Supporting Information

Promoting the Stability of Organic Photovoltaics by Planar Heterojunction optimization

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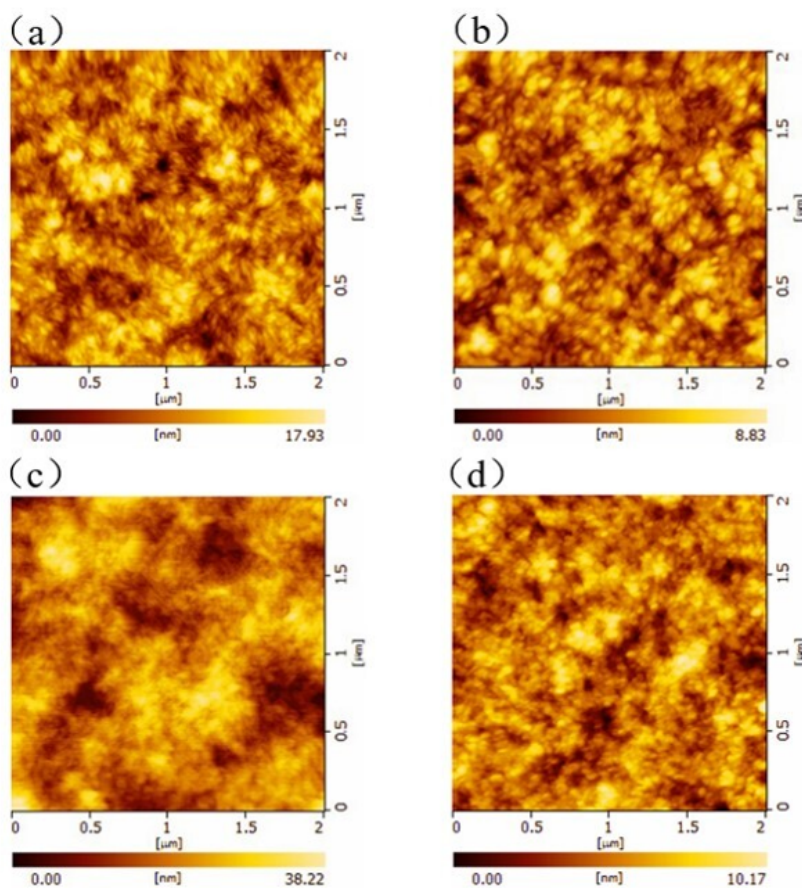E-mail: w.c.tsoi@swansea.ac.uk; bwei@shu.edu.cn

Fig. S1 AFM images of different time periods: (a) PEDOT: PSS/PBDB-T: ITIC film at 0 h, (b) PEDOT: PSS/ PBDB-T/ITIC film at 0 h, (c) PEDOT: PSS/PBDB-T: ITIC film at 120 h, (d) PEDOT: PSS/ PBDB-T/ITIC film at 120 h.

Table S1 Roughness values of PBDB-T: ITIC thin films and PBDB-T/ITIC thin films at different time periods.

Device	Time (h)	RMS (nm)
PBDB-T: ITIC	0	2.84
	120	6.10

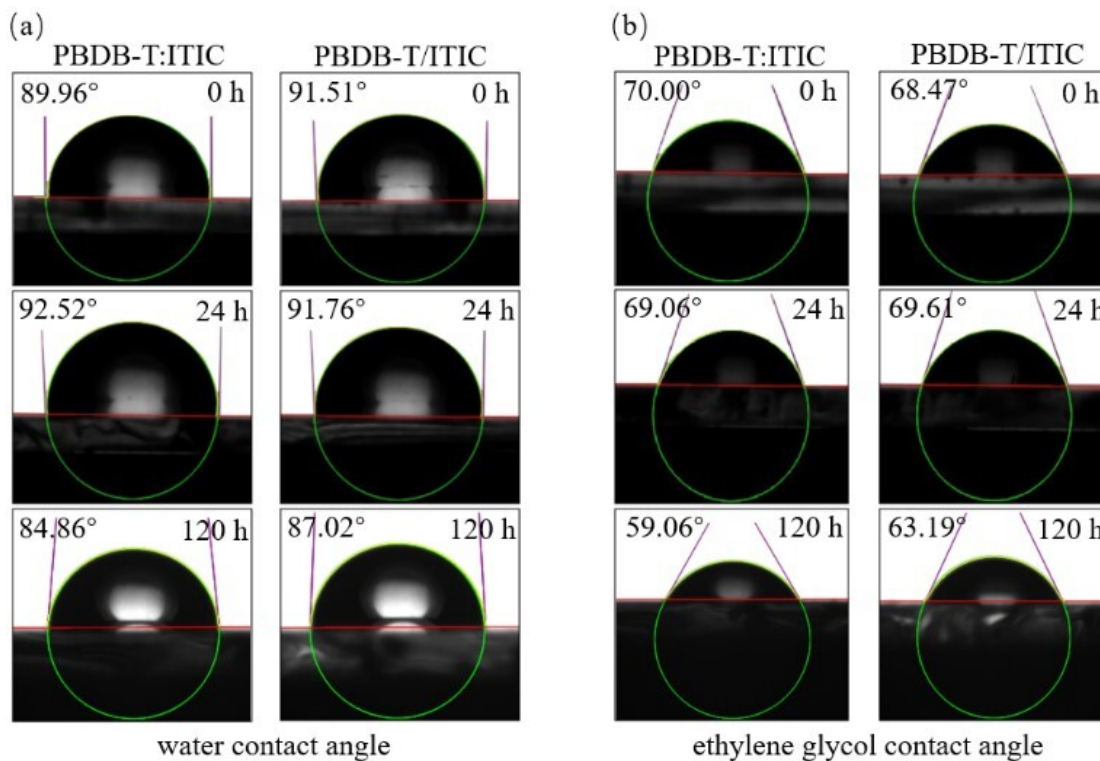|		
PBDB-T/ITIC	0	1.47
	120	1.61

Fig. S2 Contact angles of PEDOT: PSS/PBDB-T: ITIC film and PEDOT: PPS/PBDB-T/ITIC film at different time periods: (a) water contact angle, (b) ethylene glycol contact angle.

Table S2 Surface energy parameters of deionized water and ethylene glycol.

Device	Surface energy parameters		
	γ_L^d	γ_L^p	γ_L
deionized water	29.30	18.90	48.20
ethylene glycol	22.10	50.70	72.80

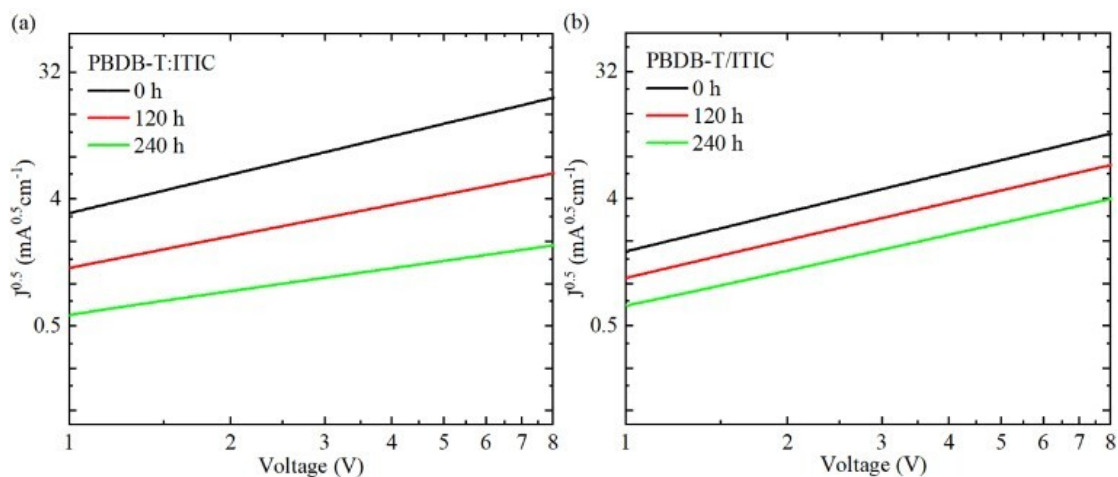Note: γ^d is the dispersion component, γ^p is the polarity component.

Fig. S3 $J^{0.5} - V$ curves for different time periods: (a) based on PBDB-T: ITIC BHJ OPV, (b) based on PBDB-T/ITIC PHJ OPV.

Table S3 Device performance results based on PBDB-T: ITIC BHJ and PBDB-T/ITIC PHJ.

Device	Time (h)	J_{SC} (mA•cm-2)	V_{OC} (V)	FF (%)	PCE (%)	Rs (mΩ)
PBDB-T: ITIC	0	15.28±0.25	0.87	68.26±0.22	9.09±0.32	1074
	120	10.21±0.15	0.60	43.01±0.28	2.64±0.21	14904
	240	4.51±0.19	0.42	35.77±0.20	0.68±0.23	19128
PBDB-T/ITIC	0	10.21±0.21	0.81	60.72±0.24	5.03±0.27	1527
	120	7.46±0.22	0.76	51.23±0.15	2.98±0.24	9989
	240	5.34±0.19	0.61	47.99±0.21	1.57±0.18	15804

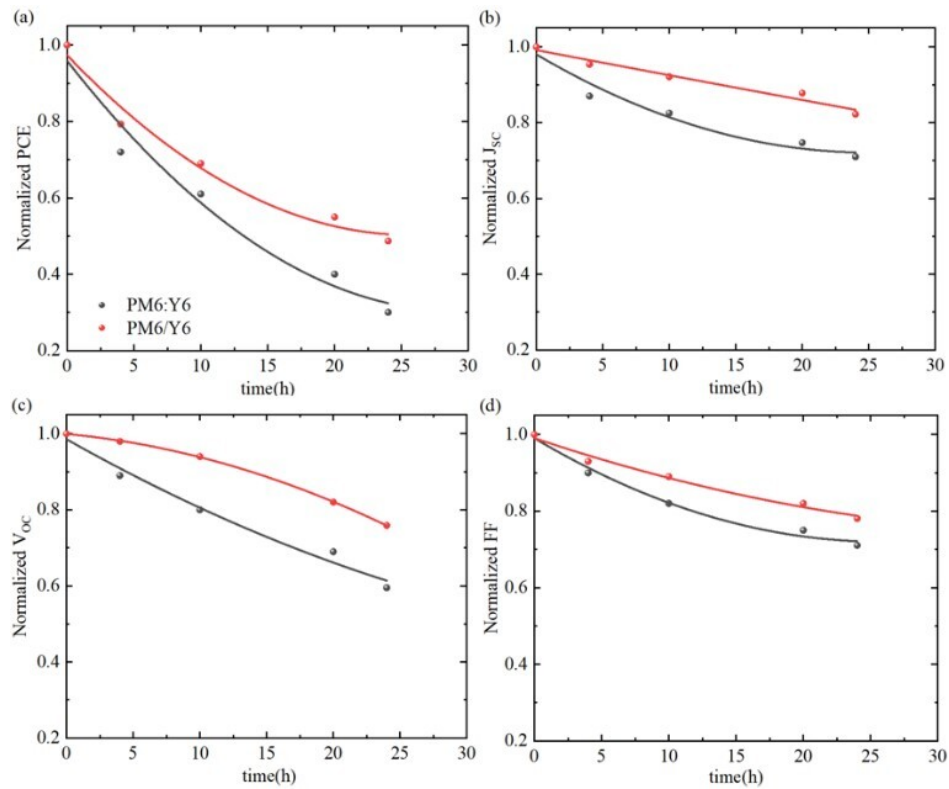Note: results are averaged from more than 20 devices.

Fig. S4 Normalized (a) PCE, (b) J_{SC}, (c) V_{OC}, and (d) FF over time based on PM6: Y6 BHJ and PM6/Y6 PHJ OPV measurements.

Table S4 Device performance results based on PM6: Y6 BHJ and PM6/Y6 PHJ OPV.

Device	Time (h)	J_{SC} (mA•cm-2)	V_{OC} (V)	FF (%)	PCE (%)
PM6: Y6	0 h	26.59±0.30	0.84	67.26±0.27	15.05±0.32
	24 h	18.88±0.26	0.50	47.80±0.25	4.52±0.28
PM6/Y6	0 h	23.36±0.22	0.83	62.43±0.30	12.13±0.28

| | 24 h | 19.21±0.24 | 0.63 | 48.75±0.26 | 5.91±0.25 |

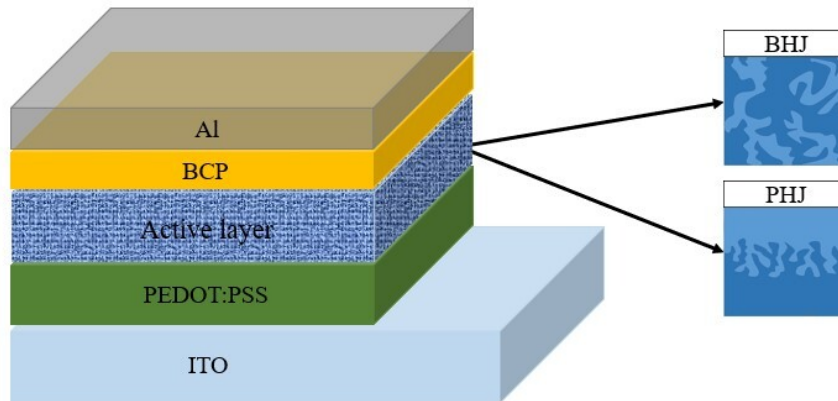Note: results are averaged form more than 20 devices.

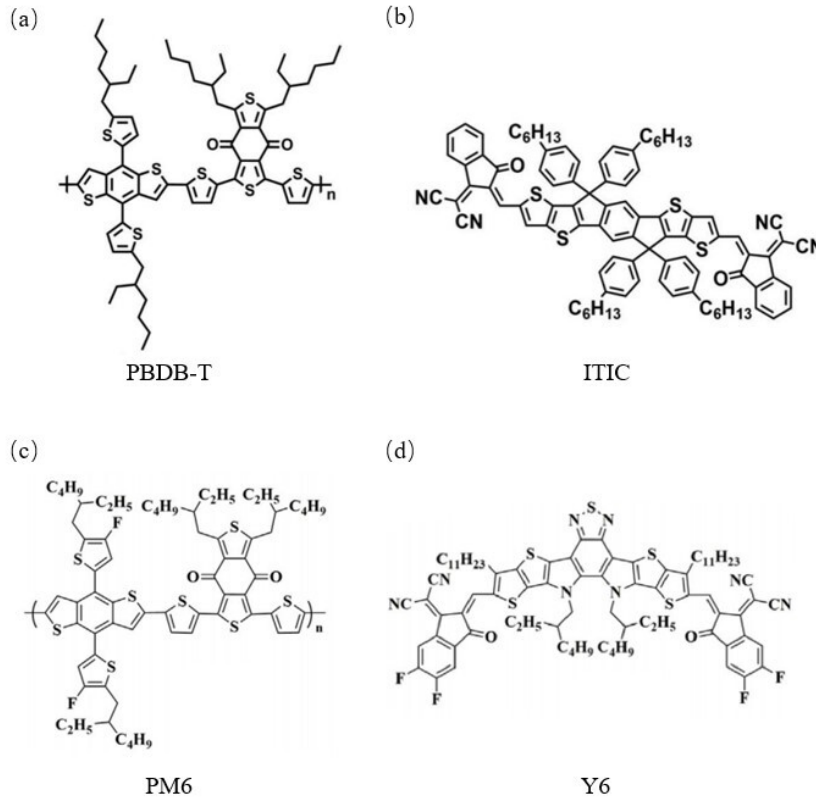**Fig. S5** The schematic diagram of the device structure prepared in this work.

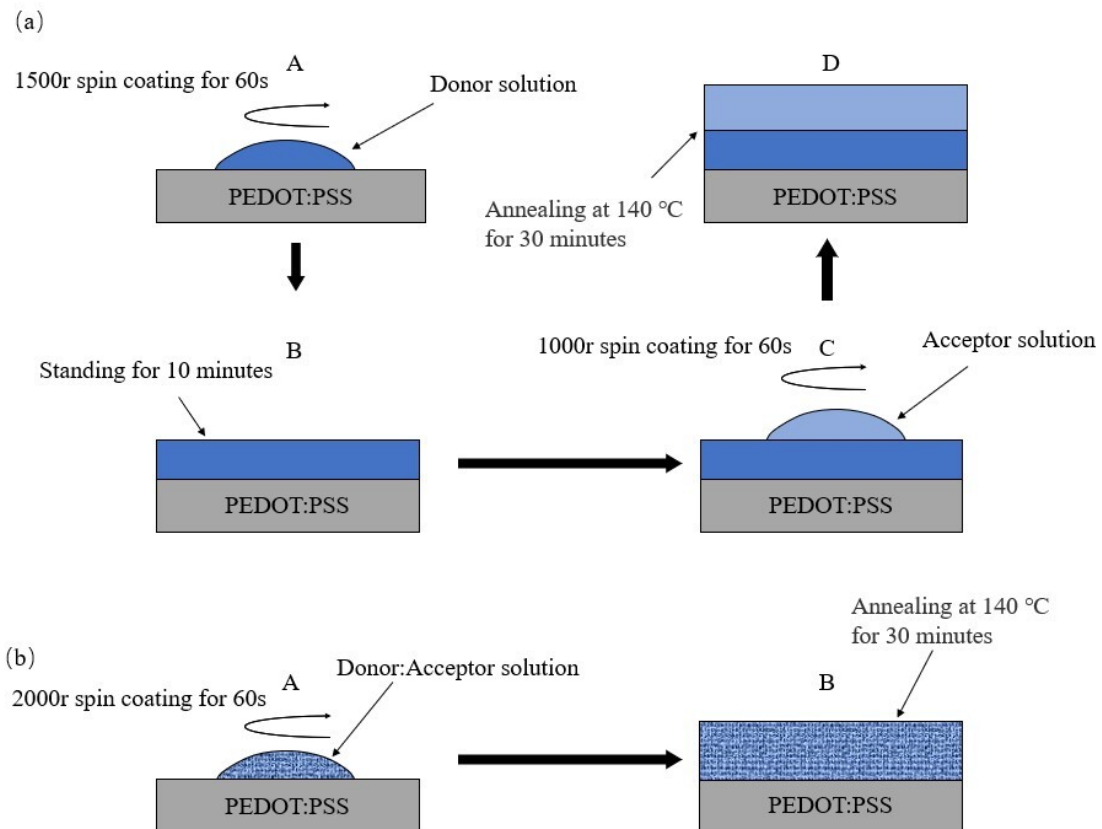**Fig. S6** Active layer materials used in this work: (a) PBDB-T, (b) ITIC, (c) PM6, (d) Y6.

Fig. S7 Flow chart of active layer preparation: (a) PHJ, (b) BHJ.