

Supporting Information

Novel wide band gap copolymers featuring excellent comprehensive performance towards practical application for organic solar cells

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General Information

1. Materials and Methods

All reagents were commercially available and were used as received without further purification unless otherwise stated. Anhydrous *N,N*-dimethylformamide (DMF) and toluene were distilled from CaH₂ and Na/benzophenone, respectively. [6,6]-phenyl C₇₁ butyric acid methyl ether (PC₇₁BM) was purchased from American Dye Source Inc. Tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄], chlorobenzene (CB, 99+% purity), acetonitrile (99.8%, purity) and 1,8-diiiodoctane (DIO) were purchased from Sigma-Aldrich. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexylthio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene, 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene and 2,2'-Bithiophene-3,3'-imide (BTI) were synthesized according to the reported literatures.^{1,2}

¹H nuclear magnetic resonance (NMR): ¹HNMR spectra were recorded on a Bruker AV-400 MHz spectrometer in *d*-chloroform with TMS as the internal standard. Chemical shifts were expressed in parts per million (ppm).

Thermogravimetric analysis (TGA): TGA was carried out on a METTLER TOLEDO TGA/DSC1/1100 LF apparatus operated at a heating rate of 10 °C min⁻¹ under N₂ atmosphere.

High temperature gel permeation chromatography (GPC): The GPC experiments were performed on a PL-GPC 220 instrument. Polymer was dissolved in 1,2,4-trichlorobenzene (TCB) at 130 °C with shaking for 1 h for complete dissolution. The obtained molecular weights were calibrated with the classical polystyrene standard.

UV-vis: UV-vis absorption spectra were recorded on a Lambda 750 spectrometer (Perkin-Elmer). The solution absorption spectra of polymers were performed on 10⁻⁵ M (based on repeating units) chlorobenzene solutions, and the film absorption spectra were collected from films spin-casted from 5 mg mL⁻¹ chlorobenzene solutions.

Differential scanning calorimetry (DSC): DSC profiles were performed on a TA Q100 DSC with a heating and cooling rate of 10 °C min⁻¹ under N₂.

Cyclic voltammetry (CV) measurements: The electrochemical properties of the polymer films were performed on a CHI600D electrochemical instrument in anhydrous acetonitrile at a scan rate 50 mV s⁻¹ under nitrogen. Tetrakis-(n-butyl)ammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) was employed as the electrolyte. A glassy carbon electrode, a Ag/AgNO₃ electrode, and a Pt wire were used as the working electrode, reference and counter electrode, respectively. Polymer films were drop-casted onto the glassy carbon working electrode from a 5 mg mL⁻¹ CB solution. The potential of Ag/AgNO₃ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc⁺). The electrochemical onsets

were determined at the position where the current starts to differ from the baseline.

The HOMO energy levels were calculated from the equation (1):

$$\text{HOMO (eV)} = - (E_{ox}^{onset} + 4.8) \text{eV} \quad (1)$$

LUMO energy levels were obtained by combining the HOMO and optical band gap values of the films.

Two-dimensional grazing incidence wide angle X-ray scattering (2D-GIWAXS):

2D-GIWAXS patterns were obtained at BL14B1 at Shanghai Synchrotron Radiation Facility (SSRF) ($\lambda = 0.69 \text{ \AA}$). The neat films were annealed at 100 °C for 10 mins.

X-ray diffraction (XRD): XRD profiles were obtained by using a Bruker D8

Discover Reflector with X-ray generation power of 40 kV tube voltage and 40 mA tube current. The samples were scanned by detector scan mode across a range of $2\theta = 2^\circ$ - 30° , with a step size of 0.05° and accounting period of 5 s step^{-1} .

Transmission electron microscopy (TEM): The TEM images were acquired at

Tecnai G2 F20 operated at an acceleration voltage of 200 KV.

External quantum efficiencies (EQE): The EQE spectra of devices were measured

using chopped monochromatic light from a xenon lamp under ambient conditions. A standard silicon solar cell was used as a reference to determine the light intensity at each wavelength.

Film thickness: Film thickness of each thin film was measured by the profiler (D-100

Stylus Profilometer, KLA Tencor).

2. Device fabrication and thermal stability testing

Polymer solar cells (PSCs) with conventional device structure of indium-tin oxide(ITO)/poly(ethylenedioxythiophene)(PEDOT):poly(styrenesulfonate)(PSS)/Polymer: PC₇₁BM/LiF/Al were fabricated as follows. The ITO-coated glass substrates were cleaned in sequence with detergent, deionized water, isopropyl alcohol and acetone. After the cleaned ITO substrates were treated with UV ozone for 25 mins, the substrates were covered with a 30 nm PEDOT:PSS layer by spin-coating. Then the substrates were thermal annealing at 150 °C for 15 mins and transferred into a glove box with N₂. Polymer/PC₇₁BM CB solutions (8 mg ml⁻¹) with/without DIO were spin-coated onto the PEDOT:PSS layer to form the active layer. Methanol treatment was carried out by spin-coating methanol onto the top of active layer at 4000 rpm for 30 s. Afterwards, the photoactive layers were thermally annealed at different conditions in a glove box. The devices were completed by evaporation of a layer of LiF (8 Å)/Al (120 nm) as cathode. The active layer area of each device was 0.09 cm². The *J-V* characteristics of photovoltaic devices were measured by Keithley-2400 source meter in a glove box using a solar simulator (SAN-EI, XES-70S1) at AM 1.5 G illumination of 100 mW cm⁻².

Device thermal stability testing. The testing devices were fabricated under the same procedure described in Device Fabrication. After spin-coating of the active layer, the devices without encapsulation were transferred to a hot plate at 100 °C in a N₂-filled glove box and annealing for 24 h, 48 h, 72 h, 96 h and 120 h, respectively. Then, the devices were quenched to room temperature and completed by evaporation of a layer of LiF (8 Å)/Al (120 nm) as cathode. The active layer area of each device was

0.09 cm². Device performance was measured under AM 1.5G solar illumination at 100 mW/cm² (1 sun). Eight devices were measured to obtain the average PCE.

3. Space charge limited current (SCLC) measurement

The hole and electron mobilities were measured by the space charge limited current (SCLC) method with a hole-only and electron-only device with structure of ITO/PEDOT:PSS/activelayer/Au/Al and ITO/ZnO/activelayer/LiF/Al, respectively. The device fabrication procedure was almost the same as that of polymer solar cells. The area for each device was 0.09 cm², as defined by a shadow mask. The SCLC hole mobility was estimated by fitting the hole-only I - V curves with SCLC model and the Mott-Gurney law:

$$\ln(I / V^2) = 0.89\beta(V / L)^{1/2} + \ln(9\mu\epsilon_0\epsilon S / (8L^3)) \quad (2)$$

where I is the current, V is the applied voltage, β is the field activation factor, L is the thickness of polymer film, μ is the mobility, ϵ_0 is the permittivity of free space, ϵ is the relative permittivity, and S is the area of polymer film. The measurement of hole mobility was conducted in the dark on a computer-controlled Keithley 2400 source-measure unit.

4. Synthesis of polymers

PBTIBDTT: An air-free flask was charged with 2,6-bis(trimethyltin)-4,8-bis (5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']-dithiophene (0.1 mmol, 90.4 mg), *N*-(2-hexyldecyl)-5'5-bis[5-bromo-3-(decylthio)thiophene-2-yl]-2'2-bithiophene-3'3-dicarboximide (0.1 mmol, 106.3 mg) and Pd(PPh₃)₄ (0.002 mmol, 2.3 mg). After 3 freeze/pump/thaw cycles with argon, anhydrous toluene (10 ml) and DMF (1 ml)

were added into the flask. The sealed reaction flask was stirred at 95 °C for 6 hours. Then, 0.2 ml 2-(tributylstannyl)thiophene was injected and the mixture was stirred at 95 °C for 10 hours. Finally, 0.3 ml 2-bromothiophene was injected and the reaction mixture was continuously stirred at 95 °C for another 10 hours. When the reactant was cooled to room temperature, the mixture was precipitated into 200 ml methanol. After filtration, the crude product was purified by soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform, successively. The chloroform fraction was precipitated into methanol with vigorous stirring. Then the precipitate was collected and dried in vacuum to get a dark solid as the product PBTIBD TT copolymer (100 mg, 67%). $M_n = 36.1$ KDa, PDI = 2.02. $^1\text{H NMR}$ (400 MHz, *o*-dichlorobenzene- d_4 , 100 °C, TMS/ppm, δ): 7.71 (br, 2H), 7.64 (br, 2H), 7.27 (br, 2H), 6.87 (br, 2H), 6.79 (br, 2H), 4.21 (br, 2H), 2.68 (br, 8H), 1.95 (br, 1H), 1.71 (br, 2H), 1.51 (br, 8H), 1.45-0.90 (br, 64H), 0.76 (br, 12H), 0.66 (br, 12H).

PBTIBD TT-S: An air-free flask was charged with 2,6-bis(trimethyltin)-4,8-bis (5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]-dithiophene (0.1 mmol, 96.9 mg), *N*-(2-hexyldecyl)-5'5-bis[5-bromo-3-(decylthio)thiophene-2-yl]-2'2-bithiophene-3'3-dicarboximide (0.1 mmol, 106.3 mg) and Pd(PPh₃)₄ (0.002 mmol, 2.3 mg). After 3 freeze/pump/thaw cycles with argon, anhydrous toluene (10 ml) and DMF (1 ml) were added into the flask. The sealed reaction flask was stirred at 110 °C for 48 hours. Then, 0.2 ml 2-(tributylstannyl)thiophene was injected and the mixture was stirred at 95 °C for 10 hours. Finally, 0.3 ml 2-bromothiophene was injected and the mixture was continuously stirred at 95 °C for another 10 hours. When the reactant was cooled

to room temperature, the mixture was precipitated into 200 ml methanol. After filtration, the crude product was purified by soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform, successively. The chloroform fraction was precipitated into methanol with vigorous stirring. Then the precipitate was collected and dried in vacuum to get a dark solid as the product PBTIBDTT-S copolymer (110 mg, 71%). $M_n = 25.8$ KDa, PDI = 2.71. ^1H NMR (400 MHz, *o*-dichlorobenzene- d_4 , 100 °C, TMS/ppm, δ): 7.68 (br, 2H), 7.59 (br, 2H), 7.28 (br, 2H), 7.10 (br, 2H), 6.87 (br, 2H), 4.21 (br, 2H), 2.81 (br, 4H), 2.63 (br, 4H), 1.96 (br, 1H), 1.71 (br, 2H), 1.65-0.90 (br, 72H), 0.85-0.5 (br, 24H).

Reference

- 1 D. Yang, T. Zhang, X. Zhao, G. Zeng, Z. Li, Y. Tian, F. He, J. Zhang, X. Yang, *Polym. Chem.* **2016**, 7, 5366.
- 2 J. Warnan, C. Cabanetos, R. Bude, A. El Labban, L. Li, P. M. Beaujuge, *Chem. Mater.* **2014**, 26, 2829.

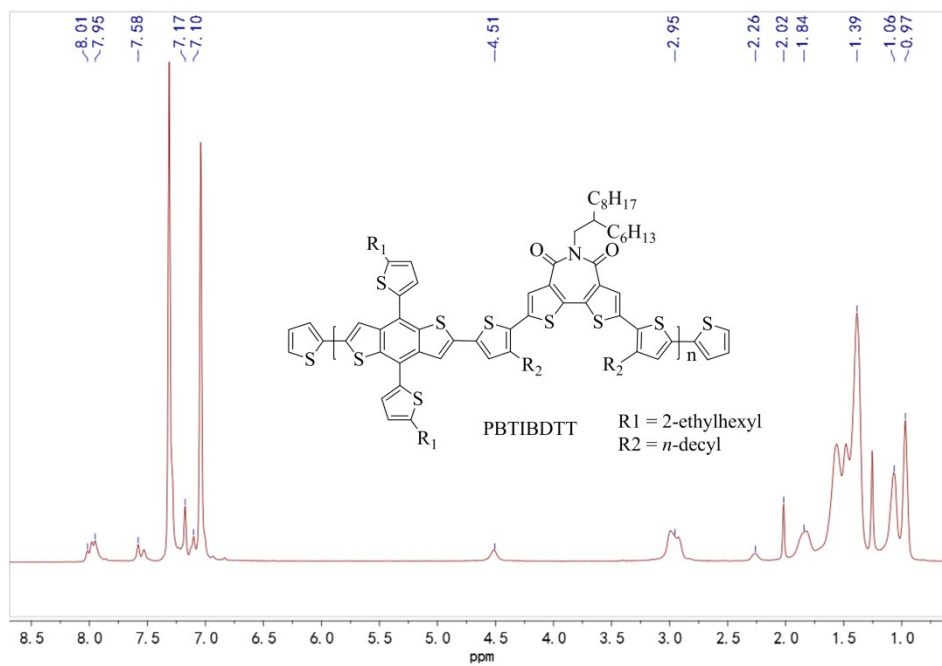


Figure S1. ¹H NMR spectrum of polymer PBTIBDTT in *o*-dichlorobenzene-*d*₄ at 100 °C.

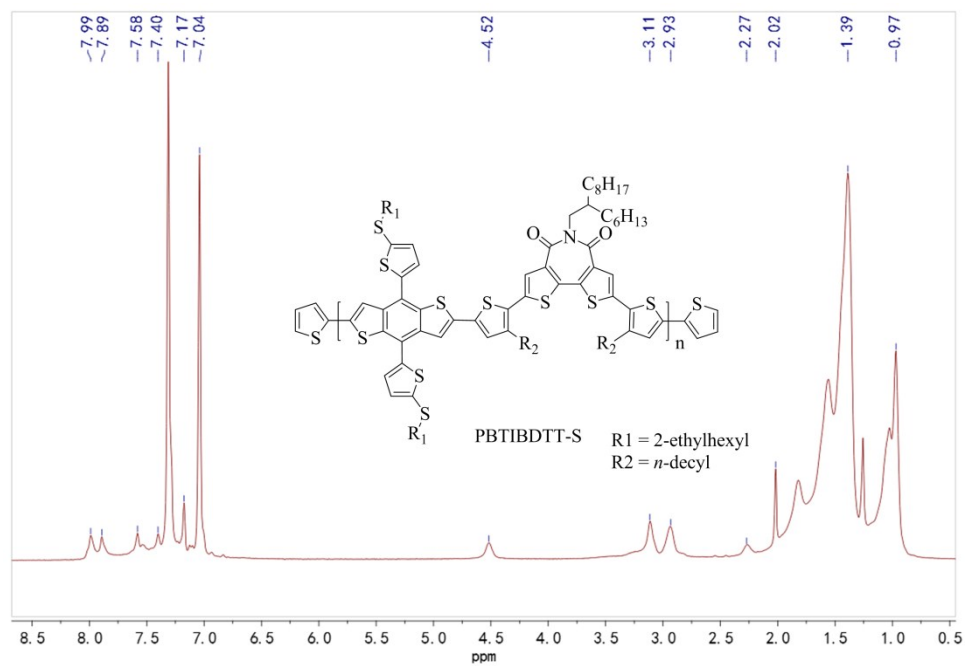


Figure S2. ¹H NMR spectrum of polymer PBTIBDTT-S in *o*-dichlorobenzene-*d*₄ at 100 °C.

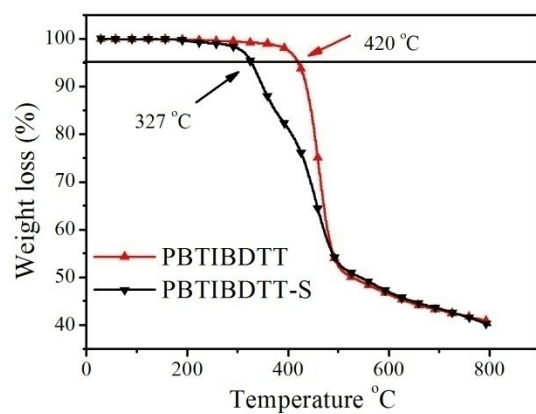


Figure S3. TGA curves of PBTIBDTT and PBTIBDTT-S at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

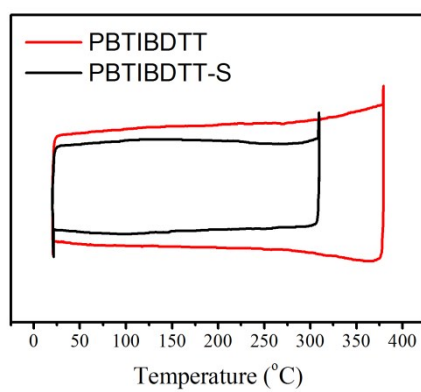


Figure S4. DSC curves of PBDTTBTI and PBDTTBTI-S with heating ramp of 10 °C min⁻¹.

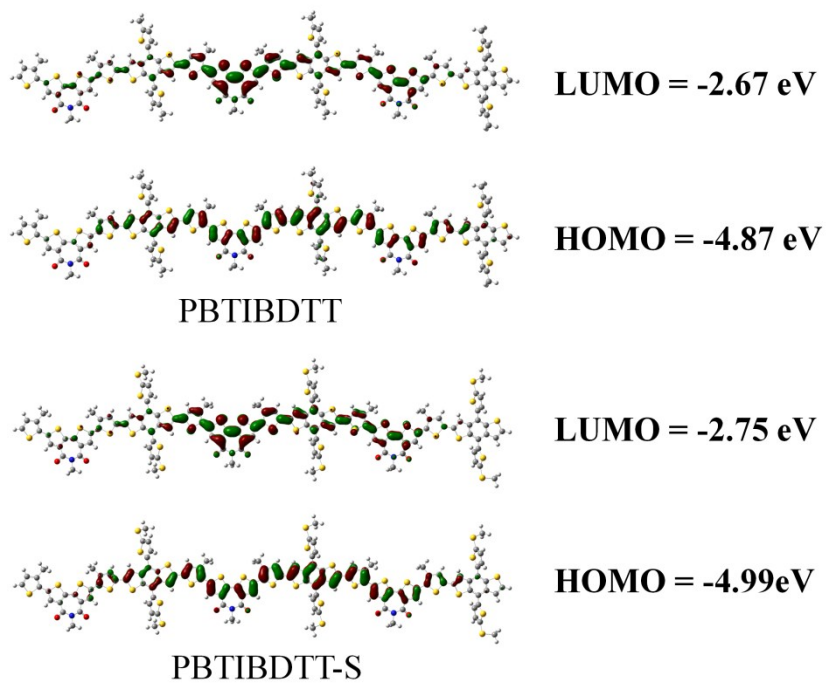


Figure S5. Electron density contours for PBTIBDTT and PBTIBDTT-S trimers.

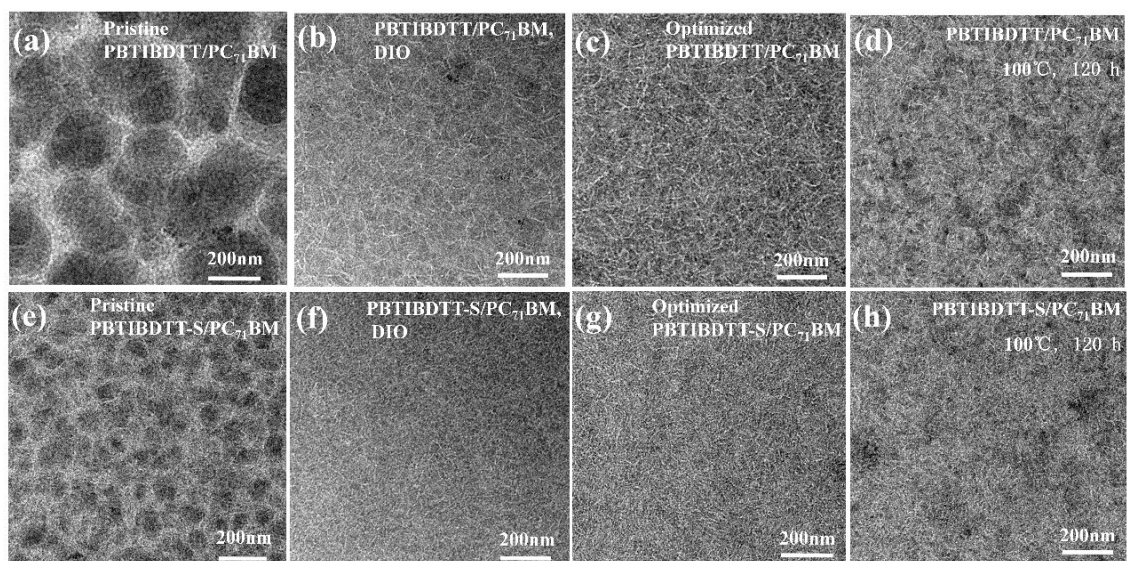


Figure S6. The course of microstructure evolution of the blend films under different treatments.

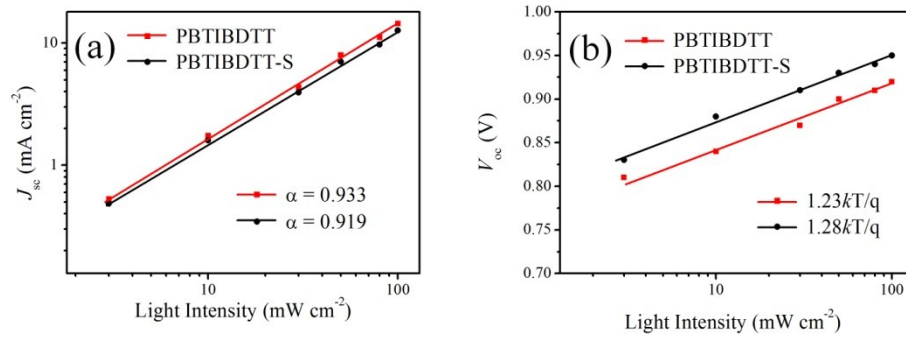


Figure S7. Light intensity of dependence of (a) J_{sc} and (b) V_{oc} in PBTIBDTT and PBTIBDTT-S devices.

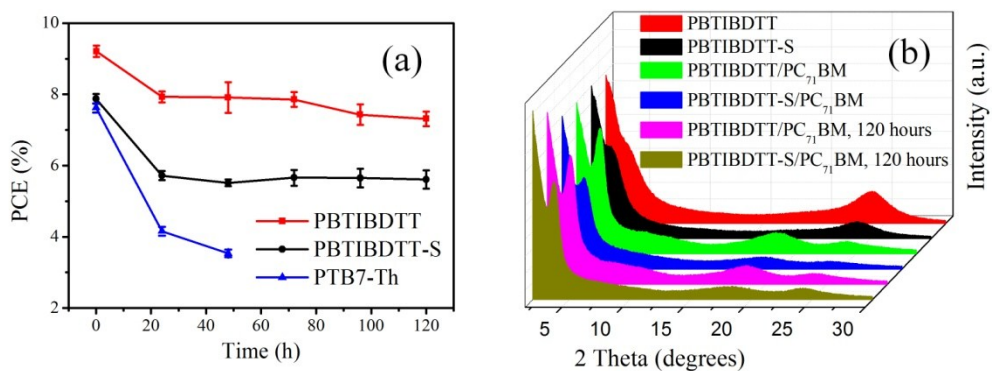


Figure S8. (a) The PCEs variation of PBTIBDTT, PBTIBDTT-S and PTB7-Th devices annealed at 100 °C for different times. (b) The out-of plane XRD spectra of PBTIBDTT and PBTIBDTT-S under different conditions.

Table S1. The number-average molecular weights (M_n), polydisperse indexes (PDI), optical and electrochemical properties of PBTIBDTT and PBTIBDTT-S.

Polymers	M_n^a [KDa]	PDI	Solution [λ_{max} , nm]	Film [λ_{max} , nm]	E_g^b [eV]	HOMO ^{c)} [eV]	LUMO ^{c)} [eV]
PBTIBDTT	36.1	2.0	365, 569, 602	366, 562, 605	1.87	-5.47	-2.79
PBTIBDTT-S	25.8	2.7	371, 568, 589	378, 568, 603	1.88	-5.53	-2.85

^{a)}Number-average molecular weight (M_n) determined by GPC at 130 °C with 1,2,4-trichlorobenzene as eluent; ^{b)}Optical band gaps were calculated from the absorption onsets (λ_{onset}) of the films; ^{c)}HOMO and LUMO energy levels were determined from cyclic voltammetry.

Table S2. The characteristics of PBTIBDTT/PC₇₁BM device under various conditions.

PBTIBDTT/PC ₇₁ BM [(w/w)]	DIO [% , v/v]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^{a)} [%]	Thickness [nm]
1:1	0	0.93	6.03	47.97	2.69 (2.31)	80
1:1	1	0.90	10.75	69.97	6.78 (6.70)	75
1:1	2	0.90	10.28	71.70	6.63 (6.40)	88
1:1	3	0.91	9.47	56.61	4.88 (4.61)	107
1:0.8	1	0.90	11.07	69.84	6.96 (6.60)	119
1:2	1	0.88	12.83	65.76	7.43 (7.22)	168
1:3	1	0.88	12.24	65.44	7.05 (6.78)	173
1:2 ^b	1	0.88	13.45	69.14	8.18 (7.88)	230
1:2 ^{b, c}	1	0.91	14.53	71.29	9.42 (9.21)	225

^aAverage PCE in parentheses from 10 devices; ^bMethanol treatment; ^cThermal annealing 10 mins at 100 °C.

Table S3. The characteristics of PBTIBDTT-S/PC₇₁BM device under various conditions.

PBTIBDTT-S /PC ₇₁ BM (w/w)	DIO [% _v , v/v]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^{a)} [%]	Thickness [nm]
1:1	0	0.91	6.41	34.46	2.01(1.88)	85
1:1	1	0.96	11.71	64.89	7.30 (7.14)	82
1:1	2	0.95	10.62	64.83	6.54 (6.35)	112
1:1	3	0.96	9.60	61.33	5.65 (5.42)	120
1:0.8	1	0.95	10.58	62.26	6.26 (6.17)	100
1:1	1	0.96	11.71	64.89	7.30 (7.14)	82
1:2	1	0.94	9.91	63.76	5.94 (5.88)	110
1:3	1	0.94	10.99	55.59	5.74 (5.52)	112
1:1 ^b	1	0.96	11.98	69.76	8.02 (7.88)	78
1:1 ^{b, c}	1	0.98	11.53	62.84	7.10 (7.01)	80

^{a)}Average PCE in parentheses from 10 devices; ^{b)}Methanol treatment; ^{c)}Thermal annealing 10 mins at 100 °C.

Table S4. The statistical data of optimized PSCs.

Polymer	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	PCE ^a (%)	Thickness (nm)
PBTIBDTT	0.91	14.53	71.29	9.42	9.21	225
	0.91	14.16	69.85	9.00		
	0.91	14.31	70.12	9.13		
	0.91	14.55	69.69	9.23		
	0.90	14.41	71.56	9.28		
	0.91	14.52	70.06	9.26		
	0.91	14.34	69.17	9.02		
	0.91	14.30	69.58	9.05		
	0.91	14.76	69.94	9.39		
	0.91	14.52	70.53	9.32		
PBTIBDTT-S	0.96	11.98	69.76	8.02	7.88	78
	0.95	11.87	69.43	7.83		
	0.95	12.04	66.59	7.61		
	0.96	12.01	68.68	7.92		
	0.97	11.78	69.42	7.93		
	0.96	11.90	69.43	7.93		
	0.96	11.74	70.21	7.91		
	0.96	11.70	69.77	7.84		
	0.96	11.49	70.82	7.81		
	0.96	11.76	70.33	7.94		

^a)Average PCE in parentheses from 10 devices.

Table S5. Mobilities of neat polymers and blend films under the optimal conditions.

Material	Hole mobilities				Electron mobilities	
	Neat film	Thickness	Blend film	Thickness	Blend film	Thickness
	[cm ² V ⁻¹ s ⁻¹]	[nm]	[cm ² V ⁻¹ s ⁻¹]	[nm]	[cm ² V ⁻¹ s ⁻¹]	[nm]
PBTIBDTT	8.26×10^{-4}	214	1.95×10^{-3}	171	1.33×10^{-4}	175
PBTIBDTT-S	5.94×10^{-5}	102	4.45×10^{-4}	106	1.11×10^{-5}	140

NOTE: The low electron mobility for PBTIBDTT-S device might result from the low PCBM content (50%, w/w) with respect to the PBTIBDTT device (66%, w/w).

Table S6. The characteristics of PBTIBDTT-S/PC₇₁BM device with different active layer thickness.

Polymer	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]	Thickness [nm]
PBTIBDTT-S	0.95	9.70	67.22	6.20 (5.83)	178
	0.96	9.75	68.01	6.37 (6.03)	157
	0.95	10.06	68.55	6.55 (6.24)	133
	0.96	10.26	69.33	6.82 (6.50)	93
	0.96	11.98	69.76	8.02 (7.88)	78
	0.96	10.50	70.08	7.07 (6.85)	65

^a)Average PCE in parentheses from 10 devices.

Table S7. The statistical data of PBTIBD TT-S/PC₇₁BM device with different active layer thickness.

Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	PCE ^a (%)
280	0.88	13.84	71.05	8.65	8.54
	0.88	13.52	70.60	8.40	
	0.88	13.91	70.42	8.62	
	0.90	13.34	70.74	8.49	
	0.88	13.64	70.20	8.43	
	0.90	13.78	69.91	8.67	
	0.91	13.62	68.99	8.55	
	0.91	13.45	70.03	8.57	
	0.91	13.72	67.84	8.47	
	0.91	13.68	68.92	8.58	
260	0.90	13.91	70.40	8.81	8.58
	0.90	13.77	67.58	8.38	
	0.90	13.76	70.81	8.77	
	0.90	13.69	68.93	8.50	
	0.90	13.63	68.95	8.46	
	0.90	13.93	68.40	8.58	
	0.91	13.46	71.05	8.70	
	0.92	13.46	67.85	8.40	
	0.92	13.87	67.68	8.64	
	0.91	13.68	68.92	8.58	
225	0.91	14.53	71.29	9.42	9.21
	0.91	14.16	69.85	9.00	
	0.91	14.31	70.12	9.13	
	0.91	14.55	69.69	9.23	
	0.90	14.41	71.56	9.28	
	0.91	14.52	70.06	9.26	
	0.91	14.34	69.17	9.02	
	0.91	14.30	69.58	9.05	
	0.91	14.76	69.94	9.39	
	0.91	14.52	70.53	9.32	
195	0.89	13.94	71.33	8.85	8.72
	0.88	13.56	69.78	8.33	
	0.92	12.98	72.77	8.69	
	0.90	13.94	70.53	8.85	

	0.91	13.65	69.82	8.67	
	0.91	13.54	71.70	8.83	
	0.91	13.65	70.90	8.81	
	0.92	13.51	71.05	8.83	
	0.91	13.42	70.22	8.58	
	0.91	13.57	71.03	8.77	
	0.90	13.02	72.96	8.55	
	0.93	12.05	73.26	8.21	
	0.90	12.65	72.67	8.27	
	0.90	12.87	72.52	8.40	
175	0.92	12.74	72.70	8.52	8.28
	0.90	11.68	74.99	7.88	
	0.92	12.45	71.50	8.19	
	0.91	12.54	71.72	8.18	
	0.93	12.05	73.26	8.21	
	0.91	12.83	71.69	8.37	

^{a)}Average PCE in parentheses from 10 devices.

Table S8. The characteristics of PBTIBDTT/PC₇₁BM device annealed at 100 °C for different times.

V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]	Time [100°C]
0.89	14.38	63.36	8.11 (7.93)	24h
0.87	14.09	67.34	8.26 (7.91)	48h
0.88	14.18	65.24	8.14 (7.85)	72h
0.87	13.65	66.14	7.85 (7.43)	96h
0.87	13.40	65.30	7.62 (7.31)	120h

^a)Average PCE in parentheses from 10 devices.

Table S9. The characteristics of PBTIBD TT-S/PC₇₁BM device annealed at 100 °C for different times.

V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]	Time [100°C]
0.93	11.10	57.30	5.91 (5.72)	24h
0.91	11.02	56.42	5.66 (5.52)	48h
0.90	11.34	57.60	5.88 (5.66)	72h
0.88	11.57	57.50	5.86 (5.65)	96h
0.90	11.23	57.66	5.83 (5.61)	120h

^a)Average PCE in parentheses from 10 devices.

Table S10. The characteristics of PTB7-Th/ PC₇₁BM device annealed at 100 °C for different times.

V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]	Time [100°C]
0.79	14.35	69.67	7.90 (7.64)	0 h
0.78	12.66	43.22	4.27 (4.16)	24 h
0.77	11.92	40.28	3.70 (3.54)	48 h

^a) Average PCE in parentheses from 10 devices.