

Supporting Information for

Conjugated block copolymer photovoltaics with near 3% efficiency through microphase separation

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1. Absorption spectra of P3HT-*b*-PFTBT block copolymers

The absorption spectra of P3HT, PFTBT, and P3HT-*b*-PFTBT are shown in Figure S1. All films were cast from chloroform solutions and not annealed. The absorption coefficients are calculated from the absorbance and film thickness. PFTBT demonstrates two absorption peaks around 390 and 540 nm with a similar absorption edge and optical bandgap (~ 2 eV) as P3HT. P3HT-*b*-PFTBT block copolymers approximately preserve the features of the constituent P3HT and PFTBT homopolymers. Hence, the absorption coefficient is enhanced at longer wavelengths

(450-600 nm) due to the overlapping absorption bands of P3HT and PFTBT, while absorption at short wavelengths (300-420 nm) is mainly attributed to the PFTBT block.

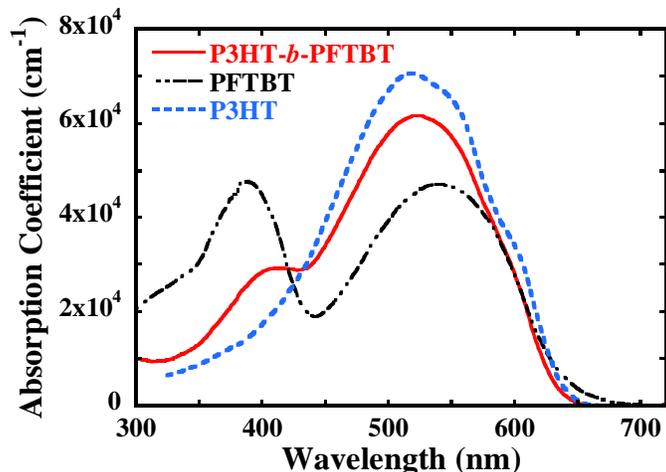


Figure S1. UV-vis absorption spectra of pristine P3HT, PFTBT and P3HT-*b*-PFTBT films.

2. X-ray absorption spectra

Near-edge X-ray absorption fine structure (NEXAFS) studies of neat P3HT and neat PFTBT films are shown in Figure S2. Both films were annealed at optimized conditions (165 °C) for device performance. The absorption spectra are normalized to 1 at 320 eV to account for thickness variations in different samples. NEXAFS spectra show that the absorption in organic materials is sensitive to small changes of the X-ray energy near the carbon absorption edge (280-320 eV). For example, significant contrast exists at 285.4 eV, where the C 1s to π^* transition differs in P3HT and PFTBT.

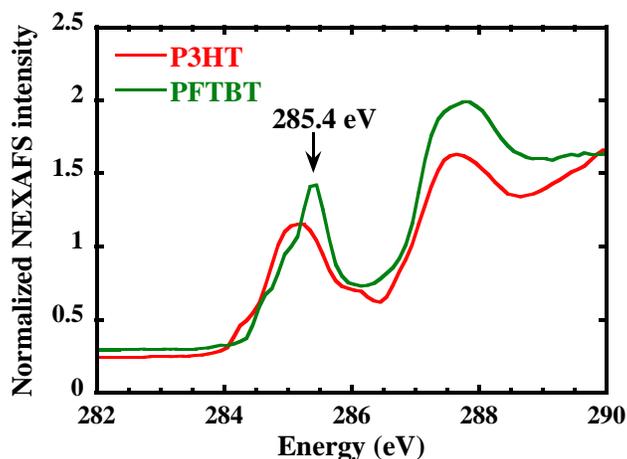


Figure S2. NEXAFS absorption spectra of neat P3HT and PFTBT films. NEXAFS spectra are normalized to 1 at 320 eV to account for thickness variations. Significant contrast is observed at 285.4 eV, where the X-ray absorption of P3HT and PFTBT differ.

3. Morphological characterization through RSOXS and GISAXS

Figure S3 presents resonant soft X-ray scattering (RSOXS) profiles of P3HT/PFTBT and P3HT-*b*-PFTBT thin films at various annealing conditions. RSOXS experiments were carried out at beamline 11.0.1.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory.¹ The X-ray energy was 285.4 eV, such that the absorption contrast between P3HT and PFTBT is significant (Figure S2). Scattering intensities are offset for clarity. Figure S3a shows the RSOXS scattering data as I vs q , where I is the scattering intensity and q is the scattering vector. Figure S3b shows the data as Kratky plots of Iq^2 vs q .

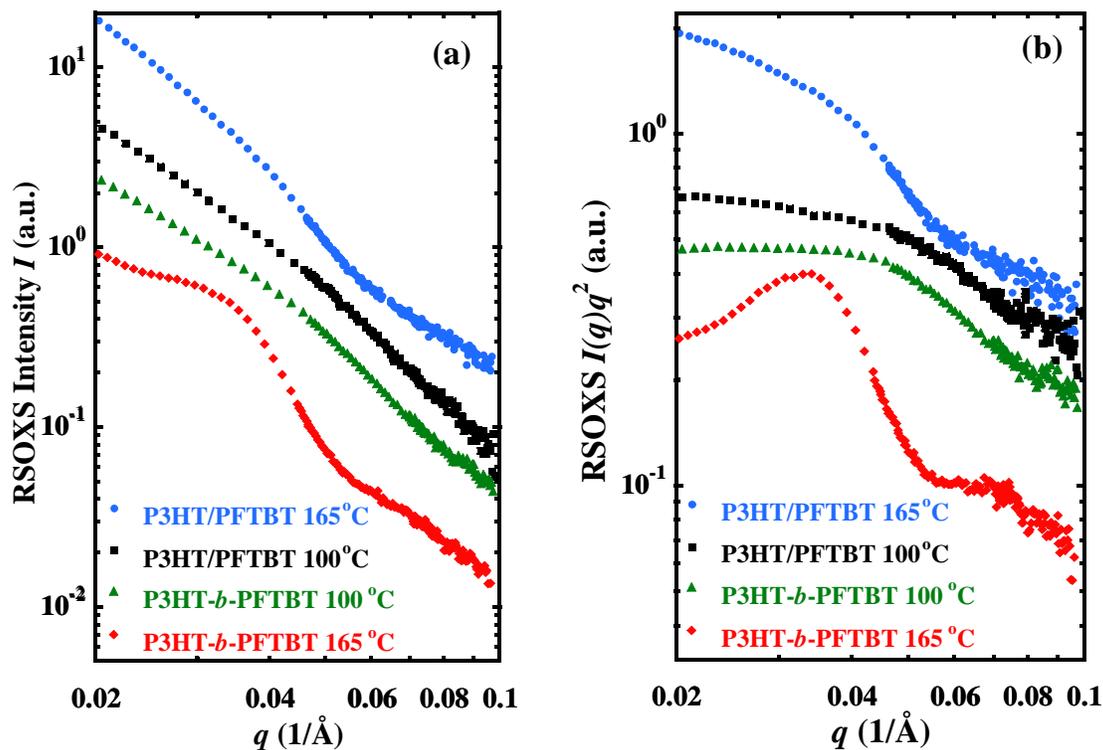


Figure S3. RSOXS intensities of P3HT-*b*-PFTBT and P3HT/PFTBT thin films under various processing conditions. (a) I vs q and (b) Iq^2 vs q . Profiles are offset for clarity. Scattering data were acquired at 285.4 eV, azimuthally integrated, and presented as both I vs q and a Kratky plot of $I(q)q^2$ vs q .

The broad peak or shoulder in the RSOXS data for blends or the block copolymer annealed at 100 °C is similar to the scattering data obtained from P3HT mixtures with fullerene derivatives,² suggesting that this scattering feature corresponds to the spacing between P3HT fibrils. Annealing blends at 165 °C instead of 100 °C leads to a shift in the scattering to lower q suggesting that the microstructure coarsens upon annealing. In contrast, a well-defined primary peak at 0.035 \AA^{-1} and its second-order reflection are identified only in block copolymer films annealed at 165 °C, suggesting the existence of alternating lamellar microdomains on a length scale of around 10 nm.

Grazing-incidence small-angle X-ray scattering (GISAXS) experiments were performed to characterize the morphology in block copolymer thin films annealed at 165 °C, as shown in Figure S4. GISAXS measurements were carried out at Beamline 8-ID-E of the Advanced Photon Source, Argonne National Laboratory ($\lambda = 1.6868 \text{ \AA}$).³ Scattering data were acquired at an incident angle of 0.2°. Using the GIXSGUI package⁴ for Matlab (Mathworks), data were corrected for X-ray polarization, detector sensitivity and geometrical solid-angle. A line cut along the in-plane direction was used to present scattering data as a function of the in-plane scattering vector, q_y . The GISAXS data clearly show that a periodic structure is present with an average domain spacing of around 16 nm, consistent with RSOXS results (Figure 2 of the main text and Figure S3). No such structure is evident from the out-of-plane GISAXS scattering data (data not shown).

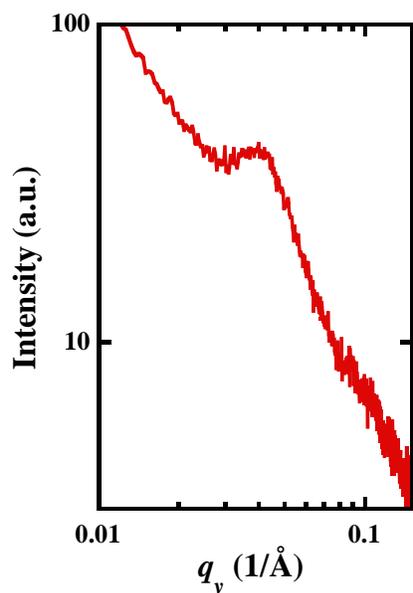


Figure S4. GISAXS intensities vs scattering vector, q_y , for a P3HT-*b*-PFTBT film annealed at 165 °C.

4. Synthesis of block copolymers

P3HT-*b*-PFTBT block copolymers were synthesized using a procedure similar to that previously described.⁵ Briefly, Br end capped P3HT ($M_w = 16.1$ kg/mol, polydispersity = 1.12, 685 mg, 0.042 mmol), 9',9'-dioctylfluorene-2',7'-diboronic acid ester (455 mg, 0.82 mmol), 4,7-bis-2'-(5'-bromo)-thienyl-2',1',3',- benzothiadiazole) (309 mg, 0.68 mmol), tetrakis-(triphenylphosphine)-palladium(0) (38 mg, 0.033 mmol), 5 mL of tetraethyl ammonium hydroxide (20% in H₂O) and aliquat 336 (3 drops) were added to a Schlenk tube loaded with nitrogen-purged toluene (25 mL). The flask was purged with three freeze-pump-thaw cycles, backfilled with nitrogen, and stirred overnight at 90 °C. Next, 5mL bromobenzene was added and stirred at 90°C for 1 h before cooling the reaction mixture. The polymer was precipitated in cold methanol and collected by filtration. The powder was then loaded into a Soxhlet thimble and washed with acetone, hexanes, and then chloroform to recover the polymer. The yield of block copolymer was 740 mg ($M_w = 28.5$ kg/mol, polydispersity = 1.3).

Polymer molecular weights and polydispersities (PDIs) were obtained by size-exclusion chromatography (SEC) as described in the next section. Refractive index (RI) SEC analyses for the P3HT macroreagent and the final P3HT-*b*-PFTBT are shown in Figure S5.

5. Size-exclusion chromatography

Polymer molecular weights and polydispersities (PDIs) were obtained by size-exclusion chromatography (SEC) using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10 000 Å pore sizes), an Agilent variable wavelength UV/visible detector, and a Wyatt Technology Optilab reX RI detector. Tetrahydrofuran was used as the mobile phase

at a flow rate of 1 mL/min at 40 °C. Weight average molecular weights (M_w) and polydispersities (PDIs) are determined relative to a set of monodisperse polystyrene standards (Astra Software Version 5.3.4). SEC-RI analysis for the P3HT macroreagent and the final P3HT-*b*-PFTBT is shown in Figure S5. Deconvolution of the constituent peaks in the block copolymer trace reveals 14 wt% of P3HT homopolymer impurities.

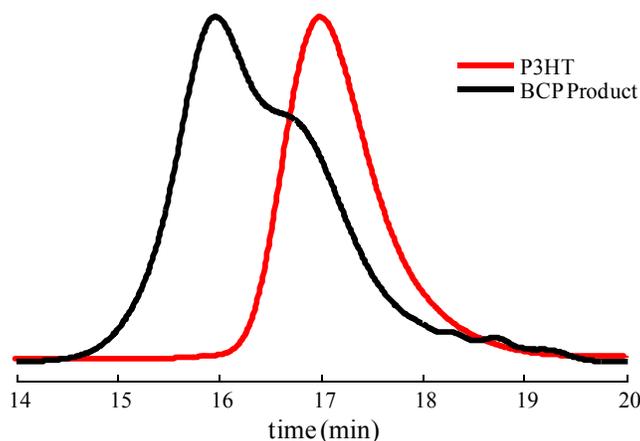


Figure S5. Size-Exclusion Chromatography (SEC) analysis of P3HT macroreagent and final block copolymer product. SEC analysis shows a clear shift of the molecular weight distribution for the final P3HT-*b*-PFTBT block copolymer compared with the starting P3HT macroreagent. The shoulder in the molecular weight distribution at long times indicates that some residual P3HT macroreagent is present (14 wt %).

6. References

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