

*Electronic Supplementary Information*

**Aggregation-mediated photochromic luminescence of cyano-stilbene based cruciform AIEgens**

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## 1. General materials

**Materials:** 2,2',7,7'-tetrabromo-9,9'-spirobi[fluorene], 4-acetylphenylboronic, 4-hydroxy - benzyl cyanide, 4-methoxyphenyl cyanide, 1-Bromododecane, K<sub>2</sub>CO<sub>3</sub>, NaOH, tetrahydrofuran, ethanol, tetrakis(triphenylphosphine)palladium, triphenylphosphine, toluene, triethylamine, dichloromethane, *n*-Hexane, ethyl acetate, and were all purchased from Energy Chemical (Shanghai, China). All these materials are analytical grade and used as received.

**Characterizations and instruments:** <sup>1</sup>H, <sup>13</sup>C NMR spectra, 2D <sup>1</sup>H-<sup>1</sup>H correlation spectroscopy (COSY), nuclear overhauser effect spectroscopy (NOESY) and heteronuclear singular quantum correlation (HSQC) were measured on a Bruker AVANCE III 400MHz, 500MHz or 600MHz spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS,  $\delta = 0$ ) as internal standard. High-resolution (HR) mass spectra were recorded on a Thermo Scientific Q-Exactive Focus (FTMS + p ESI) mass spectrometer. Absorption spectra were taken on a Thermo-fisher Evolution 220 spectrometer. Emission spectra were taken on a Thermo Lumina Fluorescent spectrometer. Powder XRD patterns were recorded on a RigakuSmartLab X-ray Diffractometer. Infrared spectroscopy (IR) were taken on a Fourier Transform Infrared Spectrometer Nicolet 6700. Gel permeation chromatography (GPC) were taken on a Waters e2695 Separations Module. Fluorescence photomicrograph were taken on a fluorescence microscope Leica DMI8.

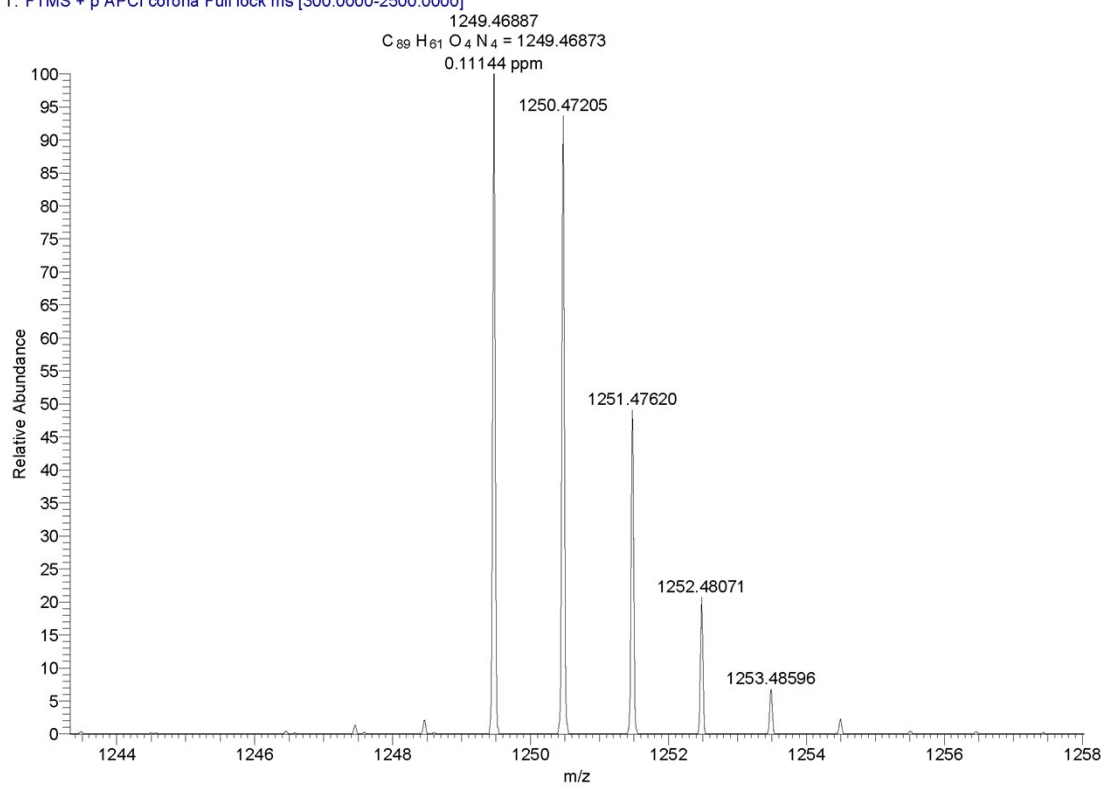
## 2. Structural characterization

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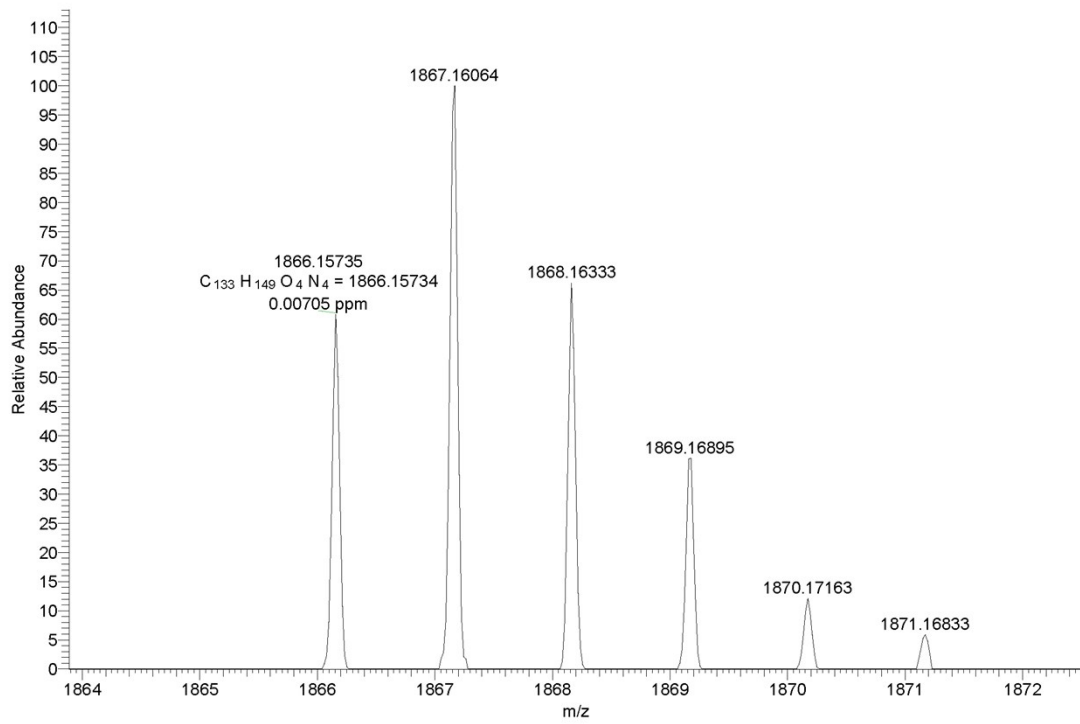
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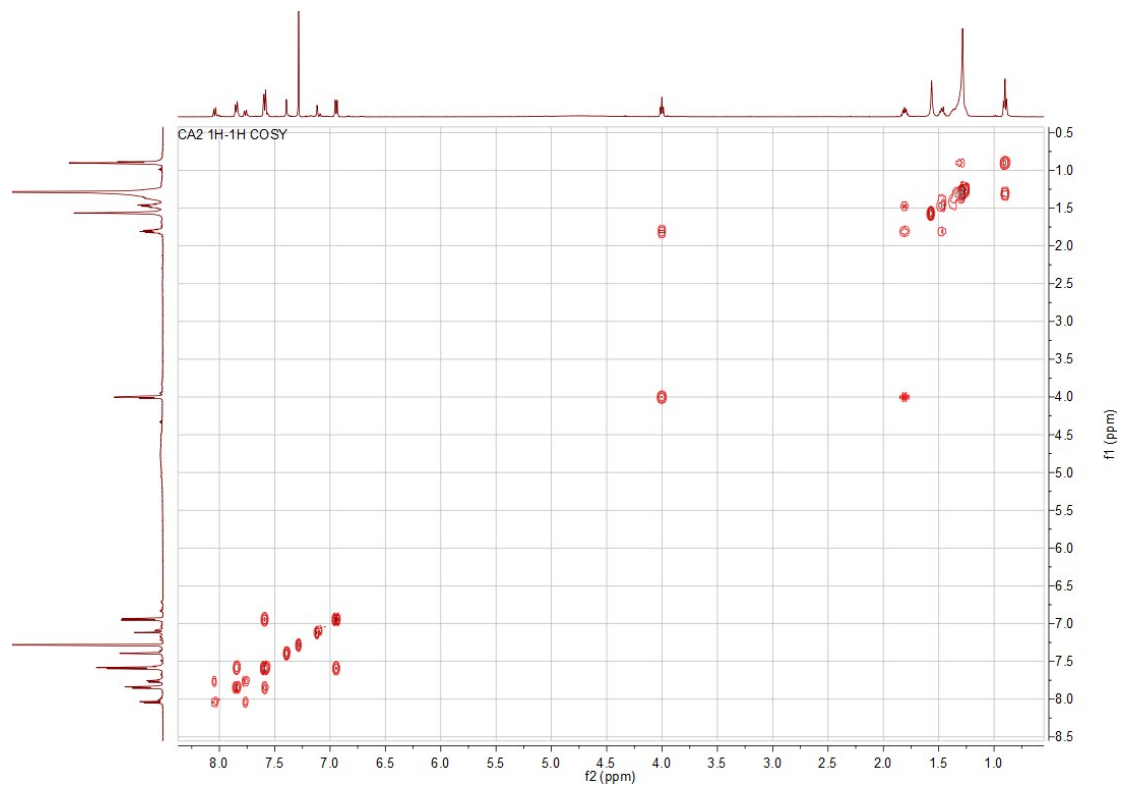


**Figure S1.** High-resolution (HR) mass spectrum of cruciform AIEgen CA1.

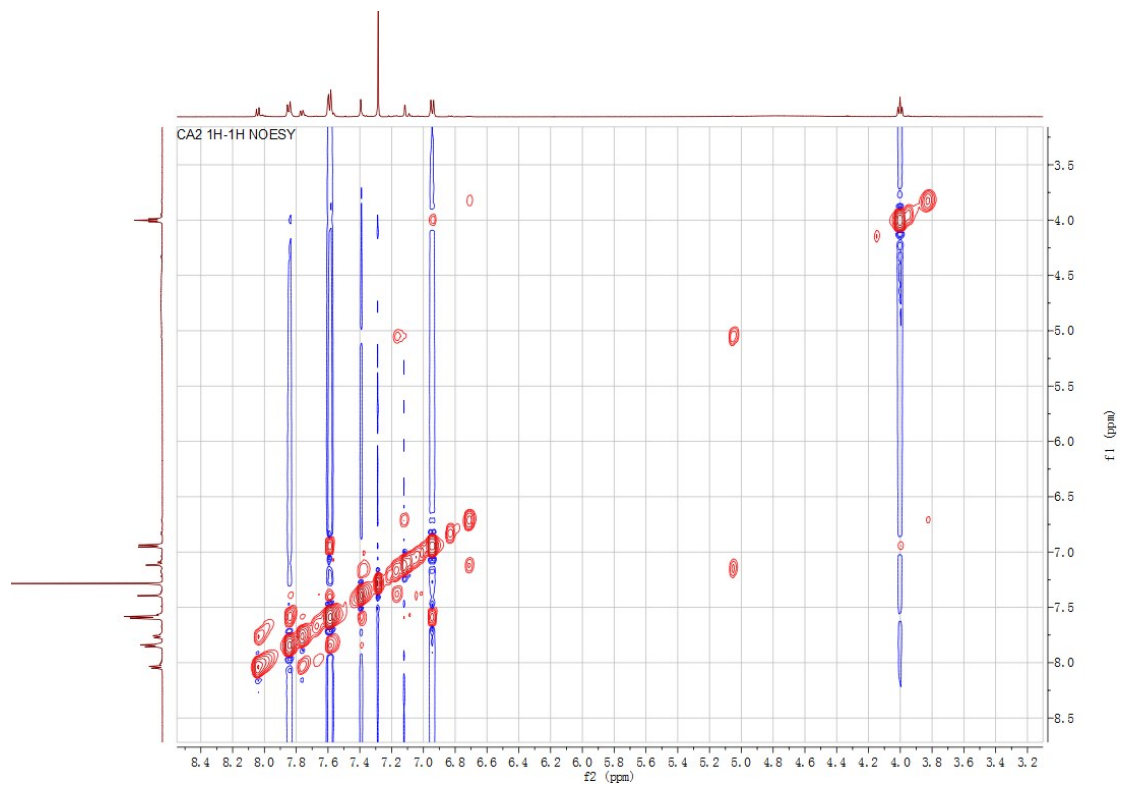
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**Figure S2.** High-resolution (HR) mass spectrum of cruciform AIEgen CA2.

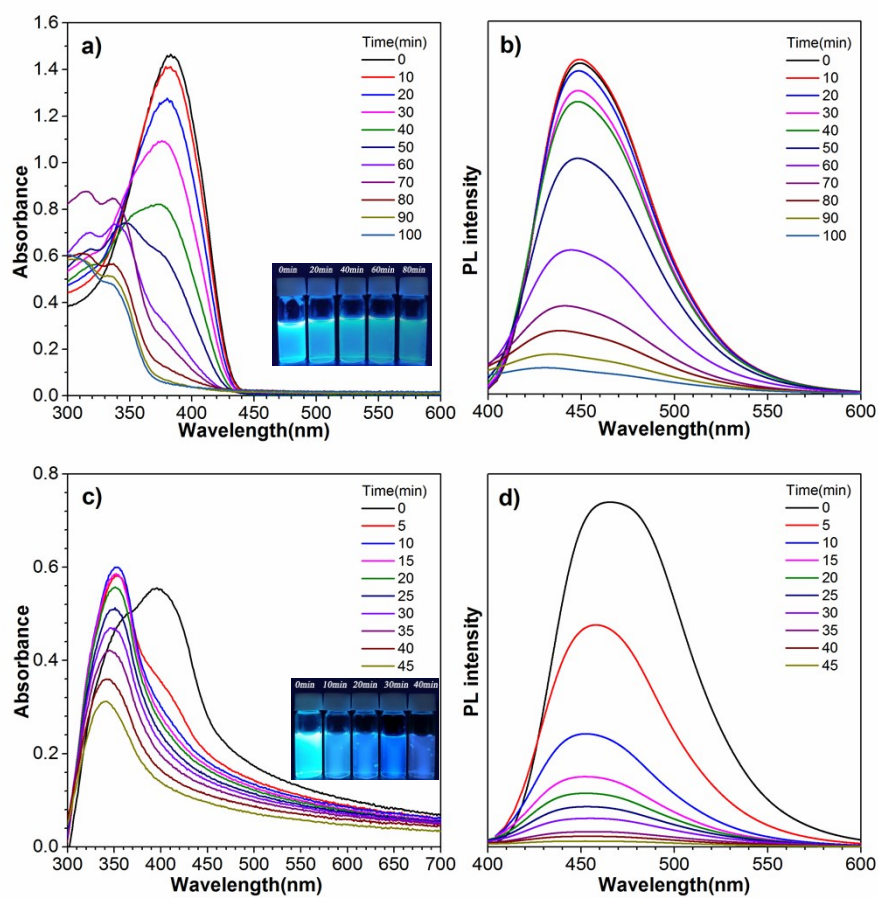


**Figure S3.** Partial 2D  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of CA2 in  $\text{CDCl}_3$ .

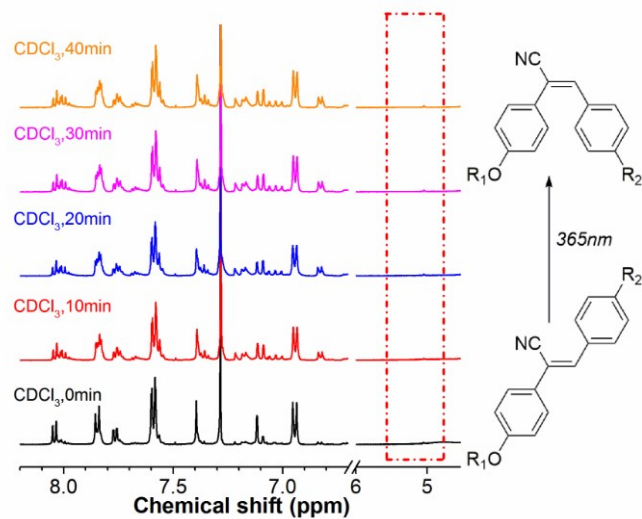


**Figure S4.** Partial 2D  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectrum of CA2 in  $\text{CDCl}_3$ .

### 3. Figures and charts

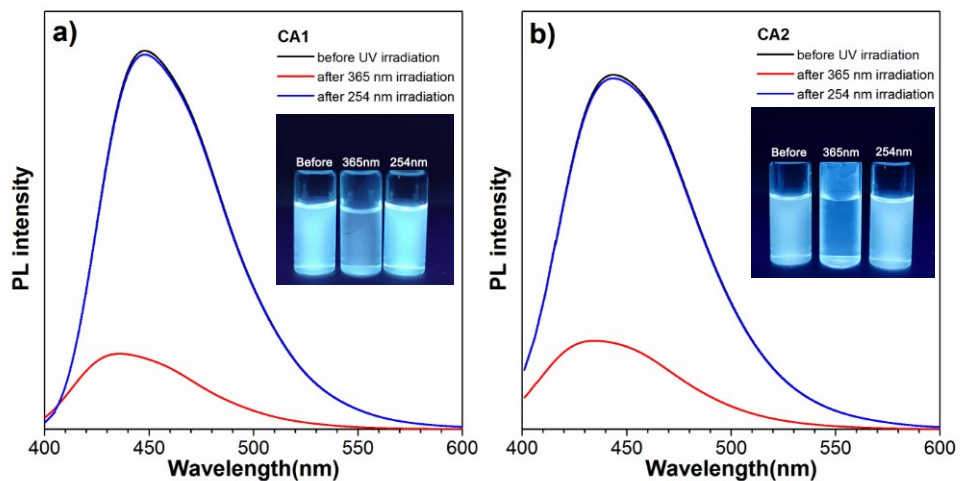


**Figure S5.** UV-Vis absorption and PL spectra of cruciform AIEgens CA2 in THF solution (a, b), and in THF/H<sub>2</sub>O mixture with  $f_W = 90\%$  (c, d) after irradiation with 365 nm UV light from a hand-held UV lamp for different time. Concentration = 10  $\mu\text{M}$ . Inset: photos of the sample in THF solution or nano-aggregates (at  $f_W = 90\%$ ) after UV irradiation.

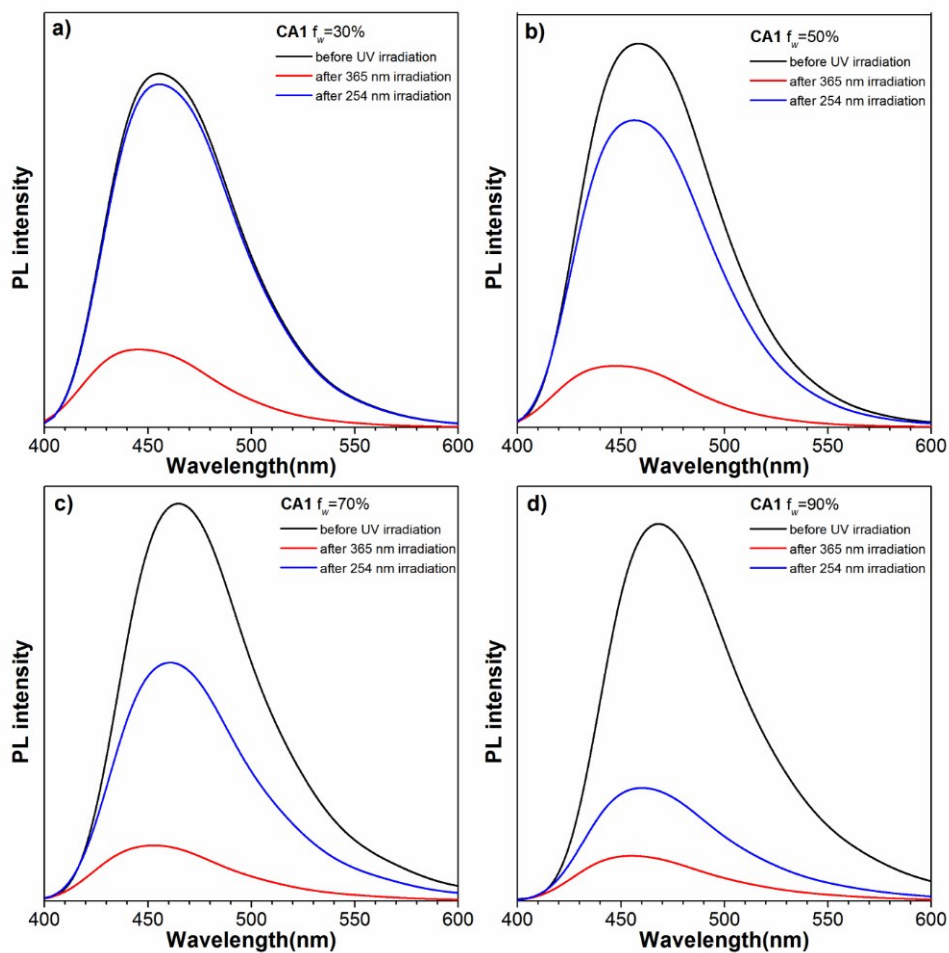


**Figure S6.** <sup>1</sup>H NMR spectrum of CA2 in CDCl<sub>3</sub> irradiated with 365 nm UV light from a hand-held UV lamp for different time. The photo-irradiation experiment was performed using 365 nm ultraviolet light from a flashlight (3W). Solution of sample CA2 in a NMR tube was placed at the distance of 1 cm from the light source.

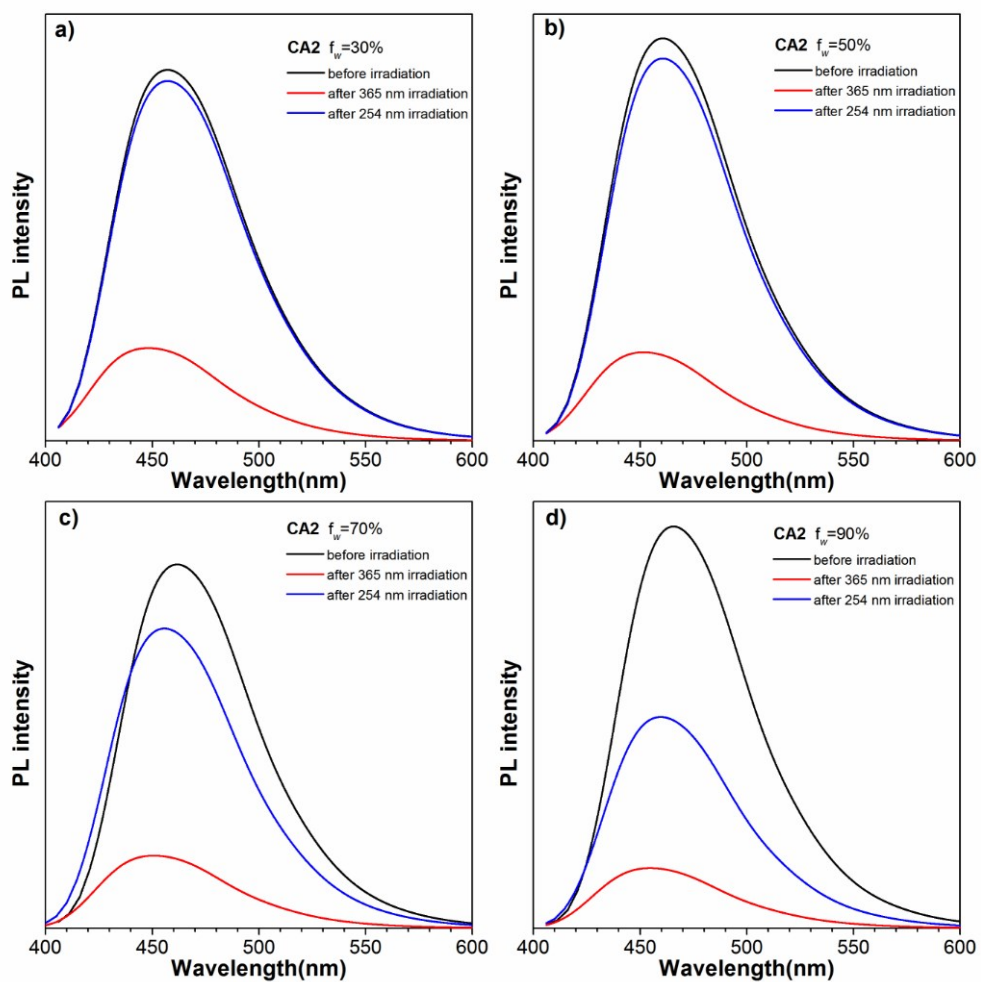




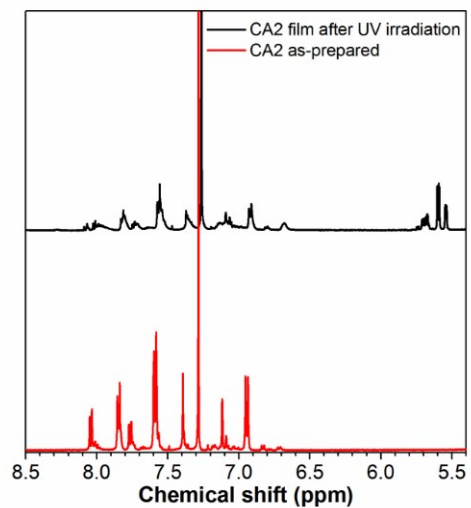
**Figure S7.** PL spectra of CA1 (a) and CA2 (b) in THF solution after 365 nm UV irradiation for 70 min and subsequent 254 nm UV irradiation for 5 hours. Concentration = 10  $\mu$ M. Inset: photos of the sample in THF solution after UV irradiation.



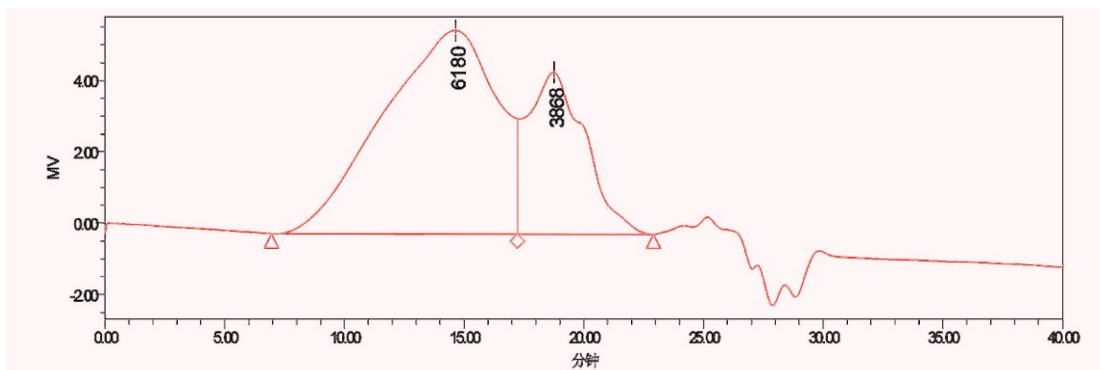
**Figure S8.** Changes of photoluminescence spectra of CA1 in THF/H<sub>2</sub>O mixtures with  $f_w$  of (a) 30%, (b) 50%, (c) 70%, and (d) 90% upon 365 nm UV light irradiation for 60, 50, 40, 30 minutes respectively, and subsequent 254 nm UV light irradiation for 5 hours from a hand-held lamp.



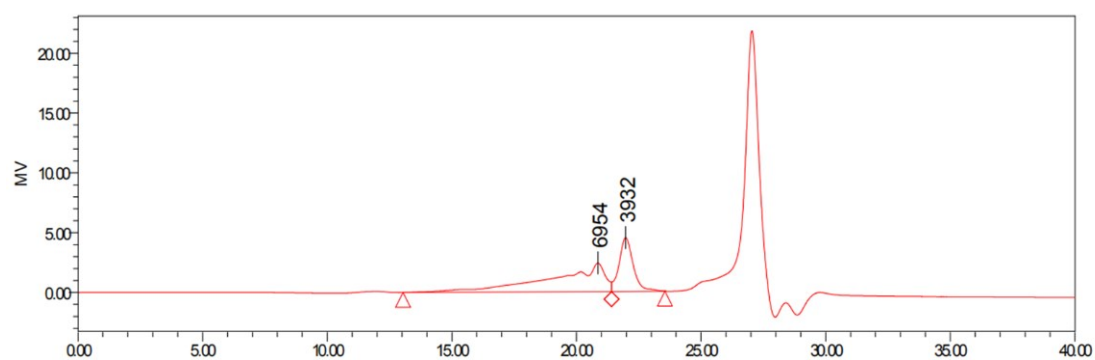
**Figure S9.** Changes of photoluminescence spectra of **CA2** in THF/H<sub>2</sub>O mixtures with  $f_w$  of (a) 30%, (b) 50%, (c) 70%, and (d) 90% upon 365 nm UV light irradiation for 60, 50, 40, 30 minutes respectively, and subsequent 254 nm UV light irradiation for 5 hours from a hand-held lamp.



**Figure S10.** <sup>1</sup>H NMR spectrum of CA2 sample in CDCl<sub>3</sub>, which was previously irradiated in the neat film. Film of sample CA2 on a glass sheet was placed at the distance of 5 cm from the light source, which could emit 365 nm UV light (3W).



**Figure S11.** GPC curve of CA1 sample, which was previously irradiated with 365 nm UV light (3W) in the neat film.



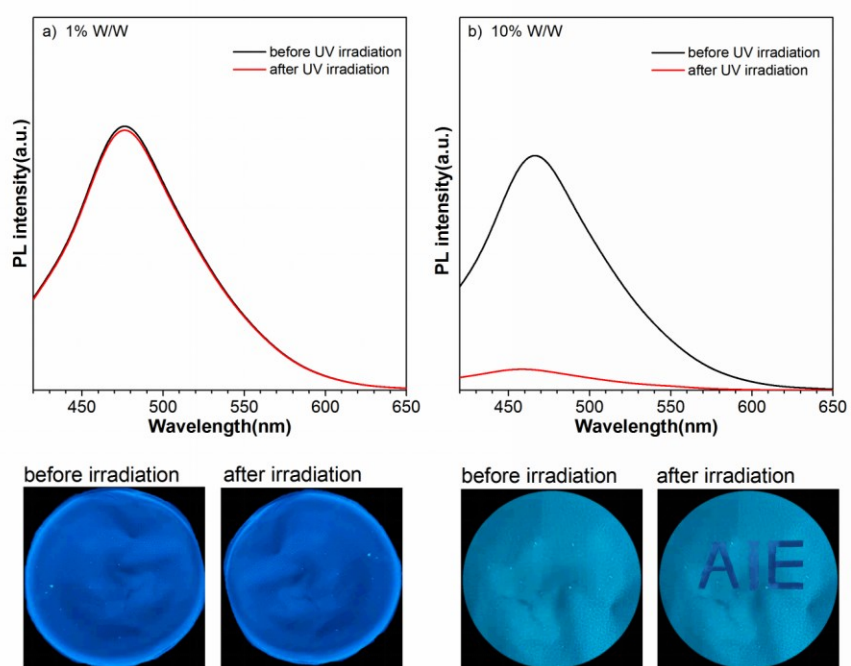
**Figure S12.** GPC curve of CA2 sample, which was previously irradiated with 365 nm UV light (3W) in the neat film.

**Table S1.** GPC data of CA1 sample, which was previously irradiated with 365 nm UV light (3W) in the neat film.

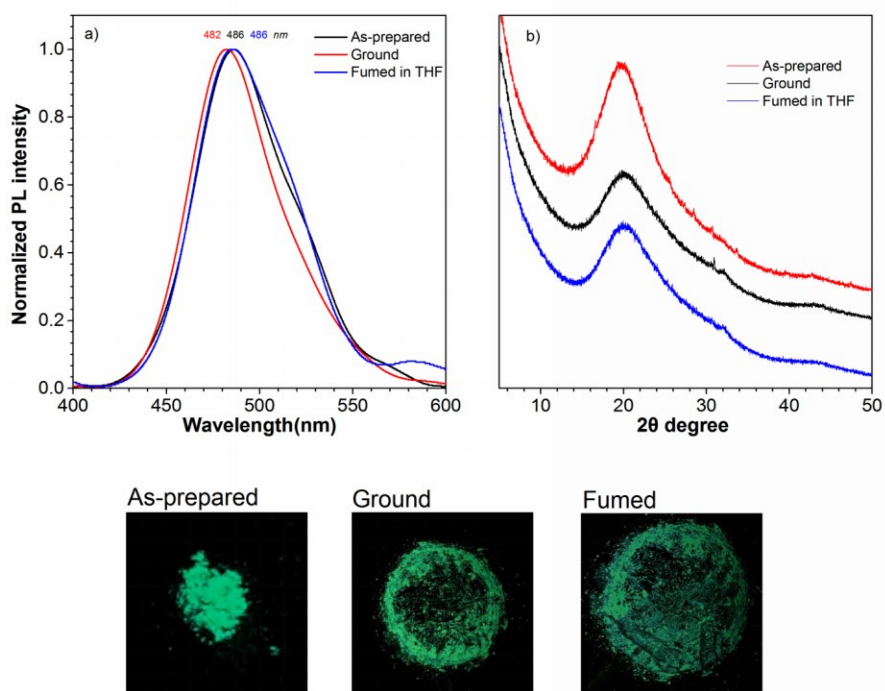
Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	10160	20090	6180	35434	47852	1.977334	1.763763	2.38188
2	3752	4667	3868	4519	5988	1,243854	0.968288	1.283051

**Table S2.** GPC data of CA2 sample, which was previously irradiated with 365 nm UV light (3W) in the neat film.

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	11899	22714	6954	72732	89580	1.908913	3.202078	3.943823
2	3841	3919	3932	3996	4073	1.020296	1.019648	1.039296

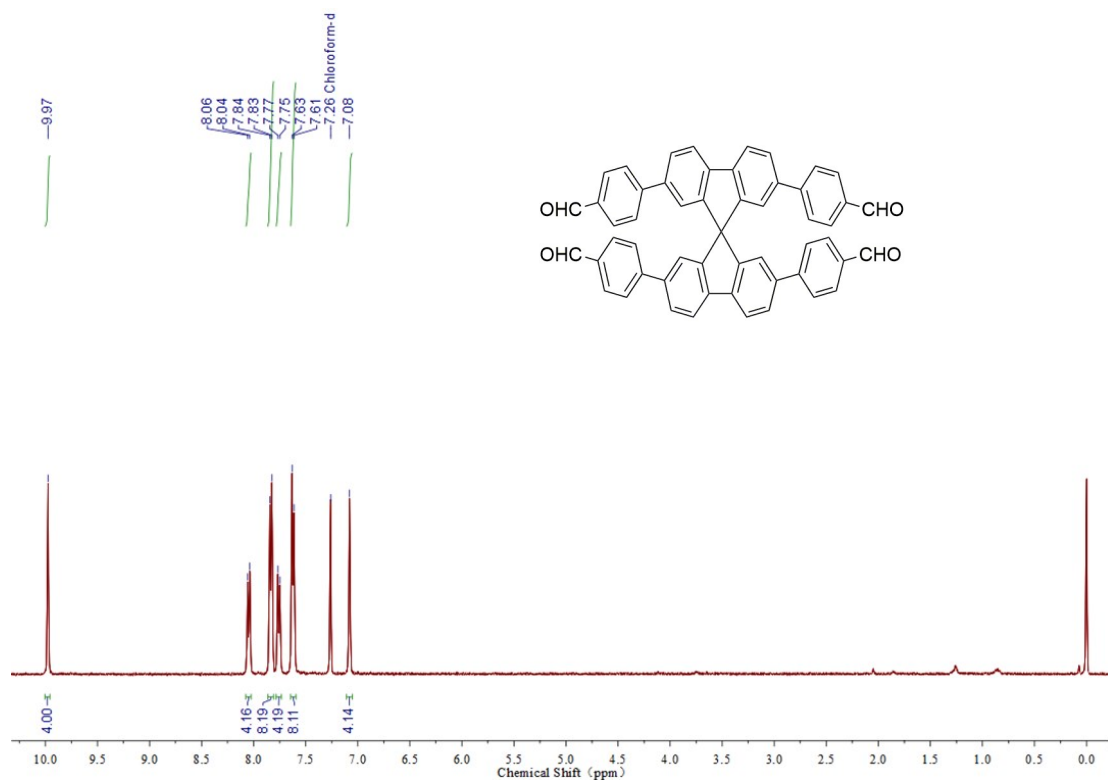


**Figure S13.** PL spectra of cruciform AIEgens CA2 dispersed in PMMA matrix (1% or 10% w/w of CA2 relative to PMMA) without and with 365 nm UV irradiation.

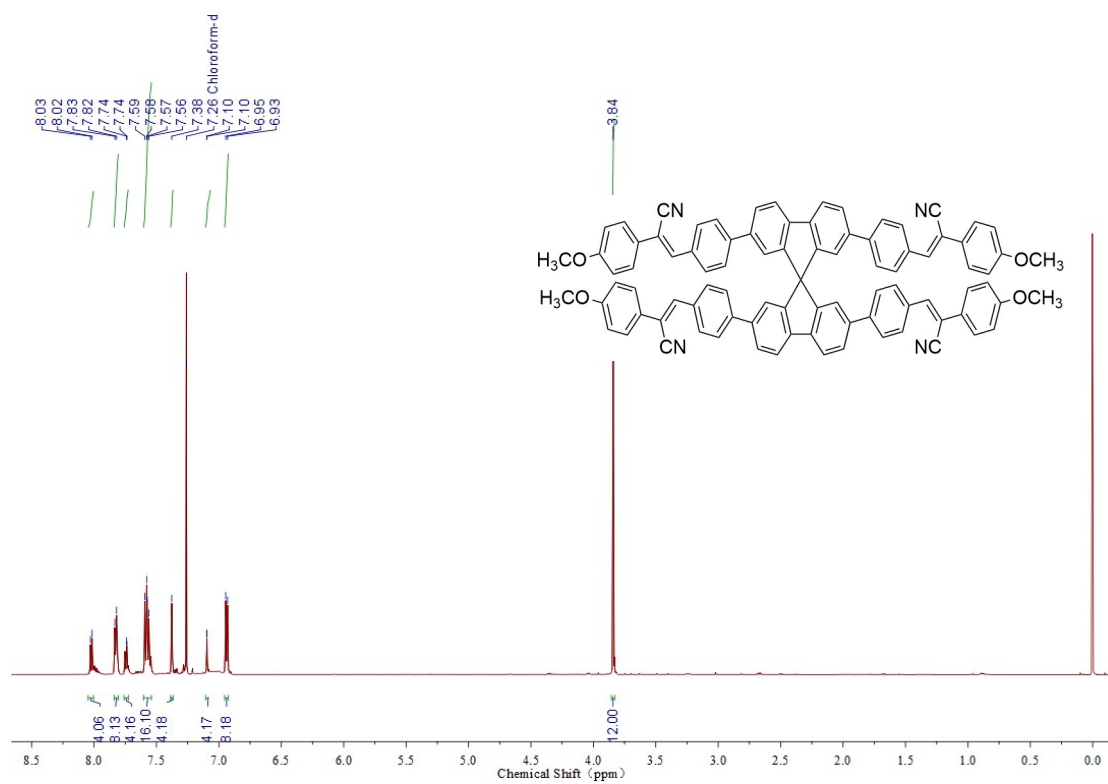


**Figure S14.** PL spectra (a), powder XRD results (b), and fluorescence images (c) of the as-prepared cruciform AIEgen CA2 samples after grinding and subsequent solvent fuming with THF for 30 min.

#### 4. NMR spectra



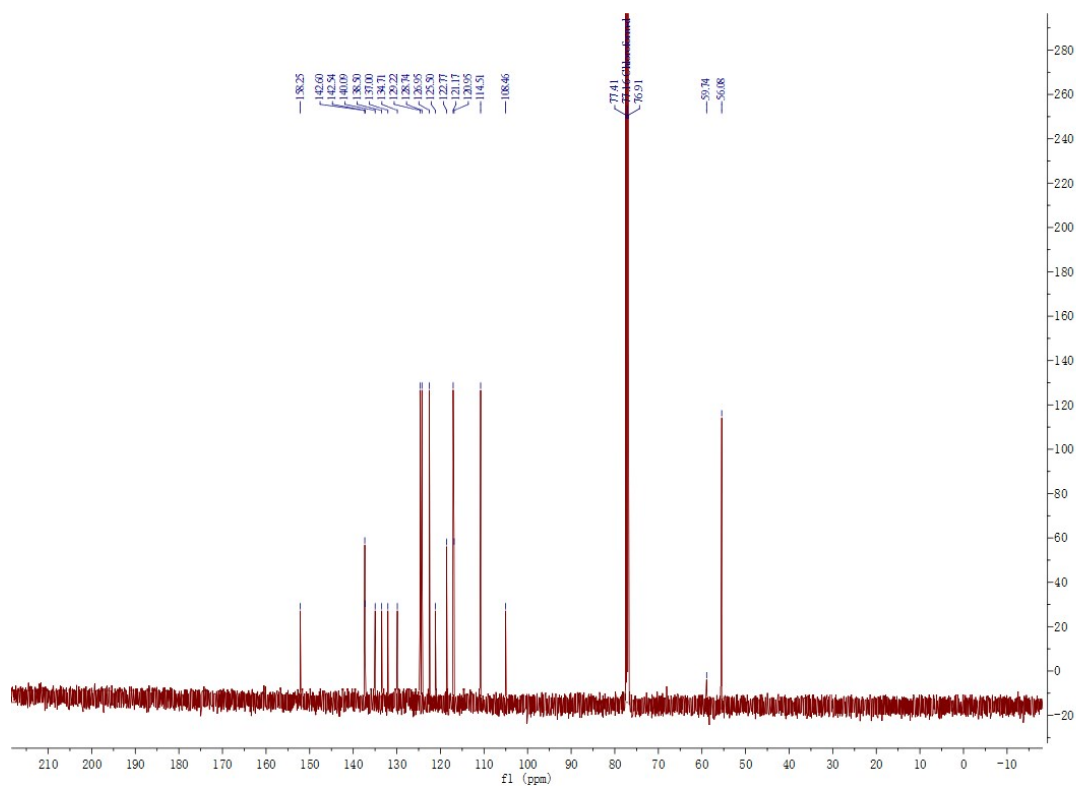
**Figure S16.** <sup>1</sup>H NMR spectrum of compound **2** in CDCl<sub>3</sub> at 298K.



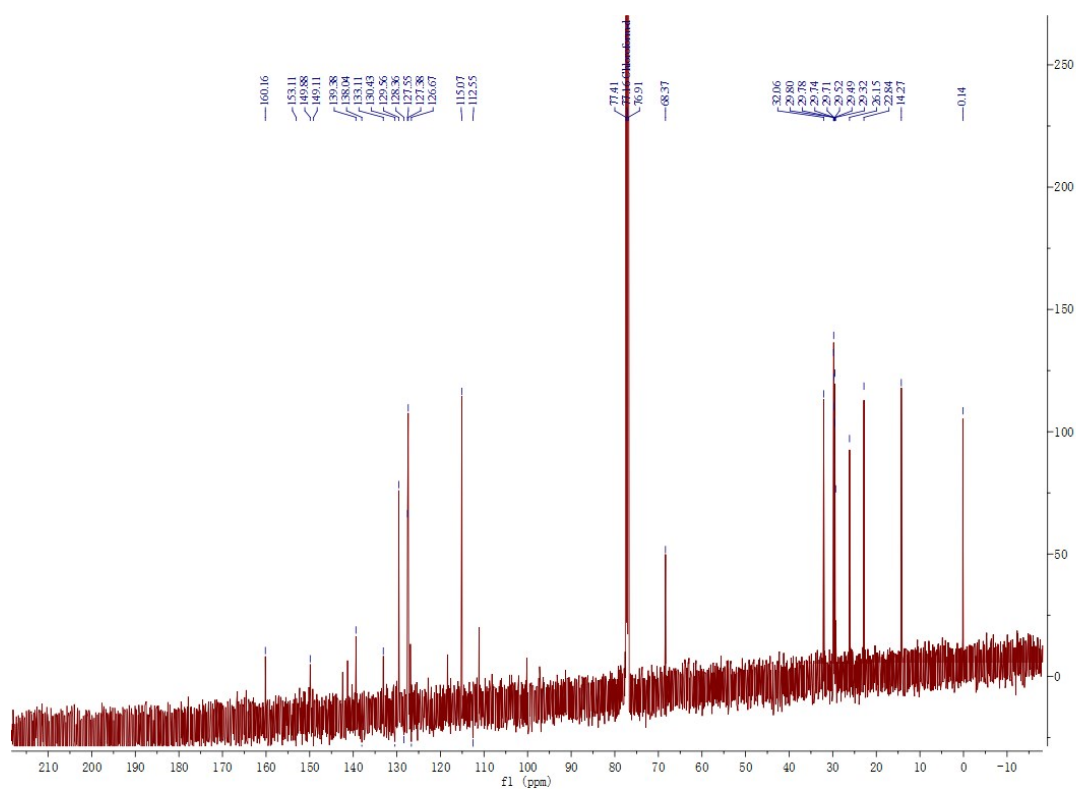
**Figure S17.** <sup>1</sup>H NMR spectrum of compound **CA1** in CDCl<sub>3</sub> at 298K.







**Figure S20.** <sup>13</sup>C NMR spectrum of compound CA1 in CDCl<sub>3</sub> at 298K.



**Figure S21.** <sup>13</sup>C NMR spectrum of compound CA2 in CDCl<sub>3</sub> at 298K.