

Supplementary Information

Photochromism via Reversible Transformation of Photoinduced Chiral Free Radicals

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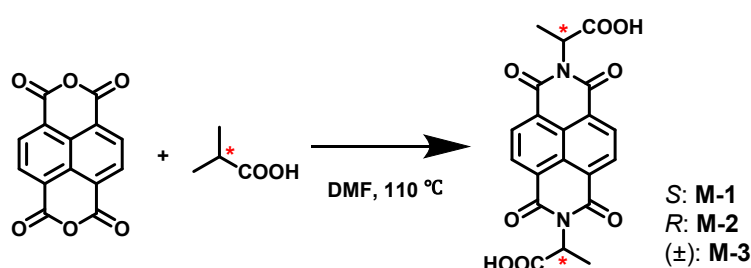
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1. General

All reactions were purchased from Aldrich and available chemicals were used without further purification. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker 500 spectrometer in $\text{DMSO-}d_6$ at room temperature. Mass spectra were measured on a Agilent 6545 QTOF. The UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 750 spectrophotometer. The emission spectra were measured using an Edinburgh FLS1000 equipped with a xenon lamp. 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 $400\text{--}4000\text{ cm}^{-1}$. The CD spectra were obtained from J1821410 Spectrophotometer.

2. Synthesis Procedures.



Scheme S1. Synthetic route of **M-1**, **M-2**, **M-3**

Synthesis of M-1: A mixture of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (268.0 mg, 1.00 mmol) and *S*-alanine (267 mg, 3.0 mmol) was dissolved in anhydrous DMF (20.0 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 12 h. After cooling to room temperature, the solution was poured into aqueous HCl (30 mL, 1 M) to precipitate the product. The resulting solid was collected and washed with diethyl ether to afford M-1 as a yellow solid (307.5 mg, 75.0% yield). ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 12.83 (s, 2H), 8.73 (s, 4H), 5.70 – 5.53 (m, 2H), 1.71 – 1.49 (m, 6H). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$): δ 171.4, 162.6, 131.4, 126.7, 126.7, 49.5, 14.9. HRMS (ESI): calculated for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_8$ $[\text{M}+\text{H}]^+$, 411.0823; found: 411.0836.

Synthesis of M-2: A mixture of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (268.0 mg, 1.00 mmol) and *R*-alanine (267 mg, 3.0 mmol) was dissolved in anhydrous DMF (20.0 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 12 h. After cooling to room temperature, the solution was poured into aqueous HCl (30 mL, 1 M) to precipitate the product. The resulting solid was collected and washed with diethyl ether to afford M-1 as a yellow solid (323.9 mg, 79.0% yield). ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 12.78 (s, 1H), 8.74 (s, 4H), 5.64 – 5.59 (m, 2H), 1.60 – 1.55 (m, 6H). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$): δ 171.5, 162.5, 131.4, 126.7, 49.5, 14.9. HRMS (ESI): calculated for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_8$ $[\text{M}+\text{H}]^+$, 411.0823; found: 411.0844.

Synthesis of M-3: A mixture of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (268.0 mg, 1.00 mmol) and alanine (267 mg, 3.0 mmol) was dissolved in anhydrous DMF (20.0 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 12 h. After cooling to room temperature, the solution was poured into aqueous HCl (30 mL, 1 M) to precipitate the product. The resulting solid was collected and washed with diethyl ether to afford M-1 as a yellow solid (299.3 mg, 73.0% yield). ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 12.83 (s, 2H), 8.73 (s, 4H), 5.70 – 5.53 (m, 2H), 1.71 – 1.49 (m, 6H). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$): δ 171.6, 162.6, 131.4, 126.7, 49.5, 14.6.

HRMS (ESI): calculated for $C_{20}H_{15}N_2O_8$ $[M+H]^+$, 411.0823; found: 411.0829.

3. Additional results

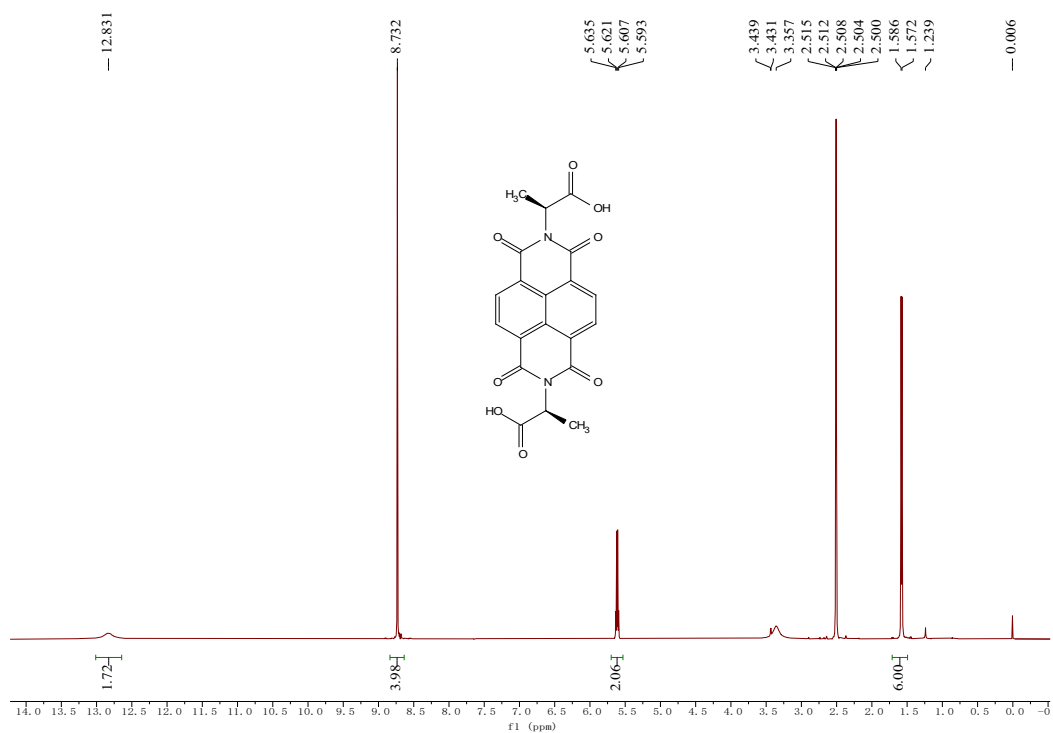


Figure S1. 1H NMR (500 MHz, $DMSO-d_6$, 298 K) spectrum of compound **M-1**.

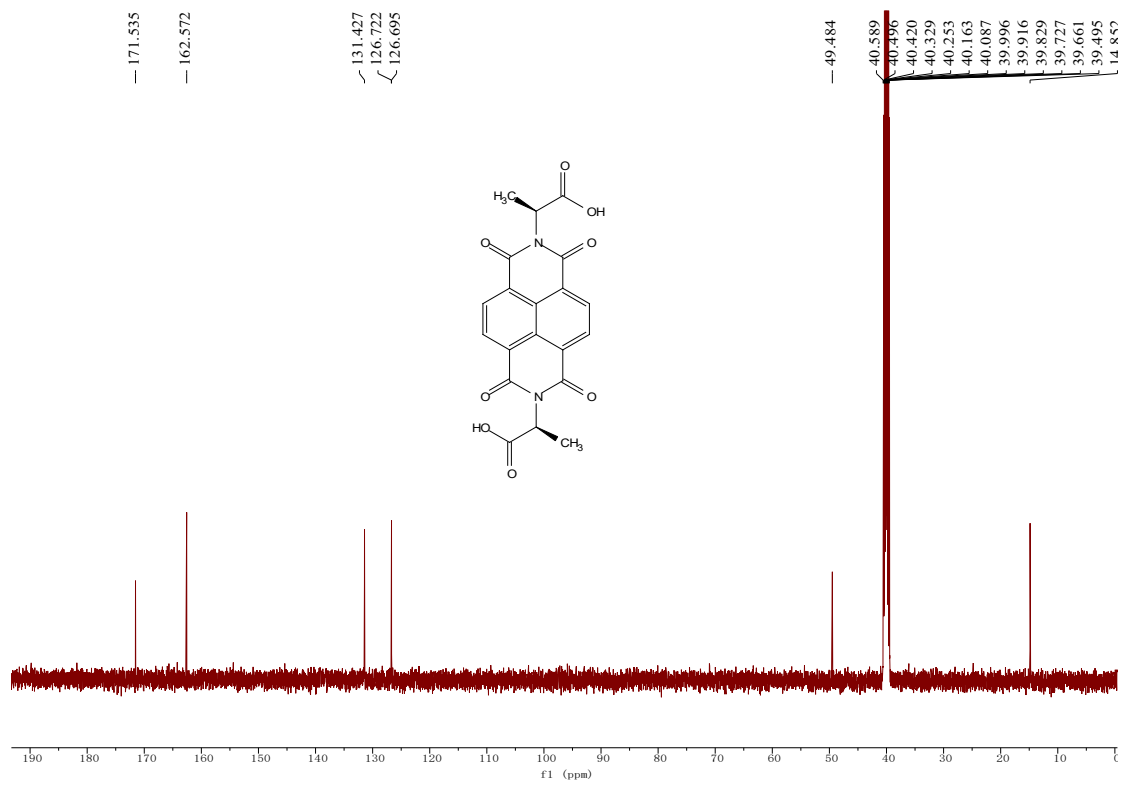


Figure S2. ¹³C NMR (125 MHz, DMSO-*d*₆, 298 K) spectrum of compound M-1.

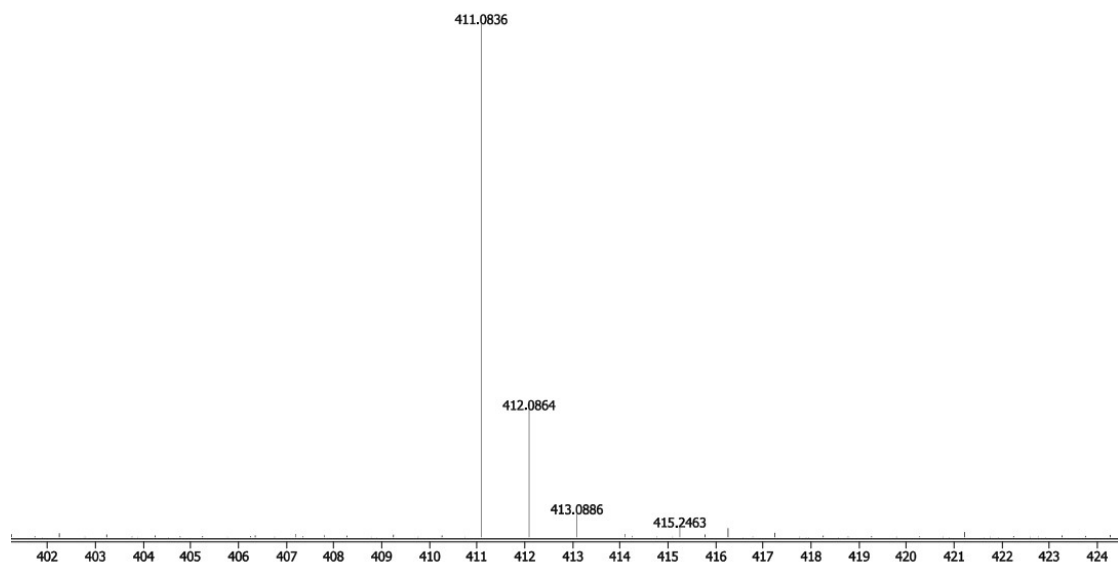


Figure S3. HRMS spectrum of compound M-1.

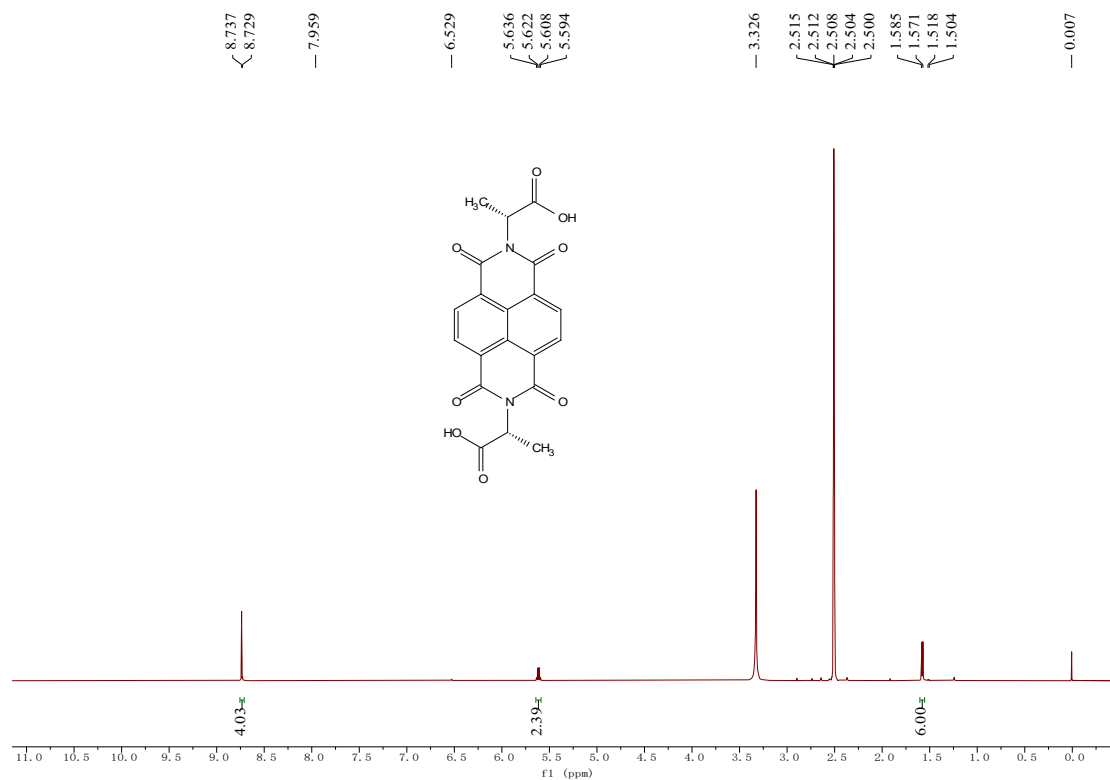


Figure S4. $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$, 298 K) spectrum of compound **M-2**.

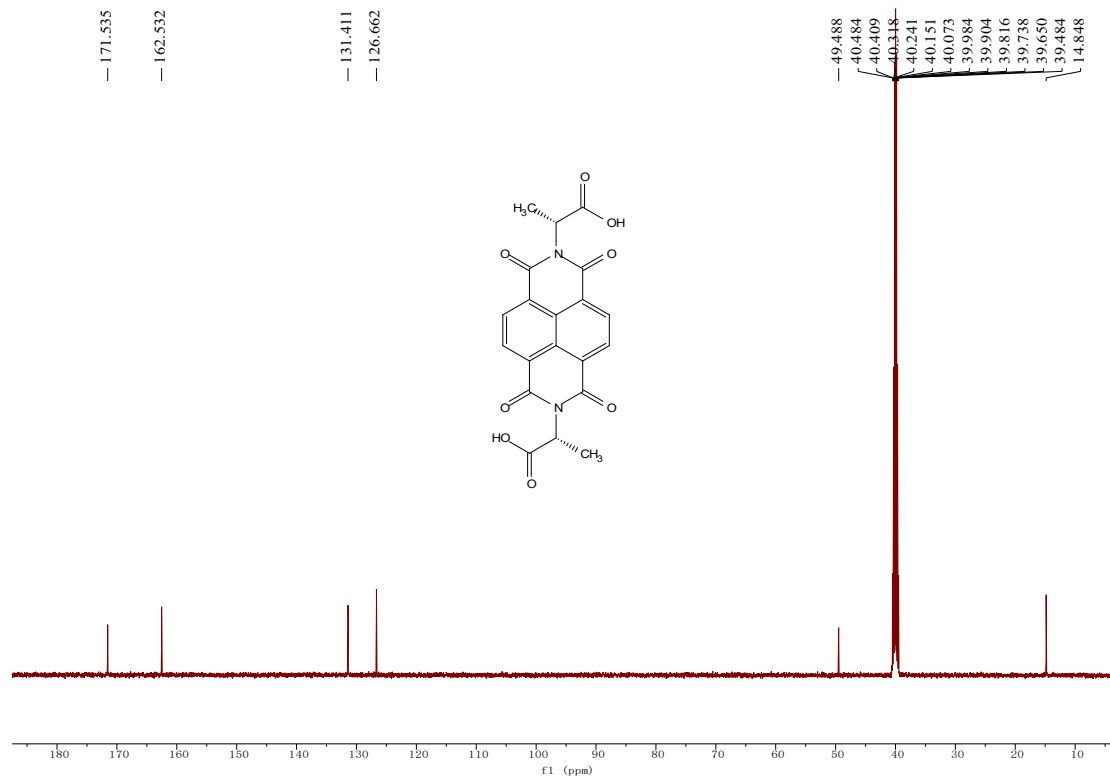


Figure S5. $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$, 298 K) spectrum of compound **M-2**.

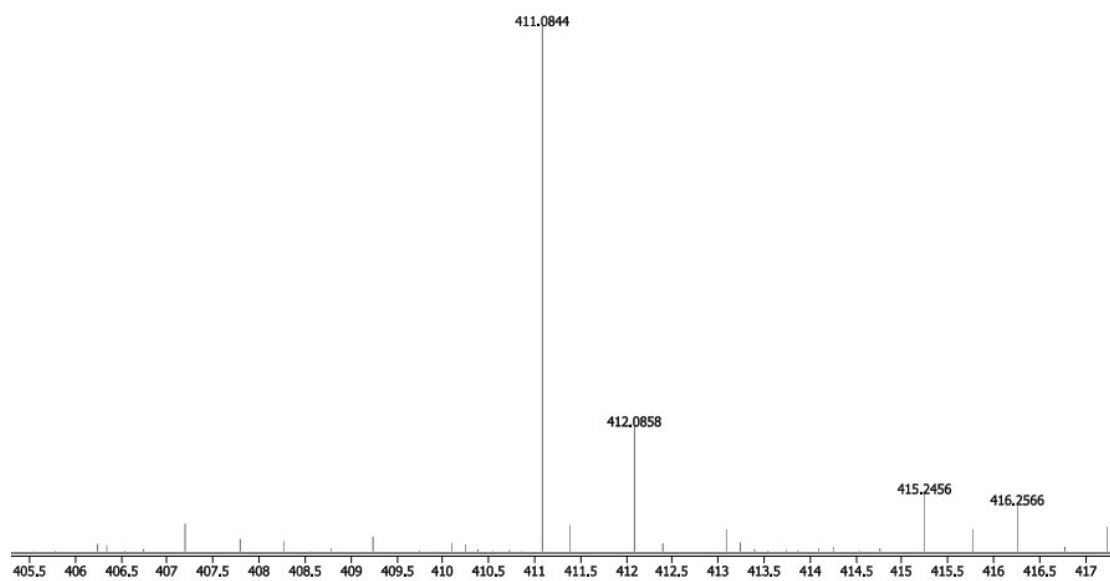


Figure S6. HRMS spectrum of compound M-2.

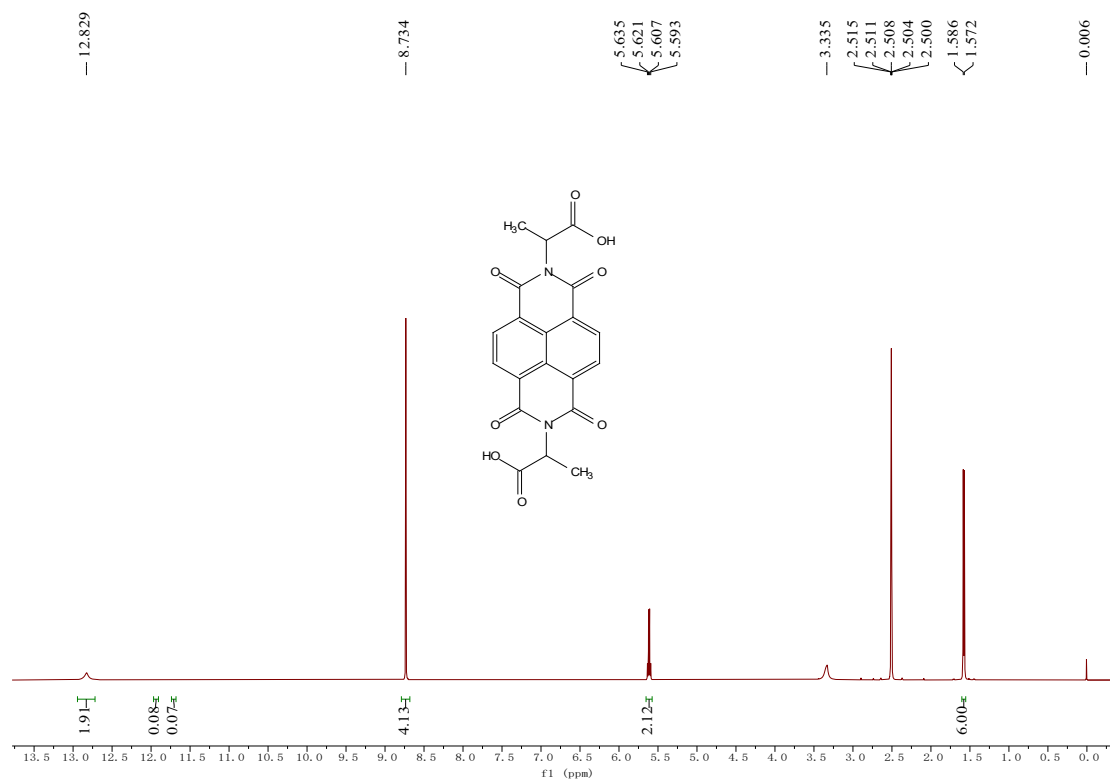


Figure S7. ¹H NMR (500 MHz, DMSO-*d*₆, 298 K) spectrum of compound M-3.

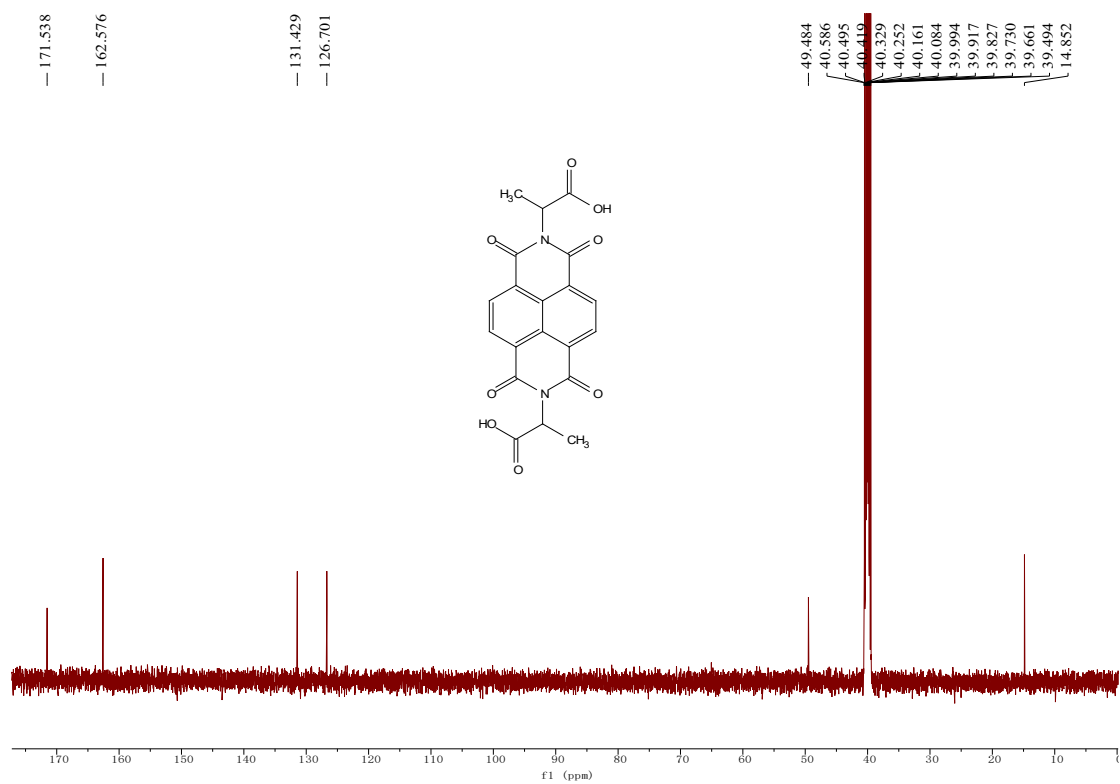


Figure S8. ¹³C NMR (125 MHz, DMSO-*d*₆, 298 K) spectrum of compound M-3.

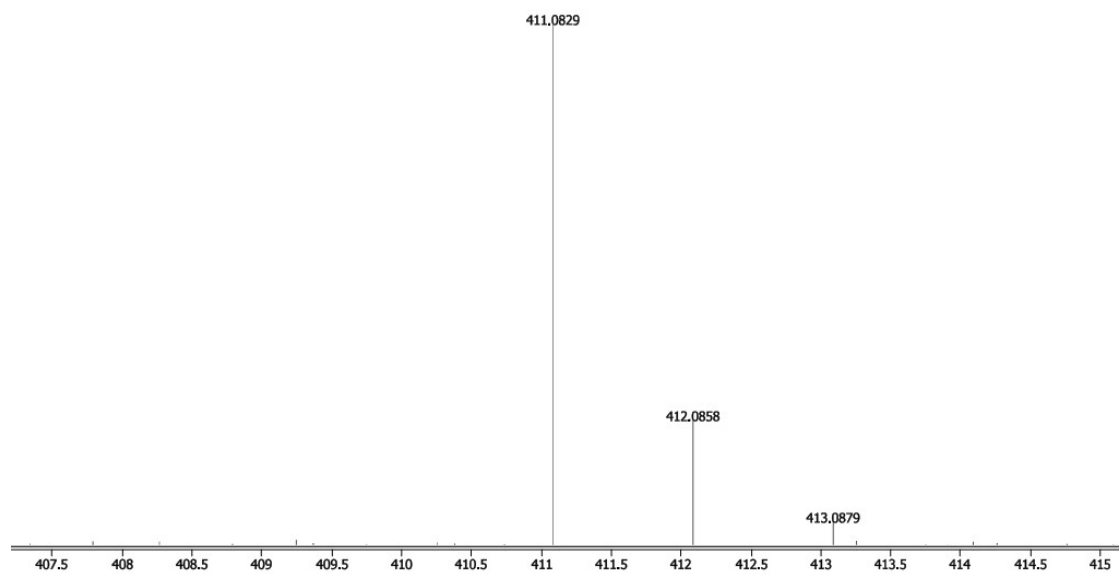


Figure S9. HRMS spectrum of compound M-3.

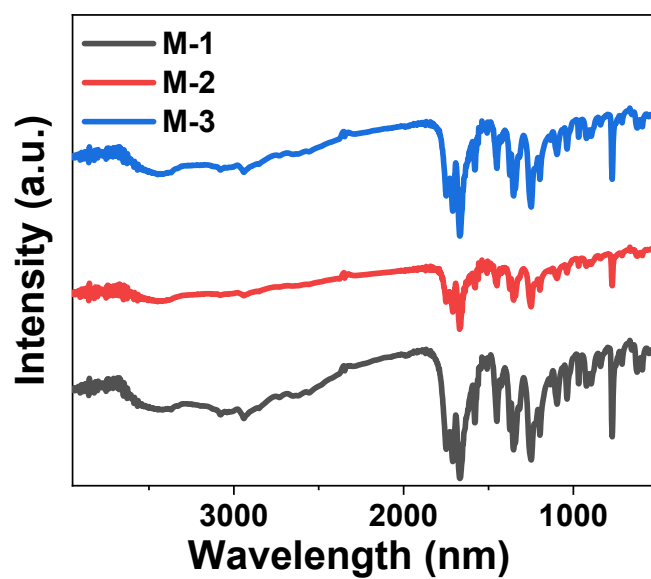


Figure S10. FT-IR spectrum of compound M-1, M-2 and M-3.

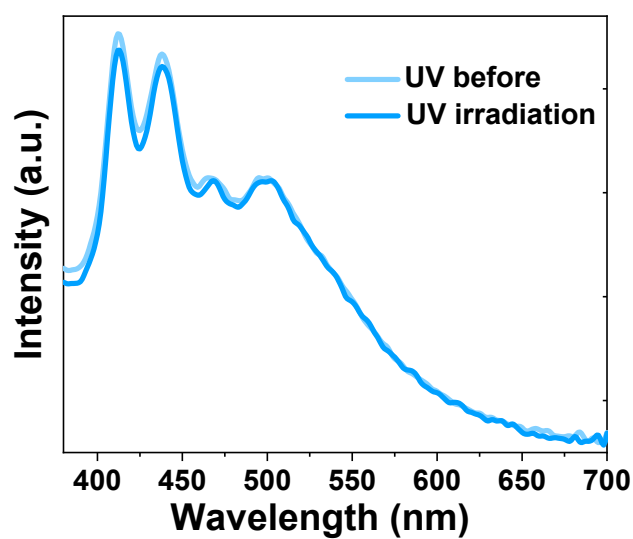


Figure S11. PL spectra of the PVA film before and after UV irradiation.

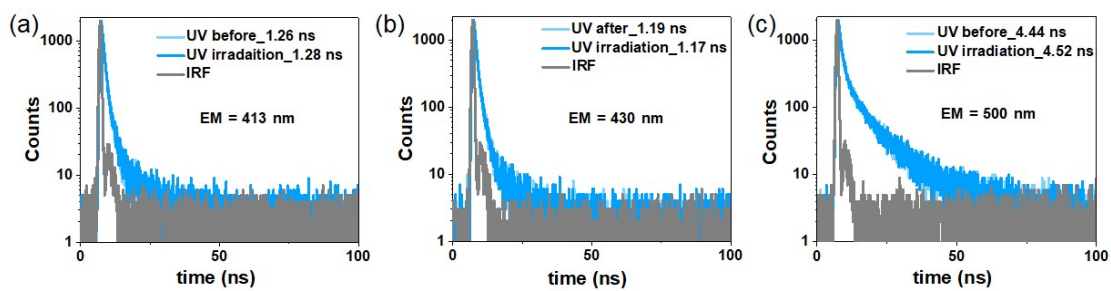


Figure S12. PL lifetime spectra of the PVA film before and after UV irradiation ($\lambda_{em} = 413, 430,$

500 nm).

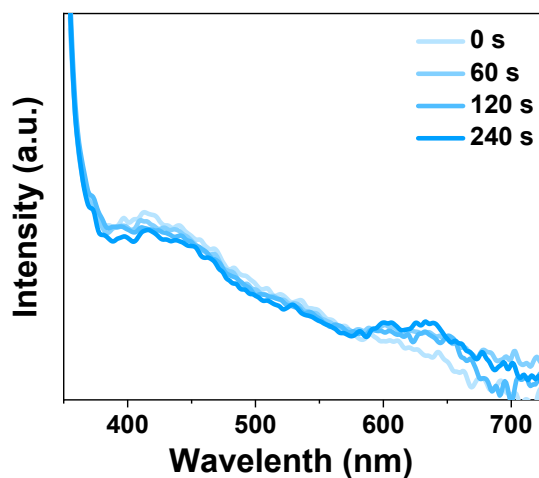


Figure S13. PL spectra of 0.2 wt% M-1@PVA film before and after UV irradiation.

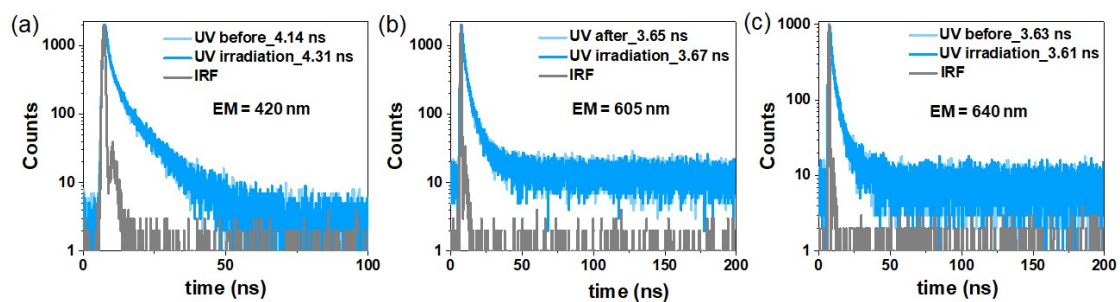


Figure S14. PL lifetime decay of 0.2 wt% M-1@PVA film before and after UV irradiation ($\lambda_{em} = 420, 605, 640$ nm).

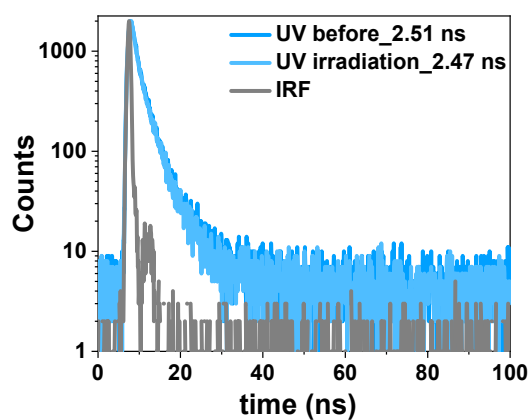


Figure S15. PL lifetime spectra of 3 wt% M-1@PVA film before and after UV irradiation ($\lambda_{em} = 640$ nm).

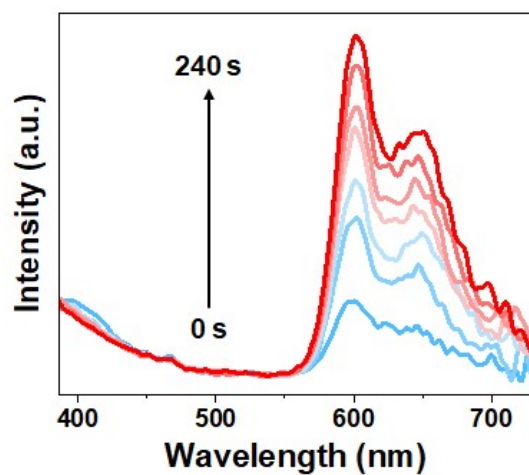


Figure S16. PL spectra of 3 wt% **M-2@PVA** film upon UV irradiation from 0 to 240 s.

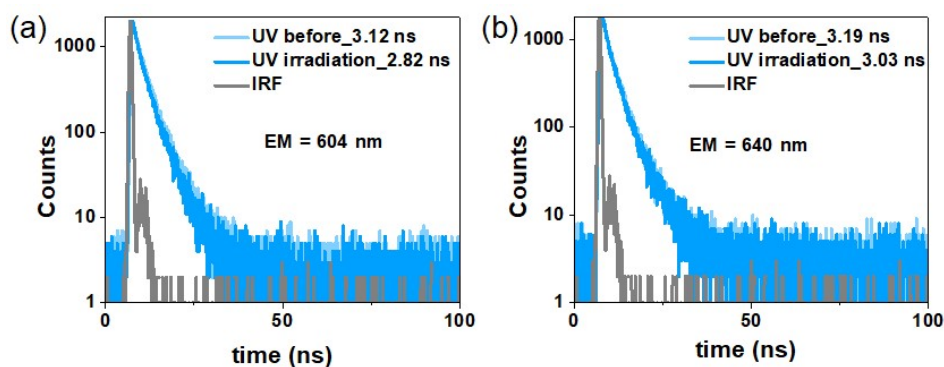


Figure S17. PL lifetime spectra of 3 wt% **M-2@PVA** film before and after UV irradiation ($\lambda_{em} = 604$ nm and 640 nm).

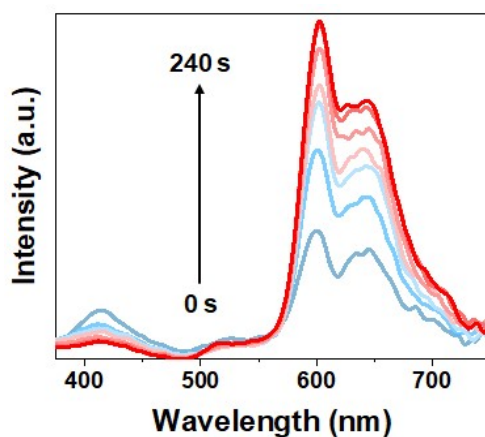


Figure S18. PL spectra of 3 wt% **M-3@PVA** film upon UV irradiation from 0 to 240 s.

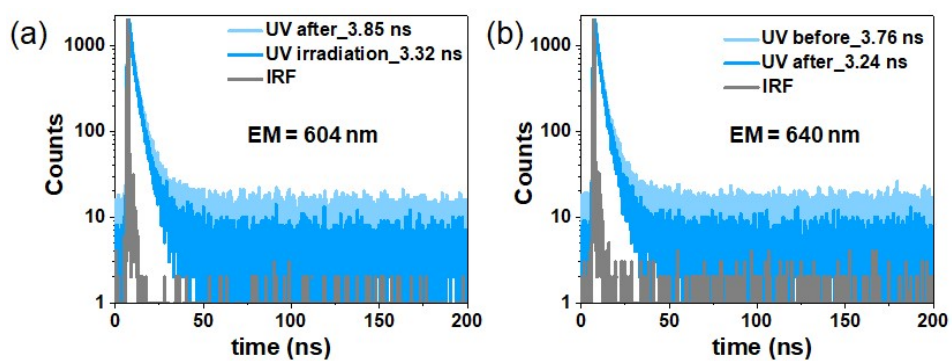


Figure S19. PL lifetime spectra of 3 wt% M-3@PVA film before and after UV irradiation ($\lambda_{em} = 604$ nm and 640 nm).

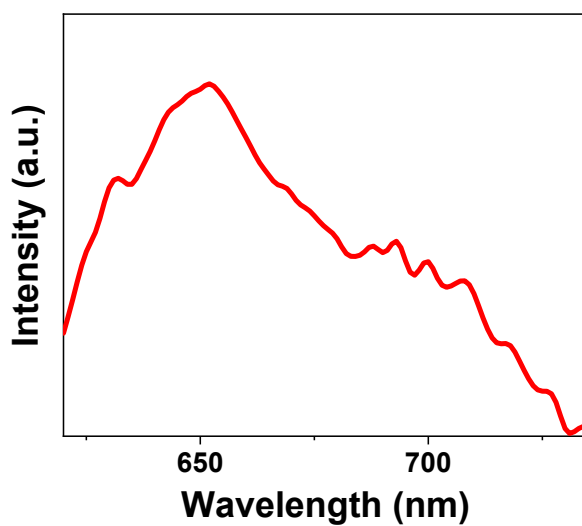


Figure S20. PL spectrum of the 3 wt% M-1@PVA film upon 600 nm excitation after UV irradiation.

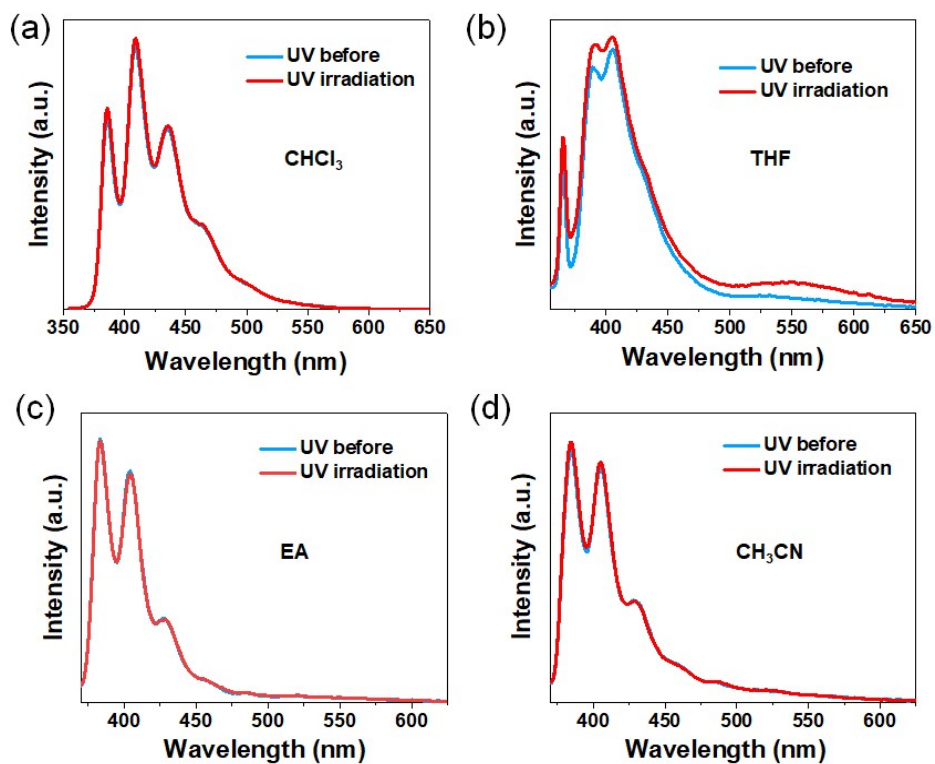


Figure S21. PL spectra of **M-1** (1x10⁻⁵ M) in various polar solvents (CHCl₃, THF, EA, ACN) before and after UV irradiation.

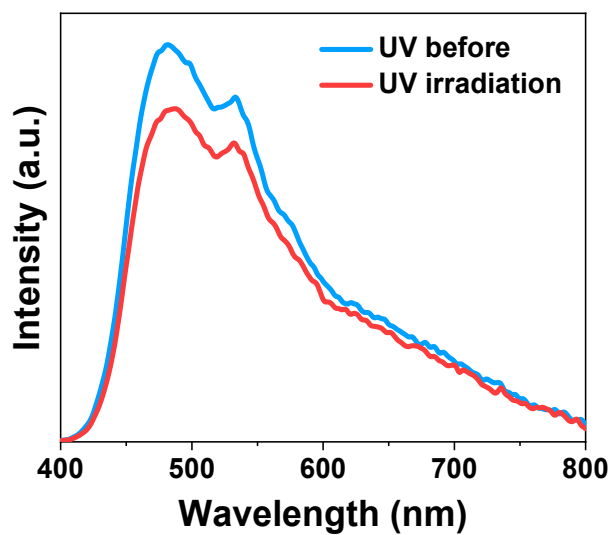


Figure S22. PL spectra of **M-1** in solid before and after UV irradiation.

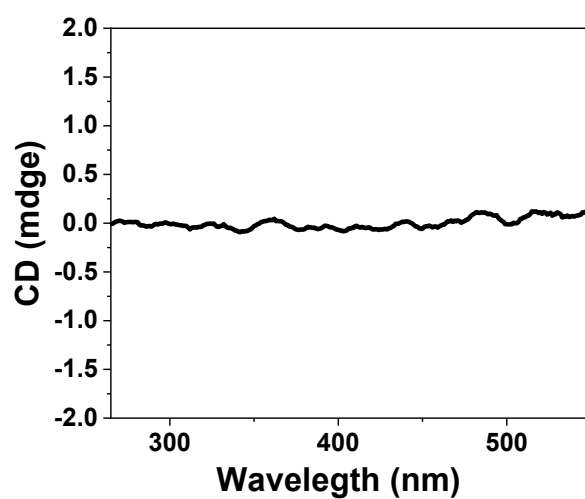


Figure S23. CD signal of M-3@PVA film.

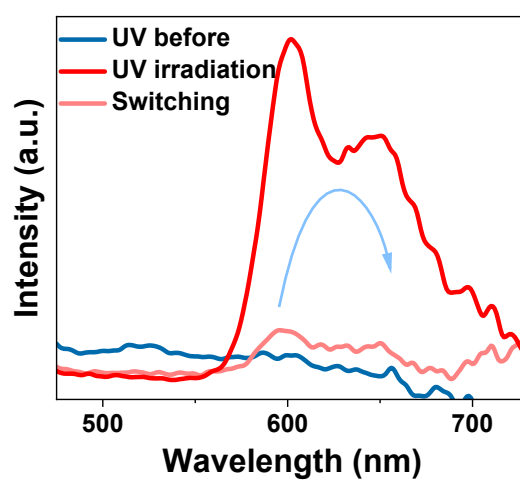


Figure S24. PL spectra of 3 wt% M-1@PVA film before and after UV irradiation ($\lambda_{em} = 640$ nm).

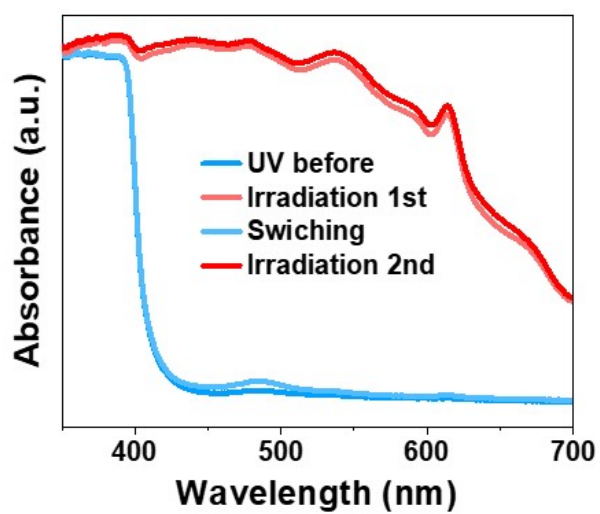


Figure S25. Absorption spectra of the **M-1@PVA** film before and after UV irradiation.

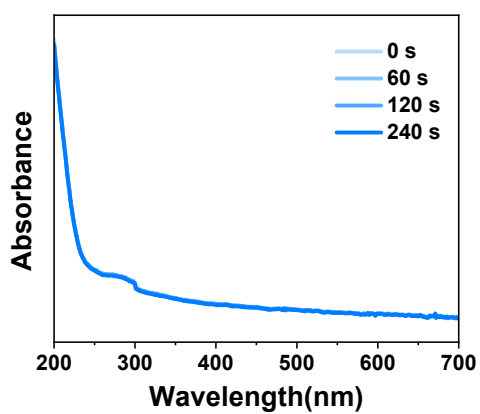


Figure S26. Absorption spectra of the pure PVA film under UV irradiation.

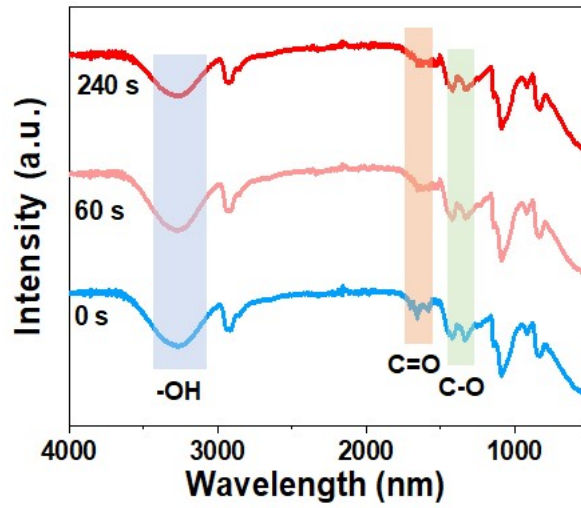


Figure S27. FTIR spectra of the M-1@PVA film under UV irradiation.

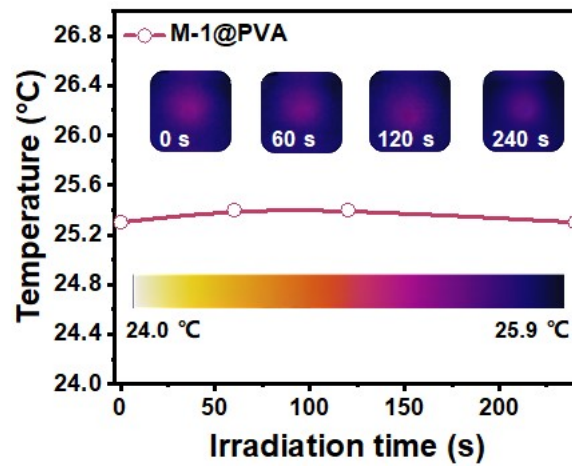


Figure S28. Photothermal measurements of the M-1@PVA film under UV irradiation.