Electronic Supplementary Information

Improving Photovotaic Performance of Ladder-type Dithienonaphthalene Containing Copolymers through Structural Isomerization

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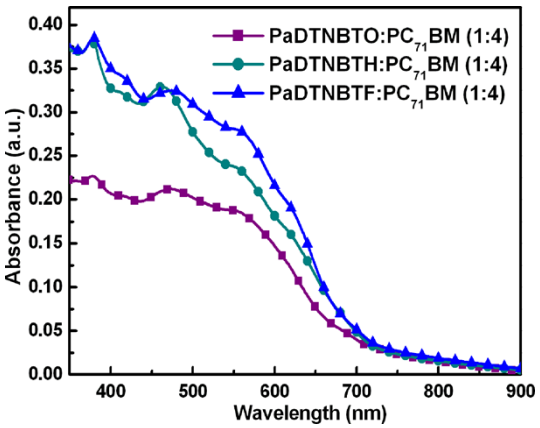

Fig. S1 Optical absorption spectra of the polymer: $PC_{71}BM$ blends.

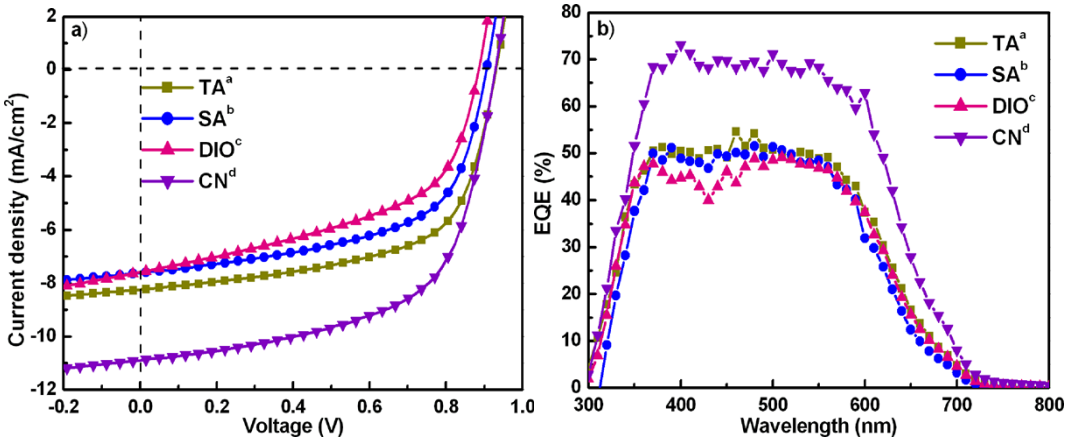

Fig. S2 (a) *J*–*V* characteristics and b) *EQE* curves of PSCs based on **PaDTNBTO**:$PC_{71}BM$ under different experiment conditions. [a]Thermal treatment (TA) at 70 °C for 5 min. [b]Solvent annealing (SA) with saturated *o*-dichorobenzene vapor for 10 min. [c]0.3% 1, 8-octanedithiol (DIO) as an additive (v/v). [d]0.3% chloro-naphthalene (CN) as an additive (v/v).

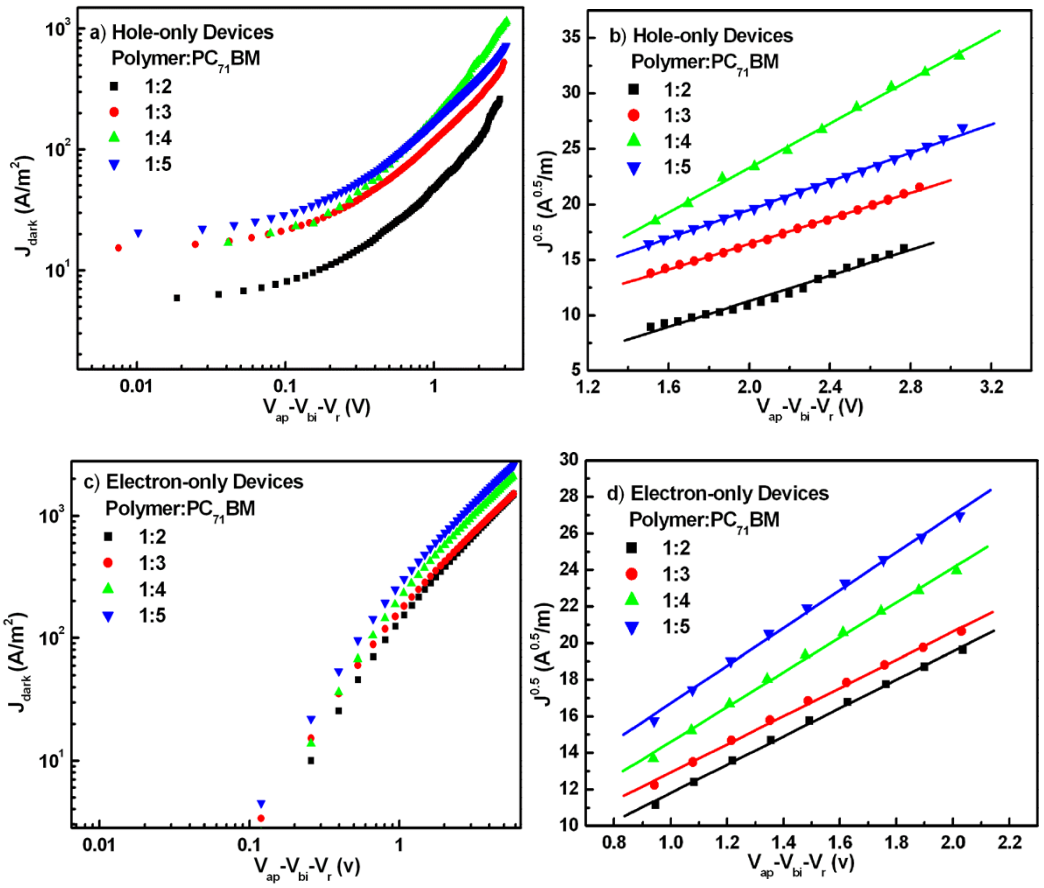

Fig. S3 (a, c) *J*~*V* characteristics, and (b, d) $J^{0.5}$~*V* characteristics of **PaDTNBTO**-based hole- and electron-only devices with different D-A ratios.

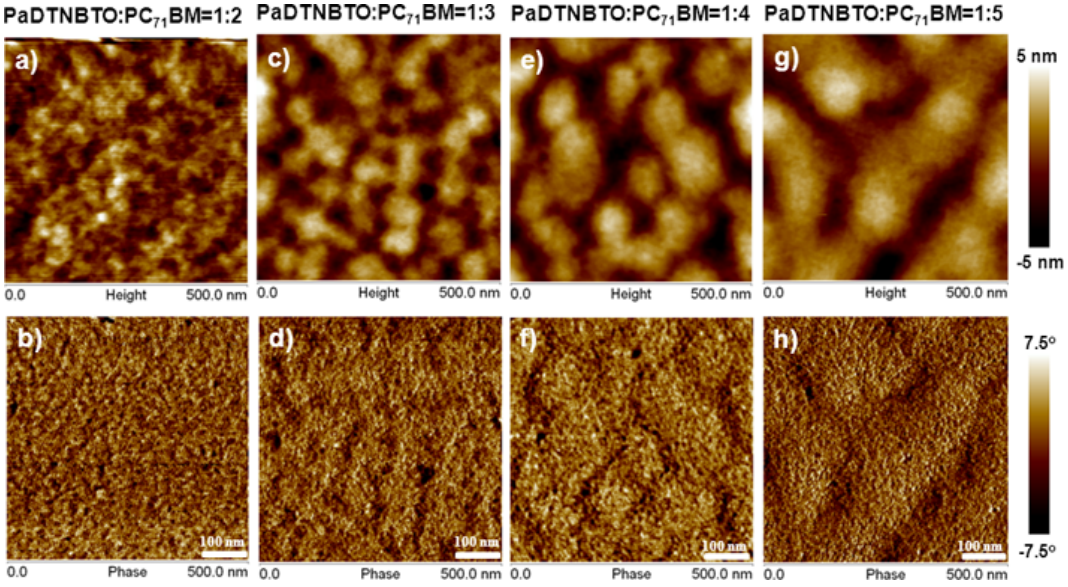

Fig. S4 AFM topography (top) and phase (bottom) images of the blend films of **PaDTNBTO** and $PC_{71}BM$ with different D/A ratios: a,b) 1:2, c,d) 1:3, e,f) 1:4, g,h) 1:5. The size of the images is 0.5 μm × 0.5 μm.

Table S1. The hole mobility of hole-only devices based on different polymer

Polymer	Polymer:$PC_{71}BM$	Thickness (nm)	Hole mobility ($cm^2 \cdot V^{-1} \cdot s^{-1}$)
PaDTNBTO	1:4	90	2.81×10^{-5}
PaDTNBTH	1:4	100	3.69×10^{-5}
PaDTNBTF	1:4	70	7.50×10^{-6}

Table S2. The electron and hole mobilities of **PaDTNBTO**:$PC_{71}BM$ blends with different D-A ratios

Polymer:$PC_{71}BM$	Electron mobility μ_e ($cm^2\ V^{-1}\ s^{-1}$)	Hole mobility μ_h ($cm^2\ V^{-1}\ s^{-1}$)	$\mu_e/\ \mu_h$
1:2	3.30×10^{-5}	7.12×10^{-6}	4.63
1:3	3.59×10^{-5}	1.10×10^{-5}	3.26
1:4	5.26×10^{-5}	2.81×10^{-5}	1.87
1:5	6.38×10^{-5}	2.12×10^{-5}	3.00

Table S3. Device parameters of PSCs based on **PaDTNBTO** under different experiment conditions

Polymer:$PC_{71}BM$	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (PCE_{ave}[a])) (%)
1:4[a]	0.93	8.22	61.6	4.71 (4.41)
1:4[b]	0.92	7.23	57.5	4.07 (3.98)
1:4[c]	0.88	7.58	51.5	3.46 (3.27)
1:4[d]	0.93	10.88	60.1	6.06 (5.91)

[a] Thermal annealing (TA) at 70 °C for 5 min. [b]Solvent annealing (SA) with saturated *o*-dichorobenzene vapor for 10 min. [c]0.3% 1, 8-octanedithiol (DIO) as an additive (v/v). [d]0.3% chloronaphthalene (CN) as an additive (v/v).