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Supplementary Information

Efficient polymer solar cells based on a cathode interlayer of dicyanomethylenated indacenodithiophene derivative with large π-conjugated and electron-deficient properties

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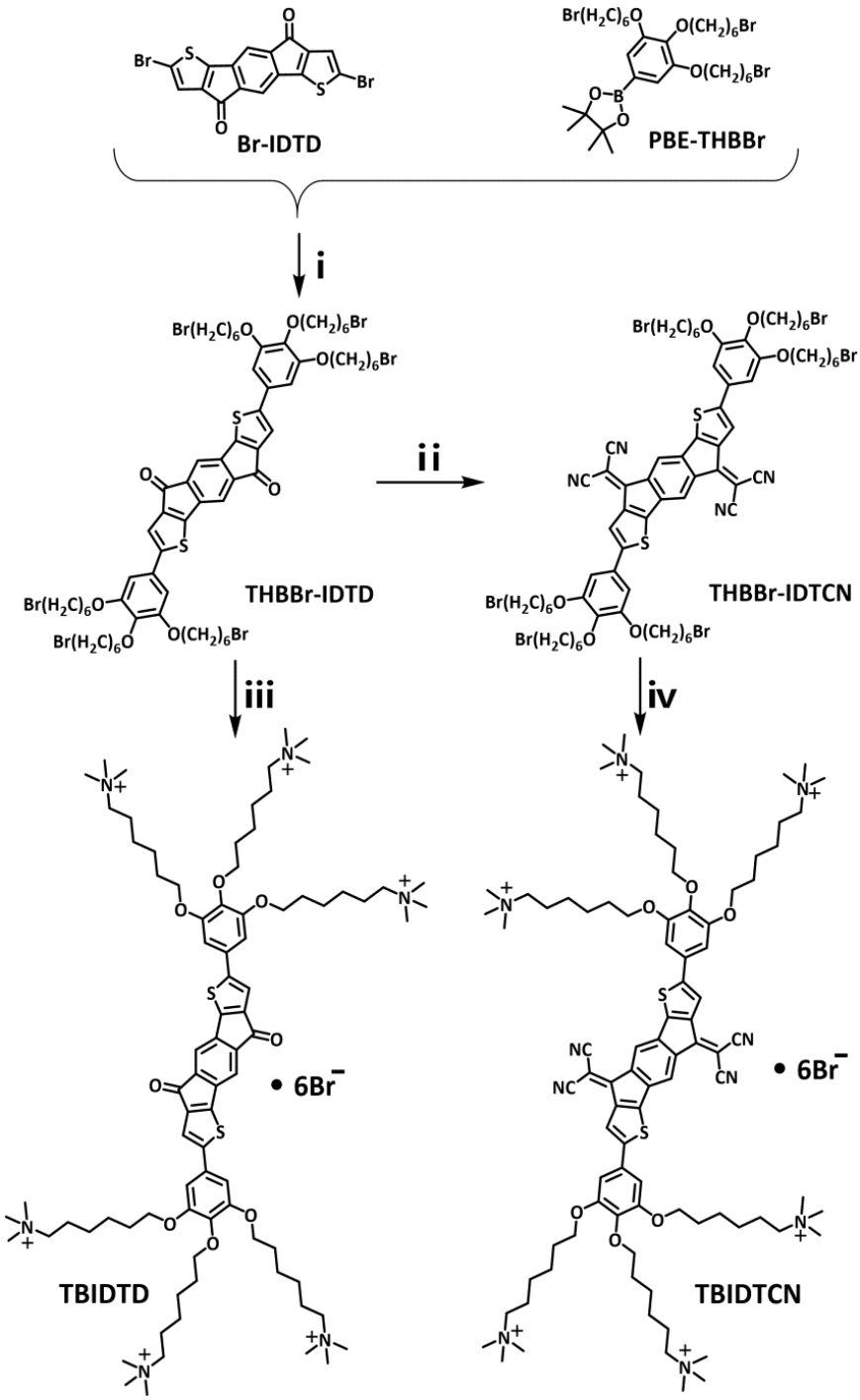
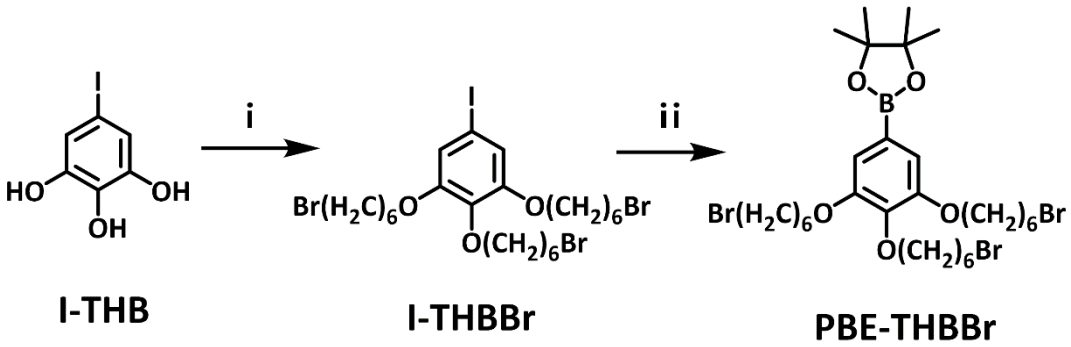
1. Synthesis and characterizations



Scheme S1. Synthesis procedures of TBIDTD and TBIDTCN. i. K_2CO_3, $Pd(PPh_3)_4$, toluene, reflux, 16 h; ii. malononitrile $TiCl_4$, pyridine, $CHCl_3$, reflux, 24 h; iii. Trimethylamine, THF, 48 h; iv. Trimethylamine, THF, 48 h.



Scheme S2. Synthesis of PBE-THBBr. **i.** 1,6-Dibromohexane, K_2CO_3, DMF, r.t., 38 h; **ii.**. n-BuLi, THF, -78 ℃, 12h.

I-THBBr: 5-Iodo-1,2,3-trihydroxybenzene (I-THB) (3.78 g, 15 mmol) was dissolved in N,N-Dimethylformamide (DMF) (80 mL), and the solution was degassed with nitrogen for 15 min. Then 1,6-Dibromohexane (18.3 g, 75 mmol) and K_2CO_3 (20.7 g, 150 mmol) were added to the system. The reaction mixture was stirred at room temperature for 38 hours, after that, water was added to quench the reaction and the mixture was extracted with ethyl acetate, then the organic phase was washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified with flash column chromatography (CH_2Cl_2/hexane 1: 2) to get the product as white solid (8.45 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 4.00-3.90 (m, 6H), 3.4-3.42 (m, 6H), 1.97-1.87 (m, 6H), 1.87-1.80 (m, 4H), 1.79-1.72 (m, 2H), 1.59-1.48 (br, 12H). GC-MS (m/z): $[M]^+$ calculated for $C_{24}H_{38}Br_3IO_3$: 741.2. Found: 741. Anal. Calcd for $C_{24}H_{38}Br_3IO_3$: C, 38.89; H, 5.17. Found: C, 38.92; H, 5.28.

PBE-THBBr: A solution of I-THBBr (7.41 g, 10 mmol) in dry THF (80 mL) was stirred under N_2 at -78 ℃. After 10 min, a solution of n-BuLi (4.6 mL, 11 mmol) in hexane was added dropwise. The mixture kept on stirring for 90 min at -78 ℃, then the formed organolithium derivative was quenched by isopropoxyboronic acid pinacol ester (2.23 g, 12 mmol). The reaction mixture was stirred at room temperature for another 12 hours, subsequently. Then an

excess aqueous solution of ammonium chloride was added to the system to quench the reaction and the mixture was extracted with Et_2O. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified with flash column chromatography (CH_2Cl_2/hexane 3:1) to get the product as white solid (5.26 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 2H), 4.10-3.92 (m, 6H), 3.42 (t, J = 6.8 Hz, 6H), 1.96-1.68 (br, 12H), 1.60-1.43 (br, 12H), 1.33 (s, 12H). GC-MS (m/z): $[M]^+$ calculated for $C_{30}H_{50}BBr_3O_5$: 741.3. Found: 741. Anal. Calcd for $C_{30}H_{50}BBr_3O_5$: C, 48.61; H, 6.80. Found: C, 48.95; H, 6.45.

2. Supplementary Figures

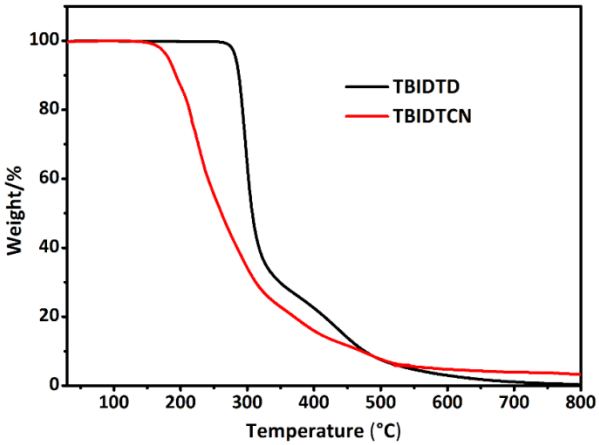


Fig. S1. TGA curves of TBIDTD and TBIDTCN.

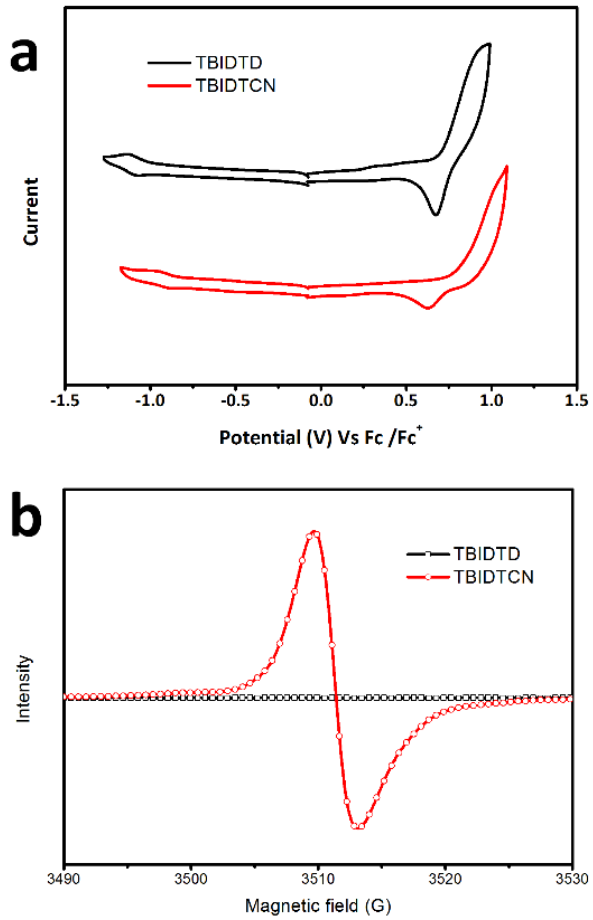


Fig S2. (a) Cyclic voltammograms of CILs at room temperature, 0.1 M TBAPF6 in CH_3CN solution; (b) EPR spectra of the CILs in the solid state.

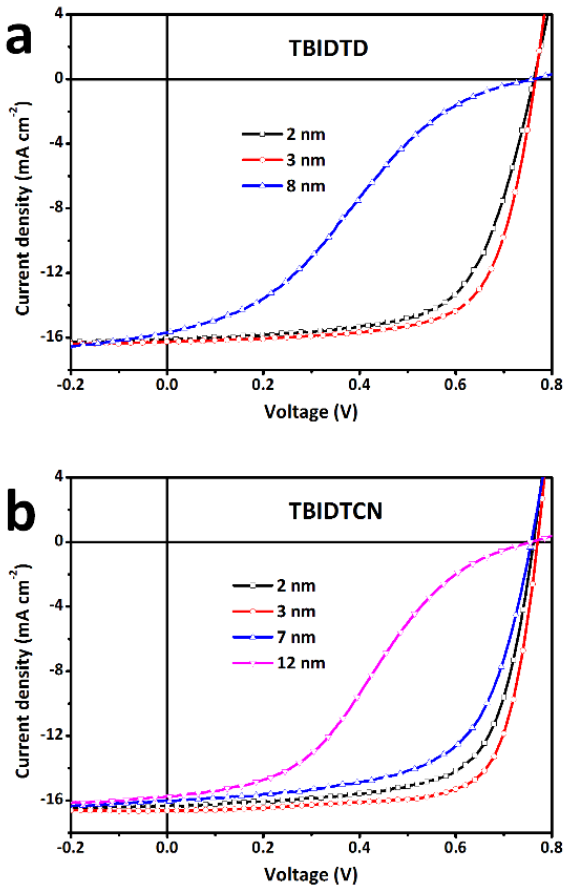


Fig. S3. Current density-voltage (J-V) curves of the PTB7:$PC_{71}BM$ based devices with different thicknesses of (a) TBIDTD and (b) TBIDTCN under the 100 mW cm^{-2} AM 1.5G irradiation.

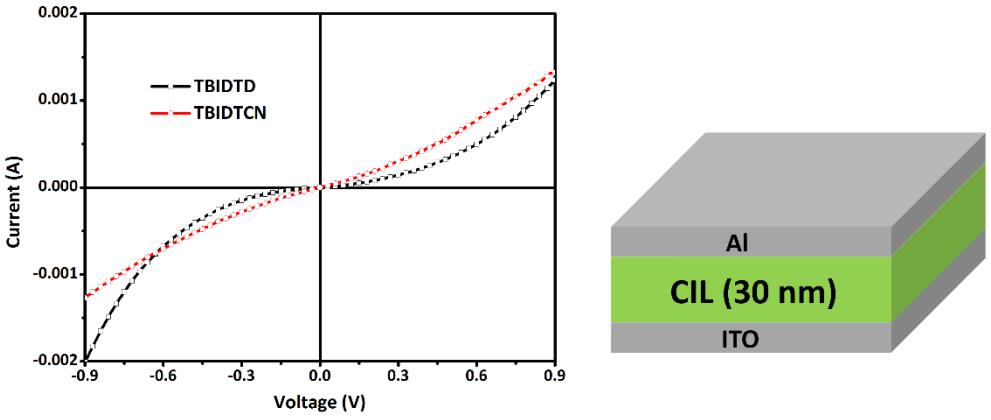


Fig. S4. (a) I–V curves of the conductivity measurements of TBIDTD and TBIDTCN with (b) a configuration of ITO/TBIDTD (TBIDTCN)/Al.

3. Supplementary Tables

Table S1. Device parameters of the PTB7:$PC_{71}BM$ based PSCs with different thicknesses of TBIDTD and TBIDTCN.

CIL	Thickness (mg ml^{-1})	Thickness (nm)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE_{max} (%)
TBIDTD	0.3	2	16.14	0.763	66.2	8.15
	0.5	3	16.23	0.766	69.3	8.62
	1	8	15.69	0.758	31.2	3.71
TBIDTCN	0.3	2	16.35	0.762	68.9	8.60
	0.5	3	16.57	0.768	72.2	9.19
	1	7	16.03	0.755	65.2	7.89
	1.5	12	15.75	0.755	35.2	4.18

Table S2 Conductivity results, the conductivities were calculated from Ohm's law at the linear regions.

CIL	Thickness (nm)	Conductivity (S m^{-1})
TBIDTD	30	2.29×10^{-5}
TBIDTCN	30	6.13×10^{-5}