

Supporting Information

In-Situ Tetrafluoroborate-Modified MAPbBr₃ Nanocrystals Showing High Photoluminescence, Stability and Self-Assembly Behavior

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Experimental Section

Materials

PbBr₂ (99%, Sigma-Aldrich), NH₄BF₄ (99%, Sigma-Aldrich), NaBF₄ (98%, Sigma-Aldrich), CH₃NH₃Br (MABr, 99%, Dyesol), oleylamine (OLA, 80-90%, Accuchem), oleic acid (OA, Analytical Reagent, Accuchem), N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), toluene (99.7%, Sigma-Aldrich).

Preparation of MAPbBr₃ NCs

MAPbBr₃ nanocrystals were prepared with the LARP technique. Typically, 0.045 mmol of MABr, 0.045 mmol of PbBr₂, 0.5 mL of oleic acid and 0.02 mL of oleylamine were added into 1 mL of DMF solution in the Ar-filled glovebox. Then, the solution were stirred at room temperature for 30 min to form a clear transparent perovskite precursor solution. Subsequently, the precursor solution was quickly injected into the 10 mL 60 °C dried toluene solution with vigorous stirring. Finally, the obtained solution was transferred to the centrifuge tube. After centrifugation at 6000 rpm for 10 min to discard the big precipitates, the bright MAPbBr₃ colloidal nanocrystal solution was obtained. For the in-situ BF₄⁻ modification approach, different amount of tetrafluoroborate salts, either NaBF₄ or NH₄BF₄ (0, 0.0225 mmol, 0.045 mmol, 0.090 mmol and 0.180 mmol) was added into the precursor solution directly. The prepared MAPbBr₃ colloidal nanocrystal solution was stored in a vial for the washing process.

Washing Process of MAPbBr₃ Nanocrystals

To remove the unreacted ions in the prepared MAPbBr₃ colloidal nanocrystal solution, the washing process was carried out. In brief, the MAPbBr₃ nanocrystals were purified by iteratively precipitating the nanocrystals using the ethyl acetate antisolvent. Typically, the MAPbBr₃ colloidal nanocrystal solution was added to an equal volume of ethyl acetate antisolvent. Then, the mixture solution was centrifuged at 10,000 rpm for 20 min to precipitate the MAPbBr₃ nanocrystals. The supernatant was discarded and the precipitation was redissolved in toluene. Such washing process was repeated twice before any further use or characterization of the MAPbBr₃ nanocrystals.

Drying Process of MAPbBr₃ Nanocrystals

To avoid the aggregation or recrystallization of MAPbBr₃ nanocrystals in the drying process, the freeze drying method was applied to prepare the dried samples for characterizations or use.

Fabrication of WLED.

In general, we used the transparent epoxy resins to encapsulate the LED. Firstly, equal amounts of epoxy JL-510-A and JL-510-B were mixed together. And then, CaAlSiN₃:Eu²⁺ (CASNE) phosphors and as-prepared MAPbBr₃ nanocrystals (NH₄BF₄-2) were added. The mixture was stirred 10 mins and subsequently coated on the InGaN LED chip, which then was annealed at 60 °C for 1h in air on the hot-stage for solidifying.

Characterizations

The X-ray diffraction (XRD) patterns were measured on a Philips X-Pert X-ray diffractometer using a Cu K α radiation source ($\lambda = 1.54056 \text{ \AA}$). The dried samples for the XRD measurement were prepared using the freeze drying method for the purified MAPbBr₃ nanocrystals. A JEOL-JEM 2100F transmission electron microscopy (TEM) machine operating at an acceleration voltage of 200 kV was used to analyze the particle size and morphology of MAPbBr₃ nanocrystals and TEM-based X-ray energy-

dispersive spectroscopy (EDS) was carried out to analyze the chemical elements. For TEM observations, the purified MAPbBr₃ nanocrystal solutions were diluted and dropped on the carbon-coated copper mesh grids and then freeze-dried overnight. Steady state and time-resolved photoluminescence (PL) spectra were measured on an F-380 fluorescence spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were taken on a UV-6100 UV-vis spectrophotometer. X-ray photoelectron (XPS) spectroscopy were carried out at a ULVAC-PHI (PHIQUANTERA-II SXM) machine with Al K α as the X-ray source. Photoluminescence quantum yield (PLQY) was tested using an FLS920 spectrometer equipped with an integrating sphere from Edinburgh Instruments. Fourier Transform infrared spectroscopy (FTIR) was recorded using a Nicolet iS50. The ¹H nuclear magnetic resonance (¹H NMR) spectra were collected on a Bruker ARX 400 NMR spectrometer. The electroluminescence spectra, CCT and luminous flux of WLEDs were measured in an integrated sphere using a HAAS-2000 high precision fast spectral radiometer.

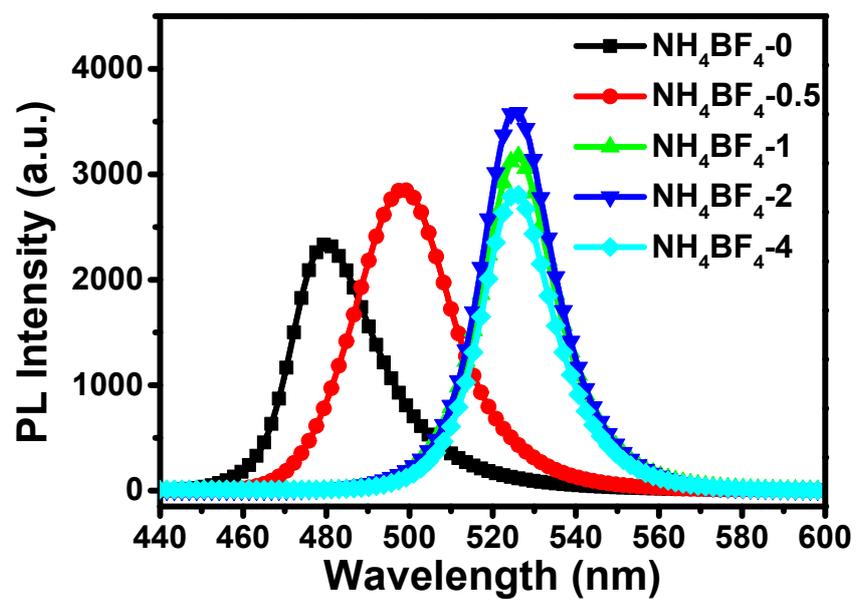


Figure S1. PL spectra of the freshly-prepared MAPbBr₃ nanocrystals using different amount of NH₄BF₄.

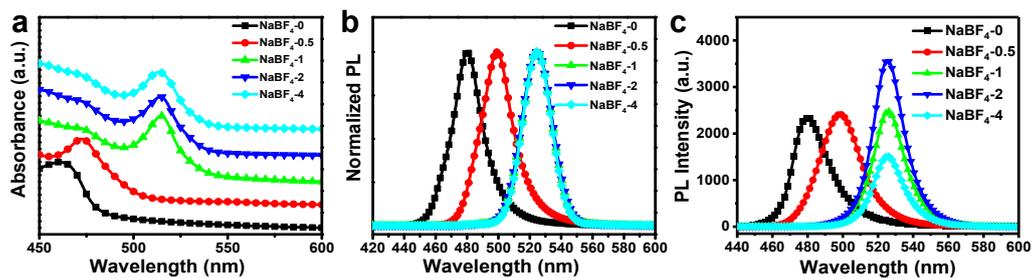


Figure S2. a) UV-vis absorption spectra and (b) normalized and (c) original PL spectra of the freshly-prepared MAPbBr₃ nanocrystals using different amount of NaBF₄.

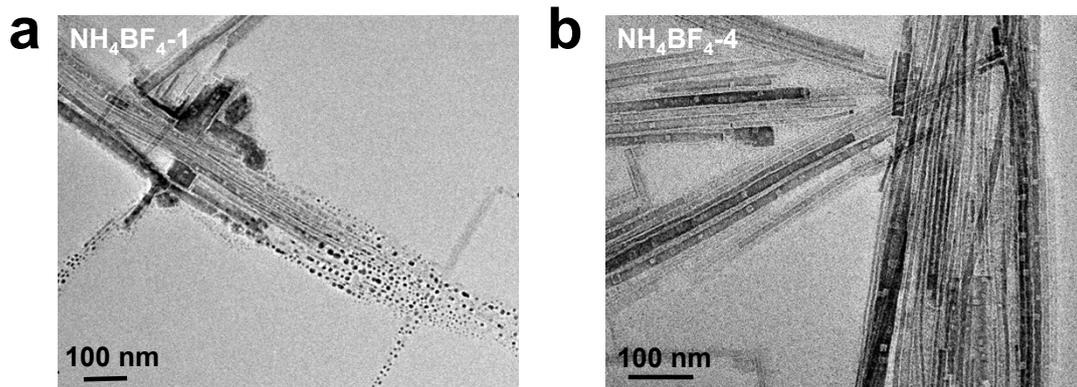


Figure S3. TEM images of (a) NH₄BF₄-1 and (b) NH₄BF₄-4.

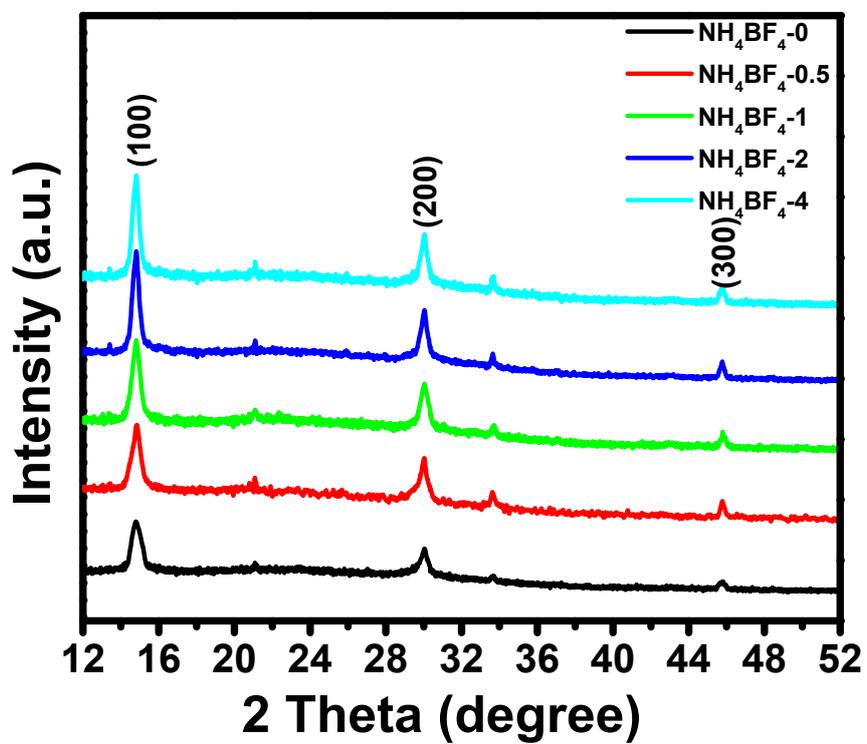


Figure S4. XRD patterns of the freshly-prepared MAPbBr₃ nanocrystals (freeze-dried sample) using different amount of NH₄BF₄.

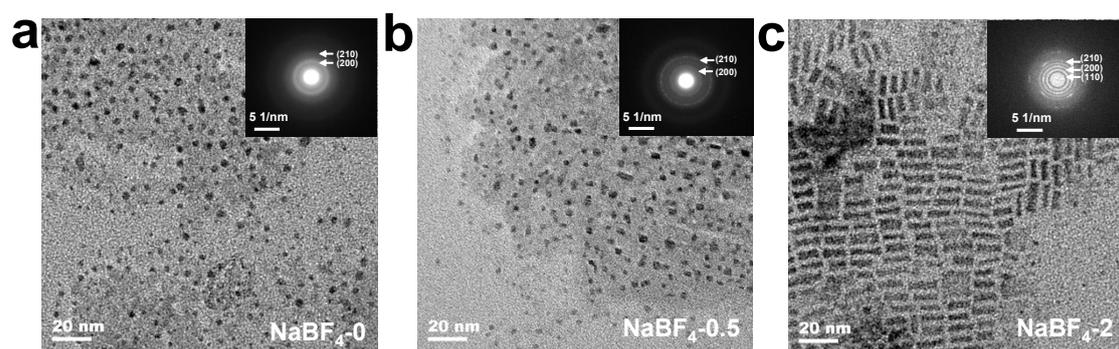


Figure S5. TEM images of NaBF₄-0, NaBF₄-0.5 and NaBF₄-2 (The insets are the selective-area electron diffraction patterns for NaBF₄-0, NaBF₄-0.5 and NaBF₄-2).

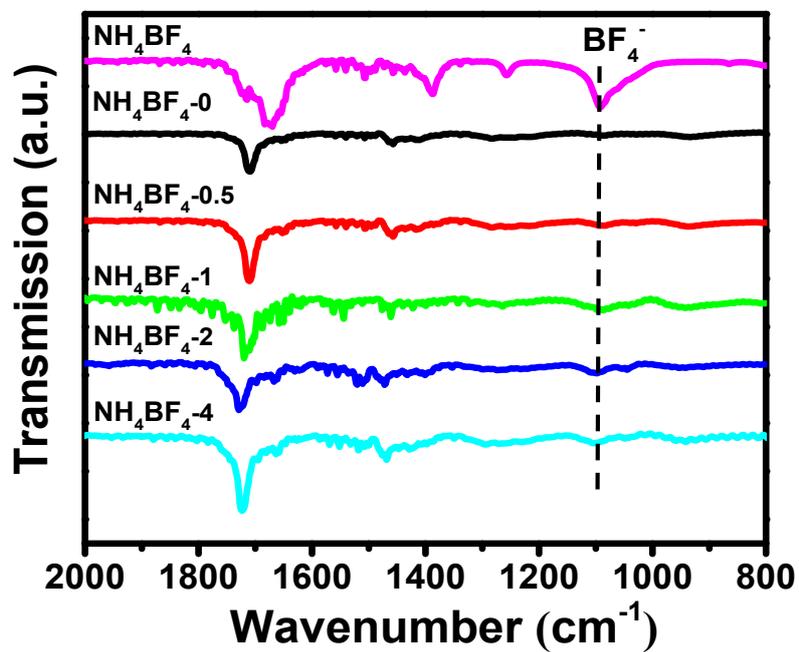


Figure S6. FTIR transmission spectra of the MAPbBr₃ nanocrystals prepared using different amounts of NH₄BF₄ and pure NH₄BF₄.

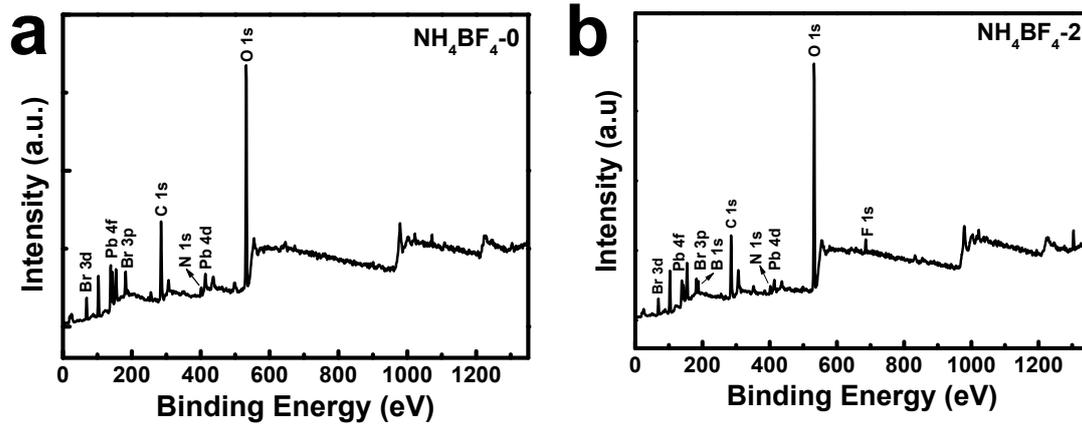


Figure S7. XPS survey scans of $\text{NH}_4\text{BF}_4\text{-0}$ and $\text{NH}_4\text{BF}_4\text{-2}$.

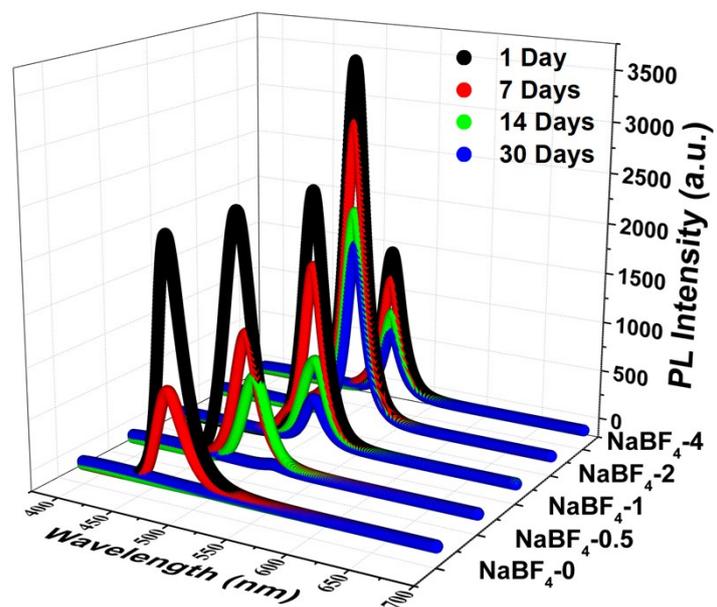


Figure S8. The relative PL intensity variation of MAPbBr₃ nanocrystals prepared using different amount of NaBF₄ as a function of the storage time in the open air.