Supporting Information

A Cocktail of Multiple Cations in Inorganic Halide Perovskite towards Efficient and Highly Stable Blue Light-Emitting Diodes

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Experimental Section

Materials and chemicals: PbCl₂ (99.999%) was purchased from Sigma Aldrich. FABr (99%) and PEABr (99%) were purchased from Borun New Material Technology LTD. CsBr (99.999%), CsCl (99.99%), RbBr (99.999%) and KBr (99.999%) were purchased from Alfa Aesar. LiF (99.99%) and bathophenanthroline (Bphen, 99%) were purchased from Nichem. All chemicals were used as received without further purification.

Preparation of multi-cation perovskite films: The multi-cation perovskite films were all prepared by a facile one-step solution deposition process. Firstly, the multi-cation perovskite precursor solutions were prepared by dissolving 0.35 M PbCl₂ and the corresponding amount of CsBr, CsCl, RbBr, FABr, PEABr, KBr in dimethyl sulfoxide (DMSO, 99.8 wt%, Alfa Aesar) with different molar ratios. Precise ratios of all these precursors were mixed to synthesize mixed halide multi-cation perovskite precursor solutions (see **Table S8** for details). The precursor solutions were continuously stirred in a nitrogen-filled glove box at room temperature for 2 h. And then the solutions were stand for 1 h at room temperature, precipitates were formed in all precursor solutions, and top transparent solutions were decanted for using. For the preparation of the perovskite films, the pre-cleaved glass substrates or indium-tin oxide (ITO)-coated patterned glass substrates were cleaned with deionized water and organic solvents, and then exposed to a UV-ozone ambient for 10 min. Then the aforementioned precursor solutions (about 200 μ L, 70 °C) were spin-coated at 1000 r.p.m for 120 s onto the mentioned substrates (70 °C) and then annealed at 100 °C for 30 min to form the perovskite films in a nitrogen-filled glove box.

Film characterizations: Film thickness of the LiF and TPBi layer was measured by an ellipsometry (SE MF-1000, Korea). The surface of the perovskite films was investigated by scanning electron microscopy (SEM, Quanta 250, FEI). Surface topography of the perovskite films was measured by an atomic force microscope (AFM, NT-MDT, Russia). The crystalline structure of the perovskite films was determined by X-ray diffraction (XRD, D/MAX-2400,

Rigaku, Japan) with Cu Ka radiation. The GIXRD measurements were performed at the BL14B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) using X-ray with a wavelength of 0.6887 Å, and the incident angle is set to be 0.3°. The 2D-GIXRD patterns were analyzed using software Fit 2D and displayed in scattering vector q coordinates with q = $4\pi \sin \theta / \lambda$, where θ is half of the diffraction angle, and λ is the wavelength of incident X-ray. The absorption and PL spectra were obtained by a UV-vis spectrophotometer (HITACHI U-3010, Japan) and a fluorescence spectrometer (Fluoromax-4 spectrofluometer), respectively. Time-resolved PL spectra were recorded with a 100 ps time resolution using a time-correlated single photon counting (TCSPC) system (FLS920 spectrometer) (excited by picosecond pulsed LEDs, pulse duration: <850 ps, repetition rate: 10 MHz). Photoluminescence quantum yield was tested using FLS920 spectrometer with an integrating sphere. The UPS characteristics were carried out by X-ray photoelectron spectroscopy (ESCALAB Xi+, Thermo Fisher Scientific). The ns pulses were delivered by a frequency-doubled Nd:YAG laser (Surelite I, Continuum Corp., USA). Face emission spectra were collected by Fiber Optic Spectrometer (Ocean Optics SpectraSuite, USB2000). The first intersection shown in the integrated PL emission intensity of different perovskite films as a function of pump energy represents the pump energy needed to fill all the traps (i.e., the threshold trap pump energy P_{Trap}). Then the trap state densities of different perovskite films will be $P_{Trap} \times \alpha / _{F}$, where α is the absorption coefficient of the perovskite films, E is the energy of the single photon absorbed by the perovskite films.

Devices Fabrication: To prepare the devices, the indium-tin oxide (ITO)-coated patterned glass substrates were cleaned with deionized water and organic solvents, and then exposed to a UV–ozone environment for 10 min. For the preparation of the PeLEDs with the structure of Glass/ITO/LiF (3 nm)/perovskite layer/LiF (8 nm)/Bphen (60 nm)/LiF (1 nm)/Al (100 nm), except the perovskite films, the rest of the layers were sequentially deposited in a vacuum

chamber at a rate of about 0.5 Å/s under a base pressure of 1×10^{-3} Pa. Film thickness was determined in-situ by a quartz-crystal sensor and confirmed by a profilometer. Emission area of the devices was about 12 mm². The experiments were carried out in a nitrogen-filled glove box or a thermal evaporation chamber without air exposure for the whole device preparation process.

Devices Characterization: The luminance-current-voltage (*L-I-V*) characteristics of the devices were measured using a computer-controlled sourcemeter (Keithley 2602) and a calibrated silicon photodiode. Electroluminescence spectra were measured using a PR650 spectrometer. For the stability of the PeLED devices, the lifetime (50% decay) was measured with 3 mA constant current under continuous operation supplied by Keithley 2602. All measurements were carried out at room temperature in a glove box with 99.999% N₂ atmosphere to protect the devices from degradation by moisture and oxygen in atmospheric environment.

The luminance (cd/m²) was directly measured using a computer-controlled sourcemeter (Keithley 2602) and a calibrated silicon photodiode (integrated over 1 s). The current density (mA/cm²) was calculated by dividing the current (mA) flowing in the device by the effective area (about $3.4 \times 3.3 \text{ mm}^2$). The current efficiency (cd/A) was calculated by dividing (the luminance (cd/m²) × the effective area) by the current *I* (A). The external quantum efficiency (*EQE*) is the ratio between the number of photons emitted from the device and the electrons injected into the device. Thus, the EQE will be:

$$EQE = \frac{\sum_{\lambda(nm)} \frac{\Phi}{hc/\lambda}}{I \times e}$$

where, Φ is the total spectral power, *h* is the Planck constant, *c* is the speed of light, λ is the EL wavelength and *e* is the unit charge.



Figure S1. PL spectra of (Cs/Rb)Pb(Cl/Br)₃ films with different Cs/Rb ratio (Cs: Rb= 1: 0, 1: 0.1, 1:







(Cs/PEA)Pb(Cl/Br)₃ film.



Figure S4. The UV-Vis measurements of the different dual-cation perovskite films.



Figure S5. Elemental maps of the corresponding element distribution (Cs, Rb, Pb, Rr and Cl) in the optimized (Cs/Rb/FA/PEA/K)Pb(Cl/Br)₃ film.



Figure S6. UV-Vis spectra of different multi-cation APb(Cl/Br)₃ perovskite films.



Figure S7. UPS measurements of the multi-cation APb(Cl/Br)₃ perovskite films.



Figure S8. PL decay curves of the multi-cation APb(Cl/Br)₃ perovskite films.



Figure S9. XRD patterns of the multi-cation APb(Cl/Br)₃ perovskite films.



Figure S10. SEM images of different multi-cation APb(Cl/Br)₃ perovskite films.



Figure S11. (a) PL spectra and (b) PL decay measurements of (Cs/Rb/FA/PEA/K)Pb(Cl/Br)₃ perovskite film deposited on ITO substrate (black line) and ITO/LiF (3 nm) substrate (red line), respectively.



Figure S12. EL spectra of different devices based on multi-cation APb(Cl/Br)₃ perovskite films.



Figure S13. The normalized EL spectra of Device 5 with (Cs/Rb/FA/PEA/K)Pb(Cl/Br)₃ perovskite film after continuously operated at 25 mA/cm² for a period of time.



Figure S14. The change of EL peak position and FWHM of Device 5 with (Cs/Rb/FA/PEA/K)Pb(Cl/Br)₃ perovskite film when bias increases from 4 V to 14 V.



Figure S15. The digital photographs of the operating Device 1-4 based on perovskite films of CsPb(Cl/Br)₃, (Cs/Rb)Pb(Cl/Br)₃, (Cs/Rb/FA)Pb(Cl/Br)₃ and (Cs/Rb/FA/PEA)Pb(Cl/Br)₃, respectively.

Sample	PL peak	FWHM	PLQY	RMS	Coverage	Grain size
(A =)	(nm)	(nm)	(%)	(nm)	(%)	(nm)
Cs	473	31	0.94	113	62	250-1100
Cs/Rb	470	20	2.19	13.3	88	50-110
Cs/K	484	18	1.31	62.6	72	200-550
Cs/FA	484	26	1.61	32.2	70	140-450
Cs/PEA	471	27	2.04	25.7	95	100-330
Cs/Rb/K	479	21	6.51	12.1	94	45-130
Cs/Rb/FA	484	20	5.20	13.1	95	50-150
Cs/Rb/PEA	477	20	7.82	6.7	98	35-100
Cs/Rb/FA/K	476	19	8.88	16.5	88	70-220
Cs/Rb/PEA/K	465	21	14.5	24.3	100	120-300
Cs/Rb/FA/PEA	484	22	12.6	7.5	98	50-120
Cs/Rb/FA/PEA/K	484	24	17.1	6.9	100	35-90

Table S1. Detailed film performance parameters of the prepared APb(Cl/Br)₃ perovskite films.

Table S2. PL lifetime obtained from fitted time-resolved PL decay data of the APb(Cl/Br)₃ perovskite films.

Sample (A =)	τ_1 (ns)	f ₁ (%)	τ_2 (ns)	f ₂ (%)	χ^2	τ_{ave} (ns)
Cs	0.42	18.35	4.32	81.65	1.238	3.61
Cs/Rb	1.42	48.98	8.56	51.02	1.221	5.09
Cs/K	1.56	61.07	10.37	38.93	1.461	5
Cs/FA	2.13	68.52	9.72	31.48	1.228	4.48
Cs/PEA	0.92	37.73	4.83	62.27	1.191	3.34
Cs/Rb/K	2.37	26.52	11.49	73.48	1.153	9.17
Cs/Rb/FA	1.75	36.61	8.54	63.39	1.097	6.05
Cs/Rb/PEA	1.89	29.28	10.15	70.72	1.122	7.76
Cs/Rb/FA/K	2.35	22.92	11.17	77.08	1.254	9.18
Cs/Rb/PEA/K	2.41	17.53	13.51	82.47	1.113	11.5
Cs/Rb/FA/PEA	2.08	22.65	13.85	77.35	1.050	11.14
Cs/Rb/FA/PEA/K	2.61	20.80	15.64	79.20	0.995	11.36

Table S3. PL lifetime of different APb(Cl/Br)₃ perovskite films with or without K.

Sample	$ au_{\mathrm{ave}}\left(\mathrm{ns} ight)$				
(A =)	without K	With K			
Cs	3.61	5			
Cs/Rb	5.09	9.17			
Cs/Rb/FA	6.05	9.18			
Cs/Rb/PEA	7.76	11.5			
Cs/Rb/FA/PEA	11.14	11.36			

Sample	$ au_{\rm ave}$ (ns)				
(A =)	without FA	With FA			
Cs	3.61	4.48			
Cs/Rb	5.09	6.05			
Cs/Rb/K	9.17	9.18			
Cs/Rb/PEA	7.76	11.14			
Cs/Rb/PEA/K	11.5	11.36			

Table S4. PL lifetime of different APb(Cl/Br)₃ perovskite films with or without FA.

Table S5. PL lifetime of different APb(Cl/Br)₃ perovskite films with or without PEA.

Sample	$ au_{\rm ave}$ (ns)				
(A =)	without PEA	With PEA			
Cs	3.61	3.34			
Cs/Rb	5.09	7.76			
Cs/Rb/K	9.17	11.5			
Cs/Rb/FA	6.05	11.14			
Cs/Rb/FA/K	9.18	11.36			

Table S6. The band parameters calculated from UPS measurement of different APb(Cl/Br)₃ perovskite films in Figure S9.

Sample (A =)	E _{Cutoff} (eV)	E _{Fermi} (eV)	Eg (eV)	E _V (eV)	E _C (eV)
Cs	16.85	1.69	2.62	6.06	3.44
Cs/Rb	18.35	3.13	2.64	6.0	3.36
Cs/Rb/FA	17.08	1.71	2.56	5.85	3.29
Cs/Rb/FA/PEA	18.11	2.65	2.56	5.76	3.20
Cs/Rb/FA/PEA/K	16.87	1.31	2.56	5.66	3.10

Emitting materials	EL peak (nm)	Max. CE (cd/A)	Max. EQE (%)	Max. Luminance (cd/m ²)	Device Stability	Ref.
$\begin{array}{c} EA_2MA_{n-1}Pb_nBr_{3n+1}\\ film \end{array}$	473, 485	/	2.6	200	$L_0=200 \text{ cd/m}^2$, $T_{50}=10-20 \text{ min}$	[1]
CsPbBr _x Cl _{3-x} QDs	470	0.18	0.07	350	N/A	[2]
CsPbBr _x Cl _{3-x} QDs	488	/	1.41	830	N/A	[3]
CsPbBr _x Cl _{3-x} QDs	490	~3	1.9	35	N/A	[4]
$\begin{array}{l} BA_2Cs_{n-1}Pb_n(Br/Y)_{3n+1}\\ film \end{array}$	487	~7	6.2	3340	N/A	[5]
$(PEOA)_2(MA)_{n-1}Pb_nBr_{3n+1}$ film	480, 494, 508	2.1	1.1	19.25	N/A	[6]
$\begin{array}{c} BA_2MA_{n-1}Pb_nBr_{3n+1}\\ film \end{array}$	~440, 460, 475	~0.006	0.005	~1	N/A	[7]
$\begin{array}{c} OLA_2MA_{n-1}Pb_nBr_{3n+1}\\ film \end{array}$	432, 480	0.0027	0.004	~1	N/A	[8]
(4-PBA) ₂ PbBr ₄ film	491	/	0.015	186	N/A	[9]
$\begin{array}{c} IPA/PEA_2MA/Cs_{n-1}Pb_nBr_{3n-1}\\ film \end{array}$	490	2.8	1.5	2480	$L_0=10 \text{ cd/m}^2$, $T_{50}=10 \text{ min}$	[10]
$\begin{array}{c} PEA_2Cs_{n-1}Pb_n(Cl_xBr_{1-x})_{3n+1}\\ film \end{array}$	480	6.1	5.7	3780	<i>T</i> ₅₀ =10 min	[11]
$\begin{array}{c} PEA_2(Rb_{0.4}Cs_{0.6})Pb_3Br_{10}\\ film \end{array}$	490	/	1.48	865.3	$L_0=20 \text{ cd/m}^2$, $T_{50}=18.7 \text{ min}$	[12]
PBABr _y (Cs _{0.7} FA _{0.3} PbBr ₃) film	483	12	9.5	700	$L_0=100 \text{ cd/m}^2,$ $T_{50}=250 \text{ s}$	[13]
(Cs/Rb/FA/PEA/K)Pb(Cl/Br) ₃ film	484	2.11	2.01	4015	$L_0=80 \text{ cd/m}^2,$ $T_{50}=300 \text{ min}$	This work

 Table S7. Device performance parameters of blue PeLEDs reported in the literatures.

Sample	PbCl ₂	CsBr	CsCl	RbBr	KBr	FABr	PEABr
(A =)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)
Cs	97.3	89.5	17.6	0	0	0	0
Cs/Rb	97.3	89.5	17.6	28.9	0	0	0
Cs/K	97.3	89.5	17.6	0	20.8	0	0
Cs/FA	97.3	89.5	17.6	0	0	21.9	0
Cs/PEA	97.3	89.5	17.6	0	0	0	35.4
Cs/Rb/K	97.3	89.5	17.6	28.9	4.2	0	0
Cs/Rb/FA	97.3	89.5	17.6	28.9	0	4.4	0
Cs/Rb/PEA	97.3	89.5	17.6	28.9	0	0	14.1
Cs/Rb/FA/K	97.3	89.5	17.6	28.9	4.2	4.34	0
Cs/Rb/PEA/K	97.3	89.5	17.6	28.9	4.2	0	14.1
Cs/Rb/FA/PEA	97.3	89.5	17.6	28.9	0	4.4	14.1
Cs/Rb/FA/PEA/K	97.3	89.5	17.6	28.9	4.2	4.4	14.1

Table S8. Detailed synthesis conditions of the prepared multi-cation APb(Cl/Br)₃ perovskite precursor solutions. All of the precursor amounts are given to make 1 mL of solution in DMSO.

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