

Supporting Information

Highly stable, luminescent core-shell type methylammonium-octylammonium lead bromide layered perovskite nanoparticles

Saikat Bhaumik, Sjoerd A. Veldhuis, Yan Fong Ng, Muduli Subas Kumar, Mingjie Li, Tze Chien Sum, Bahulayan Damodaran, Subodh Mhaisalkar and Nripan Mathews*

Experimental Section

Materials: Lead bromide, PbBr_2 (99.999%, trace metals basis, Sigma-Aldrich); oleic acid, OAc (90%, Sigma-Aldrich); oleylamine, OAm (70%, Sigma-Aldrich); N,N-Dimethylformamide, DMF (Anhydrous, 99.8%, Sigma-Aldrich); octylamine (99%, Sigma-Aldrich); butylamine (99.5%, Sigma-Aldrich); dodecylamine (99%, Sigma-Aldrich); toluene (Anhydrous, 99.7% GC, Sigma-Aldrich); hydrobromic acid, HBr (48%, Sigma-Aldrich); methylammonium bromide, MABr (Dyesol). All these chemicals were used without further purification.

Synthesis of different cationic ammonium bromide powder: OABr was synthesized by mixing octylamine and HBr. At first octylamine was precooled in a glass beaker to 0 °C under vigorous stirring condition and HBr was added dropwise. The reacted solution was stirred for 2 hours. The reaction mixture was then transferred to a rotary evaporator to remove the solvent. The resulting precipitate was washed several times with diethylether to remove impurities and then dried in a vacuum furnace overnight at 60 °C to get a purified white colored $\text{CH}_3(\text{CH}_2)_7\text{NH}_3\text{Br}$ powder. The butylammonium bromide (BABr) and dodecylammonium bromide (DDABr) powders were synthesized by same synthetic procedure while changing the methylamine to butylamine and dodecylamine respectively.

Synthesis of MAPbBr_3 and mixed cation organo lead bromide NPs: MAPbBr_3 NPs were synthesized by LARP method as reported elsewhere.¹ At first in a glass vial 0.16 mmol of MABr, 0.2 mmol of PbBr_2 were mixed in 5 mL DMF solution. Later 50 μL of OAm and 0.5 mL OAc were also mixed in the DMF solution to form the final precursor solution.

Another round bottom glass flask containing 5 mL of toluene was heated at 60°C in an oil bath. Then 250 μL of as prepared precursor solution was swiftly injected into toluene under vigorous stirring condition. The solution turned into green color confirms the formation of MAPbBr_3 NPs. The reaction was continued for 5 min and transferred into a centrifuge tube. The NPs were purified by centrifugation method that centrifuged at 7000 rpm for 10 min. The precipitate was discarded and the supernatant was collected for further characterization.

For mixed cation organo MA-OA, BA-OA and DDA-OA lead bromide NPs were synthesized by the same synthetic procedure elaborated above. Here we maintained the same total molar concentration of alkyl ammonium bromide inside the precursor solution. The molar ratio of MABr and OABr were varied to 8:2, 6:4, 4:6, 3:7, and 2:8. The molar ratio of BABr-OABr and DDABr-OABr was fixed to 8:2.

Seeded (modified) synthesis attempt of mixed cation organo lead bromide NPs: In the modified synthesis, we followed same LARP synthetic protocol as described above. Here at first we injected MABr- PbBr_2 precursor solution into toluene to grow MAPbBr_3 NPs first and later we injected desired amount of OABr- PbBr_2 precursor solution.

Synthesis of $(\text{OA})_2\text{PbBr}_4$ nanodisks: $(\text{OA})_2\text{PbBr}_4$ nanodisks were synthesized by one-pot synthetic approach as reported elsewhere.² At first in a glass vial 0.4 mmol of octylamine, 0.1mmol of PbBr_2 were mixed in 200 μL DMF solution. Later 50 μL of HBr was mixed in this DMF solution to form the final precursor solution. In another glass beaker this precursor solution was added dropwise in 2 mL of hexane under vigorous stirring condition at room temperature. After 5 min the reaction was stopped by adding 3 mL of acetone and then centrifuged at 4500 rpm for 10 min. The precipitate obtained was collected for structural and photophysical studies.

Structural and photophysical studies: The absorbance spectra of the perovskite NPs in solution phase were recorded by Shimadzu UV1800 UV-VIS Spectrophotometer and PL spectra was recorded by Shimadzu RF-5301pc Spectrofluorophotometer. The absolute PLQY was measured by Ocean-optics USB4000 spectrometer with an integrated sphere excited at 400 nm laser beam. X-Ray diffraction analysis was carried out with XRD Bruker D8 Advance. The time-resolved PL was recorded by an Optronis Optoscope streak camera system. The excitation

source is 400 nm femtosecond laser with pump intensity of $0.2 \mu\text{J}/\text{cm}^2$. The imaging of the NPs was recorded by transmission electron microscopy (TEM, Jeol JEM-2010). The morphological imaging was carried out using field emission scanning electron microscopy (FESEM, JEOL JSM-7600F).

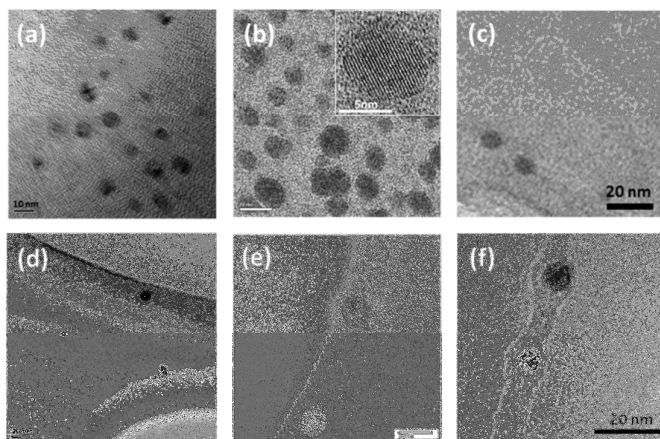


Fig. S1: TEM images of mixed organo lead bromide perovskite NPs with different MABr and OABr molar ratio : (a) 10:0, (b) 8:2, (c) 6:4, (d) 4:6, (e) 3:7 and (f) 2:8.

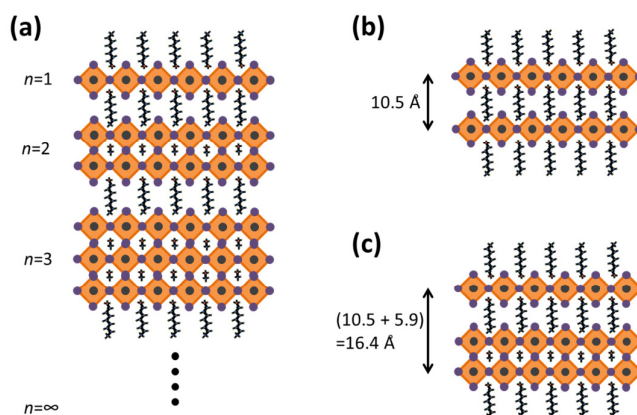


Fig. S2: Schematic diagram of perovskite structures with $[\text{PbBr}_6]^{4-}$ inorganic layer separated by octylamine (a) with different order ($n = 1, 2, 3, \dots \infty$) and (b, c) Perovskite layers with different d -spacing values.

Table S1: Details of the photophysical properties observed for mixed organo lead bromide perovskite NPs with different molar ratio of cations with oleylamine as the capping ligand.

MABr:OABr	Absorbance peak position (nm)	PL peak position (nm)	PL FWHM (nm)	PLQY (%)
10:0	513	521	24	84
8:2	433, 510	519	26	92
6:4	397, 422, 502	512	37	82
4:6	397, 433, 450, 471, 486	456, 476, 490	55	55
3:7	397, 433, 451	438, 456, 474	25	30
2:8	397, 433	438, 451	23	21

Table S2: Fitted PL lifetimes and the corresponding amplitude values. The 10:0 and 8:2 samples are fitted with single-exponential decay and the others are fitted with bi-exponential decay functions. $\tau_{avg}=A_1\tau_1+ A_2\tau_2$.

MABr:OABr	A ₁	τ_1 (ns)	A ₂	τ_2 (ns)	τ_{avg} (ns)
10:0	1	11.7±0.1	-	-	-
8:2	1	10.8±0.1	-	-	-
6:4	0.59	6.2±0.1	0.41	11.8±0.2	8.5±0.1
3:7	0.79	2.2±0.1	0.21	21.6±0.4	6.3±0.2
2:8	0.84	2.0±0.1	0.16	15.5±0.4	4.2±0.4

Table S3: PLQY obtained for the mixed organo lead bromide perovskite NPs in different time intervals.

MABr:OABr	PLQY (%) (during synthesis)	PLQY (%) (after one month)	PLQY (%) (after two months)
10:0	84	45	0
8:2	92	85	60
6:4	82	60	20
4:6	55	30	0
3:7	30	10	0
2:8	21	0	0

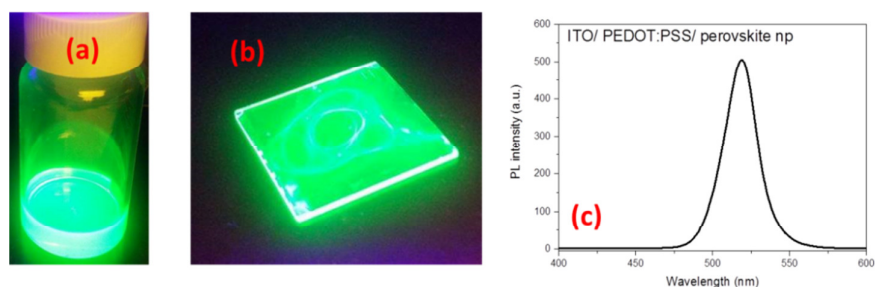


Fig. S3: Photographs of perovskite NPs under UV-lamp in (a) toluene solution and (b) thin-film. (c) Absorbance spectra of perovskite NPs spin-coated on top of ITO/PEDOT:PSS thin-film.

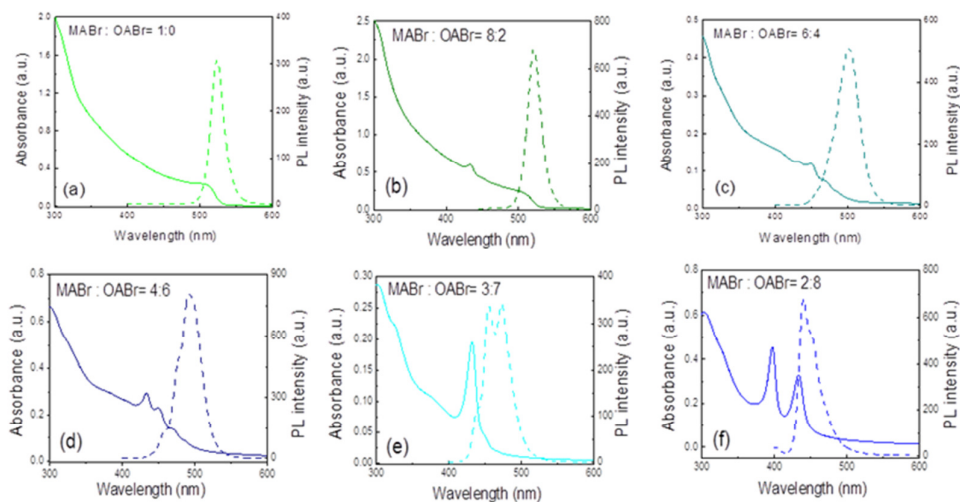


Fig. S4: (a-f) UV-vis absorption (solid line) and PL spectra (dotted line) of mixed organo lead bromide perovskite NPs with different molar ratio of MABr and OABr with octylamine as the capping ligand.

Table S4: Photospectroscopic data observed for mixed organo lead bromide perovskite NPs with different molar ratio of cations with octylamine as the capping ligand.

MABr:OABr	Absorbance peak position (nm)	PL peak position (nm)	PL FWHM (nm)	PLQY (%)
10:0	509	523	20	67
8:2	433, 507	521	22	58
6:4	433, 450, 470, 486	501	36	52
4:6	433, 450, 471, 486	457, 477, 493	38	47
3:7	433, 451	438, 455, 472	40	38
2:8	397, 433	438, 451	28	25

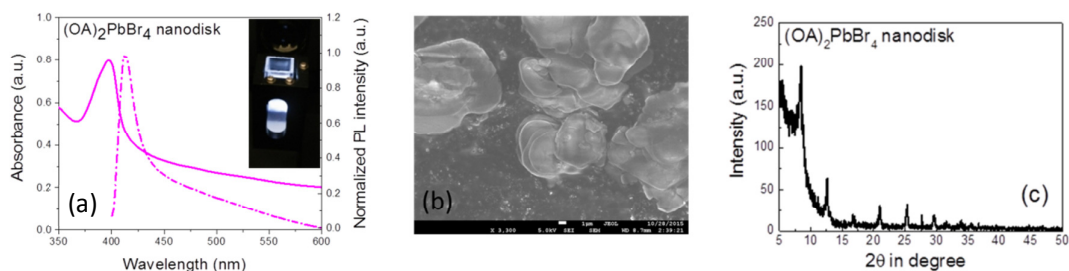


Fig. S5: (a) UV-vis absorption (solid line) and PL spectra (dotted line) of $(\text{OA})_2\text{PbBr}_4$ nanodisks. Inset of this figure is a photographic image of $(\text{OA})_2\text{PbBr}_4$ nanodisks in toluene solutions placed inside the PL spectrofluorophotometer when excited at 350 nm. (b) SEM image and (c) XRD pattern of micrometer sized nanodisks.

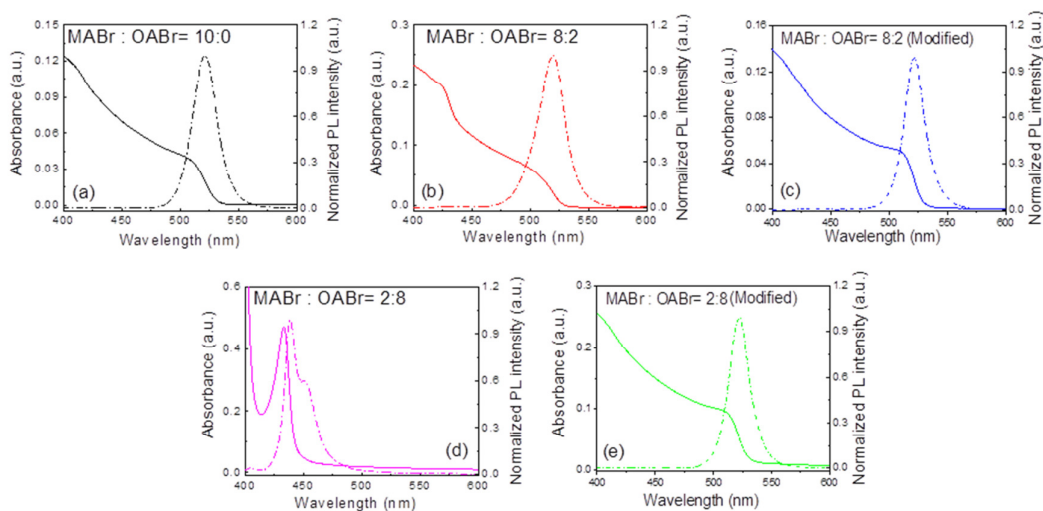


Fig. S6: UV-vis absorption and PL spectra of mixed organo lead bromide perovskite NPs with molar ratio of MABr and OABr are (a) 10:0, (b) 8:2, (c) 8:2 (seeded process), (d) 2:8 and (e) 2:8 (seeded process), respectively.

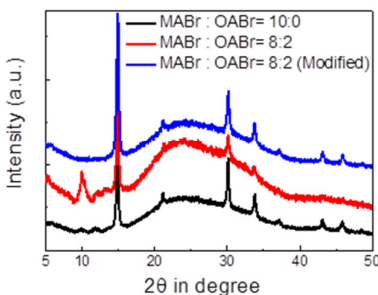


Fig. S7: XRD pattern of mixed organo lead bromide perovskite NPs with different MABr and OABr molar ratio as shown in legends. The modified process refers to the seeded synthesis procedure.

The thermo-gravimetric analysis (TGA) revealed a different thermal footprint for samples with MABr:OABr 10:0 and 8:2. The extended time necessary to remove the MABr and OABr constituents in the 8:2 sample, may explain that additional energy is required to remove the intercalated OABr. Since the weight loss of both organic molecules occur at an equal rate,³ no clear distinction between the removal of individual ammonium ligands is observed, rather a weight loss at different rates. Moreover, the weight loss associated with PbBr_2 (>400 °C) is shifted to higher temperatures, and only >450 °C its removal occurs at an equal rate as observed in 'pure' MAPbBr_3 . This further exemplifies that the removal of the MABr and OABr (in the 8:2 sample) is impeded due a structural difference with MAPbBr_3 .

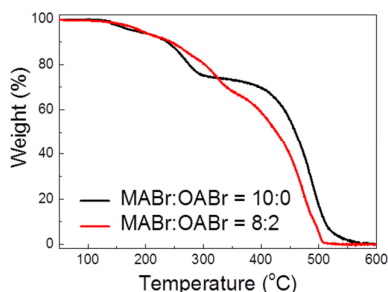


Fig. S8: Thermogravimetric analysis (TGA) heating curves of mixed organo lead bromide perovskite NPs with molar ratio of MABr and OABr shown in legends.

We have synthesized butylammonium bromide (C4; BABr) and dodecylammonium bromide (C12; DDABr). Perovskites with the respective bromides have been prepared with an MABr:XBr = 8:2 (where X = BA or DDA), optical absorption and photoluminescence spectra of these NPs are presented in Fig. S9. For both samples a photoluminescence quantum yield of approximately 70% was recorded; thus substantially lower than for both our 8:2 (92%) and 'pure' MAPbBr_3 (84%) NPs. The significant difference may be related to e.g. different interparticle spacing or packing densities, resulting in loss through self-absorption/re-emission and/or PL quenching.

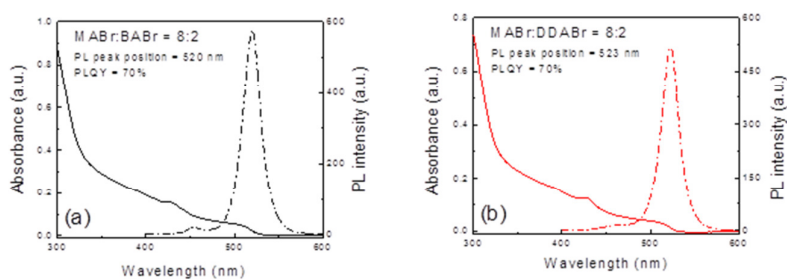


Fig. S9: UV-vis absorption and PL spectra of mixed organo lead bromide perovskite NPs with molar ratio of (a) MABr:BABr =8:2 and (b) MABr:DDABr =8:2.

Notes and references

- (1) H. Huang; A. S. Susha; S. V. Kershaw; T. F. Hung; A. L. Rogach, *Adv. Sci.*, 2015, **2**, 1500194.
- (2) Z. Yuan; Y. Shu; Y. Tian; Y. Xin; B. Ma, *Chem. Comm.*, 2015, **51**, 16385.
- (3) S. Gonzalez-Carrero; R. E. Galian; J. Perez-Prieto, *J. Mater. Chem. A*, 2015, **3**, 9187.