Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Molecule Occupancy by n-Butylamine Treatment to Facilitate the Conversion of PbI_2 to Perovskite in Sequential Deposition

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Experimental Section

Materials: Titanium isopropoxide (99.999%), ethonal (99.5%), n-butylamine (BA, 99.5%), acetonitrile (99.8%), 4-*tert*-butylpyridine (tBP, 96%), bis (trifluoromethane) sulfonimide lithium (Li-TFSI, 99.95%) and PbI_2 (99%) were all purchased from Sigma-Aldrich and used as received. Methylammonium iodide (MAI, 98%) powder was purchased from TCI. 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, 99.85%) was purchased from Advanced Election (China). Other liquid reagents including N, N-dimethylformamide (DMF, 99.8%) and chlorobenzene (CB, 99.8%) were purchased from Acros without further purification. Metal electrode materials gold (Au) was purchased from ZhongNuo Advanced Material Technology (Beijing) with a high purity of 99.999%.

Device Fabrication: The pre-patterned FTO substrates were ultrasonically cleaned with diluted detergent, deionized water, acetone, and isopropanol in succession for 20 min. Then the as-cleaned FTO substrates were treated by O_2 plasma for 5 min. A dense TiO_2 layer was prepared by spin-coating with the precursor solution (369 μl titanium isopropoxide and 0.15 ml 37 wt % HCl solution dissolved in 5 ml ethanol) on FTO substrate at 5000 rpm for 30 s, then annealed at 500 °C for 30 min. After cooling down to room temperature, PbI_2 solution (460 mg/ml in DMF) was deposited on the substrate with 4000 rpm for 30 s, followed by annealing at 70 °C for 5 min in a nitrogen-filled glove box. Subsequently, for the PbI_2 film treated with BA, the PbI_2 substrate was transferred to fuming cupboard and placed in the lower part of a home-made equipment while 500 μl BA was added to the upper part (as shown in Figure 1). The saturated vapor pressure of BA is 10.9 kPa, and the relative vapor density is 2.52 (air = 1) at room temperature (~ 25 °C). Therefore, the BA vapor would naturally flow downward to react with the PbI_2 film when the piston switch is turned on. Afterward, the sample was placed face down on a 2 cm high corundum boat in a vacuum oven preheated to 180 °C, where 120 mg MAI powder was uniformly dispersed at the bottom of the boat. Compact and uniform perovskite film was obtained as the light absorbing layer after 25 minutes reaction. Next, after cooling to room temperature, the hole transporting layer was spin-coated onto the as-prepared perovskite layer at 5000 rpm for 30 s using spiro-OMeTAD solution, which consisted of 72.3 mg spiro-OMeTAD, 35 μl Li-TFSI stock solution (260 mg Li-TFSI in 1 ml acetonitrile), 30 μl tBP and 1 ml chlorobenzene. Then, the sample was oxidized for 20 hours in a drying chamber with relative humidity near 10%. Finally, gold with 80 nm thick was deposited on the spiro-OMeTAD layer by thermal evaporation with the base pressure of $< 5 \times 10^{-4}$ Pa. The deposition rate was 0.6 Å/s.

Device Measurement: Simulated AM 1.5G irradiation ($100\ mW\cdot cm^{-2}$) was produced by a 150 W class AAA solar simulator (Zolix Sirius-SS150A) to irradiate the solar cells. The light intensity was determined by a standard monocrystalline silicon photodiode calibrated by the Newport TAC-PV laboratory. The device active area is 0.045 cm^2. A Keithley 2400 source meter was used to measure the *J-V* curves. All samples were measured in a glove box at room temperature without encapsulation.

Film Characterization: The X-ray diffraction (XRD) patterns were obtained using Cu $K\alpha_{1/2}$ source (40 kV, 40 mA, λ=0.15418 nm) by Bruker D8 ADVANCE. The ultraviolet-visible (UV-Vis) absorption spectra of PbI_2 and perovskite films were obtained by the spectrophotometer (SHIMADZU UV-2600) from 800 to 400 nm. The background noise was subtracted before testing. Scanning electron microscopy (SEM) images were obtained by using a ZEISS Ultra55 equipped with an electron beam accelerated at 5–10 kV to study the surface morphology of PbI_2 and perovskite films. The steady-state photoluminescence (PL) spectra were taken with 325 nm laser excitation at room temperature (Horiba, LabRAM HR Evolution Inc.).

Figure S1. Photogragh of PbI_2 powder dispersion in BA liquid. This result shows that PbI_2 is almost insoluble in BA.

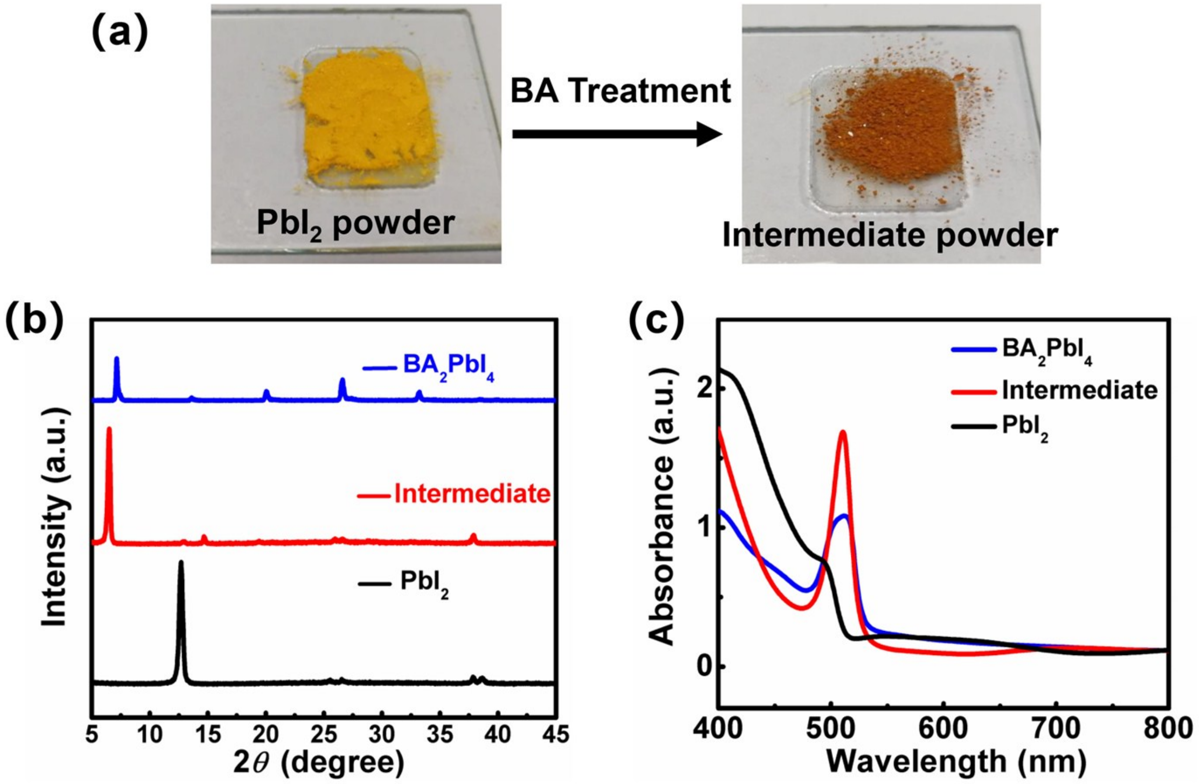

Figure S2. (a) Photographs of pristine PbI_2 powder and intermediate powder. (b) XRD paterns and (c) UV-vis absorption spectra of the pristine PbI_2, the intermediate, and the 2D perovskite BA_2PbI_4. The 2D perovskite BA_2PbI_4 showed diffraction peak at ~ 7.2°, which was indexed as the (002) plane of BA_2PbI_4 according to literatures. Absorption results of BA_2PbI_4 also agreed well with reported works. By comparing intermediate with BA_2PbI_4, we found that their XRD and absorption results were quite similar to some extent, which might be ascribed to their similar layered structures. Therefore, we speculate that BA would enter and occupy the space between PbI_6 nanolayers in PbI_2 film, self-assembling to form layer-structured intermediate or complex. One inherent difference from BA_2PbI_4 is that the edge-sharing nature of PbI_6 lead framework was maintained.

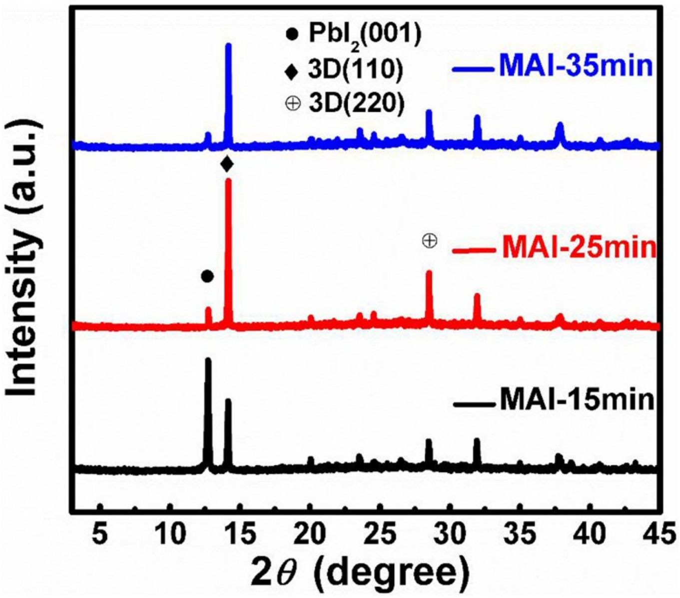

Figure S3. X-ray diffraction patterns of perovskite films obtained from pristine PbI_2 with different MAI reaction durations. After 15 minutes reaction, sharp diffraction peaks at 14.2° and 28.5° appeared, which were indexed to be the (110) and (220) planes of 3D $MAPbI_3$, respectively. However, the diffraction peak of PbI_2 (located at 12.7°, indexed to be the (001) plane of PbI_2) was also observed, indicating the residual of PbI_2. When the reaction time increased to 25 minutes, the perovskite peak intensity increased, which was due to the enhanced crystallinity of perovskite films. However, the residual of PbI_2 remained. Further increasing the reaction time to 35 minutes could reduce the PbI_2 residuals, but still could not eliminate them. Meanwhile, the intensity of perovskite diffraction peaks appeared to be weakened by prolonging the reaction time, which was probably ascribed to the perovskite crystallinity degradation in the high-temperature reaction process.

Table S1. Summary of photovoltaic parameters of PSCs

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
Reference	**19.71**	**0.989**	**74.44**	**14.52**
BA-3min	**19.95**	**1.041**	**78.81**	**16.38**
BA-10min	**22.36**	**1.031**	**76.42**	**17.63**
BA-60min	**19.49**	**1.005**	**76.89**	**15.06**

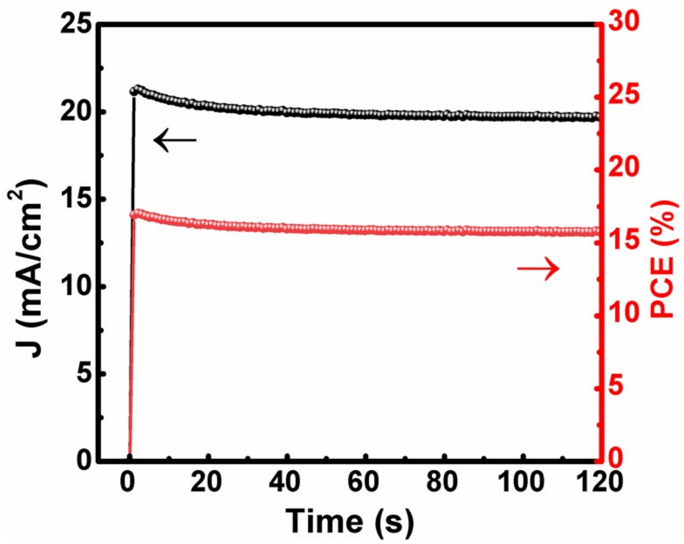

Figure S4. Stabilized steady-state photocurrent and efficiency output of the champion devices at the voltage (0.80 V) near the maximum power point.

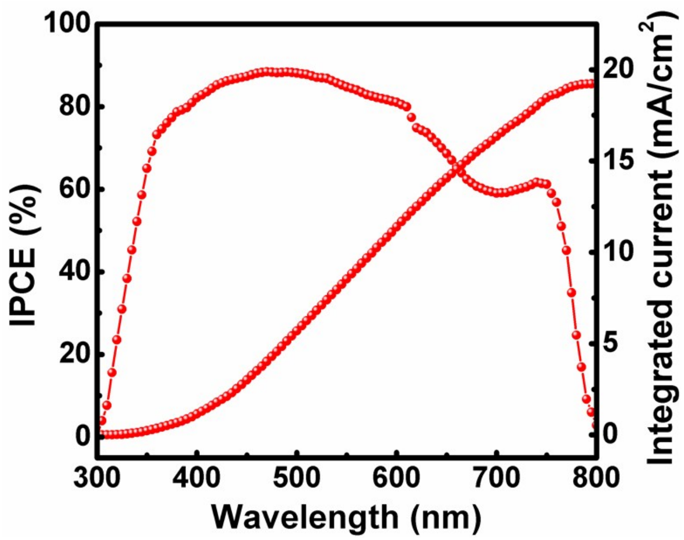

Figure S5. IPCE spectra of the best performing devices measured in atmosphere without encapsulation.

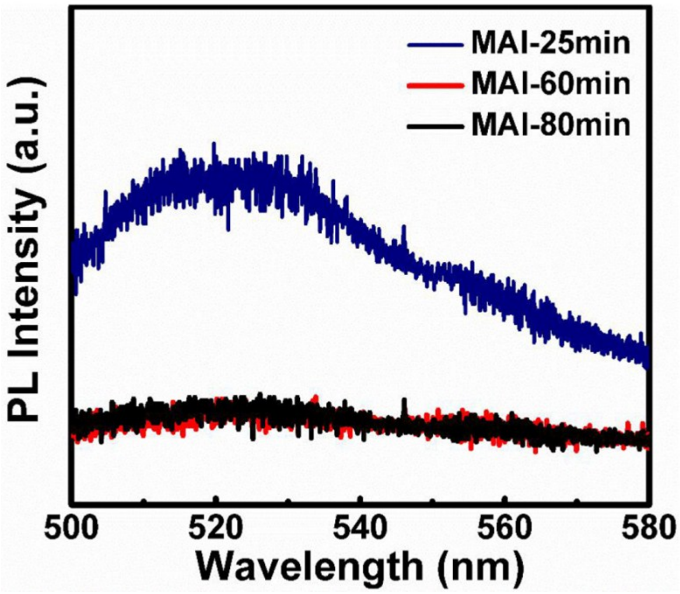

Figure S6. Magnification of the steady-state photoluminescence (PL) spectra (from 500 to 580 nm) of perovskite films by reacting BA-60min PbI_2 with MAI for different durations. The intermediate in BA-60min PbI_2 primarily transformed into 3D $MAPbI_3$ after 25 minutes reaction with MAI, as discussed in the main text. However, the signal peak at 520 nm still remained, indicating trace amount of intermediate or low-dimensional perovskite residual in the 3D $MAPbI_3$ films, since both of them exhibited PL peak at 520 nm. Prolonging the MAI reaction time could eliminate the residual completely. However, it might induce the perovskite crystallinity degradation on account of long time high-temperature reaction process. Besides, excess MAI might be deposited on the perovskite surface, which would block the interface charge transfer. Both above would lead to the deterioration of device performance.

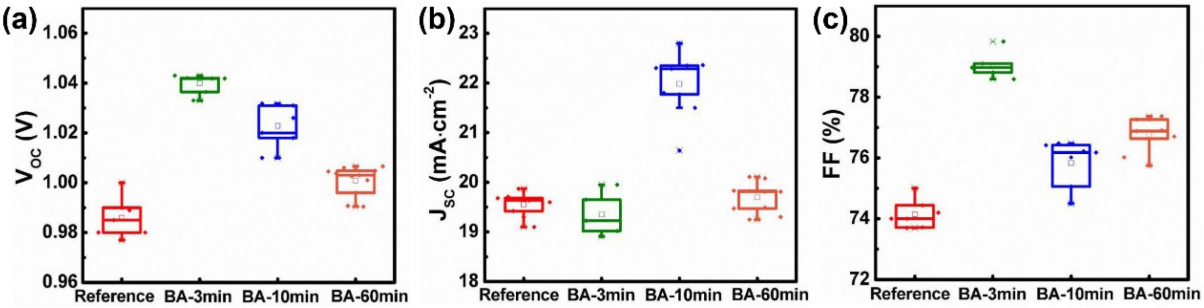

Figure S7. Detailed statistical data about the V_{oc}, J_{sc}, and FF of perovskite solar cells.

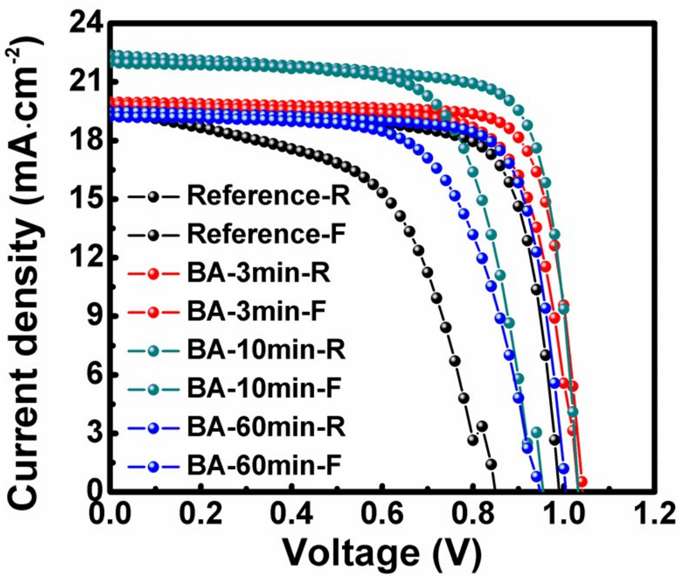

Figure S8. *J-V* curves of devices measured with both the reverse scan (from positive to negative bias) and forward scan (from negative to positive bias).