

Electronic Supplementary Information

CB[8] gated photochromism of a diarylethene derivative containing thiazole orange groups

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1. Materials and general method

All starting materials were obtained from commercial suppliers and were used as received. CB[8] (25 mg, 99%+) was purchased from Strem Chemicals, Inc. 2-Methyl thiophene and methyl iodide were supplied from Sinopharm Chemical Reagent Co. Ltd., Shanghai. 2-Methyl benzothiazole and 4-cholorquinoline were obtained from TCI.

2. Physical measurements and instrumentation

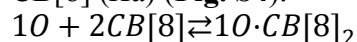
^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL instrument (JEOL, Japan). Proton chemical shifts are reported in parts per million down field from tetramethylsilane (TMS). ESI-MS data were recorded on a Micro TOFII 10257 Instrument (Bruker Daltonics Inc., Germany). UV-visible absorption spectra were recorded on a Shimadzu UV-2250 spectrophotometer. Fluorescence spectra were recorded on an Edinburgh FLS5 spectrophotometer (Germany). The HPLC (High Performance Liquid Chromatography) was conducted on Autopurification LC-MS system (Waters, America). The photo cyclization process of **1** was performed by UV light, generated by a low pressure mercury lamp with 360 nm long wavelength pass filter. In the visible light induced ring open process, a 670 nm laser ($I = 0.8$ A) was used as light source. The optical filter was the band-pass from 530-543 nm.

3. The preparation of solution samples

The stock solution of **10** (5.0×10^{-4} M) was prepared in water with 2.5% DMSO. The stock solution of Cucurbit[8]uril (CB[8], 2.5×10^{-4} M) was prepared in water. The solution samples for spectral testing were prepared by diluting the stock solution with water.

4. Binding constant calculating method

The following equations (E. 1 and E. 2) was used for the nonlinear least squares analysis of the absorption to determine the association constant¹⁻³ between **10** and CB[8] (K_a) (Fig. S4).



$$K_a = \frac{[10 \cdot CB[8]_2]}{[10][CB[8]]^2} \quad (\text{E. 1})$$

Y

$$= Y_0 + \frac{(Y_{lim} - Y_0)}{2} \left\{ 1 + \frac{C_{10}}{C_{CB[8]}} + \frac{1}{K_a C_{CB[8]}} - \left[\left(1 + \frac{C_{10}}{C_{CB[8]}} + \frac{1}{K_a C_{CB[8]}} \right)^2 - \frac{4C_{10}}{C_{CB[8]}} \right]^{1/2} \right\} \quad (\text{E. 2})$$

Y was the recorded absorbance, Y_0 was the initial absorbance without adding CB[8]; Y_{lim} was the limiting value with sufficient CB[8]; $[10 \cdot CB[8]_2]$, $[10]$ and $[CB[8]]$ were the realistic concentration of the guest molecule CB[8], host molecule **10** and the binding complex $10 \cdot CB[8]_2$ respectively, C_{10} and $C_{CB[8]}$ were the added

concentration of **10** and CB[8], respectively.

5. Calculation method of the conversion yield and cyclization quantum yield of **10**·CB[8]

- (1) The photocyclization efficiency (α) of **10**·CB[8]₂ was calculated according to the HPLC result, which was showed in **Fig. S5**. The efficiency was calculated according to the integration of the area of peaks at different retention time. The efficiency $\alpha_{O \text{ to } C}$ of **10**·CB[8]₂ with irradiation of 365 nm was estimated as 40.2% and the reversed efficiency $\alpha_{C \text{ to } O}$ was 96.9%.
- (2) Cyclization quantum yield of **10**·CB[8]₂ was calculated according to the absorbance change at 385 nm before and after UV light irradiation.^{4,5}

6. Additional data

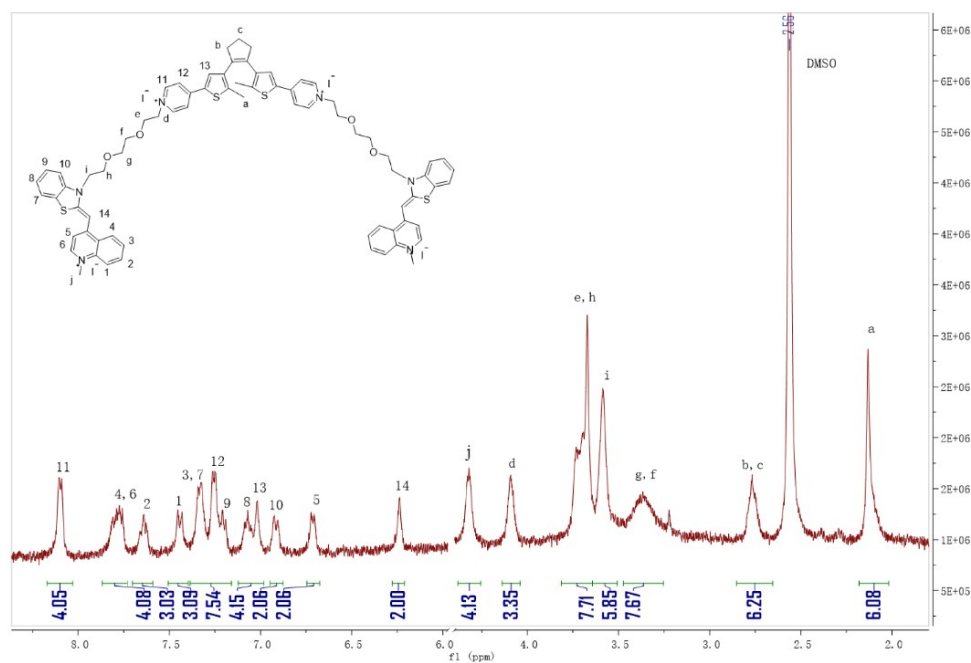


Fig. S1 ¹H NMR spectrum of **10** in d₆-DMSO/D₂O (10% of DMSO in volume).

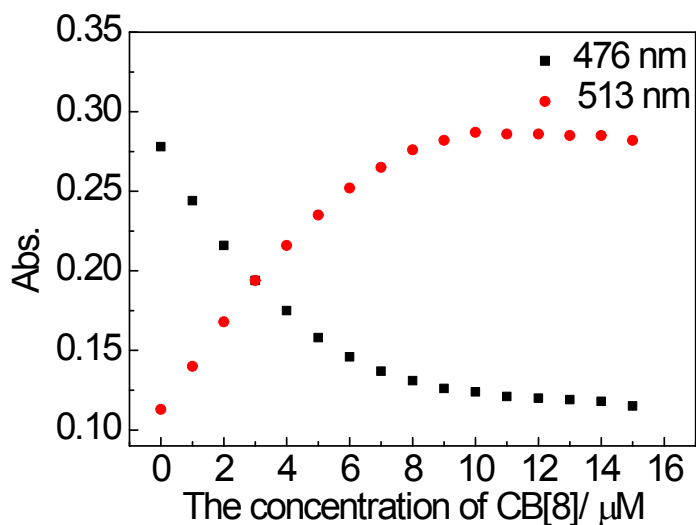


Fig. S2 The changes of absorbance at 476 and 413 nm of **10** ($5\mu\text{M}$) with addition of different concentration of CB[8].

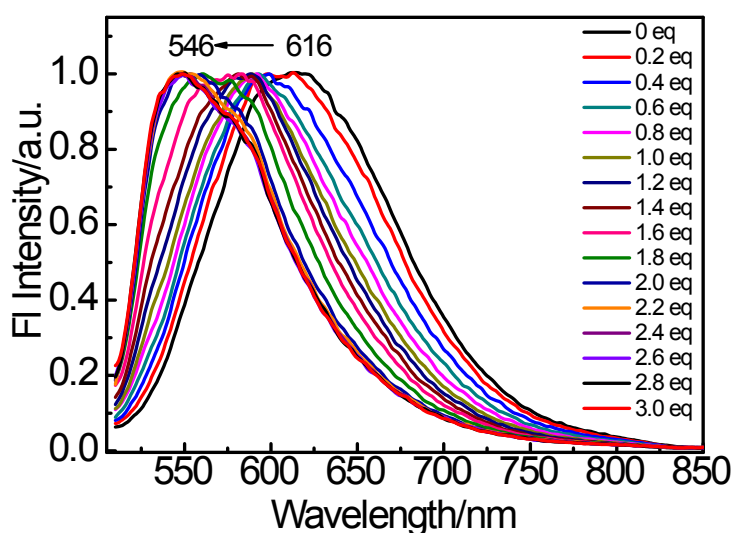


Fig. S3 The fluorescent spectra of **10** ($5\mu\text{M}$) with addition of different concentration of CB[8].

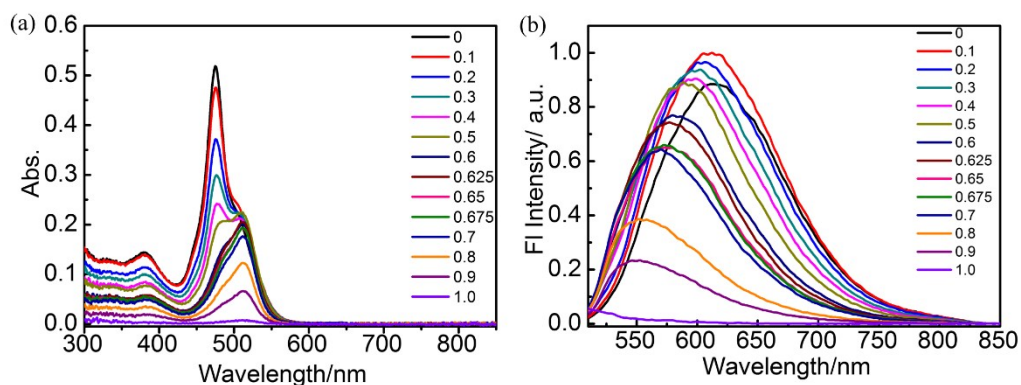


Fig. S4 (a) The absorption and (b) fluorescent spectra of the mixture solution of **10** and CB[8] with different molar ratio. The total concentration of **10** + CB[8] = 15 μM , while The concentration of CB[8] ranged from 0 to 15 μM .

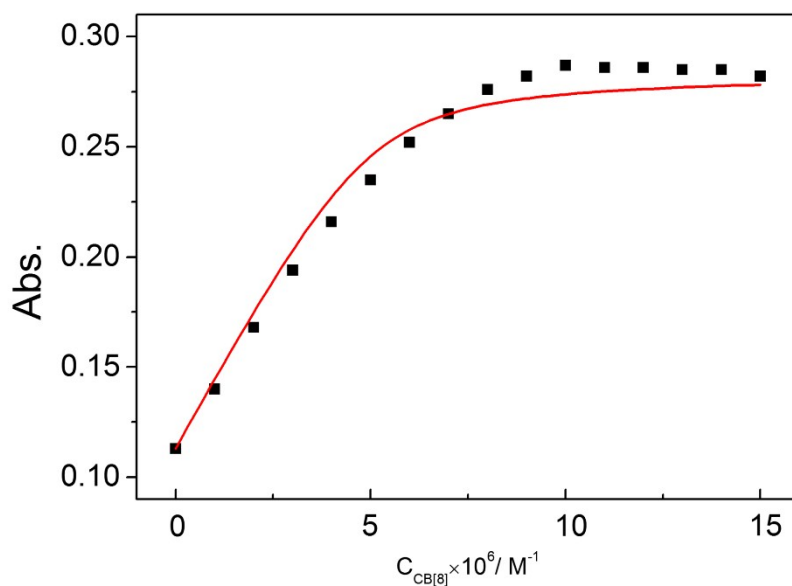


Fig. S5 The change of the absorbance at 513 nm of **10** with different concentration of CB[8] which was used for determination of association constant. The nonlinear least squares analysis (red line) gives $K_a = 3.36 (\pm 0.75) \times 10^6 \text{ L}^2\text{mol}^{-2}$ ($R^2 = 0.97847$).

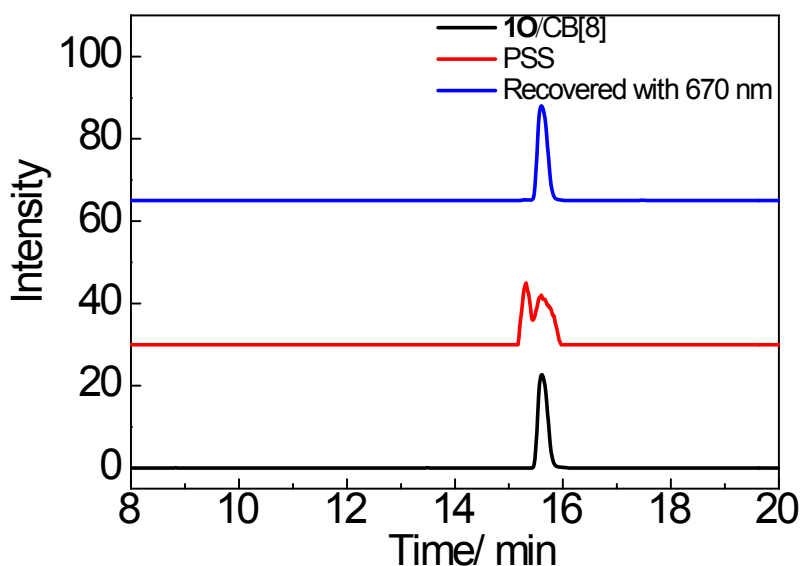


Fig. S6 HPLC of **10**·CB[8]₂ (black line), at PSS after 365 nm irradiation (red line) and recovered state after 670 nm irradiation (blue line).

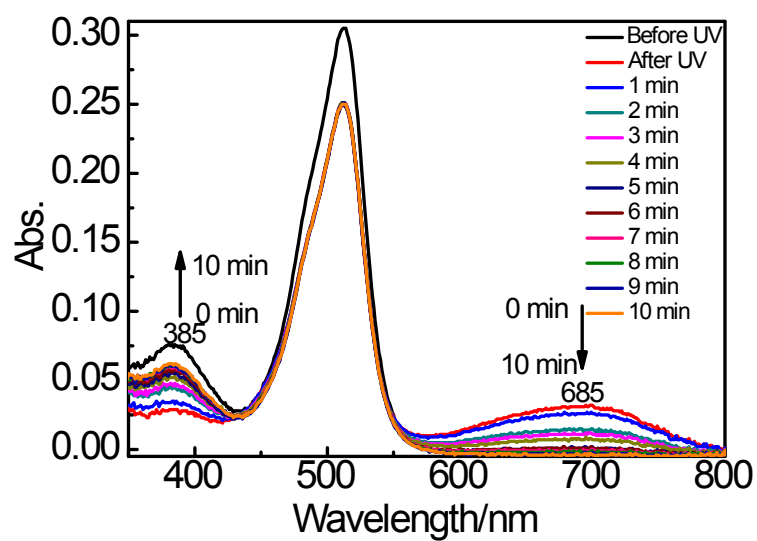


Fig. S7 The absorption spectra of $1 \cdot \text{CB}[8]_2$ at PSS with irradiation of 670 nm from 0 - 10 min

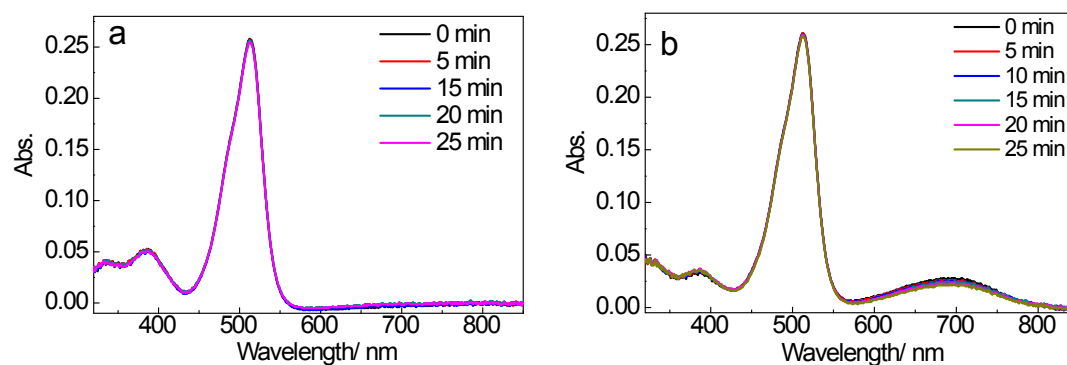


Fig. S8 The absorption changes of $10 \cdot \text{CB}[8]_2$ (a) and $1\text{C} \cdot \text{CB}[8]_2$ (b) with irradiation of 515 nm light.

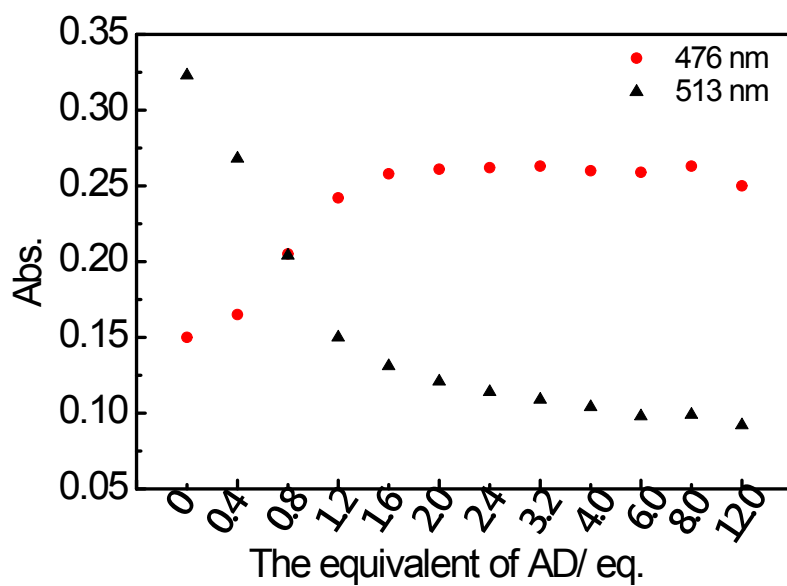


Fig. S9 The absorption changes of $10 \cdot \text{CB}[8]_2$ ($5 \mu\text{M}$) at wavelengths of 476 and 513 nm with addition of different concentration of AD.

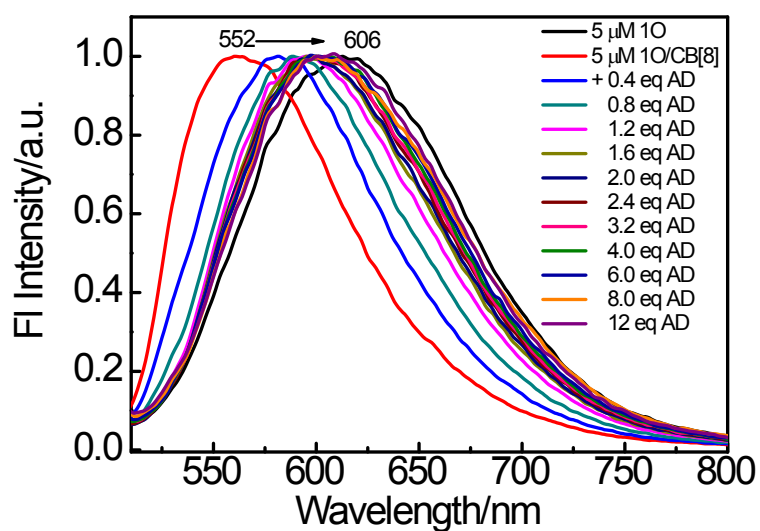


Fig. S10 The fluorescent spectra of $10 \cdot \text{CB}[8]_2$ with addition of different concentration of AD.

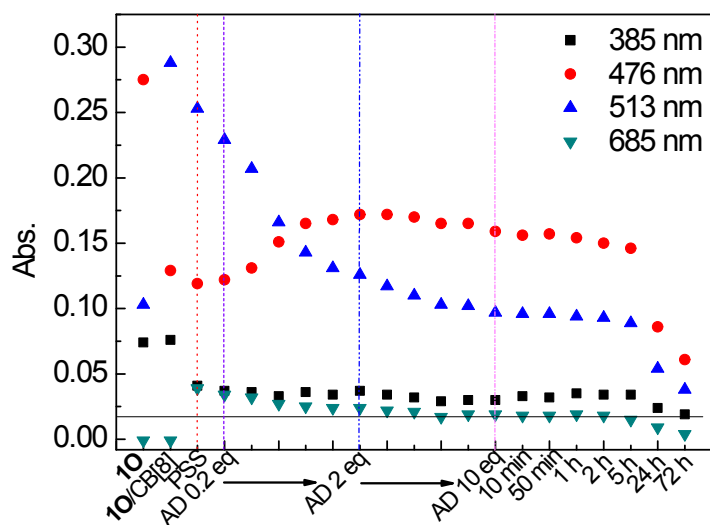


Fig. S11 The absorbance changes at different wavelengths at different processes including **10** to **10·CB[8]₂** to PSS, addition of AD from 0 – 10 eq, rest as room temperature from 0 to 72 h in dark.

7. References

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