

Electronic Supplementary Information

Effect of Incorporating Different Chalcogenophene
Comonomers into Random Acceptor Terpolymers on
the Morphology and Performance of All-Polymer Solar
Cells

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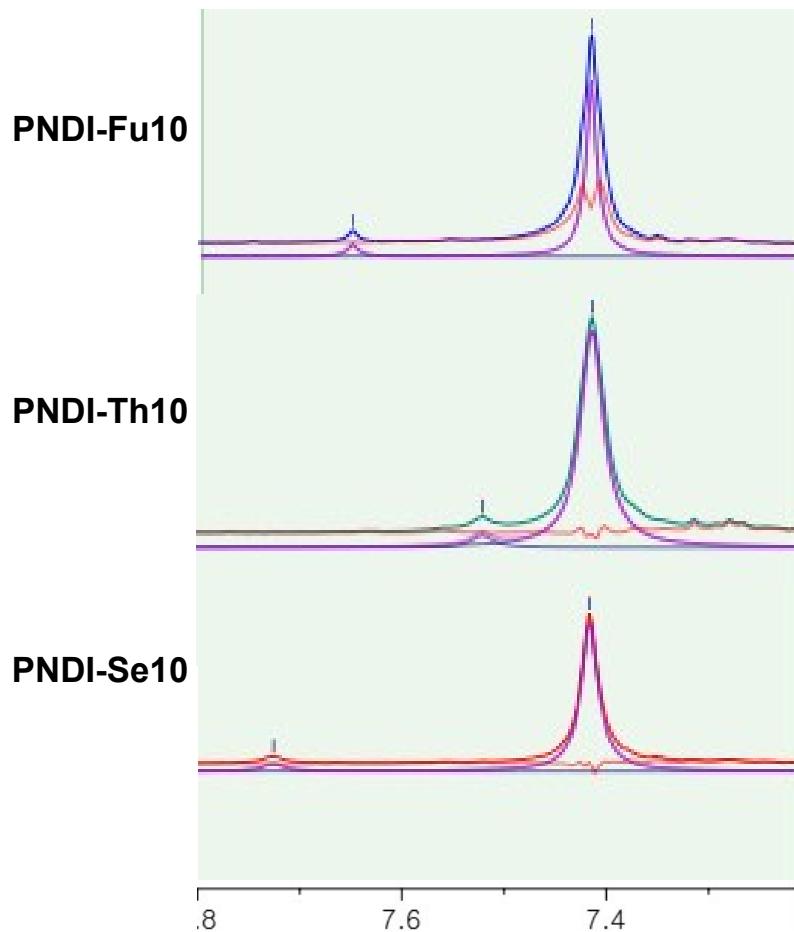


Fig. S1 Calculation of chalcogenophenes (Fu, Th, and Se) ratio in NDI-T2 units using Gaussian curves. The actual ratios of the random terpolymers were calculated based on the

following equation; the ratio of chalcogenophene (Fu, Th, or Se) (%) = $\frac{A_a}{(A_a + A_b)} \times 100 = \frac{H_a}{(H_a + H_b)} \times 100$, the ratio of T2 (%) = $\frac{A_b}{(A_a + A_b)} \times 100 = \frac{H_b}{(H_a + H_b)}$, where A_a and A_b are the area of the signals of the chalcogenophenes (7.5 -7.7 ppm) and T2 (7.41 ppm) and H_a and H_b indicate their heights, respectively.

Table S1 Comparison of theoretical ratio and actual ratio through analysis of $^1\text{H-NMR}$ at 70°C of the random terpolymers with 9:1 ratio

PNDI-Fu10	Bithiophene (T2) unit	Donor (Fu) unit
Ratio of proton	2	1
Ratio of donor unit	9	1
Theoretical ratio	18 (0.947)	1 (0.052)
Actual ratio	0.945	0.054

PNDI-Th10	Bithiophene (T2) unit	Donor (Th) unit
Ratio of proton	2	1
Ratio of donor unit	9	1
Theoretical ratio	18 (0.947)	1 (0.052)
Actual ratio	0.955	0.045

PNDI-Se10	Bithiophene (T2) unit	Donor (Se) unit
Ratio of proton	2	1
Ratio of donor unit	9	1
Theoretical ratio	18 (0.947)	1 (0.052)
Actual ratio	0.945	0.054

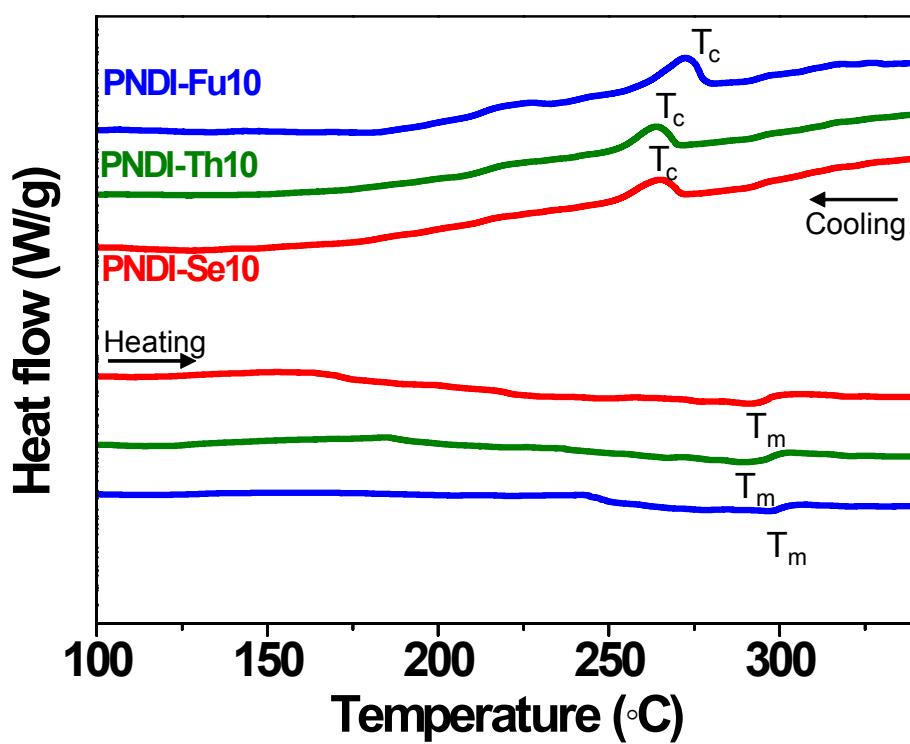
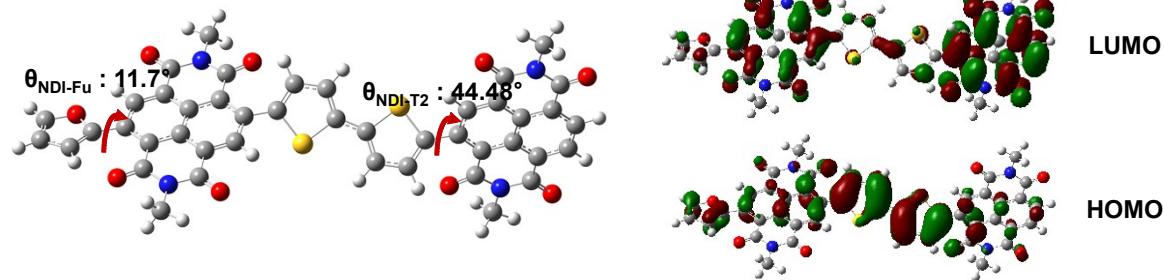
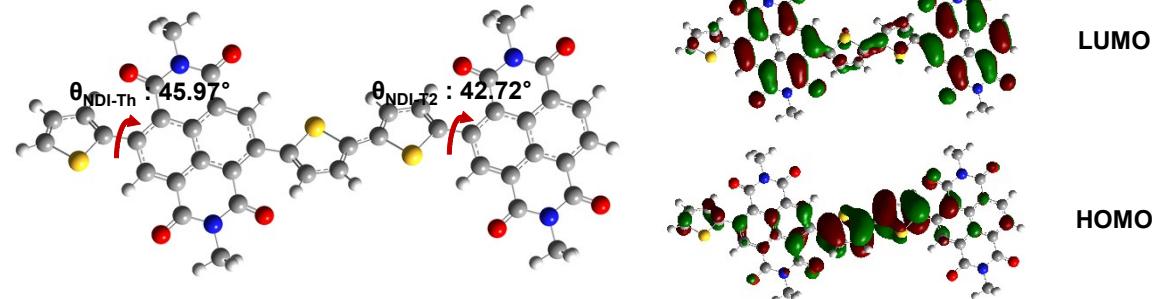


Fig. S2 DSC thermograms of neat random terpolymers measured with a scan rate of 10°C per a minute.

(a) PNDI-T2-Fu



(b) PNDI-T2-Th



(c) PNDI-T2-Se

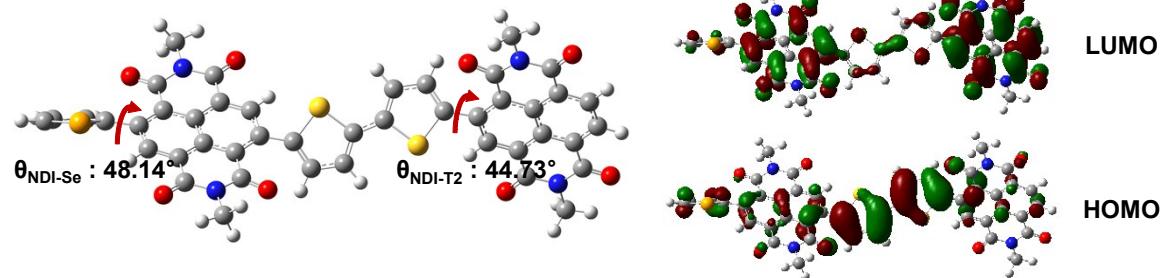


Fig. S3 Dihedral angle and charge distributions of random copolymers calculated by DFT, respectively (B3LYP/6-31G*).

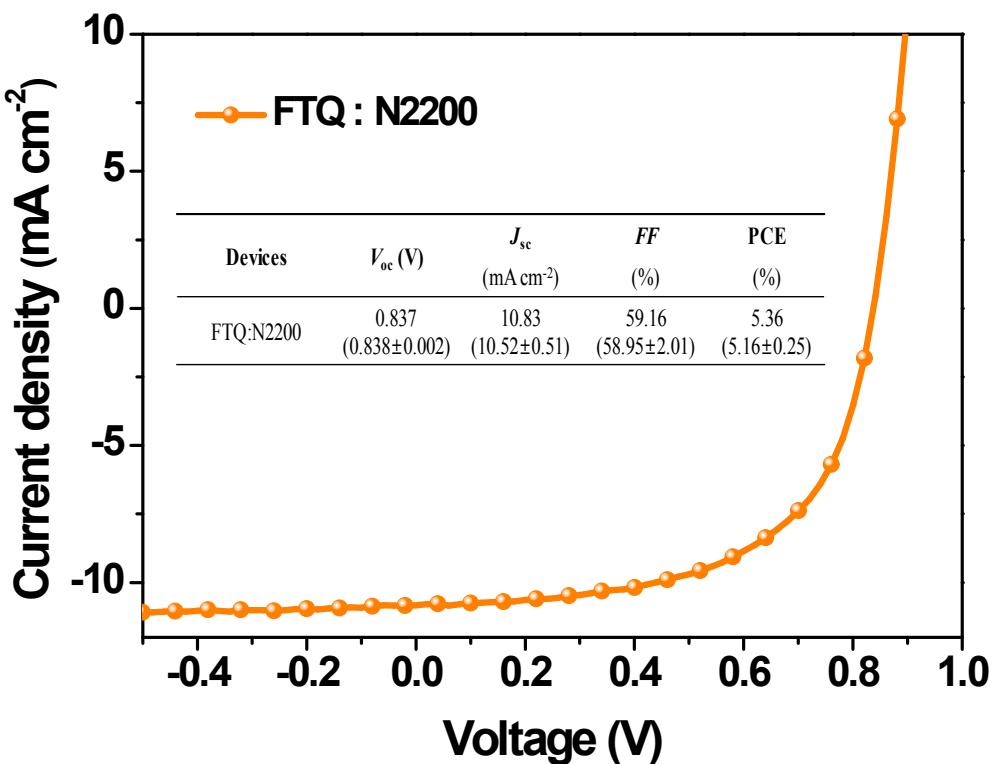


Fig. S4 Current density-voltage (J - V) curves and photovoltaics parameters of FTQ:P(NDI2OD-T2).

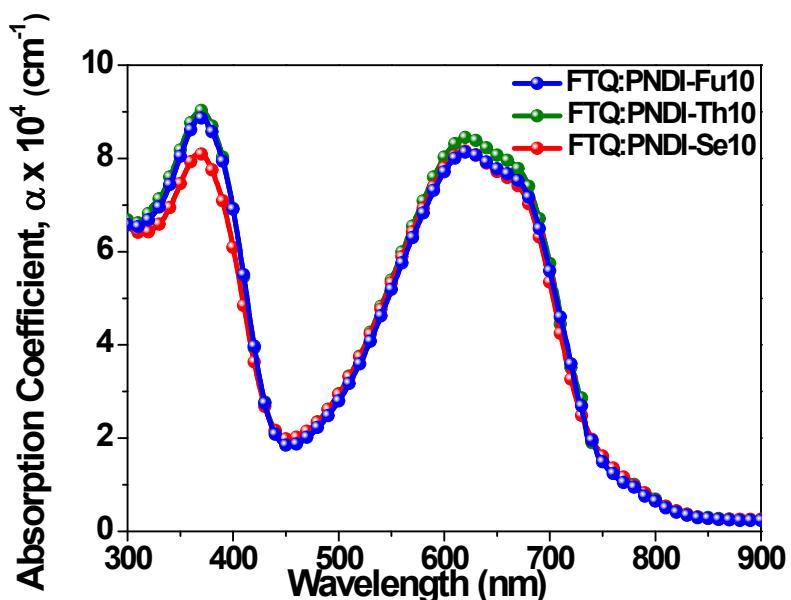


Fig. S5 The absorption spectra of the random terpolymer films blended with FTQ donor polymer.

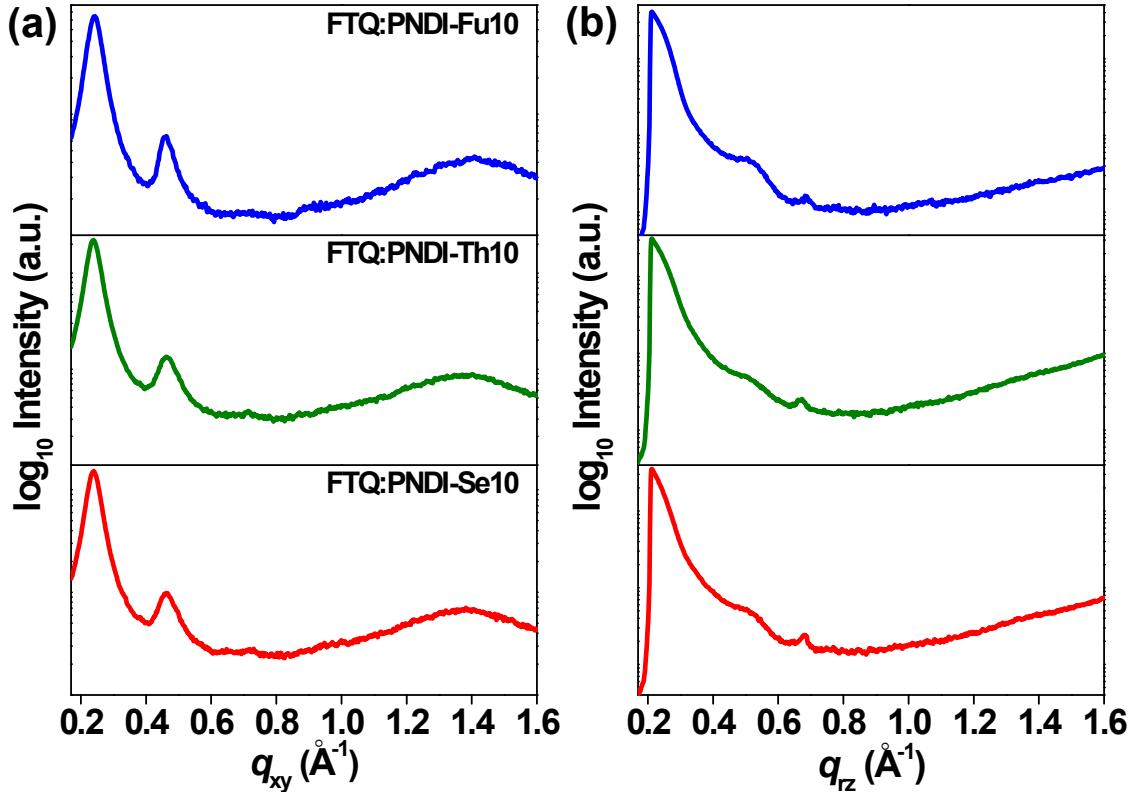


Fig. S6 GIWAXS line-cut profile of blend film (a) in-plane and (b) out-of-plane.

Table S2 The GIWAXS parameters of in-plane and out-of-plane.

Donor:Acceptor	In-Plane				Out-of-Plane	
	Unit cell long axis (100)				$\pi-\pi$ stacking cell axis (010)	
	$q (\text{\AA}^{-1})$	d -spacing (Å)	FWHM (\AA^{-1})	Correlation length (Å)	$q (\text{\AA}^{-1})$	d -spacing (Å)
FTQ: PNDI-Fu10	0.241	26.071	0.054	104.7	1.703	3.689
FTQ: PNDI-Th10	0.236	26.623	0.048	117.8	1.688	3.722
FTQ: PNDI-Se10	0.236	26.623	0.050	113.1	1.680	3.739

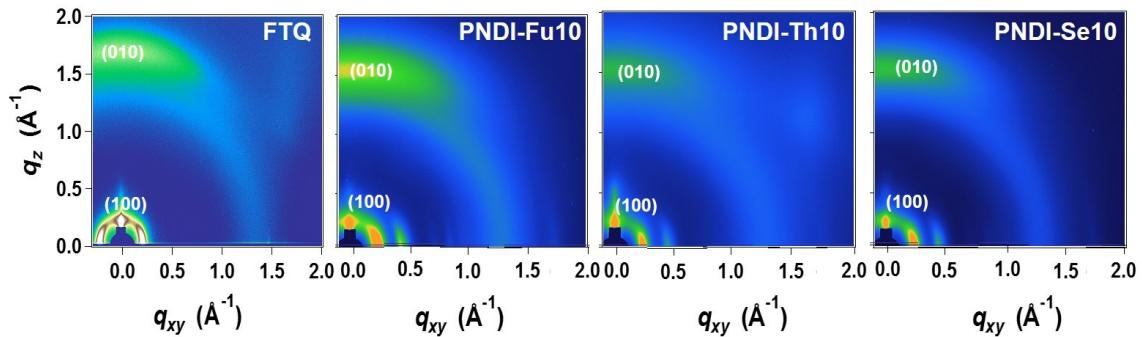


Fig. S7 2D GIWAXS images of the neat polymer films.

Table S3 The GIWAXS parameters of the neat polymers.

Polymers	In-Plane		Out-of-Plane	
	Unit cell long axis (100)		π - π stacking cell axis (010)	
	q (\AA^{-1})	d -spacing (\AA)	q (\AA^{-1})	d -spacing (\AA)
FTQ	0.228	27.557	1.69	3.71
P(NDI-Th10)	0.251	25.032	1.560	4.02
P(NDI-Se10)	0.257	24.448	1.566	4.01
P(NDI-Fu10)	0.257	24.448	1.588	3.95