## Using a Facile Processing Method to Facilitate Charge Extraction for

## **Polymer Solar Cells**

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**Fig. S1** *J-V* characteristics of devices with (a) 50 (b) 75 (c) 100 and (d) 125 Å WO<sub>3</sub> interlayer without and with post-annealing treatment.



Fig. S2 (a)  $J_{sc}$  and (b) FF of PSCs with different WO<sub>3</sub> thicknesses as a function of post-annealing treatment temperatures.



Fig. S3 AFM images of bare PTB7:PC71BM films without and with post-annealing treatment.

**i-CELIV techniques:**<sup>1-3</sup> The equivalent i-CELIV experimental setup is schematically shown in Figure S4, which is relatively simple than the photo-CELIV experimental setup, and the i-CELIV technology is more appropriate for the research of the materials with low light absorption. A waveform generator is used to offer a triangle voltage in reverse bias, and the amplitude is  $U_{max}$ . The internal electric field is compensated by a small offset voltage ( $U_{off}$ ). The signal was recorded using a digital storage oscilloscope. A constant negative  $U_{off}$  (forward bias) is used to inject the charge carrier, and the triangular voltage pulse is applied in reverse bias to extract them, effectively examining the charge extraction capacity and charge recombination in whole device.



Fig. S4 Schematics of experimental setups for the i-CELIV techniques.

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WO <sub>3</sub> thickness	Temperature (°C)	$V_{\rm oc}\left({ m V} ight)$	$J_{\rm sc}~({\rm mA/cm^2})$	FF (%)	PCE (%)
50 Å	Room temperature	0.662	15.13	63.1	6.32
	50	0.715	16.24	66.5	7.72
	60	0.731	16.52	67.4	8.14
	70	0.738	15.78	68.7	8.00
	80	0.742	14.87	66.9	7.38
75 Å	Room temperature	0.710	15.55	67.1	7.41
	50	0.734	16.48	71.1	8.60
	60	0.751	17.27	74.5	9.66
	70	0.755	16.48	73.7	9.17
	80	0.758	15.33	72.2	8.39
100 Å	Room temperature	0.732	15.89	68.5	7.97
	50	0.743	16.40	71.9	8.76
	60	0.750	16.63	73.1	9.12
	70	0.753	16.08	72.6	8.79
	80	0.755	15.24	71.3	8.21
125 Å	Room temperature	0.737	15.45	70.3	8.01
	50	0.741	15.89	71.3	8.40
	60	0.745	16.01	72.3	8.63
	70	0.748	15.65	71.0	8.31
	80	0.750	14.98	68.6	7.71

**Table S1.** The detailed photovoltaic parameters including  $V_{oc}$ ,  $J_{sc}$ , FF and PCE of devices fabricated with different thicknesses of WO<sub>3</sub> and post-annealed at different temperatures.

## References

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