## Supporting Information

# Irreversibility in Anion Exchange Between Cesium Lead Bromide and Iodide Nanocrystals Imaged by Single-Particle Fluorescence

Dong Wang<sup>1</sup>, Dongyan Zhang<sup>1</sup>, Bryce Sadtler<sup>1,2</sup>\*

<sup>1</sup>Department of Chemistry, Washington University, St. Louis, Missouri 63130

<sup>2</sup>Institute of Materials Science & Engineering, Washington University, St. Louis, Missouri 63130

\* To whom correspondence should be addressed. Email: sadtler@wustl.edu

#### **Supporting Methods**

*X-ray diffraction (XRD):* XRD patterns were measured in air with a Bruker D8 Advance x-ray diffractometer (wavelength = 0.15418 nm using Cu K $\alpha$  radiation, step size = 0.0195 in 2 $\theta$ , scan rate = 0.5 s/step). To prepare samples of the as-synthesized CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> nanocrystals (NCs) for characterization by XRD, the colloidal solutions were first concentrated by centrifuging 2 mL of the stock solution at 12000 rpm for 8 mins, removing the supernatant, and then dispersing the precipitate in 100 µL of hexane. Next, the concentrated NC solution was drop cast onto a zero-background, silicon diffraction plate in a nitrogen-filled glovebox and dried at room temperature. To minimize the exposure of the perovskite NCs to air and moisture, the XRD substrate was placed in a centrifuge tube filled with nitrogen and sealed with parafilm in a glovebox to transport the sample from our laboratory to the diffractometer.

To prepare samples of CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> NCs that had undergone anion exchange for characterization by XRD, we followed the procedure reported by Kovalenko and coworkers.<sup>1</sup> First, 60 mg of PbI<sub>2</sub> (or PbBr<sub>2</sub>), 0.2 mL of oleic acid, 0.2 mL of oleylamine, and 5 mL of ODE were added to a round-bottom flask, which was then connected to a Schlenk line. The mixture was heated to 100°C under vacuum. After the lead halide powder was completely dissolved, the flask was switched to an argon environment and allowed to cool to 40°C. Next, 1 mL of the CsPbBr<sub>3</sub> (or CsPbI<sub>3</sub>) NC stock solution was injected into the flask. After 5 mins of anion exchange, the solution in the flask was collected and centrifuged at 12000 rpm for 8 mins. The precipitate was dispersed in 1 mL of hexane and stored in a glovebox. Before XRD characterization, the solution of anion-exchanged NCs was centrifuged at 12000 rpm for 8 mins. The supernatant was removed, and the precipitate was dispersed in 100  $\mu$ L of hexane. The concentrated solution was then drop cast onto a zero-background, silicon diffraction plate and allowed to dry in a glovebox at room temperature. The sample of CsPbBr<sub>3</sub> NCs converted to iodide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> using PbI<sub>2</sub> was also used to study anion exchange back to CsPbBr<sub>3</sub> using single-particle fluorescence.

Structure files from the ICSD were used to simulate the XRD patterns for the perovskite orthorhombic  $\gamma$  phase of CsPbBr<sub>3</sub> (ICSD collection code # 243735), the perovskite cubic  $\alpha$  phase of CsPbI<sub>3</sub> (collection code # 161481), the perovskite orthorhombic  $\gamma$  phase of CsPbI<sub>3</sub> (collection code # 161481), the perovskite orthorhombic  $\delta$  phase of CsPbI<sub>3</sub> (collection code # 161480). The .cif file for each structure was used to simulate its XRD pattern using the CrystalDiffract software program. The simulated patterns used an x-ray wavelength of 0.1541 nm, a Gaussian peak profile, a peak width of 0.1°, and a particle size of 1.0 µm.

*Transmission electron microscopy (TEM):* TEM images were acquired by using a JEOL 2100F TEM operated at an acceleration voltage of 200 kV. The preparation of all TEM samples were performed in a glovebox. The CsPbI<sub>3</sub> and CsPbBr<sub>3</sub> NC stock solutions were first diluted by a factor of 10. Next, 20  $\mu$ L of the diluted solution was drop cast onto a copper TEM grid and dried at room temperature. To prepare samples of CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> NCs that had undergone anion exchange for characterization by TEM, 100  $\mu$ L of either a TBAB or TBAI solution (2 mg/mL in tert-butanol) was drop cast onto a TEM grid in which CsPbI<sub>3</sub> or CsPbBr<sub>3</sub> NCs had been deposited, respectively. The TEM grid was then washed with 100  $\mu$ L of anhydrous hexane after 10 s and dried at room temperature. To minimize the exposure of the perovskite NCs to air and moisture, the prepared TEM grids were transported to the microscope in a nitrogen-filled plastic box sealed with parafilm.

*Flow cell preparation:* In the first step, we prepared the samples for single-particle fluorescence imaging by spin-coating diluted solutions of the CsPbX<sub>3</sub> (X = Br or I) NCs onto microscope coverslips (Fisher brand, 12-544-E). The CsPbBr<sub>3</sub> or CsPbI<sub>3</sub> NC stock solution was first diluted by a factor of 500 by adding 20  $\mu$ L of the stock solution to 10 mL of anhydrous hexane. The diluted solution was then spin-coated onto a coverslip by using a home-made spin-coater in a glovebox. To prepare bromide-rich CsPbBr<sub>3-x</sub>I<sub>3</sub> NCs produced by anion exchange of CsPbI<sub>3</sub>, the CsPbI<sub>3</sub> NCs were first deposited onto a coverslip as described above. Then, the coverslip was tilted, and 1 mL of a TBAB solution (10  $\mu$ g/mL in tert-butanol) was slowly dropped onto the coverslip. The coverslip was then washed with 1 mL of anhydrous hexane to remove excess TBAB. The preparation of iodide-rich CsPbBr<sub>3-x</sub>I<sub>3</sub> NCs produced by anion exchange of CsPbBr<sub>3</sub> NCs with PbI<sub>2</sub> is described above under XRD characterization. The solution of CsPbBr<sub>3-x</sub>I<sub>3</sub> NCs after anion exchange was diluted by a factor of 500, and the diluted solution was spin-coated onto a coverslip in the glovebox.

In the next step, the coverslips with deposited CsPbX<sub>3</sub> NCs were assembled into home-made flow cells. A detailed procedure for fabricating the flow cells can be found in our previous report.<sup>2</sup> In brief, the bottom of the flow cell was the coverslip with deposited NCs, and the top was a glass slide with two drilled holes. The two slides were affixed with double-sided tape sandwiched in between them to form a flow channel, and the perimeter of the slides was sealed with epoxy. Two plastic tubes were attached to the drilled holes in order to flow solution in and out. The assembly of flow cells was performed in a glovebox.

*Image analysis:* Intensity vs. time trajectories for individual CsPbX<sub>3</sub> NCs were extracted from the recorded fluorescence videos as described in our previous work.<sup>2-3</sup> The brightness and contrast of each video was auto-adjusted by using look-up tables (LUTs) in the Nikon-NIS Elements AR software (version 4.50.00) based on the intensity distribution of all NCs in the field-of-view. This non-destructive method of brightness modification provides the best visibility of NCs in each video (see videos provided as **Supporting Information** for examples). We next excluded clusters of particles (i.e., multiple NCs emitting within a diffraction-limited spot) by analyzing the distribution of intensity values. Intensity trajectories exhibiting fluorescence intermittency with clear 'on' and 'off' states are indicative of single particles (see **Figure S10**) based on previous reports.<sup>4-8</sup> However, in a cluster of particles the intensity trajectories of multiple NCs overlap, resulting in trajectories with multiple 'on' states and without a clear 'off' state (**Figure S11**). Clusters of particles were excluded from the subsequent analysis.

We measured the 'waiting time' and 'switching time' for hundreds of single NCs at each concentration of TBAB or TBAI to quantify differences in the kinetics of anion exchange in different directions. For the transformations of as-synthesized CsPbBr<sub>3</sub> NCs to CsPbI<sub>3</sub> and assynthesized CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub>, we watched the NCs 'turn on' during anion exchange. For the back conversion of CsPbBr<sub>3-x</sub>I<sub>3</sub> NCs that had already undergone exchange prior to imaging, we watched the NCs 'turn off' under the microscope. In these cases, the intensity trajectories were reversed along the x-axis (i.e., time) so that all trajectories could be analyzed in the same way. The waiting time for each NC to 'turn on' was defined by time point where the mean intensity (averaged over 10 data points in a 200-ms window) in a trajectory reached a threshold value, *V*:

$$V = m + 5\sigma$$

where *m* is the mean intensity (averaged over 100 data points in a 2-s window) for the trajectory before the reaction starts, and  $\sigma$  is the standard deviation for a Gaussian fit to the intensity fluctuations in this region. To compare the waiting times using different concentrations of TBAB or TBAI, the waiting time for the first NC to transform was defined as 0 s, and the waiting times for all other NCs in the same field-of-view were determined relative to the first one. Each distribution of relative waiting times was plotted as a histogram, and the mean value and full width at half maximum (FWHM) were extracted from a Gaussian fit (see Figures S12 – S15).

The switching time for each NC was determined by fitting its intensity trajectory to a sigmoidal function:

$$I(t) = I_{initial} + \frac{(I_{final} - I_{initial})}{1 + e^{(b-t/\tau)}}$$

where  $I_{initial}$  and  $I_{final}$  are mean values of the intensity (averaged over 100 data points in a 2-s window) at the start and near the maximum of a single-particle trajectory, respectively, and  $\tau$  is the switching time. The values of *b* and  $\tau$  were extracted from fitting the intensity trajectory using

MATLAB. Due to the fluorescence intermittency of the NCs, some trajectories could not easily be fit to a sigmoidal function. The goodness of the fit was evaluated by the correlation coefficient between the fitted curve and the original trajectory. Only trajectories with a correlation coefficient above 0.8 were used in subsequent analysis.

The rise time in fluorescence intensity over the entire field-of-view was also measured (i.e., the ensemble intensity trajectory) for the different transformations. The ensemble rise time was defined as half the time it takes for the mean intensity (averaged over 5 adjacent data points) in an ensemble trajectory to increase from 25% to 75% of the maximum intensity (averaged over 5 data points after the maximum point). A comparison of the ensemble rise times for anion exchange in different directions vs. the mean switching time for individual NCs is shown in **Figure S9**.

*Monte Carlo simulations:* Monte Carlo simulations were used to model the reaction trajectories for anion exchange between CsPbBr<sub>3</sub> and CsPbI<sub>3</sub> NCs. The simulations were similar to our previous work on modeling anion exchange between CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub> NCs<sup>3</sup> and the intercalation of CH<sub>3</sub>NH<sub>3</sub>Br into PbBr<sub>2</sub> NCs<sup>2</sup> as well as work by Routzahn and Jain on cation exchange between CdSe and Ag<sub>2</sub>Se NCs.<sup>9</sup> Each simulation consisted of an ensemble of 500 particles, and each particle possessed 20 sites for anion exchange. At each time step, a particle among the population was chosen at random. If the particle had already completely transformed (i.e., all 20 sites had undergone exchange), then the trajectory moved on to the next step without exchange. Otherwise, the probability for the i<sup>th</sup> exchange event to occur in a particle was defined as  $p_i$ . The exchange event occurred only if  $p_i$  was larger than a randomly chosen number between 0 and 1. Each simulation ended when the average number of exchanged sites among the population of particles reached 19.998 or the total number of time steps reached 600,000. The value of  $p_i$  was determined by an equilibrium constant  $k_i$  and the change in free energy  $\Delta G_i$  for anion exchange. We developed different models based on the way each of these values evolved with consecutive reaction events in a particle as it undergoes exchange. The relationships between  $p_i$ ,  $k_i$ , and  $\Delta G_i$ are given by the following equations:

$$k_i = \exp(-\Delta G_i)$$
$$p_i = \frac{k_i}{1+k_i}$$

The change in free energy for each exchange event is given by:

$$\Delta G_i = \Delta G_1 + \Delta g_i$$

where  $\Delta G_1$  is the change in free energy for the first exchange event in a particle, and the value of  $\Delta g_i$  changes with the number of successful events. In both models described below, the initial value,  $k_1$ , was varied from 0.03 to 0.24 to simulate the concentration dependence of waiting of switching times. The initial value of k = 0.03 was adapted from our previous work,<sup>2-3</sup> which allows the code to run within in a reasonable number of time steps (i.e., 600,000 steps in these simulations). We varied the value of  $k_1$  over approximately one order of magnitude, similar to the experimental variation of concentration. A scaling factor of 0.03 was then used to convert the value of  $k_1$  into the simulated concentrations,  $k_0$ , reported in the manuscript:

$$k_0 = \frac{k_1}{0.03}$$

After conversion, the values of the simulated concentrations are comparable to experimental ones when the TBAI/TBAB concentration is given in  $\mu$ g/mL as in **Figure 4** of the main manuscript. The waiting time for each particle in a trajectory was defined as the simulated time when 50% of the sites in the particle (i.e., 10 out of 20) had undergone exchange. The switching time for each

particle was defined as half of the time difference between when 25% and 75% of the sites in the particle had undergone exchange.

*Exchange-density model*: We previously developed this model to simulate anion exchange between CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub> NCs in which the initial and final crystals possess high miscibility.<sup>3</sup> In this model, the value  $\Delta G_i$  decreases continuously as the number of successful exchange events in each particle increases.

$$\Delta g_i = -\delta i^2$$

where  $\delta$  is an empirical constant = 0.005. In this model, the probability for exchange to occur,  $p_i$ , is proportional to the density of exchanged ions in the particle. Further details of this model can be found in our previous work.<sup>3</sup>

Structural-reorganization model: This model is an adaptation of one that we previously developed to describe the intercalation of CH<sub>3</sub>NH<sub>3</sub>Br into PbBr<sub>2</sub> nanocrystals in which there is a significant change in structure during the transformation.<sup>2</sup> In this model,  $\Delta G_i$  for exchange is initially constant. After a critical threshold of successful events in a particle ( $i_c = 5$  in these simulations), the value of  $\Delta G_i$  begins to decrease with the number of events:

$$\Delta g_i = \delta \times \Delta G_1 \left( (i - i_c + 1)^{-1/5} - 1 \right) \text{ for } i \ge i_c$$

where  $\delta$  is an empirical constant = 2.4.  $\Delta G_1$  is the change in free energy for the first exchange event in a particle. In our previous phase-transformation model,  $\Delta g_i = \delta \times \Delta G_1 ((i - i_c + 1)^{-1/3} - 1)$ , and  $i_c = 4$ . Empirically, we found that the  $i^{-1/5}$  dependence gave a better match to the experimental waiting and switching times for the conversion of CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub> shown in **Figure 5** of the main manuscript. The  $i^{-1/5}$  dependence used in the current simulations provides a less abrupt change in  $\Delta G_i$ , which is expected as the degree of structural reorganization when CsPbI<sub>3</sub> NCs transform to CsPbBr<sub>3</sub> is smaller compared to when PbBr<sub>2</sub> NCs transform into CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>.

## Supporting Tables.

**Table S1**. Additional details for the fluorescence spectra shown in **Figure 1a** (i.e., transformation of CsPbBr<sub>3</sub> NCs to CsPbI<sub>3</sub>): amount of TBAI added, the emission maximum of the resulting PL spectrum, and its FWHM.

Total volume of TBAI (µL)	Total moles of TBAI (µmole)	Peak maximum (nm)	Peak maximum (eV)	FWHM (nm)	FWHM (eV)
0	0	502	2.47	24	0.13
80	0.06	537	2.31	28	0.12
160	0.13	559	2.22	35	0.12
240	0.19	608	2.04	37	0.12
320	0.26	633	1.96	36	0.12
400	0.32	643	1.93	37	0.11

**Table S2**. Additional details for the fluorescence spectra shown in **Figure 1b** (i.e., transformation of CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub>): amount of TBAB added, the emission maximum of the resulting PL spectrum, and its FWHM.

Total volume of TBAB (µL)	Total moles of TBAB (µmole)	Peak maximum (nm)	Peak maximum (eV)	FWHM (nm)	FWHM (eV)
0	0	676	1.83	40	0.11
60	0.06	674	1.84	44	0.12
120	0.11	547	2.27	27	0.11
180	0.17	533	2.33	29	0.13
300	0.28	524	2.37	24	0.11
420	0.39	519	2.39	23	0.11

Table S3. The CsPbBr3 and CsPbI3 NCs samples characterized in the main manuscript and

Supporting Figures.

		Sample characterized in the following figures				
Batch 1		Figure 1a, Figure 2b-c, Figure 3a, Figure 4a, Figure S9a, Figure S12, Figure S16a				
CsPbBr <sub>3</sub>	Batch 2	Figure 4b, Figure S2a-b, Figure S3a-b, Figure S4, Figure S5, Figure S9b, Figure S13, Figure S16b				
CsPbI <sub>3</sub>	Batch 1	Figure 1b-c, Figure 2d-e, Figure 3b, Figure 4c-d, Figure 5d, Figure S1, Figure S7, Figure S8, Figure S9c-d, Figure S10, Figure S11, Figure S14, Figure S15, Figure S16c-d, Figure S18a, Figure S18c, Figure S19				
	Batch 2	Figure S2c-d, Figure S3c-d, Figure S4, Figure S5				

**Table S4**. Fitting parameters for the concentration dependence of the mean waiting and switching times shown in Figure 4.

y = a/x + b		Figure 4a:	Figure 4b:	Figure 4c:	Figure 4d:
		CsPbBr <sub>3</sub> to	$CsPbBr_{3-x}I_x$ to	CsPbI <sub>3</sub> to	$CsPbBr_{3-x}I_x$ to
-		CsPbI <sub>3</sub>	CsPbBr <sub>3</sub>	CsPbBr <sub>3</sub>	CsPbI <sub>3</sub>
Waiting	a (s-µg/mL)	16.3	5.1	26.5	20.5
time	b (s)	2.6	1.6	2.8	2.9
Switching	a (s-µg/mL)	4.0	1.2	4.5	6.3
time	b (s)	2.2	0.47	0.3	0.8

**Table S5.** Parameters for the linear fits (y = ax + b) of the scatter plots of waiting vs. switchingtime shown in Figure S18.

Exchange-	$\mathbf{k}_0$	1	2	4	8		
density	a (slope)	0.15	0.14	0.17	0.15		
model	b (intercept)	18634	10397	5479	3872		
CsPbBr <sub>3-x</sub> I <sub>x</sub>	TBAI conc. (µg/mL)	1	2	3	4	6	10
to CsPbI <sub>3</sub>	a (slope)	0.15	0.11	0.12	0.09	0.059	0.11
	b (intercept)	14.1	4.5	3.82	5.95	1.99	3.48

**Table S6.** Tilt angles for  $PbX_6$  octahedra (X = Br or I) based on the bulk crystal structures from ICSD collection codes #243735 for CsPbBr<sub>3</sub> and #21955 for CsPbI<sub>3</sub>. Both crystals have the perovskite orthorhombic  $\gamma$  phase.

Tilt angle	CsPbBr <sub>3</sub>	CsPbI <sub>3</sub>	
In-plane Pb–X–Pb	156.51°	155.57°	
Out-of-plane Pb–X–Pb	163.79°	159.24°	

## **Supporting Figures.**



**Figure S1**. Normalized PL spectra of CsPbI<sub>3</sub> NCs before (red trace) and after (black and blue traces) adding 420  $\mu$ L of a TBAB solution (0.3 mg/mL = 0.93 mmol/L) in tert-butanol. The PL spectra were measured 30 s (black trace) and 90 s (blue trace) after the addition of TBAB. The spectra stopped blue-shifting approximately 90 s after the addition of TBAB. The excitation wavelength was 400 nm for all spectra. **Figure 1** in the main manuscript shows the resulting PL spectra when 60- $\mu$ L aliquots of the same TBAB solution were added, and a spectrum was taken between each aliquot.



**Figure S2**. Bright-field TEM images of CsPbX<sub>3</sub> NCs before and after anion exchange. (a) Assynthesized CsPbBr<sub>3</sub> NCs. (b) CsPbI<sub>3</sub> NCs produced by anion exchange of CsPbBr<sub>3</sub> NCs on a TEM grid. (c) As-synthesized CsPbI<sub>3</sub> NCs. (d) CsPbBr<sub>3</sub> NCs produced by anion exchange of CsPbI<sub>3</sub> NCs on a TEM grid.



**Figure S3**. Size distributions of the CsPbX<sub>3</sub> NCs shown in **Figure S2**. (a) As-synthesized CsPbBr<sub>3</sub> NCs. (b) CsPbI<sub>3</sub> NCs produced by anion exchange of CsPbBr<sub>3</sub> NCs on a TEM grid. (c) Assynthesized CsPbI<sub>3</sub> NCs. (d) CsPbBr<sub>3</sub> NCs produced by anion exchange of CsPbI<sub>3</sub> NCs on a TEM grid. Based on the lattice constants of the bulk crystals, the distances between Pb atoms in CsPbBr<sub>3</sub> along the edges of the NCs are 8.250 Å in the (100) direction and 8.203 Å in the (001) direction. We assume the CsPbBr<sub>3</sub> NCs in **Figure S2** are oriented with the (010) plane parallel to the substrate similar to a previous report.<sup>10</sup> In bulk CsPbI<sub>3</sub>, the distances between Pb atoms along the edges are 8.818 Å and 8.646 Å. The orientation of the unit cell is different in CsPbI<sub>3</sub>. So, these Pb–Pb distances are along the (010) and (100) directions, respectively. When CsPbBr<sub>3</sub> NCs transform to CsPbI<sub>3</sub>, the expected expansion of the lateral dimensions is 7% for the longer

dimension and 5% for the shorter dimension, which lead to changes in the lateral dimensions of less than 1 nm. A similar contraction of the lateral dimensions is expected when CsPbI<sub>3</sub> NCs transform to CsPbBr<sub>3</sub>. However, these changes in size are less than the 1<sup>st</sup> standard deviation in the size distribution of each sample. Thus, we do not observe a significant change in average edge length for either sample after anion exchange.



**Figure S4**. XRD patterns of CsPbX<sub>3</sub> NCs before and after anion exchange. From top to bottom the experimental patterns are the following: As-synthesized CsPbI<sub>3</sub> NCs (purple), iodide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs produced by anion exchange of CsPbBr<sub>3</sub> NCs (green), bromide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs produced by anion exchange of CsPbI<sub>3</sub> NCs (blue), and as-synthesized CsPbBr<sub>3</sub> NCs (red). Simulated powder XRD patterns made using ICSD collection codes #21955 for CsPbI<sub>3</sub> in the perovskite orthorhombic  $\gamma$  phase (yellow) and #243735 for CsPbBr<sub>3</sub> in the perovskite orthorhombic  $\gamma$  phase (black) are shown at the top and bottom of the plot. The peak positions in the green pattern are shifted to higher angles compared to pure CsPbI<sub>3</sub>, and the peak positions in the blue pattern are shifted to lower angles compared to pure CsPbBr<sub>3</sub> indicating that the NCs produced by anion exchange in the green and blue patterns are likely the result of aggregation of the NCs leading to a larger average crystallite size. The impurity peaks marked with \* in the green pattern are attributed to the non-perovskite orthorhombic  $\delta$  phase of CsPbI<sub>3</sub>.



**Figure S5**. Comparison of the experimental XRD pattern for iodide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs produced by anion exchange of CsPbBr<sub>3</sub> NCs (middle, green) to simulated patterns for the perovskite orthorhombic  $\gamma$  phase of CsPbI<sub>3</sub> (top, yellow) and the non-perovskite orthorhombic  $\delta$  phase (bottom, black). The simulated patterns were made using ICSD collection codes #21955 for the  $\gamma$  phase and #161480 for the  $\delta$  phase. The impurity peaks marked with \* are attributed to the non-perovskite  $\delta$  phase of CsPbI<sub>3</sub>, which results from degradation of the perovskite phase. While this impurity phase was detected in this sample, its formation may depend on the different preparation method for XRD analysis compared to fluorescence microscopy (i.e., samples for XRD were prepared at a higher concentration). Furthermore, as the  $\delta$  phase of CsPbI<sub>3</sub> is not fluorescent, this impurity phase will not be detected in the fluorescence microscopy studies.



**Figure S6**. Normalized PL spectra of different batches of CsPbBr<sub>3</sub> (blue & green traces) and CsPbI<sub>3</sub> (red & black traces) NCs. **Table S3** above matches the batch of nanocrystals used with each figure in the main manuscript and the **Supporting Information**.



**Figure S7**. Comparison of the mean value (black squares) and the FWHM (red circles) of single-NC waiting times for the transformation of CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub> measured using the same TBAB concentration (2  $\mu$ g/mL, 6.2  $\mu$ mol/L) introduced at different flow rates. The turn-on in emission of individual NCs was imaged with the green filter set (excitation window: 450 – 490 nm; emission window: 500 – 540 nm). The mean waiting time is independent of flow rate for flow rates between 10 and 25 mL/h.



**Figure S8**. Waiting and switching times as a function of particle position for the transformation of CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub> using a TBAB concentration of 1  $\mu$ g/mL (3.1  $\mu$ mol/L). The flow rate was 20 mL/h. (a, b) Waiting times for different NCs within the same field-of-view plotted vs. their pixel position along the (a) x-axis and (b) y-axis of the EMCCD camera. (c, d) Switching times for different NCs within the same field-of-view plotted vs. their and (d) y-axis of the EMCCD camera.



**Figure S9**. Comparison of the ensemble rise times in fluorescence intensity for all NCs in the field-of-view (black squares) to the mean of single-NC switching times (red circles) using different concentrations of TBAB or TBAI. (a) Transformation of as-synthesized CsPbBr<sub>3</sub> NCs to CsPbI<sub>3</sub>. (b) Back conversion of iodide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs (prepared by anion exchange of CsPbBr<sub>3</sub> prior to imaging) to CsPbBr<sub>3</sub>. (c) Transformation of as-synthesized CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub>. (d) Back conversion of bromide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs (prepared by anion exchange of CsPbBr<sub>3</sub>. (d) Back conversion of bromide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs (prepared by anion exchange of CsPbI<sub>3</sub>.



**Figure S10**. Representative intensity trajectories for single bromide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs following the transformation of CsPbI<sub>3</sub> NCs with a TBAB concentration of 1  $\mu$ g/mL (3.1  $\mu$ mol/L). Each of the black traces on the left-hand side is a segment of the trajectory after the intensity stopped increasing (i.e., following the exchange reaction). Each of the blue traces shows the background intensity in a nearby region not containing any particles. The red histograms on the right-hand side show the intensity distributions of the black traces. Intensity trajectories that exhibit fluorescence intermittency with a bimodal distribution of on and off states are indicative of single particles.



**Figure S11**. Representative intensity trajectories of clusters of CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs following the transformation CsPbI<sub>3</sub> NCs with a TBAB concentration of 1  $\mu$ g/mL (3.1  $\mu$ mol/L). Each of the black traces on the left-hand side is a segment of the trajectory after the intensity stopped increasing (i.e., following the exchange reaction). Each of the blue traces shows the background intensity in a nearby region not containing any particles. The red histograms on the right-hand side show the intensity distributions of the black traces. Unlike the trajectories for single particles shown in **Figure S10** above, clusters of particles do not show clear on and off states as each particle in the cluster blinks independently.



**Figure S12**. Histograms of the relative waiting times for the transformation of as-synthesized CsPbBr<sub>3</sub> NCs to CsPbI<sub>3</sub> using TBAI. The turn-on in emission of individual NCs was imaged with the red filter set (excitation window: 530 - 558 nm; emission window: 590 - 649 nm). The concentrations of TBAI used were (a) 1 µg/mL (2.7 µmol/L), (b) 2 µg/mL (5.4 µmol/L), (c) 3 µg/mL (8.1 µmol/L), (d) 4 µg/mL (10.8 µmol/L), (e) 6 µg/mL (16.2 µmol/L), and (f) 10 µg/mL (27 µmol/L). For each histogram, a relative waiting time of 0 seconds corresponds to the first NC to transform among the population.



**Figure S13**. Histograms of the relative waiting times for the back conversion of iodide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs to CsPbBr<sub>3</sub> using TBAB. The iodide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs were prepared by anion exchange of CsPbBr<sub>3</sub> NCs with PbI<sub>2</sub> in solution prior to imaging (see the **Supporting Methods** section above for details). The turn-off in emission of individual NCs was imaged with the red filter set (excitation window: 530 - 558 nm; emission window: 590 - 649 nm). The concentrations of TBAB used were (a) 1 µg/mL (3.1 µmol/L), (b) 2 µg/mL (6.2 µmol/L), (c) 3 µg/mL (9.3 µmol/L), (d) 6 µg/mL (18.6 µmol/L), and (e) 10 µg/mL (31.1 µmol/L). For each histogram, a relative waiting time of 0 seconds corresponds to the first NC to transform among the population.



**Figure S14**. Histograms of the relative waiting times for the transformation of as-synthesized CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub> using TBAB. The turn-on in emission of individual NCs was imaged with the green filter set (excitation window: 450 - 490 nm; emission window: 500 - 540 nm). The concentrations of TBAB used were (a) 1 µg/mL (3.1 µmol/L), (b) 2 µg/mL (6.2 µmol/L), (c) 3 µg/mL (9.3 µmol/L), (d) 4 µg/mL (12.4 µmol/L), (e) 6 µg/mL (18.6 µmol/L), and (f) 10 µg/mL (31.1 µmol/L). For each histogram, a relative waiting time of 0 seconds corresponds to the first NC to transform among the population.



**Figure S15**. Histograms of the relative waiting times for the back conversion of bromide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs to CsPbI<sub>3</sub> using TBAI. The bromide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs were prepared by anion exchange of CsPbI<sub>3</sub> NCs on a coverslip using TBAB prior to imaging (see the **Supporting Methods** section above for details). The turn-off in emission of individual NCs was imaged with the green filter set (excitation window: 450 - 490 nm; emission window: 500 - 540 nm). The concentrations of TBAI used were (a) 1 µg/mL (2.7 µmol/L), (b) 2 µg/mL (5.4 µmol/L), (c) 3 µg/mL (8.1 µmol/L), (d) 4 µg/mL (10.8 µmol/L), (e) 6 µg/mL (16.2 µmol/L), and (f) 10 µg/mL (27 µmol/L). For each histogram, a relative waiting time of 0 seconds corresponds to the first NC to transform among the population.



**Figure S16**. Examples of Gaussian fits to the distributions of relative waiting times shown above in **Figures S12** – **S15** for single CsPbX<sub>3</sub> NCs undergoing anion exchange. (a) Transformation of as-synthesized CsPbBr<sub>3</sub> NCs to CsPbI<sub>3</sub> using TBAI (example fits to histograms in **Figure S12**). (b) Back conversion of iodide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs to CsPbBr<sub>3</sub> using TBAB (example fits to histograms in **Figure S13**). (c) Transformation of as-synthesized CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub> using TBAB (example fits to histograms in **Figure S14**). (d) Back conversion of bromide-rich CsPbBr<sub>3</sub>. <sub>x</sub>I<sub>x</sub> NCs to CsPbI<sub>3</sub> using TBAI (example fits to histograms in **Figure S15**). The concentrations of TBAI shown in (a) and (d) are 1, 2, and 10 µg/mL (i.e., 2.7, 5.4, and 27.0 µmol/L). The concentrations of TBAB shown in (b) and (c) are 1, 2, and 10 µg/mL (i.e., 3.1, 6.2, and 31.1 µmol/L).



**Figure S17**. Simulated reaction trajectories for anion exchange. (a) Ensemble trajectory for the exchange-density model using a simulated concentration  $k_0 = 1$ . (b) Representative single-particle trajectories for the exchange-density model using  $k_0 = 1$ ; (c) Ensemble trajectory for the structural-reorganization model using a simulated concentration  $k_0 = 1$ . (d) Representative single-particle trajectories for the structural-reorganization model using  $k_0 = 1$ . The structural-reorganization model leads to sharper transitions for individual particles



**Figure S18**. Plots of the waiting time vs. switching time for individual particles. (a) The back conversion of bromide-rich CsPbBr<sub>3-x</sub>I<sub>x</sub> NCs to CsPbI<sub>3</sub> using a TBAI concentration of 1 µg/mL (2.7 µmol/L). (b) Exchange-density model using a simulated concentration  $k_0 = 1$ . (c) Transformation of as-synthesized CsPbI<sub>3</sub> NCs to CsPbBr<sub>3</sub> using a TBAB concentration of 1 µg/mL (3.1 µmol/L). (d) Structural-reorganization model using a simulated concentration  $k_0 = 1$ . The red dashed lines provide linear fits of the scatter plots in (a) and (b). The fitting parameters at different concentrations are provided in **Table S5**.



**Figure S19**. The slopes from linear fits to scatter plots of the waiting vs. switching time for individual particles. The red circles correspond to the back conversion of bromide-rich CsPbBr<sub>3</sub>.  $_{x}I_{x}$  NCs to CsPbI<sub>3</sub> using TBAI concentrations of 1, 2, 3, 4, 6 and 10 µg/mL (2.7, 5.4, 8.1, 10.8, 16.2 and 27 µmol/L). The black squares correspond to the exchange-density model using simulated concentrations  $k_{0} = 1, 2, 4$ , and 8. The mean slopes for the experimental and simulated results are  $0.11 \pm 0.03$  and  $0.15 \pm 0.01$ , respectively.

## **Supporting References**

- Nedelcu, G.; Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Grotevent, M. J.; Kovalenko, M. V., Fast Anion-Exchange in Highly Luminescent Nanocrystals of Cesium Lead Halide Perovskites (CsPbX<sub>3</sub>, X = Cl, Br, I). *Nano Letters* 2015, *15*, 5635-5640.
- Yin, B.; Cavin, J.; Wang, D.; Khan, D.; Shen, M.; Laing, C.; Mishra, R.; Sadtler, B., Fluorescence Microscopy of Single Lead Bromide Nanocrystals Reveals Sharp Transitions During Their Transformation to Methylammonium Lead Bromide. *Journal of Materials Chemistry C* 2019, 7, 3486-3495.
- Wang, D.; Cavin, J.; Yin, B.; Thind, A. S.; Borisevich, A. Y.; Mishra, R.; Sadtler, B., Role of Solid-State Miscibility during Anion Exchange in Cesium Lead Halide Nanocrystals Probed by Single-Particle Fluorescence. *The Journal of Physical Chemistry Letters* 2020, *11*, 952-959.
- 4. Orfield, N. J.; McBride, J. R.; Keene, J. D.; Davis, L. M.; Rosenthal, S. J., Correlation of Atomic Structure and Photoluminescence of the Same Quantum Dot: Pinpointing Surface and Internal Defects That Inhibit Photoluminescence. *ACS Nano* **2015**, *9*, 831-839.
- 5. Zhang, A.; Dong, C.; Ren, J., Tuning Blinking Behavior of Highly Luminescent Cesium Lead Halide Nanocrystals through Varying Halide Composition. *The Journal of Physical Chemistry C* 2017, *121*, 13314-13323.
- 6. Gibson, N. A.; Koscher, B. A.; Alivisatos, A. P.; Leone, S. R., Excitation Intensity Dependence of Photoluminescence Blinking in CsPbBr<sub>3</sub> Perovskite Nanocrystals. *The Journal of Physical Chemistry C* **2018**, *122*, 12106-12113.
- 7. Seth, S.; Ahmed, T.; Samanta, A., Photoluminescence Flickering and Blinking of Single CsPbBr<sub>3</sub> Perovskite Nanocrystals: Revealing Explicit Carrier Recombination Dynamics. *The Journal of Physical Chemistry Letters* **2018**, *9*, 7007-7014.
- Ryan, D. P.; Goodwin, P. M.; Sheehan, C. J.; Whitcomb, K. J.; Gelfand, M. P.; Van Orden, A., Mapping Emission from Clusters of CdSe/ZnS Nanoparticles. *The Journal of Physical Chemistry C* 2018, *122*, 4046-4053.
- 9. Routzahn, A. L.; Jain, P. K., Single-Nanocrystal Reaction Trajectories Reveal Sharp Cooperative Transitions. *Nano Letters* **2014**, *14*, 987-992.
- Lv, L.; Xu, Y.; Fang, H.; Luo, W.; Xu, F.; Liu, L.; Wang, B.; Zhang, X.; Yang, D.; Hu, W.; et al., Generalized Colloidal Synthesis of High-Quality, Two-Dimensional Cesium Lead Halide Perovskite Nanosheets and Their Applications in Photodetectors. *Nanoscale* 2016, *8*, 13589-13596.