

Indacenodithiophene-based small-molecule donor with strong crystallinity for efficient all-small-molecule organic solar cells

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Materials synthesis

All chemical reagents and solvents were purchased from commercial suppliers and used without further purification.

Synthesis of Compound 2b

Compound 1b (2 g, 3.09 mmol) and anhydrous THF (50 mL) were added into a flask and kept stirred at -78 °C under nitrogen protection, then 7.8 mL n-BuLi (2.5 M) was added dropwise. After kept stirring for 2 h at -78 °C, CBr₄ (2.56 g, 7.73 mmol) which dissolved in anhydrous THF was added into the solution, and then the mixture was stirred at room temperature for 4 h. The solution was poured into cold water to quench the reaction, and then extracted with dichloromethane (30 mL × 3). The organic layer was dried over anhydrous magnesium sulfate. After the removal of solvent, purification was carried out by silica gel column chromatography using petroleum as the eluent and **Compound 2b** (2.2 g, 90%) was obtained as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (s, 2H), 7.16 (s, 2H), 2.83 (d, J = 6.8 Hz, 4H), 1.80-1.65 (m,

2H), 1.43-1.30 (m, 13H), 1.00-0.86 (m, 15H). ¹³C NMR (100 MHz, CDCl₃): δ 140.21, 139.00, 135.91, 134.70, 128.14, 125.66, 123.09, 121.60, 117.45, 40.94, 32.51, 32.09, 28.82, 25.84, 23.03, 14.17, 10.88. MS (MALDI-TOF): *m/z* = 805.63; found 805.94.

Synthesis of Compound 3a

Compound 2a (960 mg, 1.32 mmol) and anhydrous THF (50 mL) were added into a flask and kept stirred at -78 °C under nitrogen protection, then 7.8 mL n-BuLi (2.5M) was added dropwise. After kept stirring for 2 h at -78 °C, anhydrous DMF (3.06 mL, 3.96 mmol) was added into the solution, and then the mixture was stirred at room temperature for 0.5 h. The reaction mixture was poured into water and extracted with dichloromethane (30 mL × 3). The organic layer was dried over anhydrous magnesium sulfate. After the removal of solvent, purification was carried out by silica gel column chromatography using petroleum/dichloromethane ether (3:1) as the eluent and **Compound 3a** was obtained as a yellow solid (600 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 10.05 (s, 1H), 8.31 (s, 1H), 7.64 (s, 1H), 7.27 (d, *J* = 11.0 Hz, 2H), 6.91 (d, *J* = 11.8 Hz, 2H), 2.86 (d, *J* = 6.5 Hz, 4H), 1.70-1.26 (m, 18H), 0.94 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 184.64, 147.20, 146.75, 143.60, 141.62, 140.39, 138.93, 135.41, 135.11, 134.38, 128.37, 128.26, 126.38, 126.17, 125.86, 125.67, 123.78, 119.60, 41.49, 34.26, 32.48, 28.91, 25.74, 23.03, 14.18, 10.89. MS (MALDI-TOF): *m/z* = 685.86; found 686.11

Synthesis of Compound 3b

Compound 3b (a yellow solid, 600 mg, 60%) was synthesized with similar the method as described above for the synthesis of **Compound 3a**. ¹H NMR (400 MHz, CDCl₃) δ 10.07 (s, 1H), 8.27 (s, 1H), 7.61 (s, 1H), 7.23 (s, 1H), 7.19 (s, 1H), 2.85 (d, *J* = 4.0 Hz, 4H), 1.76-1.33 (m, 18H), 0.95 (d, *J* = 9.0 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 184.39, 144.07, 141.46, 140.42, 139.73, 139.34, 138.84, 135.04, 134.08, 133.45, 128.58, 128.50, 125.95, 125.23, 123.45, 123.19, 122.90, 120.26, 40.96, 32.50, 32.12, 28.80, 25.83, 23.02, 14.16, 10.86. MS (MALDI-TOF): *m/z* = 754.74; found 754.02.

Synthesis of Compound 5a

Compound 3a (500 mg, 0.73 mmol) and **Compound 4** (450 mg, 0.36 mmol) were

charged into a flask with 50 mL toluene, and the solution was flushed with nitrogen for 10 min, and then 21 mg of Pd(PPh₃)₄ was added. The solution was flushed again for another 10 min and stirred at 110 °C for 24 h under nitrogen. Then, the reaction mixture was poured into water (100 mL) and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate. After the removal of solvent, purification was carried out by silica gel column chromatography using petroleum/dichloromethane ether (1:1) as the eluent and **Compound 5a** was obtained as a red solid (400 mg, 52%). ¹H NMR (400 MHz, CDCl₃) δ 10.03 (s, 2H), 8.28 (s, 2H), 7.65 (s, 2H), 7.39 (s, 2H), 7.31 (d, J = 3.4 Hz, 2H), 7.29 (d, J = 3.4 Hz, 2H), 7.15 (d, J = 8.2 Hz, 8H), 7.07 (d, J = 8.2 Hz, 8H), 6.93 (d, J = 3.4 Hz, 2H), 6.91 (d, J = 3.4 Hz, 2H), 2.88 (d, J = 6.1 Hz, 8H), 2.55 (t, J = 8.0 Hz, 8H), 1.71-1.34 (m, 60H), 1.03-0.78 (m, 44H). ¹³C NMR (100 MHz, CDCl₃): δ 184.64, 156.93, 153.71, 146.93, 146.51, 143.09, 142.42, 141.85, 141.76, 141.31, 140.20, 139.55, 138.58, 135.92, 135.80, 135.31, 135.22, 134.56, 128.48, 128.29, 128.18, 127.84, 126.43, 125.74, 125.65, 123.97, 121.95, 118.26, 117.57, 63.09, 41.46, 35.59, 34.30, 32.49, 31.73, 31.35, 29.15, 28.92, 25.76, 23.07, 22.60, 14.22, 14.11, 10.91. MS (MALDI-TOF): *m/z* = 2116.19; found 2116.32.

Synthesis of Compound 5b

Compound 5b (a red solid, 450 mg, 60%) was synthesized with similar method as described above for the synthesis of **Compound 5a**. ¹H NMR (400 MHz, CDCl₃) δ 10.06 (s, 2H), 8.25 (s, 2H), 7.55 (d, J = 28.3 Hz, 2H), 7.41 (s, 2H), 7.23 (s, 2H), 7.16 (d, J = 7.6 Hz, 8H), 7.08 (d, J = 7.6 Hz, 8H), 2.86 (d, J = 5.5 Hz, 8H), 2.56 (t, J = 7.3 Hz, 8H), 1.82-1.34 (m, 60H), 1.26-0.77 (m, 44H). ¹³C NMR (100 MHz, CDCl₃): δ 184.46, 157.07, 153.81, 143.49, 142.80, 141.93, 141.83, 141.79, 141.22, 140.21, 139.45, 139.23, 139.16, 139.09, 138.61, 138.54, 135.23, 135.17, 134.61, 134.50, 133.70, 128.59, 128.51, 128.40, 127.83, 125.52, 123.28, 123.11, 123.02, 122.25, 117.66, 117.58, 113.87, 63.13, 40.93, 35.58, 32.49, 32.14, 31.73, 31.35, 29.14, 28.83, 25.84, 23.05, 22.60, 14.20, 14.10, 10.87. MS (MALDI-TOF): *m/z* = 2252.92; found 2252.63.

Synthesis of Compound IDBT

Compound 5a (112 mg, 0.05 mmol) was dissolved in a solution of anhydrous CHCl_3 (50 mL) and three drops of piperidine and 2-ethyl rhodamine (85 mg, 0.52 mmol) were added subsequently and the resulting solution was stirred at 90 °C for 24 h under argon protection. The reaction mixture was then extracted with chloroform, washed with water and dried over anhydrous magnesium sulfate. After the removal of solvent, purification was carried out by silica gel column chromatography using petroleum/dichloromethane ether (1:1) as the eluent and **IDBT** was obtained as a reddish-brown solid (60 mg, 47%). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 2H), 7.64 (s, 2H), 7.39 (s, 2H), 7.30 (d, $J = 3.3$ Hz, 4H), 7.22 (s, 2H), 7.15 (d, $J = 8.2$ Hz, 8H), 7.07 (d, $J = 8.2$ Hz, 8H), 6.95 (d, $J = 3.3$ Hz, 2H), 6.92 (d, $J = 3.4$ Hz, 2H), 4.18 (q, $J = 6.8$ Hz, 4H), 2.92 (d, $J = 6.5$ Hz, 4H), 2.88 (d, $J = 6.8$ Hz, 4H), 2.56 (t, $J = 8.0$ Hz, 8H), 1.77-1.35 (m, 60H), 1.18-0.77 (m, 44H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.38, 167.14, 156.93, 153.64, 146.75, 146.51, 142.28, 141.99, 141.74, 141.35, 140.69, 139.68, 139.04, 138.75, 137.74, 136.10, 136.06, 135.88, 135.22, 131.70, 131.69, 128.48, 128.17, 128.09, 127.85, 125.97, 125.74, 125.70, 125.17, 123.44, 123.36, 121.78, 118.33, 117.58, 63.09, 41.46, 35.59, 34.30, 32.58, 31.74, 31.35, 29.72, 29.16, 28.99, 25.83, 23.11, 22.61, 14.28, 14.11, 12.29, 10.92. MS (MALDI-TOF): $m/z = 2402.01$; found 2402.04.

Synthesis of IDBT-Cl

IDBT-Cl (a red reddish-brown solid, 70 mg, 50%) was synthesized with similar method as described above for the synthesis of **IDBT**. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 2H), 7.87 (s, 2H), 7.55 (s, 2H), 7.40 (s, 2H), 7.25 (s, 2H), 7.24 (s, 2H), 7.21 (s, 2H), 7.16 (d, $J = 8.2$ Hz, 8H), 7.08 (d, $J = 8.2$ Hz, 8H), 4.18 (q, $J = 6.8$ Hz, 4H), 2.90 (d, $J = 5.7$ Hz, 4H), 2.86 (d, $J = 7.0$ Hz, 4H), 1.61-1.29 (m, 60H), 1.21-0.80 (m, 44H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.02, 167.08, 157.07, 153.79, 142.64, 141.92, 141.81, 141.26, 139.28, 139.06, 138.72, 138.21, 135.70, 135.23, 134.81, 134.72, 130.70, 128.52, 128.36, 128.30, 127.84, 125.39, 124.18, 124.09, 123.22, 123.15, 122.48, 122.10, 117.64, 63.14, 40.93, 40.81, 35.60, 32.58, 32.52, 32.25, 32.13, 31.74, 31.36, 29.16, 28.85, 28.81, 25.90, 25.83, 23.10, 23.05, 22.61, 14.26, 14.19, 14.12, 12.29, 10.96, 10.87. MS (MALDI-TOF): $m/z = 2543.05$; found 2543. 18.

Materials characterization

Cyclic voltammetry was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M Bu₄NPF₆ acetonitrile solution at a scan rate of 100 mV s⁻¹. Glassy carbon discolored with small molecules film was used as the working electrode. A Pt wire was used the counter electrode and Ag/Ag⁺ was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as the external standard and its redox potential is 0.45 V versus Ag/Ag⁺. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction potential of polymer using the following equations: HOMO = -e(φ_{ox} + 4.36) (eV); LUMO = -e(φ_{red} + 4.36) (eV).

Device Fabrication and Characterization

To investigate the photovoltaic properties of **IDBT** and **IDBT-Cl** as donor material, OSCs with a device architecture of glass/ITO/PEDOT:PSS/donor:Y6/PDIN (Scheme S1)/Al were fabricated. The ITO-coated glass was precleaned and modified by a thin layer of PEDOT:PSS which was spin-cast from a PEDOT:PSS aqueous solution (Baytron P VP AI4083 from H. C. Stark) at 5000 rpm for 40 s, and then dried at 150 °C for 15 min in air. The thickness of the PEDOT:PSS layer is ~30 nm. Then the devices were transferred to a nitrogen-filled glove-box, where the active layer was spin-coated from chloroform solution containing IDBT:Y6 (or IDBT-Cl):Y6 onto the PEDOT:PSS layer. For the optimized conditions, IDBT (or IDBT-Cl):Y6 (1:1, w/w) were dissolved in chloroform with a concentration of 9 mg/mL for donor and stirred under 30 °C for 6 h. After 0.2% (by volume) NMP was added as additive, the solution was stirred at 30 °C for another 0.5 h. The blend film was spin-coated at 2000-3000 rpm for 30 s, followed by solvent vapor annealing at rt for 30 s. The PDIN buffer layer was deposited atop the active layer from the methanol solution with a concentration of 1.0 mg/mL (1mg/mL methanol with 0.25% acetic acid) at 2000 rpm for 40 s and functions as the cathode interfacial layer. Finally, top 100 nm Al electrode was deposited at a pressure of 2.0×10^{-5} Pa onto the PDIN layer with a shadow mask.

The current density-voltage (J - V) measurement of the SM-OSCs were measured under an illumination of AM 1.5G (100 mW cm⁻²) using a SS-F5-3A solar simulator (AAA grade, 50 × 50 mm² photobeam size) of Enli Technology CO., Ltd. Masks were made using laser beam cutting technology and had well-defined areas of 0.056 cm² to define the effective areas for accurate measurement. The EQE was measured by using a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard single crystal Si solar cell.

The donor/acceptor ratio was carefully scanned and the optimal ratio was determined to be 1:1 (w/w) for the two devices (Table S1). The optimal morphology control treatment is using 0.2% (v/v) *N*-methylpyrrolidone (NMP) as solvent additive, followed by chloroform vapor annealing for 30 seconds. The optimal photovoltaic parameters are summarized in Table 1 and the corresponding current density-voltage (J - V) curves are shown in Fig. 3a.

Mobility Measurement

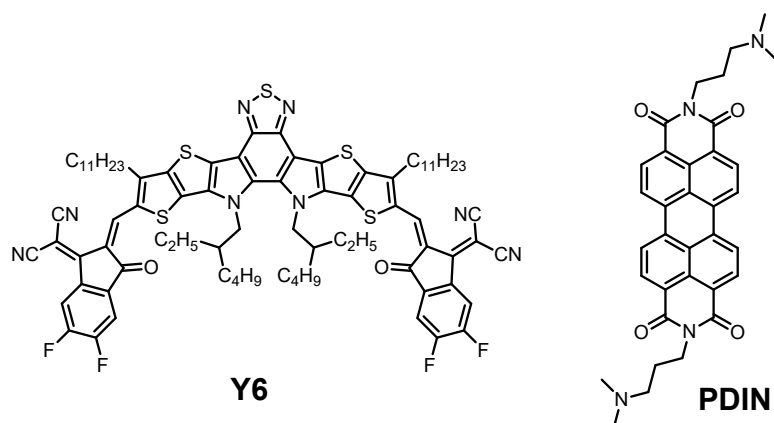
The devices with a structure of glass/ITO/PEDOT:PSS/active layer/MoO₃/Al and a structure of glass/ITO/ZnO/active layer/PDIN/Al were fabricated to measure the hole and electron mobilities, respectively. The ZnO buffer layer (thickness of 20 nm) was deposited atop the active layer from the mixed methanol: chloroform: n-butyl alcohol (1:1:14) solution of ZnO nanoparticles at a concentration of 10 mg/mL with 4000 rpm for 30 s. The fabrication of the devices is the same as that of photovoltaic devices as described above. The hole and electron mobilities were calculated by using the space-charge-limited current (SCLC) method.

$$J \cong (9/8)\epsilon\epsilon_0 \mu_0 V^2 \exp(0.89\sqrt{V/E_0 L}) / L^3$$

where ϵ is the dielectric constant of the polymers, ϵ_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, and L is the thickness of the film.

Exciton dissociation probability measurement

The device structure is glass/ITO/PEDOT:PSS/active layer/PDIN/Al. Fig. 4b plots the curves of J_{ph} ($J_{sat} = J_L - J_D$, where J_L and J_D represent the current densities under light and in the dark) versus effective voltage (V_{eff}) of the devices. It is supposed that all of the photo-generated excitons were dissociated into free charges and collected by electrodes at a high V_{eff} ($V_{eff} = 2$ V in this case). The exciton dissociation probability P_{diss} was calculated by the equation of $P_{diss} = J_{ph}/J_{sat}$.



Scheme S1 Chemical structures of Y6 and PDIN.

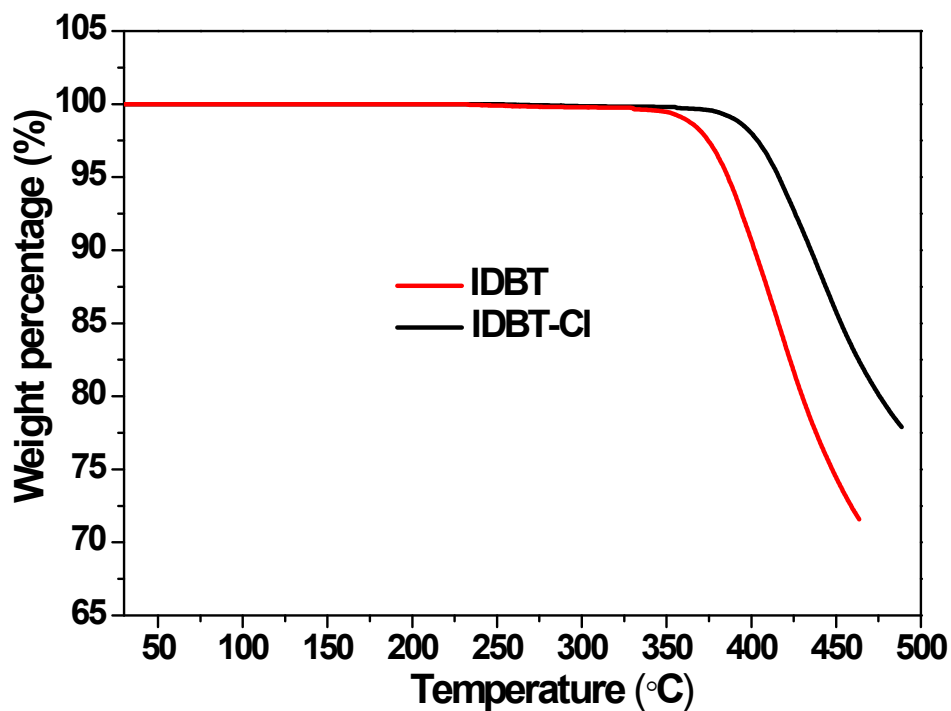


Fig. S1 TGA plots of IDBT and IDBT-Cl with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 atmosphere.

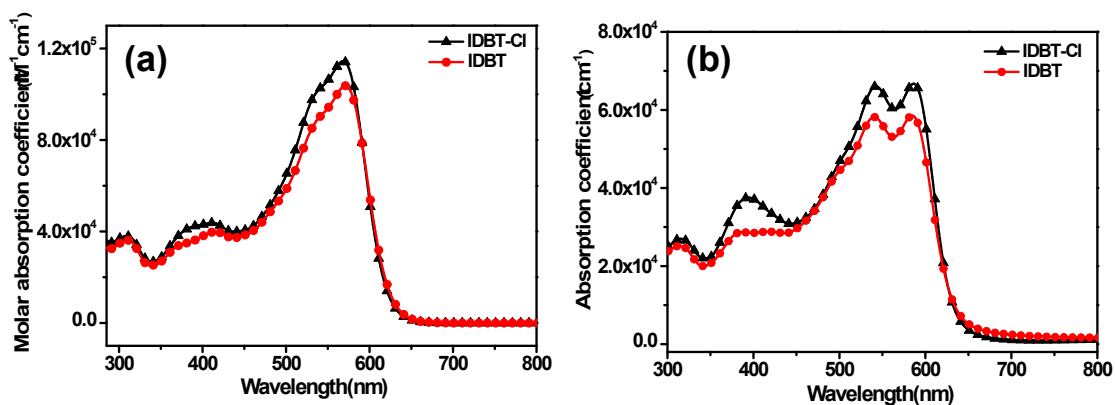


Fig. S2 Extinction coefficients of IDBT and IDBT-Cl in (a) diluted CHCl_3 solution and (b) thin film.

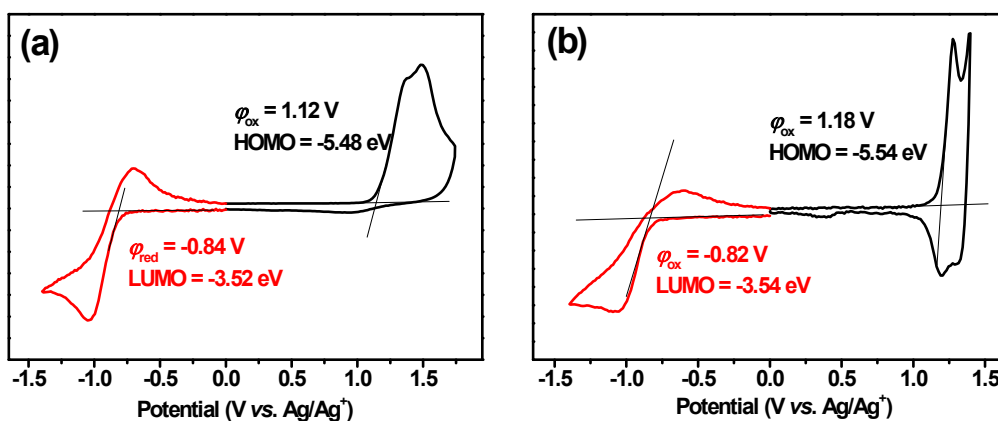


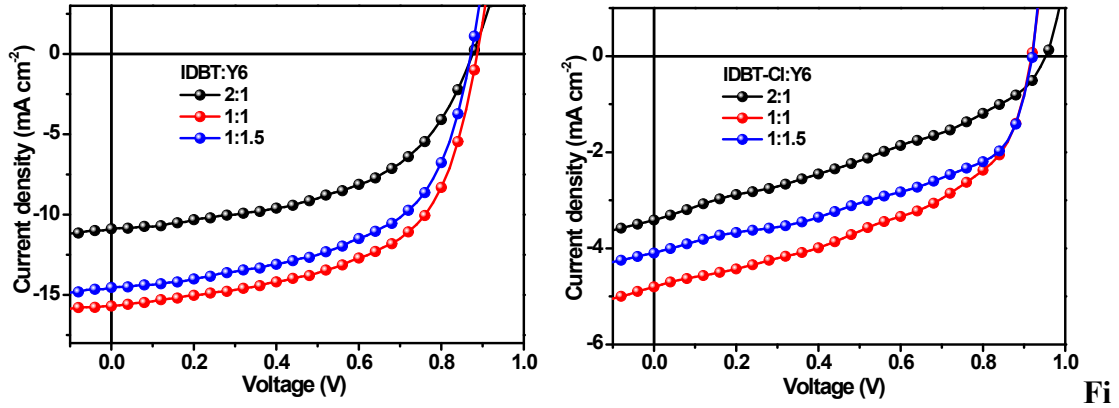
Fig. S3 Cyclic voltammograms of (a) IDBT and (b) IDBT-Cl.

Table S1 Photovoltaic performance of the OSCs based on IDBT:Y6 and IDBT-Cl:Y6 with different D/A ratio without any treatment under the illumination of AM 1.5 G at 100 mW cm^{-2} .

Active layer	D/A ratio	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
IDBT:Y6	2:1	0.881	10.89	51.8	4.94 [4.85]
	1:1	0.890	15.70	57.8	8.04 [7.95]
	1:1.5	0.872	14.53	56.6	7.17 [7.05]
IDBT-Cl:Y6	2:1	0.95	3.43	35.5	1.16 [1.05]
	1:1	0.92	4.92	44.8	2.11 [2.03]

1:1.5 0.91 3.96 49.1 1.78 [1.65]

The values in square brackets are the average PCE obtained from 6 devices.



g. S4 J - V curves the IDBT:Y6 and IDBT-Cl:Y6-based devices with various donor/acceptor weight ratios under the illumination of AM 1.5 G at 100 mW cm^{-2} .

Table S2 Photovoltaic performance of the IDBT:Y6 (1:1, w/w)-based OSCs processed by various thermal annealing temperatures for 10 min under the illumination of AM 1.5 G at 100 mW cm^{-2} .

Annealing temperature ($^{\circ}\text{C}$)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
70	0.863	17.78	62.9	9.69 [9.45]
80	0.858	19.39	62.6	10.41 [10.23]
90	0.856	19.16	61.0	9.95 [9.77]

The values in square brackets are the average PCE obtained from 6 devices.

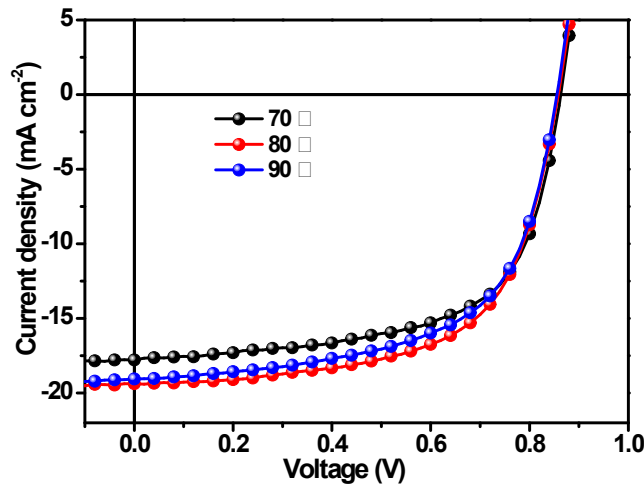


Fig. S5 J - V curves the IDBT:Y6 (1:1, w/w)-based devices processed by various

thermal annealing temperatures under the illumination of AM 1.5 G at 100 mW cm⁻².

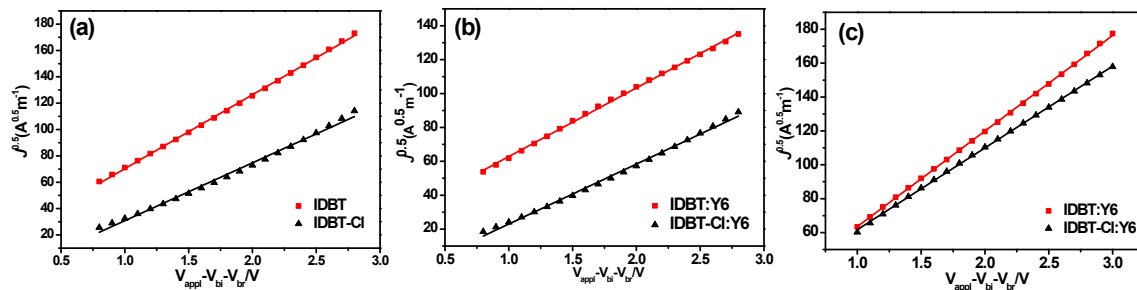


Fig. S6 $J^{0.5}$ vs $(V_{\text{app}}-V_{\text{bi}}-V_{\text{br}})$ plots of (a) hole-only device for the pristine film, (b) hole-only device for the blend film, and (c) electron only device for the blend film.

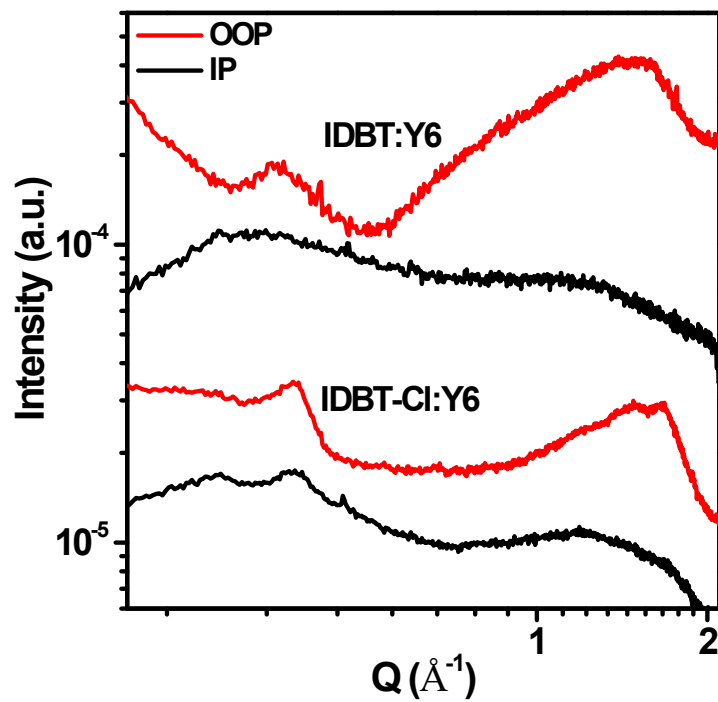


Fig. S7 The OOP and IP curves of IDBT:Y6 (1:1, w/w) and IDBT-CI:Y6 (1:1, w/w) blend films.

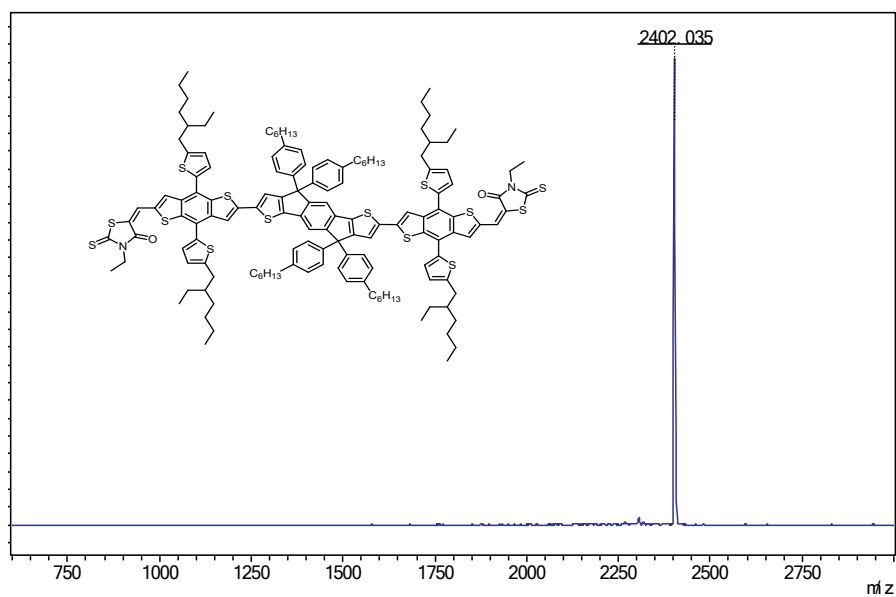


Fig. S10 MALDI-TOF spectrum of IDBT.

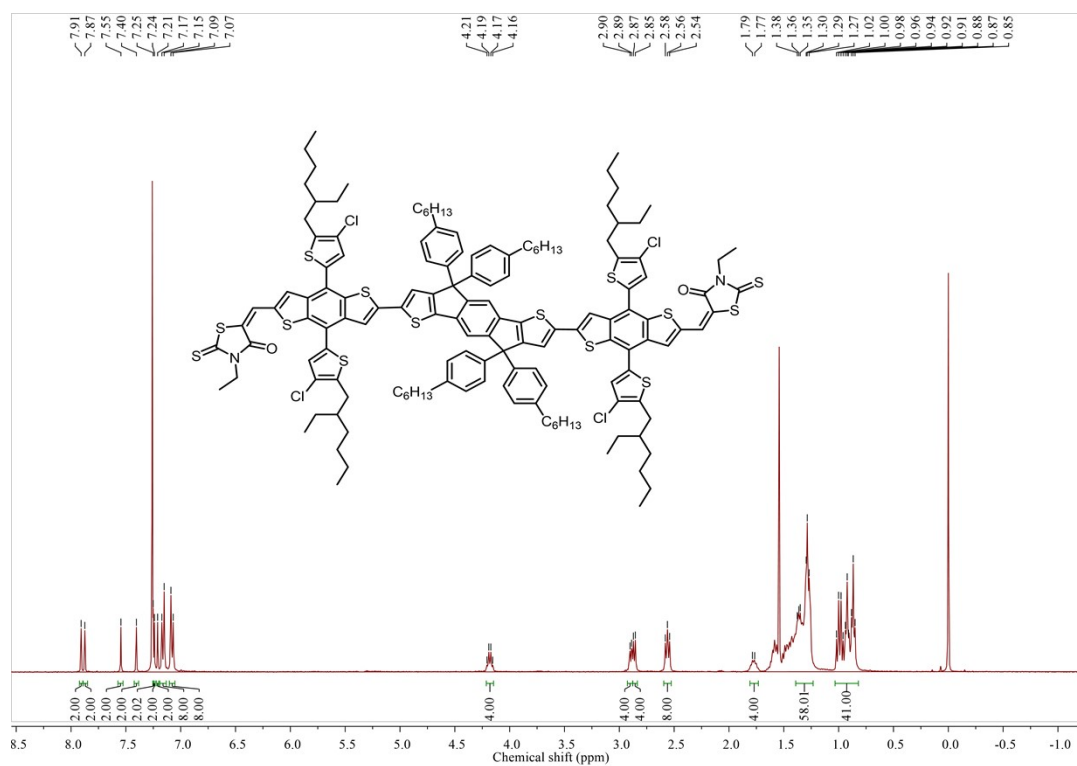


Fig. S11 ¹H NMR spectrum of IDBT-Cl in CDCl₃.

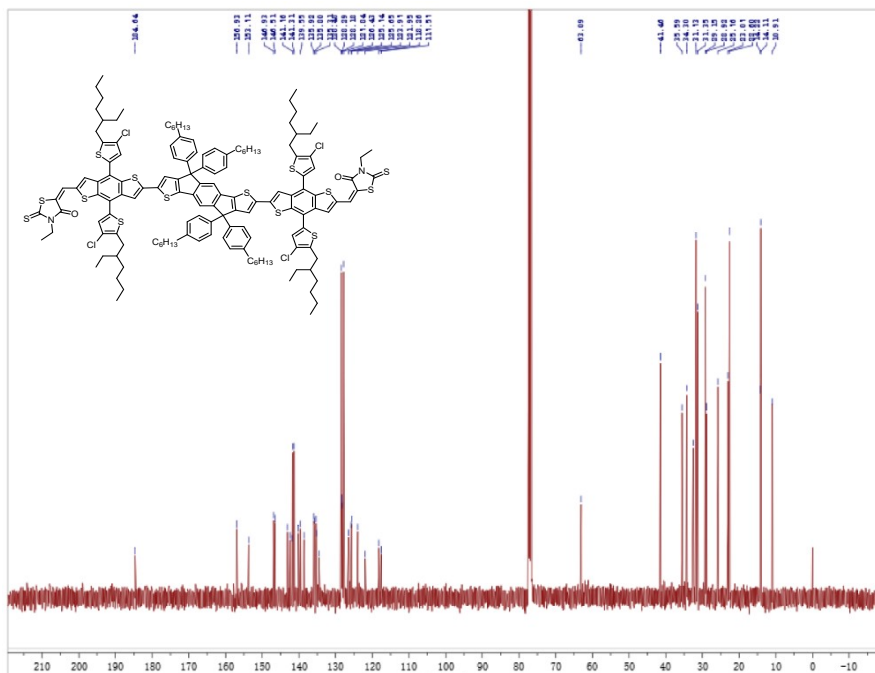


Fig. S12 ^{13}C NMR spectrum of IDBT-Cl in CDCl_3 .

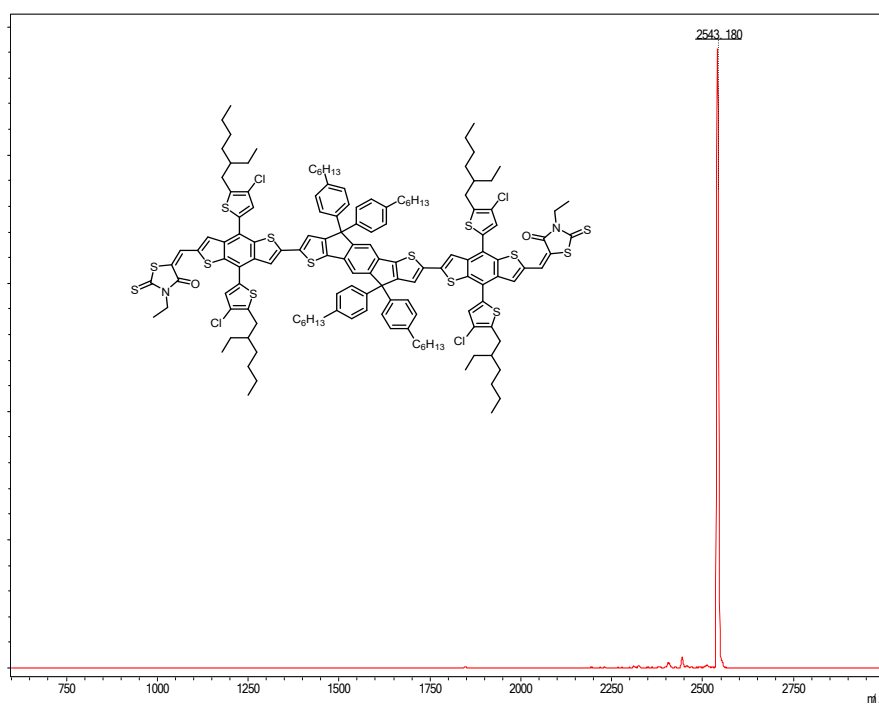


Fig. S13 MALDI-TOF spectrum of IDBT-Cl.