

<Supporting Information>

Build-up of symmetry breaking using titanium suboxide in bulk-heterojunction solar cells

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Experimental Details

Fabrication and Characterization of Organic Solar Cells: Mixtures of PCDTBT and PC₇₁BM (1:4) in chlorobenzene and dichlorobenzene (1:3 ratio) were spin coated onto a 40 nm layer of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) on ITO-coated glass substrates; the spin speed and time were 900 rpm and 60 seconds, respectively. The film was dried at 60 °C for one hour in an N₂-glove box. The active layer thickness, as measured with an Ambios XP-100 profilometer, was approximately 180 nm. Au, Ag, and Al (100 nm) electrodes were thermally evaporated at room temperature using a shadow mask. Solar cells were characterized with a Keithley 236 Source Measure Unit under simulated AM1.5G irradiation (100 mW/cm²). An aperture (9.84 mm²) was used on top of the cell to eliminate extrinsic effects.

UPS measurements: Au, Ag, and Al films (80-nm-thick) were deposited on a pre-cleaned Si substrate with a thin native oxide layer. A diluted TiO_x (1:200) solution was then spin-coated at 4000 rpm for 60 sec on the metal-coated Si substrates under ambient conditions. The

films were subsequently annealed at 80 °C for 10 min in air. The UPS analysis chamber was equipped with both a hemispherical electron energy analyzer (Kratos Ultra Spectrometer) and a UV (He I) source. The pressure in the chamber was maintained at 1×10^{-9} Torr. A sample bias of -9 V was used to acquire the high binding energy cutoff. To confirm the reproducibility of the UPS spectra, measurements were repeated twice on two sets of samples.

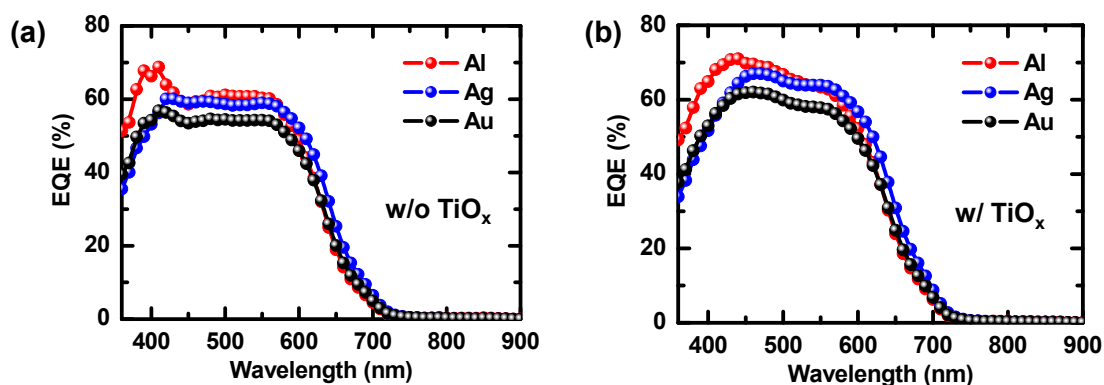


Fig. S1. EQE spectra of PCDTBT:PC₇₁BM BHJ solar cells with various cathodes (a) without and (b) with a TiO_x layer.

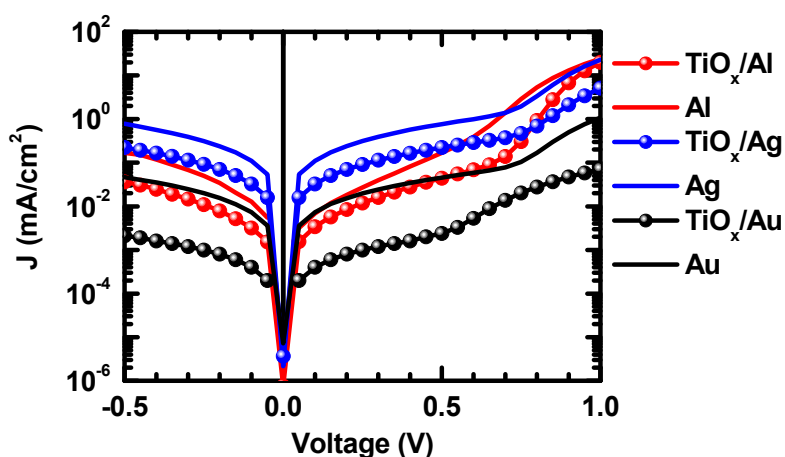


Fig. S2. Dark J-V characteristics of PCDTBT:PC₇₁BM BHJ solar cells with various cathodes without and with a TiO_x layer.