

Supporting Information

An efficient, ‘burn in’ free organic solar cell employing a non-fullerene electron acceptor

Hyojung Cha¹, Jiaying Wu¹, Andrew Wadsworth¹, Jade Nagitta¹, Saurav Limbu², Sebastian Pont¹, Zhe Li³, Justin Searl³, Mark F. Wyatt⁴, Derya Baran⁵, Ji-Seon Kim², Iain McCulloch^{1,5}, James R. Durrant,^{1,3}*

Experimental detail.

Table S1. Photovoltaic parameters of the PffBT4T-2OD-based solar cells.

Figure S1. Transient absorption spectra for (a) neat PffBT4T-2OD and (b) neat EH-IDTBR, respectively.

Figure S2. Transient absorption spectra for (a) PffBT4T-2OD:PC₇₁BM blend and (b) PffBT4T-2OD:EH-IDTBR blend, excited at 715 nm with 10 μJ cm⁻². Energy dependence of long live polaron dynamics: (c) PffBT4T-2OD:PC₇₁BM and (d) PffBT4T-2OD:EH-IDTBR.

Figure S3. The photovoltaic results (V_{oc} , J_{sc} , FF, PCE) of PffBT4T-2OD:PC₇₁BM and PffBT4T-2OD:EH-IDTBR blend solar cells under the illumination of AM 1.5G, 100 mW cm⁻².

Figure S4. The photovoltaic results (V_{oc} , J_{sc} , FF, PCE) of PffBT4T-2OD:PC₇₁BM and PffBT4T-2OD:EH-IDTBR blend solar cells under thermal stress at 85°C.

Figure S5. AFM phase images of (a) PffBT4T-2OD:PC₇₁BM and (b) PffBT4T-2OD:EH-IDTBR blend films: pristine and under thermal stress at 85°C for 2 hours.

Figure S6. Optical microscopy images of (a) PffBT4T-2OD:PC₇₁BM and (b) PffBT4T-2OD:IDTBR blend films before (left) and after thermal stress at 85 °C for 12 hours (right).

Figure S7. The photovoltaic results (V_{oc} , J_{sc} , FF, PCE) of PffBT4T-2OD:PC₇₁BM and PffBT4T-2OD:EH-IDTBR blend solar cells in the dark under ambient conditions between measurements.

Figure S8. (a) Measured open-circuit voltage as a function of illumination intensity for PffBT4T-2OD:EH-IDTBR and fresh and aged PffBT4T-2OD:PC₇₁BM. (b) Light ideality factor as a function of light intensity, calculated from the slope of V_{OC} versus light intensity.

Figure S9. Transient optoelectronic analyses of PffBT4T-2OD:EH-IDTBR devices before and after light induced burn in efficiency loss. (a) Charge extraction (CE) measurements of charge carrier density at open circuit as a function of light intensity, plotted versus open circuit voltage; (b) the corresponding charge carrier lifetimes measured by transient photovoltage (TPV) decays, plotted against the measured charge densities. Device aging (burn in) was induced by the 540 nm light source employed in the CE and TPV measurements.

Figure S10. AFM height images of (a) PffBT4T-2OD:EH-IDTBR and (b) PffBT4T-2OD:PC₇₁BM blend films: pristine (right) and under the illumination of AM 1.5G, 100 mW cm⁻² for 60 hours (left).

Figure S11. Raman Spectra of neat PffBT4T-2OD and PC₇₁BM films, respectively.

Experimental detail.

OPV devices. Bulk heterojunction solar cells were fabricated with an inverted architecture (glass/ITO/ZnO/PffBT4T-2OD:acceptor/MoO₃/Ag). Glass substrates were used with pre-patterned indium tin oxide (ITO). These were cleaned by sonication in detergent, deionized water, acetone and isopropanol, followed by oxygen plasma treatment. ZnO layers were deposited by spin-coating a zinc acetate dihydrate precursor solution (60.4 μ l 1-ethanolamine in 2 ml 2-methoxyethanol) followed by annealing at 150 °C for 10 min, giving layers of 30 nm. The PffBT4T-2OD:EH-IDTBR (1:1.4 ratio by mass) active layers were deposited from 12 mg/ml solutions in o-dichlorobenzene by spin-coating at 3,000 r.p.m. Active layer thicknesses were 70 nm. PffBT4T-2OD:PC₇₁BM (1:1.4 ratio by mass) layers were spin-coated at 1,500 r.p.m. from 12 mg/ml solutions in chlorobenzene:o-dichlorobenzene (1:1 ratio by volume) with 3 vol% of diiodooctane as a processing additive, resulting in active layer thicknesses of 300 nm. MoO₃ (10 nm) and Ag (100 nm) layers were deposited by evaporation through a shadow mask yielding active areas of 0.045 cm² in each device. (J–V) characteristics were measured using a Xenon lamp at AM1.5 solar illumination (Oriel Instruments) calibrated to a silicon reference cell with a Keithley 2400 source meter, correcting for spectral mismatch. Incident photon conversion efficiency was measured by a 100 W tungsten halogen lamp (Bentham IL1 with Bentham 605 stabilized current power supply) coupled to a monochromator with computer controlled stepper motor. The photon flux of light incident on the samples was calibrated using a UV-enhanced silicon photodiode. A 590-nm long-pass glass filter was inserted into the beam at illumination wavelengths longer than 580 nm to remove light from second-order diffraction.

UV-Vis absorption and Photoluminescence spectroscopies. UV-Visible spectra of the thin films were acquired with a PerkinElmer Lambda 25 spectrometer in air. The PL spectra were measured with a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon). All film samples were spin cast on glass substrates.

PL spectroscopy and transient absorption spectroscopy (TAS). Samples for TAS and PL spectroscopy were spin-coated onto glass using the same conditions as for solar cells. Spectra were measured using a steady state spectrofluorimeter (Horiba Jobin Yvon, Spex Fluoromax 1). The spin-

coated films were excited at 680 nm. Sub-picosecond TAS was carried out at 800 nm laser pulse (1 kHz, 90 fs) by using a Solstice (Newport Corporation) Ti:sapphire regenerative amplifier. A part of the laser pulse was used to generate the pump laser at 680 nm, 2 mJ cm^{-2} with a TOPAS-Prime (light conversion) optical parametric amplifier. The other laser output was used to generate the probe light in near visible continuum (450–800 nm) by a sapphire crystal. The spectra and decays were obtained by a HELIOS transient absorption spectrometer (450–1,450 nm) and decays to 6 ns. The samples were measured in N_2 atmosphere.

J-V Measurements as a Function of Ageing. Devices were sealed in glass fronted chambers, under N_2 without moisture, which allowed electrical contact to be made and devices to be illuminated. Light exposure was performed at equivalent 1 sun white light illumination provided by an array of white LEDs, calibrated to the device performance as measured under AM1.5 with the ultraviolet portion removed by filtering and a Keithley 2,400 source meter. The PCE was first allowed to stabilise under initial exposure to illumination and once stabilised this point is defined as time 0s. The same Keithley 2,400 source meter was used to vary the conditions from open circuit to short circuit by applying a voltage bias to the devices. A fan was used to keep the devices under 50°C during measurements.

CE and TPV. Charge extraction was performed at open circuit under different illumination intensities. Devices were illuminated by a ring of white LEDs, where the LEDs are switched off (100 ns) and the device discharged close to short circuit over a measurement resistance of 50 Ω . The resulting transients were acquired with a TDS 3032 Tektronix digital oscilloscope, converted to a current using Ohm's law and integrated with respect to time to calculate n . Transient photovoltage was recorded in an open circuit under different illumination intensities, provided by a ring of white LEDs. A Nd:YAG pulsed laser (Continuum Minilite II) was used to generate small perturbations in the device and the resulting voltage transients were recorded with a TDS 3032 Tektronix digital oscilloscope and fitted with a single exponential function to obtain a carrier lifetime.

AFM. AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All film samples were spin casted on ITO/ZnO substrates.

Table S1. Photovoltaic parameters of the PffBT4T-2OD-based solar cells.

Device (1:1.4)	Solvent	Ann. Temp. [°C]	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF	PCE [%]
Polymer:EH-IDTBR (1:1.4)	DCB	RT	14.65 (±0.2)	1.08 (±0.01)	0.60 (±0.02)	9.5 (±0.2)
	DCB	120	7.31	0.96	0.60	4.3
	CB	RT	9.12	0.95	0.52	4.5
	CB	120	6.78	0.87	0.56	3.3
	CB	140	5.73	0.86	0.42	2.0
	CB:DCB (1:1)	RT	8.58	0.96	0.56	4.7
	CB:DCB (1:1)	120	9.81	0.98	0.56	5.3
	CB:DCB (1:1)	140	5.83	0.89	0.54	2.8
	CB:DCB (1:1) 3% DIO	RT	8.58	0.96	0.56	4.7
	Polymer:PC ₇₁ BM (1:1.4)	CB:DCB (1:1) 3% DIO	RT	20.5 (±0.2)	0.76 (±0.1)	0.70 (±0.03)

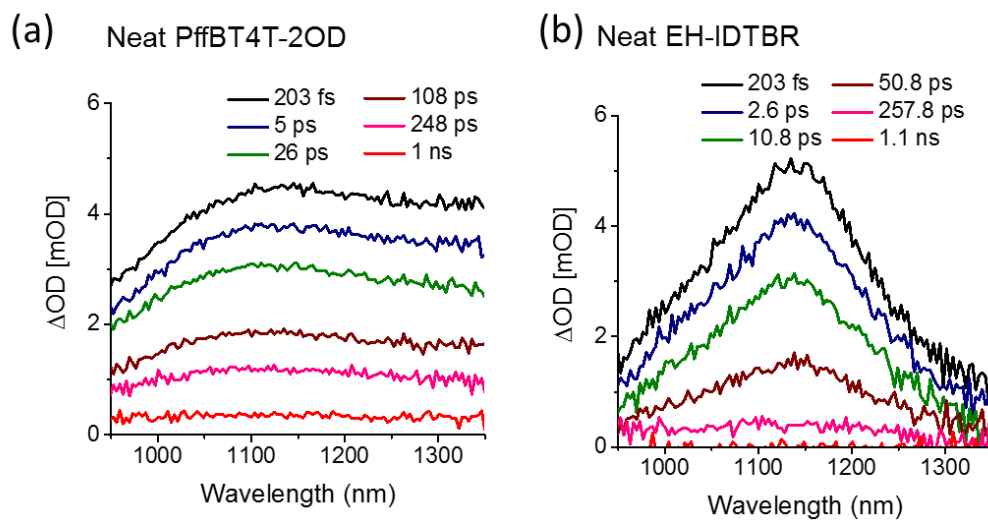


Figure S1. Transient absorption spectra for (a) neat PffBT4T-2OD and (b) neat EH-IDTBR, respectively.

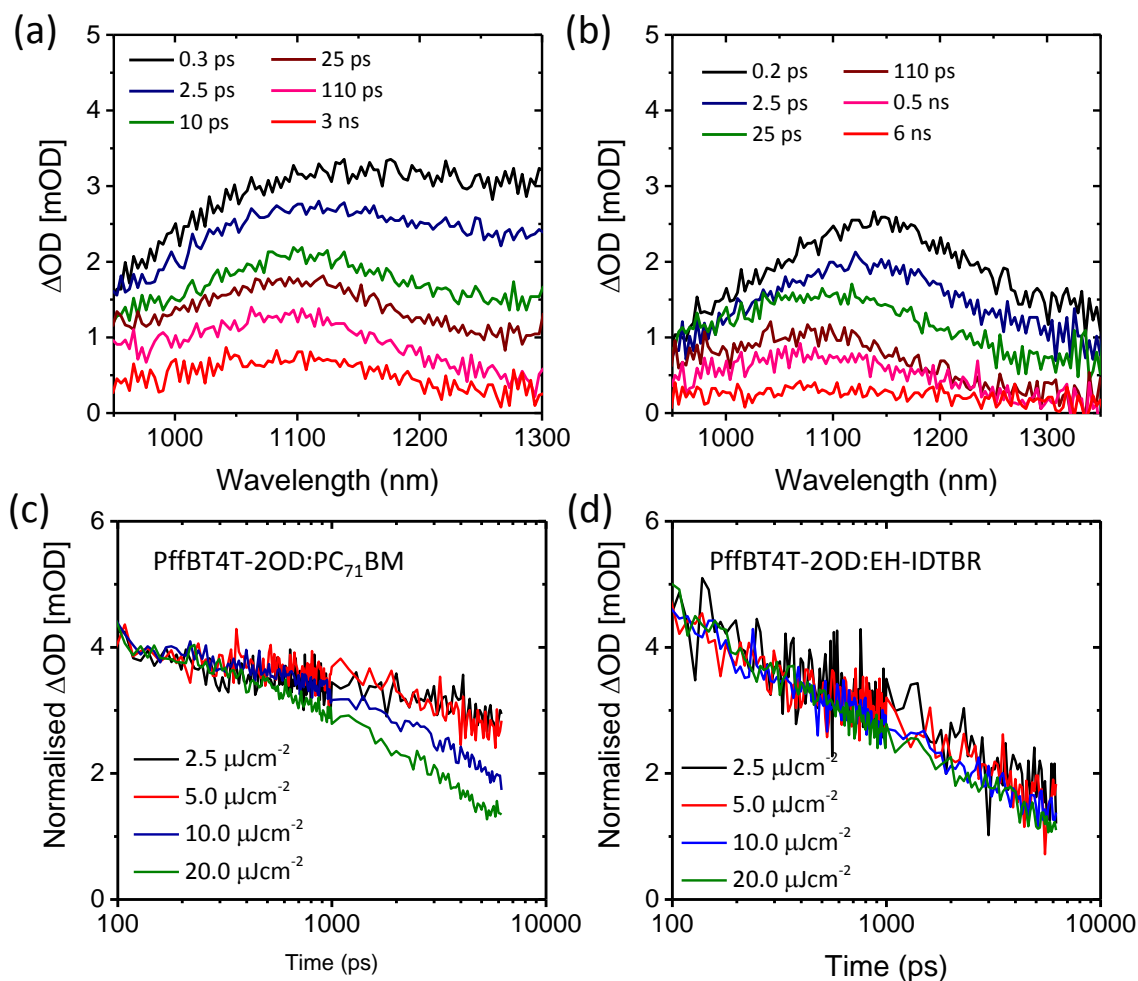


Figure S2. Transient absorption spectra for (a) PffBT4T-2OD:PC₇₁BM blend and (b) PffBT4T-2OD:EH-IDTBR blend, excited at 715 nm with 10 $\mu J cm^{-2}$. Energy dependence of long live polaron dynamics: (c) PffBT4T-2OD:PC₇₁BM and (d) PffBT4T-2OD:EH-IDTBR.

For the PffBT4T-2OD:PC₇₁BM blend data in Figure S2a, at early times (0.3 ps) a broad positive absorption is observed between 1100–1300 nm, assigned by comparison to the neat film data to the photoinduced absorption of PffBT4T-2OD excitons. By 110 ps, this broad absorption has evolved to narrower absorption feature centred at 1100 nm, assigned to polaron absorption. On the other hand, for PffBT4T-2OD:EH-IDTBR blends in Figure S2b, the transient absorption spectra at early times exhibit a similar photoinduced absorption indicative of the generation of both PffBT4T-2OD and EH-IDTBR excitons, exhibiting in particular a clear absorption maximum at 1150 nm corresponding to EH-

IDTBR singlet exciton absorption (the strength of this feature is most likely caused by the higher absorption coefficient of EH-IDTBR molecule, see Figure S1). As for the PC₇₁BM blend, this initial exciton absorption then rapidly evolves to a narrower photo-induced absorption with a maximum at 1100 nm at longer time delays, indicative of polaron formation.

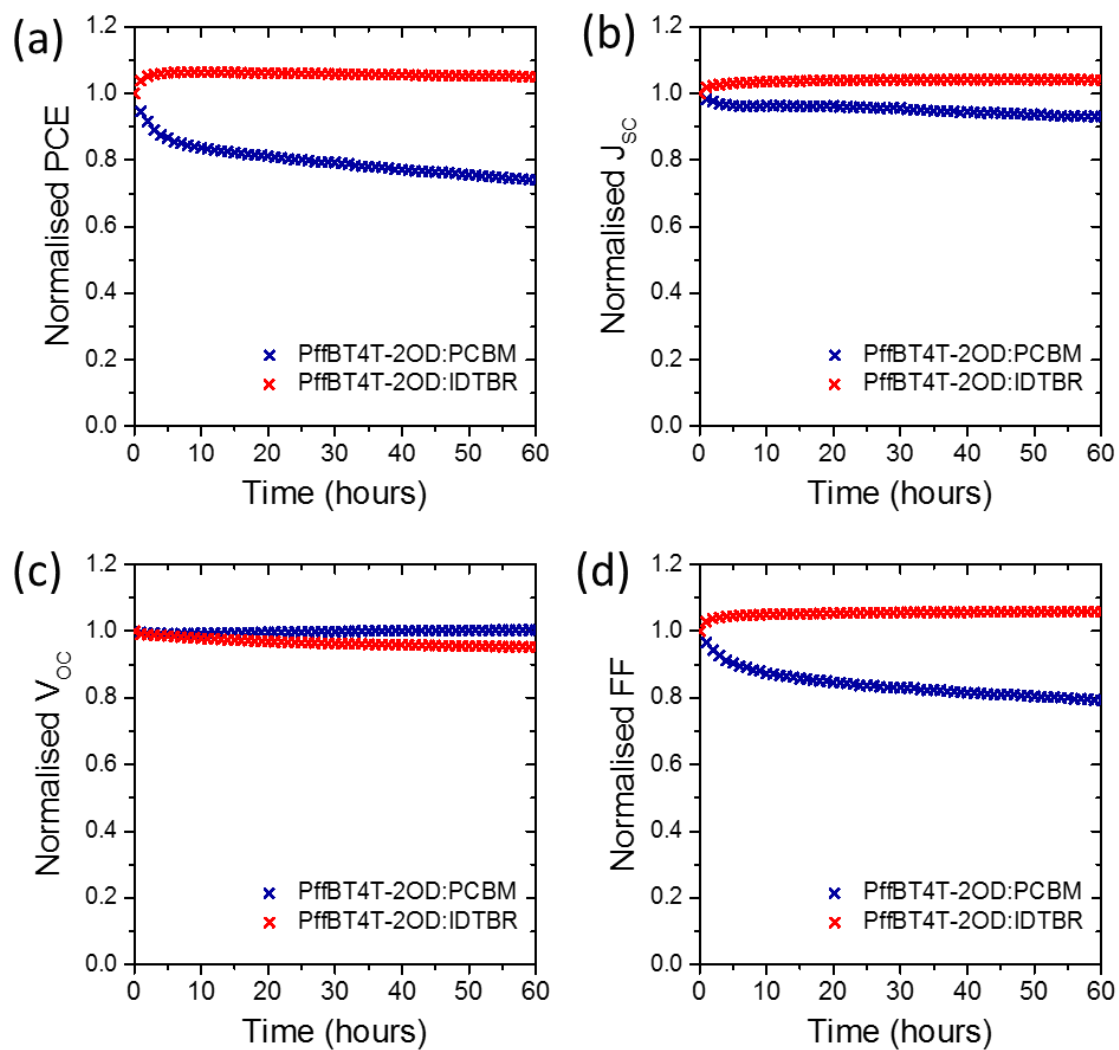


Figure S3. The photovoltaic results (V_{oc} , J_{sc} , FF, PCE) of PffBT4T-2OD:PC₇₁BM and PffBT4T-2OD:EH-IDTBR blend solar cells under the illumination of AM 1.5G, 100 mW cm⁻².

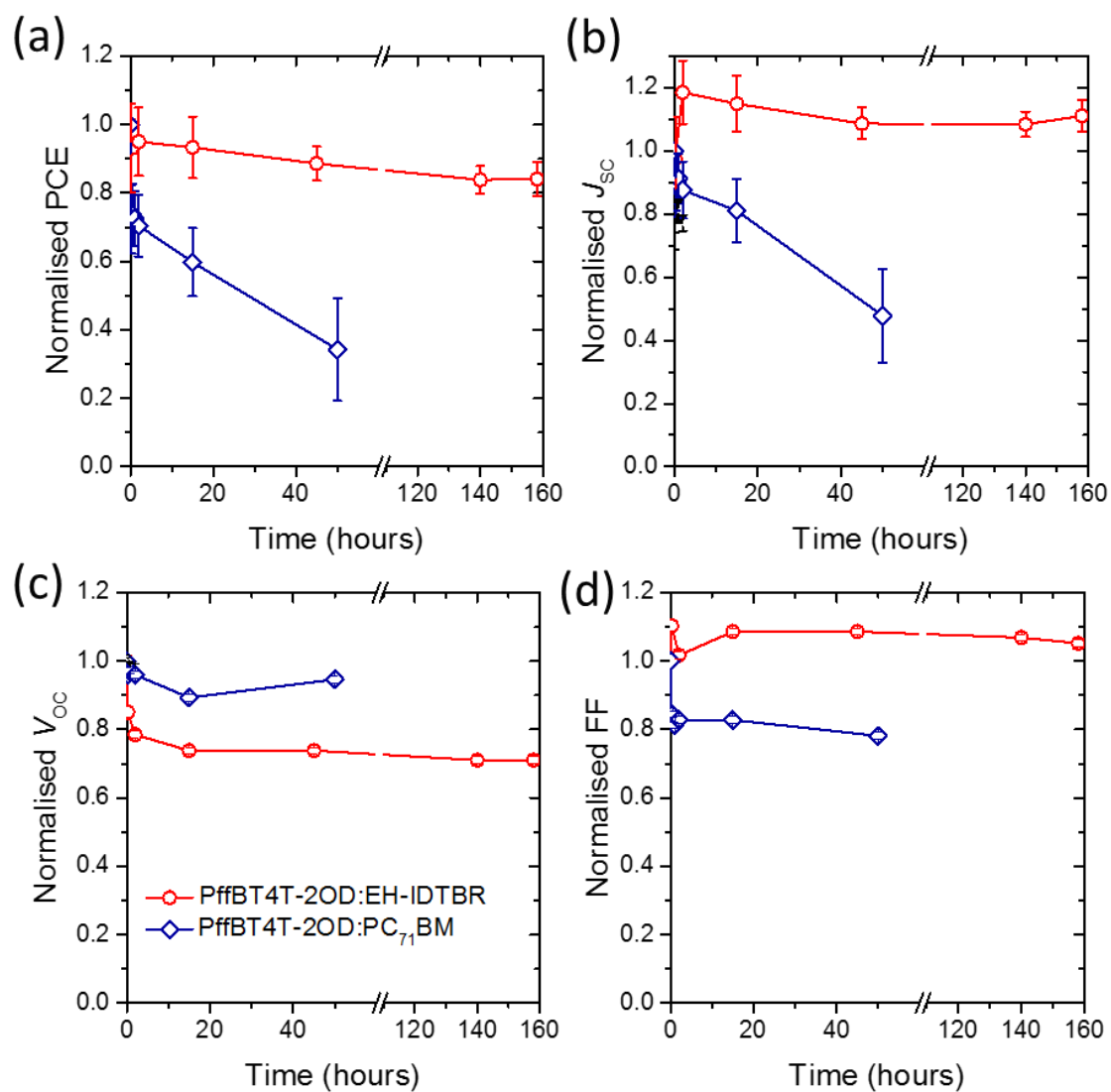


Figure S4. The photovoltaic results (V_{oc} , J_{sc} , FF, PCE) of PffBT4T-2OD:PC₇₁BM and PffBT4T-2OD:EH-IDTBR blend solar cells under thermal stress at 85°C.

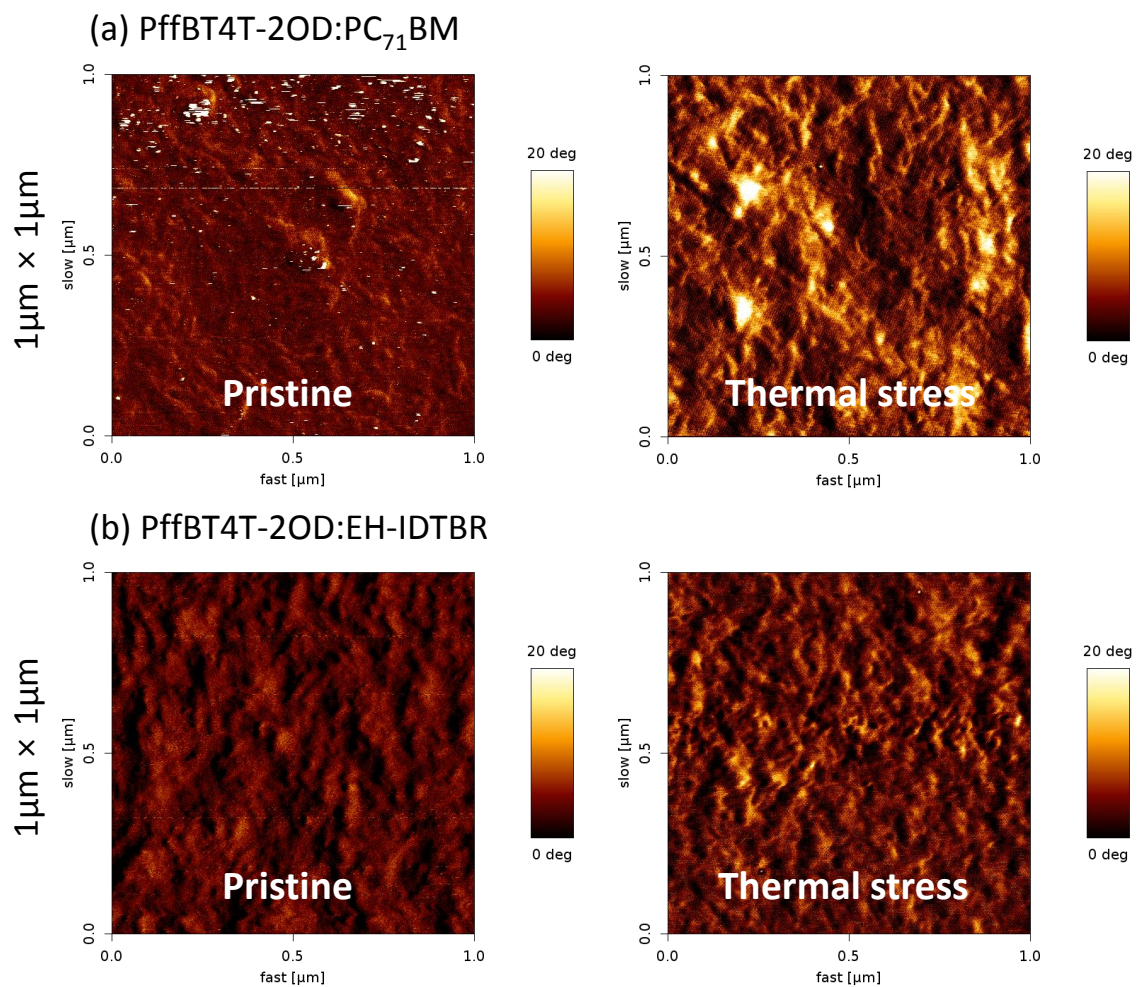


Figure S5. AFM phase images of (a) PffBT4T-2OD:PC₇₁BM and (b) PffBT4T-2OD:EH-IDTBR blend films: pristine and under thermal stress at 85°C for 2 hours.

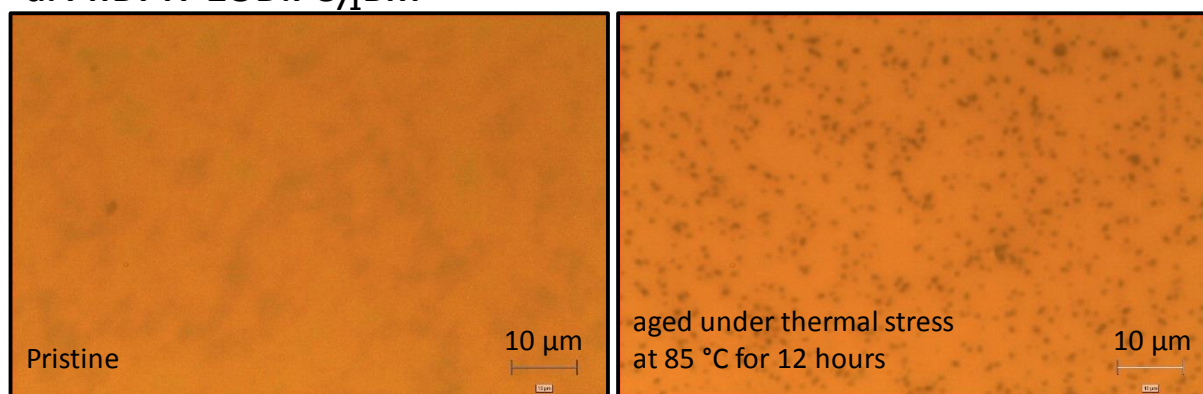
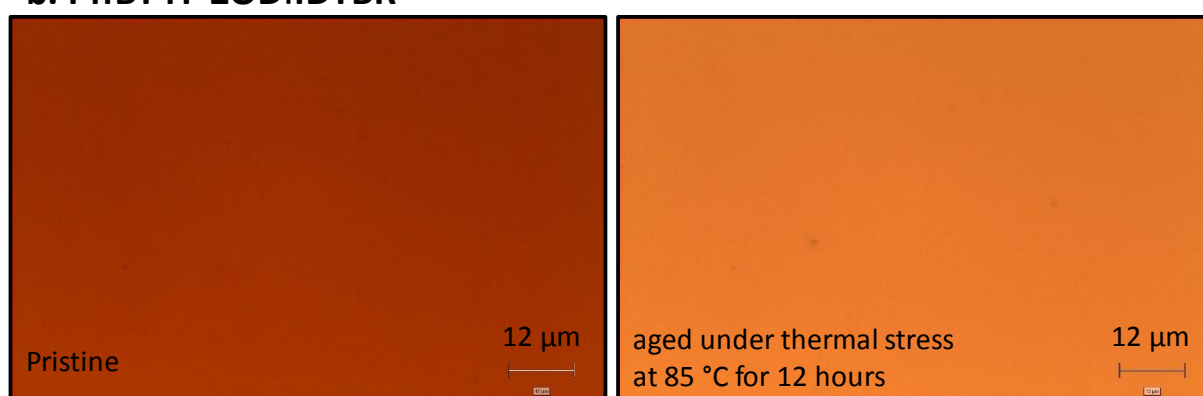
a. PffBT4T-2OD:PC₇₁BM**b. PffBT4T-2OD:IDTBR**

Figure S6. Optical microscopy images of (a) PffBT4T-2OD:PC₇₁BM and (b) PffBT4T-2OD:IDTBR blend films before (left) and after thermal stress at 85 °C for 12 hours (right).

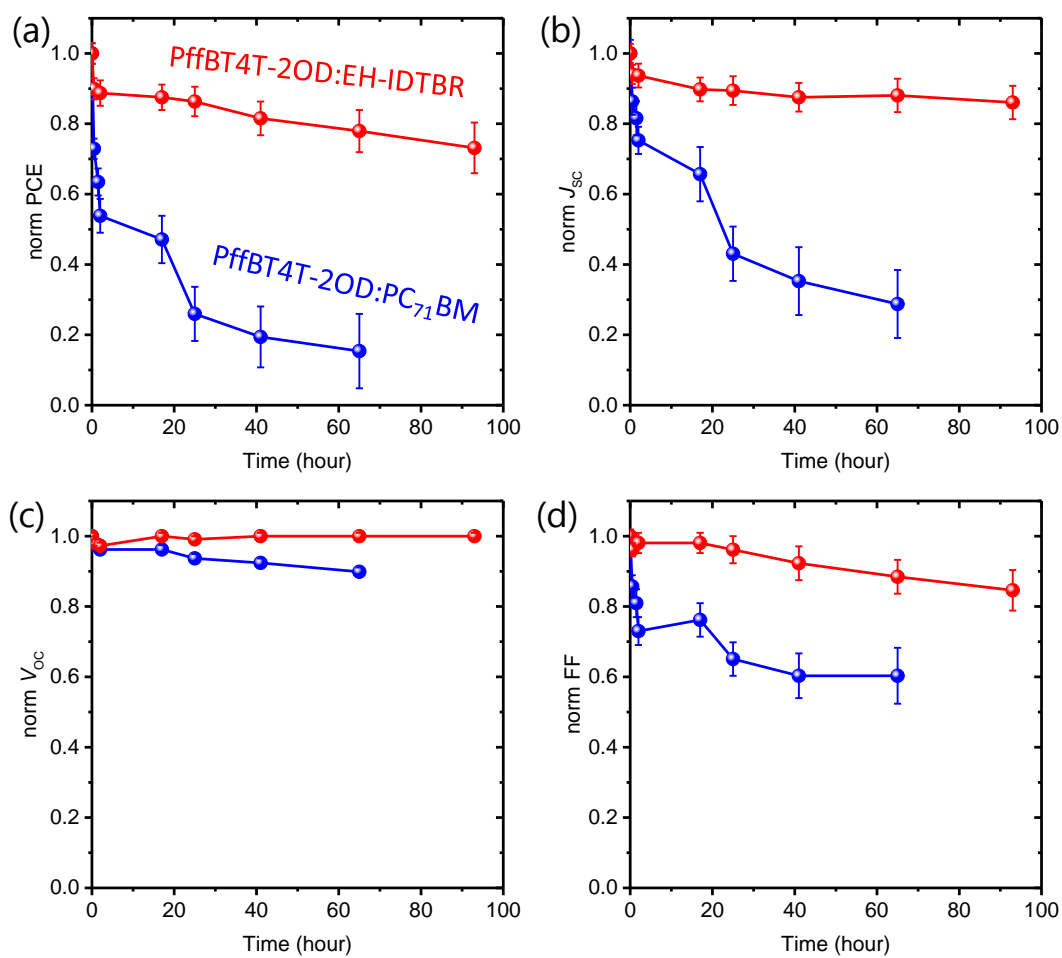


Figure S7. The photovoltaic results (V_{oc} , J_{sc} , FF, PCE) of PffBT4T-2OD:PC₇₁BM and PffBT4T-2OD:EH-IDTBR blend solar cells in the dark under ambient conditions between measurements.

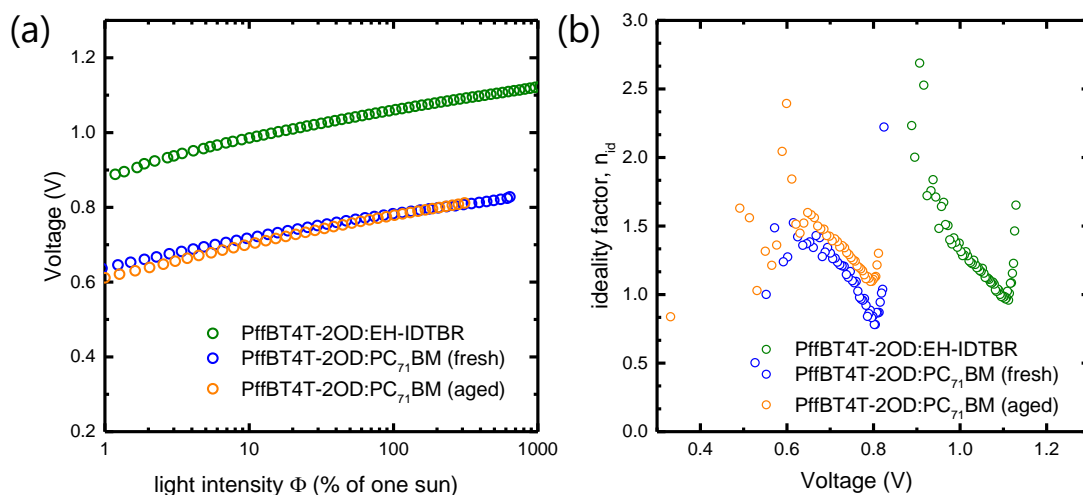


Figure S8. (a) Measured open-circuit voltage as a function of illumination intensity for PffBT4T-2OD:EH-IDTBR and fresh and aged PffBT4T-2OD:PC₇₁BM. (b) Light ideality factor as a function of light intensity, calculated from the slope of V_{OC} versus light intensity.

Figure S8b shows the light ideality factor, as calculated from the derivative of the voltage as a function of light intensity Figure S8a. A value of 1 is nominally assigned to the recombination of free charges while a value of 2 is assigned to the recombination of free charge via charge trapping in the shallow trap state. The increasing ideality factor (orange circles) for aged PffBT4T-2OD:PC₇₁BM is consistent with increasing light induced shallow trap states. We believe that the intrinsic origin of the photodegradation in PffBT4T-2OD:PC₇₁BM device is due to the light induced shallow trap states.

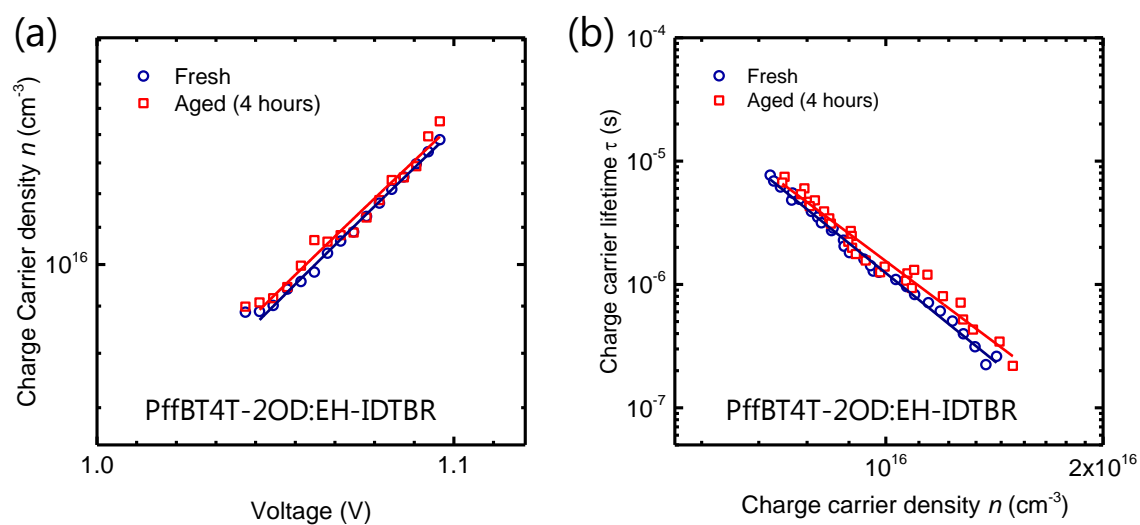


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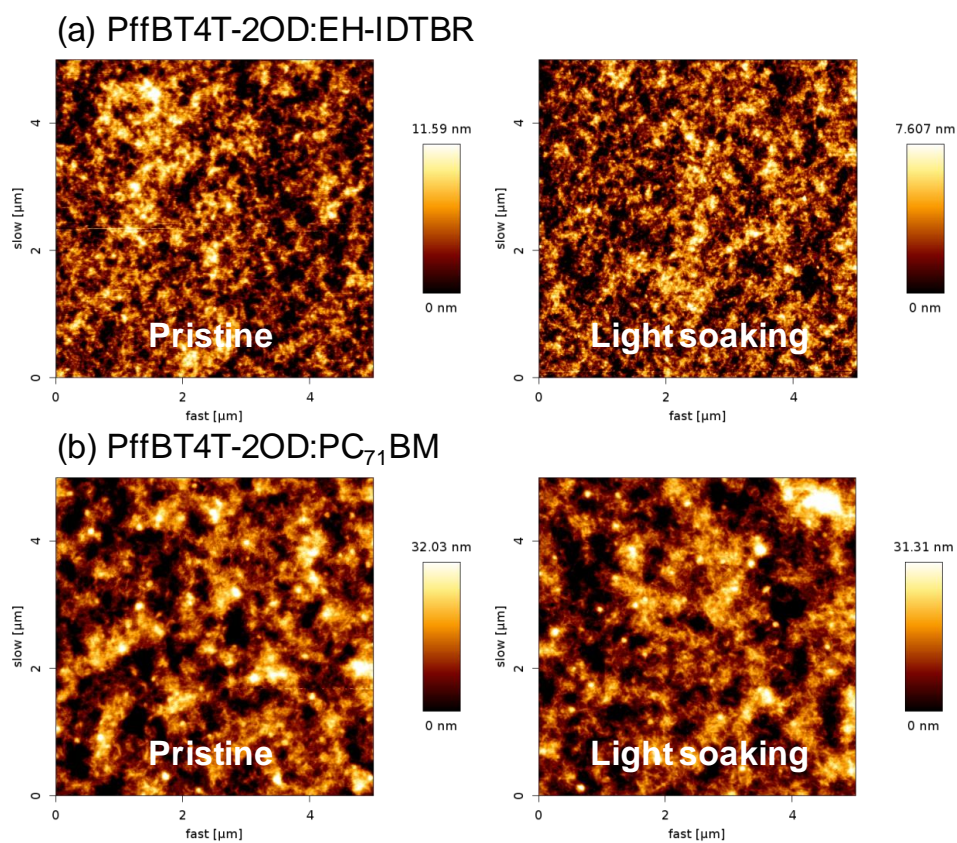


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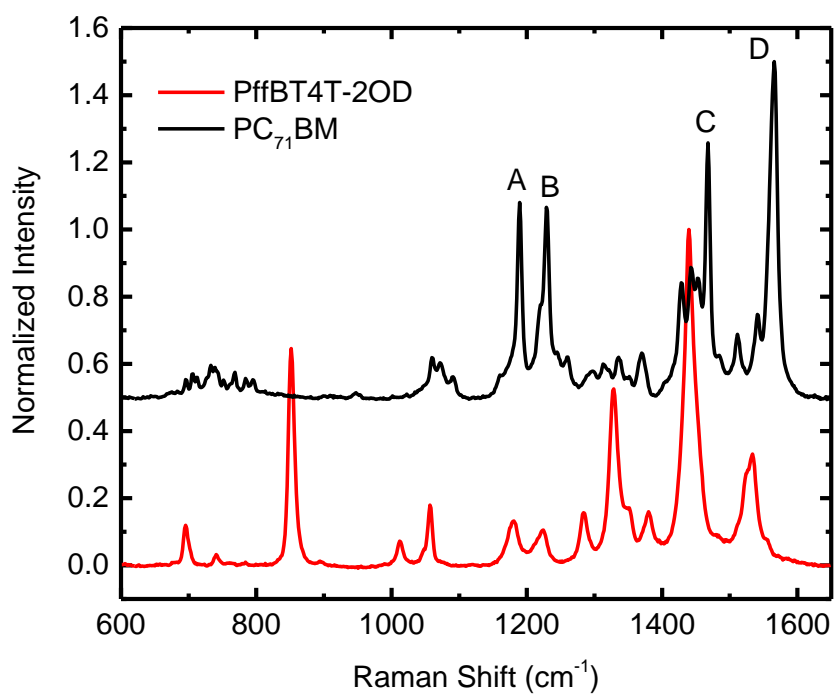


Figure S11. Raman Spectra of neat PffBT4T-2OD and PC₇₁BM films, respectively.