

Review

Innovative Materials for High-Performance Tin-Based Perovskite Solar Cells: A Review

Xiansheng Wang ^{1,2,*}, Jianjun Yang ^{1,2,*}, Jian Zhong ², Junsheng Yu ² and Xinjian Pan ¹

¹ College of Electron and Information, Zhongshan Institute, University of Electronic Science and Technology of China, Zhongshan 528402, China

² School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu 610054, China

* Correspondence: sdyman@uestc.edu.cn; Tel.: +86-0760-8831-4612

Abstract: With the rapid development of lead-based perovskite solar cells, tin-based perovskite solar cells are emerging as a non-toxic alternative. Material engineering has been an effective approach for the fabrication of efficient perovskite solar cells. This paper summarizes the novel materials used in tin-based perovskite solar cells over the past few years and analyzes the roles of various materials in tin-based devices. It is found that self-assembling materials and fullerene derivatives have shown remarkable performance in tin-based perovskite solar cells. Finally, this article discusses design strategies for new materials, providing constructive suggestions for the development of innovative materials in the future.

Keywords: self-assembling materials; material design; tin-based perovskite solar cells

1. Introduction

Solar energy is a promising renewable resource, especially perovskite solar cells (PSCs), which have rapidly advanced since Kojima et al. first proposed them in 2009 [1]. In recent years, they have reached a world-record power conversion efficiency (PCE) of 26.7% [2]. The efficiency development history of emerging photovoltaic cells is shown in Figure 1, where the efficiency of perovskite solar cells is represented by a yellow circular line graph. Organic–inorganic hybrid perovskites materials typically have the chemical formula ABX_3 , where A is an organic or inorganic cation (such as methylammonium, formamidinium, cesium, or rubidium), B is a central metal cation (such as lead, tin, or germanium), and X is a halide or pseudohalide (such as chloride, bromide, iodide, or thiocyanate) [3]. Perovskite materials exhibit excellent optoelectronic properties, including tunable bandgaps [4], high absorption coefficients [5], ambipolar charge transport [6–8], defect tolerance [9,10], and low exciton binding energies [11,12]. Lead-based PSCs have achieved the best records in photovoltaic performance, but the toxicity of lead remains a major obstacle for industrialization, making the search for non-toxic or low-toxicity alternatives especially important [13–17].

Non-toxic candidates such as germanium, bismuth, and antimony have been proposed as substitutes for lead, but their photovoltaic performance falls far short of the 26% achieved by lead-based PSCs. Tin-based perovskites, as a low-toxicity alternative, have been extensively studied, and their PCE has reached over 15% [18]. Tin, being in the same IVA group as lead, has a similar ionic electronic configuration and comparable ionic radius [19–21], requiring only slight lattice distortion for substitution [22]. Although some concerns have been raised about the environmental impact of Sn^{2+} [23,24], it is generally believed that the degradation byproduct SnO_2 is non-toxic and easier to remove from the environment compared to the degradation products of lead-based perovskites. Therefore, tin-based perovskites show great potential for the development of high-efficiency solar cells, particularly in addressing the lead toxicity issue.



Citation: Wang, X.; Yang, J.; Zhong, J.; Yu, J.; Pan, X. Innovative Materials for High-Performance Tin-Based Perovskite Solar Cells: A Review. *Polymers* **2024**, *16*, 3053. <https://doi.org/10.3390/polym16213053>

Academic Editor: Guohua Zhu

Received: 29 September 2024

Revised: 24 October 2024

Accepted: 28 October 2024

Published: 30 October 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

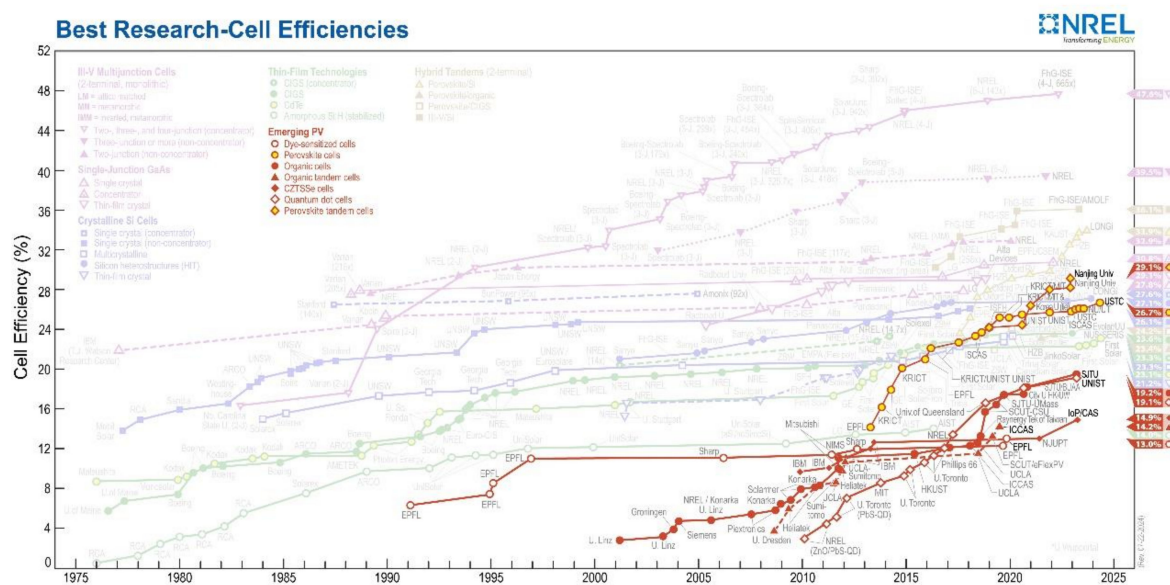


Figure 1. NREL announces latest perovskite solar cell efficiencies.

Although tin-based perovskites exhibit optoelectronic properties similar to or even superior to lead-based perovskites, such as higher carrier mobility and longer hot carrier lifetimes [25], their poor stability and the rapid oxidation of Sn^{2+} limit photovoltaic performance and reproducibility [26]. In practical fabrication processes, obtaining dense and pinhole-free films is also challenging. Tin-based perovskite films typically show poor crystallinity and rough surface morphology, with grain sizes in the range of hundreds of nanometers, unlike lead-based perovskite films that can achieve grain sizes in the range of hundreds of micrometers [27].

Review articles on tin-based PSCs have been published progressively. Among the classics, Loi focused on the structural characteristics and optoelectronic properties of 3D Sn-based perovskites, analyzing the impact of low-dimensional structures [28]. Yan et al. explored the fundamental properties of tin-based perovskites, device design, and various strategies to improve device performance [29]. Han reviewed the latest progress in efficiency, discussing the potential to enhance Sn-based PSCs' efficiency by optimizing bandgaps, enhancing light-harvesting efficiency, increasing carrier diffusion lengths, performing surface passivation, and adjusting interfacial energy level alignment, pointing out opportunities and challenges in achieving 20% PCE [30]. Huang et al. examined the recent developments in inverted Sn-based device structures, emphasizing the characteristics, device performance, charge transport layers, and crystallization processes of tin-based perovskites, and explored future obstacles and opportunities [31]. Among all TPSC structures, the inverted structure is more commonly applied, while the conventional structure typically exhibits lower V_{oc} and PCE. Due to intrinsic properties, tin-based perovskites' electron diffusion length is longer than the hole diffusion length, making the inverted structure more suitable for TPSCs [32]. This paper mainly focuses on the polymer materials used in the tin-based perovskite solar cells, analyzes their characteristics, and provides suggestions for exploring novel modification materials. It is divided into three parts: polymer materials at the buried interface of perovskite films, polymer materials in the perovskite precursor solution, and polymer materials on top of perovskite films.

2. Application of Polymeric Materials in Tin-Based Chalcogenide Solar Cells

2.1. Polymer Materials at the Buried Interface of Perovskite Films

Up to now, the highest power conversion efficiency (PCE) of tin-based perovskite solar cells (PSCs) has exceeded 15%. However, this is still significantly lower than the theoretical limit. The main bottlenecks include a large open-circuit voltage (V_{oc}) loss, uncontrollable crystallization dynamics, and poor air stability. One effective approach to address these

challenges is through modifying the buried interface. This strategy not only precisely tunes the surface properties of the buried layer to enhance interfacial compatibility, but it also interacts with the perovskite layer, regulating the crystallization process or passivating the film [33–36] (Figure 2).

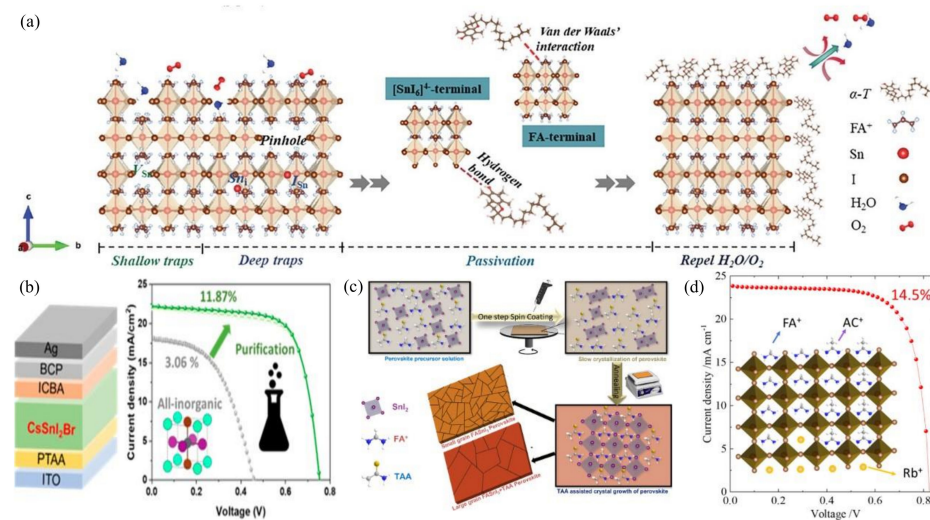


Figure 2. (a) Schematic illustration of defect profile in pristine Sn perovskite film with a variety of Sn- or I-related defects, and corresponding passivation strategy caused by hydrogen bonding and van der Waals interactions between perovskite and α -T [35]. (b) Efficient devices prepared with optimal Br content [33]. (c) Schematics of interactions and grain growth mechanism of FASnI₃ perovskite with thioacetamide [36]. (d) Adding 10% AC and 3% Rb optimizes the device ($E_1AC_{10}Rb_3$) to achieve 14.5% power conversion efficiency [37].

In the study of buried interface modifications, the choice of the buried layer varies depending on the diversity of perovskites and device structures, whether conventional or inverted. For example, in lead-based PSCs, the n-i-p structure typically adopts TiO₂/perovskite or SnO₂/perovskite interfaces [37,38], while the p-i-n structure tends to use poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA)/perovskite or self-assembled monolayer (SAM)/perovskite interfaces [39,40] (Figure 3). In the case of tin-based PSCs, the mainstream choice is the poly(3,4-ethylenedioxythiophene)(styrene sulfonate) (PEDOT:PSS)/perovskite interface.

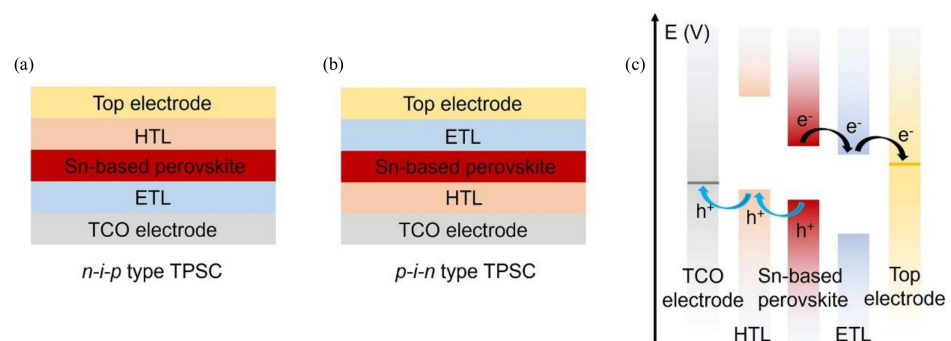


Figure 3. Schematic diagrams of (a) the n-i-p-type TPSC and (b) the p-i-n-type TPSC [38]. (c) Energy level diagram of a typical p-i-n-type TPSC [38].

PEDOT:PSS is a common choice due to its unique advantages such as high optical transparency, ease of solution processing, electrical conductivity, and energy level alignment with tin perovskites [39] (Figure 4). However, its acidic and hygroscopic nature can lead to unfavorable interactions with the tin perovskite interface, significantly affecting the

performance of tin-based PSCs [41,42]. Studies have shown that the high defect density at the Sn perovskite/PEDOT:PSS interface induces severe non-radiative recombination and low charge carrier extraction/transport efficiency, resulting in significant reductions in both Voc and short-circuit current density (Jsc) [43,44]. Additionally, the PEDOT:PSS surface is often rich in PSS, whose insulating and hygroscopic nature further worsens carrier collection efficiency and accelerates degradation processes related to the buried interface [45].

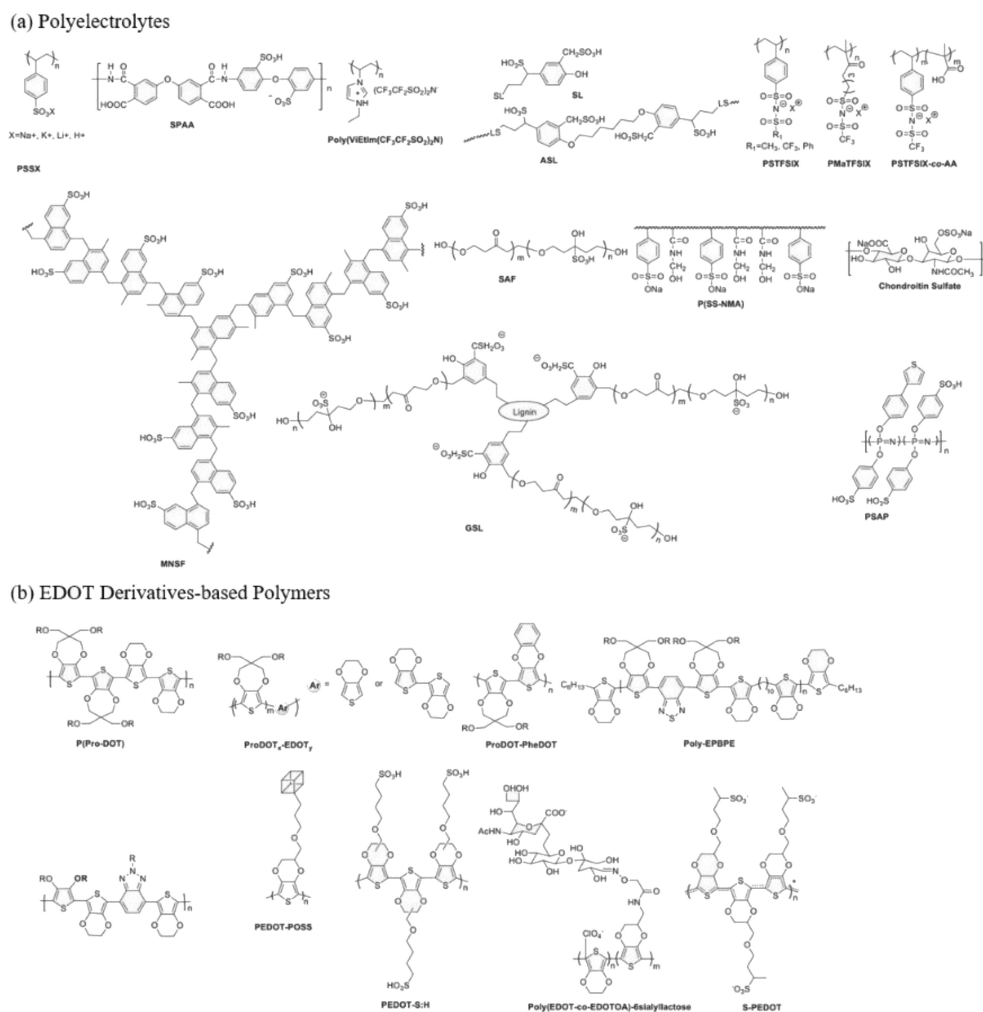


Figure 4. Schematics of representative (a) polyelectrolytes and (b) soluble processable polymers with EDOT derivatives via copolymer engineering and side-chain tailoring [39].

To address these issues, researchers have explored several alternatives to PEDOT:PSS, such as HTL-free materials, inorganic metal oxides, and novel p-type organic materials, significantly improving the stability of Sn-PSCs [46–49] (Figure 5a). However, compared to devices containing PEDOT:PSS, those without PEDOT:PSS often show poorer efficiency and reproducibility, likely due to the hydrophilic nature of PEDOT:PSS, which promotes crystal nucleation in the perovskite film. Another improvement strategy involves modifying PEDOT:PSS HTLs to enhance efficiency and stability [34,50,51]. For example, Song et al. successfully achieved a PCE of 12.1% and stability exceeding 2800 h in Sn-PSCs by post-treating the PEDOT:PSS surface with ethylenediamine [45] (Figure 5c). Further research has revealed that excess insulating PSS is partially removed during treatment, and the molecular structure of PEDOT:PSS shifts from benzenoid to quinoid form, enabling more efficient hole transport. Recently, Teng et al. used the electronic effect of an interfacial

coupling agent to treat PEDOT:PSS with trimethoxysilane, achieving the best PCE of 14.67% in Sn-PSCs [34] (Figure 5d).

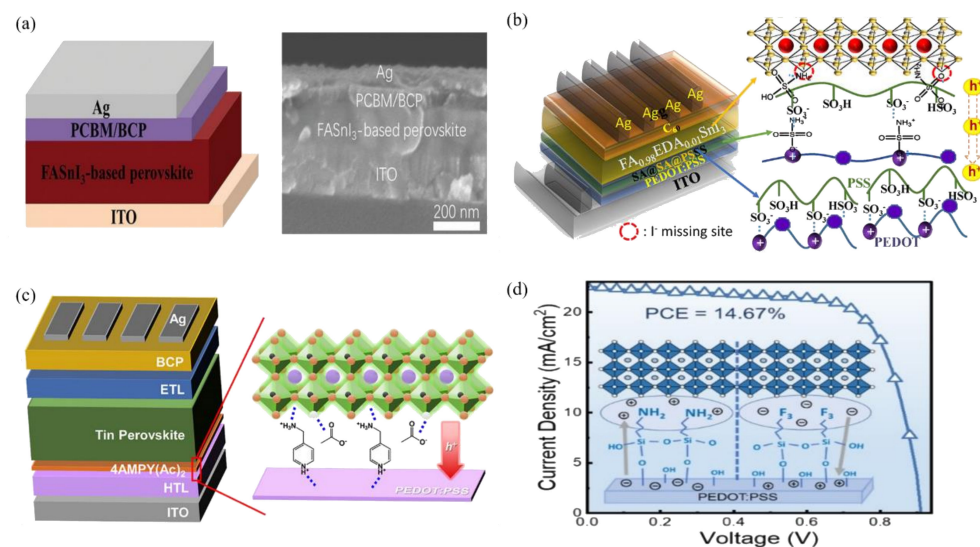


Figure 5. (a) Device configuration of the HTL-free tin PSCs with a structure of ITO/FASnI₃-based perovskite/PCBM/BCP/Ag and SEM cross-sectional image of the HTL-free tin PSCs [48]. (b) A layer of PEDOT:PSS was inserted in-between the ITO electrode and SA-modified PEDOT:PSS to form a pseudo bilayered PS/SA@PS HTL [40]. (c) Post-treatment of PEDOT:PSS surfaces using diammonium salts of aromatic acetic acid dissolved in highly volatile but interacting solvents to modify the surface [45]. (d) Trimethoxy(3,3,3-trifluoropropyl)silane (F3-TMOS) with molecular dipole moments pointing to the hole transport layer was used as a buried interface modification material [34].

In recent years, self-assembled monolayers (SAMs) have garnered considerable attention as hole transport materials (HTMs) for inverted PSCs, aiming to overcome the issues associated with traditional HTLs [52]. However, fabricating high-quality tin perovskite films on hydrophobic HTM SAMs presents a challenge due to their poor wettability [53,54]. Improved film deposition methods and the design of new SAM molecules may be key to solving this problem [55,56]. For instance, Afraj et al. developed an X-shaped quinoline-based SAM that exhibited excellent hole extraction capabilities, resulting in Sn-PSCs with a PCE of 8.3% [56] (Figure 6).

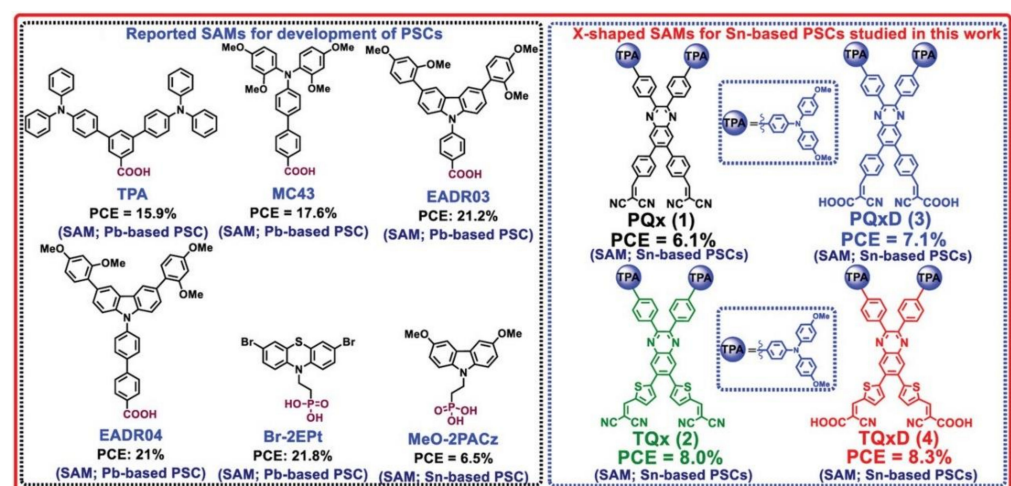


Figure 6. SAM molecules that have been reported. Right: Chemical structure of reported self-assembled monolayers (SAMs) for the PSCs. Chemical structures of SAMs: PQx (1), TQx, (2), PQxD (3) and TQxD (4) for Sn-based PSCs studied in the reference [56].

Moreover, SAM molecules can be used to modify the surfaces of conventional HTLs. Recently, Li et al. introduced 2PADBC SAM at the tin perovskite/ NiO_x interface to suppress interfacial redox reactions and reduce non-radiative recombination, achieving a PCE of 14.19% [57] (Figure 7a). Cao et al. designed a novel self-assembled molecule, 2-chloroethylphosphonic acid (CEPA), to modify the buried interface of Sn-PSCs [58]. The chemical anchoring of CEPA on PEDOT:PSS effectively reduced excess PSS and facilitated the formation of high-quality tin perovskite films, minimizing voids and impurity phases at the buried interface (Figure 7e). The reduced defects in the tin perovskite film, prepared on CEPA-modified PEDOT:PSS, significantly lowered the Urbach energy and suppressed non-radiative energy losses. As a result, the PCE of the CEPA-modified Sn-PSC based on $\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$ reached 10.65%, nearly 24% higher than that of the original perovskite device (8.57%). Similarly, Chen et al. reported high-performance tin-based PSCs with a wide bandgap of 1.62 eV and a PCE of 8.66%, using 2PACz SAM-modified PEDOT:PSS as the HTL [59] (Figure 7b). They also investigated the interaction between SAM anchoring groups ($\text{P}-\text{O}-$) and S^+ in the interface, demonstrating how phosphonic acid deprotonation at the interface improved performance. However, the high hydrophobicity of carbazole-based SAMs may lead to uncontrolled crystallization of tin perovskites in SAMs. To address this, Song et al. developed a preheating process, using a two-step sequential deposition method to fabricate uniform tin-based perovskite layers [60] (Figure 7c). Thus, tailoring the functional group design to regulate crystallization and defect passivation is crucial for buried interface modification. For instance, halogen-terminated aliphatic SAMs have been effectively used in lead-based PSCs for buried interface modification [61] (Figure 7d). Their -I end group forms electrostatic bonds with the perovskite layer, and the shorter alkyl chain ($n = 3$) provides sufficient hydrophilicity for SAM coatings, promoting perovskite film deposition. Hence, functionalized aliphatic SAMs exhibit significant advantages in multifunctional buried interface modifications, particularly in crystallization control and defect passivation, contributing to improved tin-based PSC performance.

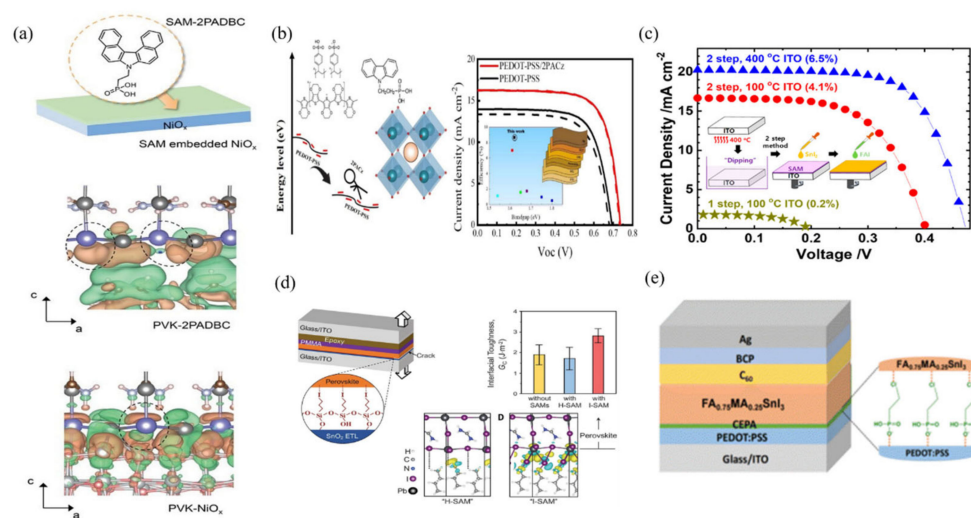


Figure 7. (a) Schematic diagram of SAM-2PADBC-embedded NiO_x film and differential charge density simulation of the perovskite– NiO_x and perovskite–2PADBC [57]. (b) The compact surface morphology of the Sn perovskite fabricated on bilayers consisting of 2PACz monolayer on PEDOT:PSS and the suppression of direct contact between PEDOT:PSS and perovskite film [59]. (c) In the two-step deposition, the SnI_2 in DMSO and FAI in a cosolvent system were sequentially deposited using spin-coating to form FASnI_3 [60]. (d) Mechanical behavior of the ETL/MHP interface [61]. (e) Schematic of the Sn-PSC based on CEPA buried interface modification [58].

As the development of SAM materials progresses, more promising new materials may emerge. For instance, SAMs based on two-dimensional materials (e.g., graphene or transition metal sulfides), with their excellent charge transport properties and tunable optical

characteristics, could become highly effective hole transport materials. The combination of these novel materials with conventional systems could lead to enhanced interfacial compatibility and improved device performance.

2.2. Polymer Materials in the Perovskite Precursor Solution

Additive engineering is widely recognized as an important means to improve the performance of tin-based perovskite solar cells (PSCs), primarily aimed at suppressing internal defects (such as tin vacancies and point defects) and external defects (such as grain boundary defects) [62,63] (Figure 8). The presence of internal defects significantly affects the optoelectronic properties of the material, while external defects can lead to decreased device stability. Therefore, the development of suitable additives is crucial for enhancing the quality of perovskite films. It is evident that the selection of additives not only impacts the fundamental properties of the materials but also directly relates to the practical application outcomes of the devices.

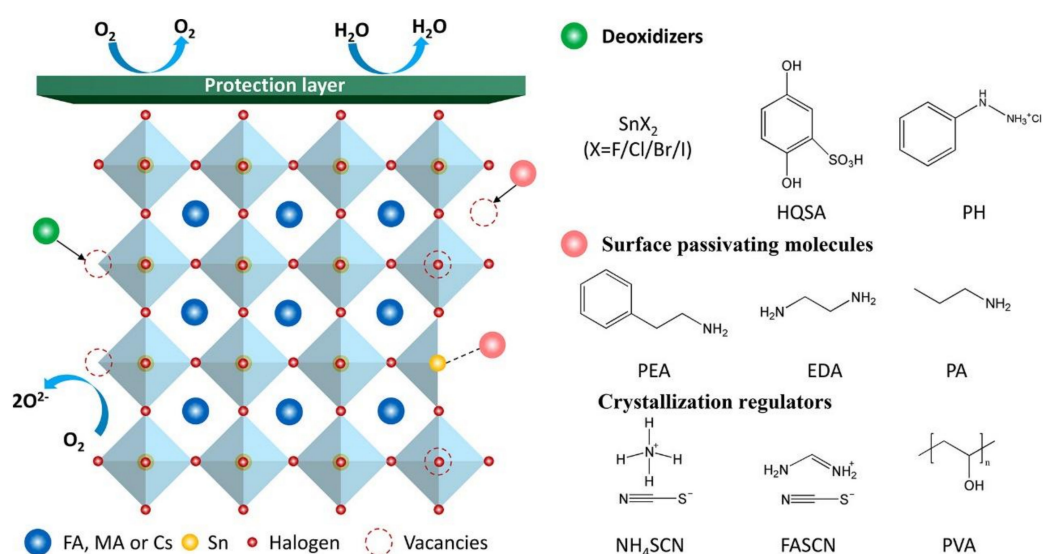


Figure 8. Schematic of the defects and functional molecules [63].

In tin-based perovskite solar cells, the most commonly used additives are inorganic SnX_2 compounds, such as SnF_2 and SnCl_2 . These inorganic additives effectively suppress the oxidation of tin by altering the crystal structure and chemical environment of the perovskite film. With the continuous development of lead-based perovskites, an increasing number of organic additives have also been introduced into the precursor solutions for tin-based perovskites, enhancing the performance of the films. For instance, additives such as gallic acid (GA) (Figure 9a), phenylhydrazine hydrochloride (PHCl), ethylenediamine (EDA), phenethylammonium (PEA), and hypophosphorous acid (H_3PO_2) have been shown to promote the efficiency of tin-based devices [64–74]. These additives not only effectively prevent the oxidation of Sn^{2+} but also improve the crystallization quality of the films, thereby enhancing device performance. In fact, these additives optimize the microstructure, contributing to improved photoconversion efficiency and demonstrating significant potential in material design. Huang et al. found that the introduction of phenylhydrazine hydrochloride into FASnI_3 perovskite films significantly reduced the generation of Sn^{4+} and inhibited the further degradation of FASnI_3 , ultimately achieving a power conversion efficiency (PCE) of 11.4% [73] (Figure 9b). This indicates that appropriate additives can effectively regulate the oxidation state of the material, thus improving its optoelectronic properties. Through this mechanism, researchers have illustrated the close relationship between the chemical stability of the material and the performance of the solar cells, providing important references for subsequent studies.

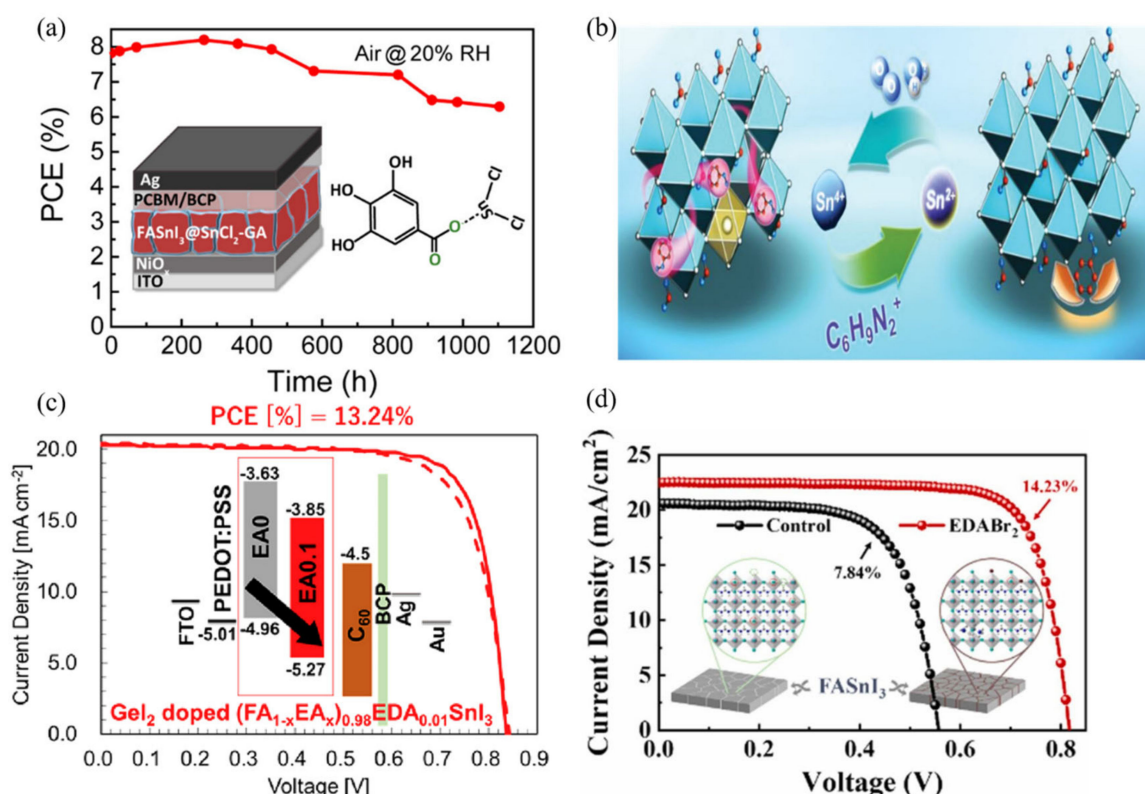


Figure 9. (a) A tin-based perovskite solar cell with significantly improved stability against oxidation was prepared by introducing hydroxybenzene sulfonic acid or a salt thereof as an antioxidant additive into the perovskite precursor solution [70]. (b) Schematic illustration of possible SRTSP mechanism for PHCl [73]. (c) Simultaneous band energy alignment and trap site passivation has been achieved by regulating the A-site cation of tin halide perovskites [71]. (d) Ethylenediammonium halide salts (i.e., EDAl2 and EDABr2) as additives in Sn perovskite [68].

Furthermore, the research by Shuzi Hayase et al. demonstrated that partially substituting ethylammonium cations for formamidinium cations could increase the efficiency of tin-based perovskite solar cells to 13.24% [71] (Figure 9c). This finding indicates that different combinations of cations can significantly affect the charge transport properties of the materials, optimizing cell performance. Zhao et al. further pointed out that the use of ethylenediamine halide salts (such as EDAl₂ and EDABr₂) as additives could enhance the PCE of the tin-based perovskite devices to 14.23% [68] (Figure 9d). This improvement may be attributed to the favorable interfacial structures formed by the additives in the films, which assist in enhancing charge transport efficiency. This illustrates the interrelationship between microstructural and macroscopic performance in material design, further advancing the field of renewable energy. Zhu et al. introduced trimethylthiourea (3T) in the spin-coating process of FASnI₃ films (Figure 10a). This bifunctional ligand significantly improved the morphology and texture of FASnI₃ films by spreading and connecting individual crystal particles. According to their findings, the carrier lifetime of the 3T-treated films reached a record 123 ns, and the open-circuit voltage was measured at 0.92 V, which is only 0.2 V lower than the theoretical limit for lead halide perovskites. These values indicate that the performance of the 3T-treated films approaches that of traditional lead-based perovskites [75]. A certified power conversion efficiency of 14.0% and excellent stability against humid air were also observed, marking these FASnI₃ solar cells as the best in their category. Such experimental results demonstrate that the microstructure of the films and the selection of additives can significantly influence the electrical performance of the devices, promoting their feasibility in practical applications. He et al.'s research further indicated that replacing a portion of FAI with FPEABr in FASnI₃ could yield an effi-

ciency of 14.81% [69] (Figure 10b). This substitution not only improved the optoelectronic performance of the films but also potentially optimized the interfacial characteristics of the materials. Optimizing interfacial characteristics is another critical factor for enhancing device efficiency, especially in multilayer structures of solar cells.

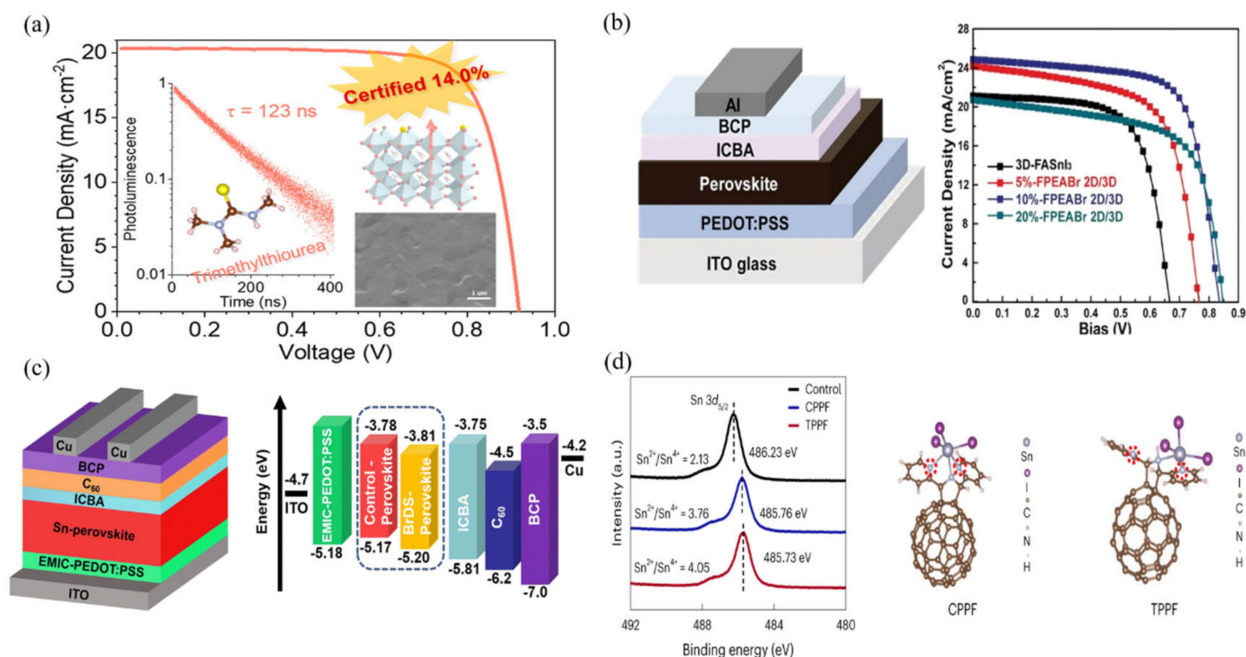


Figure 10. (a) Trimethylthiourea (3T) was introduced during spin-coating of FASnI_3 films [75]. (b) Schematic device structure of the inverted perovskite devices. Current density–voltage (J–V) curves of the champion devices containing pure 3D FASnI_3 and 2D/3D perovskite with different FPEABr [69]. (c) The structure of the Sn-based PSC device. The energy level diagram of the Sn-based PSC device [76]. (d) Sn $3d_{5/2}$ X-ray photoelectron spectroscopy spectra of the SnI_2 , CPPF- SnI_2 and TPPF- SnI_2 films. a.u., arbitrary units. Simulations of the interaction between the CPPF and perovskite components showing N (highlighted by red dashed circles) coordinating with one SnI_6^- cluster and simulations of the interaction between TPPF and perovskite components showing N coordinating with two SnI_6^- clusters [18].

Zhou et al. discovered that 2,8-dibromodibenzothiophene-S,S-dioxide (BrDS) is an ideal material for effectively reducing the high defect density in tin-based perovskite films [76] (Figure 10c). The strong interaction between the sulfone groups in BrDS and Sn^{2+} ions can effectively suppress the oxidation of Sn^{2+} , promoting film stability. Furthermore, the incorporation of BrDS can compensate for the loss of iodide ions in the films by reducing crystal aggregation and phase separation, which is crucial for forming smooth, pinhole-free films that enhance overall device performance. This indicates that the multifaceted role of additives in improving film defects and stability is of profound significance for enhancing the performance of practical devices. Chen et al. synthesized two pyridine-substituted iron-rich porphyrins (PPF) with cis (CPPF) and trans (TPPF) configurations and utilized them as precursor additives [18] (Figure 10d). The spatial configurations of CPPF and TPPF significantly influence their electron density distribution and interaction with the perovskite components. Compared to CPPF, TPPF possesses spatially separated pyridine groups, which can capture more perovskite colloids through coordination bonds, thereby slowing down the crystallization process of the perovskite. The resulting perovskite films exhibited better crystal orientation and density. TPPF also resided at the grain boundaries, improving energy level alignment at the interface and inhibiting Sn^{2+} oxidation. Consequently, TPSC based on TPPF demonstrated a certified conversion efficiency of 15.14% and excellent stability, maintaining 99% and 93% of its initial efficiency after 3000 h of storage and 500 h

of continuous illumination, respectively. This performance enhancement not only reflects the success of additive design but also provides new insights for future research.

The rational selection and regulation of additives play a crucial role in the development of tin-based perovskite solar cells. These studies not only offer new perspectives on understanding the functions of additives but also lay a solid foundation for the future industrial application of perovskite solar cells.

2.3. Polymer Materials on Top of Perovskite Films

In lead-based perovskite solar cells, surface passivation of perovskite films is a crucial method for reducing defects, improving film quality, and enhancing device efficiency. In contrast, for tin-based perovskite solar cells, surface passivation primarily addresses the issue of energy level misalignment between the perovskite layer and the electron transport layer (ETL). For example, the energy level offset associated with C60 and [6]-phenyl C61-butyric acid methyl ester (PC₆₁BM) [77,78] can lead to a reduction in the open-circuit voltage (Voc) of devices (Figure 11). Therefore, enhancing the LUMO level of the ETL can effectively increase the Voc of tin-based perovskite solar cells (TPSCs). Experimental evidence shows that the indene-C60 bisadduct (ICBA) can be utilized in tin-based perovskite solar cells [79–81], demonstrating better energy level alignment with tin-based perovskite, resulting in a larger Voc. Additionally, the shallow LUMO of ICBA hinders the injection of iodine ions, leading to a reduction in electron density and suppression of interfacial carrier recombination. In contrast, PC₆₁BM promotes increased electron density due to long-range doping by iodine ions (ionic migration), accelerating interfacial carrier recombination with the p-type tin-based perovskite film. Consequently, the devices using ICBA exhibited a Voc output of 0.94 V and a power conversion efficiency (PCE) of 12.4%, while those using PC₆₁BM showed only 0.60 V Voc and 7.7% PCE [82].

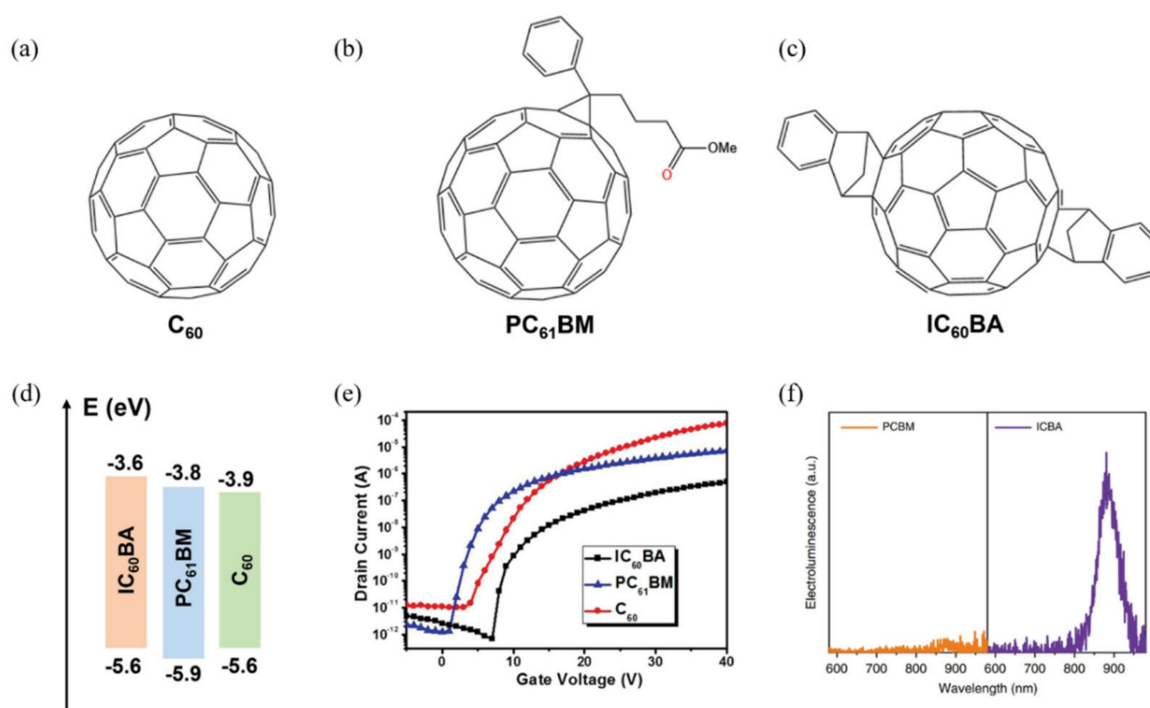


Figure 11. (a) C₆₀. (b) PC₆₁BM. (c) IC₆₀BA. (d) Band structures of C₆₀, PC₆₁BM, and IC₆₀BA. (e) The field effect transistor (FET) transfer characteristics of C₆₀, PC₆₁BM, and IC₆₀BA. (f) Electroluminescence spectra of the Sn-based perovskites films with different ETLs (PC₆₁BM and IC₆₀BA) under a bias voltage of 2 V [38].

Recently, a growing number of custom-designed materials have been employed for interfacial passivation of tin-based perovskite films. Sun et al. synthesized four well-defined

multidentate fullerene molecules, labeled FM3, FM4, FM5, and FM6, each containing three, four, five, and six diethyl malonate groups, to be used as interfacial layers in TPSCs [83] (Figure 12a). It was observed that increasing the number of functional groups on these fullerenes leads to a shallower LUMO energy level and enhances the interfacial chemical interactions. Among these, FM5 exhibited suitable energy levels and strong interactions with perovskite, effectively enhancing electron extraction and defect passivation. Furthermore, the unique molecular structure of FM5 allows for tight stacking of the exposed carbon cage with the upper fullerene cage upon interaction with perovskite, facilitating efficient charge transfer and protecting the perovskite from moisture and oxygen damage. As a result, devices based on FM5 achieved a champion efficiency of 15.05%. Hou et al. designed and synthesized a cross-linkable fullerene, thiol-functionalized C60 fulleropyrrolidine iodide (FTAI) [84], which interacts with the perovskite components to finely tune the crystallinity of the perovskite films (Figure 12b). The resulting perovskite films displayed larger grain sizes and better energy level alignment with the electron transport material, effectively improving carrier extraction efficiency (Figure 12c). The rigid devices based on FTAI achieved a champion efficiency of 14.91% and enhanced stability. In addition to this, the development of new methods is also a strategy. Zhang et al. developed a strategy using polysilanes, particularly polymethylphenylsilane (PMPS) and diphenylpentasilane (DPPS), to improve the quality of tin-based perovskites [85] (Figure 12d). Surface passivation with PMPS led to a PCE of 14.18% and better stability. Further characterization indicated that PMPS serves a dual role: it provides a smooth surface morphology and enlarged grain sizes (enhancing short-circuit current, J_{sc}) while also acting as a reducing agent for Sn^{4+} and a surface energy level regulator (enhancing V_{oc}).

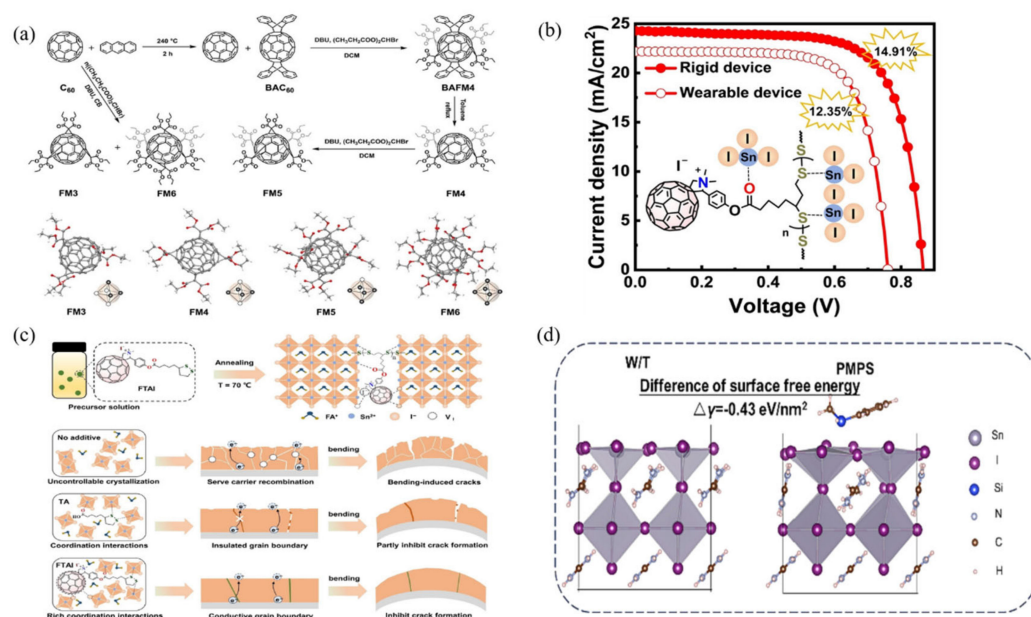


Figure 12. (a) Precise synthesis route of multidentate fullerenes, and single-crystal structures of FM3, FM4, FM5, and FM6, accompanied by corresponding fullerene structural models in the lower right corner; the solid vertex indicates that the position is occupied by a functional group, while a hollow vertex indicates that it is not occupied [83]. (b) Design and synthesis of a cross-linkable fullerene, lipoic acid-functionalized C60 fulleropyrrolidinium iodide (FTAI) for the preparation of high-efficiency devices [84]. (c) Schematic illustrations of the effect of FTAI on perovskite film. Molecular structure of FTAI and diagram of cross-linked FTAI interact with perovskite. Schematic diagrams of formation and bending performance of the control and TA- and FTAI-based perovskite films [84]. (d) Optimized slab model (1 0 0) of perovskite of W/T and PMPS [85].

The growth of a 2D film on perovskite films to form a 2D/3D structured perovskite is also an effective passivation strategy. Zang et al. constructed quasi-2D tin-based per-

ovskite films using a mixture of monoammonium and diammonium terminal ligands [86] (Figure 13a). The use of diammonium ligands reduced the total number of terminal ligands in the films and delayed the growth of the perovskite, enhancing film orientation. These improvements increased carrier mobility and diffusion lengths, resulting in a 14.3% increase in current density and power conversion efficiency. Cui et al. reported a novel cyclic organic spacer, morpholinium iodide (MPI), for developing structurally stable 2D/3D perovskites [87] (Figure 13b). The introduction of secondary ammonium and ether groups in the cyclic spacer enhances its rigidity, leading to an increase in hydrogen bonding and intermolecular interactions within the 2D perovskite. These enhanced interactions facilitate the formation of highly ordered 2D/3D perovskites with low structural disorder, effectively passivating Sn and I defects (Figure 13c). Consequently, perovskite solar cells based on MPI achieved a PCE of 12.04%, demonstrating excellent operational stability and oxidative stability.

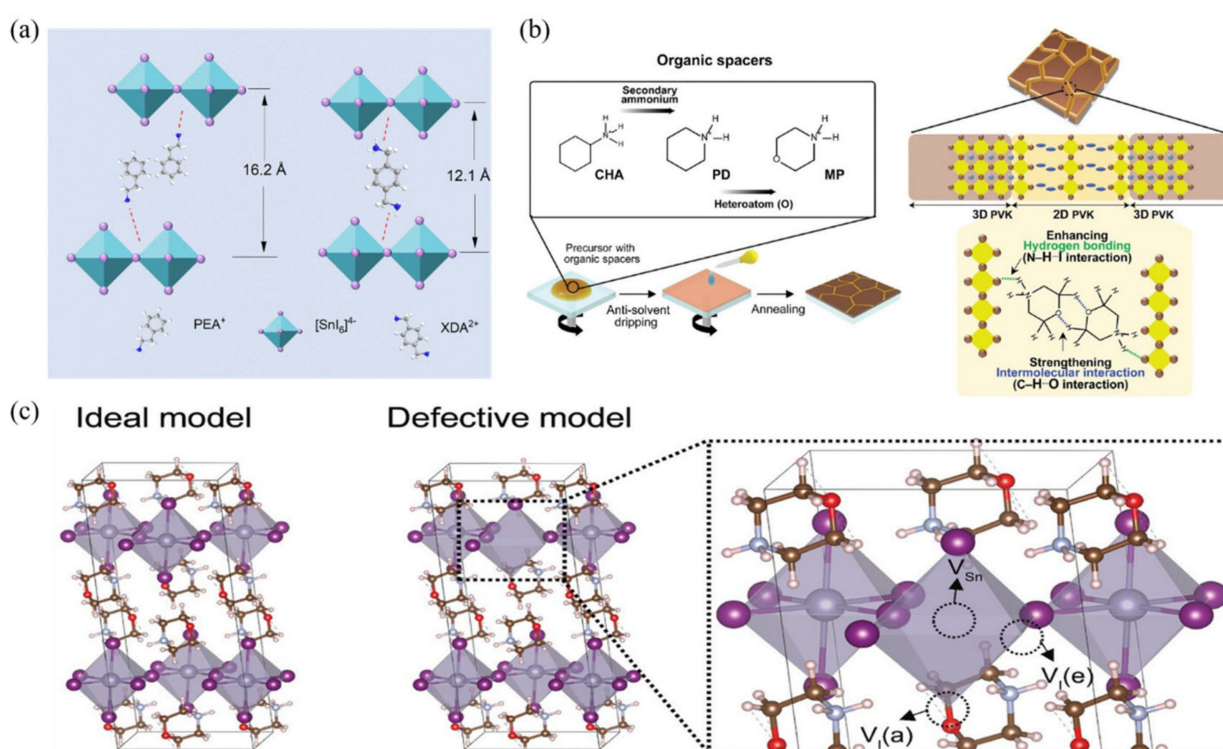


Figure 13. (a) Schematic of interaction between $[SnI_6]^{4-}$ and PEA (left) or XDA (right) [86]. (b) Left: Deposition process of 2D/3D perovskite using different organic spacers; cyclohexylammonium (CHA), piperidinium (PD), and morpholinium (MP). Right: Schematic illustration of the crystal structure of MP-based 2D/3D perovskite [87]. (c) Structural model of MP-based 2D perovskite. Structural model of 2D MP-based perovskite with vacancies. $V_1(e)$: neutral I vacancies in the equatorial position; $V_1(a)$: neutral I vacancies in the apical position; V_{Sn} : neutral Sn vacancies [87].

Additionally, there have been attempts to incorporate materials previously used in lead-based devices into tin-based devices. Recently, Chan et al. applied the commonly used ligand isobutylammonium iodide (iso-BAI) for surface treatment of tin-based perovskite [88]. Unlike the passivation effects observed in lead-based perovskites, this treatment led to surface recrystallization driven by the higher solubility of tin-based perovskite in common solvents. By carefully designing the solvent composition, effective modification of the perovskite surface was achieved while maintaining the integrity of the bulk material. This treatment improved surface crystallinity, reduced surface strain and defects, and enhanced charge transport.

Overall, these advancements in materials and strategies provide new solutions for enhancing the performance of tin-based perovskite solar cells and suggest promising avenues for future research in perovskite material development. With continuous exploration of novel materials, the potential for higher efficiency and improved stability in perovskite solar cells appears increasingly attainable.

3. Discussion

Previous studies have primarily focused on optimizing PEDOT:PSS to improve the buried interface, with numerous measures implemented in this regard. However, in recent years, the rapid development of self-assembled materials in lead-based perovskite solar cells has prompted initial attempts to apply self-assembled materials in tin-based perovskite solar cells. The surface chemical properties of self-assembled materials can be precisely tuned through the selection and arrangement of molecules, allowing for the design of interfaces suitable for perovskites, thereby enhancing the separation efficiency of electrons and holes. Additionally, a protective film can be formed at the interface, reducing the erosion of the perovskite layer by external factors such as moisture and oxygen, thus improving device stability and lifespan.

When designing novel self-assembled molecules, two main aspects should be considered. Firstly, anchoring to the transport layer can be achieved by incorporating different functional groups, such as carboxylic acids or amines, into the self-assembled molecules. These groups can chemically bond with the perovskite layer or PEDOT, enhancing interfacial adhesion and stability. Understanding the self-assembly mechanisms of these molecules (such as hydrogen bonding and hydrophobic interactions) can also aid in predicting their behavior during interface formation, facilitating better design. Secondly, modifications to the buried interface of the perovskite layer can improve charge separation and transport efficiency in tin-based perovskites, contributing to enhanced overall cell performance. The introduction of self-assembled materials not only protects the perovskite layer but also enhances its adaptability to environmental changes, thereby extending the device's operational lifespan.

In tin-based perovskite solar cells, optimizing the perovskite precursor solution is a significant research focus. This involves compositional tuning of the A, B, and X ions in the tin-based perovskite ABX_3 structure. Specifically, when adjusting the A-site ions, the use of macromolecular materials for dimensional control has emerged as an effective strategy to enhance device efficiency and stability.

Additive modulation represents another crucial method for optimizing both the perovskite precursor solution and the films. A variety of organic and inorganic materials have been incorporated into the perovskite precursor solution. In addition to traditional inorganic materials, an increasing number of researchers are exploring new organic materials for inclusion in the precursor solution. These new materials can prevent oxidation of the precursor solution and, when formed into films, can reduce defects in the active layer, thereby improving film quality.

Regarding the identification of suitable additive materials, existing research indicates that fullerene materials show considerable promise. Direct use of fullerene materials as additives is a viable research direction, with experiments aimed at finding the most effective additives. Moreover, developing new materials based on fullerene structures may become a future research hotspot. By introducing targeted functional groups to proven fullerene materials, it may be possible to further enhance the resistance to oxidation of divalent tin and improve the film quality of the perovskite layers.

Finally, we present a table summarizing the device efficiencies and electrical parameters of devices fabricated using self-assembled molecules and fullerene materials, as shown in Table 1. Most of the devices achieve efficiencies above 12%, indicating the effectiveness of the materials used.

Table 1. The device efficiencies and electrical parameters of devices fabricated using self-assembled molecules and fullerene materials.

Materials	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)	Ref.
Aromatic Diammonium Acetate Salts	0.826	20.7	70.8	12.1	[45]
Trimethoxy (3,3,3-Trifluoropropyl)-silane	0.910	22.6	70.4	14.36	[34]
X-shaped quinoxaline-based organic dyes	0.574	21.1	68.8	8.32	[56]
(4-(7H-dibenzo [c,g]carbazol-7-yl)ethyl)phosphonic acid	0.825	23.3	74.0	14.19	[57]
2-chloroethylphosphonic acid	0.640	23.2	71.8	10.65	[58]
[2-(9H-carbazol-9-yl)ethyl]phosphonic acid	0.740	16.2	73.0	8.66	[59]
Ethylenediammonium halide salts	0.817	22.5	77.4	14.23	[68]
Trimethylthiourea	0.920	20.4	76.7	14.30	[75]
2,8-dibromo-dibenzothiophene-S,S-dioxide	0.790	23.9	79.5	14.98	[76]
Pyridyl-substituted fulleropyrrolidines	0.856	24.8	72.4	15.38	[18]
[6,6]-phenyl-C61-butyric acid methyl ester	0.949	17.4	74.9	12.42	[82]
Multidentate fullerene molecules with 3, 4, 5, and 6 diethylmalonate groups	0.860	24.5	71.1	15.05	[83]
Thioctic acid functionalized C ₆₀ fulleropyrrolidinium iodide	0.866	24.6	70.0	14.91	[84]
Polymethyl-phenyl-silane	0.820	24.3	71.0	14.18	[85]
Mixed monoammonium and diammonium terminal ligands	0.900	20.7	76.9	14.31	[86]
Morpholinium iodide	0.803	20.6	73.1	12.04	[87]
Iso-butylammonium iodide	0.719	26.1	75.7	14.20	[88]

4. Conclusions

This paper summarizes the various materials recently employed in tin-based perovskite solar cells, focusing on their roles at the buried interface, within the active layer, and on the surface of the perovskite layer. Notably, self-assembled molecules and fullerene materials have shown great potential. The discussion highlights the functions of these materials within the devices and provides insights into their distinct contributions. Furthermore, suggestions are offered on how to design and utilize new materials in future research.

Funding: This research was funded by the National Key R&D Program of China (Grant No. 2018YFB0407100-02).

Data Availability Statement: The raw data can be obtained from the corresponding authors upon reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131*, 6050–6051. [CrossRef] [PubMed]
2. NREL Best Research-Cell Efficiencies. Available online: <https://www.nrel.gov/pv/assets/images/cell-pv-eff-emergingpv.jpg> (accessed on 28 September 2024).
3. Assirey, E.A.R. Perovskite synthesis, properties and their related biochemical and industrial application. *Saudi Pharm. J.* **2019**, *27*, 817–829. [CrossRef] [PubMed]
4. Gao, J.; Liang, Q.; Li, G.; Ji, T.; Liu, Y.; Fan, M.; Hao, Y.; Liu, S.; Wu, Y.; Cui, Y. Single-crystalline lead halide perovskite wafers for high performance photodetectors. *J. Mater. Chem. C* **2019**, *7*, 8357–8363. [CrossRef]
5. Sun, S.; Salim, T.; Mathews, N.; Duchamp, M.; Boothroyd, C.; Xing, G.; Sum, T.C.; Lam, Y.M. The origin of high efficiency in low-temperature solution-processable bilayer organometal halide hybrid solar cells. *Energy Environ. Sci.* **2014**, *7*, 399–407. [CrossRef]

6. Stoumpos, C.C.; Malliakas, C.D.; Kanatzidis, M.G. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. *Inorg. Chem.* **2013**, *52*, 9019–9038. [\[CrossRef\]](#)
7. Wehrenfennig, C.; Eperon, G.E.; Johnston, M.B.; Snaith, H.J.; Herz, L.M. High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites. *Adv. Mater.* **2014**, *26*, 1584–1589. [\[CrossRef\]](#)
8. Xing, G.; Mathews, N.; Sun, S.; Lim, S.S.; Lam, Y.M.; Graetzel, M.; Mhaisalkar, S.; Sum, T.C. Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science* **2013**, *342*, 344–347. [\[CrossRef\]](#)
9. Meggiolaro, D.; Motti, S.G.; Mosconi, E.; Barker, A.J.; Ball, J.; Perini, C.A.R.; Deschler, F.; Petrozza, A.; de Angelis, F. Iodine chemistry determines the defect tolerance of lead-halide perovskites. *Energy Environ. Sci.* **2018**, *11*, 702–713. [\[CrossRef\]](#)
10. Steirer, K.X.; Schulz, P.; Teeter, G.; Stevanovic, V.; Yang, M.; Zhu, K.; Berry, J.J. Defect Tolerance in Methylammonium Lead Triiodide Perovskite. *ACS Energy Lett.* **2016**, *1*, 360–366. [\[CrossRef\]](#)
11. D’Innocenzo, V.; Grancini, G.; Alcocer, M.J.P.; Kandada, A.R.S.; Stranks, S.D.; Lee, M.M.; Lanzani, G.; Snaith, H.J.; Petrozza, A. Excitons versus free charges in organo-lead tri-halide perovskites. *Nat. Commun.* **2014**, *5*, 3586. [\[CrossRef\]](#)
12. Zhang, W.; Saliba, M.; Stranks, S.D.; Sun, Y.; Shi, X.; Wiesner, U.; Snaith, H.J. Enhancement of Perovskite-Based Solar Cells Employing Core-Shell Metal Nanoparticles. *Nano Lett.* **2013**, *13*, 4505–4510. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Babayigit, A.; Ethirajan, A.; Muller, M.; Conings, B. Toxicity of organometal halide perovskite solar cells. *Nat. Mater.* **2016**, *15*, 247–251. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Hailegnaw, B.; Kirmayer, S.; Edri, E.; Hodes, G.; Cahen, D. Rain on Methylammonium Lead Iodide Based Perovskites: Possible Environmental Effects of Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2015**, *6*, 1543–1547. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Kwak, J.I.; An, Y.-J. Microplastic digestion generates fragmented nanoplastics in soils and damages earthworm spermatogenesis and coelomocyte viability. *J. Hazard. Mater.* **2021**, *402*, 124034. [\[CrossRef\]](#)
16. Li, Z.; Wu, X.; Wu, S.; Gao, D.; Dong, H.; Huang, F.; Hu, X.; Jen, A.K.Y.; Zhu, Z. An effective and economical encapsulation method for trapping lead leakage in rigid and flexible perovskite photovoltaics. *Nano Energy* **2022**, *93*, 106853. [\[CrossRef\]](#)
17. Liu, F.-W.; Biesold, G.; Zhang, M.; Lawless, R.; Correa-Baena, J.-P.; Chueh, Y.-L.; Lin, Z. Recycling and recovery of perovskite solar cells. *Mater. Today* **2021**, *43*, 185–197. [\[CrossRef\]](#)
18. Chen, J.; Luo, J.; Hou, E.; Song, P.; Li, Y.; Sun, C.; Feng, W.; Cheng, S.; Zhang, H.; Xie, L.; et al. Efficient tin-based perovskite solar cells with trans-isomeric fulleropyrrolidine additives. *Nat. Photonics* **2024**, *18*, 464–470. [\[CrossRef\]](#)
19. Meng, W.; Wang, X.; Xiao, Z.; Wang, J.; Mitzi, D.B.; Yan, Y. Parity-Forbidden Transitions and Their Impact on the Optical Absorption Properties of Lead-Free Metal Halide Perovskites and Double Perovskites. *J. Phys. Chem. Lett.* **2017**, *8*, 2999–3007. [\[CrossRef\]](#)
20. Tao, S.X.; Cao, X.; Bobbert, P.A. Accurate and efficient band gap predictions of metal halide perovskites using the DFT-1/2 method: GW accuracy with DFT expense. *Sci. Rep.* **2017**, *7*, 14386. [\[CrossRef\]](#)
21. Travis, W.; Glover, E.N.K.; Bronstein, H.; Scanlon, D.O.; Palgrave, R.G. On the application of the tolerance factor to inorganic and hybrid halide perovskites: A revised system. *Chem. Sci.* **2016**, *7*, 4548–4556. [\[CrossRef\]](#)
22. Lim, E.L.; Hagfeldt, A.; Bi, D. Toward highly efficient and stable Sn^{2+} and mixed $\text{Pb}^{2+}/\text{Sn}^{2+}$ based halide perovskite solar cells through device engineering. *Energy Environ. Sci.* **2021**, *14*, 3256–3300. [\[CrossRef\]](#)
23. Babayigit, A.; Thanh, D.D.; Ethirajan, A.; Manca, J.; Muller, M.; Boyen, H.-G.; Conings, B. Assessing the toxicity of Pb- and Sn-based perovskite solar cells in model organism *Danio rerio*. *Sci. Rep.* **2016**, *6*, 18721. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Ju, M.-G.; Chen, M.; Zhou, Y.; Dai, J.; Ma, L.; Padture, N.P.; Zeng, X.C. Toward Eco-friendly and Stable Perovskite Materials for Photovoltaics. *Joule* **2018**, *2*, 1231–1241. [\[CrossRef\]](#)
25. Fang, H.-H.; Adjokatse, S.; Shao, S.; Even, J.; Loi, M.A. Long-lived hot-carrier light emission and large blue shift in formamidinium tin triiodide perovskites. *Nat. Commun.* **2018**, *9*, 243. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Konstantakou, M.; Stergiopoulos, T. A critical review on tin halide perovskite solar cells. *J. Mater. Chem. A* **2017**, *5*, 11518–11549. [\[CrossRef\]](#)
27. Hao, F.; Stoumpos, C.C.; Guo, P.; Zhou, N.; Marks, T.J.; Chang, R.P.H.; Kanatzidis, M.G. Solvent-Mediated Crystallization of $\text{CH}_3\text{NH}_3\text{SnI}_3$ Films for Heterojunction Depleted Perovskite Solar Cells. *J. Am. Chem. Soc.* **2015**, *137*, 11445–11452. [\[CrossRef\]](#)
28. Pitaro, M.; Tekelenburg, E.K.; Shao, S.; Loi, M.A. Tin Halide Perovskites: From Fundamental Properties to Solar Cells. *Adv. Mater.* **2022**, *34*, 2105844. [\[CrossRef\]](#)
29. Cao, J.; Yan, F. Recent progress in tin-based perovskite solar cells. *Energy Environ. Sci.* **2021**, *14*, 1286–1325. [\[CrossRef\]](#)
30. Liu, X.; Wang, Y.; Xie, F.; Yang, X.; Han, L. Improving the Performance of Inverted Formamidinium Tin Iodide Perovskite Solar Cells by Reducing the Energy-Level Mismatch. *ACS Energy Lett.* **2018**, *3*, 1116–1121. [\[CrossRef\]](#)
31. Xu, L.; Feng, X.; Jia, W.; Lv, W.; Mei, A.; Zhou, Y.; Zhang, Q.; Chen, R.; Huang, W. Recent advances and challenges of inverted lead-free tin-based perovskite solar cells. *Energy Environ. Sci.* **2021**, *14*, 4292–4317. [\[CrossRef\]](#)
32. Ma, L.; Hao, F.; Stoumpos, C.C.; Phelan, B.T.; Wasielewski, M.R.; Kanatzidis, M.G. Carrier Diffusion Lengths of over 500 nm in Lead-Free Perovskite $\text{CH}_3\text{NH}_3\text{SnI}_3$ Films. *J. Am. Chem. Soc.* **2016**, *138*, 14750–14755. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Park, S.W.; Heo, J.H.; Lee, H.J.; Kim, H.; Im, S.H.; Hong, K.-H. Compositional Design for High-Efficiency All-Inorganic Tin Halide Perovskite Solar Cells. *ACS Energy Lett.* **2023**, *8*, 5061–5069. [\[CrossRef\]](#)
34. Teng, T.-Y.; Su, Z.-H.; Hu, F.; Chen, C.-H.; Chen, J.; Wang, K.-L.; Xue, D.; Gao, X.-Y.; Wang, Z.-K. Electronically Manipulated Molecular Strategy Enabling Highly Efficient Tin Perovskite Photovoltaics. *Angew. Chem.-Int. Ed.* **2024**, *63*, e202318133. [\[CrossRef\]](#) [\[PubMed\]](#)

35. Ma, X.; Zhang, Y.; Zhou, J.; Liu, L.; Ju, M.; Wang, N. Mitigating Surface Defects in Tin-Based Perovskite Films with α -Tocopherol for Enhanced Photovoltaic Performance. *Small* **2023**, *20*, e2307373. [[CrossRef](#)] [[PubMed](#)]
36. Bobba, R.S.; Ghimire, N.; Faheem, M.B.; Mabrouk, S.; Baniya, A.; Narwal, N.; Zhang, Y.; Kaswekar, P.I.; Li, H.; Saud, M.B.; et al. Thioacetamide-Assisted Crystallization of Lead-Free Perovskite Solar Cells for Improved Efficiency and Stability. *Sol. RRL* **2023**, *7*, 2300191. [[CrossRef](#)]
37. Kuan, C.-H.; Liao, T.-S.; Narra, S.; Tsai, Y.-W.; Lin, J.-M.; Chen, G.-R.; Diau, E.W.-G. Co-Cation Engineering via Mixing of Acetamidinium and Rubidium in FASnI₃ for Tin Perovskite Solar Cells to Attain 14.5% Efficiency. *J. Phys. Chem. Lett.* **2024**, *15*, 7763–7769. [[CrossRef](#)]
38. Li, T.; He, F.; Liang, J.; Qi, Y. Functional layers in efficient and stable inverted tin-based perovskite solar cells. *Joule* **2023**, *7*, 1966–1991. [[CrossRef](#)]
39. Jiang, Y.; Liu, T.; Zhou, Y. Recent Advances of Synthesis, Properties, Film Fabrication Methods, Modifications of Poly(3,4-ethylenedioxythiophene), and Applications in Solution-Processed Photovoltaics. *Adv. Funct. Mater.* **2020**, *30*, 2006213. [[CrossRef](#)]
40. Shih, C.-C.; Wu, C.-G. Synergistic Engineering of the Conductivity and Surface Properties of PEDOT:PSS-Based HTLs for Inverted Tin Perovskite Solar Cells to Achieve Efficiency over 10%. *ACS Appl. Mater. Interfaces* **2022**, *14*, 16125–16135. [[CrossRef](#)]
41. Thomas, S.A.; Hamill, J.C., Jr.; White, S.J.O.; Loo, Y.-L. Chemical and Structural Degradation of CH₃NH₃PbI₃ Propagate from PEDOT:PSS Interface in the Presence of Humidity. *Adv. Mater. Interfaces* **2021**, *8*, 2100505. [[CrossRef](#)]
42. Lanzetta, L.; Webb, T.; Zibouche, N.; Liang, X.; Ding, D.; Min, G.; Westbrook, R.J.E.; Gaggio, B.; Macdonald, T.J.; Islam, M.S.; et al. Degradation mechanism of hybrid tin-based perovskite solar cells and the critical role of tin (IV) iodide. *Nat. Commun.* **2021**, *12*, 2853. [[CrossRef](#)] [[PubMed](#)]
43. Di Girolamo, D.; Aktas, E.; Ponti, C.; Pascual, J.; Li, G.; Li, M.; Nasti, G.; Alharthi, F.; Mura, F.; Abate, A. Enabling water-free PEDOT as hole selective layer in lead-free tin perovskite solar cells. *Mater. Adv.* **2022**, *3*, 9083–9089. [[CrossRef](#)] [[PubMed](#)]
44. Ding, D.; Lanzetta, L.; Liang, X.; Min, G.; Giza, M.; Macdonald, T.J.; Haque, S.A. Ultrathin polymethylmethacrylate interlayers boost performance of hybrid tin halide perovskite solar cells. *Chem. Commun.* **2021**, *57*, 5047–5050. [[CrossRef](#)] [[PubMed](#)]
45. Song, D.; Li, H.; Xu, Y.; Yu, Q. Amplifying Hole Extraction Characteristics of PEDOT:PSS via Post-treatment with Aromatic Diammonium Acetates for Tin Perovskite Solar Cells. *ACS Energy Lett.* **2023**, *8*, 3280–3287. [[CrossRef](#)]
46. Kuan, C.-H.; Balasaravanan, R.; Hsu, S.-M.; Ni, J.-S.; Tsai, Y.-T.; Zhang, Z.-X.; Chen, M.-C.; Diau, E.W.-G. Dopant-Free Pyrrolopyrrole-Based (PPr) Polymeric Hole-Transporting Materials for Efficient Tin-Based Perovskite Solar Cells with Stability Over 6000 h. *Adv. Mater.* **2023**, *35*, 2300681. [[CrossRef](#)]
47. Zhang, Z.; Wang, L.; Bi, H.; Baranwal, A.K.; Kapil, G.; Sanehira, Y.; Liu, J.; Liu, D.; Shen, Q.; Hayase, S. Enhancement of Efficiency and Stability for Tin Halide Perovskite Solar Cells by Using Improved Doping Method. *Adv. Opt. Mater.* **2024**, *12*, 2300962. [[CrossRef](#)]
48. Liu, X.; Wu, T.; Zhang, C.; Zhang, Y.; Segawa, H.; Han, L. Interface Energy-Level Management toward Efficient Tin Perovskite Solar Cells with Hole-Transport-Layer-Free Structure. *Adv. Funct. Mater.* **2021**, *31*, 2106560. [[CrossRef](#)]
49. Wang, L.; Chen, M.; Yang, S.; Uezono, N.; Miao, Q.; Kapil, G.; Baranwal, A.K.; Sanehira, Y.; Wang, D.; Liu, D.; et al. SnO_x as Bottom Hole Extraction Layer and Top In Situ Protection Layer Yields over 14% Efficiency in Sn-Based Perovskite Solar Cells. *ACS Energy Lett.* **2022**, *7*, 3703–3708. [[CrossRef](#)]
50. Chen, L.; Li, C.; Xian, Y.; Fu, S.; Abudulimu, A.; Li, D.-B.; Friedl, J.D.; Li, Y.; Neupane, S.; Tumusange, M.S.; et al. Incorporating Potassium Citrate to Improve the Performance of Tin-Lead Perovskite Solar Cells. *Adv. Energy Mater.* **2023**, *13*, 2301218. [[CrossRef](#)]
51. Yang, W.-F.; Cao, J.-J.; Chen, J.; Wang, K.-L.; Dong, C.; Wang, Z.-K.; Liao, L.-S. Nicotinamide-Modified PEDOT:PSS for High Performance Indoor and Outdoor Tin Perovskite Photovoltaics. *Sol. RRL* **2021**, *5*, 2100713. [[CrossRef](#)]
52. Jiang, W.; Liu, M.; Li, Y.; Lin, F.R.; Jen, A.K.Y. Rational molecular design of multifunctional self-assembled monolayers for efficient hole selection and buried interface passivation in inverted perovskite solar cells. *Chem. Sci.* **2024**, *15*, 2778–2785. [[CrossRef](#)] [[PubMed](#)]
53. Pitaro, M.; Alonso, J.S.; di Mario, L.; Romero, D.G.; Tran, K.; Zaharia, T.; Johansson, M.B.; Johansson, E.M.J.; Loi, M.A.; Pitaro, M.; et al. A carbazole-based self-assembled monolayer as the hole transport layer for efficient and stable Cs_{0.25}FA_{0.75}Sn_{0.5}Pb_{0.5}I₃ solar cells. *J. Mater. Chem. A* **2023**, *11*, 11755–11766. [[CrossRef](#)]
54. Kapil, G.; Bessho, T.; Sanehira, Y.; Sahamir, S.R.; Chen, M.; Baranwal, A.K.; Liu, D.; Sono, Y.; Hirotani, D.; Nomura, D.; et al. Tin-Lead Perovskite Solar Cells Fabricated on Hole Selective Monolayers. *ACS Energy Lett.* **2022**, *7*, 966–974. [[CrossRef](#)]
55. Aktas, E.; Poli, I.; Ponti, C.; Li, G.; Olivati, A.; di Girolamo, D.; Alharthi, F.A.; Li, M.; Palomares, E.; Petrozza, A.; et al. One-Step Solution Deposition of Tin-Perovskite onto a Self-Assembled Monolayer with a DMSO-Free Solvent System. *ACS Energy Lett.* **2023**, *8*, 5170–5174. [[CrossRef](#)] [[PubMed](#)]
56. Afraj, S.N.N.; Kuan, C.-H.; Lin, J.-S.; Ni, J.-S.; Velusamy, A.; Chen, M.-C.; Diau, E.W.-G. Quinoxaline-Based X-Shaped Sensitizers as Self-Assembled Monolayer for Tin Perovskite Solar cells. *Adv. Funct. Mater.* **2023**, *33*, 2213939. [[CrossRef](#)]
57. Li, B.; Zhang, C.; Gao, D.; Sun, X.; Zhang, S.; Li, Z.; Gong, J.; Li, S.; Zhu, Z. Suppressing Oxidation at Perovskite-NiO_x Interface for Efficient and Stable Tin Perovskite Solar Cells. *Adv. Mater.* **2024**, *36*, 2309768. [[CrossRef](#)]
58. Cao, K.; Ning, H.; Xu, N.; Zuo, W.; Zhang, Y.; Yang, M.; Xia, J.; Liu, L.; Chen, S. Tailoring the buried interface with self-assembled 2-chloroethylphosphonic acid for defect reduction and improved performance of tin-based perovskite solar cells. *J. Mater. Chem. A* **2024**, *12*, 17444–17452. [[CrossRef](#)]

59. Chen, M.; Kapil, G.; Wang, L.; Sahamir, S.R.K.; Baranwal, A.; Nishimura, K.; Sanehira, Y.; Zhang, Z.; Kamarudin, M.A.; Shen, Q.; et al. High performance wide bandgap Lead-free perovskite solar cells by monolayer engineering. *Chem. Eng. J.* **2022**, *436*, 135196. [\[CrossRef\]](#)
60. Song, D.; Narra, S.; Li, M.-Y.; Lin, J.-S.; Diau, E.W.-G. Interfacial Engineering with a Hole-Selective Self-Assembled Monolayer for Tin Perovskite Solar Cells via a Two-Step Fabrication. *ACS Energy Lett.* **2021**, *6*, 4179–4186. [\[CrossRef\]](#)
61. Dai, Z.; Yadavalli, S.K.; Chen, M.; Abbaspourtamijani, A.; Qi, Y.; Padture, N.P. Interfacial toughening with self-assembled monolayers enhances perovskite solar cell reliability. *Science* **2021**, *372*, 618–622. [\[CrossRef\]](#)
62. Tai, Q.; Guo, X.; Tang, G.; You, P.; Ng, T.-W.; Shen, D.; Cao, J.; Liu, C.-K.; Wang, N.; Zhu, Y.; et al. Antioxidant Grain Passivation for Air-Stable Tin-Based Perovskite Solar Cells. *Angew. Chem.-Int. Ed.* **2019**, *58*, 806–810. [\[CrossRef\]](#) [\[PubMed\]](#)
63. Jiang, X.; Zang, Z.; Zhou, Y.; Li, H.; Wei, Q.; Ning, Z. Tin Halide Perovskite Solar Cells: An Emerging Thin-Film Photovoltaic Technology. *Acc. Mater. Res.* **2021**, *2*, 210–219. [\[CrossRef\]](#)
64. Wang, F.; Jiang, X.; Chen, H.; Shang, Y.; Liu, H.; Wei, J.; Zhou, W.; He, H.; Liu, W.; Ning, Z. 2D-Quasi-2D-3D Hierarchy Structure for Tin Perovskite Solar Cells with Enhanced Efficiency and Stability. *Joule* **2018**, *2*, 2732–2743. [\[CrossRef\]](#)
65. Chen, C.; Song, Z.; Xiao, C.; Zhao, D.; Shrestha, N.; Li, C.; Yang, G.; Yao, F.; Zheng, X.; Ellingson, R.J.; et al. Achieving a high open-circuit voltage in inverted wide-bandgap perovskite solar cells with a graded perovskite homojunction. *Nano Energy* **2019**, *61*, 141–147. [\[CrossRef\]](#)
66. Li, W.; Li, J.; Li, J.; Fan, J.; Mai, Y.; Wang, L. Additive-assisted construction of all-inorganic CsSnI₃Br₂ mesoscopic perovskite solar cells with superior thermal stability up to 473 K. *J. Mater. Chem. A* **2016**, *4*, 17104–17110. [\[CrossRef\]](#)
67. Gupta, S.; Bendikov, T.; Hodes, G.; Cahen, D. CsSnBr₃, A Lead-Free Halide Perovskite for Long-Term Solar Cell Application: Insights on SnF₂ Addition. *ACS Energy Lett.* **2016**, *1*, 1028–1033. [\[CrossRef\]](#)
68. Jiang, Y.; Lu, Z.; Zou, S.; Lai, H.; Zhang, Z.; Luo, J.; Huang, Y.; He, R.; Jin, J.; Yi, Z.; et al. Dual-site passivation of tin-related defects enabling efficient lead-free tin perovskite solar cells. *Nano Energy* **2022**, *103*, 107818. [\[CrossRef\]](#)
69. Yu, B.-B.; Chen, Z.; Zhu, Y.; Wang, Y.; Han, B.; Chen, G.; Zhang, X.; Du, Z.; He, Z. Heterogeneous 2D/3D Tin-Halides Perovskite Solar Cells with Certified Conversion Efficiency Breaking 14%. *Adv. Mater.* **2021**, *33*, 2102055. [\[CrossRef\]](#)
70. Wang, T.; Tai, Q.; Guo, X.; Cao, J.; Liu, C.-K.; Wang, N.; Shen, D.; Zhu, Y.; Lee, C.-S.; Yan, F. Highly Air-Stable Tin-Based Perovskite Solar Cells through Grain-Surface Protection by Gallic Acid. *ACS Energy Lett.* **2020**, *5*, 1741–1749. [\[CrossRef\]](#)
71. Nishimura, K.; Kamarudin, M.A.; Hirotsu, D.; Hamada, K.; Shen, Q.; Iikubo, S.; Minemoto, T.; Yoshino, K.; Hayase, S. Lead-free tin-halide perovskite solar cells with 13% efficiency. *Nano Energy* **2020**, *74*, 104858. [\[CrossRef\]](#)
72. Chen, K.; Wu, P.; Yang, W.; Su, R.; Luo, D.; Yang, X.; Tu, Y.; Zhu, R.; Gong, Q. Low-dimensional perovskite interlayer for highly efficient lead-free formamidinium tin iodide perovskite solar cells. *Nano Energy* **2018**, *49*, 411–418. [\[CrossRef\]](#)
73. Wang, C.; Gu, F.; Zhao, Z.; Rao, H.; Qiu, Y.; Cai, Z.; Zhan, G.; Li, X.; Sun, B.; Yu, X.; et al. Self-Repairing Tin-Based Perovskite Solar Cells with a Breakthrough Efficiency Over 11%. *Adv. Mater.* **2020**, *32*, 1907623. [\[CrossRef\]](#) [\[PubMed\]](#)
74. Yu, Y.; Wang, C.; Grice, C.R.; Shrestha, N.; Zhao, D.; Liao, W.; Guan, L.; Awni, R.A.; Meng, W.; Cimaroli, A.J.; et al. Synergistic Effects of Lead Thiocyanate Additive and Solvent Annealing on the Performance of Wide-Bandgap Perovskite Solar Cells. *ACS Energy Lett.* **2017**, *2*, 1177–1182. [\[CrossRef\]](#)
75. Zhu, Z.; Jiang, X.; Yu, D.; Yu, N.; Ning, Z.; Mi, Q. Smooth and Compact FASnI₃ Films for Lead-Free Perovskite Solar Cells with over 14% Efficiency. *ACS Energy Lett.* **2022**, *7*, 2079–2083. [\[CrossRef\]](#)
76. Zhou, X.; Peng, W.; Liu, Z.; Zhang, Y.; Zhang, L.; Zhang, M.; Liu, C.; Yan, L.; Wang, X.; Xu, B. Additive engineering with 2,8-dibromo-dibenzothiophene-S,S-dioxide enabled tin-based perovskite solar cells with 14.98% power conversion efficiency. *Energy Environ. Sci.* **2024**, *17*, 2837–2844. [\[CrossRef\]](#)
77. Jokar, E.; Chien, C.-H.; Tsai, C.-M.; Fathi, A.; Diau, E.W.-G. Robust Tin-Based Perovskite Solar Cells with Hybrid Organic Cations to Attain Efficiency Approaching 10%. *Adv. Mater.* **2019**, *31*, 1804835. [\[CrossRef\]](#)
78. Nishimura, K.; Hirotsu, D.; Kamarudin, M.A.; Shen, Q.; Toyoda, T.; Iikubo, S.; Minemoto, T.; Yoshino, K.; Hayase, S. Relationship between Lattice Strain and Efficiency for Sn-Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* **2019**, *11*, 31105–31110. [\[CrossRef\]](#)
79. Wheeler, S.; Bryant, D.; Troughton, J.; Kirchartz, T.; Watson, T.; Nelson, J.; Durrant, J.R. Transient Optoelectronic Analysis of the Impact of Material Energetics and Recombination Kinetics on the Open-Circuit Voltage of Hybrid Perovskite Solar Cells. *J. Phys. Chem. C* **2017**, *121*, 13496–13506. [\[CrossRef\]](#)
80. Wu, C.G.; Chiang, C.H.; Chang, S.H. A perovskite cell with a record-high-Voc of 1.61 V based on solvent annealed CH₃NH₃PbBr₃/ICBA active layer. *Nanoscale* **2016**, *8*, 4077–4085. [\[CrossRef\]](#)
81. Rajagopal, A.; Yang, Z.B.; Jo, S.B.; Braly, I.L.; Liang, P.W.; Hillhouse, H.W.; Jen, A.K.Y. Highly Efficient Perovskite-Perovskite Tandem Solar Cells Reaching 80% of the Theoretical Limit in Photovoltage. *Adv. Mater.* **2017**, *29*, 1702140. [\[CrossRef\]](#)
82. Jiang, X.; Wang, F.; Wei, Q.; Li, H.; Shang, Y.; Zhou, W.; Wang, C.; Cheng, P.; Chen, Q.; Chen, L.; et al. Ultra-high open-circuit voltage of tin perovskite solar cells via an electron transporting layer design. *Nat. Commun.* **2020**, *11*, 1245. [\[CrossRef\]](#) [\[PubMed\]](#)
83. Sun, C.; Zhang, H.; Cheng, S.; Chen, J.; Xing, Y.; Nan, Z.; Yang, P.; Wang, Y.; Zhao, X.; Xie, L.; et al. Multidentate Fullerenes Enable Tunable and Robust Interfacial Bonding for Efficient Tin-Based Perovskite Solar Cells. *Adv. Mater.* **2024**, *ahead of print*. [\[CrossRef\]](#)
84. Hou, E.; Chen, J.; Luo, J.; Fan, Y.; Sun, C.; Ding, Y.; Xu, P.; Zhang, H.; Cheng, S.; Zhao, X.; et al. Cross-Linkable Fullerene Enables Elastic and Conductive Grain Boundaries for Efficient and Wearable Tin-Based Perovskite Solar Cells. *Angew. Chem.-Int. Ed.* **2024**, *63*, e202402775. [\[CrossRef\]](#) [\[PubMed\]](#)
85. Zhang, Z.; Liu, J.; Bi, H.; Wang, L.; Shen, Q.; Hayase, S. Over 14% efficiency of highly reproducible Sn perovskite solar cell via defect passivation and morphology repairment. *Chem. Eng. J.* **2024**, *483*, 149345. [\[CrossRef\]](#)

86. Zang, Z.; Ma, M.; Jiang, X.; Zhou, W.; Seriwattanachai, C.; Kanjanaboos, P.; Ning, Z. Efficient quasi-2D tin perovskite solar cells based on mixed monoammonium and diammonium terminal molecules. *Mater. Chem. Front.* **2024**, *8*, 1827–1834. [[CrossRef](#)]
87. Choi, J.; Kim, J.; Jeong, M.; Park, B.; Kim, S.; Park, J.; Cho, K. Molecularly Engineered Alicyclic Organic Spacers for 2D/3D Hybrid Tin-based Perovskite Solar Cells. *Small* **2024**. *ahead of print*. [[CrossRef](#)]
88. Chan, P.F.; Qin, M.; Su, C.-J.; Ye, L.; Wang, X.; Wang, Y.; Guan, X.; Lu, Z.; Li, G.; Ngai, T.; et al. iso-BAI Guided Surface Recrystallization for Over 14% Tin Halide Perovskite Solar Cells. *Adv. Sci.* **2024**, *11*, e2309668. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.