Supporting Information for

Novel Perylenediimide-Based Polymers with Electron-Deficient Segment as the Comonomer for Efficient All-Polymer Solar Cells

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Characterization. ^{1}H NMR spectra were recorded on a Bruker AV400 NMR spectrometer and used tetramethylsilane (TMS) as an internal standard in $CDCl_3$. The molecular weight was determined by GPC using THF as the eluent and monodispersed polystyrene as the standard. The UV-Vis spectra of polymers were measured on with a TU-1601 spectrophotometer by using a 1 cm glass cuvette. Cyclic voltammetry (CV) was performed in 0.1M tetrabutylammonium hexafluorophosphate in acetonitrile at a scan rate of 100 mV/s with ITO as the working electrode, Pt wire as the counter electrode and Ag/Ag^{+} as the reference electrode. Atomic force microscopy (AFM) images were obtained using a NanoMan VS microscope in the tapping mode. The thickness of the active layer of the device was measured via a VeecoDektak 150 surface profiler.

All-polymer solar cell fabrication. The detailed fabrication is listed in Supporting Information. A patterned ITO was pre-cleaned by detergent, deionized water, acetone and 2-propanol for 15 min, respectively, under ultrasonic condition. The cleaned ITO was then treated by UV oxygen to form the hydrophilic surface. The PEDOT:PSS solution was spin-coated on the ITO at 3500 rpm for 30s and dried over 150 ^{o}C for 15 min under air. The PTB7-Th:polymer acceptor solution (optimized weight ratio of 1:1) in chlorobenzene with different amount solvent additives was then spin-coated above PEDOT:PSS layer at a total concentration of 20 mg/mL within glove box. The Ca (20 nm) and Al (80 nm) cathode were evaporated onto the active layer under a pressure of below 10^{-6} bar with an active area of 4 mm^2. The current density-voltage curves were collected by a Keithley 2420 under Oriel Newport 150W solar simulator (AM 1.5G).

The EQEs were measured by an Oriel Newport System. All above measurements were done at room temperature.

The hole-only device for the hole mobility was fabricated with a device structure of ITO/PEDOT:PSS/PTB7-Th:polymer acceptor/Au. The electron-only device for the electron mobility was fabricated with a device structure of ITO/TiO_x/PTB7-Th: polymer acceptor/Al. Both the hole and electron mobilities by space charge limited current (SCLC) were calculated with the following Mott-Gurney equation in the SCLC region: $J = (9/8)\varepsilon_0\varepsilon_r\mu(V^2/L^3)$, in which ε_0 is the permittivity of the vacuum, ε_r is the dielectric constant of the polymer and assumed to be 3, and L is the thickness of active layer.

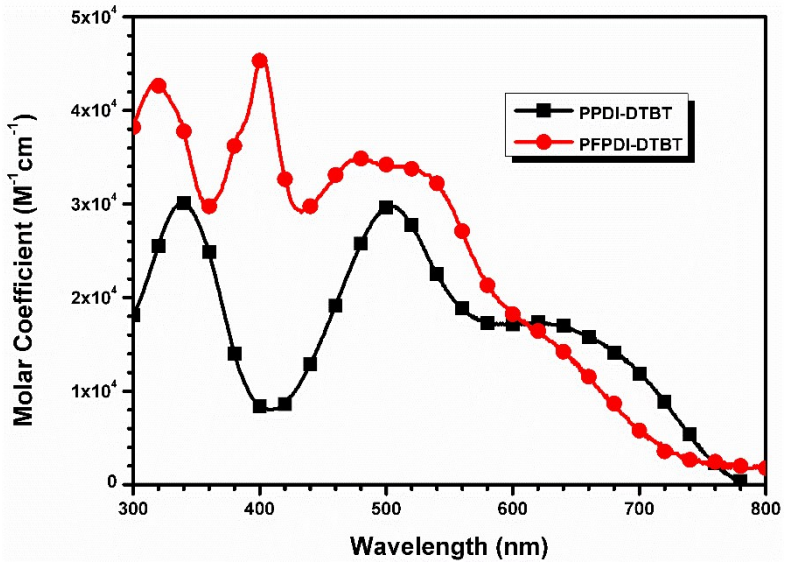

Figure S1. The molar coefficient of PPDI-DTBT and PFPDI-DTBT in chlorobenzene solution.

Table S1. Photovoltaic performance parameters of the all-PSCs based on PTB7-Th: PPDI-DTBT (or FPDI-DTBT) with various blend weight ratios, under the annealing temperature of 120 °C.

Acceptor	D/A Ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
PPDI-DTBT	1.5:1	0.77	10.09	0.43	3.34
	1:1	0.78	10.43	0.44	3.58
	1:1.5	0.79	9.70	0.44	3.37
PFPDI-DTBT	1.5:1	0.75	12.23	0.52	4.77
	1:1	0.76	12.48	0.56	5.31
	1:1.5	0.76	12.03	0.55	5.03

Table S2. Photovoltaic performance parameters of the all-PSCs based on PTB7-Th: PPDI-DTBT (or PFPDI-DTBT) with different solvent additives, under the annealing temperature of 120 °C.

Acceptor	Additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
PPDI-DTBT	no	0.78	10.43	0.44	3.58
	1%DIO	0.78	9.10	0.50	3.55
	1%DPE	0.79	8.94	0.48	3.39
	0.5%CN	0.78	10.59	0.46	3.80
	1%CN	0.78	9.79	0.50	3.82
	3%CN	0.78	10.65	0.49	4.07
	4%CN	0.78	10.50	0.47	3.85
PFPDI-DTBT	no	0.76	12.48	0.56	5.31
	1%DPE	0.76	9.63	0.62	4.54
	1%CN	0.76	11.80	0.63	5.65
	0.5%DIO	0.76	13.62	0.60	6.21
	1%DIO	0.76	13.25	0.60	6.04
	3%DIO	0.76	10.02	0.55	4.19

Table S3. Photovoltaic performance parameters of the all-PSCs based on PTB7-Th: PPDI-DTBT (or PFPDI-DTBT) with different annealing temperature.

Acceptor	**Additive**	**T(℃)**	**V_{OC} (V)**	**J_{SC} (mA cm^{-2})**	**FF**	**PCE (%)**
PPDI-DTBT	3%CN	80	0.77	10.71	0.45	3.71
		100	0.78	10.58	0.47	3.88
		120	0.78	10.65	0.49	4.07
		140	0.78	10.20	0.48	3.82
		160	0.77	9.59	0.44	3.25
PFPDI-DTBT	0.5%DIO	80	0.75	13.19	0.54	5.34
		100	0.75	14.05	0.54	5.69
		120	0.76	13.62	0.60	6.21
		140	0.76	14.13	0.58	6.23
		160	0.75	13.76	0.59	6.09

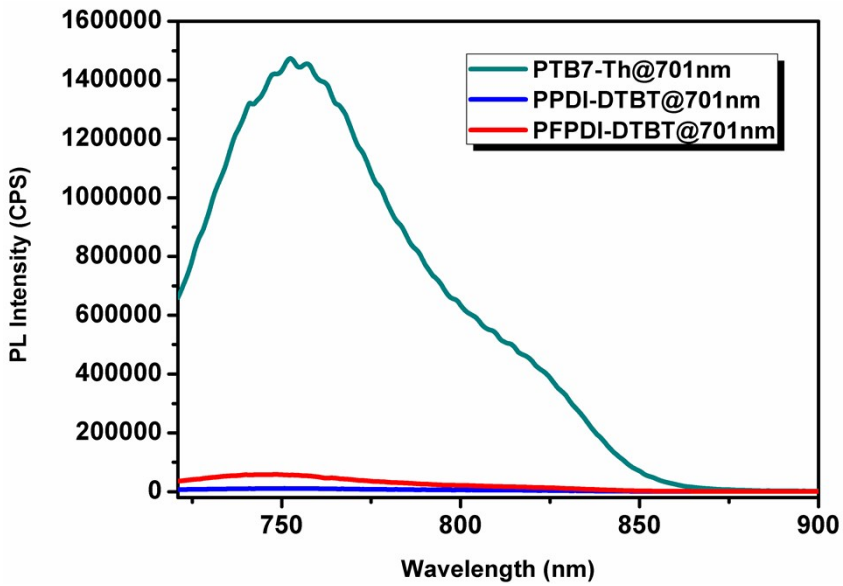

Figure S2. The PL spectra of PTB7-Th, PTB7-Th:PPDI-DTBT and PTB7-Th:PFPDI-DTBT films excited at 701nm.