Supplementary information

Cross-Conjugated n-Type Polymer Acceptors for Efficient All-Polymer Solar Cells

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1. General Experimental Details

Methods and Materials: The monomers of ((2,6-bis(trimethylstannyl)benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (compound **1**) was synthesized according to the reported procedures[1] and 4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (compound **5**) was purchased from Beijing HWRK Chem Co.,LTD. All the other materials were prepared as the following procedures as below.

^{1}H and ^{13}C NMR were characterized with Bruker-500 spectrometer in deuterated chloroform solution at 298 K. Chemical shifts were recorded as δ values (ppm) with the internal standard of tetramethylsilane (TMS). The number-average (M_n) and weight-average (M_w) molecular weights were determined with Waters GPC 2410 in THF using a calibration curve with standard polystyrene as a reference. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 under nitrogen at a heating rate of 10 ^{o}C min^{-1}. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 under nitrogen flow at heating/cooling rates of 10/20 ^{o}C min^{-1}. UV-vis absorption spectra were recorded on a HP 8453 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with an ITO-coated glass working electrodeand a Pt wire counter electrode at a scanning rate of 50 mV s^{-1} against an Ag/Ag$^+$ reference electrode with a nitrogen saturated anhydrous solution of tetra-*n*-butylammonium hexafluorophosphate in acetonitrile (0.1 mol L^{-1}). Atomic force microscopy (AFM) measurements were carried out using a Digital Instrumental DI Multimode Nanoscope

III in a taping mode.

2. Synthetic Procedures

The synthetic route for monomers and polymers are showed in Scheme S1. The Stille coupling reaction of stannylated compound ((2,6-bis(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophene-4,8-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (compound **1**) with bromized thiophene (compound **2**) gives compound **3**. By treating compound **3** with aqueous KOH (1 M) in the THF solution at 50 $^\circ$C for 6 hours, the aldehyde-bearing monomer **4** was obtained in a good yield of 80%. It is worth noting that the monomer **4** must be freshly prepared due to the photochemical instability of the alkyne.[2,3] The aldehyde-bearing polymer PNDI-CHO, which is the precursor polymer was successfully obtained from monomer **4** and monomer **5** via typical Sonogashira polymerization reactions with Pd(PPh$_3$)$_2$Cl$_2$/CuI as thecatalyst and chlorobenzene/diisopropylamine(DIPA) as the solvent. The target polymers PNDI-RDN, PNDI-BBT andPNDI-IT were prepared via the Knoevenagel condensationby treating the precursor polymerPNDI-CHO with 3-ethyl-2-thioxothiazolidin-4-one, 1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione and 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrilerespectively, with the catalysis amount of pyridine or triethylamine at 60 $^\circ$C. After pouring into methanol, the target polymers were collected by filtration and then successively purified by Soxhlet extraction with methanol, acetone and hexane.
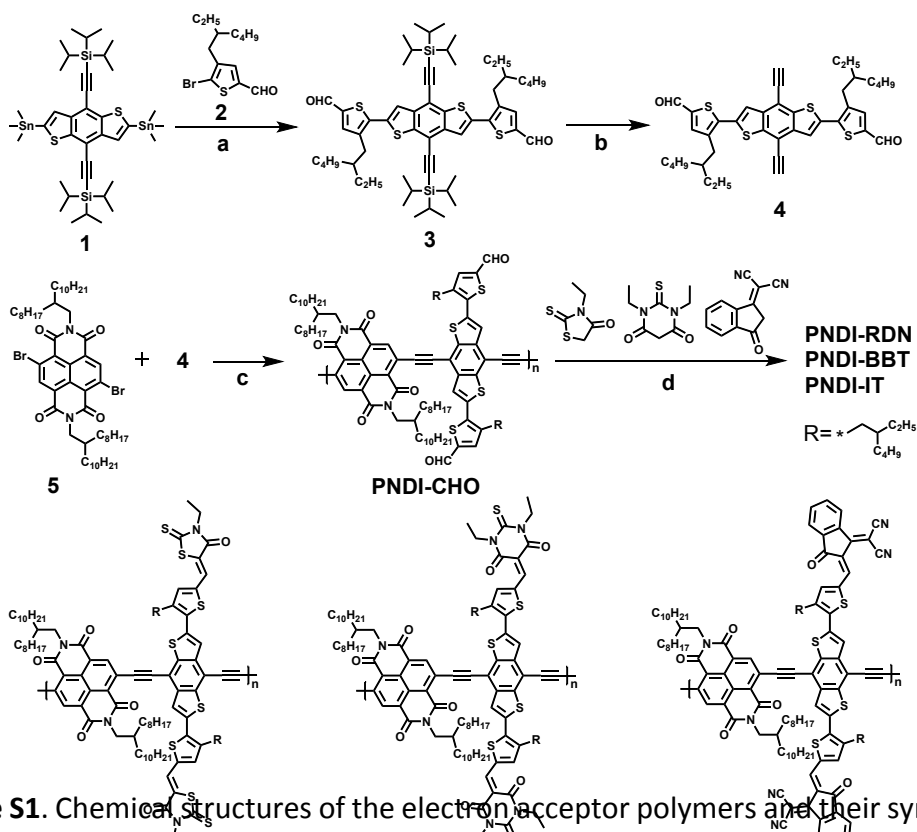
Scheme S1. Chemical structures of the electron acceptor polymers and their synthetic route. a) Pd(PPh₃)₄, toluene, 100 °C, 24 h. b) KOH, THF, 50 °C, 6 h. c) Sonogashira polymerization with Pd(PPh₃)₂Cl₂/CuI in toluene/DIPA, 80 °C, 2 h. d) Pyridine or triethylamine, CHCl₃, 60 °C, 72 h.

Synthesis of 5,5'-(4,8-bis((triisopropylsilyl)ethynyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4-(2-ethylhexyl)thiophene-2-carbaldehyde) (3).

In a two-necked, oven-dried 100 mL round bottom flask, compound**1** (1.26 g, 3 mmol) and compound **2** (1g, 9 mmol) were dissovled in 20 mL of toluene and the resulting solution was purged with argon for 20 minutes. Then Pd(PPh₃)₄ (20 mg) was added and the reaction mixture was stirred and heated to 100 °C for 24 hours. After cooling to room temperature, the material was then loaded onto silica and purified by chromatography to give 2.54 g of orange solid (78.1 %).

¹H NMR (500 MHz, CDCl₃, δ): 9.90 (s, 2H), 7.74 (s, 2H), 7.63 (s, 2H), 2.86 (qd, 4H), 1.72

(m, 2H), 1.24 – 1.21 (m, 58H), 0.86 (m, 12H).

^{13}C NMR (125 MHz, CDCl$_3$, δ): 182.73, 141.83, 141.58, 141.49, 140.96, 139.22, 138.64, 137.27, 123.22, 111.91, 103.31, 101.75, 40.25, 33.71, 32.48, 28.63, 25.80, 22.97, 18.77, 14.03, 11.28, 10.77.

Synthesis of 5,5'-(4,8-diethynylbenzo[1,2-b:4,5-b']dithioph10ene-2,6-diyl)bis(4-(2-ethylhexyl)thiophene-2-carbaldehyde) (4).

In a two-neck 100 mL argon purged flask, aqueous KOH (5 mL, 1 M) was dropwise added to the THF (50 mL) solution of compound **3** (0.85 g, 0.40 mmol), then the reaction mixture was heated to 50 ^{o}C for 6 hours. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3×50 mL). The organic phase was dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure. Purification by chromatograph yielded 0.58 g of a yellow solid (80 %)

^{1}H NMR (500 MHz, CDCl$_3$, δ): 9.89 (s, 2H), 7.74 (s, 2H), 7.60 (s, 2H), 3.90 (s, 2H), 2.86 (d, 4H), 1.71 (m, 2H), 1.39 – 1.25 (m, 16H), 0.90 – 0.84 (m, 12H).

^{13}C NMR (125 MHz, CDCl$_3$, δ): 182.60, 141.76, 141.68, 141.32, 140.45, 139.45, 138.97, 137.62, 122.81, 110.90, 87.98, 78.86, 40.19, 33.73, 32.55, 28.70, 25.67, 23.03, 14.08, 10.69.

MS (MALDI-TOF): calcd for C$_{40}$H$_{42}$O$_2$S$_4$, 683.014; found, 682.137.

Synthesis of PNDI-CHO.

In an oven-dried, magnetic-stirred, 25 mL round-bottom flask, compound **4** (269.3 mg, 0.39 mmol), compound **5** (388.6 mg, 0.39 mmol), bis(triphenylphosphine)palladium(II)

dichloride (11.5 mg), and copper iodide (2.6 mg) were added and the round-bottom flask evacuated and refilled with argon for three cycles. Then chlorobenzene (6 mL) and diisopropylamine (0.5 mL) were added by syringe, and the mixture was heated at 80 °C for 2 hours. After that, the dark green solution was precipitated in methanol. The crude polymer was collected by filtration and then successively purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform. The final product was obtained by precipitation into methanol. The product was then dried under vacuum for 1 day to get the polymer, PNDI-CHO, as a dark green solid with 89% yield (523 mg).

Synthesis of PNDI-RDN.

To a solution of PNDI-CHO (100 mg) and 3-ethyl-2-thioxothiazolidin-4-one (100 mg) in 15 mL of chloroform was added 0.5 mL of triethylamine. The mixture solution was stirred in the dark for 72 h at 60 °C after which the resulted mixture was poured into methanol and the precipitate was filtered off. The crude polymer was collected by filtration and then successively purified by Soxhlet extraction with methanol, acetone and hexane. After dried under vacuum for 1 day, the final product was obtained to be PNDI-RDN (85 mg).

Synthesis of PNDI-BBT.

Polymer PNDI-BBT was synthesized following the same procedure as that of PNDI-RDN, except 1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (80 mg) and pyridine (0.5 mL) were used. The resultant polymer PNDI-BBT was obtained as dark red solid (60 mg).

Synthesis of PNDI-IT.

Polymer PNDI-IT was synthesized following the same procedure as that of PNDI-RDN, except 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (80 mg) and pyridine (0.5 mL) were used. The resultant polymer PNDI-IT was obtained as dark blue solid (58 mg).
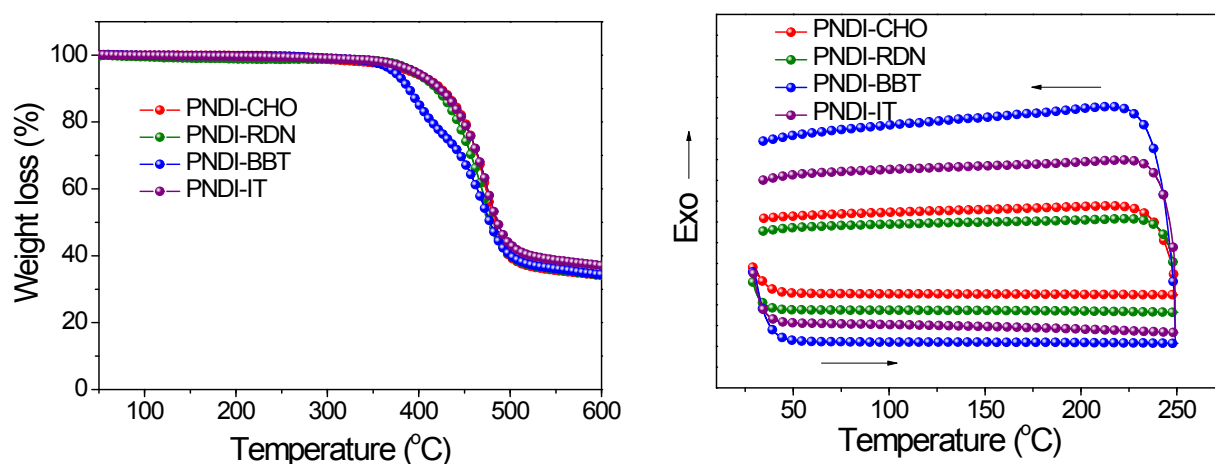
3. Thermal Properties Analyses

Fig. S1 TGA and DSC curves of PNDI-CHO, PNDI-RDN, PNDI-BBT and PNDI-IT.

The thermal properties of these polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning chromatography (DSC) under nitrogen atmosphere. TGA and DSC curves were showed in Fig. S1. All polymers exhibited excellent thermal stability with onset decomposition temperature (T_d) of over 370 °C. DSC curves were recorded by heating from 30 °C to 250 °C in second heating and cooling cycles. The glass transition of these polymers were not observed by DSC measurements, indicating both of PNDI-CHO, PNDI-RDN, PNDI-BBT and PNDI-IT are amorphous polymers. Detailed data of thermal properties are summarized in Table

S1.

Table S1. Molecular weight and the thermal properties of polymers.

Polymers	T_d (°C)	M_n (kDa)	PDI
PNDI-CHO	392	42.0	2.0
PNDI-RDN	395	45.3	2.1
PNDI-BBT	373	45.2	2.1
PPNDI-IT	396	41.2	2.0

4. UV-vis Spectroscopy
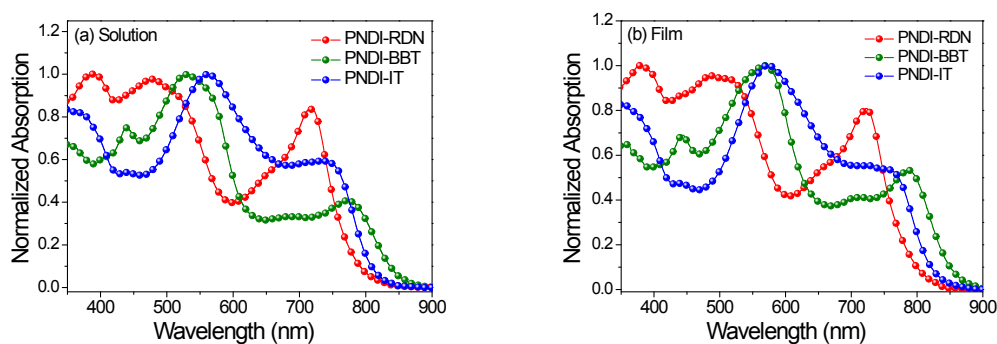
Fig. S2 UV-vis absorption spectra of polymers in chloroform solution (a) and as thin film (b).
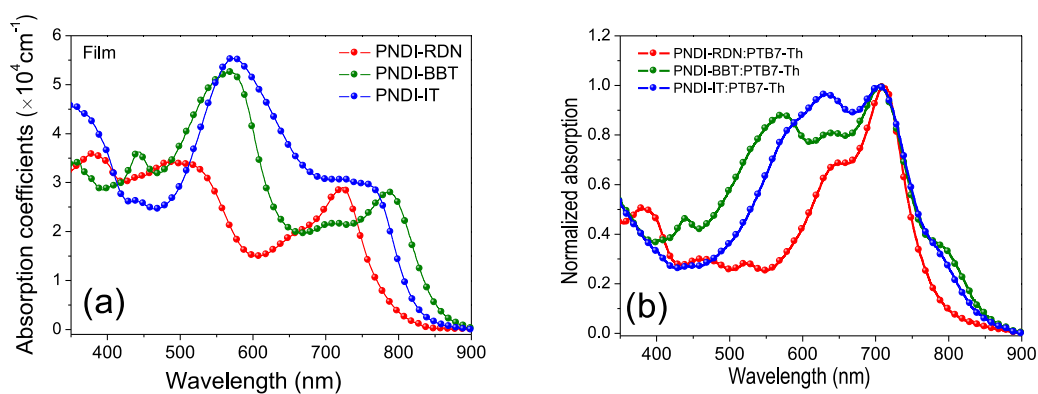
5. Cyclic Voltammetry (CV) Measurements
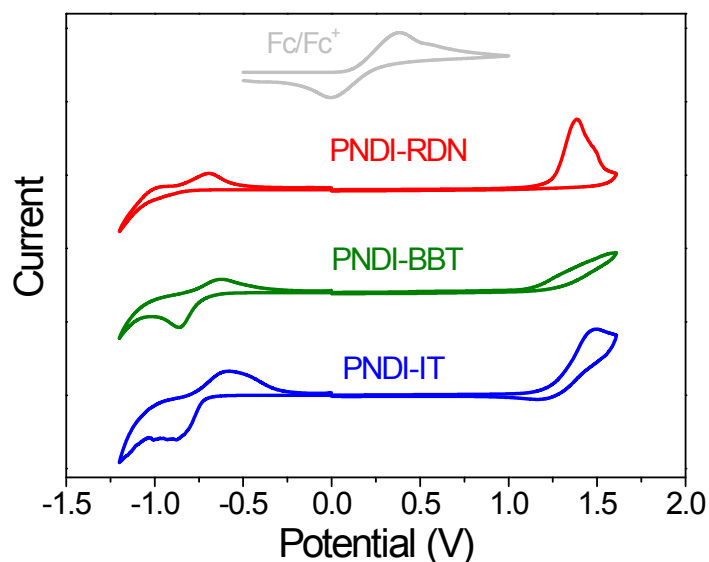
Fig. S4 Cyclic voltammograms of the polymers. Thin films of polymers were cast onto a ITO-coated glass working electrode. The cyclic voltammograms were recorded under an inert atmosphere *versus* the Ag/Ag$^+$ redox couple. The potential of ferrocene/ferrocenium (Fc/Fc$^+$) was used as the standard.

Table S2. Optophysical and electrochemical properties of polymers

Polymers	λ_{abs}(nm) solution	λ_{abs}(nm) film	[a]E_g^{opt} (eV)	E_{ox} (V)	E_{red} (V)	[b]E_{HOMO} (eV)	[c]E_{LUMO} (eV)
PNDI-RDN	385, 717	378, 724	1.60	1.23	-0.83	-5.91	-3.85
PNDI-BBT	530, 774	565, 784	1.46	1.21	-0.71	-5.89	-3.97
PPNDI-IT	562, 745	572, 764	1.50	1.22	-0.71	-5.90	-3.97

[a] Calculated from the onset of UV-vis absorption as pristine thin films; [b]$E_{HOMO} = -e(E_{ox} + 4.68)$ (eV); [c]$E_{LUMO} = -e(E_{red} + 4.68)$.

6. Devices Fabrication

All-PSCs Fabrication and Characterization

Before fabrication of the device, the indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, isopropyl alcohol and dried in oven at 80 °C for 12 h before used. After PEDOT:PSS (30 nm) layer was spin coated onto the substrate, and dried at 150 °C for 15 min in air. Then, the ITO substrates were transferred into a nitrogen protected glovebox where the H_2O concentration is≤0.5 ppm and O_2 concentration is ≤20 ppm. The thin film of active layer were spin-coated from a solution of PTB7-Th:polymer acceptor blend in chlorobenzene. A thin PFN-Br layer (5 nm) was then spin coated onto the active layer as the cathode interface layer. The substrates were then transferred to a vacuum thermal evaporator, followed by deposition of the Ag cathode at a pressure of 2×10^{-7} Torr through a shadow mask. Before the *J-V* test, a physical mask with an aperture with precise area of 0.04 cm^2 was used to define the device area. The *J-V* curves were measured on a computer-controlled Keithley 2400 source meter under 1 sun, the AM 1.5 G spectra came from a class solar simulator (Enlitech, Taiwan), and the light intensity was 100 mWcm^{-2} as calibrated by a China General Certification Center-certified reference monocrystal silicon cell (Enlitech). The EQE spectra measurements were performed on a commercial QE measurement system (QE-R3011, Enlitech).

7. SCLC Measurements

Hole and Electron Mobility Measurement by Space Charge Limited Current (SCLC) Method.

Hole-and electron-only devices were fabricated by using the device structures of ITO/PEDOT:PSS/active layer/MoO$_3$/Ag and ITO/Ag/active layer/Ag, respectively. Electron and hole mobility were measured by using the space-charge-limited current (SCLC) method. The mobility was calculated with the Mott–Gurney equation in the SCLC region: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the space charge limited current, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the material and V is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the series resistance of the whole device except for the active layers from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The hole and electron mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.
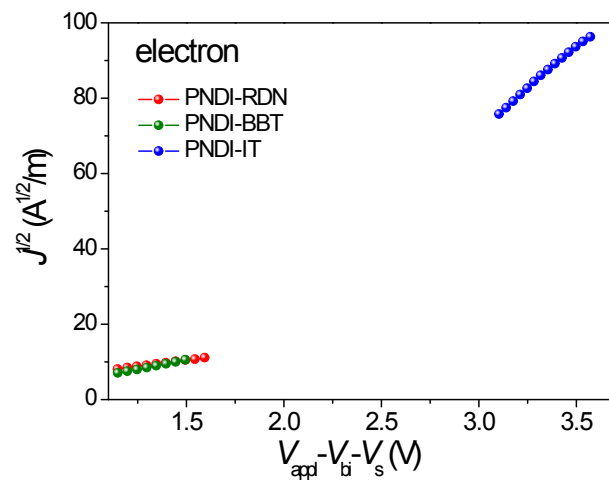
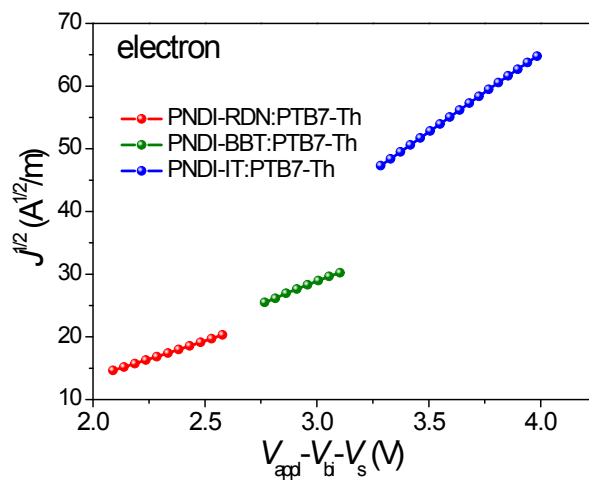**Fig. S5** $J^{1/2}$-V characteristics of the pure flims of polymer acceptors from SCLC (electron).

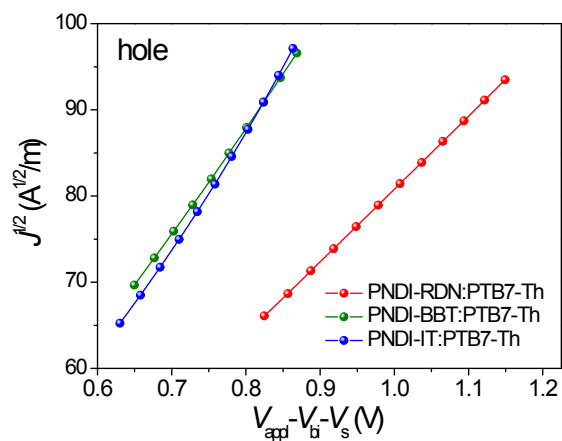**Fig. S6** $J^{1/2}$-V characteristics of polymer blend films from SCLC (electron).

Fig. S7 $J^{1/2}$-V characteristics of polymer blend films from SCLC (hole).

Table S3. Molecular weight and the thermal properties of polymers.

Polymers	$\mu_{e\ pure}$ (cm^2 V^{-1} s^{-1})	$\mu_{h\ blend}$ (cm^2 V^{-1} s^{-1})	$\mu_{e\ blend}$ (cm^2 V^{-1} s^{-1})
PNDI-RDN	5.22 ×10^{-6}	1.22 ×10^{-3}	2.28 ×10^{-5}
PNDI-BBT	1.14 ×10^{-5}	2.95 ×10^{-3}	3.48 ×10^{-5}
PNDI-IT	2.27 ×10^{-4}	3.21 ×10^{-3}	1.09 ×10^{-4}

8. AFM and TEM Images
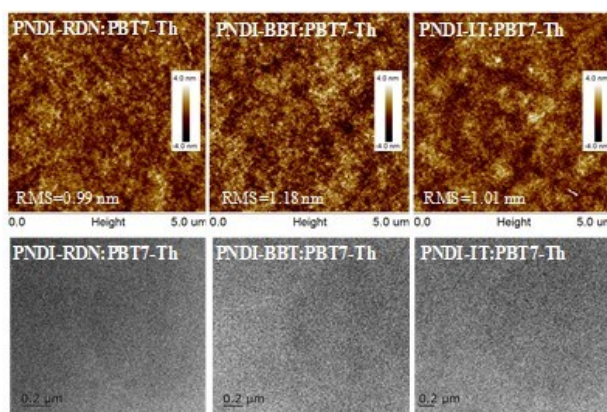
Fig. S8 AFM height images (5μm×5μm) and TEM images for PNDI-RDN:PTB7-Th, PNDI-BBT:PTB7-Th and PNDI-IT:PTB7-Th blend films.
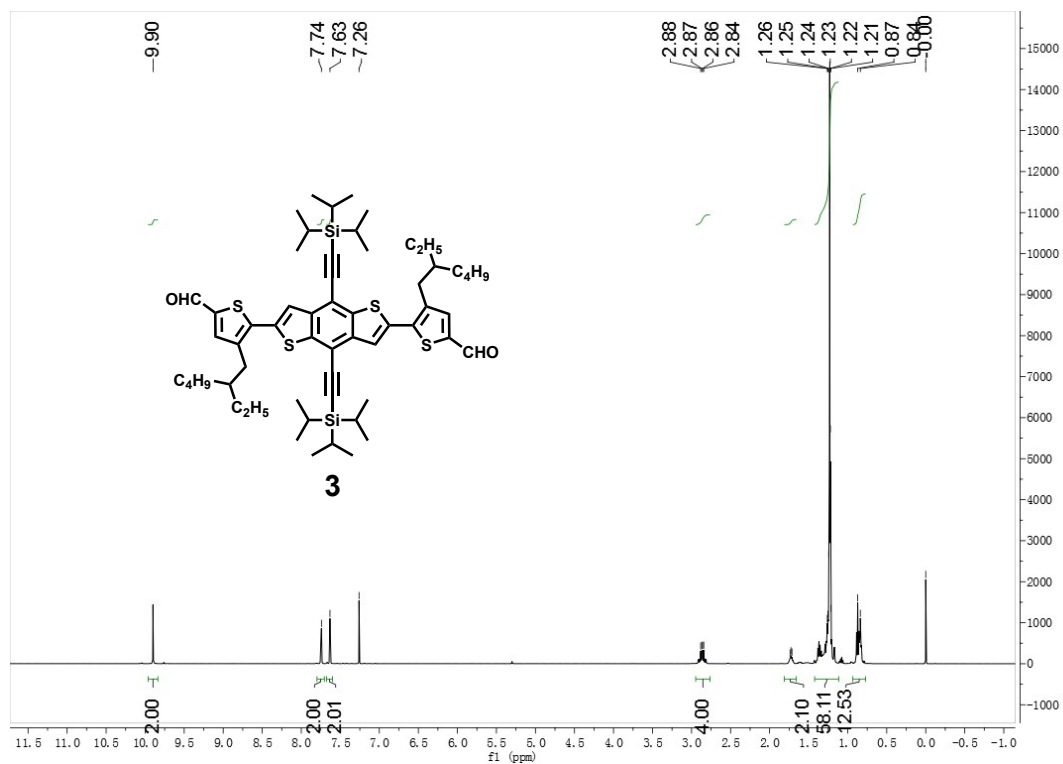
9. NMR Spectra

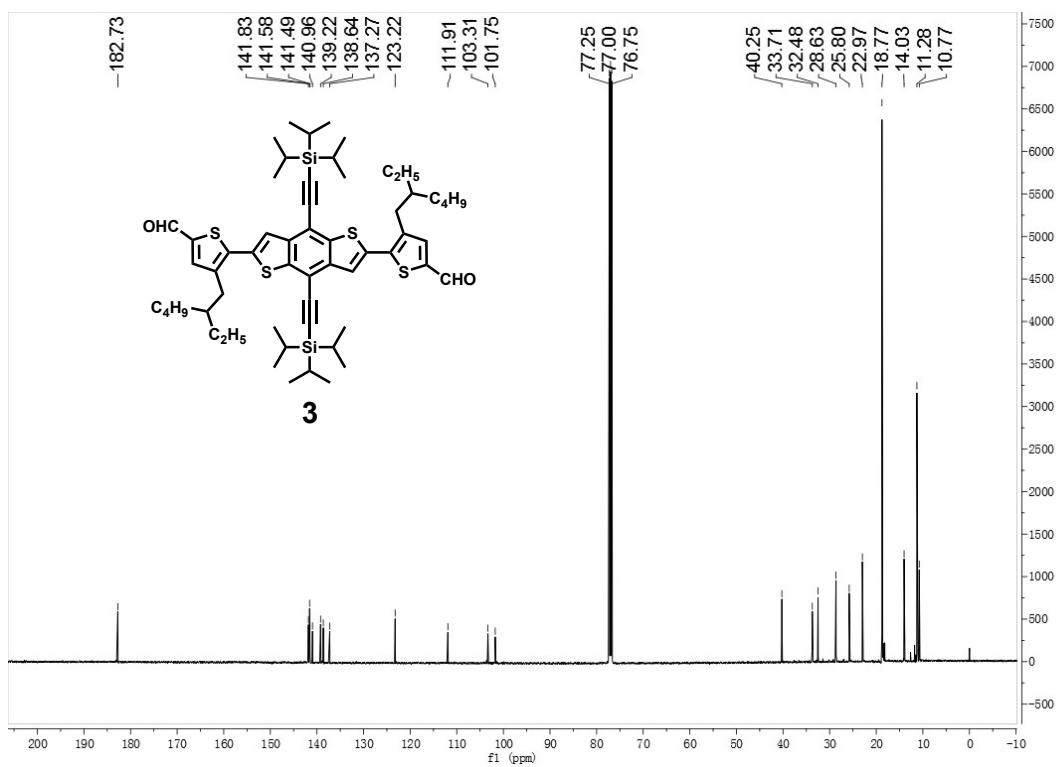**Fig. S9** ¹H NMR spectrum of compound 3.
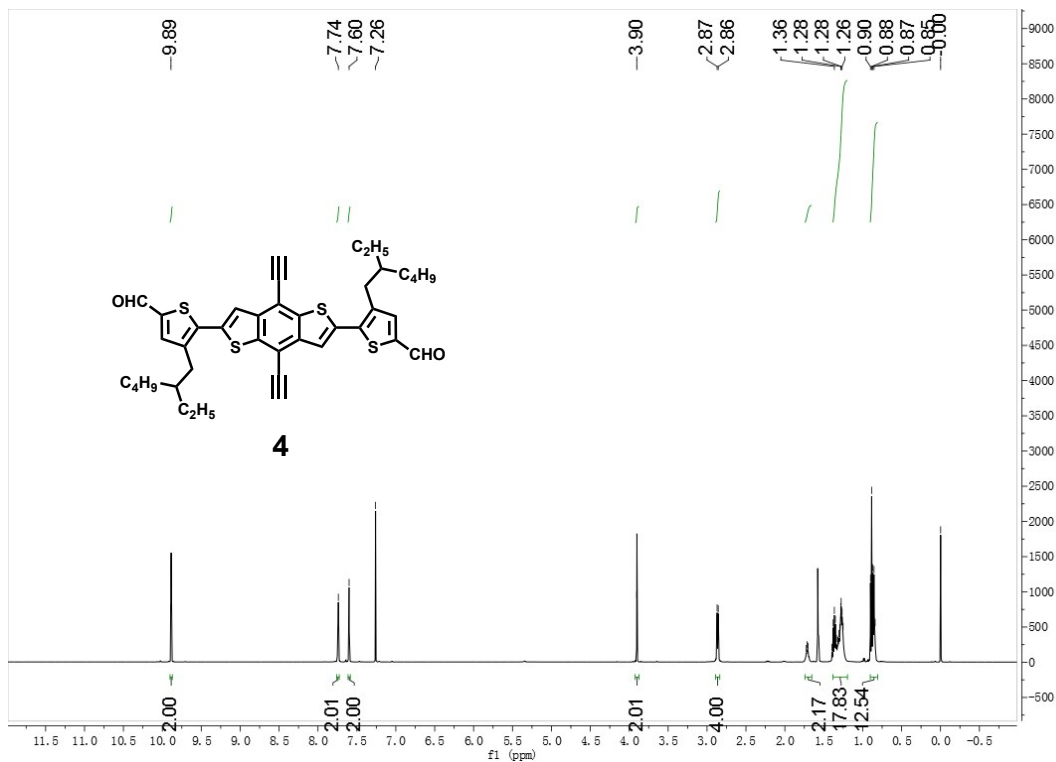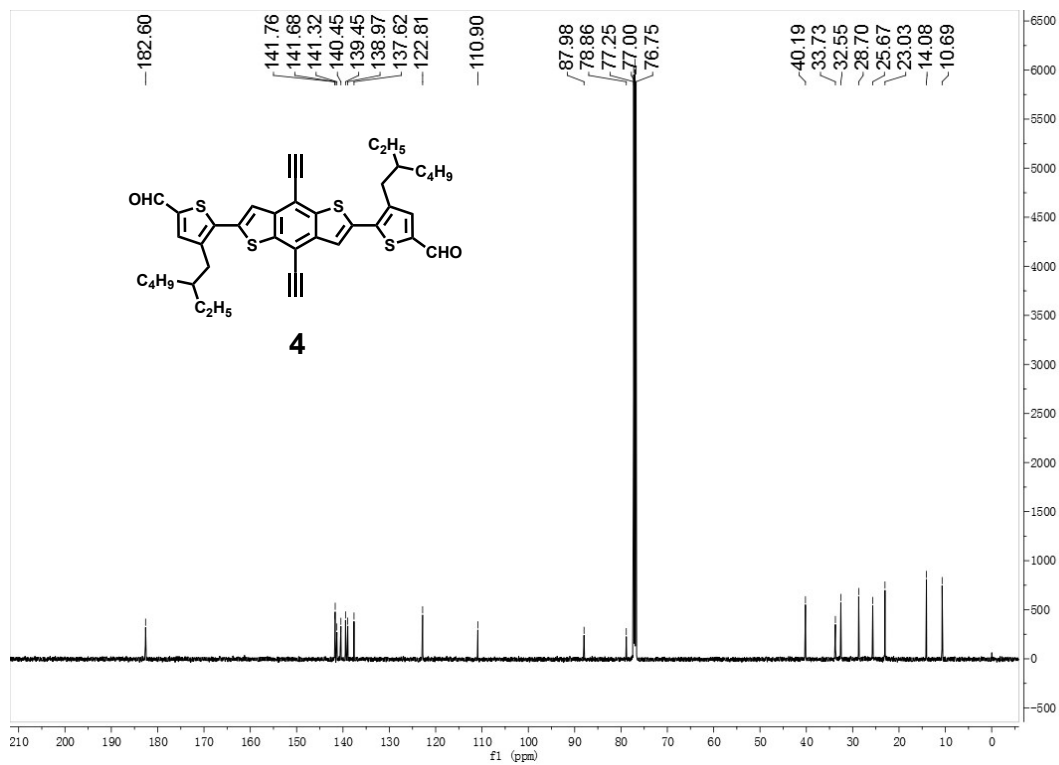

Fig. S10 ¹³C NMR spectrum of compound 3.

14

Fig. S11 ^{1}H NMR spectrum of compound 4.

g. S12 ^{13}C NMR spectrum of compound 4.
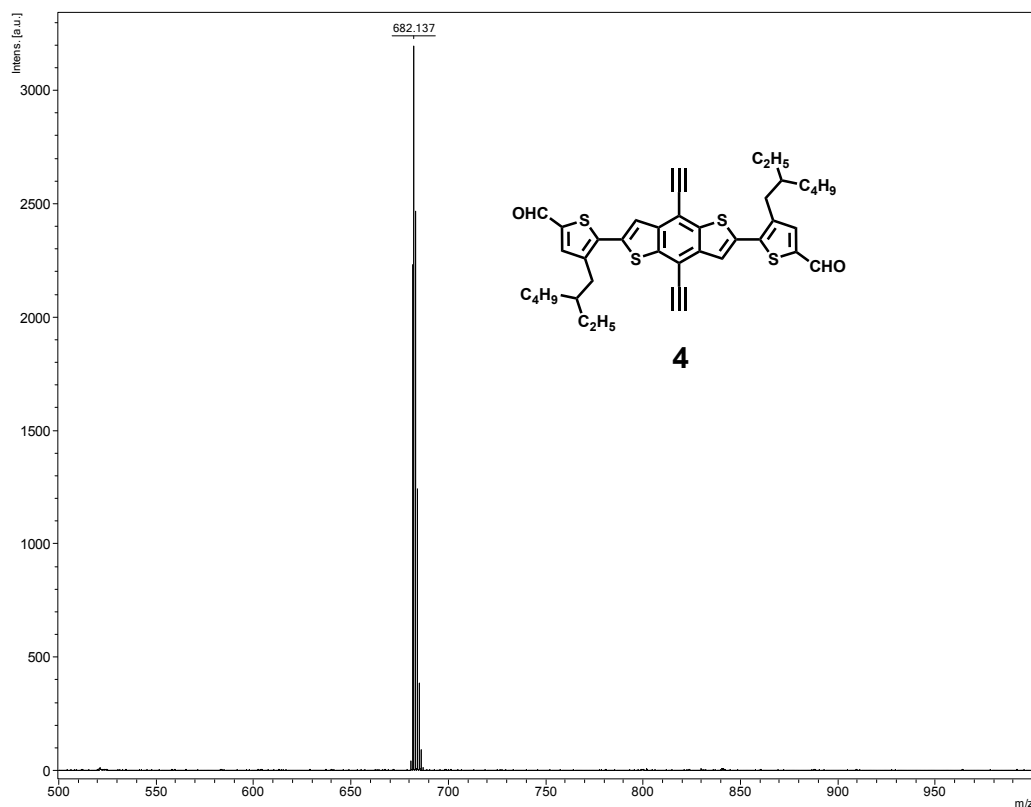
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10. MALDI-TOF Spectrum

Fig. S13   MALDI-TOF spectrum of compound 4.

11. Supplementary Information References

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