Supporting Information for

A Quinoxaline-Thiophene Based Thick Photovoltaic Device with Efficiency of ~8%

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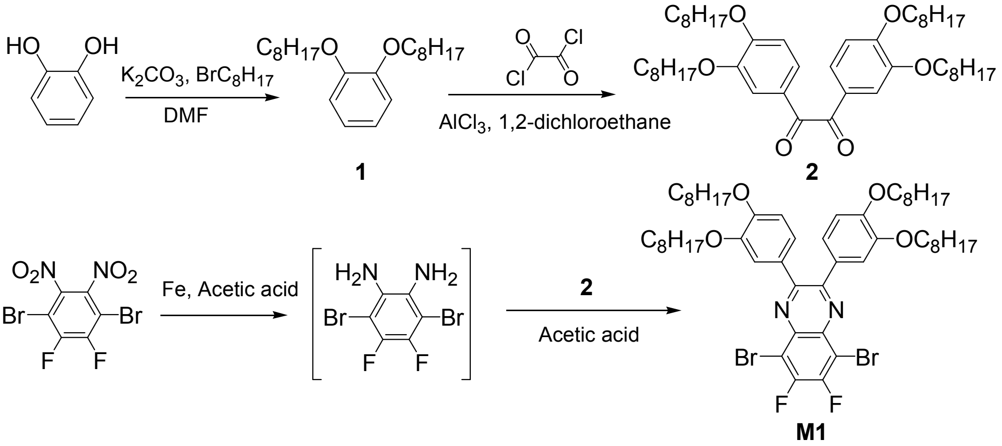
Synthesis

All chemical reagents were purchased from Aldrich, Tokyo Chemical Industry, Junsei and used without further purification. The intermediates and monomers, 2,5-bis(trimethylstannyl)thiophene, 5, 5'-bis(trimethyltin)-2,2'-bithiophene, 1,4-dibromo-2,3-difluoro-5,6-dinitrobenzene, 1,2-bis(octyloxy)benzene, 1,2-bis(3,4-bis(octyloxy)phenyl)ethane-1,2-dione were synthesized by following the procedures reported previously.[1-3] The monomers, **M1** and **M2** were prepared by modifying the previous methods (Scheme S1).[4,5]



Scheme S1 Synthetic scheme of M1.

1,2-Bis(octyloxy)benzene (1). A mixture of dihydroxybenzene (5.0 g, 45.4 mmol), 1-bromooctane (21.9 g, 113.4 mmol), and potassium carbonate (15.7 g, 113.6 mmol) in 60 mL *N,N*-dimethylformamide (DMF) was stirred overnight at 80 °C under nitrogen. After cooling the reaction solution, water (500 mL) was added. The organic layer was extracted with dichloromethane (DCM), washed with water three times, dried over anhydrous magnesium sulfate ($MgSO_4$), and then concentrated under reduced pressure. The crude compound was purified by silica gel column chromatography (hexane) to provide colorless oil (Yield: 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.89 (s, 4H), 3.97 (t, *J*=6.6 Hz, 4H), 1.81 (m, 4H), 1.47 (m, 4H), 1.28 (m, 16H), 0.88 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 149.2, 120.9, 114.1, 69.3, 31.8, 29.4, 29.3, 29.2, 26.0, 22.6, 14.1.

1,2-Bis(3,4-bis(octyloxy)phenyl)ethane-1,2-dione (2). To a mechanically stirred suspension of 1,2-bis(octyloxy)benzene (3.0 g, 8.97 mmol) and aluminum chloride (0.60 g, 4.48 mmol) in 30 mL 1,2-dichloroethane was added a solution of oxalyl chloride (0.68 g, 5.38 mmol) in 1,2-dichloroethane (20 mL) at 0 °C over a period of 30 min under nitrogen. After stirring for 30 min, the mixture was allowed to warm up to ambient temperature and further reacted overnight. The reaction mixture was poured into 1 M aqueous HCl solution and the organic layer was separated and dried over anhydrous $MgSO_4$. The concentrated residue was purified by silica gel column chromatography (hexane: DCM=1:1) to give a pure product (Yield: 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J*=1.8 Hz, 2H), 7.43 (dd, *J*=1.8 Hz, *J*=8.4 Hz, 2H), 6.83 (d, *J*=8.4 Hz, 2H), 4.04 (m, 8H), 1.82 (m, 8H), 1.45 (m, 8H), 1.28 (m, 40H), 0.87 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 193.8, 155.0, 149.3, 126.2, 126.1, 112.4, 111.6, 69.2, 69.1, 31.8, 31.7, 29.4, 29.3, 29.2, 29.1, 28.9, 26.0, 25.9, 22.6, 14.1.

2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8-dibromo-6,7-difluoroquinoxaline (M1). A mixture of 1,4-dibromo-2,3-difluoro-5,6-dinitrobenzene (3.0 g, 8.29 mmol), iron powder (5.57 g, 99.5 mmol) in acetic acid (50 mL) was stirred at 50 °C for 4 h. After filtering, 1,2-bis(3,4-bis(octyloxy)phenyl)ethane-1,2-dione (2) (6.0 g, 8.3 mmol) was added to the filtrate, followed by heating under reflux for overnight. The reaction mixture was poured into water, extracted with DCM, and dried over anhydrous $MgSO_4$. The solvent was removed via rotary evaporation and purified by column chromatography on silica gel (hexane: DCM =8:1) to afford M1 (4.3 g, 72%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.25 (m, 4H), 6.87 (d, *J*=7.8 Hz, 2H), 4.03 (t, *J*=13.5 Hz, 4H), 3.87 (t, *J*=13.5 Hz, 4H), 1.82 (m, 4H), 1.73 (m, 4H), 1.40 (m, 40H), 0.89 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) 157.5, 150.7, 148.7, 140.2, 130.2, 123.3, 115.5, 112.9, 69.2, 69.1, 32.0, 31.8, 29.4, 29.3, 29.2, 29.1, 29.0, 26.0, 22.7, 14.1. HRMS (Fast Atom Bombardment, FAB): m/z (M$^+$) = 989.4041 ($C_{52}H_{74}Br_2F_2N_2O_4$).

2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8-bis(2-thienyl)-6,7-difluoroquinoxaline (3) M1 (1.0 g, 1.01 mmol), 2-tributylstannylthiophene (0.78 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 sealed and purged with nitrogen. Toluene (12 mL) was added to the vial. The reaction mixture was heated at 80 °C for 3 min, at 100 °C for 5 min, at 120 °C for 45 min and at 140 °C for 60 min. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by column chromatography (hexane: DCM = 6:1) to provide a yellow solid (Yield: 73.6%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.02 (dd, *J*=3.9 Hz, *J*=0.9 Hz, 2H), 7.59 (dd, *J*=5.1 Hz, *J*=0.9 Hz, 2H), 7.43 (d, *J*=1.8 Hz, 2H), 7.26 (m, 4H), 6.84 (d, *J*=8.4 Hz, 2H), 4.03 (t, 4H), 3.94 (t, 4H), 1.82 (m, 8H), 1.31 (m, 40H), 0.89 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) 157.5, 150.7, 148.7, 140.2, 130.9, 130.8, 129.4, 126.5, 123.5, 123.4, 115.4, 112.5, 69.2, 69.1, 32.0, 31.8, 29.4, 29.3, 29.2, 29.1, 29.0, 26.1, 22.7, 14.1. HRMS (FAB): m/z (M$^+$) = 995.5606 ($C_{60}H_{80}F_2N_2O_4S_2$).

2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromothiophen-2-yl)-6,7-difluoroquinoxaline (M2). Compound **3** (0.74 g, 0.74 mmol) was dissolved in 25 mL DMF and *N*-bromosuccinimide (NBS) (0.33 g, 1.85 mmol) was added under nitrogen. The mixture was stirred at room temperature under dark for 14 h. After the solvent was removed under reduced pressure, water was added, extracted with DCM, and dried over anhydrous MgSO$_4$. The solvent was removed via rotary evaporation and purified by column chromatography on silica gel (hexane: DCM=7:1) to afford M2 (Yield: 64.2%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.76 (d, *J*=5.7 Hz, 2H), 7.59 (d, *J*=1.5 Hz, 2H), 7.16 (d, *J*=4.4 Hz, 2H), 7.08 (dd, *J*=1.5 Hz, *J*=8.4 Hz) 6.78 (d, *J*=8.4 Hz, 2H), 4.08 (t, 4H), 4.02 (t, 4H), 1.84 (m, 8H), 1.50 (m, 8H), 1.28 (m, 32H), 0.88 (m,12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) 151.4, 150.3, 149.2, 132.6, 130.8, 130.7, 130.3, 129.3, 123.7, 118.6, 115.3, 112.4, 69.2, 69.1, 32.0, 31.8, 29.4, 29.3, 29.2, 29.1, 29.0, 26.1, 22.7, 14.1. HRMS (FAB): m/z (M^+) = 1153.3796 ($C_{60}H_{78}Br_2F_2N_2O_4S_2$).

Poly(thiophene-*alt*-(2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-difluoroquinoxaline)) (PDFQx-T). In a N_2 filled glove box, **M1** (0.20 g, 0.202 mmol), 2,5-bis(trimethylstannyl)thiophene (82.5 mg, 1 equiv.), tris(dibenzylideneacetone)dipalladium(0) (2 mol%), tri(*o*-tolyl)phosphine (8 mol%) and toluene (1.5 mL) were added in a 5 mL microwave vial. The reaction mixture was heated at 80 °C for 3 min, at 100°C for 5 min, at 125 °C for 45 min and at 145°C for 55 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. 2-Bromothiophene (0.2 equiv.) was added by a syringe and the reaction solution was heated at 145 °C for another 20 min. After the reaction was finished, the crude PDFQx-T polymer was precipitated into 300 mL methanol, filtered and further purified by Soxhlet extraction with acetone, hexane and chloroform. The extracted polymer in chloroform was precipitated into MeOH, filtered and dried under vacuum (Yield: 58.3%). Number average molecular weight (M_n) = 36 kDa, polydispersity index (PDI) = 1.9. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.25 (br, 2H), 7.4 (br, 2H), 7.23 (br, 2H), 6.64 (br, 2H), 3.88 (br, 4H), 3.61 (br, 4H), 1.72 (br, 8H), 1.38-1.00 (br, 40H), 0.83 (br, 12H).

Poly(2,2′-bithiophene-*alt*-2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-difluoroquinoxaline) (PDFQx-2T). PDFQx-2T was synthesized similarly as PDFQx-T. Yield: 61.5%. M_n =56 kDa, PDI =2.6. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.20-7.80 (br, Ar-H 2H), 7.60-7.20 (br, 4H), 6.80-6.40 (br, 4H), 4.25-3.60 (br, 8H), 2.25-0.65 (br, 60H).

Poly(2,2':5',2"-terthiophene-*alt*-2,3-bis(3,4-bis(octyloxy)phenyl)-6,7-difluoroquinoxaline) (PDFQx-3T). PDFQx-3T was synthesized similarly as for PDFQx-T. Yield: 73%. M_n = 85 kDa, PDI = 1.8. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.20-7.80 (br, Ar-H 2H), 7.60-7.20 (br, 4H), 6.80-6.40 (br, 6H), 4.25-3.60 (br, 8H), 2.25-0.65 (br, 60H).

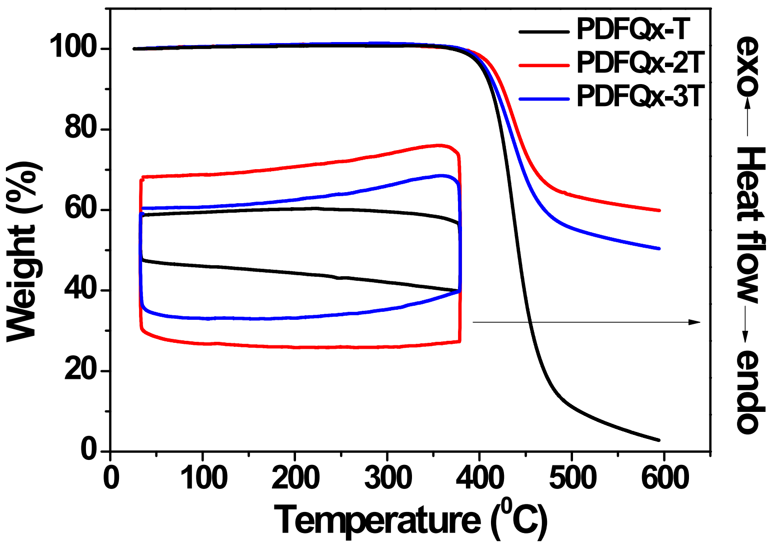


Fig. S1 TGA and DSC (insert) thermograms of PDFQx-T, PDFQx-2T and PDFQx-3T.

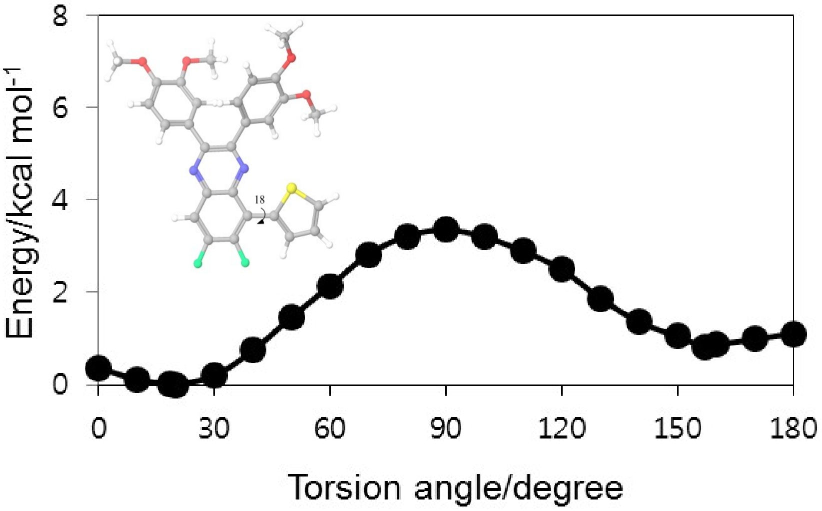


Fig. S2 Torsional profiles of difluoroquinoxaline (DFQx)-thiophene linkage.

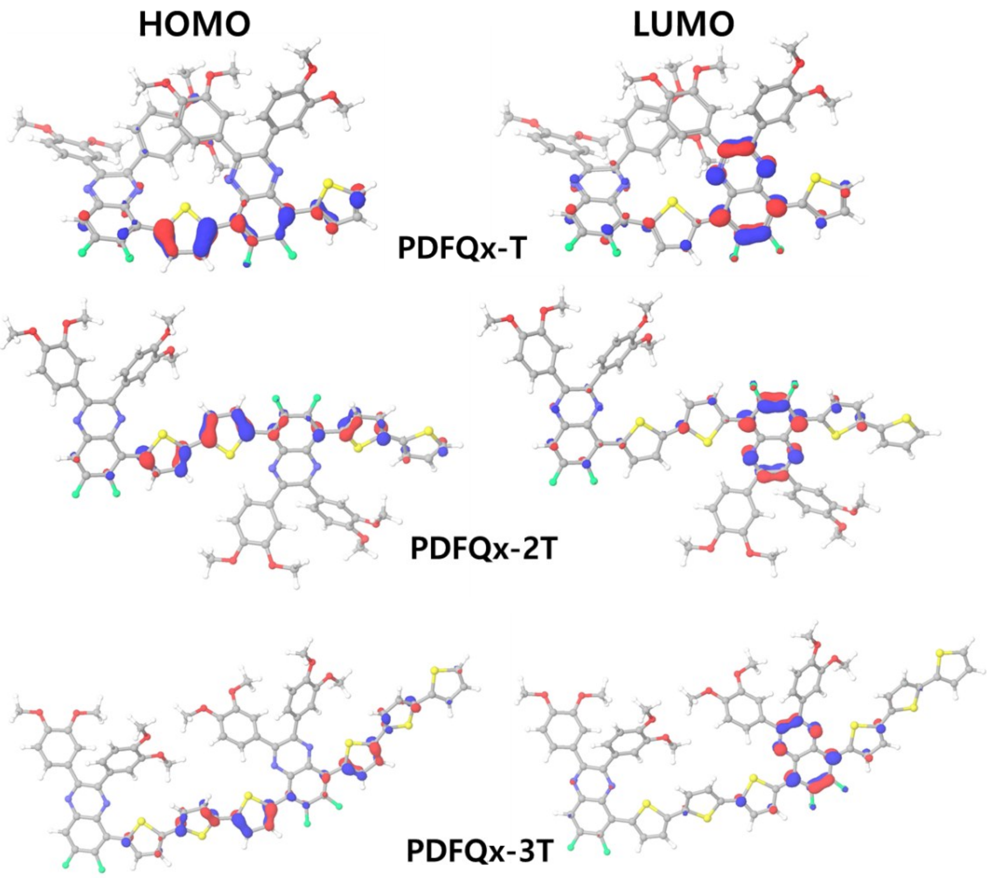
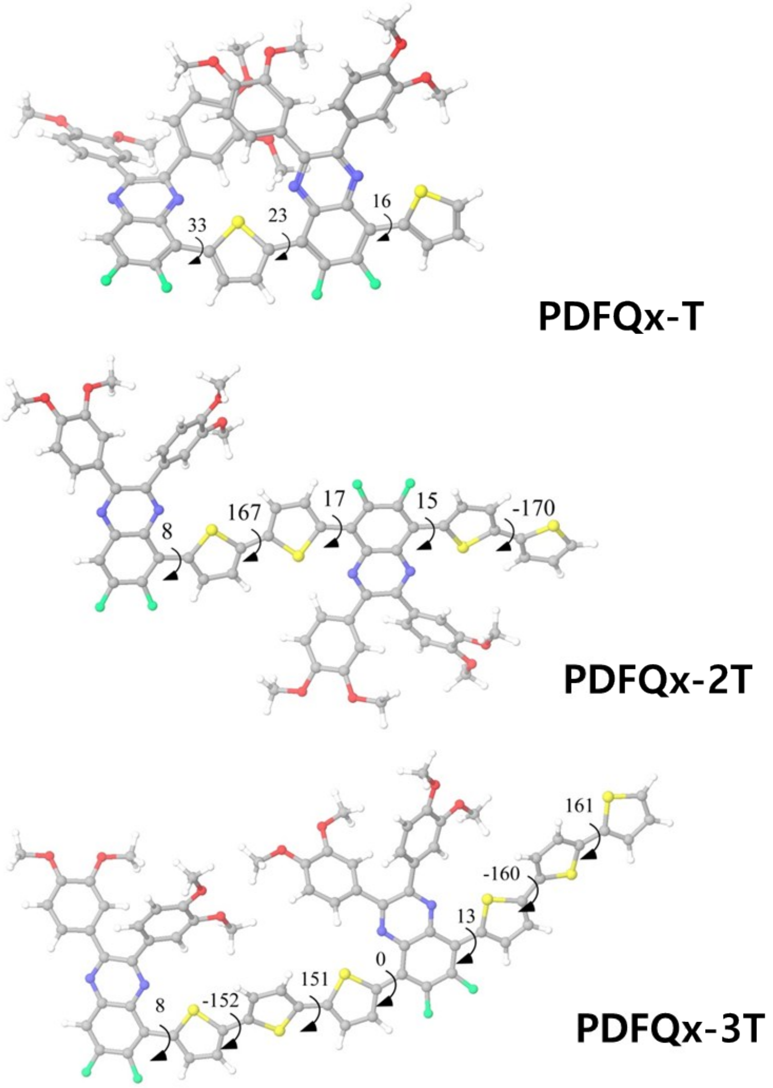


Fig. S3 HOMO and LUMO structures based on two repeat units by DFT (B3LYP/6-31G** level). Alkyl side-chains were replaced with methyl groups for simplifying calculation.


PDFQx-T

PDFQx-2T

PDFQx-3T

Fig. S4 Energy minimum conformations.

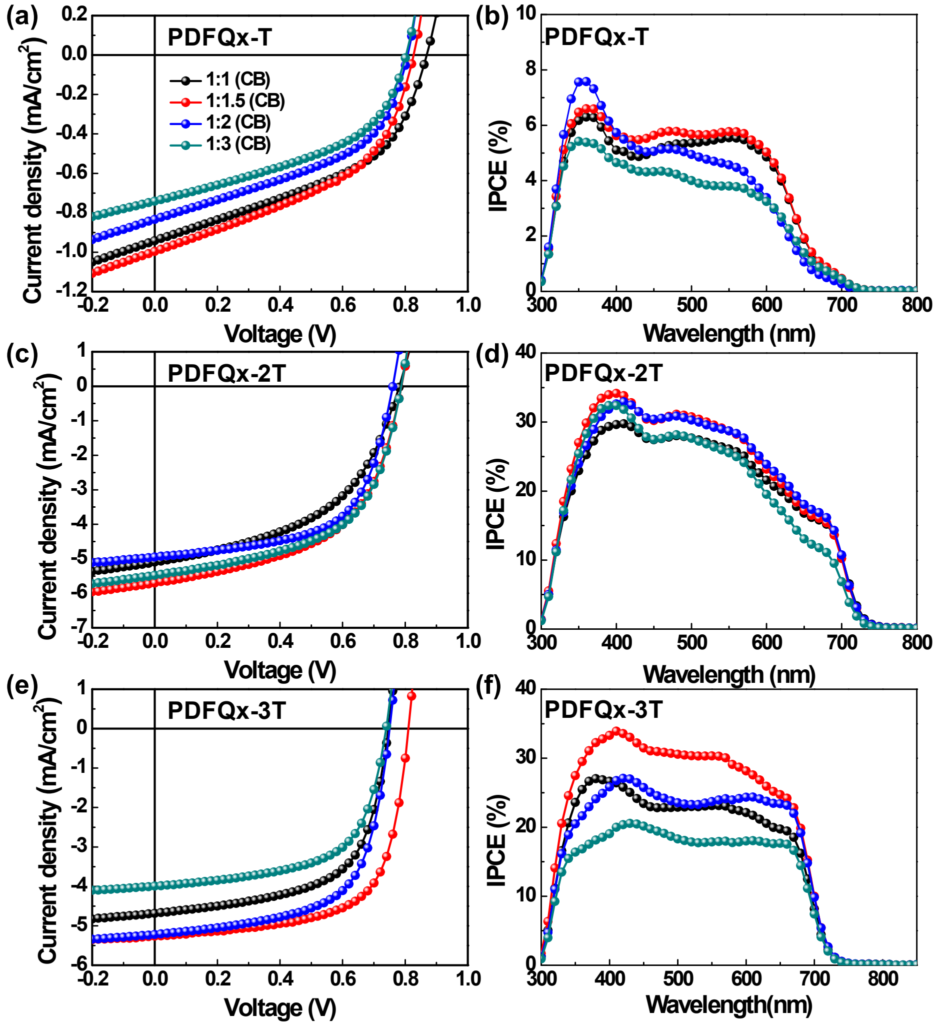


Fig. S5 a), c), e) J-V characteristics and b), d), f) IPCE curves for PDFQx-T:$PC_{71}BM$, PDFQx-2T:$PC_{71}BM$, and PDFQx-3T:$PC_{71}BM$ devices with changing blend ratios. The processing solvent is chlorobenzene (CB).

Table S1 Summary of device characteristics (CB solvent, blend ratio: 1:1 to 1:3).

Polymer:PC$_{71}$BM	D:A ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	PCE (%)	J_{SC} [Cal.] (mA/cm^2)
PDFQx-T	1:1	0.94	0.87	0.45	0.37	0.87
	1:1.5	1.00	0.83	0.45	0.37	0.92
	1:2	0.83	0.81	0.45	0.31	0.75
	1:3	0.74	0.80	0.45	0.27	0.66
PDFQx-2T	1:1	5.10	0.78	0.49	1.95	4.85
	1:1.5	5.70	0.79	0.54	2.41	5.27
	1:2	5.48	0.79	0.56	2.41	5.29
	1:3	4.95	0.76	0.60	2.27	4.56
PDFQx-3T	1:1	4.68	0.75	0.61	2.14	4.51
	1:1.5	5.26	0.81	0.66	2.81	5.81
	1:2	5.22	0.75	0.63	2.47	4.85
	1:3	3.99	0.74	0.61	1.81	3.68

Table S2 Device characteristics of PDFQx-3T with different additives (solvent: CB).

	Solvent + Additive (3%)		J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	PCE (%)
PDFQx-3T: PC$_{71}$BM (1:1.5)	CB		6.22	0.78	0.58	2.81
	CB+DIO	Thick	14.87	0.74	0.52	5.74
		Thin	13.02	0.73	0.63	6.00
	CB+ODT	Thick	13.70	0.75	0.58	5.98
		Thin	11.16	0.72	0.70	5.61
	CB+CN	Thick	12.73	0.77	0.58	5.68
		Thin	11.43	0.76	0.67	5.82
	CB+DPE	Thick	17.19	0.74	0.63	8.00
		Thin	14.06	0.76	0.72	7.73

Table S3 Summary of 2D-GIXRD packing parameters for pristine and BHJ films.

Films	Materials	2D-GIXRD parameters			
		Interlamellar scattering (q_{xy} direction)		π-π stacking (q_z direction)	
		q (Å^{-1})	d-spacing (Å)	q(Å^{-1})	d-spacing (Å)
Pristine	PDFQx-T	0.2475	25.3866	-	-
	PDFQx-2T	0.2335	26.9087	1.7129	3.6682
	PDFQx-3T	0.2371	26.2345	1.7233	3.6460
BHJ	PDFQx-T	0.2315	27.1412	-	-
	PDFQx-2T	0.2395	26.2346	1.7129	3.6682
	PDFQx-3T	0.2536	24.7759	1.7265	3.6393

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