Supporting Information for

Nanoscale phase separation control in rational design conjugated polymer solar cells processed using co-additives

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S1 Material synthesis

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted.

1,3-Dibromo-5-ethylhexylthieno[3,4-c]pyrrole-4,6-dione (TPD)[1,2] and 2,6-bis(trimethyltin)-4,8-bis(5-exylthiophene-2-yl)benzo[1,2-b:4,5-b′]dithiophene (BDT)[3,4] were prepared according to the published procedures.

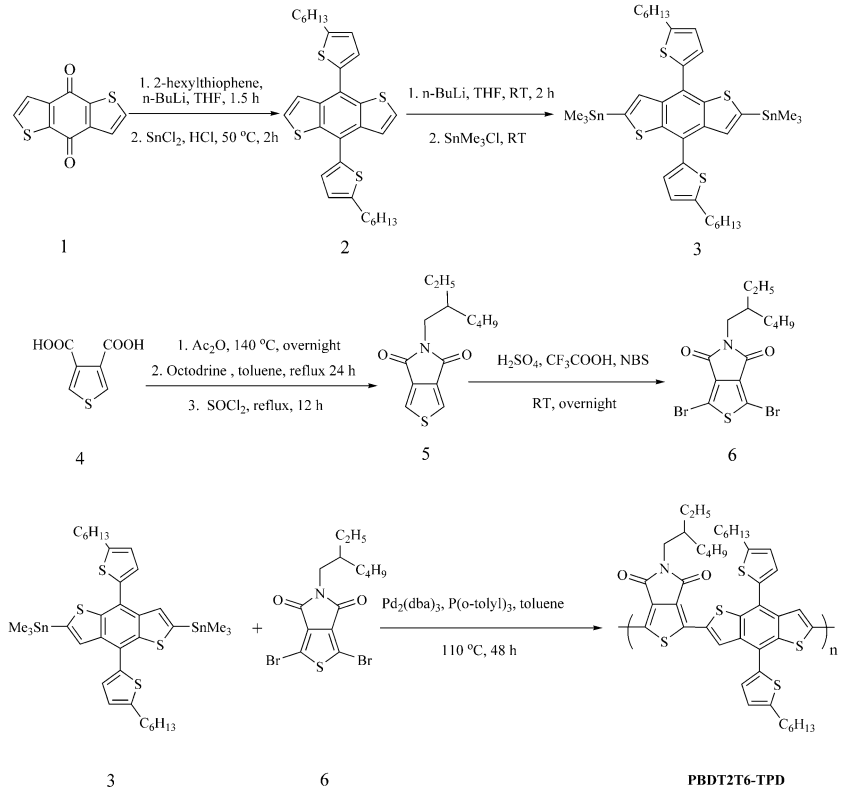
Synthesis of PBDT2T6-TPD.

The monomers TPD (211.5 mg, 0.5 mmol) and BDT (424 mg, 0.5 mmol) were dissolved in toluene (20 mL). The solution was flushed with argon for 10 min, and then $Pd_2(dba)_3$ (9.2 mg, 2 mol% with respect to the monomer) and P(*o*-tolyl)$_3$ (32.72 mg, 16%) were added into the flask. The flask was purged three times with successive vacuum and argon filling cycles. The polymerization reaction was heated to 110 °C, and the mixture was stirred for 24 h under argon atmosphere. The reaction mixture was cooled down to room temperature and precipitated in 100 mL of methanol and filtered. The crude polymer was purified by silica gel column chromatography using chloroform as the eluent. The solid was dried under vacuum for 1 day to obtain the final product (263 mg, yield: 67%, GPC: M_n = 14 kDa, M_w=32 kDa, PDI= 2.29). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.12-8.00 (br, 4H), 7.26-6.50 (br, 2H), 3.98-3.30 (br, 2H), 3.20-2.61 (br, 4H), 2.25-1.20 (br, 22H), 1.20-0.75 (br, 15H).

S2 Device fabrication and characterization

For preparing the ZnO film, the zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, AR grade) and monoethanolamine (MEA, AR grade) were dissolved in 2-ethoxyethanol, and the zinc concentration was 0.5 M. The mixture was stirred to yield a clear homogeneous ZnO precursor solution for further use. The ITO-coated glasses were cleaned in an ultrasonic bath with acetone, ITO detergent, ultra pure water, and isopropyl alcohol for 20 min. The ZnO precursor solution was spin coated at 4000 rpm for 40 s on the ITO coated glass substrate. The films (40 nm) were annealed at 100 ^{o}C for 16 h in an oven, and then the substrates were transferred into glovebox for use. Subsequently, a blend solution of PBDT2T6-TPD and $PC_{61}BM$ (American Dye Sources Inc.) with different weight ratios and additives in chlorobenzene (CB) was spin coated to form the active layers (the concentration 24 mg/mL, 1300 rpm). The thicknesses of the active layers are 90±5 nm. Next, molybdenum oxide (MoO_3, 5 nm) and silver (Ag, 80 nm) were thermally evaporated under 2.0×10^{-4} Pa. As comparison, a conventional structure PBDT2T6-TPD/$PC_{61}BM$ based solar cell with a weight ratio of 2:3 was also prepared. The active area of the device is 0.1 cm^2 defined by shadow mask.

The current density-voltage (*J-V*) characteristics were measured with a Keithley 2420 source measurement unit under simulated 100 mW/cm^2 (AM 1.5 G) irradiation from a Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. The thickness of the active layer was determined by Dektak 150 profilometer. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. Surface morphological characterizations of the films were characterized by a tapping-mode atomic force microscope (AFM, Agilent 5400).



Scheme S1 Synthetic routes of the polymer.

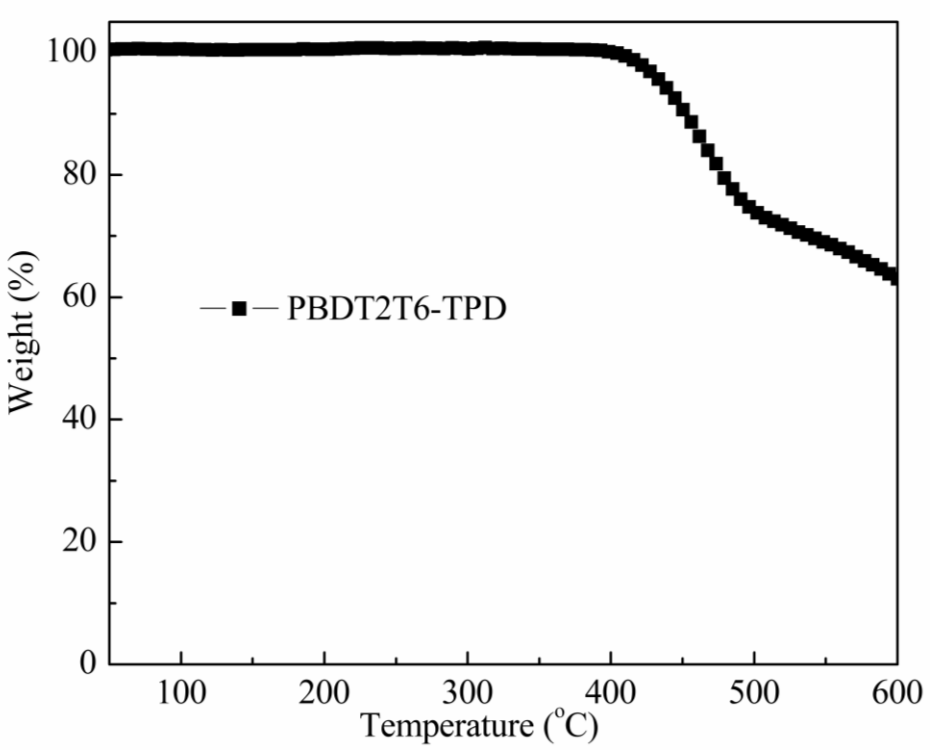


Figure S1 TGA of the polymer

Table S1 Photovoltaic properties of PBDT2T6-TPD:$PC_{61}BM$ solar cell with different conditions

Polymer	D-A ratio	Solvent	Additives	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
PBDT2T6-TPD	1:1	CB	None	0.94	9.48	43.13	3.90
PBDT2T6-TPD	2:3	CB	None	0.95	10.58	48.74	4.88
PBDT2T6-TPD	1:2	CB	None	0.91	9.80	50.25	4.46
PBDT2T6-TPD	1:3	CB	None	0.89	8.10	52.81	3.78
PBDT2T6-TPD	1:2	CB	1%DBH,1%DIO	0.90	10.40	53.84	5.02
PBDT2T6-TPD	1:2	CB	2% DIO	0.86	10.15	51.39	4.49
PBDT2T6-TPD	2:3	CB	3% DIO	0.93	11.57	54.4	5.88
PBDT2T6-TPD	2:3	CB	5%DIO	0.89	12.24	55.02	5.94
PBDT2T6-TPD	2:3	CB	6%DIO	0.90	11.91	54.43	5.80
PBDT2T6-TPD	2:3	CB	5%DBH	0.90	11.87	56.17	6.00
PBDT2T6-TPD	2:3	CB	2%DBH,3%DIO	0.93	11.88	55.20	6.12
PBDT2T6-TPD	2:3	CB	3%DBH,2%DIO	0.92	12.91	56.52	6.73
PBDT2T6-TPD	2:3	CB	3%DBH,3%DIO	0.92	12.17	54.52	6.10
PBDT2T6-TPD[&]	2:3	CB	None	0.92	8.32	53.49	4.11

[&] conventional devices

References

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