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Supporting Information

Design and synthesis of medium-bandgap small-molecule electron acceptors for efficient tandem solar cells

Qihui Yue, Zichun Zhou, Shengjie Xu, Jianyun Zhang and Xiaozhang Zhu*

Experimental Section

Materials and General Methods:

All reactions involving air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Unless stated otherwise, starting materials were obtained from Adamas, Aldrich, or J&K and were used without further purification. Anhydrous THF and toluene were distilled over Na/benzophenone prior to use. Anhydrous DMF was distilled over CaH_2 prior to use. Compounds **1** and **2** were prepared according to published procedures. ^{1}H and ^{13}C NMR spectra were measured with Bruker Fourier 300, Bruker Avance 400, or Bruker Avance 600 spectrometers. Chemical shifts for hydrogens are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent ($CDCl_3$: 7.26). ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$: 77.2). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), coupling constant in hertz (Hz), and integration. MALDI measurements were performed with a MALDI-FT 9.4 T, Bruker solariX, or MALDI-TOF MS Bruker Autoflex III. Elemental analyses were performed with a Flash EA 1112 Series from ThermoQuest. UV-vis was recorded with Jasco V-570 spectrometers. Cyclic voltammetry (CV) was performed with a CHI620D potentiostat. All measurements were carried out in a one-compartment cell under a nitrogen atmosphere, equipped with a glassy-carbon electrode, a platinum counter-electrode, and an Ag/Ag^+

reference electrode with a scan rate of 100 mV s^{-1}. The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium perchlorate (TBAP). All potentials were corrected against Fc/Fc^{+}. CV was measured with a scan rate of 100 mV s^{-1}. Thermogravimetric analysis (TGA) was performed with a Shimadzu DTG 60 instrument at a heating rate of 10 C min^{-1} under a nitrogen atmosphere with runs recorded from room temperature to 550 °C.

Device Fabrication:

Single-junction device fabrication: Devices were fabricated with a conventional structure of ITO/PEDOT:PSS/active layer/ZnO/Al. ITO-coated glass substrates (15 Ω sq^{-1}) were cleaned by sequential ultrasonication in soap deionized water, deionized water, acetone, and isopropanol. The washed substrates were further treated with oxygen plasma for 20 min to eliminate any remaining organic component. A thin layer (ca. 30 nm) of PEDOT:PSS was first spin-coated on the ITO substrates at 3,000 r.p.m. and baked at 150 °C for 30 min in air. The substrates were then transferred into a nitrogen-filled glovebox. Subsequently, the active layer was spin-coated on the PEDOT:PSS layer from a chloroform solution of 9 mg ml^{-1} PBDB-T and 9 mg ml^{-1} **YITI** at various spin rates. The resulting film thickness was measured via a surface profilometer (Dektak XT, Bruker). Here, thermal annealing (TA) was used to optimize the blend morphology and promote device performance. Then, 10 mg ml^{-1} ZnO in n-butanol was spin-coated on the active layer. At the final stage, aluminum (100 nm) was thermally evaporated onto the active layer as the top electrode. Shadow masks were used to define the OSC active area (0.04 cm^{2}) of the devices.

Tandem device fabrication: Devices were fabricated with a structure of ITO/PEDOT:PSS/PBDB-T:**YITI-2F**/ZnO/neutral PEDOT:PSS/PTB7-Th:ATT-2/ZnO /Al. The fabrication of the front cell was the same as that in single-junction device. After ZnO was spin-coated, neutral PEDOT:PSS was spin-coated at a thickness of 15 nm. Then, 7 mg ml^{-1} PTB7-Th and 10.5 mg ml^{-1} ATT-2 was spin-coated onto neutral PEDOT:PSS from its mixed solvent of chloroform/1-CN (100:1.5 v/v), after which ZnO was spin-coated as the electron transfer layer. In the end, aluminum (100 nm) was thermally evaporated onto the active layer as the top electrode. Shadow masks were used to define the OSC active area (0.04 cm^2) of the devices.

Device Characterization:

The current density–voltage (*J–V*) characteristics of photovoltaic devices were measured under N_2 using a Keithley 2400 source meter. A 300 W xenon arc solar simulator (Oriel) with an AM 1.5 global filter operated at 100 mW cm^{-2} was used to simulate the AM 1.5G solar irradiation. The illumination intensity was corrected by using a silicon photodiode with a protective KG5 filter calibrated by the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was performed using certified IPCE equipment from Enlitech, Taiwan. In the measurement of the front and rear sub-cells EQE curves for tandem devices, 750 nm and 600 nm light biases were used, respectively.

Mobility Characterization:

Space charge-limited currents were tested in electron-only devices with a configuration of ITO/ZnO/active layer/Al and hole-only devices with a configuration of ITO/PEDOT:PSS/active layer/MoO_3/Ag. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC current with field dependent mobility, which is described as

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0V^2}{8L^3} \tag{1}$$

Where J is the current, μ_0 is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, V is the effective voltage, and L is the thickness of the active layer. From the plots of $J^{0.5}$ vs V, hole and electron mobilities can be deduced.

Synthetic part

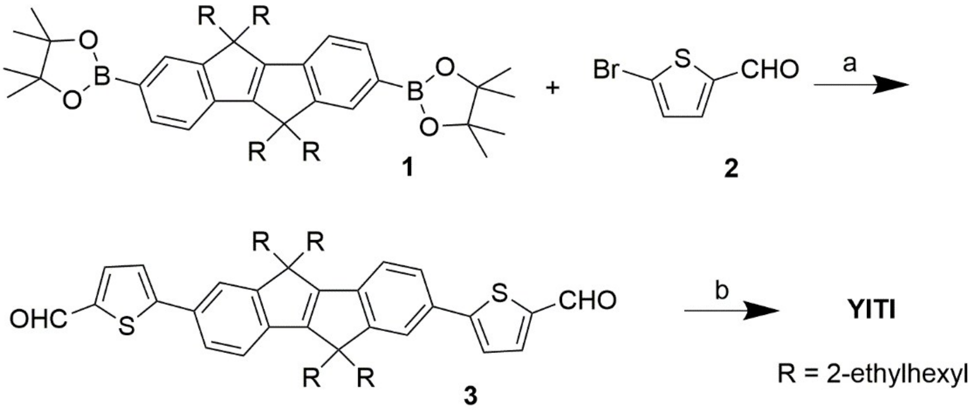


Fig. S1 Synthesis routes of **YITI**. Reagents and conditions: (a) $Pd(PPh_3)_4$, aqueous Na_2CO_3 (2.0 M) dioxane; (b) INCN or INCN-F or INCN-2F, pyridine, $CHCl_3$.

5,5'-(5,5,10,10-tetrakis(2-ethylhexyl)-5,10-dihydroindeno[2,1-a]indene-2,7-diyl)bis(thiophene-2-carbaldehyde) (3). Compounds **1** (181 mg, 0.2 mmol) and **2** (114 mg, 0.6 mmol, 3 equiv.) were added to 15 mL of a 1:2 *v*/*v* mixture of aqueous Na_2CO_3 (2.0 M) and dioxanes under nitrogen. The reaction mixture was purged with nitrogen gas for 10 minutes and then $Pd(PPh_3)_4$ catalyst (23 mg, 0.02 mmol, 0.1 equiv.) was added. The reaction solution was stirred at 90 °C overnight and then was poured into ethyl acetate. The organic layer was washed with water and brine, and was dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting orange solid was purified on a silica-gel column chromatography to give 143 mg of compound **3** as an orange solid (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 2H), 7.76 (d, ^3J = 3.6 Hz, 2H), 7.69 (s, 2H), 7.48 (d, ^3J = 7.8 Hz, 2H), 7.62 (d, ^3J = 7.6 Hz, 2H), 7.42 (m, 4H), 2.07 (s, 8H), 1.10–0.50 (m, 60H); ^{13}C NMR (100 MHz, $CDCl_3$): 182.7, 157.2, 156.8, 155.6, 141.8, 137.6, 129.0, 125.2, 123.4, 121.3, 120.4, 54.2, 42.3, 34.8, 34.7, 34.3, 33.7, 33.6, 28.4, 28.3, 27.5, 27.4, 26.9, 26.7, 23.1, 23.0, 22.9, 14.0, 13.9, 10.5, 10.4, 9.7, 9.5; HRMS (MALDI-TOF) calcd for $C_{58}H_{80}O_2S_2$ $[M]^+$: 872.5594, found, 872.5587.

YITI-0F, YITI-2F or YITI-4F. INCN or INCN-F or INCN-2F (0.285 mmol) and compound **3** (50 mg, 0.057 mmol) were added to a solvent mixture of chloroform (10 mL) and pyridine (5 drops). The reaction was placed in an oil bath at 75 °C and was stirred for overnight. The mixture was directly purified on a silica-gel column chromatography using trichloromethane as eluent to give **YITI** as black solid. **YITI-0F**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.90 (s, 2H), 8.71 (m, 0.64H), 8.71 (d, ^{3}J = 7.2 Hz, 2H), 7.96 (d, ^{3}J = 6.4 Hz, 2H), 7.91 (d, ^{3}J = 4.0 Hz, 2H),7.74–7.83 (m, 8H), 7.56 (d, ^{3}J = 3.6 Hz, 2H), 7.45 (d, ^{3}J = 8.0 Hz, 2H), 2.13 (m, 8H), 1.20–0.50 (m, 60H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 188.4, 161.9, 160.6, 158.2, 157.2, 146.6, 140.0, 138.0, 137.0, 136.2, 135.2, 134.5, 129.3, 126.5, 125.4, 124.5, 123.8, 122.2, 121.3, 120.7, 114.7, 114.6, 109.7, 73.1, 69.5, 57.4, 54.4, 42.5, 38.8, 34.9, 34.2, 32.2, 28.3, 28.2, 27.5, 23.1, 22.9, 18.2, 14.1, 13.9, 10.6, 10.5, 9.8, 9.6; HRMS (MALDI-TOF) calcd for $C_{82}H_{88}N_4O_2S_2$ [M]$^+$: 1224.6343, found, 1224.6338. **YITI-2F**: **YITI-2F** is a mixture; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.90 (s, 2H), 8.71 (m, 0.64H), 8.74 (m, 0.5H), 8.40 (m, 1.5H), 7.92–8.00 (m, 3.5H), 7.78–7.82 (m, 4H), 7.55–7.65 (m, 2.5H), 7.45 (m, 4H), 2.13 (m, 8H), 1.20–0.50 (m, 60H); HRMS (MALDI-TOF) calcd for $C_{82}H_{86}F_2N_4O_2S_2$ [M]$^+$: 1260.6155, found, 1260.6144. **YITI-4F**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.89 (s, 2H), 8.56 (m, 2H), 7.93 (d, ^{3}J = 4.4 Hz, 2H), 7.83 (s, 2H), 7.79 (d, ^{3}J = 8.0 Hz, 2H), 7.73 (t, ^{3}J = 7.6 Hz, 2H), 7.58 (d, ^{3}J = 3.2 Hz, 2H), 7.46 (d, ^{3}J = 7.6 Hz, 2H), 2.14 (m, 8H), 1.20–0.50 (m, 60H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 186.0, 162.9, 158.5, 157.2, 155.8, 153.1, 153.0, 147.3, 143.1, 138.2, 136.8, 136.0, 134.4, 129.2, 126.0, 124.6, 121.4, 121.3, 120.8, 115.0, 115.0, 114.3, 114.1, 112.8, 112.6, 70.0, 54.4, 42.5, 34.9, 34.2, 33.7, 33.6, 28.3, 27.5, 27.3, 26.9, 26.7, 23.1, 22.9, 14.1, 13.9, 10.6, 10.5, 9.8, 9.6; HRMS (MALDI-TOF) calcd for $C_{82}H_{84}F_4N_4O_2S_2$ [M]$^+$: 1296.5966, found, 1296.5946.

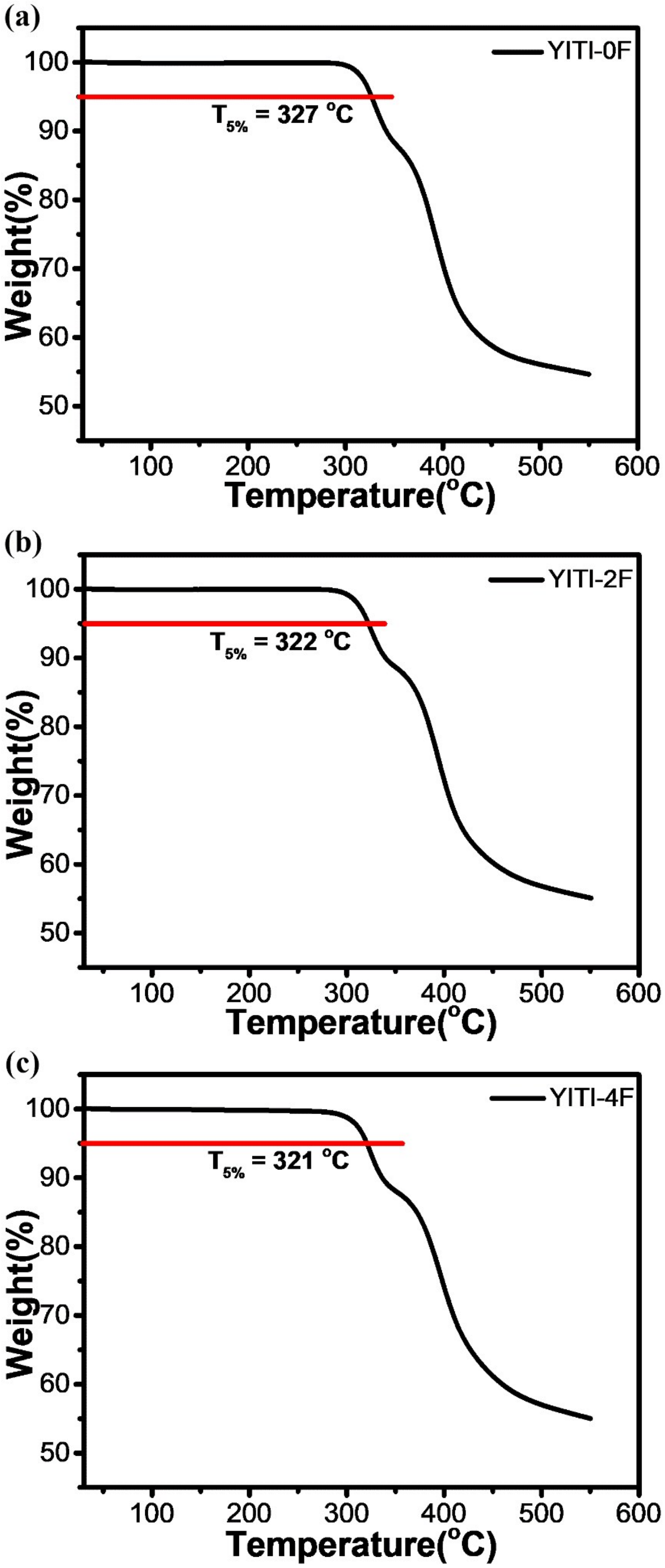


Fig. S2 Thermal gravimetric analysis (TGA) curve of (a) YITI-0F; (b) YITI-2F and (c) YITI-3F.

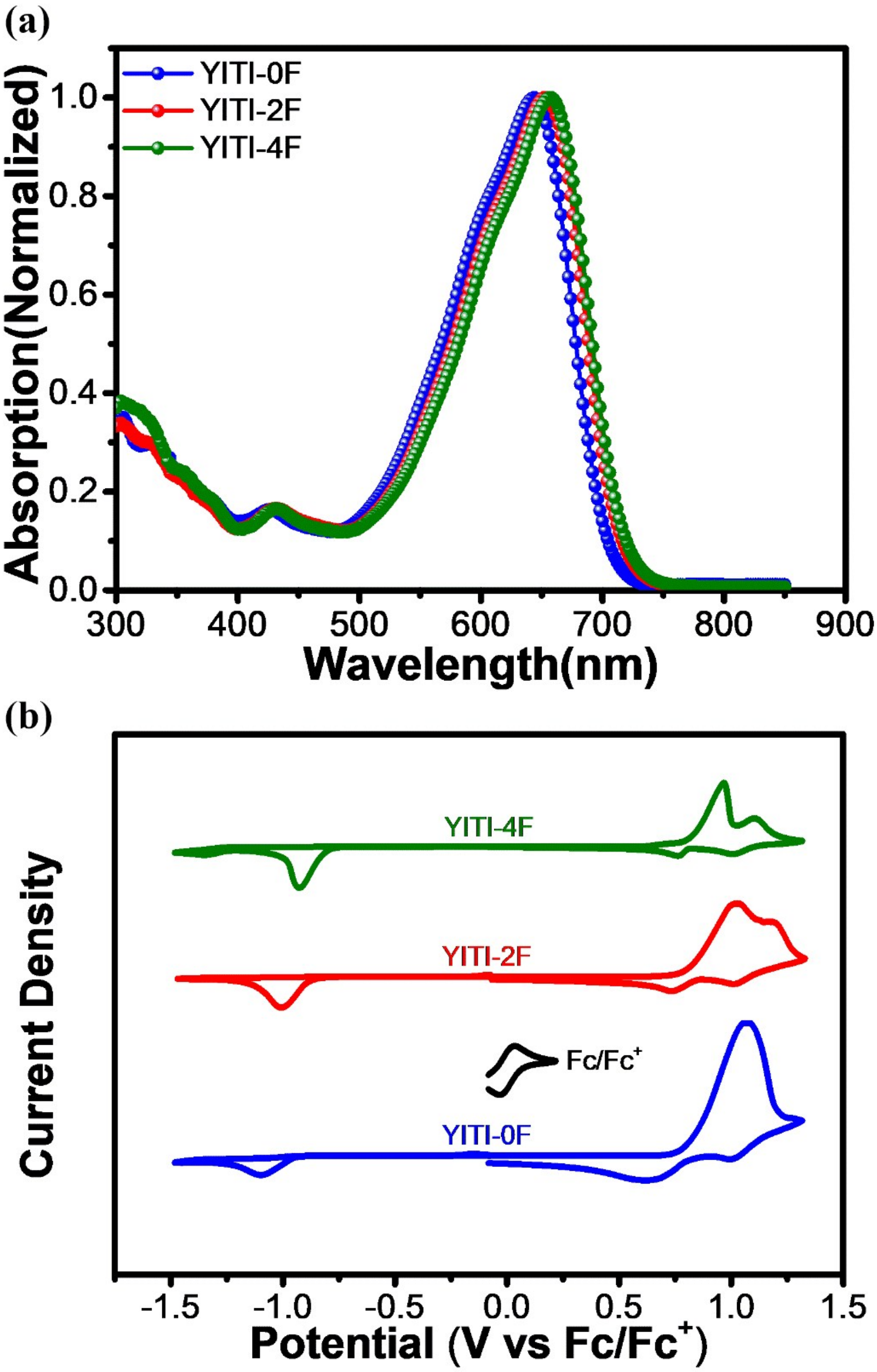


Fig. S3 (a) UV-vis absorption spectra of **YITI** in chloroform solution and (b) Cyclic voltammogram of **YITI** film in diluted CH_3CN solution with a scan rate of 100 mV s^{-1}.

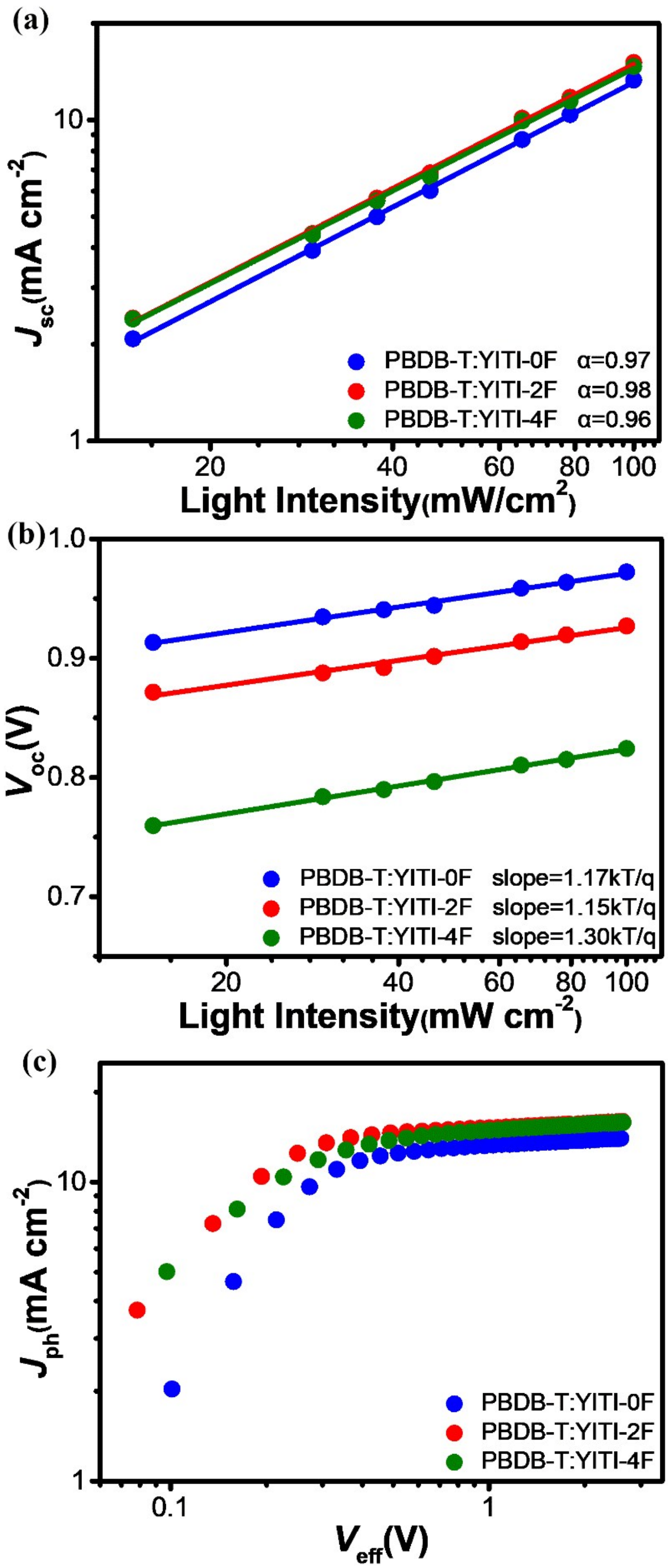


Fig. S4 (a) Plots of V_{oc} vs. natural logarithm of light intensity and (b) J_{sc} dependence on light intensity. (c) J_{ph} versus V_{eff} characteristics for the devices based on PBDB-T:**YITI** (1:1, w/w) with thermal annealing at 130°C for 10 min.

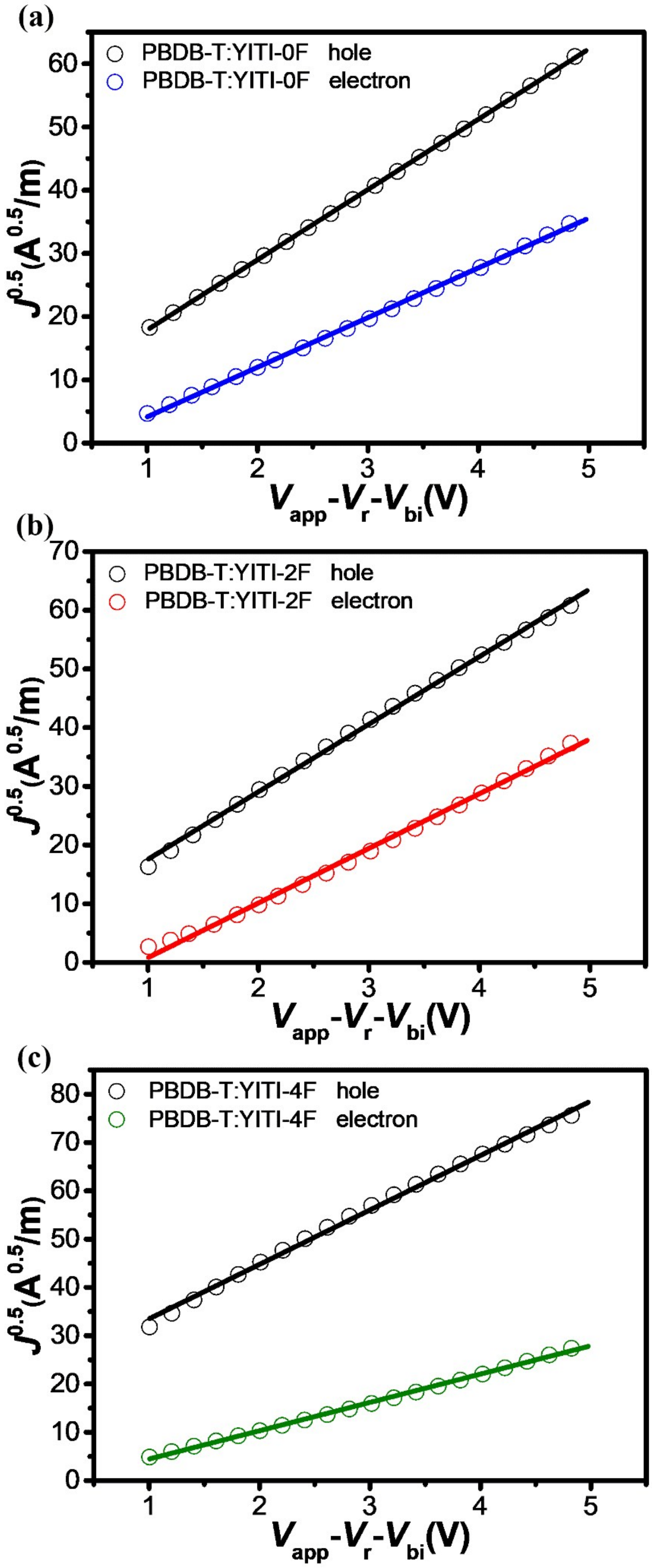


Fig. S5 $J^{0.5}$–V curves for the electron-only and hole-only devices based on (a) PBDB-T:**YITI-0F**, (b) PBDB-T:**YITI-2F** and (c) PBDB-T:**YITI-4F** (1:1, w/w) with thermal annealing at 130℃ for 10 min.

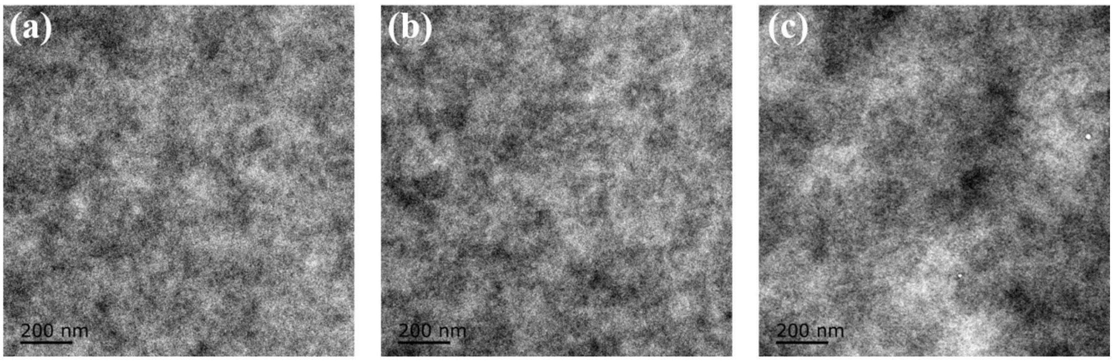


Fig. S6 Transmission electron microscopy (TEM) images of the blend films: (a) PBDB-T:**YITI-0F**; (b) PBDB-T:**YITI-2F** and (c) PBDB-T:**YITI-4F**.

Table S1 Optical and electrochemical properties of **YITI-0F**, **YITI-2F** and **YITI-4F**.

	$\lambda_{\text{max, sol}}$ [nm]	$\lambda_{\text{onset, sol}}$ [nm]	$\lambda_{\text{onset, film}}$ [nm]	HOMO [eV]	LUMO [eV]	E_g^{opt} [eV]	E_g^{elec} [eV]
YITI-0F	644	708	732	–5.59	–3.86	1.69	1.73
YITI-2F	652	719	756	–5.60	–3.92	1.64	1.68
YITI-4F	658	724	768	–5.61	–3.99	1.61	1.62

Table S2. The device parameters for the OPVs based on PBDB-T:**YITI-0F** blend with different D:A ratio.

D:A	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.8	0.972	13.18	59.30	7.60 (7.53±0.07)
1:1	0.978	13.40	67.18	8.81 (8.73±0.08)
1:1.2	0.951	13.85	61.81	8.14 (8.08±0.06)

Table S3 The device performance parameters for the OPVs based on PBDB-T:**YITI-0F** at 1:1 weight ratio with thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Treatment	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
None	0.990	11.94	53.57	6.32(6.21±0.10)
120°C	0.976	12.30	66.86	8.02(7.88±0.12)
130°C	0.978	13.40	67.18	8.81(8.73±0.08)
140°C	0.974	12.53	66.07	8.06(7.95±0.10)

Table S4 Effect of the active layer thickness on the device performance parameters for the OPVs based on PBDB-T:**YITI-0F** at 1:1 weight ratio with thermal annealing at 130°C for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Thickness (nm)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
75	0.975	12.46	67.13	8.16(8.10±0.07)

100	0.978	13.40	67.18	8.81(8.73±0.08)
125	0.971	13.47	63.43	8.43(8.29±0.13)

Table S5. The device parameters for the OPVs based on PBDB-T:**YITI-2F** blend with different D:A ratio.

D:A	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.8	0.929	14.26	60.22	7.98 (7.90±0.09)
1:1	0.928	15.54	69.69	10.05 (9.96±0.09)
1:1.2	0.911	15.62	68.37	9.73 (9.65±0.08)

Table S6 The device performance parameters for the OPVs based on PBDB-T:**YITI-2F** at 1:1 weight ratio with thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Treatment	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
None	0.934	13.73	46.99	6.03(5.90±0.13)
120℃	0.930	14.64	66.21	9.02(8.88±0.10)
130℃	0.928	15.54	69.69	10.05(9.96±0.09)
140℃	0.924	14.77	69.28	9.46(9.38±0.09)

Table S7 Effect of the active layer thickness on the device performance parameters for the OPVs based on PBDB-T:**YITI-2F** at 1:1 weight ratio with thermal annealing at 130℃ for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Thickness (nm)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
75	0.926	14.94	69.21	9.58(9.47±0.10)
100	0.928	15.54	69.69	10.05(9.96±0.09)
125	0.925	15.60	67.19	9.70(9.62±0.09)

Table S8. The device parameters for the OPVs based on PBDB-T:**YITI-4F** blend with different D:A ratio.

D:A	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.8	0.823	12.24	48.75	4.92 (4.86±0.06)
1:1	0.825	14.41	55.89	6.64 (6.54±0.11)
1:1.2	0.810	14.66	53.56	6.36 (6.27±0.10)

Table S9 The device performance parameters for the OPVs based on PBDB-T:**YITI-4F** at 1:1 weight ratio with thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Treatment	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]

None	0.892	13.56	50.16	6.06(5.96±0.08)
120°C	0.825	14.13	54.33	6.34(6.22±0.11)
130°C	0.825	14.41	55.89	6.64(6.54±0.11)
140°C	0.804	13.75	55.96	6.19(6.10±0.09)

Table S10 Effect of the active layer thickness on the device performance parameters for the OPVs based on PBDB-T:**YITI-4F** at 1:1 weight ratio with thermal annealing at 130°C for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Thickness (nm)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
75	0.824	13.52	57.18	6.36(6.29±0.08)
100	0.825	14.41	55.89	6.64(6.54±0.11)
125	0.820	13.97	52.81	6.05(5.92±0.13)

Table S11 The device performance parameters for the OPVs based on PTB7-Th:ATT-2 at 1:1.5 weight ratio in chloroform with solvent additive 1-CN, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

1-CN	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1%	0.728	17.66	59.15	7.61(7.50±0.12)
1.5%	0.721	20.76	63.58	9.52(9.39±0.14)
2%	0.723	20.03	61.33	8.89(8.79±0.10)

Table S12 Photovoltaic parameters of the tandem solar cells with different thicknesses of the front and rear cells under the irradiation of AM 1.5G, 100 mW cm^{-2}.

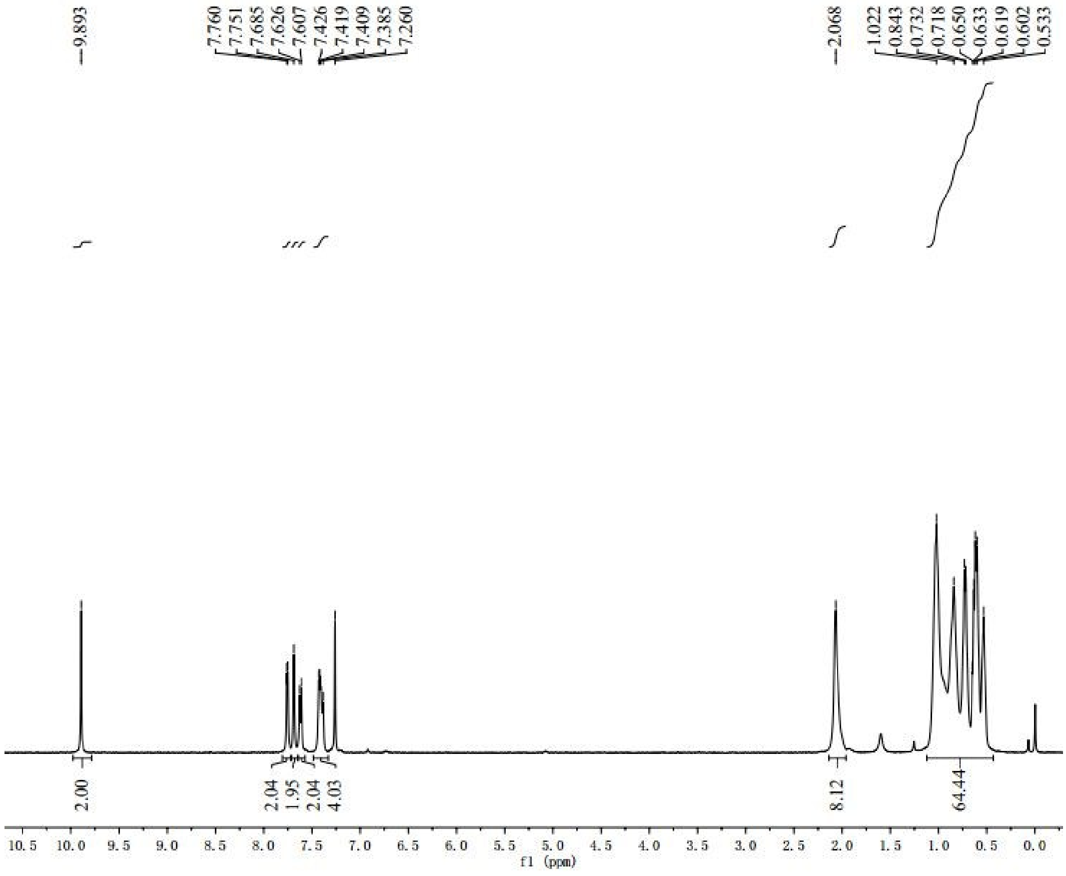
Thickness Front cell/Rear cell (nm)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
100/100	1.624	10.47	64.83	11.02(10.88±0.19)
125/100	1.628	11.33	64.31	11.86(11.64±0.20)
150/100	1.623	11.22	61.83	11.26(11.12±0.18)
125/75	1.623	11.00	64.44	11.50(11.36±0.21)
125/125	1.622	11.50	61.03	11.38(11.22±0.22)

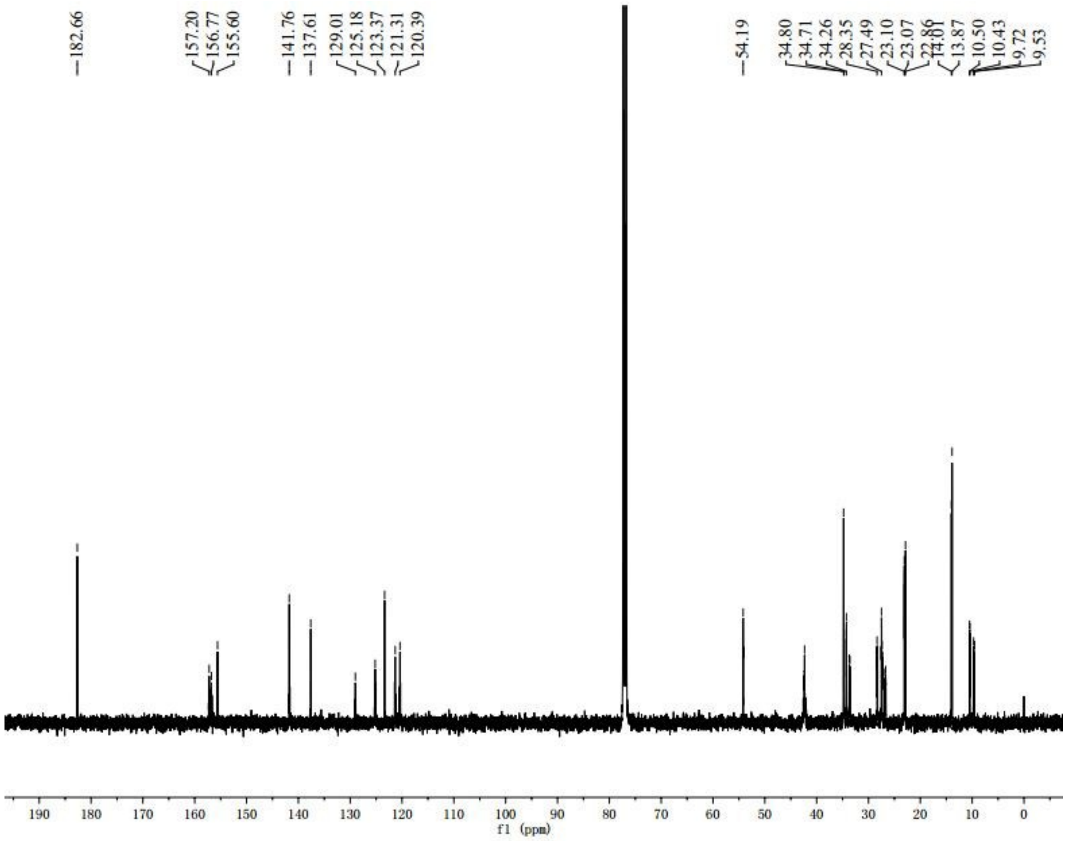
Table S13. The optimized device performance for the OPVs based on donor:**YITI-2F** blends.

Donor	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
J71	0.991	14.39	50.22	7.13 (7.06±0.07)

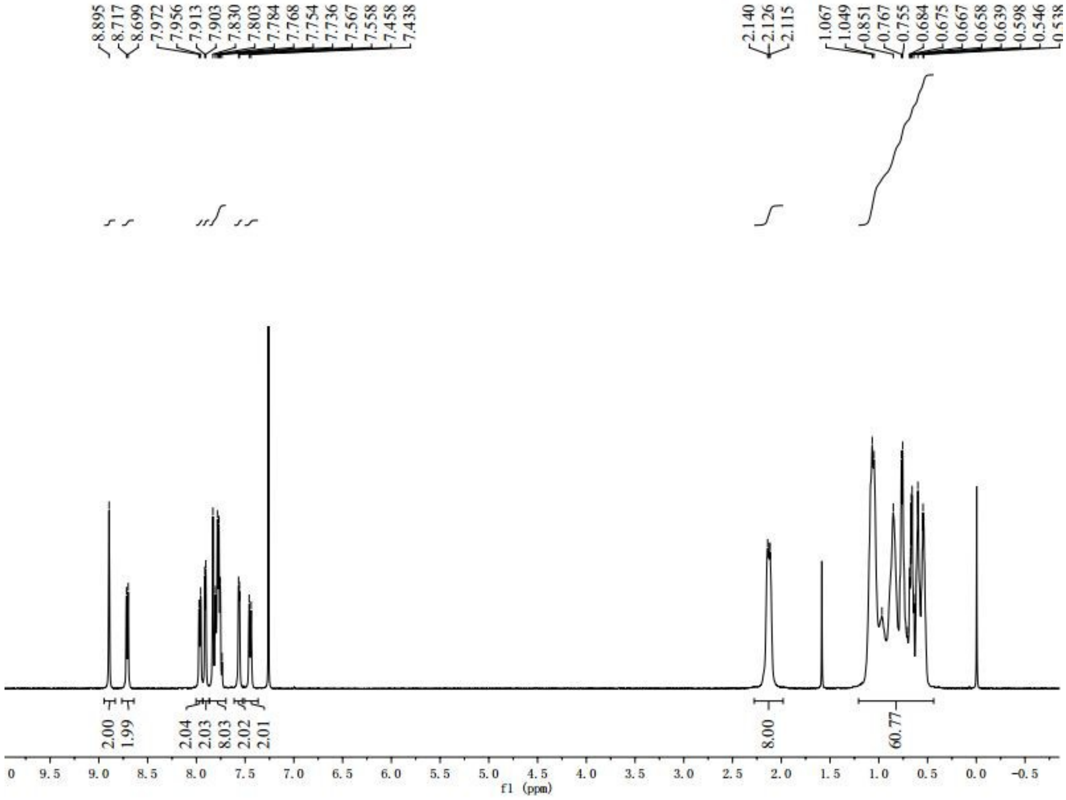
PBDB-T-F	0.985	14.11	52.99	7.31 (7.22±0.10)
PBDB-T	0.928	15.54	69.69	10.05 (9.96±0.09)

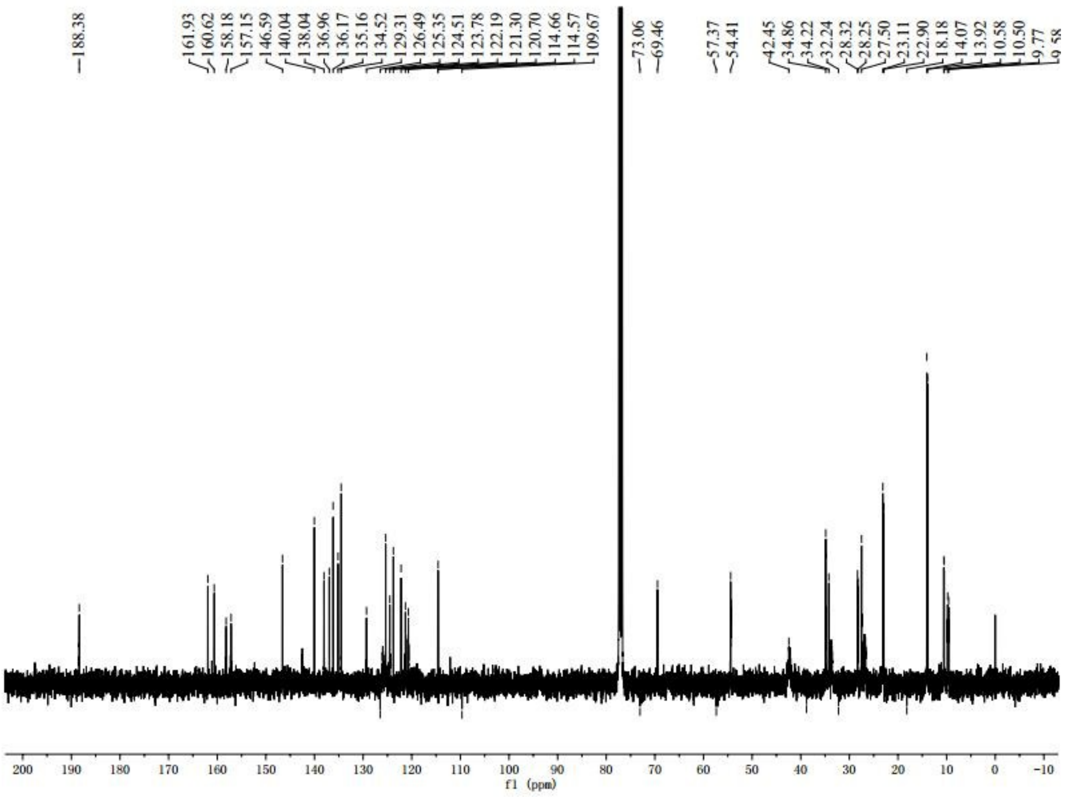
5,5'-(5,5,10,10-tetrakis(2-ethylhexyl)-5,10-dihydroindeno[2,1-*a*]indene-2,7-diyl)bis(thiophene-2-carbaldehyde) (3).



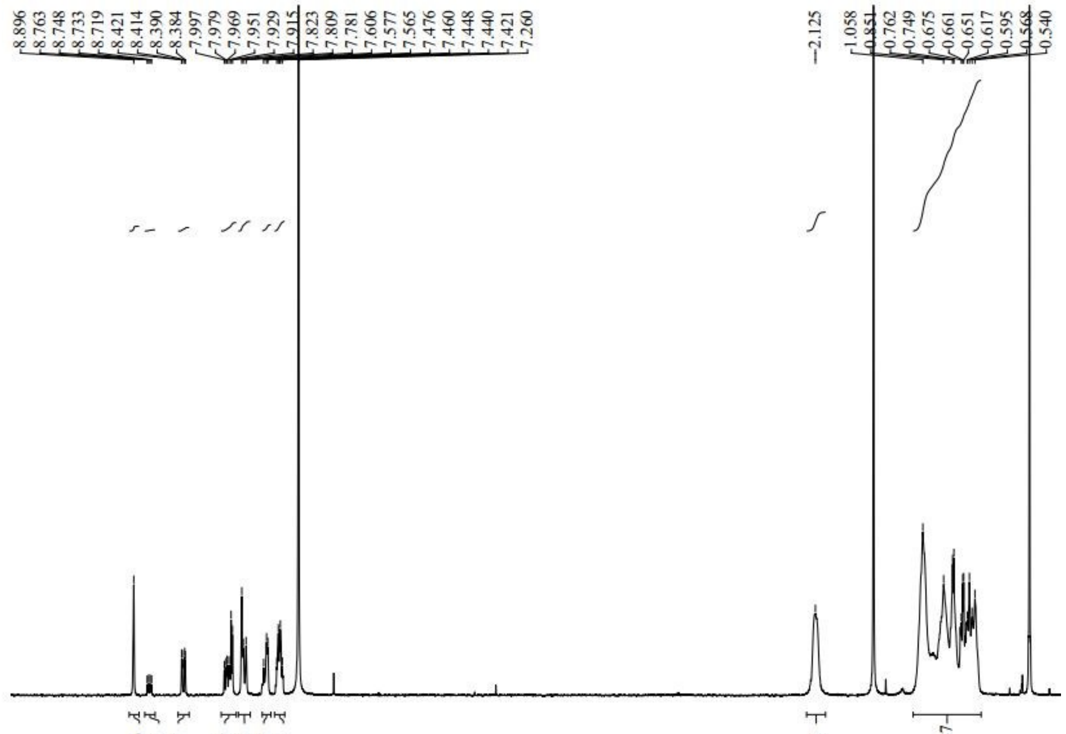


^{1}HNMR and ^{13}CNMR spectrum of YITI-0F.





^{1}HNMR spectrum of mixture of YITI-2F.



^{1}HNMR and ^{13}CNMR spectrum of YITI-4F.