Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Structural and Optical Control through Anion and Cation Exchange Processes for Sn-Halide Perovskite Nanostructures

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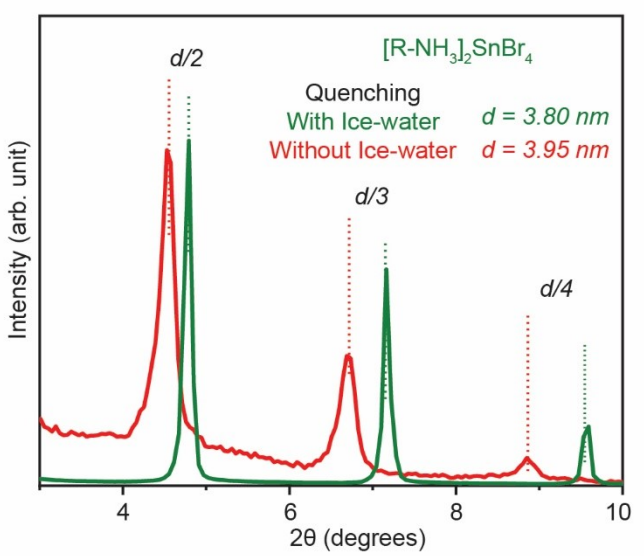

Figure S1. Powder X-ray diffraction pattern of the 2D $[R\text{-}NH_3]_2SnBr_4$ n = 1 RP nanostructures with reaction quenched with ice-water (green) and without ice-water (red).

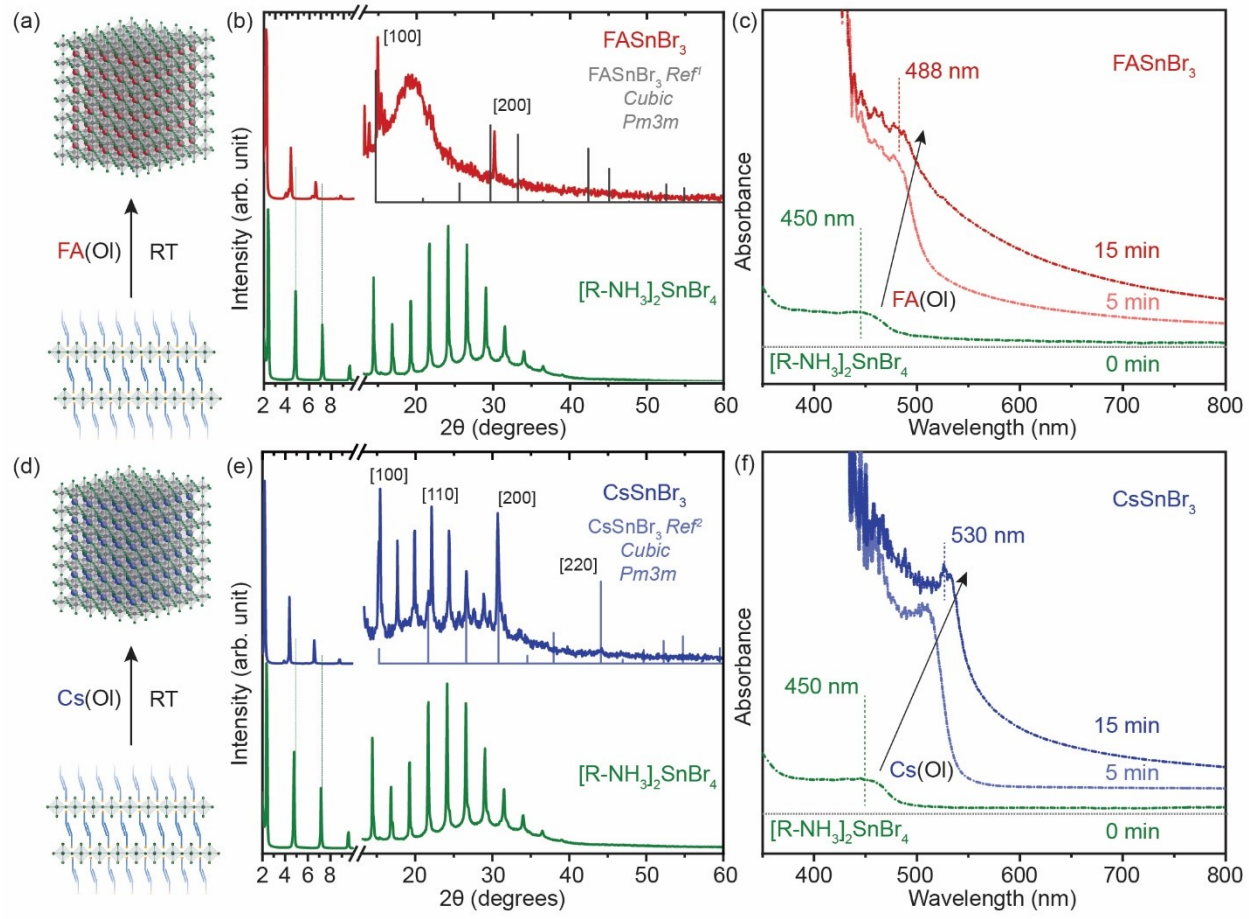

Figure S2. (a) and (d) Schematic representation of conversion of 2D $[R\text{-}NH_3]_2SnBr_4$ to 3D $FASnBr_3$ and $CsSnBr_3$ NCs respectively. (b) and (e) Powder X-ray diffraction pattern of the converted 3D $FASnBr_3$ (red) and $CsSnBr_3$ (blue) NCs from 2D $[R\text{-}NH_3]_2SnBr_4$ respectively. (c) and (f) In-situ UV-Visible spectroscopy of the formation of 3D $FASnBr_3$ (red) and $CsSnBr_3$ (blue) NCs from 2D $[R\text{-}NH_3]_2SnBr_4$ RP structure with the addition of A cation. The XRD references were adapted from ref.[1] for $FASnBr_3$ (cubic, Pm3m) and ref.[2] for $CsSnBr_3$ (cubic, Pm3m).

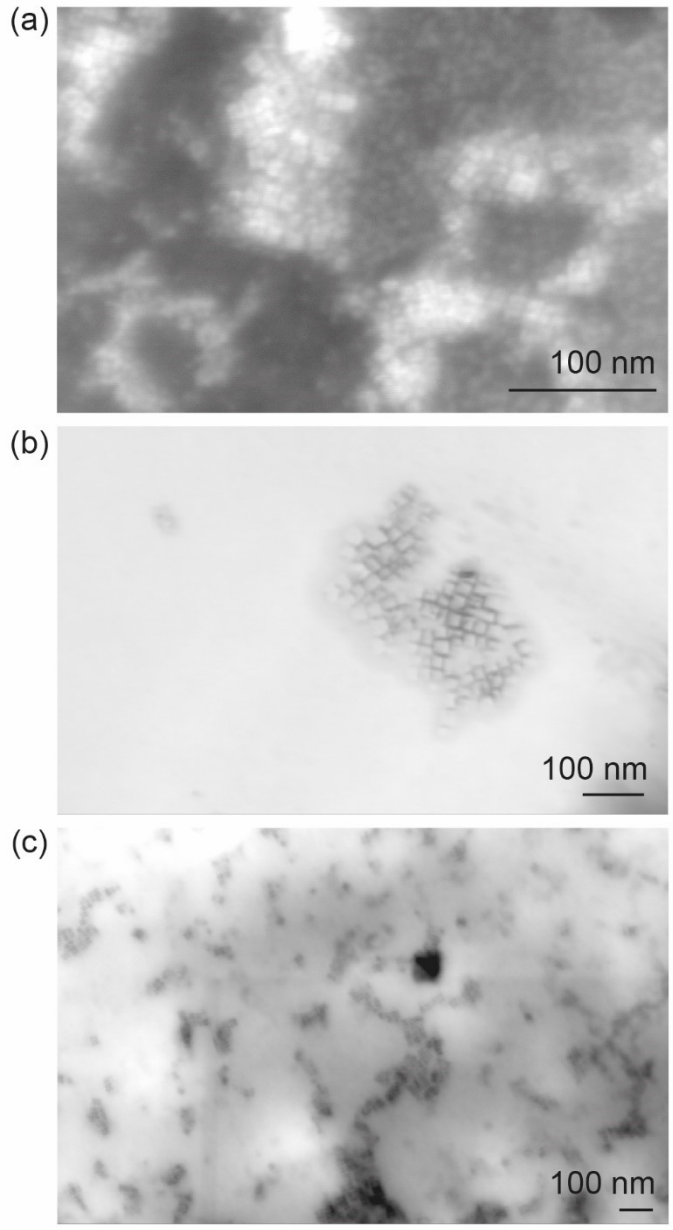

Figure S3. SEM images of $FASnI_3$ NCs formed via cation exchange of 2D $[R\text{-}NH_3]_2SnI_4$ RP nanostructures at decreasing magnifications from (a) to (c).

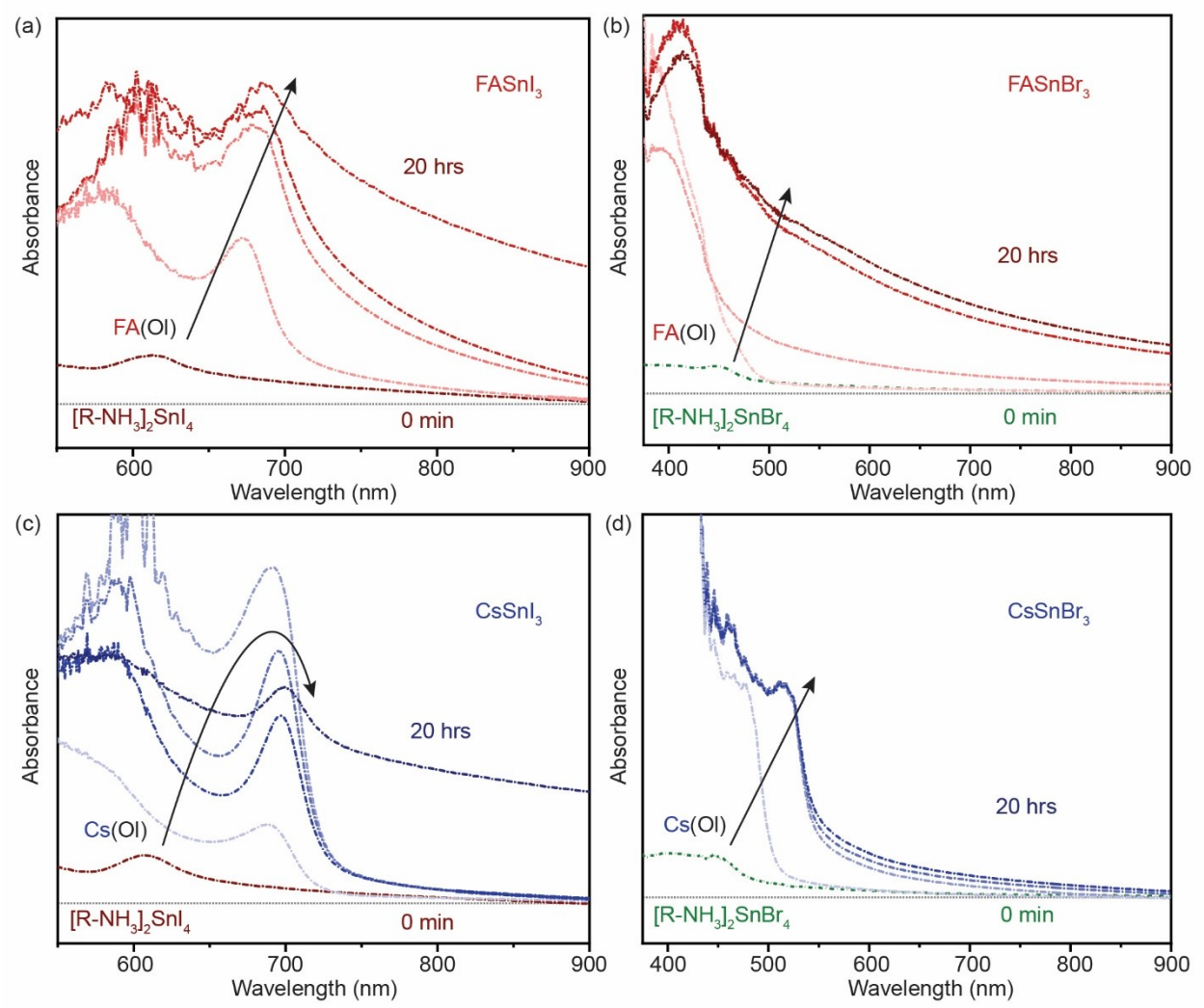

Figure S4. Extended time-dependence optical measurements (a) and (b) Insitu UV-Visible spectroscopy of the formation of 3D $FASnI_3$ and $FASnBr_3$ NCswith the addition of FA(Ol) in 2D $[R\text{-}NH_3]_2SnI_4$ and $[R\text{-}NH_3]_2SnBr_4$ RP structures respectively over the time of 30 minutes. (c) and (d) Insitu UV-Visible spectroscopy of the formation of 3D $CsSnI_3$ and $CsSnBr_3$ NCswith the addition of Cs(Ol) in 2D $[R\text{-}NH_3]_2SnI_4$ and $[R\text{-}NH_3]_2SnBr_4$ RP structures respectively over the time of 30 minutes.

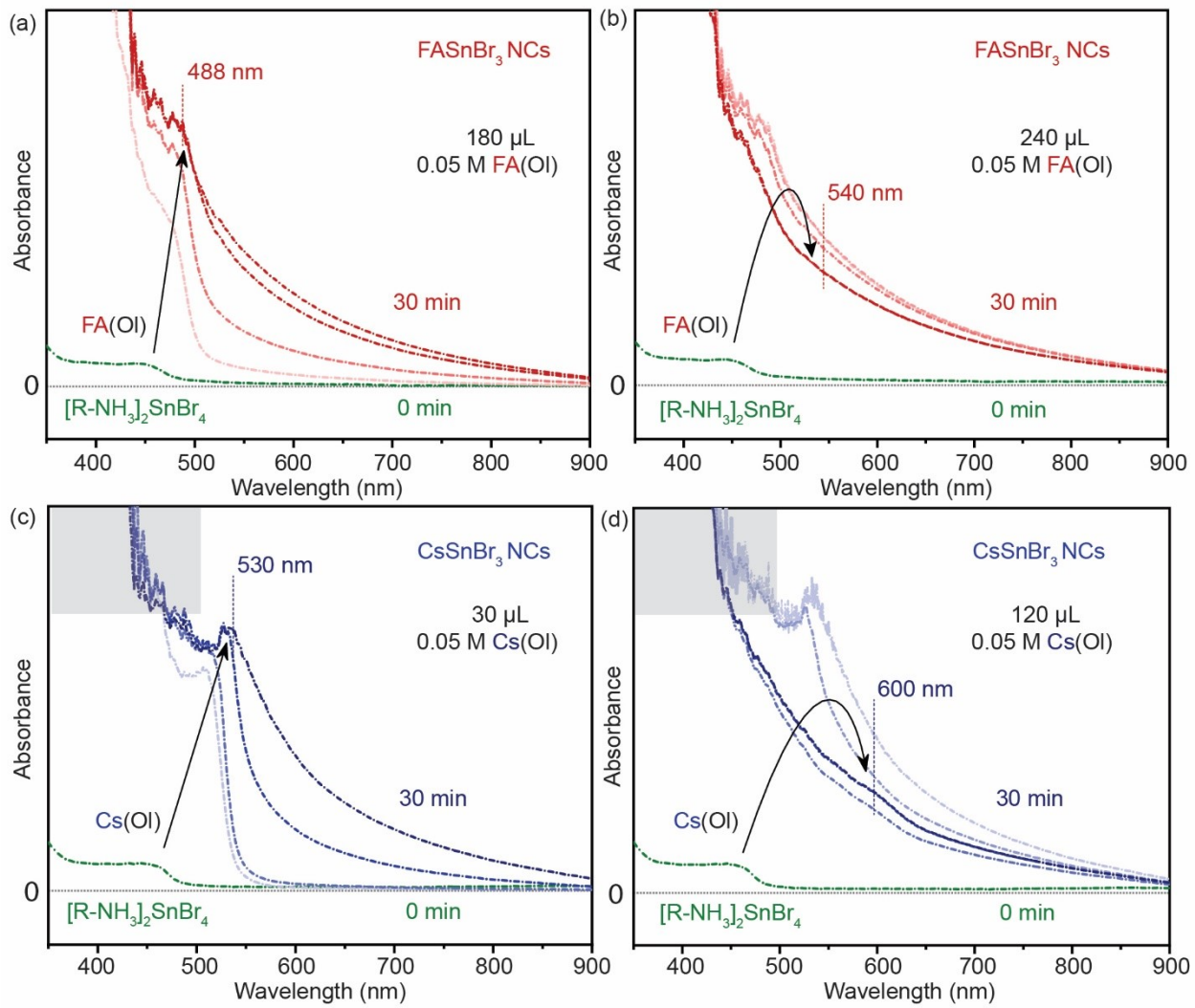

Figure S5. Concentration dependence (a) and (b) Insitu UV-Visible spectroscopy of the formation of 3D $FASnBr_3$ (red) NCswith the addition of FA(Ol) in 2D $[R\text{-}NH_3]_2SnBr_4$ RP structures over the time of 30 minutes. (c) and (d) Insitu UV-Visible spectroscopy of the formation of 3D $CsSnBr_3$ (blue) NCswith the addition of Cs(Ol) in 2D $[R\text{-}NH_3]_2SnBr_4$ RP structures over the time of 30 minutes.

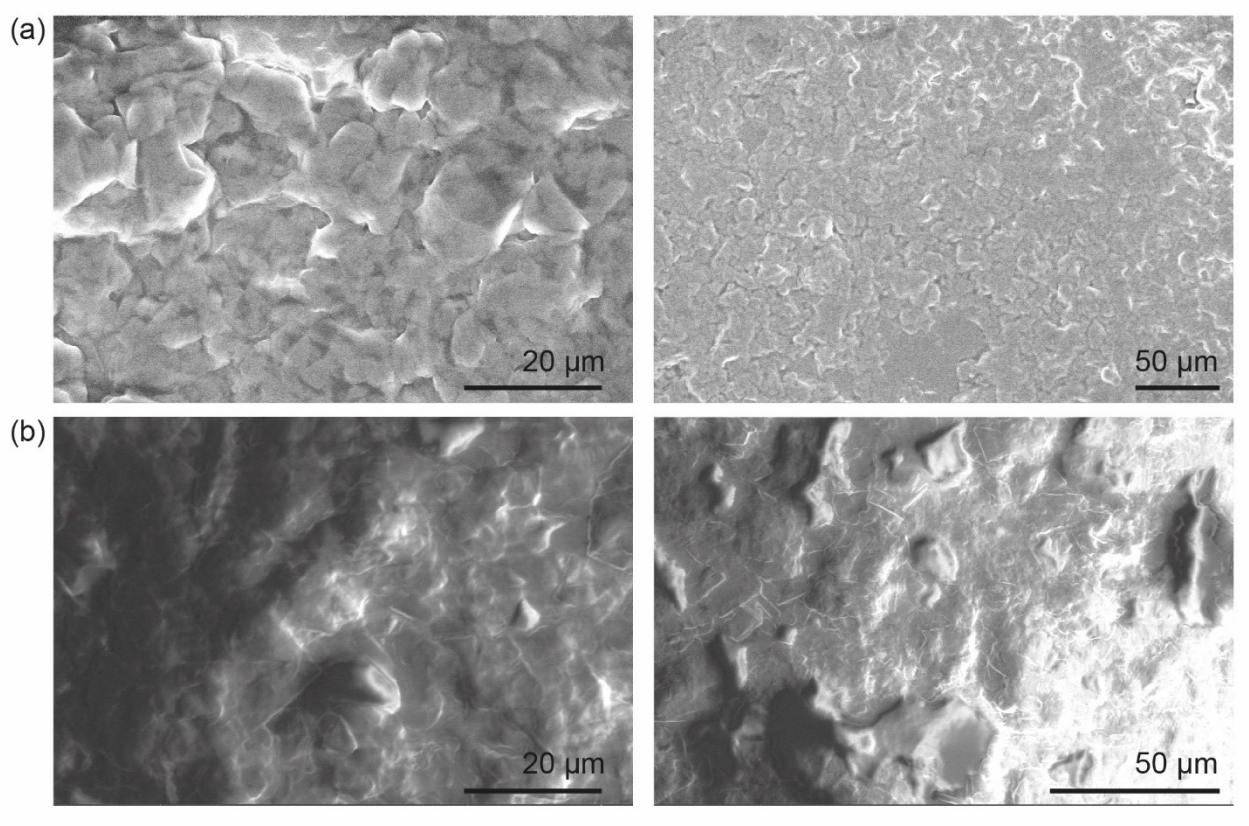

Figure S6. SEM images in the through the lens (TLD) mode. (a) Thin-film of 2D $[R\text{-}NH_3]_2SnBr_4$ RP nanostructures. (b) Thin-film of 2D $[R\text{-}NH_3]_2SnI_4$ RP nanostructures.

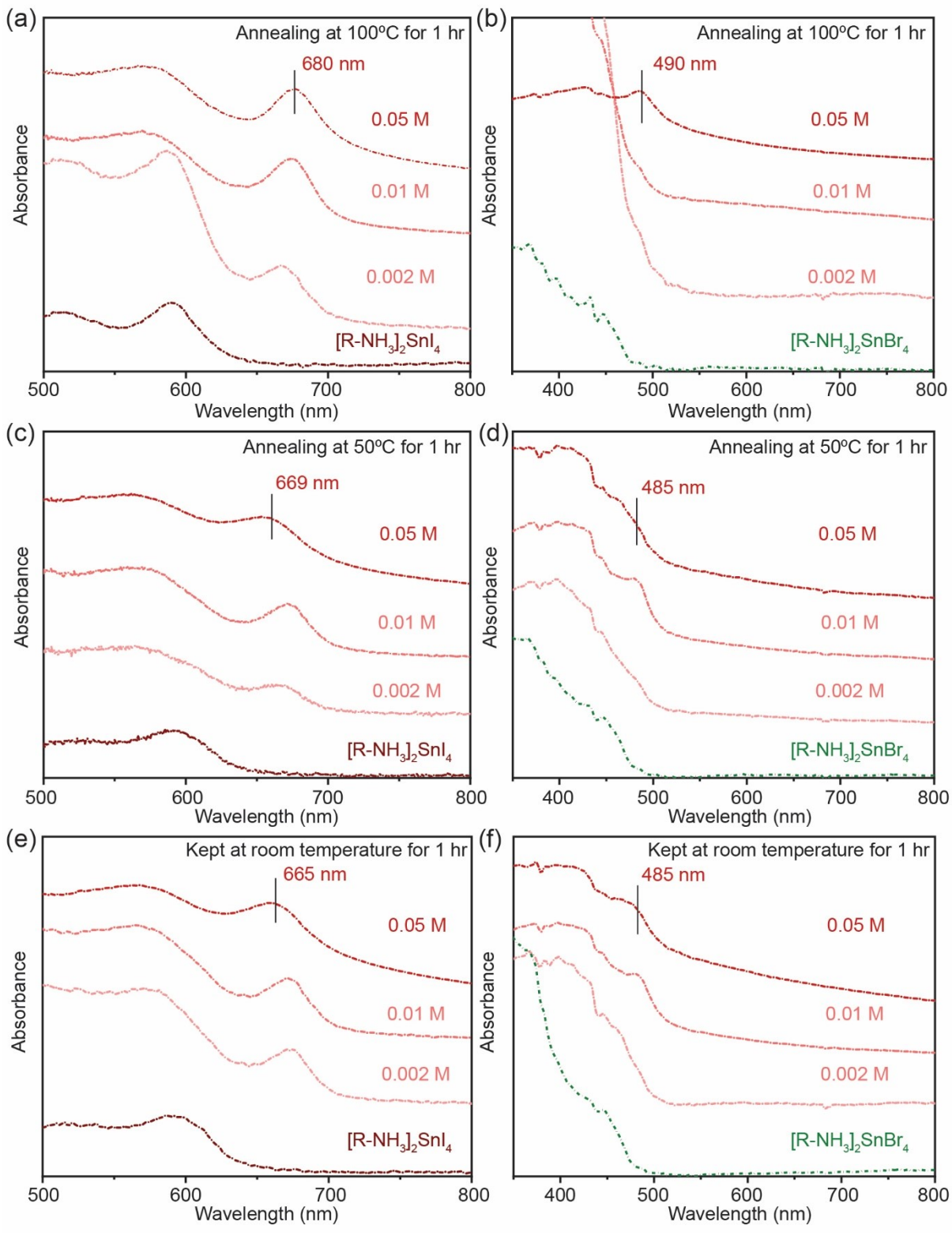

Figure S7. Annealing temperature dependence in Sn-halide perovskite thin-films with A cation addition at different concentrations. UV-Visible spectroscopy of the formation of 3D $FASnI_3$ and 3D $FASnBr_3$ nanostructures with the addition of FA(Ol) on thin-film of 2D $[R\text{-}NH_3]_2SnI_4$ RP nanostructures annealed at room temperature ((e) and (f)), 50ºC ((c) and (d)) and 100ºC ((a) and (b)) for an hour.

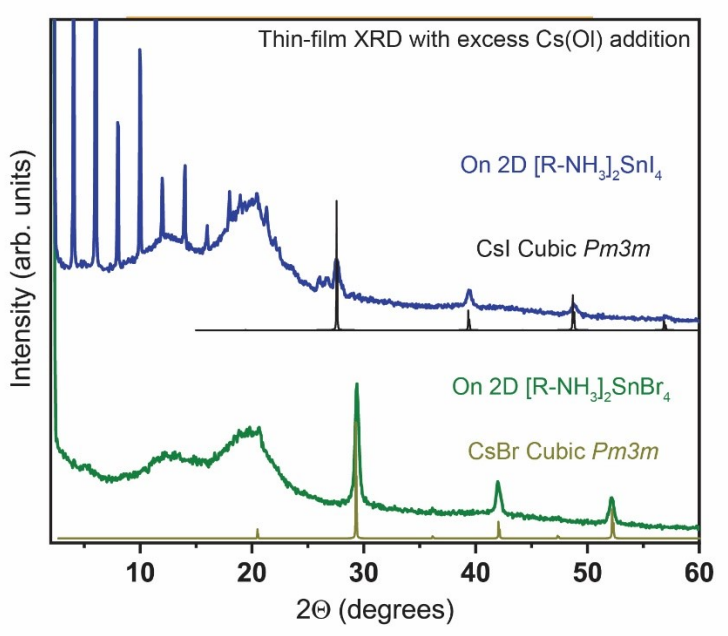

Figure S8. Powder X-ray diffraction pattern of the degraded thin-film with excess addition of Cs(Ol) solution (30 µL of 0.05 M solution) on 2D [R-NH$_3$]$_2$SnBr$_4$ (green) and 2D [R-NH$_3$]$_2$SnI$_4$ (blue). .The XRD bulk references are plotted for CsI (cubic, Pm3m) and CsBr (cubic, Pm3m).[3]

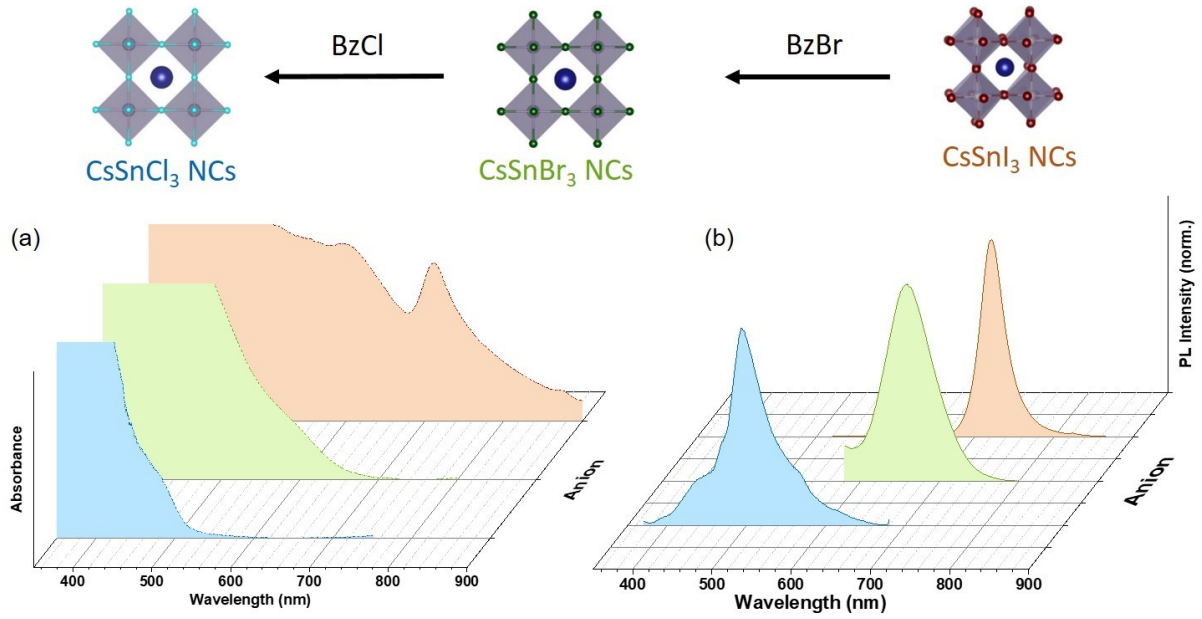

Figure S9. Anion exchange processes in solution of CsSnI$_3$ NCs. (a) UV-Visible spectroscopy of 3D CsSnBr$_3$ NCs formed via Br anion exchange of 3D CsSnI$_3$ NCs performed at room temperature which further exchanged with Cl to form 3D CsSnCl$_3$ NCs. (b) Photoluminescence spectroscopy of 3D CsSnBr$_3$ NCs formed via Br anion exchange of 3D CsSnI$_3$ NCs performed at room temperature which further exchanged with Cl to form 3D CsSnCl$_3$ NCs.

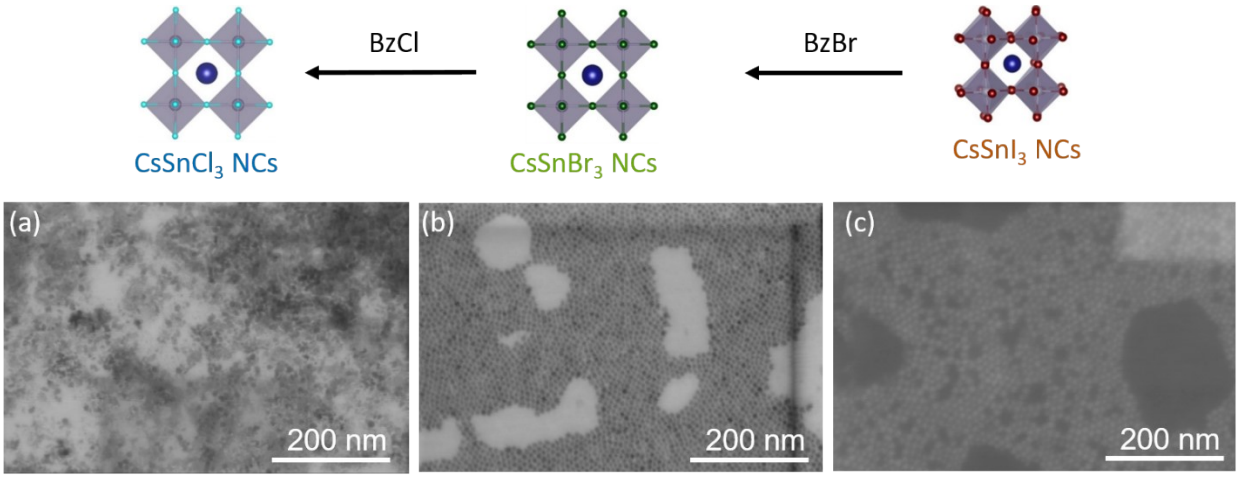

Figure S10. Anion exchange processes in solution of $CsSnI_3$ NCs. (a) and (b) show the SEM micrographs of anion-exchanged 3D $CsSnBr_3$ NCs formed via Br exchange of 3D $CsSnI_3$ NCs and 3D $CsSnCl_3$ NCs via a Cl exchange of 3D $CsSnBr_3$ NCs formed earlier respectively. (c) SEM micrographs of $CsSnI_3$ NCs before anion exchange.

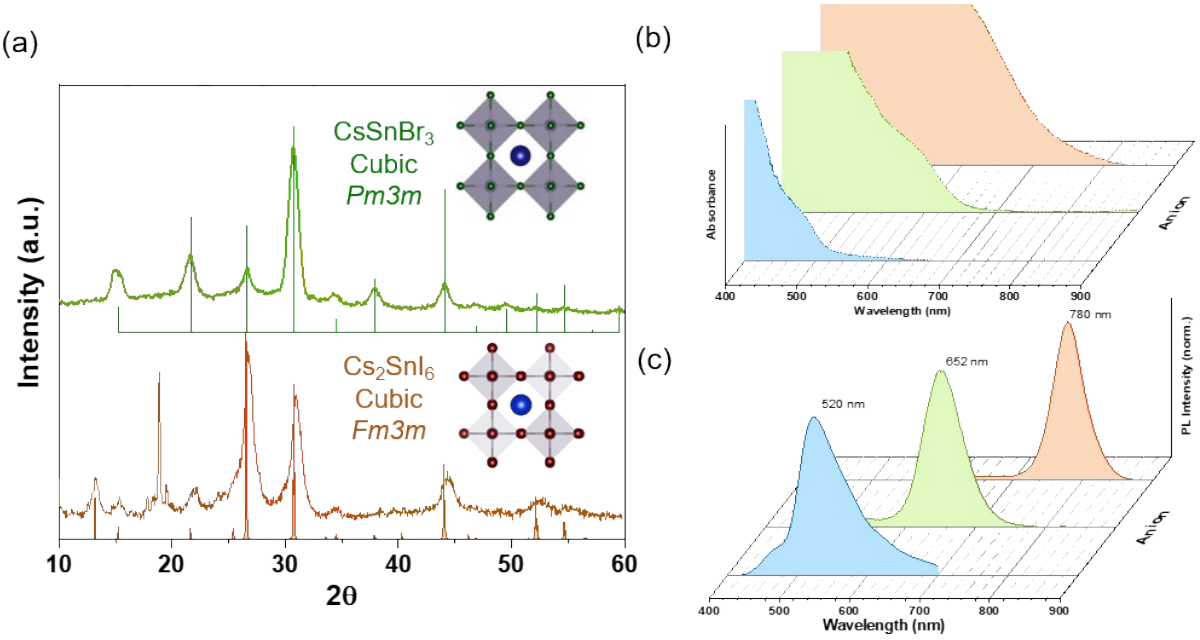

Figure S11. Anion exchange processes in solution of $CsSnBr_3$ NCs. (a) Powder X-ray diffraction pattern of the Iodide exchanged $CsSnBr_3$ NCs which yield Cs_2SnI_6 NCs with excess BzI addition. (b) and (c) UV-Visible and PL spectroscopy anion exchanged sample of $CsSnCl_3$ NCs (blue) and Cs_2SnI_6 NCs (dark orange) with starting composition $CsSnBr_3$ NCs for comparison. The XRD bulk references are plotted from $CsSnBr_3$ (cubic, Pm3m)[2] and Cs_2SnI_6 (cubic, Fm3m)[4]

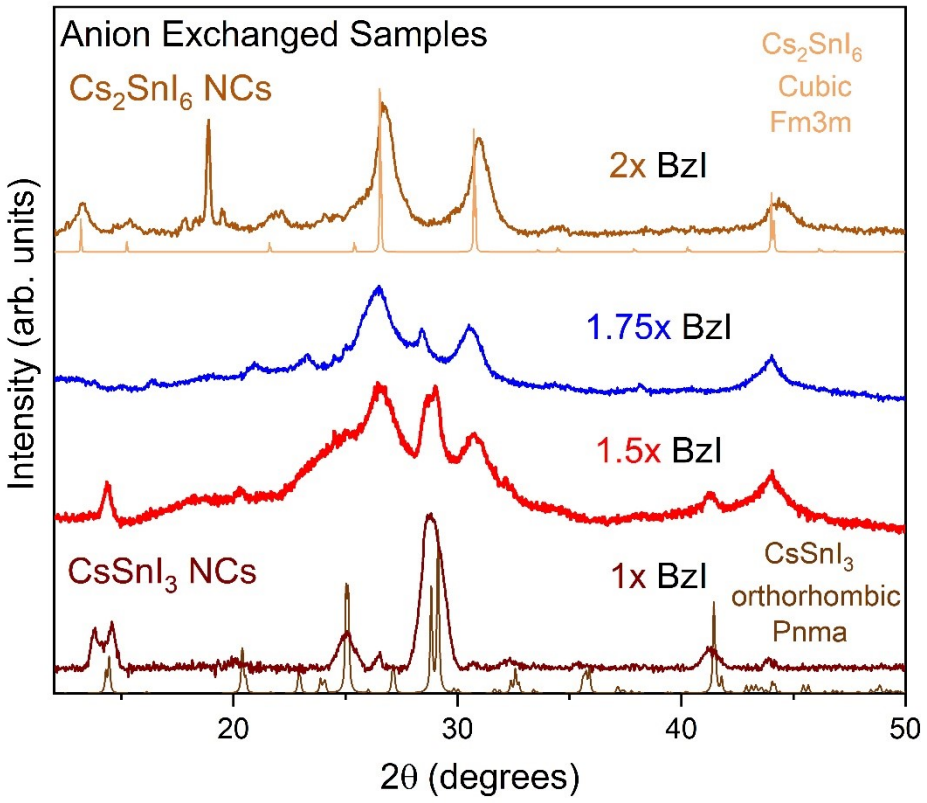

Figure S12. Evolution of powder X-ray diffraction pattern with increasing amount of BzI added for anion exchange. The XRD bulk references are plotted from $CsSnI_3$ (orthorhombic, Pnma)[5] and Cs_2SnI_6 (cubic, Fm3m)[4]

References:

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