Supporting Information

Novel indacene-1,3,5,7-tetraone-based polymerized small molecular acceptors for efficient all-polymer solar cells

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Experimental section

Materials

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. The compounds BrT-CHO and ITO were synthesized according to the reported method.[1,2] The polymer donors (like JD40-S-F and JD40-F) used in device optimization were prepared in our lab.[3]

Synthesis details

DBrT-ITO

trans-DBrT-ITO

+

cis-DBrT-ITO

DBrT-ITO (molar ratio of trans and cis isomers: 0.75/0.25)
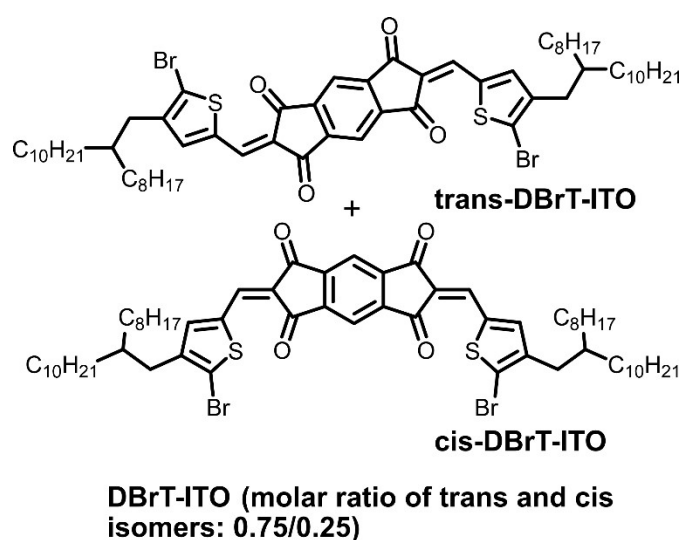
A mixture of compound BrT-CHO (3 g, 6.36 mmol) and ITO (0.59 g, 2.76 mmol) was dissolved in 135 mL acetic acid and refluxed for 48 hours. After cooling the reaction near room temperature, it was directly evaporated in vacuo to obtain the solid mixture. Then it was dissolved in CH_2Cl_2 and washed for three times with H_2O, and then dried with anhydrous Na_2SO_4. The organic phase was concentrated and further purified using column chromatography on silica gel with the eluent of petroleum ether (PE):CH_2Cl_2 (3:1, volume ratio), yielding the monomer DBrT-ITO as yellow solid, which consists of the trans and cis isomers with the molar ratio of 0.75/0.25 (2.5 g, 81%). 1H NMR

(500 MHz, CDCl$_3$) δ 8.42 (m, 2H), 7.93 (s, 2H), 7.62 (s, 2H), 2.56 (d, J = 7.1 Hz, 4H), 1.72–1.66 (m, 2H), 1.29-1.25 (m, 64H), 0.88-0.85 (m, 12H). ^{13}C-qNMR (151 MHz, CDCl$_3$) δ 188.25, 187.67, 187.57, 146.57, 146.42, 145.29, 145.20, 144.50, 144.13, 137.36, 136.93, 128.99, 124.12, 124.09, 117.87, 117.70, 117.54, 38.56, 33.91, 33.41, 32.05, 32.04, 30.11, 29.82, 29.79, 29.75, 29.50, 29.48, 26.65, 22.82, 14.26.

Polymer PBDT-ITO and PBDTCl-ITO

X=H, PBDT-ITO;
X=Cl, PBDTCl-ITO.
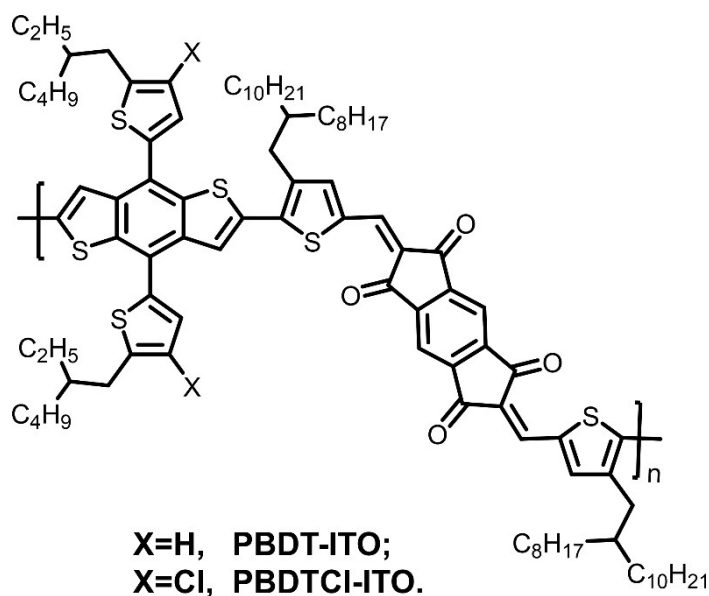
In the thick-walled tube, the monomer BDTX-Sn (0.1 mmol), DBrT-ITO (0.1 mmol) and catalyst Pd$_2$(dba)$_3$ (4.6 mg, 0.5% mmol) and P(o-tol)$_3$ (12.2 mg, 4% mmol) was added. Then the tube was transferred into the N$_2$ filled glove box, and 4 ml anhydrous chlorobenzene (CB) was injected. Next, it was sealed and heated under 80 °C for different time. When the reaction was cooled down, it was diluted to 10 mL and the mixture was precipitated into 200 mL methanol. The precipitate was filtrated, and then was extracted by Soxhlet extractor using CH$_3$OH, n-hexane, CH$_2$Cl$_2$, CHCl$_3$ and chlorobenzene (CB) successively. The CB extraction was concentrated, re-precipitated into 200 mL CH$_3$OH, filtrated, and dried to get the target polymers.

Polymer PBDT-ITO: The reaction time is 2 hours. (70 mg, 45%). GPC: Mn=50.0 kDa, PDI=2.1. ^{1}H NMR (500 MHz, 120 °C, C$_2$D$_2$Cl$_4$) δ 9.07-6.91 (m, 12H), 3.76-2.37 (m, 8H), 2.20-0.63 (m, 108H).

Polymer PBDTCl-ITO: The reaction time is 3 hours. (73 mg, 45%). GPC: Mn=45.6 kDa, PDI=1.2. ^{1}H NMR (500 MHz, 120 °C, C$_2$D$_2$Cl$_4$). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.57-6.41 (m, 10H), 3.33-2.73 (m, 8H), 1.85-0.76 (m, 108H).

Synthetic route of reference polymer PBDTCl-IDO
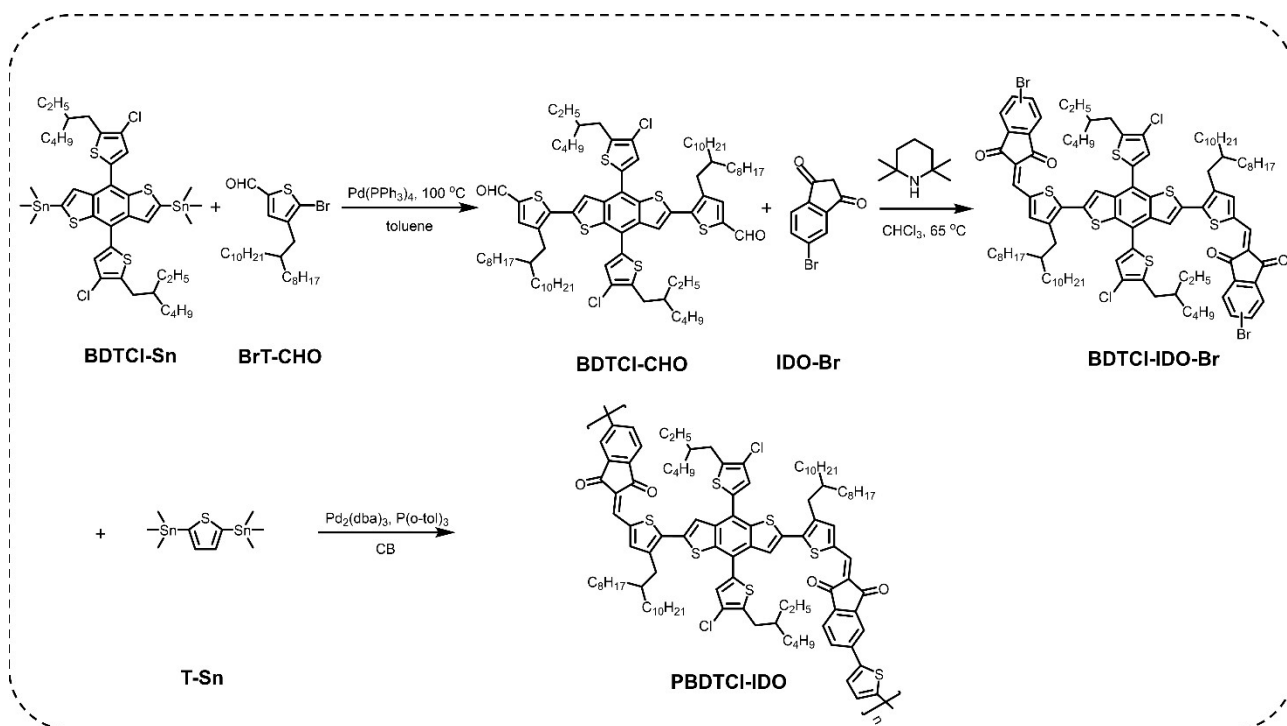
BDTCl-CHO

In the two-neck flask, compound BDTCl-Sn (0.5 g, 0.51 mmol) and BrT-CHO (0.53 g, 1.13 mmol) were dissolved in toluene under argon atmosphere. Then, Pd(PPh$_3$)$_4$ (29 mg, 0.025 mmol）was added, and the mixture was heated at 100 °C for 24 hours. After cooling the reaction, the solvent was evaporated in vacuo and the residue was directly purified by chromatography on silica gel using a PE: CH$_2$Cl$_2$ (2:1, v/v) mixture as eluent to get the compound BDTCl-CHO (0.45 g, 62%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 9.87 (s, 2H), 7.75 (s, 2H), 7.58 (s, 2H), 7.26 (s, 2H), 2.96–2.75 (m, 8H), 1.82–1.61 (m, 4H), 1.30–1.16 (m, 80H), 0.96–0.83 (m, 24H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 182.74, 141.95, 141.69, 140.87, 139.76, 139.44, 139.08, 137.21, 136.99, 135.12, 128.39, 123.44, 123.34, 123.27, 41.05, 39.21, 34.16, 33.46, 33.44, 32.68, 32.26, 32.05, 32.03, 30.16, 29.82, 29.78, 29.74,

29.49, 29.47, 28.93, 26.57, 25.94, 23.18, 22.83, 22.80, 14.28, 14.25, 10.98.

BDTCl-IDO-Br

To a solution of BDTCl-CHO (350 mg, 0.24 mmol) and IDO-Br (554 mg, 2.45 mmol) in anhydrous acetonitrile, 2,2,6,6-tetramethylpiperidine (0.3 mL) was added under argon atmosphere. The solution was stirred at 80 °C for 24 hours and then evaporated in vacuo. The resulting mixture was purified using column chromatography on silica gel, yielding the isomeric monomer BDTCl-IDO-Br (220 mg, 50%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (s, 2H), 7.92 – 7.74 (m, 10H), 7.31 (s, 2H), 2.98 – 2.74 (m, 8H), 1.83 – 1.71 (m, 4H), 1.45 – 1.14 (m, 80H), 1.00 – 0.77 (m, 24H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 189.19, 188.84, 188.58, 188.09, 146.33, 146.20, 145.16, 145.08, 143.38, 142.17, 142.11, 141.89, 140.56, 139.98, 139.11, 139.03, 138.16, 137.97, 137.41, 137.39, 137.28, 136.37, 136.20, 136.18, 135.11, 130.52, 130.30, 128.48, 126.36, 126.28, 124.56, 124.44, 124.19, 123.58, 123.39, 123.37, 40.99, 38.93, 34.09, 33.44, 32.72, 32.32, 32.05, 30.20, 29.86, 29.81, 29.76, 29.51, 28.94, 26.53, 25.90, 23.20, 22.82, 14.32, 14.24, 10.97.

PBDTCl-IDO

In the thick-walled tube, the monomer BDTCl-IDO-Br (200 mg, 0.11 mmol), T-Sn (44.5 mg 0.1 mmol) and catalyst Pd$_2$(dba)$_3$ (4.6 mg, 0.5% mmol) and P(o-tol)$_3$ (12.2 mg, 4% mmol) were added. Then the tube was transferred into the N$_2$ filled glove box, and 10 ml anhydrous chlorobenzene (CB) was injected. Next, it was sealed and heated under 110 °C for 31 hours. When the reaction was cooled down, it was precipitated into 200 mL methanol. The precipitate was filtrated, and then was extracted by Soxhlet extractor using CH$_3$OH, n-hexane, CH$_2$Cl$_2$ and CHCl$_3$ successively. The CHCl$_3$ extraction was concentrated, re-precipitated into 200 mL methanol, filtrated, and dried to yield the polymer PBDTCl-IDO. GPC: Mn=28.8 kDa, PDI=3.0.

Measurement and characterization

^{1}H and ^{13}C-NMR spectra were measured using a Bruker AV-400/500/600 instrument (Germany), where ^{13}C-quantitative NMR (^{13}C-qNMR) spectrum was tested with the assistance of inverse gated decoupling technology. Molecular weights of the polymers were obtained on an Acquity Advanced Polymer Chromatography (Waters) with high temperature chromatograph, using 1,2,4-trichlorobenzene as the eluent at 150 °C. UV-Vis absorption spectra were recorded on a PerkinElmer Lambda 950 spectrophotometer (USA). Density functional theory calculations were performed at the B3LYP/6-31G(d) level using the Gaussian 09 package 40, where polymers PBDTCl-ITO and PBDTCl-IDO were simplified as trimers and alkyl groups were replaced with methyl groups for simplification. Cyclic voltammetry (CV) data were measured on a CHI600D electrochemical workstation by using a conventional three-electrode cell with a glassy-carbon working electrode, a Pt gauze as the counter electrode, and a Ag/AgCl as the reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) in acetonitrile was the electrolyte, and CV curves were calibrated using ferrocence as the standard, whose HOMO is –4.80 eV with respect to zero vacuum level. Photoluminescence (PL) spectra were recorded on Edinburgh FLS1000 spectrofluorometer (UK). The current density−voltage ($J−V$) characteristics were measured under a computer controlled Keithley 2400 sourcemeter under 1 sun, AM 1.5G solar simulator (Taiwan, Enlitech). The illumination intensity of the light source was calibrated by a standard silicon solar cell with a KG5 filter, calibrated using a National Renewable Energy Laboratory calibrated silicon photodiode, giving a value of 100 mW cm^{-2} in the test. The $J–V$ characteristics of electron-only and hole-only devices were recorded with a Keithley 236 sourcemeter under dark. The EQE spectra were performed on a commercial EQE measurement system (Taiwan, Enlitech, QE-R). Tapping-mode atomic force microscopy (AFM) images were obtained on a Bruker Dimension Edge instrument (Germany).

Transmission electron microscopy (TEM) images were obtained by using a JEOL JEM-2100Plus Microscope (Japan). Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed using Xeuss 3.0 system (Xenocs, France) and sample to detector distance of 80 mm. Samples were measured under vacuum to avoid air scattering. The data was collected with Pilatus detecor with exposure time 1800s and pixel size 172 microns, twice exposure was performed to remove the detector gap area. Crystal coherence length (CCL) was calculated according to the reported method.[4]

The charge carrier mobilities were determined from space-charge-limited current (SCLC) devices. The structures of the hole-only devices and electron-only devices are indium tin oxide /PEDOT:PSS/PM6:polymer acceptors/MoO_3/Al and ITO/ZnO/polymer acceptors or PM6: polymer acceptors/Ca/Al, respectively. The mobilities were determined by fitting current density–voltage (J–V) curves in dark to the model of a single carrier SCLC using the equation,

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, d is the thickness of the films, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant of the transport medium, and μ is the charge carrier mobility. $V = V_{app} - V_{bi} - V_s$, where V_{app} is the applied voltage, V_{bi} is the built-in voltage, and V_s is the voltage drop from the substrate's series resistance. The carrier mobility can be calculated from the slope of the $J^{1/2}$–V curves.

Fabrication of conventional PSCs: The glass coated with indium tin oxide were precleaned sequentially by detergent once, deionized water three times and then isopropanol twice, each for 30 min, then dried at 70 °C in baking oven over 3 h. After 3 min plasma treatment, The precleaned ITO substrates were coated with PEDOT:PSS by spin-coating its' solution (3500 r.p.m. for 30 s, thickness

of about 40 nm) and then baked at 150 °C for 15 min. Next, the substrates were transferred into a

nitrogen-filled glovebox, and the solution of PM6: polymer acceptors (D:A=1:1, w/w; 12 mg/mL;

dissolved in CB: 1-chloronaphthalene (99.5:0.5, v/v)) was spin-coated at the speed of 2000 rpm onto

it to give the active layer with the thickness of 100 nm. A thin layer (~10 nm) of PFN-Br as cathode

interface was coated onto the active layer. Finally, a silver electrode (100 nm) was thermally

deposited through a shadow mask (defined active area of 0.038 cm^2) onto the prepared layer in a

vacuum chamber with base pressure of 5×10^{-7} torr.
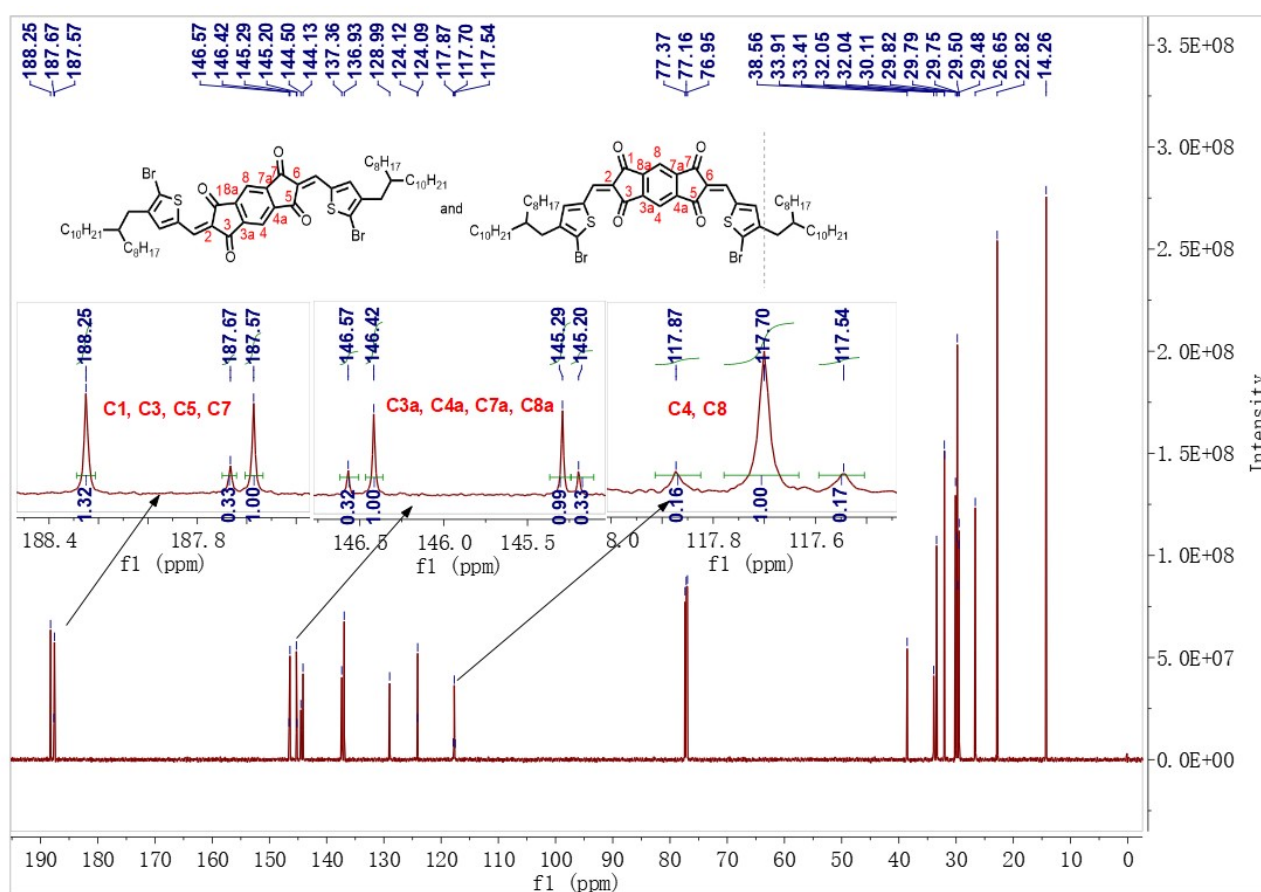
Figure S1. ^{13}C-qNMR spectra of isomeric monomer DBrT-ITO in CDCl$_3$.
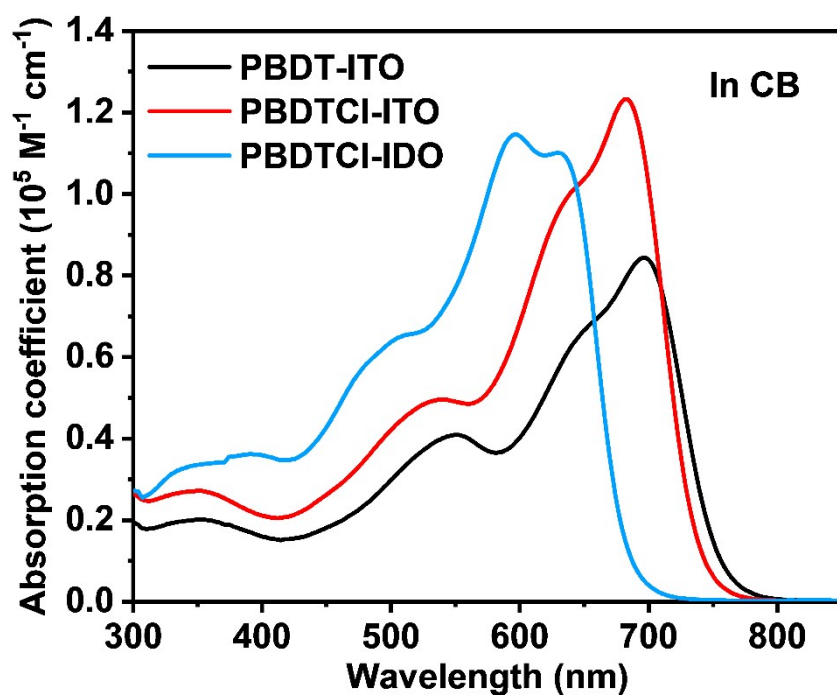
Figure S2. Absorption coefficients of three polymers in 10^{-5} M chlorobenzene solutions.
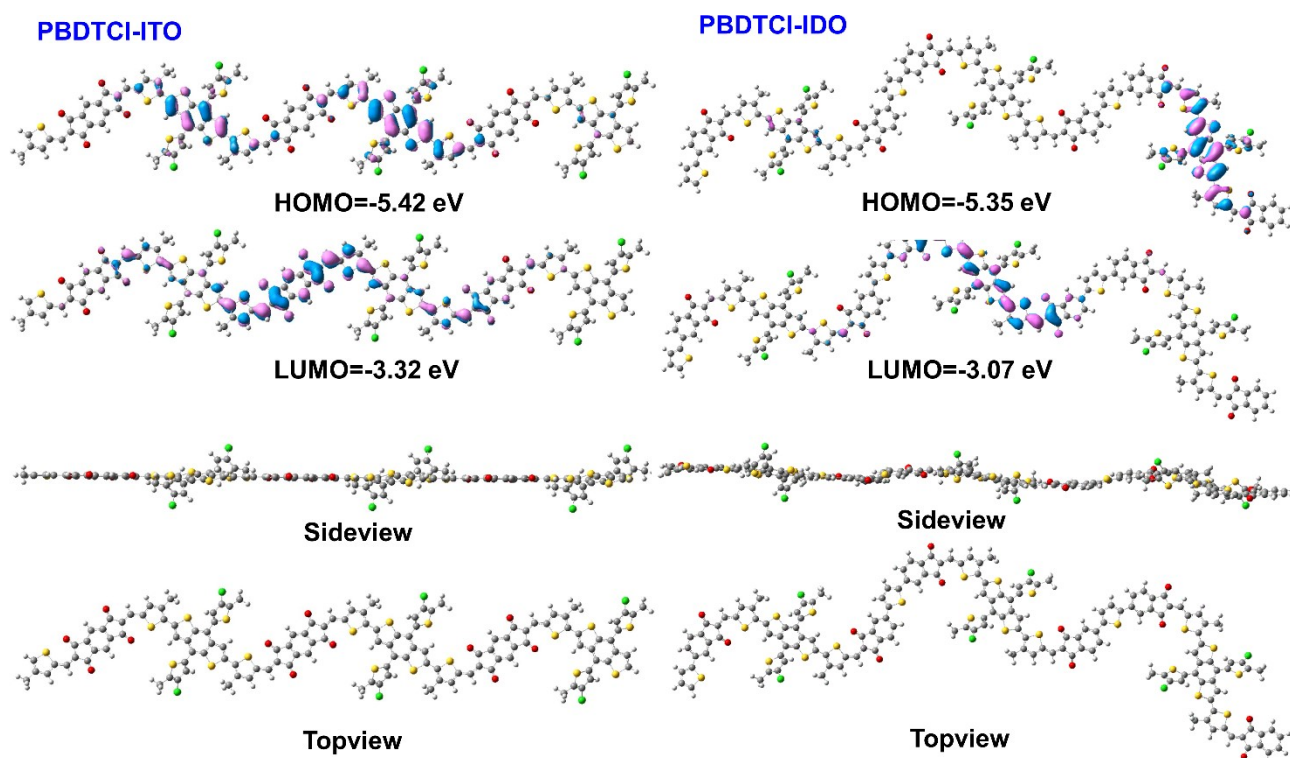
Figure S3. Calculated electronic wave-functions of the HOMO, LUMO energy level and optimized geometry of PBDTCl-ITO and PBDTCl-IDO.
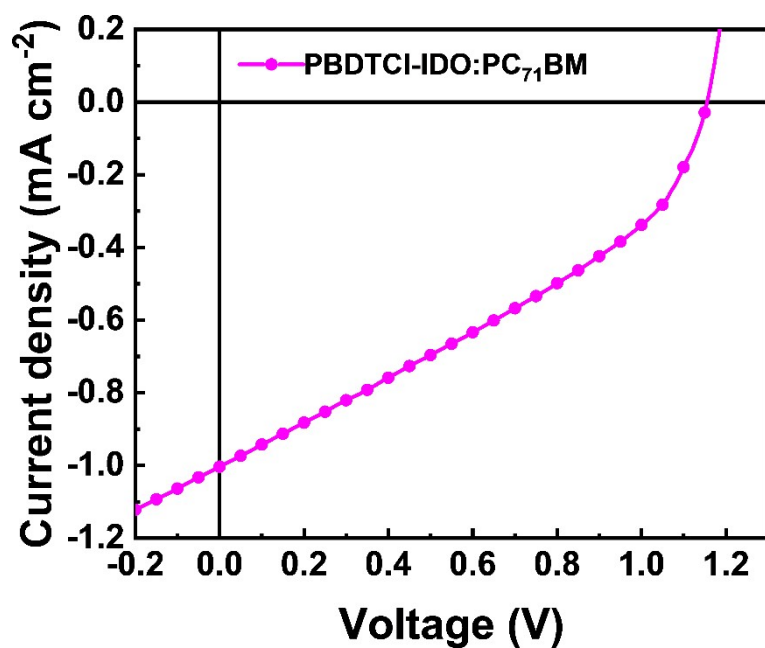
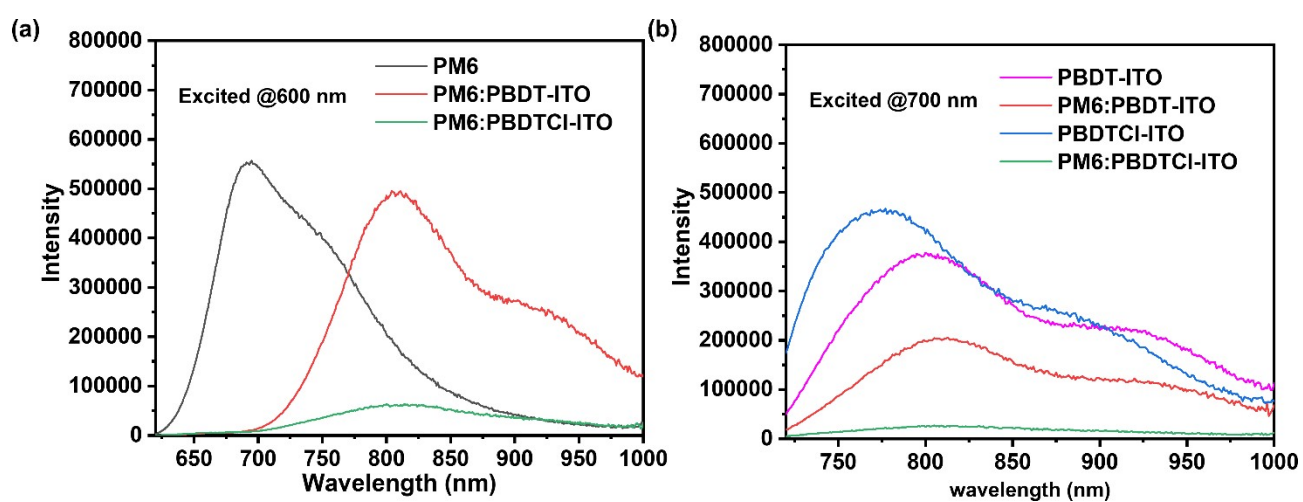**Figure S4.** *J-V* curves of PBDTCl-IDO:PC$_{71}$BM based device.

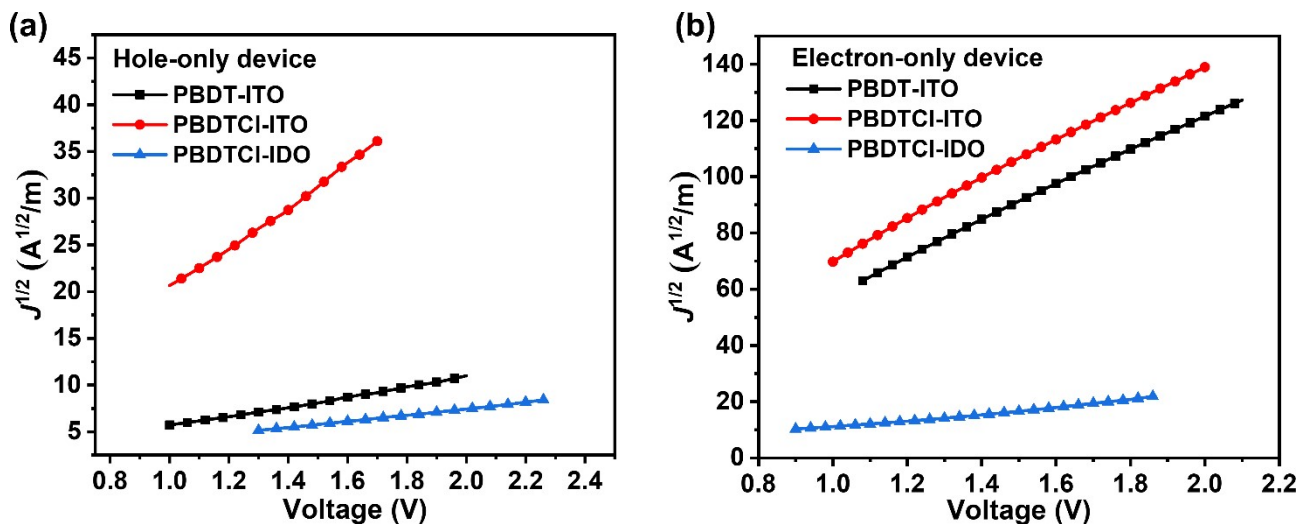**Figure S5.** Photoluminescence spectra of PBDT-ITO, PBDTCl-ITO and their blends films with polymer donor PM6.

Figure S6. $J^{1/2}$-V curves of hole-only devices (a) and electron-only devices (b) based on the polymers.

Table S1. Photovoltaic properties of PSCs based on PBDT-ITO and PBDTCl-ITO (1:1, w/w; with 5% CN, v/v; TA at 100 °C for 10 min) at AM1.5 G at 100 mW cm^{-2}

Active layer	V_{OC}(V)	J_{SC} (mA cm^{-2})	FF（%）	PCE （%）
PM6:PBDT-ITO	1.06±0.02	8.17±0.02	38.39±1.30	3.33±0.15
PM6:PBDTCl-ITO	1.01±0.00	13.19±0.17	54.62±1.44	7.32±0.21

Table S2. Photovoltaic properties of PSCs based on different polymer donors and PBDTCl-ITO (1:1, w/w; with 0.5% CN, v/v; TA at 100 °C for 10 min) at AM1.5 G at 100 mW cm^{-2}

Active layer	V_{OC}(V)	J_{SC}(mA cm^{-2})	FF（%）	PCE （%）
PM6:PBDTCl-ITO	1.01 ±0.00	13.19±0.17	54.62±1.44	7.32±0.21
PBDB-T:PBDTCl-ITO	0.90±0.00	11.33±0.21	52.77±0.99	5.42±0.15
JD40-F:PBDTCl-ITO	1.02±0.01	10.16±0.44	44.19±1.14	4.59±0.30
JD40-S-F:PBDTCl-ITO	1.02±0.01	5.49±0.01	28.47±0.15	1.60±0.02

Table S3. Photovoltaic properties of PSCs based on PM6 and PBDTCl-ITO (with 0.5% CN, v/v; TA

at 100 ºC for 10 min) with different D/A ratio under AM1.5 G at 100 mW cm^{-2}

D :A	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF（%）	PCE（%）
1.2:1	0.99±0.01	13.82±0.94	49.23±1.85	6.75±0.14
1:1	1.01 ±0.00	13.19±0.17	54.62±1.44	7.32±0.21
1:1.2	1.00±0.01	14.06±0.41	50.48±1.58	7.07±0.11

Table S4. Photovoltaic properties of PSCs based on PM6 : PBDTCl-ITO (1:1, w/w; with 0.5% CN, v/v; TA at 100 ºC for 10 min) processed with different rotation speed under AM1.5 G at 100 mW cm^{-2}

Rotation speed（r/min）	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1800	1.03±0.00	14.21±0.07	49.86±0.53	7.32±0.13
2000	1.01±0.00	13.19±0.17	54.62±1.44	7.32±0.21
2200	1.04±0.00	13.87±0.08	49.63±0.47	7.13±0.09

Table S5. Photovoltaic properties of PSCs based on PM6:PBDTCl-ITO (1:1, w/w; TA at 100 ºC for 10 min) processed with different additives under AM1.5 G at 100 mW cm^{-2}

Additive ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
0% CN	1.04±0.00	12.92±0.33	45.89±0.44	6.17±0.18
0.3% CN	1.03±0.00	14.01±0.22	49.14±0.78	7.12±0.08
0.5% CN	1.01±0.00	13.19±0.17	54.62±1.44	7.32±0.21

0.8% CN	1.03±0.00	13.40±0.38	45.90±0.11	6.32±0.19
0.5% DIO	1.03±0.00	12.95±0.14	45.52±0.30	6.05±0.07

Table S6. Photovoltaic properties of PSCs based on PM6:PBDTCl-ITO (1:1, w/w; with 0.5% CN) with thermal annealing at different temperature for 10 min under AM1.5 G at 100 mW cm^{-2}

TA (°C)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
80	1.04±0.00	13.75±0.24	49.38±0.89	7.04±0.24
100	1.01±0.00	13.19±0.17	54.62±1.44	7.32±0.21
120	1.03±0.00	13.21±0.39	45.70±0.24	6.20±0.22
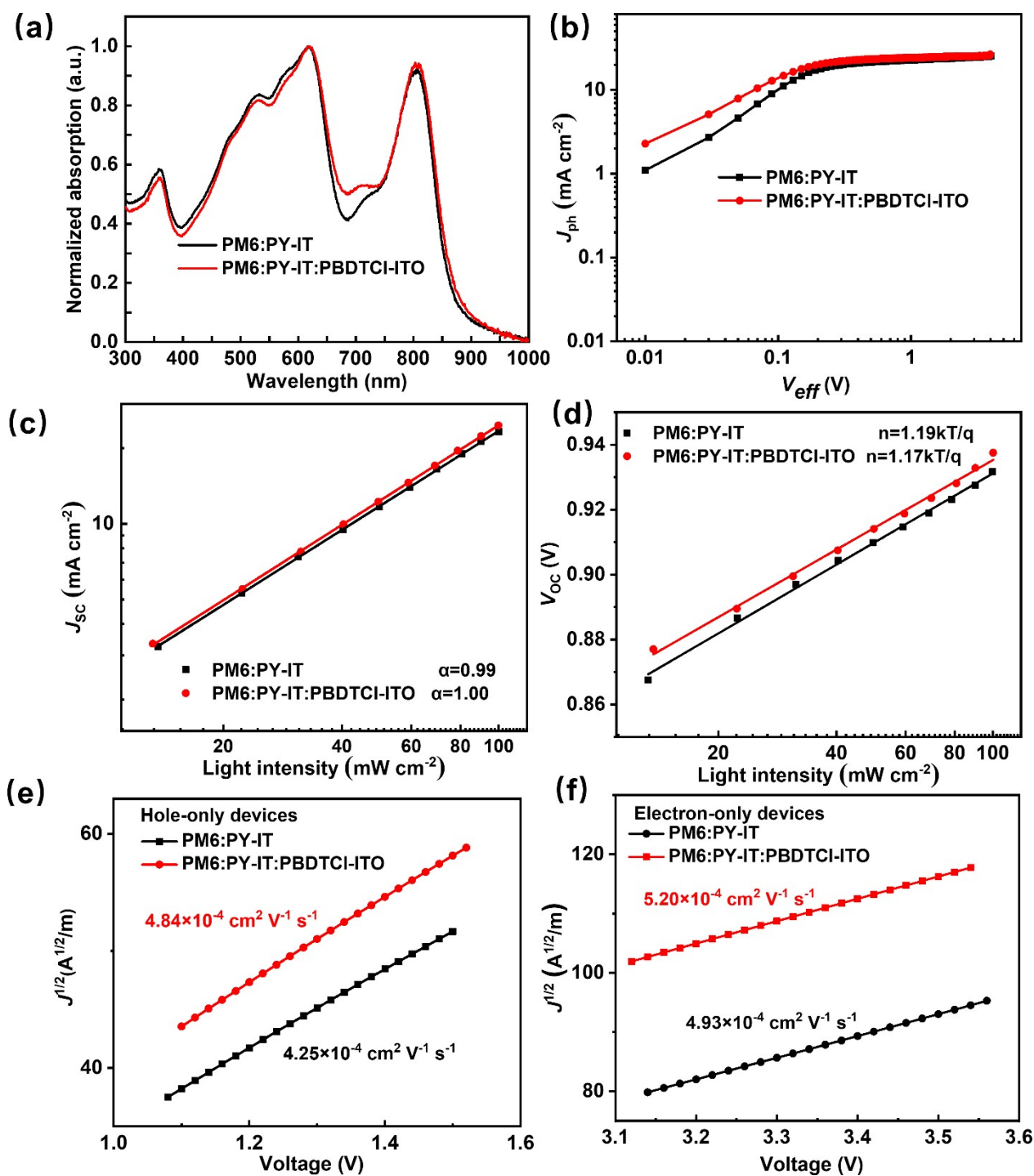
Figure S7. (a) UV-vis-NIR absorption spectra of PM6:PY-IT and PM6:PY-IT:PBDTCl-ITO blends. (b) J_{ph}-V_{eff} plot of the devices. (c) J_{SC}-P_{light} relationship of the devices. (d) V_{OC}-P_{light} relationship of the devices. (e) $J^{1/2}$-V curves of hole-only devices and (f) electron-only devices.
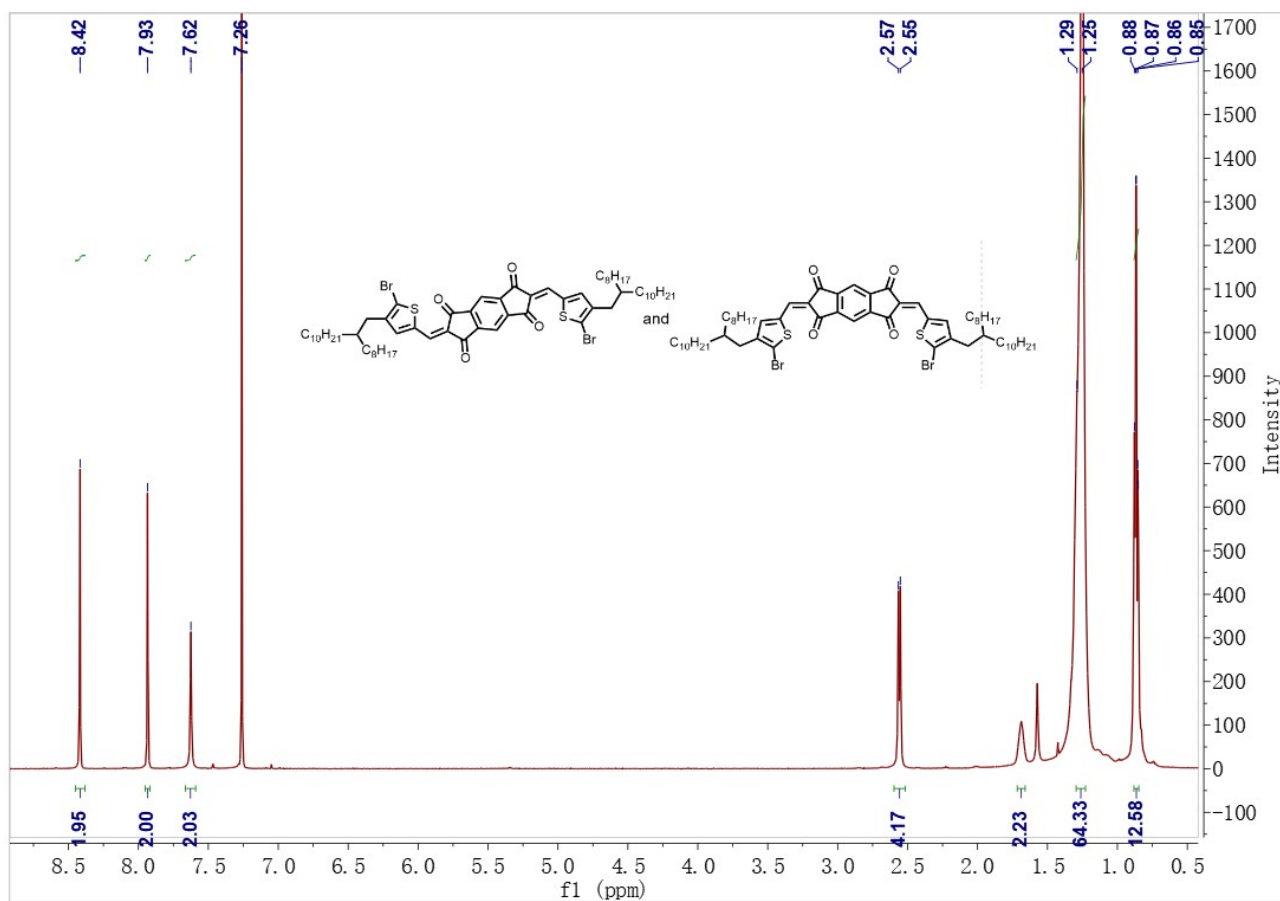
Figure S8. ^{1}H-NMR spectra of isomeric monomer DBrT-ITO in CDCl$_3$.
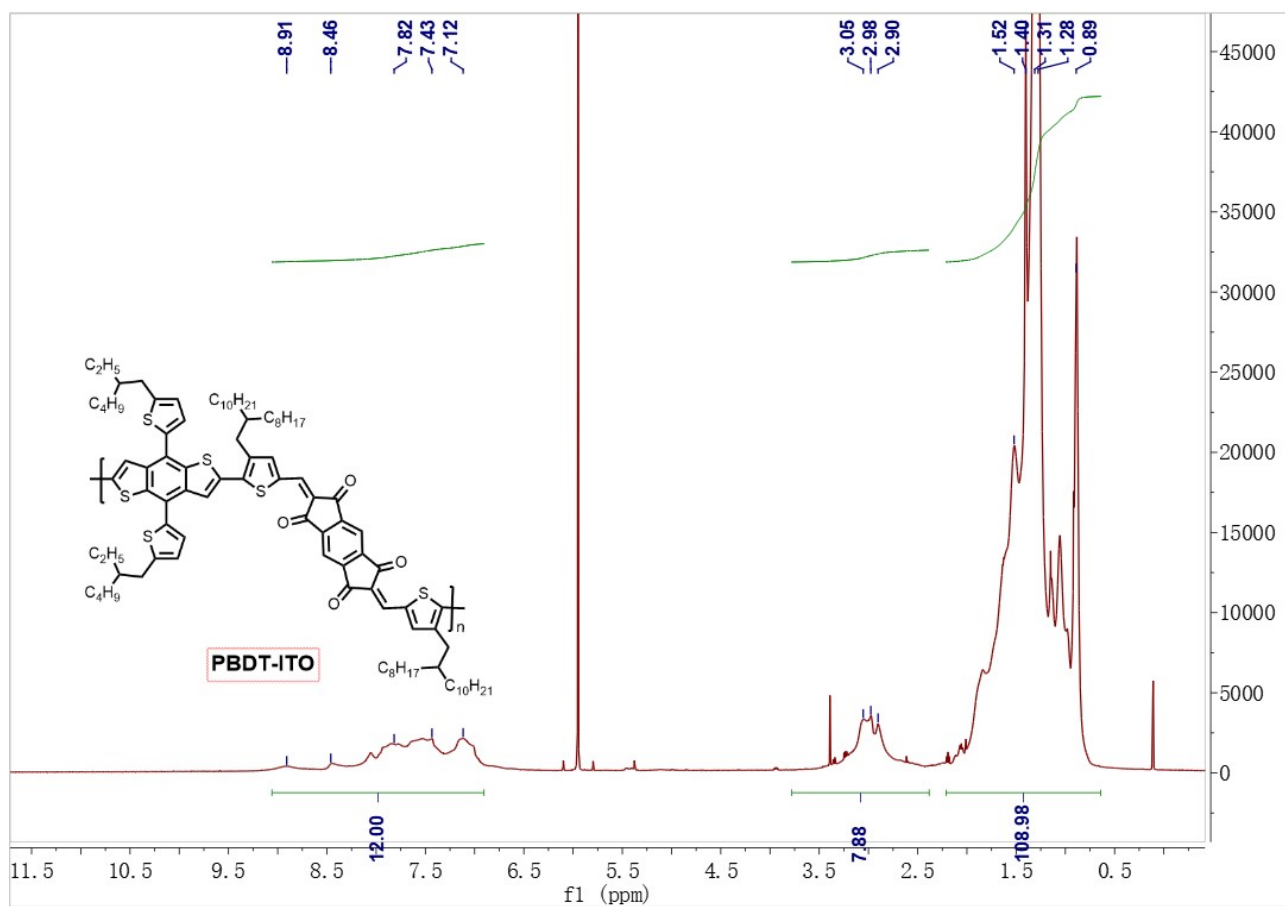
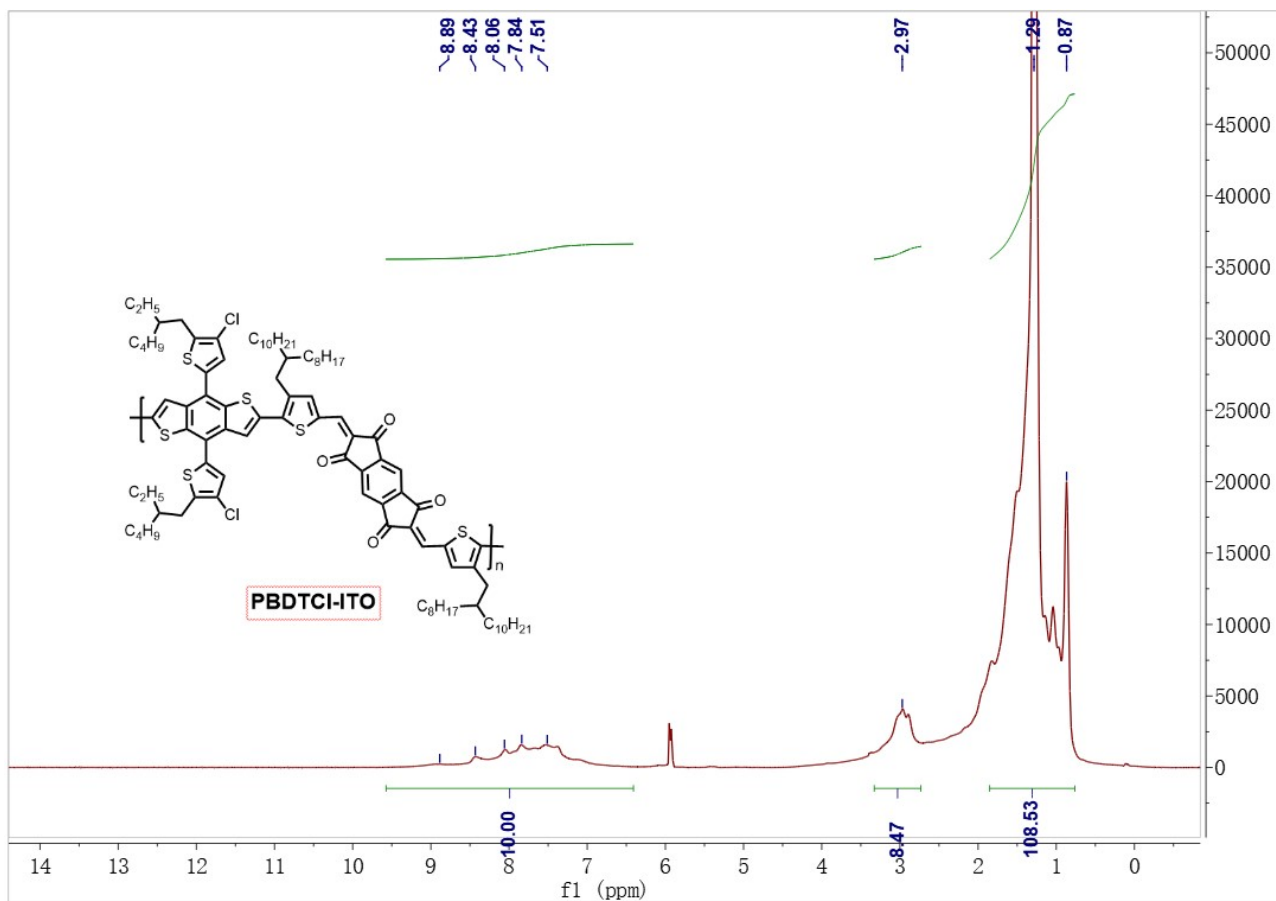**Figure S9.** ^{1}H-NMR spectra of polymer PBDT-ITO in 120 °C 1,1,2,2-tetrachloroethyane-d2.

Figure S10. ^{1}H-NMR spectra of polymer PBDTCl-ITO in 120 °C 1,1,2,2-tetrachloroethyane-d2.
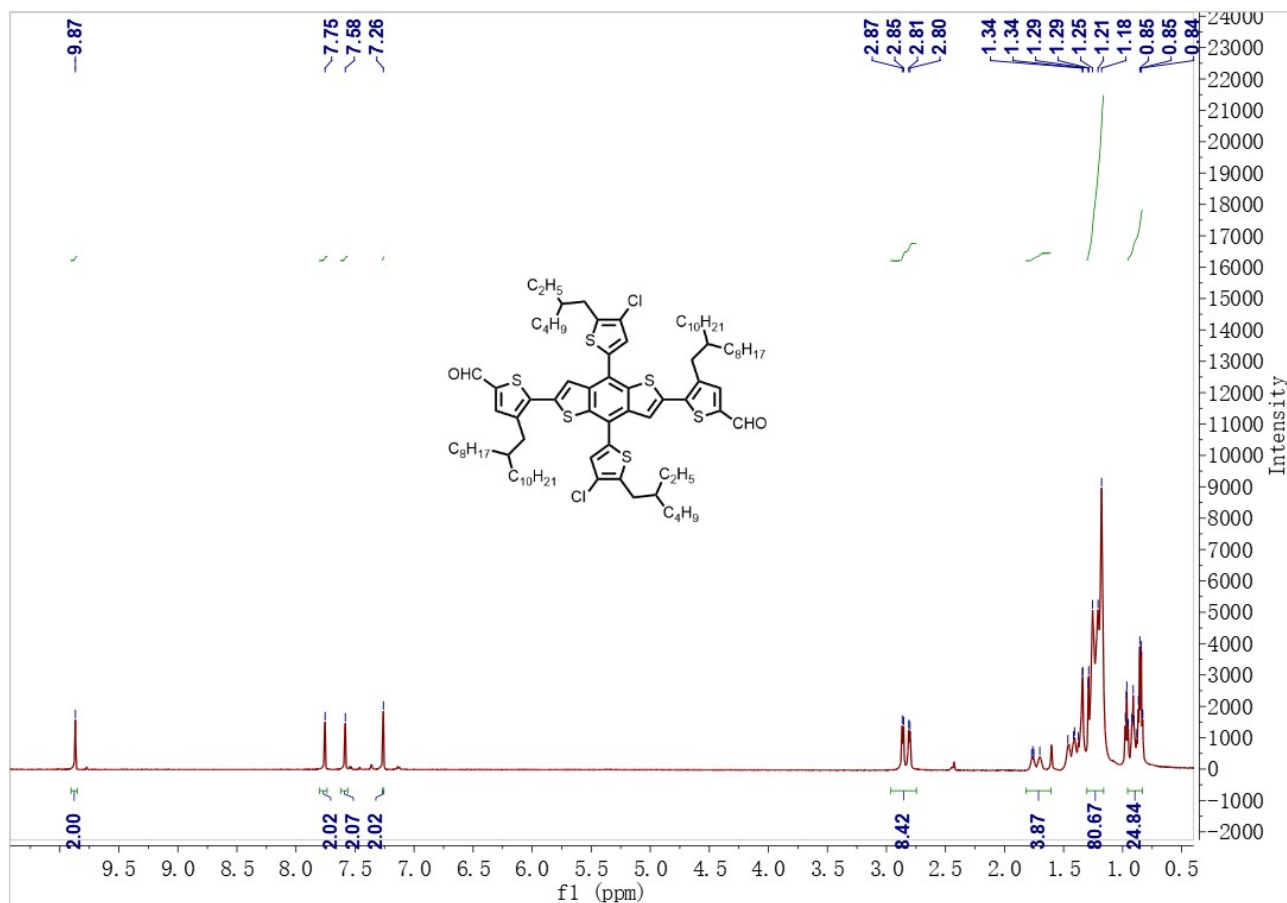
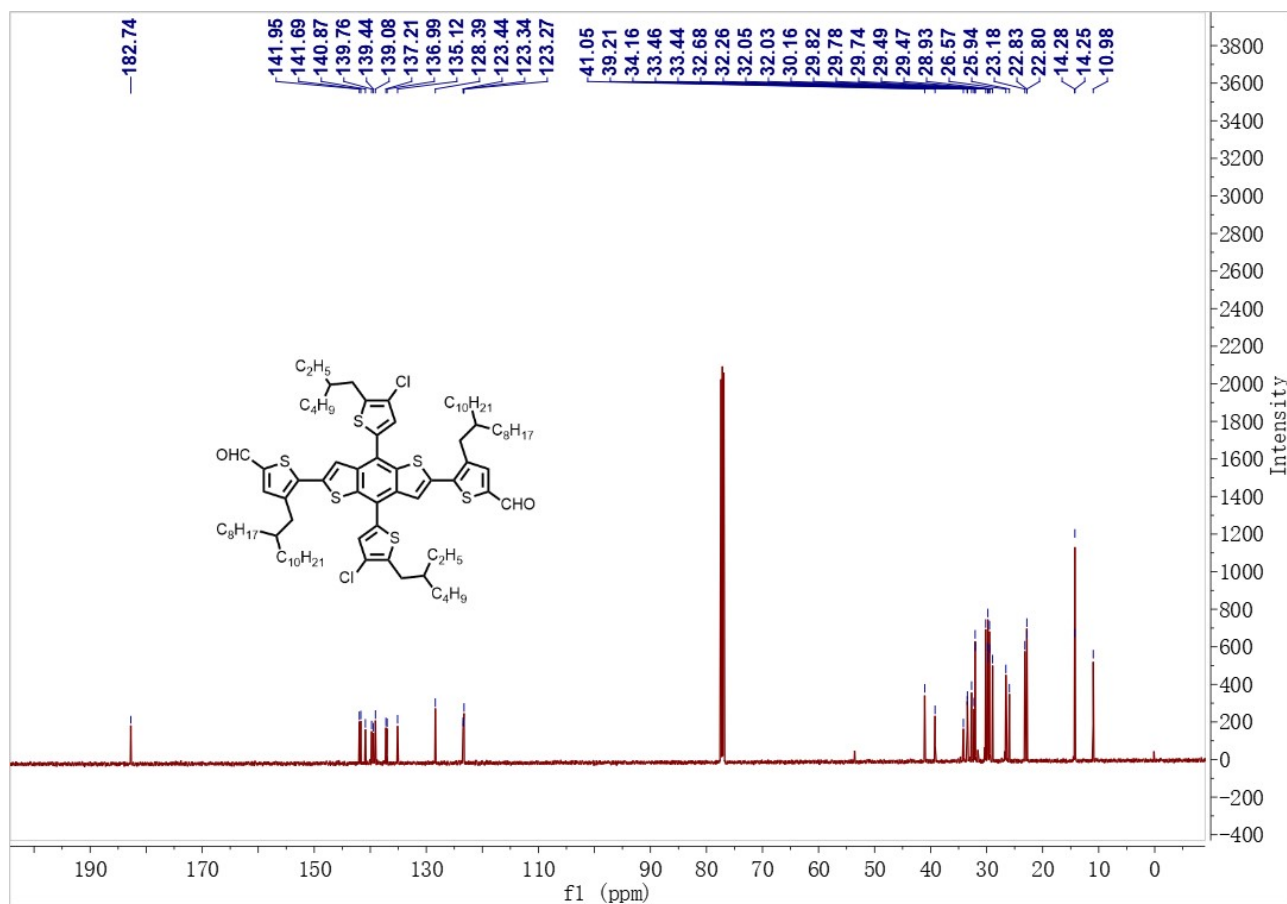**Figure S11.** ^{1}H-NMR spectra of the compound BDTCl-CHO in CDCl$_3$.

Figure S12. ^{13}C-NMR spectra of the compound BDTCl-CHO in CDCl$_3$.
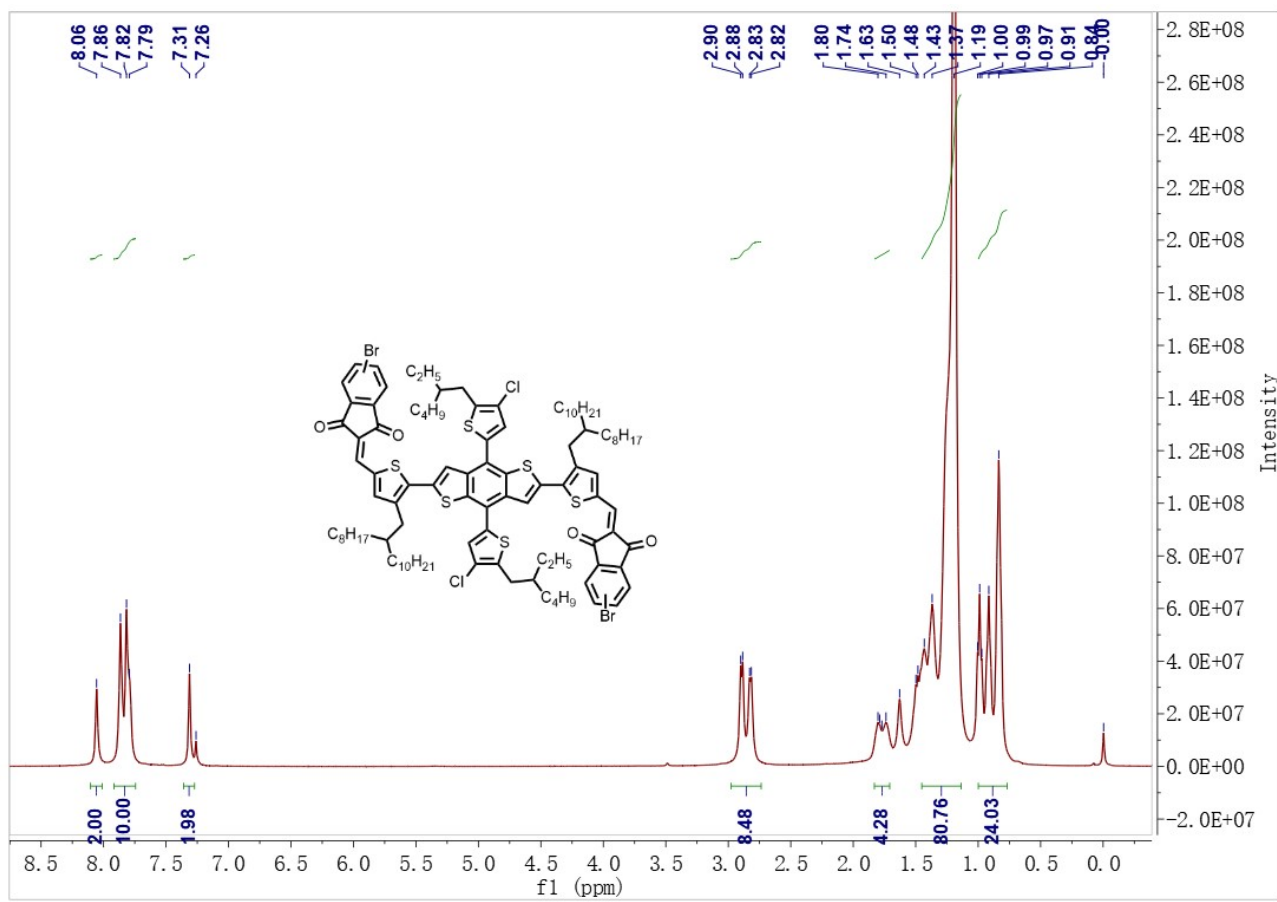

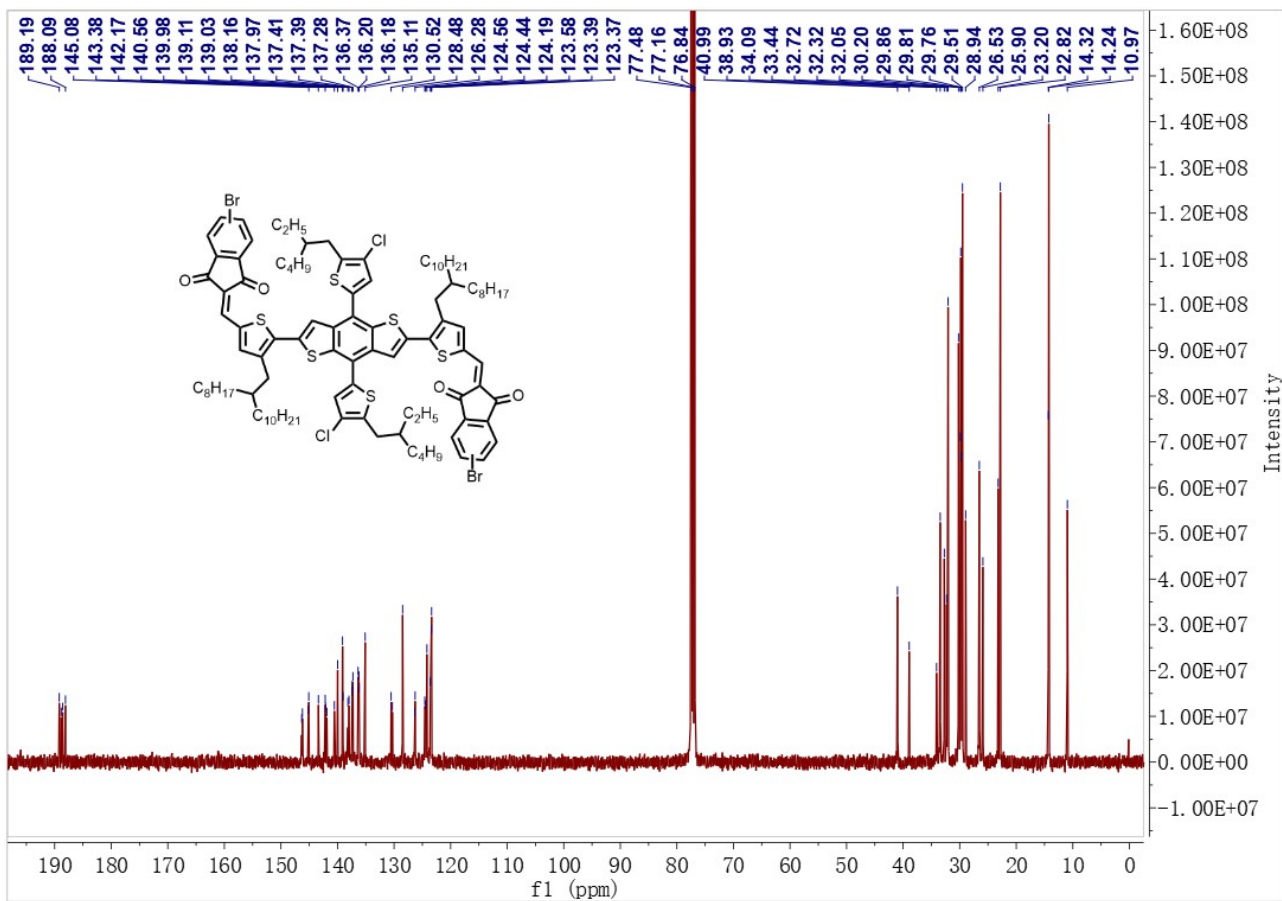**Figure S13.** ^{1}H-NMR spectra of the compound BDTCl-IDO-Br in CDCl$_3$.

Figure S14. ^{13}C-NMR spectra of the compound BDTCl-IDO-Br in CDCl$_3$.
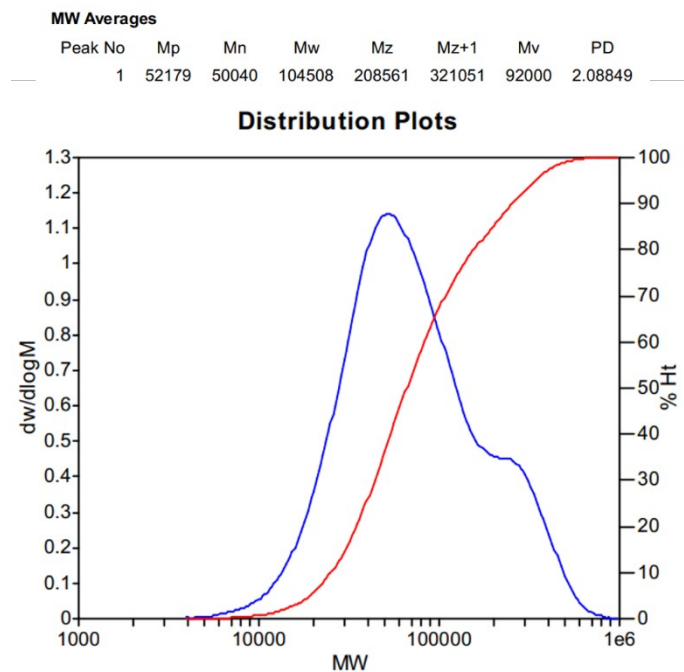

Figure S15. GPC result of polymer PBDT-ITO.

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	63452	45618	55577	64279	71407	54066	1.21831
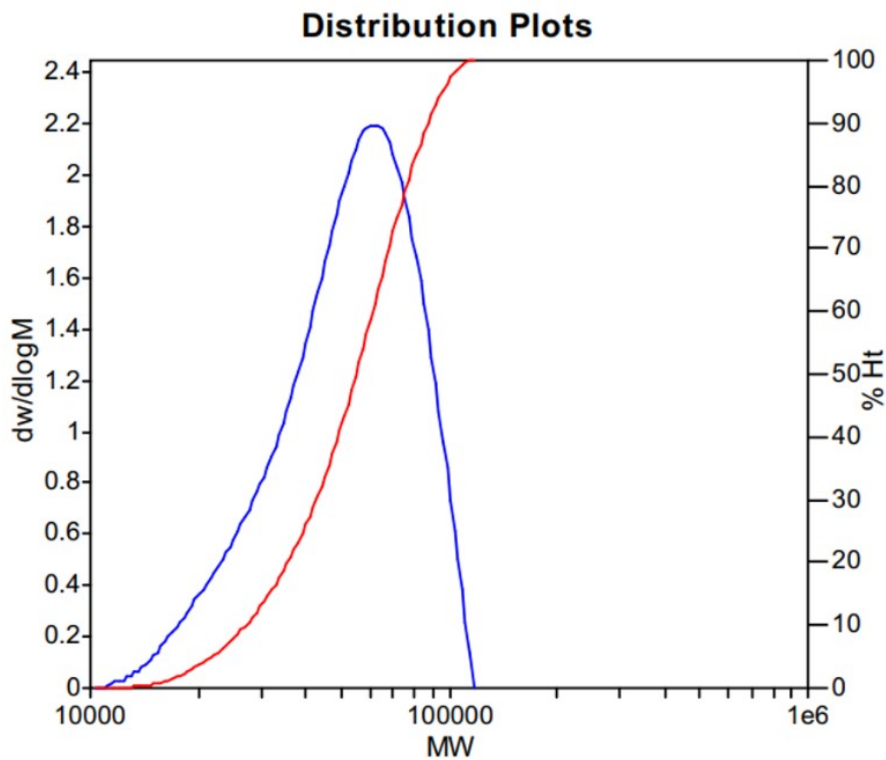
Figure S16. GPC result of polymer PBDTCl-ITO.

MW Averages

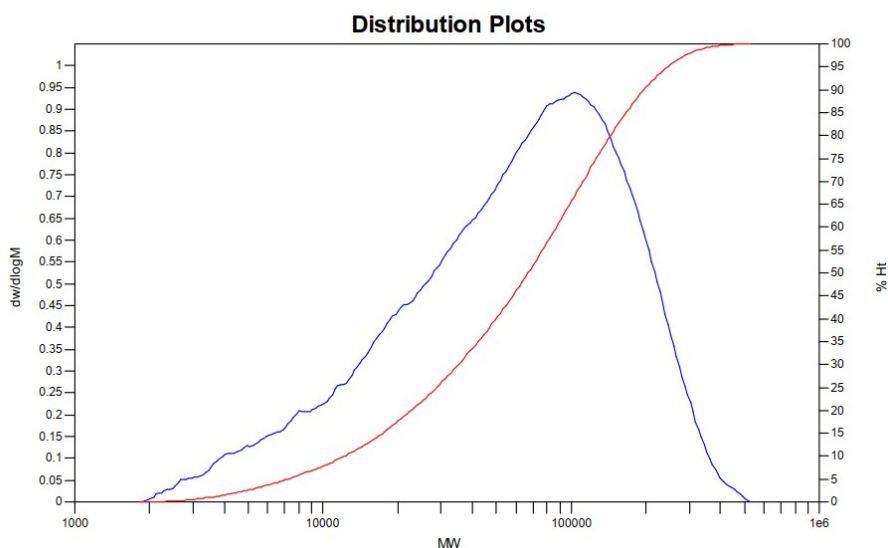| Mp: 103323	Mn: 28788	Mv: 77202	Mw: 87497
Mz: 154419	Mz+1: 210058	PD: 3.0394	

Figure S17. GPC result of polymer PBDTCl-IDO.

Reference

1   A. Tang, C. Zhan and J. Yao, *Chem. Mater.* 2015, **27**, 4719–4730.

2   G. W. Githaiga, A. W. Woodward, A. R. Morales, M. V. Bondar and K. D. Belfield, *J. Phys. Chem. C*, 2015, **119**, 21053−21059.

3   T. Jia, J. Zhang, K. Zhang, H.R. Dong, S. Dong, C.H. Tan, F. Liu, X. Wang and F. Huang, *J. Mater. Chem. A*, 2021,**9**, 8975-8983.

4   J. Jia, Q. Huang, T. Jia, K. Zhang, J. Zhang, J. Miao, F. Huang and C. Yang, *Adv. Energy Mater.*, 2021, **12**, 2103193.