Supporting information

Suppressing generation of iodine impurity via an amidine additive in perovskite solar cells

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1. Experimental Section

1.1 Materials

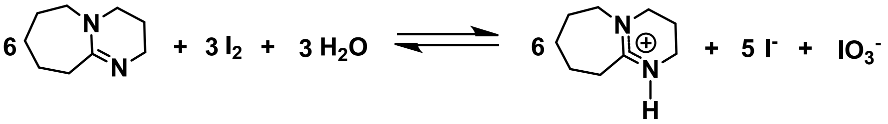
All reagents were used as received without further purification. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (98%), polyethylenimine (PEI), 1,4-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. CH_3NH_3I, PbI_2 for perovskite and PCBM (>99%, HPLC) were was purchased from Xi'an Polymer Light Technology Corp. Nickel acetate tetrahydrate, monoethanolamine and methoxyethanol were purchased from Alfa Aesar. The acetone and isopropanol for ITO cleaning were from Sinopharm Chemical Reagent Co. Ltd.

1.2 Perovskites solar cells fabrication

The ITO substrate was sequentially cleaned with acetone detergent solution, deionized water and isopropanol. NiO_x precursor solutions (0.3 g nickel acetate tetrahydrate and 0.1 g monoethanolamine in 10 g methoxyethanol) were then spin-coated onto pre-cleaned ITO substrates at 4000 rpm for 40 s. The substrate was annealed at 200 ^{o}C for 10 min and followed by 400 ^{o}C for 20 min to form a dense metal oxide film. For the perovskite absorber layer, the precursor solution (1.3 M CH_3NH_3I: 1.3 M PbI_2 in GBL:DMSO=7:3) was spin-coated on the ITO/NiO_x substrate at 4000 rpm for 30 s, and the anti-solvent toluene (approximately 400 μL) was quickly dropped onto the center of the substrate at 27th second. Then the as-prepared film was annealed at 100 °C for 10 min. As refer to the precursor solution with additive, DBU with various ratio in weight was directly added in to the referred precursor solutions. The solutions were then stirred overnight for use. Afterwards, a $PC_{61}BM$ (40 nm) and a thin layer PEI (5 nm) was deposited on top of the perovskite films successively. The samples were then transferred into the vacuum evaporation system and 100 nm of silver was evaporated with a metal aperture mask. The active area of the devices was 10.58 mm^2. The fabricated devices were measured under a simulated 100 mW cm^{-2} AM 1.5G irradiation in a N_2-filled glovebox.

1.3 Characterization

The reference precursor solution with 1.3 M CH_3NH_3I/PbI_2 (1:1) in GBL:DMSO=7:3 (Solution A) delivers a light yellow color. The color turns dark brown upon the addition of 1 mg I_2 (Solution B). Further introducing 10 μl DBU into solution B, the color of the solution turns to yellow again (Solution C), which indicates the elimination of the remnant I_2 in precursors. The reaction between the I_2 and DBU follows the equation:



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Where the trace amount of water presumably come from the precursor raw material or during sample preparation.

The UV-visible absorption spectra of the above solutions with a volume ration of 5 μl/2 ml in GBL/DMSO solvents were recorded on a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu Scientific Instruments). The perovskite films were deposited on a quartz substrate for test. The top-view morphologies of the perovskite films which were prepared on ITO/NiO_x substrates using an FEI Nova Nano-SEM 450 system. X-ray diffraction (XRD) data of the perovskite films were determined using a Philips diffractometer (X'pert PRO MRD) using Cu Kα radiation (λ = 1.540598 Å) as the X-ray source at room temperature. For the photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements, the samples were prepared on quartz substrates. The PL emission spectra were measured by a Fluorescence Spectrometer (Edinburgh Instrument, FLS 920) with an excitation wavelength of 532 nm. TRPL decay spectra were measured using a Delta Flex Fluorescence Lifetime System monitored at 770 nm.

The *J*-*V* curves of the as-prepared solar cells were tested in a nitrogen-filled glovebox with a Keithley 2400 source-measure unit. The scan rate was 20 mV s^{-1}. The light intensity is AM 1.5 G irradiation (100 mW cm^{-2}) from a 450 W solar simulator (Newport 94023A-U), which has been calibrated by using a standard silicon solar cell. The stabilized power output versus time of devices was measured by applying a bias at the maximum power output point. The EQE spectra were measured using a 150 W xenon lamp (Oriel) that was equipped with a monochromator (Cornerstone 74004) as the light source.

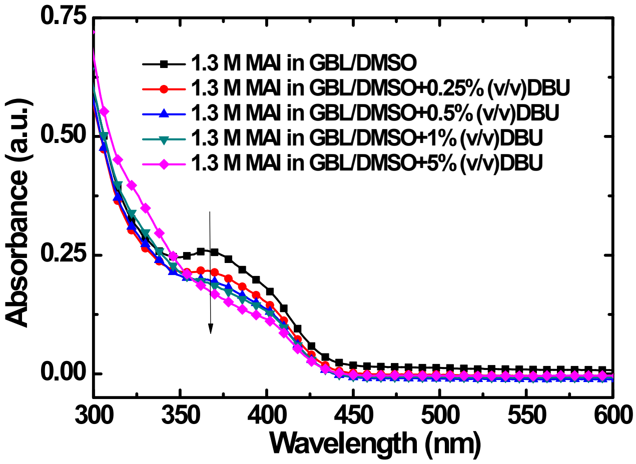

Figure S1. UV-Vis absorption spectra of the MAI solution without and with different ratios of DBU additive.

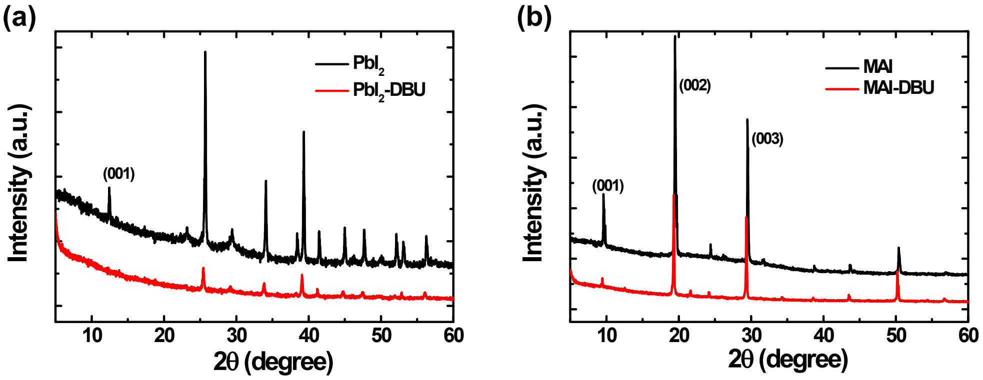

Figure S2. (a) XRD patterns of pristine PbI_2 powder and DBU treated PbI_2. **(b)** XRD patterns of pristine MAI powder and DBU treated MAI.

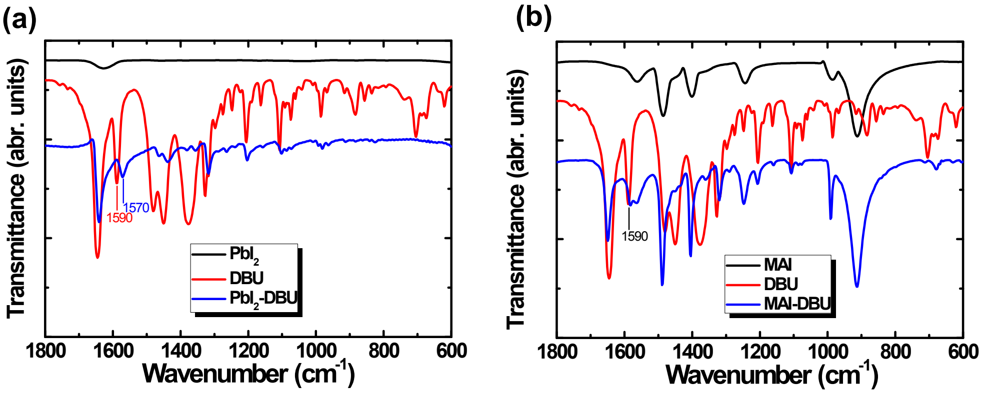

Figure S3. (a) FT-IR spectra of pristine PbI_2 powder and DBU treated PbI_2. **(b)** FT-IR spectra of pristine MAI powder and DBU treated MAI.

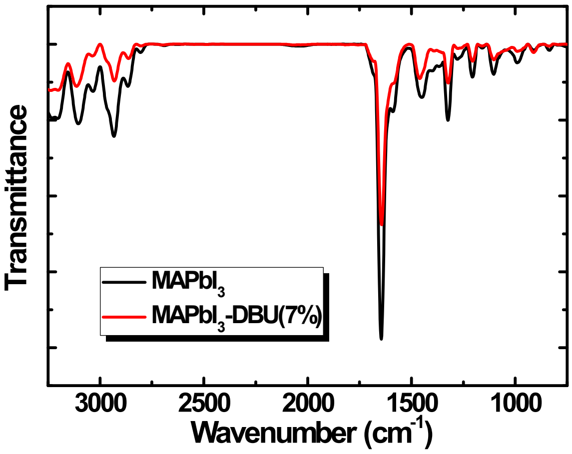

Figure S4. Fourier transform infrared (FT-IR) spectra of the reference $MAPbI_3$ and $MAPbI_3$-DBU (7%) in powder.

Table S1. Summary of the fitted parameters of time-resolved photoluminescence (TRPL) decay curves for perovskite films without and with DBU additives. The fitting functions of double exponential equation: $y = y_0 + A_1 exp(-(x-x_0)/\tau_1) + A_2 exp(-(x-x_0)/\tau_2)$. The effective lifetime is calculated by $\tau_{eff} = (A_1\tau_1 + A_2\tau_2) / (A_1 + A_2)$.[1]

Additive content	**τ_1 (ns)**	**A_1**	**τ_2 (ns)**	**A_2**	**χ^2**	**τ_{eff} (ns)**
0%	8.92	636.58	45.18	1342.67	0.998	33.52
1%	21.53	881.61	95.68	1196.04	0.997	64.22
3%	21.61	691.25	105.23	1314.72	0.997	76.41
5%	27.02	675.56	94.83	1278.11	0.996	71.38
7%	2.74	7348.61	66.22	1760.54	0.998	15.01

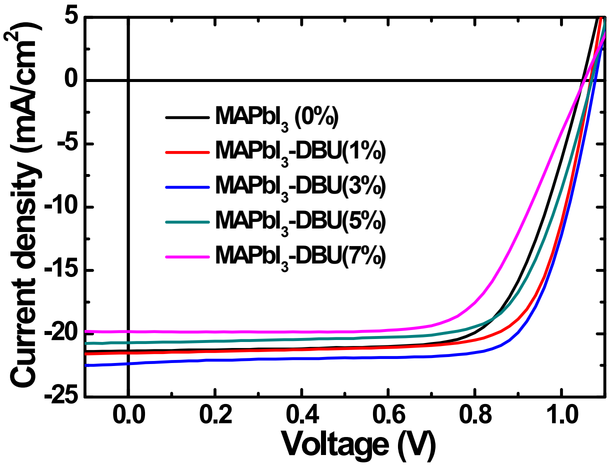

Figure S5. *J*-*V* characteristics of the perovskite solar cells prepared from the precursors without and with different molar ratios of DBU additive.

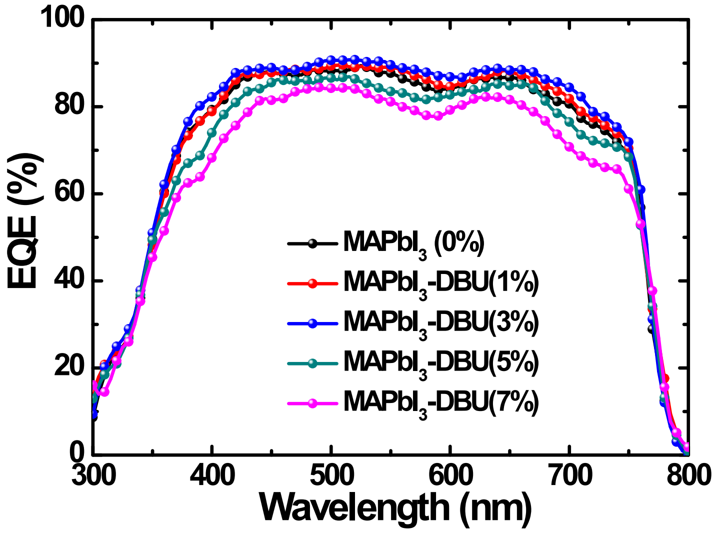

Figure S6. External quantum efficiency (EQE) spectra of the perovskite solar cells prepared from the precursors without and with different molar ratios of DBU additive.

Reference

1. X. Wen, S. Huang, S. Chen, X. Deng, F. Huang, Y.-B. Cheng, M. Green and A. Ho-Baillie, *Adv. Mater. Interfaces*, 2016, **3**, 1600467.