# Supplementary information

## Surface energy characterization

HEG-DT is a viscous liquid at room temperature and hence its surface energy can be determined by measuring its surface tension.[1] Surface tension of HEG-DT was obtained by measuring its contact angle (CA) on Teflon. Measurements were conducted on Dataphysics, OCA15EC and DSA30E measuring system with DSA4 Drop Shape Analysis program, KRUSS. The average value, extracted from 30 measurements, was ~55 mJ/m$^2$ (±25%) which is similar to that reported for other ethylene glycol moieties such as PEG (~43 mJ/m$^2$)[2].

Table S1: Surface energy and densities of P3HT, PCBM and HEG-DT materials used for P3HT:PCBM and P3HT:PCBM:HEG-DT blends

| Material | Surface Energy [mJ/m$^2$] | Densities [g/ml] |
|---|---|---|
| **P3HT** | 27 | 1.1 |
| **PCBM** | 38 | 1.3-1.5 |
| **HEG-DT** | ~55 | 1.1 |

Table S1 reveals that there is no significant difference between the densities of the system components. Hence, HEG-DT will not float onto the blend film and the composition of the blend/air interface will be governed by the thermodynamic consideration of surface energy.

**Bulk vs. Surface XPS measurements**

Bulk sensitive XPS measurement of the covered area of P3HT:PCBM:HEG-DT(4.8 %wt.) sample can further confirm that the C-O peak at 286.6 eV originates from the buried blend/Ag interface and not the Ag/air interface. The slightly higher C-O peak intensity in the bulk sensitive measurement confirms that C-O moieties are present in the deeper layers as well as close to the surface.

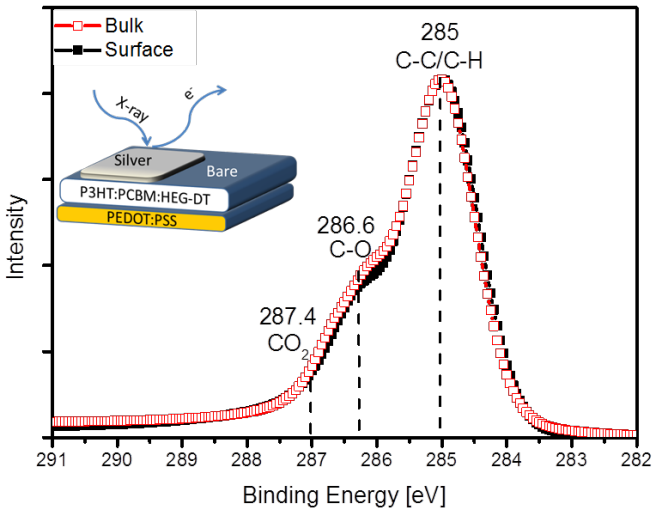


Figure S1: High energy resolution C1s XPS spectra in standard (black) and bulk (red) analysis mode, normalized to intensity of C-C/C-H peak, 285 eV obtained from the Ag-covered area of the P3HT:PCBM:HEG-DT (4.8 %wt.) film.

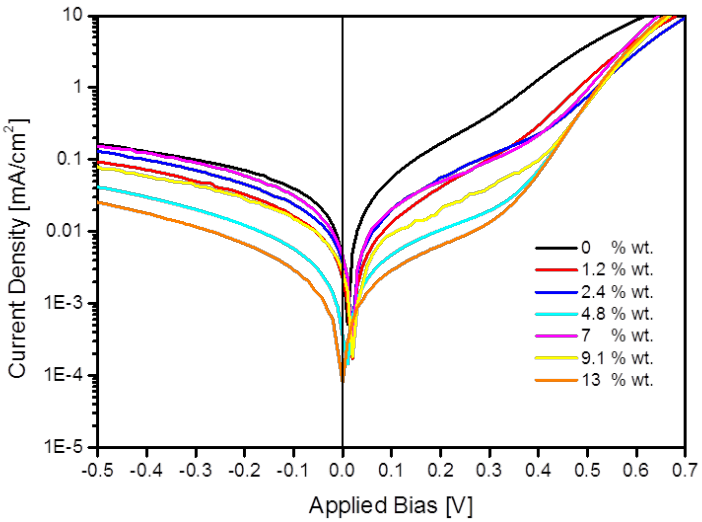


Figure S2: J-V measurement curves in dark of P3HT:PCBM and P3HT:PCBM:HEG-DT with various additive concentrations

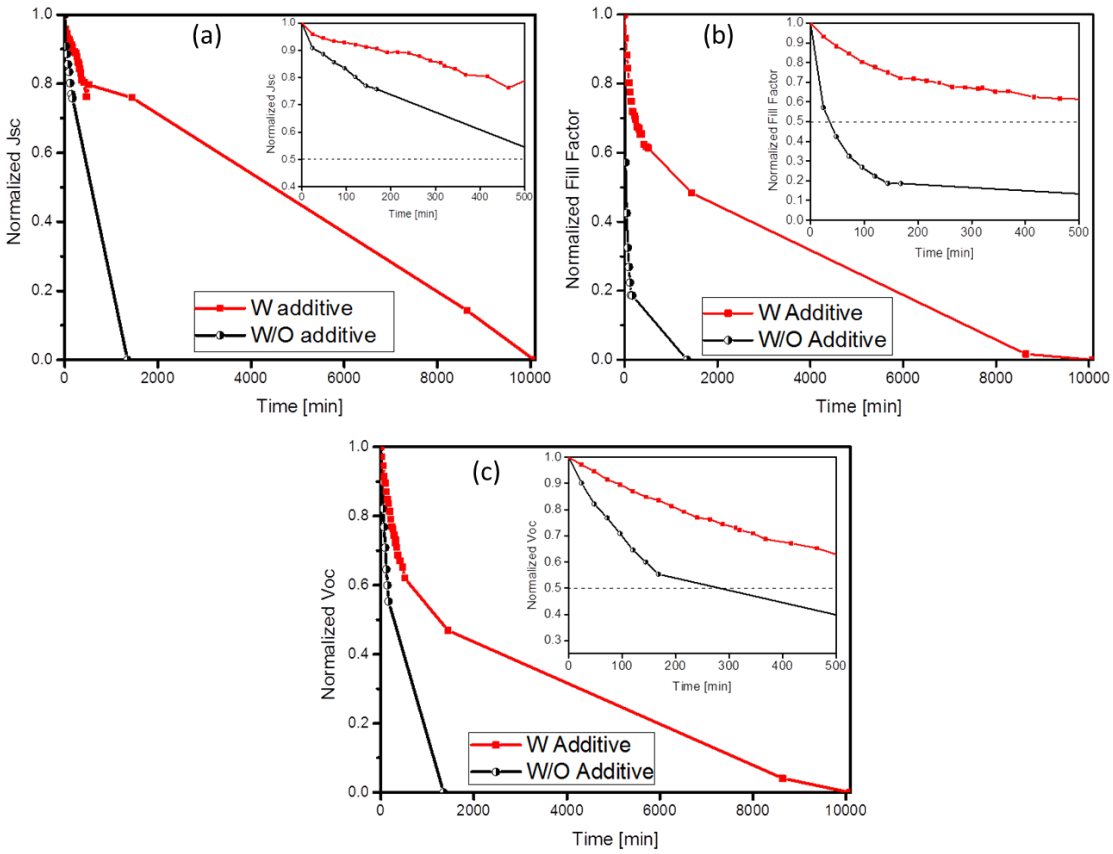


Figure S3: Normalized photovoltaic parameters under illumination of non-encapsulated devices without HEG-DT (black circles) and with 4.8 %wt HEG-DT (red squares) stored in ambient conditions and recorded over 7 days (10000 minutes). a) Short circuit current density, b) Open circuit voltage, c) FF.

Comparing the device performances of a blend with and without HEG-DT shows that the P3HT:PCBM devices (no HEG-DT) exhibit initially (t=0) a Voc of 0.42 V and a Jsc of 7.3 mA/cm$^2$, while the devices with HEG-DT at t=0 show a Voc 0.57 V and a Jsc of 9 mA/cm$^2$.

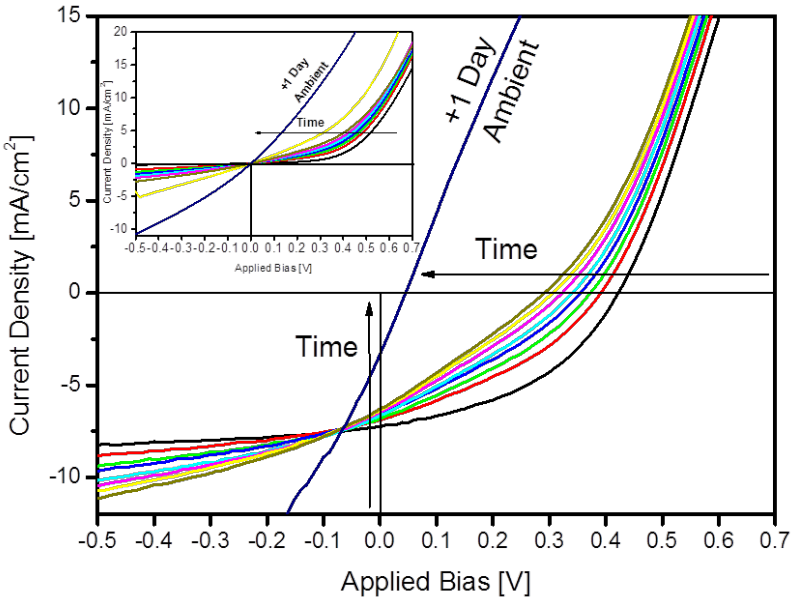


Figure S6: J-V under illumination (main figure) and dark (inset) curves of P3HT:PCBM (no HEG-DT) stored in ambient conditions and recorded over 7 days (10000 minutes).

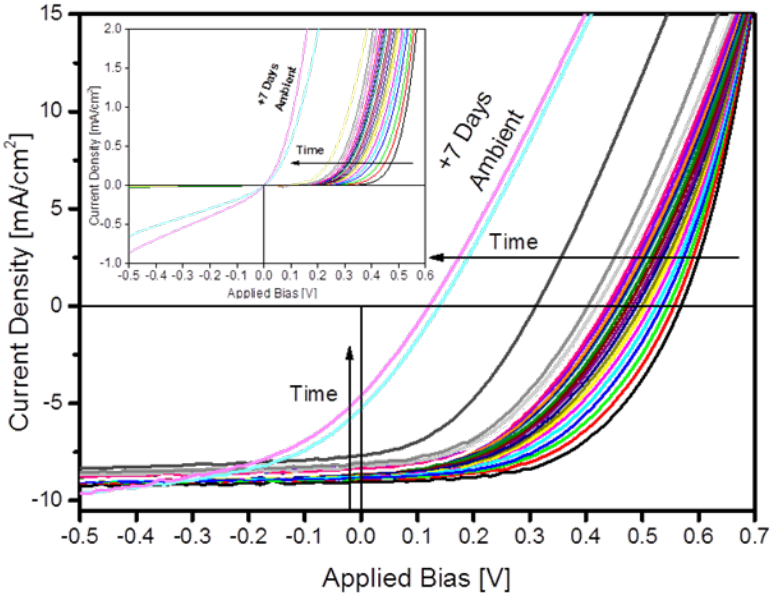


Figure S5: J-V under illumination (main figure) and dark (inset) curves of P3HT:PCBM:HEG-DT(4.8 wt%) stored in ambient conditions and recorded over 7 days (10000 minutes).

**1. Orowan, E., Surface Energy and Surface Tension in Solids and Liquids. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* 1970, *316* (1527), 473-491.**
**2. Van Oss, C.; Chaudhury, M.; Good, R., Monopolar surfaces. *Advances in colloid and interface science* 1987, *28*, 35-64.**