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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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 ($\lambda_{\text{max}}$) 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 $\pi$–$\pi$ stacking appears in DR3TSBDT films$^S$, 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$^S$, 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).