

Supporting Information

Thiazolothienyl Imide-Based Wide Bandgap Copolymers for Efficient Polymer Solar Cells

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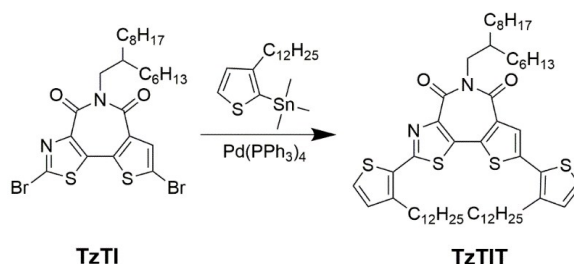
Table of Contents

1. Materials and Methods
2. Monomer and Polymer Synthesis
3. NMR and Mass Spectra of Compounds
4. Single Crystal Structure Data
5. Polymer Thermal Properties
6. PSCs Fabrication and Characterization
7. GIWAXS Measurements and Data

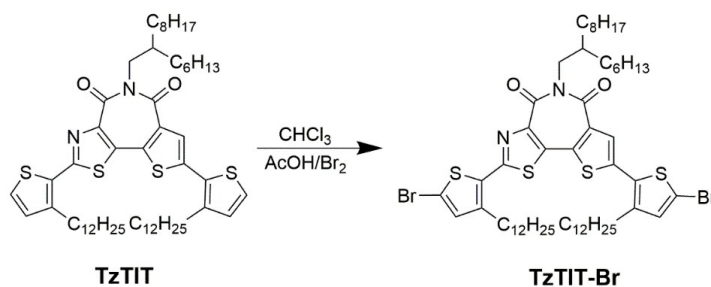
1. Materials and Methods.

All commercially available solvents, reagents, and chemicals were used as received without further purification unless otherwise stated. Anhydrous tetrahydrofuran and toluene were distilled from Na/benzophenone. The distannylated BDT monomers with distinct side chain were purchased from SunaTech Inc. (Suzhou, China). Unless otherwise stated, all operations and reactions were carried out under argon using standard Schlenk line techniques. Polymerizations were carried out on Initiator+ Microwave Synthesizer (Biotage, Sweden). ^1H and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 and 500 MHz spectrometer, and the chemical shifts were referenced to residual protio-solvent signals. C, H, N, and S elemental analyses (EAs) of monomer and polymers were conducted at Shenzhen University (Shenzhen, China). Polymer molecular weights were characterized on Polymer Laboratories GPC-PL220 high temperature GPC/SEC system (Agilent Technologies) at 150 °C vs polystyrene standards using trichlorobenzene as the eluent. Differential scanning calorimetry (DSC) curves were recorded on Mettler STARe (TA Instrument) in nitrogen with a heating ramp of 10 °C min⁻¹, and thermogravimetric analysis (TGA) curves were collected on Mettler STARe (TA Instrument). UV-vis absorption spectra were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Cyclic voltammetry (CV) measurements of polymer films were performed under argon atmosphere using a CHI760E voltammetric analyzer with 0.1 M tetra-*n*-butylammonium hexafluorophosphate in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a silver wire reference electrode were employed, and the ferrocene/ferrocenium (Fc/Fc⁺) was used as the internal reference for all measurements. The scanning rate was 100 mV s⁻¹. Polymer films were drop-casted from *o*-dichlorobenzene solutions on a Pt working electrode (2 mm in diameter). The supporting electrolyte solution was thoroughly purged with argon before all CV measurements. AFM measurements of polymer films were performed on a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone) in tapping mode.

2. Monomer and Polymer Synthesis.



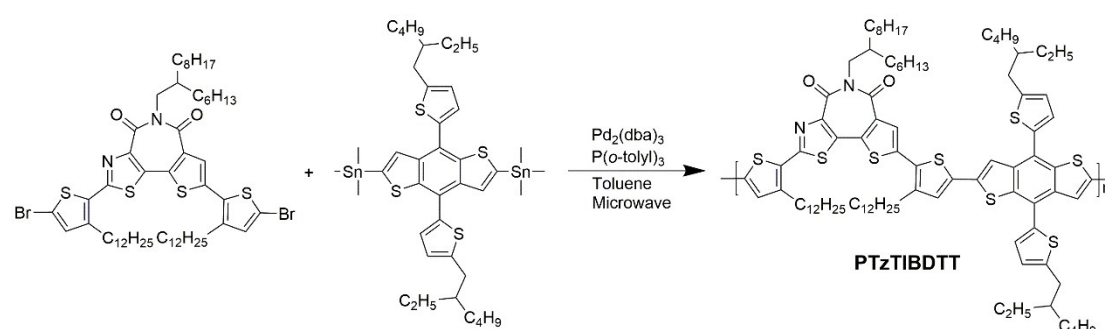
Synthesis of 2,8-bis(3-dodecylthiophen-2-yl)-5-(2-hexyldecyl)-4H-thiazolo[4,5-c]thieno[2,3-e]azepine-4,6(5H)-dione (TzTIT). The dibrominated thiazolothienyl imide (**TzTI**) (300 mg, 0.48 mmol), 2-trimethyltin-3-dodecylthiophene (604 mg, 1.45 mmol), Pd(PPh₃)₄ (30 mg, 0.024 mmol), and 5 mL DMF were combined, and the reaction mixture was stirred under microwave irradiation at 150 °C for 3 h. The solvent was then removed under a reduced pressure to afford a yellow solid, which was further purified by column chromatography over silica gel using CH₂Cl₂:Hexane (1:1 volume ratio) mixed solvent as the eluent to afford an orange solid as the product **TzTIT** (yield: 50%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.77 (s, 1H), 7.43 (d, *J* = 5.1 Hz, 1H), 7.30 (d, *J* = 5.1 Hz, 1H), 7.02 (d, *J* = 5.1 Hz, 1H), 7.00 (d, *J* = 5.1 Hz, 1H), 4.32 (d, *J* = 7.2 Hz, 2H), 3.01-2.97 (t, 2H), 2.85-2.81 (t, 2H), 2.01 (b, 1H), 1.75-1.67 (dd, 4H), 1.27 (b, 60H), 0.88 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 161.85, 160.35, 158.18, 144.70, 144.48, 141.69, 137.04, 134.17, 132.75, 132.10, 130.76, 130.60, 130.39, 130.20, 128.78, 128.30, 125.64, 77.30, 77.05, 76.79, 50.13, 36.39, 31.94, 31.89, 31.75, 31.73, 30.50, 30.38, 30.14, 30.04, 29.99, 29.82, 29.72, 29.70, 29.68, 29.63, 29.53, 29.49, 29.39, 29.36, 29.34, 26.50, 26.46, 22.71, 22.69, 14.15, 0.02. HRMS (ESI) *m/z* calcd for [C₅₇H₈₈N₂O₂S₄] 960.57, found 961.58 (M+H).



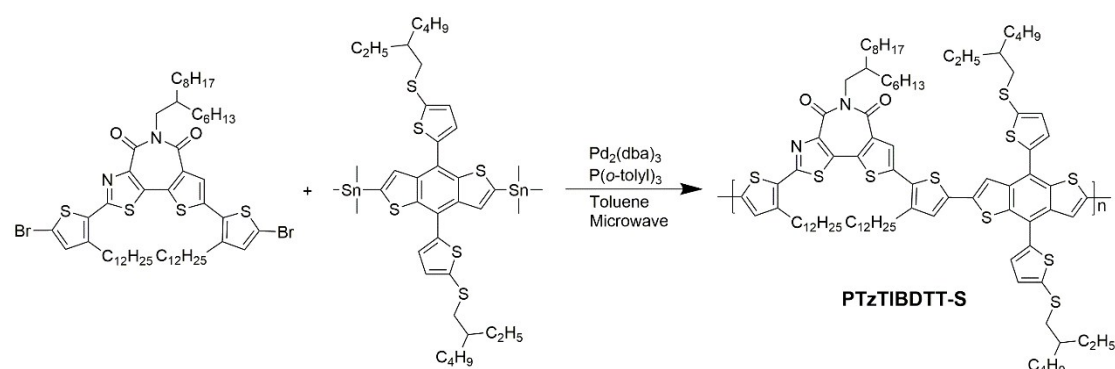
2,8-bis(5-bromo-3-dodecylthiophen-2-yl)-5-(2-hexyldecyl)-4H-thiazolo[4,5-c]thieno[2,3-e]azepine-4,6(5H)-dione (TzTIT-Br). Br₂ (200 mg, 1.24 mmol) was added to a solution of TzTIT (400 mg, 0.41 mmol) in CHCl₃:AcOH (5:1; total volume: 6 mL) in one portion. The reaction mixture was stirred at room temperature for 4 h, and 30 mL H₂O was then added. Next, the reaction mixture was extracted with 30 mL CH₂Cl₂ for 3 times, and the combined organic layer was washed with 50 mL brine and then dried over anhydrous MgSO₄. After filtration, the solvent was removed under a reduced pressure to afford an orange solid, which was purified by column chromatography over silica gel with CH₂Cl₂:Hexane (1:2 volume ratio) as the eluent. The compound TzTIT-Br was obtained as an orange solid (yield: 80%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.70 (s, 1H), 6.98(s, 1H), 6.96 (s, 1H), 4.29 (d, *J* = 7.1 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.98 (b, 1H), 1.70 (dd, 6H), 1.35 (b, 60H), 0.89-0.87 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ (ppm): 161.62, 160.14, 156.82, 144.95, 144.58, 142.34, 135.59, 134.27, 133.28, 133.02, 132.47, 132.16, 131.73, 131.22, 129.59, 117.26, 112.87, 77.30, 77.05, 76.79, 50.16, 36.39, 31.94, 31.88, 31.72, 31.69, 30.36, 30.14, 30.08, 29.80, 29.77, 29.71, 29.68, 29.63, 29.58, 29.57, 29.46, 29.44, 29.39, 29.38, 29.30, 26.46, 26.44, 22.72, 22.69, 14.15. Anal. Calcd. for C₅₇H₈₆Br₂N₂O₂S₄ (%); C, 61.16; H, 7.74; N, 2.50; S, 11.46. Found (%): C, 61.18; H, 7.75; N, 2.52; S, 11.47. HRMS (ESI) *m/z* calcd for [C₅₇H₈₆Br₂N₂O₂S₄] 1118.39, found 1119.39 (M+H).

General Procedure for Polymerizations via Stille Coupling for the Synthesis of Polymers PTzTIBDTT and PTzTIBDTT-S. To a flame-dried glass tube was charged with two monomers (0.1 mmol each), tris(dibenzylideneacetone)dipalladium (0) (Pd₂(dba)₃), and tris(*o*-tolyl)phosphine (P(*o*-tolyl)₃) (1:8, Pd₂(dba)₃:P(*o*-tolyl)₃ molar ratio; Pd loading: 0.03-0.05 equiv). The tube and its contents were subjected to 3 pump/purge cycles with argon, followed by the addition of 3 mL anhydrous toluene via syringe. The tube was sealed under argon flow and then stirred at 80 °C for 10 min, 100 °C for 10 min, and 140 °C for 3 h under microwave irradiation. Then, 0.1 mL 2-(tributylstanny)thiophene was added and the reaction mixture was stirred under microwave irradiation at 140 °C for 0.5 h. Finally, 0.2 mL 2-bromothiophene was added

and the reaction mixture was stirred at 140 °C for another 0.5 h. After cooling to room temperature, the reaction mixture was slowly dripped into 100 mL methanol, containing 5 mL 12 N hydrochloric acid, under vigorous stirring. After stirring for 1 h, the solid precipitate was transferred to a Soxhlet thimble. After drying, the crude product was subjected to sequential Soxhlet extraction with the solvent sequence depending on the solubility of the particular polymer. After final extraction, the polymer solution was concentrated to ~20 mL, and then dripped into 100 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a deep colored solid as the final product.



PTzTIBDTT. The solvent sequence for Soxhlet extraction was methanol, acetone, hexane, dichloromethane, chloroform, chlorobenzene and 1,2-dichlorobenzene. The 1,2-dichlorobenzene fraction was concentrated by removing most of solvent and precipitated into methanol. The solid was collected by filtration and dried in vacuum to afford the polymer as a deep colored solid (yield: 53%). ¹H NMR (400 MHz, CCl₄D₂, 80 °C) δ (ppm): 7.19 (s, 1H), 6.89 (s, 1H), 6.73 (s, 1H), 6.56 (s, 2H), 6.31 (d, 2H), 6.01 (d, 2H), 3.71 (d, 2H), 2.36 (d, 4H), 0.86 (m, 96H), 0.42 (m, 24H). M_n = 84 kDa, PDI = 2.2. Anal. Calcd. for C₉₁H₁₂₈N₂O₂S₈ (%) : C, 71.04; H, 8.39; N, 1.82; S, 16.67. Found (%): C, 71.08; H, 8.35; N, 1.85; S, 16.65



PTzTIBDTT-S. The solvent sequence for Soxhlet extraction was methanol, acetone, hexane, dichloromethane, chloroform, chlorobenzene and 1,2-dichlorobenzene. The 1,2-dichlorobenzene fraction was concentrated by removing most of solvent and precipitated into methanol. The solid was collected by filtration and dried in vacuum to afford the polymer as a deep colored solid (yield: 62%). ¹H NMR (400 MHz, CCl₄D₂, 80 °C) δ (ppm): 7.19 (s, 1H), 7.05 (s, 1H), 6.93 (s, 1H), 6.78(s, 2H), 6.68 (d, 2H), 6.61 (d, 2H), 3.70 (d, 2H), 2.44 (d, 4H), 0.86 (m, 96H), 0.36 (m, 24H). M_n = 67 kDa, PDI = 2.0. Anal. Calcd. for C₉₁H₁₂₈N₂O₂S₁₀ (%): C, 68.20; H, 8.05; N, 1.75; S, 20.00. Found (%): C, 68.24; H, 8.08; N, 1.72; S, 19.98.

3. NMR and Mass Spectra of Compounds.

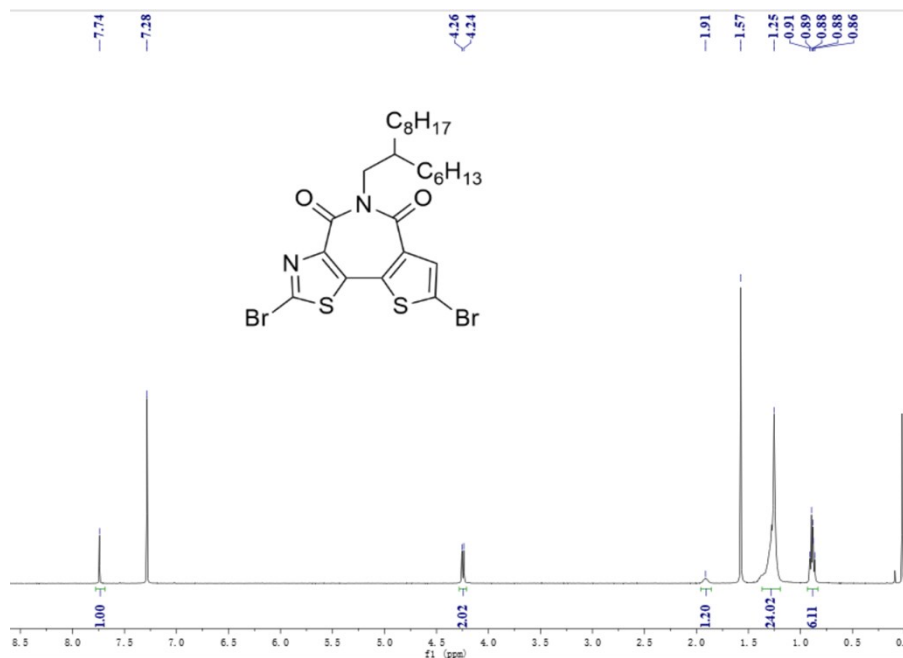


Figure S1. ¹H NMR spectrum of compound TzTI (400 M, r.t., in CDCl₃).

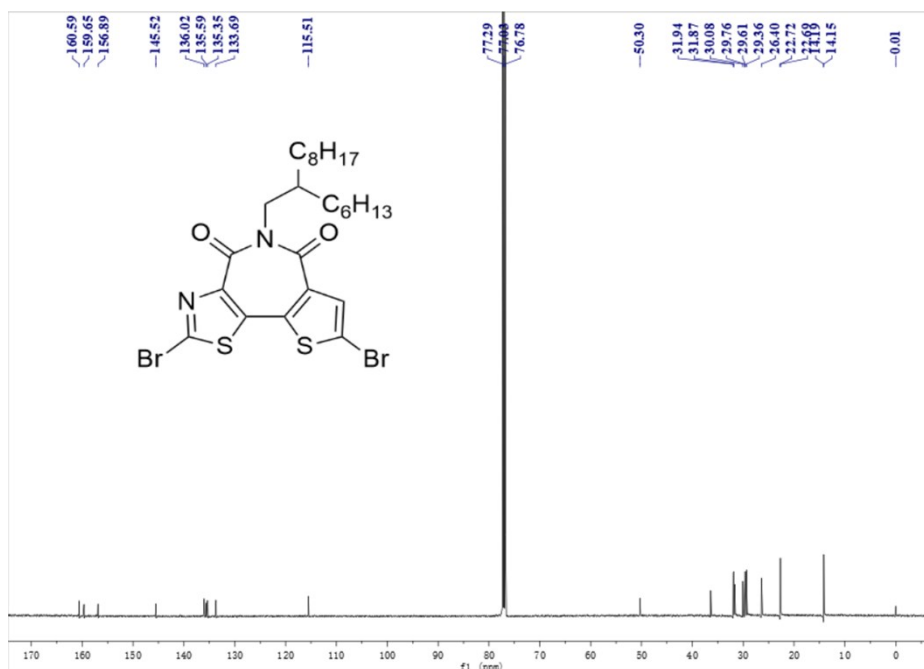


Figure S2. ¹³C NMR spectrum of compound TzTI (400 M, r.t., in CDCl₃).

[M+H]⁺

tz11_190723142359 #13 RT: 0.13 AV: 1 NL: 8.26E8
T: FTMS + p ESI Full ms [150.0000-800.0000]

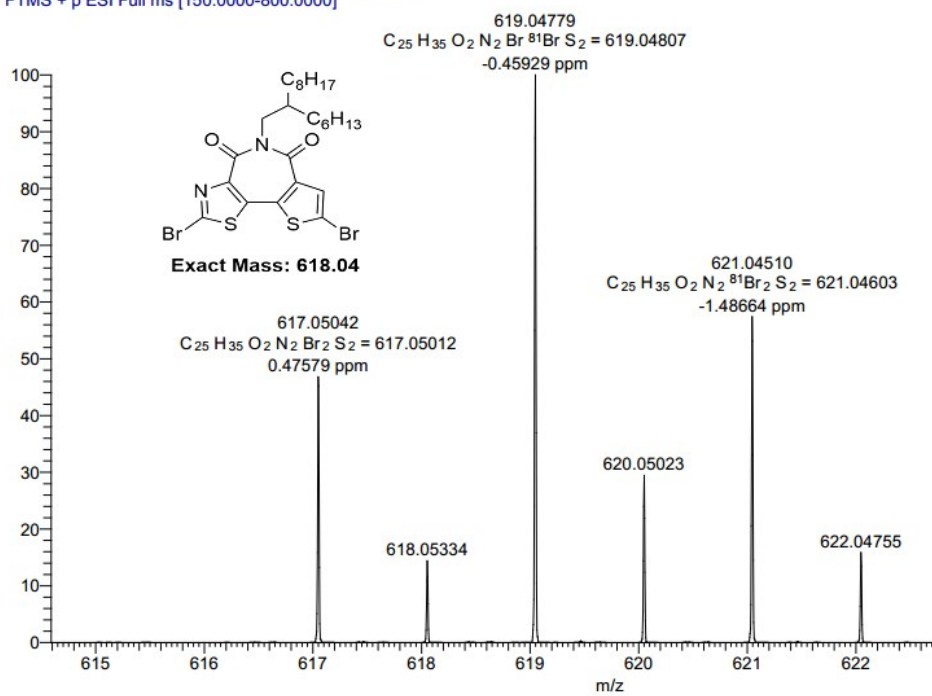


Figure S3. HRMS spectrum of compound TzTI.

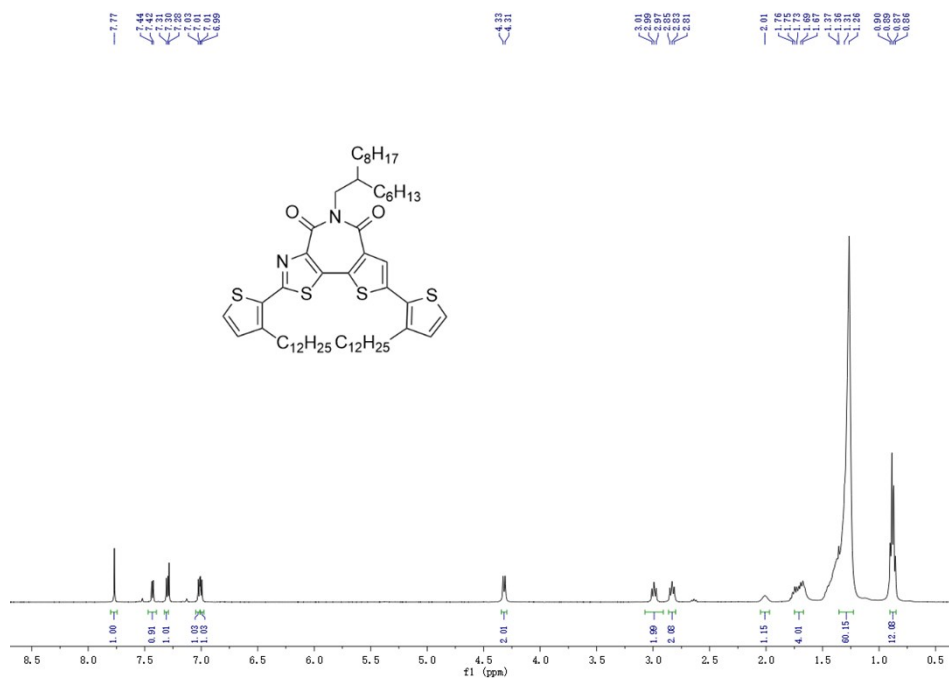


Figure S4. ¹H NMR spectrum of compound TzTIT (400 M, r.t., in CDCl₃).

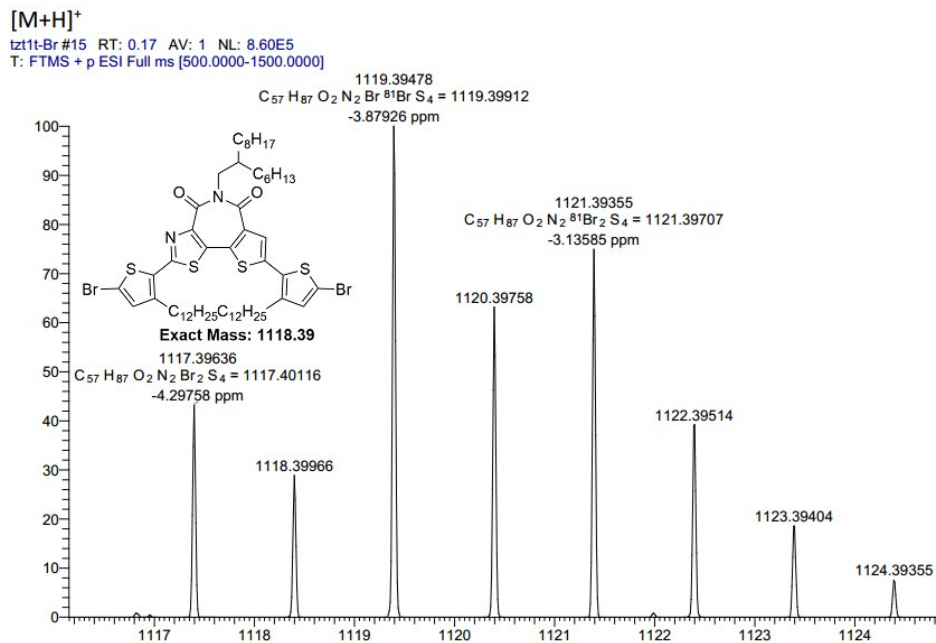


Figure S9. HRMS spectrum of compound TzTIT-Br.

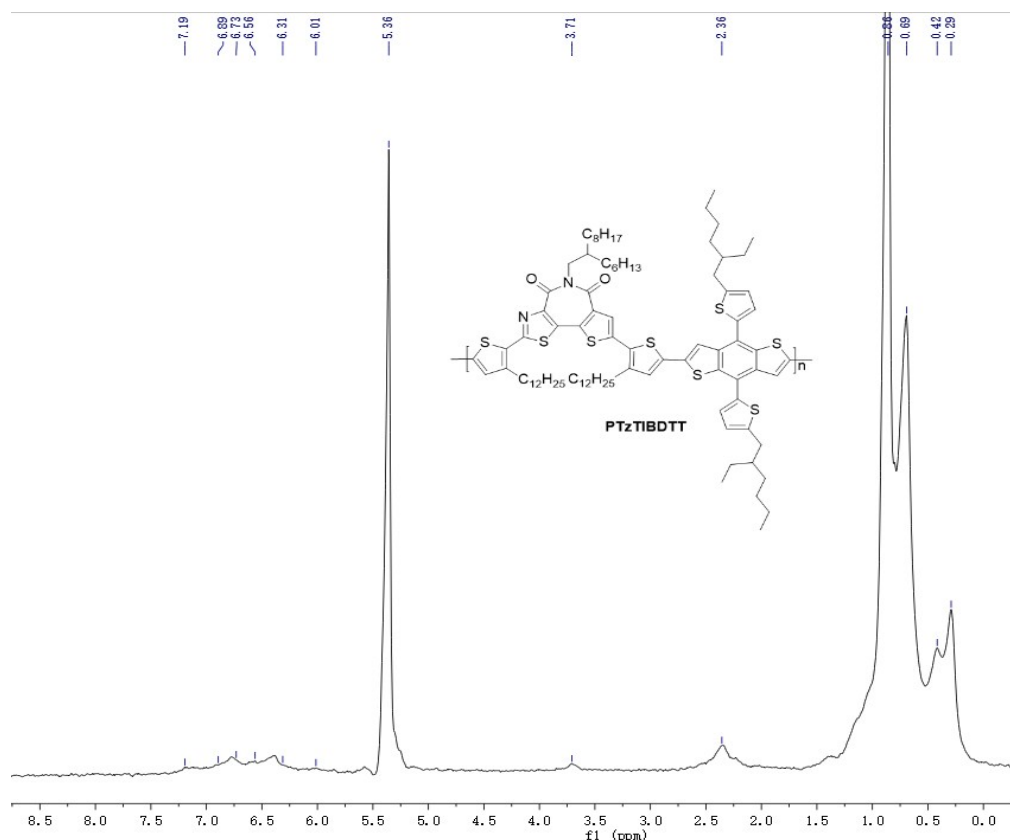


Figure S10. ¹H NMR spectrum of polymer PTzTIBDTT (400 M, 80 °C, in C₂Cl₄D₂).

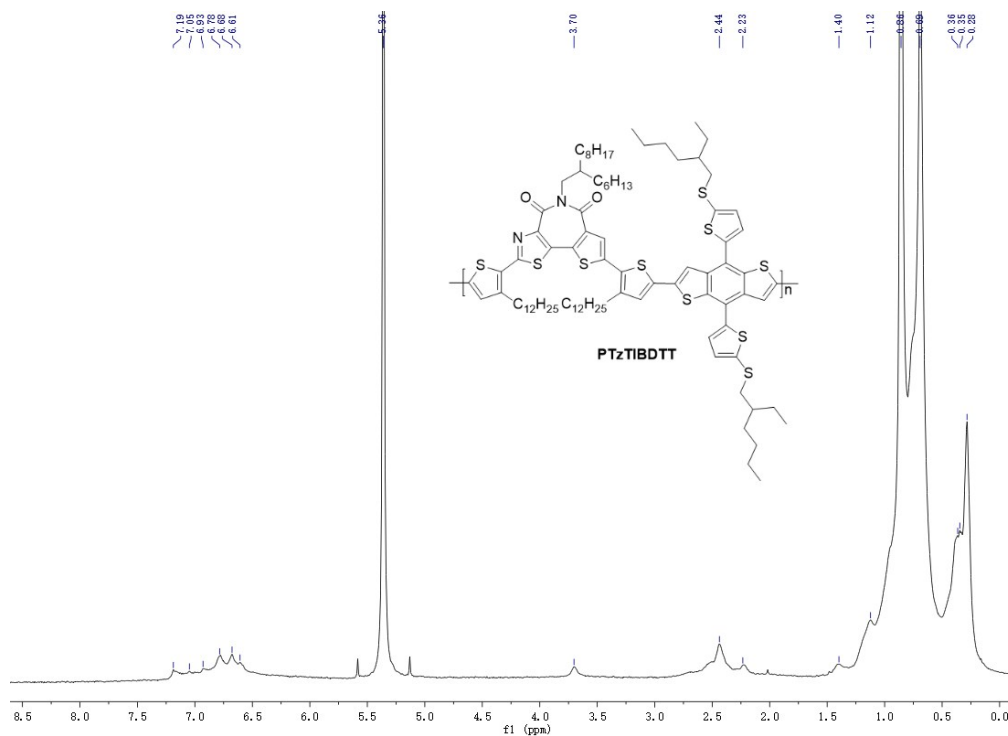
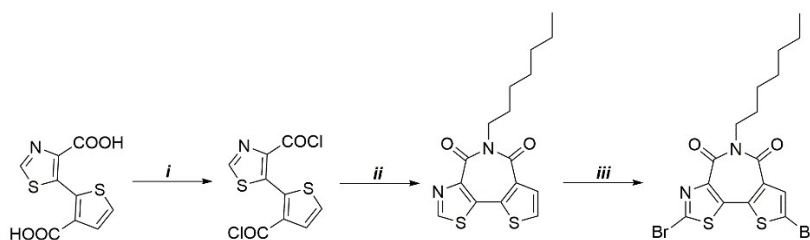


Figure S11. ^1H NMR spectrum of polymer PTzTIBDTS-S (400 M, 80 °C, in $\text{C}_2\text{Cl}_4\text{D}_2$).

4. Single Crystal Structure Data.

Note: The cif file of the crystal structures of model compound is available free of charge via the internet at <http://www.ccdc.cam.ac.uk>

Scheme S1. Synthesis route to model compound **TzTI-C7** for single crystal structure study.^[1, 2]



Reagents and conditions: (i) SOCl_2 , 80 °C; (ii) TzTI: *n*-heptane, 140 °C; (iii) LiHMDS, $\text{BrCCl}_2\text{CCl}_2\text{Br}$, -78 °C.

Computing details

Program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013).

Crystal data

CHBrNOS	$\gamma = 84.36 (9)^\circ$
$M_r = 155.00$	$V = 967.5 (13) \text{ \AA}^3$
Triclinic, P^{-1}	$Z = 9$
$a = 4.914 (4) \text{ \AA}$	$F(000) = 657$
$b = 10.850 (8) \text{ \AA}$	$D_x = 2.394 \text{ Mg m}^{-3}$
$c = 18.952 (12) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$\alpha = 74.50 (8)^\circ$	$\mu = 9.86 \text{ mm}^{-1}$
$\beta = 85.40 (7)^\circ$	$T = 566 \text{ K}$

Data collection

9480 measured reflections	$\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 2.0^\circ$
3088 independent reflections	$h = -5 \rightarrow 5$
2726 reflections with $I > 2\sigma(I)$	$k = -13 \rightarrow 12$
$R_{\text{int}} = 0.169$	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.314$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.762$	$(\Delta/\sigma)_{\max} = 0.115$
$S = 6.29$	$\Delta_{\max} = 4.01 \text{ e \AA}^{-3}$
3088 reflections	$\Delta_{\min} = -1.07 \text{ e \AA}^{-3}$
219 parameters	Extinction correction: <i>SHELXL</i> , $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.56 (16)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters
(\AA^2) for (h)*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.0804 (7)	0.3732 (3)	0.44881 (16)	0.142 (2)
Br2	1.3143 (8)	-0.2945 (3)	0.69075 (19)	0.146 (2)
S1	0.4970 (19)	0.1562 (7)	0.5256 (4)	0.133 (3)
S2	0.912 (2)	-0.0747 (7)	0.6139 (4)	0.134 (3)
O1	0.492 (4)	0.438 (2)	0.6840 (13)	0.156 (8)
O2	1.225 (6)	0.1597 (18)	0.7701 (14)	0.160 (8)
N2	0.857 (4)	0.2899 (17)	0.7189 (13)	0.123 (7)
N1	0.384 (6)	0.361 (2)	0.5747 (12)	0.153 (10)
H1	0.3103	0.4332	0.5811	0.184*
C5	0.664 (7)	0.174 (3)	0.6037 (13)	0.134 (9)
C4	0.848 (7)	0.0861 (17)	0.6370 (15)	0.119 (7)
C6	0.595 (5)	0.269 (3)	0.6211 (14)	0.130 (9)
C7	0.638 (7)	0.341 (3)	0.6822 (16)	0.139 (9)
C3	1.027 (8)	0.064 (4)	0.6936 (14)	0.179 (18)
C2	1.152 (6)	-0.047 (3)	0.719 (2)	0.161 (14)
H2	1.2401	-0.0654	0.7629	0.194*
C16	0.341 (4)	0.3095 (13)	0.5256 (14)	0.137 (9)
C8	1.015 (7)	0.176 (2)	0.7297 (13)	0.129 (9)
C9	0.924 (4)	0.365 (2)	0.7727 (11)	0.101 (6)
H9A	1.1170	0.3480	0.7821	0.121*
H9B	0.8892	0.4558	0.7504	0.121*
C10	0.761 (10)	0.330 (5)	0.8429 (15)	0.191 (17)
H10A	0.7960	0.2392	0.8667	0.229*
H10B	0.5671	0.3478	0.8349	0.229*
C11	0.851 (8)	0.412 (3)	0.8903 (12)	0.150 (11)
H11A	0.7935	0.3745	0.9410	0.180*
H11B	1.0499	0.4086	0.8872	0.180*
C12	0.742 (9)	0.550 (3)	0.8694 (13)	0.159 (12)

H12A	0.8208	0.5884	0.8208	0.191*
H12B	0.5463	0.5512	0.8649	0.191*
C17	1.156 (5)	-0.145 (2)	0.6787 (18)	0.150 (11)
C13	0.781 (9)	0.639 (8)	0.917 (2)	0.32 (5)
H13A	0.9657	0.6203	0.9333	0.382*
H13B	0.6567	0.6171	0.9598	0.382*
C14	0.734 (14)	0.791 (6)	0.880 (3)	0.32 (5)
H14A	0.5526	0.8081	0.8615	0.386*
H14B	0.8641	0.8125	0.8384	0.386*
C15	0.763 (12)	0.894 (9)	0.932 (3)	0.34 (5)
H15A	0.6629	0.9740	0.9117	0.509*
H15B	0.9522	0.9069	0.9339	0.509*
H15C	0.6890	0.8577	0.9813	0.509*

Atomic displacement parameters (\AA^2) for (h)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.157 (3)	0.141 (3)	0.124 (3)	-0.006 (2)	-0.018 (2)	-0.0233 (19)
Br2	0.164 (3)	0.128 (3)	0.139 (3)	0.007 (2)	-0.024 (2)	-0.025 (2)
S1	0.154 (6)	0.126 (5)	0.115 (5)	0.011 (4)	-0.021 (4)	-0.025 (4)
S2	0.170 (7)	0.115 (5)	0.118 (5)	0.000 (4)	-0.023 (4)	-0.029 (3)
O1	0.134 (13)	0.120 (12)	0.177 (18)	0.021 (11)	0.000 (12)	0.012 (12)
O2	0.22 (2)	0.111 (11)	0.178 (18)	0.032 (12)	-0.069 (16)	-0.088 (12)
N2	0.116 (13)	0.092 (10)	0.172 (18)	0.000 (9)	0.023 (12)	-0.066 (10)
N1	0.22 (3)	0.143 (16)	0.128 (14)	-0.100 (17)	0.055 (16)	-0.074 (13)
C5	0.19 (3)	0.119 (16)	0.086 (11)	0.031 (17)	-0.072 (14)	-0.007 (11)
C4	0.17 (2)	0.063 (8)	0.128 (16)	-0.016 (11)	-0.007 (15)	-0.028 (9)
C6	0.096 (12)	0.16 (2)	0.118 (16)	0.003 (13)	-0.066 (12)	0.002 (16)
C7	0.15 (2)	0.13 (2)	0.121 (18)	0.000 (18)	-0.027 (15)	0.001 (14)
C3	0.24 (4)	0.22 (3)	0.103 (15)	-0.16 (3)	-0.029 (18)	-0.038 (17)
C2	0.15 (2)	0.089 (12)	0.19 (3)	0.064 (16)	0.008 (18)	0.019 (16)
C16	0.095 (9)	0.043 (6)	0.23 (2)	0.062 (8)	0.027 (12)	0.008 (10)
C8	0.19 (3)	0.111 (14)	0.100 (14)	-0.051 (16)	-0.005 (15)	-0.045 (11)
C9	0.097 (10)	0.115 (13)	0.102 (11)	-0.035 (10)	0.025 (9)	-0.044 (9)

C10	0.24 (4)	0.27 (4)	0.089 (16)	-0.04 (3)	-0.015 (19)	-0.08 (2)
C11	0.25 (3)	0.142 (18)	0.077 (11)	0.003 (19)	-0.025 (14)	-0.065 (12)
C12	0.26 (4)	0.15 (2)	0.086 (13)	0.01 (2)	-0.049 (17)	-0.063 (13)
C17	0.108 (13)	0.081 (11)	0.23 (3)	0.057 (11)	0.033 (15)	-0.032 (13)
C13	0.13 (2)	0.70 (15)	0.18 (4)	0.00 (5)	-0.09 (3)	-0.21 (6)
C14	0.39 (8)	0.39 (8)	0.16 (3)	0.29 (7)	-0.06 (4)	-0.12 (4)
C15	0.28 (7)	0.67 (14)	0.16 (3)	-0.17 (9)	0.01 (4)	-0.24 (6)

Geometric parameters (Å, °) for (h)

Br1—C16	1.95 (3)	C9—C10	1.47 (4)
Br2—C17	1.695 (18)	C9—H9A	0.9700
S1—C16	1.762 (14)	C9—H9B	0.9700
S1—C5	1.81 (2)	C10—C11	1.54 (4)
S2—C17	1.76 (3)	C10—H10A	0.9700
S2—C4	1.90 (2)	C10—H10B	0.9700
O1—C7	1.21 (4)	C11—C12	1.50 (4)
O2—C8	1.30 (4)	C11—H11A	0.9700
N2—C7	1.32 (3)	C11—H11B	0.9700
N2—C8	1.37 (3)	C12—C13	1.51 (6)
N2—C9	1.53 (3)	C12—H12A	0.9700
N1—C16	1.25 (3)	C12—H12B	0.9700
N1—C6	1.53 (4)	C13—C14	1.61 (10)
N1—H1	0.8600	C13—H13A	0.9700
C5—C6	1.17 (4)	C13—H13B	0.9700
C5—C4	1.32 (4)	C14—C15	1.70 (8)
C4—C3	1.39 (4)	C14—H14A	0.9700
C6—C7	1.60 (5)	C14—H14B	0.9700
C3—C2	1.29 (5)	C15—H15A	0.9600
C3—C8	1.54 (4)	C15—H15B	0.9600
C2—C17	1.46 (5)	C15—H15C	0.9600
C2—H2	0.9300		

C16—S1—C5	83.1 (14)	C9—C10—H10A	110.5
C17—S2—C4	97.6 (13)	C11—C10—H10A	110.5
C7—N2—C8	136 (2)	C9—C10—H10B	110.5
C7—N2—C9	113 (2)	C11—C10—H10B	110.5
C8—N2—C9	111 (2)	H10A—C10—H10B	108.7
C16—N1—C6	105 (2)	C12—C11—C10	115 (3)
C16—N1—H1	127.8	C12—C11—H11A	108.6
C6—N1—H1	127.7	C10—C11—H11A	108.5
C6—C5—C4	124 (2)	C12—C11—H11B	108.6
C6—C5—S1	114.8 (17)	C10—C11—H11B	108.6
C4—C5—S1	121 (3)	H11A—C11—H11B	107.5
C5—C4—C3	140 (3)	C13—C12—C11	121 (3)
C5—C4—S2	121 (2)	C13—C12—H12A	107.0
C3—C4—S2	99 (2)	C11—C12—H12A	107.1
C5—C6—N1	117 (2)	C13—C12—H12B	107.0
C5—C6—C7	141.8 (18)	C11—C12—H12B	107.1
N1—C6—C7	101 (2)	H12A—C12—H12B	106.8
O1—C7—N2	130 (3)	C2—C17—Br2	133 (2)
O1—C7—C6	119 (3)	C2—C17—S2	101.3 (14)
N2—C7—C6	111 (2)	Br2—C17—S2	125 (2)
C2—C3—C4	121 (3)	C12—C13—C14	118 (3)
C2—C3—C8	124 (3)	C12—C13—H13A	107.9
C4—C3—C8	113 (4)	C14—C13—H13A	107.8
C3—C2—C17	119 (3)	C12—C13—H13B	107.9
C3—C2—H2	120.3	C14—C13—H13B	108.0
C17—C2—H2	120.2	H13A—C13—H13B	107.2
N1—C16—S1	121 (2)	C13—C14—C15	119 (4)
N1—C16—Br1	126.7 (17)	C13—C14—H14A	107.4
S1—C16—Br1	112.4 (15)	C15—C14—H14A	107.6
O2—C8—N2	118.4 (18)	C13—C14—H14B	107.6
O2—C8—C3	109 (3)	C15—C14—H14B	107.6
N2—C8—C3	132 (3)	H14A—C14—H14B	107.0

C10—C9—N2	112 (2)	C14—C15—H15A	109.3
C10—C9—H9A	109.1	C14—C15—H15B	109.4
N2—C9—H9A	109.1	H15A—C15—H15B	109.5
C10—C9—H9B	109.1	C14—C15—H15C	109.7
N2—C9—H9B	109.1	H15A—C15—H15C	109.5
H9A—C9—H9B	107.8	H15B—C15—H15C	109.5
C9—C10—C11	106 (3)		

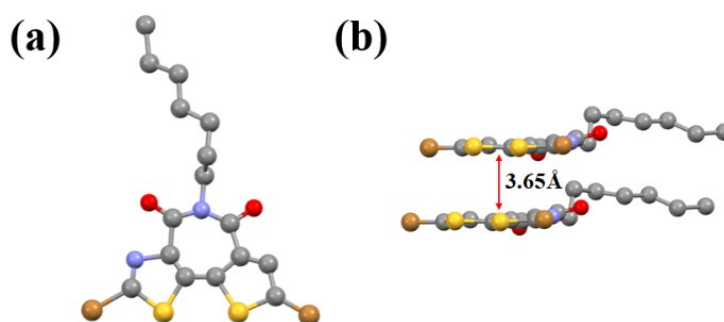


Figure S12. X-ray crystallographic structure of the model compound **TzTI-C7**, (a) top view, and (b) side view.

5. Polymer Thermal and Electrochemical Properties.

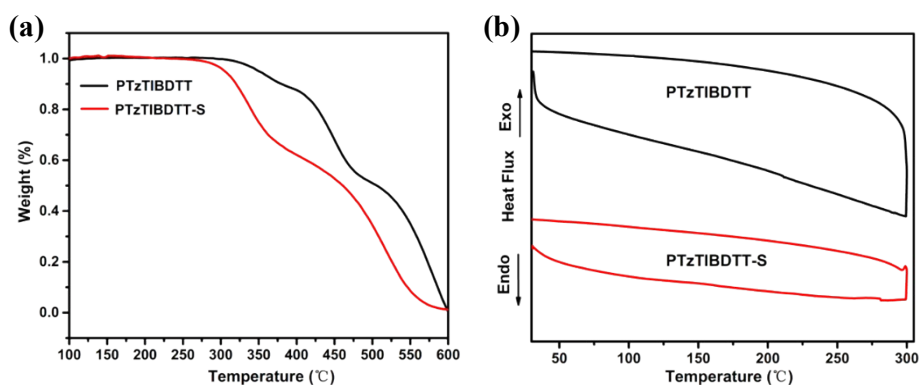


Figure S13. (a) Thermogravimetric analysis of polymers **PTzTIBDTT** and **PTzTIBDTT-S** at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. (b) DSC thermograms of polymers **PTzTIBDTT** and **PTzTIBDTT-S**. The DSC curves are from the second heating and first cooling scans with a ramp rate of $10\text{ }^{\circ}\text{C min}^{-1}$. N_2 was used as the purge gas for both TGA and DSC measurements.

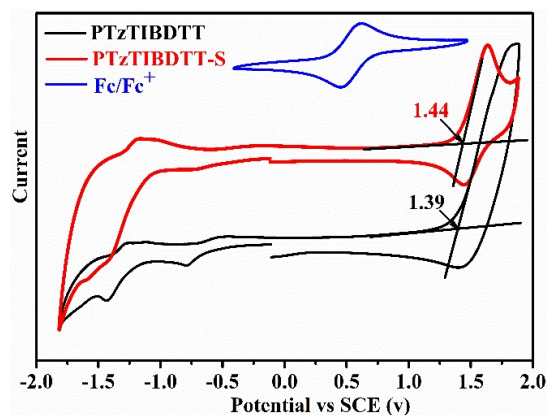


Figure S14. Cyclic voltammogram curves of PTzTIBDTT and PTzTIBDTT-S thin films measured in 0.1 M (n-Bu)₄N⁺PF₆⁻ acetonitrile solution at a scan rate of 50 mV s⁻¹, the ferrocene used as external standard.

6. Fabrication and Characterization of PSCs.

Inverted polymer solar cells with a device structure of glass/ITO/ZnO/donor:acceptor/MoO₃/Ag was used for device fabrication and optimization. Pre-patterned ITO-coated glass with a sheet resistance of < 10 Ω sq⁻¹ was used as the substrate, which was cleaned by sequential sonication in detergent H₂O, deionized H₂O, acetone, and isopropanol followed by drying in vacuum oven and then UV-ozone treatment (BZS250GF-TC, HWOTECH, Shenzhen) for 15 min. ZnO (30 nm) is deposited onto ITO glass substrates via spin-coating as the electron extraction layer, followed by thermal annealing for 30 min at 200 °C. The active layer with an optimal thickness of 110 or 180 nm was spin-coated onto ZnO from PTzTIBDTT:PC₇₁BM or PTzTIBDTT-S:PC₇₁BM blend solutions (total concentration: 30 mg mL⁻¹; D:A weight ratios of 1:2) in the mix solvent of *o*-DCB and DIO, followed by thermal annealing at 90 °C for 5min. Then, MoO₃ (10 nm) and Ag (100 nm) were sequentially deposited atop the active layer via thermal evaporation under vacuum (ca.

1×10^{-5} Pa). The effective area of PSCs was 0.045 cm^2 . For the device characterization, all current-voltage (I - V) characteristics of the devices were measured under simulated AM1.5G irradiation (100 mW cm^{-2}) using a Xe lamp-based SS-F5-3A Solar Simulator (Enli Technology, Inc.). A Xe lamp equipped with an AM1.5G filter was used as the white light source. The light intensity was controlled with an NREL-calibrated Si solar cell with a KG-5 filter. The external quantum efficiency (EQE) was recorded on a QE-R3011 measurement system (Enli Technology, Inc.).

Hole and electron mobilities were measured using the space charge limited current (SCLC) method. The structure of ITO/PEDOT:PSS/active layer/MoO₃/Ag was used for hole-only devices and the structure of ITO/ZnO/active layer/Ca/Al was used for electron-only devices, respectively. The SCLC mobilities were calculated by the MOTT-Gurney equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

Where J is the current density, ε_r is the relative dielectric constant of active layer material usually 2-4 for organic semiconductors, herein we use a relative dielectric constant of 3 for the polymers, ε_0 is the permittivity of empty space, μ is the mobility of hole or electron and d is the thickness of the active layer, V is the internal voltage in the device, and $V = V_{appl} - V_{bi}$, where V_{appl} is the voltage applied to the device, and V_{bi} is the built-in voltage resulting from the relative work function difference between the two electrodes (in the hole-only and the electron-only devices, the V_{bi} values can be neglected).

Atomic force microscopy (AFM) measurements of polymer blend films were

conducted using a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone) in the Pico Center at SUSTech under the AC-tapping mode. Transmission electron microscopy (TEM) specimens were prepared following the identical conditions as the actual devices, but were drop-cast onto a 40 nm PEDOT:PSS covered substrate. After drying, the substrates were transferred to deionized water and the floated films were transferred onto TEM grids. TEM images were obtained on a Tecnai F30 (300 kV) in the Pico Center at SUSTech.

Table S1 . Device performance parameters of PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag or ITO/PEDOT:PSS/active layer/Ca/Al. The PTzTIBDTT:PC₇₁BM films were fabricated with a D:A ratio of 1:2 (w/w) from *o*-DCB solutions (30 mg mL in total concentration).

Structure	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE max/avg (%)
Conventional	9.33	0.98	59.87	5.45/5.30
Inverted	11.84	0.92	56.55	6.1/6.01

Table S2. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:PC₇₁BM films were fabricated with different D:A ratios from 2.5:1 to 1:2.5 (w/w) from *o*-DCB solutions (30 mg mL⁻¹ in total concentration).

D:A ratio	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE max/avg (%)
2.5:1	11.76	0.89	52.42	5.53/5.42
2:1	11.92	0.90	53.81	5.80/5.66

1:1	12.02	0.94	52.48	5.90/5.78
1:2	11.84	0.92	56.55	6.1/6.01
1:2.5	11.64	0.93	54.56	5.89/5.73

Table S3. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:PC₇₁BM films were fabricated with a D:A ratio of 1:2 (w/w) from *o*-DCB solutions having different donor concentrations.

Concentration	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE max/avg (%)
10 mg mL ⁻¹	11.88	0.90	53.28	5.69/5.46
12 mg mL ⁻¹	11.84	0.92	56.55	6.10/6.01
14 mg mL ⁻¹	12.00	0.91	51.65	5.64/5.38

Table S4. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:PC₇₁BM films were fabricated with a D:A ratio of 1:2 (w/w) from *o*-DCB solutions containing distinct additive (30 mg mL⁻¹ in total concentration).

Additive	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE max/avg (%)
DIO	13.14	0.90	61.08	7.15/6.98
DPE	13.13	0.93	57.15	6.95/6.86
CN	13.24	0.89	59.31	6.93/6.79
ODT	12.30	0.92	61.71	6.96/6.82

Table S5. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBD TT:PC₇₁BM films were fabricated with a D:A ratio of 1:2 (w/w) from *o*-DCB solutions containing 3 vol % DIO (30 mg/ml in total concentration). The film was thermally annealed at different temperatures.

T _{anneal}	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE max/avg (%)
TA at 80°C	13.30	0.90	62.89	7.50/7.36
TA at 90°C	13.48	0.90	65.90	8.0/7.85
TA at 100°C	14.31	0.87	54.91	7.17/7.07

Table S6. Device performance parameters of PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag or ITO/PEDOT:PSS/active layer/Ca/Al. The PTzTIBD TT-S: PC₇₁BM films were fabricated with a D:A ratio of 1:2 (w/w) from *o*-DCB solutions (total concentration: 30 mg mL⁻¹).

Structure	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE max/avg (%)
Conventional	7.47	0.80	44.69	2.67/2.46
Inverted	7.93	0.82	46.68	3.06/2.98

Table S7. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBD TT-S:PC₇₁BM films were fabricated with different D:A ratios from 2.5:1 to 1:2.5 (w/w) from *o*-DCB solutions (total concentration: 30 mg mL⁻¹).

Ratio	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE max/avg (%)
2.5:1	7.30	0.81	43.65	2.58/2.23
2:1	7.32	0.82	45.87	2.75/2.62

1:1	7.56	0.82	48.21	3.00/2.89
1:2	7.93	0.82	46.68	3.06/2.98
1:2.5	9.05	0.78	41.94	2.90/2.78

Table S8. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT-S:PC₇₁BM films were fabricated with a D:A ratio of 1:2 (w/w) from *o*-DCB solutions having distinct donor concentrations.

Concentration	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE max/avg (%)
10 mg mL ⁻¹	7.88	0.81	44.38	2.83/2.72
12 mg mL ⁻¹	7.93	0.82	46.68	3.06/2.98
14 mg mL ⁻¹	8.02	0.82	42.68	2.80/2.67

Table S9. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT-S:PC₇₁BM films were fabricated with a D:A ratio of 1:2 (w/w) from *o*-DCB solutions with distinct additive (total concentration: 30 mg mL⁻¹).

Additive	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE max/avg (%)
DIO	9.18	0.80	48.55	3.58/3.42
DPE	9.09	0.80	48.21	3.49/3.25
CN	9.12	0.80	48.54	3.54/3.39
ODT	9.73	0.80	44.60	3.45/3.28

Table S10. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT-S:PC₇₁BM films were fabricated with a D:A ratio of 1:2 (w/w) from *o*-DCB solutions having 3 vol % DIO (30 mg mL⁻¹ in total concentration), thermal annealing at different temperatures.

T _{anneal}	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE max/avg (%)
80 °C	9.74	0.81	46.02	3.64/3.47
90 °C	9.98	0.81	45.88	3.69/3.43
100 °C	8.40	0.83	42.81	2.98/2.91

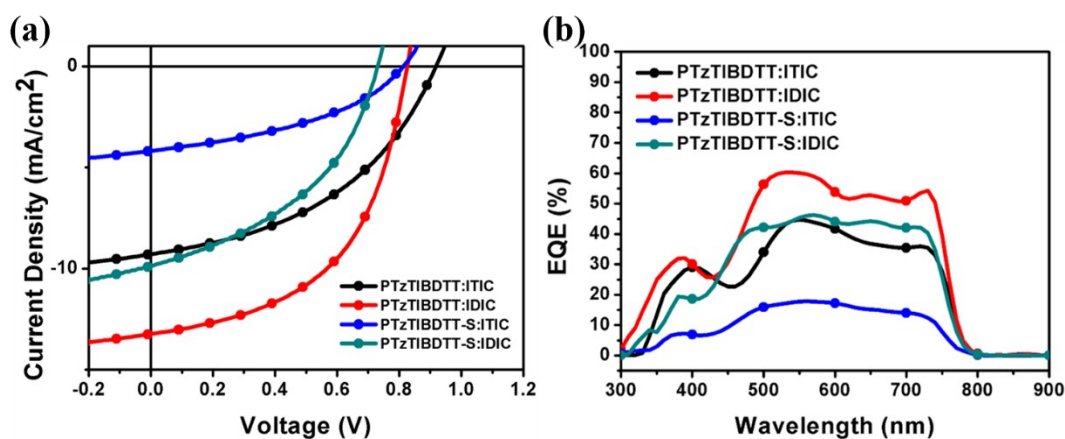


Figure S15. (a) J - V characteristics of optimized solar cells containing PTzTIBDTT:ITIC/IDIC or PTzTIBDTT-S:ITIC/IDIC active layer under AM 1.5G illumination with a light intensity of 100 mW cm⁻²; (b) EQE spectra of the optimized PSCs fabricated with PTzTIBDTT:ITIC/IDIC or PTzTIBDTT-S:ITIC/IDIC active layer.

Table S11. Photovoltaic properties of the devices based on nonfullerene acceptors ITIC and IDIC under the illumination of AM 1.5G, 100 mW cm⁻². The active layer films were fabricated with a D:A ratio of 1:1 from *o*-DCB solution having 1 vol% DIO, and thermal annealing at 100°C for 10 min.

Active layer	J _{sc} ^{JV} (mA/cm ²)	J _{sc} ^{EQE} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
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PTzTIBDTT:ITIC	8.98	8.75	0.92	43.74	3.74
PTzTIBDTT:IDIC	13.23	13.02	0.83	52.20	5.71
PTzTIBDTT-S:ITIC	4.18	4.07	0.82	41.01	1.39
PTzTIBDTT-S:IDIC	9.86	9.79	0.74	43.08	3.10

Table S12. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:ITIC/IDIC films were fabricated with a D:A ratio of 1:1 from *o*-DCB solutions.

Active layer	J_{sc}^{JV} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
PTzTIBDTT:ITIC	8.13	0.92	40.96	3.06
PTzTIBDTT:IDIC	12.37	0.83	48.92	5.02
PTzTIBDTT-S:ITIC	3.84	0.82	38.73	1.22
PTzTIBDTT-S:IDIC	9.32	0.74	41.27	2.84

Table S13. Device performance parameters of PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:IDIC films were fabricated with a D:A ratio of 1:1 from *o*-DCB solutions.

Configuration	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
Inverted	12.37	0.83	48.92	5.02
Conventional	11.57	0.84	47.79	4.65

Table S14. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:IDIC films were fabricated with a D:A ratio of 1:1 in distinct solution.

Solvent	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
<i>o</i> -DCB	12.37	0.83	48.92	5.02
CB	10.54	0.82	45.67	3.95
CF	none	none	none	none

Table S15. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:IDIC films were fabricated with a distinct D:A ratio in *o*-DCB solution.

D:A	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
2:1	10.89	0.81	45.68	4.03
1:1	12.37	0.83	48.92	5.02

1:2 12.02 0.82 47.79 4.71

Table S16. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:IDIC films were fabricated with a D:A ratio of 1:1 in *o*-DCB solution, thermal annealing at different temperature.

Thermal annealing	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
80°C	12.66	0.83	49.48	5.20
100°C	13.14	0.83	50.17	5.47
120°C	13.87	0.83	48.97	5.64

Table S17. Device performance parameters of inverted PSCs with a structure of ITO/ZnO/active layer/MoO₃/Ag. The PTzTIBDTT:IDIC films were fabricated with a D:A ratio of 1:1 from *o*-DCB solution with distinct additive.

Additive (1 vol%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
DIO	13.08	0.83	50.18	5.45
CN	12.96	0.83	48.99	5.27
DPE	12.39	0.83	49.75	5.12

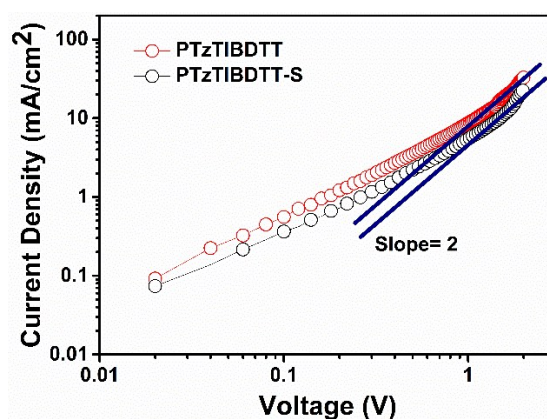


Figure S16. J - V characteristics of hole-only devices based on PTzTIBDTT and PTzTIBDTT-S.

7. GIWAXS Measurements and Data.

Two dimensional GIWAXS measurements were conducted at 23A SWAXS beamline at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan with a 10 keV primary beam, 0.15° incident angle and C9728DK area detector. The

films are prepared under the same conditions for the best-performing PSCs devices, but on silicon substrates.

Table S18. Peak positions, d-spacings of polymer blend films of **PTzTIBDTT:PC₇₁BM** and **PTzTIBDTT-S:PC₇₁BM** fabricated under the optimal conditions for PSCs devices, which were calculated via Scherrer equation.

Polymer	lamellar peak		π - π stacking peak	
	peak position (\AA^{-1})	d-spacing (\AA)	peak position (\AA^{-1})	d-spacing (\AA)
PTzTIBDTT (in-plane)	0.26	24.15		
PTzTIBDTT (out-of-plane)	0.29	21.65	1.72	3.65
PTzTIBDTT-S (in-plane)	0.25	25.12		
PTzTIBDTT-S (out-of-plane)	0.28	22.42	1.70	3.69

Reference:

- [1] Y. Shi, H. Guo, M. Qin, J. Zhao, Y. Wang, H. Wang, Y. Wang, A. Facchetti, X. Lu, X. Guo, *Adv. Mater.*, 2018, **30**, 1705745.
 [2] Y. Shi, H. Guo, M. Qin, Y. Wang, J. Zhao, H. Sun, H. Wang, Y. Wang, X. Zhou, A. Facchetti, X. Lu, M. Zhou, X. Guo, *Chem. Mater.*, 2018, **30**, 7988-8001.