

## Supporting Information

# One-Step Solution Patterning for Two-Dimensional Perovskite Nanoplate Arrays

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## Supplementary Note 1.

To confirm the importance of the shearing process on patterned substrates for synthesis of 2D perovskite arrays, we investigated the shapes of  $(\text{PEA})_2\text{PbBr}_4$  synthesized by the conventional solution dropping method on our patterned substrates (Figure S5). The synthesis of 2D perovskite crystals mainly occurs at the solution-substrate-air interface region where perovskite materials are actively precipitated by solvent evaporation. The conventional solution dropping method cannot maintain a constant solvent evaporation direction and speed due to evaporation of the solvent in all directions from the droplet. At the beginning, the evaporation speed of the solution droplet on the substrates is too fast and the solution-substrate-air interface region cannot be persisted long enough for sufficient growth to happen on the HMDS-SAM-treated patterns. Therefore, only a few  $(\text{PEA})_2\text{PbBr}_4$  crystals are synthesized. As the solvent continues to evaporate, the solution-substrate-air interface region is persisted long enough in the HMDS-SAM-treated patterns, and  $(\text{PEA})_2\text{PbBr}_4$  crystals are formed in a specific area, but this cannot be considered a proper array due to lack of periodicity and uniformity resulting from inconsistent evaporation rates and directions. As the concentration of the solution increases even more due to the continued evaporation of solvents, the aggregated 2D perovskite lumps are gradually formed and the size of the lumps become as large as the size of the patterns. Moreover, when synthesizing the crystals on the fully F-treated substrate, the synthesized 2D perovskite crystals became aggregated in one place without spreading on the substrate due to the low adhesion between the crystal and the F-treated substrate (Figure S6). These results clearly show the importance of utilizing both the shearing process and the patterned substrate for the synthesis of well defined, high quality 2D perovskite crystal arrays.

## Supplementary Note 2.

Following are the four main contributing factors to the shearing process of 2D perovskite crystal arrays: shearing speed, temperature, solvent ratio, and concentration of precursor solutions. The schematic and corresponding OM images of 2D perovskite crystal arrays resulting from various synthesis conditions are summarized in Figure S7 and Figure S8. Shearing speed is a factor that determines how long the solution stays on the patterns. Therefore, When the shearing speed is slow, the solution stays in the pattern longer, and multiple crystals are synthesized due to increased nucleation sites. On the other hand, when the shearing speed is fast, there is no crystal formation due to insufficient wetting time of the solution. The temperature of the substrate is an important factor in determining the solvent evaporation rate. For higher temperature, number of nucleation sites increase due to faster solvent evaporation, which leads to the formation of multiple crystals, and for lower temperature, small and sparse crystals are synthesized due to insufficient solvent evaporation limiting crystal growth. The ratio of solvents is also a very important factor in the synthesis of rectangular shaped 2D perovskite crystals. CB helps to reduce the solubility of perovskite materials in polar DMF solvents and promote the crystallization of the perovskite crystals while AN helps the synthesis of 2D perovskite crystals with well defined rectangular shapes.<sup>S1</sup> We confirmed that multiple crystals were formed when the solvent ratio between CB/AN of the precursor solution was increased from the optimal condition and needle-shaped crystals were formed when the ratio was decreased. Regarding the effects of solution concentrations, lower concentrations yielded small multiple crystals while higher concentrations resulted in bulky 2D perovskite material arrays.

**Table S1.** Averages, standard deviations, and relative standard deviations of sizes of (PEA)<sub>2</sub>PbBr<sub>4</sub> 2D perovskite crystals synthesized by shearing and solution dropping methods.

| Size (μm) | Ave. | Std. | Std./Ave. (%) |
|-----------|------|------|---------------|
| Shearing  | 9.27 | 2.36 | 25.5          |
| Dropping  | 3.03 | 2.06 | 80.0          |

**Table S2.** Averages, standard deviations, and relative standard deviations of thicknesses and sizes of (PEA)<sub>2</sub>PbBr<sub>4</sub> and (PEA)<sub>2</sub>PbI<sub>4</sub>-(PEA)<sub>2</sub>PbBr<sub>4</sub> 2D perovskite crystals.

|                                                                               | Thickness (nm) |      |               | Size (μm) |      |               |
|-------------------------------------------------------------------------------|----------------|------|---------------|-----------|------|---------------|
|                                                                               | Ave.           | Std. | Std./Ave. (%) | Ave.      | Std. | Std./Ave. (%) |
| (PEA) <sub>2</sub> PbBr <sub>4</sub>                                          | 169.2          | 79.2 | 46.8          | 9.3       | 2.4  | 25.4          |
| (PEA) <sub>2</sub> PbI <sub>4</sub> -<br>(PEA) <sub>2</sub> PbBr <sub>4</sub> | 114.8          | 42.0 | 36.6          | 12.1      | 1.8  | 15.0          |

**Table S3.** Device performance of (PEA)<sub>2</sub>PbBr<sub>4</sub> crystal photosensors.

| Materials               | Photo Responsivity (A W <sup>-1</sup> ) | Specific Detectivity (Jones) | Wavelength of Light Source (nm) | References                                            |
|-------------------------|-----------------------------------------|------------------------------|---------------------------------|-------------------------------------------------------|
| Single Crystal          | $2 \times 10^{-3}$                      | $\sim 1 \times 10^{13}$      | 365                             | <i>J. Mater. Chem. C.</i> <b>2019</b> , 7, 1584.      |
| Micro-Crystalline Films | $8 \times 10^{-3}$                      | $\sim 1.5 \times 10^{12}$    | 380                             | <i>Adv. Optical Mater.</i> <b>2022</b> , 10, 2101145. |
| Single Crystal          | 31.1                                    | $4 \times 10^{13}$           | 365                             | This Work                                             |

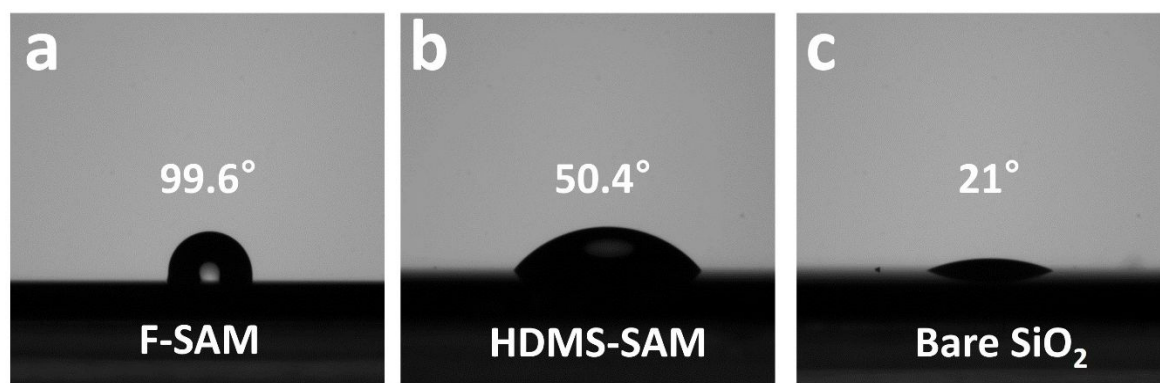


**Figure S1.** Contact angle measurements of on (a) F-, (b) HDMS-SAM and (c) bare SiO<sub>2</sub> substrates.

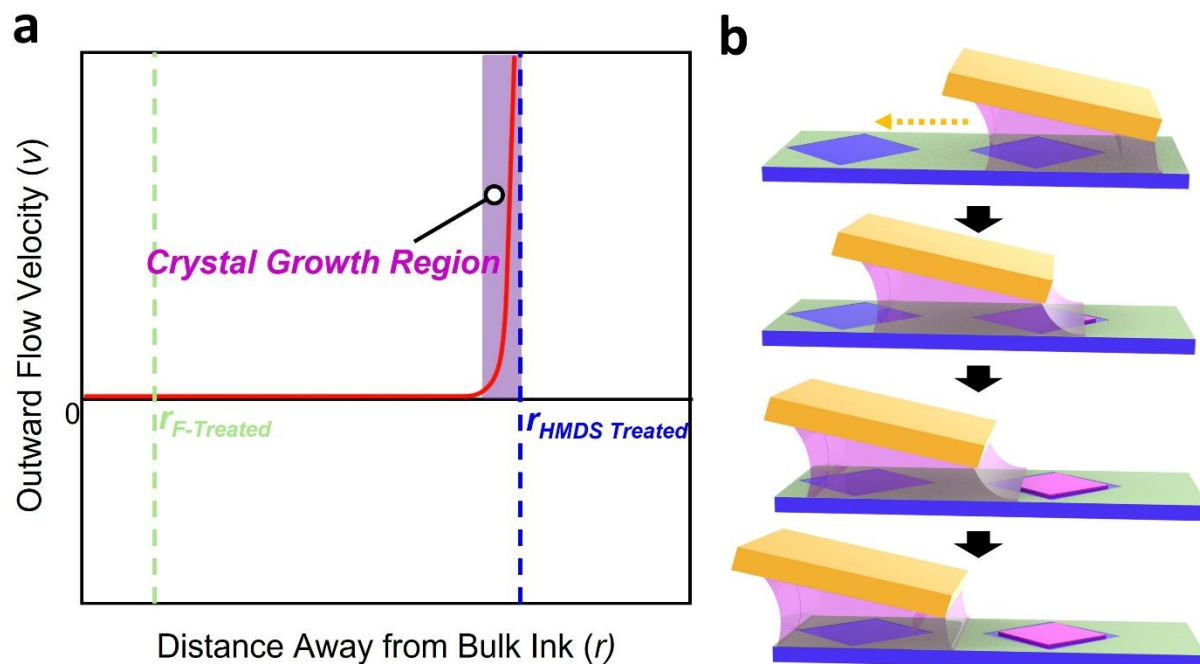


**Figure S2.** (a) Graph illustrating the velocity  $v$  of the outward convective flow as a function of the distance  $r$  of the meniscus surface away from the bulk ink. (b) Schematic images of the crystallization processing of 2D perovskite nanoplate using solution-shearing process.

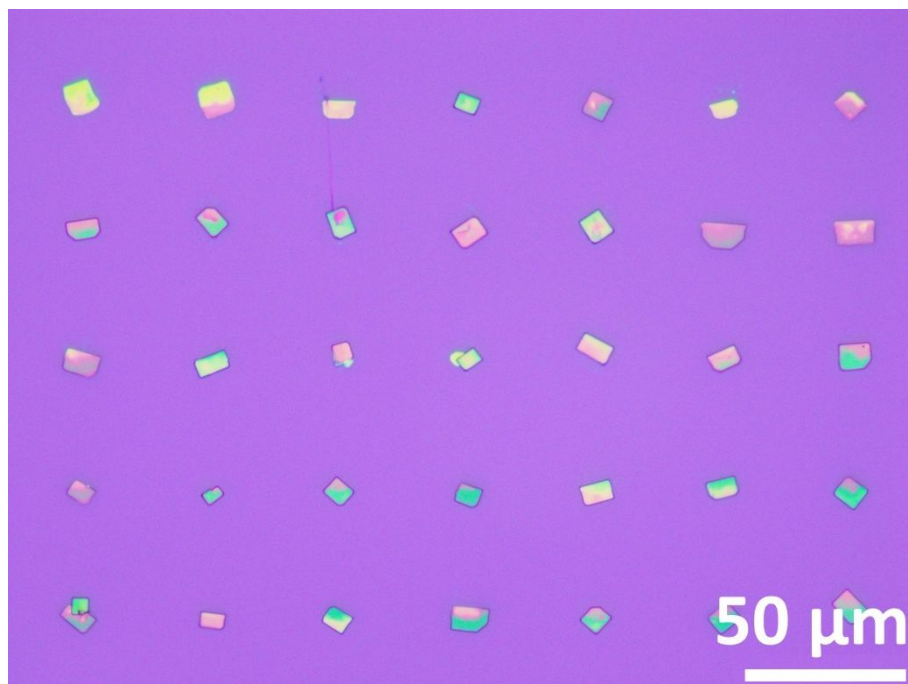


**Figure S3.** Corresponding OM image of (PEA)<sub>2</sub>PbBr<sub>4</sub> 2D perovskite crystal arrays synthesized by shearing procedure.

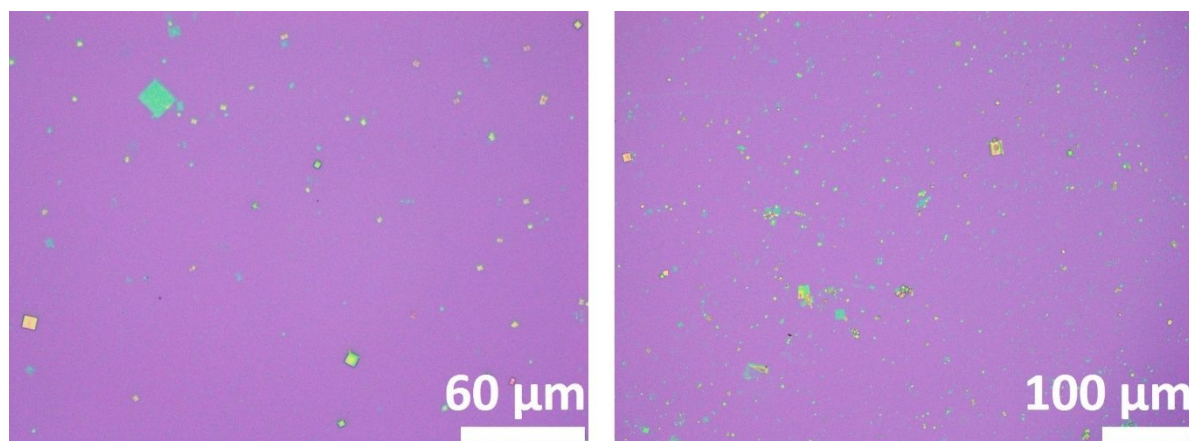


**Figure S4.** Corresponding OM images of randomly located  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystals synthesized by solution dropping method.

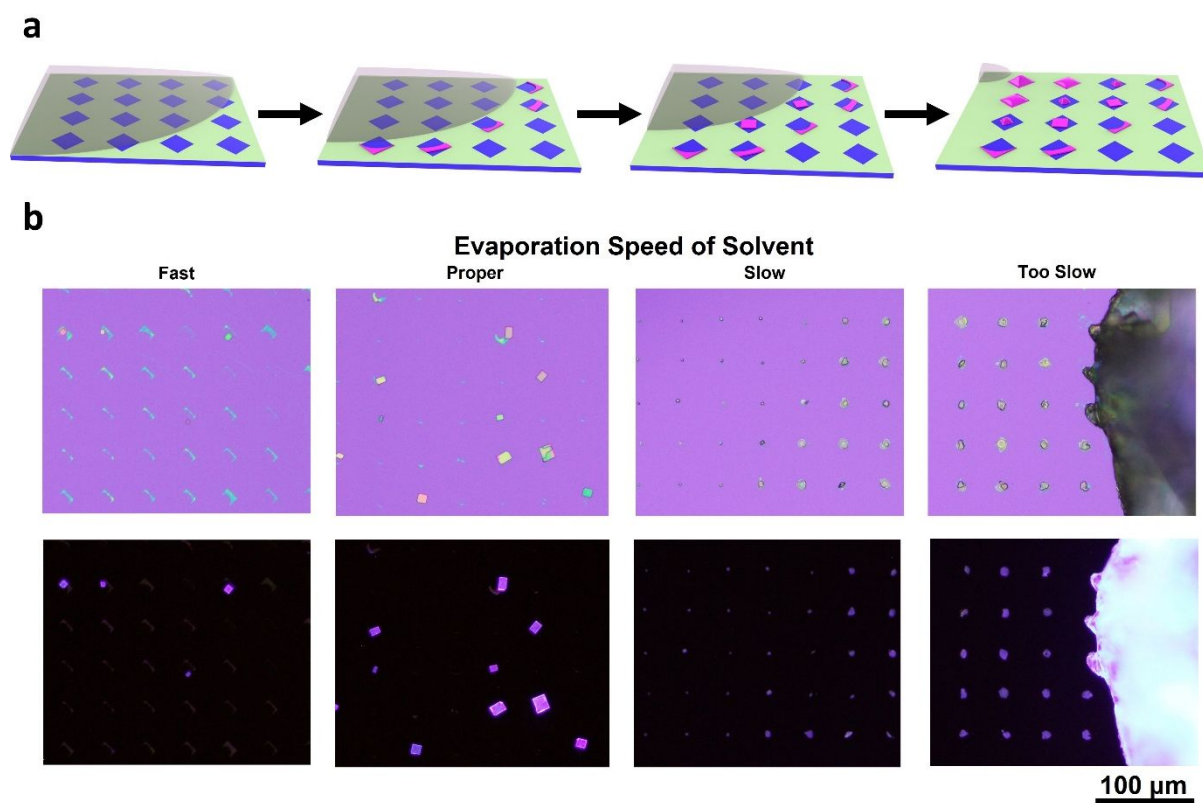


**Figure S5.** (a) Schematic image of the solvent drying process in solution dropping method on the patterned substrates. (b) OM images and corresponding PL images of  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite aggregated materials and crystals in regions with different evaporation speeds.

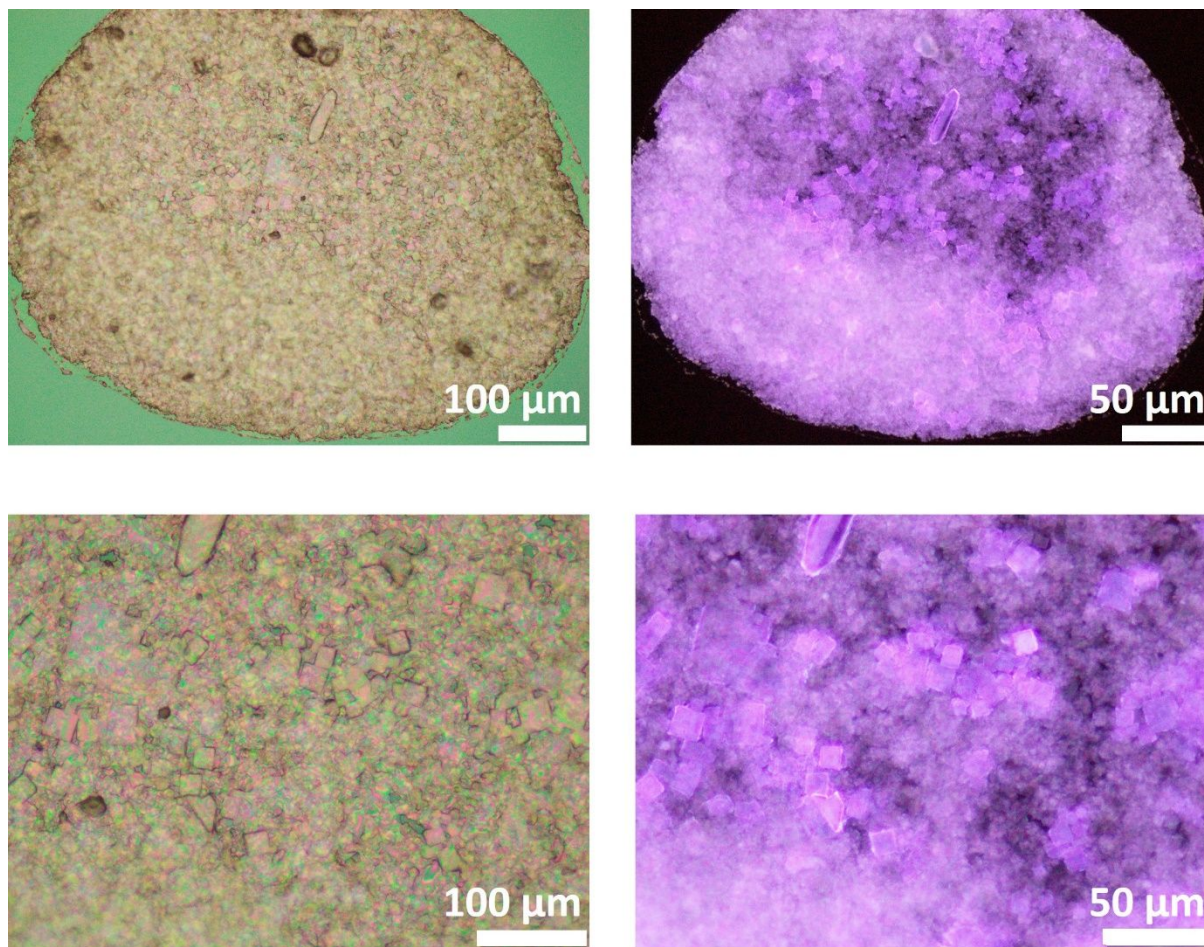


**Figure S6.** OM images and corresponding PL images of aggregated  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystals synthesized by solution dropping method on the fully fluorine-treated substrate.

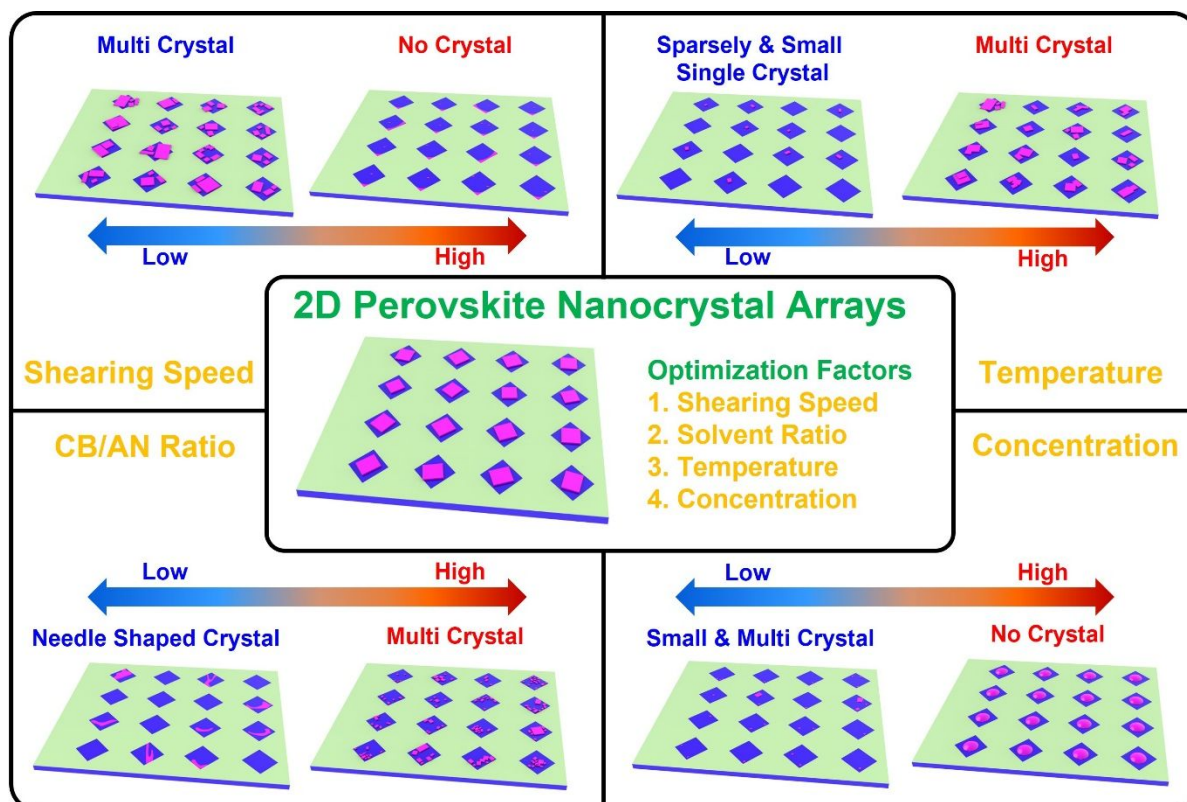


**Figure S7.** Schematic images of the  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystals under different synthesis condition for shearing process with different shearing speeds, ratios of CB/AN, substrate temperatures, and concentrations of perovskite precursor solutions.

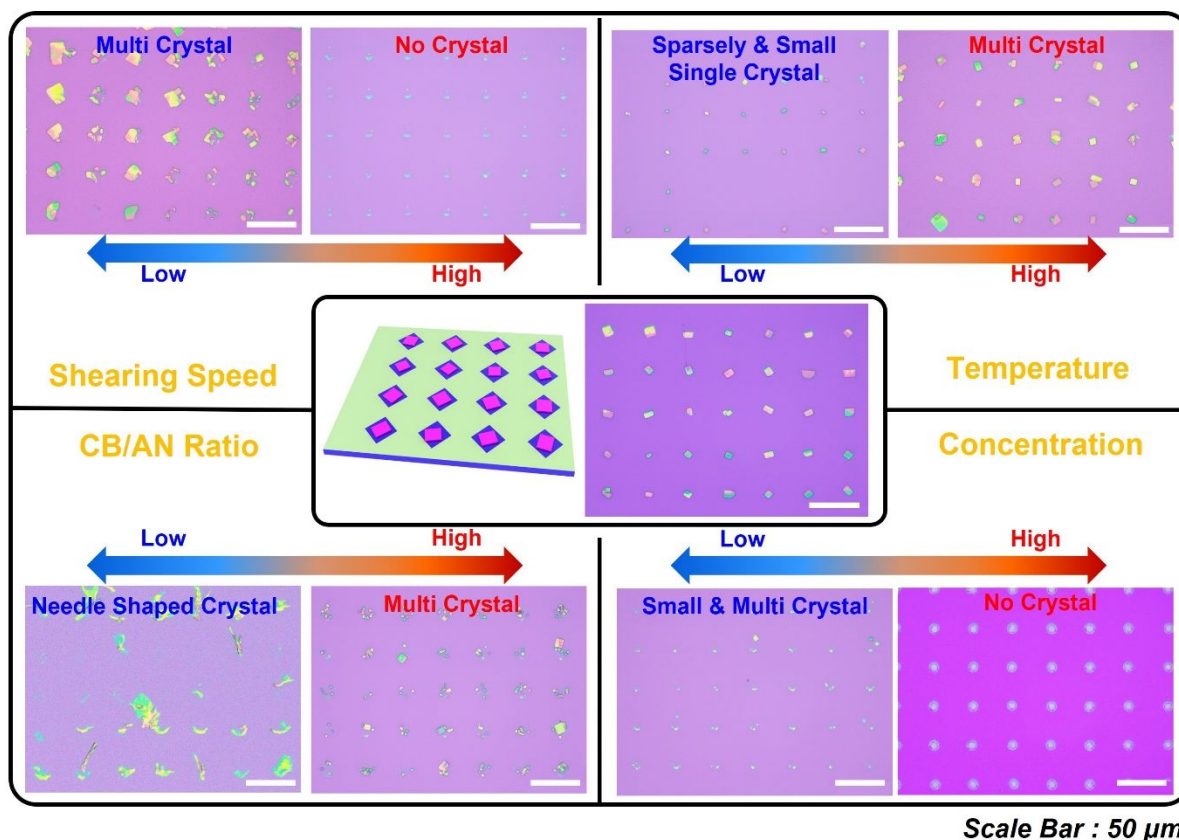


**Figure S8.** Corresponding OM images of the  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystals under different synthesis condition for shearing process with different shearing speeds, substrate temperature, ratios of CB/AN, and concentrations of perovskite precursor solutions (low/high shearing speed: 30/50  $\mu\text{m/s}$ , low/high temperature: 60/80°C, low/high CB/AN ratio: 2:1/10:1, low/high concentration: 0.5/1.5 times concentration of the optimal solution).

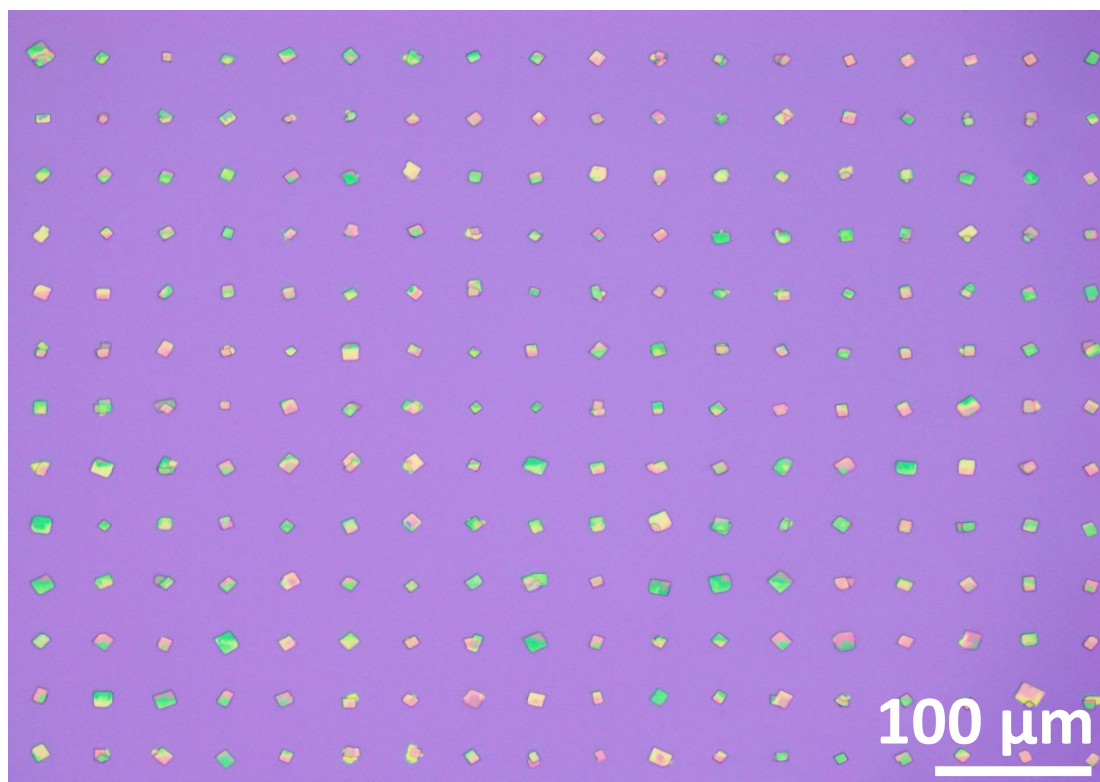


**Figure S9.** Corresponding lower-magnification OM image of  $(\text{PEA})_2\text{PbBr}_4$  perovskite crystal arrays.

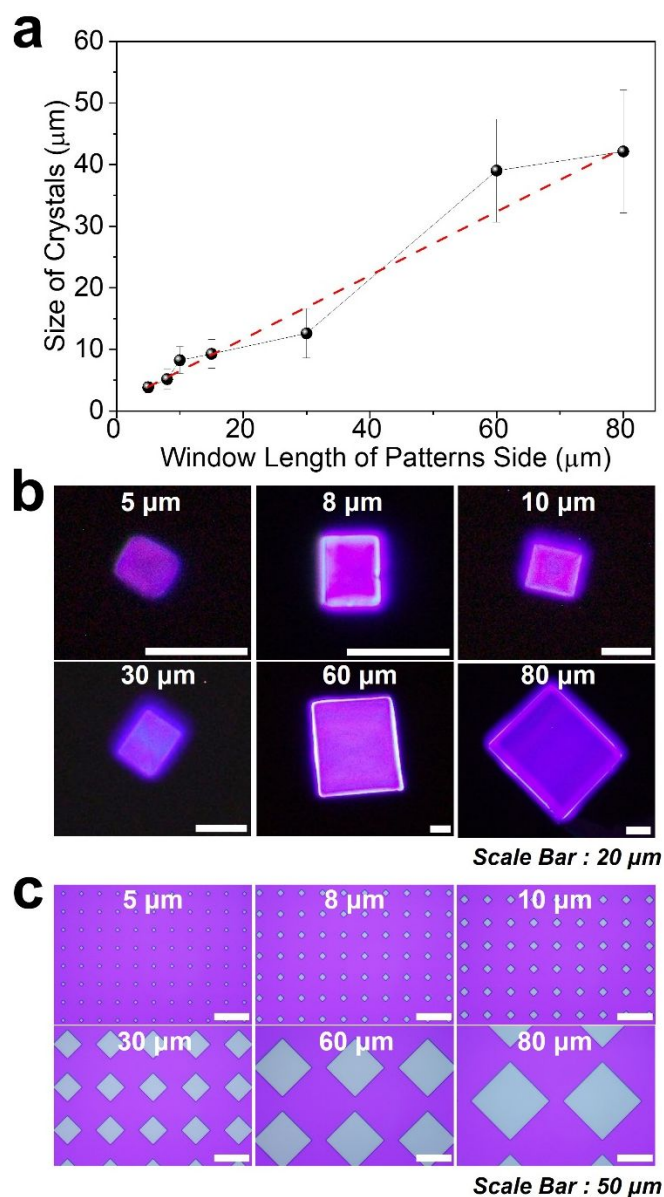


**Figure S10.** Dependence of window length of patterns to size of  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystals. (a) Sizes of  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystals dependent on size of the patterns. (b) PL images of  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystals grown on patterns of different sizes. (c) OM images of PR patterns with varying sizes fabricated by photolithography process.

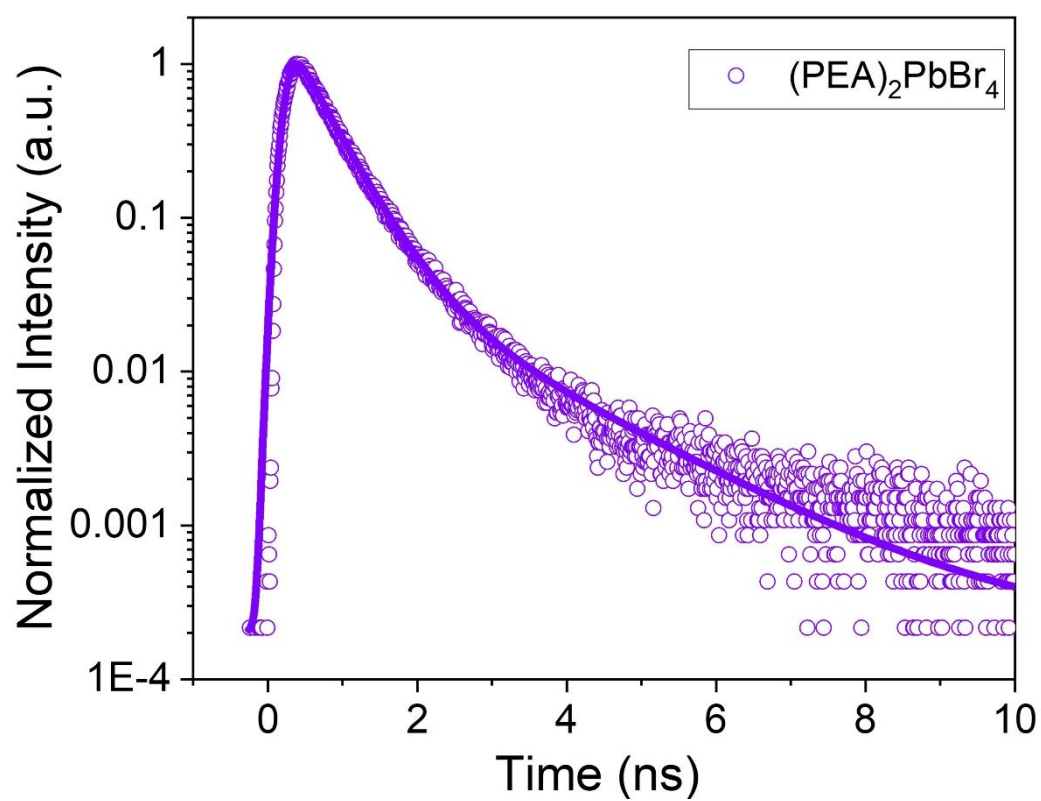


**Figure S11.** TR-PL decay at the peak emission wavelength (425 nm) for (PEA)<sub>2</sub>PbBr<sub>4</sub> 2D perovskite crystal arrays.

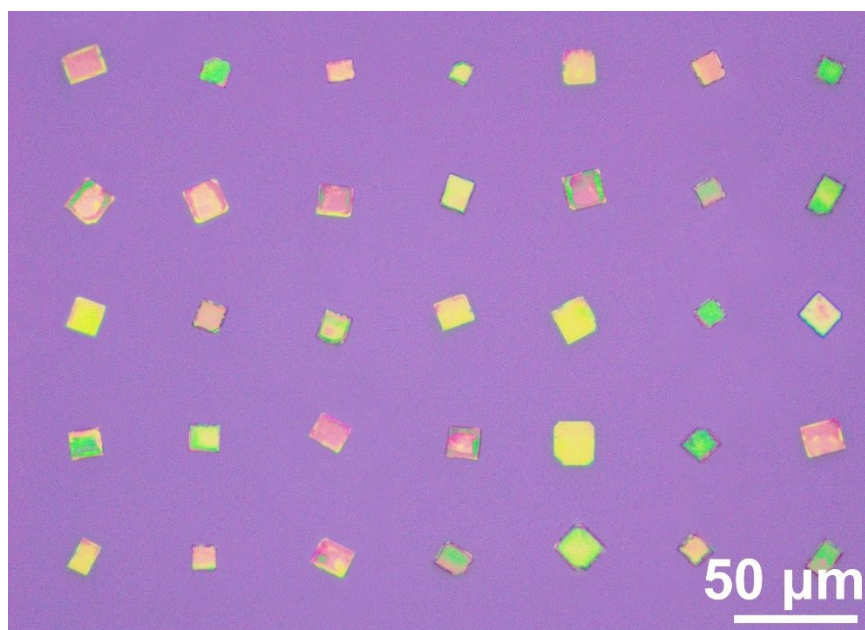


**Figure S12.** Corresponding OM image of  $(\text{PEA})_2\text{PbI}_4$ - $(\text{PEA})_2\text{PbBr}_4$  2D perovskite heterostructure crystal arrays.

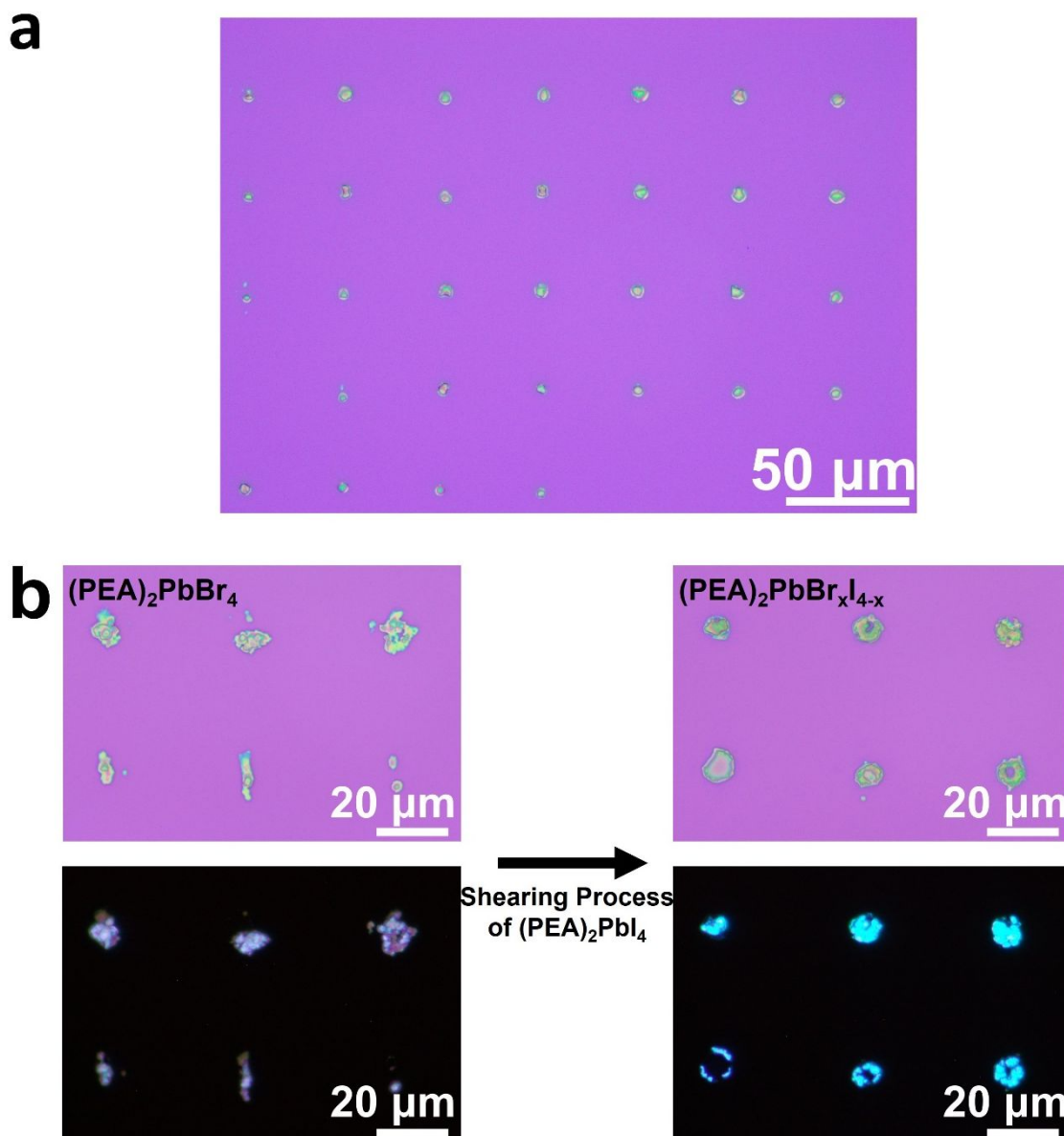


**Figure S13.** (a) Corresponding OM image of aggregated  $(\text{PEA})_2\text{PbBr}_x\text{I}_{4-x}$  2D perovskite alloy arrays synthesized by shearing process of  $(\text{PEA})_2\text{PbI}_4$  solution on the aggregated  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite array. (b) OM and corresponding PL images of the aggregated  $(\text{PEA})_2\text{PbI}_4$  arrays before the shearing process of  $(\text{PEA})_2\text{PbI}_4$  solution (left) and aggregated  $(\text{PEA})_2\text{PbBr}_x\text{I}_{4-x}$  2D perovskite alloy arrays after the shearing process of  $(\text{PEA})_2\text{PbI}_4$  solution (right).

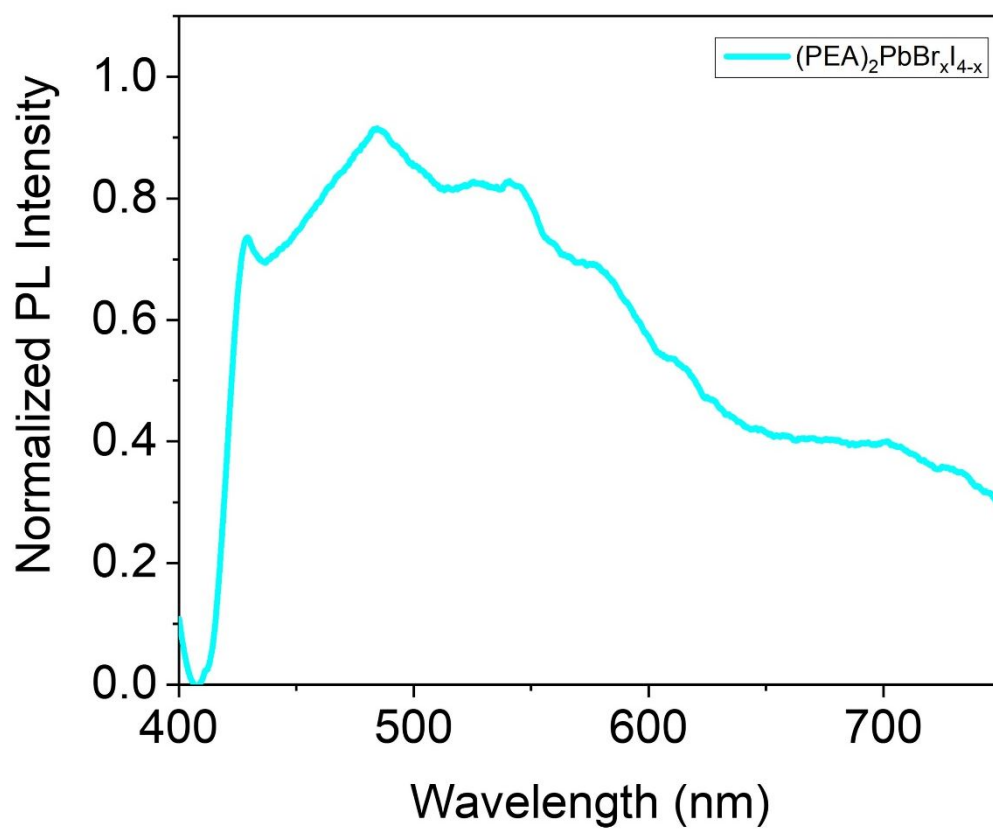


**Figure S14.** PL spectra of aggregated  $(\text{PEA})_2\text{PbBr}_x\text{I}_{4-x}$  2D perovskite alloy arrays.

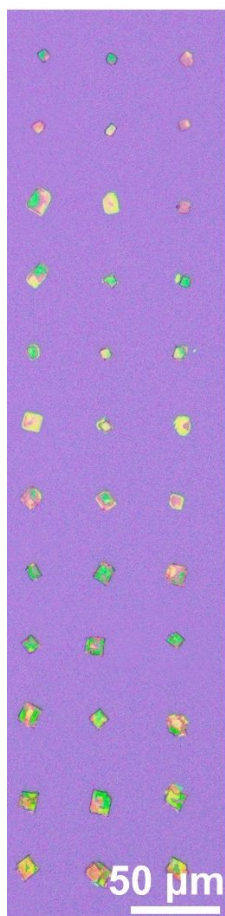


**Figure S15.** Corresponding OM image of the 2D perovskite crystal arrays synthesized by solution dropping process using  $(\text{PEA})_2\text{PbI}_4$  solution on to the  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystals arrays.

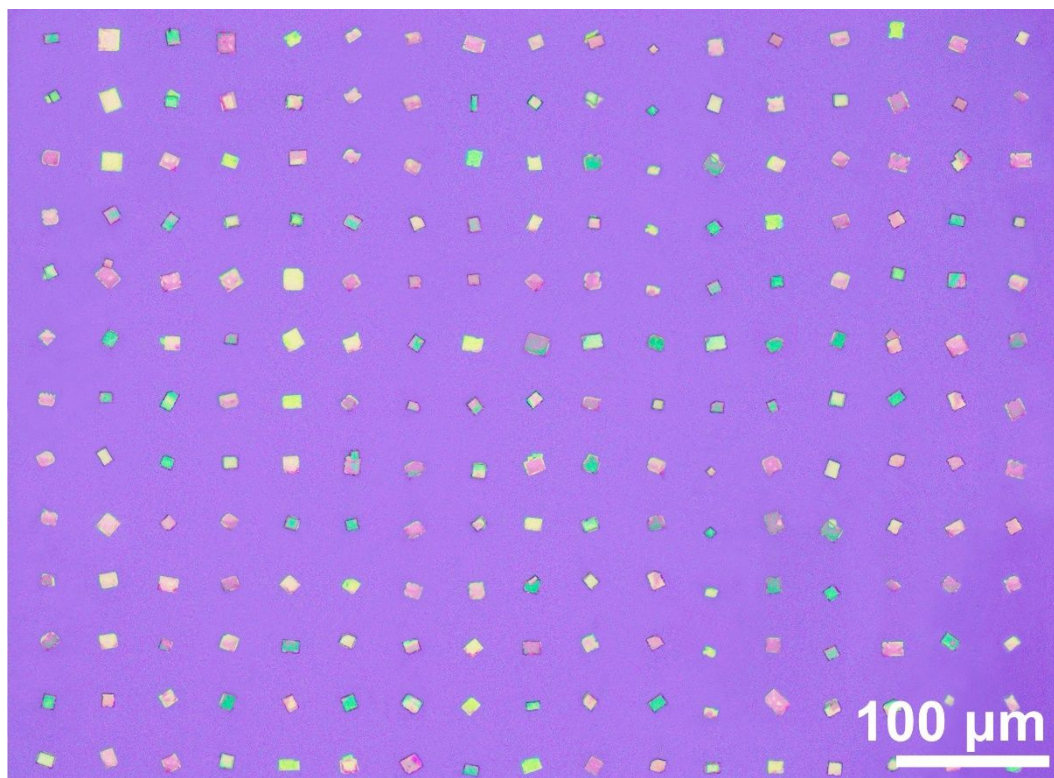


**Figure S16.** Corresponding OM image of lower-magnification  $(\text{PEA})_2\text{PbI}_4$ - $(\text{PEA})_2\text{PbBr}_4$  2D perovskite heterostructure crystal arrays.

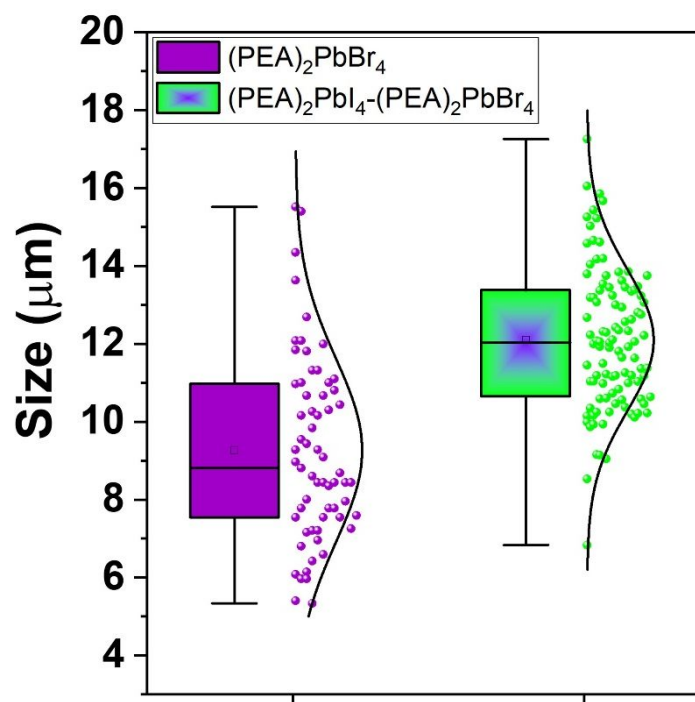


**Figure S17.** Size distributions of  $(\text{PEA})_2\text{PbBr}_4$  and  $(\text{PEA})_2\text{PbI}_4-(\text{PEA})_2\text{PbBr}_4$  2D perovskite crystal arrays.

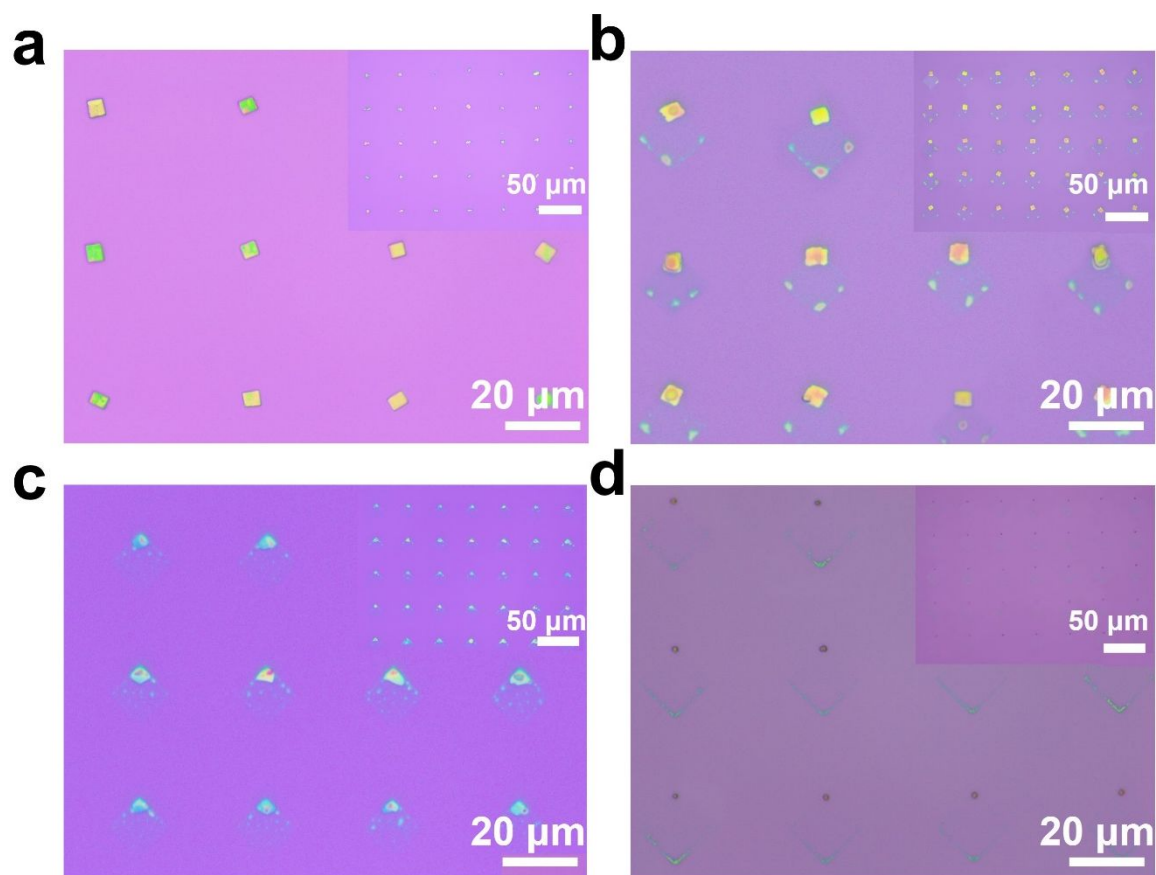


**Figure S18.** OM images of the  $(\text{PEA})_2\text{PbI}_4$ ,  $(2\text{T})_2\text{PbI}_4$ ,  $(2\text{T})_2\text{SnI}_4$ , and  $(\text{BTm})_2\text{PbI}_4$ .  
a-d) Corresponding OM images of (a)  $(\text{PEA})_2\text{PbI}_4$ , (b)  $(2\text{T})_2\text{PbI}_4$ , (c)  $(2\text{T})_2\text{SnI}_4$ , and (d)  $(\text{BTm})_2\text{PbI}_4$  2D perovskite crystal arrays (inset images: lower-magnification images).

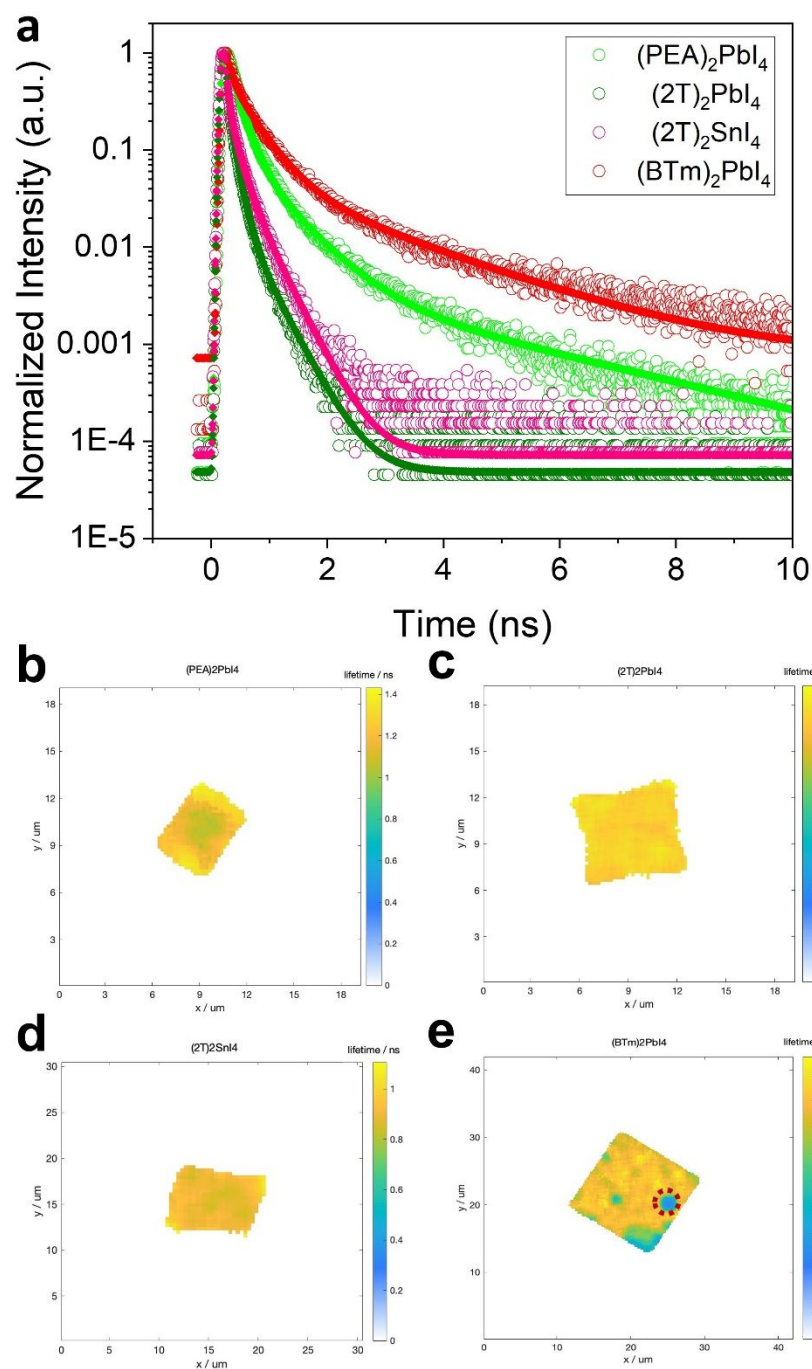


**Figure S19.** TR-PL and FLIM analysis of  $(\text{PEA})_2\text{PbI}_4$ ,  $(2\text{T})_2\text{PbI}_4$ ,  $(2\text{T})_2\text{SnI}_4$ , and  $(\text{BTm})_2\text{PbI}_4$ . (a) TR-PL decays at the peak emission wavelengths for  $(\text{PEA})_2\text{PbI}_4$ ,  $(2\text{T})_2\text{PbI}_4$ ,  $(2\text{T})_2\text{SnI}_4$ , and  $(\text{BTm})_2\text{PbI}_4$  2D perovskite crystal arrays. b-e) FLIM characterization of (b)  $(\text{PEA})_2\text{PbI}_4$ , (c)  $(2\text{T})_2\text{PbI}_4$ , (d)  $(2\text{T})_2\text{SnI}_4$ , and (e)  $(\text{BTm})_2\text{PbI}_4$  crystals (The results in red dashed circles in (e) represent the exciton lifetime of  $(\text{BTm})_2\text{PbI}_4$  crystals and remaining regions represent the lifetime of BTm molecules).

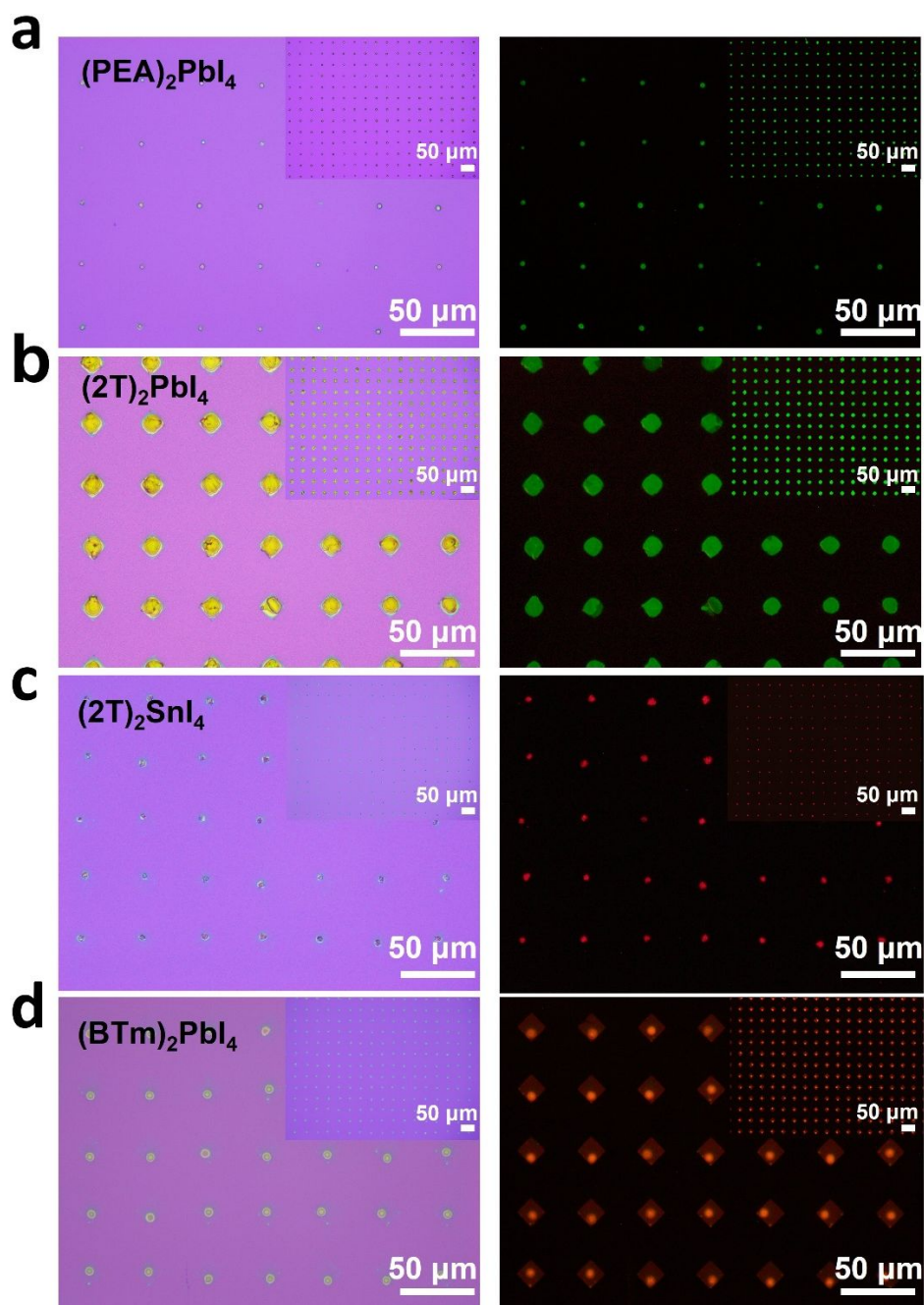


**Figure S20.** 2D perovskite bulk arrays of  $(\text{PEA})_2\text{PbI}_4$ ,  $(2\text{T})_2\text{PbI}_4$ ,  $(2\text{T})_2\text{SnI}_4$ , and  $(\text{BTm})_2\text{PbI}_4$ . a-d) OM (left) and corresponding PL (right) images of 2D perovskite bulk arrays based on (a)  $(\text{PEA})_2\text{PbI}_4$ , (b)  $(2\text{T})_2\text{PbI}_4$ , (c)  $(2\text{T})_2\text{SnI}_4$ , and (d)  $(\text{BTm})_2\text{PbI}_4$ . Inset images: Lower-magnification images.

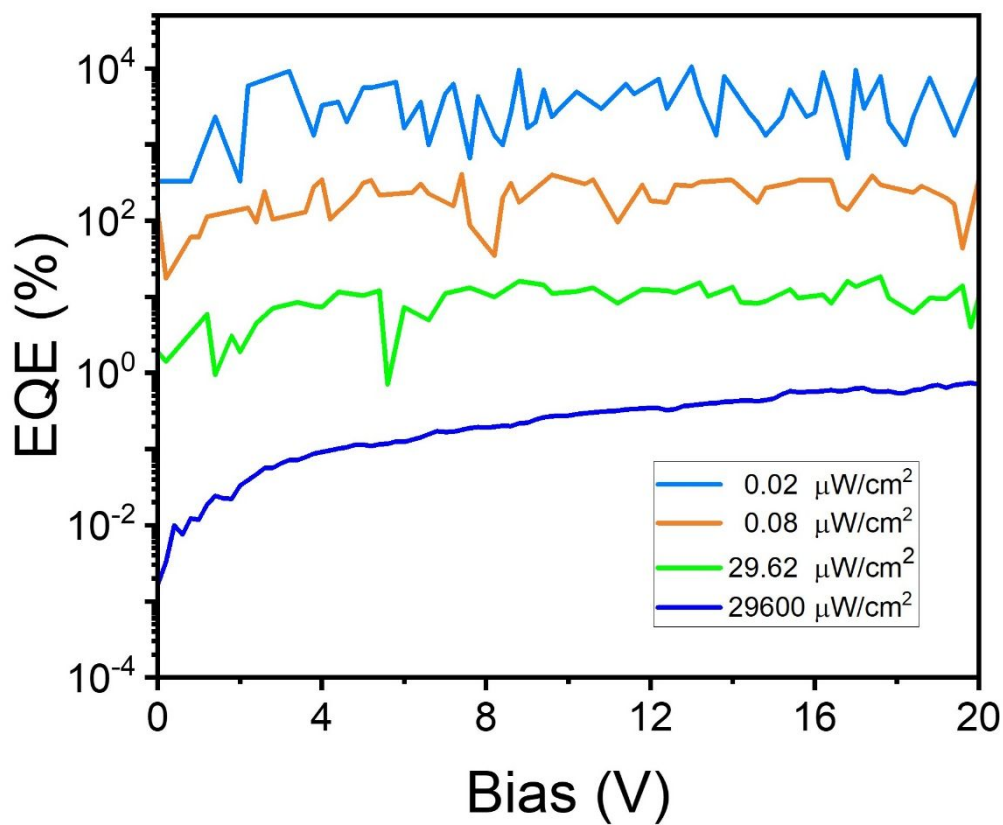


**Figure S21.** *EQE* of (PEA)<sub>2</sub>PbBr<sub>4</sub> single crystal photosensors under UV light at a wavelength of 365 nm with various light intensities.

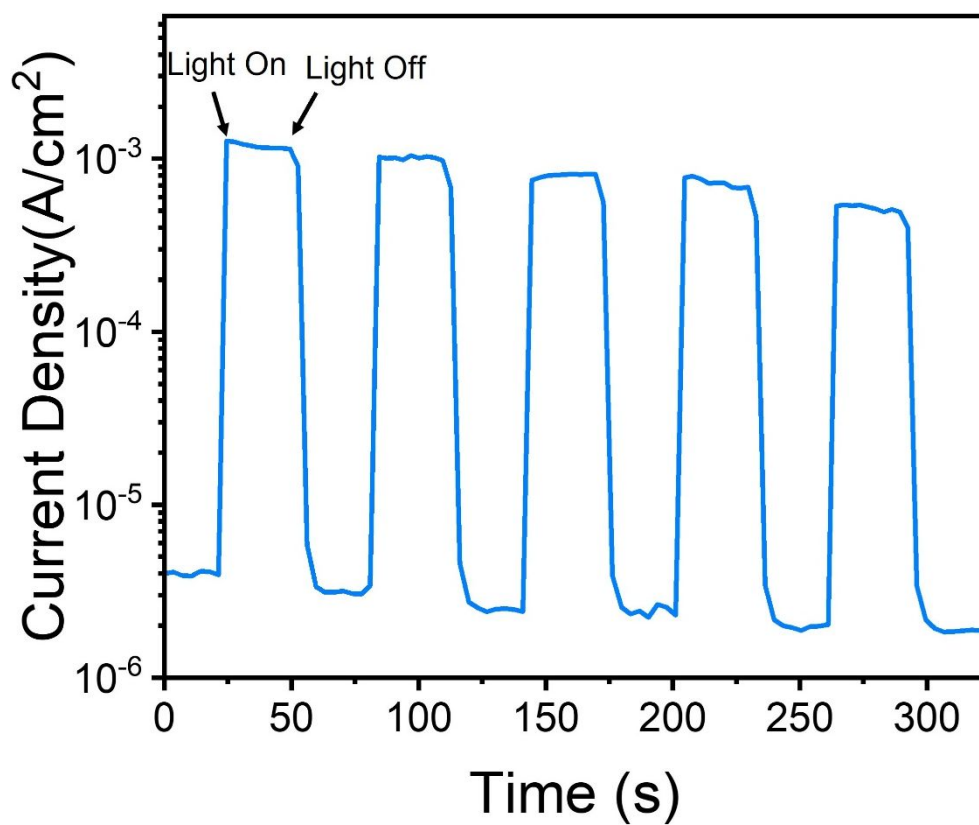


**Figure S22.** Photo-switching characteristics of (PEA)<sub>2</sub>PbBr<sub>4</sub> 2D perovskite single crystal photosensor under UV light illumination ( $\lambda = 365$  nm,  $P = 29600 \mu\text{W cm}^{-2}$ )

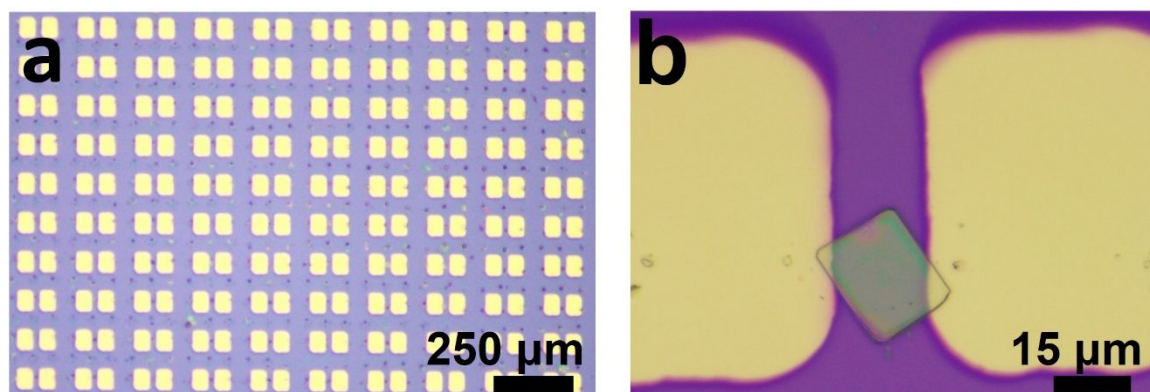


**Figure S23.** (a) OM image of  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite single crystal photosensor arrays. (b) Enlarged OM image of single photosensor showing a  $(\text{PEA})_2\text{PbBr}_4$  2D perovskite single crystal bridging two Au electrodes.

### Supplementary Reference

- S1. Dou, L.; Wong, A. B.; Yu, Y.; Lai, M.; Kornienko, N.; Eaton, S. W.; Fu, A.; Bischak, C. G.; Ma, J.; Ding, T.; Ginsberg, N. S.; Wang, L.; Alivisatos, A. P.; Yang, P. *Science*, **2015**, *349*, 1518.