A medium bandgap nonfullerene acceptor for efficient ternary polymer solar cells with high open-circuit voltage

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Experimental Part

Instruments

^{1}H NMR spectra were obtained on a Agilent 600 MHz DD2 nuclear magnetic resonance (NMR) spectrometer, and Bruker AVANCE 500VHz spectrometer using $CDCl_3$ as solvent at room temperature. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. The thermal characteristics of the polymers were investigated using thermogravimetric analysis (TGA) on a "Perkin Elmer-7" and differential scanning calorimetry (DSC-3) "Mettler-Toledo, Switzerland" at a rapid heating of 10°C/min in argon. Oxidation and reduction potentials of the compounds were determined by cyclic voltammetry (CV) experiments on a computer controlled potentiostat "Autolab type III" at a scan rate of 50 mVs[-1]. A platinum working electrode, $Ag/AgNO_3$ (0.1 M in anhydrous acetonitrile), and a platinum wire were used as the working electrode, reference electrode and counter electrode, respectively, in a nitrogen-saturated tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution (0.1 M in anhydrous acetonitrile). Assuming the absolute energy level of Fc/Fc[+] to be -4.43 eV versus vacuum level, thus the HOMO and LUMO energy levels were obtained from the equation of $E_{HOMO}/ E_{LUMO} = - (E_{ox}/E_{red}+ 4.43)$ (eV), where oxidation/reduction onset potential (E_{ox}/E_{red}) were determined from the position at which the current raised initially from the baseline.

3.2. Materials. All of the reagents and chemicals were purchased from Aldrich, Acros,TCI and used without further purification.Toluene was dried and purified by fractional distillation over sodium/benzophenone under argon.
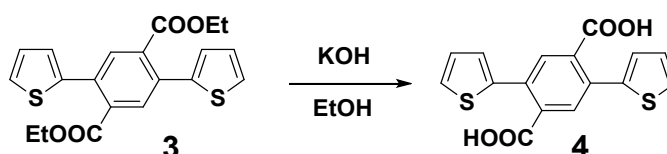
Diethyl 2,5-dibromoterephthalate (2).
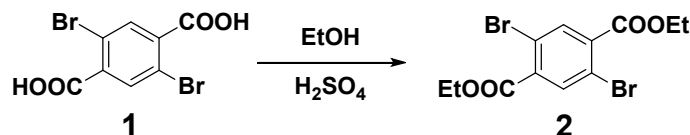
2,5-Dibromoterephthalic acid 1 (10 g, 30.87 mmol) was suspended in absolute ethanol (250 ml), 10 ml of conc. H2SO4 added and the reaction mixture were refluxed overnight. After return to room temperature, it was cooled to -20°C for several hours, the precipitate that formed was filtered off, washed with chilled ethanol, and dried. Received 10.9 g (93%) of a white substance.^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (s, ^{1}H), 4.44 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H).

Diethyl 2,5-di(thiophen-2-yl)terephthalate (3).
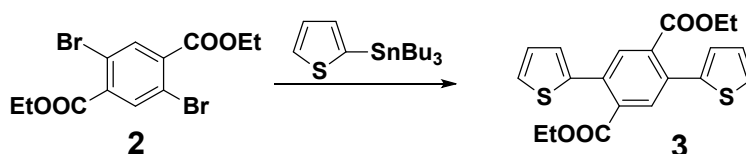
Pd (PPh3)4 (155 mg, 0.132 mmol) was added to a solution of diethyl 2,5-dibromoterephthalate 2 (5.0 g, 13.16 mmol) and 2-tributylstannylthiophene (12.27 g, 32.89 mmol) in toluene (150 ml), then the reaction mixture was boiled for 24 hours. Next, the boiling mixture was filtered through a SiO2 layer, the filtrate was evaporated dry. Petroleum ether (50 ml) was added to the oily residue, shaken and cooled to -20 ° C for several hours. The precipitated substance was filtered, washed with cooled toluene and dried. We received 4,242 g (83%) of the product .^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (s, 1H), 7.46 – 7.36 (m, 1H), 7.10 (m, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.18 (t, J = 7.1 Hz, 3H).
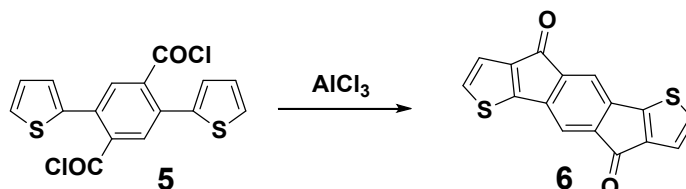
2,5-Di(thiophen-2-yl)terephthalic acid (4).

A solution of KOH (22.1 g, 394 mmol) in water (35 ml) was added to a solution of diethyl 2,5-di(thiophene-2-yl)terephthalate 3 (15.22 g, 39.39 mmol) in ethanol (450 ml), then the solution was boiled for 4 hours. After that, the mixture was cooled to -20 ° C overnight. The precipitate was filtered, washed with ethanol and dried. The resulting substance was dissolved in water (50 ml) and concentrated hydrochloric acid was added (up to pH = 1), the precipitated substance was filtered, washed with water and dried. The yield is 8.84 g (68%).^{1}H NMR (400 MHz, DMSO) δ 7.70 (s, 1H), 7.68 (d, J = 5.1 Hz, 1H), 7.26 (d, J = 3.4 Hz, 1H), 7.19 – 7.12 (m, 1H).

**2,5-Di(thiophen-2-yl)terephthaloyl dichloride (5).**
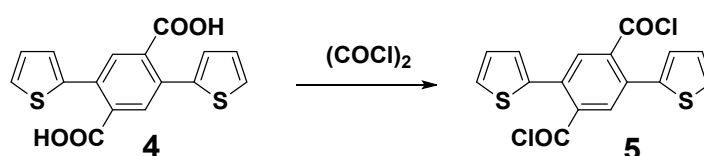
Oxalyl chloride (4.14 ml, 48.43 mmol) was added drop by drop to a suspension of 2,5-di(thiophene-2-yl)terephthalic acid 4 (4 g, 12.11 mmol) in dichloromethane (120 ml) and the mixture was stirred at room temperature overnight, after which the solvent was evaporated dry. The resulting residue was used without additional purification.

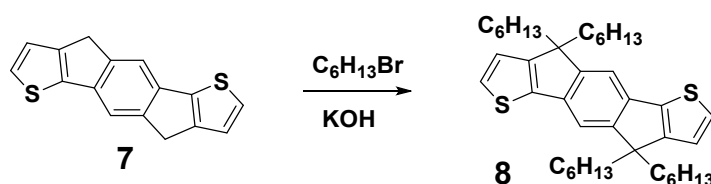**4,9-dihydro-s-Indaceno[1,2-b:5,6-b']dithiophene-4,9-dione (6)**.

A solution of 2,5-di(thiophene-2-yl)terephthaloyl dichloride 5, obtained at the previous stage, was slowly added to the suspension of AlCl3 (7.6 g, 57 mmol) in dichloromethane (180 ml) at 0 ° C, after the addition was completed, it was stirred at room temperature overnight. Next, the reaction mixture was poured into a mixture of 200 ml of concentrated hydrochloric acid and 1000 ml of water, the precipitate was filtered, washed with water, acetone and dried. We received 3.97 g (99%) of the blue substance.

**4,9-Dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (7).**
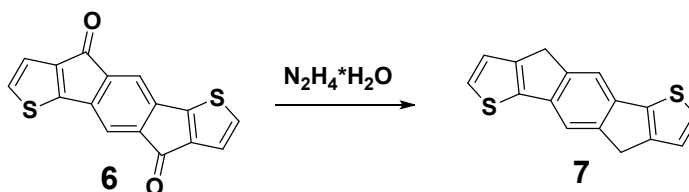
A suspension of 4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-4,9-dione 6 (4 g, 13.59 mmol), KOH (15.25 g, 272 mmol) and hydrisinghydrate (13.61 g, 272 mmol) in 150 ml of ethylene glycol was heated at 180 ° C for 24 hours. After cooling to room temperature, the mixture was poured into a mixture of ice (1 kg) and concentrated HCl (150 ml), the precipitate was filtered, washed with water and dried. The product was used without additional cleaning. Output (76%).^{1}H NMR (600 MHz, CDCl$_3$) δ 7.63 (s, 1H), 7.31 (d, J = 4.7 Hz, 1H), 7.14 (d, J = 4.7 Hz, 1H), 3.76 (s, 2H).

4,4,9,9-Tetrahexyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (8).

A suspension of 4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene 7 (6 g, 22.52 mmol), KOH (11.37 g, 202 mmol) and KI (0.934 g, 5.63 mmol) in DMSO (200 ml) was stirred at room temperature for 1 hour, Next, 1-bromohexane (22.49 g, 136 mmol) was added and the reaction mixture was heated at 80 ° C overnight. After cooling, water was added (300-400 ml) and evacuated several times with chloroform. The combined organic phases were washed with water and dried with MgSO4 and evaporated. The residue was purified by column chromatography, and 4.56 g (34%) of the target product was obtained in the form of a yellow solid.^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 (s, 1H), 7.28 (d, J = 4.8 Hz, 1H), 6.99 (d, J = 4.8 Hz, 1H), 2.05 – 1.97 (m, 2H), 1.92 – 1.84 (m, 2H), 1.22 – 1.05 (m, 13H), 0.93 – 0.76 (m, 11H).

4,4,9,9-Tetrahexyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-dicarbaldehyde (9).
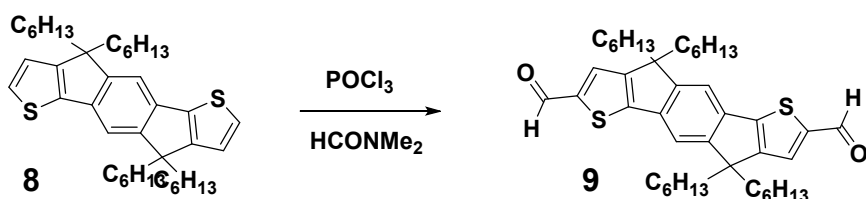
To a solution of compound 8 (2.02 g, 3.35 mmol) and DMFA (6.87 ml, 88.77 mmol) in chloroform (130 ml) at 0 ° C, POCl$_3$ (4.08 ml, 44.55 mmol) was slowly added, then the reaction mixture was boiled overnight. After cooling, the reaction mixture was poured into 150 ml of NaOAc solution and stirred at room temperature for 3 hours, then extracted with chloroform (3 × 150 ml), the combined extracts were washed with water, dried with MgSO4, filtered and evaporated. Petroleum ether was added to the semi-liquid residue and cooled to -20 °C during the night. The precipitated substance was filtered and dried. We received 1.4 g (63%) of the

product. ¹H NMR (500 MHz, CDCl₃) δ 9.94 (s, 2H), 7.67 (s, 2H), 7.48 (s, 2H), 2.00 (dtd, J = 25.4, 13.4, 4.7 Hz, 8H), 1.25 – 1.03 (m, 24H), 0.96 – 0.71 (m, 20H).
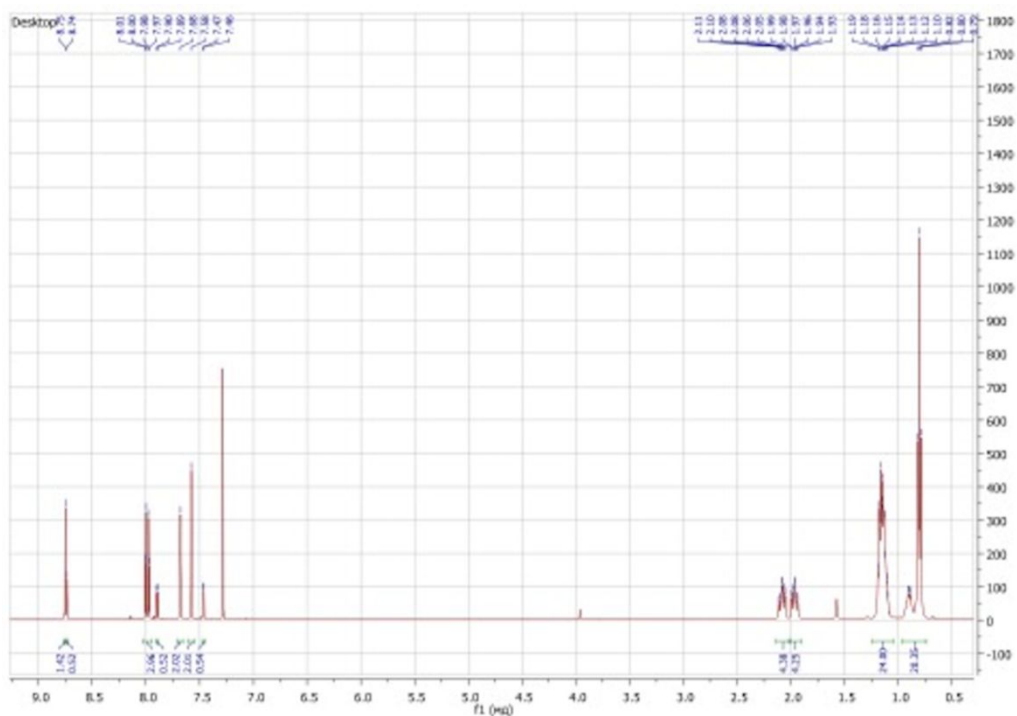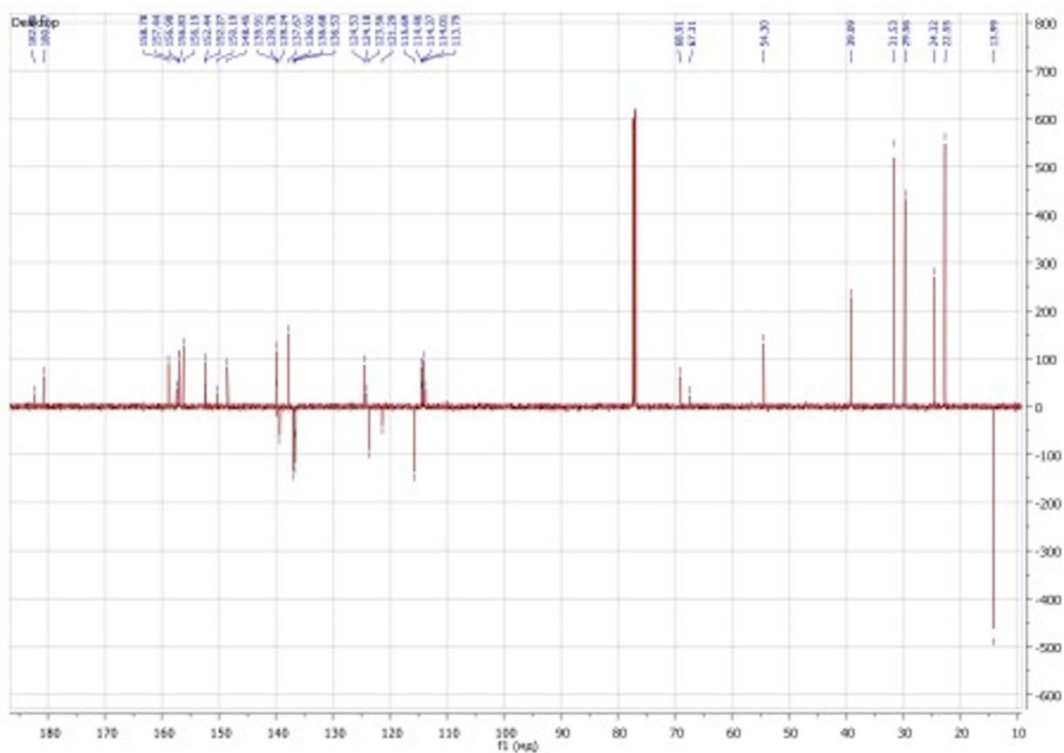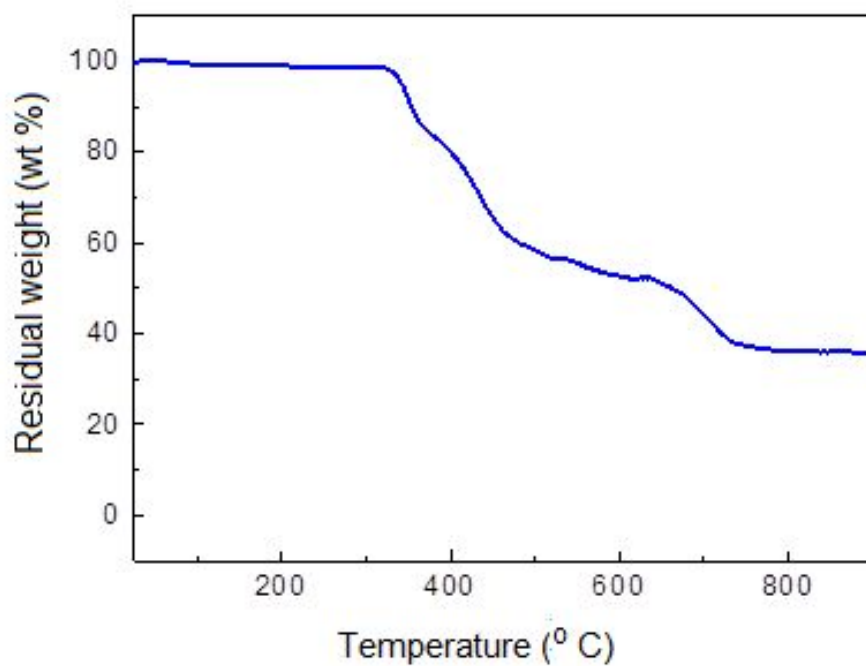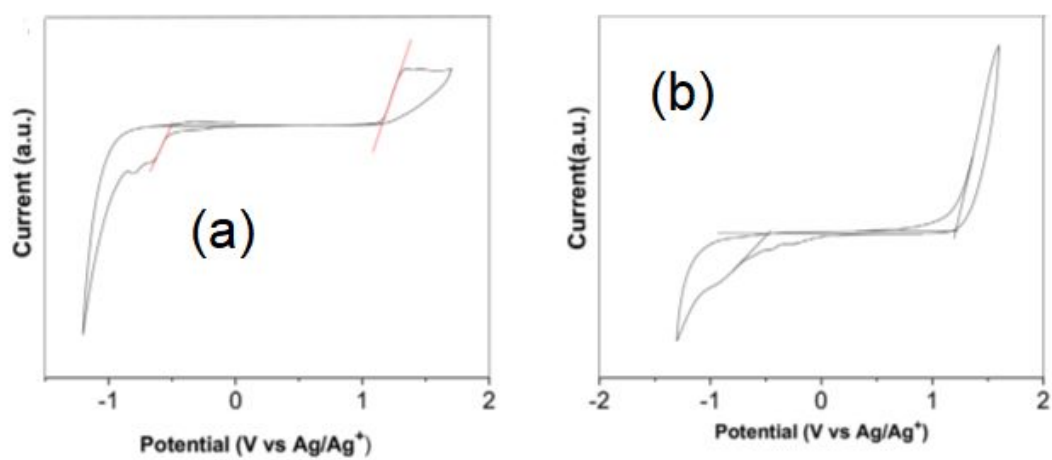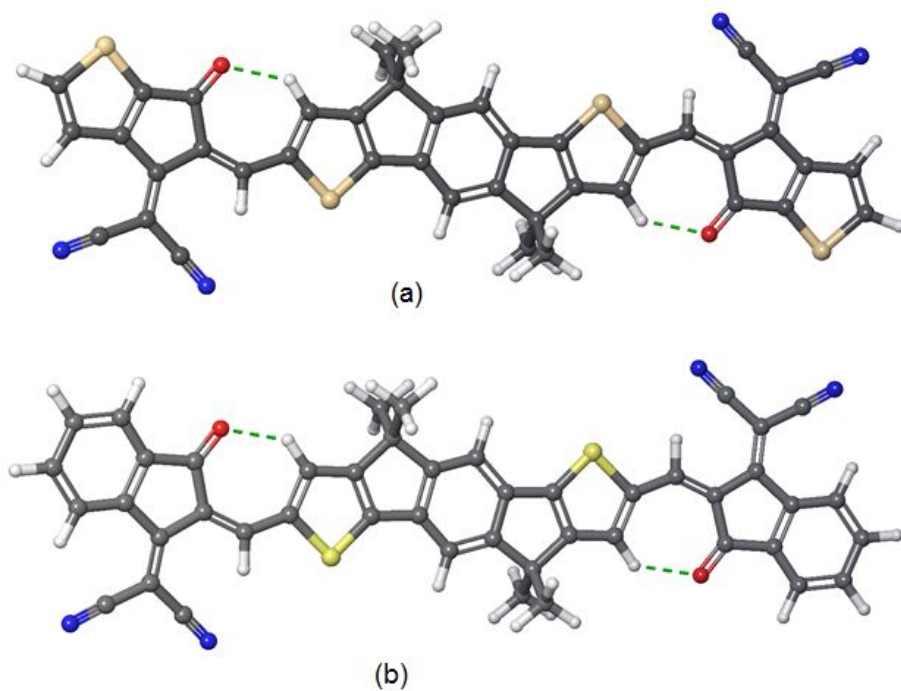

Figure S1. ¹H-NMR spectra of I**DT-IC**

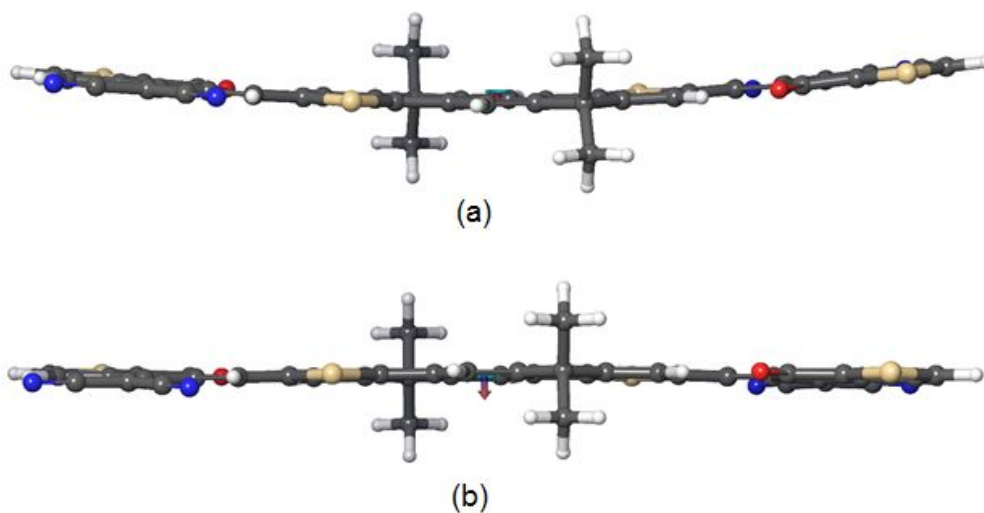**Figure S2**. ¹³C-NMR spectra of **IDT-TC**

Figure S3. TGA curves of **IDT-IC**

Figure S4. Cyclic voltammetry curves for (a) IDT-IC and (b) IDT-IC-Cl

Figure S5. Front view equilibrium geometry of (a) **IDT-TC** and (b) IDT-IC model optimized by DFT/ ωB97X-D3(BJ) / 6-31(d,p)++ method. The green dotted line indicates aromatic hydrogen bonds.

Figure S6. Side view of **IDT-TC** model (a) equilibrium geometry (b) transition state geometry optimized by DFT / ωB97X-D3(BJ) / 6-31G(d,p)++. The direction of the dipole moment is indicated.

Device Fabrication and characterization

The polymer solar cells with structure of ITO/PEODT:PSS/active layer/PFN/Al were fabricated to evaluate the photovoltaic performance of IDT-TC, IDT-IC and IDT-IC-Cl as acceptor and P as donor. PSCs were fabricated using ITO coated glass substrates (10 Ω sq-1) which were cleaned with detergent water, deionized water, acceptor and isopropyl alcohol in

an ultrasonic bath sequentially for 20 min, and dried in vacuum oven at 40° C. A thin layer (~35 nm) of PEODT:PSS was first spin coated on the pre-cleaned ITO coated glass substrates at 3500 rpm and baked at 110° C for 15 min under ambient conditions. The blend of acceptor and donor PDIF with different weight ratio (constant concentration 16 mg/mL) were prepared in chloroform solution and spin cast on to the top of PEDOT:PSS layer at speed of 2500 rpm and then dried at room temperature. For the solvent vapor annealing (SVA) treatment, optimized blended thin film were exposed to the THF vapors for 40s. The thickness of the active layers is about 90 nm (±5 nm). The PFN as electron transport layer, was spin coated on the top of active layer at 3000 rpm form a methanol solution. Finally, the Al electrode was thermally evaporated onto the top of PFN layer at the pressure less than 10-5 Pa. The shadow mask was used to define the PSC active area (16 mm2). In order to prepare the ternary active layer film, we have varied the weight ratio between two acceptor (IDT-IC and IDT-IC-CL) and kept the concentration of P same as for binary BHJ active layer. After that the optimized ternary active layer was further exposed to THF environment for 40 s to further optimize the photovoltaic performance. The current-voltage characteristics of the PSCs were measured using a Keithley 2400 source meter. A 300 W xenon solar simulator with an AM1.5 filter operated at 100 mW/cm^2 was used to simulate the AM1.5G solar irradiation. The EQE spectra of the devices were recorded on the PVE300 EQE system (Bentham make). The charge carrier mobility (hole and electron mobility) of the active layer was determined by fitting the dark current-voltage characteristics of hole-only device (ITO/PEDOT:PSS/active layer/Au and electron devices (ITO/Al/active layer/Al) to the space charge limited current (SCLC) model.

Transient photocurrent (TPC) measurements were investigated under the short circuit condition to explore the time dependent extraction of photo-generated charge carriers. The 10 ns light pulse was chosen as light source. The devices were kept in the dark between pulses in order to avoid any influence of pulse frequency on the current responses. Transient photovoltage measurements were investigated under open circuit condition to explore he photovoltage decay. The photovoltage decay kinetics of devices follow a mono-exponential decay: $\delta(v) = A \exp(-t/\tau)$ where t is the time and τ is the charge carrier lifetime and give the information about the degree of charge recombination.
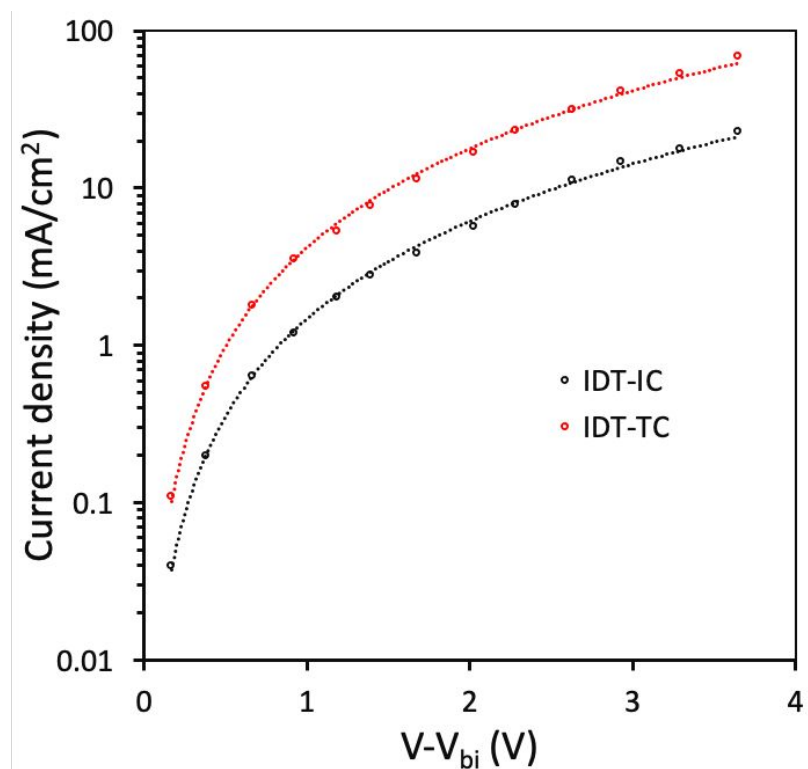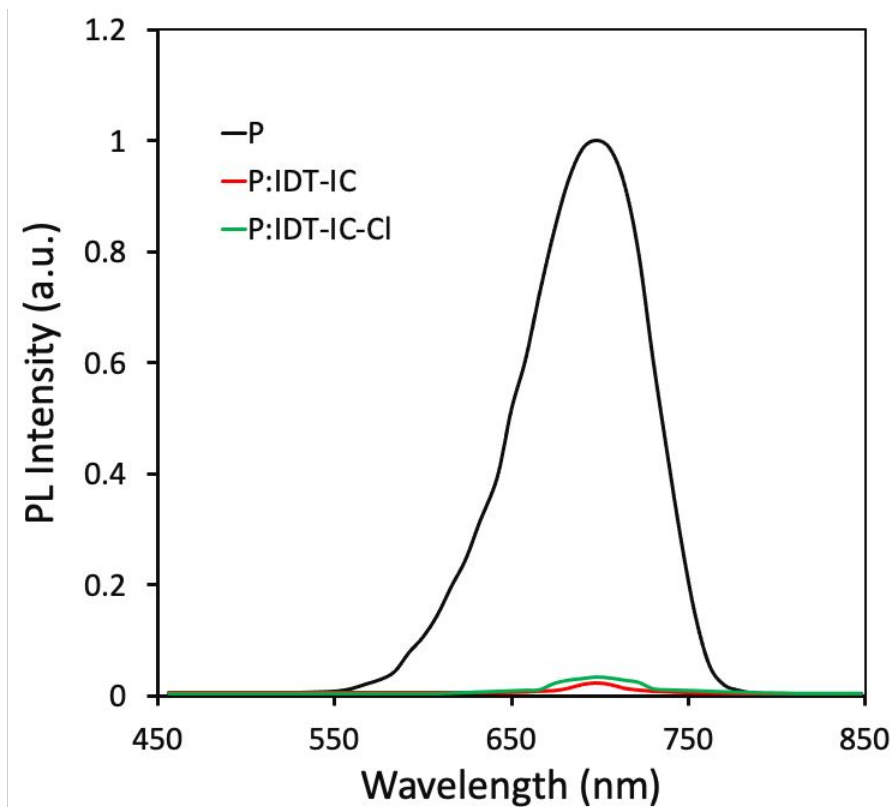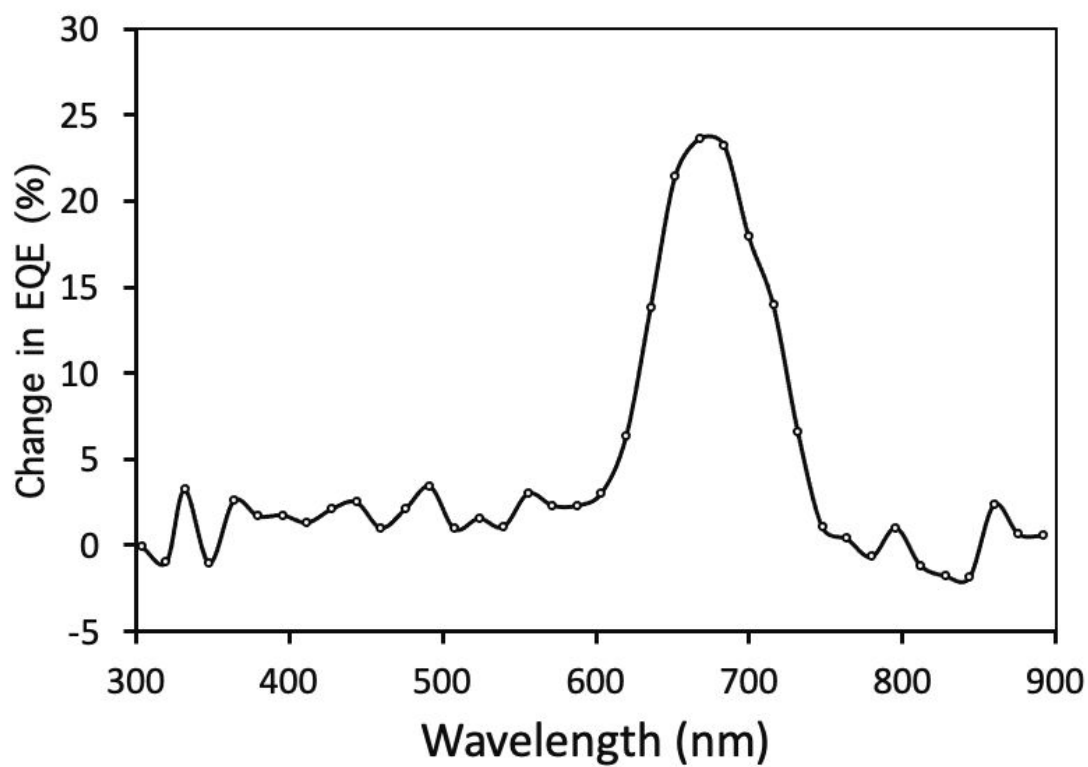
Figure S7. Dark J-V characteristics of devices based on IDT-IC and **IDT-TC** to estimate the electron mobility
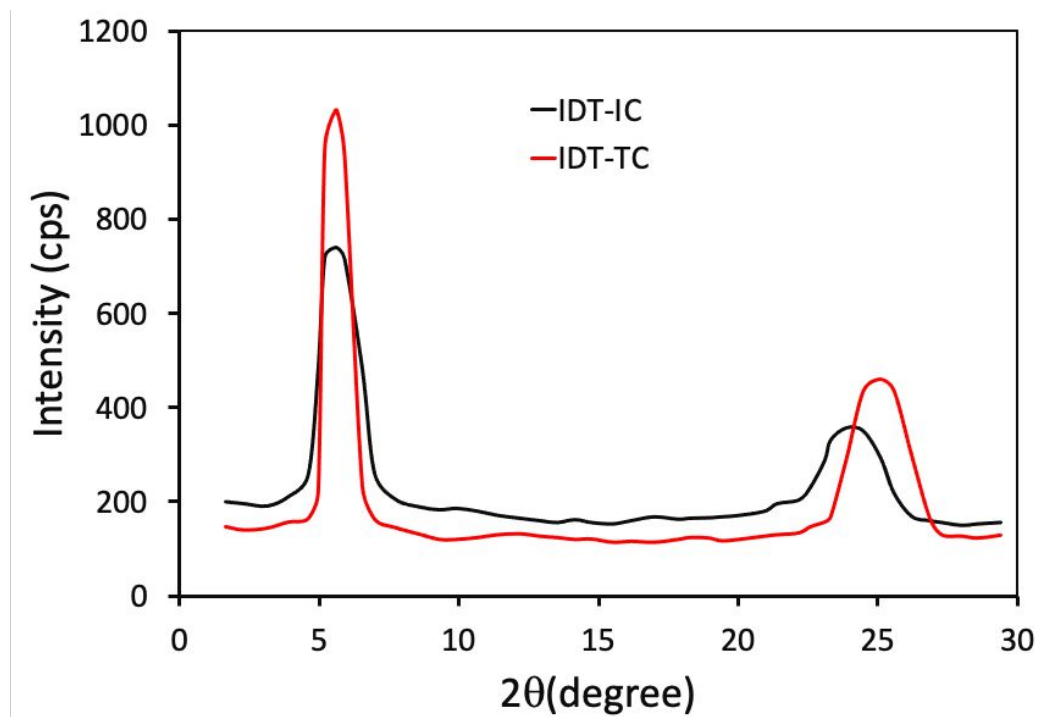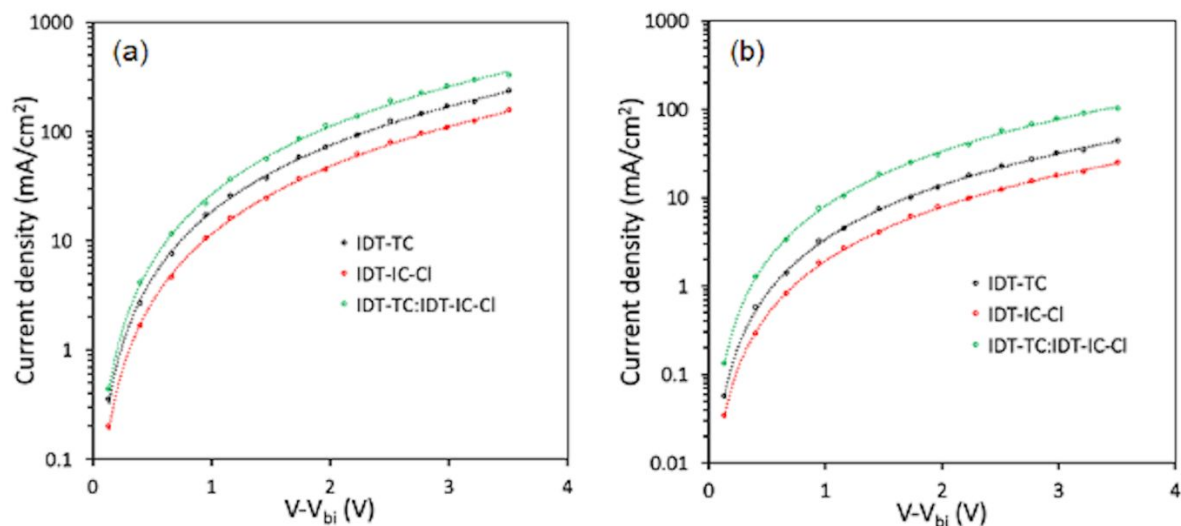

Figure S8. Thin XRD patterns of pristine IDT-IC and **IDT-TC**

Figure S9. PL spectra of pristine P and its blends with IDT-TC and IDT-IC-Cl

Figure S10. Variation in the change in EQE spectra

Figure S11. Dark J-V characteristics of (a) hole only and (b) electron only devices

Table S1a. Photovoltaic parameters of PSCs based on P:IDT-TC with different weight ratio between P and IDT-TC

P:IDT-TC weight ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1:0.4	13.38	1.07	0.58	8.30
1:0.8	14.55	1.08	0.60	9.43
1:1.2	15.23	1.09	0.61	10.13
1:1.4	14.53	1.09	0.59	9.34

Table S1b. Photovoltaic parameters of PSCs based on P:IDT-IC with different weight ratio between P and IDT-IC

P:IDT-IC weight ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1:0.4	14.34	0.93	0.52	6.93
1:0.8	15.64	0.92	0.54	5.24
1:1.2	16.98	0.92	0.55	8.59
1:1.4	15.96	0.91	0.53	7.70

Table S1c. Photovoltaic parameters of PSCs based on P:IDT-IC-Cl with different weight ratio between P and IDT-IC-Cl

P:IDT-IC weight ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1:0.4	15.83	0.92	0.58	8.45
1:0.8	16.92	0.91	0.60	9.24
1:1.2	17.76	0.91	0.61	9.86
1:1.4	17.08	0.91	0.60	9.32

Table S2a. Photovoltaic parameters of PSCs based on P: IDT-TC (1:1.2) SVA treatment at different times

SVA time	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
10 s	16.46	1.03	0.66	11.19
25 s	18.05	1.04	0.68	12.76
40 s	19.88	1.04	0.69	14.26
50 s	19.08	1.02	0.66	12.17

Table S2b. Photovoltaic parameters of PSCs based on P:IDT-IC (1:1.2) SVA treatment at different times

SVA time	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
10 s	18.23	0.87	0.61	9.67
25 s	19.45	0.86	0.623	10.43
40 s	20.52	0.88	0.64	11.56
50 s	19.83	0.86	0.612	10.44

Table S2c. Photovoltaic parameters of PSCs based on P:IDT-IC-Cl(1:1.2) SVA treatment at different times

SVA time	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
10 s	20.63	0.91	0.63	11.83
25 s	21.74	0.89	0.65	12.58
40 s	22.64	0.88	0.67	13.34
50 s	21.23	0.86	0.66	12.05

Table S3. Photovoltaic parameters of PSCs based on P:IDT-TC: IDT-IC-Cl ternary active layers with different weight ratio between IDT-TC and IDT-IC-Cl

IDT-IC :IDT-IC-Cl weight ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
0.1:1.1	19.96	1.01	0.67	13.51
0.2:1.0	20.78	1.00	0.67	13.92
0.3:0.9	21.06	0.98	0.68	14.03
0.4:0.8	20.62	0.96	0.66	13.06