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2026-08-11

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UNIVERSITY OF CALIFORNIA

Los Angeles

Molecular Control of Crystallization Pathways in Perovskite Solar Cells

A dissertation submitted in partial satisfaction of the requirements

for the degree Doctor of Philosophy

in Materials Science and Engineering

by

Haoxiang Duan

2026

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2026

ABSTRACT OF THE DISSERTATION

Molecular Control of Crystallization Pathways in Perovskite Solar Cells

by

Haoxiang Duan

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2026

Professor Yang Yang, Chair

Metal-halide perovskite solar cells have emerged as promising photovoltaic technologies because of their high absorption coefficients, long carrier diffusion lengths, defect tolerance, and compatibility with low-temperature processing. Despite rapid improvements in power conversion efficiency, their commercialization remains limited by insufficient operational stability. Many degradation pathways originate from the nonequilibrium crystallization of solution-processed perovskite films, which can introduce unfavorable crystal orientations, residual phases, compositional heterogeneity, lattice disorder, and defects that promote nonradiative recombination and ion migration. This dissertation investigates how molecular interactions can be used to control perovskite crystallization across different stages of film formation, from facet-selective crystal

growth to post-nucleation lattice reconstruction, thereby improving both photovoltaic performance and operational stability.

Chapter One introduces the fundamental properties, crystallization behavior, and stability challenges of metal-halide perovskites. Particular emphasis is placed on the multistep and nonequilibrium nature of solution-based crystallization and on how precursor coordination, intermediate-phase formation, nucleation, crystal growth, and molecular additives determine the final film structure.

In Chapter Two, a highly (111)-oriented FAPbI_3 film is developed using 3-aminopentane and propylammonium chloride as co-additives. Their cooperative effects regulate facet-selective growth and phase conversion, producing highly crystalline films with improved carrier transport and suppressed ion migration. The resulting devices exhibit enhanced photovoltaic performance and substantially improved stability under continuous illumination and elevated temperature. These results demonstrate that crystallographic orientation is a key design parameter linking film formation with electronic quality and long-term device reliability.

Chapter Three establishes a molecular framework for understanding amine-directed facet growth. Systematic screening of structurally diverse amines reveals that facet preference cannot be predicted solely from their classification as primary, secondary, or tertiary amines. Instead, it is governed by facet-specific adsorption configurations and cooperative interactions. In addition to N–Pb coordination, secondary N–H $\cdots$ I hydrogen bonding can stabilize molecular anchoring on the (100) surface. Strong, persistent adsorption blocks the incorporation of new growth units and redirects crystallization toward the (111) orientation, whereas weaker or less uniform adsorption allows continued (100)-oriented growth.

In Chapter Four, crystallization control is extended beyond early-stage nucleation through a thermally activated re-alloying pathway. The 3-APCl additive becomes active only after formation of the initial three-dimensional lattice, inducing a transient secondary intermediate and post-nucleation lattice reconstruction during annealing. This top-down reorganization heals persistent shallow defects, improves structural and optoelectronic homogeneity, suppresses ion migration, and enhances device efficiency and thermal stability.

Together, these studies demonstrate that molecular structure, adsorption geometry, and activation timing can be rationally designed to control distinct stages of perovskite crystallization. The resulting framework connects molecular-scale interactions with facet selection, lattice reconstruction, defect evolution, and device stability, providing new strategies for the development of efficient and durable perovskite solar cells.

The dissertation of Haoxiang Duan is approved.

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2026

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Acknowledgments

I would like to express my sincerest gratitude to my mentor and advisor, Professor Yang Yang, for his unwavering support and guidance throughout my five years at UCLA and one year at Westlake University. His intellectual curiosity and enduring passion for scientific discovery first inspired me to pursue a Ph.D. His command of fundamental principles impressed upon me the importance of rigorous and systematic training, while his exceptional scientific intuition taught me how to look beyond individual observations, identify the questions that truly matter, and pursue research with both depth and purpose. He has always encouraged me to speak out, be proactive, and embrace collaboration. These lessons have profoundly shaped my perspectives on research, work, and life. I feel deeply honored to have completed my Ph.D. under Professor Yang's guidance. His mentorship has had a lasting influence on both my outlook on life and the way I approach challenges. I truly believe that I have become a better version of myself during my time here.

I would also like to express my sincere appreciation to my dissertation committee members, Professor Jianwei Miao, Professor Mark Goorsky, and Professor Amartya Banerjee, for their valuable advice, support, and mentorship throughout my doctoral studies.

I am deeply grateful to Professor Chunqing Ma from Sichuan University and Dr. Zijian Huang for their inspiration and guidance in my research. They taught me how to build a systematic framework for scientific investigation and how to uncover the underlying mechanisms behind experimental observations. I benefited greatly from our many discussions, which continually challenged me to think more deeply and critically.

I would also like to thank Professor Ilhan Yavuz from Marmara University; Professor Huanping Zhou and Ms. Yuetong Wu from Peking University; Professor Gang Li from The Hong Kong Polytechnic University; Dr. Chenhui Zhu and Dr. Yunfei Wang from Lawrence Berkeley

National Laboratory; Dr. Minhuan Wang from Dalian University of Technology; and Dr. Haley Marks from the California NanoSystems Institute at UCLA for their valuable collaboration and assistance.

My heartfelt thanks also go to my wonderful colleagues and friends: Ms. Ming Gong, Ms. Kaiji Zhang, Dr. Yepin Zhao, Dr. Zhichao Shen, Ms. Mingming Xia, Dr. Ying Zhang, Mr. Tso An Yang, Mr. Wenxin Yang, Mr. Xinyang Tong, Dr. Ran Zheng, Dr. Dong Meng, Mr. Daniel Han, Dr. Yingke Zhu, and Dr. Yu-Che Lin. Thank you for your genuine support, encouragement, friendship, and companionship. We experienced many challenges and memorable moments together, and I will always cherish the time we shared. I would also like to thank Mr. Rui Sun for his companionship, especially during the final year of my Ph.D., when he provided me with invaluable emotional support through many stressful moments.

This dissertation and the related work would not have been possible without the contributions of many brilliant minds. With the support of my mentors, collaborators, colleagues, and friends, I have grown tremendously, both as a researcher and as a person. I am deeply grateful to all of you for accompanying me through these important years of my life.

Finally, I would like to thank my family, especially my parents. I have not returned home for five years. Your unconditional support and encouragement have always given me strength and reassurance.

Chapter 4 is based on a manuscript submitted to Nature Communications.

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Chapter 1 Introduction of Perovskite Solar Cells and Crystallization Control

1.1 Status and stability issues of perovskite solar cells

Solar energy represents one of the most promising routes toward sustainable electricity generation because of its abundance, broad geographic availability, and continuously declining utilization cost. Photovoltaic technologies directly convert sunlight into electrical energy and have become a central component of the global transition toward low-carbon energy systems. Among existing photovoltaic technologies, crystalline silicon solar cells currently dominate the commercial market owing to their high power conversion efficiency (PCE), mature manufacturing infrastructure, well-established supply chain, and demonstrated long-term reliability. However, conventional silicon photovoltaic manufacturing generally involves high-temperature and energy-intensive processing. These limitations have motivated the development of emerging photovoltaic technologies that may offer lower manufacturing costs, reduced energy consumption, lightweight form factors, and compatibility with flexible or tandem device architectures.

Among emerging photovoltaic materials, metal-halide perovskites have attracted exceptional attention because of their excellent optoelectronic properties, compositional tunability, and compatibility with low-temperature processing^{1,2}. The perovskites commonly used in solar cells adopt a general ABX_3 composition, in which A is a monovalent cation, B is typically a divalent metal cation, and X is a halide anion. In lead-halide perovskites, corner-sharing PbX_6 octahedra form the three-dimensional inorganic framework, while monovalent organic or inorganic cations, such as methylammonium, formamidinium, or cesium, occupy the cavities within this framework³. The inorganic metal-halide framework predominantly determines the electronic band structure, optical absorption, and charge-transport properties, whereas the A-site

cation influences lattice distortion, phase stability, crystallization behavior, and structural dynamics. This compositional flexibility allows the bandgap and other physical properties of perovskites to be tuned over a wide range.

For iodide-rich lead perovskites, the photoactive material generally adopts a dark brown or black three-dimensional perovskite phase. However, this phase should not always be described simply as cubic because its crystal symmetry depends on composition, temperature, strain, and structural distortion. Depending on the specific material system and operating conditions, the black phase may exhibit cubic, tetragonal, orthorhombic, or locally distorted structural characteristics. For example, photoactive α -FAPbI₃ is often described as a cubic-like perovskite phase, whereas the yellow δ -FAPbI₃ phase possesses a non-perovskite structure and is unsuitable for efficient photovoltaic operation⁴. Stabilizing the photoactive black phase is therefore a major materials challenge, particularly for formamidinium-rich compositions.

Metal-halide perovskites exhibit several properties that make them highly attractive as photovoltaic absorbers. Their direct and tunable bandgaps, typically around 1.5 eV for iodide-rich lead perovskites, are close to the optimal range for single-junction solar-energy conversion and can be adjusted through compositional engineering. Their optical absorption coefficients are generally on the order of 10^4 – 10^5 cm⁻¹ in the visible region, enabling effective light harvesting using films only several hundred nanometers thick. In comparison, crystalline silicon is an indirect-bandgap semiconductor and generally requires a much thicker absorber layer. Perovskites can also exhibit long carrier lifetimes, long diffusion lengths, and relatively high carrier mobilities, although the reported values depend strongly on composition, crystal quality, defect density, and measurement method. In addition, many intrinsic point defects in lead-halide perovskites form relatively shallow electronic states rather than deep recombination centers, allowing solution-

processed polycrystalline films to retain favorable optoelectronic properties despite considerable structural disorder. Their compatibility with both solution- and vapor-based deposition further provides potential advantages in processing temperature, manufacturing cost, and substrate selection.

These properties have enabled exceptionally rapid progress in perovskite solar-cell performance. Since the first reports of perovskite-based photovoltaic devices, the certified PCE of single-junction perovskite solar cells has increased from only a few percent to above 28% (**Figure 1.1**)⁵, approaching that of the best crystalline silicon cells. Perovskites are also particularly attractive for tandem solar cells because their tunable bandgaps allow them to be combined with silicon or other lower-bandgap absorbers to utilize the solar spectrum more efficiently. Perovskite–silicon tandem cells have already achieved efficiencies substantially higher than those of conventional single-junction silicon devices. This rapid development has been supported by advances in composition engineering, crystallization control, interface passivation, charge-transport materials, and device architecture.

Despite these achievements, the commercialization of perovskite solar cells remains constrained by the balance among manufacturing cost, power conversion efficiency, and operational lifetime, often described as the golden triangle of photovoltaic commercialization (**figure B1.1**). Perovskite solar cells have demonstrated competitive laboratory-scale efficiencies and offer the possibility of low-temperature and potentially low-cost manufacturing. However, their long-term operational reliability remains far less established than that of crystalline silicon photovoltaics⁶. Commercial silicon modules commonly provide performance warranties of approximately 25–30 years and are supported by decades of outdoor field data. In contrast, most perovskite devices are evaluated through accelerated laboratory tests lasting from hundreds to

several thousand hours, which cannot yet be directly translated into decades of reliable outdoor operation.

Perovskite-containing photovoltaic products have begun to enter an early stage of commercialization, particularly in perovskite–silicon tandem configurations. Nevertheless, long-term field data remain limited, and currently available product warranties are generally shorter than those of mature silicon modules. Improving operational stability while maintaining high efficiency and scalable processing therefore remains one of the central challenges for perovskite photovoltaics.

The stability limitations of perovskite solar cells originate from coupled degradation processes at the material, interface, and device levels. Metal-halide perovskites are soft ionic semiconductors in which ionic species and charged defects can migrate under thermal, optical, or electrical stimulation⁷. Mobile species may include halide ions, halide vacancies, A-site cations, and related ionic defects. Their redistribution can generate local compositional heterogeneity, accumulate ionic charge at interfaces and grain boundaries, modify the internal electric field, contribute to current–voltage hysteresis, and accelerate chemical reactions with adjacent transport layers or electrodes.

Organic and interfacial components may introduce additional instability. Volatile organic cations can undergo thermal decomposition or escape from the lattice, while organic charge-transport materials may oxidize, diffuse, absorb moisture, or react with neighboring layers. Metal electrodes can migrate into the device, and halide species can diffuse toward and corrode the contacts. These processes are particularly severe at defective interfaces and grain boundaries, where undercoordinated ions, residual precursor species, chemical incompatibility, lattice mismatch, and local mechanical stress promote charge accumulation and chemical reactivity⁸⁻¹⁰.

External environmental and operational stressors, including heat, light, moisture, oxygen, electric fields, and mechanical stress, further activate and accelerate these degradation pathways (**Figure 1.2**)^{11,12}. Moisture can coordinate with the perovskite lattice and promote the formation of hydrated intermediates, while oxygen may react with photogenerated electrons to form reactive oxygen species that attack organic components. Illumination can induce carrier accumulation, local lattice distortion, phase segregation in mixed-halide compositions, and photo-assisted ion migration. Elevated temperature enhances diffusion, volatilization, phase transformation, and interfacial reactions, whereas electric fields drive charged defects toward interfaces and electrodes. Because these stressors often act simultaneously, degradation is highly coupled and may become self-accelerating. For example, ion migration can generate interfacial defects, these defects can promote further chemical reactions, and the resulting products can create additional pathways for ionic transport and material decomposition¹³⁻¹⁵.

Strategies for improving perovskite solar-cell stability can be implemented at the device, interface, and crystal levels. Encapsulation and barrier layers reduce the ingress of moisture and oxygen and improve mechanical robustness^{16,17}, but they cannot fully suppress intrinsic ion migration, thermal decomposition, phase instability, or reactions among internal device components. Interface passivation, diffusion barriers, energy-level optimization, and more stable transport materials can reduce nonradiative recombination and detrimental interfacial reactions^{18,19}. However, degradation processes originating from the bulk perovskite absorber are strongly influenced by the crystal structure established during film formation.

The nucleation pathway, intermediate-phase formation, grain growth, crystal orientation, residual strain, defect distribution, and compositional homogeneity of the perovskite film all affect its subsequent optoelectronic properties and stability. Poorly controlled crystallization can produce

heterogeneous grains, defective grain boundaries, residual precursor phases, local compositional fluctuations, and mechanically strained regions that facilitate nonradiative recombination, ion migration, and chemical degradation. Crystallization control is therefore a key route toward improving the intrinsic quality and stability of perovskite absorbers.

1.2 Processing and crystallization of perovskite films

Solution-based spin coating remains one of the most widely used methods for fabricating metal-halide perovskite thin films because of its low cost, operational simplicity, and compatibility with laboratory-scale device fabrication. In a typical process, a precursor solution containing organic or inorganic halide salts, lead halides, coordinating solvents, and functional additives is deposited onto a rotating substrate. During spinning, centrifugal flow and solvent evaporation progressively reduce the thickness of the liquid film. An antisolvent is often introduced at a selected time to extract the host solvent, decrease the solubility of the precursor components, and induce rapid supersaturation and solidification. The resulting precursor film is subsequently transferred to a hotplate for thermal annealing, during which residual solvent removal, intermediate-phase conversion, structural reorganization, phase transformation, and crystal growth occur (**figure B1.2**)^{20,21}.

The spin-coating process is generally completed within approximately 1–2 min, whereas thermal annealing may continue from several minutes to nearly 1 h, depending on the perovskite composition and processing conditions. Nevertheless, many of the most important structural transformations occur within the first few minutes of annealing. Solvent evaporation, precursor association, nucleation, intermediate-phase formation, phase conversion, and grain growth therefore occur over short and partially overlapping timescales. The rapid and nonequilibrium

nature of this process makes perovskite film formation highly sensitive to precursor chemistry, environmental conditions, deposition parameters, and thermal history.

Perovskite film formation is governed by both thermodynamic driving forces and kinetic limitations^{22,23}. Thermodynamics determines the relative stability of different crystalline and non-crystalline states, whereas kinetics determines which structures can form within the available processing time. Although the photoactive perovskite phase may be thermodynamically favored under the final annealing conditions, the crystallization pathway often passes through multiple metastable states²⁴⁻²⁶. Rapid solvent removal drives the precursor system far from equilibrium and may kinetically trap solvent-coordinated complexes, low-dimensional structures, amorphous phases, or compositionally heterogeneous domains before the final three-dimensional lattice is established. Consequently, films with the same nominal composition may exhibit substantially different structures and properties when prepared under different processing conditions.

The crystallization of solution-processed metal-halide perovskites is often described as nonclassical (**Figure 1.3**)²⁷. In an idealized classical crystallization model, isolated ions or molecules are incorporated individually into a growing crystalline nucleus. Perovskite crystallization, however, frequently involves the prior formation of coordinated precursor complexes, iodoplumbate species, nanoscale clusters, colloidal aggregates, and structurally distinct intermediate phases. These preassembled species may aggregate, reorganize, partially dissolve, exchange ions, or transform collectively before forming the final perovskite lattice. Perovskite crystals can therefore develop through both the addition of individual building units and the structural evolution of chemically complex precursor species, rather than through a purely classical pathway.

This behavior is particularly pronounced because perovskite precursor solutions contain multiple ionic species, coordinating solvents, additives, and organic and inorganic components with different coordination strengths, diffusion rates, and chemical affinities. Lead halides can form a variety of solvent-coordinated complexes and iodoplumbate species, while A-site cations interact with these species through electrostatic interactions, hydrogen bonding, and steric effects. The balance among these interactions determines precursor speciation, aggregation behavior, intermediate-phase stability, and the subsequent crystallization pathway.

Processing solvents play a central role in controlling these interactions. Solvents such as dimethylformamide are commonly used because of their ability to dissolve precursor salts, whereas more strongly coordinating solvents, such as dimethyl sulfoxide or N-methyl-2-pyrrolidone, can bind to Pb^{2+} and stabilize solvent-containing precursor complexes²⁸. Such coordination can delay direct precipitation of the perovskite phase and promote the formation of a more homogeneous precursor film. In contrast, rapid solvent removal increases supersaturation and induces nucleation or solidification. Antisolvent treatment further accelerates this process by extracting the host solvent and reducing precursor solubility²⁹. The coordination strength, volatility, and miscibility of the solvents, together with the timing and amount of antisolvent addition, therefore, strongly influence precursor organization, nucleation density, intermediate-phase formation, and film morphology.

High-quality film formation requires an appropriate balance between nucleation and subsequent crystal growth. Excessively rapid nucleation can produce a high density of small crystallites and grain boundaries, whereas insufficient or highly localized nucleation can lead to incomplete coverage, pinholes, and spatially nonuniform films. Crystallization control should therefore not simply aim to slow the entire process. Instead, precursor solidification, nucleation,

intermediate-phase conversion, and crystal growth must be regulated in a coordinated manner to achieve uniform coverage, controlled grain formation, and sufficient time for structural relaxation and compositional redistribution.

Intermediate-phase engineering has become one of the most widely used strategies for achieving this control³⁰⁻³⁴. A variety of transient states have been identified during perovskite film formation (**Figure 1.4**)^{35,36}, including solvent-coordinated complexes, crystalline precursor phases, low-dimensional perovskite-related structures, and amorphous or poorly ordered alloy states. These species generally form during film deposition and subsequently transform into the photoactive perovskite phase during thermal annealing. By temporarily stabilizing the precursor components and delaying direct formation of the final lattice, intermediate phases can suppress uncontrolled precipitation and regulate the rates of nucleation and crystal growth.

Because many precursor complexes and intermediate phases are short-lived, *ex situ* characterization often captures only the deposited precursor film or the final annealed structure. *In situ* techniques, including photoluminescence spectroscopy, optical absorption spectroscopy, X-ray diffraction, and grazing-incidence wide-angle X-ray scattering, are therefore valuable for resolving the temporal evolution of nucleation, intermediate formation, phase conversion, and crystal growth^{37,38}. Combined with structural characterization and computational analysis, these methods can reveal how molecular-scale interactions determine macroscopic film formation.

The historical development of perovskite solar cells also illustrates the close relationship between crystallization quality and device performance. As PCE have increased, the corresponding X-ray diffraction patterns have generally evolved from relatively complex profiles containing broad peaks and reflections from residual or secondary phases toward cleaner patterns with sharper and narrower α -perovskite diffraction peaks (**figure B1.3**). Although

diffraction peak width can also be influenced by crystallite size, microstrain, instrumental broadening, and preferred orientation, this overall evolution generally indicates improved phase purity and structural order. These advances have occurred alongside reductions in compositional heterogeneity, residual phases, lattice disorder, and defect density, all of which strongly affect charge-carrier recombination and ionic transport. Crystallization quality is therefore closely associated with both photovoltaic efficiency and operational stability.

Overall, perovskite crystallization is a multistep and nonequilibrium process governed by interactions among precursor ions, solvents, additives, interfaces, and the developing crystal lattice. Molecular structure, functional-group position, steric configuration, coordination ability, hydrogen bonding, electrostatic interactions, and compatibility with the inorganic framework can all alter precursor organization and phase evolution. Understanding and controlling these molecular interactions is therefore essential for achieving reproducible formation of phase-pure, structurally ordered, and electronically high-quality perovskite films.

Vapor-deposition techniques have also advanced from the preparation of individual perovskite layers toward the fabrication of more complete device structures^{39,40}. These approaches offer advantages in process reproducibility, solvent-free manufacturing, and compatibility with large-area production. Although vapor-based processing is not investigated here, perovskite formation in both solution and vapor deposition remains governed by interactions among deposited species, surfaces, interfaces, and the evolving crystal lattice. The molecular principles discussed in this section may therefore remain relevant across different processing platforms.

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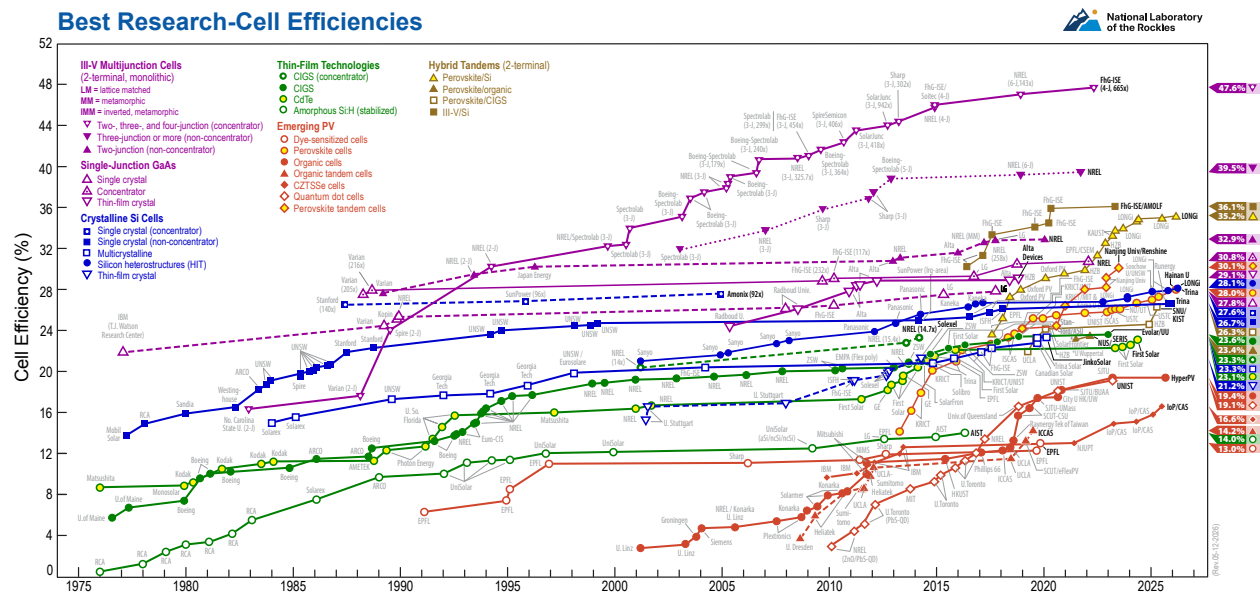


Figure 1.1. NREL Best research cell efficiency chart. ⁵

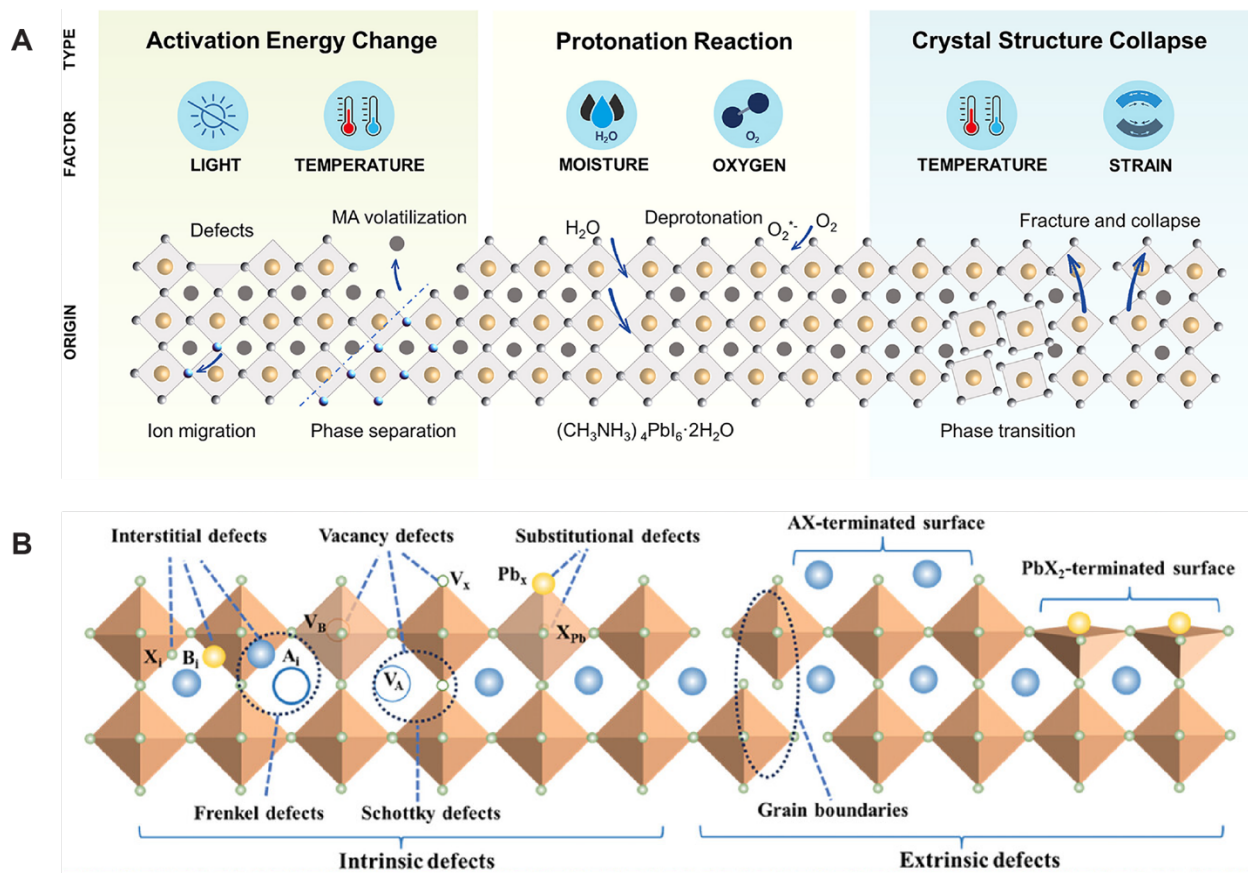


Figure 1.2. Formation and distribution of defects in metal-halide perovskites. (A) Schematic illustration of defect formation and structural degradation induced by external stressors. (B) Major intrinsic and extrinsic defects and their representative distribution within the perovskite lattice, grain boundaries, and surfaces.^{11,12}

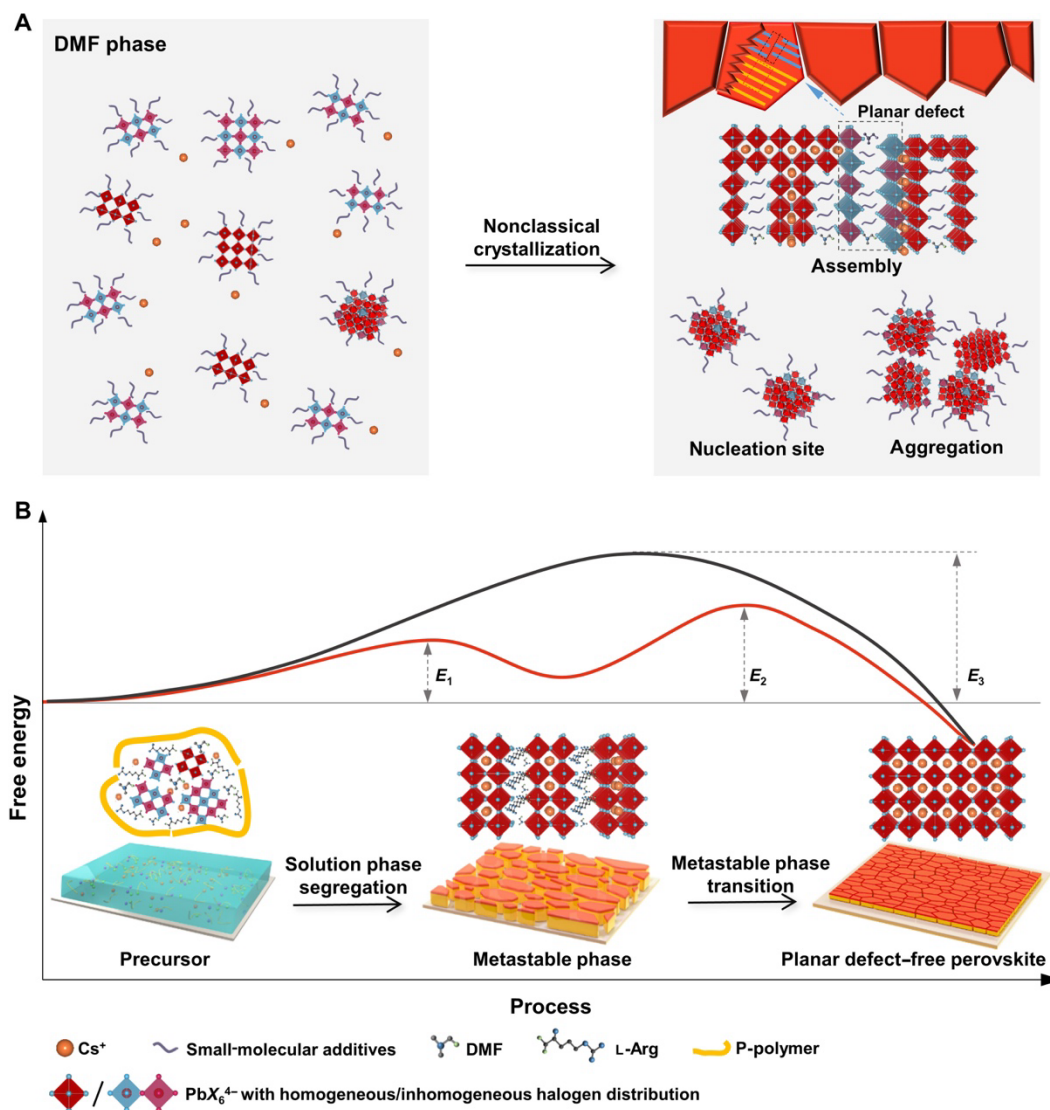


Figure 1.3. Schematic illustration of the perovskite crystallization process and the proposed crystallization pathways. (A) Nonclassical crystallization of perovskites involving the formation, aggregation, and structural reorganization of precursor clusters, followed by their transformation into the crystalline perovskite phase. (B) Schematic free-energy profiles of two possible perovskite crystallization pathways, where additive-induced intermediates lower the crystallization energy barrier.²⁷

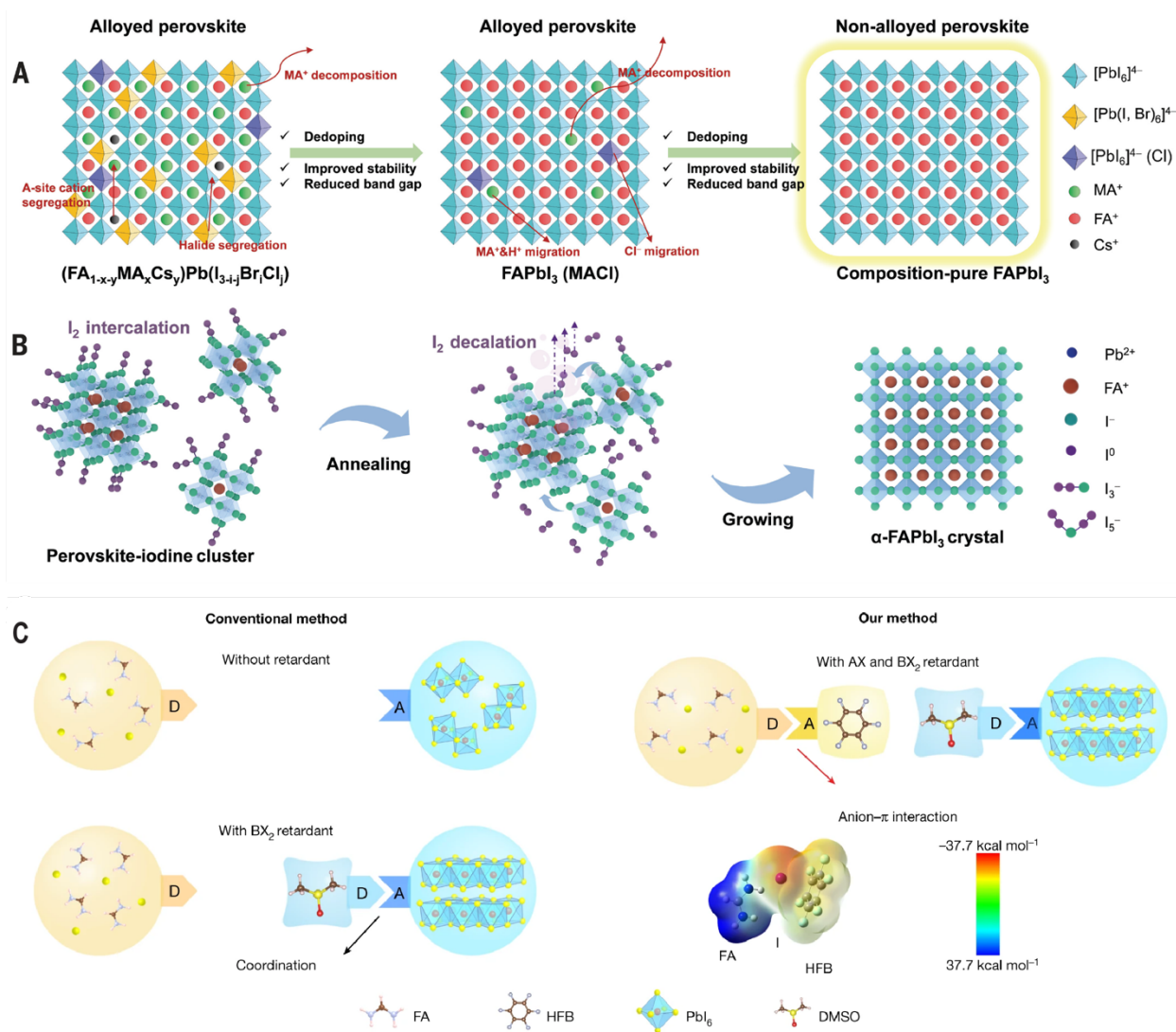


Figure 1.4. Example illustrations of additive-regulated crystallization pathways in metal halide perovskites. (A) Compositional regulation suppresses alloying-related instability and promotes the formation of compositionally uniform perovskite crystals. (B) Iodine-mediated precursor-cluster evolution and reversible iodine incorporation regulate the formation of $\alpha\text{-FAPbI}_3$. (C) Retarding additives modify precursor interactions and delay crystallization, enabling a more controlled conversion into the perovskite phase.^{35,36}

Chapter 2 Efficient and Stable (111)-Oriented Perovskite Solar Cells

The optoelectronic properties of metal-halide perovskites, including their long carrier diffusion lengths^{1,2}, compare favorably with those of conventional semiconductors such as GaAs. The theoretical carrier diffusion length in FAPbI₃ single crystals has been estimated to reach 10–100 μm ³⁻⁵, substantially exceeding the typical thickness of a perovskite solar cell absorber. In polycrystalline perovskite films, however, rapid solution-based fabrication often introduces a much higher density of surface and grain-boundary defects than that found in single crystals⁶⁻⁸. These defects enhance nonradiative recombination and carrier scattering, thereby limiting experimentally measured diffusion lengths to approximately a few micrometers. Such losses not only hinder charge transport and photovoltaic performance but may also accelerate degradation during long-term operation⁹⁻¹¹. Narrowing the gap between the intrinsic transport capability of perovskite materials and that achieved in polycrystalline films is therefore important for improving both the efficiency and operational stability of perovskite solar cells^{12,13}.

Crystallographic orientation can strongly influence carrier transport by modifying surface energetics, defect formation, electronic structure, and ion-migration behavior¹⁴⁻¹⁷. Among the commonly observed crystallographic planes, the (111) facet has attracted particular interest because of its potential to support reduced defect densities and improved carrier transport¹⁸⁻²⁰. Previous studies have shown that (111)-oriented perovskite films can exhibit enhanced environmental stability under harsh conditions²¹⁻²³. The (111) facet has also been associated with increased ion-migration activation energies and reduced sensitivity to internal electric fields during device operation. In addition, its relatively high work function may facilitate more favorable energetic alignment and balanced carrier extraction²⁴. Despite these potential advantages, the

controlled formation of highly (111)-oriented perovskite films remains challenging. Compared with the commonly observed (100) facet, the formation of the (111) surface is less readily favored during conventional solution processing, and randomly distributed nucleation sites often lead to mixed crystallographic orientations²⁵⁻²⁷. Consequently, high-quality films dominated exclusively by the (111) orientation have rarely been achieved.

Here, we develop a highly crystalline, (111)-dominated perovskite film with an exceptionally long carrier diffusion length by using 3-aminopentane (3-AP) and propylammonium chloride (PACl) as co-additives to regulate crystallization. 3-AP preferentially interacts with the (111) surface and lowers its formation energy, thereby promoting the development of the (111) orientation. PACl facilitates complete phase conversion and subsequent crystal growth. Through the cooperative effects of these two additives, a nearly pure (111)-oriented film is obtained without detectable competing preferred orientations. The resulting film exhibits high crystallinity and a carrier diffusion length of 5.42 μm , approaching that of the corresponding single-crystal material and indicating substantially reduced defect-mediated transport losses. Devices fabricated from these films achieve a high open-circuit voltage of 1.215 V, which is attributed in part to the more p-type electronic character associated with the (111)-oriented film. The devices retain 90% of their initial power conversion efficiency after 1,000 h of continuous operation at 85 °C under one-sun illumination. This work establishes a strategy for controlling facet-selective crystal growth and producing high-quality perovskite films with long carrier diffusion lengths. It further demonstrates the close relationship between crystallographic orientation, carrier transport, and device stability, providing a useful framework for the rational design of perovskite films.

2.1 Identification of (111)- dominated perovskite films

figure B2.1 compares the atomic arrangements of the (100) and (111) facets of the perovskite lattice. The (100) plane contains both Pb- and I-containing species within the exposed layers, allowing more effective charge compensation and resulting in a relatively nonpolar surface. In contrast, the (111) direction consists of alternating Pb-rich and I-rich planes, giving rise to an intrinsically polar surface with uncompensated charge. The (111) facet also exhibits a more densely packed surface atomic arrangement than the (100) facet. Such dense atomic packing may reduce the number of undercoordinated surface sites and limit the adsorption or penetration of environmental species once the surface charge is effectively compensated. At the same time, its intrinsic polarity can promote surface reconstruction, ionic redistribution, or adsorption of charged species to minimize electrostatic instability. The combined effects of surface polarity and atomic packing therefore give the two facets distinct electronic and stability characteristics.

As shown in **Figure 2.1**, the (111) facet exhibits a higher work function and a correspondingly lower local photocurrent than the (100) facet²⁸. This facet-dependent electronic behavior is further confirmed by the AFM and conductive-AFM images of an individual perovskite grain containing both (100) and (111) facets (**figure B2.2**). In addition, during exposure to 40% relative humidity, the (111) facets are preferentially preserved while the surrounding regions degrade more rapidly, indicating the higher environmental stability of the (111) surface²¹. These observations suggest that the (111) facet combines distinct electronic properties with improved resistance to degradation. On this basis, we developed a perovskite film dominated by the (111) orientation as a strategy to improve film quality and address the stability limitations of perovskite solar cells.

To selectively promote the growth of the (111)-oriented film, 3-aminopentane (3-AP) and propylammonium chloride (PACl) were introduced as co-additives to regulate crystallization. The precursor solution contained 3% 3-AP and 1.5% PACl, whereas the control precursor contained no additive. Both films were prepared using the same two-step annealing procedure. Their out-of-plane crystallographic orientations were first examined by X-ray diffraction, as shown in **Figure 2.2A**. Diffraction peaks near 14° and 25° , assigned to the (100) and (111) planes, respectively, are observed in both films. However, the (111) diffraction peak is substantially enhanced in the additive-treated film, while the relative intensity of the (100) peak is strongly suppressed. The intensity ratio of the (111) peak to the (100) peak increases from 1.09 in the control film to 25.62 in the target film, demonstrating the exceptionally high degree of (111) preferential orientation.

The change in crystallographic orientation is also reflected in the film morphology. The control film consists predominantly of irregularly shaped grains, whereas the additive-treated film exhibits characteristic triangular surface features (**Figure 2.2B**), consistent with the surface geometry expected for the (111) orientation in a cubic crystal. In addition, the (111)-oriented film displays larger grains and a narrower grain-size distribution, suggesting a more uniform and controllable crystallization process. The grazing-incidence wide-angle X-ray scattering pattern further reveals a dominant (111) diffraction feature (**figure B2.3**), and the corresponding azimuthal intensity distribution exhibits a narrow angular width, confirming the high degree of orientational alignment (**Figure 2.2C**). Transmission electron microscopy (TEM) of the target film shows a clearly resolved atomic arrangement corresponding to the (111) plane, together with a well-defined diffraction pattern, further confirming its high crystallinity and preferred orientation (**figure B2.4**).

We attribute the formation of this highly crystalline and strongly oriented film to the complementary roles of 3-AP and PACl. Screening of different amine additives showed that 3-AP

most effectively suppresses the development of the (100) orientation while promoting growth of the (111) facet. This behavior is attributed to the preferential adsorption of 3-AP on the (111) surface, which modifies the relative surface energies and stabilizes the growth of this facet. PACl, on the other side, interacts strongly with the lead–iodide framework and promotes the formation of a low-dimensional or precursor intermediate. Previous studies have shown that PACl-containing intermediates can regulate phase conversion, suppress incomplete transformation, and facilitate the formation of high-quality perovskite films^{29,30}. PACl was therefore incorporated as the second additive to promote complete phase conversion and subsequent crystal growth. The combined use of 3-AP and PACl is expected to simultaneously regulate facet selection and the overall crystallization kinetics.

To understand how the two additives regulate facet-selective crystallization, the structural evolution of the control and target films was monitored by in situ X-ray diffraction during thermal annealing. Following antisolvent treatment, the wet precursor films were transferred to a hotplate at 150 °C, which is defined as 0 s in **figure B2.5**. Immediately after antisolvent treatment, both films exhibit a diffraction feature between 11° and 12°, assigned to the δ -phase or a δ -related FAPbI_3 precursor phase. During the initial stage of annealing, the (100) and (111) diffraction peaks emerge nearly simultaneously in the control film, with the (100) peak rapidly becoming dominant. In the absence of additives, crystallization therefore preferentially proceeds toward the more commonly observed and energetically favorable (100) orientation.

A markedly different crystallization pathway is observed in the additive-treated film. The (111) diffraction peak appears preferentially, whereas the (100) peak remains nearly undetectable throughout the annealing process. In addition, the growth of the (111) peak is substantially slower than the rapid development of the (100) peak in the control film. The intensity of the (111) peak in

the target film does not become comparable to that of the control-film (100) peak until approximately 120 s of annealing. This delayed crystallization is attributed to the formation of a more stable and chemically complex precursor intermediate induced by the combined presence of 3-AP and PACl. By slowing direct crystallization, the additives extend the time available for precursor reorganization, phase conversion, and ordered crystal growth. This prolonged crystallization process promotes improved structural ordering, more complete phase conversion, and highly selective development of the (111) orientation.

The phase evolution also differs in terms of residual secondary phases. A weak PbI_2 diffraction peak near 12.5° appears in the control film after approximately 50 s and remains detectable after annealing, indicating incomplete reaction or partial precursor decomposition. In contrast, no obvious PbI_2 peak is observed in the (111)-oriented film. This result suggests that PACl facilitates more complete phase conversion, while 3-AP directs facet-selective crystal growth. The cooperative action of the two additives therefore enables the formation of a highly crystalline perovskite film with exceptional (111) orientation purity and minimal residual secondary phases.

2.2 Enhanced carrier transport

We further characterized the optoelectronic and ionic-transport properties of the control and target films. **Figure 2.3A** presents confocal photoluminescence (PL) intensity maps of the two films. Compared with the control film, the (111)-oriented target film exhibits substantially stronger PL emission and a more spatially uniform intensity distribution, indicating reduced nonradiative recombination and improved film uniformity. Consistently, the steady-state PL spectrum of the target film shows a higher emission intensity and a narrower full width at half maximum than that of the control film (**figure B2.6**), further suggesting reduced energetic disorder and a more uniform

emissive environment. The enlarged PL map of the target film also reveals distinct triangular grains, consistent with the characteristic morphology observed in the corresponding SEM images.

Time-resolved photoluminescence measurements further demonstrate the reduced recombination losses in the target film. As shown in **Figure 2.3B**, the target film exhibits a markedly slower PL decay than the control film. The fitted slow-decay lifetime, τ_2 , increases from 147.83 ns for the control film to 617 ns for the target film, suggesting a substantial reduction in defect-assisted carrier recombination.

To directly evaluate lateral carrier transport, time-resolved spatial PL measurements were performed. **Figure 2.3C** shows the PL intensity distributions of the target and control films at delay times ranging from 0 to 40 ns following localized excitation. The progressive broadening of the PL spot reflects the lateral diffusion of photogenerated carriers away from the excitation region. In the target film, the carrier distribution expands more rapidly and remains detectable for a longer period than in the control film, indicating both faster transport and slower recombination.

Analysis of the spatial broadening yields diffusion coefficients of $0.0643 \text{ cm}^2 \text{ s}^{-1}$ for the control film and $0.4784 \text{ cm}^2 \text{ s}^{-1}$ for the target film (**Figure 2.3D**). The diffusion coefficient of the target film is therefore approximately 7.4 times higher than that of the control. The combined increase in diffusion coefficient and carrier lifetime extends the carrier diffusion length from 0.97 μm in the control film to approximately 5.42 μm in the target film. This diffusion length greatly exceeds the absorber thickness used in the devices, allowing photogenerated carriers throughout the perovskite layer to reach the charge-selective contacts before recombination. These results demonstrate that the strong (111) preferential orientation is associated with a meaningful improvement in long-range carrier transport, rather than merely a change in diffraction intensity.

2.3 Improved device performance and operational stability

Ion migration was evaluated because mobile ionic species can accelerate the operational degradation of perovskite solar cells. Lateral Au/perovskite/Au structures were used to measure the temperature-dependent conductivity, $\sigma(T)$, and determine the activation energy for ion migration. The temperature dependence was described by³¹

$$\sigma(T)T = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

where E_a is the activation energy, k_B is the Boltzmann constant, σ_0 is a pre-factor, and T is the absolute temperature. Based on the linear fits of $\ln(\sigma(T)T)$ versus $1000/T$ shown in **Figure 2.4A**, the ion-migration activation energy increases from 367 meV in the control film to 624.3 meV in the target film. The higher activation energy indicates that ionic motion is substantially more difficult in the (111)-oriented perovskite film. This suppression of ion migration likely contributes to the improved stability of the target devices under prolonged illumination.

The photovoltaic performance of the control and target FAPbI₃-based n-i-p devices was evaluated using reverse-scan current density–voltage characteristics (**Figure 2.4B**). The target device achieves a power conversion efficiency of 26.50%, compared with 24.96% for the control device (**table C2.1**). The improvement is particularly evident in the open-circuit voltage, which increases from 1.186 V to 1.215 V. This enhancement is attributed to the reduced nonradiative recombination and improved carrier transport in the highly (111)-oriented film, together with the intrinsically deeper Fermi-level position associated with the (111) facet. The distinct electronic structure of the (111) facet can provide more favorable interfacial energy alignment and carrier extraction, consistent with the lower local current observed by conductive AFM. In addition, the Pb 4f peaks of the target film shift slightly toward lower binding energies compared with those of

the control film (**figure B2.7**), indicating a modified local electronic and coordination environment around Pb associated with the distinct atomic arrangement and polarity of the (111) facet.

The improved intrinsic stability of the target film was first examined under high-humidity conditions. **figure B2.8** shows photographs of the control and target perovskite films during exposure to approximately 80% relative humidity. The control film gradually changes from black to yellow, indicating transformation of the photoactive α -phase into the non-photoactive δ -phase. In contrast, the target film largely retains its original black appearance, demonstrating substantially improved resistance to moisture-induced phase degradation.

The operational stability of encapsulated devices was further evaluated by maximum power point tracking under continuous full-spectrum AM 1.5G illumination at 100 mW cm^{-2} . At $65 \pm 5 \text{ }^{\circ}\text{C}$, the target device retains more than 90% of its initial power output after 1,600 h, whereas the control device decreases to approximately 60% after about 1,400 h (**Figure 2.4C**). Under the more severe condition of $85 \text{ }^{\circ}\text{C}$, the target device still maintains approximately 90% of its initial performance after 1,000 h, while the control device retains only about 60% over the same period (**Figure 2.4D**). These results demonstrate that the highly (111)-oriented film provides substantial improvements in both photovoltaic performance and long-term operational stability.

2.4 Summary

In summary, we developed a highly (111)-oriented FAPbI₃ film by using 3-aminopentane and PACl as co-additives to regulate facet-selective growth and phase conversion. This cooperative crystallization control improved film crystallinity, carrier transport, and resistance to ion migration, leading to enhanced photovoltaic performance and operational stability. These results demonstrate that crystallographic orientation can serve as an effective design parameter for linking molecular-

level crystallization control with the electronic quality and long-term reliability of perovskite solar cells.

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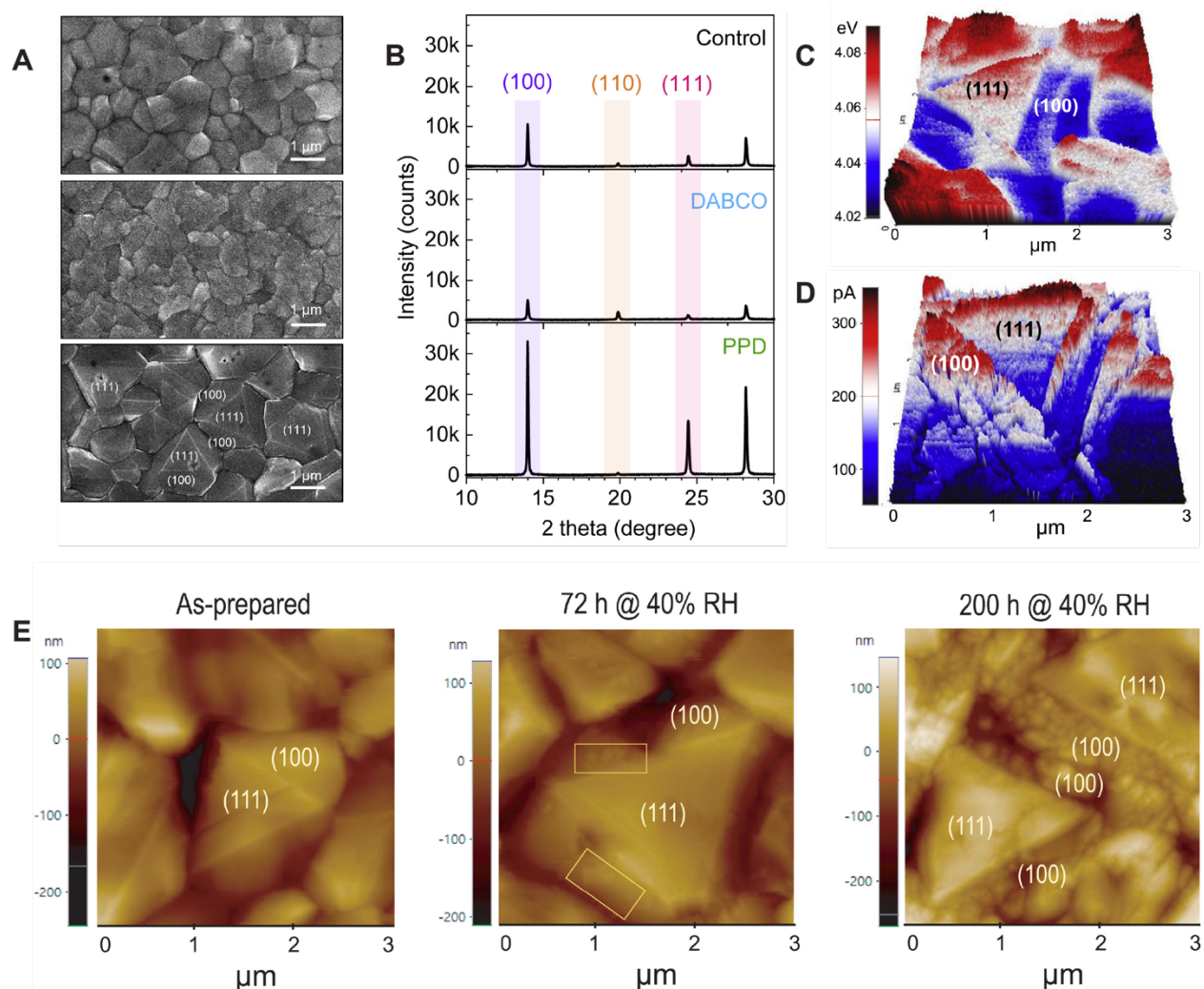


Figure 2.1. Facet-dependent characteristics and stability of perovskite films. (A) Surface morphologies of perovskite films prepared with different additives, showing distinct (100) and (111) facets in the PPD-treated film. (B) Corresponding XRD patterns of the perovskite films. (C) Schematic comparison of the work function and Fermi-level positions of the (100) and (111) facets. (D) Conductive AFM images and current distributions of the two facets. (E) Morphological evolution of the perovskite film under 40% relative humidity, showing the preferential preservation of the (111) facets.^{21,28}

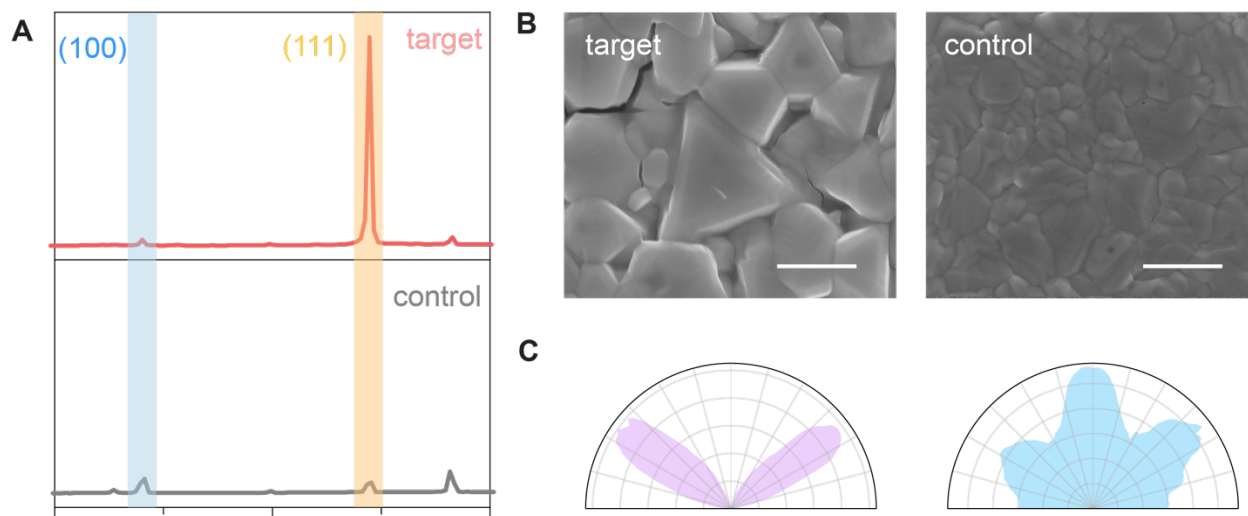


Figure 2.2. Identification of a highly (111)-dominant crystallographic texture in FAPbI₃ films. (A) XRD patterns of the control and target films. The target film exhibits a 16-fold higher (111) diffraction intensity than the control film. (B) Top-view SEM images of the target and control films. The target film shows enlarged grains with distinct triangular surface facets. Scale bars, 1 μm . (C) Fan-shaped plots of the azimuthal intensity distributions extracted from the corresponding GIWAXS diffraction signals of the target (left) and control (right) films. The target film exhibits a dominant (111) diffraction feature with a narrow azimuthal distribution.

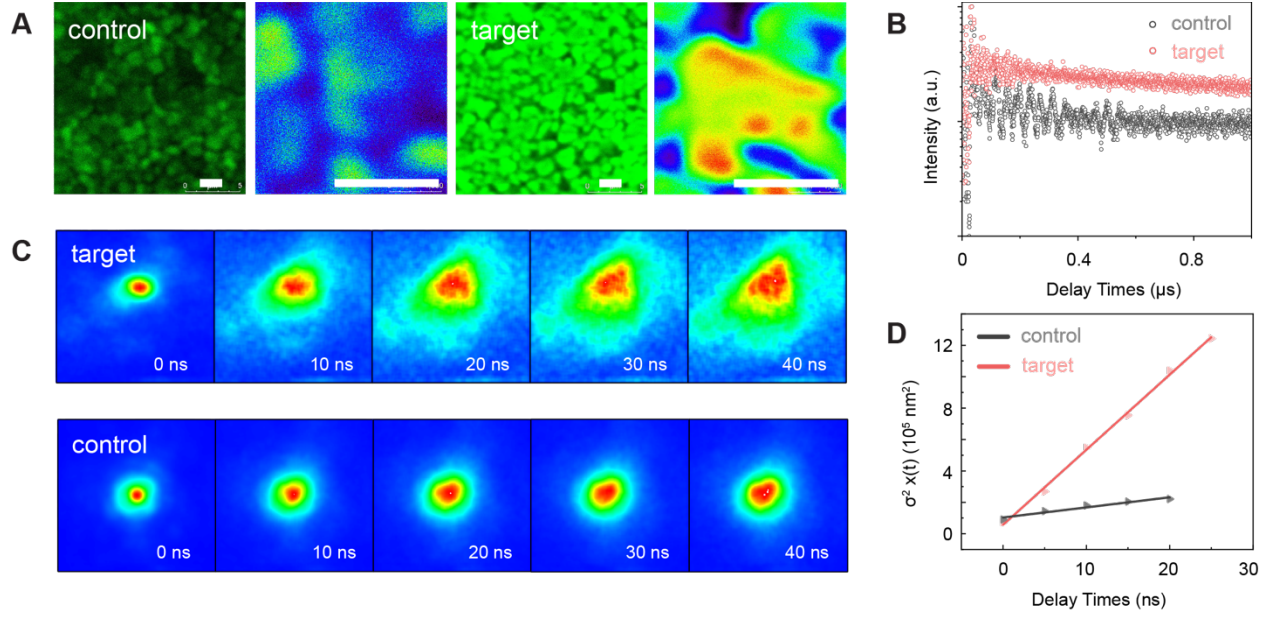


Figure 2.3. Carrier diffusion dynamics in the control and target FAPbI₃ films. (A) Confocal PL intensity maps of the control and target films. Scale bars, 2 μm . (B) TRPL decay curves of the control and target films. The fitted slow-decay lifetimes (τ_2) are 147.83 ns for the control film and 617 ns for the target film. (C) Time-resolved PL intensity images of the target (top) and control (bottom) films at delay times from 0 to 40 ns. The broadening of the PL spot with increasing delay time reflects lateral carrier transport away from the excitation site. (D) Spatial variance, $\sigma_x^2(t)$, as a function of delay time. Linear fitting yields diffusion coefficients of 0.4784 and 0.0643 $\text{cm}^2 \text{ s}^{-1}$ for the target and control films, respectively.

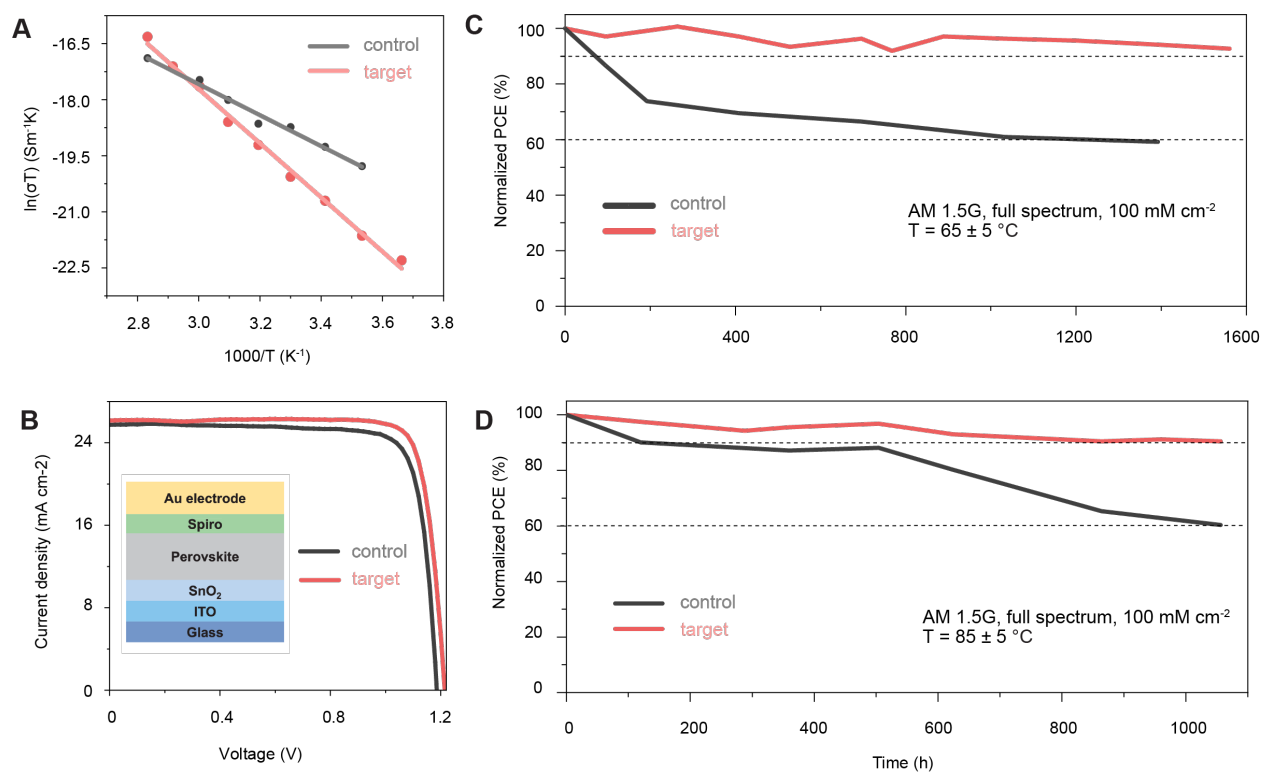


Figure 2.4. Enhanced performance and operational stability of target FAPbI3 devices. (A)

Temperature-dependent electrical conductivity of the control and target (111)-oriented perovskite films. Lateral devices with Au/perovskite/Au were used. (B) Reverse J–V characteristics of control and target FAPbI3-based n–i–p solar cells. (C, D) Evolution of the normalized power output of encapsulated devices during maximum power point (MPP) tracking under continuous illumination (AM 1.5G, full spectrum, 100 mW cm $^{-2}$) at 65 $\pm$ 5 $^{\circ}$ C (C) and 85 $^{\circ}$ C (D).

Chapter 3 Molecular Anchoring in Facet-Selective Crystallization

Amines are among the most widely used molecular additives for regulating perovskite crystallization because their Lewis-basic nitrogen atoms can interact strongly with undercoordinated Pb sites in both precursor species and growing crystals¹⁻⁵. Depending on their molecular structures, amines can alter precursor coordination, colloidal aggregation, intermediate-phase stability, nucleation density, and subsequent crystal growth⁶⁻⁸. These interactions can suppress uncontrolled precipitation and the formation of undesirable phases while modifying the kinetic barriers associated with phase conversion⁹⁻¹¹. In addition, because amine molecules can adsorb selectively on particular crystal surfaces, their influence is not limited to bulk crystallization kinetics but can also extend to facet-selective growth. Selective adsorption changes the relative surface energies and growth rates of different crystallographic planes, thereby affecting the final crystal orientation and morphology. As demonstrated in Chapter 2, 3-aminopentane promotes the preferential formation of the (111) facet. Although many previous studies have examined individual amines and proposed specific mechanisms for their effects on crystallization and facet evolution, most conclusions have been drawn from isolated molecular systems¹²⁻¹⁴. A systematic understanding of how molecular structure, functional-group position, steric configuration, and additional intermolecular interactions determine the distinct facet preferences induced by different amines remains lacking.

Here, we systematically investigate dozens of amines and evaluate their effects on facet-selective growth. Although many of these molecules exhibit similar primary interactions with the perovskite framework, they induce markedly different crystallographic preferences. In addition to the commonly recognized N–Pb coordination, we identify a possible secondary hydrogen-bonding

interaction that influences the stabilized adsorption configuration of amine molecules on perovskite surfaces. This additional interaction can act as an anchoring force, strengthening molecular adsorption and hindering the attachment of new perovskite building units to the exposed surface. Because different facets vary in their ability to support this anchoring configuration, the balance between coordination and hydrogen bonding ultimately determines facet preference. These findings provide a general molecular framework for understanding amine-directed crystal growth and offer practical guidance for the rational design of additives for facet engineering in perovskite materials.

3.1 Amine Structure Controls Facet Growth Preference

Dozens of amine additives were introduced into the perovskite precursor solution to systematically examine their effects on facet-selective crystal growth. X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were used to characterize the resulting structural and morphological differences. To directly compare the facet preferences induced by different amines, the diffraction intensities of the (100) and (111) peaks were extracted from the corresponding XRD patterns and plotted in **Figure 3.1A** and **figures B3.1–B3.4**. Amines located toward the right side of the plot exhibit a stronger preference for the (100) orientation, whereas those located toward the left favor the (111) orientation. The dashed lines indicate the neutral boundary and the position of the additive-free control film. The control film shows an intrinsic preference for the (100) orientation, consistent with the lower formation energy and more favorable growth of the (100) facet under conventional processing conditions^{15,16}.

Linear primary amines such as propylamine (PA) and butylamine (BA) generally distributed near the control region, indicating that their incorporation does not substantially alter the intrinsic facet-growth tendency of the perovskite film (**figure B3.2**). In contrast, branched and

cyclic primary amines, including 3-aminopentane (3-AP), isopropylamine (iPA), and cyclohexylamine (cyA), exhibit a clear preference for the (111) orientation (**figure B3.3**). Secondary amines display more diverse behavior. Piperidine (P2) and azetidine (H4) enhance diffraction from both the (100) and (111) planes, whereas diethylamine (DEA) preferentially promotes the (111) orientation (**figure B3.1**). Tertiary amines likewise show no consistent facet preference across the tested molecular structures (**figure B3.4**). These results demonstrate that facet selection cannot be predicted solely from the conventional classification of amines as primary, secondary, or tertiary.

Representative AFM images further reveal the morphological changes associated with the different facet preferences (**Figure 3.1B**). The control film exhibits a relatively rough surface without well-defined facet-dependent morphological features. In the P2-treated film, both (100)- and (111)-type surface features are observed within individual grains, consistent with the simultaneous enhancement of both diffraction orientations. In contrast, films treated with DEA and iPA display well-defined triangular or hexagonal grains commonly associated with (111)-dominated growth. The morphological distinction between the (100)- and (111)-dominated films is also evident in the SEM images, where square-like and triangular surface features are observed, respectively (**figure B3.5**). Conductive-AFM measurements further reveal facet-dependent local conductivity and clearly resolved boundaries between the (100) and (111) regions in both the height and current maps (**figure B3.6**).

Overall, different amine molecules induce distinct facet preferences and corresponding changes in film morphology and local electronic properties. Importantly, these trends cannot be explained by a simple classification based on primary, secondary, or tertiary amine structures. Instead, the decisive factor is likely the specific adsorption configuration and interaction strength

of each molecule on different perovskite surfaces. Facet-selective growth is therefore governed by molecular-level differences in surface binding rather than by the formal chemical category of the amine additive. To identify the origin of these differences, we next examined the adsorption configurations and interaction energies of representative amines on the (100) and (111) surfaces.

3.2 Multiple Surface Interactions Stabilize Amine Adsorption

Figure 3.2 compares the optimized adsorption configurations of PA, P2, and cyA on the perovskite (100) surface, with the corresponding structural and energetic parameters summarized in **Table 3.1**. Among the three molecules, cyA exhibits the most negative interaction energy, indicating the strongest overall adsorption on the (100) surface. This result is initially unexpected because cyA has the largest steric hindrance, which would normally weaken direct coordination between the amine group and surface Pb sites.

Consistent with this expectation, the calculated N–Pb distance of cyA is longer than that of PA, indicating weaker direct N–Pb coordination. Therefore, the stronger overall adsorption of cyA cannot be explained by the primary coordination interaction alone and likely involves additional stabilizing interactions. Examination of the optimized adsorption structures reveals geometries consistent with the formation of an additional N–H $\cdots$ I hydrogen bond between the adsorbed amine and the perovskite surface. The contribution of this secondary interaction depends strongly on the molecular adsorption configuration, particularly the H $\cdots$ I distance and the N–H $\cdots$ I bond angle. Among the three molecules, cyA exhibits the most favorable geometry, with an H $\cdots$ I distance of 3.09 Å and an N–H $\cdots$ I angle of approximately 140°, whereas PA shows the least favorable configuration. The ability to establish this additional interaction therefore follows the order PA < P2 < cyA, consistent with their experimentally observed tendency to promote the (111) orientation.

These results indicate that amine adsorption is governed by the cooperative contribution of multiple surface interactions rather than by N–Pb coordination alone. A flexible molecule dominated by a single coordination interaction can more readily change its adsorption configuration or desorb from the surface, resulting in transient and spatially nonuniform coverage. In contrast, a molecule with an appropriate and relatively constrained geometry can establish N–Pb coordination and N–H $\cdots$ I hydrogen bonding simultaneously. This multi-interaction anchoring reduces the configurational freedom of the adsorbed molecule, stabilizes its residence on the surface, and promotes more persistent and uniform surface coverage.

Strong and persistent adsorption can subsequently occupy the coordination sites required for the attachment and incorporation of incoming perovskite growth units. Rather than simply changing the thermodynamic stability of one surface, the adsorbed molecules modify both the effective surface energy and the growth kinetics of the exposed facet. The degree to which this multi-interaction anchoring can be established, however, depends strongly on the atomic arrangement and available binding geometry of the specific crystallographic surface.

3.3 Facet-Dependent Surface Geometry Governs Selective Growth

The distinct atomic arrangements of the (100) and (111) facets are illustrated by the three-dimensional crystal structures in **figure B3.7**. On the (100) surface, neighboring Pb and I sites are exposed within the same surface region, providing a suitable geometry for an amine molecule to simultaneously establish N–Pb coordination and N–H $\cdots$ I hydrogen bonding. This arrangement enables the multi-interaction anchoring described in Section 3.2. In contrast, Pb- and I-rich atomic layers are spatially separated along the (111) direction, making it more difficult for a single amine molecule to interact with Pb and I sites simultaneously. The optimized adsorption configurations shown in **figure B3.8** further illustrate this geometric difference between the two facets.

Because the (100) surface more readily supports multi-interaction adsorption, the interaction between the amine molecule and the (100) facet is expected to play a dominant role in determining the final orientation distribution. The adsorbed molecule can influence growth through two competing effects. First, a favorable molecular interaction may stabilize the attachment of incoming perovskite building units and reduce the effective barrier for their incorporation, thereby promoting continued growth along the corresponding crystallographic direction. Alternatively, strong and persistent adsorption may occupy active surface sites and hinder the attachment of additional growth units, producing a blocking effect that increases the effective growth barrier.

The conceptual energy diagram in **figure B3.9** illustrates how these two effects can alter the competition between the (100) and (111) orientations. In the additive-free film, the effective barrier for the incorporation of new perovskite units is lower for the (100) direction than for the (111) direction. The intrinsic kinetic advantage of the (100) orientation therefore results in predominantly (100)-oriented growth. When molecular adsorption facilitates the incorporation of new growth units on the (100) surface, the effective barrier is further reduced, strengthening the intrinsic (100) preference. In contrast, when strongly anchored molecules block the available incorporation sites, the effective barrier for continued (100) growth is increased. Once this barrier approaches or exceeds that associated with the (111) direction, the relative growth advantage of the (100) orientation is weakened or reversed, leading to a larger proportion of (111)-oriented domains.

Thus, the final facet preference is determined by how a particular amine modifies the effective attachment barrier on the (100) surface. Molecules that interact dynamically or facilitate precursor incorporation preserve or enhance the intrinsic (100) growth tendency, whereas

molecules capable of stable multi-interaction anchoring suppress continued (100) growth and redirect crystallization toward the (111) orientation.

3.4 Summary

In summary, this chapter establishes a molecular-level framework for understanding amine-directed facet growth in perovskite films. By systematically comparing a broad range of amine additives, we show that facet preference cannot be predicted solely from the conventional classification of primary, secondary, and tertiary amines. Instead, it is governed by the adsorption configuration and combined surface interactions of each molecule. In addition to N–Pb coordination, secondary N–H $\cdots$ I hydrogen bonding can stabilize molecular adsorption and produce a multi-interaction anchoring effect. As illustrated in **Figure 3.3**, amines with suitable geometries can strongly and persistently anchor on the (100) surface, block the incorporation of new perovskite units, and suppress continued (100) growth, thereby redirecting crystallization toward the (111) orientation. In contrast, molecules dominated by weaker or single-point interactions undergo more dynamic adsorption and provide incomplete surface coverage, allowing the intrinsic (100)-oriented growth pathway to remain dominant. These findings provide a mechanistic basis for the rational design of molecular additives for facet-selective crystallization.

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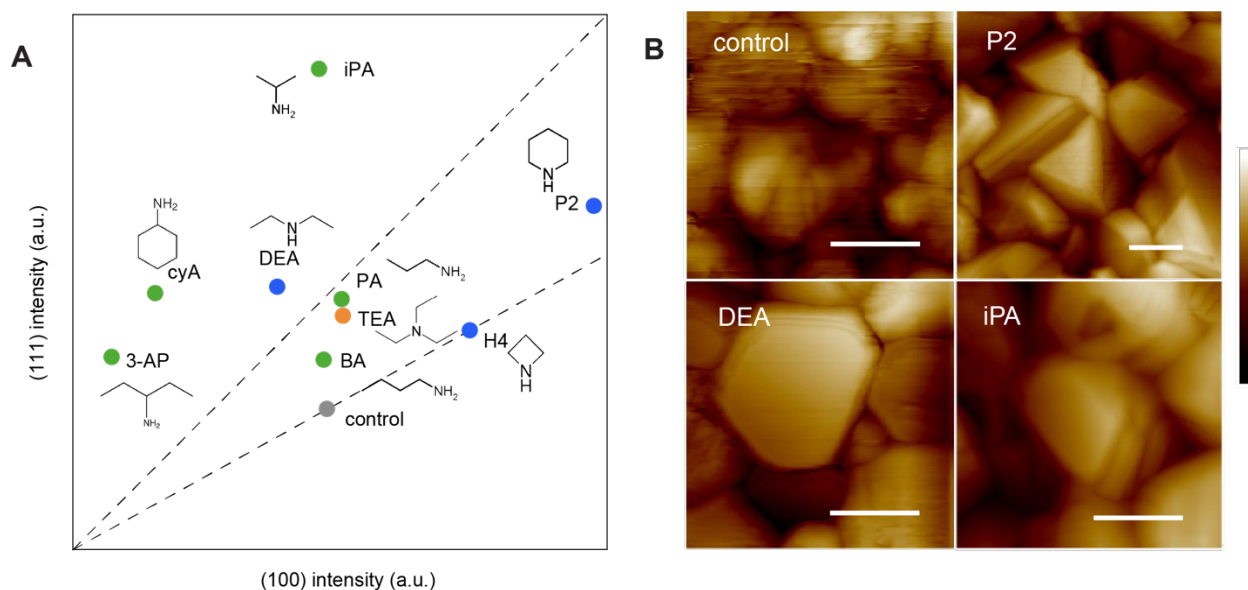


Figure 3.1. Facet preference and surface morphology of perovskite films treated with different amines. (A) Facet-preference map of the amines constructed from the relative XRD diffraction intensities of the (100) and (111) planes. Amines located toward the left preferentially promote the (111) facet, whereas those toward the right favor the (100) facet. Amines positioned near the control region exhibit weaker or more balanced facet selectivity. (B) AFM images of perovskite films prepared with different amines. The control film shows no clear facet preference based on its surface morphology. The P2-treated film displays features associated with both (100) and (111) facets, whereas the DEA- and iPA-treated films exhibit pronounced triangular grains characteristic of preferentially exposed (111) facets.

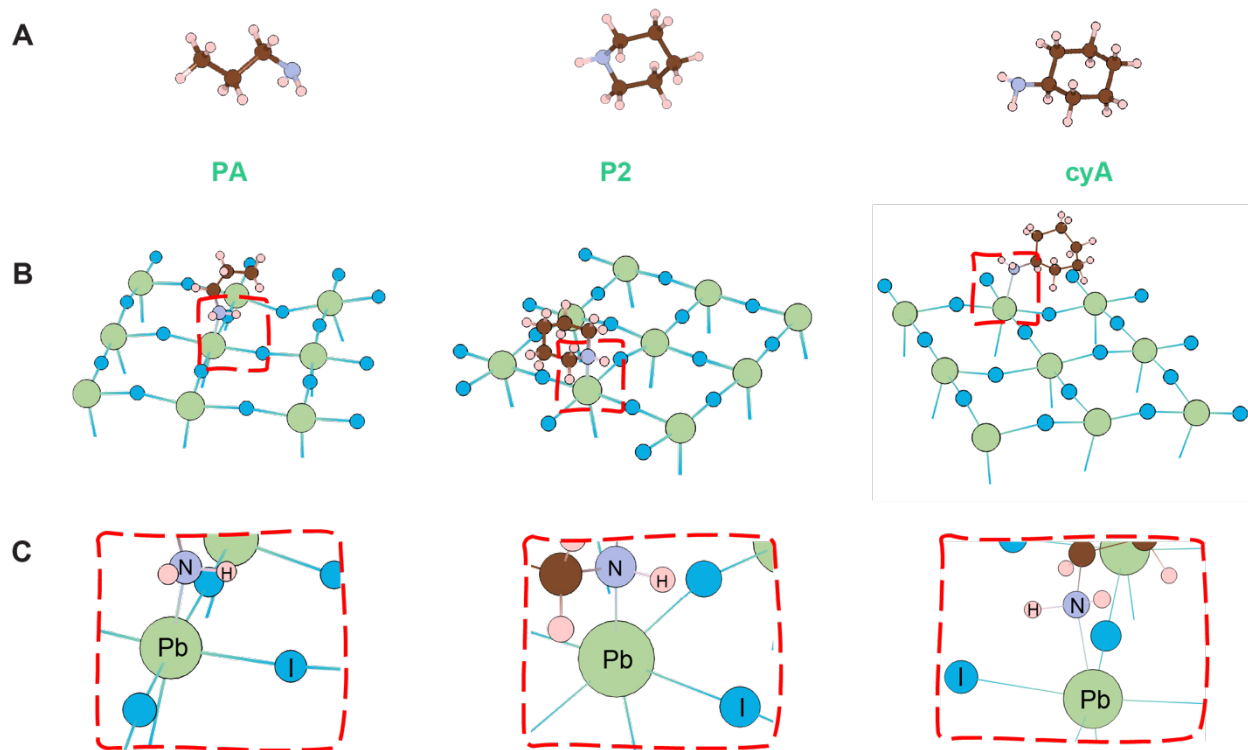


Figure 3.2. Molecular adsorption configurations of selected amines on the perovskite (100) facet. (A) Molecular structures of propylamine (PA), piperidine (P2), and cyclohexylamine (cyA). (B) Optimized adsorption configurations of the three amines on the perovskite (100) surface. (C) Enlarged views highlighting the local interactions between the amine groups and the surface Pb–I framework.

	PA	P2	cyA
E_a (eV)	-0.043	-0.046	-0.048
D_{N-Pb} (Å)	2.56	2.64	2.59
$D_{H...I}$ (Å)	3.35	3.00	3.09
N-H...I (°)	112	127	136

Table 0.1 Calculated adsorption energies and geometric parameters of PA, P2, and cyA on the perovskite (100) surface.

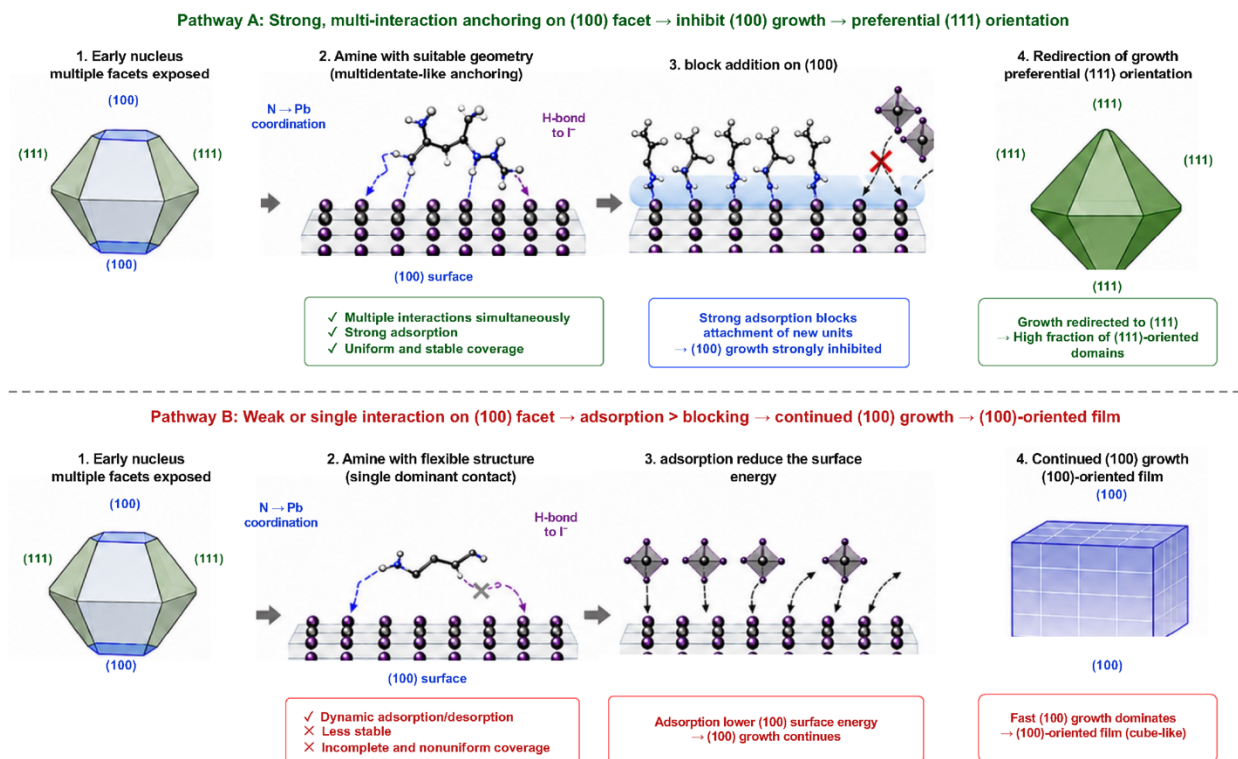


Figure 3.3. Proposed amine-mediated facet-selective growth mechanism of perovskite crystals. In pathway A, amines with suitable molecular geometry form multiple interactions with the perovskite (100) surface, including N–Pb coordination and hydrogen bonding with surface iodide. The resulting strong and stable adsorption suppresses further attachment of perovskite building units on the (100) facet, redirecting crystal growth toward the (111) direction and producing a higher fraction of (111)-oriented domains. In pathway B, flexible amines form weaker or less uniform interactions with the (100) surface. Their adsorption lowers the surface energy but does not effectively block continued growth, thereby favoring the formation of predominantly (100)-oriented, cube-like domains.

Chapter 4 Post-Nucleation Lattice Reconstruction

Halide perovskites possess a soft ionic lattice and complex crystallization chemistry, giving rise to a wide variety of imperfections with diverse spatial distributions that can limit device efficiency and operational stability¹⁻³. Substantial efforts have therefore been devoted to defect passivation in PSCs. In particular, surface and grain-boundary defects, which often introduce deep trap states, have been widely mitigated through chemical passivation and interface modification⁴⁻⁶, effectively reducing nonradiative recombination and improving device efficiency and stability. However, defects embedded within the crystalline bulk, including residual structural disorder and microstructural imperfections, remain much less accessible⁷⁻⁹. These persistent bulk defects are often associated with relatively shallow electronic states and can critically affect ion migration, lattice robustness, and operational stability^{10,11}. Nevertheless, compared with accessible surface and grain-boundary defects, buried shallow defects remain less systematically understood and more difficult to address.

The formation and spatial distribution of shallow defects are intimately coupled with the nucleation and growth dynamics of perovskite thin films, prompting extensive efforts to understand and regulate crystallization kinetics¹²⁻¹⁵. Such regulation is commonly achieved through the formation and evolution of intermediate phases, including solvent-coordinated complexes (DMSO- or NMP-based intermediates), crystalline intermediates, and amorphous alloy states¹⁶⁻²⁰. These intermediates typically form during solution deposition, and regulate crystallization pathways and film microstructure, but their structural signatures and regulatory roles gradually weaken as lattice formation proceeds during thermal annealing^{21,22}. After the initial lattice framework has formed, the film remains highly dynamic, undergoing continued ion

redistribution, grain growth, and structural relaxation throughout thermal annealing. During this stage, rapid phase transitions and solvent evaporation can still induce local lattice distortions, compositional heterogeneity, and shallow defect states²³⁻²⁵, which may become kinetically trapped within the crystalline framework. Such embedded defects are difficult to remove through strategies that mainly guide early-stage phase formation, underscoring the need for late-stage crystallization pathways that can access and heal defects within the formed lattice.

Herein, we introduce a secondary intermediate state in FAPbI₃ perovskites during the post-nucleation stage through a thermally activated re-alloying process. Rather than directing crystallization through early-stage low-dimensional intermediates, 3-APCl remains largely inactive during initial 3D lattice formation but becomes activated upon annealing, where it interacts with the pre-formed α -FAPbI₃ framework and triggers dynamic lattice dissolution followed by recrystallization. This delayed activation is enabled by the unique thermodynamic profile of 3-AP⁺, which suppresses low-dimensional phase formation while favoring high-temperature cation exchange with the 3D lattice. As a result, this process enables top-down ripening of the already formed lattice, opening a post-nucleation window for defect healing that suppresses otherwise persistent shallow defects and enhances lattice robustness. This lattice reorganization further improves optoelectronic homogeneity while reducing susceptibility to field-driven ionic redistribution. N-i-p devices enabled by this crystallization strategy deliver a champion PCE of 26.83%, while devices tested under operational aging retain ~86% of their initial efficiency after 1900 h at 85 °C. These findings extend crystallization control beyond early-stage phase formation to post-nucleation defect healing and lattice stabilization, while broadening the mechanistic understanding of intermediate-state engineering in high-efficiency perovskite solar cells.

4.1 In-situ monitoring of thermally activated re-alloying

Figure 4.1A schematically illustrates the thermally activated re-alloying pathway identified in this work. Conventionally, perovskite formation proceeds through precursor coordination that gives rise to intermediate phases during deposition, which subsequently transform into the final phase upon annealing²¹. However, this pathway confines intermediate-phase formation to the deposition stage, a restriction that is not fundamentally dictated by the thermodynamics and kinetics of material formation. In the pathway identified here, the additive initially associates with the perovskite surface without forming a detectable intermediate phase. Upon annealing, it becomes activated and interacts with the pre-formed lattice, inducing partial lattice dissolution and the formation of a secondary intermediate phase. The additive subsequently evaporates, while the lattice recrystallizes to yield the final film. This high-temperature interaction triggers a rapid dissolution–recrystallization process within the lattice, enabling defect relaxation through a post-nucleation lattice reconfiguration pathway that we term re-alloying.

To directly probe this process, 3-aminopentane hydrochloride (3-APCl, 10%) was introduced as the additive and compared with its structural isomers 1-APCl and 2-APCl, which possess identical alkyl chain lengths but differ in the position of the ammonium group along the alkyl backbone. The resulting films are denoted as control, 1-APCl, 2-APCl, and 3-APCl samples.

The crystallization dynamics and phase transitions were then tracked by in situ photoluminescence (PL) during spin-coating and subsequent annealing. Upon antisolvent dripping during spin-coating, the control and 3-APCl films exhibit PL emission near ~705 nm from their onset. In contrast, the 1-APCl film shows an initial peak at ~660 nm, characteristic of low-dimensional emission²⁶ (**figure. B4.1, B4.2**), while the 2-APCl film displays a weaker short-wavelength feature (~690 nm). All samples subsequently evolve toward the 3D perovskite

emission region (>750 nm). Upon annealing (**Figure. 4.1B**), PL emission at ~ 770 nm—characteristic of the 3D perovskite phase—emerges within 0.5 s in films containing additives, whereas the corresponding signal in the control film appears ~ 2 s later. As annealing proceeds, the PL evolution in the control and 1-APCl films remains continuous. In contrast, the 2-APCl and 3-APCl films exhibit a pronounced transient blueshift of the PL peak (~ 770 to ~ 760 nm at ~ 11 s), accompanied by substantial PL quenching (**Figure. 4.1C**, **figure. B4.3**). The PL intensity subsequently recovers within ~ 5 s, with the 3-APCl film recovering approximately 2 s later.

The PL response of the 2-APCl and 3-APCl films therefore indicates a thermally induced, rapid disruption of the emissive lattice, distinct from the 2D-intermediate-assisted pathway observed for 1-APCl. Notably, this reversible PL quenching occurs only after the 3D perovskite emission has already formed, demonstrating that the pre-formed perovskite lattice undergoes an additional transformation that is not involved in the conventionally assumed crystallization pathway^{27,28}.

To examine whether these optical behaviors are accompanied by corresponding structural changes, the temperature-dependent evolution of the films was investigated by X-ray diffraction (XRD) (**Figure. 4.1D**). Films containing 10% additive were annealed for 10 min at temperatures ranging from 40 to 120 °C. At room temperature (25 °C), all films exhibit two distinct diffraction peaks at 11.7° and 14.1° , corresponding to the δ -phase and α -phase of FAPbI₃, respectively. As annealing proceeds, the δ -phase gradually diminishes, indicating phase conversion toward the photoactive α -phase. The control film shows relatively weak α -FAPbI₃ diffraction intensity throughout the annealing process, with residual δ -phase features persisting even at 100 °C, suggesting incomplete phase conversion. In contrast, all additive-containing films exhibit stronger α -FAPbI₃ diffraction intensity from the early stages of annealing.

Among them, the 1-APCl film displays a pronounced low-dimensional (2D) diffraction peak at 13.2° over a broad temperature range from 50 to 110°C , which disappears at 120°C , consistent with the presence of a stable layered intermediate during annealing²¹. In contrast, no discernible 2D diffraction peaks are observed in either the 2-APCl or 3-APCl films across the entire annealing temperature range, implying the absence of such an intermediate and pointing to a distinct crystallization pathway from that observed in the 1-APCl system.

With increasing temperature, both the 2-APCl and 3-APCl films exhibit a slight shift of the α -FAPbI₃ diffraction peak from 14.07° to 14.01° , indicative of lattice expansion, potentially arising from partial cation incorporation or mixing within the lattice. In the 3-APCl samples, however, the established α -FAPbI₃ diffraction intensity shows a pronounced reduction between 70 and 110°C , followed by recovery at 120°C (**Figure. 4.1E**). In contrast, all other samples exhibit a monotonic increase in diffraction intensity, reflecting enhanced crystallinity during annealing. Notably, the intensity reduction and peak shift in 3-APCl are not accompanied by the emergence of any additional crystalline phase. These observations suggest a thermally activated dissolution and lattice reconfiguration within the pre-formed α -FAPbI₃ framework in the 3-APCl system, likely induced by 3-AP⁺/FA⁺ cation exchange, consistent with the transient PL blueshift and quenching during annealing, indicating a dissolution–recrystallization process.

To evaluate whether differences in additive volatility could account for the distinct crystallization behaviors, temperature-dependent nuclear magnetic resonance (NMR) measurements were performed on perovskite films containing 1-APCl, 2-APCl, or 3-APCl (**figure. B4.4**). Characteristic resonance peaks of the organic cations are clearly observed after annealing at 40 and 80°C , whereas no discernible signals remain at 120°C , indicating complete additive removal at this temperature. Quantitative integration reveals that approximately 94%, 80%, and

80% of 1-AP⁺, 2-AP⁺, and 3-AP⁺, respectively, remain in the films after annealing at 80 °C. Consistent trends are independently confirmed by thermogravimetric analysis (TGA) of the corresponding ammonium chlorides (**figure. B4.5**). Despite its greater thermal retention, the 1-APCl does not exhibit the transient lattice perturbation observed for the 3-APCl system. This comparison rules out additive volatility as the primary origin of the distinct crystallization behaviors, instead implicating intrinsic differences in the energy landscape of lattice–molecule interactions.

4.2 Structural and thermodynamic origins of re-alloyed intermediate via DFT calculation

Additives can influence intermediate formation and the crystallization pathway through distinct interactions with the Pb–I framework and the pre-formed 3D perovskite lattice. To clarify the origin of these behaviors, we systematically examined and calculated the intrinsic interactions of 1-AP⁺, 2-AP⁺, and 3-AP⁺ with both structural environments. Their ability to form low-dimensional phases was experimentally evaluated using XRD and UV–vis. Films were prepared by spin-coating and annealed at 150 °C with varying ratios of ammonium iodide (1-API, 2-API or 3-API) to PbI₂ in the precursor solution. For *n* = 1 stoichiometry (PbI₂: ammonium iodide = 1:2) (**Figure. 4.2A**), 1-AP⁺ forms a pure *n* = 1 2D perovskite, evidenced by well-resolved (0*k*0) reflections at $2\theta = 5.52^\circ$, 11.5° , and 17.5° ²⁶. In contrast, films prepared with 2-AP⁺ exhibit a dominant diffraction peak at 8.3° , characteristic of *n* = 2 phases²⁶, together with residual PbI₂, indicating an inability to stabilize *n* = 1 structures despite an identical precursor composition. For 3-AP⁺, only a weak and poorly resolved feature near 8.3° is observed, suggesting a minimal propensity to form ordered low-dimensional phases.

When extended to *n* = 2 Ruddlesden–Popper (RP) compositions (FAI: PbI₂: ammonium iodide = 1:2:2) (**Figure. 4.2B**), distinct layered *n* = 2 phases readily form for both 1-AP⁺ and 2-

AP⁺. By comparison, such phases are absent in the 3-AP⁺ system, which instead yields diffraction patterns dominated by the three-dimensional α -FAPbI₃ phase. Consistently, UV–vis absorption spectra (**figure. B4.6**) show pronounced low-dimensional excitonic features for 1-AP⁺, reduced contributions for 2-AP⁺, and exclusively 3D absorption characteristics for 3-AP⁺.

Thus, the intrinsic ability of AP cations to stabilize low-n layered phases is progressively suppressed as the ammonium group shifts from a terminal to a more internally constrained position along the alkyl backbone. This trend provides a structural basis for the emergence of low-dimensional intermediates in the 1-APCl film during spin-coating, and their absence in the 3-APCl film, as observed in the in-situ PL observations.

To further probe the interaction between 3-AP⁺ and pre-formed cubic lattice at elevated temperature, perovskite films incorporating increasing amounts of 3-APCl (0%, 1%, 3%, 5%, and 10%) were annealed at 90 °C and characterized by XRD (**Figure. 4.2C**). With increasing 3-APCl content, the main 3D diffraction peaks systematically shift toward lower angles, indicating lattice expansion and relaxation. This behavior is consistent with thermally activated incorporation and in-situ alloying of 3-AP⁺ into the α -FAPbI₃ lattice, in contrast to its inability to stabilize low-dimensional phases at lower temperature.

Density functional theory (DFT) calculations were further performed to clarify the distinct interaction behaviors of the three AP cations. As shown in **Figure. 4.2D**, differences in ammonium-group position lead to distinct molecular electrostatic potential distributions, providing an energetic basis for their interactions with the Pb–I framework during crystallization. The calculated $n = 1$ formation energy is most negative for 1-AP⁺ and becomes progressively less favorable toward 3-AP⁺ (**Figure. 4.2E, figure. B4.7**), indicating that 1-AP⁺ more strongly stabilizes low-n layered configurations. In contrast, the surface interaction energy with α -FAPbI₃ becomes

increasingly negative from 1-AP⁺ to 3-AP⁺ (**figure. B4.8**), indicating stronger additive–surface association for 3-AP⁺. Consequently, 1-AP⁺ preferentially stabilizes ordered low-dimensional intermediates during deposition, whereas 3-AP suppresses layered formation while strongly associating with the α -phase surface, facilitating early establishment of the photoactive 3D framework. 2-AP⁺ exhibits intermediate energetics in both layered stabilization and surface binding. In line with the absence of 2D diffraction features, its behavior is more consistent with a surface-associated role at this stage.

We further calculated the Gibbs free energy change associated with substitution of FA⁺ by 1-AP⁺, 2-AP⁺ and 3-AP⁺ within α -FAPbI₃ as a function of temperature (**Figure. 4.2D, 4.2F**). This substitution remains thermodynamically less favorable for 2-AP⁺ across 20–120 °C ($\Delta G > 0$), indicating its predominantly surface-associated behavior. In contrast, substitution becomes favorable for 1-AP⁺ and 3-AP⁺ above ~80 °C ($\Delta G < 0$). This is consistent with the experimental observations in 3-APCl samples, initially surface-associated, incorporates into the lattice upon annealing, enabling post-nucleation lattice reconstruction within the pre-formed α -FAPbI₃ framework. However, such incorporation is not observed for 1-AP⁺ despite being thermodynamically favorable, likely due to kinetic trapping within layered intermediates formed at early stages, which limits its subsequent incorporation into the 3D lattice.

These results suggest that the high-temperature re-alloying behavior of 3-AP⁺ arises from the combined effects of suppressed 2D intermediate formation at room temperature and thermodynamically favorable cation exchange at elevated temperatures. In the absence of stable low-dimensional phases, 3-AP⁺ remains inactive during early-stage crystallization but becomes activated upon annealing, enabling its incorporation into the pre-formed lattice. This precise thermodynamic threshold unlocks the delayed re-alloying pathway and drives recrystallization.

4.3 Re-alloying-mediated film recrystallization and structural reconfiguration

We next examined the resulting film characteristics to understand the impact of re-alloying. Slow-scan XRD measurements were performed to probe the structural characteristics of the final perovskite films (**figure. B4.9**). Compared with the control and 1-APCl films, the α -FAPbI₃ diffraction peak in the 2-APCl and 3-APCl samples shifts slightly toward lower angles ($\sim 13.89^\circ$ versus 14.05°), suggesting lattice expansion associated with partial incorporation of 2-AP⁺ and 3-AP⁺. X-ray photoelectron spectroscopy (XPS) measurements (**figure. B4.10**) show negligible Cl 2p signals for all samples, indicating the complete removal of Cl⁻ after annealing. Together, these results suggest that Cl⁻ is removed as volatile species, likely FAPbCl or MAPbCl, during annealing, while a minor fraction of 2-AP⁺ and 3-AP⁺ remains incorporated in the lattice through cation exchange. The absence of comparable retention for 1-AP⁺ is consistent with its preferential stabilization of low-dimensional intermediates during early-stage crystallization, which prevents efficient incorporation into the final 3D lattice. Consistent with this re-alloying-mediated pathway, scanning electron microscopy (SEM) images reveal a clear increase in grain size from $\sim 1\ \mu\text{m}$ to $\sim 2\ \mu\text{m}$ upon the introduction of 3-APCl (**figure. B4.11**).

To further elucidate the microstructural ordering, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed (**figure. B4.12**). The diffraction intensity of the (100) facet ($q \approx 1.0\ \text{\AA}^{-1}$) was traced along the azimuthal direction at three incident angles (0.10° , 0.14° , and 0.20°), enabling depth-dependent structural analysis²⁹ (**Figure. 4.3A**). The 3-APCl film exhibits a pronounced depth-dependent orientation evolution. At an incident angle of 0.20° , two orientation features centered at approximately 35° and 90° are observed. As the incident angle decreases, corresponding to a shallower probing depth, the 90° -oriented population progressively diminishes, while the $\sim 35^\circ$ feature becomes dominant at 0.10° , where the

measurement more strongly reflects the near-surface region. The 2-APCl film shows a similar but weaker depth-dependent trend, with the 35° and 90° features remaining comparable at 0.10° . In contrast, the control and 1-APCl films exhibit a consistently dominant 90° orientation across all incident angles. It has been reported that MA^+ incorporation thermodynamically favors the lattice configuration associated with the 90° azimuthal feature, whereas the pure FA-based lattice preferentially exhibits the $\sim 35^\circ$ feature³⁰. Therefore, we speculate that the dominant 90° orientation in the control, 1-APCl, and 2-APCl films primarily originates from MACl-assisted templated growth during precursor crystallization³¹. A similar templating effect is also present in the deeper region of the 3-APCl film, as evidenced by the dominant 90° feature at 0.20° . However, the emergence of the near-surface-dominant $\sim 35^\circ$ feature suggests that 3-APCl further drives the pre-formed lattice toward a more thermodynamically favored FA-based configuration, pointing to a unique 3-AP-mediated top-down recrystallization and ripening process. This orientation evolution is distinct from conventional template-directed crystallization through early-stage intermediates.

The steady-state PL intensity of the 3-APCl film is notably higher than that of the other samples (**figure. B4.13**), indicating suppressed non-radiative recombination arising from improved crystal quality via re-alloying. PL mapping over $40\ \mu\text{m} \times 40\ \mu\text{m}$ regions (**Figure. 4.3B**) reveals weak emission in the control film and strong spatial variations in the 1-APCl and 2-APCl films. In contrast, the 3-APCl film shows both stronger emission and markedly reduced spatial variation, indicating a more uniform composition and phase distribution. Time-resolved PL (TRPL) measurements further corroborate this trend, showing a prolonged carrier lifetime in the 3-APCl film (**Figure. 4.3C**).

We further investigated field-induced ion migration by monitoring the PL response of the perovskite films under an applied electric field³². Lateral perovskite devices with a structure of

Au/perovskite (100 μm)/Au were used, across which a constant bias of 20 V was applied while tracking the temporal evolution of the PL. A sequence of PL images recorded over time (**Figure. 4.3D**) reveals pronounced PL quenching in the control and 1-APCl films, which initiates near the electrode and progressively propagates across the channel region. The emission intensity decreases continuously, accompanied by the development of a pronounced spatial gradient, indicative of the destroyed stoichiometry and/or structure of the crystals due to migration of charged defects. In contrast, the 2-APCl and 3-APCl films exhibit minimal changes in both PL intensity and spatial distribution throughout the measurement, with no evident propagation of quenching fronts, indicating strongly suppressed ion migration.

To evaluate the structural stability of perovskite during aging, we monitored the phase evolution by XRD. Perovskite films were subjected to illumination stability testing at 55 °C, and their structural evolution was tracked by XRD (**Figure. 4.3E and figure. B4.14**). During the first 200 h, the intensity of the perovskite (100) diffraction peak in the control film decreases markedly, indicating rapid structural degradation. A similar decrease is observed in the 1-APCl and 2-APCl films after approximately 500 h. In contrast, the diffraction peak of the 3-APCl film remains nearly unchanged over 1200 h, indicating substantially improved structural stability enabled by the re-alloying crystallization pathway. Notably, the 2-APCl film shows a decrease in the PbI_2 peak intensity during the initial 100 h accompanied by an increase in the perovskite (001) peak intensity, suggesting continued reaction between residual PbI_2 and FAI species. The PbI_2 and $\sigma\text{-FAPbI}_3$ phases emerge in the control film after ~ 500 h of aging, suggesting the onset of phase degradation.

4.4 Suppressed shallow defects and efficient and stable devices

We then fabricated perovskite solar cells with the architecture $\text{FTO}/\text{SnO}_2/\text{FAPbI}_3/\text{spiro-OMeTAD}/\text{Au}$. The optimized 3-APCl devices exhibited improved photovoltaic performance

compared with the other samples. The best-performing 3-APCl device (0.0735 cm²) achieved a PCE of 26.83%, with a J_{SC} of 26.27 mA cm⁻², a V_{OC} of 1.206 V, and a fill factor (FF) of 84.71% (**Figure. 4.4A, Table. C4.1**). A stabilized power output of 26.6% at 1.06 V was obtained (**Figure. 4.4B**). By comparison, the best PCEs of the control, 1-APCl, and 2-APCl devices were 25.93%, 25.31%, and 26.09%, respectively (**table. C4.1**). Statistical analysis of 100 devices shows that the 3-APCl devices achieve an average PCE of 25.85%, compared with 25.28% for the control devices (**figure. B4.15**). Representative 3-APCl devices further exhibit negligible hysteresis (**figure. B4.16**) and EQE-integrated J_{SC} values consistent with the J–V measurements (**figure. B4.17**). The improved efficiency primarily arises from enhancements in V_{OC} and FF, which can be attributed to reduced defect density and improved carrier transport. To examine the generality of this strategy, we further applied the same approach to p-i-n structured devices (FTO/SAM/FAPbI₃/C60/BCP/Ag). A similar efficiency improvement was observed, with the PCE increasing from 25.56% for the control devices to 26.58% for the 3-APCl devices (**figure. B4.18, table. C4.2**).

To examine the effect of the re-alloying process on defect states in the perovskite absorber, we performed temperature-dependent admittance spectroscopy (TAS) and Mott–Schottky analyses³³. TAS measurements were conducted on the control, 1-APCl, 2-APCl, and 3-APCl devices over the temperature range of 210–300 K under dark conditions (**figure. B4.19**). The defect activation energies (E_a) were extracted as 0.187 eV for the control, 0.174 eV for 1-APCl, 0.121 eV for 2-APCl, and 0.127 eV for 3-APCl, respectively (**Figure. 4.4C**). The substantially reduced E_a values of the 2-APCl and 3-APCl devices indicate that the involvement of 2-AP⁺ and 3-AP⁺ during annealing shifts trap states toward shallower energy levels. The trap density-of-states (tDOS) distribution was further derived using $NT(E\omega) = -\omega V_{bi}/(qkTW) \times dC/d\omega$ and $E\omega = kT \ln(\beta T^2/\omega)$,

where q is the elementary charge, ω is the angular frequency, V_{bi} is the built-in potential, and W is the depletion width. The values of V_{bi} and W were obtained from Mott–Schottky analysis (**figure. B4.20**). Consistent with the E_a trend, the 2-APCl and 3-APCl devices exhibit an overall shallower tDOS distribution than the control and 1-APCl devices, indicating suppressed formation of deep-level trap states (**Figure. 4.4D**). Notably, although the 2-APCl and 3-APCl devices show nearly overlapping trap distributions above 0.125 eV, the 3-APCl device exhibits a pronounced reduction in trap density below 0.125 eV. This effective healing of shallow-level defects decreases the tDOS from 12.5×10^{16} to $8 \times 10^{16} \text{ cm}^{-3} \text{ eV}^{-1}$. These results highlight the broader defect-healing capability of the re-alloying mechanism, particularly in suppressing shallow defects that are less accessible through conventional crystal-growth control.

Operational stability of the PSCs was first evaluated by maximum power point (MPP) tracking under continuous 1 sun illumination at 55 °C (**Figure. 4.4E**). To ensure thermal stability of the hole transport layer, spiro-OMeTAD was replaced with the oxidized Spiro-OMeTAD ($\text{Spiro}^{2+}(\text{TFSI})_2$)³⁴. The control devices retained only ~60% of their initial efficiency after 2,209 h, whereas the 3-APCl devices maintained ~90% of their initial efficiency over the same period. We further evaluated device stability under harsher conditions of 1 sun illumination at 85 °C (**Figure. 4.4F**). The PCE of the control devices decreased by 45% after 1900 h, whereas the 3-APCl devices retained 86% of their initial efficiency after 1,909 h. The enhanced thermal stability is consistent with the improved lattice robustness and suppressed ion migration enabled by the re-alloying crystallization pathway. Notably, the 1-APCl devices show the poorest stability under both conditions.

4.5 Conclusion

Overall, we identify a thermodynamically driven re-alloying crystallization pathway that enables post-nucleation lattice reconstruction in FAPbI₃ perovskites. Unlike conventional additive strategies that mainly regulate early-stage nucleation, the temperature-dependent favorability of additive incorporation into the established 3D lattice drives lattice dissolution and recrystallization within the pre-formed α -phase framework during annealing. The resulting top-down ripening heals persistent shallow defects and suppresses ion migration, thereby improving lattice robustness and device operational stability. These findings establish post-nucleation crystallization as a critical stage for defect suppression in halide perovskites, offering a strategy beyond conventional nucleation control and surface passivation.

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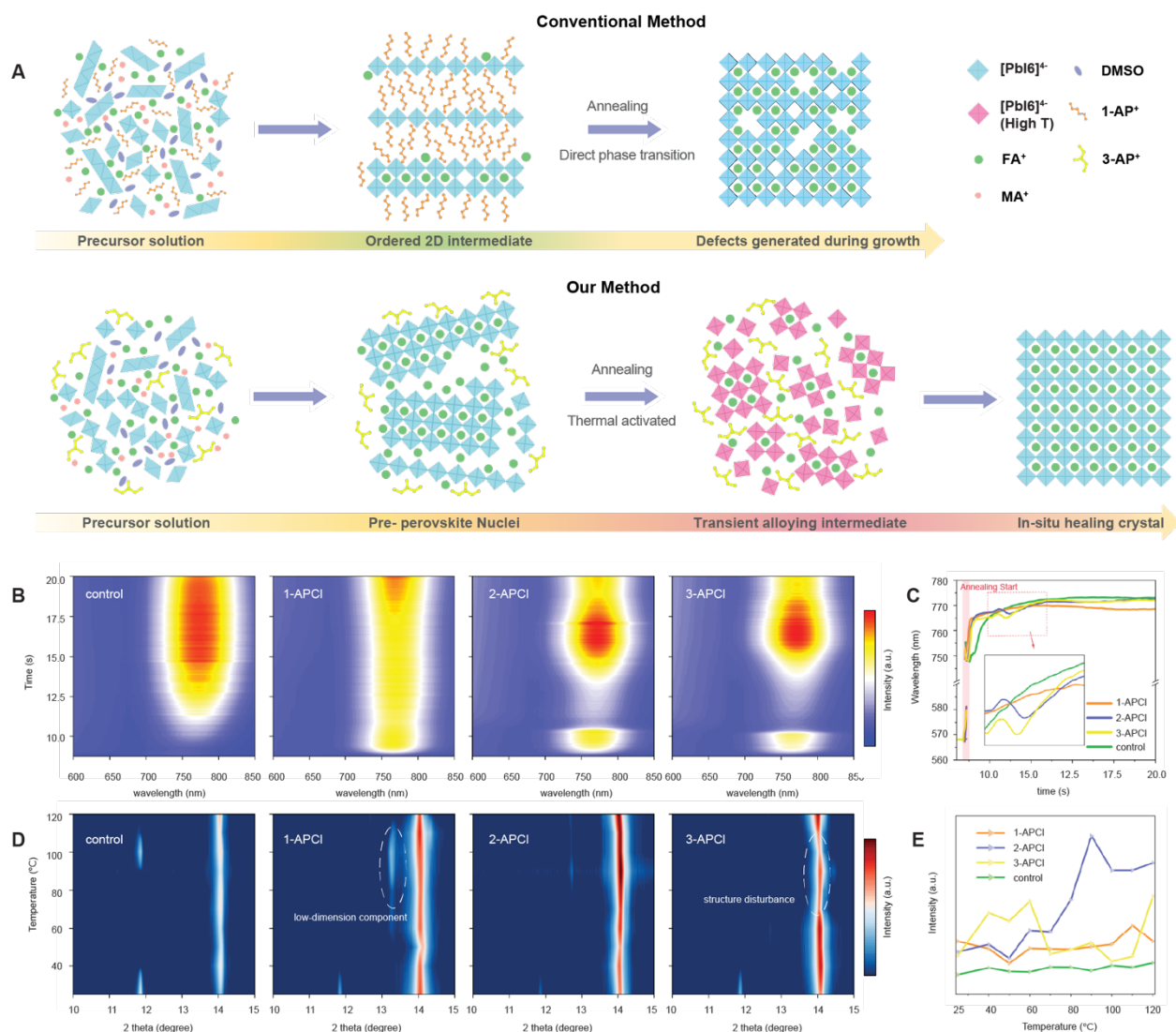


Figure 4.1. High-temperature re-alloying mechanism and experimental verification. (A)

Schematic comparison between conventional intermediate-assisted crystallization and thermally activated re-alloying. (B) In situ PL spectra of perovskite films with and without additives during thermal annealing. (C) Temporal evolution of the 3D emissive PL peak position during annealing; clear blue shifts are observed in the 2-APCI and 3-APCI samples. (D) Temperature-resolved XRD patterns of perovskite films during annealing. (E) α -phase diffraction intensity as a function of annealing temperature; a decrease is observed in the 3-APCI sample between 70–110 °C.

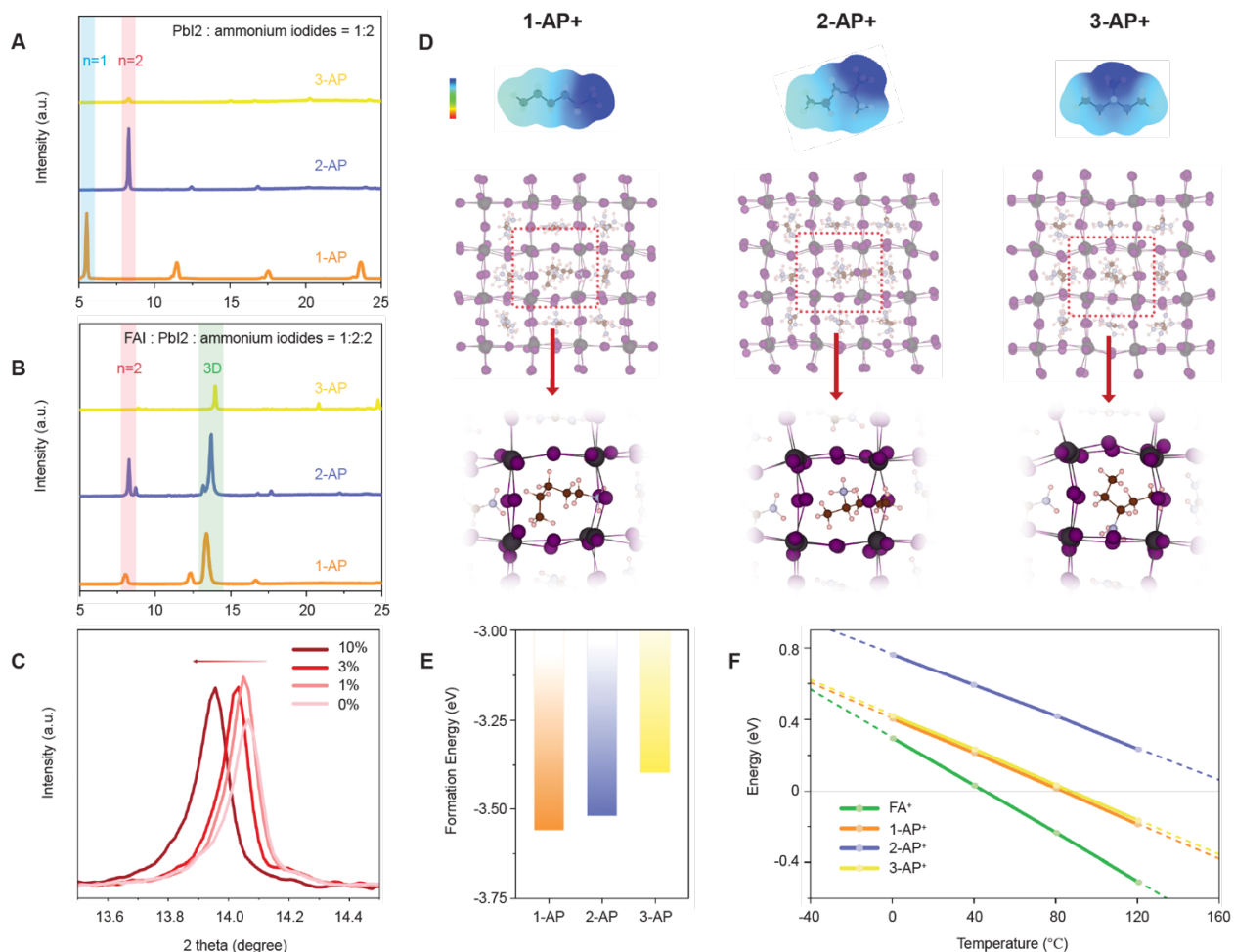


Figure 4.2. Structural preference and energetic origins of distinct crystallization behaviors among AP cations. (A, B) XRD patterns of films prepared with three ammonium cations at $n = 1$ and $n = 2$ stoichiometries, showing a reduced tendency of 3-APCl to form low-dimensional structures. (C) XRD patterns of films containing different amounts of 3-APCl; diffraction peaks shift toward lower angles with increasing 3-APCl content. (D) Calculated electrostatic potential distributions of 1-AP⁺, 2-AP⁺, and 3-AP⁺ and their optimized configurations after substitutional incorporation into the α -FAPbI₃ lattice. (E) Calculated formation energies of $n = 1$ 2D perovskites with different cations. (F) Temperature-dependent Gibbs free energies for FA⁺ substitution by different AP⁺ cations in α -FAPbI₃.

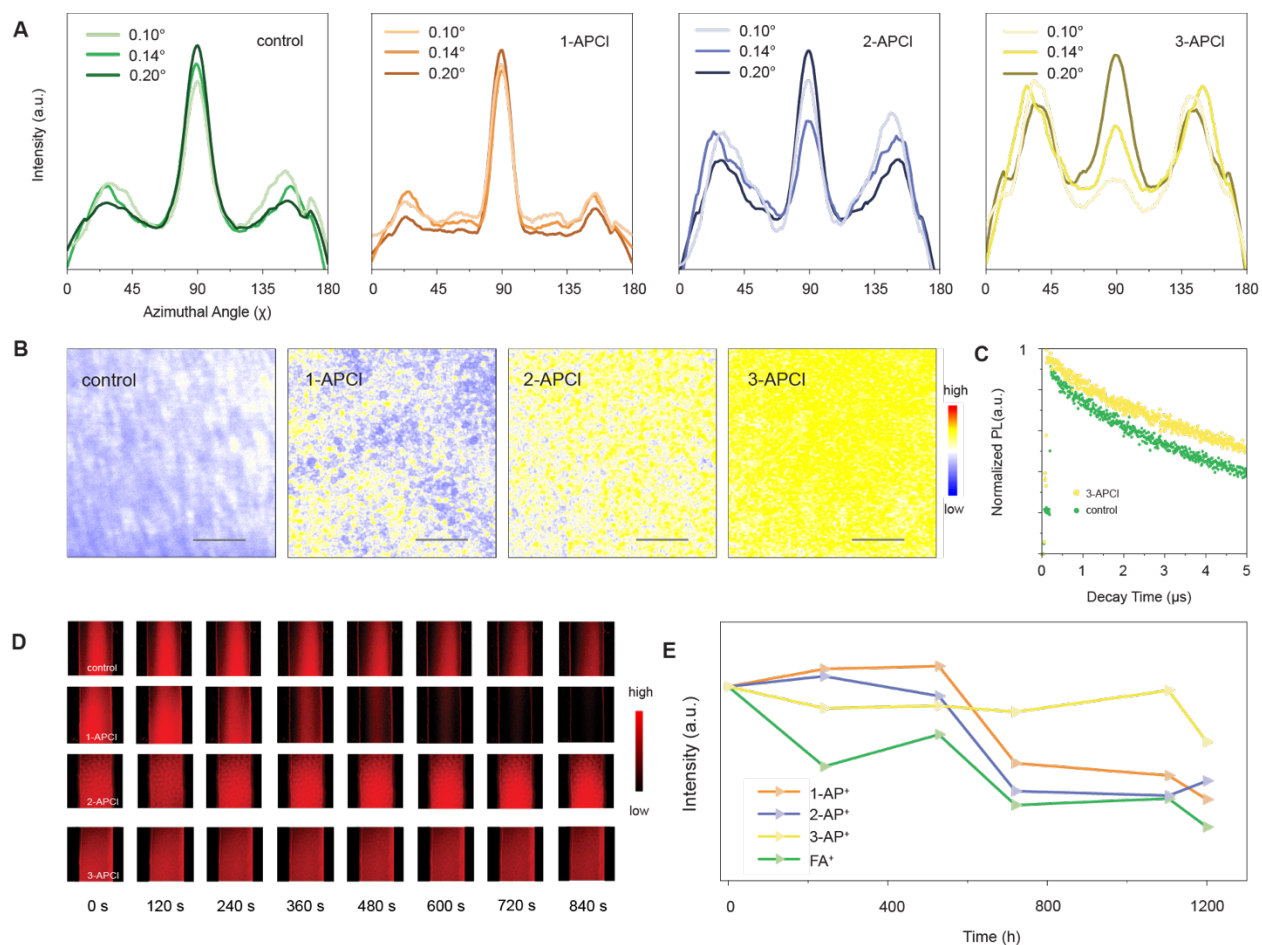


Figure 4.3. Re-alloying suppresses defects and ion migration in perovskite films. (A) Azimuthal distribution of the (100) GIWAXS diffraction at different incident angles, probing different depths from the surface to the bulk. (B) PL intensity mapping (40 $\mu\text{m} \times 40 \mu\text{m}$; scale bar, 10 μm). (C) TRPL decay curves. (D) Time-resolved PL images under a constant in-plane bias (0.2 V μm^{-1}). (E) Evolution of the perovskite (100) peak intensity during aging under 1 sun at 55 °C.

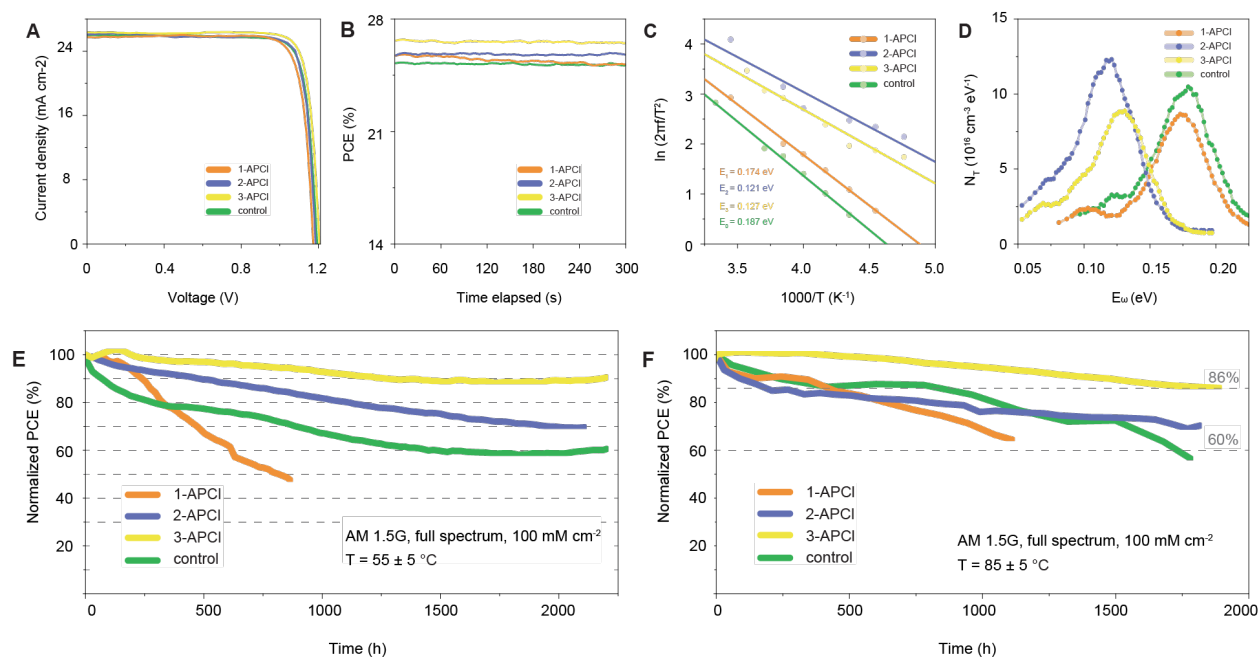


Figure 4.4. 3-APCI-enabled re-alloying reduces defect density and enhances operational stability. (A) Reverse J–V characteristics of FAPbI₃-based n–i–p solar cells with 3-APCI. (B) Stabilized power output and corresponding PCE tracking under continuous illumination. (C) Arrhenius plots (obtained by linear fitting of data points) of the characteristic transition frequencies determined from the derivative of the admittance spectra. (D) Trap state density (NT) of the perovskite solar devices. (E, F) Evolution of the normalized power output of encapsulated devices during maximum power point (MPP) tracking under continuous illumination (AM 1.5G, full spectrum, 100 mW cm⁻²) at 55 ± 5 °C (E) and 85 °C (F).

Appendix A

Materials synthesis

1-APCl powder was synthesized by reacting 30 mL of hydrochloric acid with 0.15 mol of amylamine in an ice bath for 2 h. The solvent was then evaporated at 60 °C using a rotary evaporator until powders were formed. The white powders were washed and recrystallized with ether three times and dried under vacuum for 2 days. The same procedure was used for the synthesis of 2-APCl and 3-APCl powders. FAPbI₃ single crystals were prepared by reacting 1 M FAI and 1 M PbI₂ in γ -butyrolactone at 150 °C for 3 h. The black perovskite crystals were washed sequentially with acetonitrile and ether, followed by drying at 150 °C for 30 min.

n-i-p Solar cell device fabrication

The FTO substrates were cleaned sequentially with ultrapure water, acetone, ethanol, and isopropanol. For highly efficient PSCs, SnO₂ was deposited by chemical bath deposition following a previously reported method¹ and annealed at 150 °C for 60 min in air. A 20 mM KCl aqueous solution was spin-coated onto the SnO₂ layer before perovskite deposition. Perovskite precursor solutions were prepared by mixing 1.5 M synthesized FAPbI₃ single crystals, 0.045 M MAPbBr₃, 0.3 M MAcl, and 0.075 M CsCl in a mixed solvent of DMF and DMSO with a volume ratio of 8:1. For different samples, 2 mol% 1-APCl, 2-APCl, or 3-APCl was added to the perovskite precursor solution. The perovskite layers were prepared by spin-coating with a two-step program of 1000 rpm for 5 s and 5000 rpm for 20 s. Diethyl ether (1 mL) was dropped onto the spinning substrate 10 s before the end of the spin-coating process. The perovskite films were then annealed at 120 °C for 1 h. A Spiro-OMeTAD layer was prepared by spin-coating 20 μ L of a solution containing 90 mg Spiro-OMeTAD in 1 mL chlorobenzene, with 35.5 μ L 4-tert-butylpyridine and

23 μL Li-TFSI solution added. The Li-TFSI solution was prepared by dissolving 540 mg Li-TFSI in 1 mL acetonitrile. The Spiro-OMeTAD solution was spin-coated at 3000 rpm for 20 s. A passivation layer was then deposited by spin-coating 2 mg HABr in 1 mL IPA. The device was completed by thermal evaporation of an 80 nm Au electrode under vacuum. The complete devices were stored in dry air for 2 days before testing. For the stability test, tBP and Li-TFSI were removed from the Spiro-OMeTAD layer, and 6 mg spiro(TFSI)₂ and 5 mg PTAA were added to 1 mL of the HTM solution. Devices used for stability tests were encapsulated with UV-curable epoxy and a glass coverslip.

p-i-n solar cell device fabrication

The FTO was cleaned similar to n-i-p solar cell. The cleaned FTO was treated by UV-oxygen for 15 min before use. NiO_x (10 mg/mL in water) was spin-coated at 3,000 r.p.m. and annealed at 100 °C for 20 min. SAM (MeO-4PACz 0.33 mg/mL and 2PACz 0.17 mg/mL in ethanol) was then spin-coated at 3,000 r.p.m. and annealed at 100 °C for 5 min. The perovskite precursor was prepared by dissolving 1.73 M (Cs_{0.05}FA_{0.95})_{0.98}MA_{0.02}Pb(I_{0.98}Br_{0.02})₃ with 5% PbI₂ excess and 0.27 M MACl in DMF/DMSO (5:1, v/v). The above precursor was spin-coated on SAM at 1,000 r.p.m. for 10 s and 5,000 r.p.m. for 40 s. 200 μL of chlorobenzene was used to wash the film 10 s before the end. The film was then annealed at 110 °C for 20 min. The PCBM (25 mg mL⁻¹ in chlorobenzene) solution was spin-coated at 3,000 r.p.m. for 30 s followed by annealing at 70 °C for 10 min. The BCP (1 mg mL⁻¹ in ethanol) solution was spin-coated at 5,000 r.p.m. and annealed at 70 °C for 10 min. The device was finished by thermal evaporation of Ag (150 nm) under vacuum.

Basic Material Characterization

The J–V curves of the solar cells were measured with a Keithley 2401 source meter under simulated one-sun illumination (SS-C10-3A, Enlitech) with AM 1.5G spectra. The intensity was

calibrated using a certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mW cm^{-2} . Solar cell measurements were performed in an ambient atmosphere. J–V characterizations were conducted from -0.1 V to 1.22 V at a scan rate of 0.1 V s^{-1} using a mask with an area of 0.0735 cm^2 . In-situ PL spectra were recorded using a commercial dynamic spectrometer system (Du-100, Puguangweishi Co., Ltd.) in a nitrogen-filled glovebox. X-ray diffraction (XRD) patterns were collected with a PANalytical diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Standard scans were performed at a scan rate of 4° min^{-1} , while slow scans were performed at $0.45^\circ \text{ min}^{-1}$. Ultraviolet–visible absorption spectra were obtained using a HITACHI U-4100 spectrophotometer. SEM images were collected using a Nova Nano 230 system. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical AXIS Ultra DLD system with a monochromatic $\text{Al K}\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$) as the excitation source. Nuclear magnetic resonance (NMR) spectra were collected using a Bruker AVANCE 400 MHz spectrometer. Thermogravimetric analysis (TGA) was performed using a PerkinElmer TGA 8000 system. Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) was performed at beamline 7.3.3 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. Steady-state photoluminescence (PL) spectra were acquired using a Horiba Jobin Yvon system with a 532 nm monochromatic laser for excitation. Time-resolved PL (TRPL) decay spectra were measured using a time-correlated single-photon counting (TCSPC) system (PicoHarp 300) with a pulsed laser driver (PLD 800B, PicoQuant) operating at a 100 kHz repetition frequency. PL mapping was performed using a Leica TCS SP8 MP DIVE FLIM confocal imaging system. Electrochemical impedance spectroscopy (EIS) and Mott–Schottky (M–S) measurements were performed using a precision LCR meter (Agilent 4980A). EQE test was performed on an integrated system QE-R3018 (Enlitech, Taiwan). Stability tests were performed using a Fluxim Litos Lite system.

Computational methodology

ESP calculations. Gas phase geometries and electrostatic potential (ESP) calculations were performed using the wB97-XD/6-31G(d,p) methodology implemented in Gaussian09².

Bulk and slab calculation method. For periodic bulk and slab calculations, we employed first-principles calculations using density functional theory (DFT) based on plane-wave basis set and the projected augmented wave method, as implemented in the VASP package^{3,4}. We used the PBE functional to describe the exchange-correlation functionals. A cut-off energy of 400 eV for the plane-wave basis sets and 4×4×2 for gamma-centered k-mesh are used for the self-consistent field calculations and geometry optimizations. Threshold values of 10⁻⁵ eV and 0.01 eV/Å were used for electron self-consistent field energies and geometry optimizations, respectively.

Free energy of formation. We calculated the n=1 2D perovskite formation energies via

$$\Delta H = H_{RPbI_4} - (H_R + 2H_{I_2} + H_{Pb})$$

where H_{RPbI_4} is the energy of the bulk n=1 2D perovskite, H_R , H_{I_2} and H_{Pb} is the energy of the molecule only, elemental iodine in the orthorhombic phase and fcc lead crystal, respectively.

Surface interactions. For surface interaction calculations, we constructed two types of surface terminations (PbI and I terminated) and placed three cations properly and relaxed the system. The surface interaction strength is calculated from interaction energy

$$E_{int} = H_{surf,R} - (H_{surf} + H_R)$$

where $H_{surf,R}$ is the energy of the slab+molecule geometry, H_{surf} is the surface energy only and H_R is the energy of the molecule only.

Free energy of substitution. The substitution free energies of formation of $FAI + PbI_2 + API \rightarrow AP.FAPbI_3$ (arbitrary contents) with and without AP^+ were evaluated by combining DFT total energies with phonon-derived finite-temperature entropy contributions. For each system, an FA^+ in the A-site was replaced by the corresponding AP^+ molecule and the structure was fully relaxed by DFT geometry optimizations. The free energy was estimated as

$$\Delta G_f = \Delta H_f - T\Delta S_{ph}$$

where $\Delta H_f = H_{complex} - \sum_j n_j H_j$ is the DFT energy of formation of a bare and AP^+ substituted $FAPbI_3$, $\Delta S_{ph} = S_{complex} - \sum_j n_j S_j$ is the vibrational entropy obtained from DFT phonon calculations.

References

- 1 Yoo, J. J. *et al.* Efficient perovskite solar cells via improved carrier management. *Nature* **590**, 587–593 (2021).
- 2 M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. *et al.* Gaussian 09, Revision D.01. *Gaussian, Inc., Wallingford CT* (2013).
- 3 Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys Rev B Condens Matter* **47**, 558–561 (1993).
- 4 Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **6**, 15–50 (1996).

Appendix B

B1

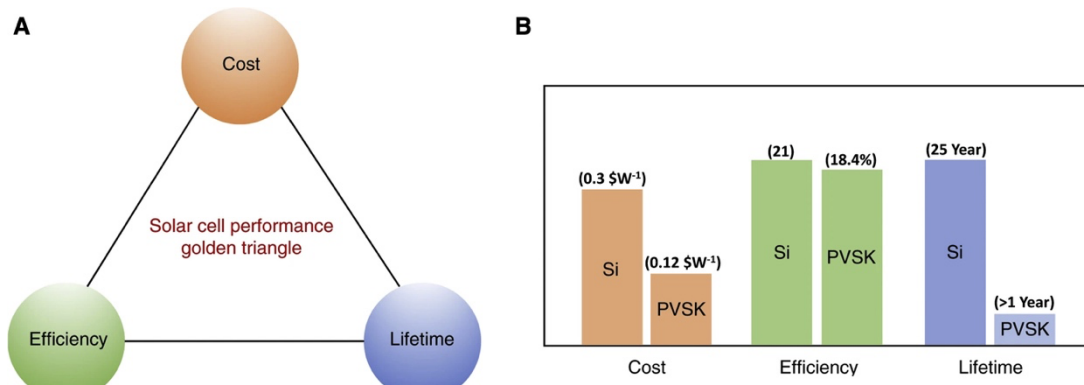


figure B1.1 Comparison of cost, efficiency, and lifetime between silicon and perovskite solar cells.¹

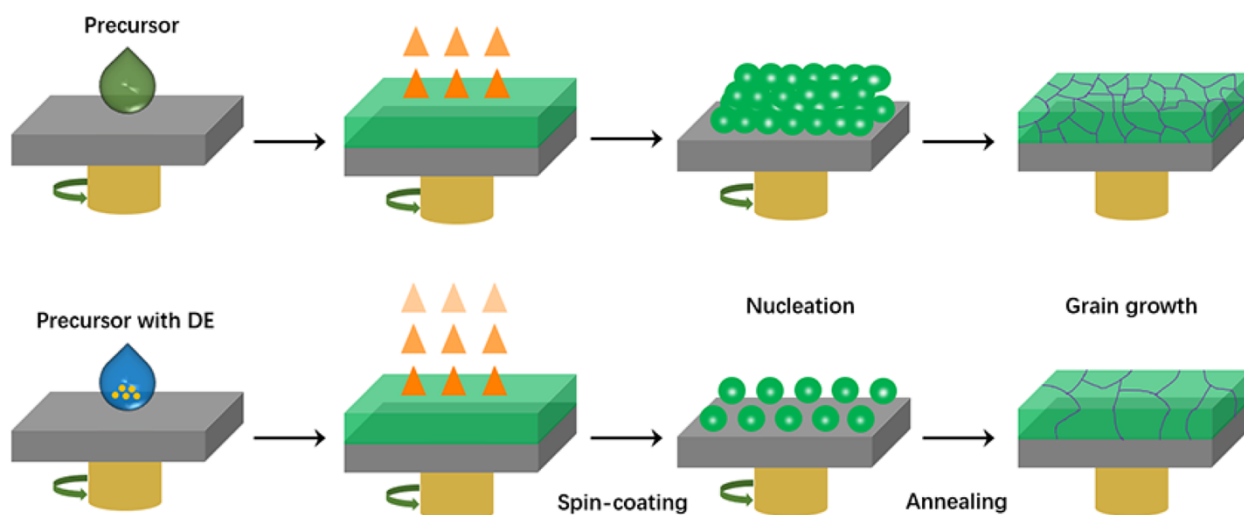


figure B1.2 Typical processing steps for spin-coated perovskite films.²

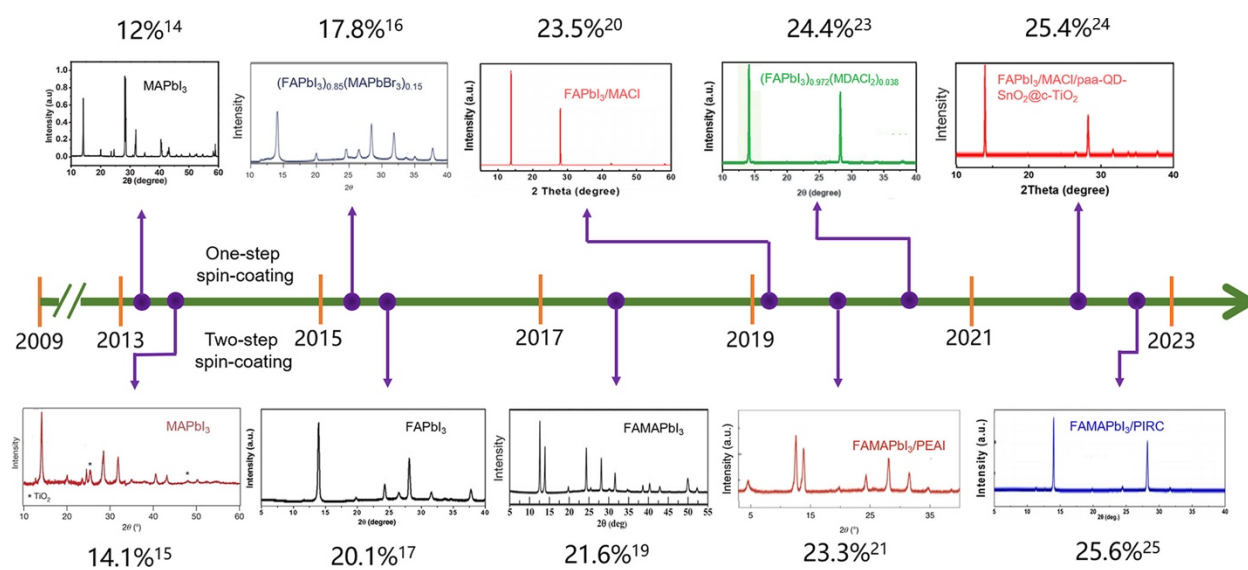


figure B1.3 Evolution of perovskite solar-cell efficiencies and the corresponding XRD patterns.³

B2

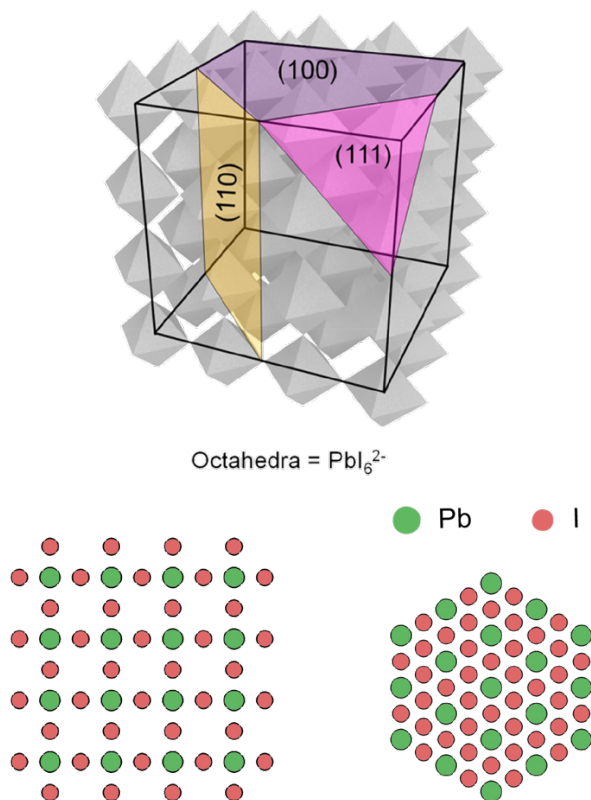


figure B2.1 Schematic illustration of different facets of cubic perovskite crystals and comparison of the atomic arrangements on the (100) and (111) facets.

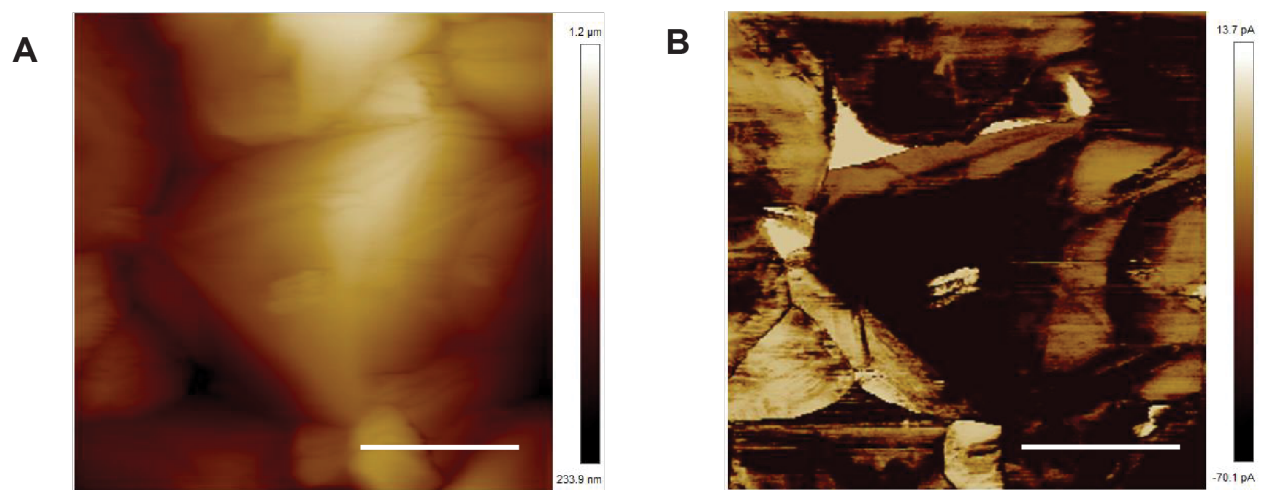


figure B2.2 AFM and corresponding conductive-AFM images of a perovskite grain containing both (100) and (111) facets. Scale bar, 1 μm .

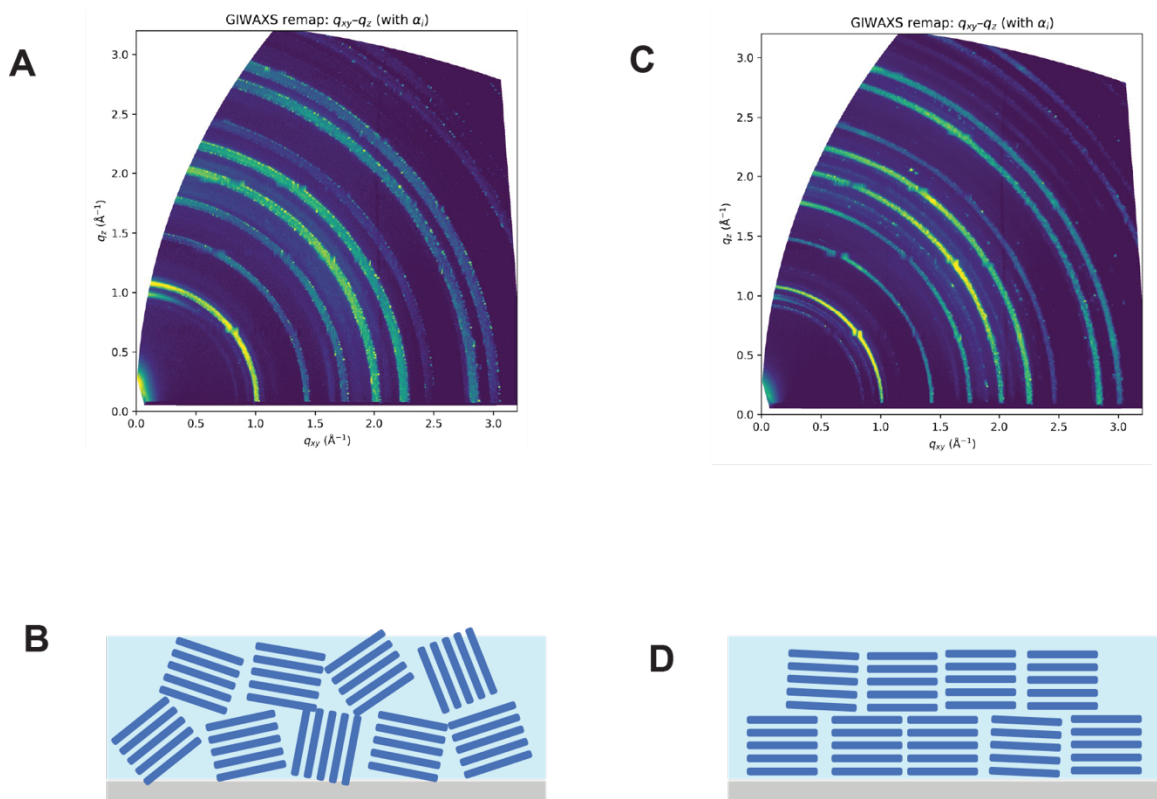


figure B2.3 GIWAXS patterns of the control and target films.

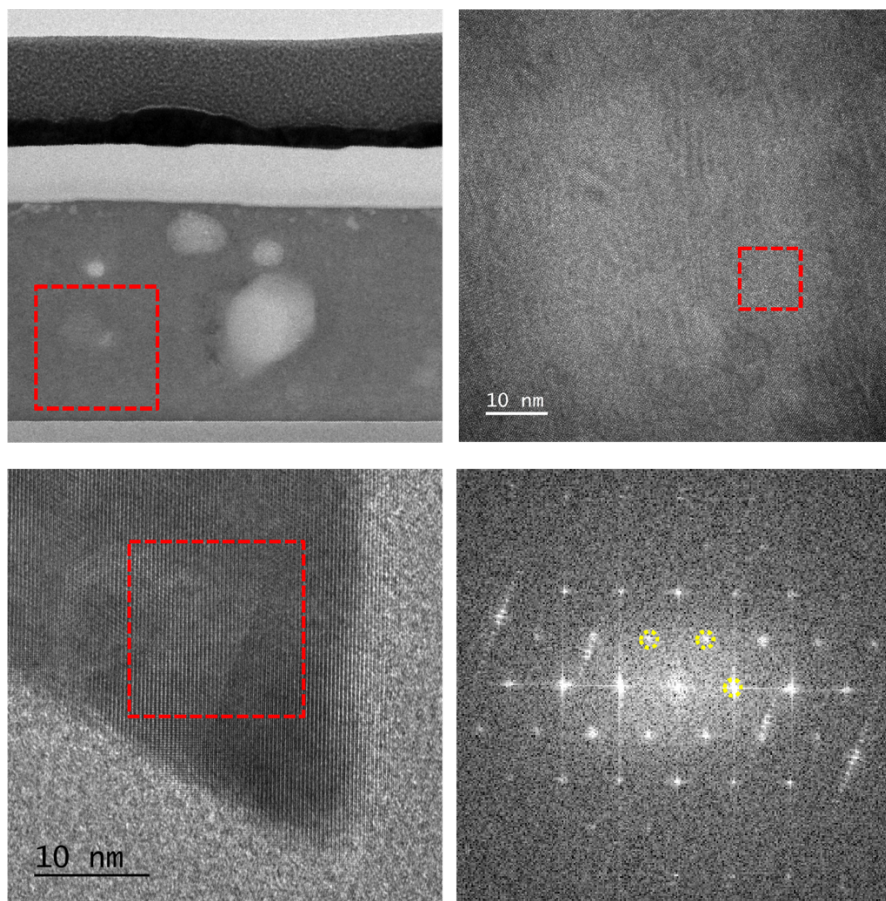


figure B2.4 TEM images and corresponding diffraction patterns identifying the (111) surface.

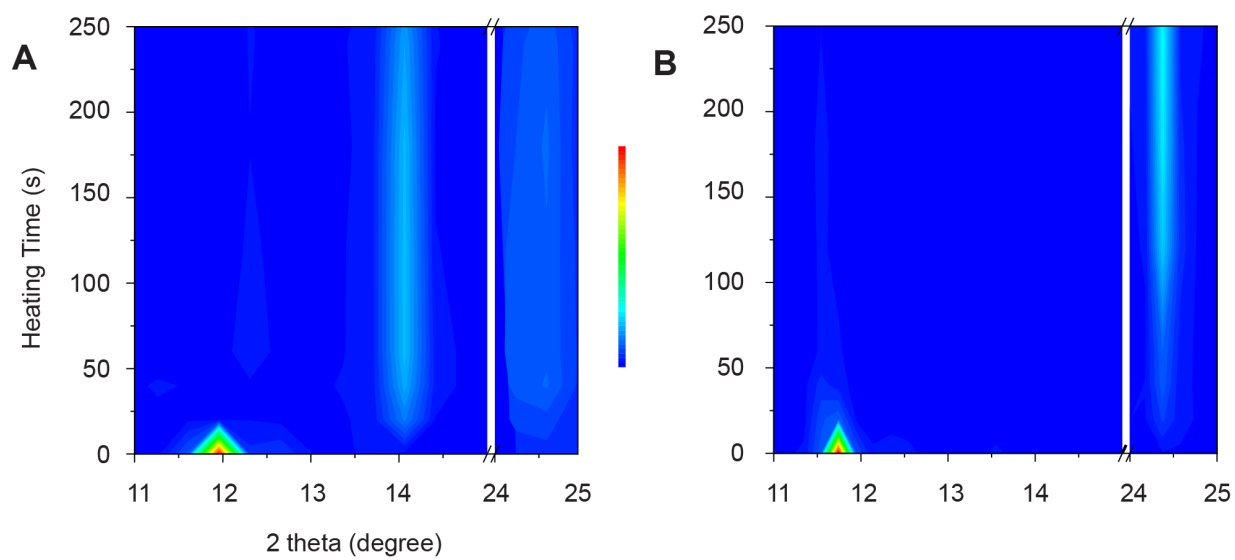


figure B2.5 In-situ XRD patterns of the control and target films during thermal annealing.

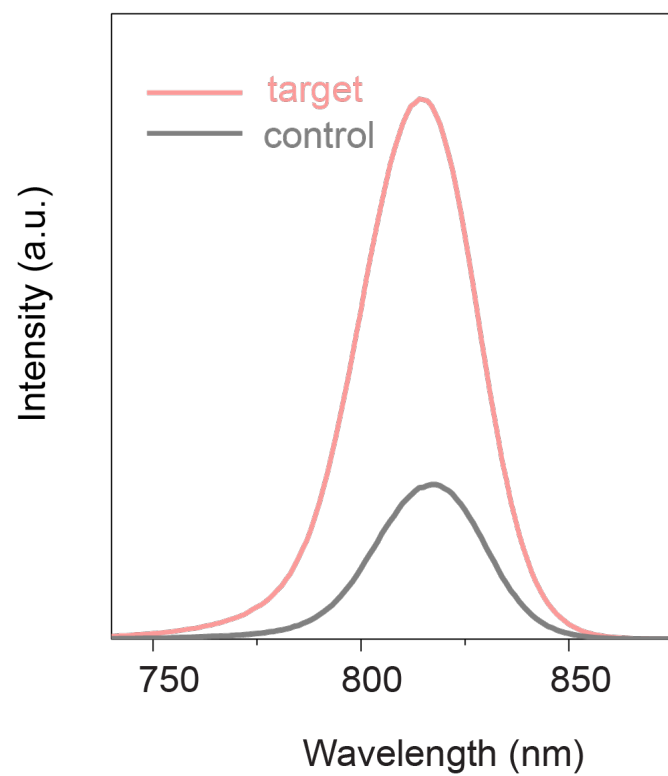


figure B2.6 PL spectra of the control and target films.

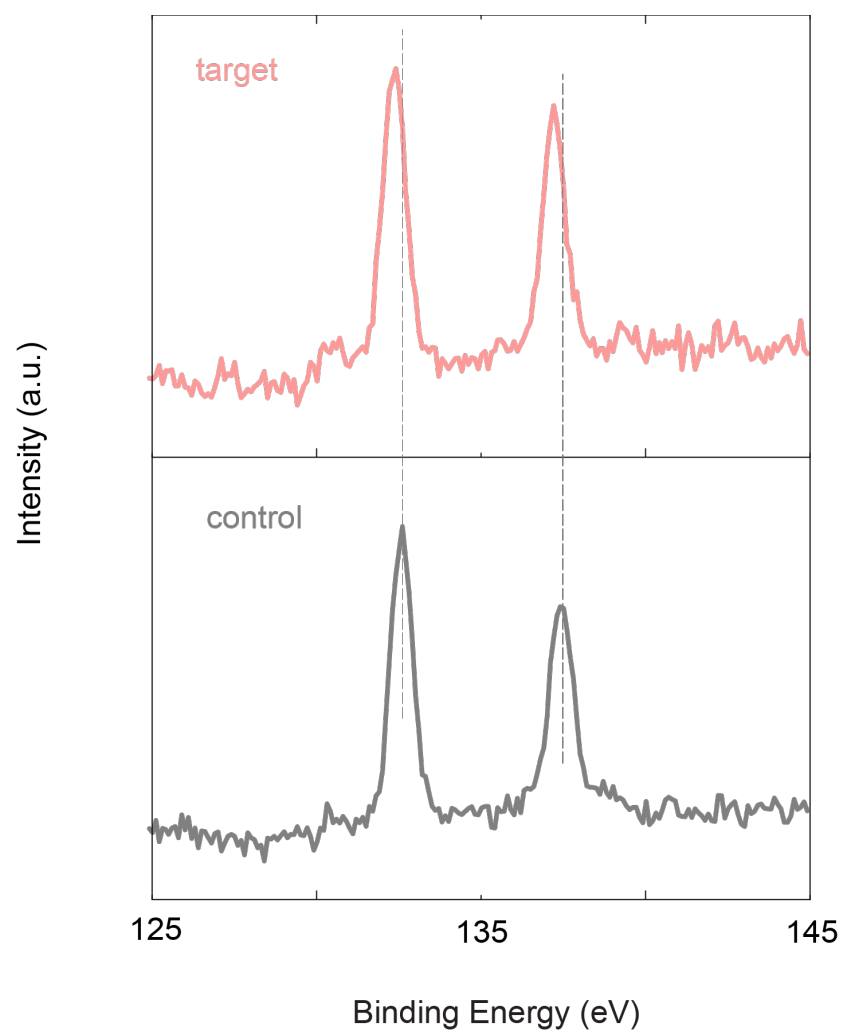


figure B2.7 Comparison of the Pb XPS spectra of the control and target films.

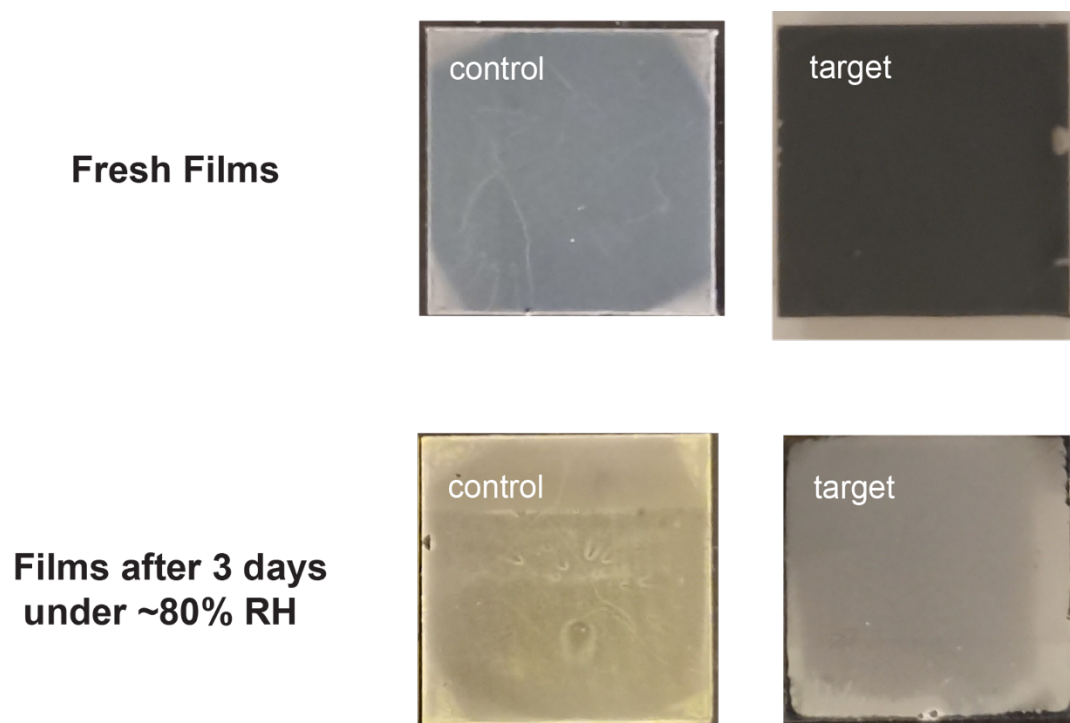


figure B2.8 Photographs showing the evolution of the control and target perovskite films under approximately 80% relative humidity.

B3

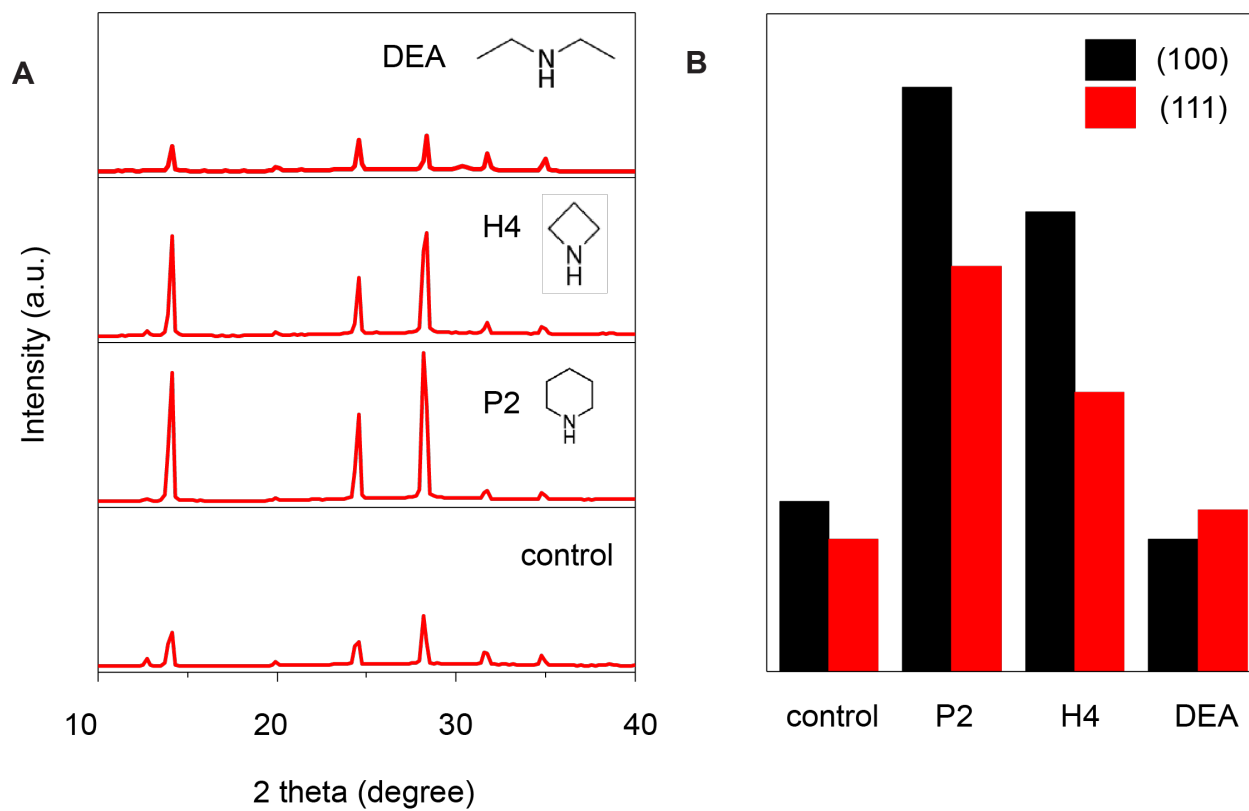


figure B3.1 XRD patterns and corresponding facet-preference analysis of perovskite films treated with secondary amines.

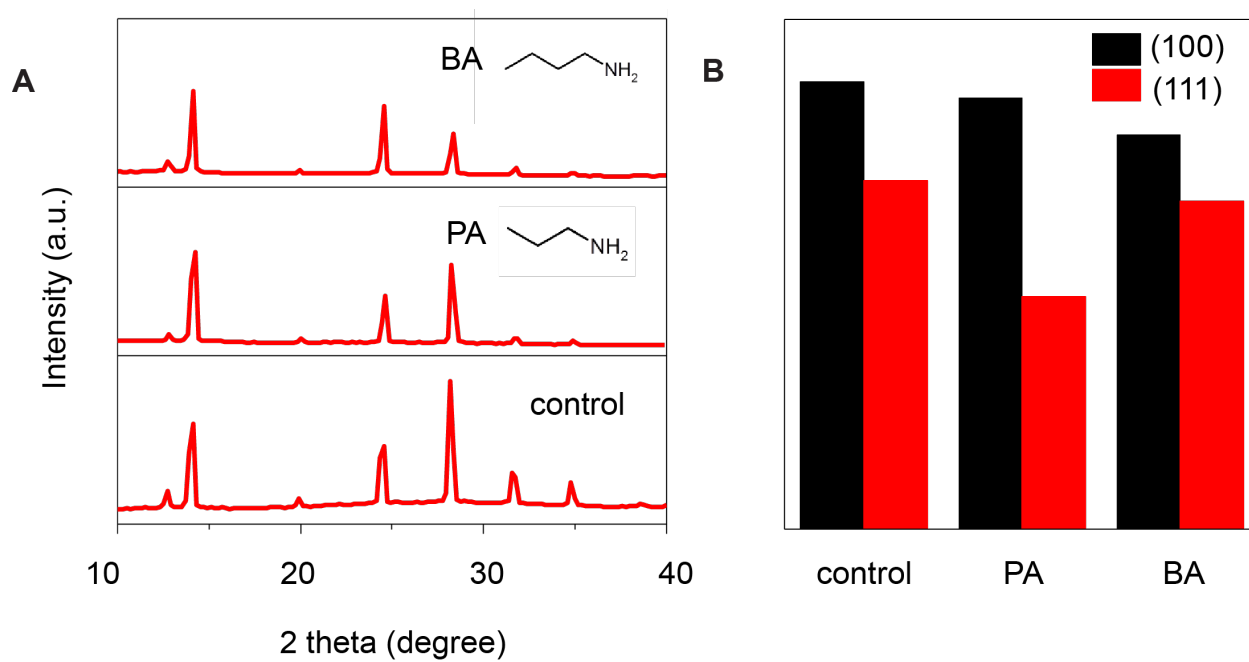


figure B3.2 XRD patterns and corresponding facet-preference analysis of perovskite films treated with linear primary amines.

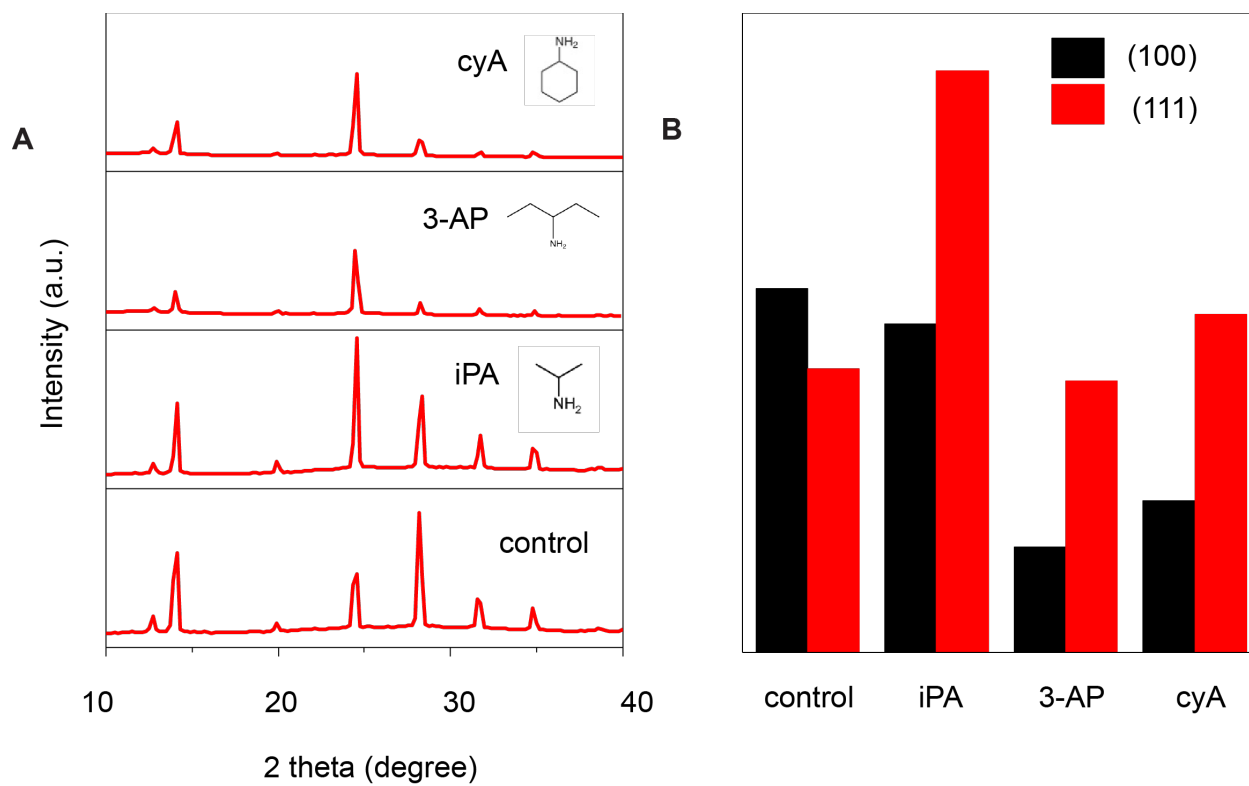


figure B3.3 XRD patterns and corresponding facet-preference analysis of perovskite films treated with branched and cyclic primary amines.

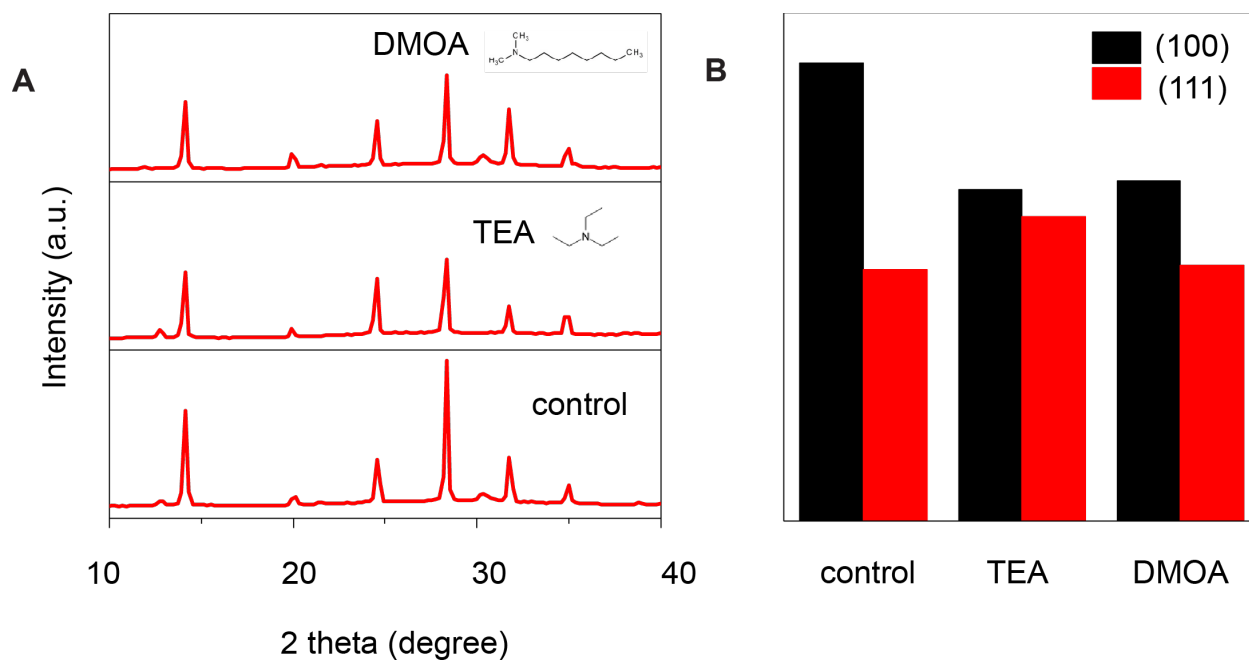


figure B3.4 XRD patterns and corresponding facet-preference analysis of perovskite films treated with tertiary amines.

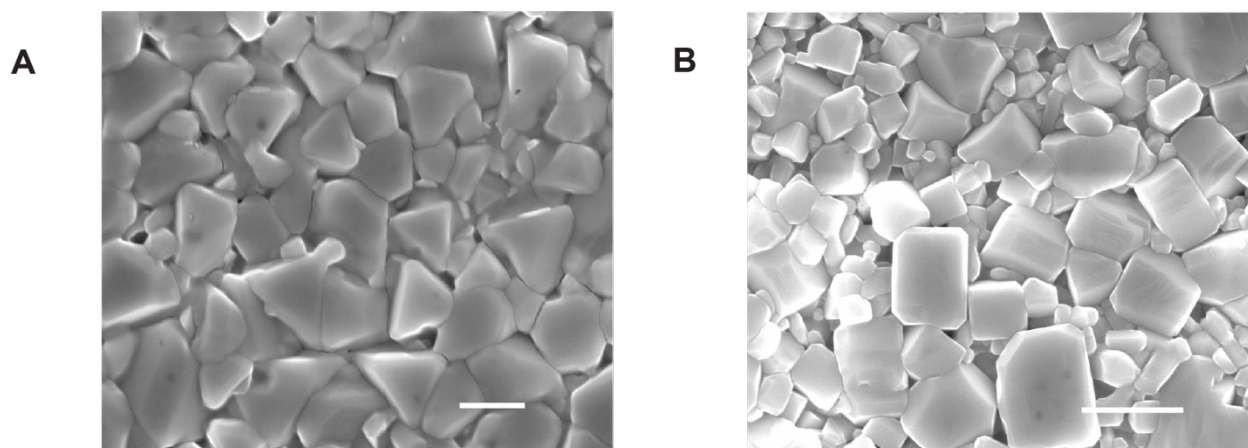


figure B3.5 Top-view SEM images of perovskite films with preferentially exposed (111) and (100) facets. Scale bar, 1 μm .

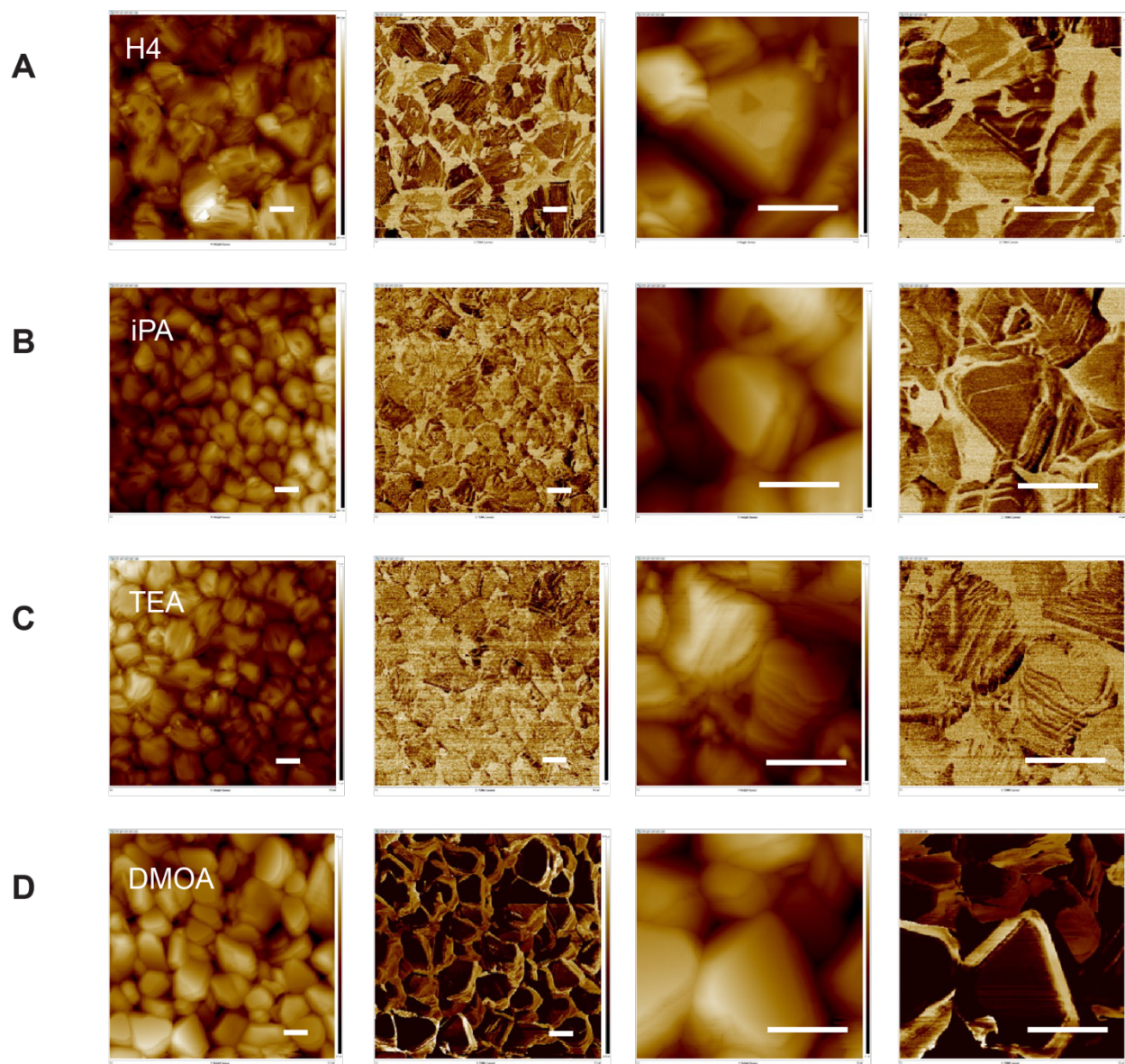


figure B3.6 AFM height and corresponding c-AFM images of perovskite films treated with H4, iPA, TEA, and DMOA at different magnifications. Scale bar, 1 μm .

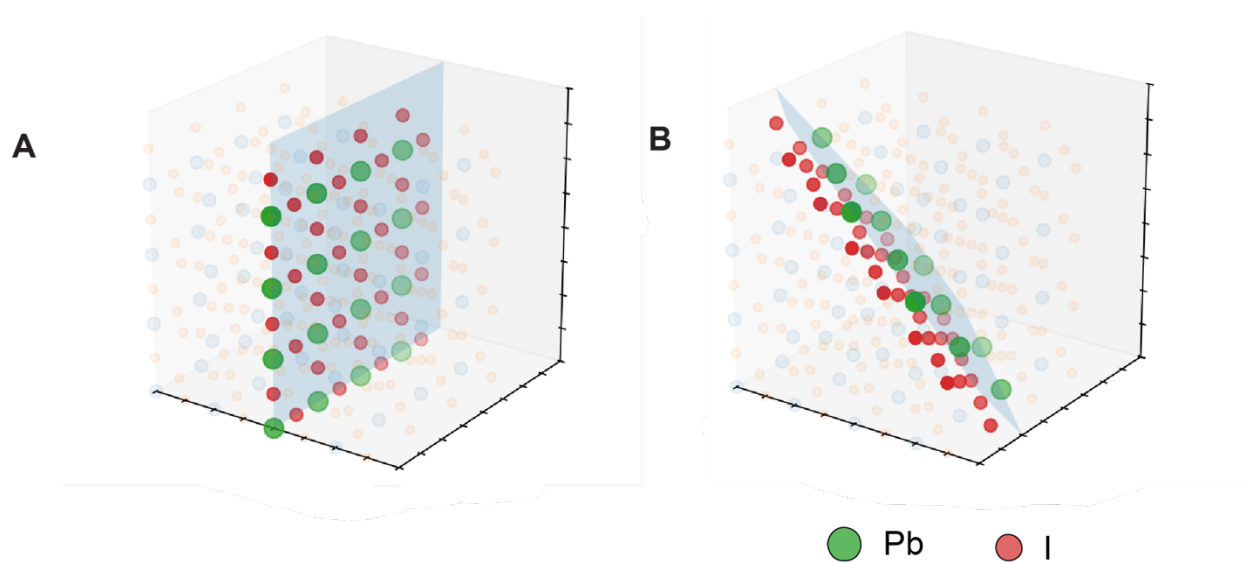


figure B3.7 Three-dimensional cross-sectional views of the perovskite (100) and (111) facets and the corresponding surface atomic distributions.

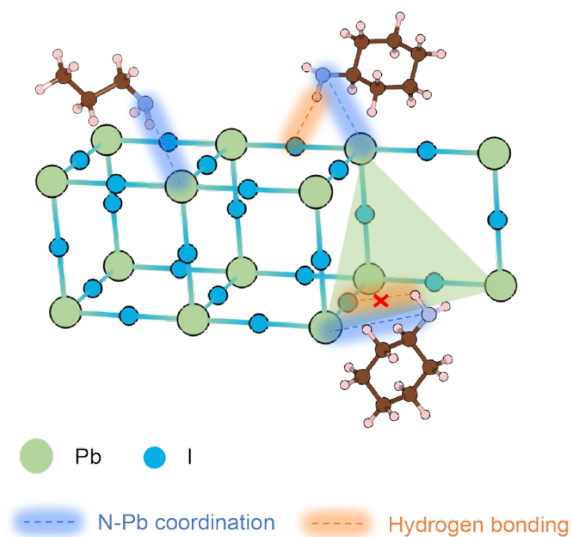


figure B3.8 Schematic illustration of the distinct interactions of amines with the perovskite (100) and (111) facets and the corresponding possible bonding configurations.

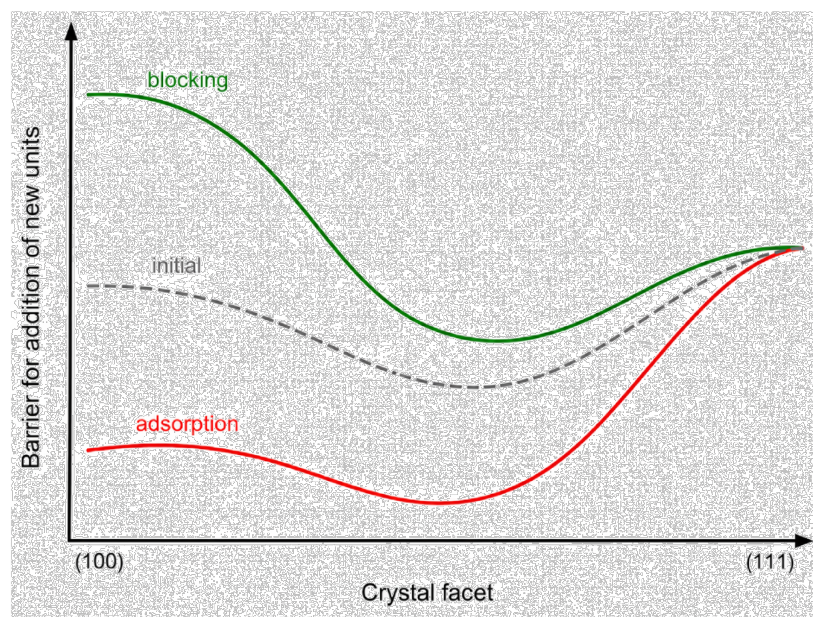


figure B3.9 Schematic relationship between amine adsorption, growth blocking, and facet-dependent incorporation of new growth units.

B4

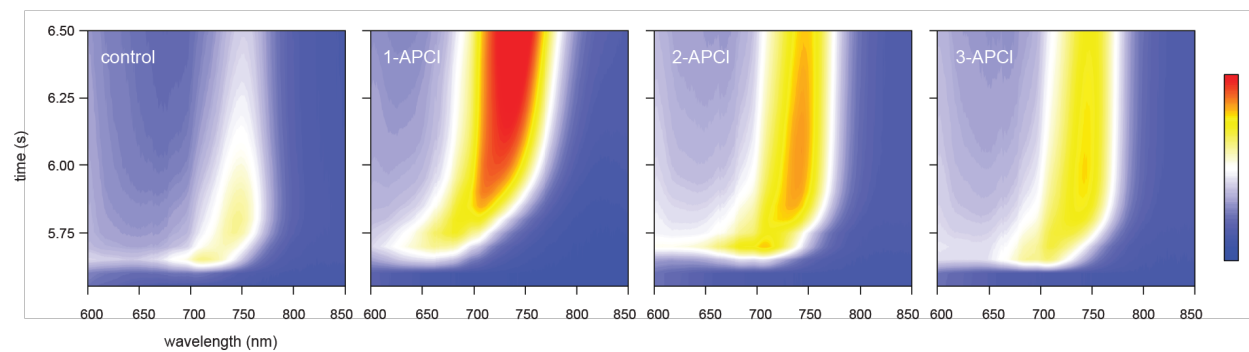


figure B4.1 In situ PL spectra of perovskite films during thermal annealing.

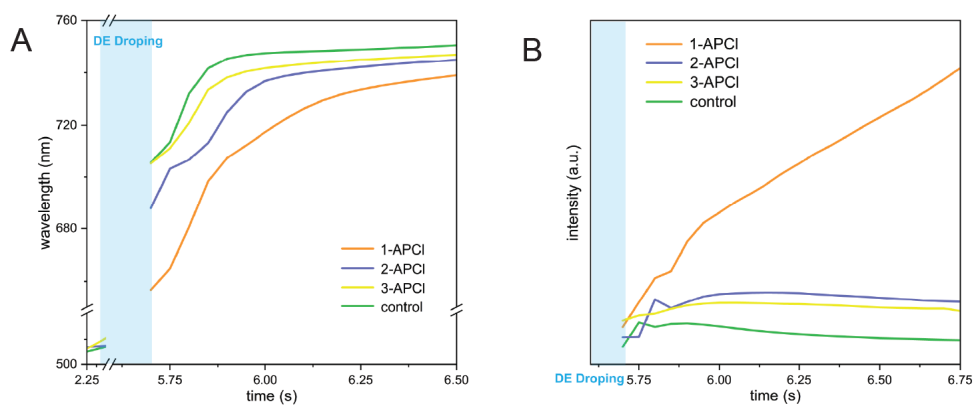


figure B4.2 Temporal evolution of PL peak position (A) and PL peak intensity (B) during spin-coating.

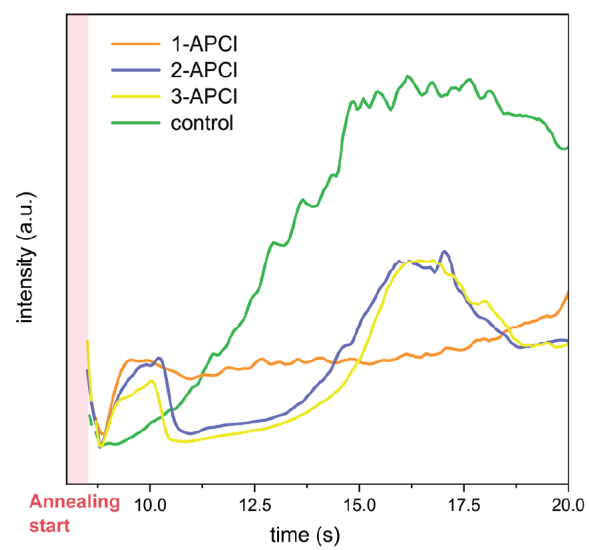


figure B4.3 Temporal evolution of PL peak intensity during thermal annealing.

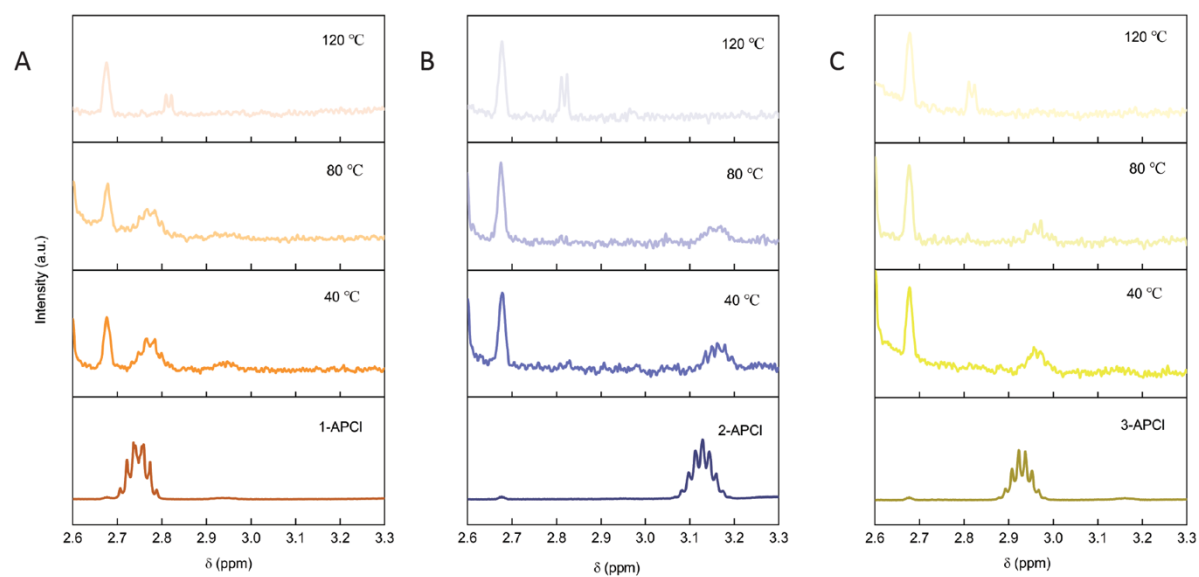


figure B4.4 Temperature-dependent ^1H NMR spectra of FAPbI₃ films containing 1-APCl, 2-APCl, and 3-APCl.

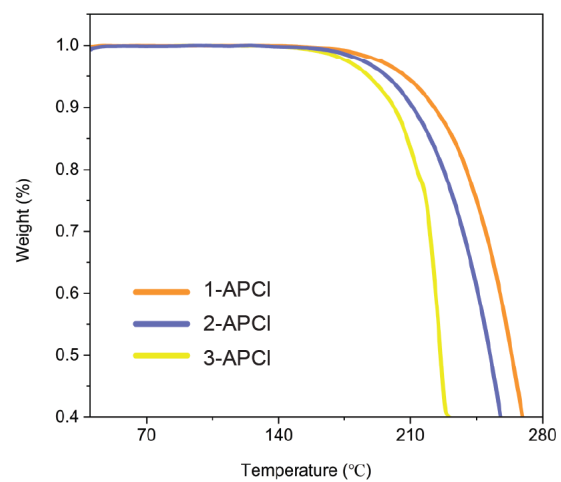


figure B4.5 Thermogravimetric analysis (TGA) curves of 1-APCl, 2-APCl, and 3-APCl powders.

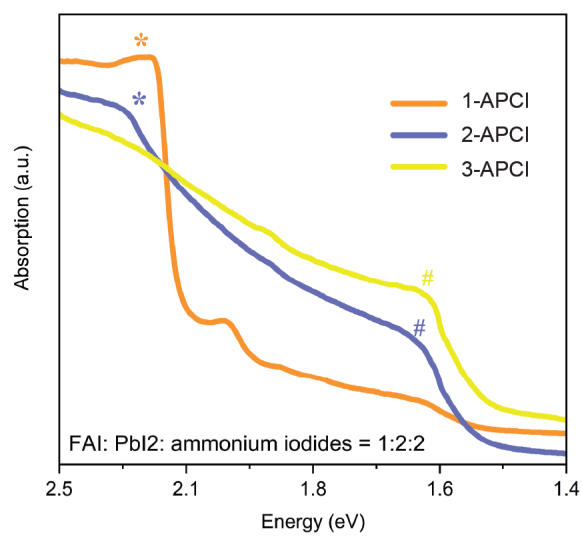


figure B4.6 UV–vis absorption spectra of films prepared with three ammonium cations at $n = 2$ stoichiometry.

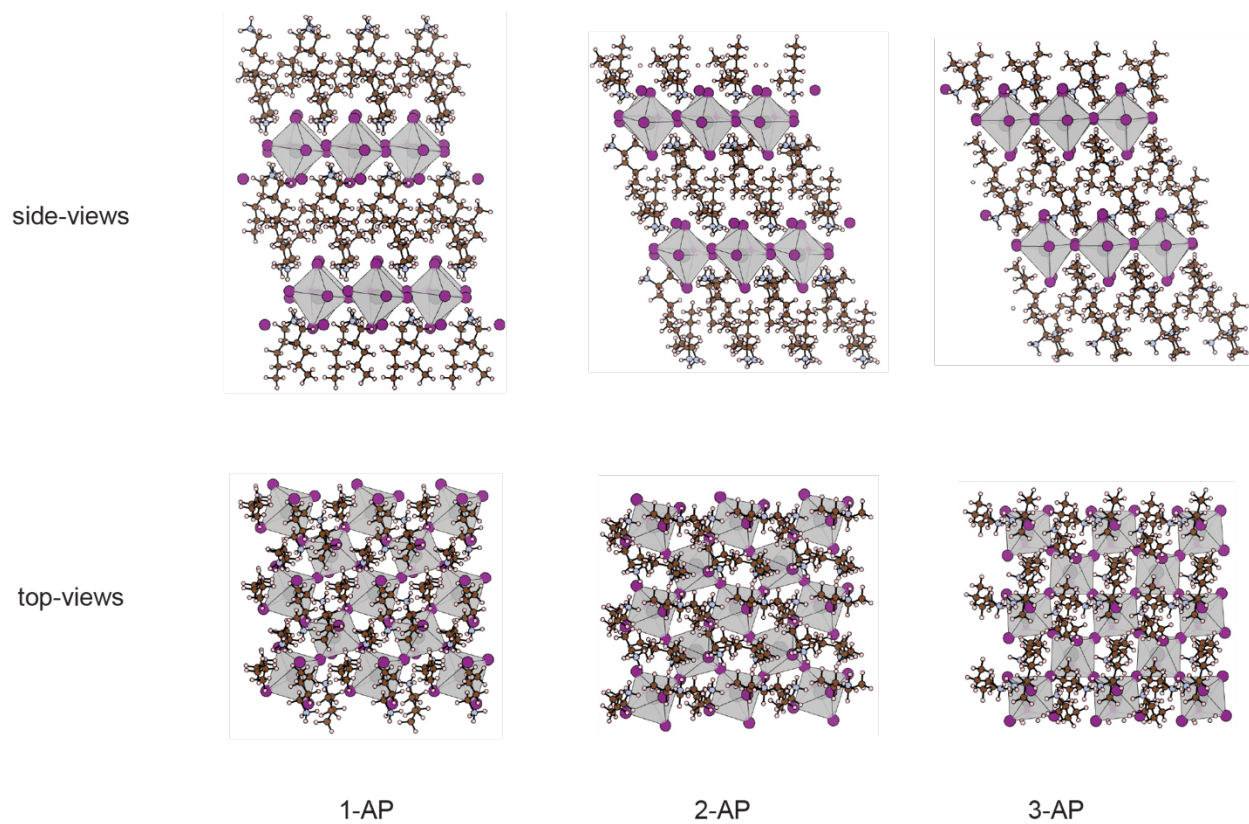


figure B4.7 Structural models of $n = 1$ two-dimensional perovskites formed with 1-AP⁺, 2-AP⁺, and 3-AP⁺ cations.

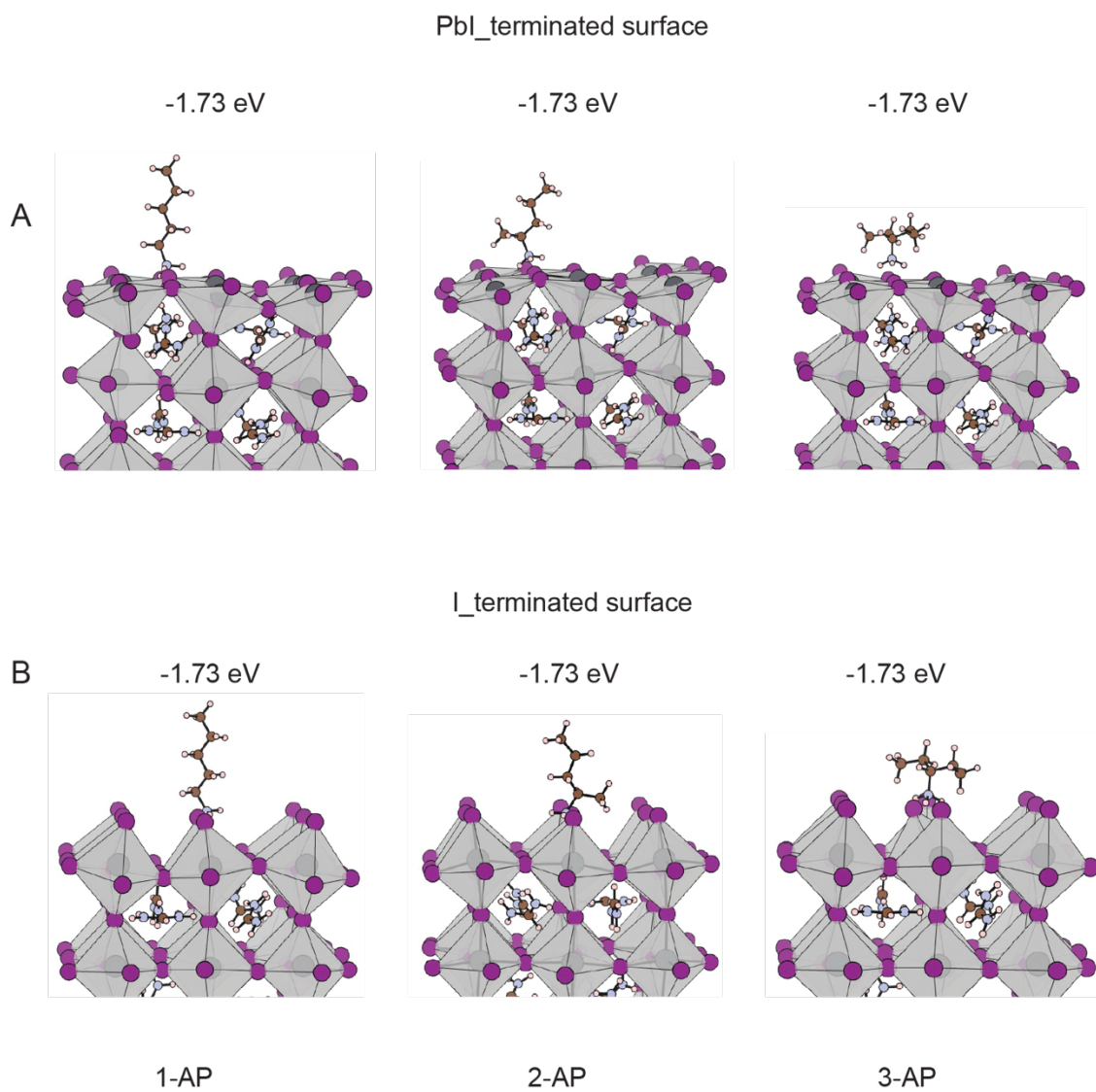


figure B4.8 Calculated surface interaction configurations and interaction energies of 1-AP⁺, 2-AP⁺, and 3-AP⁺ with α -FAPbI₃ surfaces.

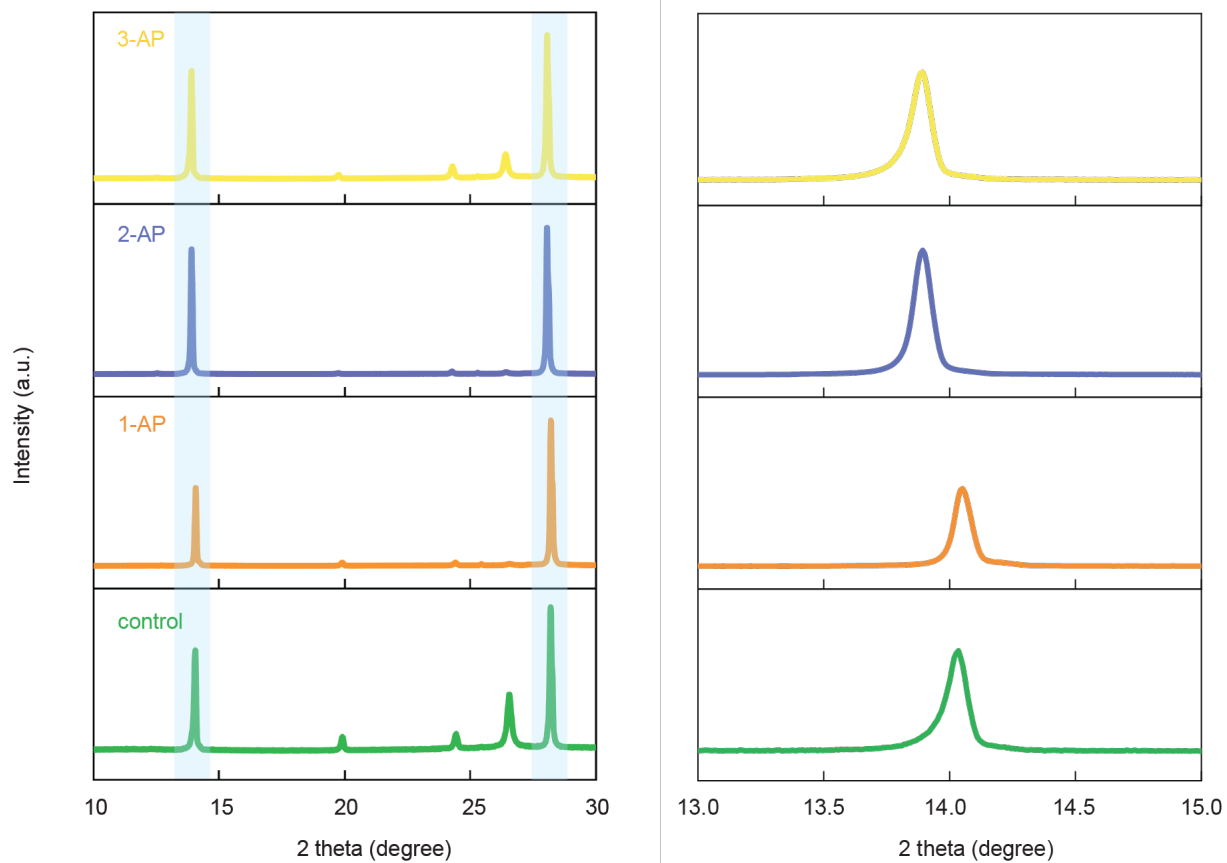


figure B4.9 Slow-scan XRD patterns of control, 1-APCl, 2-APCl, and 3-APCl perovskite films.

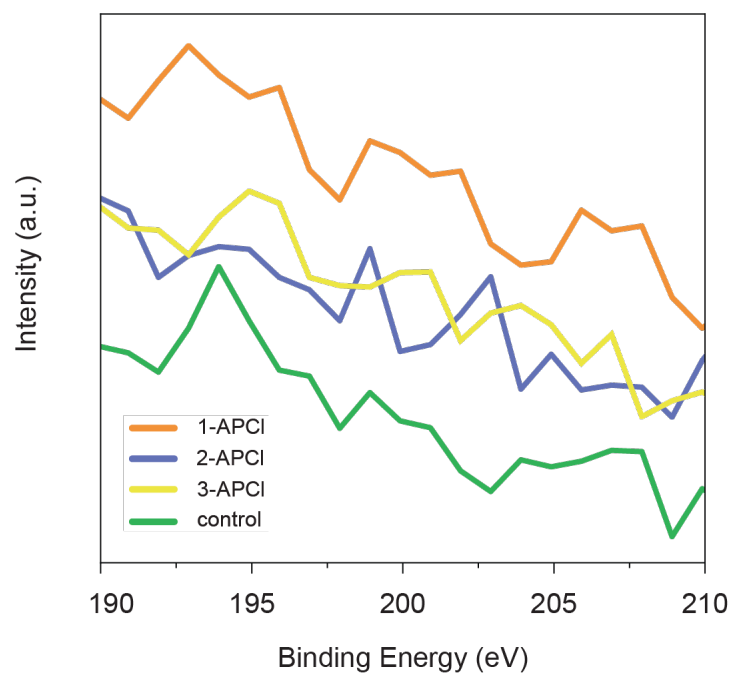


figure B4.10 Cl 2p XPS spectra of control and additive-containing perovskite films deposited on FTO glass.

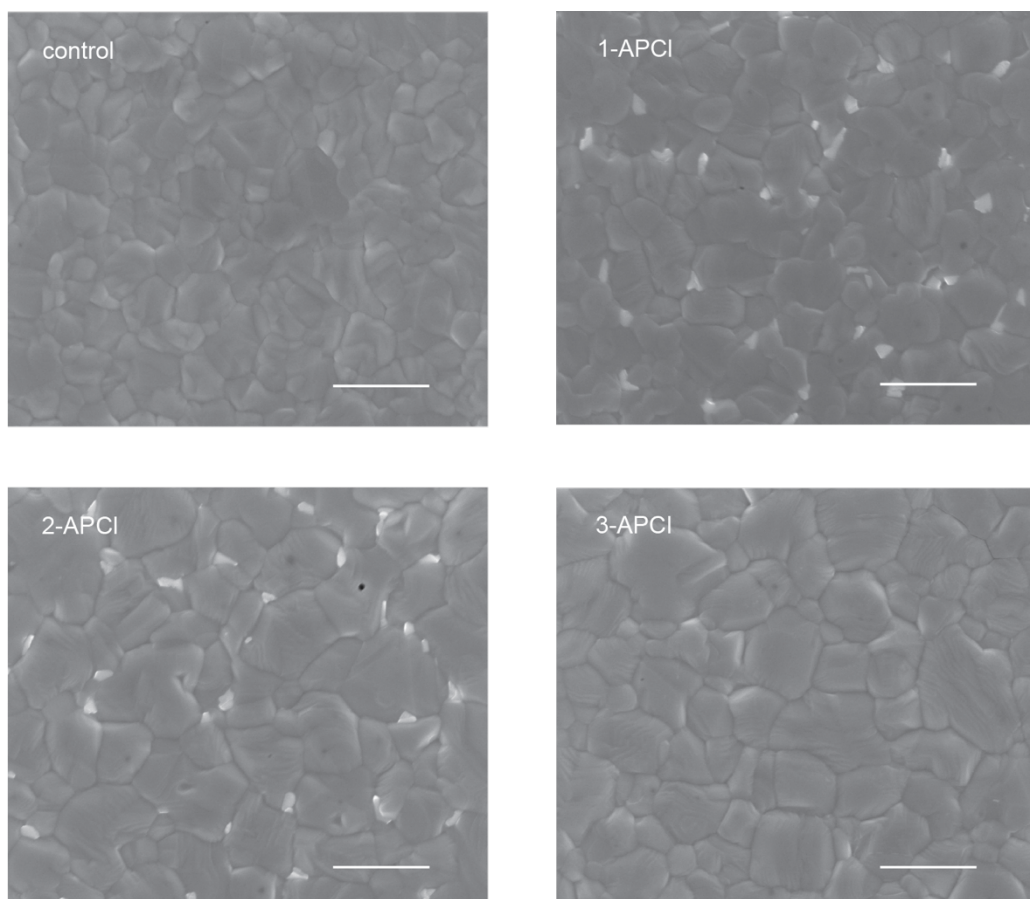


figure B4.11 Top-view SEM images of control, 1-APCI, 2-APCI, and 3-APCI perovskite films.

Scale bars, 2 μm .

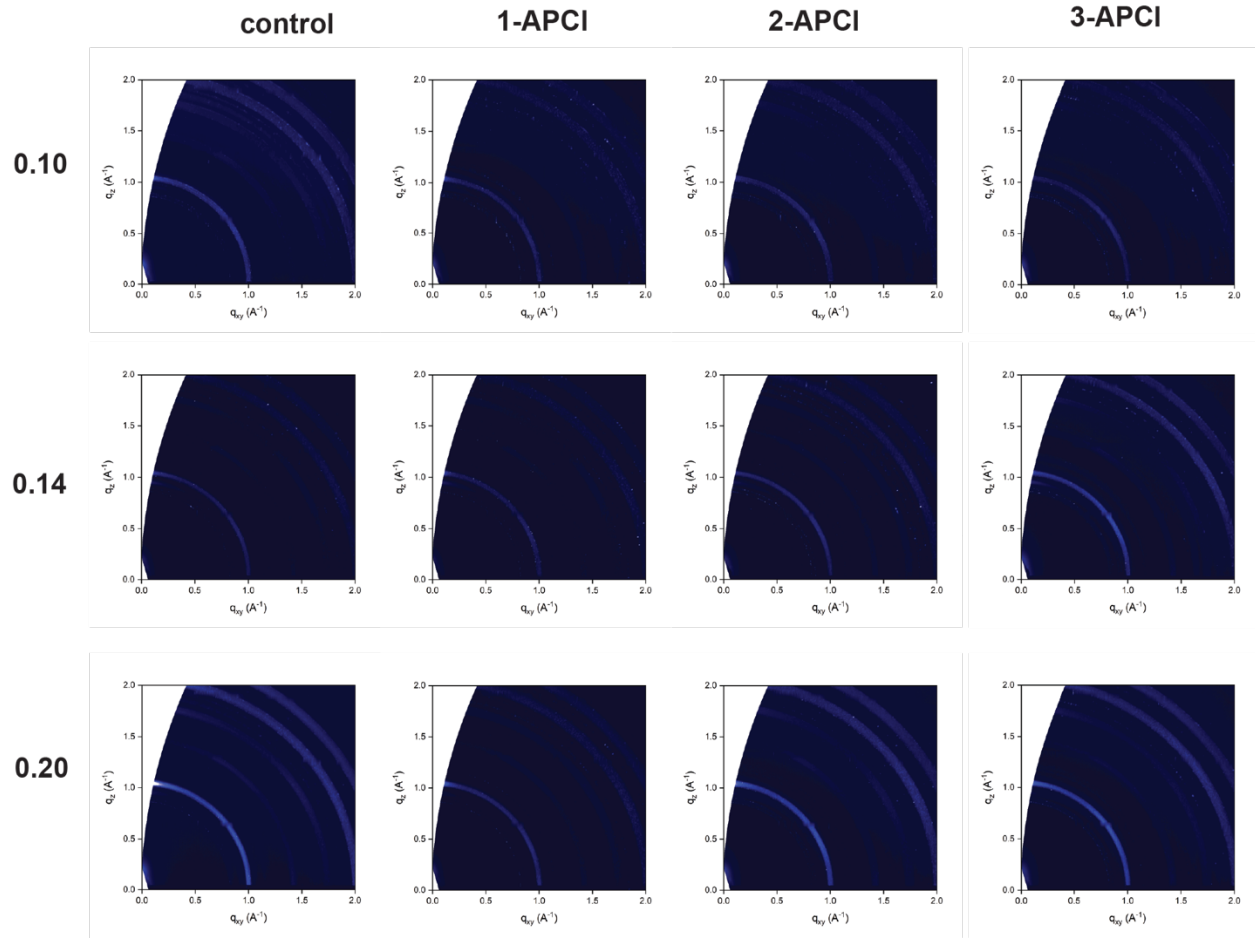


figure B4.12 GIWAXS patterns of control, 1-APCI, 2-APCI, and 3-APCI perovskite films collected at different incident angles.

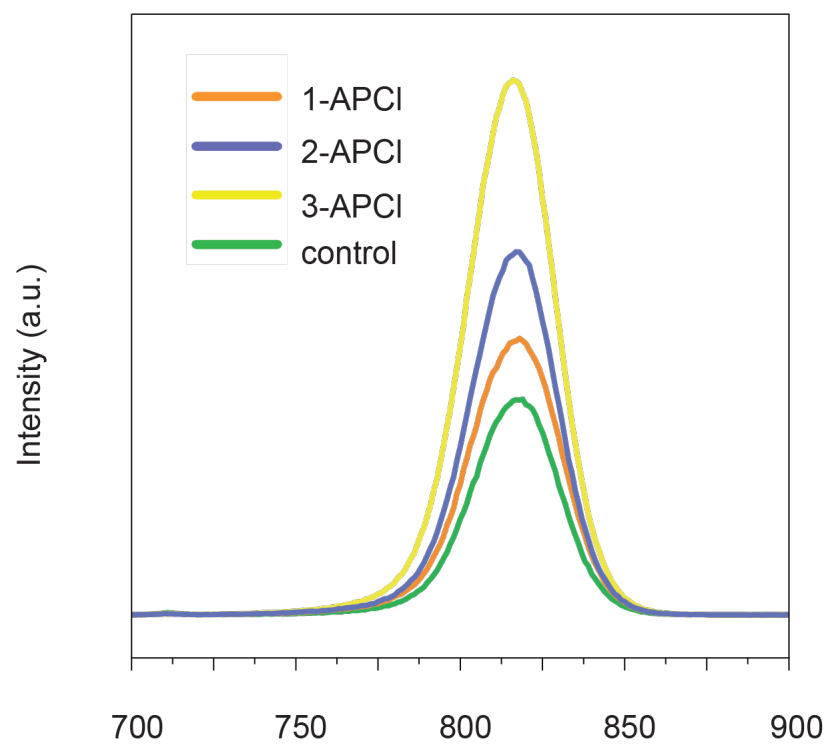


figure B4.13 Steady-state PL spectra of control, 1-APCl, 2-APCl, and 3-APCl perovskite films.

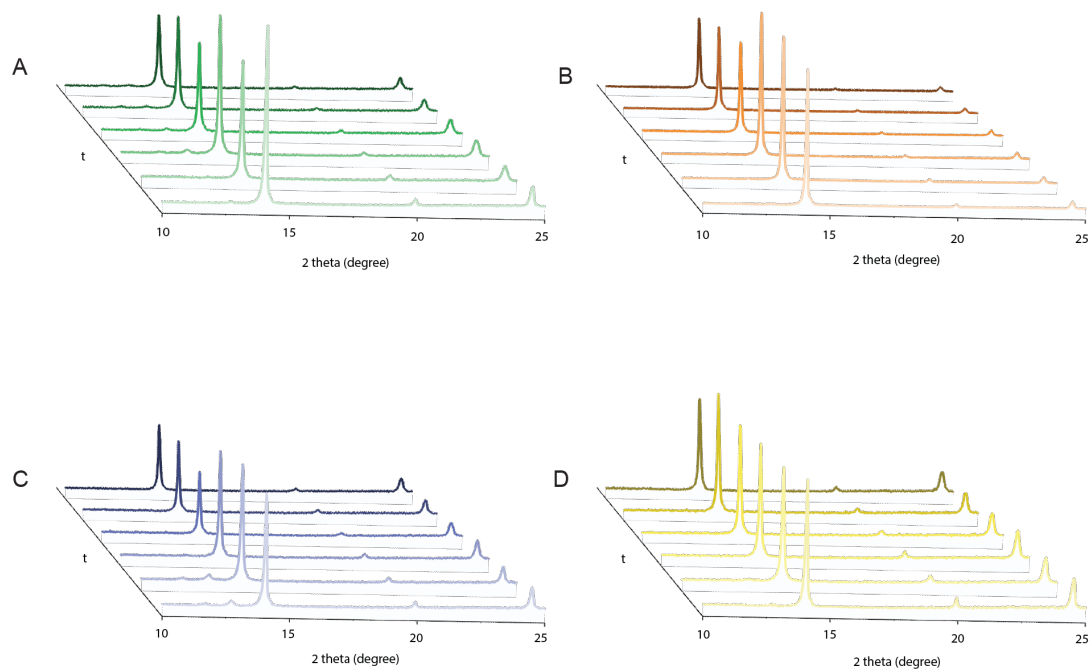


figure B4.14 Evolution of XRD patterns of control (A), 1-APCl (B), 2-APCl (C), and 3-APCl (D) perovskite films under 1 sun aging.

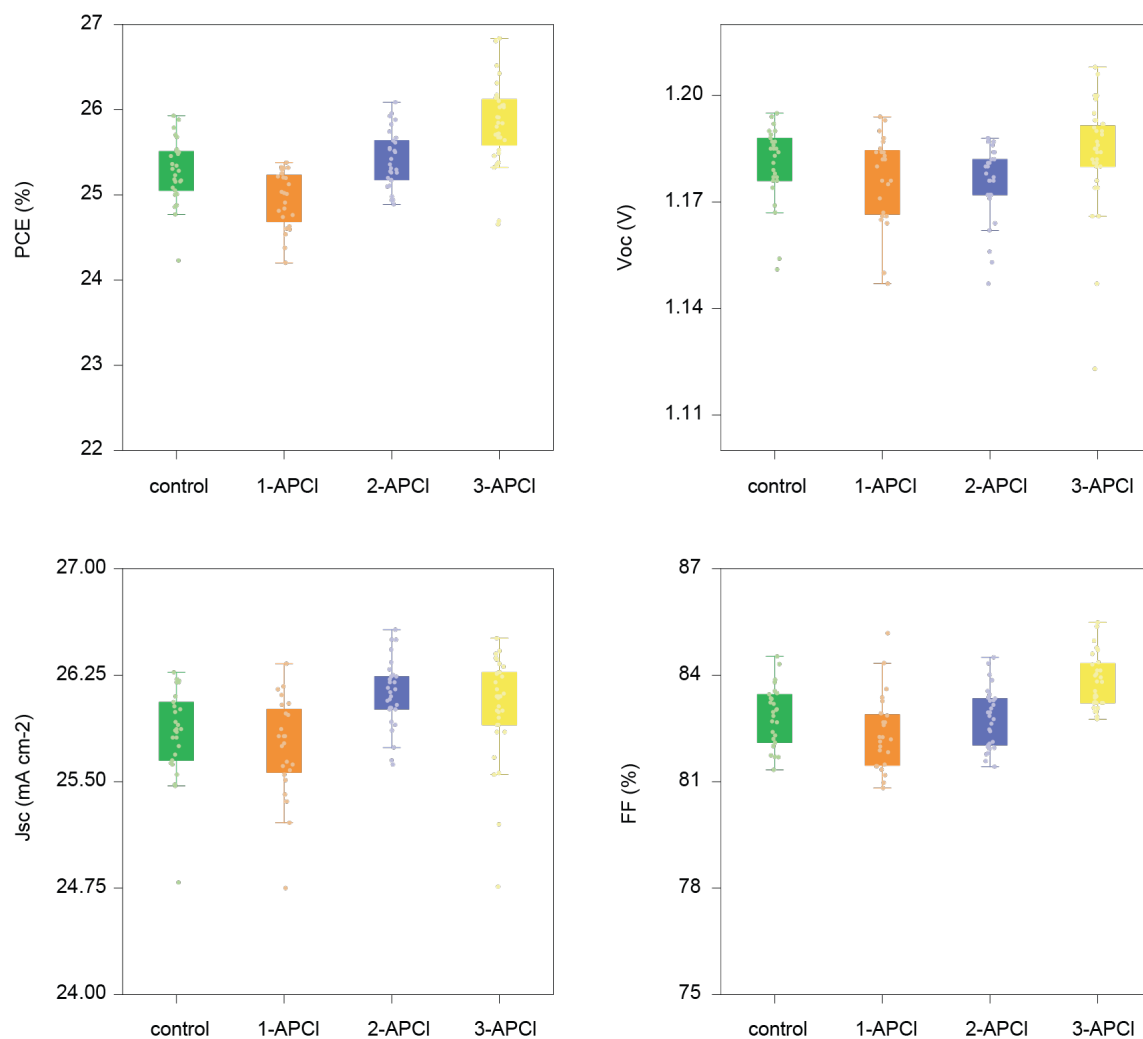


figure B4.15 Statistical distributions of PCE, V_{OC} , J_{SC} , and FF based on 100 individual devices.

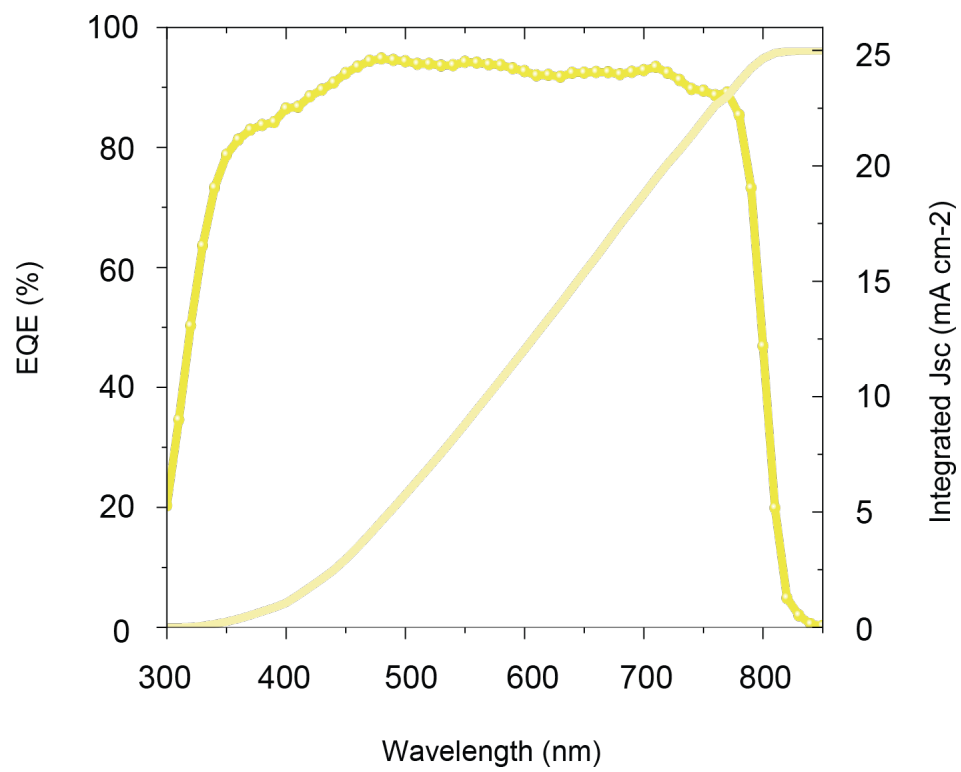


figure B4.16 EQE spectrum of the 3-APCl device.

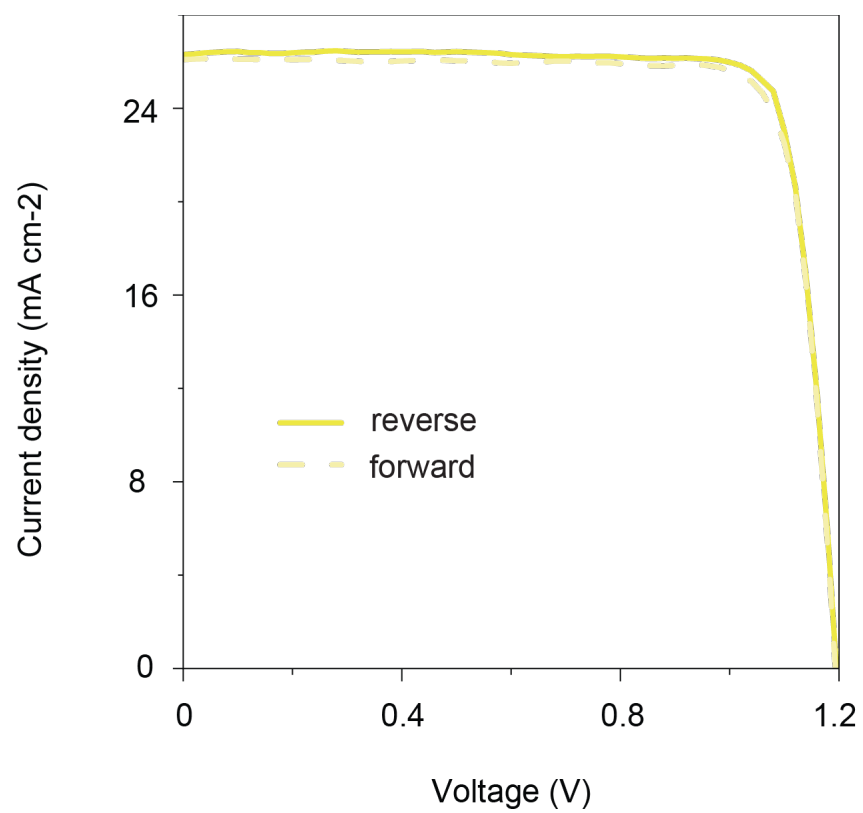


figure B4.17 Forward and reverse J–V scans of the 3-APCl device.

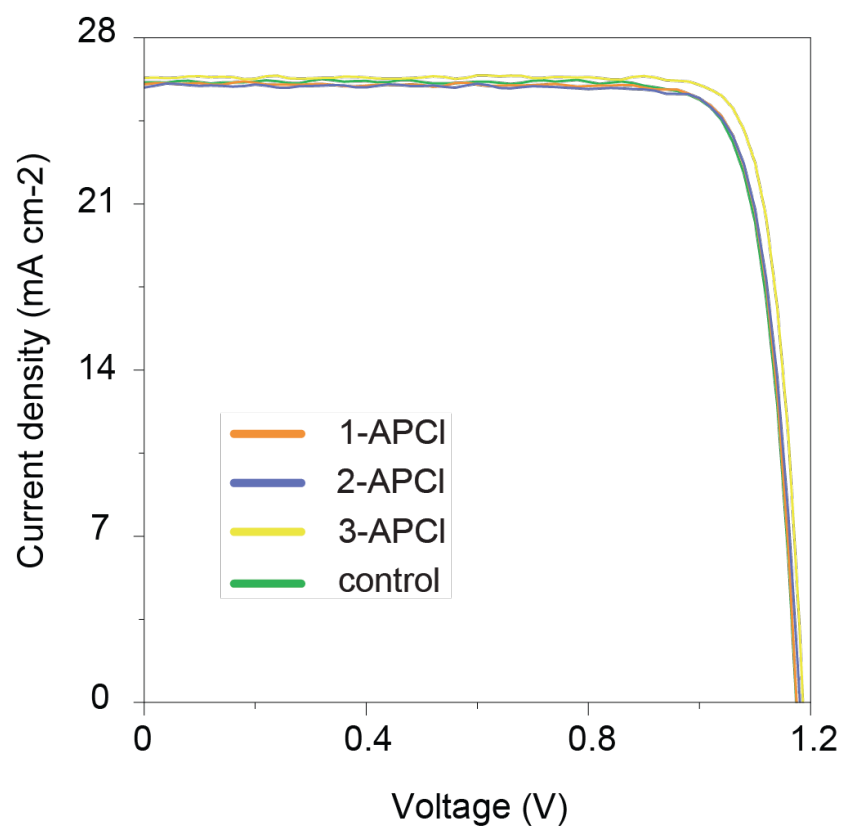


figure B4.18 Reverse-scan J–V characteristics of FAPbI₃-based p–i–n solar cells with and without APCI additives.

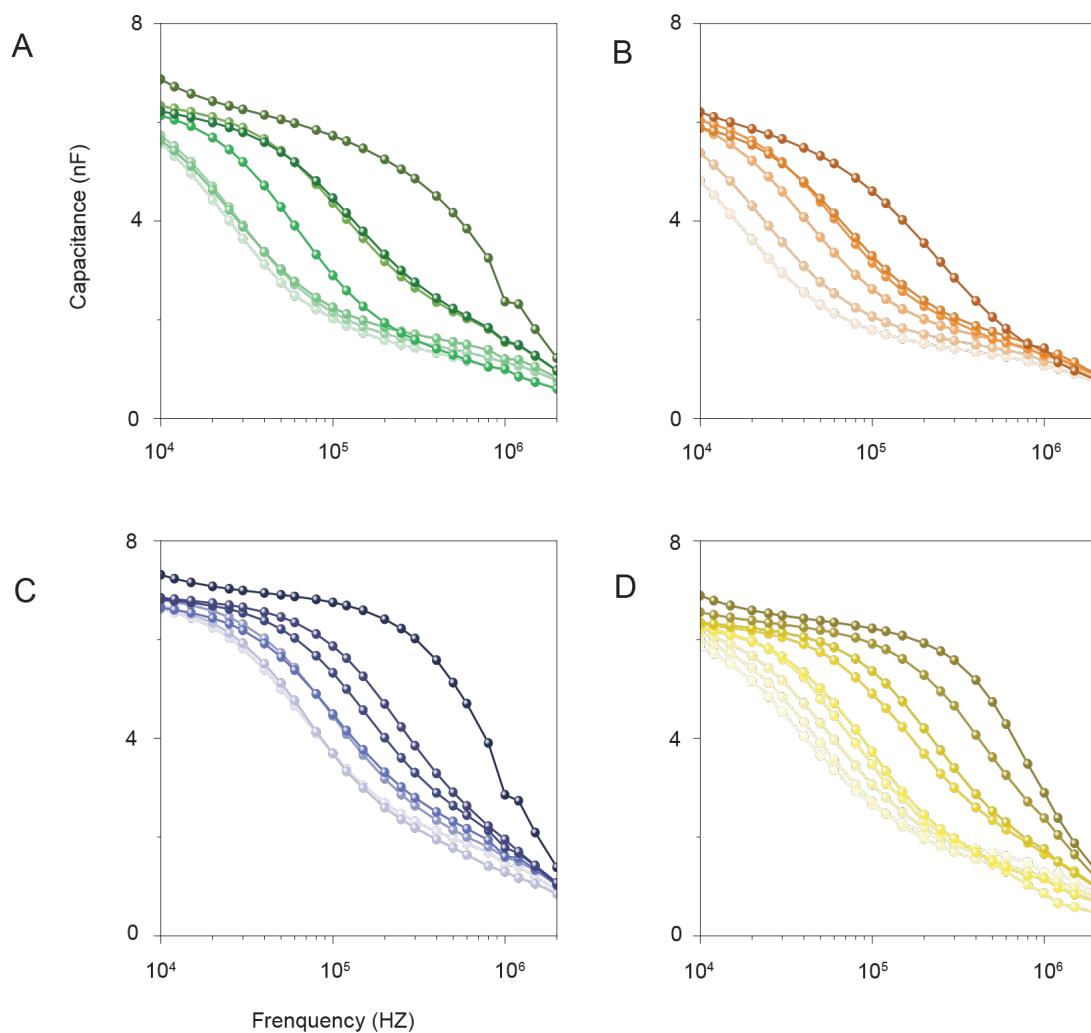


figure B4.19 Temperature-dependent admittance spectra of control (A), 1-APCl (B), 2-APCl (C), and 3-APCl (D) devices.

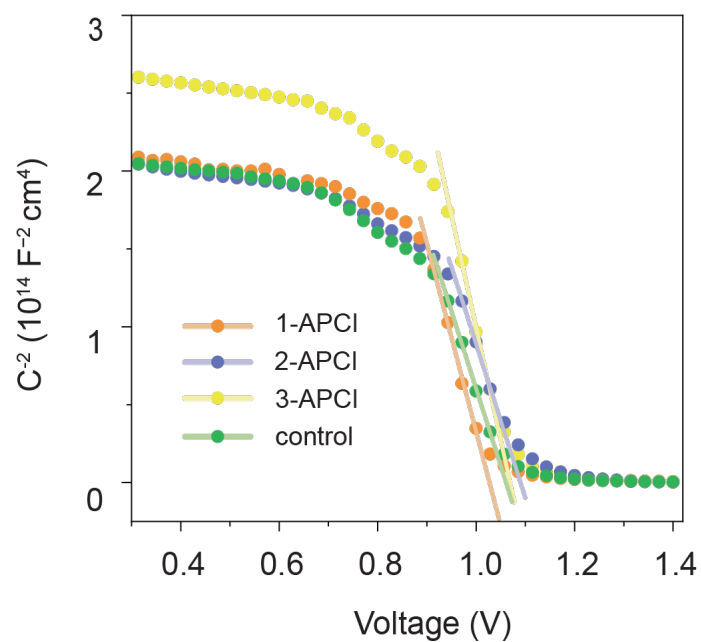


figure B4.20 Mott–Schottky analysis of control, 1-APCl, 2-APCl, and 3-APCl devices measured at 100 kHz.

Reference

- 1 Faheem, M. B. *et al.* Insights from scalable fabrication to operational stability and industrial opportunities for perovskite solar cells and modules. *Cell Reports Physical Science* **3**, 100827 (2022).
- 2 Liu, Z., Wang, L., Liu, X., Xie, X. & Chen, P. Crystallization control of wide-bandgap perovskites for efficient solar cells via adding an anti-solvent into the perovskite precursor. *Nanoscale* **16**, 7670–7677 (2024).
- 3 Gao, F. & Zhao, Q. Facet Engineering: A Promising Pathway toward Highly Efficient and Stable Perovskite Photovoltaics. *The Journal of Physical Chemistry Letters* **14**, 4409–4418 (2023).

Appendix C

Appendix C2

	VOC (V)	JSC (mA cm-2)	FF (%)	PCE (%)
control	1.186	25.75	81.73	24.96
target	1.215	26.11	83.56	26.50

table C2.1 Photovoltaic parameters of the best-performing FAPbI₃-based n-i-p control and target (111) devices.

Appendix C4

	VOC (V)	JSC (mA cm-2)	FF (%)	PCE (%)
control	1.194	26.06	83.33	25.93
1-APCl	1.176	25.82	83.37	25.31
2-APCl	1.187	26.01	84.5	26.09
3-APCl	1.206	26.27	84.71	26.83

table C4.1 Photovoltaic parameters of the best-performing FAPbI₃-based n-i-p control, 1-APCl, 2-APCl, and 3-APCl devices.

	VOC (V)	JSC (mA cm ⁻²)	FF (%)	PCE (%)
control	1.174	26.12	83.35	25.56
1-APCl	1.175	26.03	83.93	25.67
2-APCl	1.181	25.90	83.69	25.60
3-APCl	1.186	26.31	85.17	26.58

table C4.2 Photovoltaic parameters of the best-performing FAPbI₃-based p-i-n control, 1-APCl, 2-APCl, and 3-APCl devices.