## **Electronic Supplementary Information**

## Enhanced performance of perovskite solar cells with solutionprocessed n-doping of PCBM interlayer

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## Experimental

All reagents were purchased from Sigma-Aldrich and used without further purification. For the preparation of the perovskite solution (35 wt.%), methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I, MAI) and PbI<sub>2</sub> were dissolved with a molar ratio of 1:1 (0.262 g:0.759 g) in anhydrous N,N-dimethylformamide (DMF, 2 ml) with constant stirring inside an N<sub>2</sub>-filled glove box at 60 °C for 12 h. The additive solvent (5 vol.% N-cyclohexyl-2-pyrrolidone (CHP)) was then added to the precursor solution. To prepare the PCBM (Nano-C) solution, PCBM was dissolved in chlorobenzene with the concentration of 20 mg/ml. To dope the PCBM electron transport layer (PCBM/DMBI bi-layer type), different amounts of DMBI were dissolved in anhydrous isopropyl alcohol with constant stirring for 12 h at 60°C in air. To prepare a doped electron transport layer from a blended DMBI/PCBM solution, different amounts of DMBI were dissolved in PCBM solution with constant stirring for 12 h inside an N<sub>2</sub>-filled glove box at 60 °C.

For the device fabrications, patterned ITO-glass substrates (10 Ohm/sq, Samsung Corning Co, Ltd.,  $1.5 \times 1.5$  cm<sup>2</sup>) were cleaned with detergent, acetone, isopropyl alcohol, and then dried in an oven at 100 °C for 12 h. All substrates were treated with UV/O<sub>3</sub> plasma for 30 min for hole transport layer coating. The PEDOT:PSS (VP AI 4083, Clevious) was spin-coated at 5000 rpm for 40s, followed by thermal treatment at 150 °C for 10 min in air. Perovskite film was fabricated by spin coating on top of the PEDOT:PSS layer at 6000 rpm for 90 s, followed by thermal treatment at 100 °C for 5 min. To fabricate the sequential deposition type electron transport layer, PCBM solution was cast on top of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer at 1000 rpm for 60 s, and then DMBI was coated onto the PCBM layer at 4000 rpm for 30 s in air. In the case of the PCBM/DMBI blended configuration, a premixed PCBM/DMBI solution was directly coated onto the perovskite layer at 1000 rpm for 60 s in air. Finally, the top electrode (Ag, 100 nm) was evaporated using a shadow mask with 4.64 mm<sup>2</sup> by a thermal evaporator in a high vacuum of 10-6 Torr. The device photocurrent density-voltage (J-V) was measured by a Keithley 2400. Before measuring the photovoltaic performances, we calibrated the light intensity using the reference Silicon solar cell certified by the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI standards, Inc.) under the standard AM 1.5 G condition. The incident photon-to-current efficiency (IPCE) data was measured using the Oriel® IQE-200 QE measurement system. The electrical conductivity and work-function characteristics were measured by Keithley 4200 and scanning kelvin probe microscopy (SKPM, XE7, Park systems). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images were measured by field emission-SEM (FE-SEM) (Hitachi, S-4800) and XE7 (Park systems).

Depth-profile was measured using time of flight secondary ion mass spectrometry (TOF-SIMS, ION-TOF GmbH) where the analysis condition of pulsed primary ions is a 30 keV Bi<sup>+</sup>, and the analysis was done on a  $500 \times 500 \ \mu\text{m}^2$  area.

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**Figure S1.** Photographs of the DMBI dopant dissolved in (a) chlorobenzene and (b) isopropanol (c) Tyndall effects of DMBI dissolved in chlorobenzene.

|                                    | ETL           | $V_{oc}(V)$ | J <sub>sc</sub> (mA/cm <sup>2</sup> ) | FF (%) | PCE (%) |
|------------------------------------|---------------|-------------|---------------------------------------|--------|---------|
| Sequential<br>Deposition<br>Method | Pristine Cell | 0.90        | 11.74                                 | 72.27  | 7.65    |
|                                    | 0.4 wt%       | 1.00        | 14.69                                 | 73.51  | 10.79   |
|                                    | 0.7 wt%       | 0.96        | 15.49                                 | 78.84  | 11.77   |
|                                    | 1.0 wt%       | 0.93        | 11.87                                 | 76.41  | 8.42    |
| Pre-mixed<br>Method                | 0.4 wt%       | 0.77        | 12.83                                 | 76.12  | 7.54    |
|                                    | 0.7 wt%       | 0.78        | 12.73                                 | 73.17  | 7.31    |
|                                    | 1.0 wt%       | 0.77        | 11.60                                 | 71.82  | 6.39    |

**Table S1.** Photovoltaic statistic average parameters of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-based PSCs with different DMBI doping methods and concentrations.