### Supporting Information

## Towards Superior X-ray Detection Performance of Two-dimensional Halide Perovskite Crystals by Adjusting Anisotropic Transport Behavior

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#### 1. Thermodynamic study on nucleation process

According to the classical nucleation theory, the nucleation seeds generated only when the solution is oversaturated enough to overcome the nucleation barrier  $\Delta G$ . A simplified model considering a single precursor A in the solution, which could form nuclei composed of pure A-molecules coordinated with *j* solvent molecules S, that is A-S<sub>j</sub> complex. The concentration of the complex is determined by the complex binding energy  $E_c$  relative to the energies of A molecules ( $\varepsilon_A$ >0) and solvent molecules ( $\varepsilon_S$ >0), where  $\varepsilon$  is the cohesive energies in the complex. <sup>[1]</sup> Due to the surface tension, the energies are lower at the solution surface, *i.e.*  $\varepsilon_{AS} < \varepsilon_A$ ,  $\varepsilon_{SS} < \varepsilon_S$ .

The nucleation barrier could be expressed as the difference in free energy of molecules in the nucleated particle relative to their energy in the solution:

$$\Delta G = -\frac{4}{3}\pi r^3 \cdot (\varepsilon - \varepsilon_{\rm A} + k_{\rm B}T \cdot \ln N_{\rm A}) + 4\pi r^2 \cdot \sigma \tag{S1}$$

where *r* is the nucleus radius,  $N_A$  is the mole fraction of isolated A-molecules.  $k_B$  is the Boltzmann constant, *T* is the temperature, and  $\sigma$  is the crystallite's surface energy. At the critical condition of the nucleus formation  $\frac{\partial \Delta G}{\partial r} = 0$ , the critical nucleus radius could be given:

$$r = \frac{2\sigma}{\varepsilon - \varepsilon_A + k_B T \cdot \ln N_A} \tag{S2}$$

and the critical nucleation barrier:

$$\Delta G = \frac{16\pi}{3} \cdot \frac{\sigma^3}{\left(\varepsilon - \varepsilon_A + k_B T \cdot \ln N_A\right)^2}$$
(S3)

As the surface layer is only a few molecule-layers in thickness, the concentration

of individual A-molecules in the surface layer should be very close to that in the solution. Therefore, Eq. (S3) shows that the nucleation barrier decreases with decreasing molecular binding energy  $\varepsilon_{A}$ . For A-molecules in the surface layer this decrease is due to surface tension such that  $\varepsilon_{AS}=\varepsilon_{A}-\varepsilon_{Surf}$ , where  $\varepsilon_{Surf}>0$  is the surface tension-related elastic energy per A-molecule in the surface layer. <sup>[1]</sup> Then the nucleation barrier at the solution bottom and at the solution surface could be written as:

$$\Delta G_{\text{bottom}} = \frac{16\pi}{3} \cdot \frac{\sigma^3}{\left(\varepsilon - \varepsilon_A + k_B T \cdot \ln N_A\right)^2}$$
(S4)

and

$$\Delta G_{\text{surface}} = \frac{16\pi}{3} \cdot \frac{\sigma^3}{\left(\varepsilon + \varepsilon_{\text{Surf}} - \varepsilon_A + k_B T \cdot \ln N_A\right)^2}$$
(S5)

These two equations show that the critical nucleation barrier at the solution surface is lower than that at the solution bottom (Figure 2c). Therefore, the nucleation at the solution surface is easier than that at the solution bottom.

# 2. The calculation of signal-to-noise ratio of (BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> and (*i*-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystals with different directions.

As shown in Figure S11, the signal current  $(I_{signal})$  was derived by subtracting the average photocurrent  $(\overline{I}_{photo})$  by the average dark current  $(\overline{I}_{dark})$ . The noise current  $(I_{noise})$  was obtained by calculating the standard deviation of the photocurrent.

$$I_{signal} = \overline{I}_{photo} - \overline{I}_{dark}$$
(S6)

$$I_{noise} = \sqrt{\frac{1}{N} \sum_{i}^{N} (I_i - \overline{I}_{photo})^2}$$
(S7)

Then the signal-to-noise ratio (SNR) was calculated using

$$SNR = I_{signal} / I_{noise}$$
(S8)

For example, for  $(BA)_2CsPb_2Br_7$  device with 5 V bias and under 194.7 nGy·s<sup>-1</sup> (or 277.1 nGy·s<sup>-1</sup>), the calculated average photocurrent, dark current, and noise current was 19.61 pA (or 22.21 pA), 13.71 pA (or 13.71 pA), and 0.48 pA (or 0.75 pA), respectively, resulting in a SNR value of 12.3 (or 11.3).

### 3. Supporting Figures and Tables



Figure S1. The relationship between the dose rate and current of X-ray tube.



**Figure S2.** (a) and (c) are  $(i-BA)_2CsPb_2Br_7$  crystals grown with the cooling rate of 0.5 °C/h at the solution surface and solution bottom, respectively. (b) and (d) are  $(i-BA)_2CsPb_2Br_7$  crystals grown with the cooling rate of 0.1 °C/h at the solution surface and solution bottom, respectively. All scale bars are 1 mm.



**Figure S3.** Representative SEM images and the corresponding partial enlarged top-view and cross-view of as-grown (BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> (a) and (g) and (i-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> (d) and (i) crystals with block shape and rod shape, respectively. (b), (e) and (h) Top-view. (c) and (f) Cross-view.



**Figure S4.** SEM and corresponding EDS results of (BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystals grown in the solution volume, the obtained chemical composition is Cs:Pb:Br=1:1.86:7.09.



Figure S5. SEM and corresponding EDS results of (BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystals grown at the solution

surface, the obtained chemical composition is Cs:Pb:Br=1:1.86:7.07.



Figure S6. SEM and corresponding EDS results of (i-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystals grown in the solution

Element Atom (%) 000 -Cs 10.01 18.12 Pb Br mm Br 71.87 Cs 100.00 Totals ΡЬ Рb Cs Cs Cs Pb Pb Pb Pb Br

volume, the obtained chemical composition is Cs:Pb:Br=1:1.93:7.28.

Figure S7. SEM and corresponding EDS results of (i-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystals grown at the solution

surface, the obtained chemical composition is Cs:Pb:Br=1:1.81:7.18.



**Figure S8.** The typical current-voltage (*I-V*) curves of (i-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystal along (a) *ab* plane, and (b) *c* direction under dark from -100 V to 100 V. The insets are the *I-V* curves ranged from -1 V to 1 V, respectively. The typical current-time (*I-t*) curves of (i-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystal along (c) *ab* plane, and (d) *c* direction illuminated by blue light with a wavelength of 425 nm under 10 V bias. The insets are the corresponding powder-dependent ratio of on-off ratio, respectively.

<b>Table S1.</b> The corresponding electrode sizes of $(BA)_2CSPb_2Br_7$ and $(1-BA)_2CSPb_2Br_7$ crystal for
anisotropic resistivities measurement.

Crystal	Direction	Electrode area (mm <sup>2</sup> )	Electrode distance (mm)	Resistivity ( $\Omega$ ·cm)
(BA) <sub>2</sub> CsPb <sub>2</sub> Br <sub>7</sub>	ab	0.95*1.00	3.91	2.22×10 <sup>9</sup>
	С	1.27*2.48	1.00	9.87×10 <sup>10</sup>
(i-BA) <sub>2</sub> CsPb <sub>2</sub> Br <sub>7</sub>	ab	1.17*3.62	2.66	3.27×10 <sup>9</sup>
	С	3.50*3.16	0.89	3.97×10 <sup>10</sup>



**Figure S9.**  $\alpha$ -particle-induced pulse shape rise time analysis. a) Diagram of the transport process of electrons and holes in (BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> and (i-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystals illuminated under  $\alpha$ particles and the signal measurement setup. b) The typical pulse spectrum obtained from the preamplifier, and the rise time is defined as the span of 10%~90% amplitude.



**Figure S10.** TOF technique based on the  $(BA)_2CsPb_2Br_7$  crystal device using alpha particles. Transport is measured from electrons (a) or holes (b) along the *c* direction when the alpha particles are incident on the cathode and anode, respectively. The distributions of the rise time for electrons

(c) and holes (d) in  $(BA)_2CsPb_2Br_7$  crystal device under various biases along the *c* direction, respectively. The electron (e) and holes (f) drifting velocities *vs* electric field in  $(BA)_2CsPb_2Br_7$  crystal along the *c* direction, respectively.



**Figure S11.** TOF technique based on the  $(i-BA)_2CsPb_2Br_7$  crystal device using alpha particles. Transport is measured from electrons along the (a) *ab* plane, and (b) *c* direction when the alpha particles are incident on the cathode, respectively. The distributions of the rise time for electrons in  $(i-BA)_2CsPb_2Br_7$  crystal device under various biases along the (c) *ab* plane and (d) *c* direction, respectively. The electron drifting velocities *vs* electric field in  $(i-BA)_2CsPb_2Br_7$  crystal along the (e) *ab* plane and (f) *c* direction, respectively.



**Figure S12.** TOF technique based on the  $(i-BA)_2CsPb_2Br_7$  crystal device using alpha particles. Transport is measured from holes along the (a) *ab* plane, and (b) *c* direction when the alpha particles are incident on the anode, respectively. The distributions of the rise time for holes in (*i*-BA)\_2CsPb\_2Br\_7 crystal device under various biases along the (c) *ab* plane and (d) *c* direction, respectively. The hole drifting velocities *vs* electric field in (*i*-BA)\_2CsPb\_2Br\_7 crystal along the (e) *ab* plane and (f) *c* direction, respectively.



Figure S13. Device response to X-rays (194.7 or 277.1 nGy·s<sup>-1</sup> dose rate) on tuning the X-ray

source on and off.



**Figure S14.** The typical X-ray on-off curves of  $(BA)_2CsPb_2Br_7$  crystal with *ab* plane with an Xray beam bias of 40 kVp under the bias of (a) 1 V, (c) 3 V, and (e) 10 V, respectively. The insets are the corresponding signal-to-noise ration (SNR), the blue dasehed line represent the SNR of 3. Dose rate-dependent current density of  $(BA)_2CsPb_2Br_7$  crystal with *ab* plane under the bias of (b) 1 V, (d) 3 V, and (f) 10 V, respectively.



**Figure S15.** The typical X-ray on-off curves of  $(BA)_2CsPb_2Br_7$  crystal with *c* direction with an X-ray beam bias of 40 kVp under the bias of (a) 30 V, (c) 50 V, and (e) 70 V, respectively. The insets are the corresponding signal-to-noise ration (SNR), the blue dasehed line represent the SNR of 3. Dose rate-dependent current density of  $(BA)_2CsPb_2Br_7$  crystal with *c* direction under the bias of (b) 30 V, (d) 50 V, and (f) 70 V, respectively.



**Figure S16.** The typical X-ray on-off curves of (i-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystal with *ab* plane with an Xray beam bias of 40 kVp under the bias of (a) 1 V, (c) 5 V, (e) 10 V, (g) 15 V, and (i) 20 V, respectively. The insets are the corresponding signal-to-noise ration (SNR), the blue dasehed line represent the SNR of 3. Dose rate-dependent current density of (i-BA)<sub>2</sub>CsPb<sub>2</sub>Br<sub>7</sub> crystal with *ab* plane under the bias of (b) 1 V, (d) 5 V, (f) 10 V, (h) 15 V, and (j) 20 V, respectively.



**Figure S17.** The typical X-ray on-off curves of  $(i-BA)_2CsPb_2Br_7$  crystal with *c* direction with an X-ray beam bias of 40 kVp under the bias of (a) 1 V, (c) 5 V, (e) 10 V, (g) 20 V, and (i) 30 V, respectively. The insets are the corresponding signal-to-noise ration (SNR), the blue dasehed line represent the SNR of 3. Dose rate-dependent current density of  $(i-BA)_2CsPb_2Br_7$  crystal with *c* direction under the bias of (b) 1 V, (d) 5 V, (f) 10 V, (h) 20 V, and (j) 30 V, respectively.



**Figure S18.** The long-term X-ray on-off switching cycles of  $(i-BA)_2CsPb_2Br_7$  crystal with (a) *ab* plane and (b) *c* direction with an X-ray beam bias of 40 kVp and under X-ray illumination with dose rate of 278.4  $\mu$ Gy·s<sup>-1</sup>. (c) and (d) are the initial and final X-ray on-off switching cycles of (a) and (c), respectively.

### Reference

[1] a) A. A. Zhumekenov, V. M. Burlakov, M. I. Saidaminov, A. Alofi, M. A. Haque, B. Turedi, B. Davaasuren, I. Dursun, N. Cho, A. M. El-Zohry, M. D. Bastiani, A. Giugni, B. Torre, E. D. Fabrizio, O. F. Mohammed, A. Rothenberger, T. Wu, A. Goriely, O. M. Bakr, *ACS Energy Lett.* 2017, 2, 1782;
b) K. Wang, C. Wu, D. Yang, Y. Jiang, S. Priya, *ACS Nano* 2018, 12, 4919.