

Electronic Supplementary Information

Supramolecular structural control: photochemical reactions between styrylpyridine derivative and cucurbit[7,8]urils

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1. Synthesis of CHP

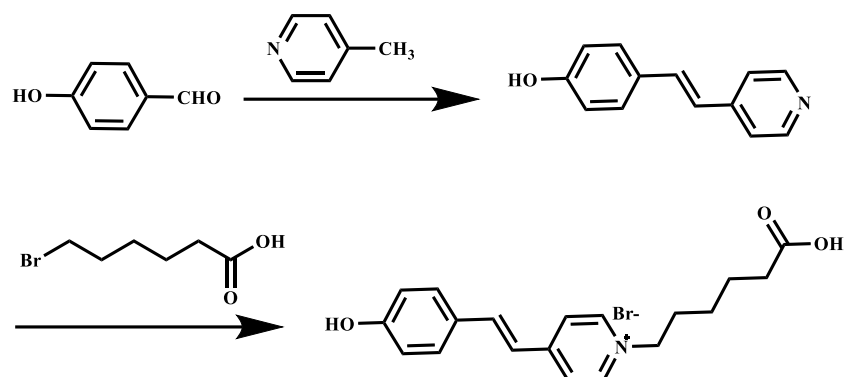


Figure S1. The synthesis route of guest CHP.

4-[2-(4-Pyridinyl)ethenyl]phenol: 2.5 g (0.020 mol) 4-hydroxybenzyl aldehyde and 2.7 g (0.029 mol) 4-methylpyridine were added to 15 ml acetic anhydride, and heated to reflux overnight. 50 ml distilled water was added to quench the reaction and the pH was adjusted to 9 using 5% NaOH. The precipitate was filtered and collected, and washed with cold ethanol 3-5 times to obtain a pale-yellow solid.

CHP: 4-[2-(4-Pyridinyl)ethenyl]phenol (0.2 g, 0.001 mol) and 6-bromohexanoic acid (1.0 g, 0.005 mol) were dissolved in acetonitrile (30 mL). The solution was stirred under an inert nitrogen atmosphere and heated to 80°C and refluxed for 12 h. The resultant solution was concentrated to approximately 5 ml by vacuum rotary evaporation, and was added dropwise to 40 ml acetone. After being filtered off, the light green precipitate (compound CHP) was washed several times with acetone and dried. ¹H NMR (D₂O, 400 MHz): δ = 8.38 (d, J = 6.8 Hz, 2H), 7.79 (d, J = 6.8 Hz, 2H), 7.58 (d, 1H), 7.52 (d, J = 8.9 Hz, 2H), 7.08 (d, J = 16.3 Hz, 1H), 6.97 (d, J = 8.5 Hz, 2H), 4.25 (t, J = 7.2 Hz, 2H), 2.05 (t, J = 7.3 Hz, 2H), 1.75 (m, 2H), 1.37 (m, 2H), 1.11 (q, J = 7.2 Hz, 2H); ¹³C NMR (DMSO-d₆, 100 MHz): δ (ppm) = 175.23, 169.97, 153.81, 152.87, 145.25, 140.77, 133.88, 130.25, 124.82, 124.31, 123.57, 60.46, 34.23, 25.84, 24.71, 21.94. HRMS calcd for [M]⁺: m/z = 312.1594, found: m/z = 312.1601.

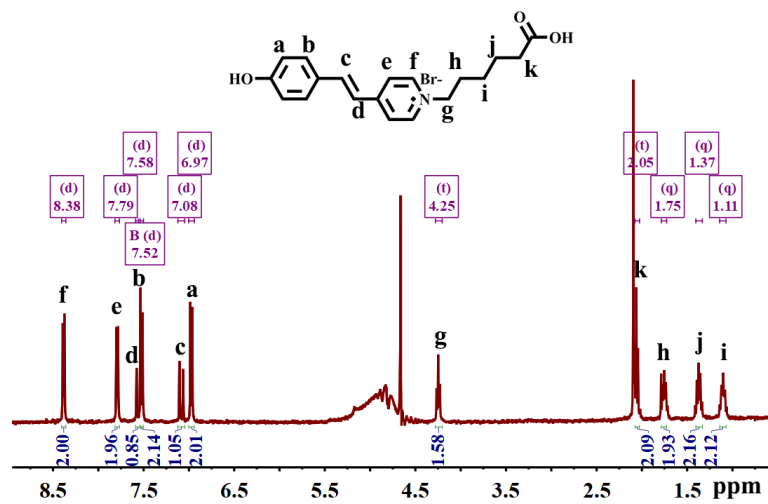


Figure S2. ^1H NMR spectra of CHP in D_2O (400 MHz).

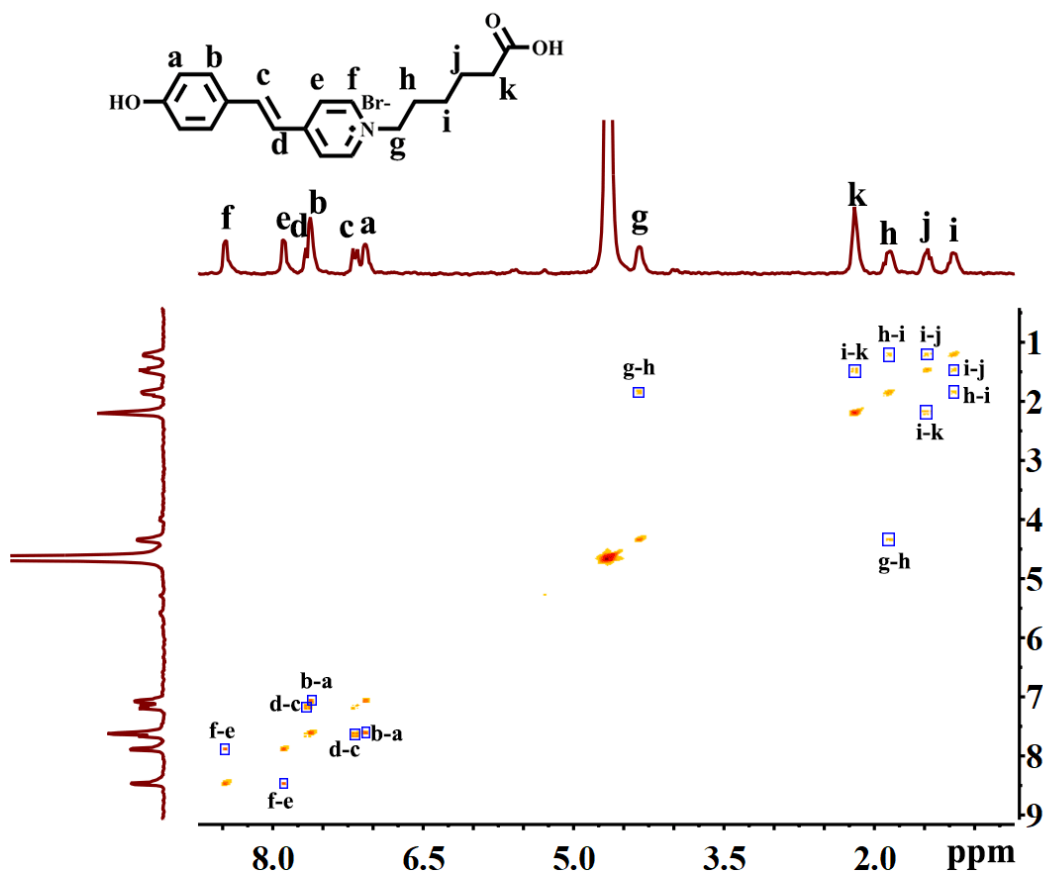


Figure S3. COSY NMR spectra of CHP in D_2O (400 MHz).

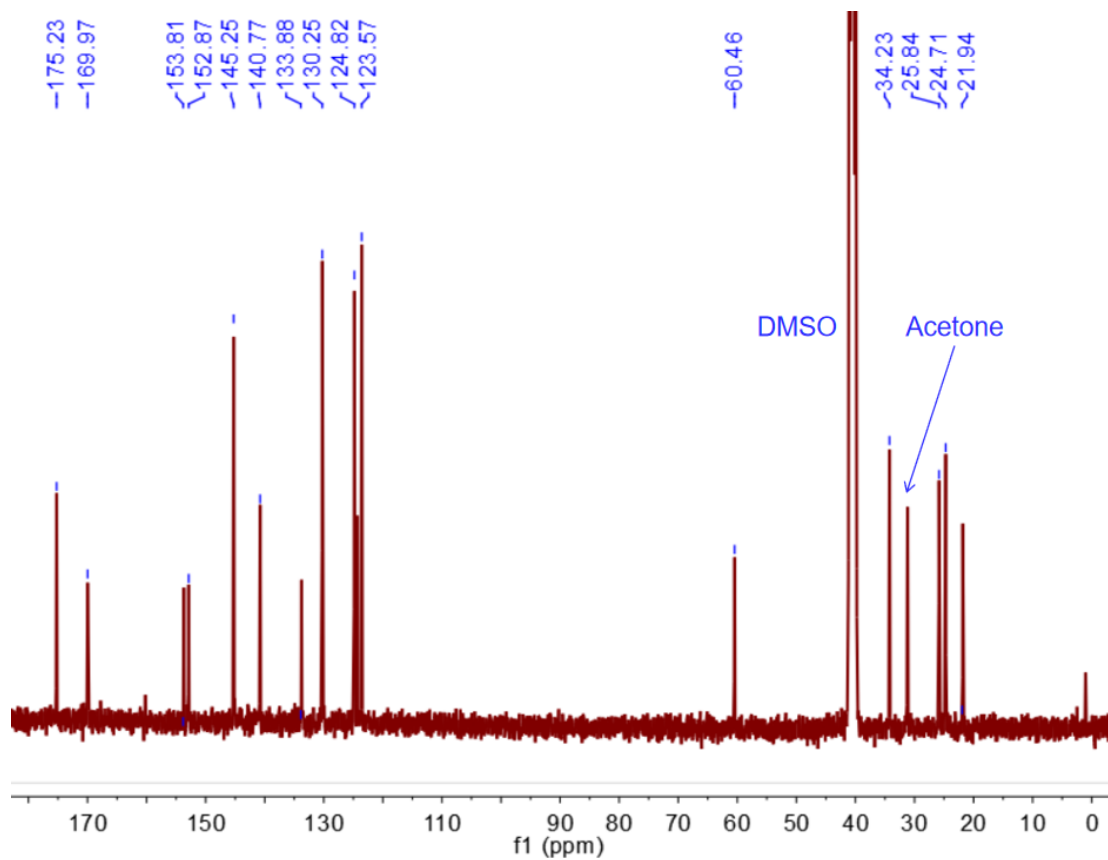


Figure S4. ^{13}C NMR spectra of CHP in DMSO- d_6 (100 MHz).

2. The interaction between CHP and Q[8]

2.1 The UV absorption spectra

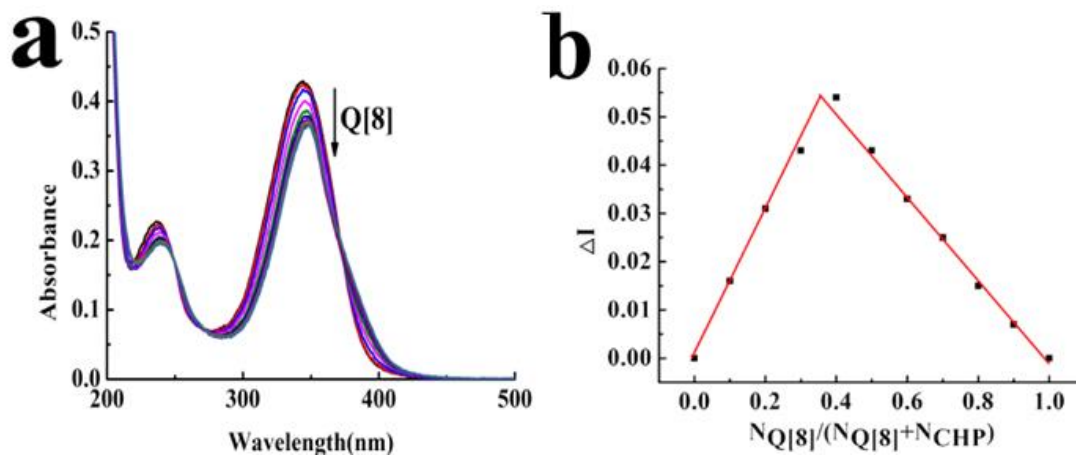


Figure S5. (a) Relationship between absorbance and $N_{\text{Q}[8]}/N_{\text{CHP}}$; (b) Corresponding curve of $\Delta I - N_{\text{Q}[8]}/(N_{\text{Q}[8]}+N_{\text{CHP}})$.

2.2 The fluorescence spectroscopy

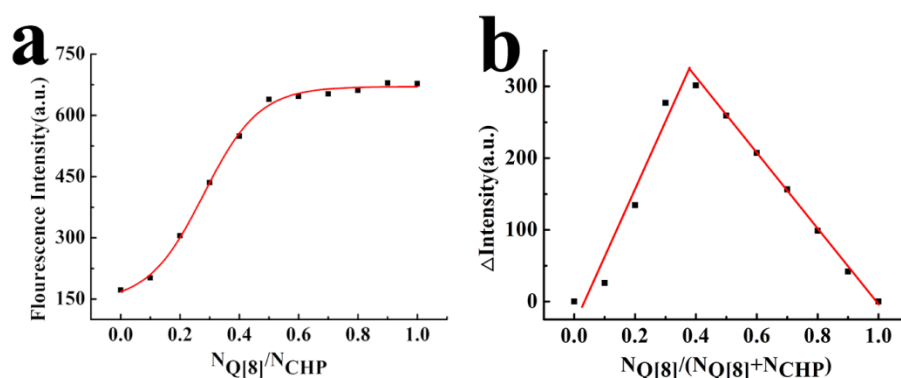


Figure S6. (a) Relationship between fluorescence intensity and $N_{Q[8]}/N_{CHP}$; (b) Corresponding curve of $\Delta A-N_{Q[8]}/(N_{Q[8]}+N_{CHP})$.

2.3 The Isothermal titration calorimetry experiment

The first binding constant K_{a1} and the second binding constant K_{a2} are obtained by fitting the ITC curve using a sequential binding model.

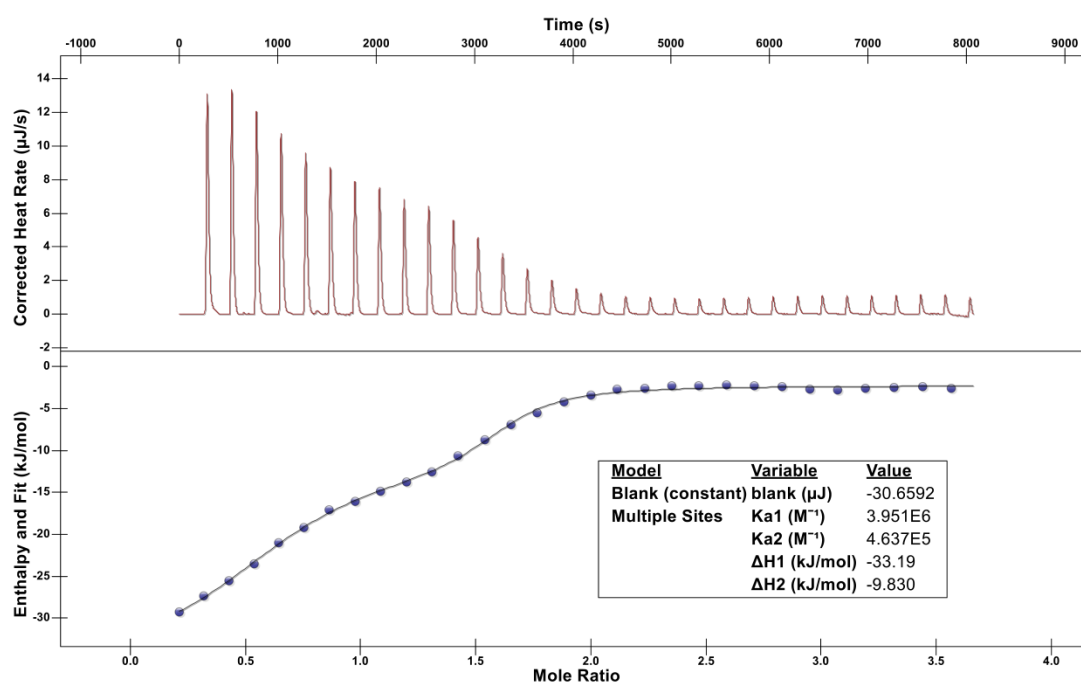


Figure S7. Isothermal titration calorimetry profiles of Q[8] in the presence of the guest CHP in aqueous solution at 298.15 K.

Table S1. ITC data of Q[8]-CHP

$K_{a1}/(M^{-1})$	$K_{a2}/(M^{-1})$	$\Delta H_1 / (kJ \cdot mol^{-1})$	$\Delta H_2 / (kJ \cdot mol^{-1})$
3.951×10^6	4.637×10^5	-33.19	-9.830

2.4 The association constants of CHP with Q[8] and Q[7]

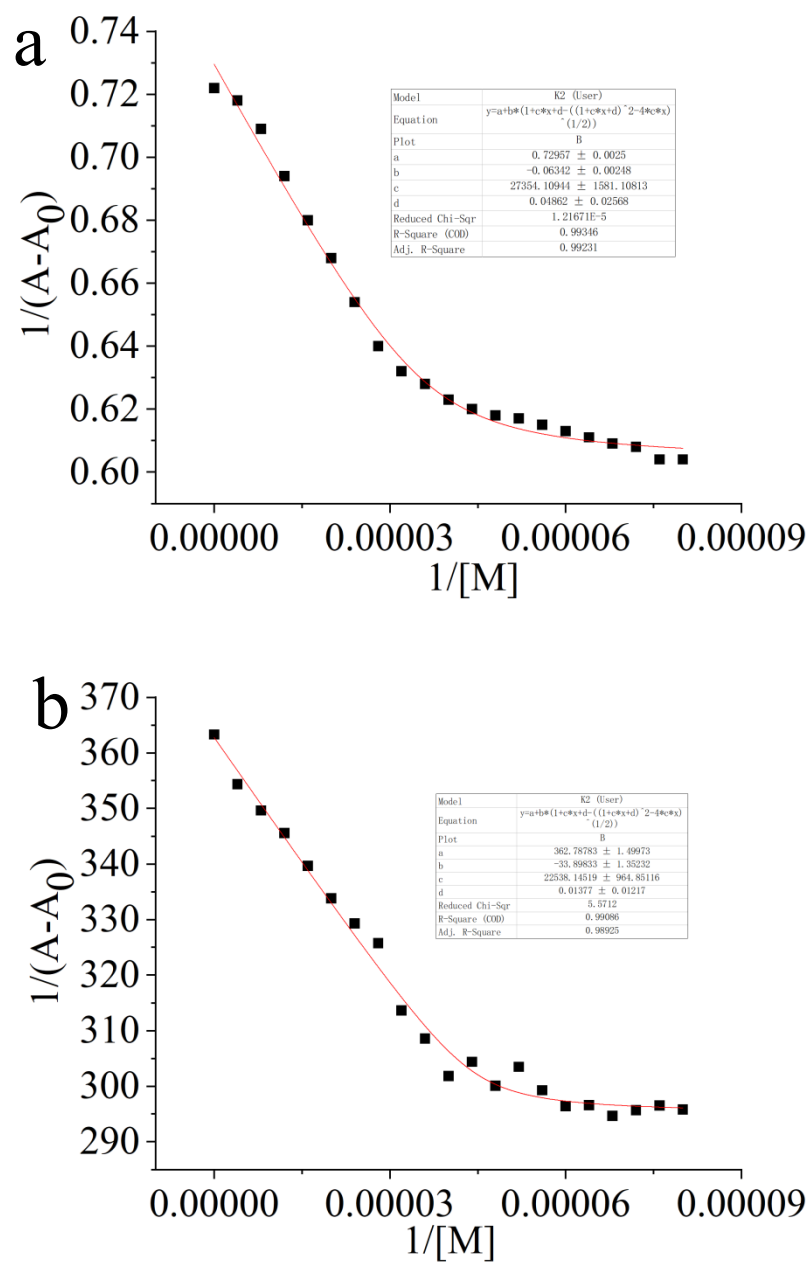


Figure S8. (a) The K_a of CHP with Q[7] by UV absorption spectra and (b) Fluorescence absorption spectra

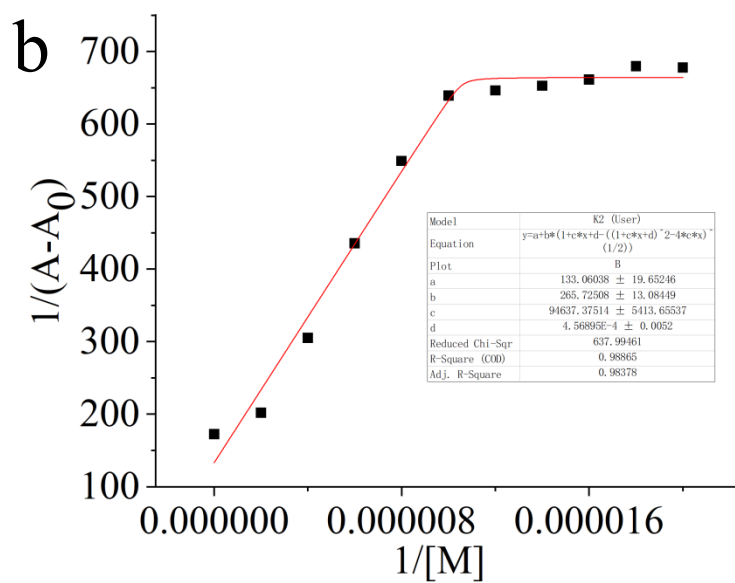
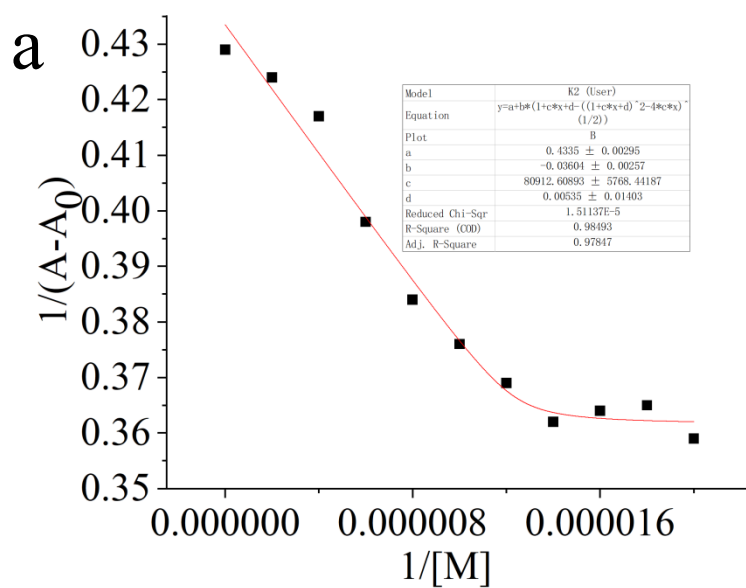


Figure S9. (a)The K_a of CHP with Q[8] by UV absorption spectra and (b) Fluorescence absorption spectra.

3. Interaction between CHP and Q[7]

3.1 COSY NMR spectra of Q[7]-CHP

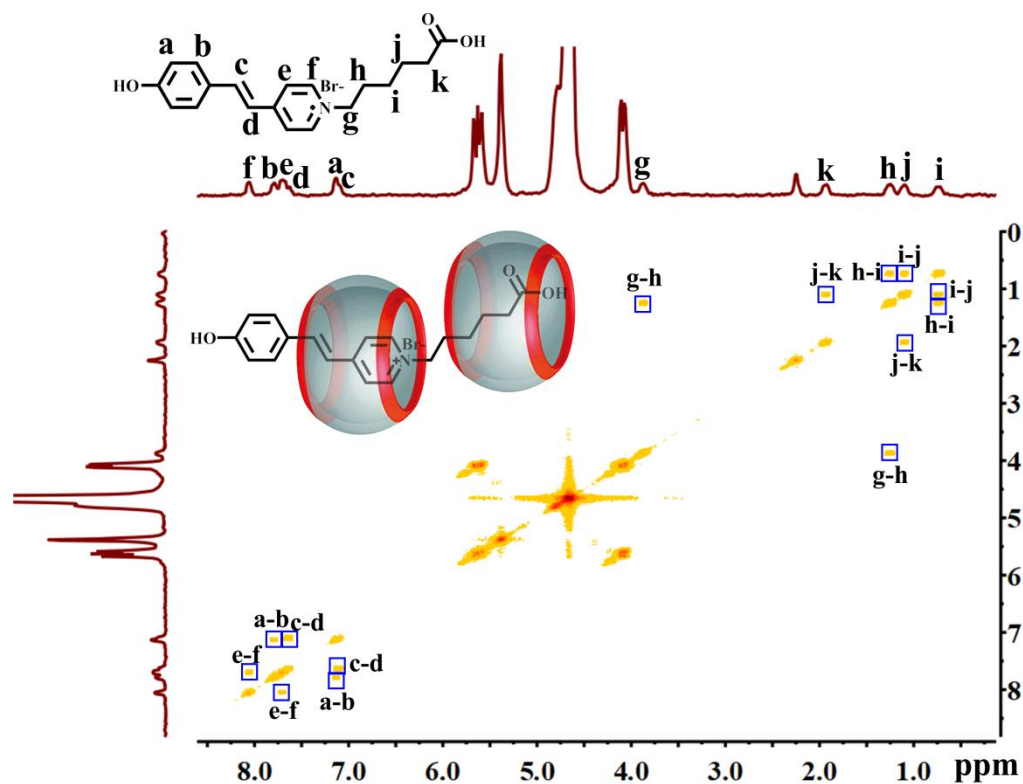


Figure S10. COSY NMR spectra of Q[7]-CHP in D₂O (400 MHz).

3.2 UV absorption spectra

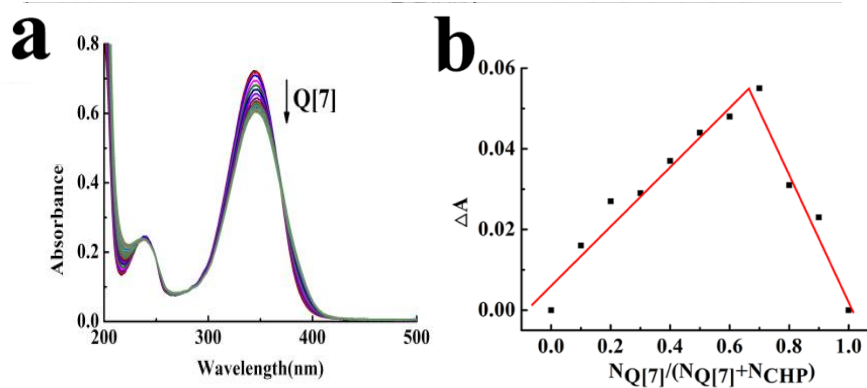


Figure S11. (a) Relationship between absorbance and $N_{Q[7]}/N_{CHP}$; (b) Corresponding curve of $\Delta A - N_{Q[7]}/(N_{Q[7]}+N_{CHP})$.

3.3 Fluorescence spectroscopy

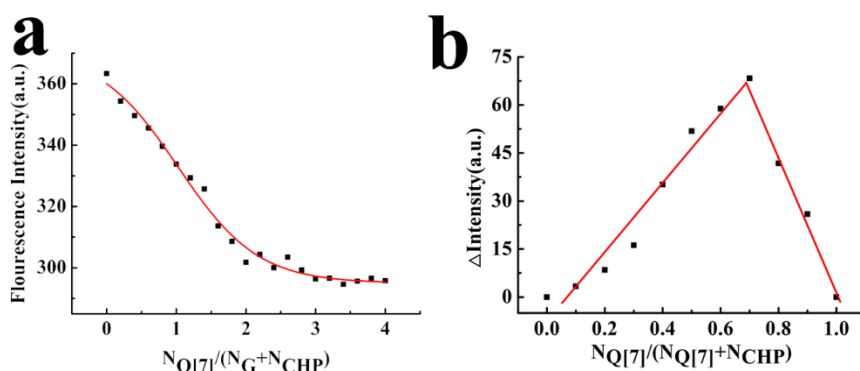


Figure S12. (a) Relationship between fluorescence intensity and $N_{Q[7]}/N_{CHP}$; (b) Corresponding curve of $\Delta A-N_{Q[7]}/(N_{Q[7]}+N_{CHP})$.

3.4 The Isothermal titration calorimetry experiment

The first binding constant K_{a1} and the second binding constant K_{a2} are obtained by fitting the ITC curve using a sequential binding model.

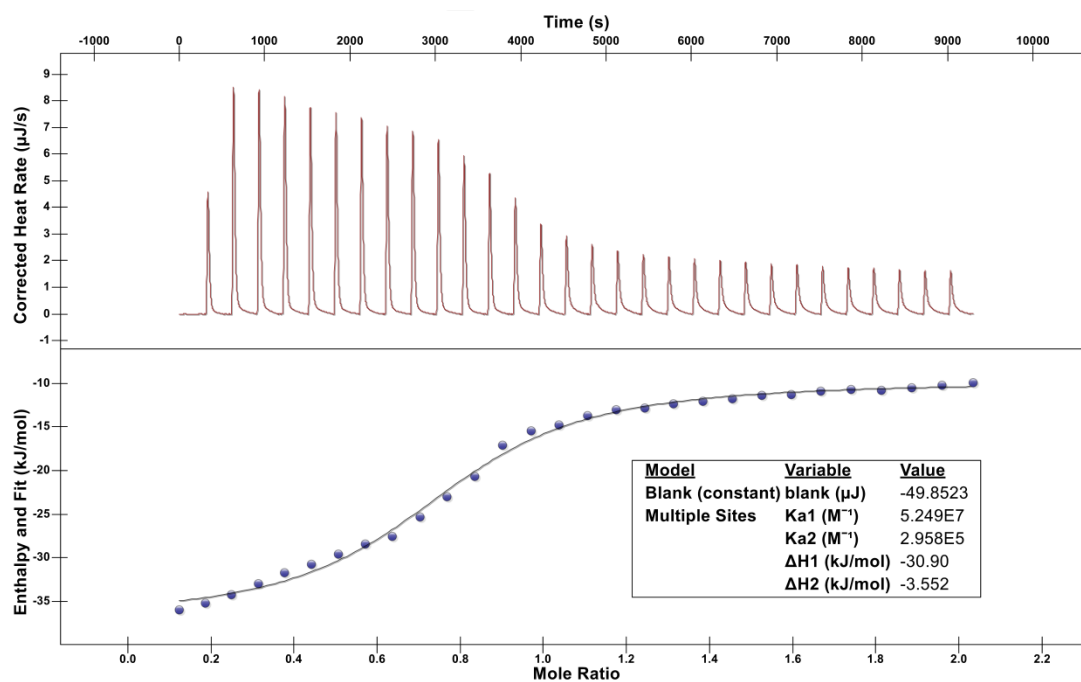


Figure S13. Isothermal titration calorimetry profiles of Q[7] in the presence of the guest CHP in aqueous solution at 298.15 K.

Table S2. ITC data of CHP@Q[7]

$K_{a1}/(M^{-1})$	$K_{a2}/(M^{-1})$	$\Delta H_1 / (kJ \cdot mol^{-1})$	$\Delta H_2 / (kJ \cdot mol^{-1})$
5.249×10^7	2.958×10^5	-30.9	-3.552

3.5 COSY NMR spectra of Q[7]-(*cis*-CHP)

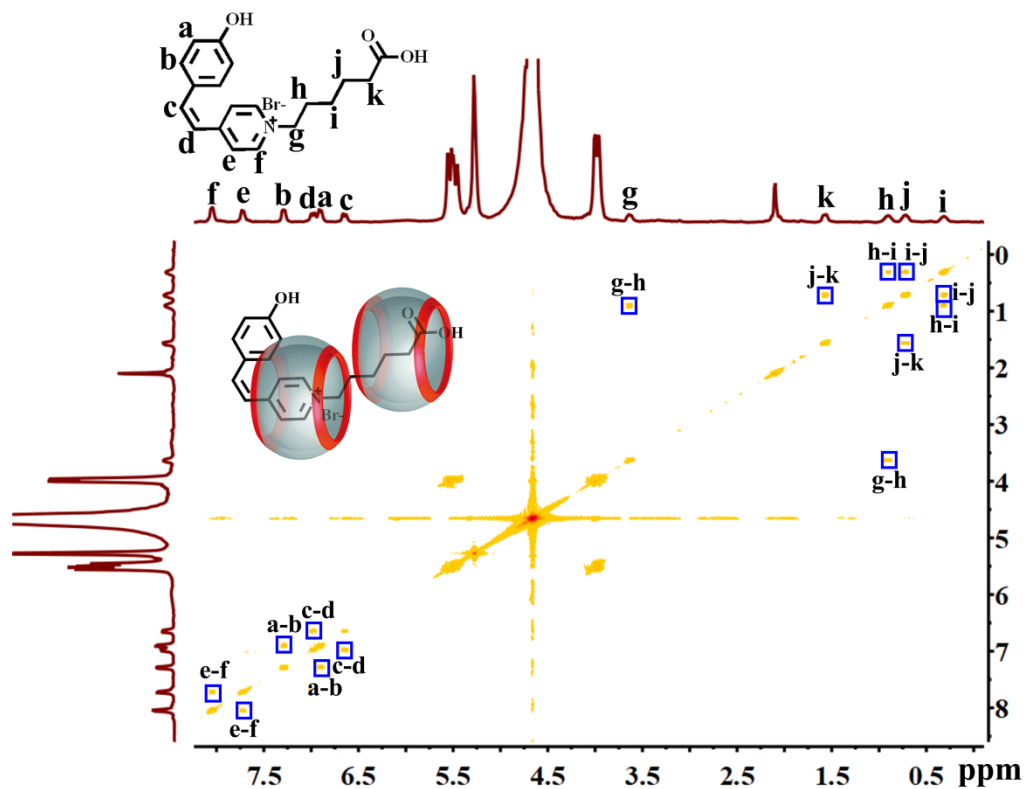


Figure S14. COSY NMR spectra of Q[7]-(*cis*-CHP) in D₂O (400 MHz).

4. Photochemical reaction of CHP

4.1 Photodimerization of CHP catalyzed by Q[8]

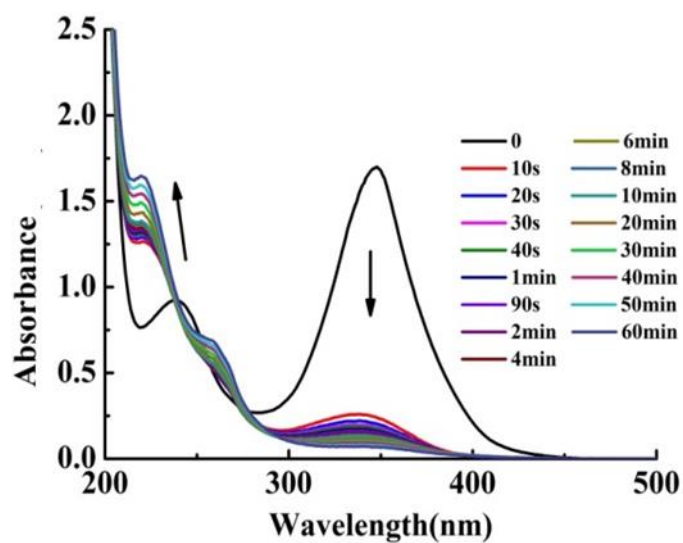


Figure S15. UV-Vis spectra of CHP solution (1×10^{-4} mol/L) with UV irradiation in the presence of Q[8].

4.2 Photodimerization of CHP inhibited by Q[7]

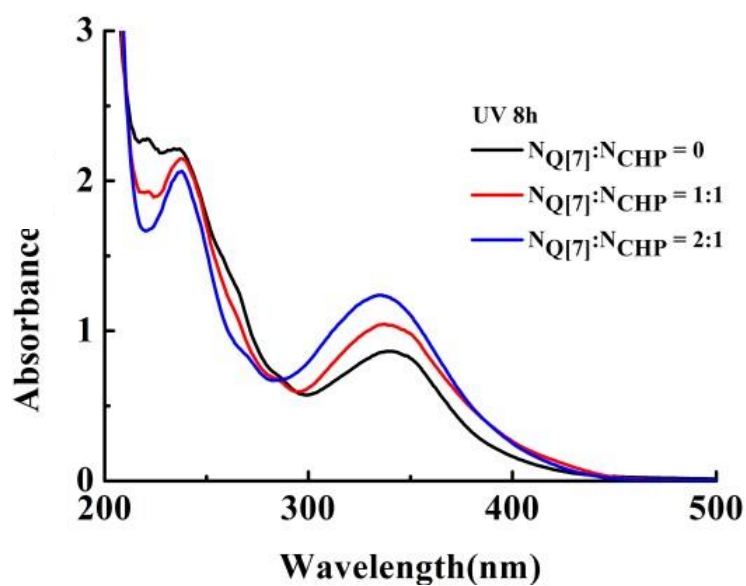


Figure S16. UV-visible spectra of CHP solutions (1×10^{-4} mol/L) with different Q[7] contents after 8h of UV irradiation.

5. Analysis of the competitive effect of Q[7] and Q[8] in the presence of CHP

5.1 ^1H NMR spectrum

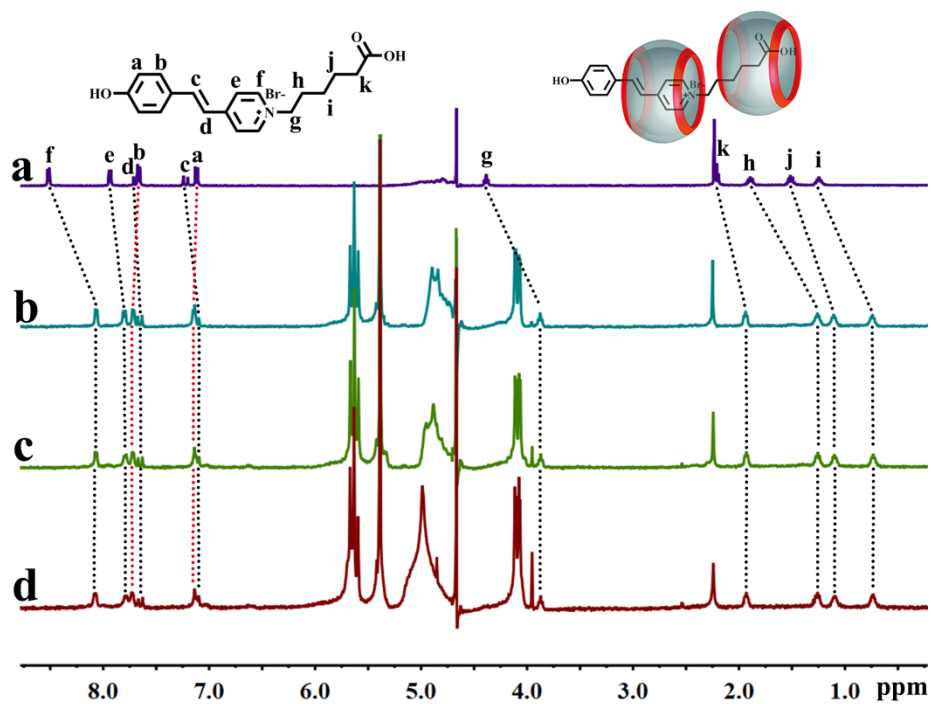


Figure S17. ^1H NMR spectrum (400MHz, D_2O) of (a) the guest CHP (1.0×10^{-3} mol/L); (b) Q[7]-CHP; (c) on adding 0.5 equivalent of Q[8]; (d) on adding 1.0 equivalent of Q[8].

5.2 The fluorescence spectroscopy

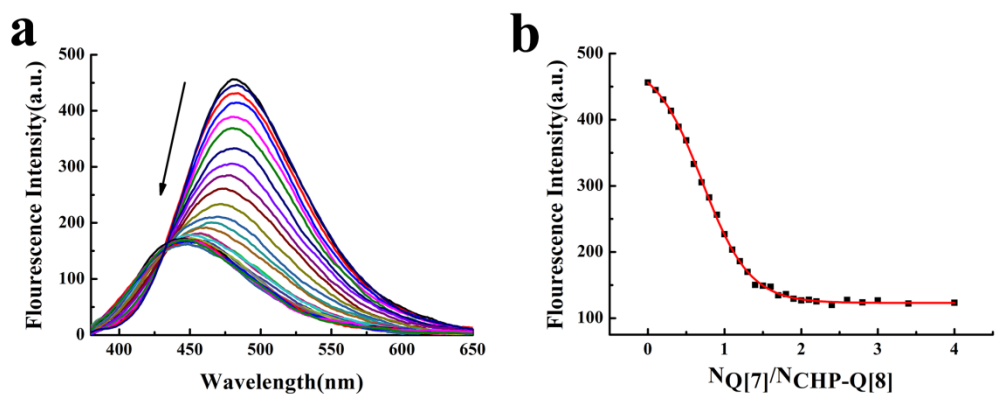


Figure S18. (a) Fluorescence spectra of Q[8]-CHP (2.0×10^{-5} mol/L) on adding increased amounts of Q[7] (0, 0.1, 0.2... 4.0 equivalents); (b) Relationship between concentration and fluorescence emission and $N_{Q[7]} / N_{CHP+Q[8]}$.

6. Comparison of fluorescence intensity

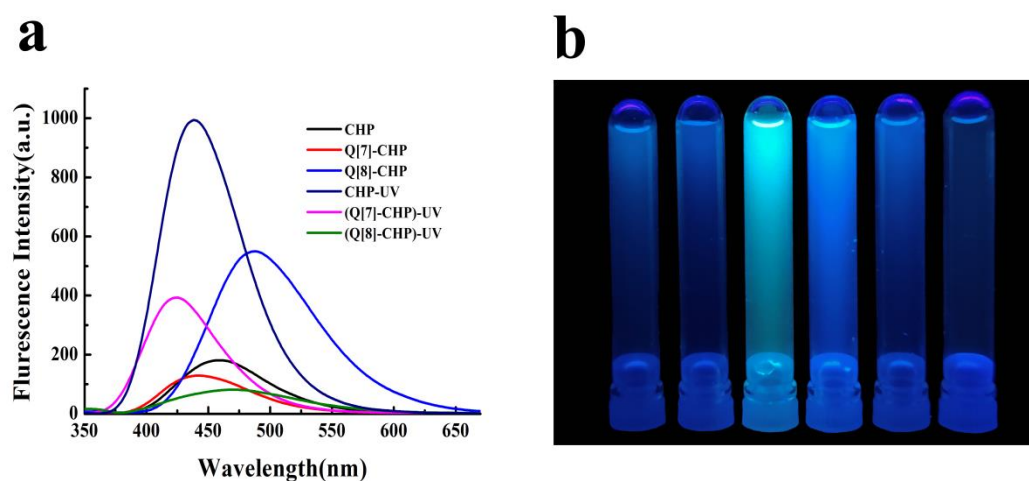


Figure S19. (a) Fluorescence spectra of CHP, CHP-Q[7], CHP-Q[8] after 8 hours of irradiation; (b) Photos under 365 nm ultraviolet light.

7. pKa of CHP

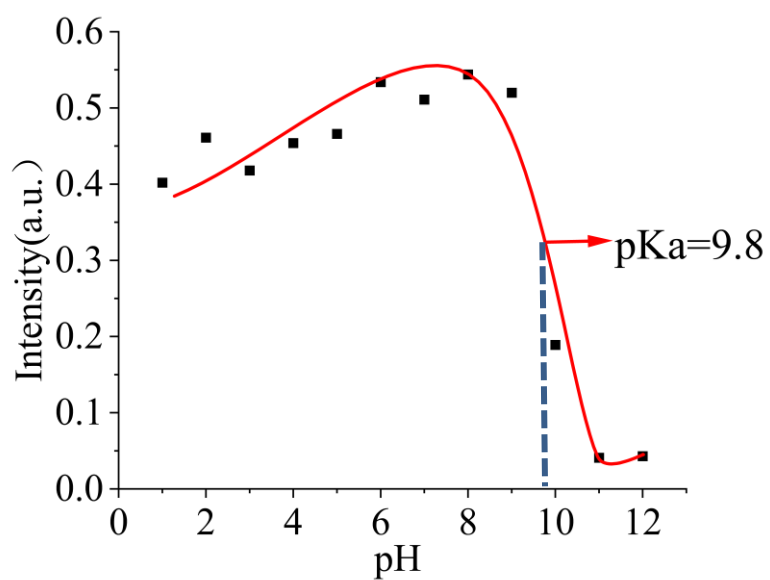


Figure S20. The pKa of CHP ($2 \times 10^{-5} \text{ mol/L}^{-1}$) in aqueous solution.

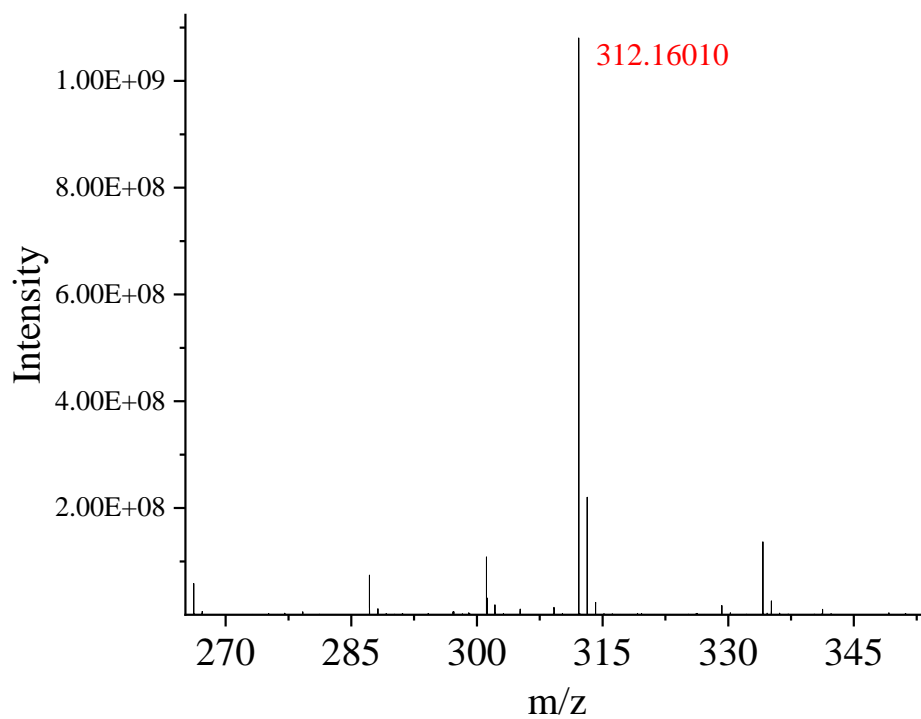


Figure S21. The HRMS spectrum of CHP.