Supporting Information

Experimental Section

Synthesis and crystal growth: All the chemical reagents and solvents were purchased and used without further purification. The raw materials were mixed according to the preset proportion, and the aqueous solution cooling method was utilized to grow $BA_2Cs_{1-x}MA_xPb_2Br_7$ single crystals with varying mixed cation concentrations (x = 0, 0.07, 0.21, 0.34). A clear transparent solution was obtained after the continuous stirring for 30 min at 353 K. Plate-like yellow crystals were obtained by the temperature cooling method (the cooling rate of 4 K/day) after about two weeks. Elemental analyzer VARIO MICRO was employed to determine the MA^+ fraction of x value.

Characterization. DSC analyses of samples were carried out using a NETZSCH DSC 200 F3 DSC instrument in the temperature range of 298-420 K. The powder samples placed in aluminum crucibles were heated and cooled with a rate of 10 $K \cdot min^{-1}$ under the N_2 atmosphere. Single crystals of samples with the surface deposited by silver paste were used for dielectric constant measurements. The dielectric analyses were performed on TongHui TH2828 analyzer in the temperature range of 298-410 K. The temperature-dependent *P-E* hysteresis loops and *I-E* curves were measured on a ferroelectric analyzer (Radiant Precision Premier II) using the double-wave method. In order to avoid electric discharge at high electric field, single crystals of samples were immersed in silicone oil to measure the *P-E* hysteresis loops.

Optical measurements: The UV absorptions in solid state were measured at room temperature on a PE Lambda 900 UV-Visible spectrophotometer. The band near 440 nm might be attributed to free exciton. The band near 475 nm can be attributed to the intrinsic luminescence peak of the substance, which is determined by the band structure of the material.[1] The fluorescence measurements were performed on an Edinbergh Analytical instrument FLS920. The temperature during measurements was controlled at 290 K using a Linkam TS1500 heating stage. *Exciton binding energy calculation: Based on the Arrhenius plot of the integrated PL intensity versus the temperature:* $I(T)=I_0/(1+Aexp(-E_a/k_bT))$, *where* $I(T)$ *and* I_0 *are integrated PL intensities at T and 77 K, respectively, A is a constant,* k_b *is the Boltzman constant, and* E_a *is the binding energy. we used the integral intensity of the PL (435-455 nm) for calculation. The exciton binding energies for x = 0 and 0.34 are calculated to be 85.8 and 58.4 meV, respectively.*

Photoelectric measurements: Electrical measurements were carried out along the polar axis of the crystal (*c*-axis), and the thickness of the crystal is ~4 mm in the *c* direction. Ag electrodes were sputtered on the flat side of a well-polished single crystal. The electrode materials were proven not to have any obvious influence on the photoelectric properties. The current vs voltage (*I*-*V*) and photocurrent vs time (*I*-*t*) with light on or off (measured at zero bias) were measured using a high precision electrometer (Keithley6517B). A THORLABS 405 nm pigtailed laser diode (LP405-MF300, 200 mW/cm^2) was used for visible light illumination. The incident light intensity was measured by light power meter. The responsivity (*R*) of and the corresponding detectivity (*D**) of the device are calculated from the following equations:

$$R = (I_{on} - I_{off})/P_{in}$$

$$D^* = R/(2qI_{off}/S)^{1/2}$$

where I_{on} is the photocurrent, I_{off} is the dark current, P_{in} is the incident light power, and q is the electron charge.

Reference

1. Su, L., Fan, X., Yin, T., Wang, H., Li, Y., Liu, F., Li, J., Zhang, H., Xie, H., Inorganic 2D Luminescent Materials: Structure, Luminescence Modulation, and Applications. *Adv. Optical Mater*. 2020, 8, 1900978.

Figures

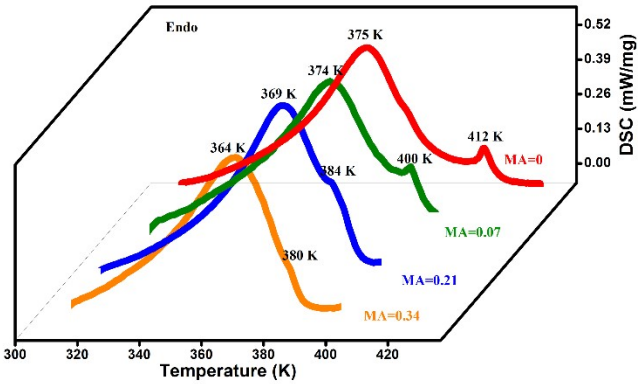

Figure S1. DSC curves of $BA_2Cs_{1-x}MA_xPb_2Br_7$ (x = 0, 0.07, 0.21, 0.34).

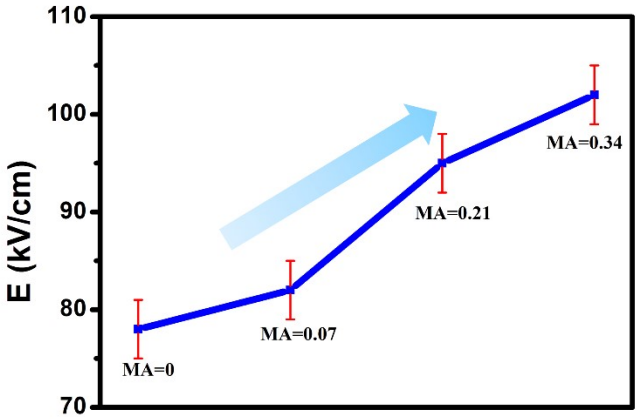

Figure S2. The breakdown resistance voltage of $BA_2Cs_{1-x}MA_xPb_2Br_7$ (x = 0, 0.07, 0.21, 0.34).

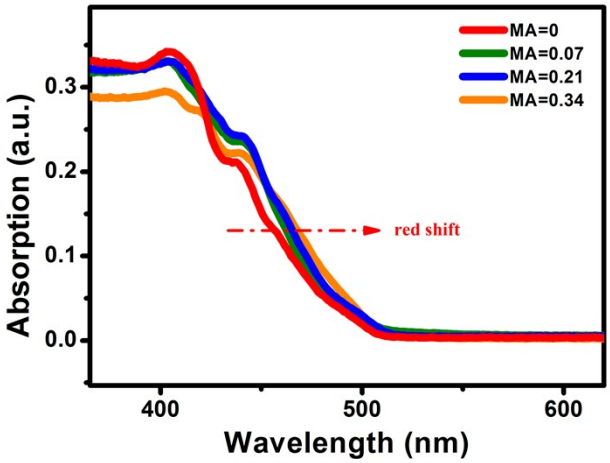

Figure S3. UV−vis absorption spectra of $BA_2Cs_{1-x}MA_xPb_2Br_7$ (x = 0, 0.07, 0.21, 0.34).

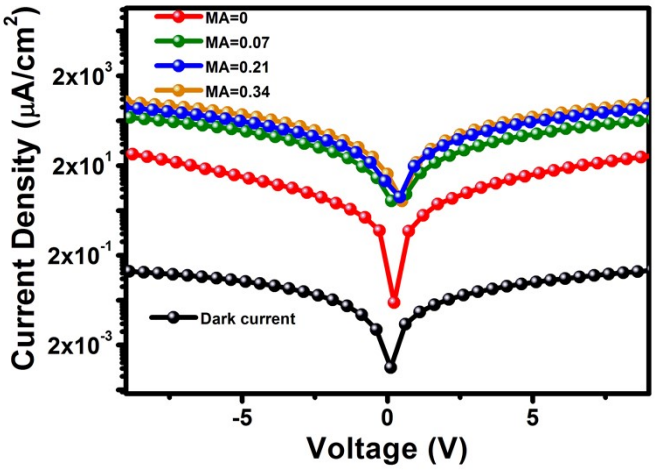

Figure S4. The photo-electric characteristics of mixed cage cation samples under 405 nm laser irradiation (10 V, 74 mW/cm^2).

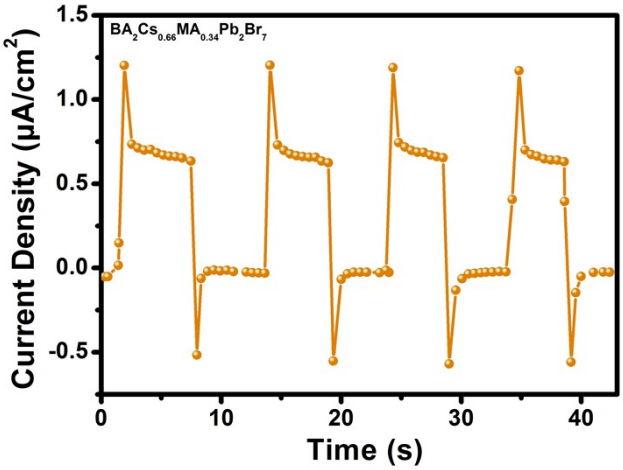

Figure S5 *I-t* curves under 450nm light illumination.

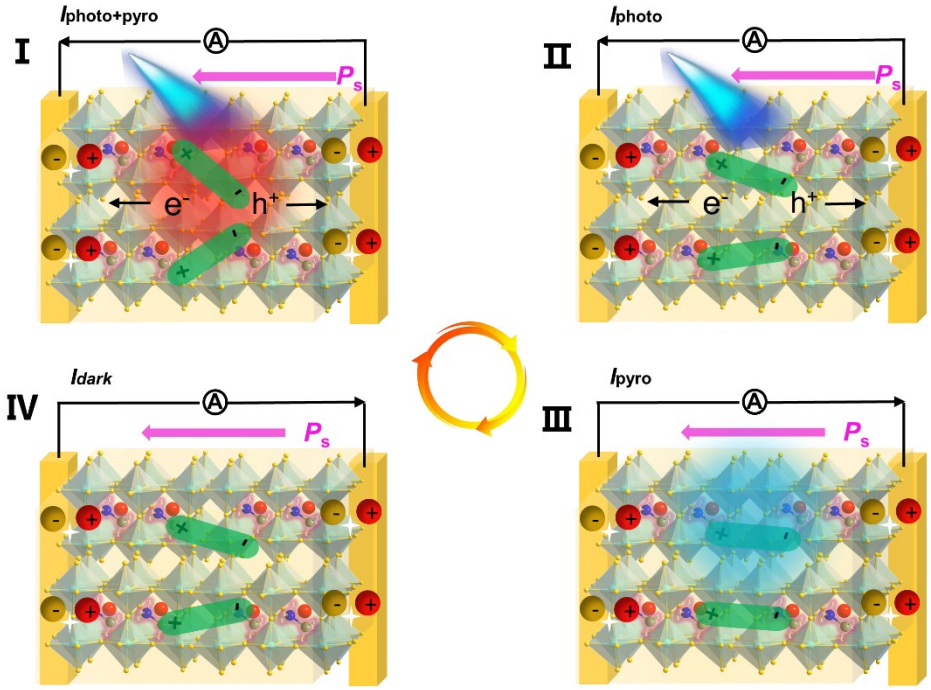

Figure S6. Schematic diagram for creating FPP effect with the laser being turned on/off.

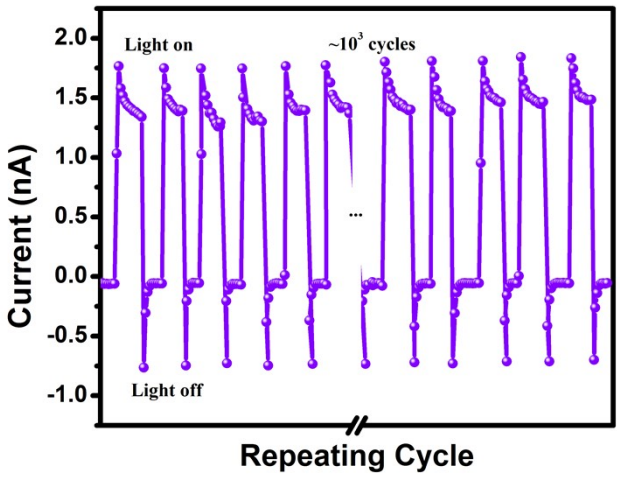

Figure S7. The long-term stability of the photodetector of $BA_2Cs_{0.66}MA_{0.34}Pb_2Br_7$.

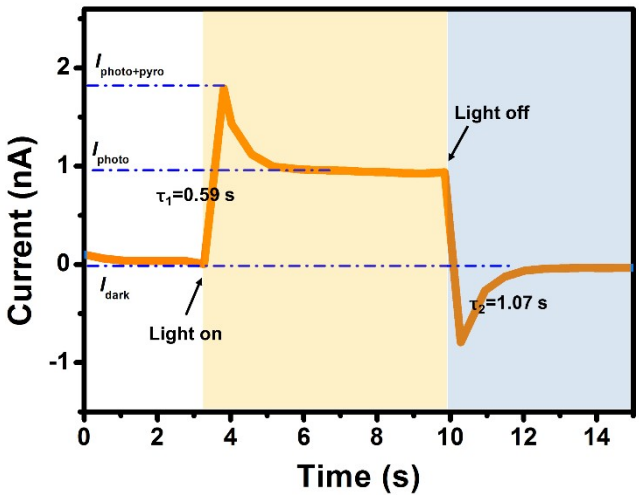

Figure S8. The response time of the device.

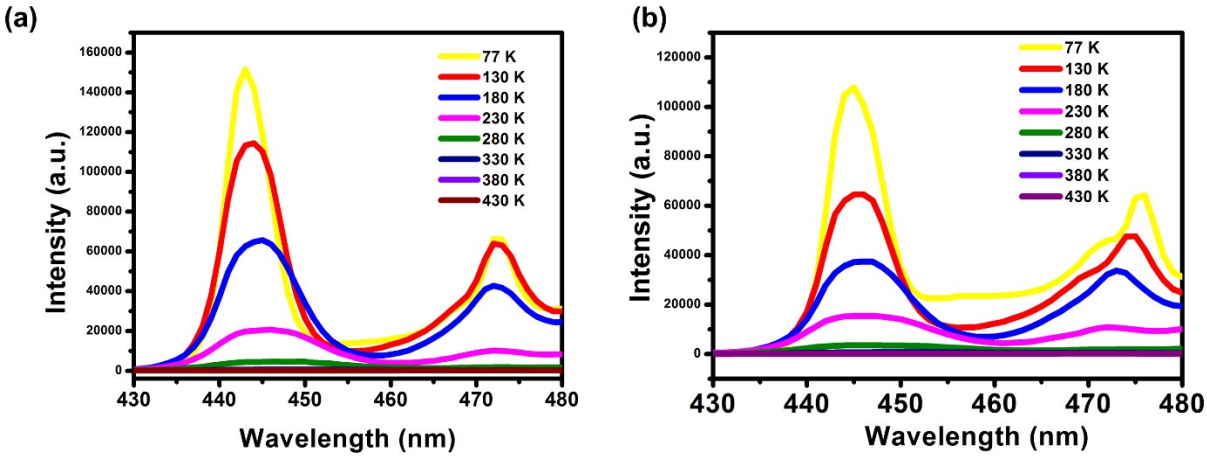

Figure S9. The temperature-dependent PL emission spectra of $BA_2CsPb_2Br_7$ (a) and $BA_2Cs_{0.66}MA_{0.34}Pb_2Br_7$ (b).

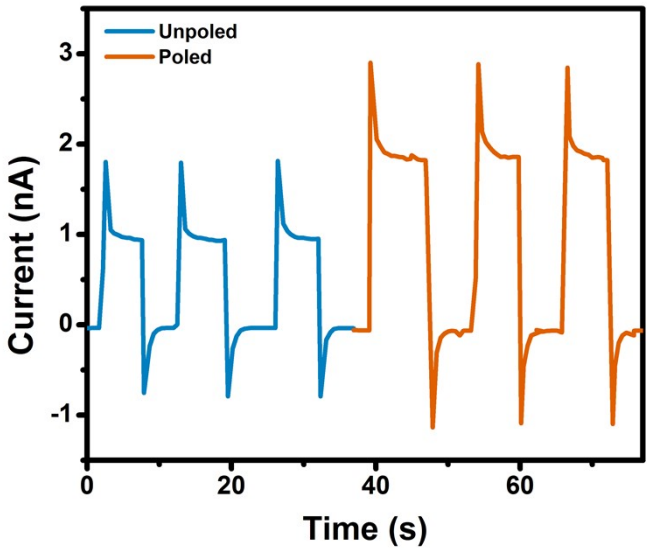

Figure S10. *I-t* curves of $BA_2Cs_{0.66}MA_{0.34}Pb_2Br_7$ before and after device electric field polarization.

Table S1. Elemental analysis results were used to determine the MA^+ fraction of x value.

Sample name	C(%)	N(%)	H(%)
$BA_2Cs_{0.93}MA_{0.07}Pb_2Br_7$	7.77	2.27	1.91
$BA_2Cs_{0.79}MA_{0.21}Pb_2Br_7$	7.99	2.53	2.08
$BA_2Cs_{0.66}MA_{0.34}Pb_2Br_7$	8.20	2.71	2.17

Table S2. Unit cell parameters for $BA_2Cs_{1-x}MA_xPb_2Br_7$.

Sample name	a(Å)	b(Å)	c(Å)	*V* (Å^3)
$BA_2CsPb_2Br_7$	39.2896	8.3153	8.1943	2677
$BA_2Cs_{0.93}MA_{0.07}Pb_2Br_7$	39.2911	8.3281	8.2024	2684
$BA_2Cs_{0.79}MA_{0.21}Pb_2Br_7$	39.2791	8.3463	8.2243	2696
$BA_2Cs_{0.66}MA_{0.34}Pb_2Br_7$	39.340	8.3563	8.2290	2705