### Supporting Information for:

# Impact of Highly-Crystalline, Isoindigo-Based Small-Molecular Additives for Enhancing Performance of All-Polymer Solar Cells

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## **Table of Contents**

#### **Supplementary Figures S1-14**

- **Figure S1**: (a) Synthetic scheme and (b) <sup>1</sup>H-NMR spectrum of DTI.
- Figure S2. (a) Reduction potential and (b) oxidation potential of DTI measured by cyclic voltammograms.
- Figure S3. (a) GIWAXS image of the DTI pristine film; (b-c) in-plane and out-of-plane linecuts.
- Figure S4. Absorption coefficient of pristine films of PTB7-Th, DTI, and P(NDI2HD-T).
- Figure S5. Transient absorption spectra for (a) PTB7-Th pristine film and (b) DTI pristine film at various delays with the excitation of 3.06 eV (405 nm), and (c) exciton dynamics at 0.87 eV for PTB7-Th with 0–20 wt% addition of DTI.
- Figure S6. PL spectra of PTB7-Th, DTI, and P(NDI2HD-T) with the excitation at 500 nm.
- Figure S7. AFM images of all-polymer blend films *via* addition of DTI with different weight contents: (a-e) 0–50 wt%.
- Figure S8. (a) GIWAXS images, (b) in-plane linecuts, and (c) out-of-plane linecuts of the P(NDI2HD-T) films with different DTI contents.
- Figure S9. (a) GIWAXS images, (b) in-plane linecuts, and (c) out-of-plane linecuts of the PTB7-Th films with different DTI contents.
- Figure S10. (a) UV-vis absorption spectra of blend films of PTB7-Th and P(NDI2HD-T) with 0-50 wt% addition of DTI; (b) UV-vis absorption spectra of blend films of PTB7-Th with 0-50 wt% addition of DTI; (c) Absorption ratio of 0-0 to 0-1 vibronic peaks (R) and 0-0 absorption wavelength with 0 50 wt% addition of DTI in PTB7-Th films.
- Figure S11. Time-resolved PL and the PL lifetimes of (a, b) PTB7-Th and (c, d) P(NDI2HD-T) with 0-20 wt% addition of DTI.
- Figure S12. (a) Hole and (b) electron mobilities of all-polymer blends with different DTI contents.
- **Figure S13**. Dependence of  $J_{SC}$  on illuminated light intensity (*P*) of all-PSCs with different weight ratios of DTI.
- Figure S14. Normalized PCEs of the all-PSC devices as a function of annealing time at 150 °C.

#### **Supplementary Tables S1-3**

- Table S1. Device performance of the neat films of PTB7-Th, DTI, and P(NDI2HD-T) and blend films of PTB7-Th:DTI and P(NDI2HD-T):DTI under AM 1.5G illumination (100 mW cm<sup>-2</sup>).
- **Table S2**. GIWAXS results of pristine films *via* addition of the DTI.
- **Table S3**. Hole and electron mobility values of the all-polymer blend devices with different weight ratios of DTI.

## **Supplementary Figures**



Figure S1. (a) Synthetic scheme and (b) <sup>1</sup>H-NMR spectrum of DTI.



Figure S2. (a) Reduction potential and (b) oxidation potential of DTI measured by cyclic voltammograms.



Figure S3. (a) GIWAXS image of the DTI pristine film; (b-c) in-plane and out-of-plane linecuts.



Figure S4. Absorption coefficient of pristine films of PTB7-Th, DTI, and P(NDI2HD-T).



**Figure S5.** Transient absorption spectra for (a) PTB7-Th pristine film and (b) DTI pristine film at various delays with the excitation of 3.06 eV (405 nm), and (c) exciton dynamics at 0.87 eV for PTB7-Th with 0–20 wt% addition of DTI.



Figure S6. PL spectra of PTB7-Th, DTI, and P(NDI2HD-T) with the excitation at 500 nm.



**Figure S7**. AFM images of all-polymer blend films *via* addition of DTI with different weight contents: (a-e) 0-50 wt%.



**Figure S8**. (a) GIWAXS images, (b) in-plane linecuts, and (c) out-of-plane linecuts of the P(NDI2HD-T) films with different DTI contents.



**Figure S9**. (a) GIWAXS images, (b) in-plane linecuts, and (c) out-of-plane linecuts of the PTB7-Th films with different DTI contents.



**Figure S10**. (a) UV-vis absorption spectra of blend films of PTB7-Th and P(NDI2HD-T) with 0-50 wt% addition of DTI; (b) UV-vis absorption spectra of blend films of PTB7-Th with 0-50 wt% addition of DTI; (c) Absorption ratio of 0-0 to 0-1 vibronic peaks (right) and 0-0 absorption wavelength (left) with 0 - 50 wt% addition of DTI in PTB7-Th films.



**Figure S11**. Time-resolved PL and the PL lifetimes of (a, b) PTB7-Th and (c, d) P(NDI2HD-T) with 0–20 wt% addition of DTI.



**Figure S12**. (a) Hole and (b) electron mobilities of all-polymer blends with different DTI contents; The films were prepared under optimized device conditions.



**Figure S13**. Dependence of  $J_{SC}$  on illuminated light intensity (*P*) of all-PSCs with different weight ratios of DTI.



**Figure S14**. Normalized PCEs of the all-PSC devices as a function of annealing time at 150 °C.

#### **Supplementary Tables**

**Table S1**. Device performance of the neat films of PTB7-Th, DTI, and P(NDI2HD-T) and blend films of PTB7-Th:DTI and P(NDI2HD-T):DTI under AM 1.5G illumination (100 mW cm<sup>-2</sup>).

Active Layers	$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA cm <sup>-2</sup> )	FF	PCE (%)
PTB7-Th	0.80	0.42	0.49	0.16
DTI	-	-	-	-
P(NDI2HD-T)	0.33	0.0012	0.58	0.00022
PTB7-Th : DTI (1 : 1 (w/w))	0.46	0.28	0.31	0.04
P(NDI2HD-T) : DTI (1 : 1 (w/w))	-	-	-	-

Table S2. GIWAXS results of pristine films via addition of the DTI.

Materials	$q_{\rm z}{ m of}(010)^{ m b}({ m \AA}^{-1})$	$d_{(010)}$ -spacing (Å)
PTB7-Th pristine	1.63	3.9
+ DTI 10 wt%	1.71	3.7
P(NDI2HD-T) pristine	1.53	4.1
+ DTI 10 wt%	1.60	3.9

**Table S3**. Hole and electron mobility values of the all-polymer blend devices with different weight ratios of DTI.

Active Layers	$\mu_{\rm h}  [{ m cm}^2  { m V}^{-1}  { m s}^{-1}]$	$\mu_{\rm e}  [{ m cm}^2  { m V}^{-1}  { m s}^{-1}]$
PTB7-Th : P(NDI2HD-T)	$1.2 \times 10^{-4}$	5.3×10 <sup>-5</sup>
+ DTI 10 wt%	3.0×10 <sup>-4</sup>	1.2×10-4
+ DTI 20 wt%	2.2×10 <sup>-4</sup>	9.8×10 <sup>-5</sup>
+ DTI 30 wt%	9.4×10 <sup>-5</sup>	4.9×10 <sup>-5</sup>
+ DTI 50 wt%	4.2×10 <sup>-5</sup>	1.8×10-5