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Supplementary Information

Fast, Tunable and Reversible Anion-Exchange in $CsPbBr_3$ Perovskite Nanocrystals with Hydrohalic Acids

V.G.Vasavi Dutt, Syed Akhil and Nimai Mishra*
Department of Chemistry, SRM University-AP, Neerukonda, Guntur(Dt)
Andhra Pradesh, India-522502
*E-mail address: nimai.m@srmap.edu.in

Materials:

Cesium Carbonate (Cs_2CO_3; 99.9%, Alfa Aesar), Octadecene (ODE; 90%, Alfa Aesar), Oleic acid (OA; Alfa Aesar), Oleylamine (OAm; Alfa Aesar), Lead (II) Bromide ($PbBr_2$; 98+%, Alfa Aesar), Hexane (99%, anhydrous), Hydrochloric acid (HCl; Finar, 36.5%), Hydrobromic acid (HBr, Emparta, 47%), Sodium chloride (NaCl; 99.5%, Finar), Potassium chloride (KCl; 99%, Finar), Ammonium chloride (NH_4Cl; 99%, Finar), Hydroxyl ammonium chloride ($HO.NH_3Cl$; 98%, Nice), Magnesium chloride hexahydrate ($MgCl_2$. $6H_2O$; 97%, Finar). All the chemicals were used without further purification.

Preparation of Cs-oleate precursor:

Cs_2CO_3 (0.2 g) was taken into 15 mL capacity vial along with ODE (7.5 mL) and OA (0.88 mL), dried for 1 hour at 120 °C under open atmospheric conditions. Cs-oleate precipitates at room temperature, hence it is pre-heated upto 100 °C before use.

Synthesis and purification of $CsPbBr_3$ perovskite nanocrystals:

In a typical synthesis, 5 mL ODE, 0.5 mL OA, 0.5 mL OAm, and 0.188 mmol (69 mg) $PbBr_2$ were taken in a 20 mL vial and dried for 1 hour at 120 °C in open atmospheric conditions. The temperature was raised to 140 °C after $PbBr_2$ was dissolved completely. To it, 0.4 mL of previously prepared Cs-oleate solution was rapid injected. Right after the injection, the colour of the solution changed from yellow to yellowish green indicating the formation of $CsPbBr_3$ NCs. The reaction was then quenched to room temperature using ice bath after 2 minutes. The crude solution was then purified via centrifugation by discarding supernatant and re-dispersing in hexane. Unlike the other synthesis reported where vacuum and nitrogen atmosphere used, here every step was carried out in open atmospheric conditions.

Anion-Exchange reactions:

Direct Salt treatment: Various inorganic salts like NaCl, KCl, NH_4Cl, $HO.NH_3Cl$, and $MgCl_2$ (Br:Cl= 1:2 molar ratio) are mixed to $CsPbBr_3$ NCs dissolved in hexane for 30 minutes to initiate the anion exchange. On the other hand, a rapid anion-exchange is observed by directly treating with hydrochloric acid (HCl) and the extent and rate of exchange is further analyzed. Similarly, HBr is also treated.

Treatment with salts in its aqueous form: In point of view of anion-exchange with HCl which is 37%, the above mentioned salts are also dissolved in water in 37% w/v. The aqueous solutions are added to $CsPbBr_3$ perovskite NCs in such a way that the Cl:Br molar ratio is 2 and mixed for 30 minutes to initiate anion-exchange reactions

Characterizations:

The UV-Vis absorbance spectra and PL spectra were collected with Tecan Multimode Reader using 96 flat plates in absorbance and fluorescence intensity scan modes respectively. The powder X-Ray Diffraction (XRD) patterns were collected for $CsPbBr_3$ perovskite NCs are drop-casted onto glass substrates by using Empyrean PANalytical X-Ray Diffractometer. Transmission Electron Microscopy (TEM) images were obtained using JEOL JEM-2100 High-Resolution Transmission Electron Microscope with 0.23 nm point resolution. Photoluminescence measurements were carried out using Time Correlated Single Photon Counting (TCSPC) accessories of Fluorolog- 3 with 370 nm excitation Laserdiode.

Figures:

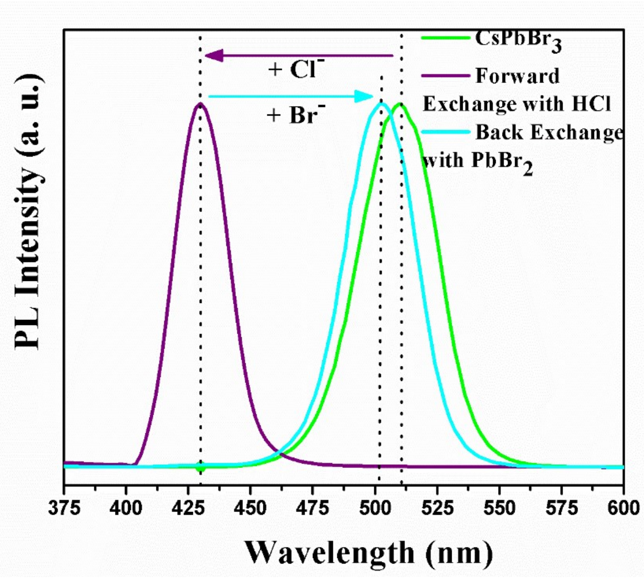

Figure S1: (a) Illustration of Cl-exchange of $CsPbBr_3$ NCs with HCl and back-exchange with $PbBr_2$ of already exchanged NCs in terms of PL emission spectra.

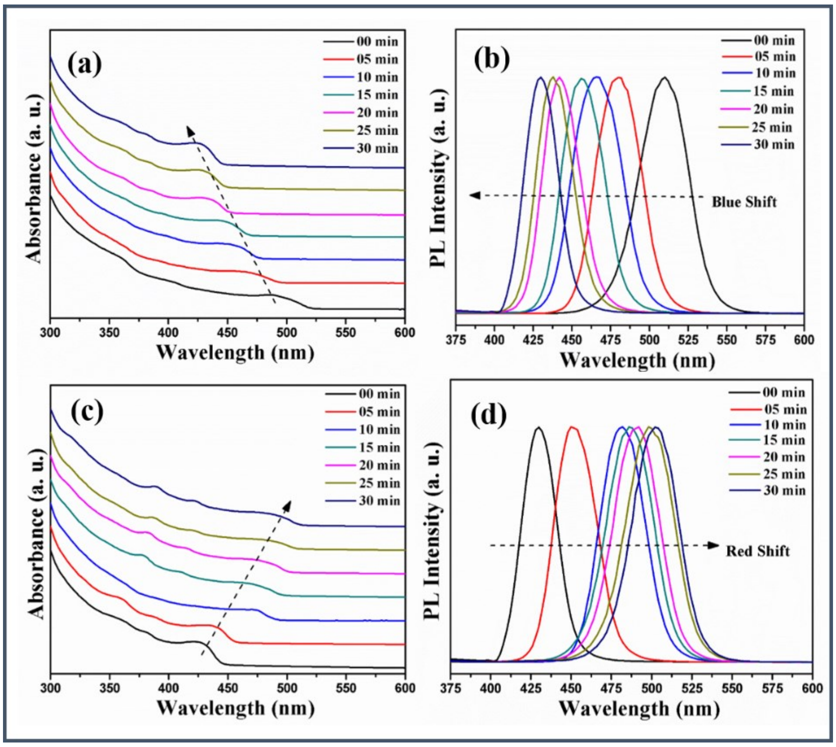

Figure S2: Representation of blue shift with respect to Cl-exchange of parental $CsPbBr_3$ NCs which is depicted in its (a) absorbance spectra and (b) PL emission spectra. Red shift is observed with respect to the back-exchange via $PbBr_2$ treatment of already Cl-exchanged $CsPbBr_3$ NCs interms of (c) absorbance and (d) PL emission spectra at regular time interval of 5 minutes.

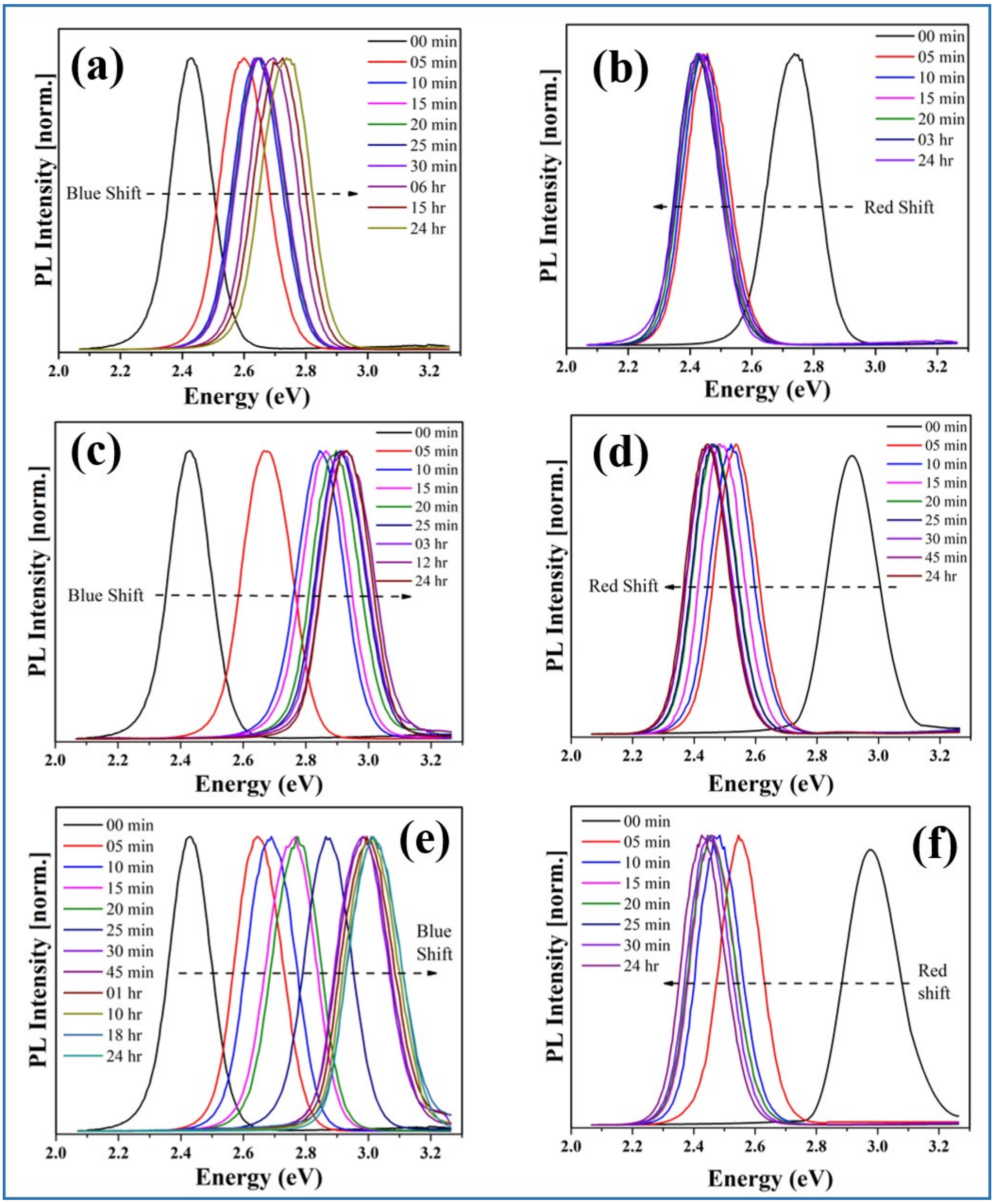

Figure S3: Graphs showing PL emission spectra of $CsPbX_3$ with HCl induced blue shift from green to blue with (a) 0.1 mmol (half the concentration), (c) 0.2 mmol (with the same concentration) and (e) 0.4 mmol (double the concentration of $PbBr_2$ used in the regular synthesis procedure). Their corresponding red shift induced with the addition of HBr are shown in (b), (d), and (f) respectively.

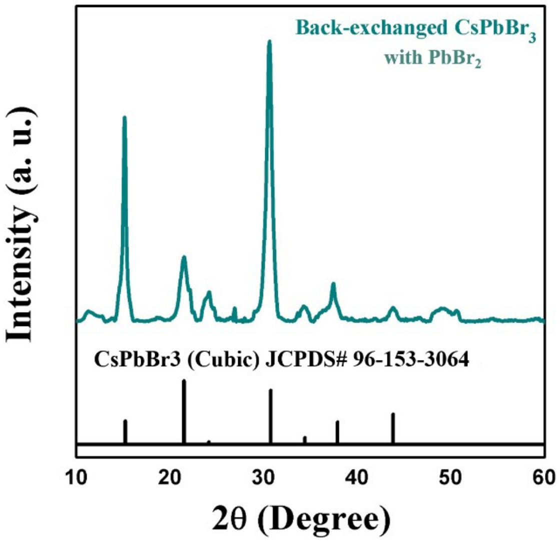

Figure S4: XRD spectra of $CsPbBr_3$ perovskite NCs (dark cyan line) obtained by back-exchanging Cl-exchanged $CsPbX_3$ NCs with $PbBr_2$ and pattern lines showing $CsPbBr_3$ orthorhombic phase (black line) from standard database.

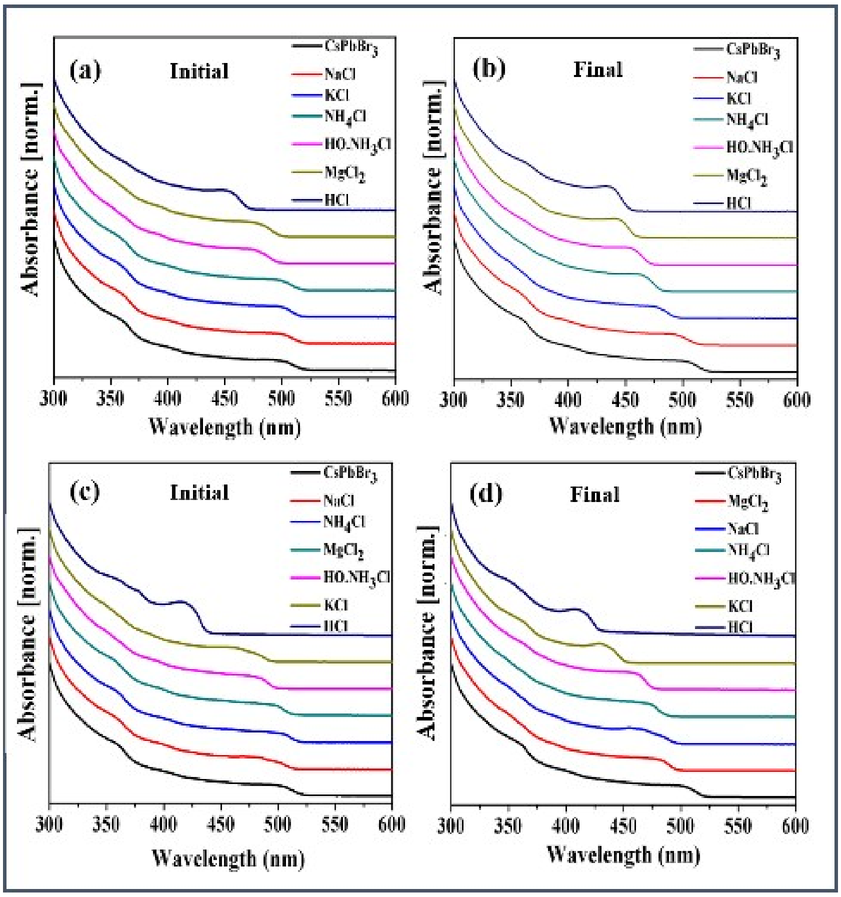

Figure S5: Absorbance spectra of $CsPbX_3$ NCs; Evolution of Cl-exchange from (a) 0 hours to (b) 72 hours with direct treatment of Cl-precursors NaCl, KCl, NH_4Cl, $HO.NH_4Cl$, $MgCl_2$ and

HCl. Evolution of Cl-exchange from (c) 0 hours to (b) 30 hours with treatment of Cl-precursors in their aqueous form.

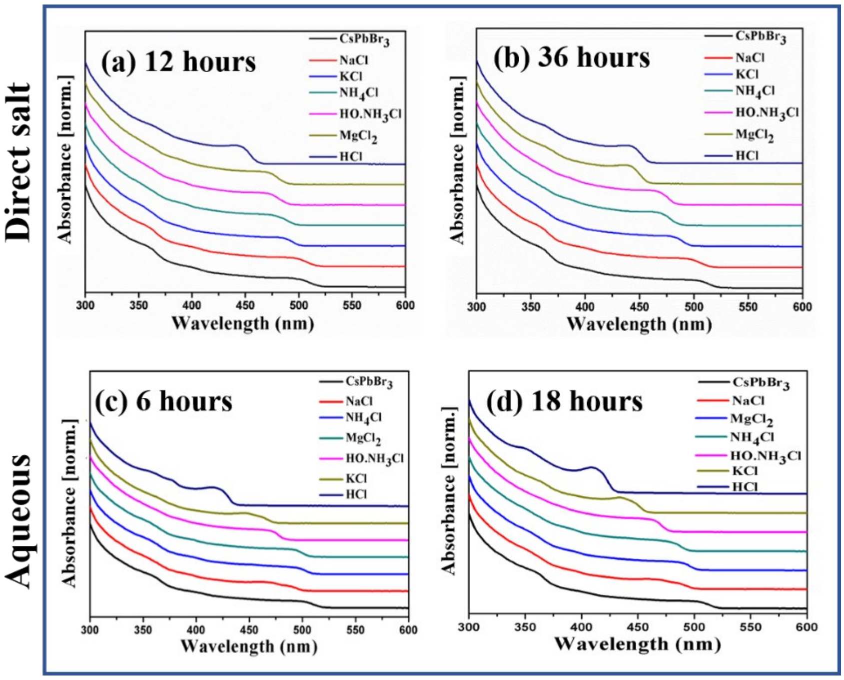

Figure S6: Absorbance spectra of CsPbX$_3$ NCs; Evolution of Cl-exchange at (a) 12 hours and (b) 36 hours with direct treatment of Cl-precursors NaCl, KCl, NH$_4$Cl, HO.NH$_4$Cl, MgCl$_2$ and HCl. Evolution of Cl-exchange at (c) 6 hours and (b) 18 hours with treatment of Cl-precursors in their aqueous form.

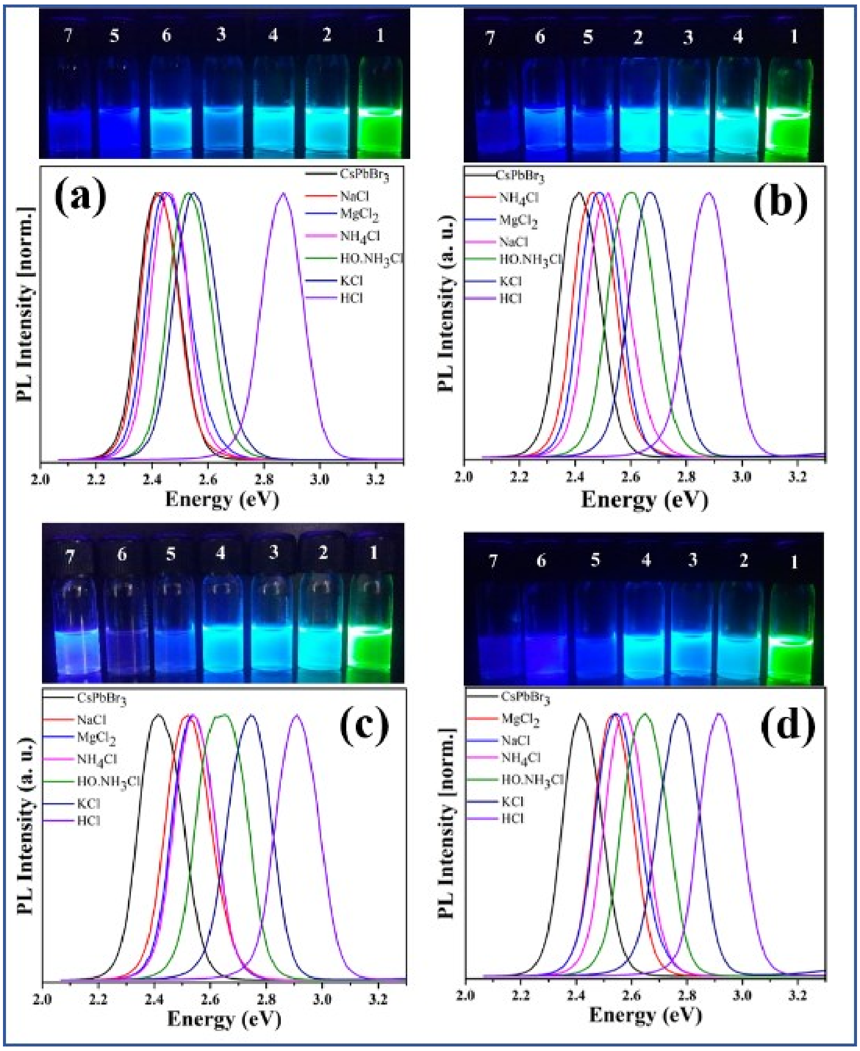

Figure S7: PL spectra of $CsPbX_3$ perovskite NCs obtained via treatment with different Cl-precursors in their aqueous form; measurements taken after (a) 30 minutes, (b) 6 hours, (c) 18 hours, and (d) 30 hours along with their respective photographs showing NCs (labelled 1: $CsPbBr_3$, 2: NaCl, 3: $MgCl_2$, 4: NH_4Cl, 5: $HO.NH_3Cl$, 6: KCl, and 7: HCl) under irradiation of UV light (λ_{ex} = 365 nm).