ANION DIFFUSION IN TWO-DIMENSIONAL HALIDE PEROVSKITES

by

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Dedicated to my parents, Veena Singh & Arun Kumar

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Figure 3.1: Optical and morphological characterizations of 2D lateral heterostructures. a, Schematic illustration of lateral heterostructures along with chemical structures of BA, PEA, 2P, and 1T organic cations. The inorganic octahedra in blue represent the bromide perovskite and the inorganic octahedra in green represent the iodide perovskite. **b, c, d, e,** BF, PL, SEM and AFM images of (BA)₂PbI₄-(BA)₂PbBr₄. **f, g, h, i,** BF, PL, SEM, and AFM images of (PEA)₂PbI₄-(PEA)₂PbBr₄. **j, k, l, m,** BF, PL, SEM, and AFM images of (1T)₂PbI₄-(1T)₂PbBr₄. **n, o, p, q,** BF, PL, SEM, and AFM images of (2P)₂PbI₄-(2P)₂PbBr₄. The dashed yellow lines in SEM and AFM images highlight the lateral heterojunctions separating the central bromide and edge iodide perovskites. All AFM images have been superimposed with height profiles along the dashed black **Figure 3.3: Quantification of halide inter-diffusion. a,** Comparison of impact of organic cations on the concentration dependent Br-I inter-diffusion coefficients across BA, PEA, 1T, and 2P based lateral heterostructures using analytical BM method at 100 °C after heating for 30 mins. The box represents data points between 25 – 75 percentiles of the range, whisker represents the minimum-to-maximum range, and the dashed line highlights the average diffusion coefficients of the sample data points. **b,** Side view and top view depiction of the two potential halide diffusion pathways in the inorganic octahedral framework of perovskites. Layer 0 represents the axial halides and layer 1 represents the equatorial halides. I, Pb, S, N, C, and H atoms are illustrated by green, orange, yellow, blue, grey, and white spheres, respectively. Organic cations have not been shown in all illustrations for the purpose of clarity. Representative free energy (FE) barrier calculation in kcal(mol)⁻¹ for the two migration pathways – layer 1 to layer 0 and layer 1 to layer 1 is also shown.

Figure 3.5: Impact of inorganic layer thickness. a, Comparison of concentration dependent Br-I inter-diffusion coefficients across (PEA)₂(MA)_{n-1}Pb_nI_{3n+1}-(PEA)₂(MA)_{n-1}Pb_nBr_{3n+1} (n = 1, 2, 3) lateral heterostructures using analytical BM method at 100 °C after heating for 30 mins. The box represents data points between 25 - 75 percentiles of the range, whisker represents the minimum

LIST OF ABBREVIATIONS

0D	Zero-dimensional
1D	One-dimensional
1T	Thiophenylethylammonium
2D	Two-dimensional
2P	Biphenylethylammonium
2T	Bithiophenylethylammonium
3D	Three-dimensional
AFM	Atomic Force Microscopy
AFOSR	Air Force Office of Scientific Research
AN	Acetonitrile
BA	Butylammonium
BF	Bright-field
BM	Boltzmann-Matano
CB	Chlorobenzene
ChEM	Center for High-resolution Electron Microscopy
CPD	Contact Potential Difference
DCB	Dichlorobenzene
DFT	Density Functional Theory
DLTS	Deep-level Transient Spectroscopy
DMF	Dimethylformamide
DOS	Density of States
EDAX	Energy Dispersive X-ray Analysis
EDS	Energy Dispersive X-ray Spectroscopy
EQE	External Quantum Efficiency
FE	Free Energy
FEG	Field Emission Gun
FIB	Focused Ion Beam
GGA	Generalized Gradient Approximation
IMPS	Intensity Modulated Photocurrent Spectroscopy

IMVS	Intensity Modulated Photovoltage Spectroscopy
IS	Impedance Spectroscopy
KMC	Kinetic Monte Carlo
KPFM	Kelvin Probe Force Microscopy
LAMMPS	Large-scale Atomic / Molecular Massively Parallel Simulator
LED	Light Emitting Diode
LSCM	Laser Scanning Confocal Microscope
MA	Methylammonium
MD	Molecular Dynamics
PA	Propylamine
PAW	Projector Augmented Wave
PBC	Periodic Boundary Conditions
PBE	Perdew, Burke and Ernzerhof
PCE	Power Conversion Efficiency
PDA	1,3-propanediamine
PDOS	Projected Density of States
PEA	Phenylethylamine
PL	Photoluminescence
PLQY	Photoluminescence Quantum Yield
PMMA	Polymethyl methacrylate
PPPM	Particle-particle-mesh
RH	Relative Humidity
RP	Ruddlesden-Popper
RT	Room Temperature
SEM	Scanning Electron Microscopy
SMD	Steered Molecular Dynamics
SOC	State of Charge
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectroscopy
UB	Umbrella Sampling

VASP	Vienna Ab initio Simulation Package
vdW	Van der Waals
WHAM	Weighted Histogram Analysis Method
XRD	X-ray Diffraction

ABSTRACT

Technological advancements in electronics industry are driven by innovations in device fabrication techniques and development of novel materials. Halide perovskites are one of the latest additions to the semiconductor family. The performance of solid-state devices based on halide perovskites is now competing with other well-established semiconductors like silicon and gallium arsenide. However, the intrinsic instability of three-dimensional (3D) perovskites poses a great challenge in their widespread commercialization. The soft crystal lattice of hybrid halide perovskites facilitates anionic diffusion which impacts material stability, optoelectronic properties, and solid-state device performance.

Two-dimensional (2D) halide perovskites with organic capping layers have been used for improving the extrinsic stability as well as suppressing intrinsic anionic diffusion. Nevertheless, a fundamental understanding of the role of compositional tuning, especially the impact of organic cations, in inhibiting anionic diffusion across the perovskite-ligand interface is missing. In our research, we first developed a library of atomically sharp and flat 2D heterostructures between two arbitrarily determined phase-pure halide perovskite single crystals. This platform was then used to perform a systematic investigation of anionic diffusion mechanism and quantify the impact of structural components on anionic inter-diffusion in halide perovskites.

Stark differences were observed in anionic diffusion across 2D halide perovskite lateral and vertical heterostructures. Halide inter-diffusion in lateral heterostructures was found to be similar to the classical Fickian diffusion featuring continuous concentration profile evolution. However, vertical heterostructures show a "quantized" layer-by-layer diffusion behavior governed by a local free energy minimum and ion-blocking effects of the organic cations. For both lateral and vertical migrations, halide diffusion was found to be faster in perovskites with larger inorganic layer thickness. The increment becomes less apparent as the inorganic layer thickness increases, akin to the quantum confinement effect observed for band gaps. Furthermore, we found that bulkier and more rigid π -conjugated organic cations. These results offer significant insights into the mechanism of anionic diffusion in 2D perovskites and provide a new materials platform for heterostructure assembly and device integration.

1. BACKGROUND AND LITERATURE REVIEW

Technological advancements in the field of electronics are driven by innovations in device architecture and discovery of novel materials. Silicon and group III-V semiconductors are the dominant materials used in commercial solid-state devices. However, there has been an increasing demand for incorporation of semiconducting materials which can offer low-cost manufacturing and new functionalities.¹ Metal halide perovskites have emerged as promising additions to the family of semiconductors owing to their facile low-temperature solution-processed synthesis and remarkable optoelectronic properties. Due to their high optical absorption coefficient, narrow-band bright photoluminescence (PL), tunable bandgap, shallow defects, low exciton binding energy, and long-range carrier diffusion, halide perovskites have already been used in fabrication of solar cells, light emitting diodes (LEDs), photodetectors, transistors, and lasers.

1.1 Origin and structure of perovskites

The name "perovskite" originates from the Russian mineralogist L. A. Perovski who discovered $CaTiO_3$ in 1839. More than half a century after the initial identification of the naturally occurring oxide perovskites, a series of halide perovskites were synthesized. Halide perovskites represent the crystallographic family with the general ABX₃ stoichiometry, where 'A' is an organic or inorganic monovalent cation, 'B' is a divalent metal cation, and 'X' is a monovalent halide anion.²⁻³

Halide perovskites offer dimensionality control as they can be networked in threedimensional (3D), two-dimensional (2D), one-dimensional (1D), and zero-dimensional (0D) morphologies through size and quantum confinement. Morphological low-dimensional perovskites are obtained by size reduction of the 3D perovskite. These low-dimensional perovskites have the same crystal structure or ABX₃ building block as 3D perovskites, but they are confined in one or more directions. Molecular low-dimensional perovskites are obtained by altering the chemical structure of ABX₃ 3D perovskites by introducing organic spacer cations. These low-dimensional perovskites have the same $[PbX_6]^{4-}$ inorganic octahedral building block as 3D perovskites but the overall structure depends on the intercalating organic cations. **Figure 1.1** shows a schematic representation of the morphological and molecular low-dimensional perovskites.⁴



Morphological Low-dimensional halide perovskites (ABX₃)

Molecular Low-dimensional halide perovskites (non-ABX₃)

Figure 1.1: Structure of low-dimensional halide perovskites. Morphological low-dimensional perovskites with ABX₃ building blocks and molecular low-dimensional perovskites with $[PbX_6]^{4-}$ building blocks. Reprinted from *Materials Science & Engineering R*, **137**, Zhou, C.; Lin, H.; He, Q.; Xu, L.; Worku, M.; Chaaban, M.; Lee, S.; Shi, X.; Du, M. H.; Ma, B., Low dimensional metal halide perovskites and hybrids, 38–65, 2019, with permission from Elsevier.⁴

1.2 Applications of halide perovskites

The first utilization of 3D halide perovskites as visible light sensitizers in solar cells was in 2009.⁵ Since then, there has been a tremendous boost of research and development in the field of halide perovskite optoelectronics. 3D perovskite-based solar cells with > 25 % power conversion efficiency (PCE) and LEDs with > 20% external quantum efficiency (EQE) have already been reported.^{6,7}

High color purity, narrow bandgap, tunable PL, and high PL quantum yield (PLQY, up to 100 %) make 0D perovskites quite promising for future display technologies.⁸ In 2019, Liang *et al.* reviewed the unique properties of 0D perovskites and their applications in the field of photoelectrochemistry. The review paper highlights the advancements made in application of perovskite quantum dots in photocatalytic degradation, photocatalytic CO₂ reduction, photoelectrochemical sensing, and photovoltaic devices.⁹

1D halide perovskites are quite promising for their potential in lighting applications owing to their large band gap and high exciton binding energy.¹⁰ Using perovskite nanowires, Zhu *et al.*

demonstrated room-temperature and wavelength-tunable lasing with very low lasing thresholds (220 nJ.cm⁻²) and high quality factors (\sim 3600). The long carrier lifetimes and low non-radiative recombination rates in 1D perovskites, make them promising candidates for applications in nanophotonics, optical computing and chemical / biological sensing.¹¹

2D halide perovskites have been extensively used in fabrication of solar cells and LEDs. In 2018, Chen *et al.* demonstrated that improvement in charge transport properties of 2D perovskite solar cells can be achieved by controlling the orientation of crystallization. Vertically orientated nucleation and growth of the 2D films led to unhindered transport of carriers across the absorbing layer, resulting in higher short circuit current density, lower series resistance and higher PCE compared to non-orientated films.¹² In their review paper, Zhang *et al.* discuss the advancements in 2D perovskite LEDs and their bright future in ultrahigh-definition displays, solid-state lighting, optical communications, *etc.*¹³ In addition to solar cells and LEDs, Sn-based 2D halide perovskites with conjugated organic cations have shown promise in thermoelectric device applications.¹⁴ Xie *et al.* demonstrated the versatility of Li doped (PEA)₂PbBr₄ scintillator as radiation detectors for a wide range of energies from keV up to MeV.¹⁵ The color tunability and solution processability of 2D halide perovskites also make them a promising gain media for lasing. In 2020, Qin *et al.* utilized 2D perovskite to fabricate a stable green laser under continuous wave optical pumping in air at room temperature.¹⁶

1.3 Stability issues in halide perovskites

High performance, low cost, and high stability are three key metrics considered for successful commercialization of a semiconductor material. The performance of perovskite-based devices is already competitive with conventional semiconductors, and compatibility with simple solution-processing offers cost-effective manufacturing opportunities. Currently the biggest hurdle for halide perovskite commercialization is their reduced device lifetimes compared to prevailing inorganic semiconductors.¹⁷⁻¹⁹ The instability of halide perovskites stems from extrinsic and intrinsic factors. The extrinsic instability leading to degradation of perovskites when exposed to ambient oxygen and moisture can be resolved by encapsulation of the devices. However, the intrinsic instability, which originates from facile ion migration in the soft crystal lattice of perovskites, can only be resolved by developing a comprehensive understanding of the diffusion kinetics. Ionic diffusion in perovskites leads to anomalous response from both the stand-alone

materials and devices under external stimuli, including light, heat, and electric bias. Depending on the operating condition, one or more of these external stimuli can play a governing role in determining the material and device stability. In turn, comparative studies of materials and devices shed light on intrinsic material susceptibilities versus device specific susceptibilities (*e.g.*, resulting from specific materials interfaces).

Figure 1.2 a, b demonstrates the typical photodegradation behavior of 2D and 3D perovskites. The Br:I mixed halide 3D perovskite, MAPb($Br_{0.6}I_{0.4}$)₃ (MA = methylammonium) thin film initially exhibits a high energy emission corresponding to bromide-rich species (Figure **1.2a**). After light soaking for two minutes, a new low energy emission associated with iodine-rich species dominates the PL spectra. This change in PL emission was observed under sequential light soaking and dark relaxation cycles. The reversible change in emission response of halide perovskite under photoexcitation shows the instability of the material under illumination and alludes to halide movement in the thin film.²⁰ Compared to 3D perovskites, 2D perovskites offer better stability due to their higher formation energies and encapsulation by organic spacer cations.²¹ However, even for 2D perovskites, ionic diffusion and stability issues are not completely resolved. Figure 1.2b shows the absorption spectra of pristine $(PEA)_2PbX_4$ (X = Br, I, PEA = phenylethlyammonium) thin films coated on glass slides. The pristine absorption spectra exhibit a 405 nm peak from (PEA)₂PbBr₄ and a 515 nm peak from (PEA)₂PbI₄. The bromide and iodide perovskite glass slides are then clamped together and annealed at 140 °C. The external heat stimulus induces Br / I halide migration leading to change in composition and thereby absorption spectra of the pristine films. After thermal annealing, both bromide and iodide thin films show a single absorption peak at 435 nm, indicating the homogenization of halide composition across the two films.²²

The intrinsic material instabilities in halide perovskites also leads to reliability issues in devices. Ahmad *et al.* tracked PCEs of three perovskite-based solar cells over a period of ~ 8 days. Over this period, the solar cells were tested for their heat stability by placing them on a 85 °C hot plate in an open atmosphere with a relative humidity (RH) of 40 - 70 %. The 3D MAPbI₃ based solar cell showed a 50 % reduction in PCE within 1 hour of operation. In contrast, the 2D propylamine (PA) perovskite solar cells maintained 95 % of their initial PCE for several hours, followed by PCE degradation to < 30 % after 168 hours. The 2D 1,3-propanediamine (PDA) based perovskite devices demonstrated the best stability and maintained 95 % of their initial PCE after

continuous heating in air for 168 hours.²³ The better stability of 2D perovskites under damp heat stress can be attributed to the stabilizing effect of the organic layers on the overall crystal structure. The thermal stability of 2D perovskites although comparatively superior to 3D perovskites, is still not at par with commercial semiconductors.



Figure 1.2: Material and device instabilities in halide perovskites. a, PL spectra of MAPb(Br_{0.6}I_{0.4})₃ thin film during sequential illumination and dark cycles. Illumination time is 2 mins, followed by dark relaxation of 5 mins. Reproduced from Ref. 20 with permission from the Royal Society of Chemistry.²⁰ **b**, Absorption spectra of $(PEA)_2PbX_4$ (X = Br, I) films before and after homogenization treatment at 140 °C. The inset shows the photographs of Br and I perovskites before and after homogenization. Reprinted with permission from ACS Materials Lett., 2, 6, Cho, J.; Dubose, J. T.; Le, A. N. T.; Kamat, P. V., Suppressed Halide Ion Migration in 2D Lead Halide Perovskites, 565–570. Copyright 2020 American Chemical Society.²² c, I-V characteristic of a halide perovskite solar cell under forward and reverse bias. Inset shows the schematic of the device architecture. Reprinted with permission from J. Phys. Chem. Lett., 6, 22, Kim, H. S.; Jang, I. H.; Ahn, N.; Choi, M.; Guerrero, A.; Bisquert, J.; Park, N. G., Control of I-V Hysteresis in CH₃NH₃PbI₃ Perovskite Solar Cell, 4633–4639. Copyright 2015 American Chemical Society.²⁴ d, Photocurrent response of a lateral perovskite device with and without electrical poling under 0.25 sun illumination. Arrows indicate the scan direction. Reprinted by permission from Springer Nature, Nature Mater, 14, 2, Xiao, Z.; Yuan, Y.; Shao, Y.; Wang, Q.; Dong, Q.; Bi, C.; Sharma, P.; Gruverman, A.; Huang, J., Giant switchable photovoltaic effect in organometal trihalide perovskite devices, 193–198. Copyright 2015.²⁵

In addition to light and heat activation, halide migration in perovskite-based devices also leads to detrimental device hysteresis when subjected to electrical bias. **Figure 1.2c** depicts the current-voltage characteristics of a MAPbI₃ based solar cell. The forward and reverse voltage scans do not follow the same curve and show hysteresis behavior. Hysteresis can be linked to halide diffusion in the absorbing layer and subsequent interaction with the other contact layers.²⁴ Another example of halide diffusion under external bias is the observation of electrical poling. Photocurrent response of a lateral perovskite device is shown in **Figure 1.2d**. The non-poled device sustains no photovoltaic effect and exhibits zero open circuit voltage (V_{OC}) because of the symmetric structure of the device. The poled device depicts a reversal in photovoltaic response upon changing the direction of the bias. Positive poling leads to accumulation of cations at the Au electrode forming a p–i–n homojunction structure. Whereas negative poling leads to formation of a n–i–p homojunction. This effect can be ascribed to the ionic movement in the perovskite layer.²⁵

1.4 Overview of halide diffusion studies in literature

Investigation into the diffusion channels and diffusing species in halide perovskites is crucial to understand and resolve the material stability challenges. The crystal lattice of halide perovskites is considered soft and tolerant to defects.²⁶ Though this defect tolerance enables facile synthesis, it also facilitates ionic diffusion. Local lattice distortions caused by charge accumulation, impurities, and strain also act as ion transport channels. Point defects tend to accumulate more at interfaces and grain boundaries than within the bulk crystal; therefore, polycrystalline films exhibit faster ionic diffusion compared to single crystals. In the bulk crystal, the predominant diffusion pathway is mediated by vacancies.²⁷

To deconvolute the impact of different mobile species on overall diffusion, many computational modeling studies have been performed. Using density functional theory (DFT), researchers have estimated the activation energies required for formation of cationic and anionic vacancies. **Figure 1.3a** provides a summary of activation energy calculations for I⁻, MA⁺, and Pb²⁺ vacancies. Based on the sample data points, average energy barriers for I⁻, MA⁺, and Pb²⁺ migration are 0.29 eV, 0.62 eV, and 1.56 eV, respectively. The lowest activation energy for iodide vacancies indicate that halide migrations predominate the diffusion in perovskite lattice.²⁸⁻³³ To experimentally validate the governing role played by anionic vacancies, Senocrate *et al.* measured ionic conductivity of a MAPbI₃ pellet under different iodine partial pressures. The ionic

conductivity decreased with increasing iodine partial pressure, which can be explained by the reduction of mobile iodide vacancies due to incorporation of I₂ from gas phase. To further demonstrate the dominant role of I⁻ rather than MA⁺ species in ionic migration, the authors performed a tracer exchange experiment. The experiment involved placing two samples of MAPbI₃ in contact with each other in which one of the samples was enriched with ¹³C- and ¹⁵N- isotopes. After annealing the two samples, a depth profile across the MAPbI₃ sample was obtained using time-of-flight secondary ion mass spectroscopy (ToF-SIMS). From the depth profile, it was evident that there is negligible diffusion of ¹³C- into the MAPbI₃ sample.³⁴ From the theoretical calculations, ionic conductivity measurements, and tracer diffusion experiments, we can conclude that the stability of perovskites is dictated by vacancy-mediated halide diffusion.



Figure 1.3: Characterizing diffusion in halide perovskites. a, Activation energy barriers for vacancy mediated diffusion of I⁻, Pb⁺, and MA⁺ ions.²⁸⁻³³ **b**, Comparison of ionic defect migration rates measured using various time domain and frequency domain methods. Reprinted from <u>https://pubs.acs.org/doi/10.1021/acsenergylett.1c02076</u>.^{37,38,39}

Diffusion studies in halide perovskites have focused on utilizing numerous electrical characterizations to probe the density of defects in the material. Impedance spectroscopy (IS) and deep-level transient spectroscopy (DLTS) are two of the most commonly used techniques to probe the ionic defect landscape in halide perovskites. In addition to IS and DLTS, which mostly capture the response to voltage perturbations, a range of electrical techniques have been developed to measure the response to light perturbations. Light stimulus has been used to measure current in intensity modulated photocurrent spectroscopy (IMVS).^{35,36} A summary of the temperature-dependent ionic migration rates extracted using IS, DLTS, IMVS, and IMPS characterizations is shown in **Figure**

1.3b. It is evident that the various perturbations (voltage or light) and observables (capacitance, current, or voltage) in both the frequency and time domain yield comparable migration rates.^{37,38,39} Utilizing electrical characterizations for diffusion studies makes it challenging to deconvolute the impact of device architecture, interlayers, cationic and anionic migrations. Therefore, it is necessary to explore characterization techniques that isolate these factors.

1.5 Research objectives

The development of heterostructure platform for visualization of halide diffusion was a major development in the 3D perovskite field. Instead of relying on indirect electrical measurements, in-situ PL mapping of the heterostructures helps in directly probing the intrinsic anionic diffusion. In my research, I have focused my attention on 2D halide perovskite materials as they offer better stability and higher compositional flexibility compared to their 3D counterparts. Specifically, I have investigated halide diffusion kinetics in the most extensively studied 2D Ruddlesden-Popper (RP) phase perovskites which can be represented by the general formula $L_2A_{n-1}B_nX_{3n+1}$, where 'L' is a monovalent spacer organic cation. The objective of my research is to understand the mechanism of halide diffusion and perform a systematic analysis of factors that impact halide diffusion in RP phase 2D perovskites.

In the following sections, I will discuss the synthesis techniques developed for 2D perovskite heterostructures, and their utilization in qualitative and quantitative diffusion studies.

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2. HALIDE DIFFUSION IN 2D PEROVSKITE VERTICAL HETEROSTRUCTURES

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2.1 Introduction

Halide perovskites are promising semiconductors for next-generation solution-processed optoelectronics, but their remarkable properties are often over-shadowed by their poor material stability.¹⁻⁷ The intrinsic instability of perovskites is dictated by the "soft" ionic framework. This soft lattice enables high ionic mobility, which results in detrimental impacts on perovskite-based optoelectronic devices, such as current-voltage hysteresis, spontaneous phase segregation in alloys, diminished transistor behavior at room temperature, and photoinduced self-poling effects.⁸⁻¹² Recently, direct visualization of ion migration in three-dimensional (3D) perovskite heterostructures has been realized and the solid-state diffusivity of halides is estimated to be in the order of $10^{-14} \sim 10^{-18}$ m²/s at a temperature slightly above room temperature, which is dramatically higher than that of Si or oxide perovskites.¹³⁻¹⁶

To address the intrinsic stability issue, two-dimensional (2D) halide perovskites incorporating hydrophobic organic capping ligands have been studied as promising alternatives.¹⁷⁻¹⁹ In the past few years, high performance optoelectronics with improved stability and suppressed anion migration have been demonstrated using polycrystalline quasi-2D perovskite thin films.²⁰⁻²² However, a comprehensive quantitative analysis of the factors impacting anionic migration in these 2D halide perovskites is still lacking. This is largely limited by the difficulty of obtaining a clean system free from uncertain variables such as defects, grain boundaries, and phase impurities. Here, we demonstrate the first quantitative investigation of the anionic inter-diffusion across atomically flat 2D perovskite vertical heterojunctions. Interestingly, the halide diffusion does not follow the classical process. Instead, a "quantized" layer-by-layer diffusion model is proposed to describe the behavior of the anionic migration in 2D perovskites and provide a new materials platform for heterostructure construction and device integration.



Figure 2.1: Assembly and characterization of $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure. **a**, Assembly of bromide-iodide perovskite vertical heterostructure by mechanical exfoliation of iodide perovskite on bromide perovskite using a ScotchTM tape. **b**, AFM image of vertical heterostructure with thicknesses of bromide and iodide layers. The blue scale bar is 2 µm. **c**, SEM image of a representative vertical heterostructure. **d**, **e**, **f**, EDS elemental mappings of Pb, Br, and I, respectively, for the SEM image in **c**. **g**, **h**, Confocal mappings of vertical heterostructure using 405 nm laser as excitation wavelength and emission channel widths of 410 – 460 nm and 560 – 650 nm, respectively. **i**, Dual-channel confocal mapping by superimposing **g** and **h**. All white scale bars are 5 µm. **j**, PL spectrum of vertical heterostructure at room temperature depicting blue emission (~ 410 nm) from bromide layer and red emission (~ 615 nm) from iodide layer.

2.2 Assembly of vertical heterostructures

The vertical heterostructures are assembled by transferring the bulk crystals of top iodide layer onto the pre-grown bromide nanocrystals using mechanical exfoliation (**Figure 2.1a and Appendix Figure A.1**). Independently synthesizing the perovskite layers before assembling the heterostructure ensures higher phase purity compared to previously reported techniques of heterostructure construction using sequential growth or chemical vapor deposition.²³⁻²⁷ Following

this synthesis strategy, a variety of high-quality bromide-iodide 2D perovskite vertical heterostructures have been constructed.



Figure 2.2: Cross-sectional characterization of $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure. a, SEM image of the vertical heterostructure (top view). The dashed rectangle highlights the area used for cross-sectional characterization. b, Carbon coating of the rectangular area of interest. Preparation of the cross-sectional lamella by c, digging a hole and d, thinning by Ga ions. e, Prepared cross-section of the vertical heterostructure. All yellow scale bars are 10 µm. f, Low-magnification STEM image of the vertical heterostructure. The blue scale bar is 1 µm. g, Enlarged STEM image of the vertical heterostructure. STEM images show a clear interface between $(BA)_2PbBr_4$ and $(BA)_2(MA)_2Pb_3I_{10}$. EDS elemental mapping of h, Pb, i, Br, and j, I. k, Overlaid bromine and iodine EDS mapping. All white scale bars are 200 nm. The brighter bromine and iodine signals in the EDS elemental mappings are mainly concentrated in the pure phase $(BA)_2PbBr_4$ and $(BA)_2(MA)_2Pb_3I_{10}$ regions, respectively. The dimmer Br signal from $(BA)_2(MA)_2Pb_3I_{10}$ region and iodine signal from $(BA)_2PbBr_4$ region can be attributed to diffusion, which is likely caused by the harsh sputtering and focused ion-beam milling during the cross-sectional sample preparation. These results suggest that electron microscopy is not an ideal tool to study the anion inter-diffusion kinetics for 2D halide perovskites due to sample damage.



Figure 2.3: Temperature dependence of halide inter-diffusion in $(BA)_2PbBr_4$ - $(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructures. **a**, **f**, **k**, Bright-field images of three independent $(BA)_2PbBr_4$ - $(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructures. **b**, **g**, **l**, Corresponding PL images of vertical heterostructures at room temperature (RT). The circled regions denote the area used for PL emission measurement of the heterostructure. **c**, **d**, PL images of the vertical heterostructure in **a** after heating at 60 °C for 1 hr and 8 hrs, respectively. **h**, **i**, PL images of the vertical heterostructure in **f** after heating at 80 °C for 1 hr and 4 hrs, respectively. **m**, **n**, PL images of the vertical heterostructure in **k** after heating at 100 °C for 1 hr and 2 hrs, respectively. Dashed lines are added in all the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) domains. All scale bars are 5 µm. **e**, **j**, **o**, Evolution of PL spectra of the three vertical heterostructures upon heating at 60 °C, 80 °C, and 100 °C, respectively.

We firstly assembled a $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure, where BA is butylammonium cation and MA is methylammonium cation. **Figure 2.1b** shows the atomic force microscopy (AFM) image of a representative vertical heterostructure with a total thickness of ~ 6.4 nm. Scanning electron microscopy (SEM) image and the corresponding energy dispersive Xray spectroscopy (EDS) elemental mappings of lead, bromine, and iodine for $(BA)_2PbBr_4 (BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure is shown in **Figure 2.1 c** – **f**. The spatial confinement of the photoluminescence (PL) emission is captured using confocal PL laser scanning microscopy (**Figure 2.1 g** – **i**). Interestingly, confocal mapping indicates that the blue emission (410 – 460 nm channel) is limited to the pure bromide region and is largely blocked by the top iodide layer in the junction area due to absorption and / or energy transfer.²⁸⁻³³ The two peaks in the PL emission spectrum shown in **Figure 2.1j** correspond to the band edge emissions from the $(BA)_2PbBr_4$ (~ 410 nm) and the $(BA)_2(MA)_2Pb_3I_{10}$ (~ 615 nm) layers, respectively. The interface of the reference $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure is elucidated by the cross-sectional scanning transmission electron microscopy (STEM) and elemental analysis (**Figure 2.2**).

2.3 Mechanism of halide diffusion

Halide inter-diffusion across the vertical heterojunction is monitored during the heating process by tracking the change in PL spectra. PL emission tracking is used for anionic diffusion study rather than cross-sectional STEM / EDS mapping due to its relative simplicity and nondestructive nature. The Br-I inter-diffusion is observed and analyzed at different temperatures. Figure 2.3a, 2.3f, and 2.3k show the bright-field images of (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructures, and Figure 2.3b, 2.3g, and 2.3l show the corresponding PL images at room temperature. The evolution of PL emissions after heating at 60, 80, and 100 °C are depicted through PL images and PL spectra in Figure 2.3 c - e, 2.3 h - j, and 2.3 m - o, respectively. The emergence of intermediate green PL emission is an indication of halide diffusion between the top and bottom 2D perovskites of the vertical heterostructure. It is important to note that irrespective of the temperature and duration of heating, the green PL emission centered at 512 - 515 nm is observed for all vertical heterostructures. The appearance of a single alloy PL emission is distinct from the PL evolution profiles reported for halide inter-diffusion in 3D perovskites.¹³⁻¹⁶ The green alloy PL emission is localized to the junction area, while non-overlapping bromide and iodide perovskites maintain their respective intrinsic blue and red PL emissions even after heating. The spatial confinement of the green PL emission is further evidenced by the confocal imaging of the reference $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure at room temperature and after heating for 4 hrs at 80 °C (Appendix Figure A.2). The localized green emission at the heterojunction area can be attributed to considerably shorter vertical thickness ('nm' scale) compared to the lateral length ('µm' scale) of the heterostructures. Additionally, the halide alloy PL progressively increases in intensity with an increase in heating time until it reaches a steady state of bromide-iodide intermixing.



Figure 2.4: Analysis of origin of halide alloy PL peak in (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure after heating at 80 °C. a, Bright-field image of vertical heterostructure. **b**, **c**, PL image of vertical heterostructure at room temperature and after heating at 80 °C for 40 hrs, respectively. The circled regions denote the area used for PL emission measurement of the heterostructure, bromide and iodide perovskite. Dashed lines are added in all the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) domains. All white scale bars are 10 μ m. **d**, PL spectrum of vertical heterostructure before and after heating at 80 °C for 40 hrs. Presence of halide alloy PL peak at ~ 511 nm (dashed blue curve) is evident in bromide perovskite layer. No new PL peak (dashed red curve) is observed in iodide perovskite layer after the heating process. e, f, Bright-field and PL image of (BA)₂PbBr₄, respectively. g, PL image of the (BA)₂PbBr_{4x}I_{4(1-x)} alloy formed after placing bulk crystal of (BA)₂(MA)₂Pb₃I₁₀ on top of (BA)₂PbBr₄ nanocrystal and heating it for 4 hrs at 80 °C. The bulk crystal of (BA)₂(MA)₂Pb₃I₁₀ is removed after the heating process to analyze the formation of $(BA)_2PbBr_{4x}I_{4(1-x)}$ perovskite in the bottom layer. All yellow scale bars are 5 µm. h, PL spectrum of (BA)₂PbBr₄ nanocrystal at room temperature and $(BA)_2PbBr_{4x}I_{4(1-x)}$ alloy formed in the bottom layer after heating (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure at 80 °C for 4 hrs.

Additional experiments were conducted to investigate the origin of halide alloy PL emission. In the first experiment, the $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure was heated at 80 °C for a prolonged duration of ~ 40 hrs to facilitate lateral halide inter-diffusion into the pristine bromide and iodide layers (**Figure 2.4 a** – **d**). Interestingly, the green emission extended outside the junction area to the bottom bromide layer, which suggests that the green emission originates from the bottom bromide layer. In the second experiment, a large bulk crystal of iodide perovskite (which could easily be removed later) was placed on top of the pre-grown bromide nanocrystals to form the vertical heterostructure. The vertical heterostructure was then heated at 80 °C for 4 hrs after which the bulk iodide crystal was removed. Strong green PL emission is observed from the bromide layer after removing the iodide bulk crystal (**Figure 2.4 e – h**). EDS mapping of the bromide crystal clearly shows dominant iodine composition after heating (**Figure 2.5**). An alternate possibility for the green emission is the formation of a new perovskite phase after heating the vertical heterostructure. To exclude this possibility, $(BA)_2PbI_4-(BA)_2(MA)_2Pb_3I_{10}$ and $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3Br_{10}$ vertical heterostructures with identical halides in both layers were assembled. No new PL emissions emerged after heating, indicating that no new perovskite phases were formed (**Figure 2.6 a – h**). Therefore, based on these control experiments, we conclude that the green emission observed during the thermal diffusion studies originates from the bottom bromide layer after alloy formation.

It is important to highlight that for the same thickness of top and bottom 2D perovskite layers in the vertical heterostructure, the number of diffusing iodide ions in $(BA)_2(MA)_2Pb_3I_{10}$ (n = 3) is significantly higher compared to bromide ions due to a larger number of organic barriers in $(BA)_2PbBr_4$ (n = 1) perovskite. If overall charge neutrality is maintained, the number of halides remain the same before and after the diffusion process. This results in a greater impact of interdiffusion on the average composition of bromide perovskite, thus potentially leading to the formation of an iodide dominant (BA)₂PbBr_{4x}I_{4(1-x)} alloy with green PL emission. The impact of relative halide concentration was investigated by assembling a (BA)₂(MA)₂Pb₃Br₁₀-(BA)₂PbI₄ vertical heterostructure which contrasts our reference case (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ since in the new system, each layer of bottom bromide perovskite $[(BA)_2(MA)_2Pb_3Br_{10}, n = 3]$ has thrice as many bromide ions as compared to the iodide ions in each layer of top iodide perovskite $[(BA)_2PbI_4, n = 1]$ (Figure 2.6 i – l). An orange-red PL emission was observed after heating the (BA)₂(MA)₂Pb₃Br₁₀-(BA)₂PbI₄ vertical heterostructure at 80 °C which is characteristic of an iodide dominant (BA)₂(MA)Pb₃Br_{10x}I_{10(1-x)} perovskite rather than a bromide dominant (BA)₂PbBr_{4x}I_{4(1-x)} perovskite. Hence, the formation of iodide dominant $(BA)_2PbBr_{4x}I_{4(1-x)}$ alloy perovskite in the reference (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure is not just related to the stoichiometric ratio of diffusing bromide-iodide ions but is also governed by the thermodynamics of the associated alloys.³⁴⁻³⁶


Figure 2.5: SEM / EDS imaging of $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure. SEM images of $(BA)_2PbBr_{4x}I_{4(1-x)}$ alloy formed after placing bulk crystal of $(BA)_2(MA)_2Pb_3I_{10}$ on top of $(BA)_2PbBr_4$ nanocrystal and heating it for **a**, 4 hrs and **e**, 10 hrs at 80 °C. EDS elemental mappings of **b**, **f**, Pb, **c**, **g**, Br, and **d**, **h**, I for the SEM images in **a** and **e**, respectively. All scale bars are 3 µm. **i**, **j**, EDS spectrum corresponding to the SEM images in **a** and **e**, respectively. The insets show the zoomed-in spectrum to highlight the bromine and iodine counts. The weak iodine signal in EDS elemental mapping and spectrum after 4 hrs of heating suggest that the iodine ions diffused to only top few layers of the bromide perovskite after 4 hrs of heating. After 10 hrs of heating, almost all the bromide perovskite layers show dominant iodine composition as evident from the EDS mapping and spectrum.

Density functional theory (DFT) calculations were performed to understand the impact of halide compositions on the band structures of $(BA)_2PbBr_{4x}I_{4(1-x)}$ and $(BA)_2(MA)Pb_3Br_{10x}I_{10(1-x)}$

perovskites. Projected density of states (DOS) highlighting the band gap for (BA)₂PbI₄, (BA)₂PbBr₄, (BA)₂(MA)₂Pb₃I₁₀ and (BA)₂(MA)₂Pb₃Br₁₀ are shown in Appendix Figure A.3a, A.3b, A.3c, and A.3d, respectively. The experimentally measured PL energies for varying bromide mole fractions (x_{Br}) in $(BA)_2PbBr_{4x}I_{4(1-x)}$ perovskites are plotted in Appendix Figure A.4a. Interestingly, both experimental data and DFT calculations predict insignificant changes in PL emissions and band gaps for $0 \le x_{Br} \le 0.5$. Therefore, once the iodide diffusion into the bottom bromide perovskite layer reaches $x_{Br} = 0.5$, changes in PL emission becomes less obvious with additional iodide influx. DFT calculated band gap vs. x_{Br} calibration curve is plotted for (BA)₂(MA)Pb₃Br_{10x}I_{10(1-x)} perovskites in Appendix Figure A.4b. It can be concluded from the plot that for the top iodide layer, no obvious change in PL energy and composition can be distinguished for $0 \le x_{Br} \le 0.3$. From the PL spectra evolution during heating of (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure, it is evident that the iodide dominant alloy $((BA)_2PbBr_{4x}I_{4(1-x)})$ with $x \le 0.5$ forms in the bottom layer within minutes of heating. Furthermore, the incremental energy required for substitution of iodine atoms in (BA)₂PbBr₄ perovskite (calculated by DFT) decreases significantly for $x_{Br} \le 0.4$ (Appendix Figure A.4c). This result indicates that it is energetically favorable to form iodide dominant halide alloys in (BA)₂PbBr_{4x}I₄₍₁₋ x_{x} perovskites once the barrier for initial energy states is overcome and therefore the diffusion to the next layer is limited by this energy threshold.

The above observations regarding the origin of the green PL emission and formation of thermodynamically preferred alloy composition provide important insights into the mechanism of halide inter-diffusion across the vertical heterojunction. **Appendix Figure A.5a** – **A.5c** and **Appendix Figure A.5g** provide a schematic illustration of the halide migration and the corresponding concentration profile evolution during the heating process as predicted by the classic Fickian diffusion model. However, this continuous concentration profile is contrary to the experimental observations of the emergence of a single halide alloy composition. To more precisely depict the experimental observations, a layer-by-layer mechanism is proposed and schematically represented in **Figure 2.7 a** – **c** and **Appendix Figure A.5d** – **A.5f**. This is based on the key findings that a preferential halide alloy composition is formed exclusively in the bottom perovskite layer and the heterostructure achieves a steady state when all bottom perovskite layers attain this preferred composition during the heating process. Meanwhile, the diffusion of bromide into the top layer only leads to a small PL shift as indicated in **Figure 2.3e, 2.3j, and 2.3o** and

Appendix Figure A.4b ($0 \le x_{Br} \le 0.3$). The corresponding concentration profile evolution for this proposed "quantized" model is captured in **Appendix Figure A.5h**.



Figure 2.6: Analysis of new phase formation in (BA)₂PbX₄-(BA)₂(MA)₂Pb₃X₁₀ (X = I, Br) and alloy formation in (BA)₂(MA)₂Pb₃Br₁₀-(BA)₂PbI₄ vertical heterostructures after heating at 80 °C. a, Bright-field image of (BA)₂PbI₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure. b, c, PL images of (BA)₂PbI₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure at room temperature and after heating at 80 °C for 4 hrs, respectively. d, PL spectrum of (BA)₂PbI₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure before and after heating at 80 °C for 4 hrs. No PL shift and no new PL emission from any new halide perovskite phases is observed after the heating process. e, Bright-field image of (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃Br₁₀ vertical heterostructure. f, g, PL images of (BA)₂PbBr₄- $(BA)_2(MA)_2Pb_3Br_{10}$ vertical heterostructure at room temperature and after heating at 80 °C for 4 hrs, respectively. h, PL spectrum of (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃Br₁₀ vertical heterostructure before and after heating at 80 °C for 4 hrs. No PL shift and no new PL emission from any new halide perovskite phases is observed after the heating process. i, Bright-field image of (BA)₂(MA)₂Pb₃Br₁₀-(BA)₂PbI₄ vertical heterostructure. **j**, **k**, PL images of (BA)₂(MA)₂Pb₃Br₁₀-(BA)₂PbI₄ vertical heterostructure at room temperature and after heating at 80 °C for 4 hrs, respectively. I, PL spectrum of (BA)₂(MA)₂Pb₃Br₁₀-(BA)₂PbI₄ vertical heterostructure before and after heating at 80 °C. Alloy peak centered ~ 605 nm observed after heating indicates formation of iodide dominant $(BA)_2(MA)_2Pb_3Br_{10x}I_{10(1-x)}$ (n = 3) alloy perovskite rather than $(BA)_2PbBr_{4x}I_{4(1-x)}$ (n = 1) alloy perovskite. Dashed lines are added in all the bright-field and PL images for the ease of distinction of bottom (light blue) and top (yellow) perovskite domains. All scale bars are 5 µm.

2.4 Diffusion coefficient calculations

Due to the complex absorption and energy transfer processes between perovskite layers, it is challenging to accurately obtain the evolution of concentration profile during the diffusion process. However, the diffusion coefficient can be estimated solely based on the initial and final equilibrium states. The halide inter-diffusion coefficient across vertical heterojunctions is calculated analytically using Fickian and non-Fickian mathematical models and estimated from Kinetic Monte Carlo (KMC) simulations.

The Fickian mathematical model utilizes Fick's second law describing a one-dimensional transient diffusion problem stated as follows.³⁷

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{1}$$

Here 'C' is the concentration of bromide, 't' is the heating time, 'x' is the diffusion length and 'D' is the halide inter-diffusion coefficient. The solution of this ideal one-dimensional diffusion problem is given by

$$C = \frac{1}{2}C_0 \operatorname{erfc} \frac{x}{2(Dt)^{\frac{1}{2}}}$$
(2)

where, 'C₀' is the initial bromide concentration in the bottom perovskite.³⁸

The non-Fickian mathematical model utilizes a concentration dependent diffusion coefficient, D(C), describing a one-dimensional transient diffusion problem stated as follows.³⁸

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D(C) \frac{\partial C}{\partial x} \right)$$
(3)

The diffusion coefficient is calculated by utilizing the fact that at equilibrium, all the bottom layers in the vertical heterostructure attain the preferred halide alloy composition as depicted by the curve ' t_f ' in **Appendix Figure A.5h**. Concentration profile at the final time step is fitted with Gaussian distribution and diffusion coefficient is then calculated by the Boltzmann-Matano (BM) method.^{38,39}

$$D(c^*) = -\frac{1}{2t} \frac{\int_{c_1}^{c^*} (x - x_M) dc}{\left(\frac{dc}{dx}\right)_{c^*}}$$
(4)

where, 'c^{*}' is the bromide mole fraction in preferred halide alloy, 'c_l' is the bromide mole fraction in the top perovskite layer, ' x_M ' is the Matano interface (a mathematical parameter which divides the concentration profile into two equal area plots), 't' is the heating time, 'x' is the diffusion length, and 'D' is the halide inter-diffusion coefficient. A representative example of the

experimental data used to obtain the equation parameters and calculate inter-diffusion coefficient for $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure using both Fickian and non-Fickian diffusion models is depicted in **Appendix Figure A.6**. Details of the calculation steps involved in converting the experimental observations to mathematical parameters are provided in Supplementary Information.

Although the non-Fickian diffusion model is based on the final concentration profile across the vertical heterostructure, it does not capture the unique layer-by-layer alloy-mediated diffusion process observed in the 2D vertical heterostructures. To model the impact of layer-by-layer preferred alloy formation on the inter-diffusion coefficient, KMC lattice-diffusion simulations were performed. The simulated lattices consisted of sites corresponding to Pb octahedra. Layers representing Br⁻ or I⁻ dominant perovskite sheets were initialized in accordance with the experimental assembly of vertical heterostructures. To capture the experimental behavior of the heterostructure to equilibrate to a preferred halide alloy composition, as well as to model the proposed layer-by-layer diffusion mechanism, a concentration threshold criterion for the interlayer diffusion was introduced. This concentration threshold criteria suppresses halide diffusion from a given layer into an adjacent layer until the experimentally observed preferred halide alloy concentration is attained in the originating layer. Thus, diffusing ions "spill over" from one layer to the next in a quantized manner instead of diffusing continuously throughout the heterostructure. The interlayer hopping rates, k, were fit so that the elapsed simulation time required for the bottom perovskite layer to reach its thermodynamically preferred alloy composition reproduced the experimental time. Once the transition rates were determined, the diffusion coefficients were calculated by $D = kx^2$, where x is the bromide layer thickness. Further details on KMC methodology is available in the 'Simulations' section.

The calculated diffusion coefficients using Fickian, BM and KMC models at 60, 70, 80, 90, and 100 °C are plotted in **Figure 2.7d**. Additionally, a plot of the average diffusion coefficient using the three mathematical models *vs*. temperature is shown in **Figure 2.7e**. The calculated diffusion coefficients (D) are compared with the theoretical prediction of the Arrhenius equation as stated below.

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \qquad \Rightarrow \ln D = \ln D_0 - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{5}$$

where, 'D₀' is a constant, 'E_a' is the activation energy for vacancy-assisted halide migration, 'R' is the universal gas constant (R = 8.314 J/(K.mol)) and 'T' is the heating temperature (**Figure 2.7e**).^{40,41} The calculated diffusion coefficients show a good fit to the exponential temperature dependence, which provides additional credibility to the mathematical models used for quantification of halide inter-diffusion coefficient.



Figure 2.7: Proposed mechanism and calculated diffusion coefficients for halide interdiffusion in 2D perovskite vertical heterostructures. a, Schematic of vertical heterostructure before heating showing direction of bromide and iodide diffusion fluxes at the interface. b, c, Schematic of vertical heterostructure depicting layer-by-layer halide diffusion during the heating process. Red to orange-red shift in iodide layer emission denotes marginal compositional change in iodide layer. Similarly, blue to green shift in bromide layer symbolizes significant compositional change in bromide layer. d, Plot of bromide-iodide inter-diffusion coefficients for $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructures at five temperature points – 60 °C, 70 °C, 80 °C, 90 °C, and 100 °C. BM refers to the non-Fickian diffusion coefficients calculated using Boltzmann-Matano method and KMC refers to diffusion coefficients obtained using Kinetic Monte Carlo simulation. The box represents data points between 25 – 75 percentiles of the range, whisker represents the minimum-to-maximum range and dashed line highlights the average diffusion coefficients of the sample data points. e, Average halide inter-diffusion coefficients (scatter points) calculated using three methods at five temperatures fitted with Arrhenius equation (dashed line).

2.5 Impact of inorganic and organic layers on halide diffusion

The halide inter-diffusion was analyzed for three additional heterostructures constructed by using different inorganic layer thicknesses for the top iodide perovskite. **Figure 2.8 a – c, Figure 2.8 d – f, and Figure 2.8 g – i** show the schematic representations, bright-field and PL images of $(BA)_2PbBr_4-(BA)_2PbI_4$, $(BA)_2PbBr_4-(BA)_2(MA)Pb_2I_7$ and $(BA)_2PbBr_4-(BA)_2(MA)_4Pb_5I_{16}$ vertical heterostructures, respectively. The bromide-iodide diffusion across the vertical heterojunctions was analyzed by heating at 80 °C and monitoring the PL (**Appendix Figure A.7, A.8 and A.9**). It is interesting to note that the emergence of a single halide alloy PL centered at 508 – 518 nm is also observed for $(BA)_2PbBr_4-(BA)_2(MA)Pb_2I_7$ (**Appendix Figure A.8**) and $(BA)_2PbBr_4-(BA)_2(MA)4Pb_5I_{16}$ (**Appendix Figure A.9**). Note, for $(BA)_2PbBr_4-(BA)_2PbBr_4$ vertical heterostructure, no intermediate PL is observed after heating. In this case, the PL emission originating from iodide diffusion into the bottom bromide perovskite is subsumed in the PL emission of top $(BA)_2PbI_4$ layer, which is centered at ~ 521 nm at room temperature (**Appendix Figure A.7**).

These observations are consistent with the conclusion that the green alloy PL emission originates from bottom perovskite (BA)₂PbBr_{4x}I_{4(1-x)} irrespective of the top perovskite $((BA)_2(MA)_{n-1}Pb_nI_{3n+1}; n = 1, 2, 3, and 5)$. The diffusion coefficients for all three heterostructures are compared using the three diffusion models in **Figure 2.8s**. The KMC predicted halide interdiffusion coefficients are in the range of $10^{-19} \sim 10^{-20} \text{ m}^2/\text{s}$. All models predict that the halide interdiffusion increases with the inorganic layer thickness ('n' number), which is consistent with the reported Br-I inter-diffusion coefficient of ~ $10^{-18} \text{ m}^2/\text{s}$ for 3D perovskite heterostructure.^{14,16} This observation suggests that a higher 'n' number facilitates slightly faster halide migration. Therefore, for a given organic cation, 2D perovskites. But overall, 2D perovskites with BA ligands do not show a significantly reduced anion diffusivity compared to 3D perovskites.



Figure 2.8: Effect of inorganic layer thickness and organic cation on halide diffusion in $(L)_{2}PbBr_{4}-(BA)_{2}(MA)_{n-1}Pb_{n}I_{3n+1}$ (L = organic cation; n = 1, 2, 3 & 5) vertical heterostructures. **a**, **d**, **g**, **j**, **m**, **p**, Schematic representations of $(BA)_2PbBr_4-(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1, 2 and 5) and $(L)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ (L = PEA, 2P, 2T) vertical heterostructures, respectively. For clarity, no hydrogen atoms have been shown in the organic cations. b, e, h, k, n, q, Bright-field images of $(BA)_2PbBr_4-(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1, 2 and 5) and $(L)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ (L = PEA, 2P, 2T) vertical heterostructures, respectively. c, f, i, l, o, r, PL images of (BA)₂PbBr₄- $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1, 2 and 5) and $(L)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ (L = PEA, 2P, 2T) vertical heterostructures, respectively. Dashed lines are added in all the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) domains. All scale bars are 5 µm. s, t, Comparison of halide inter-diffusion coefficients in $(BA)_2PbBr_4-(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1, 2, 3 and 5) and $(L)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ (L = BA, PEA, 2P, 2T) vertical heterostructures, respectively, after heating at 80 °C. BM refers to the non-Fickian diffusion coefficients calculated using Boltzmann-Matano method and KMC refers to diffusion coefficients obtained using Kinetic Monte Carlo simulation. The box represents data points between 25 - 75 percentiles of the range, whisker represents the minimum-to-maximum range and dashed line highlights the average diffusion coefficients of the sample data points.

The effect of organic cation on halide inter-diffusion in 2D perovskites is investigated by comparing BA with three larger cations – phenylethylammonium (PEA), biphenylethylammonium (2P), and bithiophenylethylammonium (2T).¹⁸ Schematic representations, bright-field and PL images of the (PEA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀, (2P)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀, and (2T)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructures are shown in **Figure 2.8 j** – **l**, **Figure 2.8 m** – **o**, **and Figure 2.8 p** – **r**, respectively. The heterostructures were heated at 80 °C and halide inter-diffusion was tracked using PL (**Appendix Figure A.10, A.11, and A.12**). Similar to previous cases, halide inter-diffusion in (PEA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ and (2P)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructures of a single halide alloy PL peak centered at 507 – 511 nm (**Appendix Figure A.10 and A.11**). The calculated inter-diffusion coefficients for several PEA and 2P based heterostructures using both analytical models and KMC simulations are shown in **Figure 2.8t**.

Interestingly, for (2T)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure, no obvious intermediate halide alloy emissions are observed even after 36 hrs of heating at 80 °C (Appendix Figure A.12), indicating that there is minimal amount of inter-diffusion. We confirmed the absence of iodine in the bromide layer after heating the heterostructure using SEM / EDS characterizations and excluded the possibility of type II band alignment (resulting in PL quenching) through a detailed PL study on a series of Br-I alloys for the 2T-based system (see Figure 2.9 for detailed discussion). The quantification of halide inter-diffusion process for the 2T system is performed by assuming that the time for alloy formation (centered at ~ 510 nm) is longer than 36 hrs and hence the model predicts an upper limit for Br-I inter-diffusion coefficient. The 2T vertical heterostructures are not exposed to longer heating periods (> 36 hrs) due to defect formation as evidenced by the origin of lower energy PL emissions in Appendix Figure A.12. The bromideiodide inter-diffusion coefficient for (2T)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructures using all three diffusion models is plotted in Figure 2.8t. The inter-diffusion coefficients for BA, PEA, 2P, and 2T based vertical heterostructures using the KMC model are in the order of ~ 10^{-19} , ~ 10^{-19} 20 , ~ 10⁻²⁰, and ~ 10⁻²² m²/s, respectively. All the diffusion models present a consistent trend which indicates that bulkier π -conjugated organic cations like 2T are much more efficient in inhibiting halide inter-diffusion compared to benzene-based π -conjugated systems like 2P and PEA or short chain aliphatic organic cations like BA. Detailed information about the morphology, structural

stability, and diffusivity calculation parameters for all heterostructures can be found in **Appendix** Figure A.13 – A.16 and **Appendix Table A.1**.



Figure 2.9: Investigation of halide inter-diffusion in (2T)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure. a, SEM image of bottom bromide perovskite layer after placing bulk crystal of (BA)₂(MA)₂Pb₃I₁₀ on top of (2T)₂PbBr₄ nanocrystal and heating it for 10 hrs at 80 °C. **b**, **c**, **d**, EDS elemental mappings of Pb, Br, and I, respectively, for the SEM image in a. All yellow scale bars are 10 µm. e, EDS spectrum corresponding to the SEM image in a. f, g, h, i, j, PL images of thin films of $(2T)_2$ PbBr_{4x}I_{4(1-x)} alloy perovskite with $x_{Br} = 0.4, 0.3, 0.2, 0.1, and 0$, respectively. All white scale bars are 20 µm. k, PL emission spectrum of alloy perovskites with $x_{Br} = 0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1$, and 0. The legend texts for $x_{Br} > 0.4$ have been shown in grey color to highlight that no PL is observed for these compositions. Note that (2T)₂PbBr₄ perovskite has no PL emission due to type II band alignment between the inorganic [PbBr₄]²⁻ and organic ligand 2T⁺ layers. The red PL emission in (2T)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure comes from the top iodide perovskite layer. However, (2T)₂PbI₄ has type I band alignment with green PL emission. Since all other heterostructures show an alloy PL emission peak which is iodide dominant, we expected the halide inter-diffusion in 2T system to be thermodynamically driven towards formation of an iodine dominated (2T)₂PbBr_{4x}I_{4(1-x)} perovskite with green PL emission. To ensure that absence of green alloy PL emission in 2T system indicates absence of iodide diffusion rather than quenched PL of iodide dominant alloy perovskite, it is important to estimate the bromide concentration at which the (2T)₂PbBr_{4x}I_{4(1-x)} alloy perovskite transitions from type II to type I band alignment. Figure 2.9 f - k shows the PL emission spectrum of (2T)₂PbBr_{4x}I_{4(1-x)} alloy perovskites obtained by spin coating the bromide and iodide precursor solutions mixed in the desired stoichiometric ratios. It is evident from Figure 2.9k that for $x_{Br} \leq$ 0.4, $(2T)_2$ PbBr_{4x}I_{4(1-x)} perovskite has type I band alignment and for $x_{Br} > 0.4$, it transitions to type II band alignment. Therefore, the absence of alloy PL emission in the diffusion studies is indicative of the inhibiting role of 2T organic cation rather than type II band alignment of iodide dominant alloy perovskites.

2.6 Conclusions

In conclusion, we have demonstrated the assembly of the first atomically flat vertical heterostructures using two 2D halide perovskites. In contrast to classical solid-state inter-diffusion models featuring continuous concentration profile evolution, a "quantized" layer-by-layer diffusion model governed by concentration threshold and ion-blocking effects of the organic cations is discovered in 2D halide perovskites. Qualitative and quantitative halide inter-diffusion analysis in $(BA)_2PbBr_4-(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ vertical heterostructures reveals that anionic migration is faster for higher 'n' number. Additionally, bulky and rigid thiophene-based conjugated organic cations are found to be much more effective stabilizers and inhibitors of halide inter-diffusion compared to short aliphatic chains. These findings provide new insights about strategies to inhibit the intrinsic inter-diffusion in halide perovskites and mitigate the instability of perovskite devices *via* molecular engineering. Moreover, the realization of vertical heterostructures also provides a materials platform for fundamental studies on the interplay between different 2D halide perovskites and their optoelectronic applications.

2.7 Methods

2.7.1 Solvent evaporation method for synthesis of bottom bromide perovskite in vertical heterostructure

For the synthesis of (BA)₂PbBr₄ nanocrystals, a concentrated precursor solution is prepared by dissolving 0.02 mmol of n-butylammonium bromide (BA·HBr) and 0.01 mmol of lead bromide (PbBr₂) in 2 mL solution of dimethylformamide (DMF) and chlorobenzene (CB) (DMF:CB = 1:1). The concentrated solution is diluted 60 times using a solvent system of CB, acetonitrile (AN) and dichlorobenzene (DCB) with CB:AN:DCB volume ratio of 2.5:1:0.01. All organic solvents (DMF, CB, AN and DCB) and PbBr₂ are purchased from Sigma Aldrich and are used as received. BA·HBr is purchased from Greatcell Solar Ltd. and is used as received. Perovskite crystal synthesis using the solvent evaporation method is carried out in a glove box maintained under nitrogen atmosphere. A sample vial containing Si / SiO₂ substrate is then placed on a hot plate maintained at 50 °C. The Si / SiO₂ substrate is cleaned by dipping in a Piranha solution for ~ 2 hrs to remove all trace impurities. 10 μ L of the diluted precursor solution along with 5 μ L of AN is then dropped on the Si / SiO₂ substrate and the sample vial is capped for slow evaporation of solvents and subsequent growth of perovskite crystals. The Si/SiO₂ substrate is then removed from the hot plate once all the solvents are evaporated which is typically within 15 mins.

The synthesis of $(PEA)_2PbBr_4$, $(2P)_2PbBr_4$, and $(2T)_2PbBr_4$ nanocrystals follow the same procedure as detailed above for $(BA)_2PbBr_4$. For $(PEA)_2PbBr_4$, instead of BA·HBr, phenylethylammonium bromide (PEA·HBr) precursor is used. For $(2P)_2PbBr_4$, instead of BA·HBr, biphenylethylammonium bromide $(2P \cdot HBr)$ precursor is used. Similarly, bithiophenylethylammonium bromide $(2T \cdot HBr)$ precursor is used for the synthesis of $(2T)_2PbBr_4$. The growth temperature used for $(PEA)_2PbBr_4$ and $(2T)_2PbBr_4$ nanocrystals synthesis is 70 °C. PEA·HBr and $(2P)_2PbBr_4$ are purchased from Greatcell Solar Ltd. and are used as received. $2T \cdot HBr$ salt is synthesized in our lab.¹⁸

2.7.2 Slow cooling synthesis of bulk bromide perovskite crystals

 $(BA)_2(MA)_2Pb_3Br_{10}$ bulk crystals are synthesized by a solution of 0.19 mmol BA·HBr, 0.40 mmol MA·HBr and 0.59 mmol PbO in 0.9 mL HBr (48 wt.% in H₂O) and 0.1 mL H₃PO₂ (50 wt.% in H₂O). PbO, HBr and H₃PO₂ are purchased from Sigma Aldrich. MA·HBr is purchased from Greatcell Solar Ltd. and is used as received. The 10 mL solution vial is magnetically stirred and heated to 120 °C in an oil bath until the solution becomes transparent. The perovskite crystals formed after controlled cooling at the rate of ~ 5 °C/hr are collected by vacuum filtration.

2.7.3 Slow cooling synthesis of bulk iodide perovskite crystals

For the synthesis of $(BA)_2PbI_4$ bulk crystals, a precursor solution is prepared by mixing 0.57 mmol of n-butylammonium iodide $(BA \cdot HI)$ and 0.57 mmol of lead oxide (PbO) in 0.9 mL hydroiodic acid (HI, 57 wt.% in H₂O) and 0.1 mL hypophosphorous acid $(H_3PO_2, 50 \text{ wt.\% in H}_2O)$. HI is purchased from Sigma Aldrich. BA · HI is purchased from Greatcell Solar Ltd. All chemicals are used as received. The sample vial containing the precursor solution is magnetically stirred and heated to 120 °C in an oil bath until all the salts are completely dissolved. Once the solution is clear, the stirring is halted, and the solution is cooled down at a rate of ~ 5 °C/hr. This controlled cooling down process leads to the nucleation and growth of perovskite crystals. The bulk crystals are extracted from the solution by vacuum filtration.

The synthesis of $(BA)_2(MA)Pb_2I_7$ bulk crystals is done by mixing 0.43 mmol of BA·HI, 0.31 mmol of methylammonium iodide (MA·HI) and 0.59 mmol of PbO in an acid solution containing 0.9 mL HI (57 wt.% in H₂O) and 0.1 mL H₃PO₂ (50 wt.% in H₂O). MA·HI is purchased from Greatcell Solar Ltd. and is used as received. The precursor solution in a 10 mL sample vial is magnetically stirred and heated to 120 °C in an oil bath until all the salts are completely dissolved. The perovskite crystals are obtained by controlled slow cooling at the rate of ~ 5 °C/hr followed by vacuum filtration.

 $(BA)_2(MA)_2Pb_3I_{10}$ bulk crystals are synthesized by a solution of 0.19 mmol BA·HI, 0.40 mmol MA·HI and 0.59 mmol PbO in 0.9 mL HI (57 wt.% in H₂O) and 0.1 mL H₃PO₂ (50 wt.% in H₂O). The 10 mL solution vial is magnetically stirred and heated to 120 °C in an oil bath until the solution becomes transparent. The perovskite crystals formed after controlled cooling at the rate of ~ 5 °C/hr are collected by vacuum filtration.

Finally, $(BA)_2(MA)_4Pb_5I_{16}$ bulk crystal synthesis involves a solution of 0.16 mmol BA·HI, 0.67 mmol MA·HI and 0.59 mmol PbO in 0.9 mL HI (57 wt.% in H₂O) and 0.1 mL H₃PO₂ (50 wt.% in H₂O). The 10 mL sample vial containing precursor solution is magnetically stirred and heated to 120 °C in an oil bath until all precursor salts are completely dissolved in the acid solution. The crystallized perovskites are formed and collected after controlled slow cooling at the rate of ~ 5 °C/hr followed by vacuum filtration.

2.7.4 2D halide perovskite vertical heterostructure assembly

One or two pieces of iodide bulk crystals synthesized using the slow cooling method is transferred on the adhesive side of the ScotchTM tape. A second ScotchTM tape is then stuck on the first tape and peeled off to exfoliate thinner layers of perovskite. This peeling off process is repeated three to four times to ensure a very thin iodide layer with good coverage over the entire adhesive tape. The Si / SiO₂ substrate with the bottom perovskite layer is then stuck on the ScotchTM tape containing exfoliated thin iodide perovskite layer. The Si / SiO₂ substrate with ScotchTM tape is kept on a hot plate at 50 °C for ~ 3 mins to ensure efficient transfer of iodide perovskite from tape to substrate. The substrate is then removed from the hot plate, and the tape is finally peeled off, resulting in the formation of 2D bromide-iodide perovskite vertical heterostructure. The mechanical exfoliation process is carried out in a nitrogen filled glovebox.

2.7.5 Spin coating of PMMA on 2D perovskite vertical heterostructures

All 2D perovskite vertical heterostructures constructed in this study are encapsulated by spin coating a layer of ~ 30 μ L of polymethyl methacrylate (PMMA) solution to protect against environmental degradation. PMMA 950K is purchased from Microchem and is used for spin coating after further dilution with CB. The diluted PMMA solution is obtained by mixing a 3:1 volume ratio of PMMA 950K:CB. Spin coating is carried out at 1500 rpm for 1 min in a nitrogen filled glove box. The spin coated substrate is then heated on a hot plate at 50 °C for ~ 2 mins to condense the PMMA and remove trace CB.

2.7.6 Spin coating of (L)₂PbBr_{4x}I_{4(1-x)} 2D halide alloy thin films

(L)₂PbBr₄ (L = BA, 2T) precursor solution is prepared by dissolving 0.05 mmol of L·HBr (L = BA, 2T) and 0.05 mmol of PbBr₂ in 0.6 mL of DMF. Similarly, (L)₂PbI₄ (L = BA, 2T) precursor solution is prepared by dissolving 0.05 mmol of L·HI (L = BA, 2T) and 0.05 mmol of PbI₂ in 0.6 mL of DMF. 100 µL of (L)₂PbBr_{4x}I_{4(1-x)} (L = BA, 2T) solutions are then prepared by mixing the (L)₂PbBr₄ and (L)₂PbI₄ (L = BA, 2T) precursor solutions in desired stoichiometric ratios. For instance, (L)₂PbBr_{1.6}I_{2.4} (x = 0.4) solution is prepared by mixing 40 µL of (L)₂PbBr₄ solution with 60 µL of (L)₂PbI₄ solution. 30 µL of the prepared (L)₂PbBr_{4x}I_{4(1-x)} solution is spin coated on Si/SiO₂ substrate. Spin coating is carried out at 1500 rpm for 1 min in a nitrogen filled glove box. The spin coated thin films are used for PL characterization of (L)₂PbBr_{4x}I_{4(1-x)} 2D halide alloys. The experimentally obtained PL energy *vs.* bromide mole fraction correlation for (BA)₂PbBr_{4x}I_{4(1-x)} is then used as the calibration for calculating alloy compositions for all heterostructures presented in this work.

2.8 Characterizations

2.8.1 Bright-field imaging

All bright-field images are collected by a custom Olympus BX53 microscope.

2.8.2 PL imaging and PL spectrum

All PL images are captured using X-Cite Series 120 Q lamp as the excitation source. Coherent OBIS 375 nm laser excitation source is used for all PL spectrum measurements. The filter cube in an Olympus BX53 microscope contains a bandpass filter (330 - 385 nm) for excitation and a dichroic mirror (cutoff wavelength: 400 nm) for light splitting. PL spectra are collected by a SpectraPro HRS-300 spectrometer.

2.8.3 Confocal imaging

A Leica SP8 inverted laser scanning confocal microscope (LSCM) with a 405 nm laser line as excitation wavelength is used for PL mapping of bromide and iodide layers in the vertical heterostructure.

2.8.4 AFM imaging

AFM images are recorded in tapping mode using a Veeco multi-mode atomic force microscope.

2.8.5 SEM imaging / EDS mapping

SEM images are captured using a Quanta 650 FEG SEM at 10 kV and 4.5 spot size with an Everhart-Thornley detector. EDS spectra and elemental mappings are collected using an EDAX Element Silicon Drift Detector at the same beam conditions as the SEM images.

2.8.6 Cross-sectional STEM imaging / EDS mapping

The cross-sectional samples were prepared by a multi beam focused ion beam (FIB) system (JEOL JIB-4700F). In order to minimize ion-beam-induced damage, the whole FIB polishing process is carried out at reduced voltage and ion-beam current. The 2 μ m-thick sample is extracted with accelerating voltage of 30 kV and reduced ion-beam less than 1 nA. After the lamella is transferred to the TEM grid, it is gradually thinned to approximately 500 nm with an ion beam of accelerating voltage of 10 kV and gradually reducing current of 100 pA and 30 pA. After that, the

voltage is reduced further to 5 kV and the current as small as 10 pA is used for final milling. STEM images and EDS elemental maps are carried out on a JEOL JEM-F200 microscope at 200 kV.

2.8.7 XRD

XRD of vertical heterostructures and pure perovskites is measured with a Rigaku Smart Lab using a Cu K α source ($\lambda = 1.54056$ Å) in Bragg Brentano mode.

2.9 Simulations

2.9.1 DFT calculations

Vienna *Ab initio* Simulation Package (VASP) version 5.4 is used to perform DFT calculations for geometry optimization and predicting electronic properties.^{42,43} The projector augmented wave (PAW) potentials are applied, with *Is* of H, *2s2p* of C and N, *4s4p* of Br, *5s5p* of I and *5d6s6p* of Pb as valence electrons.^{44,45} The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) is employed. The energy cutoff for the plane-wave basis set is set as 500eV.⁴⁶ Γ -centered 3×3×1 k-points mesh is used for structural relaxation and 6×6×1 mesh for DOS calculations. Under the applied settings, the total energy is converged to ≤ 1 meV/atom with respect to higher kinetic energy cutoff or denser k-point mesh. The convergence threshold for structural optimization is set to be 0.025 eV/Å. D3 correction method with Becke-Jonson damping is applied to account for the van der Waals (vdW) interaction.⁴⁷ The DOS calculations are performed with spin-orbital coupling corrections switched on.⁴⁸ Two materials – BA₂PbBr₄ (n = 1) and BA₂MA₂Pb₃I₁₀ (n = 3) – are investigated. 2×2×2 unit cells are used to allow for concentration variation in halide species. To model the hybrid perovskite samples in different diffusion stages, different ratios of Br atoms to I atoms are substituted in BA₂PbBr₄ (n = 1) and I atoms to Br atoms in BA₂MA₂Pb₃I₁₀ (n = 3).

2.9.2 KMC simulations

The KMC simulations consist of a two-dimensional lattice of sites corresponding to Pb octahedra, which are identified as containing either I or Br ions.^{49,50} The number of columns of simulation is arbitrarily chosen to have 100 sites for ease of implementation, while the number of

rows reflect the number of repeat octahedron layers inside each system (such that the total height is the total number of perovskite sheets). Partial periodic boundary conditions are implemented, permitting periodicity only between the first and last columns for a row. The ions can move from one site to a neighboring site by a hopping event, the rate of which is controlled by a transition rate, k. There are two types of hopping events: an exchange between an identical pair of ions and an exchange between a dissimilar pair of ions. We are interested in fitting only in the latter case (i.e. the hopping event that results in a change of occupancy), as this propagates the system to a different state that can be observed. The former case is ignored and is not available as a hopping event.

A standard KMC algorithm is used and a hopping event occurs every KMC step. There are four possible moves for a given site, each having a transition probability of k, and a list is formed which contains all possible moves and associated k. The total rate coefficient $k_{total} = \sum_{i=1}^{M} k_i$, with M being the total number of possible moves is calculated, along with a list (R) containing the cumulative rates $R_i = \sum_{j=1}^{i} k_i$, for i = 1, ..., M. The transition which satisfies $R_{i-1} < uR \le R_i$, where $u \in [0,1]$ is a uniform random deviate, is chosen and the hopping event is carried out. The rates are recalculated, and the elapsed system time is incremented with a variable time step (Δt), which is randomly chosen from a Poisson distribution:

$$\Delta t = -\ln(u)k_{total}^{-1}$$

where $u \in [0,1]$ and is independent of the u chosen for the hopping event.

To capture the experimental behavior of the Br layer to equilibrate to its preferred alloy composition, a concentration threshold constraint is implemented, such that once the concentration of the Br species in a given layer reaches its preferred concentration, diffusion from the layer is suppressed (by setting k = 0). An additional constraint is implemented in the case of $(BA)_2PbBr_4$ - $(BA)_2PbI_4$ to capture the observed population inversion. To avoid reaching a steady state concentration of 50:50, the backwards diffusion of a Br ion to its originating layer is suppressed (with k = 0). The transition rates, k, are fit so that the elapsed simulation time required for the bottom perovskite Br layer to reach its thermodynamically preferred alloy composition, as determined experimentally, reproduces the experimental time. Once the transition rates are determined, the diffusion coefficients are calculated by $D = kx^2$, where x is the experimentally measured bromide layer thickness.

2.10 References

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2.12 Author Contributions

Akriti and E.S. synthesized and characterized the 2D perovskite vertical heterostructures; Akriti performed the analytical calculations of halide inter-diffusion coefficients; S.B.S. and B.M.S. performed KMC simulations and data analysis; J.Y. and P.L. carried out DFT calculations; C.L.A. and A.J.P. participated in heterostructure fabrication and optical characterization; B.Y., X.H. and Y.Y. conducted STEM characterization; Y.G. performed organic ligand synthesis; B.P.F. performed SEM and EDS characterizations; Akriti and L.D. wrote the manuscript; all authors read and revised the manuscript. L.D. supervised the project.

3. HALIDE DIFFUSION IN 2D PEROVSKITES LATERAL HETEROSTRUCTURES

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3.1 Introduction

Facile anionic migration is a key factor in halide perovskite instability.¹⁻⁴ Attempts at limiting the anionic migration in perovskites have been mainly focused on post-synthetic treatments, passivation by organic ligands, incorporation of ion-blocking interfacial layers, and optimization of thin-film microstructures.⁵⁻⁸ These strategies, although somewhat effective, only solve the anion migration issue at the interface. Suppressing anionic migration in bulk perovskites is crucial in addressing intrinsic instability and unlocking the full potential of halide perovskites for future applications. This has led to an increasing interest in two-dimensional (2D) perovskites due to their higher enthalpy of formation and better ambient stability compared with their three-dimensional (3D) counterparts. The reduced dimensionality of 2D perovskites also offers additional flexibility for tuning the optoelectronic properties.⁹⁻¹⁴

Heterostructures of 2D materials such as graphene, transition metal dichalcogenides, and hexagonal boron nitride have been extensively used for spatial modulation of chemical, structural, and electronic properties. The exciting material properties and device physics displayed by 2D heterostructures have driven technological advancements in the electronics industry.¹⁵⁻¹⁷ Halide perovskite heterostructures have been invaluable for direct visualization of ionic migration *via* photoluminescence (PL) spectroscopy rather than relying on indirect electrical indicators such as current-voltage hysteresis and electrical poling effects.¹⁸⁻²⁴ Obtaining phase pure perovskite lateral heterostructures is challenging due to their high ionic mobility, although recently our group reported a solution-phase sequential growth approach for synthesis of phase pure and atomically sharp 2D halide perovskite lateral epitaxial heterostructures.²⁴ However, a quantitative understanding of the anionic diffusion in these 2D perovskite lateral heterostructures is still missing. In this study, we have expanded our library of heterostructures by varying the ligand chemistry and synthesizing quasi-2D (n > 1) halide perovskite lateral heterostructures. This library

of lateral heterostructures was then utilized to analyze the impact of organic cation and inorganic layer thickness on bromide-iodide (Br-I) inter-diffusion kinetics by confocal PL tracking and diffusion coefficient calculation using the Boltzmann-Matano method. Additionally, the molecular dynamics (MD) simulation predictions of diffusion free energy barriers for all the heterostructures were in good agreement with the experimental observations.



Figure 3.1: Optical and morphological characterizations of 2D lateral heterostructures. a, Schematic illustration of lateral heterostructures along with chemical structures of BA, PEA, 2P, and 1T organic cations. The inorganic octahedra in blue represent the bromide perovskite and the inorganic octahedra in green represent the iodide perovskite. **b, c, d, e,** BF, PL, SEM and AFM images of (BA)₂PbI₄-(BA)₂PbBr₄. **f, g, h, i,** BF, PL, SEM, and AFM images of (PEA)₂PbI₄-(PEA)₂PbBr₄. **j, k, l, m,** BF, PL, SEM, and AFM images of (1T)₂PbI₄-(1T)₂PbBr₄. **n, o, p, q,** BF, PL, SEM, and AFM images of (2P)₂PbI₄-(2P)₂PbBr₄. The dashed yellow lines in SEM and AFM images highlight the lateral heterojunctions separating the central bromide and edge iodide perovskites. All AFM images have been superimposed with height profiles along the dashed black lines. BF and PL images have been captured for the same heterostructure, but different samples have been used for both SEM and AFM imaging to best represent the pristine heterostructures. All scale bars are 5 μm.

3.2 2D lateral heterostructures with varying organic cations

In this work, we chose four organic cations – butylammonium (BA), phenylethylammonium (PEA), thiophenylethylammonium (1T), and biphenylethylammonium (2P) – to study the effect of ligand rigidity (BA *vs.* PEA), heteroatoms (PEA *vs.* 1T), and conjugation length (PEA *vs.* 2P) on halide diffusion. The chemical structures of organic cations and the schematics of the assembled single crystal 2D lateral heterostructures are shown in **Figure 3.1a**. The 2D lateral heterostructures were synthesized using our previously reported solution-processed solvent evaporation method.²³⁻²⁵ Details of the synthesis process can be found in the 'Methods' section. **Figure 3.1b and 3.1c** respectively show the bright-field (BF) and PL images of BA based lateral heterostructure with (BA)₂PbI₄ edge and (BA)₂PbBr₄ center. Scanning electron microscope (SEM) image of (BA)₂PbI₄-(BA)₂PbBr₄ heterostructure (**Figure 3.1d**) shows the contrast between the bromide and iodide regions. The surface morphology and height profile across the lateral heterojunction are captured in the atomic force microscopy (AFM) image (**Figure 3.1e**). Similarly, BF, PL, SEM, and AFM images of (PEA)₂PbI₄-(PEA)₂PbBr₄ lateral heterostructure are shown in **Figure 3.1 f-i**.

Both BA and PEA based lateral heterostructures were reported in our previous study.²⁴ 1T and 2P systems are new additions to our family of 2D halide lateral heterostructures, further emphasizing the versatility of the sequential solvent evaporation method for a variety of organic cations. BF, PL, SEM, and AFM images of (1T)₂PbI₄-(1T)₂PbBr₄ lateral heterostructure are shown in **Figure 3.1 j-m**. Finally, **Figure 3.1 n-q** show the BF, PL, SEM and AFM images of (2P)₂PbI₄-(2P)₂PbBr₄ lateral heterostructure.

3.3 Visualization of halide migration

To visualize the halide migration in 2D lateral heterostructures, we utilized the composition dependent PL property of perovskites. Halide migration in the lateral heterostructures was thermally activated and the consequent local PL change was monitored using confocal laser scanning microscope. The spatial variation in PL between the edge and central region of a pristine $(PEA)_2PbI_4-(PEA)_2PbBr_4$ lateral heterostructure at room temperature (RT) is shown through the four discrete emission channels (411 – 446 nm, 446 – 482 nm, 482 – 517 nm, and 517 – 553 nm) in **Figure 3.2a**. The dimensions of the emitting regions have also been added in each PL image to highlight their change upon heating the samples. Merged image depicts the combined PL emission

channels from 411 - 553 nm. Upon heating the lateral heterostructure at 100 °C for 30 mins, there is an evident movement of halide ions, depicted by the evolution of the spatial PL emission in Figure 3.2b. For instance, in the 411 - 446 nm channel, the expansion of 6.1 μ m × 6.9 μ m size PL emission region at RT to 7.1 μ m \times 7.5 μ m after heating shows the movement of bromide ions from the center to the edge of the crystal. The PL spectrum evolution after heating the (PEA)₂PbI₄-(PEA)₂PbBr₄ heterostructure is shown in **Figure 3.2c**. The intermixing and movement of halides across the heterojunction is further elucidated by the SEM imaging, EDX mapping, and EDX spectrum at RT and after heating at 100 °C for 30 hrs (Appendix Figure B.1). In addition to the PL emission evolution, the Br-I inter-diffusion upon heating also impacts the potential distribution across the heterostructure as captured by the Kelvin probe force microscopy (KPFM) images and potential profiles in Appendix Figure B.2. The confocal PL imaging, PL spectrum, SEM / EDX mapping, and KPFM imaging qualitatively illustrate Br-I inter-diffusion across the lateral heterojunctions. To quantify the diffusion rates, a correlation between PL emission and composition was established. Perovskite thin films for $(PEA)_2PbBr_{4x}I_{4(1-x)}$ (x = 1, 0.75, 0.50, 0.25, 0) were synthesized by spin coating a stoichiometric solution of bromide and iodide precursors. BF and PL images of these halide alloy perovskites are shown in Appendix Figure B.3a and B.3b, respectively. The PL emission energy vs. composition curve plotted for $(PEA)_2PbBr_{4x}I_{4(1-x)}$ perovskite was then used to obtain a linear relationship between PL emission and halide composition (Appendix Figure B.3c). This calibration curve is utilized to convert the PL emission line scans along the dotted white arrows in the merged images of Figure 3.2a and 3.2b to the concentration profiles shown in Figure 3.2d. The halide migration and the consequent compositional change after heating is evident in these concentration profiles. The evolution of confocal PL imaging, PL spectrum, and concentration profile for (BA)₂PbI₄-(BA)₂PbBr₄, (1T)₂PbI₄-(1T)₂PbBr₄, and (2P)₂PbI₄-(2P)₂PbBr₄ lateral heterostructures are shown in **Appendix** Figure B.4, B.5, and B.6, respectively.

Thermal stability of $(1T)_2PbBr_4$ and L_2PbI_4 (L = PEA, 1T, 2P) perovskites and L_2PbI_4 -L₂PbBr₄ (L = BA, PEA, 1T, 2P) lateral heterostructures was tested by XRD characterizations to ensure phase preservation even after heating at 100 °C for 10 hrs (**Appendix Figure B.7 and B.8**). Thermal stability check using XRD for L_2PbBr_4 (L = BA, PEA, 2P) and (BA)₂PbI₄ has already been reported in our previous work.²³



Figure 3.2: Confocal imaging of halide inter-diffusion in (PEA)₂PbI₄-(PEA)₂PbBr₄. Confocal image of the lateral heterostructure at **a**, RT and **b**, after heating at 100 °C for 30 mins, respectively. The PL emissions in the wavelength range 411 - 446 nm, 446 - 482 nm, 482 - 517 nm, and 517 - 553 nm are represented in violet, blue, green, and red colors, respectively. Length and width of the emitting region has been added to each of the emission channels to highlight crystal dimensions and halide migration upon heating. The merged image shows the PL emission from 411 - 553 nm. All scale bars are 5 µm. **c**, **d**, Evolution of PL spectra and halide concentration profile of the lateral heterostructure during the inter-diffusion process. PL spectrum at RT and after heating are collected from the white circled areas in the merged images. Scatter points in **d** are estimated along the dashed white arrows in the merged images. Scatter points in **d** are experimentally obtained concentration from PL emissions and line plots are Gaussian fittings to the experimental data points.

3.4 Diffusion coefficient calculations

The Br-I migration across the lateral heterojunction is considered as a one-dimensional transient diffusion problem represented by the following equation.^{26,27}

$$\frac{\partial \mathbf{x}}{\partial t} = \frac{\partial}{\partial \mathbf{y}} \left(\mathbf{D}(\mathbf{x}) \frac{\partial \mathbf{x}}{\partial \mathbf{y}} \right) \tag{1}$$

where, 'x' is the bromide concentration, 't' is the heating time, 'y' is the diffusion length, and D(x) is the concentration dependent diffusion coefficient. The analytical solution of equation (1) is as follows.^{27,28}

$$D(x^{*}) = -\frac{1}{2t} \frac{\int_{x_{L}}^{x^{*}} (y - y_{M}) dx}{\left(\frac{dx}{dy}\right)_{x^{*}}}$$
(2)

where, 'x^{*}' is the bromide concentration at the current position, 'x_L' is the bromide concentration at the boundary position, 'y_M' is the Matano interface (a mathematical parameter which represents composition weighted average position), and ' $D(x^*)$ ' is the halide inter-diffusion coefficient for x^{*} bromide concentration. The experimentally obtained concentration profile is fitted with Gaussian distribution and Boltzmann-Matano method is then used to analytically estimate the diffusion coefficient. An example explaining the procedure of extracting Matano interface, and eventually concentration dependent Br-I inter-diffusion coefficient using equation (2) is illustrated in Appendix Figure B.9. We would like to highlight that the simplified 1D mathematical model for halide inter-diffusion calculations has been utilized due to isotropy of the 2D perovskites in the in-plane direction. This is in alignment with the diffusion studies conducted for 3D perovskites.^{18,21,22} To further ensure the validity of our assumption, we estimated Br-I interdiffusion coefficients across two arbitrarily chosen directions for PEA based lateral heterostructures. Appendix Figure B.10 clearly demonstrates that the estimated diffusion coefficients are within the same order-of-magnitude irrespective of the direction chosen for diffusion analysis. Therefore, 1D model is a reasonable approximation to represent diffusion kinetics in our lateral heterostructures.

Figure 3.3a shows the concentration dependent halide inter-diffusion coefficients of all the 2D lateral heterostructures. We also collected confocal PL mapping and the consequent concentration profile evolution after 1 hr of heating at 100 °C to calculate halide inter-diffusion coefficients at 1 hr time step (**Appendix Figure B.11**). Same heterostructure samples were used for 30 mins and 1 hr diffusion to compare the resulting inter-diffusion coefficients. As expected, the diffusion rates decrease slightly with progressive heating as the concentration gradient across the lateral heterostructures reduces. Ideally, more time steps could be used to obtain the inter-diffusion coefficients. However, longer heating times and repeated confocal PL measurements using point-by-point laser scanning can damage the exposed region of the heterostructure, compromising the quality of the junction and the consequent diffusion analysis.



Figure 3.3: Quantification of halide inter-diffusion. a, Comparison of impact of organic cations on the concentration dependent Br-I inter-diffusion coefficients across BA, PEA, 1T, and 2P based lateral heterostructures using analytical BM method at 100 °C after heating for 30 mins. The box represents data points between 25 - 75 percentiles of the range, whisker represents the minimum-to-maximum range, and the dashed line highlights the average diffusion coefficients of the sample data points. **b,** Side view and top view depiction of the two potential halide diffusion pathways in the inorganic octahedral framework of perovskites. Layer 0 represents the axial halides and layer 1 represents the equatorial halides. I, Pb, S, N, C, and H atoms are illustrated by green, orange, yellow, blue, grey, and white spheres, respectively. Organic cations have not been shown in all illustrations for the purpose of clarity. Representative free energy (FE) barrier calculation in kcal(mol)⁻¹ for the two migration pathways – layer 1 to layer 0 and layer 1 to layer 1 is also shown.

BA based lateral heterostructure shows the highest diffusion rates compared with other organic cations for all halide compositions. Halide migration in BA based system is on average ~ 6 times faster than PEA and 1T systems which show similar diffusion rates. Similarly, Br-I interdiffusion in BA lateral heterostructures is on average ~ 10 times faster than 2P system. Additionally, average diffusion rates in PEA and 1T systems are ~ 2 times faster than 2P lateral heterostructures. Therefore, the best inhibition of halide migration in 2D perovskites can be achieved by using bulky π -conjugated organic cations such as 2P.

To interrogate the molecular details of halide diffusion, we computed free energy barriers for different diffusion paths in various halide perovskites using MD simulations. For vacancymediated halide migration, we analyzed two potential diffusion pathways (**Figure 3.3b**) – hopping between equatorial and axial positions (layer $1 \leftrightarrow 0$) and hopping along equatorial positions (layer $1 \leftrightarrow 1$). The free energy profiles for L₂PbX₄ (L = BA, PEA, 1T, 2P; X = Br, I) were calculated *via* umbrella sampling (detailed in the 'Methods' section). As depicted by a representative example in **Figure 3.3b**, the free energy profiles were calculated using the degree of rotation from the initial halide position as the collective variable, rather than migration distance as reported in previous works.^{4,20} As a result, the free energy profiles exhibit physically correct symmetry along the reaction coordinate for hopping along the equatorial positions. Here, we only discuss the L₂PbI₄ case, since the L₂PbBr₄ results exhibit similar trends with the main difference being lower overall free energy barriers due to the smaller halide.

For diffusion between equatorial positions (layer $1 \leftrightarrow 1$), which is the dominant path for lateral diffusion, all ligands exhibit comparable free energy barriers of ~ 12 kcal(mol)⁻¹ (**Appendix Table B.1**). This is larger than the barrier of 8.51 kcal(mol)⁻¹ for the bulk 3D system calculated using the same method (*vide infra*), which is consistent with the general suppression of halide diffusion in the reduced dimensionality systems.²⁰ However, comparing the barriers across the 2D systems is difficult due to the use of auxiliary restraints on neighboring halides to limit off-target halide diffusion during sampling (**Appendix Figure B.12**), which prevents us from directly probing the effect of the lattice softness due to ligand substitutions. Nevertheless, we observed several indirect indications that halide diffusion is more rapid in the BA-substituted systems. While the relatively mild restraint of 50 kcal(mol-Å)⁻¹ was sufficient to suppress off-target diffusion for all the π -conjugated ligands, a stronger 100 kcal(mol-Å)⁻¹ restraint was required for the BA ligand. Similarly, BA required a higher spring constant for the strong restraint on the diffusion halide during umbrella sampling. It should be noted that the mild constraint on non-target halides help in preventing undesired diffusion, however, the constraint on the target halide ensures sufficient sampling through the reaction coordinate.²⁹ The stronger constraints required for BA compared with the other ligands (PEA,1T, 2P) provides indirect evidence of the much softer lattice and facile diffusion in the BA systems. Furthermore, the same constraints work well for PEA, 1T and 2P implying that they exhibit comparable diffusion behavior.

Analyzing the free energy profiles for halide transfer between the equatorial and axial positions (layer $1 \leftrightarrow 0$) for different ligands reveals significant differences from the 'layer $1 \leftrightarrow 1$ ' profiles due to the stronger interactions between the ligands and halides in the axial position (**Appendix Figure B.13**). There is a strong preference for the vacancy to occupy the axial position compared with the equatorial position. In the case of the π -conjugated ligands, the barrier for halide transfer from the equatorial to the axial position is reduced by up to ~ 6 kcal(mol)⁻¹ compared with the BA ligand. The barrier of the 2P ligand appears to be lower than the other π -conjugated ligands, although it is difficult to resolve the barrier. We note that this is due to the use of auxiliary restraints on the neighboring halides and the rigidness of the lattice that limit the geometric relaxation of the certain states. For BA, this artifact is even more apparent due to the stronger restraints required to avoid off-target transfer in the soft lattice of BA. Nevertheless, these results suggest that the equatorial to axial hopping channel is comparable across the π -conjugated structures, with 2P exhibiting a potentially lower barrier and BA being an outlier with extremely facile halide transport that challenges our ability to resolve the barrier heights with MD.

The foregoing analysis of the activation energies for halide diffusion recapitulates the same trend that is observed experimentally; namely, that anion diffusion as a function of the ligand substitution follows the trend BA >> PEA ~ 1T > 2P. From the simulations, BA stands out as it has the softest lattice and is more likely to facilitate lateral diffusion than equatorial-to-axial diffusion. PEA and 1T yield similar free energy profiles, while 2P shows slight differences potentially linked to better lattice stability. A confounding factor in this interpretation is that vacancy concentration is unknown and cannot easily be quantified in these systems. Nevertheless, the agreement between the activation energy analysis and the experimentally observed diffusivity suggests that the vacancy concentrations are comparable across the materials or follow a similar trend to the activation energies.²⁴

3.5 Quasi-2D perovskite lateral heterostructures and diffusion kinetics

In addition to the organic cations, we analyzed the impact of inorganic layer thickness or 'n' number in $L_2A_{n-1}B_nX_{3n+1}$ (L = organic cations, A = organic / inorganic cations, B = metal cations, X = halide anions). The first challenge in studying halide diffusion in quasi-2D (n > 1) perovskites is the synthesis of phase pure quasi-2D perovskites. In our solvent evaporation method used for 2D perovskites, the organic solvent system does not offer stable and favorable growth kinetics for formation of n > 1 phases. So, we employed a different method for assembling the quasi-2D lateral heterostructures through ion exchange, which has commonly been used in the field.^{18,30-32} A schematic representation of the ion exchange method is shown in **Appendix Figure B.14**. The first step was synthesis of quasi-2D bromide perovskite using controlled slow cooling in solution. The synthesized bromide nanocrystals were then transferred on to the silicon substrate using mechanical exfoliation. Part of the exfoliated bromide nanocrystals was protected by encapsulating with drops of polymethyl methacrylate (PMMA) solution. The substrate with the bromide nanocrystals was then exposed to iodide vapors. The encapsulated bromide regions remain unaffected, and the unprotected regions undergo exchange reaction with iodide vapor leading to the formation of Br-I lateral heterostructures.

Figure 3.4a shows an illustration of (PEA)₂(MA)_{n-1}Pb_nI_{3n+1}-(PEA)₂(MA)_{n-1}Pb_nBr_{3n+1} (n = 2, 3) quasi-2D perovskite lateral heterostructures analyzed in this study. BF, PL, SEM, and AFM images of (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇ lateral heterostructure are shown in **Figure 3.4 b-e**. SEM imaging, EDX elemental mapping, and EDX spectrum in **Appendix Figure B.15** shows the spatial distribution of bromide and iodide across the (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇ lateral heterojunction. To study the Br-I inter-diffusion, (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇ lateral heterostructure was heated at 100 °C for 30 mins. The halide migration upon thermal activation was observed using confocal PL mapping as shown in **Appendix Figure B.16a and B.16b**. The change in PL emission before and after heating is captured in **Appendix Figure B.16a**. **Figure 4f** and **Appendix Figure B.16d** show the corresponding evolution of concentration profile. BF, PL, SEM, and AFM images of (PEA)₂(MA)₂Pb₃I₁₀-(PEA)₂(MA)₂Pb₃Br₁₀ lateral heterostructure are shown in **Figure 3.4 g-j**. SEM / EDX characterization of the lateral heterostructure is shown in **Appendix Figure B.17a**. The confocal PL mapping of the lateral heterostructure at RT and after heating are shown in **Appendix Figure B.18a** and **B.18b** and the

corresponding PL spectrum evolution is shown in **Appendix Figure B.18c**. **Figure 3.4k** and **Appendix Figure B.18d** demonstrate the corresponding concentration profile evolution.



Figure 3.4: Optical and morphological characterization of quasi-2D lateral heterostructures. Schematic illustration of quasi-2D lateral heterostructures (PEA)₂(MA)Pb₂I₇a. (PEA)₂(MA)Pb₂Br₇ and (PEA)₂(MA)₂Pb₃I₁₀-(PEA)₂(MA)₂Pb₃Br₁₀. The inorganic octahedra in blue represent the bromide perovskite and the inorganic octahedra in red represent the iodide perovskite. **b**, BF image, **c**, PL image, **d**, SEM image, **e**, AFM image, and **f**, concentration profile evolution upon heating for (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇ lateral heterostructure. **g**, BF image, h, PL image, i, SEM image, j, AFM image, and k, concentration profile evolution upon heating for (PEA)₂(MA)₂Pb₃I₁₀-(PEA)₂(MA)₂Pb₃Br₁₀ lateral heterostructure. The yellow dashed lines in all SEM and AFM images highlight the lateral heterojunctions. All AFM images are superimposed with a height profile along the black dashed lines. BF and PL images have been captured for the same heterostructure, but different samples have been used for SEM, AFM, and concentration profile to best represent the pristine heterostructures. All white scale bars are 5 µm and the black scale bar is 1 µm.

Using the ion exchange method coupled with PMMA protection of pristine bromide phase, we were able to synthesize high-quality quasi-2D lateral heterojunctions, however, it is difficult to ensure phase purity of the iodide region. To ascertain the validity of our diffusion analysis using ion exchange method and understand the impact of synthesis process on Br-I inter-diffusion, we

synthesized n = 2 lateral heterostructure using a second "direct bulk synthesis" approach, which is schematically depicted in **Appendix Figure B.19a**. Details of the bulk synthesis method can be found in the 'Methods' sections. BF, PL, SEM and AFM imaging of (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇ lateral heterostructure using bulk synthesis method are shown in **Appendix Figure B.19 b-e**. Elemental characterization using SEM / EDX and concentration profile evolution using confocal PL mapping are captured in **Appendix Figure B.20 and B.21**, respectively. Thermal stability of all quasi-2D bromide perovskites, iodide perovskites and bromide-iodide lateral heterostructures analyzed in this study was tested by XRD characterizations to ensure phase preservation even after heating at 100 °C for 10 hrs (**Appendix Figure B.22 and B.23**).

After extracting concentration profiles of all the quasi-2D lateral heterostructures post heating, we proceed to quantify the halide diffusion rates across the junctions using Boltzmann-Matano method described in the previous section. **Figure 3.5a** compares the concentration dependent diffusion coefficient for (PEA)₂(MA)_{n-1}Pb_nI_{3n+1}-(PEA)₂(MA)_{n-1}Pb_nBr_{3n+1} (n = 1, 2, 3) quasi-2D perovskite lateral heterostructures. **Appendix Figure B.24** also depicts the halide interdiffusion coefficient of all quasi-2D lateral heterostructures after 1 hr of heating at 100 °C. The quasi-2D systems have higher halide diffusion rates compared with the 2D perovskites which can potentially be attributed to weaker physical confinement and wider in-plane transport channels. For quasi-2D perovskites, the increment of the calculated diffusion constant becomes less apparent as the 'n' number increases from 1 to 3. This is somewhat akin to the quantum confinement effect where the band gap decrement reduces with the increasing 'n' number. Additionally, since no significant difference was observed in the calculated diffusion coefficients for n = 2 lateral heterostructures synthesized using bulk synthesis and ion exchange methods (**Appendix Figure B.25**), our analysis of Br-I inter-diffusion in quasi-2D systems holds true irrespective of the synthesis method employed for the heterostructure assembly.

Along with the graphical representation of diffusion coefficients in **Figure 3.3a and 3.5a**, average diffusion coefficient at each composition for all 2D and quasi-2D heterostructures have been listed in **Appendix Table B.2** for better readability.

To probe the thermodynamic origin of the differences in diffusion rates among the quasi-2D perovskites, free energy calculations for $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1, 2, 3) and MAPbI₃ (n = ∞) 3D perovskites, were conducted using MD simulations. The calculated free energy barrier for 3D perovskites is 8.51 kcal(mol)⁻¹, which is ~ 4 kcal(mol)⁻¹ lower than the previously reported value

from DFT calculations.⁴ It is difficult to comment on relative accuracy of these numbers, considering that the earlier DFT study was based on nudged elastic band calculations, which neglect entropic contributions to the free energy barrier, while the MD simulations use approximate interatomic potentials. Nevertheless, the histogram (**Appendix Figure B.26**) from the umbrella sampling calculation shows excellent sampling throughout the entire reaction coordinate, and analysis of the trend based on these calculations thus remains credible.



Figure 3.5: Impact of inorganic layer thickness. a, Comparison of concentration dependent Br-I inter-diffusion coefficients across $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}-(PEA)_2(MA)_{n-1}Pb_nBr_{3n+1}$ (n = 1, 2, 3) lateral heterostructures using analytical BM method at 100 °C after heating for 30 mins. The box represents data points between 25 – 75 percentiles of the range, whisker represents the minimum-to-maximum range, and the dashed line highlights the average diffusion coefficients of the sample data points. **b,** Free energy curves and barriers in kcal(mol)⁻¹ for different halide diffusion pathways (layer 1 \leftrightarrow 1 in solid lines, layer 1 \leftrightarrow 2 in dashed lines, layer 2 \leftrightarrow 3 in dashdot line, and layer 3 \leftrightarrow 3 in dotted line) for (PEA)₂(MA)_{n-1}Pb_nI_{3n+1} [n = 1 in blue, n = 2 in green, n = 3 in orange, and n = ∞ (3D MAPbI₃) in cyan] using MD simulations.
As 'n' increases, there are 1 (layer $1 \leftrightarrow 2$) and 3 (layer $1 \leftrightarrow 2$, layer $2 \leftrightarrow 3$, layer $3 \leftrightarrow 3$) additional halide diffusion pathways for n = 2 and n = 3, respectively, compared with n = 1 perovskites (**Appendix Figure B.27**). **Figure 3.5b** shows the free energy profiles and barriers of different pathways for (PEA)₂(MA)_{n-1}Pb_nI_{3n+1} (n = 1, 2, 3) perovskites. In all the diffusion pathways, n = 2 and n = 3 have similar barriers as $n = \infty$ (3D perovskites) except for the layer in contact with the surface ligands (layer $1 \leftrightarrow 1$), which has higher barriers for 2D and quasi-2D perovskites compared with 3D, suggesting that the bulky ligands at the surface increase the free energy barrier and as the number of inorganic layers increases, this surface effect reduces until it eventually achieves 3D perovskite energy barrier.

2D perovskites (n = 1) have the highest barrier of 11.94 kcal(mol)⁻¹, which is $1.5 \sim 2$ kcal(mol)⁻¹ and ~ 3.5 kcal(mol)⁻¹ higher than that of quasi-2D n = 2 and n = 3 migrations between layer 1 \leftrightarrow 1 and layer 1 \leftrightarrow 2 \leftrightarrow 3, respectively. The higher energy barrier in 2D perovskites would result in slower diffusion, which is consistent with the experiments. Among quasi-2D perovskites, n = 3 perovskites have slightly lower barrier for layer 1 \leftrightarrow 1 migrations and similar energy barrier for layer 1 \leftrightarrow 2 migrations compared with n = 2 perovskites. n = 3 perovskites also offer additional diffusion pathways for hopping between equatorial and axial positions (layer 2 \leftrightarrow 3) and within equatorial positions (layer 3 \leftrightarrow 3). Comparing the free energy barriers and available diffusion pathways, n = 3 system is expected to have faster halide diffusion than n = 2 system, which is in alignment with the experimental results.

Similar to the calculations for different ligands, the above discussed analysis is based on the calculation for $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$ instead of $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}-(PEA)_2(MA)_{n-1}Pb_nBr_{3n+1}$ due to the scaling of the interatomic potential used in MD simulations for different halide types.

3.6 Conclusion

In this study, we demonstrated the synthesis of novel 2D and quasi-2D halide perovskites lateral heterostructures. Utilizing these lateral heterostructure platforms, we tracked halide migration in perovskites using PL mapping. The halide migrations were quantified by diffusion coefficient calculations using Boltzmann-Matano method. Among the four different organic cations – BA, PEA, 1T, and 2P – bulkier π -conjugated organic cations like 2P offer better inhibition to Br-I inter-diffusion compared with straight chain aliphatic organic cations like BA. This was confirmed by MD simulations where a more rigid lattice leads to slower diffusion. Additionally, quasi-2D perovskites were found to have faster halide diffusion compared with their 2D counterparts which can be attributed to their reduced free energy barriers. MD simulations also showed that the inhibiting effect of the surface bulky organic ligands on halide diffusion in quasi-2D perovskites decreased as the number of inorganic layers increased till it finally reached 3D perovskites diffusion rates. By presenting a versatile system of halide perovskite heterostructures in this study, we aim to emphasize the importance of these platforms for unravelling fundamental material properties. Additionally, an in-depth understanding of the impact of each component in perovskite structure on halide diffusion kinetics will drive the future innovations towards novel material design and device applications.

3.7 Experimental Methods

3.7.1 Chemicals and reagents

The lead precursor salts, including lead bromide (PbBr₂), lead iodide (PbI₂), and lead oxide (PbO); solvents, including chlorobenzene (CB), dimethyl formamide (DMF), acetonitrile (AN), and dichlorobenzene (DCB); and acids, including hydrogen bromide (HBr, 48 wt% H₂O), hydrogen iodide (HI, 57 wt% H₂O), and hypophosphorous acid (H₃PO₂, 50 wt% H₂O); were purchased from Sigma Aldrich and were used as received. Perovskite precursor salts, including butylammonium bromide (BABr), butylammonium iodide (BAI), phenylethylammonium bromide (PEABr), phenylethylammonium iodide (PEAI), thiophenylethylammonium bromide (1TBr), thiophenylethylammonium iodide (1TI), biphenylethylammonium bromide (2PBr), biphenylethylammonium iodide (2PI), methylammonium bromide (MABr), and methylammonium iodide (MAI); were purchased from Greatcell Solar Ltd. and were used as received. The encapsulating polymer PMMA 950K was purchased from Microchem.

3.7.2 Synthesis of 2D perovskites nanocrystals (n = 1)

Pure phase $(1T)_2PbX_4$ (X = Br, I) perovskite nanocrystals were synthesized using solvent evaporation method for XRD characterizations. 0.02 mmol of (1T)X (X = Br, I) and 0.01 mmol of PbX₂ (X = Br, I) precursors were dissolved in 2 ml solution of DMF and CB mixed in 1:1 volume ratio. The concentrated precursor solution was then diluted 60 times using a solvent system of CB, AN, and DCB mixed in the volume ratio 2.5:1:0.01. A Si / SiO₂ substrate was placed inside a glass vial kept on a hot plate maintained at 50 °C. ~ 10 μ l of the diluted precursor was then dropped on the Si / SiO₂ substrate. The solvent evaporation is associated with the nucleation and growth of the nanocrystals on the substrate. The substrate was then removed from the hot plate in ~ 15 mins, once all the solvent was evaporated.²³⁻²⁵

3.7.3 Growth of 2D perovskites lateral heterostructures (n = 1)

All 2D perovskite lateral heterostructures were grown using sequential solvent evaporation method.²³⁻²⁵ Bromide nanocrystals were first synthesized on the Si / SiO₂ substrate followed by epitaxial growth of iodide perovskites from the bromide templates. Pure phase precursor solutions were prepared for (L)₂PbX₄ (L = BA, PEA, 1T, 2P; X = Br, I) perovskites by adding 0.02 mmol of LX and 0.01 mmol of PbX₂ in 2 ml solution of DMF and CB mixed in 1:1 volume ratio. The concentrated precursor solutions were then diluted 60 times using a ternary solvent system of CB, AN, and DCB mixed in the volume ratio 2.5:1:0.01.

 $(BA)_2PbI_4-(BA)_2PbBr_4$ lateral heterostructure: For the synthesis of $(BA)_2PbBr_4$ nanocrystals, ~ 5 µl of the 60 times diluted precursor solution was dropped on the Si / SiO₂ substrate inside a vial on a hot plate maintained at 50 °C. The solvents evaporated from the solution and the substrate was removed from the hot plate in ~ 15 mins. The synthesized bromide nanocrystals were then protected from solvents in the iodide solution by adding ~ 10 µl of CB. 120 times diluted solution of iodide precursors was made by further dilution of 60 times diluted solution using a solvent system of CB and AN in the volume ratio 2.5:1. ~ 5 µl of the 120 times diluted iodide precursor solution was then added on top of CB and the Si / SiO₂ substrate inside the vial was again put on the hot plate at 50 °C. Epitaxially grown Br-I lateral heterostructures were formed on the Si / SiO₂ substrate after ~ 15 mins of solvent evaporation.

(*PEA*)₂*PbI*₄-(*PEA*)₂*PbBr*₄ lateral heterostructure: The PEA based lateral heterostructures were synthesized using the same process as discussed for BA based heterostructures.

 $(1T)_2PbI_4-(1T)_2PbBr_4$ lateral heterostructure: The 1T based lateral heterostructures were synthesized using the same process as discussed for BA based heterostructures.

 $(2P)_2PbI_4-(2P)_2PbBr_4$ lateral heterostructure: The 2P based lateral heterostructures were synthesized using the same process as discussed for BA based heterostructures. The hot plate was maintained at a temperature of 70 °C instead of 50 °C used for BA system.

3.7.4 Synthesis of quasi-2D perovskites crystals (n = 2 and n = 3)

(*PEA*)₂(*MA*)*Pb*₂*Br*₇ (n = 2) and (*PEA*)₂(*MA*)₂*Pb*₃*Br*₁₀ (n = 3): PbO (0.59 mmol), PEABr (0.19 mmol for n = 2, 0.15 mmol for n = 3), and MABr (0.40 mmol for n = 2, 0.55 mmol for n = 3) precursors were added to an acid mixture containing 0.9 ml HBr (48 wt% H₂O) and 0.1 ml of H₃PO₂ (50 wt% H₂O) in a 10 ml glass vial. Additional 100 µL DMF was added into the solution to enhance the formation of quasi-2D bromide perovskites. The bromide perovskite precursor solution was heated in an oil bath at 120 °C under continuous magnetic stirring until the precursors were completely dissolved. The solution was then cooled at a rate of 2 °Cmin⁻¹, leading to the nucleation and growth of bromide crystals. The crystals were collected by vacuum filtration, and the residue solvent was removed *via* vacuum pumping.

<u>(PEA)₂(MA)Pb₂I₇ (n = 2) and (PEA)₂(MA)₂Pb₃I₁₀ (n = 3)</u>: PbO (0.59 mmol), PEAI (0.43 mmol for n = 2, 0.15 mmol for n = 3), and MAI (0.60 mmol for n = 2, 0.53 mmol for n = 3) precursors were added to an acid mixture containing 0.9 ml HI (57 wt% H₂O) and 0.1 ml of H₃PO₂ (50 wt% H₂O) in a 10 ml glass vial. Under continuous magnet stirring, the vial was heated to 120 °C in an oil bath. After the solid precursors were completely dissolved and the solution became transparent, the stirring is terminated, and the solution was cooled at a rate of 2 °Cmin⁻¹, during which the crystals were formed. The final crystals were collected by vacuum filtration, and the residue solvent was removed *via* vacuum pumping.

3.7.5 Growth of quasi-2D perovskites lateral heterostructures (n = 2 and n = 3)

<u>Bulk synthesis method for n = 2</u>: Quasi-2D bromide perovskites were synthesized and collected firstly using the methods described above and then ~ 0.1 g of the synthesized crystal was taken into another blank vial and used as the nucleation template for growth of quasi-2D iodide perovskites. The quasi-2D iodide solution was prepared by adding PbO (0.59 mmol), PEAI (0.43 mmol), and MAI (0.60 mmol) precursors into an acid mixture containing 0.9 ml HI (57 wt% H₂O)

and 0.1 ml of H₃PO₂ (50 wt% H₂O) in a 10 ml glass vial. The glass vial was heated to 120 °C in an oil bath under continuous magnetic stirring until all precursors were completely dissolved. The temperature was then decreased to 50 - 55 °C at a rate of 2 °Cmin⁻¹. 200 µl of iodide solution was taken out and added into the vial containing bromide perovskite crystals. After 5 mins at room temperature, the quasi-2D iodide perovskites precipitated around quasi-2D bromide perovskites. The mixed crystals were collected by vacuum filtration, and the residue solvent was removed *via* vacuum pumping. Finally, the quasi-2D perovskites lateral heterostructures were obtained using mechanical exfoliation with scotch tape.

Ion exchange method for n = 2 and n = 3: The quasi-2D bromide perovskite crystals were first mechanically exfoliated on silicon substrate. Thin bromide single crystals with large domain sizes were located using the optical microscope and were then partially protected by PMMA solution. The PMMA solution was dried using vacuum pumping for ~ 15 mins. The partially unprotected bromide crystals were exposed to iodide ions by dropping ~ 40 µl of iodide solution (such as HI or the iodide perovskite precursor solution) near the sample. The iodide solution was then dried under vacuum for ~ 15 mins, initiating the ion exchange process between the iodide ions from solution and bromide ions from unprotected crystals, leading to the formation of quasi-2D perovskites lateral heterostructures.

3.7.6 Spin coating of (PEA)₂PbBr_{4x}I_{4(1-x)} thin films

To obtain a relationship between PL emission and halide composition, $(PEA)_2PbBr_{4x}I_{4(1-x)}$ thin films were synthesized using spin coating. Pure bromide $[(PEA)_2PbBr_4]$ and iodide $[(PEA)_2PbI_4]$ perovskite precursor solutions were prepared by dissolving 0.1 mmol of PEAX (X = Br, I) and 0.05 mmol of PbX₂ (X = Br, I) in 2 ml of DMF. 100 µl of halide alloy solution was prepared by mixing the bromide and iodide precursor solutions in the desired stoichiometric ratio. For instance, 25 µl of (PEA)_2PbBr_4 solution and 75 µl of (PEA)_2PbI_4 solution was mixed to prepare 100 µl of (PEA)_2PbBrI₃ (Br:I = 25:75) halide alloy solution. 30 µl of the halide alloy solution was then spin coated at 1000 rpm for 30 sec followed by 10 mins thermal annealing at 95 °C in a nitrogen-filled glove box. Finally, PL emissions for different halide alloy thin films were captured using the spectrometer to obtain the PL vs. halide composition calibration curve.

3.7.7 PMMA encapsulation of lateral heterostructures

All lateral heterostructures analyzed in this study were protected from ambient conditions and potential degradation by encapsulating with PMMA polymer. The PMMA solution was diluted with CB (PMMA:CB volume ration of 3:1) before it was spin coated on the silicon substrates with perovskite heterostructures. The spin coating was performed at 1500 rpm for 1 min in a nitrogen-filled glove box.

3.8 Characterizations

3.8.1 BF imaging

All BF images were captured using a custom Olympus BX53 microscope.

3.8.2 PL imaging and PL spectrum

All PL images were captured using X-Cite Series 120 Q lamp as the excitation source. All PL spectra were measured using Coherent OBIS 375 nm laser as the excitation source. The filter cube in the Olympus BX53 microscope contains a 330 – 385 nm bandpass filter for excitation and a dichroic mirror with 400 nm cutoff wavelength for light splitting. All PL spectra were collected using SpectraPro HRS-300 spectrometer.

3.8.3 SEM imaging and EDX mapping

SEM images without EDS mapping were collected using an FEI Teneo Field Emission SEM using a 10 kV accelerating voltage, 0.1 nA beam current, and an in-lens back-scattered electron detector. For EDX mapping, SEM images were captured using a Quanta 650 FEG SEM at 10 kV and 4.5 spot size with an Everhart-Thornley detector. EDS spectra and elemental mappings were collected using an EDAX Element Silicon Drift Detector at the same beam conditions as the SEM images.

3.8.4 AFM imaging

AFM images were recorded in tapping mode using a Veeco multi-mode atomic force microscope.

3.8.5 Confocal PL imaging

A Zeiss 880 upright laser scanning microscope with a 405 nm laser line as excitation wavelength was used for PL mapping of bromide and iodide emissions across the lateral heterojunctions.

3.8.6 KPFM

KPFM measurements were performed using Asylum Cypher ES AFM in an AC (taping) image mode in air. Conductive AFM tips with Ti / Pt coating (ElectriLever from Asylum research, with mechanical resonance frequency and spring constant of 70 kHz and 2 Nm⁻¹, respectively) were used to obtain the topographical and contact potential difference (CPD) images simultaneously. The lift height was 300 nm. The perovskite samples were prepared on silicon substrates.

3.8.7 XRD

All XRD spectra were collected with a Rigaku Smart Lab using a Cu K α source ($\lambda = 1.54056$ Å) in Bragg Brentano mode.

3.9 Simulations

The modified MYP model was used for all simulations as described in our previous work.^[14] LAMMPS and PLUMED were used to perform the MD simulations. All simulations used 1 fs integration timestep and periodic boundary conditions (PBC).^{33,34} Long-range electrostatics were modeled using the particle-particle-particle-mesh (PPPM) algorithm and Lennard-Jones interactions were truncated at 15 Å. The initial structure of 2D, quasi-2D and 3D perovskites were generated by constructing representative unit cells of ideal perovskites (n = 1, 2, 3, ∞) with the bulky organic cations placed at the surface. The simulation was first relaxed in the NVE ensemble

with restrained atomic displacements of 0.01 Å per timestep for 50 ps, followed by a 1 ns NPT simulation with the Nose-Hoover thermostat and barostat. The boundary of y-direction, which is parallel to the bulky organic cations, is extended by 20 Å to prevent the interaction of organic cations from different sides due to PBC. During the NPT equilibration, the barostat was only applied to x and z-direction, which are normal to the bulky organic cations. After the equilibration, a randomly selected halide at the desired layer was removed to create a vacancy. Steered molecular dynamics (SMD) were used to generate the initial configurations for umbrella sampling (UB).^{29,} ³⁵ In SMD, we used a spring constant of 5000 kcal(mol-Å)⁻¹ and a constant velocity of 0.0125 rad/ps to steer the target diffusing halide to the vacancy. The halide neighbors of the target diffusing halide and the vacancy were mildly constrained with a spring constant of 50 kcal(mol-Å)⁻¹ to prevent undesired diffusion of non-target halides. In UB, the reaction coordinate (rad = 0) to $\pi/2$) was split into 40 windows with equal spacing. The initial configuration of each window is extracted from SMD trajectory by searching for the configuration with the desired reaction coordinate value of the corresponding window. Each window is then subjected to 2 ns of NVT simulation with the target diffusing halide constraint at the desired reaction coordinate using a spring constant of 1000 kcal(mol-Å)⁻¹ and neighbor halides mildly constrained to prevent undesired diffusion. A total simulation time of 80 ns is utilized for one UB calculation. The first 400 ps was discarded to serve as an equilibration period. Finally, the free energy profile was calculated with the weighted histogram analysis method (WHAM).³⁶ For each ligand (BA, PEA, 1T and 2P) and different inorganic layers (PEA n = 1, 2, 3), six independent simulations, including NPT equilibration, SMD, and UB, were conducted to extract the standard deviation of the free energy.

In this work, all the calculations and the subsequent trend analysis were conducted for L_2PbI_4 instead of $L_2PbI_4-L_2PbBr_4$. In the development of the interatomic potential used in MD simulations for iodide and bromide perovskites, that for bromide is, in principle, obtained by scaling the interatomic potential for iodide so that bromide perovskites would have shorter lattice constants, higher cohesive energy, lower phase transition temperatures, *etc.*³⁷ Thus, calculations for $L_2PbI_4-L_2PbBr_4$ and L_2PbI_4 should yield the same trend except that higher bromide composition would result in lower free energy. In addition, limited by our sampling method, *i.e.*, only one target halide is diffusing while others are oscillating at the same lattice position, it is difficult to capture the correct effect of different compositions, *e.g.*, what is the proper distribution of halide types in the

entire system and around the target diffusing halides for different compositions. Therefore, we believe that calculations of L_2PbI_4 are representative and help avoid the noise that may result from the setup for different compositions.

3.10 References

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3.11 Acknowledgements

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3.12 Author Contributions

Akriti and S.Z. synthesized and characterized the 2D and quasi-2D perovskite lateral heterostructures; E.S. developed the method for 2D perovskite synthesis using solvent evaporation method; Akriti performed the halide inter-diffusion coefficients calculations; Z.L. and B.M.S. performed MD simulations for free energy estimations; B.P.F. performed SEM / EDX characterizations; Y.G. captured all the AFM images; A.J.P. measured XRD of all perovskite

systems; K.M. performed KPFM measurements; Akriti and L.D. wrote the manuscript; all authors read and revised the manuscript.

4. CONCLUSION AND OUTLOOK

In my research, we have developed synthesis techniques for 2D halide perovskite lateral and vertical heterostructure assembly and utilized these heterostructures for analyzing diffusion behavior. Employing PL tracking of heterostructures, we have provided a simple and nondestructive method for studying the emission and concentration profile evolution. Diffusion coefficient calculations revealed the impact of different structural components on halide diffusion. The halide diffusion in perovskites was found to increase with increase in inorganic layer thickness or 'n' number. The choice of capping organic cations was found to play a dominant role in governing the diffusion behavior compared to inorganic layer thickness. Incorporation of bulkier and π -conjugated organic cations play an inhibitory role and stabilize the perovskite structure. Additionally, the in-plane diffusion in halide perovskites was found to follow a classical diffusion behavior, but the out-of-plane diffusion showed a quantized layer-by-layer diffusion. These experimental estimations were corroborated with numerical calculations. The numerical calculations emphasized the role of transport channels within the perovskite crystal and differences in surface vs. bulk diffusion behaviors. The insights gained from these investigations provide a guide for design of stable 2D perovskites. However, to develop a comprehensive understanding of the halide diffusion behavior in 2D perovskites, further studies need to be conducted.

4.1 Relationship between heat, light, and bias induced halide diffusion

Majority of the fundamental studies on understanding perovskite stability have focused on thermally activated halide diffusion. This provides a good indication of the stability performance of perovskite when subjected to normal device operating conditions. However, it is important to test the perovskite system under external stimulus of light and bias to improve the stability predictions. Photo-activated diffusion rates can be extracted by exposing the heterostructures to illumination from different light sources – lamps, lasers, solar simulators – at varying light intensities. Electrically driven ion migration can be activated by subjecting the heterostructures to an external bias via a metal contact. In addition to studying the halide diffusion, it is important to compare the response of the material under various external stimuli. For instance, answering questions whether π -conjugated organic cations also play a stabilizing role in light and bias

induced diffusions. Comparing and contrasting the stability of various perovskite systems under different external stimuli can also assist in developing a correlation between the responses. This correlation can be used to predict the behavior of a new system under different external stimuli based on their response to one of the stimuli.

4.2 Device stability performance prediction based on halide diffusion study

Deepening fundamental understanding regarding halide diffusions in 2D perovskite heterostructures is ultimately expected to contribute to preventing ionic diffusion in future device applications. However, due to the complex architecture of devices, this process leading from fundamental analysis to device stability and reliability enhancement requires us to answer multiple intermediary questions to achieve the final goal. One of the first questions that need to be answered is the prediction of the stability of layered devices based on halide diffusion studies conducted on relatively simple junction structures. Predicting halide diffusion in devices, unlike diffusion in single crystals, requires considerations from a myriad of contributing factors such as grain boundaries, surface defects, film thickness, and overall junction quality. With multiple factors in play, it is important to emphasize that device stability does not solely rely on halide diffusion. Therefore, all other contributing factors need to be carefully controlled and fixed to truly extract the relationship between halide diffusion and device stability. Finally, it is anticipated that in-situ studies of halide migration in thin film devices must be conducted to validate and improve the our mechanistic understanding of halide diffusion in 2D perovskites.

4.3 Comprehensive evaluation of structure-property relation to material and device stability

As we have discussed above, the effect of the ligand framework and the dimensionality of the 2D perovskite on the diffusivity has been well-characterized. However, a complete picture of the stability issues in 2D perovskites requires investigations into other structural components as well. Preliminary studies have shown that some 'A' cations for quasi-2D perovskites, such as FA, lead to suppressed halide diffusivity.51 The structural source of the stability should be analyzed. Another interesting area could be exploring other <100> oriented 2D perovskites. For instance, the eclipsed interlayer halide alignment and enhanced interaction of organic cations with inorganic layers in DJ perovskite may lead to suppression of the halide diffusion, thus leading to stable

device applications. Furthermore, the characterization of anion diffusivity is mostly based on 2D perovskite nanocrystals, which possess large specific surface area. Whether the large surface area assists in halide diffusion is another interesting topic worth investigating.

4.4 Estimation of vacancy concentration

The vacancy concentration plays an important role in diffusion but is difficult to directly estimate both experimentally and through simulations. Experimental characterization of charge carrier transport properties like intrinsic charge carrier density, PL lifetime, and mobility can provide an indication of the vacancy concentration. It is important to deconvolute the impact of various structural components on charge carrier transport and consequently on defects and vacancies. The choice of synthesis technique can also impact the vacancy concentration in the perovskite system. An indirect estimation can be made based on the free energy of vacancy formation. An alternative is to fit the vacancy concentration in KMC simulations so that the resulting diffusion coefficient aligns with the experiments. The former depends on the accuracy of the method / system used to calculate the free energy and the latter depends on the accuracy of the MD- or DFT-calculated input rate k for KMC. Most studies assume similar defect concentrations as the qualitative analysis of the free energy alone agrees with the experimental trend. However, the direct estimation of vacancy concentration is needed to unveil a more detailed impact on ionic diffusion. An accurate estimation of vacancy concentration can also shed light on the impact of dimensionality modulation (3D vs. 2D) on intrinsic material defects and consequently on the observed diffusion characteristics. Finally, it is crucial to analyze the correlation between vacancy concentration and device performance.

4.5 Improve the force field used for numerical diffusion estimations

DFT simulations are most widely used for calculating the free energy barrier of migration in perovskite systems. In addition to the expensive computational cost, the DFT simulations are based on nudged elastic band calculations, which neglect entropic contributions. MD simulations, compared to DFT simulations, are computationally cheaper. Furthermore, more molecular details can be probed by the MD's high flexibility in alternating properties of the system, e.g., the concentration of different anions. However, accuracy of MD simulations highly depends on the

atomic potential, i.e., force fields, used to describe the atomic interactions. To date, there are very few available validated force fields for perovskite systems, but none have considered the dynamics of electrostatics. Better atomic potential description of perovskite systems is needed to improve the accuracy of MD simulations so that more detailed quantitative analysis can be made to deduce the effect of other factors, such as vacancy concentration, involved in the diffusion process.

APPENDIX A. SUPPORTING INFORMATION FOR VERTICAL HETEROSTRUCTURES

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Appendix Figure A.1: Schematic illustration depicting synthesis procedure for top and bottom 2D halide perovskite layers of vertical heterostructure. a, Solvent evaporation method for synthesis of bottom bromide perovskite layer showing initial precursor solution on Si/SiO_2 substrate, crystal nucleation, and crystal growth. This method offers the advantage of forming single crystals with large lateral size, well-defined shape, and uniform thickness. b, Slow cooling method for synthesis of top iodide perovskite layer showing initial supersaturated precursor solution which is heated in an oil bath, crystal nucleation upon controlled cooling, and crystal growth.



Appendix Figure A.2: Confocal imaging of $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure. Confocal mappings of vertical heterostructure using 405 nm laser as excitation wavelength and emission channel widths of **a**, **e**, 410 – 460 nm, **b**, **f**, 470 – 550 nm, and **c**, **g**, 560 – 650 nm, at room temperature (RT) and after heating for 4 hrs at 80 °C, respectively. **d**, **h**, Superimposed confocal mapping for all the three emission channels at room temperature and after heating for 4 hrs at 80 °C, respectively. All scale bars are 10 µm.



Appendix Figure A.3: DFT calculated band gaps. Projected DOS plots with SOC corrections for **a**, (BA)₂PbI₄, **b**, (BA)₂PbBr₄, **c**, (BA)₂(MA)₂Pb₃I₁₀, and **d**, (BA)₂(MA)₂Pb₃Br₁₀.



Appendix Figure A.4: Trends in band gap and substitutional energy. a, Average of experimentally measured PL energy (black scatter points) and DFT calculated band gap (blue scatter points) for (BA)₂PbBr_{4x}I_{4(1-x)}. A quadratic fitting curve (black line) gives a mathematical correlation between experimentally measured PL energy and bromide mole fraction in (BA)₂PbBr_{4x}I_{4(1-x)} perovskite. b, DFT calculated band gap for (BA)₂(MA)₂Pb₃Br_{10x}I_{10(1-x)}. c, Incremental substitutional energy of iodine atom in (BA)₂PbBr₄ calculated using the formula $E_{sub} = \frac{E[BA_2PbBr_{4(1-y)}I_{4y}] - E[BA_2PbBr_{4(1-x)}I_{4x}] + 2(y-x) \times E[Br_2] - 2(y-x) \times E[I_2]}{4(y-x)}$ where y > x. The substitutional energy of adding an iodine atom reduces significantly for iodide mole fraction, $x_I \ge 0.6$.



Appendix Figure A.5: Difference in Fickian and experimentally observed halide interdiffusion mechanism in 2D perovskite vertical heterostructures. a, d, Schematic of vertical heterostructure before heating showing direction of bromide and iodide diffusion fluxes at the interface. b, Schematic of vertical heterostructure depicting a concentration gradient in bromide and iodide layers as predicted by Fick's law. The change in concentration for bromide and iodide layers decreases with increase in distance from the junction. c, Schematic of steady state concentration across all layers of the heterostructure as predicted by Fick's diffusion model. e, f, Schematic of vertical heterostructure depicting layer-by-layer halide diffusion during the heating process. Red to orange-red shift in iodide layer emission denotes marginal compositional change in iodide layer. Similarly, blue to green shift in bromide layer symbolizes significant compositional change in bromide layer. The final halide alloy concentrations in iodide and bromide layers represent the preferred alloy phase in the respective layers. g, Concentration profile evolution profile evolution across the vertical heterostructure highlighting layer-by-layer compositional change to preferred alloy phase in bottom bromide and top iodide perovskite layers.

Fickian Diffusion Model

The halide inter-diffusion coefficient is calculated by using the following ideal solution of Fick's second law.

$$C = \frac{1}{2}C_0 \operatorname{erfc} \frac{x}{2(Dt)^{1/2}}$$
(1)

Fickian model-based bromide-iodide inter-diffusion coefficient across vertical heterojunction can be calculated using the initial pure bromide PL peak, halide alloy PL peak, PL energy *vs*. halide composition calibration curve, heating time and perovskite thickness from AFM. **Appendix Figure A.6** depicts the complete set of representative experimental parameters required to solve the above equation and extract diffusion coefficient value. **Appendix Figure A.6a and A.6b** show the bright-field and PL images of $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure. The bottom layer of the heterostructure is pure bromide perovskite with initial bromide concentration, $C_0 = 1$.

The vertical heterostructure is heated at 80 °C to initiate halide migration. The evolution of PL emission is monitored by measuring PL spectrum after heating for different time durations (**Appendix Figure A.6c**). The halide alloy PL peak intensity stabilizes after 4 hrs of heating, therefore, t = 4 hrs $= 4 \times 60 \times 60 = 14400$ sec.

The PL energy (*i.e.* emission energy in electron-volts) corresponding to halide alloy PL peak (*i.e.* emission wavelength of 510 nm) is calculated as follows.

$$\frac{hc}{\lambda f} = \frac{(6.634 \times 10^{-34} \text{m}^2 \text{kg/s}) \cdot (3 \times 10^8 \text{ m/s})}{(510 \times 10^{-9} \text{ m}) \cdot (1.602 \times 10^{-19} \text{J/eV})} = 2.4314 \text{ eV}$$
(2)

where 'f' is the conversion factor from joules to electron-volts.

The final halide alloy composition is obtained by using the halide composition *vs*. PL energy quadratic calibration curve (**Appendix Figure A.4a**).

$$C = \frac{-b + \sqrt{b^2 - 4ac}}{2a} = \frac{0.2 + \sqrt{(-0.2)^2 - 4 \times 0.92 \times (2.38 - 2.4314)}}{2 \times 0.92} = 0.3715$$
(3)

Diffusion length based on thickness of the vertical heterostructure measured by AFM imaging (Appendix Figure A.6d) is given by x = 122 - 81 = 41 nm.

All the parameters (C, C₀, t and x) are plugged into the solution equation to obtain inter-diffusion coefficient, $D = 2.09 \times 10^{-18} \text{ m}^2/\text{s}.$

Non-Fickian Diffusion Model

The halide inter-diffusion calculation for non-Fickian model relies on the experimentally obtained concentration profile at the final time step. At end of the heating process all the bromide layers attain the thermodynamically preferred halide alloy composition. Therefore, for the $(BA)_2PbBr_4$ - $(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure shown in **Appendix Figure A.6**, the whole bottom layer of the heterostructure has a composition of $c^* = 0.3715$ (as calculated above based on PL peak and calibration curve). The PL evolution in **Appendix Figure A.6c** predicts insignificant change in composition of the iodide layer. Additionally, minor change in composition of the iodide layer cannot be obtained directly from the PL emission spectrum since DFT calculations predict no apparent change in band gap / PL energy for $0 \le x_{Br} \le 0.3$ for $(BA)_2(MA)_2Pb_3Br_{10x}I_{10(1-x)})$ (**Appendix Figure A.4b**). Since change in composition of the top iodide layer cannot be measured experimentally, we used conservation of mass principle to calculate the final halide concentration in the top layer. For all the mass conservation calculations, it is assumed that there is no loss of halides in the heating process and therefore, the number of bromide and iodide species remain the same before and after the thermal annealing process.

Thickness of bromide layer = h_1 (obtained from AFM) = 81 nm

Monolayer thickness of bromide perovskite = d_1 (obtained from pure phase XRD) = 1.37 nm

Number of octahedral layers in bottom bromide perovskite, $l_1 = h_1/d_1 = 59$

Thickness of iodide layer = h_2 (obtained from AFM) = 122 - 81 = 41 nm

Monolayer thickness of iodide perovskite = d_2 (obtained from pure phase XRD) = 2.57 nm

Number of octahedral layers in top iodide perovskite, $l_2 = n \times h_2/d_2 = 48$ (n = number of inorganic repeating units, i.e. (BA)₃(MA)₂Pb₃I₁₀ has 3 inorganic octahedral repeating units for every monolayer of the perovskite)

> Initial concentration of bromide layer = $x_{Br,1}^i = 1$ Initial concentration of iodide layer = $x_{Br,2}^i = 0$

Final concentration of bromide layer = $x_{Br,1}^f$ = 0.3715

(obtained from alloy PL emission and calibration curve)

Final concentration of iodide layer = $x_{Br,2}^{f}$

Average composition across the vertical heterostructure before heating

$$x_{Br,avg}^{l} = (x_{Br,1}^{l} \times l_{1} + x_{Br,2}^{l} \times l_{2})/(l_{1} + l_{2}) = (1 \times 59 + 0 \times 48)/(59 + 48) = 0.55$$
(4)

Average composition across the vertical heterostructure after heating

$$x_{Br,avg}^{f} = \left(x_{Br,1}^{f} \times l_{1} + x_{Br,2}^{f} \times l_{2}\right) / \left(l_{1} + l_{2}\right) = \left(0.3715 \times 59 + x_{Br,2}^{f} \times 48\right) / (59 + 48)$$
(5)

Assuming conservation of halide ions, the average composition across the vertical heterostructure remains the same before and after heating.

Therefore,
$$x_{Br, avg}^i = x_{Br, avg}^f$$

 $\Rightarrow 0.55 = (0.3715 \times 59 + x_{Br,2}^f \times 48)/(59 + 48)$
 $\Rightarrow x_{Br,2}^f = 0.77$

The above stated calculation steps based on mass conservation principles seem intuitive, however, the experimentally observed complexity of thermodynamically preferred halide alloy perovskite formation cannot be captured by this simplistic model. Since the change in PL emission of the top iodide layer is insignificant, the $(BA)_2(MA)_2Pb_3Br_{10x}I_{10(1-x)}$ alloy perovskite is most likely within the DFT predicted concentration range of $0 < x_{Br} < 0.3$. Therefore, to incorporate this thermodynamic limit to our mass conservation calculations, we add a constraint to the calculated $x_{Br,2}^f$ so that $x_{Br,2}^f \leq 0.3$. Therefore, for this representative case, $c_1 = x_{Br,2}^f = 0.3$.

Based on c^* and c_l values and thickness of vertical heterostructure obtained from AFM imaging (**Appendix Figure A.6d**), the concentration profile at final time step (t = 4 hrs = 14400 sec) is proposed in **Appendix Figure A.6e**. Using the Gaussian fit of the concentration profile, following graphical information is obtained.

Matano Interface,
$$x_M = 42.5 \text{ nm}$$

Area under the curve at c^{*} with respect to x_M , $-\int_{c_1}^{c^*} (x - x_M) dc = 12.77$ nm Slope of the curve at c^{*}, $(dc/dx)_{c^*} = 0.082 \text{ (nm)}^{-1}$

Finally, the inter-diffusion coefficient can be calculated using the Boltzmann-Matano method.

$$D(c^*) = -\frac{1}{2t} \frac{\int_{c_1}^{c^*} (x - x_M) dc}{(dc/dx)_{c^*}} = \frac{1}{2 \times 14400} \times \frac{12.77 \times 10^{-9}}{0.082 \times 10^9} = 5.41 \times 10^{-21} \text{ m}^2/\text{s}$$
(6)

The experimentally obtained input parameters, calculated final compositions of the bromide and iodide perovskites, and estimated diffusion coefficients using Fickian, Boltzmann-Matano (BM), and Kinetic Monte Carlo (KMC) methods have been tabulated in **Appendix Table A.1** for all the vertical heterostructures analyzed in this study. Representative AFM images of all vertical heterostructures used for thickness measurement is also shown in **Appendix Figure A.13**.



Appendix Figure A.6: Halide inter-diffusion coefficient calculation steps for (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure. **a**, Bright-field image of vertical heterostructure. **b**, PL image of vertical heterostructure at room temperature. Dashed lines are added in the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) perovskite domains. All white scale bars are 5 µm. **c**, Evolution of PL spectrum of vertical heterostructure after heating at 80 °C for varying time durations. The intensity of bromide-iodide alloy PL peak at 510 nm progressively increases till 4 hrs of heating. **d**, AFM image of the vertical heterostructure. The blue scale bar is 2 µm. **e**, Gaussian fit $y = y_0 + A \times \exp\left[\frac{-(x-x_c)^2}{2w^2}\right]$ of the concentration profile after 4 hrs of heating. The inset shows a zoomed-in image of the plot into two equal areas (red hatched area and green hatched area).



Appendix Figure A.7: Halide inter-diffusion in $(BA)_2PbBr4-(BA)_2PbI4$ vertical heterostructure at 80 °C. a, Bright-field image of vertical heterostructure. b, PL image of vertical heterostructure at room temperature. c, d, e, f, g, h, i, PL images of vertical heterostructure after heating at 80 °C for 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, 16 hrs, and 20 hrs, respectively. Dashed lines are added in the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) perovskite domains. All scale bars are 5 µm. j, Evolution of PL spectrum of vertical heterostructure after heating at 80 °C for varying time durations. Progressive blue-shift in pure iodide peak along with peak broadening is observed till ~ 20 hrs of heating at 80 °C.



Appendix Figure A.8: Halide inter-diffusion in $(BA)_2PbBr_4-(BA)_2(MA)Pb_2I_7$ vertical heterostructure at 80 °C. a, Bright-field image of vertical heterostructure. b, PL image of vertical heterostructure at room temperature. c, d, e, f, g, h, i, PL images of vertical heterostructure after heating at 80 °C for 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, 18 hrs, and 20 hrs, respectively. Dashed lines are added in the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) perovskite domains. All scale bars are 5 μ m. j, Evolution of PL spectrum of vertical heterostructure after heating at 80 °C for varying time durations. Progressive increase in alloy halide PL peak intensity is observed till ~ 20 hrs of heating at 80 °C.



Appendix Figure A.9: Halide inter-diffusion in $(BA)_2PbBr_4-(BA)_2(MA)_4Pb_5I_{16}$ vertical heterostructure at 80 °C. a, Bright-field image of vertical heterostructure. b, PL image of vertical heterostructure at room temperature. c, d, e, f, g, h, i, PL images of vertical heterostructure after heating at 80 °C for 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, 16 hrs, and 24 hrs, respectively. Dashed lines are added in the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) perovskite domains. All scale bars are 5 µm. j, Evolution of PL spectrum of vertical heterostructure after heating at 80 °C for varying time durations. Inset image is the zoomed-in PL spectrum of the halide alloy. Progressive increase in alloy halide PL peak intensity is observed till ~ 24 hrs of heating at 80 °C.



Appendix Figure A.10: Halide inter-diffusion in (PEA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀ vertical heterostructure at 80 °C. a, Bright-field image of vertical heterostructure. b, PL image of vertical heterostructure at room temperature. c, d, e, f, g, h, i, PL images of vertical heterostructure after heating at 80 °C for 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, 18 hrs, and 20 hrs, respectively. Dashed lines are added in the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) perovskite domains. All scale bars are 5 µm. j, Evolution of PL spectrum of vertical heterostructure after heating at 80 °C for varying time durations.



Appendix Figure A.11: Halide inter-diffusion in $(2P)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure at 80 °C. a, Bright-field image of vertical heterostructure. b, PL image of vertical heterostructure at room temperature. c, d, e, f, g, h, i, PL images of vertical heterostructure after heating at 80 °C for 15 mins, 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, and 16 hrs, respectively. Dashed lines are added in the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) perovskite domains. All scale bars are 5 µm. j, Evolution of PL spectrum of vertical heterostructure after heating at 80 °C for varying time durations.



Appendix Figure A.12: Halide inter-diffusion in $(2T)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructure at 80 °C. a, Bright-field image of vertical heterostructure. b, PL image of vertical heterostructure at room temperature. c, d, e, f, g, h, i, PL images of vertical heterostructure after heating at 80 °C for 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, 16 hrs, and 24 hrs, respectively. Dashed lines are added in the bright-field and PL images for the ease of distinction of bromide (light blue) and iodide (yellow) perovskite domains. All scale bars are 5 µm. j, Evolution of PL spectrum of vertical heterostructure after heating at 80 °C for varying time durations.



Appendix Figure A.13: AFM images and height profiles of vertical heterostructures. a, c, e, g, i, k, m, AFM images, and b, d, f, h, j, l, n, height profiles along the dashed white line in the AFM images of $(BA)_2PbBr_4-(BA)_2PbI_4$, $(BA)_2PbBr_4-(BA)_2(MA)Pb_2I_7$, $(BA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$, $(BA)_2PbBr_4-(BA)_2(MA)_4Pb_5I_{16}$, $(PEA)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$, $(2P)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$, and $(2T)_2PbBr_4-(BA)_2(MA)_2Pb_3I_{10}$ vertical heterostructures, respectively. All scale bars are 2 µm.

For the different types of vertical heterostructure systems analyzed in this study, it is critical to ensure that thermal annealing does not lead to change in crystal structure or formation of new perovskite. Therefore, X-ray diffraction (XRD) characterizations were performed at pristine conditions and after heating at 80 °C for all the vertical heterostructures presented in this work (Appendix Figure A.14). Additionally, 2D halide perovskites undergo degradation when exposed to light, heat, or ambient conditions. For all the vertical heterostructures studies in this work, same light source and excitation power has been used to measure the PL spectrum and perform the qualitative and quantitative diffusion analysis. The vertical heterostructures are exposed to the laser excitation source only for a few seconds to capture the PL emission spectrum, hence, any degradation due to light illumination is not expected. Furthermore, all vertical heterostructures have been assembled and heated in a glove box maintained under nitrogen atmosphere. The vertical heterostructures are protected from exposure to ambient conditions during PL measurements by PMMA (polymethyl methacrylate) encapsulation. Therefore, minimal degradation of the vertical heterostructures and the component pure phase 2D halide perovskites is expected due to exposure to ambient conditions. Nevertheless, we conducted stability test for all the pure phase 2D halide perovskites used in this study. Appendix Figure A.15 shows the XRD of the pure phase perovskites at pristine conditions and after heating at 80 °C in a nitrogen-filled glove box. No observable phase transformation or degradation is seen in the XRD spectrum even after 20 hrs of heating, indicating that the perovskite crystal structure can be assumed to be stable during the diffusion studies. Appendix Figure A.16 shows the XRD of the pure phase perovskites at pristine conditions and after storing in ambient conditions. All perovskite samples have been encapsulated by PMMA to replicate the conditions used in our diffusion studies. No apparent change in XRD spectrum is observed even after 11 days of exposure to ambient conditions. The environmental stability of the perovskites, especially (BA)₂PbBr₄ and (BA)₂PbI₄, can be attributed to the protection offered by PMMA layer. 11 days of ambient exposure is much longer compared to the limited time exposure during PL emission measurement of the vertical heterostructures, therefore, any ambient degradation during our diffusion experiments is not anticipated.



Appendix Figure A.14: XRD of vertical heterostructures. XRD spectrum of pure bottom perovskite (blue), pure top perovskite (red), vertical heterostructure before heating (orange), vertical heterostructure after heating for 10 hrs at 80 °C (green), and vertical heterostructure after heating for 20 hrs (magenta) at 80 °C for **a**, (BA)₂PbBr₄-(BA)₂PbBr₄, **b**, (BA)₂PbBr₄-(BA)₂(MA)Pb₂I₇, **c**, (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀, **d**, (BA)₂PbBr₄-(BA)₂(MA)₄Pb₅I₁₆, **e**, (BA)₂PbI₄-(BA)₂(MA)₂Pb₃I₁₀, **f**, (BA)₂PbBr₄-(BA)₂(MA)₂Pb₃Br₁₀, **g**, (BA)₂(MA)₂Pb₃Br₁₀-(BA)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀, **i**, (2P)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀, and **j**, (2T)₂PbBr₄-(BA)₂(MA)₂Pb₃I₁₀. Blue and red dots correspond to the diffraction peaks originating from bottom and top pure perovskites, respectively.



Appendix Figure A.15: Thermal stability of pure phase 2D halide perovskites. XRD spectrum of **a**, (BA)₂PbBr₄, **b**, (BA)₂PbI₄, **c**, (BA)₂(MA)Pb₂I₇, **d**, (BA)₂(MA)₂Pb₃I₁₀, **e**, (BA)₂(MA)₄Pb₅I₁₆, **f**, (PEA)₂PbBr₄, **g**, (2P)₂PbBr₄, **h**, (2T)₂PbBr₄, and **i**, (BA)₂(MA)₂Pb₃Br₁₀ at room temperature (red) and after heating at 80 °C for 5 hrs (green), 10 hrs (blue), and 20 hrs (magenta).


Appendix Figure A.16: Ambient stability check of pure phase 2D halide perovskites. XRD spectrum of **a**, $(BA)_2PbBr_4$, **b**, $(BA)_2PbI_4$, **c**, $(BA)_2(MA)Pb_2I_7$, **d**, $(BA)_2(MA)_2Pb_3I_{10}$, **e**, $(BA)_2(MA)_4Pb_5I_{16}$, **f**, $(PEA)_2PbBr_4$, **g**, $(2P)_2PbBr_4$, **h**, $(2T)_2PbBr_4$, and **i**, $(BA)_2(MA)_2Pb_3Br_{10}$ in pristine condition (red) and after storing in air for 5 days (green) and 11 days (blue). All perovskite samples were encapsulated by PMMA.

Appendix Table A.1: Experimental inputs and calculated parameters for estimation of halide inter-diffusion across different vertical heterostructures. Here, T is temperature, t is heating time, h_I is thickness of top iodide layer, h_{Br} is thickness of bottom bromide layer, λ is alloy PL emission wavelength, $C_{f,Br}$ is final concentration of bromide layer, $C_{f,I}$ is final concentration of iodide layer, x_{Br} is bromide mole fraction, and D is diffusion coefficient.

		Input Parameters Ca					Calculated Parameters					
Heterostructure	т	+	h	ha	2	Can	Car	Fickian	BM	КМС		
System	1	L	111	IIBr	<i>N</i>	Ci,Br	Ci,i	'D'	' D'	'D'		
	°C	hour	nm	nm	nm	XBr	XBr	m²/s	m²/s	m²/s		
$(\mathbf{D} \mathbf{A})_{\mathbf{z}} \mathbf{D} \mathbf{b} \mathbf{D} \mathbf{r}$	80	16	47	61	511	0.36	0.50	2.6E-19	1.2E-21	7.8E-20		
$(\mathbf{B}\mathbf{A})_{2}\mathbf{I}$ $\mathbf{B}\mathbf{B}\mathbf{I}_{4}$ -		18	30	33	500	0.46	0.50	8.7E-19	2.8E-21	1.2E-20		
(BA) ₂ P01 ₄		18	60	60	519	0.26	0.50	7.1E-20	4.3E-22	1.3E-19		
$(\mathbf{D} \mathbf{A}) \cdot \mathbf{D} \mathbf{b} \mathbf{D} \mathbf{r}$		20	70	50	513	0.34	0.30	1.1E-19	2.9E-21	3.1E-20		
$(\mathbf{DA})_{2}\mathbf{F}\mathbf{U}\mathbf{D}_{14}$ -	80	20	41	53	514	0.33	0.30	9.8E-20	2.5E-21	4.0E-20		
$(\mathbf{D}\mathbf{A})^2(\mathbf{W}\mathbf{A})\mathbf{F}\mathbf{U}^2\mathbf{I}^{\prime}$		20	65	43	514	0.34	0.30	7.1E-20	3.2E-21	2.2E-20		
		20	65	12	516	0.31	0.08	4.3E-21	1.2E-22	2.0E-21		
	60	8	111	60	510	0.37	0.21	5.9E-19	2.3E-21	3.9E-20		
		24	58	76	514	0.33	0.30	1.7E-19	2.9E-21	1.7E-19		
		20	73	55	511	0.36	0.30	1.7E-19	2.5E-21	2.6E-20		
		20	61	77	514	0.33	0.30	2.3E-19	3.4E-21	8.3E-20		
	70	16	166	171	510	0.38	0.30	2.7E-18	7.8E-21	3.5E-19		
		20	49	55	507	0.40	0.30	3.6E-19	9.2E-22	2.5E-20		
(BA)2PbBr4 - (BA)2(MA)2Pb3I10		20	136	97	509	0.39	0.27	8.0E-19	3.1E-21	7.9E-20		
		22	140	98	507	0.40	0.26	9.9E-19	1.8E-21	8.5E-20		
		20	91	70	508	0.39	0.29	4.5E-19	1.9E-21	4.0E-20		
		12	129	49	504	0.43	0.14	8.0E-19	6.1E-22	3.5E-20		
		16	103	127	513	0.35	0.30	8.9E-19	6.5E-21	2.5E-19		
		22	148	88	509	0.39	0.23	5.9E-19	1.2E-21	6.8E-20		
	80	20	68	60	507	0.40	0.30	4.3E-19	1.2E-21	1.8E-19		
		20	50	50	504	0.43	0.30	5.7E-19	7.3E-22	2.5E-20		
		16	50	50	507	0.40	0.30	3.7E-19	1.1E-21	2.1E-20		
	90	12	91	72	513	0.34	0.30	3.7E-19	6.0E-21	9.1E-20		

		Input Parameters			Calculated Parameters					
Heterostructure	т	+	hr	hn	2	Con	Cer	Fickian	BM	КМС
System	1	L		λ	Cf,Br	Cf,I	'D'	'D'	'D'	
	°C	hour	nm	nm	nm	XBr	XBr	m²/s	m²/s	m ² / s
		16	85	99	517	0.30	0.30	3.1E-19	4.0E-19	1.8E-19
		12	54	31	513	0.34	0.23	6.7E-20	4.5E-22	1.7E-20
		12	136	98	514	0.33	0.30	5.6E-19	2.4E-20	1.7E-19
		16	71	76	497	0.48	0.30	2.3E-17	9.9E-22	4.5E-20
		8	71	65	503	0.44	0.30	2.9E-18	2.3E-21	9.4E-20
	100	8	49	48	508	0.39	0.30	5.3E-19	2.4E-21	5.7E-20
		16	65	67	511	0.37	0.30	3.3E-19	2.5E-21	5.6E-20
		16	125	44	507	0.40	0.13	2.9E-19	4.6E-22	2.3E-20
		16	54	65	513	0.34	0.30	2.2E-19	3.4E-21	7.4E-20
$(BA)_2PbBr_4$ -	80	16	72	30	512	0.36	0.15	5.8E-20	3.5E-22	1.5E-20
$(BA)_2(MA)_4Pb_5I_{16}$	80	18	118	108	507	0.40	0.30	1.4E-18	3.6E-21	1.4E-19
		20	112	40	513	0.35	0.13	7.4E-19	3.7E-22	2.1E-20
	80	8	51	35	511	0.36	0.23	1.7E-19	1.3E-21	3.9E-20
(PEA) ₂ PbBr ₄ -		16	30	18	504	0.43	0.18	8.9E-20	1.5E-22	4.9E-21
$(BA)_2(MA)_2Pb_3I_{10}$	00	4	59	19	510	0.38	0.10	1.3E-19	6.2E-22	1.5E-20
		4	52	17	510	0.37	0.11	9.4E-20	5.7E-22	1.3E-20
(2P) ₂ PbBr ₄ - (BA) ₂ (MA) ₂ Pb ₃ I ₁₀	80	20	115	64	504	0.43	0.12	9.2E-19	3.0E-22	2.8E-20
		36	49	60	523	0.16	0.30	1.4E-20	2.1E-22	5.6E-20
		16	93	28	507	0.40	0.07	1.1E-19	1.4E-22	9.8E-21
		30	47	31	506	0.41	0.15	9.2E-20	1.0E-22	5.3E-21
		36	115	102	506	0.41	0.20	7.7E-19	4.5E-22	4.7E-20
$(2T)_2PbBr_4 -$	80	42	32	13	510	0.37	0.10	5.7E-21	3.1E-23	8.9E-22
		42	19	7	510	0.37	0.09	1.6E-21	4.1E-23	2.4E-22
		42	21	13	510	0.37	0.15	5.1E-21	3.7E-23	7.9E-22
		42	33	30	510	0.37	0.23	2.9E-20	2.6E-22	4.5E-21
		42	16	5	510	0.37	0.07	7.0E-22	2.2E-23	1.1E-22

APPENDIX B. SUPPORTING INFORMATION FOR LATERAL HETEROSTRUCTURES

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Appendix Figure B.1: SEM / EDX imaging of $(PEA)_2PbI_4-(PEA)_2PbBr_4$ lateral heterostructure. SEM image of the lateral heterostructure at **a**, room temperature and **e**, after heating at 100 °C for 30 hrs. Yellow dashed lines in the SEM images highlight the heterojunction. EDX elemental mapping of **b**, **f**, Pb, **c**, **g**, Br, and **d**, **h**, I before and after heating, respectively. All scale bars are 5 μ m. EDX spectrum collected from bromide and iodide regions **i**, before and **j**, after heating.



Appendix Figure B.2: KPFM imaging of (PEA)₂PbI₄-(PEA)₂PbBr₄ lateral heterostructure. a, PL image of the lateral heterostructure. b, Potential map and d, potential profile along the dashed black arrow in b before heating. c, Potential map and e, potential profile along the dashed black arrow in c after heating at 100 °C. A potential difference of ~ 0.07 V between the bromide and iodide regions is observed before and after heating. All scale bars are 5 μ m.



Appendix Figure B.3: PL calibration curve for (PEA)₂PbBr_{4x}I_{4(1-x)} halide alloy perovskites. a, BF and b, PL images of spin-coated halide alloy perovskite thin films of varying composition ($x_{Br} = 1, 0.75, 0.5, 0.25, 0$). All scale bars are 5 µm. c, Relationship between PL emission energy and halide composition. Black scatter plot is the experimentally measured average PL energy at each halide composition. Blue line is the linear fitting to the experimental data.



Appendix Figure B.4: Confocal imaging of halide inter-diffusion in $(BA)_2PbI_4-(BA)_2PbBr_4$. Confocal image of the lateral heterostructure at **a**, room temperature and **b**, after heating at 100 °C for 30 mins, respectively. The PL emissions in the wavelength range 411 - 446 nm, 446 - 482 nm, 482 - 517 nm, and 517 - 544 nm are represented in violet, blue, green, and red colors, respectively. Length and width of the emitting region has been added to each of the emission channels to highlight crystal dimensions and halide migration upon heating. The merged image shows the PL emission from 411 - 544 nm. All scale bars are 5 µm. **c**, **d**, Evolution of PL spectra and halide concentration profile of the lateral heterostructure during the inter-diffusion process. PL spectrum at RT and after heating are collected from the white circled areas in the merged images. Scatter points in **d** are experimentally obtained concentration from PL emissions and line plots are Gaussian fittings to the experimental data points.



Appendix Figure B.5: Confocal imaging of halide inter-diffusion in $(1T)_2PbI_4$ - $(1T)_2PbBr_4$. Confocal image of the lateral heterostructure at **a**, room temperature and **b**, after heating at 100 °C for 30 mins, respectively. The PL emissions in the wavelength range 411 - 446 nm, 446 - 482 nm, 482 - 517 nm, and 517 - 553 nm are represented in violet, blue, green, and red colors, respectively. Length and width of the emitting region has been added to each of the emission channels to highlight crystal dimensions and halide migration upon heating. The merged image shows the PL emission from 411 - 553 nm. All scale bars are 5 µm. **c**, **d**, Evolution of PL spectra and halide concentration profile of the lateral heterostructure during the inter-diffusion process. PL spectrum at RT and after heating are collected from the white circled areas in the merged images. Scatter points in **d** are experimentally obtained concentration from PL emissions and line plots are Gaussian fittings to the experimental data points.



Appendix Figure B.6: Confocal imaging of halide inter-diffusion in $(2P)_2PbI_4-(2P)_2PbBr_4$. Confocal image of the lateral heterostructure at **a**, room temperature and **b**, after heating at 100 °C for 30 mins, respectively. The PL emissions in the wavelength range 411 - 446 nm, 446 - 482 nm, 482 - 517 nm, and 517 - 553 nm are represented in violet, blue, green, and red colors, respectively. Length and width of the emitting region has been added to each of the emission channels to highlight crystal dimensions and halide migration upon heating. The merged image shows the PL emission from 411 - 553 nm. All scale bars are 5 µm. **c**, **d**, Evolution of PL spectra and halide concentration profile of the lateral heterostructure during the inter-diffusion process. PL spectrum at RT and after heating are collected from the white circled areas in the merged images. Scatter points in **d** are experimentally obtained concentration from PL emissions and line plots are Gaussian fittings to the experimental data points.



Appendix Figure B.7: XRD of pure phase 2D perovskites. XRD spectrum of **a**, (PEA)₂PbI₄, **b**, (1T)₂PbI₄, **c**, (1T)₂PbBr₄, and **d**, (2P)₂PbI₄ perovskites before and after heating at 100 °C.



Appendix Figure B.8: XRD of 2D perovskite lateral heterostructures. XRD spectrum of **a**, (BA)₂PbI₄-(BA)₂PbBr₄, **b**, (PEA)₂PbI₄-(PEA)₂PbBr₄, **c**, (1T)₂PbI₄-(1T)₂PbBr₄, and **d**, (2P)₂PbI₄-(2P)₂PbBr₄ lateral heterostructures before and after heating at 100 °C.



Appendix Figure B.9: Boltzmann-Matano method for Br-I inter-diffusion coefficient calculation. a, Representative concentration profile for a lateral heterostructure sample highlighting the Matano interface. The experimentally observed scatter plot is fitted with Gaussian distribution to obtain the concentration profile. Area under the curve and slope at a randomly selected point is also illustrated. **b,** Representative concentration dependent diffusion coefficient plot. Diffusion coefficient at any point is calculated using the area under the curve and the slope at that point.



Appendix Figure B.10: Comparison of Br-I halide inter-diffusion in different directions for $(PEA)_2PbI_4-(PEA)_2PbBr_4$ lateral heterostructure after heating at 100 °C for 30 mins. The box represents data points between 25 – 75 percentiles of the range, whisker represents the minimum-to-maximum range, and the dashed line highlights the average diffusion coefficients of the sample data points. The inset shows PL image of a representative lateral heterostructure with two arbitrarily chosen edges. Scale bar is 5 μ m.



Appendix Figure B.11: Comparison of impact of organic cations on the concentration dependent Br-I inter-diffusion coefficients across BA, PEA, 2P, and 1T based lateral heterostructures using analytical BM method after heating at 100 °C for 30 mins and 1 hr. The box represents data points between 25 - 75 percentiles of the range, whisker represents the minimum-to-maximum range, and the dashed line highlights the average diffusion coefficients of the sample data points.



Appendix Figure B.12: Illustration of off-target halide diffusing into the vacancy before the targeted halide. I atoms are shown as green spheres, Pb atoms are shown as orange spheres, and target halide is shown as a red sphere.



Appendix Figure B.13: Free energy curves of different ligands (BA in blue, PEA in green, 1T in orange, 2P in light blue) for the diffusion between equatorial and axial positions [layer $1 (\theta \sim 0.2 \text{ rad}) \leftrightarrow \text{layer } 0 (\theta \sim 1.7 \text{ rad})$].



Partial PMMA Protection of Br Perovskite

Br-I lon Exchange

Appendix Figure B.14: Schematic illustration of quasi-2D lateral heterostructure synthesis using ion exchange method. Ion exchange process involves partial protection of bromide perovskite by PMMA encapsulation to maintain pristine state upon exposure of the unprotected sample to iodide ions, consequently leading to quasi-2D halide perovskite lateral heterostructure synthesis.



Appendix Figure B.15: SEM imaging and EDX elemental mapping of pristine $(PEA)_2(MA)Pb_2I_7-(PEA)_2(MA)Pb_2Br_7$ lateral heterostructure synthesized using ion exchange method. a, BF and b, SEM image of the lateral heterostructure. Yellow dashed line in the BF image highlights the heterojunction. EDX elemental mapping of c, Pb, d, Br, and e, I. All scale bars are 20 µm. f, EDX spectrum collected from bromide and iodide regions.



Appendix Figure B.16: Confocal imaging of halide inter-diffusion in (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇ lateral heterostructure synthesized using ion exchange method. Confocal image of the lateral heterostructure at **a**, room temperature and **b**, after heating at 100 °C for 30 mins, respectively. The PL emissions in the wavelength range 429 - 473 nm, 473 - 517 nm, 517 - 562 nm, 562 - 606 nm, and 606 - 651 nm are represented in violet, blue, green, orange, and red colors, respectively. The merged image shows the PL emission from 429 - 651 nm. All scale bars are 5 µm. **c**, **d**, Evolution of PL spectra and halide concentration profile of the lateral heterostructure during the inter-diffusion process. PL spectrum at RT and after heating are collected from the white circled areas in the merged images. Halide concentration profiles are estimated along the dashed white arrows in the merged images. Scatter points in **d** are experimentally obtained concentration from PL emissions and line plots are Gaussian fittings to the experimental data points.



Appendix Figure B.17: SEM imaging and EDX elemental mapping of pristine $(PEA)_2(MA)_2Pb_3I_{10}-(PEA)_2(MA)_2Pb_3Br_{10}$ lateral heterostructure synthesized using ion exchange method. a, BF and b, SEM image of the lateral heterostructure. Yellow dashed line in the BF image highlights the heterojunction. EDX elemental mapping of c, Pb, d, Br, and e, I. All scale bars are 5 µm. f, EDX spectrum collected from bromide and iodide regions.



Appendix Figure B.18: Confocal imaging of halide inter-diffusion in (PEA)₂(MA)₂Pb₃I₁₀-(PEA)₂(MA)₂Pb₃Br₁₀ lateral heterostructure synthesized using ion exchange method. Confocal image of the lateral heterostructure at **a**, room temperature and **b**, after heating at 100 °C for 30 mins, respectively. The PL emissions in the wavelength range 429 – 473 nm, 473 – 517 nm, 517 – 562 nm, 562 – 606 nm, and 606 – 651 nm are represented in violet, blue, green, orange, and red colors, respectively. The merged image shows the PL emission from 429 – 651 nm. All scale bars are 5 μ m. **c**, **d**, Evolution of PL spectra and halide concentration profile of the lateral heterostructure during the inter-diffusion process. PL spectrum at RT and after heating are collected from the white circled areas in the merged images. Halide concentration profiles are estimated along the dashed white arrows in the merged images. Scatter points in **d** are experimentally obtained concentration from PL emissions and line plots are Gaussian fittings to the experimental data points.



Appendix Figure B.19: Demonstration of quasi-2D lateral heterostructure formation using bulk synthesis method. a, Schematic illustration of bulk synthesis method. The first step involves synthesis of phase pure quasi-2D bromide perovskite followed by sequential growth of iodide perovskite from the bromide template. The top iodide layers are then removed using mechanical exfoliation to expose underlying quasi-2D lateral heterostructure. b, BF, c, PL, d, SEM, and e, AFM images for (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇ lateral heterostructure formed using bulk synthesis method. The yellow dashed lines in the SEM and AFM images highlight the lateral heterojunctions. The AFM image is superimposed with a height profile along the black dashed line. BF and PL images have been captured for the same heterostructure, but different samples have been used for SEM and AFM to best represent the pristine heterostructures. All white scale bars are 5 μ m and the black scale bar is 1 μ m.



Appendix Figure B.20: SEM imaging and EDX elemental mapping of pristine $(PEA)_2(MA)Pb_2I_7-(PEA)_2(MA)Pb_2B_7$ lateral heterostructure formed using bulk synthesis method. a, BF and b, SEM image of the lateral heterostructure. Yellow dashed line in the BF image highlights the heterojunction. EDX elemental mapping of c, Pb, d, Br, and e, I. All scale bars are 5 µm. f, EDX spectrum collected from bromide and iodide regions.



Appendix Figure B.21: Confocal imaging of halide inter-diffusion in (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇ lateral heterostructure formed using bulk synthesis method. Confocal image of the lateral heterostructure at **a**, room temperature and **b**, after heating at 100 °C for 30 mins, respectively. The PL emissions in the wavelength range 429 – 473 nm, 473 – 517 nm, 517 – 562 nm, 562 – 606 nm, and 606 – 651 nm are represented in violet, blue, green, orange, and red colors, respectively. The merged image shows the PL emission from 429 – 651 nm. All scale bars are 5 μ m. **c**, **d**, Evolution of PL spectra and halide concentration profile of the lateral heterostructure during the inter-diffusion process. PL spectrum at RT and after heating are collected from the white circled areas in the merged images. Halide concentration profiles are estimated along the dashed white arrows in the merged images. Scatter points in **d** are experimentally obtained concentration from PL emissions and line plots are Gaussian fittings to the experimental data points.



Appendix Figure B.22: XRD of pure phase quasi-2D perovskites. XRD spectrum of **a**, (PEA)₂(MA)Pb₂I₇, **b**, (PEA)₂(MA)Pb₂Br₇, **c**, (PEA)₂(MA)₂Pb₃I₁₀, and **d**, (PEA)₂(MA)₂Pb₃Br₁₀ perovskites before and after heating at 100 °C.



Appendix Figure B.23: XRD of quasi-2D perovskite lateral heterostructures. XRD spectrum of **a**, (PEA)₂(MA)Pb₂I₇-(PEA)₂(MA)Pb₂Br₇, and **b**, (PEA)₂(MA)₂Pb₃I₁₀-(PEA)₂(MA)₂Pb₃Br₁₀ lateral heterostructures before and after heating at 100 °C.



Appendix Figure B.24: Comparison of impact of inorganic layer thickness on the concentration dependent Br-I inter-diffusion coefficients across n = 1, n = 2, and n = 3 PEA based lateral heterostructures using analytical BM method after heating at 100 °C for 30 mins and 1 hr. The box represents data points between 25 - 75 percentiles of the range, whisker represents the minimum-to-maximum range, and the dashed line highlights the average diffusion coefficients of the sample data points.



Appendix Figure B.25: Impact of synthesis methods – ion exchange vs. bulk synthesis on concentration dependent Br-I inter-diffusion coefficients for $(PEA)_2(MA)Pb_2I_7$ - $(PEA)_2(MA)Pb_2Br_7$ lateral heterostructure. The diffusion coefficients are calculated for concentration profiles across the lateral heterojunctions after heating at 100 °C for 30 mins. The box represents data points between 25 – 75 percentiles of the range, whisker represents the minimum-to-maximum range, and the dashed line highlights the average diffusion coefficients of the sample data points.



Appendix Figure B.26: Free energy curve and each window's corresponding histogram in the umbrella sampling for MAPbI₃. Each curve in the probability density *vs*. reaction coordinate graph represents different window's histogram.



Appendix Figure B.27: Diffusion pathways for $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1, 2, 3) perovskites. Diffusion between a, layer $0 \leftrightarrow 1$ and layer $1 \leftrightarrow 1$ in n = 1 perovskite, b, layer $0 \leftrightarrow 1$, layer $1 \leftrightarrow 1$, and layer $1 \leftrightarrow 2$ in n = 2 perovskite, and c, layer $0 \leftrightarrow 1$, layer $1 \leftrightarrow 1$, layer $1 \leftrightarrow 1$, layer $1 \leftrightarrow 3$ in n = 3 perovskite.

Organic Cations	Free Energy Barrier [kcal(mol) ⁻¹]					
	L2PbI4	L ₂ PbBr ₄				
BA	11.95 ± 0.28	10.48 ± 0.27				
PEA	11.94 ± 0.24	10.51 ± 0.26				
1T	12.11 ± 0.20	10.47 ± 0.22				
2P	12.30 ± 0.23	10.51 ± 0.18				

Appendix Table B.1: Estimated free energy barriers of diffusion between equatorial positions (layer $1 \leftrightarrow 1$) for L₂PbX₄ (X = Br, I) perovskites using different organic cations.

Appendix Table B.2: Compositional variation of average inter-diffusion coefficients for all 2D and quasi-2D Br-I lateral heterostructures after heating at 100 °C for 30 mins.

Heterostructure	Average Diffusion Coefficients (m ² s ⁻¹) at Different Bromide Concentrations (x _{Br})									
Systems	$\mathbf{x}_{\mathbf{Br}} = 0.2$	$x_{Br} = 0.3$	$\mathbf{x}_{\mathbf{Br}} = 0.4$	$\mathbf{x}_{\mathbf{Br}} = 0.5$	$\mathbf{x}_{\mathbf{Br}} = 0.6$	$\mathbf{x}_{\mathbf{Br}} = 0.7$				
n = 1, BA	4×10^{-18}	8×10 ⁻¹⁸	2×10^{-17}	3×10 ⁻¹⁷	5×10 ⁻¹⁷	1×10 ⁻¹⁶				
n = 1, PEA	9 ×10 ⁻¹⁹	2×10^{-18}	3×10 ⁻¹⁸	4×10^{-18}	6×10 ⁻¹⁸	2×10^{-17}				
n = 1, 1T	9×10 ⁻¹⁹	1×10^{-18}	2×10 ⁻¹⁸	5×10 ⁻¹⁸	9×10 ⁻¹⁸	4×10^{-17}				
n = 1, 2P	6×10 ⁻¹⁹	1×10 ⁻¹⁸	2×10 ⁻¹⁸	3×10 ⁻¹⁸	5×10 ⁻¹⁸	8×10 ⁻¹⁸				
n = 2, PEA	5×10 ⁻¹⁷	8×10 ⁻¹⁷	1×10 ⁻¹⁶	2×10 ⁻¹⁶	3×10 ⁻¹⁶	5×10 ⁻¹⁶				
(Bulk Synthesis)										
n = 2, PEA	1×10 ⁻¹⁶	1×10 ⁻¹⁶	2×10 ⁻¹⁶	3×10 ⁻¹⁶	6×10 ⁻¹⁶	1×10 ⁻¹⁵				
(Ion Exchange)										
n = 3, PEA	4×10 ⁻¹⁶	5×10 ⁻¹⁶	7×10 ⁻¹⁶	1×10 ⁻¹⁵	1×10 ⁻¹⁵	3×10 ⁻¹⁵				
(Ion Exchange)										

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