Supporting Information:

Anisotropy of Excitons in 2D Perovskite Crystals

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Sample preparation

The *n*-butylammonium iodide (BAI) solution was synthesized by mixing a 40% w/w aqueous *n*-butylamine (4 mL) and a 57% w/w aqueous hydroiodic acid (HI) (16 mL) under stirring at 0°C for 4 h. For the synthesis of $(BA)_2PbI_4$, PbO powder (0.563 g) was dissolved in a mixture of 57% w/w aqueous hydriodic acid (HI) solution (3 mL) and 50% w/w aqueous hypophosphorous acid (H₃PO₂) solution (0.5 mL) by heating to 150 °C under constant magnetic stirring. Then 2.5 mL BAI solution was injected into the resultant solution. Afterwards, the stirring was stopped, and the solution was left to naturally cool to room temperature. The resultant solution was left overnight to complete the growth and the crystals were sequentially isolated by suction filtration and thoroughly dried in the oven.



Figure S1. X-ray diffraction pattern of the as-synthesized $(BA)_2PbI_4$ perovskite powder. All peaks can be indexed according to the calculated results.



Figure S2. SEM image of the *ac*-plane from a freshly cleaved crystal. Sale bars: 200 μ m (50 μ m

for inset).



Figure S3. (a-b) Photoluminescence spectra of different polarization orientation from the *ab*-plane under an excitation with polarization orientation along *a*-axis (a) and *b*-axis (b) of the crystal. (c-d) Photoluminescence spectra of different polarization orientation from *ac*-plane under an excitation with polarization orientation along *a*-axis (c) and *c*-axis (d) of the crystal.



Figure S4. Emission intensity of 2D perovskite crystals *versus* time (a) and polarization degree (b) under a laser excitation. There is no severe degradation occurs during the measuring process.



Figure S5. Photoluminescence spectra at 100 K taken from *ab*- and *ac*-plane under a normal (N) and an oblique (O) incidence, respectively. For ab-plane, only free exciton emission can be observed. In contrast to *ab*-plane, the self-trapped exciton emission is greatly enhanced for ac-plane under an oblique incidence, which we believe is due to the different optical selection rule for self-trapped excitons compared with the free excitons. Since both PL spectra at low- and room-temperature show similar results, it is reasonable to believe that self-trapped excitons are intrinsic in 2D perovskite.



Figure S6. (a) Photoluminescence spectra of the *ac*-plane under oblique excitation with different excitation power intensity. (b) Photoluminescence intensity of free exciton (at 521 nm) and self-trapped exciton (at 554 nm) *versus* excitation power intensity, respectively. The linear increase of the emission intensity with excitation power is observed for both free exciton and self-trapped exciton with a similar slope, indicating that defects should not be responsible for the sub-bandgap emission. For the defect emission, the emission intensity should exhibit a sublinear increase and finally saturation with the excitation power due to the small density of states for defect. In addition, if the emission peak at 554 nm is indeed due to the defect emission, we should also observe this emission peak for both *ac*- and *ab*-plane under a normal excitation. Nevertheless, only the free exciton emission peak could be observed for *ac*-plane under a normal incidence (Figure 4d). Therefore, we believe the emission peak at 554 nm is not induced by defects.