Supporting Information

Efficient ternary blend all-polymer solar cells with a polythiophene derivative as hole-cascade material

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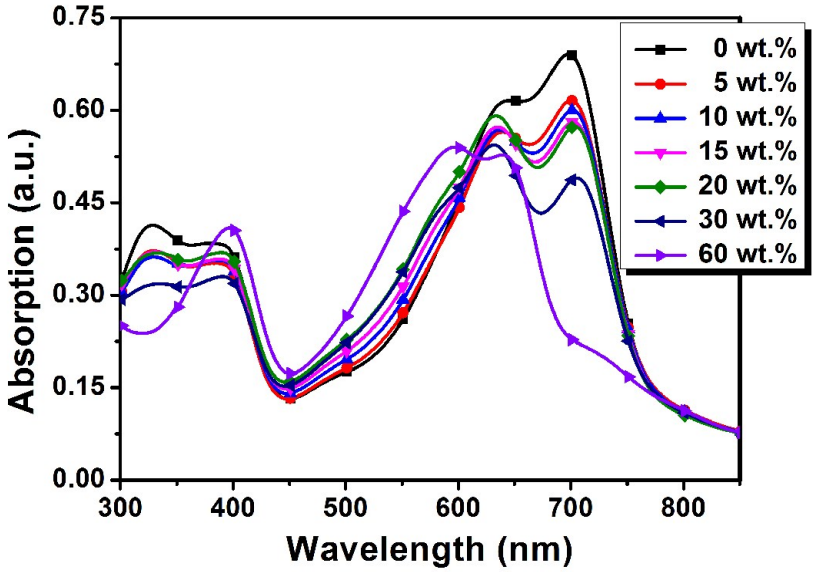

Fig. S1 UV-vis absorption spectra of the **PTB7-Th:PBDD-ff4T:N2200** blend films with different weight ratios of **PBDD-ff4T** (60 wt.% is for the binary blend film based on **PBDD-ff4T:N2200** (1.5:1, w/w)).

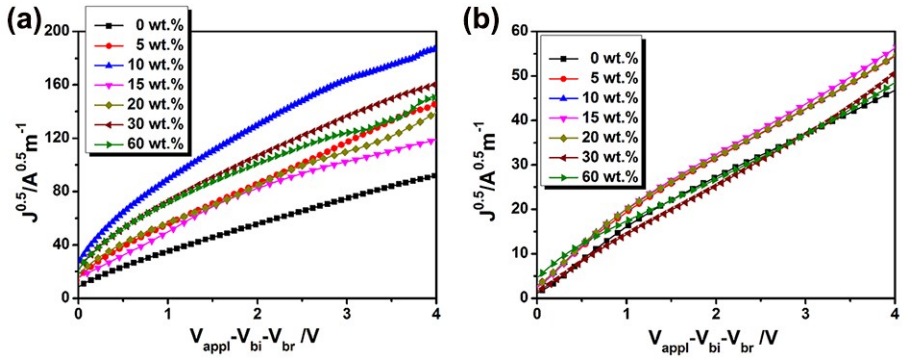

Fig. S2 The *J-V* curves of (a) the hole-only devices with the structure of ITO/PEDOT:PSS/active layer/MoO_3/Al and (b) the electron-only devices with the structure of ITO/ZnO/active layer/Ca/Al according to the SCLC model (60 wt.% is for the binary blend film based on **PBDD-ff4T:N2200** (1.5:1, w/w)).

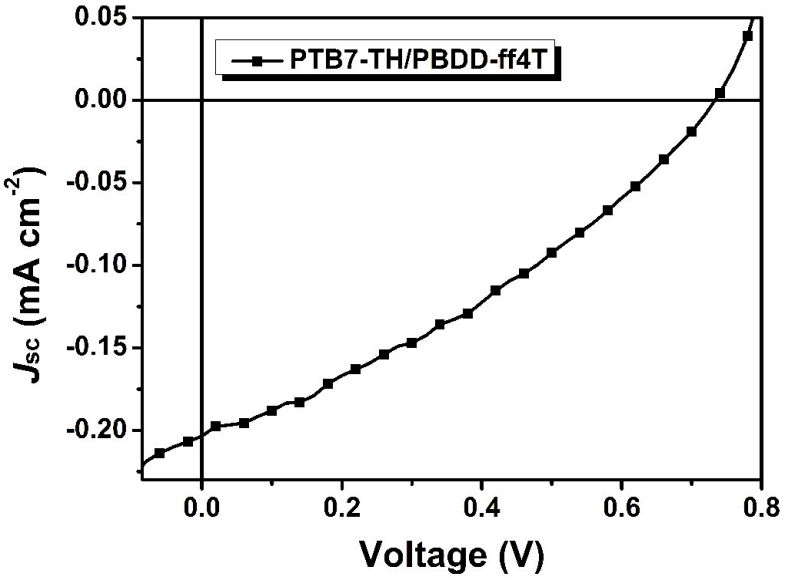

Fig. S3 The *J-V* curve of the binary all-PSC based on **PTB7-Th:PBDD-ff4T (1:1, w/w)**.

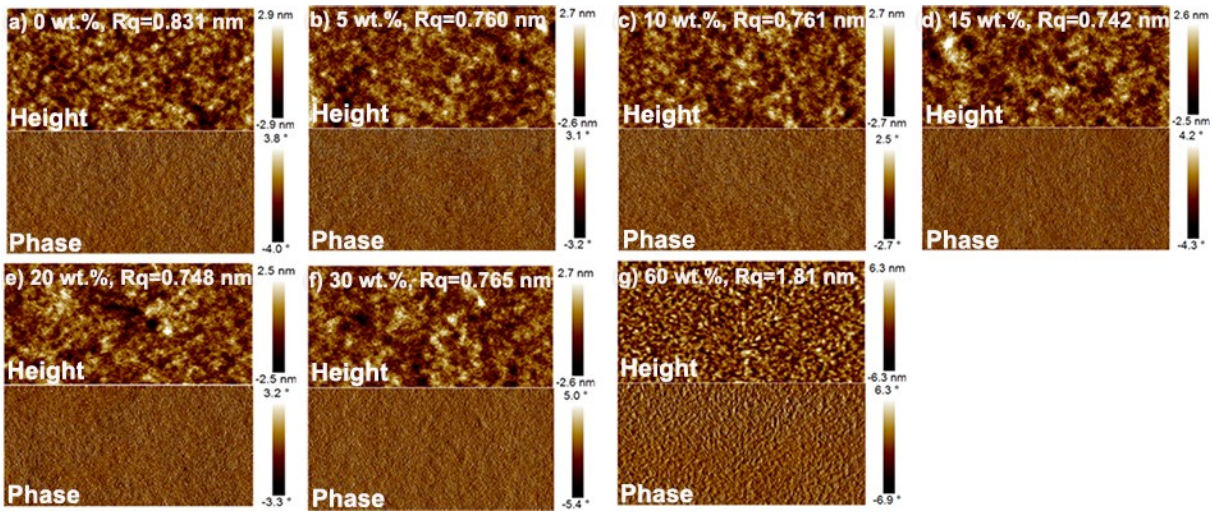

Fig. S4. AFM images of the ternary blend films based on **PTB7-Th:PBDD-ff4T:N2200** with with fixed **PTB7-Th:N2200** weight ratio of 1.5:1 and with 0 wt.% (a), 5 wt.% (b), 10 wt.% (c), 15 wt.% (d), 20 wt.% (e), and 30 wt.% (f) of **PBDD-ff4T,** and (g) the AFM images of binary blend film based on **PBDD-ff4T:N2200** with a D/A weight ratio of 1.5:1 (60 wt.% of **PBDD-ff4T**).

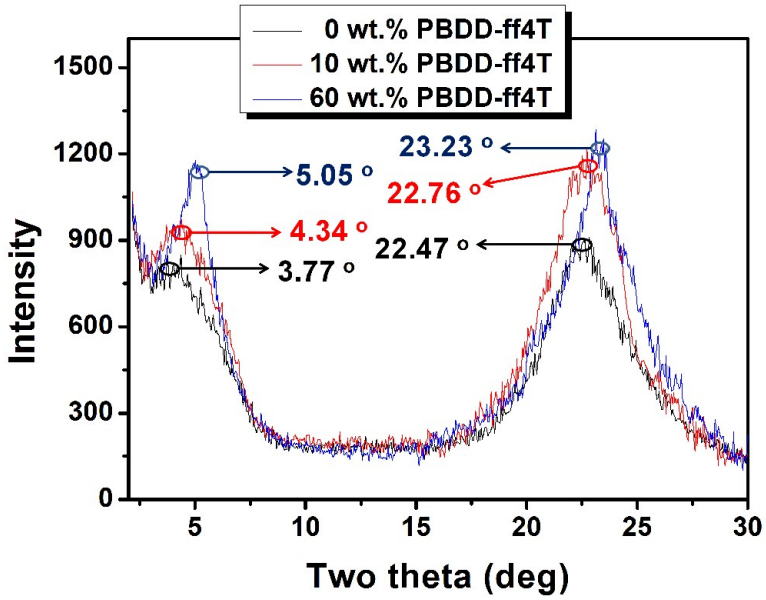

Fig. S5. The XRD curves of the binary blend films of **PTB7-Th:N2200 (0% PBDD-ff4T)** and **PBDD-ff4T:N2200** (60**% PBDD-ff4T**), and the ternary blend film with 10 wt.% of **PBDD-ff4T**.

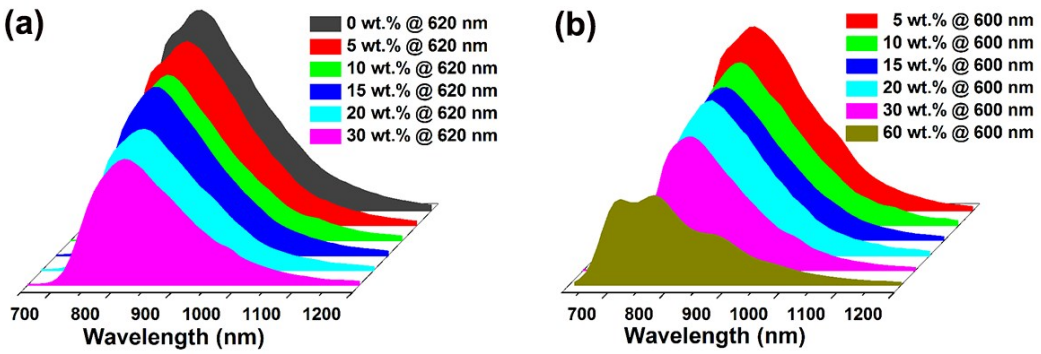

Fig. S6. The PL spectra of the **PTB7-Th/PBDD-ff4T** binary blend films with different blend ratios (where the ratio of PBT7-Th:PBDD-ff4T is consistent with that in the ternary blend films), (a) excited at 620 nm for **PTB7-Th** and the related blend films, (b) excited 600 nm for **PBDD-ff4T** and the related blend films).