

Supporting Information

Binary Ligands-Mediated Morphological Evolution of Methylammonium Lead Bromide Nanocrystals

Artavazd Kirakosyan¹, Min-Gi Jeon¹, Chang-Yeon Kim², Yeonho Kim^{3,*}, and Jihoon Choi^{1,*}

¹Department of Materials Science and Engineering, Chungnam National University,
99 Daehak-ro, Yuseong-gu, Daejeon, 34134, Republic of Korea

²Research Center for Materials Analysis, Korea Basic Science Institute, Daejeon, 34134,
Republic of Korea

³Research Institute of Basic Science, Incheon National University
119 Academy-ro, Yeonsu-gu, Incheon, 22012, South Korea

Corresponding author: Email: jihoonc@cnu.ac.kr

Email: yeonho@inu.ac.kr

Phone: +82 42 821 6632; Fax +82 42 821 5850

Table of Contents:

1. Experimental	S2-S4
2. Results	S5-S12

Contains 10 pages; Experimental procedure and Characterization Details, 8 Supporting Figures

1. Experimental

Materials

The chemicals were obtained from Sigma-Aldrich and used as received: lead (II) bromide (PbBr_2 , 99 %), *n*-octylamine (OAm, ≥ 99 %), oleylamine (OlAm, 70 %), dodecylamine (DDAm, > 97 %), octadecylamine (ODAm, > 80 %), oleic acid (OA ≥ 90 %), toluene (99 %), *N,N*-dimethylformamide (DMF, 99.5 %), methylamine water solution (CH_3NH_2 , 38-42 %), hydrobromic acid (HBr, Extra pure, 47-49 %).

Synthesis of $\text{CH}_3\text{NH}_3\text{Br}$

$\text{CH}_3\text{NH}_3\text{Br}$ (MABr) was synthesized at 0 °C for 2 hours by reacting the equivalent amount of methylamine with hydrobromic acid, respectively. The raw product was obtained by removing the solvents by a rotary evaporator at 40 ~ 45 °C. The precipitates were washed with diethyl ether for three times and dried under vacuum (60 °C, 5 h). As prepared MABr was stored for further use.

Synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr₃) NCs

The samples were prepared by the modified reverse ligand-assisted reprecipitation method. Briefly, $\text{CH}_3\text{NH}_3\text{Br}$ (MABr; 0.16 mmol) and PbBr_2 (0.2 mmol) were dissolved in DMF (2 mL) at ambient condition. Additionally, binary ligands of OAm (0.18 mmol) and OA (1.41 mmol) were added into the precursor solution. Then, neat toluene (8 mL) was added into the precursor solution (2.5 mL) while vigorously stirring. The addition of toluene induced a color

change from transparent to pale-green, and then to orange for initial 2-3 minutes indicating the formation of colloidal MAPbBr₃ perovskite NCs. After the formation of MAPbBr₃ NCs, the solutions were aged for 0-4 days in an oil bath (T = 25 and 45 °C). To achieve a wide range of morphological and size diversity, we carefully controlled the type of alkylamine (OAm, OlAm, DDAm, and ODAm) and concentration, aging duration, and toluene feed rate using Harvard Apparatus 11 plus syringe pump. For further analysis of the resulting crystals, the samples were carefully collected by decanting the upper solution and then washed three times using toluene.

Synthesis of MAPbBr₃ NCs with controlled amounts of binary ligands

MABr (0.16 mmol) and PbBr₂ (0.2 mmol) were dissolved in DMF (2 mL) at ambient condition. The controlled amounts of OAm (0.03 and 0.18 mmol) and OA (0.28, 0.57, 0.85, 1.13, and 1.41 mmol) were added into the precursor solution. Then, neat toluene (8 mL) was added into the precursor solution (2.5 mL) while vigorously stirring. The resulting MAPbBr₃ solution was aged for 1 day in an oil bath (T = 25 °C).

Characterization

The particle size and shape were observed by Hitachi S-4800 high-resolution scanning electron microscopy (SEM) equipped with HORIBA EX-250 module for energy disperse spectroscopy (EDS) analysis. Transmission electron microscopy (TEM) images and diffraction pattern were obtained on JEM2100 operated at 200 kV and High Voltage TEM (HVEM) operated at 1250 kV (JEM-ARM1300S, JEOL). Crystal structures of the drop-cast films were examined by X-Pert PRO MPD diffractometer with Cu-K α radiation at $\lambda = 1.54 \text{ \AA}$. Absorbance

and photoluminescence spectra were recorded using Shimadzu UV-2600 UV-Vis spectrometer and Hitachi F-7000 fluorescence spectrometer ($\lambda_{\text{Exc.}} = 365 \text{ nm}$), respectively.

2. Results

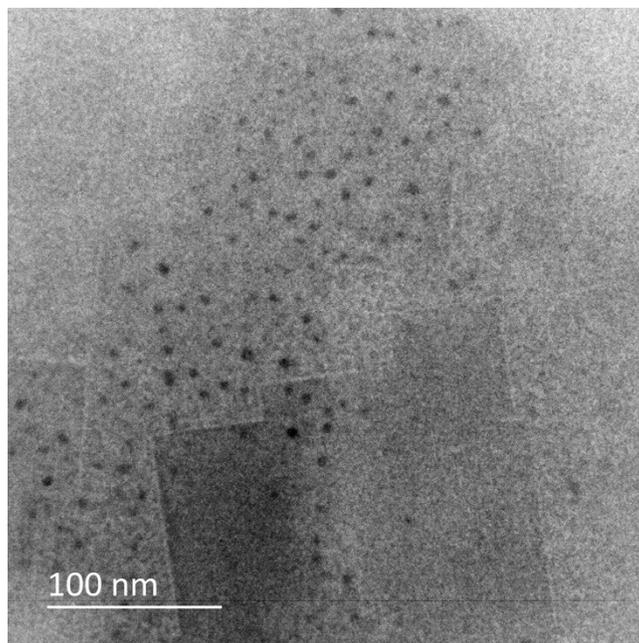


Figure S1. TEM image of MAPbBr_3 nanocrystals produced by the addition of DMF (2 mL) into the precursor solution.

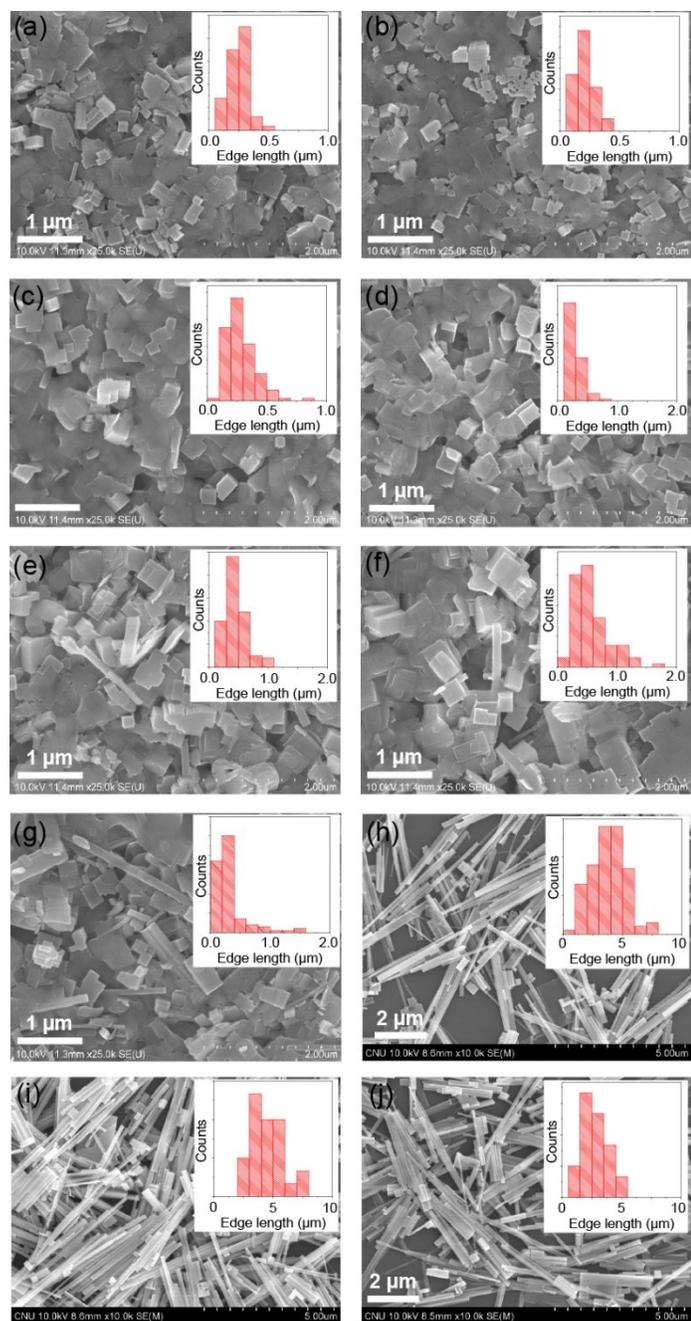


Figure S2. SEM images of the MAPbBr₃ crystals aged for (a) 0 min, (b) 1 min, (c) 5 min, (d) 10 min, (e) 30 min, (f) 60 min, (g) 3 hours, (h) 5 hours, (i) 30 hours, and (j) 96 hours at T = 25 °C.

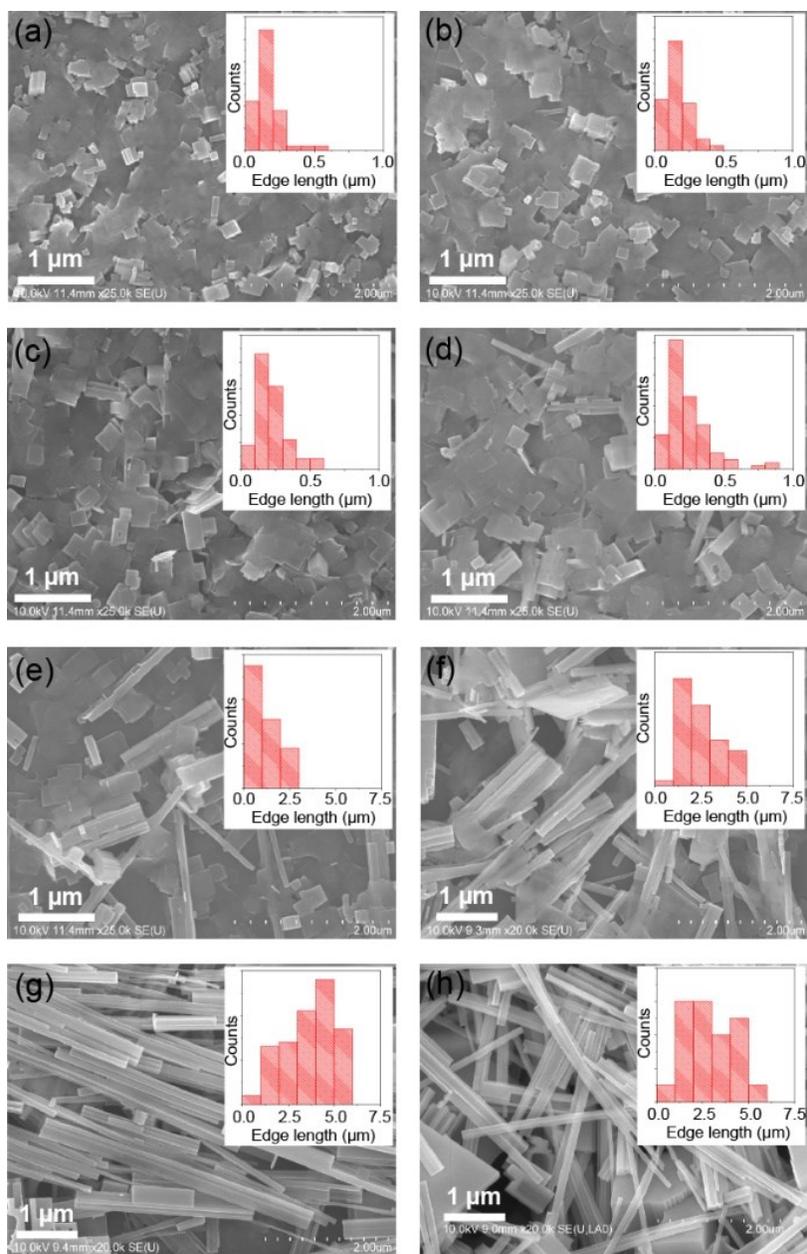


Figure S3. SEM images of the MAPbBr₃ crystals aged for (a) 0 min, (b) 1 min, (c) 5 min, (d) 10 min, (e) 30 min, (f) 60 min, (g) 3 hours, and (h) 24 hours at T = 40 °C.

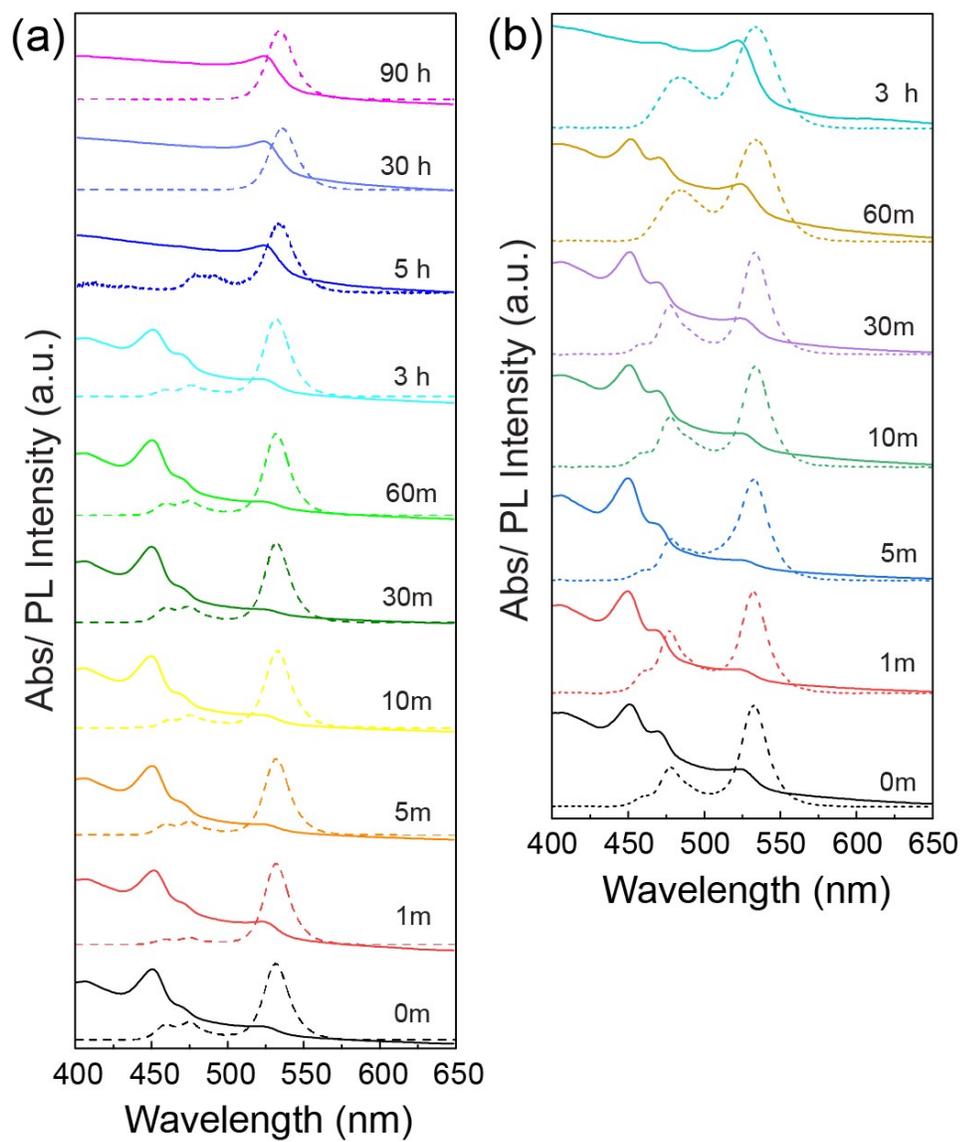


Figure S4. Time-dependent UV-Vis absorbance and PL spectra of MAPbBr₃ crystals aged at (a) T = 25 °C and (b) 40 °C.

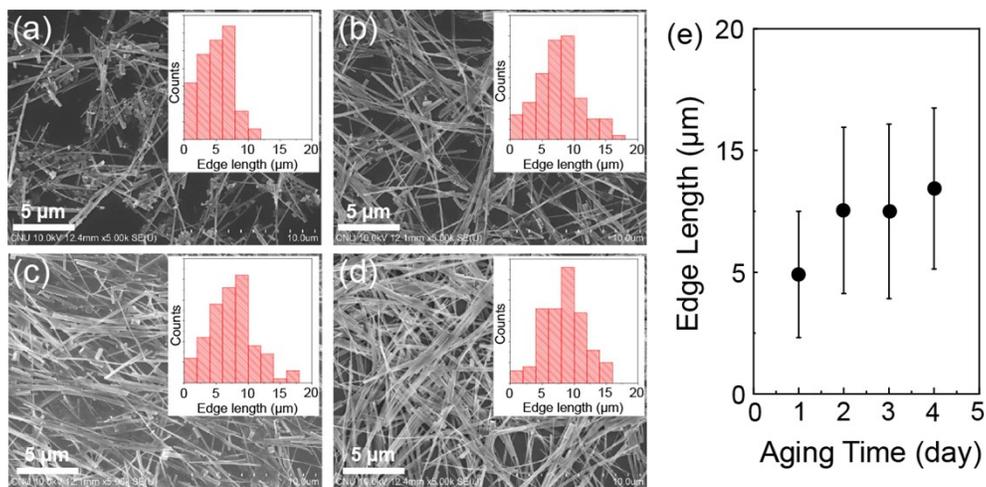


Figure S5. SEM images of MAPbBr₃ NWs aged for (a) 1, (b) 2, (c) 3, and (d) 4 days. The insets show the size distribution. (e) Average length of NWs as a function of aging time.

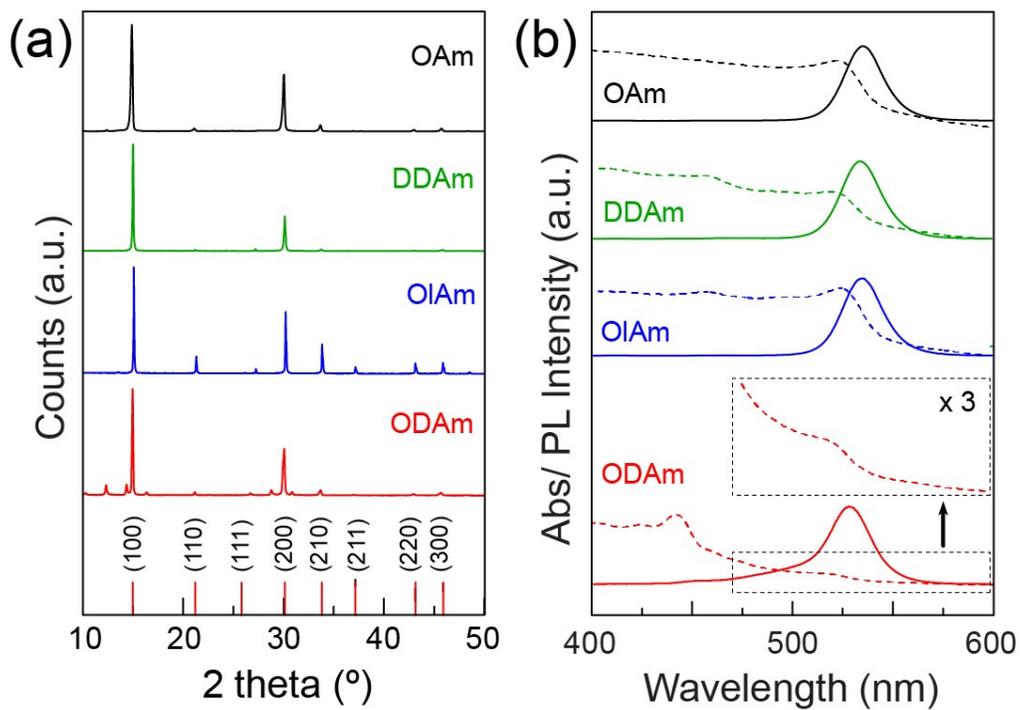


Figure S6. (a) X-ray diffraction patterns and (b) UV-Vis absorbance and PL spectra of the MAPbBr₃ crystals synthesized in the presence of *n*-octylamine (OAm), dodecylamine (DDAm), oleylamine (OlAm), and octadecylamine (ODAm).

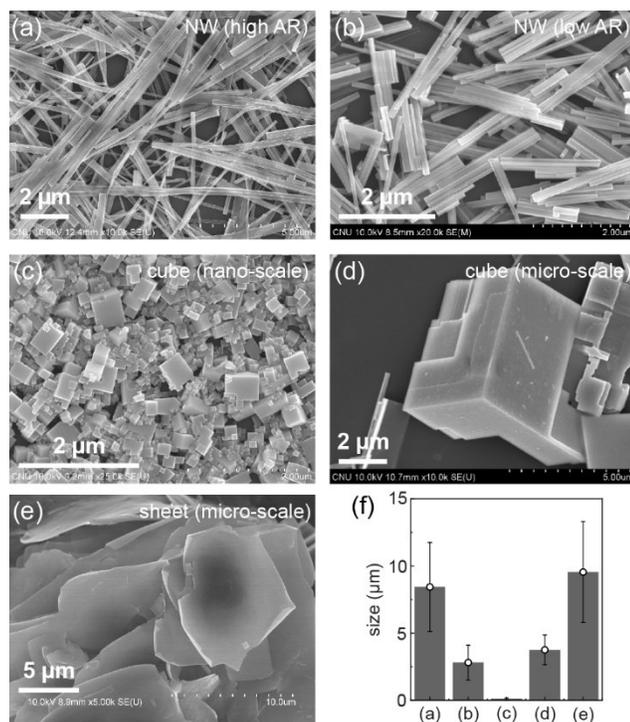


Figure S7. (a-e) SEM images and (f) the characteristic size of MAPbBr₃ crystals with the shape of (a) NW with a high aspect ratio, (b) NW with a low aspect ratio, (c) nanocube, (d) microcube, and (e) sheet.

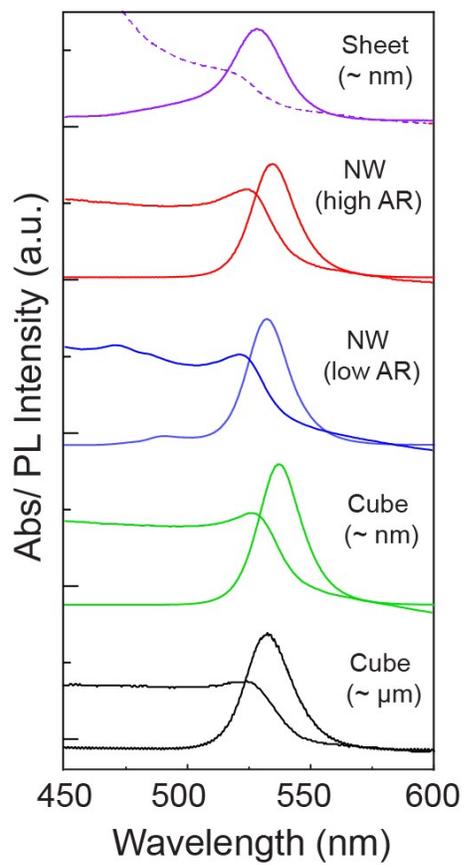


Figure S8. UV-Vis absorbance and PL spectra of MAPbBr₃ crystals with various shapes.