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Supporting information

Functionalized alkenyl side chains: a feasible strategy in improving charge transport and photovoltaic performance

Bing Zheng, Juan Liu, Xuexue Pan, Yu Zhang, Zaiyu Wang, Feng Liu, Meixiu Wan, and Lijun Huo**

B. Zheng, J. Liu, F. Qi, X. Pan, Y. Zhang, M. Wan, Prof. L. Huo
School of Chemistry
Beihang University
Beijing 100191, China.
E-mail: huolijun@buaa.edu.cn

Zaiyu Wang, Prof. Feng Liu
Department of Physics and Astronomy
Shanghai Jiao Tong University
Shanghai 200240, PR China
E-mail: fengliu82@sjtu.edu.cn

Materials: All chemical reagents and solvents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and toluene were freshly distilled from sodium/benzophenoneketyl prior to use. All reactions were performed under a nitrogen atmosphere. The monomer of (4,8-bis(5-(2-ethylhexyl)thienyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) was prepared according to the previous methods.

bis(3,7-dimethyloctyl) 2,5-dibromothiophene-3,4-dicarboxylate (1a):

A mixture of 2,5-dibromothiophene-3,4-dicarboxylic acid (6.60 g, 0.02 mol) and $SOCl_2$ (50 mL) was refluxed for 8h, and the excess $SOCl_2$ was removed under vacuum. To the residue, 3,7-dimethyloctan-1-ol (30 mL) and dry pyridine (3 mL) were added to the flask dropwise through an addition funnel. The mixture was stirred for 12 h at 60 °C and was cooled to room temperature, then was poured into a mixture of ice and chlorohydric acid (200 mL, 1 M), and stirred. The solution was washed with ether for three times, and the combined organic layer was dried over anhydrous magnesium sulfate. After removal of solvents, the afforded residues was purified by column chromatography on silica gel with dichloromethane as eluent to give colorless liquid (10.3 g, yield 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (m, 4H), 1.73 (m, 2H), 1.49 (m, 6H), 1.27 (m, 12H), 0.89 (m, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 161.56, 134.01, 115.46, 64.64, 39.38, 37.38, 35.51, 29.75, 27.93, 24.59, 22.67, 22.56, 19.35.

bis((E)-3,7-dimethylocta-2,6-dien-1-yl)2,5-dibromothiophene-3,4-dicarboxylate (1b)

A mixture of 2,5-dibromothiophene-3,4-dicarboxylic acid (4.95 g, 0.015 mol) and $SOCl_2$ (40 mL) was refluxed for 8h, and the excess $SOCl_2$ was removed under vacuum. To the residue, (E)-3,7-dimethylocta-2,6-dien-1-ol (20 mL) and dry pyridine (3 mL) were added to the flask dropwise through an addition funnel. The mixture was stirred for 12 h at 60 °C and was cooled to room temperature, then it was poured into a mixture of ice and chlorohydric acid (200 mL, 1 M), and stirred. The solution was washed with ether for three times, and the combined organic layer was dried over anhydrous magnesium sulfate. After removal of solvents, the afforded residues was purified by column chromatography on silica gel with dichloromethane as eluent to give colorless liquid (3.96 g, yield 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39 (t, 2H), 5.06 (d, 2H), 4.78 (d, 4H), 2.04 (m, 8H), 1.60 (m, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 161.50, 143.30, 133.81, 131.91, 123.66, 117.50, 115.62, 62.79, 39.57, 26.28, 25.68, 17.70, 16.58.

bis(3,7-dimethyloctyl) [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (2a):

In a 100 mL argon purged flask, 1a (1 mmol) was added into a solution of trimethyl(thiophen-2-yl)stannane (1.12 g, 3 mmol) in toluene (30 mL) at room temperature. When the flask was purged by argon for 5 minutes, 115 mg of $Pd(PPh_3)_4$ was added as a catalyst, and then the mixture was purged by argon for another 15 minutes. The reactant was heated to reflux overnight. Then the mixture was concentrated to obtain the raw compound 2a. Further purification was carried out by a silica gel column using a dichloromethane/petroleum ether (1/6) eluent to obtain pure compound 2a as an yellow liquid (0.41 g, yield 66.5%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 2H), 7.31 (d, 2H), 7.05 (dd, 2H), 4.20 (m, 4H), 1.64 (m, 2H), 1.42 (m, 6H), 1.09 (m, 12H), 0.85 (m, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 163.81, 137.82, 132.64, 130.21, 128.60, 127.69, 127.49, 64.28, 39.24, 37.14, 35.33, 29.70, 27.94, 24.57, 22.68, 22.58, 19.37.

bis((E)-3,7-dimethylocta-2,6-dien-1-yl)[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (2b):

In a 100 mL argon purged flask, 1b (1 mmol) was added into a solution of trimethyl(thiophen-2-yl)stannane(1.12 g, 3 mmol) in toluene (30 mL) at room temperature. When the flask was purged by argon for 5 minutes, 115 mg of $Pd(PPh_3)_4$ was added as a catalyst, and then the mixture was purged by argon for another 15 minutes. The reactant was heated to reflux overnight. Then the mixture was concentrated to obtain the raw compound 2b. Further purification was carried out by a silica gel column using a dichloromethane/petroleum ether (1/5) eluent to obtain pure compound 2b as an yellow liquid (0.31 g, yield 51.1%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, 2H), 7.32 (d, 2H), 7.03 (t, 2H), 5.32 (t, 2H), 5.06 (d, 2H), 4.74 (d, 4H), 2.05 (m, 8H), 1.59 (m, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 163.68, 142.82, 137.88, 132.66, 131.84, 129.95, 128.63, 127.66, 127.48, 123.74, 117.66, 62.48, 39.56, 26.32, 25.65, 17.68, 16.51.

bis(3,7-dimethyloctyl) 5,5''-dibromo-[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3a)

In a 100 mL flask, N-bromosuccinimide (NBS) (0.36 g, 2 mmol) was slowly added into a solution of compound 2a (1 mmol) in chloroform (25 mL) at room temperature and stirred for 5 hours and then poured into ice water. The mixture was extracted by dichloromethane twice and the combined organic phase was concentrated to obtain the raw product 3a. Further purification was carried out by a silica gel column using a dichloromethane/petroleum ether (1/10) eluent to obtain pure compound 3a as an yellow liquid (0.56 g, yield 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, 2H), 7.01 (d, 2H), 4.24 (m, 4H), 1.64 (m, 2H), 1.40 (m, 6H), 1.09 (m, 12H), 0.86 (m, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 163.41, 137.00, 133.80, 130.43, 130.29, 129.01, 115.22, 64.49, 39.24, 37.15, 35.35, 29.71, 27.94, 24.58, 22.69, 22.60, 19.36.

bis((E)-3,7-dimethylocta-2,6-dien-1-yl)5,5''-dibromo-[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (3b):

In a 100 mL flask, N-bromosuccinimide (NBS) (0.36 g, 2.2 mmol) was slowly added into a solution of compound 2b (1 mmol) in chloroform (25 mL) at room temperature and stirred for 10 hours and then poured into ice water. The mixture was extracted by dichloromethane twice and the combined organic phase was concentrated to obtain the raw product 3b. Further purification was carried out by a silica gel column using a dichloromethane/petroleum ether (1/10) eluent to obtain pure compound 3b as an yellow liquid (0.48 g, yield 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (d, 2H), 6.93 (d, 2H), 5.26 (t, 2H), 4.99 (d, 2H), 4.67 (d, 4H), 1.95 (m, 8H), 1.49 (m, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 163.31, 143.31, 137.02, 133.85, 131.89, 130.24, 130.18, 128.99, 123.68, 117.38, 115.22, 62.66, 39.57, 26.31, 25.65, 17.69, 16.54.

General procedure for the preparation of copolymers (LP3 and LP4)

The two monomers, 3a (or 3b) (0.17mmol), (4,8-bis(5-(2-ethylhexyl)thienyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (0.17mmol), toluene (20ml) were mixed in a 25ml two-neck flask. The reactant was purged by argon for 5 minutes, and then 5 mg of $Pd(PPh_3)_4$ was added. After being purged for 20 minutes, the reactant was heated up to 110°C under protection of inert atmosphere. After overnight, the sticky reactant was poured into methanol. The target polymer was precipitated as black powder and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol and chloroform. The polymer was recovered from the chloroform fraction as black solid. The solid was dried under vacuum to get the final polymers.

LP3: M_n: 17.6kg•mol^{-1}, PDI:2.0; elemental analysis calcd (%) for ($C_{68}H_{86}O_4S_7$): C, 68.53; H, 7.27; found: C, 68.76; H, 7.11.

LP4: M_n: 9.9kg•mol^{-1}, PDI:1.6; elemental analysis calcd (%) for ($C_{68}H_{78}O_4S_8$): C, 68.99; H, 6.64; found: C, 68.58; H, 6.71.

Instrumentation: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer using $CDCl_3$ as the solvent. The molecular weight of polymers was determined by gel permeation chromatography (GPC) relative to polystyrene standards with chloroform as the eluent. Thermal gravimetric analysis (TGA) were performed on a Perkin-Elmer Pyris 1 thermogravimetric analyzer. UV–vis absorption measurements were carried out on a Hitachi (model U-3010) UV–vis spectrophotometer. Cyclic voltammetric (CV) measurements were carried out in a conventional three-electrode cell using a platinum plate as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag^+ electrode as the reference electrode on a Zahner IM6e Electrochemical workstation in a tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) acetonitrile solution at a scan rate of 20 mV s^{-1}.

Device Fabrication and Characterization: An inverted architecture was fabricated with ITO/ZnO/active layer/MoO_3/Ag. The ITO-coated glass substrates were sequentially ultrasonicated in soap water, deionized water, acetone, and isopropyl alcohol for at least 15 min, and ultimately dried in an oven overnight. The ITO-coated glass substrates were treated by uv-ozone for 10 min. The ZnO precursor (zinc acetate dihydrate) was spin-coated on top of the pre-cleaned ITO (4000 rpm, 20 s). After coating, ZnO films were annealed at 200 °C for 30 min. The active layers were deposited in a glove box by spin coating. The solution of active layer was chloroform solution containing 8mg/mL of the donor, 8 mg/mL of the acceptor and 0.5% DIO as additive. The mixed solution was spin cast at 2000 rpm for 40s atop ZnO layer to form the active layer. Then the thin films were transferred into a vacuum evaporator connected to the glove box. MoO_3 (5nm) and Ag (100 nm) were deposited sequentially by thermal evaporation under 10^{-5} Pa. The active area of the devices is 4.50 mm^2. Current density-voltage (J-V) characteristics were measured by a Keithley 2400 Source Measure Unit, in N_2 atmosphere under an AM 1.5G solar simulator with an irradiation light intensity of 100 $mw\cdot cm^{-2}$. The external quantum efficiency (EQE) of the devices was measured by using a QEX10 solar cell EQE measurement system (PV measurements.Inc.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Atomic force microscopy (AFM) Characterization: AFM images were investigated on a Dimension Icon AFM (Bruker) in a tapping mode.

Transmission Electron Microscopy (TEM) Characterization: TEM images were performed on a JEOL JEM-1400 transmission electron microscope. TEM samples were prepared as follows: First, the active layer was spin cast on the top of ITO/PEDOT:PSS substrates; Then, the active layer film was peeled off and floated onto the surface of deionized water; Finally, the floated films were picked up on a carbon film 200 mesh copper grid for TEM measurements.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Characterization**:** GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector.

Space-Charge-Limited Current (SCLC): The current density–voltage (J–V) characteristics of the hole or electron only devices are fitted by the Mott–Gurney law:

$J = (9/8)\varepsilon_r\varepsilon_0\mu(V^2/L^3)$

where J is the current density, ε_r is the dielectric permittivity of the active layer, ε_0 is the vacuum permittivity, L is the thickness of the active layer, μ is the mobility. $V=V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here). The mobility can be calculated from the slope of the $J^{0.5}$~V curves.

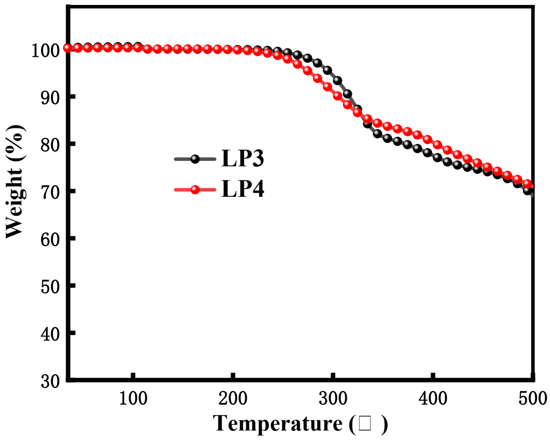

Figure S1. TGA plots of **LP3** and **LP4** with a heating rate of 20 °C/min under the inert atmosphere.

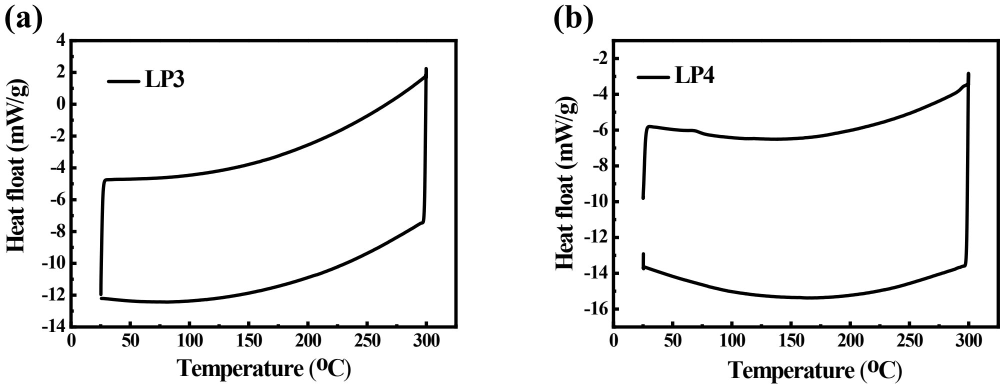

Figure S2. DSC plots of **LP3** and **LP4** with a scanning rate of 10 °C/min under the inert atmosphere.

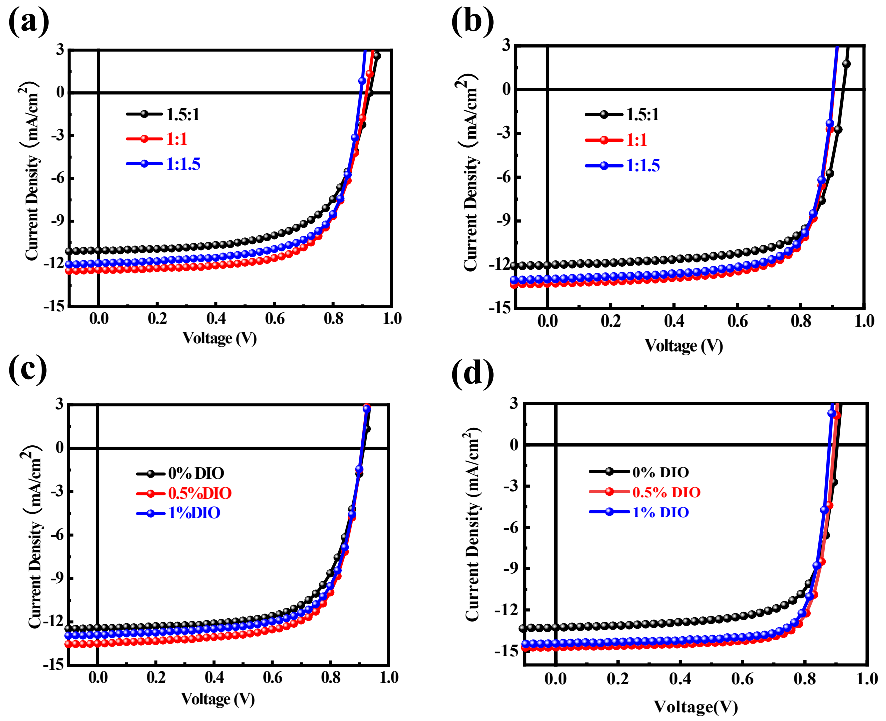

Figure S3. (a)-(d) *J–V* characteristics of **LP3**:**ITCPTC** and **LP4**: **ITCPTC** based solar cells with optimized weight ratios and additive conditions under the illumination of AM 1.5G, 100 mW/cm^2.

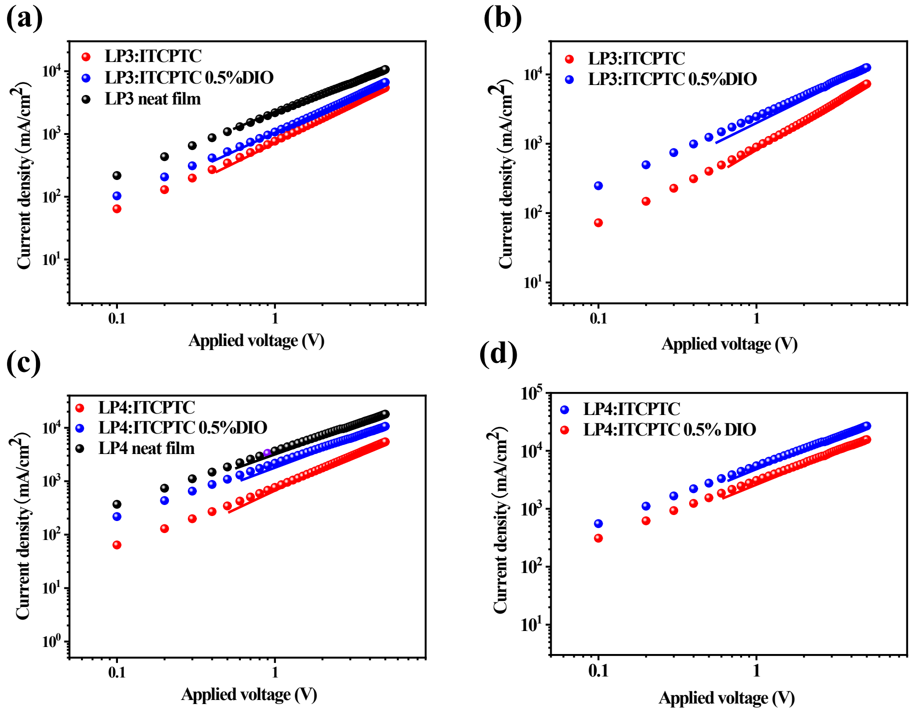

Figure S4. Current-voltage (*I-V*) characteristics of pure film and blend films in a hole-only devices: ITO/MoO$_3$/blend film/MoO$_3$/Al (a,c); electron-only devices:

ITO/Al/blend film/Al (b,d).

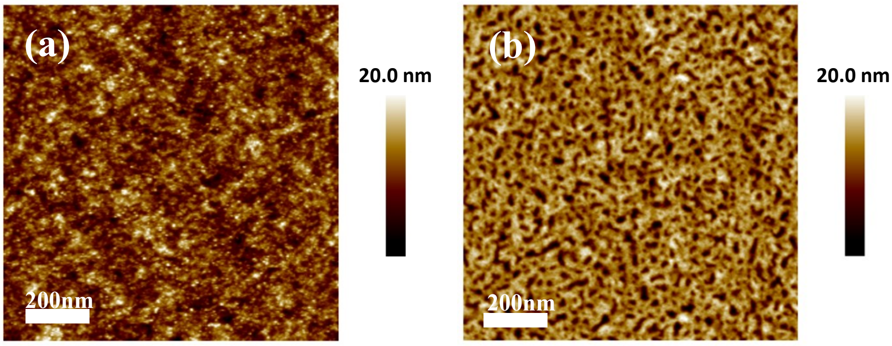

Figure S5. AFM topography images (1 × 1 μm) of **LP3** (a) and **LP4** (b) pure films.

Table S1 Photovoltaic performance of the devices based on **LP3**:**ITCPTC** without DIO under the illumination of AM 1.5G, 100 mW/cm^2.

LP3:ITCPTC	V_{oc} (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)^a
1.5:1	0.92	11.09	62	6.33 (6.31)
1:1	0.92	12.41	67	7.65 (7.49)
1:1.5	0.90	12.08	68	7.39 (7.18)

a) All average values were calculated from six devices

Table S2 Photovoltaic performance of the devices based on **LP3**:**ITCPTC** with different DIO concentrations under the illumination of AM 1.5G, 100 mW/cm^2.

DIO (%)	*Voc* (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)^a
0%	0.92	12.41	67	7.65 (7.49)
0.5%	0.91	13.50	69	8.48 (8.37)
1%	0.91	12.90	70	8.22 (7.90)

a) All average values were calculated from six devices

Table S3 Photovoltaic performance of the devices based on **LP4**:**ITCPTC** without

DIO under the illumination of AM 1.5G, 100 mW/cm^2.

LP4:ITCPTC	V_{oc} (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)^a
1.5:1	0.93	12.05	70	7.84 (7.56)
1:1	0.90	13.28	72	8.61 (8.44)
1:1.5	0.90	12.98	72	8.41(8.29)

a) All average values were calculated from six devices

Table S4 Photovoltaic performance of the devices based on **LP4**:**ITCPTC** with different DIO concentrations under the illumination of AM 1.5G, 100 mW/cm^2.

DIO (%)	*Voc* (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)^a
0%	0.90	13.28	72	8.61 (8.44)
0.5%	0.89	14.72	77	10.09 (10.03)
1%	0.88	14.43	76	9.65(9.54)

a) All average values were calculated from six devices

Table S5 Photovoltaic performance of the devices based on **LP4**:**ITCPTC** with different thickness under the illumination of AM 1.5G, 100 mW/cm^2.

thickness (nm)	*Voc* (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)^a
100	0.89	14.28	76	9.66 (9.47)
130	0.89	14.72	77	10.09 (10.03)
200	0.88	15.05	73	9.67 (9.36)
250	0.87	15.17	73	9.63 (9.31)
300	0.87	15.26	71	9.43 (9.17)
400	0.87	14.74	70	8.98 (8.76)

b) All average values were calculated from six devices

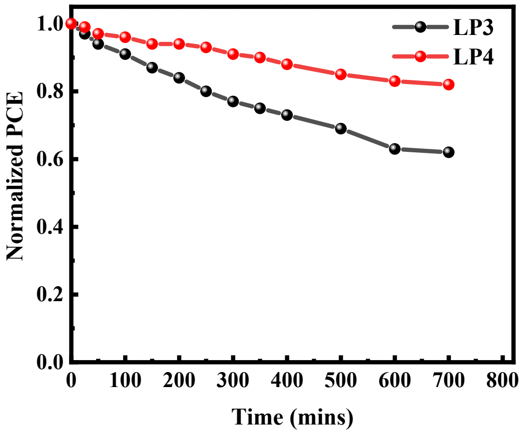

Figure S6. The PCEs for the devices based on **LP3**:**ITCPTC** and **LP4**:**ITCPTC** blended films after thermal treatment at 100 °C for different times.

Table S6 Electron/hole mobility data and the ratio μ_h/μ_e of of blend films in blend and neat films.

Samples	Additive	μ_h(cm^{2}V^{-1}s^{-1})	μ_e(cm^{2}V^{-1}s^{-1})	μ_h/μ_e
LP3:**ITCPTC**	W/O	7.03×10^{-4}	9.65×10^{-4}	0.73
LP3:**ITCPTC**	DIO	8.81×10^{-4}	1.07×10^{-3}	0.82
LP4:**ITCPTC**	W/O	1.98×10^{-3}	2.21×10^{-3}	0.90
LP4:**ITCPTC**	DIO	2.73×10^{-3}	2.62×10^{-3}	1.04
LP3		1.09×10^{-3}		
LP4		4.16×10^{-3}		