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

^{1}H 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 **1O** (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 constant[1-3] between **1O** and CB[8] (*K*a) (**Fig. S4**).

$$1O + 2CB[8] \rightleftarrows 1O{\cdot}CB[8]_2$$

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

$$Y = Y_0 + \frac{(Y_{lim} - Y_0)}{2}\left\{1 + \frac{C_{1o}}{C_{CB[8]}} + \frac{1}{K_a C_{CB[8]}} - \left[(1 + \frac{C_{1O}}{C_{CB[8]}} + \frac{1}{K_a C_{CB[8]}})^2 - \frac{4C_{1O}}{C_{CB[8}\right.\right.$$

(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]; [**1O**·CB[8]$_2$], [**1O**] and [CB[8]] were the realistic concentration of the guest molecule CB[8], host molecule **1O** and the binding complex **1O**·CB[8]$_2$ respectively, $C_{\mathbf{1O}}$ and $C_{\mathrm{CB[8]}}$ were the added

concentration of **1O** and CB[8], respectively.

5. Calculation method of the conversion yield and cyclization quantum yield of 1O·CB[8]

(1) The photocyclization efficiency (α) of **1O·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 $\alpha_{O\ to\ C}$ of **1O·CB[8]$_2$** with irradiation of 365 nm was estimated as 40.2% and the reversed efficiency $\alpha_{C\ to\ O}$ was 96.9%.

(2) Cyclization quantum yield of **1O·CB[8]$_2$** was calculated according to the absorbance change at 385 nm before and after UV light irradiation. [4, 5]

6. Additional data

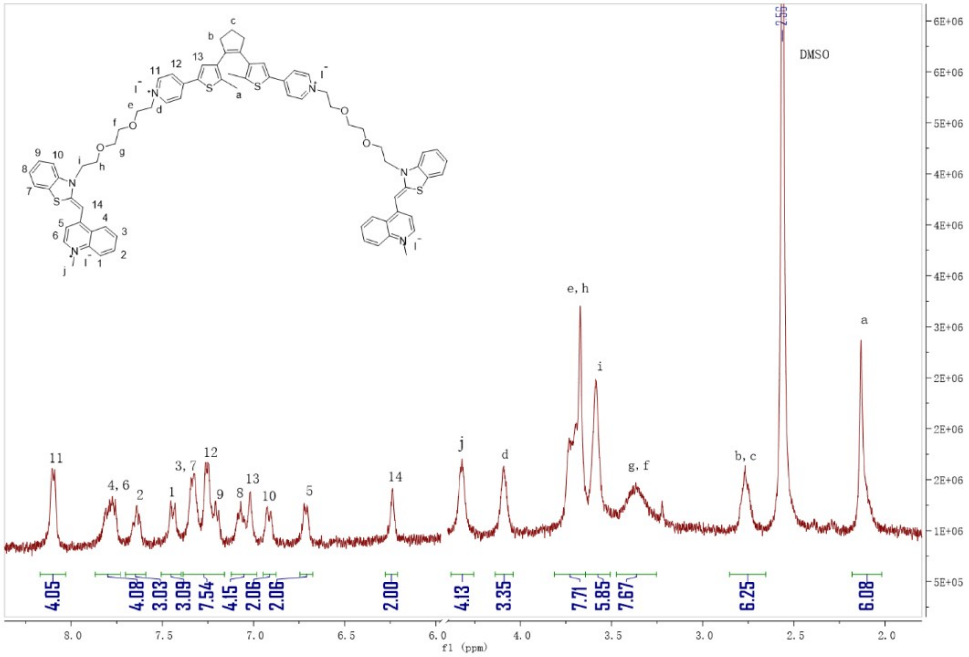

Fig. S1 ^{1}HNMR spectrum of **1O** in d_6-DMSO/D_2O (10% of DMSO in volume).

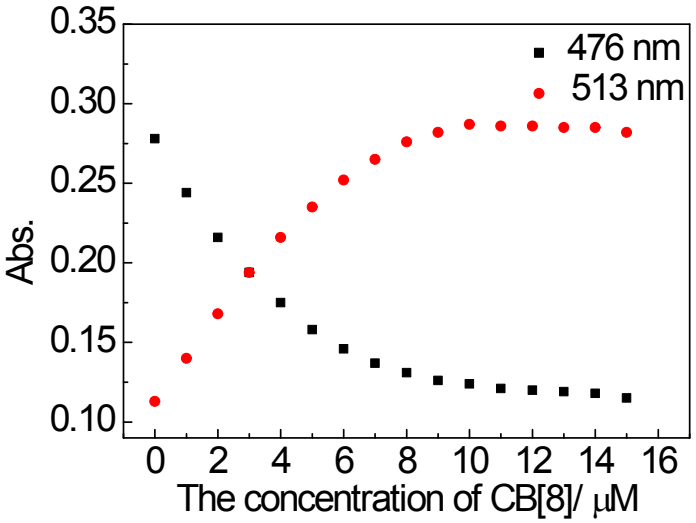

Fig. S2 The changes of absorbance at 476 and 413 nm of **1O** (5μM) with addition of different concentration of CB[8].

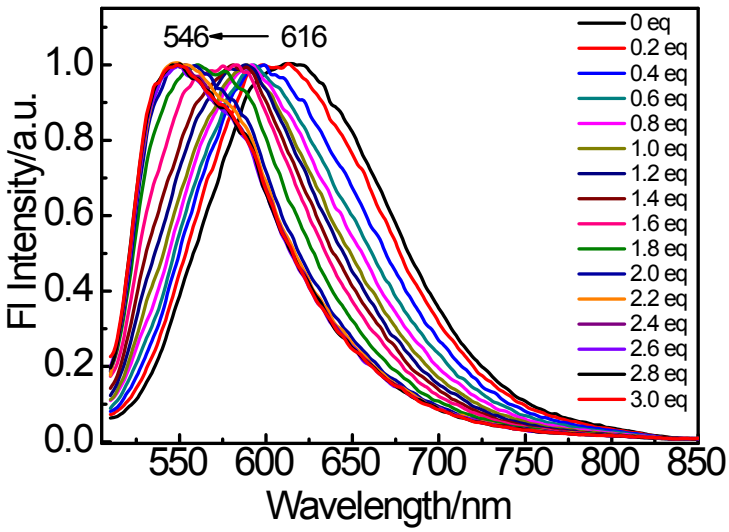

Fig. S3 The fluorescent spectra of **1O** (5μM) with addition of different concentration of CB[8].

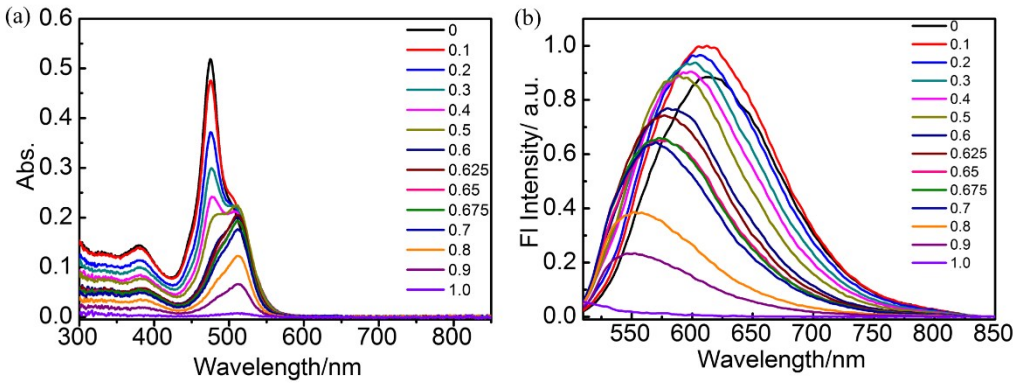

Fig. S4 (a) The absorption and (b) fluorescent spectra of the mixture solution of **1O** and CB[8] with different molar ratio. The total concentration of **1O** + CB[8] = 15 μM, while The concentration of CB[8] ranged from 0 to 15 μM.

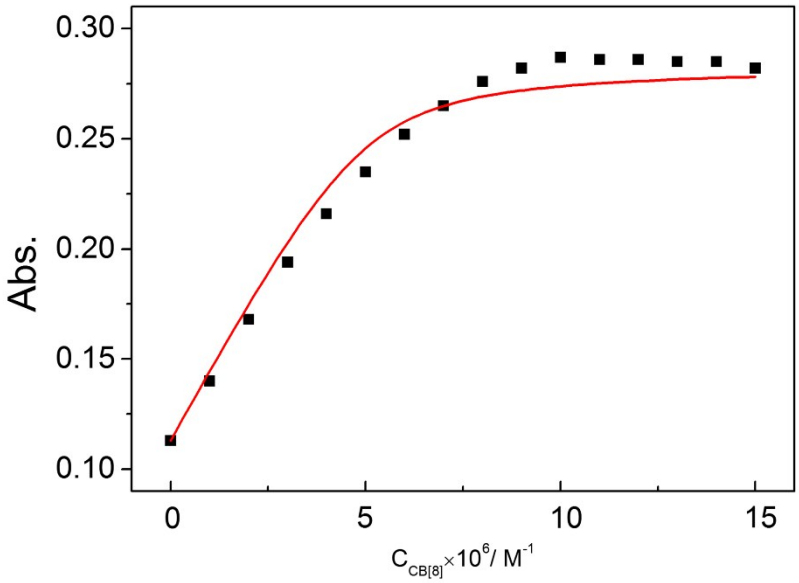

Fig. S5 The change of the absorbance at 513 nm of **1O** with different concentration of CB[8] which was used for determination of association constant. The nonlinear least squares analysis (red line) gives *K*a = 3.36 (±0.75) × 10^6 L^2mol^{-2} (R^2 = 0.97847).

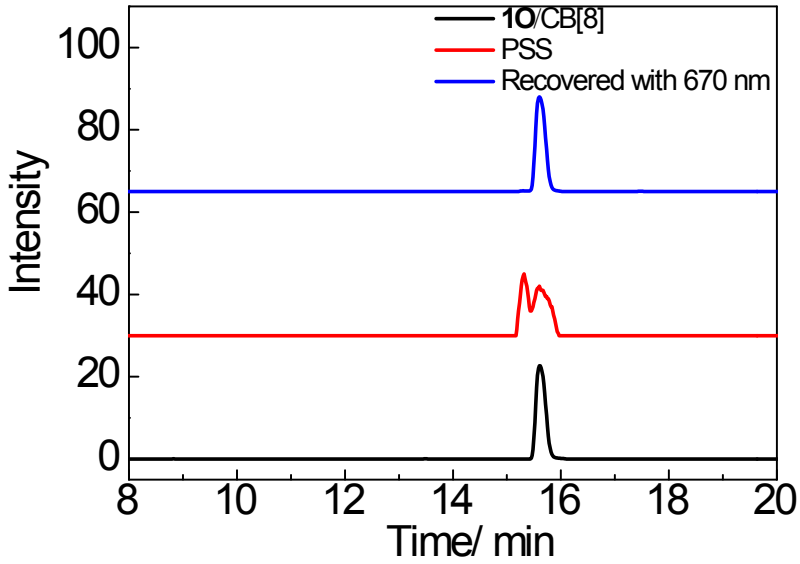

Fig. S6 HPLC of **1O·CB[8]$_2$** (black line), at PSS after 365 nm irradiation (red line) and recovered state after 670 nm irradiation (blue line).

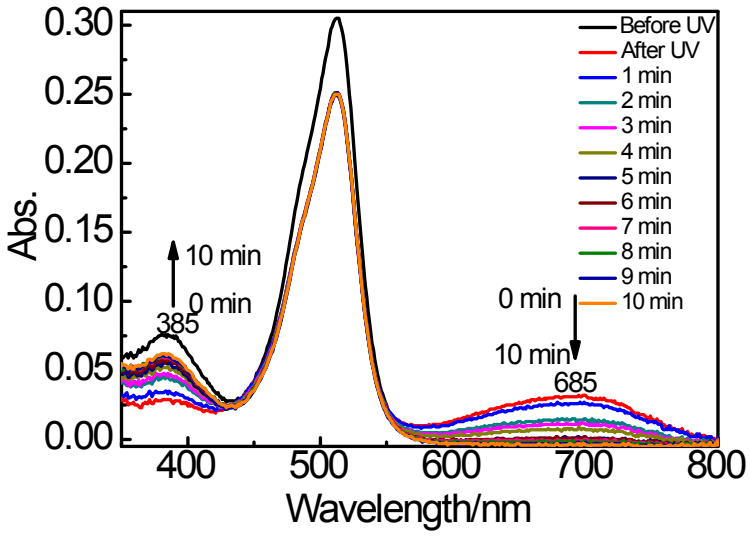

Fig. S7 The absorption spectra of **1·CB[8]$_2$** at PSS with irradiation of 670 nm from 0 - 10 min

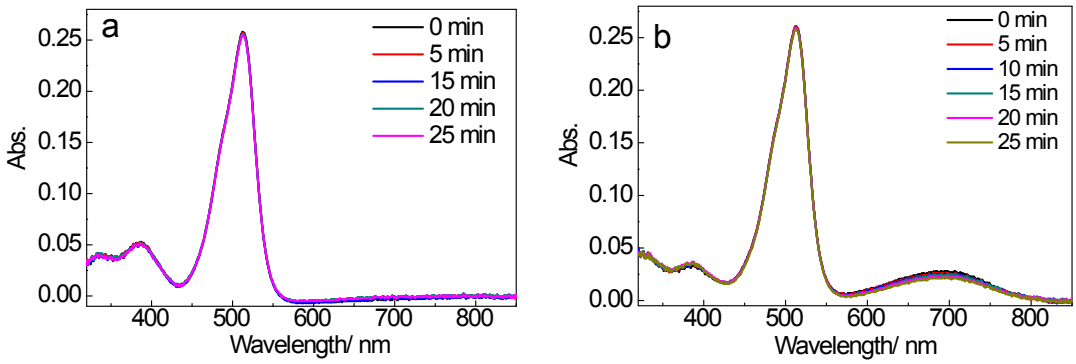

Fig. S8 The absorption changes of **1O**·CB[8]$_2$ (a) and **1C**·CB[8]$_2$ (b) with irradiation of 515 nm light.

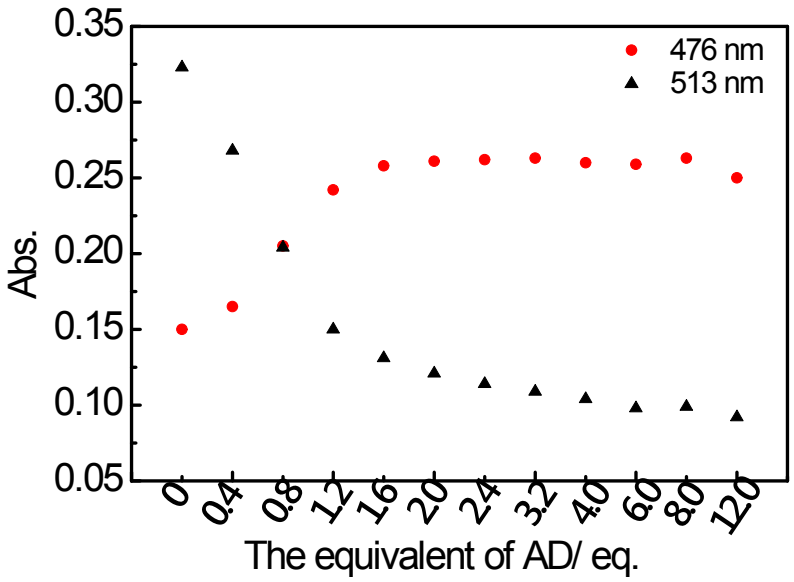

Fig. S9 The absorption changes of **1O·CB[8]$_2$** (5 μM) at wavelengths of 476 and 513 nm with addition of different concentration of AD.

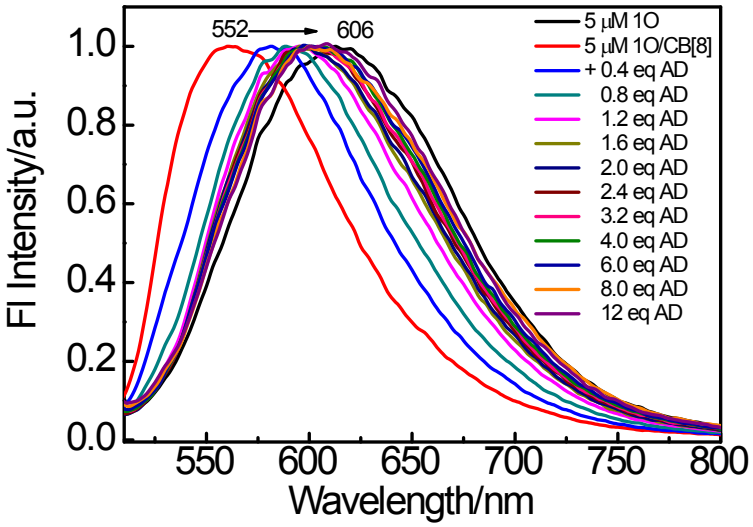

Fig. S10 The fluorescent spectra of **1O·CB[8]$_2$** with addition of different concentration of AD.

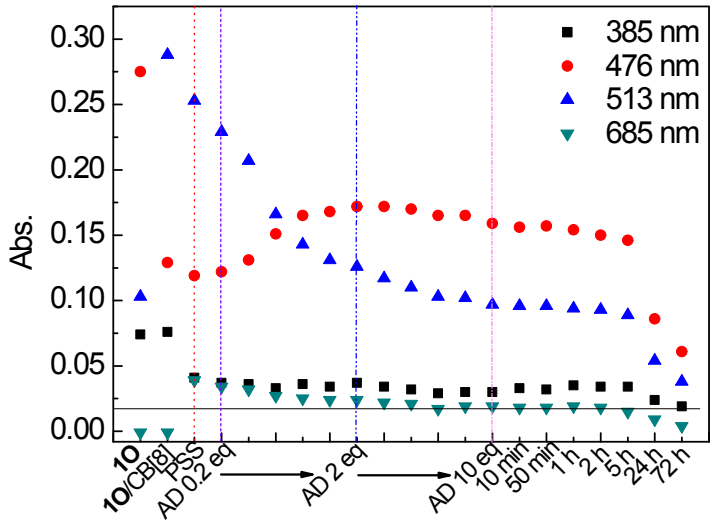

Fig. S11 The absorbance changes at different wavelengths at different processes including **1O** to **1O·CB[8]$_2$** to PSS, addition of AD from 0 – 10 eq, rest as room temperature from 0 to 72 h in dark.

7. References

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