## Supporting Information for

## High-Efficiency Ternary Nonfullerene Organic Solar Cells Enabled by a Near

## Infrared Acceptor Enhancing Exciton Utilization and Extending Absorption

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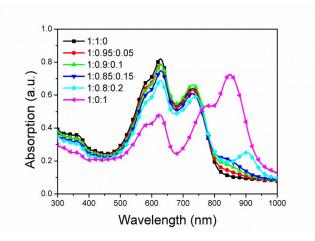
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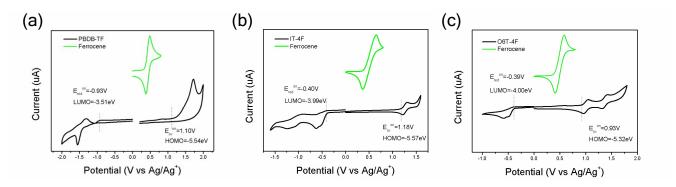
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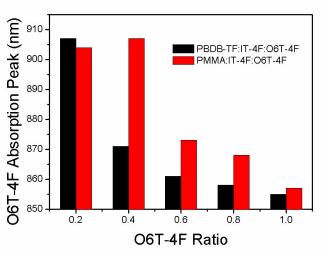
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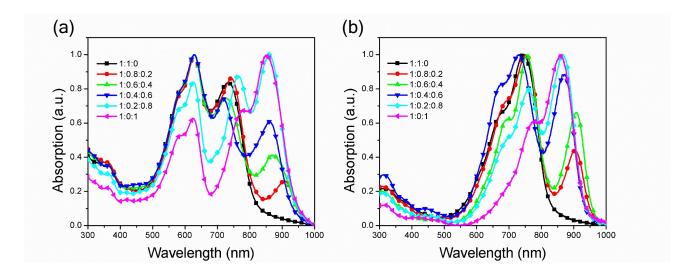
**Figure S1.** The absorption spectra of the PBDB-TF:IT-4F:O6T-4F ternary blends with different IT-4F:O6T-4F ratios. The donor/acceptor weight ratio is fixed at 1:1.



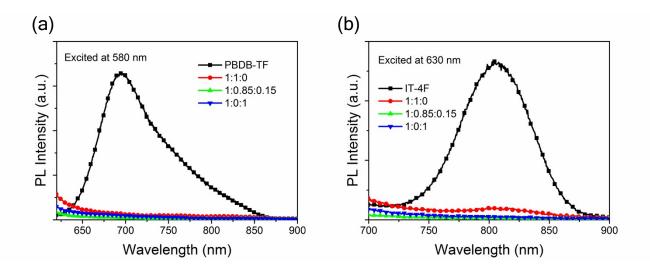
**Figure S2.** CV plots of (a) PBDB-TF, (b) IT-4F and (c) O6T-4F, respectively, from which the HOMO and LUMO levels of the respective materials are calculated.



**Figure S3.** The O6T-4F absorption peak shifts with the IT-4F:O6T-4F ratio in PBDB-TF:IT-4F:O6T-4F and PMMA:IT-4F:O6T-4F films. The ratio between PBDB-TF (or PMMA) and acceptors is fixed at 1:1.



**Figure S4.** Normalized absorption spectra of (a) PBDB-TF:IT-4F:O6T-4F blend films and (b) PMMA:IT-4F:O6T-4F blend films.



**Figure S5.** Photoluminescent quenching of (a) PBDB-TF donor (excited at 580 nm) and (b) IT-4F acceptor (excited at 630 nm) in binary and ternary blend films (PBDB-TF:IT-4F:O6T-4F=1:1:0, 1:0.85:0.15, 1:0:1).

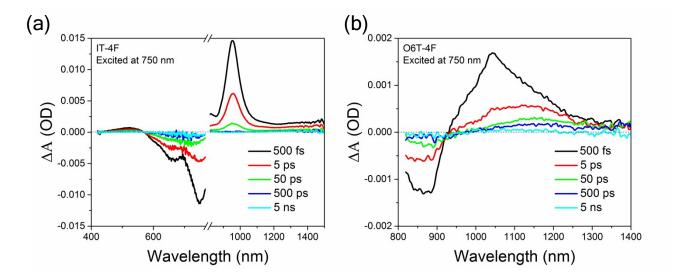


Figure S6. TA spectra of neat IT-4F and O6T-4F films pumped at 750 nm with 10 nJ pulse<sup>-1</sup>.

**Table S1.** Detailed photovoltaic performance of the OSCs based on the PBDB-TF:IT-4F:O6T-4F blendactive layers with various IT-4F:O6T-4F ratios.

PBDB-TF:IT-4F:O6T-4F (w/w/w)	V <sub>oc</sub> [V]	J <sub>SC</sub> [mA cm <sup>-2</sup> ]	FF	PCE [%]
1:1:0	0.82	19.72	0.740	11.97
1:0.8:0.2	0.81	21.33	0.699	12.08
1:0.6:0.4	0.81	19.24	0.614	9.57
1:0.4:0.6	0.80	18.73	0.562	8.42
1:0.2:0.8	0.78	17.24	0.576	7.75
1:0:1	0.77	16.43	0.547	6.92