

Supporting Information

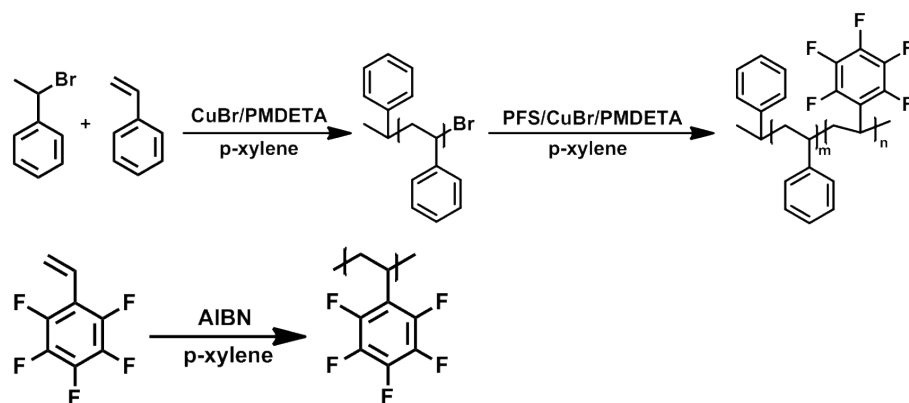
A Ring-Perfluorinated Nonvolatile Additives with a High Dielectric Constant Lead to Highly Efficient and Stable Organic Solar Cells

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Scheme S1. Synthetic routes of PS, PS-*b*-PPFS and PPFS polymer additives.

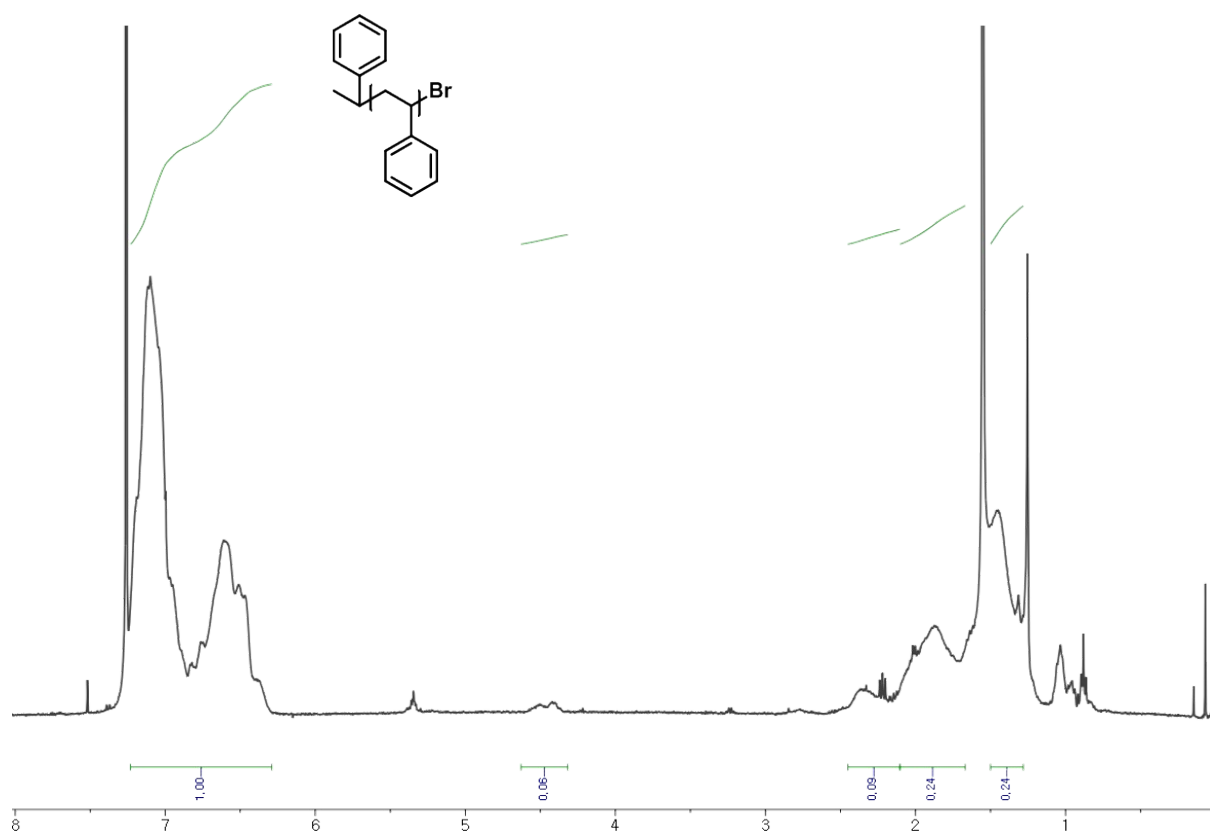


Fig. S1 ^1H NMR data of PS-br

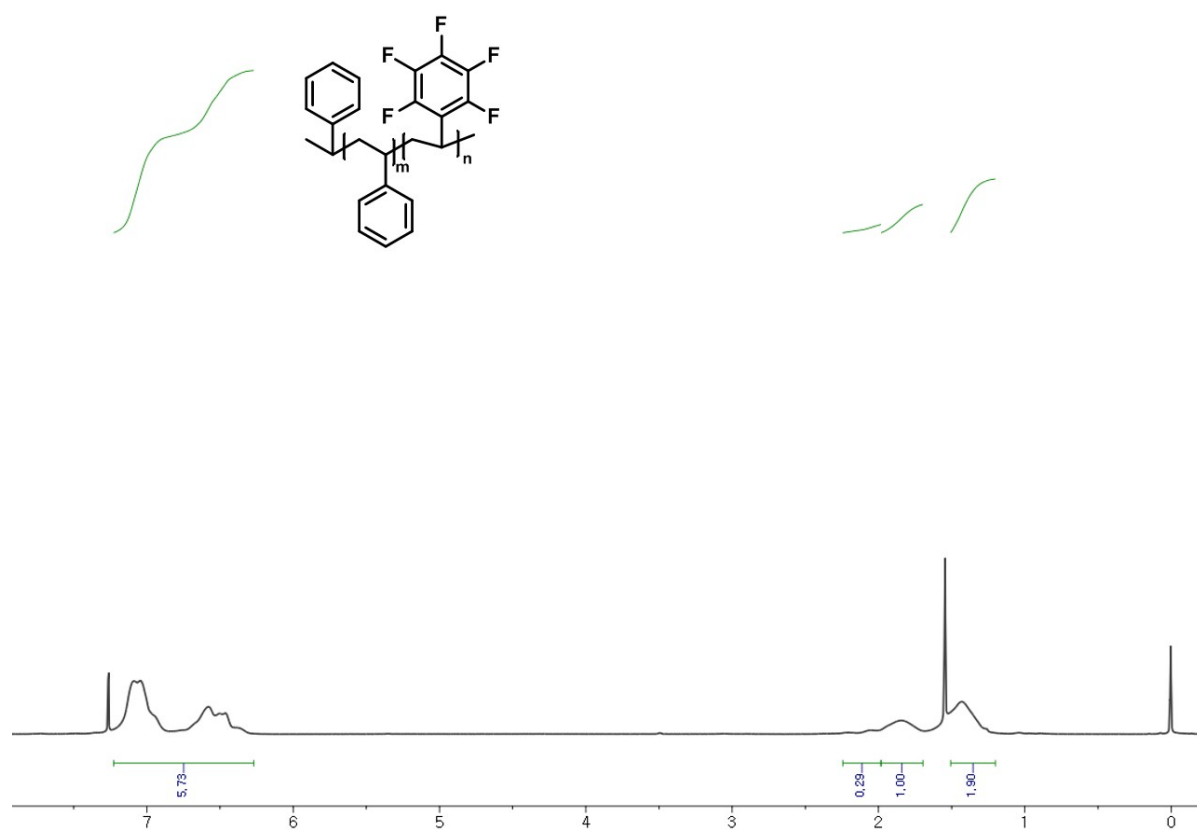


Fig. S2 ¹H NMR data of PS-*b*-PPFS

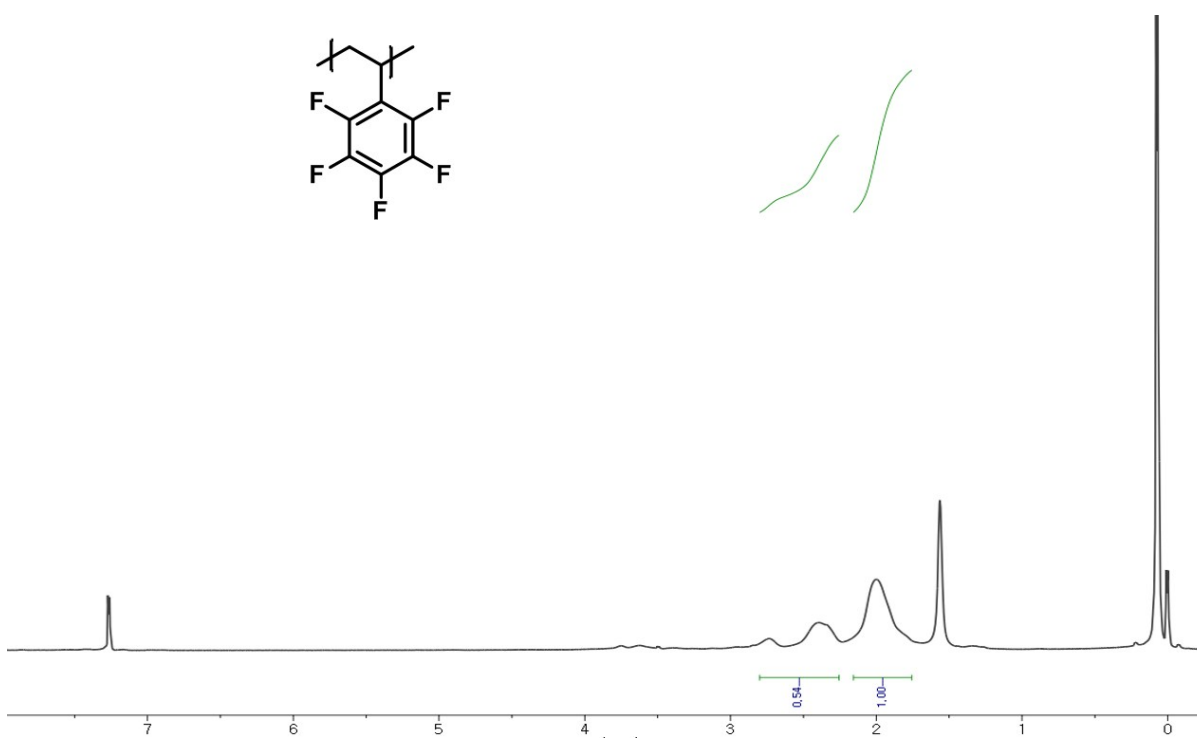


Fig. S3 ¹H NMR data of PPFS

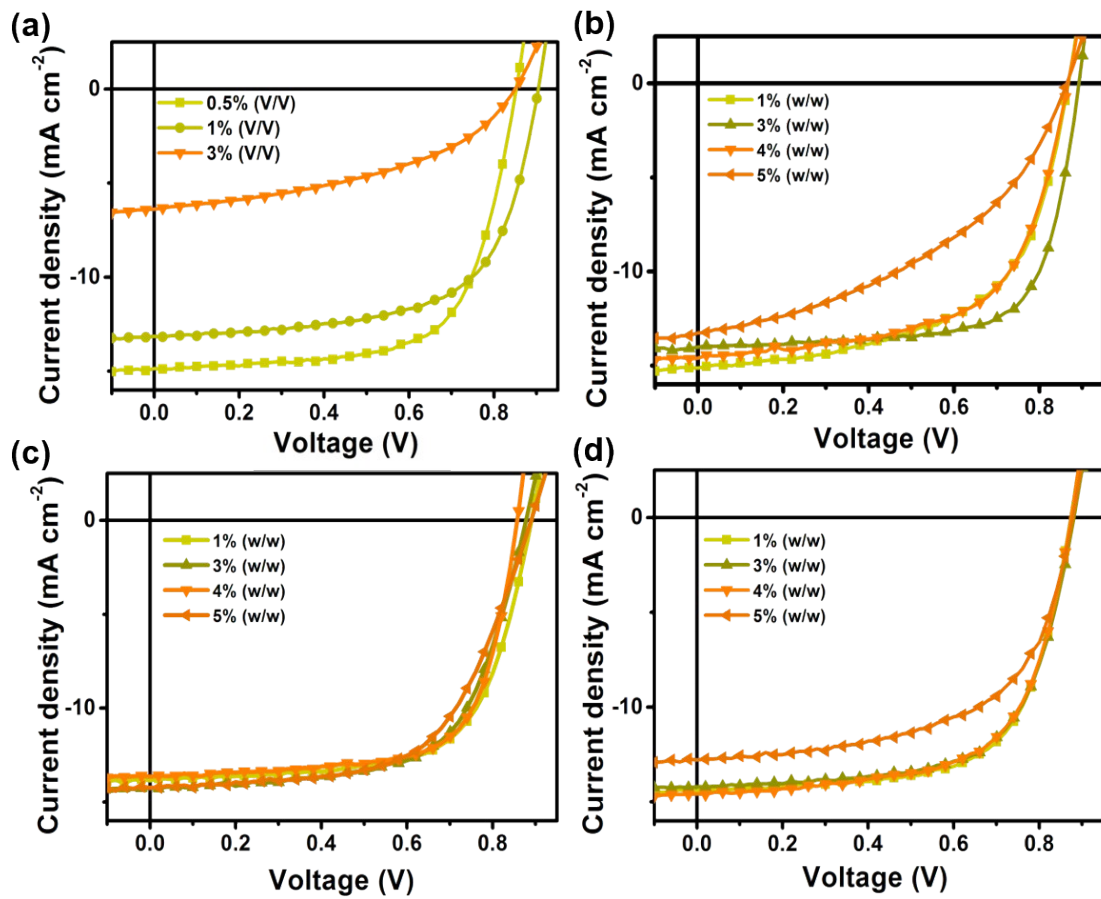


Fig. S4 The J - V curves for PBDB-TT5:ITIC films with different concentration of each additive: (a) DIO, (b) PS, (c) PS-*b*-PPFS, and (d) PPFS under AM 1.5G simulated solar radiation at 100mW cm^{-2}

Table S1. Photovoltaic parameters of NF-OSCs with different concentration of each additive.

Additive (v/v)	V_{OC}^a [V]	J_{SC}^a [mA cm ⁻²]	FF ^{a)}	PCE ^{a)} [%]
1% DIO	0.904 (0.906±0.003)	13.15 (13.09±0.18)	63.55 (62.78±0.80)	7.58 (7.50±0.07)
2% DIO	0.889 (0.887±0.001)	9.16 (8.98±0.31)	59.69 (59.42±0.28)	4.86 (4.61±0.25)
3% DIO	0.849 (0.850±0.002)	6.39 (6.16±0.14)	44.09 (44.45±0.38)	2.39 (2.35±0.04)
1% PS	0.881 (0.882±0.011)	15.02 (14.99±0.15)	63.84 (63.46±0.57)	8.45 (8.39±0.06)
3% PS	0.894 (0.886±0.008)	14.87 (14.81±0.11)	64.01 (64.46±0.40)	8.51 (8.48±0.02)
4% PS	0.872 (0.876±0.003)	14.60 (14.83±0.14)	61.51 (60.94±0.56)	8.19 (8.07±0.12)
5% PS	0.886 (0.885±0.004)	13.37 (13.18±0.21)	50.01 (49.63±0.38)	5.92 (5.87±0.06)
1% PS- <i>b</i> -PPFS	0.887 (0.884±0.004)	14.46 (14.21±0.19)	67.92 (67.71±0.26)	8.51 (8.45±0.10)
3% PS- <i>b</i> -PPFS	0.882 (0.877±0.004)	15.00 (14.85±0.15)	64.90 (64.43±0.45)	8.42 (8.39±0.05)
4% PS- <i>b</i> -PPFS	0.901 (0.879±0.03)	13.62 (13.40±0.22)	69.01 (68.85±0.12)	8.10 (8.09±0.01)
5% PS- <i>b</i> -PPFS	0.884 (0.881±0.002)	14.77 (14.62±0.11)	63.90 (63.70±0.24)	8.22 (8.07±0.15)
1% PPFS	0.882 (0.876±0.004)	15.37 (14.88±0.48)	67.20 (66.85±0.37)	8.53 (8.43±0.10)
3% PPFS	0.894 (0.889±0.005)	15.19 (15.02±0.16)	65.75 (64.88±1.0)	8.87 (8.66±0.22)
4% PPFS	0.897 (0.886±0.007)	15.10 (14.74±0.34)	68.69 (67.42±0.9)	8.70 (8.53±0.17)
5% PPFS	0.889 (0.886±0.002)	15.92 (15.73±0.22)	66.02 (66.01±0.12)	8.51 (8.38±0.14)

^{a)} The values in the parentheses are the average values obtained from over 16 devices.

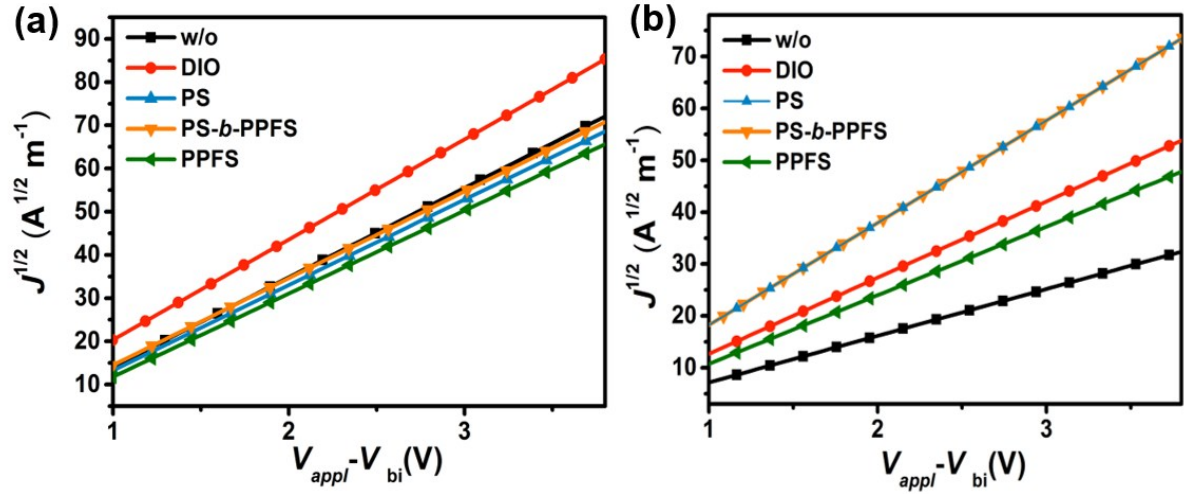


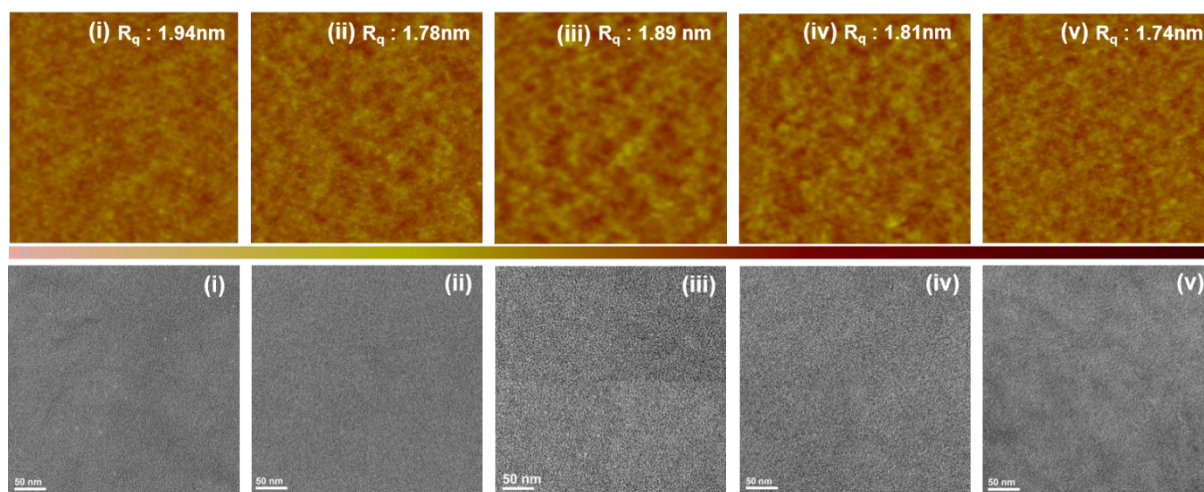
Fig. S5 Dark $J^{1/2}$ - V plots for the (a) electron-only, (b) hole-only devices based on the PBDB-TT5:ITIC blend films.

Table S2. The $P(E, T)$ values at short-circuit condition and maximum power output condition.

Devices	$P(E, T)$ [%]	
	At short-circuit condition	At maximum power output condition
w/o additive	92.3	73.2
0.5% DIO	93.5	78.1
2% PS	95.2	77.1
2% PS- <i>b</i> -PPFS	94.6	79.5
2% PPFS	95.8	82.0

Table S3. The GIWAX parameters of out-of-plane and in-plane.

Additive (w/w) or (v/v)	Out-of-Plane				In-Plane			
	π - π stacking cell axis (<i>010</i>)				Unit cell long axis (<i>100</i>)			
	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	Coherence length ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	Coherence length ($\text{\AA}$)
w/o additive	1.685	3.723	0.272	21.055	0.292	21.530	0.0442	128.067
0.5% DIO	1.692	3.713	0.245	23.380	0.295	21.332	0.0456	126.106
2% PS	1.695	3.707	0.267	21.387	0.293	21.453	0.0481	117.677
2% PS- <i>b</i> -PPFS	1.692	3.714	0.266	21.485	0.292	21.518	0.0437	129.504
2% PPFS	1.696	3.704	0.287	19.883	0.295	21.315	0.0459	123.295

**Fig. S6** The AFM height images in $4\mu\text{m} \times 4\mu\text{m}$ (top) and TEM images of the blend film (bottom): (i) w/o additive, (ii) DIO, (iii) PS, (iv) PS-*b*-PPFS, and (v) PPFS.

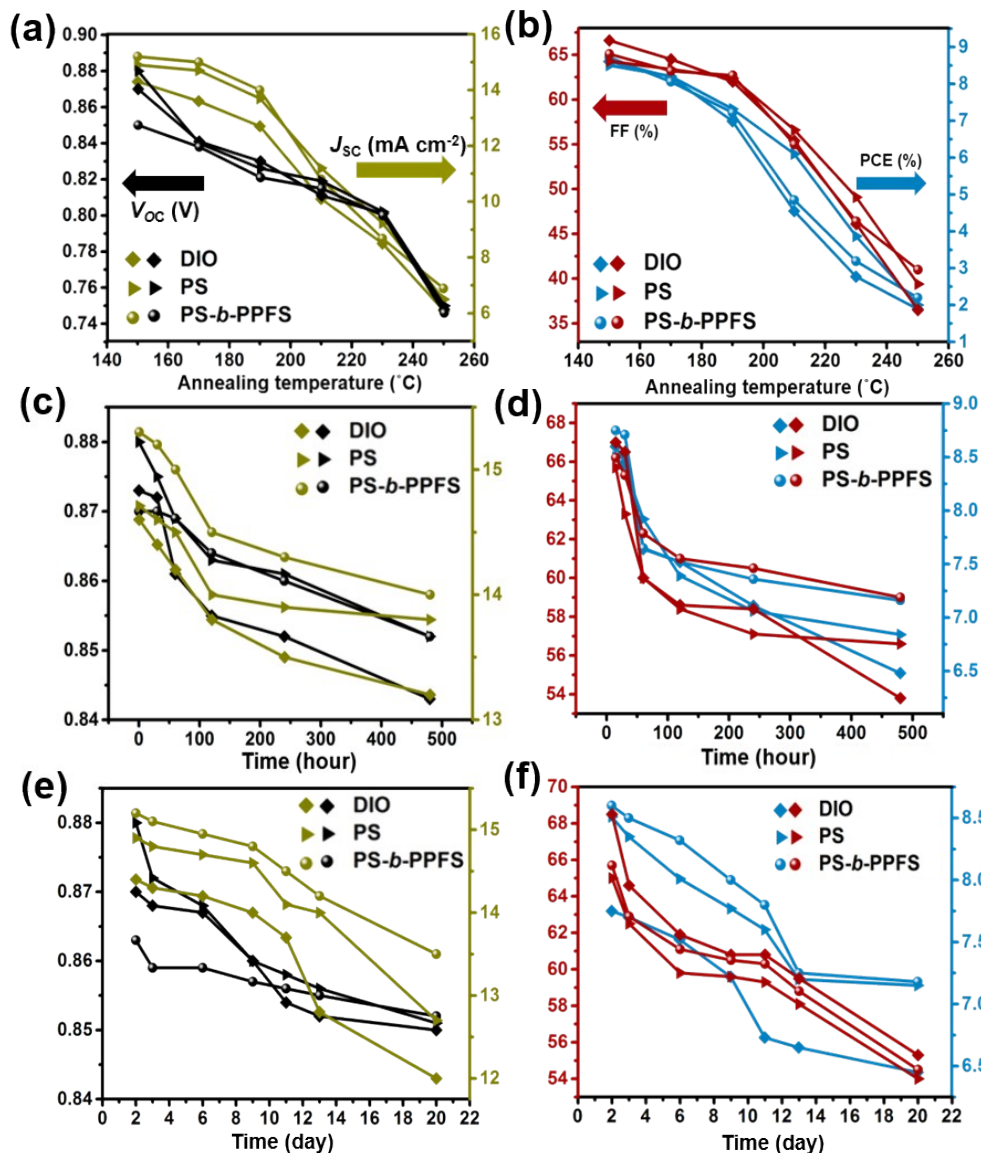


Fig. S7 Device stability of the different processing additive contained films under different conditions: (a), (b) annealing-temperature stability in the N_2 -filled glovebox; (c),(d) thermal-time stability at 150 °C; (e), (f) in the N_2 -filled glovebox without capsulation of the long-term stability.

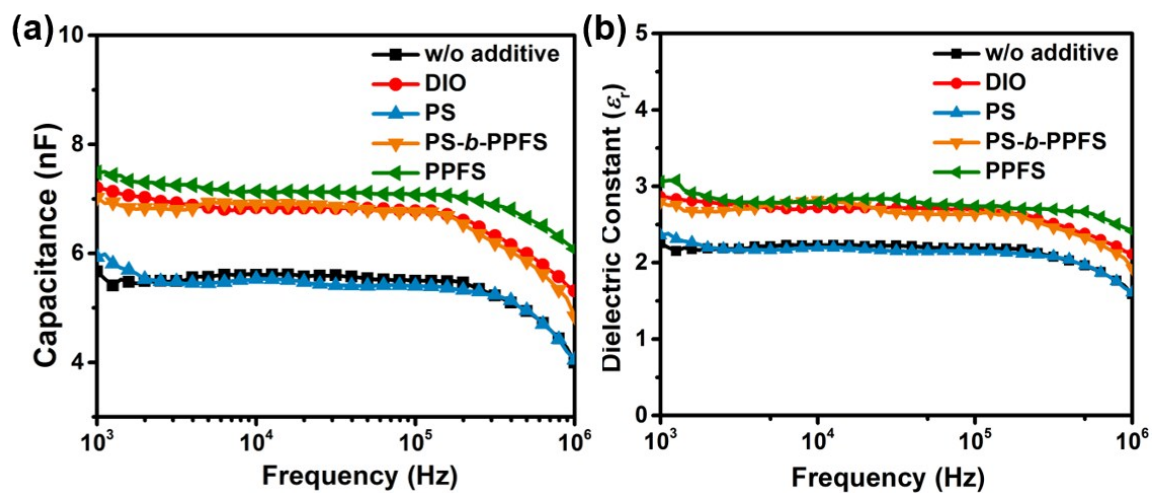


Fig. S8 Frequency dependence of the (a) capacitance and (b) dielectric constant in the blend system.

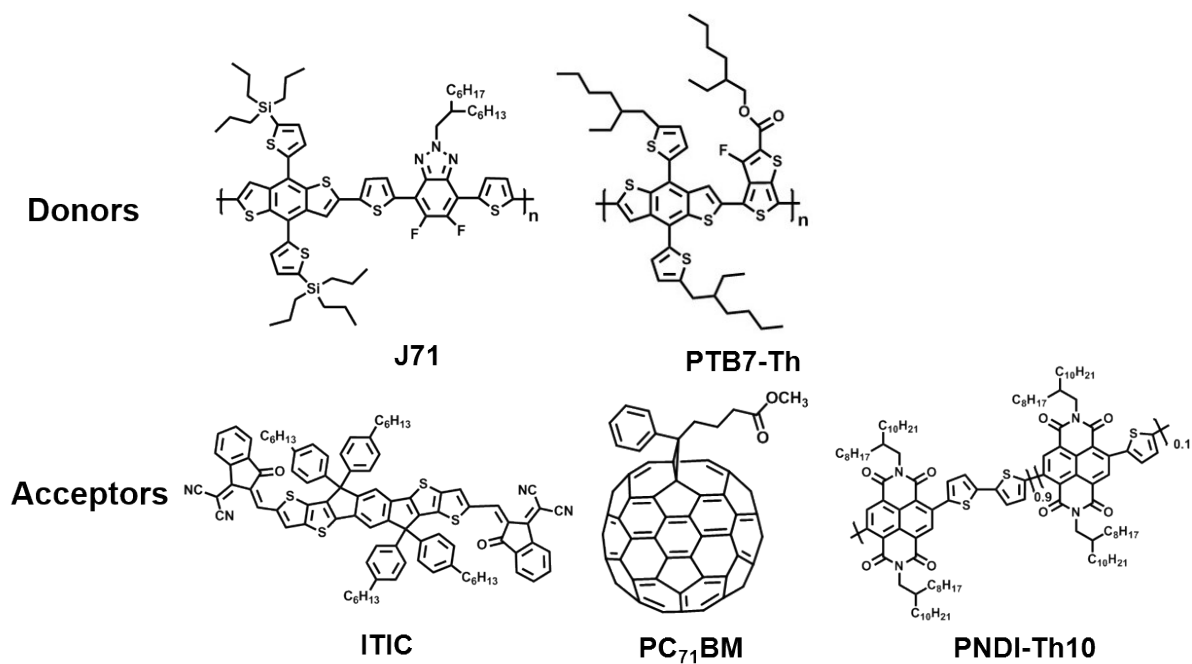


Fig. S9 Chemical structures of donors and acceptors used in other host systems.

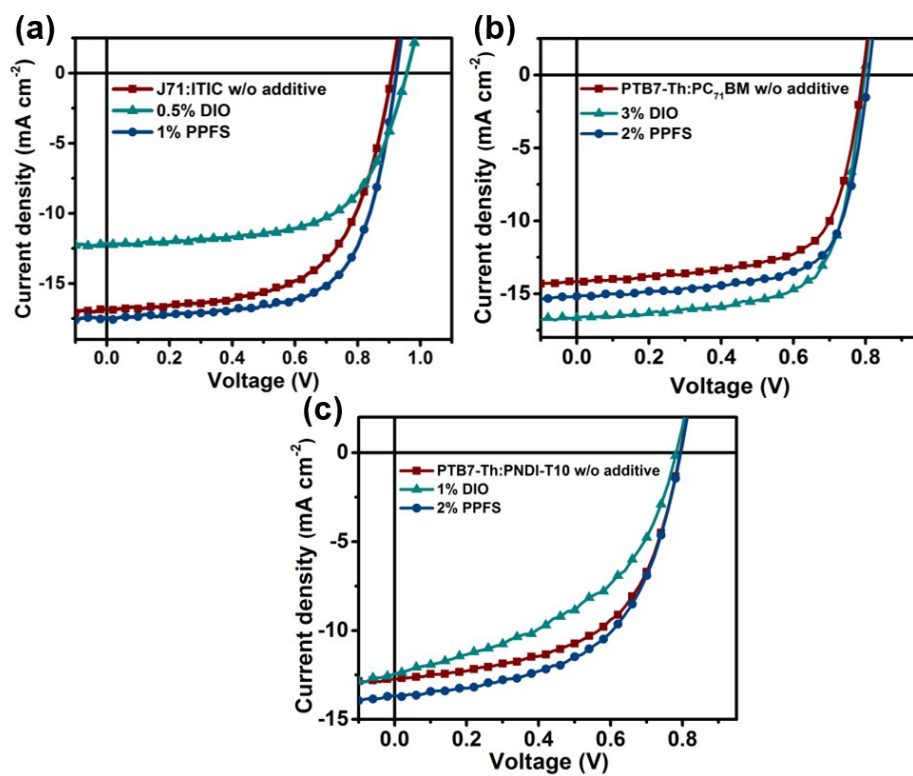


Fig. S10 The J - V curves with optimal concentration additive (a) J71:ITIC, (b) PTB7-Th:PC₇₁BM, and (c) PTB7-Th:PNDI-T10.

Table S4. Photovoltaic parameters having different types of active layers with and without additives.

Devices	Additive	$V_{OC}^{a)}$ [V]	$J_{SC}^{a)}$ [mA/cm ²]	FF ^{a)}	PCE ^{a)} [%]
J71:ITIC	X	0.919 (0.913±0.003)	17.15 (17.01±0.14)	61.30 (61.08±0.20)	9.68 (9.52±0.12)
J71:ITIC	0.5% DIO	0.922 (0.919±0.007)	15.38 (15.38±0.13)	56.01 (55.07±0.14)	7.96 (7.79±0.19)
J71:ITIC	1% PPFS	0.924 (0.927±0.006)	17.38 (17.08±0.40)	66.20 (65.75±0.17)	10.70 (10.45±0.23)
PTB7-Th:PC ₇₁ BM	X	0.785 (0.792±0.006)	15.60 15.28(0.38)	67.64 66.6(±0.66)	8.29 (8.05±0.24)
PTB7-Th:PC ₇₁ BM	3% DIO	0.792 (0.793±0.003)	17.69 17.45(±0.25)	69.21 68.85(±0.17)	9.40 (9.21±0.20)
PTB7-Th:PC ₇₁ BM	2% PPFS	0.805 (0.804±0.008)	15.49 15.76(±0.26)	69.67 68.71(±0.15)	8.70 (8.58±0.06)
PTB7-Th:PNDI-T10	X	0.793 (0.803±0.004)	12.74 (12.49±0.24)	56.21 (55.96±0.20)	5.68 (5.60±0.14)
PTB7-Th:PNDI-T10	1% DIO	0.782 (0.786±0.012)	12.44 (12.09±0.58)	46.51 (44.96±0.06)	4.52 (4.15±0.60)
PTB7-Th:PNDI-T10	2% PPFS	0.795 (0.799±0.003)	13.69 (13.52±0.17)	56.10 55.65(±0.44)	6.10 (6.01±0.12)

^{a)} The values in the parentheses are the average values obtained from over 16 devices.