## **Supporting Information**

## The Effect of Ultraviolet Radiation on Organic Photovoltaic Materials and Devices

Jay B. Patel<sup>1</sup>, Priti Tiwana<sup>2</sup>, Nico Seidler<sup>2</sup>, Graham E. Morse<sup>2</sup>, Owen R. Lozman<sup>2</sup>, Michael B. Johnston<sup>1</sup>, and Laura M. Herz<sup>1</sup>\*

 Department of Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford, OX1 3PU, United Kingdom

E-mail: <u>laura.herz@physics.ox.ac.uk</u>

 Merck Chemicals Ltd., Chilworth Technical Centre, University Parkway, Southampton, SO16 7QD, United Kingdom



**Figure S1.** Device parameters found using standard JV characterisation, for the device batch used in this study, with the open-circuit voltage ( $V_{oc}$ ), short-circuit density ( $J_{sc}$ ), fill factor (FF) and power conversion efficiency (PCE). The devices were measured promptly after fabrication. These devices were then used for the investigation.



**Figure S2. a)** Air Mass 1.5G solar spectrum, plotted using data accessed from nrel.gov.<sup>[1]</sup> The dashed lines denote the cut-off for the two categories of UV radiation found in the AM 1.5 solar spectrum, UVB ( $280 \le \lambda < 315$  nm) and UVA ( $315 \le \lambda < 400$  nm) **b**) The transmission spectrum of the long pass 331nm filter (H-BaK7 331-GY, Comar optics) used in this investigation to filter UVB radiation, and the transmission spectrum of the long pass 400 nm filter (Schott Glass GG-400, Thorlabs) that was used to filter UVB +UVA radiation, together with the simulated unfiltered AM 1.5 light spectrum (red line) generated from the Oriel class AAA solar simulator with 0.7 sun (70mWcm<sup>-2</sup>) intensity. The pink line shows the transmission curve of the glass/ITO substrates that the devices were fabricated on. The glass/ITO reflects a fraction of the incident light across the whole frequency range, and clearly transmits a significant amount of UV radiation.



**Figure S3.** Sub-bandgap changes in the EQE, as evident when spectra shown in Figure 1c are plotted on a semi-logarithmic scale. A reduction in photocurrent from the sub-bandgap region is evident when the device is exposed to UVB+UVA filtered AM1.5 light (bottom), while no change is found when the device is exposed to unfiltered AM1.5 light (top).



**Figure S4.** Ultraviolet-visible absorption spectra of the bulk heterojunction films containing PBTZT-stat-BDTT-8 and PCBM when illuminated with **a**) unfiltered **b**) UVB + UVA filtered AM 1.5 light before (fresh) and after 1070 mins (Aged).



**Figure S5:** Absorption spectra of PBTZT-stat-BDTT-8 and PCBM on Quartz. The inset shows the sub-bandgap absorbance of PBTZT-stat-BDTT-8 and PCBM along with the recorded electroluminescence spectra of the fresh device. The arrows represent the y-axis that the data corresponds to.



**Figure S6:** Current-voltage curve of a typical PBTZT-stat-BDTT-8:PCBM bulk heterojunction device.



**Figure S7:** Bias voltage applied to the OPV device and the corresponding injection current density measured during electroluminescence spectroscopy. To extract an accurate value of  $E_{CT}$  it is important to ensure that EL spectra are measured in the low injection current regime (<30 mA cm<sup>-2</sup>), as this minimizes local changes in the chemical potential of the PAL.<sup>[2]</sup> From Figure S7 it is clear that the plateauing observed in Figure 3c after 1.6 V is below the low injection regime, allowing us to extract an accurate value of  $E_{CT}$ = 1.31eV.

Illumination Condition	Initial	Aged
	$(mA cm^{-2})$	$(mA cm^{-2})$
Unfiltered Light	13.05	12.29
UVA +UVB Filtered Light	12.19	11.56

Table S1: The absolute integrated short-circuit current density values of the initial and aged devices (1070 minutes) from Figure 2.

## References

[1] NREL. NREL National Center for Photovoltaics http://www.nrel.gov/ncpv/ (accessed March 19, 2017).

[2] Vandewal, K.; Albrecht, S.; Hoke, E. T.; Graham, K. R.; Widmer, J.; Douglas, J. D.; Schubert, M.; Mateker, W. R.; Bloking, J. T.; Burkhard, G. F.; et al. Efficient Charge Generation by Relaxed Charge-Transfer States at Organic Interfaces. Nat. Mater. 2014, 13 (1), 63–68.