

Supplementary Information

Photochromic fluorescence switching in liquid crystalline polynorbornenes with α -cyanostilbene side-chains

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Materials

3,4,5-Trihydroxybenzaldehyde (97%), Protocatechualdehyde (98%), 3,5-Dihydroxybenzaldehyde (97%), p-Hydroxybenzaldehyde (99%), 4-Bromophenylacetonitrile (99%), 4-Hydroxybenzeneboronic acid (98%), 1-Bromododecane (99%), Potassium iodide (99%), Tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$), Methyl 7-aminoheptanoate hydrochloride (97%), Triethylamine (TEA) (99%, AR), 1-[3-(dimethyl amino) propyl]-3-ethylcarbodiimide hydrochloride ($\text{EDC} \cdot \text{HCl}$, 99%), 4-(dimethylamino)pyridine (DMAP, 99%) and Grubbs catalyst (third generation) were purchased from Sigma Aldrich. Dichloromethane (CH_2Cl_2) (AR, Sinopharm) and Chloroform (CHCl_3) (AR, Sinopharm) were distilled by refluxing over CaH_2 prior to use. Tetrahydrofuran (THF) (AR, Sinopharm) was heated under reflux over sodium for at least 8 h and distilled before use. All other reagents and solvents were obtained from commercial sources and used without further purification.

Measurements

Nuclear Magnetic Resonance Spectroscopy (NMR). The 1D ^1H , ^{13}C NMR spectra and 2D ^1H - ^1H COSY, ROESY were recorded on an Agilent 600MHz NMR spectrometer at ambient temperature with CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard.

Gel Permeation Chromatography (GPC). The number-average molecular weight (M_n , GPC) and polydispersity (PDI) of polymers were measured on an instrument comprised of a Waters 1515 isocratic HPLC pump, a Waters 717 plus auto sampler, a Waters 2414 refractive-index detector with three 300 mm (length) \times 7.5 mm (inner diameter) columns with a particle size of 5 μm (PL gel mixed-C, Polymer Laboratories). THF was used as the eluent at a flow rate of 1.00 mL/min at 35 $^\circ\text{C}$. The calibration was carried out with a series of polystyrene standards.

Polarized Optical Microscopy (POM). LC textures and birefringence of samples were examined under an Olympus BX51-P microscope equipped with a Linkam THMS 600 hot stage. Samples were made by sandwiching the dried polymer powder between a glass slide and a cover glass. These samples were heated to their isotropic temperature and then cooled to room temperature at a rate of 1-5 $^\circ\text{C}/\text{min}$.

Differential Scanning Calorimetry (DSC). Thermal behavior and phase transition temperatures of all monomers and polymers were observed and obtained using a TA-Q200 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at a cooling and heating rate of 10 $^\circ\text{C}/\text{min}$. Samples with a typical mass of about 5 mg were encapsulated in sealed aluminum pans. The DSC curves recorded their first cooling and second heating processes at a rate of 10 $^\circ\text{C}/\text{min}$.

Thermogravimetric Analysis (TGA). The thermal stability of all polymers was measured by TGA on a TGA Q500 (TA) instrument at a heating rate of 10 $^\circ\text{C}/\text{min}$ from room temperature to 800 $^\circ\text{C}$ under a nitrogen atmosphere.

Small Angle X-ray Scattering (SAXS). To identify phase structures of polymers, SAXS

experiments were performed using a high-flux X-ray instrument (SAXSess mc², Anton Paar) equipped with Kratky block-collimation system and a GEID3003 sealed-tube X-ray generator (CuK α). The wavelength is 0.1542 nm. Samples were wrapped into aluminum foils and sandwiched in a steel sample holder. The X-ray scattering patterns were recorded in vacuum on an imaging-plate (IP) which extended to high-angle range (the q range covered from 0.06 to 29 nm⁻¹, $q = 4\pi(\sin\theta)/\lambda$, where the λ is the wavelength of 0.1542 nm and 2θ is the scattering angle). The diffraction peak positions were calibrated with silver behenate.

Powder X-ray Diffraction (PXRD). D/MAX-3C diffractometer using a Cu tube source (CuK α , $\lambda = 1.5406 \text{ \AA}$).

Photoluminescence Spectroscopy. PL spectra of solutions and solids were recorded on a Shimadzu RF-5301 PC spectrofluorophotometer (Japan), with an excitation wavelength of 380 nm for solids, 360 or 370 nm for solutions.

UV-vis Spectroscopy. The UV-vis spectra were measured on Cary 5000 UV-vis-NIR (Agilent Technologies). All samples in dilute organic solvents ($1 \times 10^{-5} \text{ mol/L}$) were prepared in the dark.

Mass Spectrometry (MS). MS spectra of photoproducts were recorded on matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer (Ultra extreme, Bruker Co.).

Synthetic procedure

Synthesis of Precursors and Monomers. The synthetic procedures of all the monomers (M-(Z)-345, M-(Z)-34, M-(Z)-35, M-(Z)-4, M-(E)-345 and M-(E)-34) are shown in Scheme 1. Compound 2 was synthesized according to the literature. The experimental details are described as follows, taking M-(Z)-345 and M-(E)-345 as examples.

Synthesis of N-(methyl 7-aminoheptanoic acid)-*cis*-5-norbornene-*exo*-2,3-dicarb-oximide (Compound 1). *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (5.00 g, 30.46 mmol) and methyl 7-aminoheptanoate hydrochloride (5.34 g, 33.54 mmol) were charged in 250 mL three-necked flask, and then toluene (80 mL) was added to dissolve the reactant. Trimethylamine (TEA, 0.31 g, 3.06 mmol) was added stepwise to the solution. The mixture was stirred under reflux for 12 h. After reaction, the solution was concentrated under vacuum. The crude product was purified by silica gel column chromatography with dichloromethane as eluent to yield a colorless oil product 7.36 g (85%). The obtained product (3.00 g, 9.82 mmol) was then dissolved in THF (50 mL) followed by adding sodium hydroxide aqueous solution (1 mol/L, 10 mL) and then stirred for 12 h. After removing THF, the residue was washed with diluted hydrochloric acid and ethyl acetate. The resulting organic phase was dried with anhydrous sodium sulfate and removed by evaporation under reduced pressure to obtain a white solid 2.61 g (91%). ¹H NMR (CDCl₃, TMS), δ : 6.29 (s, 2H), 3.47-3.45 (t, 2H), 3.27 (s, 2H), 2.67 (s, 2H), 2.35-2.33 (t, 2H), 1.65-1.51 (m, 4H), 1.40-1.26 (m, 4H).

Synthesis of M-(Z)-345. Compound 1 (0.65 g, 2.22 mmol), Compound 2 (0.94 g, 1.11 mmol), and DMAP (15 mg, 0.12 mmol) were stirred in CH₂Cl₂ (50 mL). Then, EDC·HCl (0.53 g,

2.76 mmol) was added to the mixture and the reaction was allowed to proceed for 5 h at room temperature. CH₂Cl₂ was then evaporated under vacuum. The resulting solid was purified by silica gel column chromatography with CH₂Cl₂-ethyl acetate (50: 1) as eluent to yield luminous yellow solid 0.94 g (76%). ¹H NMR (CDCl₃, TMS), δ: 7.73-7.72 (d, 2H), 7.64-7.61 (m, 4H), 7.46 (s, 1H), 7.18-7.17 (t, 4H), 6.29 (s, 2H), 4.06-4.04 (m, 6H), 3.50-3.47 (t, 2H), 3.28 (s, 2H), 2.68 (s, 2H), 2.60-2.57 (t, 2H), 1.86-1.74 (d, 8H), 1.63-1.23 (m, 62H), 0.89-0.87 (m, 9H). ¹³C NMR (CDCl₃, TMS), δ: 178.1, 172.1, 153.2, 150.5, 142.3, 140.9, 140.6, 137.8, 137.7, 133.7, 128.6, 128.0, 127.6, 126.3, 122.1, 118.4, 109.3, 108.0, 73.6, 69.2, 47.8, 45.2, 42.7, 38.6, 34.3, 31.9, 30.4, 29.7, 29.4, 28.6, 27.6, 26.6, 26.1, 24.7, 22.7, 14.1. MS (HR-ESI): [M + NH₄]⁺/z, Calcd 1140.8338; Found, 1140.8345. Anal. Calcd for C₇₃H₁₀₆N₂O₇: C, 78.03; H, 9.51; N, 2.49. Found: C, 77.82; H, 9.13; N, 2.04.

Synthesis of M-(E)-345. M-(Z)-345 powders (0.36 g, 0.32 mmol) were added into CHCl₃ (200 mL) and then irradiated with 365nm UV light for 12 h. Finally, the Z-isomer was mostly converted to E-isomer. Pure M-(E)-345 was obtained by silica gel column chromatography with CH₂Cl₂-hexane-ethyl acetate (5: 1: 0.1). The product had the appearance of a white powder 0.26 g (73%). ¹H NMR (CDCl₃, TMS), δ: 7.59-7.55 (m, 4H), 7.49-7.43 (d, 2H), 7.25 (s, 1H), 7.17-7.15 (m, 2H), 6.38 (s, 2H), 6.29-6.28 (t, 2H), 3.95-3.93 (t, 2H), 3.67-3.64 (t, 4H), 3.50-3.47 (t, 2H), 3.28 (s, 2H), 2.68 (d, 2H), 2.59-2.56 (t, 2H), 1.79-1.23 (m, 70H), 0.89-0.86 (m, 9H). ¹³C NMR (CDCl₃, TMS), δ: 178.1, 172.0, 152.8, 150.6, 144.6, 141.1, 139.9, 137.8, 137.6, 132.1, 129.6, 128.2, 128.0, 127.6, 122.1, 120.2, 112.1, 108.5, 73.5, 68.8, 47.8, 45.2, 42.7, 38.5, 34.2, 31.9, 30.3, 29.6, 29.3, 29.1, 28.60, 27.6, 26.6, 26.0, 24.7, 22.7, 14.1. MS (HR-ESI): [M + NH₄]⁺/z, Calcd 1140.8338; Found, 1140.8341. Anal. Calcd for C₇₃H₁₀₆N₂O₇: C, 78.03; H, 9.51; N, 2.49. Found: C, 77.83; H, 9.06; N, 2.12.

All the other monomers were synthesized and characterized similarly.

M-(Z)-34. ¹H NMR (CDCl₃, TMS), δ: 7.73-7.71 (d, 2H), 7.68 (d, 1H), 7.64-7.61 (t, 4H), 7.48 (s, 1H), 7.38-7.36 (dd, 1H), 7.18-7.17 (d, 2H), 6.93-6.91 (d, 1H), 6.29 (s, 2H), 4.11-4.07 (m, 4H), 3.50-3.47 (t, 2H), 3.28 (s, 2H), 2.68 (s, 2H), 2.59-2.57 (t, 2H), 1.88-1.74 (d, 6H), 1.63-1.23 (m, 42H), 0.89-0.87 (m, 6H). ¹³C NMR (CDCl₃, TMS), δ: 178.1, 172.1, 151.5, 150.5, 149.0, 142.1, 140.6, 137.8, 137.7, 134.0, 128.0, 127.6, 126.6, 126.2, 124.3, 122.0, 118.6, 113.2, 112.8, 107.8, 69.3, 69.1, 47.8, 45.2, 42.7, 38.6, 34.3, 31.9, 29.7, 29.4, 29.2, 29.1, 28.6, 27.6, 26.6, 26.1, 26.0, 24.7, 22.7, 14.1. MS (HR-ESI): [M + NH₄]⁺/z, Calcd 956.6511; Found, 956.6515. Anal. Calcd for C₆₁H₈₂N₂O₆: C, 78.00; H, 8.80; N, 2.98. Found: C, 77.89; H, 8.50; N, 2.63.

M-(E)-34. ¹H NMR (CDCl₃, TMS), δ: 7.59-7.57 (dd, 4H), 7.49-7.48 (d, 2H), 7.27 (s, 1H), 7.17-7.16 (d, 2H), 6.84-6.82 (dd, 1H), 6.74-6.73 (d, 1H), 6.64 (d, 1H), 6.29 (s, 2H), 3.98-3.96 (t, 2H), 3.59-3.57 (t, 2H), 3.50-3.47 (t, 2H), 3.28 (s, 2H), 2.68 (s, 2H), 2.60-2.56 (t, 2H), 1.81-1.74 (m, 4H), 1.63-1.20 (m, 46H), 0.89-0.86 (m, 6H). ¹³C NMR (CDCl₃, TMS), δ: 178.1, 172.0, 150.9, 150.5, 148.3, 144.4, 140.9, 137.8, 137.6, 132.3, 129.6, 128.0, 127.6, 126.0, 124.5, 122.1, 120.6, 114.0, 112.4, 110.7, 76.8, 68.9, 68.7, 47.8, 45.2, 42.7, 38.5, 34.2, 31.9, 29.7, 29.6, 29.4, 29.3, 29.0, 28.9, 28.6, 27.6, 26.6, 25.9, 24.7, 22.7, 14.1. MS (HR-ESI): [M + NH₄]⁺/z, Calcd 956.6511; Found, 956.6515. Anal. Calcd for C₆₁H₈₂N₂O₆: C, 78.00; H, 8.80; N, 2.98. Found: C, 77.95; H, 8.71; N, 2.77.

M-(Z)-35. ^1H NMR (CDCl_3 , TMS), δ : 7.74-7.73 (d, 2H), 7.65-7.61 (m, 4H), 7.49 (s, 1H), 7.19-7.17 (m, 2H), 7.05 (d, 2H), 6.55-6.54 (t, 1H), 6.29 (s, 2H), 4.01-4.00 (t, 4H), 3.50-3.47 (t, 2H), 3.28 (s, 2H), 2.68 (s, 2H), 2.59-2.57 (t, 2H), 1.82-1.75 (m, 6H), 1.63-1.23 (m, 44H), 0.89-0.87 (t, 6H). ^{13}C NMR (CDCl_3 , TMS), δ : 178.1, 172.1, 160.5, 150.5, 145.8, 142.3, 141.1, 137.8, 137.6, 135.2, 133.5, 128.1, 127.6, 126.5, 122.1, 117.9, 111.2, 107.5, 104.3, 68.3, 47.8, 45.2, 42.7, 38.6, 34.3, 31.9, 29.7, 29.6, 29.4, 29.2, 28.6, 27.6, 26.6, 26.1, 24.7, 22.7, 14.1. MS (HR-ESI): $[\text{M} + \text{NH}_4]^+/\text{z}$, Calcd 956.6511; Found, 956.6511. Anal. Calcd for $\text{C}_{61}\text{H}_{82}\text{N}_2\text{O}_6$: C, 78.00; H, 8.80; N, 2.98. Found: C, 77.85; H, 8.49; N, 2.60.

M-(Z)-4: ^1H NMR (CDCl_3 , TMS), δ : 7.90-7.89 (d, 2H), 7.73-7.71 (d, 2H), 7.64-7.60 (m, 4H), 7.51 (s, 1H), 7.19-7.16 (m, 2H), 6.99-6.96 (m, 2H), 6.29 (s, 2H), 4.04-4.01 (t, 2H), 3.50-3.47 (t, 2H), 3.28 (s, 2H), 2.68 (s, 2H), 2.59-2.57 (t, 2H), 1.83-1.74 (m, 4H), 1.63-1.23 (m, 26H), 0.90-0.87 (t, 3H). ^{13}C NMR (CDCl_3 , TMS), δ : 178.1, 172.1, 161.1, 150.5, 145.9, 141.7, 140.6, 137.8, 137.7, 133.9, 131.2, 128.0, 127.6, 126.3, 126.2, 122.0, 118.5, 114.9, 107.9, 68.3, 47.8, 45.2, 42.7, 38.6, 34.3, 31.9, 29.7, 29.6, 29.4, 29.1, 28.6, 27.6, 26.6, 26.0, 24.7, 22.7, 14.1. MS (HR-ESI): $[\text{M} + \text{NH}_4]^+/\text{z}$, Calcd 772.4684; Found, 772.4684. Anal. Calcd for $\text{C}_{49}\text{H}_{58}\text{N}_2\text{O}_5$: C, 77.95; H, 7.74; N, 3.71. Found: C, 77.72; H, 7.18; N, 3.36.

Synthesis of Polymers. All polymers (P-(Z)-345, P-(Z)-34, P-(Z)-35, P-(Z)-4, P-(E)-345, and P-(E)-34) were obtained by similar polymerization procedures. The experimental details are described as follows which is used P-(Z)-345 as an example.

M-(Z)-345 (0.20 g, 0.18 mmol) and Grubbs third-generation catalyst (2.25 mg, 0.0025 mmol) were loaded in a dry Schlenk tube with a magnetic stirring bar. The tube was evacuated and filled with high purity nitrogen to degas. CH_2Cl_2 (3 mL) was injected to the tube. After three freeze-pump-thaw cycles, polymerization was carried out at room temperature under N_2 atmosphere. After the reaction mixture was stirred for 5 h, vinyl ethyl ether (1 mL) was added to the reaction mixture using a syringe. Then polymerization was stopped after an additional hour. The viscous liquid was diluted with 5 mL of CH_2Cl_2 and passed through a short alumina column to separate the catalyst and then the polymer was precipitated out in 300 mL of methanol. The product was collected by filtration and dried in a vacuum at 35 $^\circ\text{C}$ for 24 h. The target polymer P-(Z)-345 was obtained as an orange filamentous solid 0.16 g (80%).

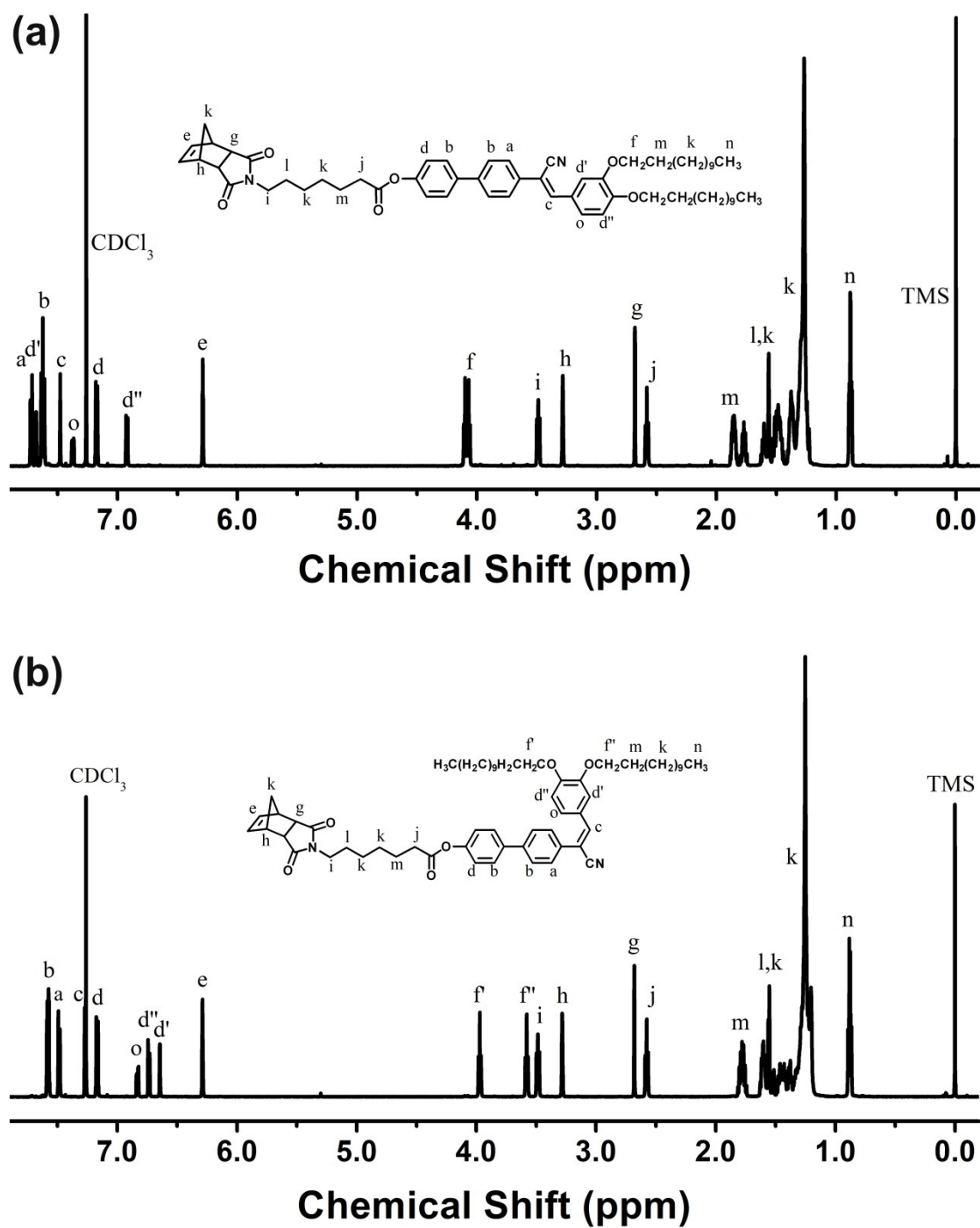


Fig. S1 ¹H NMR spectra of M-(Z)-34 (a) and M-(E)-34 (b) in CDCl₃.

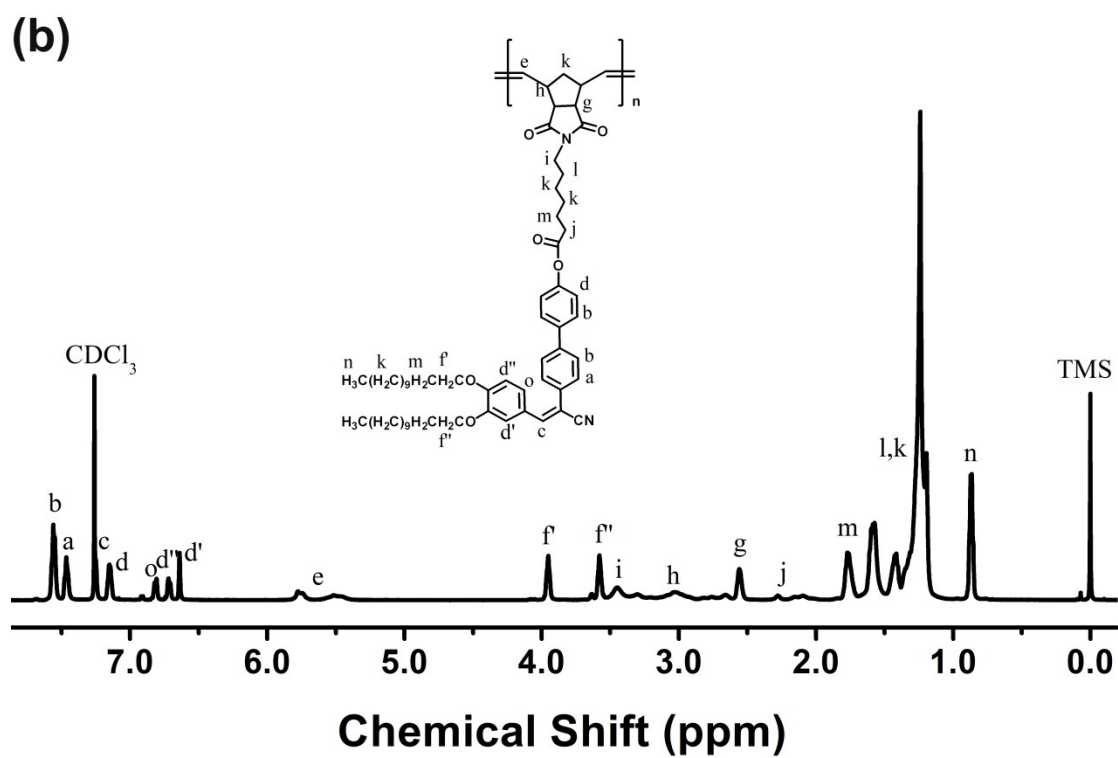
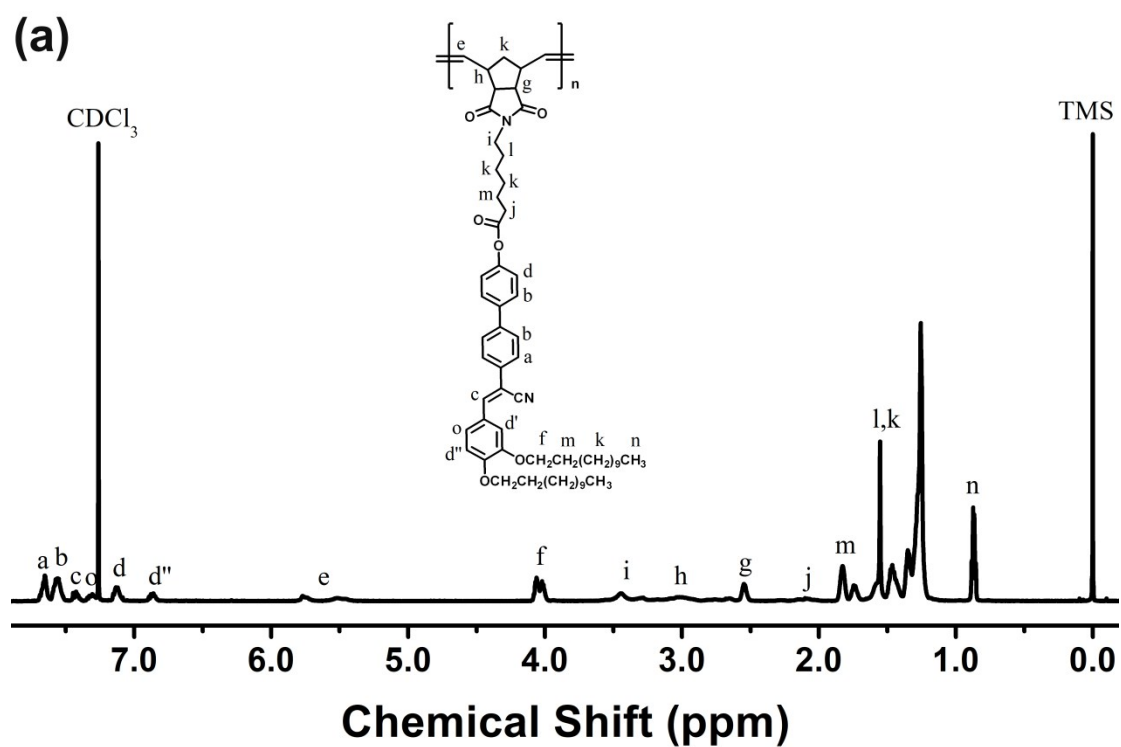


Fig. S2 ¹H NMR spectra of P-(Z)-34 (a) and P-(E)-34 (b) in CDCl₃.

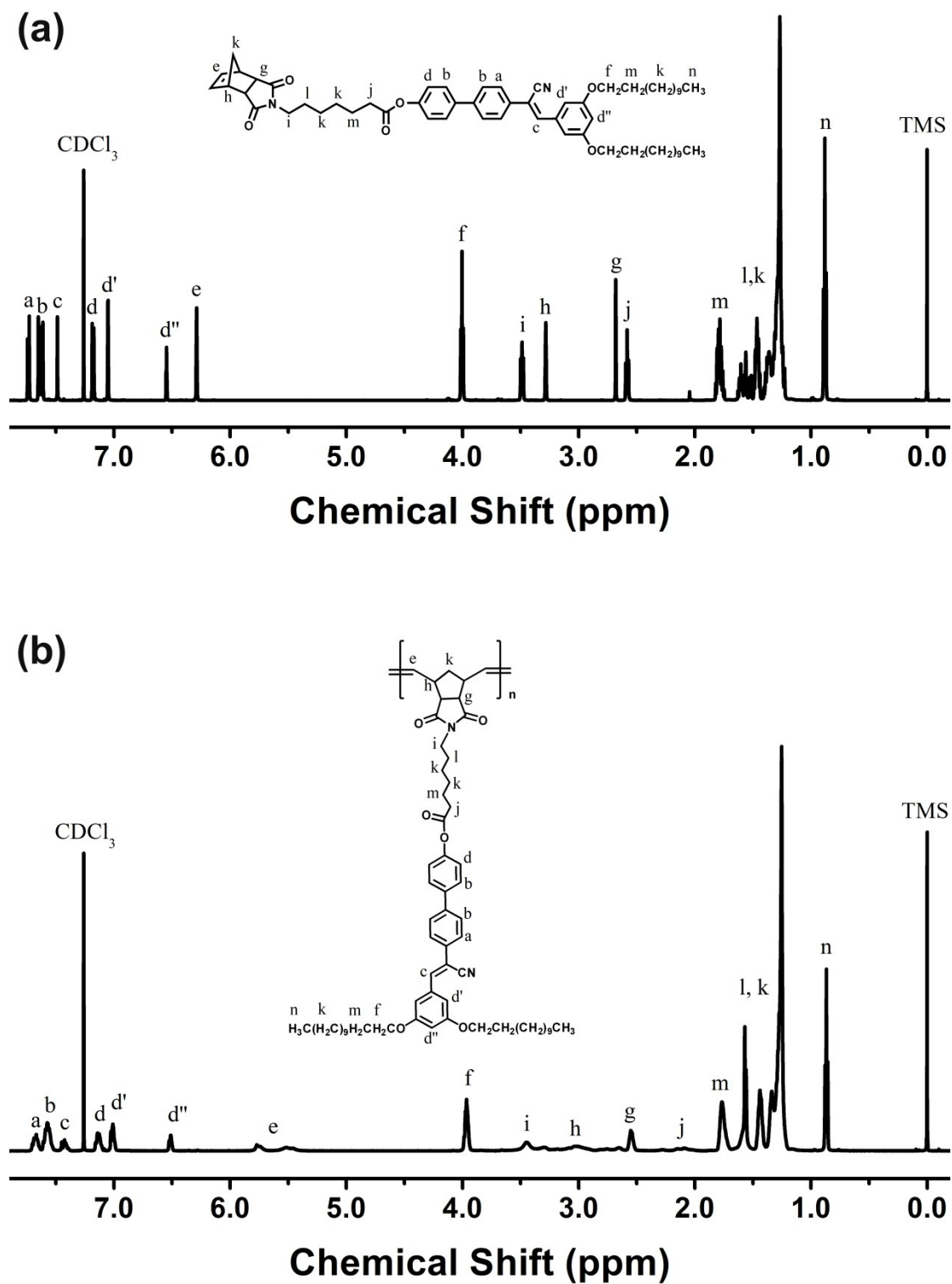


Fig. S3 ^1H NMR spectra of M-(Z)-35 (a) and P-(Z)-35 (b) in CDCl_3 .

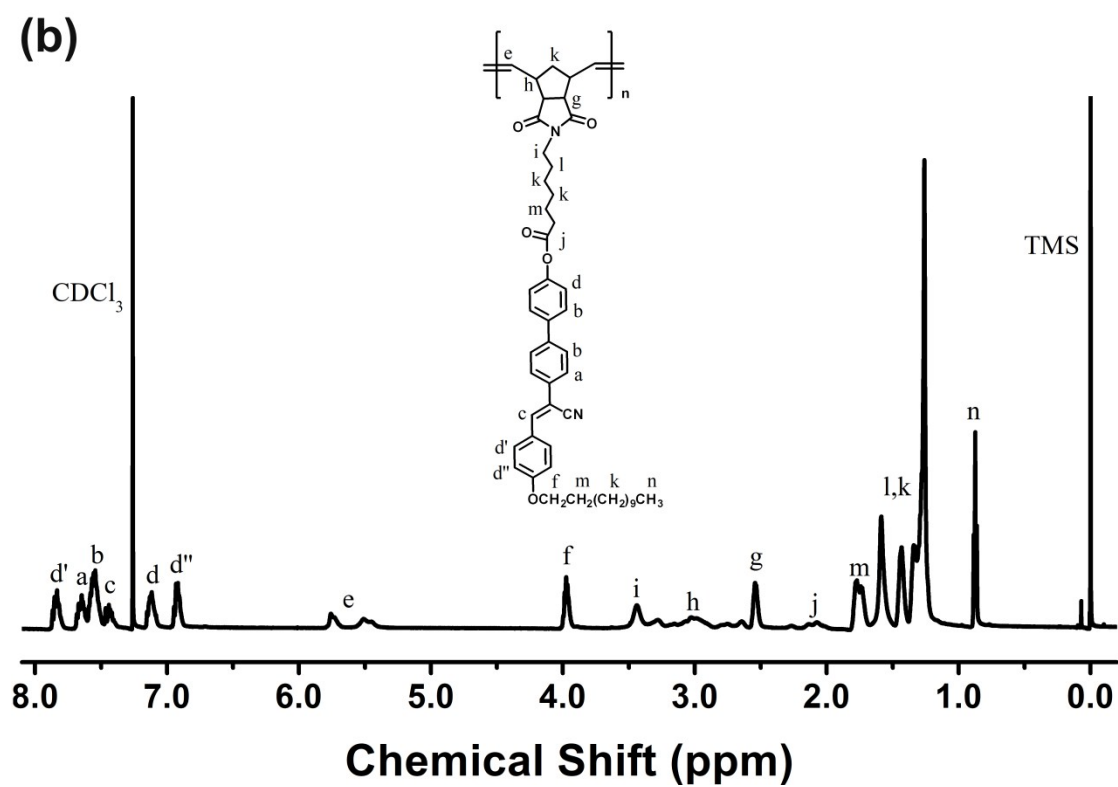
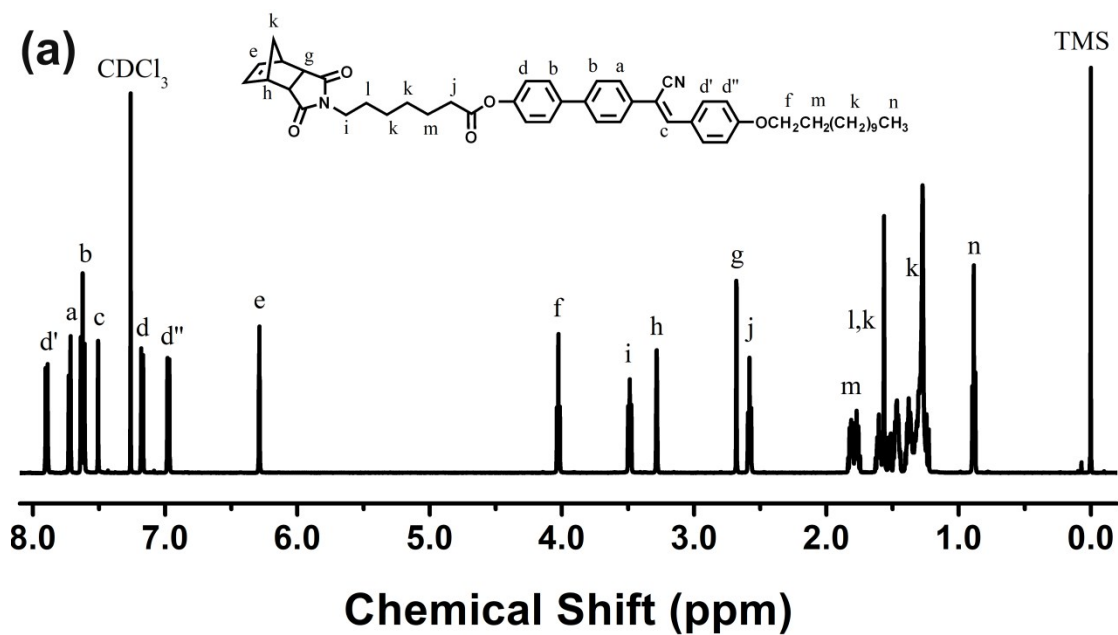


Fig. S4 ^1H NMR spectra of **M-(Z)-4** (a) and **P-(Z)-4** (b) in CDCl_3 .

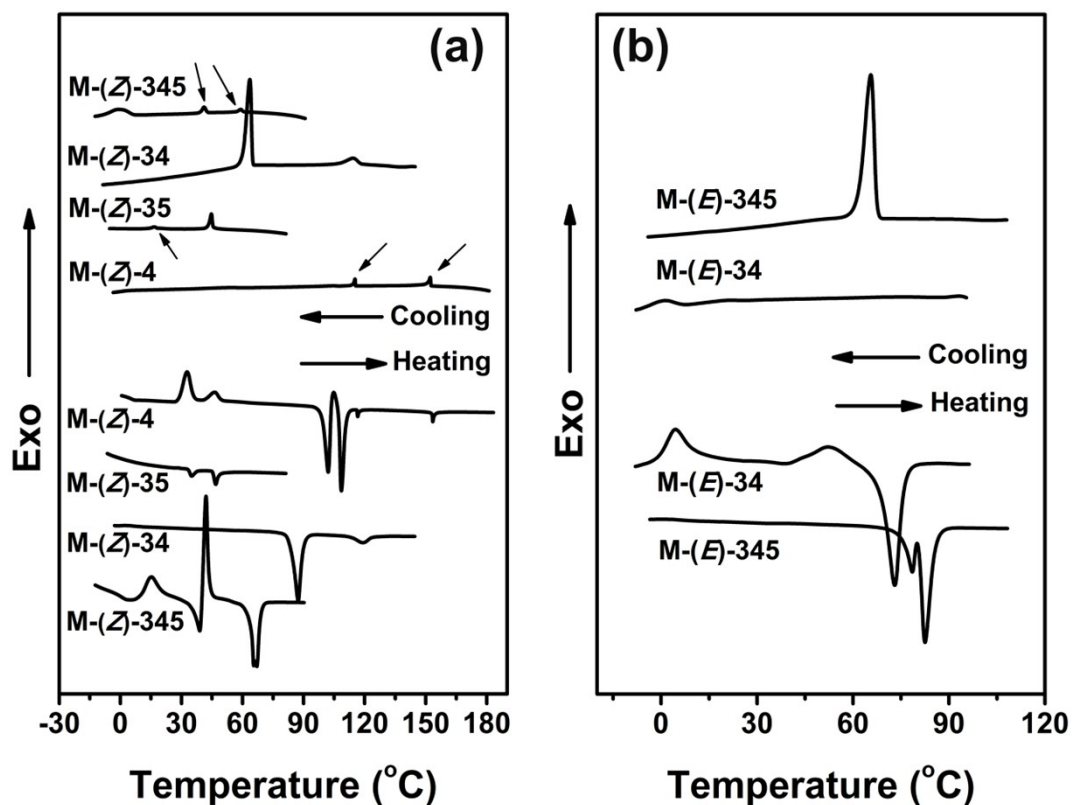


Fig. S5 DSC curves of the *Z*-monomers (a) and *E*-monomers (b) during the first cooling and the second heating cycle at a rate of 10 °C/min in the nitrogen atmosphere.

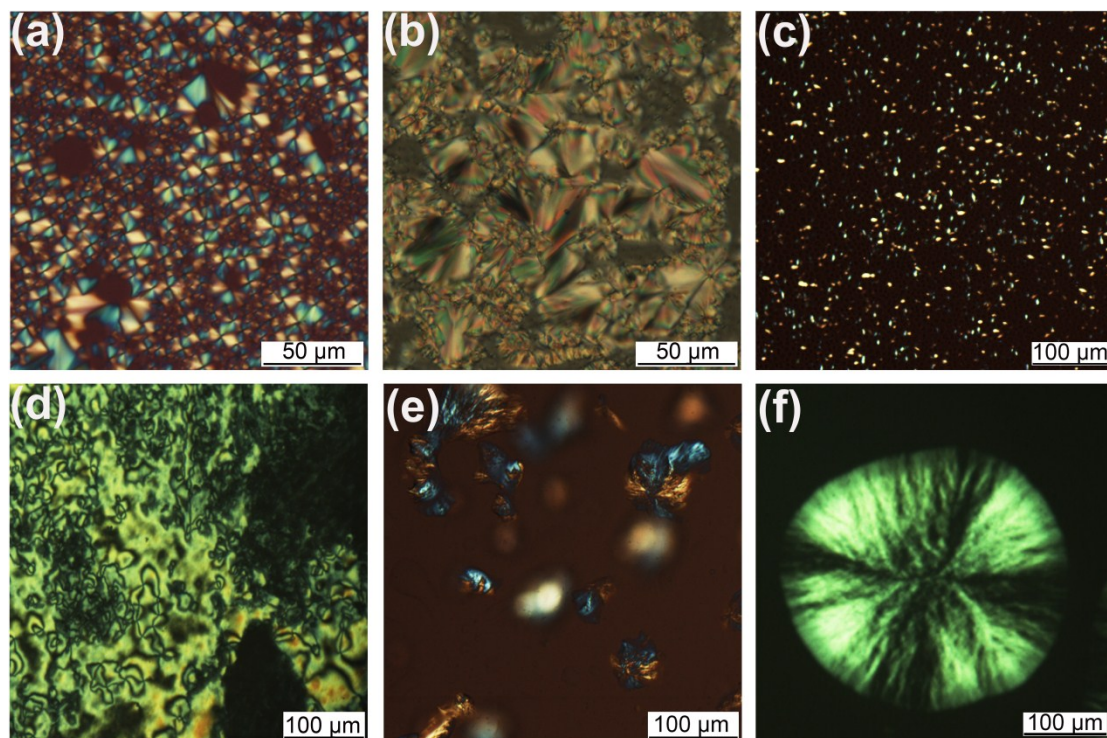


Fig. S6 POM images of the monomers. (a) M-(Z)-345 at 68°C; (b) M-(Z)-34 at 114 °C; (c) M-(Z)-35 at 45 °C; (d) M-(Z)-4 at 131 °C; (e) M-(E)-345 at 56 °C; (f) M-(E)-34 at 32 °C when cooling from isotropic state.

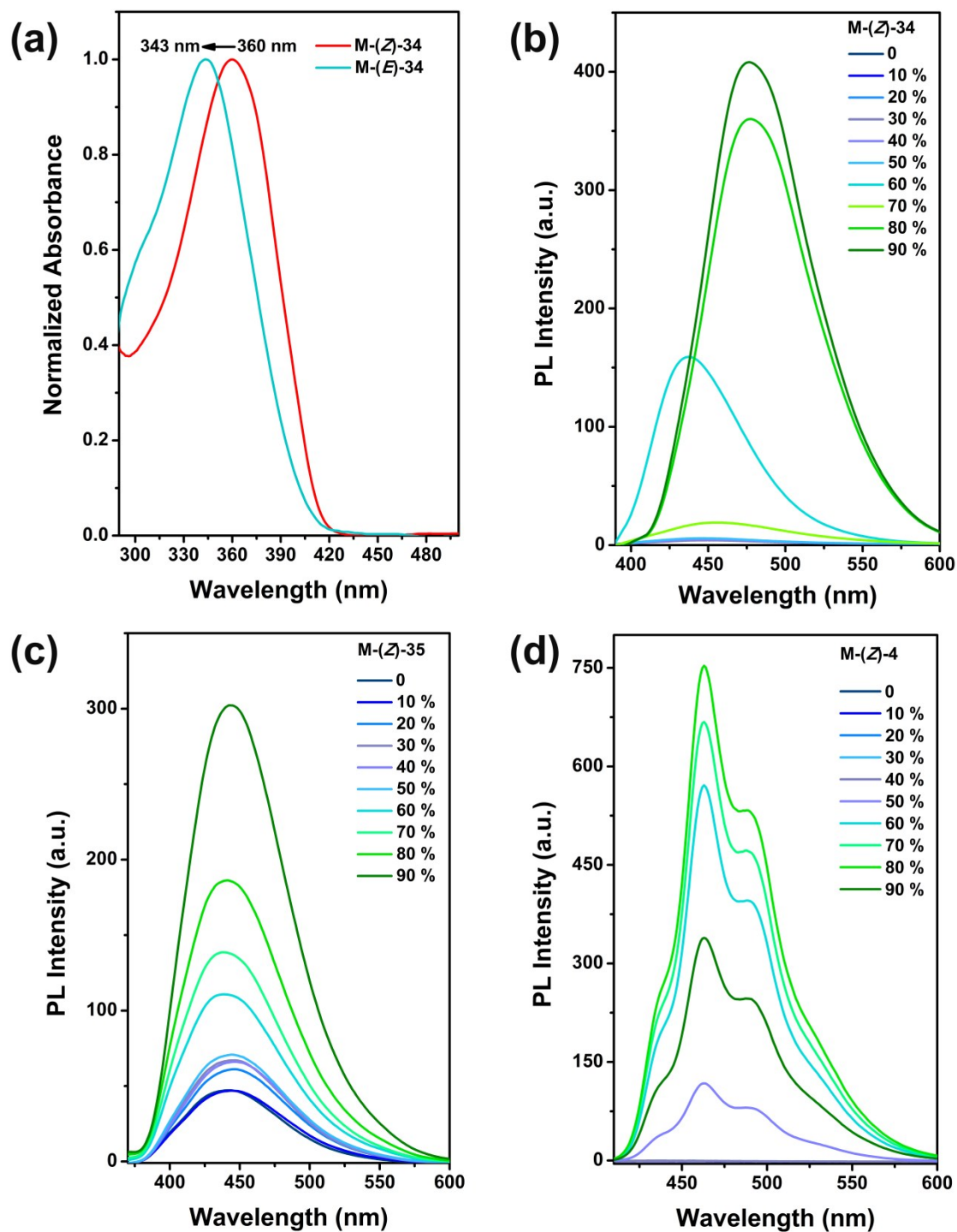


Fig. S7 UV-vis absorption spectra(a) of M-(Z)-34 and M-(E)-34 in CHCl_3 solutions. Emission spectra(b-d) of M-(Z)-34, M-(Z)-35 and M-(Z)-4 in pure THF and THF-water mixtures with different water content, respectively ($c = 1 \times 10^{-5}$ mol/L).

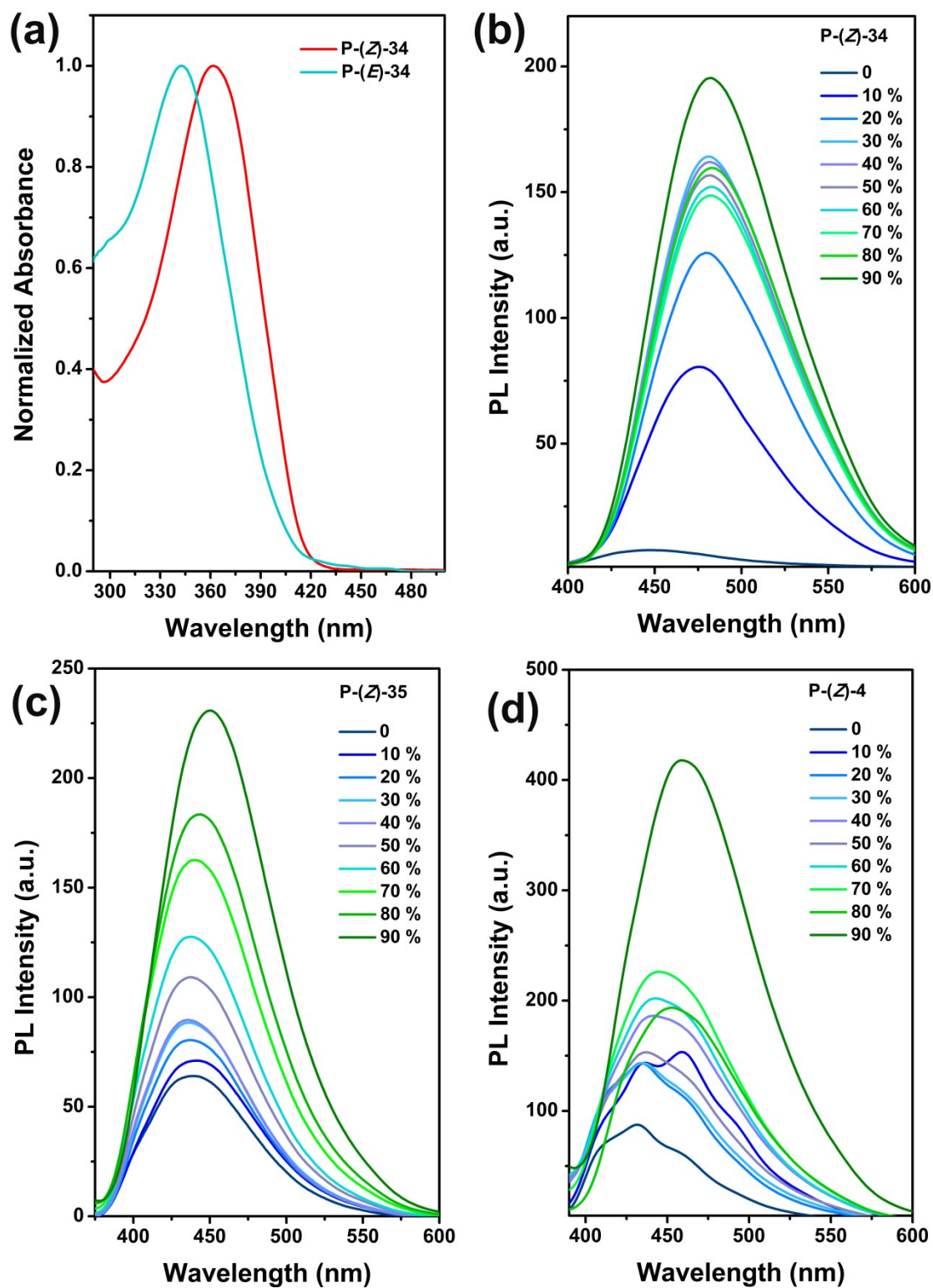


Fig. S8 UV-vis absorption spectra (a) of P-(Z)-34 and P-(E)-34 in CHCl_3 solutions. Emission spectra (b-d) of P-(Z)-34, P-(Z)-35 and P-(Z)-4 in THF-water mixtures with different water volume fractions, respectively ($c = 1 \times 10^{-5}$ mol/L).

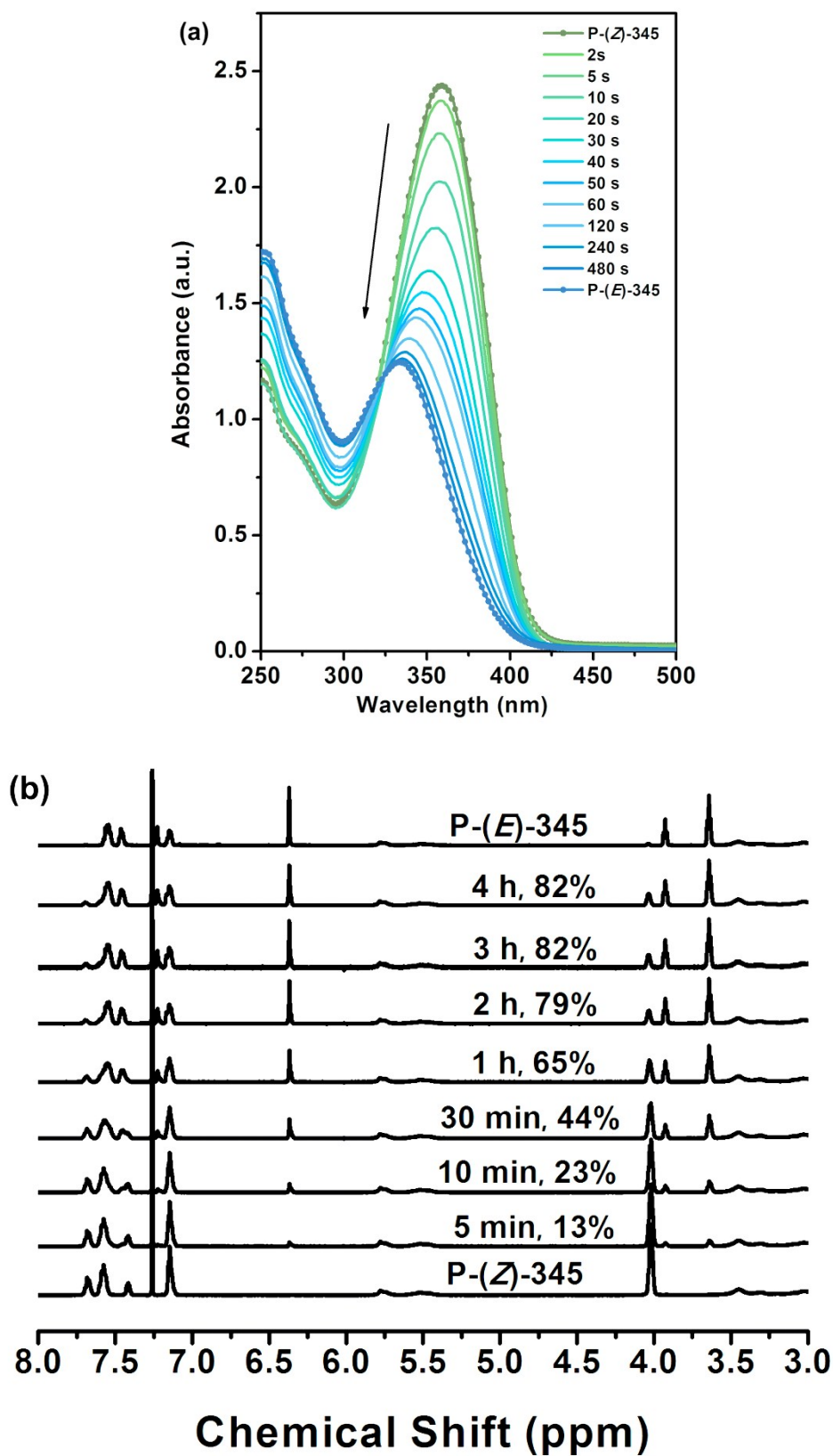


Fig.S9 (a) UV-vis absorption spectra of P-(Z)-345 in CHCl_3 (1×10^{-5} mol/L) before and after irradiation upon 365 nm UV light with different illumination time; (b) ^1H NMR of P-(Z)-345 (10 mg/mL) in CDCl_3 under 365 nm UV irradiation for different times.

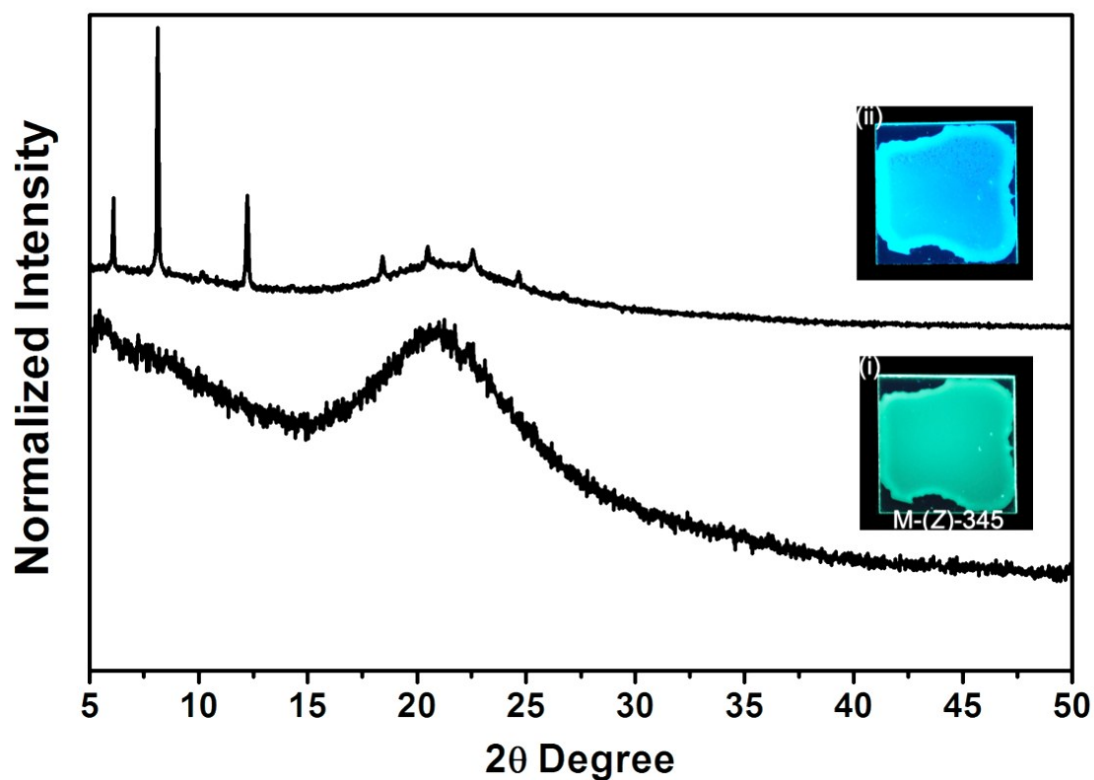


Fig. S10 PXRD profiles as-prepared M-(Z)-345 film (i) and thermal annealed film (ii) and their fluorescent images under UV light.

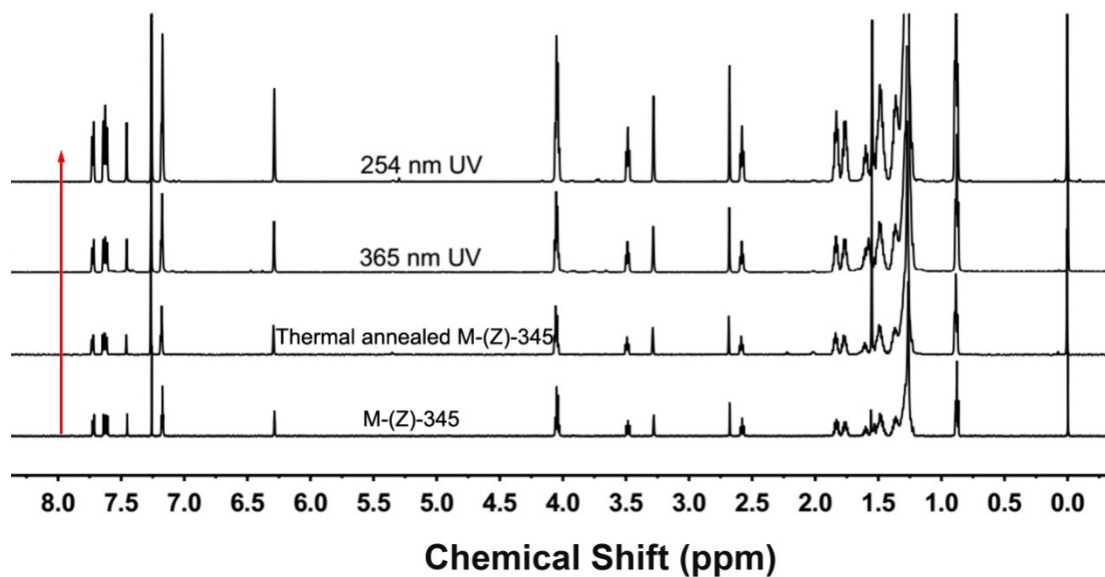


Fig. S11 ¹H NMR spectra of the M-(Z)-345 samples with different treatment: (from bottom to the top) original sample, thermal annealed sample, UV-irradiated crystalline sample (under 365 nm for 1 h and then 254 nm for 1 h).

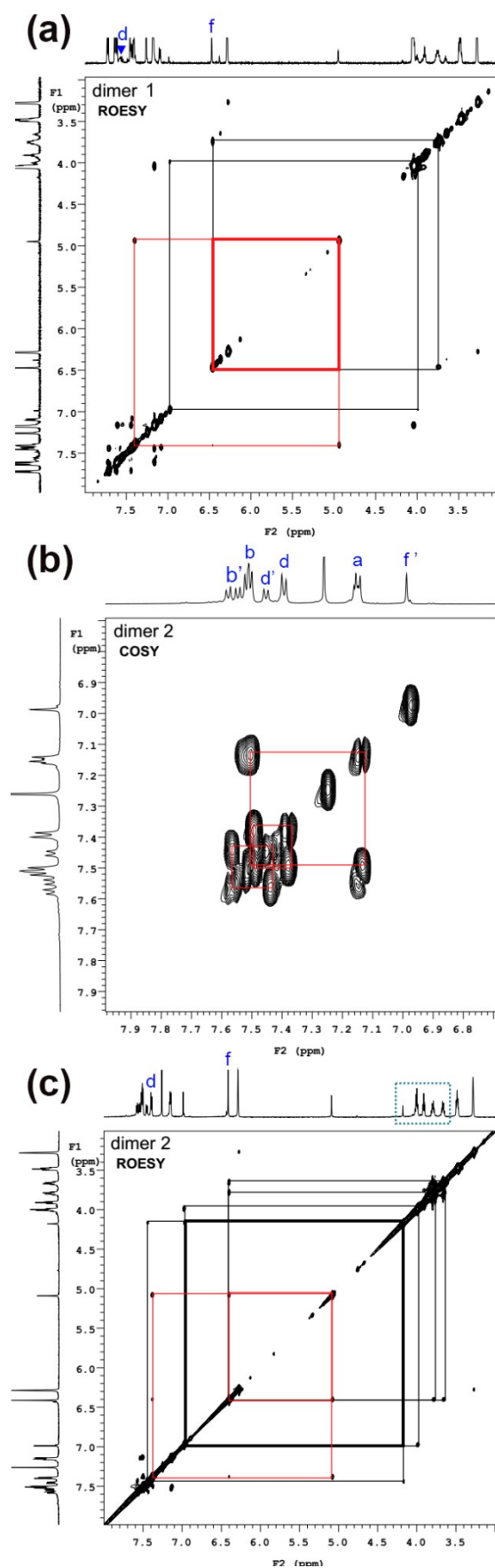


Fig. S12 ROESY spectrum (a) of dimer 1; COSY (b) and ROESY (c) spectra of dimer 2.

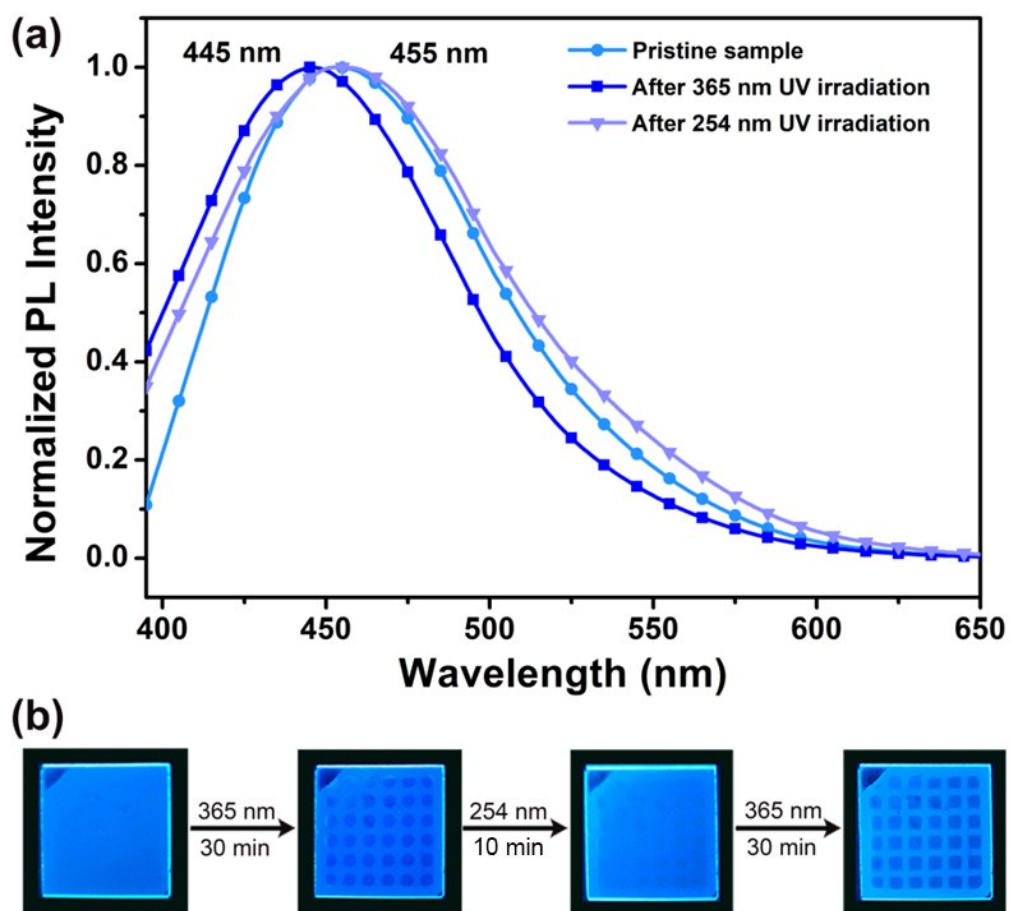


Fig. S13 Emission spectra (a) of P-(Z)-35, after 365 nm UV irradiation and then after 254 nm UV irradiation. Photos (b) of P-(Z)-35 taken under 365 nm UV light in initial state and after a period of exposure to different wavelengths of UV light.