

## Supporting information

### Nonfullerene small molecular acceptor acting as a solid additive enables highly efficient pseudo-bilayer all polymer solar cells

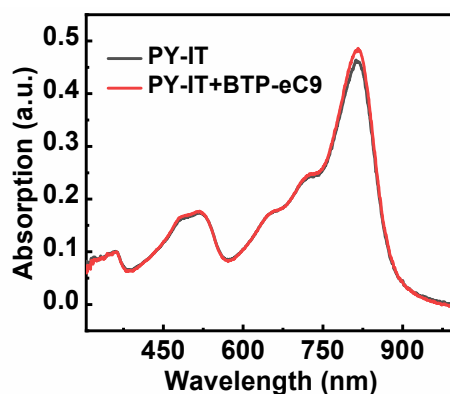
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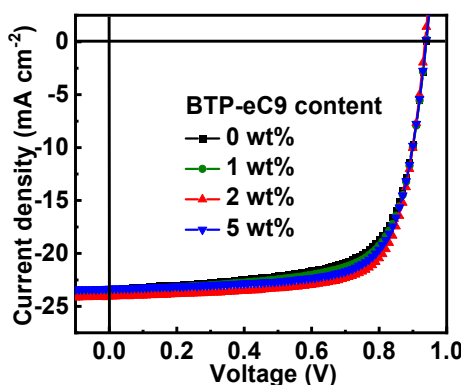
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#### Additional experimental results



**Figure S1.** The absorption spectra of PY-IT and PY-IT:BTP-eC9 films.



**Figure S2.** The  $J$ - $V$  curves of PPHJ-APSCs with different incorporation ratios of BTP-eC9.

**Table S1.** Key photovoltaic parameters of PM6/PY-IT based PPHJ-APSCs with different BTP-eC9 content in PY-IT layer.

BTP-eC9	$J_{SC}$	$V_{OC}$	FF	PCE
[wt%]	[mA cm <sup>-2</sup> ]	[V]	[%]	[%]
0	23.36	0.94	68.83	15.11
1	23.52	0.94	70.70	15.51
2	24.08	0.94	72.76	16.47
5	23.33	0.94	72.35	15.86

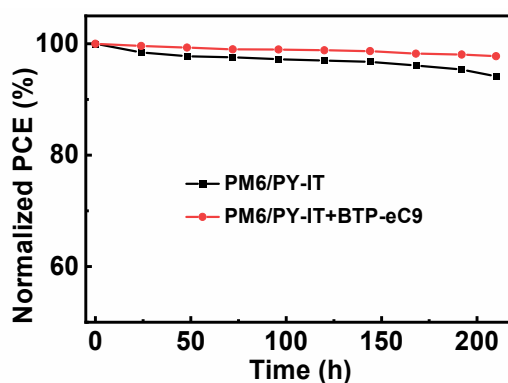
**Table S2.** The  $J_{ph}^{\&}$ ,  $J_{ph}^*$  and  $J_{ph}/J_{sat}$  of typical PPHJ-APSCs.

Active layer	$J_{ph}^{\&}$	$J_{ph}^*$	$J_{sat}$	$J_{ph}^{\&}/J_{sat}$	$J_{ph}^*/J_{sat}$
	[mA cm <sup>-2</sup> ]	[mA cm <sup>-2</sup> ]	[mA cm <sup>-2</sup> ]	[avg. ± dev.] <sup>a</sup> [%]	[avg. ± dev.] <sup>a</sup> [%]
PM6/PY-IT	19.67	23.36	23.73	98.44 (98.31±0.08)	82.89 (82.73±0.11)
PM6/PY-IT+BTP-eC9	20.36	24.08	24.36	98.85 (98.79±0.05)	83.58 (83.50±0.06)

<sup>a</sup> Statistical data obtained from 5 individual cells with different batches.

**Table S3.** The fitted parameters of PPHJ-APSCs according to the impedance spectroscopy.

Active layer	$R_{CT}$ (Ω)	$R_{os}$ (Ω)	$CPE_T$ (nF)	$CPE_P$	$\tau$
PM6/PY-IT	48.4	45.0	16.6	0.928	803.4
PM6/PY-IT+BTP-eC9	34.2	44.6	12.8	0.975	437.8



**Figure S3.** The normalized PCEs of APSCs dependence on storage time in N2 filled glovebox.