Supporting Information

Hereditary Character of Alkyl-Chain Length Effect on β-Phase Conformation from Polydialkylfluorenes to Bulky Polydiarylfluorenes

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EXPERIMENT SECTION

Materials. 2,7-dibromo-9-fluorenone, 2,2'-bipyridine, *n*-alkyl bromide, 1,5-cyclooctadiene (COD), bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$), hydrazine hydrate, alumina (Al_2O_3), and all solvents were purchased from Aldrich or J&K Chemicals without further purification. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use. Dimethylformamide (DMF) was dried over calcium hydride (CaH) and distilled under a dry nitrogen atmosphere immediately prior to use. Toluene was dried over Na and distilled under a dry nitrogen atmosphere immediately prior to use. The other solvents were distilled under a dry nitrogen atmosphere immediately prior to use. Anhydrous chloroform was pre-dried over molecular sieves.

Preparation of PnDPF Solutions and Gels for the Analysis in This Study. The toluene solutions of 0.5 and 5 mg/mL were prepared by heating and stirring repeatedly until the solutions were transparent, and then filtration by filter heads with a porosity size of 100 μm. The dilute toluene solutions (10^{-5} mg/mL) used for UV-vis, PL and low temperature measurements were all prepared by adding the concentrated solutions into toluene solvent using pipette. The preparation procedures of gels are illustrated as follow: the concentrated solutions of these polymers are heated in the ultrasonic repeatedly until the solutions turn to the transparent state, then placed the solutions standing for several days in refrigerator at -18 ^{o}C or room temperature.

Preparation of PnDPF Films for the Analysis in This Study. Films of PnDPF for the measurement of grazing incident X-ray diffraction (GIXD) and atomic force microscope (AFM)

were spin-coated on silicon chips from their chloroform ($CHCl_3$) solution (10 mg/mL) using KW-4A (from the institute of micro-electronics of Chinese Academy of Science) at 1500 rpm for 30 s. The annealing experiments were implemented on a hot plate with a temperature of 220 °C in the glovebox filled with nitrogen atmosphere. The thickness of the films were all within 100 nm.

Characterization. All ^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the interval standard at room temperature. Mass spectra were recorded on a Shimadzu GCMS 2010 PLUS. Gel permeation chromatography (GPC) analysis was performed on a HP1100 HPLC system equipped with 7911GP-502 and GP NXC columns using polystyrenes as the standard and THF as the eluent at a flow rate of 1.0 mL/min at 25 °C. DSC measurement was acquired using a Shimadzu Instruments DSC-60A. DSC data were collected from 30 to 300 °C at a rate of 10 °C/min for both of the baseline and sample. Absorbance spectra were measured with a Shimadzu UV-3600 spectrometer at 25 °C, and emission spectra were recorded on a Shimadzu RF-5301(PC) luminescence spectrometer. The low temperature emission spectra were recorded on Hitachi F-4600 luminescence spectrometer. The quartz cells of 10 mm thickness were used to measure the spectra of the dilute solutions, and quartz cells of 1 mm thickness were used for the measurement of 0.5 mg/mL solutions. The low temperature emission spectra were recorded on a Hitachi F-4600 luminescence spectrometer, and the solutions were added into a tube and dipped into a quartz container filled with liquid nitrogen. The excitation wavelength was 390 nm for PL, and 485 nm for photoluminescence excitation (PLE). The GIXD measurements were performed on Beamline 7.3.3 at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. The AFM images of the films on silicon chips were obtained by using a Dimension 3100 (Veeco, CA) in tapping model with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N/m) at a scanning rate of 1 Hz.

Raman microscopy was performed using a Renishaw 2000 CCD spectrometer coupled to an Olympus BH-2 confocal microscope, and using the 633 nm line of a He–Ne laser as the excitation source to avoid absorption and resonance effects. The thickness of the films were measured using a Bruker Dektak XT stylus profiler with the films spin-coated onto the silicon chips. The DLS measurements were carried out using an ALV/CGS-3 light scattering spectrometer equipped with an ALV/LSE-5003 multiple-τ digital correlator over the time range 10^{-8}-10^{3} s. The JDS-Uniphase solid-state He-Ne laser having the output power of *ca.* 22 mW at the operating wavelength of 632.8 nm was used as the light source. Powder diffraction patterns were performed by using a Bruker D8 X-ray diffractometer with Cu Kα radiation (λ =1.54050 Å). The operating 2θ angle ranges from 5 to 30°, with a step length of 0.02°.

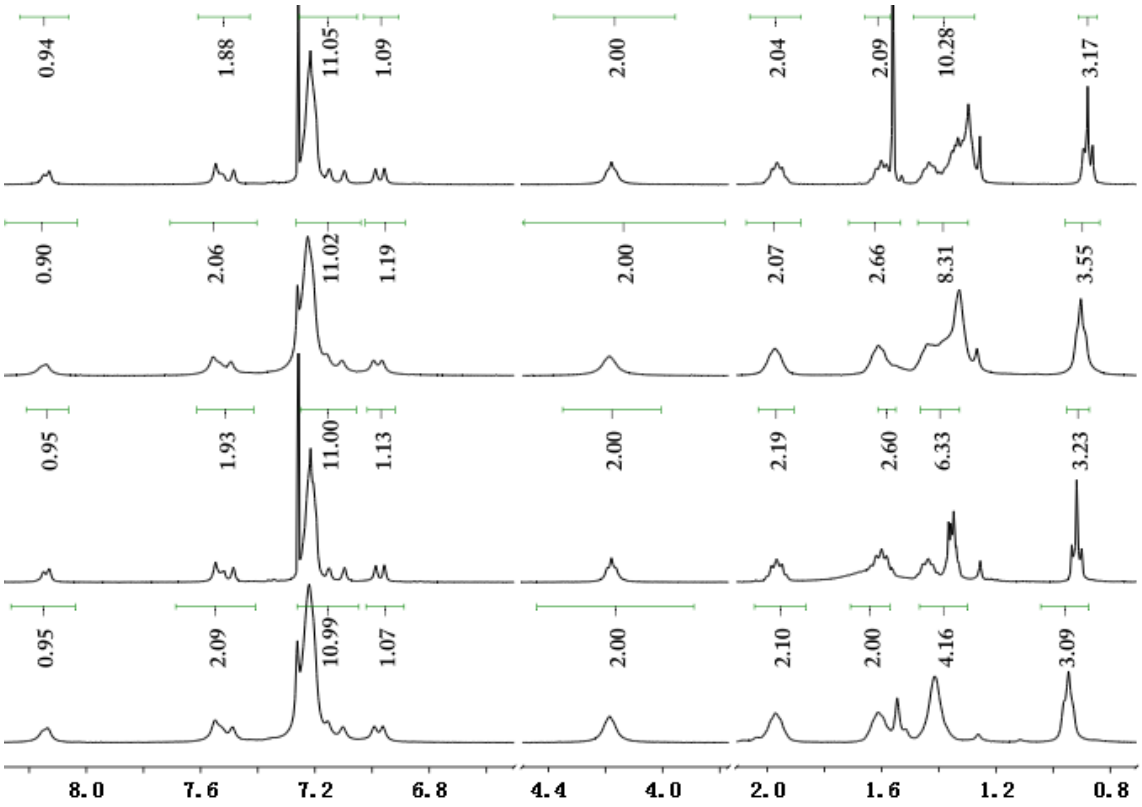

Figure S1. ^{1}H NMR of PODPF.

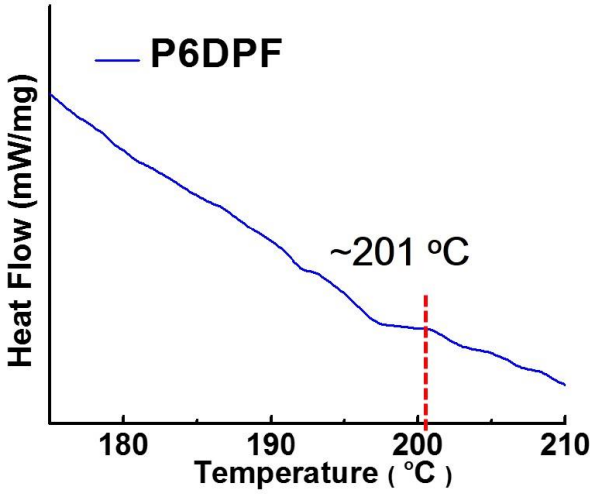

Figure S2: DSC curve of P6DPF.

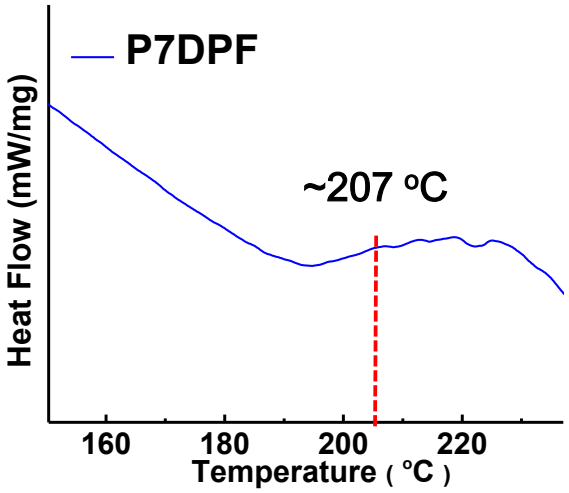

Figure S3: DSC curve of P7DPF.

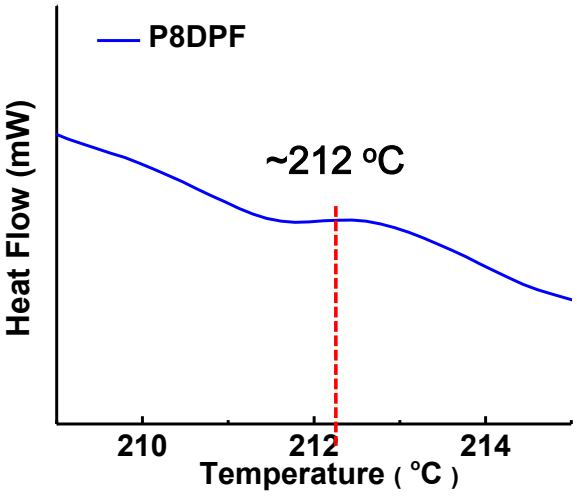

Figure S4: DSC curve of P8DPF.

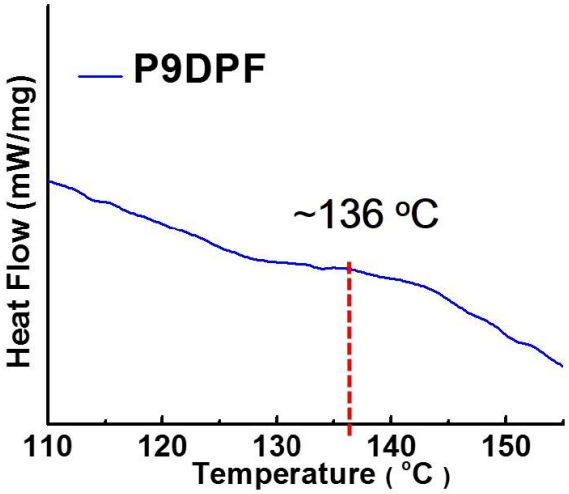

Figure S5: DSC curve of P9DPF.

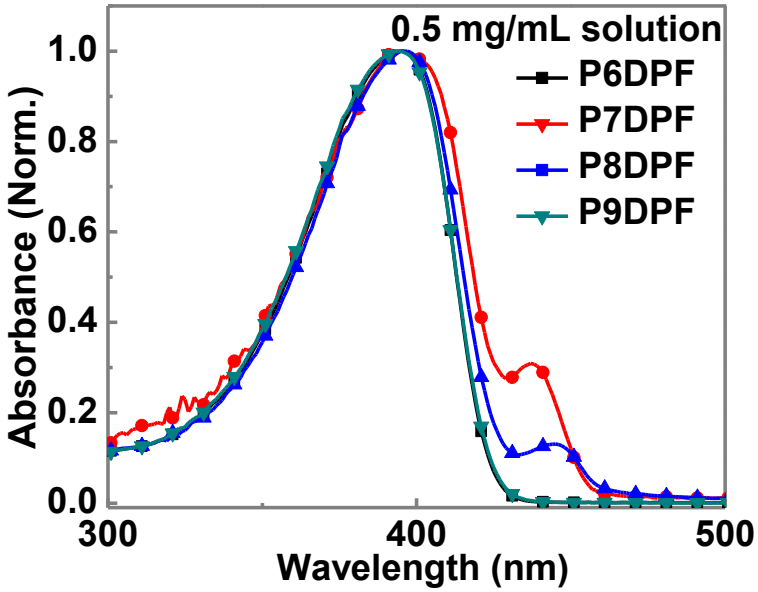

Figure S6. The UV-vis spectra of four polymers with a concentration of 0.5 mg/mL.

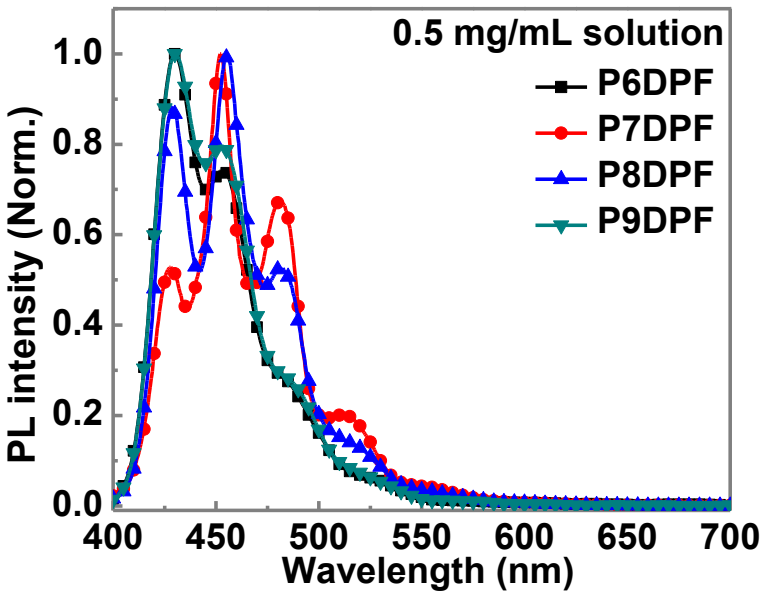

Figure S7. The PL spectra of four polymers with a concentration of 0.5 mg/mL.

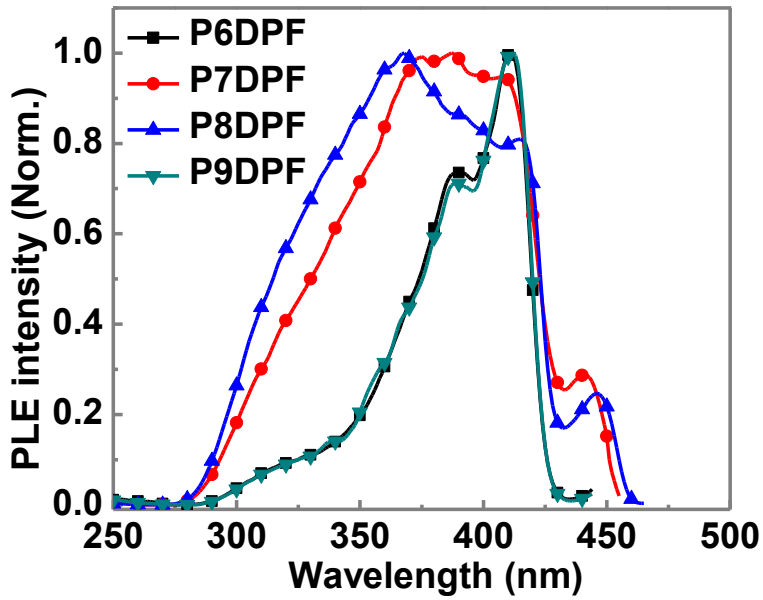

Figure S8. The PLE spectra of four polymers measured at -196 ^{o}C with a concentration of 10^{-5} mg/mL.

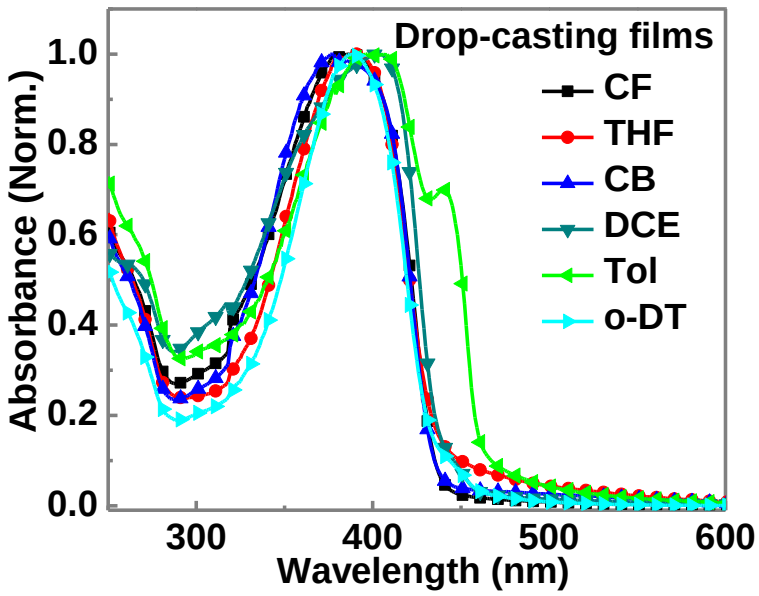

Figure S9. The UV-vis spectra of P8DPF films drop-cast from various solvents with different solubility.

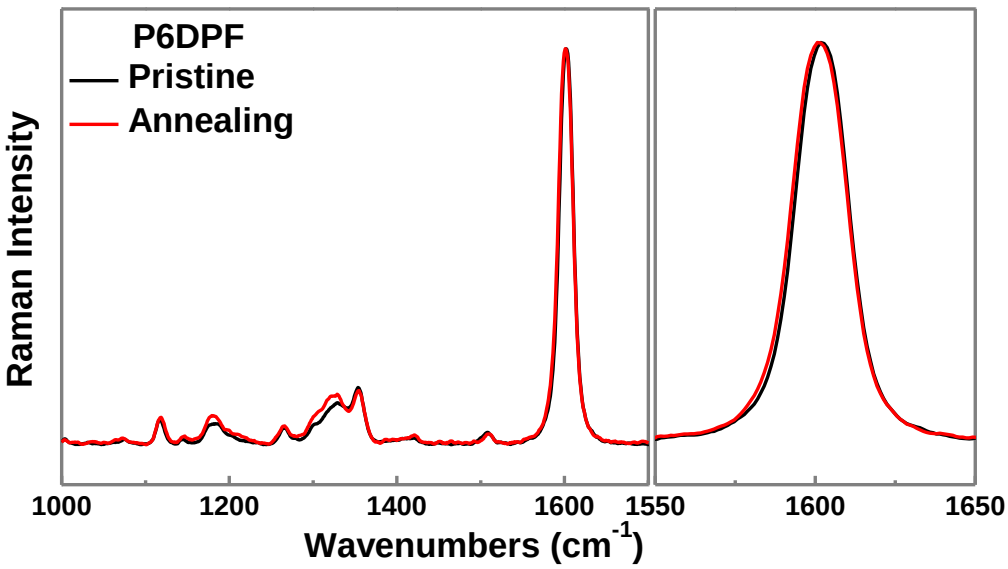

Figure S10: Raman spectra of P6DPF drop-casting films.

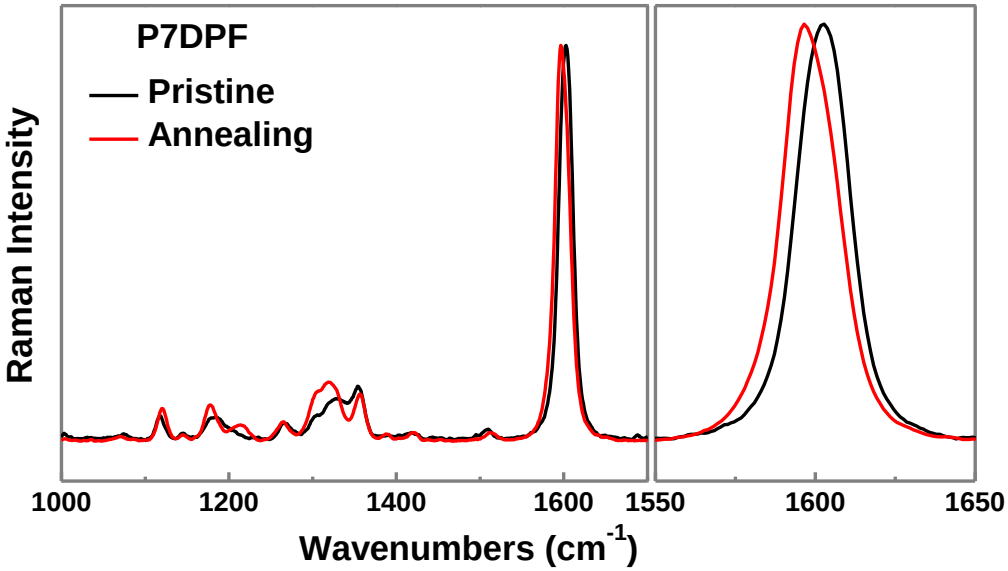

Figure S11: Raman spectra of P7DPF drop-casting films.

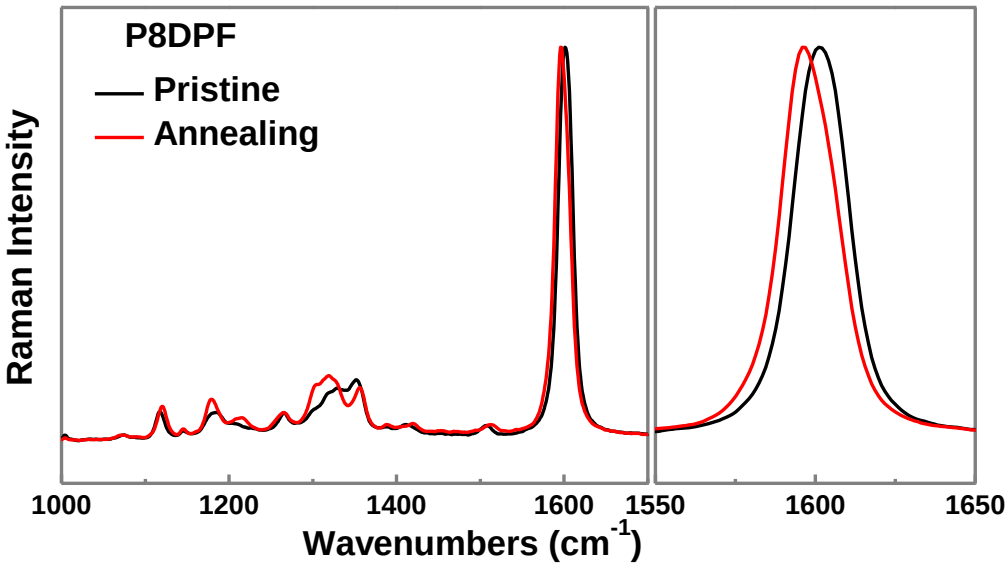

Figure S12: Raman spectra of P8DPF drop-casting films.

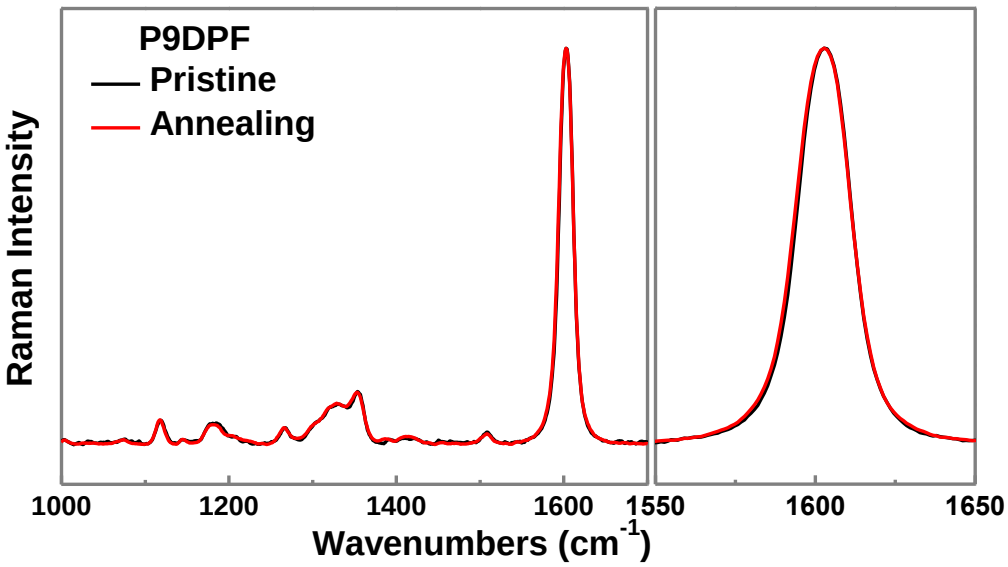

Figure S13: Raman spectra of P9DPF drop-casting films.

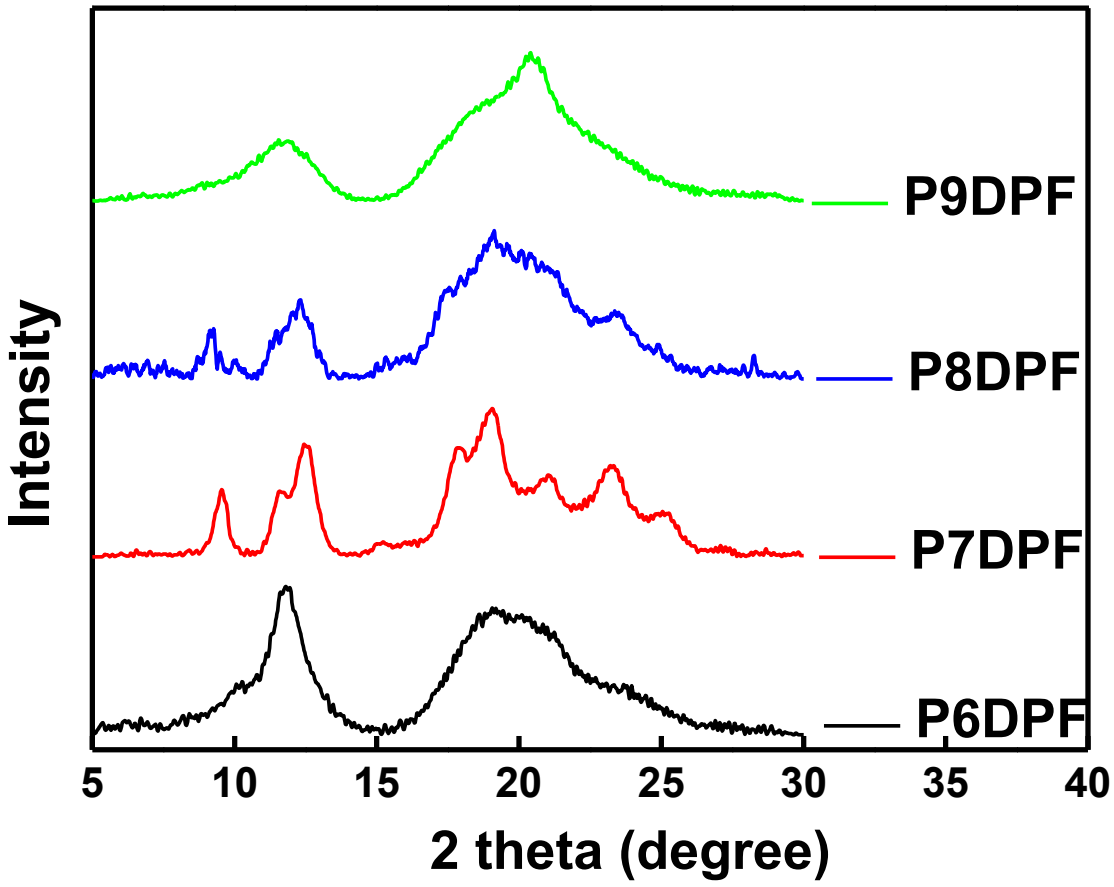

Figure S14: 1D XRD profiles of PnDPF powders.

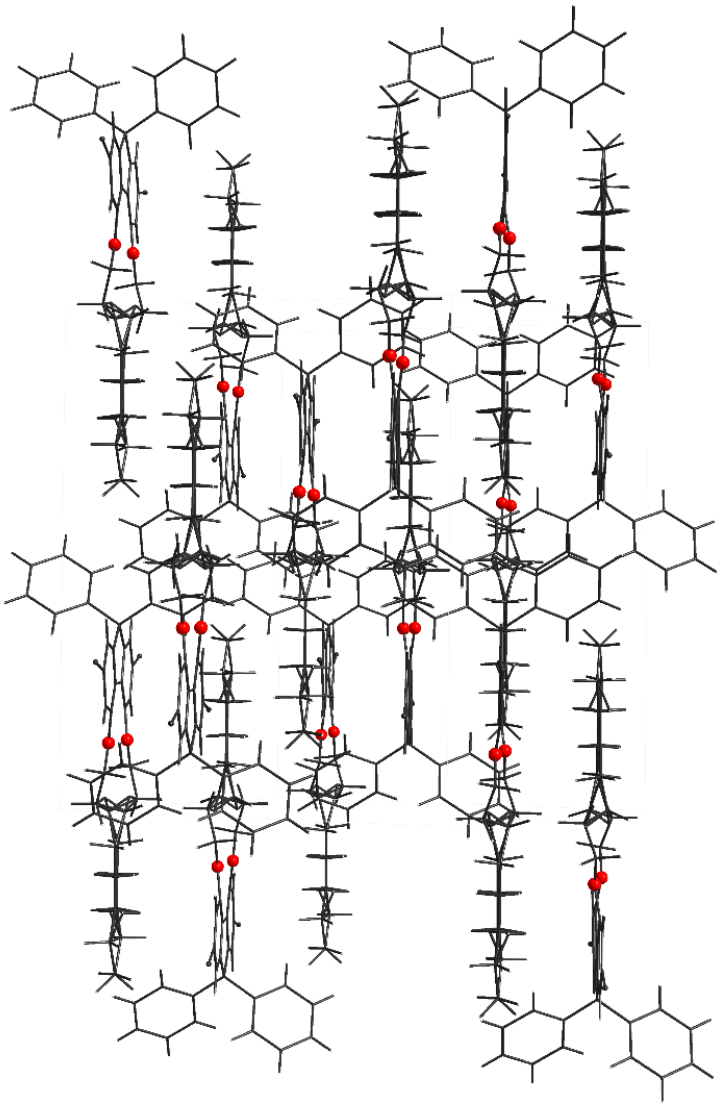

Figure S15: Packing diagram of the P8DPF monomer single crystal, the oxygen atoms are marked in red, the dual alkoxy chains at the 4 and 5-positions show symmetric disorder.