Supporting Information

Photo-Responsive Near-Infrared Circularly Polarized Luminescent Liquid Crystal Copolymers

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Materials

6-Bromo-1-hexanol (97%), 2-bromoethanol (98%), cholesteryl chloroformate (98%), methacrylic acid (99%), 4-dimethylaminopyridine (DMAP, 98%), 2,3,3-trimethyl-3H-indole (98%), 5-nitrosalicylaldehyde(98%), methacryloyl chloride (97%) were purchased from Energy Chemical Co.. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 99%), pyridine (≥99.9%), sodium chloride (99.9%), potassium carbonate (99%), potassium iodide (99%), sodium bicarbonate (99%), sodium-sulfate (99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All organic solvents with analytical purity such as N, N-dimethylformamide (DMF), methanol, acetonitrile, ethanol, dichloromethane and tetrahydrofuran (THF) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. THF was refined via sodium metal to remove trace amounts of water. Dichloromethane was refined via magnesium sulfate to remove water. All other materials were used directly without any further purification.

Measurements and characterizations

The ^1H NMR and ^{13}C NMR spectra of all samples were measured by a Bruker ARX 400 MHz spectrometer. The molecular weight of intermediates and monomers were measured by a Bruker Biflex III MALDI-TOF instrument using $CHCl_3$ as solvent. Waters 1515 gel permeation chromatography was applied to measure the number-molecular weights (M_n) and polymer dispersity index (PDI) of polymers. THF was used as solvent and the flow rate was 1.0 $mL.min^{-1}$ at 35°C. The TGA Q50 thermogravimetric analyzer was used to characterize the thermal stability of polymers under N_2 atmosphere and the heating rate was 20 $°C.min^{-1}$. The phase textures of polymers were characterized by a Mettler FP82 polarizing microscope (POM) with a hot stage. The phase transition temperature of polymers was measured by DSC-Q10 differential scanning calorimeter under N_2 atmosphere. An Anton Paar SAXSess was used for determining the specific phase structure of polymers. Absorption spectra of samples were recorded on Carry-100 spectrophotometer and the fluorescence spectra of samples were recorded on F-4700 fluorescence spectroscopy. The UV-vis diffuse reflectance spectra were evaluated by Shimadzu Solid Spec-3700 spectrometer with integrating sphere. The circular dichroism (CD) spectra of samples were recorded by an Applied Photophysics Chirascan V100 spectrometer. The CPL-300 spectrometer was used to measure the circularly polarized luminescence spectra and luminescence dissymmetry factor of samples.

Synthesis of monomer and polymers

The synthetic method of monomer MSP and polymers was shown in Figure S1 and Figure S2, respectively. The detailed process was described as follows.

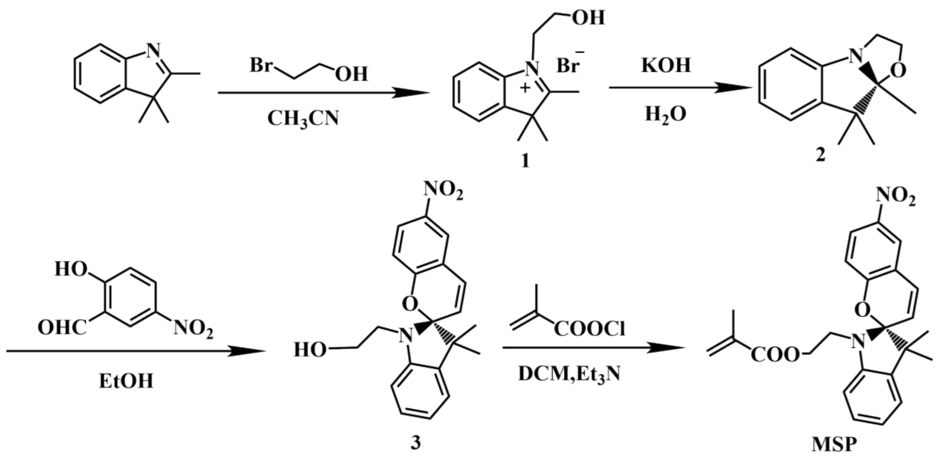

Figure S1. Synthetic route of MSP.

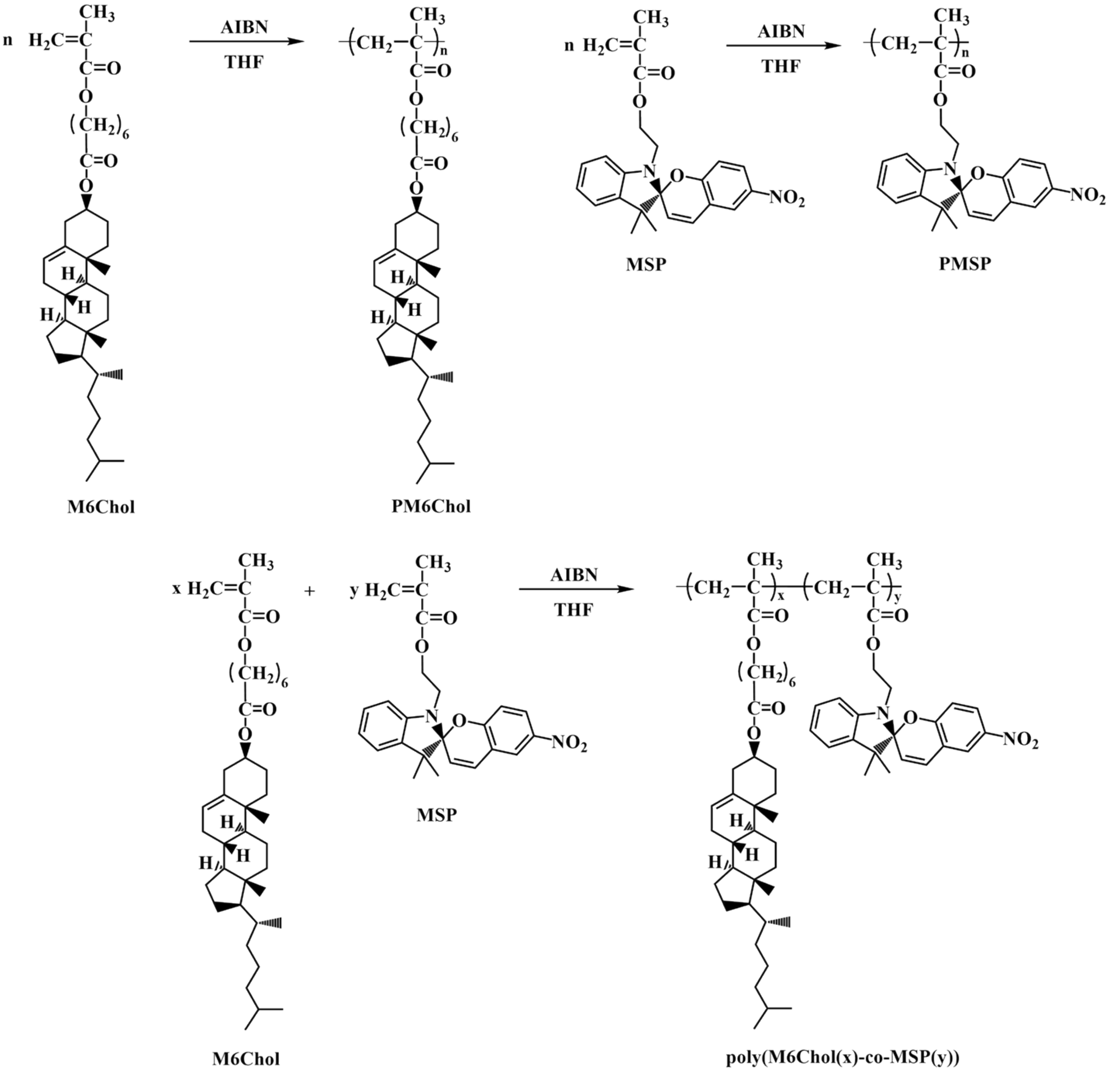

Figure S2. Synthetic routes of homopolymers and copolymers.

Synthesis of compound (1). 2,3,3-Trimethyl-3H-indole (10.00 g, 62.93 mmol), 2-bromoethanol (9.41 g, 76.12 mmol), 30.00 mL acetonitrile were successively added into a 250 mL three-necked flask, and then stirred at 83°C for 12 h under nitrogen atmosphere. When the reaction was completed, the reaction solution was naturally cooled to room temperature. Then, the reaction solution was poured into 200 mL ethyl acetate, and a large amount of solid was precipitated. The mixtures were filtered by suction to remove filtrate, and the obtained precipitate was washed with ethyl acetate for three times. After that, the pure product was collected and dried, and then 11.42 g of pink solid was obtained with a yield of 89.01%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.75 (m, 1H, Ph-H), 7.58 (m, 3H, Ph-H), 4.88 (t, J=4.9 Hz, 2H, $-CH_2-$), 4.19 (t, J=4.9 Hz, 2H, $-CH_2-$), 3.14 (s, 3H, $-CH_3$), 1.65 (s, 6H, $-CH_3$), 1.24 (s, 1H, -OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.73, 141.55, 141.02, 130.04, 129.57, 123.15, 122.60, 115.61, 58.47, 54.71, 51.99, 23.34, 22.65, 16.38. MALDI-MS: (m/z) $[M]^+$ Calcd for $C_{13}H_{18}NO$, 204.14; found, 204.32 $[M]^+$.

Synthesis of compound (2). Compound (1) (10.00 g，48.98 mmol), KOH (3.16 g，56.40 mmol) and 100 mL deionized water were added into a 250 mL flask, followed by stirring at room temperature for approximately 30 min. The solution was then extracted with anhydrous ether for four times, and the upper organic layer was collected. The mixtures were then dried over anhydrous magnesium sulfate for 3 h, filtered under suction, and subjected to rotary evaporation, resulting in 9.06 g yellow oily product with a yield of 91.05%. ^{1}H NMR (400 MHz,$CDCl_3$, δ): 7.19-7.10 (m, 1H, Ph-H), 7.09 (m, 1H, Ph-H), 6.94 (m, 1H, Ph-H), 6.78 (m, 1H, Ph-H), 3.85 (m, 1H, $-CH_2-$), 3.78-3.68 (m, 1H, $-CH_2-$), 3.64-3.46 (m, 2H, $-CH_2-$), 1.45 (s, 3H, $-CH_3$), 1.40 (s, 3H, $-CH_3$), 1.20 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.55, 140.00, 127.53, 122.44, 121.73, 112.01, 108.99, 63.00, 50.09, 46.96, 28.12, 20.82, 17.60. MALDI-MS: (m/z) $[M]^+$ Calcd for $C_{13}H_{17}NO$, 203.13; found, 203.13 $[M]^+$.

Synthesis of compound (3). Compound (2) (5.00 g, 24.61 mmol), 5-nitrosalicylaldehyde (3.50 g, 20.96 mmol) and 80 mL ethanol were added into a 250 mL three-necked flask. The mixtures were refluxed under nitrogen atmosphere for 5 h. When the reaction was completed, the reaction solution was naturally cooled to room temperature. The solvent ethanol was removed by a rotary evaporator. After recrystallization in the ethanol, 7.96 g purplish-red solid was obtained with a yield of 91.80%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.05-7.92 (m, 2H, Ph-H), 7.23-7.05 (m, 2H, Ph-H), 6.94-6.81 (m, 2H, Ph-H), 6.76 (d, J=8.7 Hz 1H, =CH-), 6.70-6.60 (m, 1H, Ph-H), 5.88 (d, J=10.3 Hz, 1H, =CH-), 4.79 (s, 2H, $-CH_2-$), 3.77 (m, 1H, $-CH_2-$), 3.64-3.28 (m, 1H, $-CH_2-$), 1.31-1.21 (s, 3H, $-CH_3$), 1.19 (s, 3H, $-CH_3$),1.13-1.07 (s, 1H, -OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.47, 147.06, 141.02, 135.86, 128.26, 127.89, 125.99, 122.83, 122.07, 121.94, 119.95, 118.65, 115.57, 106.91, 106.84, 60.79, 58.37, 52.88, 46.11, 25.93, 20.04, 18.38. MS: MALDI-MS: (m/z) $[M]^+$ Calcd for $C_{20}H_{20}N_2O_4$, 352.14, found, 353.14 $[M+H]^+$.

Synthesis of MSP. Compound (3) (5.00 g, 13.50 mmol), triethylamine (2.50 g, 24.75 mmol) and 50 mL anhydrous dichloromethane were added into a 100 mL single-necked flask in turn and the mixtures were stirred at 0°C. Then, methacryloyl chloride (2.50 g, 24.50 mmol) was slowly added dropwise to the above solution. After that, the mixtures were reacted at 0°C for 5 h. After filtration and rotary evaporation, the crude product was obtained, which was then further purified by column chromatographic method using petroleum ether and dichloromethane as eluent (PE:DCM=1:2). After that, 5.07 g pure product was obtained with a yield of 83.8%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.01 (m, 2H, Ph-H), 7.21 (t, J=7.7 Hz, 1H, Ph-H), 7.09 (d, J =7.3Hz, 1H, =CH-), 6.94-6.87 (m, 2H, Ph-H), 6.75 (d, J=8.7 Hz, 1H, Ph-H), 6.71 (d, J=7.8 Hz, 1H, Ph-H), 6.07 (s, 1H , =CH-), 5.87 (d, J=10.4 Hz, 1H, =CH-), 5.57 (s, 1H, =CH-), 4.30 (t, J=6.4 Hz, 2H, $-CH_2-$), 3.55 (m, 1H, $-CH_2-$), 3.48-3.39 (m, 1H, $-CH_2-$), 1.92 (s, 3H, $-CH_3$), 1.28 (s, 3H, $-CH_3$), 1.16 (s, 3H, $-CH_3$),^{13}C NMR (100 MHz, $CDCl_3$) δ 167.21, 159.41, 146.68, 141.14, 136.08, 135.73, 128.31, 127.86, 125.97, 125.88, 125.50, 124.92, 122.78, 121.82, 119.95, 118.46, 115.57, 106.77, 106.55, 62.65, 52.87, 52.82, 42.45, 25.86, 19.85, 18.34, 1.03. MALDI-MS: (m/z) $[M]^+$ Calcd for $C_{24}H_{24}N_2O_5$, 420.17, found, 421.17 $[M+H]^+$.

Synthesis of homopolymers and copolymers. According to the synthetic route shown in Figure S2, homopolymers PM6Chol, PMSP and a series of copolymers poly(PM6Chol(x)-co-PMSP(y)) with different copolymerization ratios were synthesized by free radical polymerization method in solution. For poly(PM6Chol(x)-co-PMSP(y)), x and y are the relative molar contents of monomers M6Chol and MSP in the feed, respectively. This article only takes the synthetic method of poly(M6Chol(0.65)-co-MSP(0.35)) as an example to illustrate: M6Chol (0.40 g, 0.67 mmol), MSP (0.15 g, 0.36 mmol), AIBN (1.69 mg, 0.01 mmol) and THF (1.02 g) were sequentially added to a clean glass polymerization tube. The polymerization tube was frozen with liquid nitrogen, vacuumed, deoxygenated with an oil pump for 5 min, and then thawed in anhydrous methanol. After that, N_2 was blown into the polymerization tube. The above operation was repeated three times before sealing the tube, and the sealed polymerization tube was placed in an oil bath at 75°C for 4 h. When the polymerization reaction was completed, the polymerization tube was opened, and 10 mL of THF was added to dilute the polymerization solution. Then, the diluted polymerization solution was slowly dropped into 400 mL of acetone to remove unpolymerized monomers. After centrifugation and drying, 0.30 g of the copolymer was obtained with a monomer conversion rate of 55%. PM6Chol, PMSP and all other copolymers were also synthesized using the same method.

Preparation of polymer films

As shown in Figure S3, a quartz glass substrate was placed on a hot stage equipped with a temperature control device. Polytetrafluoroethylene (PTFE) films with specified thicknesses were applied to both ends of the quartz glass. A certain amount of polymer sample was then deposited onto the quartz glass. The temperature was gradually increased to above the isotropization temperature (T_i) of the polymers at a heating rate of 10°C.min^{-1}. If the polymer is in an amorphous state, it will be heated to the viscous flow state. The polymer sample was melted, and another quartz glass was placed on top of the PTFE film. Uniform spreading of the polymer was achieved by applying external pressure. The sample was then cooled to the temperature range of its liquid crystal phase and held at this temperature for 30 min to allow the full development of the chiral liquid crystal phase structure. Finally, the sample was cooled to 25°C at a rate of 5 °C.min^{-1}, resulting in the successful preparation of the polymer films. By adjusting the thickness of the PTFE film, a series of polymer films with different thicknesses were obtained.

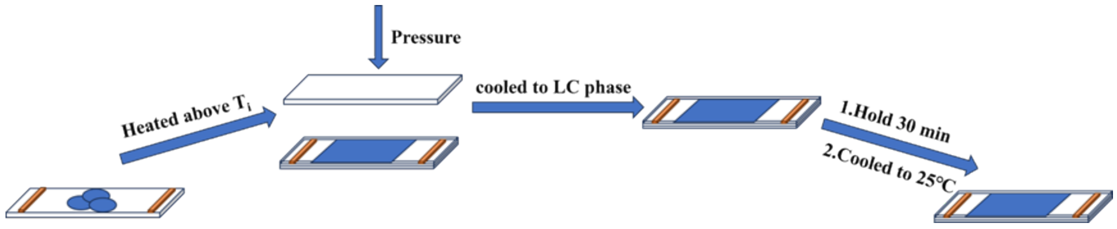

Figure S3. Preparation method of polymer films.

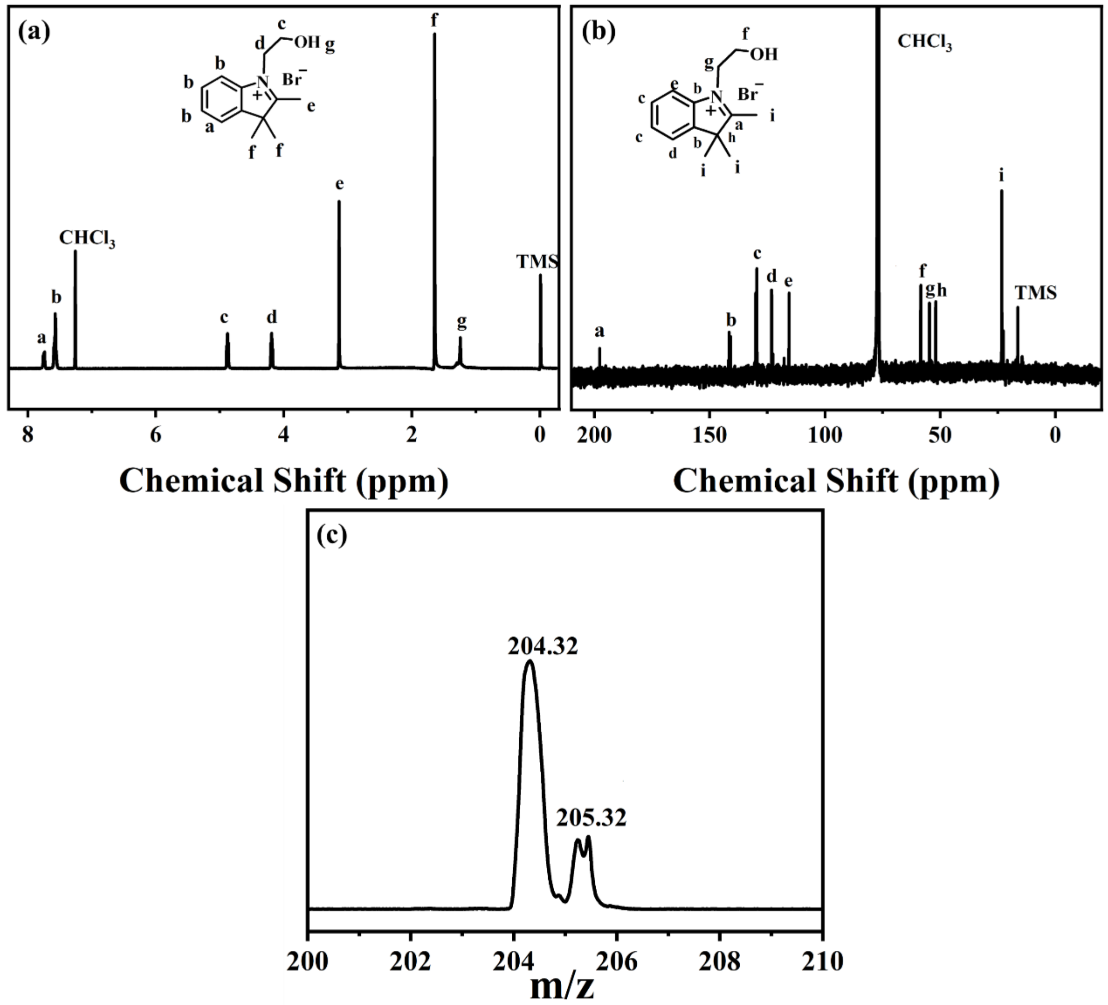

Figure S4. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of compound (1) in $CDCl_3$. (c) MS spectrum of compound (1) in $CHCl_3$.

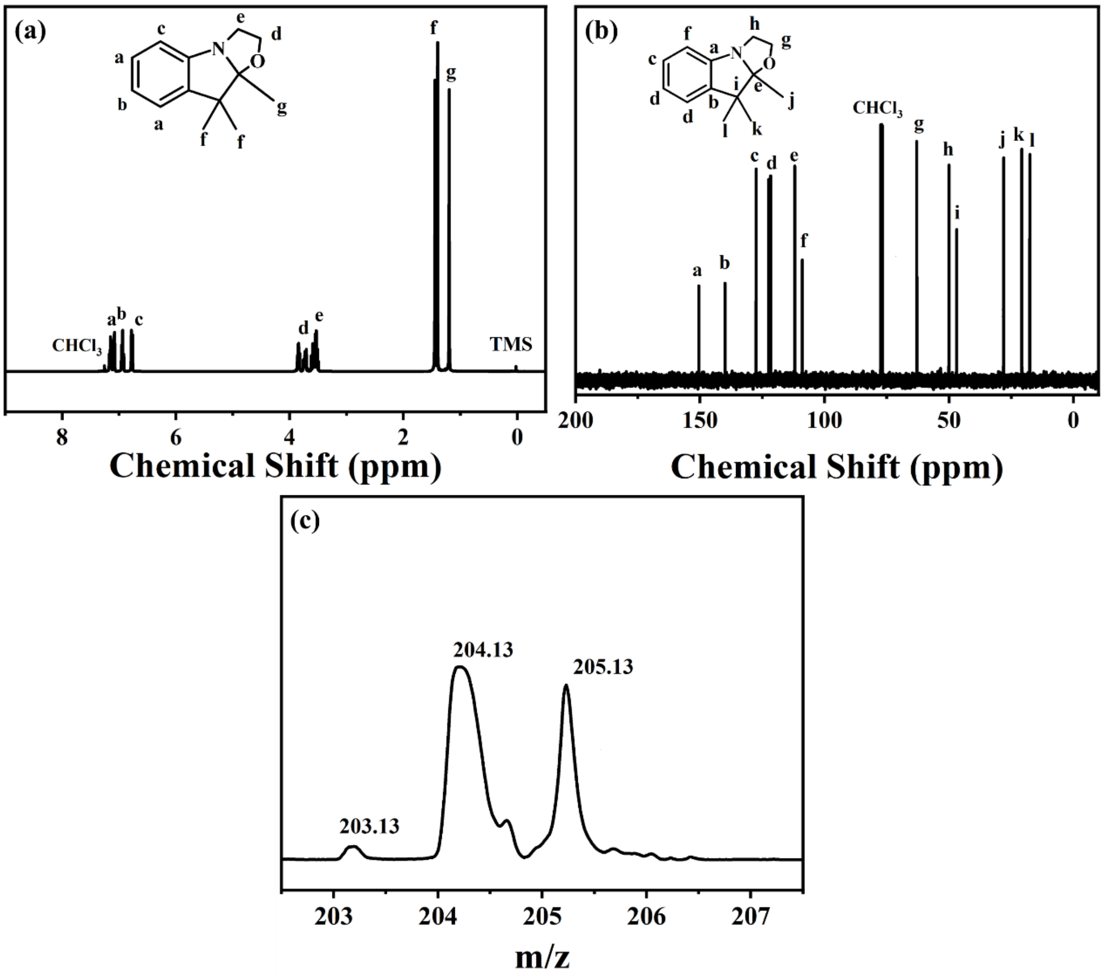

Figure S5. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of compound (2) in CDCl$_3$. (c) MS spectrum of compound (2) in CHCl$_3$.

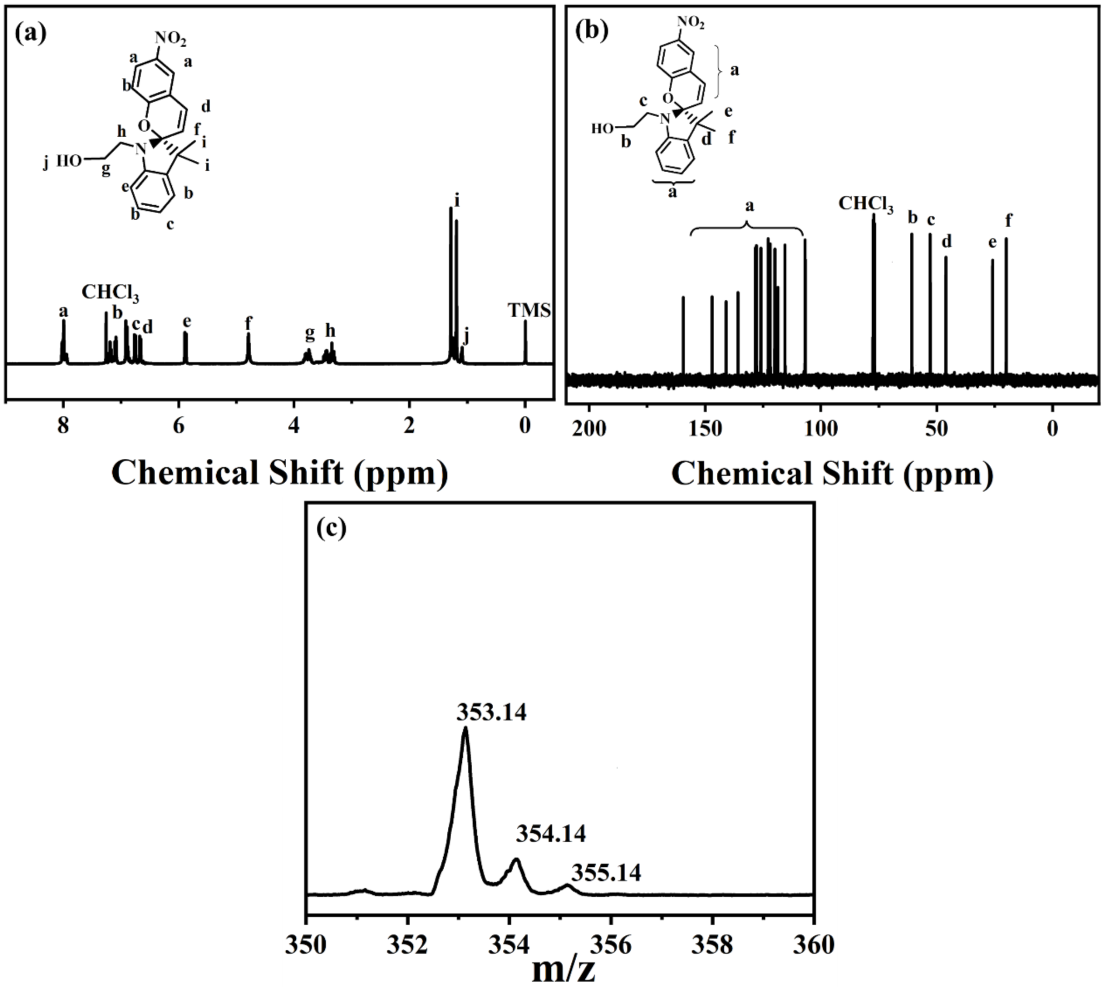

Figure S6. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of compound (3) in $CDCl_3$. (c) MS spectrum of compound (3) in $CHCl_3$.

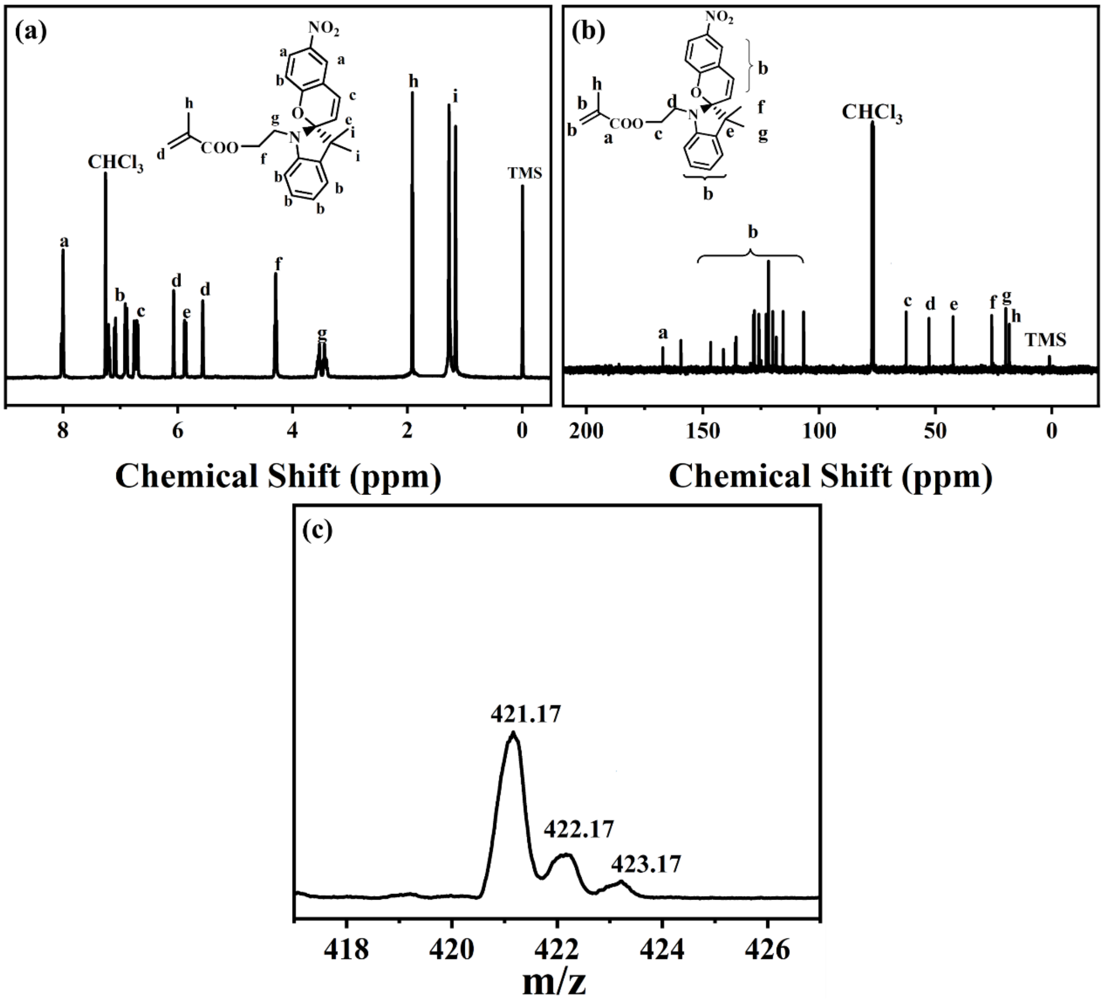

Figure S7. (a) ^1H NMR and (b) ^{13}C NMR spectra of MSP in $CDCl_3$. (c) MS spectrum of MSP in $CHCl_3$.

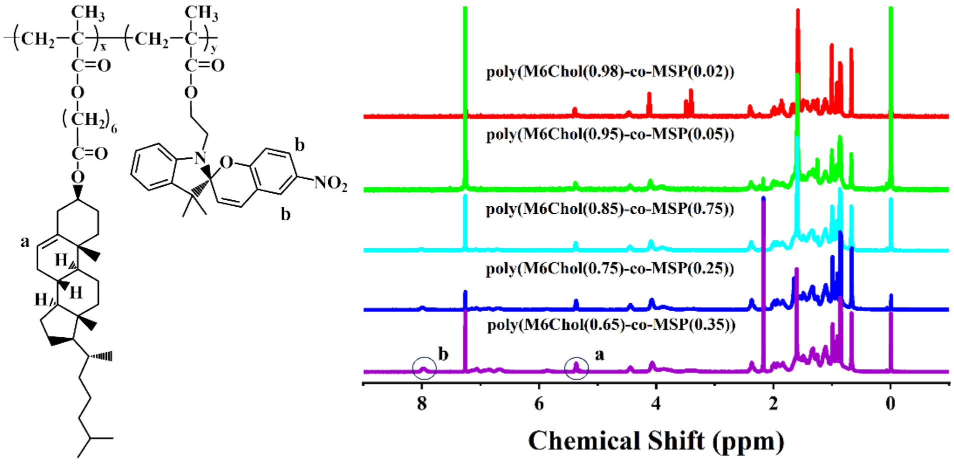

Figure S8. ^{1}H NMR spectra of poly(M6Chol(x)-co-MSP(y)) with different copolymer ratios in $CDCl_3$.

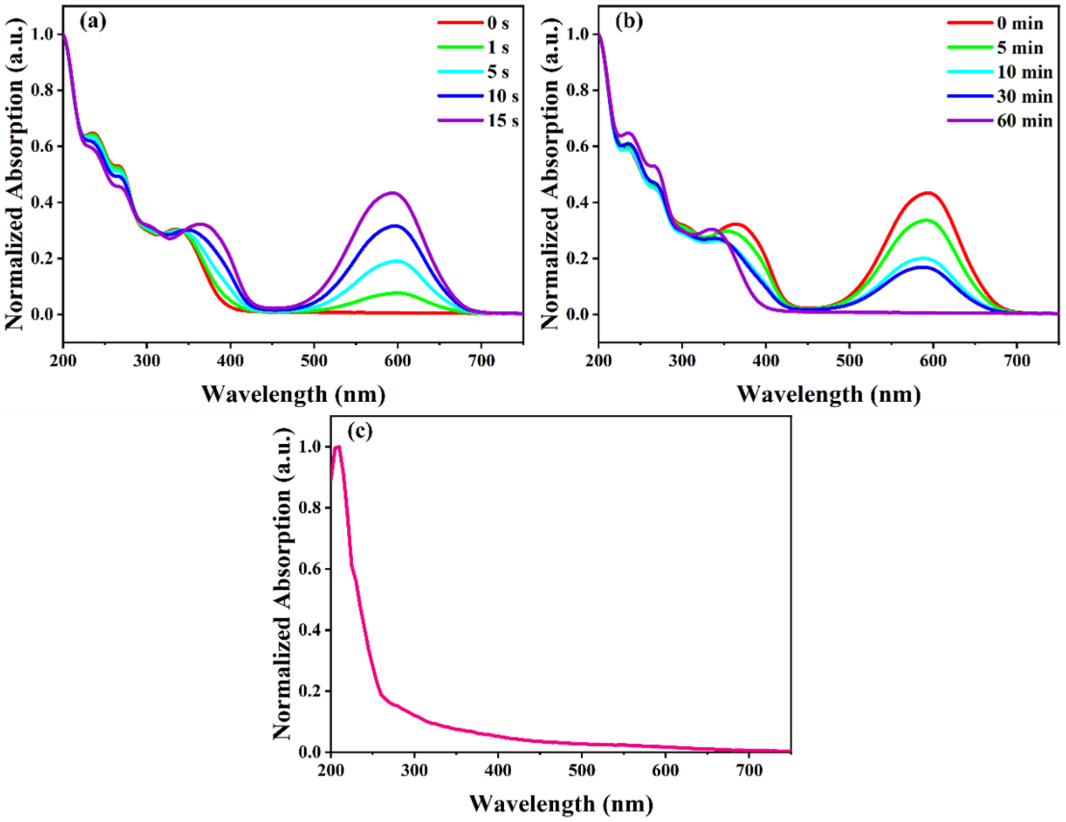

Figure S9. (a) The absorption spectra of PMSP film exposed to 365 nm light for different time and (b) then irradiated with 520 nm light for different time. (c) Absorption spectrum of PM6Chol film.

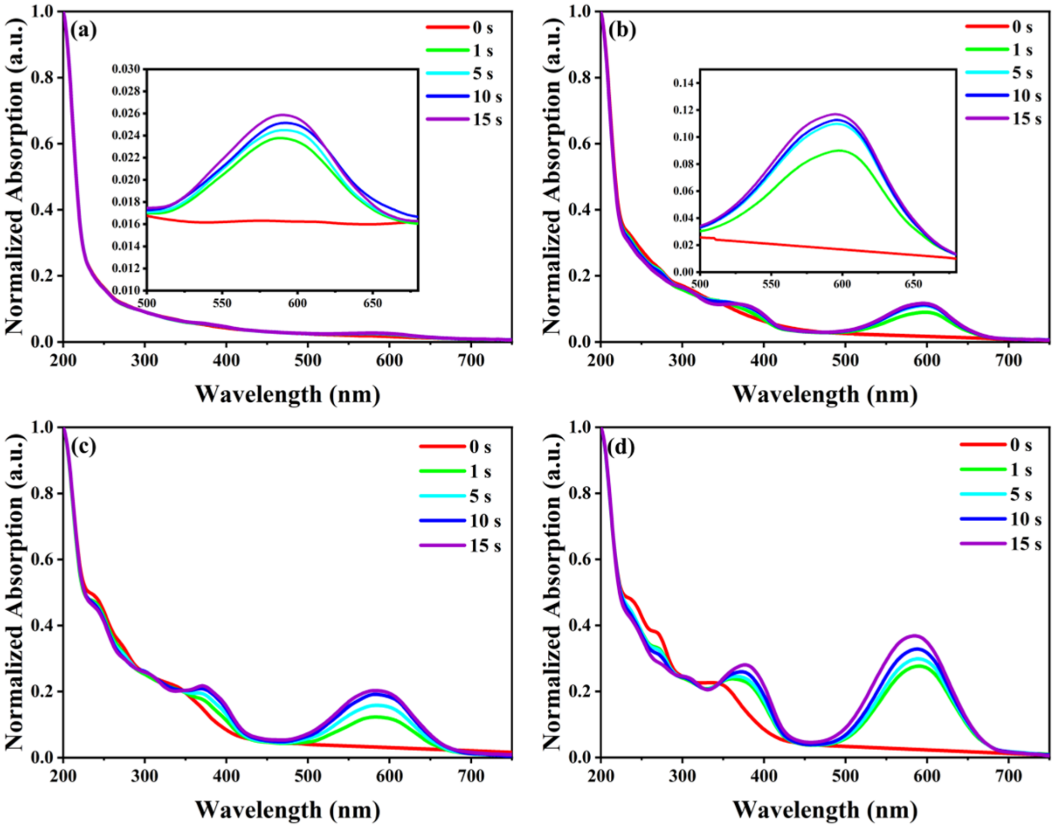

Figure S10. Absorption spectra of (a) poly(M6Chol(0.98)-co-MSP(0.02)), (b) poly(M6Chol(0.85)-co-MSP(0.15)), (c) poly(M6Chol(0.75)-co-MSP(0.25)), (d) poly(M6Chol(0.65)-co-MSP(0.35)) irradiated with 365 nm UV light for different time.

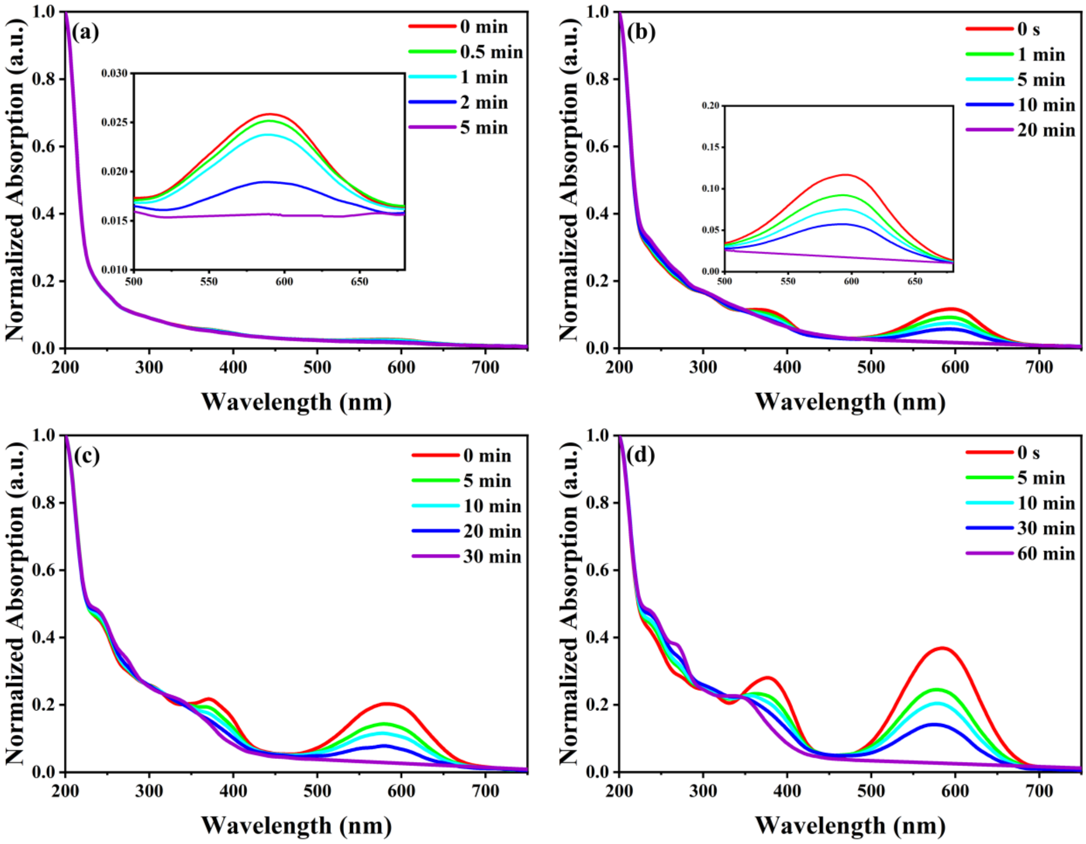

Figure S11. Absorption spectra of (a) poly(M6Chol(0.98)-co-MSP(0.02)), (b) poly(M6Chol(0.85)-co-MSP(0.15)), (c) poly(M6Chol(0.75)-co-MSP(0.25)), (d) poly(M6Chol(0.65)-co-MSP(0.35)) after 520 nm radiation.

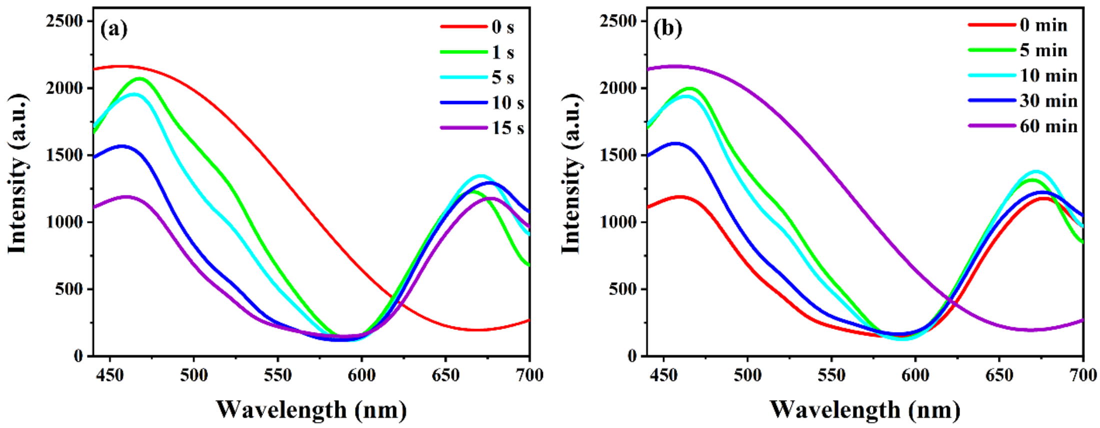

Figure S12. (a) Emission spectra of PMSP film exposed to 365 nm light for different time and (b) then irradiated with 520 nm light for different time.

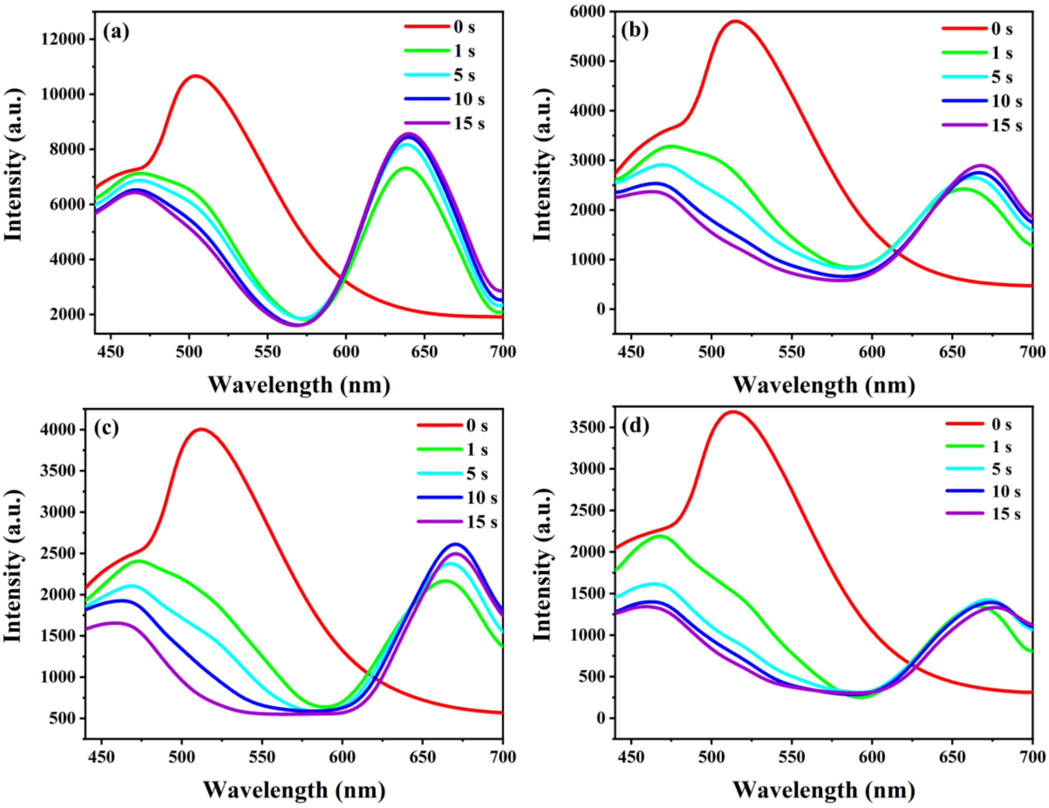

Figure S13. Emission spectra of polymer films irradiated with 365 nm UV light for different times, (a) poly(M6Chol(0.98)-co-MSP(0.02)), (b) poly(M6Chol(0.85)-co-MSP(0.15)), (c) poly(M6Chol(0.75)-co-MSP(0.25)), (d) poly(M6Chol(0.65)-co-MSP(0.35)). (λ_{ex}=370 nm).

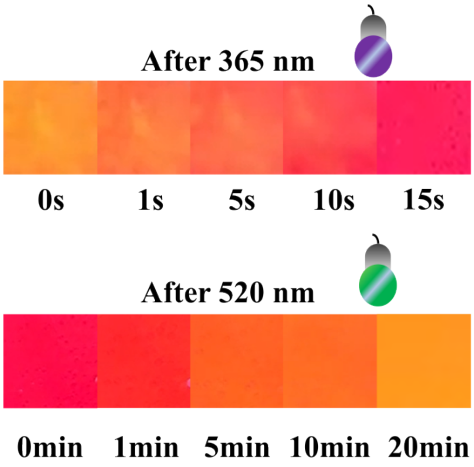

Figure S14. The reversible luminescence color change of poly(M6Chol(0.95)-co-MSP(0.05)) film under sequential irradiation with 365 nm and 520 nm light.

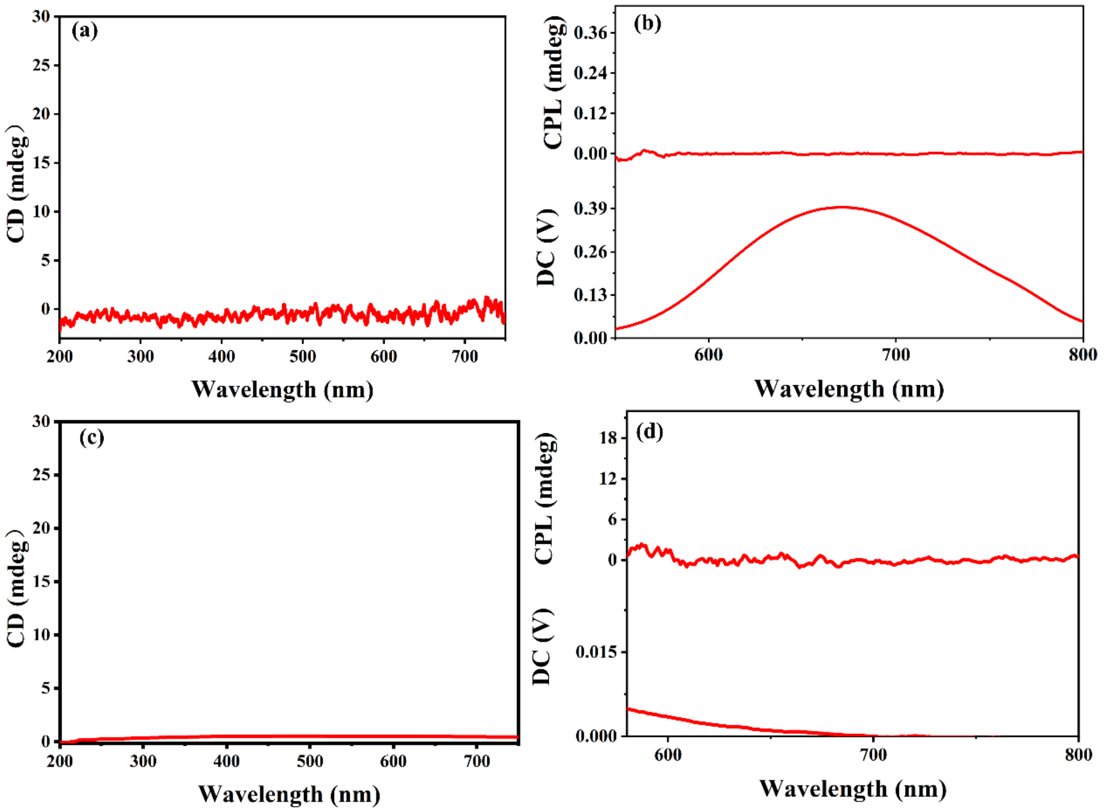

Figure S15. (a) CD spectra of PMSP and (b) CPL spectra of PMSP film. (c) CD spectra of PM6Chol and (d) CPL spectra of PM6Chol film. (λ_{ex}=370 nm).

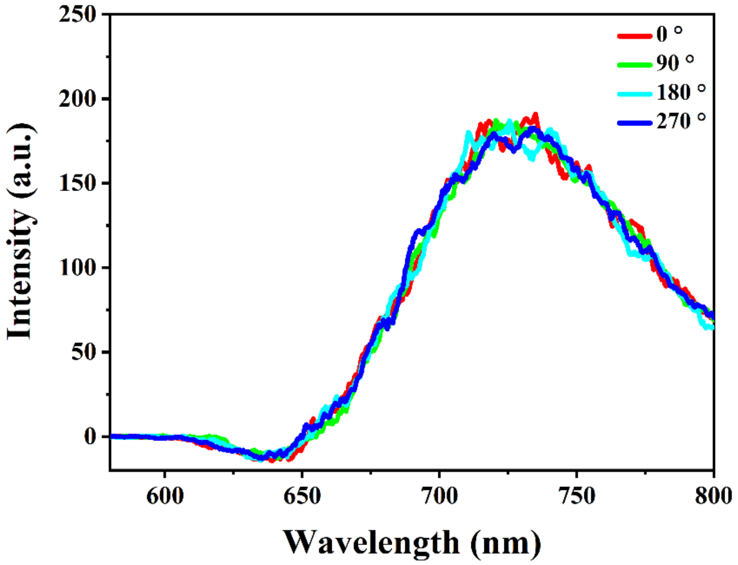

Figure S16: The CPL spectra of poly(M6Chol(0.95)-co-MSP(0.05)) with 30 um film thickness at different rotation angle (λ_{ex}=370 nm).