

Support Information

Tuning the Photovoltaic Parameters of Thiophene-Linked Donor-Acceptor Liquid Crystalline Copolymers for Organic Photovoltaics

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Characterizations

The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 600 NMR spectrometer with deuterated chloroform as the solvent and with tetramethylsilane ($\delta=0$) as the internal standard. The ultraviolet-visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. Fluorescence measurement for photoluminescence (PL) of the polymers was carried out on a Hitachi F-7000 PC spectrofluorophotometer with a xenon lamp as the light source. The gel permeation chromatography (GPC), so-called size-exclusion chromatography (SEC) analysis, was conducted with a Breeze Waters system equipped with a Rheodyne injector, a 1515 Isocratic pump and a Waters 2414 differential refractometer using polystyrenes as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min and 40 °C through a Styragel column set, Styragel HT3 and HT4 (19 mm×300 mm, 10^3+10^4 Å) to separate molecular weight (MW) ranging from 10^2 to 10^6 . Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 7 for thermogravimetry at a heating rate of 10 °C/min under nitrogen with a sample size of 8–10 mg. Differential scanning calorimetry (DSC) was used to determine phase-transition temperatures on a Perkin-Elmer DSC 7 differential scanning calorimeter with a constant heating/cooling

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rate of 10 °C/min. Texture observations by polarizing optical microscopy (POM) were made with a Nikon E600POL polarizing optical microscope equipped with an Instec HS 400 heating and cooling stage. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target ($\lambda = 1.54 \text{ \AA}$) and at a scanning rate of 1°/min. The fluorescence lifetime was determined with an Edinburgh Instrument FLS920 fluorescence spectrophotometer using a H₂ gas lamp as the light source. TEM images were recorded using a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera. The morphology observations of active layer films were made by scanning electron microscopy (SEM; FEI, QuanTA-200F environmental scanning electron microscope) with gold vapor deposition. Cyclic voltammograms (CV) were performed in a three-electrode cell using platinum electrodes at a scan rate of 50 mV s⁻¹ and a Ag/Ag⁺ (0.1 M of AgNO₃ in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in acetonitrile. Under these conditions, the onset oxidation potential ($E_{1/2 \text{ ox}}$) of ferrocene was -0.02 eV versus Ag/Ag⁺. The HOMO energy level of polymers was determined from the oxidation onset of the second scan from CV data. It is assumed that the redox potential of Fc/Fc⁺ has an absolute energy level of -4.40 eV to vacuum. The energy of HOMO and LUMO levels were calculated according to the eqs 1 and 2; the electrochemically determined band gaps were deduced from the difference between onset potentials from oxidation and reduction of copolymers as depicted in eq 3[3-4].

$$E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.42) \text{ (eV)} \quad (1)$$

$$E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{red}} + 4.42) \text{ (eV)} \quad (2)$$

$$E_{\text{gap}}^{\text{EC}} = (E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}) \text{ (eV)} \quad (3)$$

Annealing of films was conducted by heating in the setting temperature for 1 h, followed by cooling to room temperature at a cooling speed of 1 deg/min. All the thermal treatments were performed under ambient atmosphere at 160 °C (polymer PFtpTDTBT-a) and 170 °C (PFtpTDTBT-b and PFtpTDTBT-c).

Device Fabrication and Characterization

The polymer PVCs were fabricated with the active layer consisting of the copolymer **PFtpTDTBT**:PCBM in 1:2 wt/wt ratio. Prior to use, the substrates were ultrasonicated for 20 min in acetone followed by deionized water and then 2-propanol. The substrates were dried under a stream of nitrogen and subjected to the treatment of UV ozone over 30 min. A filtered dispersion of PEDOT: PSS in water (Baytron Al4083) was then spun-cast onto clean ITO substrates at 4000 rpm for 60 s and then baked at 120°C. The copolymers were dissolved in chlorobenzene to make 20 mg·mL⁻¹ solutions, followed by blending with PCBM (purchased from Lumtec. Corp) in 75 wt %. The active layers were obtained by spin-coating the blend solutions at 1000 rpm for 30 s and the thickness of films were ~ 90 nm. Subsequently, LiF (0.6 nm) and Al (100 nm) electrodes were deposited via thermal evaporation in vacuum (<10⁻⁶ Torr) in thickness of approximately. The thicknesses of all the films were measured by a Dektak profiler. Annealing of some devices was conducted by heating at different temperatures for 60 min, followed by cooling to room temperature at a cooling speed of 1 deg/min. Current-voltage (J-V) characteristics were recorded using Keithley 2400 Source Meter in the dark and under 100 mW/cm² simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000). All the measurements were performed under ambient atmosphere at room temperature. EQE were detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode.

Hole mobility measurement and fabrication of polymer solar cells. We used a device structure of ITO/PEDOT:PSS/polymer:PC70BM/Au for the hole mobility measurement, based on the space-charge-limited current (SCLC) model. According to the following equation: $\ln(JL^3/V^2) \approx 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \ln(9\epsilon\epsilon_0\mu_0/8)$, Where μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, ϵ is the dielectric constant of the polymer, ϵ_0 is the permittivity of the vacuum, L is the thickness of the polymer layer, $V = V_{\text{appl}} - V_{\text{bi}}$, V_{appl} is the applied potential, and V_{bi} is

the built-in potential (in this device structure, $V_{bi} = 0.2$ V). According to the equation, hole mobility can be calculated.

Materials. All solvents are ACS grade unless otherwise noted. Anhydrous THF and toluene were obtained by distillation from sodium/benzophenone prior to use. DMF is dried in CaH₂.

9,9-bis[6-(4'-hexyloxy-terphenyloxy)-hexyl]-fluorene (F),
2,5-bis(tributylstannyl)-3-hexylthiophene [1] and
4,7-bis(5-bromothiophen-2-yl)-[2,1,3]-benzothiadiazole (DTBT) [2] were prepared according to modified literature procedures. All reagents were purchased from Aldrich, TCI America, or Alfa Aesar, and were used without further purification.

Polymerization of PFtpTDTBT derivates. Stille cross-coupling polymerization was conducted according to a literature method. [3] The synthetic route is depicted in Scheme 1S.

Polymer PFtpTDTBT-a. 2 mol % of tris(dibenzylideneacetone)dipalladium(0), and 8 mol % of triphenylarsine were added to a mixture of 2,5-bis(tributylstannyl)-3-hexylthiophene (199 mg, 0.3 mmol), 9,9-bis[6-(4'-hexyloxy-terphenyloxy)-hexyl]-fluorene (236 mg, 0.2 mmol), and 4,7-bis(5-bromothiophen-2-yl)-[2,1,3]-benzothiadiazole (46 mg, 0.1 mmol) with the respective monomers (Ftp: DTBT = 2: 1) in dry DMF (8 mL). The reaction mixture was purged with N₂ and subjected to three freeze/pump/thaw cycle to remove O₂. The polymerization reaction was carried out at 110 °C for 48 h. The copolymers were end-capped using bromobenzene and trimethyl(phenyl)tin. The dark solution was poured into methanol, and the black precipitate was collected on a membrane filter. The random copolymer was washed using a Soxhlet extractor using acetone and then hexanes to remove catalyst residues and low molecular weight fractions. The polymers were extracted with chloroform and the polymer solid dissolved in CHCl₃ was washed with dilute aqueous HCl solution, NH₄OH(aq), and distilled water in this order to purify from metals. Then the chloroform fraction was then concentrated, and chlorobenzene was added (5 mL). The polymer solution was then precipitated into methanol at room temperature, filtered, and dried under vacuum to yield the polymer as a deep-red product (73%). ¹H-NMR (CDCl₃, 400MHz): δ 7.56-7.32 (m, aromatic, 46H), 7.01-6.79 (m, aromatic, 23H), 4.01-3.83(m, 16H, -CH₂-O-terphenyl), 2.81 (t,

6H, -CH₂-thiophene), 1.97-0.52(m, 117H, alkyl). ¹³C-NMR (600 MHz, CDCl₃): 158.62, 151.93, 138.64, 132.97, 129.86, 127.37, 126.81, 126.27, 121.81, 114.67, 113.77, 68.05, 58.32, 55.42 39.96, 33.96, 33.96, 31.43, 29.72, 28.68, 27.35, 25.24, 23.06, 22.73, 18.05, 13.73,. Anal. Calcd: C, 80.39; H, 7.33; N, 0.98; S, 6.77. Found: C, 79.92; H, 7.45; N, 1.07; S, 6.56. Other polymers were prepared in analogous fashion.

Polymer **PFtpTDTBT-b**. The polymer was synthesized following the same procedure as **PFtpTDTBT-a** with the respective monomers (F:DTBT = 1:1). Black solid, yield=75%. ¹H-NMR (CDCl₃, 400MHz): δ 7.56-7.32 (m, aromatic, 24H), 7.01-6.79 (m, aromatic, 14H), 4.01-3.83(m, 8H, -CH₂-O-terphenyl), 2.81 (t, 4H, -CH₂-thiophene), 1.97-0.52(m, 64H, alkyl). Anal. Calcd: C, 77.82; H, 6.91; N, 1.70; S, 9.70. Found: C, 77.43; H, 7.06; N, 1.73; S, 9.84.

Polymer **PFtpTDTBT-c**. The polymer was synthesized following the same procedure as **PFtpTDTBT-a** with the respective monomers (F:DTBT = 1:2). Black solid, yield=77%. ¹H-NMR (CDCl₃, 400MHz): δ 7.56-7.32 (m, aromatic, 26H), 7.01-6.79 (m, aromatic, 19H), 4.01-3.83(m, 8H, -CH₂-O-terphenyl), 2.81 (t, 6H, -CH₂-thiophene), 1.97-0.52(m, 75H, alkyl). Anal. Calcd: C, 74.36; H, 6.34; N, 2.65; S, 13.62. Found: C, 74.13; H, 6.42; N, 2.63; S, 13.54.

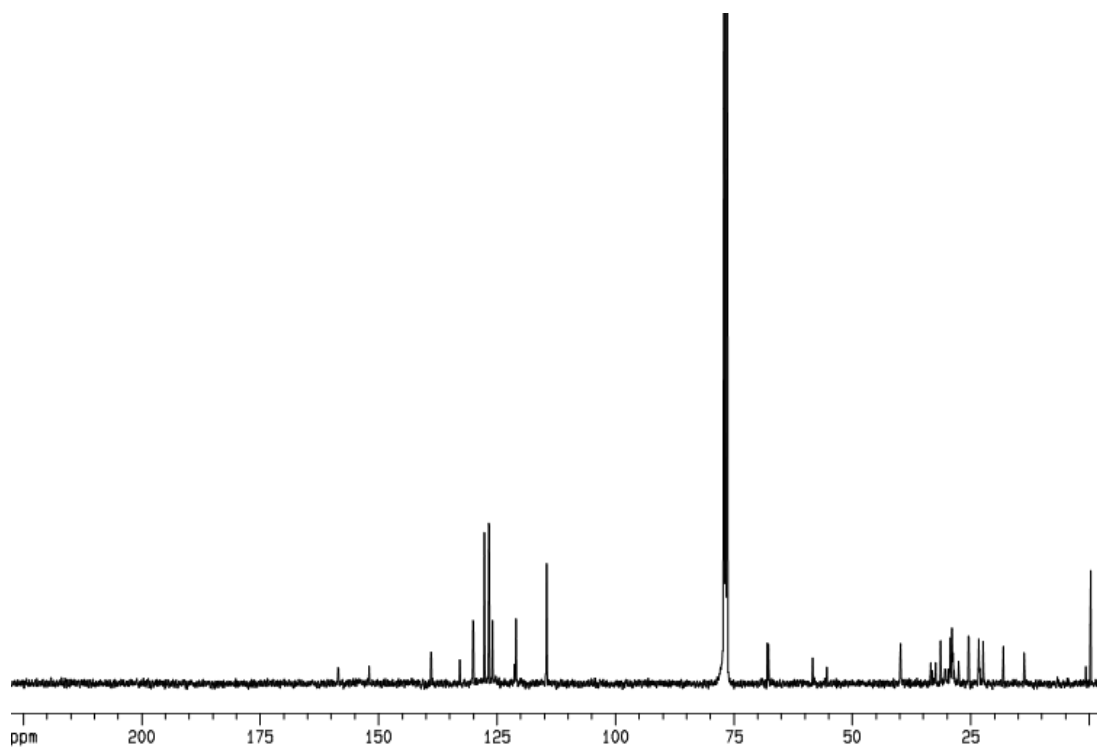


Figure S1. ^{13}C NMR spectra of polymer **PFtpTDTBT-a** in chloroform-*d*.

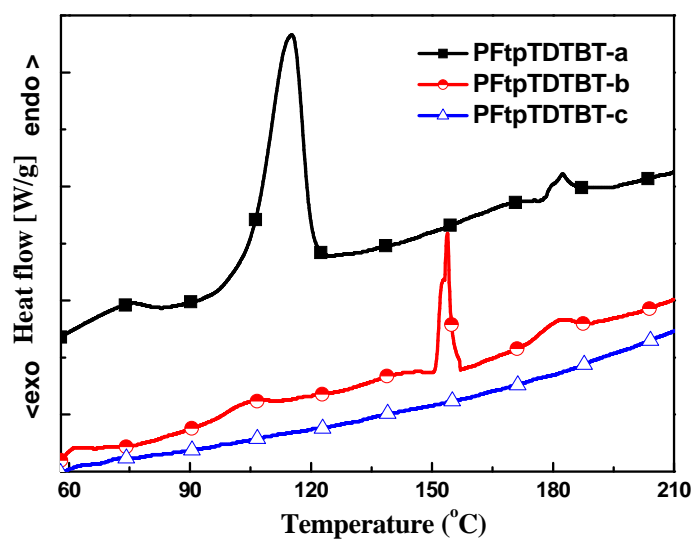


Figure S2. DSC curves of polymers during the second heating scan at 10°C/min.

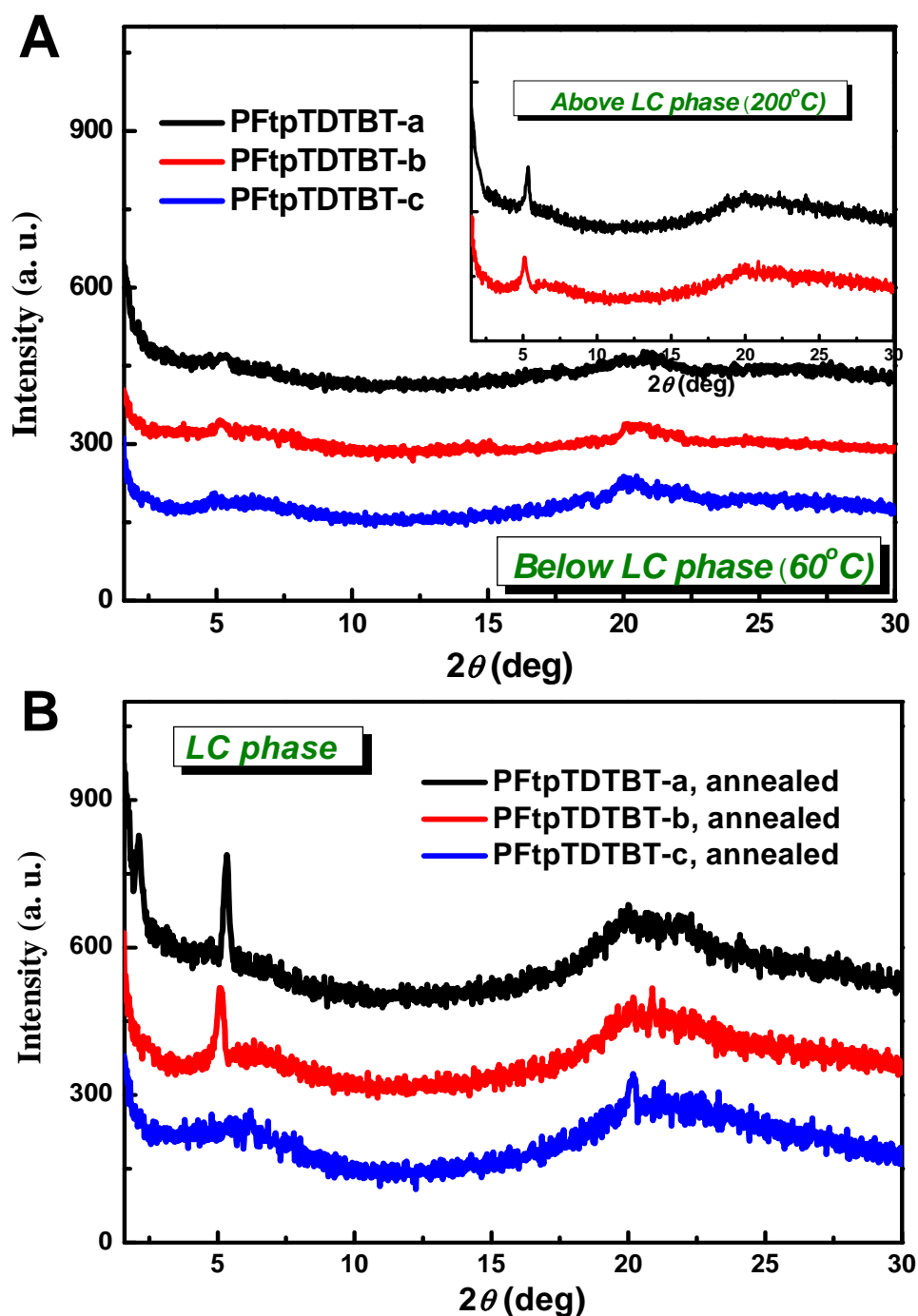


Figure S3. Powder X-ray diffraction pattern of a thin film of copolymers deposited onto a glass substrate under different temperature treatment. (A) The curves of film at 60°C (isotropic, below the mesophase transition) and 200°C annealing (isotropic, above the mesophase transition) (B) LC phase annealing.

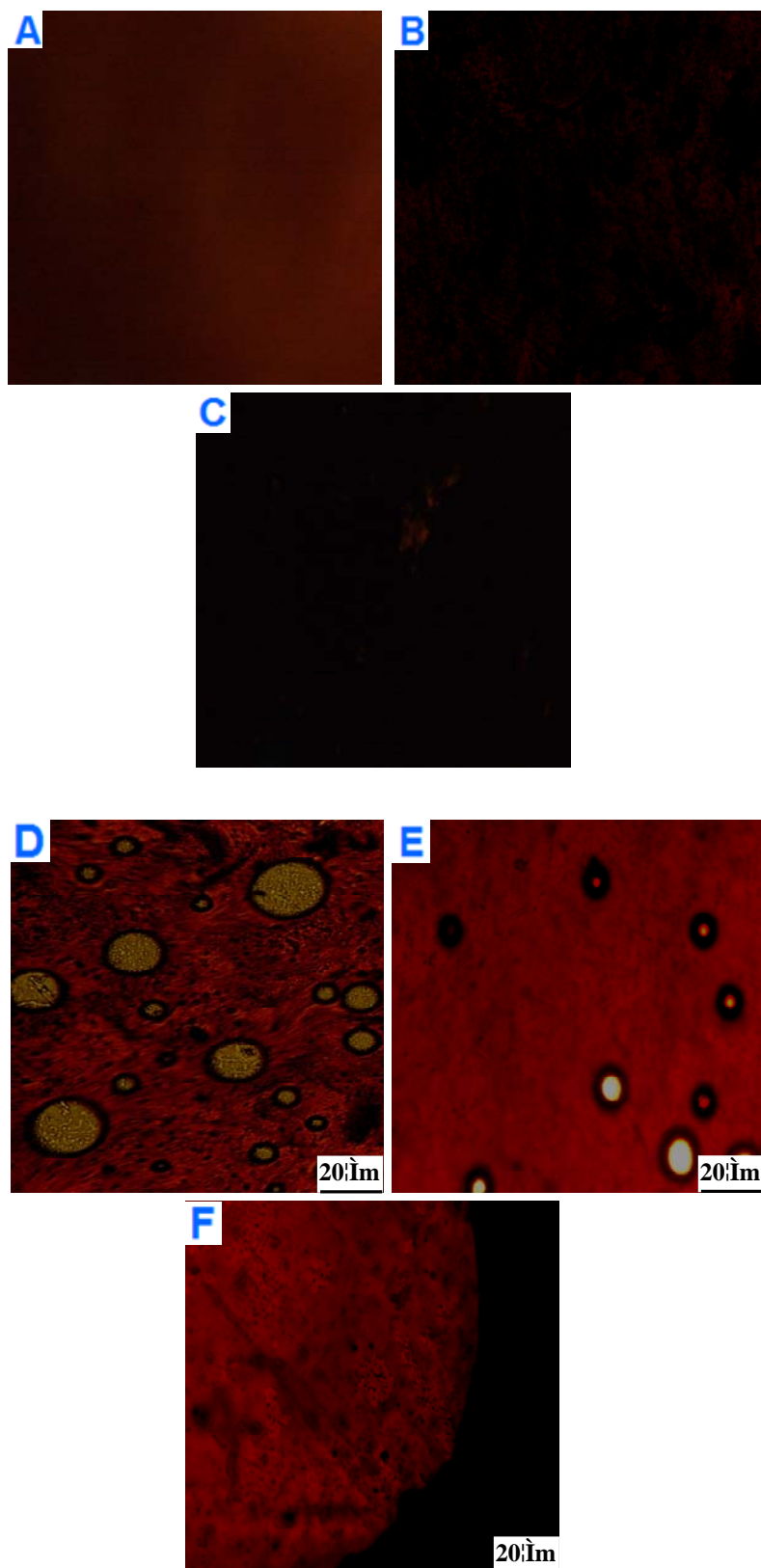


Figure S4. Polarizing optical microscopic images of **PFtpTDTBT-a** (A); **PFtpTDTBT-b** (B); **PFtpTDTBT-c** (C) at 60 °C; and the images of **PFtpTDTBT-a** (D); **PFtpTDTBT-b** (E); **PFtpTDTBT-c** (F) at 200 °C.

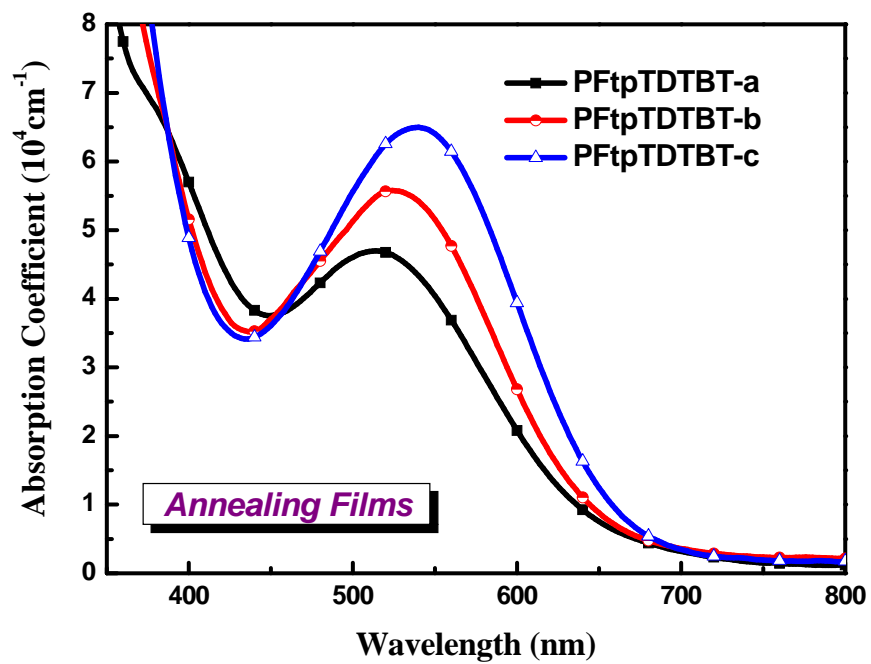


Figure S5. Absorption coefficients of the polymer films after annealing.

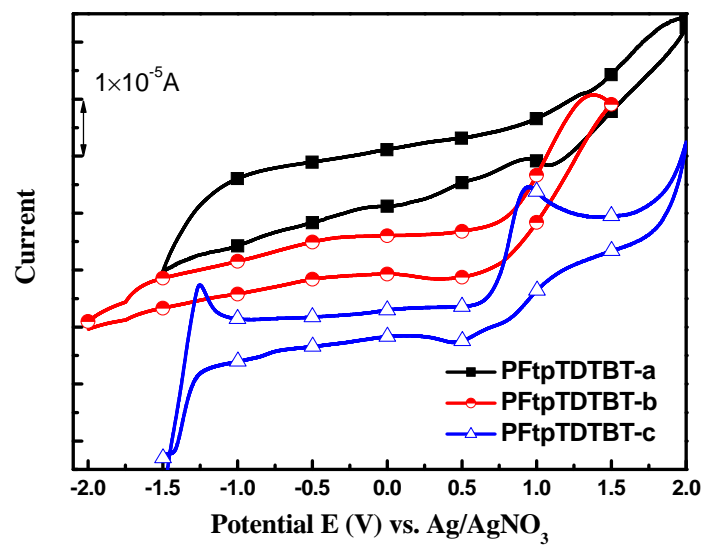


Figure S6. Cyclic voltammograms of the oxidation and reduction behavior of thin films of copolymers.

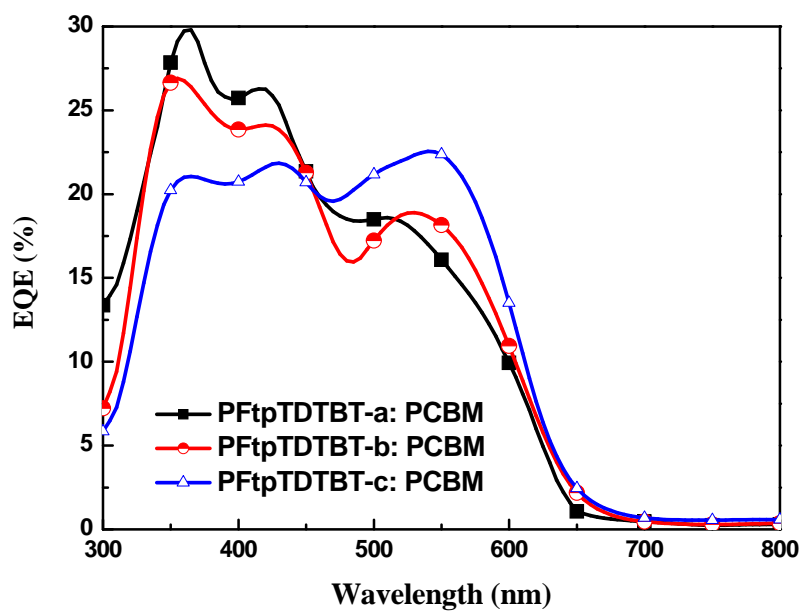


Figure S7. External quantum efficiency (EQE) of the PSCs devices of photovoltaic cells calculated from the photocurrents under short-circuit conditions based on the three polymers:PCBM blends after annealed.

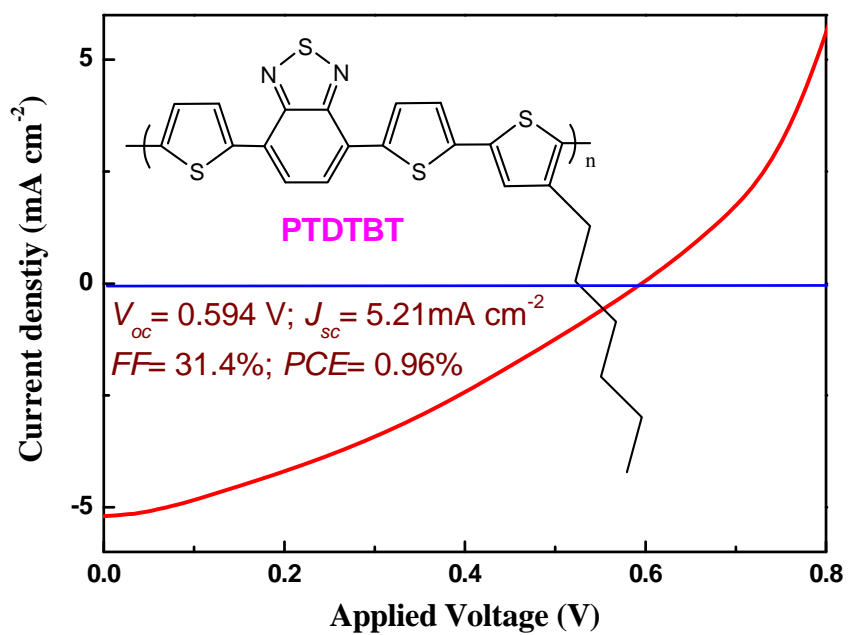


Figure S8. The chemical structure of reference polymer **PTDTBT** and *J-V* characteristics of devices based on **PTDTBT**:PC₆₁BM (1:1, w/w).

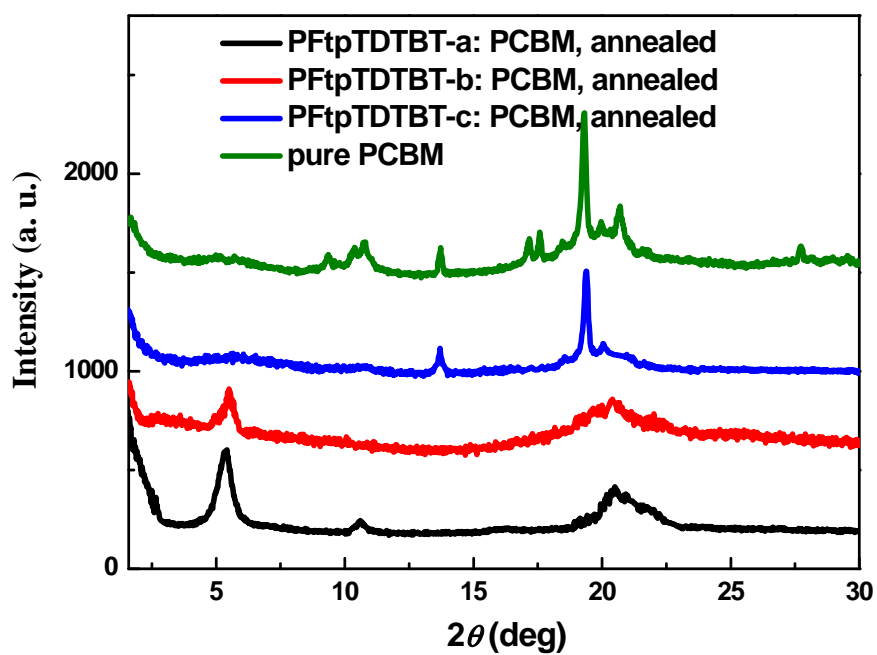


Figure S9. XRD spectra of PCBM film and polymer:PCBM (1:2 wt %) films after LC phase annealed treatment.

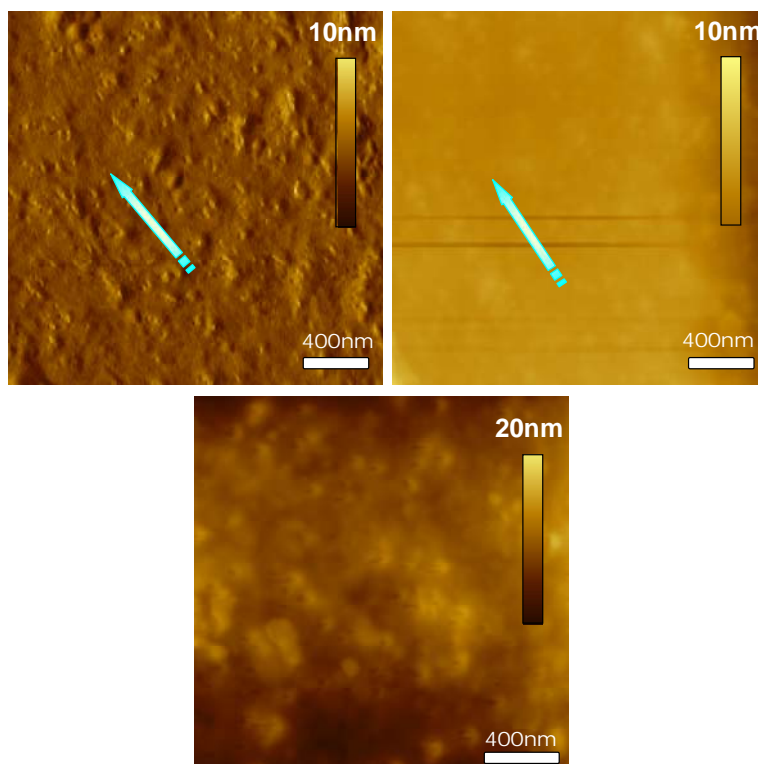


Figure S10. AFM height images of **PFtpTDTBT-a:PCBM** (a), **PFtpTDTBT-b:PCBM** (b) and **PFtpTDTBT-c:PCBM** (c) films after annealing treatment in a 1:2 ratio blend.

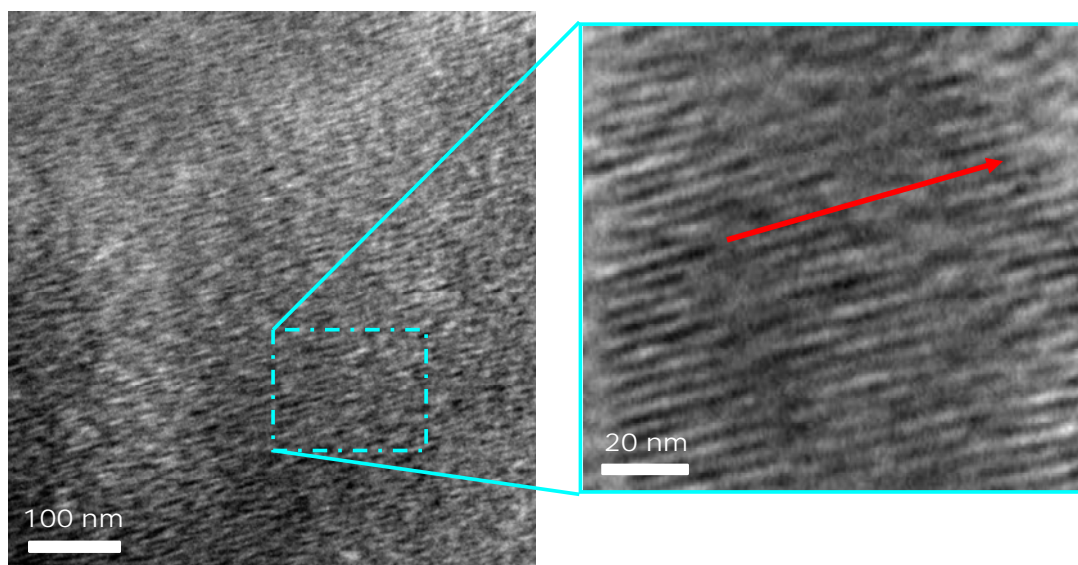


Figure S11. TEM images of PFtpTDTBT-a:PCBM films after annealed treatment and the lamellae can be seen in the zoom-in TEM image.

Reference and note

1. E. Bundgaard, and F. C. Krebs, *Macromolecules*, 2006, **39**, 2823-2831.
2. Q. Hou, Y. Xu, W. Yang, M. Yuan, J. Peng and Y. Cao, *J. Mater. Chem.*, 2002, **10**, 2887-2892.
3. (a) Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792–7799. (b) S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You, *J. Am. Chem. Soc.*, 2011, **133**, 4625–4631.