Supporting Information

Asymmetric Fused-Ring Electron Acceptor with Two Distinct Terminal Groups for Efficient Organic Solar Cells

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Characterizations of compounds

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-300, using the residual solvent resonance of $CDCl_3$. Matrix-assisted laser desorption/ ionization fourier transform ion cyclotron resonance-mass spectrometry (MALDI-FTICR-MS) was determined on IonSpec 4.7 Tesla Fourier transform mass spectrometer. UV-vis absorption spectra were measured using a UV-vis spectrophotometer (Shimadzu UV-2700). Atomic force microscopy (AFM) images were investigated on a Dimension Icon AFM (Bruker) in a tapping mode. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were accomplished with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°. Cyclic voltammetry (CV) measurements was performed on a CHI660E electrochemical workstation in a three-electrode cell in anhydrous acetonitrile solvents solution of Bu_4NPF_6 (0.1 M) with a scan rate of 50 mV/s at room temperature under argon. A Ag/Ag^+ wire, two platinum wires were used as the reference electrode, counter electrode, and working electrode, respectively. The potential of Ag/Ag^+ reference electrode was internally calibrated by using ferrocene/ ferrocenium (Fc/Fc^+) as the redox couple. Space-charge-limited current (SCLC): The current density–voltage (*J*–*V*) characteristics of the hole or electron only devices are fitted by the Mott–Gurney law:

$$J = (9/8)\varepsilon_r\varepsilon_0\mu(V^2/L^3)$$

where J is the current density, ε_r is the dielectric permittivity of the active layer, ε_0 is the vacuum permittivity, L is the thickness of the active layer, μ is the mobility. $V=V_{app}-V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here). The mobility can be calculated from the slope of the $J^{0.5}\sim V$ curves.

Organic solar cells fabrication and characterization

Organic solar cells with inverted device architecture of ITO/ZnO/Polymers: Acceptor/MoO_3/Ag were fabricated. The ITO-coated glass substrates were firstly cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol for 20 minutes, respectively. After drying at 110 ℃ for one night, ZnO precursor

solution was spin coated at 4000 rpm and the ZnO layer was generated at 200 °C for 15 min in ambient atmosphere. The active layers with a thickness of 100 nm were spin-coated from a solution of polymers: acceptor with a weight ratio 1:1 in chlorobenzene. Solution with a volume ratio DIO of 0.25% was stirred overnight prior to cast. The active layers were allowed to heat at 100 °C for 10 min in a N_2-filled glovebox. The MoO_3 were deposited by sequential thermal evaporation of 3 nm followed by 90 nm of Ag. The device area is 4.00 mm^2. Current density-voltage (*J-V*) characteristics were measured using a Keithley 2400 Source Measure Unit. The currents were measured under 100 mW cm^{-2} simulated 1.5 Global (AM 1.5 G) solar simulator (Enli Technology Co., Ltd, SS-F5-3A). The light intensity was calibrated by a standard Si solar cell (SRC-2020, Enli Technology Co., Ltd). EQE spectra were carried out by using a QEX10 Solar Cell IPCE measurement system (PV Measurements, Inc.).

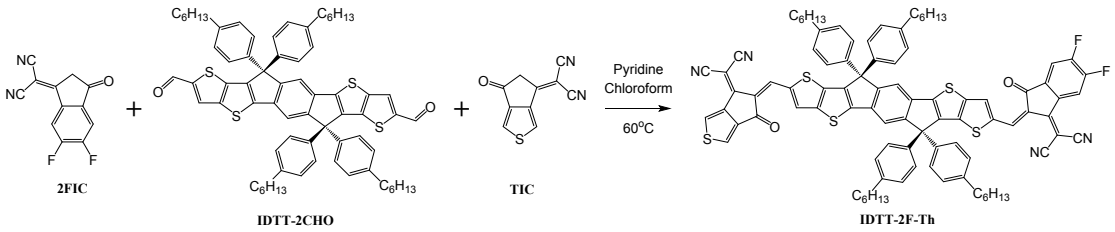
Materials

The polymer PBT1-C-2Cl and the small acceptor ITCPTC were synthesized according to the reported literatures.[1, 2] Other reagents and solvents were purchased from commercial sources and were used without further purification unless stated otherwise. Tetrahydrofuran (THF) and ether were distilled over sodium and benzophenone.

Synthesis of IDTT-2F-Th.

A solution of IDTT-2CHO (100 mg, 9.30×10^{-2} mmol), 2-(6-oxo-5,6-dihydro-4*H*-cyclopenta[*c*]thiophen-4-ylidene)malononitrile (20 mg, 10.23×10^{-2} mmol, 1.1 eq) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (21 mg, 9.30×10^{-2} mmol, 1 eq) in 20 mL chloroform was stirred at room temperature. Then pyridine (five drops) was added to the system. The reaction mixture was heated at 65 °C overnight. After cooling down to room temperature, the solvent was evaporated and the residue was purified with silica gel chromatography (eluent: petroleum ether/DCM, *v*/*v*, 2:3) to provide pure product as purple solid (0.41 g, 30%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (d, *J* = 17.3 Hz, 2H), 8.53 (dd, *J* = 9.9, 6.4 Hz, 1H), 8.35 (s, 1H), 8.22 (d, *J* =

16.9 Hz, 2H), 7.90 (s, 1H), 7.70-7.65 (m, 3H), 7.22 (d, J = 7.9 Hz, 8H), 7.15 (d, J = 7.9 Hz, 8H), 2.57 (t, J = 7.8 Hz, 8H), 1.64-1.54 (m, 8H), 1.38-1.25 (m, 24H), 0.88-0.83 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.78, 181.28, 156.06, 155.83, 155.78, 153.78, 153.09, 147.82, 147.71, 147.66, 147.47, 143.91, 143.81, 142.61, 142.57, 142.50, 142.17, 139.69, 139.44, 139.42, 138.86, 138.84, 138.45, 137.50, 137.21, 137.01, 136.88, 128.90, 128.82, 127.87, 127.75, 125.56, 121.72, 118.69, 118.65, 115.11, 114.94, 114.81, 114.25, 114.11, 112.33, 67.79, 63.24, 35.62, 31.72, 31.28, 29.20, 22.61, 14.12. MALDI-FTICR-MS [M] $C_{92}H_{78}F_2N_4O_2S_5$: m/z calcd. 1468.4696; found: 1468.4683.



Scheme S1. Synthesis route of IDTT-2F-Th.

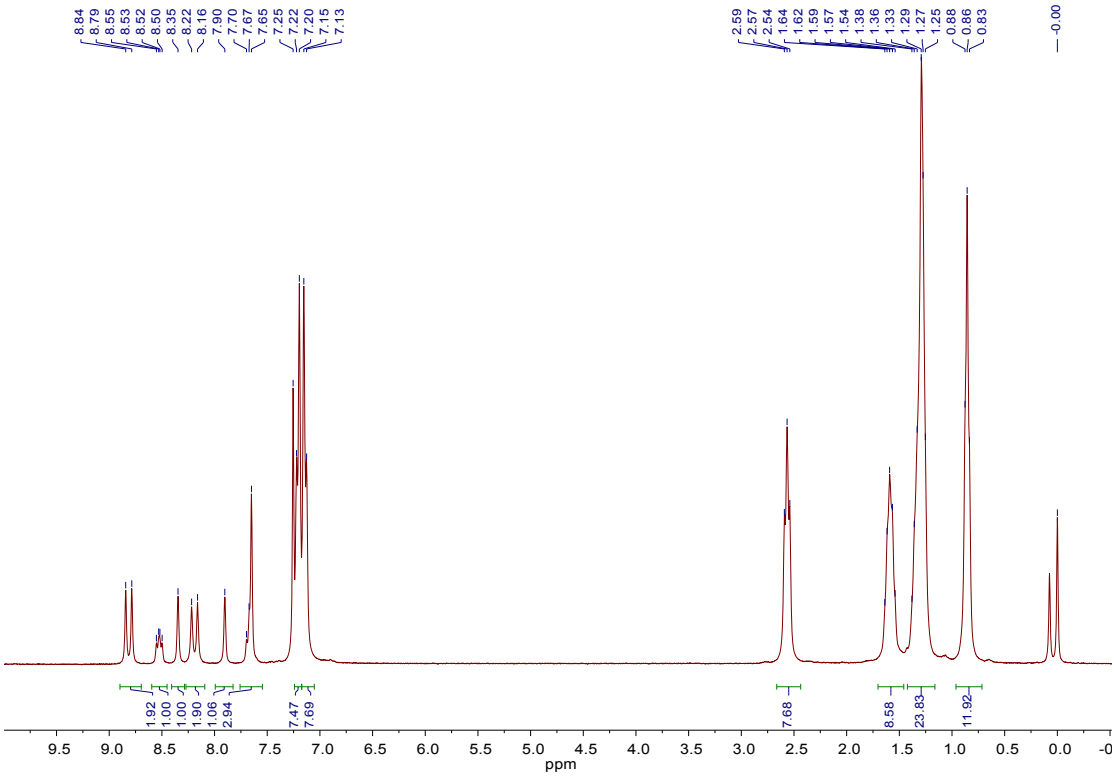


Fig. S1. The ^{1}H NMR spectra of IDTT-2F-Th in $CDCl_3$.

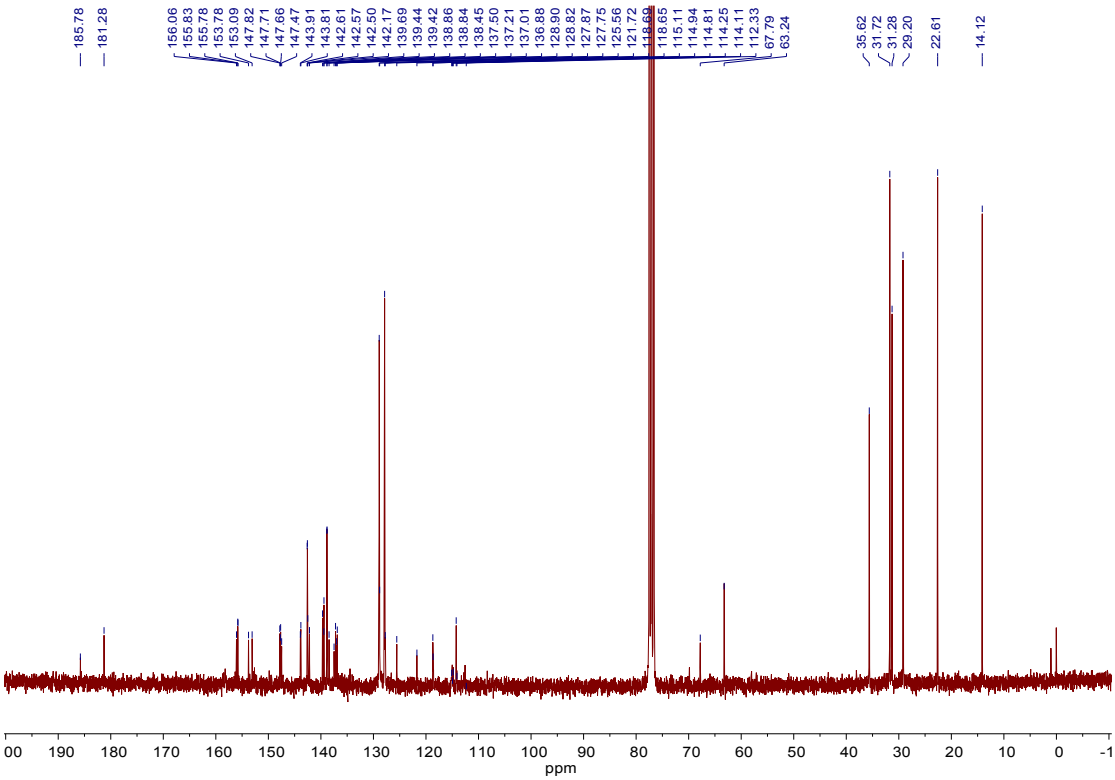


Fig. S2. The ^{13}C NMR spectra of IDTT-2F-Th in $CDCl_3$.

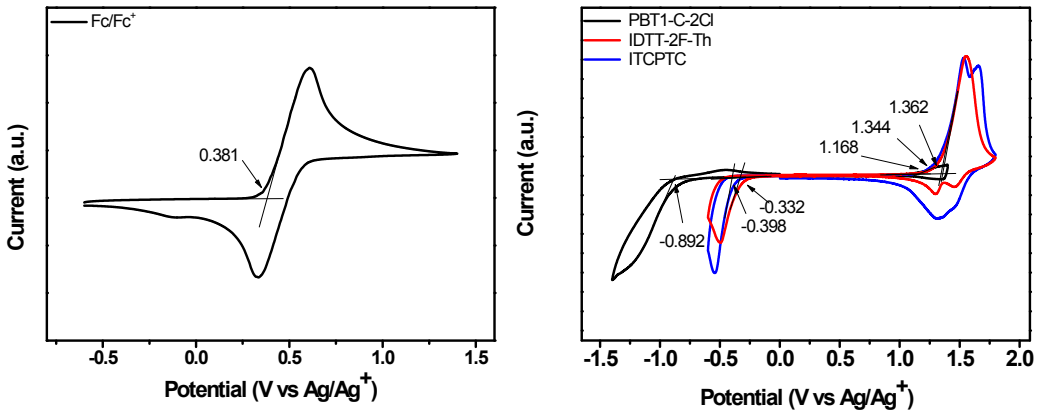


Fig. S3. The curves of the cyclic voltammetry (CV) measurements for ferrocene/ferrocenium on the left, and PBT1-C-2Cl, ITCPTC and IDTT-2F-Th on the right.

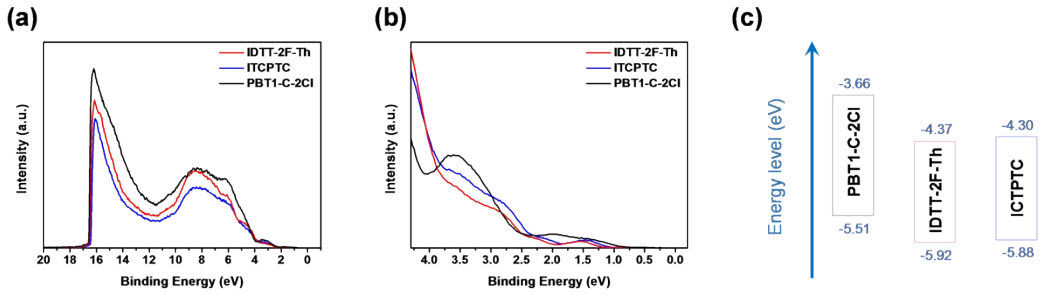


Fig. S4. (a, b) UPS spectra of PBT1-C-2Cl, ITCPTC and IDTT-2F-Th films and (c) the energy levels measured from UPS. The LUMO levels are calculated from the E_g^{opt} and the HOMO levels from UPS spectra.

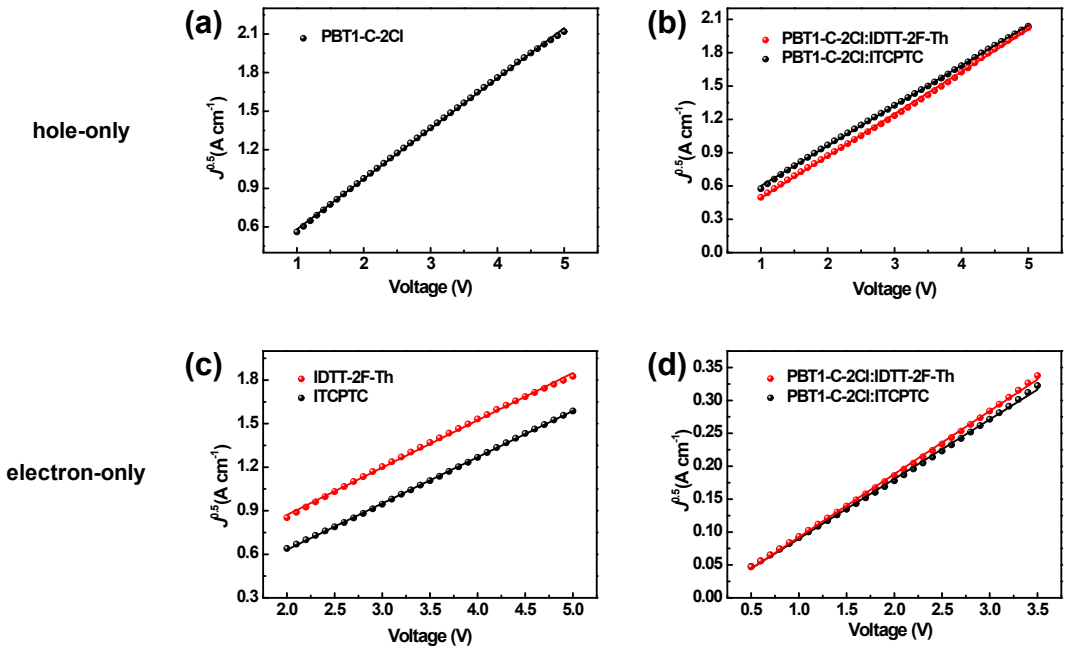


Fig. S5. (a, b) Characteristic curves of hole-only SCLC devices; (c, d) Characteristic curves of electron-only SCLC devices.

Table S1. Photovoltaic Performance of PBT1-C-2Cl:IDTT-2F-Th solar cells (10 devices).

PBT1-C-2Cl:IDTT-2F-Th	J_{sc} **(mA cm^{-2})**	V_{oc} **(V)**	FF **(%)**	PCE **(%)**
1	17.60	0.912	74.3	11.90
2	17.11	0.909	71.2	11.32
3	17.15	0.899	71.6	11.0
4	17.69	0.912	72.8	11.75
5	17.53	0.908	72.8	11.58
6	17.38	0.905	74.5	11.72
7	17.82	0.912	73.9	12.01
8	17.57	0.909	72.8	11.62
9	17.65	0.907	71.7	11.48
10	17.52	0.911	74.3	11.85

Table S2. Photovoltaic Performance of PBT1-C-2Cl:ITCPTC solar cells (10 devices).

PBT1-C-2Cl:ITCPTC	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
1	15.81	0.967	66.8	10.20
2	15.55	0.963	65.0	9.73
3	15.68	0.962	66.0	9.96
4	15.92	0.968	66.9	10.31
5	15.26	0.964	65.2	9.60
6	15.42	0.962	66.0	9.81
7	15.75	0.968	66.3	10.11
8	15.60	0.966	65.2	9.83
9	15.8	0.963	66.0	10.04
10	15.17	0.961	63.8	9.30

Table S3. The hole and electron mobilities according to SCLC measurements.

	μ_h/μ_e	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})
PBT1-C-2Cl	/	1.20×10^{-3}	/
ITCPTC	/	/	3.4×10^{-4}
IDTT-2F-Th	/	/	3.1×10^{-4}
PBT1-C-2Cl : ITCPTC	11.5	1.07×10^{-3}	9.3×10^{-5}
PBT1-C-2Cl : IDTT-2F-Th	10.3	9.0×10^{-4}	8.7×10^{-5}

1. D. Xie, T. Liu, W. Gao, C. Zhong, L. Huo, Z. Luo, K. Wu, W. Xiong, F. Liu, Y. Sun and C. Yang, *Solar RRL*, 2017, **1**, 1700044.
2. T. Liu, L. Huo, S. Chandrabose, K. Chen, G. Han, F. Qi, X. Meng, D. Xie, W. Ma, Y. Yi, J. M. Hodgkiss, F. Liu, J. Wang, C. Yang and Y. Sun, *Adv. Mater.*, 2018, **30**, 1707353.