

Supporting Information

A zigzag fused-ring building block for polymer solar cells

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1. General characterization

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters 1515 series GPC coupled with UV-vis detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was done by using a Perkin-Elmer Diamond TG/DTA thermal analyzer under nitrogen. Cyclic voltammetry was done on a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). A glassy carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag⁺ electrode was used as the reference electrode. Polymers were coated onto glassy carbon electrode and all potentials were corrected against Fc/Fc⁺. AFM was performed on a Dimension 3100 microscope (Veeco) using tapping mode. X-ray diffraction (XRD) of thin films was performed on a Rigaku D/max-2500 X-ray diffractometer in reflection mode by using Cu K α radiation (40 kV, 200 mA).

2. Synthesis

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co., Lyntech Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. 1,5-Dibromonaphthalene-2,6-dicarboxylic acid (**1**)¹ and *N*-(2-octyldodecyl)thiophen-3-amine² were prepared according to literatures.

1,5-Dibromo-*N*²,*N*⁶-bis(2-octyldodecyl)-*N*²,*N*⁶-di(thiophen-3-yl)naphthalene-2,6-dicarboxamide (2**).** To a solution of 1,5-dibromonaphthalene-2,6-dicarboxylic acid (**1**) (0.99 g, 2.65 mmol) in dry CH₂Cl₂ (50 mL) were added oxalyl chloride (3 mL, 45.6 mmol) and 2 drops of DMF. The mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure to obtain 1,5-dibromonaphthalene-2,6-dichloride, which was used in next step without purification. To the solution of 1,5-dibromonaphthalene-2,6-dichloride in dry CH₂Cl₂ (30 mL) was slowly added a solution of *N*-(2-octyldodecyl)thiophen-

3-amine (2.5 g, 14.5 mmol) and Et₃N (2 mL) in dry CH₂Cl₂ (30 mL) at 0 °C. The mixture was stirred at room temperature overnight. Then the mixture was poured into water and extracted with CHCl₃ for three times. The organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was then purified via silica gel column by using CH₂Cl₂ as eluent to give compound **2** as a yellow solid (2.38 g, 81.8%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.05 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.00-7.02 (m, 2H), 6.93 (br, 2H), 6.81 (d, *J* = 4.8 Hz, 2H), 4.03 (br, 2H), 3.69 (br, 2H), 1.65-1.59 (br, 2H), 1.35-1.26 (m, 64H), 0.90-0.87 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 168.71, 139.66, 138.67, 131.95, 127.05, 126.18, 125.41, 120.80, 119.89, 52.09, 36.17, 31.91, 31.90, 31.20, 30.05, 29.63, 29.58, 29.34, 29.31, 26.31, 22.68, 14.11.

7,14-Bis(2-octyldodecyl)thieno[3',2':3,4]isoquinolino[6,5-*f*]thieno[3,2-*c*]isoquinoline-6,13(7*H*,14*H*)-dione (zTITI). To a solution of compound **2** (1.28 g, 1.17 mmol) in N,N-dimethylacetamide (60 mL) were added PCy₃·HBF₄ (300 mg, 0.81 mmol), Cs₂CO₃ (1.5 g, 4.6 mmol) and Pd(OAc)₂ (150 mg, 0.67 mmol) under Ar. The mixture was stirred at 120 °C overnight and then cooled to room temperature. The mixture was poured into ice water and extracted with CHCl₃ for three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was then purified via silica gel column by using petroleum ether/CH₂Cl₂ (1:4) as eluent to give zTITI as a yellow solid (719 mg, 65.7%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 9.10 (d, *J* = 9.0 Hz, 2H), 8.85 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 5.6 Hz, 2H), 7.28 (d, *J* = 5.7 Hz, 2H), 4.39 (br, 4H), 2.09 (br, 2H), 1.42-1.20 (m, 64H), 0.86-0.81 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 161.51, 141.36, 131.51, 130.31, 127.65, 126.69, 124.06, 123.42, 117.13, 115.64, 49.72, 37.15, 31.88, 31.84, 31.65, 29.95, 29.59, 29.53, 29.49, 29.29, 29.25, 26.64, 22.64, 22.62, 14.06.

2,9-Dibromo-7,14-bis(2-octyldodecyl)thieno[3',2':3,4]isoquinolino[6,5-*f*]thieno[3,2-*c*]isoquinoline-6,13(7*H*,14*H*)-dione (zTITI-Br). To a solution of zTITI (109 mg, 0.117 mmol) in mixed solvents of CHCl₃ (15 mL) and DMF (10 mL) was added NBS (45.6 mg, 0.256 mmol) under Ar. The mixture was stirred at room temperature for 24 h in the dark, and then

was poured into water and extracted with CHCl₃ for three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was then purified via silica gel column by using petroleum ether/CH₂Cl₂ (1:3) as eluent to give **zTITI-Br** as a yellow solid (86 mg, 67.7%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.79 (br, 4H), 7.25 (s, 2H), 4.31 (br, 4H), 2.05 (br, 2H), 1.38-1.21 (m, 64H), 0.87-0.82 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 161.04, 140.90, 130.98, 130.03, 126.88, 123.85, 123.59, 120.17, 117.03, 116.60, 49.92, 37.10, 31.90, 31.86, 31.66, 29.97, 29.61, 29.54, 29.50, 29.30, 29.26, 26.59, 22.65, 22.62, 14.03. MALDI-TOF MS (m/z): 1093.6 (M⁺).

Poly{2,5-thiophene-alt-2,9-(7,14-bis(2-octyldodecyl))thieno[3',2':3,4]isoquinolino[6,5-f]thieno[3,2-c]isoquinoline-6,13(7H,14H)-dione} (PThzTITI). **zTITI-Br** (87.6 mg, 0.080 mmol) and 2,5-bis(trimethylstannyl)thiophene (32.8 mg, 0.080 mmol) were dissolved in 30 mL toluene, and the solution was flushed with argon for 15 min, then 8 mg Pd(PPh₃)₄ was added into the solution. The mixture was flushed again with argon for 20 min. The reaction solution was heated to reflux for 24 h. Then the solution was cooled to room temperature and added dropwise to 150 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, hexane and chloroform in sequence. The chloroform fraction was concentrated and added dropwise into methanol. Then the precipitate was collected and dried under vacuum overnight to give **PThzTITI** as a dark red solid (62 mg, 76.3%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.86 (br, 4H), 7.52-6.17 (br, 4H), 4.37 (br, 4H), 2.11-0.81 (br, 78H). Elemental analysis (%) calcd for C₆₄H₉₀N₂O₂S₃: C, 75.69; H, 8.93; N, 2.76. Found: C, 75.54; H, 8.91; N, 2.81.

Poly{2,5-selenophene-alt-2,9-(7,14-bis(2-octyldodecyl))thieno[3',2':3,4]isoquinolino[6,5-f]thieno[3,2-c]isoquinoline-6,13(7H,14H)-dione} (PSezTITI). **PSezTITI** was synthesized by following the same procedures for **PThzTITI**. **zTITI-Br** (97.3 mg, 0.087 mmol) and 2,5-bis(trimethylstannyl)selenophene (40.6 mg, 0.087 mmol) were used as start materials. **PSezTITI** was obtained as a dark purple solid (90 mg, 95.2%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.85 (br, 4H), 7.52-6.28 (br, 4H), 4.40 (br, 4H), 2.11-0.81 (br, 78H). Elemental analysis

(%) calcd for $C_{64}H_{90}N_2O_2S_2Se$: C, 72.35; H, 8.54; N, 2.64. Found: C, 72.37; H, 8.35; N, 2.77.

3. ^1H NMR

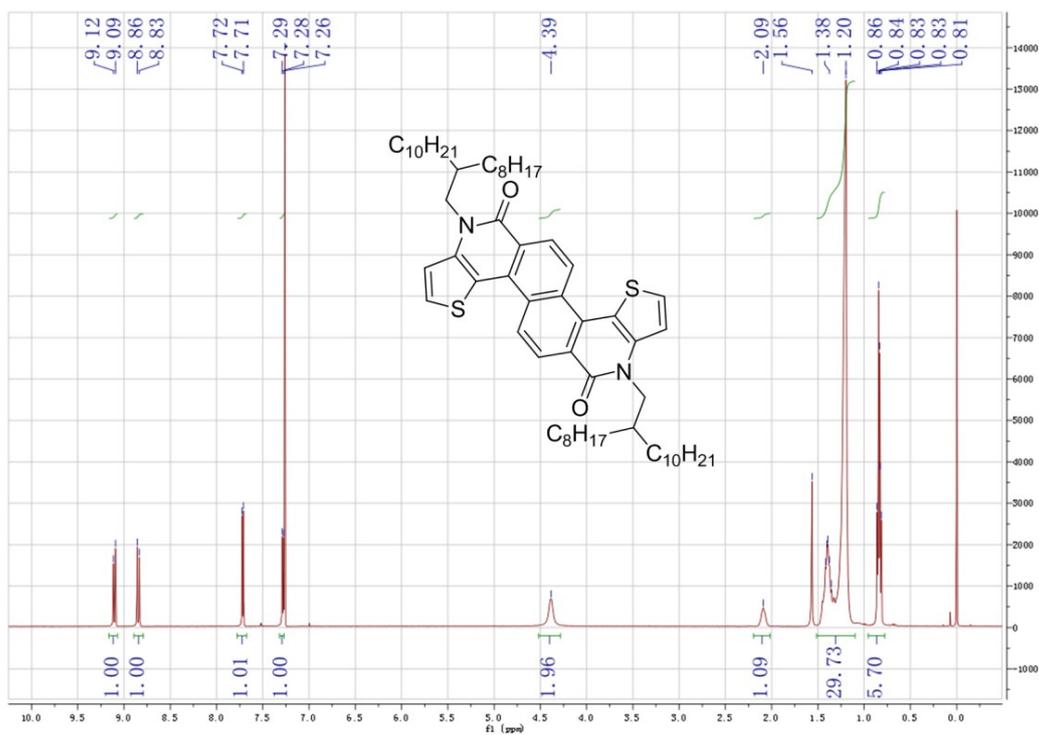


Fig. S1 ^1H NMR spectrum of zTITI.

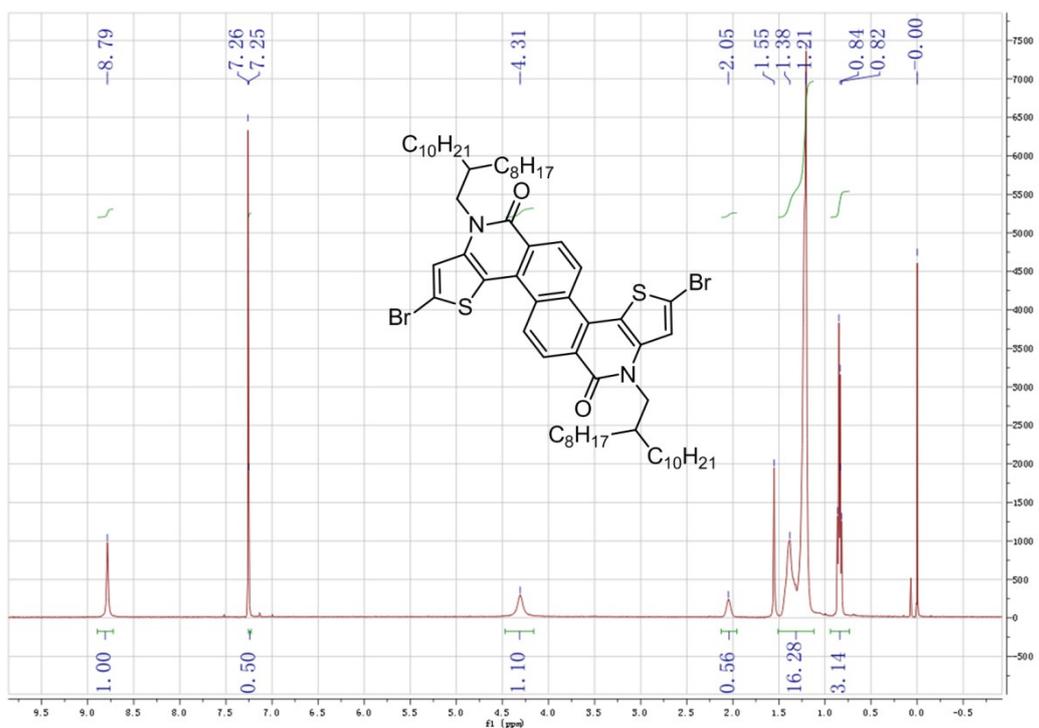


Fig. S2 ^1H NMR spectrum of zTITI-Br.

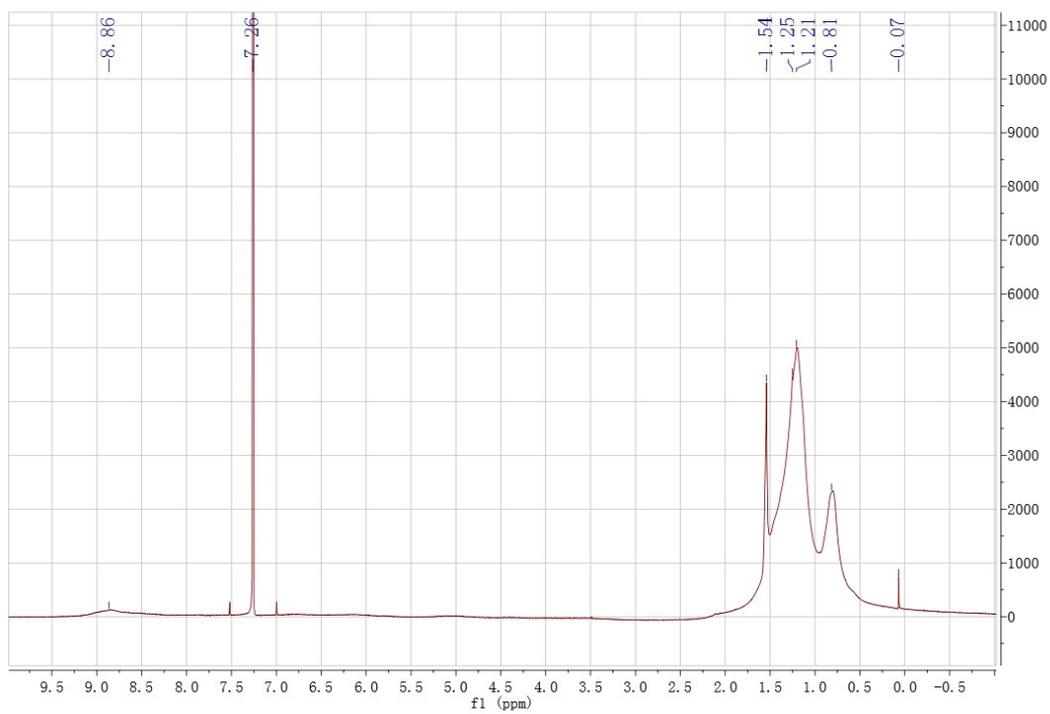


Fig. S3 ^1H NMR spectrum of PThzTITL.

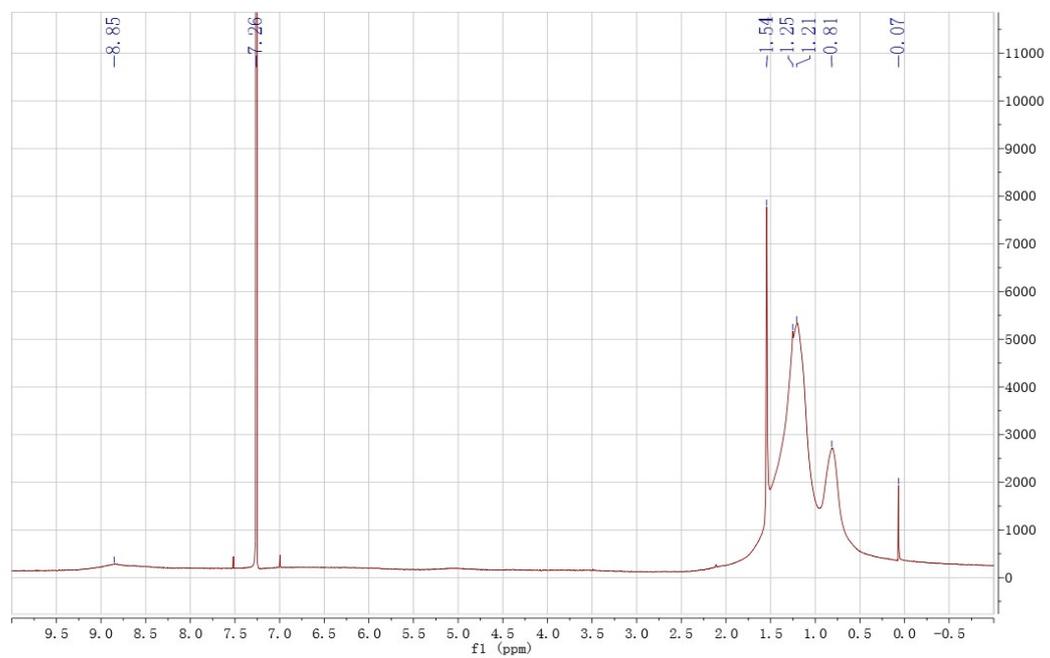


Fig. S4 ^1H NMR spectrum of PSezTITL.

4. TGA

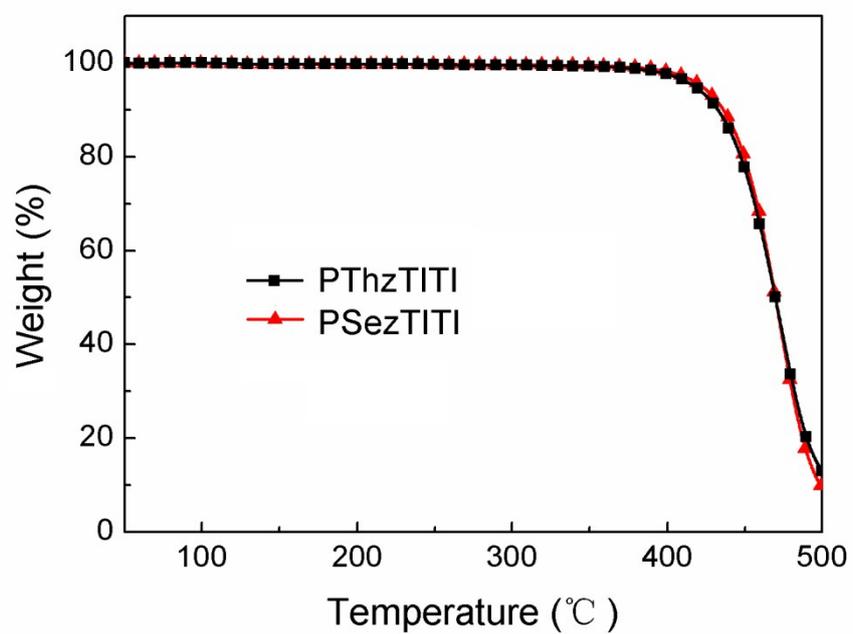


Fig. S5 TGA curves for PThzTITI and PSezTITI.

5. CV

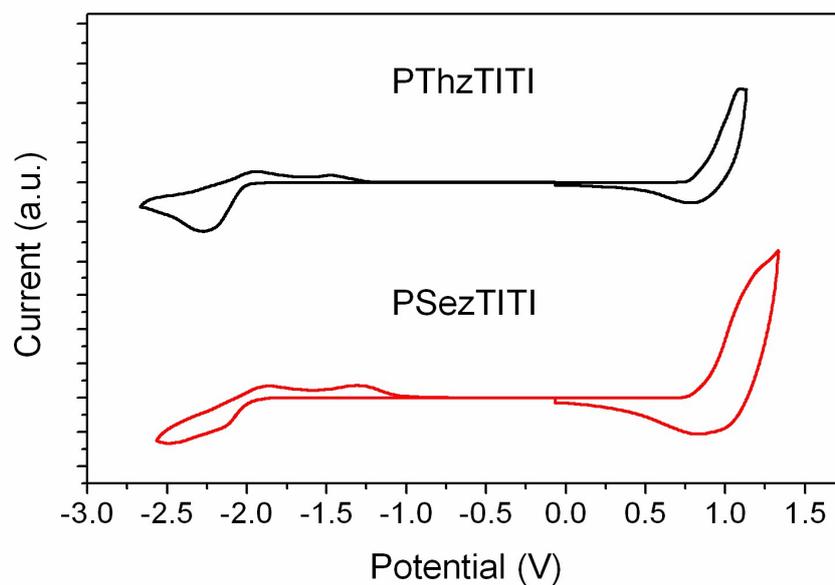


Fig. S6 Cyclic voltammograms for PThzTITI and PSezTITI.

6. Device fabrication and measurements

Hole-only devices

The structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Al. A 30 nm thick PEDOT:PSS layer was made by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A polymer:PC₇₁BM blend in CB with 3 vol% DIO was spin-coated onto PEDOT:PSS layer. Finally, MoO₃ (~6 nm) and Al (~100 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10⁻⁴ Pa). *J-V* curves were measured by using a computerized Keithley 2420 SourceMeter in the dark.

Space-charge limited current (SCLC) measurements

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of holes (μ_h), ϵ_0 is the permittivity of the vacuum, ϵ_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage, $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode workfunction difference. The mobilities were calculated from the slope of $J^{1/2}$ - V plots.

7. Optimization of device performance

Table S1 Optimization of D/A ratio for PThzTITI:PC₇₁BM solar cells.^a

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.6	1.07	1.47	55.4	0.87
1:0.8	1.06	1.53	56.1	0.91
1:1.0	1.07	1.61	55.5	0.96
1:1.2	1.08	1.46	56.7	0.90
1:1.4	1.08	1.35	57.8	0.84

^a Blend solution: 14 mg/mL in CB with 3 vol% DIO; spin coating: 1200 rpm for 60 s.

Table S2 Optimization of the active layer thickness for PThzTITI:PC₇₁BM solar cells.^a

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
90	1.04	1.41	56.1	0.82
97	1.04	1.53	60.2	0.96
110	1.05	1.48	60.3	0.94
119	1.05	1.48	59.6	0.93
127	1.07	1.37	59.8	0.88
132	1.04	1.32	59.4	0.82

^a D/A ratio: 1:1 (w/w); blend solution: 14 mg/mL in CB with 3 vol% DIO.

Table S3 Optimization of the additive content for PThzTITI:PC₇₁BM solar cells.^a

DIO	V_{oc}	J_{sc}	FF	PCE
[v/v, %]	[V]	[mA/cm ²]	[%]	[%]
0	0.94	0.54	46.4	0.24
1	0.99	1.24	51.0	0.63
2	1.04	1.48	57.2	0.89
3	1.08	1.60	56.8	0.98
4	1.03	1.30	56.7	0.76

^a D/A ratio: 1:1 (w/w); blend solution: 14 mg/mL in CB; spin coating: 1500 rpm for 40 s.

Table S4 Optimization of D/A ratio for PSezTITI:PC₇₁BM solar cells.^a

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.6	1.06	3.21	57.3	1.95
1:0.8	1.07	3.43	60.7	2.23
1:1.0	1.04	3.29	63.8	2.19
1:1.2	1.04	3.09	64.0	2.05
1:1.4	1.04	2.58	60.2	1.62

^a Blend solution: 16 mg/mL in CB with 3 vol% DIO; spin coating: 1200 rpm for 60 s.

Table S5 Optimization of the active layer thickness for PSezTITI:PC₇₁BM solar cells.^a

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
87	1.03	3.37	56.0	1.95
95	1.05	3.68	54.4	2.10
104	1.06	3.60	55.5	2.12
109	1.02	3.81	56.4	2.20
115	1.03	3.66	53.5	2.03

^a D/A ratio: 1:0.8 (w/w); blend solution: 16 mg/mL in CB with 3 vol% DIO.

Table S6 Optimization of the additive content for PSezTITI:PC₇₁BM solar cells.^a

DIO	V_{oc}	J_{sc}	FF	PCE
[v/v, %]	[V]	[mA/cm ²]	[%]	[%]
0	1.02	0.48	45.4	0.22
1	1.03	1.30	55.1	0.74
2	1.04	3.25	57.3	1.93
3	1.05	3.75	59.6	2.36
4	1.04	3.21	57.6	1.93
5	1.03	3.16	55.0	1.80

^a D/A ratio: 1:0.8 (w/w); blend solution: 16 mg/mL in CB; spin coating: 1000 rpm for 60 s.

8. AFM

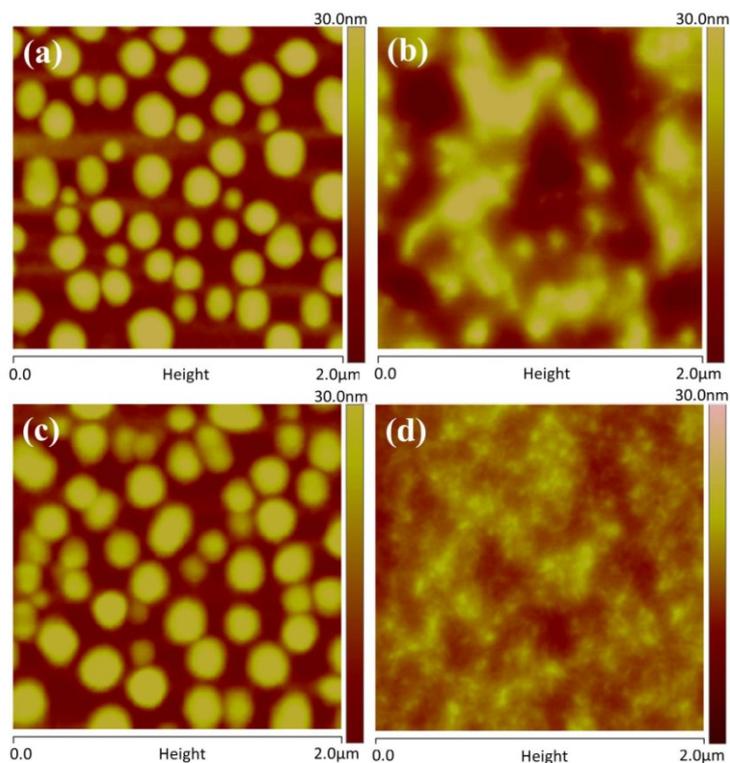


Fig. S7 AFM height images for PThzTITI:PC₇₁BM (top) and PSezTITI:PC₇₁BM (bottom) blend films without ((a), (c)) or with 3% DIO ((b), (d)).

9. XRD

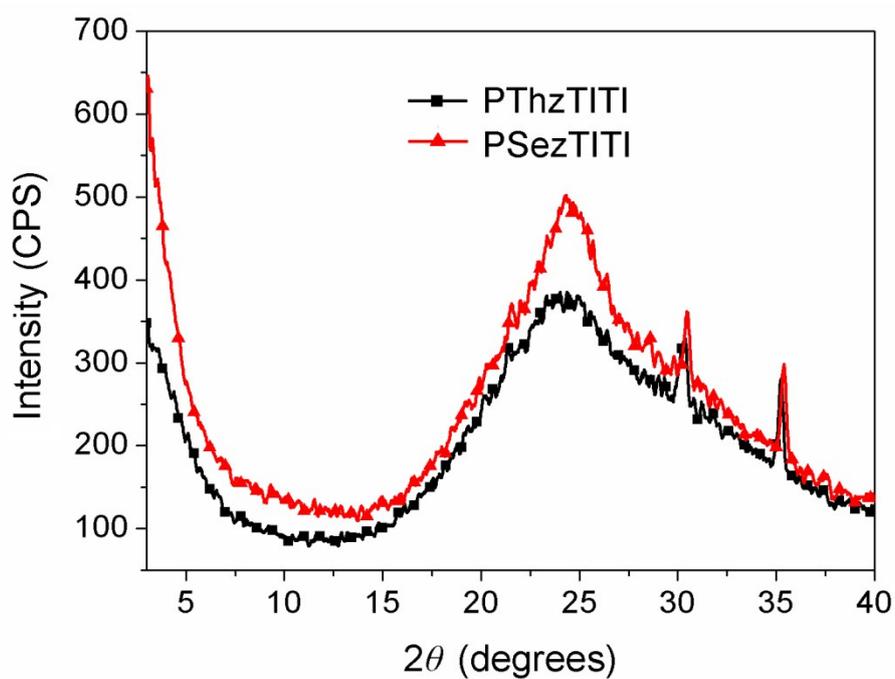


Fig. S8 XRD patterns for as-cast polymer films on ITO glass.

References

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- [2] R. S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus and I. McCulloch, *Chem. Commun.*, 2012, **48**, 3939.