

Supporting Information for

Fast anion-exchange in highly luminescent nanocrystals of cesium lead halide perovskites (CsPbX_3 , $\text{X}=\text{Cl}$, Br , I)

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Materials and Synthesis

Materials and chemicals. Cesium carbonate (Cs_2CO_3 , Aldrich, 99.9%), oleic acid (OA, Sigma-Aldrich, 90%), 1-octadecene (ODE, Sigma-Aldrich, 90%), ethanol (EtOH, Aldrich), oleylamine (OAm, Acros Organics, 80-90%), $\text{HCl} \geq 37\%$ (Aldrich), HBr 48% (Aldrich), HI 57% (Aldrich), lead chloride (PbCl_2 , ABCR, 99.999%), lead bromide (PbBr_2 , ABCR, 98%), lead iodide (PbI_2 , ABCR, 99.999%), n-trioctylphosphine (TOP, Strem, 97%), methylmagnesium chloride (MeMgCl , 3M in THF, Aldrich), methylmagnesium bromide (MeMgBr , 3M in ether, Strem), methylmagnesium iodide (MeMgI , 33% in ethylether, ca. 2 mol/L, TCI), toluene (Fischer Scientific, HPLC grade), hexane (Sigma-Aldrich, $\geq 95\%$).

Preparation of Cs-oleate: Cs_2CO_3 (0.814 g, Aldrich, 99.9%), OA (2.5 mL, Sigma-Aldrich, 90%) and ODE (40 mL, Sigma-Aldrich, 90%) were added into a 100 mL 3-neck flask, dried for 1h at 120 °C and then heated under N_2 to 150 °C until all Cs_2CO_3 reacted with OA. Since Cs-oleate precipitates out of ODE at room-temperature, it must be preheated to 100 °C before injection.

Preparation of oleylammonium halides (OAmX): Ethanol (100 mL, Aldrich) and OAm (0.038 mol, Acros Organics 80-90%) were combined in a 250 mL 2-neck flask and vigorously stirred. The reaction mixture was cooled in an ice-water bath and HX (0.076 mol, $\text{HCl} \geq 37\%$, Aldrich; HBr 48%, Aldrich; HI 57%, Aldrich) was added. The reaction mixture was left to react overnight under N_2 flow. Then the solvent was evaporated under vacuum and the obtained product was purified by rinsing multiple times with diethylether. The product was left under vacuum overnight in a vacuum oven at 80 °C resulting in a white powder for OAmCl and OAmBr and a dark orange waxy-powder for OAmI.

Synthesis of CsPbX_3 NCs: ODE (5 mL) and 0.188 mmol of PbX_2 (PbCl_2 – 0.052 g, ABCR, 99.999%; PbBr_2 – 0.069 g, ABCR, 98%; PbI_2 – 0.086 g, ABCR, 99.999%) were loaded into a 25 mL 3-neck flask and dried under vacuum at 120 °C for 1h. Dried OA (1.5 mL for PbCl_2 , 0.5 mL for PbBr_2 and 0.7 mL for PbI_2) and OAm (1.5 mL for PbCl_2 , 0.5 mL for PbBr_2 and 0.7 mL for PbI_2) were injected at 120 °C under N_2 flow. After complete solubilisation of a PbX_2 salt, the temperature was raised to 180-190 °C and Cs-oleate solution (0.4 mL of stock solution prepared as described above) was swiftly injected and 1 minute later the reaction mixture was cooled down by a water bath. For obtaining CsPbCl_3 NCs, a higher temperature of 170 °C and 1 mL of n-Trioctylphosphine (TOP, Strem, 97%) are necessary to solubilize PbCl_2 . After reaction, the aggregated NCs were separated by centrifugation. After centrifugation, the supernatant was discarded and the precipitate was redispersed in dried toluene for further use in anion-exchange reactions.

Anion-exchange reactions (Table S1). The anion exchange reactions were conducted using a Schlenk line. PbBr_2 , PbI_2 and OAmX as anion sources were mixed with ODE (5 mL) in a 25 mL 3-neck flask and kept under vacuum at 120 °C for 10 minutes. Dried OA and OAm (0.2 mL each) were injected at 120 °C under N_2 flow. After complete solubilisation of the anion source, the temperature was lowered to 40 °C and CsPbX_3 NCs (20-25 mg) dispersed in toluene were injected to initiate the anion-exchange. When using PbCl_2 as the anion source, 1 mL TOP was

added and it was necessary to raise the temperature to 150-170 °C for short time in order to solubilize PbCl₂. When using MeMgX as the anion source, it should be injected after the solvent and ligands are dried, just prior to addition of NCs. After reaction, the NCs were isolated by centrifugation. The supernatant was discarded and the precipitate was dispersed in hexane (0.3 mL) and centrifuged again. The supernatant was mixed with toluene (0.9 mL). NCs were precipitated by adding 0.3 mL acetonitrile, followed by centrifuging. The obtained precipitated NCs were redispersed in toluene for further analysis.

Characterization Methods

Absorbance: UV-VIS absorption spectra were collected using a Jasco V670 spectrometer in transmission mode.

Photoluminescence (PL) and absolute quantum yield (QY) measurements. Fluorolog iHR 320 Horiba Jobin Yvon spectrofluorimeter equipped with a PMT detector was used to acquire steady-state PL spectra from solutions and films. PL QYs were estimated according to standard procedure using appropriate dye molecules for blue, green and red spectral regions (coumarine 343, fluorescein, and rhodamine 6G).¹

In-situ photoluminescence measurements were performed with excitation light from a CW laser ($\lambda=405$ nm, P= 300 mW) delivered through one branch of a Y-shaped fiber optic bundle or UV-LED ($\lambda=365$ nm, power of 3 W) mounted to the flask during the anion-exchange. The emission light was collected with the second branch of the fiber optic bundle. PL spectra were recorded with a compact CCD spectrometer (LR1, Aseq-Instruments) or Acton SP-2350 spectrometer equipped with Si CCD Array (Thorlabs, LC100).

Powder X-ray diffraction (XRD) patterns were collected with a STOE STADI P powder diffractometer, operating in transmission mode. A germanium monochromator, Cu K α_1 irradiation and Dectris Mythen silicon strip detector were used.

Transmission electron microscopy (TEM) images were recorded using a JEOL JEM-2200FS microscope operated at 200 kV.

Energy dispersive X-ray (EDX) Elemental analysis was performed with two scanning electron microscopes (Zeiss Gemini 1530 and Hitachi, S-4800).

Rutherford backscattering spectrometry (RBS) was performed at the ETH Laboratory of Ion Beam Physics. Measurements were conducted using a 2 MeV 4He beam and a silicon PIN diode detector under angle of 168°. The collected RBS data was analyzed using simulations by the RUMP code.²

Supporting References:

- (1) Grabolle, M. *et al.* Determination of the Fluorescence Quantum Yield of Quantum Dots: Suitable Procedures and Achievable Uncertainties. *Anal. Chem.* **2009**, *81*, 6285-6294.
- (2) Doolittle, L. R. A semiautomatic algorithm for Rutherford backscattering analysis. *Nucl. Instr. and Meth. B* **1986**, *15*, 227-231

Table S1. All Cl \leftrightarrow Br and Br \leftrightarrow I anion exchange reactions were conducted in dry ODE (5 mL) at 40 °C. 1 mL TOP was added in all experiments where PbCl₂ was used as halide source. The evolution of the PL peak maxima as a result of anion exchange has been completed within several seconds to several minutes (faster for Cl/Br systems).

starting NCs [mmol] in 1 mL toluene	halide precursor [mmol]	resulting PL peak [nm]	OA [mL]	OAm [mL]
CsPbCl ₃ – 0.047	PbBr ₂ – 0.019	470	0.1	0.1
CsPbCl ₃ – 0.098	PbBr ₂ – 0.098	494	0.4	0.4
CsPbCl ₃ – 0.035	OAmBr – 0.035	467	0.2	0.2
CsPbCl ₃ – 0.05	OAmBr -0.15	508	0.6	0.6
CsPbCl ₃ – 0.058	MeMgBr – 0.058	467	0.2	0.2
CsPbCl ₃ – 0.055	MeMgBr -0.165	508	0.4	0.4
CsPbBr ₃ – 0.044	PbCl ₂ – 0.025	468	0.3	0.3
CsPbBr ₃ – 0.044	PbCl ₂ – 0.132	410	0.8	0.8
CsPbBr ₃ – 0.05	PbCl ₂ – 0.05	432	0.7	0.7
CsPbBr ₃ – 0.025	OAmCl – 0.025	484	0.2	0.2
CsPbBr ₃ – 0.034	OAmCl – 0.062	456	0.3	0.3
CsPbBr ₃ – 0.034	OAmCl – 0.1	404	0.4	0.4
CsPbBr ₃ – 0.046	MeMgCl – 0.023	465	0.1	0.1
CsPbBr ₃ – 0.046	MeMgCl – 0.046	443	0.2	0.2
CsPbBr ₃ – 0.046	MeMgCl – 0.139	419	0.4	0.4
CsPbBr ₃ – 0.048	PbI ₂ – 0.014	550	0.2	0.2
CsPbBr ₃ – 0.056	PbI ₂ – 0.022	584	0.2	0.2
CsPbBr ₃ – 0.043	PbI ₂ – 0.025	604	0.2	0.2
CsPbBr ₃ – 0.05	PbI ₂ – 0.038	632	0.2	0.2
CsPbBr ₃ – 0.06	PbI ₂ – 0.06	650	0.4	0.4
CsPbBr ₃ – 0.037	PbI ₂ – 0.112	680	0.6	0.6
CsPbBr ₃ – 0.025	OAmI – 0.025	610	0.1	0.1
CsPbBr ₃ – 0.034	OAmI – 0.1	675	0.3	0.3
CsPbBr ₃ – 0.027	MeMgI – 0.027	570	0.1	0.1
CsPbBr ₃ – 0.031	MeMgI – 0.077	628	0.2	0.2
CsPbBr ₃ – 0.035	MeMgI – 0.122	688	0.3	0.3
CsPbI ₃ – 0.058	PbBr ₂ – 0.017	658	0.1	0.1
CsPbI ₃ – 0.031	PbBr ₂ – 0.016	636	0.1	0.1
CsPbI ₃ – 0.049	PbBr ₂ – 0.049	578	0.2	0.2
CsPbI ₃ – 0.048	PbBr ₂ – 0.064	548	0.3	0.3
CsPbI ₃ – 0.033	OAmBr – 0.033	628	0.1	0.1
CsPbI ₃ – 0.034	OAmBr – 0.069	545	0.2	0.2
CsPbI ₃ – 0.035	OAmBr – 0.105	516	0.2	0.2
CsPbI ₃ – 0.043	MeMgBr – 0.043	628	0.1	0.1
CsPbI ₃ – 0.045	MeMgBr – 0.090	543	0.2	0.2
CsPbI ₃ – 0.040	MeMgBr – 0.120	508	0.3	0.3

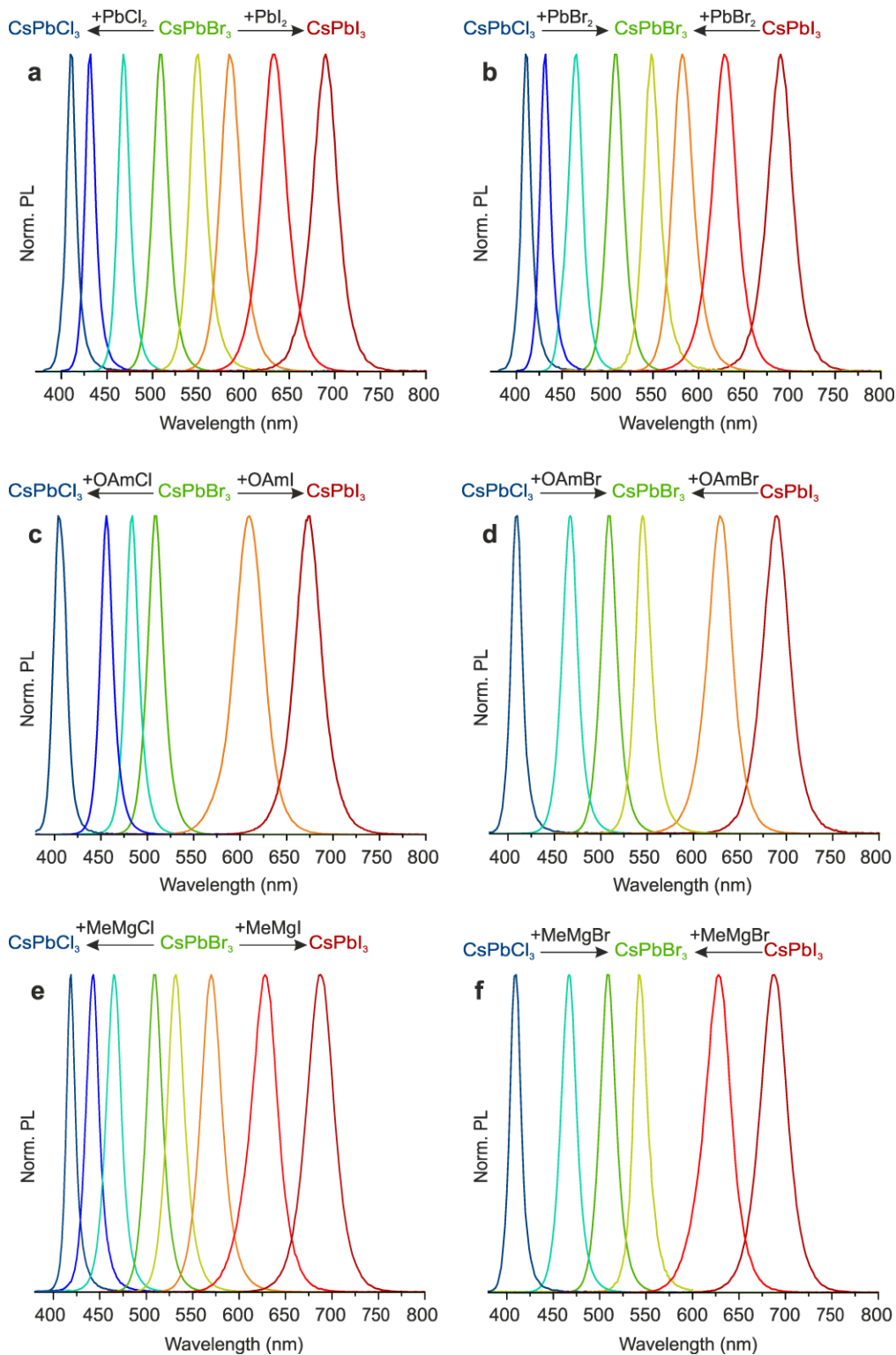


Figure S1. PL spectra for anion-exchange reactions in CsPbX₃ NCs using various halide sources. Gradual change in the PL peak wavelengths reflect the ease of halide mixing within the perovskite lattice for Cl/Br and Br/I systems.

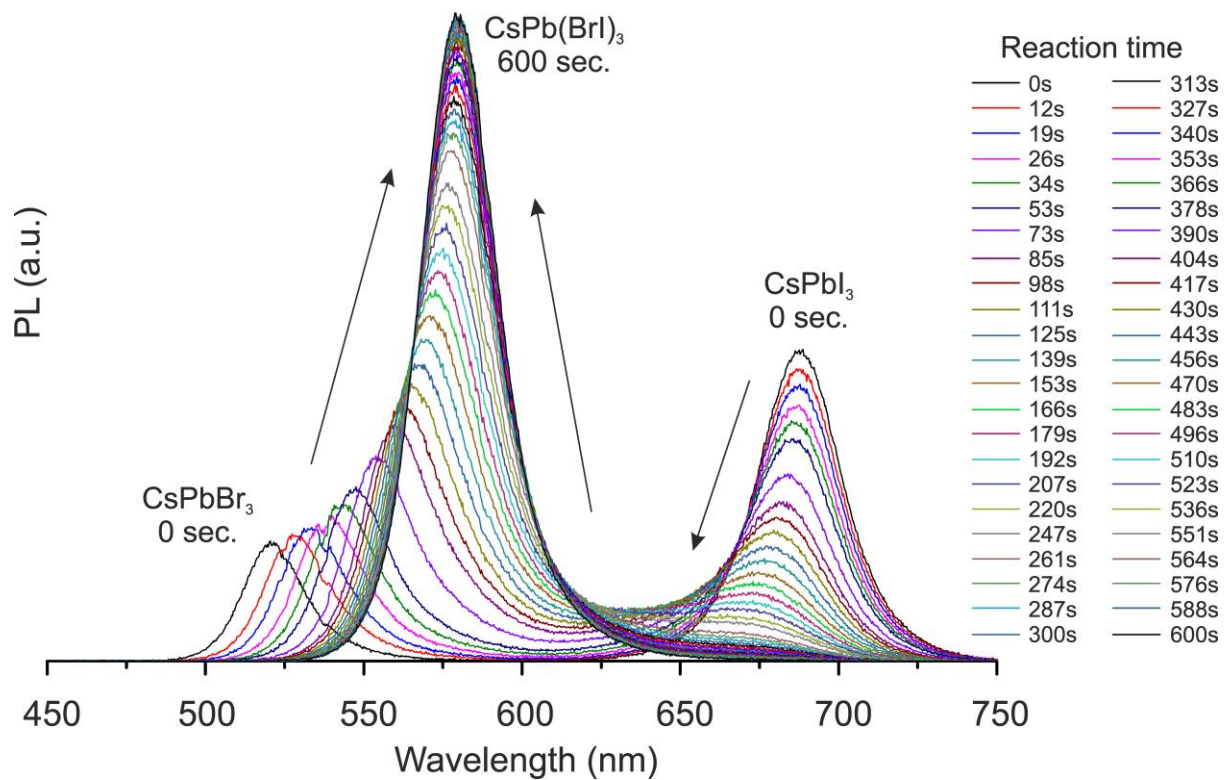


Figure S2. *In-situ* PL study of the anion-exchange between CsPbBr₃ and CsPbI₃ NCs in toluene.