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Supporting Information

Solvent-free, mechanochemical syntheses of bulk trihalide perovskites and their nanoparticles

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Experimental Procedures

Materials: Lead (II) bromide ($PbBr_2$, 99.999%, Alpha Aeser), methylamine solution (CH_3NH_2, 40%, Sd fine chemical limited), n-octylamine ($CH_3(CH_2)_7NH_2$, 99%, Spectrochem), hydrobromic acid (HBr, 48%, SRL), formamidine acetate [$(NH=CH(NH_2).\ CH_3COOH$, 99%, Sigma-Aldrich], acetone (99%, EMPLURA), toluene (99.5%, Fisher Scientific) and ether (98%, Fisher Scientific). All chemicals were used as received.

Methods:

Methylammonium bromide (CH_3NH_3Br) and n-octylammonium bromide ($CH_3(CH_2)_7NH_3Br$): Bromide salt of methylamine and n-octylamine were synthesized by previously reported method.[1] HBr (83.33 mL, 0.5 mol) was added drop-wise to methylamine (42.86 mL, 0.5 mol) or n-octylamine (82.74 mL, 0.5 mol) dissolved in 50 mL ethanol at 0 °C under magnetic stirring and it was continued for 3 hr. Excess ethanol was removed by rotary evaporator keeping the water bath temperature at 60 °C. The solid was redissolved in ethanol and then it was reprecipitated by adding ether. This process was repeated for four times. At last, the solid was dried under vacuum, a snow-white crystalline material was formed, which was stored inside the glove box for further use.

Formamidinium bromide (FABr): FABr was synthesized according to a literature method.[2] Formamidine acetate (10 gm, 0.096 mol) was dissolved in 32 ml (0.0192 mol) 48% HBr under stirring condition and stirring was continued for another 30 minutes. The solvent was removed by evaporation. Then, it was dissolved in ethanol and reprecipitated with ether. The process was repeated for three times and the white product was dried in vacuum at 60 °C.

Bulk $APbBr_3$ (A= Cs/FA/MA): $PbBr_2$ (36.7 mg, 0.1 mmol) and CH_3NH_3Br (11.2 mg, 0.1 mmol) were grinded with a mortar and pestle at room temperature. An orange color solid was immediately formed. The grinding was continued for another 10 minutes to achieve complete conversion. Then 2 ml acetone was added to it and centrifuged at 5000 rpm for 2 minutes. Supernatant was discarded. The product was dried in vacuum.

$FAPbBr_3$ and $CsPbBr_3$ were prepared according to the above procedure. Formamidine bromide (12.5 mg, 0.1 mmol) and CsBr were taken instead of MABr to prepare yellowish orange colored $FAPbBr_3$ and light yellow colored $CsPbBr_3$ respectively. In all the cases yield is more than 98%.

$APbBr_3$ (A= Cs/FA/MA) NPs: In a typical synthesis of $MAPbBr_3$, $PbBr_2$ (36.7 mg, 0.1 mmol), CH_3NH_3Br (11.2 mg, 0.1 mmol) and n-octylammonium bromide (12.6 mg, 0.06 mmol) were grinded with a mortar and pestle at room temperature. An orange color solid was observed immediately. This colored solid was grinded for another 10 minutes. Then 2 ml acetone was added to it and centrifuged at 5000 rpm for 2 minutes. Supernatant was discarded. The product was dried in vacuum.

$FAPbBr_3$ and $CsPbBr_3$ were prepared according to the above procedure. Formamidine bromide (12.5 mg, 0.1 mmol) and CsBr (21.2 mg, 0.1 mmol) were taken instead of MABr to prepare $FAPbBr_3$ and $CsPbBr_3$ NPs, respectively. In all the cases yield is more than 98%.

Spectroscopy and Microscopy Characterization

UV-visible measurements: Absorption spectra were collected with a Perkin-Elmer Lambda 1050 spectrophotometer using 1 cm quartz cuvette over the range of 320-800 nm. **Photoluminescence studies:** The fluorescence spectra were recorded on Perkin-Elmer LS-55 spectrometer with constant 10 nm excitation and 5 nm emission slit width with an excitation wavelength of 377 nm. The photoluminescence quantum yields (PL-QY) of the synthesized NPs were calculated using fluorescein as a standard (QY 0.79 in ethanol).

Thermogravimetry (TGA) Instruments: The thermogravimetric analyses were performed using Perkin Elmer instruments. The data was collected from 40 ^{0}C to 900 ^{0}C at a heating rate of 10 ^{0}C/min under N_2 flow.

Transmission Electron Microscopy images (TEM): TEM images were captured using JEOL instruments.

X-ray Diffraction (XRD): Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance Diffractometer with Ni-filtered Cu K_α radiation.

Energy dispersive X-ray (EDX). Elemental analysis was performed using TM3000 table top microscope Hitachi with an accelerating voltage of 15kV equipped with an EDX detector.

Time resolved photoluminescence: Luminescence lifetime decays were performed using time correlated single photon counting (TCSPC) using Edinburgh Instruments FLSP920. A pulsed laser diode (377 nm) with a pulse repetition rate of 500 kHz was employed for the lifetime measurements. The PL emission decay was collected at the PL peak maximum for each sample. The instrument response function was done using a Ludox scattering solution in water. The samples were excited at 377 nm and the lifetime decays were measured at the emission wavelength maximum. The PL decay spectrum has been collected using a time-correlated single photon counting (TCSPC) technique, and the numerical fit is formatted with the F900 software. The TRPL spectra were fitted according to the equation,

$$I(t) = \sum_{i=1}^{n} \alpha_i \exp\left(- t/\tau_i \right)$$

where α_i and τ_i are amplitude and lifetime of i^{th} component respectively whereas n is number of components. The amplitudes bear the total contribution of individual lifetime towards the average lifetime. Average fluorescence lifetimes were enumerated using the following equation:[3]

$$\tau_{av} = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i}$$

in which α_i is the pre-exponential factor corresponding to the i^{th} decay time constant, τ_i.

We examine the photophysical behavior of $APbBr_3$ NPs as a function of A-site cation. Time resolved photoluminescence studies were carried out in solution phase shown in Figure S6. The average life-times were estimated to be 29 ns, 151 ns and 383 ns for $CsPbBr_3$, $MAPbBr_3$ and $FAPbBr_3$ NPs, respectively after fitting the decays with a sum of three exponentials. This tri-exponential fitting indicates the contribution of multi-channel radiative recombination of excitons.

Table S1: Amount of starting materials

Products	$PbBr_2$	A-site cations			OABr	Yield (%)
		CsBr	MABr	FABr		
Bulk $CsPbBr_3$	36.7 mg, 0.1 mmol	21.2 mg, 0.1 mmol	×	×	×	98
$CsPbBr_3$ NPs	36.7 mg, 0.1 mmol	21.2 mg, 0.1 mmol	×	×	12.6 mg, 0.06 mmol	98
Bulk $MAPbBr_3$	36.7 mg, 0.1 mmol	×	11.2 mg, 0.1 mmol	×	×	99
$MAPbBr_3$ NPs	36.7 mg, 0.1 mmol	×	11.2 mg, 0.1 mmol	×	12.6 mg, 0.06 mmol	98
Bulk $FAPbBr_3$	36.7 mg, 0.1 mmol	×	×	12.5 mg, 0.1 mmol	×	99
$FAPbBr_3$ NPs	36.7 mg, 0.1 mmol	×	×	12.5 mg, 0.1 mmol	12.6 mg, 0.06 mmol	98

Table S2: Time-resolved photoluminescence parameters for $APbBr_3$ NPs

Perovskite NPs	$\tau_1\ (ns)$	α_1	$\tau_2\ (ns)$	α_2	$\tau_3\ (ns)$	α_3	$\tau_{av}\ (ns)$
$CsPbBr_3$	0.88	0.44	5.3	0.11	30.35	0.44	28.53
$MAPbBr_3$	3.21	0.9	29	0.05	209	0.05	151.15
$FAPbBr_3$	10	0.708	94	0.25	705	0.04	383.41

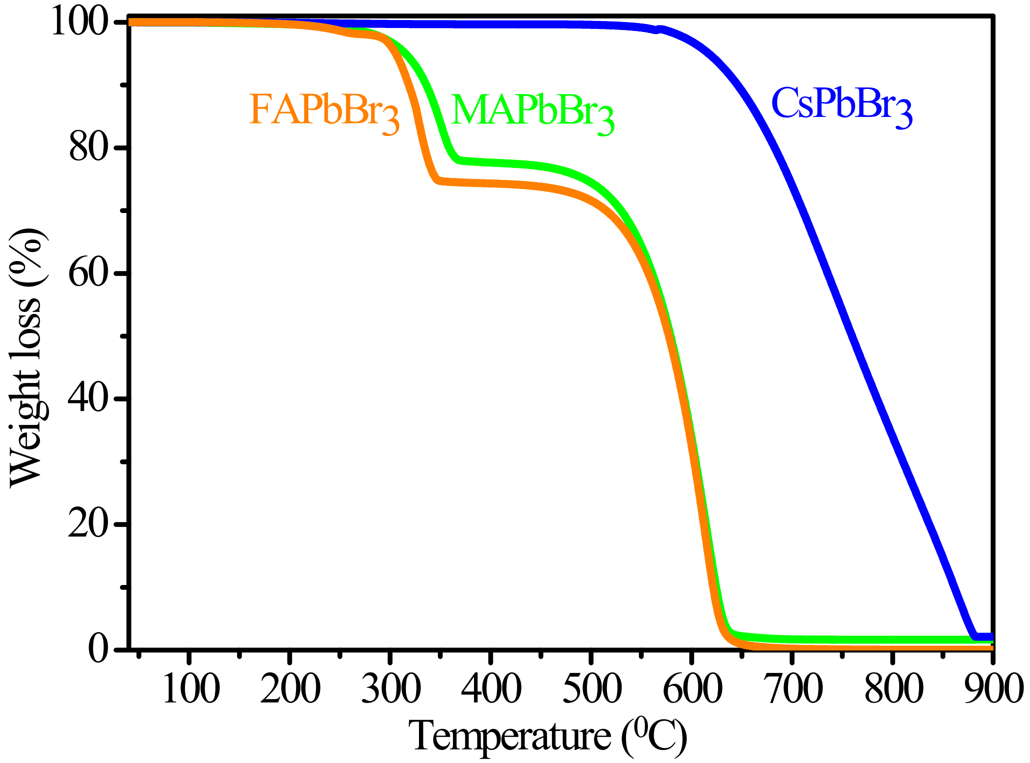
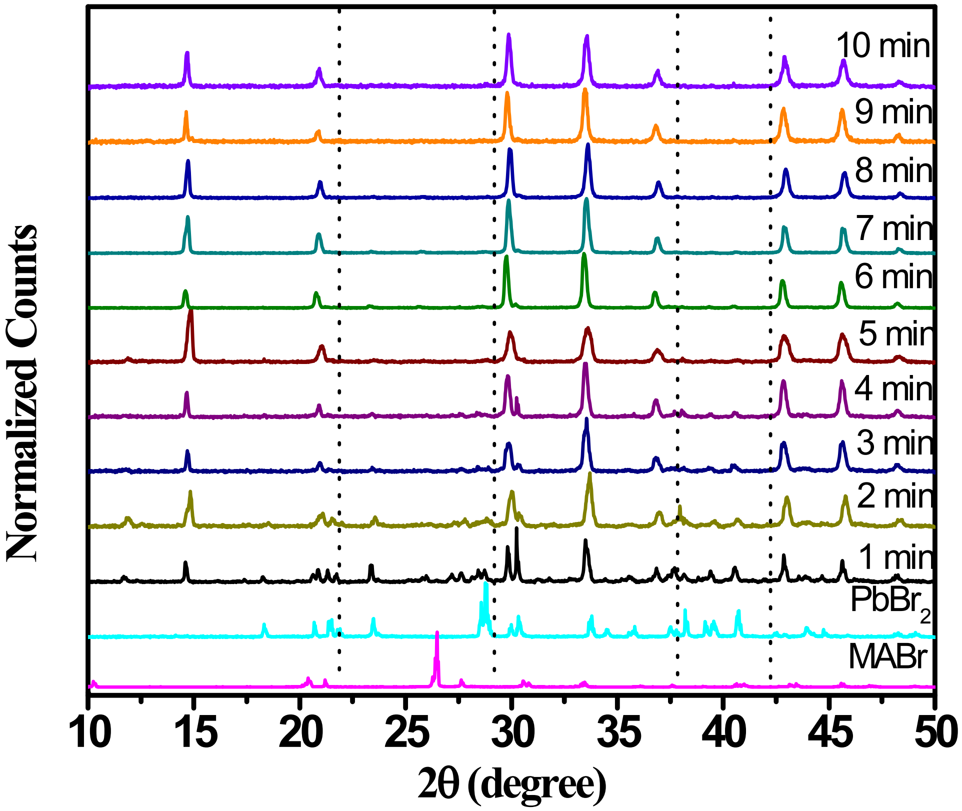


Figure S1: Thermogravimetric analyses of bulk $MAPbBr_3$, $FAPbBr_3$ and $CsPbBr_3$. More ionic nature of CsBr than MABr/FABr results in highest thermal stability of $CsPbBr_3$.[4] The smaller radius of MA^+ than FA^+,[5] enhances the thermal stability of $MAPbBr_3$ than $FAPbBr_3$.



Figures S2: PXRD patterns of $MAPbBr_3$ during the course of reaction, $PbBr_2$ and MABr precursors. The powder X-ray diffraction peaks of $PbBr_2$ and MABr gradually disappear over the grinding time and the peaks for $MAPbBr_3$ appear within 1 minute, supporting the incorporation of MA^+ into the $PbBr_2$ crystal lattice. PXRD pattern of $MAPbBr_3$ exhibits only the peaks of $MAPbBr_3$ after 10 min.

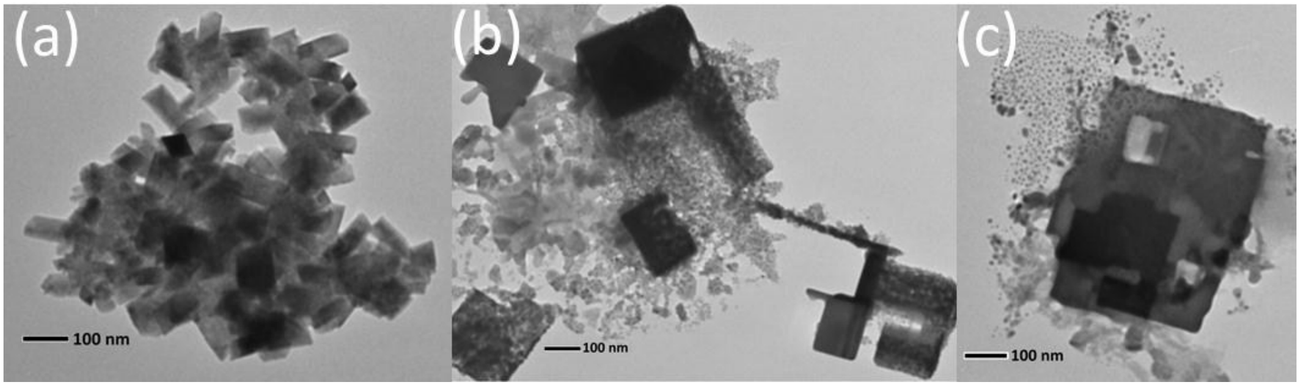


Figure S3: TEM images of (a) $FAPbBr_3$ (b) $CsPbBr_3$, and (c) $MAPbBr_3$ NPs. Degradation of $CsPbBr_3$ nanoplatelets occur under the electron beam exposure.

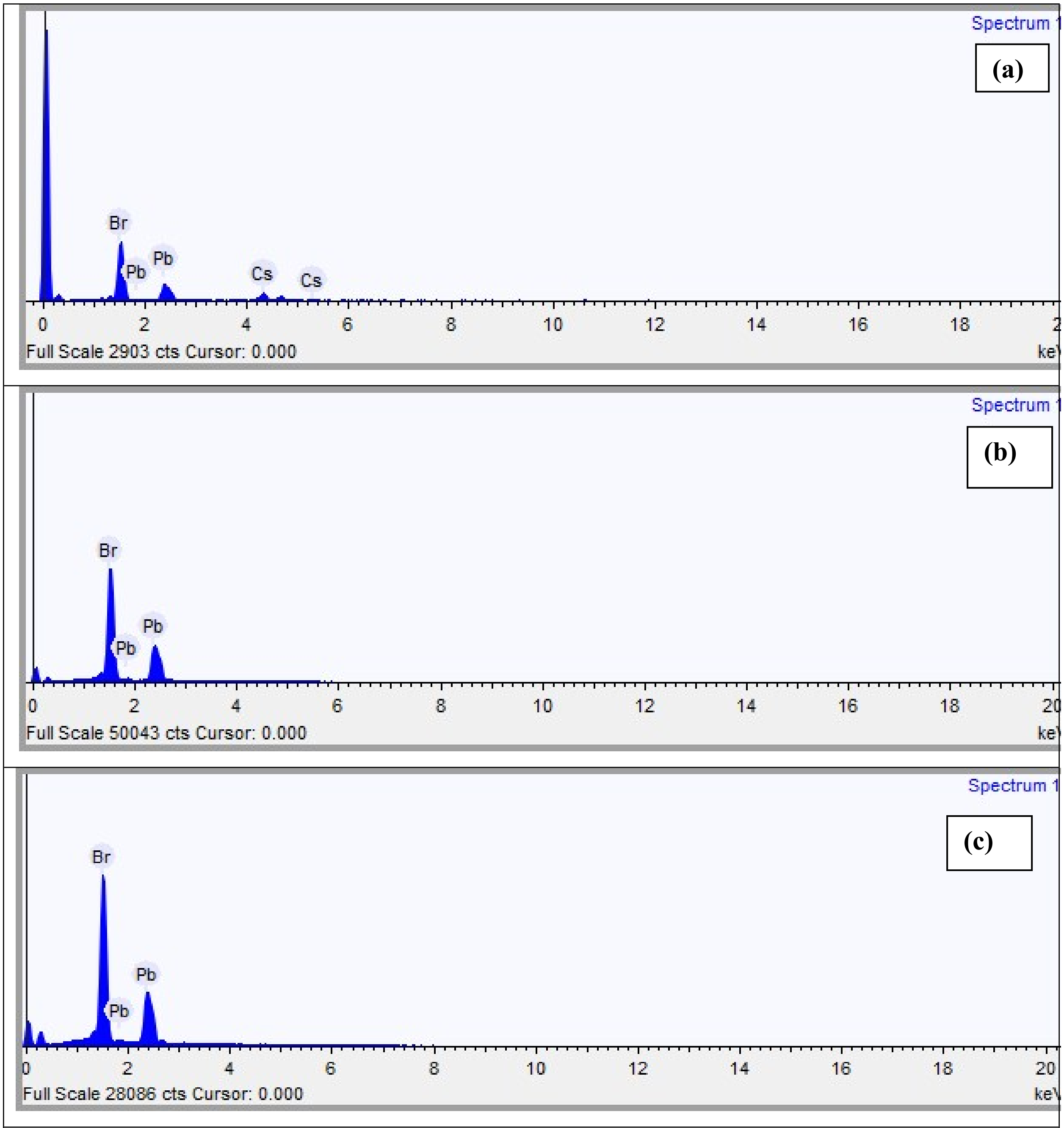
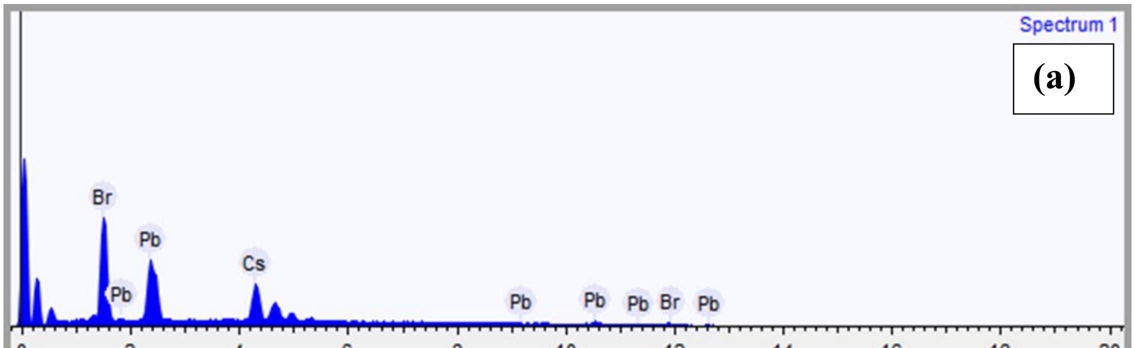


Figure S4. A representative energy dispersive X-ray (EDX) spectroscopy analysis of bulk (a) $CsPbBr_3$, (b) $MAPbBr_3$ and (c) $FAPbBr_3$. The Cs:Pb:Br ratio in $CsPbBr_3$ equal to 1:1:3. The Br:Pb ratio is 1:3 for both bulk $MAPbBr_3$ and $FAPbBr_3$.



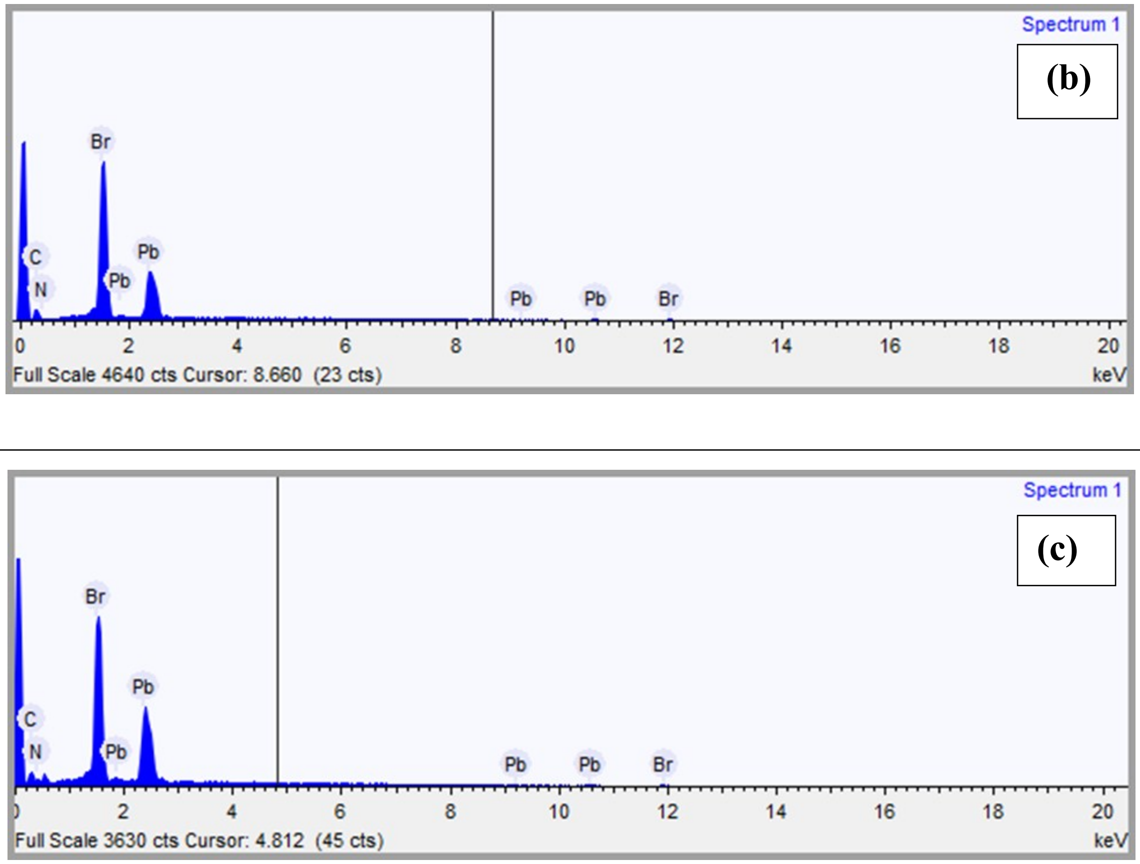


Figure S5. A representative energy dispersive X-ray (EDX) spectroscopy analysis of (a) CsPbBr$_3$, (b) MAPbBr$_{3,}$ and (c) FAPbBr$_3$ NPs. The Cs:Pb:Br ratio in CsPbBr$_3$ equal to 1.12:1.00:3.97. The Br:Pb ratio is 1:3.8 and 1:3.7 for MAPbBr$_3$ and FAPbBr$_3$ NPs, respectively.

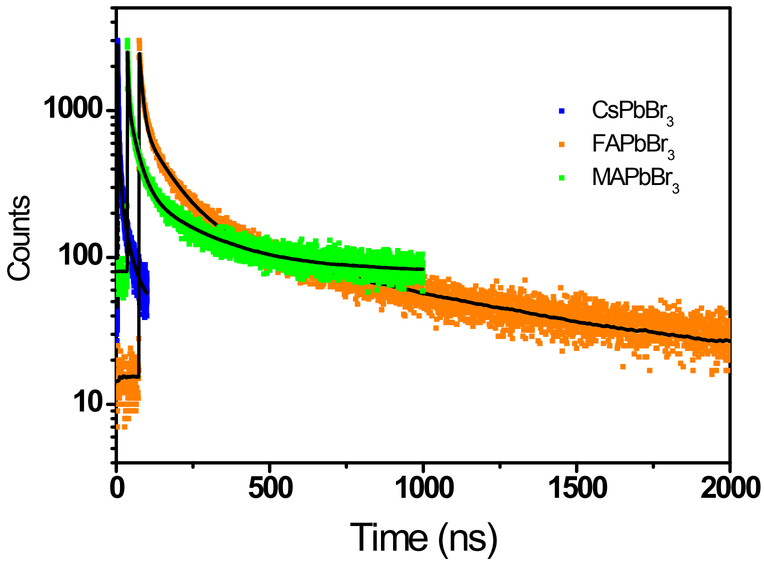


Figure S6. Time-resolved photoluminescence decay curves of $APbBr_3$ NPs

Equation S1. Calculation of quantum yield of $APbBr_3$ NPs[3]

$$\emptyset_s = \frac{OD_{standard}}{OD_{sample}} \times \frac{A_{sample}}{A_{standard}} \times \frac{\eta^2{}_{sample}}{\eta^2{}_{standard}} \times \emptyset_{standard}$$

OD is the optical density/absorbance of the standard/sample at the excitation wavelength of 377 nm, A is the area under fluorescence spectral curve, η is the refractive index of different solvents.

References

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