Electronic Supplementary Information (ESI)

Following the nano-structural molecular orientation guidelines for sulfur versus thiophene units in small molecule photovoltaic cells

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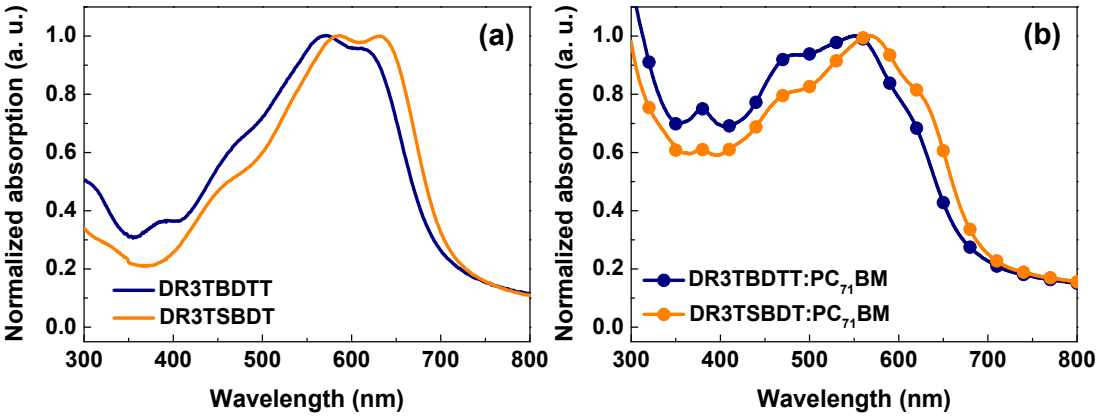

Fig. S1 Normalized UV-vis absorption spectra of pure small molecule (a) and small molecule:$PC_{71}BM$ films (b).

We investigated the UV-vis absorption spectra of active films (pure small molecule (a) and small molecule:$PC_{71}BM$ films (b)). In the pure small molecule films, the **DR3TSBDT** absorption spectrum more red-shifted relative to that in **DR3TBDTT** film. Furthermore, the absorption maximum peak (λ_{max}) at ca. 630 nm appears with shaper and more intense in pure **DR3TSBDT** film. These results indicate that the presence of more ordered aggregation and stronger π–π stacking appears in **DR3TSBDT** films[S1], which are agree with AFM and 2D-GIWAXS analyses. Moreover, in the small molecule:$PC_{71}BM$ films, the absorption spectrum of **DR3TSBDT** blends also slightly red-shifted with higher shoulder peak at ca. 635 nm than that of **DR3TBDTT**:$PC_{71}BM$ film. However, in short absorption range (300 – 500 nm), which is due to PCBM domains[S2], absorption band are revealed with stronger and higher intensity in the **DR3TBDTT**:$PC_{71}BM$ films. All Two findings are quite consistent with line-cut profiles of 2D-GIWAXS (Fig. 4g-h).

S1 Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell and Y. Cao, *Nat. Photonics* 2015, **9**, 174-179.

S2 C. Dyer-Smith, I. A. Howard, C. Cabanetos, A. E. Labban, P. M. Beaujuge and F. Laquai, *Adv. Energy Mater*., 2015, **5**, 1401778.