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Supporting Information

Green solvent-processed efficient non-fullerene organic solar cells enabled by low band gap copolymer donors with EDOT side chains

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1. Experimental section

1.1. Materials and synthetic procedures

PTB7-Th was purchased from 1-Materials. J71 and ITIC-Th were purchased from Derthon Optoelectronic Materials Science Technology. All the other chemicals were purchased from Aladdin, Adamas, Sigma-Aldrich, and Alfa Asear Chemical Co., and used without further purification. All solvents were freshly distilled immediately prior to use. 2-Ethyhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (**M3**) was synthesized according to previously reported procedures.[1]

*Synthesis of 2-(2-ethylhexyl)-3,4-ethylenedioxythiophene (**2a**):* 3,4-Ethylenedioxythiophene (**1**) (2.0 g, 14.1 mmol) in anhydrous THF (30 mL) was firstly cooled to 0 °C. *n*-Butyllithium (5.6 mL, 14.1 mmol, 2.5 M in hexane) was dropwise added in above solution under argon protection. After the mixture was stirred at 0 °C for 2 h, 2-ethylhexylbromine (2.7 g, 14.1 mmol) was then dropwise added. The reaction mixture was continuously stirred overnight at room temperature. After the reaction was finished, NH_4Cl aqueous solution was added and the solution was extracted with diethyl ether. The organic phase was combined and washed with water for three times, then dried over anhydrous $MgSO_4$. After removal of solvent, the residue was purified by column chromatography (silica gel; eluent: dichloromethane/petroleum ether = 1:10) to give purified compound **2a** as colorless oil (2.4 g, 67%). ^1H NMR (400 MHz, $CDCl_3$, δ/ppm): 6.16 (s, 1H, ArH), 4.16 (s, 4H, CH_2), 2.57 (d, 2H, J=6.88, CH_2), 1.55 (m, 1H, CH_2), 1.31 (m, 8H, CH_2), 0.88 (m, 6H, CH_3), ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 141.35, 138.05, 117.44, 95.33, 64.73, 64.52, 40.53, 32.39, 29.91, 28.77, 25.65, 23.06, 14.14, 10.82. Elemental analysis calcd (%) for $C_{14}H_{22}O_2S$: C 66.10, H 8.72; found: C 66.13, H 8.74. HR-MS: $[M+1]^+$: Calcd: 255.1419; found: 255.1417.

*Synthesis of 2-[(2-ethylhexyl)thio]-3,4-ethylenedioxythiophene (**2b**):* 3,4-Ethylenedioxythiophene (**1**) (3.0 g, 21.1 mmol) in anhydrous THF (40 mL) was firstly cooled to 0 ^{o}C. *n*-Butyllithium (8.4 mL, 21.1 mmol, 2.5 M in hexane) was dropwise added in above solution under argon protection. After the mixture was stirred at 0 ^{o}C for 1.5 h, sulfur powder (0.67 g, 21.15 mmol) was added in one portion, and then the resulting mixture was stirred at 0 ^{o}C for another 2 h. Subsequently, 2-ethylhexylbromine (4.0 g, 21.15 mmol) was dropwise added in the reaction mixture. The reaction solution was then stirred overnight at room temperature. After the reaction was finished, NH_4Cl aqueous solution was added and the solution was extracted with diethyl ether. The organic phase was combined and washed with water for three times, then dried over anhydrous $MgSO_4$. After removal of solvent, the residue was purified by column chromatography (silica gel; eluent: dichloromethane/petroleum ether=1:10) to give purified compound **2b** as colorless oil (2.0 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 6.36 (s, 1H, ArH), 4.27 (m, 4H, CH_2), 4.18 (m, 4H, CH_2), 2.72 (d, J=7.00, 2H, CH_2), 1.36 (m, 9H, CH_2), 0.86 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 143.59, 141.26, 107.94, 102.19, 64.97, 64.36, 42.43, 39.01, 31.96, 28.75, 25.16, 22.99, 14.19, 10.73. Elemental analysis calcd (%) for $C_{14}H_{22}O_2S_2$: C 58.70, H 7.74; found: C 58.80, H 7.90. HR-MS: $[M+1]^+$: Calcd: 287.1137; found: 287.1139.

*Synthesis of 4,8-bis[5-(2-ethylhexyl)-3,4-ethylenedioxythiophene-2-yl]benzo[1,2-b:4,5-b']dithiophene (**3a**):* Compound **2a** (2.3 g, 9.05 mmol) in anhydrous THF (25 mL) was added into a three-necked round-bottom flask with a condenser. When the solution was cooled to 0 °C under argon atmosphere, *n*-butyllithium (4 mL, 10.0 mmol, 2.5 M in hexane) was dropwise added to above mixture. The mixture was kept at room temperature for 1.5 h, and then cooled to 0 °C again. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (0.66 g, 3.02 mmol) was added in one portion. The mixture was stirred at 50 °C overnight, and then cooled to ambient temperature. $SnCl_2 \cdot 2H_2O$ (5.5 g, 12.1 mmol) in 10 mL HCl (10%) was added, and the mixture was stirred for another 2 h. After the reaction was finished, the ice water was added and extracted with dichloromethane. The combined extracts were dried over anhydrous $MgSO_4$. After removal of solvent, the residue was purified by column chromatography (silica gel; eluent: dichloromethane/petroleum ether=1:1) to afford purified compound **3a** as light yellow oil (0.8 g, 38%). ^1H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.43 (s, 4H, ArH), 4.23 (dd, 8H, J=6.31 CH_2), 2.69 (d, 4H, J=7.48, CH_2), 1.66 (m, 2H, CH_2), 1.40 (m, 8H, CH_2), 1.29 (m, 8H, CH_2), 0.93 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 139.38, 138.33, 138.01, 137.12, 127.12, 123.72, 121.14, 117.98, 109.17, 64.81, 64.54, 40.54, 32.56, 30.06, 29.72, 28.85, 25.93, 23.08, 14.18, 10.92. Elemental analysis calcd (%) for $C_{38}H_{46}O_4S_4$: C 65.67, H 6.67; found: C 65.63, H 6.68. MALDI-TOF-MS m/z: calcd for $C_{38}H_{46}O_4S_{6,}$ $[M]^+$, 694.228; found, 694.230.

*Synthesis of 4,8-Bis{5-[(2-ethylhexyl)thio]-3,4-ethylenedioxythiophene-2-yl}benzo[1,2-b:4,5-b']dithiophene (**3b**):* The synthesis of compound **3b** was similar to compound **3a** with a yield of 20%. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.48 (d, 2H, J=5.80, ArH), 7.39 (d, 2H, J=5.80, ArH), 4.35 (br, 4H, CH_2), 4.30 (br, 4H, CH_2), 2.85 (m, 4H, CH_2), 1.64 (m, 2H, CH_2), 1.40 (m, 16H, CH_2), 0.91 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 143.42, 139.30, 138.34, 137.02, 127.65, 123.40, 120.71, 115.33, 108.70, 64.98, 64.48, 42.31, 39.29, 32.09, 28.87, 25.31, 22.98, 14.25, 10.89. Elemental analysis calcd (%) for $C_{38}H_{46}O_4S_6$: C 60.12, H 6.11; found: C 60.83, H 6.22. MALDI-TOF-MS m/z: calcd for $C_{38}H_{46}O_4S_6$: $[M]^+$: 758.172; found: 758.181.

*Synthesis of 2,6-bis(tributylstannanyl)-4,8-bis[5-(2-ethylhexyl)-3,4-ethylenedioxythiophene-2-yl]benzo[1,2-b:4,5-b']dithiophene (**M1**):* Compound **3a** (0.75 g, 1.08 mmol) was dissolved in 20 mL of anhydrous THF and cooled to -78 °C under nitrogen protection. Lithium diisopropylamide (LDA) (1.62 mL, 3.24 mmol, 2M in hexane solution) was added with stirring. After the addition of LDA, the mixture was kept in the same temperature for 30 min. Tri-*n*-butyltin chloride (1.05 g, 3.24 mmol) was then added dropwise, and the mixture was stirred overnight at room temperature. The mixture was quenched with 10 mL of water and extracted with diethyl ether for three times, then dried over anhydrous $MgSO_4$. After removal of solvent, the crude product was purified by column chromatography (silica gel; eluent: petroleum ether) to afford compound **M1** as light yellow oil (1.0 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.46 (s, 2H, ArH), 4.23 (br, 8H, CH_2), 4.23 (m 4H, CH_2), 2.71 (d, 4H, J=6.52, CH_2), 1.64 (m, 10H, CH_2), 1.54 (m, 2H, CH_2), 1.39 (br, 2H, CH_2), 1.13 (m, 12H, CH_2), 0.91(m, 30H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 143.37, 140.70, 137.96, 137.89, 137.67, 131.89, 118.98, 117.45, 110.20, 64.62, 64.54, 40.50, 32.48, 30.02, 28.95, 28.80, 27.27, 25.89, 23.08, 14.21, 13.71, 10.92. Elemental analysis calcd (%) for $C_{62}H_{98}O_4S_4Sn_2$: C 58.49, H 7.76; found: C 58.92, H 8.09. MALDI-TOF-MS m/z: calcd for $C_{62}H_{98}O_4S_4Sn_2$: $[M]^+$: 1274.445; found:1274.445.

*Synthesis of 2,6-bis(tributylstannanyl)-4,8-bis{5-[(2-ethylhexyl)thio]-3,4-ethylenedioxythiophene-2-yl]benzo[1,2-b:4,5-b']dithiophene (**M2**):* The synthesis of compound **M2** was similar to compound **M1** with a yield of 69%. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.46 (s, 2H, ArH), 4.23 (br, 8H, CH_2), 4.23 (br, 4H, CH_2), 2.71 (d, J=6.52, 4H, CH_2), 1.64 (m, 10H, CH_2), 1.54 (m, 2H, CH_2), 1.39 (br, 2H, CH_2), 1.13 (m, 12H, CH_2), 0.91 (m, 30H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 143.41, 143.38, 141.62, 138.03, 137.61, 131.44, 118.58, 116.56, 108.06, 65.01, 64.32, 42.28, 39.31, 32.09, 29.07, 28.97, 28.86, 28.82, 27.29, 25.31, 22.96, 14.22, 13.75, 10.90, 10.82. Elemental analysis calcd (%) for $C_{62}H_{98}O_4S_6Sn_2$: C 55.69, H 7.39; found: C 56.44, H 7.68. MALDI-TOF-MS m/z: calcd for $C_{62}H_{98}O_4S_6Sn_2$: $[M+1]^+$: 1337.391; found: 1337.396.

*Synthesis of **PTB-EDOT***: **M1** (0.3819 g, 0.3000 mmol) and **M3** (0.1417 g, 0.3000 mmol) was first dissolved in degassed toluene (10 mL). $Pd_2(dba)_3$ (5.06 mg, 2% mmol) and P(*o*-tol)$_3$ (6.71 mg, 8% mmol) were then added in above solution under argon atmosphere. The mixture was stirred at 110 °C for 24 h in dark and then cooled down to room temperature. The reaction solution was dropped slowly into 500 mL methanol. The precipitated solid was collected by filtration, and then subjected to Soxhlet extraction successively with methanol, acetone, and hexane to remove the oligomers and impurities. The remaining polymer was dissolved in chloroform and precipitated again from methanol to yield **PTB-EDOT** as a dark solid (yield: 86.4%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.89 (m, 1H, ArH), 7.59 (m, 1H, ArH), 4.30 (t, 8H, CH_2), 2.79 (s, 3H, CH), 1.67 (m, 6H, CH_2), 1.60 (m, 24H, CH_2), 0.96 (m, 18H, CH_3). Elemental analysis calcd (%) for $C_{53}H_{61}FO_6S_6$: C 63.31, H 6.12, S 19.13; found: C 63.34, H 6.31, 19.10.

*Synthesis of **PTB-EDOTS***: **PTB-EDOTS** was synthesized as a dark solid with a yield of 87.5% similar to the synthetic procedures of **PTB-EDOT**. In this experiment, **M2** (0.4012 g, 0.3000 mmol) and **M3** (0.1417 g, 0.3000 mmol) were used as the monomers, and the reaction mixture was heated at 110 °C for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.90 (m, 1H, ArH), 7.59 (m, 1H, ArH), 4.30 (t, 8H, CH_2), 2.80 (s, 3H, CH), 1.67 (m, 6H, CH_2), 1.60 (m, 24H, CH_2), 0.97 (m, 18H, CH_3). Elemental analysis calcd (%) for $C_{53}H_{61}FO_6S_8$: C 59.52, H 5.75, S 23.98; found: C 59.40, H 5.81, 23.77.

1.2. Instruments and measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer with *d*-chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as internal standard. The molecular mass was confirmed by using a Q-TOF Ultima Global liquid chromatography mass spectrometer (LC-MS), or a Autoflex III matrix-assisted laser desorption ionization mass spectrometer (MADI-TOF-MS), or a 9.4T Solarix fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS). Elemental analyses (EA) were performed on Thermo Electron SPA Flash EA 1112 series analyzer. Thermogravimetric analysis (TGA) was conducted on a TA Instrument

Model SDT Q600 simultaneous TGA/DSC analyzer at a heating rate of 10 °C min^{-1} and under the N_2 flow rate of 90 mL min^{-1}. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC equipment at a heating rate of 10 °C min^{-1} under the N_2 flow rate of 90 mL min^{-1}. UV-vis spectra were obtained on a Hitachi U2910 spectrophotometer. Cyclic voltammetry measurements were carried out on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s^{-1}, with the platinum wire as counter electrode and the Ag/AgCl as reference electrode, which was calibrated by the ferrocene/ferrocenium (Fc/Fc^{+}) redox couple to be -4.34 eV. AFM images were obtained by using a Bruker Inova atomic microscope in tapping mode. Carrier mobility was estimated using the SCLC method, which was described by $J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3$. J is the current density, L is the film thickness of the active layer, μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), V is the internal voltage and $V = V_{appl}-V_{bi}-V_a$, where V_{appl} is the applied voltage to the device, V_{bi} is the built-in voltage and V_a is the voltage drop.

Grazing incident wide-angle X-ray diffraction (GIWAXS): GIWAXS characterization of the thin films was performed at the SSRL on beamline 11-3, Standford Synchrotron Radiation Lab. Thin film samples were spin-casted on to PEDOT:PSS covered SiO2 wafers. The scattering signal was recorded on a 2D detector (MarCCD). The samples were ≈ 15 mm long in the direction of the beam path, and the detector was located at a distance of ≈ 300 mm from the sample center (distance calibrated using a silver behenate standard). The incidence angle of 0.16° was chosen which gave the optimized signal-to-background ratio. The beam energy was 8 keV. All GIXD experiments were done in helium atmosphere. The data was processed and analyzed using waxdiff software package.

1.3. Device fabrication and measurement

The ITO (sheet resistance = 15 Ω square^{-1}) glass substrates were ultrasonicated sequentially with detergent, deionized water, acetone and isopropanol. After that, the ITO glasses were treated with UV for 30 min in a UV-ozone chamber. The zinc oxide (ZnO) precursor solution (diethylzinc solution 2M in toluene, diluted by tetrahydrofuran) was then spin-coated on the surface of ITO substrate at a spinning rate of 5000 rpm for 30 s in dry air. The ZnO covered ITO plate was baked in dried air at 180°C for 30 min to form a thin ZnO film (~30 nm) as an electron extraction layer. The copolymer:ITIC-Th (1:1.5 w/w) solution was prepared by dissolved in CB/CN (98:2 v/v) with a in total concentration of 20 mg/mL or in MeTHF with a total concentration of 16 mg mL^{-1}. For the ternary blends, PTB-EDOT$_{(1-x)}$:J71$_x$:ITIC-Th$_{1.5}$ was dissolved in MeTHF with a total concentration of 16 mg mL^{-1}, and the D/A ratio was kept at 1:1.5. The prepared solutions were spin-coated on the top of ZnO layer at a speed of 2000 rpm for 60 s. The MeTHF-processed active layers were then baked on a hot plate at 100 ^{o}C for 5 min. The thickness of active layer was 100 nm. A molybdenum trioxide (MoO_3, 10 nm) and an aluminum anode (Al, 100 nm) were finally deposited onto the top of the active layer in an evaporation chamber under high vacuum (~10^{-4} Pa). The device area was exactly fixed at 4.00 mm^2. The I-V characterization was performed on a computer-controlled Keithley 2400 Source under

AM1.5G (100 mW cm^{-2}) using a solar simulator (XES-70S1, SAN-EI), which was calibrated by a standard Si solar cell (AK-200, Konica Minolta, INC.). The EQE values were measured with a Newport QE test Model 77890 (Newport Co. Ltd.) during illumination with monochromatic light from a xenon lamp. All fabrication and characterization processes, except for the ZnO layer preparation and EQE measurements, were conducted in a high purity argon filled glove box (< 0.1 ppm O_2 and H_2O).

2. Supplementary Figures

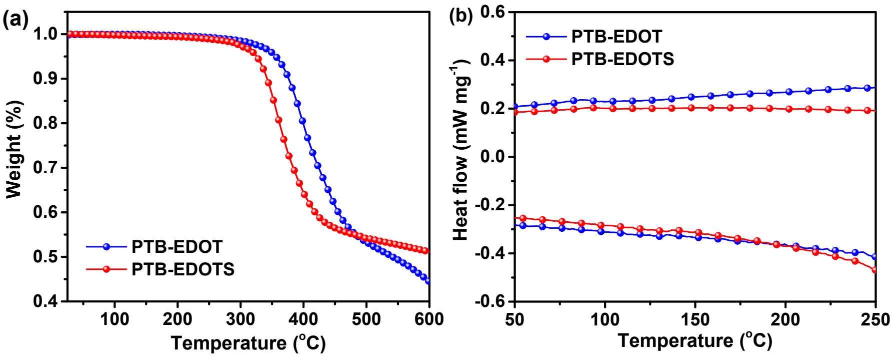

Fig. S1 (a) TGA curves of the copolymers. (b) DSC curves of the copolymers.

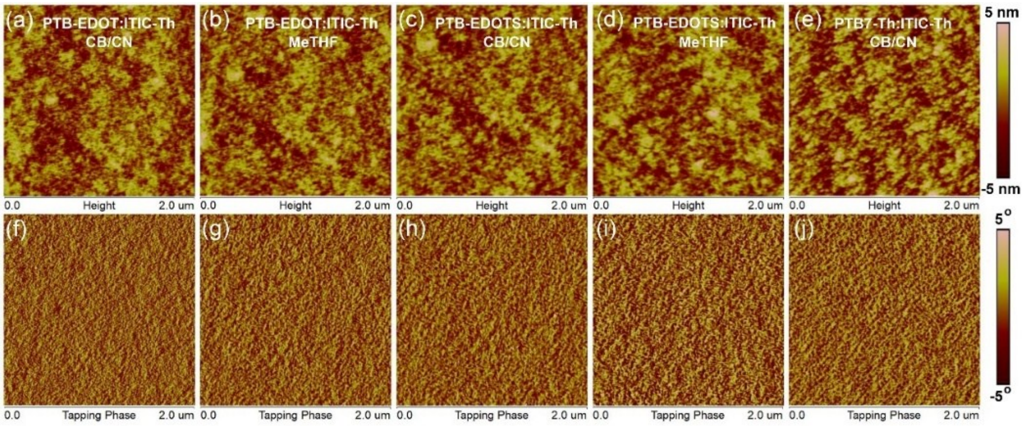

Fig. S2 AFM height (a-e) and phase (f-j) images of the blend films casted from different solvents.

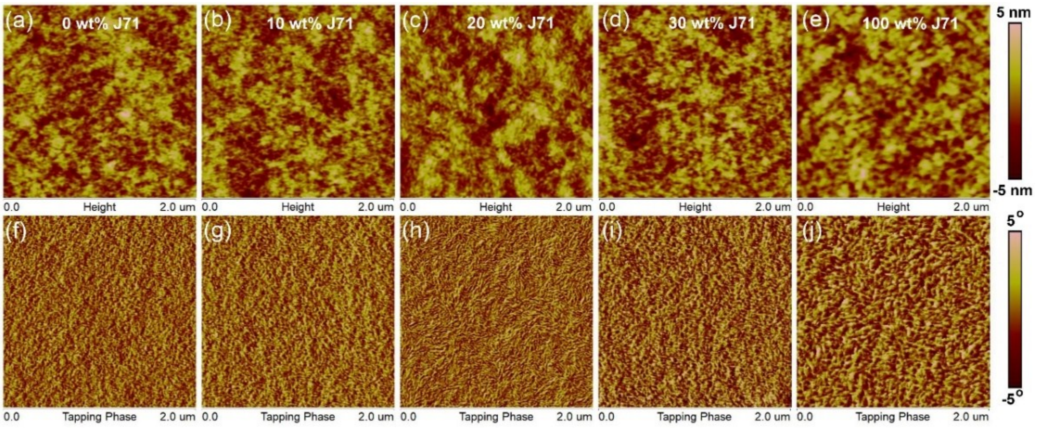

Fig. S3 AFM height (a-e) and phase (f-j) images of the ternary blend films with different J71 content.

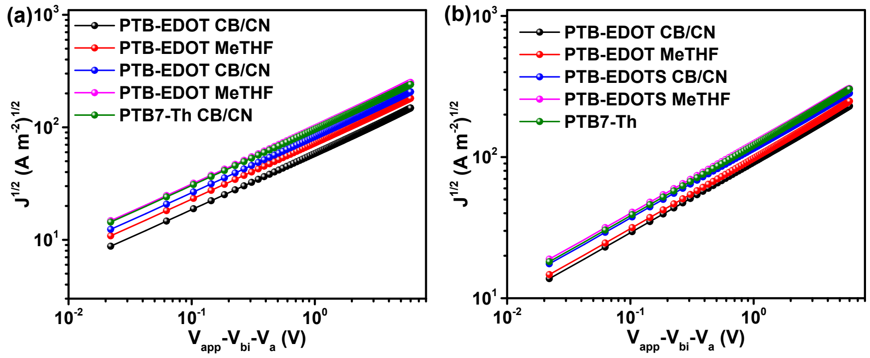

Fig. S4 $J^{1/2}$-V curves of the blend films casted from different solvents. (a) hole-only devices. (b) electron only devices.

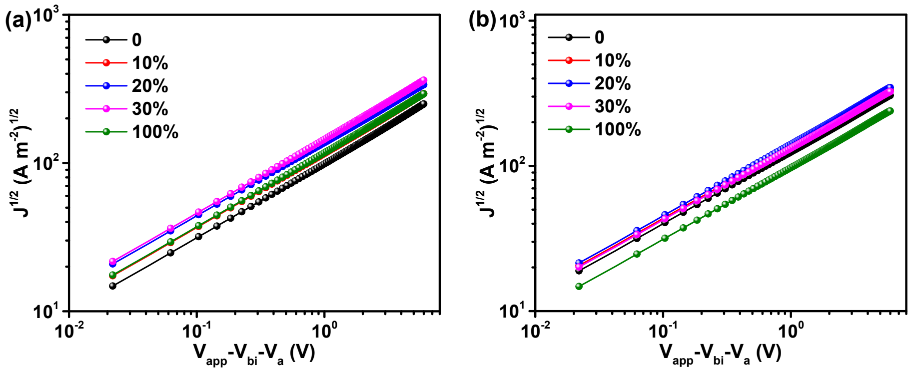

Fig. S5 $J^{1/2}$-V curves of the blend films casted from different solvents. (a) hole-only devices. (b) electron only devices.

3. Supplementary Tables

Table S1 Photovoltaic parameters of non-fullerene OSCs based on halogen free solvents.

active layer	solvent	additive	V_{oc} (V)	J_{sc} (mA cm-^{2})	FF (%)	PCE (%)	ref
FTAZ:IT-M	TMB[a]		0.94	14.40	61.90	9.1	1
	o-xylene		0.943	15.70	62.30	9.6	1
	toluene		0.95	16.80	66.10	11.0	1
PBDTS-TDZ:ITIC	*o*-xylene		1.10	17.78	65.40	12.80	2
3MT-Th:ITIC	toluene	DPE[b]	0.95	17.01	60.08	9.73	3
	mesitylene	DPE	0.89	6.21	66.09	3.65	3
	o-xylene	DPE	0.94	11.95	63.38	7.13	3
PBDB-BzT:IT-M	THF		0.96	17.63	69.00	12.10	4
PBTA-TF:IT-M	o-xylene	PN[c]	0.96	18.71	70.00	13.10	5
PBQ-4F:ITIC	THF/IPA		0.95	17.87	66.80	11.34	6
PBDB-T:IT-M	o-xylene	PN	0.94	17.10	72.10	11.60	7
PB3T:IT-M	anisole		1.00	18.90	63.00	11.90	8
PTzBI:N2200$_{HW}$	Me-THF		0.849	15.17	70.36	9.16	9
PTzBI-Si:N2200	Me-THF		0.87	15.57	73.39	10.10	10
PBTA-Si:PTzBI-Si:N2200	Me-THF		0.85	14.89	75.65	9.56	11
PBDTTS1:PPDIODT	*o*-MA[d]		0.74	13.77	52.46	5.60	12
	anisole		0.76	14.67	48.73	5.43	13
PiI-2T-PS10:P(TP)	toluene	MN[e]	0.98	9.77	51.00	5.00	14

[a] 1,2,4-Trimethylbenzene; [b] Diphenylether; [c] 1-Phenylnaphthalene; [d] o-methylanisole; [e] 1-Methylnaphthalene.

Table S2 Summarized charge carrier mobilities of the blend films.

Blend film	solvent	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})

PTB7-Th:ITIC-Th	CB/CN	2.21×10^4	3.50×10^4
PTB-EDOT:ITIC-Th	CB/CN	0.87×10^4	2.01×10^4
PTB-EDOT:ITIC-Th	MeTHF	1.25×10^4	2.43×10^4
PTB-EDOTS:ITIC-Th	CB/CN	1.63×10^4	3.05×10^4
PTB-EDOTS:ITIC-Th	MeTHF	2.45×10^4	3.56×10^4
10wt% J71	MeTHF	3.42×10^4	4.21×10^4
20wt% J71	MeTHF	4.35×10^4	4.57×10^4
30wt% J71	MeTHF	5.01×10^4	4.02×10^4
100wt% J71	MeTHF	4.01×10^4	2.17×10^4

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