

Morphology-Dependent Photoresponsive Behaviors of a Self-Assembled System based on a Single Cyanostilbene Derivative

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Experimental details

Materials

All solvents were purchased from commercial suppliers and used directly without further purification unless otherwise stated. Tetraethyleneglycol monomethyl ether, 4-Methoxybenzenesulfonyl chloride (TsCl), 5-Hydroxy-isophthalic acid dimethyl ester, 2-(4-nitrophenyl)acetonitrile and 4-(dimethylamino)benzaldehyde were all purchased from Energy Chemical Co., Ltd.

Characterizations

^1H NMR and ^{13}C NMR spectra were conducted with a Bruker Avance III 400 MHz NMR spectrometer. UV/Vis absorption spectra were recorded on a Shimadzu 3600 UV-Vis-near-IR spectrophotometer. Scanning electron microscope (SEM) images were obtained from a JEOL JEM-6700F scanning electron microscope with 3 kV operating voltage. Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker VERTEX 70 FTIR spectrometer. Mass spectra were measured using a Bruker Autoflex speed TOF/TOF mass spectrometer. X-ray powder diffraction (XRD) investigation was carried out using Siemens D5005 diffractometer. Elemental analysis (C, H, N) was carried out on an Elementar Vario micro cube. The light source used to trigger photoreactions was a commercially used blue LED (420 nm wavelength emission) with the power of 20 W.

Synthesis

2,5,8,11-tetraoxatridecan-13-yl 4-methylbenzenesulfonate (1). 2.58 g NaOH (64.46 mmol) was dissolved in 10 mL deionized water and cooled to 0 °C. Under ice bath, NaOH solution was slowly dropped into the mixture of Tetraethyleneglycol monomethyl ether (8 mL, 37.9 mmol) and TsCl (10.84 g, 56.85 mmol) in 40 mL THF. The whole mixture was stirred for two days under room temperature. 30 mL water was added into the mixture and stirred for another 5 hours. Then, THF was removed under reduced pressure and the resultant mixture was extracted with DCM. The organic layer was collected and dried over in the presence of anhydrous Na₂SO₄. After evaporation, the transparent oil **1** was obtained with no further purification.

Dimethyl 5-((2,5,8,11-tetraoxatridecan-13-yl)oxy)isophthalate (2). **1** (1.76 g, 4.68 mmol), 5-Hydroxy-isophthalic acid dimethyl ester (1.12 g, 5.34 mmol) and K₂CO₃ (3.11 g, 24.3 mmol) were mixed with 50 mL anhydrous MeCN and refluxed for 24 hours. After filtration, the clear solution was filtrated to get the yellow oil **2**. ¹H NMR (400 MHz, DMSO-*d*₆) δ/ppm = 8.07 (s, 1H), 7.69 (d, *J* = 1.3 Hz, 2H), 4.26–4.20 (m, 2H), 3.89 (s, 6H), 3.80–3.75 (m, 2H), 3.60 (dd, *J* = 6.0, 3.4 Hz, 2H), 3.57–3.47 (m, 8H), 3.41 (dd, *J* = 5.7, 3.6 Hz, 2H), 3.23 (d, *J* = 2.8 Hz, 3H).

5-((2,5,8,11-tetraoxatridecan-13-yl)oxy)isophthalic acid (3). The above oil **2** and NaOH (0.973 g, 24.3 mmol) were mixed with 100 mL EtOH/H₂O mixture (v:v = 1:1) and then refluxed for a night. After evaporating most of EtOH under reduced pressure, 1 M HCl was dropped until pH was adjust below 2. Finally, EtOAc was applied to extracted for 3 times and the organic layer was dried and concentrated by rotary evaporation to give the white product. ¹H NMR (400 MHz,

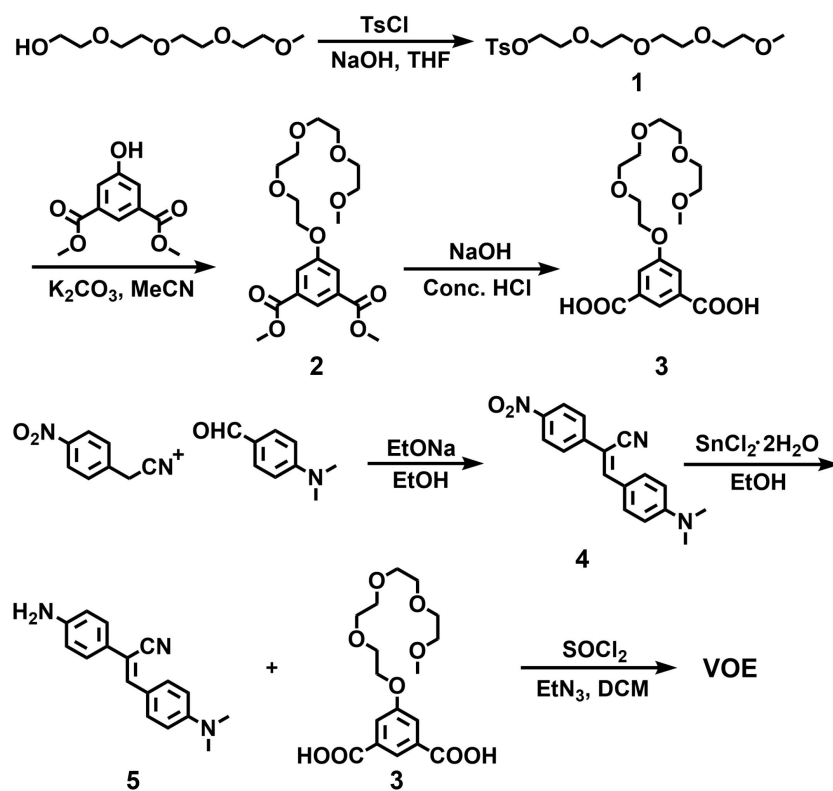
DMSO-*d*₆), δ /ppm = 13.28 (s, 2H), 8.08 (s, 1H), 7.66 (s, 2H), 4.28–4.16 (m, 2H), 3.79–3.75 (m, 2H), 3.60 (dd, *J* = 6.0, 3.4 Hz, 2H), 3.55–3.47 (m, 8H), 3.41 (dd, *J* = 5.4, 3.8 Hz, 2H), 3.22 (s, 3H).

3-(4-Dimethylamino-phenyl)-2-(4-nitro-phenyl)-acrylonitrile (4). 2-(4-nitrophenyl)acetonitrile (2.43 g, 15.0 mmol) and 4-(dimethylamino)benzaldehyde (2.24 g, 16.3 mmol) were added to dried methanol (30 mL). Then gradually drop pyrrolidine until the solution color turned purple. White precipitate was filtered after 4 hours and washed with methanol for three times (3.52 g, yield: 80%). ¹H NMR (400 MHz, DMSO-*d*₆), δ /ppm = 8.31 (d, *J* = 8.7 Hz, 2H), 8.11 (s, 1H), 7.96 (t, *J* = 8.9 Hz, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.07 (s, 6H).

2-(4-Amino-phenyl)-3-(4-dimethylamino-phenyl)-acrylonitrile (5). 3 g compound **4** (10.2 mmol) and stannous chloride (9.2 g, 46.07 mmol) were added in 80 mL EtOH. The mixture was refluxed in dark for 12 hours. After cooling, NaHCO₃ was added to adjust the pH to above 7. Then the mixture was extracted with EtOAc. The organic layer was dried with MgSO₄ and evaporated under vacuum to obtain the yellow powder **5** (1.94 g, yield: 72%). ¹H NMR (400 MHz, DMSO-*d*₆), δ /ppm = 7.77 (d, *J* = 8.6 Hz, 2H), 7.48 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.59 (dd, *J* = 27.8, 8.5 Hz, 2H), 5.43 (s, 2H), 2.99 (s, 6H).

(5-((2,5,8,11-tetraoxatridecan-13-yl)oxy)-N¹,N³-bis(4-((Z)-1-cyano-2-(4-(dimethylamino)phenyl)vinyl)phenyl)isophthalamide (VOE). 0.7 g compound **5** (1.88 mmol) was dissolved in 5 mL THF. Then SOCl₂ (1.37 mL, 18.80 mmol) was added and the whole mixture was refluxed for 3 hours. The solution was evaporated many times for removing excess SOCl₂. Next, the obtained dark yellow liquid drop was added with **3** (1.76 g, 5.64 mmol) and 20 mL DCM. Slowly drop 0.78 mL (5.64 mmol) Et₃N into above mixture under ice bath. The solution was then stirred in dark

under room temperature for 2 days. After evaporating DCM under reduced pressure, the yellow precipitates were washed with methanol and water until no **5** existed. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ/ppm = 10.54 (s, 2H), 8.18 (s, 1H), 7.90 (dd, J = 18.8, 8.8 Hz, 8H), 7.79 (s, 2H), 7.76 (s, 2H), 7.70 (d, J = 8.6 Hz, 4H), 6.83 (d, J = 8.9 Hz, 4H), 4.31 (s, 2H), 3.84 (s, 2H), 3.64 (s, 2H), 3.59–3.48 (m, 8H), 3.42 (d, J = 5.0 Hz, 2H), 3.22 (s, 3H), 3.03 (s, 12H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ/ppm = 165.15, 158.90, 152.05, 142.22, 139.33, 136.80, 131.43, 125.84, 121.51, 121.11, 119.91, 117.15, 112.11, 102.74, 71.75, 70.46, 70.32, 70.26, 70.05, 69.35, 68.28, 58.50, 40.08.



Scheme S1 The detailed synthetic route of VOE.

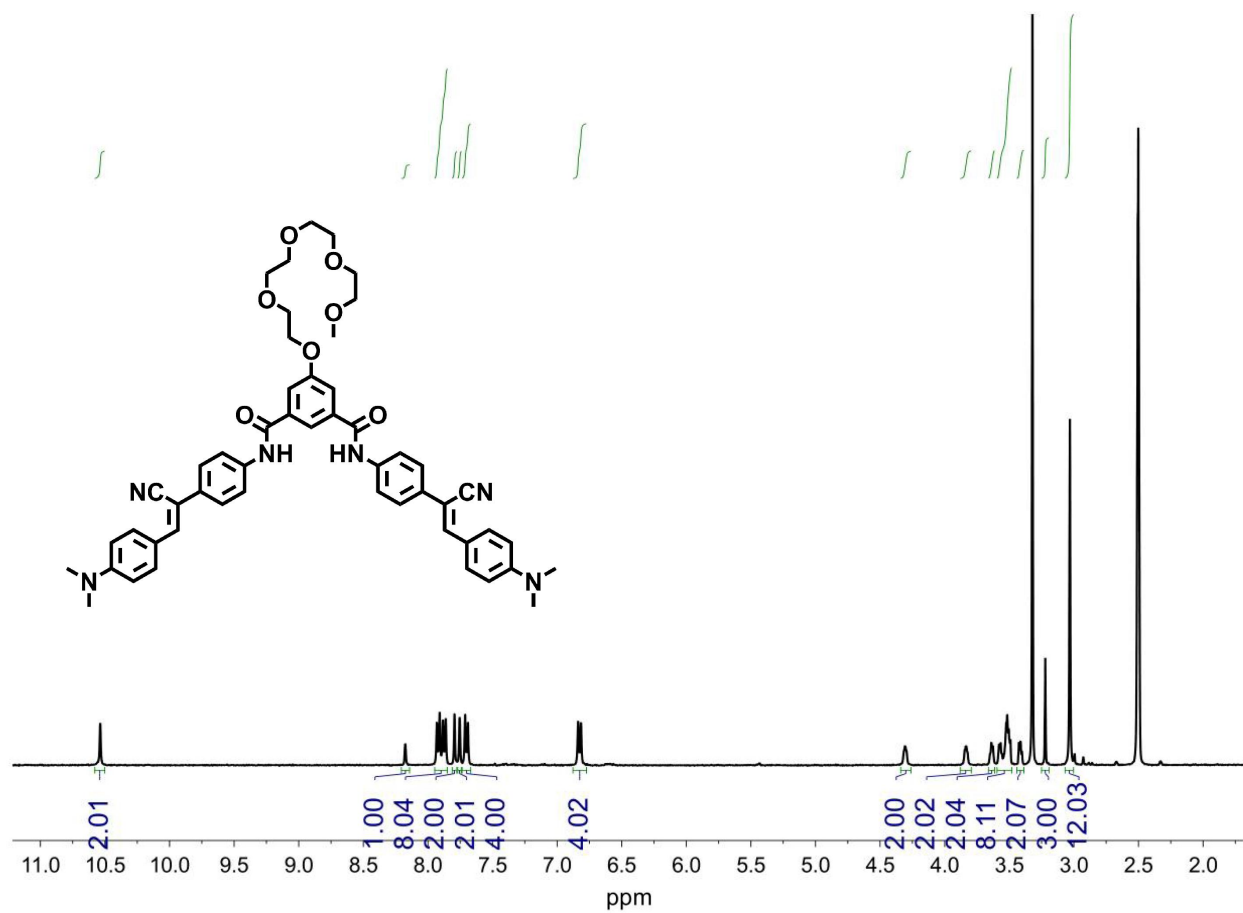


Fig. S1 ¹H NMR spectrum of VOE in DMSO-d₆.

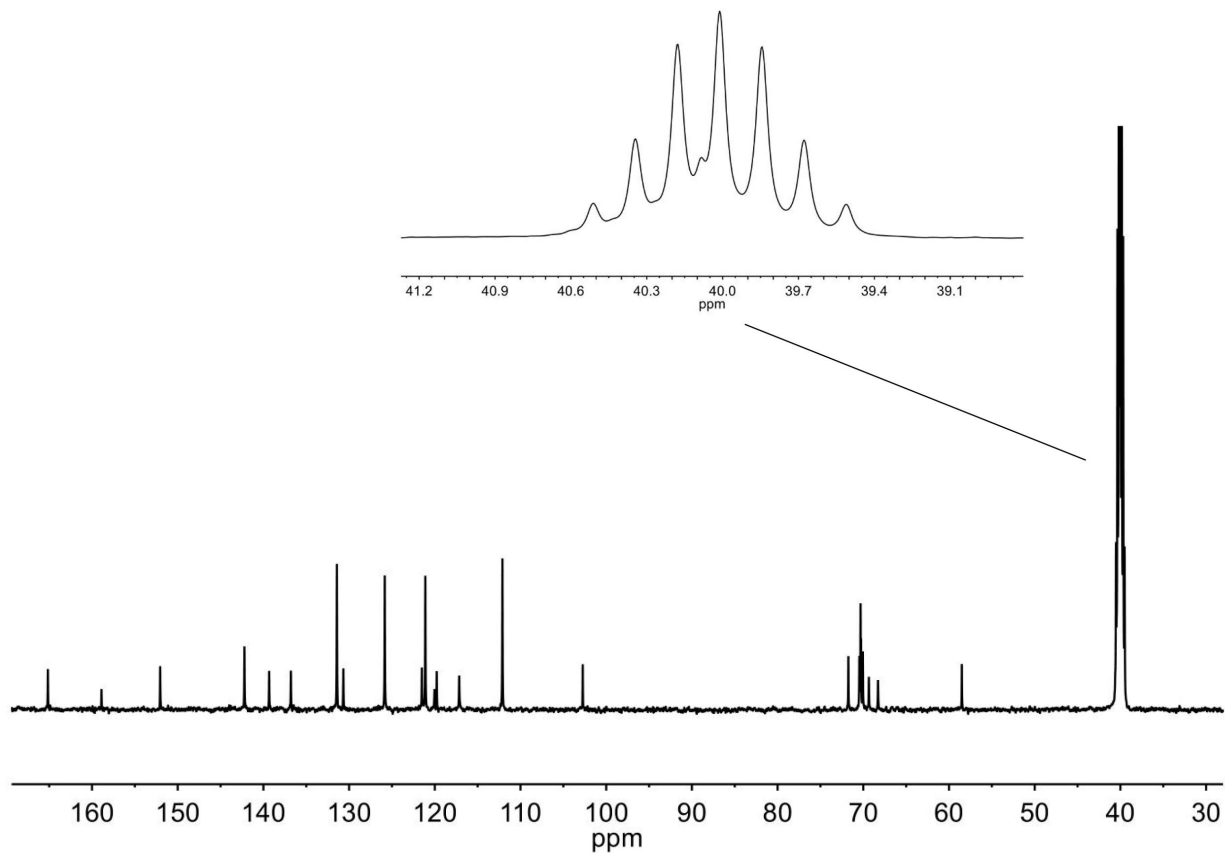


Fig. S2 ^{13}C NMR spectrum of VOE in $\text{DMSO-}d_6$.

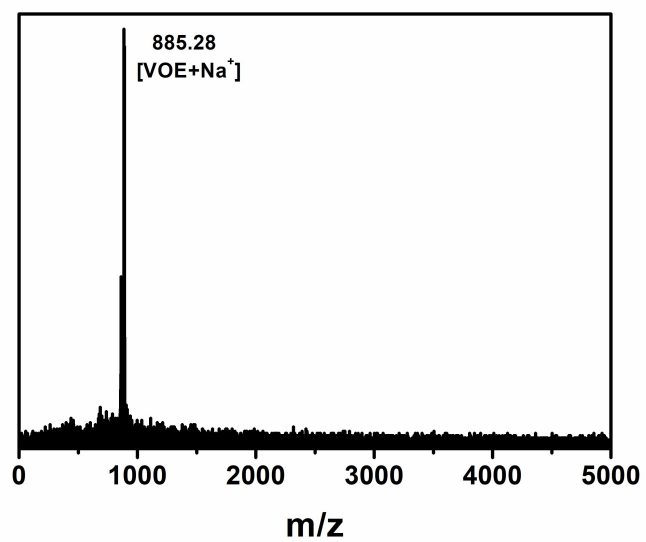


Fig. S3 MALDI-TOF mass spectrum of VOE.

Table S1 Elemental analysis results of VOE.

VOE	C	H	N
Calculated (%)	70.98	6.31	9.74
Found (%)	70.97	6.56	9.75
Error (%)	0.01	0.25	0.01

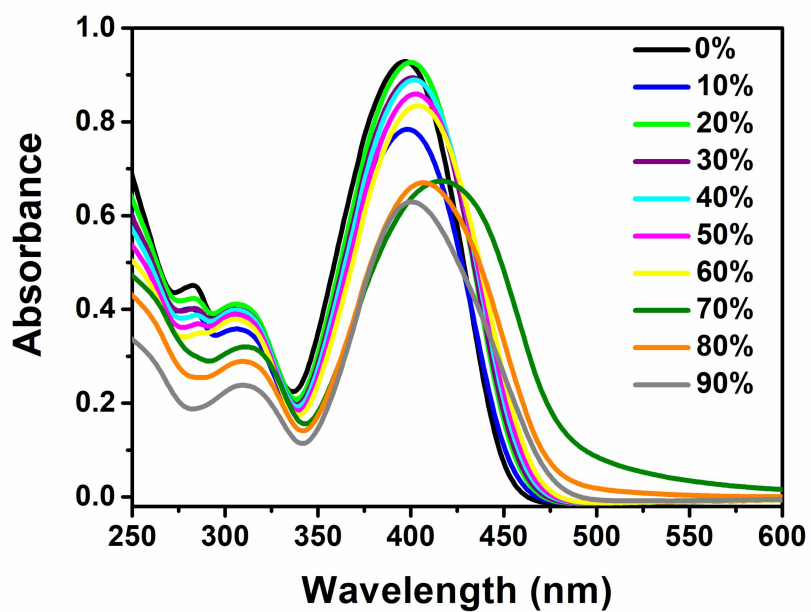


Fig. S4 UV/Vis absorption spectra of the freshly prepared VOE in H₂O/THF mixtures with different water fractions.

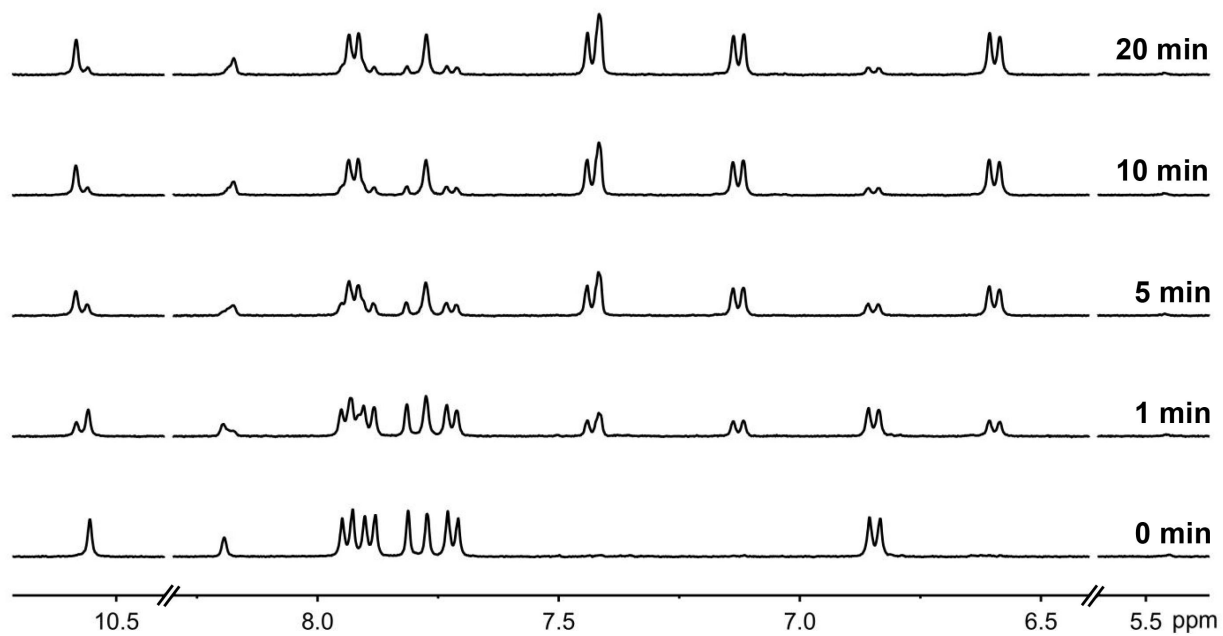


Fig. S5 ^1H NMR spectra variations of VOE in $\text{DMSO-}d_6$ solution with the increase of the blue light irradiation time up to 20 minutes.

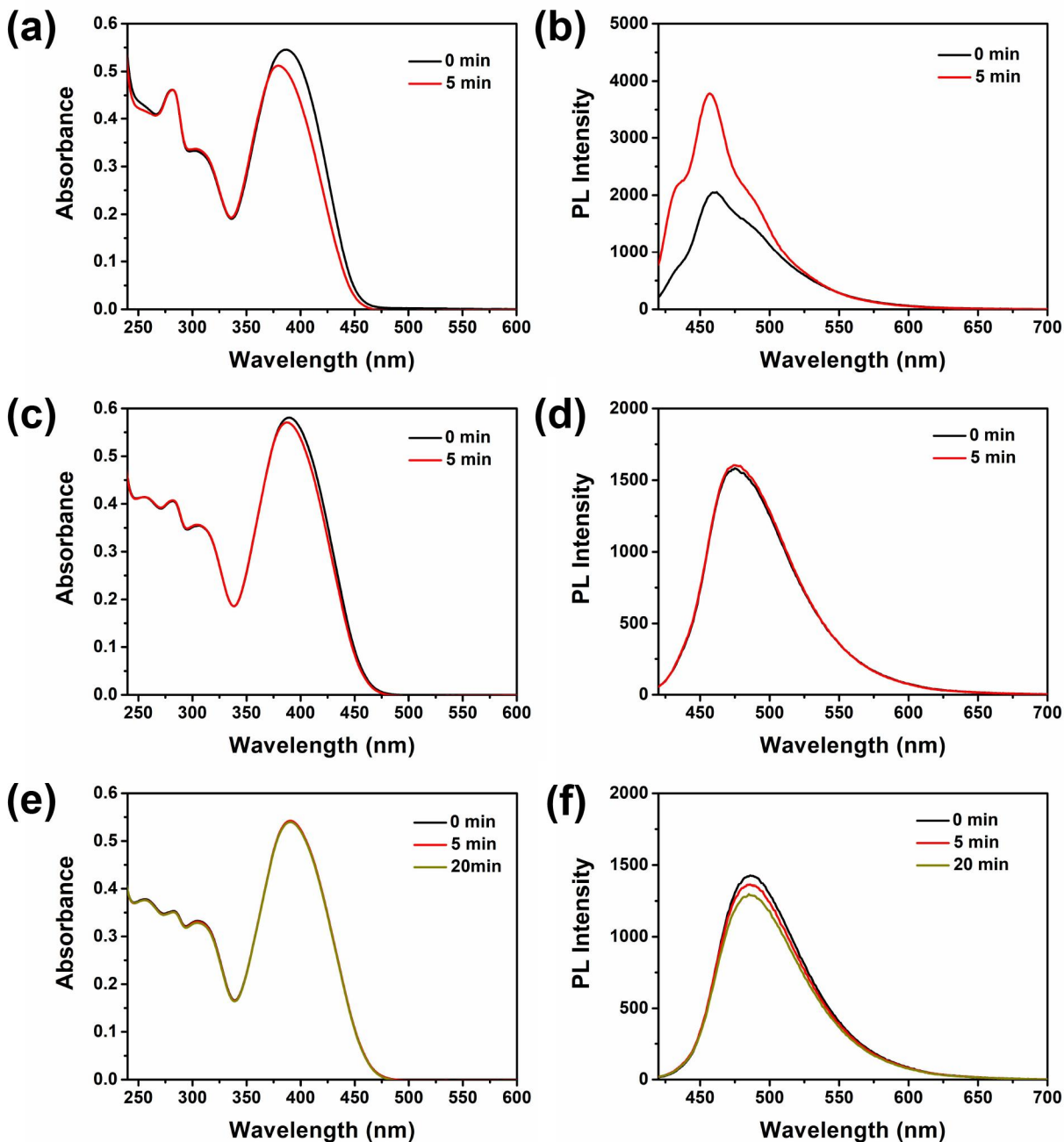


Fig. S6 Changes of UV/Vis spectra of VOE in H₂O/THF mixtures with water fractions of (a) 0%, (c) 30% and (e) 50% upon blue light irradiation for different time. Changes of fluorescence spectra of VOE in H₂O/THF mixtures with water fractions of (b) 0%, (d) 30% and (f) 50% upon blue light irradiation for different time. ([VOE] = 5*10⁻⁵ M, λ_{ex} = 400 nm)

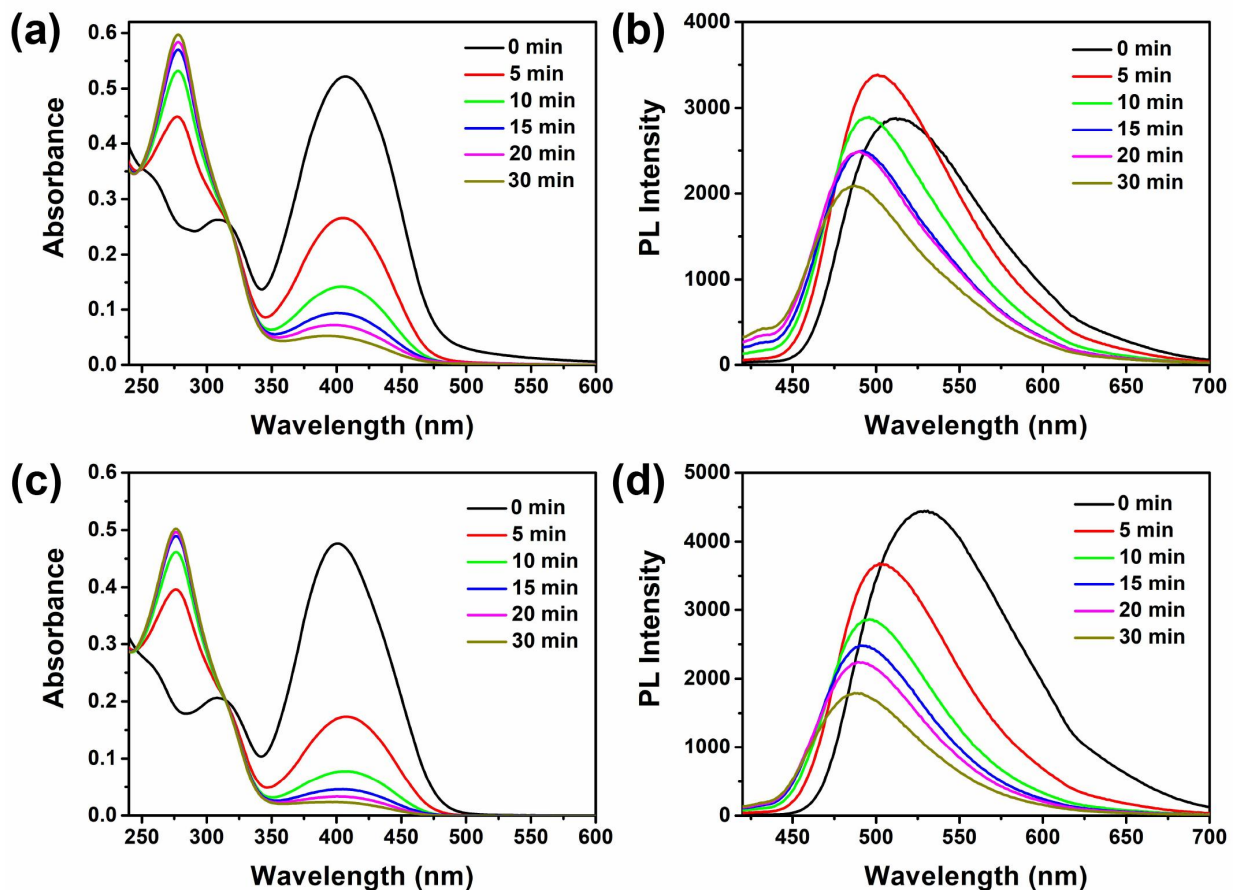


Fig. S7 Changes of UV/Vis spectra of VOE in H₂O/THF mixtures with water fractions of (a) 80% and (c) 90% upon blue light irradiation for different time. Changes of fluorescence spectra of VOE in H₂O/THF mixtures with water fractions of (b) 80% and (d) 90% upon blue light irradiation for different time. ([VOE] = 5*10⁻⁵ M, λ_{ex} = 400 nm)

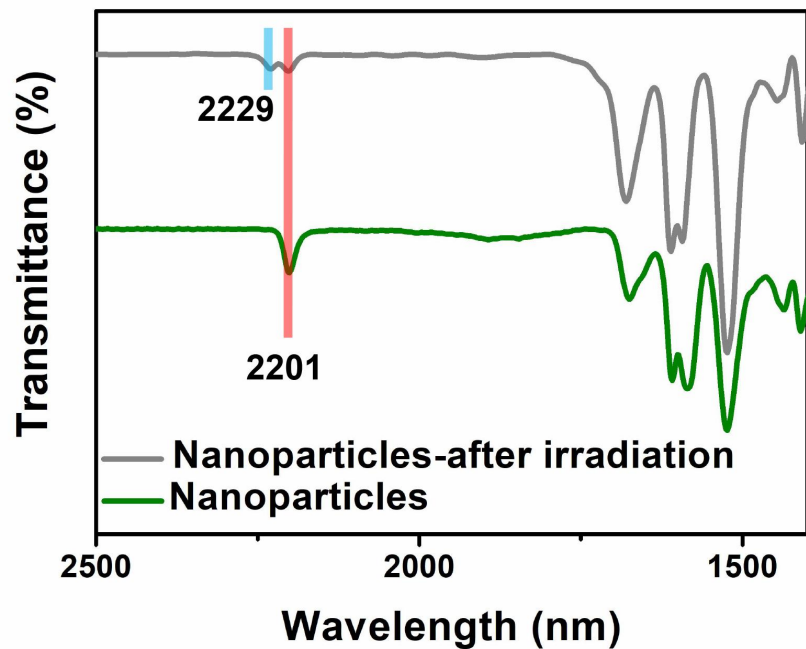


Fig. S8 FT-IR spectra of nanoparticles before and after irradiation.

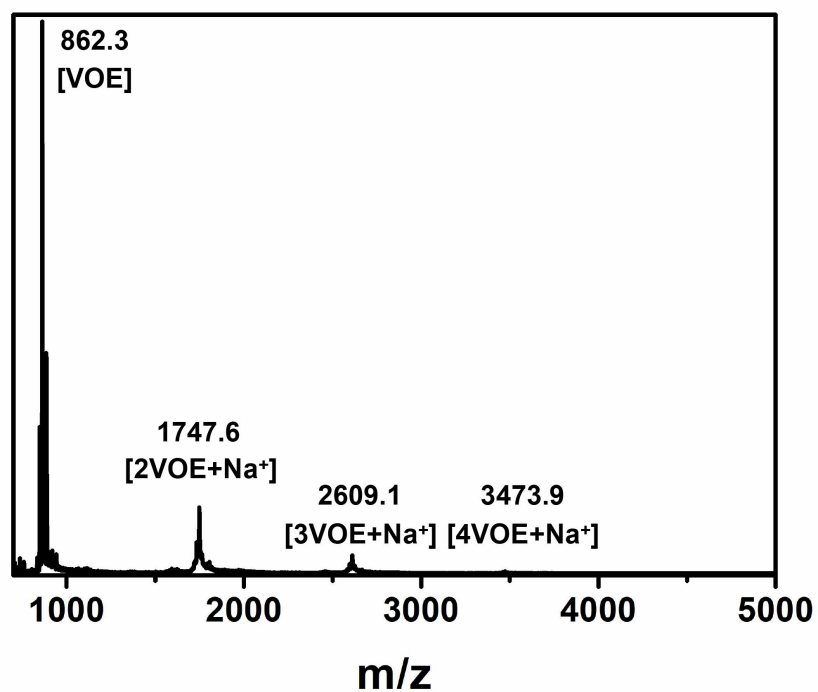


Fig. S9 MALDI-TOF mass spectrum of nanoparticles after irradiation.

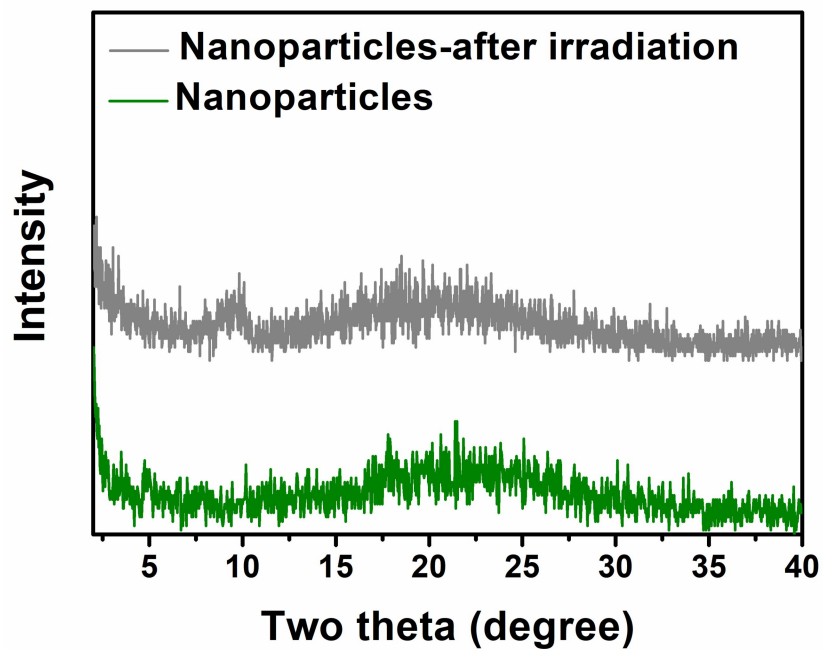


Fig. S10 XRD patterns of nanoparticles before and after blue light irradiation.

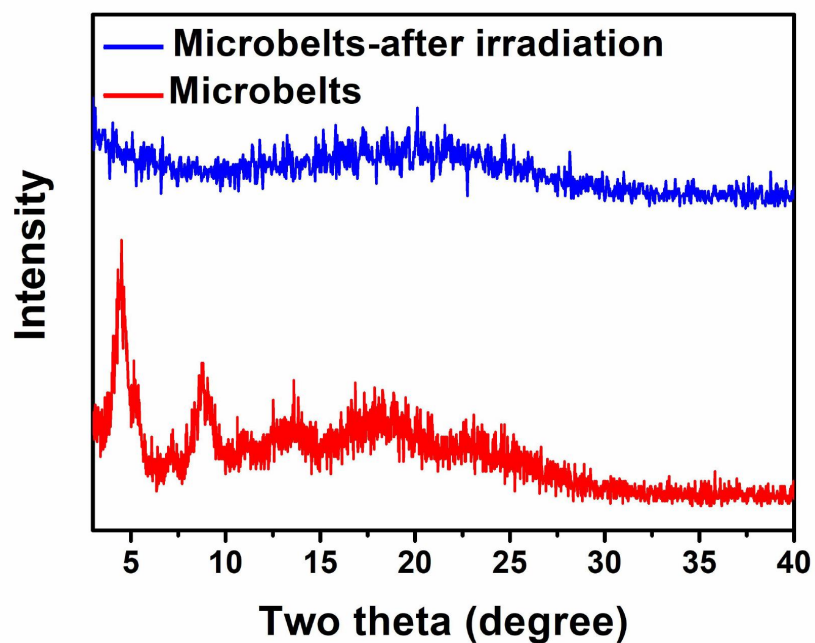


Fig. S11 XRD patterns of microbelts before and after blue light irradiation.

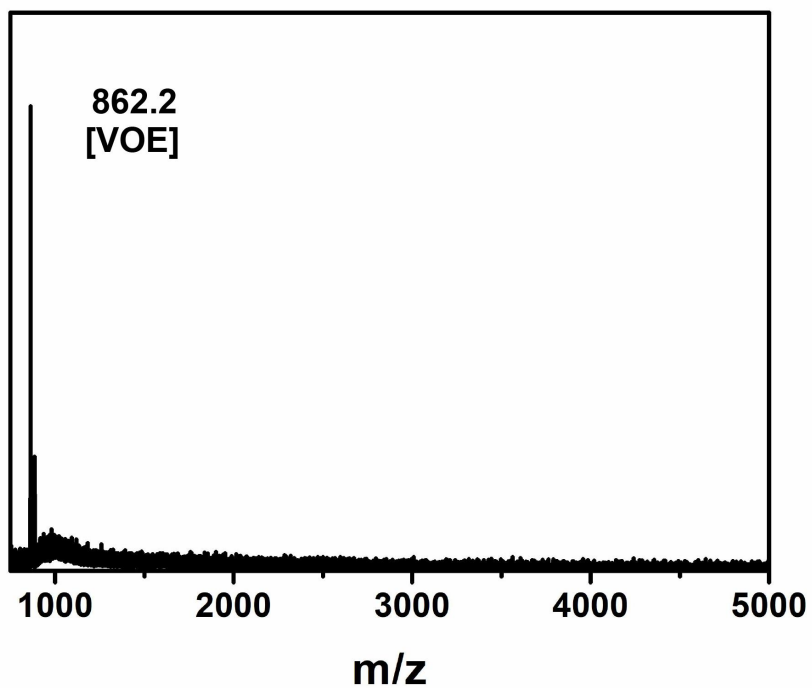


Fig. S12 MALDI-TOF mass spectrum of microbelts after irradiation.

Table S2 Gelation properties and critical gelator concentrations (CGC) of VOE in various organic solvents at 25 °C. The values in parentheses are CGC (mg mL⁻¹). G: gel; I: insoluble; S: solution; P: precipitate.

Solvent	State	Solvent	State
MeCN	G (20)	Methanol	I
DCM	S	Cyclohexane	I
Chloroform	S	n-Hexane	I
1,4-Dioxane	S	Toluene	I
THF	S	m-Xylene	I
DMSO	S	Ethyl acetate	I
DMF	S	Acetone	P

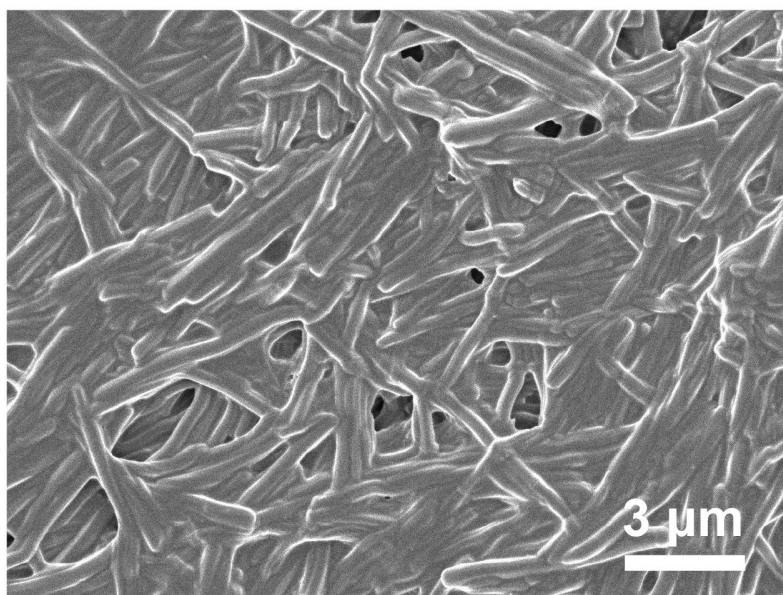


Fig. S13 SEM image of VOE xerogels formed in acetonitrile (20 mg mL^{-1}).

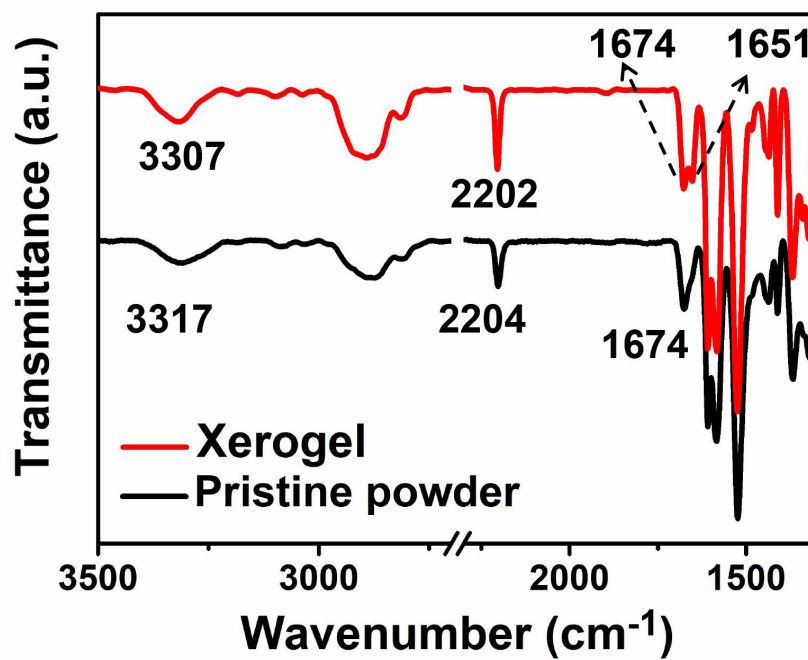


Fig. S14 FT-IR spectra of VOE xerogel and pristine powder.

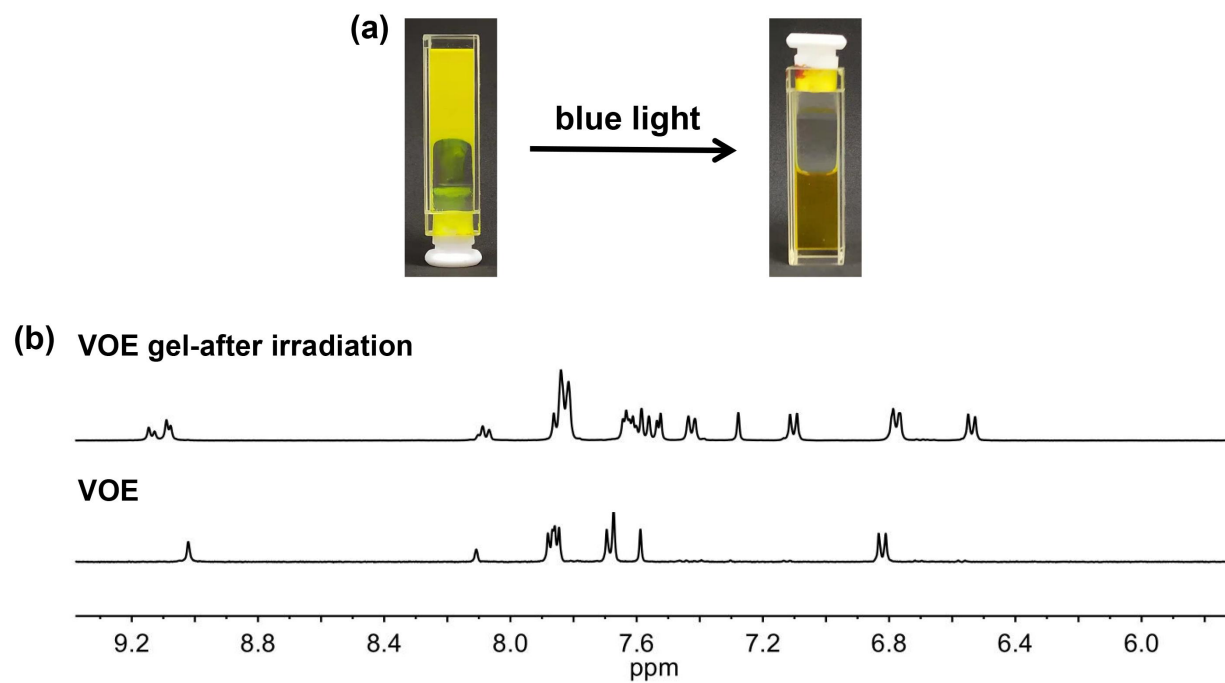


Fig. S15 (a) Photographs of VOE gel before and after blue light irradiation. (b) ^1H NMR spectra of pure Z configurations of VOE and product of VOE gel after blue light irradiation in CD_3CN .