Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Electronic Supplementary Information

Experimental Section

Materials: Hydrobromic acid (HBr) (48 wt.% in water), hydroiodic acid (HI) (57 wt.% in water), methylamine (CH_3NH_2) (40 wt.% in water), $PbBr_2$ (99%), PbI_2 (99%), N,N-dimethylformamide (DMF, 99.9%) and γ-butyrolactone (GBL, 99%) were purchased from Sigma-Aldrich and used as received without further purification.

Synthesis of CH_3NH_3X (X= Br, I) Crystals: CH_3NH_3Br was synthesized by reacting CH_3NH_2 and HBr with the molar ratio of 1.2:1. The HBr was added dropwise into the CH_3NH_2 in a flask under nitrogen atmosphere in an iced bath for 2.5 h, the resulting solution was evaporated at 60 °C in a rotary evaporator to remove the solvent. CH_3NH_3I were synthesized with the same procedure as above except by replacing the HBr using HI. The white CH_3NH_3X (X= Br, I) crystalline powder was collected using Büchner funnel filtration after being washed for three times with anhydrous ethanol and recrystallized in anhydrous diethyl ether, then dried in a vacuum oven at 60 ^oC overnight.

Single crystal growth process for $CH_3NH_3Pb(Br_xI_{1-x})_3$: To grow the dual-halide perovskite single crystals $CH_3NH_3Pb(Br_xI_{1-x})_3$ (x = 0~1), precursor solutions were prepared first. The solution concentration was controlled at 0.7 M in DMF for $CH_3NH_3PbBr_3$ and 1.3 M in GBL for $CH_3NH_3PbI_3$. Specifically, equimolar mixture of the CH_3NH_3Br and $PbBr_2$ were dissolved in DMF at 50 °C for $CH_3NH_3PbBr_3$, equimolar mixture of the CH_3NH_3I and PbI_2 in GBL for $CH_3NH_3PbI_3$. For $CH_3NH_3Pb(Br_xI_{1-x})_3$, measured volume of $CH_3NH_3PbBr_3$ (0.7 M) solution and $CH_3NH_3PbI_3$ (1.3 M) were mixed to form the double-halide precursor solution with desired Br:I ratio. (Supplementary Table 1). The $CH_3NH_3Pb(Br_xI_{1-x})_3$ solution were heated to 95 °C and maintained

at the temperature until desired $CH_3NH_3Pb(Br_xI_{1-x})_3$ single crystals formed.

The fabrication of photodetector: Planar-type photodetectors were fabricated by depositing ~200 nm interdigital Au electrodes via vacuum evaporation on the single crystalline $CH_3NH_3Pb(Br_xI_{1-x})_3$, respectively. Each electrode consists of a group of 15 fine Au wires (2 mm in length, 50 μm in width). The effective illumination area was controlled at ~3 mm^2.

Characterizations: Powder XRD patterns were collected using a Rigaku (Smartlab-9kW) X-ray diffractometer equipped with a Cu Kα X-ray (λ = 1.54186 Å) tube operated at 40 kV and 30 mA. The $CH_3NH_3Pb(Br_xI_{1-x})_3$ powder was produced by grinding a large piece of crystal into fine powder; Vis-NIR diffuse reflectance spectrum was measured at room temperature using a Vis-NIR spectrophotometer (PerkinElmer Lambda 950) with an integrating sphere attachment operating in the 400~1000 nm region. A highly refined barium sulfate ($BaSO_4$) plate was used as the standard (100% reflectance); The photoresponse characteristics for the $CH_3NH_3Pb(Br_xI_{1-x})_3$ photodetectors were collected by a Keithley 2400 source meter under various bias voltage and LED light illumination.

The procedures to extract the bandgaps: The optical absorption coefficient (α) is alculated using reflectance data according to the Kubelka−Munk equation, $F(R)= \alpha/S = (1 - R)^2/2R$, where R is the percentage of reflected light, *S* is the scattering coefficient. The incident photon energy (hν) and the optical band gap (Eg) are related to the transformed Kubelka−Munk function, $\alpha h\nu^p = A(h\nu - Eg)^n$, where A and p are constants. As all three kinds of $CH_3NH_3PbX_3$ (x=Cl, Br, I) are direct-bandgap semiconductor materials, the n value is 1/2. By extrapolating the linear region of the $[F(R)h\nu]^2$ vs. hν curve, the intercept is shown in Fig. S2, Eg is established.[1-3]

Table 1 The mixed volumetric ratio of $CH_3NH_3PbBr_3$, $CH_3NH_3PbI_3$ for the $CH_3NH_3Pb(Br_xI_{1-x})_3$ solution.

dual-halide perovskites	composition (x)	$CH_3NH_3PbBr_3$ (0.7M) Volume (mL)	$CH_3NH_3PbI_3$ (1.3M) Volume (mL)
$CH_3NH_3Pb(Br_xI_{1-x)3}$	0	0	15
	0.08	2	13
	0.21	5	10
	0.38	8	7
	0.52	10	5
	0.6	11	4
	0.68	12	3
	0.78	13	2
	0.87	14	1
	1	15	0

Table S2. Comparison of the photocurrent response speed of the photodetector as reported in literature and our measurements.

Material	Rise time	Fall time	Reference
$CH_3NH_3PbBr_3$ single crystal	70 us	150 us	46
$CH_3NH_3PbBr_3$ single crystal		25 us	47
$CH_3NH_3PbBr_3$ nanowires	120 ms	86 ms	48
$CH_3NH_3PbI_3$–$CH_3NH_3PbBr_3$ heterojunctions	120 ms	94 ms	49
$MAPb(Br_{0.78}I_{0.22})_3$ single crystal	3.4 ms	3.6 ms	Present work

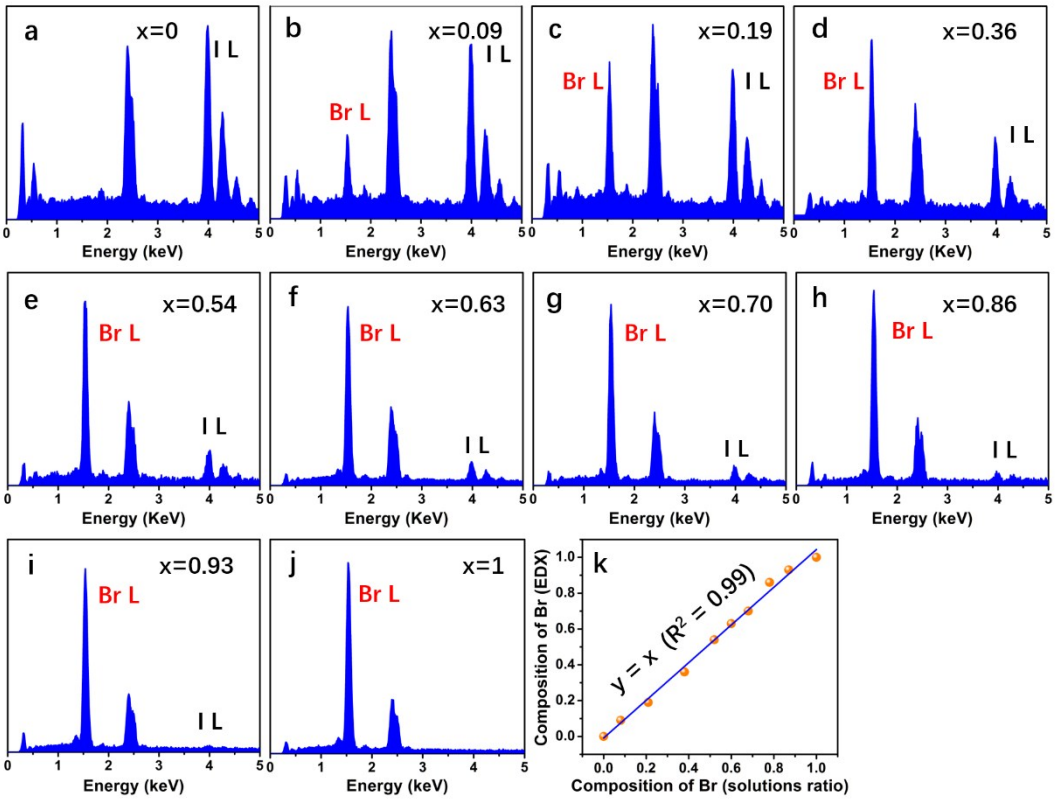

Fig. S1. (a-j) EDX spectra of $MAPb(Br_xI_{1-x})_3$ (x= 0, 0.08, 0.21, 0.38, 0.52, 0.60, 0.68, 0.78, 0.87 and 1) samples. The corresponding x value was calculated using the Br K and I L shell peaks, which are shown in the inset (x= 0, 0.09, 0.19, 0.36, 0.54, 0.63, 0.70, 0.86, 0.93 and 1). (k) The correlation of the x values determined by the ratio of precursor solution between the x values determined by the EDX spectra.

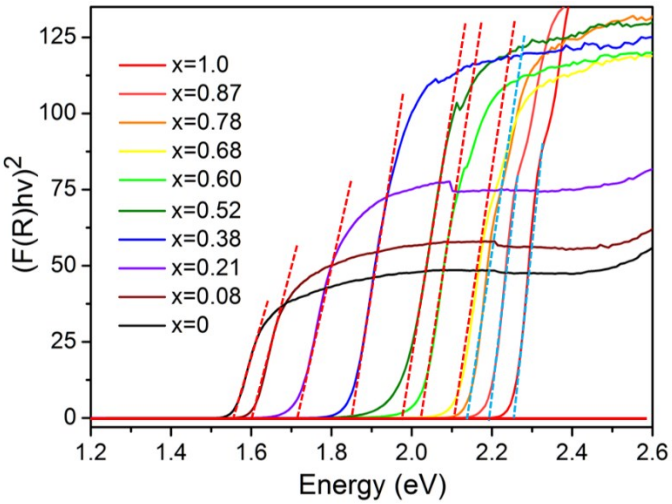

Fig. S2 The K-M plots with the tangent line to determine the bandgap.

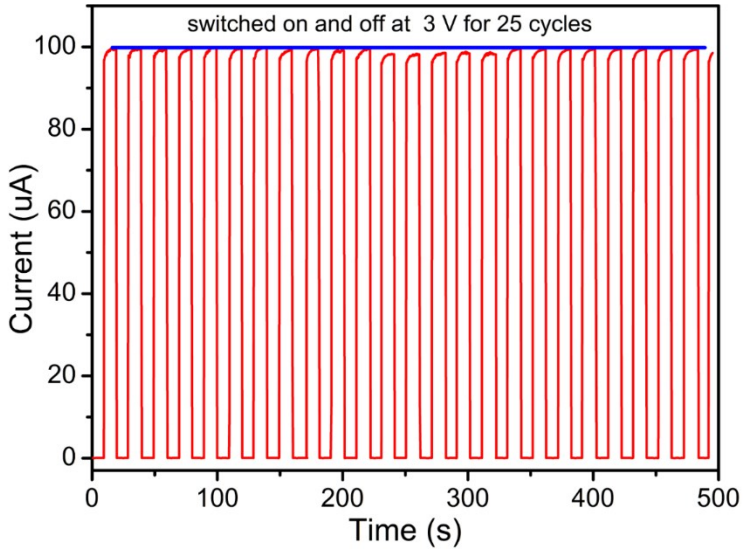

Fig. S3 Photocurrent response measured at 3 V bias for 25 cycles under the illumination (460 nm,7.96 mW cm^{-2}) switched on and off.

references

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