

Supporting Information

Strain Relaxation and Phase Regulation in Quasi-2D Perovskites for Efficient Solar Cells

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Experimental Section

Materials: All solvents were purchased from Sigma-Aldrich except special state. PEA ($\geq 98\%$), iso-BAI ($\geq 98\%$) were purchased from Aladdin. HI (analytical reagent, $\geq 57\%$) and PEI were purchased from Sigma-Aldrich., MAI ($\geq 99.5\%$), PTAA (Mw = 6000–15000 by GPC), PC₆₁BM ($\geq 99\%$) were both purchased from Xi'an Polymer Light Technology Corp. Pbl₂ (99.999%) was purchased from TCI. Synthesis of Organic Ammonium Cations: F-PEAI was prepared by mixing stoichiometric quantity amounts of PEA and HI in 1:1.2 under ice bath condition and stirring for 2 h. Then, the solution was evaporated in a solvent to obtain yellow power. The powder was subsequently washed by diethylether and recrystallized in ethanol for three times to obtain white power. Finally, the white power was dried under vacuum conditions at 60 °C overnight.

Preparation of Perovskite Solutions: (F-PEA_xiso-BA_{1-x})₂MA₃Pb₄I₁₃ based perovskite precursor solution was prepared by dissolving MAI (0.75 mmol), Pbl₂ (1.0 mmol), F-PEAI (0.5x mmol), iso-BAI (0.5(1-x) mmol), MAcl (0.1 mmol), and PbCl₂ (0.1 mmol) in 0.95 mL DMF and 0.05 mL DMSO mixture solvent and stirred at 60 °C overnight before using.

Device Fabrication: The device structure is ITO/PTAA/Q-2D perovskite/PC₆₁BM/PEI/Ag. The detailed experiment processes are as follows: ITO glass substrates were first treated with ultra-sonication in detergent, acetone, isopropanol, and ethanol, followed by UV-ozone for 15 min after drying in N₂ stream. PTAA with 4 mg/mL in CB solvent was spin-coated at 5000 rpm for 40 s on cleaned ITO substrate (thickness ~20 nm), then dried at 100 °C for 10 min. The perovskite solutions were dropped on 80 °C preheated ITO/PTAA substrates and spin-coated at 5000 rpm for 70 s (thickness increases from ~463 to ~650 nm with increasing F-PEA content). PC₆₁BM (25 mg/mL in CB solvent) was spin coated at 2000 rpm for 60 s on the surface of perovskite films (thickness ~76 nm). Then, the perovskite and PC₆₁BM bilayer films were annealed at 100 °C for 10 min and remained for 1 h at room temperature. PEI (0.7 mg/mL in isopropyl alcohol (IPA)) was spin-coated at 5000 rpm for 30 s before thermal

evaporation. Finally, Ag electrode (120 nm) was thermally evaporated at a base pressure of 3.0×10^{-4} Pa at a growth rate of 1 Å/s. The active area for the PSCs is 0.04 mm², defined using a shadow mask.

Film and Device Characterizations: For Q-2D perovskite films, the X-ray diffraction (XRD) patterns were measured by using a Bruker D8 advance diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). UV–vis absorption spectral was measured by using SHIMADZU-UV-2600. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images were collected by using FEI Inspect F50 electron microscope and Thermo Fisher Scientific Escalab 250Xi system. GIWAXS measurements were conducted on beamline 7.3.3 at Advanced Light Source, Lawrence Berkeley National Laboratory. Transient absorption measurements (infrared) were performed using a Helios setup. The transient dynamics in fs–ns time region (50 fs~7 ns) was acquired by Helios that works in a nondegenerate pump-probe configuration. 800 nm wavelength laser pulses were from the regenerative amplifier's output while 400 nm wavelength laser pulses were obtained with a BBO doubling crystal. A mode lock Ti-sapphire oscillator (Coherent Vitesse, 80 MHz) was used to seed the amplifier. For 800 nm pump, the laser from the regenerative amplifier was directly used. The probe pulses were a white light continuum generated by passing the 800 nm fs pulses through a sapphire plate for the infrared part (420–780 nm). The time-of-flight secondary-ion mass spectrometry (TOF-SIMS) spectra were recorded on a TOF-SIMS V instrument (Ion-TOF, GmbH, Germany) to track the depth distributions of iso-BA⁺, F-PEA⁺, Pb²⁺, MA⁺ and In³⁺ from the top of the perovskite down to the ITO substrate. Dual beam depth profiling used a pulsed 30 keV Bi³⁺ liquid metal ion gun as a primary ion source and a 10 keV argon gas cluster ion beam with the beam current being lowered to 1 nA as a sputtering ion source in an interlaced mode. Grazing incident angle X-ray diffraction (GIXRD) was performed on D8-discover 25 diffractometer (PANalytical). The initial incident angle φ of GIXRD is selected as 5°. For the PSCs, *J*–*V* curves of the devices were measured using Keithley 2400 source meter interfaced with a xenon lamp (Newport) at 100 mW/cm² under the AM 1.5G condition. The external quantum

efficiency (EQE) spectra were measured using a QTEST HIFINITY 5 (Crowntech Inc., USA).

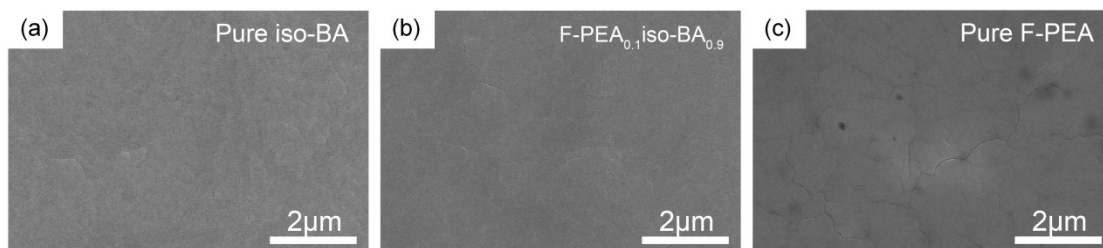


Figure S1 Top-view SEM images of Pure iso-BA, iso-BA:F-PEA and Pure F-PEA based quasi-2D perovskite films.

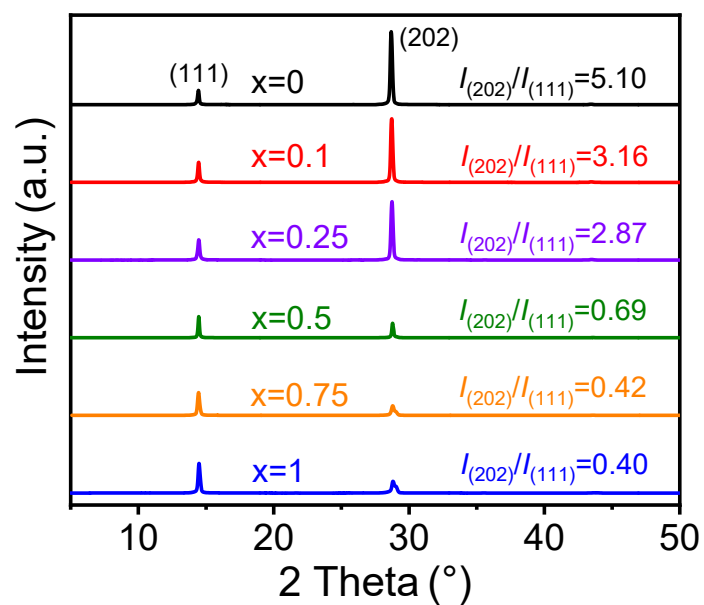


Figure S2 XRD patterns of $(\text{F-PEA}_x\text{iso-BA}_{1-x})_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ ($n = 4$) with different spacer cation ratio.

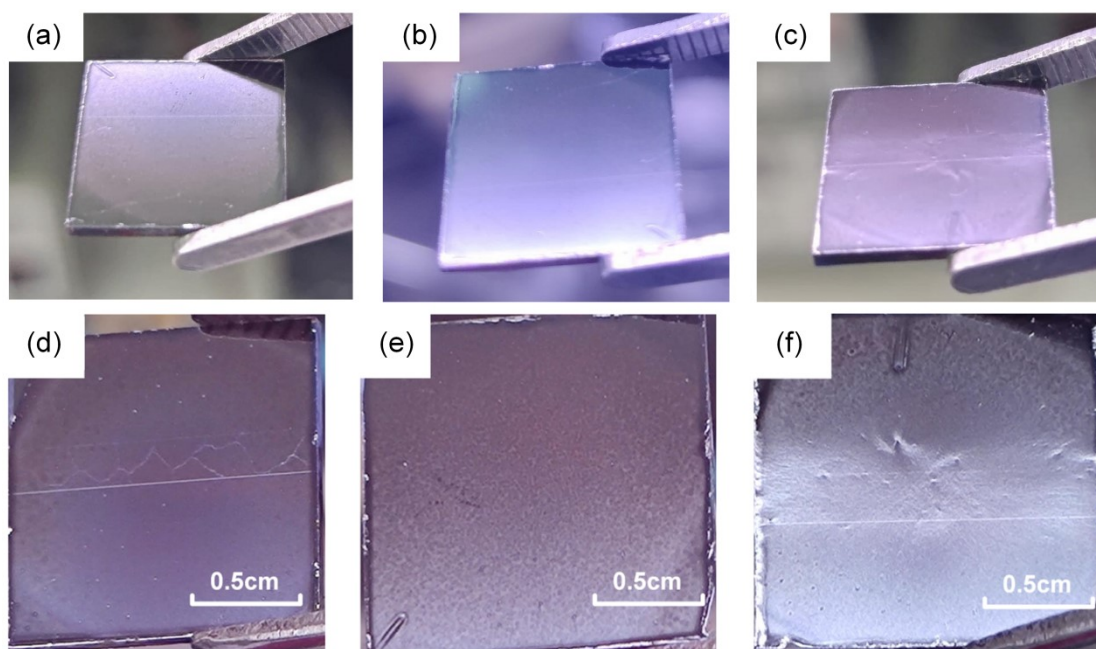


Figure S3 Different perovskite film morphology from (a,d) Pure iso-BA, (b,e) iso-BA:F-PEA, (c,f) Pure F-PEA on PTAA (a-c) w/ and (d-f) w/o coating CB.

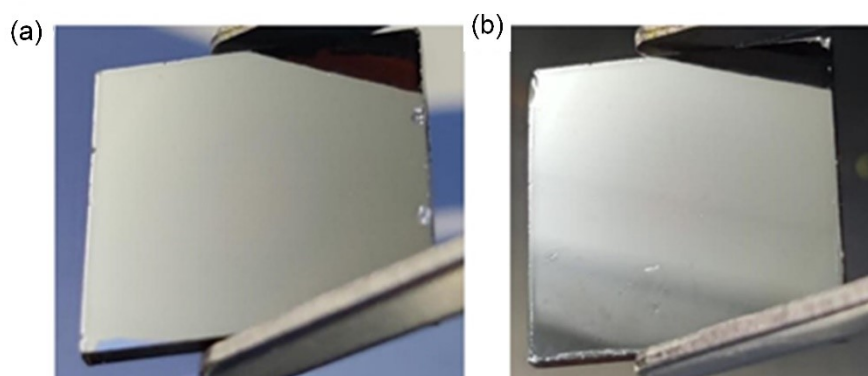


Figure S4 Photographs of the ITO/PEDOT:PSS/(iso-BA)₂MA₃Pb₄I₁₃ films (a) before and (b) after spin coating CB on top of the film.

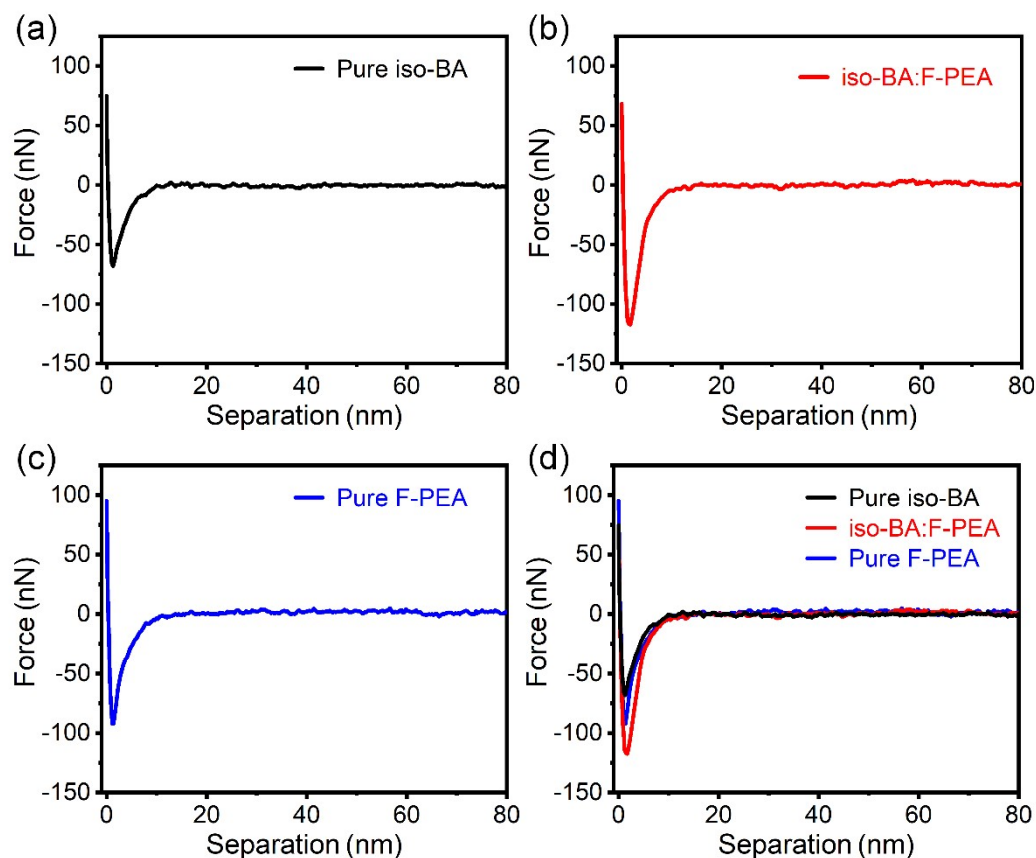


Figure S5 PFYQ-AFM force curves of different perovskite films. Fit the falling part of the force curve to obtain the corresponding Young's modulus of each film which showed in Table S1.

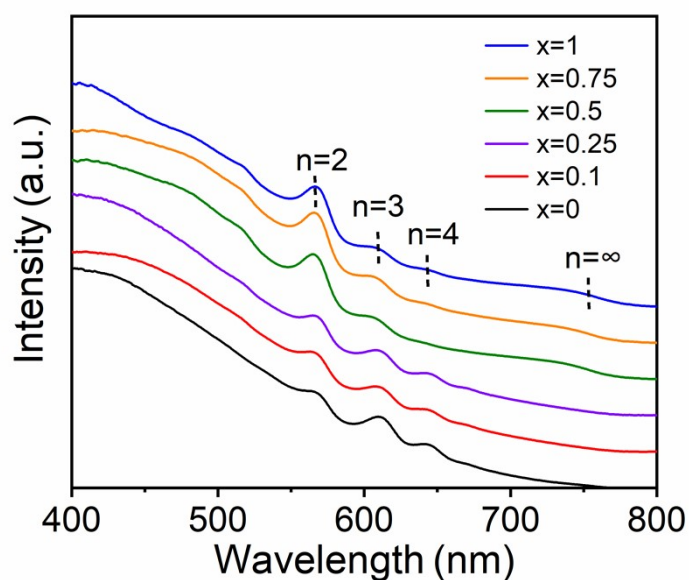


Figure S6 UV-vis absorptions of the $(\text{F-PEA}_x \text{iso-BA}_{1-x})_2 \text{MA}_3 \text{Pb}_4 \text{I}_{13}$ -based quasi-2D perovskite films. The thicknesses of pure iso-BA, $(\text{iso-BA})_{1-x}(\text{F-PEA})_x$ ($x = 0.1, 0.25, 0.5$)

and 0.75), and pure F-PEA based perovskite films are 463 ± 20 nm (pure iso-BA), 559 ± 26 nm ($x = 0.1$), 563 ± 37 nm ($x = 0.25$), 598 ± 19 nm ($x = 0.5$), 623 ± 22 nm ($x = 0.75$), and 650 ± 36 nm (pure F-PEA), respectively.

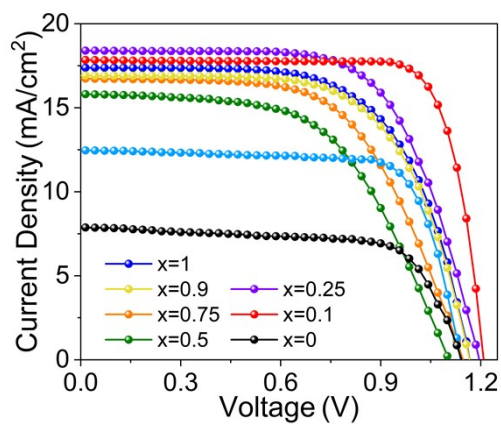


Figure S7 J - V curves of the $(\text{F-PEA}_x \text{iso-BA}_{1-x})_2 \text{MA}_3 \text{Pb}_4 \text{I}_{13}$ based Q-2D PSCs with various x values. The concentration of Pb^{2+} is 1.0 mmol/ml.

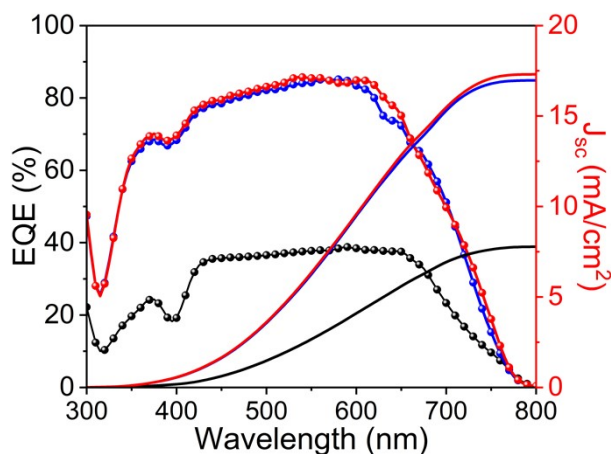


Figure S8 EQE spectra and the integrated J_{sc} of Pure iso-BA- (black), iso-BA:F-PEA (red), Pure F-PEA- (blue) based PSCs.

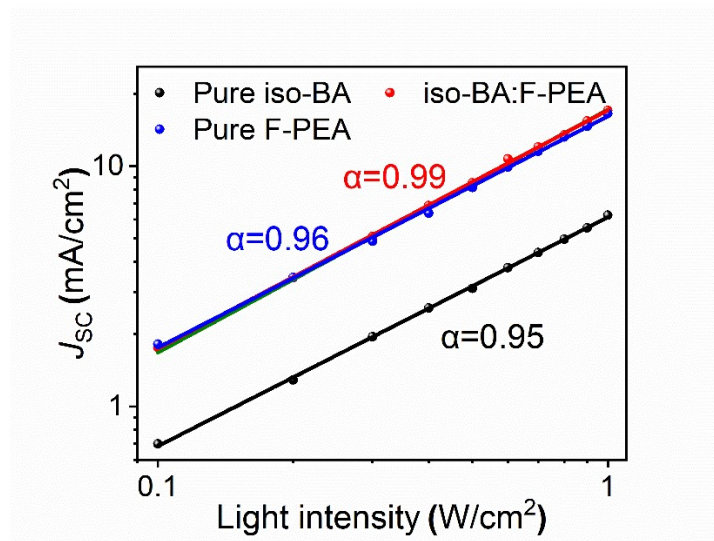


Figure S9 Light-dependent J_{sc} of Pure iso-BA-, iso-BA:F-PEA-, and Pure F-PEA-based PSCs.

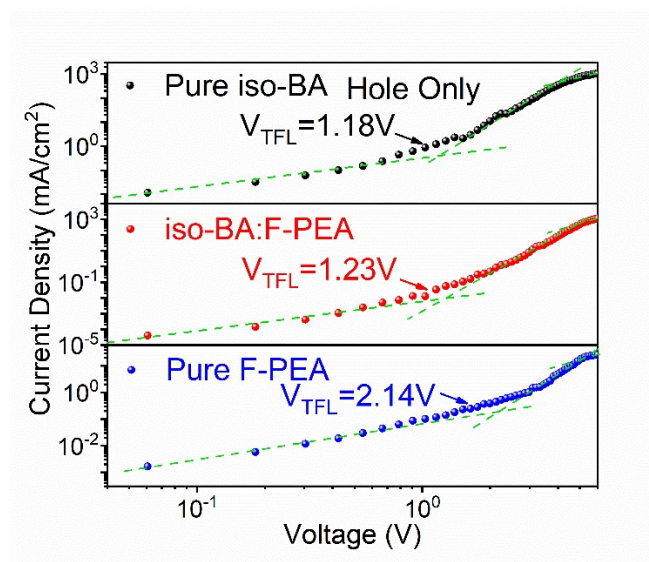


Figure S10 Dark J - V curves of hole-only device based on Pure iso-BA-, iso-BA:F-PEA-, and Pure F-PEA-based perovskite.

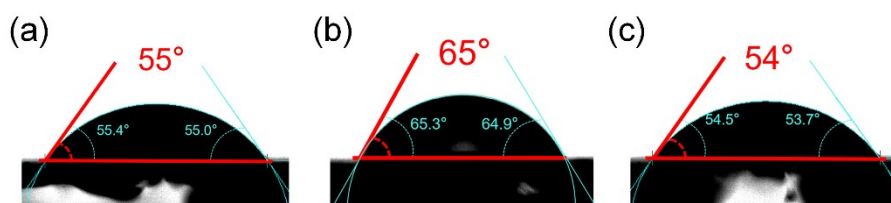


Figure S11 Water contact angle test of (a) pure iso-BA, (b) iso-BA:F-PEA and (c) pure F-PEA based perovskite film.

Table S1 Performance comparison between our devices in this work and other representative iso-BA⁺ based Q-2D PSCs.

	Perovskite materials	Device architecture	PCE	Stability	Article information
1	iso-BA ₂ MA ₃ Pb ₄ I ₁₃ (<i>n</i> = 4)	ITO/C ₆₀ /perovskite/Spiro-OMeTAD/Au	10.63%	Preserve initial color, 840 h, 20 °C, 60% RH	<i>Adv. Energy Mater.</i> , 2017, 7 , 1700162
2	iso-BA ₂ MA ₃ Pb ₄ I ₁₃ (<i>n</i> = 4)	ITO/PEDOT:PSS/perovskite/C ₆₀ /BCP/Al	8.22%	NA	<i>Chem. Sci.</i> , 2020, 11 , 12139-12148
3	iso-BA ₂ MA ₄ Pb ₅ I ₁₆ (<i>n</i> = 5)	ITO/m-PEDOT:PSS/perovskite/PC ₆₁ BM/PEIE/Ag	16.0%	91% of initial PCE, 500 h, 1-sun illumination, 40 °C, 30-40% RH (Encapsulated cell)	<i>Commun. Mater.</i> , 2020, 1 , 33
4	iso-BA ₂ MA ₄ Pb ₅ I ₁₆ (<i>n</i> = 5)	ITO/PEDOT:PSS/perovskite/PC ₆₁ BM/BCP/Ag	~15%	NA	<i>Small</i> , 2023, 19 , 2206787
5	(iso-BA _{0.9} F-PEA _{0.1}) ₂ MA ₃ Pb ₄ I ₁₃ (<i>n</i> = 4)	ITO/PTAA/perovskite/PC ₆₁ BM/PEI/Ag	17.17%	85% of initial PCE, 30 days, 25 °C, 40-50% RH (Unencapsulated cell)	<i>This work</i>

Table S2 Young's modulus in (F-PEA_{1-x}iso-BA_x)₂MA₄Pb₅I₁₆ perovskite films ($x = 0, 0.1, 1$).

x	0	0.1
Young's modulus (GPa)	23.065	7.224
	20.504	7.830
	22.454	7.614
	30.998	7.343
	24.146	7.631
	16.858	8.576
	16.602	8.283
	16.057	7.836
	26.048	8.218
	23.423	7.639
Average	22.016	7.819

Table S3 Fitting components from TA kinetics of the (F-PEA_xiso-BA_{1-x})₂MA₃Pb₄I₁₃ based quasi-2D perovskites films.

Table S2-1 Fitting components from TA kinetics of the Pure iso-BA perovskites films

	A_1	$t_{\text{delay},1}$ (ns)	A_2	$t_{\text{delay},2}$ (ns)	t_{delay} (ns)
n=3	0.93	3.51	0.18	63.21	13.2
	A_1	t_{rise} (ns)			
n=∞	-	1.34			

Table S2-2 Fitting components from TA kinetics of the iso-BA:F-PEA perovskites films

	A_1	$t_{\text{delay},1}$ (ns)	A_2	$t_{\text{delay},2}$ (ns)	t_{delay} (ns)
n=3	0.13	0.54	0.02	1.17	0.62
	A_1	t_{rise} (ns)			
n=∞	-	0.56			

Table S3-3 Fitting components from TA kinetics of the Pure F-PEA perovskites films

	A_1	$t_{\text{delay},1}$ (ns)	A_2	$t_{\text{delay},2}$ (ns)	t_{delay} (ns)
n=3	0.29	0.43	0.52	0.51	0.49
	A_1	t_{rise} (ns)			
n=∞	-	0.52			

The kinetics extracted from TA spectra are fitted with multiple-exponential decay function:

$$I(t) = 1/2 \sum_{i=1}^N H_i(t) A_i e^{-\frac{t}{\tau_i}}$$

where t is the probe time delay, $H_i(t) = [1+\text{erf}(-t/r-r/2\tau_i)]$ is the rising function, r (0.1 ps) is the Gaussian laser pulse width, A_i is the amplitude or pre-exponential function, and τ_i is the decay time.

Table S4 Photovoltaic parameters of the quasi-2D PSCs with various value of x in (F-PEA_xiso-BA_{1-x})₂MA₃PbI₁₃.

x value	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
1	1.17	17.38	63.9	12.93
0.9	1.17	16.92	64.1	12.63
0.75	1.15	16.74	59.6	11.44
0.5	1.10	15.82	56.7	9.91
0.25	1.19	18.37	65.4	14.36
0.1	1.21	17.77	79.9	17.17
0	1.14	7.94	69.3	6.28