Electronic Supplementary Information (ESI)

Sifting α,ω-di(thiophen-2-yl)alkanes as Solvent Additive to Boost Photovoltaic Performance of PTB7-Th:PC$_{71}$BM Blend

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1. Measurements and Instruments

^1H and ^{13}C NMR spectra were recorded in deuterated chloroform ($CDCl_3$) on a Bruker Avance III-HD-500 MHz spectrometer. UV−Vis spectra of the BHJ blend films spin-coated on pre-cleaned glass were recorded on a SHIMADZU UV-1750 spectrophotometer. The photoluminescence (PL) spectrum of films spin-coated on precleaned quartz glass were recorded on a Fluoro Max-3-P spectrometer. The atomic force microscopy (AFM) images (5.0 μm × 5.0 μm) were obtained through tapping mode on Multimode 8 SPM at ambient conditions. RTESPA (0.01 - 0.025 ohm-cm Antimony (n) doped silicon) tips with a spring constant of 20 - 80 N m^{-1} and a frequency of 305 - 356 kHz was used in imaging.

2. Fabrication and Characterization of Polymer Solar Cells

The PSC devices were fabricated with inverted configuration of ITO/ZnO/PTB7-Th:$PC_{71}BM/MoO_3$(8 nm)/Ag(100 nm). Prior to be used, indium tin oxide glass substrates were sequentially cleaned in ultrasonic bath for 10 minutes with distilled water, acetone, isopropyl alcohol and were treated by UV-Ozone for 10 min. For BHJ devices, the ZnO films were spin-coated onto cleaned ITO substrates and annealed at 170 °C for 30 min before the substrates were transferred into a glove box under N_2. Subsequently, the layer of PTB7-Th:$PC_{71}BM$ blends were spin-coated from the solution with a fixed donor concentration of 10 mg mL^{-1} in *o*-dichlorobenzene/1,8-diodooctane (97:3, v/v) *or* *o*-dichlorobenzene with certain amount of α,ω-di(thiophene-2-yl)alkanes. Finally, MoO_3(8 nm) and Ag(100 nm) were sequentially deposited on the top of the active layers as the anode at a pressure of 2×10^{-6} mbar through a shadow mask that defines 8 devices with each active area of 0.09 cm^2. Current versus potential (*J*-*V*) curves were recorded with a Keithley 2420 digital source meter in a glovebox under AM 1.5 G irradiation (100 mW cm^{-2}) from a 450 W solar simulator (Newport 94023A-U) calibrated by a NREL certified standard silicon cell. The EQE measurement was performed on a QEX10 (PV Measurements, Inc.) system equipped with a standard Si solar cell (Oriel, VLSI standards) across a wavelength range of 300–900 nm.

The SCLC *J*-*V* curves were obtained in the dark from the electron-only and hole-only device of ITO/ZnO/active-layer/Ca/Al and ITO/PEDOT:PSS/active-layer/MoO_3/Ag, respectively. The electron and hole mobility were calculated using the Mott-Gurney square law:

$$J_{SCLC} = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

where ε_0 is vacuum permittivity, ε_r is the dielectric constant of the polymer used, μ is the charge carrier mobility, V is the effective applied voltage, and L is the thickness of the active film in the device.

3. Supplementary figures and tables

Table S1. The optimized photovoltaic properties of PTB7-Th:$PC_{71}BM$ PSCs processed with various additives (v/v, *o*-DCB) (parenthesized with the average values and standard deviations over 15 devices)

Additive (%)		Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{max} (%)
DIO	3%	103 ± 2	0.796 (0.789 ± 0.007)	17.25 (17.01 ± 0.29)	62.85 (62.54 ± 0.73)	8.65 (8.51 ± 0.18)
DTB	5%	108 ± 2	0.754 (0.749 ± 0.006)	19.02 (18.76 ± 0.31)	55.08 (54.46 ± 0.85)	7.89 (7.73 ± 0.21)
	6%	109 ± 2	0.773 (0.766 ± 0.009)	19.29 (19.06 ± 0.27)	54.98 (54.42 ± 0.81)	8.21 (8.03 ± 0.24)
	7%	110 ± 2	0.782 (0.776 ± 0.006)	19.61 (19.38 ± 0.25)	56.80 (56.20 ± 0.92)	8.76 (8.59 ± 0.18)
	8%	110 ± 2	0.755 (0.750 ± 0.008)	18.29 (18.02 ± 0.29)	53.30 (52.66 ± 0.94)	7.32 (7.16 ± 0.17)
DTH	5%	112 ± 2	0.793 (0.789 ± 0.007)	18.96 (18.75 ± 0.23)	56.94 (56.22 ± 0.96)	8.54 (8.39 ± 0.20)
	6%	114 ± 2	0.795 (0.790 ± 0.006)	19.72 (19.53 ± 0.28)	58.37 (57.85 ± 0.87)	9.03 (8.88 ± 0.18)
	7%	115 ± 2	0.803 (0.799 ± 0.005)	20.43 (20.15 ± 0.32)	59.20 (58.62 ± 1.03)	9.64 (9.42 ± 0.25)
	8%	116 ± 2	0.792 (0.785 ± 0.009)	20.16 (19.95 ± 0.27)	57.89 (57.35 ± 0.98)	9.24 (9.07 ± 0.23)
DTO	5%	113 ± 2	0.792 (0.787± 0.006)	19.86 (19.67 ± 0.26)	57.23 (56.78 ± 0.72)	8.96 (8.78 ± 0.23)
	6%	115 ± 2	0.805 (0.799± 0.008)	20.26 (20.01 ± 0.29)	57.12 (56.58 ± 0.83)	9.30 (9.13 ± 0.19)
	7%	115 ± 2	0.805 (0.801± 0.005)	20.78 (20.51 ± 0.30)	59.43 (58.70 ± 0.75)	9.87 (9.68 ± 0.20)
	8%	117 ± 2	0.802 (0.796± 0.009)	19.01 (18.75 ± 0.32)	55.94 (55.21 ± 0.89)	8.54 (8.38 ± 0.18)
DTD	5%	114 ± 2	0.802 (0.798 ± 0.007)	17.52 (17.28 ± 0.28)	53.33 (52.80 ± 0.76)	7.45 (7.27 ± 0.21)
	6%	116 ± 2	0.805 (0.802 ± 0.005)	17.91 (17.69 ± 0.25)	55. 06 (54.40 ± 0.92)	7.93 (7.78 ± 0.17)
	7%	117 ± 2	0.806 (0.800 ± 0.008)	18.22 (18.01 ± 0.23)	54.70 (54.30 ± 0.87)	8.07 (7.93 ±0.14)
	8%	117± 2	0.807 (0.802 ± 0.009)	17.06 (16.81± 0.30)	52.17 (51.56 ± 0.90)	7.16 (7.01 ± 0.19)

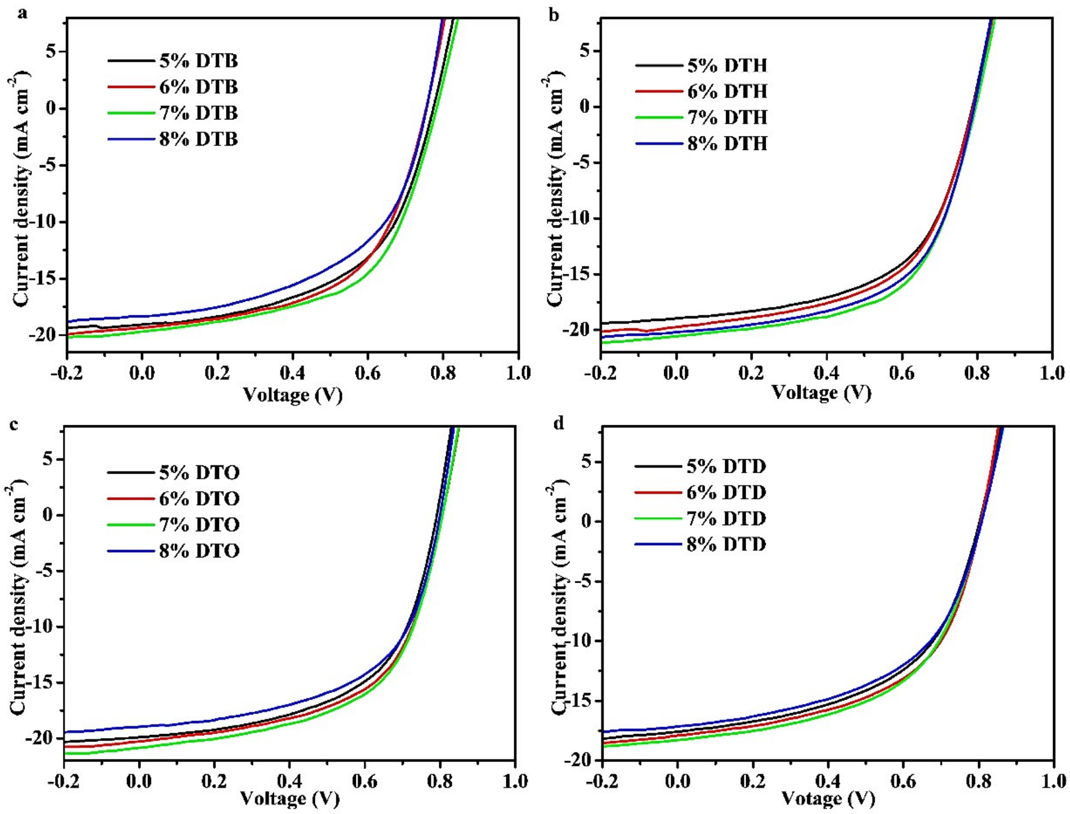

Fig. S1. Typical *J–V* curves of BHJ PSCs with the blend of PTB7-Th:PC$_{71}$BM (1:1.5, w/w) with various volume ratios of additives a) DTB, b) DTH, c) DTO, and d) DTD.

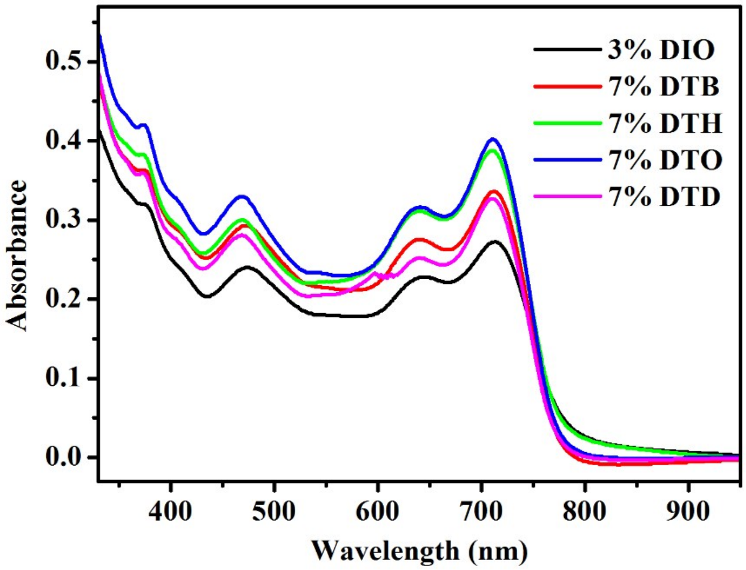

Fig. S2. The absorption spectra of optimized PTB7-Th:PC$_{71}$BM blend films with different solvent additives of DIO and α,ω-di(thiophen-2-yl)alkanes.

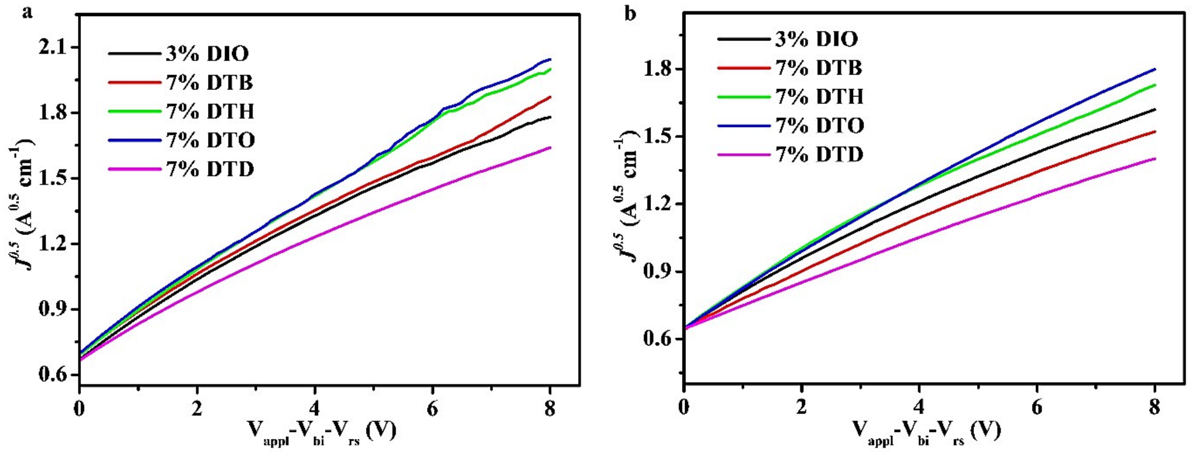

Fig. S3. $J^{0.5}$ *vs* V_{appl}-V_{bi}-V_{rs} plots for a) hole-only and b) electric-only devices of PTB7-Th:$PC_{71}BM$ blend films processed with DIO and α,ω-di(thiophen-2-yl)alkanes.

Table S2. Physical parameters of PTB7-Th:$PC_{71}BM$ PSC devices processed with additives in this work.

Additive	$J_{sc,\ integrated}$[a] (mA cm^{-2})	$J_{ph,sat}$ (A m^{-2})	G_{max} (10^{28} m^{-3} s^{-1})	μ_h[b] (10^{-4} cm^2 V^{-1} s^{-1})	μ_e[b] (10^{-4} cm^2 V^{-1} s^{-1})
DIO	16.99	180.64	1.08	1.38 ± 0.15	1.08 ± 0.10
DTB	18.73	204.21	1.16	1.57 ± 0.20	1.02 ± 0.09
DTH	19.41	213.82	1.18	3.01 ± 0.23	2.31 ± 0.15
DTO	19.86	216.57	1.20	3.08 ± 0.17	2.37 ± 0.10
DTD	17.47	194.68	1.05	1.09 ± 0.16	0.68 ± 0.14

[a] Integrated J_{sc}s from the EQE spectra; [b] average values and standard deviations from 6 devices.

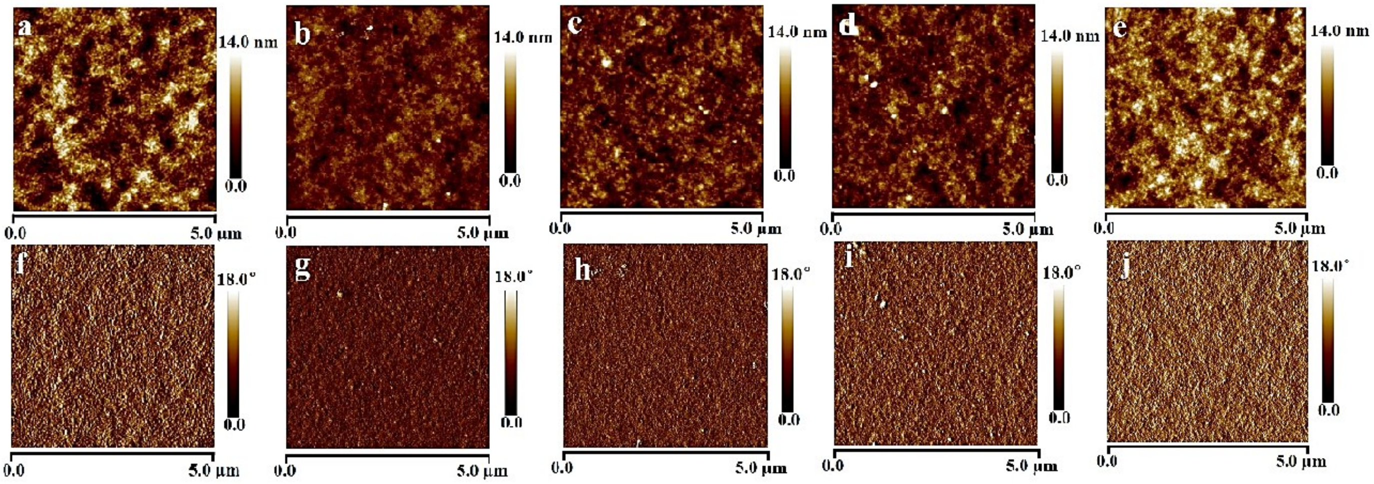

Fig. S4. Tapping-mode AFM height (a, b, c, d and e) and phase images (f, g, h, I and j) of the optimized PTB7-Th:PC$_{71}$BM blend films processed with the additives of DIO (a and f), DTB (b and g), DTH (c and h), DTO (d and i) and DTD (e and j), respectively.

Table S3. The molecular packing parameters from GIWAXS along both the OOP and IP directions of the PTBT-Th:PC$_{71}$BM BHJ blend films processed with the additives in this work.

Additives	OOP				IP	
	(100) (Å^{-1})	d-spacing (Å)	(010) (Å^{-1})	d-spacing (Å)	(100) (Å^{-1})	d-spacing (Å)
DIO	0.31	20.26	-	-	0.28	22.43
DTB	0.32	19.62	1.67	3.76	0.29	21.66
DTH	0.32	19.62	1.67	3.76	0.30	20.93
DTO	0.32	19.62	1.68	3.74	0.31	20.26
DTD	0.32	19.62	-	-	-	-

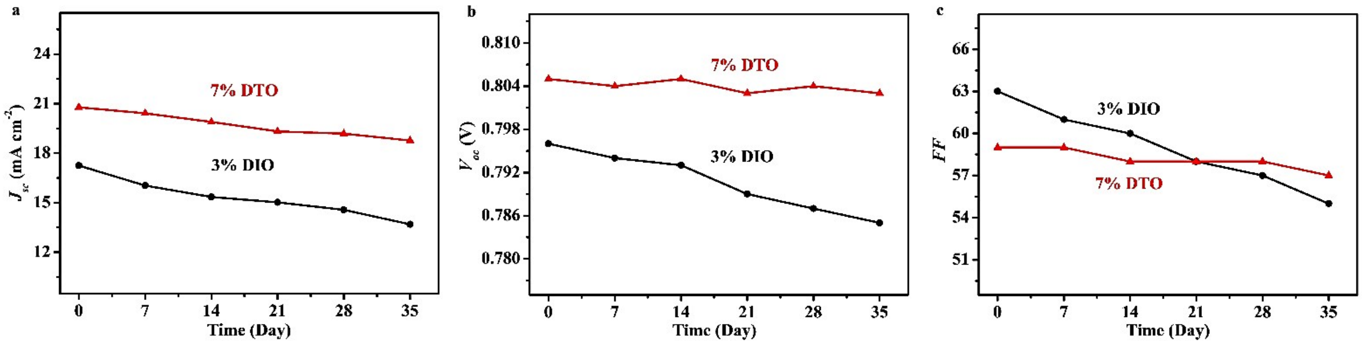

Fig. S5. Photovoltaic parameters of the PTBT-Th:PC$_{71}$BM solar cells processed with DIO and DTO respectively as a function of storage time in nitrogen-filled glove box: a) J_{sc}, b) V_{oc} and c) FF.

Table S4. The optimized device parameters of the PTB7-Th:PC$_{71}$BM solar cells processed with DIO and DTO respectively stored in nitrogen-filled glove box over 35 days (parenthesized with the average values and standard deviations from 6 devices).

Additive	Time (Day)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
DIO	1	0.796 (0.794 ± 0.003)	17.25 (17.22 ± 0.08)	62.85 (62.78 ± 0.36)	8.65 (8.59 ± 0.07)
	35	0.785 (0.784 ± 0.002)	13.69 (13.56 ± 0.15)	55.49 (55.24 ± 0.45)	5.96 (5.83 ± 0.14)
DTO	1	0.805 (0.804 ± 0.001)	20.78 (20.68 ± 0.12)	59.43 (59.06 ± 0.29)	9.87 (9.82 ± 0.07)
	35	0.803 (0.802 ± 0.001)	18.77 (18.61 ± 0.17)	57.28 (57.05 ± 0.26)	8.63 (8.51 ± 0.12)