Supporting Information

Intrinsic Photo-degradation and Mechanism of Polymer Solar Cells: The crucial role of Non-fullerene Acceptor

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\textbf{General:} Unless otherwise noted, all of the chemicals and solvents for the device fabrications and characterizations were purchased from Sigma-Aldrich and used without further purification process. The active layer materials such as PTB7, PC\textsubscript{71}BM, PBDB-T, and ITIC were purchased from 1-Material Inc. \textsuperscript{1}H-nuclear magnetic resonance (NMR) spectra were obtained on a Bruker Ascend 400 spectrometer using CD\textsubscript{2}Cl\textsubscript{2} as a solvent at 298 K. The mass spectra were obtained by the matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF MS) at the Korea Basic Science Institute (Seoul) using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix. The ultraviolet-visible (UV/vis) absorption spectra of the active layers were obtained by a PerkinElmer Lambda 35 UV/vis spectrometer at room temperature and an integrating sphere accessory was used for encapsulated ultra-thin films. The atomic force microscopy (AFM) images of the active layers were obtained using XE-100 AFM Park systems Inc. with a non-contact mode. Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained by measuring ITIC or degraded ITIC on the surface of KBr crystal window using PerkinElmer Spectrum 100 FT-IR spectrometer. Transmission electron microscopy (TEM) images were recorded on a FE-TEM (JEM-2100F). To prepare the TEM samples, the blend solution for active layer was spin coated on ITO/PEDOT:PSS substrate, and then floating the blend film at the surface of deionized water, followed by lifting on a carbon film 200 mesh copper grid. To procure quantities of degraded ITIC sufficient for analyses such as \textsuperscript{1}H-NMR, FT-IR, MALDI-TOF MS, and cyclic voltammetry (CV), a large number of ultra-thin ITIC films were exposed to UV in a N\textsubscript{2}-filled glove box, dissolved in dichloromethane, concentrated, and dried under vacuum.
Polymer solar cell device fabrication

Polymer solar cell devices with an inverted device architecture of glass/indium tin oxide (ITO)/ZnO/active layer/MoO$_3$/Ag were fabricated by procedures below. Pre-patterned ITO glass substrates were cleaned with ultra-sonication in diluted detergent (Hellmanex III), deionized water, acetone, and isopropyl alcohol sequentially 10 min in each step and dried in 100 °C oven over 1 h. The dried ITO substrates were treated with an UV/O$_3$ for 20 min. To prepare a ZnO precursor solution, zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, 1 g) and ethanolamine (NH$_2$CH$_2$CH$_2$OH, 0.28 g) were dissolved in 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, 10 mL) under vigorous stirring for 24 h. The ZnO precursor solution was spin-coated on the pre-treated ITO glass substrates and then followed 200 °C annealing in air. The blend solution for PBDB-T:ITIC active layer was prepared by dissolving the active materials in 1:1 blend ratio (wt:wt) in a mixture of chlorobenzene and 1% of DIO. For PTB7:PC$_{71}$BM active layer, 1:1.3 blend ratio of solution was prepared in a mixture of chlorobenzene and 3% of DIO. In both blend solutions, each polymer concentration was 10 mg/mL. The completely dissolved solution was spin-coated on ZnO coated ITO substrate to form the active layer and PBDB-T:ITIC coated films were treated by thermal annealing at 160 °C for 10 min in N$_2$ filled glove box. The active layer coated substrates were transferred into a thermal evaporator chamber in the glove box and 3 nm of MoO$_3$ and 100 nm of Ag were deposited sequentially. A shadow mask was used in the electrode deposition to decide an active area and the active area was 0.2 cm$^2$.

Characterization of polymer solar cell devices

Class A solar simulator with a 1000 W xenon ramp of Yamashita equipped with an AM1.5G filter was employed as a light source and a Keithley model 2400 sourcemeter was used to record current density versus voltage (J-V) characteristics of the polymer solar cell devices. A NREL-calibrated Si solar cell was used to adjust the 1 sun light intensity (100 mW·cm$^{-2}$, AM1.5G). External quantum efficiency (EQE) spectra were recorded as a function of wavelength on incident photon-to-current using an equipment of Mcscience. A NIST-
calibrated silicon photodiode G425 was used as a standard for calibration.

**Photo-stability test**

Polymer solar cell devices for photo-stability test were encapsulated by a glass through UV curable resin in the N₂ filled glove box to prevent effects of oxygen and moisture in air. The encapsulated devices were exposed under 1 sun light using solar cell reliability test system (Polaronix K3600, Mcscience) and J-V characteristics of the devices were recorded several times during the light exposure. To track UV-vis absorption changes of the active layers during the light exposure, the active layers of optimized conditions were prepared with same procedures of the device fabrication without the electrode deposition and encapsulated in inert condition. AFM topography images of light exposed samples were obtained with opening and measuring the encapsulated samples using a blade. Ultra-thin films of PBDB-T:ITIC blend and ITIC on bare glass or ZnO coated glass were prepared by spin coating with total 2 mg/mL blend solution and 2 mg/mL ITIC solution, respectively. To prevent the effect of solvent to active layer stability, all of stability test samples were completely dried in vacuum chamber before encapsulation.

**Degraded ITIC characterization**

To analyze degraded ITIC with enough amount, 16 pieces of ultra-thin ITIC film on ~20 cm² substrates were prepared by same procedures of stability test samples and degraded in nitrogen filled glove box by using UV lamp. Degraded ITIC was obtained by dissolving the degraded film in dichloromethane, concentrating, and drying in vacuum. Degraded ITIC was characterized by ¹H-NMR, FR-IR, MALDI-TOF MS, and cyclic voltammetry (CV).

**Electrochemical properties**

Cyclic voltammogram of ITIC and degraded ITIC were obtained to estimate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level using a CH instruments electrochemical analyzer. Electrolyte for measurement was used of
0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in degassed acetonitrile. For CV measurement, the three electrode system was employed consisted of glassy carbon as a working electrode, Ag/AgCl as a reference electrode, and Pt wire as a counter electrode. The samples were loaded on the surface of glassy carbon working electrode by drop-casting. The CV measurements were performed with a 20 mV·s⁻¹ potential sweep rate. Ferrocene was used as an internal standard to calibrate the energy levels in same measurement system, and the redox potential of ferrocene/ferrocenium (Fc/Fc⁺) was located at 0.52 V vs. Ag/AgCl reference electrode.

**Electron mobility measurements**

Electron-only devices with a structure of ITO/ZnO/PBDB-T:ITIC/Al was prepared. The electron mobility of the fresh and degraded device were calculated using a space charge limited current (SCLC) model as following equation.

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J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_e V^2 \frac{1}{L^3}
\]

Where, \(\varepsilon_r\) is the relative permittivity of conjugated molecules (typically, \(\varepsilon_r = 3\)), \(\varepsilon_0\) is absolute permittivity in free space, \(\mu_e\) is the electron mobility, \(L\) is the thickness of blend film, and \(V\) is the voltage drop across the electron-only device. \(V = V_{app} - V_{bi} - V_r\), where \(V_{app}\) is the applied voltage to the device, \(V_{bi}\) is the built-in voltage from the difference of work function, and \(V_r\) is the voltage drop from the contact and series resistance across the electrodes.\(^{1,2}\) The \(J\)-\(V\) characteristics were obtained using Keithley model 2400 sourcemeter under N₂ and dark condition.
Fig. S1 (a) UV-vis absorption spectra and (b) AFM topography images of encapsulated active layer films on ZnO with various 1 sun illumination time. Variations in (c) JSC with different light intensity for BHJ solar cells of initial and 400 h 1 sun illuminated.
Fig. S2 UV-vis absorption spectra of encapsulated ~100 nm or ~10 nm BHJ active layer films with various 1 sun illumination times.
Fig. S3 UV-vis absorption spectra of encapsulated ~100 nm or ~10 nm BHJ active layer films of P3HT:ITIC, PCDTBT:ITIC, and PTB7-Th:ITIC with various 1 sun illumination times.
Fig. S4 UV-vis absorption spectra of fresh and UV exposed PBDB-T film (~10 nm) on ZnO under N₂.

Fig. S5 UV-vis absorption spectra of fresh and UV exposed ITIC film (~10 nm) on ZnO under N₂.
Fig. S6 Current density–voltage characteristics of fresh and UV exposed electron only device.

Fig. S7 UV-vis absorption spectra of fresh and UV exposed ultra-thin ITIC (~10 nm) on (a) TBA (b) MBA and (c) EDT self-assembled monolayer (SAM) treated ZnO, and (d) glass under N₂. (e) Absorption maximum changes of ultra-thin ITIC film on different conditions of ZnO under UV exposure and N₂ condition.
Fig. S8 Degraded ITIC compounds detected in MALDI-TOF MS.
Fig. S9 Dark current density-voltage ($J-V$) curves of fresh and 471 h 1 sun light-soaked PBDB-T:ITIC solar cell devices.

Fig. S10 Energy diagram of degraded PBDB-T:ITIC solar cell.
Fig. S11 Chemical structure of non-fullerene acceptors.

Fig. S12 Absorption maximum changes of non-fullerene acceptor thin films (~10 nm) on ZnO under UV exposure and N$_2$ condition.
Reference
