Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Contents

1. Materials and measurements

All synthetic procedures were performed under argon atmosphere. Commercial chemicals were used as received. NMR spectra were recorded at 400 MHz and on a Bruker AVANCE spectrometer with CF-d_1 as the solvent and tetramethylsilane (TMS) as the internal standard. Optical absorption spectra were recorded on a JASCO V-570 spectrometer with a slit width of 2.0 nm and a scan speed of 1000 nm min^{-1}. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of 0.1 V s^{-1} and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode.

Atomic force microscopy (AFM) images were recorded using a Digital Inst ruments Nano scope llla multimode atomic force microscope in tapping mode under ambient conditions.

GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector.

Photovoltaic devices with inverted configuration were made by spin-coating a ZnO sol-gel at 4000 rpm for 60 s onto pre-cleaned, patterned ITO substrates. The photoactive layer was deposited by spin coating a chloroform solution containing **PMBBDT** and **ITIC-2Cl** or **BTP-2Cl** under nitrogen atmosphere. The thin films were then transferred into the N_2-filled glove box. MoO_3 (10 nm) and Ag (100 nm) were deposited by vacuum evaporation at ca. 4×10^{-5} Pa as the back electrode. The active area of the cells was 0.04 cm^2. The *J-V* characteristics were measured by a Keithley 2400 source meter unit under AM1.5G spectrum from a solar simulator (Enlitech model SS-F5-3A). Solar simulator illumination intensity was determined at 100 mW cm^{-2} using a monocrystal silicon reference cell with KG5 filter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The external quantum efficiency was measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak XT profilometer. The carrier mobilities were measured by space charge limit current (SCLC), where the device configuration of ITO/PEDOT:PSS/active layer/MoO_3/Ag was used for hole-only devices and ITO/ZnO/active layer/Ca/Al was used for electron-only devices.

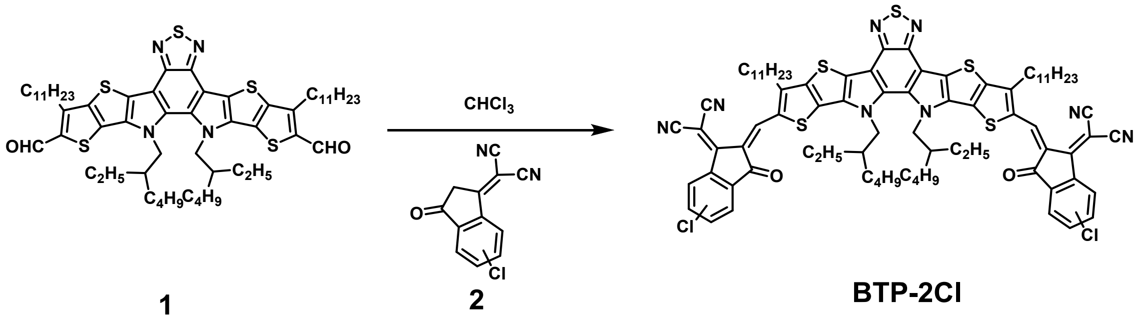
IQE: IQE spectra were obtained by the Transfer Matrix Model (TMM). The optical constants n and k for the active layer were collected by measuring reflectance and transmittance using a UV/VIS spectrometer (Lambda 950) with an integrating sphere of three films with different thickness. The same optical constants n and k were also used to model the Jsc-max by TMM with 100% IQE.

sEQE: The light of a quartz halogen lamp was chopped with 170Hz and coupled into the monochromator from Newport Inc.. The resulting monochromatic light was focused on the solar cells through the ITO side; Current of the device at short-circuit conditions was collected using a lock-in amplifier (Stanford Research System SR830) after through a pre-amplifier (Stanford Research System SR570). Then the EQEPV was obtained by the help of a calibrated silicon (Si) photodiode.

EL: Electroluminescence measurements were measured with a Shamrock sr 303i spectrograph from Andor Tech., and a Newton EM-CCD Si array detector and a Newton InGaAs detector.

EQE_{EL} was determined by a Hamamatsu silicon diode 1010B, a Keithley 6482 current meter and a Keithley 2400 source meter.

2. Synthesis of the BTP-2Cl acceptor



Scheme S1. Synthesis of the BTP-2Cl.

Compound 1 (0.15 g, 0.15 mmol), **Compound 2** (0.21 g, 0.9 mmol), pyridine (1 mL) and chloroform (45 mL) were added in a round bottom flask under nitrogen. The mixture was stirred at 65 °C overnight. After cooling to room temperature, the mixture was poured into methanol and filtered. The residue was purified with column chromatography on silica gel using dichloromethane/petroleum ether (1/1, v/v) as the eluent to give a dark blue solid BTP-2Cl (0.12 g, 58% yield).^{1}H NMR δ (ppm): 9.18 (s, 2H), 8.64-8.69 (t, 2H), 7.87-7.89 (d, 2H), 7.69-7.72 (t, 2H), 4.77-4.78 (d, 4H), 3.22-3.26 (t, 4H), 2.08-2.11 (t, 2H), 1.85-1.93 (m, 4H), 1.48-1.55 (d, 4H), 1.17-1.52 (m, 44H), 1.02-1.03 (d, 6H), 0.85-0.88 (t, 6H), 0.75-0.77 (m, 6H). ^{13}C NMR δ (ppm): 187.10, 159.81, 159.39, 153.66, 147.52, 145.12, 141.67, 141.33, 141.00, 138.42, 138.11, 137.84, 137.79, 135.89, 135.81, 135.44, 135.08, 134.74, 134.29, 133.77, 133.41, 126.35, 125.30, 124.51, 120.40, 115.13, 113.60, 68.91, 68.35, 55.72, 40.41, 31.92, 31.18, 29.82, 29.72, 29.65, 29.63, 29.52, 29.46, 29.34, 27.71, 23.31, 22.84, 22.69, 14.11, 13.74, 10.29, 10.24. MS(MALDI-TOF) m/z: $[M]^+$, Calcd for $C_{82}H_{88}Cl_2N_8O_2S_5$: 1446.5; found: 1446.6.

3. CV curves

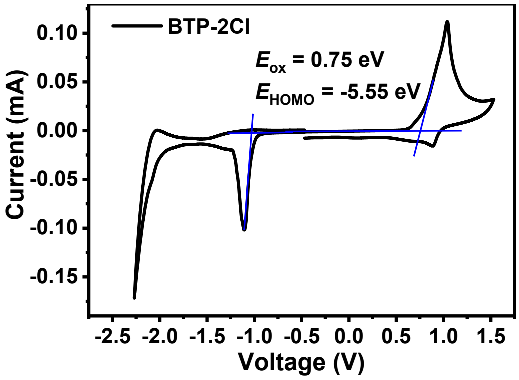


Figure S1. Cyclic voltammograms of BTP-2Cl in thin films. The HOMO level was determined by using a work function value of - 4.8 eV for Fc/Fc$^+$.

Table S1. Optical and electrochemical properties of the PMBBDT, ITIC-2Cl and BTP-2Cl.

Materials	E_g^{film} (eV)[a]	HOMO (eV)[b]	LUMO (eV)[c]
PMBBDT	1.41	-5.31	-3.90
ITIC-2Cl	1.56	-5.70	-4.14
BTP-2Cl	1.38	-5.55	-4.17

[a] Optical band gap calculated from the absorption edge of thin films. [b] Determined using a work function value of - 4.8 eV for Fc/Fc$^+$. [c] Determined as $E_{HOMO} + E_g^{film}$.

4. Solar cells

Table S2. Characteristics of PMBBDT:ITIC-2Cl solar cells spin coated from different proportions of additives.

Ratio	Solvent	Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	TA (°C)
1:1	CF	50	12.52	0.72	47.75	4.31	130

1:1	CF:0.2% DIO	65	14.75	0.71	50.20	5.27	130
1:1	CF:0.5% DIO	60	15.72	0.72	59.50	6.72	130
1:1	CF:1% DIO	75	7.58	0.63	50.50	2.41	130

Table S3. Characteristics of PMBBDT:ITIC-2Cl solar cells spin coated from different ratio of donor to acceptor.

Ratio	Solvent	Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	TA (°C)
1:1	CF:0.5% DIO	65	15.72	0.72	59.50	6.72	130
1:1.5	CF:0.5% DIO	60	17.40	0.72	60.81	7.56	130
1:2	CF:0.5% DIO	80	16.54	0.71	50.34	5.94	130
1.2:1	CF:0.5% DIO	50	9.77	0.71	52.63	3.64	130

Table S4. Characteristics of PMBBDT:ITIC-2Cl solar cells spin coated from different thickness.

Ratio	Solvent	Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	TA (°C)
1:1.5	CF:0.5% DIO	55	11.664	0.733	51.2	4.38	130
1:1.5	CF:0.5% DIO	65	15.716	0.718	59.5	6.72	130
1:1.5	CF:0.5% DIO	100	9.476	0.735	45.3	3.15	130

Table S5. Characteristics of PMBBDT:BTP-2Cl solar cells spin coated from different proportions of additives.

Ratio	Solvent	Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	TA (°C)
1:1.5	CF	70	17.486	0.773	54.6	7.38	130
1:1.5	CF	70	16.247	0.802	49.15	6.4	none
1:1.5	CF:0.5% DIO	60	20.224	0.752	63.61	9.67	130
1:1.5	CF:1% DIO	65	18.666	0.737	58.54	8.05	130

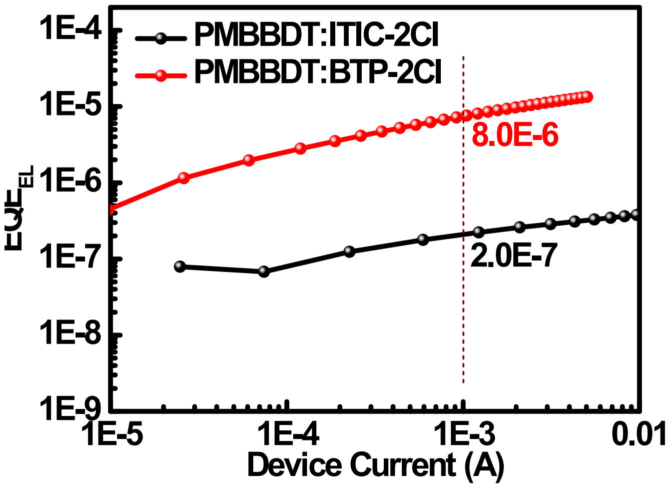


Figure S2. EQE$_{EL}$ of photovoltaic devices related to current.

5. AFM

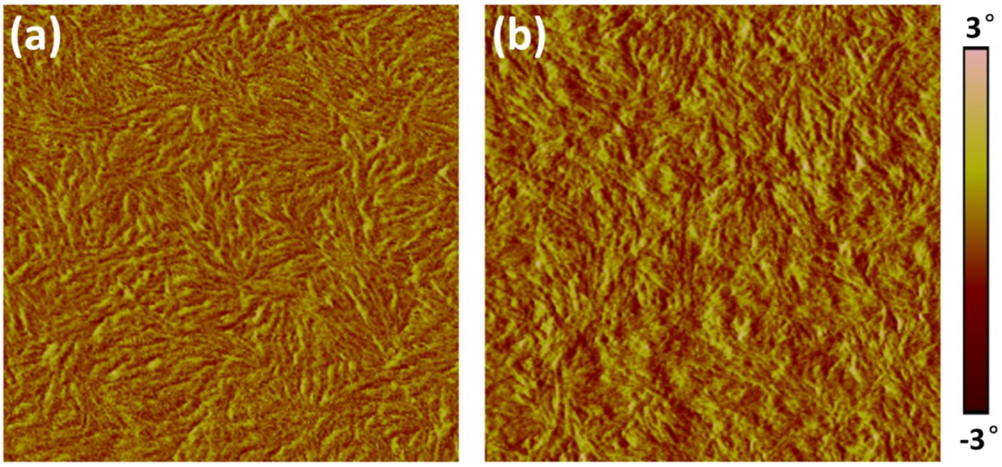


Figure S3. AFM phase images. (a) PMBBDT:ITIC-2Cl, (b) PMBBDT:BTP-2Cl.

6. GIWAXS

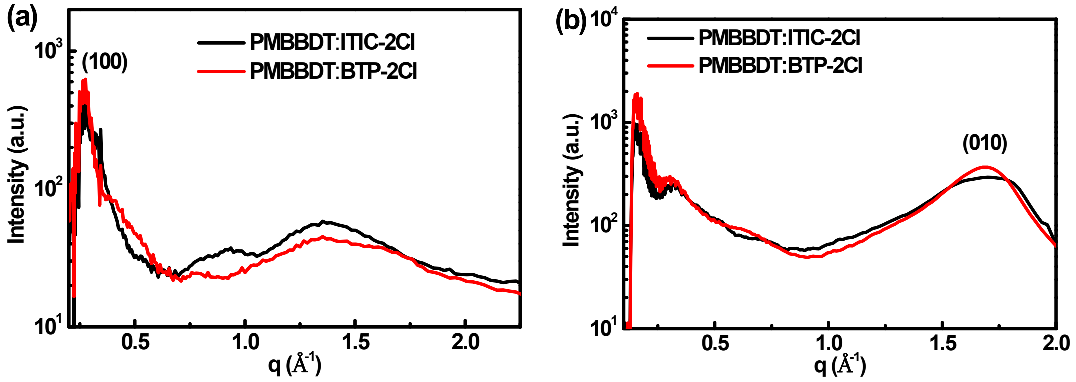


Figure S4. The (a) IP and (b) OOP cuts of the corresponding GIWAXS patterns.

Table S6. Crystallographic parameters of the blended thin films fabricated from CF with thermal annealing at 130 °C for 10 min. IP: in-plane. OOP: out-of-plane.

	(100) (IP)			(010) (OOP)		
	q (Å^{-1})	*d*(Å)	CL(Å)	*q* (Å^{-1})	*d*(Å)	CL(Å)
PMBBDT:ITIC-2Cl	0.29	21.59	58.83	1.67	3.74	14.10
PMBBDT:BTP-2Cl	0.27	22.59	110.60	1.66	3.77	17.70

7. SCLC

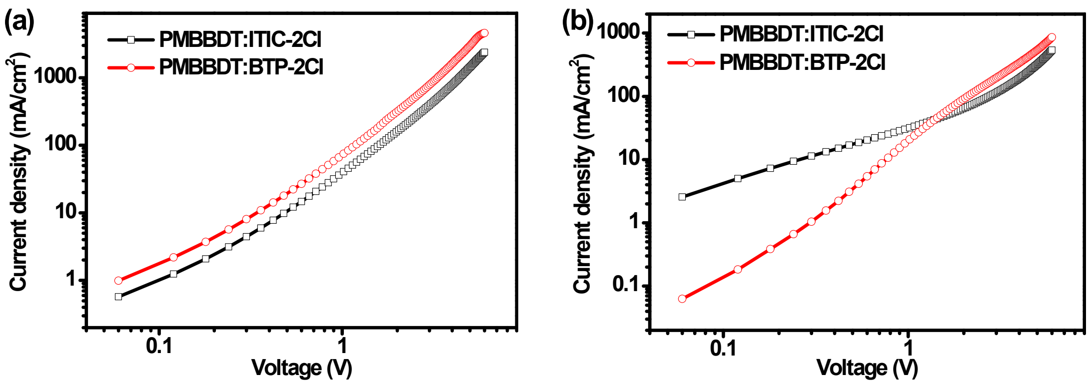


Figure S5. *J*-*V* characteristics in the dark for (a) hole-only devices and (b) electron-only devices. The device configuration of ITO/PEDOT:PSS/active layer/MoO_3/Ag was used for hole-only devices and ITO/ZnO/active layer/Ca/Al was used for electron-only devices.

Table S7. Hole and electron mobility of optimized Solar Cells. The values are exacted from SCLC measurement.

Active layer	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h /μ_e
PMBBDT:ITIC-2Cl	1.12×10^{-3}	1.15×10^{-4}	9.73
PMBBDT:BTP-2Cl	1.42×10^{-3}	2.47×10^{-4}	5.74

8. NMR spectra and MALDI-TOF

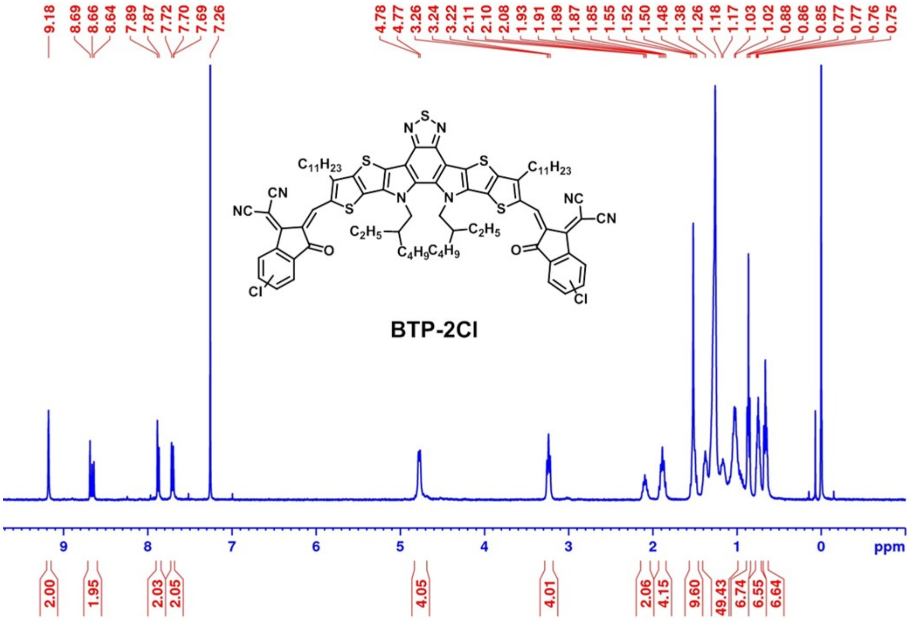


Figure S6. ^{1}H NMR of BTP-2Cl in $CDCl_3$.

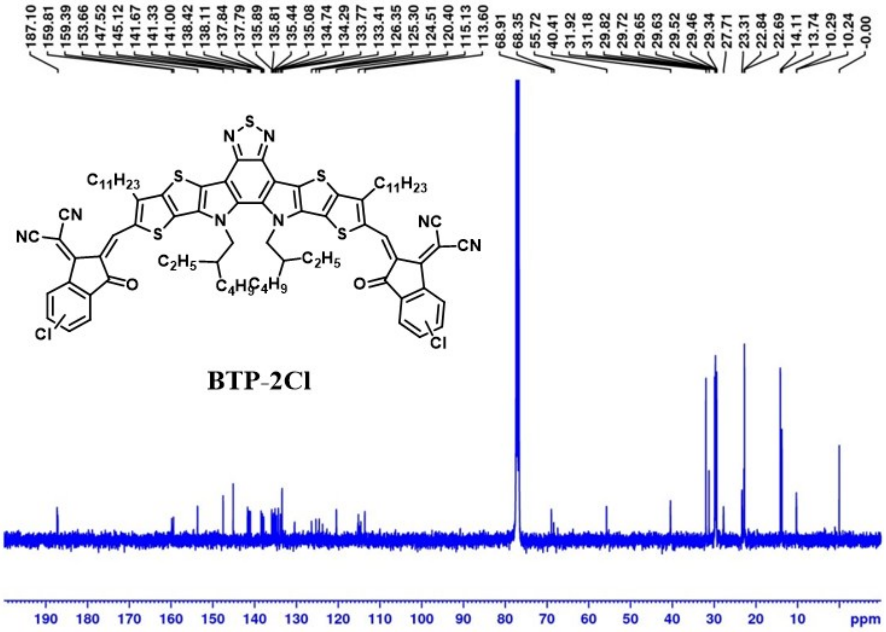


Figure S7. ^{13}C NMR of BTP-2Cl in $CDCl_3$.

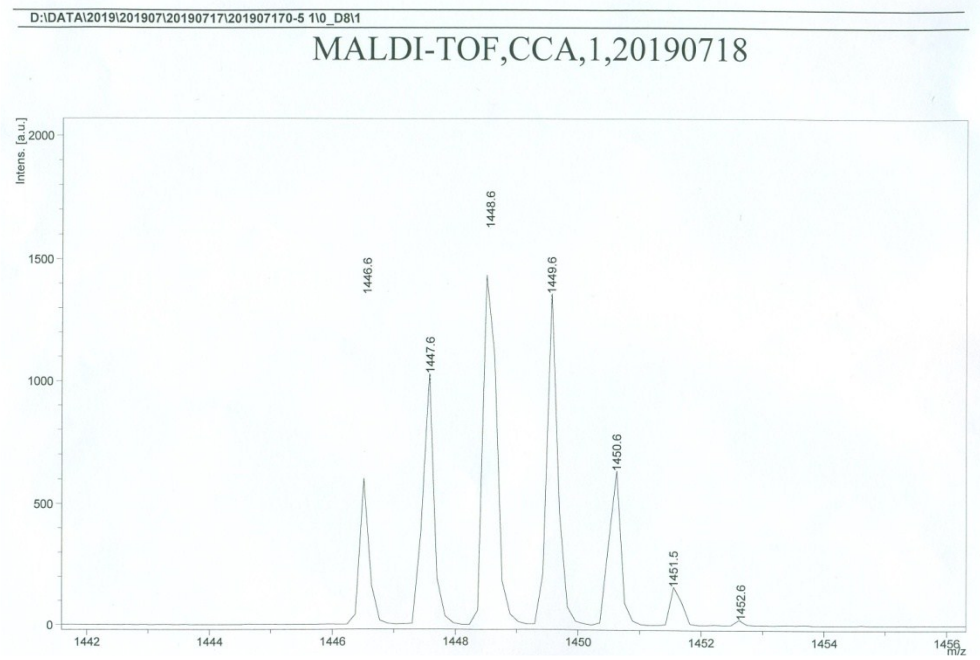


Figure S8. The low resolution mass spectrometry (MALDI-TOF) of BTP-2Cl.