

Supporting Information

Formamidinium-based Ruddlesden-Popper perovskite films fabricated via two-step sequential deposition: quantum well formation, physical properties and film-based solar cells

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Experimental Section

Materials preparation: N, N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%) and isopropanol (IPA, 99.8%) were purchased from Sigma-Aldrich. 4-tert-butylpyridine (96%), acetonitrile (99.7+%), chlorobenzene (CB, 99.8%) and lithium bis(trifluoromethanesulfonyl)imide (99%) were purchased from Aladdin Reagent. Lead iodide (PbI_2 , 99.9985%), and formamidinium iodide (FAI, 99.5%) were obtained from Advanced Election Technology CO., Ltd.. PMAI (benzylamine hydroiodide, 99.5%) was obtained from p-OLED. 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD, $\geq 99.0\%$) was purchased from Shenzhen Feiming Science and Technology Co., Ltd.. The purity of gold wire is 99.99%. All chemicals were used as received without further purification.

Solution preparation: 1.5 mmol PbI_2 dissolved in 1 mL of mixture solvent with DMSO and DMF (volume ratio of 1:9), then the PbI_2 solution was stirred at 60°C for 6 hours. The molar ratio of PMAI:FAI in IPA increasing from 2:3 to 2:9 and 2:59 were prepared and stirred overnight at room temperature, according to the formula Ruddlesden-Popper (RP) type $\text{PMA}_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n=4, 10, 60$). The Spiro-OMeTAD solution was prepared by dissolving 90 mg Spiro-OMeTAD and 22 μL lithium bis(trifluoromethanesulfonyl)imide in acetonitrile and 36 μL 4-tert-butylpyridine in 1 mL CB. All solutions filtered with a 0.45 μm pore size polytetrafluoroethylene filter membrane. In addition, all progresses were conducted under an N_2 atmosphere inside a glove box.

Device fabrication: The FTO-coated glass (2.5 cm \times 2.5 cm) was cleaned by sequential sonication in acetone, isopropanol and ethanol for 30 min each and then dried under N_2 flow and treated by O_3 plasma for 15 min. The TiO_2 was prepared by chemical bath deposition with the clean substrate immersed in a TiCl_4 (CP, Sinopharm Chemical Reagent Co., Ltd.) aqueous solution with the volume ratio of $\text{TiCl}_4:\text{H}_2\text{O}$ equal to 0.0225:1 at 70°C for 1 hour. The spin-coating was accomplished under inert atmosphere inside a nitrogen glove box. The PbI_2 film was deposited using a 1.5 M precursor solution spin-coated at 1500 rpm for 30 s and then placed on a hotplate for 1 min at 70°C . The 300 μL IPA containing three kinds of ratio for PMAI:FAI was cast on the PbI_2 film during spin-coating at 2000 rpm for 30 s, followed by thermal annealing at 150°C for 15 min under 30–40% relative humidity. Subsequently, the Spiro-OMeTAD layer

was deposited on top of the perovskite by spin-coating at 5000 rpm for 30 s followed by evaporation of 100 nm gold electrodes on top of the stack.

Device Characterization: UV–visible absorption spectra were acquired on a PerkinElmer UV-Lambda 950 instrument. Steady-state photoluminescence (PL) (excitation at 510 nm, front-side excitation) and time-resolved photoluminescence (TRPL) were measured with a PicoQuant FT-300. Femtosecond pump-probe transient absorption (TA) measurements were performed at appropriate power density ($29.88 \mu\text{J cm}^{-2}$). The pump pulse with a wavelength of 450 nm and duration of 290 fs generated via a second harmonic generator (SHG) was used to excite all the samples and the probe beam (from 450 to 950 nm) was detected by a high-speed spectrometer. All experiments were carried out at room temperature (i.e. $T = 300\text{K}$). The surface morphology and structure of the perovskite films were characterized by scanning electronic microscopy (SEM) (FE-SEM; SU-8020, Hitachi) at an acceleration voltage of 3 kV. X-ray diffraction (XRD) measurements were carried out in a θ - 2θ configuration with a scanning interval of 2θ between 3° and 60° on a Rigaku Smart Lab (X-ray Source: Cu $K\alpha$; $\lambda = 1.54 \text{ \AA}$). Grazing incidence wide angle X-ray scattering (GIWAXS) images were collected using a Xeuss 2.0 spectrometer (Xenocs company) with MetalJet-D2 (Excillum) as the X-ray source and Pilatus 3R 1M (Dectris) as the detector placed 216.723 mm away from the sample position. The incidence angle of the X-ray beam was 0.15° . Electron-only devices (FTO/c-TiO₂/Perovskite/PCBM/Ag) were fabricated to calculate the electron mobility of the devices. The dark J - V characteristics of the electron-only devices were measured on a Keithley 2400 SourceMeter. The mobility is extracted by fitting the J - V curves to the Mott-Gurney equation. The trap-state density was determined by the trap-filled limit voltage using the equation in the text. The J - V curves of the perovskite solar cells were analyzed using a Keithley 2400 SourceMeter under ambient conditions at room temperature, and the illumination intensity was 100 mw cm^{-2} (AM 1.5G Oriel solar simulator). The scan rate was 0.3 V s^{-1} , the delay time was 10 ms, and the scan step was 0.02 V. The power output of the lamp was calibrated against an NREL-traceable KG5 filtered silicon reference cell. The device area of 0.09 cm^2 is defined by a metal aperture to avoid light scattering from the metal electrode into the device during the measurement. The EQE was characterized on the QTest Station 2000ADI system (Crowntech. Inc., USA), and the light source is a 300 W xenon lamp. The monochromatic light intensity for EQE measurement was calibrated using a reference silicon

photodiode. All measurement were carried out without any encapsulation in ambient condition unless otherwise stated.

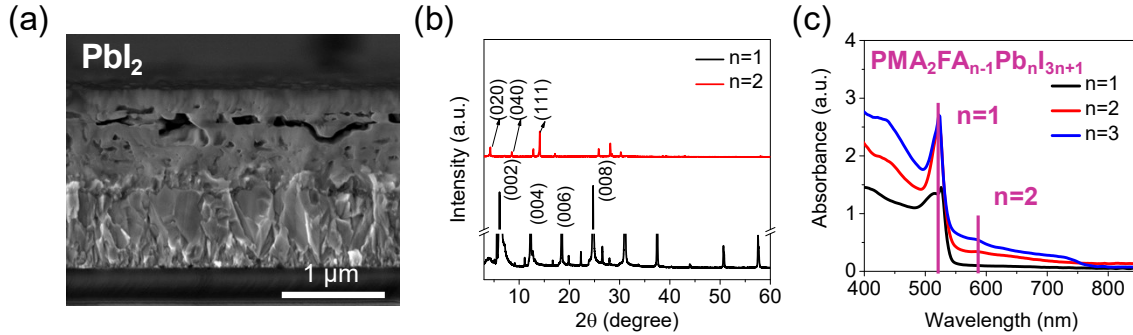


Fig. S1 (a) Cross-sectional SEM images of the PbI_2 . (b) XRD pattern of $\text{PMA}_2\text{FA}_{n-1}\text{Pb}_{n-1}\text{I}_{3n+1}$ ($n = 1, 2$) two-dimensional perovskite film prepared by one-step method. (c) The optical absorption spectrum of $\text{PMA}_2\text{FA}_{n-1}\text{Pb}_{n-1}\text{I}_{3n+1}$ ($n = 1, 2, 3$) two-dimensional perovskite film prepared by one-step method.

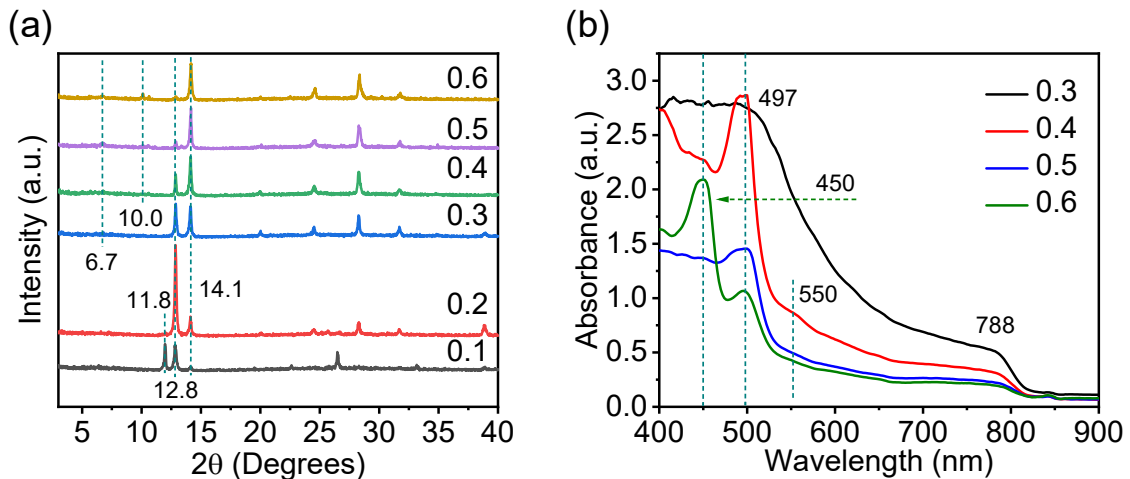


Fig. S2 (a) and (b) XRD patterns and UV-Vis spectra of $\text{FA}_2\text{FA}_{n-1}\text{Pb}_{n-1}\text{I}_{3n+1}$ films prepared via two-step sequential deposition of PbI_2 (ca. 400 nm) and various concentrations of FAI.

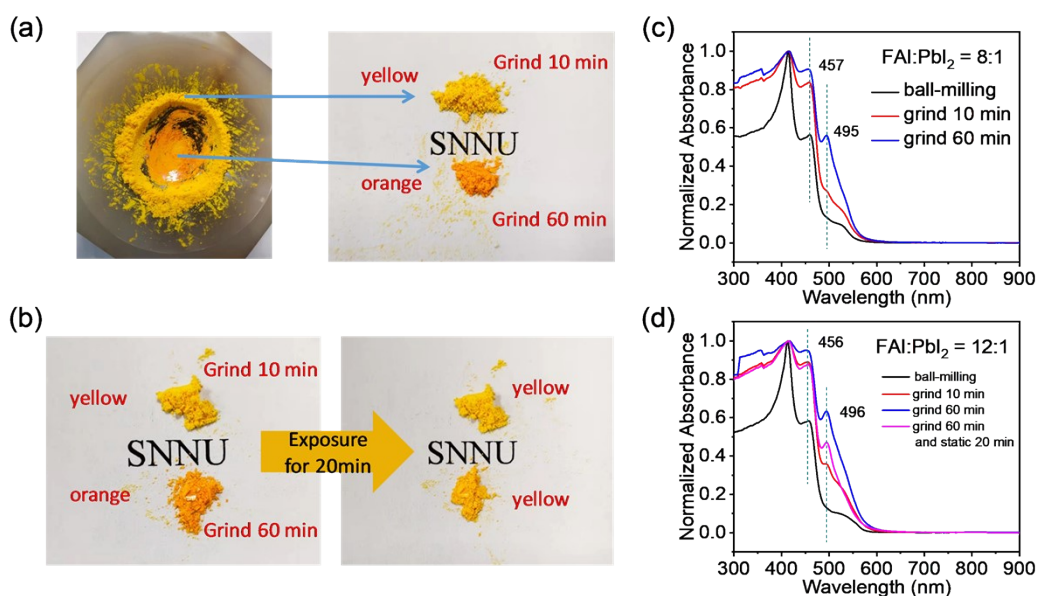


Fig. S3 (a, b) The photos and corresponding. (c, d) UV-Vis spectra of $\text{FA}_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ powders fabricated using ball-milling from $\text{FAI}:\text{PbI}_2$ powders with molar ratio of 8:1 and

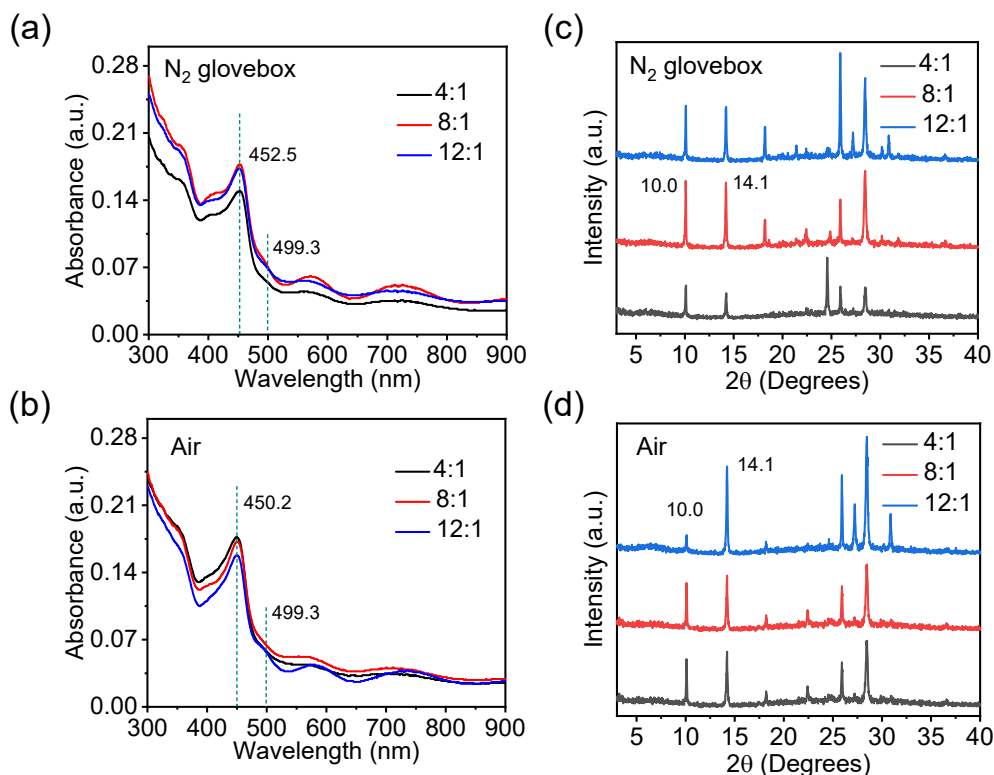


Fig. S4 (a) and (b) UV-Vis spectra of $\text{FA}_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ films prepared using one-step spin-coating from DMSO solvent in inert conditions and under ambient conditions, respectively. (c) and (d) XRD patterns of $\text{FA}_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ films prepared using one-step spin-coating from DMSO solvent in inert conditions and under ambient conditions, respectively.

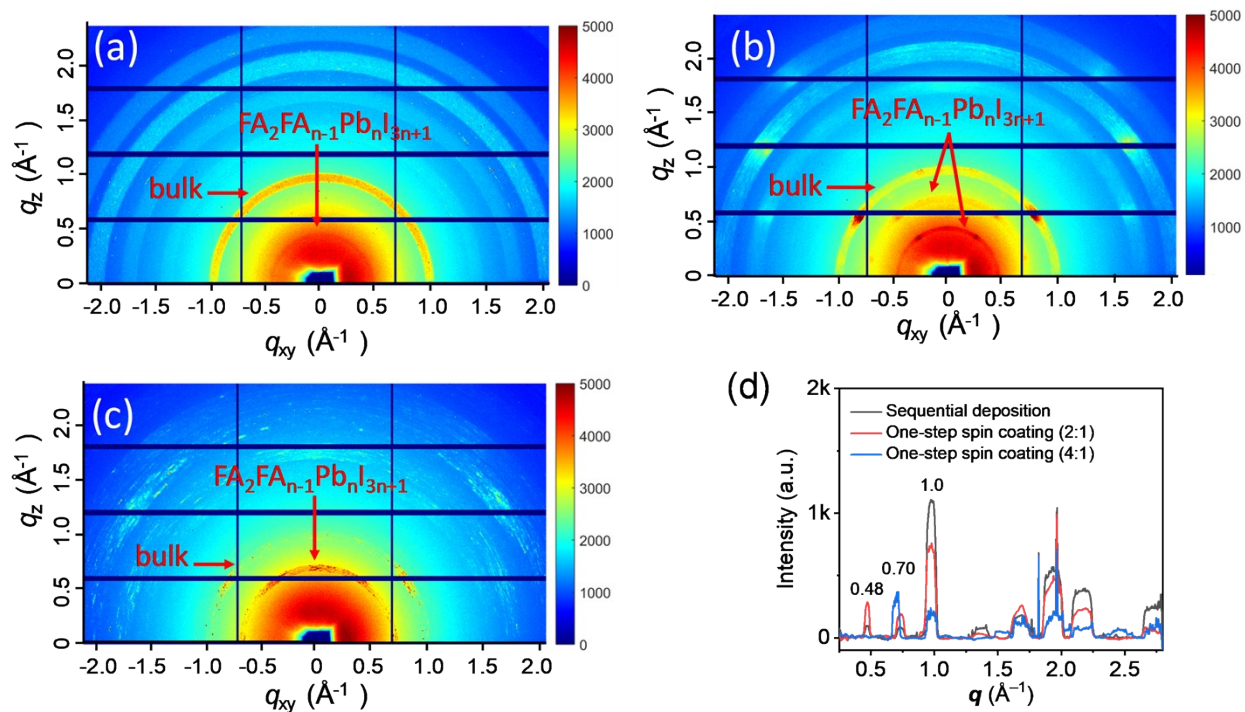


Fig. S5 GIWAXS 2D images for (a) $\text{FA}_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ films prepared via two-step sequential deposition of PbI_2 (ca. 400 nm) and FAI 0.6 mol L^{-1} , (b) $\text{FA}_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ films prepared from FAI: PbI_2 (2:1 molar ratio) from DMSO via one-step spin-coating, (c) $\text{FA}_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ films prepared from FAI: PbI_2 (4:1 molar ratio) from DMSO via one-step spin-coating. (d) Corresponding line-profiles of 2D GIWAXS images for the three films.

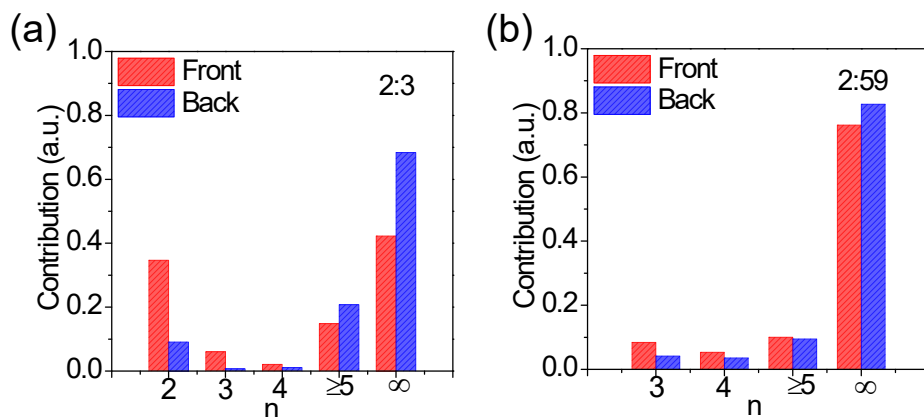


Fig. S6 The composition of QWs in the (a) 2:3 and (b) 2:59 films estimated from the TA spectroscopy with 0.54 ps delay time.

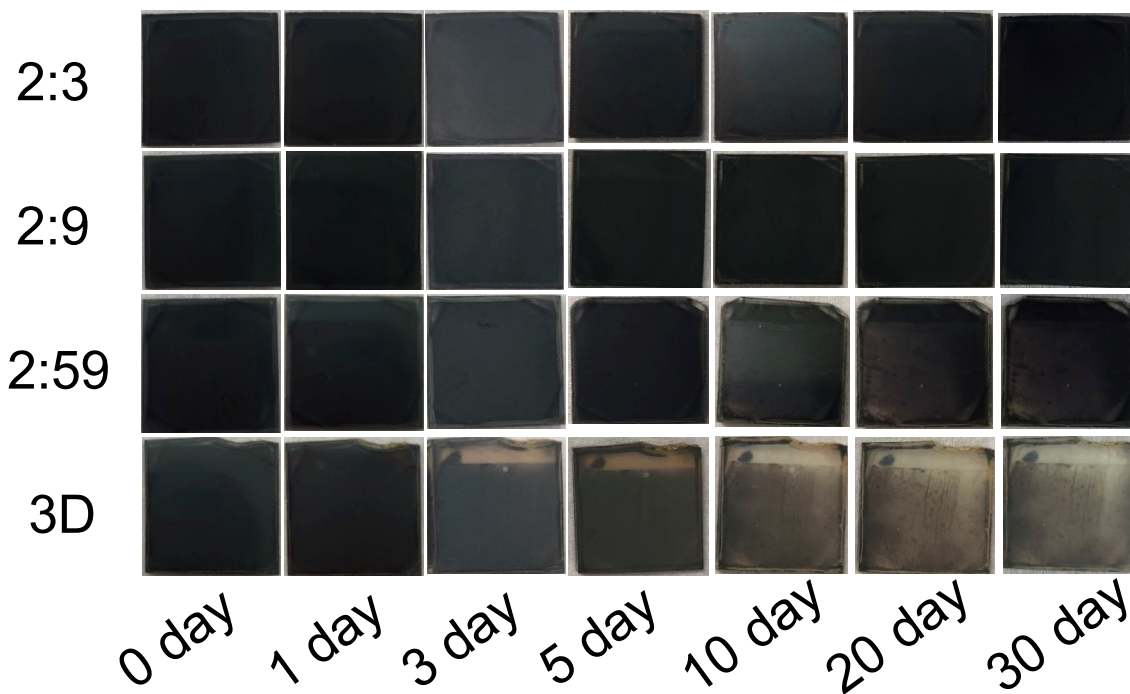


Fig. S7 Photographs of 2:3, 2:9, 2:59 and 3D films after aging under ambient 40-50% relative humidity at room temperature for 30 days.

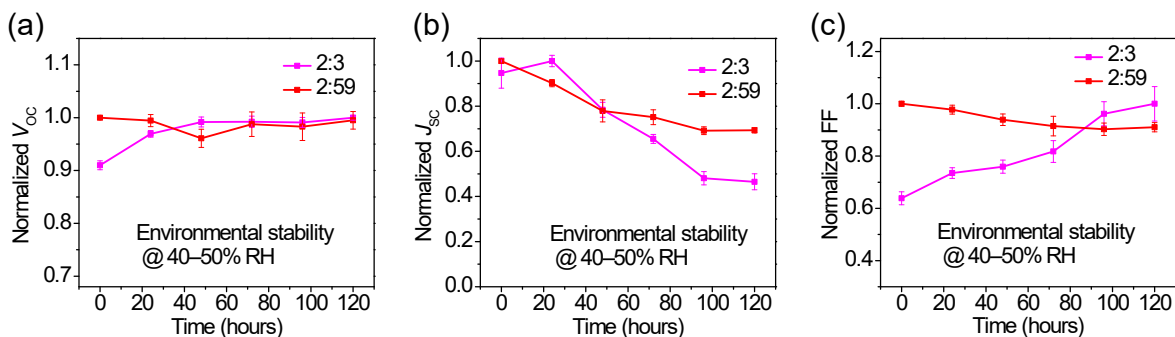


Fig. S8 Environmental stability of devices parameters (a) V_{OC} , (b) J_{SC} and (c) FF, under ambient about 40-50% relative humidity at room temperature.

Table S1 The phases detected as a function of the proportion of FA⁺ in the synthesis and their main characteristic diffraction peaks and excitonic peaks. FA₂FA_{n-1}Pb_nI_{3n+1} films prepared via two-step sequential deposition of PbI₂ (ca. 400 nm) and various concentrations of FAI.

FAI (mol L ⁻¹)	phases detected			XRD Diffraction peaks				UV-Vis (nm)	
	δ -FAPbI ₃	PbI ₂	α -FAPbI ₃	FA ₂ FA _{n-1} Pb _n I _{3n+1}	δ -FAPbI ₃	PbI ₂	α -FAPbI ₃	FA ₂ FA _{n-1} Pb _n I _{3n+1}	
0.1	☺	☺	☺		11.8	12.8	14.1		
0.2	☺	☺	☺		11.8	12.8	14.1		
0.3		☺	☺	n=2		12.8	14.1	6.7	788, 497
0.4		☺	☺	n=2, n=1		12.8	14.1	6.7, 10.0	788, 497, 450
0.5		☺	☺	n=2, n=1		12.8	14.1	6.7, 10.0	788, 497, 450
0.6		☺	☺	n=2, n=1		12.8	14.1	6.7, 10.0	788, 497, 450

Table S2 Fitting parameters for time-resolved photoluminescence of perovskite films on glass substrate.

	τ_1 (ns)	Intensity τ_1 (%)	τ_2 (ns)	Intensity τ_2 (%)	average τ (ns)
2:3	3.8	18.6	36.4	81.4	30.3
2:9	5.5	2.0	84.0	98.0	82.4
2:59	12.6	0.9	296.9	99.1	294.4

Table S3 PV performance parameters of perovskite solar cells in all conditions.

		V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
2:3	average	1.11±0.02	16.87±1.77	45.36±5.1	8.46±0.87
	max	1.14	17.55	51.95	10.36
2:9	average	1.09±0.01	21.84±0.97	54.06±2.41	12.81±0.55
	max	1.08	23.42	55.12	14.00
2:59	average	1.06±0.02	24.51±0.57	67.50±2.00	17.46±0.73
	max	1.07	25.04	71.98	19.33