

## Supplementary Material (ESI)

### Impacts of Metal Oxide Diffusion and Materials Design on Thermal Stabilities of Non-Fullerene Polymer Solar Cells

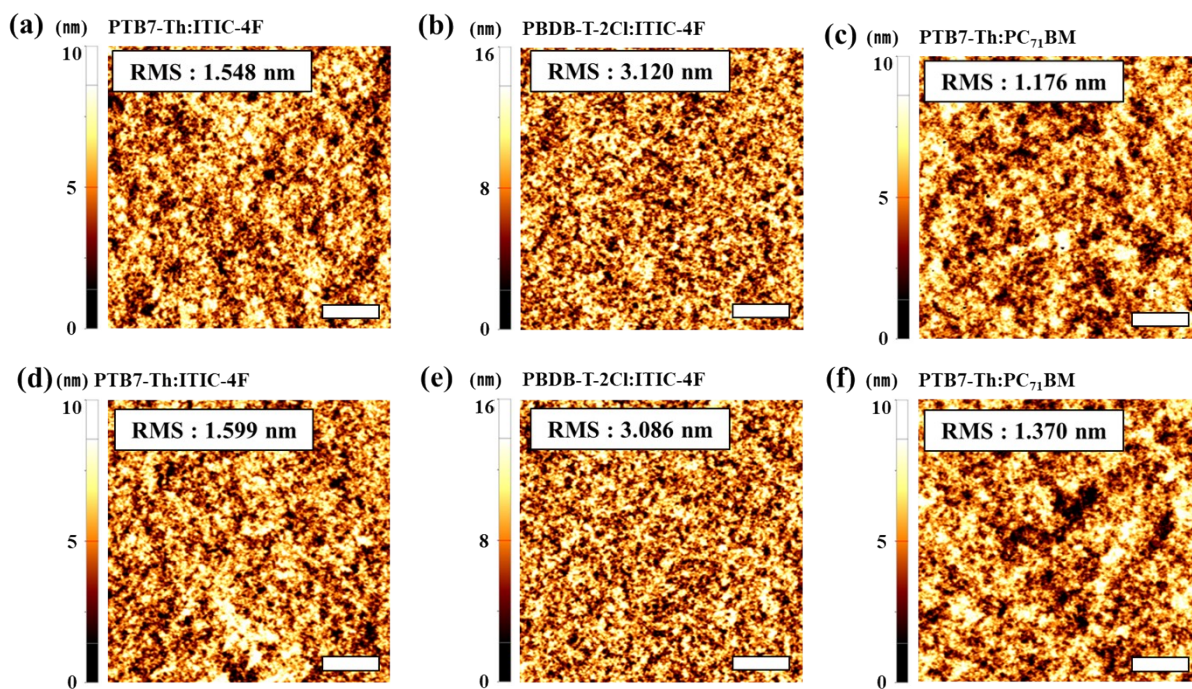
*Dongmin Lee, Yongchan Jang, Jeonga Kim, Sang Young Jeong, Han Young Woo, Donggu Lee, Jongbok Kim, Youngmin Lee, Changyeon Lee\*, and Wonho Lee\**

#### **Experimental Section**

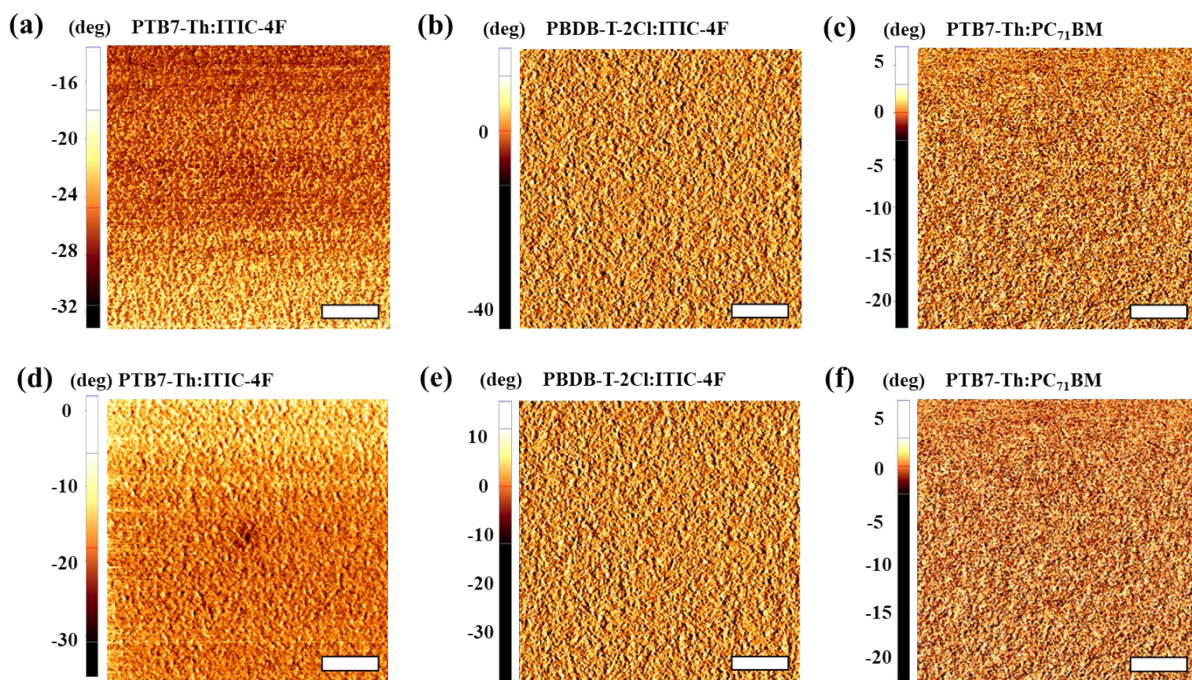
**Materials:** PTB7-Th (the number average molecular weight ( $M_n$ ) = 57.1 kg mol<sup>-1</sup> and dispersity ( $\mathcal{D}$ ) = 1.95) and ITIC-4F were purchased from Ossila. PC<sub>71</sub>BM was purchased from Nano-C. PBDB-T-2Cl ( $M_n$  = 36.0 kg mol<sup>-1</sup> and  $\mathcal{D}$  = 4.47) was synthesized according to previous literature.<sup>1</sup>

**Measurements:** AFM images were obtained using an XE-100 (Park System) with an AC160TS probe in tapping mode. GIWAXS measurements were performed using synchrotron radiation on beam line 6D at the Pohang Accelerator Laboratory (PAL), Pohang, Korea. The XPS and UPS measurements were performed using a VersaProbe III (ULVAC-PHI). For the XPS measurements, an Al K $\alpha$  X-ray source ( $h\nu$  = 1486.7 eV), with path energy of 1 eV, was used. The He I (21.2 eV) radiation line from a discharge lamp was used in UPS measurements to identify the HOMO level of MoO<sub>3</sub>. For the ToF-SIMS depth profile data, Cs<sup>+</sup> primary ions (2 keV, ~58 nA) were used for sapping, and a Bi<sup>+</sup> pulsed primary ion beam was used for the analysis (30 keV, 1 pA). EIS was measured under ambient and dark conditions by using a WizEIS-1200 (Wizmac); the frequency range was from 10<sup>6</sup> – 1 Hz with an oscillation amplitude of 10 mV. The UV-vis absorption spectra were analyzed using a UV-1900 (Shimadzu). The tDOS was calculated using capacitance measurements according to the previous literature.<sup>2</sup> The capacitance behavior with a full configuration of ITO/ZnO/active layer/MoO<sub>3</sub>/Ag was not properly recorded, so ITO/active layer/MoO<sub>3</sub>/Ag structure was fabricated to obtain capacitance (**Fig. S7c**). However, because the device without ZnO exhibited a very low built-in potential ( $V_{bi}$ ) (**Fig. S7a**), it was assumed that the  $V_{bi}$  of ITO/active layer/MoO<sub>3</sub>/Ag was identical to the value extracted from the full-configuration device (**Fig. S7b**). From the data of **Fig. S7b** and **S7c**, the distribution of the tDOS was plotted (**Fig. S7d**).

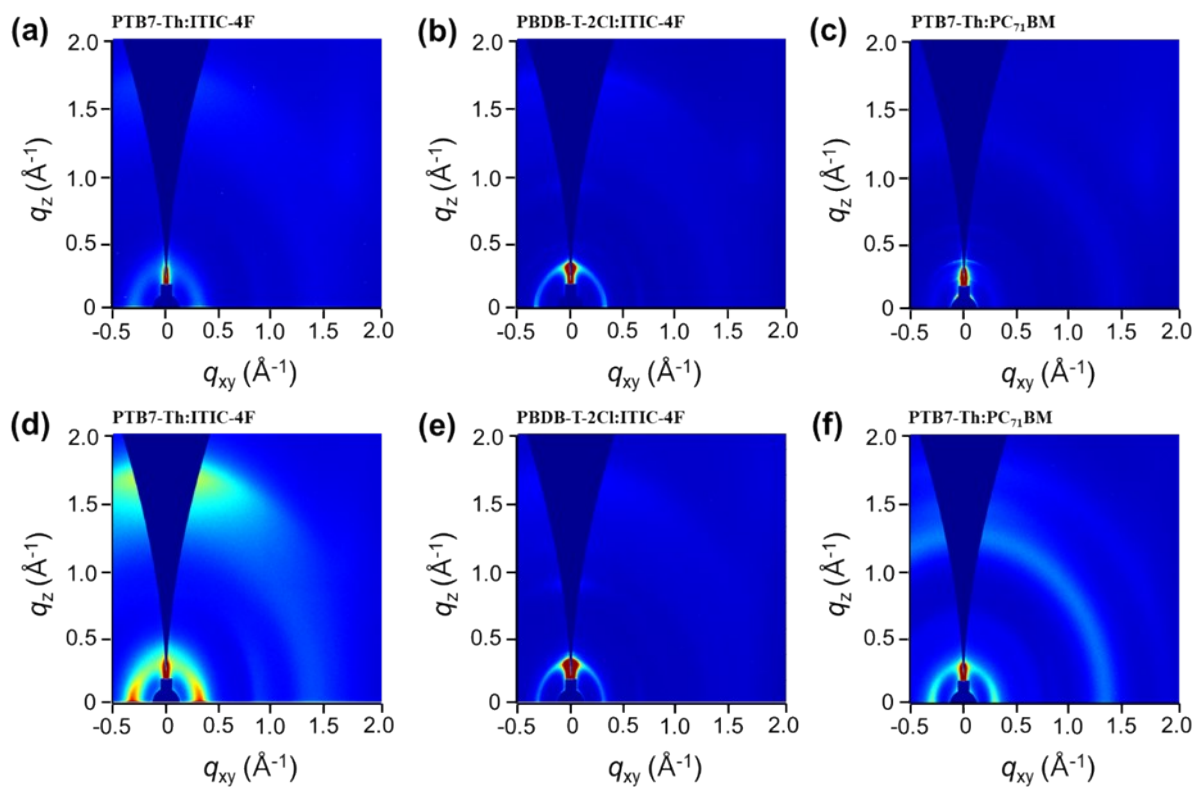
*Device fabrication and characterization of PSCs:* The device structure used in this study was ITO/ZnO/active layer/MoO<sub>3</sub>/Ag. The ITO coated glass substrates were cleaned by sequential ultrasonication with acetone, deionized water, and isopropanol. The ITO glass was dried in an oven at 100 °C for 12 h. The ZnO precursor solution was prepared according to a previously reported procedure.<sup>3</sup> Before deposition of the ZnO precursor solution, the ITO/glass substrates were processed with O<sub>2</sub> plasma for 20 min. Thereafter, the ZnO layer was deposited by spin-casting the precursor solution at 2000 rpm for 40 s, followed by annealing at 200 °C for 10 min under ambient conditions. For the PTB7-Th:PC<sub>71</sub>BM blend, the optimized donor:acceptor (D:A) ratio was 1:1.5, and the concentration of the donor material was 10 mg mL<sup>-1</sup> in CB with 3.0 vol% 1,8-diiodooctane (DIO). For the PTB7-Th:ITIC-4F blend, the optimized D:A ratio was 1:1.5, and donor concentration was 8 mg mL<sup>-1</sup> in CB with 0.5 vol% DIO. For the PBDB-T-2Cl:ITIC-4F blend, the optimized D:A ratio was 1:1, and the donor concentration was 12 mg mL<sup>-1</sup> in CB with 0.5 vol% DIO. The blended solutions were stirred for 1 h at 85 °C and spin-coated at 2000 rpm (PTB7-Th:PC<sub>71</sub>BM and PTB7-Th:ITIC-4F) or 1000 rpm (PBDB-T-2Cl:ITIC-4F) for 60 s in an N<sub>2</sub>-filled glove box. MoO<sub>3</sub> (10 nm) and Ag (100 nm) were sequentially deposited using a thermal evaporator under high vacuum conditions (<1×10<sup>-6</sup> torr) to complete the device fabrication. The active area of the fabricated device was 0.168 cm<sup>2</sup>. The current density-voltage (J-V) characteristics of the devices were measured using a Keithley 2400 Source Meter under the ambient conditions under AM 1.5G (100 mW cm<sup>-2</sup>, ORIEL LCS-100, Newport). Both pre- and post-annealing were performed in an N<sub>2</sub>-filled glove box to exclude the effects of moisture and oxygen on the degradation mechanism.



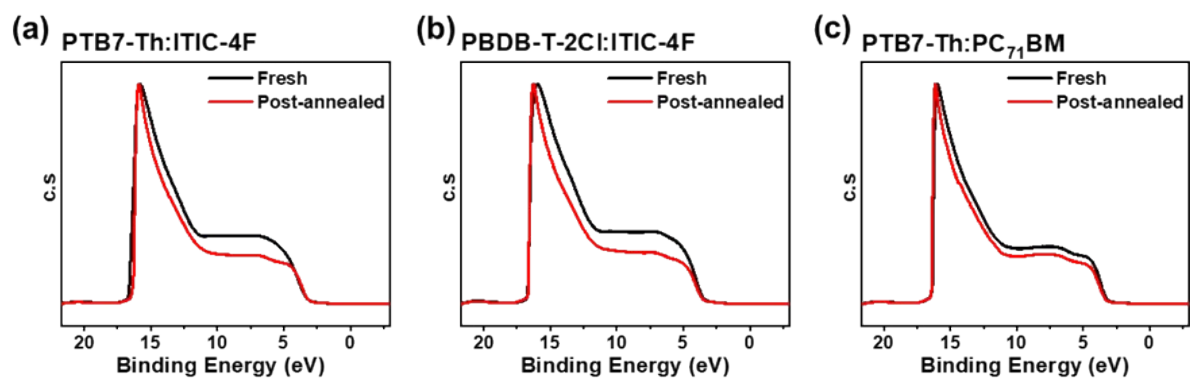
**Fig. S1.** AFM height images of fresh and pre-annealed (a, d) PTB7-Th:ITIC-4F, (b, e) PBDB-T-2Cl:ITIC-4F, and (c, f) PTB7-Th:PC<sub>71</sub>BM blend films (size: 10 μm × 10 μm). The scale bar in the AFM images is 2 μm.



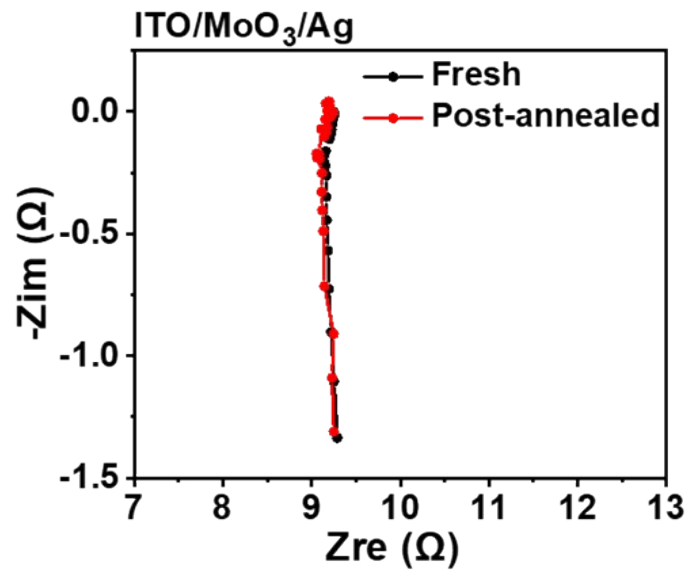
**Fig. S2.** AFM phase images of fresh and pre-annealed blend films. The scale bar in the AFM images is 2 μm.



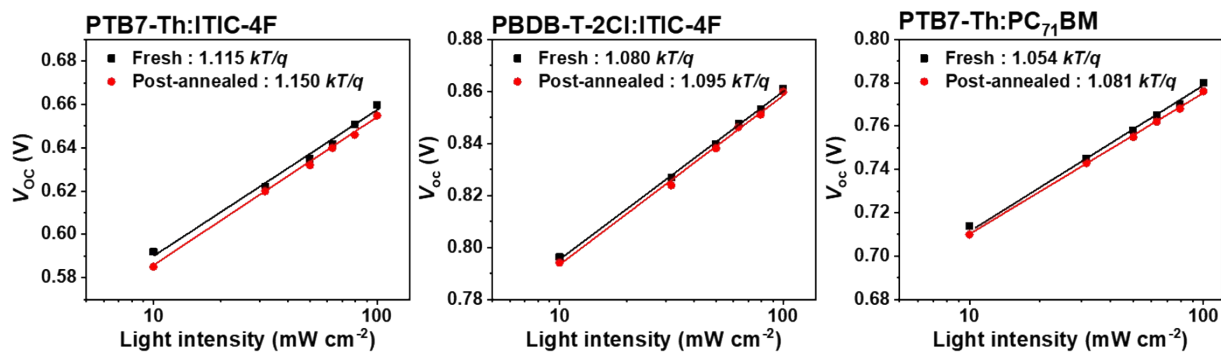
**Fig. S3.** GIWAXS scattering patterns of fresh and pre-annealed (a, d) PTB7-Th:ITIC-4F, (b, e) PBDB-T-2Cl:ITIC-4F, and (c, f) PTB7-Th:PC<sub>71</sub>BM blend films.



**Fig. S4.** UPS spectra of fresh and post-annealed (a) PTB7-Th:ITIC-4F, (b) PBDB-T-2Cl:ITIC-4F, and (c) PTB7-Th:PC<sub>71</sub>BM devices with ITO/ZnO/active layer/MoO<sub>3</sub> structure.

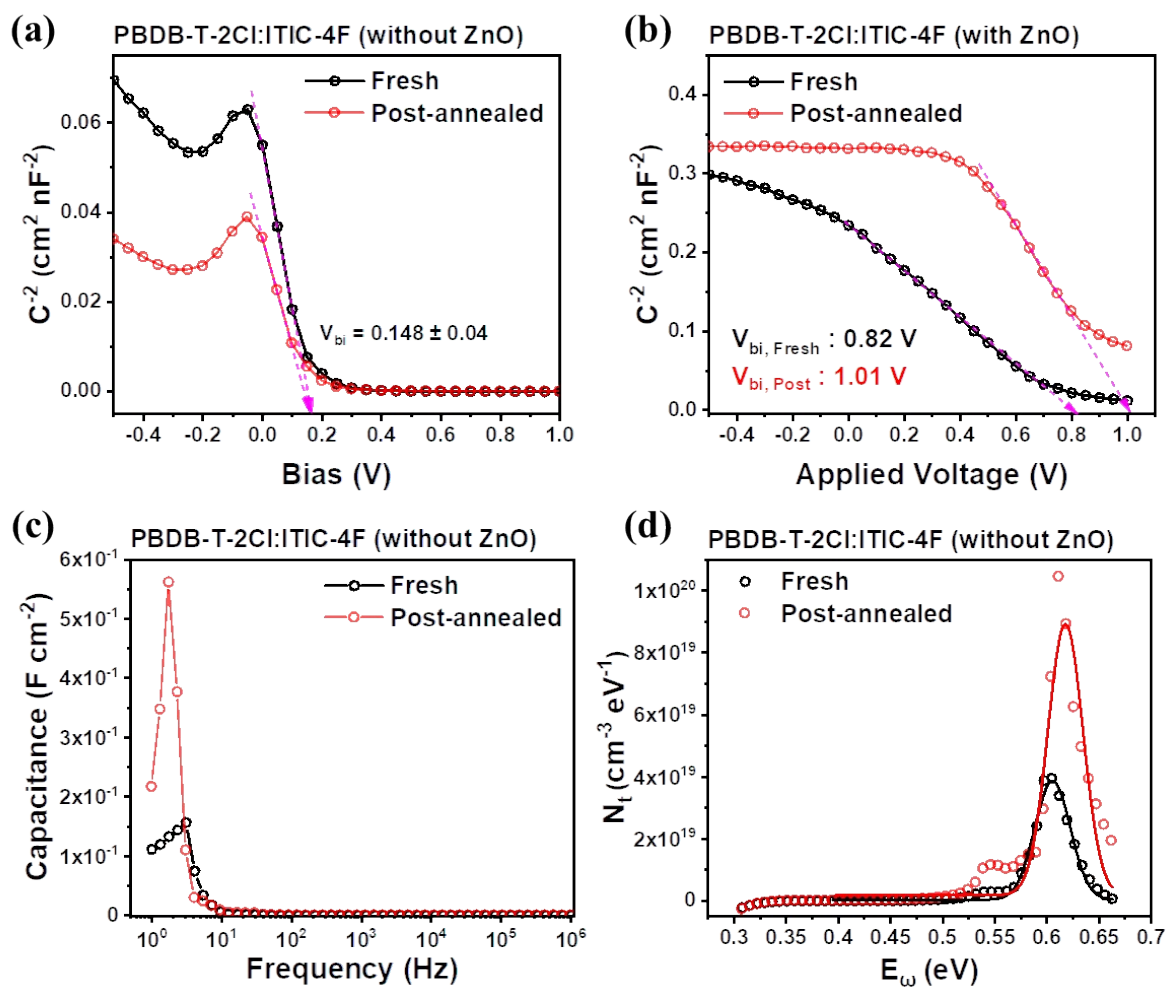


**Fig. S5.** Nyquist plot for ITO/MoO<sub>3</sub>/Ag device annealed at 110 °C for 10 min (frequency: 1M ~ 1 Hz at 0 V, ambient, R.T and dark).

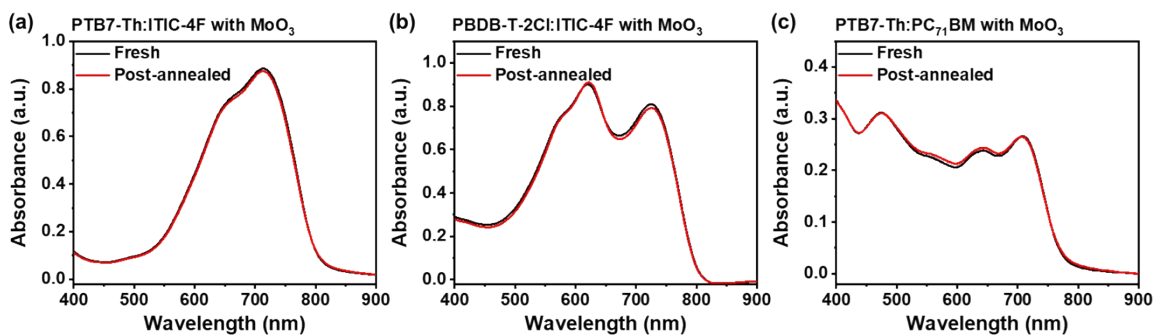


**Fig. S6.** Plots of  $V_{OC}$  vs. light intensity for the fresh and post-annealed PTB7-Th:ITIC-4F, PBDB-T-2Cl:ITIC-4F, and PTB7-Th:PC<sub>71</sub>BM devices.





**Fig S7.** Mott-Schottky plot measured at 10 kHz (a) without ZnO and (b) with ZnO device. The linear fit reveals the built-in potential. (c) Capacitance spectra of fresh and post-annealed devices measured at zero bias. (d) The distribution of tDOS. The continuous line denotes the fit using a Gaussian distribution.



**Fig. S8.** UV-Vis absorbance of fresh and post-annealed samples: (a) glass/PTB7-Th:ITIC-4F/MoO<sub>3</sub>, (b) glass/PBDB-T-2Cl:ITIC-4F/MoO<sub>3</sub>, and (c) glass/PTB7-Th:PC<sub>71</sub>BM/MoO<sub>3</sub>.

**Table S1.** Photovoltaic performances of fresh and pre-annealed devices. The average values were obtained from at least ten different devices.

| Active layer (D:A)                            | $V_{OC}$ (V) | $J_{SC}$ (mA cm <sup>-2</sup> ) | FF          | PCE (%)      |
|---|--------------|---------------------------------|-------------|--------------|
| <b>PTB7-Th:ITIC-4F</b> <sup>a</sup>           | 0.65 ± 0.01  | 17.92 ± 0.40                    | 0.68 ± 0.01 | 8.14 ± 0.12  |
| <b>PTB7-Th:ITIC-4F</b> <sup>b</sup>           | 0.63 ± 0.02  | 17.95 ± 0.60                    | 0.70 ± 0.01 | 8.16 ± 0.17  |
| <b>PBDB-T-2Cl:ITIC-4F</b> <sup>a</sup>        | 0.87 ± 0.01  | 18.13 ± 0.39                    | 0.67 ± 0.01 | 10.52 ± 0.14 |
| <b>PBDB-T-2Cl:ITIC-4F</b> <sup>b</sup>        | 0.84 ± 0.01  | 18.04 ± 0.60                    | 0.71 ± 0.01 | 10.63 ± 0.38 |
| <b>PTB7-Th:PC<sub>71</sub>BM</b> <sup>a</sup> | 0.78 ± 0.01  | 17.22 ± 0.44                    | 0.65 ± 0.01 | 8.67 ± 0.21  |
| <b>PTB7-Th:PC<sub>71</sub>BM</b> <sup>b</sup> | 0.78 ± 0.01  | 17.20 ± 0.56                    | 0.65 ± 0.01 | 8.77 ± 0.10  |

<sup>a</sup> Fresh device; <sup>b</sup> pre-annealed device

**Table S2.** Photovoltaic performances of fresh and post-annealed devices.

| Active layer (D:A)                               | $V_{OC}$ (V) | $J_{SC}$ (mA cm <sup>-2</sup> ) | FF          | PCE (%)      |
|--|--------------|---------------------------------|-------------|--------------|
| PTB7-Th:ITIC-4F <sup>a</sup>                     | 0.65 ± 0.01  | 17.92 ± 0.40                    | 0.68 ± 0.01 | 8.14 ± 0.12  |
| PTB7-Th:ITIC-4F <sup>b</sup> (60°C)              | 0.65 ± 0.01  | 17.74 ± 0.42                    | 0.67 ± 0.02 | 8.11 ± 0.22  |
| PTB7-Th:ITIC-4F <sup>b</sup> (80°C)              | 0.65 ± 0.01  | 17.56 ± 0.38                    | 0.67 ± 0.02 | 7.81 ± 0.40  |
| PTB7-Th:ITIC-4F <sup>b</sup> (100°C)             | 0.64 ± 0.01  | 17.20 ± 0.44                    | 0.65 ± 0.03 | 7.49 ± 0.34  |
| PTB7-Th:ITIC-4F <sup>b</sup> (110°C)             | 0.63 ± 0.01  | 16.49 ± 0.53                    | 0.62 ± 0.01 | 7.16 ± 0.25  |
| PTB7-Th:ITIC-4F <sup>b</sup> (120°C)             | 0.61 ± 0.01  | 14.69 ± 0.52                    | 0.58 ± 0.01 | 5.94 ± 0.30  |
| PBDB-T-2Cl:ITIC-4F <sup>a</sup>                  | 0.87 ± 0.01  | 18.13 ± 0.39                    | 0.67 ± 0.01 | 10.52 ± 0.14 |
| PBDB-T-2Cl:ITIC-4F <sup>b</sup> (60°C)           | 0.86 ± 0.01  | 18.00 ± 0.43                    | 0.68 ± 0.01 | 10.49 ± 0.42 |
| PBDB-T-2Cl:ITIC-4F <sup>b</sup> (80°C)           | 0.87 ± 0.01  | 18.02 ± 0.25                    | 0.66 ± 0.02 | 10.61 ± 0.30 |
| PBDB-T-2Cl:ITIC-4F <sup>b</sup> (100°C)          | 0.87 ± 0.01  | 18.10 ± 0.51                    | 0.67 ± 0.01 | 10.51 ± 0.37 |
| PBDB-T-2Cl:ITIC-4F <sup>b</sup> (110°C)          | 0.83 ± 0.01  | 16.57 ± 0.17                    | 0.63 ± 0.02 | 9.30 ± 0.50  |
| PBDB-T-2Cl:ITIC-4F <sup>b</sup> (120°C)          | 0.78 ± 0.03  | 15.52 ± 0.38                    | 0.52 ± 0.03 | 7.06 ± 0.55  |
| PTB7-Th:PC <sub>71</sub> BM <sup>a</sup>         | 0.78 ± 0.01  | 17.22 ± 0.44                    | 0.65 ± 0.01 | 8.67 ± 0.21  |
| PTB7-Th:PC <sub>71</sub> BM <sup>b</sup> (60°C)  | 0.78 ± 0.01  | 16.88 ± 0.33                    | 0.63 ± 0.02 | 8.24 ± 0.18  |
| PTB7-Th:PC <sub>71</sub> BM <sup>b</sup> (70°C)  | 0.77 ± 0.01  | 16.70 ± 0.45                    | 0.63 ± 0.01 | 8.15 ± 0.12  |
| PTB7-Th:PC <sub>71</sub> BM <sup>b</sup> (80°C)  | 0.78 ± 0.01  | 16.19 ± 0.39                    | 0.62 ± 0.01 | 7.80 ± 0.26  |
| PTB7-Th:PC <sub>71</sub> BM <sup>b</sup> (90°C)  | 0.78 ± 0.01  | 15.67 ± 0.19                    | 0.59 ± 0.01 | 7.11 ± 0.19  |
| PTB7-Th:PC <sub>71</sub> BM <sup>b</sup> (100°C) | 0.78 ± 0.01  | 14.98 ± 0.33                    | 0.54 ± 0.03 | 6.33 ± 0.44  |

| Active layer (D:A)                                | $V_{OC}$ (V) | $J_{SC}$ (mA cm <sup>-2</sup> ) | FF          | PCE (%)      |
|---|--------------|---------------------------------|-------------|--------------|
| PTB7-Th:ITIC-4F <sup>a</sup>                      | 0.65 ± 0.01  | 17.92 ± 0.40                    | 0.68 ± 0.01 | 8.14 ± 0.12  |
| PTB7-Th:ITIC-4F <sup>c</sup> (1 min)              | 0.65 ± 0.02  | 17.56 ± 0.51                    | 0.67 ± 0.02 | 7.89 ± 0.14  |
| PTB7-Th:ITIC-4F <sup>c</sup> (5 min)              | 0.64 ± 0.02  | 17.20 ± 0.32                    | 0.66 ± 0.02 | 7.49 ± 0.28  |
| PTB7-Th:ITIC-4F <sup>c</sup> (10 min)             | 0.63 ± 0.01  | 16.49 ± 0.53                    | 0.62 ± 0.01 | 7.16 ± 0.25  |
| PTB7-Th:ITIC-4F <sup>c</sup> (60 min)             | 0.62 ± 0.01  | 14.69 ± 0.27                    | 0.62 ± 0.01 | 5.94 ± 0.26  |
| PBDB-T-2Cl:ITIC-4F <sup>a</sup>                   | 0.87 ± 0.01  | 18.13 ± 0.39                    | 0.67 ± 0.01 | 10.52 ± 0.14 |
| PBDB-T-2Cl:ITIC-4F <sup>c</sup> (1 min)           | 0.86 ± 0.01  | 18.21 ± 0.58                    | 0.66 ± 0.02 | 10.21 ± 0.37 |
| PBDB-T-2Cl:ITIC-4F <sup>c</sup> (5 min)           | 0.87 ± 0.01  | 17.81 ± 0.20                    | 0.66 ± 0.01 | 10.30 ± 0.07 |
| PBDB-T-2Cl:ITIC-4F <sup>c</sup> (10 min)          | 0.83 ± 0.01  | 16.57 ± 0.17                    | 0.63 ± 0.02 | 9.30 ± 0.50  |
| PBDB-T-2Cl:ITIC-4F <sup>c</sup> (60 min)          | 0.77 ± 0.02  | 15.52 ± 0.38                    | 0.52 ± 0.01 | 6.58 ± 0.08  |
| PTB7-Th:PC <sub>71</sub> BM <sup>a</sup>          | 0.78 ± 0.01  | 17.22 ± 0.44                    | 0.65 ± 0.01 | 8.67 ± 0.21  |
| PTB7-Th:PC <sub>71</sub> BM <sup>c</sup> (1 min)  | 0.78 ± 0.01  | 16.53 ± 0.16                    | 0.63 ± 0.02 | 8.13 ± 0.14  |
| PTB7-Th:PC <sub>71</sub> BM <sup>c</sup> (5 min)  | 0.78 ± 0.01  | 16.18 ± 0.27                    | 0.59 ± 0.02 | 7.80 ± 0.18  |
| PTB7-Th:PC <sub>71</sub> BM <sup>c</sup> (10 min) | 0.78 ± 0.01  | 15.67 ± 0.19                    | 0.59 ± 0.01 | 7.11 ± 0.19  |
| PTB7-Th:PC <sub>71</sub> BM <sup>c</sup> (60 min) | 0.78 ± 0.01  | 14.81 ± 0.36                    | 0.57 ± 0.02 | 6.53 ± 0.10  |

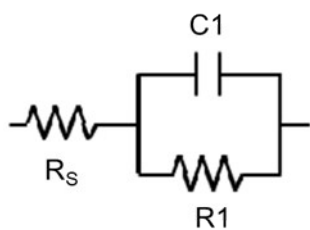
<sup>a</sup> Fresh device; <sup>b</sup> all the devices were post-annealed for 10 min; <sup>c</sup> all the devices were post-annealed at  $T_D$

**Table S3.** HOMO energy levels of MoO<sub>3</sub> calculated from UPS data. (HOMO = 21.2 eV – ( $E_{\text{cutoff}} - \text{HOMO}_{\text{onset}}$ ))

| <b>Active layer (D:A)</b>                    | <b>HOMO (eV)</b> | <b><math>\Delta E_{\text{HOMO}}</math><br/>(eV, annealed-fresh)</b> |
|--|------------------|---|
| <b>PTB7-Th:ITIC-4F<sup>a</sup></b>           | -7.87            | -0.09   |
| <b>PTB7-Th:ITIC-4F<sup>b</sup></b>           | -7.96            |   |
| <b>PBDB-T-2Cl:ITIC-4F<sup>a</sup></b>        | -7.89            | -0.07   |
| <b>PBDB-T-2Cl:ITIC-4F<sup>b</sup></b>        | -7.96            |   |
| <b>PTB7-Th:PC<sub>71</sub>BM<sup>a</sup></b> | -7.93            | -0.07   |
| <b>PTB7-Th:PC<sub>71</sub>BM<sup>b</sup></b> | -8.01            |   |

<sup>a</sup> Fresh devices; <sup>b</sup> post-annealed devices

**Table S4.** Summary of EIS results with equivalent circuit models.



| Active layer (D:A)                           | $R_s$ (Ohm) | $R1$ (Ohm) |
|--|-------------|------------|
| <b>PTB7-Th:ITIC-4F<sup>a</sup></b>           | 19.2        | 528.2      |
| <b>PTB7-Th:ITIC-4F<sup>b</sup></b>           | 19.0        | 298.6      |
| <b>PBDB-T-2Cl:ITIC-4F<sup>a</sup></b>        | 15.0        | 2902.0     |
| <b>PBDB-T-2Cl:ITIC-4F<sup>b</sup></b>        | 10.4        | 1288.0     |
| <b>PTB7-Th:PC<sub>71</sub>BM<sup>a</sup></b> | 14.5        | 1456.0     |
| <b>PTB7-Th:PC<sub>71</sub>BM<sup>b</sup></b> | 9.4         | 966.2      |

<sup>a</sup> Fresh devices; <sup>b</sup> post-annealed devices

**Table S5.**  $T_g$  of donor and acceptor materials used in this study.

|                          | $T_g$ (°C)  | Ref. |
|--------------------------|-------------|------|
| <b>PTB7-Th</b>           | ~ 130       | [4]  |
| <b>PBDB-T-2Cl</b>        | ~ 130 – 180 | [5]  |
| <b>ITIC-4F</b>           | ~ 185       | [6]  |
| <b>PC<sub>71</sub>BM</b> | ~ 150       | [7]  |

## References

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