Supporting information

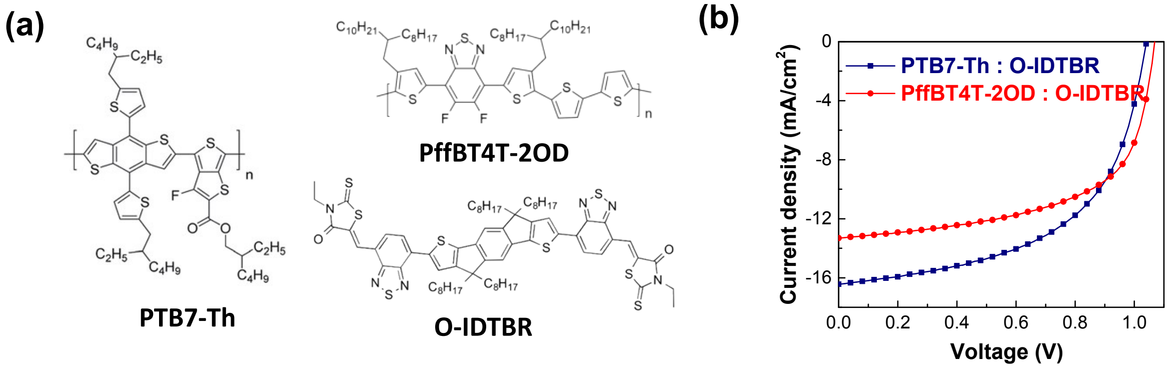

Figure S1 (a) The chemical structures of PTB7-Th, PffBT4T-2OD, and O-IDTBR (b) Current-voltage (J-V) curves for PTB7-Th:O-IDTBR and PffBT4T-2OD:O-IDTBR fresh devices.

Table S1 Summary of device performance for solar cells based on fresh polymer:O-IDTBR active layers.

Active layer	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
PTB7-Th:O-IDTBR	1.03 ± 0.01	15.2 ± 0.2	56 ± 1	8.8 ± 0.2
PffBT4T-2OD:O-IDTBR	1.05 ± 0.04	12.7 ± 0.6	60 ± 1	8.2 ± 0.3

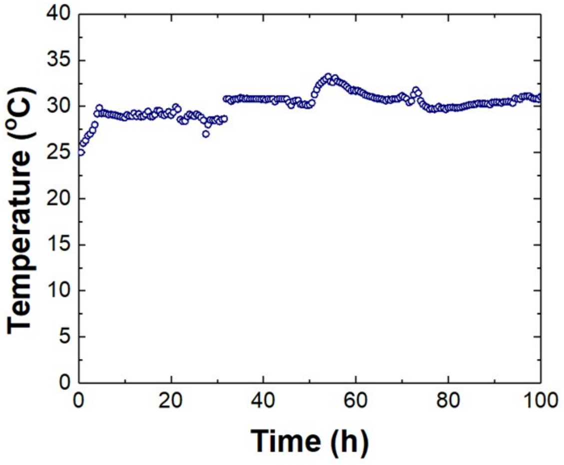

Figure S2 Device temperature monitored by thermal sensor when devices are under continuous 1 sun illumination.

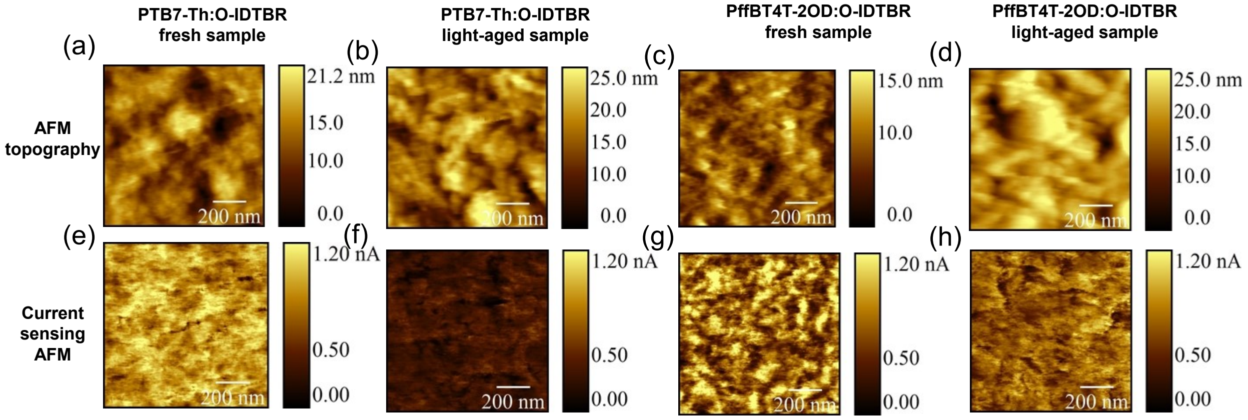

Figure S3 Contact mode AFM topography (a-d) and current sensing AFM (C-AFM) images (e-f) of PTB7-Th: O-IDTBR and PffBT4T-2OD: O-IDTBR samples.

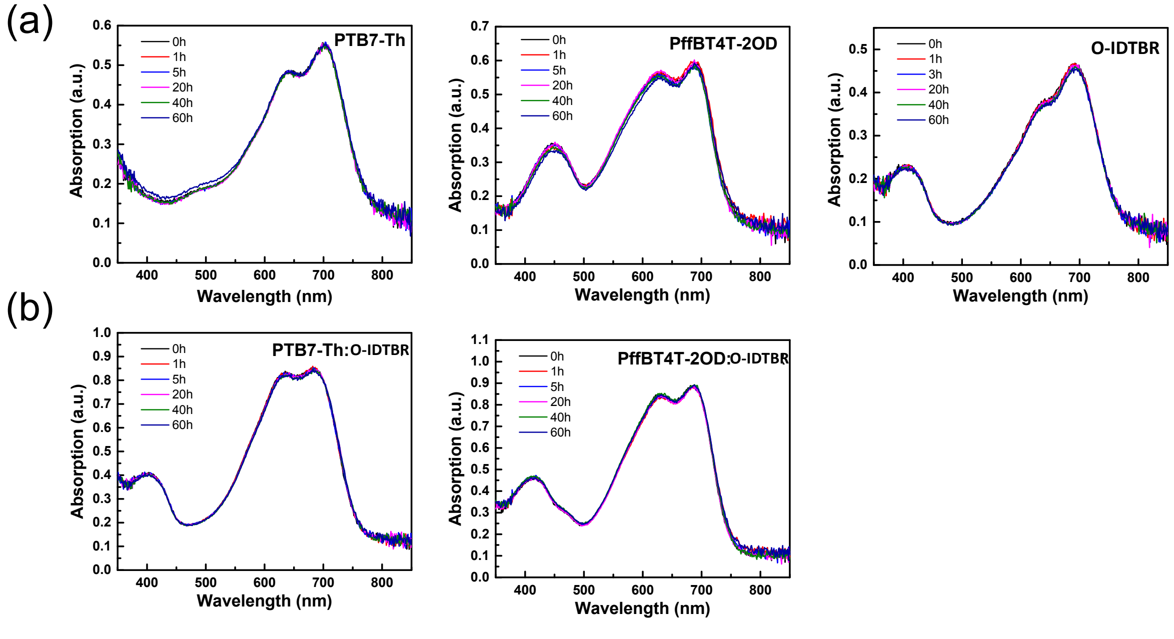

Figure S4 Normalized absorbance spectra of (a) pristine materials and (b) polymer:O-IDTBR blend films.

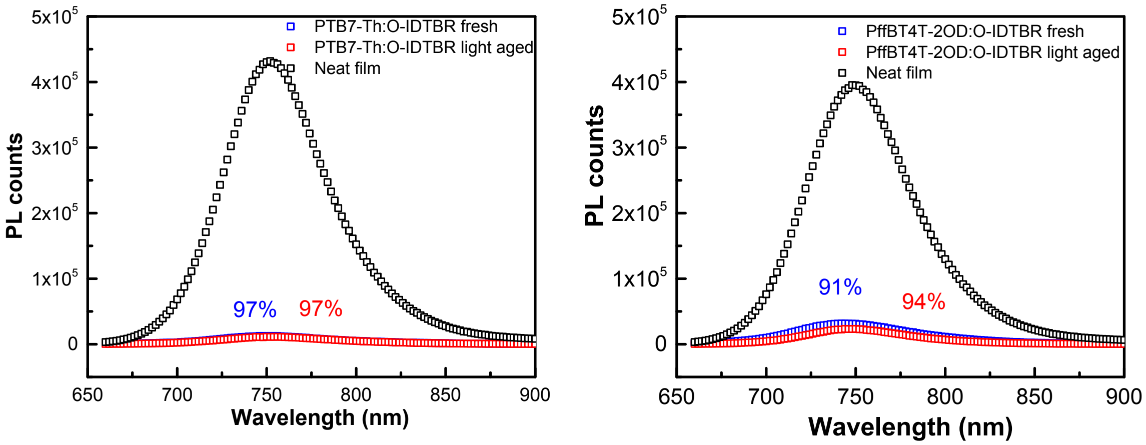

Figure S5 PL emission spectra for BHJ blend films and their corresponding pristine donor polymer film emissions.

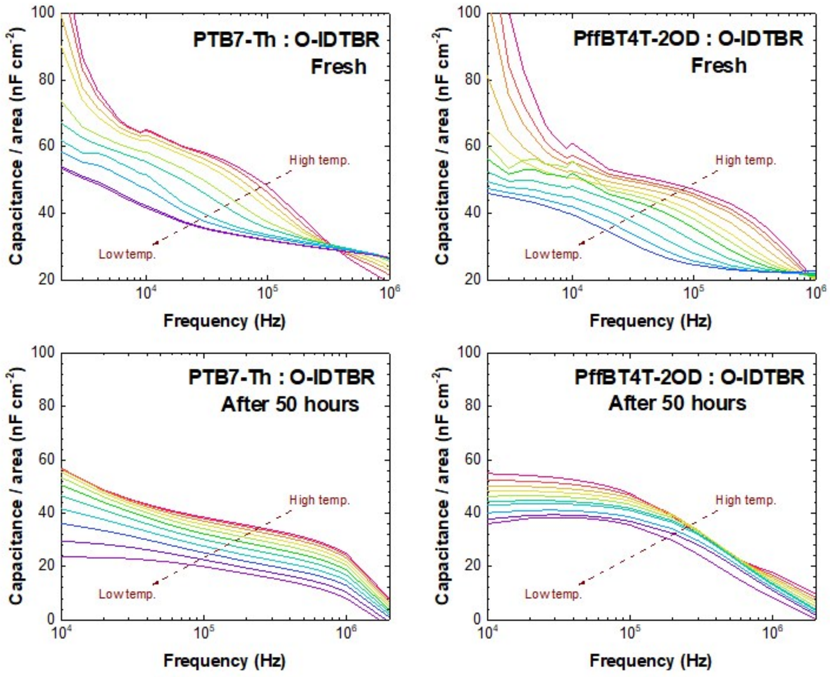

Figure S6. Capacitance−frequency curves at different temperatures.

The frequency-dependent capacitance is a combination of depletion capacitance (C_{dep}) and trap capacitance (C_{trap}) given by the following equation:

$$C(\omega) = C_{dep} + \frac{1}{1+\omega^2\tau^2} C_{trap}$$

where τ is the time constant of charging and discharging process, which can be extracted from the measured capacitance−frequency (C−f) curve shown in **Figure S5**. From the equation, we observe that there is a clear step in the C−f curve, and the characteristic transition frequency $\omega_t = 1/\tau$ is where the step occurs. As trap states are thermally activated, the thermal emission rate of a trap state in a semiconductor is quantified by

$$\omega_t = \beta T^2 exp(\frac{-E_a}{kT})$$

where β is a constant, k is the Boltzmann constant, and E_a is the activation energy of the defect, which is the energy of hole trap energy level above valence band or electron trap below conduction band.

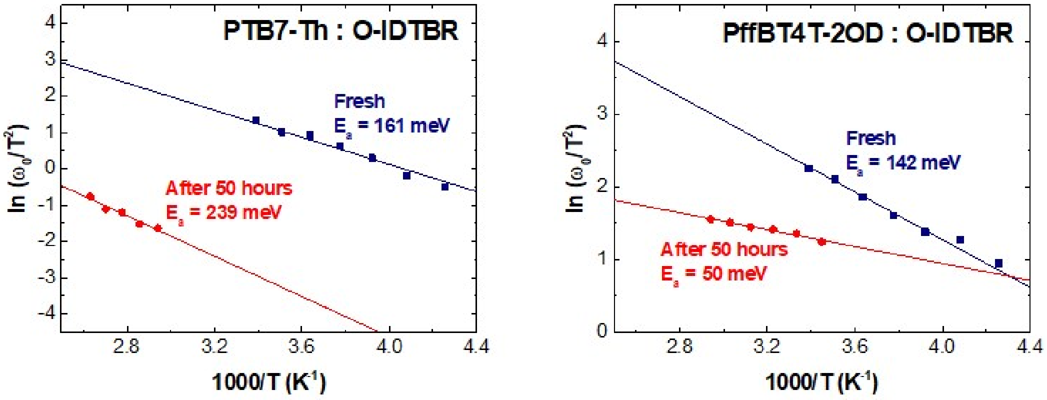

Figure S7 Linear fitting of characteristic frequency versus temperature.

As shown in **Figure S6**, the activation energy (E_a) can be extracted through linear fit of $\ln\left(\frac{\omega_t}{T^2}\right)$ versus $\frac{1}{T}$. Based on the extracted activation energy, the charge trap density can be quantitatively obtained from the measured C-f curves through the following equation:

$$N_t(E_\omega) = -\frac{V_{bi}\, dC\ \omega}{eWd\omega kT}$$

where N_t is the trap density, V_{bi} is the built-in potential, e is the elementary charge, W is the depletion width, and E_ω is the defect energy. Through integration of the traps over energy, the total trap densities of devices are shown in **Figure 4(b)**.

Table S2: Simulation parameters based on TAS and SCLC experimental results.

	Electron mobility/(cm^2/Vs)	Hole mobility/(cm^2/Vs)	Trap state energy level (eV)
PffBT4T-2OD:O-IDTBR fresh	10^{-3}	10^{-3}	0.14
PffBT4T-2OD:O-IDTBR photoaged	10^{-4}	10^{-3}	0.05
PTB7-Th:O-IDTBR fresh	10^{-4}	10^{-3}	0.16
PTB7-Th:O-IDTBR photoaged	10^{-6}	10^{-3}	0.24

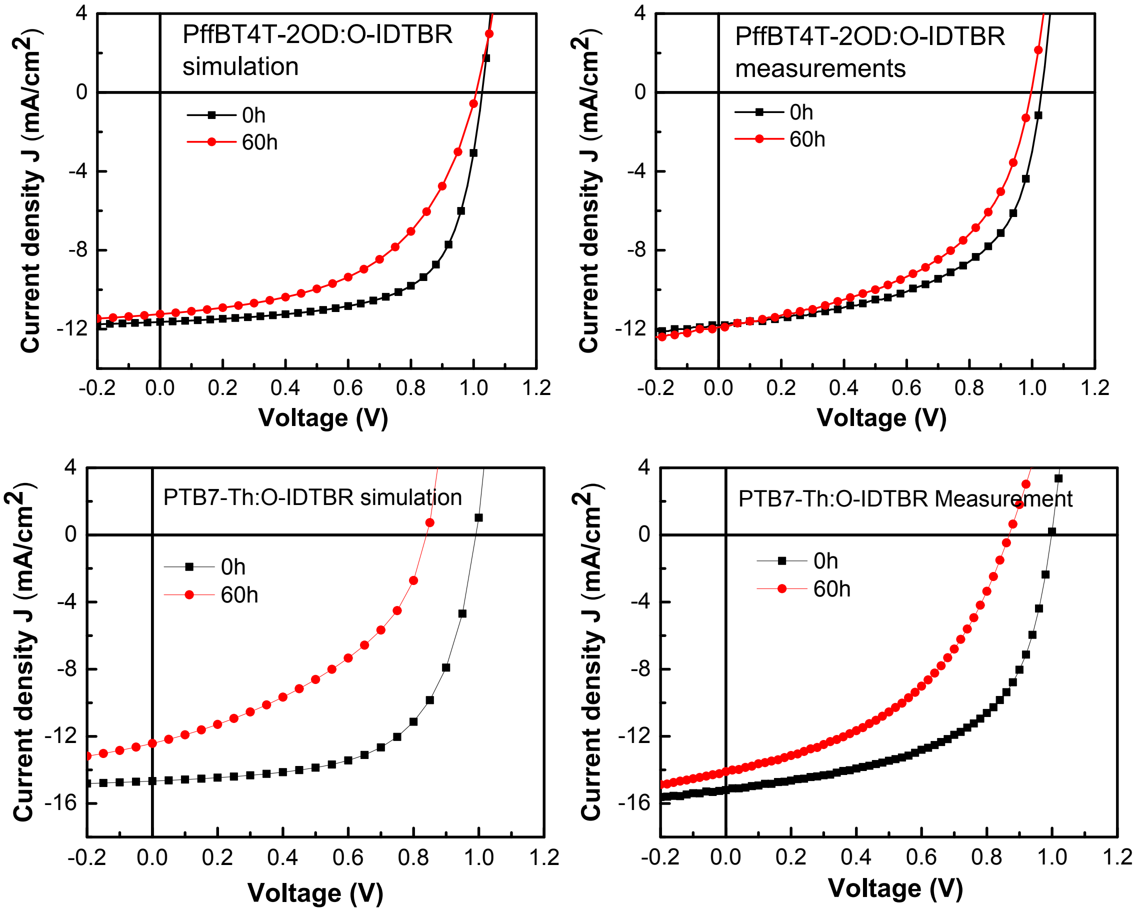

Figure S8 Comparison of simulated and experimental J-V curves for PffBT4T-2OD:O-IDTBR fresh and light aged devices and PTB7-Th:O-IDTBR fresh and light aged devices.

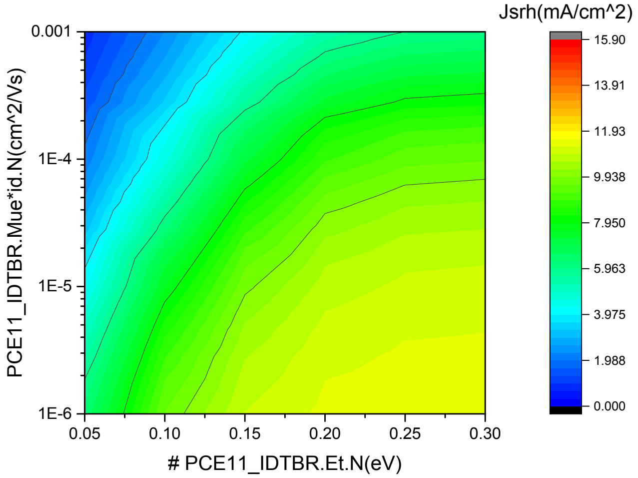

Figure S9 Shockley–Read–Hall (SRH) recombination current density as a function of trap energy level and electron mobility.

Table S3. Derived simulation parameters based on experimental JV data.

Parameters	Values
Langevin recombination rate	10^{-12} cm^{3}s^{-1}
Bandgap	1.4 eV (PffBT4T-2OD:O-IDTBR); 1.3 eV (PTB7-Th:O-IDTBR)
Dielectric constant	3.5
Optical generation efficiency	0.8

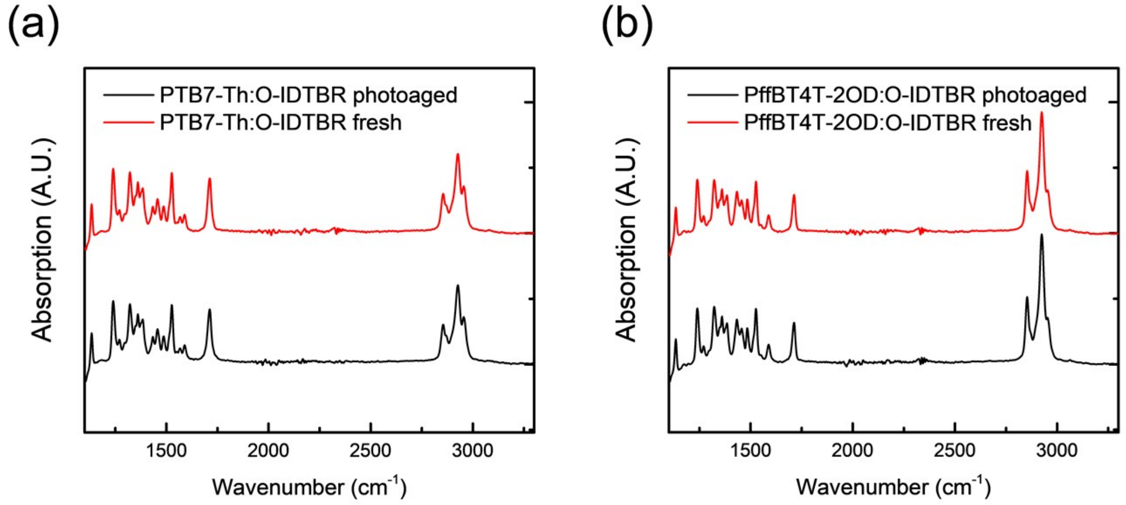

Figure S10 FTIR spectra of (a) PTB7-Th:O-IDTBR and (b) PffBT4T-2OD:O-IDTBR before and after light exposure (60 h).