

SYNTHETIC FACTORS AFFECTING THE STABILITY OF METHYLAMMONIUM LEAD HALIDE PEROVSKITE NANOCRYSTAL DISPERSIONS PRODUCED BY LIGAND-ASSISTED REPRECIPITATION

ELECTRONIC SUPPORTING INFORMATION

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1. Sample composition

Table S1. Summary of the synthetic reagents used for the fabrication of $\text{MAPbBr}_{3-x}\text{I}_x$ PNC precursor solutions. OY samples indicate variation of the oleylamine capping ligand concentration, R samples indicate variation of the halide ratio and/or halide source and S samples indicate variation of the antisolvent.

Sample ID	PbBr ₂ (mmol)	PbI ₂ (mmol)	MAI (mmol)	MABr (mmol)	OY (mmol)	OA (mmol)	Ratio (Br:I ⁻)	Solvent
OY ₅₀	0.2		0.16		0.15	1.6	2:0.8	Toluene
OY ₆₀	0.2		0.16		0.18	1.6	2:0.8	Toluene
OY ₇₀	0.2		0.16		0.21	1.6	2:0.8	Toluene
OY ₈₀	0.2		0.16		0.24	1.6	2:0.8	Toluene
OY ₉₀	0.2		0.16		0.27	1.6	2:0.8	Toluene
OY ₁₀₀	0.2		0.16		0.30	1.6	2:0.8	Toluene
R ₁	0.13	0.7	0.056	0.104	0.15	1.6	2:1.1	Toluene
R ₂	0.13	0.7	0.07	0.13	0.15	1.6	2:1.1	Toluene
R ₃	0.1	0.1		0.16	0.15	1.6	2:1.1	Toluene
R ₄	0.1	0.1		0.2	0.15	1.6	2:1	Toluene
R ₅		0.2		0.16	0.15	1.6	0.8:2	Toluene
R ₆	0.1	0.1	0.08	0.08	0.15	1.6	1:1	Toluene
R ₇	0.2		0.08	0.08	0.15	1.6	5:1	Toluene
S ₁	0.2		0.16		0.15	1.6	2:0.8	CHCl ₃

MAI = methyl ammonium iodide, MABr = methyl ammonium bromide, OY = oleyl amine, OA = oleic acid.

2. Analysis of size and composition

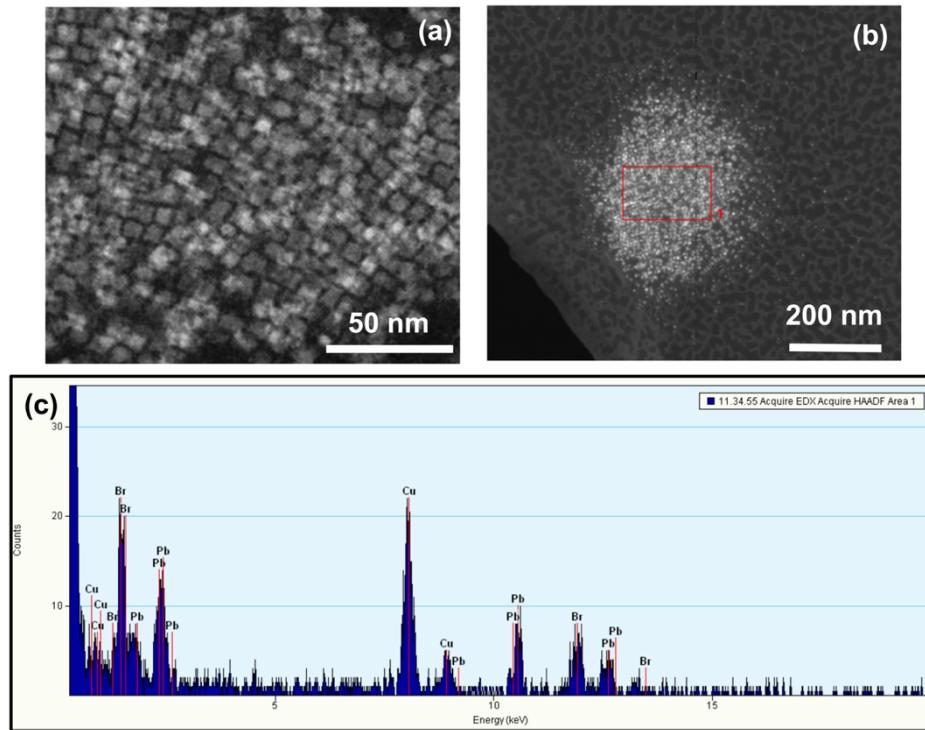


Figure S1. Compositional analysis of the parent solution of a standard $\text{MAPbBr}_{3-x}\text{I}_x$ PNC sample by STEM. (a) and (b) STEM images of PNCs under different magnification. The red box in (b) represents the area investigated by EDX. (b) Corresponding EDX spectrum indicating the absence of iodide in the $\text{MAPbBr}_{3-x}\text{I}_x$ PNC sample at the detection limits of the technique.

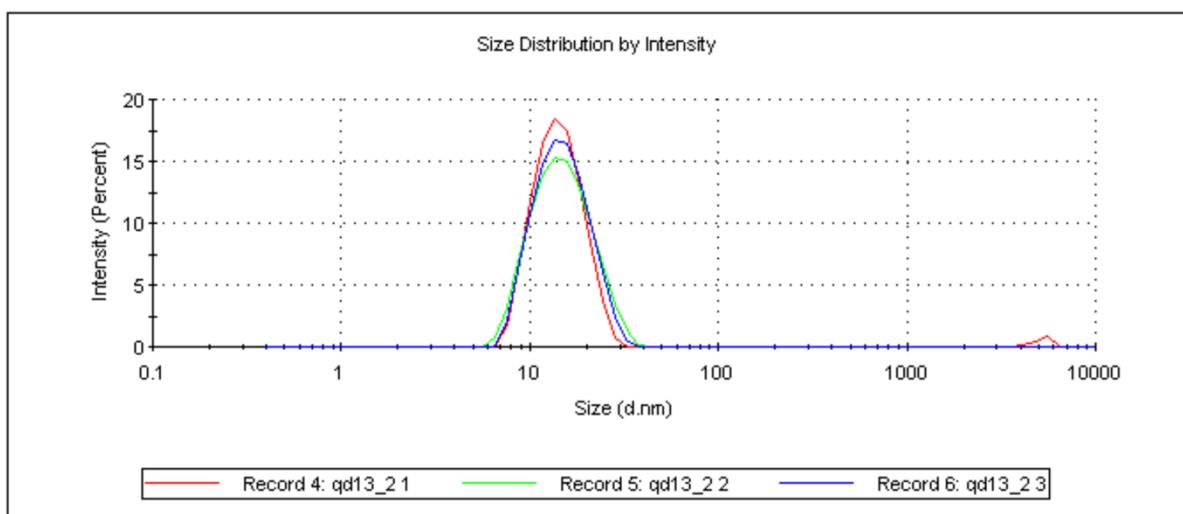


Figure S2. Dynamic light scattering size-intensity distribution plot for $\text{MAPbBr}_{3-x}\text{I}_x$ PNCs in toluene (standard sample). The mean hydrodynamic diameter is ca. 14 nm.

3. Photoluminescence properties

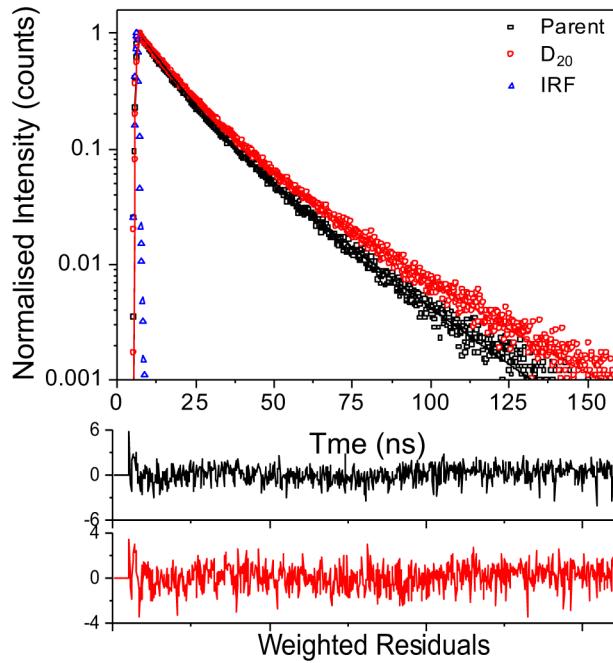


Figure S3. Emission decay curves, biexponential fits (solid lines) and instrument response function (IRF, blue triangles) for a standard MAPbBr_{3-x}I_x PNC dispersion in toluene upon excitation at 458 nm, before (black squares, $\lambda_{\text{em}} = 525$ nm) and after dilution D₂₀ (red circles, $\lambda_{\text{em}} = 560$ nm). For each fit the residuals are also shown.

Table S2. Photoluminescence properties of standard MAPbBr_{3-x}I_x PNC dispersions before and after dilution. Lifetimes (τ), pre-exponential amplitudes (A), and chi-squared (χ^2) values obtained from bi-exponential fits to the emission decays of parent ($\lambda_{\text{em}} = 525$ nm) and dilute (D₂₀) ($\lambda_{\text{em}} = 560$ nm) samples. $\lambda_{\text{ex}} = 400$ nm.

	τ_1 (ns)	τ_2 (ns)	A_1	A_2	χ^2	PLQY (%)
Parent	10.7 ± 0.1	24.2 ± 0.2	0.66 ± 0.02	0.34 ± 0.01	1.14	54 ± 4
D ₂₀	12.4 ± 0.2	28.8 ± 0.2	0.72 ± 0.01	0.28 ± 0.01	1.2	10 ± 0.5

4. Effect of dilution

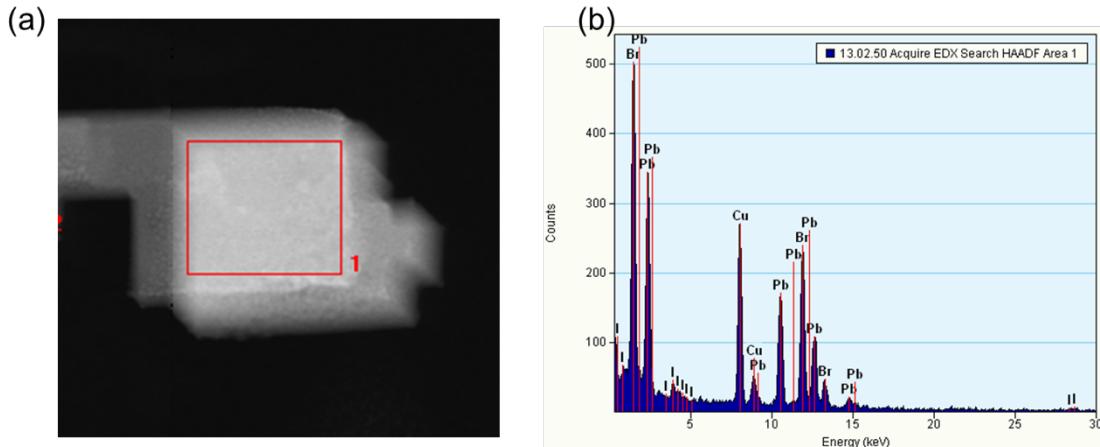


Figure S4. Compositional analysis of a dilute dispersion of $\text{MAPbBr}_{3-x}\text{I}_x$ PNCs by STEM (dilution factor, D_{20}). (a) STEM image of large population of the sample; the red box represents the area investigated by EDX. (b) Corresponding EDX spectrum.

5. Effect of halide ratio

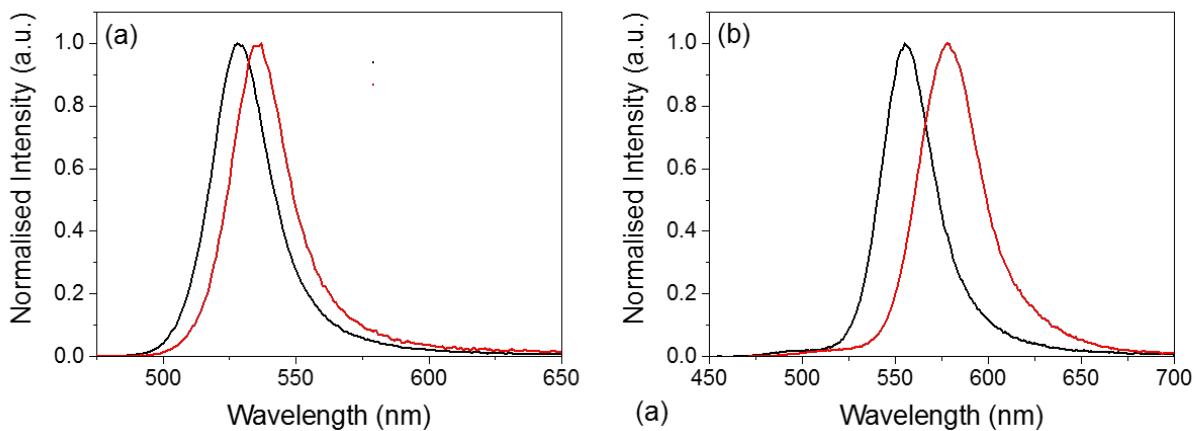


Figure S5. Photoluminescence spectra of standard ($\text{Br}^-:\text{I}^- = 2:0.8$, black line) and stoichiometric ($\text{Br}^-:\text{I}^- = 2:1$, red line) $\text{MAPbBr}_{3-x}\text{I}_x$ PNCs before (a) and after (b) dilution by a factor D_{20} . $\lambda_{\text{ex}} = 400$ nm.

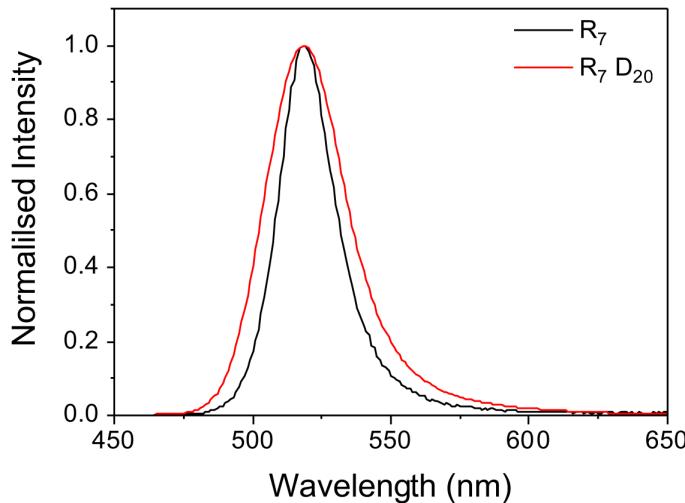


Figure S6. Photoluminescence spectra of $\text{MAPbBr}_{3-x}\text{I}_x$ PNCs prepared with excess bromide (R_7 , $\text{Br}^-:\text{I}^- = 5:1$) before and after dilution by a factor D_{20} . $\lambda_{\text{ex}} = 400 \text{ nm}$.

6. Effect of capping ligand concentration

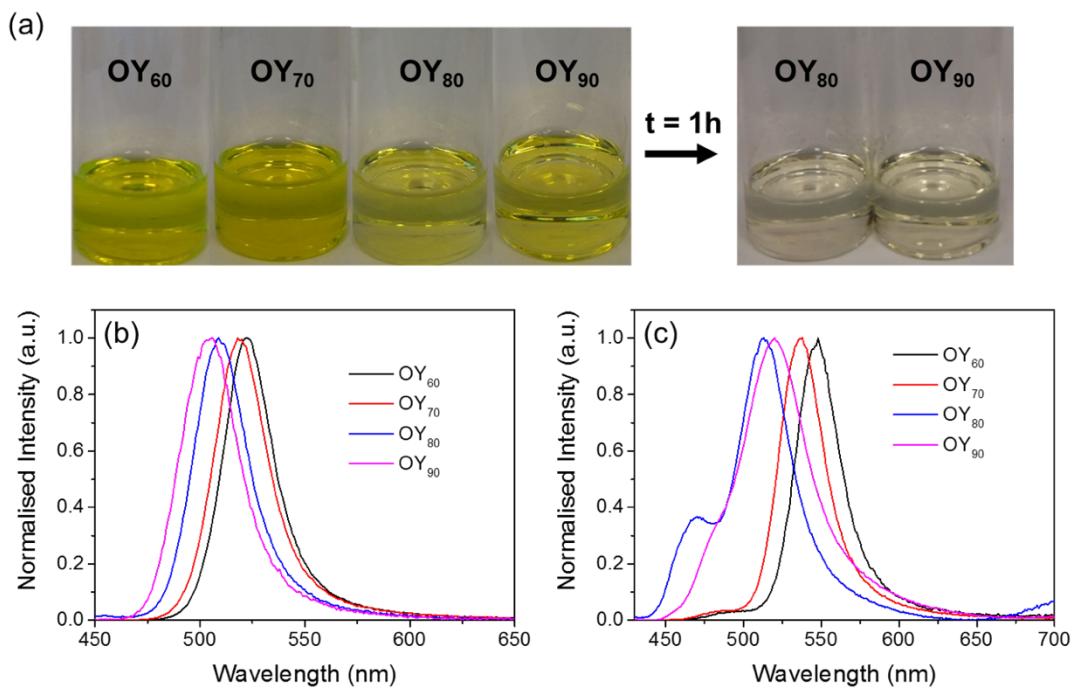


Figure S7. (a) Photographs of $\text{MAPbBr}_{3-x}\text{I}_x$ PNC dispersions synthesised with different oleylamine (OY) capping ligand volumes. Photoluminescence spectra of (b) parent PNC dispersions and (c) diluted dispersions (D_{20}). $\lambda_{\text{ex}} = 400 \text{ nm}$.

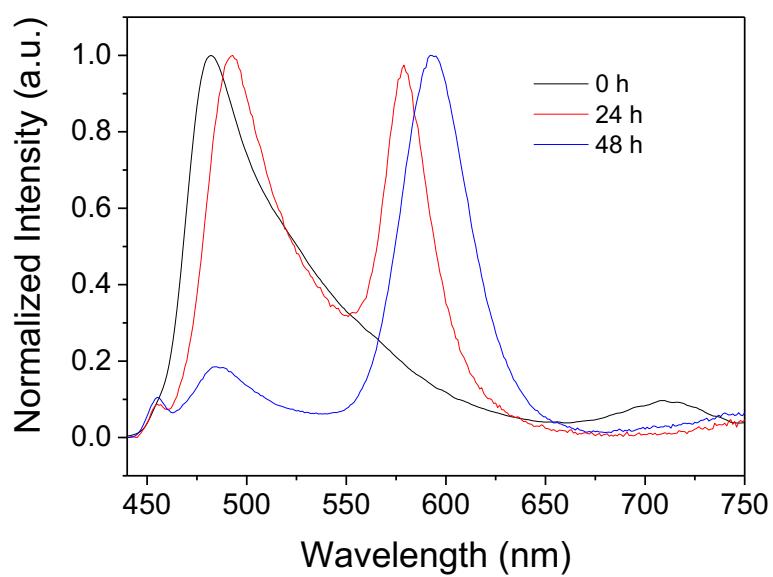


Figure S8. Photoluminescence spectra of OY₁₀₀ MAPbBr_{3-x}I_x PNCs upon dilution by a factor D20 after 0 hours, 24 hours and 48 hours. $\lambda_{\text{ex}} = 400$ nm.