Supporting Information for:

Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions

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Additional Experimental Data

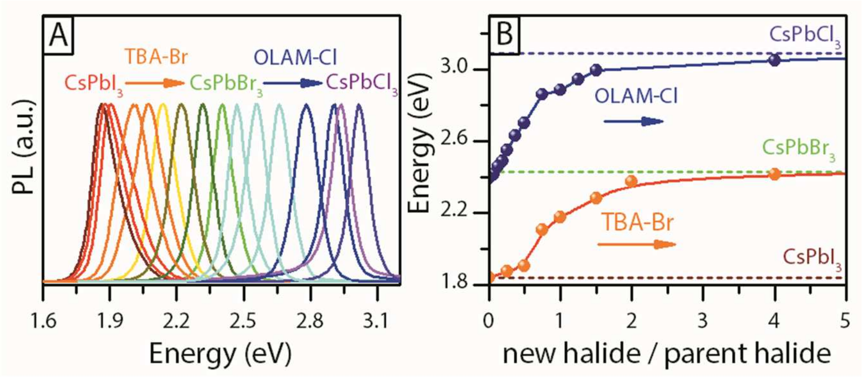

Figure SI1. PL spectra of the CsPbX$_3$ NCs prepared by anion exchange, using TBA-Br and OLAM-Cl. (B) PL calibration curves based on the I$^-$ (for using TBA-Br) and Br$^-$ (for using OLAM-Cl) amount in the starting NCs. The curves are reported as a function of the molar ratio between the added halide and the Br amount in the starting NCs.

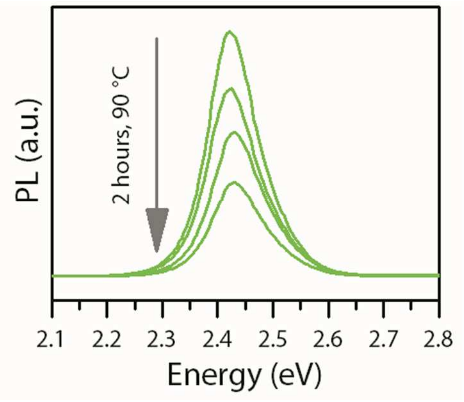

Figure SI2. PL spectra measured overtime (2 hours) on CsPbBr$_3$ NCs dispersed in TOL and heated at 90°C.

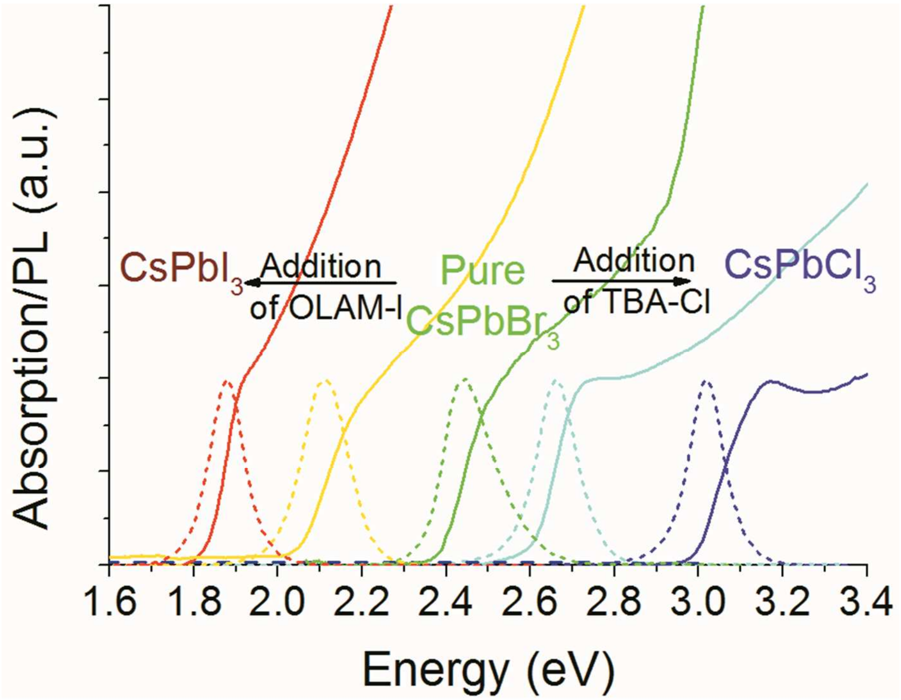

Figure SI3. Optical Absorption and PL spectra of $CsPbX_3$ NCs prepared by anion exchange.

Comparison of optical properties and diffraction patterns of the NCs prepared by direct synthesis with those prepared by anion exchange.

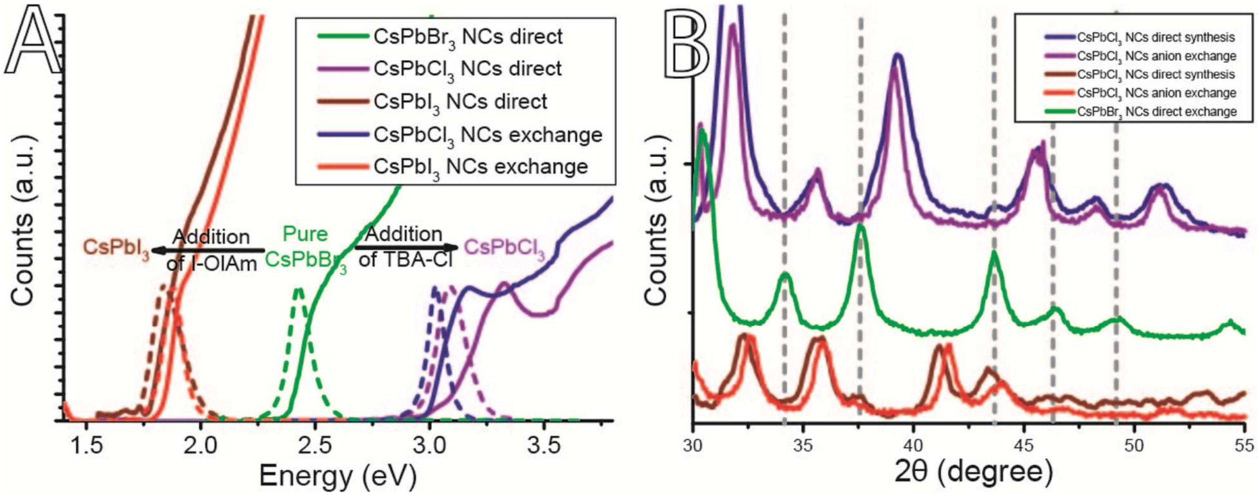

Figure SI4. Optical absorption and PL spectra (A) and XRD patterns (B) of directly synthesized $CsPbX_3$ NCs (X=Cl, Br, I) and of $CsPbX_3$ NCs (X=Cl, Br) prepared by anion exchange. Only minor differences can be seen in both optical spectra and XRD patterns of the NCs prepared by anion exchange with respect to the spectra and XRD patterns of the corresponding NCs prepared by direct synthesis, corroborating the almost complete anion exchange

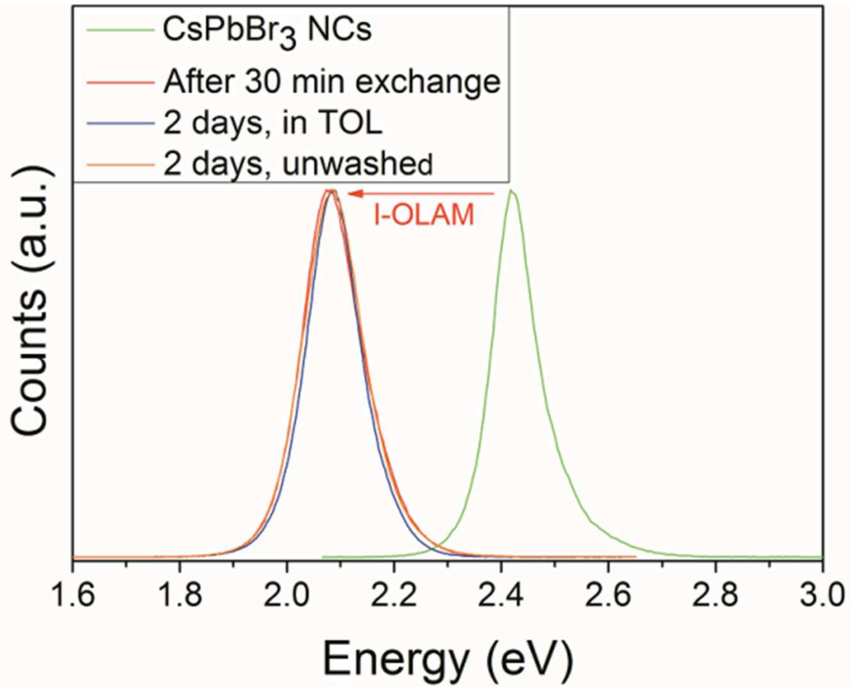

Figure SI5. Green spectrum: PL of initial $CsPbBr_3$ NCs. Red spectrum: PL of the exchanged NCs (with I-OLAM), recorded 30 minutes after the exchange reaction; Orange spectrum: PL of the same sample of exchanged NCs, recorded 2 days later; Blue spectrum: PL of a sample of NCs cleaned after exchange (by centrifugation and re-dispersion in toluene), recorded 2 days later. All exchanged samples had the same PL emission peak and linewidth, regardless of the time from exchange at which the PL was recorded and regardless of whether the samples were crude solutions or cleaned ones.

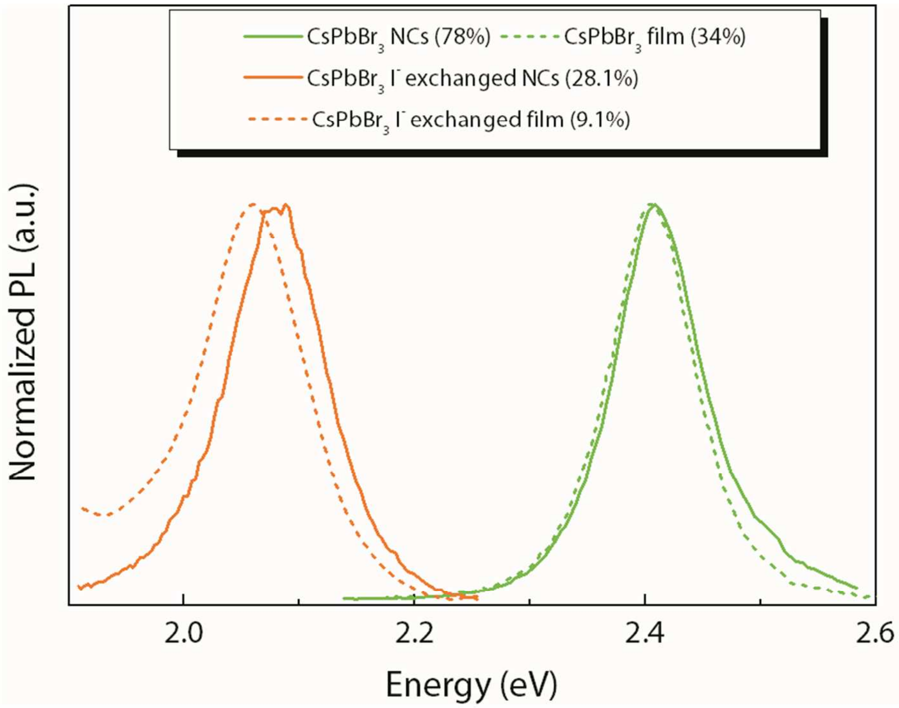

Figure SI6. PL spectra of $CsPbBr_3$ (green) and I^- exchanged $CsPb(Br:I)_3$ (orange) recorded from solutions (continuous lines) and from thin films of NCs deposited on a substrate (dotted lines). The parent $CsPbBr_3$ retain their PL with a drop of PLQY from 78% to 34% whereas the exchanged NCs exhibit a small 5 nm red shift and a PLQY drop from 28% to 9.1 %.

TEM analysis of anion exchanged NCs

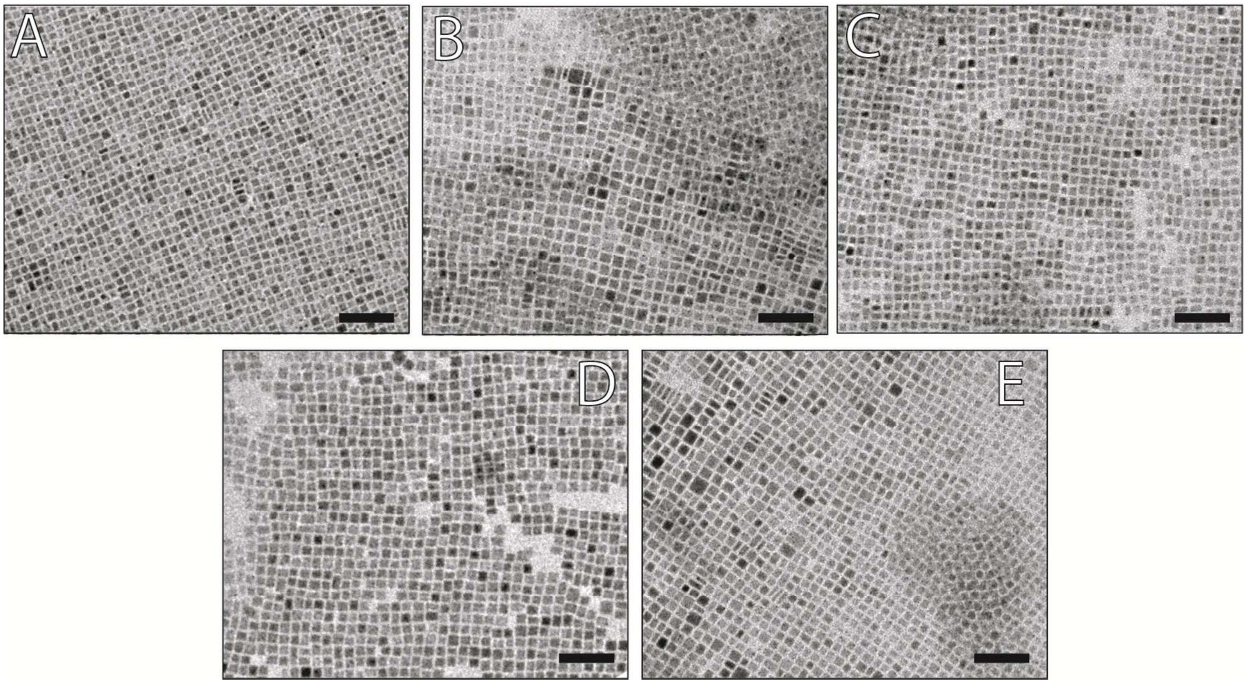

Figure SI7. TEM images of pristine $CsPbBr_3$ NCs (panel C), of the anion exchanged $CsPbCl_3$ (panel A), $CsPbI_3$ (panel E) and of two intermediate Cl^- (panel B) and I^- (panel D) exchanged samples. Scale bars correspond to 50 nm.

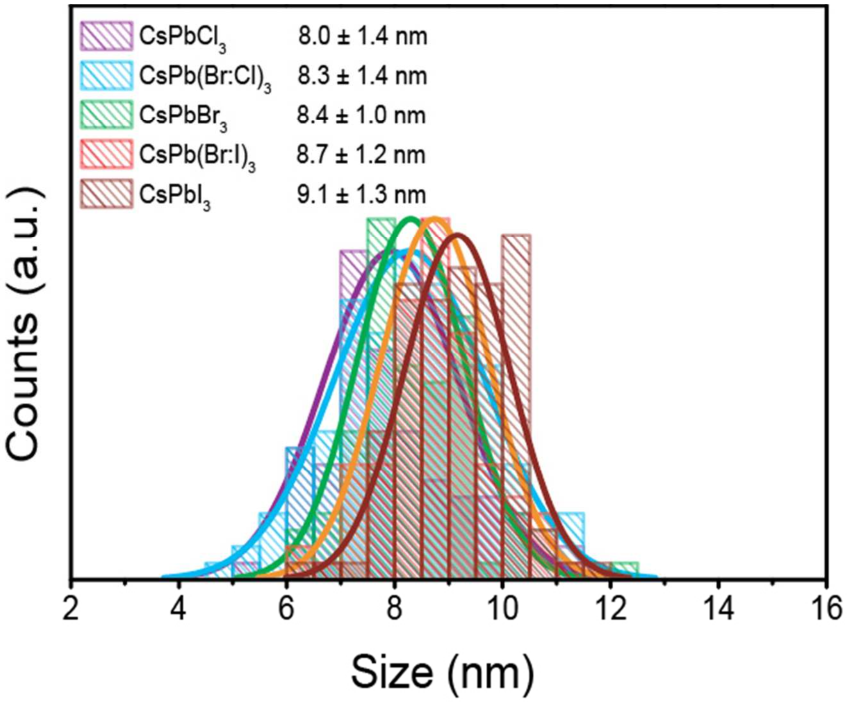

Figure SI8. Size distribution of the $CsPbX_3$ NCs whose TEM images are reported in figure SI7, as determined by size analysis on more than 100 NCs.

Comparison of full XRD patterns of $CsPbX_3$ NCs obtained by direct synthesis with those of the NCs prepared by anion exchange reactions.

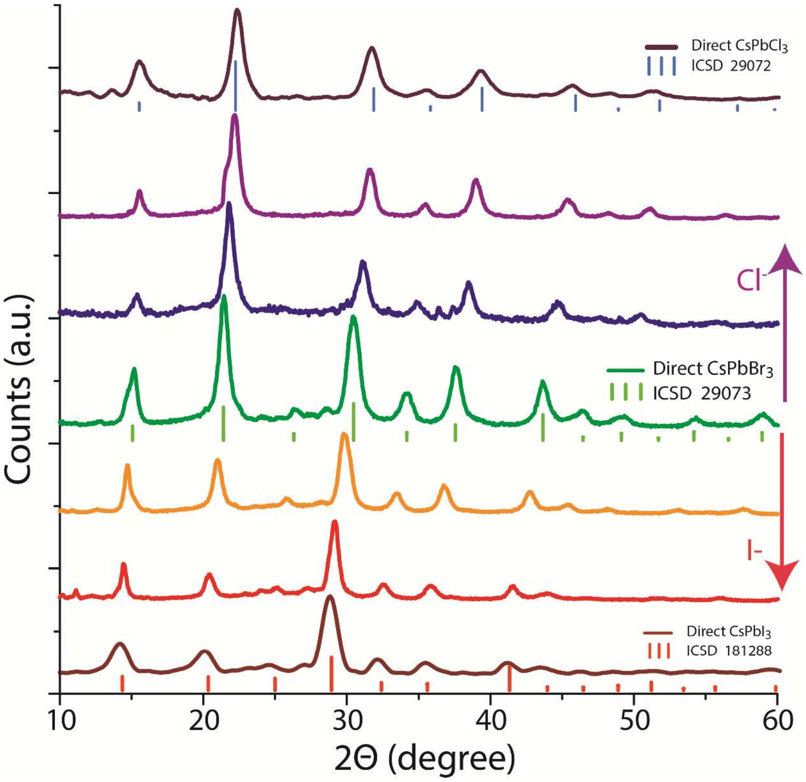

Figure SI9. Full XRD patterns of directly synthesized $CsPbX_3$ NCs (top: $CsPbCl_3$, middle: $CsPbBr_3$; bottom: $CsPbI_3$), together with those of the NCs prepared by anion exchange, starting from $CsPbBr_3$.

Exchange reaction with MA-Br.

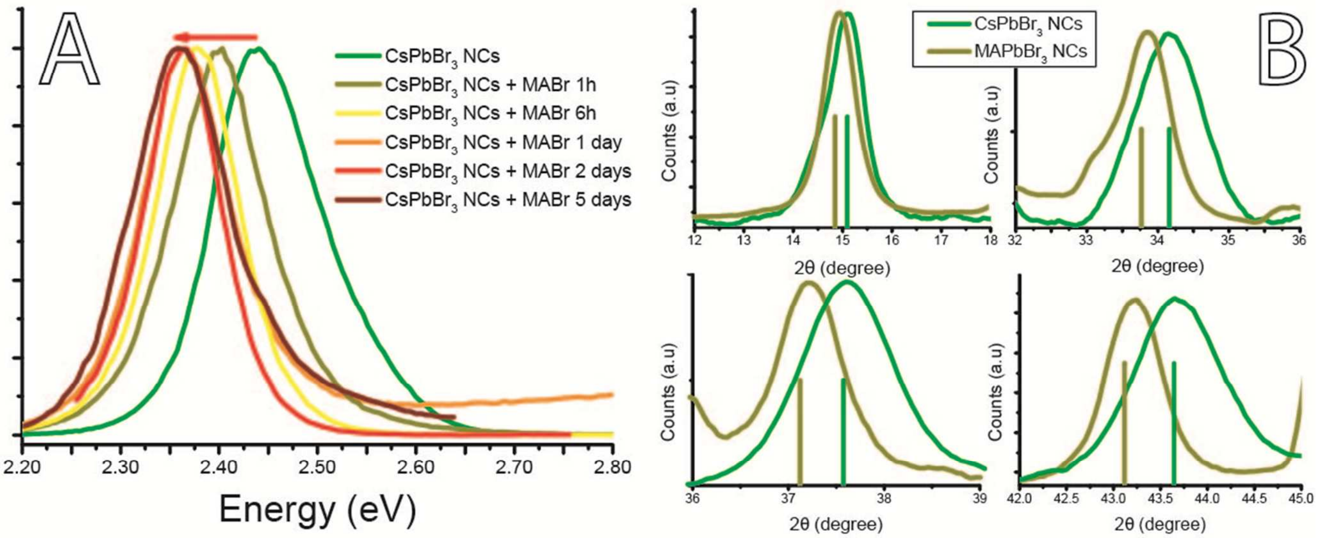

Figure SI10. (A) Photoluminescence (PL) spectra of $CsPbBr_3$ NCs upon reaction with MA-Br. A shift from 2.43 eV to 2.36 eV could be observed 24 h after mixing the NCs with MA-Br (due to the exchange of Cs^+ ions with MA^+ ions), with no further shift over the following days. (B) Details of XRD patterns. A shift of the diffraction peaks to lower angles was observed, due to the expansion of the crystal structure with the increasing cationic radius, from Cs^+ (1.81 Å) to MA^+ (2.70 Å) (see Figure SI10B).[4] The straight lines correspond to the bulk peak positions of $CsPbBr_3$ (ICSD 29073) and of $MAPbBr_3$, as reported by Schmidt et al.[5]

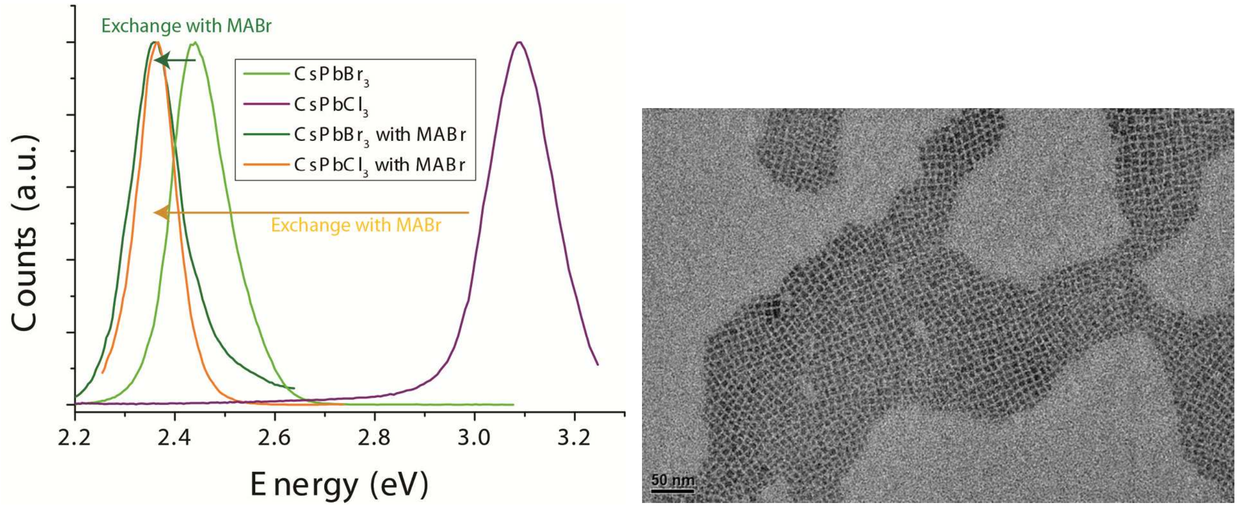

Figure SI11. (Left) PL spectra of starting $CsPbX_3$ (X = I, Cl) NCs and of the corresponding final samples obtained by reaction with MA-Br. (Right) TEM image of $CsPbBr_3$ NCs after exposure to MA-Br. The average size of the NCs is 7.2 ± 0.8 nm.

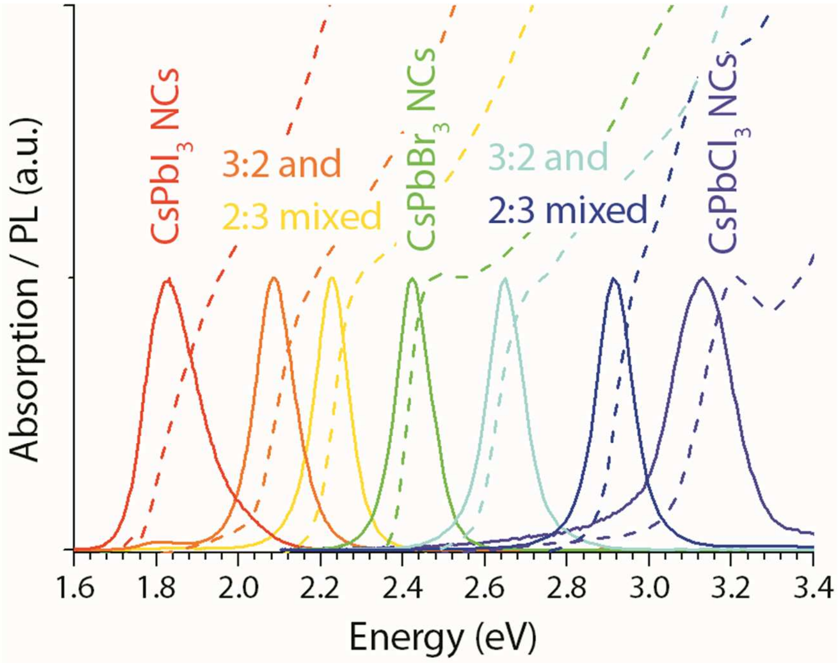

Figure S12. Absorption and PL spectra of solutions prepared by mixing two solutions of $CsPbBr_3$ and $CsPbCl_3$ (or $CsPbI_3$) NCs. Here, crude solution were mixed in either 3:2 or 2:3 ratios and resulted in $CsPb(Br{:}Cl)_3$ and $CsPb(Br{:}I)_3$ NC samples emitting in spectral regions that were intermediate compared to those of the parent solutions. A 1:1 mixing ratio was instead used for the samples reported in Figure 4C of the main text.

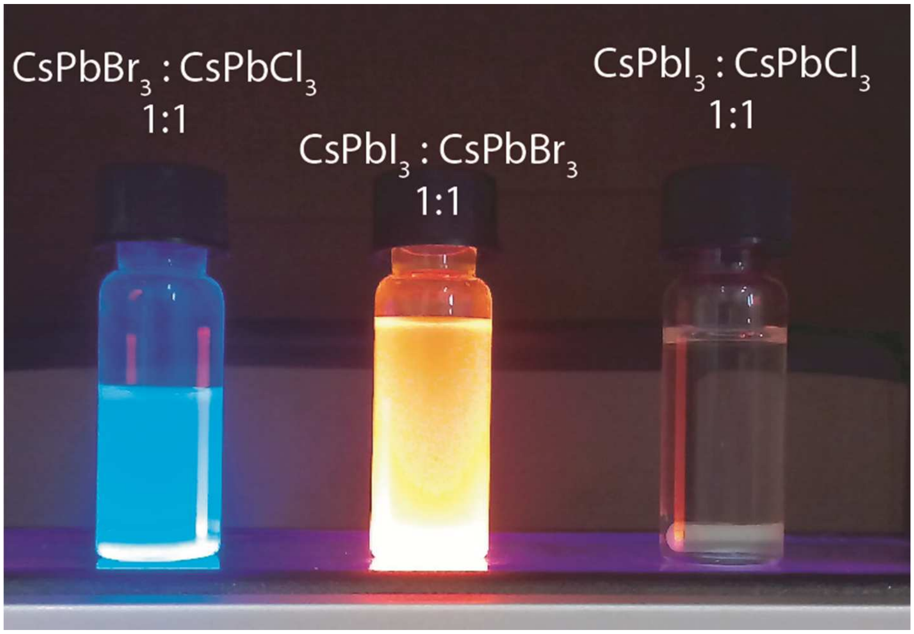

Figure S13. A photograph of vials containing mixtures of 1:1 $CsPbCl_3$:$CsPbBr_3$ NCs (left), $CsPbI_3$:$CsPbBr_3$ NCs (middle) and $CsPbCl_3$:$CsPbI_3$ NCs (right). A magnetic stir bar is present in each vial. The vials are sitting on a UV lamp. No PL was observed from the sample on the right.

Additional References

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(3) Edri, E.; Kirmayer, S.; Kulbak, M.; Hodes, G.; Cahen, D. *J. Phys. Chem. Lett.* **2014**, 5, 429-433.

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