

Rapid synthesis of hybrid methylammonium lead iodide perovskite quantum dots and rich MnI₂ substitution favouring Pb- free warm white LED applications

Rajan Kumar Singh^{a,b}, Sudipta Som^b, Somrita Dutta^c, Neha Jain^a, Mei-Tsun Kuo^b,
Jai Singh^a, Ranveer Kumar^{a,*} and Teng-Ming Chen ^{c,*}

^a Department of Physics, Dr. Harisingh Gour Central University, Sagar, 470003,
M. P., India

^b Department of Chemical Engineering, National Taiwan University, Taipei,
Taiwan, ROC

^cDepartment of Applied Chemistry, National Chiao Tung University, 1001
University Road, Hsinchu 30010, Taiwan

*To whom all correspondence should be addressed.

Email: tmchen@mail.nctu.edu.tw, ranveerssi@yahoo.com,

Tel: +88635731695, Fax: +88635723764.

Table S1 Detailed composition and amount of ingredients required for the synthesis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ based HPQDs.

S.N	PQDs	CH_3NH_3 I (gm)	PbI_2 (gm)	MnI_2 (gm)	Oleic Acid (μl)	Oleyla mine (μl)	Perovskite Precursor (μl)	Equal mixture of Toluene and chloroform(ml)
1	$\text{CH}_3\text{NH}_3\text{PbI}_3$	0.0159	.0461	0	200	200	40	6
2	$\text{CH}_3\text{NH}_3\text{Pb}_{0.90}\text{Mn}_{0.05}\text{I}_3$	0.0159	.0438	.0015	200	200	40	6
3	$\text{CH}_3\text{NH}_3\text{Pb}_{0.90}\text{Mn}_{0.10}\text{I}_3$	0.0159	0.415	.0031	200	200	40	6
4	$\text{CH}_3\text{NH}_3\text{Pb}_{0.85}\text{Mn}_{0.15}\text{I}_3$	0.0159	0.392	.00464	200	200	40	6
5	$\text{CH}_3\text{NH}_3\text{Pb}_{0.80}\text{Mn}_{0.20}\text{I}_3$	0.0159	.0369	.0062	200	200	40	6
6	$\text{CH}_3\text{NH}_3\text{Pb}_{0.75}\text{Mn}_{0.25}\text{I}_3$	0.0159	.0346	.0077	200	200	40	6
7	$\text{CH}_3\text{NH}_3\text{Pb}_{0.70}\text{Mn}_{0.30}\text{I}_3$	0.0159	.0323	.0093	200	200	40	6
8	$\text{CH}_3\text{NH}_3\text{Pb}_{0.65}\text{Mn}_{0.35}\text{I}_3$	0.0159	0.03	.0108	200	200	40	6
9	$\text{CH}_3\text{NH}_3\text{Pb}_{0.60}\text{Mn}_{0.40}\text{I}_3$	0.0159	.0278	.0124	200	200	40	6
10	$\text{CH}_3\text{NH}_3\text{Pb}_{0.55}\text{Mn}_{0.45}\text{I}_3$	0.0159	.0254	.014	200	200	40	6
11	$\text{CH}_3\text{NH}_3\text{Pb}_{0.50}\text{Mn}_{0.50}\text{I}_3$	0.0159	.0231	.0155	200	200	40	6
12	$\text{CH}_3\text{NH}_3\text{Pb}_{0.40}\text{Mn}_{0.60}\text{I}_3$	0.0159	.0184	.01854	200	200	40	6

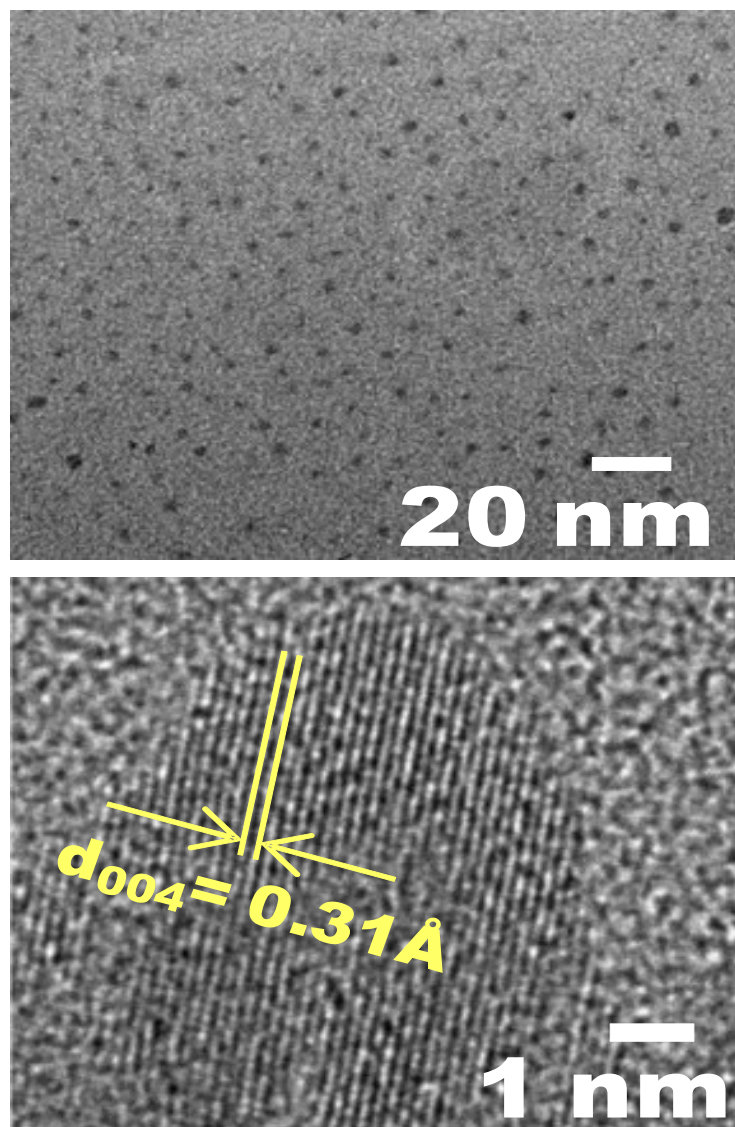


Figure S1: TEM and HR-TEM image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) hybrid perovskite quantum dots synthesized via a modified low temperature route.

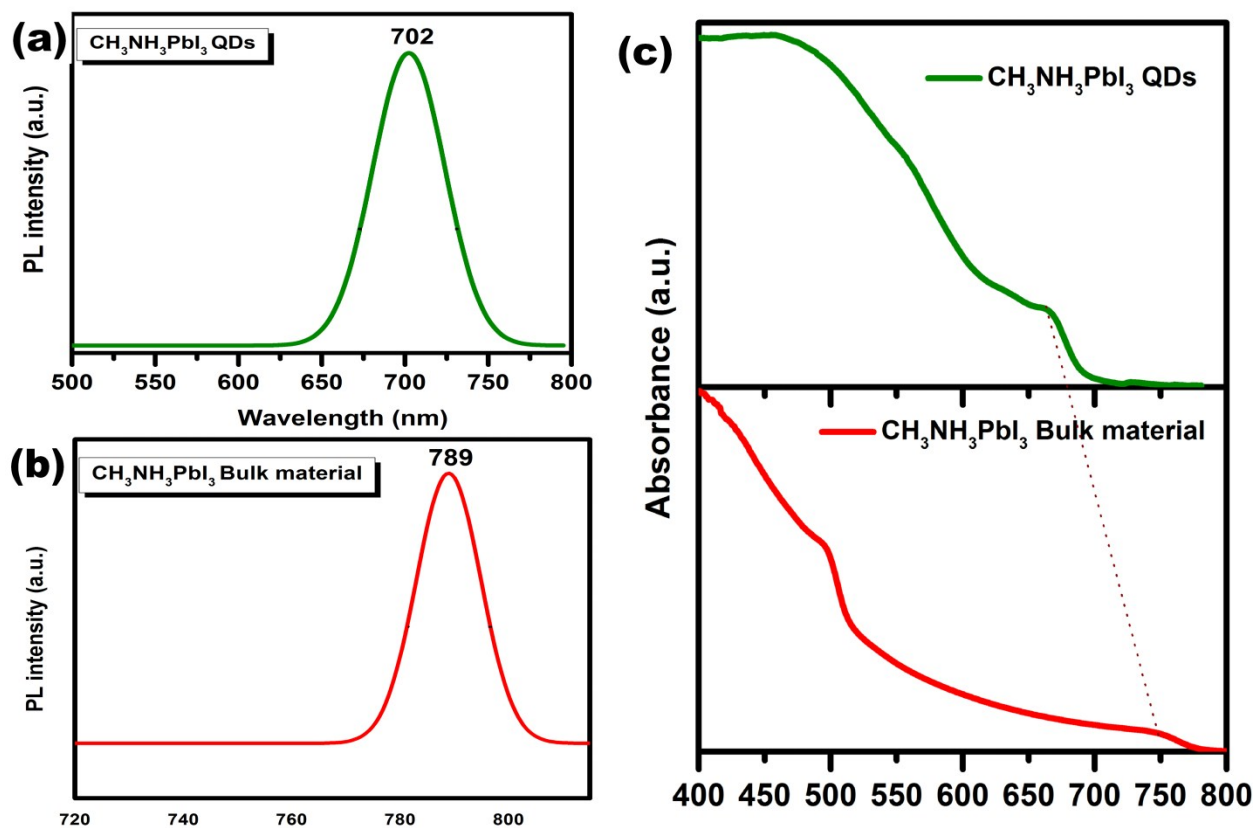


Figure S2: Comparison of bulk and PQDs of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (a and b) PL emission of $\text{CH}_3\text{NH}_3\text{PbI}_3$ QDs and bulk material respectively and (c) UV-visible absorbance spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ QDs and bulk material.

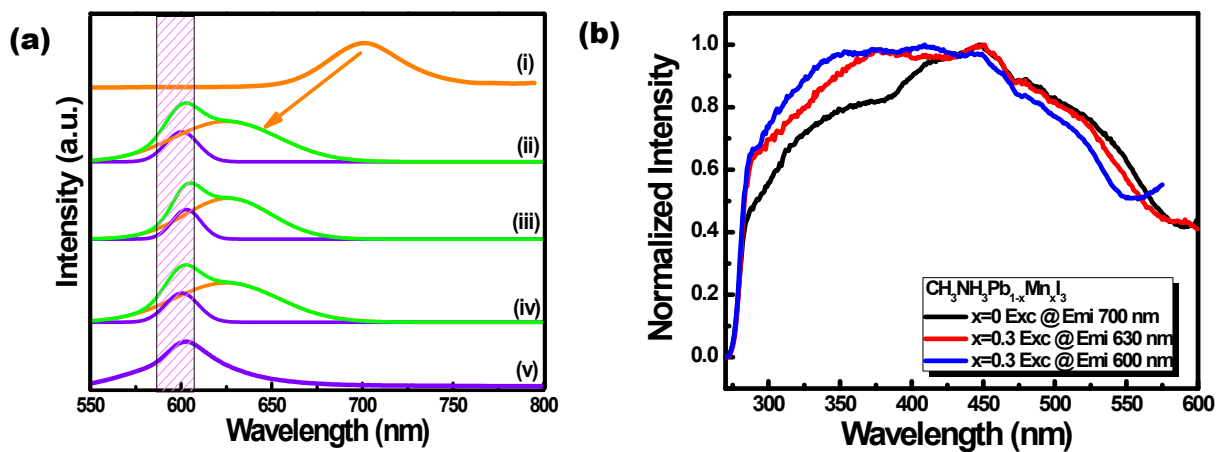


Figure 3: (a) Variation of PL emission spectra from 0% to 60% and decomposition of PL peaks into two Gaussian curves, and the (b) comparison of PL excitation spectra for pure and 30% doped $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Mn}_x\text{I}_3$ PQDs by monitoring the excitonic and Mn^{2+} related emissions.

Color coordinate diagram:

The influence of Pb^{2+} to Mn^{2+} cation exchange on color coordinates of $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Mn}_x\text{I}_3$ PQDs is shown in the commission International de l'Eclairage (CIE) chromaticity diagrams to better enable the comparison of color variation (Fig. S2(d)). With the gradual substitution of Pb^{2+} by Mn^{2+} , the emission color changed from red/pink to orange for the 5 to 60% Mn^{2+} doped PQDs and CIE co-ordinates lies between ($x= 0.67$ to 0.60 and $y= 0.30$ to 0.40).

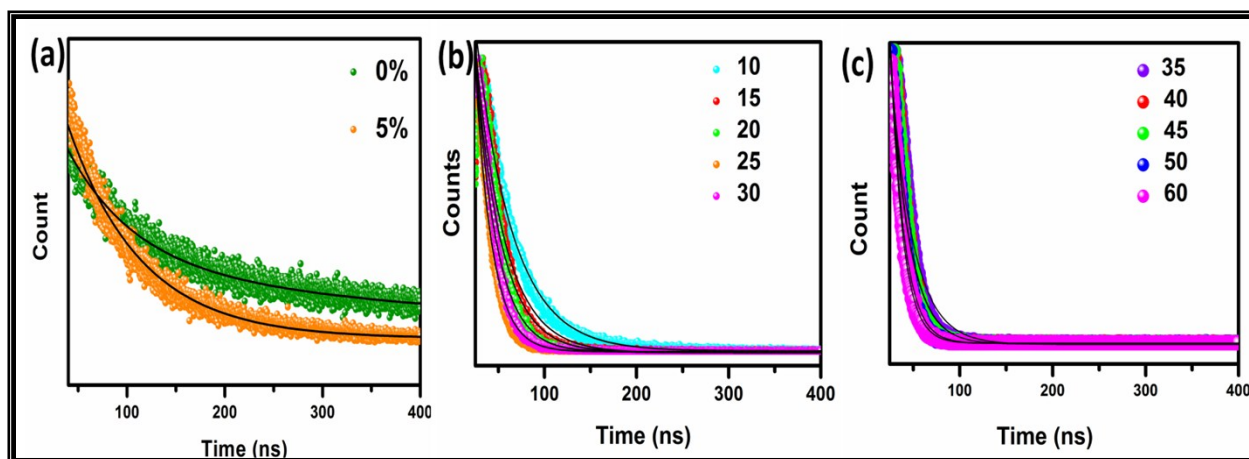


Figure S4: PL life time decay curves (a)TRPL of pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 5% Mn^{2+} doped PQDs fitted with mono-exponential fitting (b) TRPL of 10 – 30% and (c) 35-60% Mn^{2+} incorporated emplace of Pb^{2+} in $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Mn}_x\text{I}_3$ PQDs with dual-exponential fitting, (d) graph between average life-time and Mn^{2+} concentration in $\text{CH}_3\text{NH}_3\text{Pb}_{1-x}\text{Mn}_x\text{I}_3$ PQDs

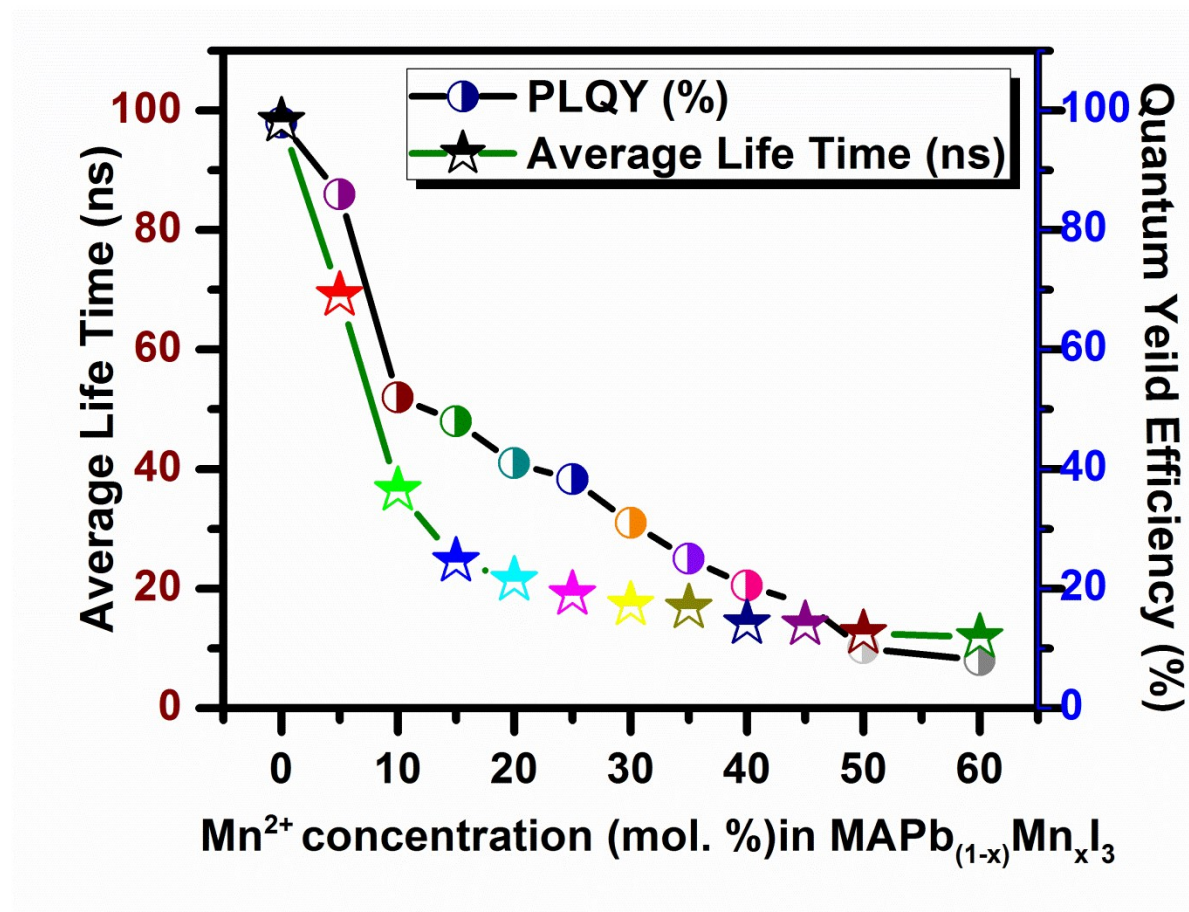


Figure S5: Graph between PLQY and average life-time for different concentration of Mn²⁺ concentration in CH₃NH₃Pb_{1-x}Mn_xI₃ PQDs

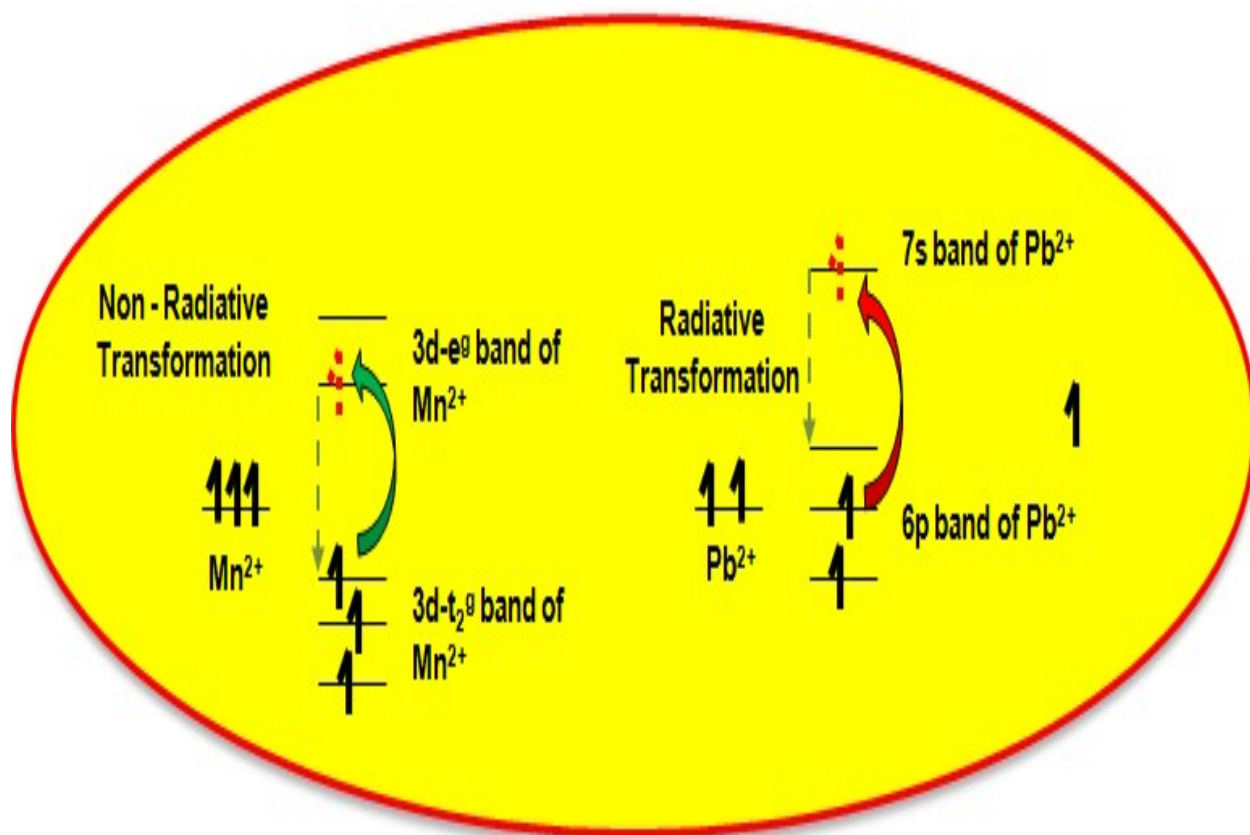


Figure S6: Transition mechanism in perovskite with Mn incorporation