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Electronic Supplementary Information

For

A Donor–Acceptor Semiconducting Polymer with a Random Configuration for Efficient, Green-Solvent-Processable Flexible Solar Cells

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Experimental details

Materials

All chemicals were purchased from Sigma-Aldrich and used without purification except tetrahydrofuran (THF) which was purified using J.C. Meyer solvent dispensing system.

Characterization

The synthesized compounds were characterized using ^{1}H NMR spectra obtained using a Bruker DPX-400 NMR Spectrometer and ^{13}C, ^{19}F NMR spectra obtained using Bruker AvanceⅢ-500 NMR Spectrometer. Elemental analyses were recorded on a Vario ELⅢ element analysis with 20 mg samples. Number-average (M_n) molecular weights were determined by a size exclusion chromatography (SEC) with SHIMADZU LC solution with chloroform eluent using a calibration curve of polystyrene standards. The UV-Vis absorption spectra were measured with a Mecasys Optizen Pop UV/Vis spectrophotometer. Thermogravimetric analysis (TGA) was performed under argon atmosphere at a heating rate of 10 ^{o}C/min with TGA Q500 instrument. Differential scanning calorimetry (DSC) was performed under a nitrogen atmosphere at a heating rate of 10 ^{o}C/min with a Dupont 9900 analyzer. Cyclic voltammetry (CV) was performed using a PowerLab/AD instrument model system in 0.1 M solution of tetrabutylammonium hexafluorophospate (Bu_4NPF_6) in anhydrous acetonitrile as supporting electrolyte at a scan rate of 50 mVs^{-1}. A glassy carbon disk (~0.05 cm^{2}) coated with a thin polymer film, an Ag/$AgNO_3$ electrode, and a platinum wire were used as working electrode, reference electrode, and counter electrode, respectively. Film thickness was measured using P-6 stylus profiler. The atomic force microscope (AFM) (Multimode IIIa, Digital Instruments) was operated in tapping mode to acquire images of the surfaces of blend and neat films. Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were carried out using a synchrotron radiation on the beam line 3C at the Pohang Accelerator Laboratory (PAL), Pohang, Korea.

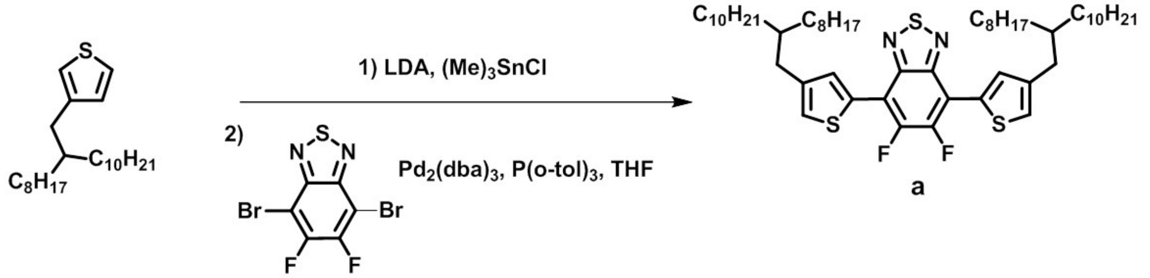
Solar cell fabrication and measurement

The device structure was designed as inverted structure of ITO/ZnO/polymer:$PC_{71}BM$/MoO_3/Ag. We fabricated the device as follow. The ITO-coated glass substrates were cleaned with distilled water, acetone, and isopropyl alcohol with ultra-sonication, sequentially, and dried in oven over 12 hours. Zinc oxide was prepared by a solution of diethylzinc (5 wt%) dissolved in a 1:2 mixture of THF. The zinc oxide film was spin-casted at 3000 rpm for 30 sec on top of ITO, and annealed at 110 °C for 15 min in air condition. For active layer, the solution (18 mg ml^{-1}) was prepared with mixture of polymer:$PC_{71}BM$ with 1:0.8 weight ratio either in DCB with DIO (3 vol%) or in 2MA.

Active layers were spin-casted with 1000 rpm on top of zinc oxide layer in nitrogen filled glove box. The PffBT-T4:$PC_{71}BM$-DCB, PffBT-RT4:$PC_{71}BM$-DCB, PffBT-RT4:$PC_{71}BM$-2MA film thickness is 400-450 nm. After transferring samples into thermal evaporator, the molybdenum oxide (5 nm) and silver (80 nm) were deposited, subsequently, on top of active layer under vacuum ($<10^{-6}$ Torr). The area of the silver electrode was defined as 3.67 mm^2. The measurement was carried out inside nitrogen filled glove box, using high quality optical fiber guide simulated 100 mW cm^{-2} AM 1.5G light from xenon arc lamp with a Keithley 2635A source measurement unit. EQE measurement was calculated using a Model QEX7 system (PV Measurements Inc.) under ambient conditions.

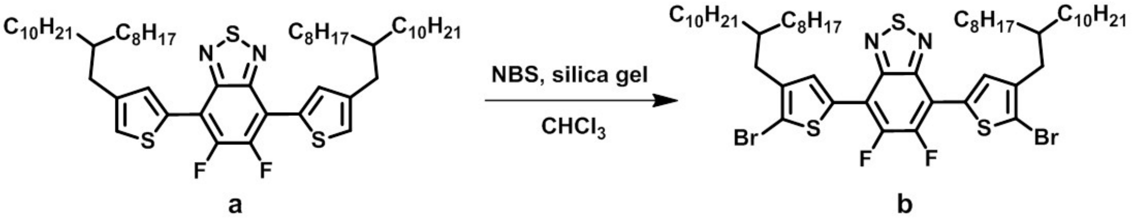
Synthesis

Synthesis of 5,6-Difluoro-4,7-bis(4-(2-octyldodecyl)-2-thienyl)-2,1,3-benzothiadiazole (a)



A solution of 3-(2-octyldodecyl)thiophene (2.00g, 5.48 mmol) in 15 mL THF was cooled to -78 °C under N_2. A solution of lithium diisopropylamide (LDA, 2 M, 2.74 mL, 5.48 mmol) was added dropwise and the mixture was stirred for 1 h at -78 °C followed by stirring for additional 1 h at 0 °C. Then, the mixture was cooled again to -78 °C and Bu_3SnCl (2.14 g, 6.58 mmol) was added in one portion. The mixture was stirred overnight at room temperature. To the mixture an aqueous potassium chloride solution was added. The mixture was washed with distilled water, then dried by $MgSO_4$. The solvent was removed by evaporation under reduced pressure to give yellow oil. To this product, 4,7-dibromo-5,6-difluoro-2,1,3-benzothiadiazole (300mg, 1.0 mmol), $Pd_2(dba)_3$ (10 mg, 0.01 mmol), and P(*o*-tol)$_3$ (12 mg, 0.04 mmol) in 10 mL THF were added and the mixture was refluxed overnight under N_2. The reaction mixture was then cooled to room temperature and the solvent was removed by evaporation. The residue was purified by flash column chromatography (eluent: *n*-hexane) to give the product (**a**) as a yellow solid (0.78 g, 78%).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10 (s, 2H), 7.20 (s, 2H), 2.64(d, 4H), 1.77 – 1.62 (m, 2H), 1.42 – 1.14 (m, 64H), 0.97 – 0.84 (m, 12H).
^{19}F NMR (500 MHz, $CDCl_3$, ppm) δ -128.23 (s, 2F).
^{13}C NMR (500 MHz, $CDCl_3$, ppm) δ 149.70 (dd), 148.94 (t), 143.05, 133.00 (t), 140.06, 124.90, 112.00 (dd), 39.10, 35.00, 33.34, 32.01, 30.05, 29.68, 29.67, 29.40, 26.67, 22.70, 14.12.

Synthesis of 5,6-Difluoro-4,7-bis(5-bromo-4-(2-octyldodecyl)-2-thienyl)-2,1,3-benzothiadiazole (b)



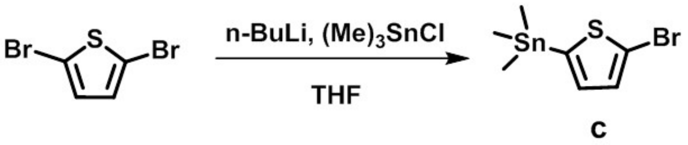
N-Bromosuccinimide (605 mg, 3.40 mmol) was added to a mixture of **a** (1.5 g, 1.67 mmol) and silica gel (20 mg) in 20 mL chloroform at 0 °C. The reaction mixture was warmed to room temperature and then stirred overnight. The reaction mixture was washed with distilled water, the organic layer was dried with $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The residue was purified with flash column chromatography (eluent: *n*-hexane) to give the product (d) as a orange solid (1.3 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.94 (s, 2H), 2.60 (d, 4H), 1.80 – 1.70 (m, 2H), 1.40 – 1.15 (m, 64H), 0.90 – 0.77 (m, 12H).

^{19}F NMR (500 MHz, $CDCl_3$, ppm) δ -128.10 (s, 2F).

^{13}C NMR (500 MHz, $CDCl_3$, ppm) δ 149.54 (dd), 148.26, 141.70, 132.25, 130.99, 124.83, 115.13 (t,), 110.85 (dd), 38.53, 34.08, 33.35, 31.94, 30.05, 29.73, 29.69, 29.67, 29.39, 26.56, 22.71, 14.13.

Synthesis of (5-bromothiophen-2-yl)trimethylstannane (c)

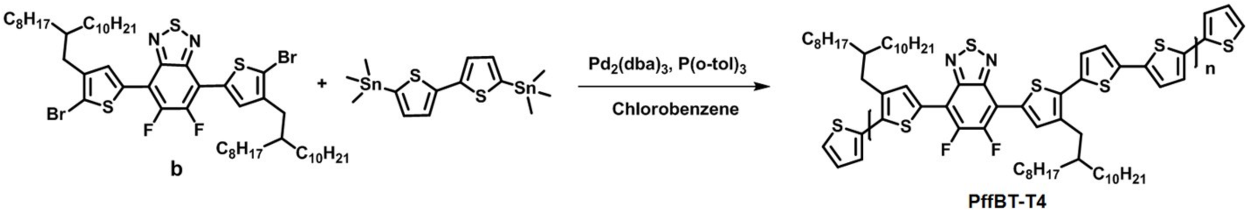


A solution of 2,5-dibromothiophene (2.00g, 8.27 mmol) in 20 mL THF was cooled to -78 °C under N_2. A solution of n-Butyllithium (2.5M in hexane, 5.30 mL, 8.27 mmol) was added into the solution dropwise and the mixture was stirred for 1 h at -78 °C followed by stirring for 30 min at 25 °C. The mixture was cooled to -78 °C and trimethyltin chloride (9.93 ml, 9.93 mmol) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The mixture was extracted with chloroform, and then washed with distilled water. The organic layer was dried with $MgSO_4$. The solvent was removed by evaporation under reduced pressure, and then the product (**c**) was obtained.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.13 (d, 1H), 6.95 (d, 1H), 0.37 (s, 9H)

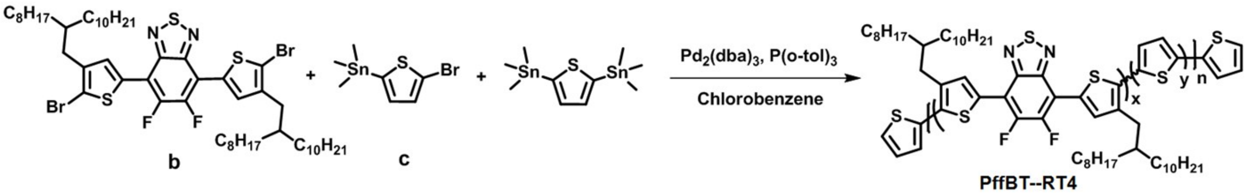
^{13}C NMR (500 MHz, $CDCl_3$, ppm) δ 140.5(s), 135.8(s), 131.0(s), 116.5(s), -4.75 (s, 3C)

Polymerization of PffBT-T4



A 30 ml microwave vial was charged with **b** (200 mg, 0.19 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (93.2 mg, 0.19 mmol), $Pd_2(dba)_3$ (10 mg, 0.01 mmol), P(*o*-tol)$_3$ (12 mg, 0.04 mmol) and chlorobenzene (2 ml) in a glove box protected with N_2. The vial was sealed and heated with stirring at 200 °C for 2 h in a microwave reactor. After precipitation in methanol, polymer was purified by Soxhlet extraction in acetone, dichloromethane, and chloroform. The polymer was collected from chlorobenzene. The chlorobenzene solution was then concentrated by evaporation. Then the polymer was reprecipitated in methanol and dried in vacuum oven for 24 h at an ambient temperature. Finally, the polymer was obtained as a dark green solid (150 mg, 70%).

Polymerization of PffBT-RT4



A 30 ml microwave vial was charged with **b** (211 mg, 0.2 mmol), **c** (65.2 mg, 0.2 mmol), 2,5-bis(trimethylstannyl)thiophene (82.4 mg, 0.2 mmol), $Pd_2(dba)_3$ (10 mg, 0.01 mmol) and P(*o*-tol)$_3$ (12 mg, 0.04 mmol), and chlorobenzene (2 ml) in a glove box protected with N_2. The vial was sealed and heated with stirring at 200 °C for 2 h in a microwave reactor. After precipitation in methanol, polymer was purified by Soxhlet extraction in acetone, dichloromethane, and chloroform. The polymer was collected from chlorobenzene. The chlorobenzene solution was then concentrated by evaporation. Then the polymer was reprecipitated in methanol and dried in vacuum oven for 24 h at an ambient temperature. Finally, the polymer was obtained as a dark green solid (130 mg, 65%).

Fig. S1 GPC profiles of PffBT-T4 and PffBT-RT4.

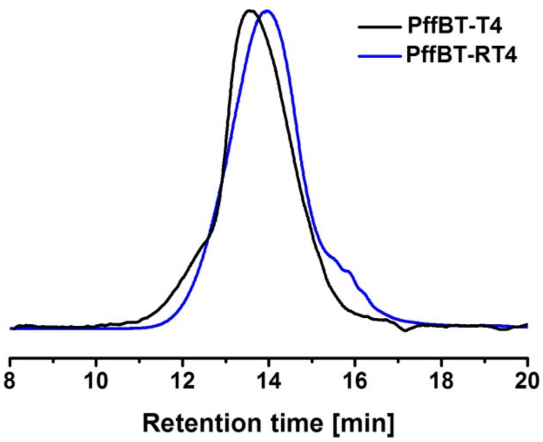


Fig. S2 ^{1}H NMR spectrum of PffBT-T4.

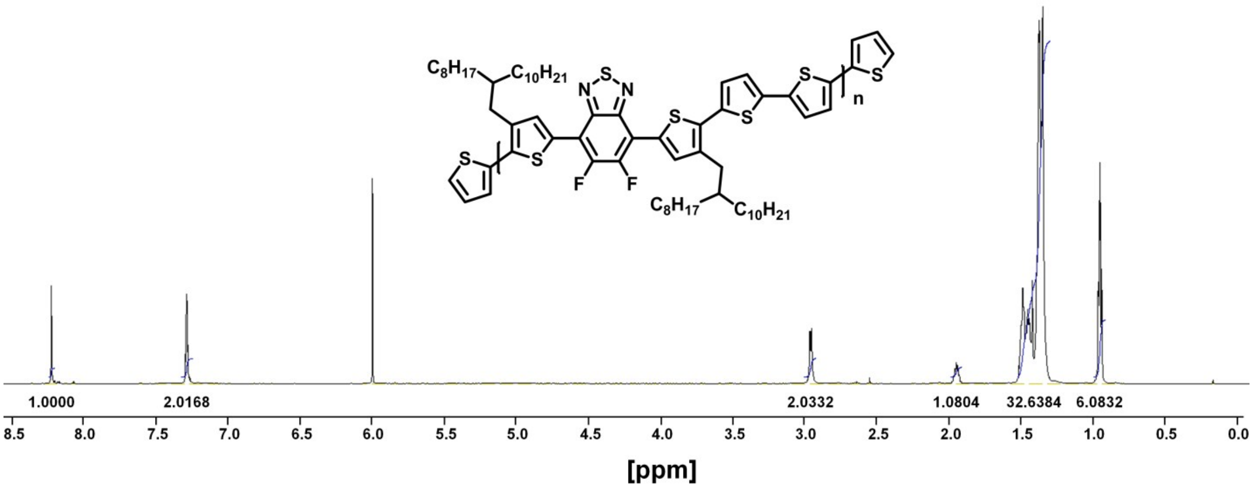


Fig. S3 ^{1}H NMR spectrum of PffBT-RT4.

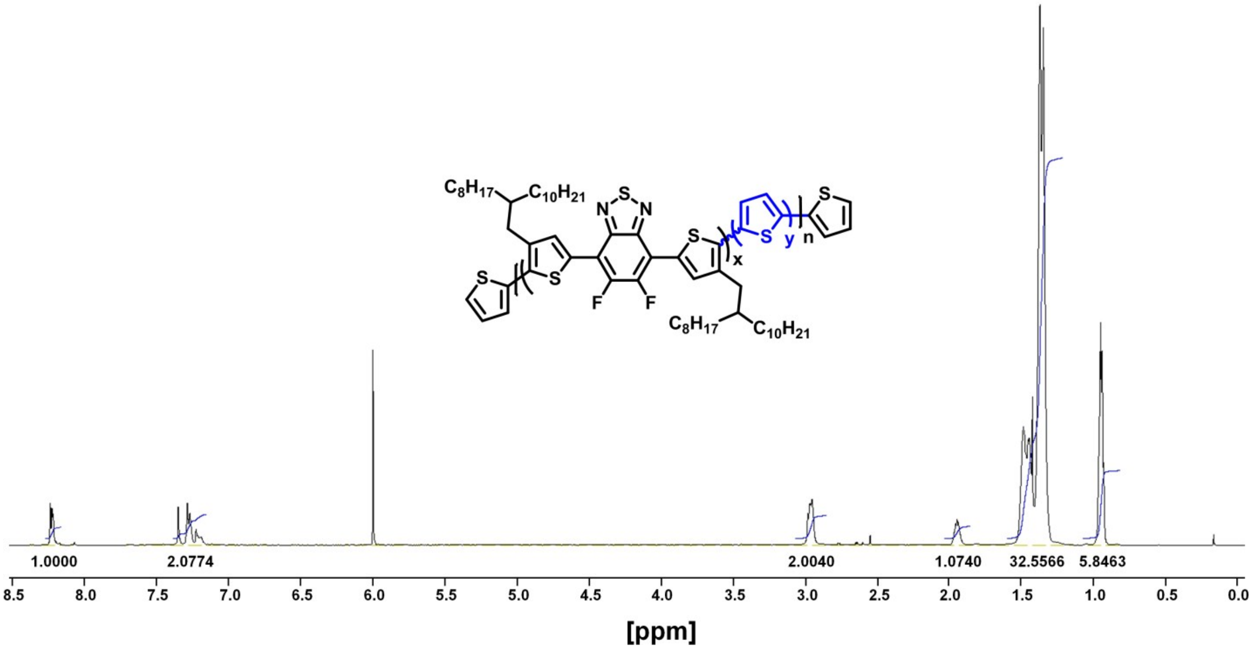


Fig. S4 GPC profiles of PffBT-RT4(#2), (#3), and (#4).

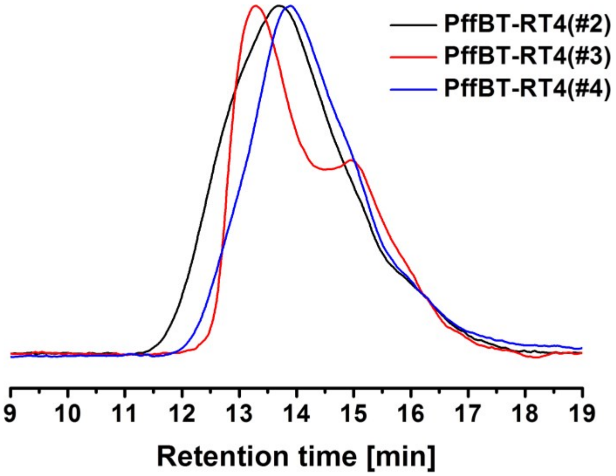


Fig. S5 ^{1}H NMR spectra of PffBT-RT4(#2), (#3), and (#4) between 7.0 and 8.5 ppm.

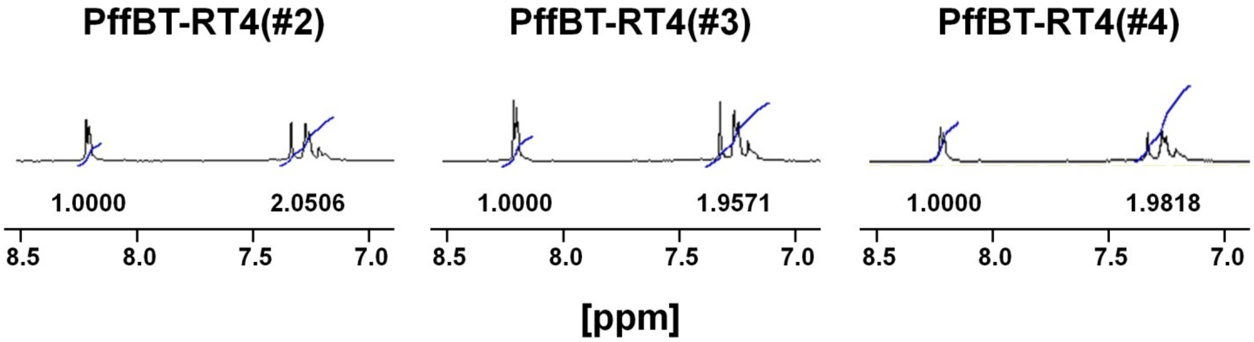


Fig. S6 TGA thermograms of PffBT-T4 and PffBT-RT4.

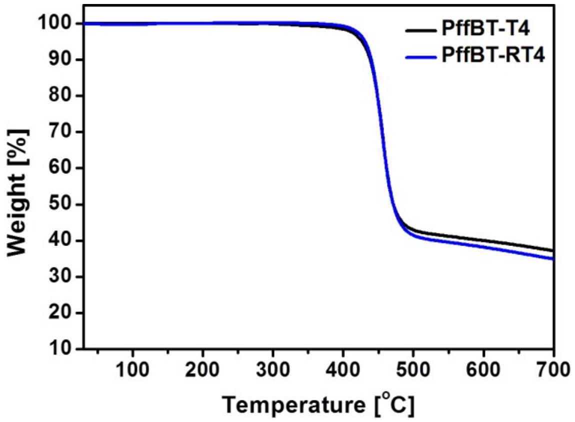


Fig. S7 DSC heat-only thermograms of PffBT-T4:PC$_{71}$BM and PffBT-RT4:PC$_{71}$BM blends.

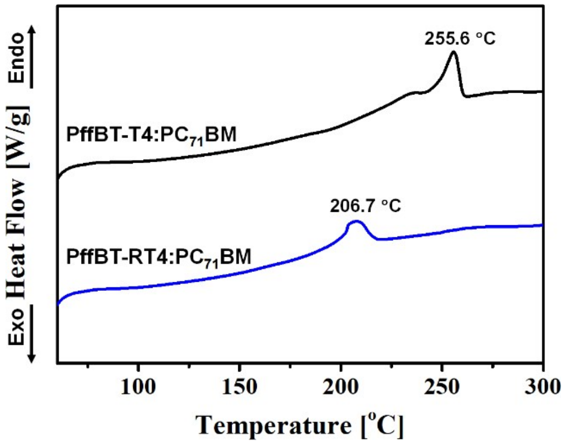


Fig. S8 Tapping mode AFM height images of PffBT-T4 and PffBT-RT4 films.

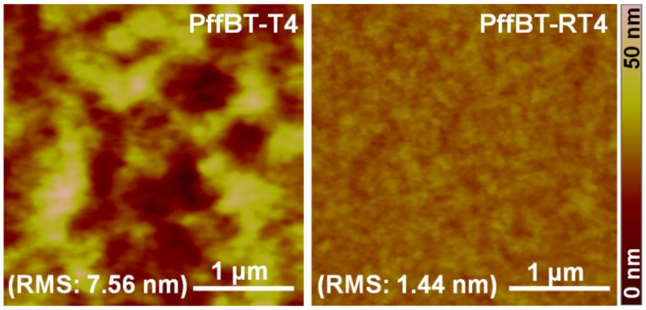


Fig. S9 Cyclic voltammograms of PffBT-T4 and PffBT-RT4.

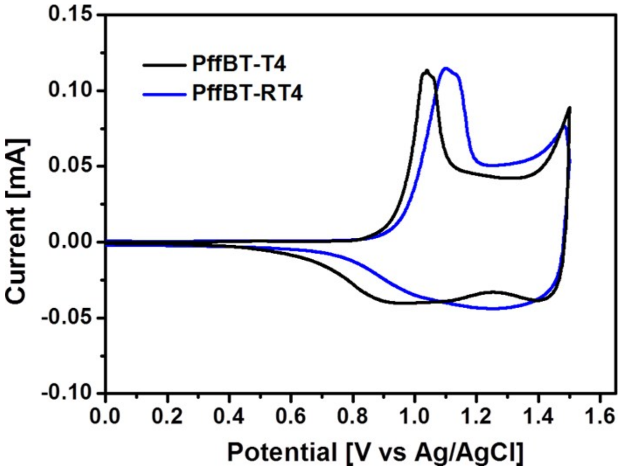


Fig. S10 Normalized UV-vis absorption spectra of PffBT-T4 and PffBT-RT4 solutions in 2MA.

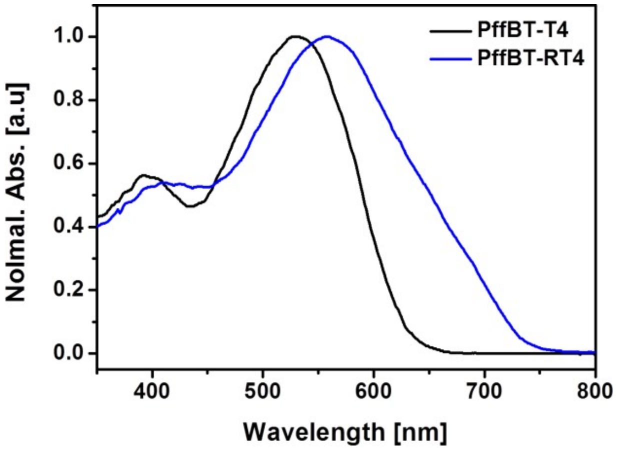


Fig. S11 Normalized UV-vis absorption spectra of PffBT-RT4 films coated using 2MA and DCB, respectively.

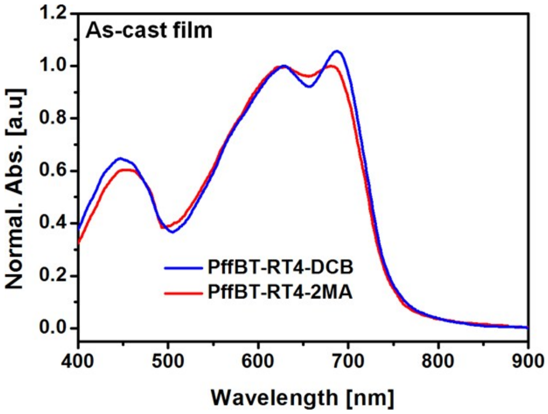


Fig. S12 *J–V* curves of PffBT-RT4(#2), (#3), and (#4) PSCs. The PSCs were prepared using the identical conditions as PffBT-RT4:PC$_{71}$BM-DCB.

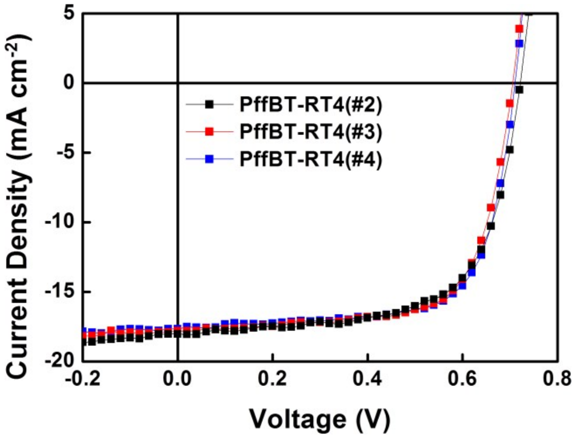


Fig. S13 GIWAXS patterns of neat polymer films.

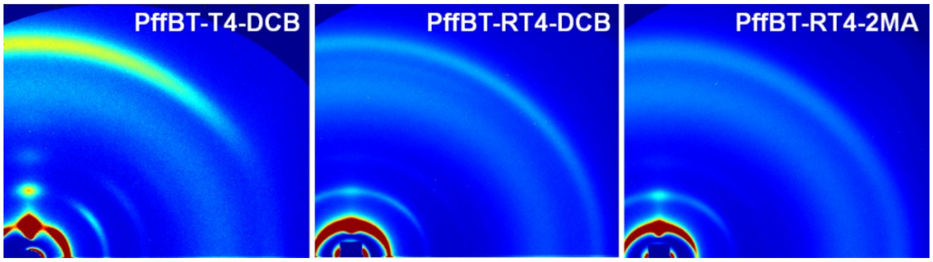


Fig. S14 Out-of-plane and in-plane GIWAXS spectra of neat polymer and blend films of PffBT-T4-DCB, PffBT-RT4-DCB and PffBT-RT4-2MA.

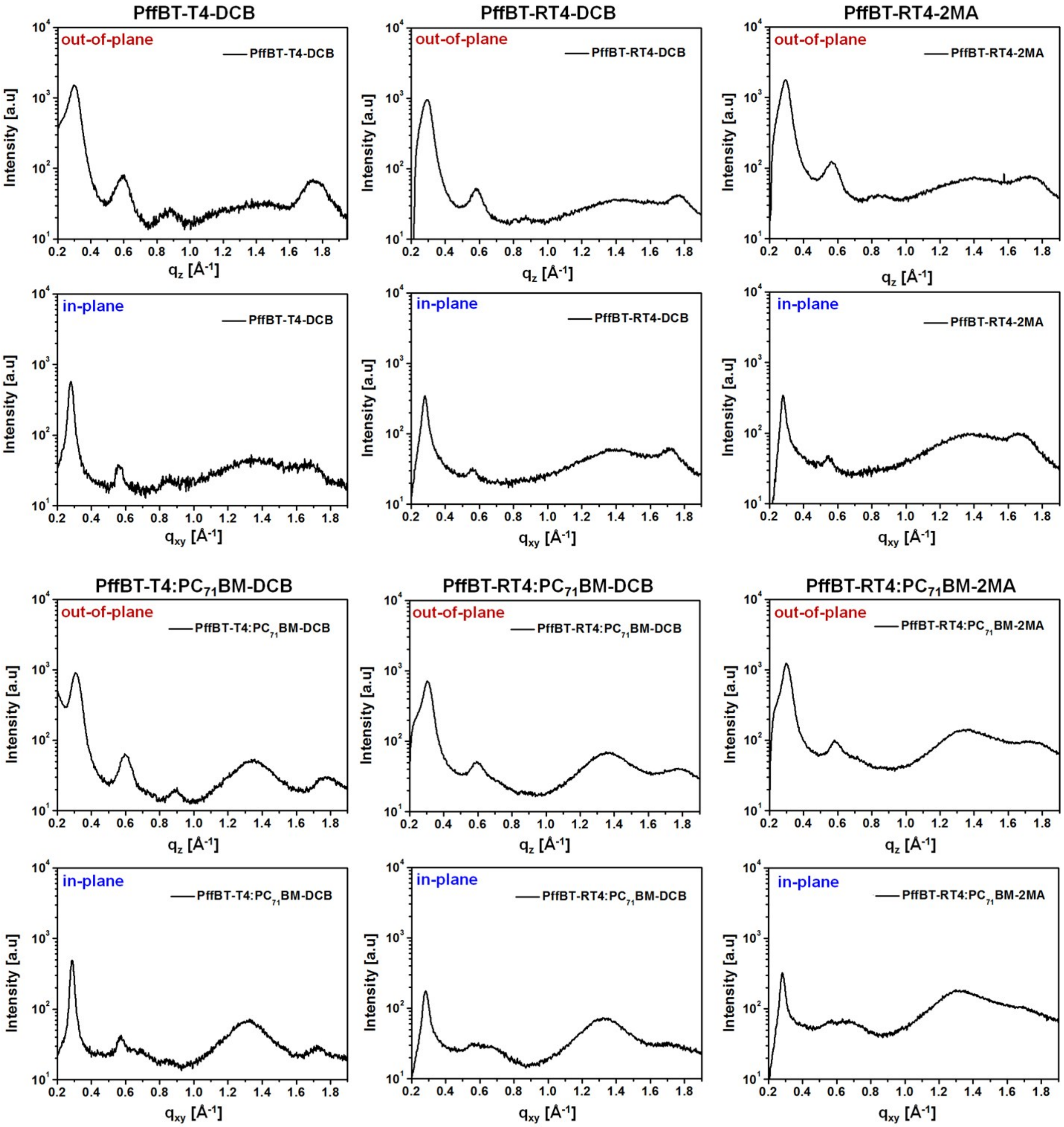


Table S1 Polymerization information PffBT-RT4(#2), (#3), and (#4) and photovoltaic performance of corresponding PSCs.

Polymer	Polymerization information		Photovoltaic performance			
	M_n (kg/mol)	PDI	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
PffBT-RT4(#2)	27.2	2.86	18.04	0.72	0.66	8.53
PffBT-RT4(#3)	26.4	2.67	17.80	0.71	0.69	8.71
PffBT-RT4(#4)	25.5	2.4	17.67	0.71	0.70	8.78

Table S2 Lamellar packing and π-π stacking distances of neat polymer films.

Polymer	Lamellar packing distance[a] [Å]		π-π stacking distance[a] [Å]	
	out-of-plane	in-plane	out-of-plane	in-plane
PffBT-T4-DCB	21.16	22.52	3.64	3.75
PffBT-RT4-DCB	21.3	22.36	3.55	3.65
PffBT-RT4-2MA	21.3	22.44	3.63	3.75

[a] Calculated using distance = 2π/q. The q values were obtained from the GIWAXS spectra.