Supporting information

Red-light-responsive cucurbit[8]uril based host-guest interaction for photoswitchable supramolecular polymeric hydrogel

Yan-Yan Yuan, Yu Hai, Li-Juan Liu, Tian-Guang Zhan*, Li-Chun Kong and Kang-Da Zhang*

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Materials Science, Zhejiang Normal University, 688 Yingbin Road, Jinhua 321004, China.

E-mails: tgzhan@zjnu.cn; Kangda.Zhang@zjnu.cn

Table of Contents

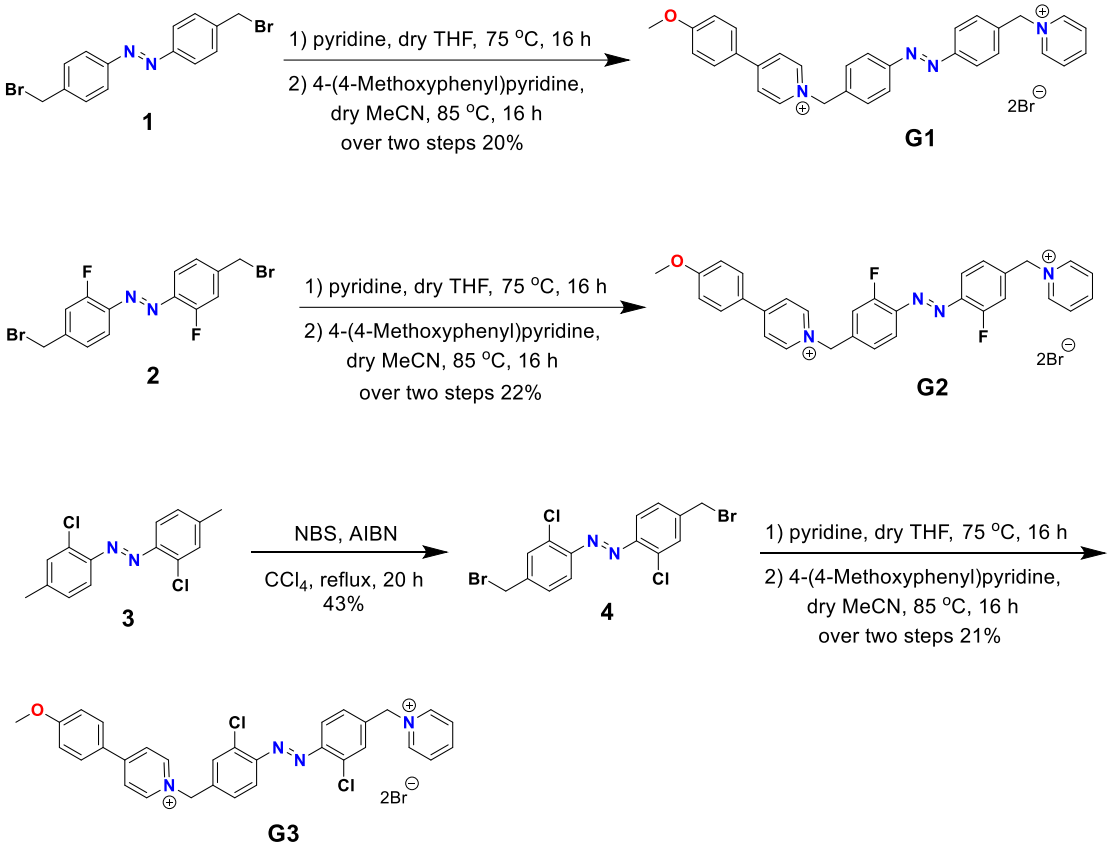
Section 1: experimental and materials

All the chemical reagents were used as received from the commercial suppliers and used without further purification. Compounds **1**[1], 4-(4-methoxyphenyl)pyridine[2], **2**[3], **3**[4], **5**[5] and **11**[6] were synthesized according to published procedures.

Nuclear Magnetic Resonance (NMR) Spectroscopy: the solution phase ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 and 600 spectrometers, and the chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard.

UV-Vis Absorption Spectroscopy: the UV-Vis spectra were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer.

Section 2: synthesis of guest molecules and polymer



Scheme S1. The synthetic route for the guest molecules **G1**-**G3**.

Synthesis of G1. Compound **1**[1] (200 mg, 0.543 mmol) and pyridine (27.9 mg, 0.353 mmol) were dissolved in dry THF (15 mL) in a sealed tube, and the resulting mixture was heated at 75 °C with stirring for 16 hours. After cooling to the room temperature, the reaction mixture was filtrated. The remaining filter cake was washed by THF to give light yellow solid (90.0 mg), which was further dissolved in dry CH_3CN (1.0 mL) with compound 4-(4-methoxyphenyl)pyridine[2] (45.2 mg, 0.244 mmol) in a sealed tube. The mixture was then heated to 85 °C for another 16 hours. After cooling down, the solvent was discarded by filtration and the solid residue was washed by CH_3CN for several times to remove the remaining starting material. The collected filter cake was dried to give **G1** as yellow solid (70.5 mg, 20%).

^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 9.26 (d, J = 5.6 Hz, 2 H), 9.17 (d, J = 6.8 Hz, 2 H), 8.67 (t, J = 8.0 Hz, 1 H), 8.53 (d, J = 7.2 Hz, 2 H), 8.23 (t, J = 7.2 Hz, 2 H), 8.13 (d, J = 8.8 Hz, 2 H), 7.98-7.93 (m, 4 H), 7.78-7.74 (m, 4 H), 7.20 (d, J = 8.8

Hz, 2 H), 5.99 (s, 2 H), 5.92 (s, 2 H), 3.89 (s, 3 H).

^{13}C NMR (150 MHz, DMSO-d_6, 298 K) δ (ppm): 163.33, 154.98, 152.52, 152.45, 146.68, 145.49, 145.06, 138.53, 138.08, 130.70, 130.61, 130.44, 129.04, 125.72, 124.06, 123.76, 115.68, 62.97, 61.78, 56.21.

HRMS (ESI) *m/z*: Calcd. for $C_{31}H_{28}N_4O$ ($[M-2Br^-]^{2+}$): 236.1126, Found: 236.1129.

Synthesis of G2. Compound **2**[3] (300 mg, 0.742 mmol) and pyridine (38.2 mg, 0.4783 mmol) were mixed in dry THF (20 mL) in a sealed tube, the resulting mixture was then heated at 75 ºC with stirring for 16 hours. After cooling to the room temperature, the reaction mixture was filtrated. The remaining filter cake was washed by THF to give light yellow solid (128 mg), which was further dissolved in dry CH_3CN (4.0 mL) with compound 4-(4-methoxyphenyl)pyridine[2] (58.9 mg, 0.318 mmol) in a sealed tube. The mixture was then heated to 85 ºC for another 16 hours and then cooling down. The reaction mixture was filtrated to discard the solvent, and the solid residue was washed by CH_3CN for several times to remove the remaining starting material. The collected filter cake was dried to give **G2** as yellow solid (109 mg, 22%).

^{1}H NMR (400 MHz, D_2O, 298 K) δ (ppm): 8.86 (d, J = 6.0 Hz，2 H), 8.69 (d, J = 6.8 Hz, 2 H), 8.50 (t, J = 7.6 Hz, 1 H), 8.16 (d, J = 6.4 Hz, 2 H), 8.01 (t, J = 7.2 Hz, 2 H), 7.85 (d, J = 8.8 Hz, 2 H), 7.67-7.63 (m, 2 H), 7.35 (d, J = 10.4 Hz, 2 H), 7.27-7.22 (m, 2 H), 7.07 (d, J = 8.4 Hz, 2 H), 5.81 (s, 2 H), 5.71 (s, 2 H), 3.80 (s, 3 H).

^{13}C NMR (150 MHz, DMSO-d_6, 298 K) δ (ppm): 162.92, 159.26 (d, $J_{C\text{-}F}$ = 256.5 Hz), 159.20 (d, $J_{C\text{-}F}$ = 256.7 Hz), 154.65, 146.32, 145.13, 144.68, 140.80 (d, $J_{C\text{-}F}$ = 8.4 Hz), 140.28 (d, $J_{C\text{-}F}$ = 8.4 Hz), 140.14 (d, $J_{C\text{-}F}$ = 6.9 Hz), 140.05 (d, $J_{C\text{-}F}$ = 6.6 Hz), 130.26, 128.60, 125.75 (d, $J_{C\text{-}F}$ = 3.3 Hz), 125.55 (d, $J_{C\text{-}F}$ = 3.2 Hz), 125.25, 123.61, 118.52, 118.48, 118.23 (d, $J_{C\text{-}F}$ = 21 Hz), 118.00 (d, $J_{C\text{-}F}$ = 20.7 Hz), 115.24, 62.00, 60.84, 55.75.

^{19}F NMR (376 MHz, DMSO-d_6, 298 K) δ (ppm): -122.90, -122.94.

HRMS (ESI) *m/z*: Calcd. for $C_{31}H_{26}F_2N_4O$ ($[M-2Br^-]^{2+}$): 254.1036, Found: 254.1034.

Synthesis of Compound 4. After the compound **3**[3] (2.00 g, 7.16 mmol), NBS (3.83 g, 21.5 mmol) and AIBN (0.294 g, 1.79 mmol) were dissolved in CCl_4 (80 mL), the

resulting mixture was degassed by bubbling nitrogen gas for 30 min, after which the mixture was refluxed under nitrogen gas atmosphere for 20 hours. The reaction mixture was allowed to cool down and filtrated, the collected filtrate was concentrated via evaporation under reduced pressure to give yellow solid, which was further dissolved in ethyl acetate (55 mL) and washed by water (80 mL × 2). The organic phase dried by anhydrous Na_2SO_4, which was further removed by filtration. After concentration, the remaining residue was submitted to flash column chromatography for purification by using petroleum ether as eluent to give compound **4** as yellow solid (1.35 g, 43%).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ (ppm): 7.77 (d, *J* = 8.4 Hz, 2 H), 7.63 (s, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 4.51 (s, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ (ppm): 148.54, 142.36, 136.09, 131.15, 128.04, 118.46, 31.13.

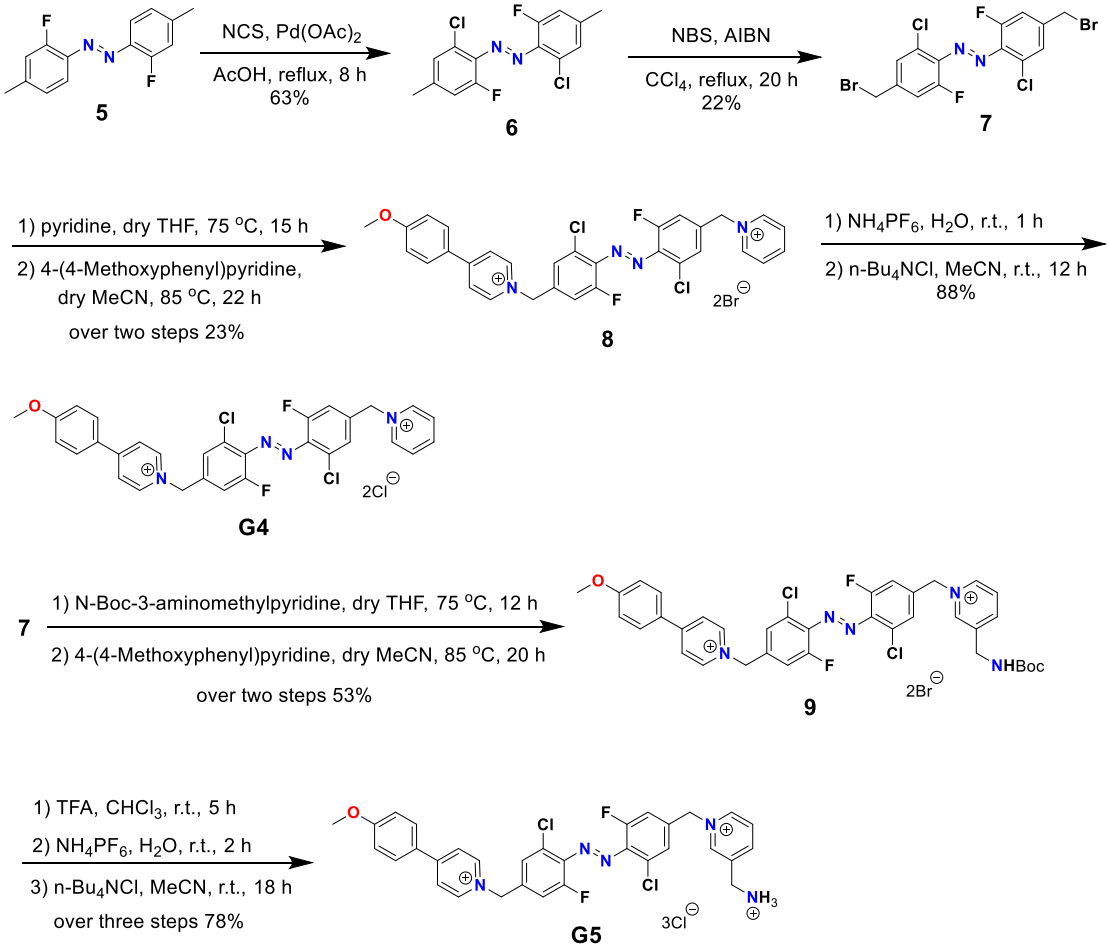
HRMS (ESI) *m/z*: Calcd. for $C_{14}H_{11}Br_2Cl_2N_2$ ($[M+H]^+$) 434.8661, Found: 434.8624.

Synthesis of G3. A sealed tube was charged with compound **4** (200 mg, 0.458 mmol), pyridine (23.5 mg, 0.298 mmol) and anhydrous THF (15 mL), after which the tube was sealed and then heated to 75 °C for 15 hours. After cooling down, the reaction mixture was filtrated to discard the solvent, the solid residue was then washed by THF to remove the unconsumed starting material. The collected yellow solid was then mixed with compound 4-(4-methoxyphenyl)pyridine[2] (36.4 mg, 0.197 mmol) and anhydrous acetonitrile (4 mL) in a sealed tube, and heated up to 85 °C for 22 hours. The reaction mixture was allowed to be cooled down and filtrated, the isolated solid was further washed by THF to remove the unconsumed reactants. After dried, **G3** could be obtained as yellow solid (66.8 mg, 21%).

^{1}H NMR (600 MHz, D_2O, 298 K) δ (ppm): 8.85 (d, *J* = 6.4 Hz, 2 H), 8.60 (d, *J* = 6.4 Hz, 2 H), 8.51 (t, *J* = 7.6 Hz, 1 H), 8.04-7.99 (m, 4 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 7.55 (s, 1 H), 7.48 (s, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 8.4 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 7.16 (d, *J* = 8.4 Hz, 1 H), 6.91 (d, *J* = 7.2 Hz, 2 H), 5.75 (s, 2 H), 5.57 (s, 2 H), 3.74 (s, 3 H).

^{13}C NMR (150 MHz, DMSO-d_6, 298 K) δ (ppm): 163.33, 155.04, 148.66, 148.58,

146.74, 145.55, 145.09, 140.36, 139.87, 135.23, 135.18, 131.99, 131.79, 130.70, 129.40, 129.22, 129.04, 125.69, 124.06, 118.98, 118.95, 115.66, 62.22, 61.05, 56.20. **HRMS (ESI)** *m/z*: Calcd. for $C_{31}H_{26}Cl_2N_4O$ ($[M\text{-}2Br^-]^{2+}$) 270.0737, Found: 270.0740.



Scheme S2. The synthetic route for the guest molecules **G4** and **G5**.

Synthesis of Compound 6. After mixing compound **5**[5] (2.00 g, 8.12 mmol), $Pd(OAc)_2$ (0.183 g, 0.812 mmol) and NCS (3.32 g, 24.4 mmol) in AcOH (80 mL), the resulting mixture was heated to 120 °C with stirring for 8 hours under nitrogen gas atmosphere. When the TLC suggested the reaction was completed, it was allowed to cool down and filtrated. The collected filtrate was concentrated to give yellow solid, which was further dissolved in ethyl acetate (160 mL), and then conscientiously washed by saturated $NaHCO_3$ aqueous solution (80 mL × 2) and brine. The organic layer was dried by anhydrous Na_2SO_4, which was further removed by filtration. After concentration, the

remaining residue was submitted to flash column chromatography for purification by using petroleum ether as eluent, to give compound **6** as orange yellow solid (1.62 g, 63%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.99 (s, 2 H), 6.97 (dd, J_1 = 11.6 Hz, J_2 = 0.8 Hz, 2 H), 2.41 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 152.46 (d, $J_{C\text{-}F}$ = 260.7 Hz), 142.20 (d, $J_{C\text{-}F}$ = 9.3 Hz), 137.11 (d, $J_{C\text{-}F}$ = 9.2 Hz), 132.41 (d, $J_{C\text{-}F}$ = 3.7 Hz), 126.71 (d, $J_{C\text{-}F}$ = 3.1 Hz), 116.38 (d, $J_{C\text{-}F}$ = 20.3 Hz), 21.33.

^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ (ppm): -124.00 (d).

HRMS (ESI) *m/z*: Calcd. for $C_{14}H_{11}Cl_2F_2N_2$ ($[M+H]^+$) 315.0262, Found: 315.0263.

Synthesis of Compound 7. The solution of compound **6** (1.00 g, 3.17 mmol), NBS (1.69 g, 9.52 mmol) and AIBN (0.130 g, 0.790 mmol) in CCl_4 (50 mL) was degassed by bubbling nitrogen gas for 30 min. After cooling down, the mixture was filtrated and the collected filtrate was concentrated to give yellow-brown solid, which was further dissolved in ethyl acetate (50 mL) and then washed by water (80 mL × 2). The collected organic phase was dried by anhydrous Na_2SO_4, which was removed by filtration. The filtrate was concentrated via evaporation under reduced pressure and the remaining residue was further purified by flash column chromatography using petroleum ether as eluent, to give compound **7** as yellow-brown solid (0.329 g, 22%).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ (ppm): 7.43 (s, 2 H), 7.22 (dd, J_1 = 10.8 Hz, J_2 = 1.8 Hz, 2 H), 4.46 (s, 4 H).

^{13}C NMR (150 MHz, DMSO-d_6, 298 K) δ (ppm): 151.82 (d, $J_{C\text{-}F}$ = 259.7 Hz), 143.74 (d, $J_{C\text{-}F}$ = 9.3 Hz), 138.23 (d, $J_{C\text{-}F}$ = 9.6 Hz), 131.41 (d, $J_{C\text{-}F}$ = 2.4 Hz), 127.73 (d, $J_{C\text{-}F}$ = 3.0 Hz), 117.72 (d, $J_{C\text{-}F}$ = 21 Hz), 31.81.

^{19}F NMR (564 MHz, $CDCl_3$, 298 K) δ (ppm): -122.26.

HRMS (ESI) *m/z*: Calcd. for $C_{14}H_9Br_2Cl_2F_2N_2$ ($[M+H]^+$): 470.8472, Found: 470.8507.

Synthesis of Compound 8. The compound **7** (400 mg, 0.846 mmol), pyridine (43.5 mg, 0.549 mmol) were mixed in anhydrous THF (25 mL) in a glass tube, which was

sealed and then heated to 75 °C with stirring for 15 hours. After cooling down, the reaction mixture was filtrated to discard the solvent, and the solid residue was then washed by THF to remove the unconsumed starting material. The collected yellow solid (170 mg) was dissolved in anhydrous acetonotrile (3 mL) with compound 4-(4-methoxyphenyl)pyridine[2] (68.4 mg, 0.369 mmol). The resulting mixture was then heated to 85 °C with stirring for another 22 hours. After cooling down, the reaction mixture was filtrated and the collected solid residue was further washed by THF to remove the unconsumed reactants. Finally, the received solid was dried to give compound **8** as yellow solid (142 mg, 23%).

^{1}H NMR (400 MHz, DMSO-d_6, 298 K) d (ppm): 9.26 (d, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 2 H), 9.17 (d, J = 6.8 Hz, 2 H), 8.67 (tt, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 8.52 (d, J = 7.2 Hz, 2 H), 8.21 (dd, J_1 = 7.6 Hz, J_2 = 6.8 Hz, 2 H), 8.14 (d, J = 8.8 Hz, 2 H), 7.93 (s, 1 H), 7.91 (s, 1 H), 7.82-7.77 (m, 2 H), 7.20 (d, J = 9.2 Hz, 2 H), 5.95 (s, 2 H), 5.88 (s, 2 H), 3.89 (s, 3 H).

^{13}C NMR (150 MHz, DMSO-d_6, 298 K) d (ppm): 163.37, 155.13, 151.89 (d, $J_{C\text{-}F}$ =259.5 Hz), 151.86 (d, $J_{C\text{-}F}$ = 259.4 Hz), 146.78, 145.64, 145.16, 139.48 (d, $J_{C\text{-}F}$ = 9.2 Hz), 139.06 (d, $J_{C\text{-}F}$ = 9.8 Hz), 138.94 (d, J = 9.6 Hz), 131.54 (d, $J_{C\text{-}F}$ = 2.6 Hz), 131.49 (d, $J_{C\text{-}F}$ = 2.7 Hz), 130.71, 129.02, 127.94 (d, $J_{C\text{-}F}$ = 3.3 Hz), 127.70 (d, $J_{C\text{-}F}$ = 3.0 Hz), 125.74, 124.06, 118.09 (d, $J_{C\text{-}F}$ = 21.5 Hz), 117.86 (d, $J_{C\text{-}F}$ = 21.5 Hz), 115.69, 61.80, 60.67, 53.20.

^{19}F NMR (376 MHz, DMSO-d_6, 298 K) d (ppm): -123.08, -123.11.

HRMS (ESI) *m/z*: Calcd. for $C_{31}H_{24}Cl_2F_2N_4O$ $[M\text{-}2Br^-]^{2+}$ 288.0642, Found: 288.0647.

Synthesis of G4. To the solution of compound **8** (71.0 mg, 0.0963 mmol) in water (10 mL), was dropwise added the saturated NH_4PF_6 aqueous solution to generate yellow peripatetics, the mixture was keep stirring at room temperature for another one hour, and then filtrated. The collected solid was further dissolved in dried acetonitrile (2 mL), to which tetrabutylammonium chloride (TBACl) (600 mg, 2.16 mol) was added to generate yellow peripatetics. After stirring at room temperature for another 12 hours, the mixture was filtrated and the isolated solid was washed by acetonitrile (3 mL × 3),

and dried. **G4** could be obtained as yellow solid (54.9 mg, 88%).

Synthesis of Compound 9. The compounds **7** (200 mg, 0.423 mmol) and N-Boc-3-aminomethylpyridine (106 mg, 0.508 mmol) were mixed in dry THF (50 mL) in a glass tube, and then heated to 75 ºC with stirring for 12 hours. After cooling down, the reaction mixture was filtrated and the solid was washed by THF to remove the the unconsumed reactants. The obtained yellow solid was then mixed with 4-(4-methoxyphenyl)pyridine[2] (69.4 mg, 0.333 mmol) in dry acetonitrile (2.5 mL) in a glass tube. After heating at 85 ºC with stirring for another 20 hours, the reaction mixture was allowed to cool down and filtrated. The collected solid residue was then washed by acetonotrile to remove the the unconsumed reactants, and the received yellow solid was further dried to give compound **9** (194 mg, 53%).

^{1}H NMR (600 MHz, DMSO-d_6, 298 K) δ (ppm): 9.17-9.14 (m, 3 H), 9.09 (s, 1 H), 8.53 (d, J = 7.2 Hz, 2 H), 8.50 (d, J = 7.8 Hz, 1 H), 8.19 (dd, J_1 = 7.8 Hz, J_2 = 6.0 Hz, 1 H), 8.14 (d, J = 9.0 Hz, 2 H), 7.92 (s, 1 H), 7.87 (s, 1 H), 7.79 (dd, J_1 = 11.4 Hz, J_2 = 1.8 Hz, 1 H), 7.74 (d, J = 11.4 Hz, 1 H), 7.66 (t, J = 6.0 Hz, 1 H), 7.20 (d, J = 9.0 Hz, 2 H), 5.94 (s, 2 H), 5.86 (s, 2 H), 4.34 (d, J = 6.0 Hz, 2 H), 3.89 (s, 3 H), 1.37 (s, 9 H).

^{13}C NMR (150 MHz, DMSO-d_6, 298 K) δ (ppm): 163.38, 156.21, 155.13, 151.89 (d, $J_{C\text{-}F}$ = 259.5 Hz), 151.85 (d, $J_{C\text{-}F}$ = 259.4 Hz), 145.17, 145.11, 144.27, 143.77, 141.81, 139.49 (d, $J_{C\text{-}F}$ = 9.0 Hz), 139.05 (d, $J_{C\text{-}F}$ = 9.9 Hz), 139.00 (d, $J_{C\text{-}F}$ = 4.2 Hz), 138.93 (d, $J_{C\text{-}F}$ = 3.9 Hz), 131.51, 130.71, 128.69, 127.83 (d, $J_{C\text{-}F}$ = 2.3 Hz), 127.71 (d, $J_{C\text{-}F}$ = 3.0 Hz), 125.74, 124.06, 117.97 (d, $J_{C\text{-}F}$ = 21.6 Hz), 117.86 (d, $J_{C\text{-}F}$ = 21.5 Hz), 115.69, 79.14, 61.88, 60.88, 56.20, 41.22, 28.54.

^{19}F NMR (564 MHz, DMSO-d_6, 298 K) δ (ppm): -123.13, -123.15.

HRMS (ESI) *m/z*: Calcd. for $C_{37}H_{35}Cl_2F_2N_5O_3$ $[M\text{-}2Br^-]^{2+}$ 352.6037, Found: 352.6049.

Synthesis of G5. The suspension mixture of compound **9** (80.0 mg, 0.0928 mmol) in a binary solvent of TFA/$CHCl_3$ (11 mL, v/v = 1/10) was stirred in an ice bath for 10 min, after which the reaction mixture was kept stirring at room temperature until TLC suggested the consumption of starting reactants. The reaction mixture was concentrated

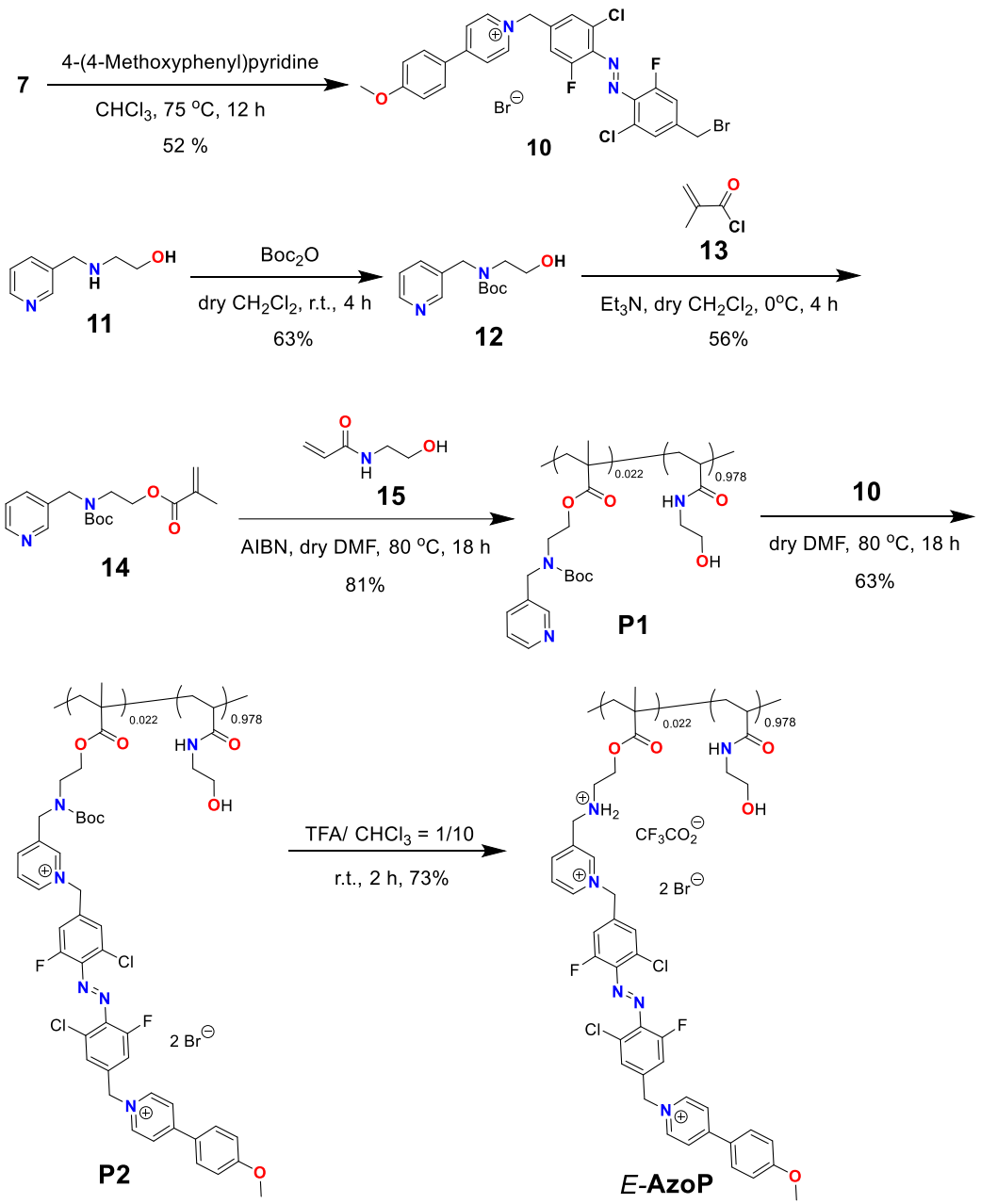
via evaporation under reduced pressure to give yellow-brown solid, which was then redissolved in water (10 mL). To this solution was dropwise added saturated NH_4PF_6 aqueous solution to generate yellow precipitates, which was isolated by filtration and further dissolved in dry acetonitrile (2 mL). Then, tetrabutylammonium chloride (TBACl) was further added to this solution to regenerate yellow precipitates, and the mixture was kept stirring at room temperature for another 18 hours. After filtration, the collected yellow solid was washed by acetonitrile (3 mL × 3) and then dried, to give **G5** as yellow solid (52.0 mg, 78%)

^{1}H NMR (400 MHz, D_2O, 298 K) δ (ppm): 9.04 (s, 1 H), 8.96 (d, J = 6.4 Hz, 2 H), 8.70 (d, J = 6.8 Hz, 2 H), 8.64 (d, J = 8.0 Hz, 1 H), 8.17 (d, J = 6.8 Hz, 2 H), 8.12 (t, J = 6.8 Hz, 1 H), 7.85 (d, J = 8.8 Hz, 2 H), 7.48 (s, 1 H), 7.44 (s, 1 H), 7.32 (d, J = 11.2 Hz, 1 H), 7.27 (d, J = 11.2 Hz, 1 H), 7.07 (d, J = 8.8 Hz, 2 H), 5.85 (s, 2 H), 5.71 (s, 2 H), 4.37 (s, 2 H), 3.81 (s, 3 H).

^{13}C NMR (150 MHz, DMSO-d_6, 298 K) δ (ppm): 163.29, 155.01, 151.81 (d, $J_{C\text{-}F}$ = 259.2 Hz), 151.76 (d, $J_{C\text{-}F}$ = 259.7 Hz), 147.36, 146.45, 145.18, 139.57 (d, $J_{C\text{-}F}$ = 9.3 Hz), 139.07 (d, $J_{C\text{-}F}$ = 9.6 Hz), 138.89 (d, $J_{C\text{-}F}$ = 9.6 Hz), 138.59 (d, $J_{C\text{-}F}$ = 9.5 Hz), 135.64, 131.41 (d, $J_{C\text{-}F}$ = 13.4 Hz), 130.71, 128.39, 128.12 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.79 (d, $J_{C\text{-}F}$ = 3.0 Hz), 125.71, 124.04, 118.33 (d, $J_{C\text{-}F}$ = 21.5 Hz), 117.96 (d, $J_{C\text{-}F}$ = 21.9 Hz), 115.64, 61.86, 60.31, 56.20, 39.30.

^{19}F NMR (376 MHz, DMSO-d_6, 298 K) δ (ppm): -123.08, -123.10

HRMS (ESI) *m/z*: Calcd. for $C_{32}H_{27}Cl_2F_2N_5O$ $[M\text{-}2Cl^{-}\text{-}HCl]^{2+}$ 302.5775, Found: 302.5781.



Scheme S3. The synthetic route for polymer **AzoP**.

Synthesis of compound 10. A glass tube was charged with compound **7** (300 mg, 0.634 mmol), compound 4-(4-methoxyphenyl)pyridine[2] (82.3 mg, 0.444 mmol) and chloroform (15 mL), the resulting mixture was then heated at 75 °C for 12 hours. After cooling down, the reaction mixture was filtrated and the filter cake was washed by chloroform to remove the remove the unconsumed reactants. The remaining solid was collected and dried to give compound **10** as yellow solid (216 mg, 52%).

^{1}H NMR (600 MHz, DMSO-d_6, 298 K) δ (ppm): 9.24 (d, J = 7.2 Hz, 2H), 8.54 (d, J =

7.2 Hz, 2H), 8.15 (d, J = 9.0 Hz, 2H), 7.96 (s, 1H), 7.84 (dd, J_1 = 11.4 Hz, J_2 = 1.2 Hz, 1H), 7.74 (s, 1H), 7.62 (dd, J_1 = 11.4 Hz, J_2 = 1.2 Hz, 1H), 7.19 (d, J = 9.0 Hz, 2H), 5.93 (s, 2H), 4.77 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (150 MHz, DMSO-d_6, 298 K) δ (ppm): 163.37, 155.14, 151.97 (d, J_{C-F} = 259.2 Hz), 151.78 (d, J_{C-F} = 259.7 Hz), 145.16, 143.97 (d, J_{C-F} = 9.3 Hz), 139.23 (d, J_{C-F} = 9.2 Hz), 139.06 (d, J_{C-F} = 10.1 Hz), 138.13 (d, J_{C-F} = 9.6 Hz), 131.53 (d, J_{C-F} = 2.4 Hz), 131.44 (d, J_{C-F} = 2.1 Hz), 130.70, 127.76 (d, J_{C-F} = 3.0 Hz), 127.64 (d, J_{C-F} = 3.2 Hz), 125.74, 124.07, 117.80 (d, J_{C-F} = 21.5 Hz), 117.75 (d, J_{C-F} = 21 Hz), 115.68, 60.74, 56.19, 31.79.

^{19}F NMR (564 MHz, DMSO-d_6, 298 K) δ (ppm): -123.01, -123.25.

HR-MS(ESI) *m/z*: Calcd. for $C_{26}H_{19}BrCl_2F_2N_3O$ $[M\text{-}Br^-]^+$ 576.0057, Found: 576.0053.

Synthesis of compound 12. To a solution of compound **11**[6] (3.00 g, 19.7 mmol) in CH_2Cl_2 (25 mL) was added Boc_2O (4.73 g, 21.7 mmol), the mixture was then allowed to be stirred at room temperature for 4 hours. The reaction mixture was concentrated to remove the solvent, and the residue was redissolved in CH_2Cl_2 and washed by water (60 mL × 2) and brine (60 mL), respectively. The combined organic phase was dried by anhydrous Na_2SO_4, which was further removed by filtration. After the filtrate was concentrated via evaporation under reduced pressure, the remaining crude was purified by flash column chromatography by using a binary eluent of CH_2Cl_2/MeOH = 30/1, to afford compound **12** as colorless liquid (3.10 g, 63%).

^{1}H NMR (600 MHz, CD_3CN, 298 K) δ (ppm): 8.47-8.44 (m, 2H), 7.64 (d, J = 7.8 Hz, 1H), 7.30 (t, J = 6.0 Hz, 1H), 4.48 (s, 2H), 3.59 (t, J = 6.0 Hz, 2H), 3.36-3.24 (d, 2H), 3.09 (br, 1H), 1.46-1.34 (d, 9H).

^{13}C NMR (150 MHz, CD_3CN, 298 K) δ (ppm): 156.88, 149.80, 149.25, 136.11, 135.83, 135.58, 124.44, 80.52, 80.37, 61.03, 50.45, 50.35, 50.18, 49.49, 28.52.

HR-MS (ESI) *m/z*: Calcd. for $C_{13}H_{21}N_2O_3$ $[M + H]^+$ 253.1552, Found:253.1546.

Synthesis of compound 14. To a solution of compound **12** (0.300 g, 1.20 mmol) and Et_3N (0.250 g, 2.00 mmol) in 10 mL anhydrous CH_2Cl_2 cooled at 0 ºC with an ice bath,

was added another solution of compound **13** (0.186 g, 1.80 mmol) in 3 mL anhydrous CH_2Cl_2. The resulting mixture was kept stirring at 0 ºC for another 4 hours, and then allowed to warm up at room temperature. Then, the reaction mixture was poured into 80 mL cold water and extracted by CH_2Cl_2 (60 mL × 2), the combined organic phase was continuously washed by water (60 mL × 2) and brine (60 mL × 2). The collected organic phase was dried by anhydrous Na_2SO_4, which was further removed by filtration. The filtrate was concentrated via evaporation under reduced pressure, and the remaining crude residue was submitted to flash column chromatography for purification by using a binary solvent of CH_2Cl_2/MeOH = 15/1 as eluent, after which compound **14** could be isolated as colorless liquid (0.215 g, 56%).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ (ppm): 8.49-8.46 (m, 2H), 7.59-7.50 (m, 1H), 7.23 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 1H), 6.05 (s, 1H), 5.54 (d, 1H), 4.48 (d, 2H), 4.23 (d, 2H), 3.48 (d, 2H), 1.90 (s, 3H), 1.42 (d, 9H).

^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ (ppm): 167.10, 155.64, 155.21, 149.04, 148.80, 135.96, 135.44, 134.66, 133.97, 133.67, 126.01, 125.91, 123.59, 123.47, 80.62, 62.67, 49.28, 48.49, 45.85, 45.62, 28.32, 18.29.

HR-MS (ESI) *m/z*: Calcd. for $C_{17}H_{25}N_2O_4$ $[M + H]^+$ 321.1814, Found: 321.1809.

Synthesis of polymer P1. Compounds **14** (0.0200 g, 0.06 mmol), **15** (0.276 g, 2.40 mmol) and AIBN (2.00 mg, 0.0122 mmol) were mixed in 0.5 mL anhydrous acetonitrile in the mole ratio of 1/0.025/0.005. Then, the glass tube charged with reaction mixture was sealed by a rubber cover with aluminum foil and degassed by three freeze-pump-thaw cycles in liquid N_2 through a long needle, after which the pinhole on the rubber cover was sealed with paraffin. The tube was then allowed to worm up to room temperature and heated up to 70 ºC with stirring for another 18 hours. After cooling down, the polymer solution was poured into acetone to generate viscous precipitates, which were isolated by centrifugation and filtration, and then dried to give polymer **P1** as white solid (0.250 g, 81%).

Synthesis of polymer P2. Polymer **P1** (49.0 mg) and compound **10** (8.30 mg) was mixed in 0.5 mL anhydrous acetonitrile in a glass tube, which was then sealed and heated up to 85 ^{o}C with stirring for 18 hours. The cooled polymer solution was poured into diethyl ether to generate precipitates, and then centrifugated for twice. After filtration, the precipitates were dried to afford polymer **P2** as orange solid (35.0 mg, 63%).

Synthesis of polymer AzoP. The polymer **P2** (35.0 mg) was suspended in a binary solvent of TFA/$CHCl_3$ (1/10, v/v), the resulting mixture was then stirred in an ice bath for 10 min. After removing the ice bath, the reaction mixture was allowed to be stirred at room temperature for another 2 hours. The reaction mixture was concentrated under reduced pressure to remove the solvent, the remained orange solid was further dissolved in 15 mL methanol, which was dropwise added into diethyl ether to generate precipitates. The collected precipitates were redissolved in methanol and precipitated in diethyl ether again, after which it was allowed to be filtrated. The obtained product was dried under vacuum to give polymer **AzoP** as orange solid (25 mg, 73%).

Section 3: Photocontrolled complexation behavior of G1 and CB[8]

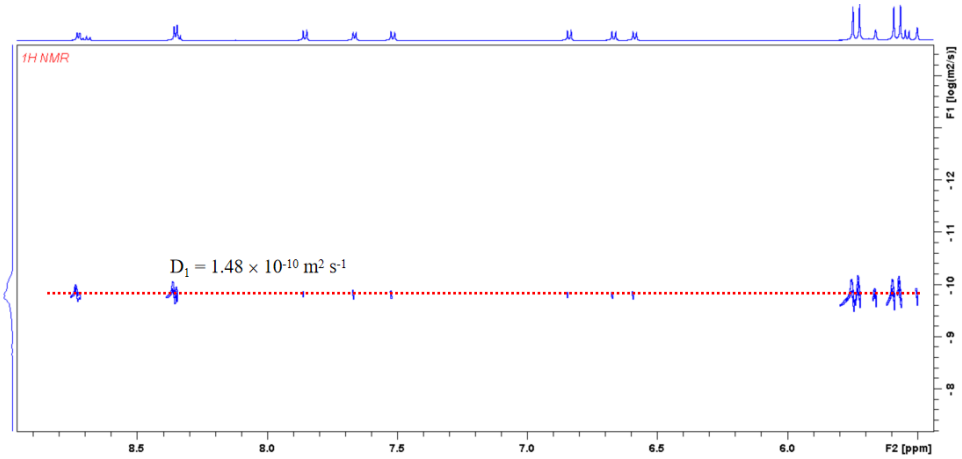


Fig. S1 The 2D DOSY-NMR spectrum (600 MHz, D_2O, 298 K) for the solution of the mixture of *E*-**G1** and CB[8] (2:2, 5.0 mM)

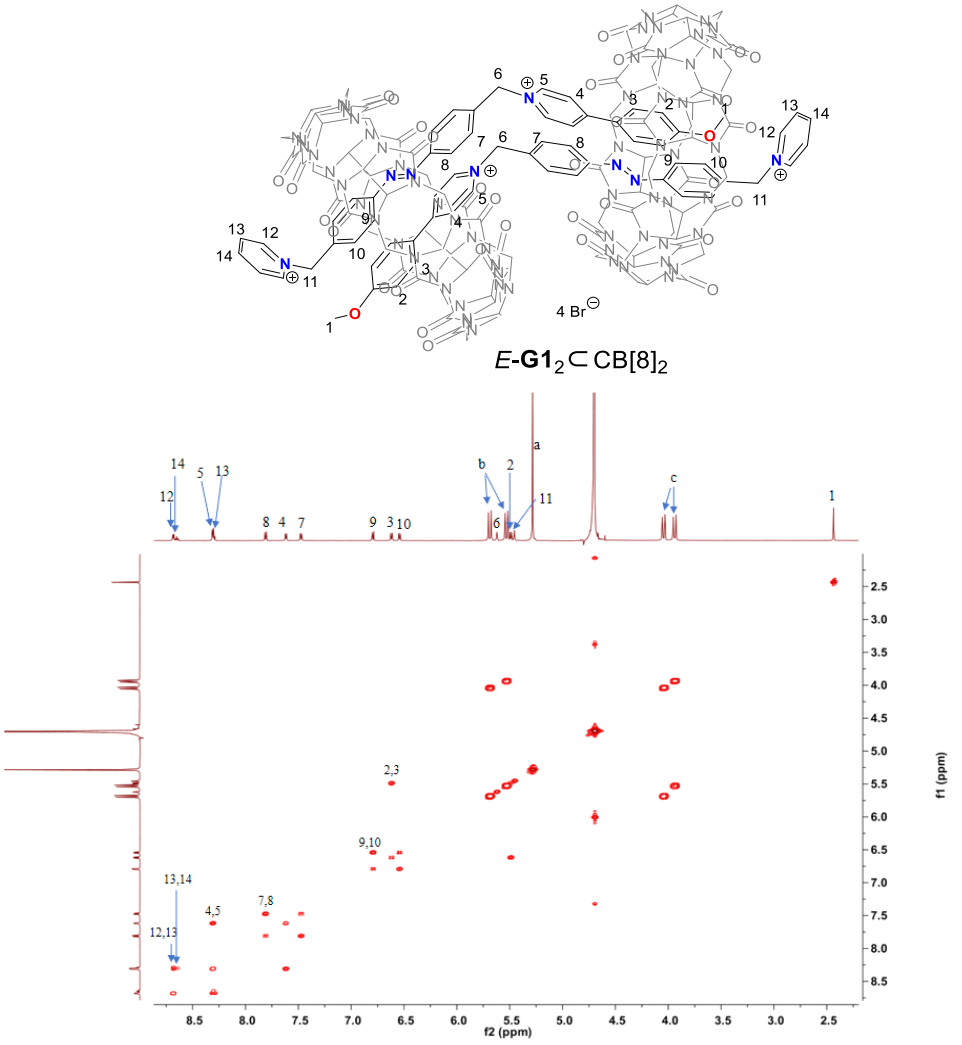


Fig. S2 The 2D COSY spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G1** and CB[8] (2:2, 10 mM).

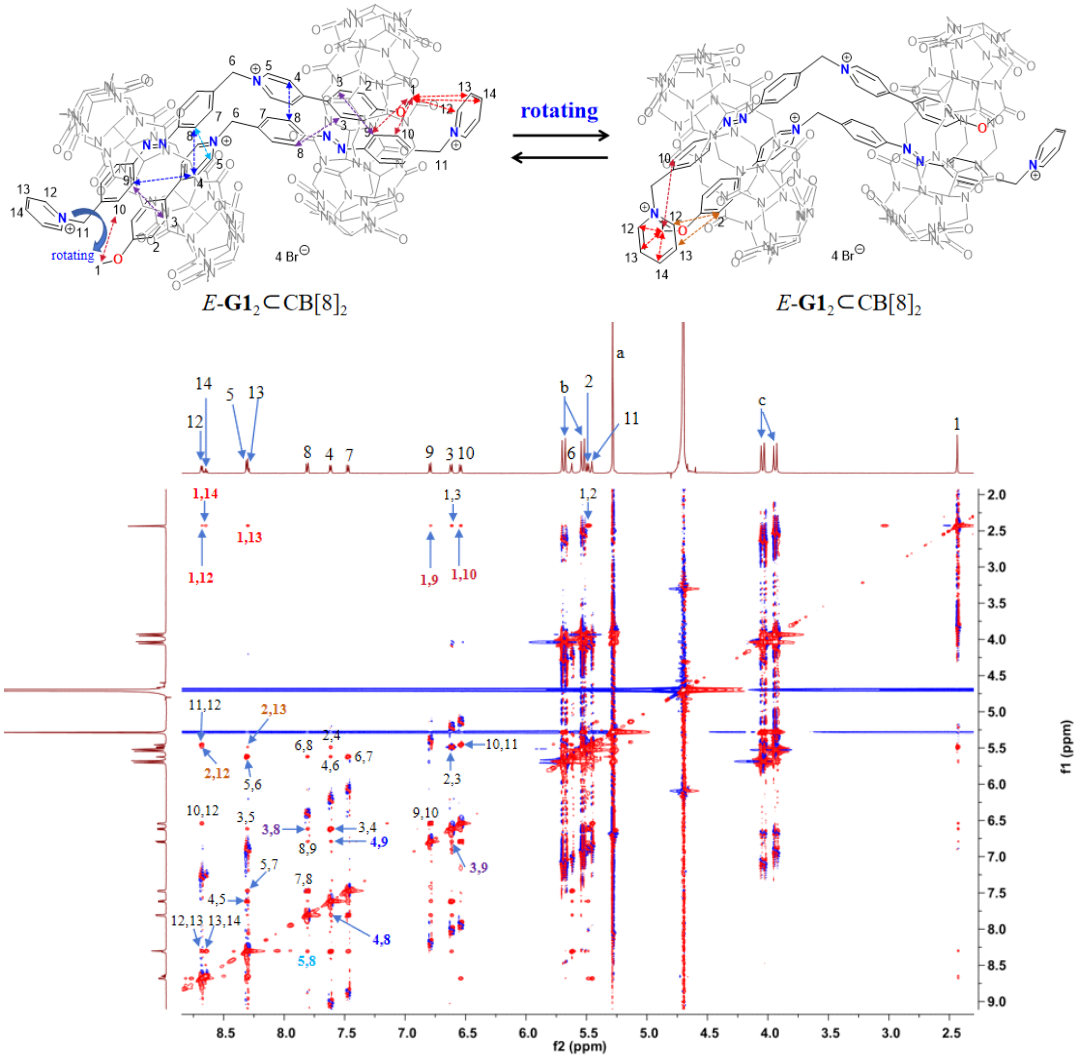


Fig. S3 The 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G1** and CB[8] (2:2, 10 mM).

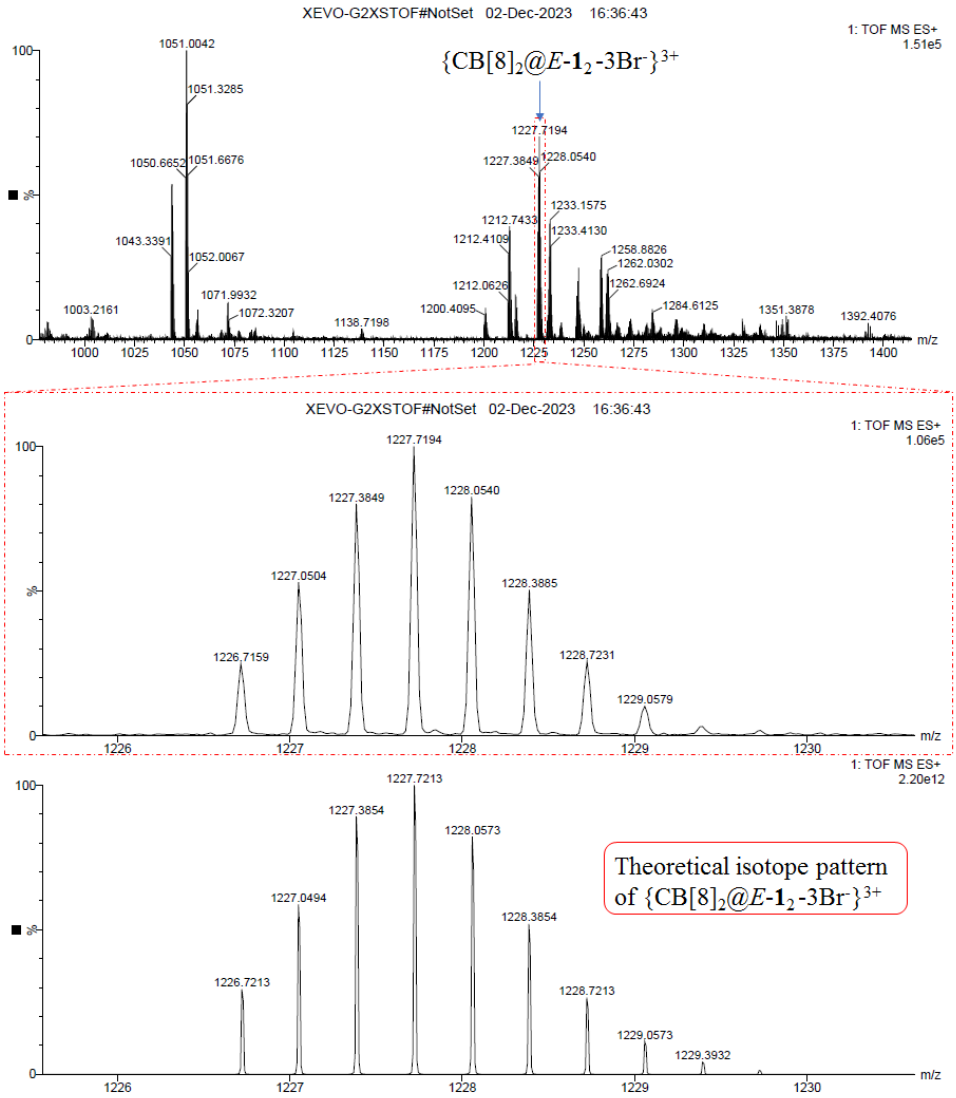


Fig. S4 The high-resolution ESI-mass spectrum of the host-guest complex formed between *E*-**G1** and CB[8] (2:2).

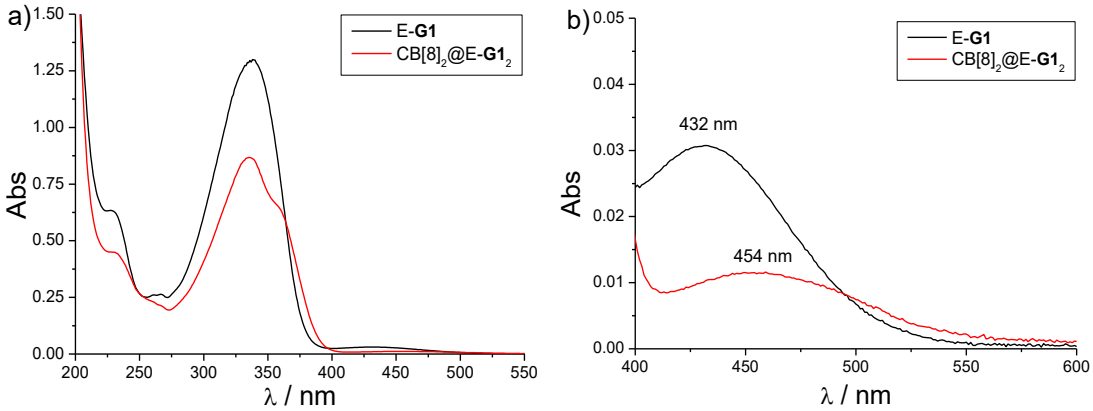


Fig.S5 The UV-Vis absorption spectra for *E*-**G1** (0.025 mM) (black line), and the mixture of *E*-**G1** and CB[8] (2:2, 0.025 mM) (red line) in H_2O at 25 °C.

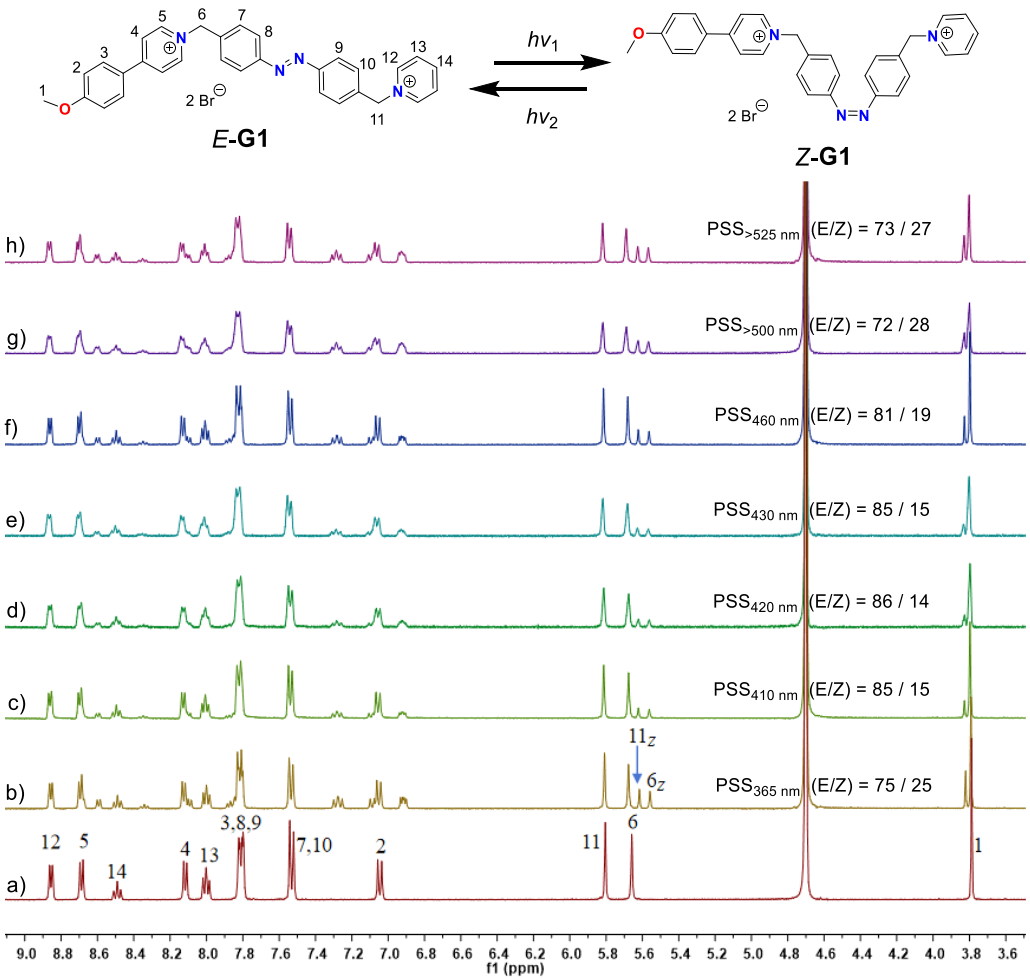


Fig.S6 Partial ^{1}H NMR spectra (400 MHz, D_2O, 5 mM, 298K) of **G1** recorded under conditions of a) before, and b) to h) after irradiation by light sources with different wavelengths.

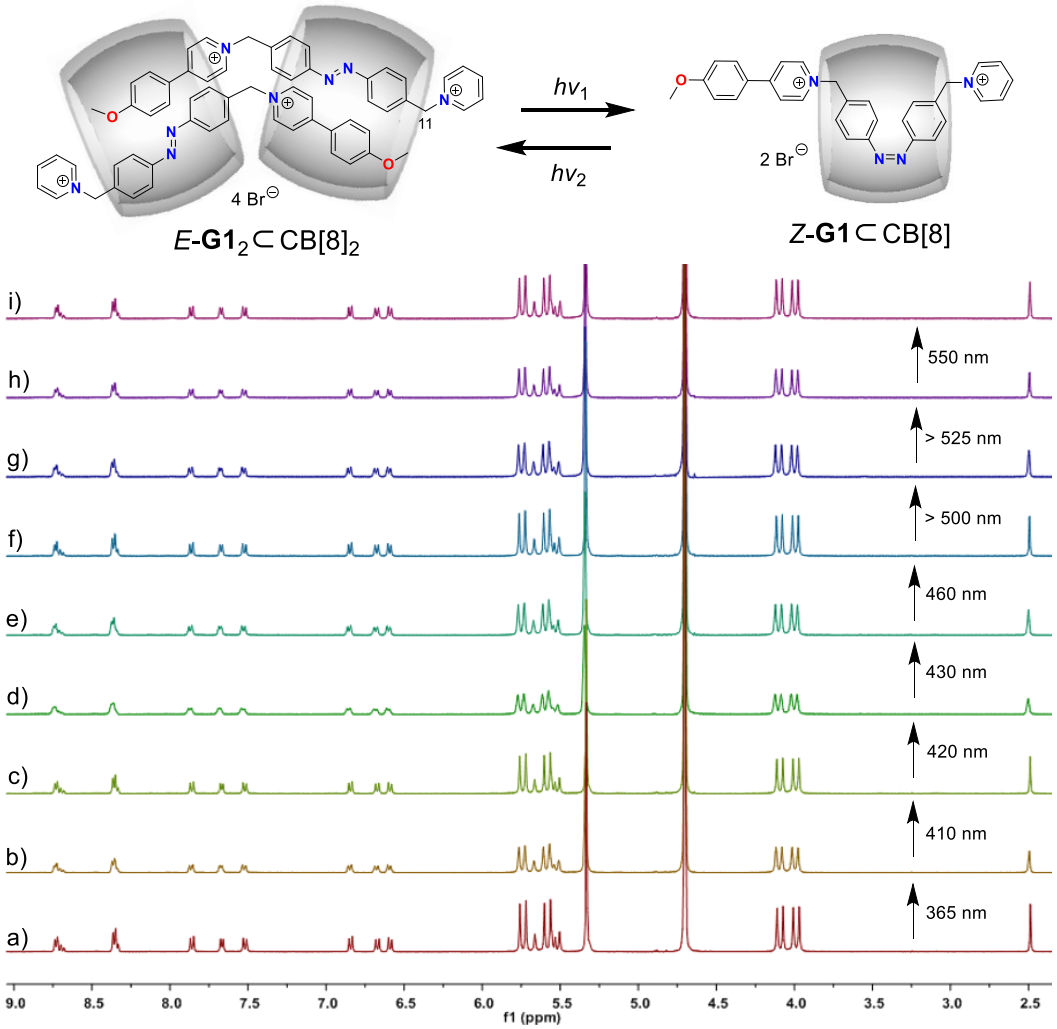


Fig.S7 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298K) for the mixture of *E*-**G1** and CB[8] (2:2, 5.0 mM) recorded under conditions of a) before, and b) to i) after irradiation by light sources with different wavelengths.

Section 4: The photocontrolled complexation behavior of G2 and CB[8]

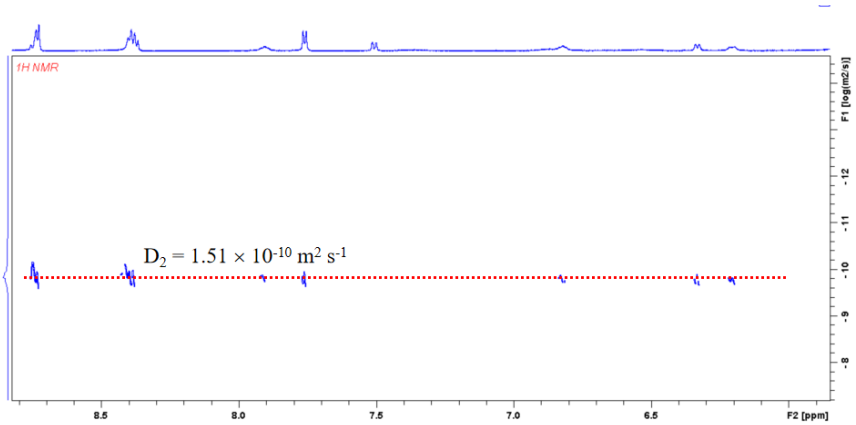


Fig. S8 The 2D DOSY-NMR NMR spectrum (600 MHz, D_2O, 298 K) for the solution of the mixture of *E*-**G2** and CB[8] (2:2, 5.0 mM)

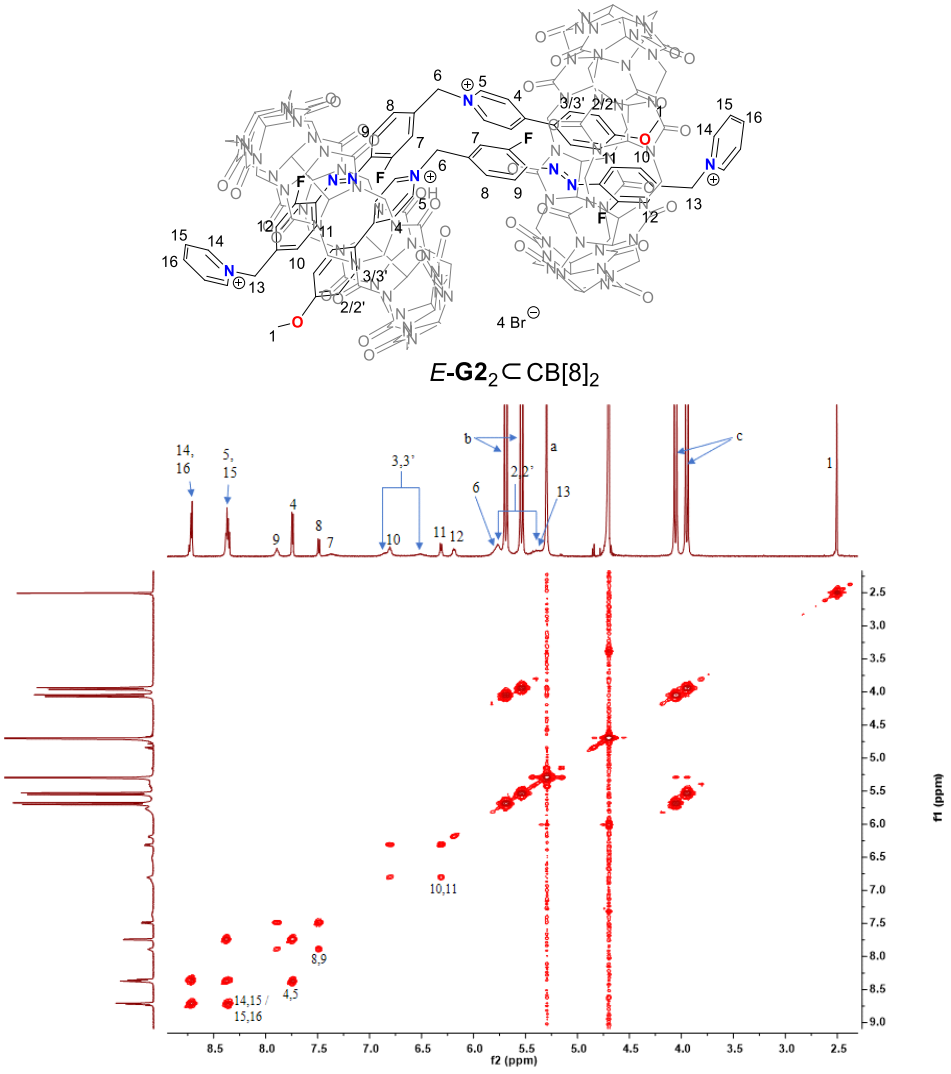


Fig. S9 The 2D COSY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G2** and CB[8] (2:2, 10 mM).

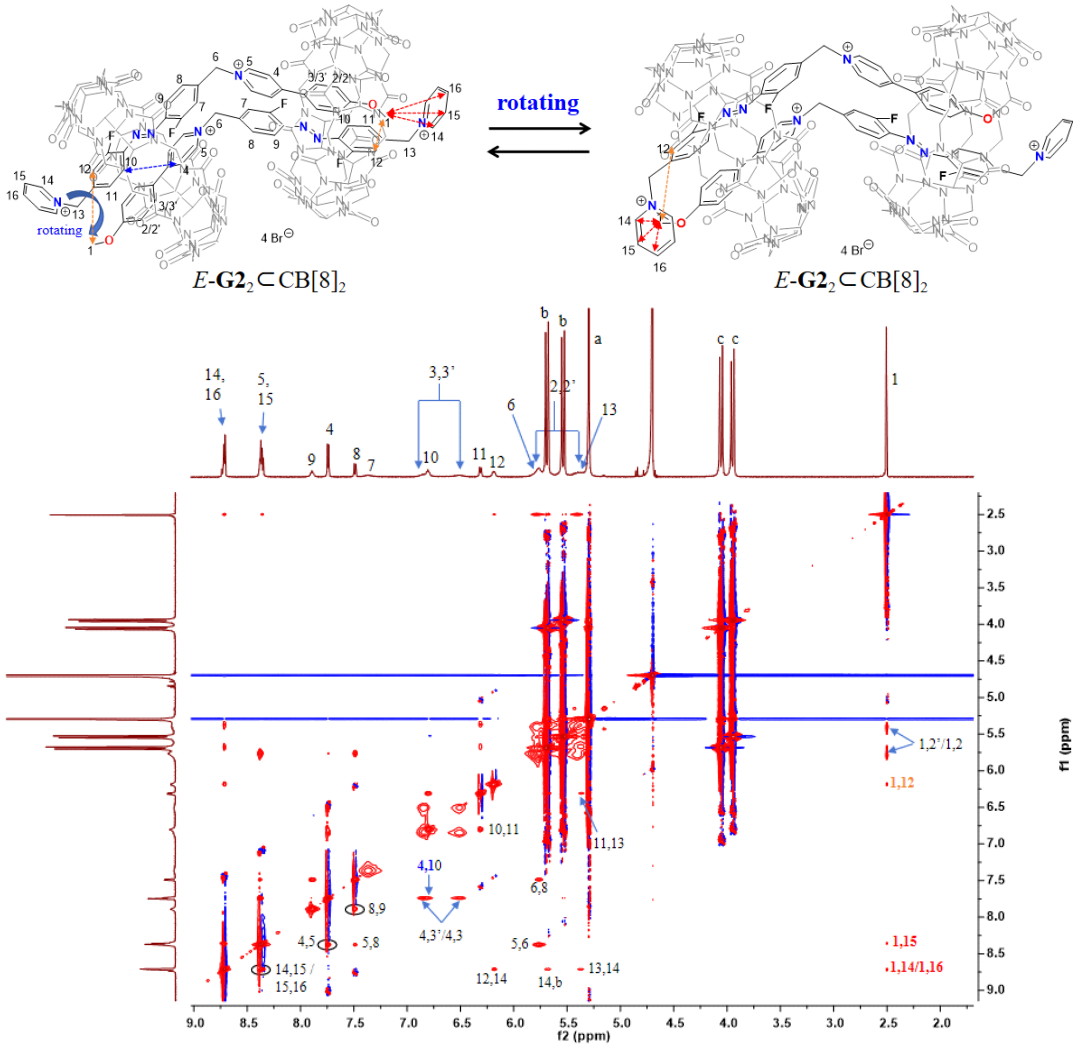


Fig. S10 The schematic structural representation for the 2:2 host-guest complex *E*-**G2**$_2$⊂CB[8]$_2$ with heat-to-tail encapsulated *E*-**G2**, and the 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G2** and CB[8] (2:2, 10 mM).

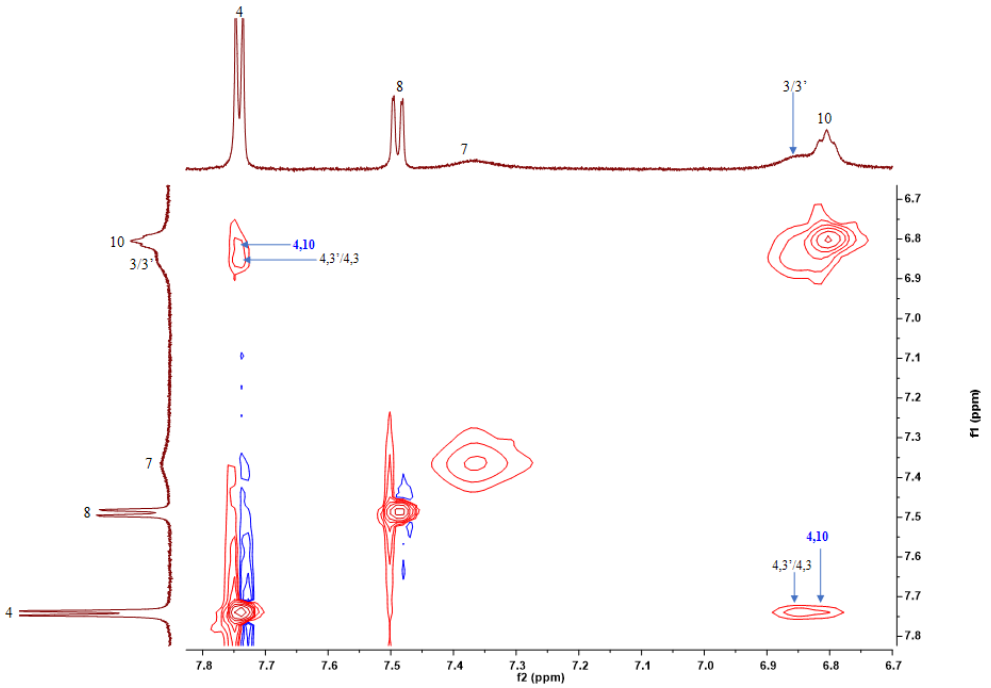


Fig. S11 Partial 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G2** and CB[8] (2:2, 10 mM).

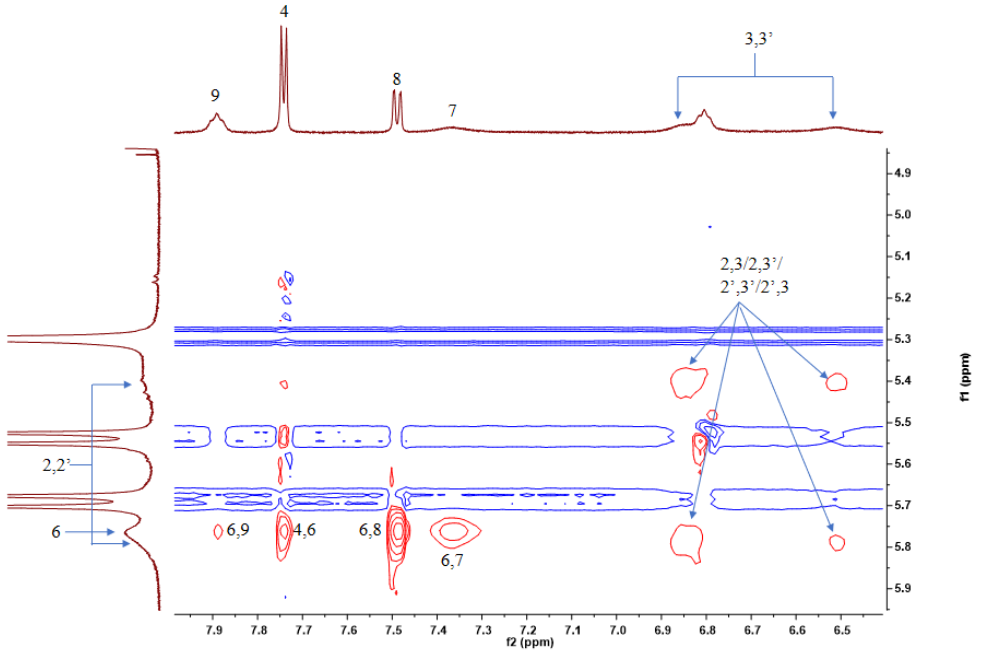


Fig. S12 Partial 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G2** and CB[8] (2:2, 10 mM).

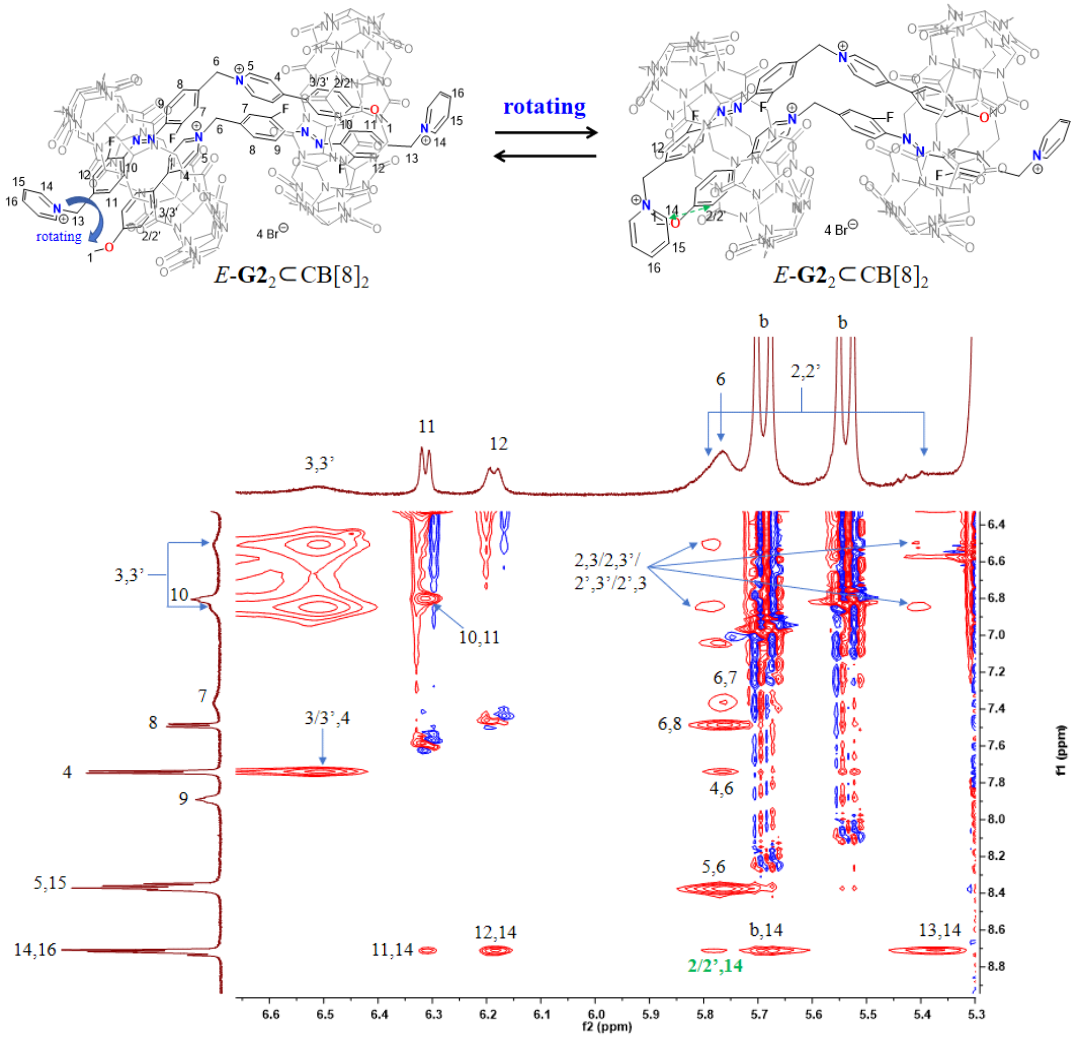


Fig. S13 Partial 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G2** and CB[8] (2:2, 10 mM).

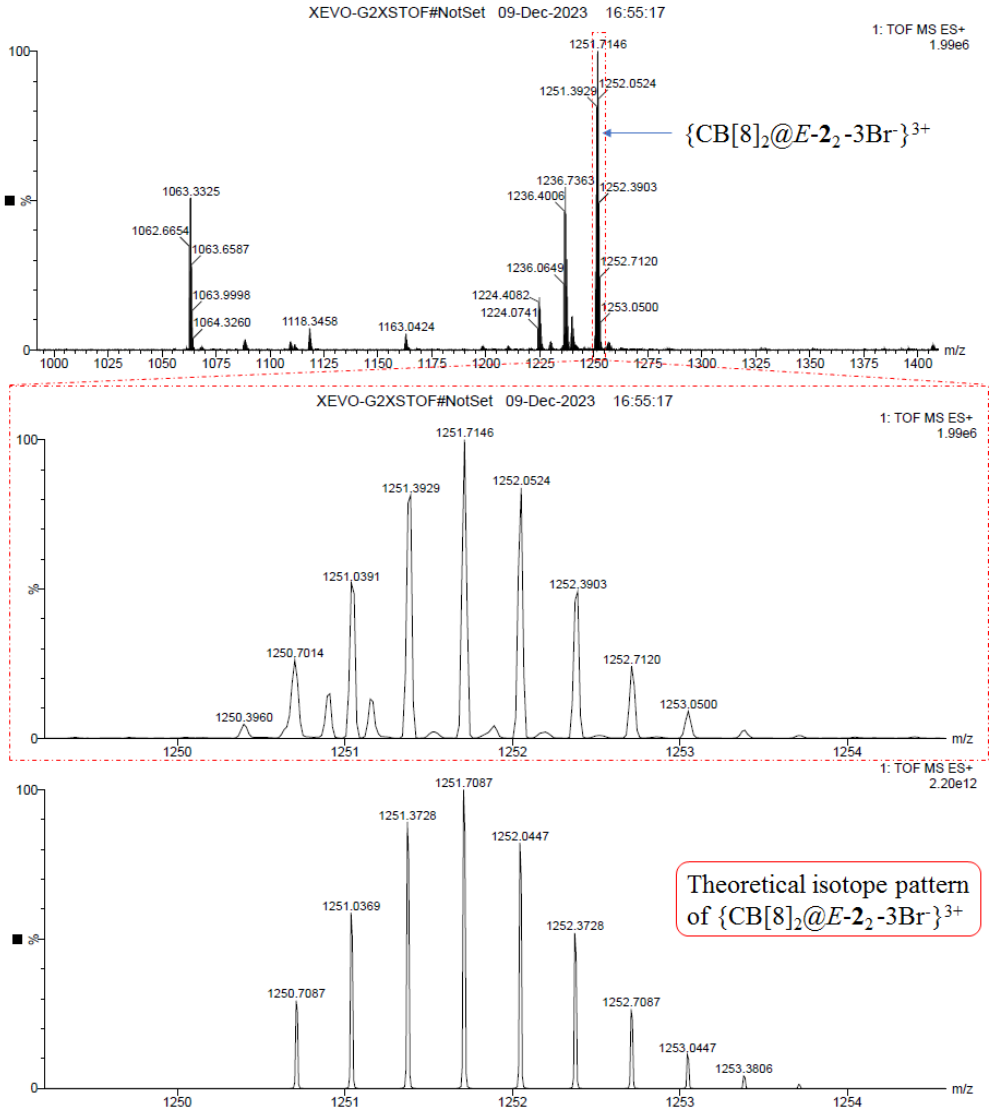


Fig. S14 The high-resolution ESI-mass spectrum of the host-guest complex formed between *E*-**G2** and CB[8] (2:2).

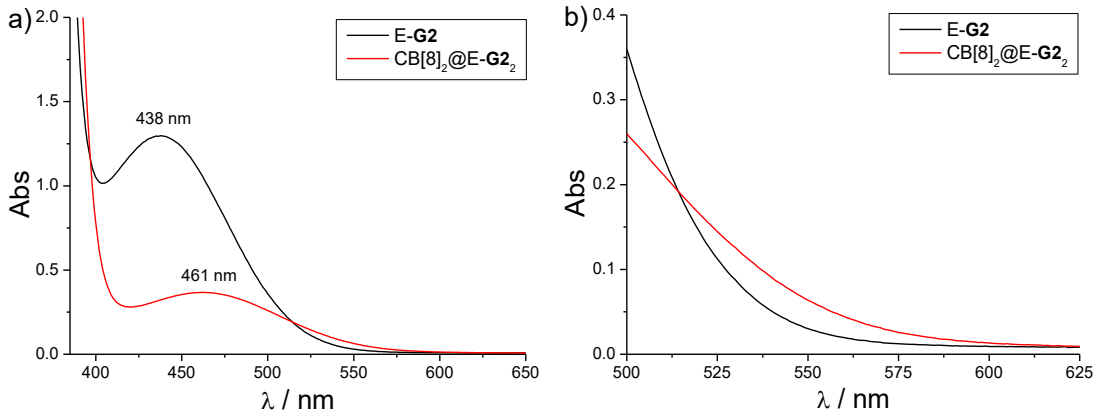


Fig.S15 The UV-Vis absorption spectra for *E*-**G2** (1.0 mM) (black line), and the mixture of *E*-**G2** and CB[8] (2:2, 1.0 mM) (red line) in H_2O at 25 °C.

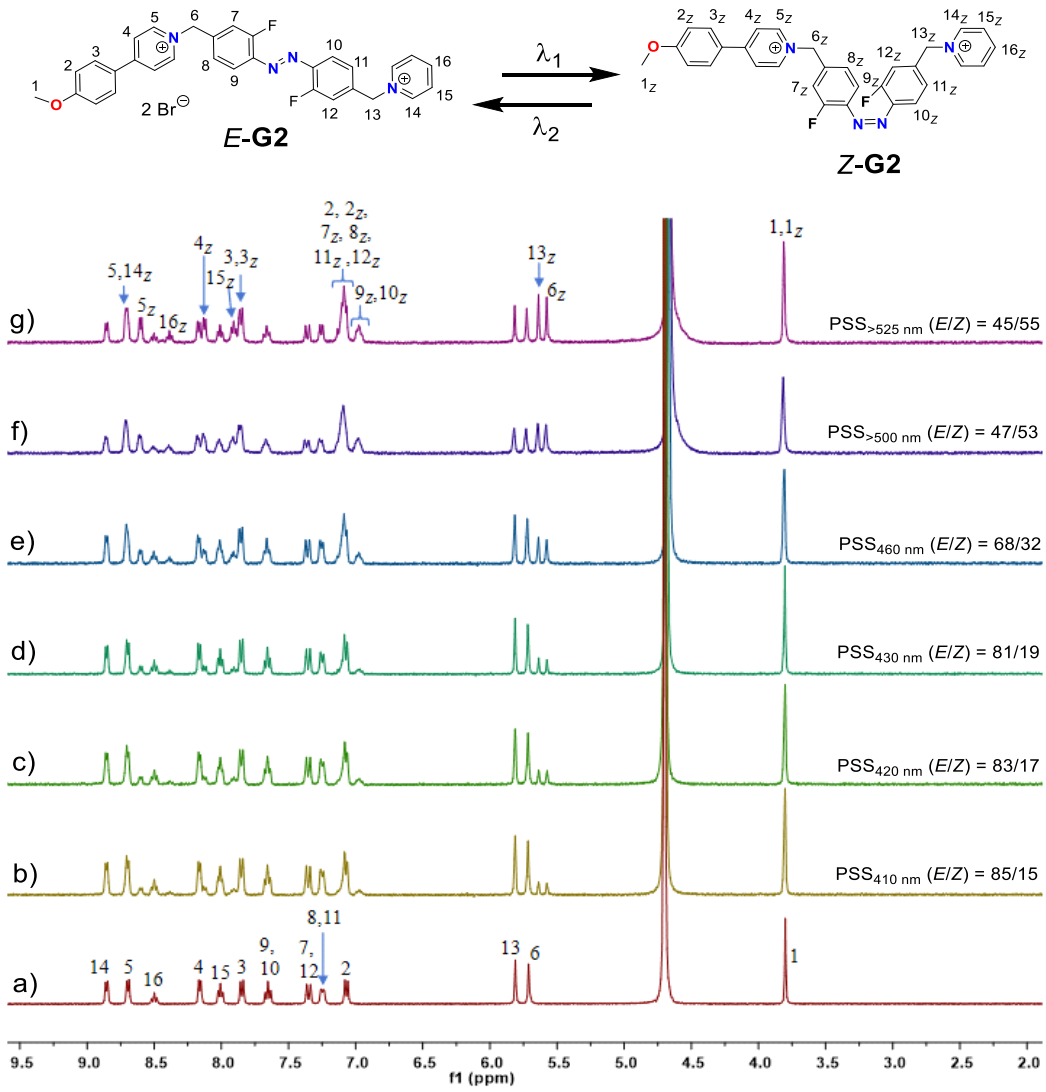


Fig.S16 Partial ^{1}H NMR spectra (400 MHz, D_2O, 5 mM, 298K) of **G2** recorded under conditions of a) before, and b) to g) after irradiation by light sources with different wavelengths.

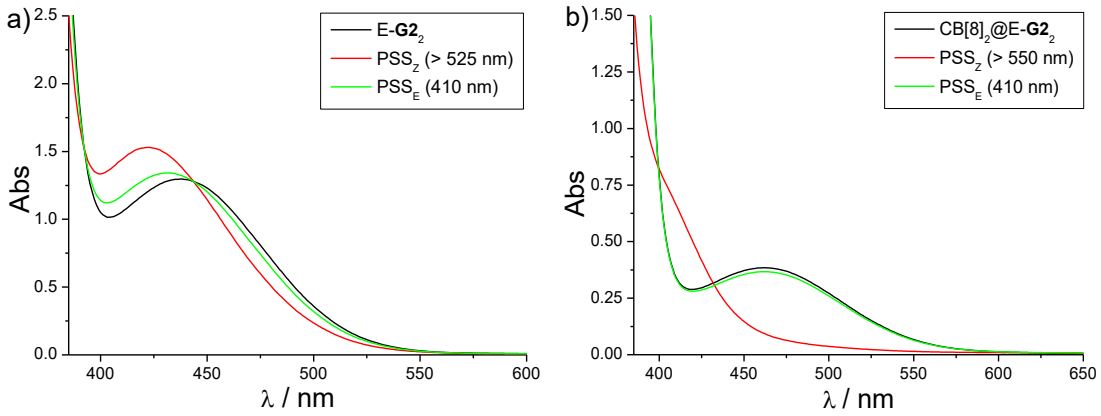


Fig.S17 The UV-Vis absorption spectra for a) *E*-**G2** (1.0 mM) and b) the mixture of *E*-**G2** and CB[8] (2:2, 1.0 mM) under conditions of before light irradiation (black line) and after irradiated by light sources with different wavelengths (red line and green line) in H_2O at 25 °C.

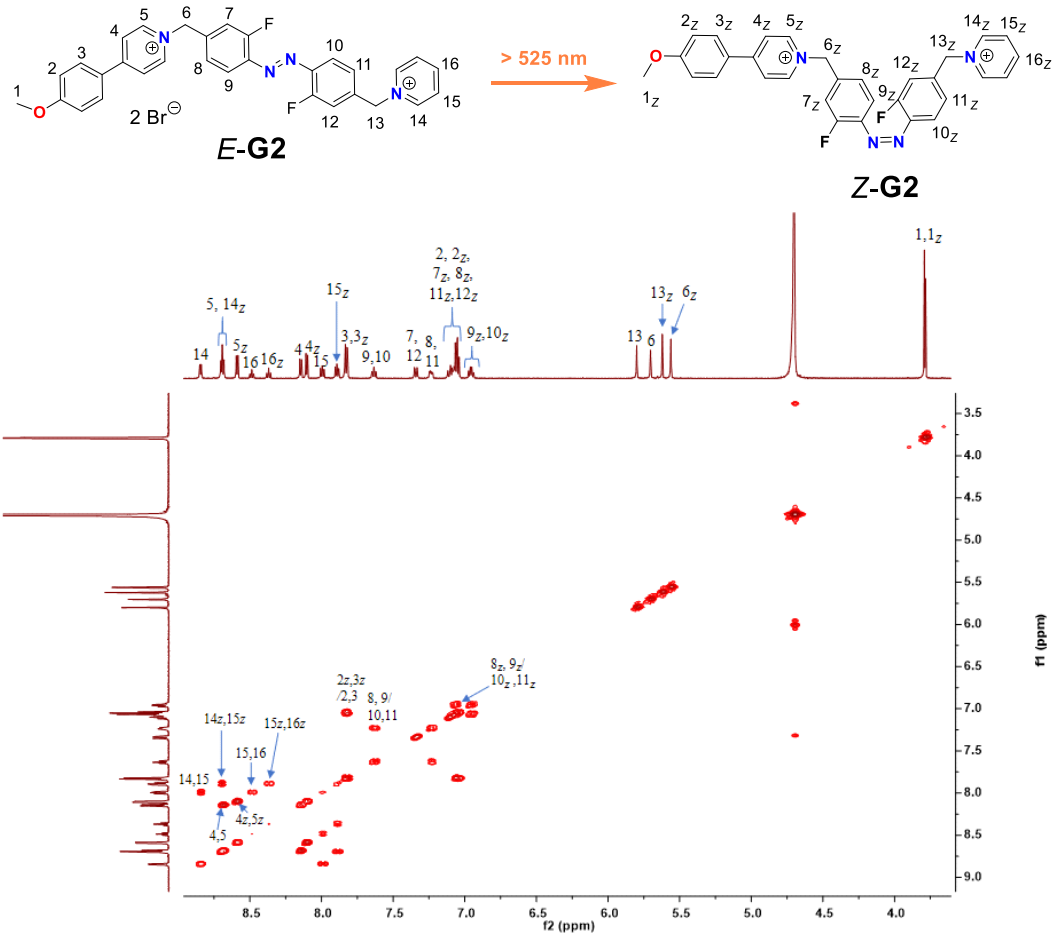


Fig.S18 The 2D COSY NMR spectrum (600 MHz, D_2O, 298 K) for the PSS_Z (> 525 nm) mixtures of **G2** (5.0 mM).

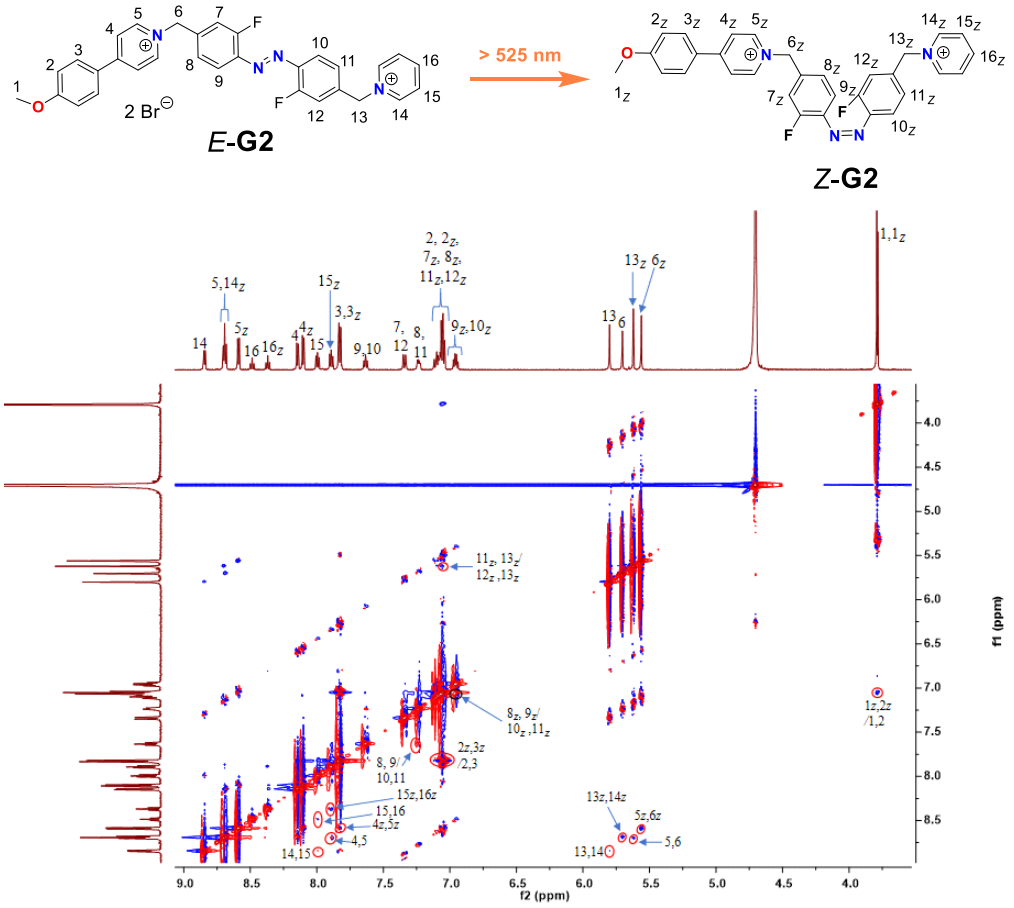


Fig.S19 The 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the PSS_Z (> 525 nm) mixtures of **G2** (5.0 mM).

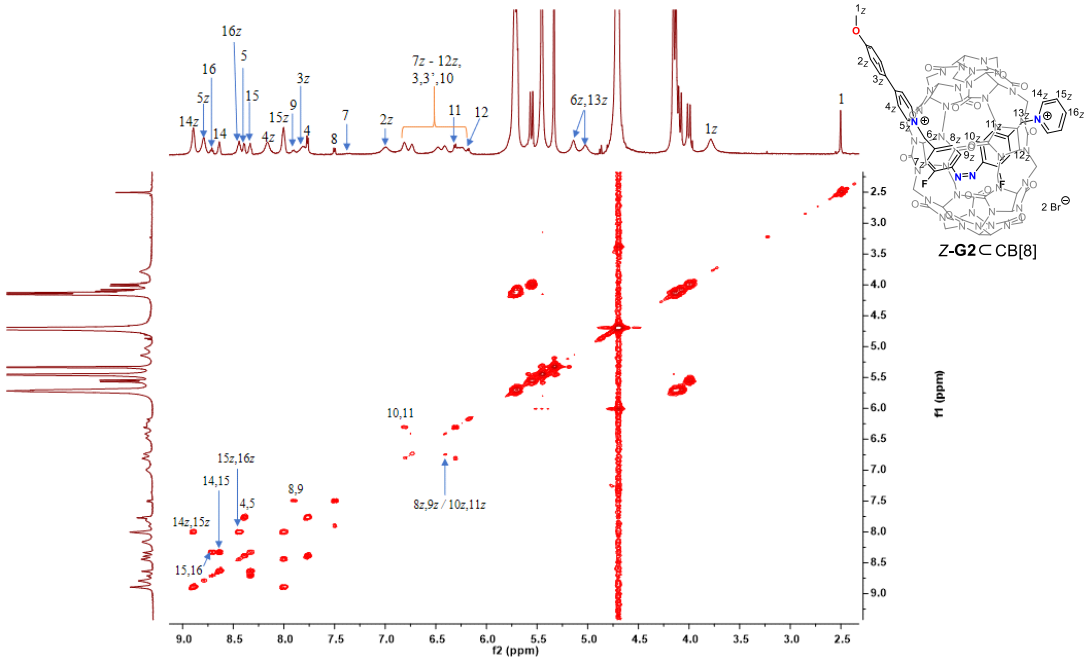


Fig.S20 The 2D COSY NMR spectrum (600 MHz, D_2O, 298 K) for the PSS_Z (> 550 nm) mixtures of **G2** and CB[8] (2:2, 5.0 mM).

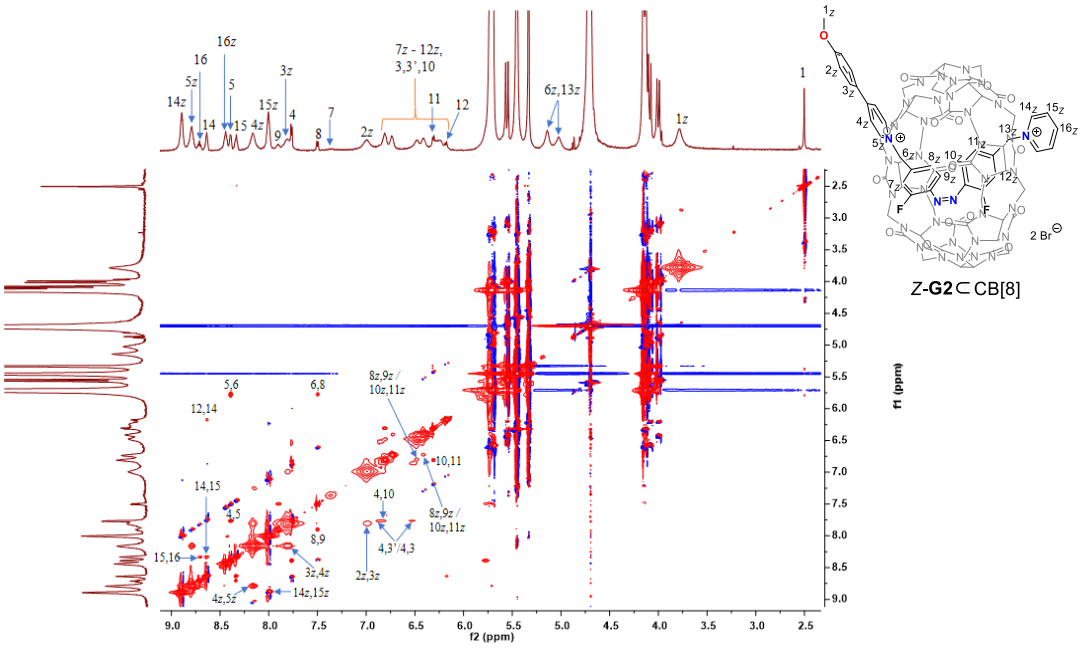


Fig.S21 The 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the PSS_Z (> 550 nm) mixtures of **G2** and CB[8] (2:2, 5.0 mM).

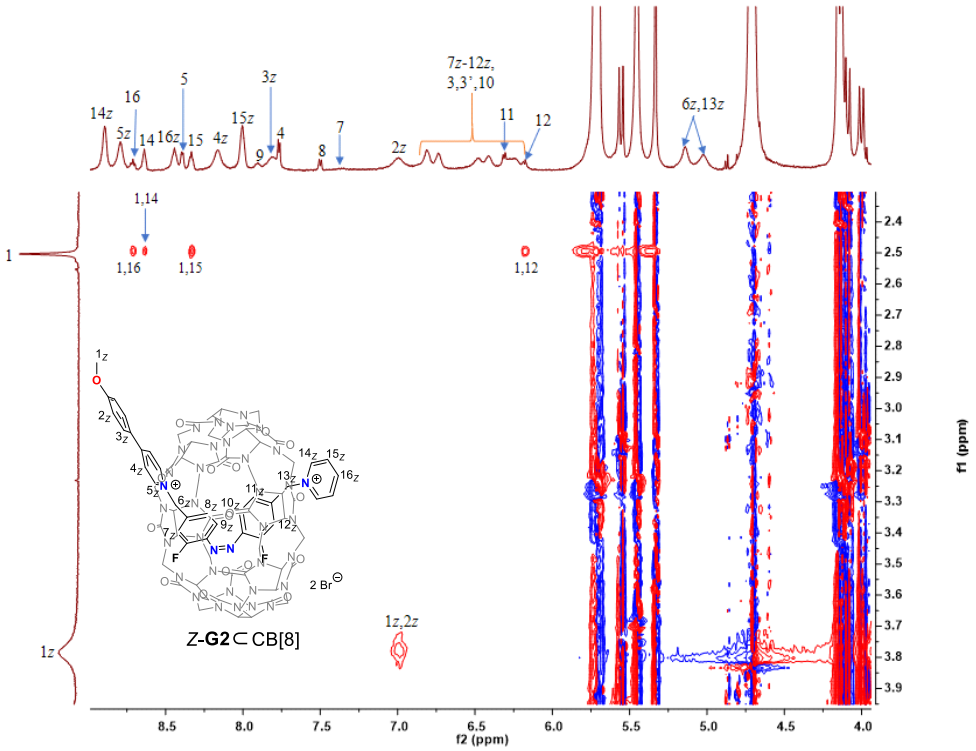


Fig.S22 Partial 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the PSS_Z (> 550 nm) mixtures of **G2** and CB[8] (2:2, 5.0 mM).

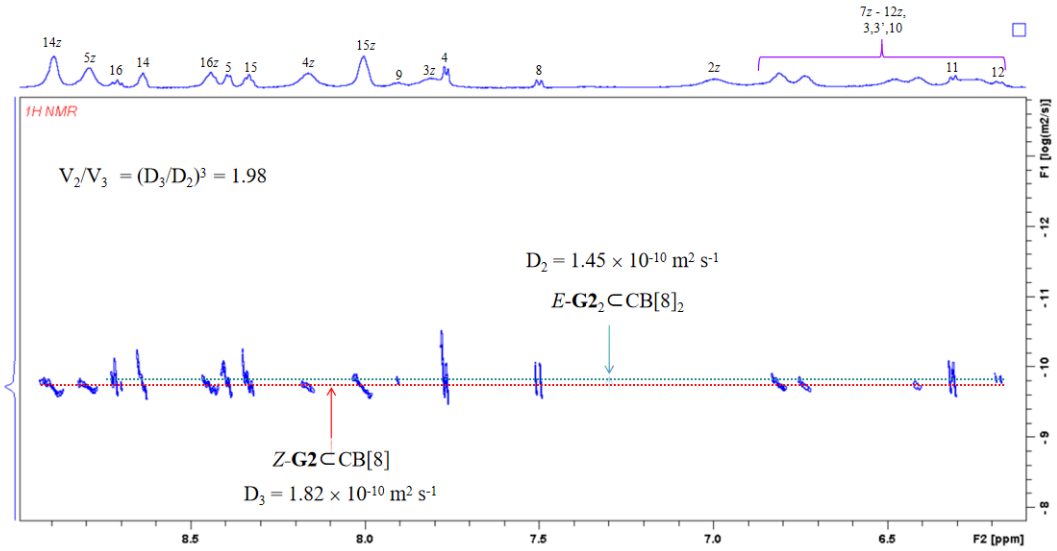


Fig.S23 The 2D DOSY NMR spectrum (600 MHz, D_2O, 298 K) for the PSS_Z (> 550 nm) mixtures of **G2** and CB[8] (2:2, 5.0 mM).

Section 5: The photocontrolled complexation behavior of G3 and CB[8]

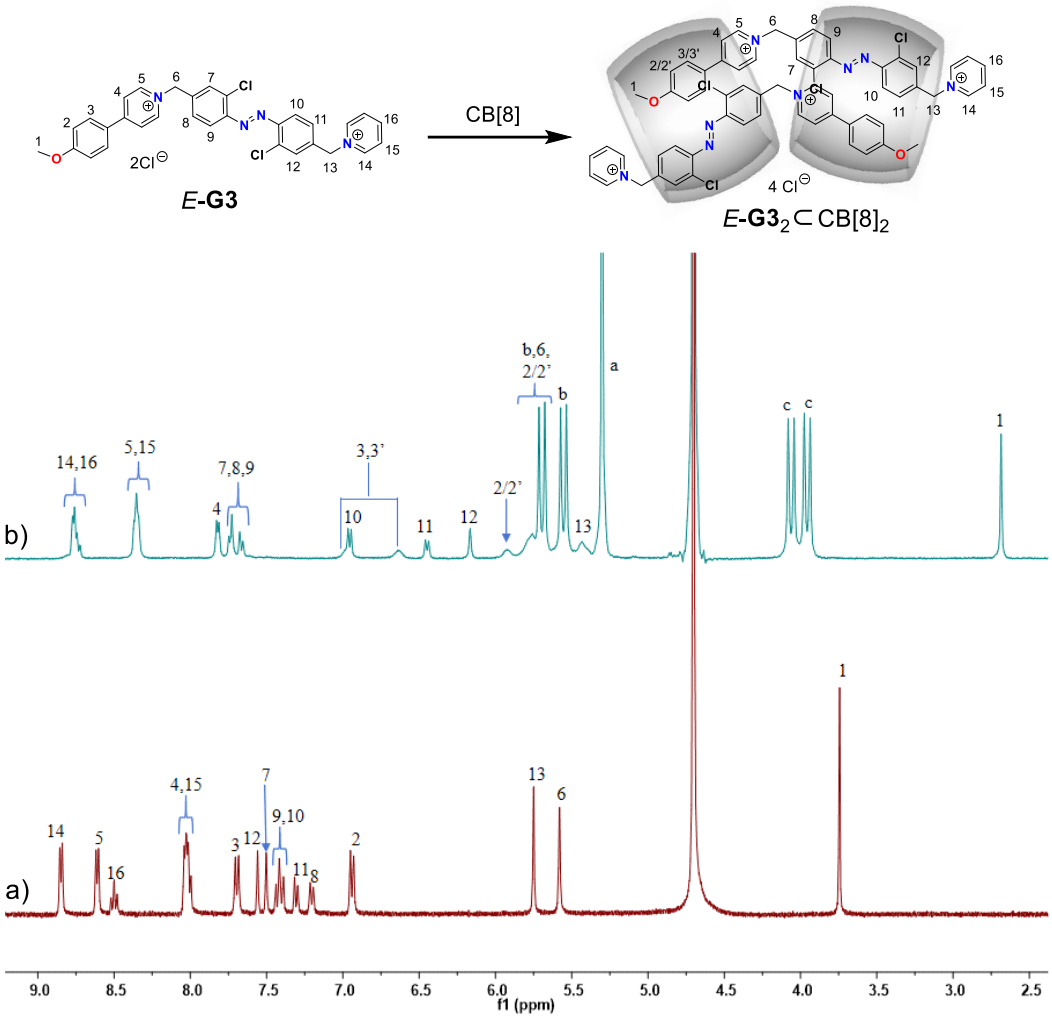


Fig.S24 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) for the solution of a) *E*-**G3** (5.0 mM), and b) the mixture of *E*-**G3** and CB[8] (2:2, 5.0 mM).

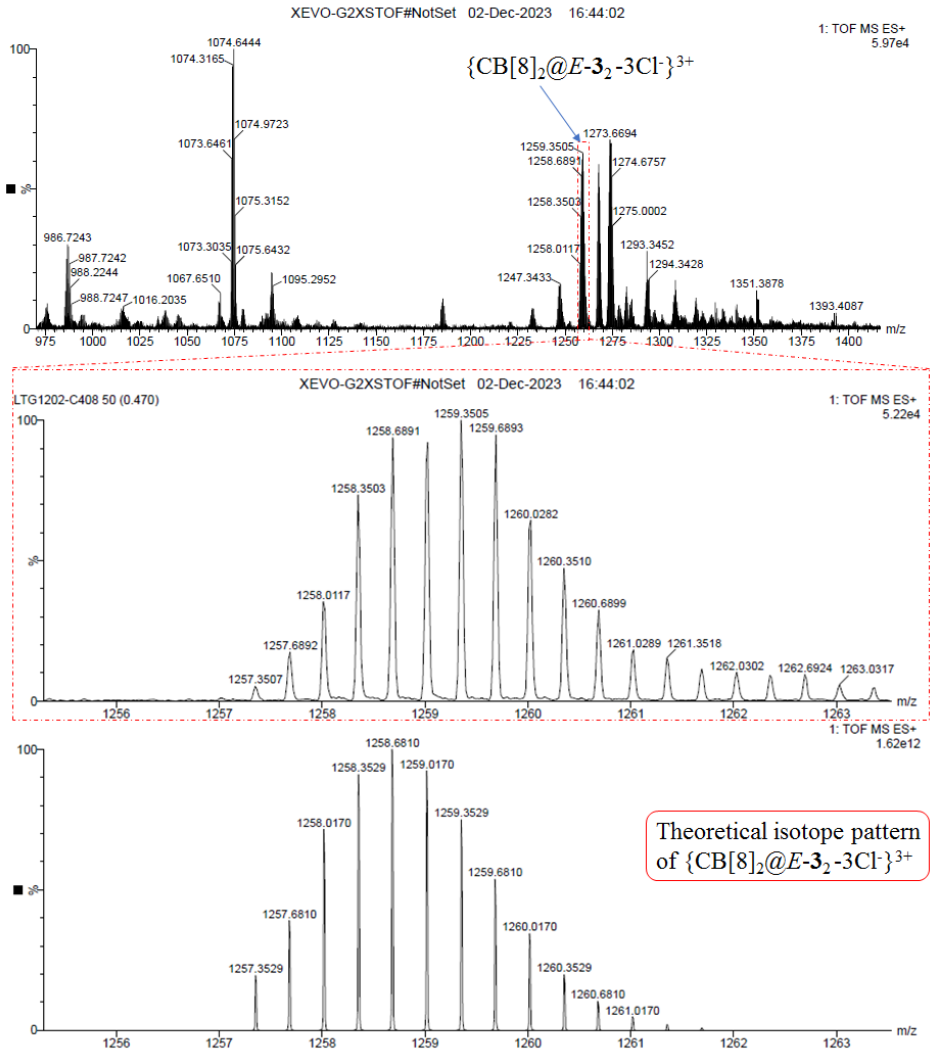


Fig. S25 The high-resolution ESI-mass spectrum of the host-guest complex formed between *E*-**G3** and CB[8] (2:2).

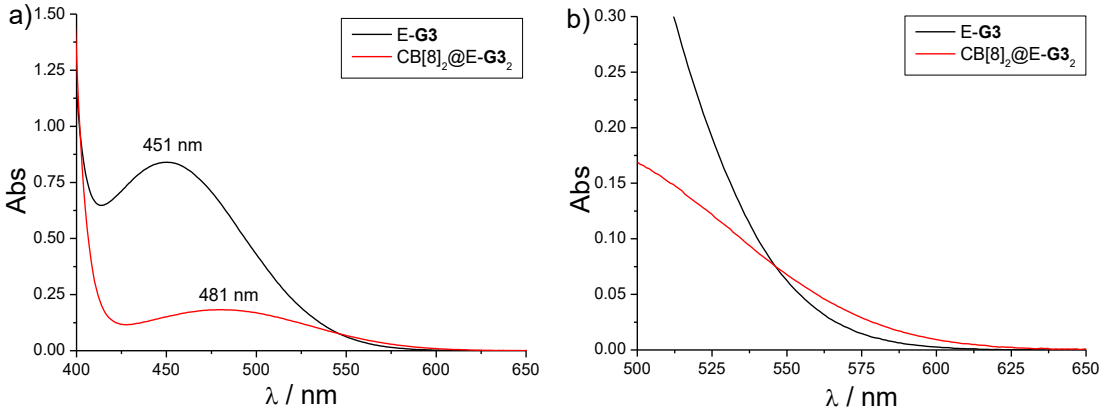


Fig.S26 The UV/Vis absorption spectra of *E*-**G3** (1.0 mM) (black line), and the mixture of *E*-**G3** and CB[8] (2:2, 1.0 mM) (red line) in H_2O at 25 °C.

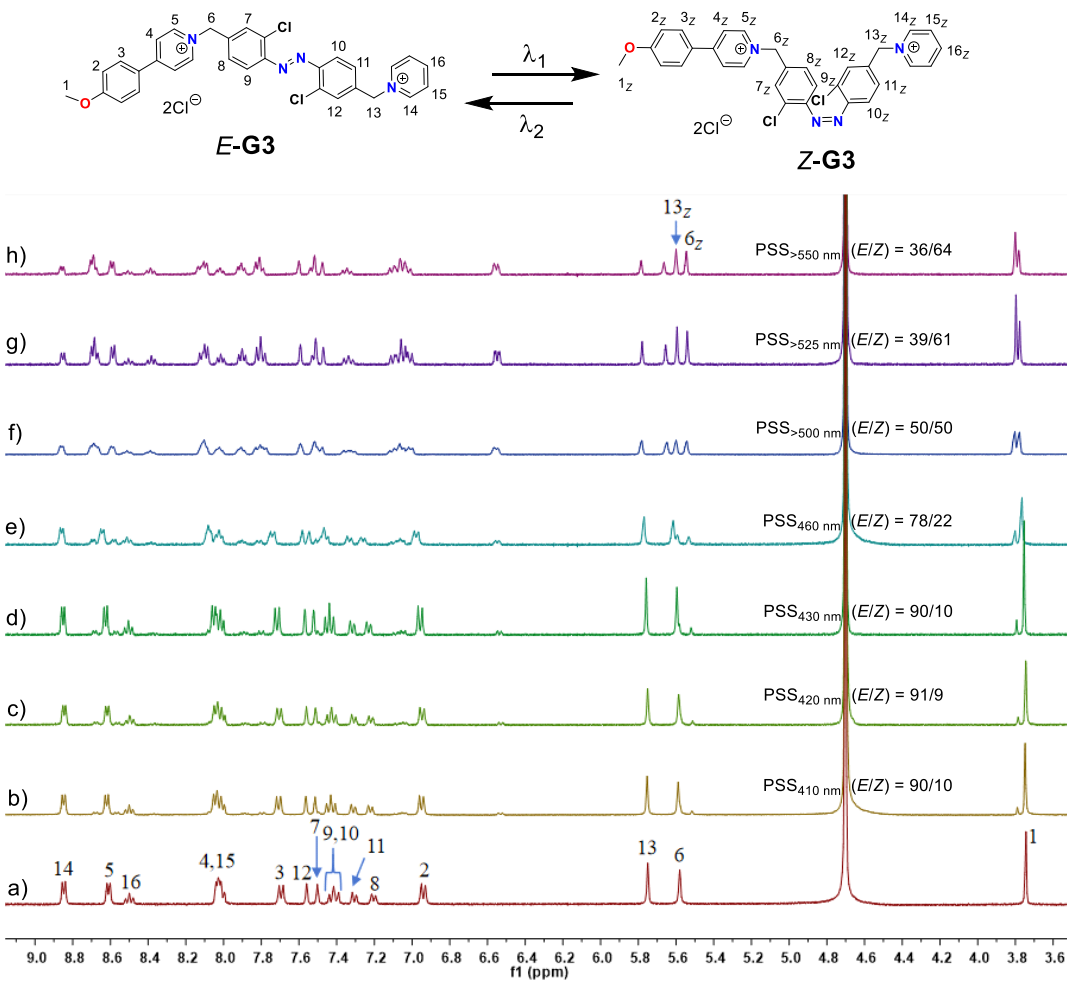


Fig.S27 Partial ^{1}H NMR spectra (400 MHz, D_2O, 5 mM, 298K) of **G3** recorded under conditions of a) before, and b) to h) after irradiation by light sources with different wavelengths.

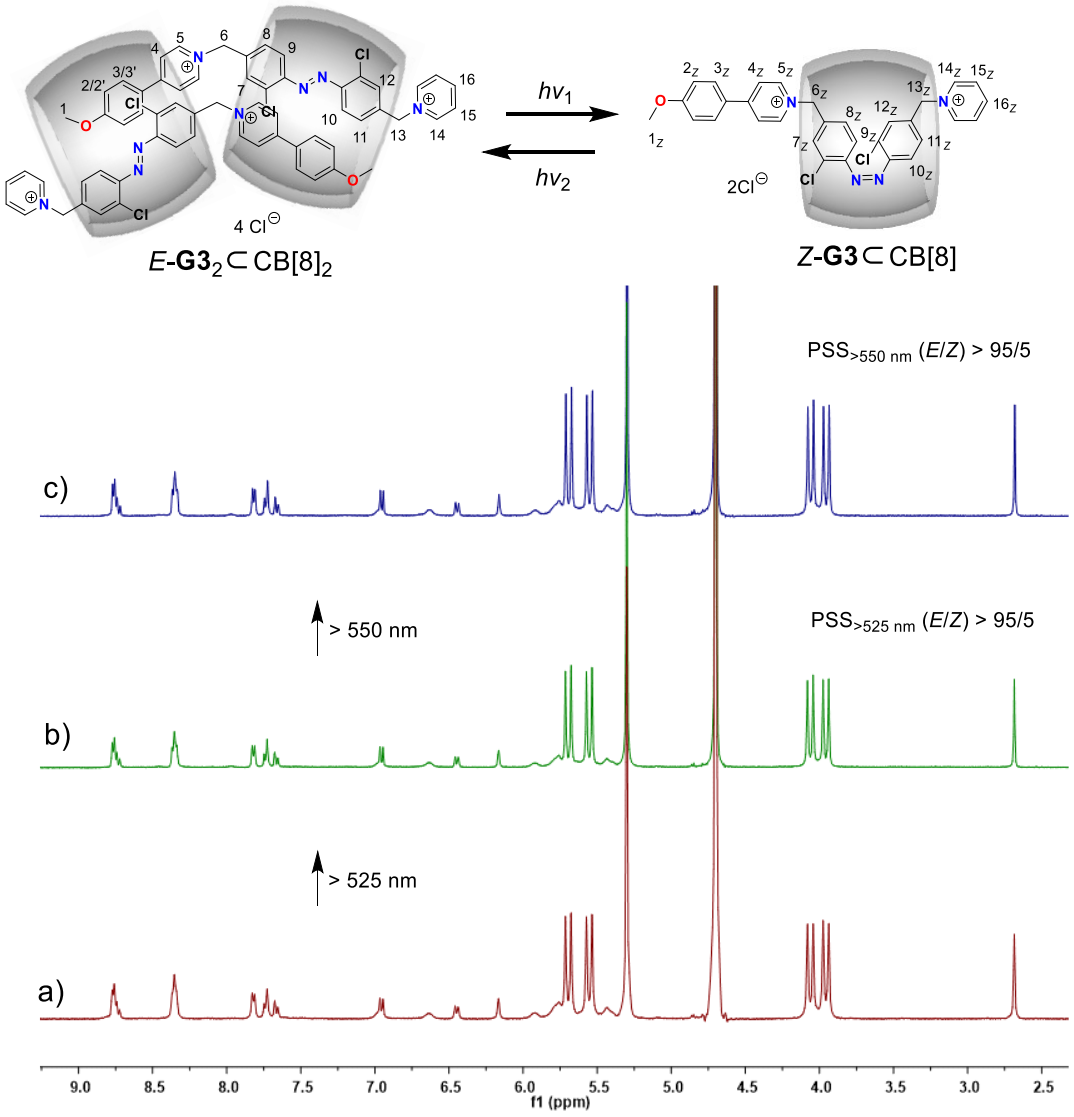


Fig.S28 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298K) of *E*-**G3** and CB[8] (2:2, 5.0 mM) recorded under conditions of a) before, and b) to c) after irradiation by light sources with different wavelengths.

Section 6: The photocontrolled complexation behavior of G4 and CB[8]

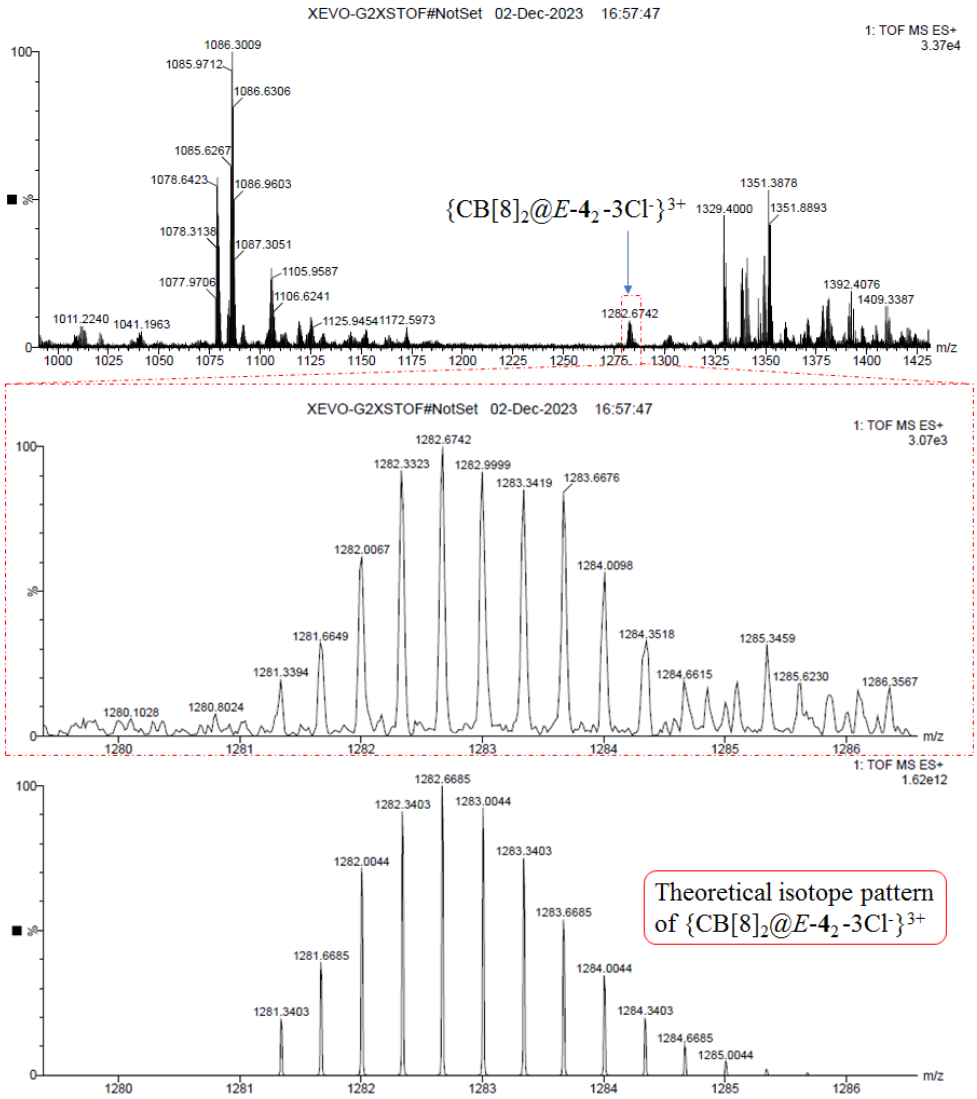


Fig. S29 The high-resolution ESI-mass spectrum of the host-guest complex formed between *E*-**G4** and CB[8] (2:2).

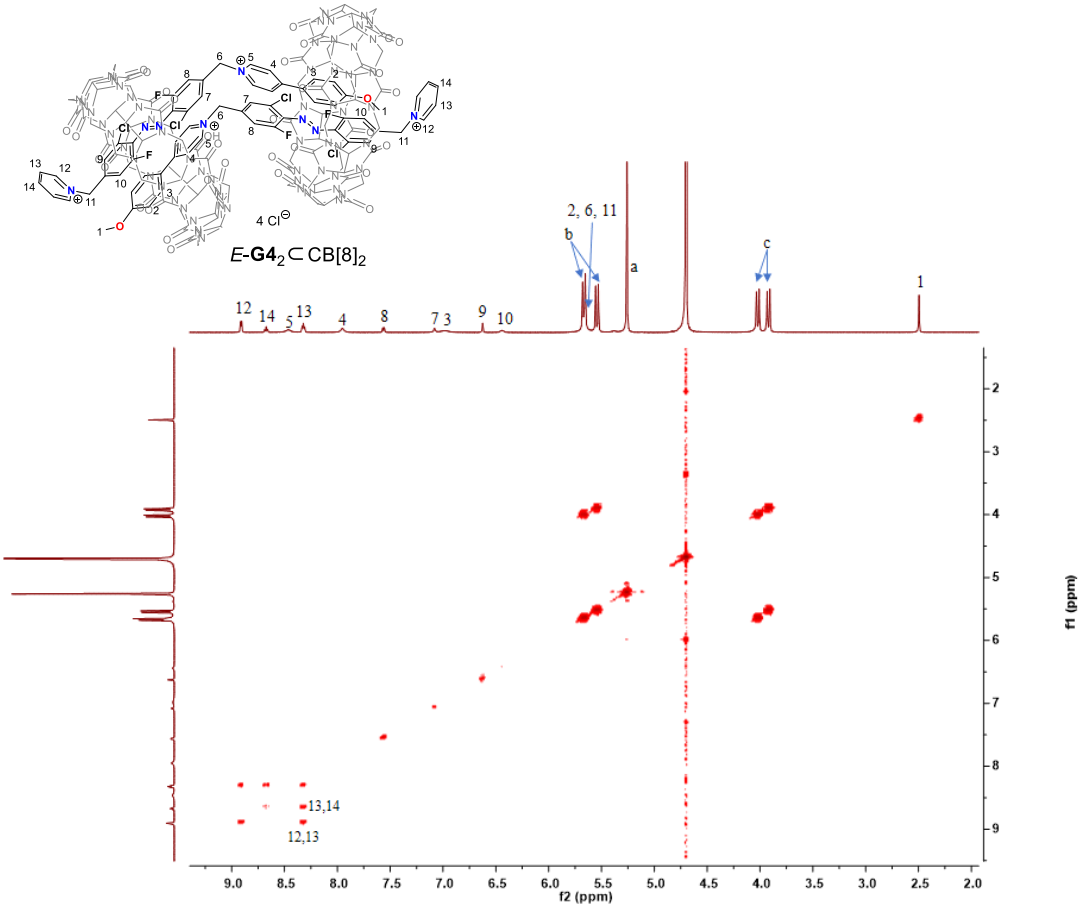


Fig. S30 The 2D COSY spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G4** and CB[8] (2:2, 5.0 mM).

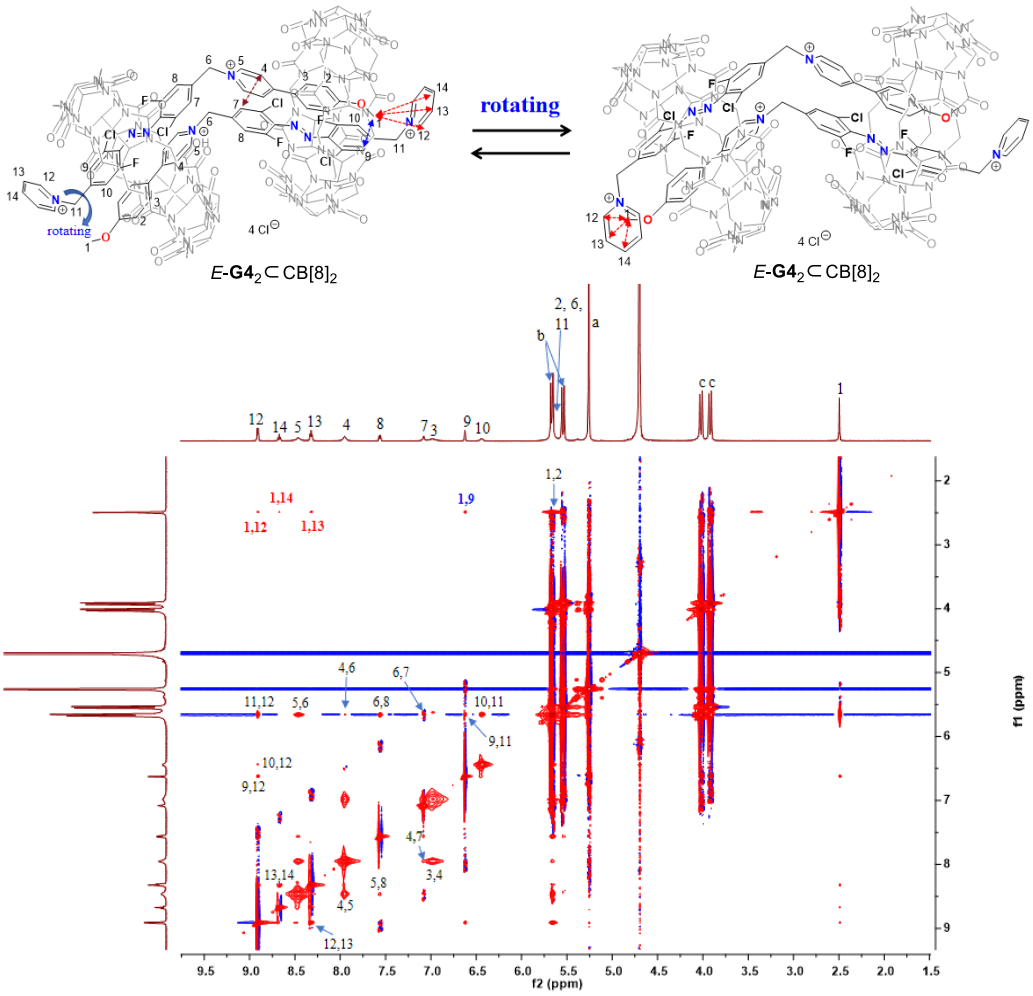


Fig. S31 The 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G4** and CB[8] (2:2, 5.0 mM).

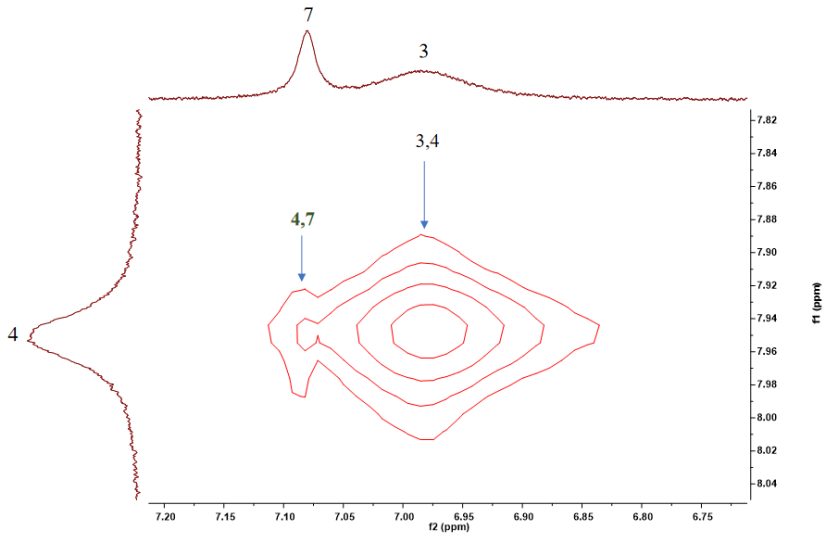


Fig. S32 Partial 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G4** and CB[8] (2:2, 5.0 mM).

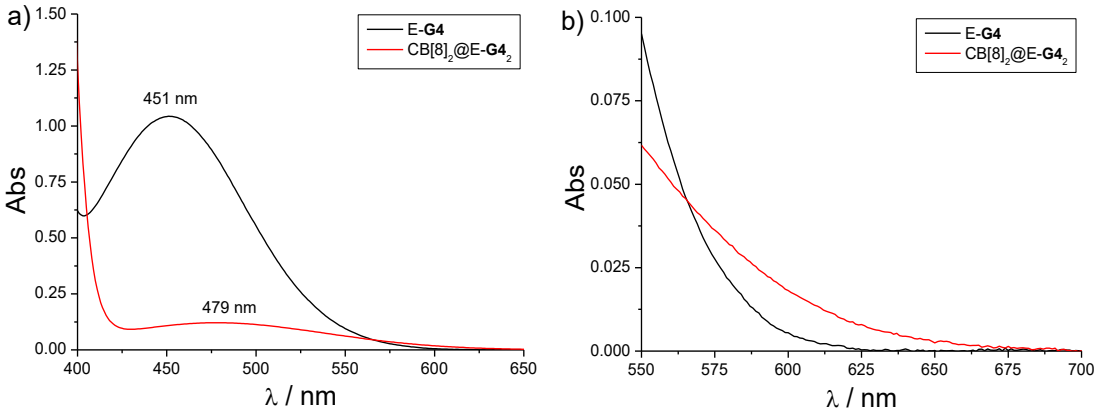


Fig.S33 The UV/Vis absorption spectra of *E*-**G4** (1.0 mM) (black line), and the mixture of *E*-**G4** and CB[8] (2:2, 1.0 mM) (red line) in H_2O at 25 °C.

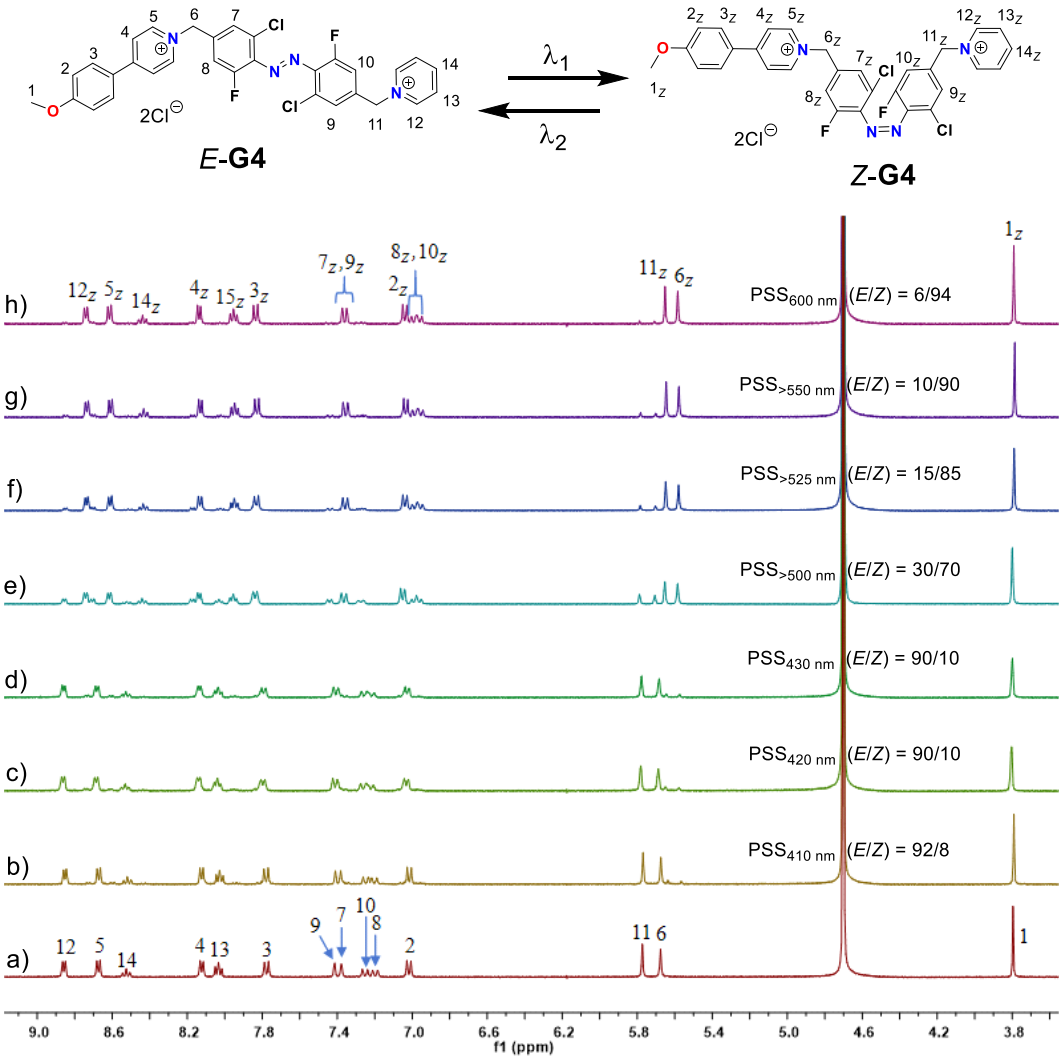


Fig.S34 Partial ^{1}H NMR spectra (400 MHz, D_2O, 5 mM, 298K) of **G4** recorded under conditions of a) before, and b) to h) after irradiation by light sources with different wavelengths.

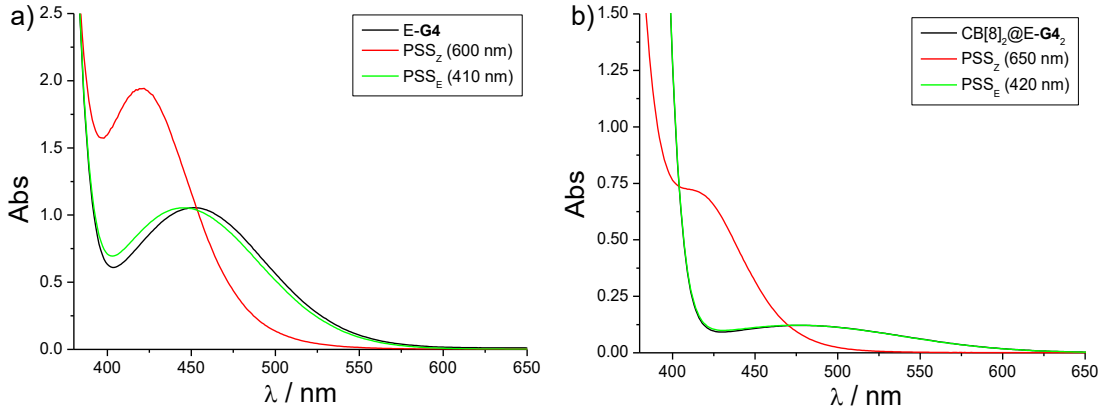


Fig.S35 The UV/Vis absorption spectra for a) *E*-**G4** (1.0 mM) and b) the mixture of *E*-**G4** and CB[8] (2:2, 1.0 mM) under conditions of before (black line) and after irradiation by light sources with different wavelengths (red line and green line) in H_2O at 25 ºC.

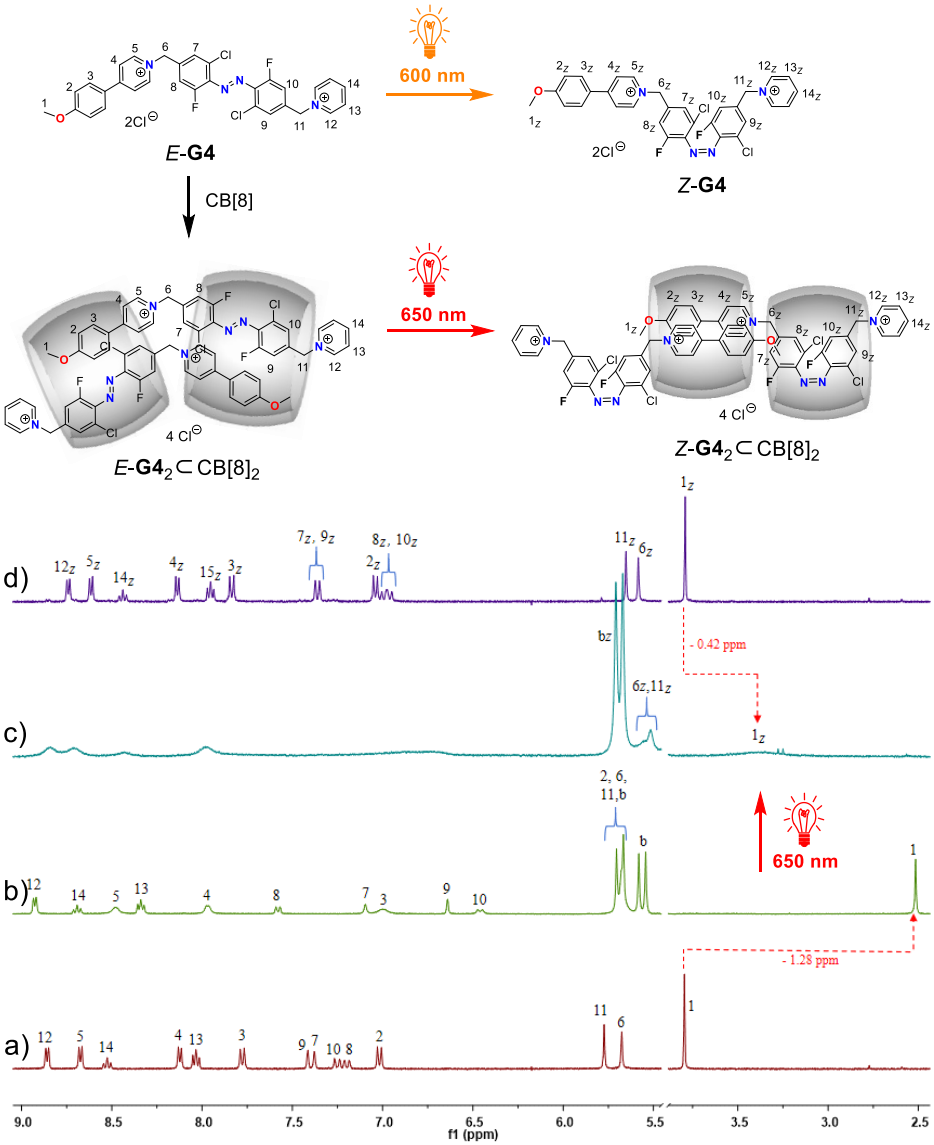


Fig. S36 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) for the solution of *E*-**G4** (5.0 mM) under conditions of a) before and d) after irradiation by orange light (600 nm), as well as for the mixture of *E*-**G4** and CB[8] (2:2, 5.0 mM) b) before and c) after irradiation by red light (650 nm).

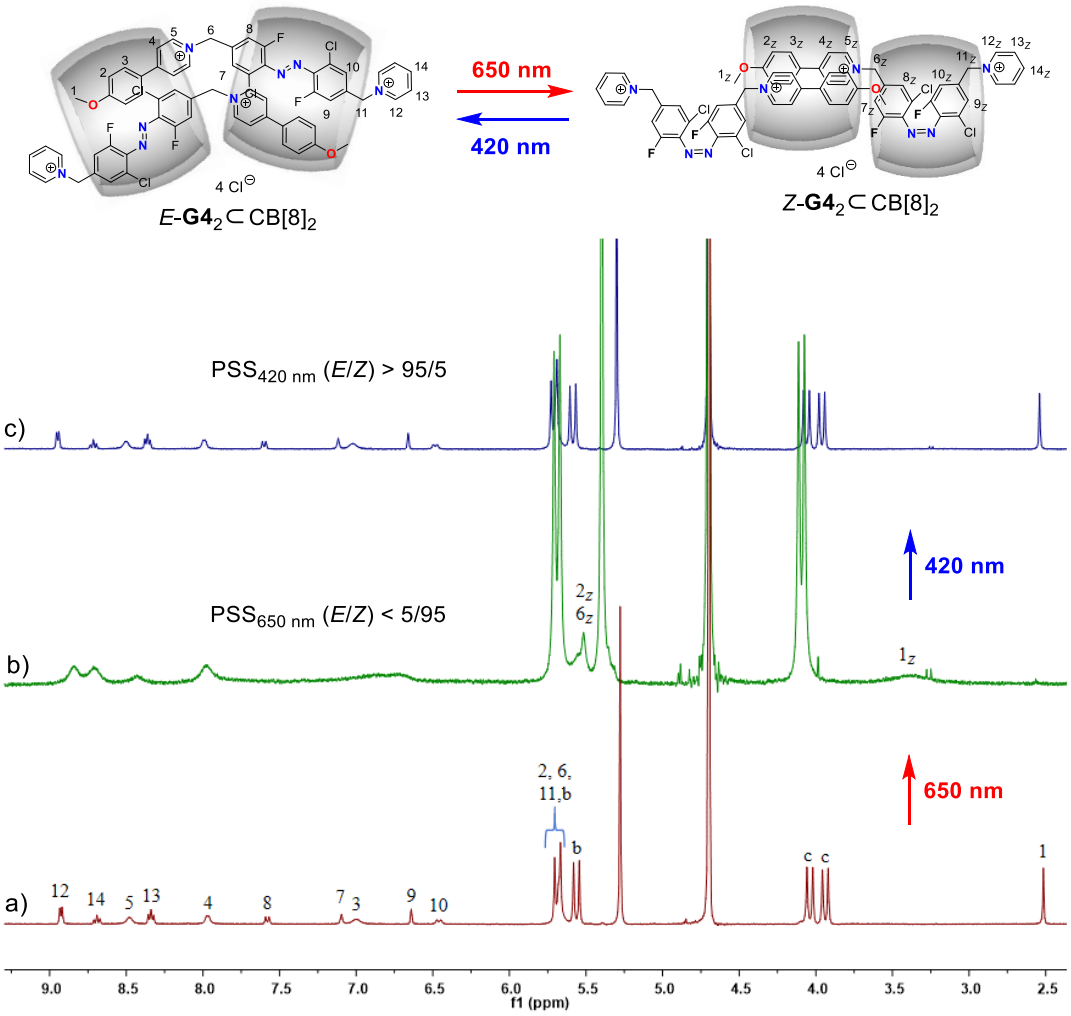


Fig.S37 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) for the solution of the mixture of *E*-**G4** and CB[8] (2:2, 5.0 mM) under conditions of a) before irradiation, b) after irradiation by red light (650 nm), and c) the red-light-irradiated solution of *E*-**G4** and CB[8] (2:2, 5.0 mM) after irradiation by blue light (420 nm).

Section 7: The photocontrolled complexation behavior of G5 and CB[8]

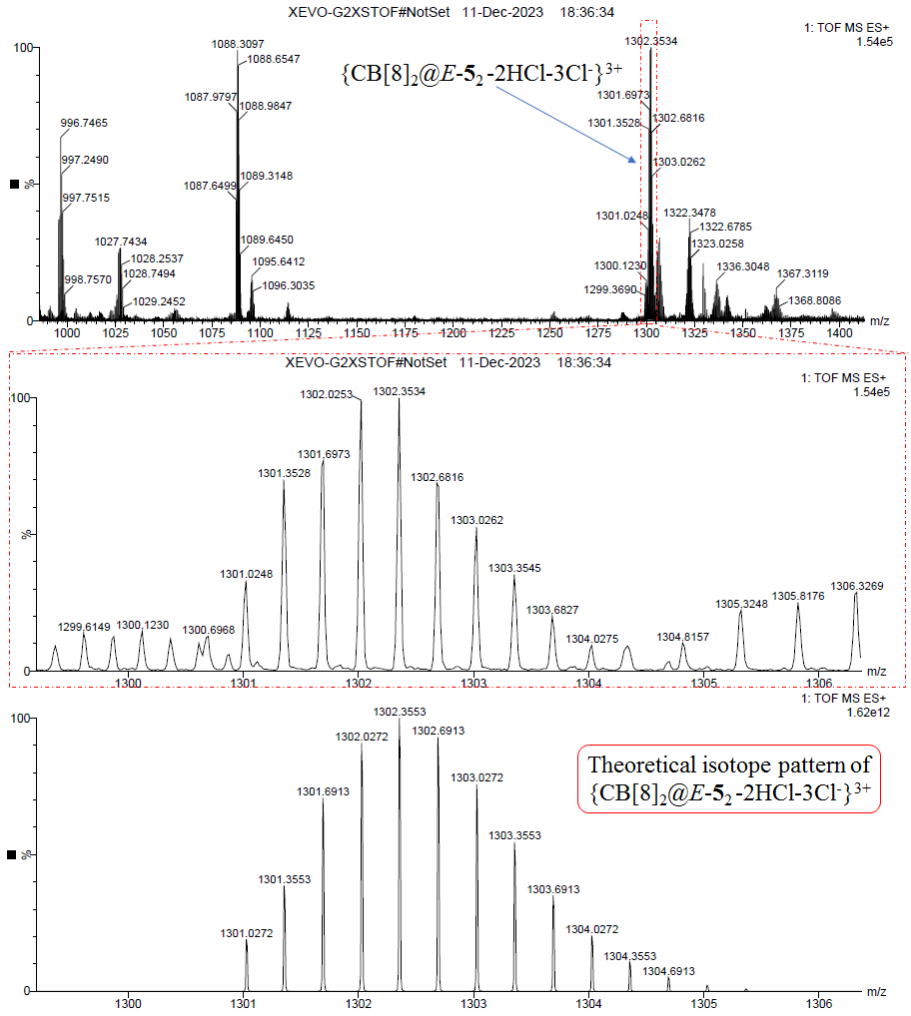


Fig. S38 The high-resolution ESI-mass spectrum of the host-guest complex formed between *E*-**G5** and CB[8] (2:2).

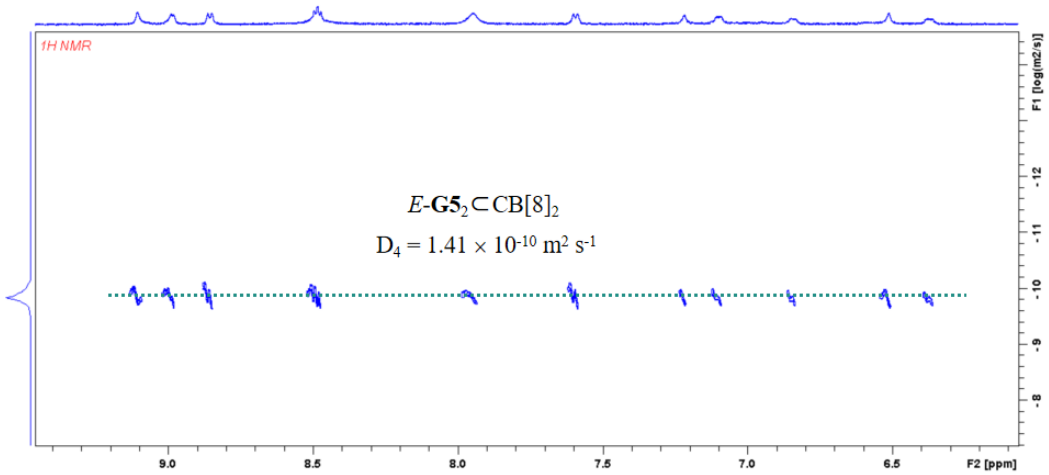


Fig.S39 The 2D DOSY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G5** and CB[8] (2:2, 2.5 mM).

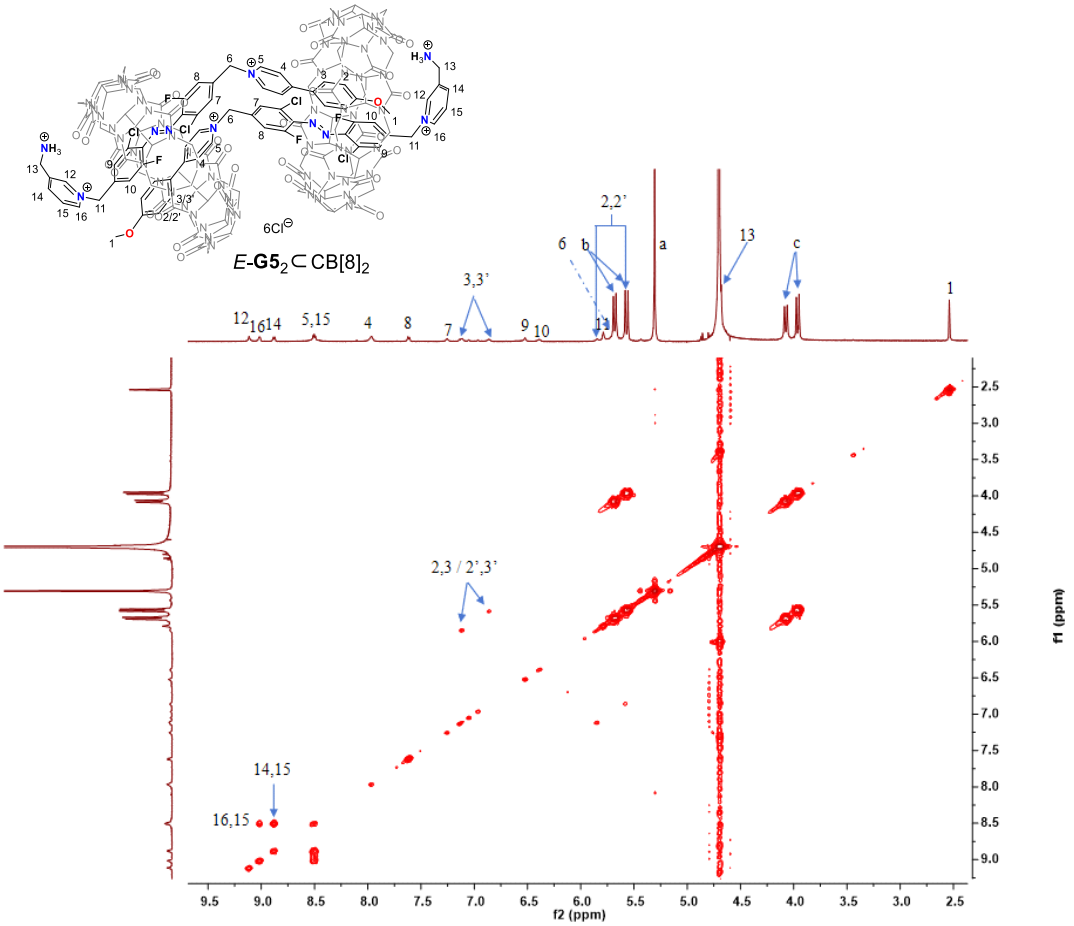


Fig. S40 The 2D COSY spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G5** and CB[8] (2:2, 10 mM).

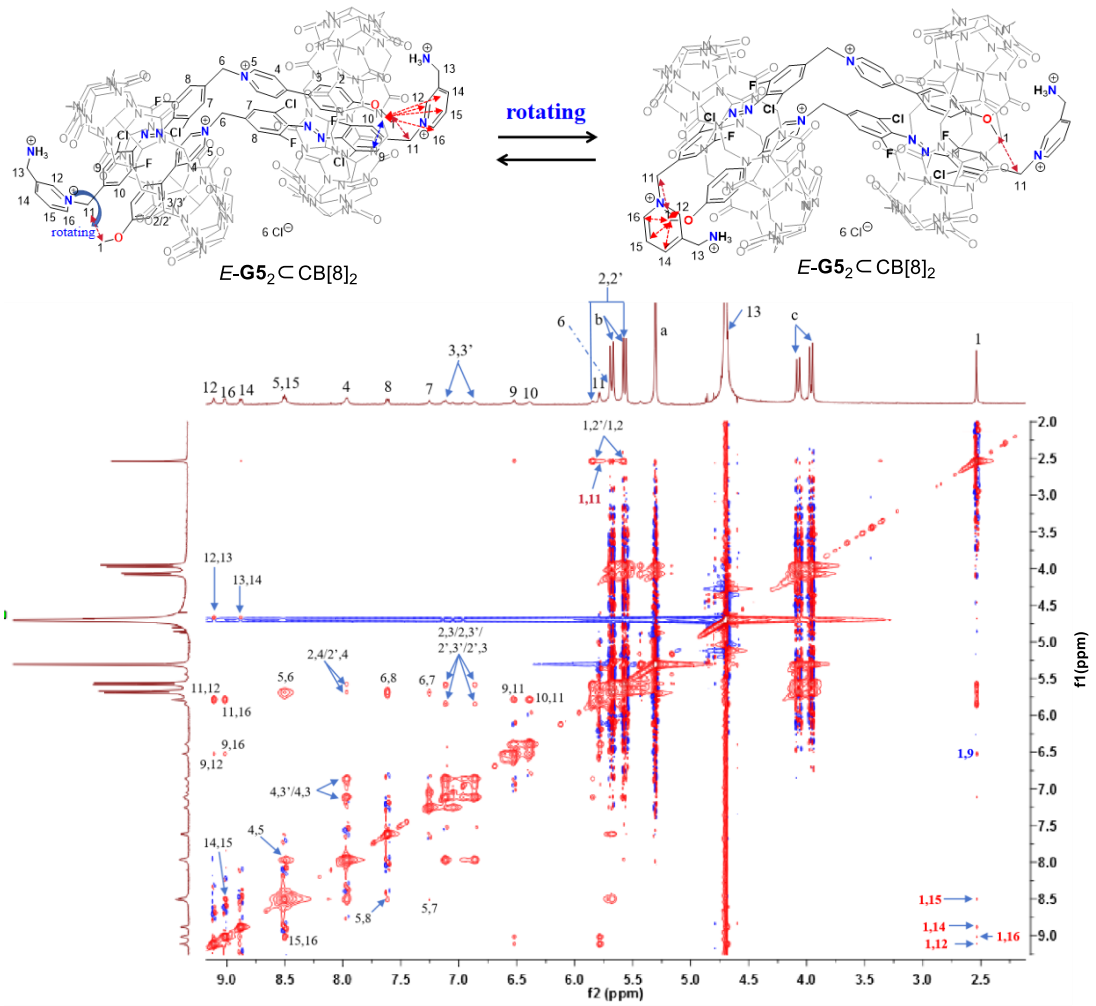


Fig. S41 The 2D NOESY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G5** and CB[8] (2:2, 10 mM).

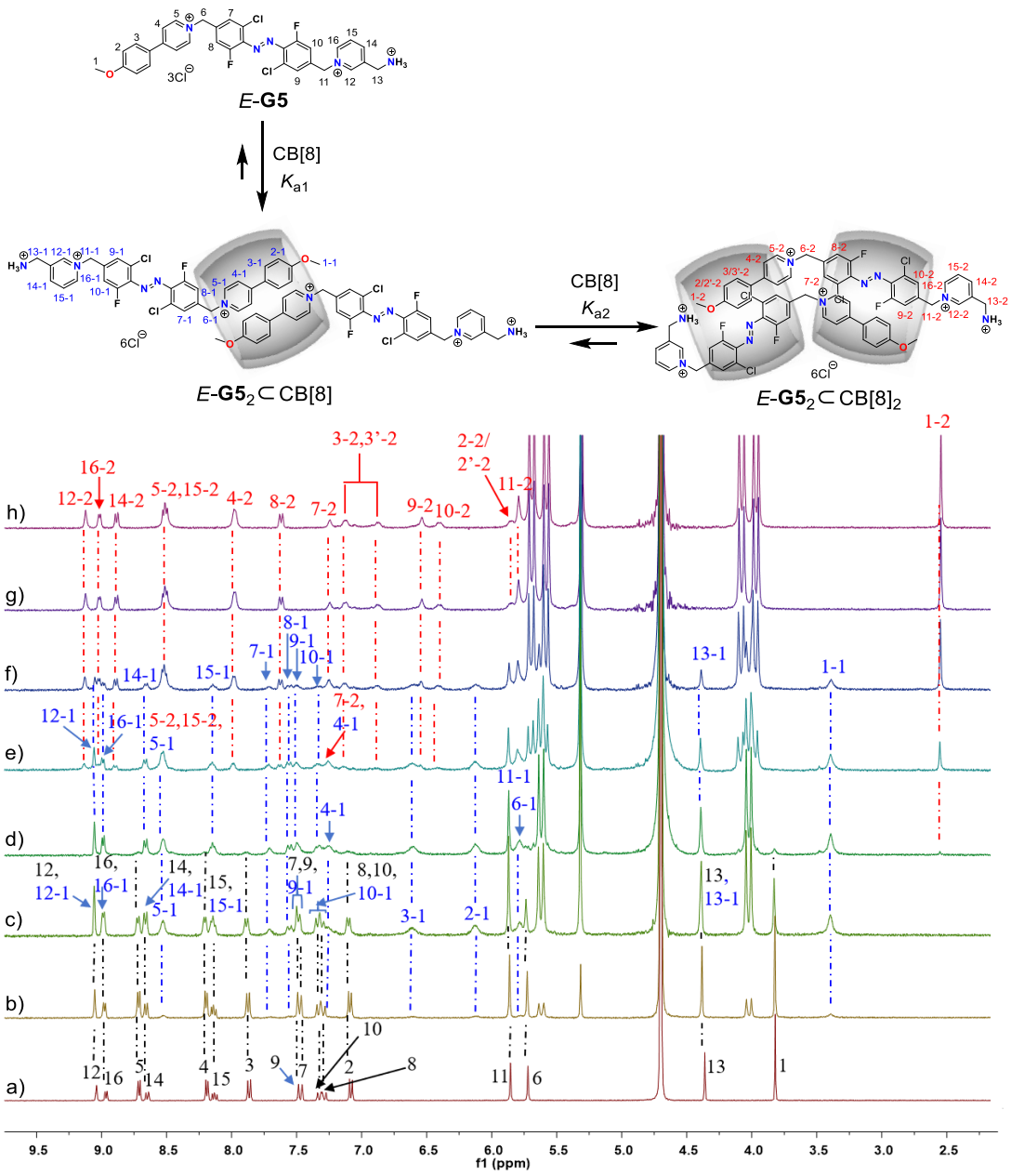


Fig. S42 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) for the solution of *E*-**G5** (2.5 mM) in the presence of a) 0, b) 0.1, c) 0.3, d) 0.5, e) 0.7, f) 0.8, g) 1.0, and h) 1.5 equiv. of CB[8].

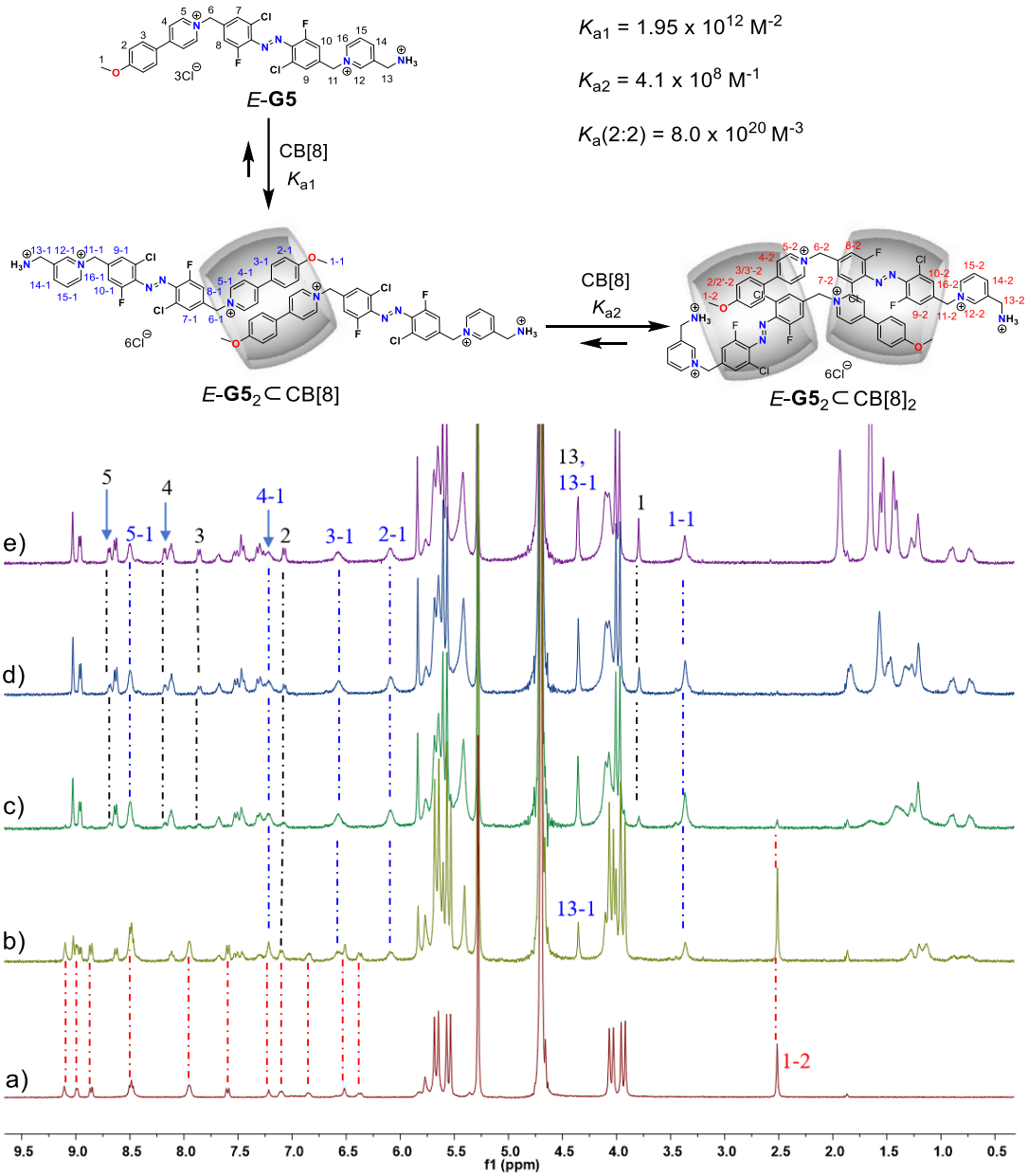
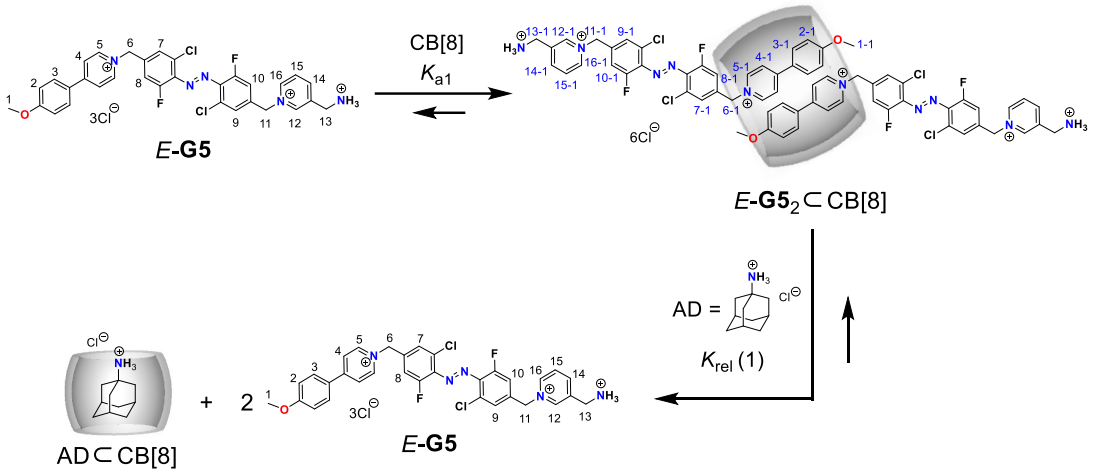


Fig. S43 Partial ^{1}H NMR spectra (400 MHz, 50 mM NaO_2CCD_3 buffer, pD = 4.74, 298 K) for the solution of the mixture of *E*-**G5** and CB[8] (2:2, 2.5 mM) in the presence of a) 0, b) 0.25, c) 0.75, d) 1.25, and e) 2.25 equiv. of 1-adamantanamine hydrochloride.

The apparent association constant K_a (2:2) for the formation of 2:2 stoichiometric *E*-**G5**$_2$⊂CB[8]$_2$ complex could be determined by performing the ^{1}H NMR competition experiments according to the reported method (Figs. S44 and S45)[7]. The 1-adamantanamine (AD) hydrochloride was selected as the competitive guest, its binding constant with CB[8] was previously determined as K_a(AD⊂CB[8]) = 8.2 × 10^8 M^{-1} in

the CD_3CO_2Na buffer (50 mM, pD = 4.74)[7]. The calculation procedure for K_{a1} (1:1) of *E*-**G5**$_2$⊂CB[8] complex and K_{a2} (2:2) of *E*-**G5**$_2$⊂CB[8]$_2$ complex are presented in Fig. S43 and Fig. S44, respectively.



K_a(AD⊂CB[8]) = 8.2 x 10^8 M^{-1}

K_{rel} (1) = K_a(AD⊂CB[8]) / K_{a1} = {$C_{(AD⊂CB[8])}$ x $C_{(E\text{-}G5)}^2$ } / {$C_{(2E\text{-}G5⊂CB[8])}$ x $C_{(AD)}$} = 4.2 x 10^{-4} M

K_{a1} = 1.95 x 10^{12} M^{-2}

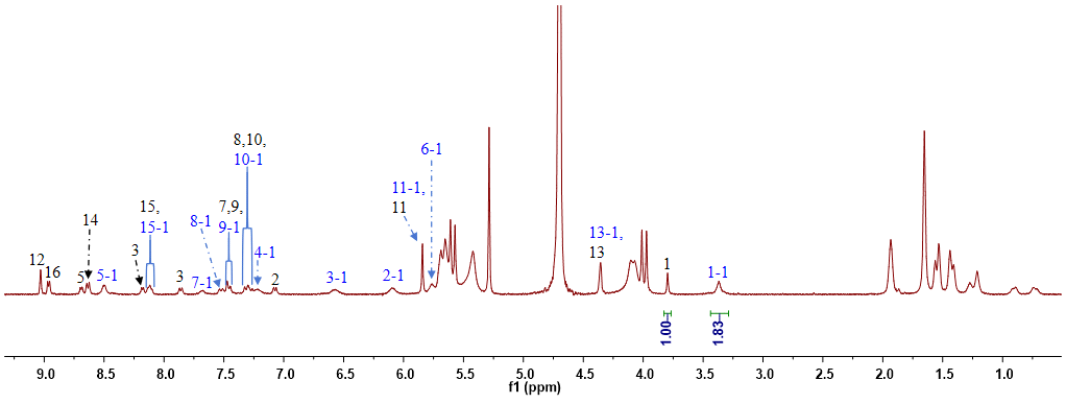
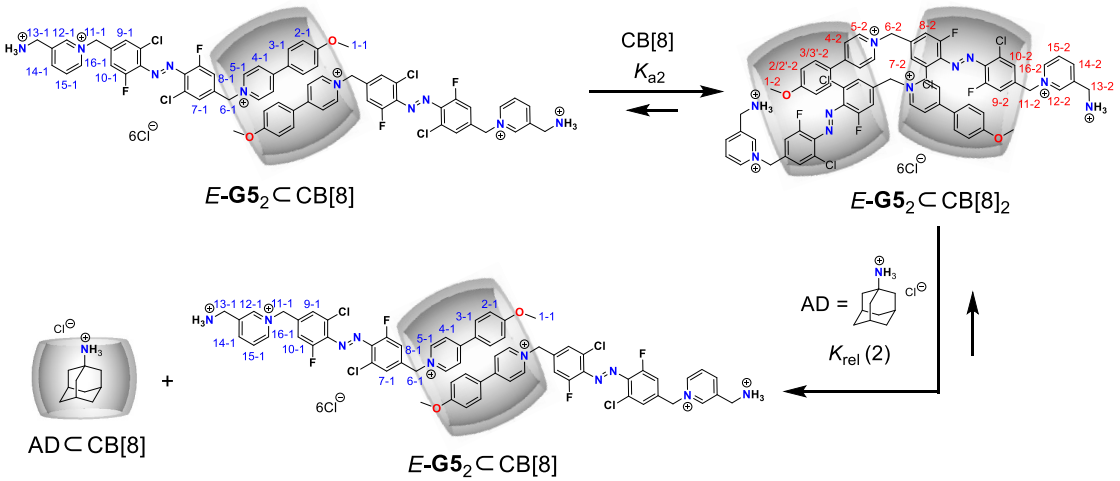


Fig. S44 The schematic representation for the calculation of association constant of K_{a1} in forming *E*-**G5**$_2$⊂CB[8] complex, and the corresponding partial ^{1}H NMR spectrum (400 MHz, 50 mM NaO_2CCD_3 buffer, pD = 4.74, 298 K) for the solution of the mixture of *E*-**G5** and CB[8] (2:2, 2.5 mM) in the presence of 2.25 equiv. of 1-adamantanamine (AD) hydrochloride.



K_a(AD⊂CB[8]) = 8.2 x 10^8 M^{-1}

K_{rel} (2) = K_a(AD⊂CB[8]) / K_{a2} = {$C_{(AD⊂CB[8])}$ x $C_{(2E\text{-}G5⊂CB[8])}$} / {$C_{(2E\text{-}G5⊂2CB[8])}$ x $C_{(AD)}$} = 2.0

K_{a2} = 4.1 x 10^8 M^{-1}

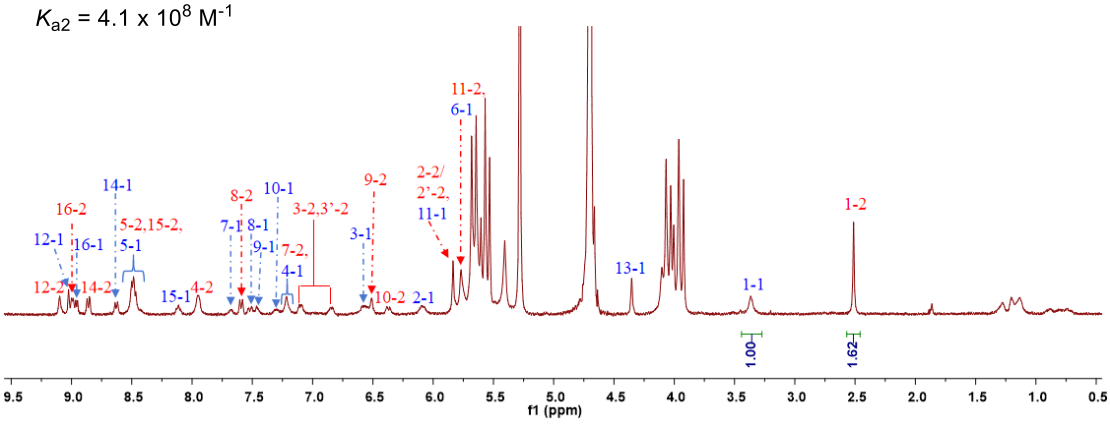


Fig. S45 The schematic representation for the calculation of association constant of K_{a2} in forming *E*-**G5**$_2$⊂CB[8]$_2$ complex, and the corresponding partial ^{1}H NMR spectrum (400 MHz, 50 mM NaO_2CCD_3 buffer, pD = 4.74, 298 K) for the solution of the mixture of *E*-**G5** and CB[8] (2:2, 2.5 mM) in the presence of 0.25 equiv. of 1-adamantanamine (AD) hydrochloride.

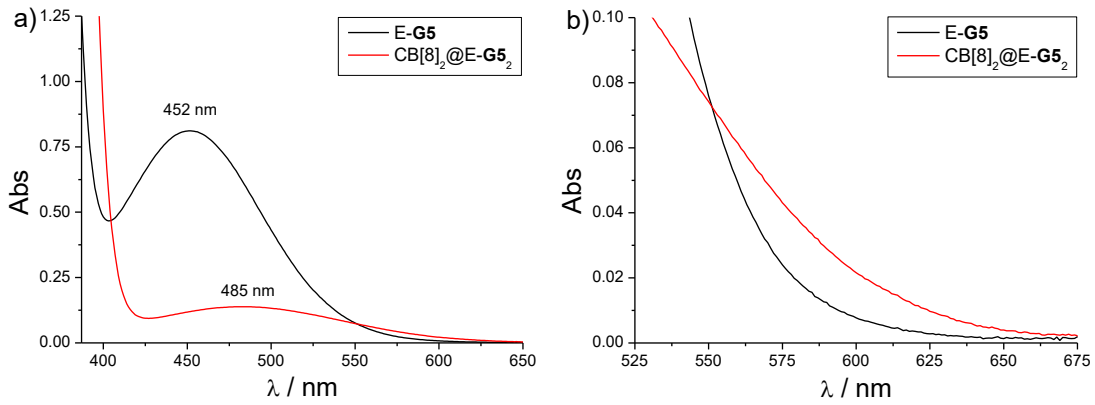


Fig.S46 The UV/Vis absorption spectra of *E*-**G5** (1.0 mM) (black line), and the mixture of *E*-**G5** and CB[8] (2:2, 1.0 mM) (red line) in H_2O at 25 °C.

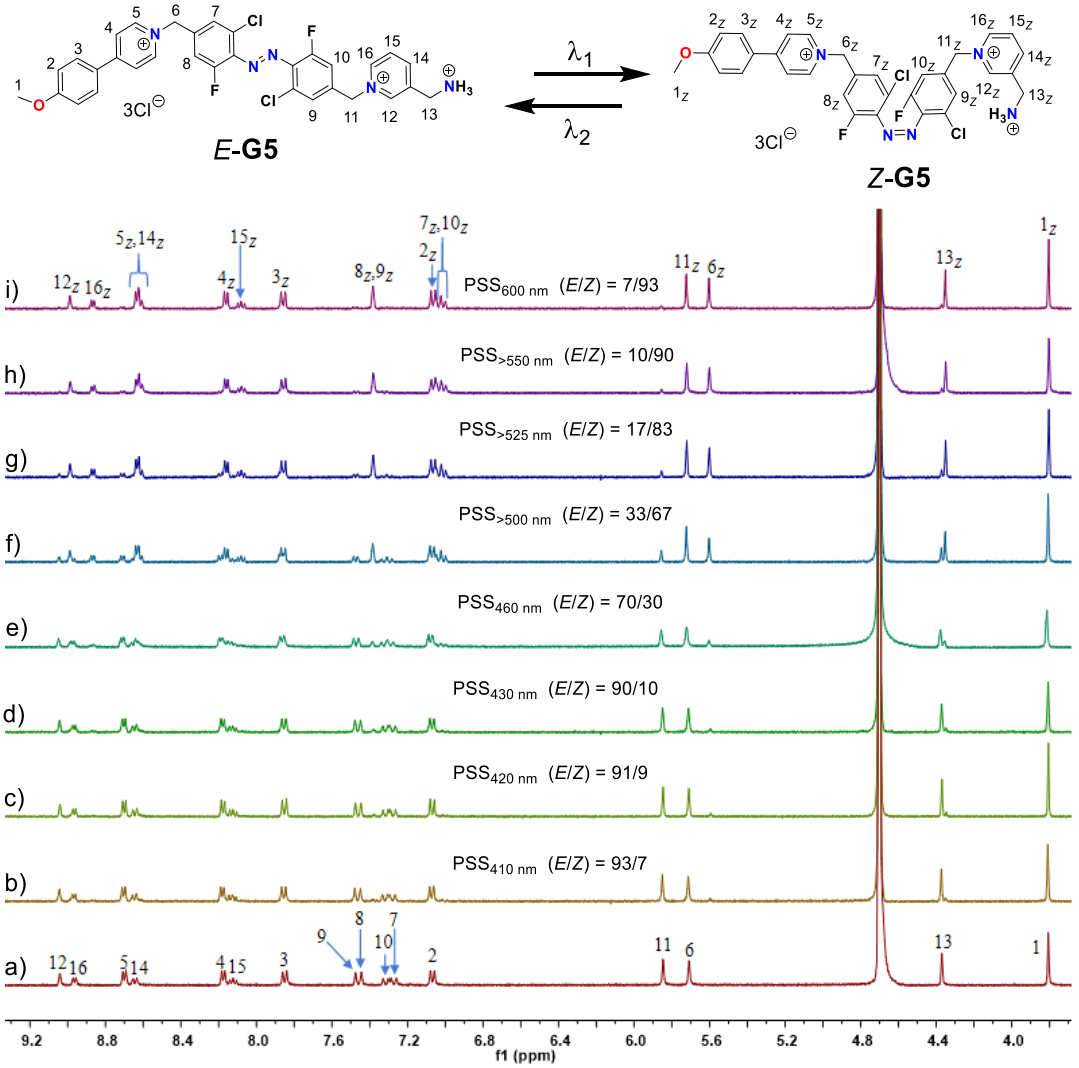


Fig.S47 Partial ^{1}H NMR spectra (400 MHz, D_2O, 5.0 mM, 298K) of **G5** recorded under conditions of a) before, and b) to i) after irradiation by light sources with different wavelengths.

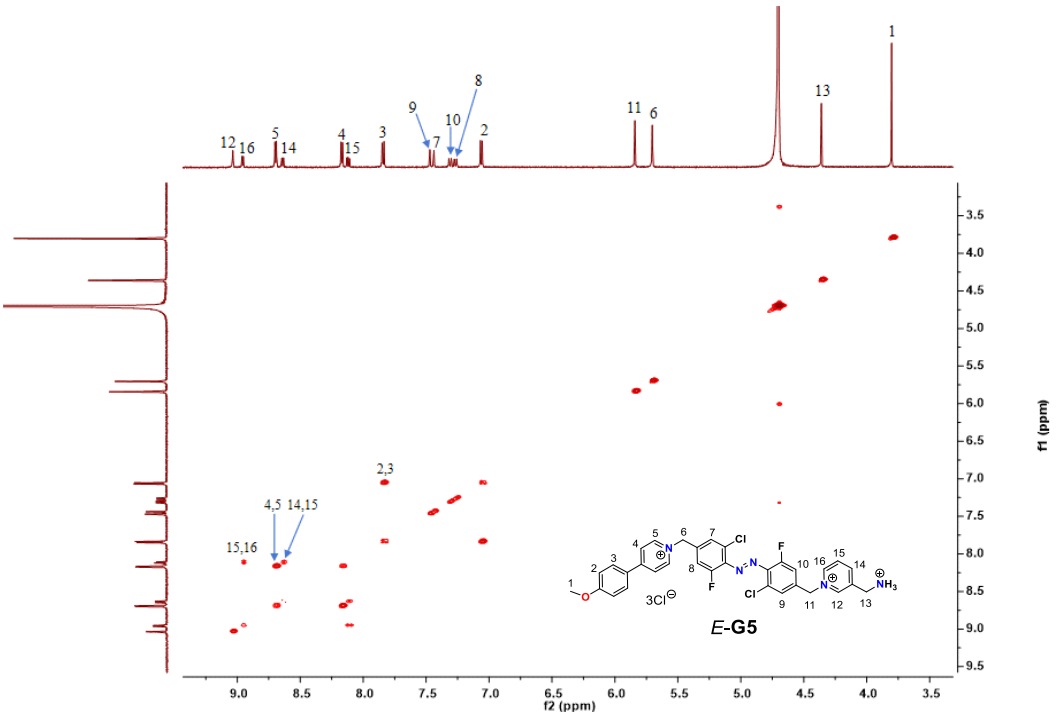


Fig. S48 The 2D COSY spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G5** (5.0 mM).

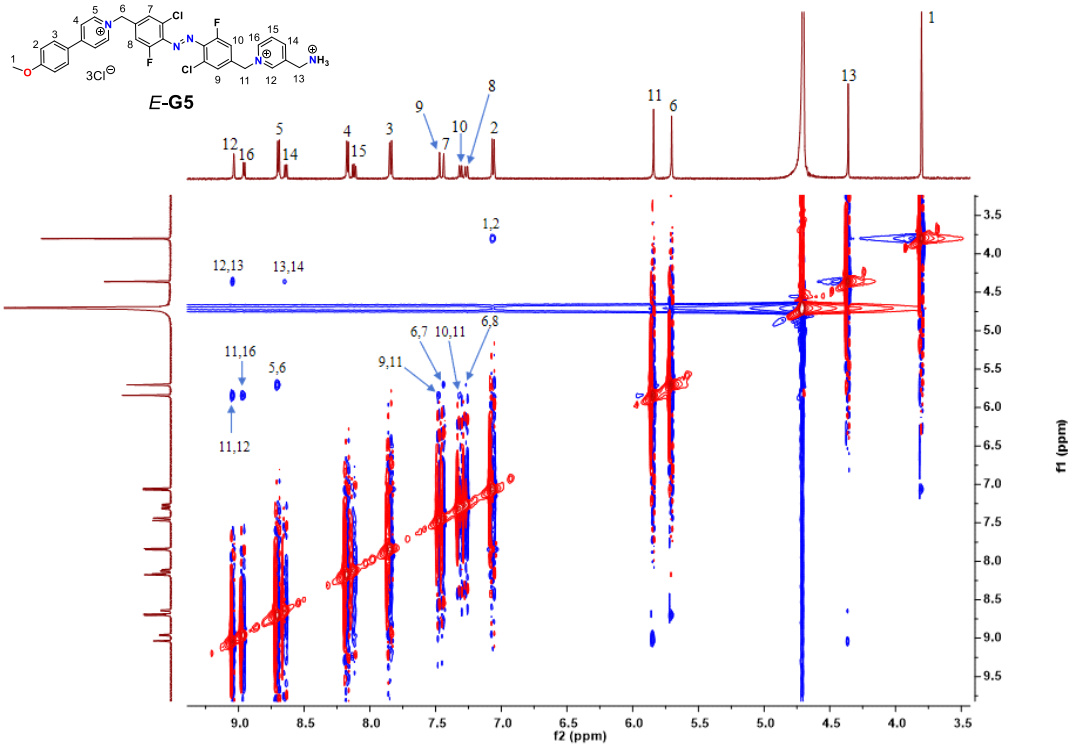


Fig. S49 The 2D NOESY spectrum (600 MHz, D_2O, 298 K) for the mixture of *E*-**G5** (5.0 mM).

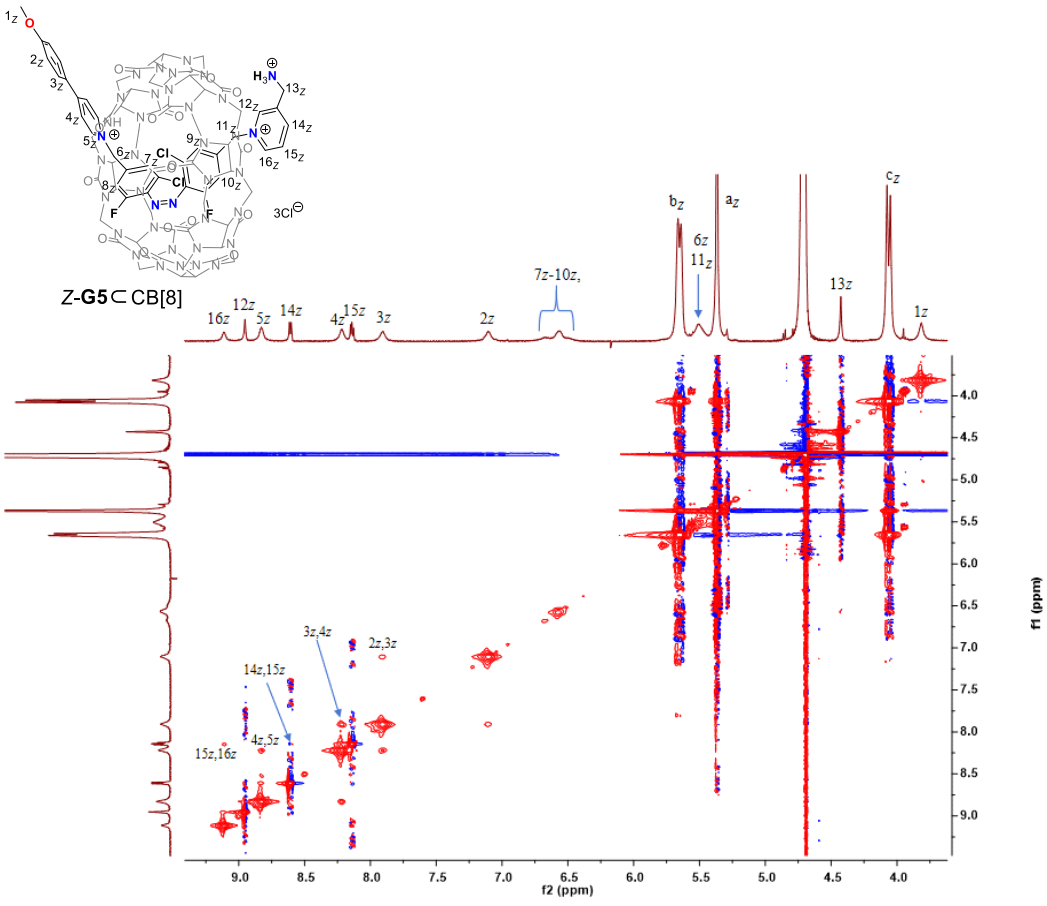


Fig. S50 The 2D NOESY spectrum (600 MHz, D_2O, 298 K) for the mixture of PSS_Z (650 nm) mixtures of **G5** and CB[8] (2:2, 2.5 mM).

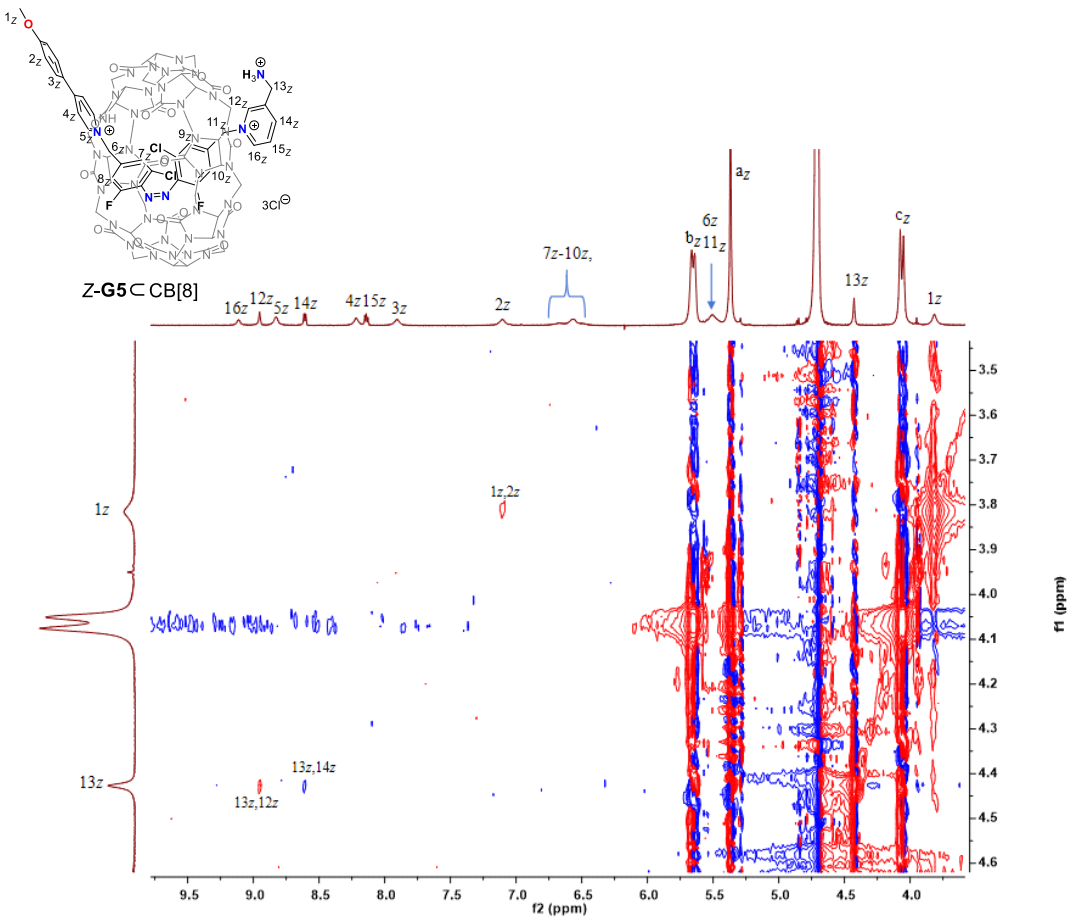


Fig. S51 Partial 2D NOESY spectrum (600 MHz, D_2O, 298 K) for the mixture of PSS_Z (650 nm) mixtures of **G5** and CB[8] (2:2, 2.5 mM).

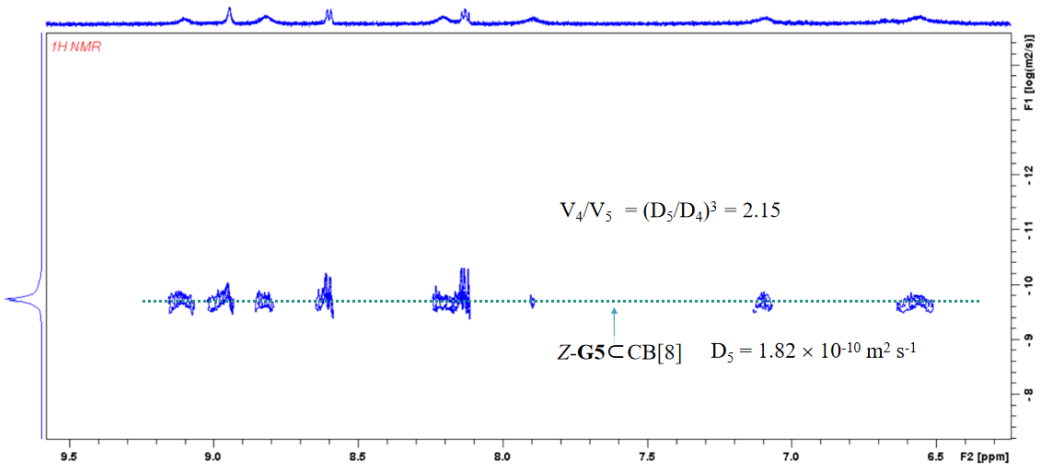


Fig.S52 The 2D DOSY NMR spectrum (600 MHz, D_2O, 298 K) for the mixture of PSS_Z (650 nm) mixtures of **G5** and CB[8] (2:2, 2.5 mM).

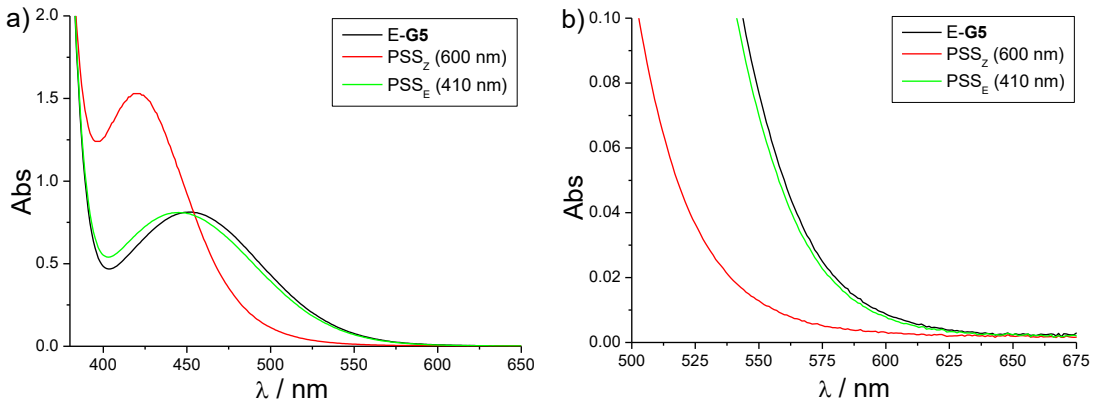


Fig.S53 The UV/Vis absorption spectra for *E*-**G5** (1.0 mM) under conditions of before (black line) and after irradiation by light sources with different wavelengths (red line and green line) in H_2O at 25 ºC.

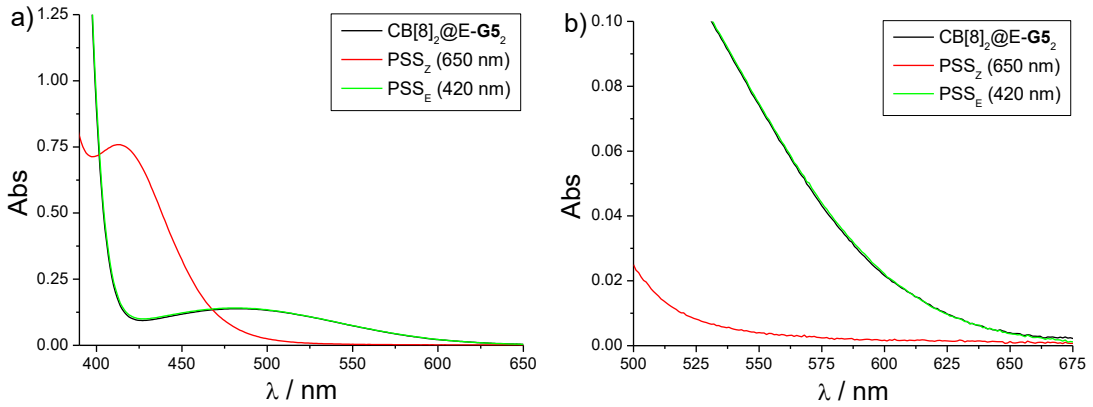


Fig.S54 The UV/Vis absorption spectra for the mixture of *E*-**G5** and CB[8] (2:2, 1.0 mM) under conditions of before (black line) and after irradiation by light sources with different wavelengths (red line and green line) in H_2O at 25 ºC.

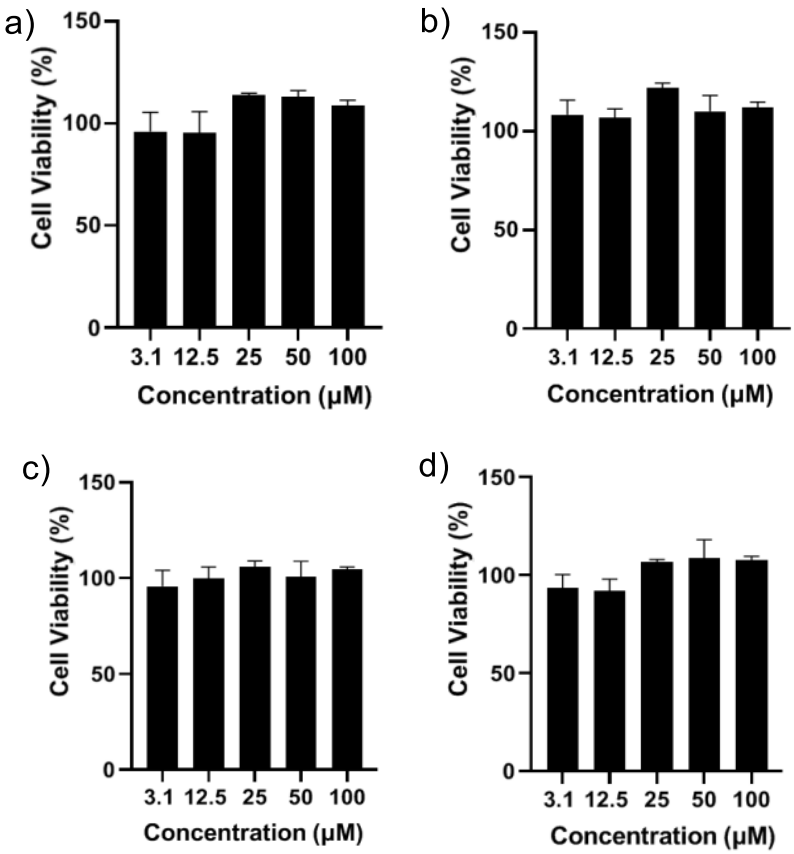


Fig.S55 Cell viability of H9C2 cells estimated by CCK-8 *versus* incubation concentrations of a) *E*-**G5**, b) PSS$_Z$(600 nm) mixtures of **G5**, c) mixture of *E*-**G5** and CB[8] (2:2), d) PSS$_Z$(650 nm) mixtures of **G5** and CB[8] (2:2).

Section 8: Photocontrolled complexation behavior of polymer AzoP and CB[8]

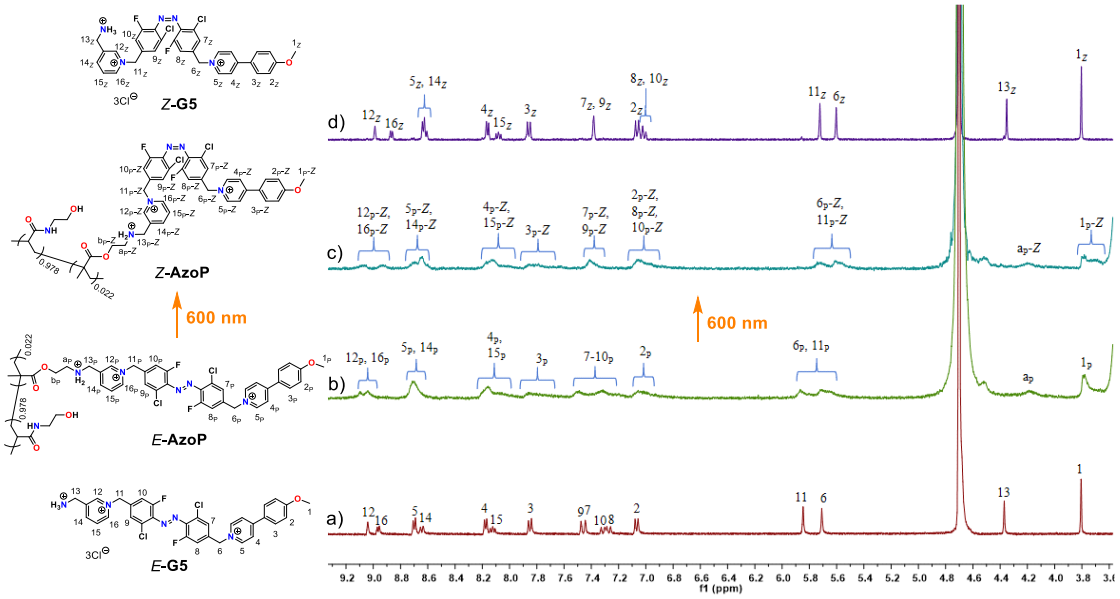


Fig.S56 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) for the solution of *E*-**G5** (5.0 mM) under conditions of a) before and d) after irradiation by orange light (600 nm), b) the pristine polymer solution of *E*-**AzoP** (13.3 mg/mL), c) the PSS$_Z$(600 nm) mixtures of polymer **AzoP** (13.3 mg/mL).

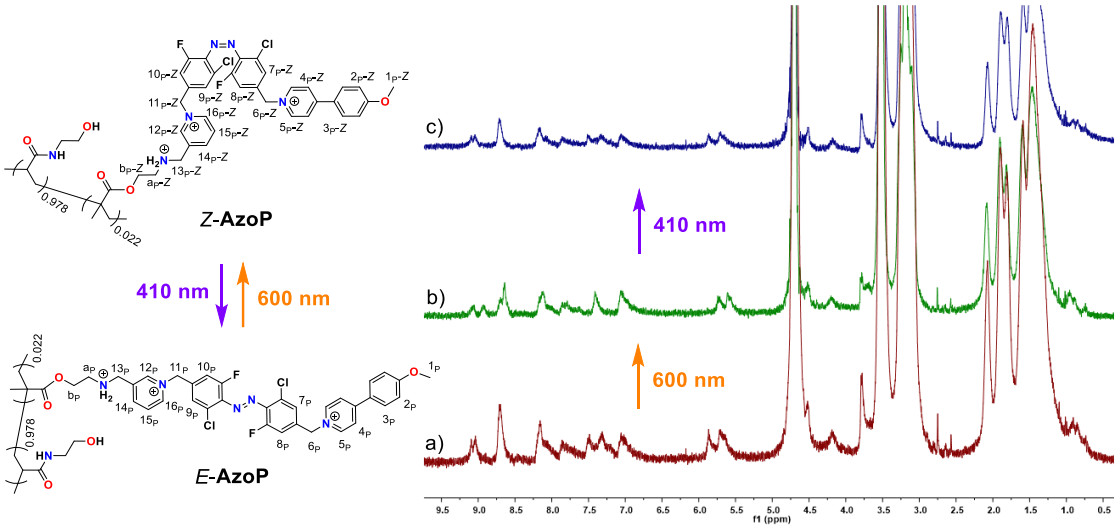


Fig.S57 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) for the solution of a) pristine polymer *E*-**AzoP** (13.3 mg/mL); b) the PSS$_Z$(600 nm) mixtures of polymer **AzoP** (13.3 mg/mL), and c) the PSS$_E$(410 nm) mixtures of polymer **AzoP** (13.3 mg/mL).

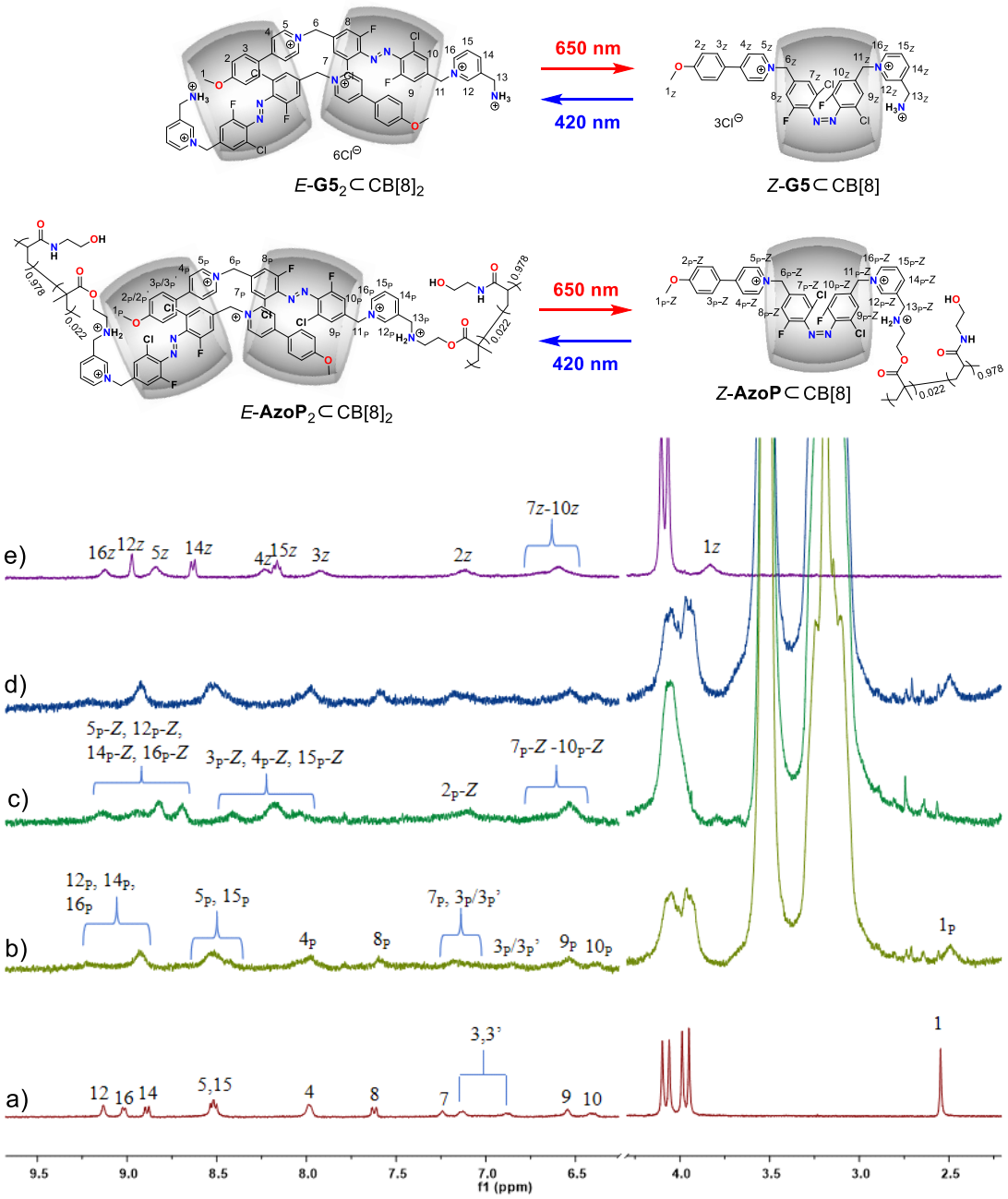


Fig.S58 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) for the solution of *E*-**G5** and CB[8] (2:2, 2.5 mM) under conditions of a) before and e) after irradiation by orange light (600 nm); b) the mixture of CB[8] (2.0 mM) and pristine polymer *E*-**AzoP** (13.3 mg/mL, 2.0 mM of Azo unit), c) the PSS_Z(650 nm) mixtures of CB[8] (2.0 mM) and polymer **AzoP** (13.3 mg/mL, 2.0 mM of Azo unit), d) the PSS_E(410 nm) mixtures of CB[8] (2.0 mM) and polymer **AzoP** (13.3 mg/mL, 2.0 mM of Azo unit).

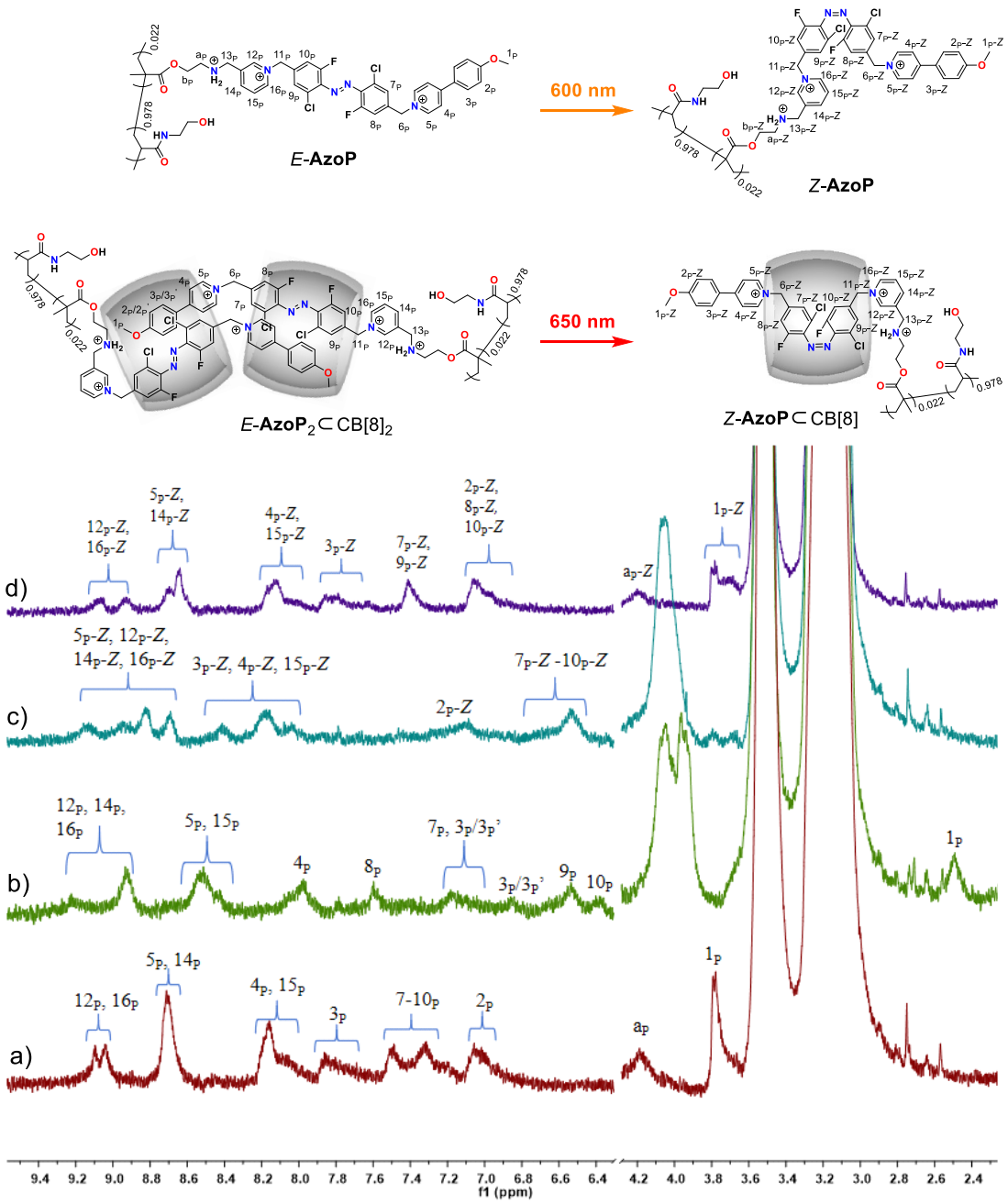


Fig.S59 Partial ^{1}H NMR spectra (400 MHz, D_2O, 298 K) for the solution of *E*-**AzoP** (13.3 mg/mL) under conditions of a) before and d) after irradiation by orange light (600 nm); b) the mixture of CB[8] (2.0 mM) and pristine polymer *E*-**AzoP** (13.3 mg/mL, 2.0 mM of Azo unit), c) the PSS$_Z$(650 nm) mixtures of CB[8] (2.0 mM) and polymer **AzoP** (13.3 mg/mL, 2.0 mM of Azo unit).

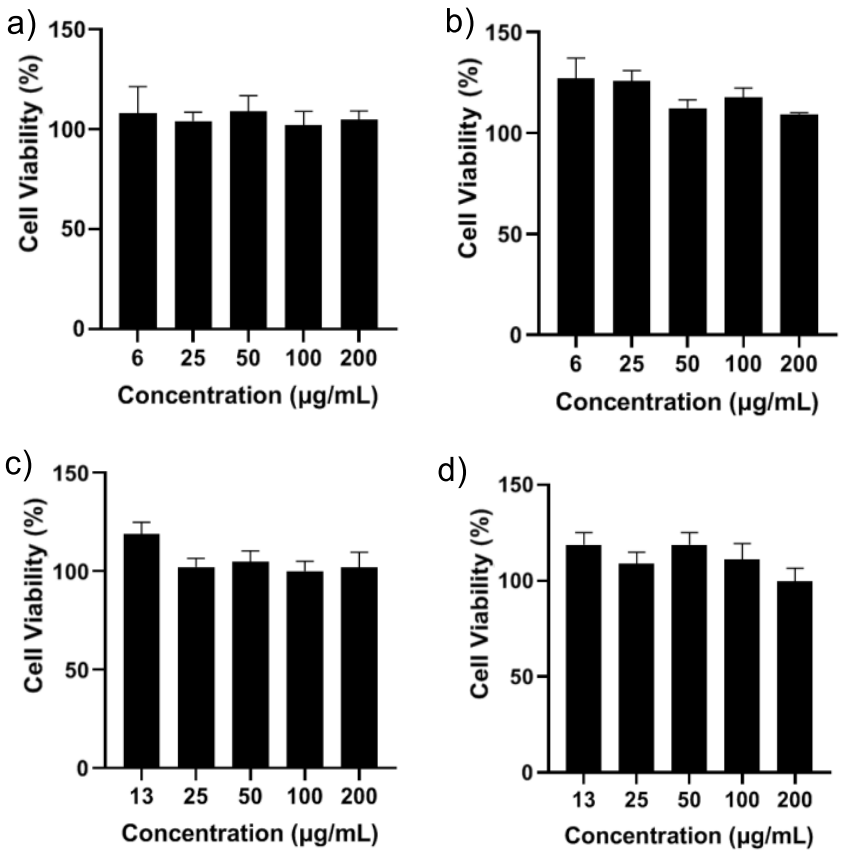
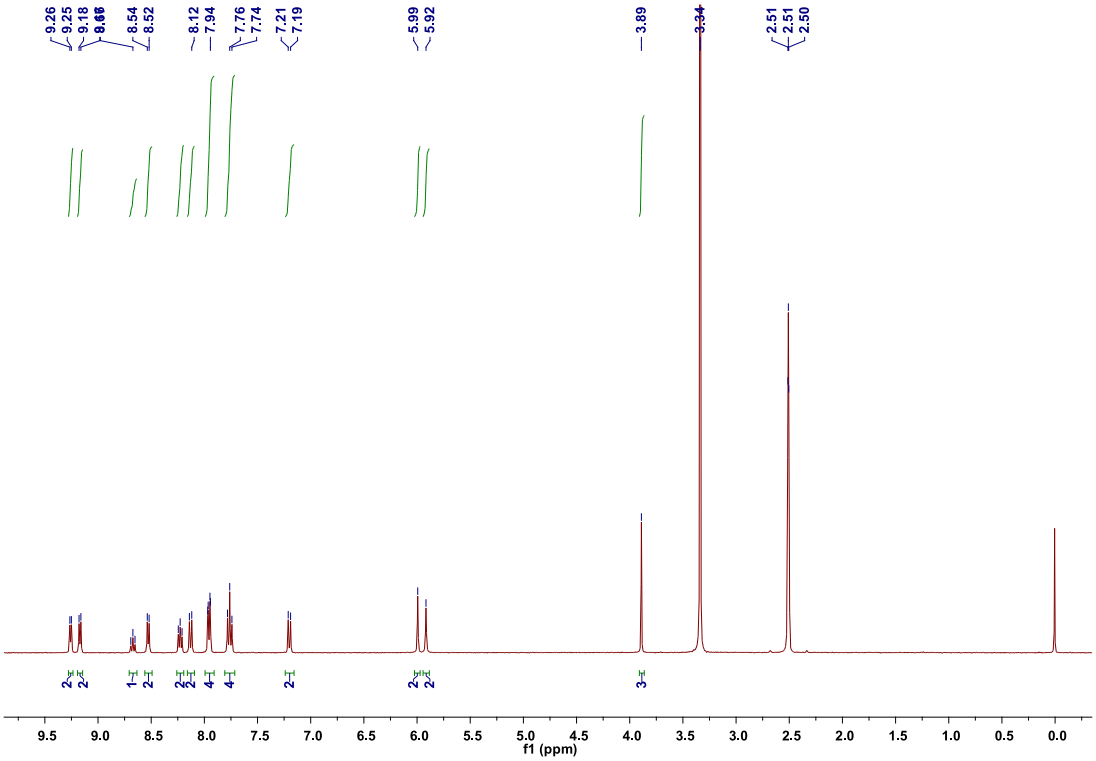
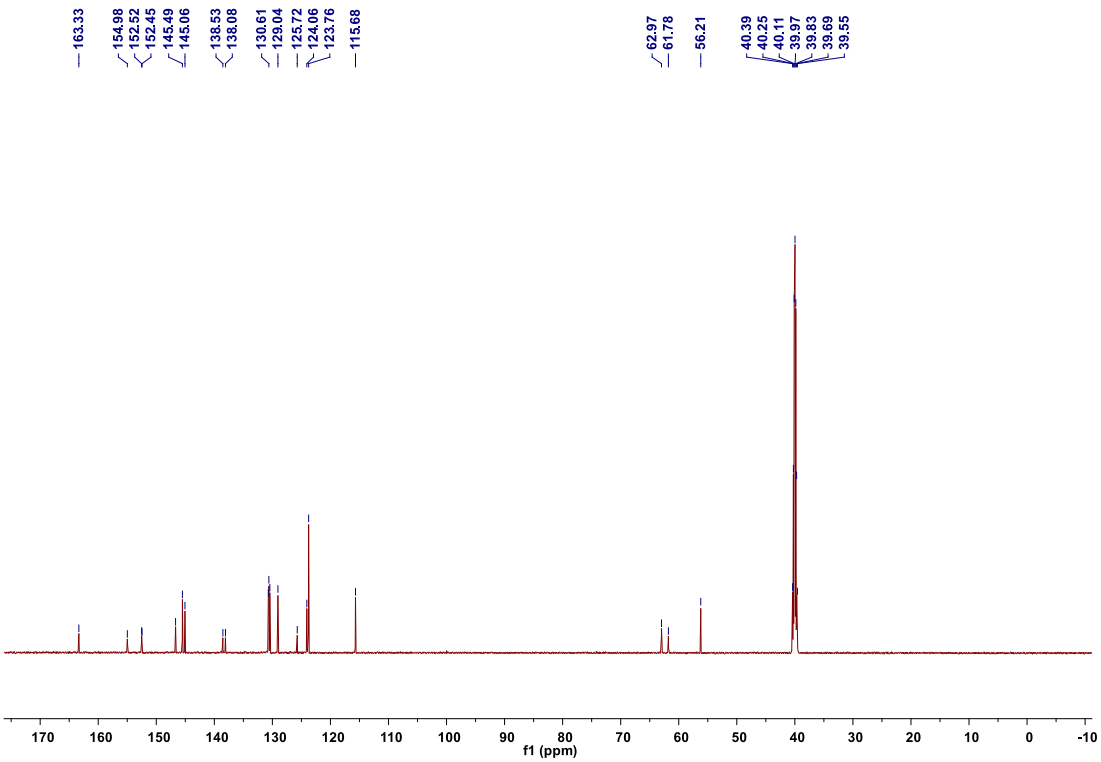


Fig.S60 Cell viability of H9C2 cells estimated by CCK-8 *versus* incubation concentrations of a) *E*-**AzoP**, b) PSS*z*(600 nm) mixtures of **AzoP**, c) mixture of *E*-**AzoP** and CB[8], d) PSS*z*(650 nm) mixtures of **AzoP** and CB[8]. The azo unit of **AzoP** and CB[8] are adjusted to 1:1 in experiments c and d.

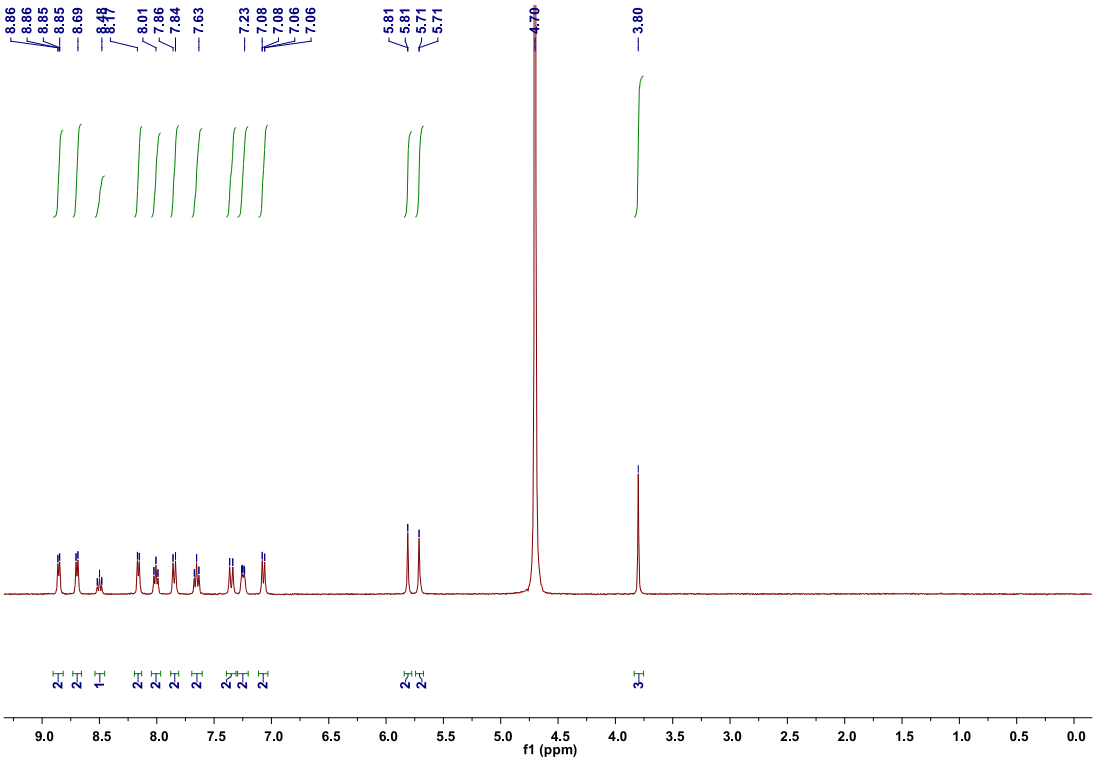
Section 9: The ^{1}H NMR, ^{13}C NMR and MS spectra for new compounds



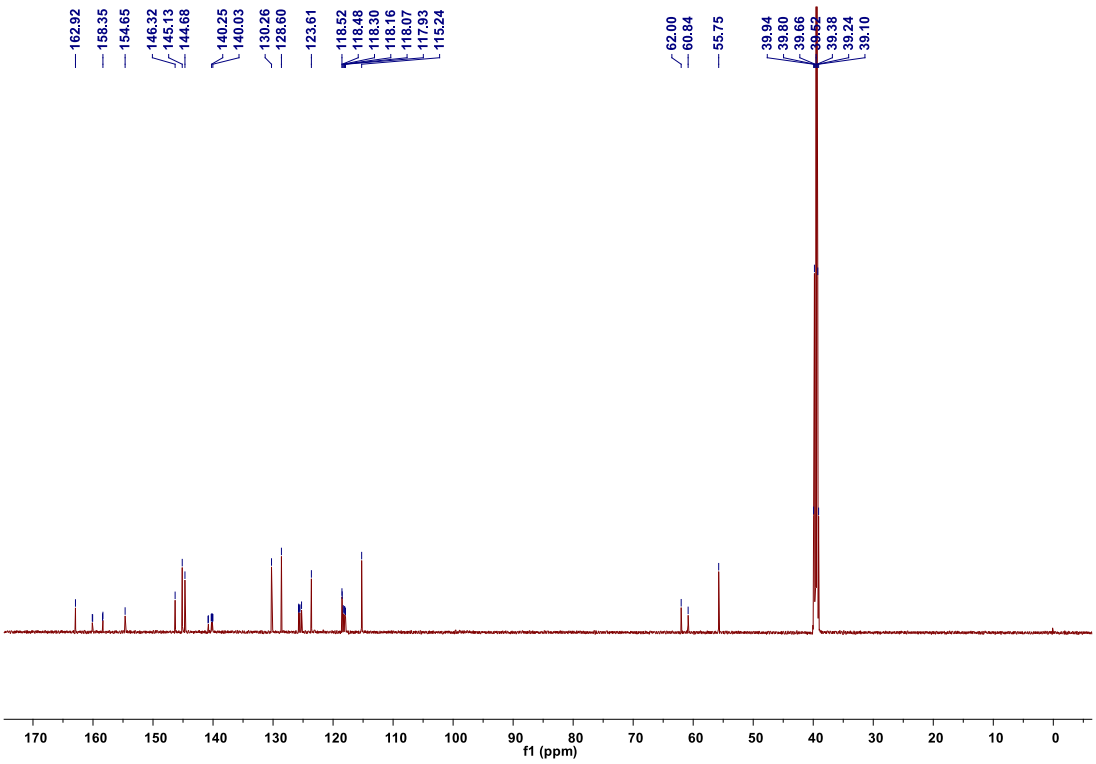
^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **G1**.



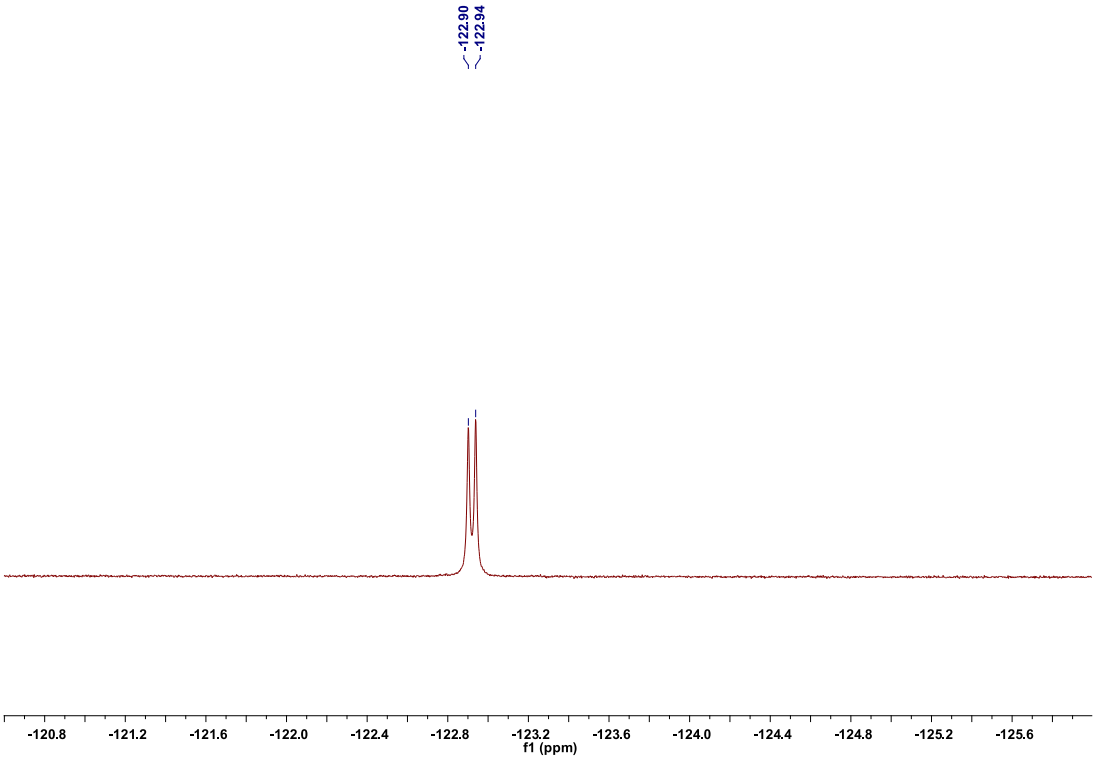
^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **G1**.



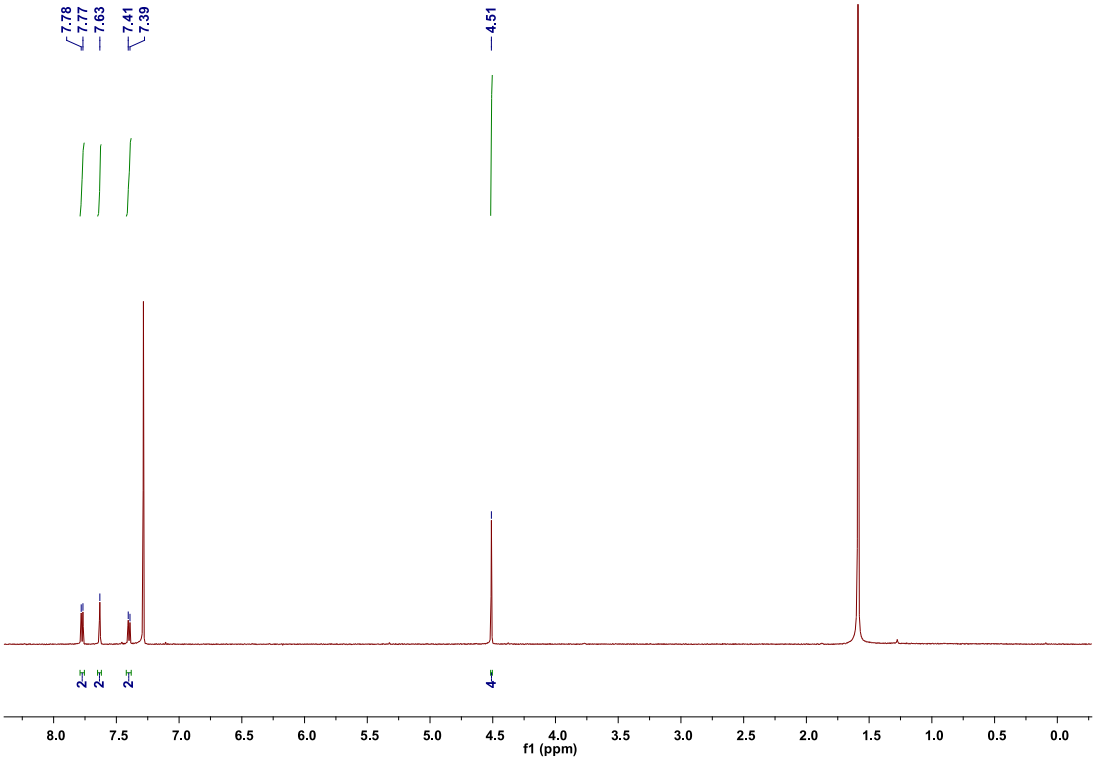
^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of compound **G2**.



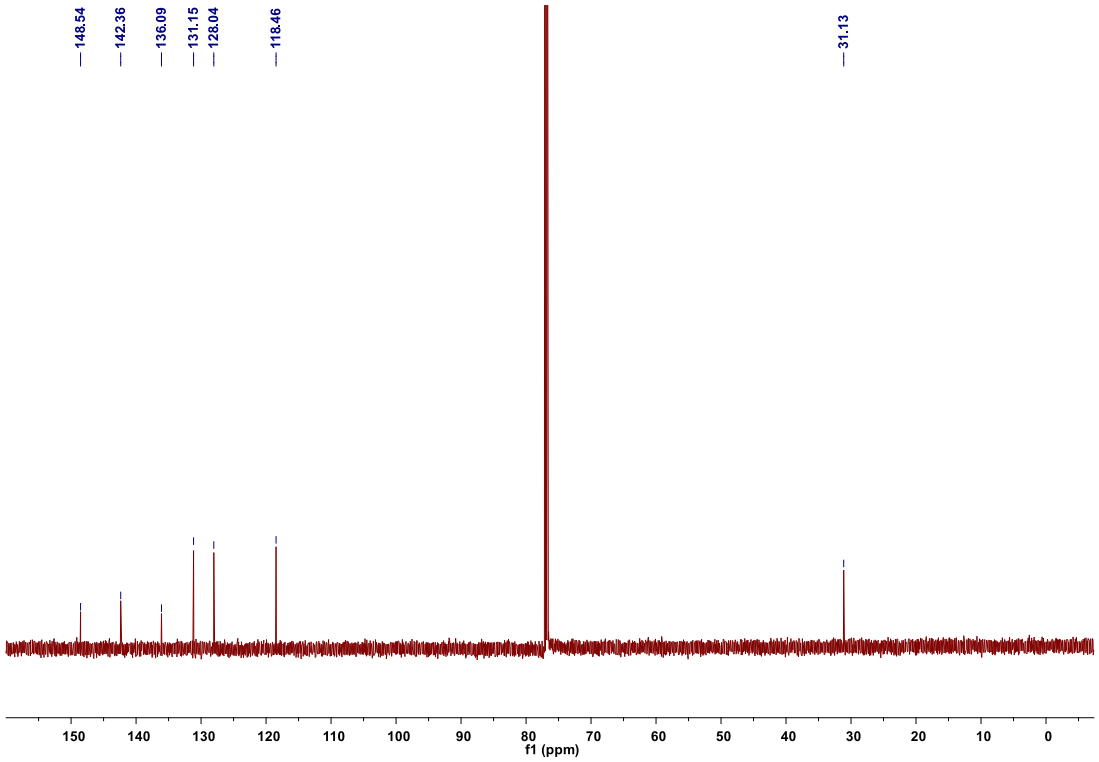
^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **G2**.



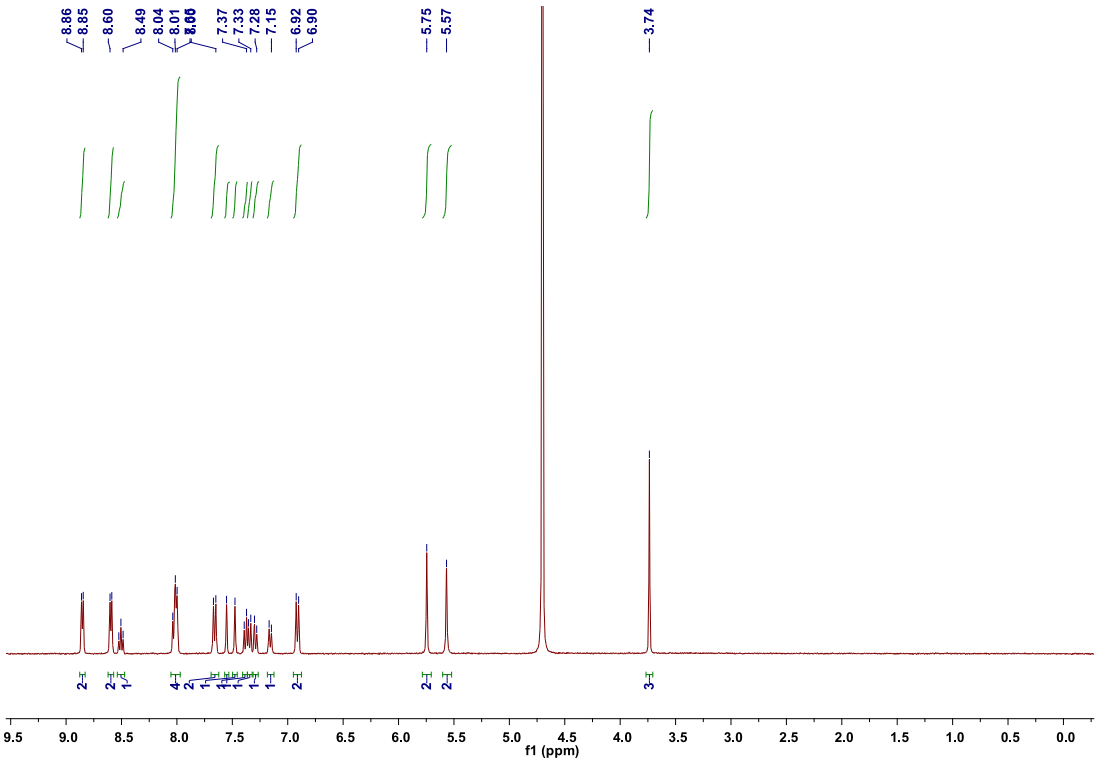
^{19}F NMR spectrum (376 MHz, DMSO-d_6, 298 K) of compound **G2**.



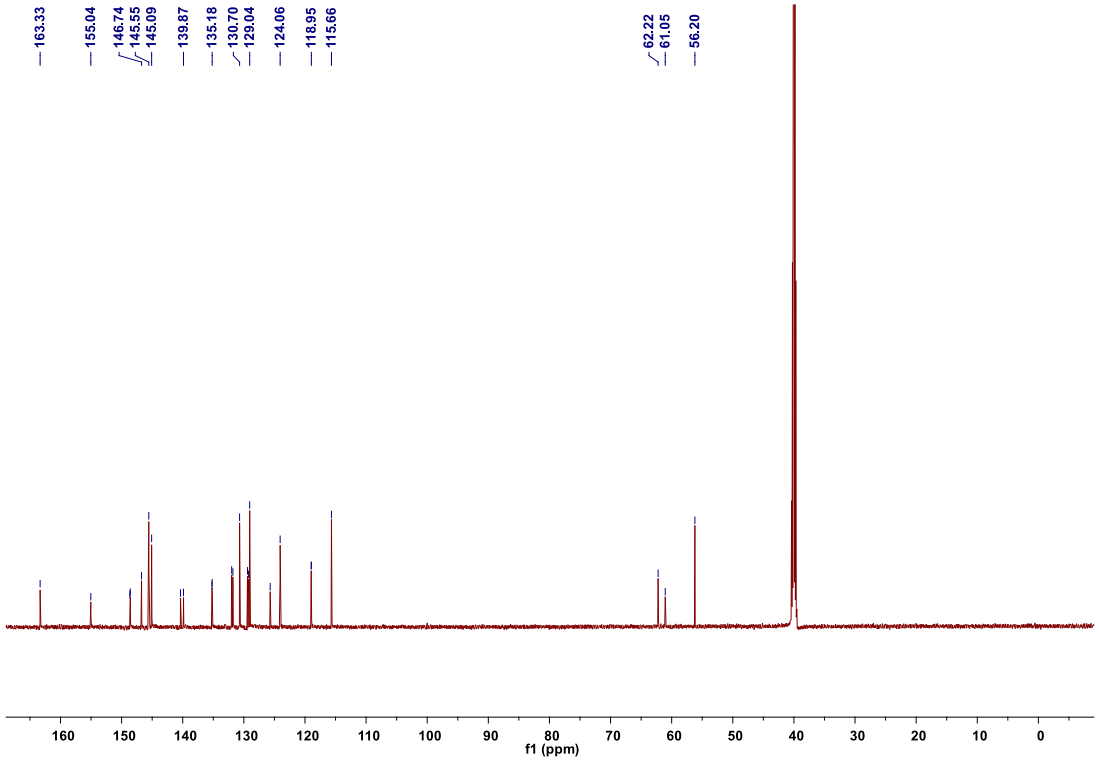
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **4**.



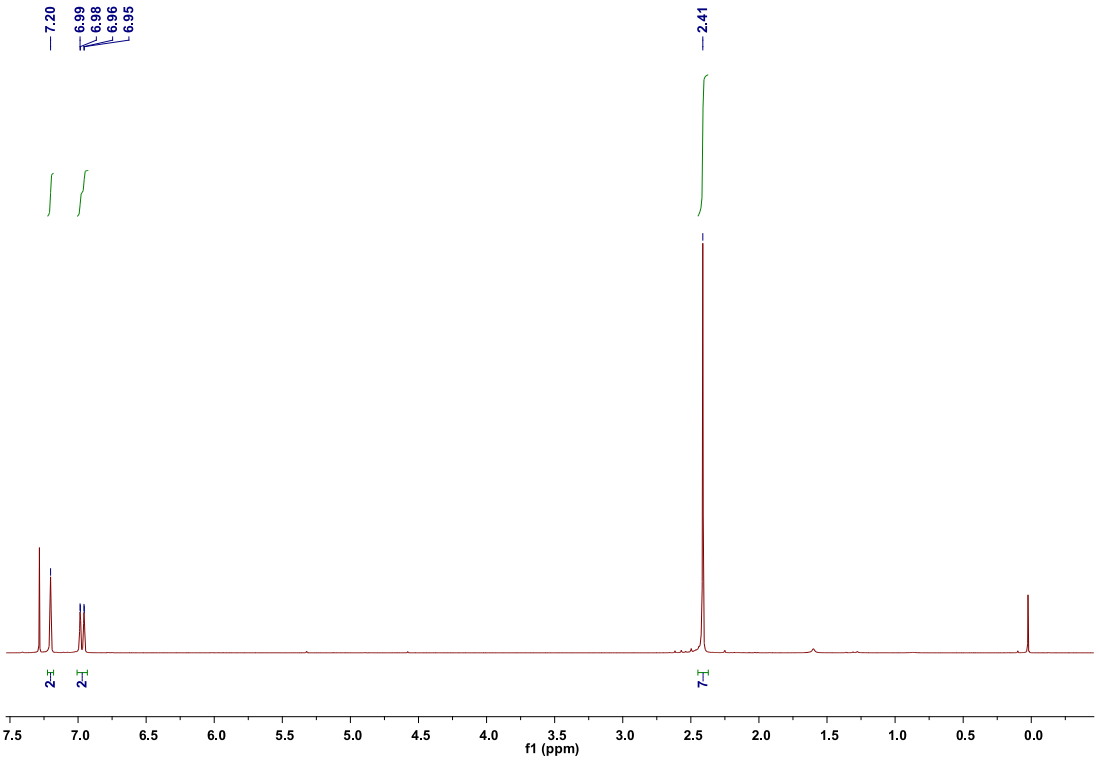
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **4**.



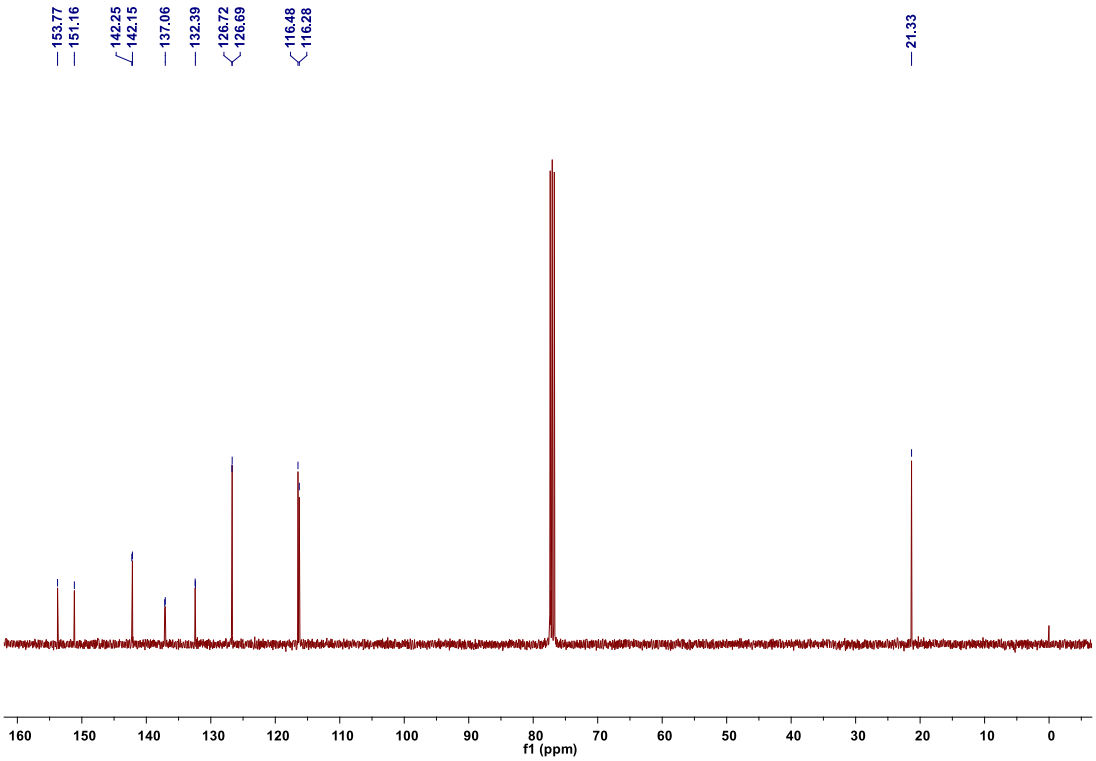
^{1}H NMR spectrum (600 MHz, D_2O, 298 K) of compound **G3**.



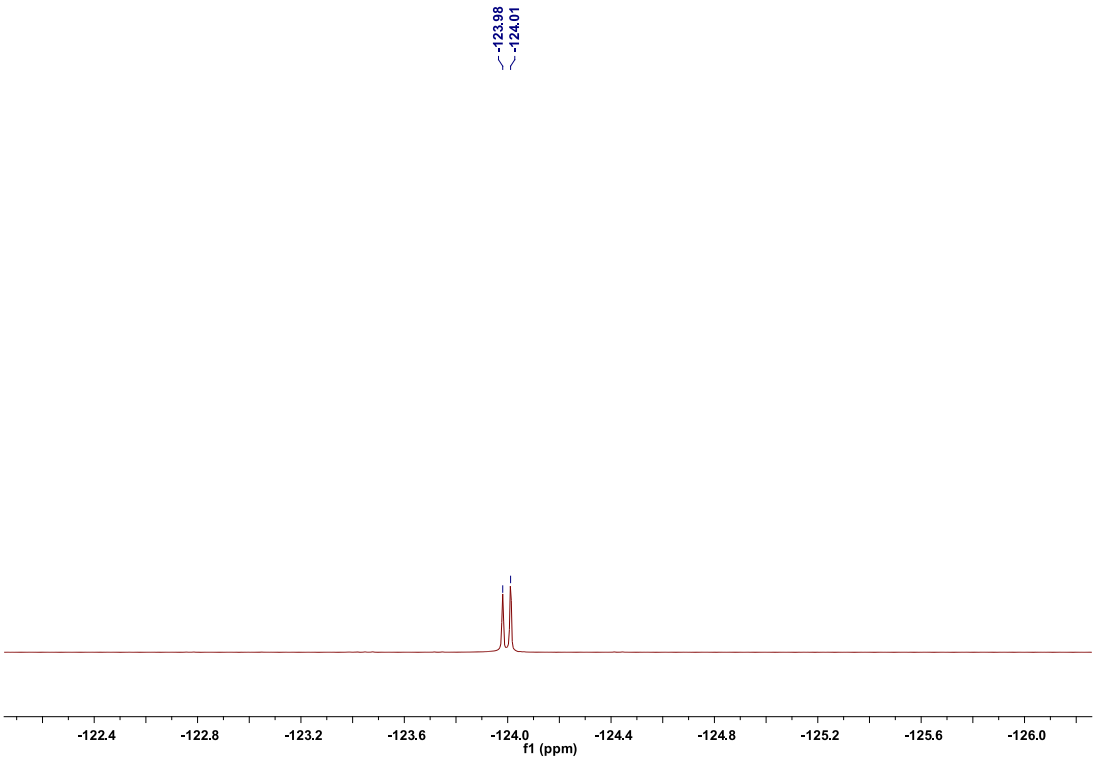
^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **G3**.



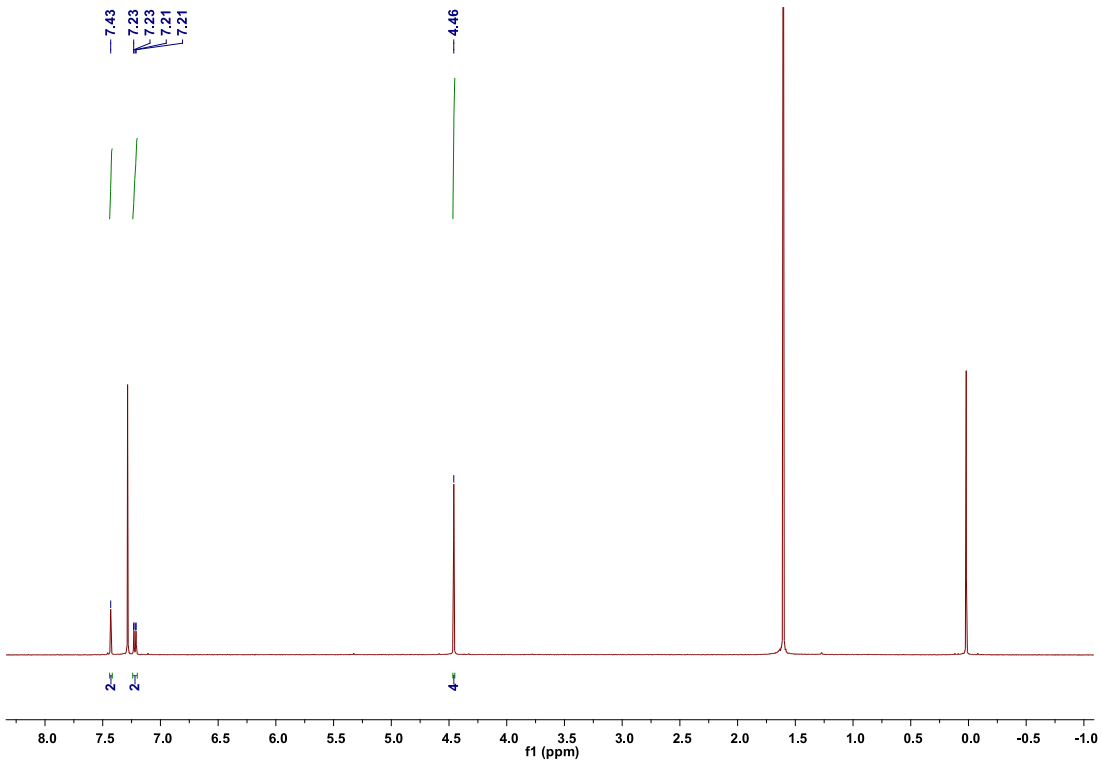
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **6**.



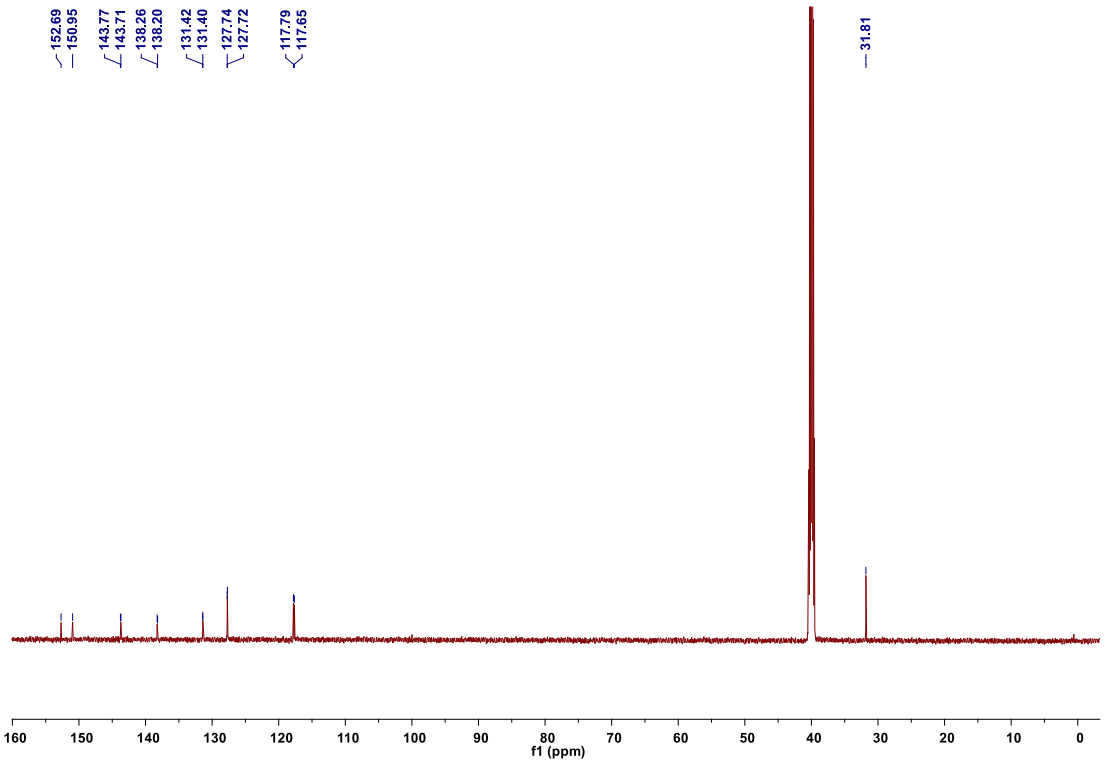
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **6**.



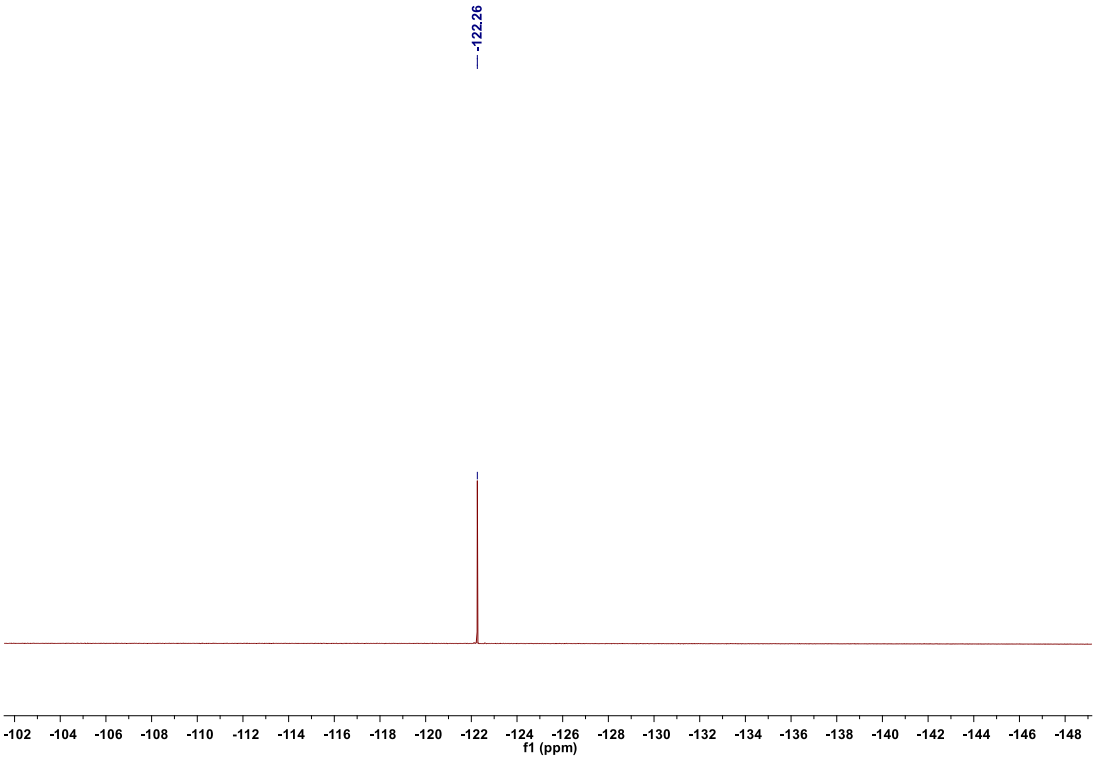
^{19}F NMR spectrum (376 MHz, $CDCl_3$, 298 K) of compound **6**.



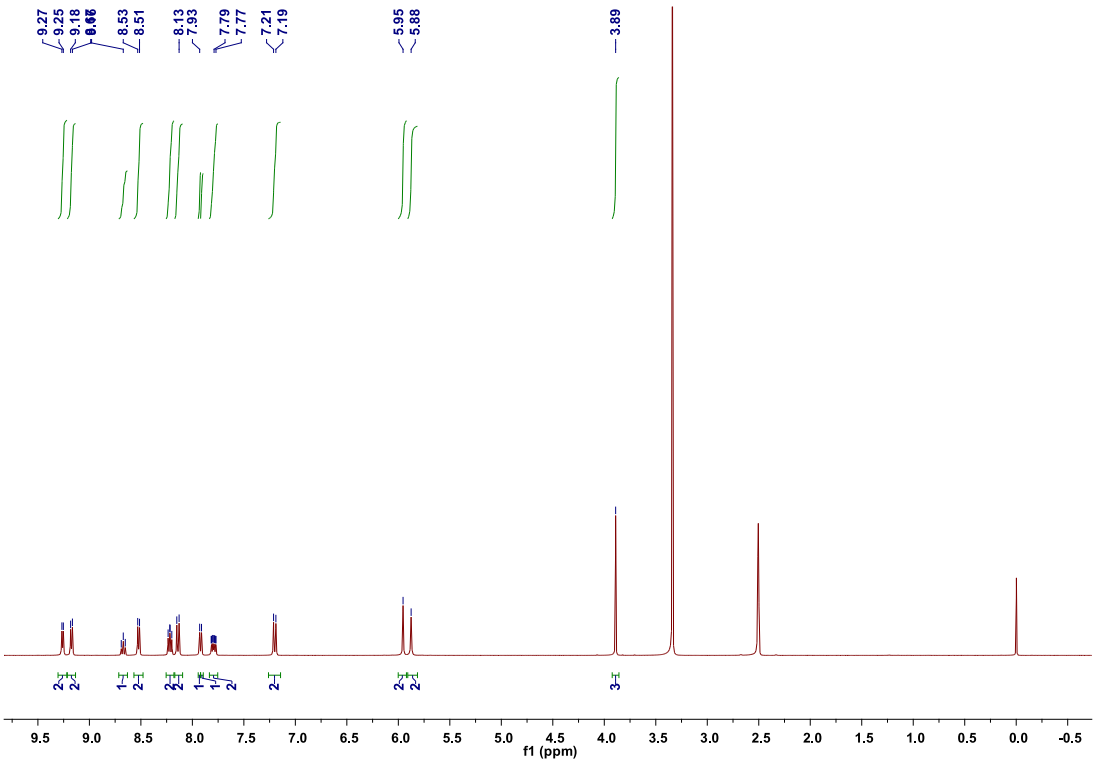
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **7**.



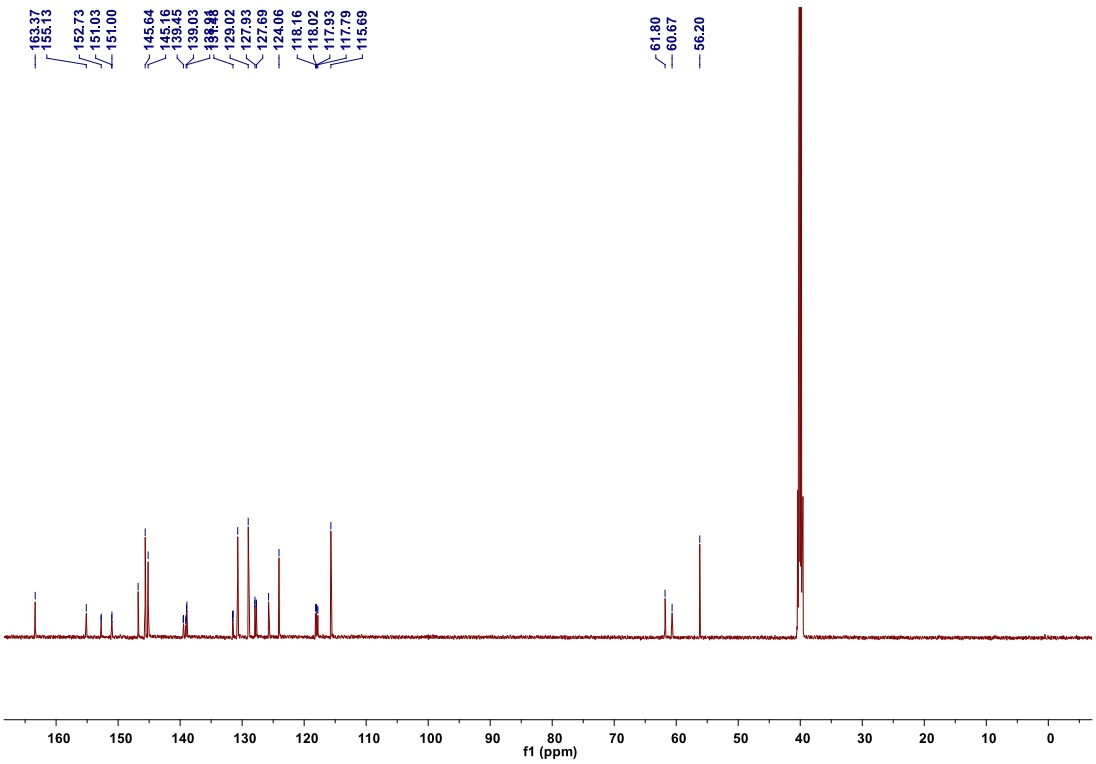
^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **7**.



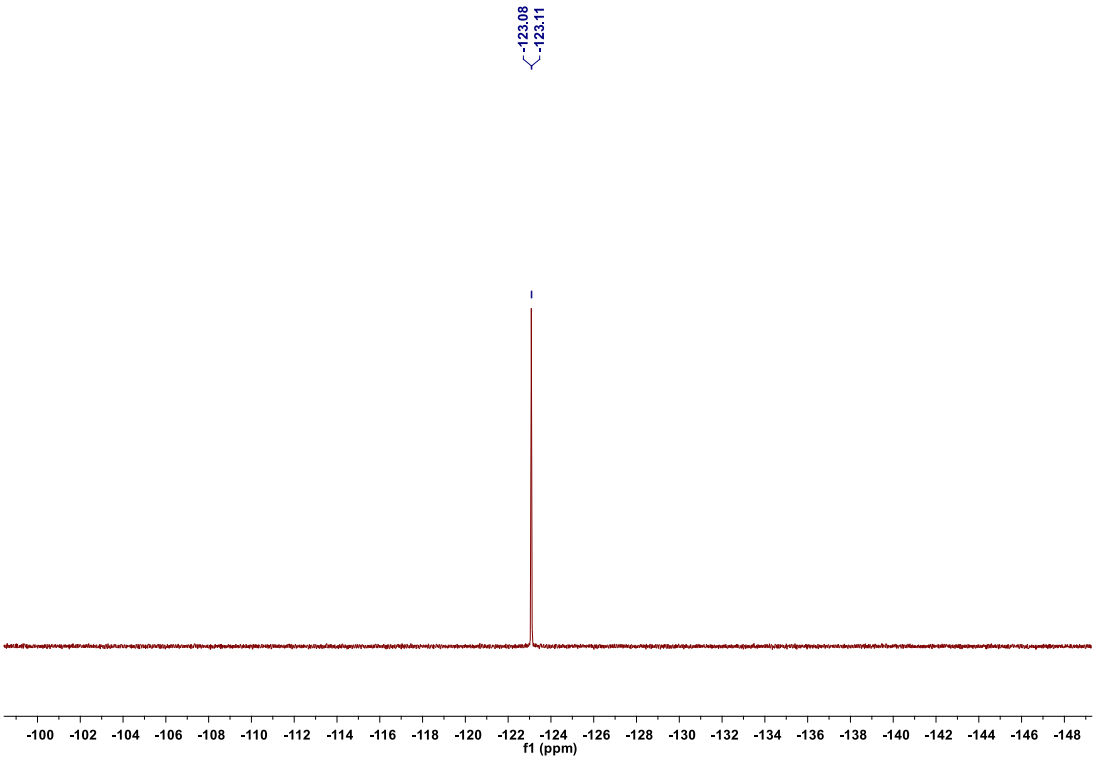
^{19}F NMR spectrum (564 MHz, $CDCl_3$, 298 K) of compound **7**.



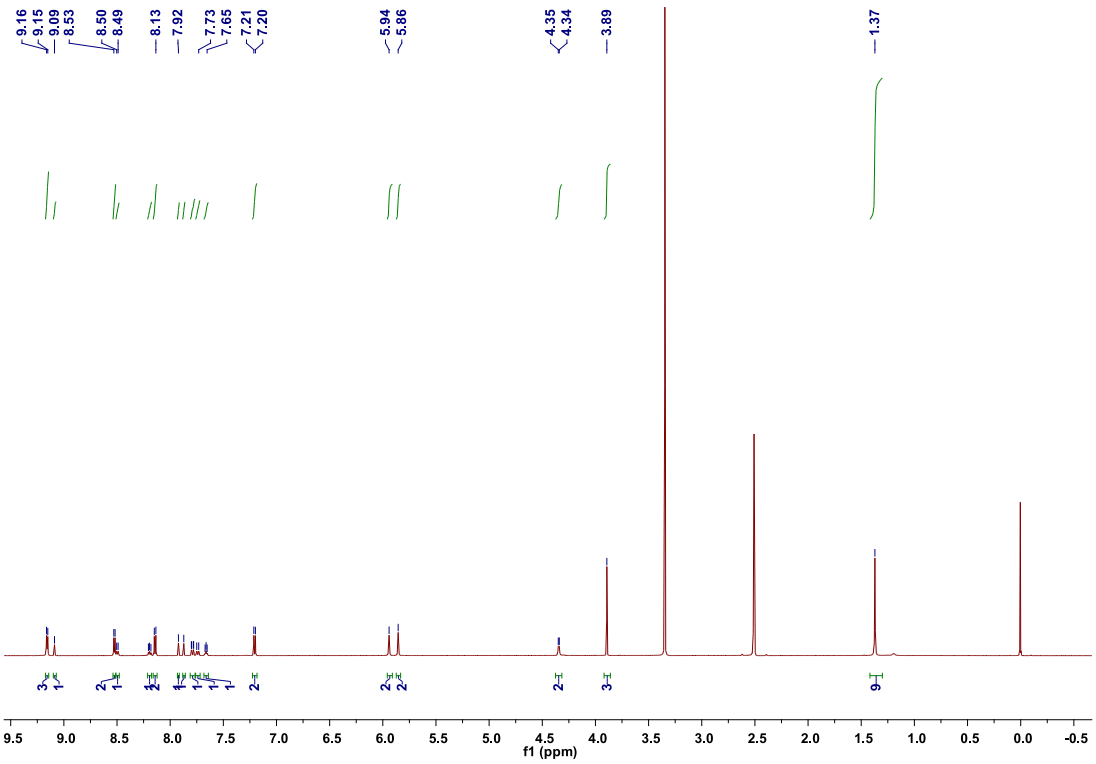
^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **8**.



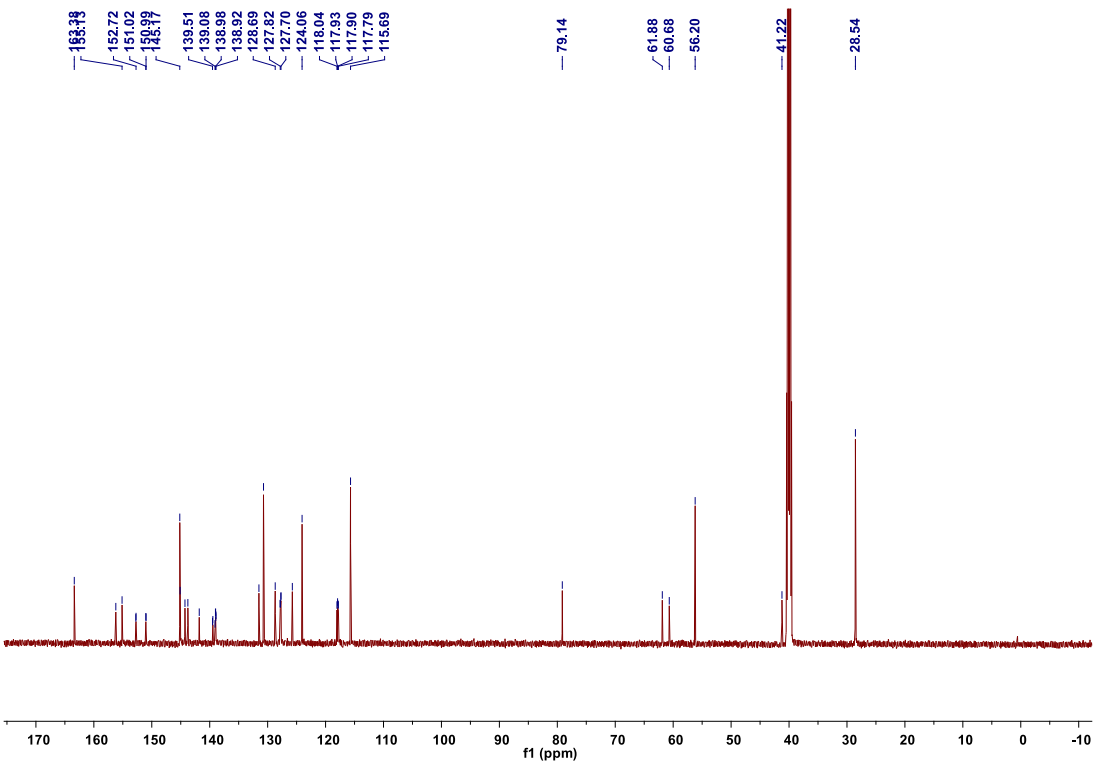
^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **8**.



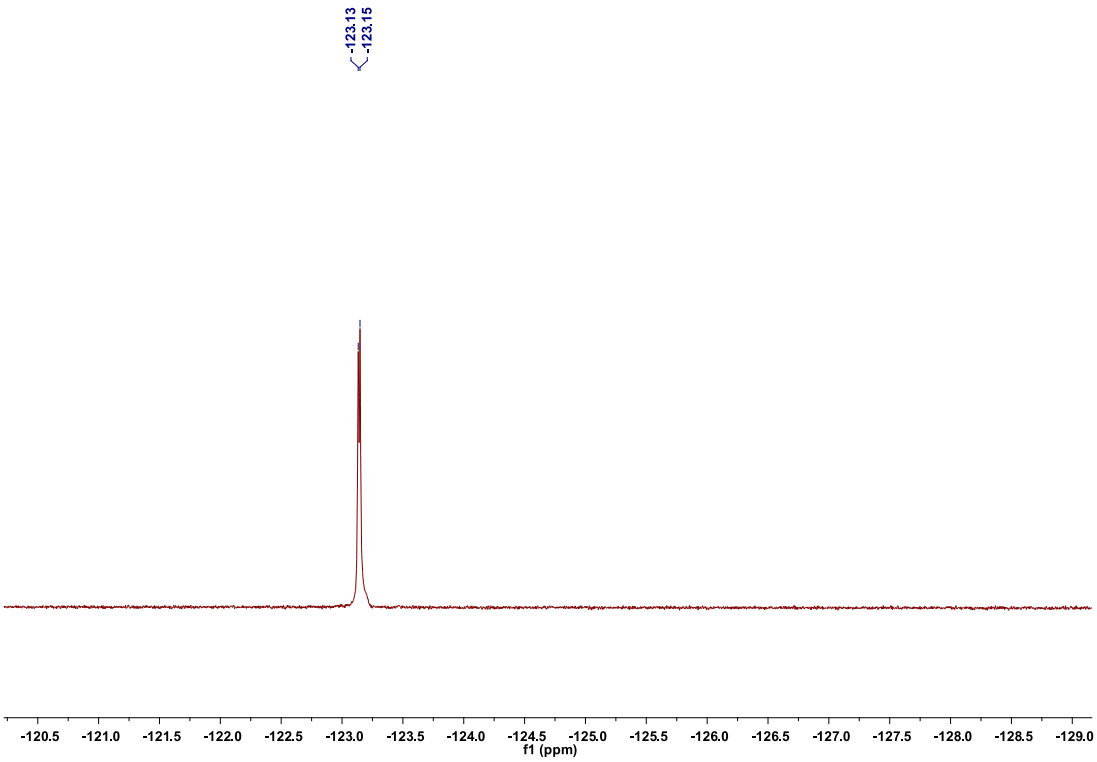
^{19}F NMR spectrum (376 MHz, DMSO-d_6, 298 K) of compound **8**.



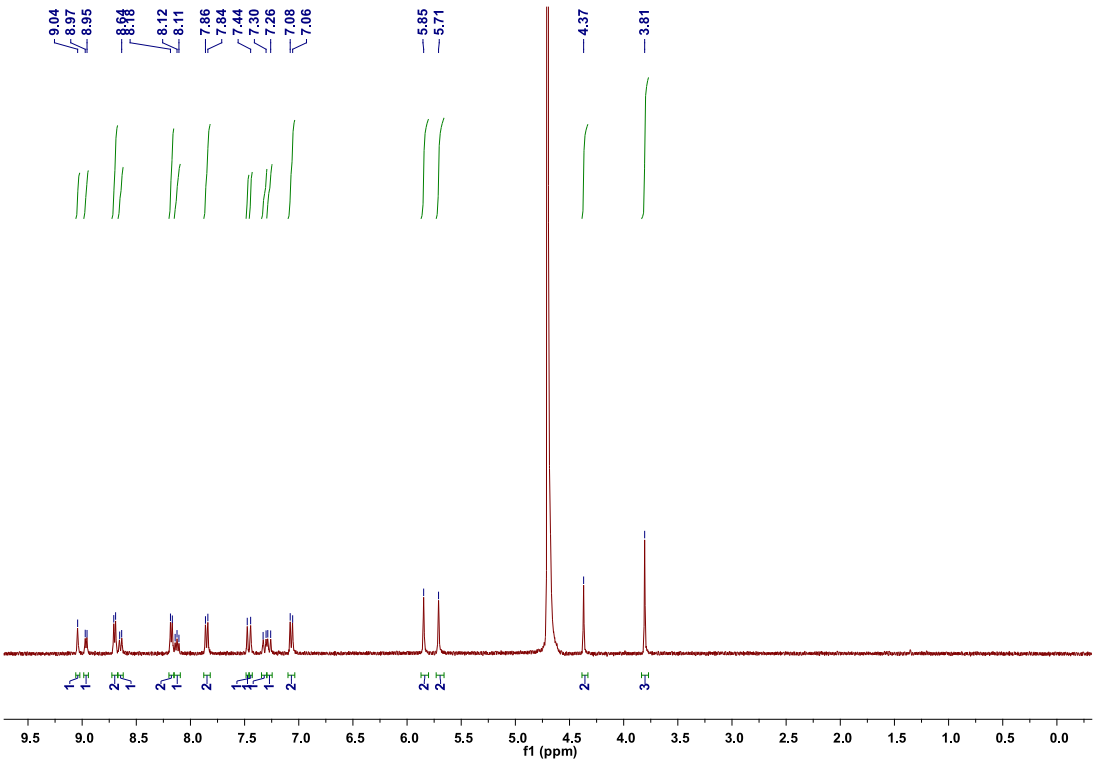
^{1}H NMR spectrum (600 MHz, DMSO-d_6, 298 K) of compound **9**.



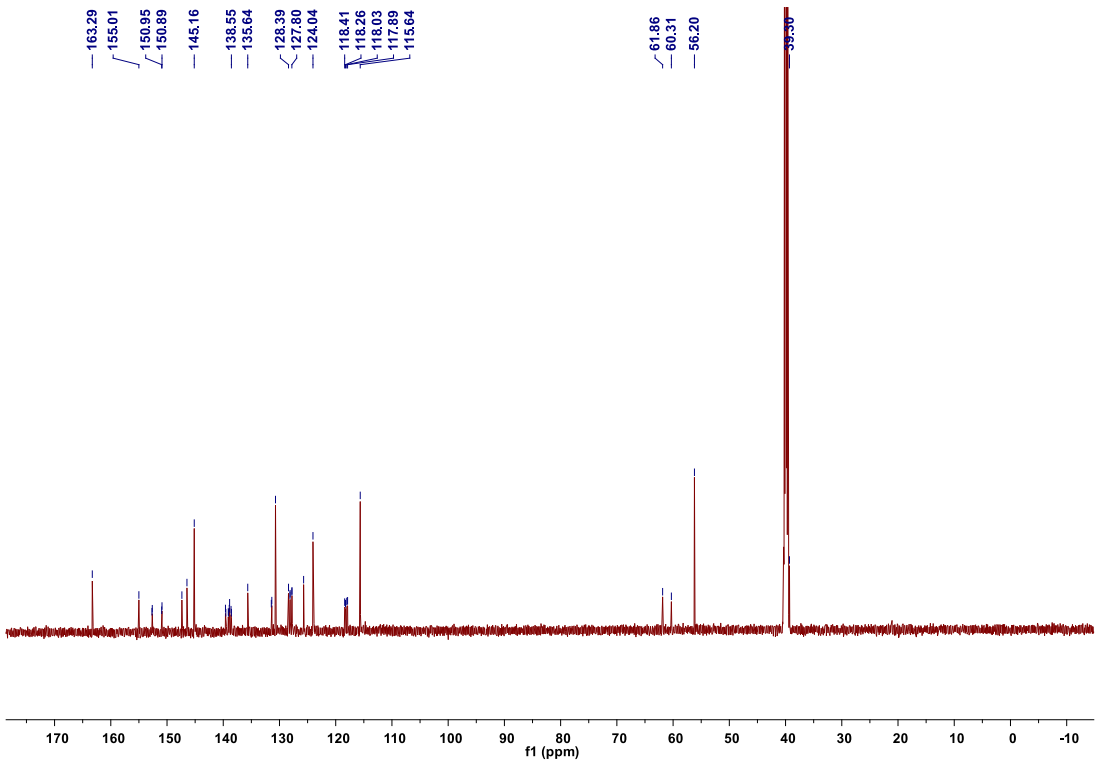
^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **9**.



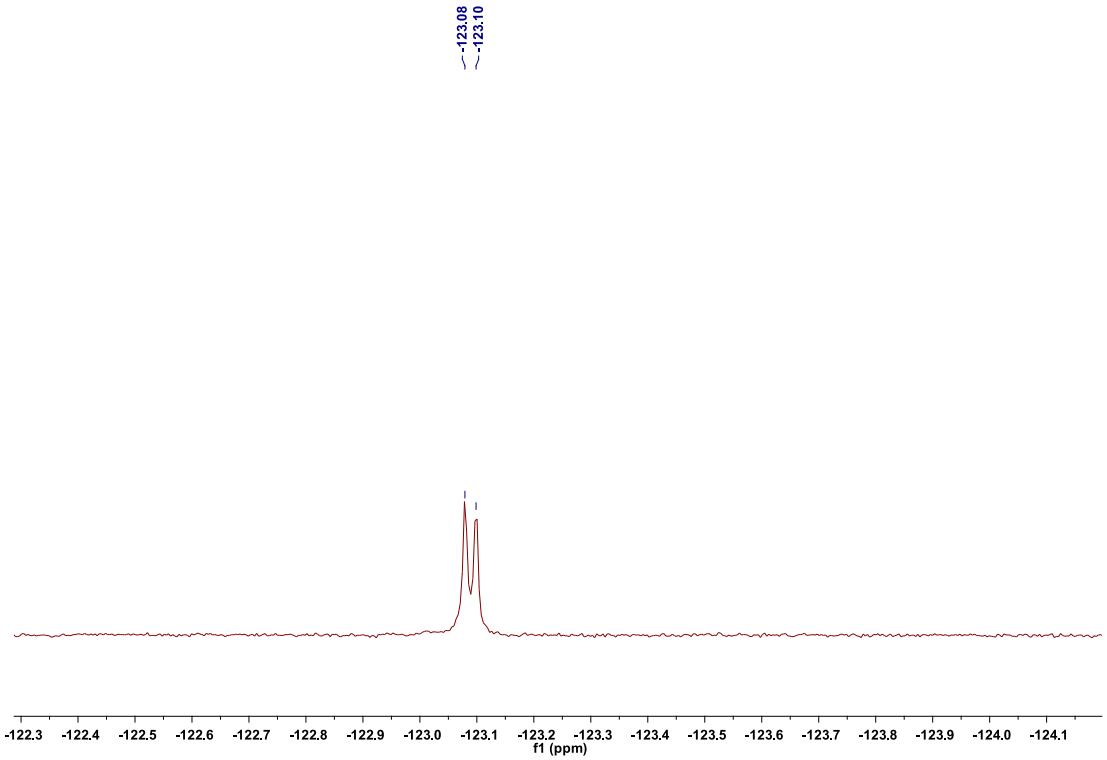
^{19}F NMR spectrum (564 MHz, DMSO-d_6, 298 K) of compound **9**.



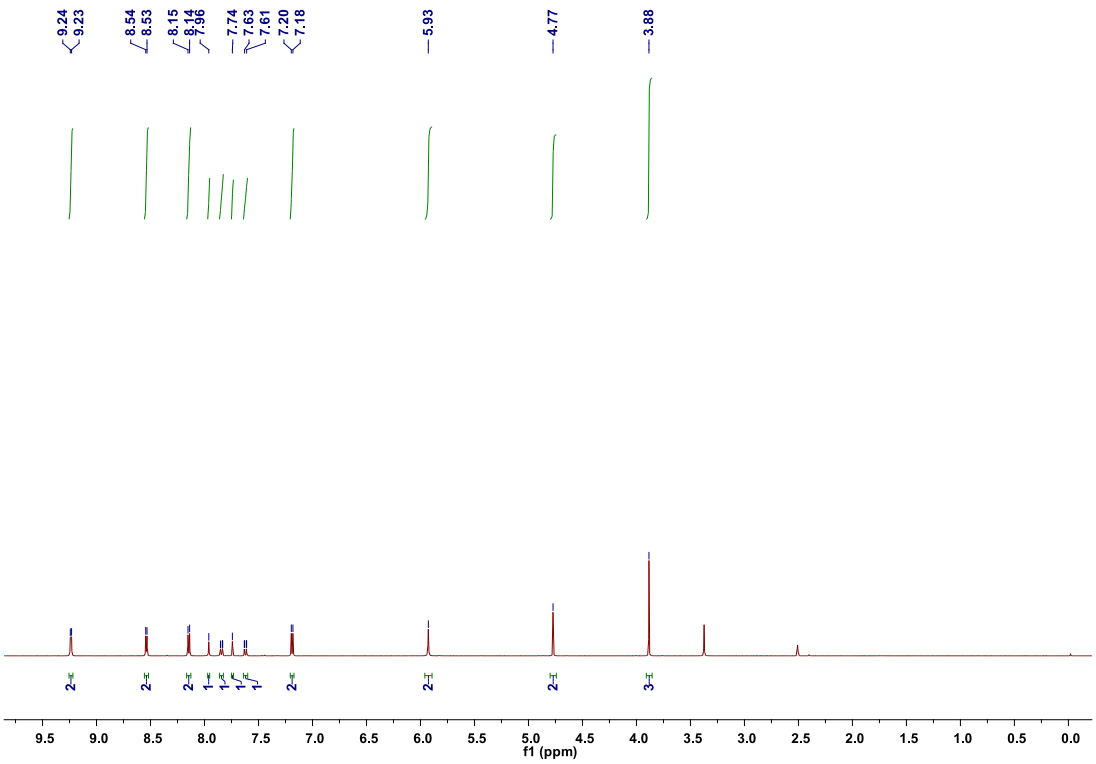
^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of compound **G5**.



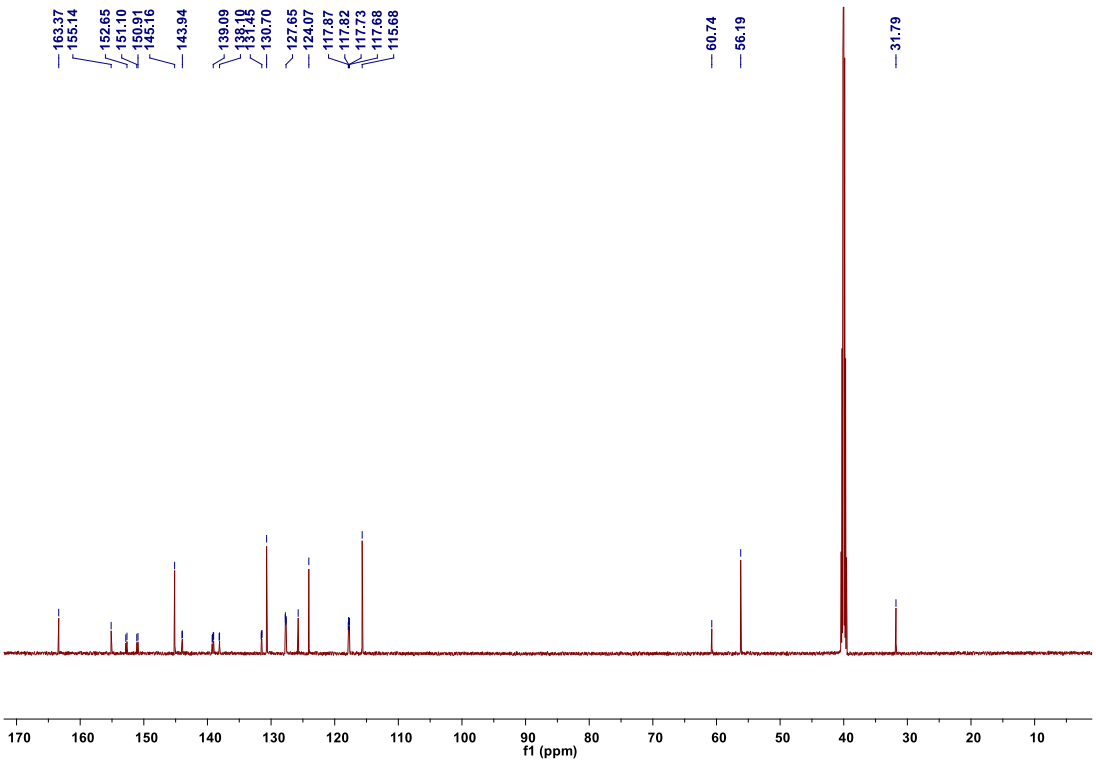
^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **G5**.



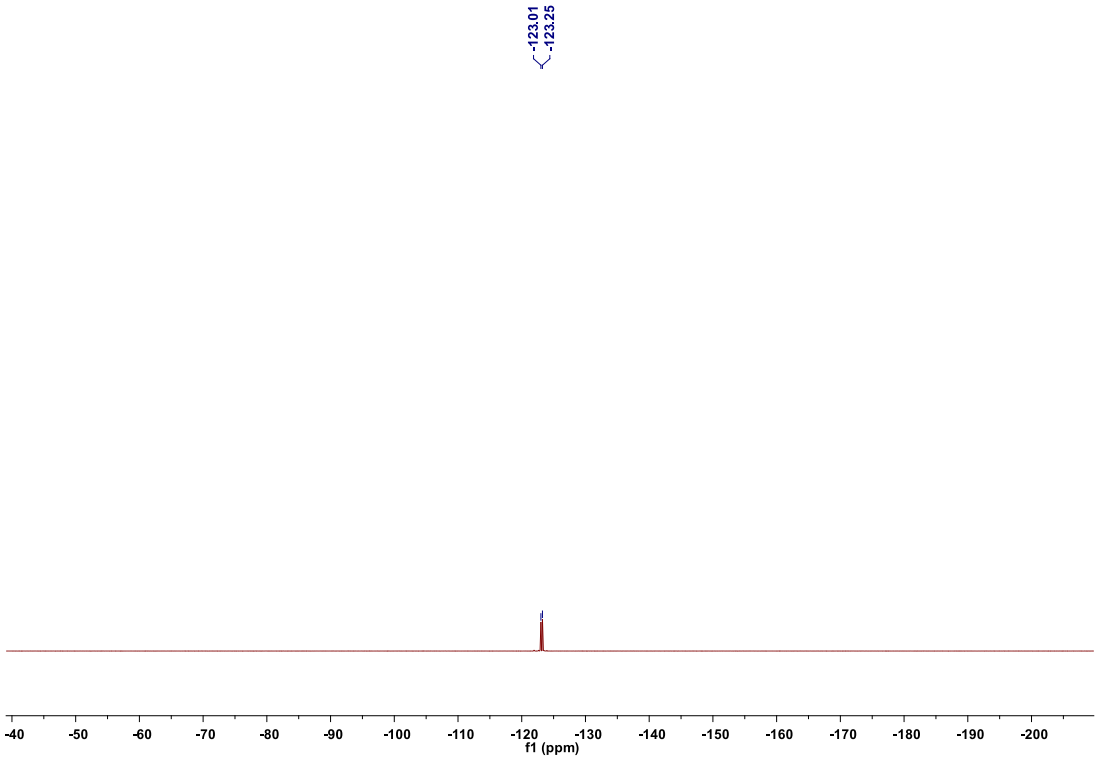
^{19}F NMR spectrum (376 MHz, DMSO-d_6, 298 K) of compound **G5**.



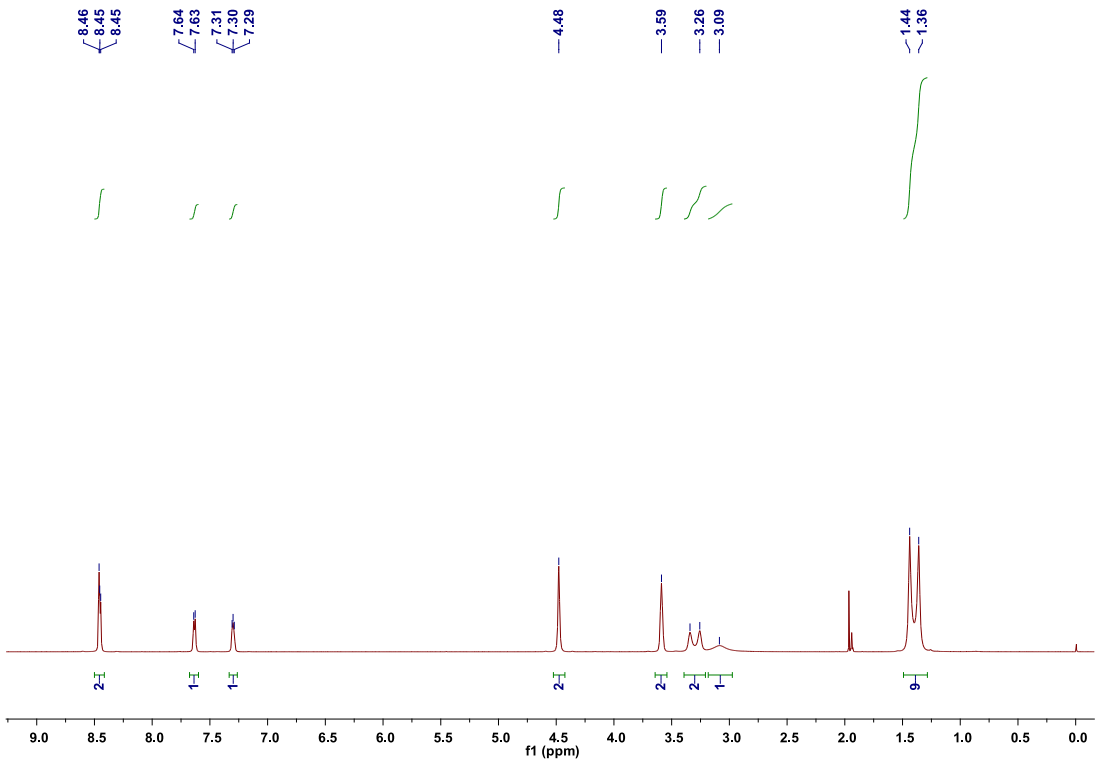
^{1}H NMR spectrum (600 MHz, DMSO-d_6, 298 K) of compound **10**.



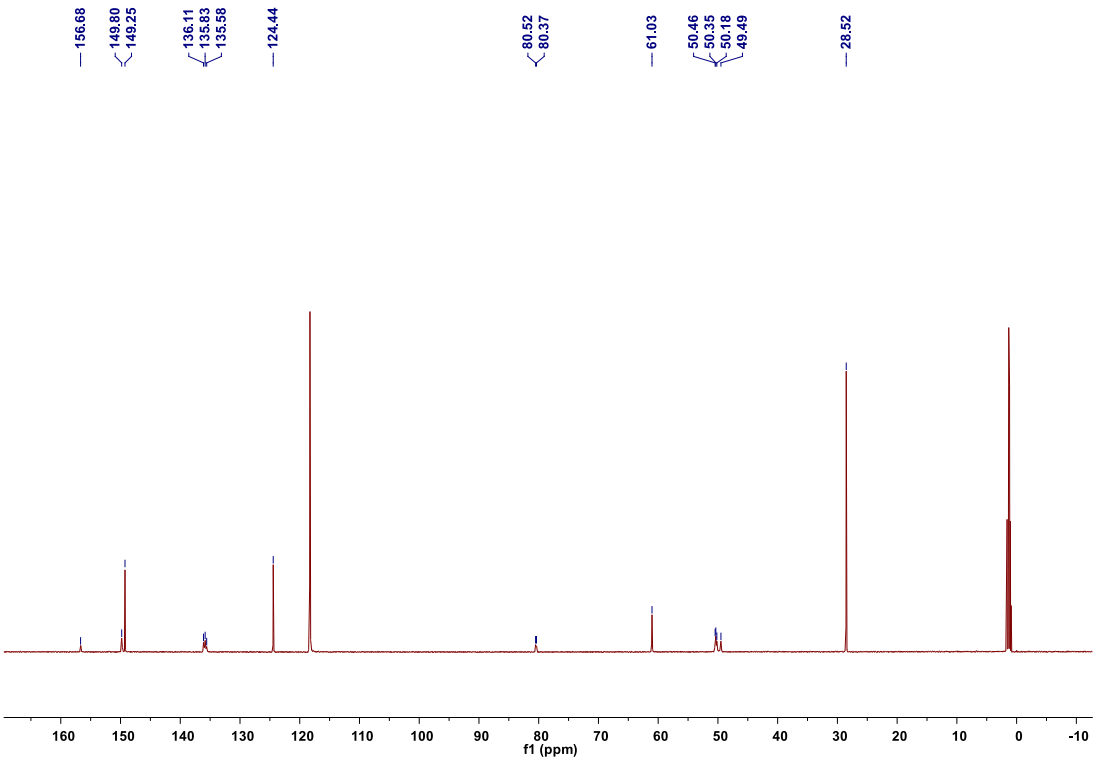
^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **10**.



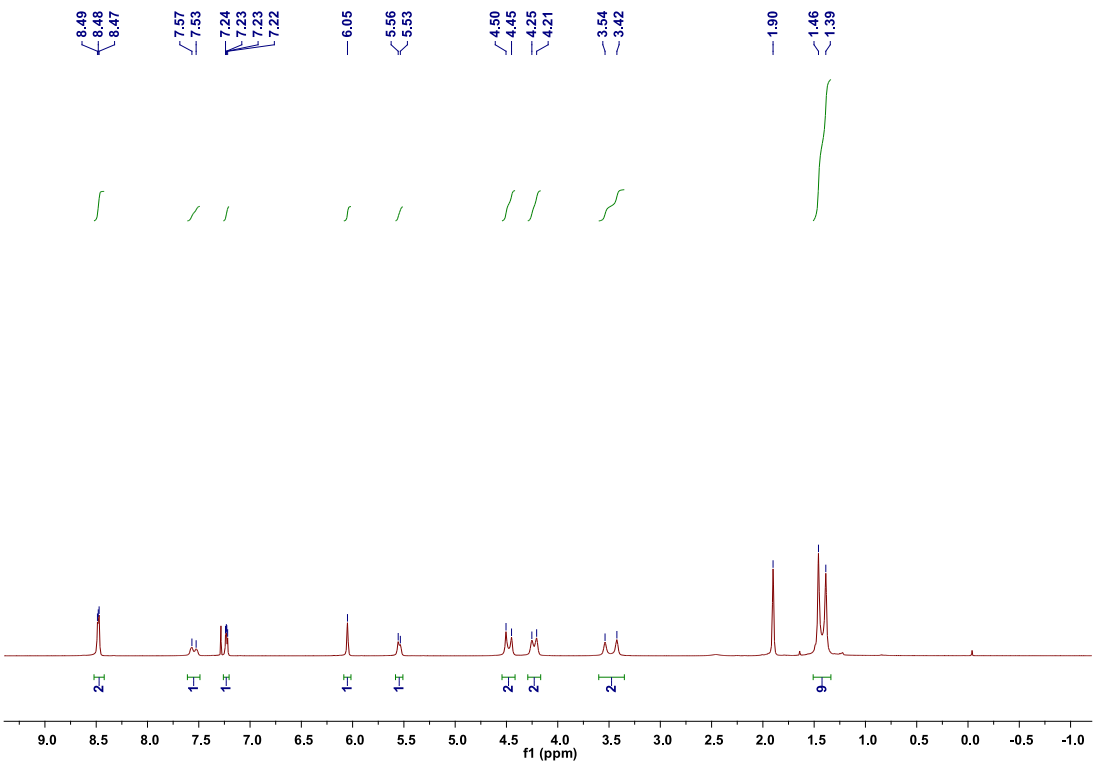
^{19}F NMR spectrum (564 MHz, DMSO-d_6, 298 K) of compound **10**.



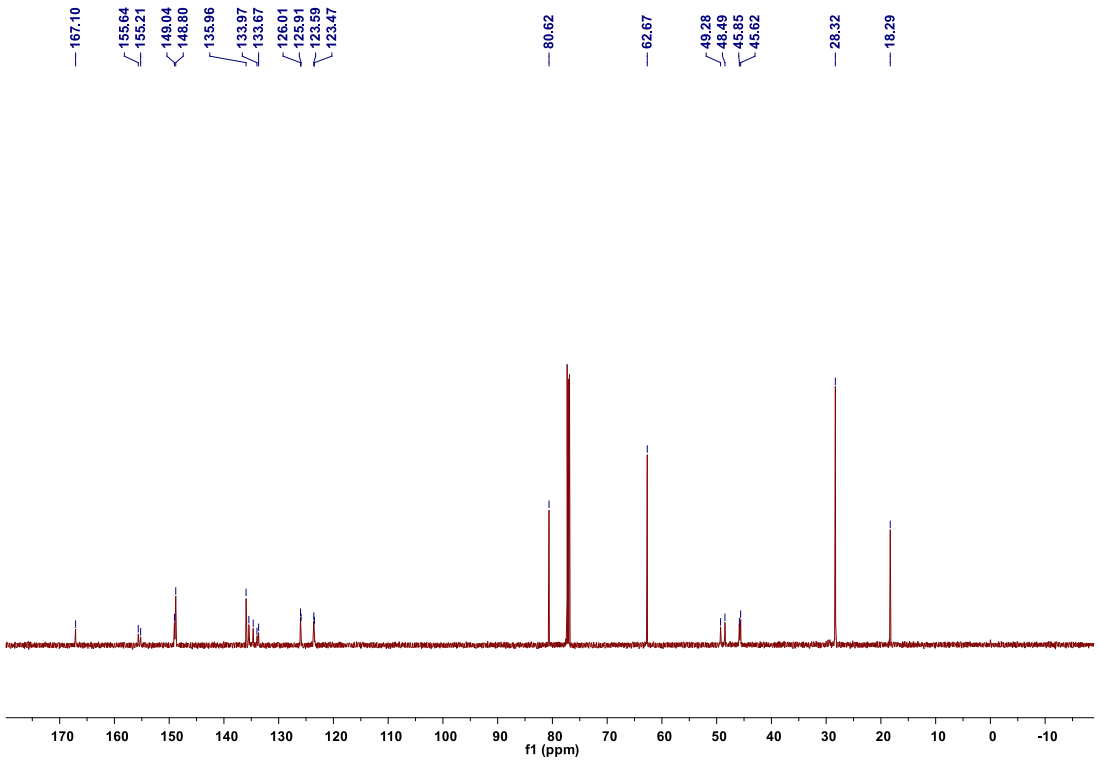
^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of compound **12**.



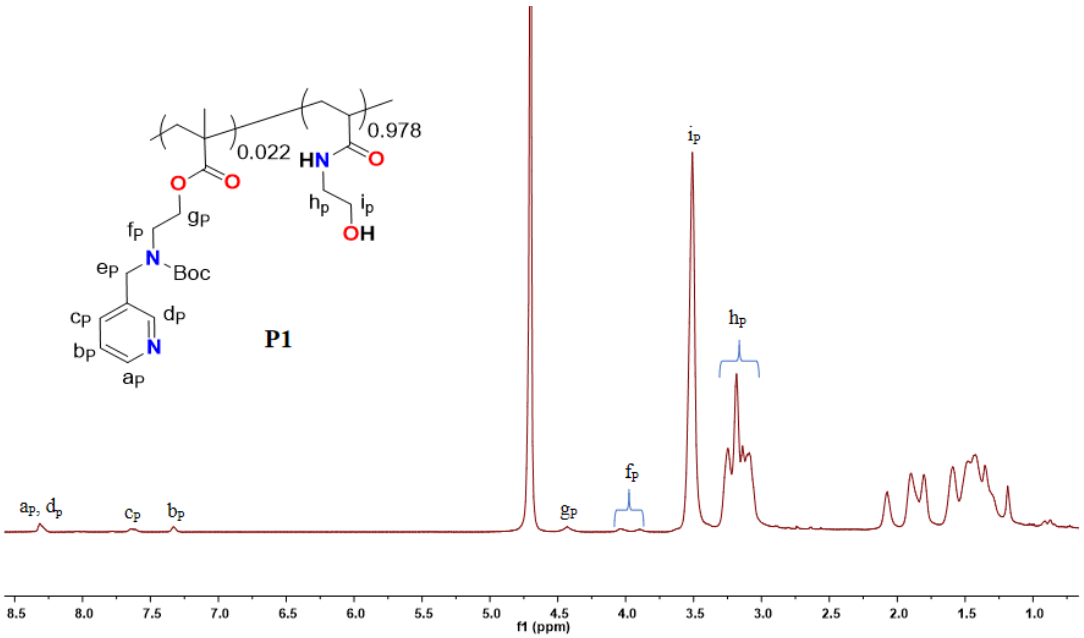
^{13}C NMR spectrum (150 MHz, CD_3CN, 298 K) of compound **12**.



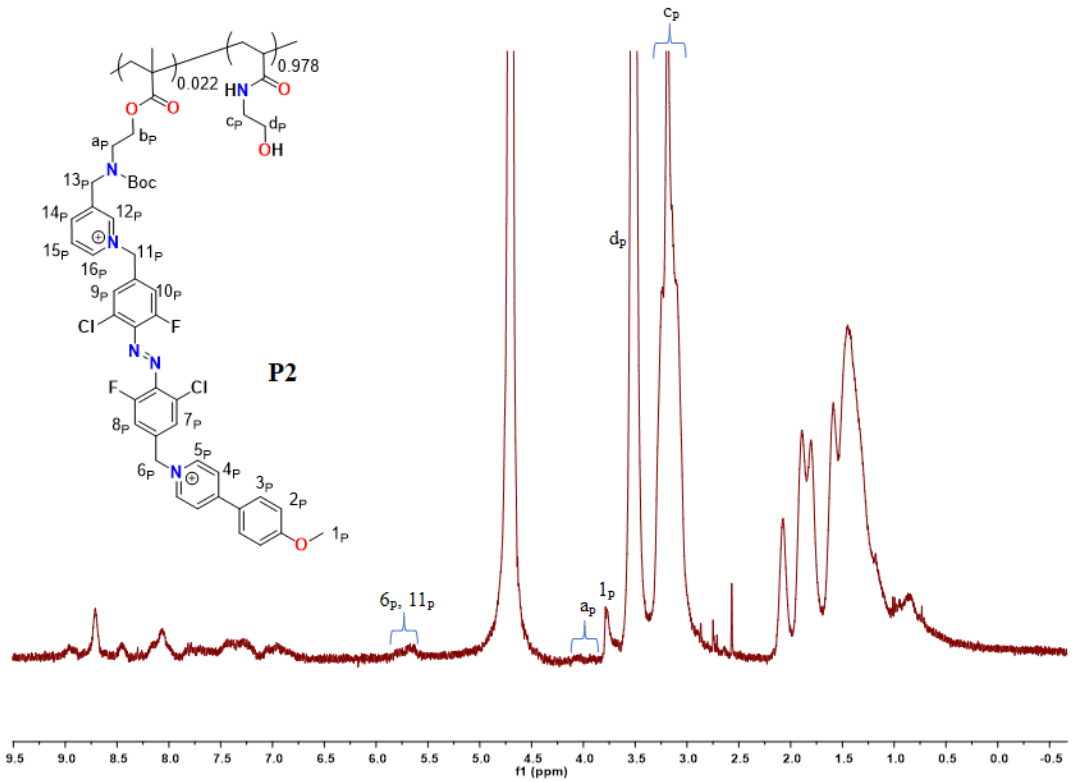
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **14**.



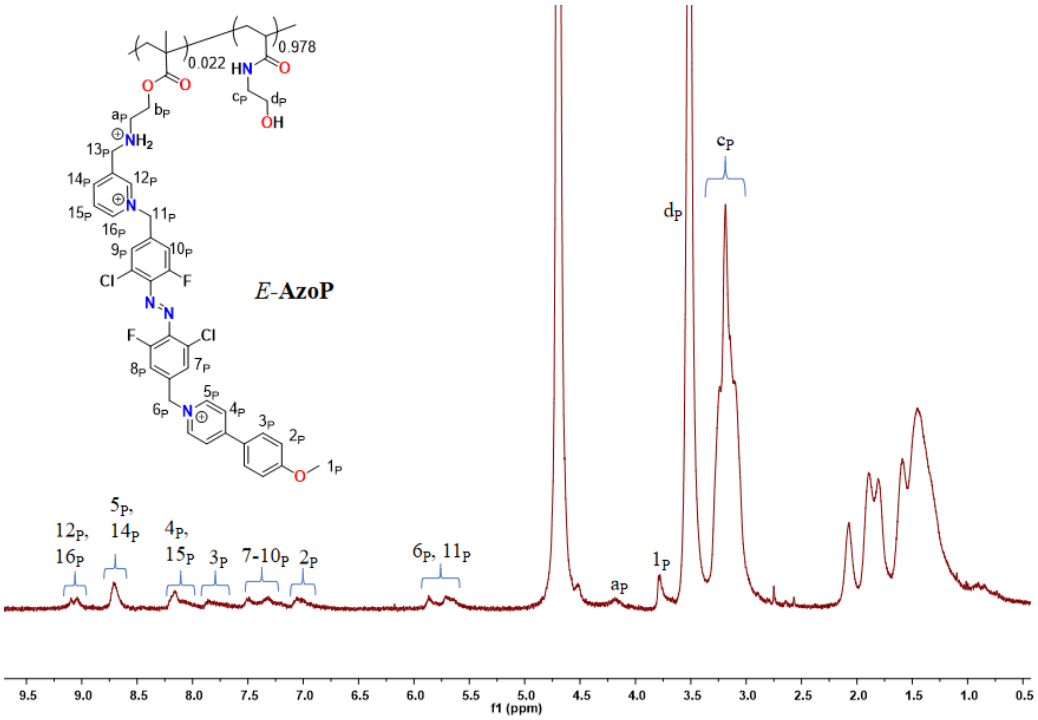
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **14**.



^{1}H NMR spectrum (600 MHz, D_2O, 298K) of the solution of polymer **P1**.



^{1}H NMR spectrum (600 MHz, D_2O, 298K) of the solution of polymer **P2**.



^{1}H NMR spectrum (400 MHz, D_2O, 298K) of the solution of polymer *E*-**AzoP**.

References

[1] L. Agnetta, M. Bermudez, F. Riefolo, C. Matera, E. Claro, R. Messerer, T. Littmann, G. Wolber, U. Holzgrabe and M. Decker, *J. Med. Chem.*, 2019, **62**, 3009-3020.

[2] X. Duan, R. Sun, J. Tang, S. Li, X. Yang, X. Zheng, R. Li, H. Chen, H. Fu and M. Yuan, *J. Org. Chem.*, 2022, **87**, 7975-7988.

[3] J. Wei, T.-T. Jin, Y.-F. Yin, X.-M. Jiang, S.-T. Zheng, T.-G. Zhan, J. Cui, L.-J. Liu, L.-C. Kong and K.-D. Zhang, *Org. Chem. Front.*, 2019, **6**, 498-505.

[4] T. H. L. Nguyen, N. Gigant, S. Delarue-Cochin and D. Joseph, *J. Org. Chem.* 2016, **81**, 1850-1857.

[5]. K. Pothula, L. Tang, Z. Zha and Z. Wang, *RSC Adv.*, 2015, **5**, 83144-83148.

[6] G. Li, X. Qian, S. Yan, J. Cui, R. Zhang and Y. Xiao, *Monatsh. Chem.*, 2008, **139**, 169-178.

[7] S. Liu, C. Ruspic, P. Mukhopadhyay, S. Chakrabarti, P.Y. Zavalij and L. Isaacs. *J. Am. Chem. Soc.*, 2005, **127**, 15959-15967.