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Effect of Metal/Bulk-Heterojunction Interfacial Properties on Organic Photovoltaic Device Performance

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Figure S1a shows the dark *J-V* measurements of the pristine devices shown in **Figure 1**. **Figure S1b** shows the dark *J-V* measurements of the devices shown in **Figure 3**, which were processed through electrode delamination and re-deposition of ZnO ETL and metals.

Figure S2 shows ATR-FTIR absorbance spectra from pure P3HT and PCBM films, buried Al and Ag electrodes, and clean Al and Ag films. Peak assignments for P3HT and PCBM follow published literatures.^[1-4]

Figure S3 shows the summary of XPS signal (C 1s, O 1s, S 2p) collected on pristine active layer (black), and buried active layers previously under Al (red) or Ag (blue). We note no carbonyl signature from PCBM (~533 eV) is observed on pristine active layers, which is consistent with previous reports showing that as the P3HT:PCBM film dries, P3HT becomes highly enriched at the air-film interface due to the lower surface energy of P3HT compared to PCBM.^{[5][6][7]} The P3HT enrichment extends at least 5 nm into the film.^[5] and thus XPS of P3HT:PCBM surface is not able to detect PCBM. As a result, the oxygen signal at \sim 534 eV is probably caused by ambient contamination. On the active layers after electrode delamination, we observe the carbonyl signature under Ag but not Al. A recent report shows that deposition of Al electrode at room temperature on top of an organic film induces movement of oxygen-containing molecules, in their case poly(ethylene glycol), toward the electrode due to metal-oxygen interaction.^[6] In our case, during the metal deposition, the oxygen-contained molecules (PCBM) in bulk are probably induced to the metal/organic interface. As Al reacts with the methyl ester and Al-O-C complex is delaminated with the electrode, we do not observe carbonyl signatures on the active layer under Al. On the other hand, Ag does not react with methyl ester, so that we observe the carbonyl signature under Ag.



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Figure S1. Dark J-V curves of devices shown in **Figure 1** and **Figure 3** (main text) with different cathodes. (a) Al (black squares), Ag (red circles), ZnO NPs/Al (green triangles), and ZnO NPs/Ag (blue diamonds) cathodes deposited on pristine BHJ. (b) Delaminated BHJ originally under Al electrodes with re-deposited ZnO NPs/Al (black squares) and ZnO NPs/Ag (red circles) cathodes, and delaminated BHJ originally under Ag electrodes with re-deposited ZnO NPs/Ag (blue diamonds) cathodes.



Figure S2. ATR-FTIR absorbance spectra for pure P3HT (black, bottom), PCBM (black, 2nd bottom), clean Al film (orange), buried Al electrode (red), clean Ag film (green) and buried Ag electrode (blue).



Figure S3. XPS spectra of (a) C 1s, (b) O 1s, and (c) S 2p signal collected on the pristine active layer (black), and active layer after delamination of Al (red) or Ag (blue) electrode.

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