

Supporting Information

Stabilizing the Electroluminescence of Halide Perovskites with Potassium Passivation

Anil Kanwat,¹ Natalia Yantara,¹ Yan Fong Ng,^{1,2} Thomas J. N. Hooper,¹ Prem Jyoti

Singh Rana,¹ Benny Febriansyah,¹ Padinhare Cholakkal Harikesh,¹ Teddy Salim,² Parth

*Vashishtha,² Subodh G. Mhaisalkar,^{1,2} and Nripan Mathews^{*1,2}*

¹ Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, 50

Nanyang Drive, Singapore, 637553 Singapore

² School of Materials Science and Engineering, Nanyang Technological University, 50

Nanyang Avenue, Singapore, 639798 Singapore

AUTHOR INFORMATION

Corresponding Author

*Email: nripan@ntu.edu.sg

Films and device Characterization:

The XRD measurements were performed with Bruker D8 Advance X-ray diffractometer using Ni-filtered Cu K α radiation.

The absorption spectra were recorded using UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu) equipped with an integrating sphere.

The steady state PL spectra were measured using Fluoromax-4 (Horiba Jobin Yvon) spectrofluorometer at an excitation wavelength of 350 nm.

The FESEM imaging of perovskite films (on ITO/PEDOT:PSS substrates) was performed using a JEOL JSM-7600F scanning electron microscope at 5-10 kV with a working distance of $\sim$ 8 mm.

A JEOL 2100F was used for the HR-TEM analyses at an accelerating voltage of 200 kV and beam current of 146 μ A. Samples were prepared by spin coating the precursor solution on carbon support copper grids. To collect the HRTEM micrograph, the perovskite samples were exposed not more than 10 seconds to minimize beam damage.

Capacitance–voltage (C–V) measurements were carried out at 200 kHz in Autolab PGSTAT302N. The measurements were done under dark at an AC voltage of 20mV at room temperature.

Auger electron spectroscopy (AES) was performed with a field-emission Auger microprobe (JEOL JAMP-7830F) with a primary electron beam having an accelerating voltage of 10 keV and a probe current of 10 nA. The sample was tilted at 55° throughout the analysis. Auger mapping was collected from an area of 5x5 μ m² corresponding to magnification of 300x, with a dwell time of 5 ms and averaged over 10 accumulations for Cs/Br and 1 accumulation for K. The analyser was operated at a constant retarding ratio (CRR) mode (energy resolution < 0.5%) for both spectroscopy and mapping. The surface composition was determined by considering the peak-to-peak distance of the differentiated Auger spectra and the relative sensitive factor (RSF) for the elements of interest, i.e., K, Cs, and Br.

All solid state NMR experiments in this study were completed on a 14.1 T Bruker Avance III HD 600 MHz spectrometer with a Bruker 4mm HX MAS probe operating at an MAS frequency of 14 KHz. The ¹³³Cs NMR ($\nu_0(^{133}\text{Cs}) = 78.73$ MHz) experiments employed a one-pulse sequence,

utilising a selective $\pi/2$ pulse of 7.5 μs (determined on $\text{CsCl}_{(\text{s})}$) and a recycle delay of 1025 s. The resulting data was referenced with respect to 0.1 M $\text{CsNO}_{3(\text{aq})}$ ($\delta_{\text{iso}} = 0$ ppm). The ^{133}Cs spin-lattice relaxation times (T_1) were determined using a saturation recovery pulse sequence with a 200 pulse saturation pulse train. The ^{207}Pb NMR ($\nu_0(^{207}\text{Pb}) = 125.55$ MHz) experiments employed a Hahn-echo pulse sequence, utilising $\pi/2$ and π pulses of 5.0 and 10.0 μs (determined on 1.1 M $\text{Pb}(\text{NO}_3)_{2(\text{aq})}$), a recycle delay of 10 s, and a rotor synchronised echo delay of 63.9 μs . The resulting data was referenced with respect to 1.1 M $\text{Pb}(\text{NO}_3)_{2(\text{aq})}$ ($\delta_{\text{iso}} = -2965.7$ ppm). The ^{79}Br NMR ($\nu_0(^{79}\text{Br}) = 150.38$ MHz) experiments employed a one-pulse sequence, utilising a selective $\pi/2$ pulse of 3.6 μs (determined on $\text{KBr}_{(\text{s})}$) and a recycle delay of 0.25 s. The resulting data was referenced with respect to 0.01 M $\text{NaBr}_{(\text{aq})}$ ($\delta_{\text{iso}} = 0$ ppm). Spectra simulation was performed using the DMFit software package (Ref. 10.1002/mrc.984).

The electrical poling was performed using the same Keithley 2612B by applying a fixed constant bias (1, 2 and 3 V) for a set duration of 1 min.

All PeLED devices were tested at ambient conditions. The characteristic current density–voltage–luminance (J-V-L) were recorded with a Keithley 2612B source meter and an OceanOptics QE Pro spectrometer connected to an integrating sphere and operated using Ciemo LabVIEW software.

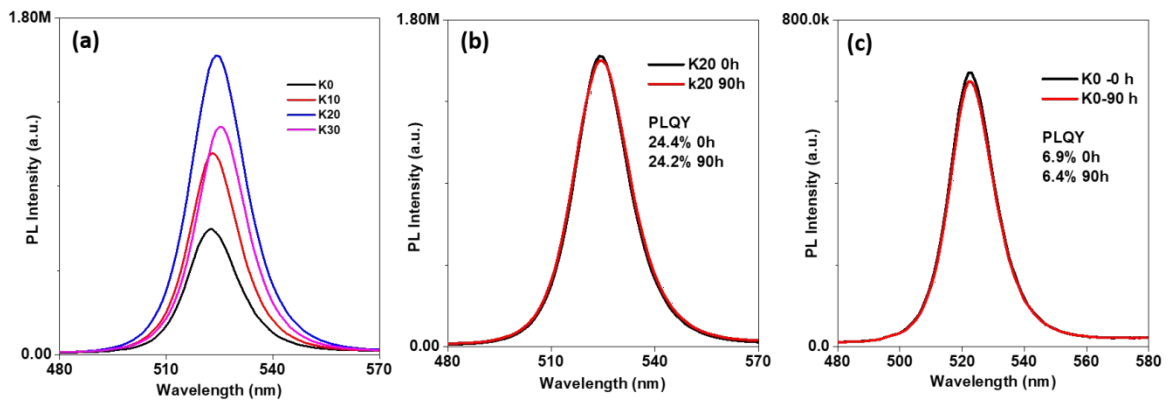


FIG. S1 (a) Photoluminescence intensity with increasing K^+ concentration in KBr mixed $CsPbBr_3$ films; K0, K10, K20, and K30. The PL intensity increases 1.6, 1.8, and 2.4 fold with respect to K0 in K10, K20, and K30, respectively. PL and PLQY stability for 90 hr of (b) K20, and (c) K0 perovskite films.

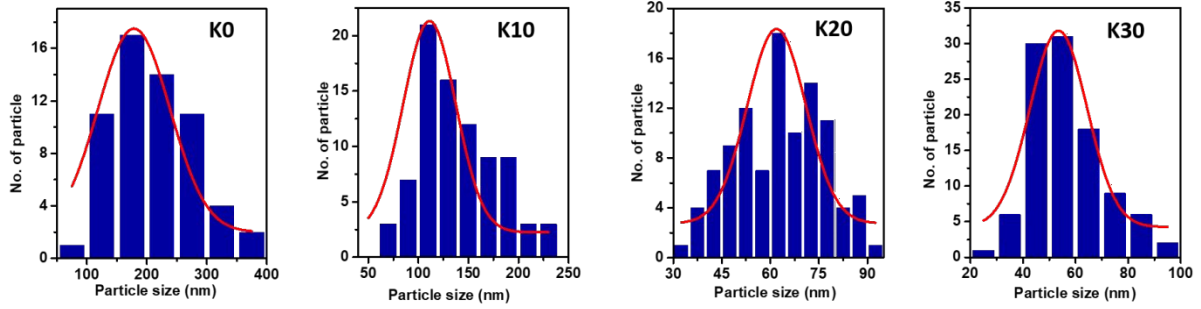


FIG. S2 Histogram of crystallite size calculated from field emission scanning electron microscopy (FIG 2) of perovskite films with increasing KBr concentration; K0, K10, K20, and K30.

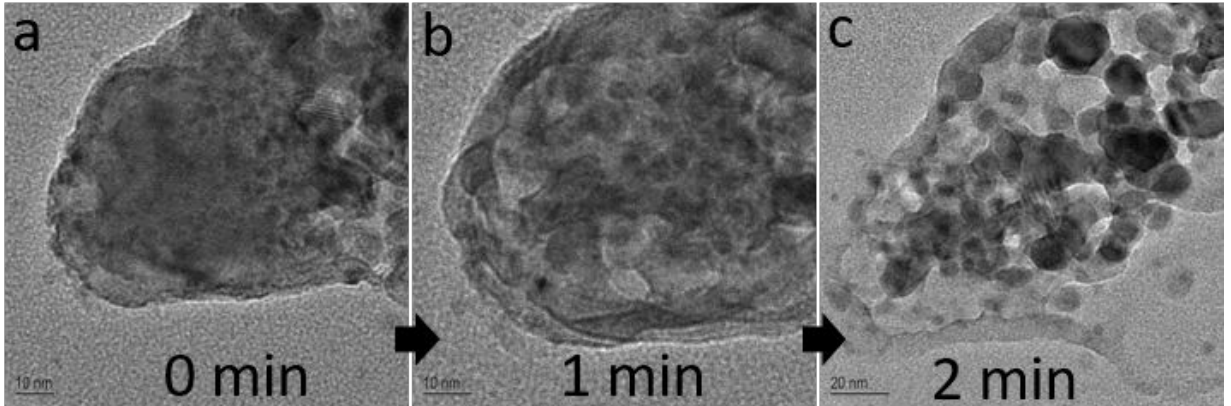


FIG. S3 HR-TEM images of K20 sample with increasing electron beam exposure time on the specimen for (a) 0 min (b) 1 min, and (c) 2 min.

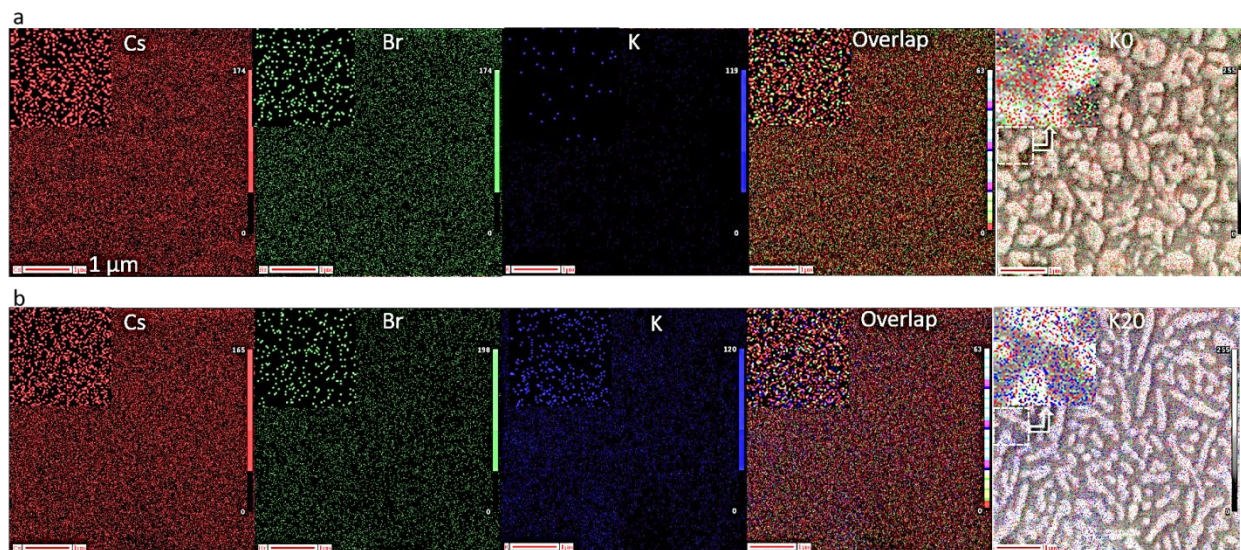


FIG. S4 Auger electron spectroscopy (AES) of (a) K0 (unmodified) and (b) K20 (KBr modified) films. The inset depicts the zoomed AES elemental mapping of Cs, Br, K, and overlapped area of these elements.

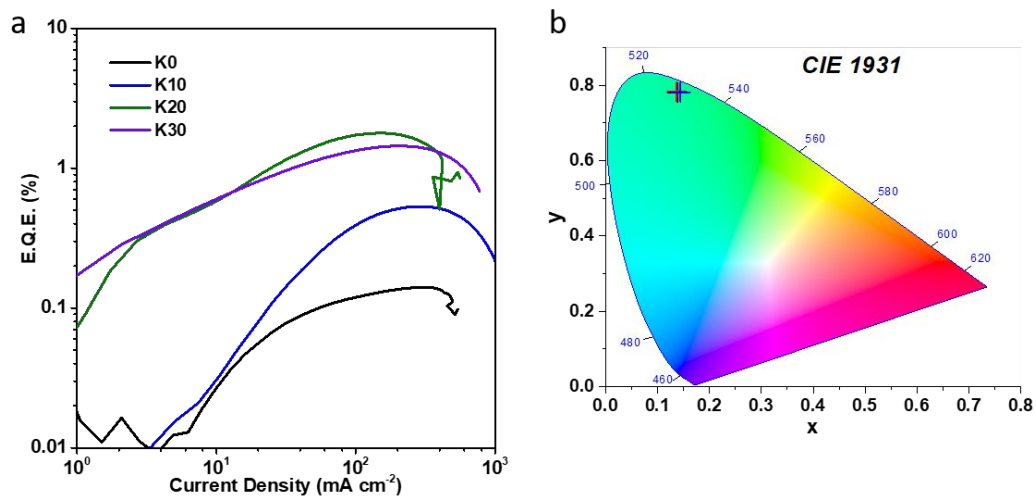


FIG. S5 (a) EQE, and (b) CIE- co-ordinate of PeLEDs with increasing KBr concentration.

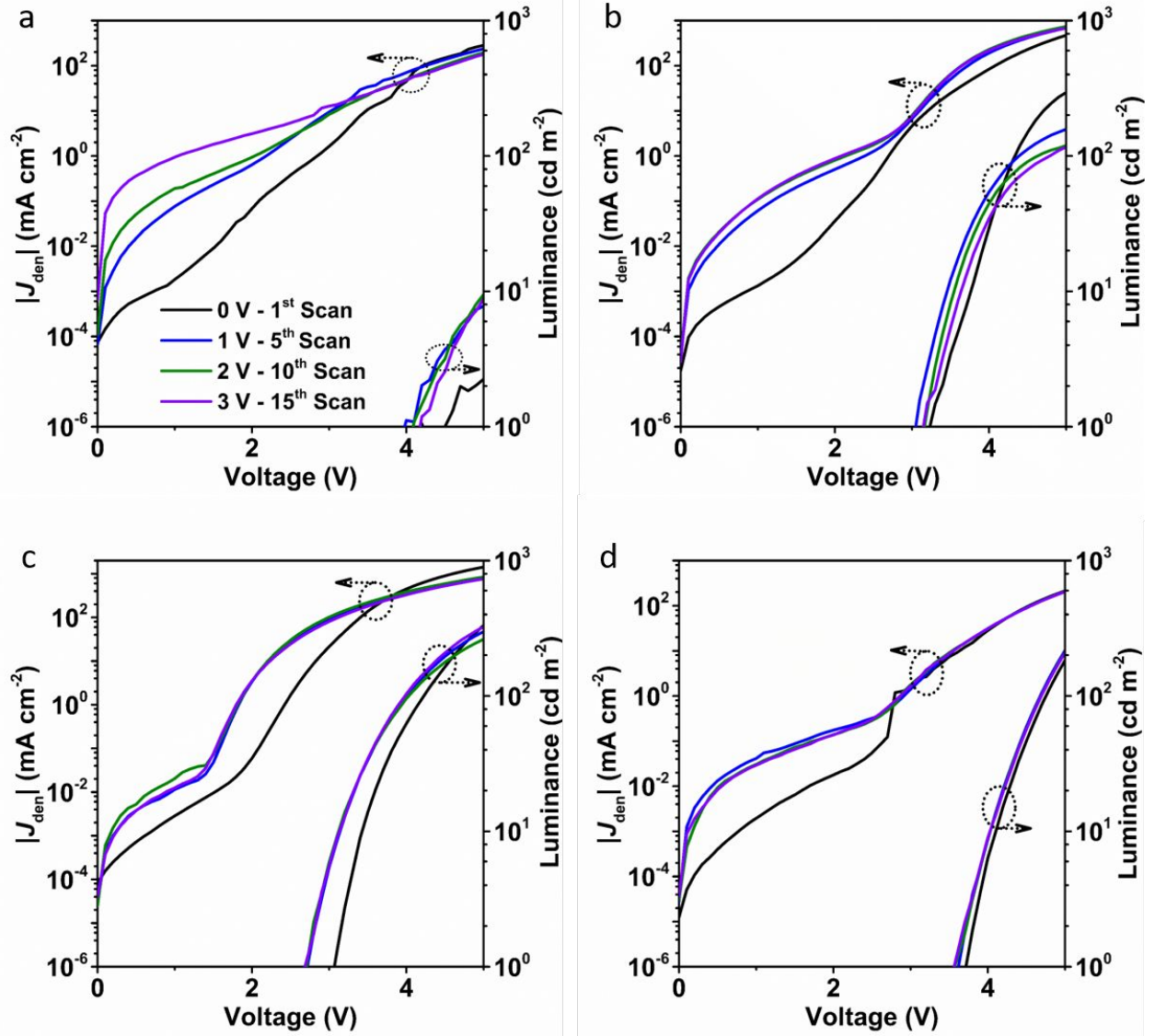


FIG. S6 J-V-L plots before (0) and after electrical poling at 1 V, 2 V, and 3 V with increasing KBr concentration; (a) K0, (b) K10, (c) K20, and (d) K30.

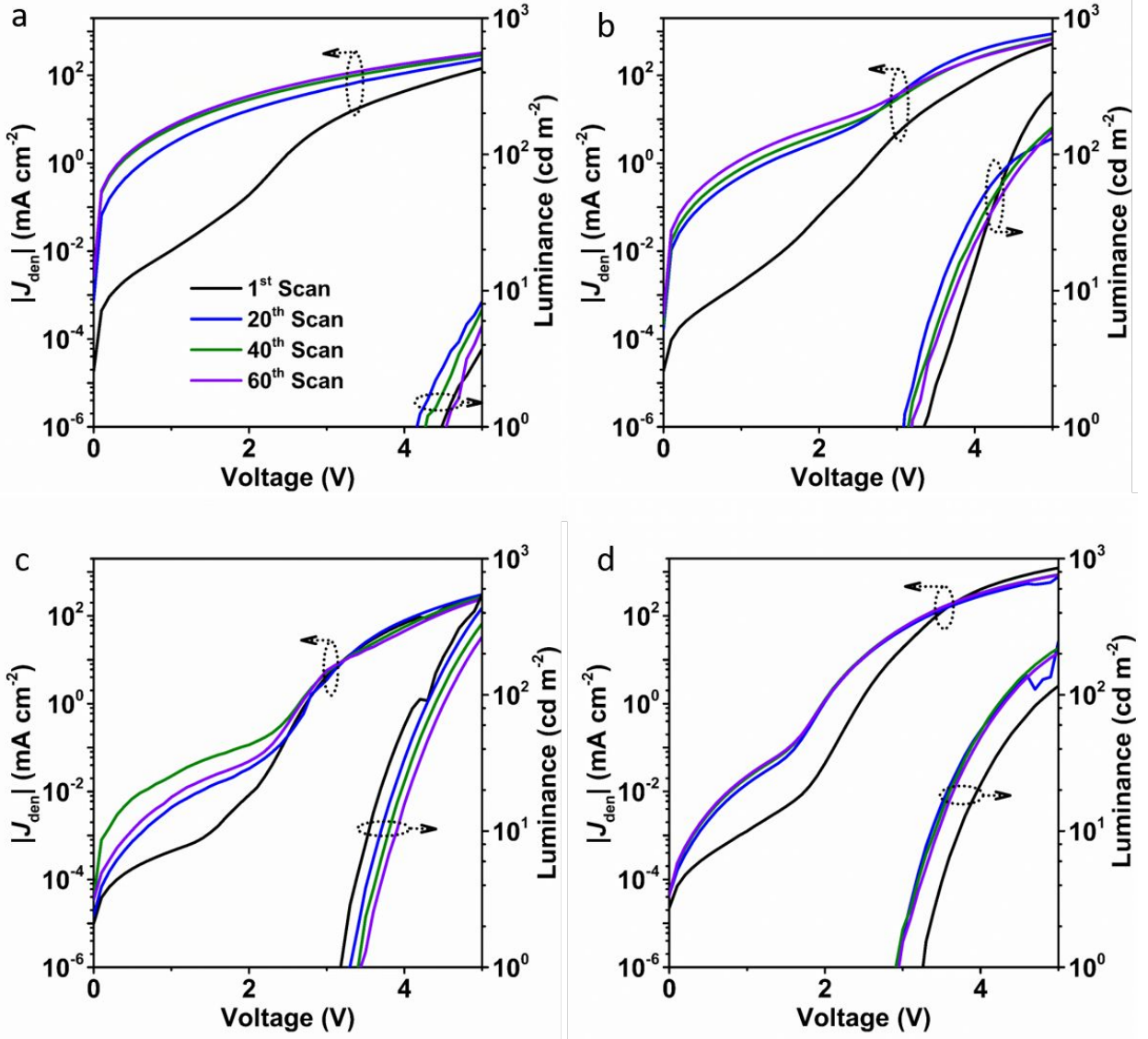


FIG. S7 J-V-L plots with multiple scan of PeLED devices from 0-5V with increasing KBr concentration; (a) K0, (b) K10, (c) K20, and (d) K30.

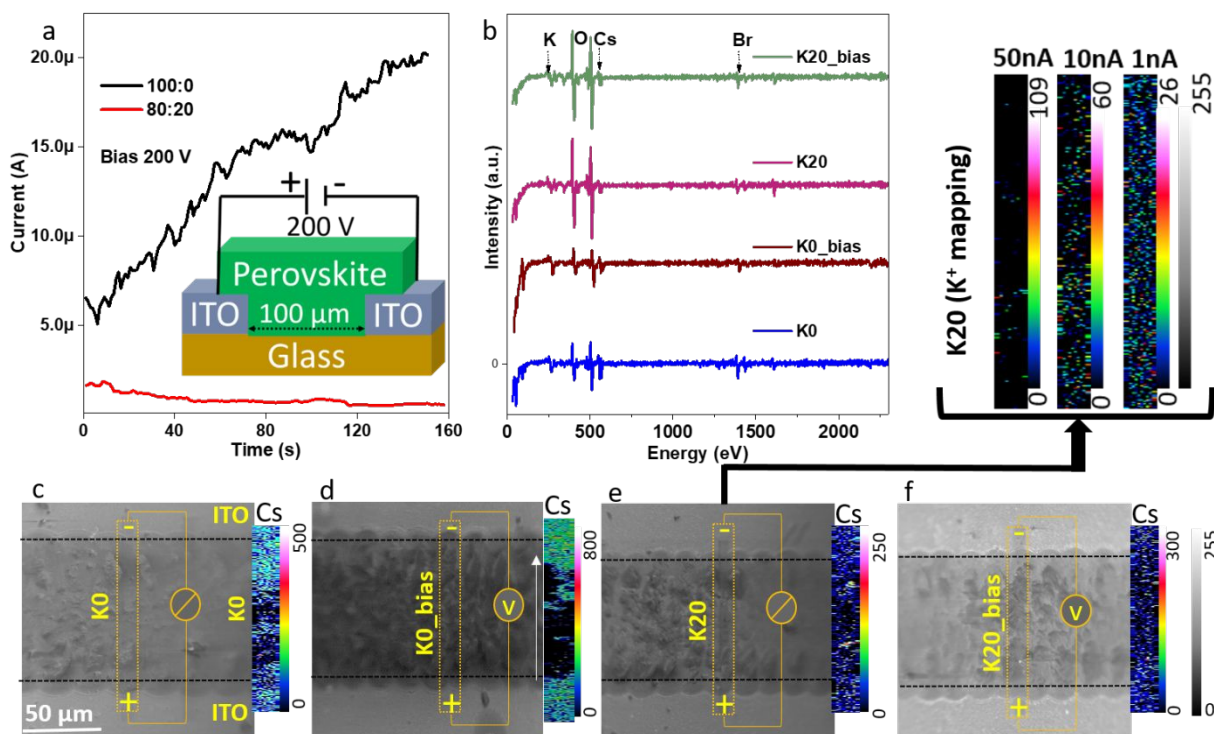


FIG. S8 (a) Current plots of K0 (unmodified) and K20 (KBr modified) films at applied constant bias of 200V for 150 sec. The inset depicts the device preparations for Auger electron spectroscopy (AES). (b) AES full scan of K0 and K20 perovskite films before and after applied bias. Cs^+ mapping of (c,d) K0 and (e,f) K20 perovskite films before (c,e) and after (d,f) applied bias. Extended figure of (e) depicts K^+ elemental mapping with decreasing Auger current from 50 nA to 1nA.

Table S1. The ^{133}Cs NMR parameters of the K0, and K20 thin film samples determined via Gaussian/Lorentzian fitting and saturation recovery relaxation experiments.

Sample	Assignment	$\delta_{\text{iso}}(^{133}\text{Cs})$ (ppm)	FWHM (KHz)	T_1 relaxation (s)	Relative intensity (%)
K0	CsPbBr ₃	117.6 ± 0.6	0.36 ± 0.04	175 ± 8	59
	Cs ₄ PbBr ₆	235.5 ± 0.9	0.57 ± 0.07	190 ± 20	41
K20	CsPbBr ₃	117.6 ± 0.6	0.36 ± 0.04	160 ± 10	32
	Cs ₄ PbBr ₆	239 ± 3	2.3 ± 0.3	200 ± 60	68

Table S2: The ^{207}Pb NMR parameters of the K0 and K20 thin film samples determined via J -coupling spectral simulation.

Sample	Assignment	$\delta_{\text{iso}}(^{207}\text{Pb})$ (ppm)	FWHM (KHz)	$^1J(^{207}\text{Pb} - ^{79/81}\text{Br})$ (KHz)	Relative intensity (%)
K0	CsPbBr ₃	269 ± 3	2.6 ± 0.3	2.3 ± 0.3	83
	Cs ₄ PbBr ₆	-349 ± 2	1.5 ± 0.2	2.0 ± 0.2	17
K20	CsPbBr ₃	270 ± 3	2.8 ± 0.3	2.3 ± 0.3	62
	Cs ₄ PbBr ₆	-366 ± 4	>4	2.0	38