Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Straight Chain D-A Copolymers Based on Thienothiophene and Benzothiadiazole for Efficient Polymer Field Effect Transistors and Photovoltaic Cells

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Synthesis and characterization

All chemical reagents were purchased from Aldrich, Tokyo Chemical Industry, Junsei Chemical and used without further purification. The compound, 2-(tributylstannyl)thieno[3,2-b]thiophene, 1,4-bis(decyltetradecyloxy)benzene and benzothiadiazole (BT)-based monomers were synthesized according to previously described methods.[1, 2]

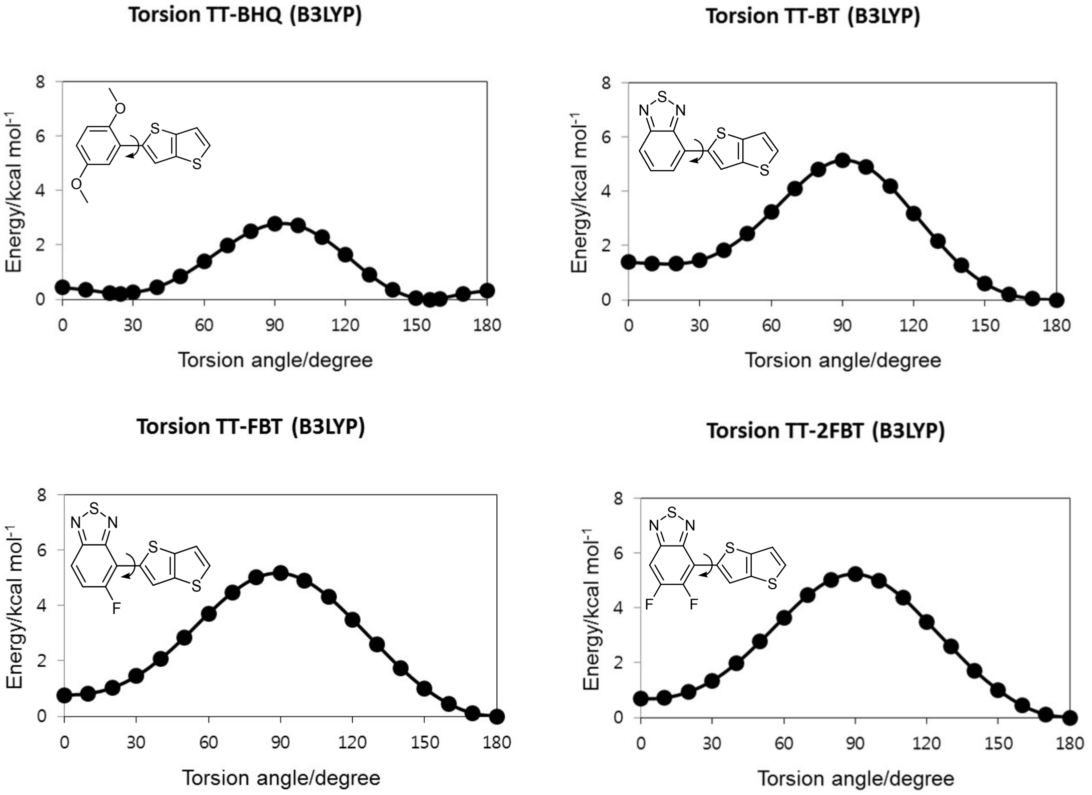
1,4-Bisthieno[3,2-b]thiophene-2,5-bis(decyltetradecyloxy)benzene (3). Compound 1 (1.0 g, 1.06 mmol), 2-tributylstannylthieno[3,2-b]thiophene (1.10 g, 2.4 equiv.), tris(dibenzylideneacetone)dipalladium(0) (4 mol%) and tri(*o*-tolyl)phosphine (8 mol%) were added in a 30 mL microwave vial. The vial was purged with nitrogen for 0.5 h and sealed. Anhydrous toluene (12 mL) was added to the vial and the reaction mixture was heated stepwise, at 80 °C for 5 min, 100 °C for 5 min, 130 °C for 45 min and at 150 °C for 60 min in a microwave reactor. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by column chromatography with hexane/dichloromethane (DCM) = 6:1 (v/v) as eluent to provide a yellow solid. Yield: 0.86 g (76.2%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.73 (s, 2H), 7.36 (d, J = 5.1 Hz, 2H), 7.25 (d, J = 6.3 Hz, 2H), 7.21 (s, 2H), 3.97 (d, J = 5.1 Hz, 4H), 1.90 (m, 2H), 1.24 (m, 80H), 0.88 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 149.6, 141.6, 139.5, 139.3, 126.8, 123.4, 119.4, 117.9, 112.7, 72.4, 38.1, 31.9, 31.5, 30.0, 29.7, 29.6, 29.4, 26.9, 22.7, 14.1. Elemental analysis. Calcd. for ($C_{66}H_{106}O_2S_4$): C, 74.80; H, 10.08; S, 12.10. Found: C, 74.80; H, 10.23; S, 11.43.

1,4-Bis(5-trimethylstannylthieno[3,2-b]thiophene-2-yl)-2,5-bis(decyltetradecyloxy)benzene (M1). To a solution of compound 3 (1.5 g, 1.42 mmol) in dry THF (50 mL) was added a 2.5 M solution of n-BuLi in hexane (1.3 mL, 2.3 equiv.) dropwise at -78 °C. After stirring at -78 °C for 1.5 h, 1.0 M solution of trimethylstannyl chloride in THF (3.54 mL, 2.5 equiv.) was introduced by syringe to the solution. The reaction mixture was warmed up to room temperature and stirred for overnight. The reaction mixture was extracted with diethyl ether and washed with water three times. The combined organic extracts were dried with anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The product was obtained by recrystallization from hot methanol. Yield: 1.60 g (81.6%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.71 (s, 2H), 7.26 (s, 2H), 7.22 (s, 2H), 3.97 (d, J = 5.1 Hz, 4H), 1.87 (m, 2H), 1.22 (m, 80H), 0.85 (m, 12H), 0.39 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 149.6, 145.1, 141.6, 141.4, 140.8, 126.5, 123.5, 117.5, 112.6, 72.3, 38.1, 31.9, 31.5, 30.0, 29.7, 29.6, 29.4, 26.9, 22.7, 14.1. Elemental analysis. Calcd. for ($C_{72}H_{122}O_2S_4Sn_2$): C, 64.42; H, 8.88; S, 9.26. Found: C, 62.94; H, 9.21; S, 9.41.

Poly[2,5-bis(decyltetradecyloxy)benzene-*alt*-4,7-bis(thieno[3,2-b]thiophene)-2,1,3-benzothiadiazole] (PPDTTBT). In a N_2 filled glove box, M1 (0.20 g, 0.144 mmol), M2 (42.4 mg, 1.0 equiv.), tris(dibenzylideneacetone)dipalladium(0) (2 mol%), tri(*o*-tolyl)phosphine (8 mol%) and anhydrous toluene (1.5 mL) were added in a 5 mL microwave vial. The reaction mixture was heated stepwise, at 80 °C for 5 min, 100 °C for 5 min, 130 °C for 45 min and 150 °C for 60 min in a microwave reactor. The polymer was end-capped by addition of 2-tributylstannylthiophene (0.1 equiv.) and the mixture was further reacted at 145 °C for 20 min. The reaction solution was cooled down and 2-bromothiophene (0.2 equiv.) was added by a syringe and the solution was heated at 140 °C for another 20 min. After the reaction was finished, the crude polymer was precipitated into 300 mL methanol, filtered and further purified by Soxhlet extraction with acetone, hexane and chloroform. The extracted portion with chloroform was precipitated into methanol, filtered and dried under vacuum to afford PPDTTBT (192 mg, yield: 79.2%). Number average molecular weight (M_n) = 61 kDa, polydispersity index (PDI) = 4.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09 (br, 2H), 7.68 (br, 2H), 7.34 (br, 2H), 7.21 (br, 2H), 4.02(br, 4H), 2.03 (br, 2H), 1.54-1.31(br, 80H), 0.85-0.66 (br, 12H).

Poly[2,5-bis(decyltetradecyloxy)benzene-*alt*-4,7-bis(thieno[3,2-b]thiophene)-5-fluoro-2,1,3-benzothiadiazole] (PPDTTFBT). The polymer was prepared similarly as for PPDTTBT. Yield: 72.6%. M_n = 57 kDa, PDI = 3.2. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09-7.21 (br, 7H), 4.02 (br, 4H), 2.03 (br, 2H), 1.54-1.31 (br, 80H), 0.85-0.66 (br, 12H).

Poly[2,5-bis(decyltetradecyloxy)benzene-*alt*-4,7-bis(thieno[3,2-b]thiophene)-5,6-difluoro-2,1,3-benzothiadiazole] (PPDTT2FBT). The polymer was prepared similarly as for PPDTTBT. Yield: 86%. M_n = 67 kDa, PDI = 3.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80-7.21 (br, 6H), 4.02 (br, 4H), 2.03 (br, 2H), 1.54-1.31 (br, 80H), 0.85-0.66 (br, 12H).


Torsion TT-BHQ (B3LYP)

Torsion TT-BT (B3LYP)

Torsion TT-FBT (B3LYP)

Torsion TT-2FBT (B3LYP)

Figure S1. Torsional profiles.

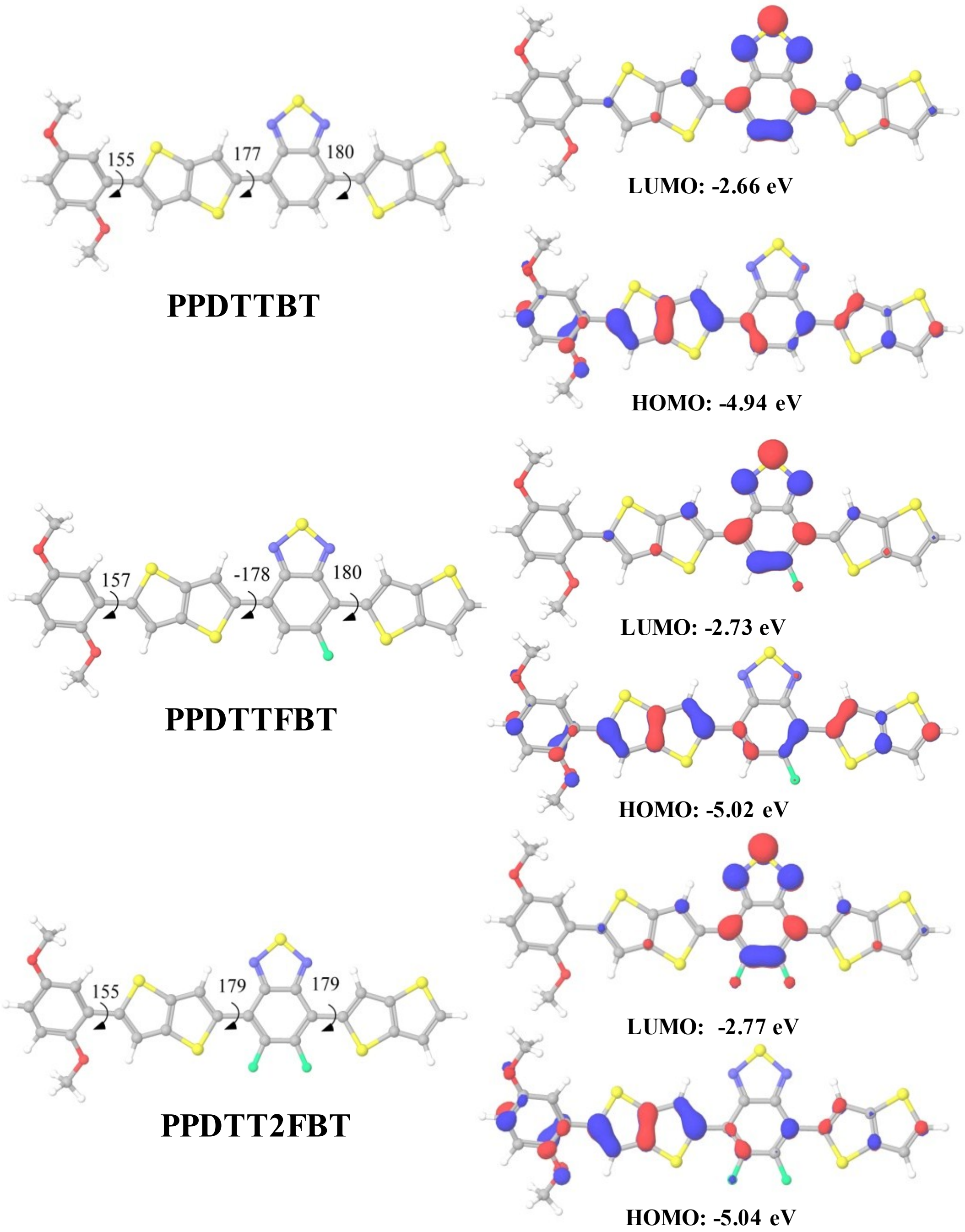


Figure S2. Energy minimum conformations and HOMO/LUMO structures of polymers by DFT calculation (B3LYP/6-31G** level). Alkyl side-chains were replaced with methyl groups for simplifying calculation (yellow, sulfur; red, oxygen; green, fluorine; blue, nitrogen).

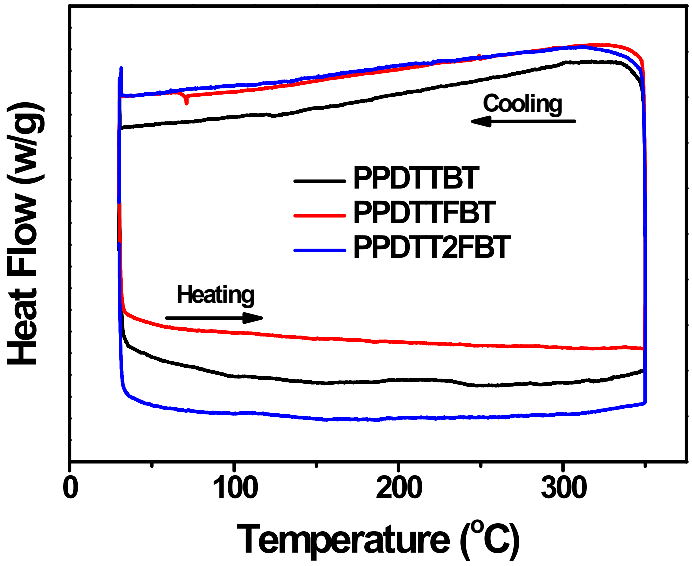


Figure S3. DSC thermograms of PPDTTBT, PPDTTFBT and PPDTT2FBT.

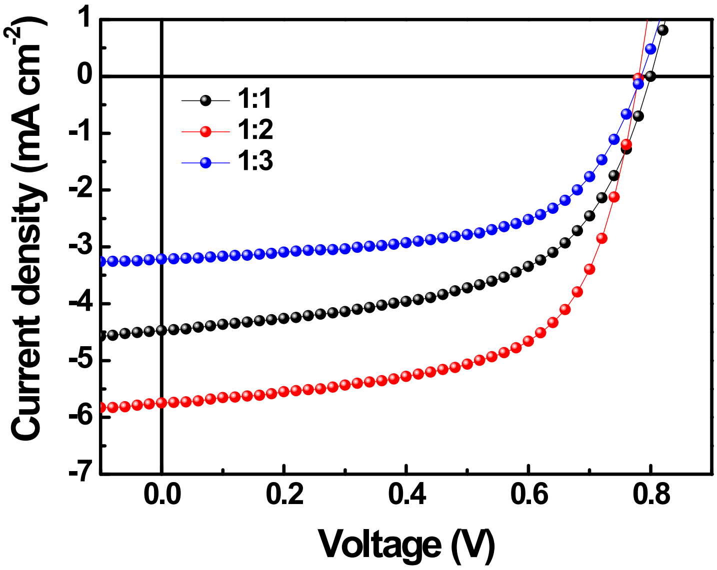


Figure S4. *J*-*V* characteristics for PPDTT2FBT:$PC_{71}BM$ PSCs with different D:A blend ratios.

Table S1. Summary of PFET characteristics by varying thermal annealing temperatures.

Polymer	Thermal annealing [^{o}C]	Mobility [cm^2/Vs]	I_{off} [A]	I_{on} [A]	I_{on}/I_{off}	V_T [V]
PPDTTBT	None	7.76E-04	5.24E-11	8.22E-07	1.57E+04	-11.64
	100	0.014	4.38E-11	1.49E-05	3.40E+05	-10.48
	150	0.020	1.66E-11	2.71E-05	1.63E+06	-4.24
	200	0.025	9.08E-11	3.57E-05	3.94E+05	-3.22
	250	0.028	2.10E-11	4.34E-05	2.07E+06	-0.85
	300	0.021	1.93E-10	3.19E-05	1.66E+05	-0.67
PPDTTFBT	None	8.70E-05	1.33E-11	9.58E-08	7.20E+03	-8.30
	100	0.012	1.07E-11	1.63E-05	1.52E+06	-5.66
	150	0.028	1.44E-11	4.91E-05	3.42E+06	2.53
	200	0.044	8.10E-11	7.45E-05	9.19E+05	2.97
	250	0.050	1.11E-11	8.14E-05	7.30E+06	1.01
	300	0.042	2.90E-11	7.04E-05	2.43E+06	1.58
PPDTT2FBT	None	6.89E-04	8.60E-12	8.11E-07	9.43E+04	-4.12
	100	0.029	3.61E-12	4.61E-05	1.28E+07	1.63
	150	0.052	6.04E-11	8.92E-05	1.48E+06	2.75
	200	0.062	6.99E-11	1.20E-04	1.72E+06	8.00
	250	0.103	5.56E-11	1.35E-04	2.42E+06	7.70
	300	0.046	1.42E-11	1.64E-04	1.16E+07	30.9

Table S2. Summary of photovoltaic parameters for PPDTT2FBT:PC$_{71}$BM with different D:A blend ratios.

D:A ratio	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF*	PCE [%]
1:1	4.47	0.800	0.561	2.01
1:2	5.75	0.781	0.624	2.80
1:3	3.21	0.785	0.600	1.51

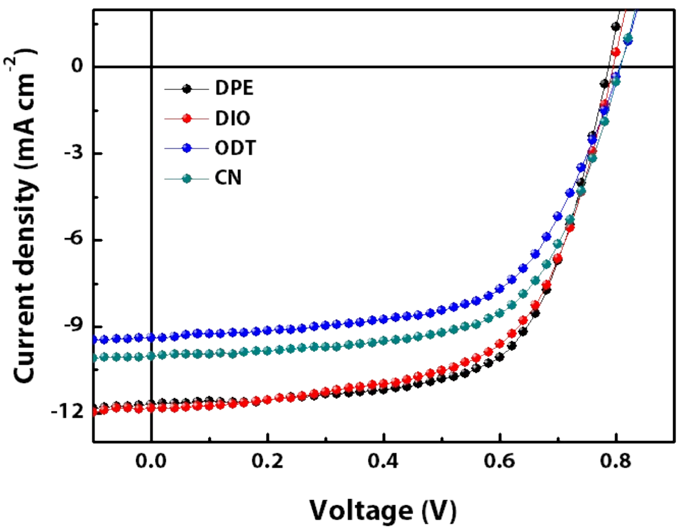


Figure S5. *J-V* characteristics for PPDTT2FBT:PC$_{71}$BM PSCs with different solvent additives.

Table S3. Summary of photovoltaic parameters for PPDTT2FBT:PC$_{71}$BM PSCs with different solvent additives.

Additive (3 vol%)	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF*	PCE [%]
Diphenyl ether (DPE)	13.3	0.742	0.649	6.40
1,8-Diiodooctane (DIO)	11.8	0.795	0.613	5.77
1,8-Octanedithiol (ODT)	9.38	0.806	0.610	4.62
1-Chloronaphthalene (CN)	10.0	0.807	0.632	5.12

Table S4. Photovoltaic characteristics of PPDTTBT, PPDTTFBT, PPDTT2FBT BHJ solar cells without and with DPE.

Polymers	Solvent additive (3vol% DPE)	J_{sc} [mA cm^{-2}]	J_{sc}(Calc.) [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
PPDTTBT	X	3.95	3.80	0.640	0.569	1.44
	O	9.82	9.18	0.605	0.596	3.54
PPDTTFBT	X	4.72	4.43	0.725	0.599	2.05
	O	11.7	10.7	0.705	0.629	5.20
PPDTT2FBT	X	5.75	5.46	0.781	0.624	2.80
	O	13.3	12.5	0.742	0.649	6.40

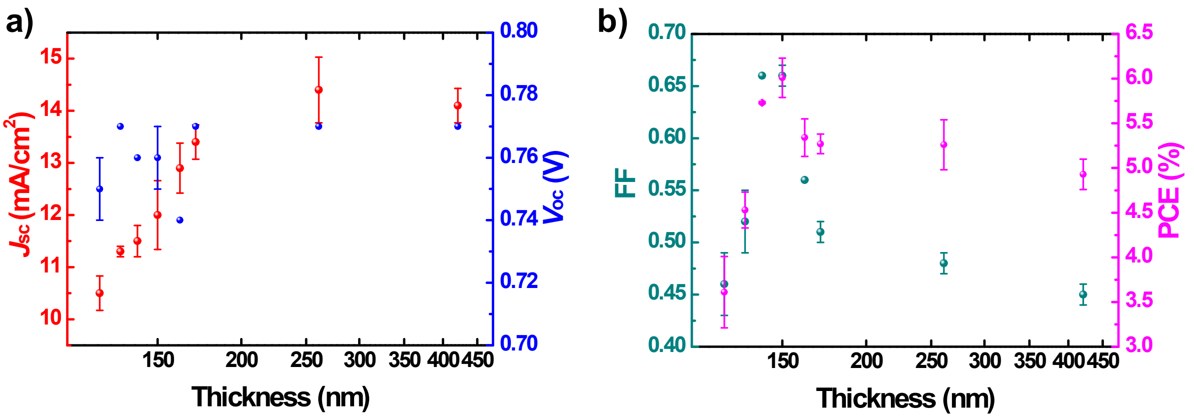


Figure S6. Photovoltaic parameters of PPDTT2FBT:PC$_{71}$BM PSCs as a function of active layer thickness. Dots and error bars indicate averages and standard deviations respectively, calculated based on 10 devices for each condition.

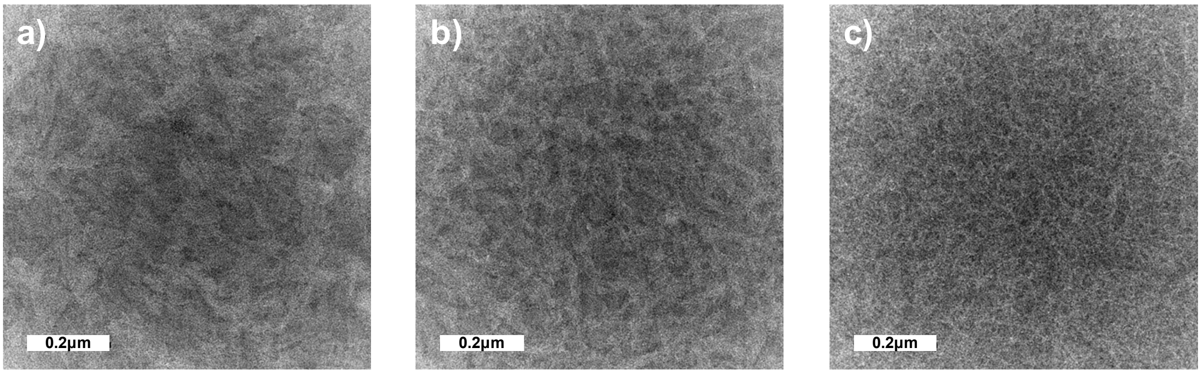


Figure S7. HR-TEM images for (a) PPDTTBT:PC$_{71}$BM, (b) PPDTTFBT:PC$_{71}$BM, and (c) PPDTT2FBT:PC$_{71}$BM BHJ films with DPE.

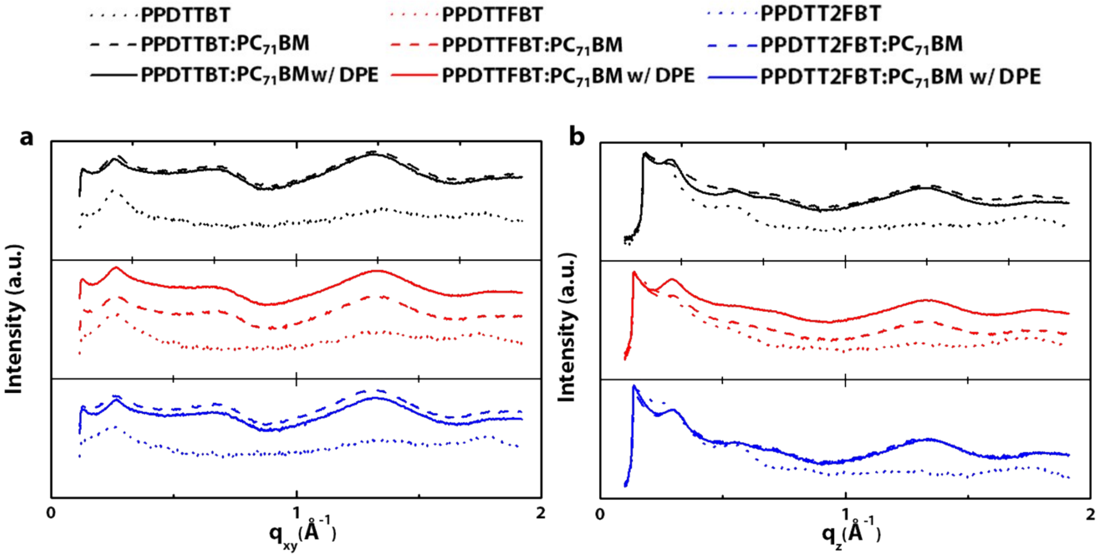


Figure S8. (a) In-plane and (b) out-of-plane GIWAXS line-cut data.

Table S5. Summary of GIWAXS packing parameters.

Direction	Polymer	Film	Lamellar stack		π-π stack	
			Scattering vector (q) [Å^{-1}]	d-spacing [Å]	Scattering vector (q) [Å^{-1}]	d-spacing [Å]
In-plane	PPDTTBT	Pristine	0.2593	24.23	1.753	3.584
		Blend w/ DPE	0.2601	24.16	-	-
	PPDTTFBT	Pristine	0.2563	24.51	1.754	3.582
		Blend w/ DPE	0.2665	23.58	-	-
	PPDTT2FBT	Pristine	0.2390	26.29	1.802	3.487
		Blend w/ DPE	0.2670	23.53	-	-
Out-of-plane	PPDTTBT	Pristine	0.2685	23.40	1.753	3.584
		Blend w/ DPE	0.2920	21.52	1.779	3.532
	PPDTTFBT	Pristine	0.2787	22.54	1.739	3.613
		Blend w/ DPE	0.2955	21.26	1.788	3.514
	PPDTT2FBT	Pristine	0.2736	22.96	1.740	3.611
		Blend w/ DPE	0.3021	20.80	1.784	3.522

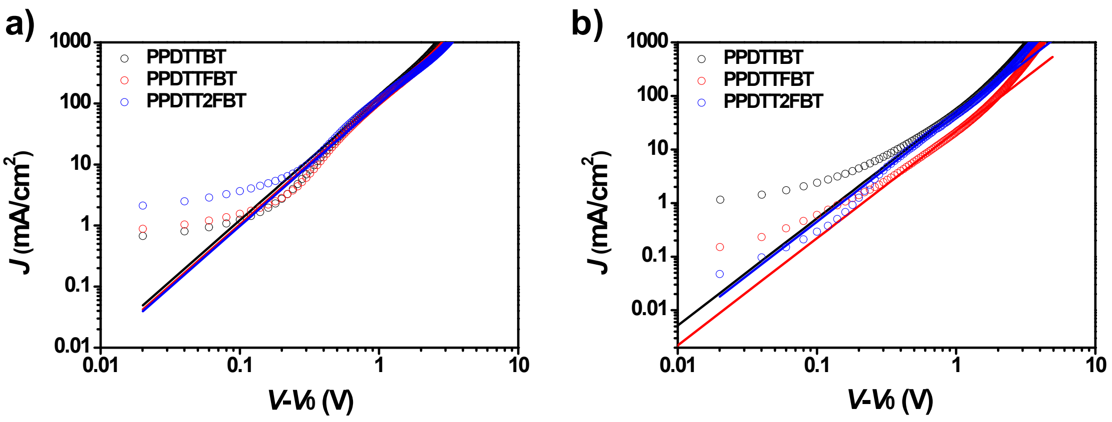


Figure S9. *J*-*V* characteristic of a) hole-only and b) electron-only devices based on polymer:PC$_{71}$BM BHJ films. Lines represent fits of the curves using the Mott-Gurney relationship. BHJ films were prepared under the same condition for the optimized polymer solar cells.

Table S6. Charge carrier mobility by PFET and SCLC measurements.

Polymer	μ_h(PTFT) [cm^2/Vs]	μ_h(SCLC) [cm^2/Vs]	μ_e(SCLC) [cm^2/Vs]	μ_h(SCLC)/μ_e(SCLC)
PPDTTBT	0.028 (0.027 ± 0.001)	2.88×10^{-5}	2.34×10^{-4}	8.13
PPDTTFBT	0.050 (0.049 ± 0.002)	1.44×10^{-5}	2.07×10^{-4}	14.38
PPDTT2FBT	0.103 (0.094 ± 0.011)	6.86×10^{-4}	2.16×10^{-4}	3.15

References:

1. H. S. Kim, Y. H. Kim, T. H. Kim, Y. Y. Noh, S. Pyo, M. H. Yi, D. Y. Kim and S. K. Kwon, *Chem. Mater.*, 2007, **19**, 3561-3567.

2. T. L. Nguyen, H. Choi, S. J. Ko, M. A. Uddin, B. Walker, S. Yum, J. E. Jeong, M. H. Yun, T. J. Shin, S. Hwang, J. Y. Kim and H. Y. Woo, *Energy Environ. Sci.*, 2014, **7**, 3040.