## Supporting Information

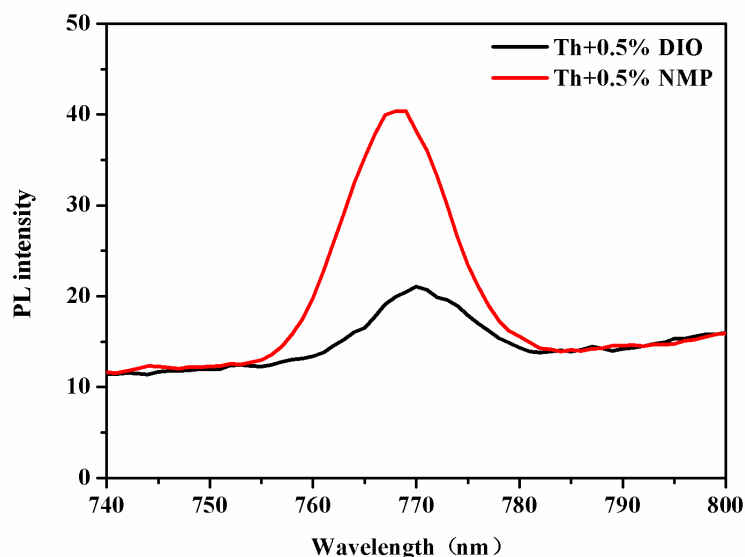## S1



**Figure S1.** Photoluminescence spectrum (PL) of thin films based on pure DTS(PTTh$_2$)$_2$ processed from thiophene solutions incorporating 1% (v/v) NMP or 1% (v/v) DIO.

The photoluminescence (PL) spectroscopy for films of DTS(PTTh$_2$)$_2$ alone prepared from solution in Th containing NMP and DIO were performed, respectively. Here, pure DTS(PTTh$_2$)$_2$ films were chosen because, excitons dissociate at the interface between DTS(PTTh$_2$)$_2$ and PC$_{70}$BM in their blend film, which would lead to almost no PL signal detected. The PL signal of H-aggregation is weaker than J-aggregation due to fluorescence quenching in H-aggregation, and the emission of H-aggregation is red-shifted because indeedly the excited electrons transfer back to ground state from lower excited state after an inner conversion from higher excited state to a lower one. The two excited state is attributed to the large splitting of H-aggregation caused by stronger coupling interaction arising from the larger π-π overlap in H-aggregation. The PL intensity of the film prepared by adding NMP is higher a lot than that by adding DIO, and the latter peak is a little red-shifted from 768 nm to 770 nm. In accordance with the results of absorption spectra, both the shift of emission spectra and the change of emission intensity are also support our view convincingly that the H- and J-aggregation indeed coexist in DTS(PTTh$_2$)$_2$ and their proportion could be controlled effectively by
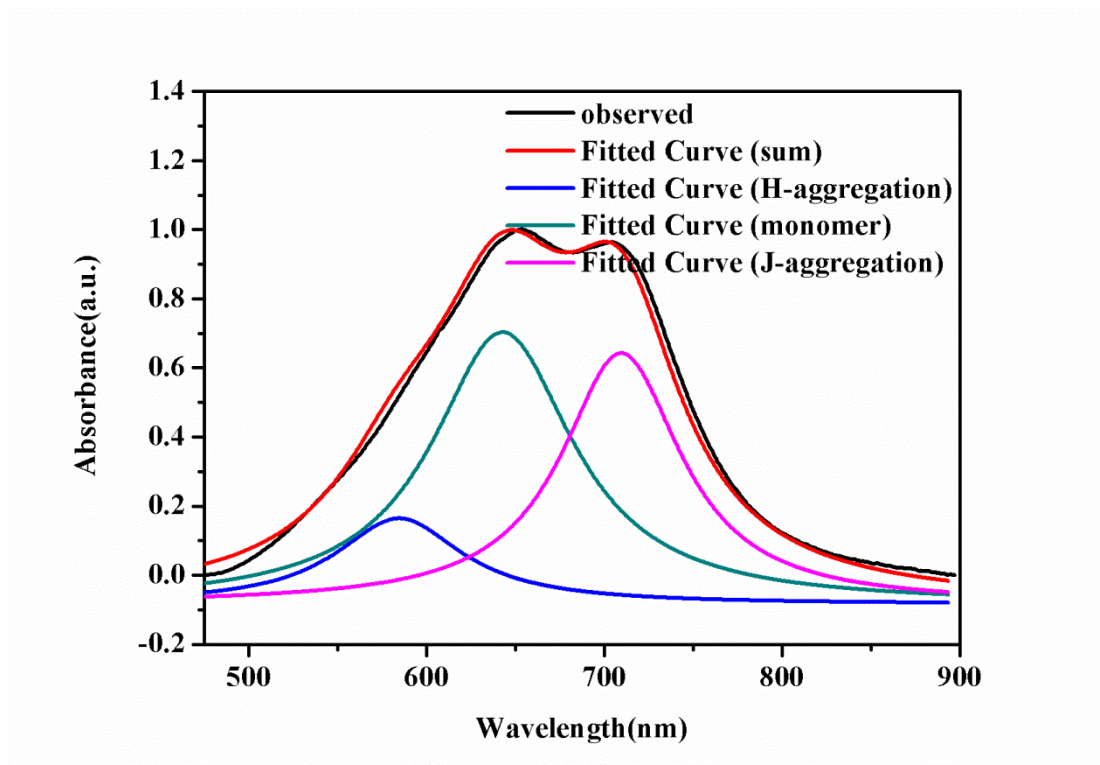
using additives.

**S2**



**Figure S2** The ultraviolet–visible absorption (UV-vis) spectrum after deducting the absorbance of PCBM of spin-coated $DTS(PTTh_2)_2/PC_{70}BM$ (7/3, w/w) blend film processed from thiophene solution and the corresponding fitted curves.

In order to get the ratio of H-aggregation and J-aggregation (H/J), the spectra after deducting the absorbance of PCBM were fitted into three peaks. Take the spectrum of thin film made from Th for example (shown in **Figure S2)**. The peak areas of fitted curves of H-aggregation, monomer and J-aggregation are 34, 120 and 94, respectively. The peak area represents the amount of the corresponding aggregation. So H/J=34/94=0.36.
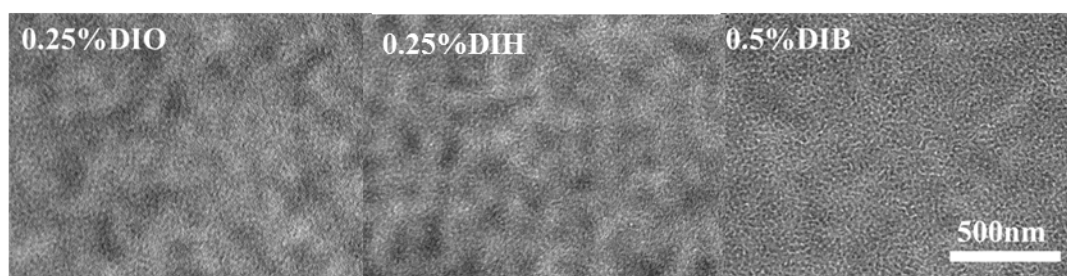
**S3**

**Figure S3.** TEM images of spin-coated DTS(PTTh$_2$)$_2$/PC$_{70}$BM (7/3, w/w) blend films processed from thiophene solutions incorporating 0.25% (v/v) DIO, 0.25% (v/v) DIH, 0.5% (v/v) DIB, respectively.