Supporting Information

A low-cost wide bandgap polymer based on carboxylate-substituted thiazole enables efficient organic solar cells with remarkable batch-to-batch reproducibility

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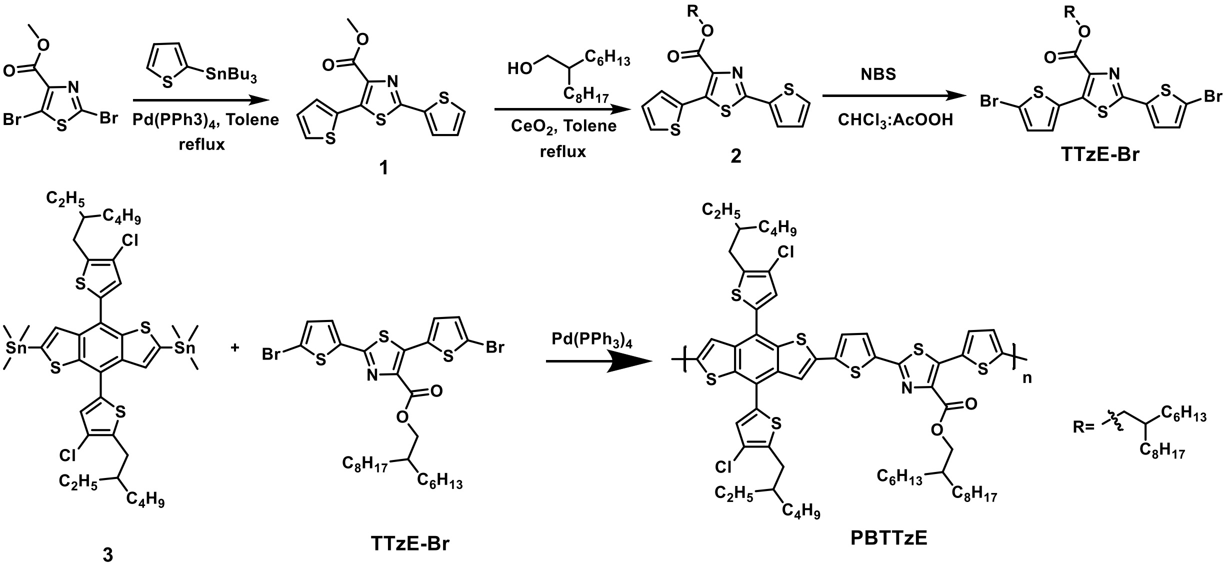
Experimental section

1. Materials

Methyl-2,5-dibromothiazole-4-carboxylate was purchased from Energy Chemical. Tributyl(thiophen-2-yl)stannane and (4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl)bis(trimethylstannane) were prepared according to the previous methods [1, 2]. The materials of PM6, IT-4F, BTP-eC9, Y6 and L8-BO were purchased from Solarmer. Other reagents were obtained from JK Chemical, Energy Chemical or Acros and used as received. Anhydrous THF and toluene were obtained by distillation over sodium/benzophenone under nitrogen atmosphere. The detailed synthetic procedures are as follows.



Scheme S1 Synthetic routes of TTzE-Br and PBTTzEs

2. Synthesis of the monomer and polymers

methyl 2,5-di(thiophen-2-yl)thiazole-4-carboxylate (1): Anhydrous toluene (60 mL) was injected through a septum to a 250 mL three-necked flask charged with Methyl-2,5-dibromothiazole-4-carboxylate (0.75 g, 2.50 mmol), 2-(tributylstannyl) thiophene (2.33 g, 6.25 mmol) and $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol). The mixture was then heated to 110 °C under argon for 16 h. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane three times. The organic phase was washed with brined, dried with anhydrous Na_2SO_4, and then evaporated to dryness under reduced pressure. The crude product was purified by column chromatography using dichloromethane and petroleum ether (v/v, 2/1) as the eluent. Pure product was obtained after vacuo as a yellow solid (0.61 g, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.54 (d, J = 3.5 Hz, 2H), 7.46 (t, J = 6.2 Hz, 2H), 7.10 (t, J = 4.4 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm): 162.45, 158.67, 139.38, 138.85, 135.89, 130.76, 130.37, 128.96, 128.76, 127.96, 127.68, 127.43, 52.46. EIMS (ESI, m/z): [M^+], calcd. for $C_{13}H_9NO_2S_3$: 307.40; found: 307.00.

2-hexyldecyl 2,5-di(thiophen-2-yl)thiazole-4-carboxylate (2): Compound **1** (0.15 g, 0.50 mmol), 2-hexyl-1-decanol (0.45 g, 2.0 mmol), and CeO_2 (0.34 g, 2.0 mmol) were dissolved in 15 mL toluene, and the solution was purged with argon for 20 min. Then the mixture was heated at 110 °C. After 48 h, the solution was cold to room temperature and the redundant 2-Hexyl-1-decanol was removed by vacuum distillation. The crude product was dissolved in dichloromethane and extracted with water, and dried over anhydrous Na_2SO_4. After removing organic solvent by rotary evaporator, the crude product was purified by column chromatography with dichloromethane and petroleum ether (v/v, 1/1) as the eluent. The pure product was obtained after vacuo as a yellow oil (0.22 g, yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.53 (d, J = 3.6 Hz, 2H), 7.44 (d, J = 4.4 Hz, 2H), 7.09 (q, J = 4.4 Hz, 2H), 4.22 (d, J = 6.0 Hz, 2H), 1.71 (m, 1H), 1.25 (m, 24H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm): 162.37, 158.89, 140.78, 137.40, 136.22, 130.52, 130.32, 128.67, 128.52, 127.89, 127.48, 127.38, 68.54, 37.24, 31.90, 31.81, 31.18, 30.94, 29.95, 29.61, 29.55, 29.33, 26.67, 26.64, 22.67, 14.11. EIMS (ESI, m/z): [M$^+$], calcd. for $C_{28}H_{39}NO_2S_3$: 517.81, found: 517.20.

2-hexyldecyl 2,5-bis(5-bromothiophen-2-yl)thiazole-4-carboxylate (TTzE-Br): To a solution of Compound **2** (0.52 g, 1.0 mmol) in chloroform and acetic acid (v/v, 1:1, 10 mL) was added *N*-Bromosuccinimide (0.36 g, 2.0 mmol) in ice bath under darkness. After stirring for overnight under reflux conditions, water was poured into the mixture to quench the reaction. Then, the solution was extracted twice with dichloromethane, and washed with $NaHCO_3$ and water. The organic extract was dried over anhydrous Na_2SO_4, condensed at reduced pressure and purified with silica gel column chromatography using dichloromethane and petroleum ether (v/v, 1:2) as the eluent to give a yellow oil product (0.60 g, yield 89%). ^{1}H NMR (400 MHz, CDCl3), δ(ppm): 7.25 (d, J = 4.0 Hz, 1H), 7.19 (d, J = 4.0 Hz, 1H), 7.04 (dd, J = 4.0 Hz, J = 4.0 Hz, 2H), 4.23 (d, J = 6.4 Hz, 2H), 1.74 (m, 1H), 1.27 (m, 24H), 0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm): 162.14, 157.45, 140.52, 137.46, 137.14, 131.84, 130.81, 130.70, 130.04, 127.50, 116.79, 116.56, 68.79, 37.27, 31.90, 31.83, 31.27, 31.25, 29.97, 29.64, 29.57, 29.35, 26.70, 26.67, 22.68, 14.12. EIMS (ESI, m/z): [M$^+$], calcd. for $C_{28}H_{37}Br_2NO_2S_3$: 675.60, found: 675.05.

Polymerization of PBTTzE (M_n = 43 kDa): Into a 50 mL Schlenk tube was added TTzE-Br (0.14 g, 0.20 mmol) and (4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis (trimethylstannane) (0.20 g, 0.20 mmol). The flask was then transferred to a glovebox where anhydrous toluene (6.0 mL) was injected to dissolve the mixture. Then the $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol) was added as a catalyst, and the flask was heated at 110 °C for 48 h under nitrogen. After cooling, the mixture was poured into methanol (50 mL). The precipitate was collected and further purified by Soxhlet extraction with acetone, hexane, dichloromethane and chloroform. The chloroform fraction was then concentrated via rotavapor evaporation and precipitated in methanol. The solid was filtered and dried under vacuum to offer the final product (148 mg, yield 62%). GPC: M_n = 43 kDa, PDI = 2.3.

Polymerization of PBTTzE (M_n = 54 kDa): The polymer was prepared using a similar procedure for PBTTzE (M_n = 43 kDa) from TTzE-Br (0.14 g, 0.20 mmol), (4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (0.20 g, 0.20 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol), and a mixed solvent of anhydrous toluene (3.56 mL) and *N,N*-dimethylformamide (0.44 mL). The mixture was stirred at 120 °C for 48 h, and then 175 mg of the final product was obtained from the chloroform fraction after Soxhlet extraction with a yield of 73.4%. GPC: M_n = 54 kDa, PDI = 2.4.

Polymerization of PBTTzE (M_n = 57 kDa): The polymer was prepared using a similar procedure for PBTTzE (M_n = 43 kDa) from TTzE-Br (0.14 g, 0.20 mmol), (4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6diyl)bis(trimethylstannane) (0.20 g, 0.20 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol), and a mixed solvent of anhydrous toluene (3.35 mL) and *N,N*-dimethylformamide (0.65 mL). The mixture was stirred at 130 °C for 72 h, and then 183 mg of the final product was obtained from the chloroform fraction after Soxhlet extraction with a yield of 76.8%. GPC: M_n = 57 kDa, PDI = 2.0.

Polymerization of PBTTzE (M_n = 76 kDa): The polymer was prepared using a similar procedure for PBTTzE (M_n = 43 kDa) from TTzE-Br (0.14 g, 0.20 mmol), (4,8-bis(4-chloro-5-(2-ethylhexyl)thiophen -2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6diyl)bis(trimethylstannane) (0.20 g, 0.20 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol), and a mixed solvent of anhydrous *o*-xylene (3.35 mL) and *N,N*-dimethylformamide (0.65 mL). The mixture was stirred at 140 °C for 96 h, and then 169 mg of the final product was obtained from the chloroform fraction after Soxhlet extraction with a yield of 71%. GPC: M_n = 76 kDa, PDI = 2.3.

3. Measurements and Instruments

Nuclear magnetic resonance (NMR): ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer using deuterated chloroform ($CDCl_3$) as the solvent at room temperature.

Electron impact mass spectrum (EI-MS): EI-MS were determined using GCMS-QP2020 Mass Spectrometer.

Gel permeation chromatography (GPC): The molecular weights and Polydispersity of PBTTzEs with different molecular weight were measured by high temperature chromatography with trichlorobenzene as the eluent at 150 °C relative to a polystyrene standard on an Agilent PL-GPC 220 system.

Thermogravimetric analysis (TGA): The TGA measurements were carried out on with a NETZSCH (449F3/F5) apparatus at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

UV-vis spectroscopy: The UV-vis absorption spectra of polymers in chloroform solution and thin films were conducted on a Perkin-Elmer Lambda 365 spectrophotometer from 300 nm to 900 nm. The temperature-dependent experiments of polymers in chlorobenzene solution were measured through stepwise increasing temperature from room temperature to fully disaggregate temperature.

Cyclic voltammetry (CV): The CV experiments were performed with CHI 600 electrochemical workstation by using a conventional three-electrode configuration employing a platinum wire as a counter electrode, platinum electrode as a working electrode, and Ag/Ag$^+$ electrode as a reference electrode at a scan rate of 100 mV s^{-1} in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1M) in anhydrous acetonitrile. A ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was used as internal standard and was assigned an absolute energy of –4.8 eV versus vacuum. The HOMO and LUMO energies of materials were determined according to the equation $E_{\mathrm{HOMO}} = -(E_{\mathrm{ox\ onset}} + 4.8 - E_{\mathrm{Fc/Fc+}})$ and $E_{\mathrm{LUMO}} = -(E_{\mathrm{red\ onset}} + 4.8 - E_{\mathrm{Fc/Fc+}})$, where $E_{\mathrm{ox\ onset}}$ and $E_{\mathrm{red\ onset}}$ are the onsets of oxidation and reduction potential, respectively.

Steady-state photoluminescence (PL): The PL spectrum of films spin coated on precleaned quartz glasses were recorded on a Fluoro Max-3-P spectrometer.

Atomic force microscopy (AFM): The AFM images were obtained through tapping mode on Multimode 8 SPM at ambient condition. RTESPA (0.01-0.025 ohm-cm Antimony (n) doped silicon) tips with a spring constant of 20 - 80 N m^{-1} and a frequency of 305-356 kHz were used in imaging.

Transmission electron microscope (TEM): TEM measurement was performed by using a HITACHI H-7650 electron microscope with an acceleration voltage of 110 kV.

Surface energies: Surface energies were measured using a HITACHI H-7650 drop shape analyzer with water and glycerol as testing liquids.

Grazing incidence wide-angle X-ray scattering (GIWAXS): The GIWAXS measurements of the pristine polymers and polymer:IT-4F/BTP-eC9 blend films were conducted at a Xeuss 3.0 SWAXS beamline at the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan, using a Cu X-ray source 8.05 keV beam incident at 0.20° and a Eiger2R 1M detector.

Transient absorption spectroscopy: Femtosecond transient absorption spectroscopy was measured on an Ultrafast Helios pump-probe system in collaboration with a regenerative amplified laser system from Coherent. An 800 nm pulse with a repetition rate of 1kHz, a length of 100 fs, and an energy of 7 mJ pluse^{-1}, was generated by an Ti:sapphire amplifier (Astrella, Coherent). Then the 800 nm pulse was separated into two parts by a beam splitter. One part was coupled into an optical parametric amplifier (TOPAS, Coherent) to generate the pump pulses at 400 nm, 600 nm, and 900 nm. The other part was focused onto a sapphire plate and a YAG plate to generate white light supercontinuum as the probe beams with spectra covering 430-800 nm and 800-1500 nm, respectively. The time delay between pump and probe was controlled by a motorized optical delay line with a maximum delay time of 8 ns. The samples films were spin-coated onto the 1 mm-thick quartz plates and are encapsulated by epoxy resin in nitrogen filled glove box to resist water and oxygen in the air. The pump pulse is chopped by a mechanical chopper with 500 Hz and then focused on to the mounted sample with probe beams. The probe beam was collimated and focused into a fiber-coupled multichannel spectrometer with CCD sensor. The energy of pump pulse was measured and calibrated by a power meter (PM400, Thorlabs).

4. Fabrication and Characterization of Polymer Solar Cells

The PSC devices were fabricated with the conventional configuration of ITO/PEDOT:PSS/active layer/PDINN/Ag. Prior to be used, indium tin oxide glass substrates were cleaned with detergent and ultrasonicated in deionized water, acetone, iso-propanol for 10 min each and were again treated by UV-Ozone for 15 min. Subsequently, the PEDOT:PSS layer was spin-coated onto the ITO substrate and annealed at 150 °C for 15 min in air. The substrates were then transferred to the glove-box containing a nitrogen atmosphere. For the BHJ films, the polymers were blended with non-fullerene acceptor in chlorobenzene or chloroform, and further optimize the donor:acceptor weight ratios, thickness, solvent additive and thermal annealing temperature and duration. For the optimal binary OSC devices, the polymer:IT-4F (1:1, w/w) blends was dissolved in chlorobenzene with a concentration of 10 mg mL^{-1} (for polymer), with DIO (0.75% by volume) as additive. The optimal ternary OSC devices were dissolved in chloroform by introducing PBTTzE (54 kDa) into the optimal binary system of PM6:BTP-eC9 with weight ratio of 0.9:1.2:0.1 and a total concentration of 16.5 mg mL^{-1}. The solution was stirred for 4 hours at 40 °C and then spin-coated on the surface of PEDOT: PSS layer. The active layer was thermal annealed for10 min at 100 °C. Afterwards, an electron transport layer of PDINN was spin-coated from a mixture solution of methanol and acetic acid (200:1). Finally, a 100 nm Ag was deposited on the top of the active layers as the cathode by thermal evaporation in a vacuum chamber at a pressure of 2×10^{-6} mbar through a shadow mask that defines 4 devices with each active area of 0.042 cm^2.

Current-voltage measurements were carried out in a glovebox under AM 1.5 G irradiation (100 mW cm^{-2}) from a 450 W solar simulator calibrated by a NREL certified standard silicon cell. Current versus potential (J-V) curves were recorded with a Keithley 2450 digital source meter.

External quantum efficiencies (EQEs): The EQE spectra were measured by an integrated system (LST-QE) with the light intensity calibrated by a standard single-crystal silicon photovoltaic cell.

Light-intensity dependence measurements: The light-intensity dependence measurements were carried out with illumination between 10-100 mW cm^{-2}, which was calibrated by a standard single-crystal silicon solar cell. The current density and voltage were recorded with a Keithley 2450 source meter.

Electroluminescence (EL) measurements: Electroluminescence (EL) quantum efficiency ($\mathrm{EQE_{EL}}$) measurements were performed by applying external voltage/current sources through the devices (LST-QE).

Fabrication and characterization of single-carrier devices: The charge mobilities of the devices were measured by the space-charge limited current (SCLC) method. The SCLC *J-V* curves were obtained in the dark from the electron-only and hole-only devices of ITO/ZnO/active layer/PDINN/Ag and ITO/PEDOT:PSS/active layer/MoO_3/Ag, respectively. The electron and hole mobility were calculated using the Mott-Gurney square law, $J = (9/8)\varepsilon_0\varepsilon_r\mu(V^2/L^3)$, where ε_0 is vacuum permittivity, ε_r is the dielectric constant of the polymer used, μ is the charge carrier mobility, V is the effective applied voltage, and L is the thickness of the active film in the device.

5. ^{1}H and ^{13}C-NMR spectrum and Electron impact mass spectrum of new compounds in this work

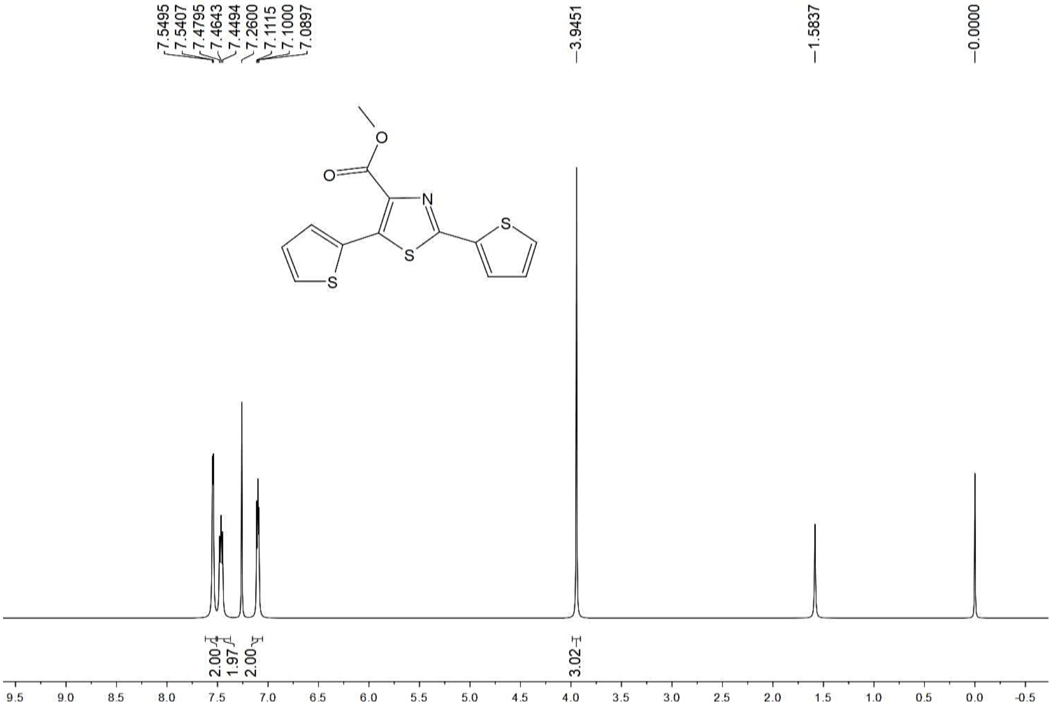


Figure S1 ^{1}H NMR spectrum of methyl 2,5-di(thiophen-2-yl)thiazole-4-carboxylate.

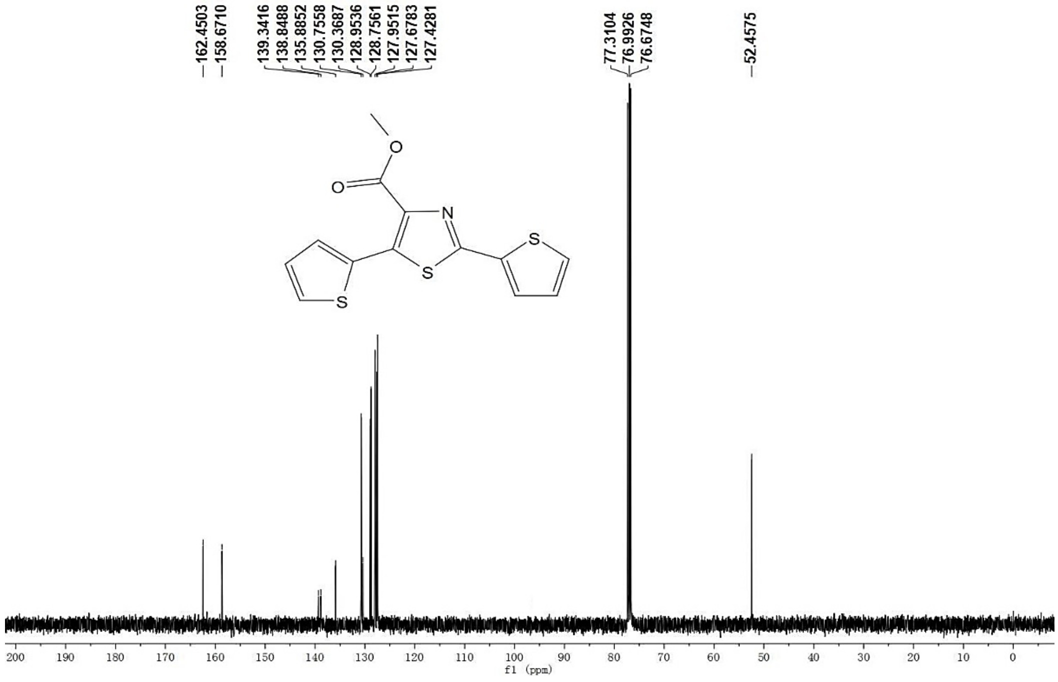


Figure S2 ^{13}C NMR spectrum of methyl 2,5-di(thiophen-2-yl)thiazole-4-carboxylate.

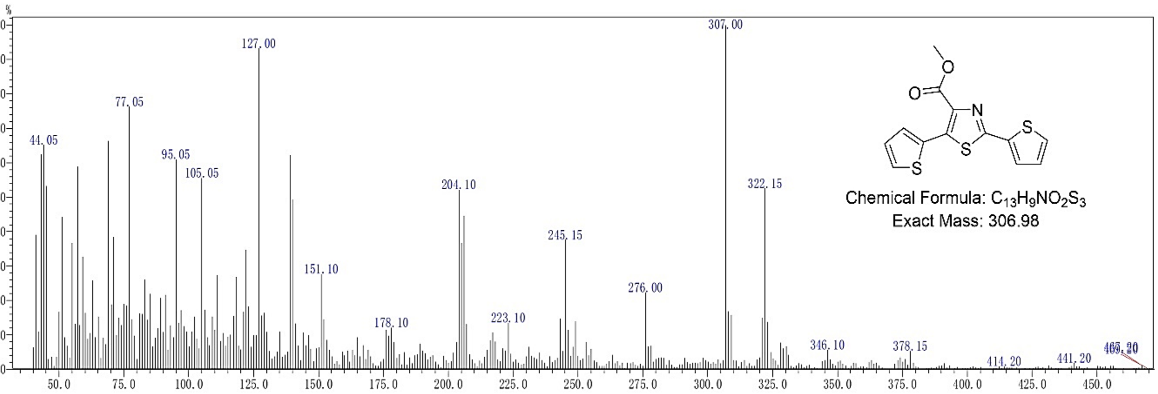


Figure S3 Electron impact mass spectrum of methyl 2,5-di(thiophen-2-yl)thiazole-4-carboxylate.

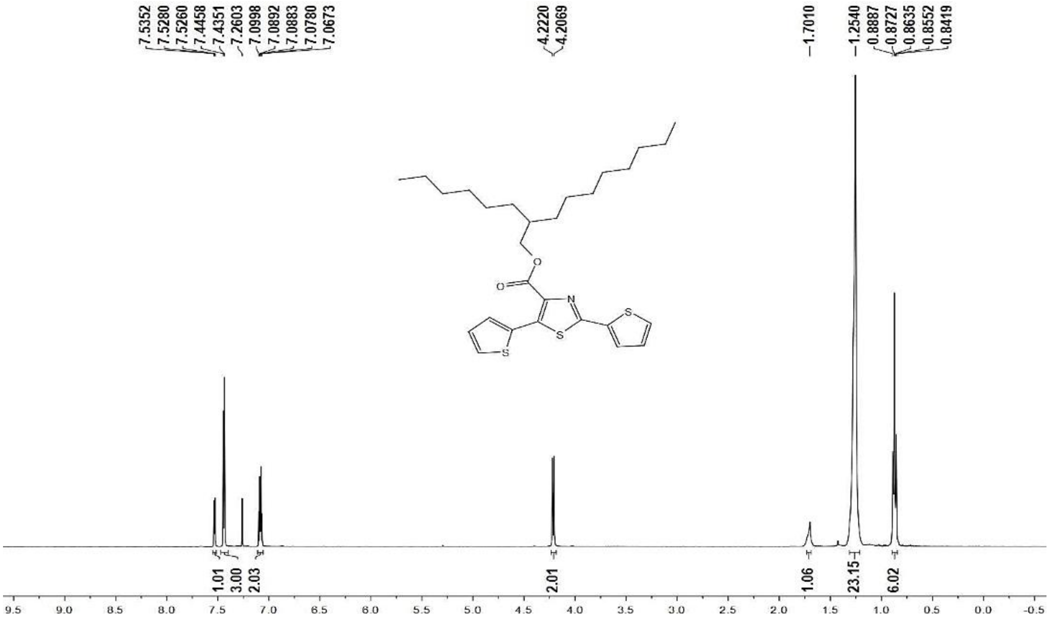


Figure S4 ^{1}H NMR spectrum of 2-hexyldecyl 2,5-di(thiophen-2-yl)thiazole-4-carboxylate.

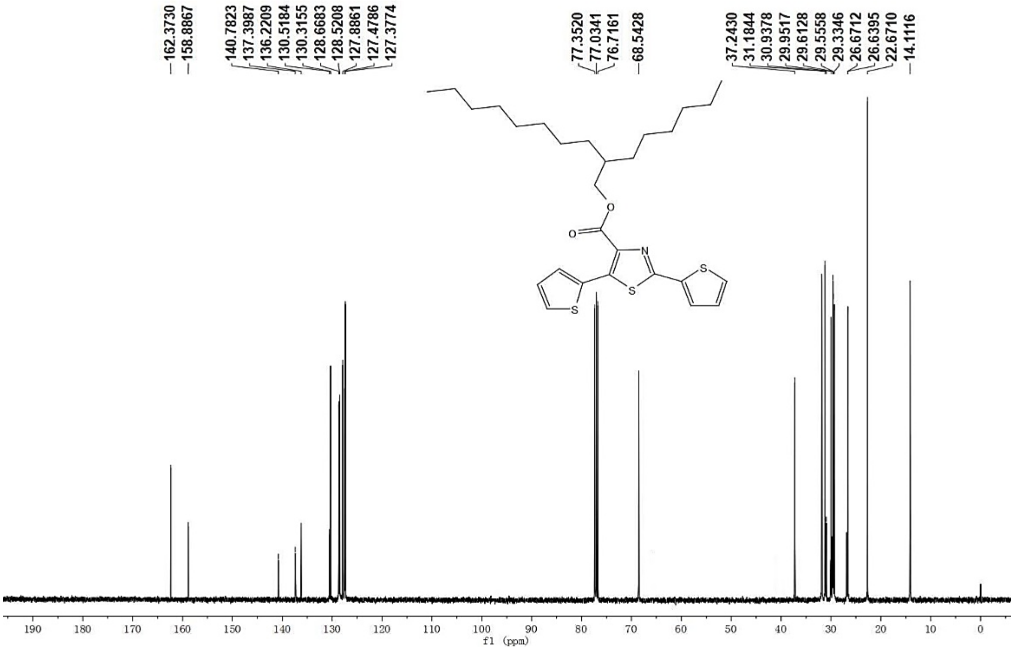


Figure S5 ^{13}C NMR spectra of 2-hexyldecyl 2,5-di(thiophen-2-yl)thiazole-4-carboxylate

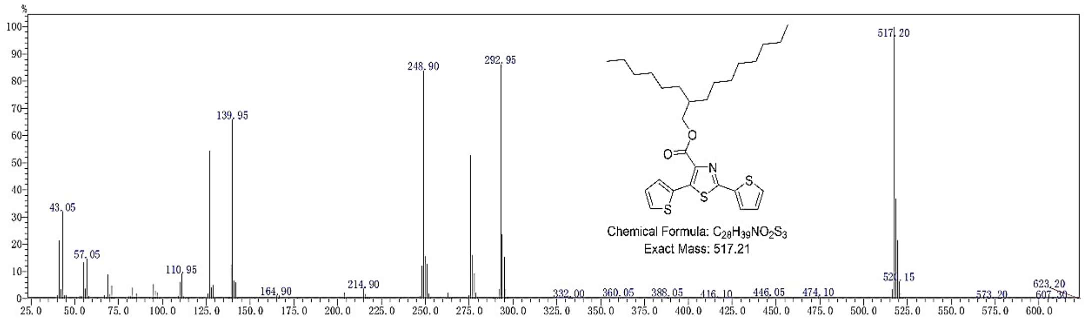


Figure S6 Electron impact mass spectrum of 2-hexyldecyl 2,5-di(thiophen-2-yl)thiazole-4-carboxylate.

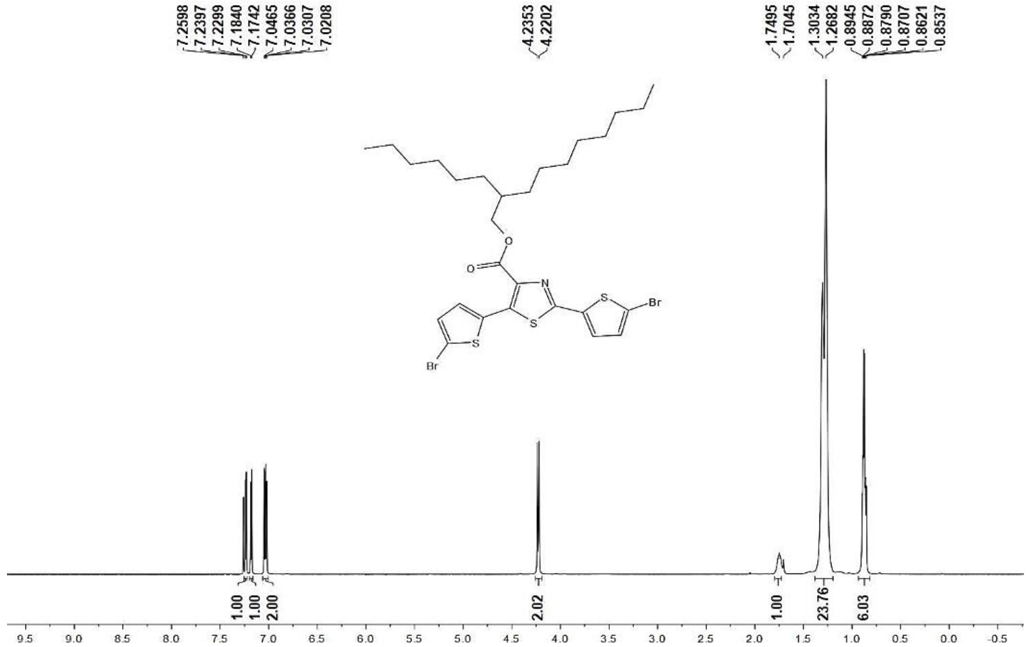


Figure S7 ^{1}H NMR spectrum of 2-hexyldecyl 2,5-bis(5-bromothiophen-2-yl)thiazole-4-carboxylate.

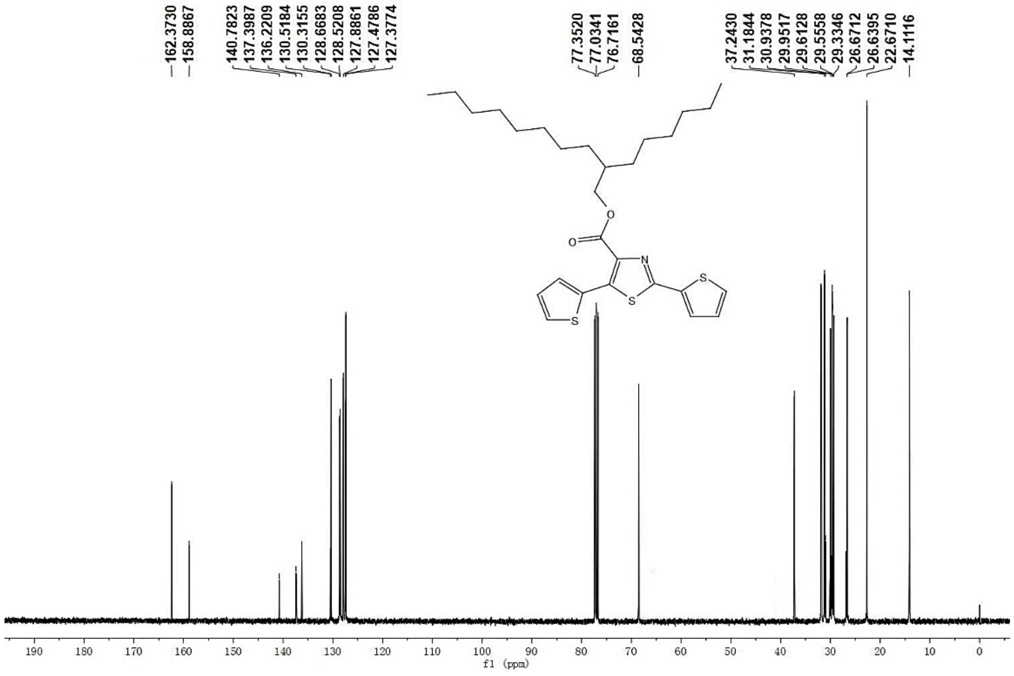


Figure S8 ^{13}C NMR spectrum of 2-hexyldecyl 2,5-bis(5-bromothiophen-2-yl)thiazole-4-carboxylate.

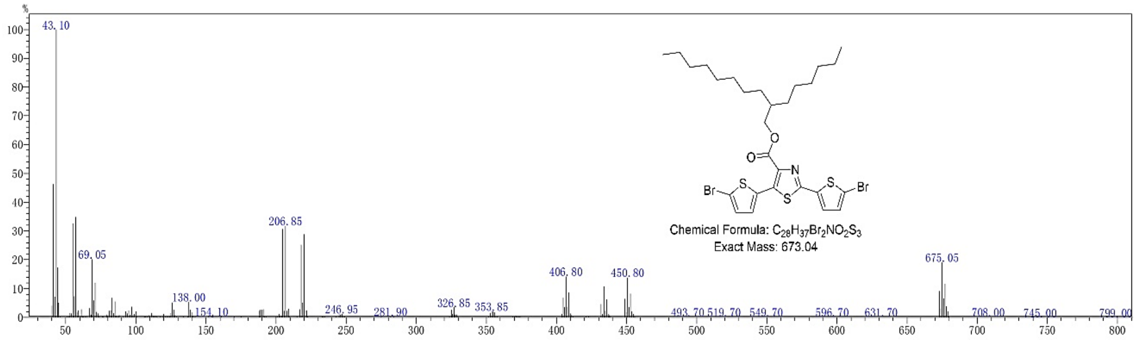


Figure S9 Electron impact mass spectrum of 2-hexyldecyl 2,5-bis(5-bromothiophen-2-yl)thiazole-4-carboxylate.

6. Additional Figures and Tables

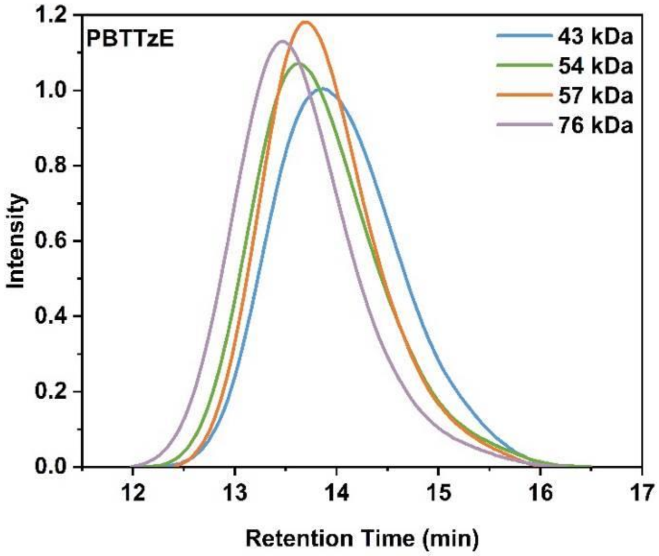


Figure S10 High temperature GPC chromatograms for PBTTzEs eluted by 1,2,4-trichlorobenzene at 150 ºC.

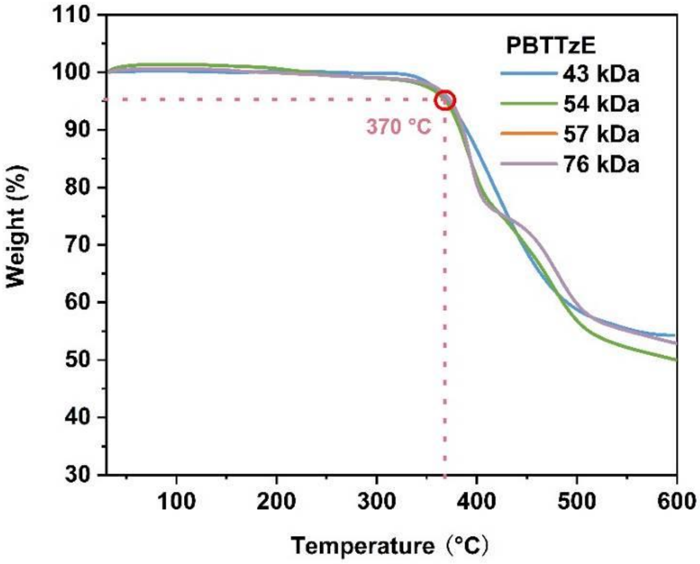


Figure S11 TGA curves of PBTTzEs with a heating rate of 10 ºC min^{-1} under a nitrogen atmosphere.

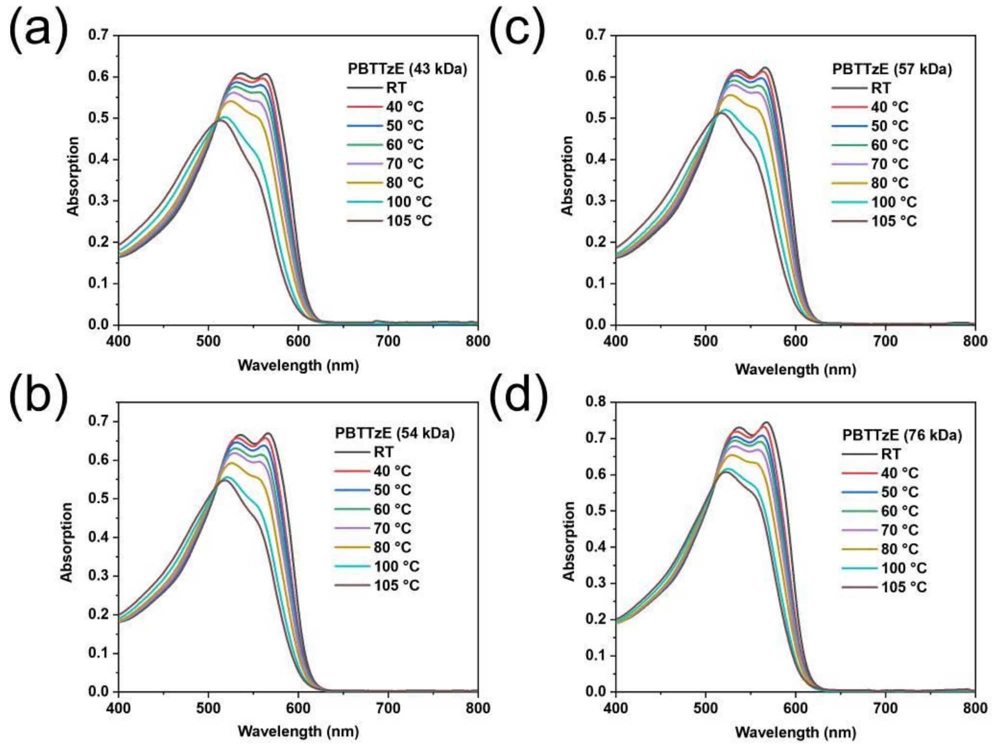


Figure S12 Temperature-dependent UV-vis absorption spectra of PBTTzE with different M_n in chlorobenzene solutions: (a) 43 kDa; (b) 54 kDa; (c) 57 kDa; (d) 76 kDa.

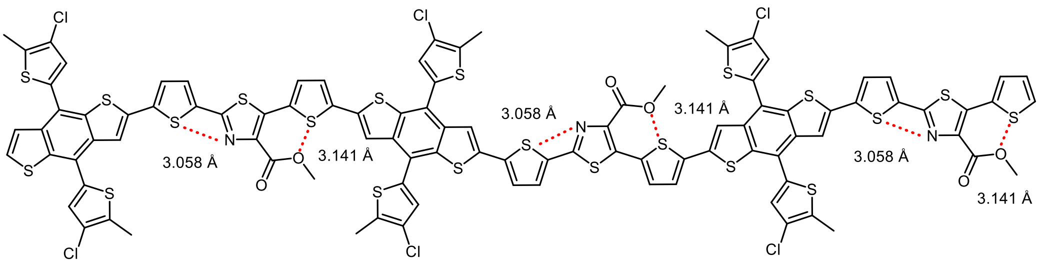


Figure S13 Calculated molecular structure of trimers of PBTTzE using density functional theory (DFT). The alkyl chains are replaced with methyl chains for computational simplicity.

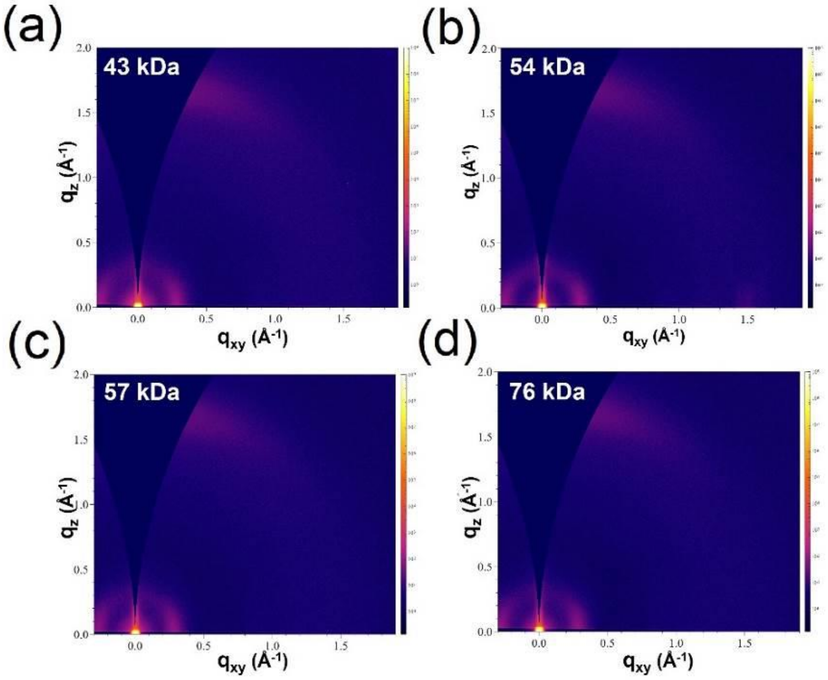


Figure S14 2D-GIWAXS patterns of different molecular weights PBTTzE: (a) 43 kDa; (b) 54 kDa; (c) 57 kDa; (d) 76 kDa.

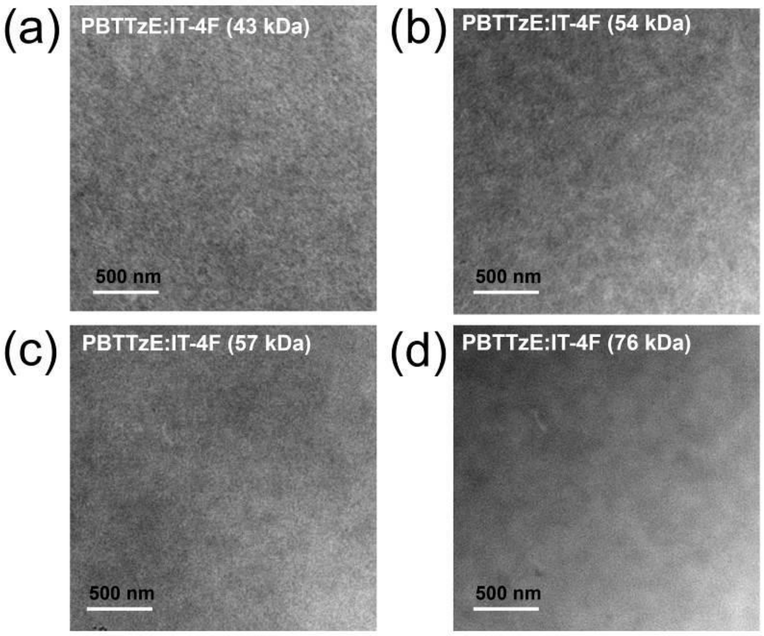


Figure S15 TEM images of the blend films based on different polymer molecular weights: (a) 43 kDa; (b) 54 kDa; (c) 57 kDa; (d) 76 kDa.

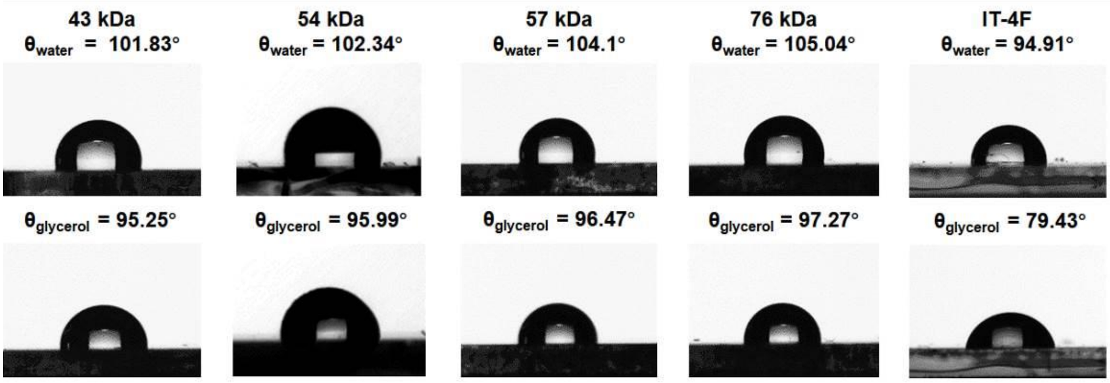


Figure S116 Photographs of water and glycerol droplets on the top surfaces of PBTTzE with different molecular weight and IT-4F.

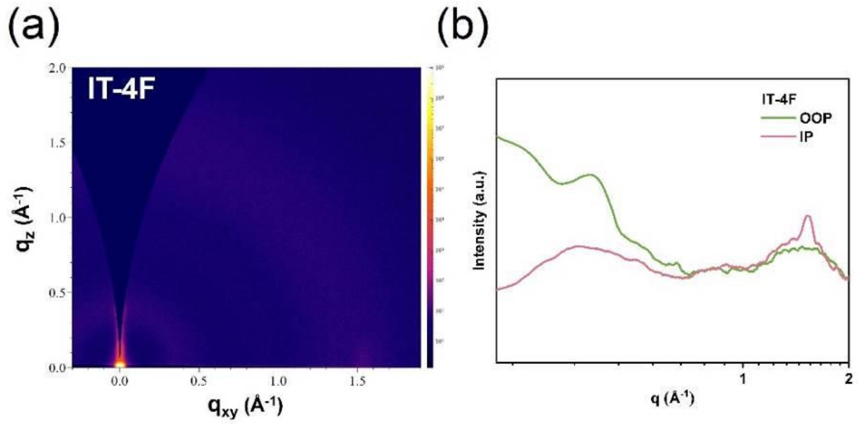


Figure S17 (a) 2D-GIWAXS patterns of IT-4F; (b) Corresponding line-cut profiles in IP and OOP directions.

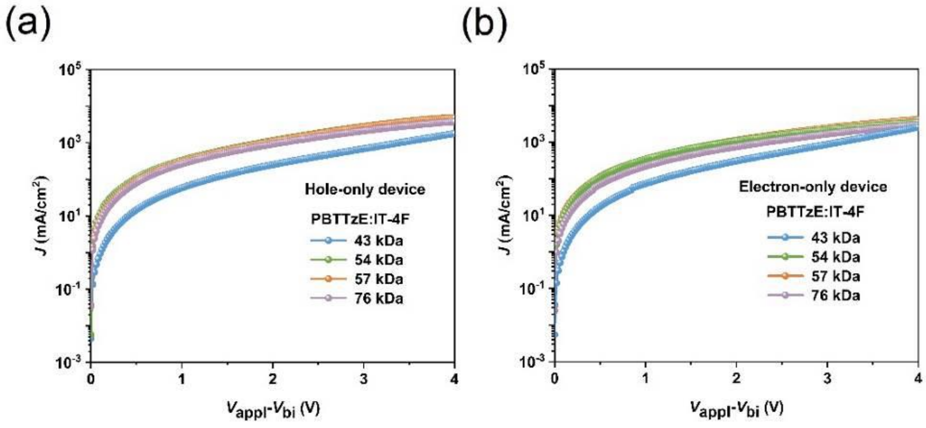


Figure S18 (a) Hole-only and (b) Electron-only of PBTTzEs:IT-4F with different polymer molecular weights.

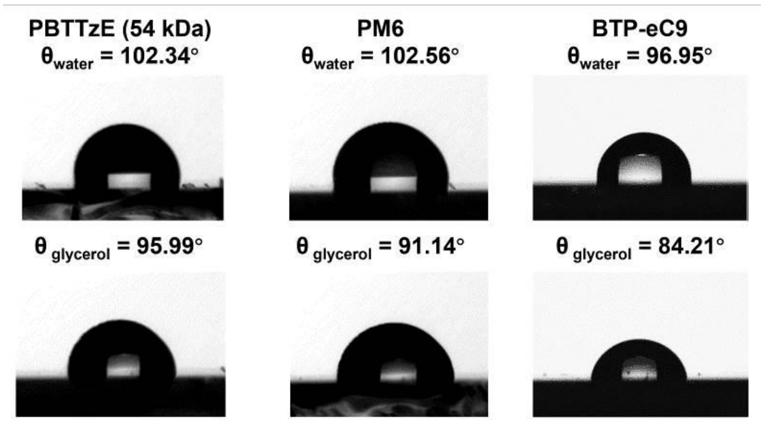


Figure S19 Photographs of water and glycerol droplets on the top surfaces of PBTTzE (54 kDa), PM6, and BTP-eC9

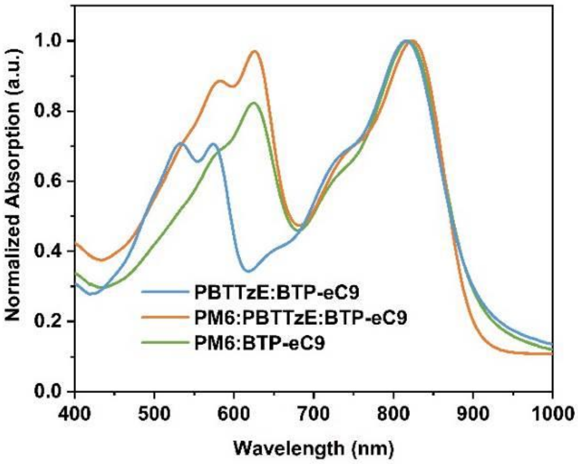


Figure S20 Normalized absorption of the binary and optimized ternary blend films.

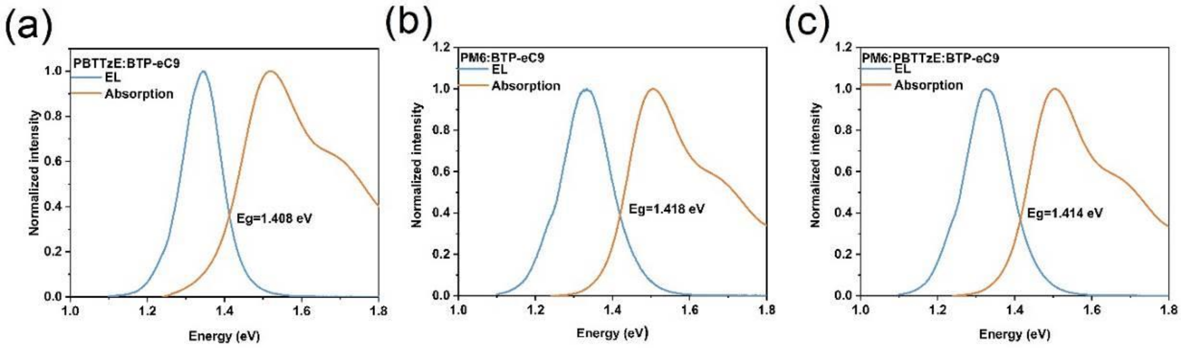


Figure S21 The normalized absorption and EL spectra for the blend films and devices based on (a) PBTTzE:BTP-eC9; (b) PM6:BTP-eC9; and (c) ternary, respectively.

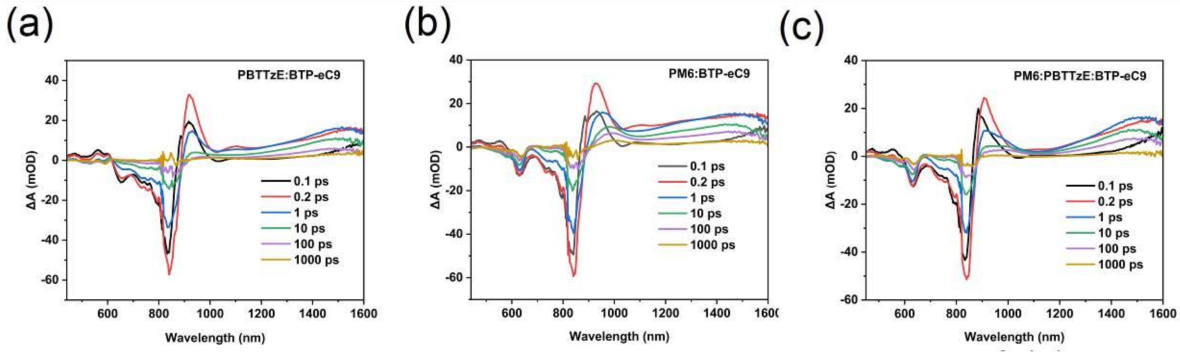


Figure S22 TA spectra of the blend films at different delay times (pump@800 nm, 4 μJ cm^{-2}). (a) PBTTzE:BTP-eC9; (b) PM6:BTP-eC9; (c) PM6: PBTTzE:BTP-eC9.

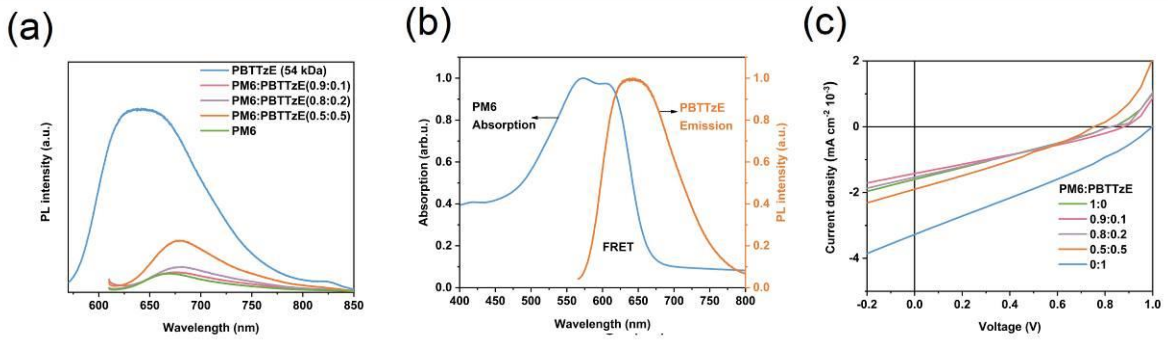


Figure S23 (a) PL spectra of PM6:PBTTzE blend films with varied weight ratios; (b) The normalized absorption spectrum of PM6 and emission spectrum of PBTTzE; (c) *J-V* curves of the donor-only devices based on pristine PM6 and PBTTzE, and binary PM6:PBTTzE blend films.

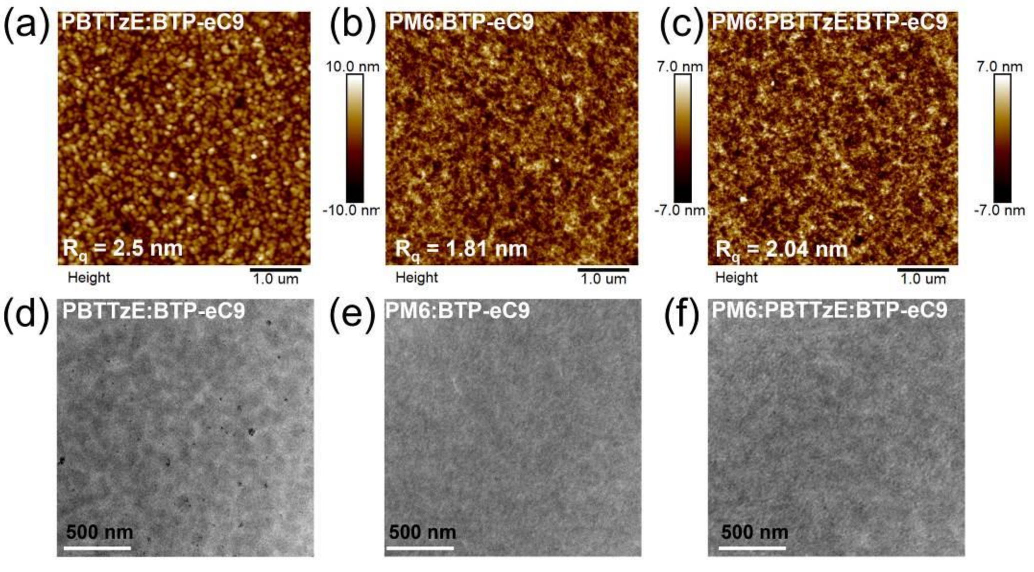


Figure S24 (a-c) AFM height images and (d-f) TEM images of the blend films. (a, d) PBTTzE:BTP-eC9; (b, e) PM6:BTP-eC9; (c, f) PM6:PBTTzE:BTP-eC9.

Table S1 FOM and efficiency of organic solar cells based on different polymer donors and IT-4F acceptor.

Polymer	NSS a)	RY a)	NUO a)	NHC a)	NCC a)	SC b)	FOM c) of Acceptor Unit	PCE [%]	Ref.
PBTTzE	4	1.65	3	0	3	34.86	0.45	15.9	This work
PBTz-TC	7	23.25	12	7	5	95.13	0.13	12.8	62
PFBCPZ	4	5.55	3	0	2	41.08	0.37	15.3	63
PM6	5	32.25	7	5	3	73.38	0.18	13.2	64
PM7	5	32.25	7	5	3	73.38	0.20	14.7	64
PB2F	7	5.88	6	3	6	74.53	0.19	14.1	65
PBDF-S-BZ	5	32.25	7	5	3	73.38	0.18	13.7	66
PBSF-D12	5	32.25	7	5	3	73.38	0.18	13.4	67
PBTPBD-50	7	2.38	4	0	3	53.74	0.25	13.6	68
PBDT-F-C4T	4	1.65	3	0	3	34.86	0.35	12.5	69

a) NSS is the number of synthetic steps, RY is the reciprocity yields, NUO is the number of unit operations required for the isolation/purification, NCC is the number of column chromatography, NHC is the number of hazardous chemicals used for their preparation, and NSS$_{max}$, RY$_{max}$, NUO$_{max}$, NCC$_{max}$, and NHC$_{max}$ are the maximum values of the corresponding parameters; b) SC = 35*NSS/NSS$_{max}$ + 25*log（RY）/log（RY$_{max}$） + 15*NUO/NUO$_{max}$ + 15*NCC/NCC$_{max}$ + 10*NHC/NHC$_{max}$; c) FOM = PCE/SC [3].

Table S2 Detailed data of the fitting patterns of line-cuts from the GIWAXS measurements for PBTTzE series.

Sample	OOP (010) Peak				IP (100) Peak	
	q [$Å^{-1}$]	d [Å]	FWHM [$Å^{-1}$]	Lc [Å]	q [$Å^{-1}$]	d [Å]
PBTTzE (43 kDa)	1.65	3.81	0.23	24.57	0.28	22.43
PBTTzE (54 kDa)	1.66	3.78	0.23	24.57	0.28	22.43
PBTTzE (57 kDa)	1.67	3.76	0.21	26.91	0.28	22.44
PBTTzE (76 kDa)	1.69	3.72	0.20	28.26	0.29	21.66

Table S3 Photovoltaic performance of the devices based on PBTTzE(43 kDa):IT-4F with different DIO, weight ratios, film thickness, and thermal annealing temperature under the illumination of AM 1.5G, 100 mW cm^{-2}.

PBTTzE:IT-4F	Thicknesses [nm]	TA[a)] [°C]	Additive [%]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
1:1 (20 mg/mL)	100	100 °C	**0.5% DIO**	0.889	23.39	70.29	14.62
1:1 (20 mg/mL)	100	100 °C	**0.75% DIO**	0.894	22.79	73.12	14.91
1:1 (20 mg/mL)	100	100 °C	**1% DIO**	0.870	23.21	68.88	13.91
1.2:1 (22 mg/mL)	100	100 °C	0.75% DIO	0.888	19.49	72.45	12.54
1:1.2 (18.3 mg/mL)	100	100 °C	0.75% DIO	0.873	23.33	69.39	14.14
1:1 (20 mg/mL)	**120**	100 °C	0.75% DIO	0.855	21.46	64.56	11.85
1:1 (20 mg/mL)	**85**	100 °C	0.75% DIO	0.890	21.02	70.64	13.22
1:1 (20 mg/mL)	100	**25 °C**	0.75% DIO	0.911	19.74	69.56	12.51
1:1 (20 mg/mL)	100	**80 °C**	0.75% DIO	0.873	21.01	70.3	12.90
1:1 (20 mg/mL)	100	**120 °C**	0.75% DIO	0.922	20.55	67.11	12.72

a) All devices were fabricated with thermal annealing treatment for 10 min.

Table S4 Contact angles of water and glycerol and their parameters for active layer materials.

Surface	θ_{water} [°]	θ_{Gl} [°]	γ [mN m^{-1}]	Relative χ
PBTTzE (43 kDa)	101.83	95.25	21.29	0.44
PBTTzE (54 kDa)	102.34	95.99	20.93	0.50
PBTTzE (57 kDa)	104.1	96.47	20.27	0.60
PBTTzE (76 kDa)	105.04	97.27	19.77	0.69
IT-4F	94.91	79.43	27.86	

Table S5 Detailed data of the fitting patterns of line-cuts from the GIWAXS measurements for PBTTzE:IT-4F blend films with different polymer molecular weights.

Sample	OOP (010) Peak				IP (100) Peak	
	q [Å^{-1}]	d [Å]	FWHM [Å^{-1}]	Lc [Å]	q [Å^{-1}]	d [Å]
PBTTzE:IT-4F (43 kDa)	1.74	3.61	0.30	18.84	0.31	20.26
PBTTzE:IT-4F (54 kDa)	1.75	3.59	0.25	22.61	0.32	19.62
PBTTzE:IT-4F (57 kDa)	1.74	3.61	0.26	21.74	0.31	20.26
PBTTzE:IT-4F (76 kDa)	1.71	3.67	0.28	20.19	0.31	20.26

Table S6 Contact angles of water and glycerol and their parameters for active layer materials.

Surface	θ_{water} [°]	θ_{Gl} [°]	γ [mN m^{-1}]	Relative χ (with BTP-eC9)	Relative χ (with PM6)
PBTTzE (54 kDa)	102.34	95.99	20.93	0.26	0.018
PM6	102.56	91.14	22.19	0.14	-
BTP-eC9	96.95	84.21	25.87	-	-

Table S7 Photovoltaic performance of the devices based on PM6:PBTTzE(54 kDa):BTP-eC9 with different weight ratios and film thickness under the illumination of AM 1.5G, 100 mW cm^{-2}.

PM6:PBTTzE: BTP-eC9	Thicknesses [nm]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]
0.9:0.1:1.2	114	0.846	28.38	0.782	18.76
0.8:0.2:1.2	114	0.850	28.01	0.721	17.17
0.92:0.08:1.2	114	0.838	27.94	0.756	17.73
0.9:0.1:1.2	**128**	0.840	28.61	0.743	17.87
0.9:0.1:1.2	**102**	0.840	28.06	0.762	17.98

Table S8 Scattering parameters obtained from the GIWAXS measurements for pristine and blend films.

Sample	OOP (010) Peak				IP (100) Peak	
	q [Å^{-1}]	d [Å]	FWHM [Å^{-1}]	Lc [Å]	q [Å^{-1}]	d [Å]
PBTTzE	1.66	3.78	0.23	24.57	0.28	22.43
PM6	1.64	3.83	0.25	22.61	0.28	22.43
BTP-eC9	1.71	3.67	0.30	18.84	0.39	16.10
PBTTzE:BTP-eC9	1.71	3.67	0.27	20.93	0.31	20.25
PM6:BTP-eC9	1.68	3.74	0.29	19.49	0.30	20.93
PM6:PBTTzE:BTP-eC9	1.69	3.72	0.28	20.19	0.30	20.93

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