Supplementary Information

Performance enhancement of planar heterojunction perovskite solar cells by *n*-doping of electron transporting layer

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Materials and Characterization

CH_3NH_3I and DMBI were synthesized by following the methods reported in the literature.[1,2] PbI_2 was purchased from Sigma-Aldrich. Poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevious P VP AI 4083) was purchased from H. C. Stark and passed through a 0.45 μm PVDF syringe filter before spin-coating. PCBM was obtained from Nano-C. The absorption spectra were obtained by an UV-Vis spectrophotometer (Lambda 25, Perkin Elmer). UPS measurement was performed using a hemispherical electron energy analyzer (RESOLVE 120, PSP). The base pressure of analysis chamber was maintained under low 10^{-9} Torr. He I ($h\nu$ = 21.22 eV) discharge lamp was used as an excitation source with sample bias of −15 and −10 V for secondary electron cutoff and valence band region, respectively. Fermi level was calibrated through Ar^+-sputtered clean Au. The electrical conductivity was measured with device configuration of glass substrate/PCBM or PCBM:DMBI/Au. PCBM or PCBM:DMBI solution was spin-coated on the top of pre-cleaned glass followed by thermal deposition of Au electrode (80 nm thick) in a vacuum below 10^{-7} Torr. The electrical conductivity was measured in N_2-filled glove box by a probe

station with a computer-controlled Keithley 4200 source measurement unit. Devices for electrical conductivity measurement had a channel length of 50 μm and a channel width of 1 mm. Film thickness was measured by AFM measurement. *J–V* curves of photovoltaic cells were obtained using the Keithley 4200 source measurement unit under AM 1.5G (100 mW cm^{-2}) simulated by an Oriel solar simulator (Oriel 91160A). The light intensity was calibrated using a NREL-certified photodiode prior to each measurement. The EQE spectra were obtained using Polaronix K3100 IPCE measurement system (McScience). The light intensity at each wavelength was calibrated with a standard single-crystal Si cell.

Device Fabrication

The configuration of the solar cell device used in this work is glass/ITO/PEDOT:PSS/$CH_3NH_3PbI_3$/PCBM or PCBM:DMBI/Ca/Al. The ITO-coated glass was cleaned with acetone and isopropyl alcohol for 30 min each. After complete drying, the ITO-coated glass was treated with UV-ozone for 15 min. A 40 nm thick PEDOT:PSS was spin-coated on the ITO-coated glass at 3000 rpm for 40 s and annealed at 150 ℃ for 30 min in ambient condition. Then, substrates were transferred to N_2-filled glove box for further processing. For the perovskite layer, a 1:1 ratio of CH_3NH_3I:PbI_2 was dissolved in DMSO. The precursor solution was spin-coated onto the PEDOT:PSS layer at 3000 rpm. The substrate was immediately transferred onto a hot plate and heated at 110 ℃ for 30 s. For the ETL, various ratios of PCBM/DMBI were dissolved in chloroform and then spin-coated on $CH_3NH_3PbI_3$ layer at 3000 rpm. Finally, Ca (40 nm) and Al (120 nm) as top electrode were thermally deposited on the ETL under 10^{-6} Torr. The device area is 0.1 cm^2.

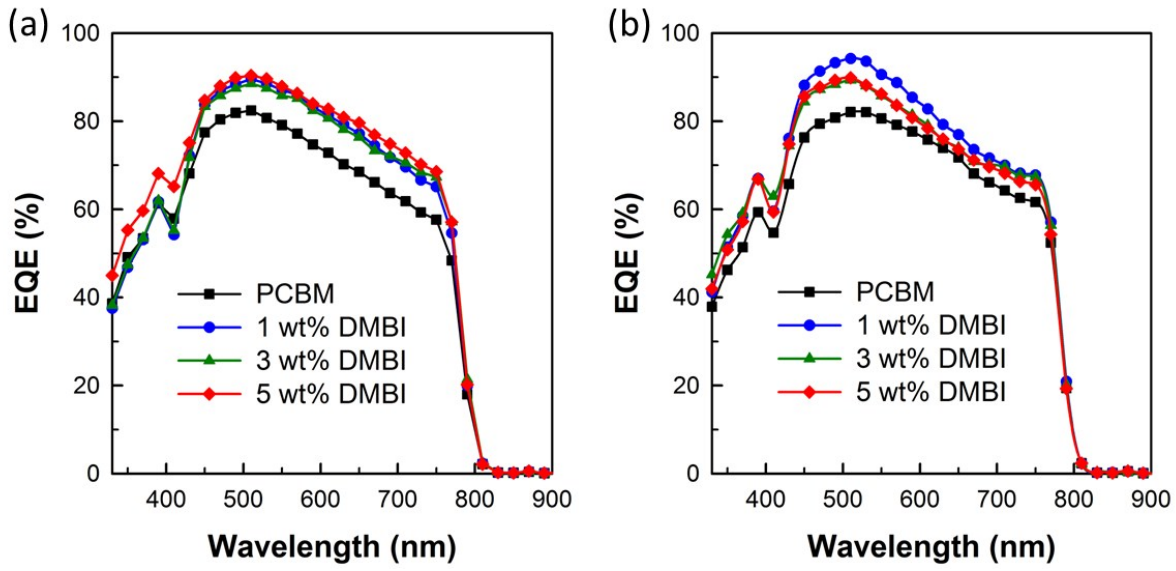

Fig. S1 EQE spectra of devices with (a) thin ETL and (b) thick ETL which are doped with various DMBI concentrations.

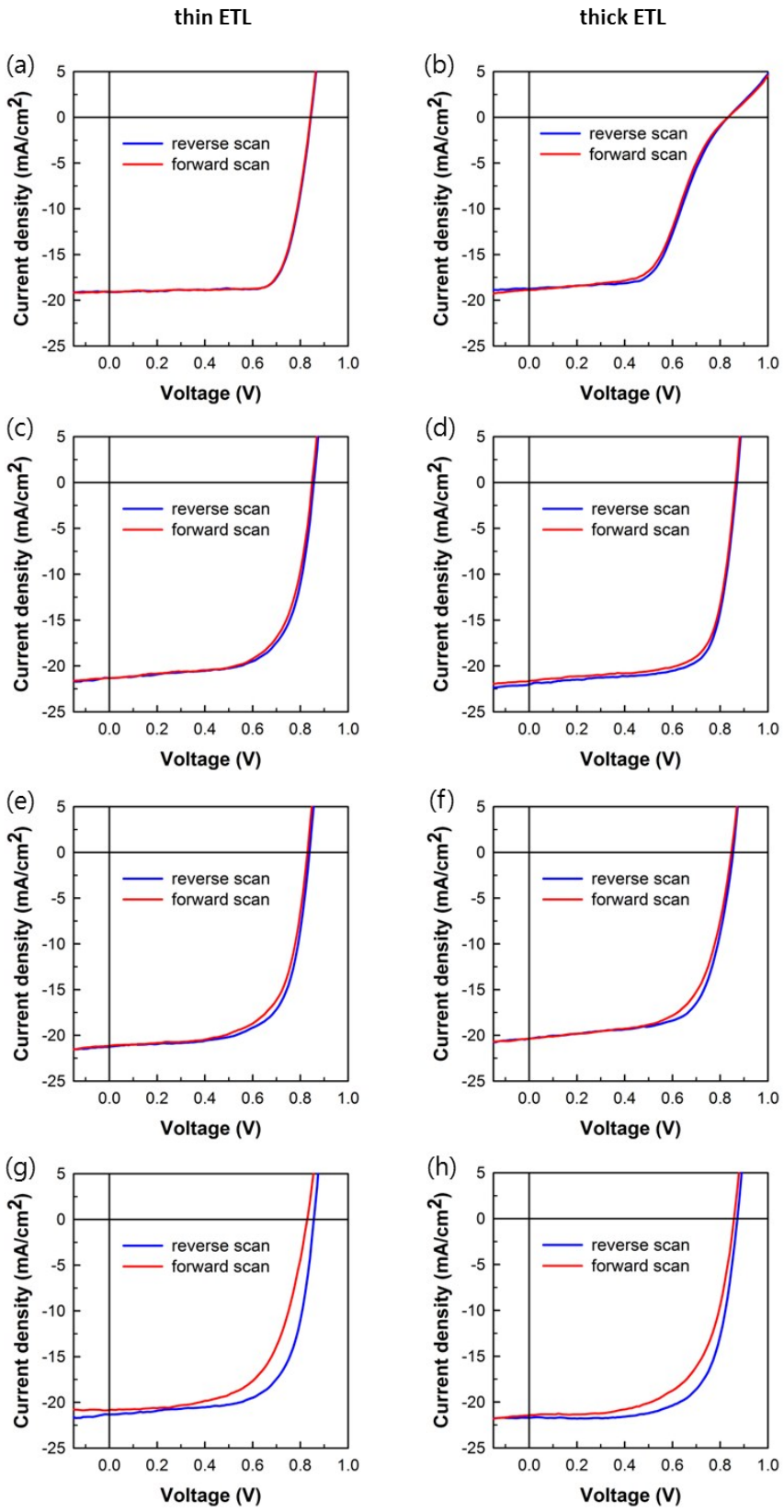

Fig. S2 Hysteresis curves for devices with (a), (b) pure PCBM, (c), (d) 1 wt% doped PCBM, (e), (f) 3 wt% doped PCBM, (g), (h) 5 wt% doped PCBM.

Table S1. Average device parameters and their standard deviations based on at least 10 devices.

Solution conc.[a] (mg/mL)	Dopant conc. of ETL	J_{SC}[b] (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)	R_{Sh}[c] (Ω cm^2)	R_S[c] (Ω cm^2)
10	Pure PCBM	18.2±1.1 (18.2)	0.82±0.05	0.72±0.05	11.0±1.0	1.42×10^3	3.52
10	1 wt% DMBI	20.3±0.8 (20.0)	0.84±0.02	0.70±0.05	12.1±0.8	9.97×10^2	3.60
10	3 wt% DMBI	20.3±1.3 (20.0)	0.83±0.03	0.67±0.04	11.1±1.0	5.88×10^2	3.62
10	5 wt% DMBI	20.5±1.2 (20.6)	0.83±0.03	0.65±0.05	11.1±0.9	4.01×10^2	3.85
20	Pure PCBM	18.4±0.9 (18.6)	0.82±0.04	0.52±0.07	7.9±1.2	4.11×10^2	35.1
20	1 wt% DMBI	20.6±0.8 (20.6)	0.86±0.02	0.69±0.05	12.2±0.7	5.04×10^2	3.71
20	3 wt% DMBI	20.0±0.7 (19.9)	0.84±0.03	0.69±0.03	11.2±0.7	5.35×10^2	3.96
20	5 wt% DMBI	19.9±1.0 (19.8)	0.84±0.05	0.67±0.04	11.6±1.0	5.17×10^2	4.24

[a]10 and 20 mg/mL chloroform solutions are used for fabrication of 50 and 105 nm thick ETL, respectively.

[b]J_{SC} values calculated from EQE spectra are indicated in parenthesis.

[c]The series and shunt resistance were calculated by the slopes of *J-V* curves.

References

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2. J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C. -S. Lim, J. A. Chang, Y. H. Lee, H. -J. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel and S. I. Seok, *Nat. Photonics*, 2013, **7**, 486-491.