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Electronic Supplementary Information

Red-light responsive molecular encapsulation in water: An ideal combination between photochemistry and host-guest interaction

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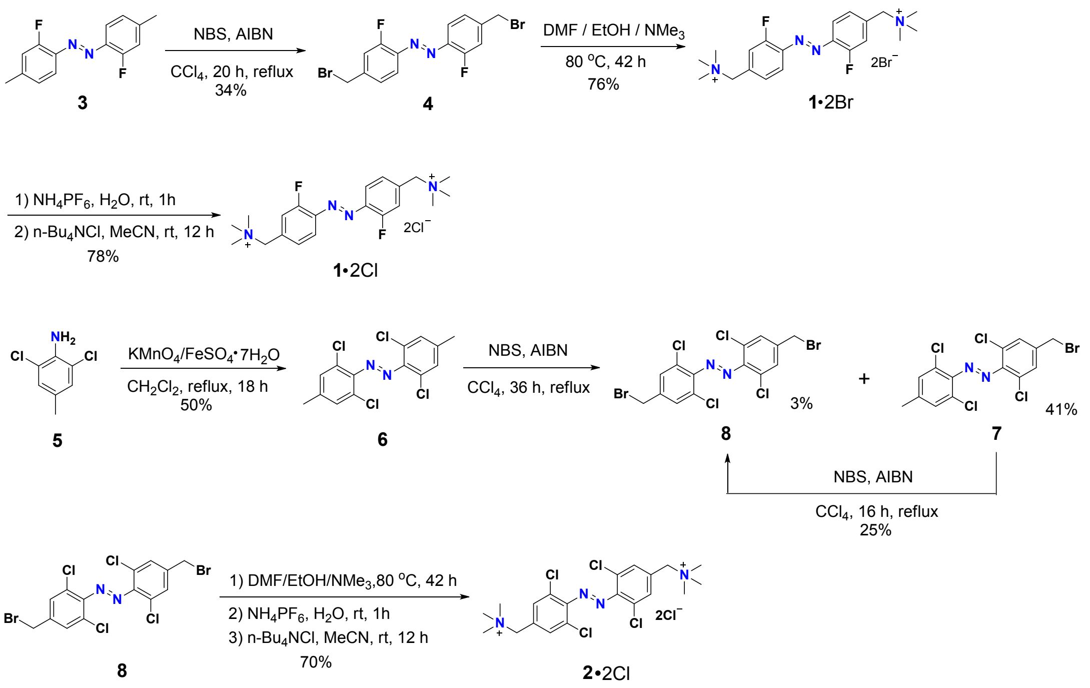
Section 1: Materials and General Methods

All reagents were used as received from the commercial suppliers without further purification; the solvents have been purified by standard procedures before use. Compounds **3**[1] was synthesized according to the literatures.

The ^1H NMR, ^{13}C NMR and 2D DOSY spectra were recorded on a Bruker AVANCE 600 spectrometer. UV-Vis absorption spectra were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer.

The irradiation experiments were performed by using a 100 W LED lamp (white light) and a 60 W LED lamp (650-660 nm) equipped with a long pass filter (> 500 nm) and a narrow band pass filter (650 nm), respectively.

Section 2: Synthetic Procedures



Scheme S1. Synthetic route of **1** and **2**.

Compound 4. Compound **3**[1] (68.6 mg, 0.279 mmol) was dissolved in 12 mL carbon tetrachloride, to which NBS (136 mg, 0.764 mmol) and AIBN (11.2 mg, 0.0682 mmol) were further added, and the resulting mixture was refluxed for 20 hours under nitrogen atmosphere. After cooling down to the room temperature, the precipitates was removed by filtration and washed with 30 mL ethyl acetate. The filtrate was collected and washed with water (3 × 30 mL) and brine (30 mL) consecutively; the combined organic phase was dried by anhydrous sodium sulfate. After removing the desiccant by filtration, the solvent was evaporated and the remaining residue was further purified by flash column chromatography using petroleum ether as eluent. Compound **4** (38.3 mg, 0.0949 mmol) could be obtained as yellow solid in the yield of 34%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.77 (t, J = 8.4 Hz, 2H), 7.32 (dd, J_1 = 10.8 Hz, J_2 = 1.8, 2H), 7.24 (dd, J_1 = 8.4 Hz, J_2 = 1.8, 2H), 4.50 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 106.14 (d, $J_{C\text{-}F}$ = 258 Hz), 143.32 (d, $J_{C\text{-}F}$ = 8 Hz), 140.45 (d, $J_{C\text{-}F}$ = 7 Hz), 125.09 (d, $J_{C\text{-}F}$ = 3 Hz), 118.30, 117.73 (d, $J_{C\text{-}F}$ = 21 Hz), 31.56. ^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): -128.09. MS (ESI) *m/z*: 403.0 $[M+H]^+$. HRMS (ESI): Calcd for $C_{14}H_{11}Br_2F_2N_2$ $[M+H]^+$: 402.9252. Found: 402.9249.

Compound 1•2Br. Compound **4** (100 mg, 0.248 mmol) was dissolved in binary solvent of DMF (2.8 mL) and trimethylamine (31-35% wt.% in ethanol, 1.34 mL), the resulting mixture was heated at 80 °C for 48 hours. After the reaction was complete as monitored by TLC, the reaction mixture was cooling down to room temperature. The yellow precipitates were collected by filtration and washed with acetonitrile (15 mL) and ether (30 mL). After dried, compound **1**•2Br (98.2 mg, 0.188 mmol) could be prepared as orange solid I the yield of 76%. ^{1}H NMR (600 MHz, D_2O) δ (ppm): 7.76 (t, J = 8.4 Hz, 2H), 7.54 (dd, J_1 = 11.4 Hz, J_2 =1.8 Hz, 2H), 7.42 (dd, J_1 = 8.4 Hz, J_2 = 1.8Hz, 2H), 4.51 (s, 4H), 3.09 (s, 18H). ^{13}C NMR (150 MHz, D_2O) δ (ppm): 159.09 (d, $J_{C\text{-}F}$ = 256 Hz), 141.49 (d, $J_{C\text{-}F}$ = 7 Hz), 133.13 (d, $J_{C\text{-}F}$ = 8 Hz), 129.48 (d, $J_{C\text{-}F}$ = 3 Hz), 121.72 (d, $J_{C\text{-}F}$ = 21 Hz), 119.06, 68.33, 52.70. ^{19}F NMR (564 MHz, D_2O) δ (ppm): -123.12. MS (ESI) *m/z*: 181.2 $[M-2Br^-]^{2+}$. HRMS (ESI): Calcd for $C_{20}H_{28}F_2N_4$ $[M-2Br^-]^{2+}$: 181.1135. Found: 181.1142.

Compound 1•2Cl. Compound **1**•2Br (90.0 mg, 0.172 mmol) was dissolved in 10 mL water, to which saturated ammonium hexafluorophosphate aqueous solution was added, and yellow precipitates were generated. The precipitates were collected by filtration and dissolved in 5 mL anhydrous acetonitrile; the tetrabutylammonium chloride (700 mg, 2.52 mmol) was then added to generate yellow precipitates and the suspension was stirred for another 12 hours. The precipitates were collected and washed with 25 mL acetonitrile and dried. Compound **1**•2Cl (58.1 mg, 0.134 mmol) was obtained as orange solid in the yield of 78%.

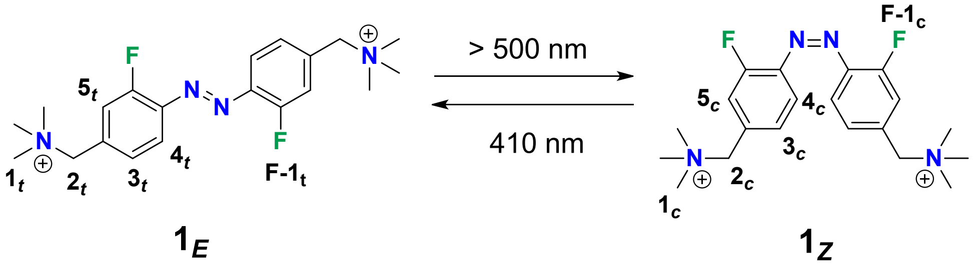
Compound 6. $KMnO_4$ (960mg, 6.08 mmol) and $FeSO_4$•$7H_2O$ (960 mg, 3.45 mmol) were mixed and grinded, the resulting solid mixture was further suspended in 17 mL CH_2Cl_2, compound **5** (100 mg, 0.568 mmol) was then added and the resulting mixture was refluxed for 16 hours under nitrogen atmosphere. After the reaction was complete as monitored by TLC, the reaction mixture was cooling down to room temperature.

The solid was removed by filtration and the filtrate was collected, the solvent was evaporated and the remaining residue was further purified by flash column chromatography by using petroleum ether as eluent. Compound **6** (49.4 mg, 0.142 mmol) was prepared as orange solid in the yield of 50%. ^{1}H NMR (600 MHz, CD_3CN) δ (ppm): 7.41 (s, 4H), 2.39 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 145.28, 140.55, 129.66, 127.28, 20.85. MS (ESI) *m/z*: 347.0 $[M+H^+]^+$. HRMS (ESI): Calcd for $C_{14}H_{11}Cl_4N_2$ $[M+H^+]^+$: 346.9671. Found: 346.9681.

Compound 8. Compound **6** (300 mg, 0.861 mmol), N-bromosuccinimide (405 mg, 2.29 mmol) and Azobisisobutyronitrile (30.0 mg, 0.183 mmol) were mixed in 20 mL carbon tetrachloride. The resulting mixture was refluxed for 36 hours under nitrogen atmosphere, after cooling down, the solvent was evaporated and the remaining residue was purified by flash column chromatography using the binary solvent of CH_2Cl_2:PE (1:60→1:20). The mono-brominated compound **7** (150 mg, 0.351 mmol) and bi-brominated compound **8** (13.2 mg, 0.0258 mmol) were isolated in the yields of 40% and 3%, respectively. The as-synthesized compound **7** (150 mg, 0.351 mmol) was further with N-bromosuccinimide (82.6 mg, 0.469 mmol) and azobisisobutyronitrile (15.0 mg, 0.0916 mmol) in another 15 mL carbon tetrachloride. The resulting mixture was further refluxed for another 16 hours under nitrogen atmosphere. After cooling down, the solvent was removed by evaporation and the remaining residue was further purified by flash column chromatography using the binary solvent of CH_2Cl_2:PE (1:60→1:20→1:0). The crude compound **8** was collected and recrystallized in CH_2Cl_2, compound **8** (44.4 mg, 0.0878 mmol) was then obtained as yellow solid in the yield of 25%. After combining the purified products from these two steps, compound **8** (57.6 mg, 0.114 mmol) could prepared in a total yield of 13%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.49 (s, 4H), 4.43 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 147.13, 140.00, 129.90, 127.70, 30.35. MS (MALDI) *m/z*: 502.8 $[M+H]^+$. HRMS (DART Positive Ion Mode): Calcd for $C_{14}H_9Br_2Cl_4N_2$ $[M+H]^+$: 502.7881. Found: 502.7871.

Compound 2•2Cl. Compound **6** (160 mg, 0.316 mmol) was dissolved in binary solvent of DMF (3.5 mL) and trimethylamine (31-35% wt.% in ethanol, 1.8 mL), the resulting mixture was heated at 80 ^{o}C for 48 hours. The solid was completely dissolved when the temperature of the oil bath was raised to 75 °C, and yellow solid was precipitated as the reaction progressed. After the reaction was complete as monitored by TLC, the reaction mixture was cooling down to room temperature. 30 mL ether was then added to the reaction mixture and generating black precipitates, which were collected by filtration. The obtained solid product was further purified by flash column chromatography using the ternary solvent of MeOH/H_2O/saturated $NH_4Cl_{(aq)}$ = 6:3:0.01 as eluent. The yellow crude product was isolated and further dissolved in 20 mL water, to which saturated NH_4PF_6 aqueous solution was added to generate yellow precipitates. After filtrating, the solid was collected and further dissolved in 6 mL anhydrous acetonitrile. NH_4Cl (1.30 g, 4.68 mmol) was then added into the resulting solution and yellow solid was precipitated. This suspension was further stirred for another 12 hours at room temperature, and the precipitates were collected by filtration and washed by 25 mL acetonitrile. After dried under vacuum, compound **2**•2Cl (112 mg, 0.221 mmol) could be obtained as yellow solid in the yield of 70%. ^{1}H NMR (600 MHz, D_2O) δ (ppm): 7.75 (s, 4H), 4.49 (s, 4H), 3.10 (s, 18H). ^{13}C NMR (150 MHz, D_2O) δ (ppm): 148.01, 133.78, 130.50, 127.11, 67.55, 52.74. MS (ESI) *m/z*: 231.1 $[M\text{-}2Cl^{-}]^{2+}$. HRMS (ESI): Calcd for $C_{20}H_{26}Cl_4N_4$ $[M\text{-}2Cl^{-}]^{2+}$: 231.0451. Found: 231.0461.

Section 3: Photochromic Behaviors of 1 in Water



Scheme S2

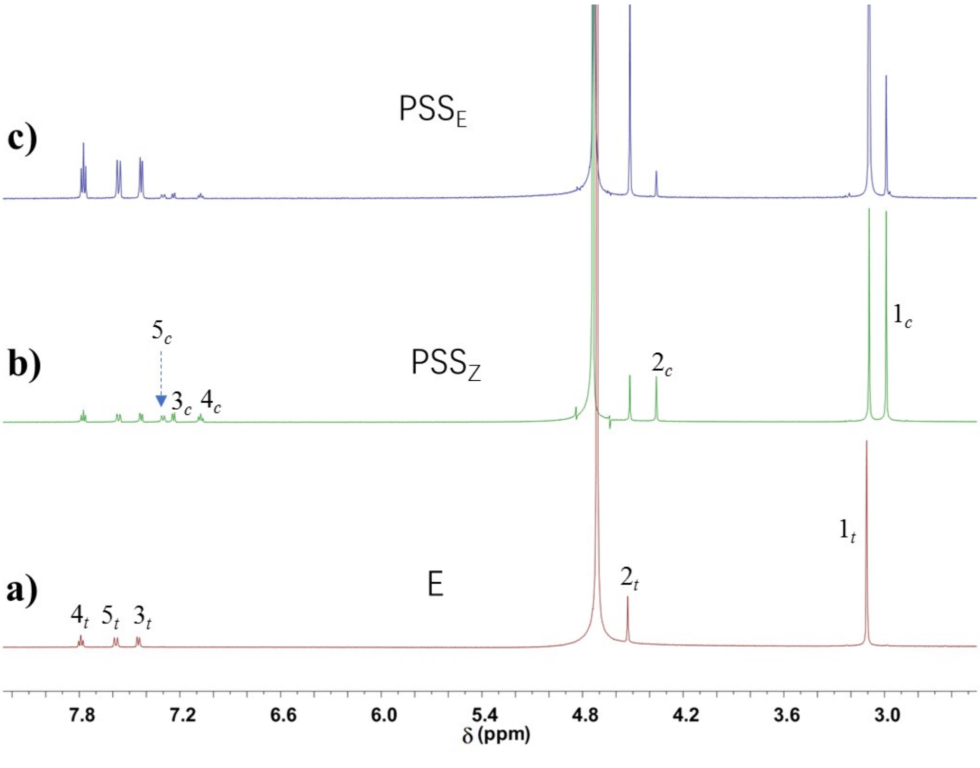


Fig. S1 ^{1}H NMR spectra (600 MHz, D_2O, 4.0 mM, 298K) of the solution of **1** a) before and b) after irradiation with yellow light (λ > 500 nm, 220 W / m^2) for 1.5 h; and the irradiated solution of **1** c) after irradiation by blue light (λ = 410 nm, 21 W / m^2) for 1 h.

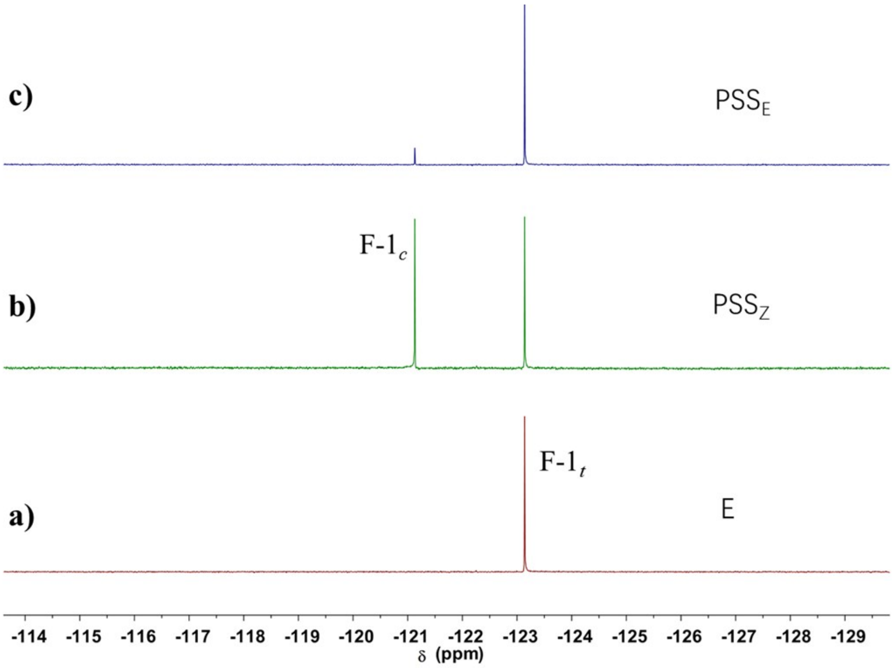


Fig. S2 ^{19}F NMR spectra (564 MHz, D_2O, 4.0 mM, 298K) of the solution of **1** a) before and b) after irradiation with yellow light (λ > 500 nm, 220 W / m^2) for 1.5 h; and the irradiated solution of **1** c) after irradiation by blue light (λ = 410 nm, 21 W / m^2) for 1 h.

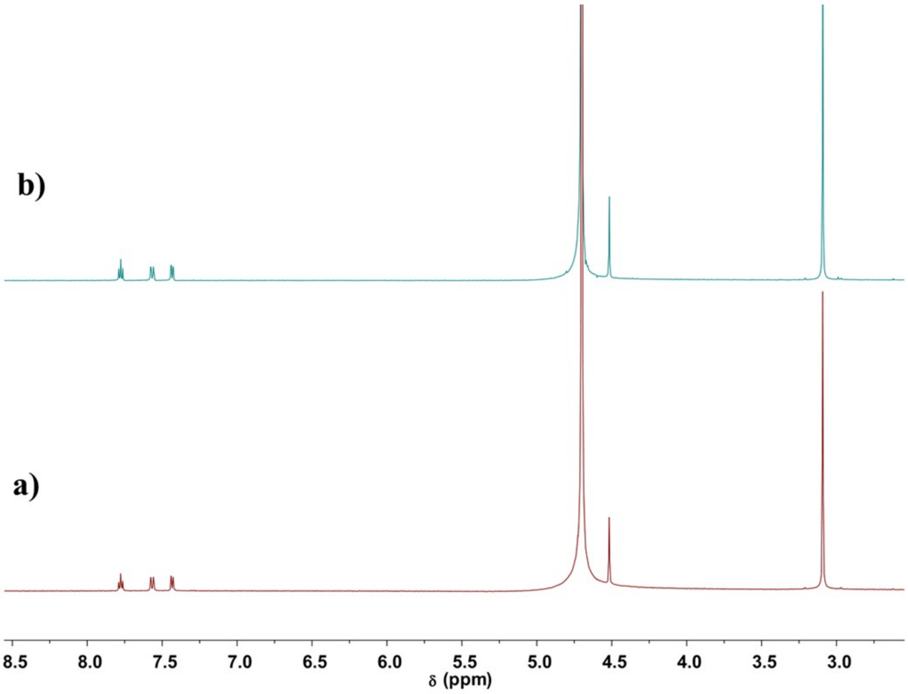


Fig. S3 ^{1}H NMR spectra (600 MHz, D_2O, 4.0 mM, 298K) of the solution of **1** a) before and b) after irradiation with red light (λ = 650 nm, 120 W / m^2) for 6 h.

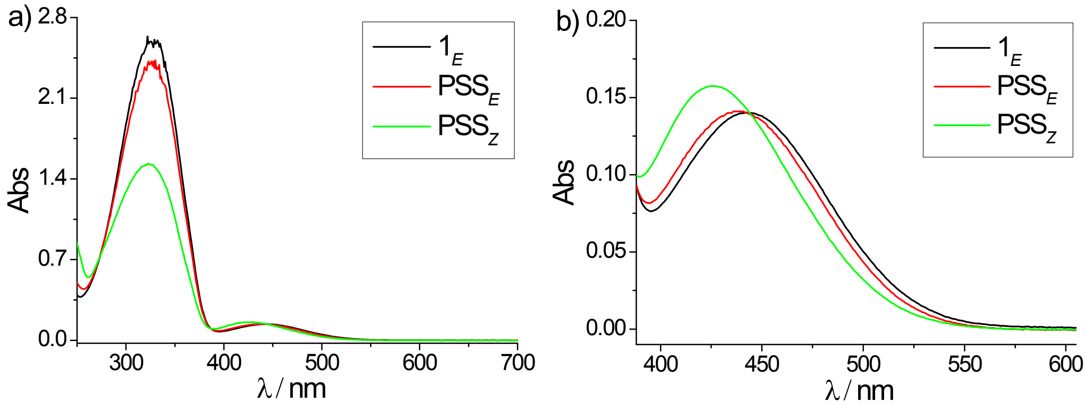


Fig. S4 The (a) full and (b) partial UV/Vis absorption spectra of **1** (0.128 mM) before (black line) and after (red line) irradiation with blue light (λ = 410 nm, 21 W / m^2) in H_2O at room temperature for 10 min, and the blue light-irradiated solution of **1** after irradiation by yellow light (λ > 500 nm, 220 W / m^2) for 30 min (green line).

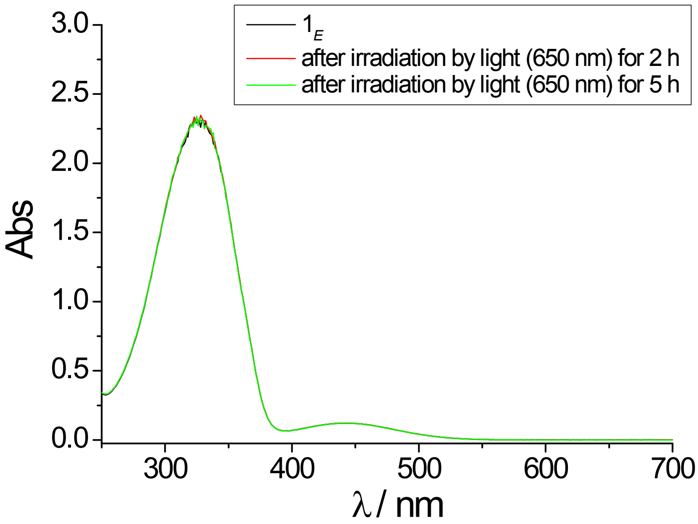


Fig. S5 UV/Vis absorption spectra of **1** (0.128 mM) before (black line) and after irradiation with red light (λ = 650 nm, 120 W / m^2) in H_2O at room temperature for 2 h (red line), and 5 h (green line).

Section 4: Photochromic Behaviors of 1 in the Presence of CB[8] in Water

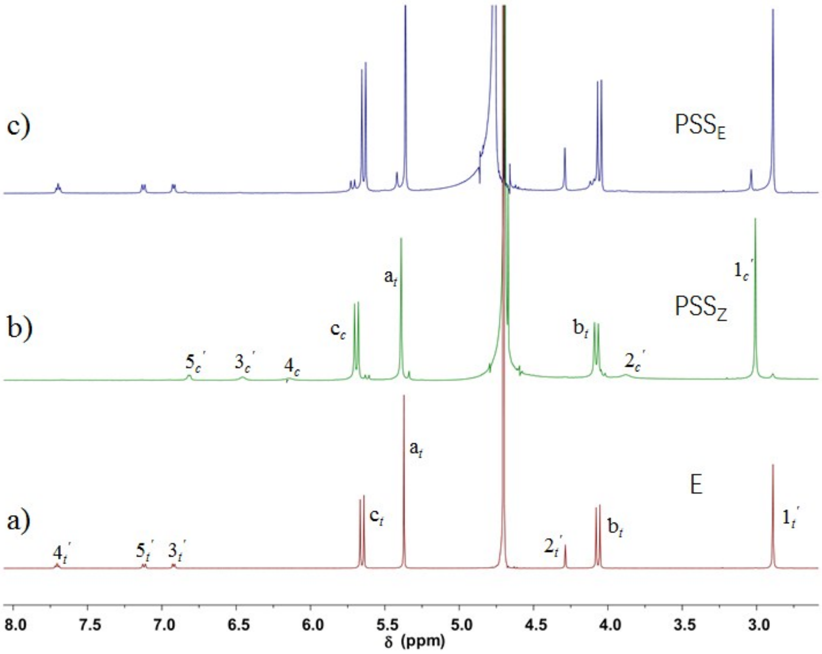


Fig. S6 ^{1}H NMR spectra (600 MHz, D_2O, 4.0 mM, 298K) of the solution of CB[8]•**1**$_E$ a) before and b) after irradiation with yellow light (λ >500 nm, 220 W / m^2) for 1.5 h; and c) the irradiated solution of CB[8]•**1**$_E$ after irradiation by blue light (λ = 410 nm, 21 W / m^2) for 1 h.

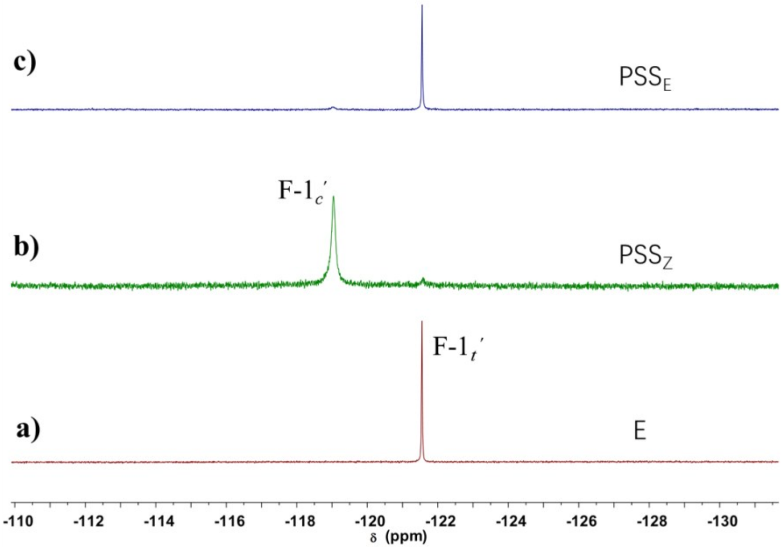


Fig. S7 ^{19}F NMR spectra (564 MHz, D_2O, 4.0 mM, 298K) of the solution of CB[8]•**1**$_E$ a) before and b) after irradiation with yellow light (λ >500 nm, 220 W / m^2) for 1.5 h; and c) the irradiated solution of CB[8]•**1**$_E$ after irradiation by blue light (λ = 410 nm, 21 W / m^2) for 1 h.

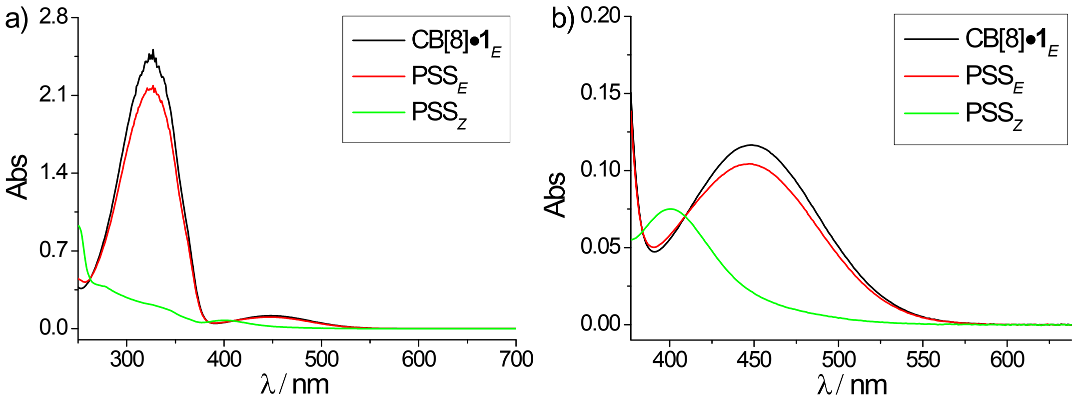


Fig. S8 The (a) full and (b) partial UV/Vis absorption spectra of CB[8]•**1**$_E$ (0.15 mM) before (black line) and after (red line) irradiation with blue light (λ = 410 nm, 21 W / m^2) in H_2O at room temperature for 10 min, and the blue light-irradiated CB[8]•**1**$_E$ solution after irradiation by yellow light (λ > 500 nm, 220 W / m^2) for 30 min.

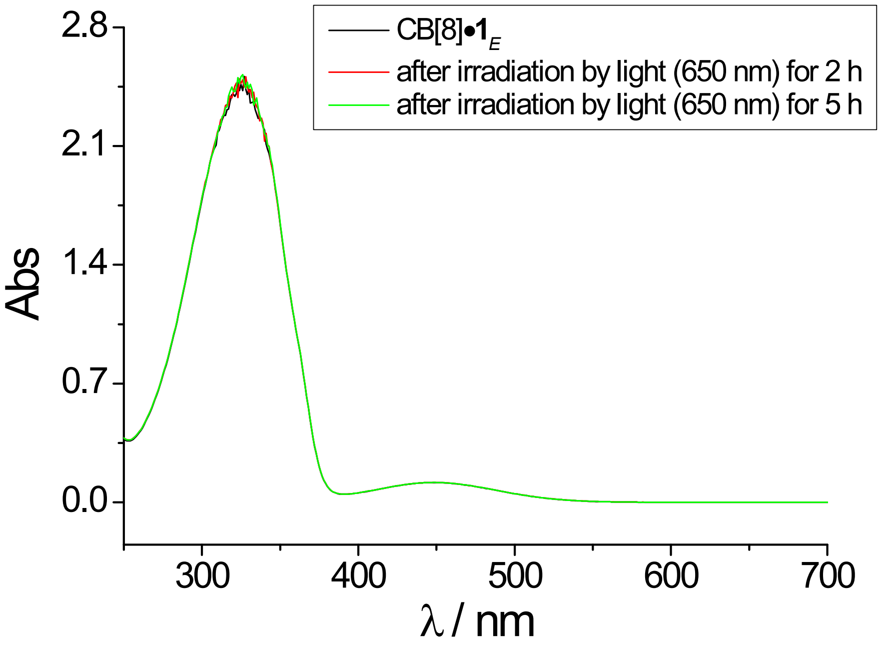


Fig. S9 UV/Vis absorption spectra of CB[8]•**1**$_E$ (0.15 mM) before (black line) and after irradiation with red light (λ = 650 nm, 150 W / m^2) in H_2O at room temperature for 2 h (red line), and 5 h (green line).

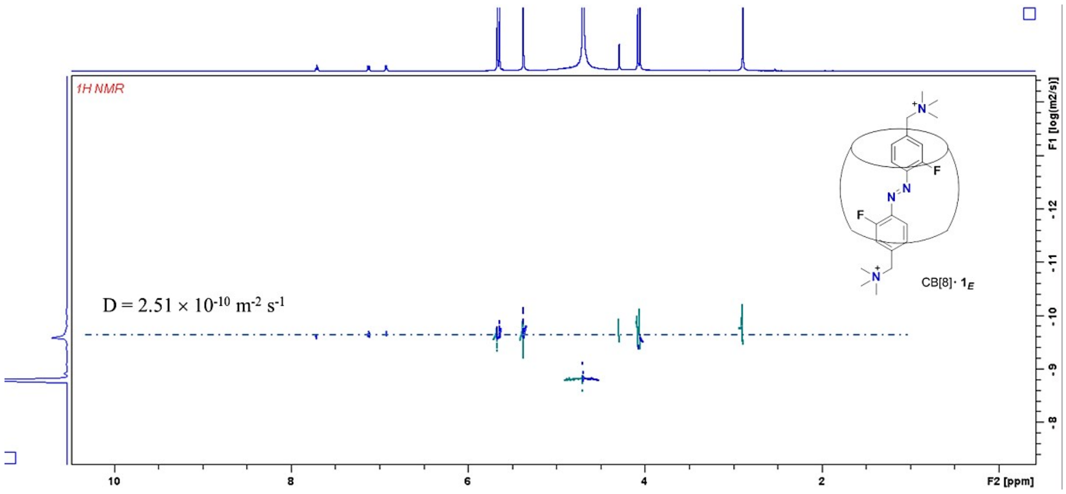


Fig. S10 DOSY-NMR spectrum (600 MHz, D_2O, 298 K) of the solution of CB[8]•$\mathbf{1}_E$ (4.0 mM). The ordinate represents the log value of the diffusion constant.

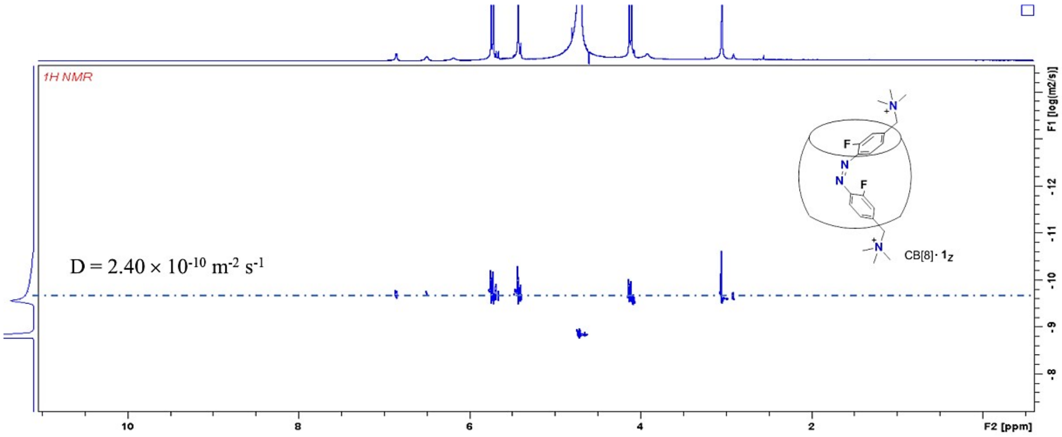


Fig. S11 DOSY-NMR spectrum (600 MHz, D_2O, 298 K) of the solution of CB[8]•$\mathbf{1}_Z$ (4.0 mM) after irradiation with yellow light ($\lambda > 500$ nm, 220 W/m^2) for 1.5 h. The ordinate represents the log value of the diffusion constant.

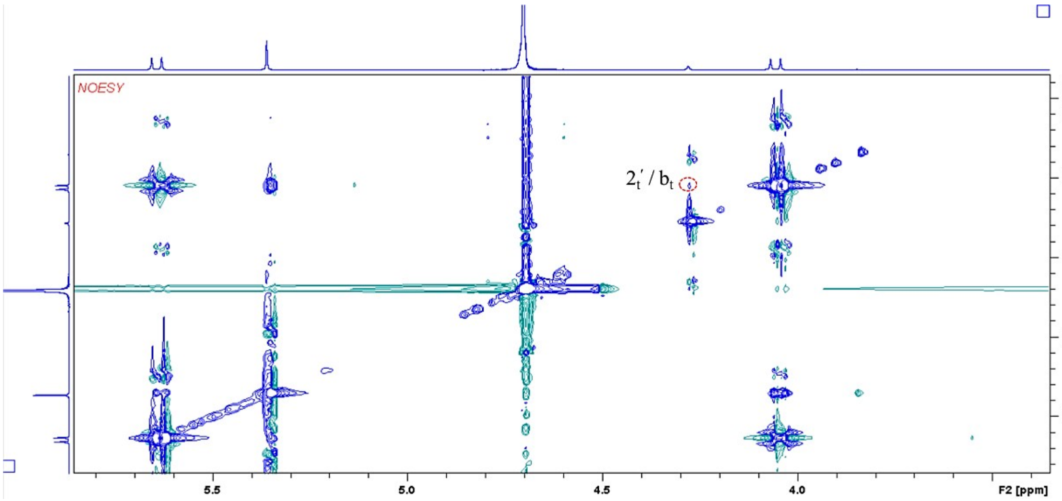
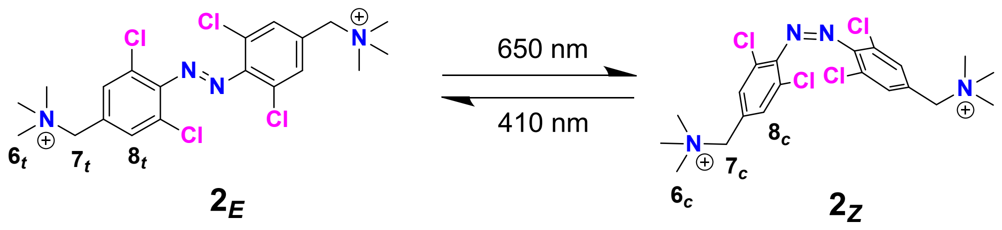


Fig. S12 NOESY-NMR spectrum (600 MHz, 4.0 mM in D_2O, 298 K) of CB[8]•$\mathbf{1}_E$.

Section 5: Photochromic Behaviors of 2 in the Absence and Presence of CB[8] in Water



Scheme S3.

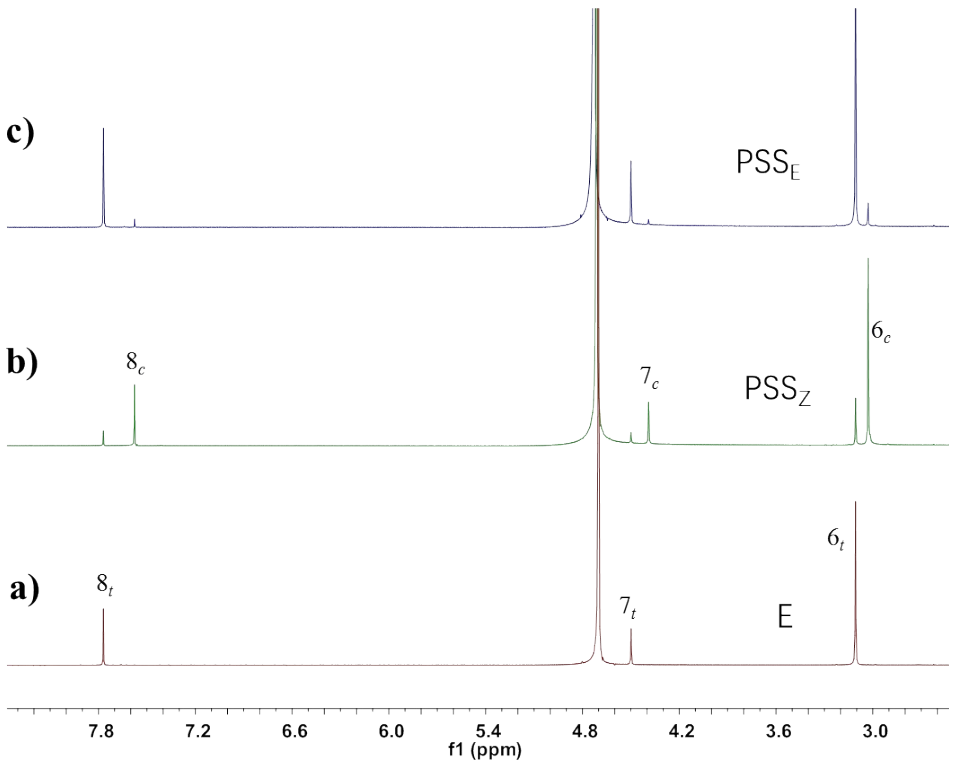


Fig. S13 ^{1}H NMR spectra (600 MHz, D_2O, 4.0 mM, 298K) of the solution of $\mathbf{2}_E$ a) before and b) after irradiation with red light (λ = 650 nm, 150 W / m^2) for 6 h; and the irradiated solution of **2** c) after irradiation by blue light (λ = 410 nm, 21 W / m^2) for 1 h.

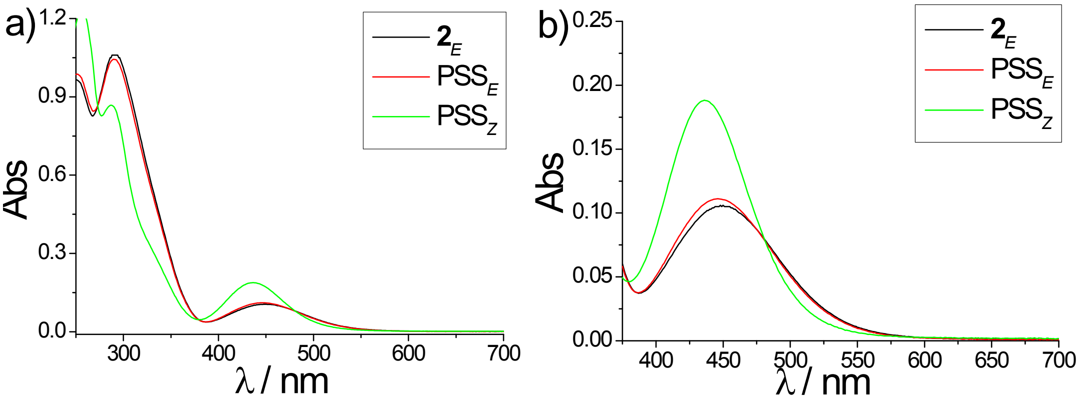


Fig. S14 The (a) full and (b) partial UV/Vis absorption spectra of $\mathbf{2}_E$ (0.128 mM) before (black line) and after (green line) irradiation with red light (λ = 650 nm, 150 W / m^2) in H_2O at room temperature for 4 h, and the red-light-irradiated **2** solution after irradiation by blue light (λ = 410 nm, 21 W / m^2) for 10 min (red line).

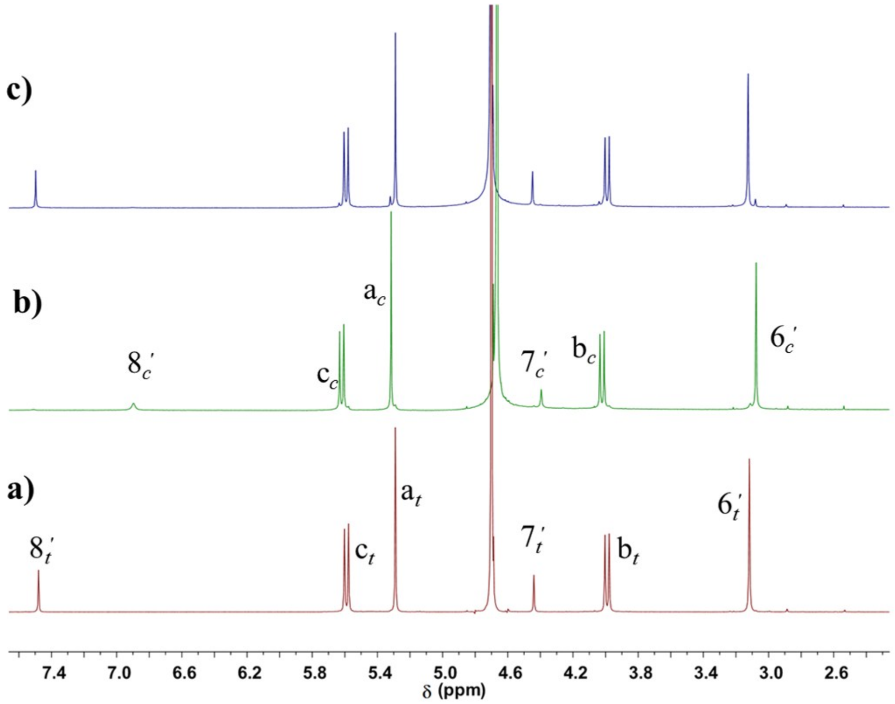


Fig. S15 ^{1}H NMR spectra (600 MHz, D_2O, 4.0 mM, 298K) of the solution of CB[8]•$\mathbf{2}_E$ a) before and b) after irradiation with red light (λ = 650 nm, 150 W / m^2) for 6 h; and the irradiated solution of **2** c) after irradiation by blue light (λ = 410 nm, 21 W / m^2) for 1 h.

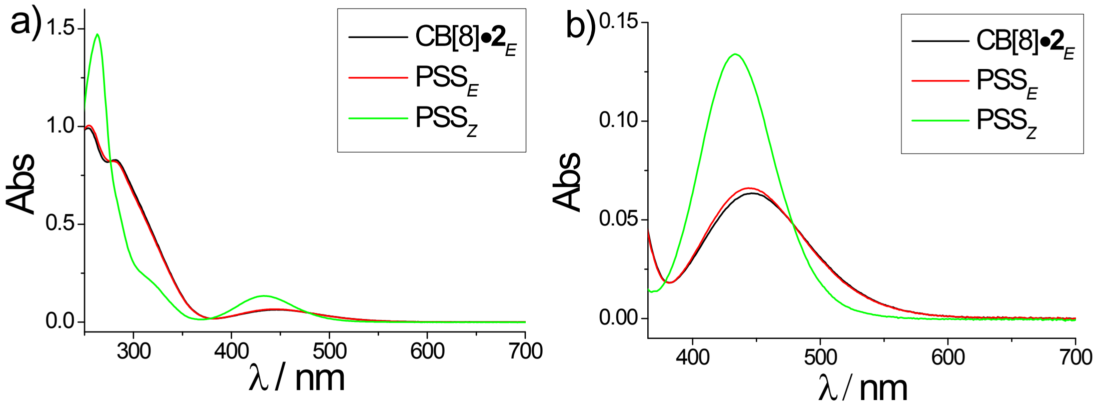


Fig. S16 The UV/Vis absorption spectra of CB[8]•**2**$_E$ (0.15 mM) before (black line) and after (red line) irradiation with blue light (λ = 410 nm, 21 W / m^2) in H_2O at room temperature for 10 min, and the blue light-irradiated CB[8]•**2**$_E$ solution after irradiation by red light (λ = 650 nm, 150 W / m^2) for 4 h.

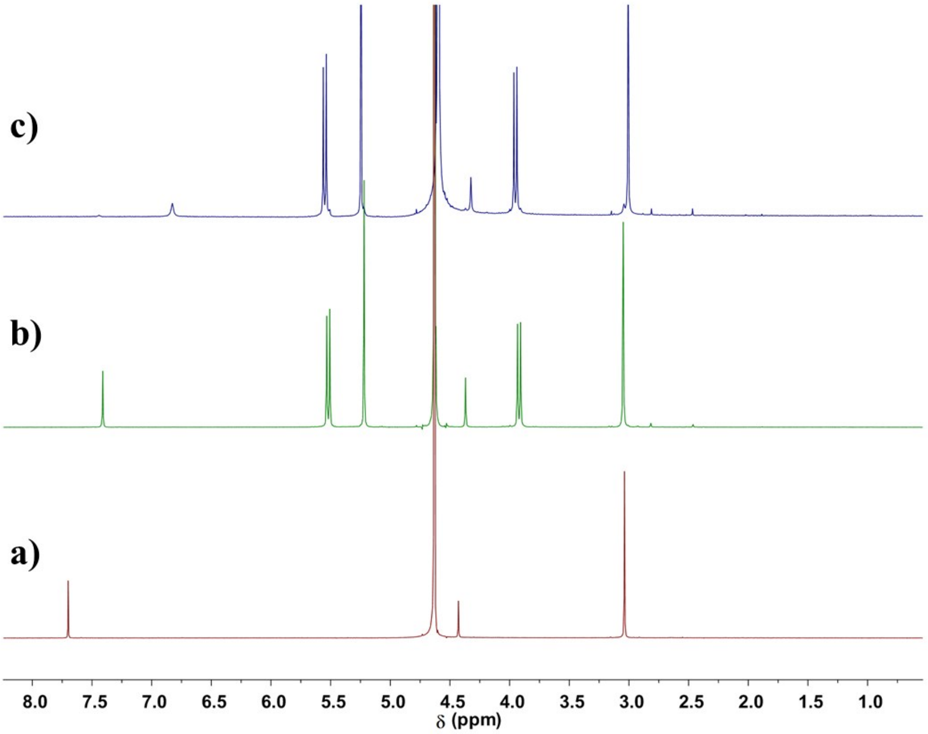


Fig. S17 ^{1}H NMR spectra (600 MHz, D_2O, 4.0 mM, 298K) of the solution of a) **2**$_E$, b) CB[8]•**2**$_E$, and c) CB[8]•**2**$_E$ after irradiation (λ = 650 nm, 150 W / m^2) for 6 h.

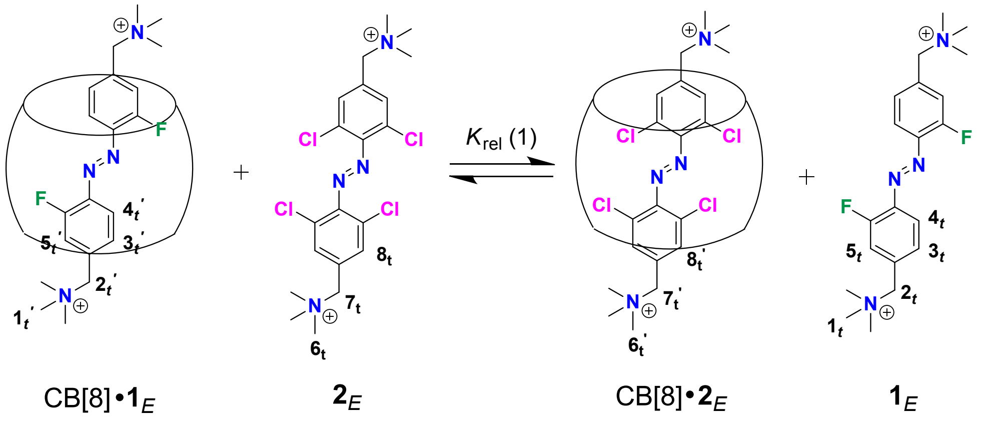
Section 6: Determination of the Association Constants for CB[8]•$\mathbf{1}_E$, CB[8]•$\mathbf{1}_Z$, CB[8]•$\mathbf{2}_E$ and CB[8]•$\mathbf{2}_Z$.

We use ^{1}H NMR competition experiments to determine the association constants (K_a) for these binary host-guest complexes. [S. Liu, C. Ruspic, P. Mukhopadhyay, S. Chakrabarti, P. Y. Zavalij and L. Isaacs. *J. Am. Chem. Soc*. 2005, **127**, 15959.]

For CB[8]•$\mathbf{1}_E$, as showed in Scheme S4, compound $\mathbf{2}_E$ was used as the competitive guest.

$$K_{\mathrm{rel}}\ (1) = K(\mathrm{CB[8]}\bullet\mathbf{2}_E) \,/\, K(\mathrm{CB[8]}\bullet\mathbf{1}_E) = 0.97 \qquad (1)$$

Substitution the value of K(CB[8]•$\mathbf{2}_E$) = 1.04 × 10^5 M^{-1} (see Scheme S6, Figure S20) to equation (1), the association constant value of K(CB[8]•$\mathbf{1}_E$) could be calculated as 1.07 × 10^5 M^{-1}.



$$\mathrm{CB[8]}\bullet\mathbf{1}_E + \mathbf{2}_E \xrightleftharpoons{K_{\mathrm{rel}}\ (2)} \mathrm{CB[8]}\bullet\mathbf{2}_E + \mathbf{1}_E$$

Scheme S4.

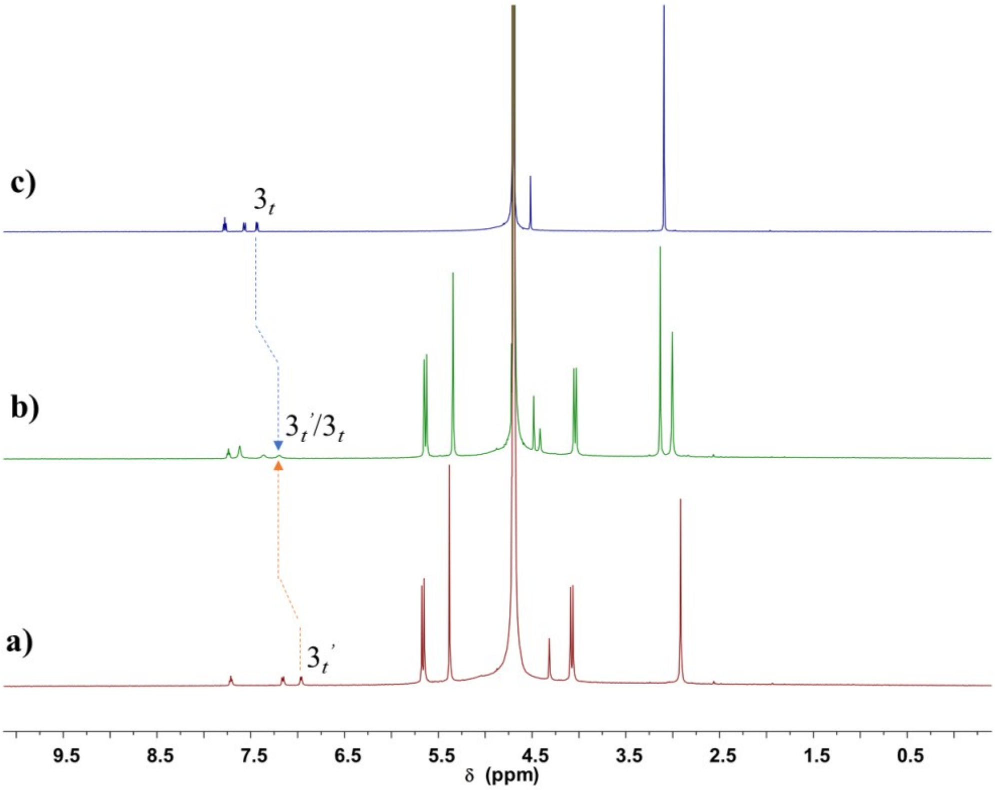
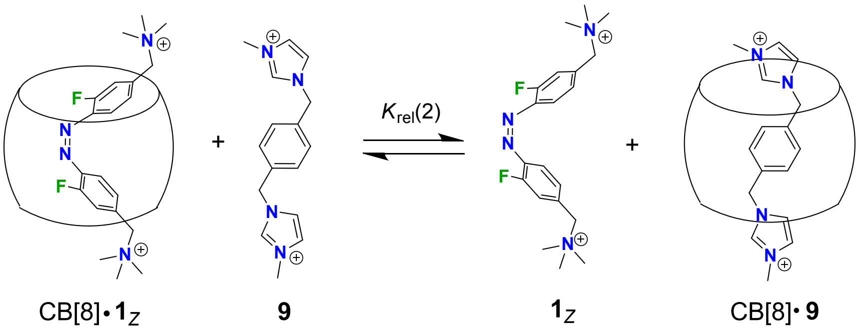


Fig. S18 ^{1}H NMR spectra (600 MHz, 10 mM sodium phosphate buffer, pD = 7.0, 298 K) of the solution of a) CB[8]•$\mathbf{1}_E$ (1.5 mM), b) the mixtures of CB[8], $\mathbf{1}_E$ and $\mathbf{2}_E$ (1:1:1, 1.5 mM), and c) $\mathbf{1}_E$ (1.5 mM).

For CB[8]•$\mathbf{1}_Z$, as showed in Scheme S5, compound $\mathbf{2}_E$ was used as the competitive guest.

$$K_{\mathrm{rel}}\ (2) = K(\mathrm{CB[8]}{\bullet}\mathbf{9})\ /\ K(\mathrm{CB[8]}{\bullet}\mathbf{1}_Z) = 0.0171 \qquad (2)$$

Substitution the value of K(CB[8]•**9**) = $1.9 \times 10^6\ \mathrm{M}^{-1}$ (*Ref S2*) to equation (2), the association constant value of K(CB[8]•$\mathbf{1}_Z$) could be calculated as $1.1 \times 10^8\ \mathrm{M}^{-1}$.



$$\mathrm{CB[8]}{\bullet}\mathbf{1}_Z + \mathbf{9} \xrightleftharpoons{K_{\mathrm{rel}}\ (2)} \mathrm{CB[8]}{\bullet}\mathbf{9} + \mathbf{1}_Z$$

Scheme S5.

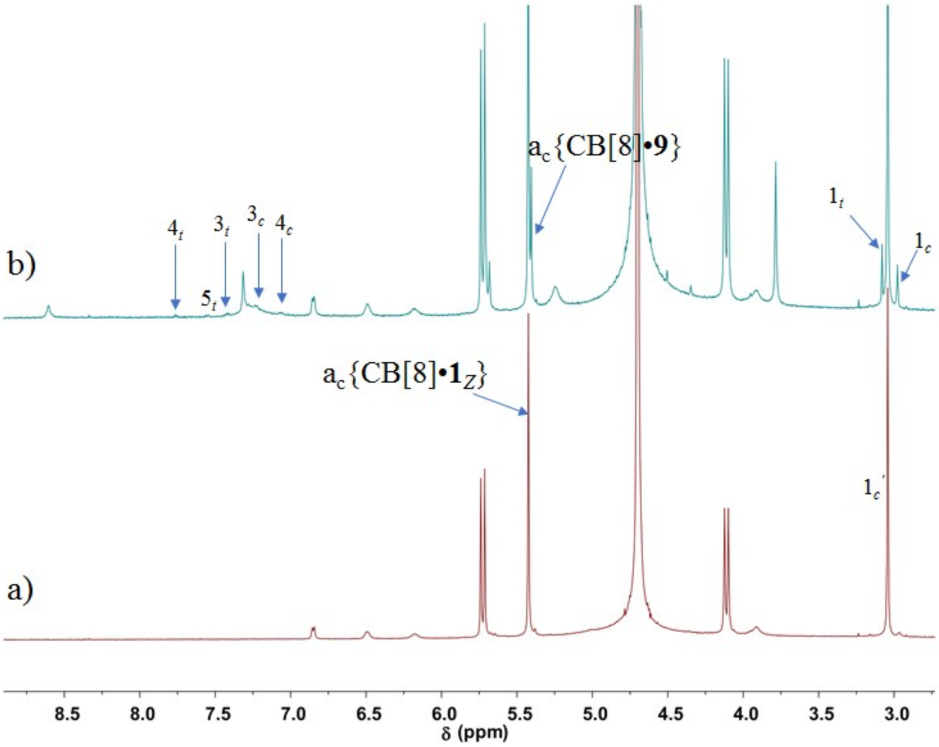
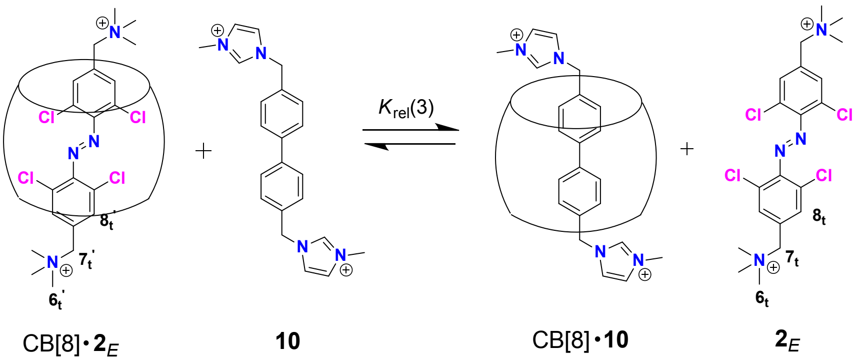


Fig. S19 ^{1}H NMR spectra (600 MHz, 10 mM sodium phosphate buffer, pD = 7.0, 298 K) of the solution of a) the PSS_Z mixtures of CB[8]•**1** (1.5 mM), and b) after addition of 1 equiv. of **9**.

For CB[8]•$\mathbf{2}_E$, as showed in Scheme S6, compound **10** was used as the competitive guest.

$$K_{\mathrm{rel}}\,(3) = K(\mathrm{CB[8]}\bullet\mathbf{10}) \,/\, K(\mathrm{CB[8]}\bullet\mathbf{2}_E) = 1.92 \qquad (3)$$

Substitution the value of K(CB[8]•**10**) = 2.0 × 10^5 M^{-1} (*Ref S2*) to equation (3), the association constant value of K(CB[8]•$\mathbf{2}_E$) could be calculated as 1.04 × 10^5 M^{-1}.



$$\mathbf{2}_E\cdot\mathrm{CB[8]} + \mathbf{10} \xrightleftharpoons{K_{\mathrm{rel}}(3)} \mathbf{10}\cdot\mathrm{CB[8]} + \mathbf{2}_E$$

Scheme S6.

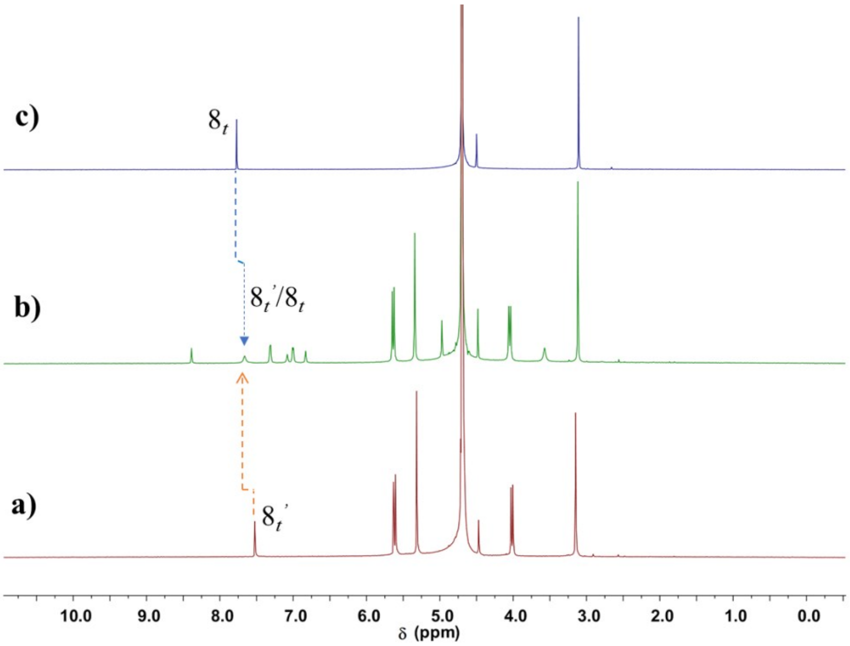
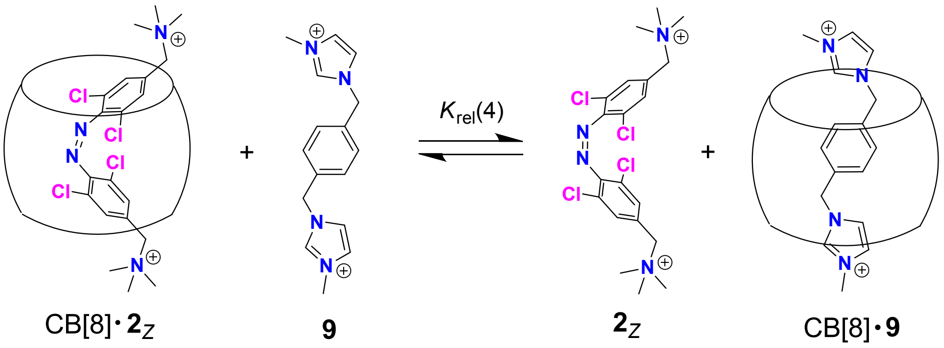


Fig. S20 ^{1}H NMR spectra (600 MHz, 10 mM sodium phosphate buffer, pD = 7.0, 298 K) of the solution of a) CB[8]•$\mathbf{2}_E$ (1.5 mM); b) the mixtures of **10**, CB[8] and $\mathbf{2}_E$ (1:1:1, 1.5 mM); and c) $\mathbf{2}_E$ (1.5 mM).

For CB[8]•**2**$_Z$, as showed in Scheme S7, compound **9** was used as the competitive guest.

$$K_{\text{rel}}\,(4) = K(\text{CB[8]}\bullet\mathbf{9}) \,/\, K(\text{CB[8]}\bullet\mathbf{2}_Z) = 0.217 \qquad (4)$$

Substitution the value of K(CB[8]•**9**) = 1.9 × 10^6 M^{-1} (*Ref S2*) to equation (4), the association constant value of K(CB[8]•**2**$_Z$) could be calculated as 8.7 × 10^6 M^{-1}.



$$\mathbf{2}_Z\cdot\text{CB[8]} + \mathbf{9} \underset{}{\overset{K_{\text{rel}}(4)}{\rightleftharpoons}} \mathbf{9}\cdot\text{CB[8]} + \mathbf{2}_Z$$

Scheme S7.

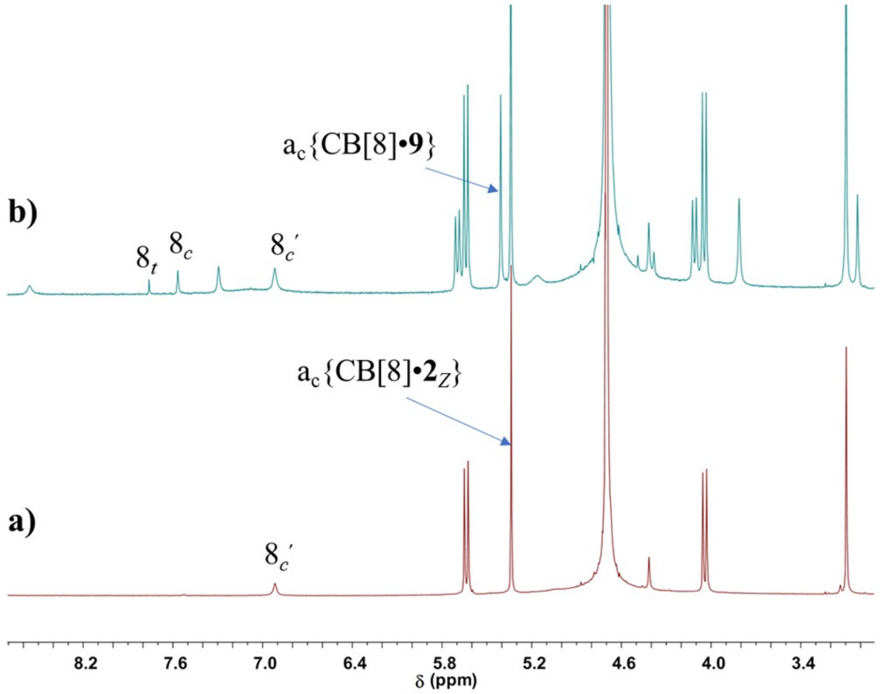
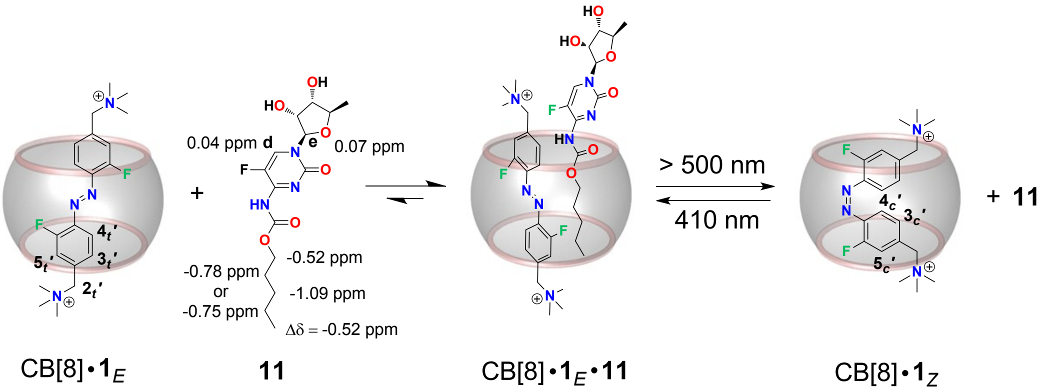


Fig. S21 ^{1}H NMR spectra (600 MHz, 10 mM sodium phosphate buffer, pD = 7.0, 298 K) of the solution of a) the PSS$_Z$ mixtures of CB[8]•**2** (1.5 mM), and b) after addition of 1 equiv. of **9**.

Section 7: The Light-Regulated Capture and Release Behaviors of CB[8]•1$_E$ Complex with the Selected Second Guest Molecules



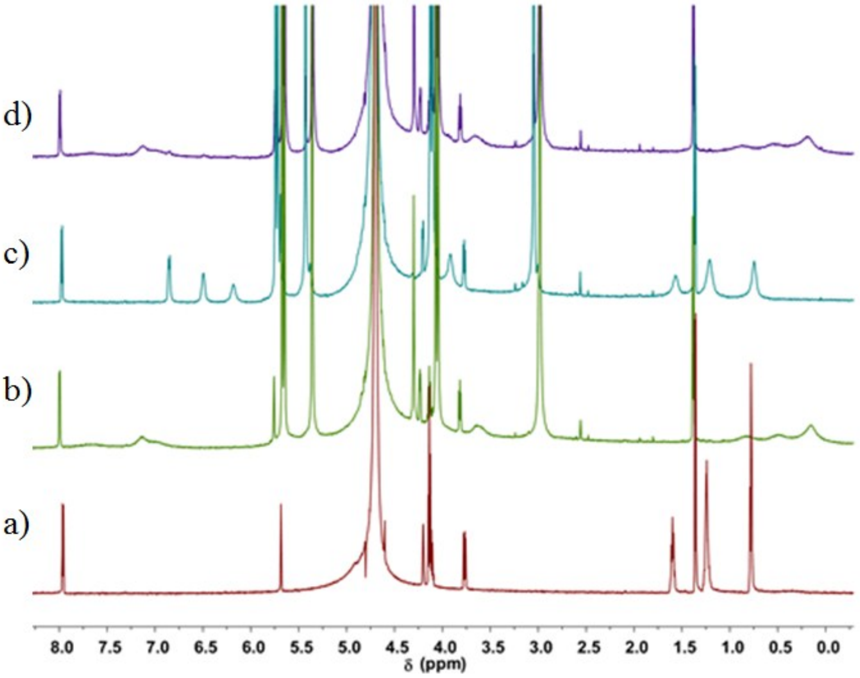


Fig. S22 ^{1}H NMR spectra (600 MHz, D2O, 4.0 mM, 298K, 10 mM sodium phosphate buffer, pD = 7.0) of the solution of a) **11**, CB[8]•**1**$_E$ and **11** (1:1) before (b) and after (c) irradiation with yellow light (> 500 nm, 220 W / m^2) for 1.5 h; and d) the yellow light irradiated the solution of CB[8]•**1**$_E$ and **11** after irradiation by purple light (λ = 410 nm, 21 W / m^2) for 1 h.

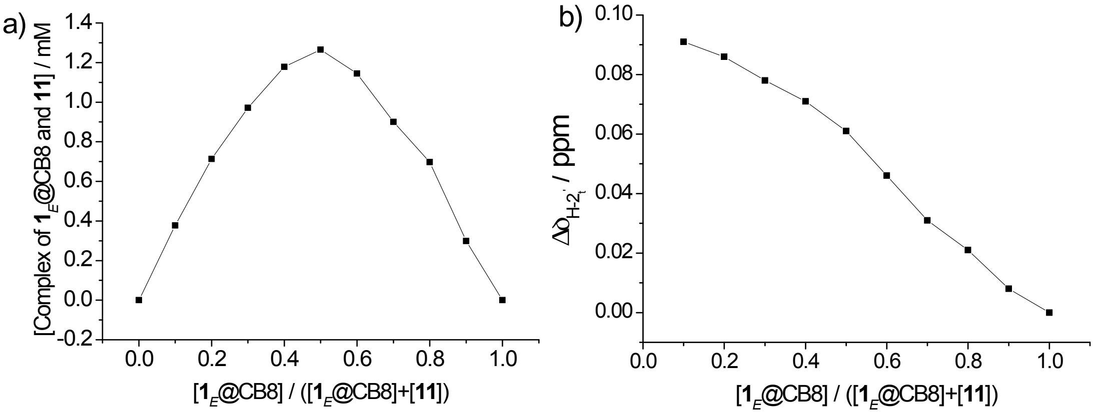


Fig. S23 (a) Job's plot of CB[8]•$\mathbf{1}_E$ / **11** host-guest interaction (^{1}H NMR at 298 K); (b) Plot of the changes of the chemical shifts of CB[8]•$\mathbf{1}_E$ *versus* [CB[8]•$\mathbf{1}_E$] / ([CB[8]•$\mathbf{1}_E$] + [**11**]) in 10 mM sodium phosphate buffer, pD = 7.0, at 298 K ([CB[8]•$\mathbf{1}_E$]$_{tot}$ + [**11**]$_{tot}$ = 4.0 mM).

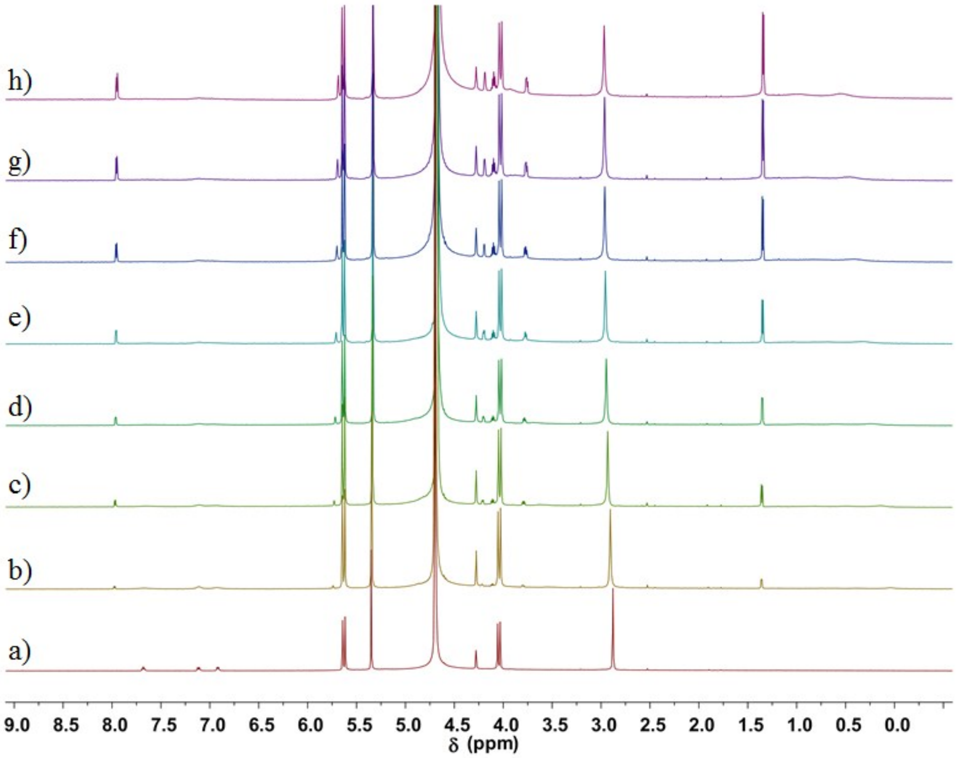


Fig. S24 ^{1}H NMR spectra (600 MHz, 298K, 10 mM sodium phosphate buffer, pD = 7.0) of the solution of CB[8]•$\mathbf{1}_E$ (1.5 mM) in the presence of a) 0, b) 1/3, c) 2/3, d) 1.0, e) 4/3, f) 5/3, g) 2.0, and h) 8/3 equiv. of capecitabine (**11**).

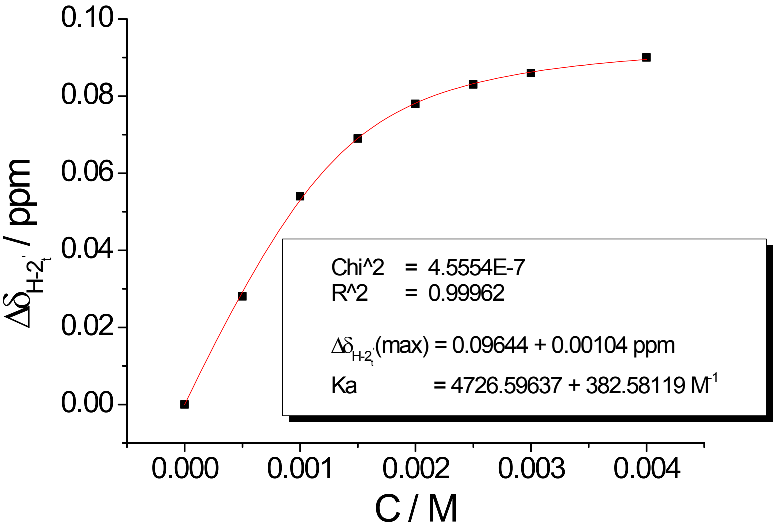


Fig. S25 Plot of the changes of the chemical shifts of CB[8]•**1**$_E$ (1.5 mM) *versus* the concentration of capecitabine (**11**) (0 ~ 4.0 mM) in 10 mM sodium phosphate buffer, pD = 7.0, at 298 K. The solid line represents the best least-squares fit of the data to a 1:1 binding model (K_a = 4727 M^{-1}).

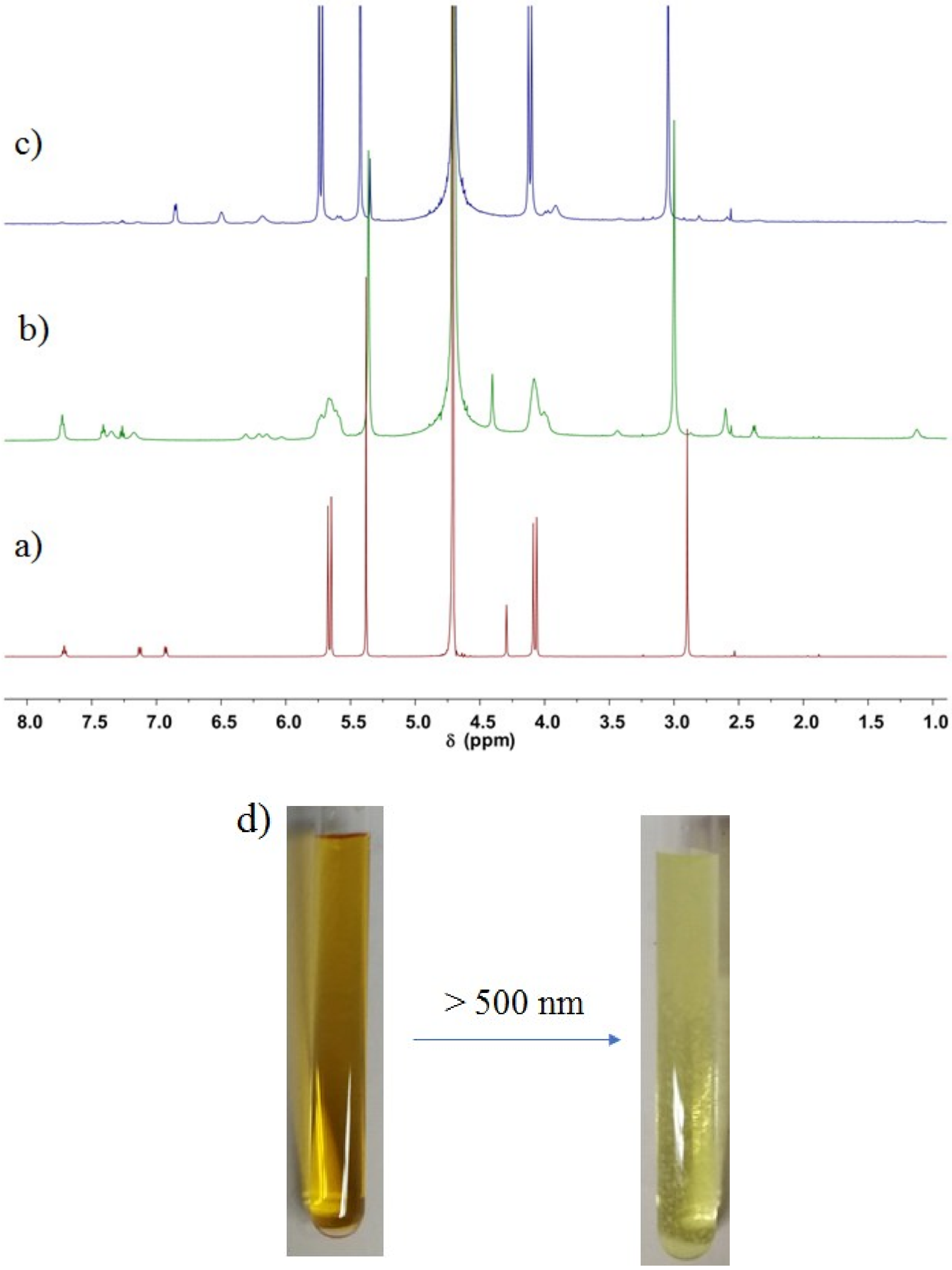


Fig. S26 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of the solution of a) CB[8]•$\mathbf{1}_E$ (4.0 mM); b) CB[8]•$\mathbf{1}_E$ (4.0 mM) and tamoxifen (**12**); c) CB[8]•$\mathbf{1}_E$ and tamoxifen (**12**) after irradiation yellow light (λ > 500 nm, 220 W / m^2) for 6 h; and d) the tamoxifen (**12**) was precipitated from the solution, after the solution of CB[8]•$\mathbf{1}_E$ and tamoxifen (**12**) was irradiation by yellow light (λ > 500 nm).

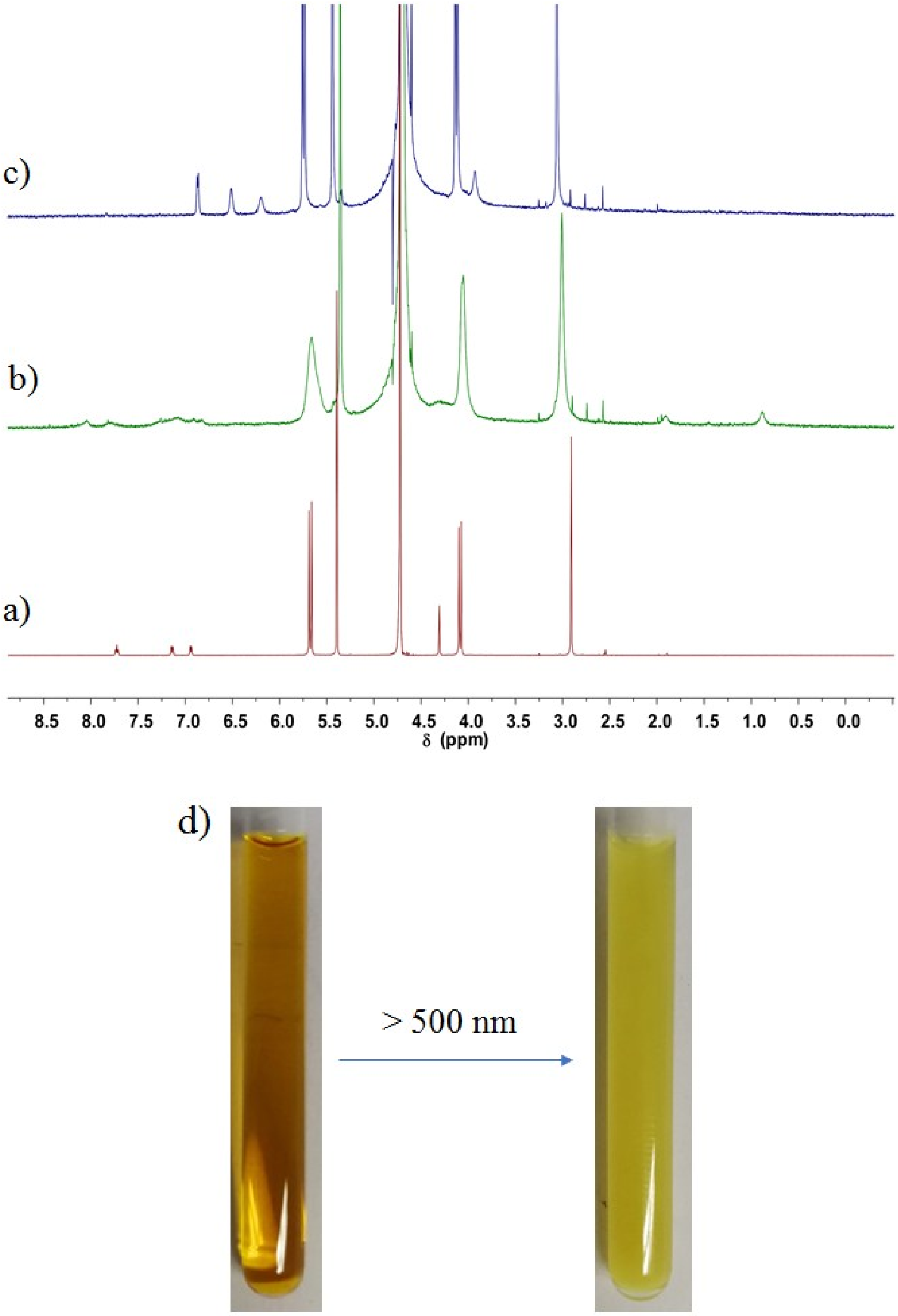


Fig. S27 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of the solution of a) CB[8]•$\mathbf{1}_E$ (4.0 mM); b) CB[8]•$\mathbf{1}_E$ (4.0 mM) and camptothecin (**13**); c) CB[8]•$\mathbf{1}_E$ and camptothecin (**13**) after irradiation with yellow light ($\lambda > 500$ nm, 220 W / m^2) for 6 h; and d) the camptothecin (**13**) was precipitated from the solution, after the solution of CB[8]•$\mathbf{1}_E$ and camptothecin (**13**) was irradiation by yellow light ($\lambda > 500$ nm).

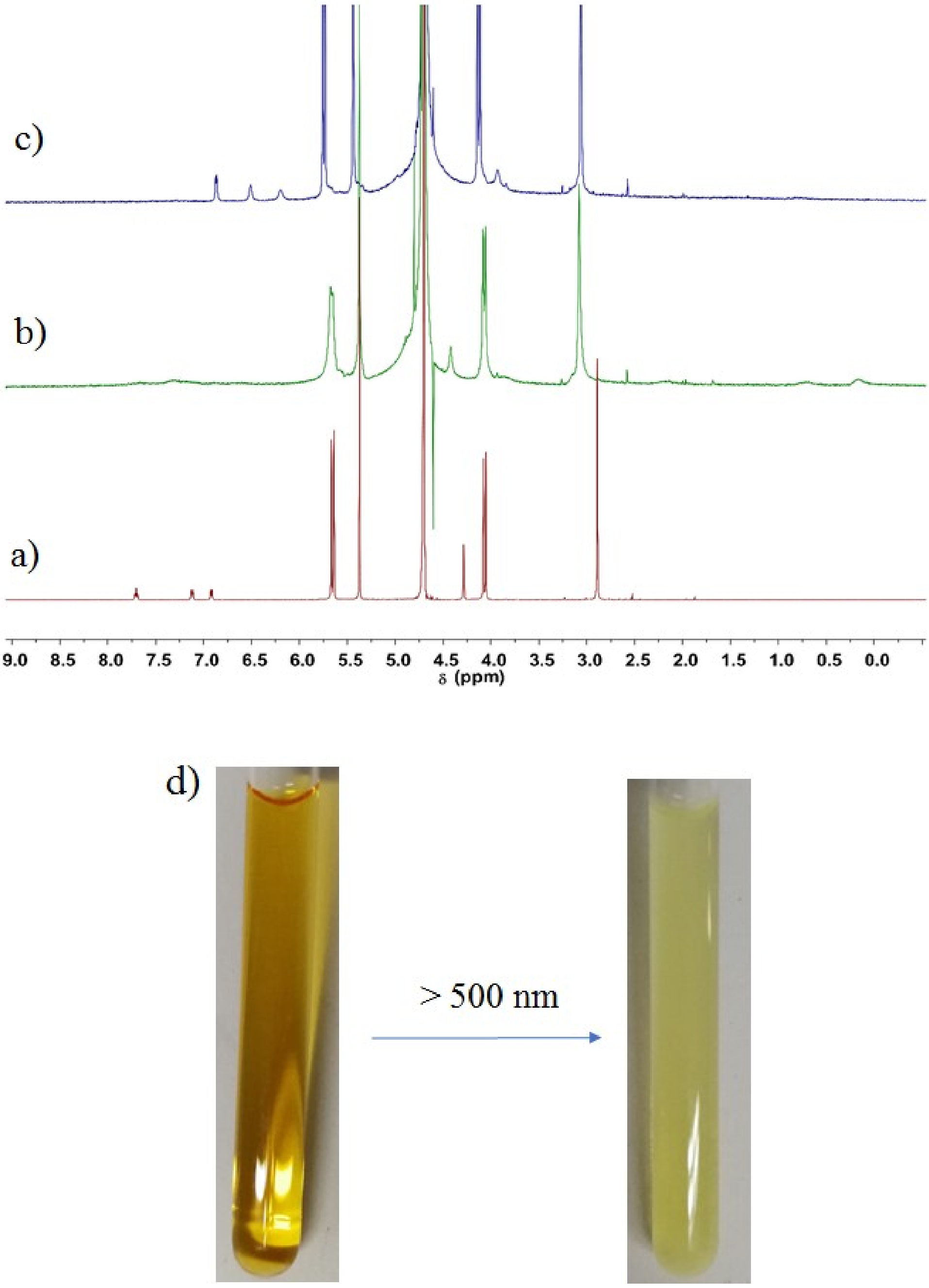


Fig. S28 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of the solution of a) CB[8]•$\mathbf{1}_E$ (4.0 mM); b) CB[8]•$\mathbf{1}_E$ (4.0 mM) and albendazole (**14**); c) CB[8]•$\mathbf{1}_E$ and albendazole (**14**) after irradiation with yellow light ($\lambda > 500$ nm, 220 W / m^2) for 6 h; and d) the albendazole (**14**) was precipitated from the solution, after the solution of CB[8]•$\mathbf{1}_E$ and albendazole (**14**) was irradiation by yellow light ($\lambda >$ 500 nm).

Section 8: The Light-Regulated Capture and Release Behaviors of CB[8]•**2**$_E$ Complex with the Selected Second Guest Molecules

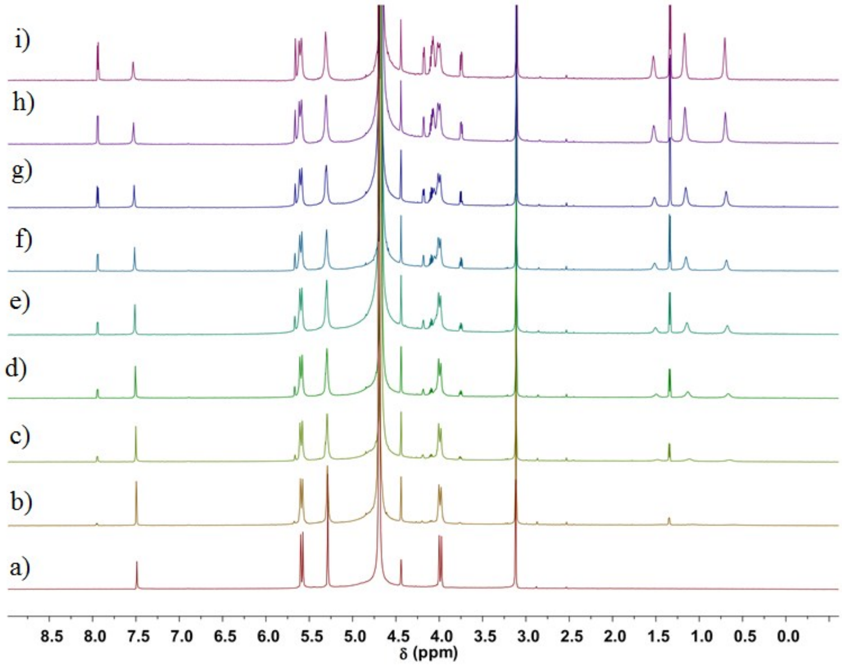


Fig. S29 ^{1}H NMR spectra (600 MHz, 298K, 10 mM sodium phosphate buffer, pD = 7.0) of the solution of CB[8]•**2**$_E$ (1.5 mM) in the presence of a) 0, b) 1/3, c) 2/3, d) 1.0, e) 4/3, f) 5/3, g) 2.0, and h) 8/3 equiv. of capecitabine (**11**).

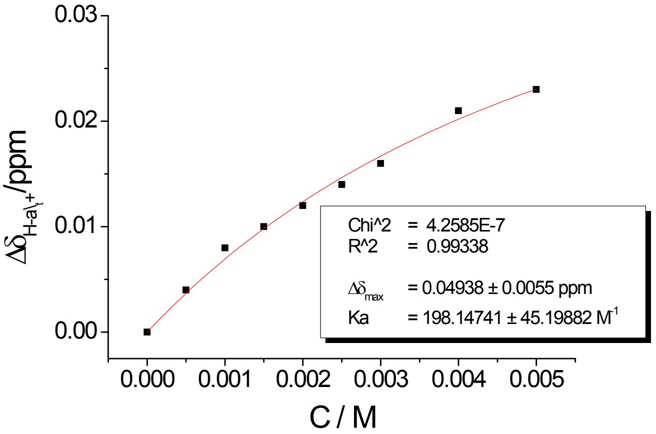


Fig. S30 Plot of the changes of the chemical shifts of H-a$_t$ of CB[8]•**2**$_E$ (1.5 mM) *versus* the concentration of capecitabine (**11**) (0-5.0 mM) in 10 mM sodium phosphate buffer, pD = 7.0, at 298 K. The solid line represents the best least-squares fit of the data to a 1:1 binding model (K_a = 198 M^{-1}).

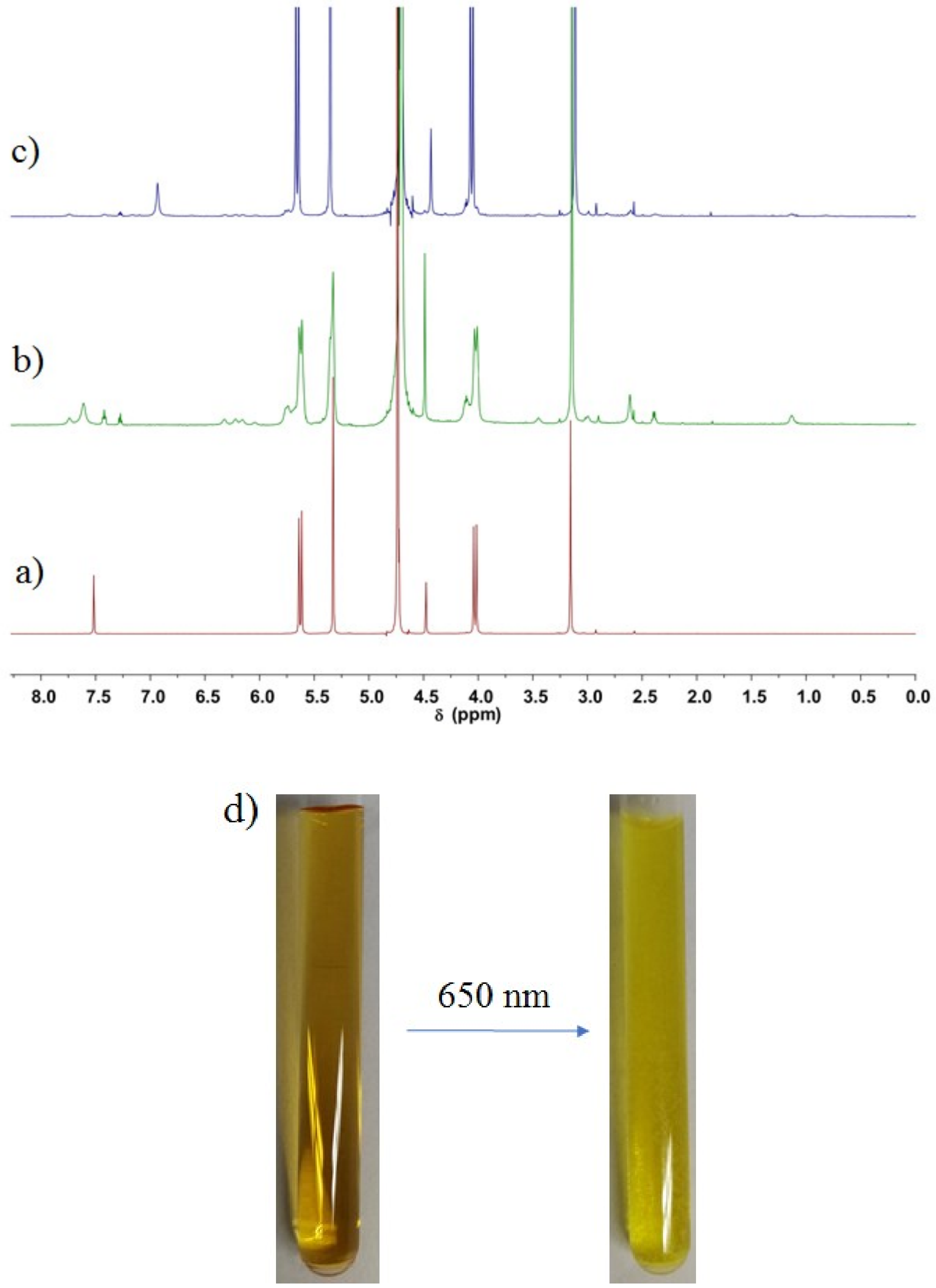


Fig. S31 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of the solution of a) CB[8]•$\mathbf{2}_E$ (4.0 mM); b) CB[8]•$\mathbf{2}_E$ (4.0 mM) and tamoxifen (**12**); c) CB[8]•$\mathbf{2}_E$ and tamoxifen (**12**) after irradiation with red light (λ = 650 nm, 150 W / m^2) for 6 h; and d) the tamoxifen (**12**) was precipitated from the solution, after the solution of CB[8]•$\mathbf{2}_E$ and tamoxifen (**12**) was irradiation by red light (λ = 650 nm).

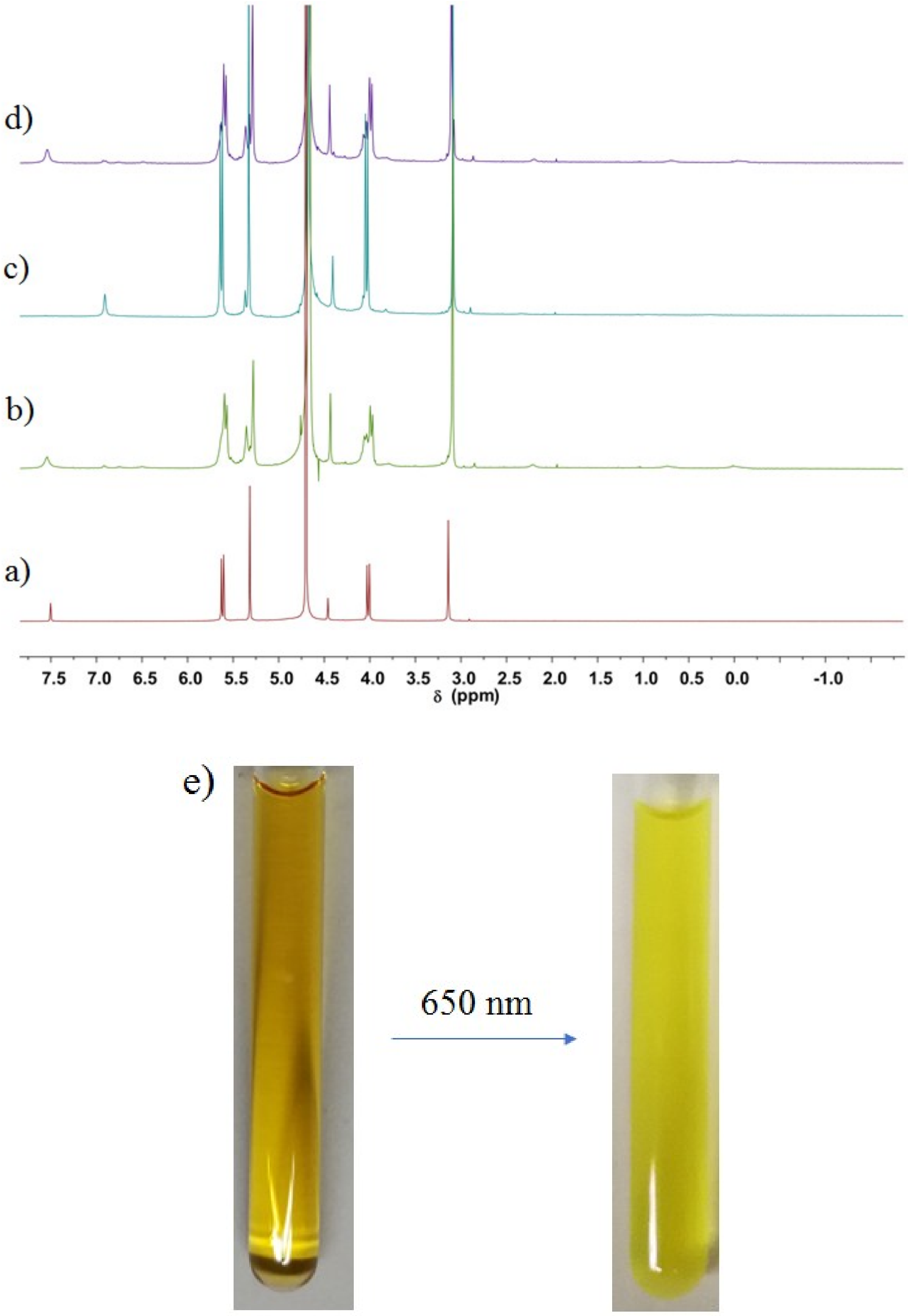


Fig. S32 ^{1}H NMR spectra (600 MHz, D_2O, 298K) of the solution of a) CB[8]•$\mathbf{2}_E$ (4.0 mM); b) CB[8]•$\mathbf{2}_E$ (4.0 mM) and **14** before (b) and after (c) irradiation with red light (λ = 650 nm, 150 W / m^2) for 6 h; d) the red light irradiated mixutre of CB[8]•$\mathbf{2}_E$ and **14** after irradiation by purple light (λ = 410 nm, 21 W/m^2) for 1 h; and e) the albendazole (**14**) was precipitated from the solution, after the solution of CB[8]•$\mathbf{2}_E$ and albendazole (**14**) was irradiation by red light (λ = 650 nm).

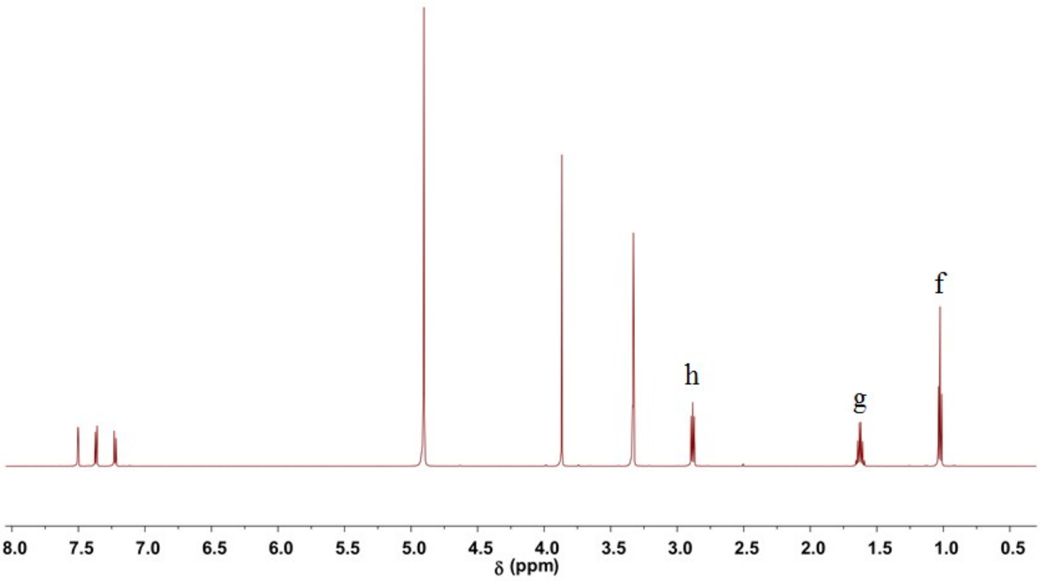
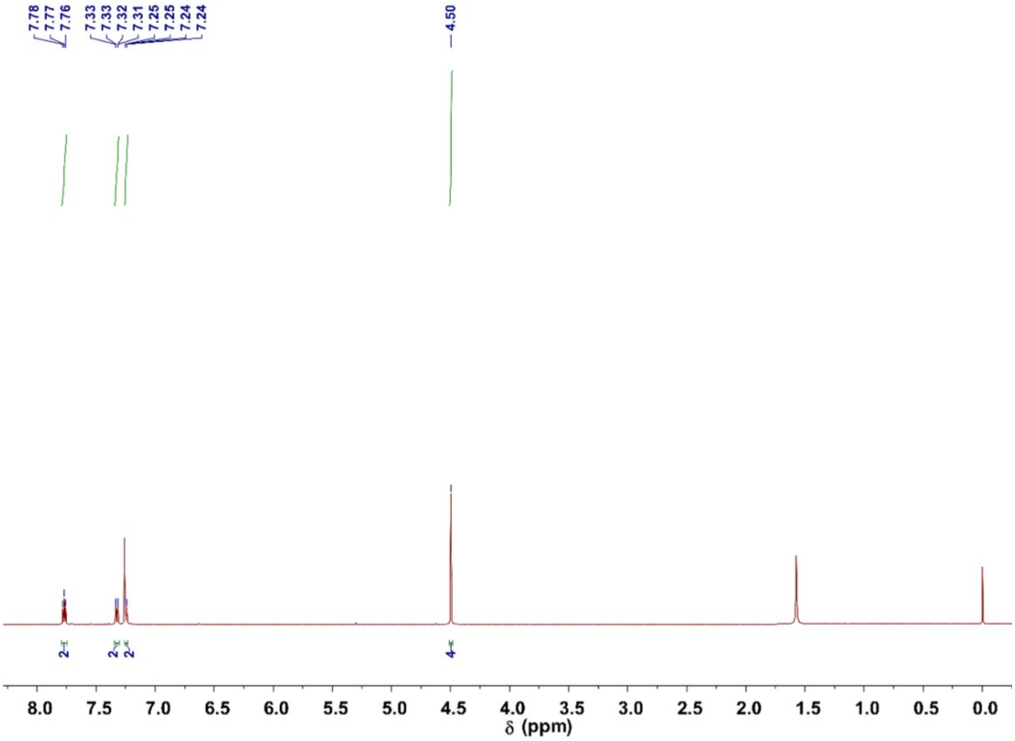
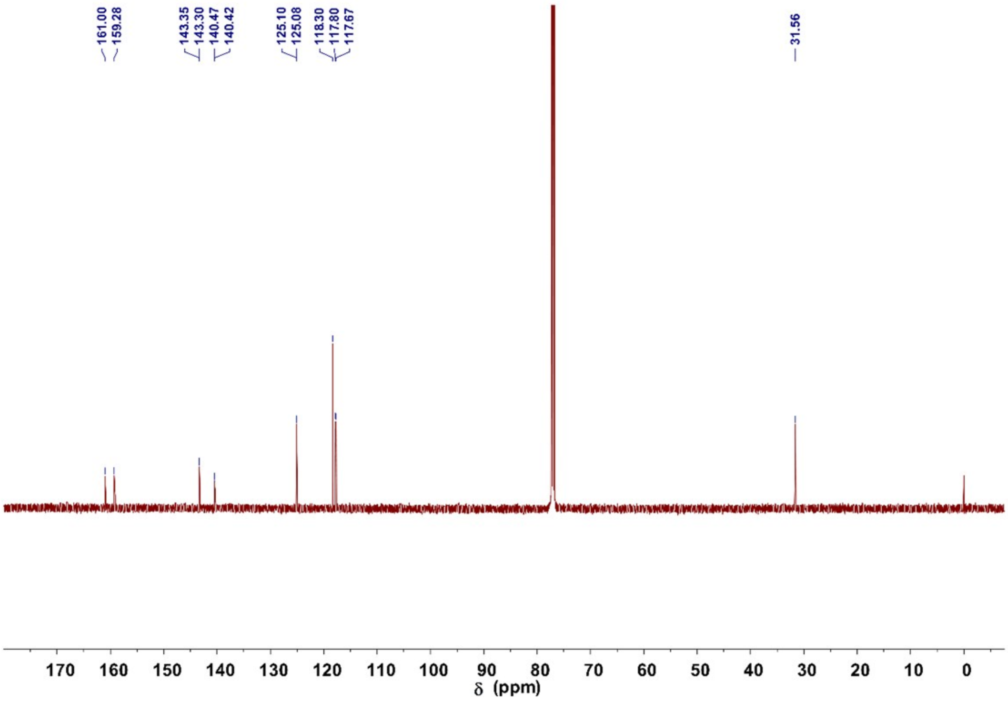


Fig. S33 ^{1}H NMR spectra (600 MHz, 298 K) of **14** (4.0 mM) in CD_3OD.

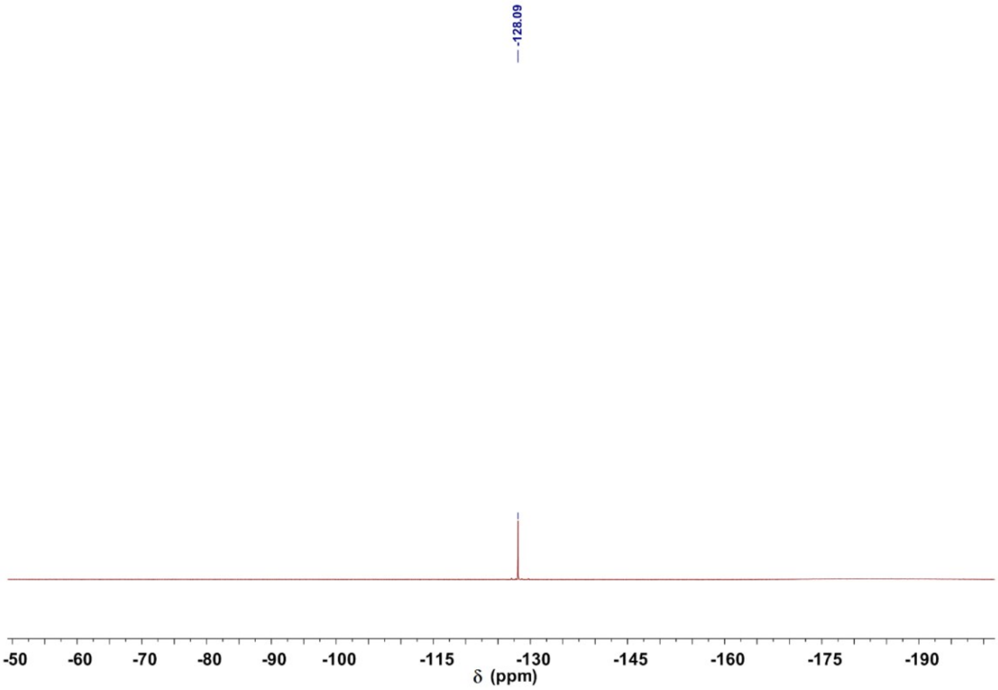
Section 9: The Characterization Data of the New Compounds



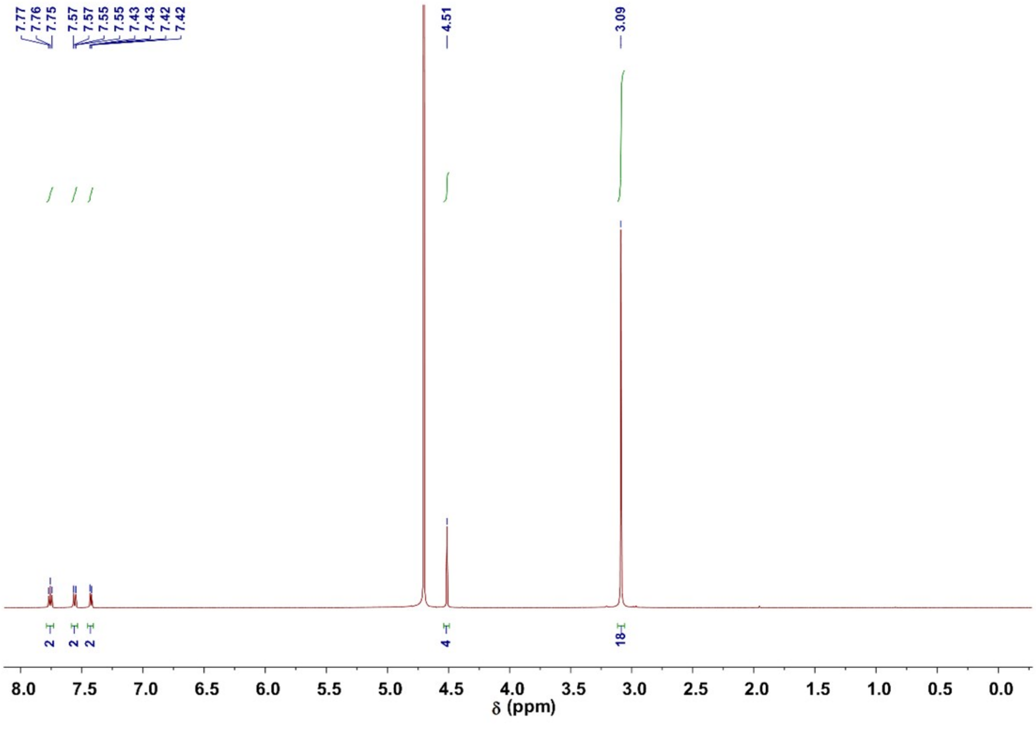
^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of compound **4**.



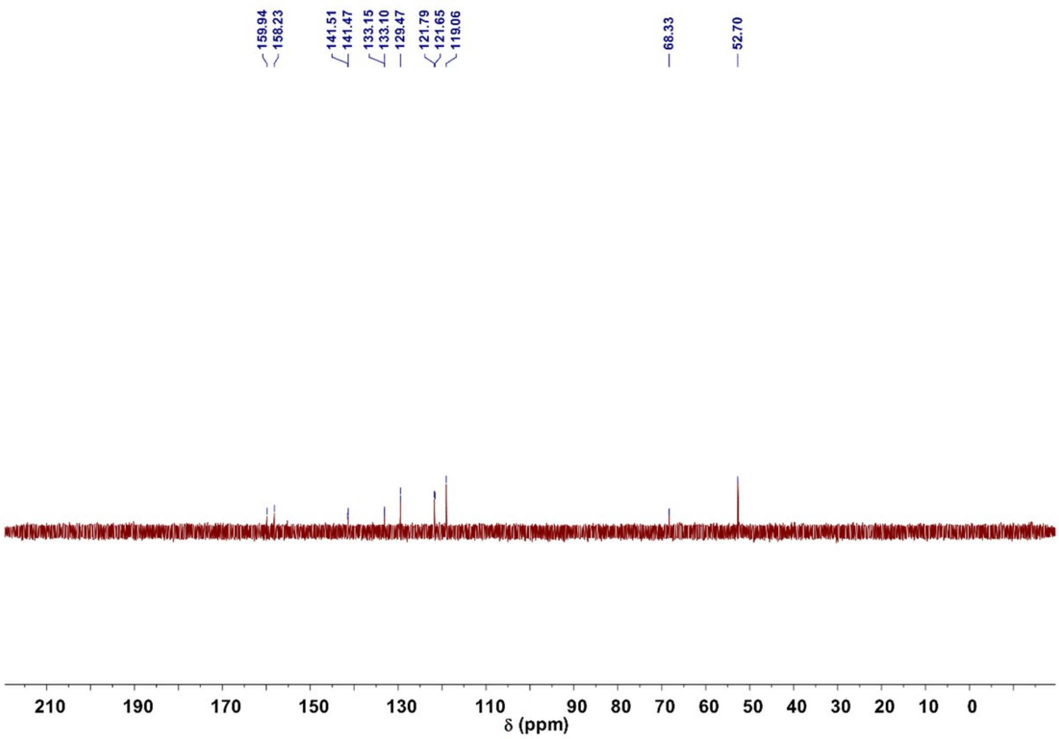
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **4**.



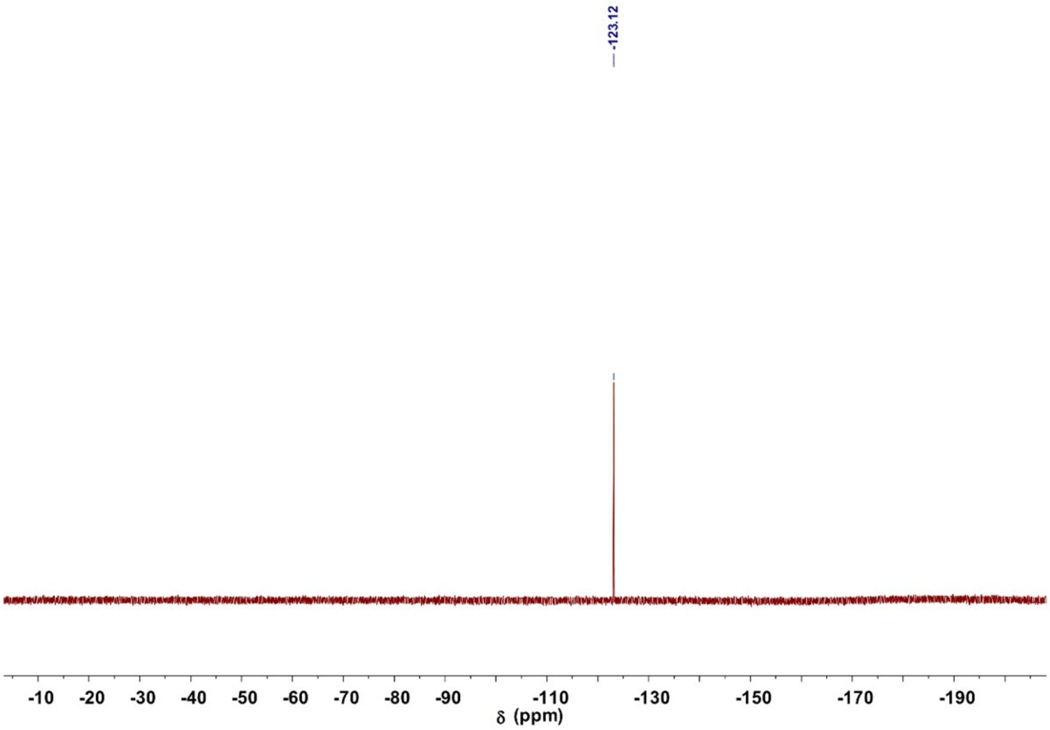
^{19}F NMR spectrum (564 MHz, $CDCl_3$, 298 K) of compound **4**.



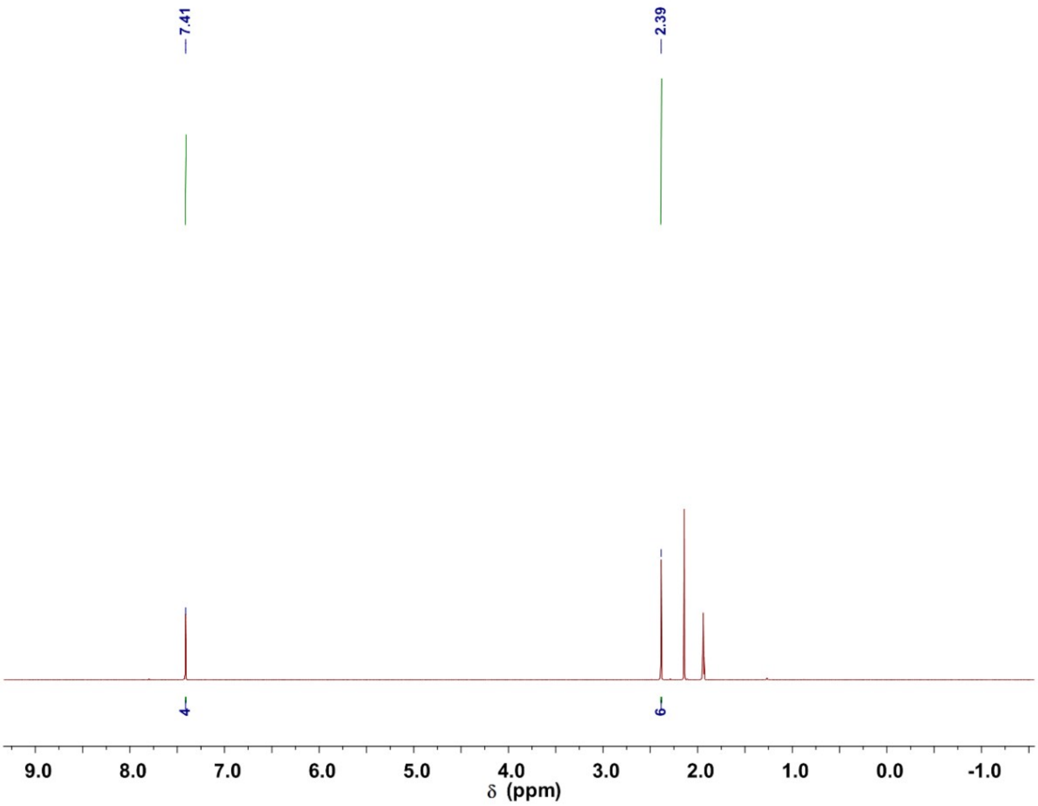
^1H NMR spectrum (600 MHz, D_2O, 298 K) of compound **1**·2Br.



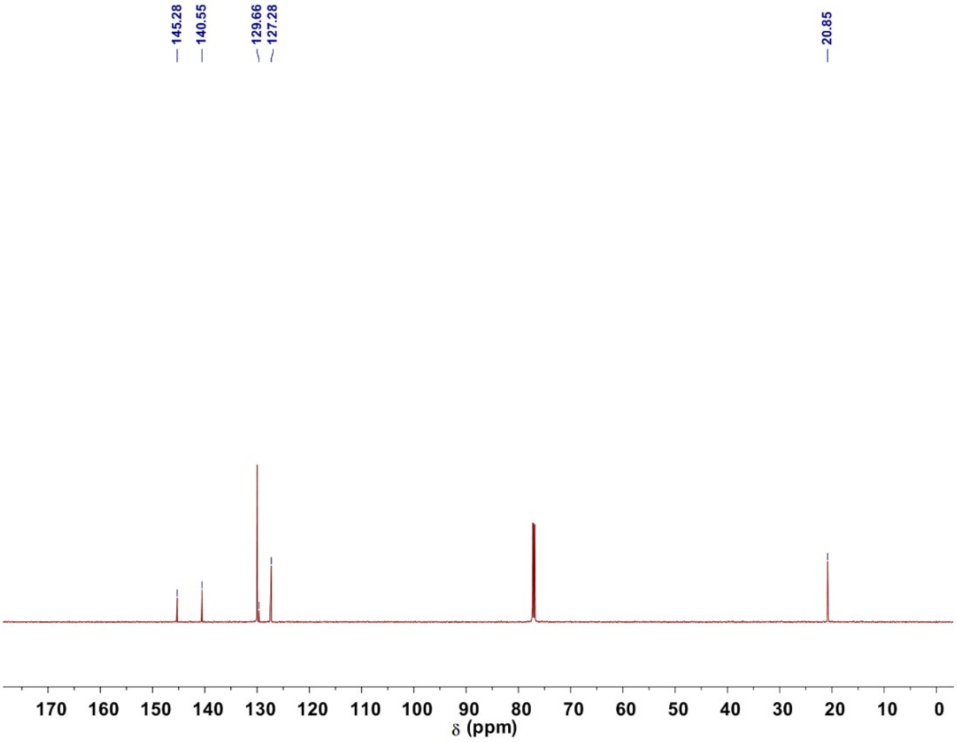
^{13}C NMR spectrum (150 MHz, D_2O, 298 K) of compound **1**·2Br.



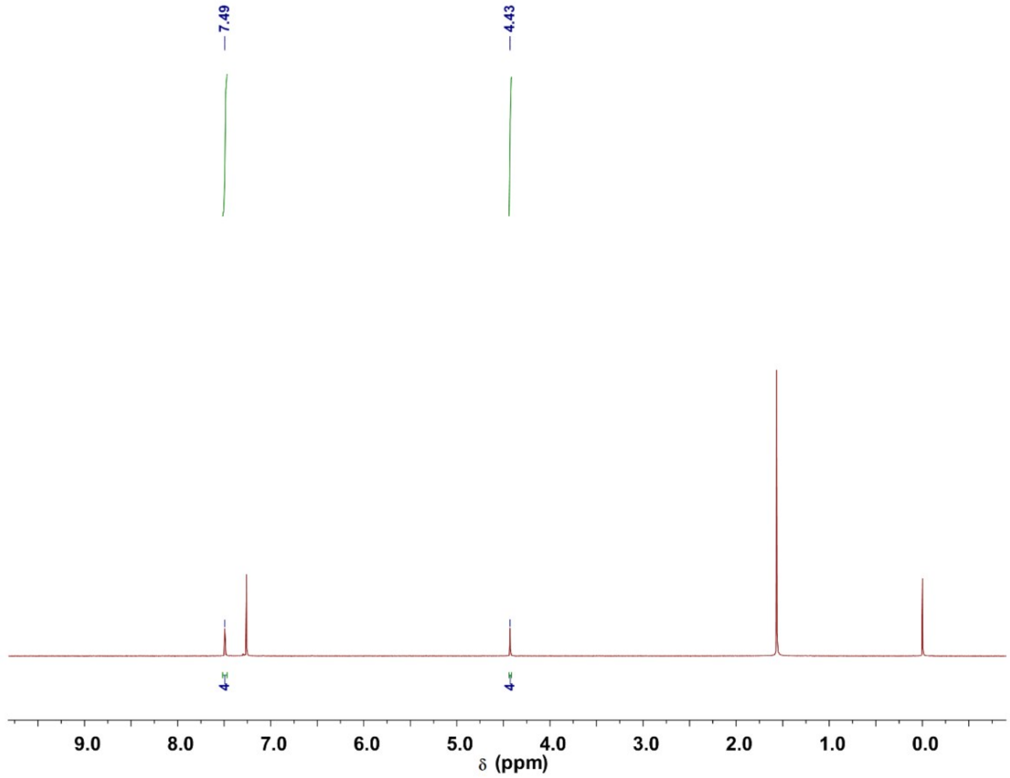
^{19}F NMR spectrum (564 MHz, D_2O, 298 K) of compound **1**·2Br.



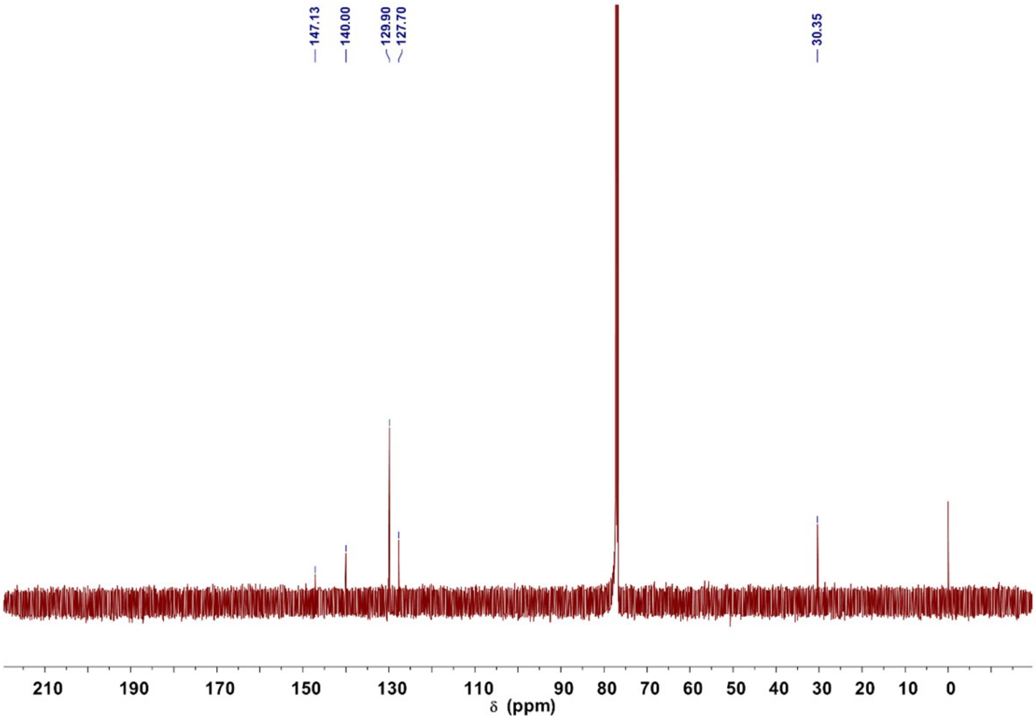
^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of compound **6**.



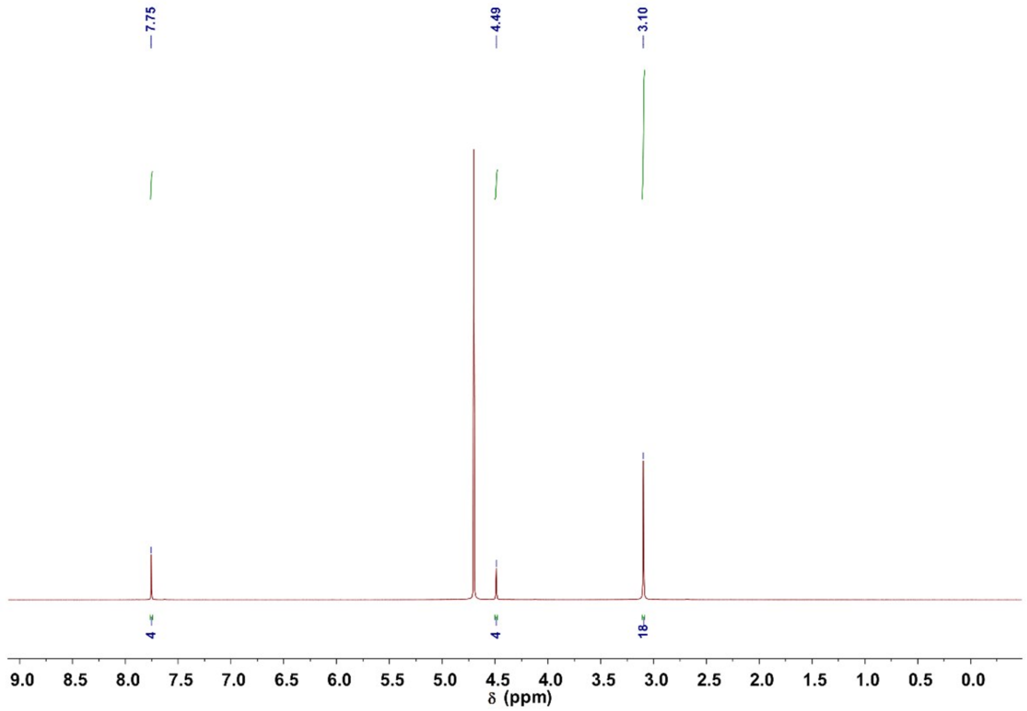
^{13}C NMR spectrum (150 MHz, $CDCl_3$, 298 K) of compound **6**.



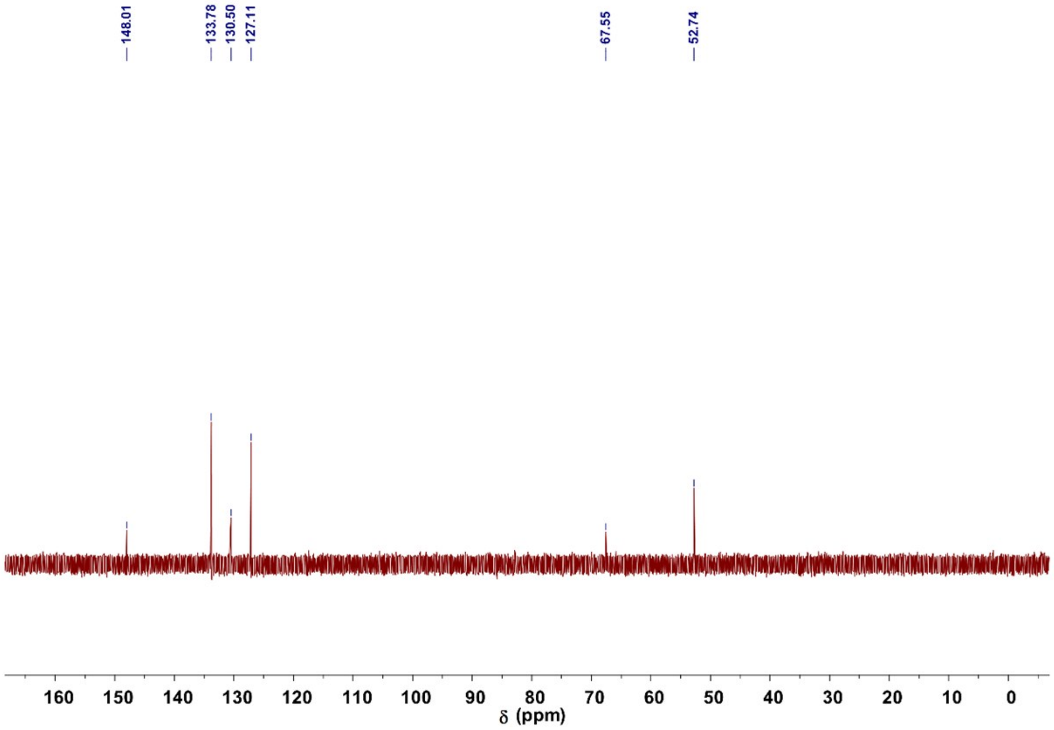
^{1}H NMR spectrum (600 MHz, CDCl$_3$, 298 K) of compound **8**.



^{13}C NMR spectrum (150 MHz, CDCl$_3$, 298 K) of compound **8**.



^{1}H NMR spectrum (600 MHz, D_2O, 298 K) of compound **2**·2Cl.



^{13}C NMR spectrum (150 MHz, D_2O, 298 K) of compound **2**·2Cl.

References

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

[2] D. Jiao, F. Biedermann and O. A. Scherman, *Org. Lett.*, 2011, **13**, 3044-3047.