Supporting Information

Mixed Perovskite Based on Methyl-ammonium and Polymericammonium for Stable and Reproducible Solar Cells

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Experimental Section

Materials: Polymeric ammonium (PEI·HI) was synthesized by reacting was synthesized by reacting 2 g of 2.5 mmol Polyethylenimine, ethylenediamine branched (PEI, $M_w \sim 800$, Aldrich), 10 mL of 0.04 mol hydroiodic acid (57 wt% in water with 1.5% hypophosphorous acid, Alfa Aesar), and 100 mL methanol in a 250 mL round bottom flask under nitrogen at 0 °C for 12 h with stirring. After reaction, the light yellow precipitate of PEI·HI was recovered by rotary evaporation at 40 °C and then was washed with diethyl ether. The raw product was recrystallized in ethanol and dried at 40 °C in a vacuum oven for 48 h. CH₃NH₃I (MAI) was synthesized according to the reported method.

Perovskite Device Fabrication: All the devices were fabricated on inverted planar heterojunction (PHJ) structure at humidity levels $50 \pm 2\%$ unless special instructions. ITO (15 ohm/sq) on glass and ITO on PET (30 ohm/sq) were cleaned sequentially with detergent and deionized water, acetone, and isopropanol under sonication for 10 min. Commercial aqueous dispersion of PEDOT:PSS (Clevios PVP AI 4083) was spin-coated (4k rpm) on pre-cleaned and dry ITO substrate. PbI₂ and MAI were dissolved in DMF and 2-propanol with concentrations of 460 mg/ml and 40 mg/ml, respectively. For the mixed perovskite, PEI·HI was added in the solution PbI₂ at the molar ratio of 2% or 4%. A solution of PbI₂ or PbI₂:PEI·HI mixture was spin-coated onto the substrate at 2000 rpm for 60 s and CH₃NH₃I solution was spin-coated onto the first layer at 3000 rpm for 40 s. Subsequently, the film was annealed at 100 °C for 5 min to obtain the perovskite films. Afterward, the PC₆₁BM (20 mg/mL in chlorobenzene) was then sequentially deposited by spin coating at 1.2 k rpm for 60 s. LiF interlayer and Ag electrode were thermally evaporated on top of the film under high vacuum ($<2 \times 10^{-6}$ Torr) through a shadow mask with the thickness of 1 nm and 200 nm, respectively.

The device area was defined as 10 mm². It is noteworthy that all device fabrications were conducted below 50 % of relative humidity. A Keithley 2400 source meter unit was used to record *J-V* characteristics in this study. A 300 W xenon arc solar simulator equipped with an AM 1.5G filter was used to simulate an light intensity of 100 mW cm⁻². The illumination intensity of the light source was accurately calibrated employing a standard Si photodiode detector equipped with a KG-5 filter, which can be traced back to the standard cell of the National Renewable Energy Laboratory (NREL). The EQE spectra performed here were obtained from an IPCE setup consisting of a Xenon lamp (Oriel, 450 W) as the light source, a monochromator, a chopper with a frequency of 100Hz, a lock-in amplifier, and a Si-based diode for calibration. The calculated J_{SC} values obtained by integrating the EQE spectrum under the AM 1.5G illumination condition agreed well with the measured J_{sc} value from J-V characteristics and the differences were within 3%.

Characterization: The ultraviolet–visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. Fluorescence measurement for photoluminescence (PL) of the polymers was carried out on a Hitachi F-7000 PC spectrofluorophotometer with a xenon lamp as the light source. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target ($\lambda = 1.54$ Å) and at a scanning rate of 1°/min. Scanning Electron Microscopy (SEM) images were acquired on a JEOL JSM-6701F field-emission SEM at an accelerating voltage of up to 30kV. Film thicknesses were measured using a KLA Tencor profilometer, which showed a similar thickness around 400 nm for all the (MAPbI₃)_{1-x}[(PEI)₂PbI₄]_x (x = 0%, 2% or 4%) films.



Fig. S1 The chemical structure of PEI·HI.



Fig. S2 Images of three different $(MAPbI_3)_{1-x}[(PEI)_2PbI_4]_x$ perovskite films (x = 0%, 2% or 4%) before and after exposure to humidity (around 50%) for two weeks.

Table S1 Performance of perovskite devices under AM 1.5G illumination (100 mW cm⁻

 ²). The fabrication procedure was similar for all device in optimized condition.

Precursor	$J_{\rm sc}~({\rm mA~cm}^{-2})$	$V_{ m oc}\left({ m V} ight)$	FF	PCE $(\%)^a$
x = 0%	18.80 ± 1.14	1.01 ± 0.03	0.68 ± 0.03	$12.96 \pm 0.94^{b} (14.59)^{c}$
x = 2%	18.92 ± 0.45	1.07 ± 0.01	0.72 ± 0.01	$14.57 \pm 0.35 \; (15.20)$
x = 4%	15.86 ± 0.41	1.09 ± 0.01	0.66 ± 0.01	$11.41 \pm 0.32 \ (12.01)$

^{*a*} Maximum PCE in the brackets; ^{*b*} Error values represent the standard deviation of the mean of 50 devices. ^{*c*} The best device performance values of the PeSCs.



Fig. S3 XRD patterns of perovskite $(MAPbI_3)_{1-x}[(PEI)_2PbI_4]_x$ films of before and after exposed to 50 % relative humidity for 2 weeks. Peaks marked with \star are assigned to the PbI₂.



Fig. S4 *J*–*V* curves of forward and reverse bias sweep for the solar cell using the MAPbI₃ and $(MAPbI_3)_{1-x}[(PEI)_2PbI_4]_x$ (x = 2%) perovskite active layer.



Fig. S5 Experimental data for V_{OC} as a function of illumination light intensity for cells using $(MAPbI_3)_{1-x}[(PEI)_2PbI_4]_x$ as light-absorbing layer along with the linear fit. The large slope of 1.67 k_BT/q of $(MAPbI_3)_{1-x}[(PEI)_2PbI_4]_x$ (x = 4%) is an indicator of trapassisted recombination.



Fig. S6 *J*–*V* curves of forward and reverse bias sweep for the solar cell using the $(MAPbI_3)_{1-x}[(PEI)_2PbI_4]_x$ (x = 4%) perovskite active layer.



Fig. S7 EQE spectra for different for best cells using $(MAPbI_3)_{1-x}[(PEI)_2PbI_4]_x$ perovskite materials.



Fig. S8 Stacked plot of the normalized performance parameters as a function of exposure time to ambient atmosphere (humidity levels $50 \pm 2\%$) for (MAPbI₃)_{1-x}[(PEI)₂PbI₄]_x (x = 0%, 2% or 4%) based solar cells.



Fig. S9 Device performance of of $(MAPbI_3)_{1-x}[(PEI)_2PbI_4]_x$ (x = 2%) solar cell at conventional architecture (FTO/TiO₂ compact/TiO₂ mesoporous/mixed perovskite/spiroOMeTAD/Ag) : (A) *J-V* curves of best cell; (B) Histograms of the solar cell reproducibility; (C) Plot of the normalized PCE values as a function of exposure time to ambient atmosphere.