# Thermal metal deposition induces polymer segregation in thin films: a demonstration on OPVs

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## Supporting Information

Film and device processing and analysis:

Polymer blend solution was prepared by dissolving P3HT (purchased from Rieke Metals and used as received) and PCBM (purchased from Nano-C and used as received) in 1,2-dichlorobenzene (DCB) to obtain a 1:1 wt/wt ratio (20 mg/ml) solution. The solution was stirred for ~10 h at 80◦C under N2 atmosphere. For preparation of poly(ethylene glycol) (PEG) containing films, the PEG (Mw=200; purchased from Fluka and used as received) was added into the blend solution at weight ratio of 10% (2 mg/ml) or 25% (5 mg/ml) and stirred for ~5 h at room temperature under N2 atmosphere. The active layers were spun at 1000 rpm for 20 s under N2 atmosphere onto PEDOT:PSS/ITO/glass substrates. The spun films were then left in a covered glass petri dish for 1 hour. The films were then either subjected to XPS analysis or completed to devices. For device fabrication glass plates (12×12 mm2 ) covered with patterned indium tin oxide (ITO) (~80 nm) stripes defining device area of 3 mm2 were cleaned by sonication in acetone, methanol, and 2-propanol, followed by 15 min of UV-ozone treatment. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) (Clevios PVP AL 4083 purchased from Haraeus) was filtered through a 0.45 mm PVDF filter and spun at 5000 rpm onto the ITO coated glass, followed by drying at 120°C for 15 min in ambient conditions. Then the organic active layer was deposited as explained above. The processing was completed by thermal deposition of Al or Au through a shadow mask at a system pressure of ~10-6 Torr. The thickness of the evaporated metals stripes was ~3 nm and ~100 nm for XPS measurements and devices, respectively. The evaporation time of the thin (3 nm) stripes was extremely short, less than 30s, and a temperature controller was used to maintain the samples' temperature below 25oC. All stripes of a specific metal (Al or Au) were evaporated simultaneously in one batch in order to minimize thickness deviation. Device characterization was performed in inert atmosphere in dark and under 100 mW/cm2 AM1.5G class A sun simulator (Science Tech Inc. ss150 solar simulator) by use of a Keithley 2400 source meter. X-ray Photoelectron Spectroscopy (XPS), was performed in a Thermo VG Scientific Sigma Probe fitted with a monochromatic Al Kα (1486.6 eV) source. A 100W X-ray beam of 400 μm in diameter was used for high energy resolution scans of C1s spectra with pass energy of 30eV. Line-shape analysis was done using XPSPEAK4.1 software after a Shirley-type background subtraction. The binding energy scale calibration of C 1s spectra was done by referencing the C-C/C-H bonds to 285eV. For all samples, the C 1s spectra were measured in the standard and bulk-sensitive modes at an angle between the direction of the analyzer and the specimen normal of 53o ±30o and 30.5o ±7.5o , respectively. We used the bulk sensitive mode to obtain maximum depth information and to enhance the contribution from the blend/Al interface region relative to the contribution of the Al electrode carbon-based surface contamination. The higher intensity of the C-O peak (286.6 eV) obtained in the bulk-sensitive measurement, compared to that obtained in the standard mode measurement, clearly indicates that the main origin of the C-O signal is from the berried organic/Al interface and not from contaminations at the Al surface. Based on inelastic mean free path estimations in the Al/blend system, the information depth of C 1s electrons includes ~5nm thick organic film beneath the Al layer.[1]

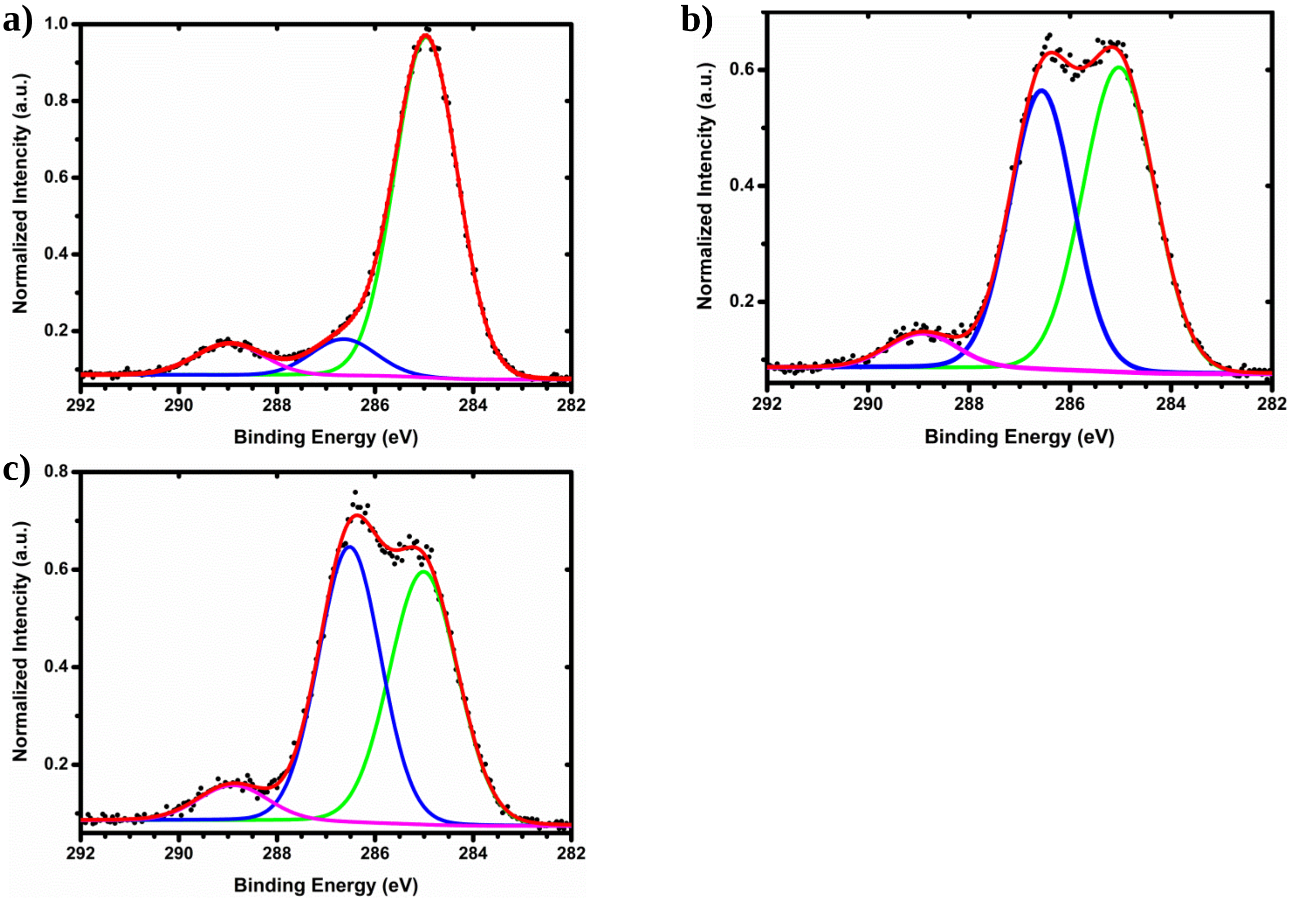

Figure S1- Line fitting of high energy resolution C 1s XPS spectra of Al covered P3HT:PCBM:PEG blends with different PEG content a) 0 wt%, b) 10 wt% and c) 25 wt%. Three peaks are fitted to each spectra: the green line associated with the C-C and C-H bonding in all polymers (285.0 eV); the blue line associated with the C-O bonding in PEG (286.6 eV); and the magenta line associated with O-C=O contamination moieties (288.6 eV). The red lines in each graph show the cumulative fitted spectra.

**Table S1-** Electrical characteristics of devices fabricated with various PEG content.

| | Jsc [mA/cm²] | Voc [V] | FF | Efficiency [%] |
|---|---|---|---|---|
| **P3HT:PCBM** | 9.3±09 | 0.46±0.01 | 0.46±0.01 | 1.9±0.3 |
| **P3HT:PCBM:PEG(10%)** | 9.4±0.8 | 0.61±0.01 | 0.69±0.01 | 3.9±0.3 |
| **P3HT:PCBM:PEG(25%)** | 9.7±0.6 | 0.61±0.01 | 0.67±0.02 | 4.0±0.2 |

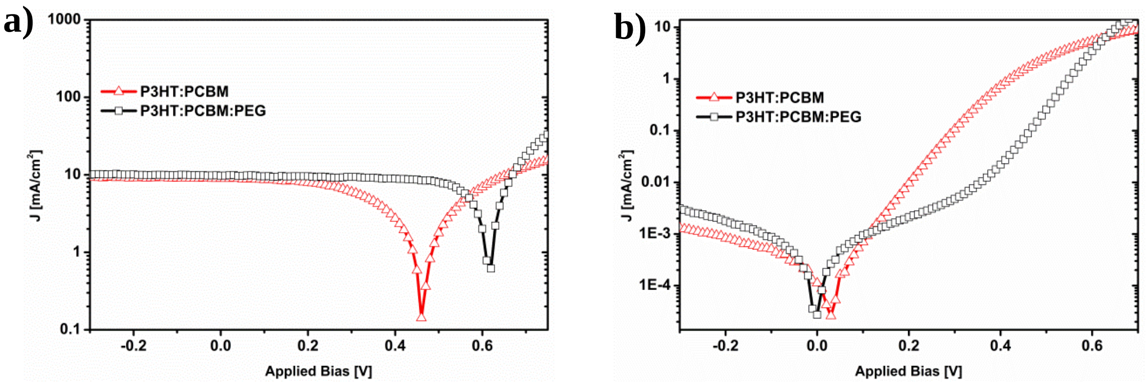

Figure S2-Current density-voltage (J-V) curves under illumination and (a) in the dark (b) of a P3HT:PCBM:PEG(25wt%) device (red triangles) and a corresponding P3HT:PCBM reference device (black squares).

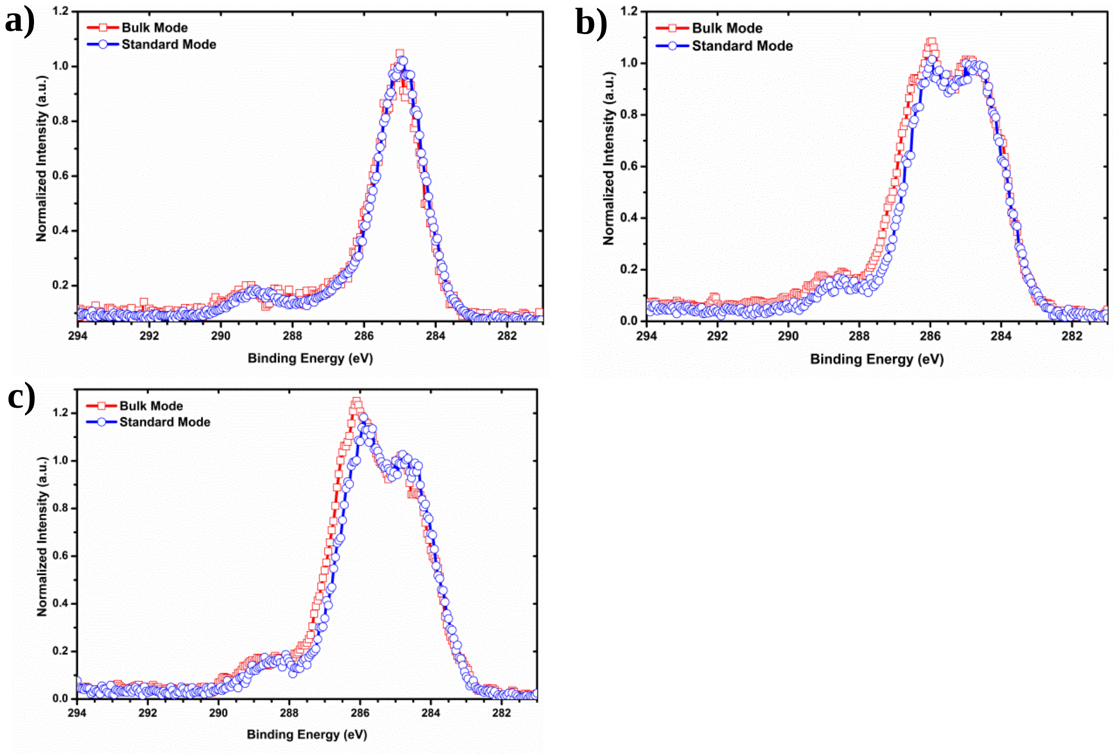

Figure S3-High energy resolution C 1s XPS spectra in the standard and bulk analysis mode normalized to intensity of C-C/C-H peak (285 eV) obtained from Al-covered areas of films prepared from P3HT:PCBM (a), P3HT:PCBM:PEG(10wt%) (b) and P3HT:PCBM:PEG(25wt%) (c) blends.

References:

[1] S. Tanuma, C.J. Powell, D.R. Penn, Surface and Interface Analysis, 17 (1991) 927-939.