

## Direct Insight into Crystallization and Stability of Hybrid Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ via Solvothermal Synthesis

### Electronic Supplementary Information:

#### Experimental Section

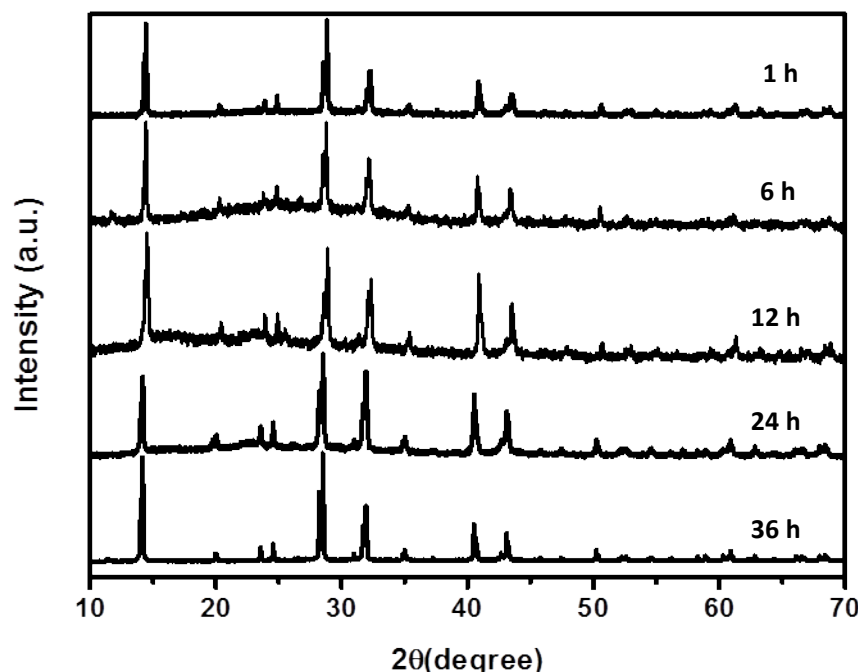
In a typical experimental process, 15 mg lead(II) of acetatetrihydrate ( $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ ) (99.8%, Aldrich) was completely dissolved in 1 mL of hydriodic acid (45% in water, J&K Scientific) with the help of continuous magnetic stirring, then 30 mL of isopropanol (99.9%, J&K Scientific) was added and stirred violently. The solution was stirred for 15 min, then it turned into yellow. 300  $\mu\text{L}$  of methylamine solution (33 wt. % in absolute ethanol, Aldrich) was added dropwise. The mixture was further stirred for 15 min and then transferred into Teflon-lined autoclave, sealed and kept at 120  $^\circ\text{C}$  for 12 h in a furnace, and cooled to room temperature. The black precipitates were collected and washed with isopropanol, and then dried in a vacuum oven at 55  $^\circ\text{C}$  for 12 h. The equipment with the total volume of isopropanol was kept constant.

#### Material Characterization

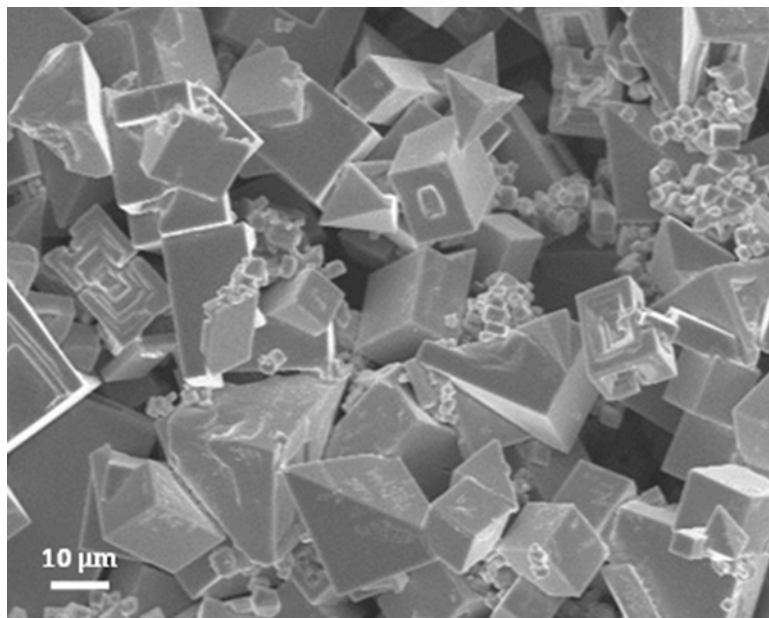
Crystallographic information on  $\text{CH}_3\text{NH}_3\text{PbI}_3$  crystals was investigated by powder X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer,  $\text{Cu K}\alpha$  radiation, 40 kV). The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FESEM, HITACHI S4800) and transmission electron microscopy (TEM, JEOL JEM-2100, 100 kV).

Perovskite samples were dispersed in isopropanol, and then dropped on a conductive SEM sample holder, or a carbon-coated copper grid with irregular holes, for electron microscopy (SEM/TEM) analysis.

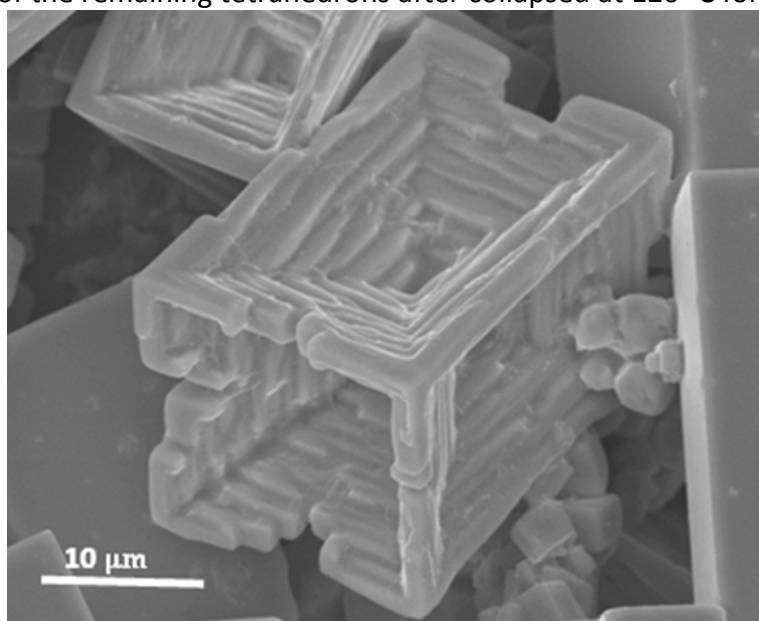
The optical absorption spectra were measured by using a Cary 500 Spectrophotometer. The photofluorescence spectra were obtained from a Fluorolog-3-P molecular fluorescence spectrometer with excitation wavelength of 460 nm



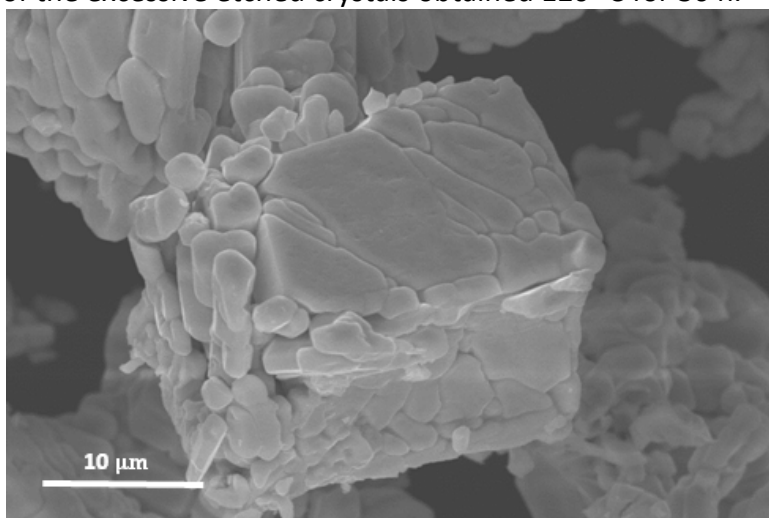
**Figure S1.** PXRD patterns of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  crystals synthesized with different time of reaction. From top to bottom are 36 h, 24 h, 12 h, 6 h and 1 h respectively.



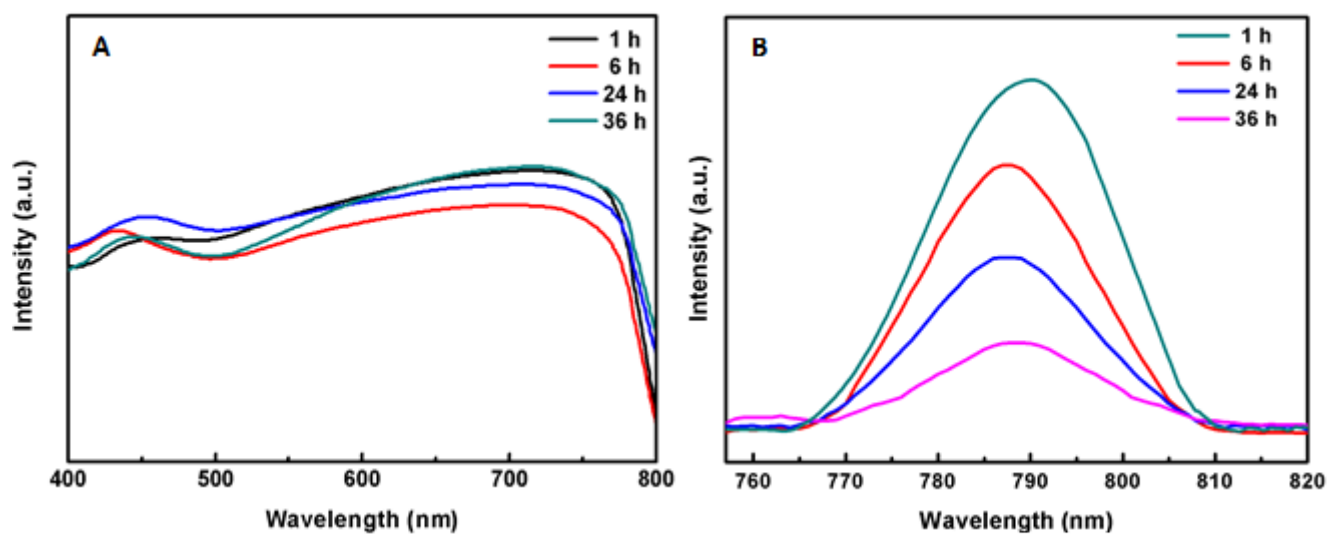
**Figure S2.** SEM image of the remaining tetrahedrons after collapsed at 120 °C for 60 h.



**Figure S3.** SEM image of the excessive etched crystals obtained 120 °C for 36 h.



**Figure S4.** The SEM image of the crystals preserved in the humidity of sixty percent for 3 h.



**Figure S5.** (A) UV-vis absorption and (B) photoluminescence spectrum of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  products prepared with different reaction time.