Supporting Information

Approach to high open-circuit voltage polymer solar cells via alcohol/water-soluble cathode interlayer based on anthrathiadiazole derivatives

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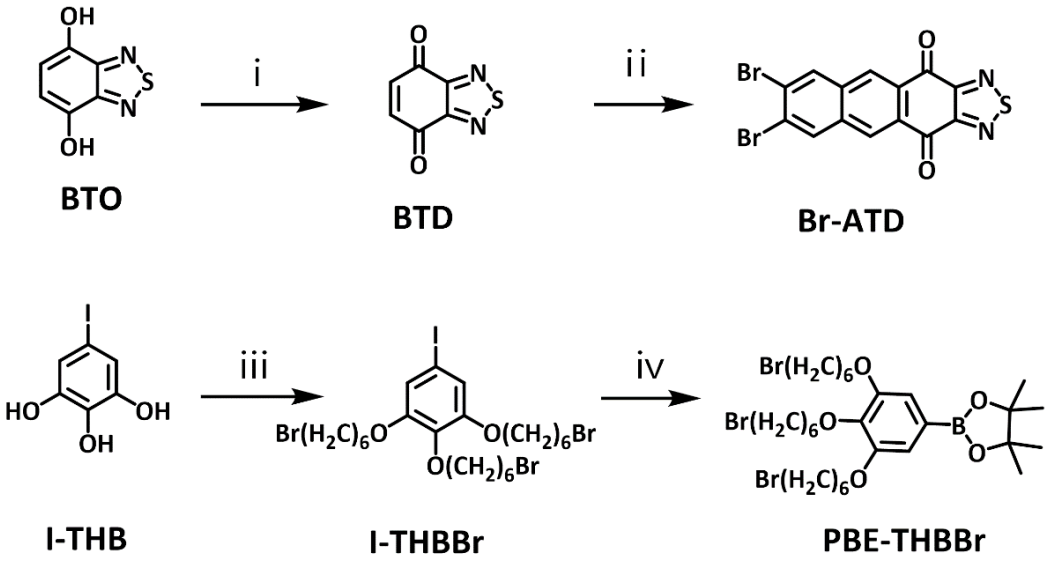
1. Synthesis and characterizations



Scheme S1 Synthesis of Br-ATD and PBE-THBBr. **i.** Ag_2O, dioxane, r.t., 12h; **ii.** 1,2-dibromo-4,5-bis(bromomethyl)benzene, KI, DMF, 90 °C 20 h; **iii**. 1,6-Dibromohexane, K_2CO_3, DMF, r.t., 38 h; **iv**. n-BuLi, THF, -78°C, 12h.

BTD: To a 100 ml flask 4,7-dihydroxylbenzothiadiazole (BTO) (3.36 g, 20 mmol), silver oxide (6.5 g, 28 mmol), anhydrous sodium sulfate (1.42 g, 10 mmol), and 40 ml dioxane were added. The mixture was stirred over night at room temperature (r.t.), and filtered through a Celite pad. The filter cake was washed with 50 ml dioxane and the filtrates were concentrated under reduced pressure. Recrystallization of the residue from carbon tetrachloride-chloroform (8: 1) afforded needles of PTD as a yellowish solid (2.66 g, 80%). ^{1}H NMR (500 MHz, DMSO) δ 7.22 (s, 2H). GC-MS (m/z): $[M]^+$ calculated for $C_6H_2N_2O_2S$: 166.2. Found: 166. Anal. Calcd for $C_6H_2N_2O_2S$: C, 43.37; H, 1.21; N, 16.86; S, 19.30. Found: C, 43.02; H, 1.31; N, 16.52; S, 19.08.

Br-ATD: 3.32 g BTD (20 mmol), 1,2-dibromo-4,5-bis(bromomethyl)benzene (9.28 g, 22 mmol) and 150 ml N,N-Dimethylformamide (DMF) were heated to 90 °C in nitrogen atmosphere, then 22.1 g KI (133 mmol) was added to the mixture. After vigorously stirring and heating for 20 hours at 90 °C, the mixture was cool down to room temperature and filtered, the filter cake was washed

with acetone, tetrahydrofuran, ethyl ether in turn, and the product was obtained as a yellowish solid after drying under vacuum (5.21 g, 61%). ^{1}H NMR (500 MHz, DMSO) δ 8.96 (s, 2H), 8.93 (s, 2H). GC-MS (m/z): $[M]^+$ calculated for $C_{14}H_4Br_2N_2O_2S$: 424.1. Found: 424. Anal. Calcd for $C_{14}H_4Br_2N_2O_2S$: C, 39.65; H, 0.95; N, 6.61; S, 7.56. Found: C, 36.45; H, 1.05; N, 6.65; S, 7.85.

I-THBBr: 5-Iodo-1,2,3-trihydroxybenzene (I-THB) (2.52 g, 10 mmol) was dissolved in DMF (70 mL), and the solution was degassed with nitrogen for 15 min. Then 1,6-Dibromohexane (12.2 g, 50 mmol) and K_2CO_3 (13.8 g, 100 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 (5.56 g, 75%). ^{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 (3.71 g, 5 mmol) in dry tetrahydrofuran (THF) (60 mL) was stirred under N_2 at -78 °C. After 10 min, a solution of n-Butyllithium (n-BuLi) (2.5 mL, 6 mmol) in hexane was added dropwise. The mixture was kept stirring for 90 min at -78 °C, then the formed organolithium derivative was quenched by isopropoxyboronic acid pinacol ester (1.12 g, 6 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

(2.6 g, 70%). ^{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. TGA curves of PBATD and TBATD

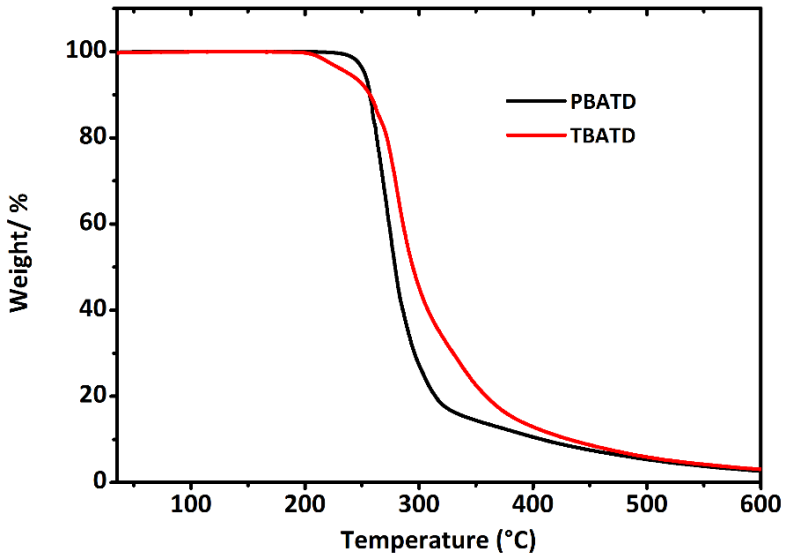


Fig. S1. TGA curves of PBATD and TBATD.

3. Thickness tests through the absorption spectra of PBATD and TBATD

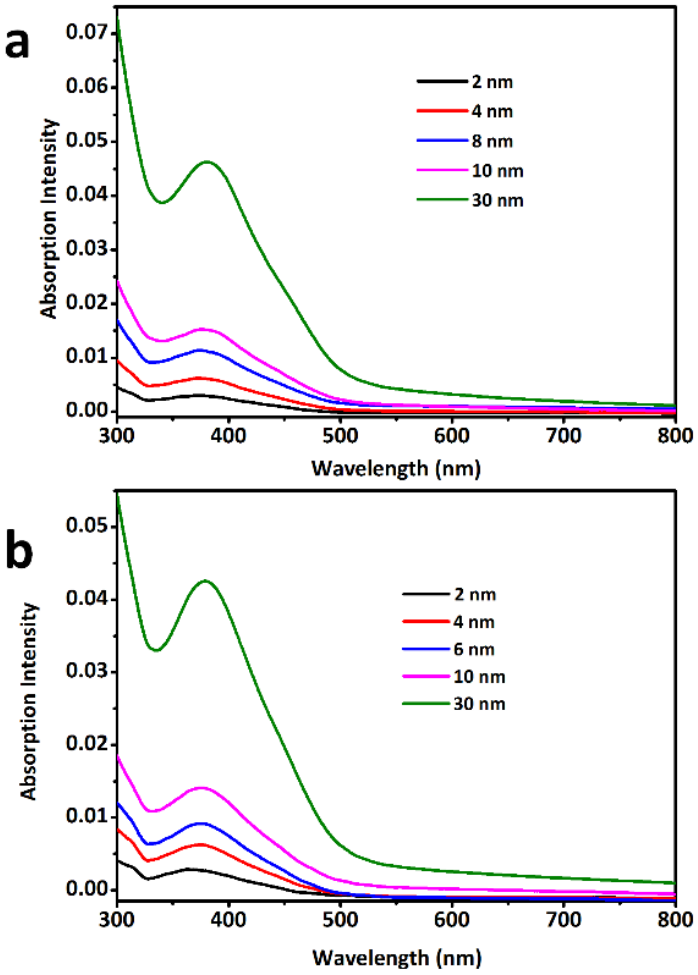


Fig. S2. The absorption spectra of (a) PBATD and (b) TBATD films with different thicknesses on the quartz substrates. The thicknesses of 30 nm for PBATD film and TBATD film were determined by the profilometer.

Table S1 The film thicknesses of PBATD and TBATD monitored by different concentrations.

CIL	**PBATD**					**TBATD**				
Concentration (mg ml^{-1})	0.4	0.8	1.2	1.6	5.0	0.4	0.8	1.2	1.6	5.0
Thickness (nm)	2	4	8	10	30	2	4	6	10	30

4. Device characteristics of the PCDTBT:$PC_{71}BM$ based PSCs with different thicknesses of PBATD and TBATD

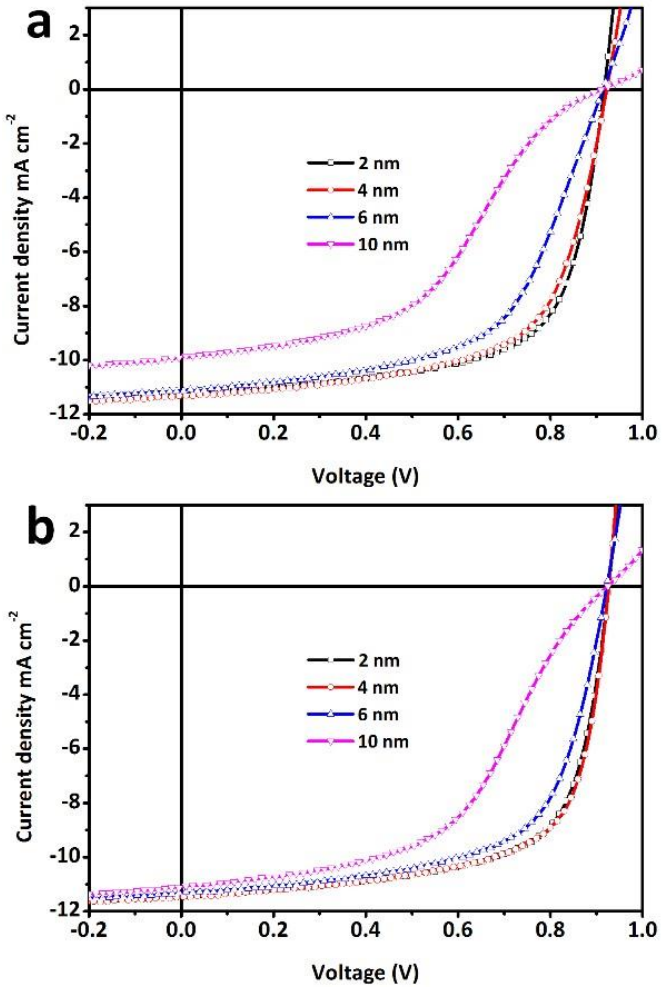


Fig. S3. Current density-voltage (J-V) curves of the PCDTBT:$PC_{71}BM$ based devices with different thicknesses of (a) PBATD and (b) TBATD under the 100 mW cm^{-2} AM 1.5G irradiation.

Table S2. Device parameters of the PCDTBT:$PC_{71}BM$ based PSCs with different thicknesses of PBATD and TBATD.

CIL	Thickness (nm)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE_{max} (%)	R_s (Ω cm^2)
PBATD	2	11.27	0.92	67.3	6.98	7.3
	4	11.34	0.92	64.5	6.73	10.6
	8	11.12	0.91	59.5	6.02	21.2
	10	10.14	0.91	45.3	4.18	135.8
TBATD	2	11.43	0.93	67.7	7.20	6.6
	4	11.46	0.93	68.1	7.26	5.5
	6	11.30	0.92	64.2	6.67	10.3
	10	11.10	0.92	50.3	5.14	63.3