THESIS ABSTRACT
FOR
ANION DIFFUSION IN TWO-DIMENSIONAL HALIDE PEROVSKITES

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 to 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 inhibit halide inter-diffusion much more effectively compared to short chain aliphatic 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.