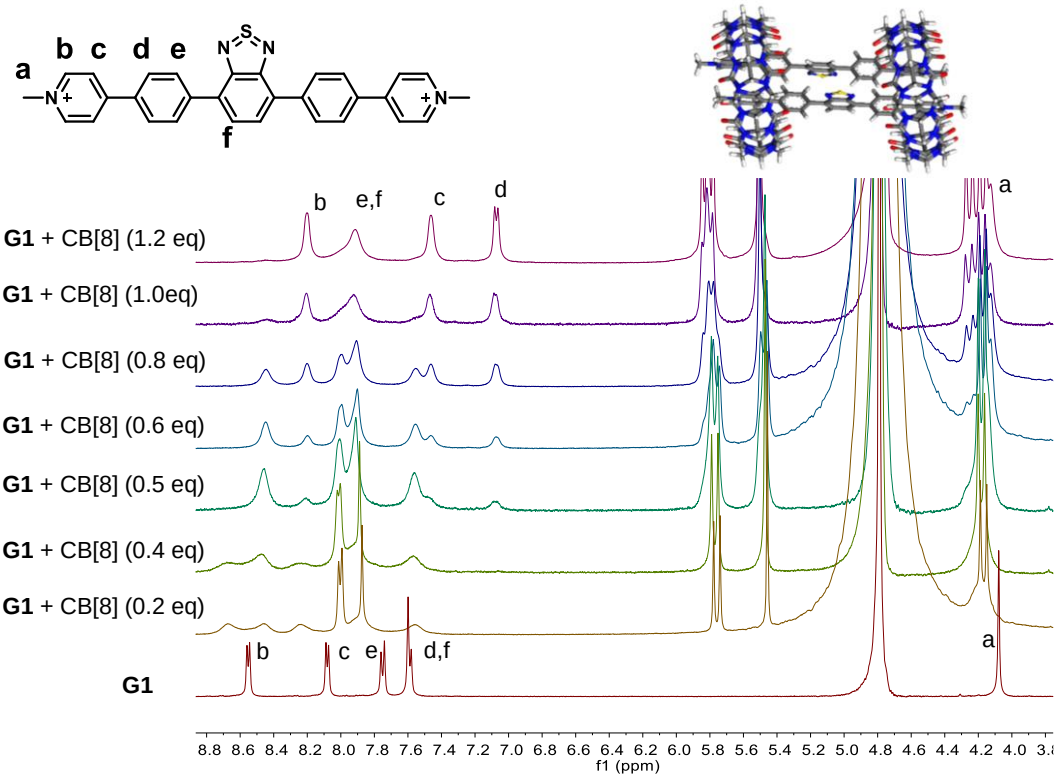


Figure S8. [1]H NMR spectra (400 MHz) of the mixture of **G1** (1.0 mM) and CB[8] (0 to 1.2 equiv.).

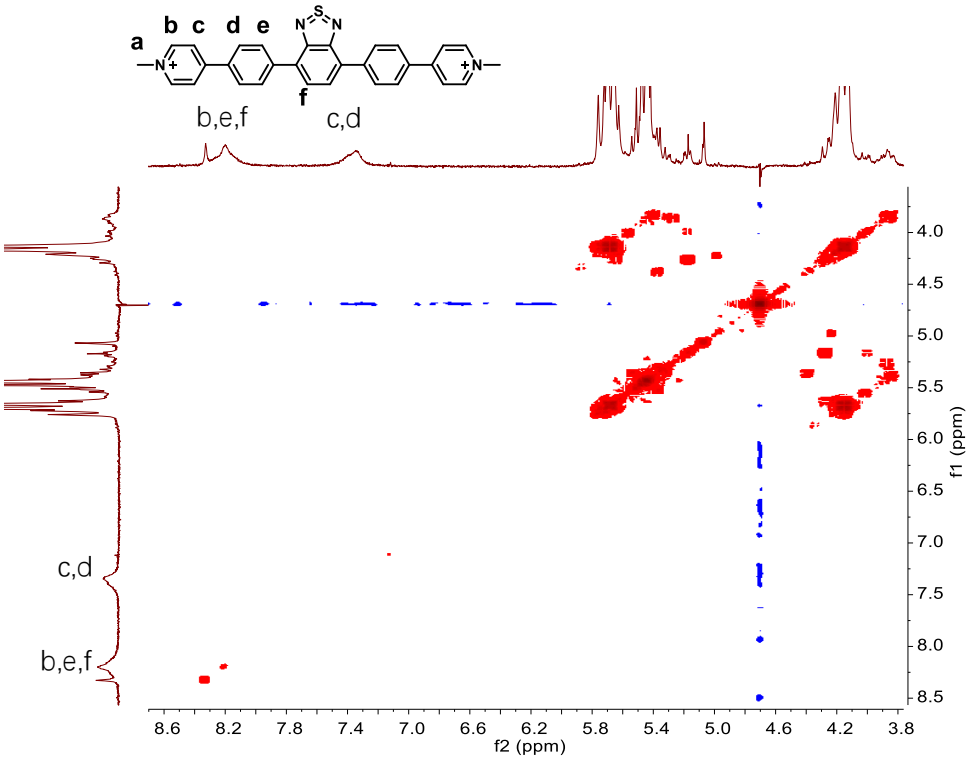


Figure S9. 2D ^{1}H–^{1}H COSY NMR spectrum (400 MHz, D_2O, 298 K) of **G1**⊂(CB[7])$_2$.

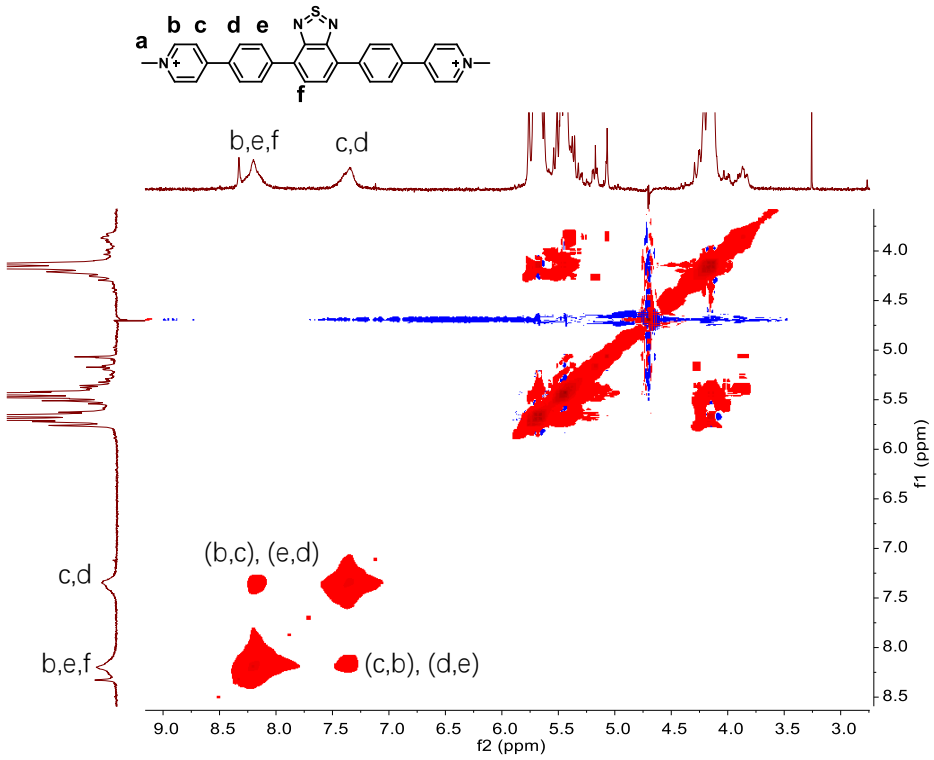


Figure S10. 2D ^{1}H–^{1}H NOESY NMR spectrum (400 MHz, D_2O, 298 K) of **G1**⊂(CB[7])$_2$.

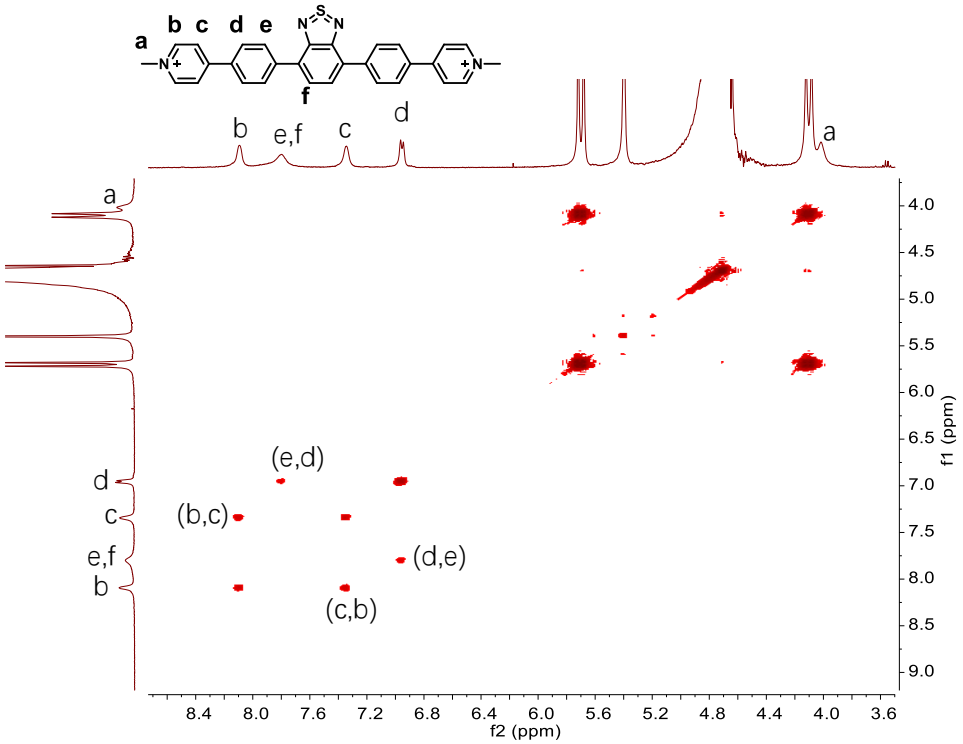


Figure S11. 2D ^{1}H–^{1}H COSY NMR spectrum (400 MHz, D_2O, 298 K) of (**G1**)$_2$⊂(CB[8])$_2$.

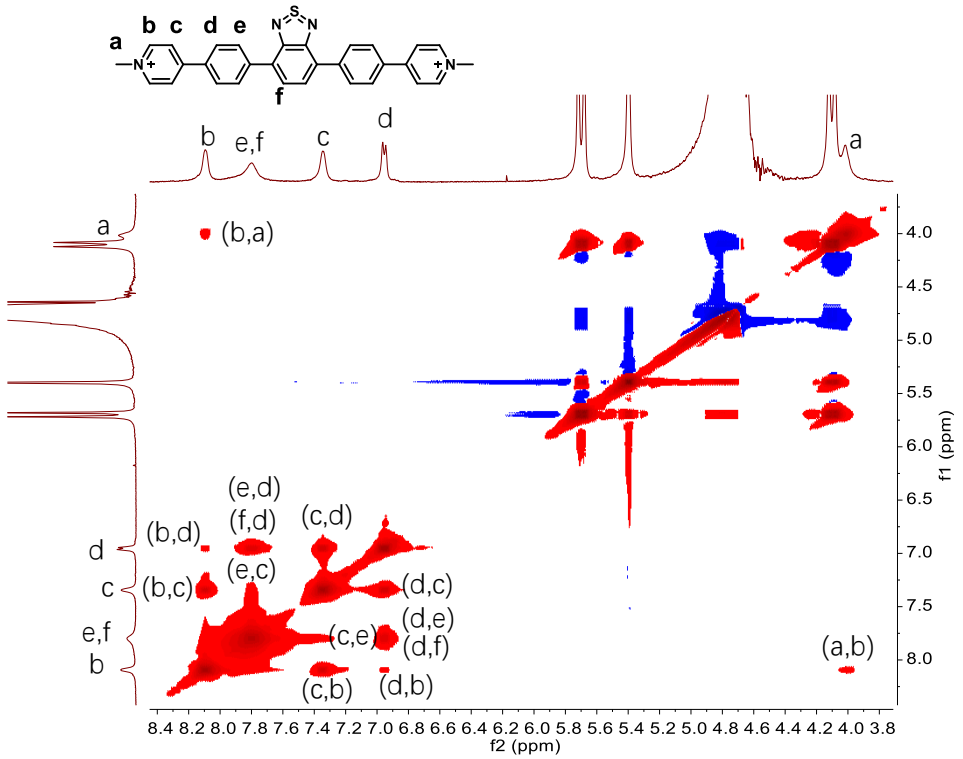


Figure S12. 2D ^{1}H–^{1}H NOESY NMR spectrum (400 MHz, D_2O, 298 K) of (**G1**)$_2$⊂(CB[8])$_2$.

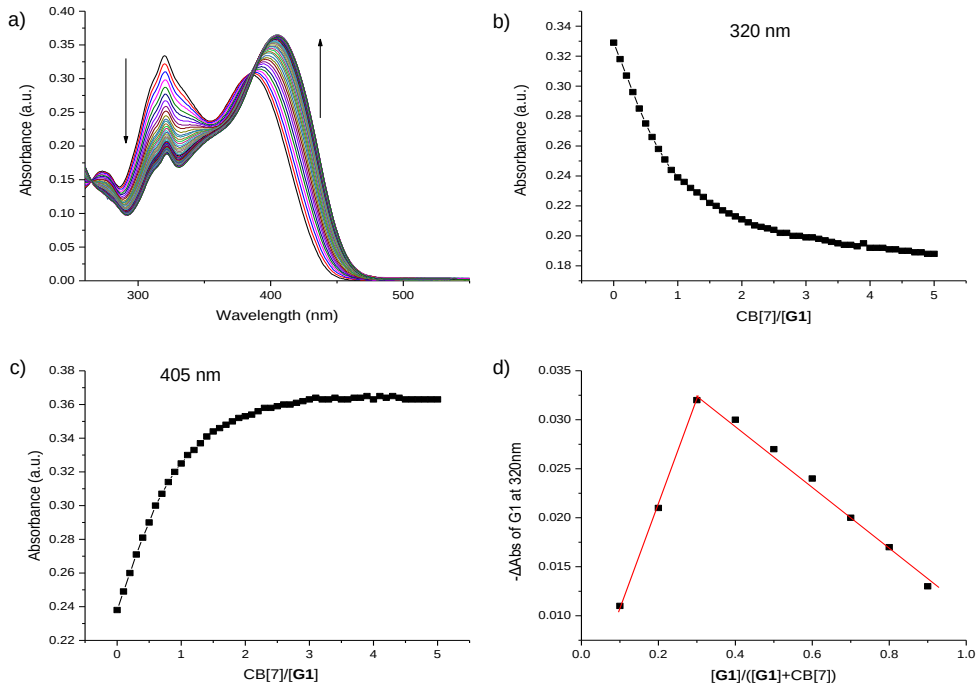


Figure S13. a) UV-vis spectroscopy of **G1** (10 μM) with the addition of CB[7] (0-5.0 equiv.) in water at 25 °C, b,c) the plot of the absorbance change at 320 nm and 405 nm, Job's plot indicated a stoichiometry of 1:2 of **G1** and CB[7]. [**G1**] + [CB[7]] = 0.01 mM, T = 296 K.

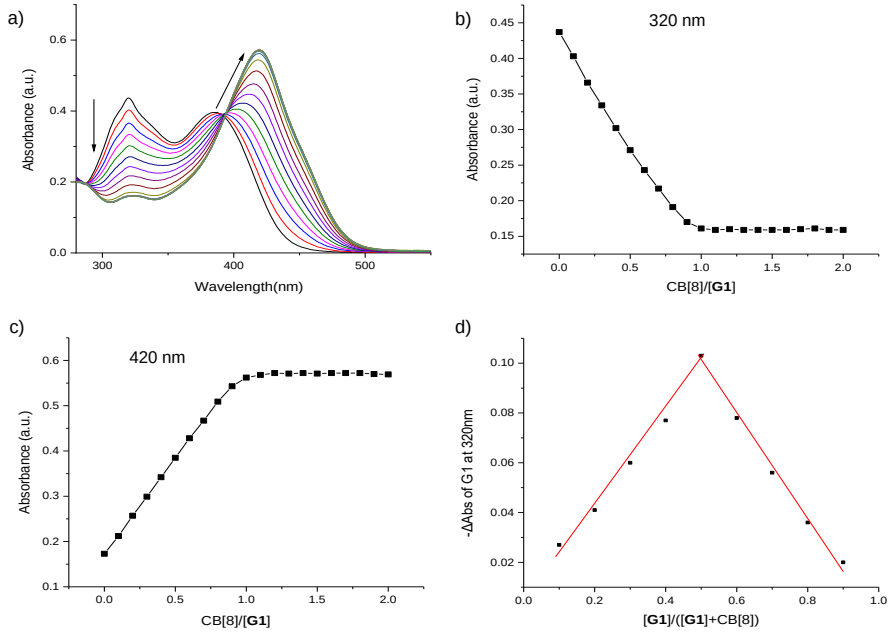


Figure S14. a) UV-vis spectroscopy of **G1** (10 μM) with the addition of CB[8] (0-2.0 equiv.) in water at 25 °C, b,c) the plot of the absorbance change at 320 nm and 420 nm, Job's plot indicated a stoichiometry of 1:1 of **G1** and CB[8]. [**G1**] + [CB[8]] = 0.01 mM, T = 298 K.

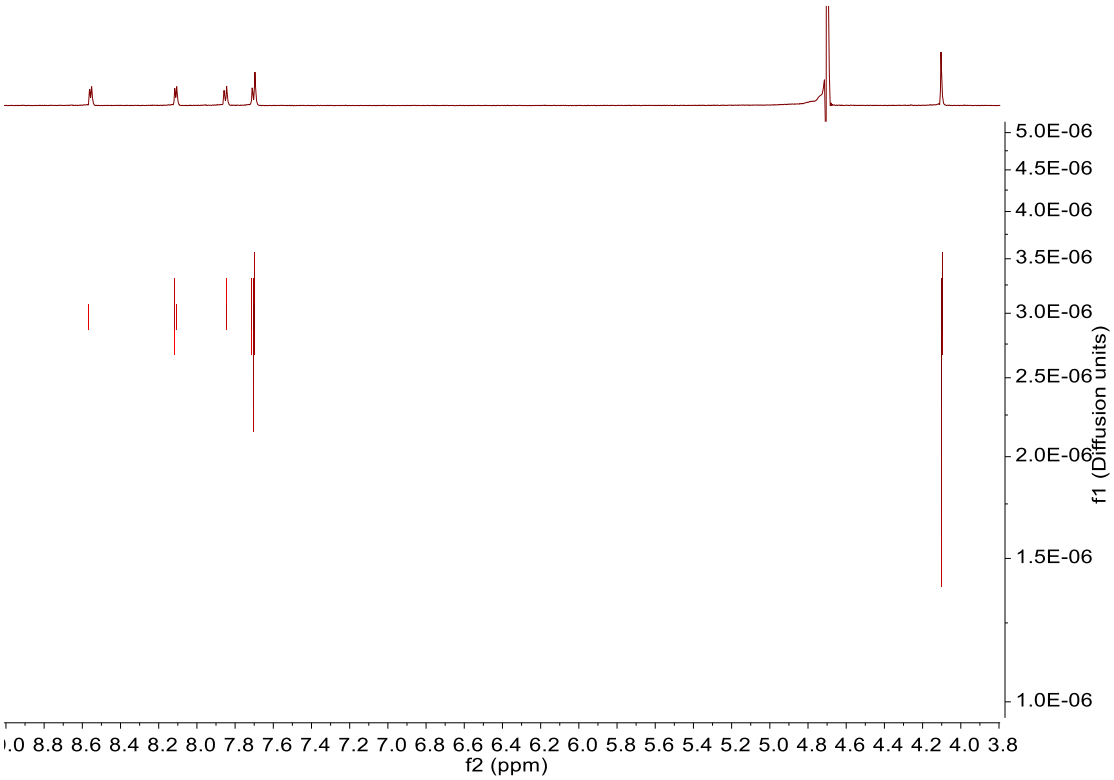


Figure S15. 2D diffusion-ordered NMR spectroscopy (DOSY) of **G1** (600 MHz, D_2O, 298 K).

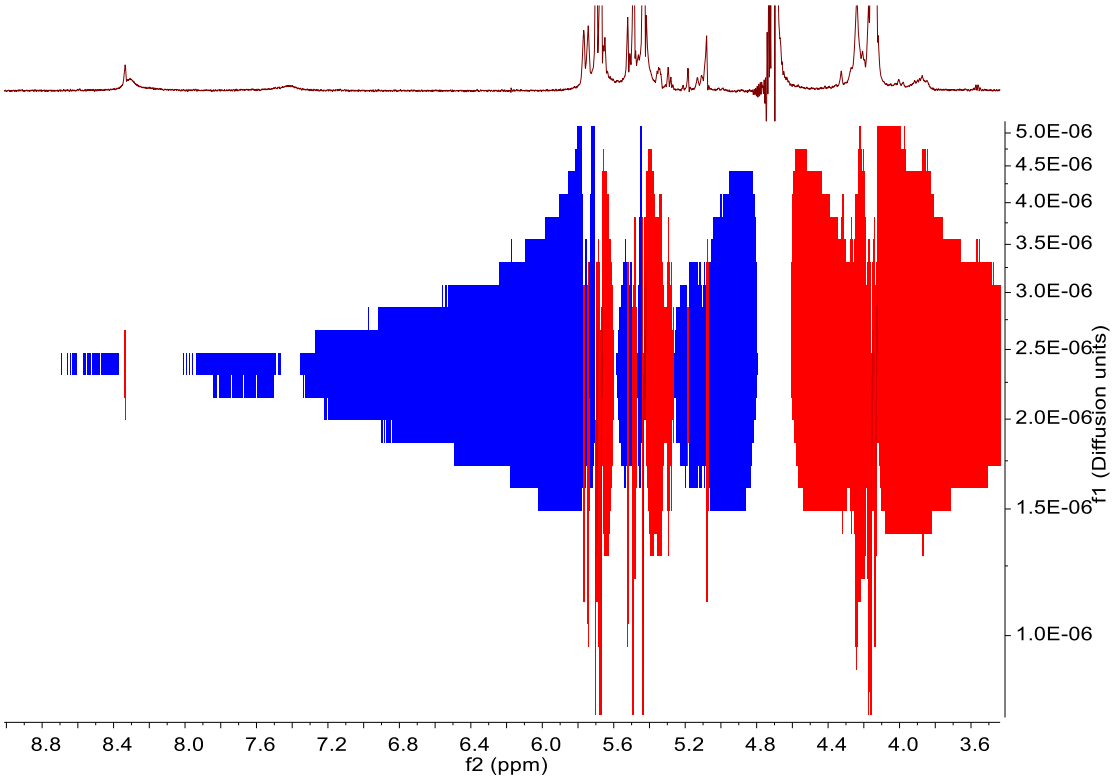


Figure S16. 2D diffusion-ordered NMR spectroscopy (DOSY) of **G1**⊂$(CB[7])_2$ (600 MHz, D_2O, 298 K).

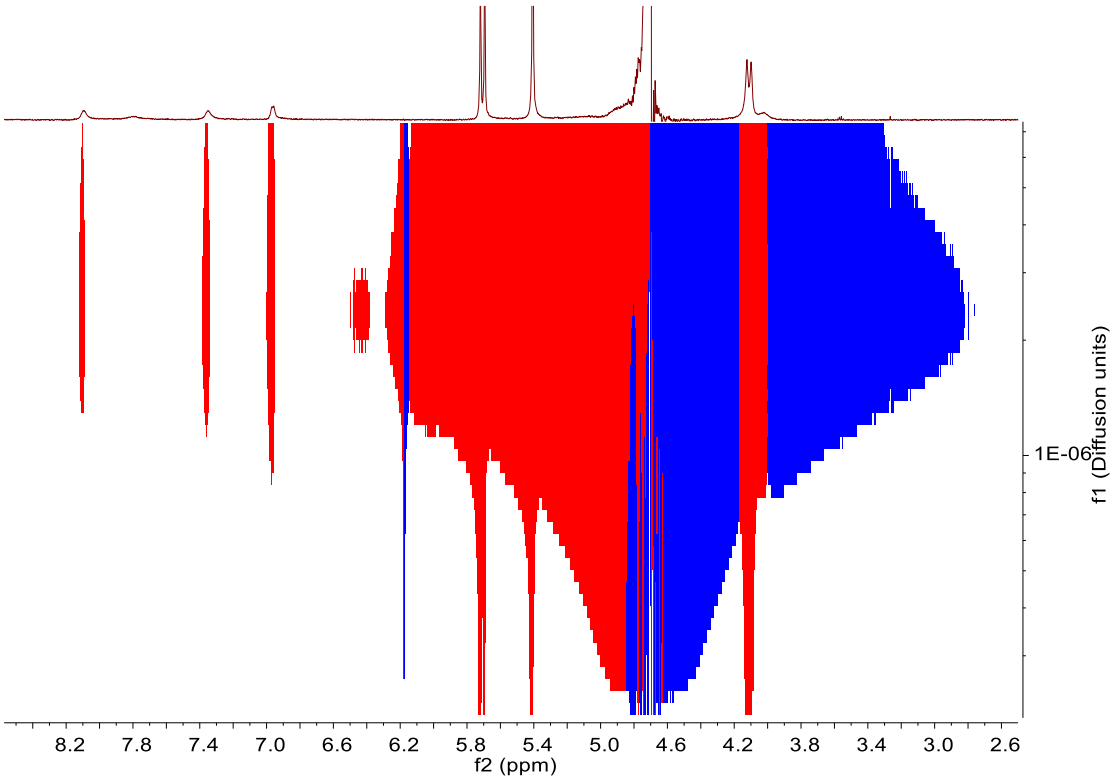


Figure S17. 2D diffusion-ordered NMR spectroscopy (DOSY) of (**G1**)$_2$⊂(CB[8])$_2$ (600 MHz, D_2O, 298 K).

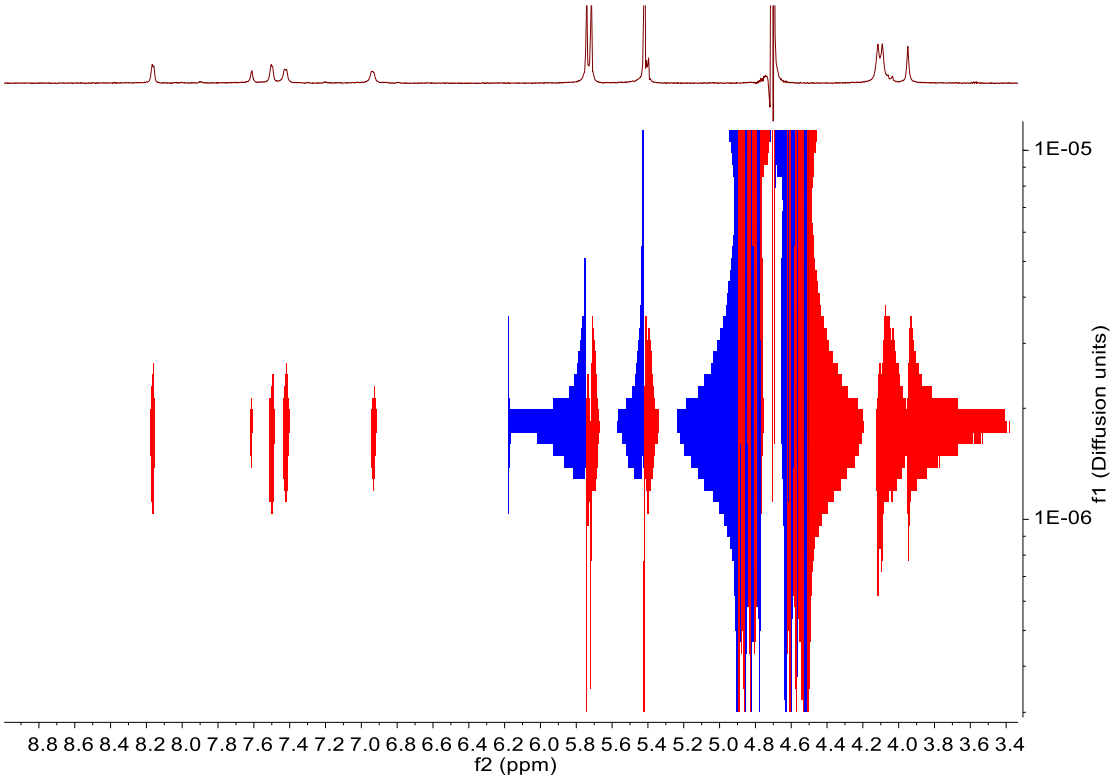


Figure S18. 2D diffusion-ordered NMR spectroscopy (DOSY) of (**G1**)$_3$⊂(CB[10])$_2$ (600 MHz, D_2O, 298 K).

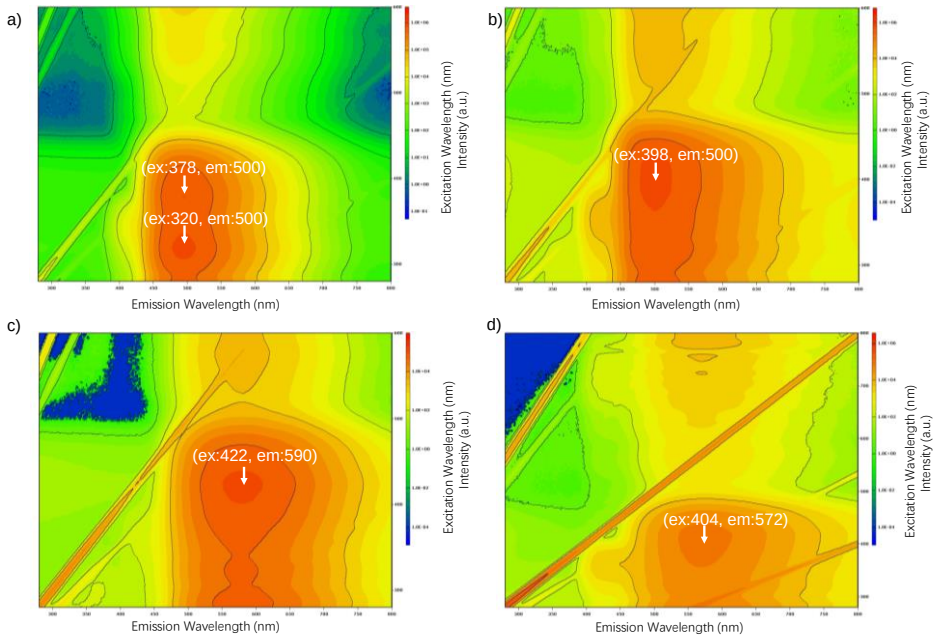


Figure S19. 2D fluorescence spectroscopy of (a) **G1**, (b) **G1**⊂(CB[7])$_2$, (c) (**G1**)$_2$⊂(CB[8])$_2$ and (d) (**G1**)$_3$⊂(CB[10])$_2$ in water ([**G1**] = 10 μM).

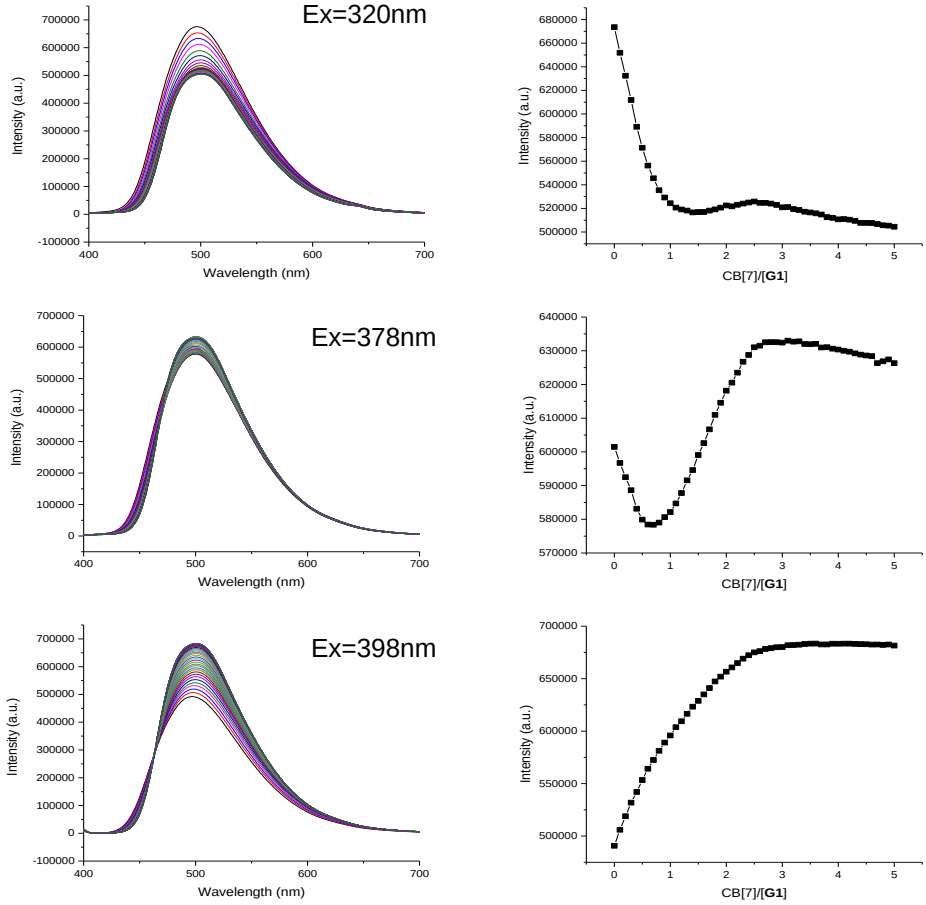


Figure S20. Fluorescence spectroscopy of **G1** (10 μM) with the addition of CB[7] (0-5.0 equiv.) in water at 298 K (λ_{ex} = 320, 378 and 398 nm).

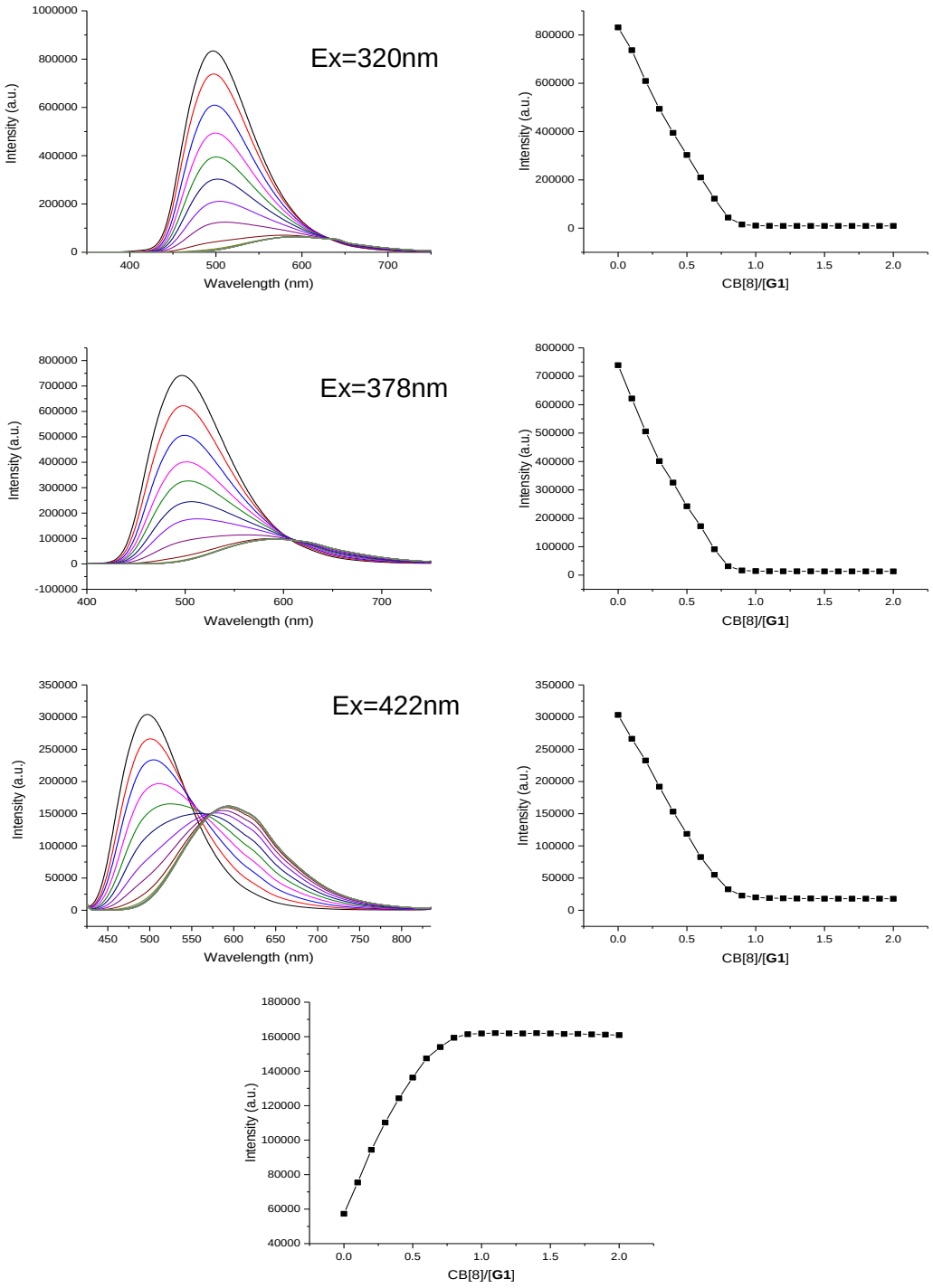


Figure S21. Fluorescence spectroscopy of **G1** (10 μM) with the addition of CB[8] (0-2.0 equiv.) in water at 298 K (λ_{ex} = 320, 378 and 422 nm).

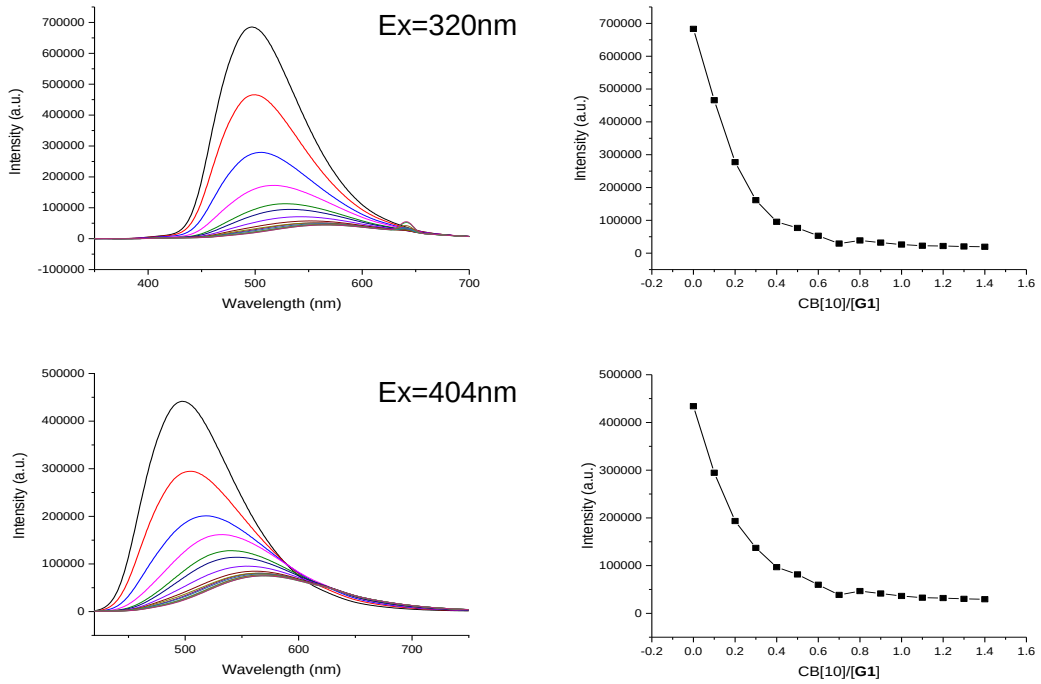


Figure S22. Fluorescence spectroscopy of **G1** (10 μM) with the addition of CB[10] (0-1.4 equiv.) in water at 298 K (λ_{ex} = 320, 404 nm).

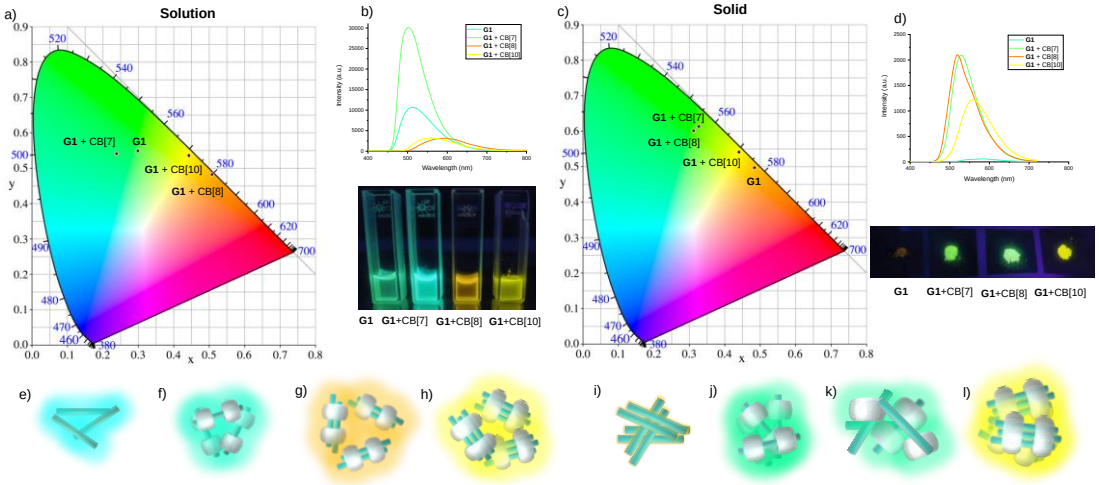


Figure S23. The fluorescence spectra of **G1**, **G1**⊂(CB[7])$_2$, (**G1**)$_2$⊂(CB[8])$_2$ and (**G1**)$_3$⊂(CB[10])$_2$ in solution (1.0 mM) (b) and solid state (d). The 1931 CIE chromaticity diagram illustrating the luminescent color changes of **G1**, **G1**⊂(CB[7])$_2$, (**G1**)$_2$⊂(CB[8])$_2$ and (**G1**)$_3$⊂(CB[10])$_2$ in solution (1.0 mM) (a) and solid state (c), corresponding to (b) and (d), respectively. The schematic Illustrations of **G1**, **G1**⊂(CB[7])$_2$, (**G1**)$_2$⊂(CB[8])$_2$ and (**G1**)$_3$⊂(CB[10])$_2$ in solution (e-h) and solid state (i-l).

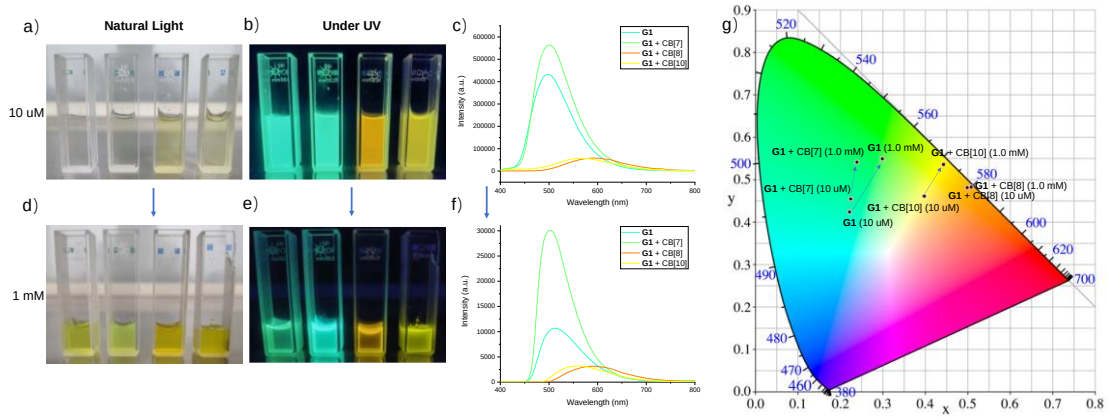


Figure S24. (a-b) The solution of **G1**, **G1**⊂(CB[7])$_2$, (**G1**)$_2$⊂(CB[8])$_2$ and (**G1**)$_3$⊂(CB[10])$_2$ under natural light and UV(365 nm) ([**G1**] = 10 μM). (c) Emission spectra ([**G1**] = 10 μM, λ_{ex} = 365 nm, H_2O, 298 K) of **G1**, **G1**⊂(CB[7])$_2$, (**G1**)$_2$⊂(CB[8])$_2$ and (**G1**)$_3$⊂(CB[10])$_2$. (d-e) The solution of **G1**, **G1**⊂(CB[7])$_2$, (**G1**)$_2$⊂(CB[8])$_2$ and (**G1**)$_3$⊂(CB[10])$_2$ under natural light and UV(365 nm) ([**G1**] = 1.0 mM). (f) Emission spectra ([**G1**] = 1.0 mM, λ_{ex} = 365 nm, H_2O, 298 K) of **G1**, **G1**⊂(CB[7])$_2$, (**G1**)$_2$⊂(CB[8])$_2$ and (**G1**)$_3$⊂(CB[10])$_2$. (g) Chromaticity coordinate (CIE) of **G1**, **G1**⊂(CB[7])$_2$, (**G1**)$_2$⊂(CB[8])$_2$ and (**G1**)$_3$⊂(CB[10])$_2$ in different concentration, corresponding to c) and f).

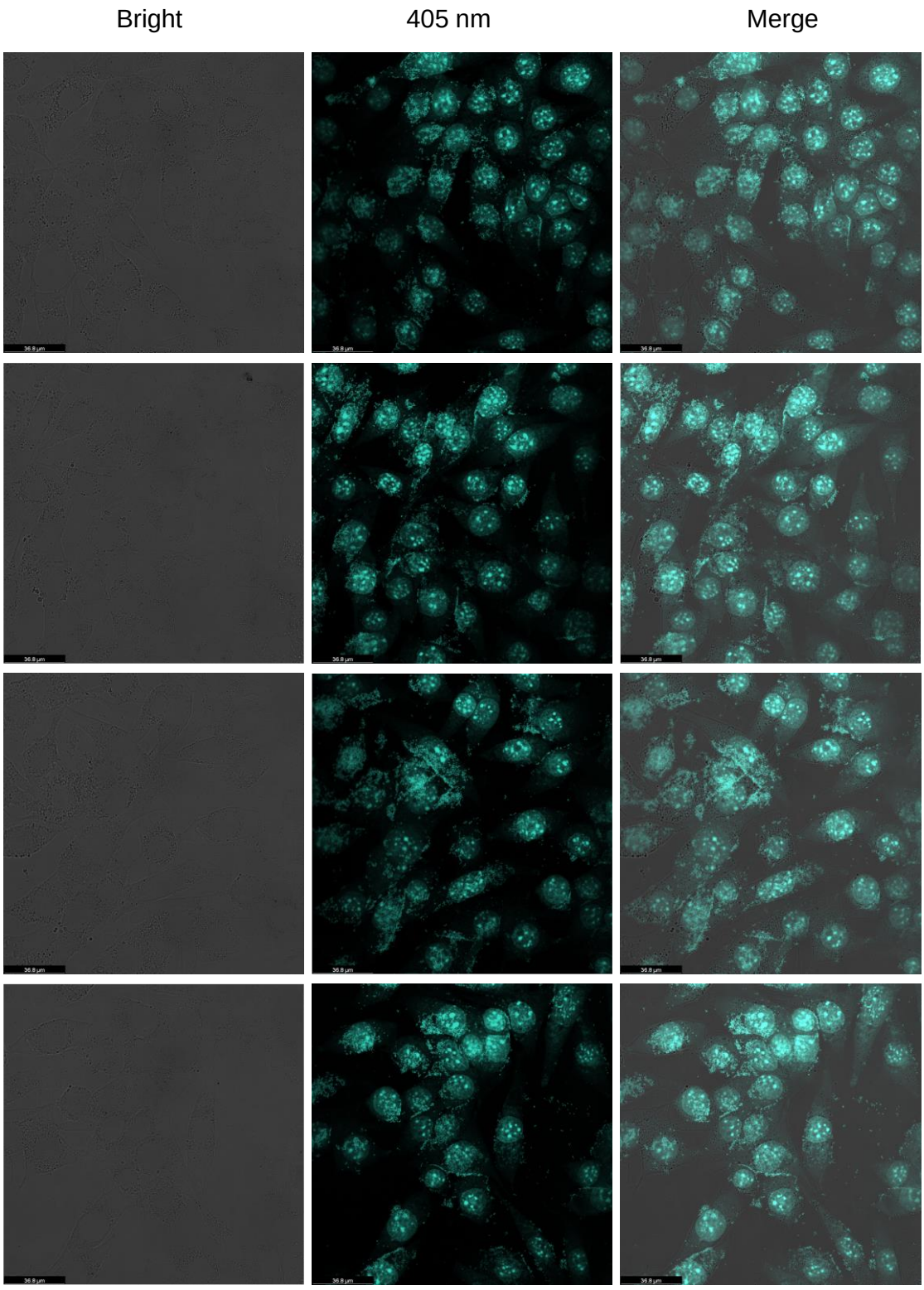


Figure S25. Bright field (left), **G1** (middle), and merge (right) confocal microscopic images of B16 cells.

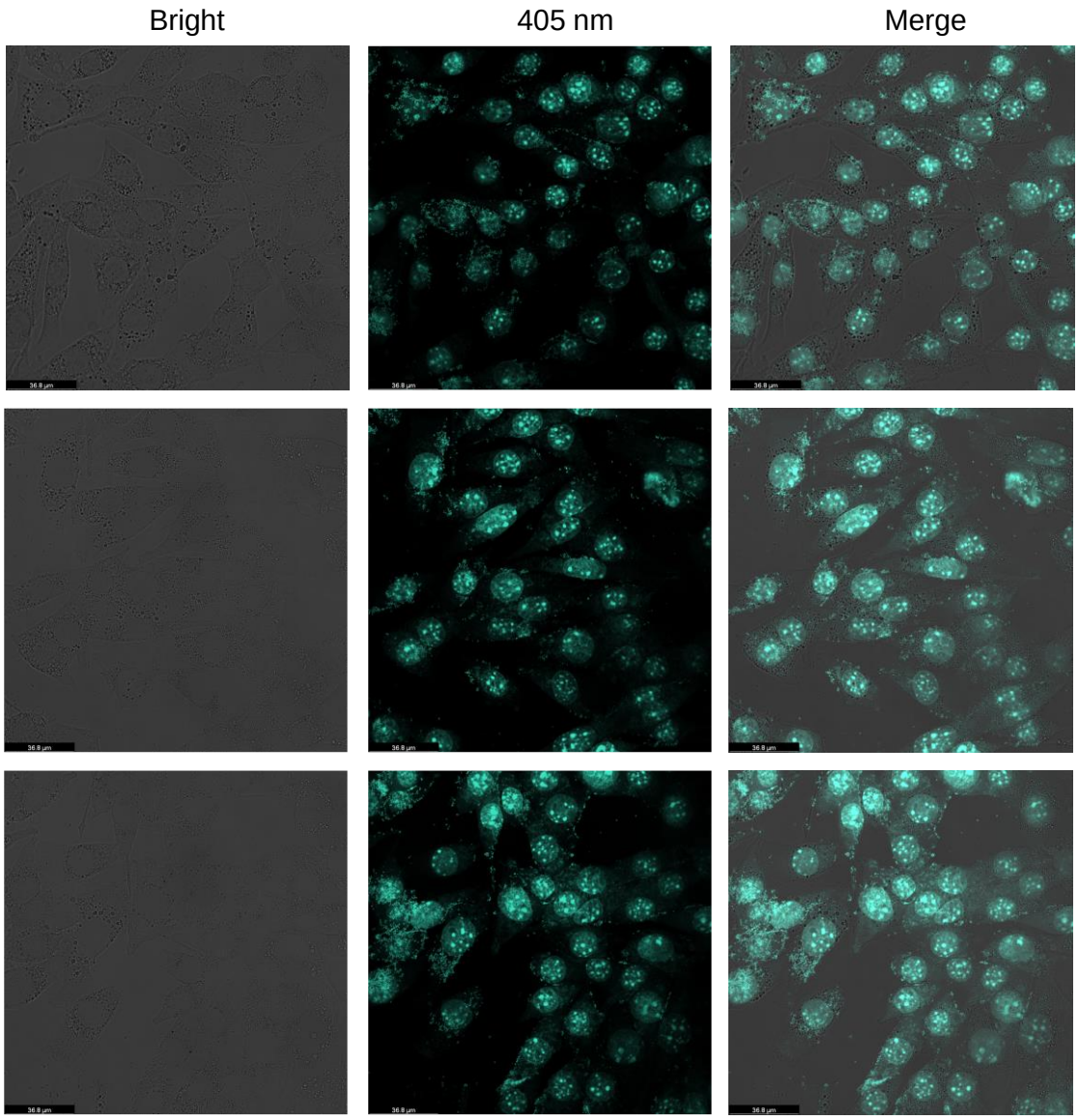


Figure S26. Bright field (left) of **G1**⊂(CB[7])$_2$ complex (middle), and merge (right) confocal microscopic images of B16 cells.

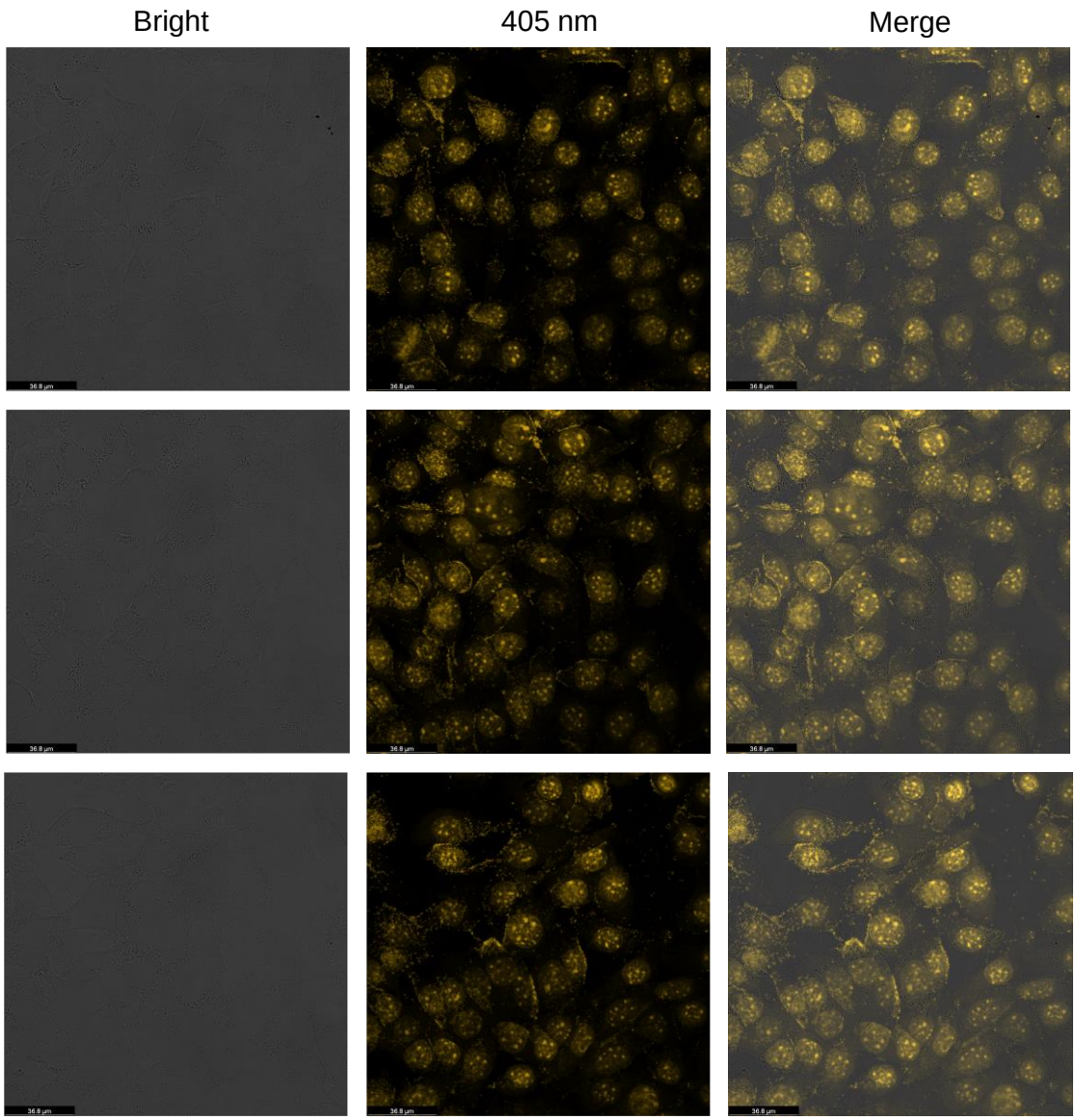


Figure S27. Bright field (left), $(\mathbf{G1})_2 \subset (CB[8])_2$ complex (middle), and merge (right) confocal microscopic images of B16 cells.

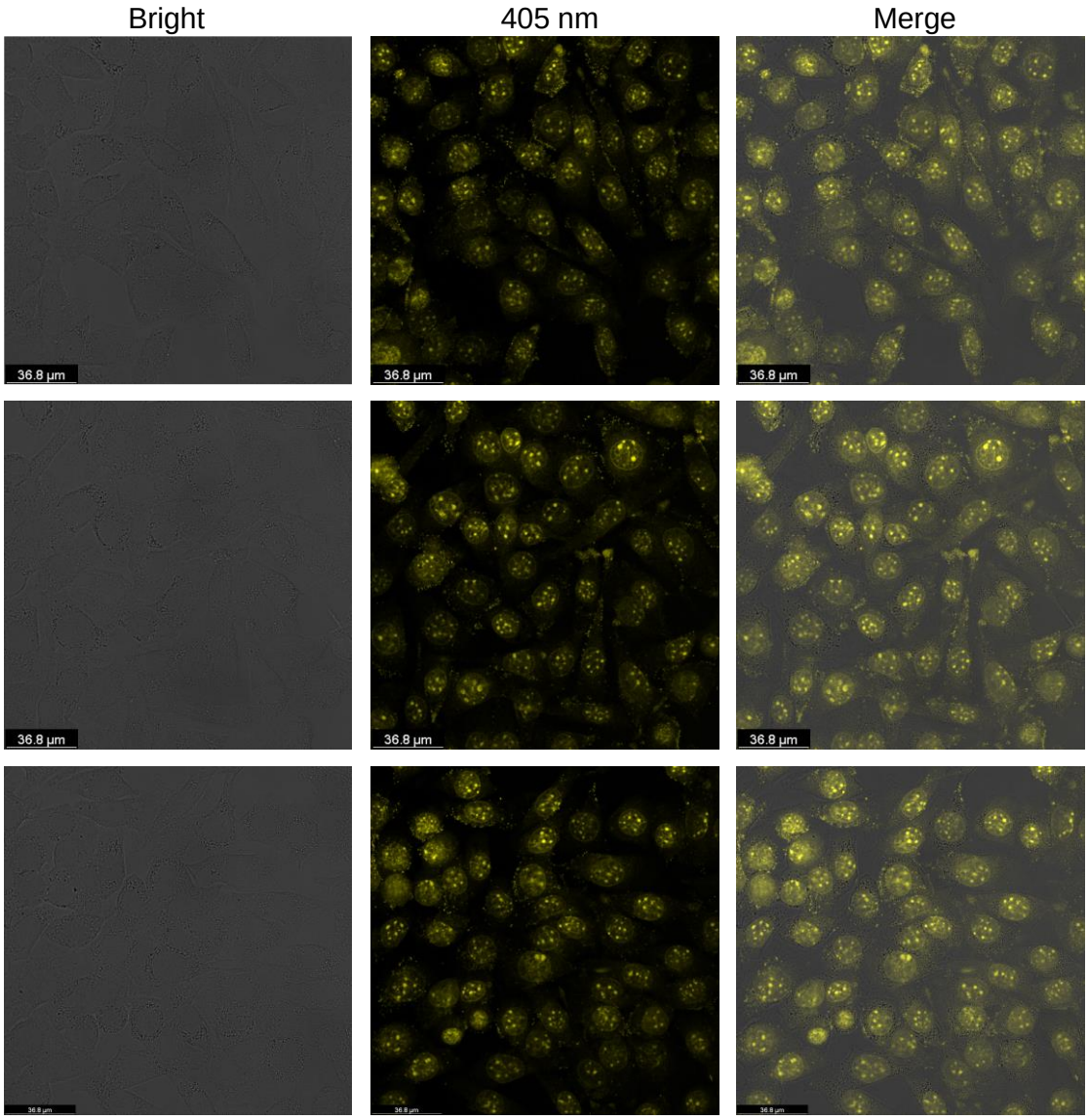


Figure S28. Bright field (left), $(\mathbf{G1})_3\subset(CB[10])_2$ complex (middle), and merge (right) confocal microscopic images of B16 cells.

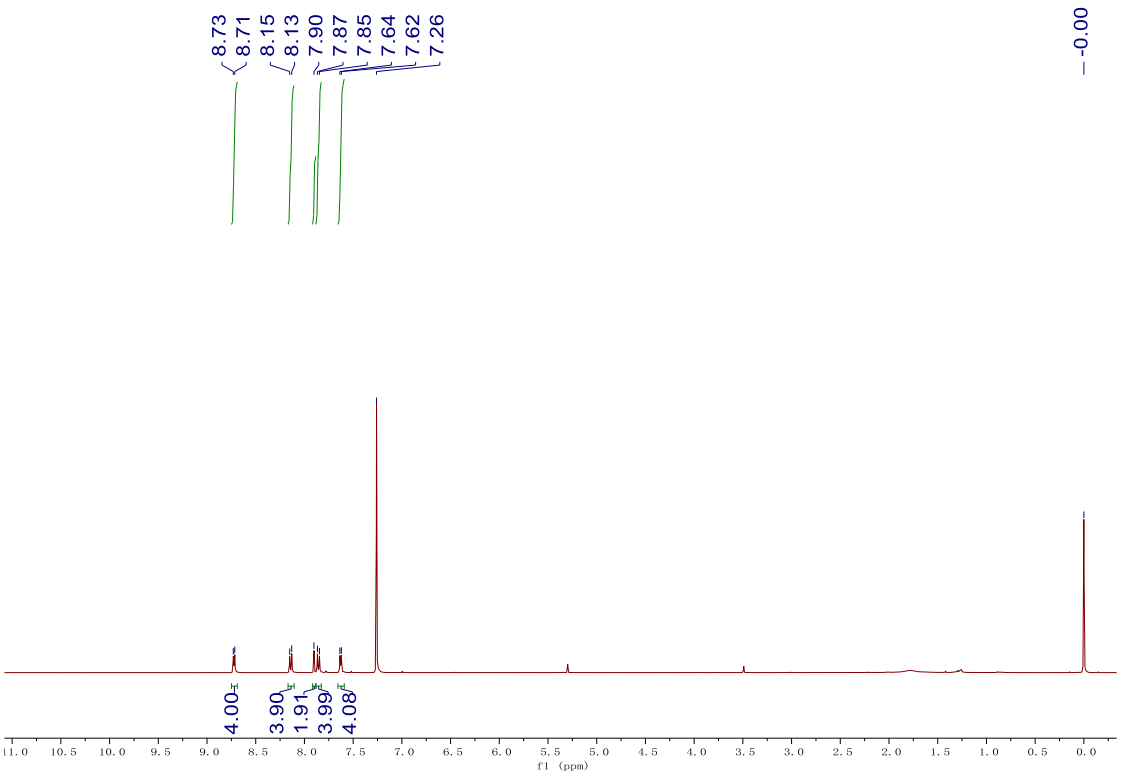


Figure S29. ^{1}H NMR spectrum (400 MHz) of compound **2** in $CDCl_3$

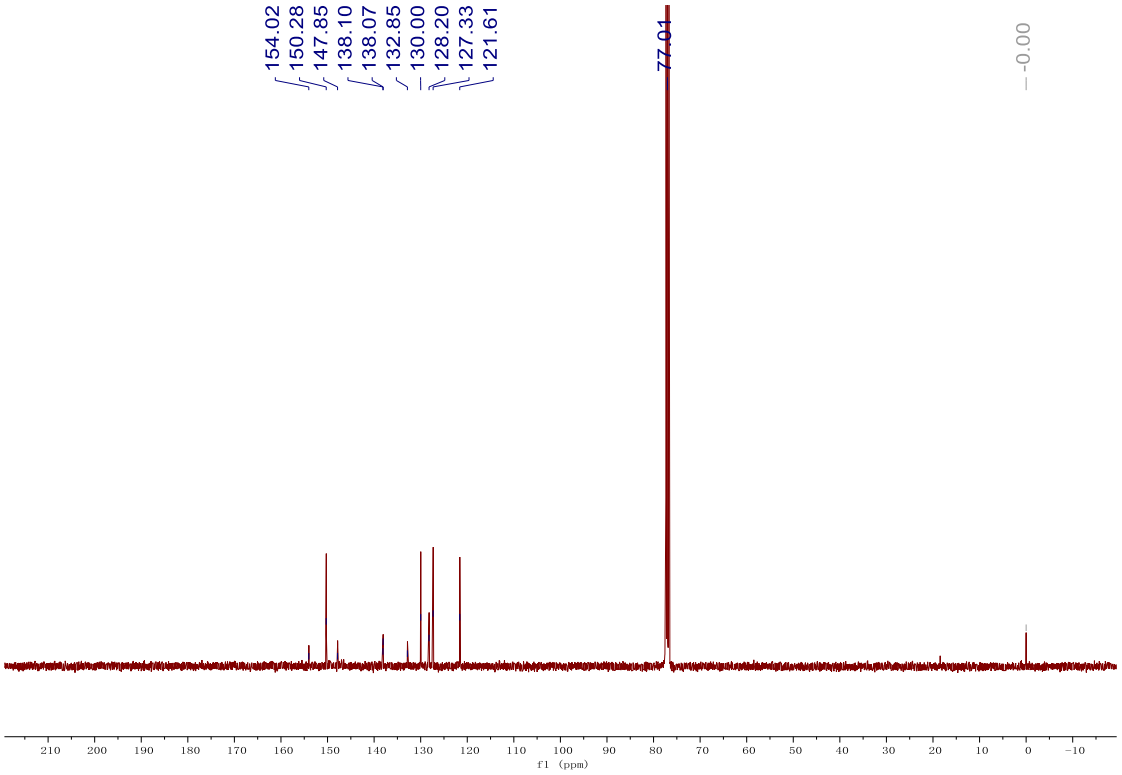


Figure S30. ^{13}C NMR spectrum (100 MHz) of compound **2** in $CDCl_3$.

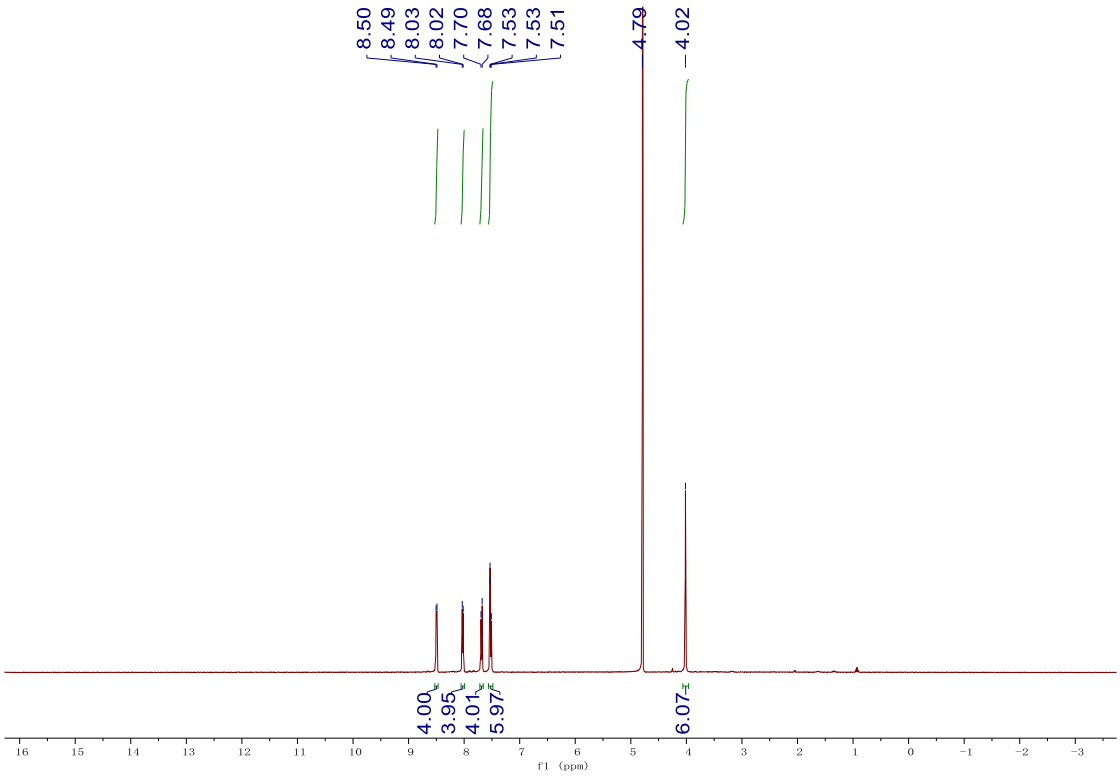


Figure S31. ^{1}H NMR spectrum (400 MHz) of compound **G1** in D_2O.

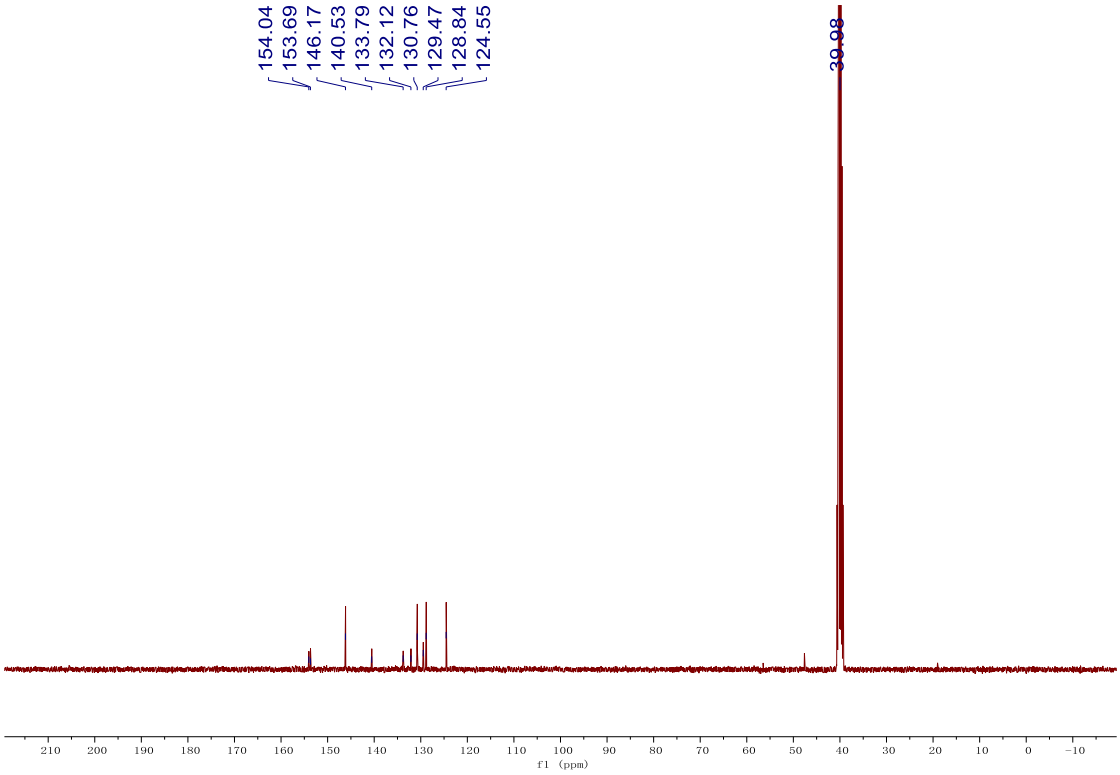
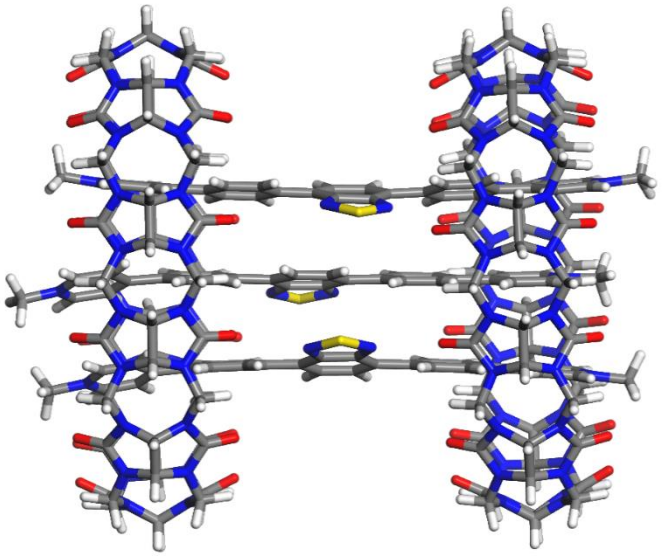


Figure S32. ^{13}C NMR spectrum (100 MHz) of compound **G1** in DMSO-d6.

Atomic coordinates of the minimized 3**G1**⊂2CB[10] complex:



537

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C	-37.40900	15.80300	25.13700
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H	-38.32100	15.99800	25.69600
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C	-37.28500	15.53600	29.48000
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C	-37.95600	15.70700	19.41500
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H	-41.40300	10.85600	29.92700
C	-41.65700	13.25200	30.67800
N	-37.76700	24.51600	33.61700
N	-39.85700	23.28100	33.57500
N	-41.07300	21.40700	33.62500
N	-41.80000	19.10500	33.66200
N	-41.93200	16.86000	33.71300
O	-39.75600	21.93400	35.48000
O	-40.89800	17.97600	35.49300
C	-39.11900	24.40700	34.11000
H	-39.66500	25.33300	33.87500
H	-39.06100	24.27500	35.19700
C	-40.17100	22.17800	34.34800
C	-41.88200	20.41000	34.28200
H	-42.93700	20.73500	34.28600
H	-41.51800	20.31800	35.31200
C	-41.47200	17.98200	34.40400
N	-37.71900	24.33700	31.16500
N	-39.86500	23.19700	31.11800
N	-41.10000	21.32600	31.17700
N	-41.89100	19.02300	31.21600
N	-42.15500	16.78400	31.27500
O	-39.83900	21.77900	29.26200
O	-41.46800	17.78400	29.27600

C	-39.04000	24.25500	30.57500
H	-39.55500	25.21700	30.71800
H	-38.91400	24.05500	29.50400
C	-40.21400	22.06700	30.39600
C	-41.95000	20.32200	30.56700
H	-42.99600	20.67800	30.56900
H	-41.60600	20.18700	29.53500
C	-41.79300	17.85700	30.45600
N	-37.87100	6.77900	34.42700
N	-39.97200	7.98500	34.24400
N	-41.13900	9.88500	34.11900
N	-41.82600	12.19600	33.95600
N	-41.93000	14.43900	33.82900
O	-39.95700	9.43200	36.07900
O	-40.99200	13.45400	35.73400
C	-39.24100	6.90000	34.86600
H	-39.76400	5.95300	34.66700
H	-39.22800	7.09300	35.94500
C	-40.30800	9.13300	34.93700
C	-41.95800	10.94100	34.66500
H	-43.01800	10.63300	34.65000
H	-41.63800	11.10300	35.70100
C	-41.51800	13.37200	34.62400
N	-35.53700	24.46400	33.64700
N	-33.38900	23.34000	33.80800
N	-32.13000	21.49400	33.94300
N	-31.33200	19.20500	34.11200
N	-31.15400	16.96400	34.24300
O	-33.44700	22.09000	35.78000
O	-32.04800	18.13000	36.06100
C	-34.22000	24.44300	34.24500
H	-33.70600	25.38900	34.01500
H	-34.34700	24.34800	35.33000
C	-33.04500	22.28500	34.63400
C	-31.27500	20.55800	34.64100
H	-30.23000	20.91000	34.59300
H	-31.60100	20.52700	35.68700
C	-31.56300	18.10600	34.93000
N	-35.49800	6.68500	32.06700
N	-33.44600	7.98300	32.16600
N	-32.26000	9.88200	32.12100
N	-31.47700	12.17000	32.02500
N	-31.13400	14.39100	31.91600
O	-33.43800	9.25400	30.20600

O	-31.99900	13.29400	30.04200
C	-34.13100	6.82500	31.62600
H	-33.57100	5.91800	31.89900
H	-34.15000	6.93500	30.53500
C	-33.09900	9.06200	31.37100
C	-31.40100	10.83700	31.45800
H	-30.35300	10.48800	31.50400
H	-31.72300	10.89700	30.41200
C	-31.58500	13.28400	31.19900
O	-36.88100	7.90500	36.21900
C	-36.80800	7.28100	35.16200
O	-36.56200	23.35000	29.39300
C	-36.58500	23.94100	30.47000
O	-36.51600	7.55600	30.15500
C	-36.57400	7.06300	31.27900
O	-36.69700	23.63900	35.49700
C	-36.67100	24.13500	34.37300
C	-35.89600	6.09000	33.32800
H	-35.44300	5.09400	33.44700
C	-31.90100	9.28100	33.39400
H	-30.81300	9.12200	33.45600
C	-32.71900	7.95600	33.42400
H	-32.09500	7.05100	33.48400
C	-30.55500	14.01000	33.19400
H	-29.48800	14.28200	33.23200
C	-30.79500	12.48100	33.26900
H	-29.86400	11.89900	33.35600
C	-35.84600	25.12200	32.38600
H	-35.40200	26.12900	32.36200
C	-31.74900	22.08300	32.66700
H	-30.66700	22.28800	32.64800
C	-32.62300	23.36900	32.57600
H	-32.03600	24.29900	32.51200
C	-30.45300	17.30400	33.01000
H	-29.40000	16.98400	33.06000
C	-30.61300	18.84500	32.90300
H	-29.65100	19.38000	32.85500
C	-37.45400	6.06300	33.23600
H	-37.88100	5.04900	33.23100
C	-41.48800	9.19200	32.89100
H	-42.57600	9.03200	32.83300
C	-40.67400	7.86700	32.97700
H	-41.30100	6.96100	32.97300
C	-42.68900	13.97800	32.66900

H	-43.74100	14.29800	32.74200
C	-42.52700	12.43700	32.71200
H	-43.48800	11.89800	32.70100
C	-37.40600	25.12400	32.35000
H	-37.84500	26.13000	32.26700
C	-41.48400	22.04300	32.38600
H	-42.56900	22.23500	32.39100
C	-40.62600	23.34300	32.34400
H	-41.22400	24.26800	32.31600
C	-42.71000	17.24000	32.53800
H	-43.75500	16.90700	32.64500
C	-42.57200	18.78400	32.47900
H	-43.54200	19.30800	32.49900
C	-30.80400	15.76500	34.98800
H	-29.70700	15.72000	35.11600
H	-31.27900	15.83300	35.97300
C	-30.64300	15.55400	31.20700
H	-29.53800	15.53100	31.18100
H	-31.02900	15.51400	30.18400
C	-42.60300	15.53500	30.68400
H	-43.70800	15.51800	30.66400
H	-42.22200	15.49400	29.65900
C	-42.29300	15.68400	34.47700
H	-43.38400	15.69100	34.66100
H	-41.76400	15.73100	35.43500