Supporting formation

Effects of Additives *n*-Propylammonium or *n*-Butylammonium Iodide on the

Performance of Perovskite Solar Cells

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Device Fabrication and Characterization

Perovskite solar cells (PSCs) were prepared using the following device fabrication procedure. Glass/ITO substrates [Sanyo, Japan (8 Ω/\Box)] were sequentially patterned lithographically, cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, dried on a hot plate at 140 °C for 10 min, and treated with oxygen plasma for 5 min. PEDOT:PSS (Baytron P-VP AI4083) was passed through a 0.45- μ m filter and deposited onto ITO (thickness: *ca.* 40 nm) through spin-coating (3000 rpm) in air; the sample was then dried at 140 °C for 20 min inside a glove box. The perovskite precursor solution was prepared by dissolving MAI and lead(II) chloride (molar ratio,

3:1) at 25 wt% (with various vol% of PAI or BAI) in DMF and then stirring continuously overnight at 60 °C in the dark. PVSK devices were made with layered configuration of glass/ITO/PEDOT:PSS/MAPbI_{3-x}Cl_x/PC₆₁BM/Al. Prior to deposition of the perovskite layer, the PEDOT:PSS film was preheated at 60 °C for 5 min. The precursor solution was also pre-heated at 60 °C for 5 min and then deposited on top of the PEDOT:PSS layer. To study the effects of the additive on the morphology, absorption, and crystallization of the perovskite films, we fabricated such films under the same conditions as those described above, but with different concentrations (1, 2.5, and 5 vol%) of PAI and BAI in the precursor solutions and variations of the annealing time, respectively. Prior to deposition of the perovskite layer, the PEDOT:PSS film was preheated at 60 °C for 5 min. The precursor solution was also preheated at 60 °C for 5 min and then deposited on top of the PEDOT:PSS. We used the annealing temperature of 90 °C, with the time necessary to fully crystallize MAPbI_{3-x}Cl_x being between 2.5 and 3.5 h.³² The fully generation of perovskite films can be observed clearly with the naked eye, with a color change from yellow to dark brown. An optimized annealing times for our normal (no PAI or BAI) and PAI and BAI-derived perovskite films were 2.5 and 3.5 h, respectively.PCBM was spin-coated (2000 rpm) from a chlorobenzene solution (10 mg mL⁻¹). The layers of Al (100 nm) were deposited thermally under vacuum. The active area of the device was 10 mm². The cell performance was measured inside a glove box. The current–voltage (I-V) properties of

the devices were measured using a computer-controlled Keithley 2400 source measurement unit (SMU) and a Newport solar simulator (Oriel® Sol2A Class ABA Solar Simulators) under AM 1.5 illumination (100 mW cm⁻²). The illumination intensity was calibrated using a standard Si reference cell and a KG-5 filter. EQEs were measured using an Enlitech QE-R spectral response measurement system to calibrate the current densities of the devices. UV–vis absorption spectra were recorded using a Hitachi U-3300 spectrophotometer. ImageJ was used to calculate the surface coverages of the films. GIWAXS patterns were collected using a Philips Panalytical-x'PertPROMRD instrument; the incident beam angle was above the critical angle (ca. 0.5°). SEM images were measured using a JEOL JSM 6701F field-emission scanning electron microscope.



Figure S1. FE-SEM image of CH₃NH₃PbI_{3-x}Cl_x perovskite thin film of magnification

by 8000 times.