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Comparative Analysis of Burn-in Photo-degradation in Non-fullerene COi8DFIC Acceptor based High-efficiency Ternary Organic Solar Cells

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Support information

Materials Preparation

The pre-patterned ITO glasses with the area of 12 mm × 12 mm were purchased from Lumtec. The chemical materials PTB7-Th was purchased from Solarmer. The chemical materials COi8DFIC was obtained from Ding's group.[1-3] The chemical material $PC_{71}BM$, zinc nanoparticles, reagent alcohol (anhydrous, <0.003% water), chlorobenzene (99.8%), 1,8-diiodooctane, and MoO_3 are purchased from Sigma-Aldrich.

Device Fabrication

In this paper, we have used an inverted device structure of ITO Glass/ZnO/PTB7-Th:COi8DFIC:$PC_{71}BM$ or PTB7-Th:$PC_{71}BM$ or PTB7-Th:COi8DFIC /MoO_3/Ag to fabricate devices. ITO glass substrates were cleaned through soapy deionized (DI) water, pure DI water, acetone and isopropanol in sequence by 10 min ultrasonication. The ZnO nanoparticle solution (3%) was made by adding 50 μL zinc dispersion into 1622 μL reagent alcohol. The ZnO nanoparticles solution was stirred overnight in the N_2 filled glove box and then spin-coated on the top of the cleaned ITO glass with a spin rate of 4000 rpm for the 60s. After coated ZnO solution, all the samples were annealed at 120 ℃ on the hot plate inside the N_2 filled glove box for 10 min. The PTB7-Th:$PC_{71}BM$ or PTB7-Th:COi8DFIC binary active layer solutions were made by 10 mg PTB7-Th and 15 mg $PC_{71}BM$ or 15 mg COi8DFIC with a 1:1.5 wt. ratio in a 25 mg/mL chlorobenzene solution with 3 vol% DIO. The PTB7-Th:COi8DFIC:$PC_{71}BM$ ternary active layer solutions were made by 10mg PTB7-Th, 10.5 mg COi8DFIC and 4.5 mg $PC_{71}BM$ with a 1:1.05:0.45 wt. ratio in a 18 mg/mL chlorobenzene. The PTB7-Th:$PC_{71}BM$ or PTB7-Th:COi8DFIC active layer solution was stirred overnight under room temperature

inside an N_2-filled glovebox and then spin-coated at a rate of 1800 rpm for 2 min. on samples to reach an around 100 nm thickness. The PTB7-Th:COi8DFIC:$PC_{71}BM$ ternary active layer solution was stirred overnight on the 100 ℃ hot plate inside an N_2-filled glovebox and then spin-coated at a rate of 1800 rpm for 1min on samples to reach an around 100 nm thickness. After that, the coated samples were put into a vacuum chamber at a pressure of 10^{-5} Pa. The 10 nm film of MoO_3 and 100 nm film of silver were deposited to the sample surface through a shadow mask by thermal evaporation. The device area fabricated was 0.045 cm^2.

Device Characterization

Fresh samples were stored in an N_2-filled glove box to avoid degradation before characterizations. For aged samples, it has been operated under one-sun test condition at ambient for 5 hours. The current density-voltage (J–V) measurements were conducted by using a solar cell I–V testing system from PV Measurements, Inc. (using a Keithley 2400 source meter) under illumination power of 100 mW/cm^2 by an AM 1.5G solar simulator. A dehumidifier from Ausclimate (model no: WDH-930DA) and a forced air flow were applied to control the temperature and humidity to minimize the thermal and moisture effects during the IV measurement. The device temperature was measured by GM1350 50:1 LCD infrared thermometer digital gun and maintained at around 25 ℃. The relative humidity of the test area was around 35%. An Autolab PGSTAT-30 was used as the EIS and capacitance-voltage (C-V) characterization machine. This characterization was conducted in the glove box with a frequency range of 10^6-100 Hz by using a frequency analyzer module. A QEX10 spectral response system from PV measurements was used as a characterization machine for external quantum efficiency (EQE) measurements. The optical characterization was conducted by a UV–VIS–NIR spectrometer (Perkin Elmer –Lambda 950). A Bruker Dimension ICON SPM with a scan size of "5 μm × 5 μm", the scan rate of 0.812 Hz was used as the atomic force microscopy (AFM) to characterize the film surface morphology. Scanning electron microscopy (SEM) images were taken using a Nano SEM 450 system. The micro-photoluminescence (μPL) characterisation was conducted on a self-developed μPL system. The sample is excited by a pulsed OPO laser at 532 nm. For steady state spectral PL, the signal was detected by Glacier X TE Cooled CCD Spectrometer with a detection range of 200 nm to 1050 nm. For time-resolved PL (TRPL), the signal was detected by id110 VIS 100 MHz Photon Detector operated in free running mode.

Space-charge limited current (SCLC) Characterization

The electron mobilities of both binary and ternary devices were also verified by the space charge limited current (SCLC) characterization. The electron-only devices were fabricated by using the device structure of ITO/ZnO nanoparticles/active layer/ZnO nanoparticles/Ag. The electron mobilities were estimated by fitting the current-voltage curves of the electron-only devices in the range from 1V to 3V of the space charge limited range. The estimation equation is shown below:

$$J = \frac{9\varepsilon_r\varepsilon_0\mu_0(V - V_{bi})^2}{8L^3}$$

where ε_0 notes as the free space permittivity (8.85×10^{-12} F m^{-1}), ε_r notes as the relative permittivity, μ_0 notes as the electron mobility, V represents the applied bias voltage, V_{bi} represents the built-in voltage and L is the thickness of the active layer. The built-in voltage used in estimation are 0.8V for PTB7-Th:$PC_{71}BM$ based devices and 0.6V for PTB7-Th:COi8DFIC and ternary devices which are consistent with the build-in potential estimated from C-V measurement. The root square root of the electron current to bias voltage curves of devices were shown in Figure S1 and the corresponding obtained electron mobility were shown in Table S5.

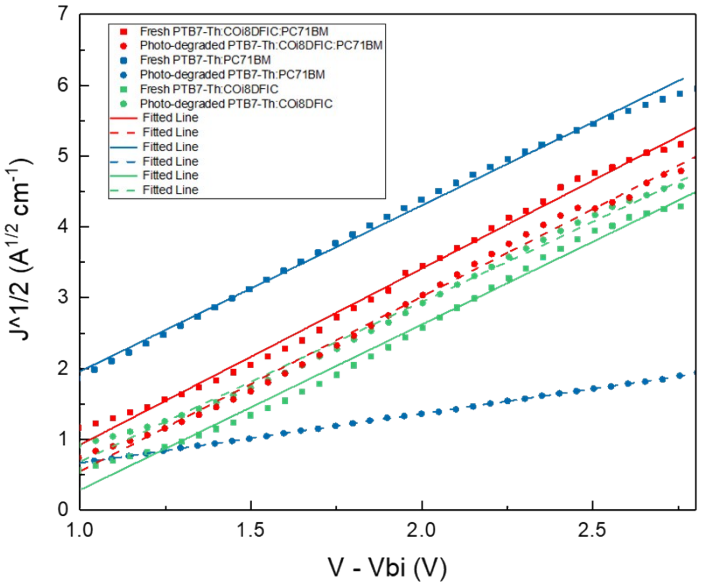

Figure S1. Root square plots of the electron current density to bias voltage curve of the electron-only devices for both fresh and photo-degraded PTB7-Th:$PC_{71}BM$, PTB7-Th:COi8DFIC and PTB7-Th:COi8DFIC:$PC_{71}BM$ devices.

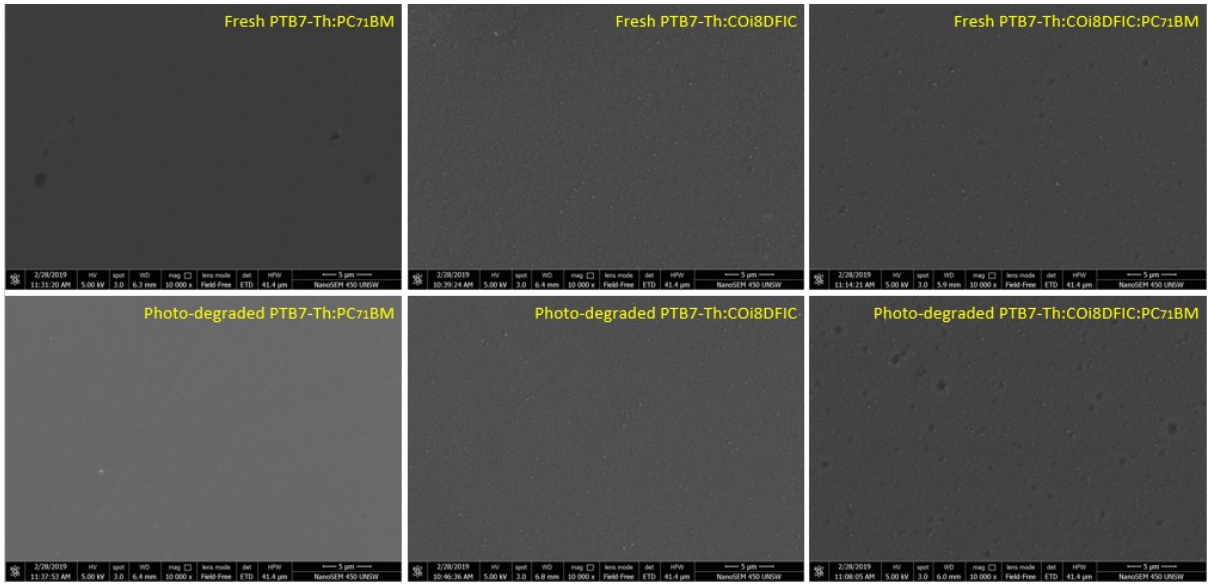

Figure S2. The SEM images of both both fresh and photo-degraded PTB7-Th:PC71BM, PTB7-Th:COi8DFIC and PTB7-Th:COi8DFIC:PC71BM blend films deposited on top of ITO surface.

Table S1. Normalized photovoltaic parameters for 5 hours of continuous light illumination under one-sun test condition (AM1.5G illumination at 100 mW cm^{-2}) for PTB7-Th:$PC_{71}BM$ binary devices obtained from at least 5 devices.

Degradation Time	**V_{OC} (V)**	**J_{SC} (mA/cm²)**	**FF**	**PCE**	**RSH (Ω cm²)**	**RS (Ω cm²)**
0H	0.819±0.001	15.26±0.26	0.62±0.01	7.74±0.26%	525±31	5.57±0.50
1H	0.793±0.005	14.17±0.78	0.60±0.02	6.69±0.42%	507±48	6.70±0.59
2H	0.783±0.005	13.89±0.81	0.58±0.02	6.32±0.41%	507±45	7.26±0.82
3H	0.780±0.006	13.93±0.84	0.56±0.02	6.09±0.37%	452±54	7.69±0.44
4H	0.778±0.005	13.11±0.98	0.55±0.03	5.56±0.56%	445±49	9.15±1.46
5H	0.775±0.006	13.08±0.69	0.52±0.03	5.28±0.39%	401±74	9.87±1.43

Table S2. Normalized photovoltaic parameters for 5 hours of continuous light illumination under one-sun test condition (AM1.5G illumination at 100 mW cm^{-2}) for PTB7-Th:COi8DFIC ternary devices obtained from at least 5 devices.

Degradation Time	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE	RSH (Ω cm^2)	RS (Ω cm^2)
0H	0.701±0.003	22.32±1.05	0.60±0.01	9.40%±0.48%	552±48	7.15±0.43
1H	0.639±0.008	21.37±1.12	0.46±0.02	6.29%±0.19%	239±23	10.95±0.76
2H	0.633±0.012	19.30±1.64	0.45±0.02	5.44%±0.14%	232±28	12.91±0.77
3H	0.626±0.007	18.37±1.20	0.44±0.01	5.09%±0.27%	222±23	14.13±0.83
4H	0.621±0.012	17.13±1.90	0.43±0.03	4.58%±0.42%	226±37	16.677±2.14
5H	0.606±0.022	16.99±1.17	0.41±0.04	4.24%±0.75%	212±75	19.764±0.44

Table S3. Normalized photovoltaic parameters for 5 hours of continuous light illumination under one-sun test condition (AM1.5G illumination at 100 mW cm^{-2}) for PTB7-Th:COi8DFIC:$PC_{71}BM$ ternary devices obtained from at least 5 devices.

Degradation Time	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE	RSH (Ω cm^2)	RS (Ω cm^2)
0H	0.712±0.001	25.87±0.45	0.63±0.01	11.54±0.12%	468±45	3.82±0.06
1H	0.688±0.004	24.60±0.19	0.61±0.01	10.27±0.26%	313±41	3.88±0.07
2H	0.693±0.004	23.12±0.55	0.58±0.02	9.30±0.50%	289±56	4.80±0.39
3H	0.688±0.011	22.98±0.59	0.56±0.03	8.79±0.69%	248±59	5.60±0.47
4H	0.690±0.007	22.23±0.65	0.55±0.02	8.50±0.53%	257±42	6.00±0.53
5H	0.686±0.013	21.51±0.80	0.52±0.03	7.73±0.46%	215±51	7.24±0.68

Table S4. Extracted amplitudes (A_1 and A_2), fast and slow lifetime (τ_1 and τ_2) and constant (y_0) for binary and ternary, fresh and photo-degraded blend films from the normalized TRPL curves by fitting with the bi-exponential decay equation

Device	**Fast Lifetime τ_1 (ns)**	**Slow Lifetime (ns) τ_2**	**Amplitudes A_1**	**Amplitudes A_2**	**Constant y_0**
Fresh PTB7-Th:$PC_{71}BM$	0.152	2.313	0.907	0.122	-0.035
Photo-degraded PTB7-Th:$PC_{71}BM$	0.174	2.894	0.894	0.140	-0.050
Fresh PTB7-Th:COi8DFIC	0.103	0.930	0.931	0.089	0.0007
Photo-degraded PTB7-Th:COi8DFIC	0.109	1.040	0.956	0.081	0.0005
Fresh PTB7-Th:COi8DFIC: $PC_{71}BM$	0.182	3.259	0.990	0.094	-0.022
Photo-degraded PTB7-Th:COi8DFIC: $PC_{71}BM$	0.186	3.348	0.873	0.107	-0.038

Table S5. Extracted average electron mobility of both fresh and photo-degraded PTB7-Th:$PC_{71}BM$, PTB7-Th:COi8DFIC and PTB7-Th:COi8DFIC:$PC_{71}BM$ devices over at least 3 devices from the SCLC characterization.

Device	**Electron mobility (cm^2/Vs)**
Fresh PTB7-Th:$PC_{71}BM$	$1.14 \pm 0.19 \times 10^{-4}$
Photo-degraded PTB7-Th:$PC_{71}BM$	$1.30 \pm 0.03 \times 10^{-5}$
Fresh PTB7-Th:COi8DFIC	$8.81 \pm 1.29 \times 10^{-5}$
Photo-degraded PTB7-Th:COi8DFIC	$8.10 \pm 1.49 \times 10^{-5}$
Fresh PTB7-Th:COi8DFIC: $PC_{71}BM$	$1.40 \pm 0.26 \times 10^{-4}$
Photo-degraded PTB7-Th:COi8DFIC: $PC_{71}BM$	$1.20 \pm 0.35 \times 10^{-4}$

References

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