Supporting information for

Simple approach for an electron extraction layer in all-vacuum processed *n-i-p* perovskite solar cell

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Device fabrication

ITO pre-patterned substrates were cleaned following a standard procedure in which they are sequentially cleaned with soap, water, deionized water, and isopropanol in a sonication bath. The UV treatment was not performed. All the solar cell layers were prepared by thermal vacuum deposition performed in vacuum chambers evacuated to a pressure of ~10^{-6} mbar, which were integrated into a nitrogen-filled glovebox (H_2O and O2 < 0.1 ppm). C_{60}, BCP, TaTm and TPBi were sublimed in the same vacuum chamber at temperatures ranging from 100 to >300 °C, depending on the material, and the precise evaporation rate and deposited film thickness were controlled by the QCM sensors. The C_{60} and BCP ratios were controlled by their deposition rates from pre-calibrated thickness monitor (QCM) respectively. For the perovskite deposition, MAI and PbI_2 were co-evaporated at the same time, also

controlled by the thickness monitors. The MoO_3 and Ag were evaporated in another vacuum chamber using aluminum boats as sources by applying currents ranging from 2.0 to 4.5 A.

Characterization

Absorption spectra were collected using a fiber optics based Avantes Avaspec2048 Spectrometer. Characterization of the solar cells was performed as follows, using two different methods for double check. For the first, the external quantum efficiency (EQE) was measured using the cell response at different wavelength (measured with a white light halogen lamp in combination with band-pass filters), where the solar spectrum mismatch is corrected using a calibrated Silicon reference cell (MiniSun simulator by ECN, the Netherlands). Solar cells were illuminated by the halogen lamp in combination with interference filters for the EQE and J–V measurements. An estimation of the short-circuit current density (J_{SC}) under standard test conditions was calculated by convolving the EQE spectrum with the AM1.5G reference spectrum, using the premise of a linear dependence of J_{SC} on light intensity. J–V characteristics of the solar cells were recorded using a Keithley2400 Source Meter, in a −0.2 and 1.2 V voltage range, with 0.01 V steps. The layout used to test the solar cell has 4 pixels of equal areas (0.0651cm^2 , defined as the overlap between the ITO and the top metal contact) and measured through a shadow mask with 0.06 cm^2 aperture. A schematic and a photograph of the layout and the cells is shown in Fig. S1)
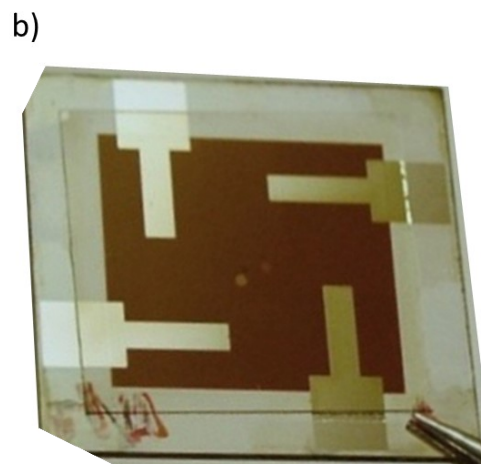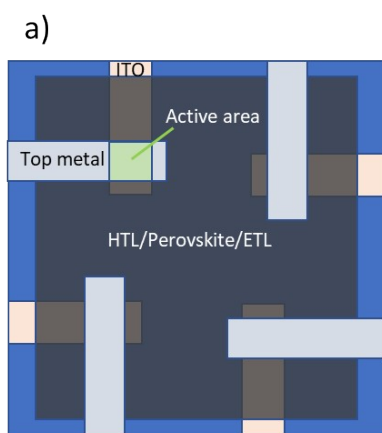
a)

b)

Figure S1. (a) Schematic of our device areas and (b) a photograph of a cell.

The series resistances (R_S) are fitted by diode equivalent circuit model from dark J-V curves (Fig. S4). X-ray diffraction (XRD) patterns were collected in Bragg-Brentano geometry on an Empyrean PANalytical powder diffractometer with a copper anode operated at 45 kV and 40 mA. The photoluminescence of the film stacks was measured through the glass side using a home-built setup to illuminate a spot of 0.091 cm2 with power densities in between 5.9 and 1700 mW/cm^2 (0.08-23 suns) generated by a diode laser of integrated optics, emitting at 405 nm. The emitted signal passed through a 600 nm long-pass filter before being collected and measured by an Avantes Avaspec2048 spectrometer. The collection path was calibrated to absolute intensity by a calibration lamp with the same emission profile as the samples (AvaLight-HAL-CAL-Mini). The integration times ranged from 100 ms with 10 averages for 23 suns laser intensity to 20 s with 1 average for 0.08 suns.
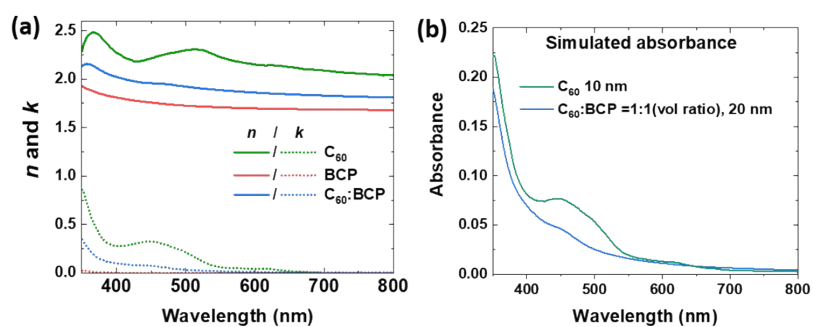
Figure S2. (a) Refractive index of C_{60}, BCP and C_{60}:BCP films and (b) simulated absorbance using transfer matrix method.
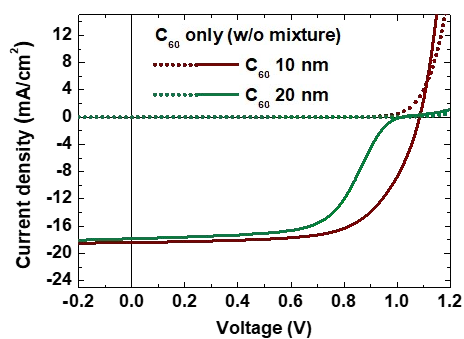

Figure S3. *J-V* curve with only C_{60} intrinsic layers. The curve for 10 nm of C_{60} is displayed in Fig. 3b, to compare with the mixture layers.
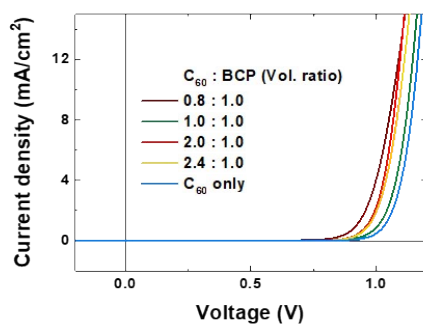

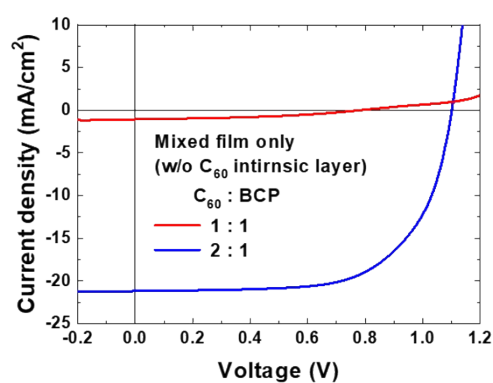**Figure S4.** Dark *J-V* curve for the devices shown in Fig. 3d.

Figure S5. *J-V* curve without C_{60} intrinsic layers. The curve for 1:1 mixed film is displayed in Fig. 3b.
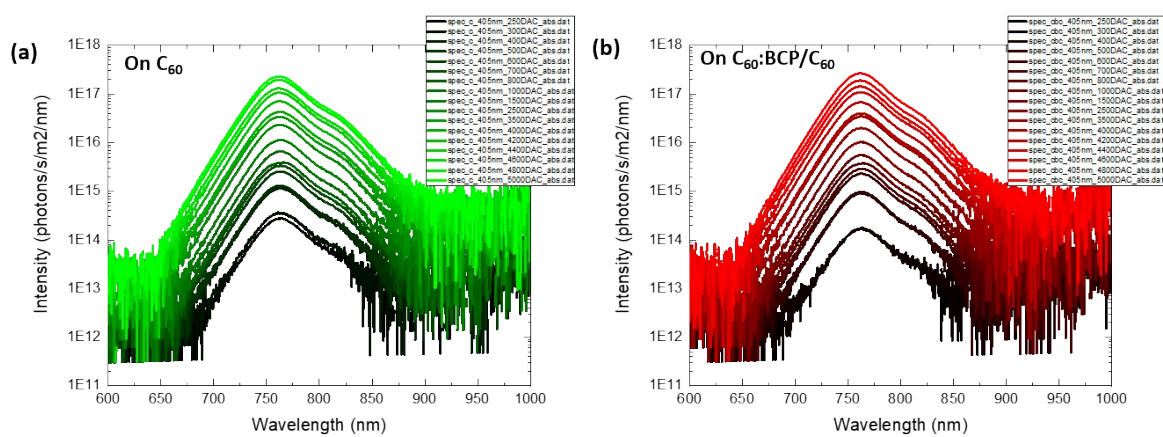

Figure S6. The PL spectrum of the $CH_3NH_3PbI_3$ films with different excitation power, used to calculate PLQY shown in Fig. 5b.
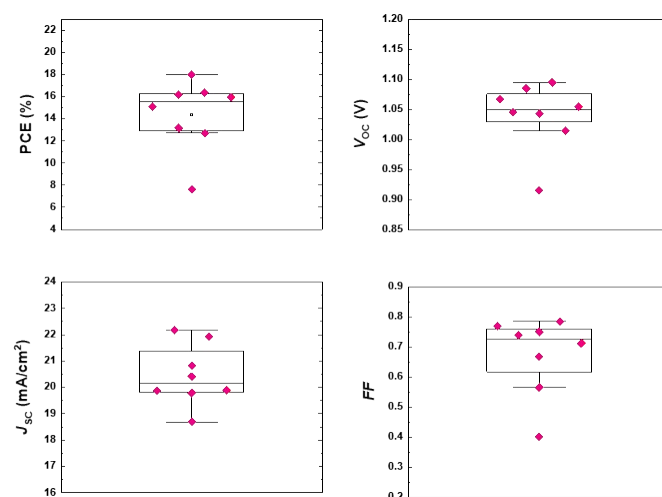
Figure S7. Device performance statistics of the fabricated solar cell with the optimum condition (C_{60} : BCP=1:1 + intrinsic C_{60} 5 nm) from 3 different batches.