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Supplementary Information

Alkyl Chain Engineering of Low-Dimensional Perovskite Seeds for High-Efficiency Perovskite Solar Cells

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Experimental details.

Materials. The FTO substrate was purchased from Beijing Huamin New Materials Technology Company Limited. Lead (II) iodide (PbI_2, 99.9%), formamidinium iodide (FAI, 99.99%), Methylammonium iodide (MAI, 99.9%) and methylammonium chloride (MACl, 99.9%) were bought from Xi'an Shuoyuan Photoelectric Technology Corp. N, N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%) and isopropyl alcohol (IPA, 99.9%) were got from Sigma–Aldrich. [4-(3,6-dimethyl-9H-carbazol9-yl)butyl] phosphonic acid (Me-4PACz) was obtained from TCI. C_{60} was gain from Liaoning Advanced Election Technology Company Limited.1,3-Dimethylimidazolium Chloride(DMIMCl, ⩾98%) and 1-Ethyl-3-methylimidazolium chloride (EMIMCl, ⩾98%) were received from Aladdin. All chemicals were used without any further purification.

Fabrication of single-junction perovskite solar cells. Laser-patterned FTO glass (2.2 cm × 2.2 cm, 8 Ω sq-1) was cleaned with deionized water, isopropanol, and ethanol in the ultrasonic bath for 20 min respectively. The FTO glass was dried with N_2 gas and then treated with UV-ozone for 15 min to increase hydrophilicity. 80 μl dispersion of NiO_x (20 mg ml^{-1} in deionized water, sonicated for 10 min and filtered through a 0.22 μm PES before use) was spin-coated on the FTO at 2000 rpm for 30 s, followed by annealing at 150°C for 30 min. After cooling to room temperature, it was exposed to ozone for 5 minutes and then transferred to a N_2-filled glovebox. 100 μl solution of Me-4PACz (0.5 mg·ml^{-1} in ethanol) was spin-coated at 3000 rpm for 30 seconds and annealed at 100°C for 10 minutes. PbI_2 solution (1.5 ml) in DMF/DMSO (v:v = 9:1) was spin-coated on FTO/NiO_x/Me-4PACz at 2800 rpm for 30 s, followed by annealing at 70°C for 1 min. Then, a solution of FAI: MAI: MACl (79mg: 6.4mg: 10mg in 1ml IPA) was spin-coated onto the PbI_2 at a spin rate of 2300 r.p.m. for 30 s to form a wet the precursor film, followed by rapid transfer to air ambient (30 ~ 40% RH) for annealing at 150 °C for 15 min. For modified devices, 4% molar ratios of DMIMCl and EMIMCl were dissolved in the PbI_2 solution and stirred at room temperature for 6 hours.After the deposition of perovskite layers, the samples were transferred into a nitrogen-filled glovebox. Finally, 25 nm C_{60} at a rate of 0.5 Å·s^{-1}, 6 nm BCP a rate of 0.5 Å·s^{-1} and 120 nm silver electrode a rate of 1.0 Å·s^{-1} were thermally evaporated, respectively, under high vacuum ($<1\times10^{-4}$ Pa).

Fabrication of perovskite/perovskite/silicon triple-junction solar cells. The bottom Si solar cell with 20 nm ITO at the front surface was obtained from Hiking PV Technology Co. Ltd. The EMIMCl-treated middle perovskite subcell was fabricated as described above. Instead of BCP, 20 nm of ALD-SnOx was deposited on the top of the C_{60} layer. For ALD-SnOx deposition, the substrate temperature was maintained at 80 ℃. The TDMASn precursor source was set at 60℃, and the H_2O source at 70℃. The pulse and purge times for TDMASn were 1 and 20 s, respectively, with a 120 sccm carrier gas of nitrogen. For H_2O, the pulse and purge times were 0.2 and 20 s, with a 120 sccm N_2 flow; 210 cycles for this process were conducted. Then ITO (20 nm) and NiO_x (15 nm) were prepared by magnetron sputtering. Then the samples were transferred to a glovebox filled with N_2. The Me-2PACz (0.5 mg ml^{-1} in MeOH) was spin-coated at 3000 rpm for 30 s and annealed at 100°C for 10 min. The 1.1 M perovskite ($Cs_{0.22}FA_{0.78}Pb(I_{0.4}Br_{0.6})_3$) stock solution contains 62.87 mg CsI, 147.55 mg FAI, 50.71 mg PbI_2, 363.35 mg $PbBr_2$ and 3.67 mg MACl, 9.17 mg $PbCl_2$ that were dissolved in 1 ml mixed solvent of DMF : DMSO (v : v = 4 : 1). The 1.96-eV $Cs_{0.22}FA_{0.78}Pb(I_{0.4}Br_{0.6})_3$ perovskite film was deposited as same method as the 1.55-eV perovskite. PDADI (2.5 mg ml^{-1} in IPA) was spin-coated at 5000 rpm for 30 s and annealed at 100 ℃ for 5 min. Finally, C_{60} (20 nm)/SnO_2 (20 nm)/IZO (150 nm)/Ag frame (500 nm)/MgF_2 (100 nm) were deposited sequentially by the same method.

Film characterization. SEM images of perovskite films, and cross-sectional devices were obtained using Gemini SEM 300. AFM and KPFM were conducted on Oxford Instruments Asylum Research, Cypher S. XRD patterns were characterized on a Rigaku SmartLab diffractor attached with Cu K-alpha radiation (λ = 1.5405 Å). Optical absorption spectra measurement was performed on a UV–vis spectrophotometer (Shimadzu UV2600). XPS measurements were performed on a Thermo Fisher ESCALAB 250Xi instrument with a monochromatic Mg K Alpha (1.254 keV) X-ray source, and the samples were measured under an ultrahigh vacuum ($<10^{-7}$ Pa). UPS spectra were measured with an ESCALAB 250Xi (Thermo Scientific) with a He I α photon source (21.22 eV), and a -10 V voltage bias was applied between the sample and detector. The binding energy scale calibration of the UPS spectrometer was performed using clean gold film. PL spectra and TRPL spectra were recorded by FluoTime 300, Picoquant.

Device characterization. Electrochemical impedance spectroscopy (EIS) and capacitancevoltage spectrum (C-V) were performed by an electrochemical workstation (PAR-Ametek, VersaSTAT 3). The trap density measurements were conducted by using an Agilent B1500A precision meter in the drive-level capacitance profiling (DLCP) module. EQE_{EL} and V_{OC} loss measurements were carried out by applying external voltage/current sources through the devices (REPS, Enlitech). EQE spectra of the PSCs were recorded from QE-R3011 (Enli Tech) using Czerny-Turner monochromatic incident light. The PCE and SCLC of perovskite solar cells were calculated by recording the current density-voltage (J-V) curves on a solar simulator connected to a Keithley 2400 Digital Source Meter under AM1.5G irradiation in the dark. The light intensity was calibrated with a standard silicon photodiode. The scan rate was fixed at 20 $mV \cdot s^{-1}$ while the delay time was set to 0.01 s. A metal mask defined the active area with a size of 0.06 cm^2. For the stability test, unencapsulated devices are stored in a nitrogen (N_2) environment or in an environment with a humidity of 40%-50%. They were periodically taken out for measurements. After the measurements are completed, they are returned to their respective storage environments to be preserved for subsequent measurements.

Supporting Figures

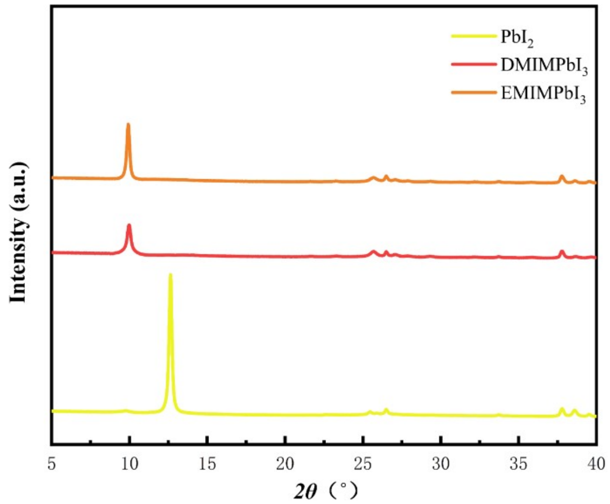

Figure S1. XRD patterns of PbI_2 films, $DMIMPbI_3$ films and $EMIMPbI_3$ films.

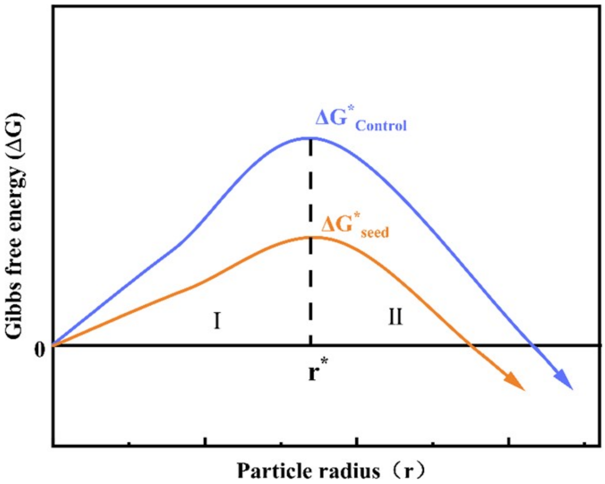

Figure S2. Gibbs free energy mechanism diagram of perovskite crystallization with seed-mediation.

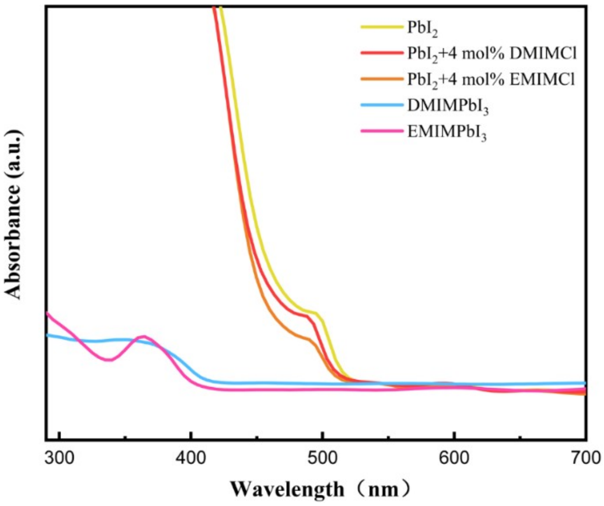

Figure S3. UV-Vis of PbI$_2$ films with different amount of DMIMCl, EMIMCl and DMIMPbI$_3$, EMIMPbI$_3$ films.

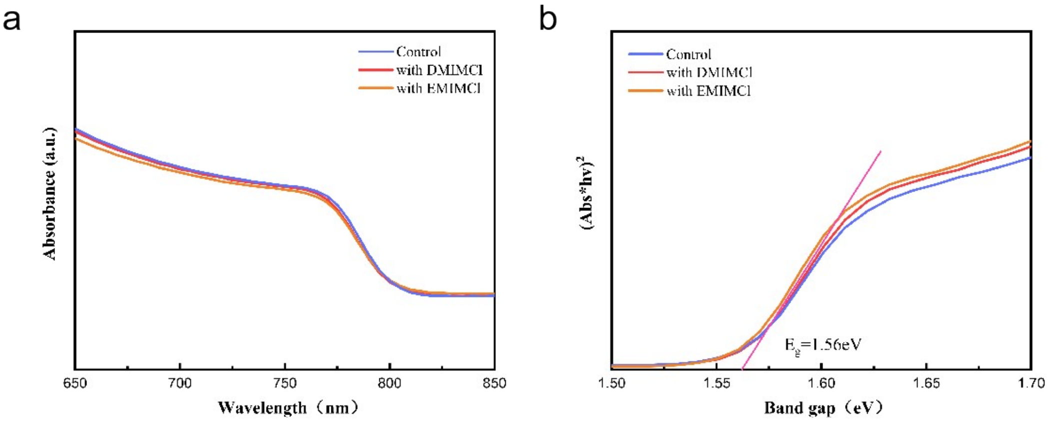

Figure S4. a) UV-vis absorption spectra and b) the bandgap of control, DMIMCl and EMIMCl treated perovskite.

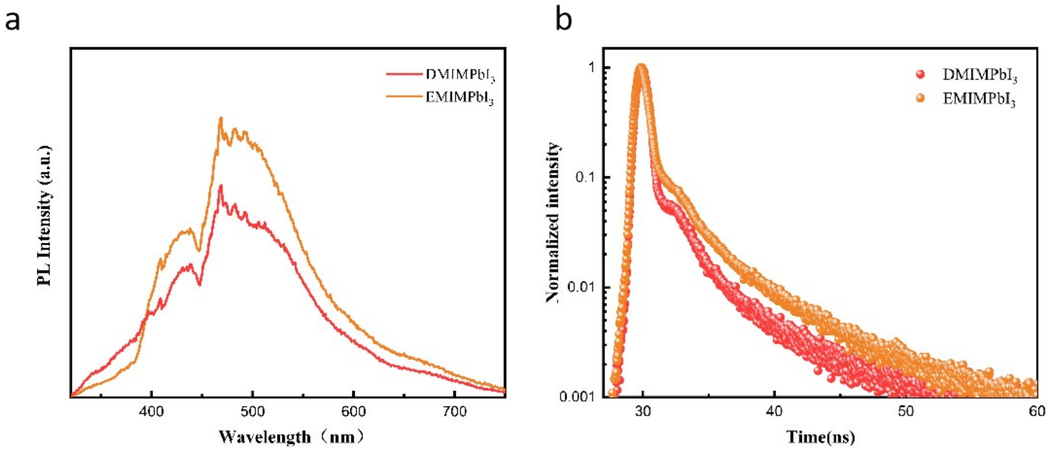

Figure S5. a) PL and b) TRPL spectra of $DMIMPbI_3$ and $EMIMPbI_3$ seed films.

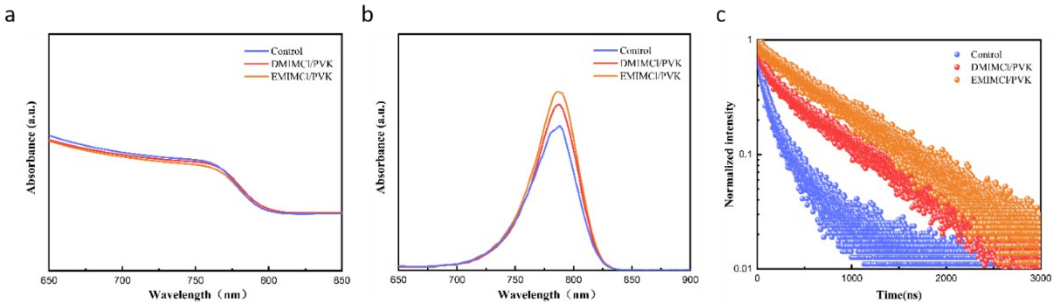

Figure S6. a). UV-vis, b) PL and c) TRPL spectra of the perovskite films based on free imidazolium ligand of EMIMCl and DMIMCl.

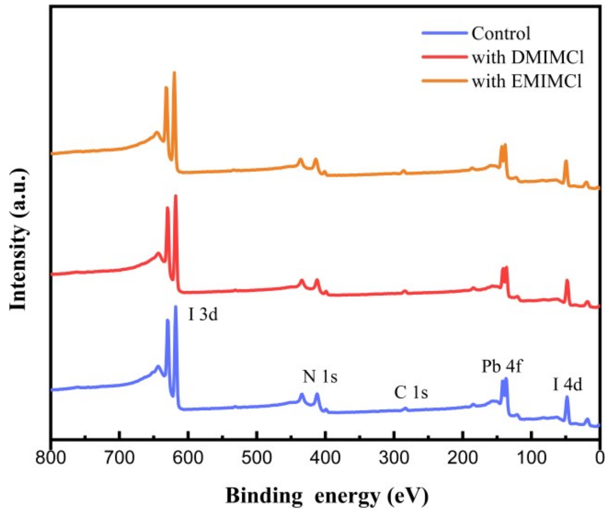

Figure S7. Overview XPS spectra of seed-mediated perovskite films compared with control.

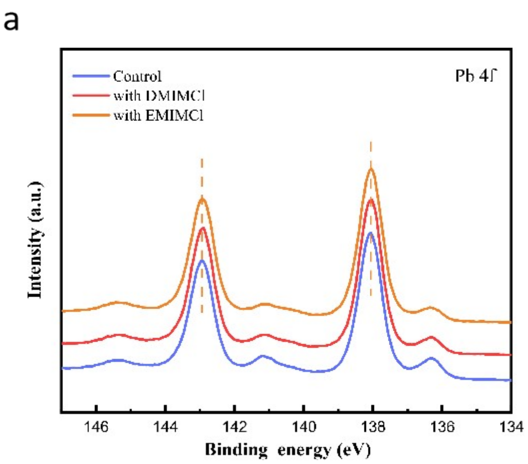

Figure S8. a) Pb 4f and b) I 3d XPS spectra of the DMIMCl and EMIMCl modified PbI_2 films compared with bare PbI_2.

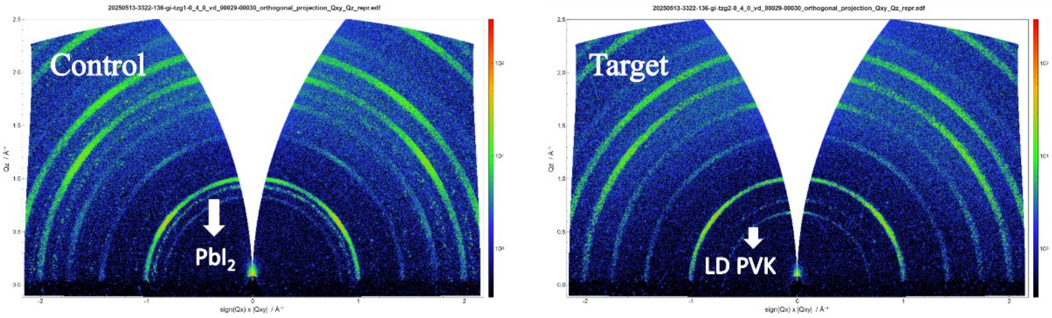

Figure S9. GIWAXS mapping of EMIMCl passivated perovskite (right) and bare perovskite (left) films as control.

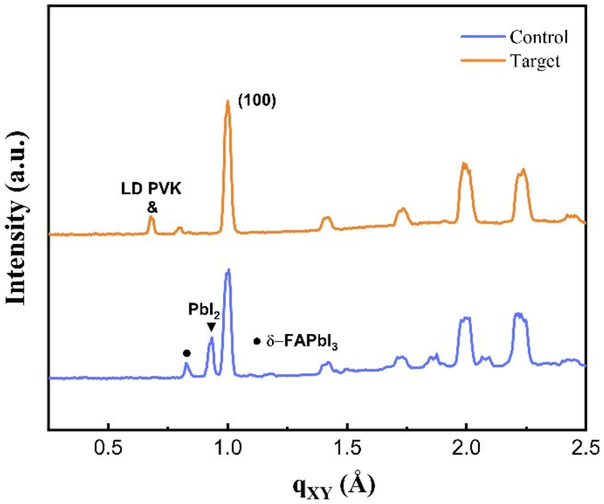

Figure S10. IIntegrated line files corresponding to the GIWAXD patterns.

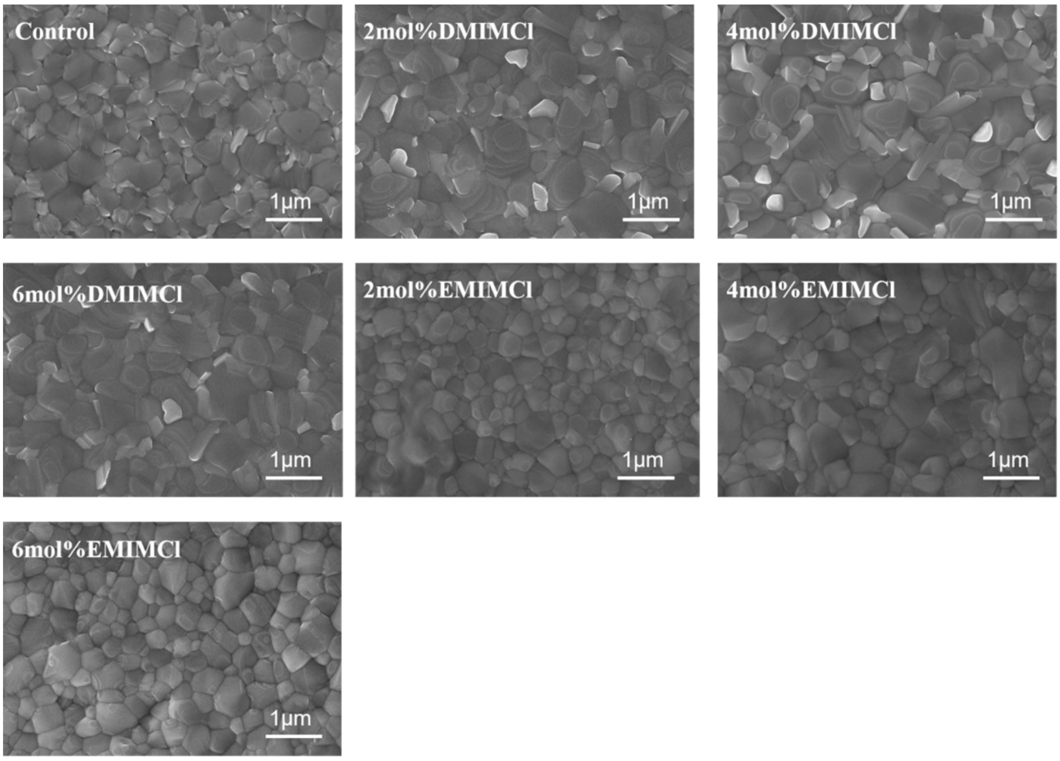

Figure S11. SEM images of perovskite films containing different seed concentrations.

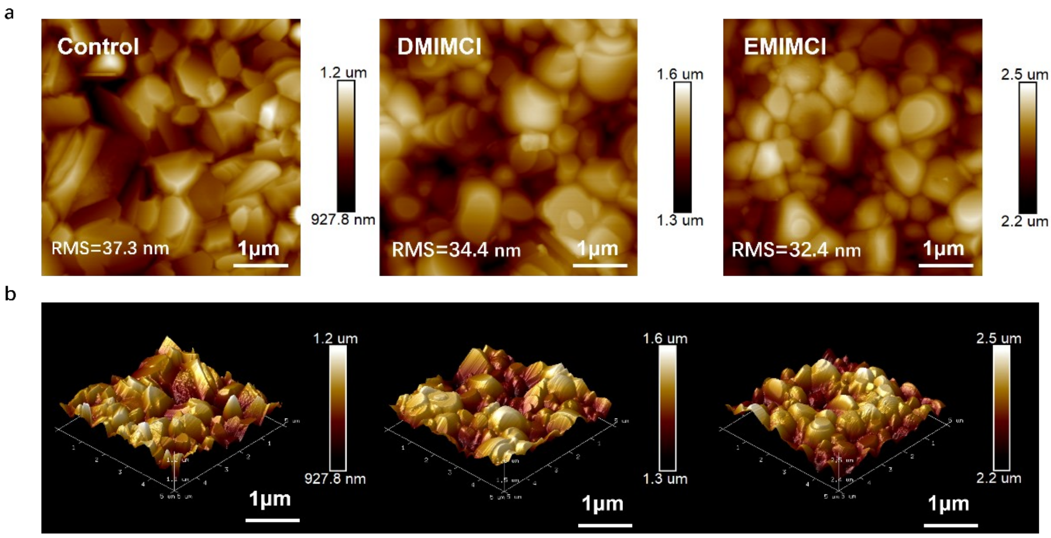

Figure S12. 3D AFM morphology of 4 mol% seed-mediated perovskite films and the non-mediated perovskite films.

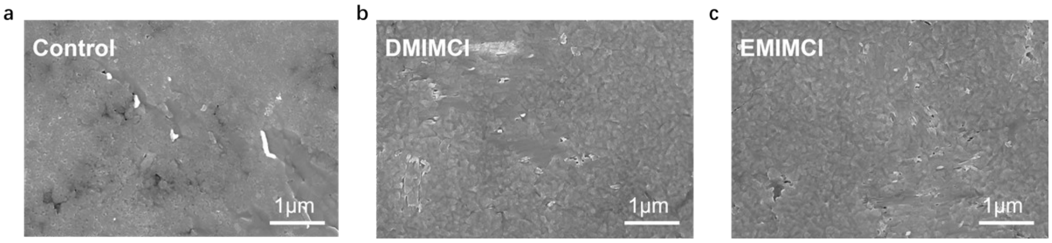

Figure S13. SEM images of bottom surface for a) the control b) DMIMCl and c) EMIMCl treated perovskite film

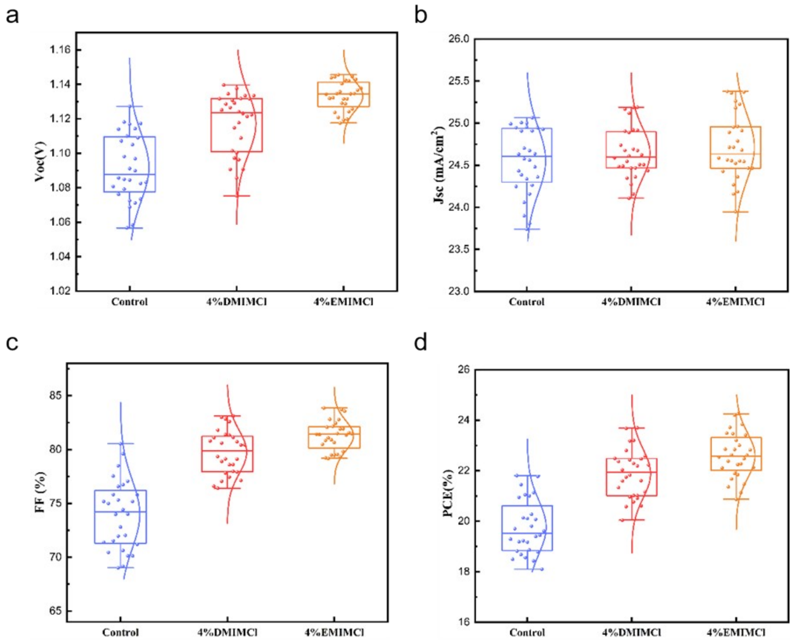

Figure S14. Statistic photovoltaic parameter of a) V_{OC}, b) J_{SC}, c) FF and d) PCE for 26 PSC devices fabricated with different imidazolium seed-mediated perovskite.

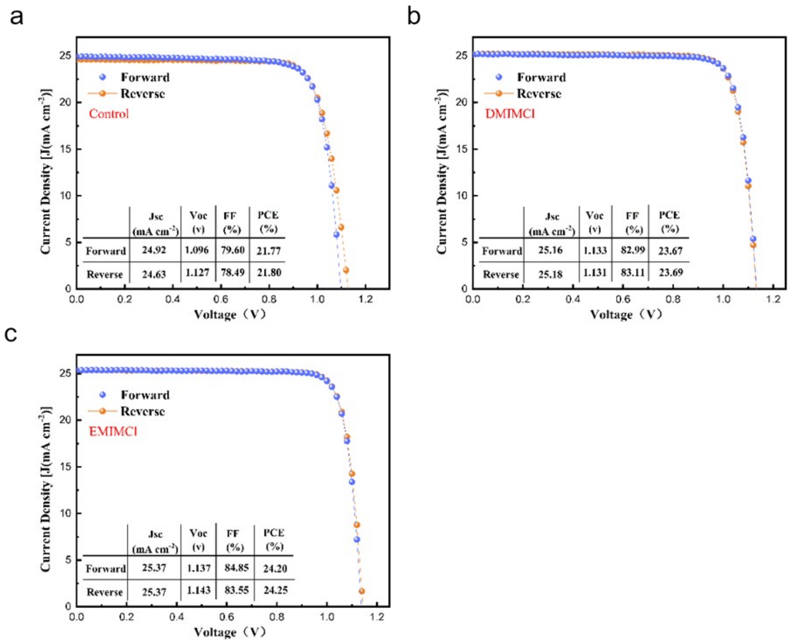

Figure S15. J-V curves of the best performing devices of a) control, b) DMIMCl based device and c) EMIMCl based device.

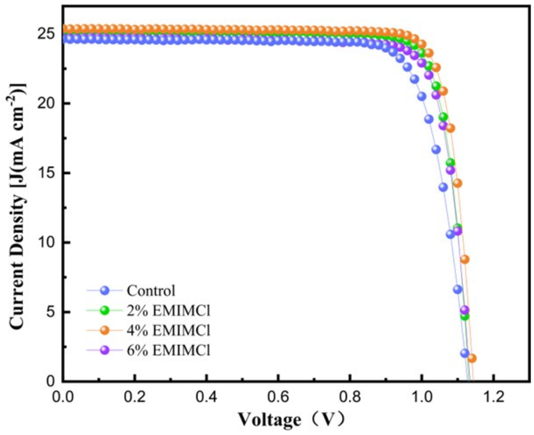

Figure S16. J-V curves of the best performing devices of different concentrations treatment by EMIMCl based seed, compared with the control.

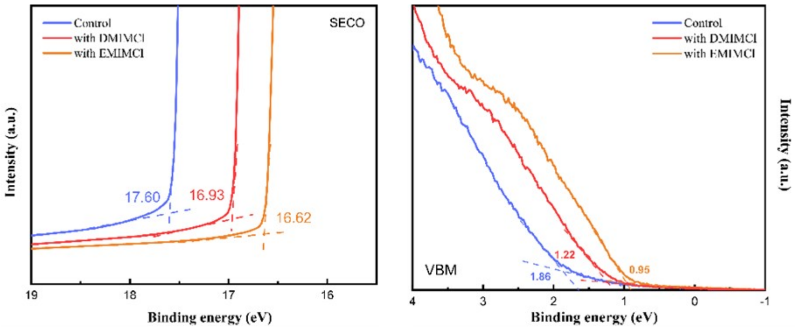

Figure S17. UPS spectra of seed-mediated perovskite compared with the control, including secondary electron cutoff region (SECO) and valence band region with logarithmic intensity scale.

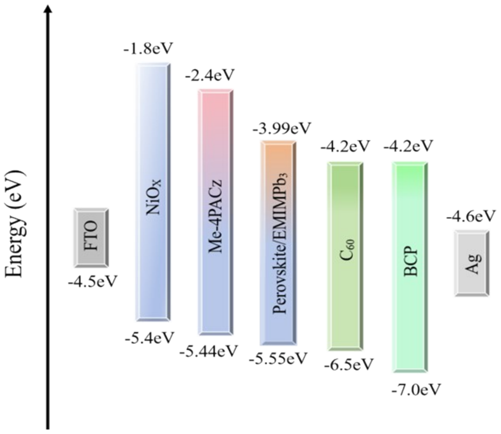

Figure S18. Energy band level diagram of the EMIMCl based PSC.

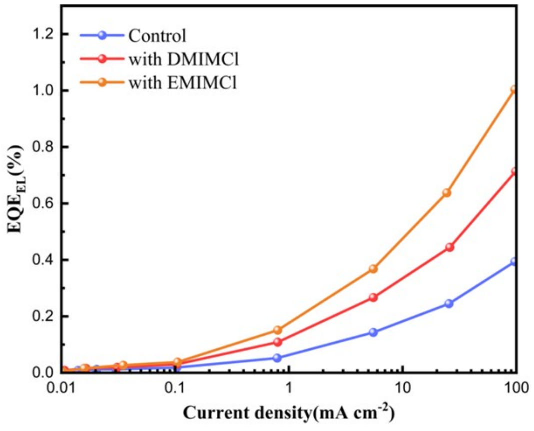

Figure S19. EQE_{EL} spectra of imidazolium seed-mediated devices.

Supporting Figures

Table S1. The fitted carrier lifetime of LD perovskite seed based perovskite films obtained from the TRPL measurements.

	τ_1 (ns)	**τ_2 (ns)**	**τ_{ave} (ns)**
Control	**7.04**	**146.08**	**147.33**
DMIMCl	**56.91**	**375.52**	**345.62**
EMIMCl	**244.42**	**1520.69**	**1521.94**

Table S2. The fitted carrier lifetime of LD perovskite seed films obtained from TRPL measurements.

	τ_1 (ns)	**τ_2 (ns)**	**τ_{ave} (ns)**
$DMIMPbI_3$	**5.09**	**5.08**	**5.09**
$EMIMPbI_3$	**5.14**	**5.15**	**5.16**

Table S3. The fitted carrier lifetime of the free imidazolium ligand based perovskite film obtained from TRPL measurements.

	τ_1 (ns)	**τ_2 (ns)**	**τ_{ave} (ns)**
Control	**26.61**	**246.72**	**245.44**
DMIMCl/perovskite	**66.79**	**523.35**	**524.39**
EMIMCl/perovskite	**104.92**	**784.96**	**785.46**

Table S4. Photovoltaic parameters of different concentrations treatment by EMIMCl based seed, compared with the control.

	J_{SC} (mA cm^{-2})	**V_{OC} (V)**	***FF* (%)**	**PCE (%)**
Control	**24.63**	**1.127**	**78.49**	**21.80**
2% EMIMCl	**25.28**	**1.132**	**83.24**	**23.84**
4% EMIMCl	**25.37**	**1.143**	**83.55**	**24.25**

6% EMIMCl	24.71	1.134	81.92	22.97

Table S5. Fitted values of EIS measurement from the equivalent circuit components.

	R_s (Ω)	R_{rec} (Ω)	C (nF)
Control	25.66	1999	11.15
DMIMCl	17.34	3818	8.72
EMIMCl	15.33	4631	7.87

Table S6. V_{OC} loss calculation of of the control PSC and imidazolium seed-mediated devices.

	E_g (eV)	V_{OC}, SQ (V)	V_{OC} (V)	ΔV_1 (V)	ΔV_2 (V)	ΔV_3 (V)	V_{OC}□ (V)
Control	1.553	1.312	1.127	0.277	0.036	0.145	1.126
DMIMCl	1.553	1.311	1.131	0.276	0.037	0.130	1.130
EMIMCl	1.553	1.311	1.143	0.276	0.033	0.121	1.142