Supporting Information

## Dual Förster Resonance Energy Transfer Effects in Non-Fullerene Ternary Organic Solar Cells with the Third Component Embedded in Donor and Acceptor

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Figure S1. (a) PL spectra of neat PCDTBT, PTB7-Th, ITIC, 20 wt% PCDTBT:PTB7-Th and 20 wt% PCDTBT:ITIC films with an excitation wavelength of 500 nm. (b) Absorption spectra of PTB7-Th:ITIC with various PCDTBT doping ratios of 10 wt%, 20 wt%, 30 wt% and 40 wt%, respectively.



Figure S2. 2D GIWAXS scattering patterns of pure films of (a) PTB7-Th, (b) PCDTBT, (c) ITIC and (d) in-plane and out-of-plane profiles of each neat films.



Figure S3. (a) 2D GIWAXS scattering patterns of PTB7-Th:ITIC blended with 40 wt% PCDTBT. (b) 2D GISAXS scattering patterns of PTB7-Th:ITIC blended with 40 wt% PCDTBT.



Figure S4. 2D GISAXS scattering patterns of (a) PTB7-Th, (b) PCDTBT and (c) ITIC. (d) In-plane profiles of the pristine films.



Figure S5. AFM images (5  $\mu$ m × 5  $\mu$ m) of ternary blends films with different PCDTBT weight ratio doped of (a)-(e) 0, 10, 20, 30, 40 wt% respectively. (f) Roughness distribution image of the ternary films.



Figure S6. (a) J-V curves of the binary organic solar cells under AM 1.5G illumination at 100 mW cm<sup>-2</sup>. (b) The corresponding EQE spectra.



Figure S7. The J-V curves of hole-only ITO/PEDOT:PSS/PTB7-Th:PCDTBT:ITIC/MoO<sub>3</sub>/Ag devices with different PCDTBT doping ratios and corresponding hole mobility.

Table S1. Parameters of GIWAXS results of neat PTB7-Th, PCDTBT, ITIC and ternary films with various doping ratios of PCDTBT.

|         | PTB7-Th | PCDTBT | ITIC | 0 wt% | 10 wt% | 20 wt% | 30 wt% | 40 wt% |
|---------|---------|--------|------|-------|--------|--------|--------|--------|
| q (Å-1) | 1.61    | 1.55   | 1.54 | 1.55  | 1.62   | 1.68   | 1.72   | 1.74   |
| d (Å)   | 3.90    | 4.05   | 4.08 | 4.05  | 3.88   | 3.74   | 3.65   | 3.61   |

Table S2. Parameters of GIWAXS results of pristine PTB7-Th, ITIC blended with various ratios of PCDTBT.

|         | 10 wt%    | 20 wt%    | 30 wt%    | 10 wt%    | 20 wt%    | 30 wt%    |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|
|         | PCDTBT in |
|         | PTB7-Th   | PTB7-Th   | PTB7-Th   | ITIC      | ITIC      | ITIC      |
| q (Å-1) | 1.68      | 1.73      | 1.75      | 1.65      | 1.74      | 1.77      |
| d (Å)   | 3.74      | 3.63      | 3.59      | 3.81      | 3.61      | 3.55      |

Table S3. Device performance parameters of the binary organic solar cells.

|                | V <sub>oc</sub> (V) | J <sub>sc</sub> (mA cm <sup>-2</sup> ) | FF (%) | PCE (%) |
|----------------|---------------------|--|--------|---------|
| PCDTBT:ITIC    | 0.97                | 2.15                                   | 33.08  | 0.69    |
| PCDTBT:PTB7-Th | 0.90                | 0.12                                   | 37.04  | 0.04    |