

Supporting Information

Switchable Circularly polarized luminescence in supramolecular gels through photo-modulated FRET

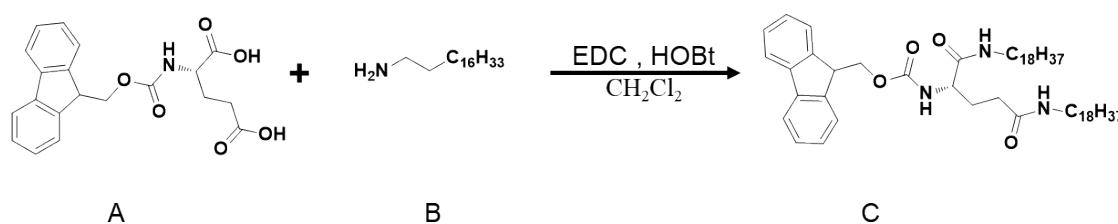
Sifan Du,^{†,‡} Xuefeng Zhu,[†] Li Zhang,^{*,†} and Minghua Liu^{*,†,‡}

[†] Beijing National Laboratory for Molecular Science (BNLMS), CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China

[‡] University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

Corresponding author: zhangli@iccas.ac.cn, liumh@iccas.ac.cn

1. Synthesis of chiral Fmoc-L-Glu-2C18 (FLG)



Scheme S1. Synthetic route of FLG. A: Fmoc-L-glutamic acid; B: 1-octadecylamine; C: FLG.

The mixture of 9-fluorenylmethoxycarbonyl-L-glutamic acid (A, 1.0 g, 369.12, 2.71 mM) and 1-octadecylamine (B, 1.46 g, 269.31, 5.42 mM) were firstly stirred for 30 min in dichloromethane (200 mL). Thereafter, 1-hydroxybenzotriazole (HOBt; 0.74 g,

135.12, 5.42 mM) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl; 1.56 g, 191.7, 8.13 mM) were added to the reaction mixture. Then the mixture was stirred for 5 days. The crude white product was isolated by evaporation with rotated-dried dichloromethane. The crude product was then dissolved in tetrahydrofuran (50 mL) and the solution was poured into saturated NaHCO₃ aqueous solution (500 mL) with stirring for 20 mins and setting for 2 hours. Then the solution was removed by filtration. After the washed product dried, the white product was dissolved in ethanol (50 mL) by heating and then the hot solution was poured into HCl aqueous solution (500 mL). After filtration and dried, the white product was purified by recrystallization for four times in ethanol solution to give the target compounds FLG (C, 1.5 g, 63.6% yield) .

¹H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 6.68 (s, 1H), 6.24 (s, 1H), 5.78 (s, 1H), 4.37 (d, *J* = 7.2 Hz, 2H), 4.22 (t, *J* = 7.2 Hz, 1H), 4.18 – 4.10 (m, 1H), 3.24 (m, 4H), 2.30 (t, *J* = 7.7 Hz, 2H), 2.08 (m, 1H), 1.95 (m, 1H), 1.50 (m, 4H), 1.25 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 6H).

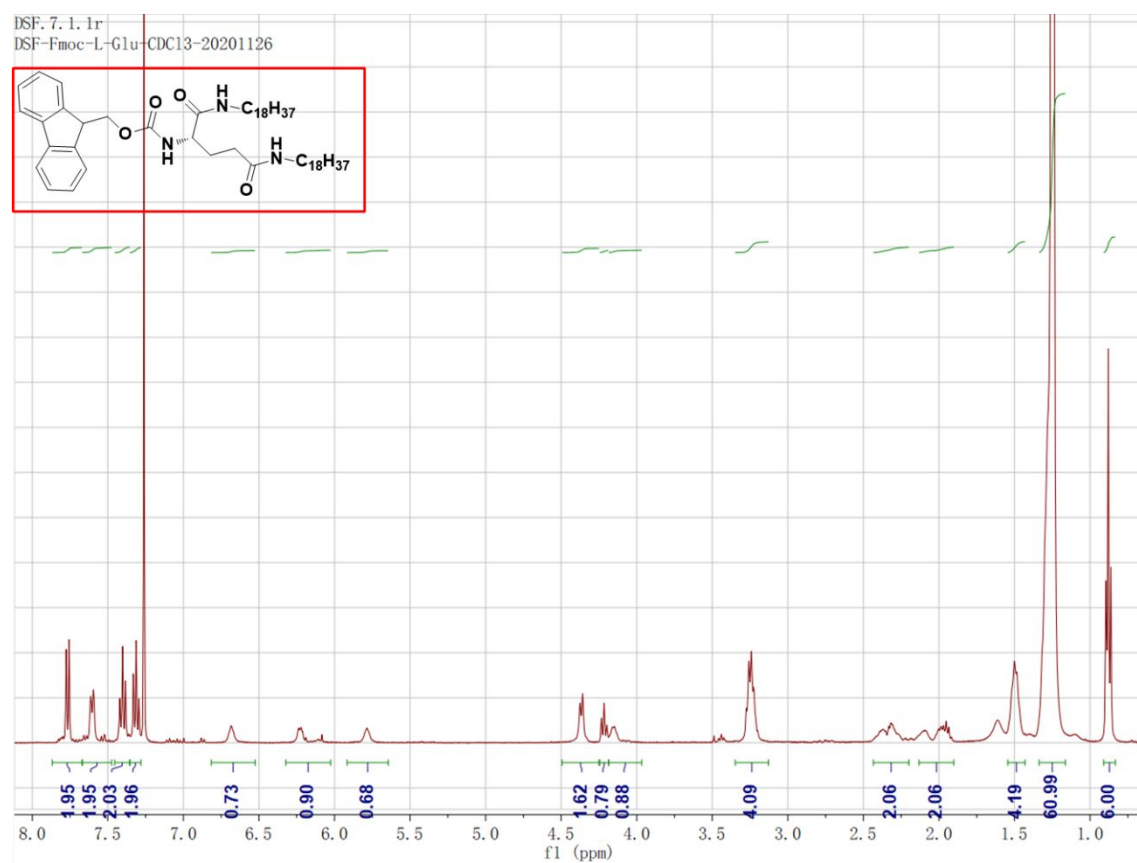


Figure S1. ¹H NMR spectrum of FLG. Note that the peak at 7.27 ppm and 1.76 ppm are attributed to the residual solvent peak of CD₃Cl and D₂O respectively.

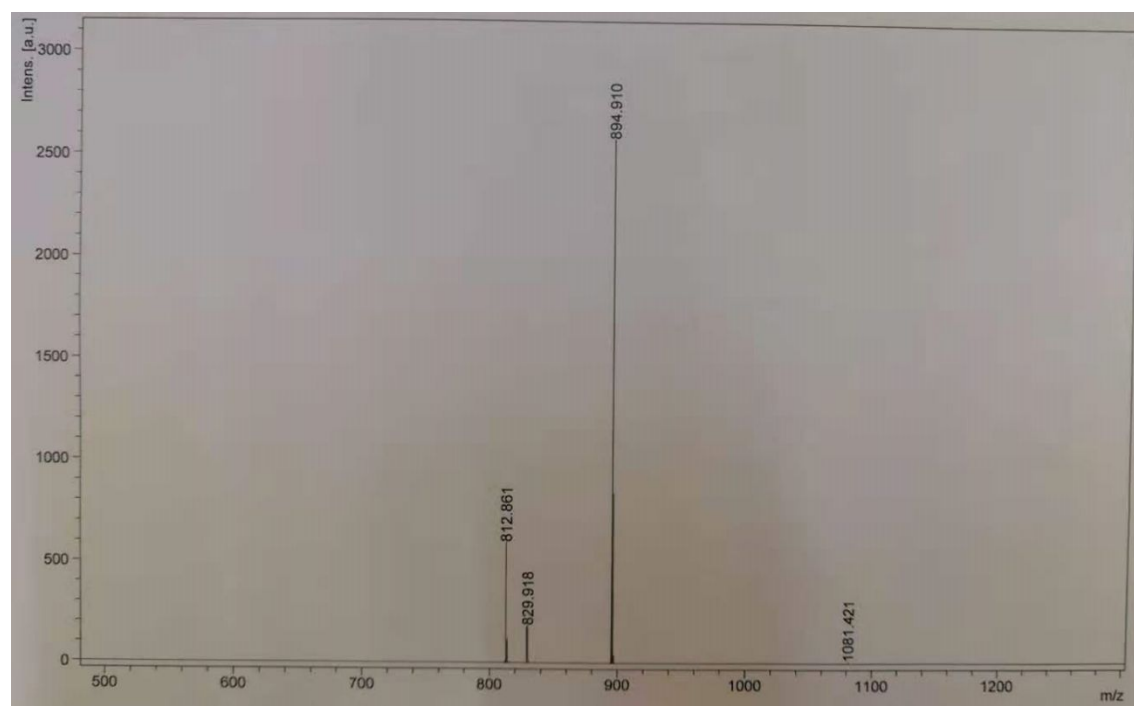


Figure S2. MALDI-TOF MS of FLG.

2. Supplementary Figures

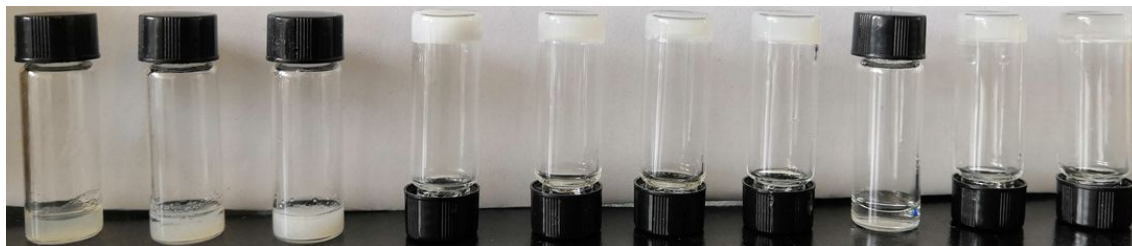


Figure S3. Pictures of FLG assembled in different solvents. From left to right are DMSO, DMF, methanol, acetonitrile, ethanol, acetone, ethyl acetate, THF, dichloromethane, methyl cyclohexane. Note that the concentration of FLG in all solvents is kept at 10 mg/ml.

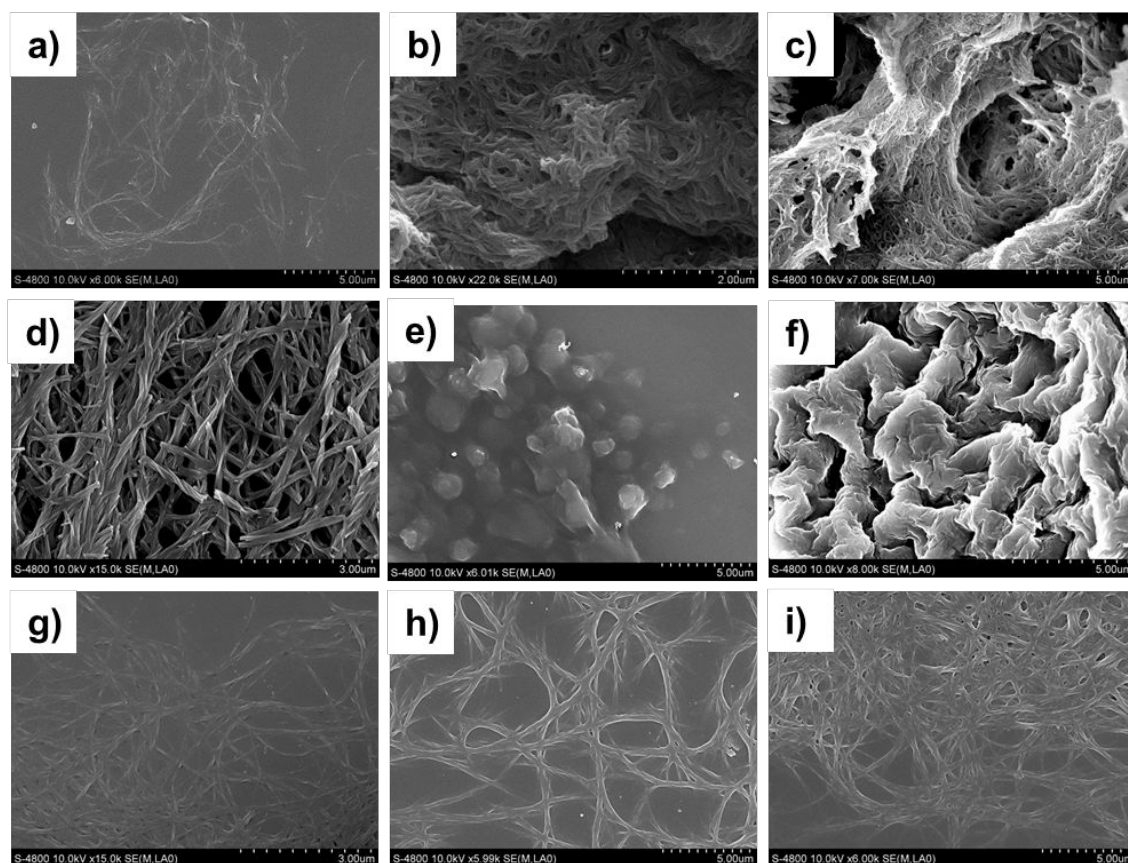


Figure S4. SEM images of FLG in different solvents. a-i) DMSO, DMF, MeOH, acetonitrile, methyl cyclohexane, acetone, ethyl acetate, THF, dichloromethane. The concentration of FLG in all solvents is kept at 10 mg/ml.

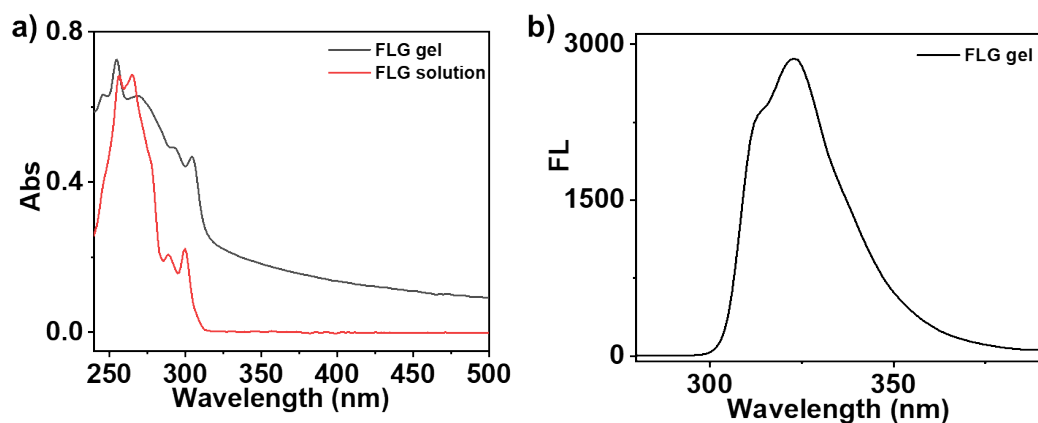


Figure S5. a) UV-vis spectra of FLG in the solution state and gel state. b) Fluorescence spectrum of FLG in the gel state. The concentration FLG gel was kept at 11.5 mM and the FLG solution was kept at 0.23 mM.

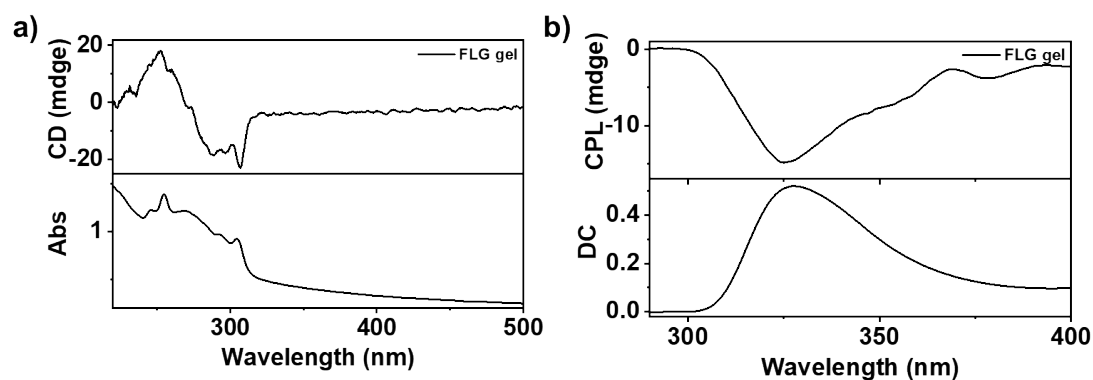


Figure S6. a, b) CD and CPL spectra of FLG in the ethanol gel.

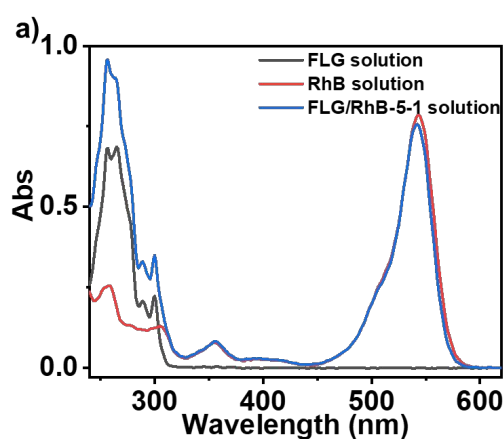


Figure S7. a) UV-vis spectra of FLG, RhB and their mixed solutions in ethanol. The concentration FLG solution was kept at 0.23 mM and the RhB solution was kept at 0.046 mM.

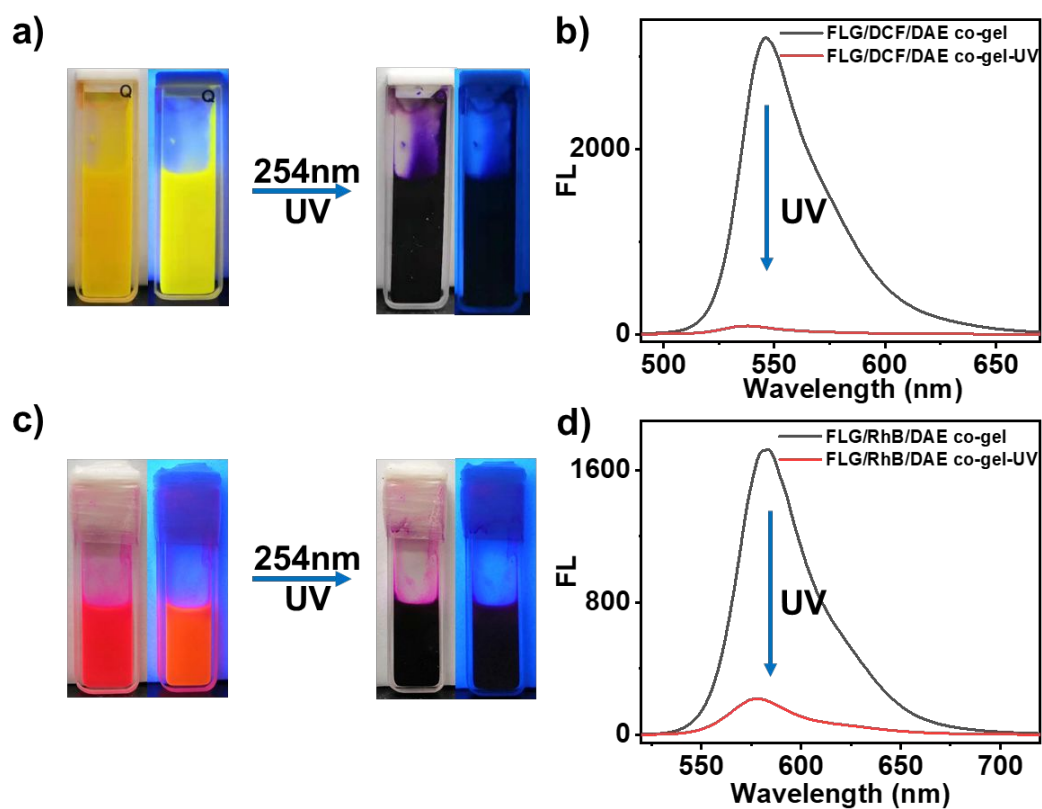


Figure S8. a, c) Photos of FLG/DCF/DAE and FLG/RhB/DAE three-component co-gels in a quartz cell before and after irradiated with UV (under natural light (left) and 365 nm UV light (right)). b, d) Fluorescence spectra for the three-component co-gel upon UV light irradiation.

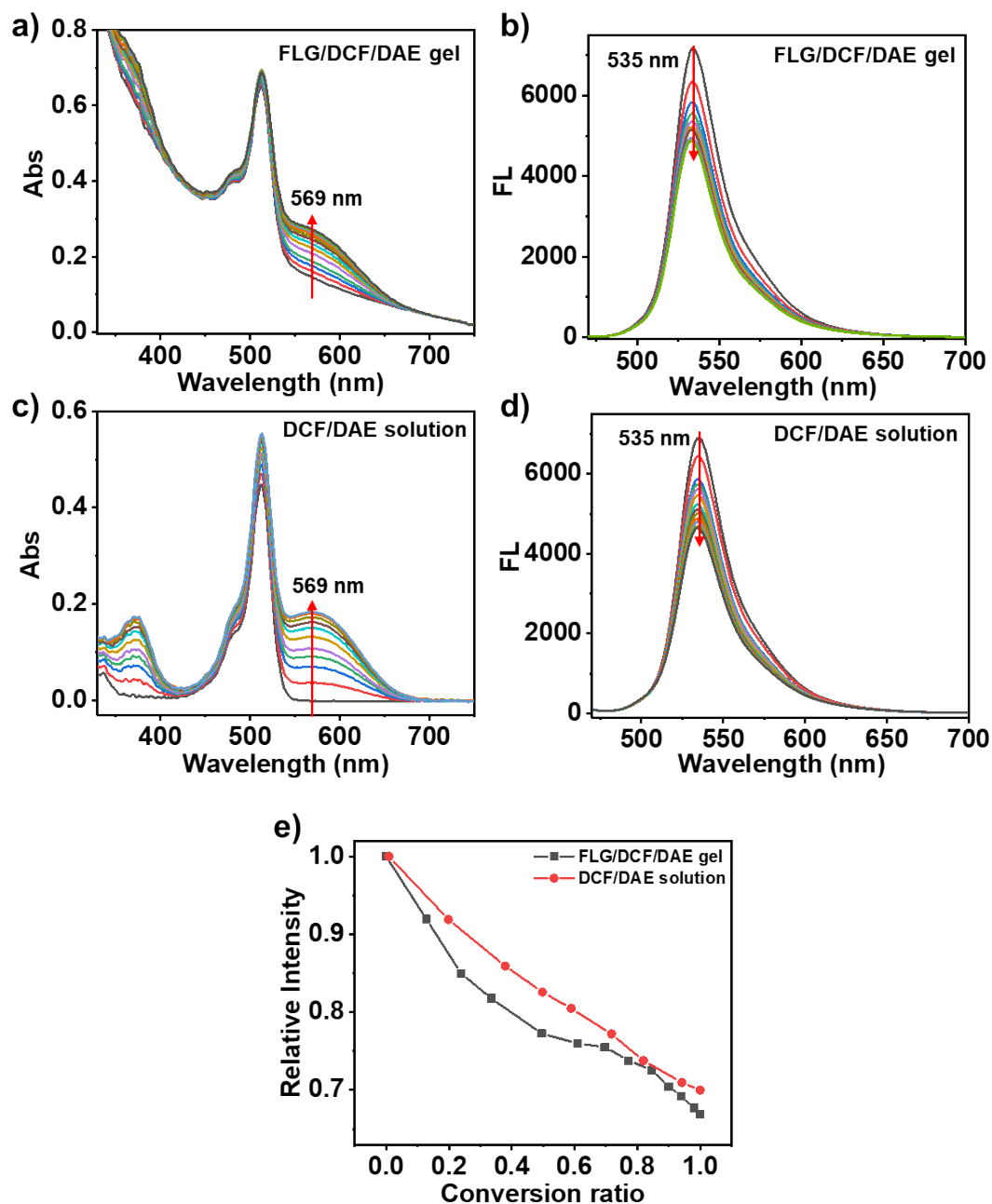


Figure S9. a, c) UV-vis spectra and b, d) Emission spectra of the FLG/DCF/DAE co-assembled gel and DCF/DAE solution in ethanol upon irradiation with 254 nm light ($\lambda_{\text{ex}}=470$ nm). e) Fluorescence intensity versus conversion yield (CY) of C-DAE correlation plots, plotted from DCF/DAE solution (red dots) and FLG/DCF/DAE gel (black squares). The concentration of DCF and DAE in DCF/DAE solution and FLG/DCF/DAE gel was kept at 0.046 mM and 0.14 mM, respectively. The concentration of FLG in FLG/DCF/DAE gel was kept at 3.8 mM.

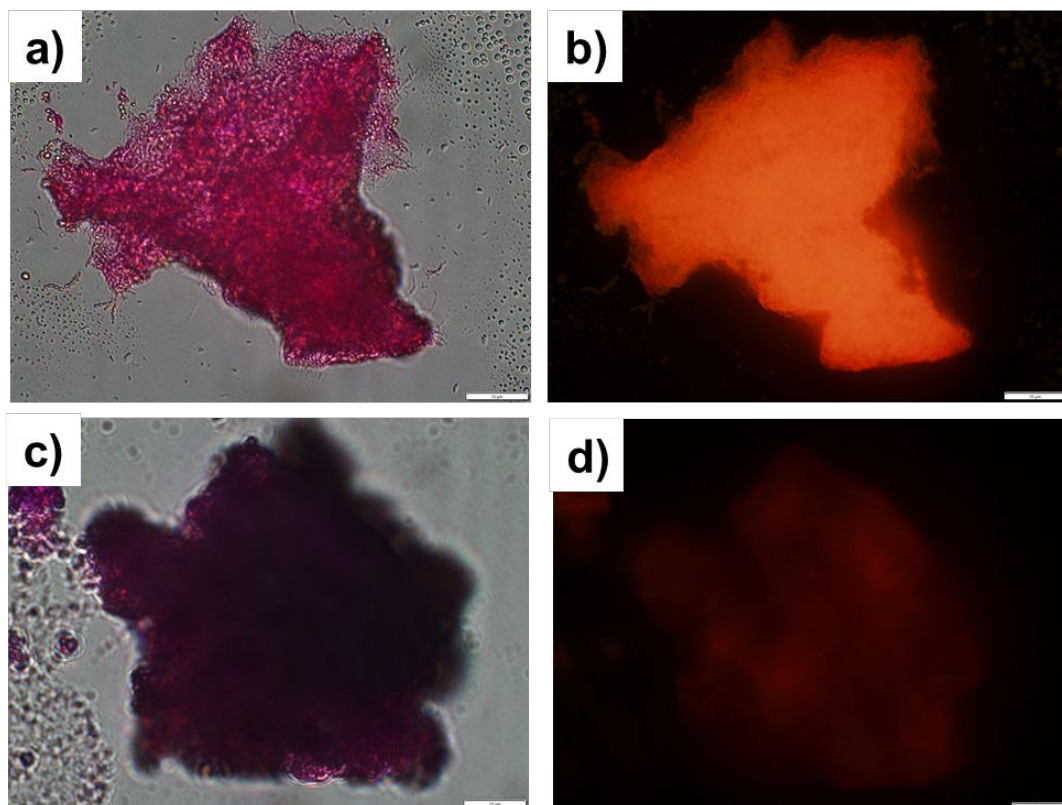


Figure S10. a, c) Optical microscopy images and b, d) Fluorescence microscopy images of FLG/RhB/DAE ethanol co-gel before and after irradiated with UV light.

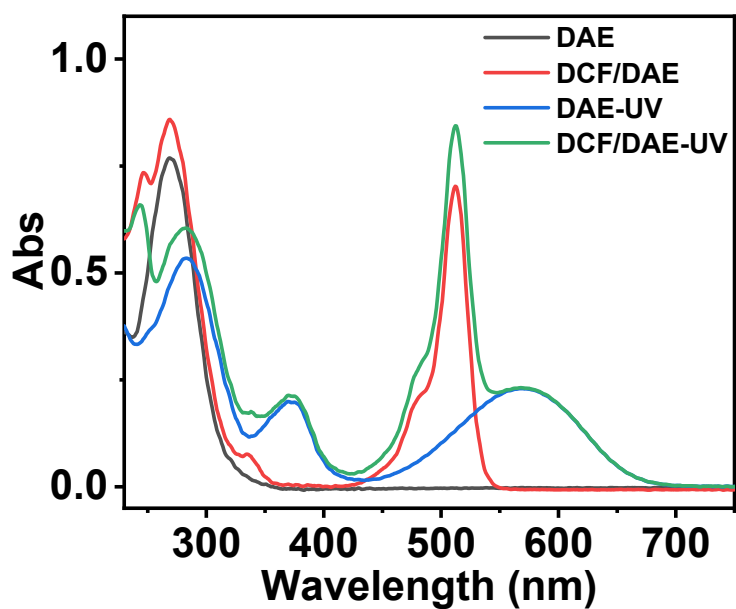


Figure S11. UV-vis spectra of DAE solution and DCF/DAE mixture solution in ethanol before and after UV irradiation with 254nm light. The concentration of DAE in both DAE solution and DCF/DAE solution was kept at 0.14 mM and the DCF in DCF/DAE solution was kept at 0.046 mM.

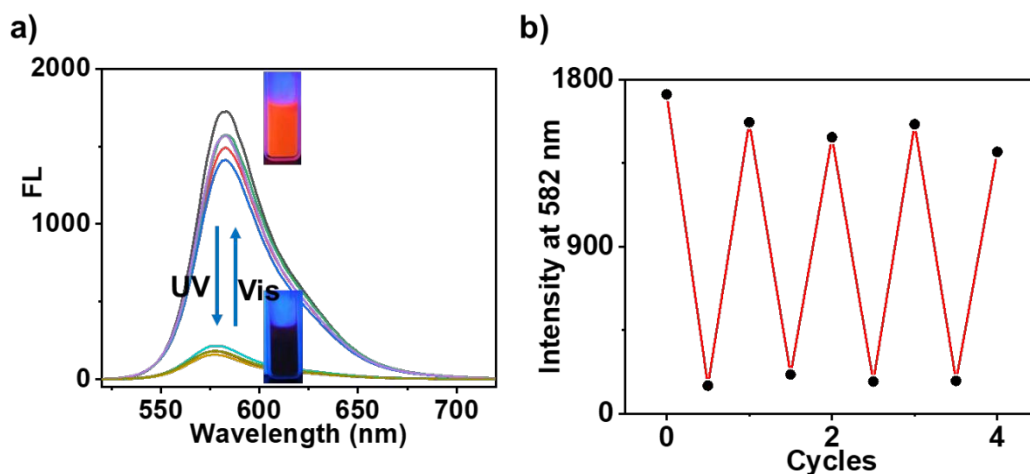


Figure S12. a, b) Fluorescence spectra and intensity changes at 582 nm for the three-component co-gel upon alternating UV and visible light irradiation. The inset represented fluorescent images of three-component co-gel before and after irradiated with UV, observed under 365 nm light.

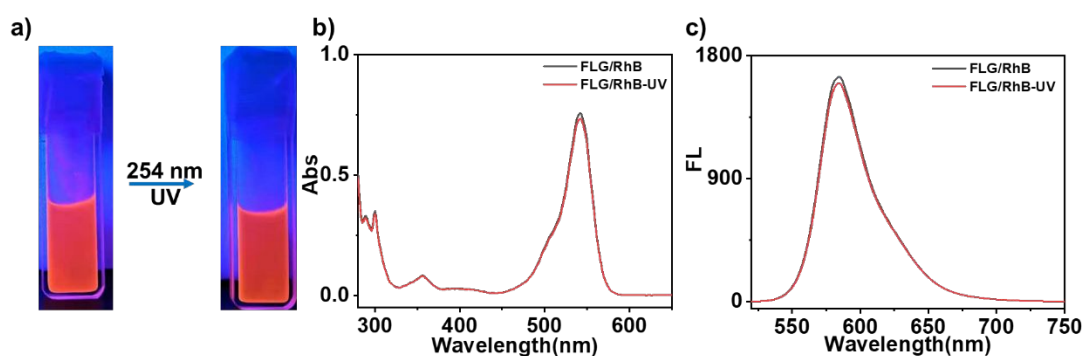


Figure S13. a) Fluorescence images of FLG/RhB co-gel before and after UV irradiation, observed under 365 nm light. b, c) UV-Vis and Fluorescence spectra for the FLG/RhB co-gel upon before and after UV light irradiation.

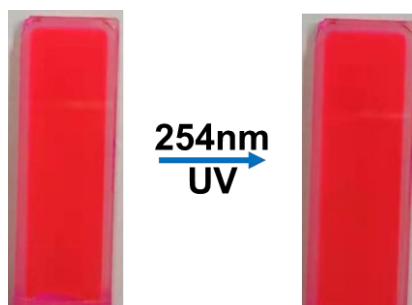


Figure S14. Photos covered with characters of FLG/RhB two-component co-gel in a quartz cell before and after irradiated with UV.