## **Supporting Information**

## Unique insight on phase separation in polymer solar cells from its

## electric characteristics

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The **Fig. S1** shows absorption spectra of neat PBDT-TS1 film, PBDT-TS1:ICBA and PBDT-TS1:PC<sub>61</sub>BM blend films prepared with different solution processing ways, consisting of room temperature (20 °C, cool) solution, hot (70 °C) solution, cool solution with solvent additive 1,8-diiodideoctane (DIO) and hot solution with solvent additive DIO. All of the films were dried under the vacuum condition (~ 1 Pa) for 10 minutes. PBDT-TS1:ICBA and PBDT-TS1:PC<sub>61</sub>BM blend films show the similar absorption range, and the absorption spectra of the blend films prepared with different solution processing methods were almost kept constant.



Fig. S1 The absorption spectra of PBDT-TS1 film, PBDT-TS1:ICBA and PBDT-TS1:PC<sub>61</sub>BM

blend films prepared with different solution processing methods.

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More than one hundred PSCs were prepared to confirm the solution processing methods on PSCs performance. The detailed *J-V* curves of part cells based on PBDT-TS1:ICBA (1:1.5, wt/wt) are shown in **Fig. S2**. The PCE of the PSCs are increased to 4.32% form 3.25% by optimizing the D/A phase separation with hot (70 °C) solution with DIO solvent additive. The detailed *J-V* curves of part cells based on PBDT-TS1:PC<sub>61</sub>BM (1:1.5, wt/wt) are shown in **Fig. S3**. The PCE of the PSCs are increased to 5.56% form 5.97% by optimizing the D/A phase separation with cool solution with DIO solvent additive. The average PCE was calculated based on 20 cells prepared under the same condition.



**Fig. S2** The *J-V* curves measured under AM 1.5 light (100 mW/cm<sup>2</sup>) and in dark condition of PSCs based on different PBDT-TS1:ICBA blend films.



Fig. S3 The J-V curves measured under AM 1.5 light (100 mW/cm<sup>2</sup>) and in dark condition of PSCs based on different PBDT-TS1:PC<sub>61</sub>BM blend films.

The **Fig. S4** shows PL spectra of neat PBDT-TS1 film, PBDT-TS1:ICBA and PBDT-TS1:PC<sub>61</sub>BM blend films prepared with different solution processing ways, consisting of cool (20  $^{\circ}$ C, room temperature) solution, hot (70  $^{\circ}$ C) solution, cool solution with solvent additive DIO and hot solution with solvent additive DIO. All of the films were dried under the vacuum condition (~ 1 Pa) for 10 minutes. The PL spectra were measured under the excitation wavelength of 680 nm.



**Fig. S4** PL spectra of neat PBDT-TS1, PBDT-TS1:ICBA and PBDT-TS1:PC<sub>61</sub>BM blend films prepared with different solution processing methods.

The **Fig. S5** shows phase images of PBDT-TS1:ICBA and PBDT-TS1:PC<sub>61</sub>BM blend films prepared with different solution processing ways, consisting of cool (20 °C, room temperature) solution, hot (70 °C) solution, cool solution with solvent additive DIO and hot solution with solvent additive DIO. All of the films were dried under the vacuum condition (~ 1 Pa) for 10 minutes.



Fig. S5 Phase images of PBDT-TS1:ICBA and PBDT-TS1:PC<sub>61</sub>BM blend films prepared with different solution processing methods.

The **Fig. S6** shows the schematic image of phase separation of active layer with different film drying process. The D/A phase separation strongly depends on the solution conditions, post treatment conditions on the active layer as well as the intrinsic factor of electron donor and acceptor molecular chemical structures.



Fig. S6 The schematic image of phase separation of active layer with different film drying

process.