Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

# Study on Photo-Degradation of Inverted Organic Solar Cells Caused by Generation of Potential Barrier between PEDOT:PSS and PBDB-Ts.

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Contents

# 1. Experimental

## 1-1. Materials

All chemicals and solvents are of reagent grade unless otherwise indicated. Zinc acetylacetonate hydrate (99.995%, trace metals basis), regioregular P3HT (MW 42,000), and chlorobenzene (CB) were purchased from Sigma-Aldrich, Japan. A PEDOT:PSS dispersion in water (Clevios P) (1.3 wt%) was purchased from H. C. Starck. The indium tin oxide (ITO) substrates (sheet resistance = 10 Ω sq) and Au wires were purchased from Furuuchi Chemical Corporation. $PC_{61}BM$ were purchased from Frontier Carbon Corporation, Japan. PBDB-T and PBDB-T-2F were synthesized following the reported procedure.[1,2] $MoO_X$ nanoparticle solution was prepared by reported method.[3] PB-62 was supplied by Nissan Chemical Corporation.

## 1-2. Fabrication of inverted organic solar cells

A patterned ITO (sheet resistance = 10 Ω sq)-coated glass substrate was cleaned by ultrasonication in 2-propanol. A ZnO layer was prepared by spin coating (1000 rpm, 60 s) a precursor solution prepared from zinc acetylacetonate (0.103 g) and acetylacetone (120 μL) in 1.0 mL of 2-methoxyethanol and subsequent thermal annealing at 250 °C. Then, a chlorobenzene solution of the active materials (PBDB-T and $PC_{61}BM$, 1:1, 16 g/L or PBDB-T-2F and $PC_{61}BM$, 1:1, 16 g/L) was spin-coated onto an ITO/ZnO substrate at 1500 rpm for 65 s. After the spin coating, the substrate was annealed at 160 °C for 10 min, then, hole transport layer (HTL) was fabricated by spin coating (2000 rpm for 60 s for PEDOT:PSS, 1000 rpm for 30 s for $MoO_X$ using nanoparticle solution, 4000 rpm for 60 s for PB-62). An Au electrode was deposited by thermal evaporation under vacuum (approximately $10^{-2}$ Pa) through a metal mask (active area: 1.0 $cm^2$). Finally, the device covered with barrier film (Cellel, Kureha Extech) was thermo-compressed at 30 N $m^{-2}$ for 30 s. All fabrication steps except the Au deposition step were performed in an $N_2$-air mixed atmosphere to control the relative humidity to less than 30%. The active area of the device was defined by using a 1.0 $cm^2$ photo mask.

### 1-3. Fabrication of donor polymer/PEDOT:PSS bilayer devices

A patterned ITO-coated glass substrate was cleaned by ultrasonication in 2-propanol. A chloroform solution of the donor polymer (1 g/L) was spin-coated onto an ITO substrate at 1500 rpm for 60 s. A PEDOT:PSS layer was fabricated by spin coating at 2000 rpm for 60 s using water-diluted solution (×10). An Au electrode was deposited by thermal evaporation under vacuum (approximately $10^{-2}$ Pa). All fabrication steps except the Au deposition step were performed in an $N_2$-air mixed atmosphere to control the relative humidity to less than 30%.

## 2. Predicted photo-decomposition of non-fullerene acceptors

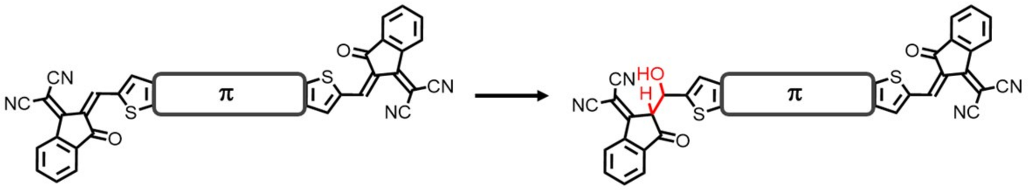

**Figure S1.** Predicted photo-decomposition of state-of-the-art acceptors under photo-irradiation by the photocatalytic effect of ZnO films.

## 3. Change of PCE values of *i*-OSC devices

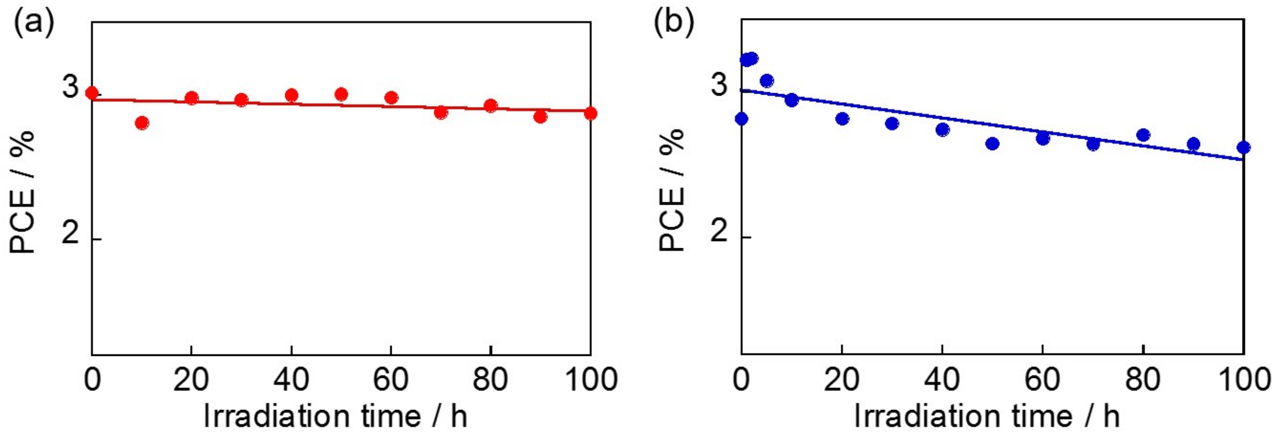

**Figure S2.** Change of PCE values of an *i*-OSC device with ITO/ZnO/active materials/ PEDOT:PSS/Au/barrier film structure upon photo-irradiation for 100 h under ambient conditions. The P3HT:$PC_{61}BM$-based device (a) and PBDB-T:$PC_{61}BM$-based one (b).

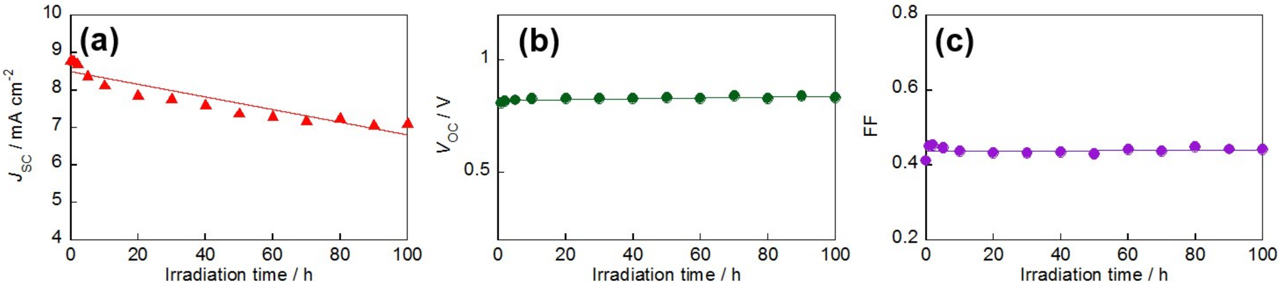

**Figure S3.** Changes of $J_{SC}$ (a), $V_{OC}$ (b), and FF (c) values of an *i*-OSC device with ITO/ZnO/PBDB-T:$PC_{61}BM$/PEDOT:PSS/Au/barrier film structure upon photo-irradiation for 100 h under ambient conditions.

## 4. Investigation of active layer materials in OSCs after photo-irradiation

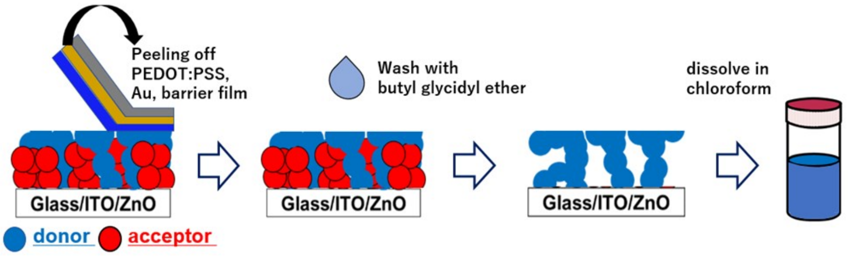

**Figure S4.** Schematic illustration of the sample preparation method for spectral measurements.

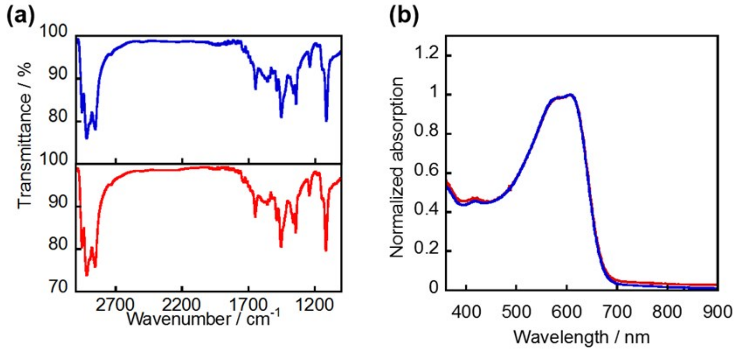

**Figure S5.** ATR-IR spectra of PBDB-T films after extraction of $PC_{61}BM$ from bulk-heterojunction layer in the *i*-OSCs (a) and UV-vis-NIR absorption spectra of chloroform solution of PBDB-T extracted from the OSCs (b) (blue traces: without photo-irradiation, red traces: after photo-irradiation for 100 h).

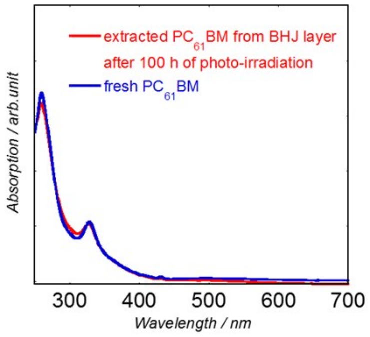

**Figure S6.** Absorption spectra of solution of extracted $PC_{61}BM$ from the bulk-heterojunction layer of OSCs after photo-stability testing (AM1.5, 100 mW/cm$^2$, 100 h, ambient conditions) and fresh $PC_{61}BM$.

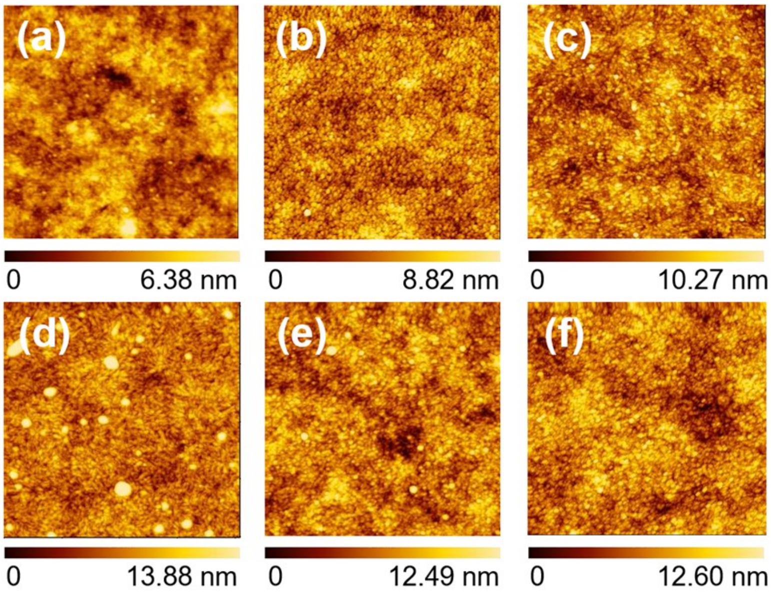

**Figure S7.** AFM images (2 × 2 μm$^2$) of active layer films after peeling off barrier film with Au and PEDOT:PSS layer from photo-irradiated *i*-OSCs (a,b,c) and PBDB-T films after removing PC$_{61}$BM from the active layer (d,e,f). Without photo-irradiation (a,d), after photo-irradiation for 2 h (b,e) and 100 h (c,f).

## 5. Solubility test of PBDB-T

Solubility test of PBDB-T in butyl glycidyl ether was conducted by following procedure. PBDB-T and filter paper (pore size: <1 μm) were dried carefully in a desiccator under vacuum, and the PBDB-T was stirred in 1 mL of butyl glycidyl ether for 3 h at 25 ˚C. The suspension was filtered using the dried solid with the filter paper was dried carefully in a desiccator under vacuum, then, the weights of PBDB-T before and after this test were compared (Table S1). This test was conducted three times.

To detect small amounts of soluble component in PBDB-T, we used gas chromatography. 30.0 mg of PBDB-T in 1.0 mL of butyl glycidyl ether was stirred at 25 ˚C for 3 h. After removing of residual solids by filtration, the filtrated butyl glycidyl ether was analyzed by gas chromatography. The resulting chromatogram shows that the impurity pattern of the filtrated butyl glycidyl ether is almost the same to that of butyl glycidyl ether before it was used for this test (Figure S8). With these results, we conclude that PBDB-T does not dissolve in butyl glycidyl ether.

**Table S1.** Results of solubility test of PBDB-T in butyl glycidyl ether.

| run | 1 | 2 | 3 |
|---|---|---|---|
| weight of PBDB-T before washing / mg | 10.2 | 10.4 | 10.6 |
| weight of PBDB-T after washing / mg | 10.2 | 10.4 | 10.7 |

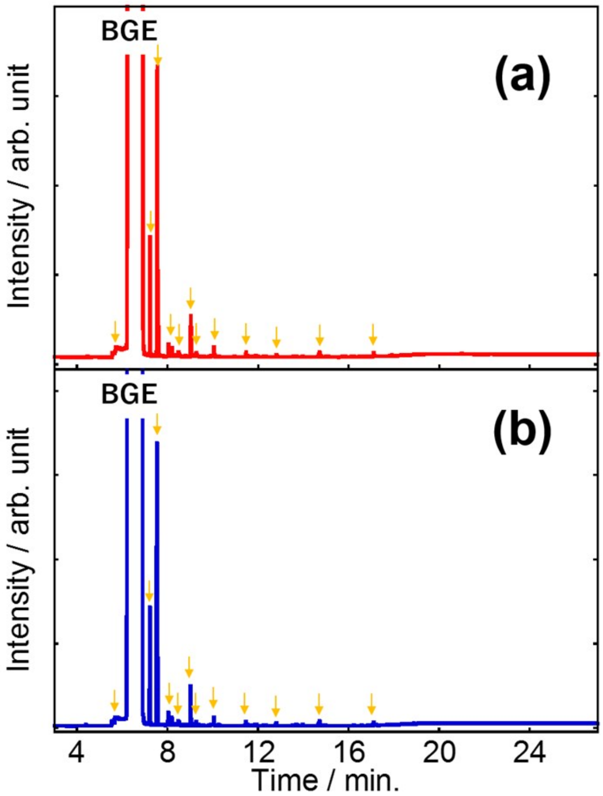

**Figure S8.** Chromatogram obtained by gas chromatography of the filtrated butyl glycidyl ether from the suspension with butyl glycidyl ether and PBDB-T (a) and butyl glycidyl ether before it was used for the solubility test (b). The orange arrows indicate impurity patterns.

## 6. *I-V* characteristics of devices with ITO/donor polymer/PEDOT:PSS/Au

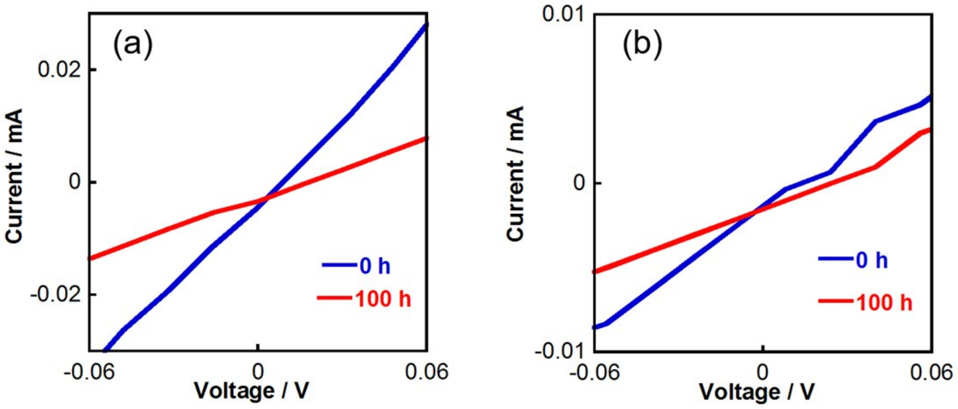

**Figure S9.** *I-V* characteristics of devices with ITO/PBDB-T/PEDOT:PSS/Au/barrier film (a) and ITO/P3HT/PEDOT:PSS/Au/barrier film (b) as prepared and after photo-irradiation for100 h.

## 7. Schematic illustration of the Kelvin-probe measurements of the interface between PEDOT:PSS and donor material

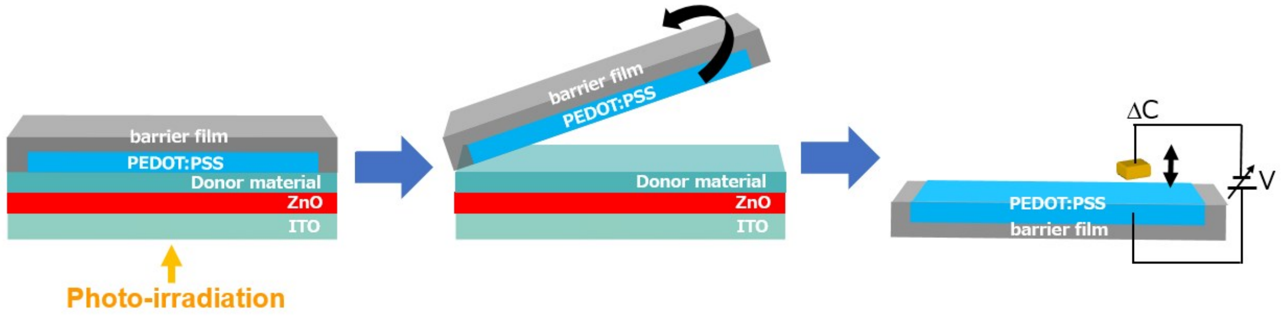

**Figure S10.** Schematic illustration of the Kelvin-probe measurements of the interface between PEDOT:PSS and donor material. The fabricated bilayer devices have ITO/ZnO/donor material (PBDB-T, or P3HT or no donor material)/PEDOT:PSS/barrier film structure.

## 8. *J*-*V* characteristics of *i*-OSCs with PB-62

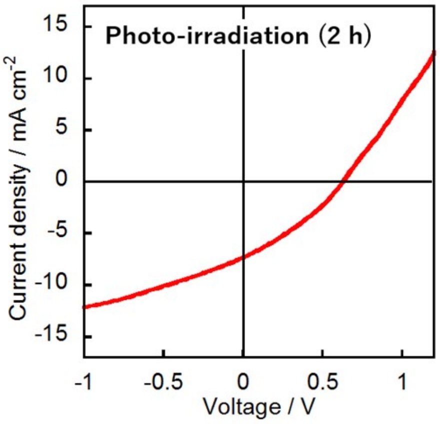

**Figure S11.** *J*-*V* characteristics of OSC device with ITO/ZnO/PBDB-T:PC$_{61}$BM/PB-62/Au/barrier film structure after 2 h of photo-irradiation.

## 8. References

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[1] D. Qian, L. Ye, M. Zhang, Y. Liang, L. Li, Y. Huang, X. Guo, S. Zhang, Z. Tan and J. Hou, *Macromolecules*, 2012, **45**, 9611–9617.

[2] M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, *Adv. Mater.*, 2015, **27**, 4655-4660.

[3] J. Meyer, R. Khalandovsky, P. Görrn and A. Kahn, *Adv. Mater.*, 2011, **23**, 70–73.