

Supporting Information

Precision synthesis of diblock copolymers via free radical photopolymerization

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Materials

N-methyl-2-pyrrole formaldehyde, tetrahydrofuran(THF, superdry), triethyl phosphoacetylacetate were obtained from Macklin. Lithium bis(trimethylsilyl)amide (LiHMDS), Dimethylaminopyridine(DMAP), 1-ethyl-3-(3-dimethylamino) carbodiimide hydrochloride(EDCI) were purchased from Aladdin. 2-Hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone(Iragcure 2959) was sourced from JIURI NEW MATERIALS(Tianjin, China). Methyl alcohol, NaOH, dichloromethane, ethyl acetate, acetonitrile(ACN) and other developing solvents were obtained from Energy Chemical (Shanghai, China). Monomer including 1,6-hexadiol diacrylate(HDDA), phenyl methacrylate(PMA) and Butyl Methacrylate(BMA) purified and commercial photoinitiator CQ were supported by Jiangsu Jicui Photosensitive Electronic Materials Research Institute limited company(Jiangsu, China).

Methods

UV-Vis spectroscopy (UV-Vis)

UV-Vis absorption spectra were recorded on a GENESYS150 spectrophotometer (Thermo Fisher Scientific, American) using quartz cells with 1cm path length. The analysis covered a range of 200-600nm. A baseline correction was performed using ACN in a separate cell as a blank.

Steady state photolysis study

Steady state photolysis studies related to compounds were performed in ACN upon the irradiation of LED@325nm(70mW/cm²), LED@465nm(70mW/cm²) and LED@275nm(15mW/cm²) in the absence of air at room temperature. The incident

light intensity was determined using radiometers provided by Photoelectric Instrument Factory of the Beijing Normal University. In addition, LED lamps were purchased from LAMPLIC(Shenzhen, China).

Nuclear Magnetic Resonance (NMR)

NMR spectra were collected by an AVANCE III(400M Hz) spectrometer(Bruker, Germany) operating at room temperature using DMSO- d_6 as the solvent. Chemical shifts (δ) were determined following IUPAC guidelines and are expressed in parts per million (ppm), with reference to tetramethyl silane(TMS) for ^1H and ^{13}C . Multiplicities of the signals are identified by s(singlet), d(doublet), t(triplet), and m(multiplet). The absolute values of coupling constants (J) are denoted in Hertz (Hz).

EPR spin-trapping (EPR-ST)

The electron paramagnetic resonance(EPR) spectrum was collected on a Bruker 500 spectrometer. The radicals aroused by initiating system CQ/PAA-2959 were generated upon LED@465nm without air at room temperature and trapped with agent N-tert-butyl- α -phenylnitroketone and upon LED@275nm at the same chemical environment condition trapped with agent 5,5-dimethyl-1-pyrrolin-n-oxide(DMPO), respectively. ACN was chosen as the solvent. The concentration of CQ/PAA-2959 was 5×10^{-3} mol/L. a_{N} and a_{H} stand for the hyperfine coupling constants for nitrogen and hydrogen, respectively.

Gel Permeation Chromatography(GPC)

Volumetric exclusion chromatographic outflow curves were recorded on an Agilent PL-GPC50. The experimental temperature was maintained at 40 °C. DMF served as the solvent throughout the analysis, and the flow rate of the solvent was set at 1.0 mL/min. Polystyrenes were utilized as reference standards.

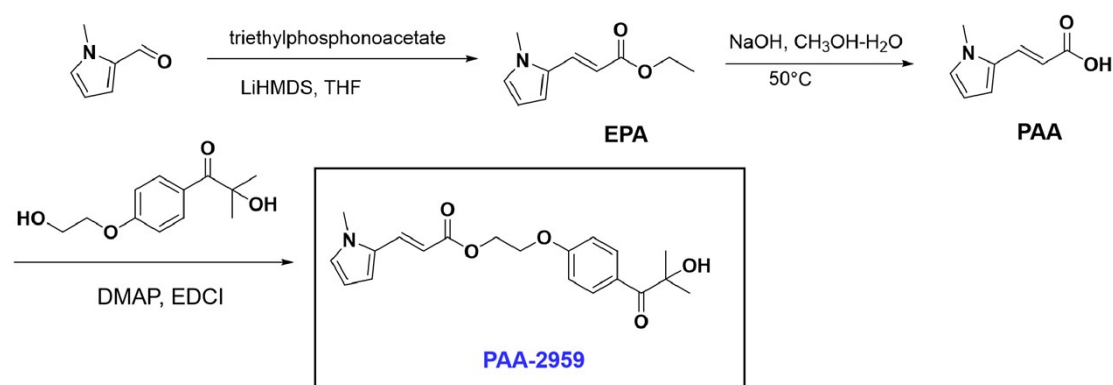
Photopolymerization kinetics

A real-time Fourier transform IR (FT-IR) spectrometer (Nicolet 5700) equipped with an MCT/A KBr detector-beam splitter combination ($650\text{-}4000\text{ cm}^{-1}$, 4 scans s^{-1}) was used to monitor the photopolymerization kinetics. Mixtures stirred for 10min including CQ(1wt%)/PAA-2959(2wt%)/HDDA were dropped onto a piece of KBr crystal with a thickness of 2 ± 0.1 mm, covered by another clear piece of KBr crystal and then exposed upon LED@465nm or LED@275nm in the absence of air. The double bond conversion of the monomer HDDA was calculated based on the decrease in the area of the acrylate absorption peak at $800\text{-}850\text{ cm}^{-1}$ using the following equation:

$$DC\%=[1-A_t/A_0]\times 100\%$$

where A_t corresponds to the area of the absorbance peak area of acrylate at 800-850 cm^{-1} of at time t during the polymerization and A_0 corresponds to the initial area of the absorbance peak before the polymerization.

Synthesis



Synthesis of EPA

LiHMDS (8.9 mL of a 1 M solution in THF, 8.9 mmol) was added to a solution of triethyl phosphonoacetate (1.78 mL, 8.9 mmol) in THF maintained at 0 °C. After 0.5 h at 0°C, N-methyl-2-pyrrole formaldehyde(0.75 mL, 7.0 mmol) was added and the solution was maintained at 0°C for 20 min then allowed to warm to room temperature. After 4 h, the reaction was quenched with NH₄Cl (10mL of a saturated aqueous solution) and H₂O (10mL) and the ensuing aqueous phase was extracted with CH₂Cl₂ (2×40mL). The combined CH₂Cl₂ extracts were washed by brine water, dried over anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography using petroleum ether/ethyl acetate as eluent to obtain the intermediate **ethyl(E)-3-(1-methyl-1H-pyrrol-2-yl)acrylate(EPA)** as a colorless oil (1.14 g), yield: 91%.

¹H-NMR (400 MHz, DMSO-*d*₆) δ[ppm]=7.52 (dd, $J = 15.7, 2.6$ Hz, 1H), 6.99 (s, 1H), 6.78 (s, 1H), 6.19 (dd, $J = 15.7, 2.6$ Hz, 1H), 6.10 (d, $J = 3.4$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 1.23 (t, $J = 7.2$ Hz, 3H).

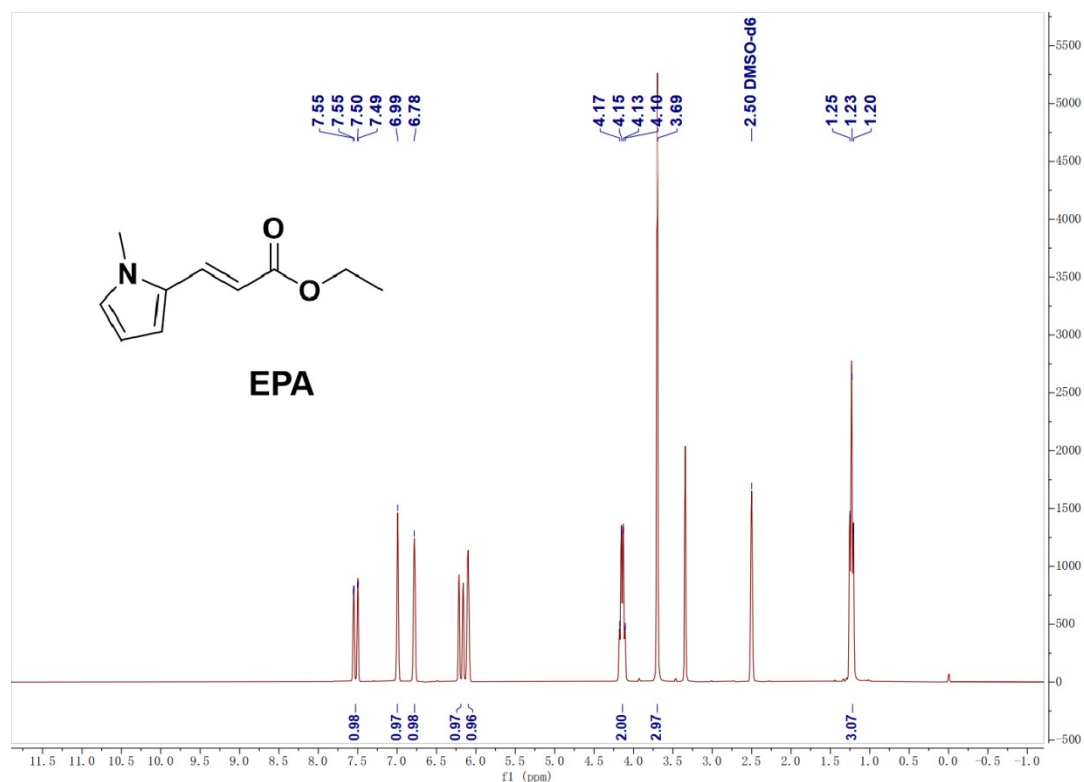


Figure S1. $^1\text{H-NMR}$ of EPA

Synthesis of PAA

To a solution of intermediate **EPA**(2.5 g, 13.9mmol) in methanol(20mL) and the solution of NaOH (2.78 g, 69.5 mmol)/H₂O(10 mL) was added. The reaction mixture was stirred at 50 °C for 4 h until complete as it was indicated by TLC. Then the mixture was acidified by adding 1M HCl solution and precipitated a white solid product (**E**)-3-(1-methyl-1H-pyrrol-2-yl)acrylic acid(**PAA**) 1.90 g, yield: 90 %.

$^1\text{H-NMR}$ (400 MHz, DMSO-*d*₆) δ [ppm]=12.03 (s, 1H), 7.48 (d, J=16.0 Hz, 1H), 6.97 (s, 1H), 6.73 (s, 1H), 6.14-6.06 (m, 2H), 3.69 (s, 3H).

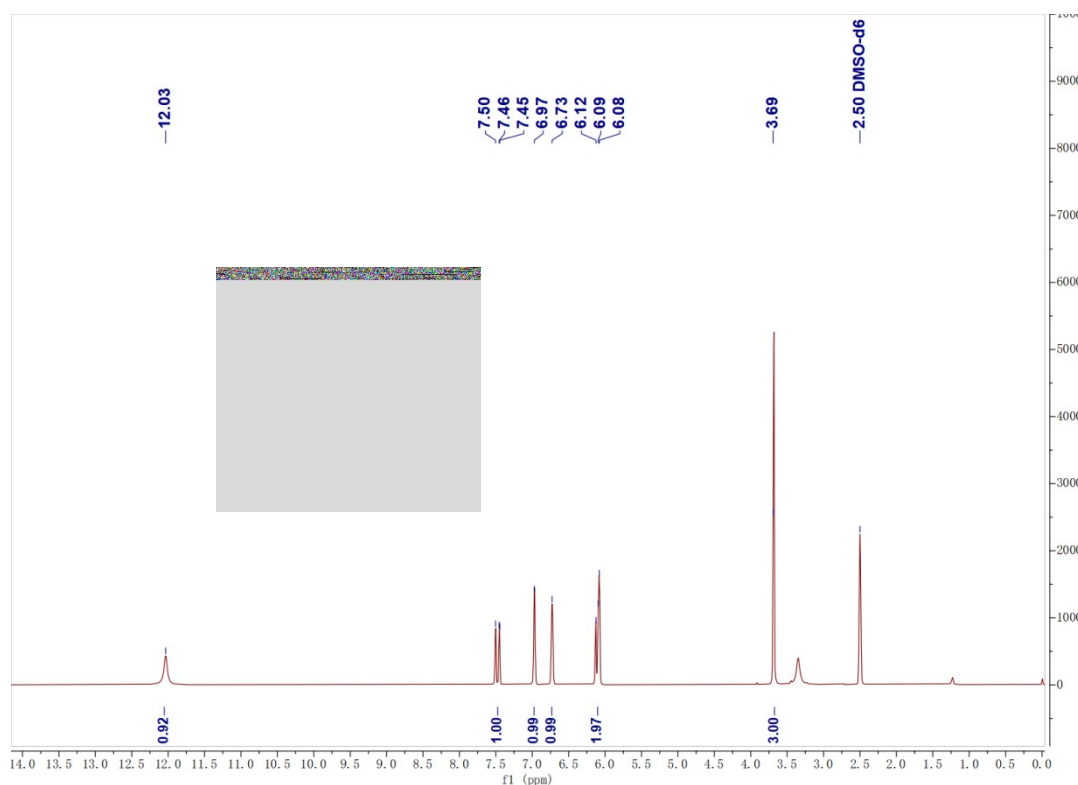


Figure S2. $^1\text{H-NMR}$ of PAA

Synthesis of PAA-2959

DMAP (201mg, 1.65mmol) and EDCI (315mg, 1.65mmol) were added into a solution of intermediate **PAA**(500mg, 3.31mmol) and Iragure 2959(1.11 g, 4.90mmol) in dichloromethane(20mL). The reactions mixture was stirred at room temperature for 6 h until complete as it was indicated by TLC. Then the mixture was quenched with water and extracted with dichloromethane. The organic layers were combined and dried over Na_2SO_4 , filtered, and then concentrated under reduced pressure to give the crude product, which was purified by column chromatography eluting with petroleum ether/ethyl acetate (10/1, v/v) to give **2-(4-(2-hydroxy-2-methylpropanoyl)phenoxy)ethyl(E)-3-(1-methyl-1H-pyrrol-2-yl)acrylate(PAA-2959)** as a white solid product 968 mg, yield: 82 %.

$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ [ppm]=8.21 (d, $J=8.9\text{Hz}$, 2H), 7.56(d, $J=15.6\text{ Hz}$, 1H), 7.04(d, $J=8.9\text{ Hz}$, 1H), 7.00(d, $J=2.1\text{Hz}$, 1H), 6.85-6.77(m, 1H), 6.24(d, $J=15.7\text{ Hz}$, 1H), 6.10(m, 1H), 5.67(s, 1H), 4.51-4.41(m, 2H), 4.37-4.27(m, 2H), 3.69(s, 3H), 1.38(s, 6H).

$^{13}\text{C-NMR}$ (75 MHz, DMSO) δ [ppm]=202.09, 166.92, 161.44, 133.22, 132.53, 128.54, 128.12, 127.79, 113.81, 112.84, 110.88, 109.11, 76.73, 66.18, 62.20, 33.97, 28.17;
ESI-MS calculated for $\text{C}_{20}\text{H}_{23}\text{NO}_5[\text{M}+\text{H}]^+$: 358.2; Found $\text{C}_{20}\text{H}_{23}\text{NO}_5[\text{M}+\text{Na}]^+$: 380.6.

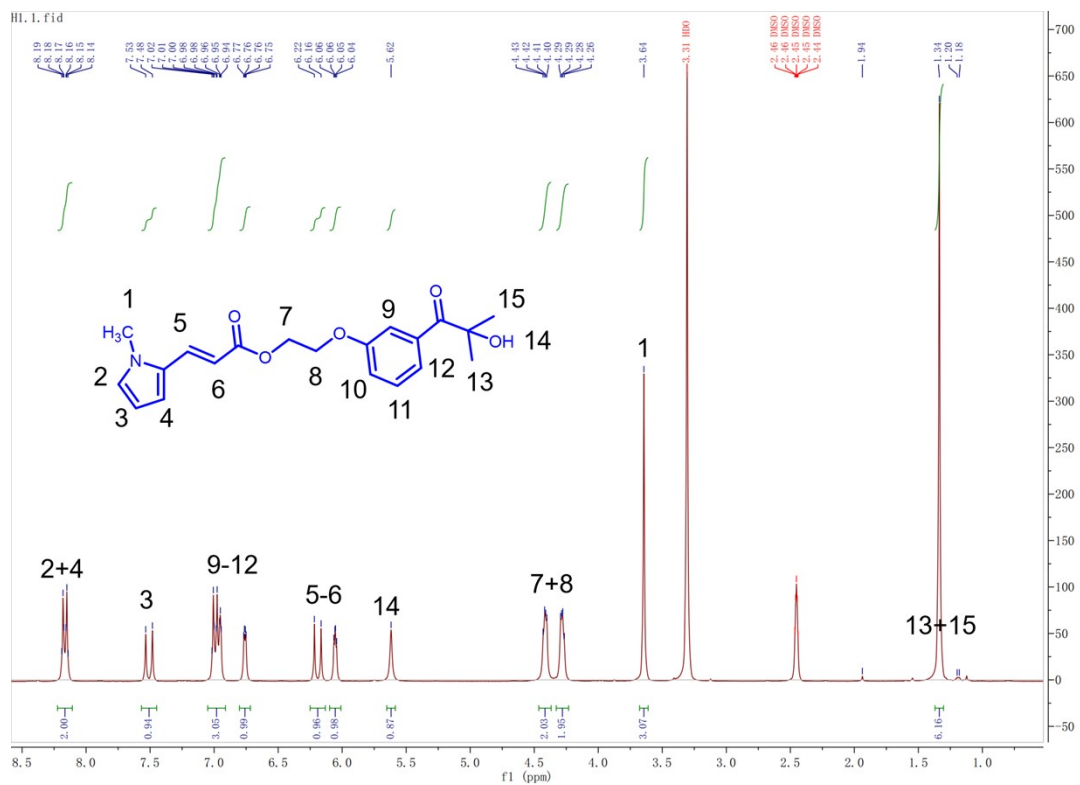


Figure S3. $^1\text{H-NMR}$ of PAA-2959

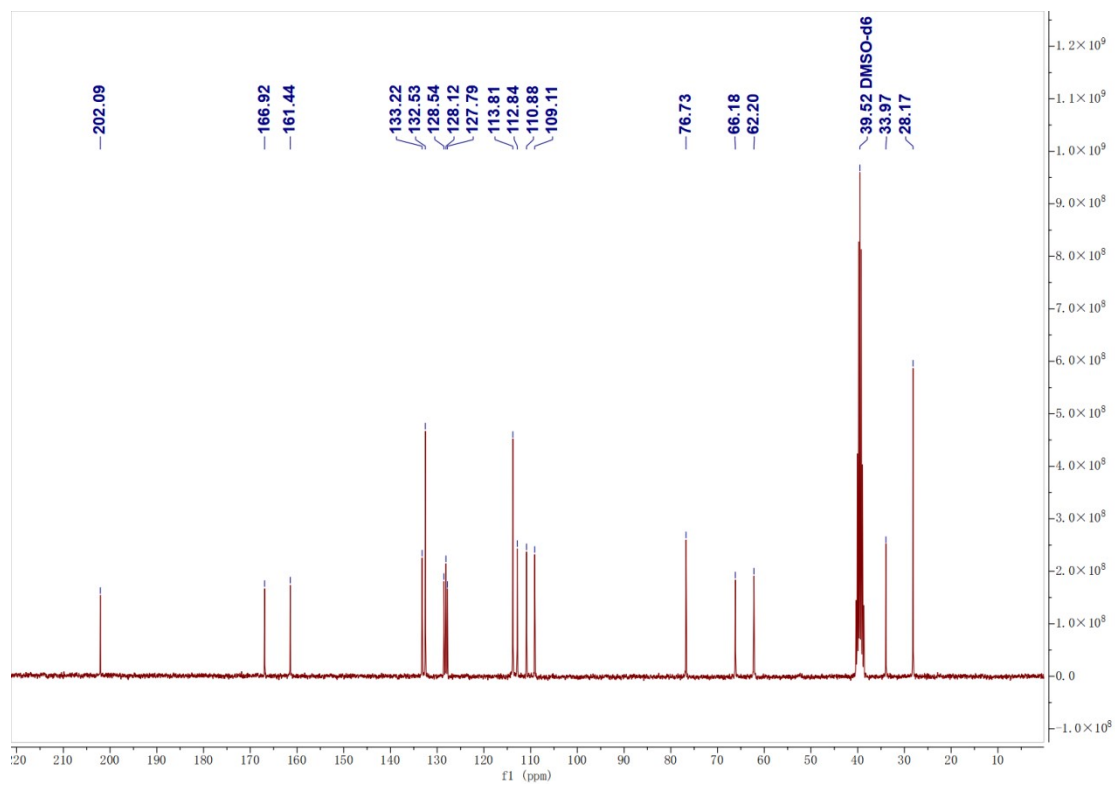


Figure S4 $^{13}\text{C-NMR}$ of PAA-2959

Spectrum RT 7.72 - 8.57 (34 scans) - Background Subtracted 4.77 - 6.66
2024-05-05-1_Scan1_is1.dat;
ESI + Settings for tune mix using source type ESI Positive.

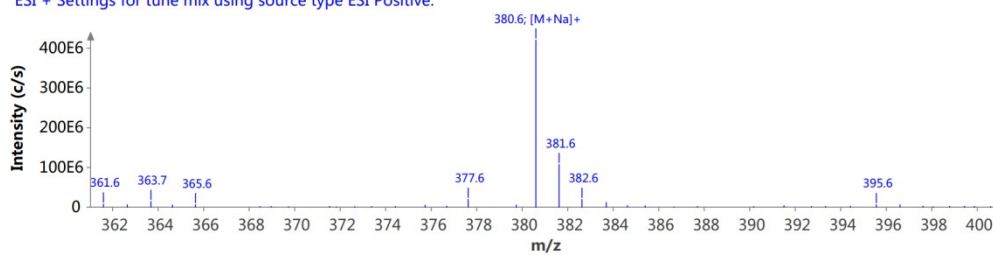


Figure S5. ESI-MS of PAA-2959

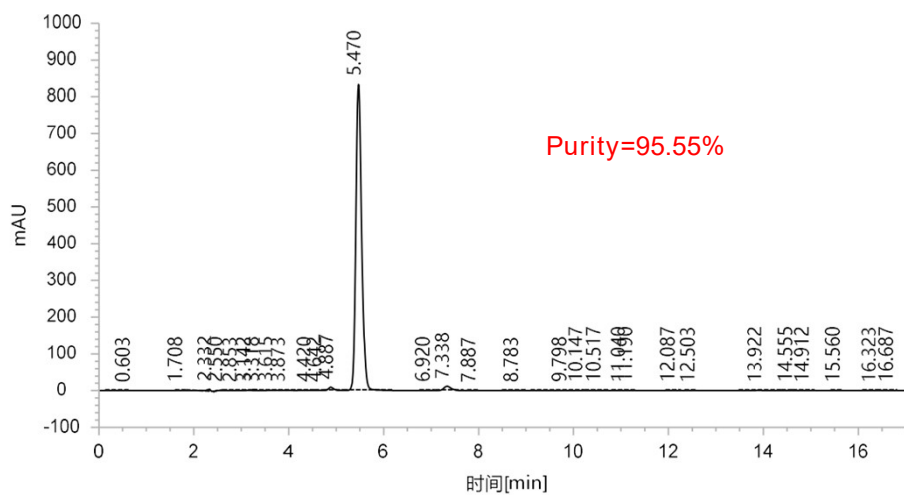


Figure S6. HPLC of PAA-2959

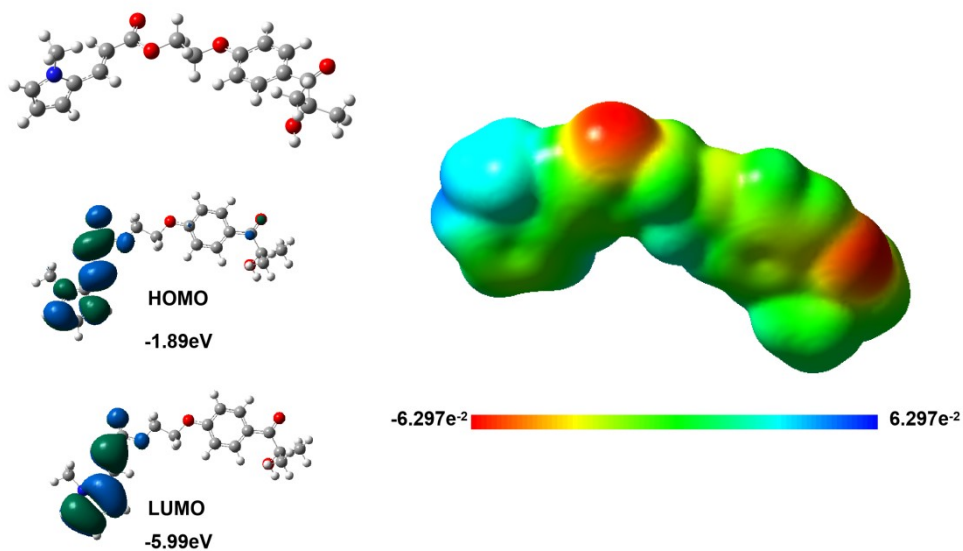


Figure S7. Optimized chemical structure, orbitals and electrostatic potential of PAA-2959

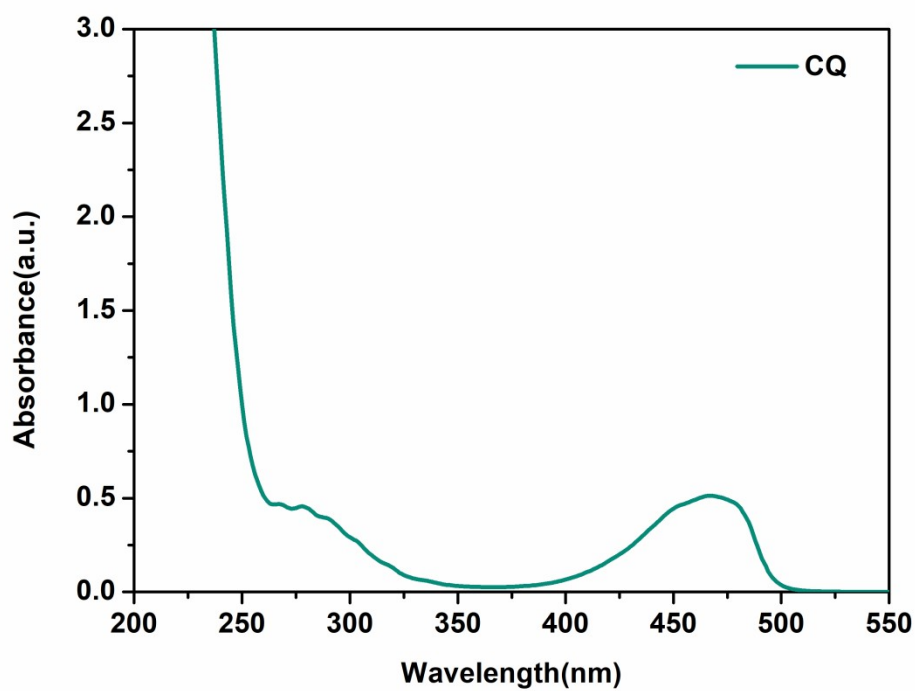


Figure S8. UV-Vis absorption spectrum of photoinitiator CQ(1.25×10^{-2} mol/L) in ACN

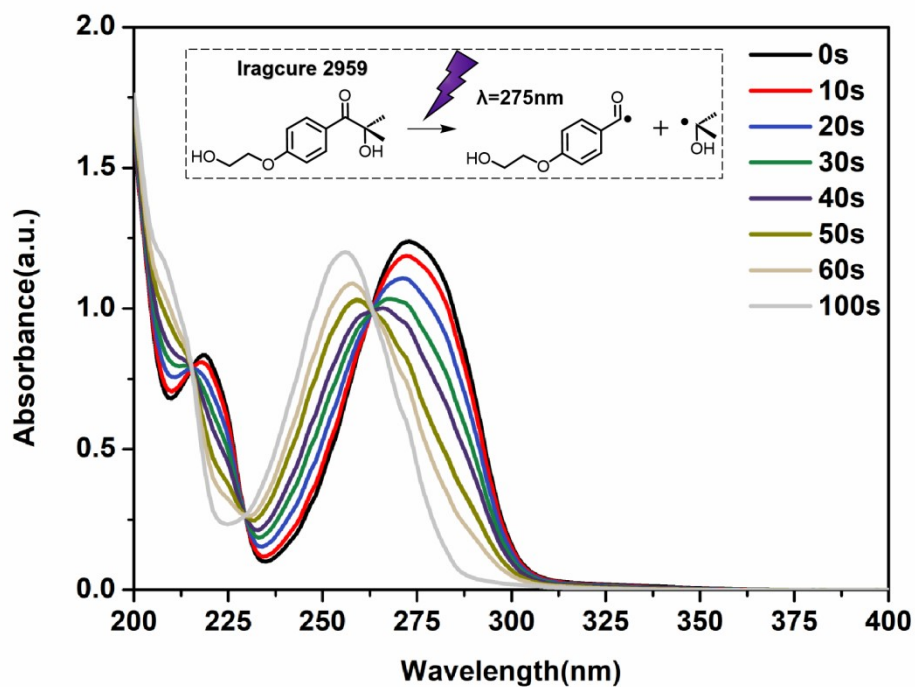


Figure S9. Steady state photolysis spectrum of Iragcure 2959 in ACN

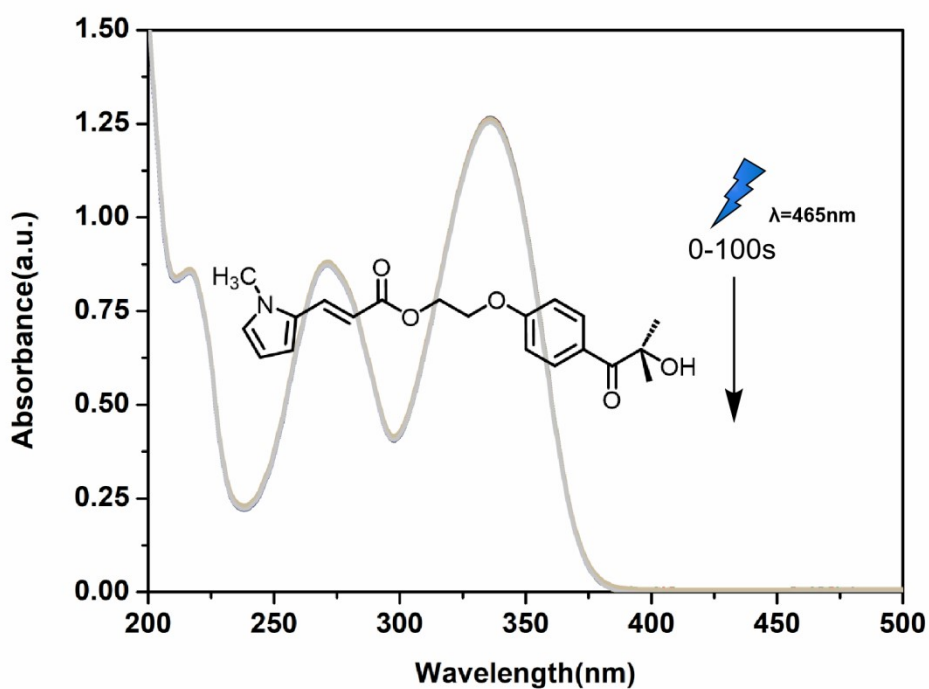


Figure S10. Steady state photolysis spectrum of PAA-2959(2.5×10^{-3} mol/L) in ACN under LED@465nm irradiation

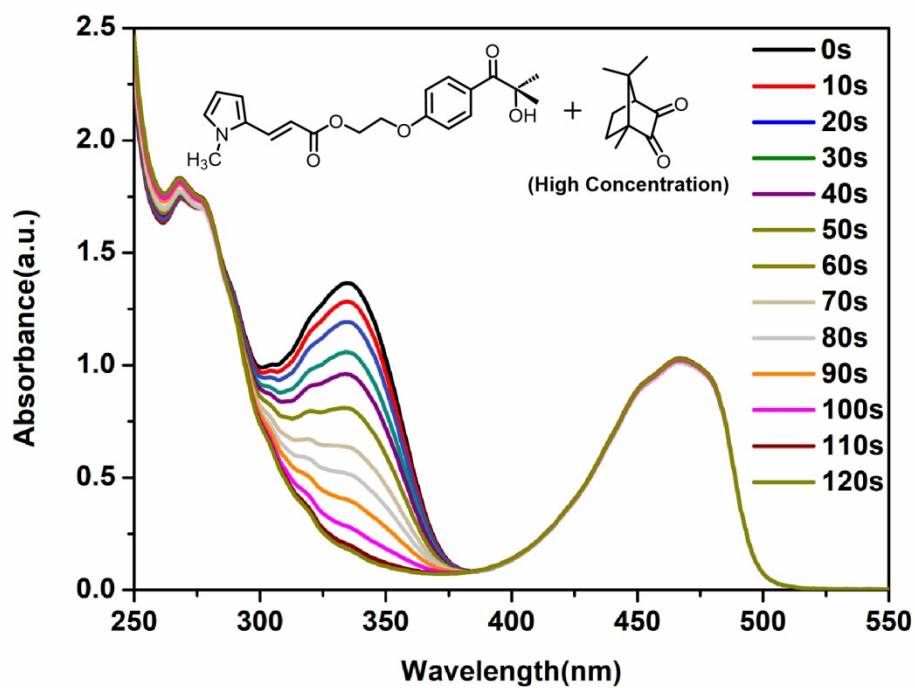


Figure S11. Steady state photolysis spectrum of initiating system PAA-2959(4×10^{-3} mol/L)/CQ(2.5×10^{-2} mol/L) in ACN under LED@275nm irradiation

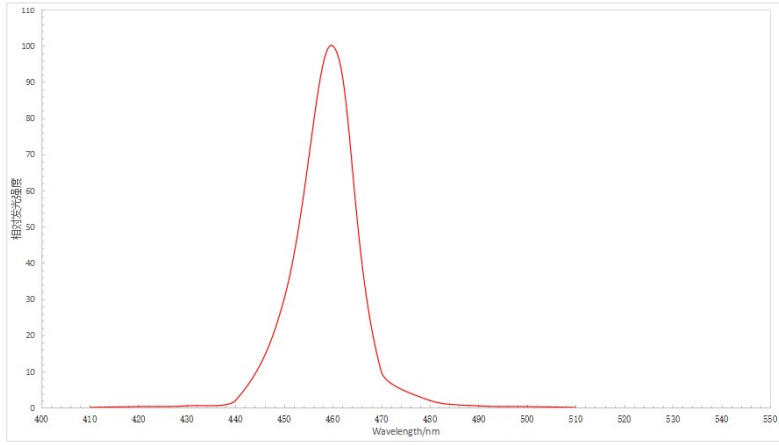


Figure S12. Emission spectra of LED@465nm

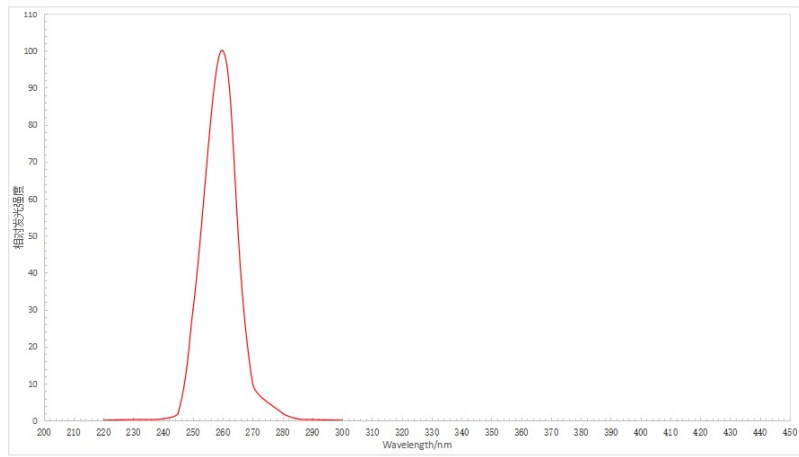


Figure S13. Emission spectra of LED@275nm