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The nonhalides in perovskite solar cells

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Recently, halide perovskite solar cells (PSCs) have accomplished the most remarkable progress in emerging photovoltaic technology. However, their poor stability hinders the route to commercialization. Notably, the high chemical activity of halides such as I⁻ and Br⁻ and the formed halide-related vacancy defects lead to the instability of PSCs. In spite of the importance of X-site anions, more and more works have been devoted to the polyatomic pseudohalides and superhalogens in perovskites. In this context, this review will focus on the basic understanding of the structural and photoelectric properties of pseudohalides and superhalogens. We comprehensively summarize the current research progress of SCN-, $HCCO^-$, Ac^- , BF_4^- , BH_4^- , and PF_6^- anions to realize high structurally stable perovskites and related solar cells. Based on these observations, some perspectives on future efforts toward achieving highly stable PSCs are proposed and discussed.

1. Introduction

Perovskite solar cells (PSCs) have driven much interest in the development of photovoltaic devices since they first emerged in 2009.^{1,2} The hybrid organic-inorganic halide perovskites act as a classical solar absorber material. Their great merits such as high carrier mobility, high absorption coefficient, low carrier recombination rate, low exciton binding energy, high defect tolerance, and tunable band-gap properties enabled an outstanding performance within a decade.³⁻⁶ The certified power conversion efficiency (PCE) has been pushed to 25.7% with superior longterm operational stability.7

In general, the halide perovskite has a ABX3 scaffold, where the A site denotes a monovalent cation (such as CH₂NH₃⁺ (MA⁺), CH(NH₂)₂⁺ (FA⁺), and Cs⁺), the B site denotes a divalent metal cation (such as Pb2+ and Sn2+), and the X site denotes a monovalent anion (such as I-, Cl-, and Br-).8 The cornershared [BX₆]⁴⁻ octahedra form a cuboctahedral cavity to accommodate the A site that satisfies the three-dimensional (3D) perovskite structure. The electronic and optical properties of the halide perovskite show a great relationship to the composition and structural variations. The exploration of the possible range of A-site cations has been widely investigated. The alternative Asite cations to yield the 3D perovskite lattice only are Cs⁺, FA⁺, and MA⁺. Other large organic spacer cations (such as PEA⁺

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 $(C_6H_5(CH_2)_2NH_3^+)$, BA^+ $(CH_3(CH_2)_3NH_3^+)$, or EDA^{2+} $((CH_2)_2-$ (NH₃)₂²⁺)) could be incorporated into perovskites to form a low-dimensional structure like the RP (Ruddlesden-Popper) phase with a formula of $A'_{2}A_{n-1}B_{n}X_{3n+1}$ or the DJ (Dion-Jacobson) phase with a $A'A_{n-1}B_nX_{3n+1}$ framework. However, a preferred vertical orientation of a low-dimensional perovskite is hard to achieve owing to its different quantum well thickness with different n values. The small n-value perovskite is more likely to orient parallel to the substrate, and the high *n*-value perovskite tends to achieve a vertical orientation.9

In addition, the Pb²⁺ of the B-site cation has high toxicity, which is very concerning in terms of environmental and human health concerns. Other metal cations with similar electron configurations in the IVA/VA group, such as Sn²⁺, Ge²⁺, Sb³⁺, Bi³⁺, Ag⁺, Cu⁺, and Au⁺, still show poor performance. ^{10,11} Meanwhile, I-, Cl-, and Br- are the most widely used X-site anions, which react with BX2 to form the ABX3 perovskite materials. However, the halide anion of I shows high chemical activity and the corresponding I vacancy defects could form easily. The existing I vacancy defects have a negative impact on the device stability owing to the unwanted increase in ion



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conductivity. 12 Partial substitution of I by Br could tune the band gap and improve the structural stability. As for Cl⁻, the Cl incorporation could affect the nucleation and crystallization of the perovskite film, although it is too small to incorporate into a perovskite lattice.¹³

Other efforts have also been reported to form stable perovskites such as SCN (thiocyanate), Ac , HCOO , BF₄ (tetrafluoroborate), and PF₆⁻ (hexafluorophosphate). ^{2,14-17} Yan et al. delivered efficient and stable PSCs by using Pb(SCN)2 in a perovskite precursor. 18 This SCN--modulated perovskite film is a high-quality perovskite film with increased grain size. Other studies with the HCCO- anion have also been investigated. Estroff and Abate et al. enabled an excellent coverage and large crystal domains with the use of MAHCOO. 19,20 Grätzel et al. used FAHCOO to suppress the anion-vacancy defects and nonradiative recombination in FAPbI₃ perovskites. The BF₄ anion plays a key role in improving charge extraction in the interface and reducing the voltage deficiency. 17,21 An appropriate amount of PF₆⁻ addition could stabilize the Pb-X-Pb octahedral frame in perovskites, which is beneficial for the less nonradiative recombination and enlarged carrier lifetime. 21 Notably, these nonhalides have shown various functions in realizing superiorly stable and high-performance PSCs. However, the effects of anions beyond I-, Cl-, and Br- on perovskites have yet to be fundamentally understood.

In this review, we first describe the basic understanding of the structural and photoelectric properties in nonhalides including pseudohalides and superhalogens. Then we comprehensively summarize the current research progress of SCN-, HCCO-, Ac-, BF₄-, BH₄-, and PF₆- anions to realize highly structurally stable perovskite materials and devices. Their functions in perovskites are systematically summarized, including the strong interaction with perovskites, nucleation and growth, phase stability, efficiency, stability enhancement, and defect passivation. Finally, based on these observations, we propose our perspectives on the future efforts towards achieving highly stable PSCs and devices.



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2. Overview of nonhalide anions

To obtain a typical 3D perovskite crystal, the crystallographic stability is determined by Goldschmidt's tolerance criteria (t) and octahedral factor (μ) :²²

$$t = \frac{R_{\rm A} + R_{\rm X}}{\sqrt{2}(R_{\rm B} + R_{\rm X})}\tag{1}$$

$$\mu = \frac{R_{\rm B}}{R_{\rm X}} \tag{2}$$

where R_A , R_B , and R_X are the ion radii of A, B, and X site ions. To form a stable perovskite crystal with a 3D framework, the value of t and μ must be in the range of 0.81 < t < 1.11, and 0.44 < μ < 0.90, respectively. ^{23,24}

The X-site anions are not limited to the three halides (I-, Cl⁻, and Br⁻), alternatively, it can be defined as negative monovalent anions or polyatomic anions with -1 charge. The ion radius shows a decreasing trend: $R_{\rm Cl}$ (181 pm) $< R_{\rm Br}$ (196 pm) $< R_{\rm I}^-$ (220 pm). There are two types of nonhalides in perovskites (Fig. 1a). On the one hand, the stable pseudohalides (e.g. SCN⁻, Ac⁻, and HCOO⁻) have gained much attention. SCN⁻ has a similar ion radius to I⁻ (217 pm for SCN⁻).²⁵ The linear Lewis structure of SCN- showed stable resonance, rendering a strong Lewis acid-base interaction with Pb²⁺ or Sn²⁺ when considering the long pairs of electrons from N and S atoms. 26,27 HCOO has a stronger bonding with FA than BF₄, I⁻, Br⁻, and Cl⁻ owing to the hydrogen bonding.² The most deleterious defects of I- vacancies can be eliminated with HCOO⁻. On the other hand, superhalogens such as BH₄⁻, PF₆⁻, and BF₄⁻ have a higher electronegative and electron affinity than halides.^{28,29} The use of superhalogens greatly enhances the structural stability via partial substitution of halides. Therefore, the recent emergence of pseudohalides or superhalogens can significantly mitigate the defect-related instability in PSCs.

2.1 Pseudohalides

The effective ion radii of polyatomic anions usually satisfy the following criteria:30

$$R_{\text{Xeff}} = \sqrt[3]{\text{volume} \times \frac{3}{4\pi}}$$
 (3)

It is reliable to apply a general comparison of the relative ion size of the pseudohalides. To satisfy Goldschmidt's tolerance criteria, the range of A-site cations increased with the size of X-site anions (Fig. 1b). The maximum value of spherical X anions is $R_{\rm X}$ = 2.42 $R_{\rm B}$ ($\mu \geq 0.414$) to stabilize the $[{\rm BX_6}]^{4-}$ octahedral. Therefore, the X-site anions with a size up to 287 pm can form a stable $[BX_6]^{4-}$ octahedral, which allows the size of A sites up to 288 pm in lead perovskites. For nonspherical X anions, the effective R_X may be greater than 2.42 R_B , which depends on how the ligands of the X site coordinate to the B site. 30 The pseudohalides mainly contain N_3^- (azides), 31 CN $^-$ (cyanides), 32 N(CN) $_2^-$ (dicyanamides), 33 SCN $^-$, 29 HCOO $^-$, 2 Ac $^-$, 34 and I_3^- (triiodides).35 Beside the Pb- and Sn-based perovskites, the perovskite-like lattice can accommodate other B-site cations, such as $[(CH_3)_4N]Mn(N_3)_3$, $Ni(NH_3)(CN_2)\cdot C_6H_6$, $[NH_3(CH_2)_7NH_3]_2Au_2I_6$ (I₃)₂, MAMn(HCOO)₃, etc. 31,32,35,36 The polyatomic HCOO anion has a similar size to Br and a planar structure.

SCN⁻ has been extensively investigated for improving the stability of perovskites. Yan et al. calculated the crystal structure of MAPbIx(SCN)3-x perovskites by density functional theory (DFT) calculation (Fig. 1c and d).³⁷ The incorporation of the SCN group delivered a thermodynamically stable lattice with a pseudo-orthorhombic framework.37 Ganose et al. also verified

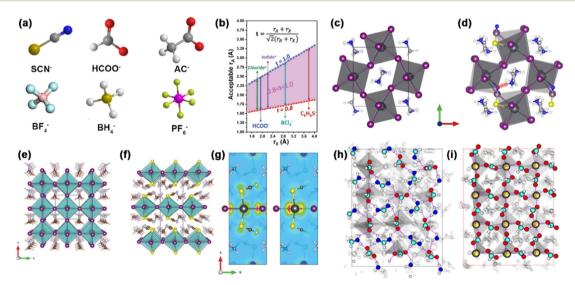


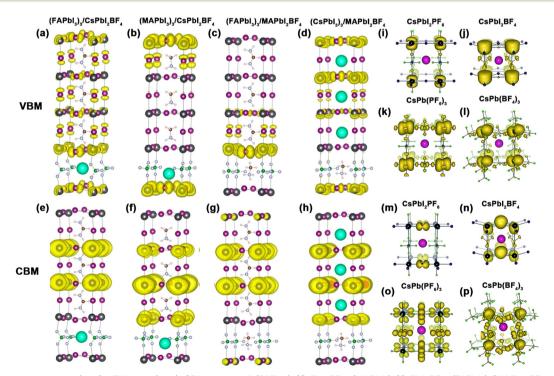
Fig. 1 (a) The structure of nonhalides in perovskites. (b) The range of ion radii of A-site and X-site ions that satisfy 0.81 < t < 1.11. Reproduced with permission. 30 Copyright 2019, Wiley-VCH Publications. Crystal structure of (c) MAPbI₃ and (d) MAPb(SCN)I_{3-x}. Reproduced with permission. 37 Copyright 2015, Springer Nature. Crystal structure of (e) MAPbI₃ and (f) MA₂Pb(SCN)₂I₂. (g) Charge density isosurface of VBM (left) and CBM (right) in MA₂Pb(SCN)₂I₂. Reproduced with permission.³⁸ Copyright 2015, American Chemical Society. Top view of surface atoms in (h) the FA⁺-terminated surface and (i) Pb²⁺terminated surface. Reproduced with permission.² Copyright 2020, Springer Nature.

the thermodynamically stable structure in 2D hybrid perovskites (Fig. 1e and f).³⁸ The 2D MA₂Pb(SCN)₂I₂ layered perovskite has a space group of Pnm21, where the Pb atom octahedrally coordinated to two apical (or trans) S-bonded SCN anions and four axial I⁻ anions. Meanwhile, the MA⁺ molecule was sandwiched between the layers, forming an orthorhombic pattern like the K₂NiF₄ compound. SCN⁻ has a great role in bonding, where the valence band maximum (VBM) and conduction band minimum (CBM) is determined by Pb 6p-I 5p and Pb 6p orbitals, respectively (Fig. 1g). There is also a small contribution of S 3p and N 2p in the SCN⁻ in VBM. HCOO⁻ was rarely reported in the inorganic-organic hybrid perovskites. Instead, it can coordinate with Mn²⁺ cations and form a MAMn(HCOO)₃ structure. It plays a significant role in eliminating halide vacancy defects and alleviates the adverse ionic conductivity of perovskites (Fig. 1h and i).2

2.2 Superhalogens

Superhalogens have a higher electron affinity than halides, such as BH₄⁻, BF₄⁻, and PF₆⁻. ³⁹ Ogale et al. first applied them to solid-state dye-sensitized solar cells as a component of the X site by using MABF₄. ⁴⁰ BF₄ and PF₆ could partially substitute I[−] to form stable organic-inorganic perovskite superlattices, which provide a large variety of possibility to expand the possible perovskite formulations. 41,42 The addition of BF $_4$ in FAPbI₃ could enhance the formation energy of FA⁺-related vacancies to improve the structural stability.42 BF4- has a higher electronegativity than the F⁻, implying that the bonding between BF4- and its neighboring Pb atom would be more ionic. Li et al. calculated the VBM and CBM of the minimumenergy superlattice structures of (FAPbI₃)₃/CsPbI₂BF₄, $(MAPbI_3)_3/CsPbI_2BF_4$, $(FAPbI_3)_3/MAPbI_2BF_4$, and $(CsPbI_3)_3/MAPbI_2BF_4$ MAPbI₂BF₄ (Fig. 2a-d and e-h).⁴³ The charge density in (MAPbI₃)₃/CsPbI₂BF₄, (FAPbI₃)₃/MAPbI₂BF₄ illustrated that the VBM and CBM states were distinctly separated in space and had no slap. While the charge density of VBM and CBM value in (FAPbI₃)₃/CsPbI₂BF₄ and (CsPbI₃)₃/MAPbI₂BF₄ had a slight overlap on the Pb atoms and was far away from the CsPbI₂BF₄ and MAPbI₂BF₄ layers. They also calculated the layers of FAPbI₃, MAPbI₃, and CsPbI₃ from one to three along the direction of the base vector a. The complete separation of charge density in VBM and CBM states is beneficial to the electrons/holes collection owing to the effective electrons/holes restriction in different atomic layers. Increasing the number of layers could solve the incomplete separation of the charge density of the VBM and CBM states.

For perovskite superlattices, the electrons are distributed in the potential well and holes in the potential barrier. For instance, the superlattice with BF₄⁻ is a type-II superlattice.⁴³ The great spatial separation of electrons/holes with superhalogens has a significant effect on carrier transport and collection. In addition, Hendon et al. simulated the crystal structure with VBM and CBM states of $CsPbI_{3-x}(PF_6)_x$ and $CsPbI_{3-x}(BF_4)_x$ perovskites as shown in Fig. 2d-p.41 Compared to the octahedral CsPbI₃ perovskite (pm3m), CsPb(PF₆)₃ maintained a cubic lattice by the linear coordination through the axial termini. $CsPb(BF_4)_3$ had C_s symmetry with C1m1 space group. The B-F bond in CsPb(BF₄)₃ was not inline owing to the linear



 $\textbf{Fig. 2} \quad \text{Charge density in the (a-d) VBM and (e-h) CBM states of } (\text{FAPbl}_3)_3/\text{CsPbl}_2\text{BF}_4, \\ \text{(MAPbl}_3)_3/\text{CsPbl}_2\text{BF}_4, \\ \text{(FAPbl}_3)_3/\text{MAPbl}_2\text{BF}_4, \\ \text{and } (\text{CsPbl}_3)_3/\text{MAPbl}_2\text{BF}_4, \\ \text{(SPbl}_3)_3/\text{MAPbl}_2\text{BF}_4, \\ \text{(SPbl}_3)_3/\text{MAPbl}_2\text{BP}_4, \\$ MAPbl₂BF₄, respectively. Reproduced with permission. ⁴³ Copyright 2020, American Chemical Society. Charge density in the (i–I) VBM and (m–p) CBM states of CsPbl₂PF₆, CsPbl₂BF₄, CsPb(PF₆)₃, and CsPb(BF₄)₃, respectively. Reproduced with permission.⁴¹ Copyright 2015, The Royal Society of Chemistry.

coordination occurring by two edges of the tetrahedron. As for BH₄⁻, it consists of two elements and has one extra electron satisfying the electronic shell closure.44 In addition to the suppression of I vacancy defects, BH₄ has a strong dihydrogen interaction with MA⁺. The existence of BH₄⁻ could substitute the I⁻ anion or compensate for the I⁻ vacancy defects.45,46

3. SCN⁻

3.1 Acting as an X-site anion in halide perovskites

Bilaji et al. first used a pseudohalide salt of Pb(SCN)2 and Pb(NO₃)₂ with MAI vapors through a sequential vapor-assisted solution process⁴⁷ to achieve the ion exchange of SCN⁻ and I⁻, or NO₃⁻ and I⁻, respectively. Yan et al. used Pb(SCN)₂ precursor and prepared a high-quality MAPbI_{3-x}SCN_x perovskite film.³⁷ The S and N atoms with long pairs of electrons in SCN have strong interaction with Pb atoms, which in turn stabilized the frame structure of MAPbI(SCN)2. Jiang et al. compared the X-ray

diffraction (XRD) patterns of MAPbI₃ and MAPbI(SCN)₂ (Fig. 3a). 48 The characteristic peaks at 14°, 20°, 29°, 32°, and 41° for the MAPbI(SCN)₂ film could be indexed to the formed perovskite structure. They designed moisture-tolerance tests via the reflection spectrum in Fig. 3b and c. There is no obvious variation in the film color of the MAPbI(SCN)₂ film for 0-1.5 h. Moreover, the black MAPbI(SCN)₂ film still maintained the original morphology for months in air with 40% relative humidity. After exposure to air with 95% humidity, the MAPbI(SCN)₂ remained the stable perovskite structure with an E_{g} of 1.532 eV. The resulting PSC device with MAPbI(SCN)₂ delivered a PCE of 8.3%. Yan et al. indicated that adding $Pb(SCN)_2$ below 1.0 mmol% did not change the E_g value of FA_{0.8}Cs_{0.2}Pb(I_{0.7}Br_{0.3})₃ perovskites. 49 Lou et al. also illustrated that the pure $CsPb(SCN)_3$ displayed the highest E_g compared with CsPbBr3 and CsPbI3 perovskites.50 The up-shifted VBM was responsible for the increase of E_g . The strong interaction between SCN⁻ and Pb²⁺ (like Pb-S, Pb-N, and Pb-C bonds) lead to a rather high-energy anti-bonding orbital when compared to CsPbBr3 and CsPbI3.

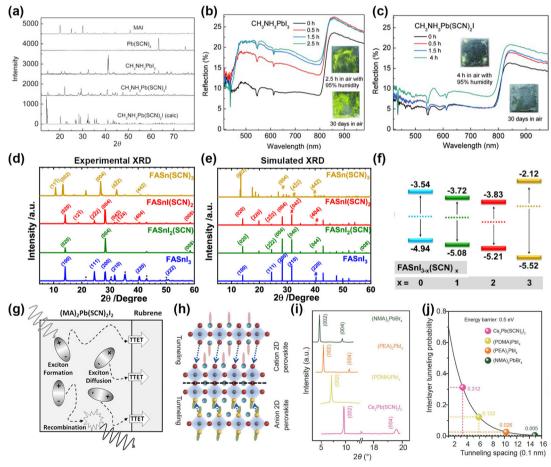


Fig. 3 (a) XRD patterns of MAPbI₃ and MAPbI₂(SCN) perovskite films. (b and c) Reflection spectrum with stability tests of MAPbI₃ and MAPbI₂(SCN) in the air with 95% humidity. Reproduced with permission. 48 Copyright 2015, Wiley-VCH Publications. (d and e) Experimental and simulated XRD patterns of $FASnl_{3-x}(SCN)_x \ perovskite \ films. \ (f) \ Energy \ level \ diagrams \ of \ FASnl_{3-x}(SCN)_x \ perovskites. \ Reproduced \ with \ permission. \ ^{52} \ Copyright \ 2020, \ American \ Particle \ Parti$ Chemical Society. (g) Exciton diffusion and triplet-triplet energy transfer at the 2D perovskites/rubrene interface. Reproduced with permission.⁵⁵ Copyright 2017, Wiley-VCH Publication. (h) The lattice structure of Cs₂Pbl₂(SCN)₂ perovskites. (i) XRD patterns of four types of 2D perovskites. (j) Relationship between charge channeling probability and interlayer spacing. Reproduced with permission.⁵⁷ Copyright 2021, Springer Nature.

Meanwhile, SCN⁻ has a strong ionic interaction with Sn²⁺.⁵¹ Owing to the π -conjugated electron system, the incorporation of SCN⁻ showed great enhancement in photoelectron transfer.^{52,53} Diau et al. observed the enhanced structural stability in FASnI_{3-x}(SCN)_x perovskites and a maximum was reached in FASnI(SCN)₂.⁵² Indeed, SCN⁻ was deemed as a bridging ligand to construct a stable octahedra framework due to its ambident nucleophilicity. The XRD patterns in Fig. 3d and e showed three main perovskite peaks around 14°, 28°, and 41° in FASnI_{3-x}(SCN)_x perovskites. However, the diffraction peaks of FASn(SCN)₃ shifted to smaller angles with the increase of lattice spacing. Similar to the other mixed-halide substitution, 54 adding SCN^- in $FASnI_{3-x}(SCN)_x$ films showed a decreased VBM value when increasing x from 0 to 3 (Fig. 3f). Besides, $FASnI_{3-x}(SCN)_x$ has enhanced oxidation resistance, which is attributed to the enhanced hydrophobicity and strong interaction with Sn²⁺.

The 2D (MA)₂Pb(SCN)₂I₂ perovskites exhibit a photoactive triplet state.⁵⁵ After spin-coating rubrene, a small organic molecule, the obvious triplet energy transfer from (MA)2 Pb(SCN)₂I₂ to rubrene was observed (Fig. 3g). This phenomenon exhibited unique photophysical behavior with triplet state phosphorescence. Therefore, 2D perovskites with SCN have great potential in the use of triplet sensitizer. Moreover, 2D Cs₂PbI₂(SCN)₂ shows high thermal stability.^{56,57} Meng et al. explored the photoelectric properties of Cs2PbI2(SCN)2 perovskites.⁵⁷ The charge transport across the inorganic layers is determined by the quantum tunneling effect. The space between inorganic layers showed negligible contributions to VBM and CBM. It was observed that Cs₂PbI₂(SCN)₂ had a crystal orientation along the [001] direction like (NMA)₂PbBr₄, (PEA)PbI₄, and (PDMA)PbI₄. However, the (002) and (004) peaks shifted to larger angles with decreasing size of the cation or anion (Fig. 3i). Meanwhile, the interlayer tunneling probability of the Cs₂PbI₂(SCN)₂ perovskite reached 0.312, which was ten times higher than those of (NMA)₂PbBr₄ and (PDMA)PbI₄ (Fig. 3j). Large tunneling probability and small interlayer spacing contributed to fast charge transport with high conductivity. Therefore, 2D Cs₂PbI₂(SCN)₂ perovskites have super small interlayer spacing and interlayer nano channels, which will promote the charge transport.

Ning et al. employed PEAI and Sn(SCN)₂ to form 2D PEA₂Sn₂I_{4-x}SCN_x perovskites as an intermediate template for the growth of 3D CsSnBrI_{2-x}SCN perovskites.⁵⁸ This approach enabled the preferred out-of-plane growth of a 2D-3D mixed structure with homogeneous inclusion of SCN- in the 3D CsSnBrI_{2-x}SCN perovskite structure, further contributing to the suppressed defect density and retarded Sn2+ oxidation. The pseudohalide-modulated 2D perovskites also show great potential in tuning the electronic properties of perovskites. Liu et al. adopt the 2D Sn perovskites with pseudohalide to adjust the electronic and excitonic properties.⁵⁹ The 2D BA₂SnI₂SCN₂ and BA₂SnI₄ perovskites had the smallest exciton binding energy and effective mass compared with the Pb- and Br-based 2D perovskites. The strong exciton effect in pseudohalide-substituted 2D tin perovskites could enhance PL performance as well as photocurrent when applied in PSCs according to the J-V curve.

3.2 Acting as additives in halide perovskites

3.2.1 Amine-type additives

GUASCN (guanidinium thiocyanate). The strong binding affinity of SCN- could recover the oxidized sites and coordinate with undercoordinated sites to passivate the defects, which cannot be reached by classical halides. 27,60,61 The strong hydrogen bonding between GUA⁺ and SCN⁻ further contributes to the additional stabilization of perovskites. Pham et al. elucidated the grain growth mechanism with GUASCN:62

$$MAPbI_3 + GUASCN \rightarrow GUAI(s) + PbI_2(s) + MA(g) + HSCN(g) \uparrow$$
(4)

With the surface treatment of GUASCN, the HSCN gas was expelled from the film rapidly and the formed GUAI, PbI₂, or the $((GUAI)_x(PbI_2)_y)$ compound accumulated at GB as a secondary phase. The MA gas enhanced the de-nucleation rate and solubility of unwanted small MAPbI₃ crystals, thus facilitating grain coarsening. Zhu et al. proved that adding 7 mol% GUASCN can substantially improve the carrier lifetime up to 1 μs in Sn-Pb perovskite films. 14,63 The calculated surface recombination velocity (S) and carrier diffusion coefficient (D) from the transient reflection (TR) spectrum in Fig. 4a and b illustrated that the fitted S increased from $10-100 \text{ cm s}^{-1}$ to 1.0 s^{-1} \times 10² cm s⁻¹. GUASCN is a common additive to reduce the pinholes and small grains in hybrid halide perovskites. Zhang et al. claimed that GUASCN could inhibit the 1D solvate intermediate phase and form high-quality quasi-2D films.64 The following reaction revealed the potential mechanism:

$$MAPbI_3 \cdot DMF + yGUASCN \rightarrow y/xPbI_{2-x}SCN_x + (1 - y/x)PbI_2 + MAI + yGUAI + DMF$$
 (5)

The decomposition products of GUAI and $PbI_{2-x}SCN_x$ enlarged the grain size and enhanced the crystalline quality of thin films. The fitted rapid rise time (τ) by ultrafast transient absorption (TA) spectroscopy in Fig. 4c and d indicated that the perovskite film with GUASCN had faster τ of 4.43 ps, 4.78 ps, and 107.90 ps for n = 3, 4, and 5, respectively, where the control films had τ of 0.15 ps (n = 2), 6.78 ps (n = 3), 8.86 ps (n = 4), and 13.21 ps (n = 5), respectively. Therefore, GUASCN significantly improved the energy/charge transfer efficiency due to a suppressed recombination center and effective energy/charge transfer. A similar approach was also reported in colloidal quantum dot (CQD) photovoltaics. 65 The bidentate nature of SCN- leads to improved electronic coupling in the CQD matrix. 2,66,67 GUASCN has nearly zero dipole moment, thus benefiting charge transport. By surface reconstruction, GUASCN played a key role in surface passivation via epitaxial surface bridges with CQD. The oxidized species were eliminated with GUASCN by substituting Pb-O to the Pb–SCN bond (Fig. 4e). The upshifted C≡N stretch in Fig. 4f proved the surface reconstruction between the SCN and CQD surface.

NH₄SCN. The pseudohalide SCN⁻ anion could drive the secondary formation of thin films as the intermediate catalyst, therefore ensuring the composition purity both in the original

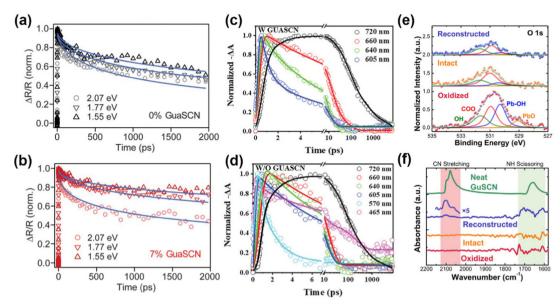


Fig. 4 (a and b) TA spectra of 0% and 7% GUASCN addition under different pump photon energies. Reproduced with permission.¹⁴ Copyright 2019, American Association for the Advancement of Science. (c and d) TA kinetics of quasi-2D perovskites without/with GUASCN. Reproduced with permission.⁶⁴ Copyright 2022, Wiley-VCH Publication. (e) XPS peaks of O 1s. (f) FTIR spectra of the CQD solids and neat GUASCN. Reproduced with permission. 65 Copyright 2022, American Chemical Society.

films and final polycrystals. The SCN group in NH₄SCN was not incorporated into the perovskite lattice in the final-state perovskite films. Jen et al. proposed the recrystallization process with NH₄SCN:⁶⁸

$$MAPbI_3 + SCN^- \rightarrow PbI_6^{4-} + MA^+ \cdot SCN^-$$
 (dipping) (6)

$$MA^{+}SCN^{-} + NH_{4}^{+} \rightarrow MA^{+} + HSCN (g) \uparrow$$

+ $NH_{3} (g) \uparrow$ (annealing) (7)

$$PbI_6^{4-} + MA^+ \rightarrow MAPbI_3 \tag{8}$$

Therefore, the undissolved polycrystals could recrystallized and form new MAPbI3 crystal. The SCN- anions in NH4SCN can strongly interact with Pb²⁺/Sn²⁺ and the organic cations, where $\mathrm{NH_4}^+$ cations could interact with $[\mathrm{PbI_6}]^{4-}$ or $[\mathrm{SnI_6}]^{4-}$. Chou et al. revealed the role of in 2D tin perovskites by time-of-flight secondary ion mass spectrometry (ToF-SIMS) to detect the location of SCN⁻ anions (Fig. 5a and b).⁷¹ The positive and negative signals of Sn, I, SCN, and TEA (2-thiophene-ethylammonium) were located at the same region, which indicated the SCN can coordinate with Sn²⁺. Zhang et al. investigated the NH₄SCN concentration in the orientation and crystallinity of 2D $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$ films (Fig. 5c-e).⁷² The 2D perovskites in the absence of NH₄SCN showed random orientation and weak preferential orientation, while the film with 2% SCN had sharp and discrete Bragg spots and a considerable increase in orientation.

MASCN and FASCN. MASCN can significantly reduce the reaction activity via the strong interaction with Sn²⁺/Pb²⁺.⁷³⁻⁷⁵ For instance, Lian et al. proved that MASCN can retard the reaction between FAI and Sn²⁺ and also suppress the Sn²⁺ oxidation.74 Zhang et al. added 5% MASCN into (PA)2(MA)4Pb5I16 (PA is *n*-pentylammonium) perovskite precursor to regulate the phase distribution.⁷⁵ The TA patterns in Fig. 5f at various delay times indicated that the peaks at 570 nm, 606 nm, 640 nm, 666 nm, and 720 nm attributed to n = 2, n = 3, n = 4, n = 5, and 3D-like phases in $(PA)_2(MA)_4Pb_5I_{16}$ film, respectively. The n=2phase disappeared and the 3D-like phase enhanced remarkably in MASCN-modified films (Fig. 5g), further proving that the perovskite film with SCN⁻ obtained a high n-value phase and large grain. Moreover, the improved water contact implied great hydrophobicity of perovskite films in Fig. 5h. The XRD patterns in pseudohalide-induced perovskite films had barely changed 2D phases after storing for 60 days. Different from the previous report, Grätzel et al. used MASCN and FASCN vapor to achieve phase transition and obtain stable black-phase FAPbI₃ perovskites.⁷⁶ The formed corner-sharing Pb-I-SCN structures at the interface could maintain kinetically stable perovskites. The vapor-treated FAPbI₃ devices maintained 94.4% PCE of the original value after 500 h testing at the maximum power point (MPP).

PEASCN and TEASCN. Compared to pure PEAI treatment, the PEASCN source conformed to a more crystalline film.⁷⁷ The PEASCN sample can reach a carrier lifetime of over 2 µs and carrier mobility over 40 cm⁻² V⁻¹ s⁻¹. Khadka et al. introduced PEASCN into pure FASnI₃ perovskites to achieve defect suppression in the bulk and interface.⁷⁸ These polyatomic pseudohalides delivered a high PCE of 9.65% with a V_{oc} of 667 mV in the corresponding devices. Therefore, the PEASCN not only acts as a 2D additive but also as a crystallization regulator. Ning et al. synthesized a new pseudohalide molecule TEASCN (TEA is 2-thiopheneethylamine) to construct a bilayer quasi-2D structure on the Sn-Pb perovskite surface.⁷⁹ The TEASCN-

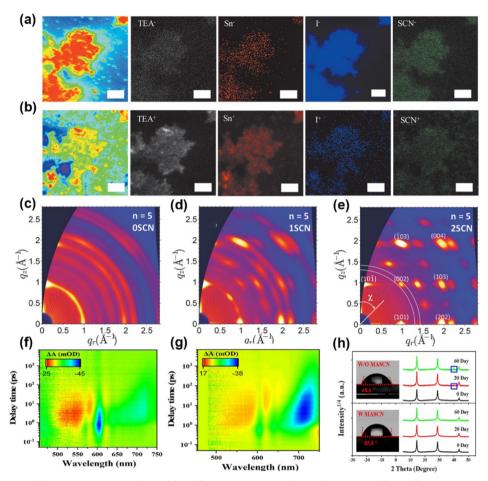


Fig. 5 ToF-SIMS mapping of 2D perovskites with 7% NH₄SCN: (a) negative signals of TEA⁻, Sn⁻, I⁻, and SCN⁻; (b) positive signals of TEA⁺, Sn⁺, I⁺, and SCN⁺. Reproduced with permission.⁷¹ Copyright 2020, Wiley-VCH Publication. (c-e) 2D GIWAX patterns of 2D perovskite films with various amounts of NH₄SCN. Reproduced with permission.⁷² Copyright 2018, Wiley-VCH Publication. TA patterns of (PA)₂(MA)₄Pb₅I₁₆ film (f) without and (g) with MASCN. (h) XRD images and contact angle tests with or without MASCN. Reproduced with permission.⁷⁵ Copyright 2022, American Chemical Society.

introduced films enabled a high n-value (n = 2) phase while the TEAI-introduced films formed a low n-value phase of n = 1.

3.2.2 Metal-type additives. KSCN and NaSCN are the most commonly used additives in perovskites.80-84 Zhang et al. used the two additives to improve the microstructure perovskite structure and crystallinity of thin films. 18 The NaSCN treatment could suppress the Br vacancies and decreased the surface defect density, thus further increasing the device stability.⁸² Besides the effect of SCN-, K+ could also passivate defects. Xu et al. found that KSCN can enlarge perovskite grains to an average diameter of 11 µm.81 This attempt enabled the carrier diffusion length to around 25 µm in slot-die-coated perovskite films. Additionally, Cao et al. used KSCN as an interlayer between PEDOT:PSS and FA_{0.75}MA_{0.25}SnI₂Br perovskites to better match the energy alignment and optimize carrier transport in the interface.⁸³ The resulting tin perovskite device delivered a high PCE of over 11% with a $V_{\rm oc}$ of 840 mV. On the one hand, K⁺ diffused into the lattice and passivate defects in the GB. On the other hand, SCN⁻ anions coordinate with Sn²⁺ and restrain Sn²⁺ oxidation.

4. HCOO⁻ and Ac⁻

Pseudohalides HCOO and Ac anions could affect the crystallization and optoelectronic properties of perovskites. Adding a small amount of HCOO⁻ and Ac⁻ anions in precursors could achieve compact surface coverage and improve the crystallinity of perovskite thin films. 85 Interestingly, formic acid (FAH) is identified as one of the degradation products of DMF.86 Introducing additional FAH in the precursor enables the reduction of the hydrolysis of DMF. A 70–80 mV increased V_{oc} was achieved with 7.5 vol% FAH. Increasing the acidity would raise the concentration of all solutes and decrease the strength of solvents in the precursor, thus inducing supersaturation and crystal growth.87 Meng et al. observed dense nuclei with the snowflake-like crystal of FAHinduced perovskite film within 3.5 min as shown in Fig. 6a and b.88 The control film showed almost no nucleation after the spincoating process. Meanwhile, FAH is an ideal redox potential and has no negative effects in nucleation and crystal growth. Liu et al. pointed out the following reactions of FAH effect in precursor:⁸⁹

$$HCCO^{-} + 2I^{0} \rightarrow 2I^{-} + H^{+} + CO_{2}(g) \uparrow$$
 (9)

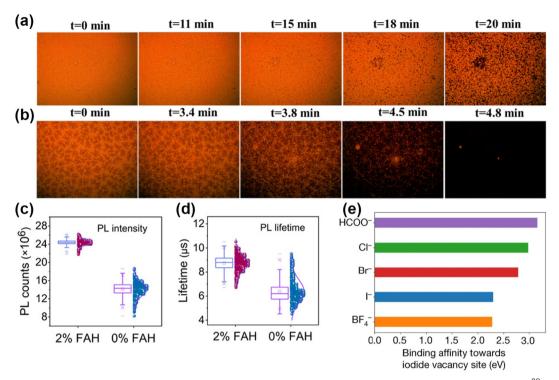


Fig. 6 (a and b) In situ microscopy patterns with 0 M and 0.764 M FAH-treated perovskite films. Reproduced with permission.⁸⁸ Copyright, 2020, Elsevier Publication. (c and d) PL intensities and lifetimes of perovskite films with or without FAH treatment. Reproduced with permission.⁸⁹ Copyright 2021, American Association for the Advancement of Science. (e) The interaction strengths of different anions with I⁻-vacancy defects at the perovskite surface. Reproduced with permission.² Copyright 2021, Springer Nature.

$$\text{HCCO}^- + \text{I}_3^- \rightarrow 3\text{I}^- + \text{H}^+ + \text{CO}_2 (g) \uparrow$$
 (10)

HCOO in FAH can react with adverse I and form I, H, and CO₂ gas. The generated H⁺ further inhibited the deprotonation of FA⁺. In addition, the FAMACs films with 2 mol% FAH showed higher photoluminescence intensity (Fig. 6c) and longer lifetime (Fig. 6d). Han et al. further reported that FAH enhanced the crystallinity of Sn-based perovskites and exhibited high reproducibility and PCE in the corresponding devices.⁹⁰

Estroff et al. first used MAFA (methylammonium formate), an ionic liquid (IL), in MAPbI₃ perovskites. 19 In addition to the advantages of HCOO⁻, the property of ILs also played a key role in film growth due to their outstanding thermal stability. 16,91 Abate et al. indicated that the crystallization and growth process with MAFA went through the following steps:²⁰ (i) the coordination of Pb2+ and HCOO- in precursor; (ii) the HCOO-Pb bond replaced by I-Pb bond when annealing at 100 °C; (iii) complete replacement by I-Pb bond and crystal growth. The MAFA was presented at the surface in the final form. By utilizing the pseudohalide anion, Jeong et al. attained a certified PCE of 25.2% and remarkable operational stability over 450 h.2 HCOO anions showed a strong affinity with Pb2+ and can form a stable bonding network at the Pb2+-terminated surface. As exhibited in Fig. 6e, the highest binding energy with I vacancies in HCOO also proved the strong defect passivation of anion vacancies via strong binding affinity.

Similar to HCOO-, volatile Ac- anions also can form an intermediate with perovskite and modulate the crystallization

process.^{34,92} Zhou et al. proposed a novel strategy to suppress adverse I₂ to reduce the energy and voltage loss. 92 FAAc (formamidine acetate) as a "residual free" weak alkaline can reduce the defect density at a deep level and in particular manipulate the stoichiometry at A sites in perovskite precursors. The characteristic peak of I2 at 360 nm showed a decreased tendency with the increasing amount of FAAc (Fig. 7a). As for the alkalinity, FAAc has a p K_a of around 7.64, whereas other alkaline additives such as NaAc (sodium acetate) and NaHCO3 have a pKa of 9.24 and 10.33, respectively. Therefore, a large range of FAAc can regulate the absorbance of I₂ (Fig. 7b), which indicated that the weak alkaline had a great potential to regulate the α-phase perovskites on a large scale. Additionally, the volatile Acfacilitated grain growth with enlarged grain size and film quality. Lv et al. further used MAAc in the Sn–Pb perovskite precursor. 93 The strong hydrogen bonding between MAI and MAAc can not only stabilize the perovskite lattice but also increase the viscosity and solubility of the solute in the solution.

PbAc₂ as a pseudohalide lead source has also been attempted to improve the perovskite growth and film morphology. 15 Compared to PbCl₂ and PbI₂ as displayed in Fig. 7c, the perovskite film from PbAc2 revealed better crystallinity. The transition process can be described as:

$$PbX_2 + 3MAI \rightarrow MAPbI_3 + 2MAX (X = Cl, I, Ac)$$
 (11)

The thermally unstable MAAc tends to evaporate more rapidly than MACl and MAI under annealing. The nucleation density with PbAc2 was higher than others and the film showed full

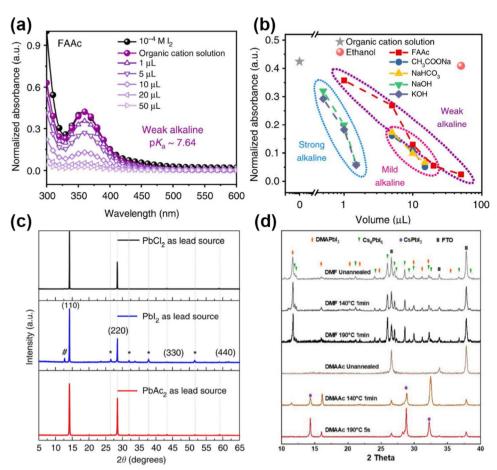


Fig. 7 (a) UV-Vis absorption of perovskite film with different amounts of FAAc. (b) Normalized absorbance with different additives. Reproduced with permission. ⁹² Copyright 2019, Springer Nature. (c) XRD patterns of perovskite films with PbCl₂, Pbl₂, and PbAc₂ sources. Reproduced with permission. ¹⁵ Copyright 2015, Springer Nature. (d) XRD patterns of CsPbl₃-DMAAc precursor with different annealing times. Reproduced with permission. 94 Copyright 2022, Wiley-VCH Publication.

coverage on the substrate. Meng et al. eliminated the Cs₄PbI₆ intermediate phase by DMAAc (dimethylamine acetate) and stabilized the lattice structure of DMAPbI₃. 94 As shown in Fig. 7d, after annealing at 140 °C for 1 min, some DMAPbI₃ crystalline phase appeared in the absence of the Cs₄PbI₆ phase. After annealing at 190 °C for 5 s, there was no Cs₄PbI₆ phase either. Thus, the incorporation of DMAAc can shorten the crystal growth time. When annealing further, the coexisting of DMAPbI2Ac and DMAPbI3 affords a dynamically stable DMAPb(I, Ac)₃ as follows:

$$PbI_2 + DMAAc \rightarrow DMAPbI_2Ac$$
 (12)

$$DMAPbI_3 + DMAPbI_2Ac \rightarrow DMAPb(I,Ac)_3$$
 (13)

$$DMAPb(I,Ac)_3 + Cs^+ + I^- \rightarrow CaPbI_3 + DMA(g) \uparrow + HAc + HI(g) \uparrow$$
(14)

Therefore, DMAAc can accelerate the phase transformation from intermediate to thermally stable CsPbI₃ phase. Additionally, Huang et al. achieved a high $V_{\rm oc}$ up to 1.31 V and superior air stability for 4680 h with *n*-butylamine acetate (BAAc). 95 The hydrogen bonding of N-H···O=C-O in BAAc has a stronger shielding effect than N-H···I⁻ in BAI. The vertically aligned

grains can be crystallized from the uniformly distributed intermediate.

5. BF_4^- and BH_4^-

An interesting strategy to introduce F in perovskite with BF₄ anion has been investigated. 28,96-98 BF₄ contributes to large perturbation to the electronic structure. Considering the similar ion radii of I and BF4, Han et al. investigated MAP $bI_{3-x}(BF_4)_x$ perovskites with different BF_4 concentrations.²⁸ All MAPbI_{3-x}(BF₄)_x perovskites had the same tetragonal crystal structure like the MAPbI₃ perovskites. The introduction of BF₄ leads to an obvious change in frequency-dependent electrical conductivity. In the same vein, Nagane et al. studied the mechanism of BF₄⁻ modulation *via* solid-state NMR (ssNMR) at the atomic level.⁹⁹ It was reported that BF₄⁻ anion was not incorporated into the perovskite lattice, but reacted with MAI like a scavenger. As shown in Fig. 8a, the F⁻ signal of BF₄⁻ was located at -147.8 ppm with a broadened signal after mixing equimolar amounts of MAI and MABF4, indicating the formed MAI-MABF4 cocrystal. Additionally, 10 mol% excess MAI was added with BF₄ and the F signal was the characteristic peak

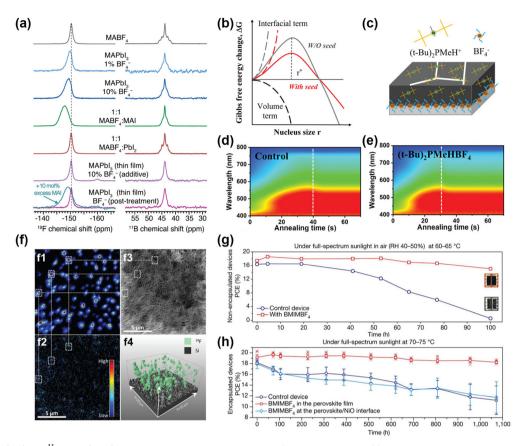


Fig. 8 (a) The ¹⁹F (left) and ¹¹B NMR (right) spectra of MABF₄, MAPbl₃: 1% MABF₄, MAPbl₃: 10%MABF₄, MABF₄: MAI, MABF₄: Pbl₂, and the MAPbl₃ film treated with 10% MABF₄, respectively. Reproduced with permission. 99 Copyright 2021, Wiley-VCH Publication. (b) Gibbs free energies of perovskite nucleation with or without (t-Bu)₂PMeHBF₄. (c) Growth modulation pattern by (t-Bu)₂PMeHBF₄. (d and e) In situ UV-Vis absorption spectra with or without (t-Bu)₂PMeHBF₄. Reproduced with permission. ¹⁰¹ Copyright 2022, Wiley-VCH Publication. (f): (f1) ¹⁹F⁻ and (f2) ¹¹B¹⁶O²⁻ anion maps for the perovskite films with BMPBF₄ additives. (f3) Secondary electron map for the sputtered surface morphology. (f4) 3D maps of F⁻ signals. Reproduced with permission. 102 Copyright 2020, American Association for the Advancement of Science. Thermal stability with (g) non-encapsulated devices and (h) encapsulated devices with or without BMIMBF₄ additives. Reproduced with permission.²¹ Copyright 2019, Springer Nature.

of MAI-MABF₄ cocrystals. The δ peak at 43.9 ppm in the ¹¹B spectrum had no change in Fig. 8b, further proving that the BF₄ was not incorporated into the perovskite lattice.

Additionally, imidazolium tetrafluoroborate (IMBF₄) containing imidazolium cation and BF4- anion to passivate the Sn-Pb perovskite was achieved by Kim et al. 12 The morphological effect and charge carrier dynamics with IMBF4 verified the role of BF4 in optoelectronic properties. Meanwhile, the functional π -conjugated QAPy $^+$ (1,1'-((7,14-dioxo-7,14-dihydroquinolino[2,3-b]acridine-5,12diyl)bis(octane-8,1-diyl))bis(pyridin-1-ium)) cooperating with BF₄ lead to a higher endothermic decomposition temperature, therefore exhibiting better stability compared to the control PSCs device. 97 The QAPyBF₄ not only suppressed the defects of organic cation vacancies but also improved the interface contact and the adhesion of the buried interface. A signature PCE of 23.1% and $V_{\rm oc}$ up to 1.2 V was achieved with markedly improved thermal stability by the buried QAPyBF₄ interface. To demonstrate the crystallization process with BF₄⁻, Zhang et al. applied (t-Bu)₂PMeHBF₄ ((t-Bu)₂ PMeH⁺ is di-tert-butyl(methyl)phosphonium) and analyzed the free energy in the surface/bulk by classical theory (Fig. 8b and c). 100 With the assistance of (t-Bu)₂PMeHBF₄, the PbI₂–(t-Bu)₂PMeBF₄

intermediate was prenucleated as the nucleation center and greatly reduced the interface energy. Thus, the nuclei of perovskite films can occur at a lower saturation due to the low nucleation barrier, further forming small and contact nuclei during the solvent evaporation process (Fig. 8b). Besides the faster nucleation process in the precursor, a faster crystallization process in the thin films was also observed as shown in the in-situ absorption spectra in Fig. 8d and e. The absorption signal of (t-Bu)₂PMeHBF₄-modified film reached the peak value 10s earlier than the control film.

Snaith et al. claimed that BMPBF₄ (BMP⁺ is 1-butyl-1-methylpiperidinium) could suppress the deep trap states significantly.²¹ To understand the distribution of BMPBF₄ in the perovskites, they utilized the nano SIMS (nanoscale secondary ion mass spectrometry) and analyzed the 19F and 11B16O2 signals as displayed in Fig. 8f. The ¹⁹F⁻ signals were consistent with ¹¹B¹⁶O²⁻ signals. F⁻ anions were distributed over the surveyed volume in the perovskite layers to play the role of defect passivation. Snaith et al. also incorporated BMIMBF₄ (BMIM⁺ is 1-butyl-3-methylimidazolium) into perovskite layers and achieved superior long-term thermal stability both in non-encapsulated and encapsulated devices (Fig. 8g and h).²¹ The BMIM⁺ was not only located in the bulk

perovskites but also accumulated at the buried interface. However, the BF₄ was only located at the buried interface. Both the BMIM⁺ and BF₄⁻ suppressed the ion migration in the perovskite films in return.

Compared to halide anions, BH₄ is composed of two elements and needed one extra electron for electronic shell closure. 46,103,104 The strong dihydrogen interaction between ionic hydrogen in BH₄ and the proton hydrogen in MAI can prevent the decomposition of MAI. BH₄⁻ has an ion radius of 202 pm, which is similar to halides and can partially substitute these heavy halides such as I⁻, Br⁻, or Cl^{-,41,46} A stable MAPbI_x(BH₄)_{3-x} was reported by Xu et al.45 The superhalogen BH4 can release anion vacancies and reduce defects such as halide vacancies or organic cation vacancies by partial substitution of I-. Sanchez-Diaz et al. reported the addition of NaBH₄ into Sn perovskites for achieving the oxidation resistance from Sn2+ to Sn4+ during the solution processing, which lead to a PCE of 10.61% with superior operational stability over 1300 h in an N₂ atmosphere. ¹⁰⁵ The FASnI₃ perovskite film emerged with a compact and pinhole-free morphology with NaBH4 incorporation. In this respect, this new type of superhalogen anion provides a novel design in complex perovskites.

6. PF₆⁻

For the F-type superhalogen PF₆, it has an ion radius of 225 pm and also can be incorporated into a perovskite lattice. 41,106 Tao et al. achieved a PCE of 27.35% in 4T (four terminal) perovskite-Si tandem devices by F-type PF₆⁻ with a perovskite $framework \quad \ of \quad \ FA_{0.65}MA_{0.20}Cs_{0.15}Pb(I_{0.8}Br_{0.2})_{3-x}(PF_6)_x.^{106}$ When partial substitution of I-/Br by PF6 occurred, the perovskite showed lattice expansion. Meanwhile, there was a released tensile strain with PF₆ addition. Therefore, a high-quality perovskite film formed with strain relaxation, which had a positive effect on charge transport and passivation of defect density. Moreover, Hao et al. adopted BMIMPF₆ to enhance the phase stability of CsPbI2Br and delivered a PCE of 16.2% with a Voc of 1.28 V.16 The CsPbI2Br with BMIMPF₆ had a lower formation energy than the pure α-CsPbI₂Br as shown in Fig. 9a, therefore stabilizing the α-CsPbI₂Br perovskite. The average Br-I-Br angle (Fig. 9c and d) with BMIMPF₆ increased from 78.1° to 88.3°, thus contributing to the enhanced phase stability of α-CsPbI₂Br perovskite by restraining the distortion of $[BX_6]^{4-}$ octahedrons. With KPF₆-assisted crystallization, Bu et al. achieved a high PCE of 23.35% in MA-free PSCs. 107 The interface between perovskite and Spiro-OMeTAD was intersected without KPF6 treatment, whereas it had no obvious change after KPF₆ treatment as shown in cross-sectional SEM images (Fig. 9d and e). Meanwhile, PF₆ stayed on the surface and passivated the grain boundaries and the signals of K⁺ and F⁻ throughout the perovskite films (Fig. 9f). As a result, the device with KPF6 showed negligible ion migration after thermal aging.

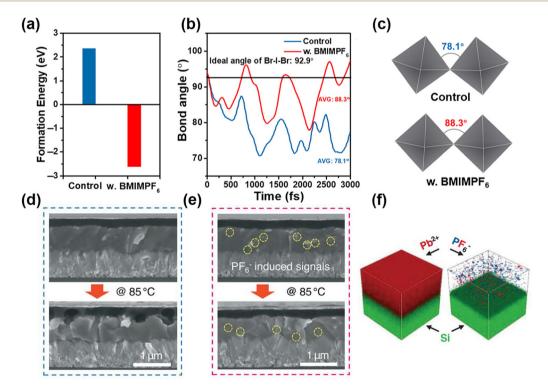


Fig. 9 (a) Formation energy of α -CsPbl₂Br with or without BMIMPF₆ treatment. (b) Time-dependent bond angle of Br-I-Br angle and (c) the corresponding crystal schematic. Reproduced with permission. ¹⁶ Copyright 2021, Wiley-VCH Publication. Cross-sectional SEM patterns of perovskite/ Spiro-OMeTAD interface (d) without and (e) with KPF₆ treatment. (f) TOF-SIMS pattern of Pb, P, and F ions in perovskites after KPF₆ addition. Reproduced with permission.¹⁰⁷ Copyright 2021, Springer Nature.

7. Conclusions and outlooks

The nonhalides act as emerging candidates for tuning the optoelectronic properties of perovskites and their applications in photovoltaics and beyond. The ambient light and thermal stability were greatly enhanced through this strategy. Meanwhile, they can tune the nucleation and crystal growth process and modulate the film growth process. Their positive effects on morphology, stability, electrical conductivity, carrier density, and charge transport properties provide another perspective for the future selection of the X-site anions. To achieve highefficiency and stable PSCs with this strategy, more fundamental research studies need to be carried out.

- (i) More theoretical and experimental studies should determine whether pseudohalides or superhalogens can be incorporated into a perovskite lattice. The propensity of the position in the bulk perovskite lattice or the interface/surface can offer an in depth understanding of halide management including the halide composition and halide defect regulation.
- (ii) Due to the high volatile properties of SCN⁻, the chemical inhomogeneity by local evaporation may be caused by unusual planar defects like edge dislocation or the bending of interlayers. The development of an elaborate vapor treatment method with SCN⁻ can improve the phase transition and the crystallization kinetics.
- (iii) Pseudohalides contribute to enlarged grains and few boundaries with high n-value distribution for low-dimensional perovskites. The role of organic cations in such a system cannot be ignored. On the one hand, functionalized organic cations containing both electron-rich atoms and electron-donating chains show a strong passivation effect on the net positive charge in perovskites. On the other hand, the characteristics of the cationic component should also be investigated.
- (iv) The passivation effect of HCOO⁻ and Ac⁻ is mostly reflected in the halide vacancies. Meanwhile, they have a strong interaction with B-site cations to stabilize the perovskite lattice structure. The hydrogen bonding network with organic cations further enables the unique role of HCOO and Ac in passivating anion-vacancy defects. Though volatile FAH and HAc have no residues in perovskite films after annealing, 85,90 long-term passivation from the precursors to thin films at high temperature is missed. Therefore, ionic liquids can be designed with various functional organic cations with pseudohalide anions in this regard. Their special properties with non-volatility and low toxicity will benefit the realization of efficient and stable PSCs.
- (v) The passivation with BF₄ or PF₆ can mainly be embodied in blocking the invasion of H₂O and O₂, thereby facilitating moisture stability. Designing the functional hydrophilic groups with BF₄ or PF₆ to meet the appropriate polarity, conductivity, melting point, viscosity, and chirality is an important issue in the development of more efficient and stable PSCs soon.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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