Supporting Information

Regulating Photochromic Behavior of Cyanostilbene by Cucurbit[*n*]uril Hosts in Aqueous Solution

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General Experimental Section.

ESI-HRMS measurements: ESI-HRMS were performed on a Solarix 9.4T. Nicomp 380 Z3000 at room temperature, and the concentration of the samples are 0.5 mM.

Fluorescence measurements: Fluorescence spectra were measured on a PerkinElmer LS-55 machine at room temperature, a Suprasil Quartz (QS) cuvette with 1 cm path length was used for all fluorescence spectra measurements.

UV/Vis measurements: The experiments were performed on a SHIMADZU UV-36002 instrument with 1 cm pathlength cells at 298 K.

^{1}H NMR measurements: All ^{1}H NMR spectra were collected on Agilent 600 MHz DD2 at 298 K.

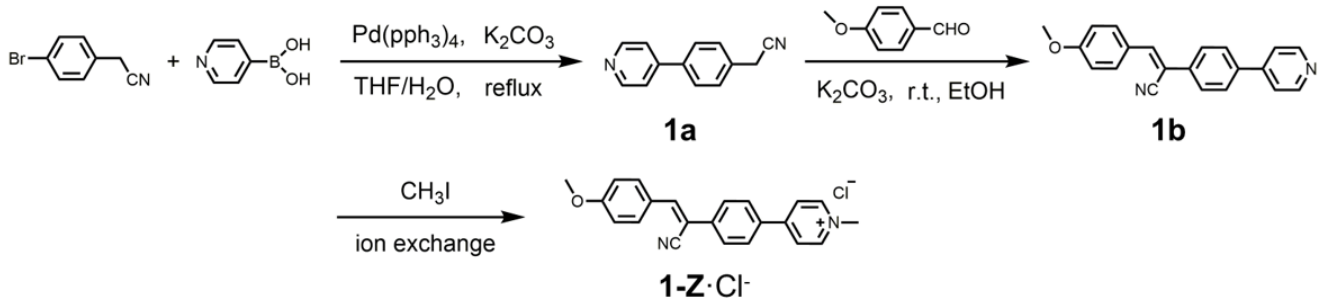
ITC measurements: ITC experiments were carried out on a Nano ITC (TA Instruments) at 298 K.

Light sources and light Irradiation experiments: The UV light irradiation experiments were performed using a Xenon Peak Integrated Light Source System MC-X10 (the irradiation wavelength for photoreaction process is 365 nm, and output power of the light is 200 W) equipped with a cutoff filter (365 nm, Shenyang HB optical Technology). All the irradiation experiments were performed in cuvettes directly, which was entirely and evenly exposed in light. Both of **1-Z** and the host-guest systems were performed in the same solvent, temperature and other conditions. The aqueous solutions used for all UV-Vis absorption spectroscopy and fluorescence spectroscopy tests involving photoreactions are initially exposed to the respective photoreactions at high concentrations (2 mM), and then diluted to the concentration required for spectroscopic testing (20 μM).

Fluorescence quantum yield: The absolute fluorescence quantum yield was determined by using a Hamamatsu C9920-02G Instruments Integrating Sphere Module (SC-30) on the FS5 spectrofluorometer. Fluorescence spectra analysis software Fluoracle and Quantum Yield Wizard were used to quantum yields. The 1.5 mL Suprasil Quartz (QS) cuvette with 1 cm path length was used for all measurements at 298K. Fluorescence quantum yield measurements were done for 1 mL aqueous solution of **1-Z** with CB[*n*] with an optical density in the range of 0.06-0.1.

Fluorescence lifetime: The fluorescence lifetime was measured on FS5 instrument (Edinburg Instruments, Livingstone, UK).

Synthesis and characterization.



Scheme S1. Synthesis route of **1-Z**·Cl^-.

Synthesis and characterization of 1a and 1b:

Synthesis and characterization of **1a** and **1b** have been reported in previous literature.[1]

Synthesis and characterization of 1-Z·Cl^-:

1b (0.50 g, 1.53 mmol) was dissolved in dry DCM (10.00 mL) and CH_3I (0.50 mL) was injected. The mixture was stirred at room temperature for 12 h. Then resulting yellow solid and the reaction mixture was filtered, washed with DCM and diethyl ether, dried in vacuum at 60°C to give yellow solid. Then the yellow solid was dissolved in MeOH:H_2O (1:1, 20 mL), added sufficient NH_4PF_6 to the mixed solution, vibrated and the solid was produced immediately, the filter cake was filtered, the obtained solid was washed for three times with H_2O in order to wash off excessive NH_4PF_6, dried in vacuum at 60°C to give yellow solid. Using a similar method, we dissolved the yellow solid in acetone solution, added excess tetrabutylammonium chloride, shaked well, solid was produced immediately and filtered, and the acquired solid is washed for three times with acetone in order to wash off excessive tetrabutylammonium chloride, dried in vacuum at 60°C to give bright yellow solid **1-Z**·Cl^- (0.40 g, 72.20%).

1-Z·Cl^-: ^{1}H NMR (600 MHz, D_2O) δ 8.56 (d, *J* = 6.4 Hz, 2H), 8.03 (d, *J* = 6.4 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.42 (s, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.26 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (150 MHz, D_2O) δ 160.78, 153.06, 144.03, 142.66, 136.49, 131.70, 131.56, 128.01, 125.73, 125.56, 123.52, 117.88, 113.89, 104.37, 55.26, 46.72.

HRMS (ESI; m/z): [**1-Z**]$^+$ calcd. for $[C_{22}H_{19}N_2O]^+$, 327.1492; found, 327.1478.

Synthesis and characterization of 1-D·$2Cl^-$:

1-D·$2Cl^-$ solid was obtained by **1-Z**·Cl^- being exposed to UV irradiation in aqueous solution for 2 hours and then freeze-dried.

1-D·$2Cl^-$: ^{1}H NMR (600 MHz, D_2O) δ 8.78 (d, *J* = 6.4 Hz, 1H), 8.27 (d, *J* = 6.5 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 5.74 (s, 1H), 4.39 (s, 1H), 3.81 (s, 2H).

^{13}C NMR (150 MHz, D_2O) δ 157.12, 152.78, 142.77, 135.64, 132.16, 129.37, 127.19, 126.02, 123.06, 122.69, 119.57, 111.76, 53.11, 50.56, 46.11, 45.11.

HRMS (ESI; m/z): [**1-D**]$^{2+}$ calcd. for $[C_{44}H_{38}N_4O_2]^{2+}$, 327.1492; found, 327.1427.

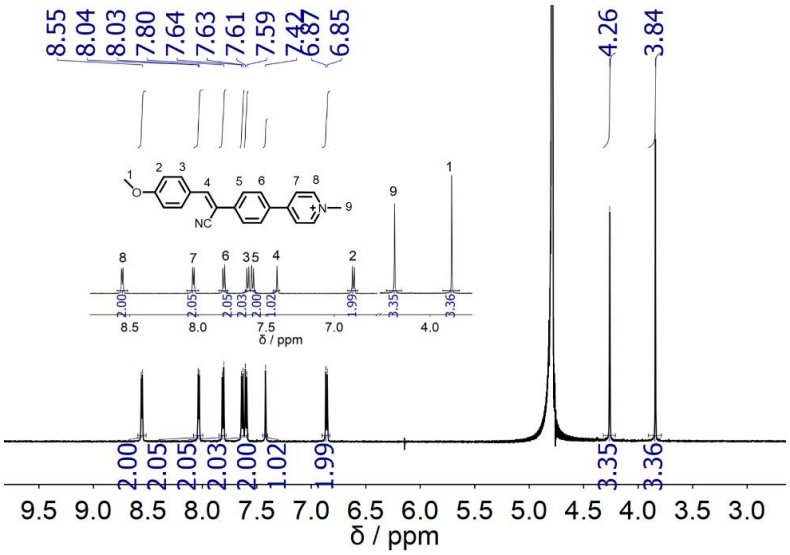


Fig. S1 ^{1}H NMR spectrum of **1-Z** (600 MHz, 298 K, D_2O).

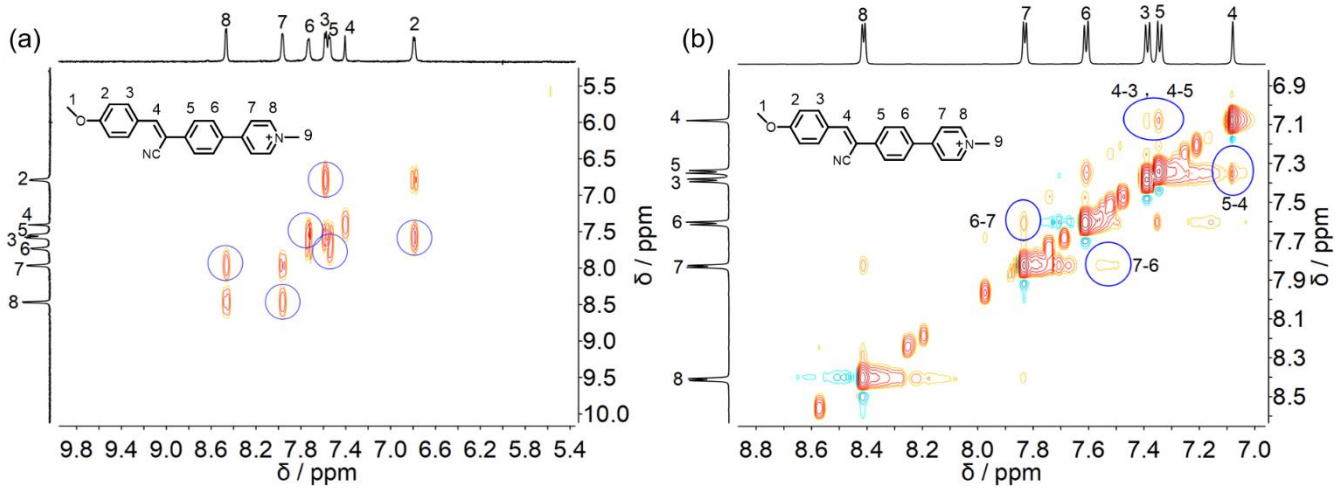


Fig. S2 (a) COSY and (b) NOESY NMR spectra of **1-Z** (600 MHz, D_2O, 298 K).

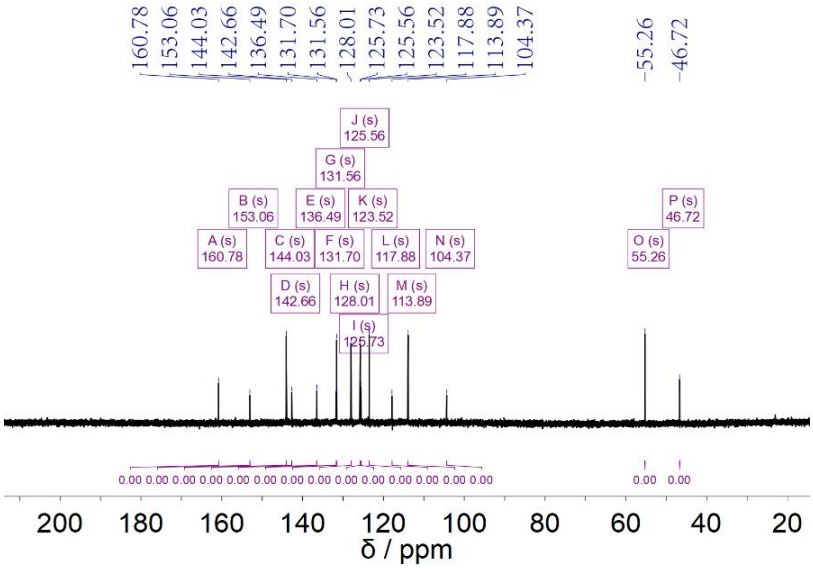


Fig. S3 ^{13}C NMR spectrum of **1-Z** (150 MHz, 298 K, D_2O).

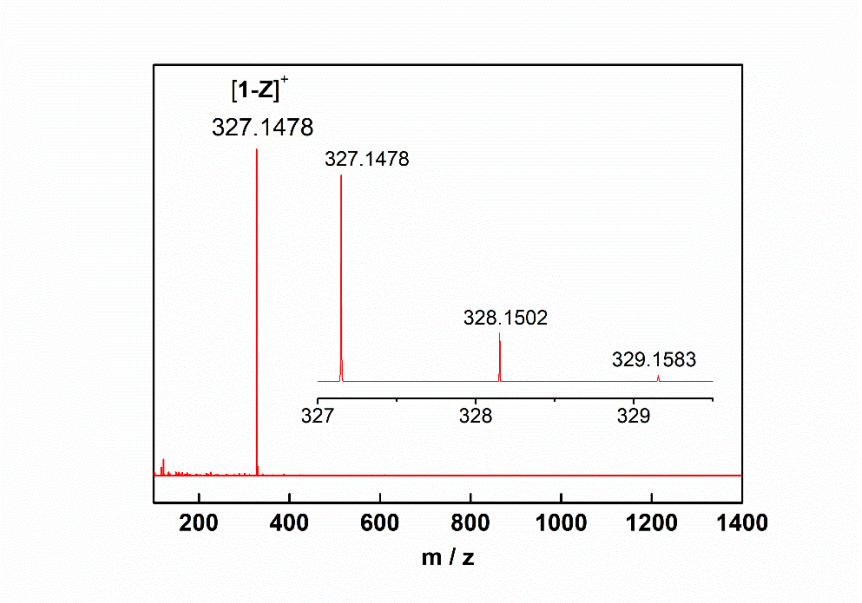


Fig. S4 ESI-HRMS spectrum of **1-Z**.

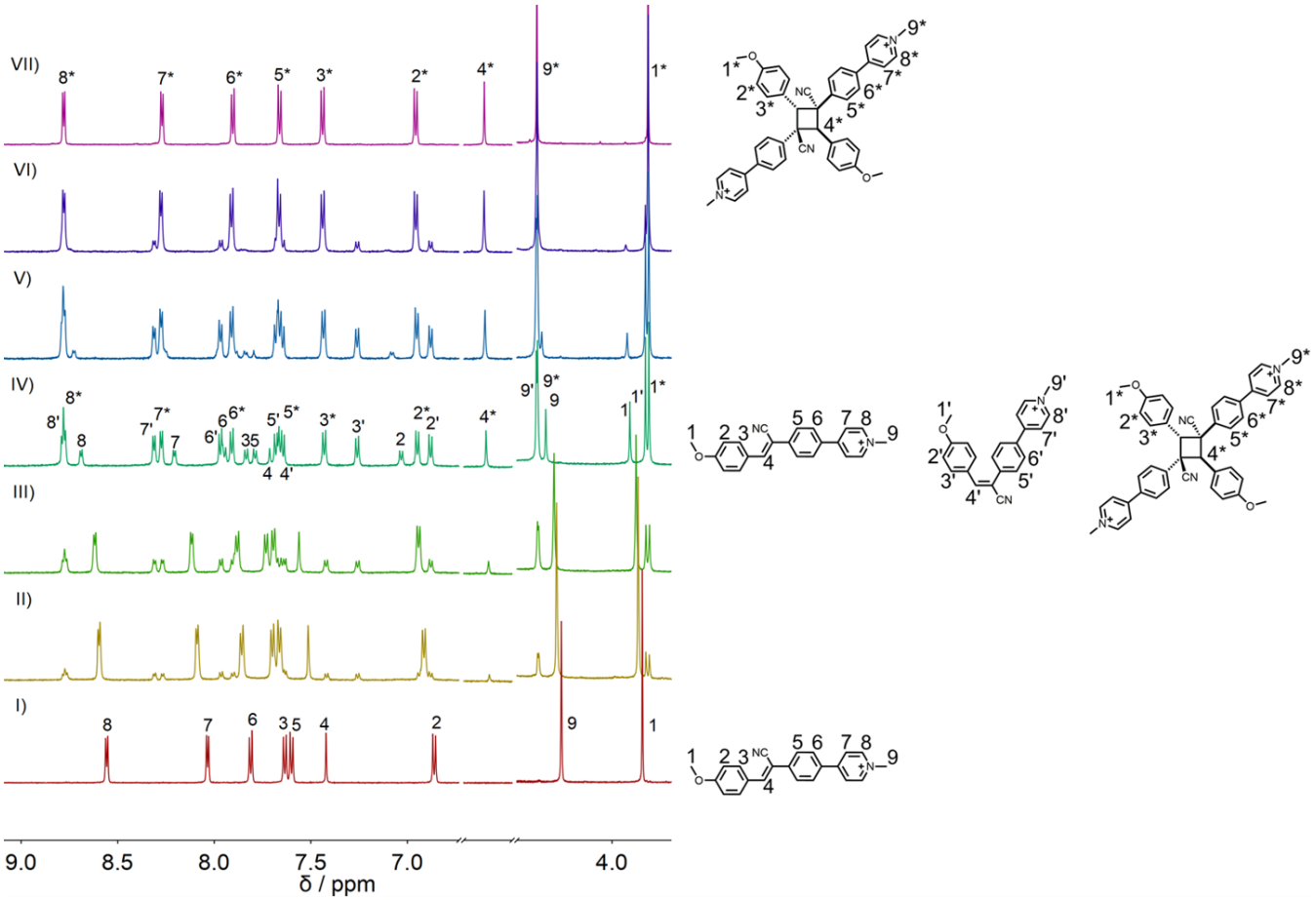


Fig. S5 ^{1}H NMR spectra of **1-Z** in aqueous solution (2 mM, 600 MHz, D_2O, 298 K) after irradiation for I) 0, II) 2, III) 5, IV) 15, V) 30, VI) 60, VII) 120 min (Resonances of **1-Z**, **1-E**, and **1-D** are labeled with number 1-9, 1'-9' and 1*-9*).

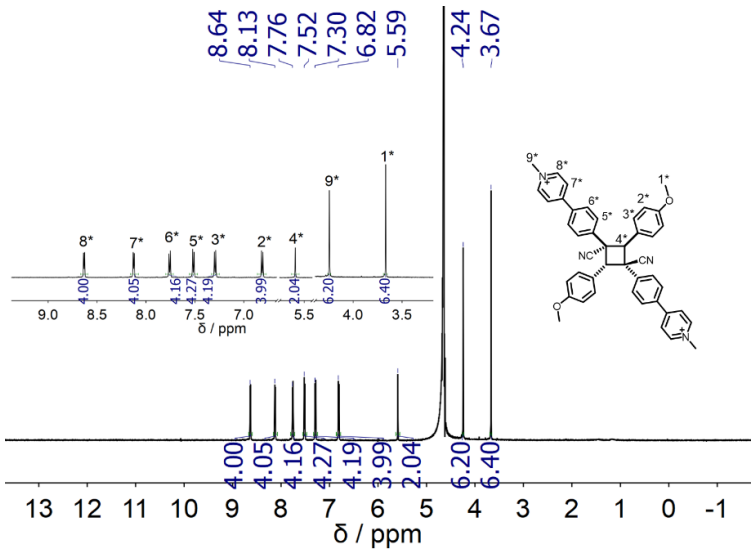


Fig. S6 ^{1}H NMR spectrum of **1-D** (600 MHz, 298 K, D_2O).

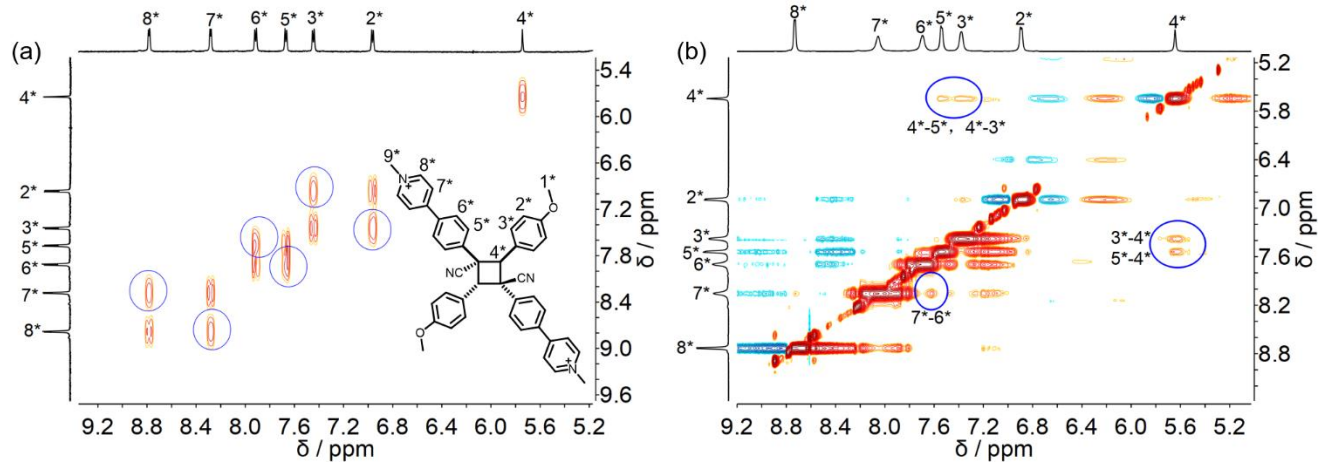


Fig. S7 (a) COSY and (b) NOESY NMR spectra of **1-D** (2 mM, 600 MHz, D_2O, 298 K).

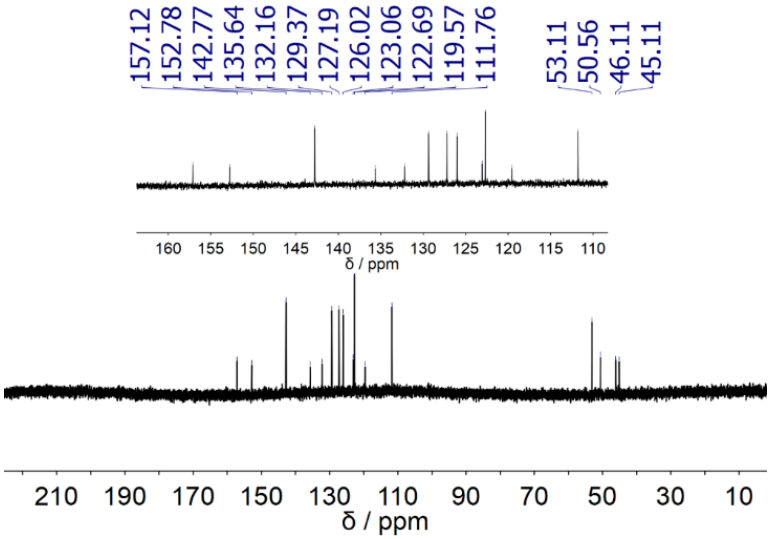


Fig. S8 ^{13}C NMR spectrum of **1-D** (150 MHz, 298 K, D_2O).

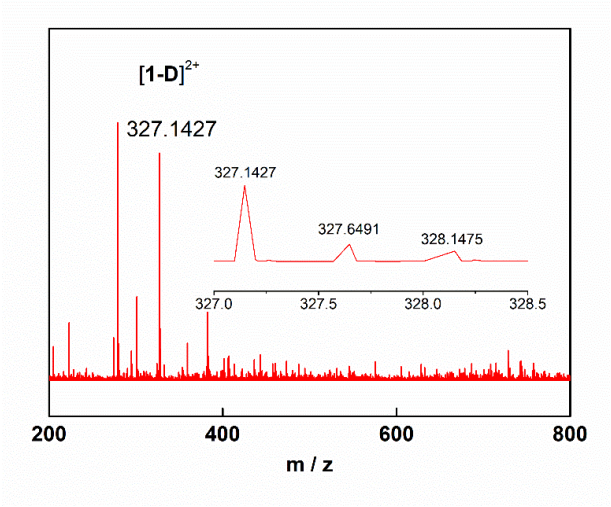


Fig. S9 ESI-HRMS spectrum of **1-D**.

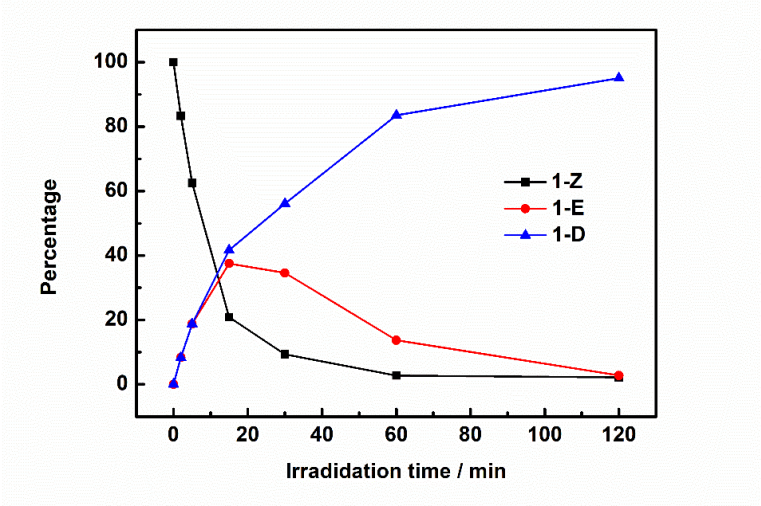


Fig. S10 Percentage of **1-Z**, **1-E**, and **1-D** upon different irradiation time according to the integrals of corresponding signals in Fig. S5.

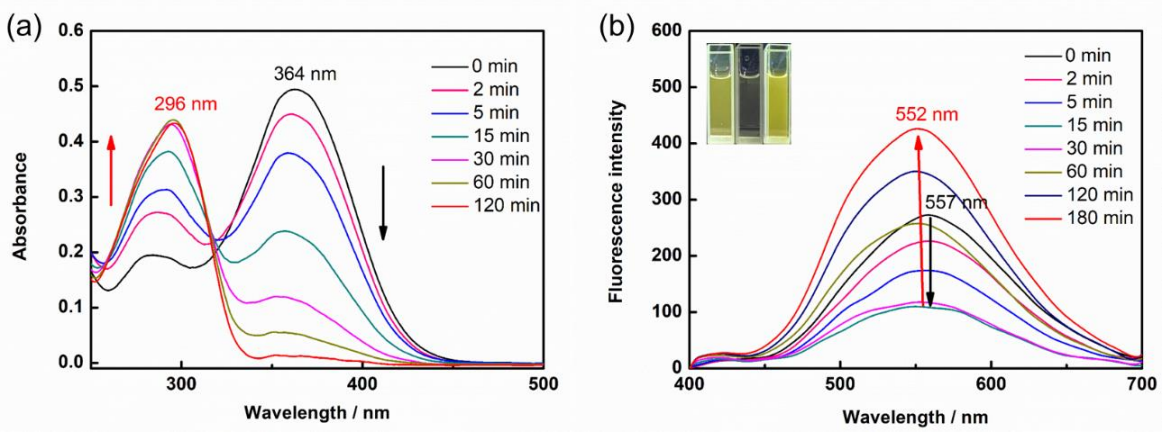


Fig. S11 (a) UV-vis absorption spectra of **1-Z (**20 μM, 298 K**)** in aqueous solution upon irradiation for different time. (b) Emission spectra of **1-Z (**20 μM, 298 K**)** in aqueous solution upon irradiation for different time (insert: photographs of **1-Z** after irradiation for 0, 30, 180 min) (λ_{ex} = 365 nm).

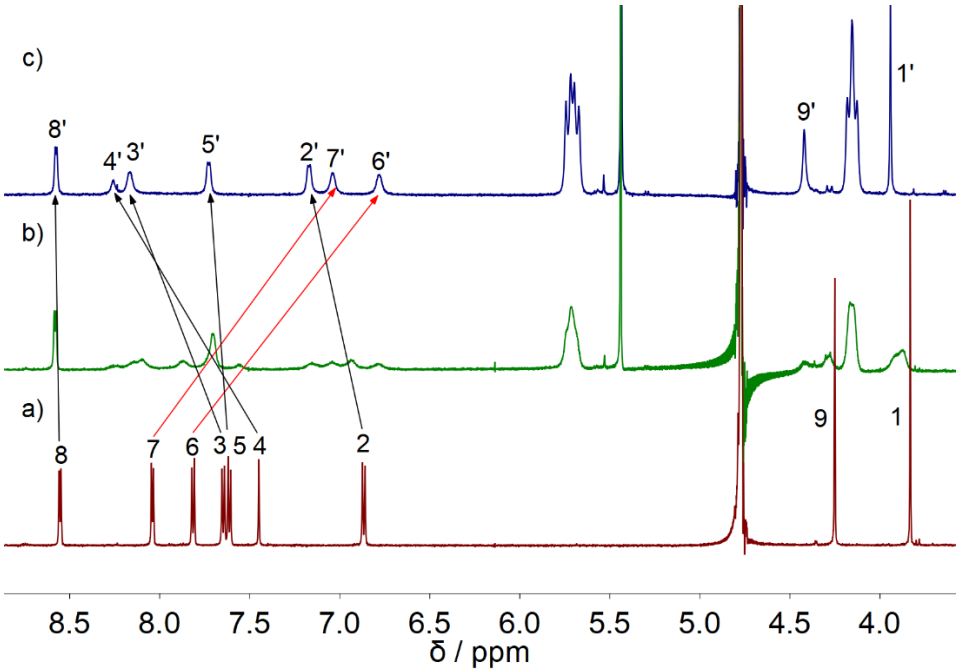


Fig. S12 ^{1}H NMR spectra of **1-Z** (2 mM, 600 MHz, D_2O, 298 K) with a) 0 equiv., b) 0. 5 equiv., c) 1 equiv. of CB[7]. Characters 1-9, 1'-9' represent the resonance signals of **1-Z** as free and in CB[7]·(**1-Z**), respectively.

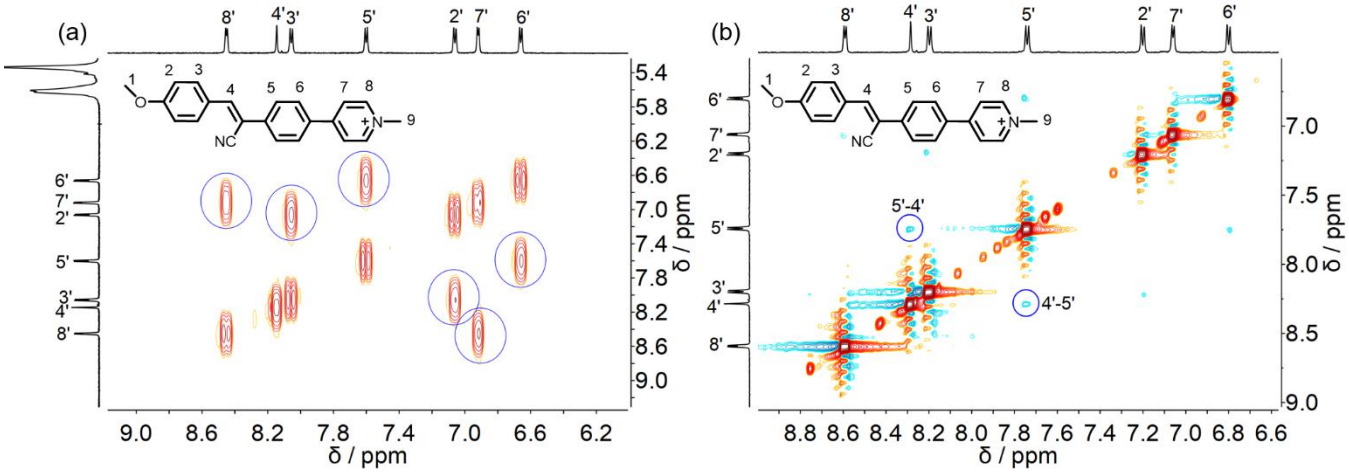


Fig. S13 (a) COSY and (b) ROESY NMR spectra of **1-Z** (2 mM, 600 MHz, D_2O, 298 K) with 1 equiv. of CB[7].

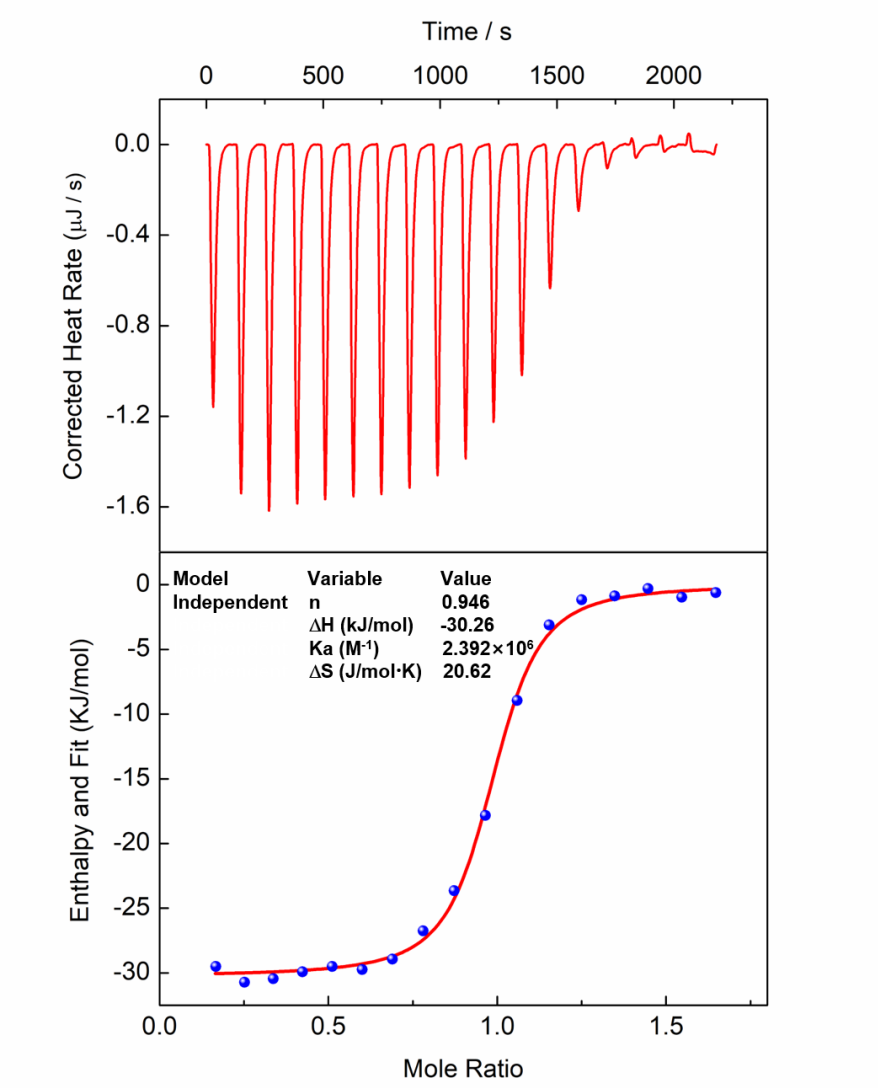


Fig. S14 Isothermal titration calorimetry data for compound **1-Z** with CB[7] in H_2O ([**1-Z**] (syringe) = 6.0×10^{-4} M, [CB[7] (cell) = 1.0×10^{-4} M).

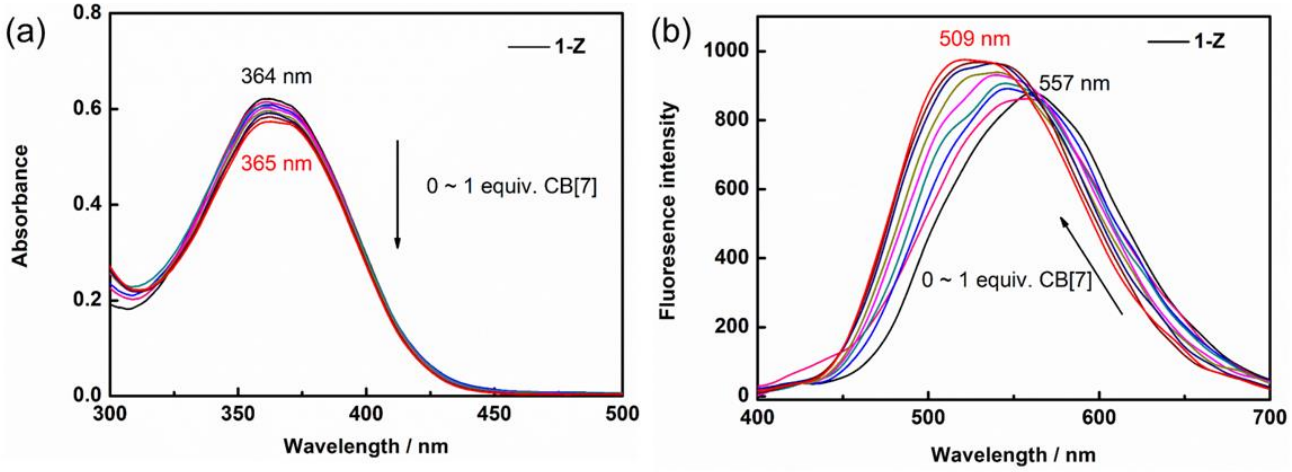


Fig. S15 UV-vis absorption spectra (a) and fluorescence spectra (b) of **1-Z** (20 μM in H_2O, 298 K) with different equiv. of CB[7] (0 ~ 1 equiv.) (λ_{ex} = 365 nm).

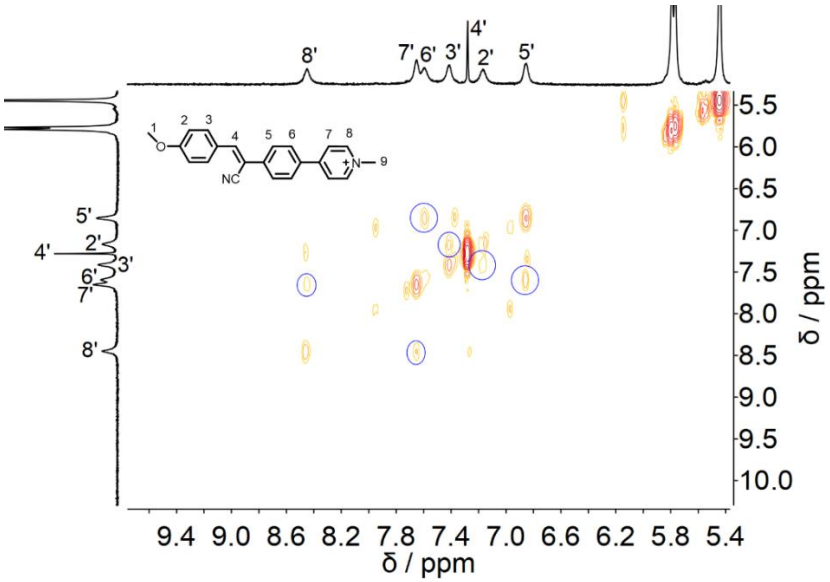


Fig. S16 COSY NMR spectrum of **1-Z** (2 mM, 600 MHz, D_2O, 298 K) with 0.5 equiv. of CB[8].

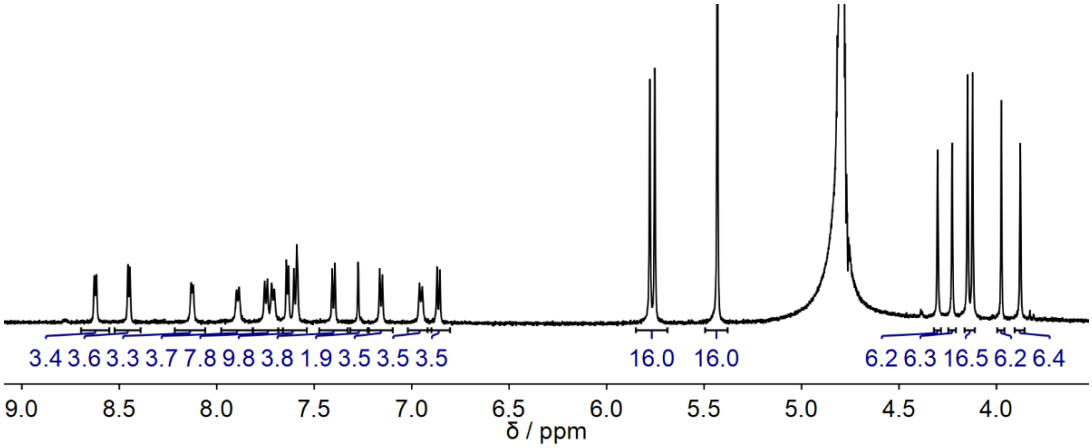


Fig. S17 ^{1}H NMR spectrum of **1-Z** (2 mM, 600 MHz, D_2O, 298 K) with 0.25 equiv. of CB[8] (this spectrum corresponds to Figure 3a).

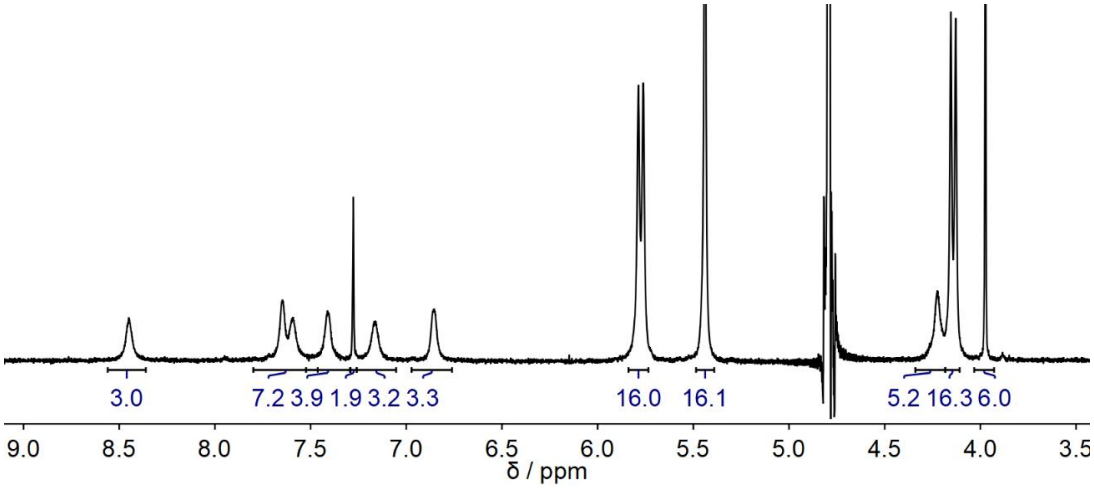


Fig. S18 ^{1}H NMR spectrum of **1-Z** (2 mM, 600 MHz, D_2O, 298 K) with 0. 5 equiv. of CB[8] (this spectrum corresponds to Figure 3a).

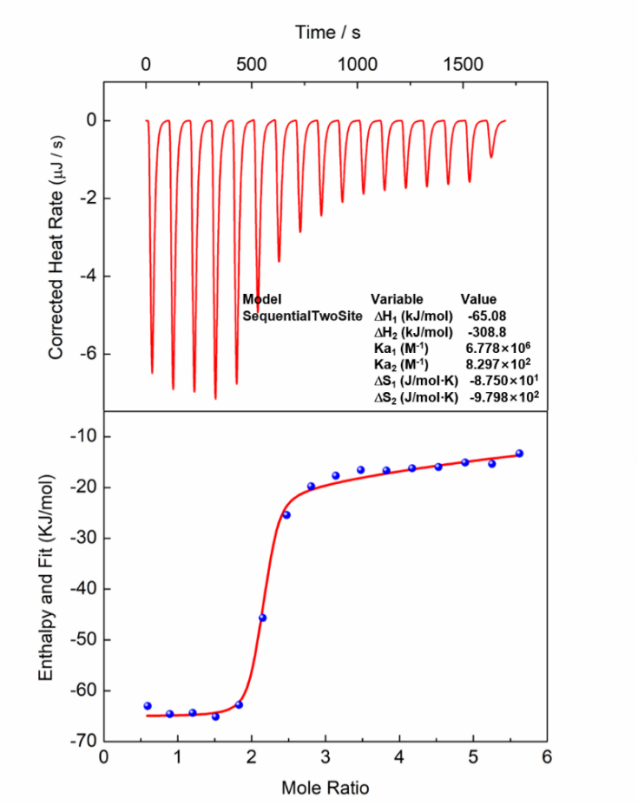


Fig. S19 Isothermal titration calorimetry data for compound **1-Z** with CB[8] in H_2O ([**1-Z**] (syringe) = 1.0×10^{-3} M, [CB[8]] (cell) = 1.0×10^{-4} M). The binding constant of CB[8]·(**1-Z**)$_2$ is estimated as 5.62×10^9 M^{-2}. However, considering the unusual enthalpy change in the second binding step, the K_a value may not be reliable.

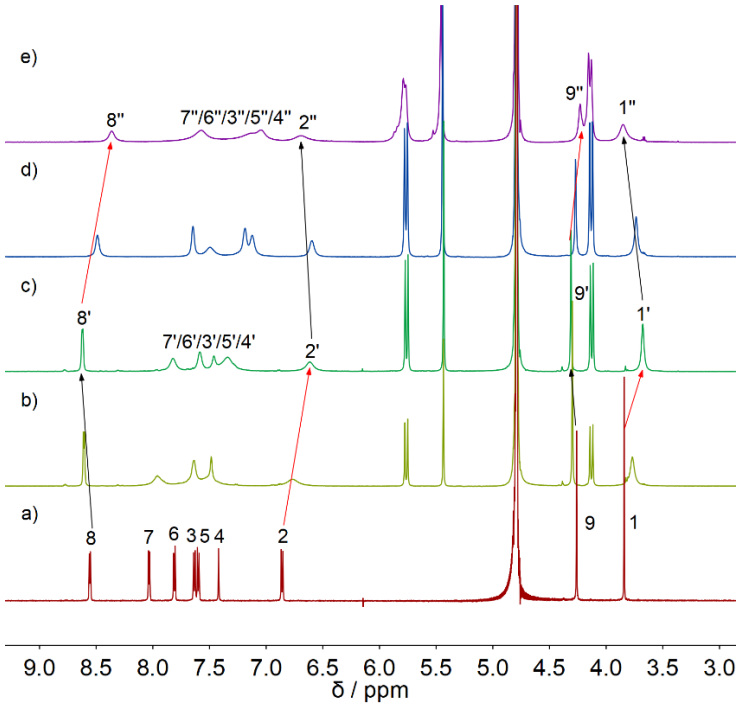


Fig. S20 ^{1}H NMR spectra of **1-Z** (2 mM, 600 MHz, D_2O, 298 K) with a) 0 equiv., b) 0.165 equiv., c) 0.33 equiv., d) 0.415 equiv., e) 0.5 equiv. of CB[10]. Characters 1-9, 1'-9', 1''-9'' represent the resonance signals of **1-Z** as free, in the presence of 0.33 equiv. of CB[10], and in the presence of 0.5 equiv. of CB[10], respectively.

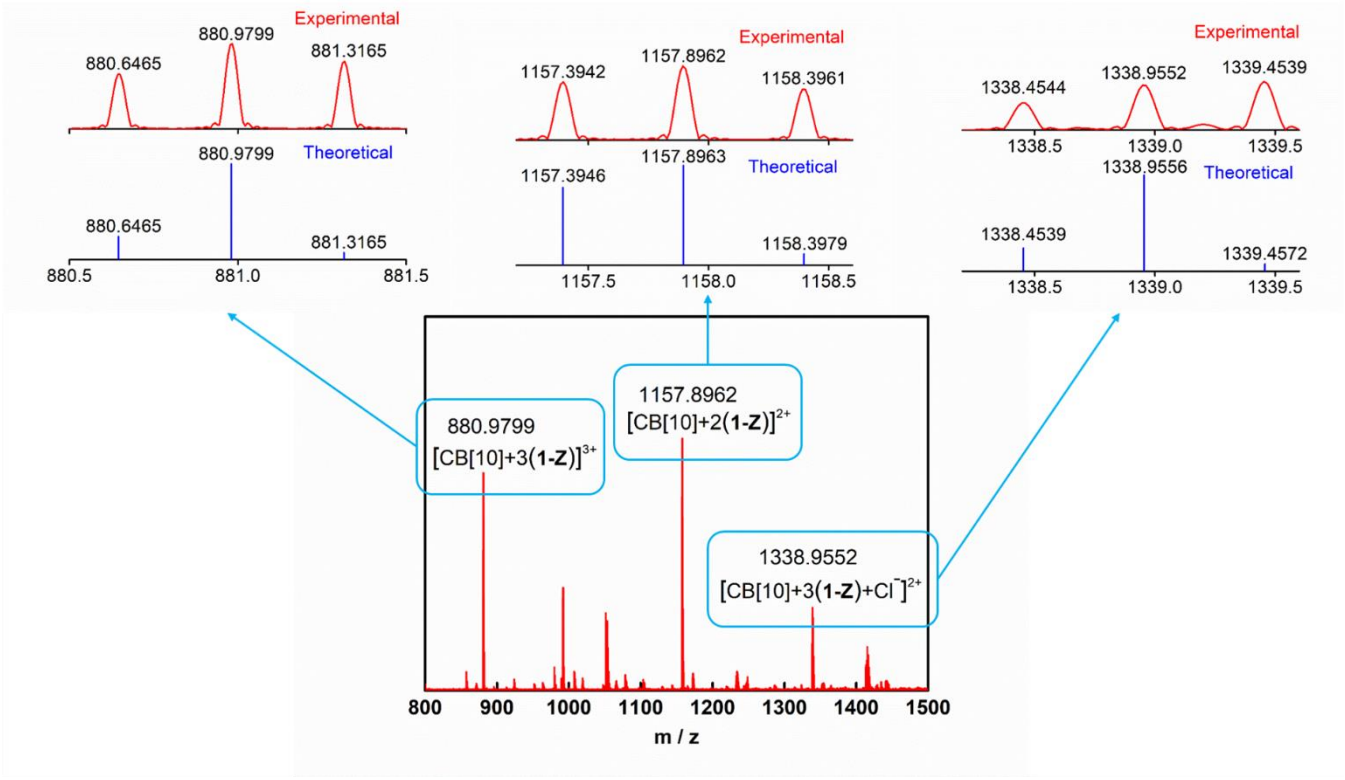


Fig. S21 ESI-HRMS spectrum of **1-Z** with CB[10].

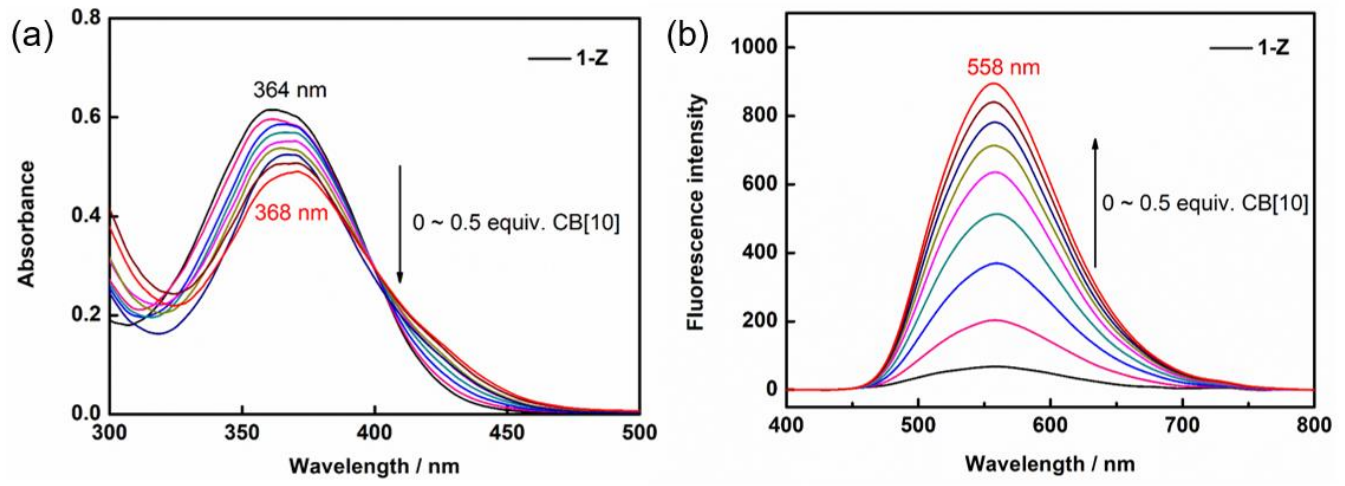


Fig. S22 UV-vis absorption spectra (a) and fluorescence spectra (b) of **1-Z** (20 μM in H_2O, 298 K) with different equiv. of CB[10] (0 ~ 0.5 equiv.) (λ_{ex} = 365 nm).

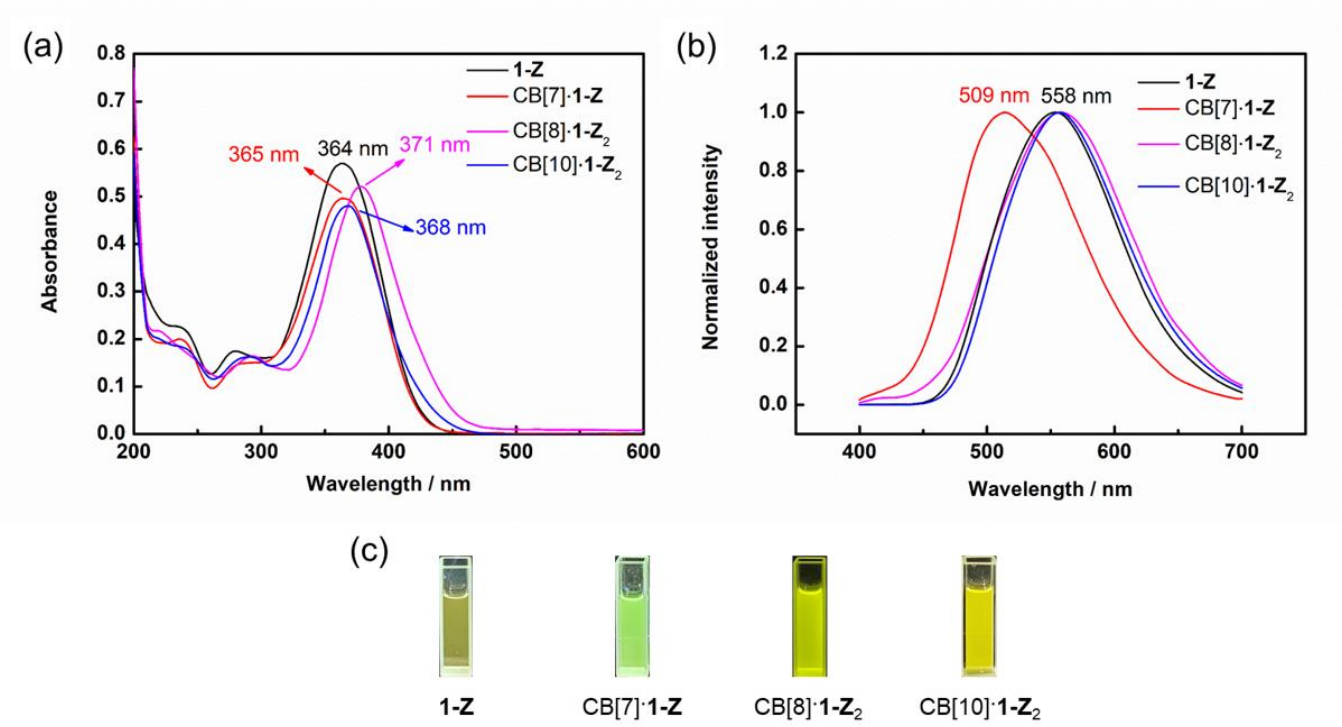


Fig. S23 UV-vis absorption spectra (a) and emission spectra (b) of free **1-Z**, CB[7]·(**1-Z**), CB[8]·(**1-Z**)$_2$, and CB[10]·(**1-Z**)$_2$ (20 μM in H_2O, 298 K, λ_{ex} = 365 nm). (c) Photographs of **1-Z** and its host-guest complexes under photoexcitation at 365 nm.

Table S1. Photoluminescence data of **1-Z** and its host-guest complexes in aqueous solution (c = 2.0 × 10^{-5} M, 298 K).

	Before irradiation				After irradiation for 2h				
	λ_{Abs}[a] (nm)	λ_{FL}[b] (nm)	τ[c] (ns)	Φ[d] (%)	λ_{Abs}[a] (nm)	λ_{FL}[b] (nm)	τ[c] (ns)	Φ[d] (%)	$\Delta\lambda_{FL}$[e] (nm)
1-Z	364	557	2.20	0.01	296	552	7.26	3.06	5
CB[7]·**1-Z**	365	509	3.95	0.09	294	509	4.96	0.03	0
CB[8]·**1-Z**$_2$	371	558	11.78	25.59	292	558	12.05	25.69	2
CB[10]·**1-Z**$_2$	368	558	4.53	3.17	300	507	11.54	6.87	51

[a] UV-vis absorption wavelength. [b] Fluorescent emission wavelength. [c] Fluorescence lifetime. [d] Quantum yields. [e] The difference value of fluorescence emission wavelength.

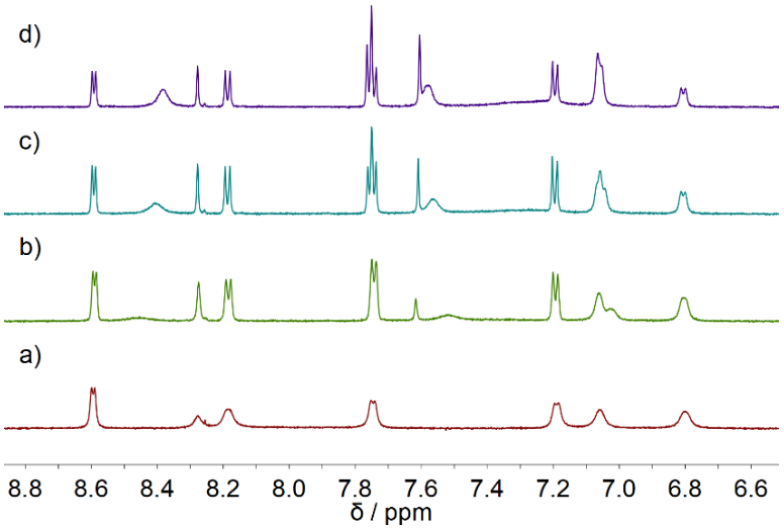


Fig. S24 ^{1}H NMR spectra of **1-Z** in the presence of 1 equiv. of CB[7] in aqueous solution (2 mM, 600 MHz, D_2O, 298 K) after irradiation for a) 0, b) 15, c) 30, d) 60 min.

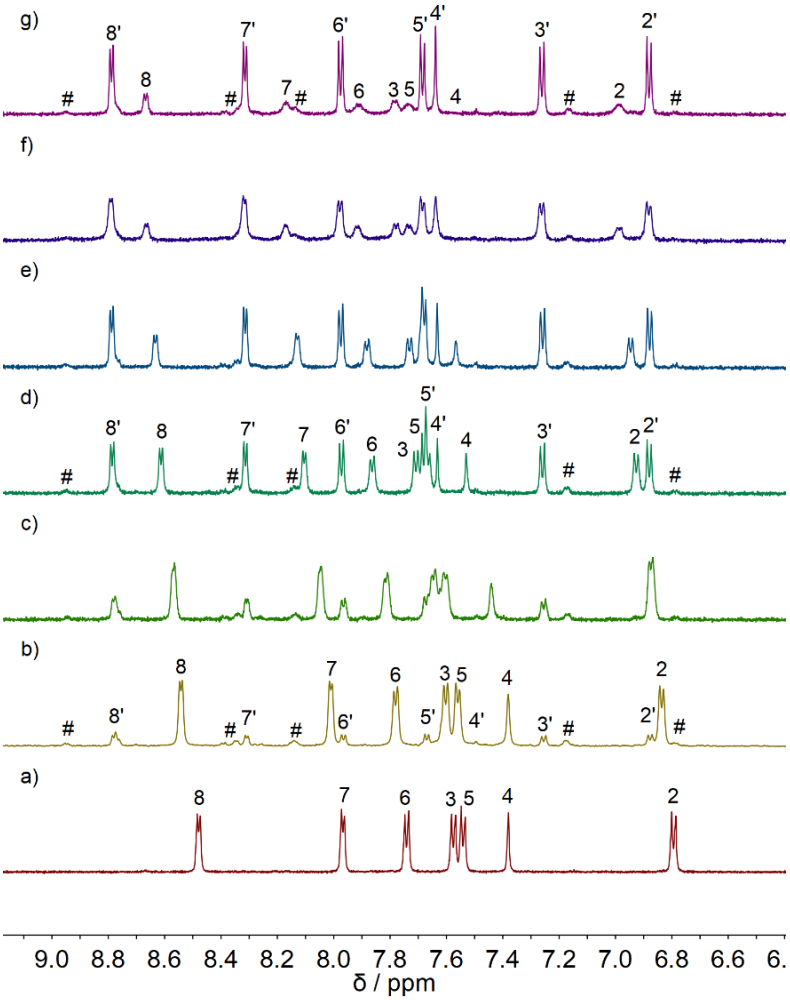


Fig. S25 ^{1}H NMR spectra of **1-Z** in the presence of 1 equiv. of CB[7] in aqueous solution (2 mM, 600 MHz, D_2O, 298 K) after irradiation for a) 0, b) 2, c) 5, d) 15, e) 30, f) 60, g) 120 min and subsequently introducing a competitive guest (**AD**) for competition (Resonances of **1-Z**, **1-E**, and **1-D** are labeled with number 1-9, 1'-9' and #; **AD** (1.1 equiv.) was added to each sample after light irradiation).

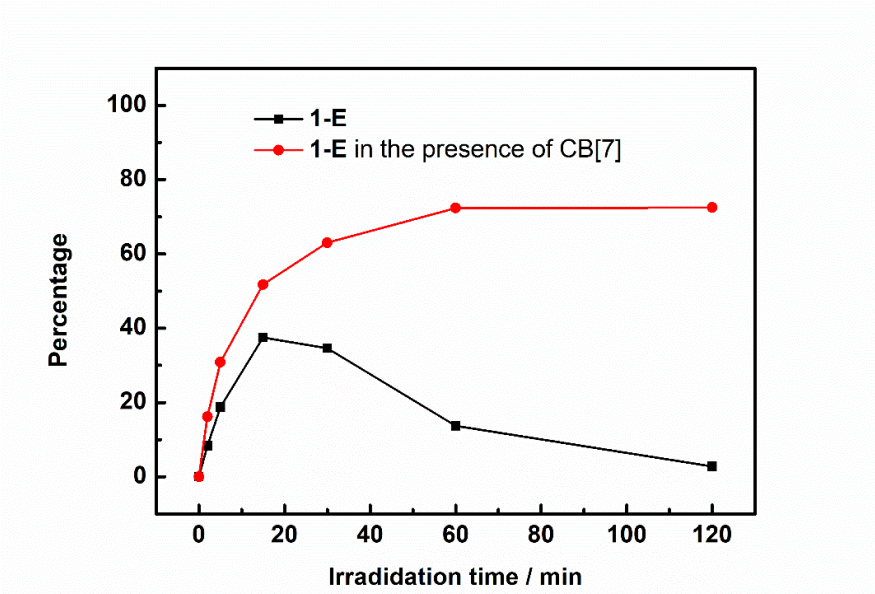


Fig. S26 Percentage of **1-E** upon irradiating **1-Z** in the absence/presence of 1 equiv. of CB[7] with different irradiation time according to the integrals of corresponding signals.

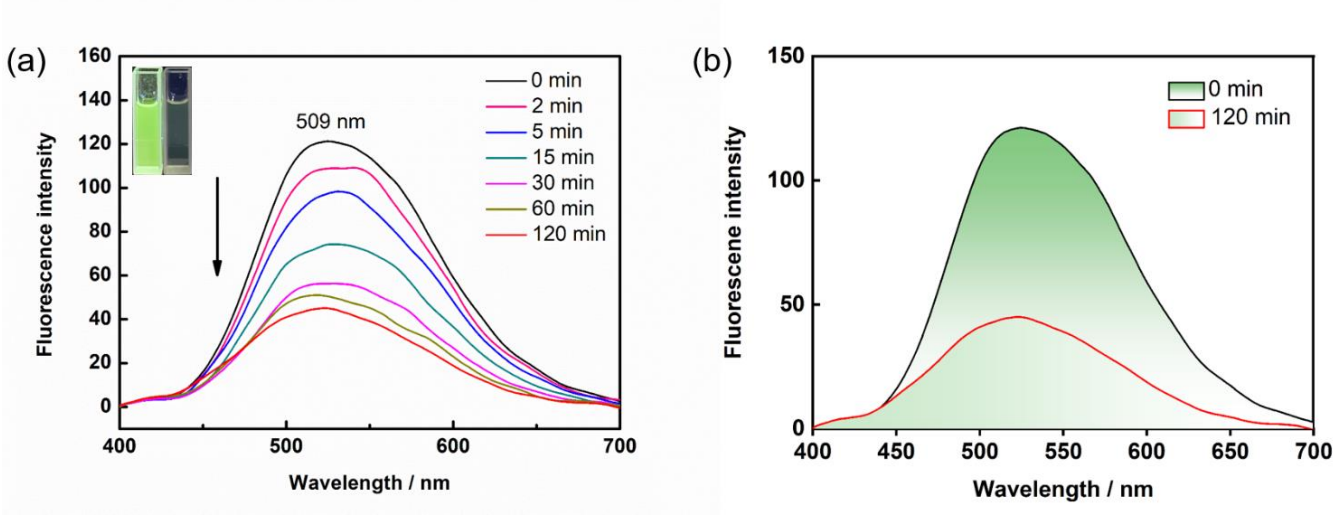


Fig. S27 (a) Emission spectra of **1-Z (**20 μM, 298 K**)** in the presence of 1 equiv. of CB[7] in aqueous solution after irradiation for different time (insert: photographs of **1-Z** in the presence of 1 equiv. of CB[7] after irradiation for 0 and 120 min) (λ_{ex} = 365 nm). (b) Fluorescence intensity changes of **1-Z** (20 μM, 298 K) in the presence of 1 equiv. of CB[7] in aqueous solution upon irradiation (λ_{ex} = 365 nm).

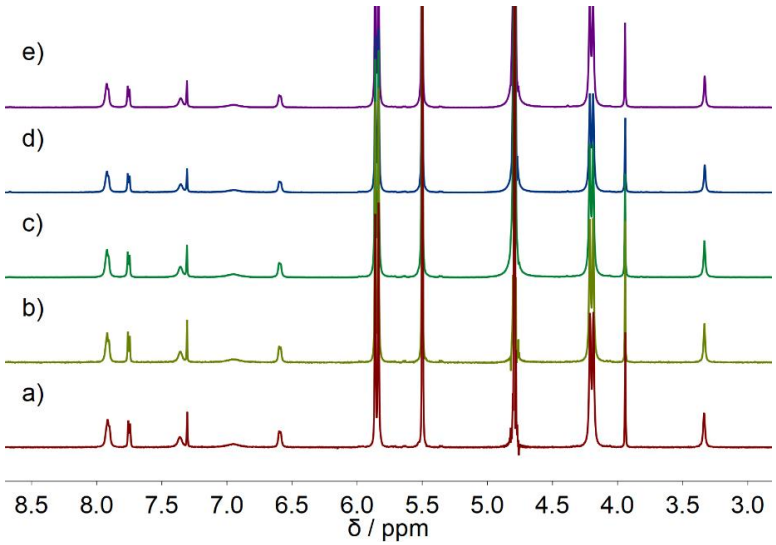


Fig. S28 ^{1}H NMR spectra of **1-Z** in the presence of 0.5 equiv. of CB[8] in aqueous solution (2 mM, 600 MHz, D_2O, 298 K) after irradiation for a) 0, b) 15, c) 30, d) 45, e) 60 min.

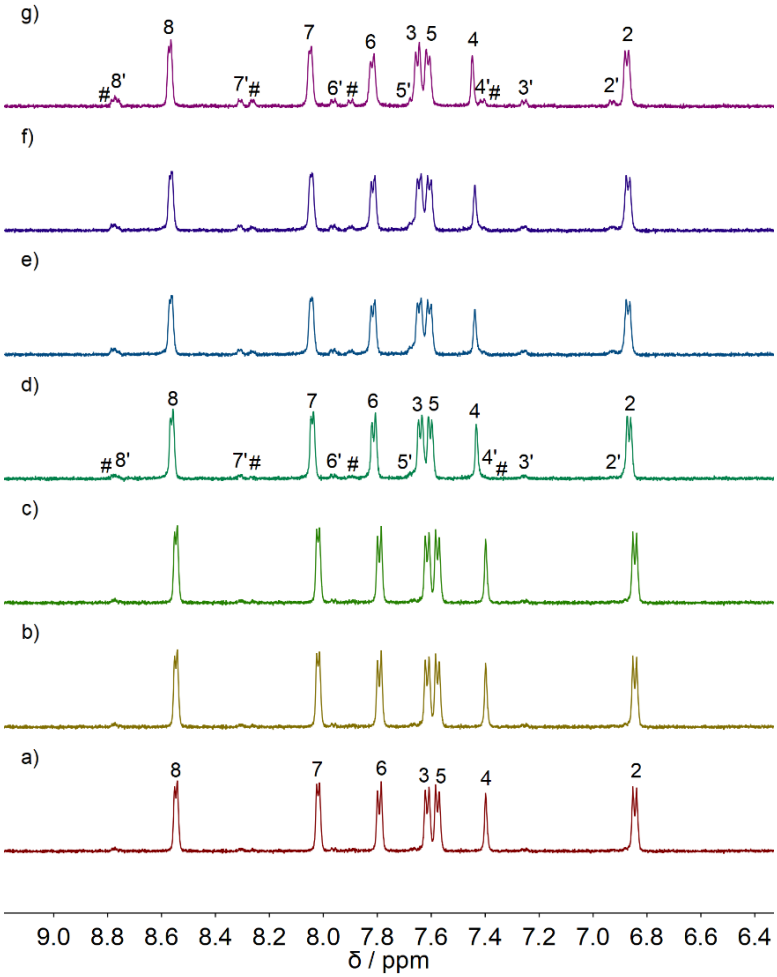


Fig. S29 ^{1}H NMR spectra of **1-Z** in the presence of 0.5 equiv. of CB[8] in aqueous solution (2 mM, 600 MHz, D_2O, 298 K) after irradiation for a) 0, b) 2, c) 5, d) 15, e) 30, f) 60, g) 120 min and subsequently introducing a competitive guest 3,5-dimethyladamantan-1-amine hydrochloride (**3,5-DMADA**) for competition (Resonances of **1-Z**, **1-E**, and **1-D** are labeled with number 1-9, 1'-9' and #; **3,5-DMADA** (1.1 equiv.) was added to each sample after light irradiation).

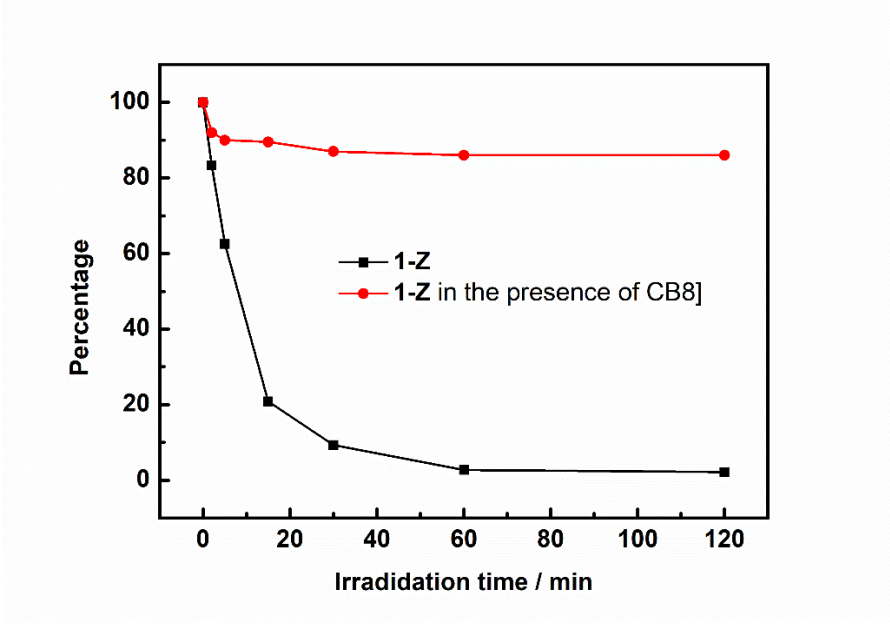


Fig. S30 Percentage of **1-Z** in the absence/presence of 0.5 equiv. of CB[8] upon different irradiation time according to the integrals of corresponding signals.

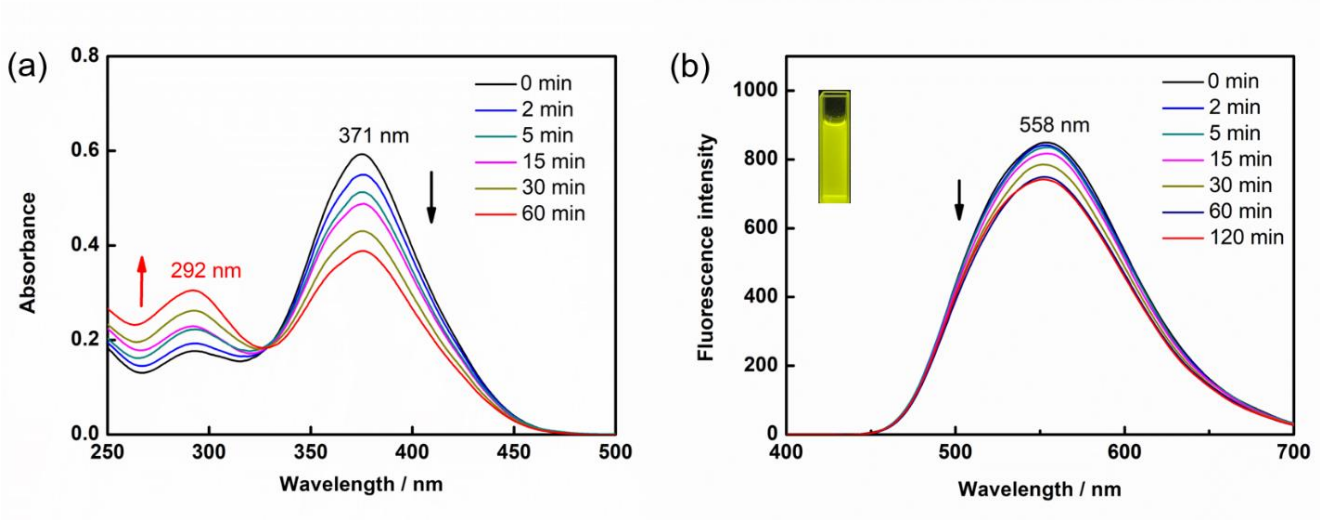


Fig. S31 UV-vis absorption spectra (a) Emission spectra (b) of **1-Z (**20 μM, 298 K**)** in the presence of 0.5 equiv. of CB[8] in aqueous solution after irradiation for different time (insert: photographs of **1-Z** in the presence of 0.5 equiv. of CB[8] after irradiation for 0, 180 min) (λ_{ex} = 365 nm).

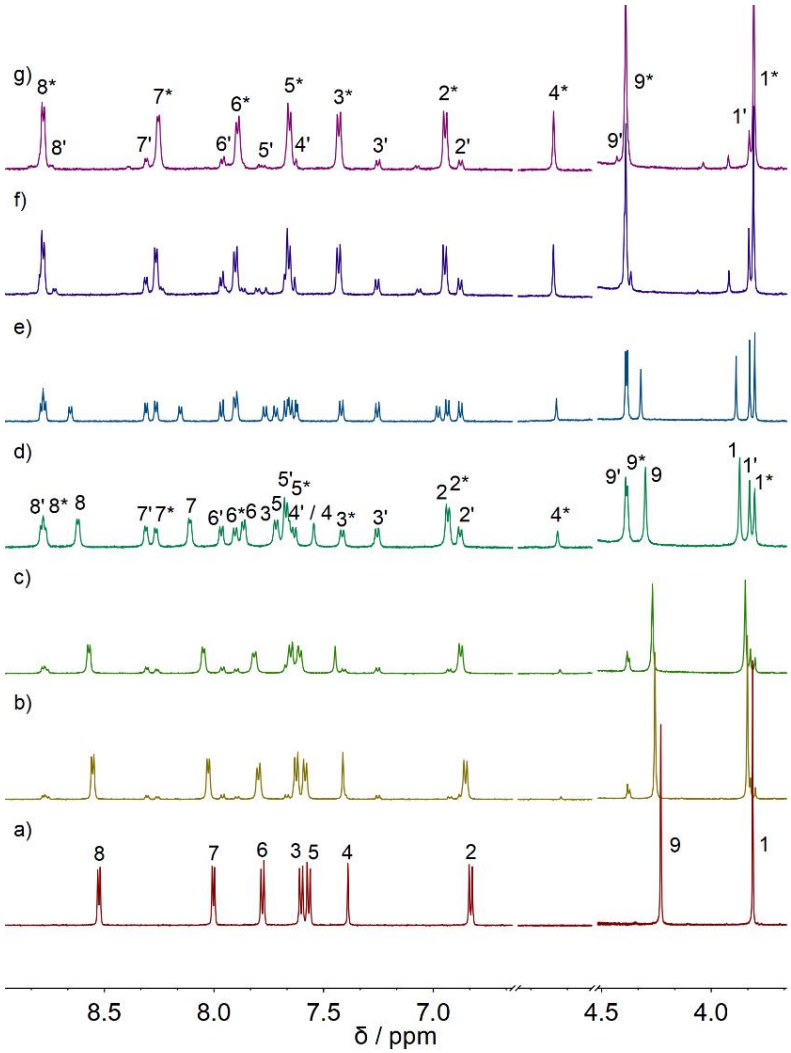


Fig. S32 ^{1}H NMR spectra of **1-Z** in the presence of 0.5 equiv. of CB[10] in aqueous solution (2 mM, 600 MHz, D_2O, 298 K) after irradiation for a) 0, b) 2, c) 5, d) 15, e) 30, f) 60, g) 120 min and subsequently introducing a competitive guest (**3,5-DMADA**) for competition (Resonances of **1-Z**, **1-E**, and **1-D** are labeled with number 1-9, 1'-9' and 1*-9*; **3,5-DMADA** (2.2 equiv.) was added to each sample after light irradiation).

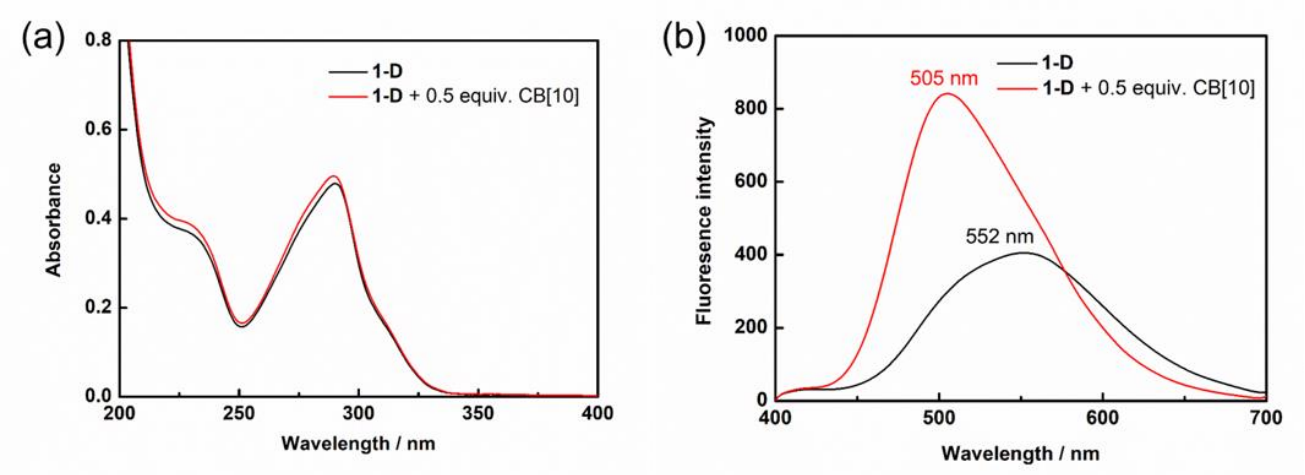


Fig. S33 UV-vis absorption spectra (a) and fluorescence spectra (b) of **1-D** (20 μM in H_2O, 298 K) with different equiv. of CB[10] (0 ~ 0.5 equiv.) (λ_{ex} = 365 nm).

References:

1. Y. Wang, Y. Zhong, X. Zhang, D.-H. Qu, D. Mei, and J. Mei, *Mater. Chem. Front.,* 2022, **6**, 2103.