Electronic Supplementary Information

Effect of Cyano (CN)–group on the Properties of Benzodithiophene–Based Polymers in Planarity, Photovoltaic Performance and Film Morphologies

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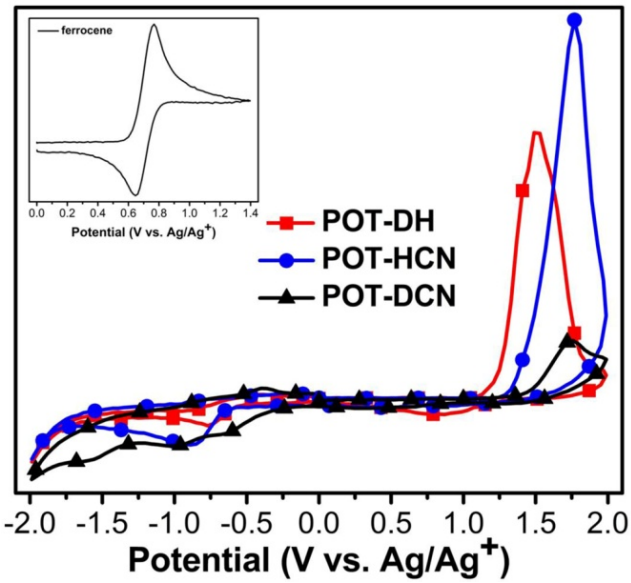

Fig. S1 Cyclic voltammograms of polymer films on a platinum electrode in acetonitrile solution containing 0.1 M Bu_4NPF_6 at a scan rate of 50 mV/s.

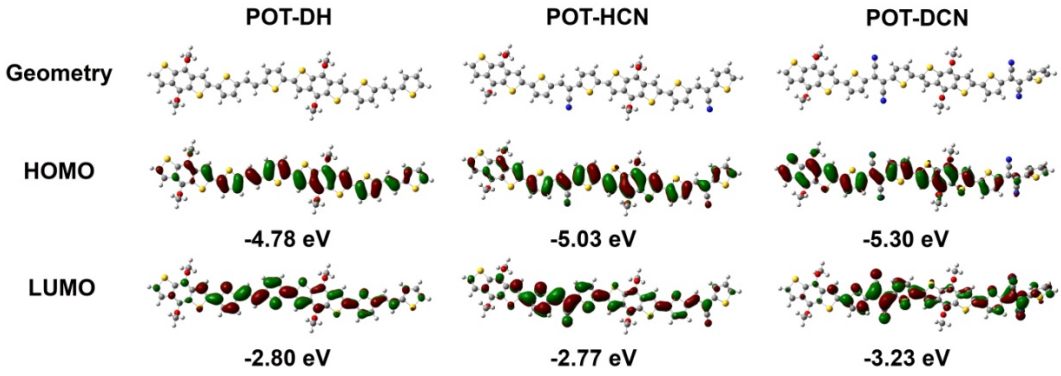

Fig. S2 Optimized geometries, molecular orbital surfaces and calculated HOMO/LUMO energy levels of the model compounds, obtained at the DFT/B3LYP/6-31GD level.

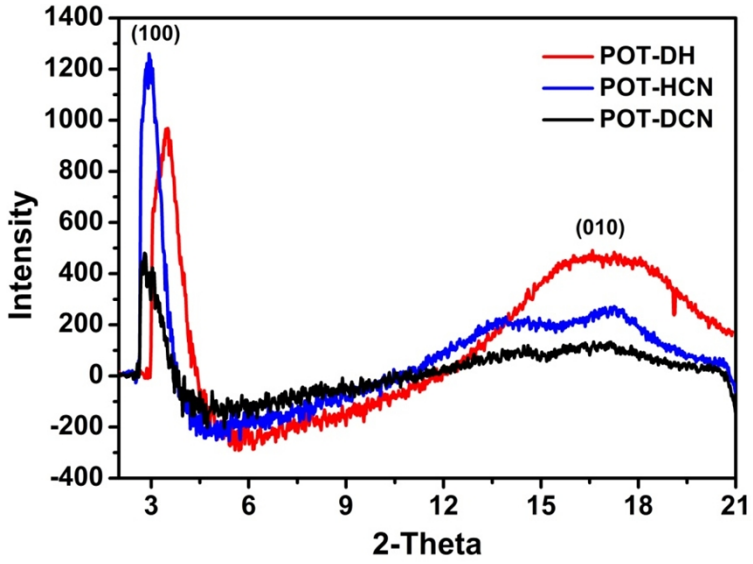

Fig. S3 1D-graph of GIXD of polymers.

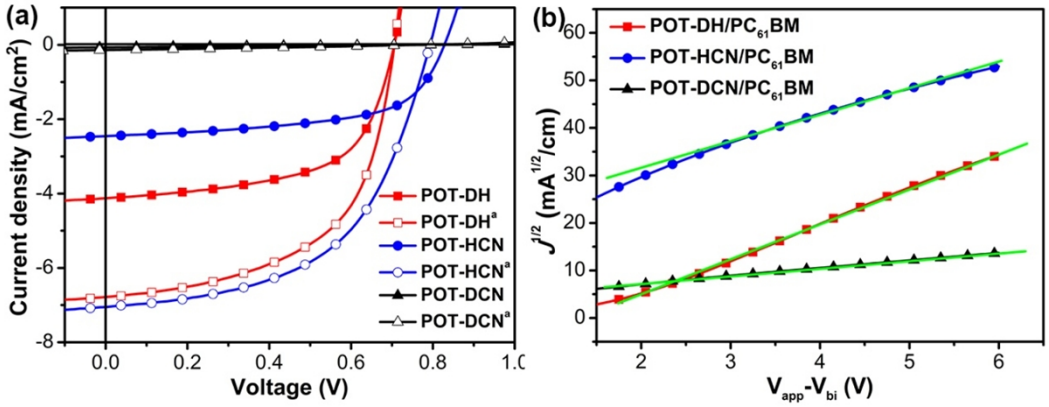

Fig. S4 (a) Current density−voltage (I−V) curves of the PSCs based on polymer/$PC_{61}BM$ (1:1.5, w/w) with ([a], empty symbol) and without DIO (full symbol); (b) $J^{1/2}$~V characteristics of the hole–only devices based on polymer/$PC_{61}BM$ measured at ambient temperature.

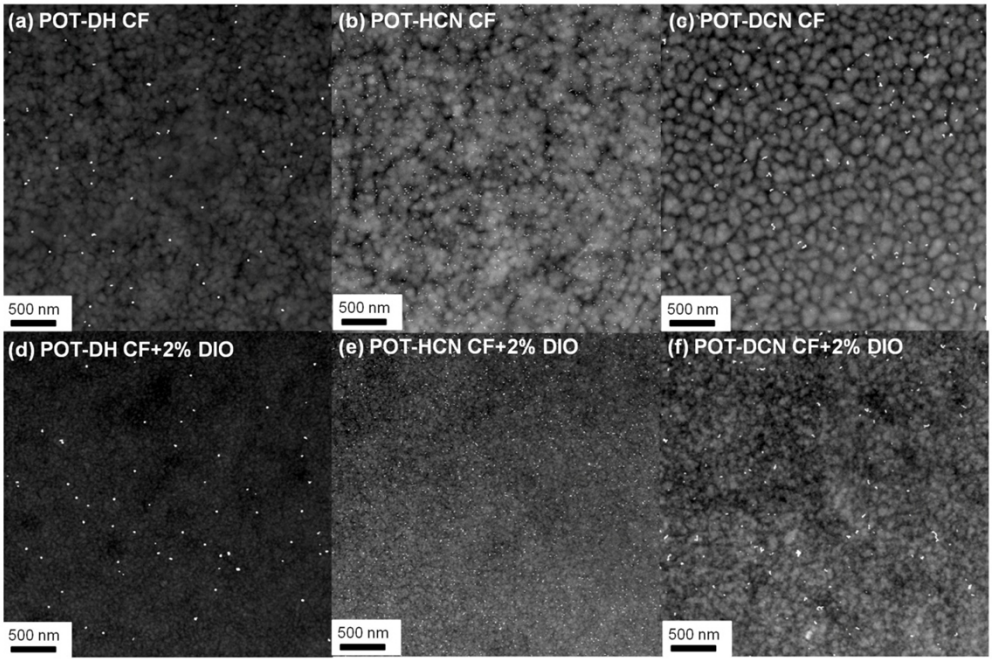

Fig. S5 HAADF–STEM images of polymer/$PC_{61}BM$ blends (1:1.5 w/w) cast from chloroform or chloroform with 2% DIO.

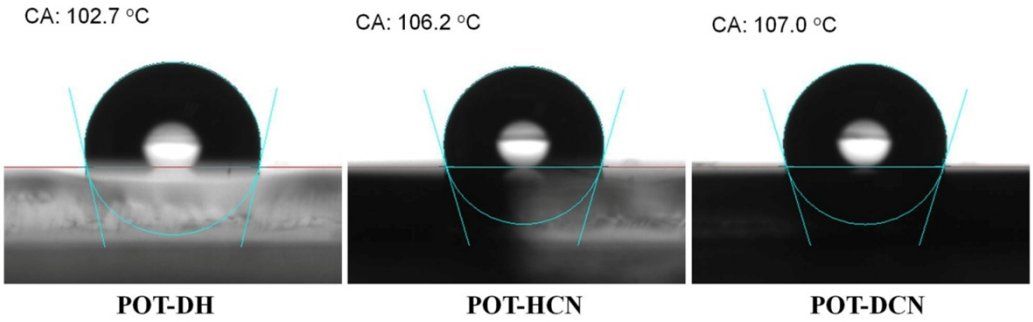

Fig. S6 Contact angles of three polymers by dropping water on the polymer films cast from $CHCl_3$ solutions.

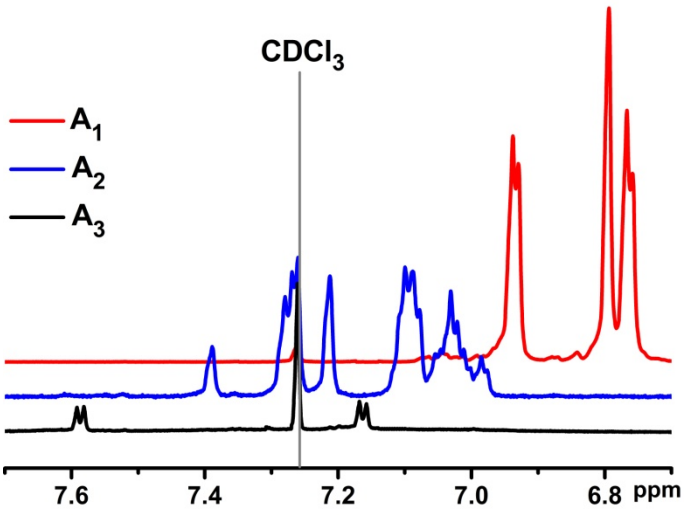

Fig. S7 ^1H NMR spectrum of monomer $\mathbf{A_1}$, $\mathbf{A_2}$ and $\mathbf{A_3}$.

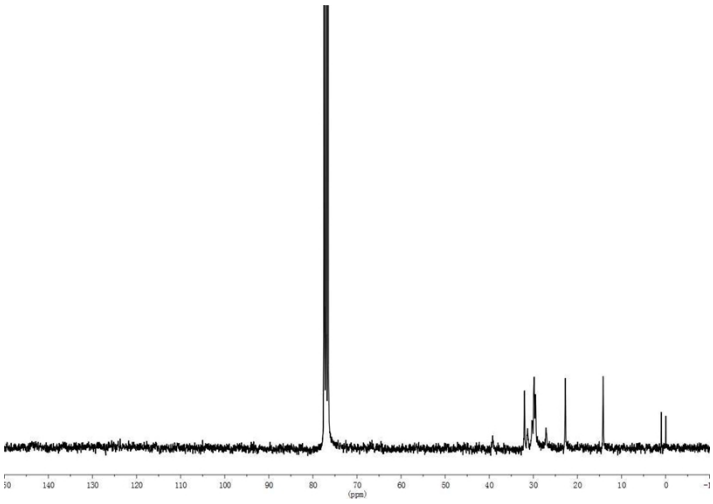

Fig. S8 ^{13}C NMR spectrum of **POT-DH**.

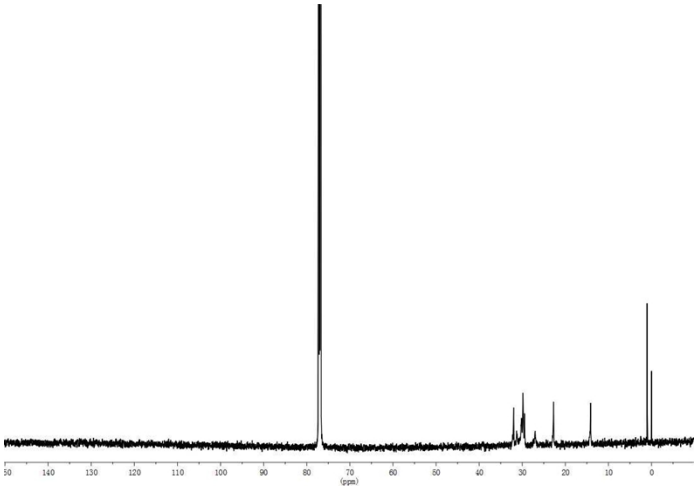

Fig. S9 ^{13}C NMR spectrum of **POT-HCN**.

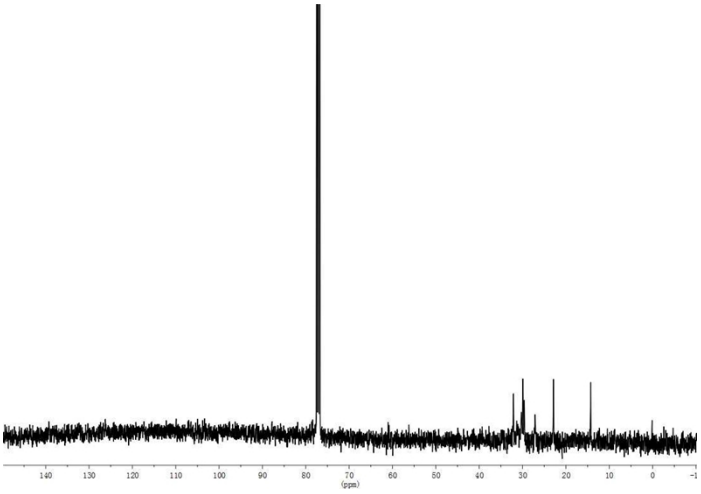

Fig. S10 ^{13}C NMR spectrum of **POT-DCN**.

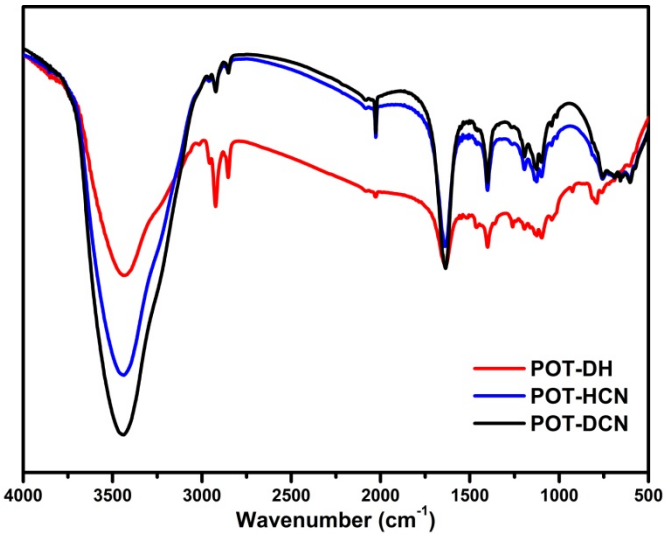

Fig. S11 Infrared spectra of three polymers. The spectra were recorded using KBr pellets.

Table S1. Optimization of donor/acceptor ratio and solvent for polymer/$PC_{61}BM$ solar cells.

Polymer	D/A	Solvent	Speed (r)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
POT–DH	1:3	CF	1500	0.69	4.52	66.2	2.06
	1:3	CF+2% DIO	1500	0.70	6.82	56.1	2.68
	1:2	CF	1500	0.73	3.35	68.1	1.67
	1:2	CF+2% DIO	1500	0.69	6.43	56.5	2.51
	1:1.5	CF	1500	0.70	4.12	60.5	1.74
	1:1.5	CF+2% DIO	1500	0.70	6.77	57.5	**2.72**
	1:1	CF	1500	0.70	3.85	61.5	1.66
	1:1	CF+2% DIO	1500	0.69	6.14	57.3	2.42
	1:3	CB	800	0.70	1.89	34.9	0.46
	1:3	CB +2% DIO	800	0.70	3.85	65.9	1.78
	1:2	CB	800	0.69	1.04	37.5	0.27
	1:2	CB +2% DIO	800	0.73	4.45	64.3	2.09
	1:1.5	CB	800	0.65	1.09	38.4	0.27
	1:1.5	CB +2% DIO	800	0.74	4.60	64.9	**2.21**
	1:1	CB	800	0.68	0.83	34.0	0.19
	1:1	CB +2% DIO	800	0.75	4.16	67.6	2.11
	1:3	ODCB	800	0.70	2.94	67.0	1.38
	1:3	ODCB +2% DIO	800	0.71	3.44	68.7	1.68
	1:2	ODCB	800	0.74	3.17	68.2	1.60
	1:2	ODCB +2% DIO	800	0.74	3.72	68.8	1.89
	1:1.5	ODCB	800	0.74	3.40	69.0	1.74
	1:1.5	ODCB +2% DIO	800	0.71	3.84	70.0	**1.91**
	1:1	ODCB	800	0.74	3.20	67.6	1.60
	1:1	ODCB +2% DIO	800	0.70	3.84	64.3	1.73

POT–HCN	1:3	CF	1500	0.79	2.34	61.0	1.13
	1:3	CF+2% DIO	1500	0.76	7.04	47.3	2.53
	1:2	CF	1500	0.80	2.13	61.3	1.04
	1:2	CF+2% DIO	1500	0.76	6.27	50.8	2.42
	1:1.5	CF	1500	0.83	2.45	59.6	1.21
	1:1.5	CF+1% DIO	1500	0.75	5.71	51.3	2.20
	1:1.5	CF+2% DIO	1000	0.76	5.57	50.9	2.15
	1:1.5	CF+2% DIO	1200	0.78	5.29	51.4	2.12
	1:1.5	CF+2% DIO	1400	0.78	5.93	48.6	2.25
	1:1.5	CF+2% DIO	1500	0.79	7.05	54.4	**3.03**
	1:1.5	CF+3% DIO	1500	0.76	5.97	51.5	2.34
	1:1	CF	1500	0.75	1.23	55.4	0.51
	1:1	CF+2% DIO	1500	0.78	6.32	49.9	2.46
	1:3	CB	800	0.65	1.69	44.8	0.49
	1:3	CB+2% DIO	800	0.73	4.67	55.6	1.90
	1:2	CB	800	0.64	1.61	50.0	0.52
	1:2	CB+2% DIO	800	0.70	5.39	54.8	2.07
	1:1.5	CB	800	0.65	1.51	49.4	0.48
	1:1.5	CB+2% DIO	800	0.74	5.15	59.8	**2.28**
	1:1	CB	800	0.69	1.29	47.0	0.42
	1:1	CB+2% DIO	800	0.75	4.68	58.2	2.04
	1:3	ODCB	800	0.74	2.33	52.2	0.90
	1:3	ODCB+2% DIO	800	0.74	2.55	55.0	1.04
	1:2	ODCB	800	0.74	3.92	58.2	1.69
	1:2	ODCB+2% DIO	800	0.76	3.50	58.1	1.55
	1:1.5	ODCB	800	0.79	3.82	58.2	1.76
	1:1.5	ODCB+2% DIO	800	0.75	3.95	57.7	1.71
	1:1	ODCB	800	0.75	3.88	61.7	1.80
	1:1	ODCB+2% DIO	800	0.78	4.20	59.5	**1.95**
POT–DCN	1:1.5	CF	1500	0.80	0.07	24.0	0.01
	1:1.5	CF+2% DIO	1500	0.77	0.14	28.8	**0.03**
	1:1.5	CB	800	0.75	0.09	25.0	0.02
	1:1.5	CB+2% DIO	800	0.72	0.15	27.5	0.03
	1:1.5	ODCB	800	0.78	0.10	28.9	0.02
	1:1.5	ODCB +2% DIO	800	0.74	0.13	30.1	0.03