

Perovskite Photovoltaics: The Significant Role of Ligands in Film Formation, Passivation, and Stability

Hong Zhang, Mohammad Khaja Nazeeruddin, and Wallace C. H. Choy*

Due to their outstanding optoelectronic properties, metal halide perovskites have been intensively studied in recent years. The latest certificated efficiency of 23.3% recently achieved in perovskite solar cells (PVSCs) enables them to be used as a very promising candidate for next-generation photovoltaics. The morphology, defect density, and water resistance of perovskite films have an enormous impact on the performance and stability of PVSCs. Ligands, with coordinating capability, have been widely developed to improve the quality and stability of perovskite materials significantly. In the first section of this review, the role of ligands in fabricating perovskite films by different methods (one-step, two-step, and postdeposition treatment) is discussed. In the second section, the progress on ligand-passivated perovskites via post-treatment, in situ passivation during perovskite formation, and modifying the substrates before perovskite formation is reviewed. In the third section, a discussion of ligand-stabilized perovskite films from the perspectives of crystal crosslinking, dimensionality engineering, and interfacial modification is presented. Finally, a summary and an outlook are given.

1. Introduction

Metal halide perovskites AMX_3 ($A^+ = CH_3NH_3$ (MA), $HC(NH_2)_2$ (FA), Cs, Rb; $M^{2+} = Pb, Sn$; $X^- = Cl, Br, I$) have recently become one of the most intensively investigated optoelectronic materials due to their merits of high absorption coefficient,^[1,2] high carrier mobility,^[3,4] long electron-hole diffusion length,^[5] tunable direct bandgap,^[6–9] and low exciton binding energy.^[10,11] The power conversion efficiency (PCE) of perovskite solar cells (PVSCs) has rocked from an initial 3.8%^[12] to a certified 23.3 %^[13] approaching that of the established photovoltaic technologies, such as crystalline silicon (c-Si), cadmium telluride (CdTe), and copper indium

gallium selenide (CIGS) solar cells (see Figure 1a).^[14,15] Meanwhile, as shown in Figure 1b, PVSCs present opportunities to significantly reduce manufacturing costs due to their use of low cost raw materials, low-temperature and scalable solution fabrication processes,^[16,17] and the potential for roll-to-roll manufacturing on flexible substrates.^[18–21] These advantages render PVSC as a potential cost-effective photovoltaic technology in the future.

The perovskite film quality crystallinity, defect density and morphology, which depend on the fabrication conditions have significant impact on the PVSC performance. Figure 1a shows the efficiency roadmap for PVSCs and the relevant methods employed for perovskite formation. In the initial development period of PVSCs, one-step spin-coating method was employed to fabricate perovskite film by using single solvent γ -butyrolactone (GBL),^[1] dimethylformamide (DMF),^[8] and dimethyl sulfoxide (DMSO).^[22] The PCE of PVSCs increased slowly from 9.7%^[1] to 12.3%^[7] in 2 years, which is mainly limited by the perovskite film quality and morphology. Although precursor composition/concentration,^[7,9,23,24] and annealing temperature/duration^[25,26] have been proposed to control the morphology of perovskite film, there is still many cracks/pinholes in perovskite film by one-step spin-coating method. While this situation has been resolved in the middle of 2013 with the development of two new techniques, namely vacuum deposition^[27] and two-step sequential deposition.^[28] Two-step sequential deposition method was first reported by Liang et al.^[29] and first applied the method to fabricate PVSCs by Burschka et al.^[28] Using this technique for the fabrication of n-i-p mesoscopic PVSCs, good reproducibility and a very high PCE approaching 15% (certified 14.14%) have been achieved. However, the main drawback of two-step deposition is the incomplete conversion of PbI_2 when deposited on flat substrate. In 2014, Seok and co-workers reported a new strategy of solvent engineering (DMSO as ligand) to control the morphology of perovskite films through forming a stable and uniform MAI-PbI₂-DMSO intermediate complex.^[30] After the introduction of a ligand in the perovskite precursor solution, the record efficiencies of PVSCs rapidly increase from 16.2% to over 20% within 2 years (Figure 1a).^[6,31–34] From the development of PVSCs, we can easily conclude that the ligand plays a significant role in controlling the formation of high-quality perovskite films.

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DOI: 10.1002/adma.201805702

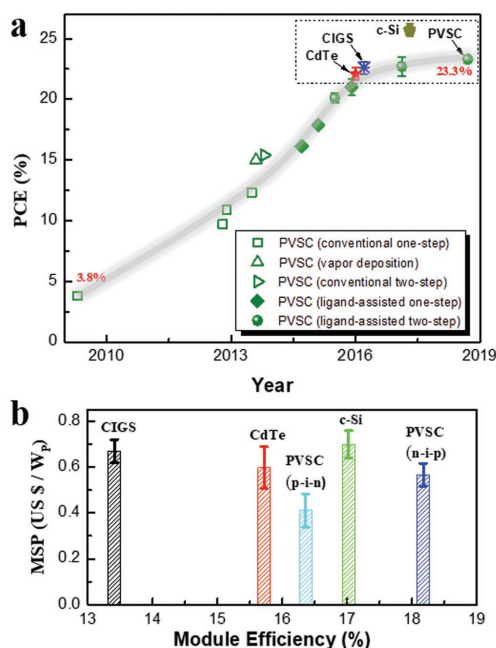


Figure 1. a) Efficiency progress of PVSCs, and the relevant methods for perovskite formation. The efficiency values are taken from “Solar cell efficiency tables”^[14] and NREL’s latest chart on record cell efficiencies.^[13] The record efficiencies of CIGS, CdTe, and c-Si are also presented for comparison. b) Minimum sustainable price (MSP) of different photovoltaic devices manufactured in the United States as a function of module efficiency. The calculated MSPs are adopted from the literature.^[16]

In addition to the film formation, passivating the defects perovskite is a powerful strategy to reduce the nonrelative recombination loss and thus enhance the PCE of PVSCs toward their efficiency limit ($\approx 31\%$).^[35] Taking silicon as an example, the understanding and control of defects has been a cornerstone of their successful photovoltaic applications.^[36] It has been widely reported that the perovskite crystal contains under-coordinated ions at its crystal surfaces and at the grain boundaries (GBs) between individual crystals.^[37] For example, the under-coordinated Pb ions have been frequently found in the perovskite films prepared by thermal annealing.^[38,39] In principle, these defects incur trap-assisted nonradiative recombination losses and hence impair the performance of PVSCs. In addition, vacancy defects provide a pathway for ion (defect) migration, which results in current-voltage hysteresis.^[40–42] Additionally, several studies have indicated that surface defects and GBs can serve as photoluminescence quenching sites and thus result in loss of photogenerated carrier.^[11]

Stability of PVSCs is one of the bottleneck issues before its commercialization. It has been reported that the degradation of PVSCs is caused by moisture,^[43] oxidation,^[44] thermal stress,^[39] and ion migration.^[40,45] Some strategies have been reported to solve this issue. For example, encapsulation [e.g., hydrophobic materials,^[46] epoxy resins,^[47] fluoropolymers^[48] and interface engineering (e.g., using metal oxides to replace organic carrier transport layers^[18,49]) have been proposed to enhance the operational stability of



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devices, plasmonic structures, metal oxides, and nano-material devices.

PVSCs by blocking the away detrimental molecules (e.g., water, oxygen, and iodide ion), but the devices still degrade at high humidity environment.^[50] Another emerging strategy is to stabilize the perovskite materials by cation engineering (e.g., reducing the dimensionality of perovskite materials, tailor-making the perovskite surface with hydrophobic cations, forming 3D/2D stacking structure).

In review we discuss the significant role of ligand in the perovskite photovoltaics from the perspective of film formation, defect passivation and stability. In the first section, we will discuss the roles of ligand in fabricating high-quality perovskite films by different solution-processed methods, including one-step, two-step, and postdeposition treatment. In the second section, we will review the progress on ligand-passivated perovskites via post-treatment, in situ passivation during perovskite formation, and modifying the substrates before perovskite formation. In the third section, a discussion of ligand-stabilized perovskite films from the perspectives of crystal crosslinking, dimensionality engineering, and interfacial modification will be presented. Finally, we will give a summary and an outlook.

2. Ligand-Assisted Perovskite Formation

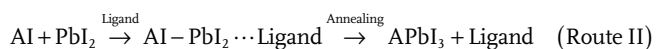
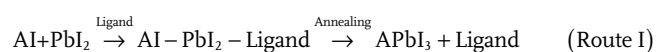
In this section, we will review the role of ligands in fabricating perovskite films by different solution-processed techniques (one-step, two-step, postdeposition treatment) for photovoltaic devices. The representative ligands are listed in Table 1.

2.1. One-Step Deposition

In conventional one-step method, due to the fast evaporation of solvent and weak interaction between solvent and perovskite precursors, the perovskite crystal forms too rapidly. As a result, an inhomogeneous and uncontinuous perovskite film with many pinholes is produced (Figure 2a).^[1,23,51] Perovskite films with poor morphology and low-quality lead to serious current leakage or interfacial recombination, thus reducing the device performances. Encouragingly, introduction of ligand in perovskite precursors significantly modulates the crystallization kinetics, and thus improving the film morphology, phase purity, and crystallographic orientation.

2.1.1. Morphology Control

In ligand-assisted pathway, ligand interacts with metal ions in perovskite framework in precursor solution and form an intermediate phase, which slows down the crystallization rate of perovskite and produces homogeneous nucleation, thus finally producing a uniform and dense perovskite crystalline film through the release of ligand during the post-treatment step (e.g., thermal annealing,^[30] antisolvent bath,^[52,53] vacuum treatment,^[32,54] gas-quenching,^[55] and pressure treatment^[56]). According to the chelation capacity of ligand, the morphology of perovskite films fabricated by using one-step deposition could be improved through the formation of I) stoichiometric intermediate films or II) nonstoichiometric intermediate phases in precursor solution



In the following parts, we will review the ligand-improved morphology of perovskite films fabricated by one-step methods from these two aspects.

I) *Formation of Stoichiometric Intermediate Films*: Besides acting as solvent, DMF can also interact with MAI and PbI₂ to form a metastable MAPbI₃·DMF intermediate.^[57] However, this intermediate prepared by conventional one-step methods has a needle-like morphology,^[28,58] which leads to a very rough perovskite film with many pinholes. To avoid the formation of needle-like MAPbI₃·DMF intermediate, Cheng and co-workers reported a fast crystallization deposition method to form smooth and highly uniform MAPbI₃ film.^[59] This approach involves the spin-coating of a DMF solution of MAPbI₃ on a substrate, followed immediately by exposure of the wet film to chlorobenzene^[59] or a dry argon gas flow^[55,60] to induce crystallization. Choy and co-workers reported a vacuum-assisted thermal annealing method to prepare pinhole-free and uniform MAPbI₃ films by modulating the thermal kinetics of 3MAI:PbCl₂ precursor films.^[54] Later, Seok and co-workers reported a solvent engineering method to prepare high-quality (smooth and highly crystalline) perovskite film, where the ligand DMSO was used to retarding the rapid reaction between MAI and PbI(Br)₂ via formation of a stable and uniform MAI(Br).PbI₂.DMSO intermediate phase.^[30] The extremely homogeneous intermediate film was converted into a pure crystalline MAPbI_{3-x}Br_x perovskite film after annealing at 100 °C (Figure 2b). A certified power-conversion efficiency of 16.2% and no hysteresis PVSCs has been achieved, which is also a milestone in the field of PVSCs. The mechanism of DMSO-assisted perovskite formation was unveiled by Rong et al.^[61] They demonstrated that the formation of stable intermediate MA₂Pb₃I₈(DMSO)₂ (see Figure 2c) is the key to controlling the crystallization kinetics of MAPbI₃. As of now, DMSO has been widely used to control the morphology of other types of perovskites, such as (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15},^[6] (FASnI₃)_{0.6}(MAPbI₃)_{0.4},^[62,63] Rb₅(Cs₅FAMA)₉₅Pb(I_{0.83}Br_{0.17})₃.^[33] Besides, some other studies demonstrated that the dropping time and properties (e.g., boiling point, miscibility, dipole moment) of the anti-solvent also have great influence on the composition and morphology of intermediate film and hence the quality of resulting perovskite films.^[64]

In addition to DMF and DMSO, other ligands have also been developed to control the perovskite morphology. For example, Cao and co-workers reported that thiourea is also an effective ligand to control the MAPbI₃ perovskite morphology.^[65] The thiourea-controlled MAPbI₃ films shown a compact micro-sized and monolithically morphology by forming the MAI.PbI₂.S=C(NH₂)₂ intermediate phase. The resulting PVSCs offered an impressive 18.46% PCE and excellent stability in ambient air. N-methyl-pyrrolidone (NMP) is another effective morphology controller for preparing smooth perovskite films. Zhou et al. reported that high-quality, smooth MAPbI_{1-x}Br_x perovskite films can be formed at room temperature by using NMP as solvent and ether as antisolvent.^[52] Zhu and co-workers employed NMP to modulate the properties (volatility and viscosity) of perovskite precursor inks to enable a wide precursor-processing window (up to ≈8 min) and a rapid grain growth rate (as short as ≈1 min). Coupled with antisolvent extraction, this precursor ink delivers high-quality perovskite films with

Table 1. Representative of ligand utilized for improving the performance and stability of perovskite photovoltaics.

Ligand	Molecular structure	The role of ligand			Perovskite	PCE [%]	V _{OC} loss [V]	Year/Ref
		Film formation	Passivation	Stability (test conditions/ retained PCE)				
O-Donor ligands								
N,N-Dimethyl-formamide (DMF)		Solvent and morphology controller	–	–	MAPbI ₃	16.2	0.51	2014 ^[59]
Dimethylsulfoxide (DMSO)		Solvent and morphology controller	–	–	MAPbI ₃	19.7	≈0.46	2015 ^[58]
N-Methyl-2-pyrrolidone (NMP)		Solvent and morphology controller	–	–	MAPbI ₃	15.2	0.47	2015 ^[52]
N-Cyclohexyl-2-pyrrolidone (CHP)		Morphology controller	–	–	MAPbI ₃	10	0.73	2014 ^[87]
Tetrahydrothiophene oxide (THTO)		Crystallo-graphic orienta-tion controller	–	–	MAPbI _{3-x} Cl _x	12.6	≈0.62	2016 ^[113]
Polyvinyl pyrrolidone (PVP)		Morphology and crystallo-graphic orienta-tion controller	–	Shelf life test in air in the dark, > 80% after 820 h	MAPbI _{3-x} Cl _x (85 nm)	5.36 (34% AVT)	≈0.62	2016 ^[91]
Poly(2-thyl-2-oxazoline) (PEOXA)		Morphology controller	–	–	MAPbI ₃ (50 nm)	6.16	0.48	2015 ^[90]
Polyethylene glycol (PEG or PEO)		–	Surface defects	MPP tracking under illumination in air,>95% after 15 h	MAPbI ₃	16.46	0.45	2018 ^[211]
		Morphology controller	–	Shelf life test in the dark under 70% RH, > 65 after 300 h	MAPbI ₃	≈16	0.57	2016 ^[183]
Benzoquinone (BQ)		Morphology controller	Bulk defects	MPP tracking under illumination (AM1.5G), > 80% after 950 h	MAPbI ₃	15.58	0.53	2017 ^[88]
Citric acid		Morphology and crystallo-graphic orienta-tion controller	–	–	MAPbI _{3-x} Cl _x	28.1 (1000-l _x white LED)	≈0.62	2017 ^[85]
Ascorbic acid (AA)		Morphology controller	Bulk defects	Shelf life test in the dark in N ₂ glovebox, > 80% after 30 d	FA _{0.5} MA _{0.5} Sn _{0.5} Pb _{0.5} I ₃	14.01	0.46	2015 ^[98]
Heparin sodium (HS)	(See Figure S1, Supporting Information)	Morphology controller	Bottom defects	Shelf life test, under dark in N ₂ glovebox, > 85% after 70 d	MAPbI ₃	20.1	≈0.44	2018 ^[169]
Methylammo-nium acetate (MAAc)		Morphology and phase purity controller	Bulk defects	Shelf life test, under dark at 85 °C, > 80% after 500 h	MAPbI ₃	19.19 (1 cm ²)	0.43	2017 ^[84]

Table 1. Continued.

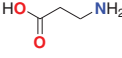
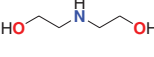
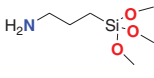
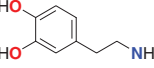
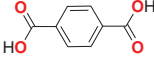
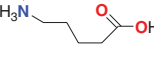
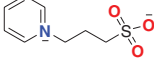
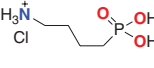
Ligand	Molecular structure	The role of ligand			Perovskite	PCE [%]	V _{OC} loss [V]	Year/Ref
		Film formation	Passivation	Stability (test conditions/ retained PCE)				
Urea		Morphology controller	Bulk defects	Shelf life test, under dark, > 65% after 27 d	MAPbI ₃	18.25	≈0.46	2017 ^[70]
Sulfamic acid		Morphology and band structure controller	–	Shelf life test, under dark, > 65% after 81 d	MAPbI ₃	16.02	≈0.55	2016 ^[86]
3-Aminopropionic acid		Morphology controller	Bottom defects	–	MAPbI ₃	≈12	≈0.72	2014 ^[164]
Diethanolamine (DEA)		Morphology controller	Bottom defects	Shelf life test, under dark in N ₂ glovebox, > 85% after 60 d	MAPbI _{3-x} Cl _x	≈16	0.60	2016 ^[167]
Aminopropyl trimethoxysilane		Morphology controller	Bottom defects	–	MAPbI ₃	15.67	0.47	2015 ^[165]
Dopamine		Morphology controller	Bottom defects	Shelf life test, under ambient conditions, > 80% after 250 h	MAPbI ₃	18.5	0.47	2018 ^[170]
Polyurethane (PU)		Morphology controller	Bulk defects	Shelf life test, under ambient conditions, > 90% after 400 h	MAPbI ₃	18.7	0.50	2017 ^[92]
Terephthalic acid (TPA)		Morphology controller	Bulk defects	Shelf life test, under ambient conditions with 30% humidity, > 80% after 15 d	MAPbI ₃	18.5	0.45	2017 ^[184]
5-Ammonium valeric acid (5-AVA ⁺)		Morphology controller	Bulk/ bottom defects	MPP tracking under illumination (AM1.5G) in ambient air, ≈100 after 1000 h	MAPbI ₃	12.84 (certified)	0.69	2014 ^[21]
		Morphology controller	Bulk/ bottom defects	MPP tracking under illumination (AM1.5G), ≈100 after 10 000 h	MAPbI ₃	11.2 module (10 × 10 cm ²)	0.69	2017 ^[206]
3-(1-Pyridinio)-1-propanesulfonate (NDSB 201)		Morphology and phase purity controller	–	Shelf life test, in air, > 85% after 30 d	CsPbI ₃	11.4	0.57	2017 ^[110]
4-phosphonobutan-1-aminium		Morphology controller	–	Shelf life test, in ambient air at ≈55% humidity in the dark, > 80% after 500 h	MAPbI ₃	16.7	0.55	2015 ^[181]
N-Donor ligands								
Formamidinium (FA)		Cation exchange	–	–	MAPbI ₃ →FAPbI ₃	18.1	0.44	2016 ^[147]
Graphitic carbon nitride (g-C ₃ N ₄)	(see Figure S1, Supporting Information)	Morphology controller	Bulk defects	–	MAPbI ₃	19.49	0.48	2018 ^[176]
Nitrogen-doped reduced graphene oxide (N-RGO)	(see Figure S1, Supporting Information)	Morphology controller	Surface and bulk defects	–	FA _{0.85} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃	18.7	0.42	2016 ^[175]

Table 1. Continued.

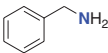
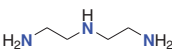
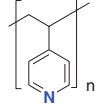
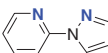
Ligand	Molecular structure	The role of ligand			Perovskite	PCE [%]	V_{OC} loss [V]	Year/Ref
		Film formation	Passivation	Stability (test conditions/ retained PCE)				
Benzylamine		–	Surface defects	Shelf life test, in air at $55 \pm 5\%$ RH in the dark, > 50% after 2900 h	FAPbI ₃	19.0	0.36	2016 ^[156]
1-Adamantylamine (ADA)		Post treatment	Surface defects	MPP tracking under illumination in ambient air, > 80% after 300 h	Cs _{0.04} MA _{0.16} FA _{0.8} PbI _{0.85} Br _{0.15}	21.3	≈0.45	2018 ^[209]
Diethylenetriamine (DETA)		Postdevice treatment	Surface defects	MPP tracking under illumination in N ₂ at 30°C, > 96% after 300 h	MAPbI ₃	20.13	0.48	2018 ^[217]
4-tert-butylpyridine (TBP)		Morphology controller	–	Shelf life test, in ambient air at ≈55% humidity in the dark, > 80% after 35 d	MAPbI ₃	16.70	0.48	2015 ^[118]
Pyrazine		Morphology controller	–	Shelf life test, encapsulated cells stored in the dark under ambient condition, > 98% after 100 d	FASnI ₃	4.80	1.08	2016 ^[97]
Pyridine (Py)		Morphology controller	–	Shelf life test, encapsulated cells stored in the dark under ambient condition, > 95% after 1000 h	MAPbI ₃	17.10	0.50	2017 ^[19]
Poly(4-vinylpyridine) (PVPy)		–	Surface defects	Shelf life test, unencapsulated cells stored under ambient condition, > 85% after 30 d	MAPbI ₃	≈15	0.50	2017 ^[160]
2-(1H-pyrazol-1-yl)pyridine		Morphology controller	Bulk defects	Shelf life test, unencapsulated cells stored in ambient environment (85 °C/55% RH), > 80% after 35 h	Cs _{0.04} MA _{0.16} FA _{0.8} PbI _{0.85} Br _{0.15}	18.1	0.55	2018 ^[223]
Dimethylammonium (DI)		Morphology controller	–	Shelf life test, unencapsulated cells stored in ambient atmosphere (RH 80%), > 80% after 200 h	(DI) ₂ (FA) ₈ Pb ₉ I ₂₈	15.02	0.54	2018 ^[204]
Trimethylammonium chloride (TACl)		Morphology controller	Bulk defects	–	MAPbI ₃	20.7	0.40	2018 ^[82]
Hydrazinium chloride		Morphology controller	–	–	MAPbI ₃	11.4	0.63	2017 ^[81]
Choline chloride		Post treatment	Surface defects	Shelf life test, unencapsulated cells stored in ambient atmosphere (RH 50–85%), ≈100% after 30 d	FA _{0.85} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃	20.59 ± 0.45% (certified)	0.41	2017 ^[161]

Table 1. Continued.

Ligand	Molecular structure	The role of ligand			Perovskite	PCE [%]	V _{OC} loss [V]	Year/Ref
		Film formation	Passivation	Stability (test conditions/ retained PCE)				
Guanidinium (GA ⁺)		Morphology controller	Bulk defects	Shelf life test, cells stored under a dry oxygen environment, T ₈₀ >300 h	MAPbI ₃	17	0.48	2016 ^[173]
		Morphology controller	Bulk defects	MPP tracking at 60 °C under continuous light illumination (AM 1.5G) in an argon atmosphere, > 60% after 1000 h	MA _{0.86} GA _{0.14} PbI ₃	20.15	≈0.52	2017 ^[174]
Ethylenedi-ammonium (EDA ²⁺)		Morphology and Phase purity	—	Shelf life test, unencapsulated cells stored in a dark dry box, > 85% after 30 d	CsPbI ₃	11.8	0.58	2017 ^[111]
Propane-1,3-diaminium (PR)		Morphology controller	—	Shelf life test, unencapsulated cells stored in ambient atmosphere (RH 80%), > 80% after 150 h	(PR) ₂ (FA) ₈ Pb ₉ I ₂₈	12.92	0.53	2018 ^[204]
Butane-1,4-diaminium (BU)		Morphology controller	—	Shelf life test, unencapsulated cells stored in ambient atmosphere (RH 80%), > 80% after 150 h	(BU) ₂ (FA) ₈ Pb ₉ I ₂₈	11.71	0.58	2018 ^[204]
C8 diammonium iodide		Morphology controller	Bulk and Surface defects	—	MAPbI ₃	17.60	0.445	2016 ^[157]
Octylammonium (OA)		Morphology and crystallographic orientation controller	—	Shelf life test, unencapsulated cells stored at 85 °C in ambient atmosphere, > 80% after 760 h	MAPbI ₃	20.6	0.44	2018 ^[117]
Tetrabutylammonium (TBA ⁺)		Morphology controller	—	Shelf life test, unencapsulated cells stored in ambient atmosphere, > 95% after 45 d	MAPbI ₃	≈10	≈0.72	2017 ^[202]
iso-Butylammonium (iso-BA ⁺)		—	—	unencapsulated films stored in ambient (60% RH) maintain its initial color after 840 h	(iso-BA) ₂ (MA) ₃ Pb ₄ I ₁₃	10.63	0.54	2017 ^[201]
Butylammonium (BA ⁺)		Crystallographic orientation controller	—	Shelf life test, unencapsulated cells stored under continuous light illumination (AM1.5G), > 60% after 2250 h	(BA) ₂ (MA) ₃ Pb ₄ I ₁₃	12.52	0.64	2016 ^[198]
2,2,2-Trifluoroethanaminium (FEA ⁺)		Morphology controller	—	Shelf life test, unencapsulated cells stored in ambient atmosphere, > 90% after 120 d	MAPbI ₃	18	0.47	2016 ^[200]

Table 1. Continued.

Ligand	Molecular structure	The role of ligand			Perovskite	PCE [%]	V_{OC} loss [V]	Year/Ref
		Film formation	Passivation	Stability (test conditions/ retained PCE)				
Polyethylenimine (PEI)	(see Figure S1, Supporting Information)	Morphology controller	Bottom defects	Shelf life test, unencapsulated cells stored in ambient atmosphere under continuous illumination, > 90% after 200 h	MAPbI ₃	13.8	0.48	2015 ^[203]
Benzylammonium (BE ⁺)		Morphology controller	–	Shelf life test, unencapsulated cells stored in ambient atmosphere (RH 80%), > 80% after 500 h	(BE) ₂ (FA) ₈ Pb ₉ I ₂₈	17.40	≈0.44	2018 ^[204]
Phenylethylammonium (PEA)		–	–	Perovskite materials show no change after stored in 52% RH environment for 46 d	(PEA) ₂ (MA) ₂ Pb ₃ I ₁₀	4.73	0.72	2014 ^[187]
		Phase purity	–	Shelf life test, unencapsulated cells stored in air (RH 40 ± 5%), > 90% after 16 d	FA _x PEA _{1-x} PbI ₃	17.7	0.47	2017 ^[193]
Cyclopropanaminium (CA)		Morphology controller	–	Shelf life test, unencapsulated cells stored in air (RH 63 ± 5%), > 54% after 220 h	MAPbI _{3-x} Cl _x	13.86	0.63	2016 ^[214]
S-Donor ligands								
2-Aminoethanethiol (2-AET)		Morphology controller	–	Maintain perovskite structure after immersion in water for a long time (>10 min)	MAPbI ₃ ·(2-AET) _{0.75}	–	–	2016 ^[182]
Thiourea		Morphology and phase purity controller	–	–	FAPbI ₃	13.6	≈0.52	2016 ^[68]
Thio-semicarbazide (TSC)		Morphology and phase purity controller	Bulk defects	Shelf life test in the dark at 85 °C, > 80% after 500 h	MAPbI ₃	19.19 (1 cm ²)	0.43	2017 ^[84]
2-Pyridylthiourea		Morphology controller	Bulk and surface defects	Shelf life test, under ambient air of 55 ± 5% RH in the dark and under 65 °C, > 90% after 30 d	MAPbI ₃	18.2	0.45	2017 ^[72]
1,3,4-Thiadiazolidine-2-thione (TDZT)		Morphology controller	Bulk defects	Shelf life test, in 30% RH ambient air at 60–75 °C under dark, > 90% after 400 h	MAPbI ₃	17.89	0.46	2018 ^[67]
1,3,4-Thiadiazolidine-2,5-dithione (TDZDT)		Morphology controller	Bulk defects	Shelf life test, in 30% RH ambient air at 60–75 °C under dark, > 90% after 800 h	MAPbI ₃	19.04	0.45	2018 ^[67]

Table 1. Continued.

Ligand	Molecular structure	The role of ligand			Perovskite	PCE [%]	V _{OC} loss [V]	Year/Ref
		Film formation	Passivation	Stability (test conditions/ retained PCE)				
Methimazole (MMI)		Morphology controller	Surface defects	Shelf life test, under continuous illumination in N ₂ atmosphere, > 80% after 670 h	MAPbI ₃	20.10	≈0.42	2018 ^[212]
Thiophene		–	Surface defects	–	MAPbI _{3-x} Cl _x	14.1	0.53	2014 ^[38]
Dimethylsulfide		Morphology controller	Bulk defects	Shelf life test, in 35% RH ambient air in the dark, > 80% after 60 d	MAPbI ₃	18.40 (flexible)	0.45	2018 ^[83]
2,3,4,5,6-pentafluorobenzethiol (HS-PhF ₅)		–	Surface defects	Shelf life test, in 45% RH ambient air, > 80% after 10 d	MAPbI ₃	13.20	0.53	2015 ^[208]
4-Mercaptobenzonitrile		–	Surface defects	MPP tracking at 50 °C under continuous light illumination (AM 1.5G) in air, > 85% after 185 h	Cs _{0.05} FA _{0.79} MA _{0.16} PbI _{2.49} Br _{0.51}	19.6	≈0.42	2018 ^[163]
4-Mercaptobenzoic acid (HS-Ph-COOH)		–	Bottom defects	Shelf life test, in 45% RH ambient air, > 50% after 100 h	MAPbI ₃	14.1	≈0.52	2015 ^[208]
Other ligands								
1,8-diiodooctane (DIO)		Morphology controller	–	–	MAPbI _{3-x} Cl _x	≈12	0.50	2014 ^[77]
1-Chloronaphthalene (CN)		Morphology controller	–	–	MAPbI _{3-x} Cl _x	≈9	0.58	2015 ^[79]
Tetraphenylphosphonium iodide (TPPI)		Morphology controller	–	–	MAPbI _{3-x} Cl _x	11.7	0.65	2015 ^[78]
Trioctylphosphine (TOP)		Solvent of PbI ₂ for metal cation exchange	–	–	FASnI ₃ →FAPbI ₃	–	–	2017 ^[148]
Trioctylphosphine oxide (TOPO)		Post treatment	Surface defects	Shelf life test, in 75% RH ambient air in the dark, > 36% after 48 h	MAPbI ₃	12.8	0.63	2018 ^[210]
Rubrene	(see Figure S1, Supporting Information)	Post treatment	Surface and bulk defects	Shelf life test, in 70% RH environment at 25 °C, > 98% after 30 d	FA _{0.15} MA _{0.85} PbI ₃	20.80 (certified)	≈0.46	2018 ^[213]
Iodopentafluorobenzene (IPFB)		–	Surface defects	–	MAPbI _{3-x} Cl _x	15.7	0.47	2014 ^[153]

Table 1. Continued.

Ligand	Molecular structure	The role of ligand			Perovskite	PCE [%]	V_{OC} loss [V]	Year/Ref
		Film formation	Passivation	Stability (test conditions/ retained PCE)				
2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4TCNQ)		–	Surface defects	Shelf life test, unencapsulated cells stored in ambient air, > 75% after 40 d	MAPbI ₃	18.1	0.49	2016 ^[154]
IDIC	(see Figure S1, Supporting Information)	–	Surface defects	Shelf life test, cells stored in a dry inert atmosphere, > 90% after 30 d	MAPbI ₃	19.5	0.44	2016 ^[159]
PFN-2TNDI	(see Figure S1, Supporting Information)	–	Surface defects	Shelf life test, unencapsulated cells stored in ambient atmosphere (RH 50 ± 10%, 25 ± 2 °C), > 50% after 160 h	MAPbI _{3-x} Cl _x	16.7	0.57	2016 ^[155]
PCDTBT	(see Figure S1, Supporting Information)	Morphology controller	Bulk defects	Shelf life test, unencapsulated cells stored in ambient atmosphere (RH 30%, 28 °C), > 80% after 192 h	MAPbI _{3-x} Cl _x	14.62	0.63	2017 ^[177]

large-scale uniformity.^[66] Recently, Li and co-workers reported that two thiadiazole derivatives (1,3,4-thiadiazolidine-2-thione, TDZT and 1,3,4-thiadiazolidine-2,5-dithione, TDZDT) are added into a perovskite precursor to modulate MAPbI₃ perovskite crystal growth and enlarge grain size.^[67]

The emerging binary ligand strategy has been reported to effectively control the morphology of perovskite films by combining their individual advantages. Park and co-workers investigated the synergistic effect of DMSO and thiourea on modulating the morphology and crystallization of FAPbI₃ film via the new formed FA.PbI₂.(DMSO_{1-x} thiourea_x) intermediate phase.^[68] Compared with small domains and rough surface of the FAPbI₃ film prepared without thiourea ($x = 0$), the FAPbI₃ film prepared from the FA.PbI₂.(DMSO_{0.8} thiourea_{0.2})

intermediate shows larger domains with highly smooth surface. The DMSO can help to form uniform perovskite films with full coverage morphology and thiourea is capable to enlarge the crystal size. Similarly, Kim and co-workers reported that using NMP and DMSO binary ligands can improved the morphology of perovskite film via forming a mixed intermediate phase, which contains a NMP.PbI₂.MAI intermediate, a DMSO.PbI₂.MAI intermediate and MAPbI₃ crystals.^[69] Recently, Urea was reported to enlarge the grain size of MAPbI₃ through the formation of MAI.PbI₂.DMSO.urea intermediate.^[70,71] This new binary ligand (DMSO and urea)-controlled MAPbI₃ film displayed single interfaces of large grains along the direction perpendicular to the substrate, whereas the single ligand (DMSO)-controlled MAPbI₃ film showed multiple interfaces between

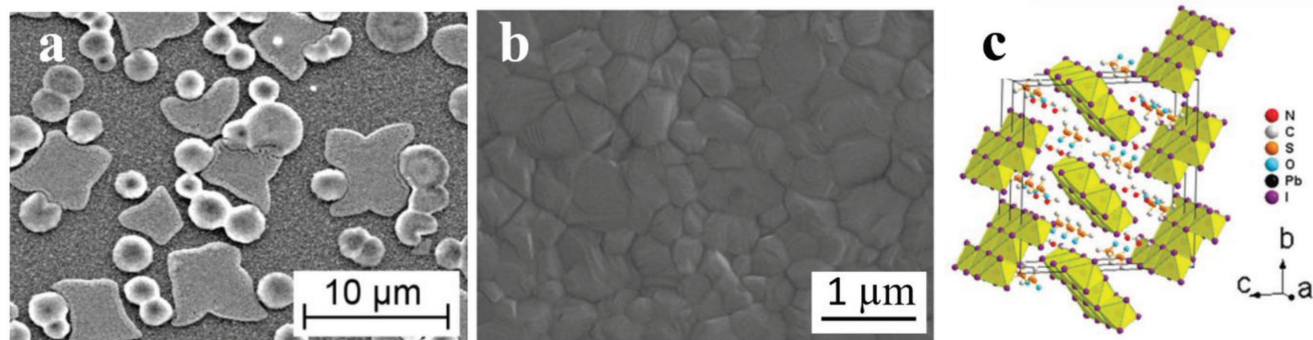


Figure 2. a) Scanning electron microscopy (SEM) images of the conventional one-step deposition of perovskite film without ligand engineering. The solvent used in (a) is GBL. Reproduced with permission.^[28] Copyright 2013, Nature Publishing Group. b) SEM image of perovskite film with ligand assistant. Reproduced with permission.^[30] Copyright 2014, Nature Publishing Group. c) Crystal structure of the intermediate phase MA₂Pb₃I₈·(DMSO)₂. Reproduced with permission.^[61] Copyright 2015, Royal Society of Chemistry.

several smaller grains. Wang and co-workers reported that binary ligand system (2-pyridylthiourea and DMSO) could also effectively control the growth of uniform and compact MAPbI₃ film with large grains in ambient air due to the strong interaction between 2-pyridylthiourea and PbI₂.^[72]

II) Formation of Nonstoichiometric Intermediate Phases in Precursor Solution: Chloride is a very effective ligand to modulate the crystallization and improve the morphology of perovskite films by using one-step deposition method. Initially, inorganic chloride additives (e.g., PbCl₂,^[23,25] MACl,^[54,73] NH₄Cl^[74]) were used to improve the morphology of perovskite films. The Cl⁻ anions provided by those ionic additives slowed down the crystallization rate of perovskite and improve film morphology, conductivity and charge diffusion length of the perovskite without affecting its optical properties.^[4,75] Organic halogenated additives (e.g., alkyl halides,^[76,77] phosphonium halides,^[78] 1-chloronaphthalene (CN),^[79,80] hydrazinium chloride,^[81] and trimethylammonium chloride (TACl)^[82]) could temporarily chelate with Pb²⁺ during crystal growth, which promoted homogenous nucleation and likely modified interfacial energy favorably, ultimately altering the kinetics of crystal growth and led to improved film morphology. Jen and co-workers reported that the bidentate halogenated additives (e.g., 1,8-diiodooctane (DIO)) modified the morphology of MAPbI_{3-x}Cl_x perovskite films by modulating the crystallization rate.^[77] As a result, the morphology of the perovskite films processed from the solution with 1wt% DIO showed a smoother and more continuous surface than that obtained from the pristine DMF solution. Song et al. demonstrated that crystallinity and morphology of MAPbI_{3-x}Cl_x perovskite could be improved by introducing CN additive in the perovskite precursor solution, which resulted in a 30% efficiency improvement compared with the reference devices.^[79] Later, the CN was used to improve the crystallization and surface coverage of the FAPbI₃ films by Liu and co-workers.^[80] As a result, with the addition of the CN additive, the efficiency of the FAPbI₃ planar-type solar cells was enhanced by 15%, from 14.33% to 16.53%. Recently, Liu and co-workers demonstrated that S-donor ligand (dimethyl sulfide) can react with Pb²⁺ to form a chelated intermediate, which slows down the crystallization rate, leading to a larger grain size for resultant perovskite film. The enhanced morphology of perovskite film pushes the record PCE of the flexible PVSCs up to 18.40%.^[83]

A binary ligand additive (methylammonium acetate (MAAc) and thio-semicarbazide (TSC)) has been reported to modulate the film morphology and crystalline quality by Wu et al.^[84] The MAAc could help to form uniform perovskite films with full coverage morphology and TSC was capable to enlarge the crystal size. Their combination resulted in a uniform MAPbI₃ perovskite film with large crystals, low density of defects, and ultrasmooth surface over inch-sized planar substrates. A certified PCE of 19.19% had also been achieved for large-area (1.025 cm²) MAPbI₃ PVSCs. As listed in Table 1, other organic acids (e.g., citric acid,^[85] sulfamic acid,^[86] 5-ammoniumvaleric acid^[21]) and small organic molecules (e.g., N-cyclohexyl-2-pyrrolidone (CHP),^[87] benzoquinone (BQ),^[88] 4-tert-butylpyridine (TBP)^[89]) have also been used to improve the film morphology and crystalline quality of perovskite films by one-step deposition method.

Polymer with functional groups can also effectively control the morphology of perovskite films by retarding the crystallization rate of perovskite through strong chelation with lead ions in the perovskite structure. For instance, Yip and co-workers first reported poly(2-ethyl-2-oxazoline) (PEOXA) as the polymer additive to control the morphology of MAPbI₃ films.^[90] At optimized conditions, the planar PVSCs composed of a thin layer of perovskite film (≈50 nm) exhibits a PCE 6.35%, which outperformed that of the devices with pristine perovskite film. Nakamura and co-workers employed poly-vinylpyrrolidone (PVP) to reduce the grain size and stabilize the cubic phase of MAPbI_{3-x}Cl_x nanocrystal films.^[91] Using this PVP-capped perovskite nanocrystal films, a high performance semi-transparent PVSCs with 5.36% PCE at 34% average visible transmittance (AVT) was realized. Chen and co-workers have recently reported the MAPbI₃ morphology could be improved by incorporating the elastomer polyurethane (PU) into the perovskite precursor solution to retard the crystallization rate.^[92] Interestingly, the doping of PU significantly enhanced the bendability of perovskite films, due to the formation of a crosslinked network at the grain boundaries by PU.

Ligand-assisted strategies can also control the morphology of lead-free perovskites. Kanatzidis and co-workers^[93] and Snaith and co-workers^[94] have reported that 5–6% efficiencies MASnI₃ PVSCs can be achieved by using DMF as solvent. However, owing to the greater Lewis acidity of Sn²⁺ versus Pb²⁺, the tin perovskites crystallize much more rapidly than those of lead perovskites when DMF is the solvent, which leads to an uncontrolled film morphology. Kanatzidis and co-workers later reported that highly uniform, pinhole-free MASnI₃ films were obtained from a DMSO solution via a transitional SnI₂·3DMSO intermediate phase.^[95] Similarly, Yan and co-workers employed DMSO as morphology controller to form an uniform pinhole-free FASnI₃ film for high performance lead-free PVSCs with efficiency of 6.22%.^[63] Although the oxidation of Sn²⁺ to Sn⁴⁺ in tin perovskites could be inhibited by the addition of SnF₂,^[63,96] excess SnF₂ will induce phase separation on the surface of the perovskite film. Seok and co-workers reported a new strategy for the homogeneous dispersion of SnF₂ in FASnI₃ film by forming a complex with pyrazine.^[97] The introduction of pyrazine provided beneficial effects for improving the surface morphology and preventing the unwanted Sn oxidation. Consequently, reproducible FASnI₃ PVSCs with a high PCE of 4.8% has been achieved. Recently, Jen and co-workers demonstrated that ascorbic acid (AA) can serve as an antioxidant for retarding the oxidation of Sn²⁺ and a morphology controller of tin-based perovskite films by forming intermediate complexes with SnI₂.^[98] Using AA as additive, MA_{0.5}FA_{0.5}Pb_{0.5}Sn_{0.5}I₃ PVSC showed a high PCE of 14.01% with improved stability, better than the control device (12.18%) processed with the regular SnF₂ additive.

Furthermore, ligand engineering has also successfully applied to control the film morphology of Bismuth (Bi)-based perovskites. A₃Bi₂I₉ (A: MA or Cs) perovskites was first applied to solar cells by Park et al.^[99] Although PCEs of 0.12% and 1.09% has been achieved in MA₃Bi₂I₉ and Cs₃Bi₂I₉ PVSCs, the morphology of the formed Bi-based perovskite films was nonuniform and with many pinholes. Recently, Miyasaka and co-workers modulated the morphology of MA₃Bi₂I₉ perovskites by bringing in a small amount of NMP into the precursor

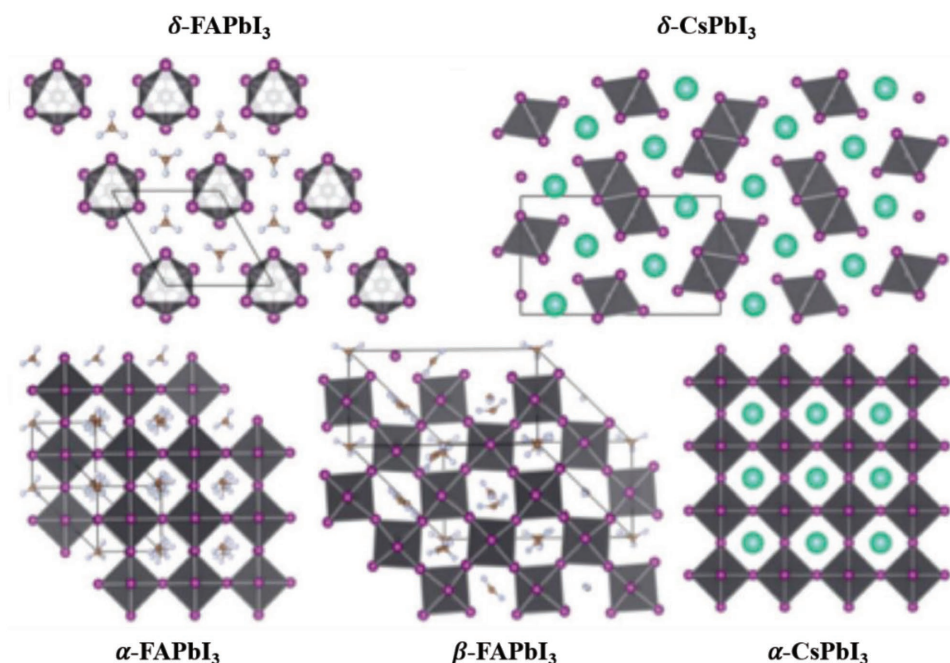


Figure 3. Various phases of FAPbI₃ and CsPbI₃ perovskites. Reproduced with permission.^[103] Copyright 2016, Royal Society of Chemistry.

solution as a morphology controller.^[100] Because of high boiling point and low vapor pressure, NMP slowed down the evaporation of solvent mixture during the spin-coating process and facilitated slow crystallization with uniform film formation of MA₃Bi₂I₉ perovskite. An optimal low concentration of 2.5% NMP added to the precursor solution improved the power conversion efficiencies of MA₃Bi₂I₉ PVSCs up to 0.31%.

2.1.2. Phase Purity

Compared to MAPbI₃, the black perovskite FAPbI₃ (α -phase) was considered to be a promising light harvester owing to its narrow bandgap (≈ 1.48 eV).^[101] However, it is phase-unstable in an ambient humid atmosphere and tends to turn into the yellow FAPbI₃ (δ -phase) with hexagonal nonperovskite structure (Figure 3), which limits its practical applications to stable photovoltaic devices. Seok and co-workers reported the formation of phase-pure mixed-organic-cation perovskite (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} by incorporating 15% bromine.^[6] A certified efficiency of 17.9% has been achieved by using this phase-pure, stable perovskite in mesoporous TiO₂-based solar cells. However, the incorporation of bromine is expected to increase the bandgap, resulting in a loss of light harvesting at longer wavelengths and thus a decrease in photocurrent. Wang et al. employed HI to develop a new precursor HPbI₃, which enables formation of highly crystalline phase FAPbI₃ films with strong (110) preferred orientation through a one-step spin-coating process.^[102] Adding small amounts of inorganic cesium (Cs) into precursor could form phase-pure FA-based perovskite. First principles calculations showed that the remarkable stabilization of the perovskite phase by mixing Cs and FA cations stems from entropic gains and the small internal energy input required for the formation of their solid solution (Figure 3).^[103]

Lee et al. demonstrated that incorporation of 10% Cs⁺ into FAPbI₃ to form phase-pure perovskite Cs_{0.1}FA_{0.9}PbI₃, which substantially improve irradiation- and moisture stability along with photovoltaic performance compared to pristine FAPbI₃ film.^[104] Saliba et al. incorporated 5% Cs⁺ into FA/MA precursors to prepare triple cations perovskite films, which were thermally more stable, contained less phase impurities and were less sensitive to processing conditions. This strategy enables more reproducible device performances to reach a stabilized power output of 21.1% and $\approx 18\%$ after 250 h under operational conditions.^[105] Recently, Xie et al. proposed a vertical recrystallization method to prepare high-quality FA-based perovskite film with vertically orientated single-grain-like morphology.^[106] Unlike conventional methods involving the introduction of additives in precursors, they controlled the recrystallization process of the pre-deposited yellow δ -phase FAPbI₃ film by deposition of a certain amount of MACl on top to trigger homogeneous nucleation. Upon annealing, MACl vertically diffused into the δ -phase FAPbI₃ films to realize the phase transformation to black α -phase FA perovskite (Figure 3). As a result, the FA-based PVSCs achieved a PCE of 20.65%.

All-inorganic perovskite α -CsPbI₃ is another promising candidate for stable and efficient wide-bandgap PVSCs due to its super thermal stability and suitable bandgap (≈ 1.73).^[107] However, the phase transition from yellow δ phase to black α phase has been reported to occur at temperature of ≈ 310 °C. Upon cooling, the CsPbI₃ material suffers from a spontaneously phase transition from black α phase to yellow δ phase under ambient conditions at room temperature (Figure 3).^[108] Many ligands have been developed to stabilize the α -phase of CsPbI₃ at room temperature. For example, Snaith and co-workers first reported a working CsPbI₃ solar cell with PCE of 2.9% by using HI-induced α -CsPbI₃ films.^[107] The addition of HI into precursor solution decreases the energy barrier for film formation

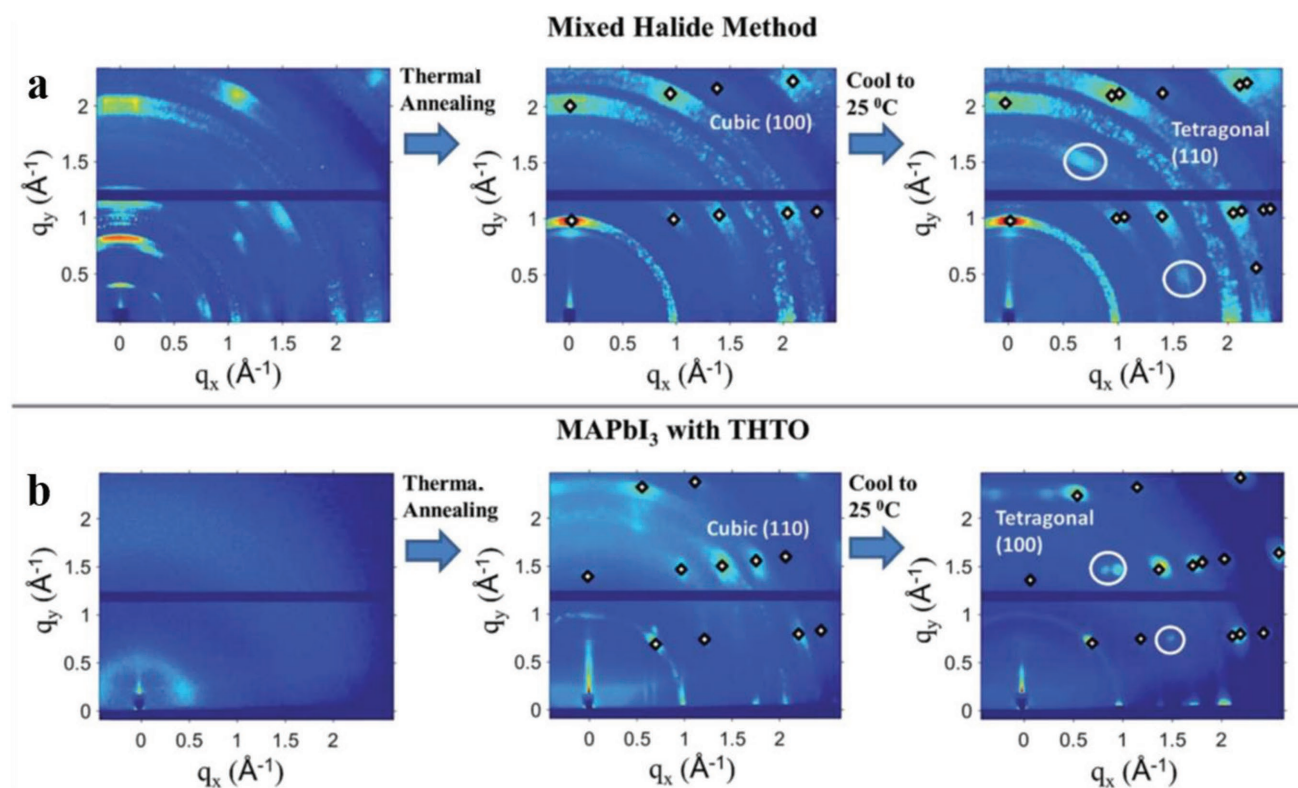


Figure 4. Ligand-controlled crystallographic orientation in perovskite films. In situ grazing incidence X-ray diffraction patterns during MAPbI₃ thin film growth a) without and b) with THTO. Diamonds indicate the calculated peak positions from the MAPbI₃ lattice for a given orientation. Circles indicate the visible new peaks arising from the cubic to tetragonal phase transition. Reproduced with permission.^[113] Copyright 2017, Royal Society of Chemistry.

and improves the phase stability of α -CsPbI₃ due to the reduced grain sizes. The introduction of surface capping ligands into precursor solution is another effective strategy to stabilize the α -CsPbI₃ films at room temperature. Jin and co-workers demonstrated that two different metastable CsPbI₃ perovskite polymorphs in the cubic (α -CsPbI₃) and the orthorhombic (β -CsPbI₃) structures can be directly synthesized in a one-step spin coating film deposition by using oleylammonium (OA⁺) or phenylethylammonium (PEA⁺), respectively.^[109] Both phases are stable at room temperature for months. As a proof-of-concept, a planar heterojunction solar cell based on stabilized α -CsPbI₃ perovskite thin film was demonstrated to show a PCE of $\approx 6.5\%$. At almost the same time, Huang and co-workers reported that sulfobetaine zwitterion could serve as efficient ligand to stabilize the cubic phase of CsPbI₃ by the formation of small CsPbI₃ grains with average size of ≈ 30 nm. The zwitterions were also found to inhibit the crystallization of CsPbI₃ films via electrostatic interaction with the ions and colloids in the CsPbI₃ precursor solution. The PVSCs with these cubic CsPbI₃ nanocrystals achieved a high efficiency of 11.4% and super stability.^[110] More recently, Zhao and co-workers stabilized the α -CsPbI₃ perovskite films by introducing ethylenediamine cations (EDA²⁺).^[111] The terminal NH₃⁺ groups of EDA were expected to cross-link the CsPbI₃ crystal units, rendering them less prone to unwanted phase transition to the yellow δ phase. PVSCs based on the α -CsPbI₃ films showed improved performance and achieved a highly reproducible PCE of 11.8% (a record for CsPbI₃ PVSCs). Besides, the resulting α -CsPbI₃

films are highly robust at room temperature for months and can retain their phase even after annealing at 100 °C for a week.

2.1.3. Crystallographic Orientation

Controlling the crystallographic orientation of perovskite polycrystalline films is quite important in PVSCs, as recently shown, there is a large variation of photovoltaic performance with different crystal facets.^[112] However, it is difficult to control the growth process and crystallographic orientation of perovskite films simultaneously with the homogeneous nucleation as well as crystallization from intermediate structures. Ligand engineering is an effective way to avoid the uncontrolled crystallographic orientation of perovskites by tuning the surface energies of different facets. For instance, addition of tetrahydrothiophene oxide (THTO) in MAPbI₃ precursor solution could result in a dramatically reduced nucleation density of as few as one per square millimeter, and a smooth perovskite film with a strong tetragonal (100) crystallographic orientation.^[113] By examining the growth process in situ with grazing incidence X-ray diffraction (Figure 4b), it was found that the THTO suppressed homogeneous nuclei as well as crystalline intermediate structures. Instead, heterogeneous nucleation at the interface and growth of a highly oriented MAPbI₃ thin film occur directly from the precursor solution. Density functional theory (DFT) calculations show that the THTO additives selectively lower the surface energy of a

particular facet, which results in the tetragonal (100) crystallographic orientation. The crystallographic orientation of the MAPbI₃ thin film was found to significantly impact the open circuit voltage of solar cell devices, which highlighted the importance of controlling the thin film orientation. Diau and co-workers reported a one-step room-temperature crystallization method to grow uniform and compact perovskite nanocrystals using NMP as solvent.^[114] The NMP-based perovskite films shown a preferred orientation at facet (004) with large crystalline grains, whereas those produced with other solvents or via thermal annealing methods showed greater intensity at facet (220) with small crystals. Snaith and co-workers demonstrated that introduction of *n*-butylammonium cations into perovskite precursor greatly favored the formation of 3D FA/Cs mixed cation perovskites with the orientation of the^[100] direction parallel to the film normal.^[115] The synergy of NH₄Cl and moisture on the crystallization of MAPbI₃ has been reported to improve the performance of printable carbon-based PVSCs.^[116] The formation and transition of intermediate MAX.NH₄PbX₃(H₂O)₂ (X=I or Cl) enables high-quality perovskite MAPbI₃ crystals with preferential growth orientation along the^[110] direction. Correspondingly, the intrinsic perovskite devices based on MAPbI₃ achieved an efficiency of 15.6% and a lifetime of over 130 days in ambient condition with 30% relative humidity. Recently, octylammonium (OA) was employed to improve degree of preferential orientation of MAPbI₃. Adding a small amount of OA (e.g., 3.3 wt%), the intense scattering intensity

of grazing incidence wide angle X-ray scattering (GIWAXS) was found at the azimuthal angle of 90°, suggesting that the crystal planes are highly oriented parallel to the substrate, which is responsible for improved charge transport property.^[117]

2.2. Two-Step Deposition

For the two-step sequential deposition, the conversion and film morphology of the final perovskite film strongly depend on the initial PbX₂ film during the first step of the process.^[20,28,29,118] Conventionally, PbX₂ from DMF solution tends to form a layered and dense crystalline film on a flat substrate (see Figure 5a). However, the complete conversion of PbX₂ to perovskite on exposure to the MAX solution usually requires several hours.^[28,29] However, this long reaction time in MAI solution could lead to the dissolution of perovskites. The introduction of ligand has been demonstrated favor the conversion of PbX₂ film into perovskites through the formation of metal halides nanostructures, metal halide adducts, nanostructured metal halide adducts, and the modification of organic ammonium halide solutions.

2.2.1. Ligand-Induced Formation of Metal Halides Nanostructures

Constructing PbX₂ nanostructures is a very effective strategy to fully convert PbX₂ into perovskites due to the increased

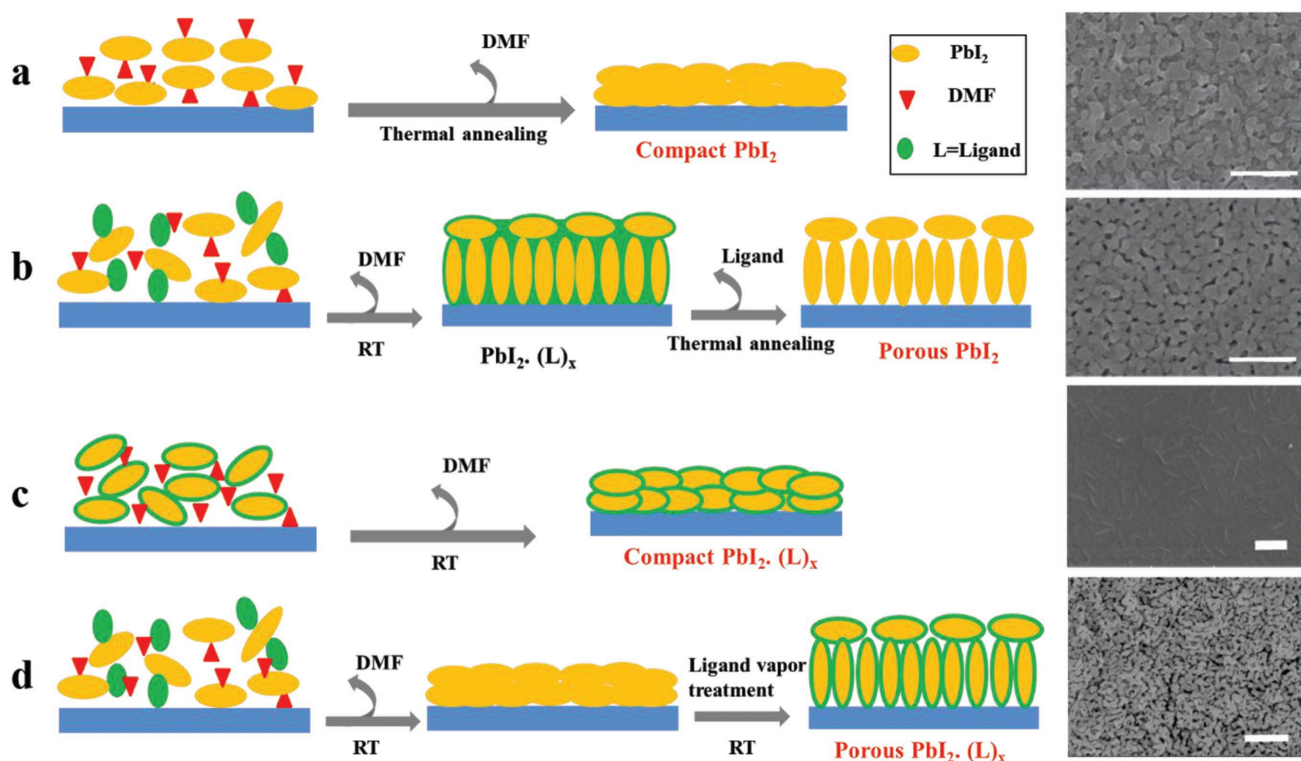


Figure 5. Two-step deposition of perovskite films through a) conventional route and b–d) ligand-assisted pathways. The SEM images of compact PbI₂ film and porous PbI₂ film are reproduced with permission.^[118] Copyright 2015, Wiley-VCH. The SEM image of compact PbI₂(L)_x film is reproduced with permission.^[128] Copyright 2015, American Association for the Advancement of Science (AAAS). The SEM image of porous PbI₂(L)_x film is reproduced with permission.^[19] Copyright 2017, Wiley-VCH.

reaction surface area with organic ammonium halides (AX) in comparison to the conventional PbX_2 films with dense morphology.

For example, Zhang et al. developed a very simple and effective method to readily form high-quality perovskite (without PbI_2 residue) through strategic design of PbI_2 nanostructures and MAI concentrations (Figure 5b).^[118] On one hand, the conversion rate of PbI_2 was facilitated by incorporating ligand (4-*tert*-butylpyridine, TBP) into its precursor solution via self-assembly method to form a porous PbI_2 film (SAP- PbI_2). On the other hand, properly increasing the concentrations of MAI in the second step, smooth and pinhole-free perovskite thin films could be obtained. Compared to the conventional PbI_2 film (C- PbI_2), the planar PVSCs fabricated from the nanostructured SAP- PbI_2 film showed a dramatically performance improvement from 1.51% to 16.21%. Furthermore, the devices based on the high-quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ film without PbI_2 residue show a better long-term stability. Later, Yi et al. reported that DMSO can also induce the formation of mesostructured bilayer $\text{TiO}_2/\text{PbX}_2$ films, which also facilitates the transformation of mixed cation perovskite films.^[119] Cao et al. identified that the PbI_2 nanostructures induced by DMSO showed better reproducibility and performance than $\text{PbI}_2(\text{DMSO})_x$ adducts via two-step deposition.^[120] Other ligands (e.g., NMP,^[121] MAACl,^[122] MACl ,^[123] H_2O ^[124]) have also been reported to induce the formation of PbI_2 nanostructures by thermal annealing post-treatment. Besides, controlling the evaporation rate of ligand in PbI_2 precursor film^[125] and removing excess ligands by anti-solvent treatment^[126] and gas-quenching treatment^[20] are also effective strategies to prepare porous PbI_2 films.

2.2.2. Ligand-Assisted Formation of Metal Halide Adducts

Ligand exchange reaction is also a powerful tool to fully convert metal halides (MX_2) into high-quality perovskite films. Thanks to the sandwich-type layered structure of MX_2 , the ionic bonds within X-M-X layers are strong while the *van der Waals* force between adjacent sandwiched layers is weak. The weak bonding between interlayers allows the insertion of various ligand molecules (see Equation (1))^[127,128]



where M refers to Pb, Sn, Bi, or alloy; L refers to ligand for perovskite precursor formation; X = I, Br, Cl, or mixture; $0 \leq \gamma \leq 2$.

The crystallized perovskite films can be fabricated at low temperature by dipping the as-formed $\text{MX}_2(\text{L})_\gamma$ films into AX isopropanol solution. During the conversion of $\text{MX}_2(\text{L})_\gamma$ to perovskite, the ligand molecules intercalated in MX_2 will be replaced by external AI whenever its coordination toward MX_2 is stronger compared to the intercalated ligands (Equation (2)). Then, the resulting perovskite film was treated by thermal annealing to improve its crystallinity and remove the residual ligand^[19,127,128]



where A cations can be organic cations (e.g., MA^+ , FA^+) or inorganic cations (e.g., Rb^+ , Cs^+).

Choy and co-workers investigated the reaction mechanisms of ligand-assisted two-step deposition of perovskite films through thermodynamics and kinetics studies.^[19,127] In conventional pathway, the formation of perovskite needed to overcome a large energy barrier. Interestingly, in ligand-assisted pathway, the formation of perovskite undergoes two-stage reactions: $\text{MX}_2(\text{L})_\gamma$ formation and perovskite formation. Both activation energy E_{a1} and E_{a2} of ligand-assisted pathway were lower than that of conventional pathway, and thus favor the perovskite formation.

The effective ligands used for the formation of highly reactive $\text{MAX}_2(\text{L})_\gamma$ adducts were summarized in Table 1. For instance, Wu et al. first employed DMSO to inhibit the fast crystallization of PbI_2 by forming an amorphous $\text{PbI}_2(\text{DMSO})_x$ films.^[129] This extremely uniform and amorphous featured wet precursor film allowed the fully transformation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite on planar substrate within 10 min. The resultant perovskite films showed a small distribution of crystal sizes and smooth surface morphology. Seok and co-workers developed a new highly uniform and dense $\text{PbI}_2(\text{DMSO})$ complex to form high-quality FAPbI₃ films (Figure 5c).^[31,128] The $\text{PbI}_2(\text{DMSO})$ film has typically been obtained in three steps: i) synthesizing the $\text{PbI}_2(\text{DMSO})_2$ complexes by pouring toluene into PbI_2 solution dissolved in DMSO; ii) producing $\text{PbI}_2(\text{DMSO})$ complexes by annealing the as-prepared $\text{PbI}_2(\text{DMSO})_2$ complex in vacuum; iii) dissolving $\text{PbI}_2(\text{DMSO})$ complexes in DMF and spin-coating this solution on the substrate. FAPbI₃ films with high-crystalline, large grain size, and smooth morphology can be readily formed by the intramolecular exchange process of DMSO intercalated in PbI_2 with FAI. As a result, FAPbI₃-based PSCs with a certificated PCE of over 20.1% were fabricated. The $\text{PbI}_2(\text{DMSO})_x$ film could be simply prepared by tuning the molar ratio of PbI_2/DMSO in the precursor solution.^[130] The *N*-Methyl-2-pyrrolidone (NMP) has also been reported to prepare $\text{PbI}_2(\text{NMP})$ layers for forming high-quality FAPbI₃-based perovskite films by intramolecular exchange process.^[131] The perovskite films deposited from $\text{PbI}_2(\text{NMP})$ film showed larger grain size and smaller volume expansion ratio than that from the $\text{PbI}_2(\text{DMSO})$ film. As a result, the NMP-based PVSCs showed higher PCE than DMSO-based and conventional PVSCs. A small amount of organic ammonium iodides (AI) (e.g., MAI,^[132] FAI,^[133] and NH_4I ^[134]) have been reported to form nonstoichiometric $\text{PbI}_2 \cdot x\text{AI}$ intermediate complexes to replace PbI_2 precursor in the two-step deposition of perovskite films. The pre-expansion of PbI_2 into $\text{PbI}_2 \cdot x\text{AI}$, which favored the formation of smooth perovskite films with pure phase and large grains within a short period of time. Recently, Vak and co-workers have demonstrated that nonstoichiometric $\text{PbI}_2 \cdot x\text{MAI}$ precursor solution could be used to fabricate high-performance flexible PVSCs with efficiency up to 11.0% via real roll-to-roll process.^[135]

2.2.3. Ligand-Induced Formation of Nanostructured Metal Halide Adducts

Although organic ligands have been reported to control the crystallization of perovskite by forming $\text{PbX}_2(\text{L})_\gamma$ intermediates, high temperature thermal annealing is still utilized

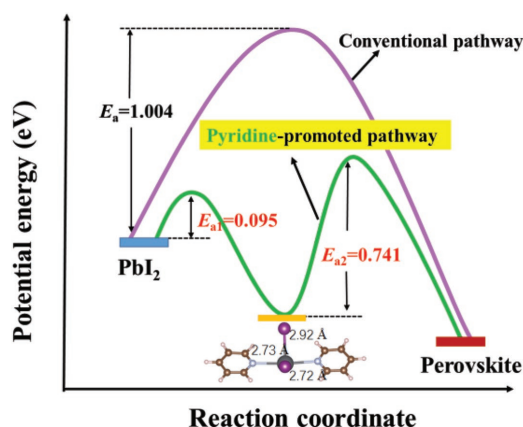
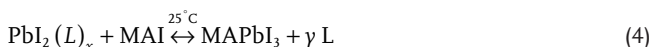
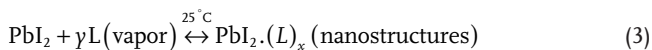


Figure 6. The reaction coordinate diagram of the perovskite formation via conventional pathway and pyridine-promoted pathway. Reproduced with permission.^[19] Copyright 2017, Wiley-VCH.

to remove the ligands for forming pure perovskite crystals. Recently, Choy and co-workers have reported a new scheme of ligand-assisted formation of high-quality perovskite films at room temperature through facile design of nanostructured and highly reactive $\text{PbI}_2(\text{L})_x$ intermediates (Figure 5d).^[19,127] This new scheme mainly contains two stages, namely i) ligand-vapor-induced formation of $\text{PbI}_2(\text{L})_x$ nanostructures at room temperature (Equation (3)) and ii) room temperature formation of perovskite film by ligand exchange reactions (Equation (4))



Different representative ligands with different features (molecular size, volatility, solubility, and reactivity) were comprehensively investigated to unravel the ligand effects on the film quality, morphology, and optoelectronic properties of perovskites. They found that by employing pyridine (Py) as ligand to form $\text{PbI}_2(\text{Py})_2$ nanostructures, highly crystalline and pure MAPbI_3 films could be formed. Based on the DFT calculation results, the reaction coordinate diagram of the perovskite formation via different pathways was presented in Figure 6. In the conventional pathway, the formation of perovskite needs to overcome a large energy barrier ($E_a = 1.004$ eV). Interestingly, the pyridine-promoted pathway showed lower activation energy than that of the conventional pathway, which indicates that the formation rate of perovskite was faster through the pyridine-promoted pathway. Remarkably, the devices based on $\text{PbI}_2(\text{Py})_2$ film showed the best photovoltaic performance with PCE of 17.10% on rigid substrate. Besides, this room-temperature solution-processed technique enabled the fabrication of lightweight flexible PVSCs with high PCE of 14.19% and remarkable power-per-weight of 23.26 W g^{-1} .^[19] This work demonstrated that low-cost PVSCs could be achieved by strategic selection of ligand for perovskite formation.

2.2.4. Ligand-Modified Organic Ammonium Halide Solutions

Traditionally, MAI, FAI, or their mixtures have been widely used to transform perovskite from PbX_2 precursor film. However, the fast-crystalline perovskite on the surface of PbX_2 will inhibit the diffusion of ammonium into the bulk, which results in forming perovskite film with many impurities. In addition to modifying metal halides, ligand-modified organic ammonium halide solution strategy has also been reported to be a very powerful strategy. For example, the introduction of additional chloride (e.g., MAI) in ammonium iodide solution is widely reported to improve crystallinity, phase purity, and surface coverage of perovskite and enlarge the grain sizes.^[4,118,136,137] The PbI_2 first reacts with chloride to afford $[\text{PbI}_2\text{Cl}]^-$, which then reacts with MAI (or FAI) to form the lead triiodide perovskites (MAPbI_3 or FAPbI_3). The first step accelerates the conversion of PbI_2 with the assistant of chloride, which leads to a higher surface coverage and a more compacted perovskite film.^[137] While the second step slows down the crystallization of final perovskites, which contributes to the improved crystallinity. A small amount of acetate (CH_3COO^-) has also been reported to incorporate in MAI solution to improve the surface coverage of MAPbI_3 film.^[138] Meng and co-workers reported that add a small amount of organic ligand (DMF was demonstrated in their work) in FAI/MAI/IPA solution for two-step spin-coating method to form smooth and pinhole-free mixed cation perovskite films.^[139] An new formed amorphous phase $\text{PbX}_2\text{-AI-DMSO-DMF}$ ($\text{X} = \text{I}, \text{Br}$; $\text{A} = \text{FA}, \text{MA}$) was suggested to help FAI/MAI penetrate into the PbX_2 framework to completely convert into the perovskite. Compared to the 0% DMF sample, the perovskite film prepared with 2% DMF additive presents larger grain sizes, smooth surface, and better performance. As a result, as high as 20.1% PCE has been achieved with a steady-state PCE of 19.1% by 2% DMF-modified FAI/MAI/IPA solution. Recently, Seok and co-workers demonstrated that introduction of triiodide ions (I_3^-) into the organic cation solution decreased the concentration of deep-level defects of perovskite film.^[31] The defect-engineered thin perovskite layers enable the fabrication of PVSCs with a new record certified PCE of 22.1% in small cells and 19.7% in 1 cm^2 cells.

2.3. Postdeposition Treatment

The morphology and quality of as-formed perovskite films can be tuned by ligand-assisted postdeposition treatment. Table S1 (Supporting Information) lists the ligands utilized in postdeposition of perovskite films.

2.3.1. Grain Boundaries and Defects Healing

Huang and co-workers first proposed a ligand-vapor-assisted post-treatment (or solvent-annealing) method^[140] to enlarge the grain sizes of the perovskite film as shown in Figure 7a₁. Since both PbI_2 and MAI have high solubility in the selected ligand (e.g., DMF, DMSO), the ligand vapor provided a wet environment so that the precursor ions and molecules could diffuse a longer distance than in all solid-state

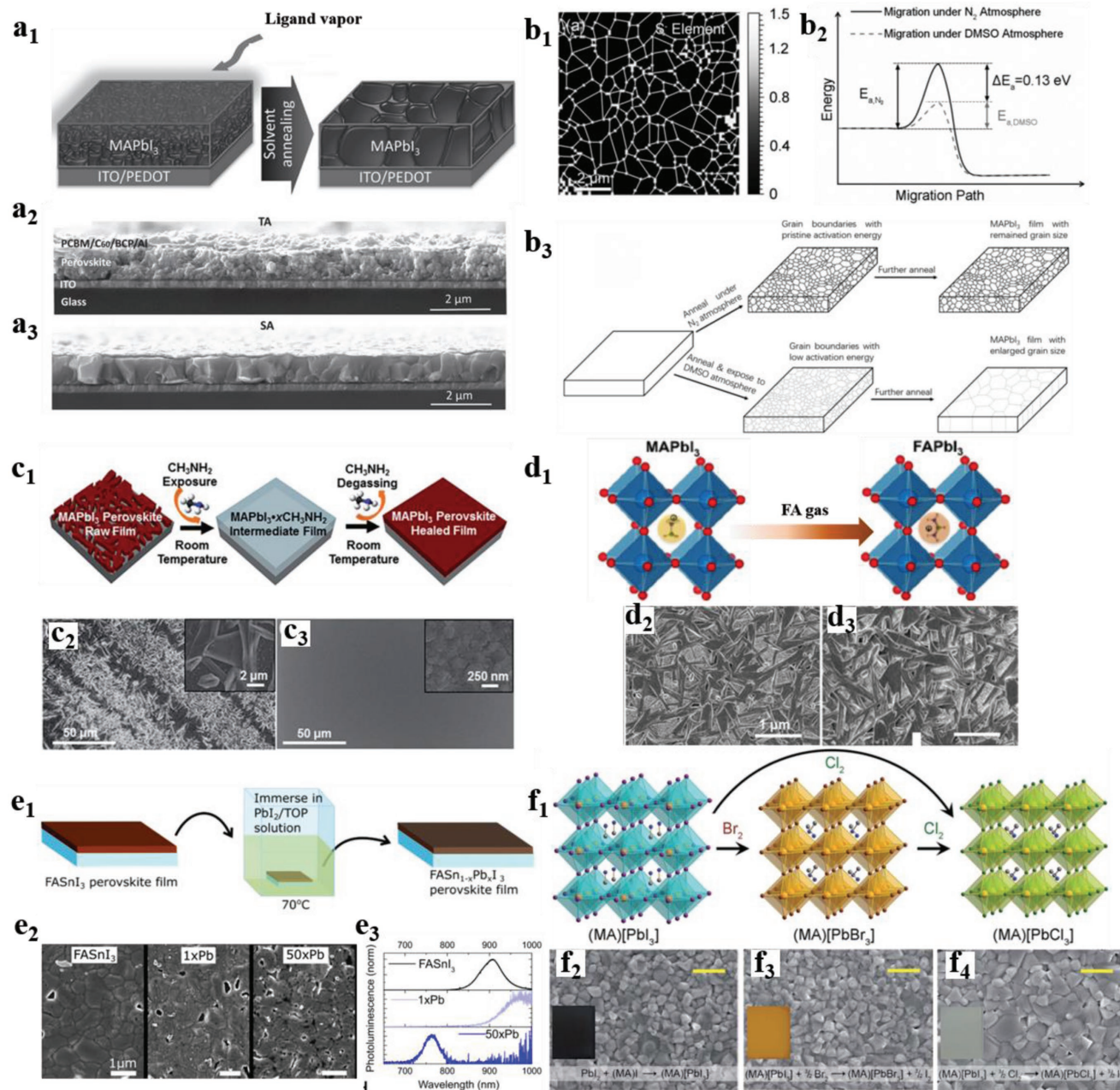
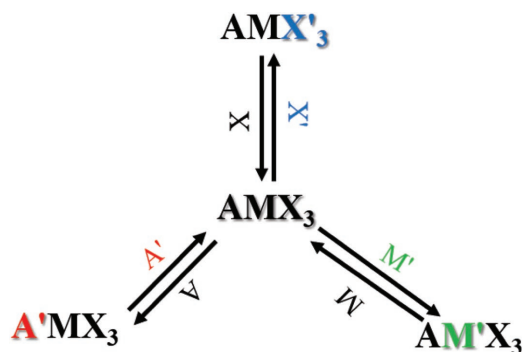


Figure 7. Ligand-assisted postdeposition treatment of perovskite films. a₁) Schematic of the ligand vapor-annealing-induced grain size increase and cross-sectional SEM images of the a₂) thermally annealed and a₃) ligand vapor-annealed perovskite films. Reproduced with permission.^[140] Copyright 2014, Wiley-VCH. b₁) Time-of-flight secondary ion mass spectrometry (ToF-SIMS) elemental mapping images of MAPbI₃ films annealed under DMSO atmosphere for 1 h. The sulfur (S⁻) element reflects the location of MA₂Pb₃I₈(DMSO)₂ intermediate. b₂) Proposed energy diagram and b₃) scheme of the proposed morphology evolution of MAPbI₃ grains under different atmosphere. Reproduced with permission.^[141] Copyright 2017, Wiley-VCH. c₁) Schematic illustration of methylamine-induced defect-healing of MAPbI₃ surfaces of MAPbI₃ perovskite thin films and the SEM images of c₂) raw film and c₃) healed film. Reproduced with permission.^[142] Copyright 2015, Wiley-VCH. d₁) Schematic illustration depicting organic cation exchange from MAPbI₃→FAPbI₃ perovskite conversion by FA gas treatment and SEM images of MAPbI₃ film d₂) before and d₃) after FA gas treatment. Reproduced with permission.^[147] Copyright 2016, American Chemical Society. e₁) Illustration of the M-site cation exchange process. e₂) Top-view SEM images and e₃) photoluminescence (PL) spectra of the pristine and exchanged films. Reproduced with permission.^[148] Copyright 2017, American Chemical Society. f₁) Halide exchange of MAPbX₃ with Br₂ and Cl₂ gas. Pb: orange, I: purple, Br: brown, Cl: green, N: blue, C: gray. SEM images of f₂) as-formed MAPbI₃ film, f₃) MAPbI₃ film treated by Br₂ gas, f₄) MAPbI₃ film treated by Cl₂ gas. The scale bar is 1 μm. Reproduced with permission.^[150] Copyright 2015, Royal Society of Chemistry.

thermal annealing, which promoted the grain growth and yielded a larger grain size, as illustrated in Figure 7a₂,a₃. Recently, the intrinsic working mechanism of this method

had been revealed by Yang and co-workers.^[141] They identified an MA₂Pb₃I₈(DMSO)₂ intermediate phase formed during the annealing process of MAPbI₃ in DMSO atmosphere



Scheme 1. Different routes for ions substitution in perovskite materials.

and located the reaction sites at perovskite grain boundaries (Figure 7b₁), which reduced the activation energy for grain boundary migration (Figure 7b₂). As shown in Figure 7b₃, with a lower activation energy, the grain boundaries moved from the large grain side to the small grain side, since the surface energy of large grains was lower than that of small ones. Therefore, high-quality perovskite films with large grains were obtained by the ligand-vapor-assisted post-treatment. Another effective strategy is methylamine (MA)-induced defect-healing of perovskite films.^[142–145,23,184–188] Cui and co-workers first reported that exposing the raw MAPbI₃ perovskite to methylamine gas at room temperature as shown in Figure 7c₁.^[142] A liquid intermediate phase MAPbI₃·xMA was formed during the methylamine gas exposure. The liquid phase spread instantaneously owing to wetting of the substrate and forms an ultra-smooth intermediate. Upon removal of the MA gas, the liquid phase released MA molecules rapidly

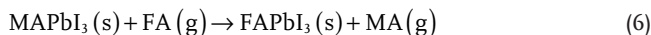


This release resulted in volume contraction, and rebuilding of the perovskite structure by rapid nucleation and growth. Notably, this process was independent of the morphology and size of the starting film, where raw MAPbI₃ films with different types of “defective” morphologies and different sizes can be healed to ultrasmooth film (Figure 7c₂,c₃). Boyen and co-workers demonstrated that the MA gas treatment improved not only the film morphology and electronic quality, but also improving electron injection from perovskite layer into TiO₂.^[143] Design rules for the broad, rational extension of MA treatment process had also been established by Jen and co-workers^[145] Choy and co-workers employed the MA gas treatment to improve the film quality of room-temperature processed MAPbI₃ perovskite film for solar cells^[19] and form highly crystalline periodic MAPbI₃ patterns for perovskite light-emitting diodes (PeLED).^[144] Recently, Nazeeruddin and co-workers reported a novel MAPbI₃/δ-FAPbI₃ structure via treating a mixed organic cation MA_xFA_{1-x}PbI₃ perovskite film with MA gas.^[146] In addition to the morphology healing, MA gas can also induce the formation of δ-FAPbI₃ phase within the perovskite film. The in situ formed 1D δ-FAPbI₃ polymorph behaves like an organic scaffold that can passivate the trap state, tunnel contact, and restrict organic-cation diffusion. As a result, the device efficiency is easily boosted to 21%.

2.3.2. Ions Substitution

Besides assisting the perovskite formation during crystallization process, some ligands have been reported to assist or directly displace the cations/anions of the as-formed AMX₃ perovskite films (A = organic cations; M = metal cations; X = halides) as shown in Scheme 1.

Organic Cation Exchange (A-Site): Zhou et al. reported a single-cation displacement route (Figure 7d₁) to realize MAPbI₃→FAPbI₃ conversion by simply exposing an as-deposited MAPbI₃ perovskite thin film to formamidine (FA) gas, which can be considered as a proton exchange reaction (Equation (6)).^[147]



By controlling the duration time of FA gas treatment, the, the MA in MAPbI₃ was partial and complete conversion into MA_{1-x}FA_xPbI₃ and FAPbI₃, respectively. Interestingly, this strategy showed a unique “morphology-preservation” feature as shown in Figure 7d₂,d₃.

Metal Cation Exchange (M-Site): Eperon and Ginger demonstrated that triethylphosphine (TOP) was able to dissolve PbI₂ and SnI₂ in reasonable concentrations and these solutions did not dissolve the perovskite films upon exposure.^[148] Using this new solutions, the Sn in FASnI₃ perovskite film was exchanged by Pb to form FASn_xPb_{1-x}I₃ alloys with partial substitution and fully convert the film into MAPbI₃ perovskite with a large excess of Pb²⁺ (Figure 7e₁). Besides, the conversion was uniform throughout the film as depicted in Figure 7e₂,e₃.

Anion Exchange (X-Site): Pellet et al. reported a rapid substitution of halide within the 3D MAPbX₃ (X = I, Br, and Cl) perovskites through MAX dipping method.^[149] No matter what the initial perovskite is, the halide exchange process can occur. However, the morphology of perovskite films cannot be always well-preserved (e.g., chloride-iodide exchange reactions). Karunadasa and co-workers reported a halogen gas treatment to exchange the halides in the organic-inorganic hybrid perovskites using redox chemistry (Figure 7f₁).^[150] This reaction provided a convenient method of converting 3D MAPbI₃ perovskite films to high-quality (smooth and highly crystalline) MAPbBr₃ or MAPbCl₃ perovskite films without further annealing or purification steps (Figure 7f₂–f₄). This strategy was extended to the 2D perovskites. The limitation of this strategy is that the halogen gas must have a more positive reduction potential than the halide in the perovskite.

3. Ligand-Passivated Perovskite Films

Similar to other ionic materials, as shown in Figure 8a, the defects (e.g., under-coordinated halide anions and metal cations) at surfaces (top and bottom)^[11] and bulk (including grain boundaries)^[41,151,152] of perovskite films could induce serious charge carrier recombination and thus greatly restrict the performance of PVSCs. It has been reported that judicious selection of ligands can effectively passivate these defects or trap states in the perovskite crystal via coordinate bonding. In this section, we will review the progress on ligand-passivated perovskites via post-treatment, in situ passivation during

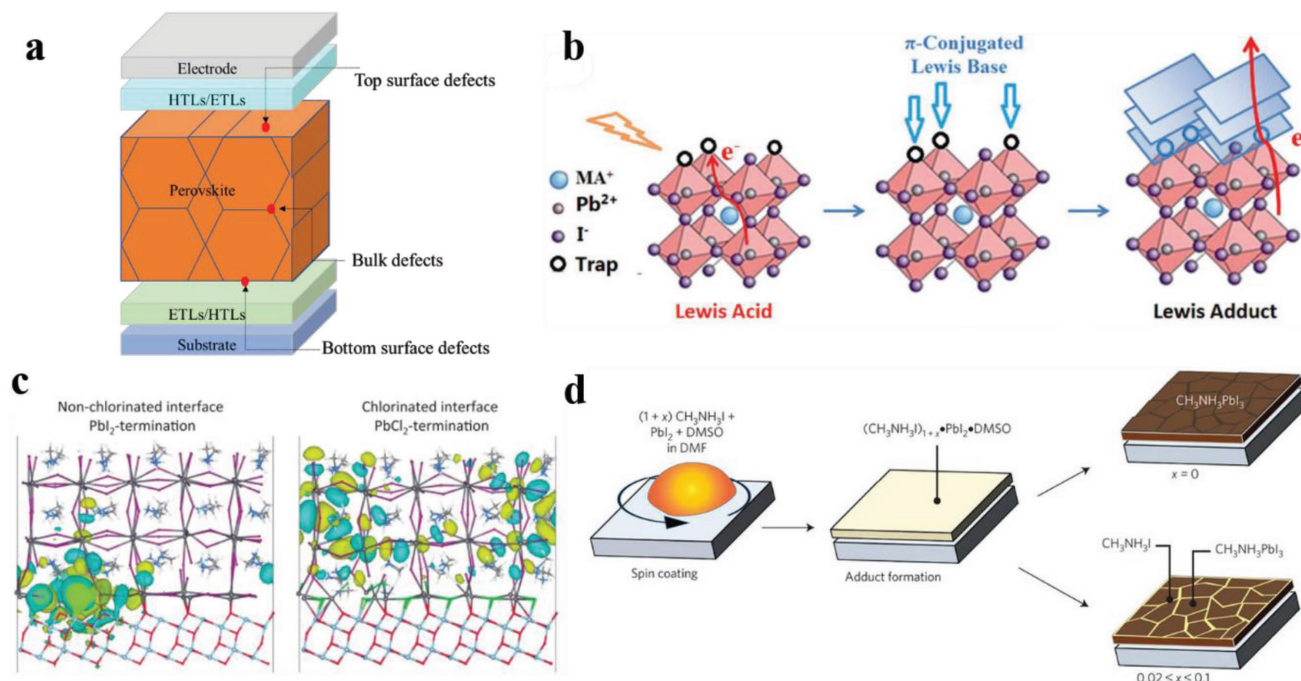


Figure 8. Passivation of perovskite films by ligand engineering. a) Three typical defect sites in perovskite films. b) Post-treatment of perovskite films with the π -conjugated Lewis base. Reproduced with permission.^[159] Copyright 2016, Wiley-VCH. c) The effect of Cl on interface quality between perovskite and TiO_2 . The effect of Cl on interface quality between perovskite. Trap-like localized antisite defects form near the valence band edge for the PbI_2 -terminated TiO_2 /perovskite interface (left); Shallow and delocalized Pb-Cl antisite defects are seen for the PbCl_2 -terminated interface (right). Reproduced with permission.^[168] Copyright 2017, American Association for the Advancement of Science (AAAS). d) Schematic representation of the coating process used to form the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films with and without grain boundary healing layer. Reproduced with permission.^[172] Copyright 2016, Nature Publishing Group.

perovskite formation, and modifying the substrates before perovskite formation.

3.1. Passivating Perovskite Films via Post-Treatment

It is hypothesized that an excess of uncoordinated ions (e.g., halide anions and Pb cations) within perovskite structure are responsible for forming trap states on the perovskite surface. To passivate the under-coordinated halide anions on the perovskite surface, some supramolecular halogen (e.g., iodopentafluorobenzene (IPFB)^[153] and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ)^[154] has been proposed to coordinate with these iodine tapping sites, and thus significantly increases the PVSC performances. For the uncoordinated metal cations (can be regarded as a Lewis acid), a series of Lewis bases (act as ligand) have been employed to treat the perovskite films to passivate these surface defects (Figure 8b). For example, Snaith and co-workers demonstrated that pyridine and thiophene were effective for passivating the trap states on the surface of perovskite films due to their interaction with the under-coordinated lead atoms.^[38] These passivated perovskite films exhibited order-of-magnitude longer photoluminescence lifetimes and improved device efficiencies. Yip and co-workers reported an amino-functionalized conjugated polymer (PFN-2TNDI) as ETLs to replace PCBM in p-i-n planar inverted PVSCs. It was found that the amines on the polymer side chains not only passivated the surface traps of perovskite to improve the electron extraction properties, but also reduced the work function of

the metal cathode by forming desired interfacial dipoles. The resulted solar cells outperformed those based on PCBM with PCE increased from 12.9% to 16.7% based on PFN-2TNDI.^[155] Zhao and co-workers reported that benzylamine effectively passivated the surface trap states, reduced the recombination centers and improved device performances through the interaction between the amino anchoring group and the Pb-I lattice.^[156] Jen and co-workers proposed a series of bifunctional diammonium iodides to passivate perovskite surfaces and grain boundaries considering their bilateral ammonium iodide end simultaneously passivated the perovskite layer and doped the adjacent electron-transporting layer (PCBM) in derived PVSCs.^[157] Sun and co-workers employed the small molecule of boron subphthalocyanine chloride (SubPc) to passivate the defects by filling up the pinholes at the perovskite surface and grain boundaries.^[158] Huang and co-workers employed a π -conjugated Lewis base (indacenodithiophene end-capped with 1,1-dicyanomethylene-3-indanone, IDIC) with n-type semiconductor property to the MAPbI_3 based solar cells as an interlayer between MAPbI_3 and cathode (Figure 8b). The carbonyl and cyano groups of IDIC passivated the under-coordinated Pb of MAPbI_3 polycrystalline films through coordination between the Lewis acid and base. The IDIC-passivated device showed lower trap density, higher open-circuit voltage and enhanced device stability compared with the control devices without IDIC layer.^[159] Miyasaka and co-workers suggested that the hydrophobic polymer (poly(4-vinylpyridine) passivated the under-coordinated Pb atoms on the surface of perovskite by its pyridine Lewis base side chains and thereby eliminates surface-trap states and nonradiative

recombination.^[160] Huang and co-workers demonstrated that quaternary ammonium halides could effectively passivate ionic defects in several different types of hybrid perovskite. The efficient defect passivation reduced the charge trap density and elongated the carrier recombination lifetime. The defect passivation reduced the open-circuit-voltage deficit of the p-i-n-structured PVSC to 0.39 V, and boosted the efficiency to a certified value of $20.59 \pm 0.45\%$.^[161,162] A chemical modified graphene oxide (rGO-4FPH) was also employed to passivate the trap states (e.g., under-coordinated Pb ions and Pb clusters) on the surface and at the GBs of $\text{MAPbI}_{3-x}\text{Cl}_x$.^[162] Recently, Cheng et al. demonstrated that passivation of the interface between the perovskite and a spiro-OMeTAD hole-transporting material with commercially available cyano-substituted benzenethiol facilitates fabrication of cm-sized PVSCs with both improved efficiency and stability.^[163]

3.2. Modifying the Substrates before Perovskite Formation

Using ligands with tailored moiety to modify the substrates has also been reported to effectively passivate the trap states on the bottom surface of perovskite films. Hayase and co-workers^[164] and Chen and co-workers^[165] applied amino acids to form an $\text{HOOC-R-NH}_2\text{I}$ monolayer as an anchor to connect the surface of metal oxides (TiO_2 , Al_2O_3 , and ZnO) with perovskite layer. The bifunctional $\text{HOOC-R-NH}_2\text{I}$ could remarkably improve the device performance via reduction of the trap states in the perovskite films as well as improving the morphology of perovskite films on these metal oxides. Similarly, a self-assembled aminopropyl trimethoxysilane monolayer has been incorporated between the TiO_2 and perovskite crystal, which helped tune the interface electronic structure and passivate the recombination process.^[166] Yang and co-workers employed diethanolamine (DEA) molecules to modify the surfaces of sol-gel processed NiO_x films before perovskite deposition. The amine groups and $-\text{OH}$ groups of DEA molecules tended to complex with NiO_x and perovskite, respectively, which improved the NiO_x /perovskite contact as well as the perovskite crystalline film quality with a reduced trap state density.^[167] Contact-passivation strategy using chlorine-capped TiO_2 (Cl-TiO_2) colloidal nanocrystal film has been reported to mitigate interfacial recombination and improves interface binding in low-temperature planar PVSCs. The incorporation of Cl atoms at the TiO_2 /perovskite interface resulted in a lower density of interfacial trap states, as well as stronger binding between TiO_2 and perovskite (Figure 8c). Using Cl-TiO_2 as ETLs, a very high PCE of 20.3% (certified PCE of 19.5%) had been achieved in large-area (1.1 cm^2) planar PVSCs.^[168] Insertion of biopolymer heparin sodium (HS) interfacial layer between the perovskites and the TiO_2 cathode could also passivating the interfacial traps and thus improve device performance and stability.^[169] Recently, Yip and co-workers demonstrated that dopamine (DA) semi-quinone radical modified poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (DA-PEDOT:PSS) as a hole transporting layer to passivate the interfacial traps. The amino and hydroxyl groups in DA can interact with the under-coordinated Pb atoms on the perovskite crystal, reducing charge-recombination rate and increasing charge-extraction efficiency.^[170]

3.3. Passivating Perovskite during Film Formation

It has been reported that bulk defects (e.g., trap states, voids, and pinholes) at grain boundaries and within grains were responsible for causing recombination and trapping of charge carriers.^[37] In addition to the self-passivation method through decomposition of perovskite into PbI_2 ,^[171] and fullerene passivation approaches,^[41,151] incorporation of small molecule ligands into perovskite precursor solution to passivate defects during the formation of perovskite film has also been widely investigated. Park and co-workers reported that excess $\text{CH}_3\text{NH}_3\text{I}$ layer passivated perovskite grain boundaries and significantly improved device performance due to the suppressed nonradiative recombination and improved hole and electron extraction at the grain boundaries by forming highly ionic-conducting pathways (Figure 8d).^[172] Similarly, guanidinium (GA) ions suppressed the formation of iodide vacancies and passivate under-coordinated iodine species at grain boundaries and within the bulk through their hydrogen bonding capability.^[173,174] The guanidinium-passivated perovskite exhibited one order of magnitude longer carrier lifetime and higher open circuit voltages. Hagfeldt and co-workers incorporated nitrogen-doped reduced graphene oxide (N-RGO) into mixed perovskites to passivate the surface and retard the electron-hole recombination through the interaction between the hydrogen atoms of the FA and basic sites on N-RGO. As a result, the N-RGO-passivated perovskite films showed larger grain sizes. The resulting device exhibits an almost hysteresis-free PCE of 18.7% as compared to the reference cell with 17.3%.^[175] Similarly, incorporation of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) into the perovskite precursor solution also improved the crystalline quality of perovskite film with large grain size by retarding the crystallization rate, and reduced intrinsic defect density by passivating charge recombination centers around the grain boundaries.^[176]

Incorporating polymers with electron donor groups into perovskite precursors is another effective strategy to passivate perovskites. Ma and co-workers reported that incorporation of PCDTBT into mixed perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_{1-x}$ precursor to improve the photovoltaic performances and stability of PVSCs.^[177] The PCDTBT contained lone pairs of electrons due to the presence of S and N atoms, which interacted with perovskite, passivated the trap states of perovskite layer and improved its morphology. Unfortunately, some polymers with low solubility in the perovskite precursor made it challenging to form a homogenous perovskite films with these polymers via the conventional one-step or two-step method. Recently, Zuo et al. reported a modified two-step spin-coating method to resolve this issue.^[178] The polymer coordinated perovskite film was prepared by three stages: i) forming a mesoporous PbI_2 layer; ii) dripping the MAI/polymer isopropanol solution onto the mesoporous PbI_2 film; iii) thermal annealing the perovskite films containing polymers. It is likely that the polymers are being incorporated at some level throughout the depth of the films and passivating the grain boundaries. The use of polymer poly(4-vinylpyridine) (PVP) could effectively passivate the grain boundaries and significantly enhance the performance of PVSCs from $16.9 \pm 0.7\%$ to $18.8 \pm 0.8\%$ compared to controls without any passivation. Furthermore, the PVP-passivated perovskite film enabled PVSCs with a V_{oc} of up to 1.16 V, which was among the best reported for a MAPbI_3 -based solar cells. A series

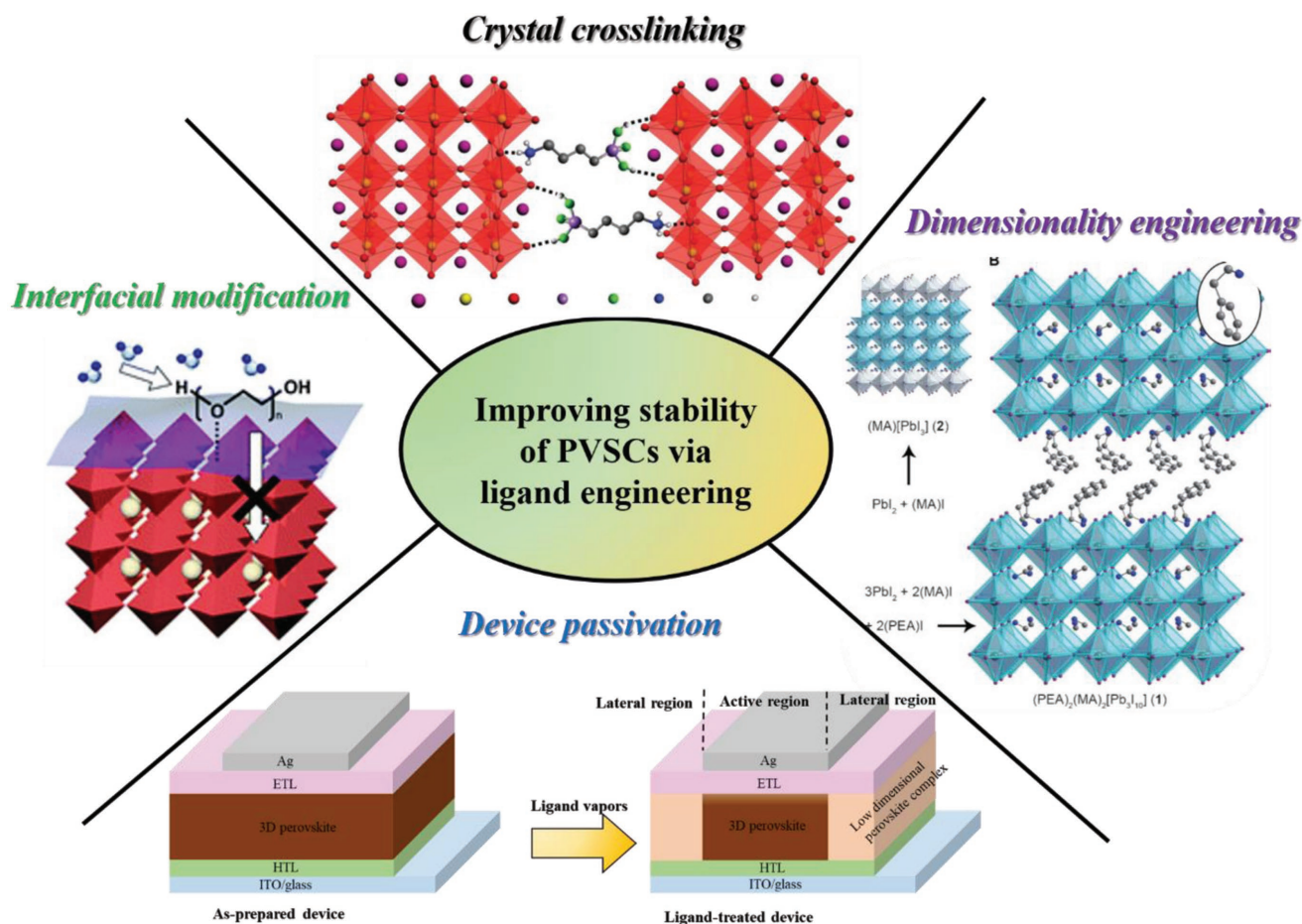


Figure 9. The strategies for improving long-term stability of perovskite solar cells via ligand engineering. Figures in the section of device passivation are reproduced with permission.^[217] Copyright 2018, Royal Society of Chemistry. Figures in the section of dimensionality engineering are reproduced with permission.^[187] Copyright 2014, Wiley-VCH. Figures in the section of crystal crosslinking are reproduced with permission.^[181] Copyright 2015, Nature Publishing Group. Figure in the section of interfacial modification is reproduced with permission.^[211] Copyright 2018, Royal Society of Chemistry.

of p-type copper salts (e.g., CuSCN ,^[179] CuI ,^[180] $\text{Cu}(\text{thiourea})\text{I}$ ^[180]) have also been reported to effectively interact with the under-coordinated metal cations and halide anions at perovskite crystal surface and thus shallow the trap state energy level of perovskite. Meanwhile, the incorporated p-type copper salts formed bulk heterojunctions with perovskite, which further facilitated hole transport and decreased charge carrier recombination. Using $\text{Cu}(\text{Tu})\text{I}$ passivated perovskite, a very high PCE of 19.9% in the inverted PVSCs has been obtained.^[180]

4. Ligand-Stabilized Perovskite Films

Different to other encapsulation strategies, organic ligands could form a capping layer on the perovskite crystals to inhibit the diffusion of some harmful molecules (e.g., moisture). These significantly improve the intrinsic stability of perovskites, which benefits the commercialization of perovskite-based optoelectronic devices. In this section, we will review the progress on ligand-stabilized perovskite films from the perspectives of crystal crosslinking, dimensionality engineering, and interfacial modification.

4.1. Crystal Crosslinking

Crystal crosslinking is an effective approach to improve the film morphology by modulating the crystallization rate and enhance the moisture-resistance of perovskite films by passivating the grain boundaries. Li et al. first demonstrated a bifunctional alkylphosphonic acid ω -ammonium chloride (ABPA) could be used to cross-link the MAPbI_3 perovskite grains through strong hydrogen bonding of the $-\text{PO}(\text{OH})_2$ and $-\text{NH}_3^+$ terminal groups to the perovskite surface (Figure 9).^[181] The adjacent crystals cross-linking by ABPA blocked the access of water to the perovskite and thus enhanced the moisture stability of PVSCs. Tian and co-workers reported an excellent and intrinsic water-resistant $\text{MAPbI}_{3-x}(\text{2-AET})$ perovskite films by incorporating 2-aminoethanethiol (2-AET) to interconnect the MAI and PbI_2 in the precursor solution. The resulting perovskite films remained the MAPbI_3 perovskite crystal structure for a long time (>10 min) after immersion in water.^[182] Zhao et al. demonstrated that the hygroscopic polyethylene glycol (PEG) scaffold stabilized the perovskite film, rendering the devices resistant to moisture with strong self-healing property. The unencapsulated devices

retained high output for up to 300 h in highly humid environment (70% RH). The improved stability and self-healing effect of the PEG-based devices was ascribed to the excellent hygroscopicity of the PEG molecules and their strong interaction with the perovskite.^[183] Similarly, another polymer polyurethane (PU) was developed to crosslink the grain boundaries between neighboring perovskite crystals to effectively improve the moisture-resistance. Interestingly, the PU-based perovskite films showed better bendability. The perovskite film without PU had some cracks after bending 200 times, whereas the PU-based perovskite displayed an unbroken and uniform morphology.^[92] Recently, terephthalic acid (TPA) has been reported to improve the moisture-resistance of MAPbI₃ films by interconnecting the perovskite grains.^[184]

4.2. Dimensionality Engineering

In addition to developing water-resistant 3D perovskite materials, another effective approach to improving device stability is to employ 2D layered perovskites as absorbers. The general formula of 2D perovskites is (RNH₃)₂(A)_{n-1}MX_{3n+1}, where RNH₃ is a primary aliphatic or aromatic alkylammonium cation acting as a spacer between the perovskite layers, A is small organic cation (i.e., MA⁺) and M is metal cations such as Pb²⁺ and Sn²⁺, X is a halide anion, and n is the number of [MX₆]⁴⁻ octahedra within each quantum well.^[185] The hydrophobic nature of spacer cation and the van der Waals force interactions between the neighboring layers impair the 2D perovskites with superior moisture stability.^[186–189] However, the introduction of organic spacers with long alkyl chain decreased the absorption coefficient and carrier transport of perovskite materials,^[190] and thus undermine the photovoltaic performance.^[191] Therefore, many groups have devoted to break the trade-off between stability and performance of 2D perovskites-based photovoltaics.^[192,193] The molecular structure of organic spacers employed in 2D perovskites for photovoltaics is summarized in Table 1.

4.2.1. Phenylethylammonium (PEA⁺)

Karunadasa and co-workers demonstrated the first-generation PVSCs based on 2D perovskite (PEA)₂(MA)₂PbI₁₀ by using PEA⁺ as spacer cation and achieved a moderate PCE of 4.73%.^[187] Significantly, the (PEA)₂(MA)₂PbI₁₀ perovskites showed superior moisture stability with almost no changes on XRD patterns after humidity (52% RH) exposure of 46 d. The n values in the (PEA)₂(MA)_{n-1}Pb_nI_{3n+1} have been modulated to enhance the stability and photovoltaic performance of PVSCs simultaneously.^[186,194] After optimization, Quan et al. demonstrated a 15.3% certified 2D PVSC with enhanced moisture stability.^[186] Later, Ning and co-workers demonstrated that this strategy can be used to form highly oriented 2D tin-based perovskite (PEA)₂(FA)₈Sn₉I₂₈ films, which exhibit significantly enhanced air stability compared to their 3D counterparts.^[195] By optimizing the amount of 2D tin-based perovskite, Loi and co-workers demonstrated all-tin-based PVSCs with a record efficiency as high as 9%.^[196]

4.2.2. n-Butylammonium (BA⁺)

n-Butylammonium (BA⁺) is another widely used spacer cation for forming 2D Ruddlesden-Popper perovskites ((BA)₂(MA)_{n-1}Pb_nI_{3n+1}). Kanatzidis and co-workers first demonstrated a moderate PCE of 4.02% for the (BA)₂(MA)₃Pb₃I₁₃ based solar cells.^[197] Later, Tsai et al. reported a hot-casting technique to fabricate near-single-crystalline (BA)₂(MA)₃Pb₃I₁₃ films with a strongly preferential out-of-plane alignment with respect to the contacts.^[198] Using this 2D perovskites as absorber in planar PVSCs, a breakthrough PCE of 12.52% with no hysteresis was achieved. A recent study further improved the PCE of (BA)₂(MA)₃Pb₄I₁₃ PVSCs up to 13.7% via cesium doping.^[199] Besides, the (BA)₂(MA)₃Pb₃I₁₃ based PVSCs exhibited greatly improved stability against accelerated aging tests (i.e., humidity, light soaking, and heat stress), in comparison to their 3D. Recently, Snaith and co-workers demonstrated an strategy to improve the photovoltaic performance and stability of FA_{0.83}Cs_{0.17}Pb(I_yBr_{1-y})₃ 3D by introducing a small amount of BA cations to form 2D perovskites at the 3D perovskite grain boundaries. The enhanced stability of the BA-based perovskites might be attributed to the hydrophobicity of the long BA cation chain, the highly oriented and dense nature of the 2D perovskite films, and the suppressed ion migration in 2D perovskites.^[115]

4.2.3. Other Types

In addition to the PEA⁺ and BA⁺, other hydrophobic cations (see Table 1) such as 5-ammonium valeric acid (AVA⁺),^[21] 1,1,1-trifluoro-ethyl ammonium (FEA⁺),^[200] iso-butylammonium (iso-BA⁺),^[201] tetrabutylammonium (TBA⁺),^[202] polyethylenimine (PEI) cations,^[203] octylammonium (OA⁺),^[117] benzylammonium (BE⁺)^[204] and the emerging dications (i.e., ethylenediammonium, EDA²⁺)^[111,204,205] have been successfully developed to enhance the moisture resistance of PVSCs. Very recently, Nazeeruddin and co-workers demonstrated one-year stable PVSCs by engineering an ultrastable 2D/3D (AVA)₂PbI₄/MAPbI₃ perovskite junction. As shown in Figure 10a, the fabricated 10 × 10 cm² solar modules exhibited superior stability by maintaining a PCE of 11.2% over 10 000 h with zero loss under controlled standard conditions.^[206]

4.3. Interfacial Modification

Strategically creating a molecular protection layer on 3D perovskite films is also an effective method to stabilize PVSCs against humidity and ion migration. In principle, the additional layer is desirable to hinder the permeation of moisture/detrimental ions and keep the capacity of carrier transport at the interface.

4.3.1. Formation of Molecular Protection Layer on the Top of Perovskite Film

Water-Resisting Layer: Given the fact that the inorganic framework of perovskites can offer unique hydrogen and ionic

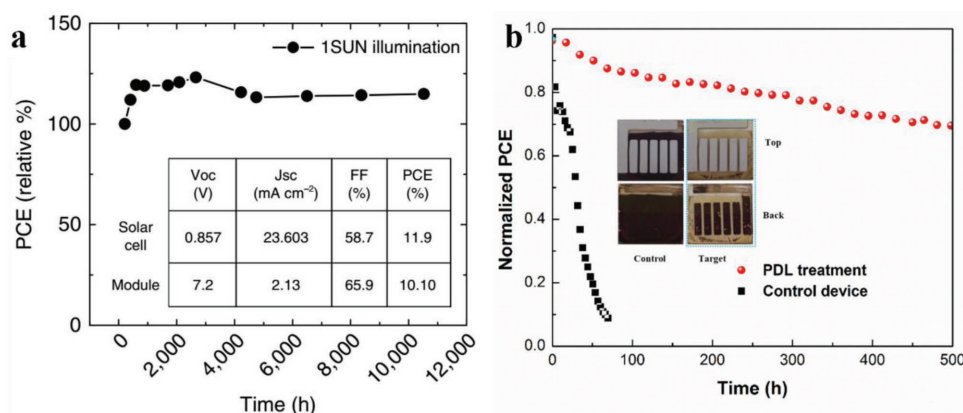


Figure 10. a) One-year stable perovskite solar cell module via ligand engineering. The test was conducted under 1 sun AM 1.5 G conditions at stabilized temperature of 55° and at short circuit conditions. Reproduced with permission.^[206] Copyright 2017, Nature Publishing Group. b) Maximum power point tracking for 500 h of the unencapsulated devices with and without postdevice ligand (PDL) treatment under continuous 1 sun illumination. The humidity and temperature are 50 ± 5% and 25 ± 1 °C, respectively. Reproduced with permission.^[217] Copyright 2018, Royal Society of Chemistry.

bonding to anchor ammonium cations or uncoordinated metal atom to anchor electron-donor ligands, it is envisaged that surface organic cation and metal atom sites can be mostly substituted by other ligands and may give rise to new water-resisting layer. For example, A series of hydrophobic alkylammonium cations could be assembled on the perovskite surface as an efficient water-resisting layer.^[207] The functionalized perovskite films exhibit enhanced surface hydrophobicity as well as superior moisture stability under a high relative humidity of 90 ± 5% for more than 30 days. The relationship between chemical structure of alkyl ammonium cations and moisture-resistant capacity has also been unveiled. Similarly, choline chloride could also effectively enhance the stability of the perovskite films in ambient environment by covering the defective sites on the film surface with quaternary ammonium halides ions and thus inhibiting the permeation of moisture and oxygen through the defects.^[161] In addition to alkylammonium cations, some organic molecules with hydrophobic moieties have been employed to modify the surface of perovskite films. For example, hydrophobic thiols (e.g., pentafluorobenzenethiol, HS-C₆F₅) have been reported to enhance the moisture stability of the PVSCs.^[208] The S-donor ligand, such as thiols, could form a fully hydrophobic molecular layer on the MAPbI₃ perovskite surface by Pb-S coordination, which enhanced the moisture-resistance of perovskite films and thus the device stability. The benzylamine with hydrophobic aromatic group could also be employed to simultaneously improve the moisture-resistance and electronic properties of the FAPbI₃ perovskite films.^[156] 1-Adamantylamine (ADA) with amine group could also anchor to an A-cation vacancy of perovskites, which makes the perovskite surface more hydrophobic. The formed molecular layer protects the perovskite film from water ingress which enhances the device stability.^[209] Trioctylphosphine oxide (TOPO) with P=O bonds has been reported to selectively anchor onto the perovskite surface through the coordination between O atom and halide-deficient sites. Thanks to the hydrophobicity of the long chain alkyls of TOPO, the humidity stability of the treated PVSCs could be enhanced.^[210] Differently, a hygroscopic polymer,

poly(ethylene oxide) (PEO), was reported to prevent water inclusion into perovskite film by screening water molecules, thus enhancing the device stability in the ambient atmosphere without encapsulation.^[211]

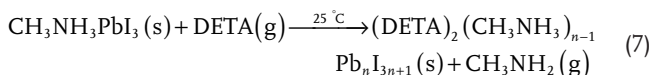
Ion Diffusion Barrier Layer. Ion migration is another important issue for PVSCs stability. Tailoring molecular layer on the surface of perovskite film could neutralize or inhibit the ion migration in PVSCs by reduction of surface defects. For example, methimazole (MMI) could be employed to construct a surface “patch” by in situ converting residual PbI₂ at grain boundaries. The resultant MMI-PbI₂ complex can effectively suppress ion migration and inhibit diffusion of the metal electrodes, thus significantly improve the device stability.^[212] The supramolecular cation- π interaction between aromatic rubrene and organic cations (e.g., MA⁺) in perovskites has been demonstrated to effectively inhibit the ion migration, and thus contribute to an outstanding stability in devices.^[213]

4.3.2. In Situ Formation of 2D/3D Perovskites Heterojunction

In situ formation of 2D/3D bilayer perovskites by alkyl ammonium halides treatment has been reported to significantly enhance the moisture-resistance of PVSCs. For instance, Yao et al. reported the in situ formation of layered perovskites (PEI)₂[PbI₄]/MAPbX₃ heterojunction enhanced the long-term stability of PVSCs.^[203] Docampo and co-workers demonstrated the formation of 2D/3D bilayer perovskites by PEA solution treatment significantly improve the moisture stability as well as photovoltaic performance of MAPbI₃-based PVSCs.^[189] Shi and co-workers demonstrated the 2D/3D perovskite hybrids (CA₂PbI₄/MAPbI₃Cl_{3-x}) delivered significantly improved moisture stability of films and devices without encapsulation in a high humidity of 63 ± 5%, as compared with the 3D perovskites (MAPbI₃Cl_{3-x}).^[214] Nazeeruddin and co-workers further improved the stability of PVSC by employing a thin 2D perovskite (PEAI)₂PbI₄ on the top of a 3D mixed cation (CsFAMA) perovskite film. The modified devices retained 85% of the initial PCE stressed under one sun illumination for 800 h at 50 °C.^[215]

4.3.3. Selective Formation of Low-Dimensional Perovskites

When the perovskite devices exposed to ambient environment, the perovskite materials in lateral region of PVSCs (without protection of metal electrode) will be damaged by moisture and decomposed to iodine containing volatile species (e.g., MAI and/or HI).^[216] Low-dimensional perovskites show higher moisture stability than conventional 3D perovskites. Meanwhile, recent study shows that the low-dimensional perovskites slow ion migration properties. Recently, Choy and co-workers proposed the first kind of simple postdevice ligand (PDL) treatment (or device passivation treatment) to selectively formation of low-dimensional perovskites to encapsulate 3D perovskite of active region (see Figure 9), which significantly improve the air stability of PVSCs.^[217] A nitrogen-donor ligand, diethylenetriamine (DETA) with three amine groups is taken as the ligand example to treat PVSCs as depicted in Table 1. Specifically, the ligand vapors are employed to directly treat the as-prepared (completed) PVSC devices. The DETA molecule can interact with $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite by substitution of the surface CH_3NH_3^+ ion, resulting in a modified $\text{CH}_3\text{NH}_3\text{PbI}_3$ or a stable non- $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase (e.g., layered perovskite). The perovskite layer in lateral regions (uncovered by metal electrode) of PVSC would directly react with ligand vapors to form a stable low-dimensional perovskite complexes (see Equation (7)), while the perovskite in active region covered by metal electrode will not be changed dramatically



As shown in Figure 10b, the control device completely degraded within 100 h by the maximum power point (MPP) tracking. In contrast, the LPD treated device maintained $\approx 70\%$ of the initial PCE under 1 sun continuous illumination for 500 h. The PDL treatment enhances the long-term stability of the PVSCs through molecular encapsulation of 3D perovskite of active region achieved by: i) forming the low-dimensional perovskites in the lateral region, which block the moisture diffusion into the operational region; ii) forming the low-dimensional perovskites at the interface between 3D perovskites and ETLs, which neutralized and suppressed the ion migration preventing damages to the electrode.

5. Summary and Outlook

In this article, we have summarized the roles of ligand in perovskite photovoltaics from the perspectives of film formation, passivation, and stability.

1) **Film Formation:** For ligand-assisted one-step deposition of perovskite film, ligand interacts with metal ions in perovskite framework in precursor solution and form an intermediate phase, which slows down the crystallization rate of perovskite and produces homogeneous nucleation, thus finally producing a high-quality (good morphology and highly crystalline) perovskite film by controlling the release of ligand from the intermediate complex. For ligand-assisted two-step deposition of perovskite

film, ligand interacts with lead halide to form adducts, which benefit the perovskite formation through two perspectives: i) increase the number of active sites toward ammonium halide; ii) changing the reaction pathways and reducing the activation energy.

Although many groups had investigated the possible mechanism of ligand-assisted perovskite formation, some in situ characterization techniques (e.g., FTIR, Raman, XRD) shall be developed to understand how the ligand control the perovskite crystallization. The crystal structure of coordination complexes is also important to reveal the role of ligand in perovskite formation. Meanwhile, comprehensive studies shall be conducted to unveil the effect of the ligand with different molecular structures and category the ligand with various functions. These properties of the ligand are suggested to share with all the scientists, which may benefit the material optimization by machine learning in the future.

Ligand engineering can also be applied to prepare high-quality lead-free perovskites. Until now, the champion efficiency of tin perovskites, bismuth perovskites, double perovskites is 9%,^[196] 1.64%,^[218] and 2.5%,^[219] respectively. We speculate that ligand-assisted perovskite formation strategy will significantly improve the performance of lead-free perovskites, which is also a critical issue before the commercialization of perovskite photovoltaics.^[220] Meanwhile, some ligands utilized for forming perovskite film could also be employed to synthesize high-quality perovskite single crystals and quantum dots.

- 2) **Passivation:** Tailoring functional ligands to passivate the defects in perovskite films and interfacial traps have been demonstrated to effectively reduce the energy loss and thus improve the PVSCs performance. To guide the design of efficient ligands, a fundamental understanding of the types and density defects that form in different perovskite materials and their impact on electronic transport properties and photovoltaic performance should be lucubrated. A molecular library should be established by investigating the effect of coordination atom, length of alkyl chain, conjugated system, and the substituent of the ligand on the passivation capacity.
- 3) **Stability:** Judicious design of ligand has been demonstrated to significantly enhance the stability via the reduction of defects and the formation of a water-resistant layer on perovskite crystals. Other factors (e.g., oxygen, thermal stress, ion migration) cause the degradation of perovskite may also be addressed by ligand engineering. For example, recent studies show that the redox-oxidation chemistry may be a potential tool to inhibit the oxidation of perovskite caused by oxygen.^[88,221] Ligand-stabilized FAPbI_3 and inorganic perovskite (e.g., $\alpha\text{-CsPbI}_3$) is a promising candidate for fabricating thermal stable solar cells.^[110,111,222,223] The suppressed ion migration of low-dimensional may be used as a buffer layer to avoid the degradation of 3D perovskites caused by the movable ion species (e.g., iodide).^[224]

We noticed that most of the previous stability results are obtained by shelf life test, which cannot reflect the effectiveness of ligand under operational conditions. Therefore, standard protocols to characterize the effectiveness of ligand in improving the stability of PVSCs shall be developed.

A reliable way to investigate PVSC stability is under 1 sun illumination (AM 1.5G), preferably at maximum power point (MPP) and both under room and elevated temperatures (e.g., 85 °C). The atmospheric environment of the experiment should be carefully controlled (e.g., 85% relative humidity).^[225] The stability data obtained by standard protocols will be helpful for eventually developing efficient ligands for stabilizing PVSCs.

Finally, the combined experimental and theoretical methodologies (e.g., DFT calculations) are also very helpful for us to design the molecular structure of ligands. We hope through the facile design of the ligand molecules, we believe that PVSCs with long-term stability of 5 years and PCE of 25% can be simultaneously achieved in the near future.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the University Grant Council of the University of Hong Kong (Grant No. 104003113), the General Research Fund (Grant Nos. 17211916, 17204117, and 17200518), and the Collaborative Research Fund (Grant No. C7045-14E) from the Research Grants Council of Hong Kong Special Administrative Region, China. Z.H. thanks Zhifu Liang for proof-reading.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

device stability, ligands, metal halide perovskites, passivation, perovskite solar cells

Received: September 2, 2018
Published online:

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