Supporting Information

Strong Addition Effect of n-type Polymer with Mid-Energy Level in Polymer:Fullerene Solar Cells with Power Conversion Efficiency Exceeding 10%

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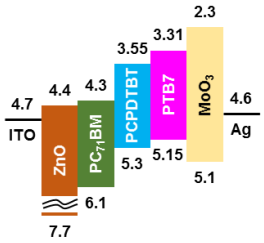
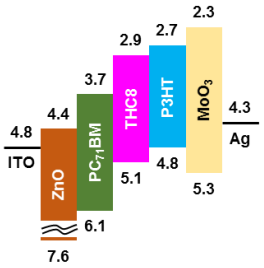
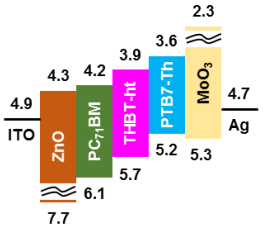
Table S1. Summary of recent reports on the inverted-type polymer:fullerene solar cells with conjugated polymer additives. Note that both minus (-) sign and energy unit (eV) in the energy band diagrams are omitted.

Authors (Affiliation)	Polymer Additive*	Device Structure	Features & Energy Band Diagrams	PCE (%)	Year	Ref
R. Lin, et al. (U. New South Wales, Australia)	PTB7	ITO/ZnO/PTB7:PCPDTBT:$PC_{71}BM$/MoO_3/Ag	▪Electron-donating polymer ▪NOT mid-energy level additive (close to an electron donor) ▪Amount: 5 wt% 	4.28	2014	34
C.-Y. Chi, et al. (NTUST, Taiwan)	THC8	ITO/ZnO/P3HT:THC8:$PC_{61}BM$/MoO_3/Ag	▪Bifunctional copolymer ▪NOT mid-energy level additive (close to an electron donor) ▪Amount: 0.15 wt% 	3.88	2014	37
This work	THBT-ht	ITO/ZnO/PTB7-Th:THBT-ht:$PC_{71}BM$/MoO_3/Ag	▪Electron-accepting polymer ▪Mid-energy level additive ▪Amount: 0.5 wt% 	10.02	2017	-

*Full names of the polymer additives:
- PTB7: Poly[[4.8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4 b]thio-phenediyl]
- THC8: Not provided from original paper (Unit names are only given) (see ref. 37)
- THBT-ht: Poly(3-hexyltiophene-*co*-benzothiadiazole) end-capped with hexylthiophene

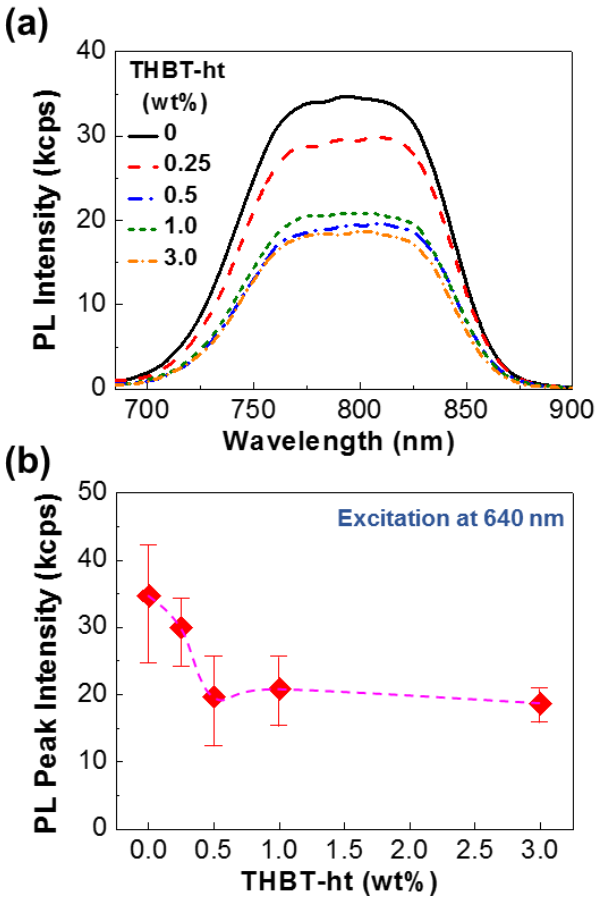


Fig. S1. (a) PL spectra for the binary blend (PTB7-Th:THBT-ht) films coated on the quartz substrates (excitation wavelength = 640 nm). (b) PL peak intensity as a function of the THBT-ht content for the binary blend (PTB7-Th:THBT-ht) films.

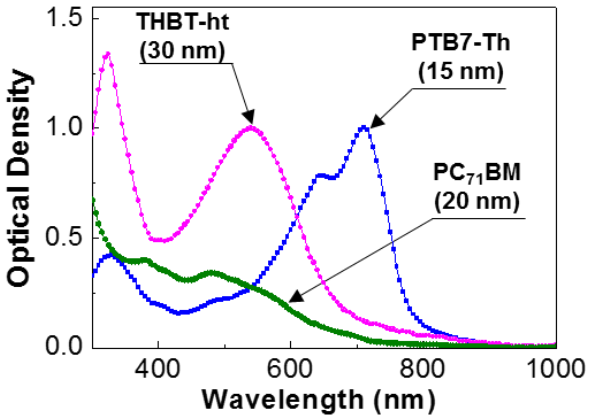


Fig. S2. Optical absorption spectra for the pristine films (PTB7-Th, $PC_{71}BM$, and THBT-ht) coated on the quartz substrates. The thickness of each film is given below the name of material.

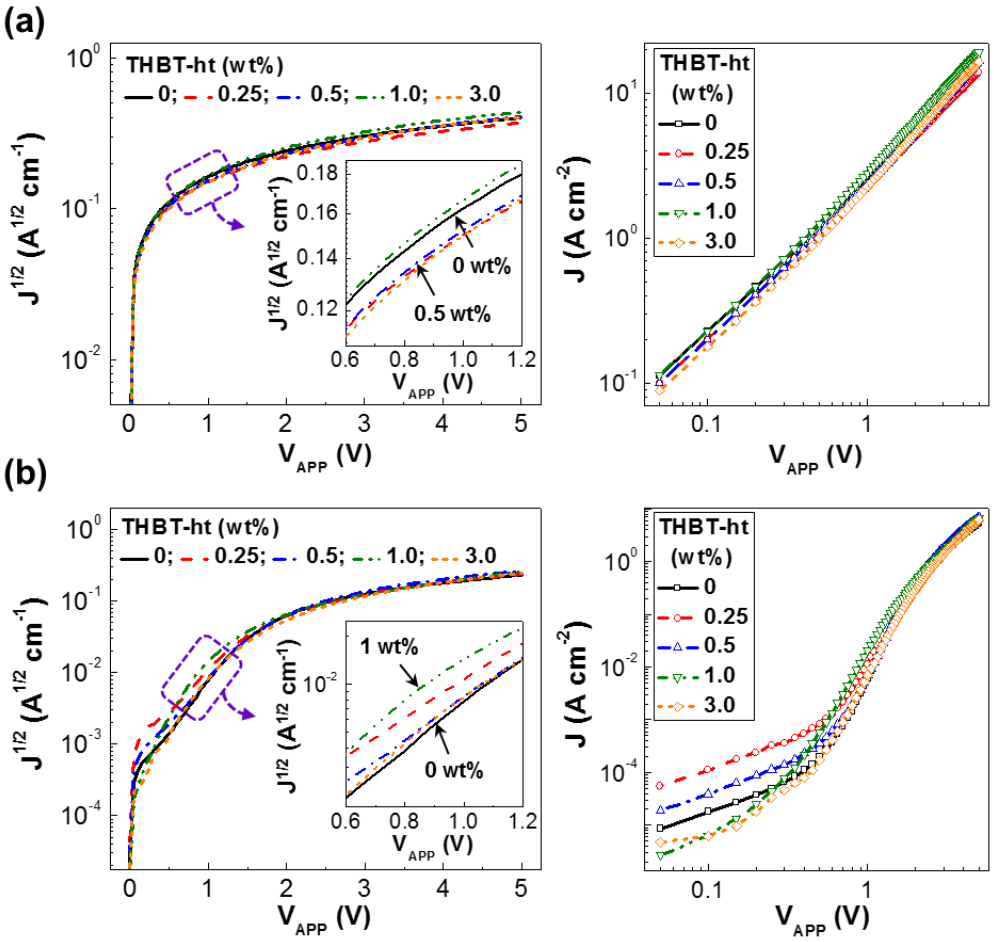


Fig. S3. Current density (J) – applied voltage (V_{APP}) characteristics of (a) hole-only devices (HODs) and (b) electron-only devices (EODs): (left) semi-logarithmic scale, (right) full logarithmic scale. The holes in the HODs are transported mainly through the HOMO levels of the PTB7-Th component, while the electrons in the EODs are transported mainly through the LUMO levels of the $PC_{71}BM$ component in the presence of marginal contribution by the THBT-ht component. Note that the effective voltage obtained by subtracting the built-in voltage from the applied voltage (V_{APP}) was used for the calculation of charge carrier mobility using the space-charge limited current (SCLC) model (see the references 43 and 44 in the manuscript).

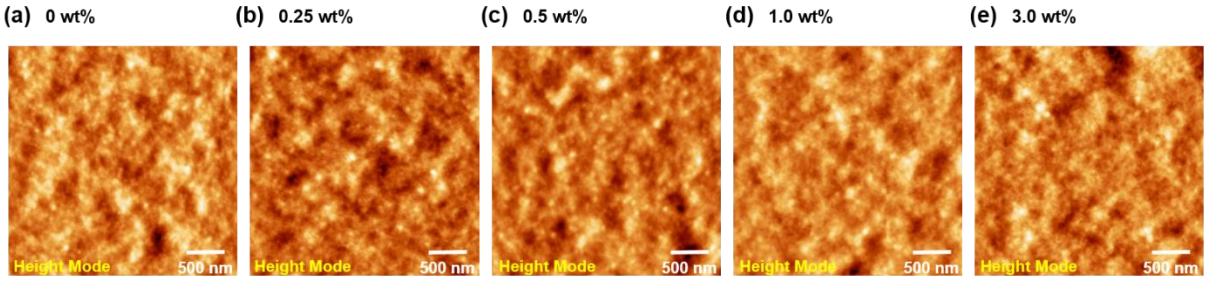


Fig. S4. 2D height-mode AFM images for the BHJ (PTB7-Th:$PC_{71}BM$) layers with the THBT-ht additive, which were coated on the ZnO/ITO-glass substrates: (a) THBT-ht = 0 wt%, (b) 0.25 wt%, (c) 0.5 wt%, (d) 1.0 wt%, (e) 3.0 wt%. The scan size of the AFM images was 3 μm × 3 μm.

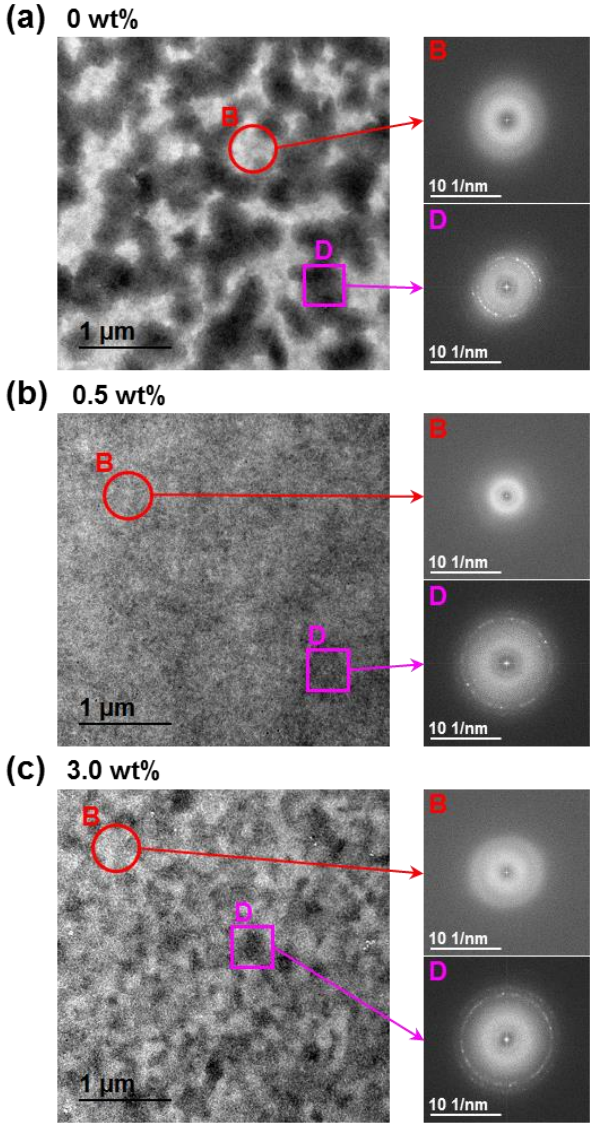


Fig. S5. TEM images, which were measured on the different position from Figure 5, for the BHJ (PTB7-Th:$PC_{71}BM$) films with the THBT-ht additive. The selected-area electron diffraction (SAED) patterns (right) were measured by focusing on the bright (B) and dark (D) parts in the BHJ films.

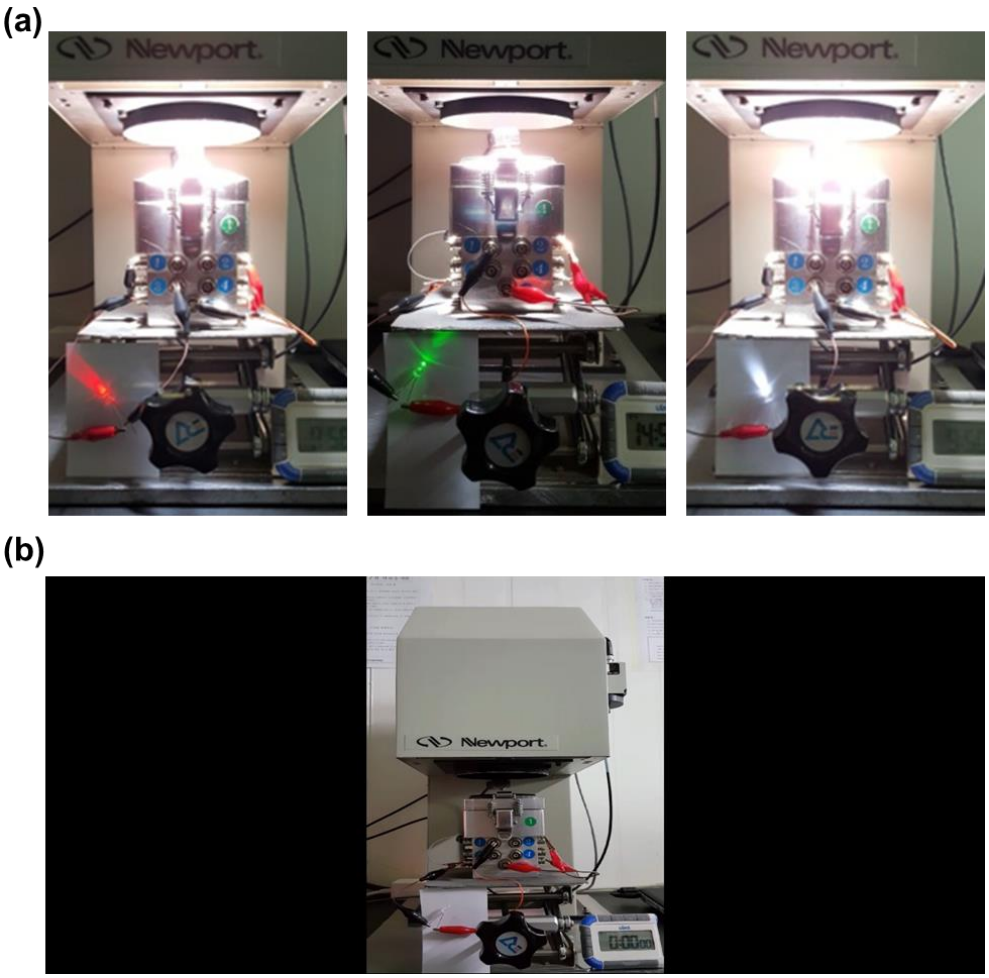


Fig. S6. (a) Photographs for the operation of three different color LEDs (left: red, middle: green, right: blue) by using the semi-solar module made by series connection of four individual inverted-type PTB7-Th:$PC_{71}BM$ solar cells with the THBT-ht additive (0.5 wt%). The simulated solar light (air mass 1.5 G, 100 mW/cm^2) was continuously exposed to the top part of the semi-solar module for 10 h. (b) Video clip for the operation of the semi-solar module under continuous illumination with the simulated solar light for 10 h (filename: video_clip_fig. S6b).