Supporting Information

Reduced Non-radiative Voltage Loss in Terpolymer Solar Cells

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Experimental Section

Materials and device measurements

ITIC was purchased from Solarmer Material Inc, Beijing, China. $PC_{71}BM$ was purchased from Sigma-Aldrich.

Binary and ternary devices were prepared in the normal device configuration ITO/PEDOT:PSS (40 nm)/active layer (100 nm)/LiF(0.6 nm)/Al(90 nm). PEDOT:PSS (Baytron P VP Al 4083) was spun-cast and baked at 140 °C. The active layer was spin-coated from a 10 mg mL^{-1} chlorobenzene solution. LiF (0.6 nm) and Al (100 nm) were used as a cathode, was thermally evaporated under vacuum ($<10^{-7}$ torr). The hole only devices were prepared in the device configuration ITO/PEDOT:PSS/active layer/MoO_3/Ag.

Low-temperature measurement

Normal devices and single-carrier devices were mounted in a liquid-nitrogen cryostat for temperature-dependent measurements. The *J-V* curves were measured using a Keithley 2400 source meter at temperatures ranging from 90K to 300K. The temperature was monitored and controlled using a LakeShore 330 Autotuning Temperature Controller. The light source was a blue laser (532 nm), and the light intensity was tuned to give a V_{oc} similar to one-sun conditions at room temperature for V_{oc}-Ttest. Photoluminescence (PL) and electroluminescence (EL) spectra were detected using a light guide positioned close to the cryostat window. The emission detection system was a Newton EM-CCD Si array detector cooled at -60°C in conjunction with a Shamrock sr 303i spectrograph from Andor Tech.

Photoluminescence (PL) and EQE_{EL}

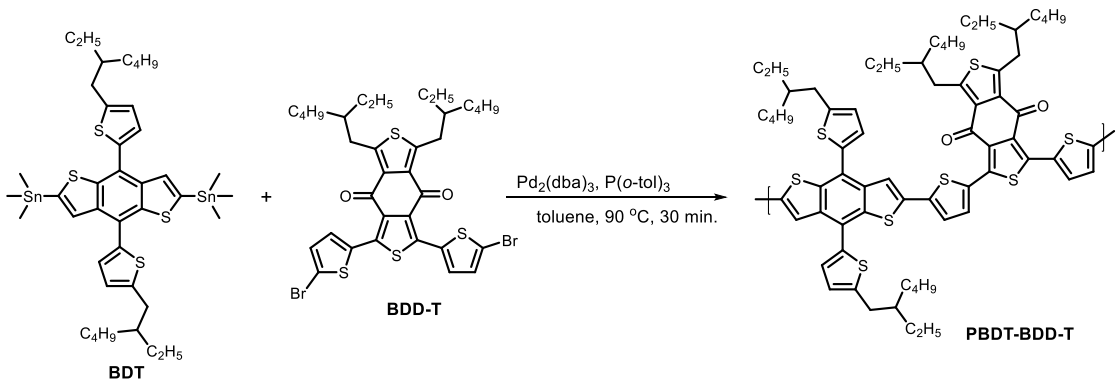
PL emission spectra measurements were recorded with an Andor Solis SR393i-B spectrograph with a Newton EM-CCD Si array detector at -60 ºC with a Shamrock SR-303i spectrograph from Andor Tech. A calibrated Oriel 63355 lamp was used to correct the spectral response. The film under study was excitd with a 520 nm laser under steady state illumination conditions. EQE_{EL} values were obtained from an inhouse-built system including a Hamamatsu silicon photodiode 1010B, a Keithley 2400 SourceMeter to apply the voltage and record the injected current, and a Keithley 485 Picoammeter to measure the emitted light intensity.

Materials Synthesis

All the reagents and monomers such as (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c*']dithiophene-4,8-dione (BDD-T) and 1,3-dibromo-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (BDD) were purchased from commercial sources and used without further purification.

The polymers were synthesized by using palladium-catalyzed Stille coupling reactions as shown in Scheme 1. To synthesize PBDT-BDD, the 4,8-di(thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-based monomer BDT and the benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione-based monomer BDD were refluxed under nitrogen atmosphere in toluene for 24 h. While, the terpolymer PBDT-BDD-*co*-BDT-BDD-T was synthesized from the polymerization reaction of 2 equivalents of electron donor monomer BDT and one equivalent each of electron acceptor benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione-based monomers BDD and BDD-T. The polymers showed high solubility in common organic solvents such as chloroform, chlorobenzene, and *ortho*-dichlorobenzene.

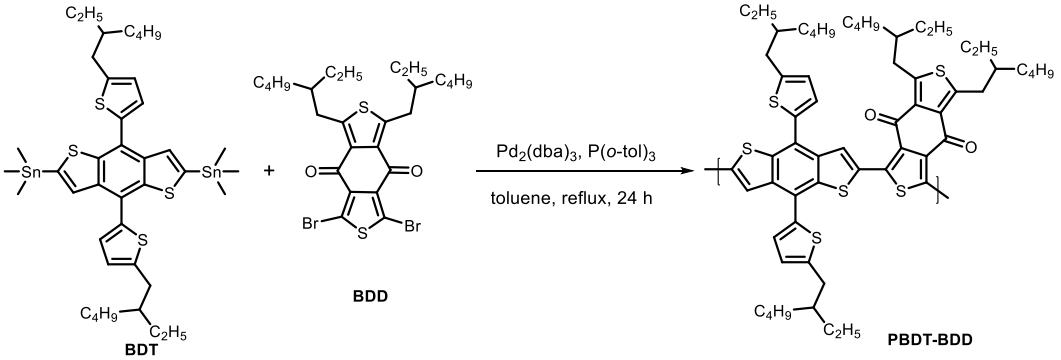
Synthesis of PBDT-BDD-T



In a 25 mL two-necked round-bottomed flask, (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethyl-stannane) (BDT) (226.1 mg, 0.25 mmol), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (BDD-T) (191.68 mg, 0.25 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol) and P(*o*-tol)$_3$ (6.1 mg, 0.020 mmol) were dissolved in dry toluene (10 mL) and the mixture was heated at 90 °C for 30 min. The polymer was then end-capped by adding two drops of 2-bromothiophene and 2-tributyl(thiophen-2-yl)stannane in 30 min interval. The mixture was allowed to cool to room temperature and the polymer was precipitated from methanol, filtered through a thimble and was Soxhlet-extracted with acetone, diethyl ether, and

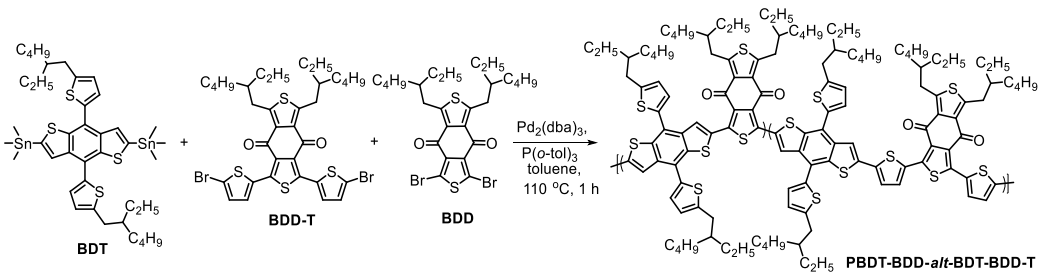
chloroform. The chloroform extract was concentrated and passed through a short column of silica gel using chloroform as eluent. Then it was precipitated from methanol, filtered and dried to afford PBDT-BDD-T (260 mg, 79%).

Synthesis of PBDT-BDD



To a 25 mL two-necked round-bottomed flask were added 1,3-dibromo-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c′*]dithiophene-4,8-dione (BDD) (150.6 mg, 0.25 mmol), (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene-2,6-diyl)bis(trimethyl-stannane) (BDT) (226.1 mg, 0.25 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), P(*o*-tol)$_3$ (6.1 mg, 0.020 mmol) and dry toluene (10 mL). The mixture was purged with nitrogen for 10 min and the mixture was heated under reflux for 24 h. The polymer was then end-capped by adding 2-bromothiophene followed by 2-tributyl(thiophen-2-yl)stannane in 1 h interval. The mixture was cooled to room temperature, poured into methanol and the polymer was filtered through a Soxhlet thimble and was subjected to Soxhlet extraction with methanol, diethyl ether, and chloroform. The chloroform fraction was passed through a short column of silica gel and the polymer was precipitated from acetone, dried in an oven at 40 ^{o}C overnight to yield PBDT-BDD (240 mg, 91%).

Synthesis of PBD-BDD-*co*-BDT-BDD-T



(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene-2,6-diyl)bis-(trimethylstannane) (BDT) (226.1 mg, 0.25 mmol), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c′*]dithiophene-4,8-dione (BDD-T) (95.84 mg, 0.125

mmol), 1,3-dibromo-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c′*]dithiophene-4,8-dione (BDD) (75.3 mg, 0.125 mmol), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol) and P(*o*-tol)$_3$ (6.1 mg, 0.020 mmol) were added into a two-necked round-bottomed flask and were dissolved in dry toluene (12 mL). The mixture was heated at 110 ºC for 1 h and the polymer was end-capped by adding two drops of 2-bromothiophene and 2-tributyl(thiophen-2-yl)stannane in 40 min interval. After cooling to room temperature, the polymer was precipitated from methanol, filtered through a thimble and was subjected to Soxhlet extraction with acetone, diethyl ether and chloroform. The chloroform extract was concentrated and passed through a short column of silica gel using chloroform as eluent and the polymer was precipitated from methanol, filtered and dried to yield PBD-BDD-*alt*-BDT-BDD-T (260 mg, 94%).

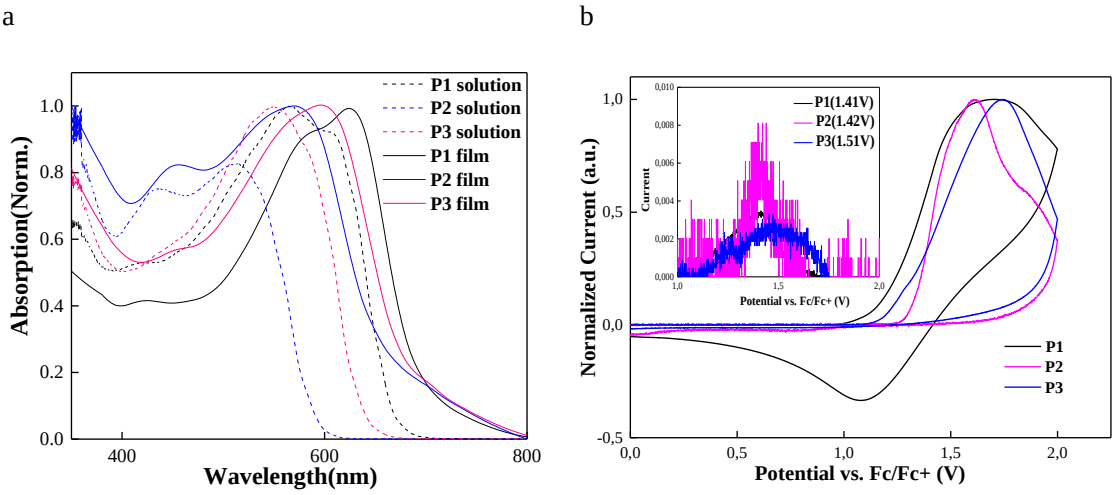


Figure S1. (a) Optical absorption spectra of solutions and thin films of the polymers. (b) Electrochemical cyclic voltammetry curves of the polymers, inset is the derivative of the cyclic voltammetry curves. Related parameters are summarized in Table S1.

The absorption onsets of P1, P2 and P3 were at 689, 650, 679 nm in the solid state corresponding to E_g^{opt}s of 1.80, 1.90 and 1.83 eV, respectively. The absorption of P1 was red-shifted compared to P2 and P3. The blue-shifted absorption of P2 was due to the absence of thiophene spacer units on the backbone of the polymer. As expected, the absorption of the terpolymer, P3, was between the absorptions of P1 and P2.

Table S1. Optical and electrochemical properties of the polymers

Polymer	Optical properties				Electrochemical properties		
	λ_{max}[nm]		λ_{onset}nm	E_g^{opt} [eV]	E_{ox}^{on} [eV]	HOMO [eV]	LUMO [eV]
	Solution	Film					
P1 (PBDT-BDD-T)	565.6	623.8	689	1.80	1.41	–5.81	–4.01
P2 (PBDT-BDD)	515.4	570.0	650	1.90	1.42	–5.82	–3.92
P3 (PBDT-BDD-*co*-BDT-BDD-T)	549.0	596.0	679	1.83	1.52	–5.91	–4.08

The frontier molecular orbital energy levels of the polymers were measured using electrochemical cyclic voltammetry (CV). The HOMO levels of the polymers were estimated by using the formula HOMO = –(4.4 + E_{onset}^{ox}) eV where $E_{max}$was the potential of maximum

dI/dV relative to ferrocene/ferrocenium (Fc/Fc^+) redox couple. The LUMO levels were calculated from the differences between the optical bandgaps and the HOMO levels of the polymers.[1] PBDT-BDD and PBDT-BDD-*co*-BDT-BDD-T had HOMO energy levels of –5.82 and –5.91 eV, respectively, while their LUMO levels were estimated to be –3.92 and –4.08 eV, respectively (Table S1).

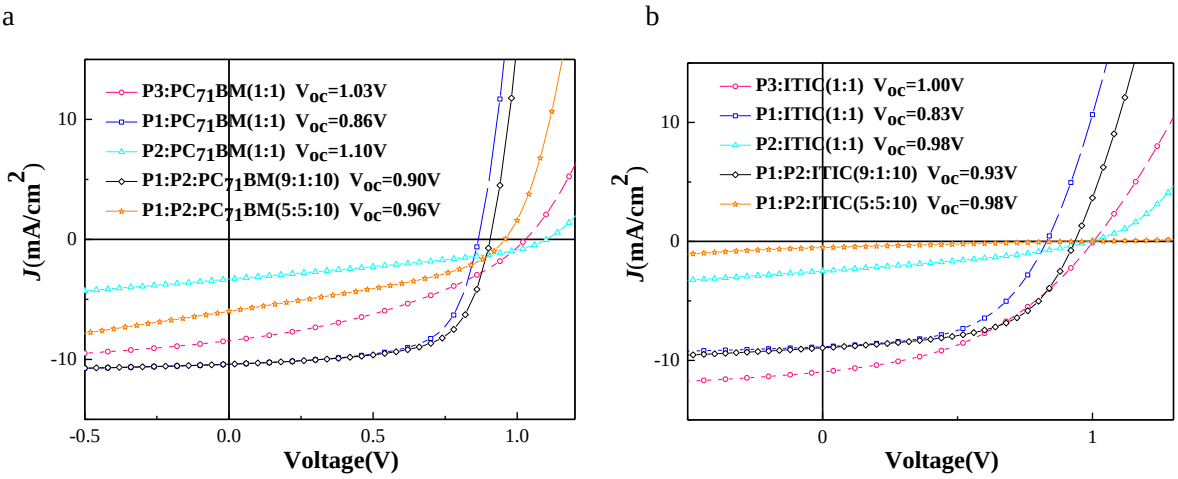


Figure S2. (a) Fullerene-based device performance. (b) ITIC-based device performance. Inset is the voltage value. Compared to Ternary devices (9:1:10 and 5:5:10), high voltages were extracted from the P3-based devices.

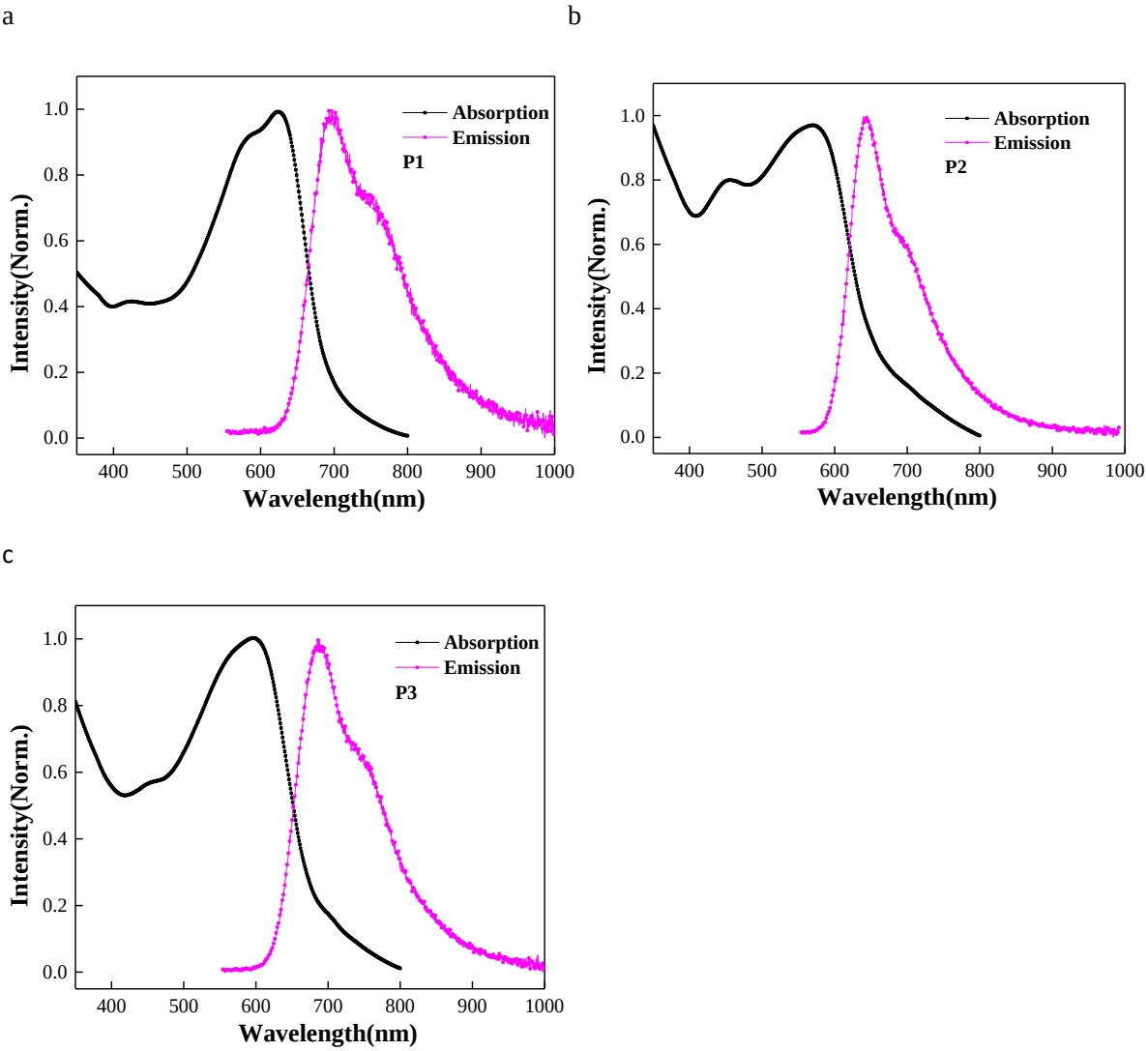


Figure S3. Photoluminescence emission and optical absorption spectra of (a) polymer P1 (PBDT-BDD-T); (b) polymer P2 (PBDT-BDD); and, (c) polymer P3 (PBDT-BDD-*co*-BDT-BDD-T).

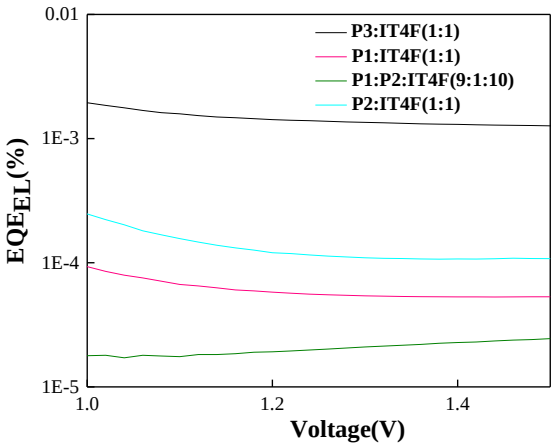


Figure S4. EL-EQE results for IT4F-based devices. The nonradiative loss[2] according to $Voc(\text{nonradiative loss}) = -\frac{kT}{q} ln(EQE_{EL})$, where k is the Boltzmann's constant, T is the absolute temperature.

a b

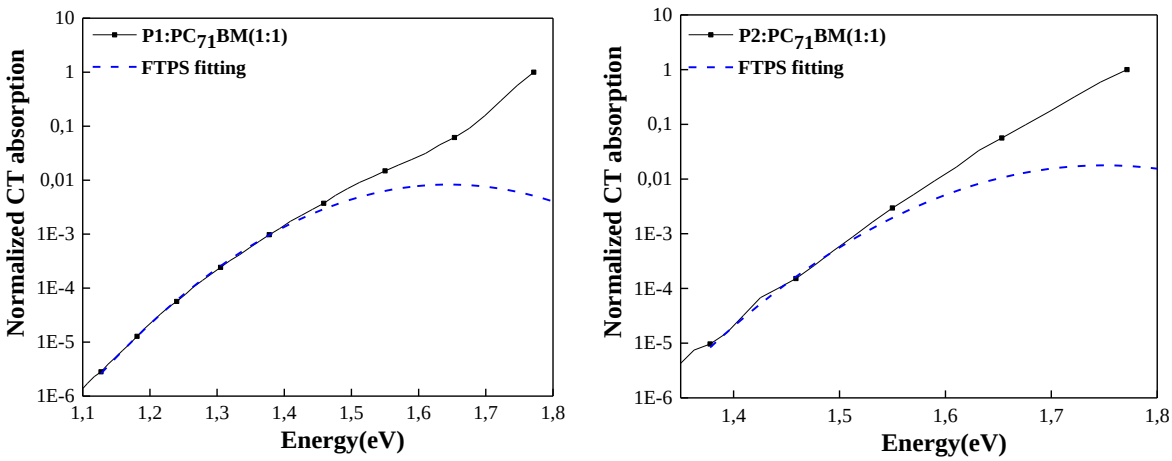


Figure S5. Fourier transform photocurrent spectrum of (a) P1 (PBDT-BDD-T):$PC_{71}BM$ device. (b) P2 (PBDT-BDD):$PC_{71}BM$ device. Dashed lines are the fitting results according to the modified Marcus formula.

The CT region of the EQE spectra obtained by using Fourier transform photocurrent spectrum (FTPS),[2] and fits the CT band using Equation:

$$EQE(E) \propto \frac{f_\sigma}{E\sqrt{4\pi\lambda kT}} exp\left(\frac{-(E_{ct}+\lambda-E)^2}{4\lambda kT}\right)$$

Where k is the Boltzmann's constant, T is the absolute temperature, E_{ct} is the energy of CT state, f_σ is proportional to the square of the electronic coupling matrix element, and λ is related to the width of the CT absorbance band, with contribution from internal/environmental reorganization and/or energetic disorder. The fitting results summarized in Table S2.

Table S2 The fitting results of FTPS

Sample	$\lambda(eV)$	f_σ	E_{ct}(eV)
P1:$PC_{71}BM$	0.33	$4.4*10^{-3}$	1.32
P2:$PC_{71}BM$	0.18	$7.4*10^{-3}$	1.57
P3:$PC_{71}BM$	0.21	$3.4*10^{-3}$	1.46
P1:P2:$PC_{71}BM$	0.32	$7.9*10^{-3}$	1.39

Note here that the EQE tail of the P2:$PC_{71}BM$ and P3:$PC_{71}BM$ blend overlaps almost completely with that of the pristine materials, the fitting in Figure S5b is not Gaussian approximation. The calculated fitting results, like the energy of CT excitons, is just an approximation, to display that the CT energy is close to the LE states.

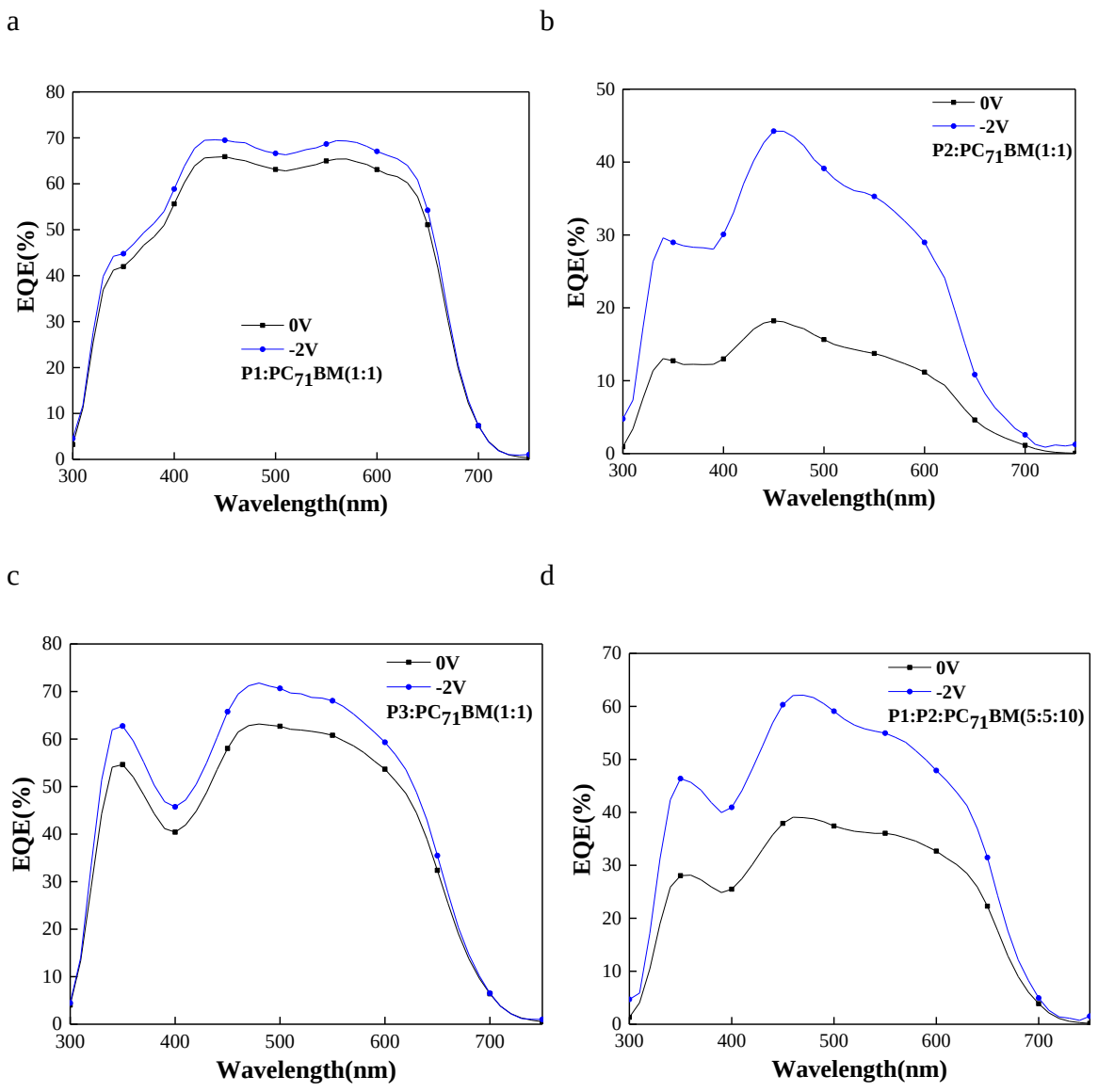


Figure S6. External quantum yield of (a) P1:$PC_{71}BM$ (1:1) device. (b) P2:$PC_{71}BM$ (1:1) device.(c) P3:$PC_{71}BM$(1:1) device. (d)Ternary (P1:P2:$PC_{71}BM$=5:5:10) device. Compared to the reference P2:$PC_{71}BM$ and ternary (P1:P2:$PC_{71}BM$=5:5:10) devices, a weak negative bias dependent (increasing electric field) was obtained in the P3:$PC_{71}BM$ and P1:$PC_{71}BM$ devices, indicating a weak electric field depending charge generation. The reference P2:$PC_{71}BM$ and ternary (P1:P2:$PC_{71}BM$=5:5:10) devices demonstrates a higher EQE value in the higher energy range (450 nm), indicates that the photocurrent generation is strongly dependent on the nature of the primary excited states.

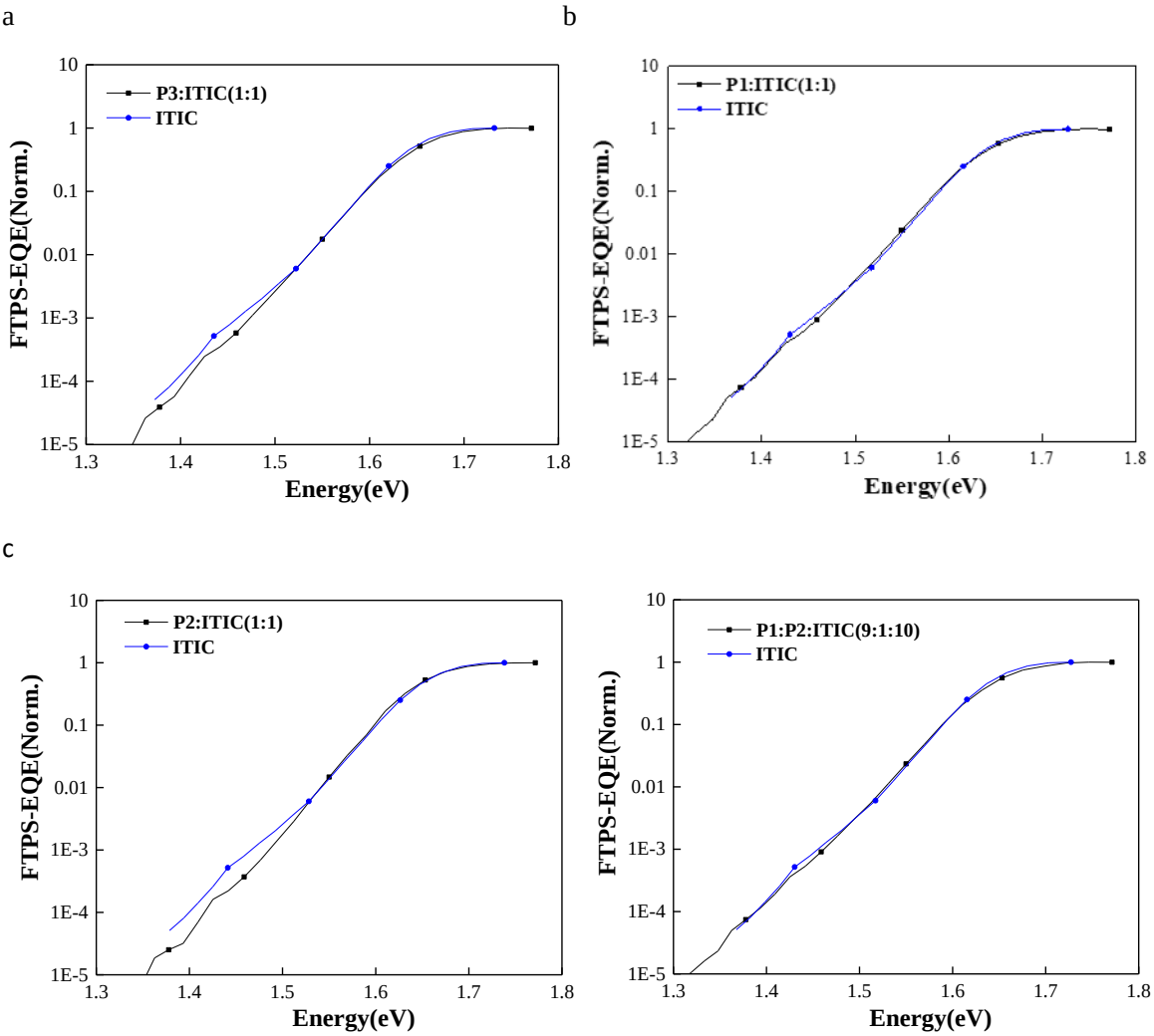
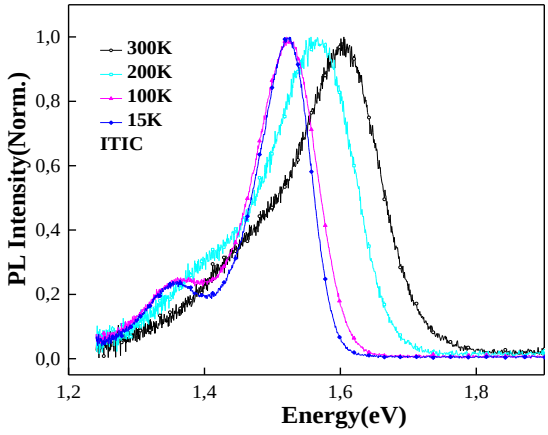
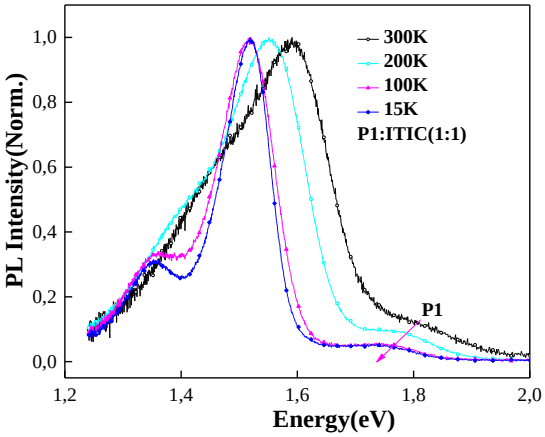


Figure S7. Fourier transform photocurrent spectrum of (a) P3 (PBDT-BDD-*co*-BDT-BDD-T):ITIC device. (b) P1 (PBDT-BDD-T):ITIC device. (c) P2 (PBDT-BDD):ITIC device. (d) the ternary (P1:P2:ITIC=9:1:10) device.

a



b



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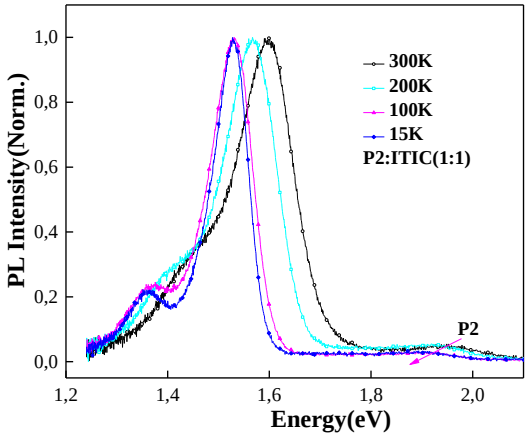

Figure S8. (a) Temperature-dependent photoluminescence of ITIC film. (b) Temperature-dependent photoluminescence of P1 (PBDT-BDD-T):ITIC film. (c) Temperature-dependent photoluminescence of P2 (PBDT-BDD):ITIC film.

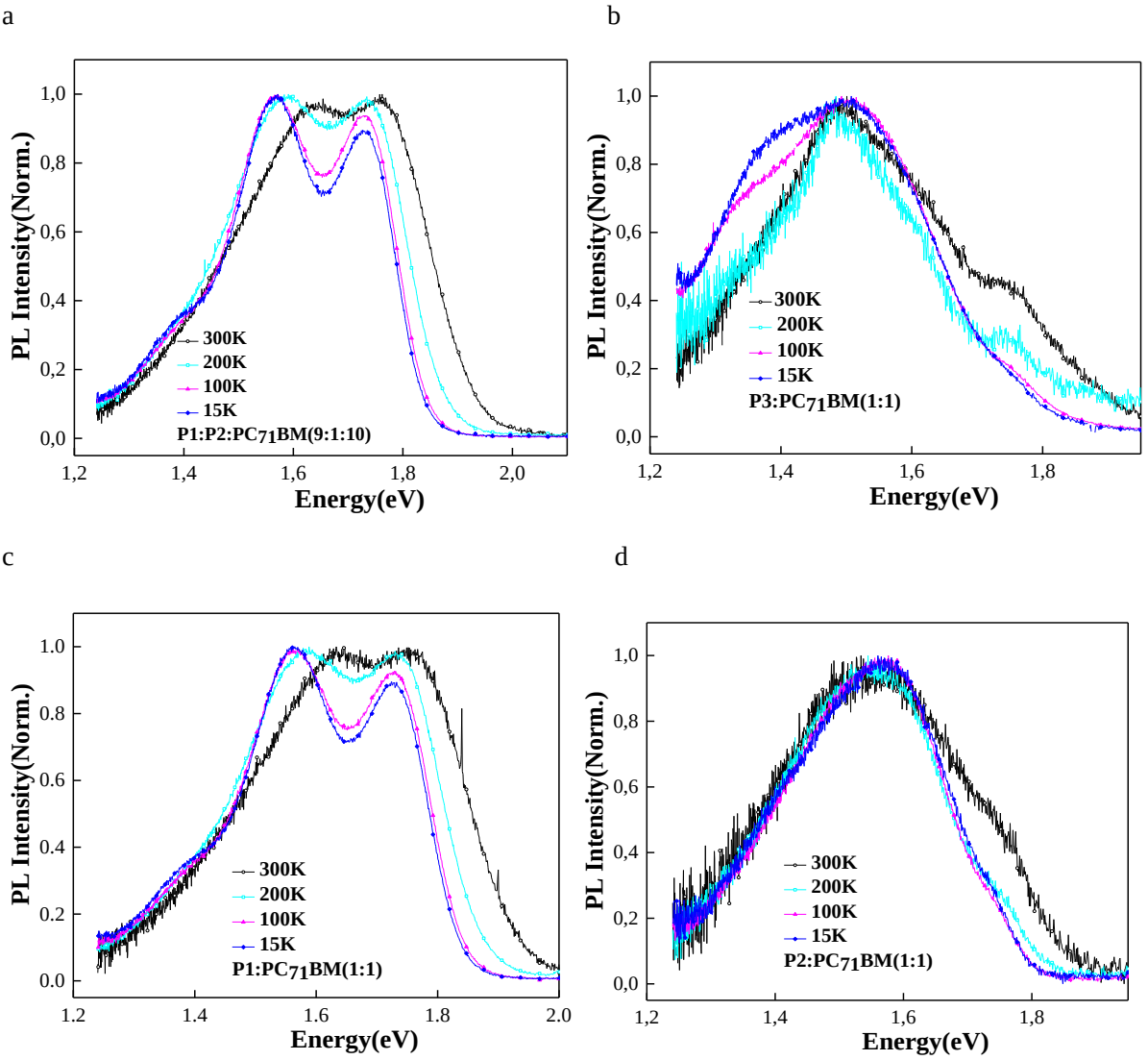

Figure S9. Temperature-dependent photoluminescence of (a) $PC_{71}BM$ based ternary blends;(b) P3 (PBDT-BDD-*co*-BDT-BDD-T):$PC_{71}BM$ blends; (c) P1 (PBDT-BDD-T):$PC_{71}BM$ blends; and, (d) P2 (PBDT-BDD):$PC_{71}BM$ blends.

a b

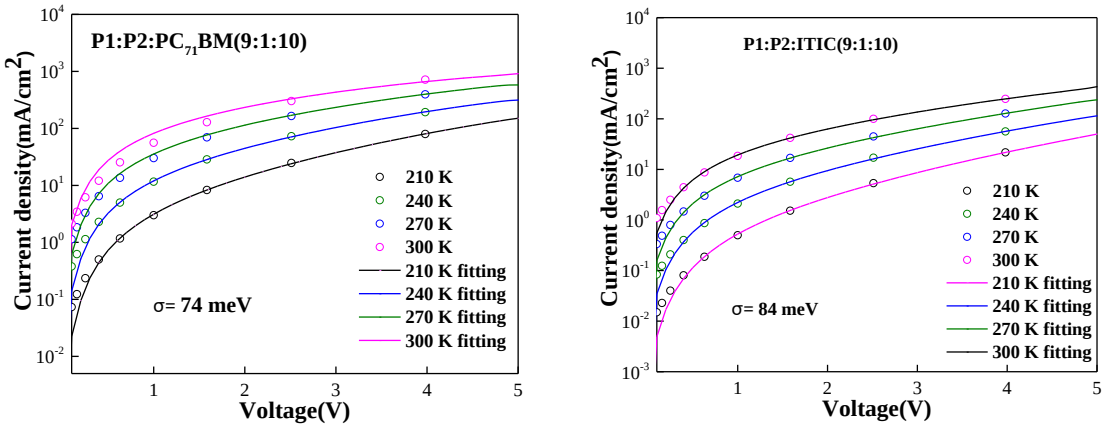

Figure S10. Temperature-dependent space-charge limited current for the (a) ternary (P1:P2:$PC_{71}BM$=9:1:10) and (b) ternary (P1:P2:ITIC=9:1:10) devices. The energetic disorder σ can be calculated from[3] $\mu_0(T) = \mu_\infty \exp\left[-\left(\frac{2\sigma}{3\kappa_B T}\right)^2\right]$. The built-in voltage is a free parameter for the Murgatroyd-Gill fitting.[3] In this study, for all studied materials, the built-in voltage did not exceed 0.1V.

Supplementary references

(1) Admassie, S.; Inganäs, O.; Mammo, W.; Perzon, E.; Andersson, M. R., Electrochemical and Optical Studies of The Band Gaps of Alternating Polyfluorene Copolymers. *Synth. Met.* **2006,** *156* (7), 614-623.

(2) Vandewal, K.; Tvingstedt, K.; Gadisa, A.; Inganäs, O.; Manca, J. V., Relating The Open-Circuit Voltage to Interface Molecular Properties of Donor:Acceptor Bulk Heterojunction Solar Cells. *Phys. Rev. B* **2010,** *81* (12), 125204.

(3) Felekidis, N.; Melianas, A.; Kemerink, M., Automated Open-Source Software for Charge Transport Analysis in Single-Carrier Organic Semiconductor Diodes. *Org. Electron.* **2018,** *61*, 318-328.