Supplementary Information

# Mesomorphic and photochromic luminescent behaviour of side-chain liquid crystalline polymers containing di-substituted cyanostilbene groups with the different number of alkyl tail chain

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## Experimental section

### Materials

4-Hydroxy benzaldehyde (AR 98%), Protocatechualdehyde (98%), 3,4,5-Trihydroxybenzaldehyde (98%), 1-Bromododecane (97%), Potassium iodide (99%), Methyl 4-(cyanomethyl)benzoate (98.87%), Methyl 2,3-dihydroxybenzoate (99.83%), 1-[3-(Dimethylamino) propyl]-propyl]-3-ethylcarbodiimide hydrochloride (EDC·HCl, 99%), 4-(Dimethylamino) pyridine (DMAP, 99%), and Grubbs catalyst (third generation) were purchased from Sigma Aldrich. Dichloromethane ($CH_2Cl_2$) (AR, Sinopharm) and Trichloromethane ($CHCl_3$) (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. N-(6-hydroxyhexyl)-cis-5-nor-bornene-exo-2,3-dicarboximide were prepared according to literature procedure. All other reagents and solvents were obtained from commercial sources and used without further purification.

### Measurements

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

**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.).

**Gel Permeation Chromatography (GPC)** The number-average molecular weight ($M_n$) 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) × 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 ºC. The calibration was carried out with a series of polystyrene standards.

**Infrared spectrometer (IR)** IR spectra were measured on an attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) (Bruker Vertex 70).

**Thermogravimetric Analysis (TGA)** The thermal stability of all polymers was measured by TGA on a TGA55 instrument at a heating rate of 10 ºC /min from room temperature to 800 ºC under a nitrogen atmosphere.

**Differential Scanning Calorimetry (DSC)** Thermal behavior and phase transition temperatures of all monomers and polymers were observed and obtained using a DCS 250 instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at a cooling and heating rate of 10 ºC /min. Samples with a typical mass of about 6 mg were encapsulated in sealed aluminum pans. The DSC curves recorded their first cooling and second heating processes at a rate of 10 ºC /min.

**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 polymer powder between a glass slide and a cover glass. These samples were heated to their isotropic temperature and cooled at a rate of 1 ºC/min.

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

experiments were performed using a high-flux X-ray instrument (SAXSess mc$^2$, Anton Paar) equipped with Kratky block-collimation system and a GEID3003 sealed-tube X-ray generator (CuKα). 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 $q$ is the scattering vector). The diffraction peak positions were calibrated with silver behenate.

**Photoluminescence Spectroscopy** PL spectra of solutions and solids were recorded on a RF-6000, with excitation wavelength of 350 nm for solids, 335 nm for solutions.

**UV-Vis Spectroscopy** UV-Vis spectra of solids were recorded on a Shimadzu UV3600 spectrophotometer.

**Absolute PL Quantum Yield Spectrometer (PLQY)** The fluorescence absolute values of $\Phi_F$ were obtained on a Hamamatsu QY-Plus C13534-11 with an integrating sphere.

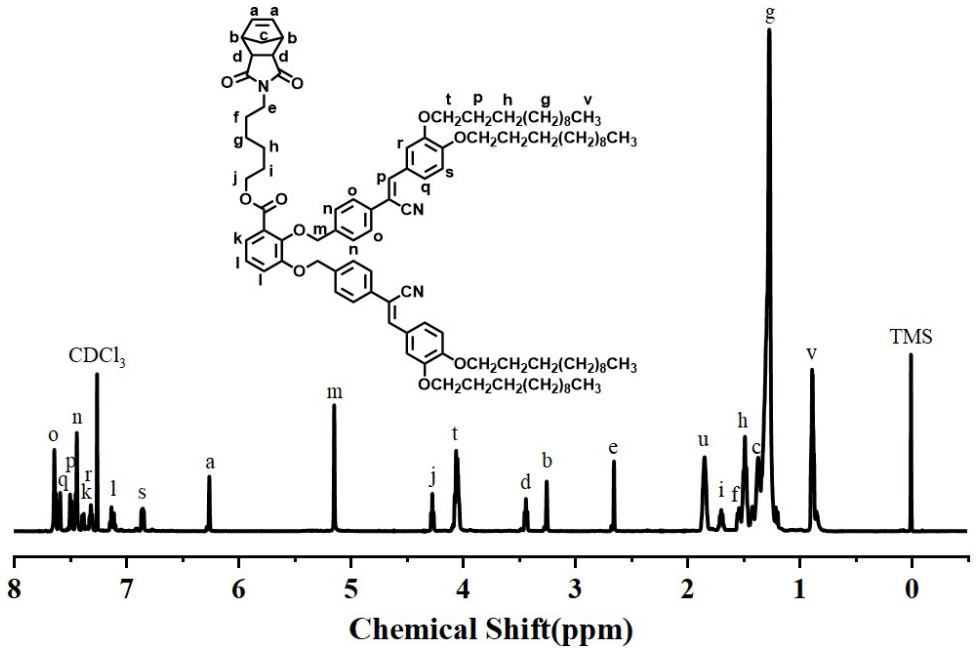


**Fig. S1** $^1$H NMR spectrum of NB-Z-34 in $CDCl_3$.

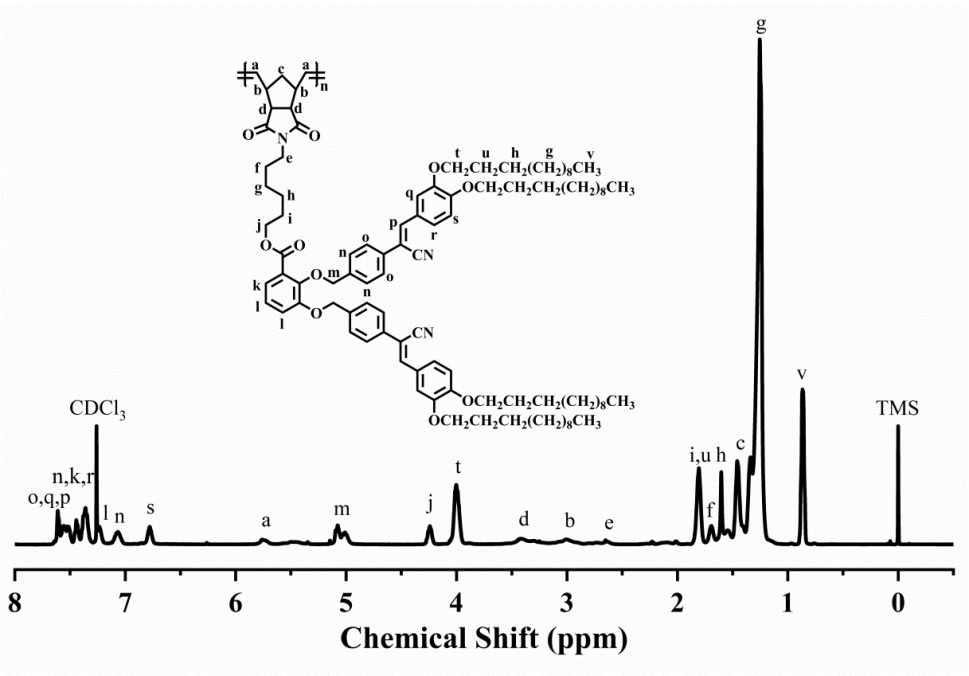


**Fig. S2** $^{1}$H NMR spectrum of PNB-Z-34 in $CDCl_3$.

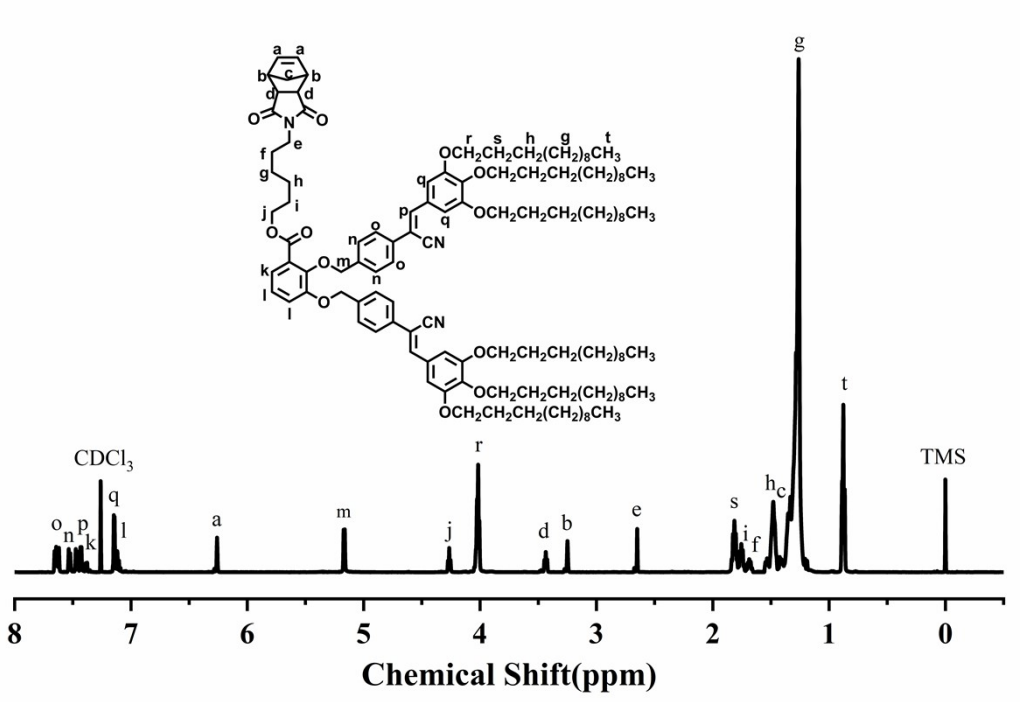


**Fig. S3** $^{1}$H NMR spectrum of NB-Z-345 in $CDCl_3$.

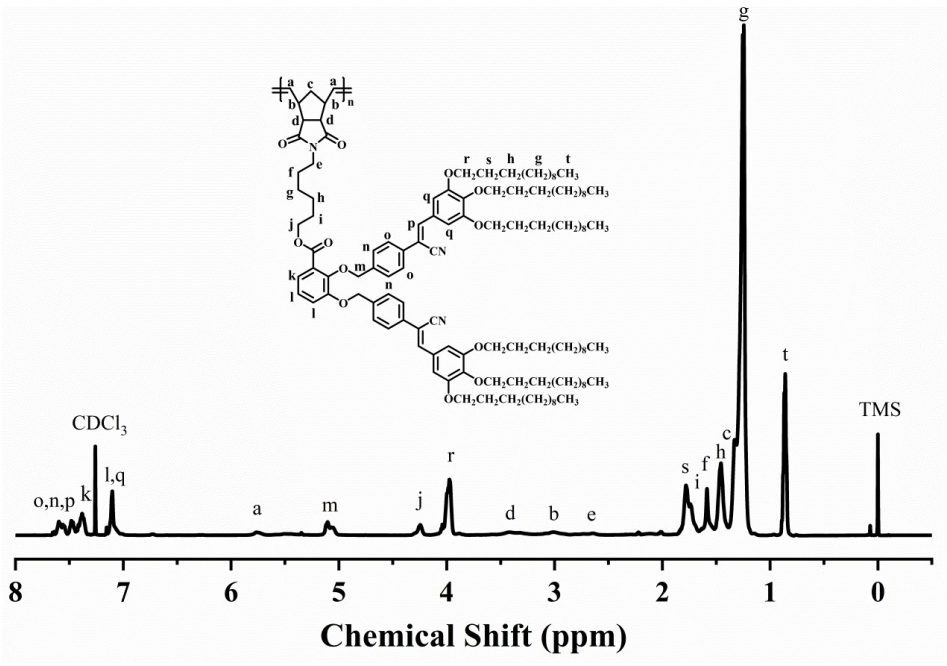


**Fig. S4** $^{1}$H NMR spectrum of PNB-Z-345 in $CDCl_3$.

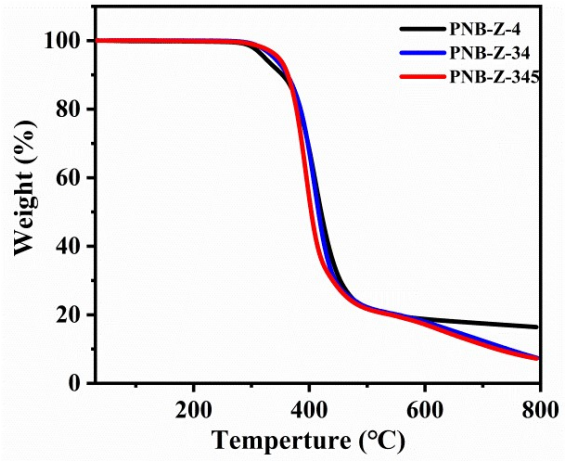


**Fig. S5** TGA curves of PNB-Z-4, PNB-Z-34 and PNB-Z-345.

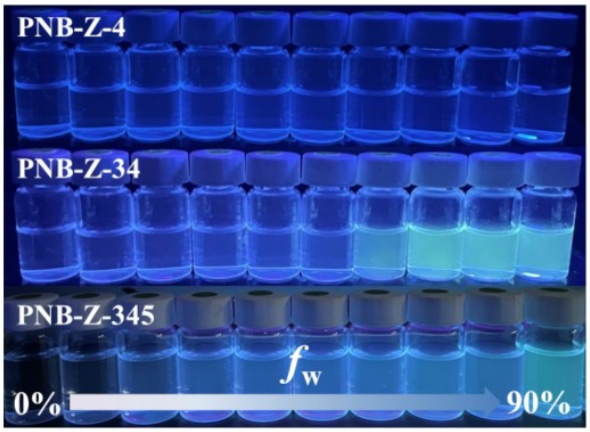


**Fig. S6** Fluorescence pictures of PNB-Z-4, PNB-Z-34 and PNB-Z-345 in THF/$H_2O$ with $f_w$ from 0% to 90% under 365 nm UV light.

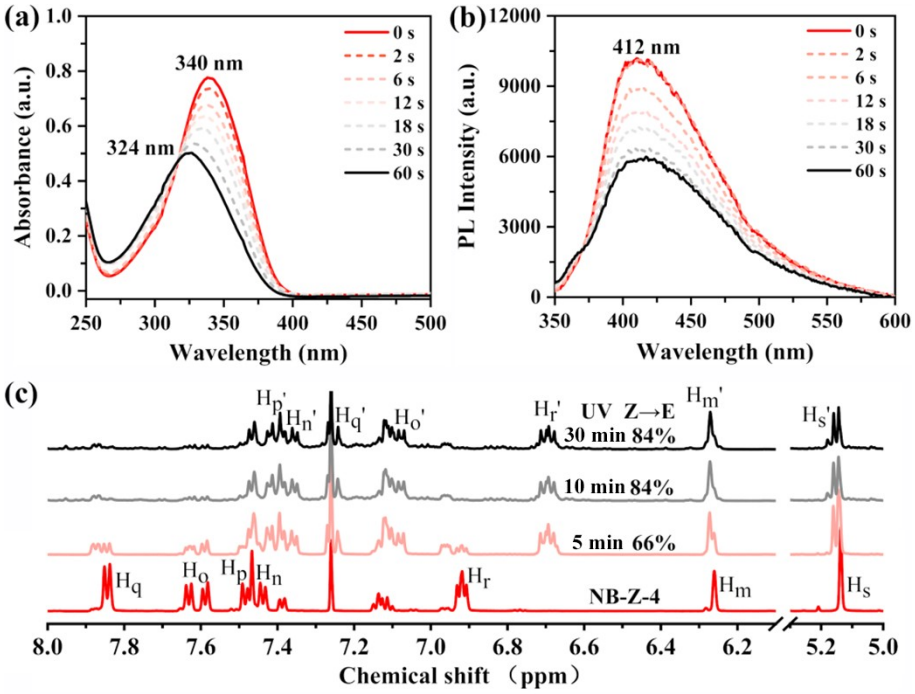


**Fig. S7** UV-Vis spectra (a) and PL spectra (b) of NB-Z-4 in $CHCl_3$ before and after 365 nm UV irradiation for different time (c = $2\times10^{-5}$ mol·$L^{-1}$). (c) $^1H$ NMR spectra of NB-Z-4 in $CDCl_3$ before and after UV irradiation for 5 min, 10 min and 30 min.

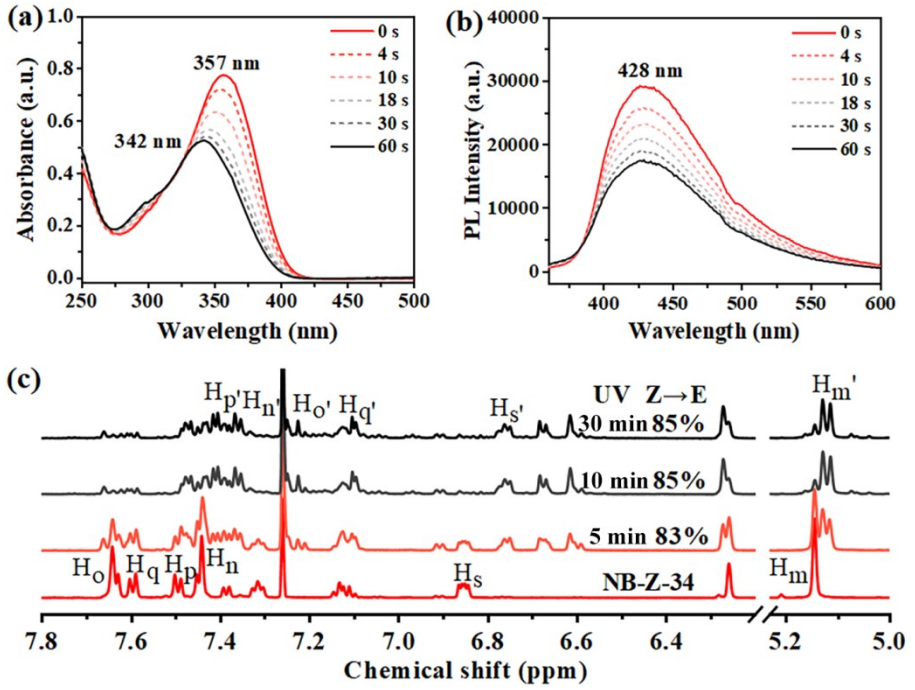


**Fig. S8** UV-Vis spectra (a) and PL spectra (b) of NB-Z-34 in $CHCl_3$ before and after 365 nm UV irradiation for different time (c = $2\times10^{-5}$ mol·$L^{-1}$). (c) $^1H$ NMR spectra of NB-Z-34 in $CDCl_3$ before and after UV irradiation for 5 min, 10 min and 30 min.

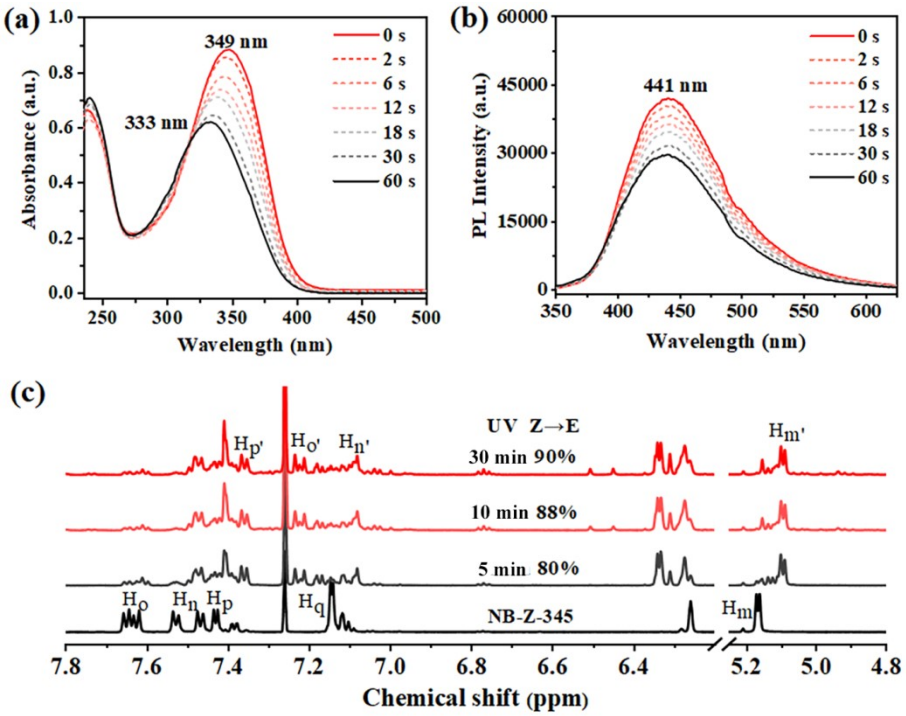


**Fig. S9** UV-Vis spectra (a) and PL spectra (b) of NB-Z-345 in $CHCl_3$ before and after 365 nm UV irradiation for different time ($c = 2\times10^{-5}$ mol·L$^{-1}$). (c) $^1$H NMR spectra of NB-Z-345 in $CDCl_3$ before and after UV irradiation for 5 min, 10 min and 30 min.

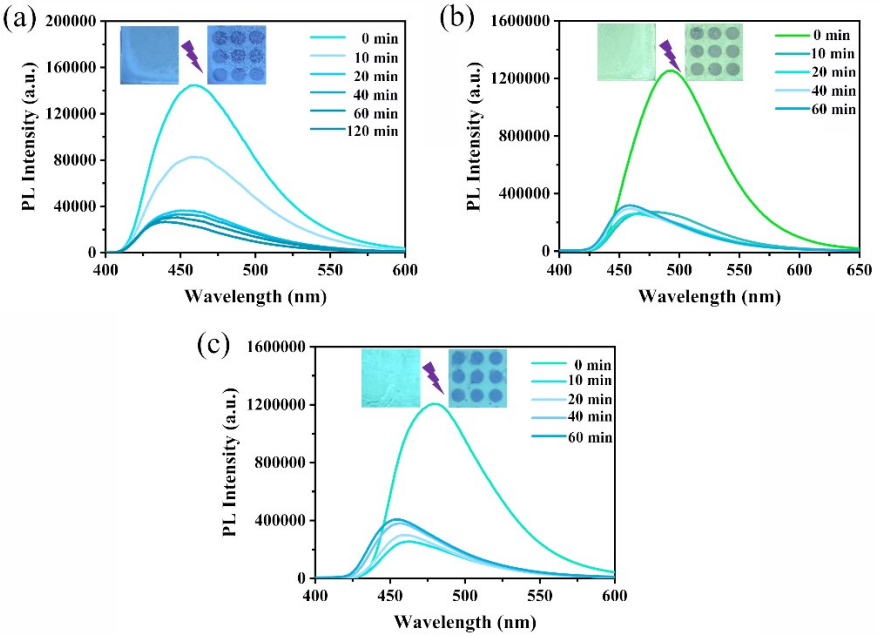


**Fig. S10** PL spectra change of NB-Z-4 (a), NB-Z-34 (b) and NB-Z-345 (c) films under 365 nm UV irradiation for different time. (inset: Fluorescent pictures of the initial monomer films (left) and irradiated monomer films with photomask for 60 min (right)).

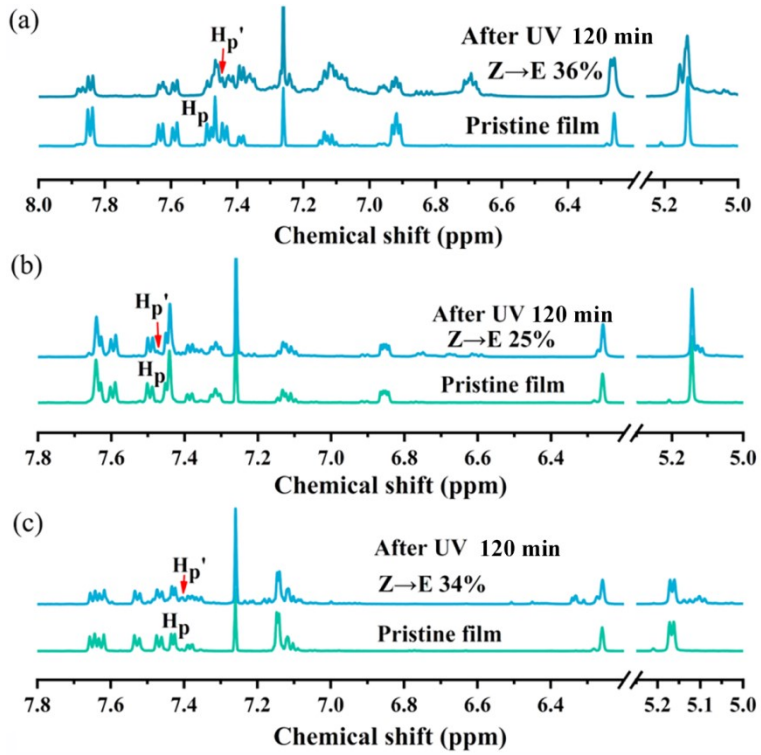


**Fig. S11** $^{1}$H NMR spectra of NB-Z-4 (a), NB-Z-34 (b) and NB-Z-345 (c) films before and after UV irradiation for 120 min.

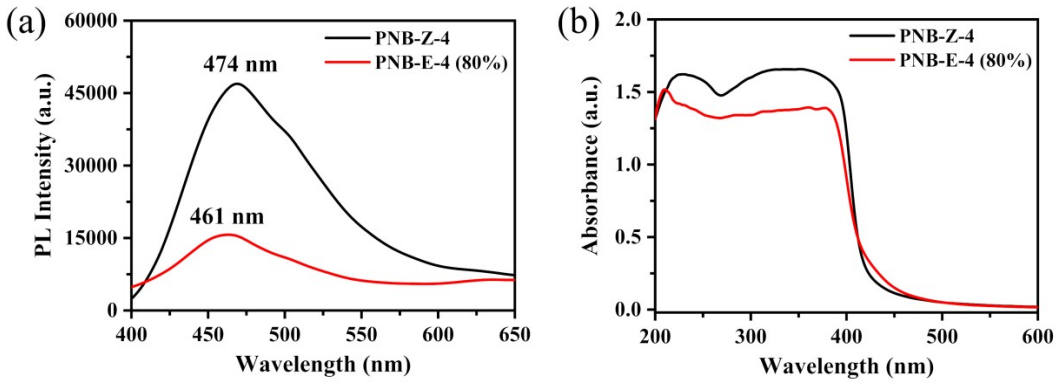


**Fig. S12** UV-Vis spectra (a) and PL spectra (b) of pristine and "irradiated" PNB-Z-4 film (The content of PNB-E-4 is more than 80%).

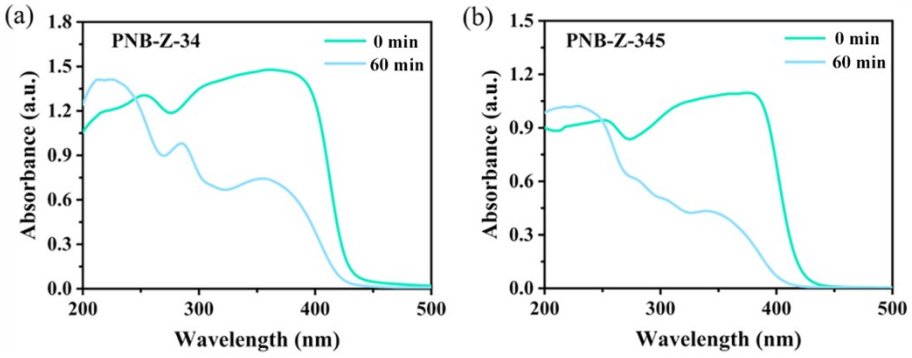


**Fig. S13** UV-Vis spectra of PNB-Z-34 (a) and PNB-Z-345 (b) films before and after UV irradiation.

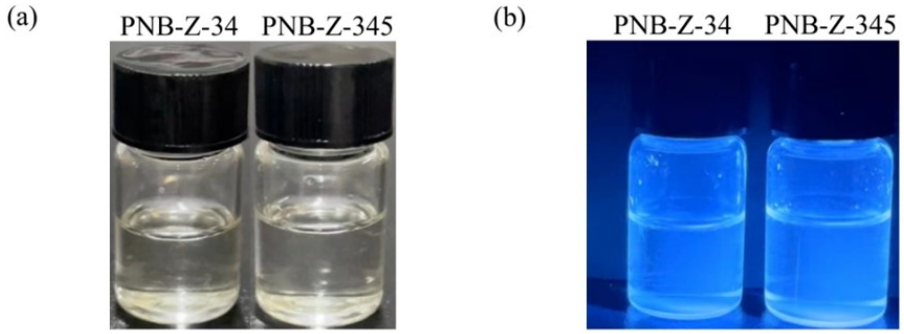


**Fig. S14** Dissolution of irradiated PNB-Z-34 and PNB-Z-345 films in $CHCl_3$ under daylight (a) and UV light (b).

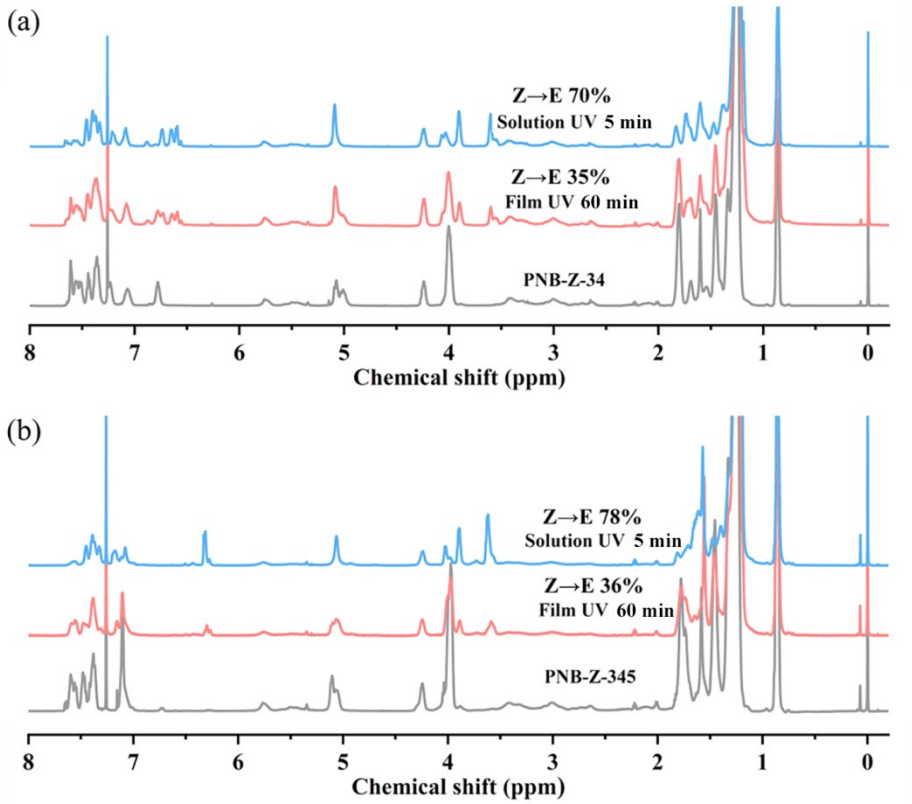


**Fig. S15** $^{1}$H NMR spectra of PNB-Z-34 (a) and PNB-Z-345 (b) solution and films before and after UV irradiation.

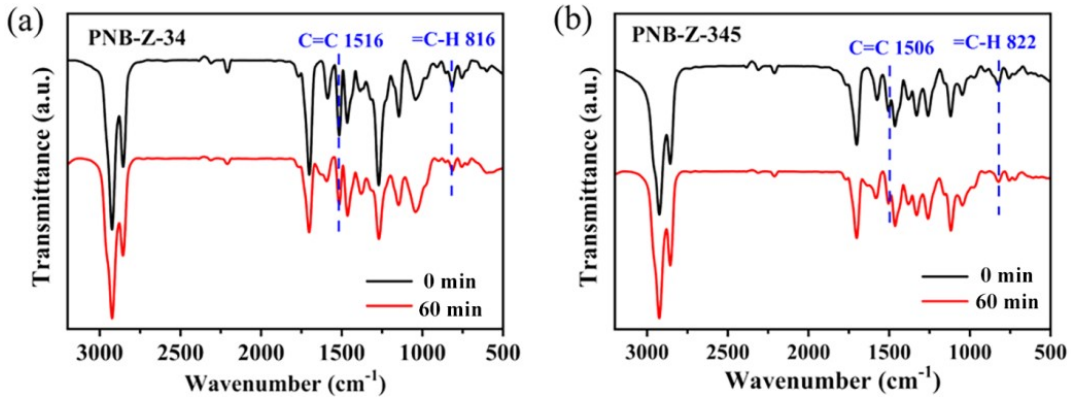


**Fig. S16** FT-IR spectra of PNB-Z-34 (a) and PNB-Z-345 (b) film before and after irradiation.