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# Supplementary Information for

## Photoexcitation-Controlled Self-Recoverable Molecular Aggregation for Flicker Phosphorescence

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**Other supplementary materials for this manuscript include the following:**





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## 1. Experimental Details

**General.** All reagents were purchased from Aldrich and used without additional purification. $^{1}$H NMR and $^{13}$C NMR spectra were measured on a Bruker 400L spectrometer. High‐resolution mass spectrometry (HRMS) data was measured by Matrix assisted laser desorption ionization-time of flight/time of flight mass spectrometer (5800). The UV-vis absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. The emission spectra were recorded on Shimadzu RF-5301, and the lifetime spectra were recorded on FLS 920 (Edinburgh Instruments). The photoirradiation was carried out using a hand-held UV lamp (with the irradiation wavelength of 365 nm in a sealed 10 mm quartz cell. Transmission electron microscopy (TEM) was performed on a Jeol JEM 2100 with an accelerating voltage of 200 kV. The confocal microscopic images were captured by Nikon C2+ confocal microscope. Raman spectroscopy were recorded on a Horiba Jobin Yvon XploRA spectrometer equipped with a 10 objective and a laser with a wavelength of 532 nm. Fourier transform infrared (FTIR) spectroscopy was carried out with a Thermofisher Nicolet 6700 spectrometer using KBr pellets as the sample matrix in the wavenumber range of 400-4000 $cm^{-1}$. Dynamic light scattering (DLS) experiments were carried out with Nano-Zeta Potential Analyzer ZS-90.

**Synthesis of compound 1:** Hexachlorobenzene (0.284 g, 1 mmol, 1.00 eq.), dry $K_2CO_3$ (2.48 g, 18 mmol, 9 eq.) and ethyl 4-mercaptobenzoate (1.68 g, 18 mmol, 9 eq.) were added into a round bottom flask capped with a septum under an argon atmosphere. Dry DMF (30 mL) was injected via a syringe and the mixture was stirred at 60 ℃ for 40h. Water (200 mL) was poured into the flask while stirring, and a yellow precipitate appeared. After collecting the solid by filtration, it was rinsed with ethanol (10 mL), diethyl ether (20 mL), and then dried under high vacuum (1.2g, 52%). $^{1}$H NMR (400 MHz, DMSO, 298 K): δ = 1.32 (t, 18H), 4.28 (m, 12H), 7.12 (m, 12H), 7.77 (m,12H).$^{13}$C NMR (100 MHz, DMSO, 298 K): δ = 14.31, 61.09, 126.98, 128.57, 130.31, 142.55, 147.93, 165.74. HRMS (ESI) calculated for $[M + Na]^+$ m/z: 1181.5631, found: 1181.6528.

**Synthesis of compound 2:** Compound 1 (1.15g, 1 mmol) was dissolved in THF (30 mL), and an aqueous solution of NaOH (2 M, 5 mL) was poured into the flask while stirring. The reaction mixture was kept at 40 ℃ for 10h when stirred with a magnetic bar, followed by addition of a HCl (1M, 200 mL) solution. The solid was collected by filter and washed by water, EA, ethanol to obtain yellow powder (600 mg), which was used for the next step directly without purification.$^{1}$H NMR (400 MHz, DMSO, 298 K): δ = 7.12 (m, 12H), 7.78 (m,12H), 12.85 (s, 6H).$^{13}$C NMR (100 MHz, DMSO, 298 K): δ = 14.31, 61.09, 126.98, 128.57, 130.31, 142.55, 147.93, 165.74. HRMS (ESI) calculated for $[M - H]^-$ m/z: 989.7368, found: 989.6521

**Synthesis of compound 3:** Compound 2 (9.9 mg, 0.1 mmol) was dissolved in 10 mL deionized water, excess KOH was added in to get compound 3. $^{1}$H NMR (400 MHz, $D_2O$, 298 K): δ = 6.92 (m, 12H), 7.59 (m,12H).$^{13}$C NMR (100 MHz, DMSO, 298 K): δ = 126.94, 129.85, 134.29, 139.62, 147.31, 174.39. HRMS (ESI) calculated for $[M - 6H]^-$ m/z: 984.6123, found $[M - 6H\text{-}C_7H_5O_2]^-$: 863.2451

**Computational Details.** Compound 3 was optimized with the density functional theory (DFT) at B3LYP/6-311+G(d) level by Gaussian 09 program, and the solvent effect was included with the polarizable continuum model (PCM).

**Transient absorption spectroscopy.** The pump laser light (~100 fs pulse width) comes from an optical parametric amplifier pumped by a Yb:YAG femtosecond regenerative amplifier (1030 nm, 100 kHz rep-rate). The probe light is a white-light supercontinuum, 450–900 nm. The pump and probe beams overlapped under a small angle. The detection consists of a pair of high-resolution multichannel detector arrays coupled to a high-speed data acquisition system.

**In Vitro Cytotoxicity Assay.** The cell viability of compound 3 was quantitatively determined by cell counting kit-8 (CCK-8) assays. Hela cells were obtained from the cell bank of the Chinese academy of sciences (Shanghai, China), and were seeded into a 96-well plate at a density of $1 \times 10^{-4}$ cells per well in Dulbecco's modified eagle medium (DMEM) containing 10% FBS under 5% $CO_2$ at 37°C. After the cells grew for 12 h, the medium was changed into a new medium (200μL/well) containing compound 3 with different concentrations. After the cells were incubated with the sample for 24 h, the medium was replaced with 100 μL of fresh medium. Subsequently, 10 μL of CCK-8 was added to each well and homogeneously mixed, followed by incubation at 37 ℃ for 4 h in a $CO_2$ incubator, and finally, 80 μL of the solutions were put into a new 96-well plate. After incubation for 3 h, the absorbance at 450 nm in each well was determined using a microplate reader (Multiskan Mk3). The relative cell viability was calculated to quantify the cytotoxicity.

**Confocal Microscopic Images.** Hela cells were seeded in 35 mm plastic-bottomed m-dishes and grown in DMEM medium for 24 h. Then the cells were treated with compound 3 (10 μmol) for another 4 h. The cells were washed with a phosphate buffer saline (PBS) solution (pH 7.4) three times and fixed with polyformaldehyde at 4 ℃ for 15 min. The luminescence images of the cells were captured using a Nikon laser scanning confocal microscope C2+ with FITC channel. The intensities were always read under the same gain.

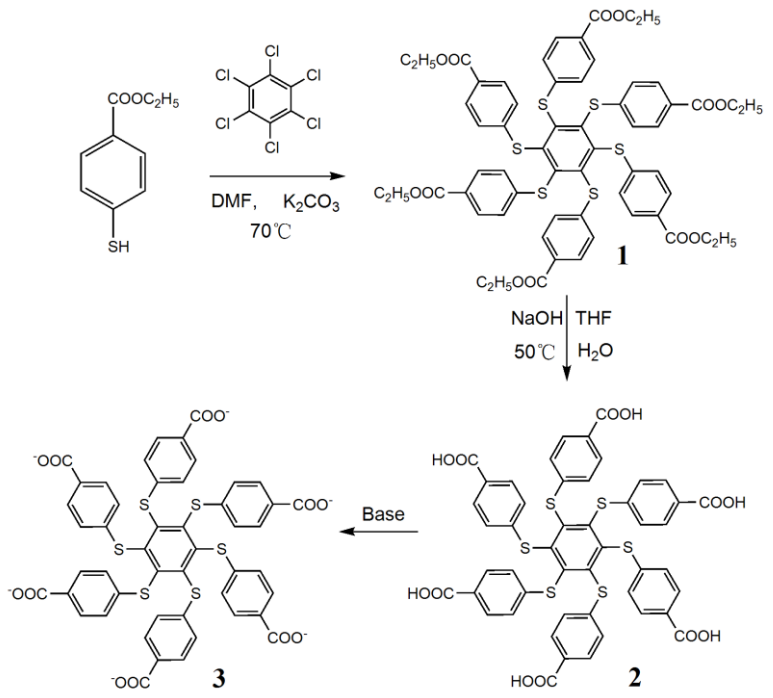


**Figure S1.** Synthetic route for compounds **1**, **2** and **3.**

## 2. Additional Computational Data

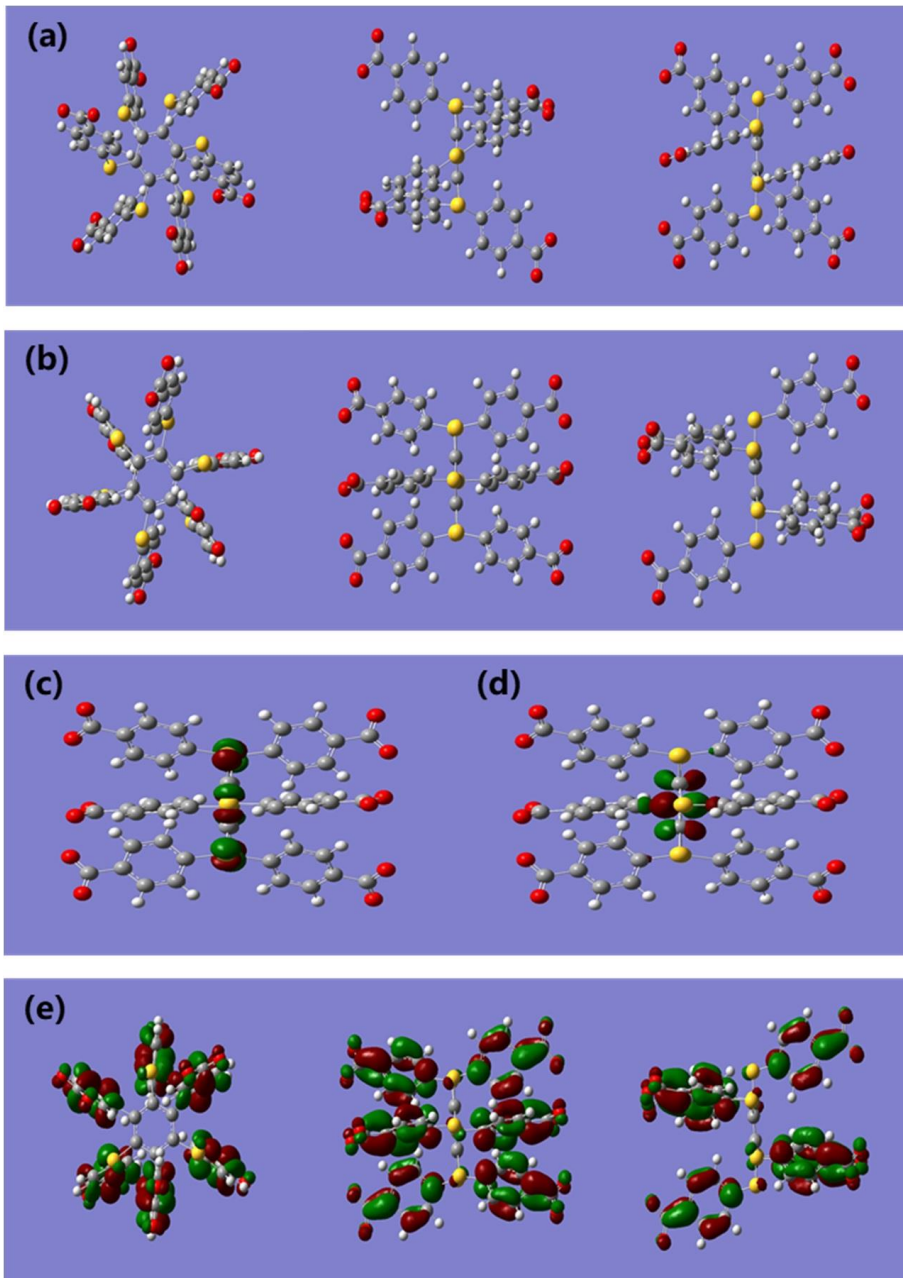


**Figure S2. Equilibrium structures before and after irradiation and relevant molecular orbitals.** (a) The GS geometries at different observational perspectives: torsion 1 = 120 °and torsion 2 = 35 °. (b) The ES1 geometries at different observational perspectives: torsion 1 = 90 °and torsion 2 = 15 °. (c) HOMO, (d) LUMO, and (e) LUMO+7 at different observational perspectives at the equilibrium geometry of ES1. The lowest excited state is a non-emissive state, which is mostly contributed by HOMO to LUMO transition. As a representative emissive state, the 54th excited state is dominated by HOMO to LUMO+7 transition. In this case, there exists significant overlap between HOMO and LUMO+7 around the sulfur atoms.

## 3. Additional Photophysical Experimental Data

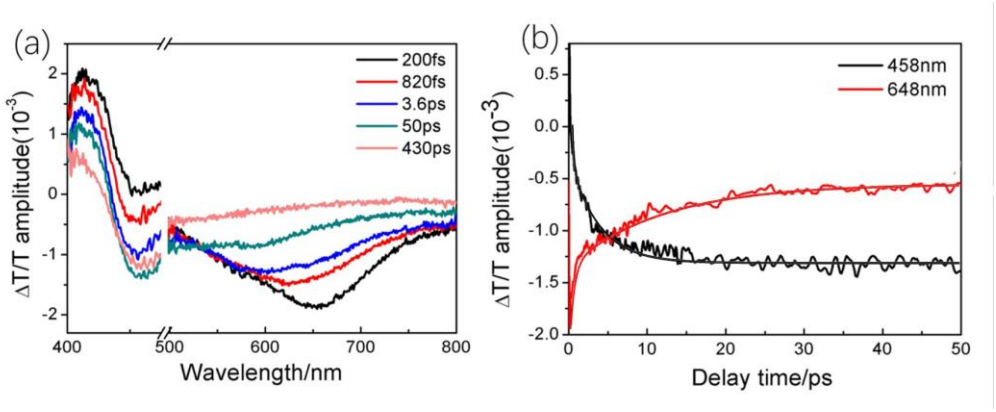


**Figure S3**. **Transient absorption data.** (a) Femtosecond transient absorption spectral signatures of 3 and (b) two-exponential fitting of the kinetics of signals at 458 nm and 648 nm in water, pumped by 370 nm

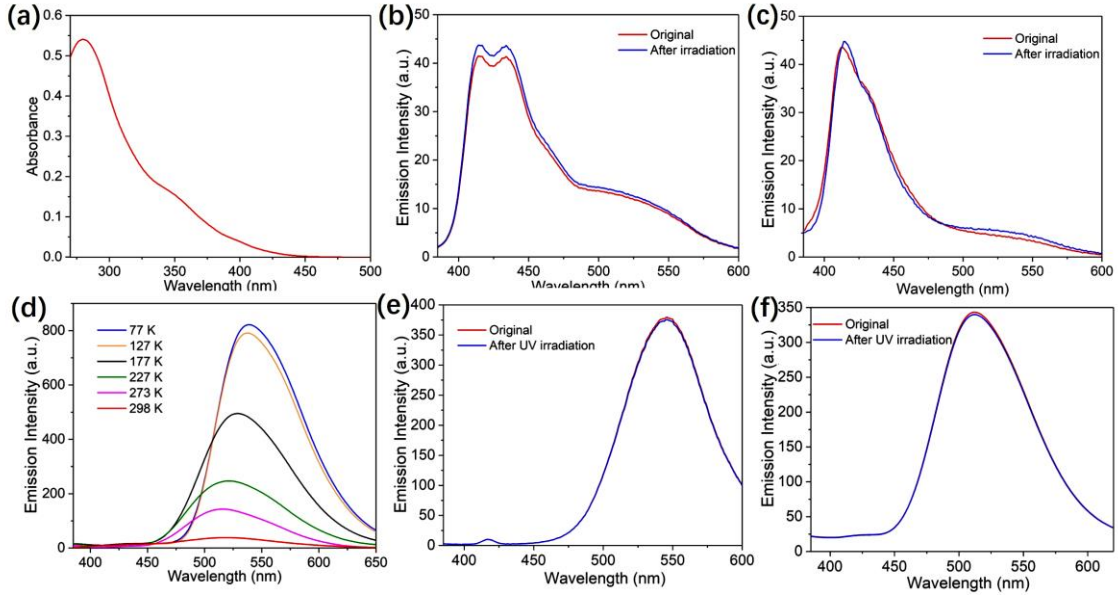


**Figure S4**. **Additional photophysical data of 2 and 3.** (a) Absorption spectra of 2 in DMF ($1 \times 10^{-5}$ M). (b) Emission spectra of 2 in DMF before and after irradiation for 5 min ($1 \times 10^{-5}$ M). (c) The emission spectra of 3 in DMF before and after irradiation for 5 min ($1 \times 10^{-5}$ M). (d) Temperature-dependent (From 77K to 298K) emission spectra of 3 in aqueous solution. (e) Emission spectra of 2 in $H_2O$ before and after irradiation for 5 min ($1 \times 10^{-5}$ M). (f) The emission spectra of 3 in solid power state before and after irradiation for 5 min.

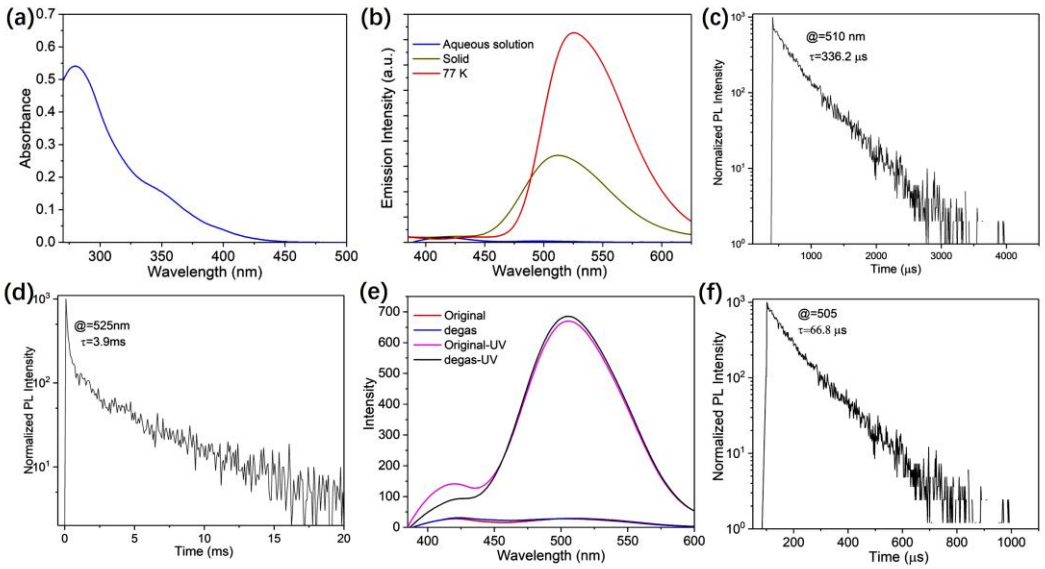


**Figure S5. Photophysical properties of 3.** (a) Absorption spectra in aqueous solution ($1 \times 10^{-5}$M). (b) Photoluminescence spectra in different states. (c)Photo-luminescent (PL) lifetimes of 3 for its powder state. (d) PL lifetimes of 3 in rigid matrices at 77 K. (e) The Emission spectra of 3 in $H_2O$ before and after degassing and followed by irradiation for 5 min. It was degassed by three cycles of freeze-pump-thaw. After the final thaw cycle, the flask was backfilled with $N_2$. (f) PL lifetimes of compound 3 after degassed.

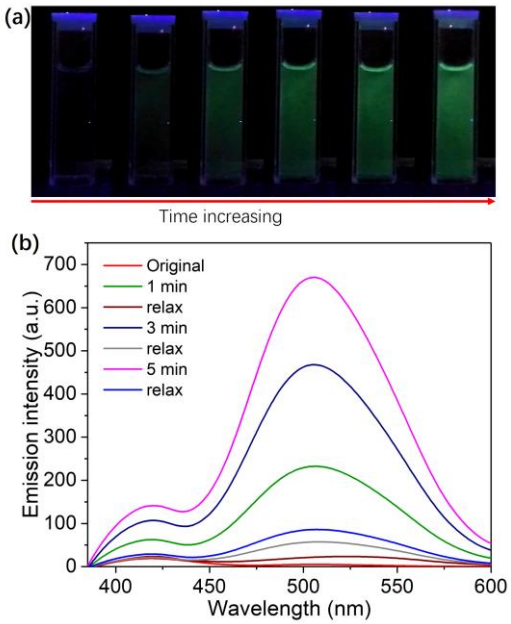


**Figure S6.** (a) The increase of the emission signal of 3 in aqueous solution along with the irradiation time prolonged. (b) The emission change of 3 in aqueous solution after irradiation for different time, followed by the relax without irradiation for the same period.

## 4. Additional Fundamental Characteristics

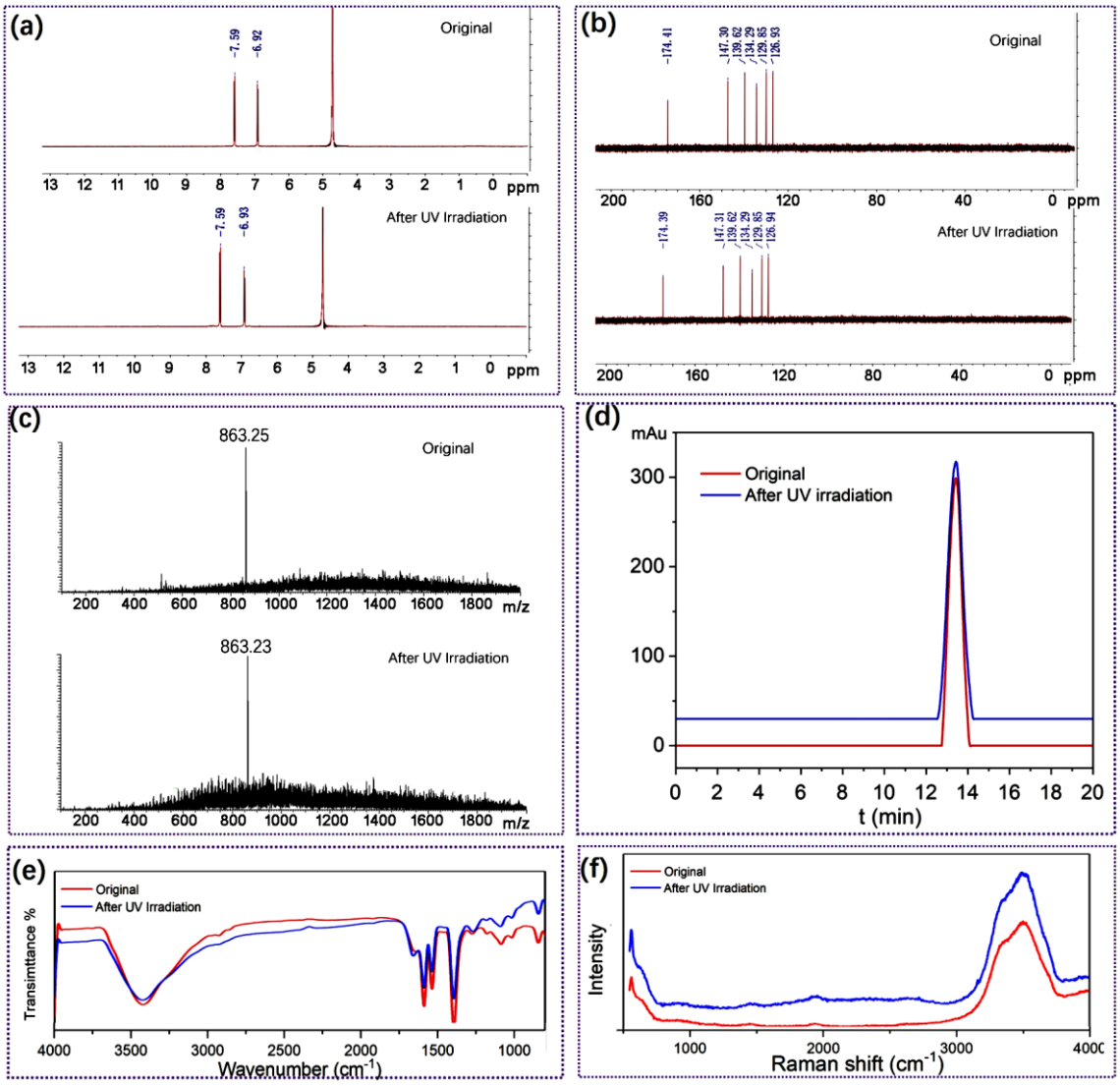


**Figure S7. Additional fundamental characteristics before and after irradiation.** (a) The $^{1}$HNMR spectra of 3 in $D_2O$ before and after UV irradiation for 5 min. (b) The $^{13}$CNMR spectra of 3 in $D_2O$ before and after UV irradiation for 5 min. (c) The ESI-MS spectra of 3 before and after UV irradiation for 5 min. (d) The HPLC spectra of 3 before and after UV irradiationfor 5 min. (e) The FTIR spectra of 3 before and after UV irradiation for 5 min. (f) The Raman spectra of 3 before and after UV irradiation for 5 min.

## 5. Additional Dynamics Study

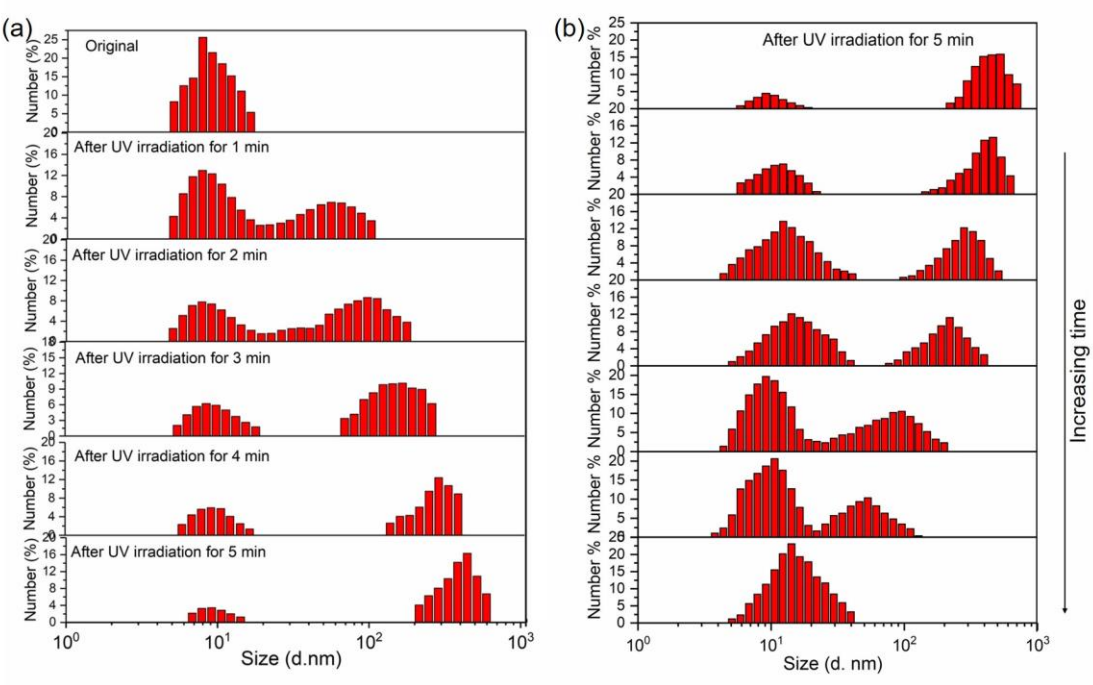


**Figure S8. Time dependent DLS signal of 3.** (a) The aggregation data in water upon irradiation. (b) The dissociation data of 3 after irradiation with relax time increasing.

## 6. Additional Bioimaging Study

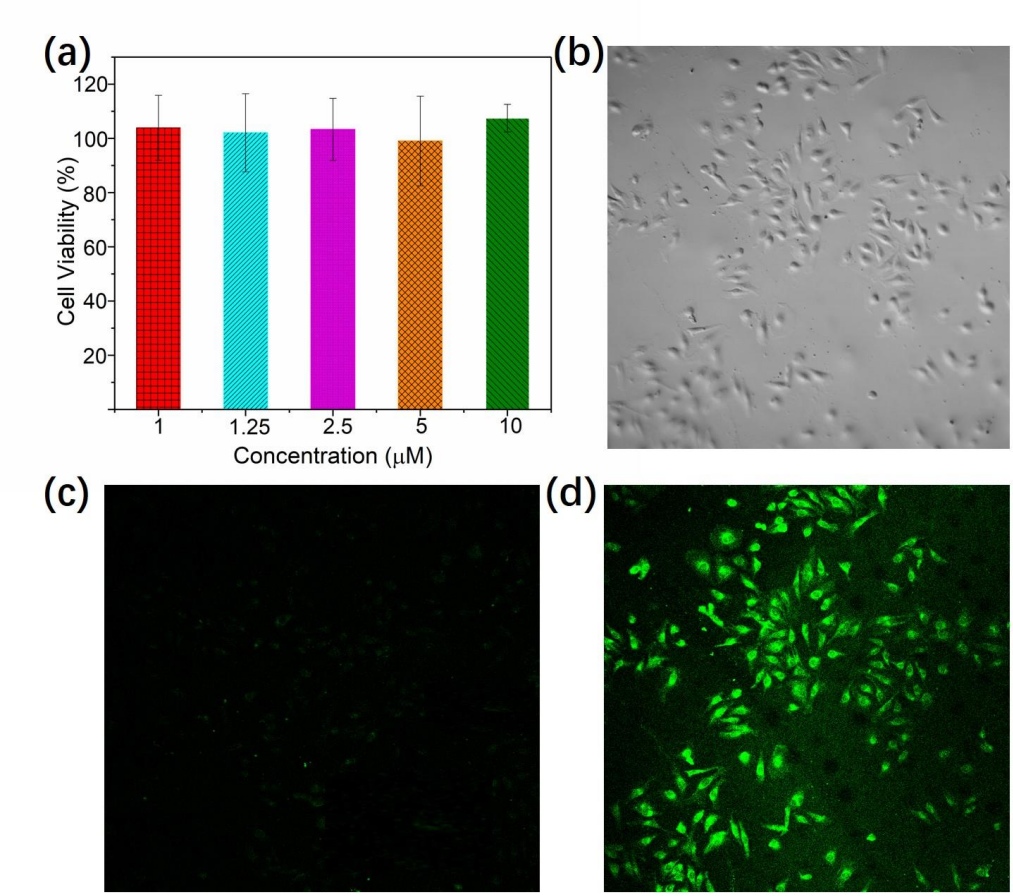


**Figure S9**. **Cell toxicity and cell imaging.** (a) Cell viability examination at different concentrations of 3. (b) CLSM images of cells under bright field. CLSM images of cells under channel of 488 nm (c) before and (d) after irradiation.

## 7. Visualized Patterning Experiment

A video (speed x10) for the visualized patterning experiment was uploaded separately: We can see an "F" character by emission flicker effect since the cell solution dyed with 3 is in the corresponding wells, whereas the cell solution dyed with any green-light emitters is in the rest of wells as luminescent surrounding. In contrast, if the probe emission is static, it will be difficult to distinguish.

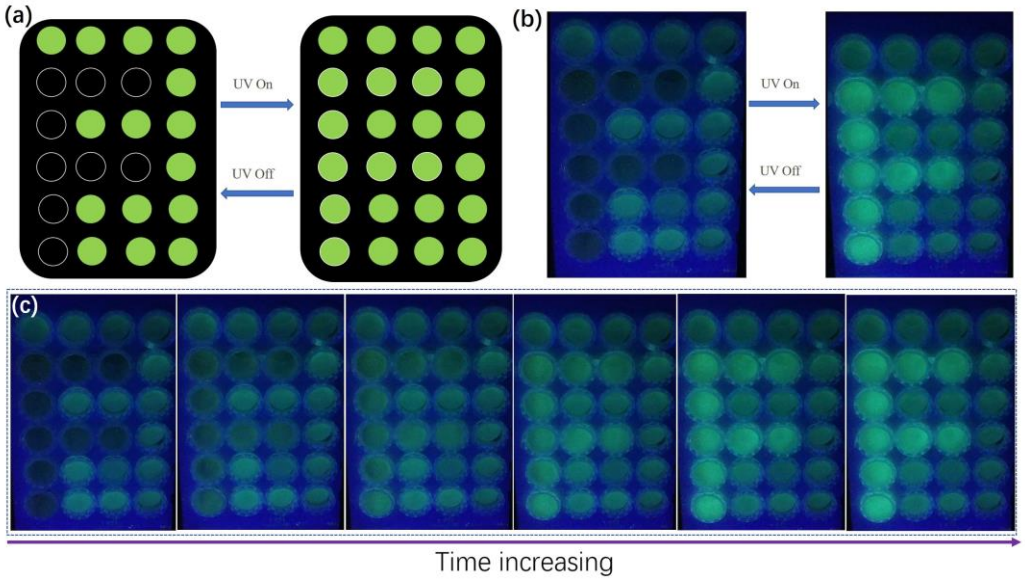


**Figure S10**. **Visualized patterning experiment.** (a) Simulated flickering emission strategy to identify the label from luminescent surrounding. (b) The exact experiment to identify the cell solution from luminescent surrounding. (c) Continuous enhancement of luminescence of the cell solution dyed with 3 with prolonging the irradiation time. Cell solution dyed with any green-light emitters show green luminescence at 365 nm before and after UV irradiation，while Cell solution dyed with solution of 3 show no luminescence before UV irradiation and green luminescence after UV irradiation.

**Movie S1.** Flicker emission effect in the visualized patterning experiment in 10 cycles.