

Supplementary Information

High Luminescence Color Gradient by Physical Mixing of Two Perovskite Nanocrystals

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1. Experimental Section:

1.1 Synthesis of MAI and MABr

Methylammonium Iodide/Bromide (MAI/ MABr) synthesis. Briefly, in a 50 ml flask, 5.14 ml CH_3NH_2 , 40% in methanol, was mixed with 10 ml of ethanol. Then, at room temperature, 6 ml 57% water solution of the HI/ HBr was added dropwise with continuous stirring. Obtained solution was placed in rotary evaporator at 60°C for removing all solvents. Then after several time washing with diethyl ether, MAI was dissolved in ethanol and precipitated with diethyl ether twice. Then, Recrystallised product was obtained.

$\text{CH}_3\text{NH}_3\text{PbI}_3$ Nanocrystals

0.1 mmol of $\text{CH}_3\text{NH}_3\text{I}$ and 0.1 mmol of PbI_2 were dissolved in 1ml of DMF forming 0.1mM solution. 100 μL of oleic acid and 200 μL of oleylamine has been added simultaneously. Next 100 μL of this mixture was injected into 3ml of anti-solvent chloroform media. Obtained solution was observed under UV chamber showing Red color.

$\text{CH}_3\text{NH}_3\text{PbBr}_3$ Nanocrystals

0.1 mmol of $\text{CH}_3\text{NH}_3\text{Br}$ and 0.1 mmol of PbBr_2 were dissolved in 1ml of DMF forming 0.1mM solution. 100 μL of oleic acid and 200 μL of oleylamine has been added simultaneously. Next 100 μL of this mixture was injected into 3ml of anti-solvent chloroform media. Obtained solution was observed under UV chamber was showing blue color.

Now further we have prepared 9 solutions by varying the compositions of already prepared above $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Preparation of P1 In the borosil glass tube 2.5ml of chloroform was taken. 100ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 900ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to light blue.

Preparation of P2 In the borosil glass tube 2.5ml of chloroform was taken. 200ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 800ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to cyan blue.

Preparation of P3 In the borosil glass tube 2.5ml of chloroform was taken. 300ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 700ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to dark cyan.

Preparation of P4 In the borosil glass tube 2.5ml of chloroform was taken. 400ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 600ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to light greenish .

Preparation of P5 In the borosil glass tube 2.5ml of chloroform was taken. 500ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 500ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to green.

Preparation of P6 In the borosil glass tube 2.5ml of chloroform was taken. 600ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 400ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to green.

Preparation of P7 In the borosil glass tube 2.5ml of chloroform was taken. 700ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 300ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to green-yellow.

Preparation of P8 In the borosil glass tube 2.5ml of chloroform was taken. 800ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 200ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to yellow.

Preparation of P9 In the borosil glass tube 2.5ml of chloroform was taken. 900ul of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 100ul of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ added successively. Suddenly color will change to yellow-orange .

Table S1 represents preparation of samples

Name of Sample	$\text{CH}_3\text{NH}_3\text{PbI}_3$ added	$\text{CH}_3\text{NH}_3\text{PbBr}_3$ added	Solvent added
P1	100 μL	900 μL	2.5 ml
P2	200 μL	800 μL	2.5ml
P3	300 μL	700 μL	2.5ml
P4	400 μL	600 μL	2.5ml
P5	500 μL	500 μL	2.5 ml
P6	600 μL	400 μL	2.5 ml
P7	700 μL	300 μL	2.5 ml
P8	800 μL	200 μL	2.5 ml
P9	900 μL	100 μL	2.5 ml

2. Material characterization

2.1 UV Vis Absorption Spectroscopy and Photoluminescence Spectroscopy Shimadzu UV-Vis 2450 spectrophotometer was used for recording UV-Vis absorption spectra in the range of 200-650 nm. Photoluminescence spectra were taken by Horiba scientific Fluoromax-4C spectrophotometer. A quartz cuvette of 10 mm path length and volume 3.5 ml (prepared by using table S1) was used for collecting the spectra.

2.2. TCSPC studies

Fluorescence lifetime decay measurements were recorded on 1cm quartz cell on a Horiba Jobin Yvon , " Fluorocube Fluorescence Lifetime System" equipped with NanoLEDs and LDs as the excitation source and an automated polarization accessory (Model 5000 U-02).

2.3 Fourier Transform Infrared Spectroscopy (FTIR) Infra red spectra (IR) of material were recorded by using Thermo scientific Nicolet 6700. The use of the spectral subtraction provided reliable and reproducible results.

2.4 X-Ray Photoelectron Spectroscopy (XPS) Thin film of perovskites has been studied on XPS with model no. PHI 5000 VersaProbe III for surface analysis.

2.5 Transmission Electron Microscopy (TEM) TEM study was carried out by TEM TECHNAI G2 20 S-TWIN. A drop (5-10 μ L) of diluted samples was placed on Carbon coated Copper grid. Again a drop was added before drying it. Afterwards drying was carried at ambient temperature.

2.6 Atomic Force Microscopy (AFM) was performed on model NT-MDT-Integra on tapping mode.

2.7 Powder XRD was carried out on Bruker -D8 Advance having Target Cu and accelerating voltage 40kV from 5 to 50° at the rate of 2°/min. Thin film samples by concentrating the sample (using centrifuge) were prepared on silica glass.

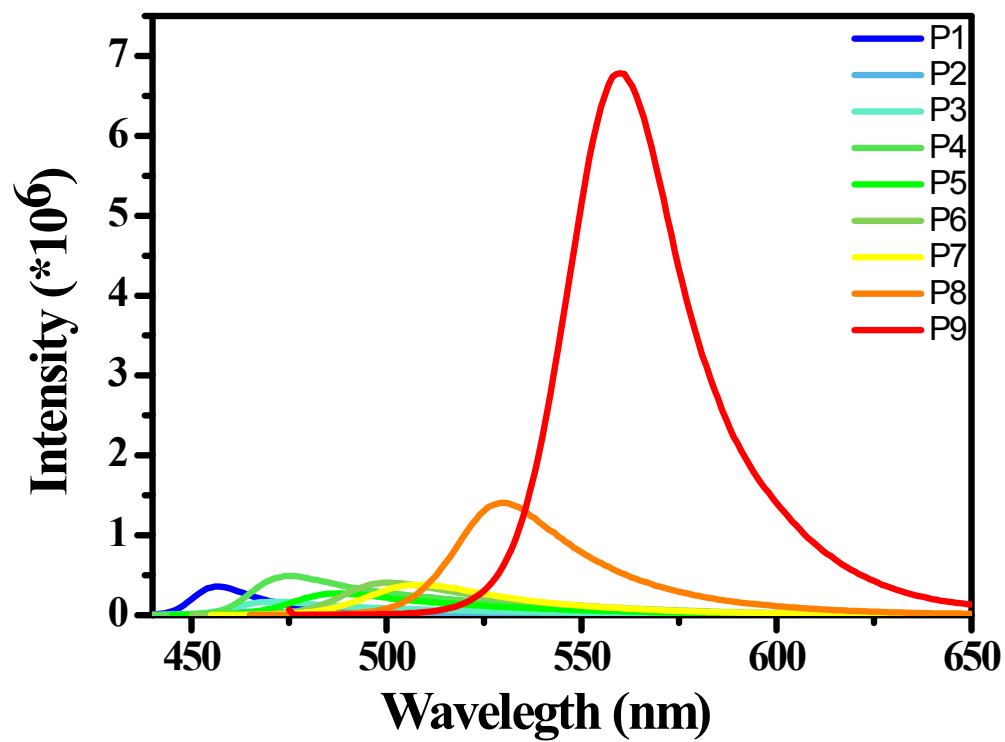


Fig. S1 PL spectra of samples P1 to P9 showing increasing intensity from P1 to P9

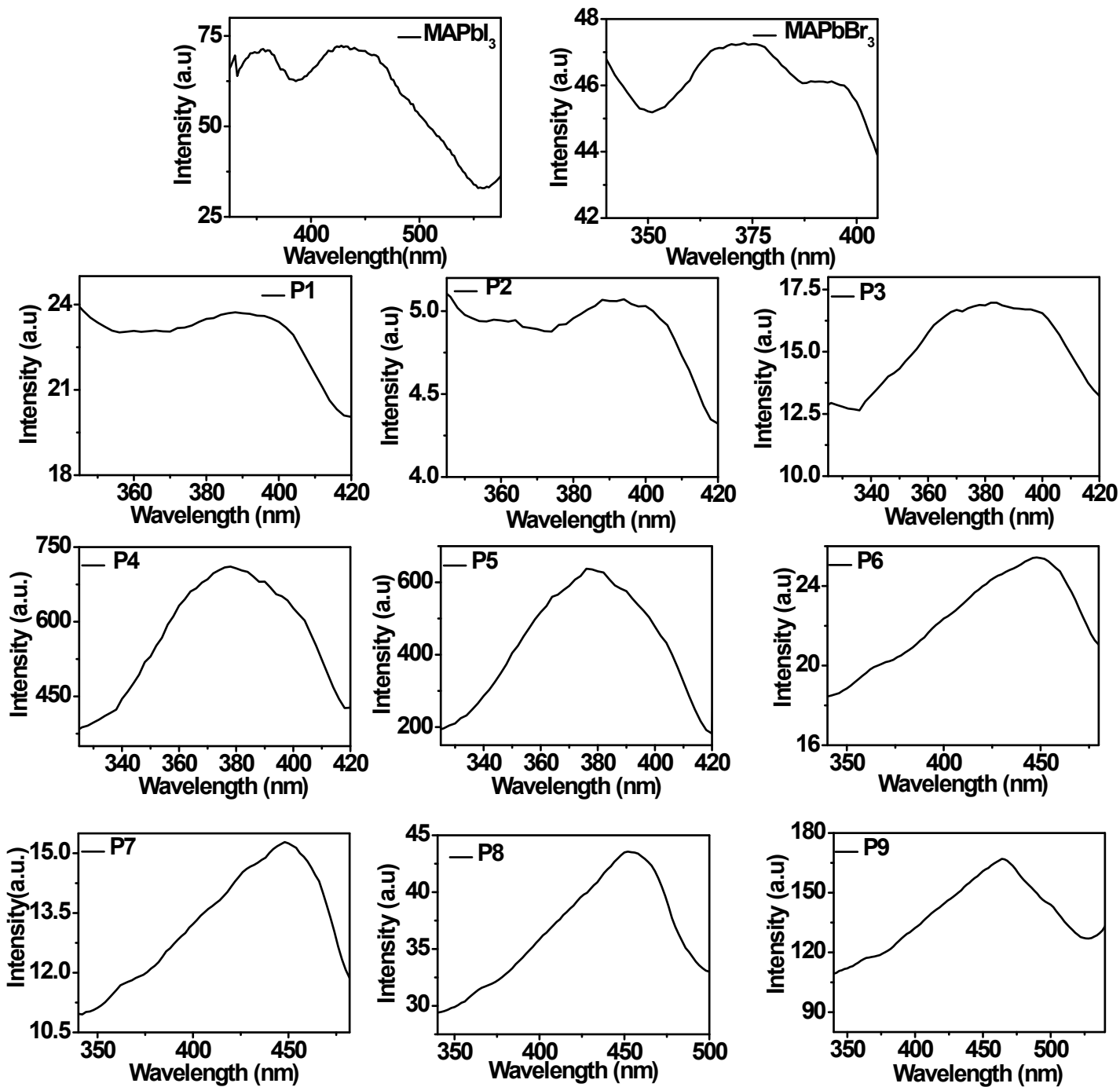


Fig. S2 shows the excitation spectra of all the samples including MAPbI₃ and MAPbBr₃ PNCs

Table S2. shows absolute Photoluminescence Quantum Yield values for all the samples

Samples	PLQY
MAPbBr ₃	47.85%
P1- P5	<5%
P6	9.02%
P7	12.39%
P8	15.05%
P9	37.03%
MAPbI ₃	49.78%

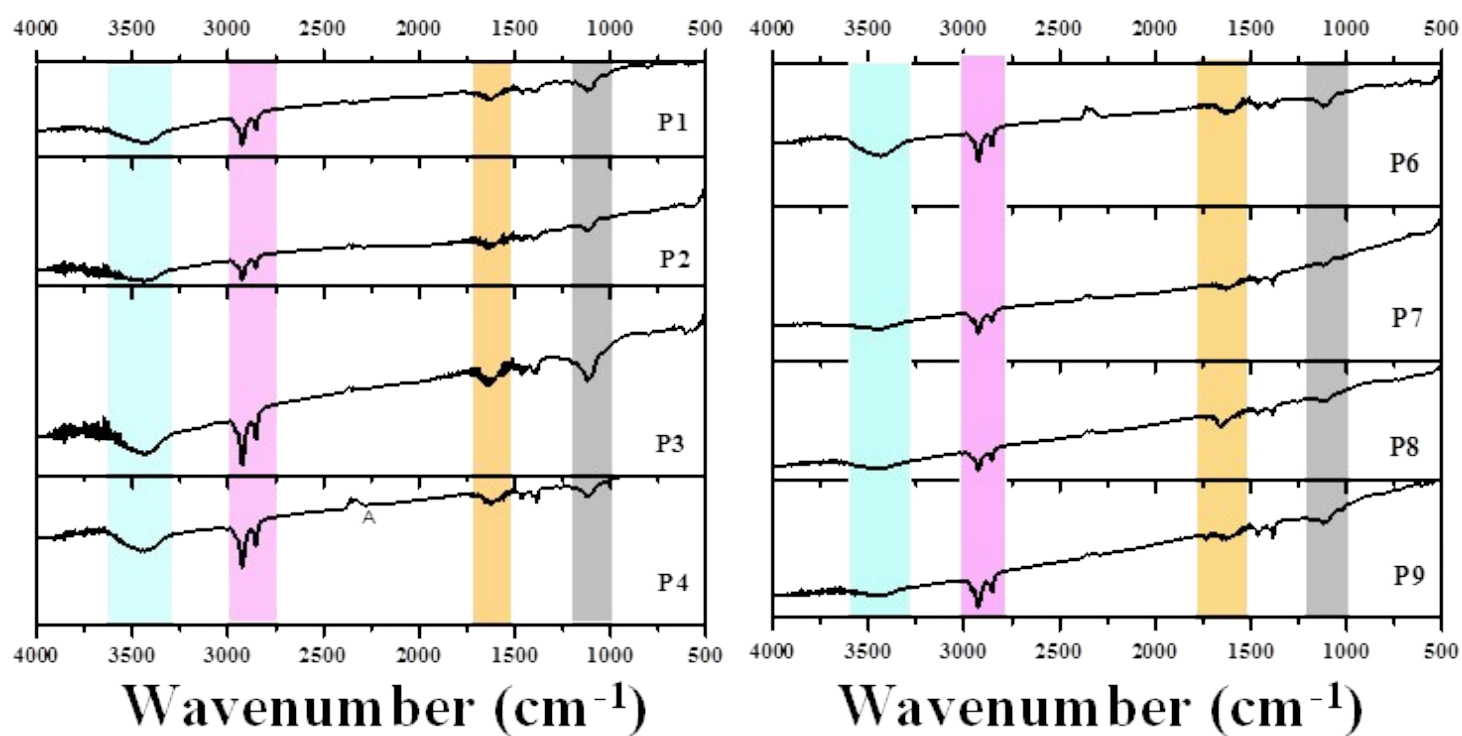


Fig.S3 shows FT-IR spectra of P1-P9 samples

Details of PXRD sample preparation

Sample solutions prepared in CHCl_3 were concentrated with the help of centrifugation and then drop-casted on silica substrate.

MAPbBr₃

2 Θ	Θ	sin Θ	sin ² Θ	Ratio	(hkl)	d (Å)	a (Å)
15.02	7.51	0.13	0.0169	1	100	5.92	5.91
30.19	15.09	0.26	0.0676	4	002	2.96	5.92

$$a^3 = 206.42 (\text{Å})^3$$

P1

2 Θ	Θ	sin Θ	sin ² Θ	Ratio	(hkl)	d (Å)	a (Å)
15.00	7.50	0.1305	0.0170	1.00	100	5.90	5.90
21.17	10.58	0.1836	0.0337	1.99	011	4.19	5.92
30.16	15.08	0.2606	0.0676	3.97	002	2.95	5.92
33.88	16.94	0.2913	0.0848	4.98	021	2.64	5.91
45.95	22.97	0.3902	0.1523	8.94	300	1.97	5.91

$$a^3 = 206.63 (\text{Å})^3$$

P2

2 Θ	Θ	sin Θ	sin ² Θ	Ratio	(hkl)	d (Å)	a (Å)
14.96	7.48	0.130	0.0169	1.00	100	5.92	5.92
21.18	10.59	0.184	0.0337	1.99	011	4.19	5.93
30.08	15.04	0.259	0.0673	3.98	002	2.96	5.93
33.73	16.86	0.290	0.0841	4.98	021	2.65	5.93

$$a^3 = 208.52 (\text{Å})^3$$

P4

2 Θ	Θ	sin Θ	sin ² Θ	Ratio	(hkl)	d (Å)	a(Å)
14.68	7.34	0.128	0.0163	1.00	100	6.02	6.02
29.70	14.85	0.256	0.0656	4.02	002	3.00	6.01
33.28	16.64	0.286	0.0819	5.03	210	2.68	6.01

$$a^3 = 217.08 (\text{Å})^3$$

P6

2 Θ	Θ	sin Θ	sin ² Θ	Ratio(*2)	(hkl)	d (Å)	a/ $\sqrt{2}$ (Å)
14.66	7.33	0.127	0.0162	2.00	110	6.062	6.05
29.60	14.80	0.256	0.0652	8.01	220	3.007	6.15

P7

2 Θ	Θ	sin Θ	sin ² Θ	Ratio(*2)	(hkl)	d (Å)	a/ $\sqrt{2}$ (Å)
14.56	7.28	0.127	0.0160	2.00	110	6.06	6.09
29.40	14.7	0.253	0.0643	8.01	220	3.002	6.12

P8

2 Θ	Θ	sin Θ	sin ² Θ	Ratio(*2)	(hkl)	d (Å)	a/ $\sqrt{2}$ (Å)
14.49	7.25	0.126	0.0159	2.00	110	6.12	6.12
29.13	14.56	0.251	0.0632	7.97	220	3.06	6.18

P9

2 Θ	Θ	sin Θ	sin ² Θ	Ratio(*2)	(hkl)	d(Å)	a/ $\sqrt{2}$ (Å)
14.11	7.055	0.122	0.01488	2.00	110	6.31	6.31
20.02	10.01	0.17382	0.030201	4.06	200	4.45	6.29
28.62	14.31	0.2471	0.061088	8.20	220	3.11	6.32
40.8	20.40	0.3485	0.121501	16.01	004	2.21	6.31

MAPbI₃

2 Θ	Θ	sin Θ	sin ² Θ	Ratio	(hkl)	d Å	a/ $\sqrt{2}$ (Å)
14.04	7.02	0.121	0.0148	2.00	110	6.32	6.34
24.60	12.30	0.213	0.0449	6.04	211	3.63	6.32
28.48	14.24	0.245	0.0605	8.00	220	3.14	6.34
43.09	21.55	0.367	0.1348	18.21	330	2.09	6.33

$$a^2c = 254.03 \text{ \AA}$$

using $\sin^2\Theta = A(h^2+k^2)$ gives $A = 0.014849$ and $\sin^2\Theta = Cl^2$ gives $C = 0.00371225$

which gives two lattice parameters $a = 8.95 \text{ \AA}$ and $c = 12.64 \text{ \AA}$.

Also $a/\sqrt{2} = 6.34 \text{ \AA}$ and $c/2 = 6.32 \text{ \AA}$ for MAPbI_3 .

$a/\sqrt{2}$ and $c/2$ parameters in tetragonal phase are compared with cubic lattice parameter, a , for comparing and plotting data of two different phases i.e. tetragonal and cubic.

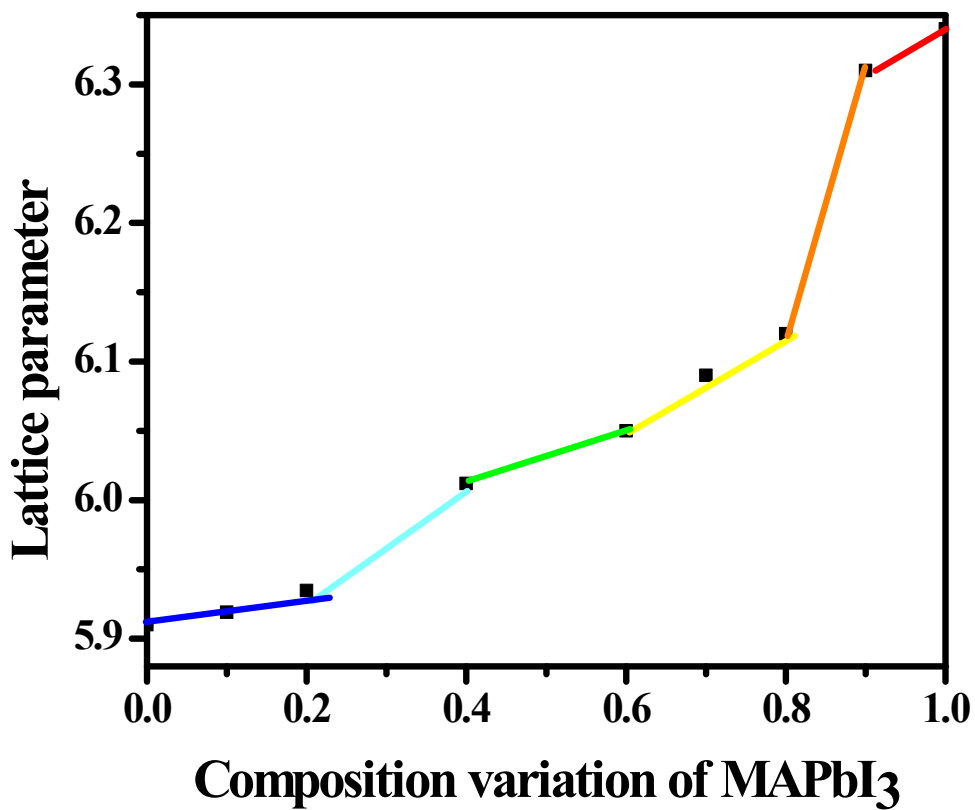


Fig.S4 shows variation of lattice parameter in samples ($a/\sqrt{2}$ is plotted for tetragonal phases)

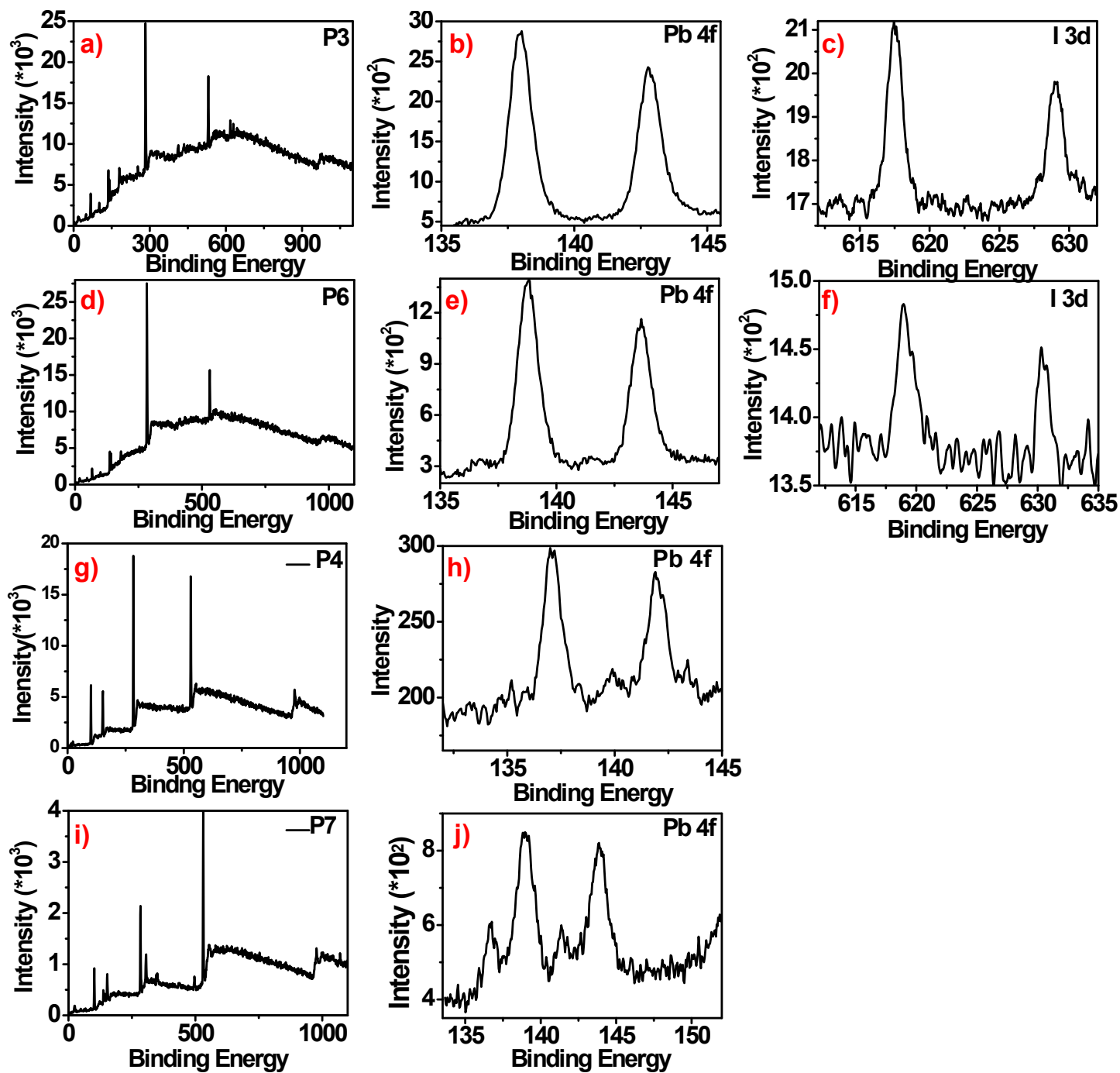


Fig. S5 a) shows survey scan of sample P3 b) Narrow scan of Pb^{2+} of sample P3 c) Narrow scan of I 3d d) shows survey scan of sample P6 e) Narrow scan of Pb^{2+} of sample P6 f) Narrow scan of I 3d g) shows survey scan of sample P4 h) Narrow scan of Pb^{2+} of sample P4 i) shows survey scan of sample P7 j) Narrow scan of Pb^{2+} of sample P7

TCSPC details

For $\text{CH}_3\text{NH}_3\text{PbBr}_3$ 405nm laser has been used at $\lambda_{\text{max}}=448.5$ nm and for $\text{CH}_3\text{NH}_3\text{PbI}_3$ 460nm laser has been used at $\lambda_{\text{max}}=602$ nm. Samples P1-P9 were performed at laser 440nm and their respective λ_{max} from emission spectra. Average lifetime is calculated using

$$\tau_{\text{avg}} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2) / (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$$

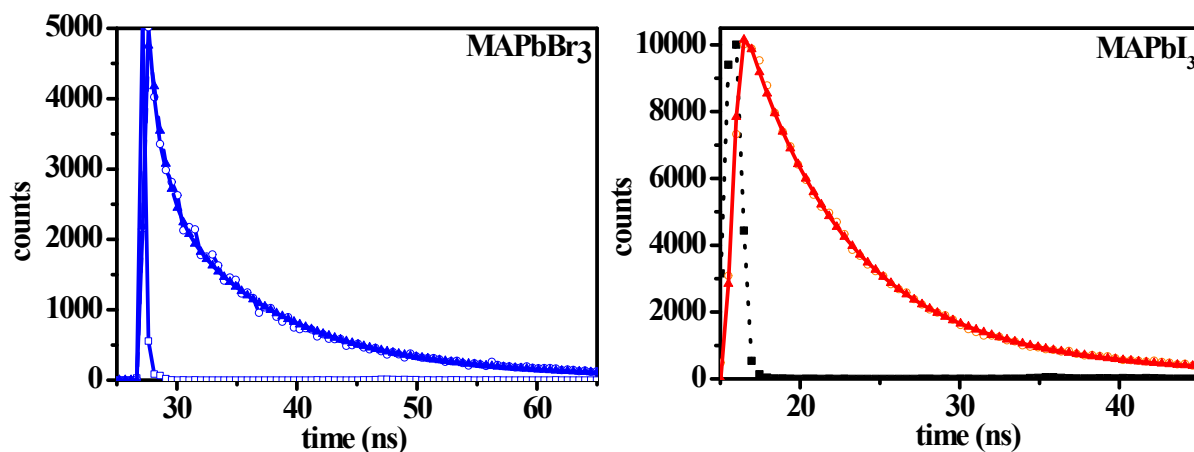


Fig. S6 TCSPC data for MAPbBr_3 and MAPbI_3

Table S3 details of weighing parameters and lifetimes for MAPbBr_3 and MAPbI_3 NCs

Sample	A_1	A_2	A_3	τ_1	τ_2	τ_3
$\text{CH}_3\text{NH}_3\text{PbBr}_3$	13.11	68.65	18.24	1.13 ns	9.23 ns	32.3 ns
$\text{CH}_3\text{NH}_3\text{PbI}_3$	27.45	8.59	63.96	14.87 ns	108.96 ns	5.97 ns

Table S4 summarizes the details of parameters of TCSPC.

Sample	τ_1 (ns)	τ_2 (ns)	A_1	A_2	τ_{avg} (ns)
P1	0.20	2.88	91.23	8.77	1.73
P2	1.38	8.02	70.33	29.67	6.08
P3	1.87	11.74	47.45	52.55	10.50
P4	1.32	10.81	62.81	37.19	9.20
P7	6.69	24.40	72.65	20.35	15.64
P8	6.30	15.30	41.94	58.06	13.24
P9	6.65	14.4	50.90	49.10	11.90

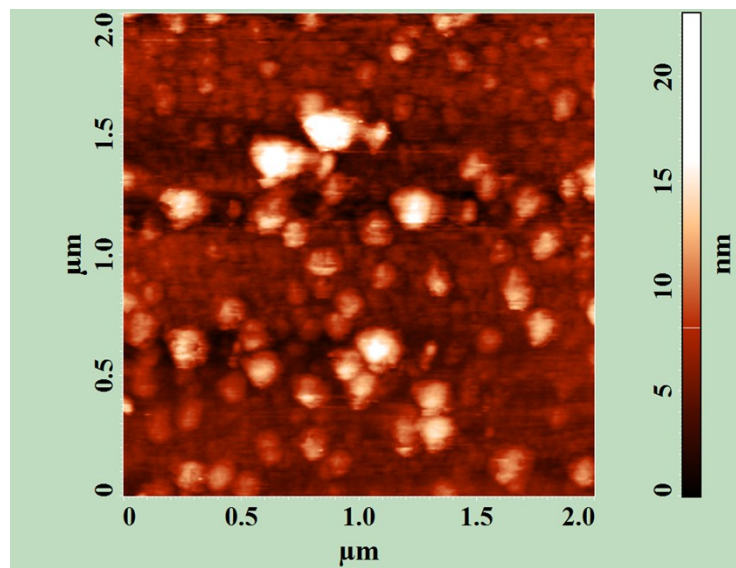
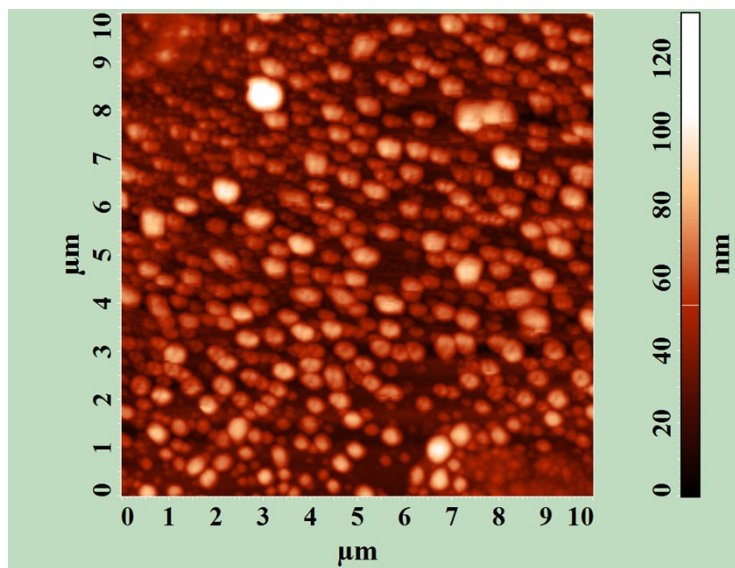


Fig. S7 represents AFM data of sample P9 and P8