## **Supporting Information**

PbI<sub>2-x</sub>Cl<sub>x</sub> Seed layer for obtaining efficient planar heterojunction perovskite solar cells via interdiffusion process

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## Materials and device fabrication

CH<sub>3</sub>NH<sub>3</sub>I was synthesized by mixing 28 mL methylamine (40% in methanol, Junsei Chemical Co., Ltd.) and 30mL hydroiodic acid (57 % in water, Aldrich) in ice-bath for 2h with stirring. The CH<sub>3</sub>NH<sub>3</sub>I was recovered by rotary evaporation at 50°C for 1h. The product was washed with diethyl ether and dried in vacuum oven at 60°C for 24h. Laser etched fluorine doped tin oxide (FTO, TEC 8) coated glasses were used as the substrates. The FTO were cleaned by sonication in acetone, ethanol and 2-propanol for 5min, respectably. A TiO<sub>2</sub> blocking layer was formed by immersing into 200mM TiCl<sub>4</sub> solution at 70°C for 50min and dried at 120°C in air. For the preparation of Pbl<sub>2-x</sub>Cl<sub>x</sub> precursor solution (1M), the mixture of Pbl<sub>2</sub> (99.999%, Aldrich) and PbCl<sub>2</sub> (99.999%, Aldrich) (the mole ratio of the precursor solution (Pbl<sub>2</sub>:PbCl<sub>2</sub>) was 1:0, 1:0.25, 1:0.5, 1:0.75 and 1:1 respectively) were dissolved in DMF (N, N -dimethylformamide) and stirring at 60°C. To form the Pbl<sub>2-x</sub>Cl<sub>x</sub> seed layer, the mixture of PbI<sub>2</sub> and PbCl<sub>2</sub> solution was spin-coated at 5000rpm for 30s in glove box and dried on a hotplate at 70°C. To stack MAI onto the Pbl<sub>2-x</sub>Cl<sub>x</sub> seed layer, 120  $\mu$ l of MAI solution dissolved in 2-propanol (40mg/mL) was loaded at 0 rpm for 25s and then spin-coated at 4000rpm for 20s, which was annealed isothermally at 90°C for 120min in ambient condition (RH 30%). A spiro-OMeTAD solution was prepared by dissolving 80 mg of spiro-OMeTAD in 1 mL chlorobenzene containing 28.8 µL of 4-tert-butyl pyridine and 17.5 mL of lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) solution (520 mg/mL acetonitrile). The spiro-OMeTAD solution was spin-coated on the perovskite film at 4000rpm for 30s. Finally, a gold counter electrode was thermally evaporated. The active area was fixed at 0.145cm<sup>2</sup>

## Characterization

Surface morphologies of the perovskite films were characterized using field emission scanning electron microscopy (FESEM, Hitachi S-4800) equipped with an energy dispersive X-ray spectrometer (EDX) to obtain information on surface chemical composition ratios. X-ray diffraction (XRD) data were collected on a diffractometer (D/MAX-2500V, Rigaku) using Cu Ka radiation. UV-vis absorption spectra were recorded using a spectrometer (V-670, Jasco). All films for XRD and UV-vis were prepared on TiO<sub>2</sub>/FTO; poly (methyl methacrylate) (PMMA) was spread on the samples to prevent further reaction with atmospheric H<sub>2</sub>O. Timeresolved photoluminescence (TRPL) spectra was measured using a time correlated single photon counting system (Fluo Time 300, Picoquant) with excitation at 520nm. ToF-SIMS was conducted with a TOF-SIMS 5. The perovskite layer was sputtered with a low energy Cs+ (500eV) beam on 200 x 200 µm2 area and the analysis (Bi3+) was conducted on a 50 x 50 µm2 area of the sputtered field. The J-V curves of Perovskite solar cells were obtained using a electrochemical station(Bio-Logic VSP) under 100 mW/cm<sup>2</sup> AM 1.5G light (Sun 3000 class AAA, ABET Technology) with a metal mask of area 0.098 cm<sup>2</sup>. Devices were scanned from J<sub>sc</sub> to forward bias (forward, blue) and from forward bias to J<sub>sc</sub> (reverse, red) with a 20 mV/s scan rate. The oriel-calibrated Si solar cell (SRC-1000-TC-KG5-N) was used to adjust light intensity to one sun illumination. The external quantum efficiency (EQE) was measured by a combination of an Ivium potentiostat (IVIUM) and a monochromator (DONGWOO OPTRON co., Ltd.,) under a Light Support (ABET 150W Xenon lamp, ABET Technology). EQE data acquisition was carried out in DC mode. Intensity-modulated photocurrent and photovoltage were measured by an Ivium potentiostat (IVIUM) with LED MODULIGHT (IVIUM).



**Fig.** S1 Photograph of the different ratio precursors ( $PbI_2:PbCI_2$ ). The concentration of all the precursors is 1M and the lead mole in the all solutions was fixed as 1 mole. The relative halide ratio in the precursors was controlled. This retrograde solubility is probably caused by the less solubility of  $PbCI_2$  in DMF solvent or the size disparity between the Cl<sup>-</sup> and l<sup>-</sup> ions



Fig. S2 XRD patterns of 1:0.75 ratio perovskite films with varied annealing time.

The peak at 15.6° corresponds to the MAPbCl<sub>3</sub> (100) orientation (Fig. S1 b). The peak of MAPbCl<sub>3</sub> (200) at 31.5° is shown as shifted MAPbI<sub>3</sub> (310) due probably to the fact that formation of MAPbCl<sub>3</sub> is dependent of the molar ratios of chloride and iodide halide species.<sup>1</sup> Interestingly, as annealing time goes by, the peak of MAPbCl<sub>3</sub> (200) is shifted to MAPbI<sub>3</sub> (310).



**Fig. S3** SEM images of  $PbI_{2-x}CI_x$  layer for (a) 1:0, (b) 1:0.25, (c) 1:0.5 and (d) 1:0.75 ratio. The microchannel of seed layer beneficial for the conversion of perovskite materials was identified in  $PbCI_2$  added seed layer.

Samples	A <sub>1</sub> (%)	τ <sub>1</sub> (ns)	A <sub>2</sub> (%)	τ <sub>2</sub> (ns)	τ <sub>avg</sub> (ns)
1:0	42.3	15.697	57.70	47.643	34.13
1:0.25	53.26	2.482	46.74	7.858	4.87
1:0.5	50.59	2.015	49.41	4.091	2.70
1:0.75	43.23	1.385	56.77	6.090	4.06
			$ au_{avg}$	$=\sum_{i}A_{i}\tau_{i},w$	here $\sum_{i} A_i = 1$

**Table. S1** Time-resolved photoluminescence (TRPL) parameters fitted using a bi-exponential decay function.



**Fig. S4** PL spectra of perovskite films on different substrate with different PbI<sub>2</sub>:PbCl<sub>2</sub> ratios and excitation at 530 nm.



Fig. S5 SEM images of 1:1 ratio perovskite films for (a) as-spun, (b) annealed and (c) the corresponding J-V



Fig. S6 The photovoltaic performance parameters for PSCs based on different seed layers.

		As-spun		
Sample	Pb	I	CI	Excess I
1:0	23.44	76.56	0	6.24
1:0.25	21.83	72.64	5.54	12.70
1:0.5	22.30	68.88	8.90	10.81
1:0.75	21.96	64.71	13.33	12.15

**Table. S2** EDX data of As-spun perovskite films to demonstrate stacking layer for interdiffusion process. Excess I ratio was determined by considering Pb:Cl and Pb:I ratio based on ideal MAPbCl<sub>3</sub> and MAPbI<sub>3</sub> ratio. Excess I stands for the stacked organic species onto the seed layer of each ratio.



**Fig. S7** SEM images of the perovskite film as a function of annealing time. This figure demonstrates the perovskite transition including coarsening of the crystal domains, diffusion of the spectator ions and removal of the excess spectator ions.



**Fig. S8** XRD spectra of a 1:0.75 ratio perovskite film on  $TiO_2/FTO$  fashioned from reduced spin rate to load more MAI solution onto 1:0.75 PbI<sub>2-x</sub>Cl<sub>x</sub> seed layer and annealed.

To corroborate the idea that the accessibility and amount of stacked intercalating species have an effect on perovskite film composition, we fabricated a perovskite film at reduced spin rate from 4000rpm to 2500rpm so as to stack a more amount of MAI species onto 1:0.75 ratio  $PbI_{2-x}CI_x$  seed layer. As seen in Figure S4, the peak intensity of  $PbI_2$  is significantly reduced compared to the perovskite film fabricated from 4000rpm (Fig. 1c). Consequently, this data support that the accessibility and diffusion rate of halide species govern the conversion of perovskite materials, as reported by Pellet et al.<sup>2</sup>

- 1. B.-w. Park, B. Philippe, T. Gustafsson, K. Sveinbjörnsson, A. Hagfeldt, E. M. J. Johansson and G. Boschloo, *Chemistry of Materials*, 2014, **26**, 4466-4471.
- 2. N. Pellet, J. Teuscher, J. Maier and M. Grätzel, *Chemistry of Materials*, 2015, 27, 2181-2188.