Intrinsic anion diffusivity in lead halide perovskites is facilitated by a soft lattice

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Facile ionic transport in lead halide perovskites plays a critical role in device performance. Understanding the microscopic origins of high ionic conductivities has been complicated by indirect measurements and sample microstructural heterogeneities. Here, we report the direct visualization of halide anion interdiffusion in CsPbCl$_2$–CsPbBr$_3$ single crystalline perovskite nanowire heterojunctions using wide-field and confocal photoluminescence measurements. The combination of nanoscale imaging techniques with these single crystalline materials allows us to measure intrinsic anionic lattice diffusivities, free from complications of microscale inhomogeneity. Halide diffusivities were found to be between $10^{-13}$ and $10^{-12}$ cm$^2$/sec at about 100 °C, which are several orders of magnitude lower than those reported in polycrystalline thin films. Spatially resolved photoluminescence lifetimes and surface potential measurements provide evidence of the central role of halide vacancies in facilitating ionic diffusion. Vacancy formation free energies computed from molecular simulation are small due to the easily deformable perovskite lattice, accounting for the high equilibrium vacancy concentration. Furthermore, molecular simulations suggest that ionic motion is facilitated by low-frequency lattice modes, resulting in low activation barriers for vacancy-mediated transport. This work elucidates the intrinsic solid-state ion diffusion mechanisms in this class of semisof and offers guidelines for engineering materials with long-term stability in functional devices.

Lithium halide perovskites are a class of soft ionic crystals with excellent optoelectronic properties ideally suited for photovoltaic and light-emitting applications (1–4). Significant ionic migration has been reported in these materials (5, 6) and is considered to play an important role in anomalous charging hysteresis, light-induced phase segregation, and photostability (7–13). The current understanding of ionic transport in lead halide perovskites is based primarily on conventional charge transport studies (14, 15), where the contribution from electrons and comovement of cations and anions is difficult to separate. Furthermore, ionic diffusion has been measured in polycrystalline thin films, replete with grain boundaries where the ion transport is usually faster than in the interior lattice (16), and thus the high ionic conduction reported may not be representative of intrinsic material properties. Although the fast anion-exchange was achieved in cesium lead halide nanocrystals at solid–liquid interfaces (17, 18), high anion diffusivity may not be necessary due to the short solid–solid diffusion path (<10 nm). Therefore, the intrinsic ion diffusion in this class of materials has remained largely unknown.

Traditional solid-state transport characterization techniques provide either direct (e.g., trace diffusion and secondary ion mass spectrometry) or indirect (e.g., nuclear magnetic relaxation and impedance spectroscopy) information of ion diffusion (19). However, most of them only reveal transport properties averaged over macroscopic scales with complications from microstructural heterogeneities. Direct microstructural observation and atomic-scale mechanism of the lattice diffusion are still highly challenging. Recently, well-defined heterostructures of two different halide species in CsPbX$_3$ nanowires were realized through a localized anion exchange reaction (20). The sharp interface with well-defined physical properties (composition, optical, electronic, etc.), controllable geometry, and single crystalline nature make these nanowire heterojunctions ideal platforms to study the intrinsic halide anion interdiffusion. In addition, different halide compositions afford an excellent bandgap tunability with high fluorescence efficiency, which allows for halide anion interdiffusion to be directly monitored by photoluminescence (PL). We combine these measurements with multiscale modeling to elucidate the relationships between mesoscale transport processes and their molecular underpinnings. Together with spatially resolved PL lifetime and surface potential mappings, we further demonstrate how anionic diffusion in lead halides is determined by low barriers to vacancy hopping and facilitated by elastic properties that render the perovskite lattice soft and deformable.

Significance

Understanding and controlling the ion migration in a solid-state semiconductor is essential for device performance in modern photonics, electronics, and optoelectronics. Direct microstructural observation and atomic-scale mechanism of the intrinsic lattice diffusion are still highly challenging. Here, we report the direct visualization of halide anion interdiffusion in CsPbCl$_2$–CsPbBr$_3$ single crystalline nanowire heterojunctions via nanoscale imaging, allowing for the direct measuring of intrinsic lattice diffusivities. The intrinsic halide diffusivities were found to be several orders of magnitudes lower than those reported in polycrystalline thin films. Together with multiscale modeling, we further demonstraex how anionic diffusion in lead halides is determined by low barriers to vacancy hopping and facilitated by the soft perovskite lattice.


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The CsPbCl₃–CsPbBr₃ nanowire heterojunctions were synthesized using our previously reported anion exchange chemistry and supported on SiO₂/Si substrates (SI Appendix). Heating the nanowires initiated halide anion interdiffusion. The in situ interdiffusion process in the single nanowire was monitored using wide-field PL imaging (Fig. 1A). Utilizing a relatively low pump power density and short exposure time, the PL measurement should be negligible to anion interdiffusion. To quantitatively relate the PL emission with Br concentration, we measured the PL spectrum of different uniform CsPb(BrₓCl₃₋ₓ) nanowires and the corresponding Br concentration by energy-dispersive X-ray spectroscopy (SI Appendix, Figs. S1 and S2). As-synthesized heterojunction nanowires featured a blue/green emission with a clear interface in the PL image (Fig. 1C). Two distinct peaks in the wide-field spectrum were observed and identified with the Cl- and Br-rich ends of the nanowire (SI Appendix). The exchange of Br/Cl between the two halide segments induced a time-dependent change of the emission spectrum. After 1.5 h, under a constant temperature of 100 °C, the blue PL peak shifted from 435 to 445 nm, indicating a local change in halide composition, while the green PL peak position remained unchanged (SI Appendix, Fig. S3A). The PL image taken at that time shows that the peak of in situ PL visualization of thermal-driven anion interdiffusion CsPbCl₃–CsPbBr₃ nanowires (SI Appendix, Figs. S1 and S2). As-synthesized heterojunction nanowires featured a blue/green emission with a clear interface in the PL image (Fig. 1B). Two distinct peaks in the wide-field spectrum were observed and identified with the Cl- and Br-rich ends of the nanowire (Fig. 1C). The exchange of Br/Cl between the two halide segments induced a time-dependent change of the emission spectrum. After 1.5 h, under a constant temperature of 100 °C, the blue PL peak shifted from 435 to 445 nm, indicating a local change in halide composition, while the green PL peak position remained unchanged (SI Appendix, Fig. S3A). The PL image taken at that time shows that the interface between the Cl- and Br-rich regions moved in the direction of the Br-rich end (Fig. 1B). From 1.5 to 5 h, the blue peak continued to red shift, and its relative intensity to the green peak increased (SI Appendix, Fig. S3B). With further heating after 5 h, the green peak began to show a gradual blue shift (SI Appendix, Fig. S3C), implying Cl diffusion into the Br-rich region. Fig. 1 F and G shows the PL image and spectrum at 7 h. In solid-state interdiffusion, with concentration-dependent transport coefficients, the equal-molar or Matano plane moves toward the more diffusive species. Furthermore, the slow change of the green emission peak further suggests Cl does not migrate far into the Br end of the wire for times up to 5 h at 100 °C. After 10 h, only one peak in the emission spectrum was present and no interface was evident along the nanowire in the wide-field PL image (Fig. 1 H and I).

Confocal PL resolves the spatial distribution of emissive sites at different wavelengths and can provide higher spatial resolution than conventional wide-field PL. With confocal PL and composition PL tunability in SI Appendix, Fig. S2, we could generate a spatial mapping of the local Br concentration along our heterojunction nanowires (SI Appendix, Fig. S4). Fig. 2A shows the evolution of the bromide concentration profile. After 1.5 h at 100 °C, the Br-rich region shrank by about 1 μm without evolving its composition, which is consistent with the green peak observed in situ PL (Fig. 1 C and E). The Br concentration in the Cl-rich region increased homogeneously from 0.22 to 0.27. After 5 h, the length of the Br-rich end was about 0.5 μm and the Br concentration in the Cl-rich part continued increasing to 0.38. After 10 h, a smooth concentration profile persisted along the nanowire along with a single peak of the wide-field PL shown in Fig. 1I. Confocal PL was also performed to study interdiffusion at different temperatures (SI Appendix, Figs. S5 and S6), indicating the same qualitative behavior. At each temperature, the total Br amount across the whole nanowire stayed almost the same, indicating no halide transport into the environment (SI Appendix, Fig. S7). Additionally, we also studied the dependence of anion interdiffusion on the sample preparation by fabricating the “reverse” CsPbCl₃–CsPbBr₃ nanowire heterojunctions, which are created by anion exchange from CsPbCl₃ templates. Fig. 2B shows the concentration profile evolution for a reverse heterojunction at 125 °C. With the same qualitative behavior as the “normal” heterojunction (SI Appendix, Fig. S8), therefore, the heterojunction fabrication process preserves the crystal quality and has no effect on the dynamics of anion interdiffusion. The evolution of concentration profiles strongly suggests a slower anionic diffusion in the Br region, which acts as a “reservoir” for Br. The time needed to deplete the Br-rich part is longer than the time for the Br in the Cl-rich part to distribute homogeneously. Thus, the Br concentration of the whole Cl-rich part increases uniformly in evolution profiles.

To understand the molecular origin of the interdiffusion mechanism, we performed molecular-dynamics (MD) calculations (SI Appendix). Previous work has demonstrated that the diffusion of the halide anions is vacancy mediated (7) due to the large formation energies of interstitial defects. To estimate the diffusivity, we computed the free energies to create a vacancy, anion-vacancy exchange rates, and the prefactors associated with the length of the exchange, and its characteristic timescale. This vacancy-mediated process is rendered in Fig. 3 A–C. We used steered MD (21) with the Jarzynski equality (22) to compute the free energy barriers anions have to overcome to diffuse by exchanging their positions with vacancies. Examples for an equal-molar mixture are shown in Fig. 3D for Br and Cl, which exhibit notable asymmetry along the reaction coordinate. This asymmetry arises because vacancies are stabilized by a local enhancement of Br ions, whose correlations decay over two to three unit cells as indicated by the vacancy–halide pair correlation function. An entropic contribution to the barrier accounts...
for up to one-third of its height. In addition, purely dynamical effects arise due to the slow energy diffusion of the halide perovskite lattice. This is quantified by small values of the transmission coefficient, illustrated in Fig. 3E. A significant dynamical correction occurs for all compositions and is largest for the equal-molar mixture (SI Appendix). This correction is a result of the weak coupling between the low-frequency octahedral tilting modes that are excited by the hopping vacancy, and the surrounding lattice, and has been noted before as resulting in low thermal conductivities (23) and low photocexcitation cooling rates (24). We have additionally computed the barrier heights for vacancy-mediated transport of Cs, which are 1.25 and 1.4 eV for the pure Br and Cl phases, respectively. These barriers put Cs diffusion on a significantly different timescale compared with anion diffusion. The black line in Fig. 3F shows the concentration-dependent hopping rate computed by the Bennet–Chandler procedure, where the hopping rate in the pure Br phase is found to be about three times faster than in the Cl phase. This small difference is insufficient to explain the enhanced diffusion noted in the PL measurements.

Vacancy-mediated diffusion additionally depends on the concentration of vacancies, which is determined by the free energy to form a vacancy in the lattice. Because the lattice is ionic, charge neutrality demands that equilibrium point defects are created in pairs. We used thermodynamic integration to compute the vacancy formation energy of a Schottky defect pair of Cs + X, as a function of composition and temperature. To study the composition dependence, we employed Monte Carlo swapping moves to sample halide compositions. We find from MD calculations that the lattice contribution to the formation free energy is 1.32 and 1.44 eV for Br and Cl, respectively (SI Appendix). Together with the appropriate standard state conditions ($\mu_\text{Br} = -0.9$ eV and $\mu_\text{Cl} = -1.09$ eV) with excess of Cl (SI Appendix), the total formation energy is 0.42 and 0.35 eV for Br and Cl, respectively. This results in an equilibrium vacancy concentration of $3 \times 10^{-7}$ and $2 \times 10^{-9}$ per unit cell for the pure chloride and bromide phases, respectively, at the conditions considered experimentally in the synthesis of the nanowires (red line in Fig. 3F). This equilibrium vacancy concentration is large despite the ionic character of the lattice. This is due to the highly anharmonic lattice with accompanying low-frequency modes and small elastic moduli (25). We find the binding energy of the Schottky defect pairs is below 0.1 eV (SI Appendix), on the order of thermal energies, which means that halide ion diffusion is expected to be uncorrelated with cesium diffusion. Therefore, we conclude that it is the enhanced vacancy concentration in the Cl part relative to the Br part that results in the large diffusivity measured experimentally in the Cl region.

To validate the role of the equilibration vacancy concentration along the nanowire, we used Kelvin probe force microscopy (6) to monitor the net flow of vacancies during interdiffusion. Fig. 2C shows the 2D surface potential map and corresponding nanowire potential profiles of the as-synthesized (Top), 1.5 h at 100 °C annealed (Middle), and 5 h at 100 °C annealed (Bottom) heterojunction nanowire, respectively. (Scale bar: 2 μm.) A distinct surface potential change ($\Delta \Phi \sim 110$ meV) is observed at the initial CsPbBr$_3$–CsPbCl$_3$ interface. The electronic junction moves $\sim 1.2 \mu$m into the initial CsPbBr$_3$ region with a smaller surface potential change ($\Delta \Phi \sim 100$ meV) after 1.5 h at 100 °C. Further extending the thermal annealing time to 5 h at 100 °C, the KPFM surface potential maps do not reveal any distinct electronic junction. (D) Fluorescence lifetime mapping images of a CsPbBr$_3$–CsPbCl$_3$ nanowire heated for 0 h (Top), 1.5 h (Middle), and 5 h (Bottom) at 100 °C. The axial size of long lifetime component (CsPbBr$_3$ region) becomes shorter after heating, exhibiting a consistent correlation with the evolution of confocal PL images. (Scale bar: 2 μm.) The Bottom of D shows the PL lifetime profiles with correlated Br/(Br + Cl) profiles. The open dots represent the lifetime distribution along the nanowire, 0 h (black square), 1.5 h (red circle), and 5 h (blue triangle). The solid lines are corresponding Br concentration profiles. The normalized PL lifetime is closely associated with composition evolutions (detail plots in SI Appendix, Fig. S12).
confocal PL can be exploited to calculate the interdiffusion concentration profiles during interdiffusion measured from concentration where the standard-state chemical potentials have been fitted against the experimental interdiffusion coefficients (300 K, 1 bar). The dashed line corresponds to the effective rate with linear fits for the Br and Cl rates (averaged over different realizations of the composition. The corresponding to the energy barriers shown in Fig. 3. The activation energy of anion diffusion is 2.5 μm after 5 h at 100 °C, the surface potential maps do not reveal any distinct electronic junction. No grain boundaries or cracks within the nanowire crystal were observed in the atomic force microscopy images after thermal annealing (SI Appendix, Fig. S10). Vacancies generally serve as nonradiative recombination centers with distinct local PL lifetimes (26). We measured local PL lifetimes with fluorescent lifetime imaging microscopy (FLIM) as shown in Fig. 2D. The Br-rich region exhibited a longer PL lifetime compared with the Cl-rich part (SI Appendix, Fig. S11A). The axial size of the long lifetime region becomes shorter after heating (Fig. 2D), exhibiting a consistent correlation with the evolution of confocal PL images (SI Appendix, Fig. S11 B and C). As shown in Fig. 2 C and D, both local PL lifetimes and surface potential show a close dependence on the concentration evolution, suggesting the correlated diffusion of vacancies during interdiffusion. These two measurements qualitatively indicate that the vacancy concentration is locally at equilibrium and depends only on the Br concentration.

A constant interdiffusion coefficient $D$ may be estimated by the average diffusion length $L \approx 2\sqrt{Dt}$ for an ideal seminfinite model (27). The interdiffusion length is around 1–2.5 μm after 1.5 h of constant heating, resulting in interdiffusion coefficient around $10^{-13}–10^{-12}$ cm$^2$/s at 75–125 °C. The evolution of the concentration profiles during interdiffusion measured from confocal PL can be exploited to calculate the interdiffusion coefficient as a function of the Br concentration. In principle, this transport coefficient depends on the hopping rates of Cs, Br, and Cl, as well as geometrical factors and the relative activities of

Fig. 3. MD simulation of interdiffusion. (A–C) Snapshots of a chloride anion swapping with a vacancy in an equal-molar mixture, in the initial position (A), on top of the energy barrier (B), and in the final position (C). Color code: cesium in orange, lead in black, bromide in green, and chloride in blue. The sticks represent the strong lead halide ionic bonds. (D) Free energy along halides’ trajectories for Cl and Br with given lattice compositions in an equal-molar mixture. $\lambda = (z - z_f)/(z_i - z_f)$ is the dimensionless reaction coordinate, with $z$ the coordinate of the ion. (E) Time-dependent transmission coefficient corresponding to the energy barriers shown in D. D and E show results for single trajectories that depend on the local anion composition. Thus, the rates must be averaged over different realizations of the composition. (F) Effective hopping rate (gray symbols) corresponding to the interdiffusion coefficient (MD results, 300 K, 1 bar). The dashed line corresponds to the effective rate with linear fits for the Br and Cl rates (SI Appendix). The red solid line is the vacancy concentration where the standard-state chemical potentials have been fitted against the experimental interdiffusion coefficients (SI Appendix).

Fig. 4. Concentration-dependent interdiffusivity. (A) Experimental interdiffusion coefficient at different temperatures as function of Br concentration by Boltzmann–Matano method at 125 °C (black circles), 100 °C (red circles), and 75 °C (blue circles). The solid lines correspond to the theoretical model fitted against experimental data (SI Appendix), which lead to the vacancy concentration shown by Fig. 3F. The solid squares are interdiffusion coefficients from molecular simulations where the vacancy concentration is given by Fig. 3F. (B) Intrinsic diffusion coefficients of pure CsPbBr$_3$ (green) and CsPbCl$_3$ (blue) as a function of inverse temperature. The diffusion coefficients of the pure phases are obtained by extrapolation of the experimental data via the theoretical model. The solid lines stand for the exponential fits $D = D_0e^{-E/RT}$. The activation energy of anion diffusion is 0.28 eV for both CsPbBr$_3$ and CsPbCl$_3$. Lai et al.
the vacancies in the two phases. However, the simulation results suggest that the vacancies are dilute, the Cs-halide Schottky pairs are unbound, and the hopping rates of both anions are nearly the same and are orders of magnitude larger than the analogous cation hopping rate. Under these assumptions, anion interdiffusion can be regarded as decoupled from Cs migration, and the corresponding coefficient \( D(c) \) fully characterizes the dynamics (28). Fick’s second law gives the evolution of the Br concentration, \( c \), at a time and with spatial coordinate \( x \), and with concentration-dependent interdiffusion coefficient \( D(c) \) as follows:

\[
\frac{\partial c}{\partial t} = D(c) \frac{\partial^2 c}{\partial x^2} + \frac{dD(c)}{dx} \left( \frac{\partial c}{\partial x} \right) .
\]

We use the classical Boltzmann–Matano method to extract \( D(c) \) from the concentration profiles, shown in SI Appendix, Fig. S13 (29–31). Our experimental estimates of the interdiffusion coefficient are shown as function of the bromide concentration and the temperature in Fig. 4A. Since the Boltzmann–Matano method is sensitive to the boundary conditions of the Br concentration profiles (SI Appendix, Fig. S14), the calculated interdiffusion coefficient in SI Appendix, Fig. S15 shows a decreasing trend for the concentration profiles of the longer annealing time. The “reverse” nanowire heterojunction has similar diffusion coefficients in SI Appendix, Fig. S15C to the “forward” CsPbCl\(_3\)–CsPbBr\(_3\) nanowire at 125 °C, which quantitatively confirms insignificant effects of the preparation of heterojunctions on anion interdiffusion.

Following Belova and Murch (28), when the anion rates are larger than the cesium rate \( (k_B, k_{CI} \gg k_c) \), the interdiffusion coefficient can be further expressed as function of the Br concentration \( c \) in a simple way:

\[
D(c) = \alpha(c)^2 \nu(c) k_e f(c) ,
\]

where \( \alpha, \nu \), and \( k_{ef} \) are the lattice spacing, the vacancy concentration per unit cell, and an effective rate that depends on the Br and Cl rates via a specific mixing rule (SI Appendix). Here, we have considered the crystal CsPbBr\(_3\)Cl\(_{1.3}\) as an ideal solid solution since the halide anions are randomly distributed throughout the lattice. We should emphasize that, in our case, the interdiffusivity is a direct measure of the off-diagonal Onsager coefficient correlating the diffusion of Br and Cl (28). In addition, the intrinsic diffusivities of the anions are the same and are equal to the interdiffusion coefficient. Despite an increasing hopping rate with the Br fraction (black line in Fig. 3F), CsPbCl\(_3\) has a higher interdiffusivity than CsPbBr\(_3\), owing to a higher vacancy concentration that dominates interdiffusion. Each quantity entering Eq. 2 is obtained by MD, but the experimental vacancy concentration also depends on the synthesis conditions through the standard-state chemical potentials for the pure Br and Cl phases (SI Appendix). Therefore, combining the experimental and MD interdiffusion coefficients (Fig. 4A) gives us the standard states and thus the vacancy concentration (red line in Fig. 3F). We found activation energies for both pure phases to be 0.28 eV by fitting the diffusion coefficients of pure CsPbBr\(_3\) and CsPbCl\(_3\) as a function of temperature with an Arrhenius law (Fig. 4B). This activation energy slightly differs from the one directly computed from MD simulations (0.3 eV) because the small differences of the fitted standard states at different temperatures add a contribution to the activation energy. This result is close to the value reported by Koscher et al. (32) (0.33 eV) from anion exchange in nanocrystals but lower than that by Pan et al. (33) (0.44 eV) found from interdiffusion experiments in nanowires. Comparing to polycrystalline thin films, our results clearly show low interdiffusion coefficients. The high grain boundary diffusivity can be attributed to high defect density and disordered interfaces of polycrystals, as evidenced by Huang and coworkers (6), who showed a lower ion migration in larger grain size perovskite thin films. By eliminating grain boundaries and other extended defects in the single-crystal nanowires, our study has clarified a lower intrinsic anion diffusivity in lead halide perovskites. This finding suggests improving crystallization processes and reducing grain boundaries might be an effective approach to enhance the long-term stability of these materials in real devices.

We have developed a robust combination of experimental and numerical techniques to unravel halide migration during interdiffusion in lead halide perovskites. Additional surface/interface processes may involve with anion interdiffusion, such as interfacial strain, surface defect, doping level change (carrier concentration), the band structure alignment, built-in electrical field, etc. The unique properties of CsPbX\(_3\) make these materials invaluable to show the strength of the theory of solid-state diffusion. Similarly, the cation diffusion dynamics can be further investigated in other heterosystems with two different cation species, such as CsPbBr\(_3\)–CsSnBr\(_3\) and CsPbBr\(_3\)–FAPbBr\(_3\). This work elucidates the intrinsic solid-state ion diffusion mechanisms in this class of soft materials. The clear picture of ion diffusion dynamics may enable the precise tailoring of ion transport properties combining with defect chemistry at microscopic, even atomic, scales, which stimulates a direction to extensive nanionic and optoionic applications in halide perovskites.

**Materials and Methods**

Additional details regarding the materials and methods may be found in SI Appendix.

**PL Measurements.** PL measurements were performed using OBIS 375 nm LX 50-mW laser. The full intensity of the beam is 1 mW. Using an iris diaphragm and a focusing lens, a Gaussian beam spot with a waist of ~30 μm was obtained. The output power of the excitation source was adjusted by a neutral density filter (normally 0.001–1 mW). Emission from nanowires was collected with a bright-field microscope objective (Nikon 50×, N.A. 0.55, in a Nikon ME600 optical microscope) and routed via optical fibers to a UV-vis spectroscopy spectrometer (Princeton Instruments/Acton) equipped with a 1,200 groove/mm grating blazed at 300 nm and a liquid N\(_2\)-cooled CCD. A layer of poly(methyl methacrylate) (PMMA) was coated on the sample in a glovebox, and then put in vacuum for about 10 min for solidification. The PMMA layer can protect the perovskite samples from the air during the heating. For in situ PL measurements, a heating stage (INSTEC STC200) was coupled to the wide-field PL setup. The heating stage takes about 5–10 min to reach the setting temperature. We used relatively low power density (about 1–100 W/cm\(^2\)) for the PL measurements. The sample was kept in the dark during the heating process except for a very short exposure time (a few seconds) to the laser before starting the PL collection. Considering a low pump power density and very short laser exposure time compared with the long annealing time, the light effect should be negligible to anion interdiffusion. The PL images were taken using a Zeiss Axio Scope.

**Confocal PL Mapping.** Confocal PL mapping was performed using a Carl Zeiss LSM710 confocal microscope, using a 20×, 0.8 N.A. objective and a 405-nm laser excitation source. All images were collected with the default optimal setting for XY pixels and scanning time from Zen2010 software. Lambda scans were performed by collecting a series of images while scanning the emission grating in 5-nm spectral windows to vary the collected wavelength range. To get high spatial resolution, 1-AU pinhole was applied and the gain was tuned accordingly to get optimized signal. The confocal PL images were lambda-coded with Zen2010 software. The samples were coated with PMMA. The measurements were performed at room temperature after being heated in a glovebox for a certain time.

**FLIM Measurements.** SiO\(_2\)/Si substrates with CsPbCl\(_3\)–CsPbBr\(_3\) nanowire heterojunctions are attached on glass slides for the measurements using a 50×, 0.55 N.A. air objective by a LSM 510 NLO Axiovert200M confocal laser-scanning microscope equipped with a Mai-Tai HP tunable laser. The excitation wavelength is 405 nm, which is from the second harmonic of 810 nm (~100 fs, 80 MHz). Lifetime measurements were performed using Becker-Hickl SPC-150 time-correlated single-photon counting. The electrical time resolution is 6.6-ps fwhm, 2.5-ps rms. The lifetime decay is collected and
analysis using Becker-Hickl SPCM software. The samples were coated with PMMA and heated in a glovebox for a certain time before the measurement at room temperature.

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Supplementary Materials for

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Materials and Methods

Synthesis of the CsPbBr$_3$ and CsPbCl$_3$ nanowires and plates.

Reagents: Unless otherwise stated, all of the chemicals were purchased from Sigma-Aldrich Chemical and used as received.

**Synthesis of CsPbBr$_3$ and CsPbCl$_3$ nanowires (1):** To grow CsPbBr$_3$ nanowires and nanoplates, 460 mg PbI$_2$ (99.999%) was dissolved in 1 mL anhydrous dimethylformide (DMF) and stirred at 70 °C overnight before further use. The PbI$_2$ solution was spun onto a PEDOT:PSS-coated glass substrates at 1000–3000 rpm for 120 s, then annealed at 100 °C for 15 min. The PbI$_2$ film was carefully submerged into a glass vial with 8 mg/mL CsBr (99.999%) solution in methanol (anhydrous, 99.8%), with the PbI$_2$ side facing up. The capped reaction vial was heated at 50 °C for 12 h, and the substrate was removed after cooling for some time. Then the substrate was washed twice in anhydrous isopropanol (each time for 30 s). The sample was then dried by heating to 50 °C for 5 min. For the synthesis of CsPbCl$_3$ nanowires, 6mg/mL CsCl solution in methanol was used.

**Preparation of oleylammonium halide:** Oleylammonium chloride and iodide were prepared via a reported approach developed by Nedelcu (2). 100 mL ethanol and 0.038mol oleylamine were added into a 3-neck flask under vigorous stirring. The reaction mixture was cooled by an ice-water batch, and certain amount of HX (X = Cl, Br, I) (0.076 mol, HCl 37%; HBr 48%; HI 57%) was added. The reaction was kept under N$_2$ flow for overnight. Then the solvent was evaporated under vacuum, and the obtained product was purified by rinsing multiple times with diethylether. The product was then dried in a vacuum oven overnight at room temperature.

**Anion exchange of CsPbX$_3$ nanowires:** To convert the CsPbBr$_3$ to CsPbCl$_3$, 10 mg of oleylammonium chloride was dissolved in 10 mg of 1-Octadecene (ODE) to make the conversion solution. Individual CsPbBr$_3$ nanowires were transferred onto a clean Si/SiO$_2$ substrate using a nano manipulator. The chip with nanowires was immersed into the
conversion solution at room temperature for 16 hours for complete conversion. Then, the chip was taken out from the solution and washed with chlorobenzene twice and hexanes once to remove the extra salts left on the chip. To convert the CsPbCl$_3$ to CsPbBr$_3$, 10 mg of oleylammominium chloride was dissolved in 10 mg of ODE to make the conversion solution and the reaction was carried out at room temperature for 12 hours.

**Fabrication of the nanowire heterojunctions.**

To fabricate heterojunction devices, the as-grown nanowires were first transferred onto a 300 nm SiO$_2$ coated Si substrate by a micromanipulator. The substrate was then spin-coated with PMMA, and baked at 130°C for 6 minutes. Electron beam lithography (EBL) was performed in a Crestec CABL-9510CC High Resolution Electron Beam Lithography System with acceleration voltage of 50 keV and beam current of 500 pA. After EBL, the substrate was dipped into developer (MIBK:IPA = 1:3) for 60 s followed by washing in IPA for another 20 s. The developer and IPA were dried with molecular sieves (Sigma-Aldrich) to remove water molecules. Subsequently, the NWs with partially coated PMMA was immersed in the conversion solution. The conversion reaction was carried out using the same recipe as described above. After conversion, the PMMA mask was removed by dipping the substrate into chlorobenzene and hexanes, respectively.

**Characterization of the perovskite heterojunctions.**

**Photoluminescence (PL) measurements:** Photoluminescence measurements were performed using OBIS 375nm LX 50mW Laser. The full intensity of the beam is 1 mW. Using an iris diaphragm and a focusing lens, a Gaussian beam spot with a waist of approximately 30 µm was obtained. The output power of the excitation source was adjusted by neutral density filters (normally 0.001 ~ 1mW). Emission from nanowires was collected with a bright-field microscope objective (Nikon 50×, N.A. 0.55, in a Nikon ME600 optical microscope) and routed via optical fibers to a UV-vis spectroscopy spectrometer (Princeton Instruments/Acton) equipped with a 1200 groove/mm grating blazed at 300 nm and a liquid N2-cooled CCD. A layer of PMMA was coated on the sample in glovebox, then put in
vacuum for about 10 min for solidification. The PMMA layer can protect the perovskite samples from the air during the heating. For in-situ PL measurements, a heating stage (INSTEC STC200) was coupled to the wide filed PL setup. The heating stage takes about 5~ 10 min to reach the setting temperature. We used relatively low power density (about 1~ 100 W/cm2) for the PL measurements. The sample was kept in dark during the heating process except very short exposure time (a few seconds) to the laser beam during the PL collection. Considering a low pump power density and very short laser exposure time comparing the long annealing time, the light effect should be negligible to anion interdiffusion. The PL images were taken using a Zeiss Axio Scope.

Scanning electron microscopy measurements (SEM): SEM images were obtained using a JEOL JSM-6340F field emission SEM.

SEM energy-dispersive X-ray spectroscopy (EDS): EDS spectra and images were obtained using a Zeiss Ultra-55 field emission SEM equipped with an EDAX EDS detector using a beam energy of 10 kV.

Confocal PL mapping: Confocal PL mapping was performed using a Carl Zeiss LSM710 confocal microscope, using a 20x 0.8 NA objective and a 405 nm laser excitation source. All images were collected with the default optimal setting for XY pixels and scanning time from Zen2010 software. Lambda scans were performed by collecting a series of images while scanning the emission grating in 5 nm spectral windows to vary the collected wavelength range. In order to get high spatial resolution, 1AU pinhole was applied and the gain was tuned accordingly to get optimized signal. The confocal PL images were lambda-coded with Zen2010 software. The samples were coated with PMMA. The measurements were performed at room temperature after heated in a glovebox for a certain time.

Fluorescent lifetime imaging microscopy (FLIM) measurements. SiO2/Si substrates with CsPbCl3-CsPbBr3 nanowire heterojunctions are attached on a glass slides for the measurements using a 50× 0.55 N.A. air objective by a LSM 510 NLO AxioVert200M Confocal Laser Scanning Microscope equipped with a Mai-Tai HP tunable laser. The
excitation wavelength is 405 nm, which is from the second harmonic of 810 nm (<100 fs, 80 MHZ). Lifetime measurements were performed using Becker-Hickl SPC-150 Time-Correlated Single Photon Counting. The electrical time resolution is 6.6 ps fwhm 2.5 ps rms. The lifetime decay is collected and analysis using Becker-Hickl SPCM software. The samples were coated with PMMA and heated in a glovebox for a certain time before the measurement at room temperature.

Atomic force microscopy (AFM) and scanning Kelvin probe force microscopy (KPFM) measurements.
AFM and scanning KPFM measurements were performed on an AFM system (MFP-3D Asylum Research, Oxford Instruments) equipped with an acoustic isolation chamber (AEK 2002). The samples were transferred from the preparation glovebox into the AFM chamber operated in nitrogen atmosphere. The AFM/KPFM measurements were performed at room temperature employing conductive platinum coated silicon cantilevers (Olympus AC240TM-R3). KPFM measurements were performed in a two-pass mode: the first scan for topographical imaging in AC mode followed by the interleave mode in which the conductive tip was lifted with constant separation relative to the specimen surface while acquiring the contact potential difference (CPD) $V_{\text{CPD}}$. To achieve highest lateral resolution, the influence of the lift height on the measured surface potential ($\delta$) was carefully checked by surface potential vs z spectroscopy, while only a minor influence of the lift height on the measured CPD signals was observed in the delta lift height region of -10 to 30 nm. Accordingly, for all surface potential measurements the delta lift height was set to result in a tip apex – surface distance of approximately 20 nm. An AC bias of 3 V amplitude at the first contact resonance frequency and a DC bias of 1 V was applied to the conductive probe. All measurements were performed at low scan rate of 0.2 Hz at a resolution of 256-by-256 pixel. During measurements, ambient light is minimized by the AFM isolation chamber, while a low-intensity ~ 5 mW infrared (IR) diode (860 nm) is used to detect probe deflection. Prior each KPFM measurement, we performed tip calibration on highly ordered pyrolytic graphite (HOPG) as detailed in our previous work (5). In the underlying work, we focus on the relative changes of the contact potential
differences with the Au-coated SiO$_2$/Si substrate as reference. The samples were heated inside a glovebox open to the environment (without PMMA coating).

Estimation of halide diffusion coefficients (D) in CsPbBr$_3$ and CsPbCl$_3$ polycrystalline thin film: The ion conductivity ($\sigma$) is $10^{-5} \sim 10^{-6} (\Omega \cdot \text{cm})^{-1}$ in (6) at about 400K. The halide defect concentration ($n$) is expected in the order of $\sim 10^{19} \text{cm}^{-3}$ in halide perovskites(7). According to Nernst–Einstein equation: $D = \frac{\sigma k_b T}{q^2 n}$, D is estimated around $10^{-8} \sim 10^{-7} \text{cm}^2/\text{s}$.

Numerical Model.

Hopping diffusion model. Since migration of ions in the lattice structure is mediated by anion vacancies via a hopping mechanism, we define the self diffusion coefficient for a halide X (Br or Cl) as

$$D_X(x) = l(x)^2 \rho_v(x) k_X(x)$$  \hspace{1cm} (S1)

where $l$ is the typical hop length that corresponds to $a/2$ whith $a$ the lattice spacing (Fig. S16A), $\rho_v$ is the vacancy concentration (the probability that there is a vacancy in a unit cell, Fig. S16B) and $k_X$ is the rate of an activated process that an anion X jump to a vacant site (Fig. S17C). We focus our attention on the dependence of these quantities on the bromide fraction $x = [\text{Br}] / ([\text{Br}] + [\text{Cl}])$, but each is also dependent on temperature and pressure.

Assuming that an anion can migrate only when a vacancy is available immediately next to it, and that the concentration of such vacancies is low, the diffusion coefficient is simply proportional to the vacancy concentration. The vacancy concentration for binary mixtures of halides is given by the composition rule

$$\rho_v(x) = x e^{-\beta \left[ \Delta F^{(f)}_{\text{Br}}(x) + \mu_{\text{Br}} \right]} + (1 - x) e^{-\beta \left[ \Delta F^{(f)}_{\text{Cl}}(x) + \mu_{\text{Cl}} \right]}$$  \hspace{1cm} (S2)

expressed as the number of vacancy per unit cell of the perovskite crystal, where $\beta^{-1} = k_b T$ and $\Delta F^{(f)}_X(x)$ is the free energy needed to move an anion X from a pristine perovskite lattice to the vacuum and $\mu_X$ are standard state chemical potentials that account for the chemical equilibrium between the perovskite nanowire and its environment during synthesis. We use Non-Equilibrium Thermodynamic Integration (NETI) to compute the
free energies of formations (see below for details). We found that the formation free energies of vacancies are independent of the bromide fraction $x$, and are equal to $1.324 \pm 0.004$ eV and $1.438 \pm 0.003$ eV for bromide and chloride anions respectively. The resulting halide vacancy concentration (Eq. S2) is shown on Fig. S16, for $\mu_{Br} = \mu_{Cl} = 0$.

The slow diffusion encountered in crystalline solids is due to the succession of activated processes that are typical rare events. Formally, we use the Bennett-Chandler method (8, 9) to compute the rates of transitions $k_x(x)$. In this framework the rates are written as

$$k(x) = \kappa \ k_{\text{TST}}(x) \quad (S3)$$

where a first estimation of the rate is given by Transition State Theory (TST) [7]:

$$k_{\text{TST}} = \frac{k_B T}{2 \pi m_x} \frac{e^{-\beta \Delta F_x^{(m)}(z^*)}}{\int_0^{z^*} e^{-\beta \Delta F_x^{(m)}(z)} dz} \quad (S4)$$

where $\Delta F_x^{(m)}(z)$ is the free energy profile along the coordinate $z$ that interpolates between equilibrium lattice positions, $z^*$ is the position of the maximum of the free energy barrier and $m_x$ is the mass of the transitioning halide. TST neglects the possibility of recrossings of the free energy barrier that lowers the effective rate. Because CsPbX$_3$ perovskites are soft crystals, entropic effects are important as are purely dynamical effects. In the Bennett-Chandler method, accounting for these effects is achieved by computing a non-dimensional correction factor called the transmission coefficient $\kappa$ that depends in our case on the configuration used. By introducing the indicator function, $H[z(t)] = \{0 \text{ if } z < z^* \text{ or } 1 \text{ if } z \geq z^*\}$ where $z < z^*$ means that the anion is at its initial site, the time dependent transmission coefficient is given by

$$\kappa_t = \frac{\langle v(0)H[z(t)] \rangle}{\langle |v(0)|/2 \rangle_{eq}} \quad (S5)$$

where $v(0)$ is the initial velocity ($\partial_t z(0)$) of the anion equilibrated at the top of the free energy barrier ($z^*$). The numerator is the time correlation of the velocity of the anion and the function that indicates whether or not the ion swapped with the vacancy. If no barrier recrossing occurs then the transmission factor is equal to one. The denominator is simply equal to $\sqrt{k_B T / 2 \pi m_x}$. The correction factor used to correct the TST rate is the long time limit of $\kappa_t$. Typically, the long time limit is reached in a few picoseconds and few
thousands of trajectories are needed to obtain reliable statistics (details in the simulation protocols section below).

The free energy barrier along a hop trajectory (Fig. 3 main text) needed for the TST estimate of the rate is obtained using the Jarzynski equality (10):

\[ e^{-\beta \Delta F_X^{(m)}(z)} = \langle e^{-\beta \Delta W(z)} \rangle_{\text{neq}} \quad \text{(S6)} \]

where \( \Delta W(z) = W(z) - W(0) \) is the work needed to move the system through the free energy barrier. In practice, we use the Steered Molecular Dynamics (SMD) method where the system is driven out of equilibrium by the use of a time dependent harmonic potential (spring) following Park et al. (11) (see below). This non-equilibrium technique allows us to perform free energy calculations with practically no post-processing burden. In the case of mixtures, the free energy profiles are not symmetric because of the quenched disorder due to the fluctuating halide composition. In general, for a mixture, when the hopping ion has swapped with the vacancy, the free energy of the new configuration differs from the initial one. To compute the TST rate for a given free energy profile, we average the rates from the forward and backward trajectories to account for the free energy offset between the two states. We thus have

\[ k_{\text{TST}} = \frac{\sqrt{k_B T / \pi m_X}}{1 + e^{-\beta \Delta F_X^{(m)}(1)}} \left[ \frac{e^{-\beta \Delta F_X^{(m)}(z^*)}}{\int_{z_0}^{z^*} e^{-\beta \Delta F_X^{(m)}(z)} dz} + \frac{e^{-\beta \Delta F_X^{(m)}(z_1)}}{\int_{z_1}^{z^*} e^{-\beta \Delta F_X^{(m)}(z)} dz} \right] \quad \text{(S7)} \]

where we specify the free energy differences for the forward and backward trajectories as \( \Delta F_X^{(m)}(z) = F_X^{(m)}(z) - F_X^{(m)}(z_0) \) and \( \Delta F_X^{(m)}(z) = F_X^{(m)}(z) - F_X^{(m)}(z_1) \) respectively. \( z_0 \) and \( z_1 \) are the initial and the final coordinates of the hopping ion in the forward sense.

In the case of interdiffusion in perovskites with Schottky pairs of vacancies that are not strongly bound the interdiffusion coefficient can be obtained from kinetics theory following the analysis of Belova and Murch (12). Within this framework, when the ion-vacancy exchange rate of the cesium is negligible compared to those of the halides the interdiffusivity only depends on the halides’ rates. Indeed, estimates from nudged elastic bond of the lower bound of the free energy barrier for cesium hopping give 1.25 and 1.4 eV (pure Br and Cl case, resp.) which is four times larger than typical values for halides.
In the dilute vacancy limit and for an ideal binary alloy the interdiffusion coefficient simply reads (12-14)

\[ D(x) = a(x)^2 \rho_v(x) \ k_{\text{eff}}(x) \]  

(S8)

where we have defined the effective rate \( k_{\text{eff}} = F(f_0)k_{\text{Br}}k_{\text{Cl}}/\Lambda \) with \( f_0 = 0.7272 \) the geometrical correlation factor of the halide sublattice that is a body centered cubic lattice and \( \Lambda \) a function of \( k_{\text{Br}}, k_{\text{Cl}}, x = x_{\text{Br}} \) and \( F(f_0) = 2f_0/(1 - f_0) \) that is written as

\[
\Lambda = \frac{F + 2}{2} (x_{\text{Br}}k_{\text{Br}} + x_{\text{Cl}}k_{\text{Cl}}) - k_{\text{Br}} - k_{\text{Cl}} + 2(x_{\text{Br}}k_{\text{Cl}} + x_{\text{Cl}}k_{\text{Br}})
+ \sqrt{\left[\frac{F+2}{2} (x_{\text{Br}}k_{\text{Br}} + x_{\text{Cl}}k_{\text{Cl}}) - k_{\text{Br}} - k_{\text{Cl}}\right]^2 + 2Fk_{\text{Br}}k_{\text{Cl}}} .
\]  

(S9)

Finally, the relations S8-S9 allows us for a comparison with the experimental results. No significant temperature dependence was observed for the lattice spacing and the free energies of formation for the temperature range considered in experiments (348, 373, 398 K). Assuming that the vacancy concentration is established at the temperature of synthesis, then the temperature dependence for the rate is explicitly given by Eq. S7, namely the activation energy in the transition rate. The analytical model used to fit the experimental data (Fig. 2 main text) is Eqs. S8-S9 with \( a(x) = 5.625 + 0.245 x - 0.019 x^2, \rho_v(x) \) given by Eq. S2 with \( \Delta F_{\text{Br}}^{(f)}(x) = 1.324 \text{eV}, \Delta F_{\text{Cl}}^{(f)}(x) = 1.438 \text{eV}, \mu_{\text{Br}} \) and \( \mu_{\text{Cl}} \) as adjustable parameters. The interdiffusion coefficient is a function of the transition rate (Eqs. S8 and S9) where the Br and Cl rates are linearly interpolated as function of the bromide content \( x \) as \( k(x) = k(0) + x[k(1) - k(0)] \) with \( k(0) \) and \( k(1) \) that are fitted for Br and Cl at the three temperatures considered experimentally. The standard state chemical potentials are fitted against the experimental data at the highest temperature, and are set to \( \mu_{\text{Br}} = -0.9 \) eV and \( \mu_{\text{Cl}} = -1.09 \) eV.

Since the BM inversion method is sensitive to the boundary conditions of the concentrations profiles we fit the experimental datapoints in an inner range of Br fraction \( (x_{\text{Br}} \text{ between 0.5 and 0.65}) \). Fig. S15 shows that the BM method leads to different estimates of the interdiffusion coefficients at different times. In order to show that the decay of the interdiffusion coefficient with time comes from the sensitivity of the Boltzmann-Matano
method and not from an additional time dependence we test the BM inversion method on density profiles (Fig. S14) generated numerically by solving the diffusion equation with a discrete element method for a given diffusion coefficient $D = 1 - 0.9 x_{\text{Br}}$ (adimensional units). Fig. S14 shows that for early concentration profiles the BM method overestimates the diffusion coefficient while at late times, when the boundary concentration increases, the BM method underestimates the interdiffusivity and even leads to a wrong trend. This sensitivity study of the BM method motivates us to use the earliest measurements we have (Fig. S14A) to evaluate the interdiffusion coefficients and to eliminate the data close to the endpoints.

**Force field.** To study anion diffusion in the mixed halides perovskite case with molecular dynamics (MD) we first parametrized a classical force field for CsPb[Br$_x$Cl$_{1-x}$]$_3$ that borrows from Mattoni et al (15) designed for MAPbI$_3$. The pair interatomic potentials for all the ions are of the Buckingham type for the short range repulsive part with a long range part dominated by Coulomb interactions. The interaction potential for two ions $i$ and $j$ separated by a distance $r$ is thus written as:

$$U_{ij}(r) = A_{ij} e^{-r/\sigma_{ij}} + \frac{q_i q_j}{4 \pi \varepsilon_0 r} \tag{S10}$$

with $\varepsilon_0$ the vacuum permittivity, $q_i$ the electric charge of the ion $i$, $A_{ij} = \sqrt{A_i A_j}$ and $\sigma_{ij} = 0.5(\sigma_i + \sigma_j)$ the parameters of the Buckingham potential using the Lorentz-Berthelot mixing rules for interactions involving different types of ions $i$ and $j$. The parameters $q_i$, $A_i$ and $\sigma_i$ of our force field are indicated in Tab. 1. The parameters for the lead ion are directly taken from (15). The cesium interaction parameters are taken independently from (16). The parameters for the halides (Br, Cl) are derived from the iodide parameters of Mattoni et al. by scaling $A_i$ and $1/\sigma_i$ in proportion to the ratio of the known ionic radii (15). Small adjustments have been made for the energy parameters $A_{\text{Cl}}$ and $A_{\text{Br}}$ in order to reproduce the experimental values for the lattice spacing of the pure perovskites CsPbBr$_3$ (6.85 Å) and CsPbCl$_3$ (~5.625 Å) (17-19). All the calculations of this study have been performed using simulation box of 6×6×6 unit cells which is sufficient to avoid finite size effects.
Tab. S1. Parameters of the molecular force field (Eq. S10) to be completed by the following combining rules $A_{ij} = \sqrt{A_i A_j}$ and $\sigma_{ij} = 0.5(\sigma_i + \sigma_j)$.

<table>
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<th></th>
<th>$A_i$ (kcal/mol)</th>
<th>$\sigma_i$ (Å)</th>
<th>$q_i$ (e)</th>
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<tr>
<td>Cs</td>
<td>384185.64295958</td>
<td>0.27155</td>
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<tr>
<td>Pb</td>
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<td>0.131258</td>
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<tr>
<td>Br</td>
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<td>-1.13</td>
</tr>
<tr>
<td>Cl</td>
<td>25418.749309</td>
<td>0.4324822</td>
<td>-1.13</td>
</tr>
</tbody>
</table>

**Simulation protocols.** MD simulations are run in a constant pressure and temperature ensemble (NPT) for equilibration purposes for 100 ps at 300 K and 1 bar using the coupled thermostat/barostat MTK method (20) with time parameters of 100 and 400 fs for the thermostat and the barostat respectively. The same thermostat value has been used for constant volume and temperature simulations (NVT) using the Nosé-Hoover thermostat except for the computation of the transmission coefficient where a time parameter of 2 ps has been used so that the thermostat does not influence artificially the heat exchange between the hopping ion and the rest of the system. The equations of motion were integrated with a timestep of 2 fs using the LAMMPS software (21).

We find that the local composition of halides (Cl and Br) are correlated to the equilibrium location of a vacancy. In order to sample the local halide compositions and compute expectation values with the correct equilibrium weights, we performed hybrid MD/Monte-Carlo simulations by regularly (every 50 MD steps) attempting swap moves between 50 random pairs of chloride and bromide. In the spirit of the semi-grand canonical Monte-Carlo method, these trial moves are accepted according to a Metropolis criterion (22). The successful swaps are performed while ensuring the conservation of the kinetic energy by scaling their velocities by the ratio of the ion masses. Equilibrium is obtained when the rate of successful swaps remains constant as function of the time (around 13% for all the mixtures considered after ~1ns of equilibration). The local configurations used for the transmission coefficient and the free energy profile calculations are extracted from hybrid MD-MC equilibration runs while the hybrid procedure has been used during the Non-
Equilibrium Thermodynamics Integration runs for the estimations of the free energies of vacancy formation.

Overall, the diffusion model (Eq. S1) requires the numerical estimation of the lattice spacings, the free energies of vacancy formation, the free energy profiles along the hop trajectories and the transmission coefficients. Lattice spacings are obtained with NPT simulations and are shown on Fig. S16-A. The free energies of vacancy formations are obtained by Non-Equilibrium Thermodynamics Integration (NETI) in the NVT ensemble (23). The free energy is given by:

$$\Delta F^{(f)} = \int_0^\tau dt \ \langle \frac{\partial H_{\alpha}}{\partial \alpha} \rangle \frac{d\alpha(t)}{dt}$$  \hspace{1cm} (S11)

with $\alpha(t)$ a time varying parameter that slowly turns off the interactions for the ion to be removed. The averaged quantity thus corresponds to the potential energy of the ion during the alchemical transformation. In practice we use a total time of integration $\tau = 2$ ns that is slow enough to obtain the free energies in single trajectory calculations (quasistatic paths). The switching function is

$$\alpha(t) = \left(1 - \frac{t}{\tau}\right)^5 \left[70 \left(1 - \frac{t}{\tau}\right)^4 - 315 \left(1 - \frac{t}{\tau}\right)^3 + 540 \left(1 - \frac{t}{\tau}\right)^2 - 420 \left(1 - \frac{t}{\tau}\right) + 126\right]$$

with zero time derivatives when $t$ tends to 0 or $\tau$. Such a choice prevents energy spikes during the calculations.

The free energy profiles along the hopping trajectories are computed via the Jarzynski equality from SMD (10, 11) by biasing the Hamiltonian of the system with a time dependent harmonic potential (spring) acting on the hopping ion:

$$U_s(x) = \frac{K}{2} [z(t) - z_s(t)]^2, \text{ with } z_s(t) = z(0) + \nu_s t$$  \hspace{1cm} (S12)

the rest position of the spring and $z(t)$ the coordinate of the ion. We used a spring constant $K = 5000 \text{ kcal mol}^{-1} \text{ Å}^{-1}$ and a constant velocity $\nu_s = 0.06 \text{ Å/ps}$ to drive the hopping anion along the $z$ coordinate from its equilibrated initial position to the vacancy location, and in the backward trajectory. The work performed by the spring is then recorded during the trajectories to compute the free energy. We use 5 independent pairs of forward and backward steered trajectories to compute the non-equilibrium average (Eq. S6). The equilibration before a steered trajectory is done while tethering the halide neighbors of the vacancy with a soft spring so as to prevent the vacancy to diffuse. These constraints are
removed during the steering process. We checked that the spring constant (50 kcal mol$^{-1}$ Å$^{-1}$) used during the equilibration was low enough to have no influence on the free energy calculation. We used 20 different mixtures configurations for each halide species (Br, Cl) at a given bromide fraction $x$ in order to average the rates and the transmission coefficients (Fig. S17).

The transmission coefficients are obtained by computing the correlation function (Eq. S5) averaged over 5000 small trajectories of 2 ps long initiated at the top of the free energy barriers so as to sample the Maxwell-Boltzmann distribution. The free energy maximum being known from the previous calculation. The system is equilibrated in NVT with a time constant of 100 fs at the top of the barrier to generate the initial configurations.

References:

Fig. S1 PL emission and corresponding SEM EDS mapping of two typical CsPbBr$_3$-xCl$_x$ nanowires with different Br/(Br+Cl). (A, C) A nanowire with PL peak emission at 458nm show Br/(Br+Cl) = 0.5 from EDS. (B, D) A nanowire with PL peak emission at 509 nm show Br/(Br+Cl) = 0.8 from EDS.
Fig. S2. The plot of PL peaks with different $\text{Br}/(\text{Br}+\text{Cl})$ ratio from EDS. It shows an approximate linear relationship. Therefore, the Br concentration can be calculated with PL emission wavelength.
Fig. S3 *In-situ* PL spectrum evolution of the CsPbBr$_3$-CsPbCl$_3$ nanowire at 100°C. (A) From 0 h to 1.5 h. The inset is enlarged spectrum for Cl rich part (B) from 1.5 h to 5 h. (C) 5 h to 7 h. (D) The PL peak shift of the Cl rich part during the annealing process.
Fig. S4 Halide distribution profile through confocal PL wavelength scanning. (A) Lambda scan of a nanowire after heating for 2.5 h at 125 °C (interval 5 nm). The scale bar is 2 µm. (B) Spatial Br/(Br+Cl) profile along the nanowire in (A). Br/(Br+Cl) is calculated with PL emission wavelength. The error bar is calculated from the scan wavelength interval. The concentration profile has good Gaussian fitting $y = y_0 + Ae^{-\frac{(x-x_c)^2}{2w^2}}$. 
**Fig. S5** Confocal PL evolution of CsPbBr$_3$-CsPbCl$_3$ heterojunction nanowires under 125 °C and 75 °C heating. (A-D) at 125 °C: (A) 0 h (B) 1.5 h (C) 2.5 h. (D) 5 h. (E-H) at 75 °C: (E) 0 h (F) 1.5 h (G) 5.5 h. (H) 18 h. The scale bar is 2 µm. E was blue colored from 405 nm to 450 nm and green colored from 450 nm to 550 nm. The other images were generated with Zen 2010 software with lambda coded.
**Fig. S6.** Evolutions of $\text{Br}/(\text{Br}+\text{Cl})$ profiles of heterojunction nanowires at different temperature in Fig.S5. (A) 75 °C. (B) 125 °C.
Fig. S7 Axially integral of Br concentration of heterojunction nanowires in Fig. 2A and Fig. S6. (A) 75 °C. (B) 100 °C. (C) 125 °C. The Br concentration is reasonably conserved during the annealing, indicating there is no halide transport into the environment. The volume differences between CsPbBr$_3$ and CsPbCl$_3$ is not taken into account when integrating Br concentration. The real Br concentration might be 9% larger than integral in a simplified model: the length of CsPbBr$_3$ and CsPbCl$_3$ is equal axially and the volume of CsPbCl$_3$ is $\sim$ 13% smaller than CsPbBr$_3$. The blue circle shows the correction. There are also other factors which may contribute to the deviation, such as spatial limitation in confocal PL.
Fig. S8 Confocal PL evolution of a “reverse “CsPbBr3-CsPbCl3 heterojunction nanowire at 125°C. The heterojunction was made via anion exchange from CsPbCl3 nanowire templates. The Br⁻-Cl⁻ interdiffusion process is the same as the “normal” heterojunctions from CsPbBr3 templates: The Br rich part got shorter and the pristine Cl part became expanded due to the higher diffusivity of Br⁻. The Br⁻ could diffuse into the far end of pristine CsPbCl3. The scale bar is 2 µm. The PL images is lambda colored based on the emission wavelength.
Fig. S9 KPFM surface potential profiles in Figure 4D with corresponding concentration of Br/(Br+Cl) profiles. (A) The initial hetero-junction showed distinguishing interface in surface potential and concentration at approximately the same position. (B) After 1.5 h heating at 100 ºC, the electronic interface resolved in surface potential mapping shifted to the CsPbBr$_3$ part, which closely correlated with the concentration distribution. (C) The surface potential appears to be overall homogeneous without distinct interface after 5 h heating. The relatively smaller concentration gradient along the nanowire may make it challenging to resolve the electronic differences by KPFM technique.
Figure S10. AFM topographical imaging of the CsPbBr$_3$-CsPbCl$_3$ heterojunction nanowire analyzed in Figure 4D by KPFM. AFM topography (top) and corresponding height profile (bottom) of the (A) as-synthesized, (B) 1.5 h annealed at 100 °C, and (C) 5 h annealed at 100 °C sample, respectively. The surface roughness factors are (A) 3.55 nm, (B) 4.35 nm, and (C) 6.91 nm, respectively. Upon consecutive thermal annealing of the heterojunction nanowire at 100 °C for 1.5 h and 5 h, respectively, we observe structural relaxation of the CsPbBr$_3$-CsPbCl$_3$ interface. The lattice-mismatch-induced strain release at the CsPbBr$_3$-CsPbCl$_3$ interface is inherently linked to a gradual height transition extending over ~ 1 µm. All scale bars are 2 µm.
Fig.S11 Fluorescence lifetime evolution with corresponding confocal PL images of a CsPbBr$_3$-CsPbCl$_3$ heterojunction nanowire at 100 °C. (A) Initial heterojunction before annealing (0 h). The below is corresponding confocal PL image. (B) After 1.5 h annealing. (C) After 5 h annealing. The long lifetime region shows a close correlation with shrinking of CsPbBr$_3$. The scale bar is 2 µm. Time-resolved PL decay curves corresponding to locations (red, blue, purple squares) along the hetero-nanowire are shown for 0 h, 1.5 h, and 5 h respectively, fitted with single nearly single-exponential dynamics. For the initial heterojunction, the Cl rich part (purple square) features a fast PL decay ($\tau \sim 340$ ps), owing to the intrinsic short lifetime of CsPbCl$_3$. The Br rich parts have longer lifetime, 2153 ps and 2093 ps for red and blue squares respectively. After 1.5h heating, the lifetimes are 1432 ps, 987 ps, 511ps for red, blue, purple squares. The lifetimes become 1379 ps, 984 ps, 489 ps after 5 h heating.
Fig. S12. Normalized PL lifetime profiles (black line) with correlated Br/(Br+Cl) profiles (red line). The PL lifetime distribution is closely associated with composition evolutions.
Fig. S13 An illustration of Boltzmann-Matano method to calculate inter-diffusion coefficient. The concentration profile has good Gaussian fitting $y = y_0 + Ae^{-\frac{(x-x_0)^2}{2\sigma^2}}$ for the profile between $C_L$ and $C_H$. The Matano plane is $X_M$ where the area $S_1 = S_2$. The inter-diffusion coefficient at $C^*$ is calculated from $D^-(C^*) = -\frac{1}{2t} \int_{C_L}^{C^*} \frac{(x-x_M) dC}{(dC/dx)_C}$. 
Fig. S14. (A) Bromide concentration profiles obtained from the discrete element solution of the diffusion equation at different time steps indicated by colors. The concentration dependent inter-diffusion coefficient used to generate the dynamics is indicated by a dashed line in B. The other solid lines in panel B are the results of the BM inversion method applied to the concentration profiles shown in A.
Fig. S15 Interdiffusion coefficients calculated by the Boltzmann-Matano method (symbols in A, B, C) at 75, 100 and 125 °C in blue, red and black, respectively, after different times. Additionally, in (C), we gather all the data for 125 °C including the diffusion coefficients measured from a heterojunction processed initially from a Cl perovskite instead of a Br one (indicated by (r) for reverse heterojunction). The solid lines in panels A and B stand for the analytical model fitted against the datapoints between 0.5 and 0.65.
Fig. S16. (A) Size of the perovskites unit cells. (B) vacancy concentration (Eq. S2) per unit cell, computed from MD simulations (300K, 1 bar) as function of the bromide fraction. The solid line (A) stands for a polynomial fit of second order ($5.625 + 0.245 x - 0.019 x^2$). The free energies of formation for bromide and chloride vacancies are 1.324 eV and 1.438 eV, respectively.
Fig. S17. (A) Hopping rate as given by the Transition State Theory (Eq. S7); (B) transmission coefficient; (C) hopping rate corrected by the transmission coefficients, as function of the bromide fraction (MD simulations, 300 K, 1 bar). Results for bromide and chloride are respectively in green and blue. Standard errors are computed over the 20 independent samples (mixtures case) used to average the results. The corrected rates (C) stand for the average of the product of the TST rates and the transmission coefficients \( k = \frac{1}{N} \sum_{i=1}^{N} \kappa^{(i)} k^{(i)}_{TST} \) with \( N = 20 \) the number of mixtures configurations).