Supporting Information

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

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Experimental Section

Materials: Polymeric ammonium (PEI-HI) was synthesized by reacting 2 g of 2.5 mmol Polyethylenimine, ethylenediamine branched (PEI, M_w ~ 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. CH_3NH_3I (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 ± 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. PbI_2 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 PbI_2 at the molar ratio of 2% or 4%. A solution of PbI_2 or PbI_2:PEI-HI mixture was spin-coated onto the substrate at 2000 rpm for 60 s and CH_3NH_3I 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 PC_61BM (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 ×10^{-6} Torr) through a shadow mask with the thickness of 1 nm and 200 nm, respectively.

The device area was defined as 10 mm^2. 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 (MAPbI_{3})_{1-x}[(PEI)_{2}PbI_{4}]_{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)$_2$PbI$_4$]$_x$ 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.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)$^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0%</td>
<td>18.80 ± 1.14</td>
<td>1.01 ± 0.03</td>
<td>0.68 ± 0.03</td>
<td>12.96 ± 0.94$^b$ (14.59)$^c$</td>
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<tr>
<td>x = 2%</td>
<td>18.92 ± 0.45</td>
<td>1.07 ± 0.01</td>
<td>0.72 ± 0.01</td>
<td>14.57 ± 0.35 (15.20)</td>
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<tr>
<td>x = 4%</td>
<td>15.86 ± 0.41</td>
<td>1.09 ± 0.01</td>
<td>0.66 ± 0.01</td>
<td>11.41 ± 0.32 (12.01)</td>
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</table>

$^{a}$ 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 \((\text{MAPbI}_3)_{1-x}\{(\text{PEI})_2\text{PbI}_4\}_x\) films of before and after exposed to 50 % relative humidity for 2 weeks. Peaks marked with ★ are assigned to the \(\text{PbI}_2\).

Fig. S4 \(J–V\) curves of forward and reverse bias sweep for the solar cell using the \(\text{MAPbI}_3\) and \((\text{MAPbI}_3)_{1-x}\{(\text{PEI})_2\text{PbI}_4\}_x\) \((x = 2\%)\) perovskite active layer.
**Fig. S5** Experimental data for $V_{OC}$ as a function of illumination light intensity for cells using $(\text{MAPbI}_3)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$ as light-absorbing layer along with the linear fit. The large slope of $1.67 \ k_B T/q$ of $(\text{MAPbI}_3)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$ ($x = 4\%$) is an indicator of trap-assisted recombination.

**Fig. S6** $J$–$V$ curves of forward and reverse bias sweep for the solar cell using the $(\text{MAPbI}_3)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$ ($x = 4\%$) perovskite active layer.
**Fig. S7** EQE spectra for different for best cells using $(\text{MAPbI}_3)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$ perovskite materials.

**Fig. S8** Stacked plot of the normalized performance parameters as a function of exposure time to ambient atmosphere (humidity levels 50 ± 2%) for $(\text{MAPbI}_3)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$ (x = 0%, 2% or 4%) based solar cells.
Fig. S9 Device performance of (MAPbI\textsubscript{3})\textsubscript{1-x}[(PEI)\textsubscript{2}PbI\textsubscript{4}]\textsubscript{x} (x = 2\%) solar cell at conventional architecture (FTO/TiO\textsubscript{2} compact/TiO\textsubscript{2} 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.