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Supporting Information

The Roles of Alkyl Halide Additives in Enhancing Perovskite Solar Cell Performance

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Material and Sample Preparation: Methylammonium iodide (MAI) was synthesized by reacting 24 ml, 0.20 mole methylamine (33 wt% in absolute ethanol, Aldrich) and 10 ml, 0.04 mole hydroiodic acid (57 wt% in water with 1.5% hypophosphorous acid, Alfa Aesar) in 100 ml ethanol under nitrogen at ice bath for 2 h with stirring. Methylammonium chloride (MACl) was synthesized by the similar procedures with the same stoichiometric amounts of methylamine and hydrochloric acid (ACS reagent, 37%, Aldrich). After reaction, the white precipitate of MAI/MACl was recovered by rotary evaporation at 40 °C and recrystallized by ethanol for three times. The MAI/MACl powders were finally collected and dried at 50 °C in a vacuum oven for 24 h. To prepare the perovskite precursor solution, MAI and lead chloride ($PbCl_2$, Aldrich) powders were mixed in anhydrous dimethylformamide (DMF, Aldrich) with a molar ratio of 1:3, and MACl/$PbCl_2$ powders were mixed with a molar ration of 1:1. The perovskite/additive solutions were prepared via adding 1 mol% studied alkyl-halide additives with respect to perovskite mole into the perovskite precursor solution. The solution (40 wt%) were stirred overnight at 80 °C and filtered with 0.20 μm PVDF filters before thin-film deposition. The absorption spectra were measured using a Perkin-Elmer Lambda-9 UV-visible spectrophotometer.

Fabrication of thin-film perovskite solar cells: The devices were fabricated in the configuration of ITO/PEDOT:PSS/perovskites/[6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$)/fullerene surfactant (Bis-C_{60})/Ag. ITO-coated (15 Ω/sq) glass substrates were cleaned sequentially with a detergent, DI-water, acetone, and isopropanol. After dried by nitrogen blower, the ITO surface was treated by air plasma for 30 s. PEDOT:PSS (Baytron 4083) (~40 nm) was first spin-coated onto clean ITO substrates followed by annealed at 150 °C for 10 min in air. The perovskite thin-films were spin-coated from the targeted precursor solution at 4000-6000 rpm for 45 s and then annealed at 90 °C for 2-3 h in the N_2-filled glovebox. Afterward, the $PC_{61}BM$ (15 mg/ml in chloroform) and Bis-C_{60} surfactant (2 mg/ml in isopropyl alcohol) were sequentially spin-coated at 1000 rpm for 60 s and 4000 rpm for 40s respectively. Finally, a 150 nm thick top Ag electrode was evaporated under high vacuum ($< 2\times 10^{-6}$ Torr). For all devices, the active area was defined as 3.14 mm^2.

Characterization of thin-film perovskite solar cells: All the J-V curves were recorded by using Keithley 2400 source meter inside the N_2-filled glovebox and the scan rate was kept at 1.0 V/s. The photocurrent was measured under illumination from a 450 W thermal Oriel solar simulator (AM 1.5G). The illumination intensity of the light source was accurately calibrated by a standard Si photodiode detector equipped with a KG-5 filter, which can be traced back to the standard cell of National Renewable Energy Laboratory (NREL). The EQE spectra performed here were obtained through the IPCE setup including a Xenon lamp (Oriel, 450 W) as the light source, a monochromator, a chopper with frequency of 100 Hz, a lock-in amplifier (SR830, Stanford Research Corp), and a Si-based diode (J115711-1-Si detector) for calibration.

Table S1. Statistic of the photovoltaic performance of the studied perovskite solar cells.[a]

	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
Pristine Perovskite	0.86 ± 0.03	15.98 ± 1.46	0.63 ± 0.05	8.65 ± 0.78
Perovskite + 1,8-DIO	0.90 ± 0.02	17.13 ± 0.55	0.72 ± 0.02	11.03 ± 0.38
Perovskite + 1,4-DIB	0.94 ± 0.01	18.27 ± 0.30	0.71 ± 0.02	12.22 ± 0.49
Perovskite + 1,4-DBrB	0.93 ± 0.01	17.82 ± 0.78	0.73 ± 0.02	12.20 ± 0.47
Perovskite + 1,4-DClB	0.92 ± 0.02	17.92 ± 0.51	0.68 ± 0.04	11.14 ± 0.41

[a] Average values with standard deviation over 10 devices.

Table S2. The photovoltaic performance of the studied perovskite solar cells fabricated from the solution containing di-iodo based additives with different chain lengths.[a]

	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
Pristine Perovskite	0.88	17.15	0.65	9.79
Perovskite + 1,10-DID	0.89	17.25	0.65	10.01
Perovskite + 1,8-DIO	0.92	17.40	0.73	11.62
Perovskite + 1,4-DIB	0.94	18.47	0.75	13.09

[a] Best power conversion efficiencies (PCEs).

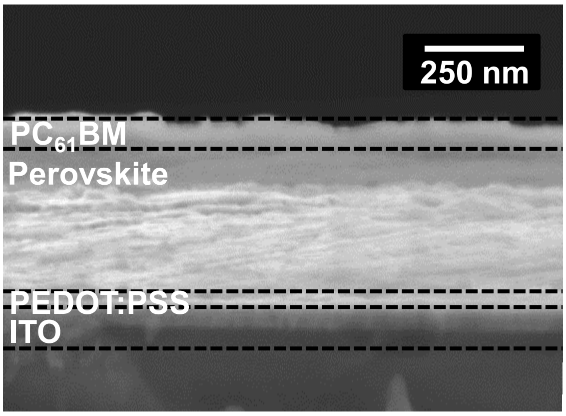

Figure S1. Cross-section images of the device made with 1% 1,4-DIB.

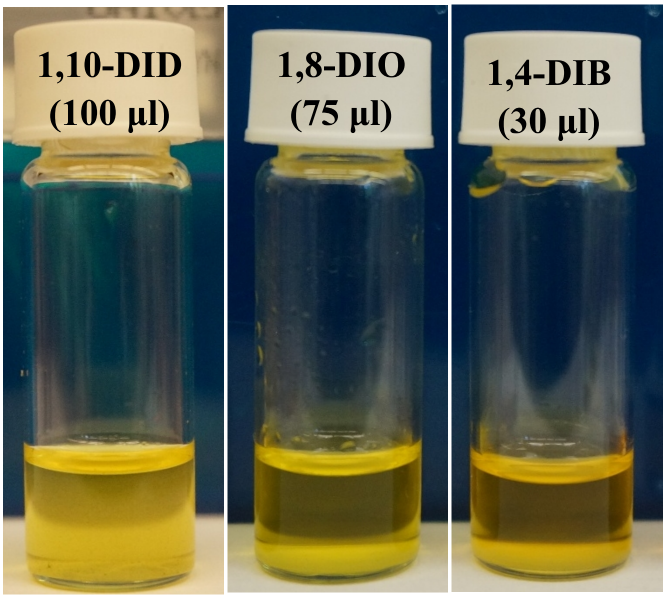

Figure S2. Solubility of $PbCl_2$ in the mixed solvents consisting of DMF and targeted additives. The concentration herein is 70 mg $PbCl_2$ in 1 ml DMF + the marked volume for each additive (1,10-DID: 100 μ l; 1,8-DIO: 75 μ l; 1,4-DIB: 30 μ l).

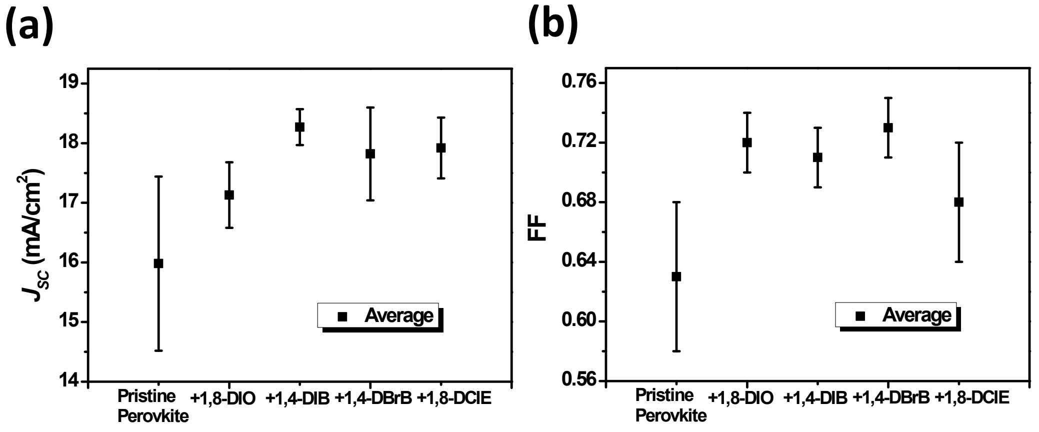

Figure S3. Statistics of (a) J_{SC} and (b) FF of the studied perovskite solar cells.

$$CH_3NH_3I \rightleftarrows CH_3NH_3^+ + I^- \qquad (1)$$

$$CH_3NH_3PbI_XCl_{3-X} \rightleftarrows CH_3NH_3^+ + Pb^{2+} + x\,I^- + (3-x)\,Cl^- \qquad (2)$$

$$CH_3NH_3^+ + I^- \rightleftarrows CH_3NH_2 + HI \qquad (3)$$

$$CH_3NH_3^+ + Cl^- \rightleftarrows CH_3NH_2 + HCl \qquad (4)$$

Scheme S1. Reactions involved for methylamine formation in perovskite precursor solution or during the degradation of perovskite.