

Supplementary information for

B-site Metal Cation Exchange in Halide Perovskites

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Materials and Methods

Materials

Unless otherwise stated, all materials were purchased from Sigma Aldrich or Alfa Aesar and used as received. Formamidinium iodide and Methylammonium iodide were purchased from Dyesol Ltd.

Perovskite thin film fabrication

Thin films were fabricated on glass or ITO substrates (TFD inc.). These were sequentially cleaned by sonicating in dilute detergent, acetone, and propan-2-ol, and subsequently treated with oxygen plasma for 10 minutes. Perovskite thin films were fabricated in a nitrogen-filled glovebox using a 'precursor-phase antisolvent immersion' technique as we have reported previously.¹ In short, for FASnI₃, a precursor solution containing 1M SnI₂, 1M FAI and 0.2M SnF₂ was dissolved in a mixed solvent of 65% dimethylformamide/35% dimethylsulfoxide, and filtered before use. For FAPbI₃, 1M PbI₂ and 1M FAI was dissolved in the same mixed solvent. For the FASn_{0.5}Pb_{0.5}I₃ reference films, these solutions were mixed in an equimolar ratio. Precursor solutions were spin-coated at 10,000rpm and transferred immediately into an anisole bath, where they were held for 20 seconds before blowing dry with an N₂ gun. Films were then heated at 70°C for 15 minutes (for FASnI₃ and FASn_{0.5}Pb_{0.5}I₃) or 70°C for 5 minutes followed by 170°C for 10 minutes (for FAPbI₃).

We note that especially the tin-containing materials are highly air-sensitive, so all materials were kept under nitrogen at all times.

Perovskite nanocrystal fabrication

Methylammonium tin iodide nanocrystals were fabricated via a hot injection method using standard air-free schlenk line techniques. Initially, an injection precursor of 744mg SnI₂ was dissolved in 2ml TOP (95%, Sigma). A reaction flask containing 10ml octadecene (90%, Sigma) and 0.32ml oleylamine (70%, Sigma) and 0.32ml oleic acid (90%, Sigma) was degassed at 100°C under vacuum for an hour, then turned to 60°C and nitrogen flow. 344μl of methylamine in tetrahydrofuran was then added to the reaction flask (2M), followed by a hot injection of 2ml of the SnI₂ precursor. The reaction was allowed to run for 1 minute before cooling with an ice water bath. The reaction was then centrifuged at 11,000rpm for 10 minutes, the supernatant discarded, the pellet dried and then redispersed in 4ml anhydrous toluene. This gave a solution of approximately 128mg/ml. Quantum yields were measured as typically 1-3%.

Methylammonium lead iodide nanocrystals were fabricated by following the method of Vybornyi et al.² The MAPbI₃ nanocrystals used in this work were synthesized at 80°C.

Cation exchange

Tin iodide and lead iodide were dissolved in TOP (95%, Sigma) at 100mg/ml and 20mg/ml respectively. For film exchange, films were immersed in 3ml toluene in large vials and this solution added in the appropriate volume. The vials were placed on a hotplate in a glovebox for the exchange to take place. For nanocrystal exchange, nanocrystals were diluted in toluene (typically 4μl nanocrystal concentrate in 3ml toluene) in a quartz cuvette and the lead or tin iodide solution added in the appropriate volume under heat and stirring in a glovebox.

To prepare samples for GDOES and XRD characterization, the exchanged solution was centrifuged at 11,000rpm for 10 minutes to precipitate the nanocrystals out, the supernatant discarded and the pellet allowed to dry in nitrogen. The product was then re-suspended in a small volume of toluene and films were drop-cast on glass or ITO-coated slides and dried under nitrogen atmosphere.

Characterization

Absorbance was measured using an Agilent 8453 spectrometer. We note that no integrating sphere was used in this measurement so scattering will be present in the measurements. The reference used for absorption measurements was the solvent (anhydrous toluene) in the same quartz cuvettes used for sample measurement. Photoluminescence was measured using both a Perkin-Elmer Fluorolog spectrophotometer and a home-built setup based on an OceanOptics 2000+ spectrometer. We note that quantum yields decreased by a factor of approximately two during each exchange. X-ray diffraction was carried out using a Bruker D8 diffractometer. Samples were sealed in nitrogen under a polyimide sheet. Scanning electron microscope images were acquired using a FEI Sirion SEM. Thicknesses and roughnesses were measured using a Bruker Dektak XT profilometer.

Transmission electron microscopy was carried out using an FEI Tecnai TEM on diluted samples (approx. 50μl of concentrated QDs in 3ml toluene) drop-cast on lacey carbon grids and allowed to dry in a glovebox overnight. We were exceptionally careful not to expose the Sn-containing films to air when loading into microscopes for longer than was unavoidable (~30s).

Glow discharge optical emission spectroscopy

GDOES measurements were performed using a Horiba GD-Profilier 2 instrument with a 4mm anode. Elemental counts were calibrated using pure FASnI₃ and FAPbI₃ films of known thickness, to allow determination of the Sn/Pb fraction. Calibration was additionally validated with a FASn_{0.5}Pb_{0.5}I₃ film which gave a Pb percentage of 52±2%. Errors were determined from repeat samples and from background noise inherent in the measurement.

Supplementary data

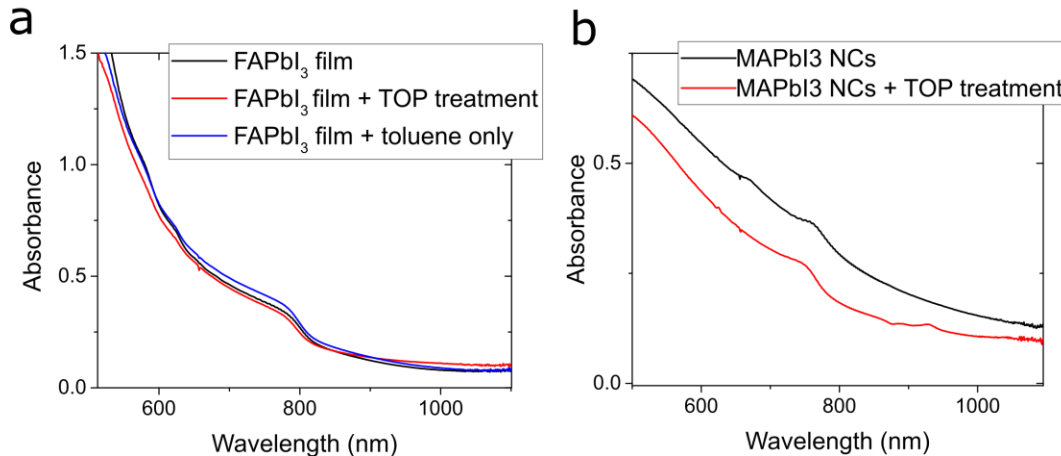


Fig. S1. Effect of TOP addition on thin films of $\text{CH}(\text{NH}_2)_2\text{PbI}_3$ (a) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals (b). Films were immersed in an equivalent concentration of TOP in toluene as used for the cation exchange (red) or pure toluene (blue) and heated at 70°C for 5 hours. Nanocrystals were diluted in an equivalent TOP/toluene solution as used for cation exchange and heated for 24 hours at 70°C .

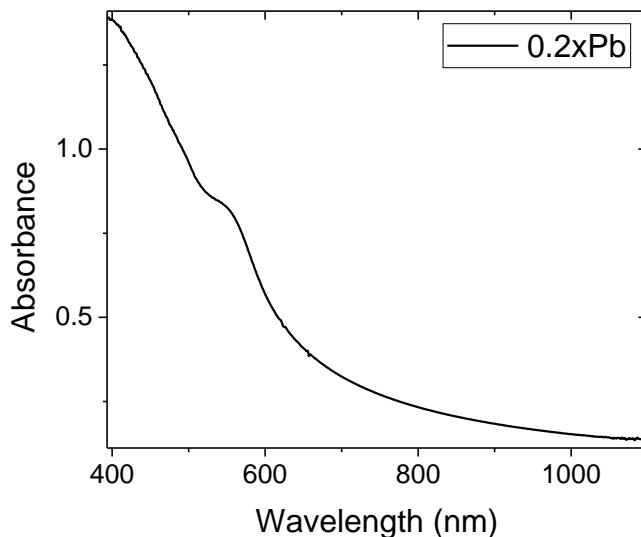


Fig S2. Absorption spectrum of FASnI_3 film immersed in low concentration of Pb (0.2 molar equivalents), showing predominantly yellow-orange phase. The film was heated at 70°C for 96 hours in the exchange solution.

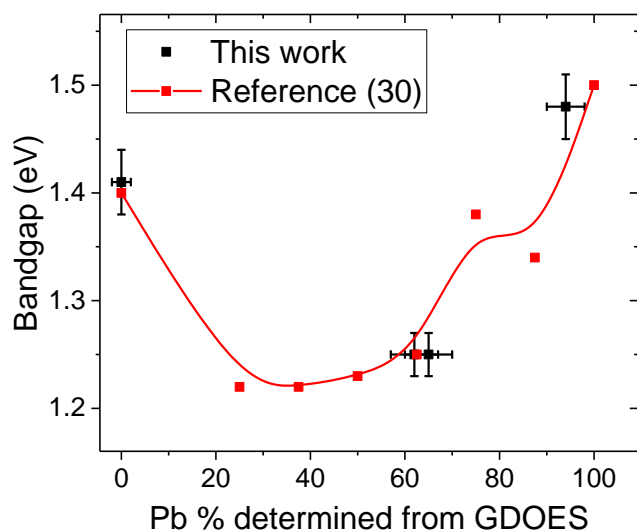


Fig S3. Comparison of bandgap values for the compositions of $\text{CH}(\text{NH}_2)_2\text{Pb}_x\text{Sn}_{1-x}\text{I}_3$ made here, with composition determined from GDOES, with bandgap data for $\text{CH}(\text{NH}_2)_2\text{Pb}_x\text{Sn}_{1-x}\text{I}_3$ taken from literature.¹ A B-spline fit is applied to the literature values.

Sample / treatment	Thickness (nm)	Roughness (RMS / Rq) (nm)
FASnI ₃	195±14	17
1xPb	225±22	18
10xPb	199±18	28
50xPb	225±64	20

Table ST1. Film thickness and roughness for FASnI₃ films and Pb-exchanged samples. Errors determined from repeat measurements (at least 3 per sample).

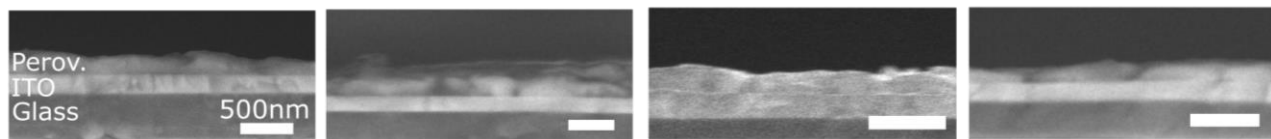


Fig. S4. Cross-sectional SEM images of (left to right) FASnI₃, 1xPb exchange, 10xPb exchange, 50xPb exchange. Films were fabricated on ITO-glass. Scale bar is 500nm in all cases.

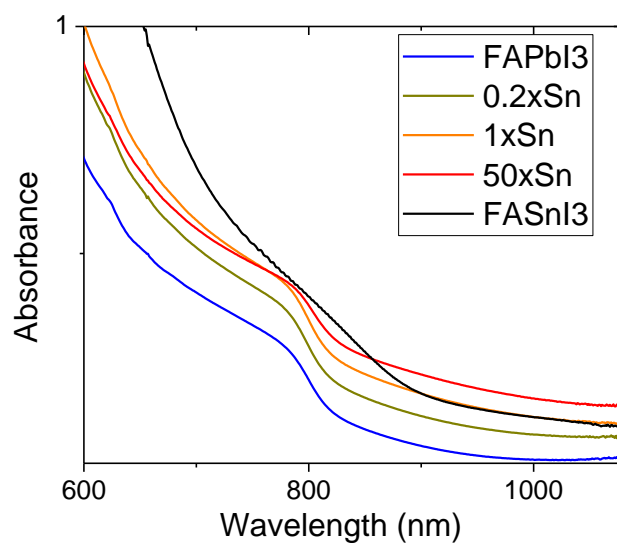


Fig S5. Attempt to exchange FAPbI₃ thin film with SnI₂. Absorbance spectra measured after heating at 70°C with the relative molar concentration of Sn shown in the legend, for 50 hours, show very little change in onset. An increase in baseline scatter with increased Sn concentration is attributed to some surface precipitation of SnI₂.

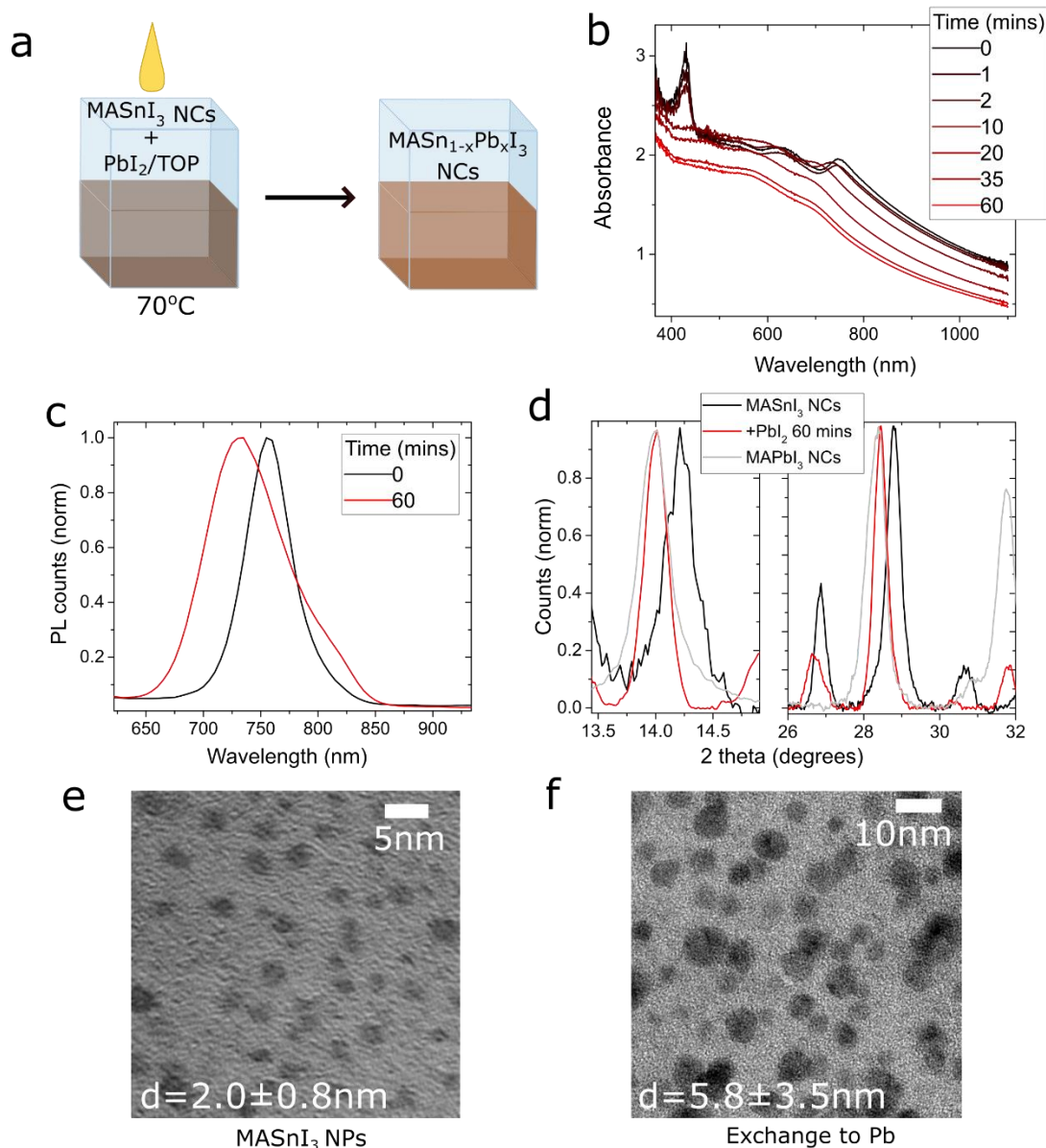


Fig S6. B-site cation exchange in nanocrystals. a) Diagram of the exchange of CH₃NH₃SnI₃ nanocrystals with Pb. b) Absorbance spectra of the cation exchange reaction, taken at various time intervals, when 1x equivalent of Pb was added to the nanocrystals. c) PL spectra of the initial nanocrystals, and the nanocrystals post-exchange reaction. d) Magnified X-ray diffraction spectra of drop-cast films of neat CH₃NH₃SnI₃, CH₃NH₃PbI₃, and Pb-exchanged CH₃NH₃SnI₃ nanocrystals, showing the peaks centered near 14° (left) and 28° (right). e) and f) Transmission electron microscope images of CH₃NH₃SnI₃ nanocrystals (e) and nanocrystals after exchange to Pb (f). Histograms of sizes used to determine average size are shown in Fig S6.

Sample	Pb/(Pb+Sn) %
MASnI ₃ nanocrystals	0±5
Exchange to Pb	75±5
Re-exchange to Sn	20±10

Table ST2. Tin-lead composition determined from Glow Discharge Optical Emission Spectroscopy (GDOES) for neat and exchanged nanocrystals.

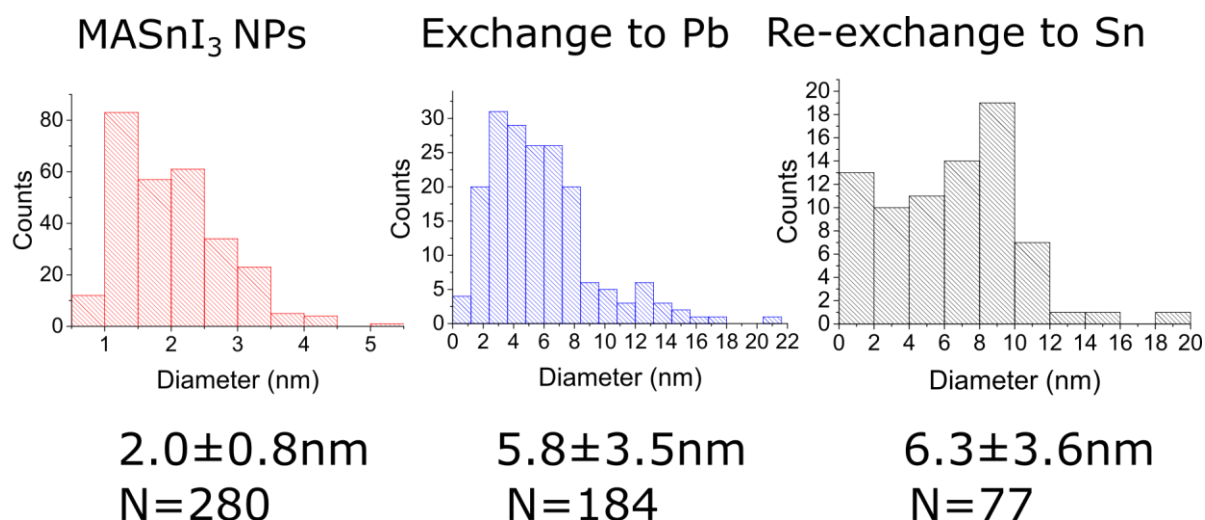


Fig S7. Size distributions of nanocrystals before and after exchange. Red = MASnI₃ nanocrystals as synthesized; blue = MASnI₃ nanocrystals exchanged with Pb; grey = reverse-exchanged nanocrystals (Sn->Pb->Sn). Average sizes are shown below the plots. We note that the average size monotonically increases with each heat/exchange step.

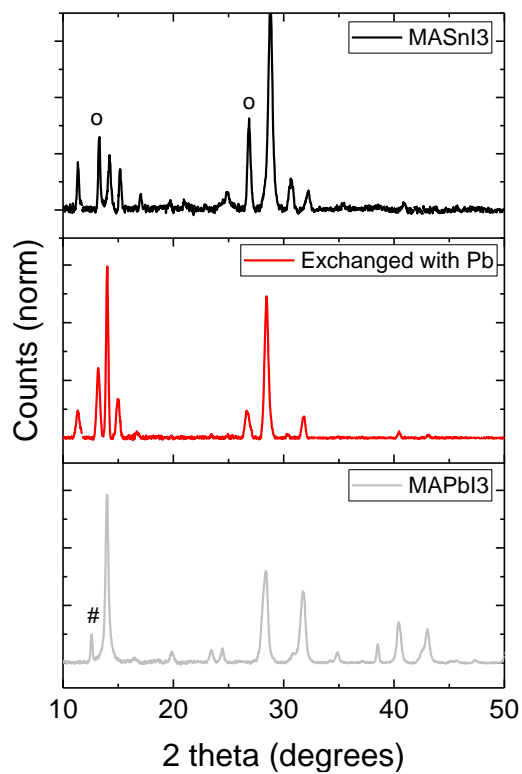


Fig S8. Full X-ray diffraction spectra for the exchange from $\text{CH}_3\text{NH}_3\text{SnI}_3$ nanocrystals with PbI_2 . We also show XRD spectra of MAPbI_3 nanocrystals as a reference (bottom). We assign peaks marked with a 'o' to SnI_2 and those marked with '#' to PbI_2 .³ It is noted that some impurities present in the initial $\text{CH}_3\text{NH}_3\text{SnI}_3$ synthesis remain in the ion-exchanged product.

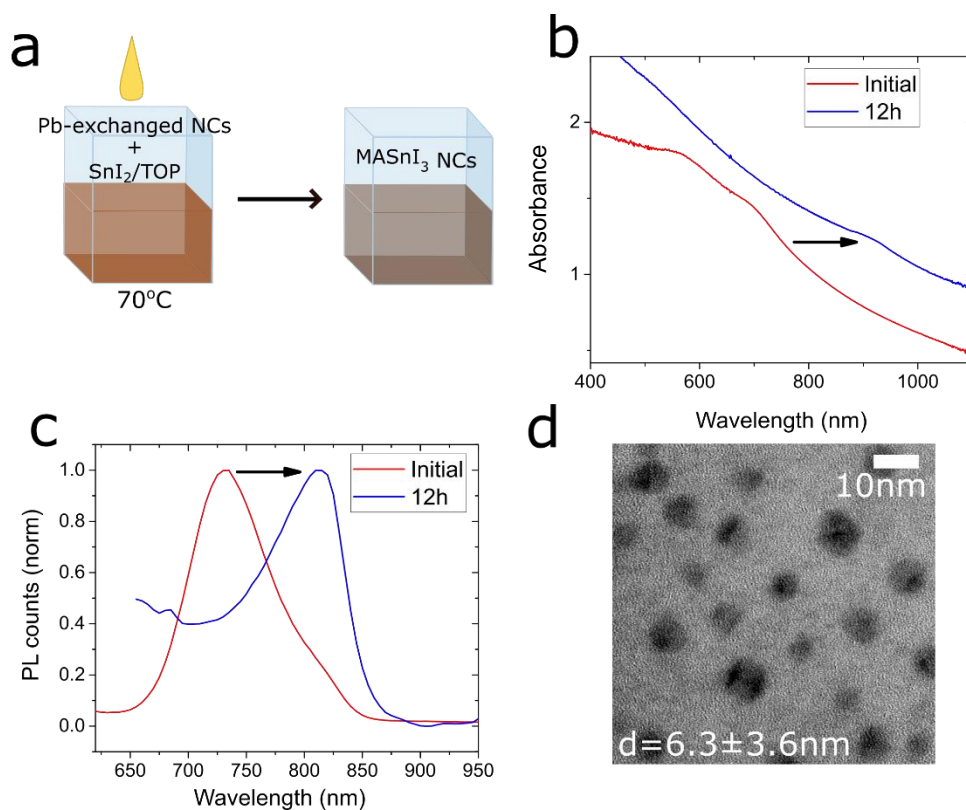


Fig S9. Reversibility of B-site cation exchange reaction in colloidal suspension. a) Diagram showing the reverse exchange process. b) Absorbance spectra of the Pb-exchanged nanocrystals before and after exchange with SnI_2 . Here a 100x Sn excess was used and the reaction run for 12 hours at 70°C . c) PL spectra of the Pb-exchanged nanocrystals before and after exchange with SnI_2 . d) Transmission electron microscope image of the reverse Pb-exchanged nanocrystals after additional reverse exchange with Sn.

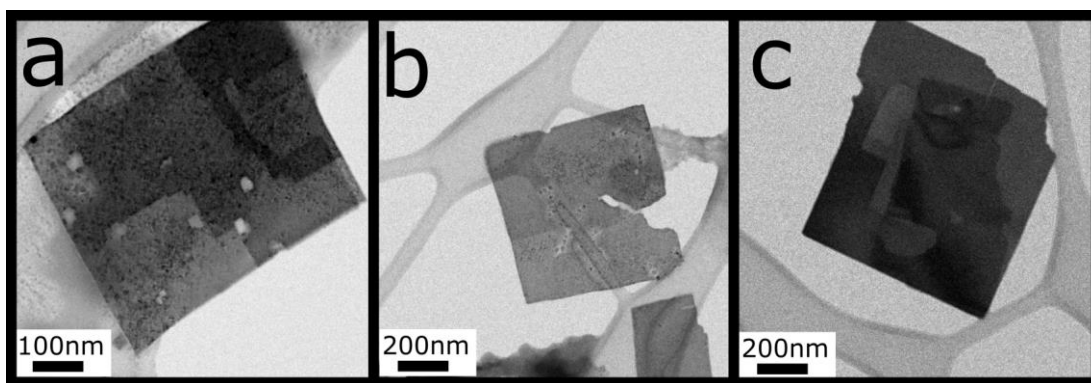


Fig. S10. Platelet structures observed in exchanged nanocrystal solutions via transmission electron microscopy (TEM). a) Platelet in Pb-exchanged FASnI₃ nanocrystals reaction; b) and c) Platelets observed in Sn-re-exchanged Pb-exchanged MASnI₃ nanocrystals (i.e. Sn->Pb->Sn).

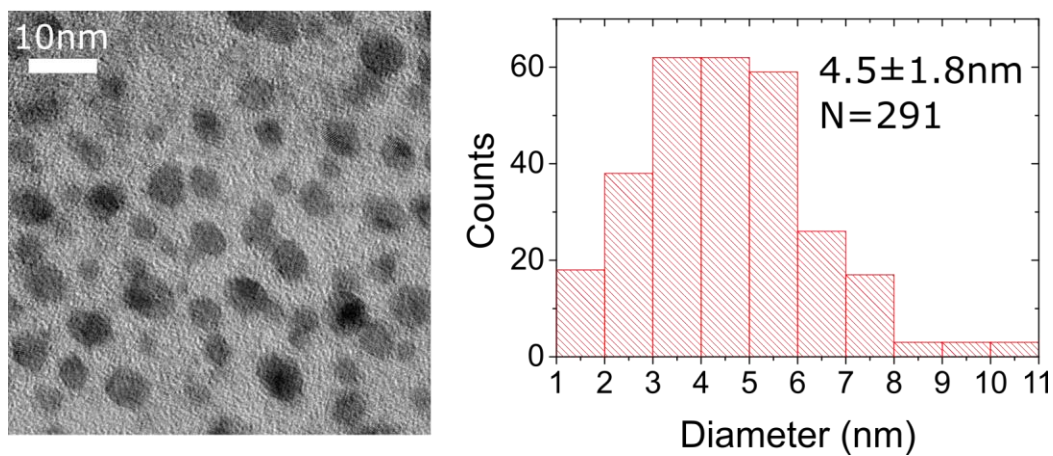


Fig S11. TEM characterization of MAPbI₃ nanocrystals. Left: TEM image of typical MAPbI₃ nanocrystals. Right: Size distribution of MAPbI₃ nanocrystals.

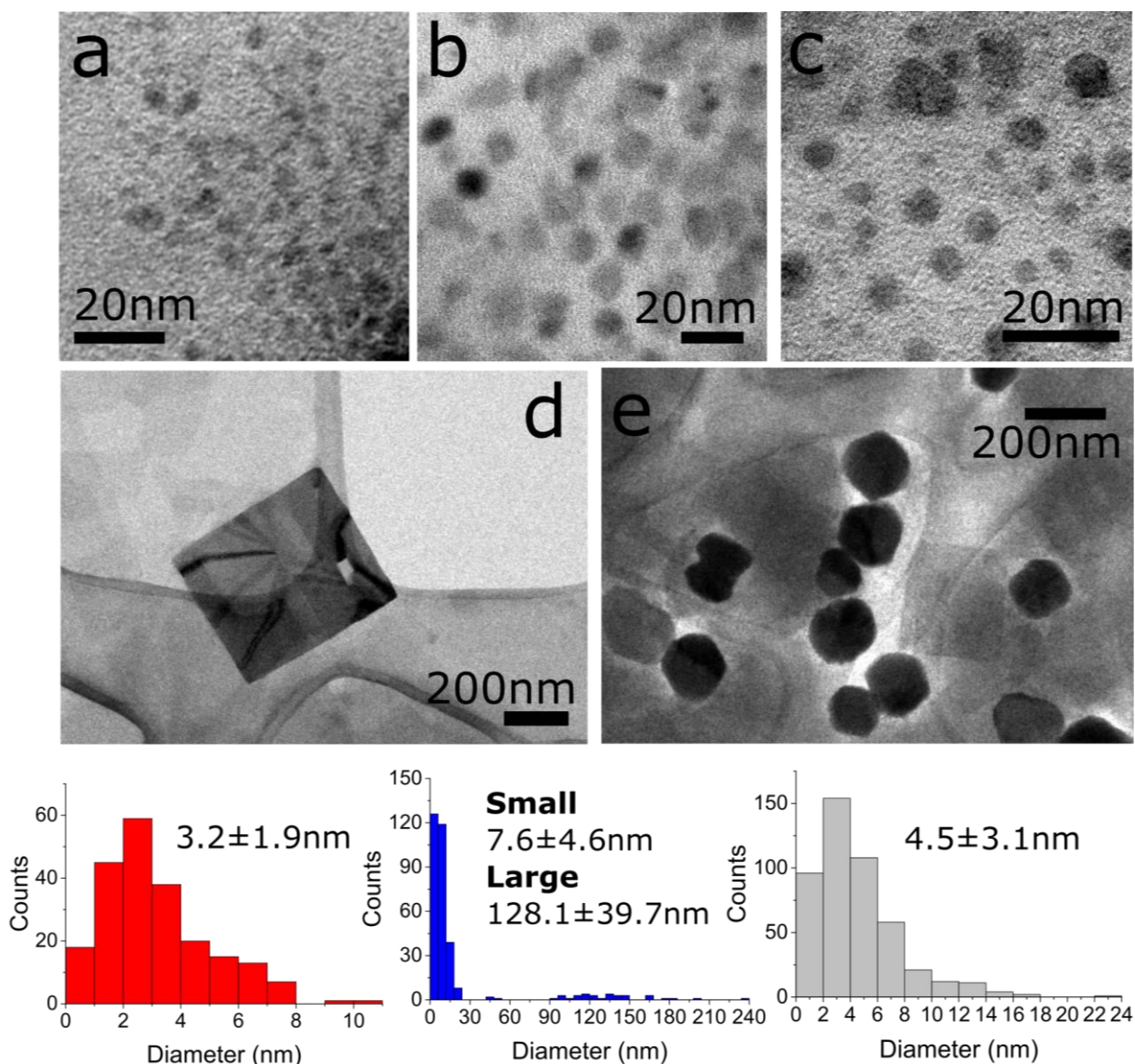


Fig. S12. Impact of heating and TOP on nanocrystal shape and size. a) MASnI₃ nanocrystals heated for 24h at 70°C. b) MAPbI₃ nanocrystals heated for 24h at 70°C. c) MAPbI₃ nanocrystals heated for 24h at 70°C with addition of TOP in equivalent quantity as for exchange reactions. d) Larger platelet observed in heated MASnI₃ nanocrystals. e) larger three-dimensional particles formed in heated MAPbI₃ nanocrystals. Below: size distributions for reactions a-c, in the order left to right. The heated MAPbI₃ nanocrystals show a bimodal distribution due to the larger particles, so we classified the average size for the two distributions separately.

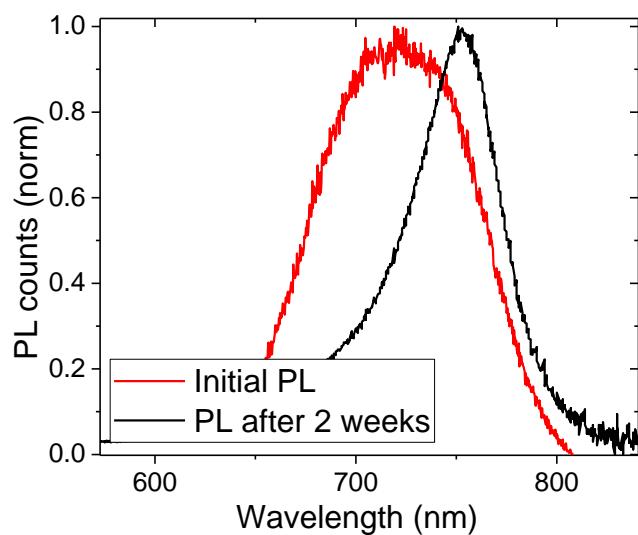


Fig S13. Growth of MA-containing nanocrystals over time. Change in PL spectra of small MAPbI₃ nanocrystals when stored in glovebox, at room temperature, for 2 weeks.

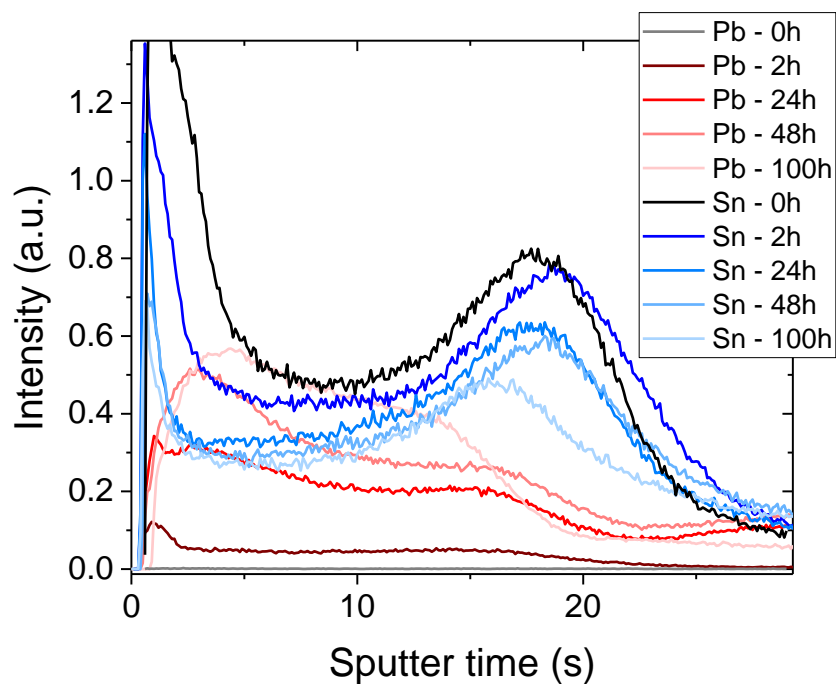


Fig. S14. GDOES line profiles for Sn and Pb after carrying out exchange reaction on identical FASnI₃ films for certain times as indicated in the legend. The increased concentration of Sn near the surface (and deficit near the center) may be due to Sn²⁺ reacting with oxygen in the air at the surface to form Sn⁴⁺, and Sn

from further into the bulk diffusing towards the surface consequently – these measurements necessitated exposing the samples to air for a matter of tens of minutes.

References

- (1) Eperon, G. E.; Leijtens, T.; Bush, K. A.; Prasanna, R.; Green, T.; Wang, J. T.-W.; McMeekin, D. P.; Volonakis, G.; Milot, R. L.; May, R.; *et al.* Perovskite-Perovskite Tandem Photovoltaics with Optimized Band Gaps. *Science* (80-.). **2016**, *354*, 861–865.
- (2) Vybornyi, O.; Yakunin, S.; Kovalenko, M. V. Polar-Solvent-Free Colloidal Synthesis of Highly Luminescent Alkylammonium Lead Halide Perovskite Nanocrystals. *Nanoscale* **2015**, 2–7.
- (3) Kostko, V. S.; Kostko, O. V.; Makovetskii, G. I.; Yanushkevich, K. I. Thin Film Structure of tin(II) Iodide. *Phys. Status Solidi Basic Res.* **2002**, *229*, 1349–1352.