

Support Information

An asymmetric small-molecule donor enables over 18% efficiency in ternary organic solar cells

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Experimental Section

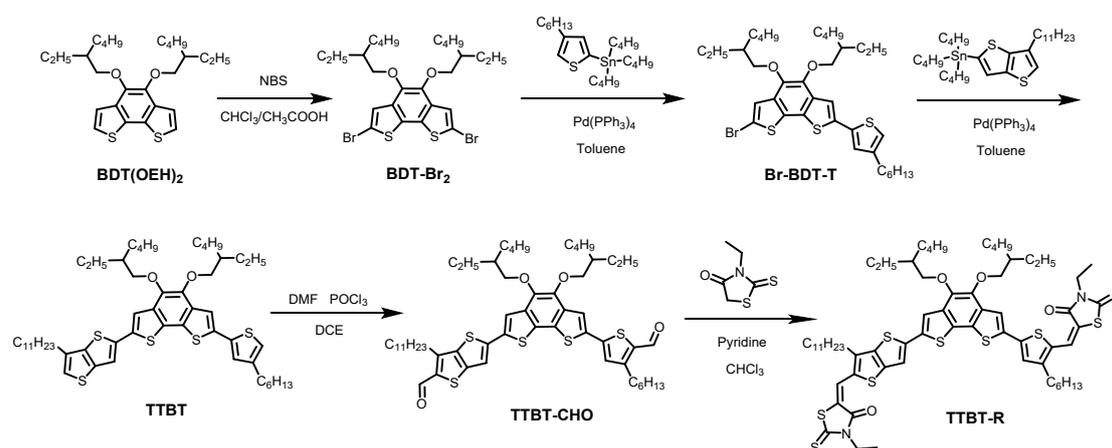
Materials and instruments

All reagents and solvents were purchased from Energy Chemical, Bide Pharmatech, Tianjin Kemiou, Hunan Huihong Reagent Co., Ltd and were used without further purification unless otherwise specified. PM6 and Y6 were purchased from Solarmer Energy Inc. and eFlexPV Ltd. Respectively. Nuclear magnetic resonance (NMR) spectra of the compounds were collected on Bruker AVANCE spectrometer by using deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the internal reference. High Resolution Mass spectrometry (HRMS) data were measured on a Bruker solanX 70 FT-MS with APCI as the ion source. The photophysical and electrochemical properties of the materials were measured on UV-visible-near infrared spectrograph (Agilent Cary 60 spectrometer) and electrochemistry workstation (CHI660A, Chenhua Shanghai) respectively. Thermogravimetric analyses (TGA) and differential scanning calorimetric (DSC) measurements were carried out on TA50 and

Q10 under nitrogen gas flow with a 15 °C min⁻¹ and a 10 °C min⁻¹ heating rate, respectively. The DSC samples were prepared by scraping and collecting the blend films on quartz slice, which were prepared by coating and drying the blend solutions. Atomic force microscopy (AFM) images were characterized by a Bruker Dimension Icon in a tapping mode. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were accomplished at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory beamline using an in-door Cu X-ray source (8.05 keV) and a Pilatus3R 300K detector.

Synthesis and characterization of TTBT-R

The detail synthetic route of TTBT-R was exhibited as follows. BDT(OEH)₂, tributyl(4-hexylthiophen-2-yl)stannane and tributyl(6-undecylthieno[3,2-*b*]thiophene-2-yl)stannane were synthesized according to the reported reference.^[1-3]



Scheme S1 The synthetic route of TTBT-R.

Synthesis of compound BDT-Br₂

The mixture of NBS (2.002 g, 11.25 mmol) in chloroform/acetic acid (20 mL, v/v=2:1) was added dropwise into a solution of BDT(OEH)₂ (2.011 g, 4.50 mmol) in chloroform/acetic acid (60 mL, v/v=2:1) under ice bath. After stirred for 24 h in dark, the mixture was poured into water and extracted with dichloromethane (100 mL × 3), then washed by water. The organic phase was dried over anhydrous MgSO₄, and then the solvent was removed by rotary evaporation. The crude product was purified on silica gel chromatography using a petroleum ether as eluent to afford a pale-yellow oil (1.387 g, 51%). ¹H NMR (400 MHz, CDCl₃): δ = 7.43 (s, 2H), 4.03-4.00 (dd, 4H), 1.81-1.75 (m, 2H), 1.66-1.36 (m, 16H), 1.00-0.93 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ = 143.10, 134.04, 129.03, 124.64, 112.84, 40.59, 30.41, 29.17, 23.81, 23.20,

14.20, 11.26.

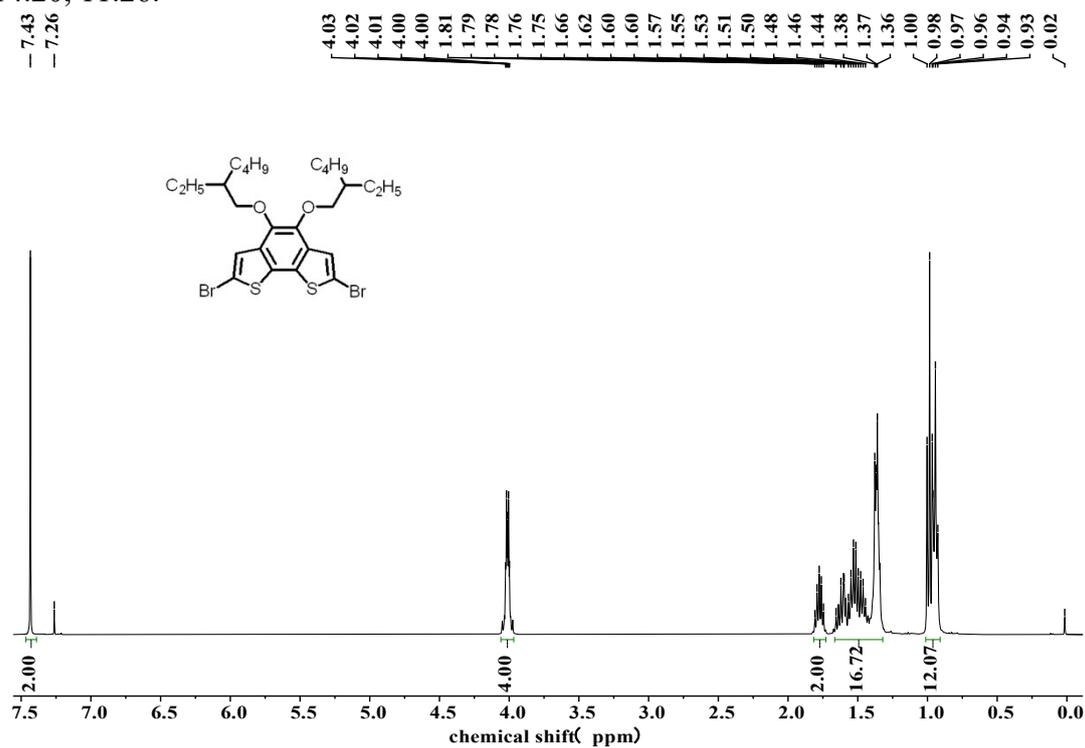


Fig. S1 ¹H NMR spectrum of BDT-Br₂ in CDCl₃.

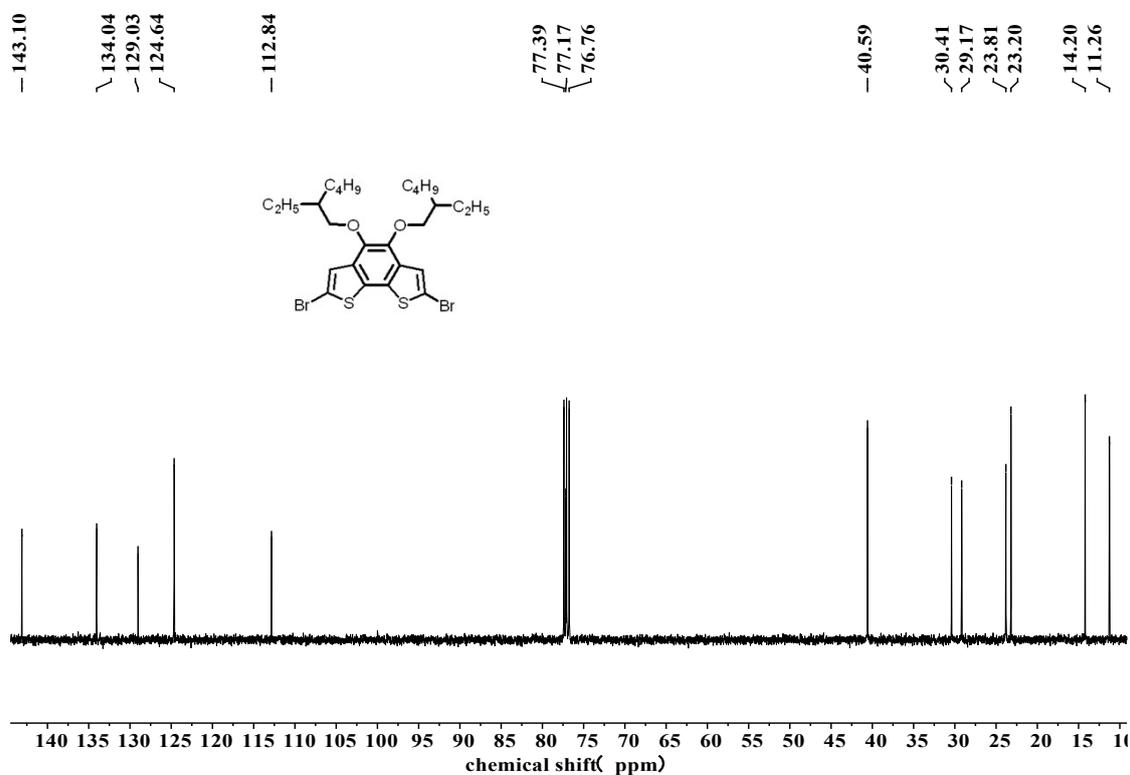


Fig. S2 ¹³C NMR spectrum of BDT-Br₂ in CDCl₃.

Synthesis of compound Br-BDT-T

BDT-Br₂ (1.172 g, 1.94 mmol) and tributyl(4-hexylthiophen-2-yl)stannane (0.928 g, 2.03 mmol) were dissolved in anhydrous toluene (13 mL) and deoxygenated with argon for 15 min. Pd(PPh₃)₄ (0.092 g, 0.08 mmol) was added under nitrogen. Then the reaction mixture was stirred at 110 °C for 36 h. After cooled to room temperature, the mixture was quenched with water and extracted with dichloromethane (150 mL × 3). The organic phase was dried over anhydrous MgSO₄. After concentrated, the crude product was purified on silica gel chromatography using petroleum ether as eluent to give a yellow liquid (0.618 g, 46%). ¹H NMR (400 MHz, CDCl₃): δ = 7.46 (s, 1H), 7.43 (s, 1H), 7.10 (s, 1H), 6.87 (s, 1H), 4.04-4.01 (dd, 4H), 2.62-2.58 (m, 2H), 1.82-1.75 (m, 2H), 1.65-1.33 (m, 24H), 1.01-0.88 (m, 15H). ¹³C NMR (100 MHz, CDCl₃): δ = 144.33, 143.75, 143.20, 136.76, 136.24, 135.05, 133.98, 129.62, 127.10, 126.36, 124.79, 120.24, 117.18, 112.53, 40.68, 40.65, 31.77, 30.59, 30.56, 30.48, 30.41, 29.27, 29.23, 29.10, 23.88, 23.29, 23.24, 22.71, 14.26, 14.22, 14.19, 11.31.

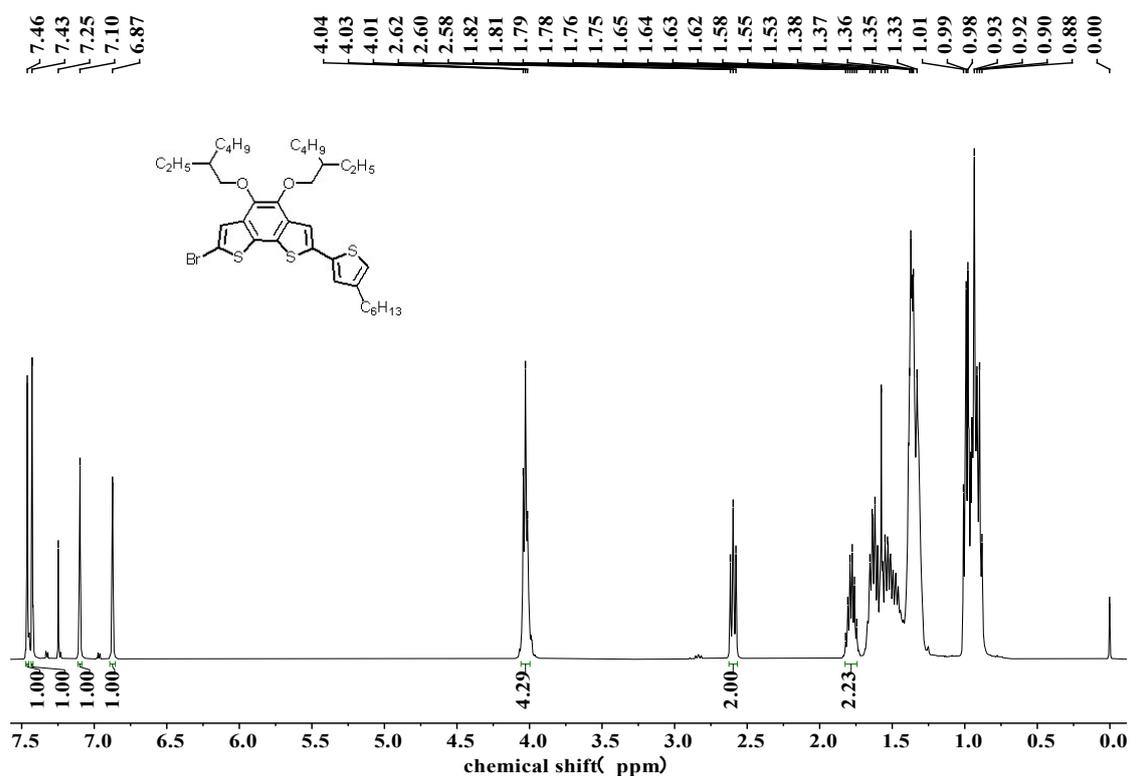


Fig. S3 ¹H NMR spectrum of Br-BDT-T in CDCl₃.

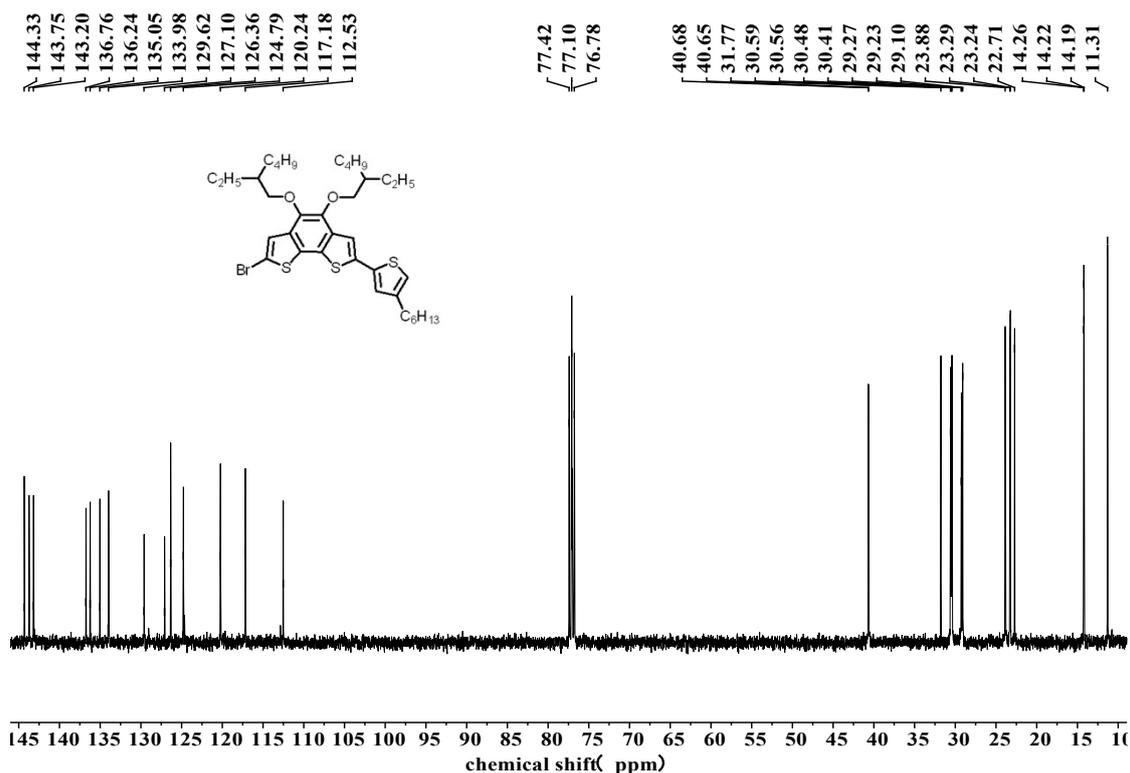


Fig. S4 ¹³C NMR spectrum of Br-BDT-T in CDCl₃.

Synthesis of compound TTBT

Br-BDT-T (0.578 g, 0.84 mmol) and tributyl(6-undecylthieno[3,2-*b*]thiophen-2-yl)stannane (0.782 g, 1.34 mmol) were dissolved in anhydrous toluene (12 mL) and deoxygenated with argon for 15 min, then Pd(PPh₃)₄ (0.085 g, 0.07 mmol) was then added under protect of argon. The reaction mixture was stirred at 110 °C for 24 h. After cooled to room temperature, the mixture was quenched with water and extracted with dichloromethane (100 mL × 3). The organic phase was dried over anhydrous MgSO₄ and concentrated, then the crude product was purified on silica gel chromatography using petroleum ether as eluent to give an orange liquid (0.523 g, 69%). ¹H NMR (400 MHz, CDCl₃): δ = 7.55 (s, 1H), 7.50 (s, 1H), 7.40 (s, 1H), 7.13 (s, 1H), 6.99 (s, 1H), 6.88 (s, 1H), 4.12-4.09 (t, 4H), 2.74-2.71 (t, 2H), 2.64-2.60 (t, 2H), 1.86-1.82 (m, 2H), 1.80-1.30 (m, 42H), 1.08-0.90 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): δ = 144.29, 143.89, 143.86, 139.17, 138.37, 137.02, 136.12, 135.95, 135.19, 135.02, 134.96, 128.63, 128.51, 127.79, 127.65, 126.18, 122.28, 120.06, 117.67, 117.36, 40.75, 32.09, 31.84, 30.67, 30.62, 30.44, 29.97, 29.87, 29.83, 29.78, 29.61, 29.59, 29.55, 29.34, 29.19, 28.71, 23.93, 23.42, 23.38, 22.86, 22.79, 14.37, 14.33, 14.26, 11.40.

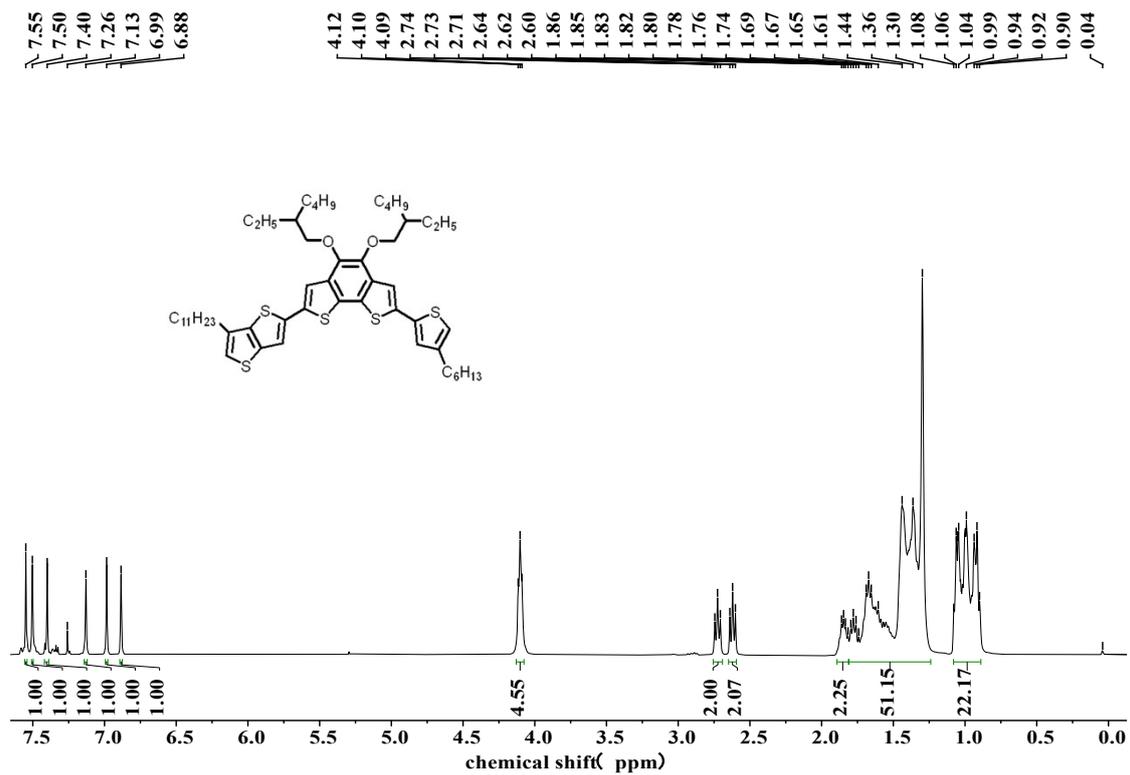


Fig. S5 ¹H NMR spectrum of TTBT in CDCl₃.

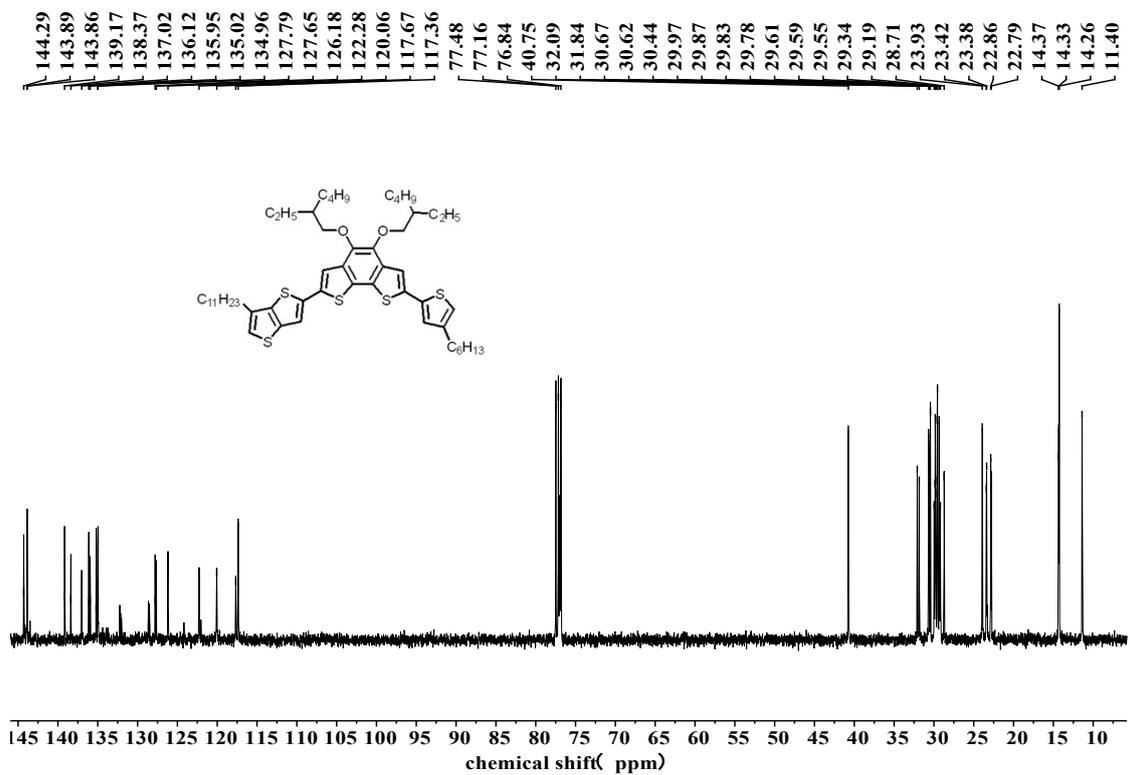


Fig. S6 ¹³C NMR spectrum of TTBT in CDCl₃.

Synthesis of compound TTBT-CHO

TTBT-CHO was synthesized by Vilsmeier-Haack reaction. Under argon atmosphere, anhydrous DMF (0.4 mL, 5.17 mmol) and POCl₃ (0.5 mL, 5.36 mmol) was slowly added to a solution of TTBT (0.463 g, 0.51 mmol) in 1,2-dichloroethane (20 mL) under ice bath. After stirred for 15 min, the mixture was heated to 85 °C and stirred for 24 h. After cooled to room temperature, sodium acetate solution (100 mL) was added to hydrolyze for 2 h. The mixture was washed with water and extracted with DCM (100 mL × 3). The organic phase was dried over anhydrous MgSO₄, and the solvent was removed by rotary evaporation. The crude product was purified on silica gel chromatography (petroleum ether/dichloromethane, 1:2) to afford an orange solid (0.450 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ = 10.04 (s, 1H), 9.99 (s, 1H), 7.63 (s, 1H), 7.58(s, 1H), 7.38 (s, 1H), 7.11 (s, 1H), 4.08-4.05 (m, 4H), 3.08-3.04 (t, 2H), 2.94-2.91 (t, 2H), 1.82-1.78 (m, 2H), 1.75-1.24 (m, 42H), 1.02-0.84 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): δ = 181.95, 181.45, 153.77, 145.32, 144.97, 144.75, 144.13, 144.10, 144.03, 139.88, 139.13, 136.66, 135.67, 135.50, 135.27, 134.66, 128.40, 128.04, 127.55, 120.20, 119.39, 117.33, 40.65, 31.93, 31.59, 31.35, 30.55, 30.51, 30.49, 29.93, 29.65, 29.63, 29.53, 29.36, 29.23, 29.08, 28.58, 28.28, 23.82, 23.79, 23.30, 23.24, 22.71, 22.59, 14.26, 14.21, 14.14, 14.09, 11.31, 11.27, 11.25.

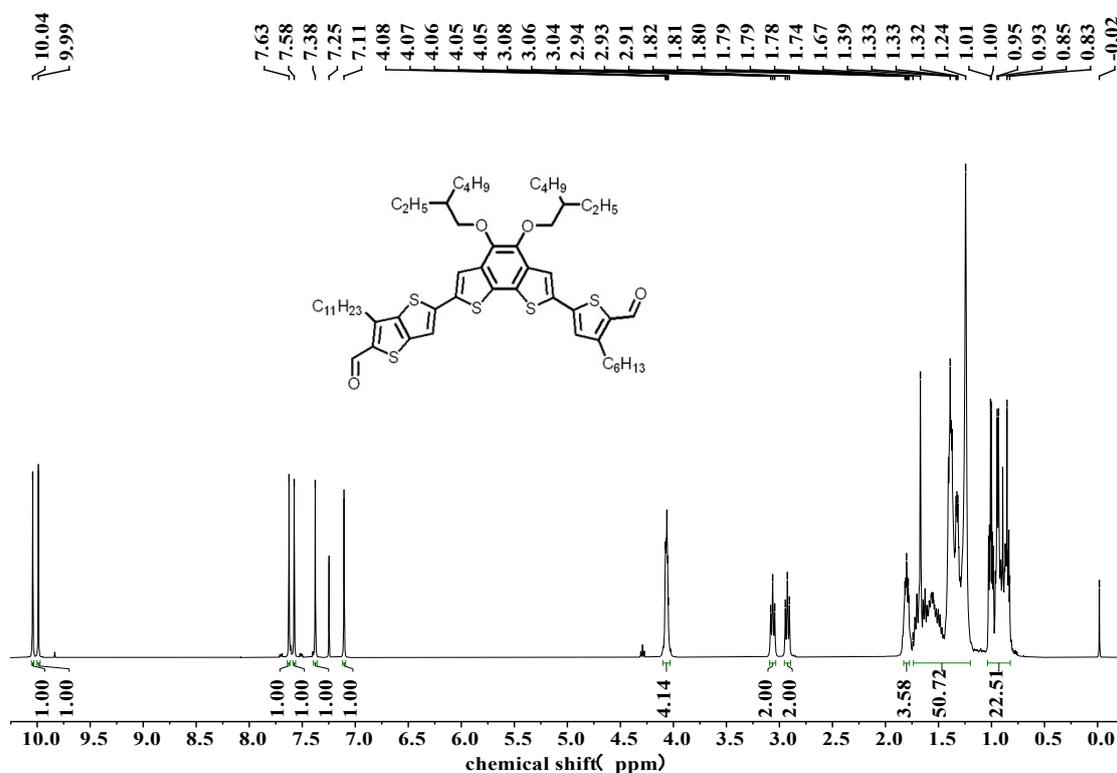


Fig. S7 ¹H NMR spectrum of TTBT-CHO in CDCl₃.

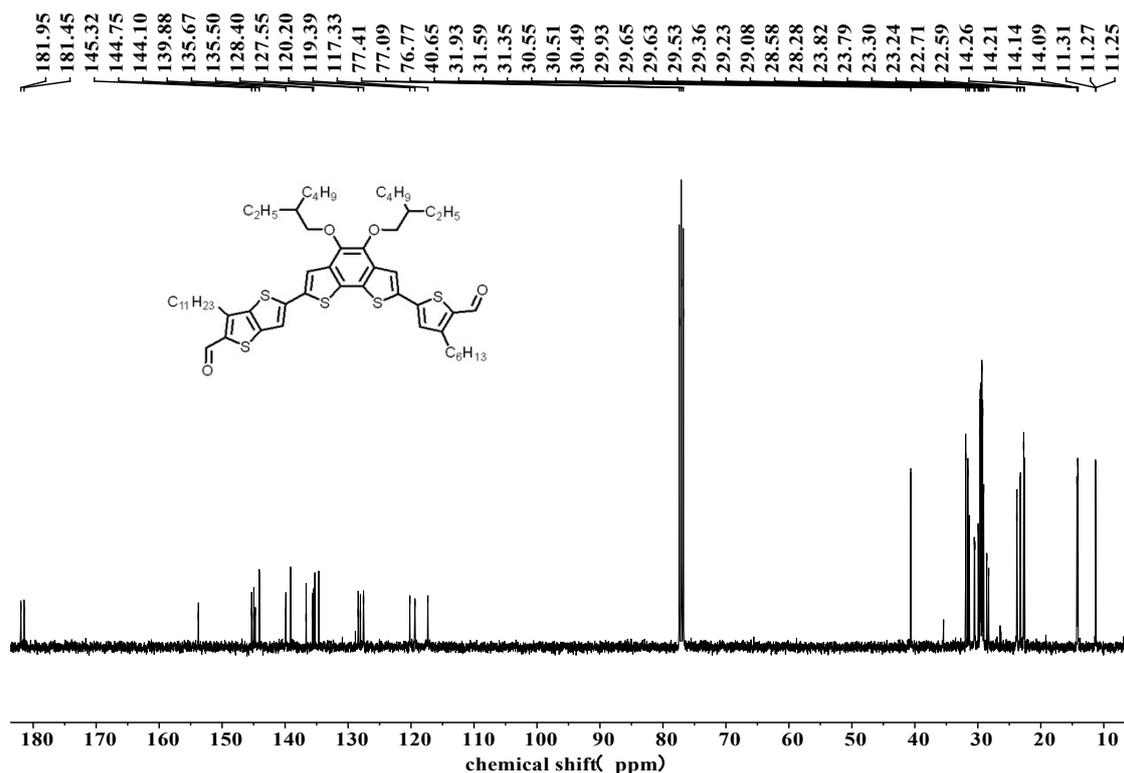


Fig. S8 ¹³C NMR spectrum of TTBT-CHO in CDCl₃.

Synthesis of compound TTBT-R

TTBT-CHO (0.112 g, 0.12 mmol), 3-ethylrhodanine (0.187 g, 1.16 mmol) was dissolved in chloroform (15 mL) under protection of argon, and pyridine (0.5 mL) was added to the mixture, then the mixture was heated to 60 °C and stirred overnight. After cooled to room temperature, the mixture was concentrated by evaporation under reduced pressure. The crude product was purified on silica gel chromatography (petroleum ether/dichloromethane, 3:1) to afford a dark brown solid (0.094 g, 63%). ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (s, 1H), 7.82 (s, 1H), 7.49 (s, 1H), 7.44 (s, 1H), 7.24 (s, 1H), 7.06 (s, 1H), 4.18-4.06 (m, 8H), 2.87-2.83 (t, 2H), 2.77-2.74 (t, 2H), 1.89-1.81 (m, 2H), 1.73-1.27 (m, 48H), 1.08-0.85 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): δ = 191.84, 191.81, 167.27, 167.21, 151.00, 144.03, 143.99, 143.56, 143.33, 142.26, 141.01, 140.48, 135.57, 135.52, 135.39, 134.57, 134.55, 132.14, 128.10, 127.89, 127.33, 123.59, 122.72, 119.96, 119.71, 119.26, 118.78, 116.78, 77.33, 77.02, 76.70, 40.71, 39.91, 31.93, 31.64, 30.97, 30.58, 29.71, 29.65, 29.59, 29.42, 29.36, 29.24, 29.19, 29.10, 28.80, 23.83, 23.36, 23.31, 22.70, 22.63, 14.35, 14.27, 14.12, 14.10, 12.29, 11.39, 11.36, 11.32. HRMS (APCI) m/z: [M+H]⁺ calcd for C₆₅H₈₆N₂O₄S₉, 1247.41467; found, 1247.41211.

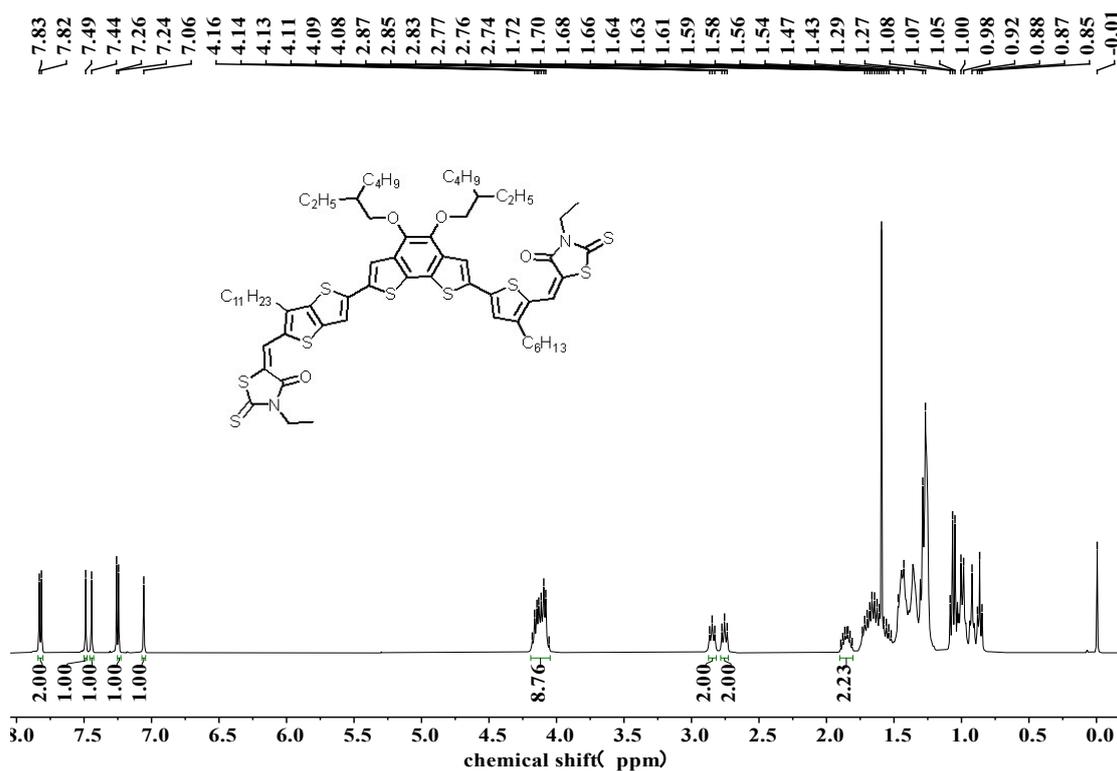


Fig. S9 ¹H NMR spectrum of TTBT-R in CDCl₃.

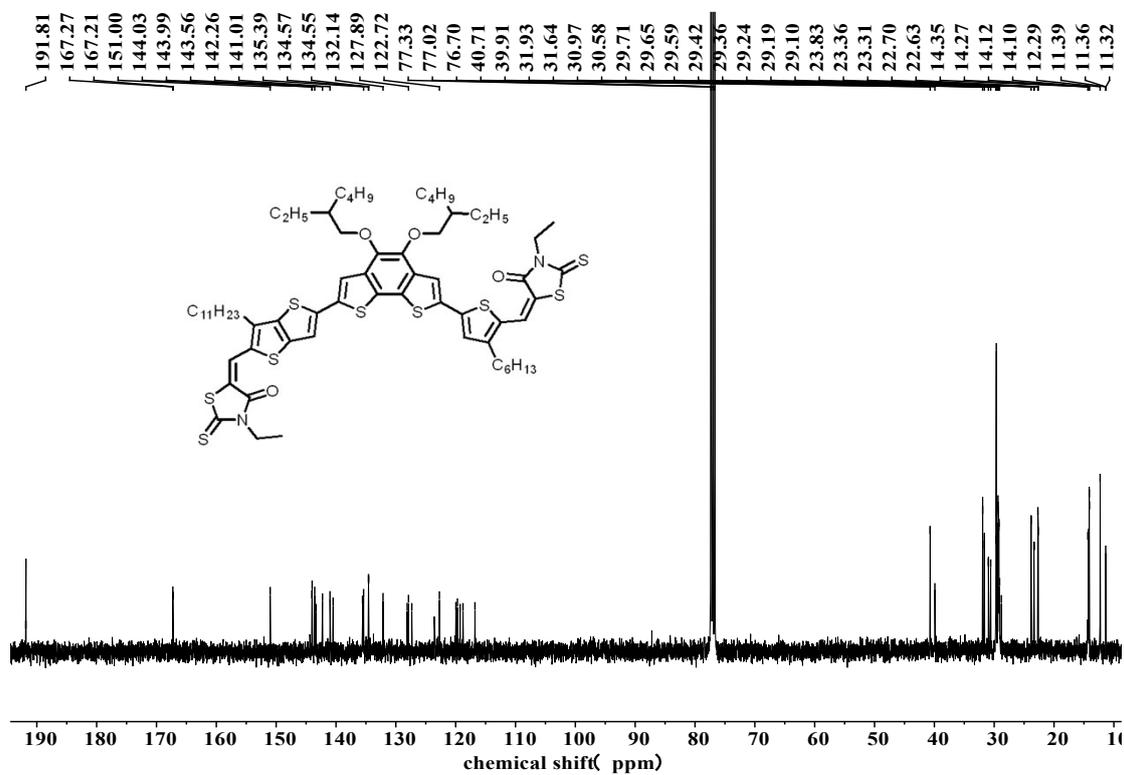


Fig. S10 ¹³C NMR spectrum of TTBT-R in CDCl₃.

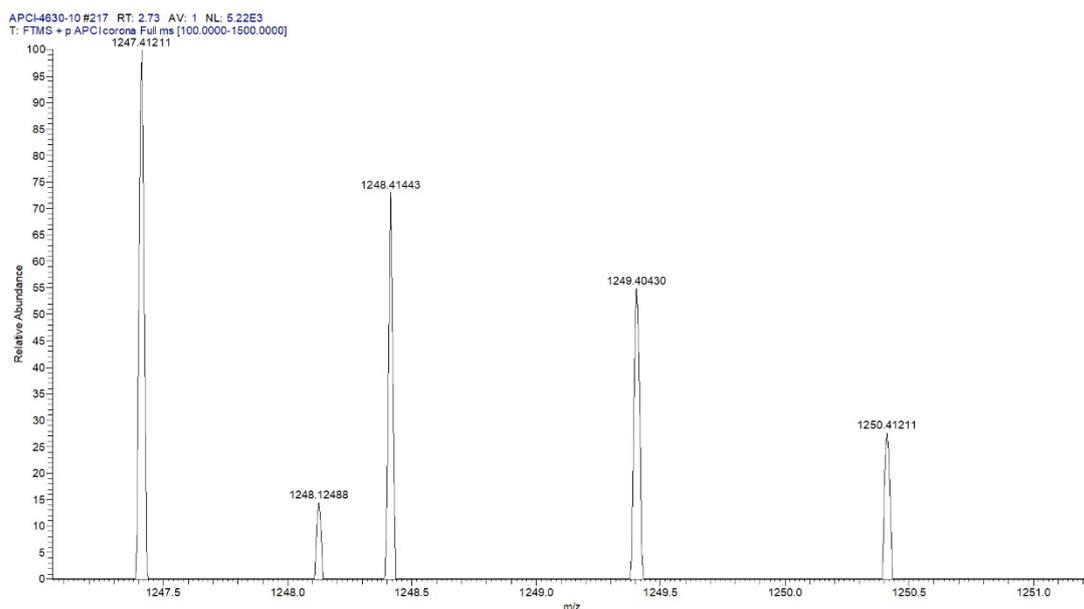


Fig. S11 HRMS of TTBT-R.

Fabrication and characterization of OSCs devices

All OSCs devices were fabricated with the conventional structure of ITO/PEDOT:PSS/Active layer/PDIN/Ag. The ITO-glass substrates was carefully washed by acetone, water, ethanol and isopropanol in sequence, and then treated by UV-ozone cleaning for 15 min. PEDOT:PSS was spin-coated at 2000 rpm onto the cleaned ITO substrate, subsequently annealed at 170°C for 30 min in air to obtain a PEDOT:PSS-covered (30 nm) ITO. The active layer (100 nm) was spin-coated from chloroform solution (12.6 mg mL⁻¹ in total) with 0.5 vol% of 1-chloronaphthalene as additive, and then annealed at 110 °C for 10 min. Subsequently, PDIN layer (5 nm) and Ag electrode (100 nm) were slowly evaporated onto the surface of active layer under a vacuum pressure of 2×10⁻⁴ Pa. The *J-V* plots were measured using a Keithley 2400 source meter, and an Enlitech SS-F5-3A solar simulator with 1.5 G solar spectrum filters was used as the light source. The charge mobilities of blend films were investigated by the space-charge-limited current (SCLC) method. The structure of electron-only devices is ITO/ZnO/active layer/ PDIN/Ag, while the hole-only device configuration is ITO/PEDOT:PSS/active layer/MoO₃/Ag. The mobility was determined by fitting SCLC curves according to the equation: $J = 9\mu\epsilon_0\epsilon_r V^2/8L^3$, where *J* is the current density, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the materials, *V* is the applied voltage, and *L* is the active layer thickness.

Table S1. Photovoltaic parameters of the reported TOSCs based on a SM molecule as

second donor.

Polymer donor	SM donor	Acceptor	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Ref.
PBDB-T	IBC-F	IE4F-S	0.887	22.83	74.4	15.06	[19]
PM6	C1	IT-4F	1.02	16.42	69.0	11.56	[35]
PM6	BPR-SCl	BTP-eC9	0.856	27.13	77.6	18.02	[41]
PM6	SM1	Y6	0.831	25.7	77.5	16.55	[42]
PM6	ECTBD	Y6	0.848	25.54	76.24	16.51	[43]
PM6	BTBR-2F	Y6	0.859	27.30	74.11	17.38	[44]
PM6	DRTB-T-C4	Y6	0.85	24.79	81.3	17.13	[45]
PM6	TiC12	Y6	0.853	26.80	75.4	17.25	[46]
PM6	BPR-SCl	Y6	0.87	25.77	75.0	16.74	[47]
PM6	BTTzR	Y6	0.87	26.2	77.7	17.7	[48]
D18-Cl	G19	Y6	0.871	27.36	77.72	18.53	[49]
PTB7-Th	DRCN5T	PC ₇₀ BM	0.78	20.10	69.8	11.1	[57]

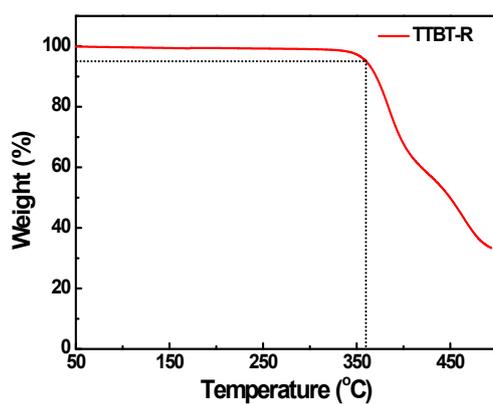


Fig. S12 Thermogravimetric curve of TTBT-R.

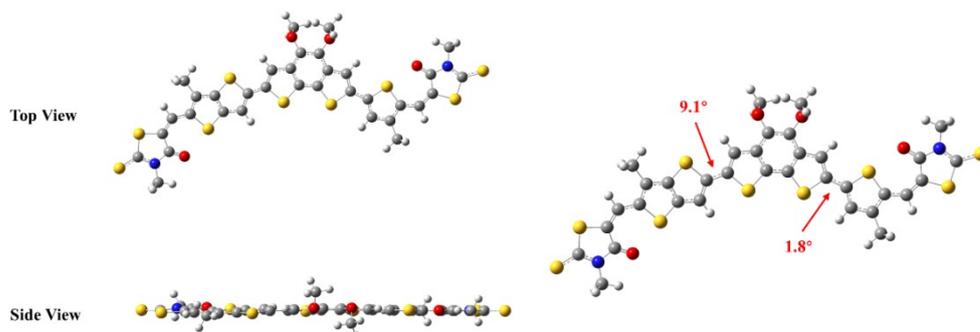


Fig. S13 Molecular geometry and dihedral angle of TTBT-R obtained by DFT calculation.

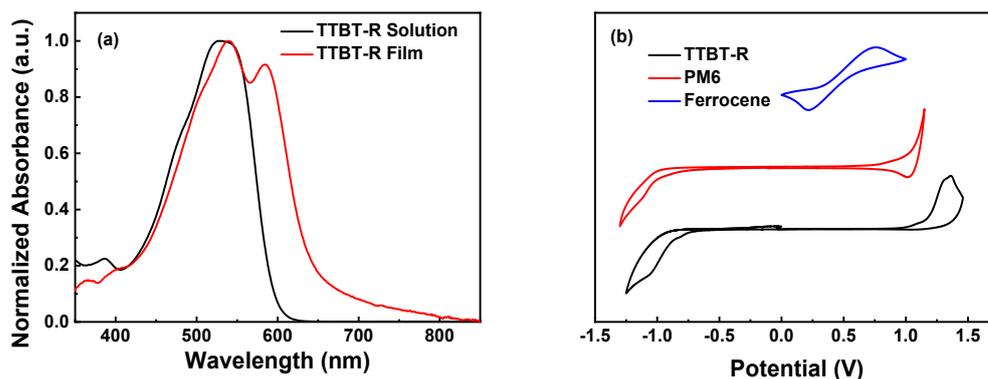


Fig. S14 (a) Normalized absorbance of TTBT-R in solution and film and (b) cyclic voltammetry curves of PM6, TTBT-R and Ferrocene.

Table S2. Optical and electrochemical parameters of PM6 and TTBT-R.

Materials	$\lambda_{\max}^{\text{film}}$ (nm)	$\lambda_{\max}^{\text{solution}}$ (nm)	$\lambda_{\text{onset}}^{\text{film}}$ (nm)	$\varepsilon_{\max}^{\text{film}}$ (10^4 cm^{-1})	E_g^{opt} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
PM6	619	-	680	5.72	1.82	-5.47	-3.46
TTBT-R	539	531	643	7.10	1.93	-5.56	-3.55

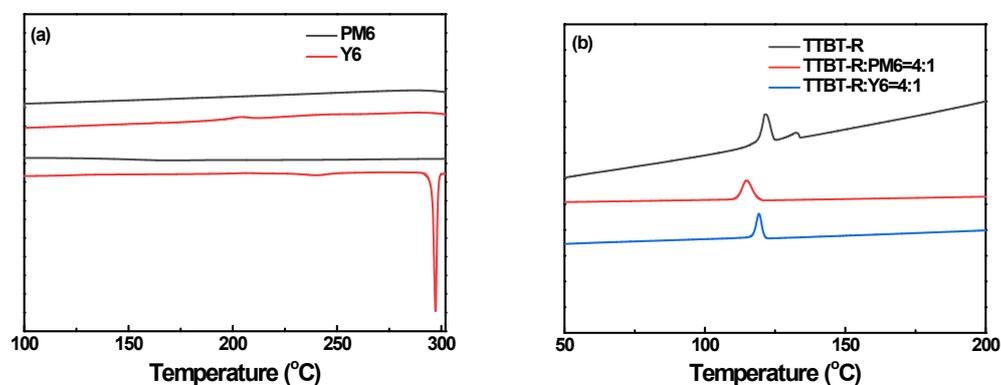


Fig. S15 (a) DSC curves of PM6 and Y6 and (b) DSC curves of TTBT-R, TTBT-R:PM6 (4:1 by weight) and TTBT-R:Y6 blends (4:1 by weight) in the cooling process.

Table S3. Contact Angles, Surface Tensions (γ), and Interaction Parameters (χ).

Materials	θ_{water} ($^{\circ}$)	θ_{EG} ($^{\circ}$)	γ^{d} [mN m $^{-1}$]	γ^{p} [mN m $^{-1}$]	γ [mN m $^{-1}$] ^a	$\chi_{\text{PM6-Ab}}$	$\chi_{\text{TTBT-R-A}}$ _b
PM6	93.3	70.8	18.94	3.83	22.77	-	0.008
TTBT-R	95.3	71.3	20.94	2.67	23.61	0.008	-
Y6	88.5	62.8	23.37	4.28	27.65	0.237	0.159

^a The surface tension of each pure material was calculated by Owens model.

^b The Flory-Huggins interaction parameters between donor (D) and acceptor (A) were calculated by using the equation $\chi \approx (\sqrt{\gamma_{\text{D}}} - \sqrt{\gamma_{\text{A}}})^2$.

Table S4. Photovoltaic parameters based on PM6:TTBT-R:Y6 (0.9:0.1:1) blends at different thermal annealing times.

Annealing time (min)	V_{oc} (V)	J_{sc} (mA cm $^{-2}$)	FF (%)	$\text{PCE}_{\text{max}}/\text{PCE}^{\text{a}}$ (%)
0	0.888 ± 0.001	24.50 ± 0.42	73.52 ± 0.32	16.36/16.08
5	0.863 ± 0.002	26.77 ± 0.34	74.48 ± 0.47	17.58/17.27
10	0.862 ± 0.001	27.01 ± 0.37	76.13 ± 0.33	18.07/17.86
15	0.858 ± 0.002	26.57 ± 0.48	74.47 ± 0.41	17.42/17.19

^a Average parameters are calculated from more than 15 independent cells.

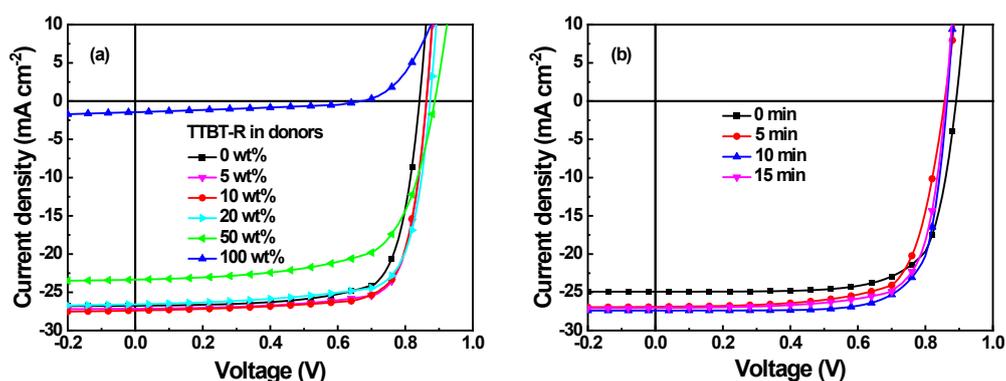


Fig. S16 (a) J - V curves of the binary devices and PM6:TTBT-R:Y6 ternary devices with different TTBT-R content, (b) J - V curves of the TOSCs based on PM6:TTBT-R:Y6 (0.9:0.1:1) blends annealed at 110 °C with different thermal annealing times.

Table S5 Photovoltaic parameters the inverted binary and ternary OSCs based on (a) PBDB-T:ITIC, (b) PM6:IT-4F and (c) PM6:Y6 blends

D/A ratio	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF (%)	PCE _{max} /PCE ^a (%)
PBDB-T:ITIC (1:1)	0.888 ± 0.002	16.86 ± 0.21	64.64 ± 0.53	9.94/9.76
PBDB-T:TTBT-R:ITIC (0.9:0.1:1)	0.927 ± 0.003	18.98 ± 0.27	68.46 ± 0.47	12.32/12.15
PM6:IT-4F (1:1)	0.829 ± 0.001	21.96 ± 0.31	74.62 ± 0.43	13.16/12.86
PM6:TTBT-R:IT-4F (0.9:0.1:1)	0.862 ± 0.002	22.96 ± 0.43	72.30 ± 0.50	14.70/14.52
PM6:Y6 (1:1)	0.838 ± 0.002	25.76 ± 0.28	70.35 ± 0.42	15.48/15.21
PM6:TTBT-R:Y6 (0.9:0.1:1)	0.855 ± 0.003	27.12 ± 0.39	70.02 ± 0.26	16.57/16.37

^a Average parameters are calculated from 10 devices.

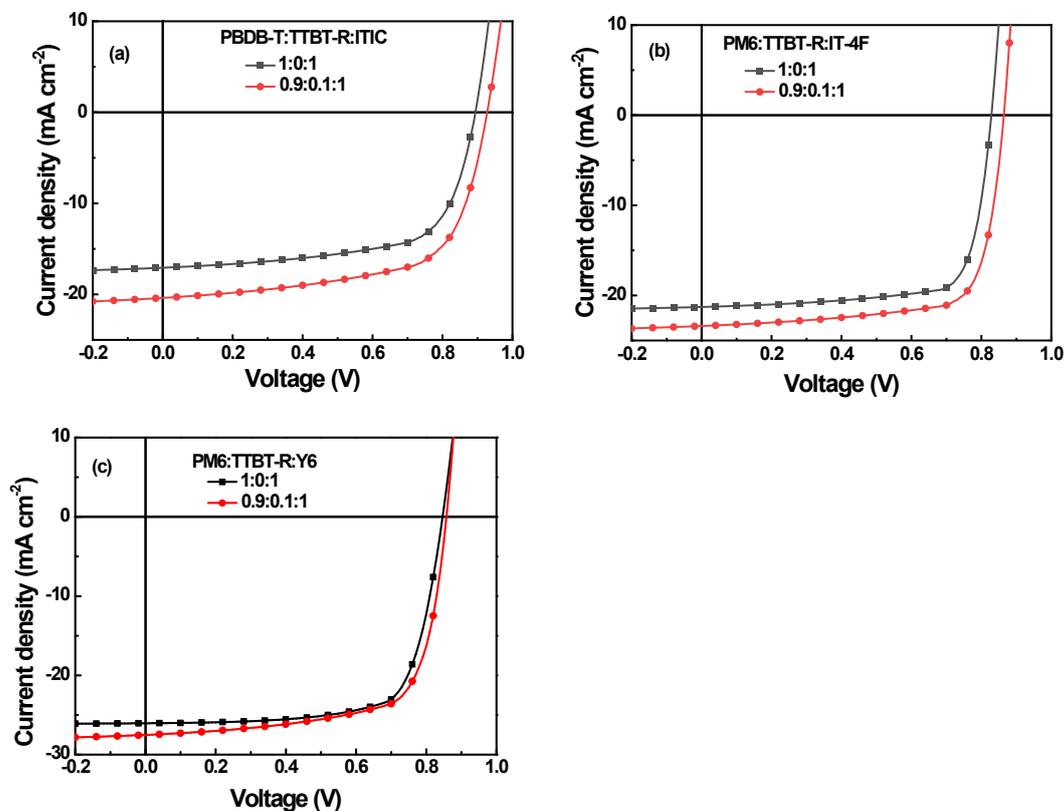


Fig. S17 J - V curves of the inverted binary and ternary OSCs based on (a) PBDB-T:

ITIC, (b) PM6: IT-4F and (c) PM6: Y6 blends.

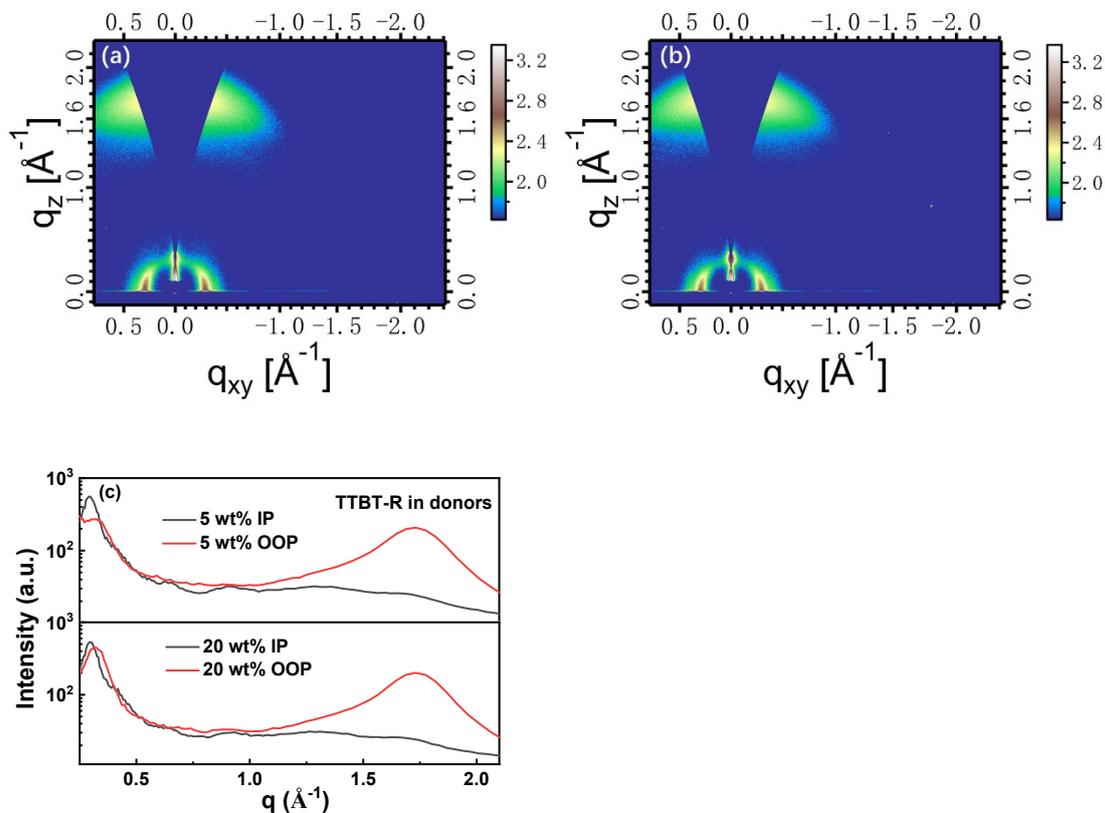


Fig. S18 2D GIWAXS patterns of PM6:TTBT-R:Y6-based blend films with different contents of TTBT-R (a) 5%, (b) 20% and (c) the corresponding in-plane and out-of-plane line-cuts of the ternary blends.

Table S6 GIWAXS parameters of the pure films and the corresponding blend films in the IP direction.

TTBT-R in donors (wt%)	in plane (100)		
	Location (\AA^{-1})	d (\AA)	CCL (\AA)
0	0.288	21.82	76.00
5	0.293	21.44	81.46
10	0.299	21.01	81.91
20	0.293	21.44	84.16
100	0.293	21.44	83.74

Table S7 GIWAXS parameters of the pure films and the corresponding blend films in the OOP direction.

TTBT-R in donors (wt%)	out of plane (010)		
	Location (\AA^{-1})	d (\AA)	CCL (\AA)
0	1.732	3.63	24.52
5	1.732	3.63	24.68
10	1.732	3.63	24.76
20	1.732	3.63	26.06
100	1.732	3.63	29.27

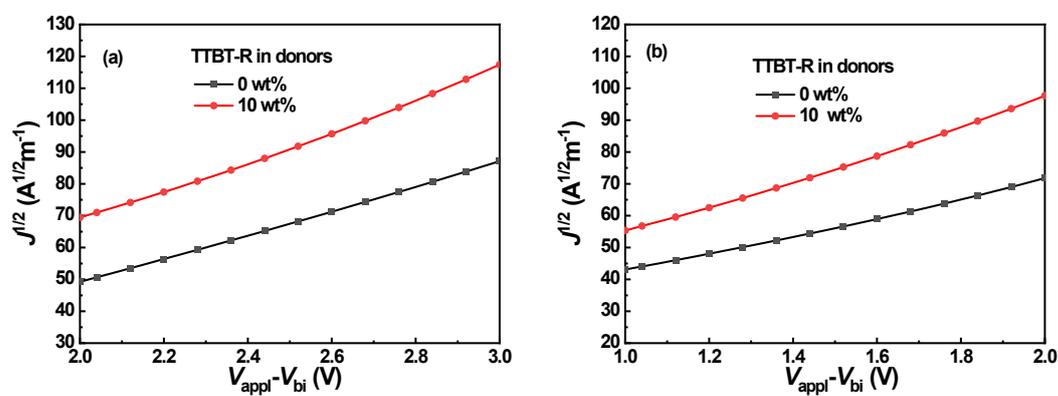


Fig. S19 $J^{1/2}$ -V curves of (a) hole-only devices and (b) electron-only devices based on the binary and ternary devices.

Table S8 Charge mobilities of the binary and ternary SCLC devices.

TTBT-R in donors (wt%)	μ_h ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	μ_e ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	μ_h/μ_e
0	4.78	2.86	1.67
5	5.63	3.68	1.53
10	7.67	5.96	1.29
20	4.38	3.04	1.44
50	2.27	1.20	1.89

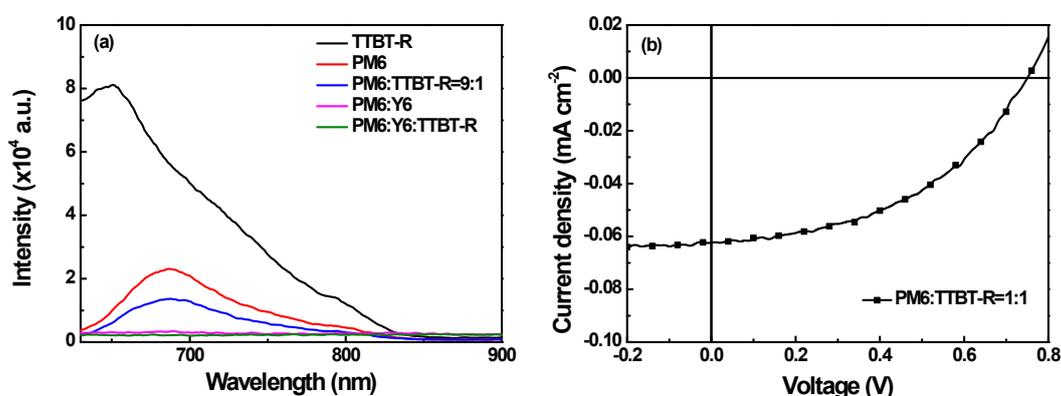


Fig. S20 (a) PL spectra of the pure and blend films excited at 619 nm and (b) J - V curve of the OSC based on PM6:TTBT-R (1:1).

Reference:

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