

Supplementary materials

Experimental section

Chemicals

All reagents from commercial sources were used without further purification, unless otherwise noted. All dry reactions were performed with glassware that was flamed under high vacuum and backfilled with N₂.

Characterization

The structures of the synthesized intermediate products and the final product were characterized by proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectroscopy. The testing instrument is JOEL nuclear magnetic resonance spectrometer (JNM-ECZ400S, 400 MHz, Japan). The obtained polymers were tested by gel permeation chromatograph (GPC) to obtain the corresponding number-average molecular weight (M_n) and polydispersity index (PDI). The decomposition temperature (T_d) and glass transition temperature (T_g) of the polymers were measured by thermogravimetric analyzer (TGA2, Mattler Instruments) and differential scanning calorimeter (DSC214 Polyma, NETZSCH Instruments), respectively. Ultraviolet-visible absorption spectra and photoluminescence spectra of the polymers in dilute solution and thin film states were collected by Shimadzu UV-1750 spectrophotometer and Hitachi F-4600 spectrometer, respectively. The morphology of the polymer thin films was obtained by photographing with an Olympus IX71 optical microscope and testing with Bruker's Dimension Icon atomic force microscope. The cyclic voltammetry test was carried out using CHI660C electrochemical workstation.

Preparation and tensile testing of free-standing film

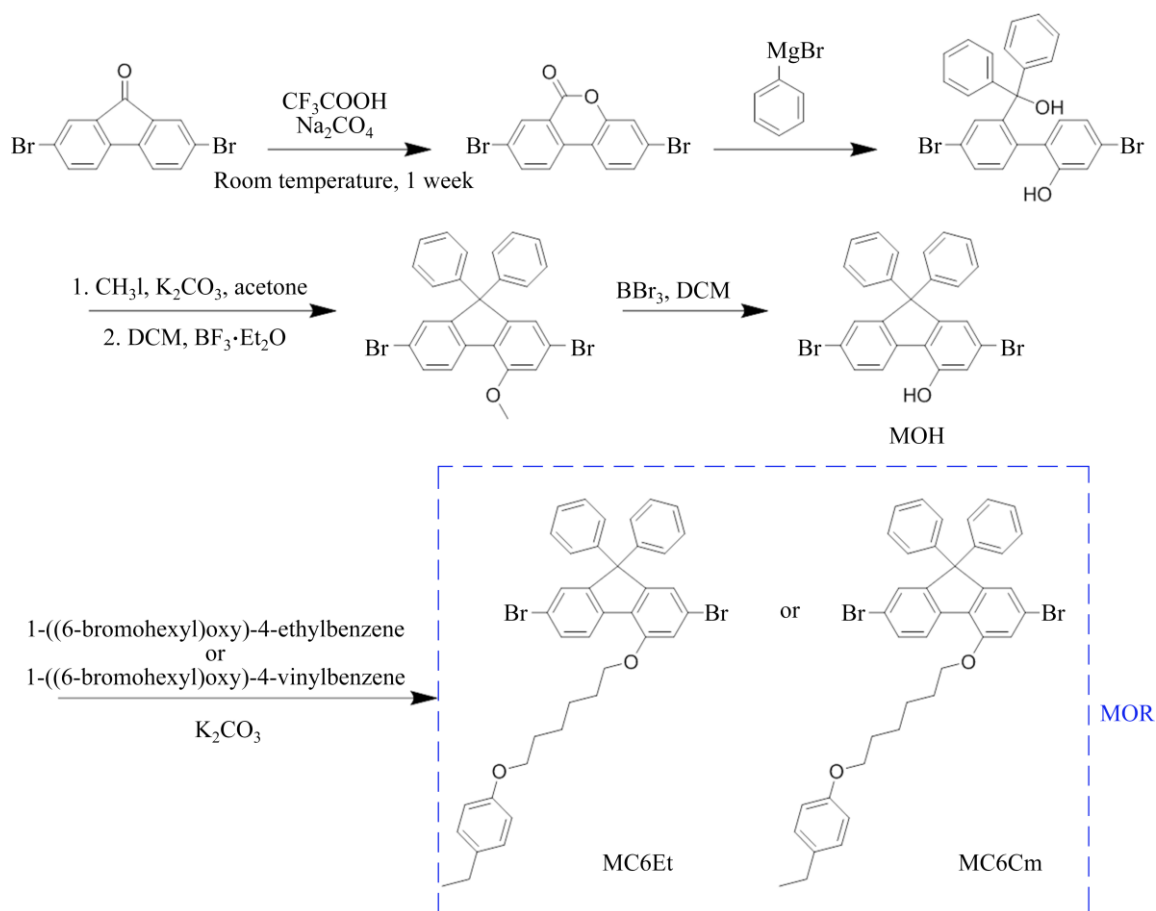
PEDOT:PSS was spin-coated onto clean quartz slice with sizes of 2 mm×5 mm at rotation speed of 3000 r/min for 60 s. Subsequently, it was placed on hot stage at 120 °C and heated for 10 min to remove the residual solvent. Then, the sample was prepared into toluene solution with concentration of 25 mg/mL and spin-coated onto the PEDOT:PSS layer. Double-sided tape was pasted on the auxiliary support and adhered to the prepared film. The film with the support was immersed in water. After the substrate naturally peeled off, the support was fished out of the water and the moisture was drained, thus obtaining substrate-free film. For the tensile testing, the stress–strain curve of the film was tested using the tensile platform built within the group. The auxiliary support loaded with the substrate-free film was mounted on the tensile fixture. The connections on both sides of the support were fused, and then the tensile test could be carried out. The stress loading rate during the tensile process was 0.005 N/min.

Device preparation based on mechanoluminescent layer

First, treat the ITO substrate. Place clean and transparent ITO substrate in ultraviolet ozone cleaner for 15 min. Spin-coat layer of PEDOT:PSS on the ITO, and then place it on heating stage at 120 °C for 15 min for later use. Second, treat the luminescent layer. Spin-coat layer of PEDOT:PSS on quartz slice, and then spin-coat the luminescent layer solution on the PEDOT:PSS. After spin-coating, the original film of the luminescent layer is obtained. To prepare the annealed film, place the original film on heating stage and treat it at the annealing temperature for certain period (anneal at 180 °C for 10 min). Adhere the PDMS elastomer to the film and place it in deionized water. After the PEDOT:PSS layer dissolves and the quartz slice falls off, the luminescent layer is transferred to the PDMS elastomer. Then, take out the PDMS elastomer and place it in oven to dry at low temperature for later use. Then, transfer the luminescent layer: Place the PDMS with the transferred luminescent layer on sliding stage and stretch it to the required ratio for uniaxial stretching. Stick the ITO substrate with spin-coated PEDOT:PSS on the stretched luminescent layer, and place it on heating stage at 120 °C for 10 min to transfer the luminescent layer onto the PEDOT:PSS layer. Finally, perform

evaporation. Place the previously treated sample in the evaporation chamber and evaporate the electron-transport layer (TPBi), the modification layer (LiF), and the electrode (Al).

Synthesis



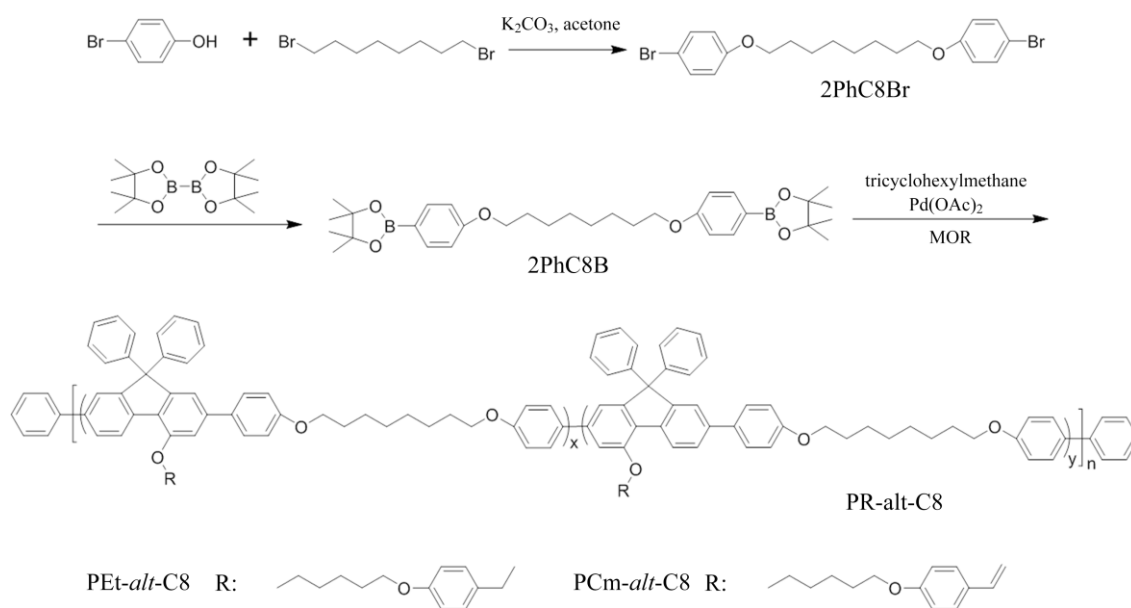
Scheme S1 Detailed synthesis procedure for target molecules

MOH. Weigh MOCH₃ (1 g, 1.97 mmol) into a round-bottom flask, seal the device, evacuate and fill with nitrogen three times. Add 40 mL of DCM to dissolve the raw materials. Place the device in ice-water bath and stir. Add boron tribromide (0.75 g, 3 mmol) and let the reaction proceed for 12 h. After stopping the stirring, add water to quench the reaction. Extract with DCM. Remove the residual moisture from the obtained organic phase with anhydrous sodium sulfate. After concentrating the solution, perform column chromatography separation (eluent: PE:EA=6:1). As a result, 0.82 g of the product is obtained, with a yield of 85%. ¹H ((CD₃)₂SO, ppm) δ: 10.92 (s, 1 H), 7.98 (d, *J*=8.2 Hz, 1 H), 7.57 (d, *J*=8.4 Hz, 1 H), 7.52 (s, 1 H), 7.32–7.22 (m, 6 H), 7.10 (d, *J*=7.5 Hz, 4 H), 7.04 (s, 1 H), 6.99 (s, 1 H). ¹³C NMR ((CD₃)₂SO, ppm) δ: 155.0, 154.6, 152.6, 144.9, 138.1, 131.4, 129.2, 128.8, 128.2, 127.6, 124.9, 121.8, 120.4, 119.9, 117.9, 66.0.

MC6Et. Weigh EtC₆Br (0.82 g, 2.87 mmol), MOH (1 g, 1.93 mmol), and potassium carbonate (0.97 g, 7 mmol) into a round-bottom flask, and add 20 mL of acetone to dissolve the raw materials. Place the reaction in an oil bath at 40 °C and stir for 24 h. After stopping the stirring, add water to quench the reaction and extract with DCM. Remove the residual moisture from the obtained organic phase with anhydrous sodium sulfate. After concentrating the solution, perform column chromatography separation (eluent: PE:DCM=4:1). As a result, 1.07 g of the product is obtained, with a yield of 80%. ¹H (CDCl₃, ppm) δ: 7.96 (d, *J*=8.2 Hz, 1 H), 7.50–7.43 (m, 2 H), 7.30–7.26 (m, 4 H),

7.26–7.25 (m, 2 H), 7.18–7.11 (m, 7 H), 7.00 (d, $J=1.2$ Hz, 1 H), 6.85 (d, $J=8.6$ Hz, 2 H), 4.15 (t, $J=12.8$ Hz, 2 H), 3.99 (t, $J=12.7$ Hz, 2 H), 2.61 (q, $J=15.2$ Hz, 2 H), 2.05–1.96 (m, 2 H), 1.91–1.83 (m, 2 H), 1.69–1.61 (m, 4 H), 1.23 (t, $J=15.2$ Hz, 3 H). ^{13}C NMR (CDCl_3 , ppm) δ : 157.0, 155.5, 154.0, 152.4, 144.4, 137.6, 136.3, 130.8, 128.7, 128.4, 128.0, 127.1, 126.2, 125.2, 122.1, 121.3, 120.8, 114.3, 113.8, 68.4, 67.7, 65.8, 29.2, 29.1, 27.9, 26.0, 25.9, 15.9).

MC6Cm. Weigh CmC6Br (0.82 g, 2.89 mmol), MOH (1 g, 1.93 mmol), and potassium carbonate (0.97 g, 7 mmol) into round-bottom flask, and add 20 mL of *N,N*-dimethylformamide to dissolve the raw materials. Wrap the reaction device with tin foil and place it in an oil bath at 60 °C, stirring the mixture in the dark for 24 h. After stopping the stirring, add water to quench the reaction and extract the mixture with DCM. Remove the residual moisture from the obtained organic phase with anhydrous sodium sulfate. After concentrating the solution, perform column chromatography separation (eluent: PE:DCM=4:1). As a result, 1.07 g of the product is obtained, with a yield of 80%. ^1H (CDCl_3 , ppm) δ : 7.94 (d, $J=8.1$ Hz, 1 H), 7.47–7.42 (m, 2 H), 7.36–7.32 (m, 2 H), 7.28–7.26 (m, 2 H), 7.25–7.23 (m, 4 H), 7.17–7.13 (m, 4 H), 7.11 (d, $J=1.4$ Hz, 1 H), 6.99 (d, $J=1.4$ Hz, 1 H), 6.88–6.84 (m, 2 H), 6.66 (dd, $J=17.6$ Hz, 1 H), 5.61 (dd, $J=17.6$ Hz, 1 H), 5.12 (dd, $J_1=10.8$ Hz, $J_2=10.9$ Hz, 1 H), 4.14 (t, $J=12.7$ Hz, 2 H), 4.00 (t, $J=12.7$ Hz, 2 H), 2.04–1.96 (m, 2 H), 1.91–1.83 (m, 2 H), 1.69–1.60 (m, 4 H). ^{13}C NMR (CDCl_3 , ppm) δ : 158.8, 155.4, 154.0, 152.4, 144.4, 137.6, 136.2, 130.8, 130.3, 128.7, 128.5, 128.0, 127.4, 127.1, 126.2, 125.1, 122.1, 121.3, 120.8, 114.4, 113.8, 111.5, 68.4, 67.9, 65.8, 29.1, 29.1, 25.9, 25.8.



Scheme S2 Synthetic routes of PCm-*alt*-C8 and PEt-*alt*-C8

2PhC8Br. Weigh 1,8-dibromooctane (0.54 g, 2 mmol), 4-bromophenol (0.69 g, 4 mmol), and potassium carbonate (0.41 g, 3 mmol) into a dry round-bottom flask, and then add 20 mL of acetone. Place the reaction in an oil bath in the dark and stir at 40 °C for 24 h. After stopping the stirring, add water to quench the reaction and extract with DCM. Remove the residual moisture from the obtained organic phase with anhydrous sodium sulfate. After concentrating the solution, perform column chromatography separation (eluent: PE:DCM=6:1). As a result, 0.68 g of the product is obtained, with a yield of 75%. ^1H NMR (CDCl_3 , 10^{-6}) δ : 7.36 (dt, $J_1=8.8$ Hz, $J_2=5.5$ Hz, 4 H), 6.77 (dt, $J_1=8.9$ Hz, $J_2=5.5$ Hz, 4 H), 3.91 (t, $J=13.0$ Hz, 4 H), 1.81–1.73 (m, 4 H), 1.50–1.43 (m, 4 H), 1.41–1.35 (m, 4 H). ^{13}C NMR (CDCl_3 , ppm) δ : 158.1, 132.2, 116.2, 112.5, 68.1, 29.2, 29.1, 25.9.

2PhC8B. Weigh 2PhC8Br (1 g, 2.19 mmol), bis(pinacolato)diboron (1.67 g, 6.57 mmol), [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride dichloromethane complex (0.03 g), and

potassium acetate (0.5 g) into a round-bottom two-necked flask. Set up a reflux device. After sealing the reaction system, evacuate it and fill it with nitrogen three times. Add toluene (40 mL) to dissolve the raw materials. Place the device in an oil bath and carry out reflux condensation at 85 °C for 36 h. After stopping the stirring, add water to quench the reaction and extract with DCM. Remove the residual moisture from the obtained organic phase with anhydrous sodium sulfate. After concentrating the solution, perform column chromatography separation (eluent: PE:DCM=3:1). As a result, 0.61 g of the product is obtained, with a yield of 51%. ¹H (CDCl₃, ppm) δ: 7.74 (dt, *J*₁=8.7 Hz, *J*₂=4.2 Hz, 4 H), 6.88 (dt, *J*₁=8.7 Hz, *J*₂=4.2 Hz, 4 H), 3.97 (t, *J*=13.1 Hz, 4 H), 1.82–1.75 (m, 4 H), 1.50–1.44 (m, 4 H), 1.41–1.37 (m, 4 H), 1.33 (s, 24 H). ¹³C NMR (CDCl₃, ppm) δ: 161.7, 136.4, 113.8, 83.5, 67.7, 29.3, 29.1, 25.9, 25.0, 24.8.

PEt-*alt*-C8. Weigh MC6Et (0.35 g, 0.50 mmol), 2PhC8B (0.28 g, 0.50 mmol), palladium acetate (4 mg), and tricyclohexylphosphine (8 mg) and add them into Schlenk tube. Seal the reaction system and conduct three cycles of vacuuming and filling with nitrogen. Inject deoxygenated toluene (8 mL). Place the reaction device in an oil bath at 75 °C and activate it in the dark for 30 min. Then inject 2 mL of a 25% aqueous solution of tetraethylammonium hydroxide, and subsequently raise the temperature to 85 °C to carry out the reaction in the dark. After 3 days, first use bromobenzene (0.3 mL) for end-capping. After 6 h, use pinacol phenylboronate (0.3 mL) for end-capping. Stop the reaction after another 6 h and perform post-treatment. Directly precipitate the mother liquor in methanol and filter to obtain a solid. Dissolve the solid in DCM, add water for liquid-liquid extraction to remove water-soluble substances such as inorganic salts. Add anhydrous sodium sulfate to the separated organic phase to remove residual water. Then, pass the organic phase through neutral alumina chromatography column for purification. Concentrate the obtained liquid to thick state using vacuum rotary evaporator, precipitate it in methanol, and then perform suction filtration to obtain solid. Wrap the obtained solid and extract it in Soxhlet extractor for 3 d using acetone as the eluent. Vacuum-dry the remaining solid to obtain 280 mg of white product. The obtained polymer has number-average molecular weight (*M*_n) of 17 kDa and polydispersity index (PDI) of 1.64. ¹H (CDCl₃, ppm) δ: 8.16 (d, *J*=8.5 Hz, 1 H), 7.56–7.52 (m, 2 H), 7.49–7.44 (m, 4 H), 7.31–7.27 (m, 4 H), 7.25–7.17 (m, 8 H), 7.10–7.06 (m, 2 H), 7.02 (s, 1 H), 6.94–6.90 (m, 4 H), 6.85–6.81 (m, 2 H), 6.24 (t, *J*=12.5 Hz, 2 H), 3.98 (t, *J*=12.8 Hz, 6 H), 2.59 (q, *J*=15.2 Hz, 2 H), 2.09–2.00 (m, 2 H), 1.91–1.84 (m, 2 H), 1.83–1.76 (m, 4 H), 1.73–1.61 (m, 4 H), 1.52–1.45 (m, 4 H), 1.42–1.37 (m, 4 H), 1.19 (t, *J*=15.2 Hz, 3 H).

PCm-*alt*-C8. Weigh MC6Cm (0.62 g, 0.90 mmol), 2PhC8B (0.49 g, 0.90 mmol), potassium tert-butoxide (0.61 g, 5.40 mmol), sodium chloride (0.15 g, 2.55 mmol), tetrabutylammonium bromide (small amount, 20 mg), palladium acetate (8 mg), and tricyclohexylphosphine (16 mg) and add them into a Schlenk tube. Seal the reaction system and perform three cycles of vacuuming and filling with nitrogen. Inject deoxygenated THF (6 mL) and water (2 mL). Place the reaction device in an oil-bath at 60 °C and carry out the reaction in the dark. After 3 d, first use bromobenzene (0.3 mL) for end-capping. After 6 h, use pinacol phenylboronate (0.3 mL) for end-capping. Stop the reaction after another 6 h and conduct post-treatment. Directly precipitate the mother liquor in methanol and filter to obtain solid. Dissolve the solid in DCM, add water for liquid-liquid extraction to remove water-soluble substances such as inorganic salts. Add anhydrous sodium sulfate to the separated organic phase to remove residual water. Then, pass the organic phase through neutral alumina chromatography column for purification. Concentrate the obtained liquid to thick state using vacuum rotary evaporator, precipitate it in methanol, and then perform suction filtration to obtain solid. Wrap the obtained solid and extract it in Soxhlet extractor for 3 d using acetone as the eluent. Vacuum-dry the remaining solid to obtain 268 mg of white product. The obtained polymer has number-average molecular weight (*M*_n) of 19 kDa and a polydispersity index (PDI) of 2.08. ¹H (CDCl₃, ppm) δ: 8.16 (d, *J*=7.8 Hz, 1 H), 7.56–7.51 (m, 2 H), 7.49–7.43 (m, 2 H), 7.33–7.27 (m, 6 H), 7.25–7.17 (m, 8 H), 7.03 (s, 1 H), 6.95–6.83 (m, 6 H), 6.64 (dd, *J*=17.6 Hz, 1 H), 5.58 (d, *J*=17.6 Hz, 1 H), 5.11 (d, *J*=11.0 Hz, 1 H),

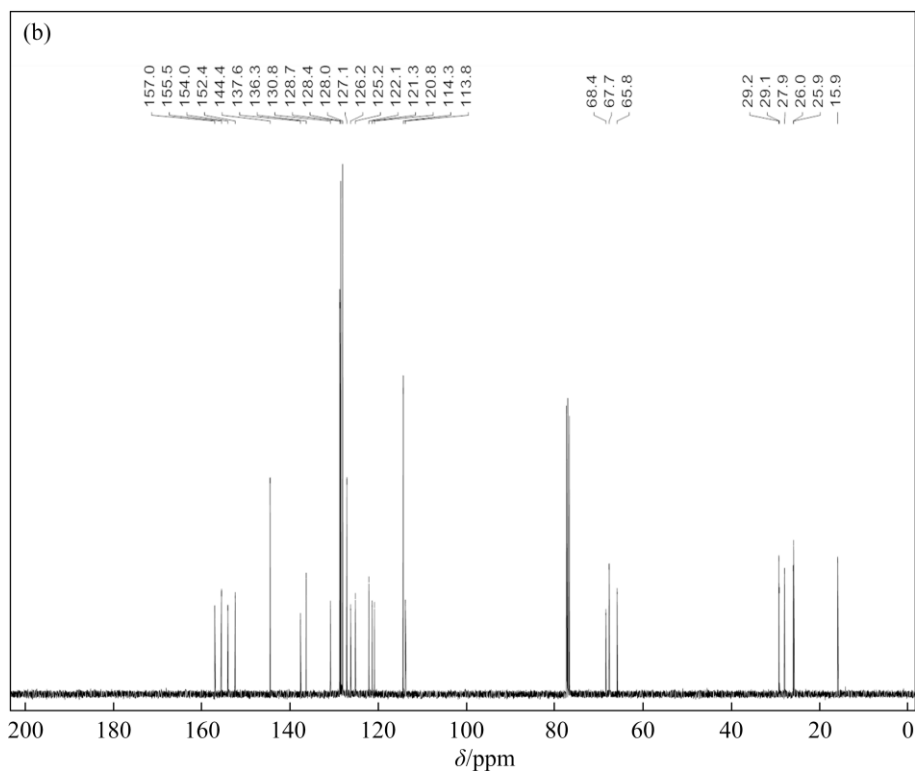
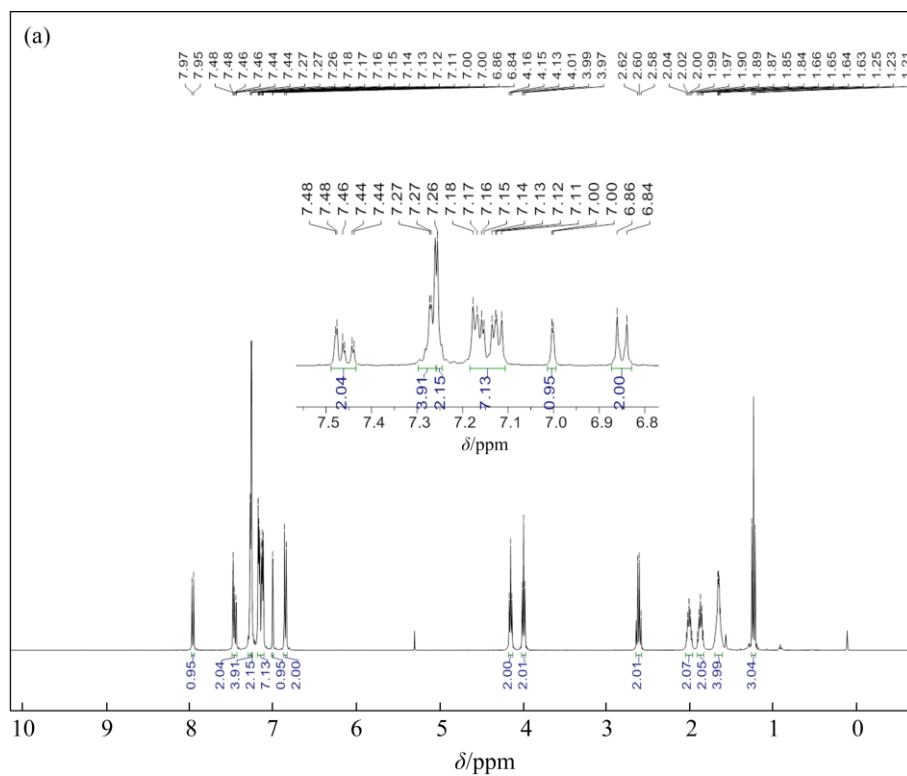


Figure S2 ^1H NMR spectra (a) and ^{13}C NMR spectra (b) of MC6Et

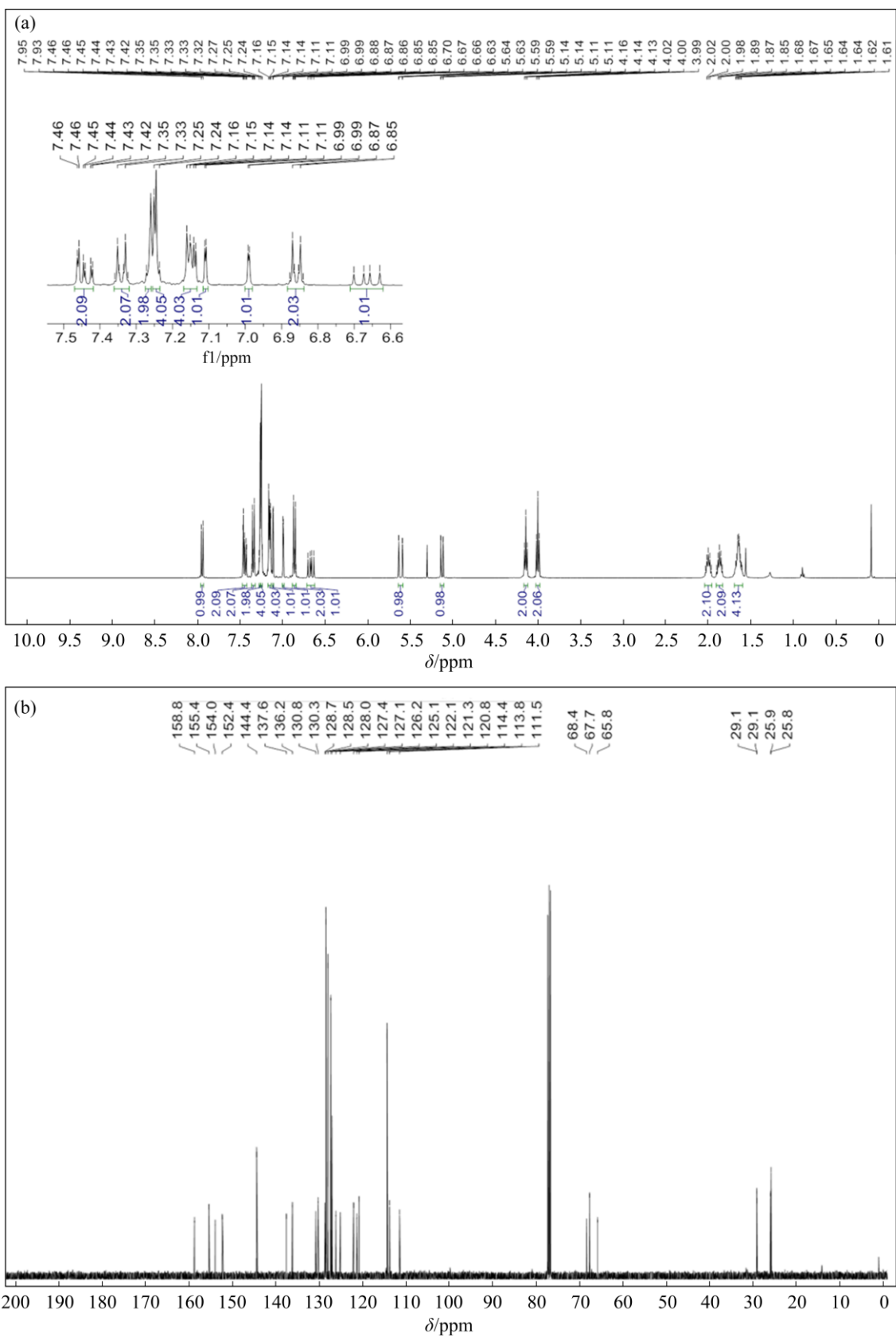


Figure S3 ^1H NMR spectra (a) and ^{13}C NMR spectra (b) of MC6Cm

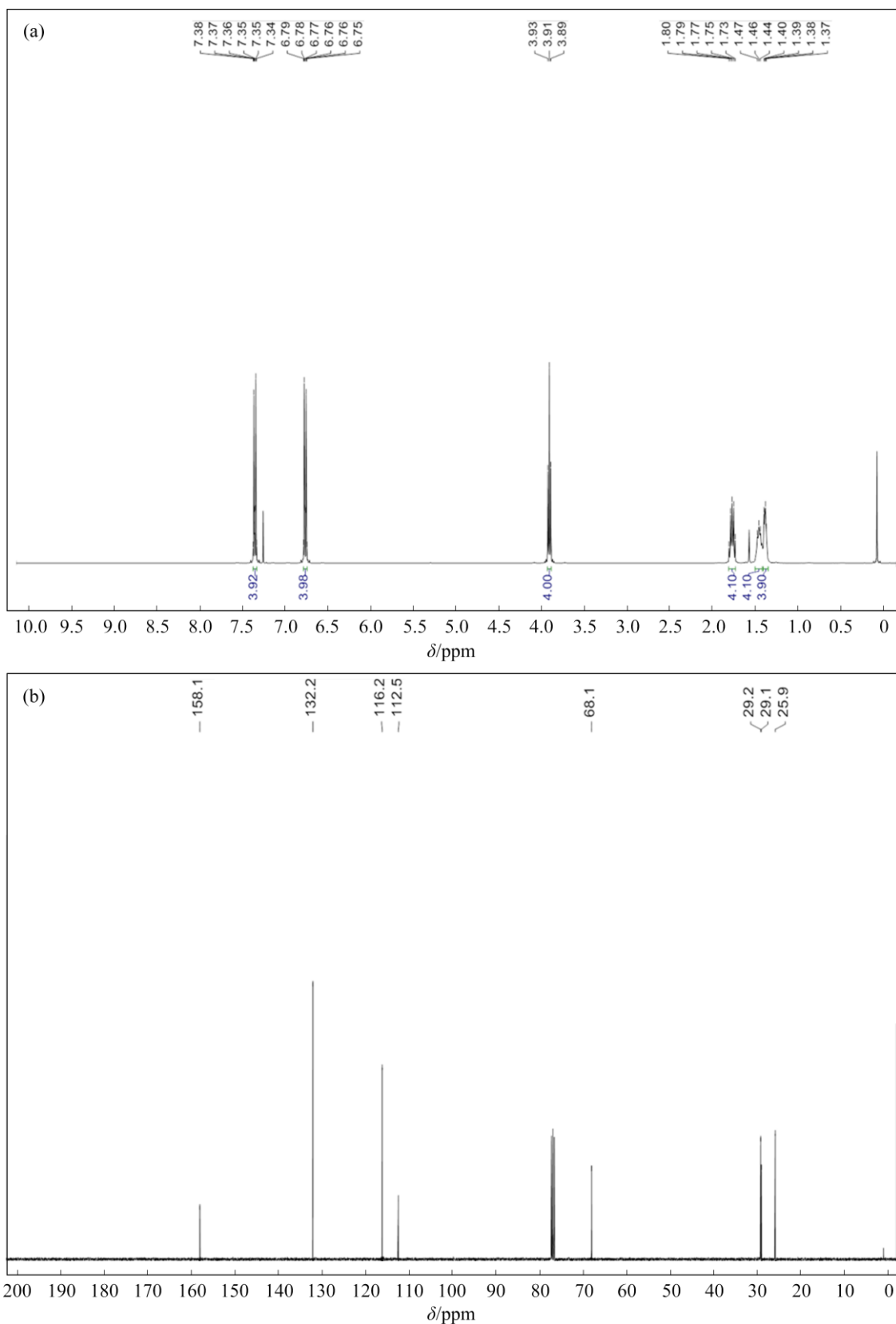


Figure S4 ^1H NMR spectra (a) and ^{13}C NMR spectra (b) of 2PhC8Br

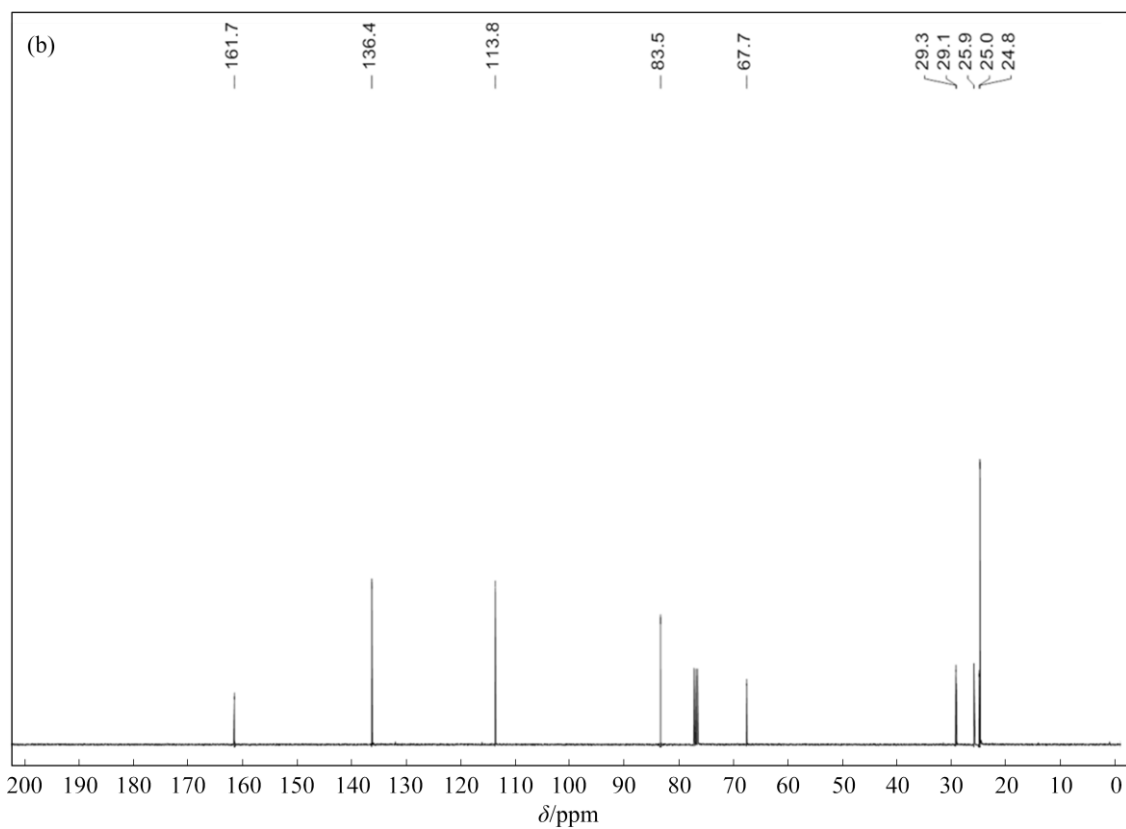
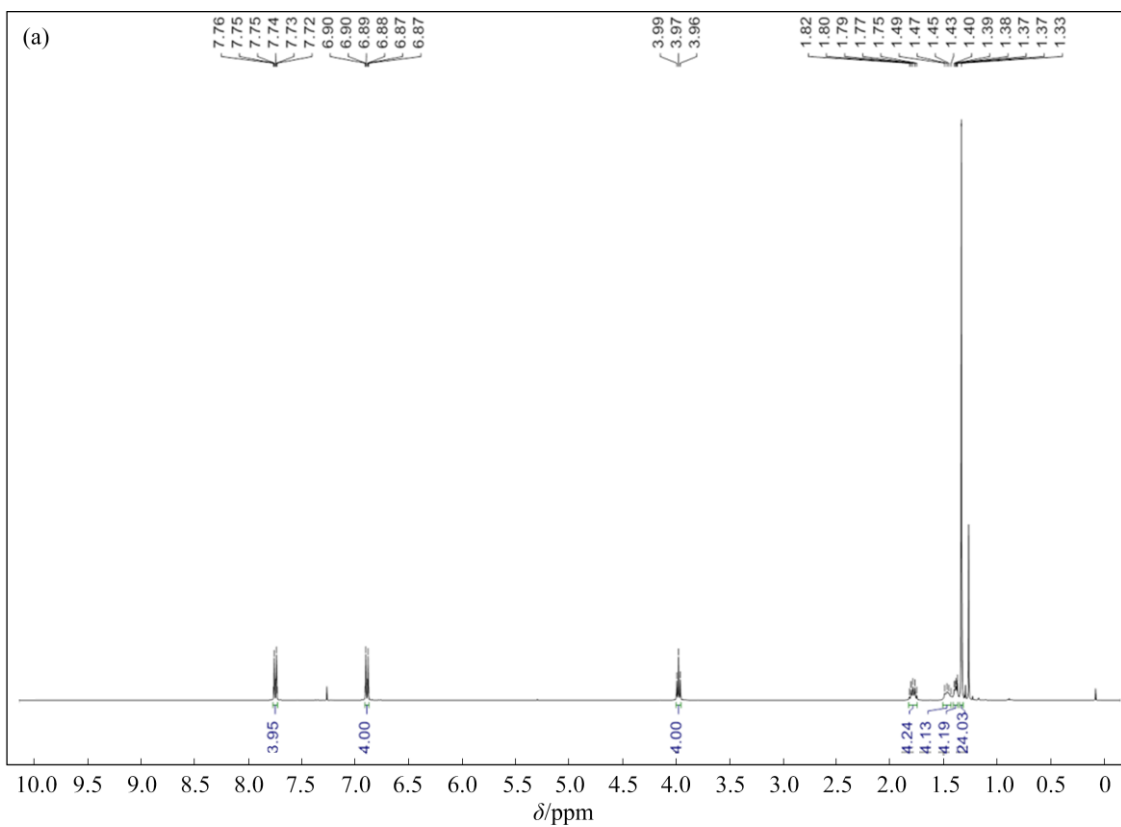


Figure S5 ^1H NMR spectra (a) and ^{13}C NMR spectra (b) of 2PhC8B

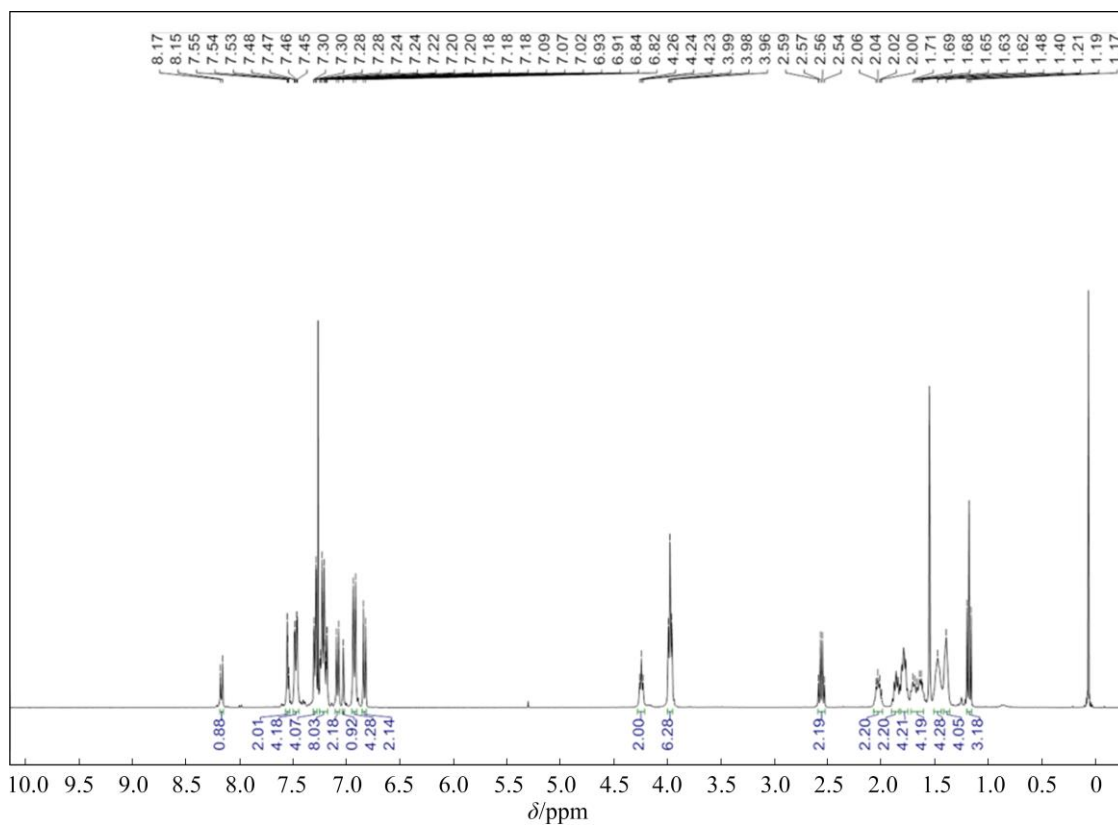


Figure S6 ^1H NMR spectra of PET-*alt*-C8

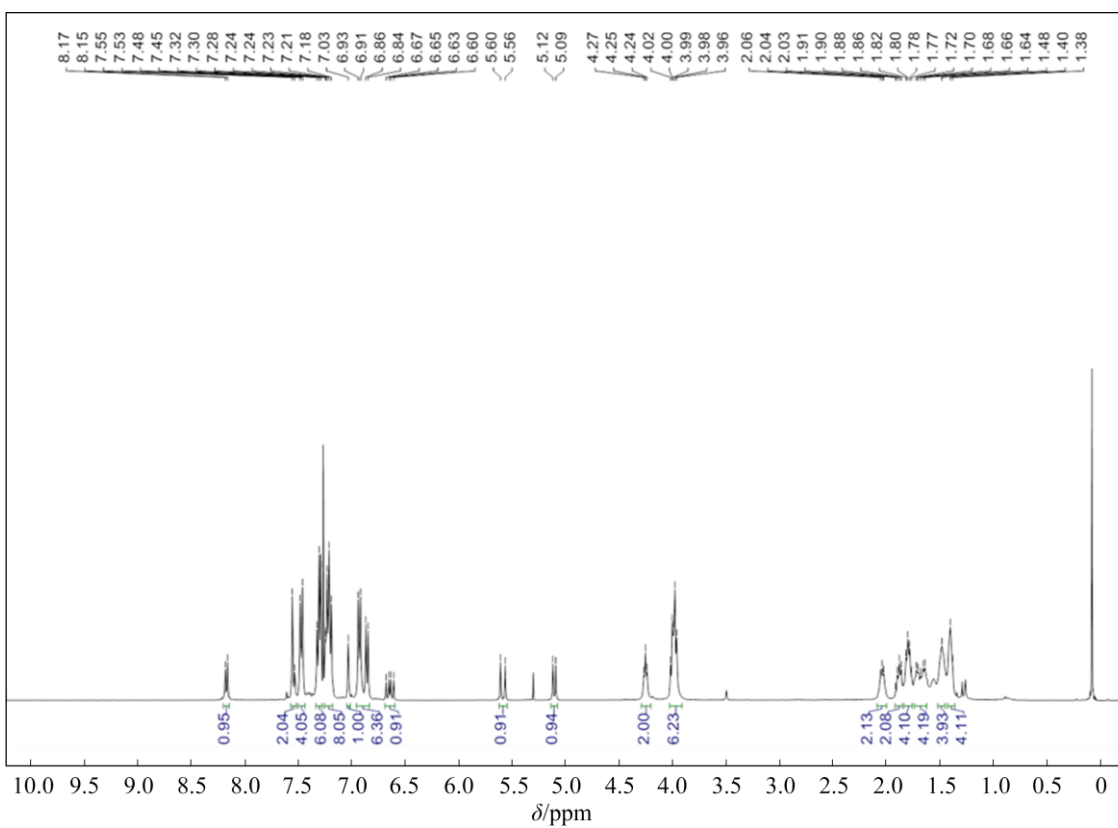


Figure S7 ^1H NMR spectra of PCm-*alt*-C8

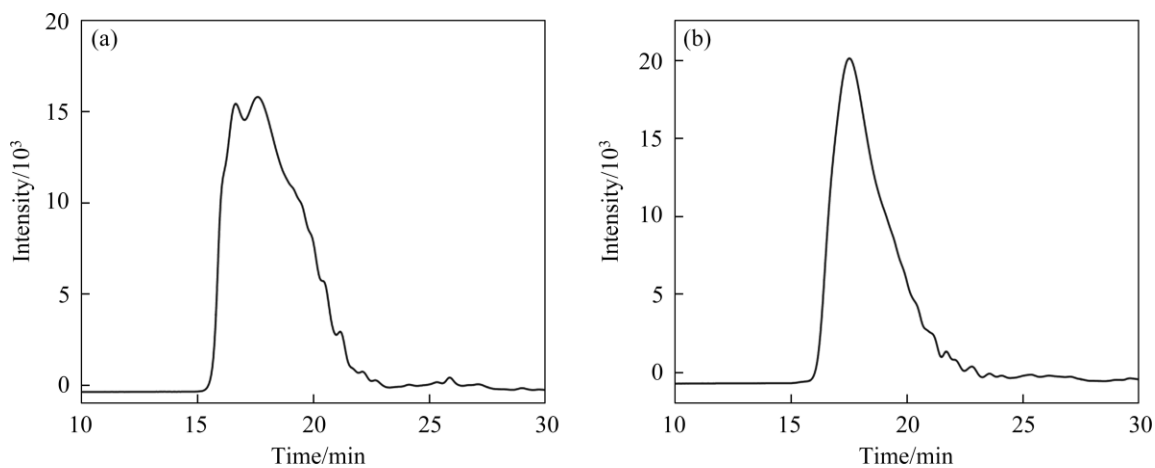


Figure S8 GPC curve of PCm-*alt*-C8 (a) and PEt-*alt*-C8 (b)

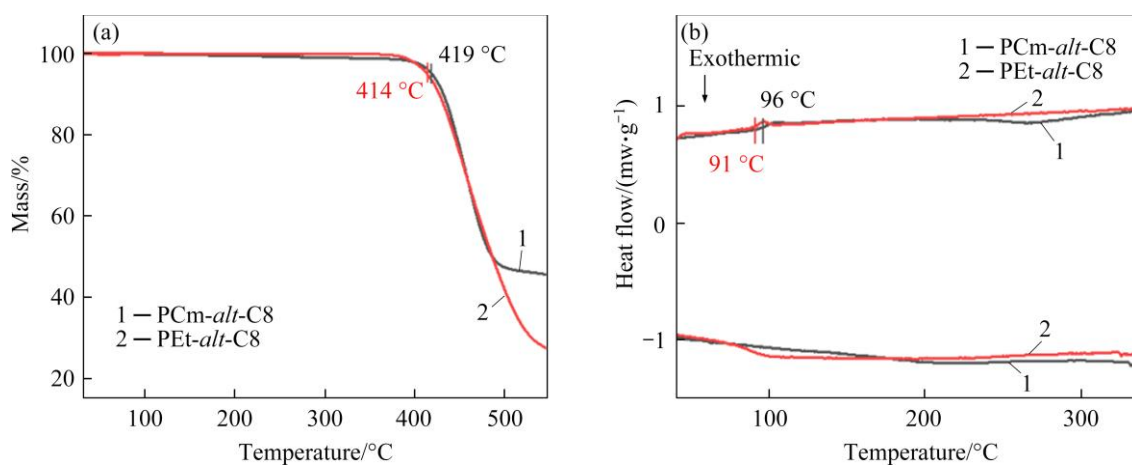


Figure S9 TGA and DSC curves of PCm-*alt*-C8 (a) and PEt-*alt*-C8 (b)

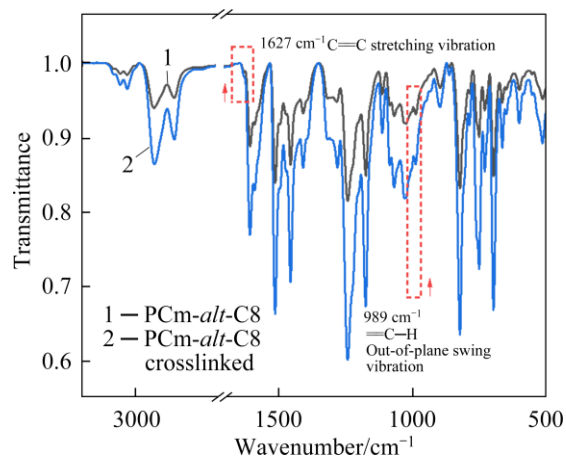


Figure S10 FT-IR spectra of PCm-*alt*-C8 powder before and after thermal cross-linking

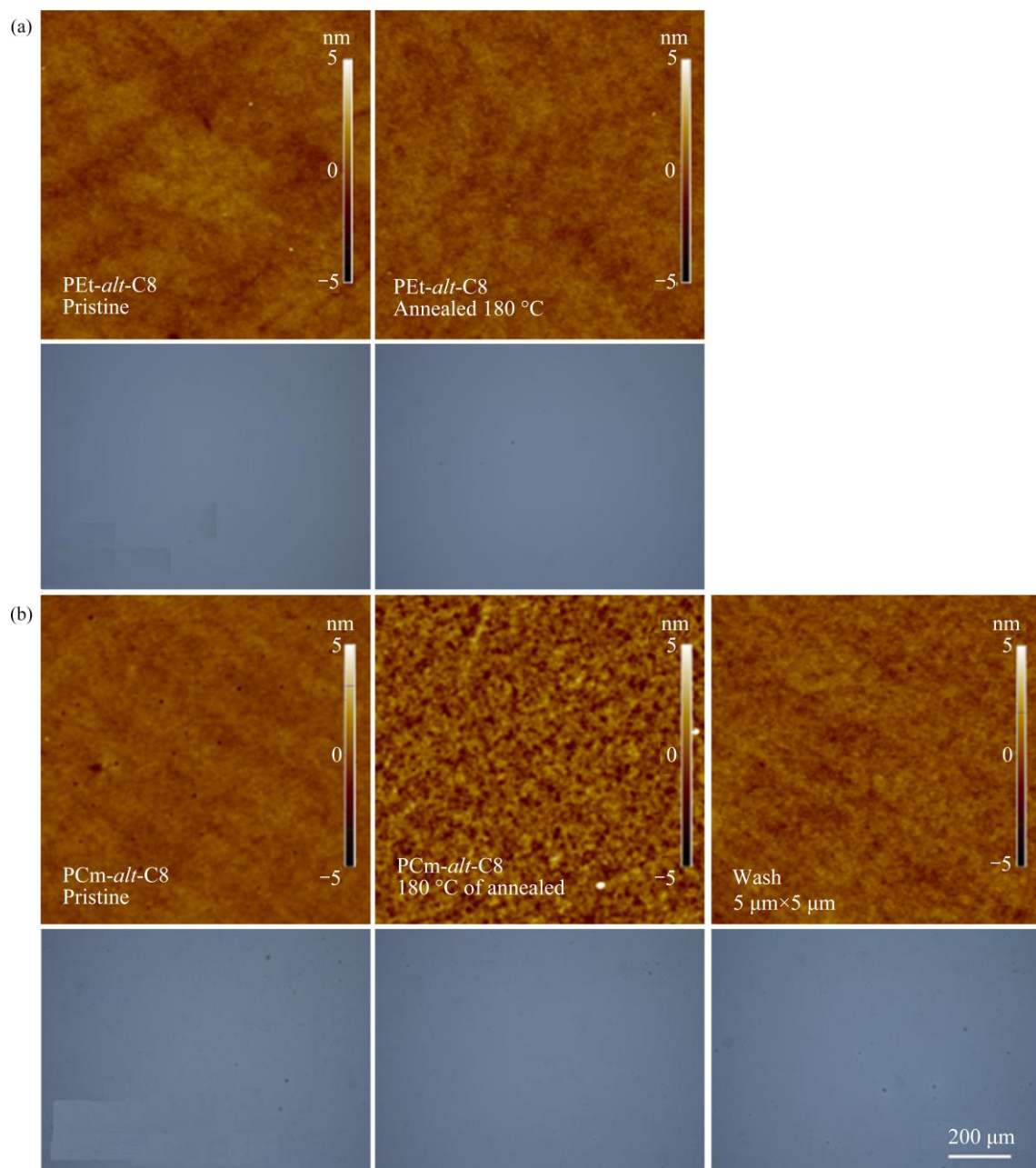


Figure S11 AFM and optical microscopy morphology of PEt-*alt*-C8 (a) and PCm-*alt*-C8 (b)

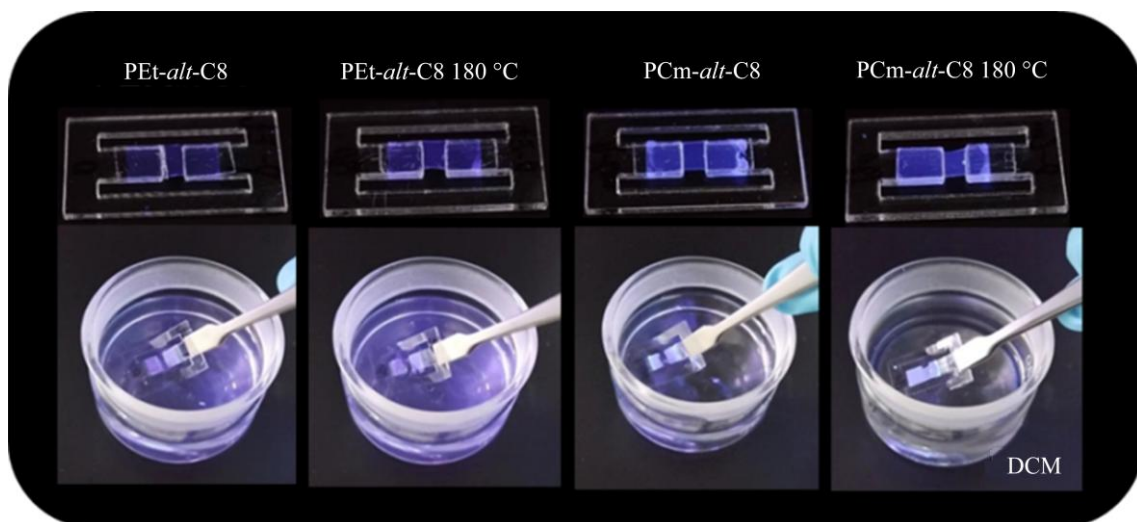


Figure S12 Solvent resistance experiments of the pristine and 180 °C annealed films of PET-*alt*-C8 and PCm-*alt*-C8

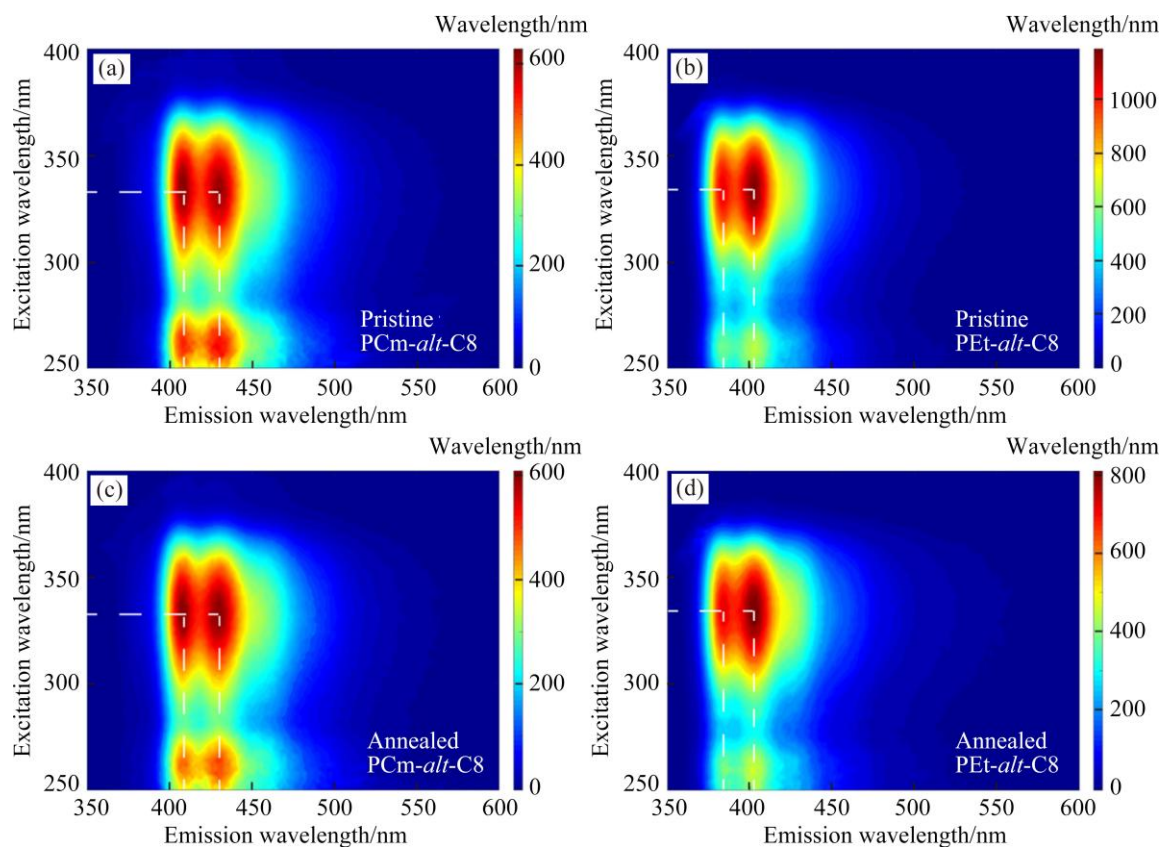


Figure S13 3D PL spectra: (a) Pristine film and (b) 180 °C annealed film of PCm-*alt*-C8; (c) Pristine film and (d) 180 °C annealed film of PET-*alt*-C8

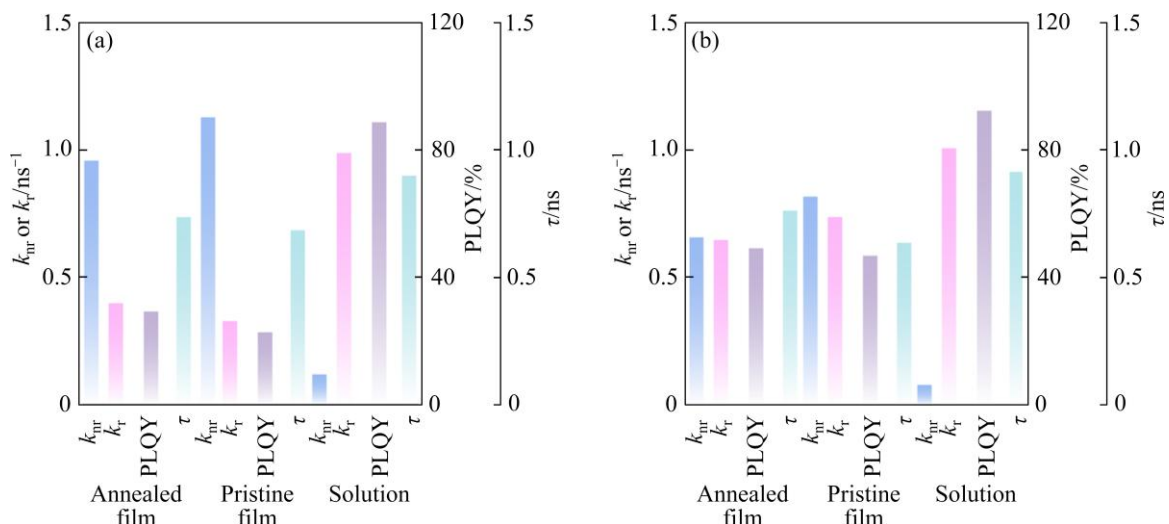


Figure S14 Fluorescence emission lifetime, PLQY, k_r and k_{nr} of PCm-*alt*-C8 (a) and PEt-*alt*-C8 (b) in different states (dilute solution, pristine film and 180 °C annealed film)

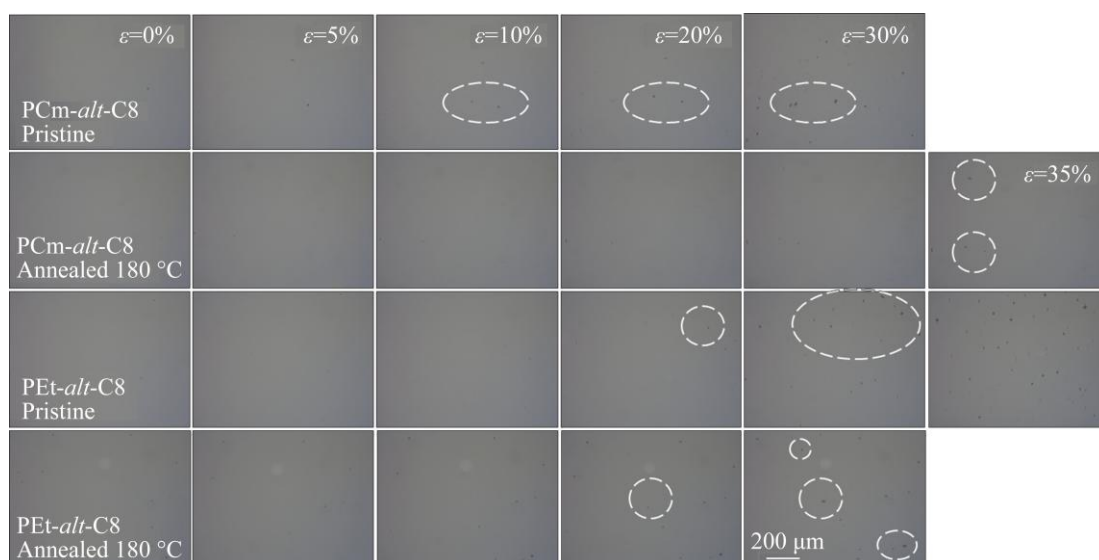


Figure S15 Optical microscopy images of PCm-*alt*-C8 and PEt-*alt*-C8 pristine and 180 °C annealed films stretched on PDMS substrates at strain levels of 0%, 5%, 10%, 20%, 30% and 35%

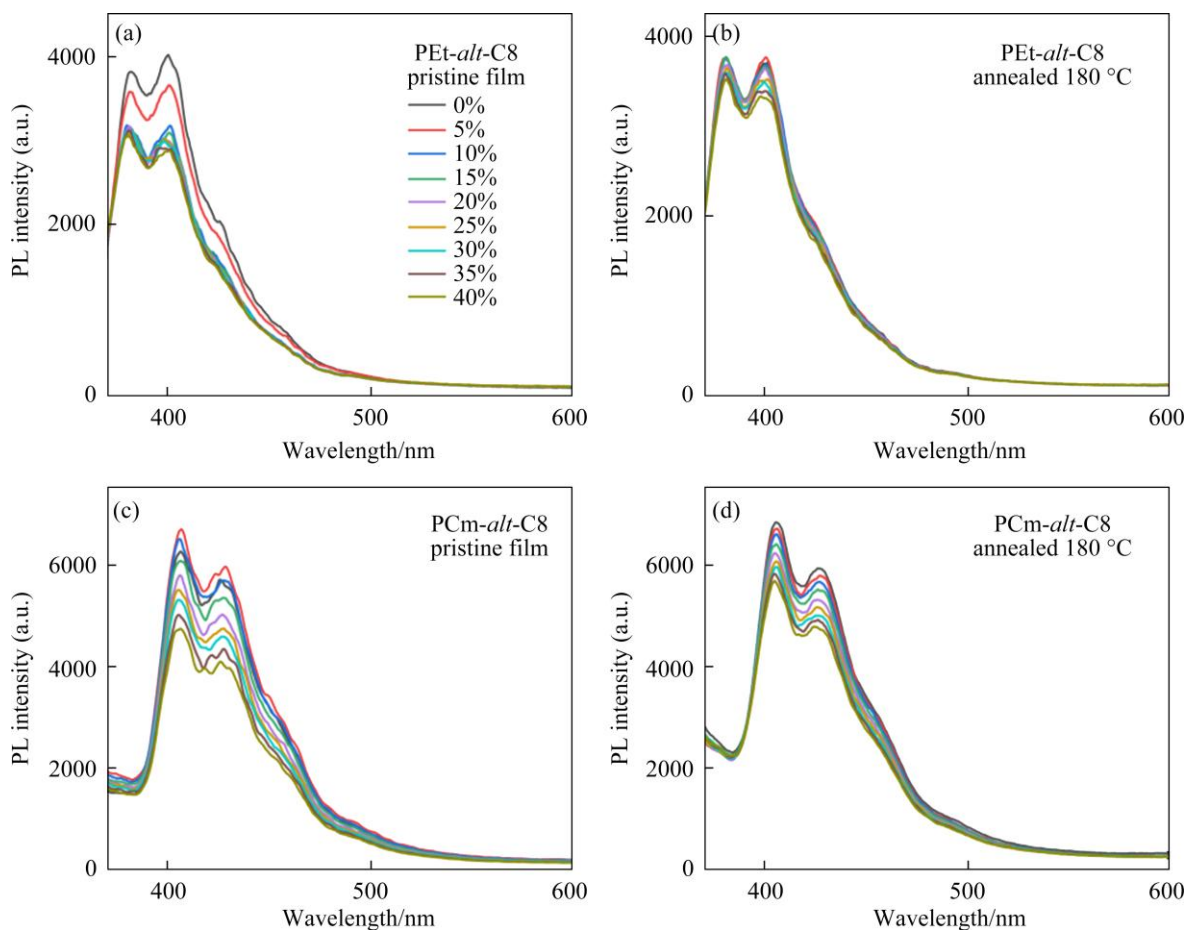


Figure S16 Original PL spectra of PET-*alt*-C8 pristine (a) and 180 °C annealed films (b) stretched on PDMS substrates at strain levels of 0%, 5%, 10%, 15%, 20%, 25%, 30%, 35% and 40% ($\lambda_{\text{ex}}=340$ nm). The original PL spectra of PCm-*alt*-C8 pristine (c) and 180 °C annealed films (d) stretched on PDMS substrates at strain levels of 0%, 5%, 10%, 15%, 20%, 25%, 30%, 35% and 40% ($\lambda_{\text{ex}}=340$ nm)

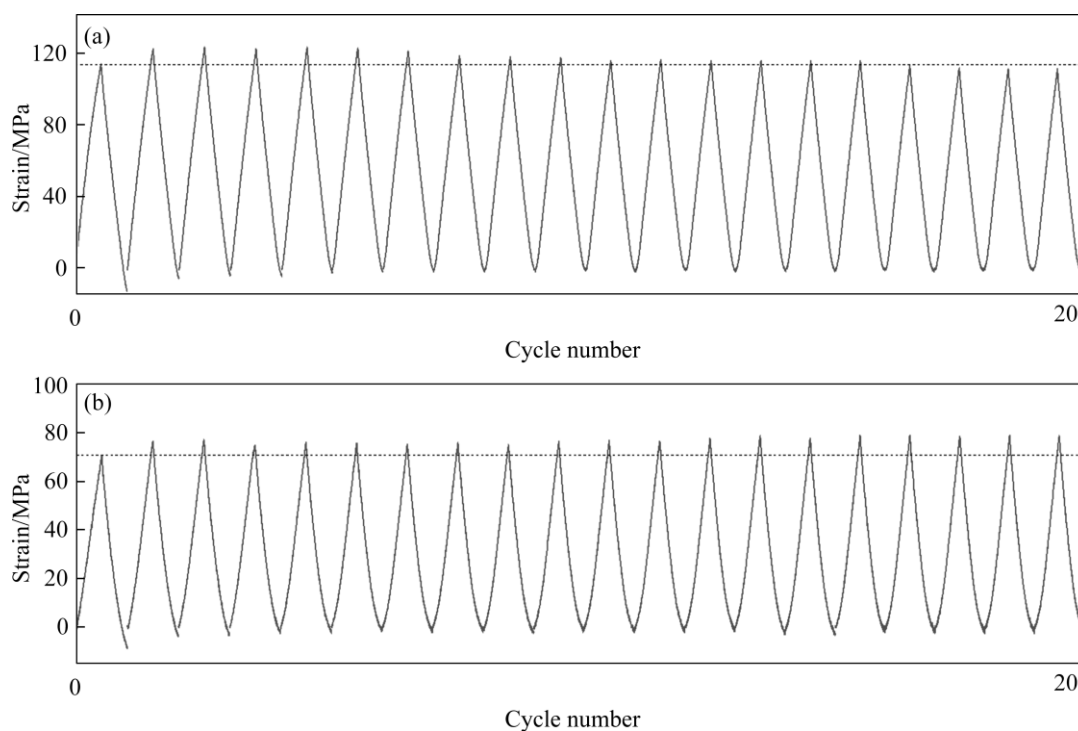


Figure S17 Stress-strain curves of PCm-*alt*-C8 (a) and PET-*alt*-C8 (b) pristine films under cyclic loading (20 cycles)

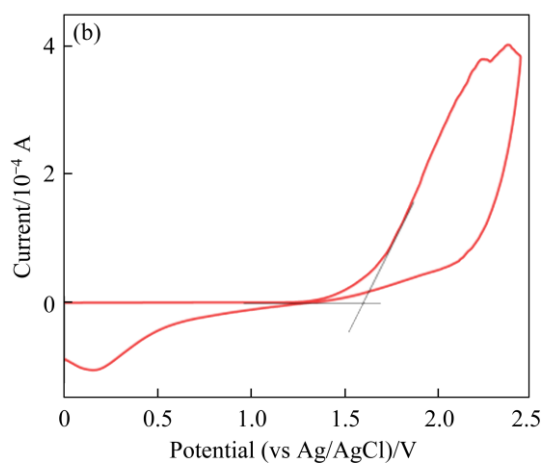
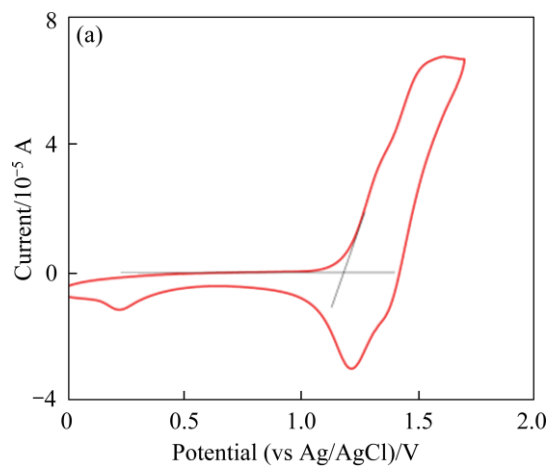


Figure S18 CV curves of PCm-*alt*-C8 (a) and PEt-*alt*-C8 (b)

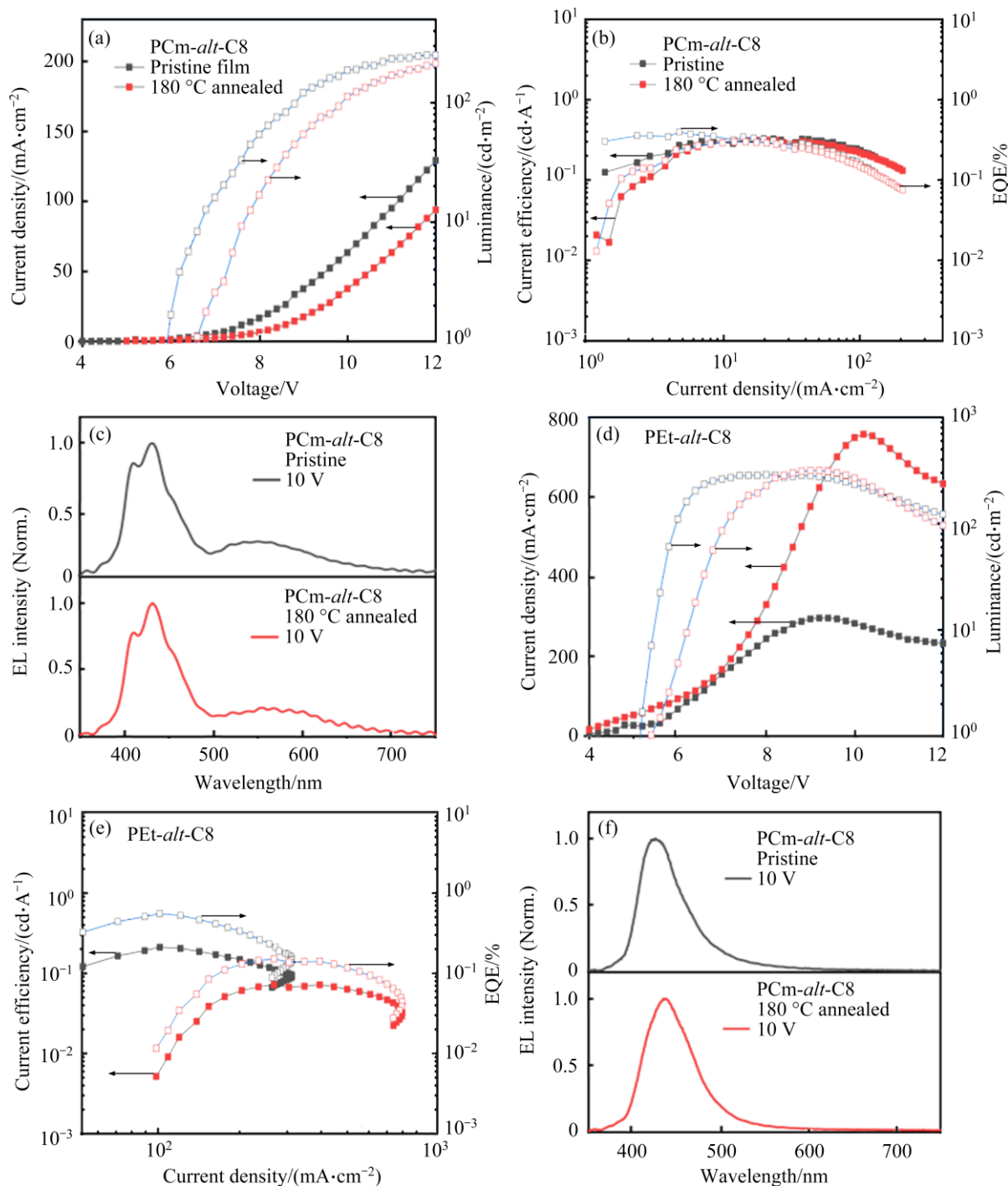


Figure S19 Current density–luminance–voltage curves (a), current efficiency–current density curves (b), and external quantum efficiency–current density curves (c) of PLED devices fabricated using pristine film and 180 °C annealed film of PCm-*alt*-C8; Current density–luminance–voltage curves (d), current efficiency–current density curves (e), and external quantum efficiency–current density curves (f) of PLED devices fabricated using pristine film and 180 °C annealed film of PEt-*alt*-C8

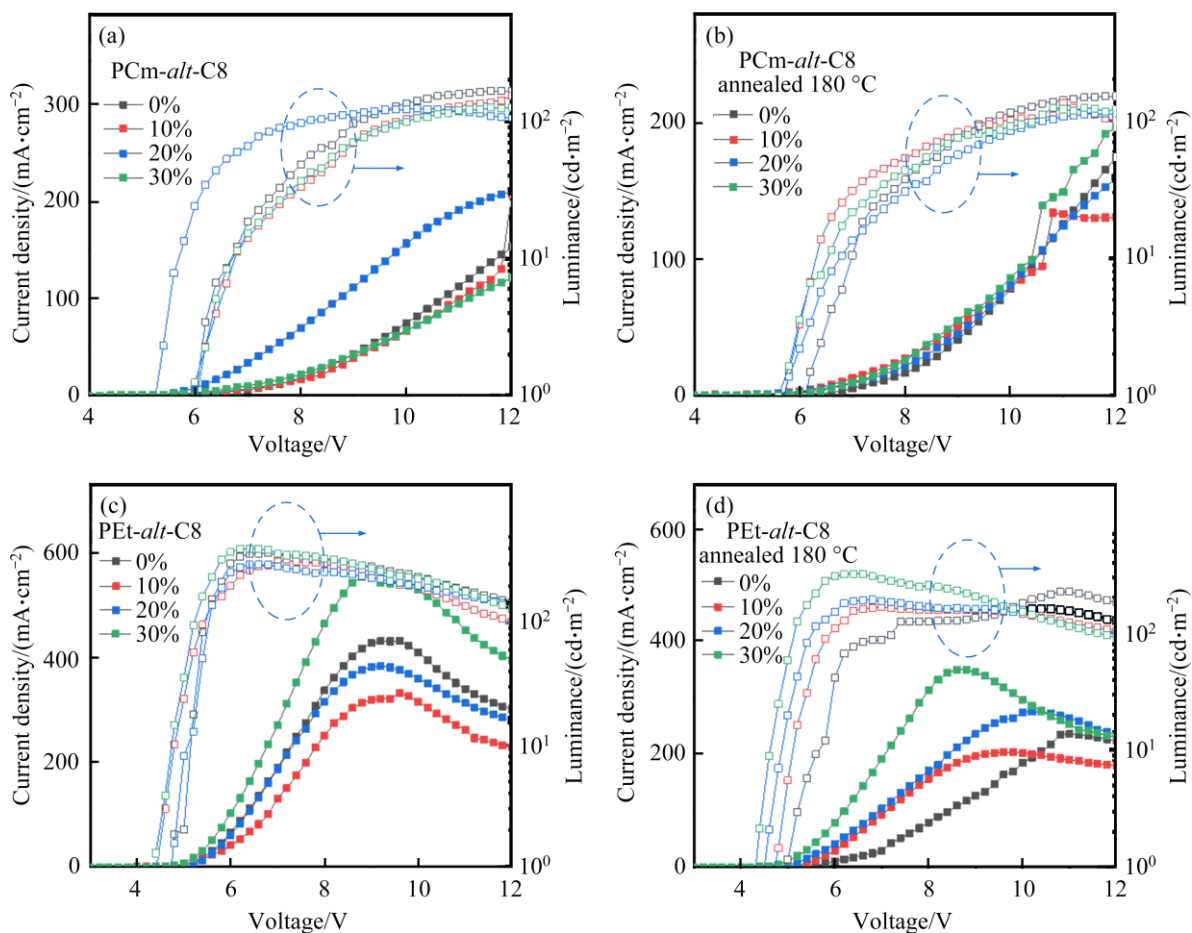


Figure S20 The performance of PLED devices based on PCm-*alt*-C8 pristine film (a) and 180 °C annealed film (b) under stretching and transfer conditions; The performance of PLED devices based on PEt-*alt*-C8 pristine film (c) and 180 °C annealed film (d) under stretching and transfer conditions. The strains applied are 0%, 10%, 20% and 30%.

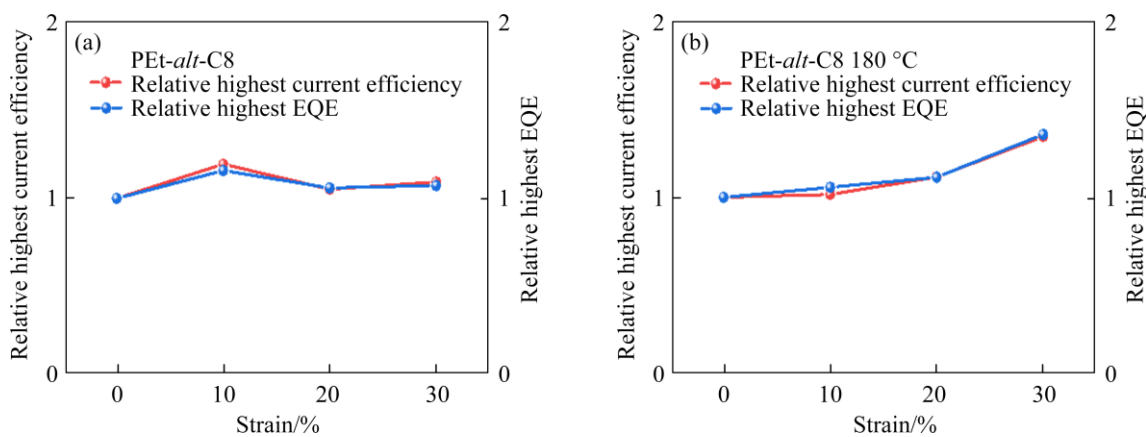


Figure S21 Trend of change in current efficiency (CE) and external quantum efficiency (EQE) relative to the unstretched samples for PLED devices based on PEt-*alt*-C8 pristine film (a) and 180 °C annealed film (b) under stretching and transfer conditions. The applied strains are 0%, 10%, 20 and 30%.