

Polymers for Perovskite Solar Cells

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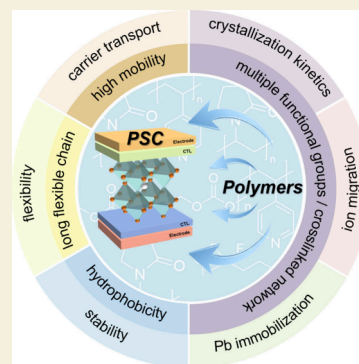
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ABSTRACT: Perovskite solar cells (PSCs) are recognized as one of the most promising next-generation photovoltaics, primarily due to their exceptional power conversion efficiency, ease of processing, and cost-effectiveness. Despite these advantages, challenges remain in achieving high-quality films and ensuring the long-term stability of PSCs, which hinder their widespread commercialization. Polymers, characterized by multifunctional groups, superior thermal stability, flexible long chains, and cross-linking capabilities, offer significant potential to enhance the performance and reliability of PSCs. This review comprehensively presents the multifaceted roles that polymers play in PSCs. Through carefully controlling interactions between polymers and perovskites, crucial aspects such as film crystallization kinetics, carrier transport process, ion migration issues, and mechanical properties under bending can be effectively regulated to maximize the device performance. Furthermore, the hydrophobic properties and strong chelated cross-linking networks of polymers significantly enhance the stability of PSCs under various environmental conditions while effectively mitigating lead leakage, thereby addressing environmental concerns and long-term durability. Moreover, this Perspective identifies potential pathways for further advancing polymer-based strategies in PSC applications.

KEYWORDS: perovskite solar cells, polymers, chemical interaction, stability, Pb immobilization



1. INTRODUCTION

Perovskite solar cells (PSCs) have emerged as highly promising photovoltaic devices due to their exceptional properties such as high mobility, strong absorption coefficient, tunable band gaps and low exciton binding energy.^{1–5} Over the past decades, their power conversion efficiency (PCE) has skyrocketed from 3.8%⁶ to 26.41%,⁷ rivaling traditional monocrystalline silicon solar cells. However, the inherent soft lattice structure of perovskite renders them susceptible to instability under conditions like high temperature, humidity and light exposure.^{8–10} Film defects, inefficient carrier transport, ion migration, and phase separation further challenge the performance and durability of PSCs. To address these issues,^{11,12} innovative organic molecule-based strategies have been utilized to enhance the performance and stability of PSCs. Polymers, in particular, have proven to be highly effective compared to small molecule materials and inorganic materials due to their superior thermal stability, customizable diversity structure, elastic properties, and cross-linking capabilities.^{13–15} Polymers functionalized with various groups play a pivotal role in regulating the crystallization kinetics of perovskite films, thereby enhancing the film crystallization and decreasing defect density, which is responsible for facilitating carrier transport^{16,17} and reducing nonradiative recombination loss and voltage deficit for enhancing the device performance.^{18–21} The strong chemical interactions derived from multifunctional groups in polymers inhibit defect

formation, passivate existing defects, and enhance the barrier against ion migration, resulting in suppressive phase separation and strengthening both photo and thermal stability.²² Additionally, the long flexible chains and superior elastic properties of polymers enhance the mechanical characteristics of films and serve as strain regulators during device bending. Their hydrophobic nature, high transparency, gas impermeability, and chemical inertness make them ideal for both the internal and external encapsulation of perovskite solar cells (PSCs). Furthermore, dendritic spatial structures and cross-linking networks significantly improve the polymers' capacity to capture Pb²⁺, thereby mitigating lead leakage and ensuring safety during operation.

This review focuses on the multifaceted roles of polymers in PSCs, including their ability to regulate crystallization kinetics, improve film flexibility, control carrier transport, inhibit ion migration, and prevent lead leakage (Figure 1). Moving forward, optimizing polymer structures to perovskite requirements, and

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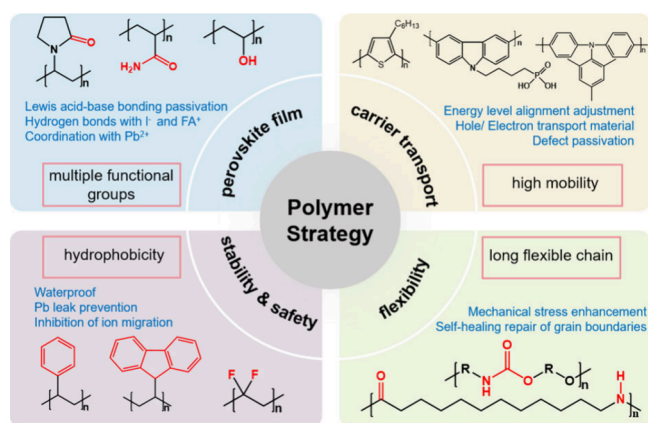


Figure 1. Summary of polymer strategies in PSCs.

exploring novel polymer functionalities are crucial for advancing the application of polymers in next-generation PSCs.

2. THE FUNCTIONS OF POLYMERS IN PSCS

2.1. Crystallization Kinetics Regulation

The quality of the perovskite absorbing layer significantly influences the photovoltaic performance of PSCs, encompassing crystallinity, uniformity, surface morphology, film coverage and defect density.²³ In the solution-processed perovskite films, film quality is heavily influenced by the precise control of crystallization kinetics during the film formation process, which is associated with the balance between nucleation and growth process as the solvent evaporates.^{24–26} Besides conventional solvent engineering techniques used to manage solvent removal rate, the functional polymers with adjustable chemical groups, lone pair electrons, and hydrogen bond donors are capable to regulate the crystallization by forming an intermediated phase that retards the crystallization process. Therefore, the crystallization kinetics could be effectively controlled through the rational design of polymers and intermolecular interaction to achieve high-quality and less-defect perovskite films.^{27–30}

For example, Li et al. designed a multifunctional fluorination additive (Figure 2a), 3-fluoro-4-methoxy-4',4'-bis((4-vinylphenyl ether)methyl)-triphenylamine (FTPA), which suppressed the

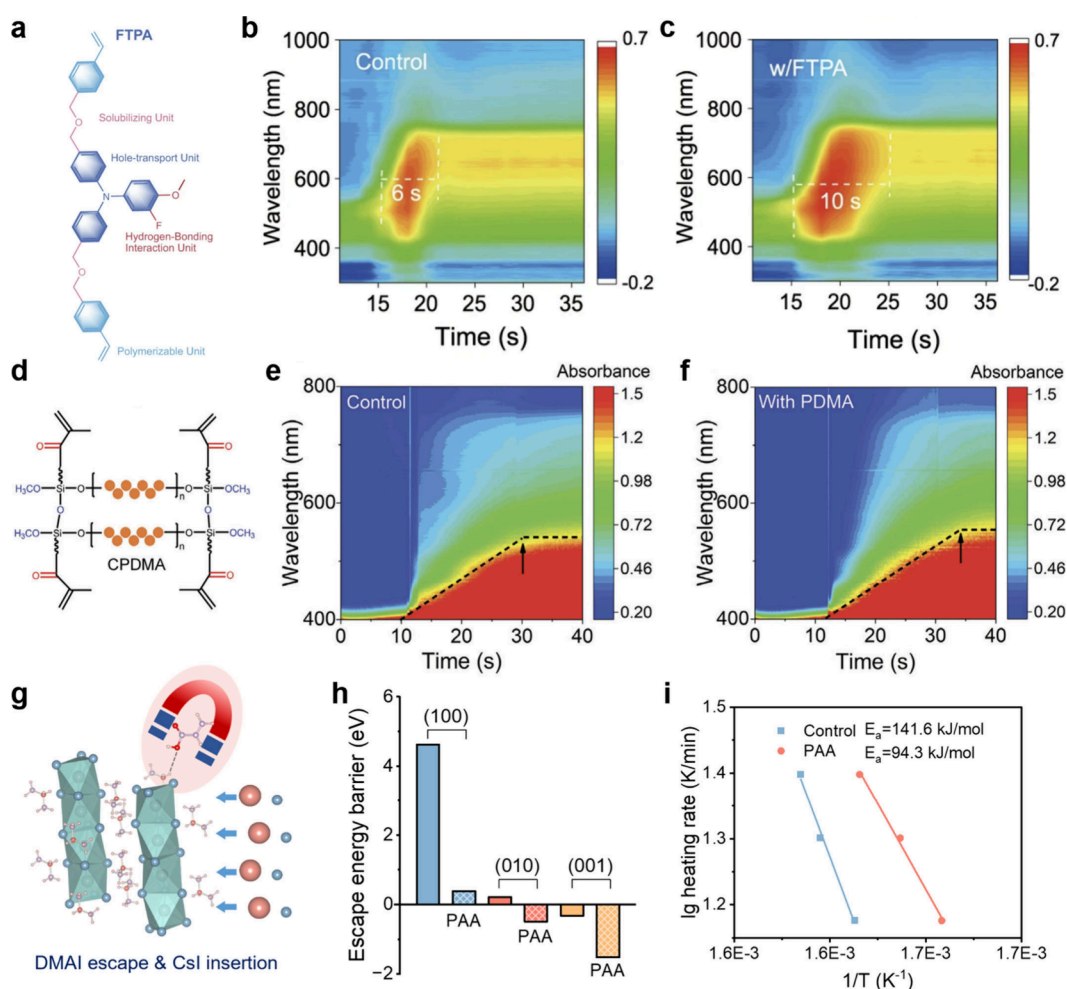


Figure 2. Crystallization kinetics regulation. (a) Chemical structure of FTPA. In-situ UV absorption spectra of (b) control and (c) FTPA films. Reproduced with permission from ref 31. Copyright 2023 Spring Nature. (d) Chemical structure of CPDMA. In-situ UV absorption spectra of (e) control and (f) PDMA films. Reproduced with permission from ref 32. Copyright 2023 Wiley-VCH. (g) Schematic hydrogen-bonding facilitated CsPbI₃ crystallization mechanism. (h) Escape energy barrier at (100), (010), and (001) surfaces with and without PAA treatment. (i) Active energy of control and PAA-treated films. Reproduced with permission from ref 30. Copyright 2023 Cell Press.

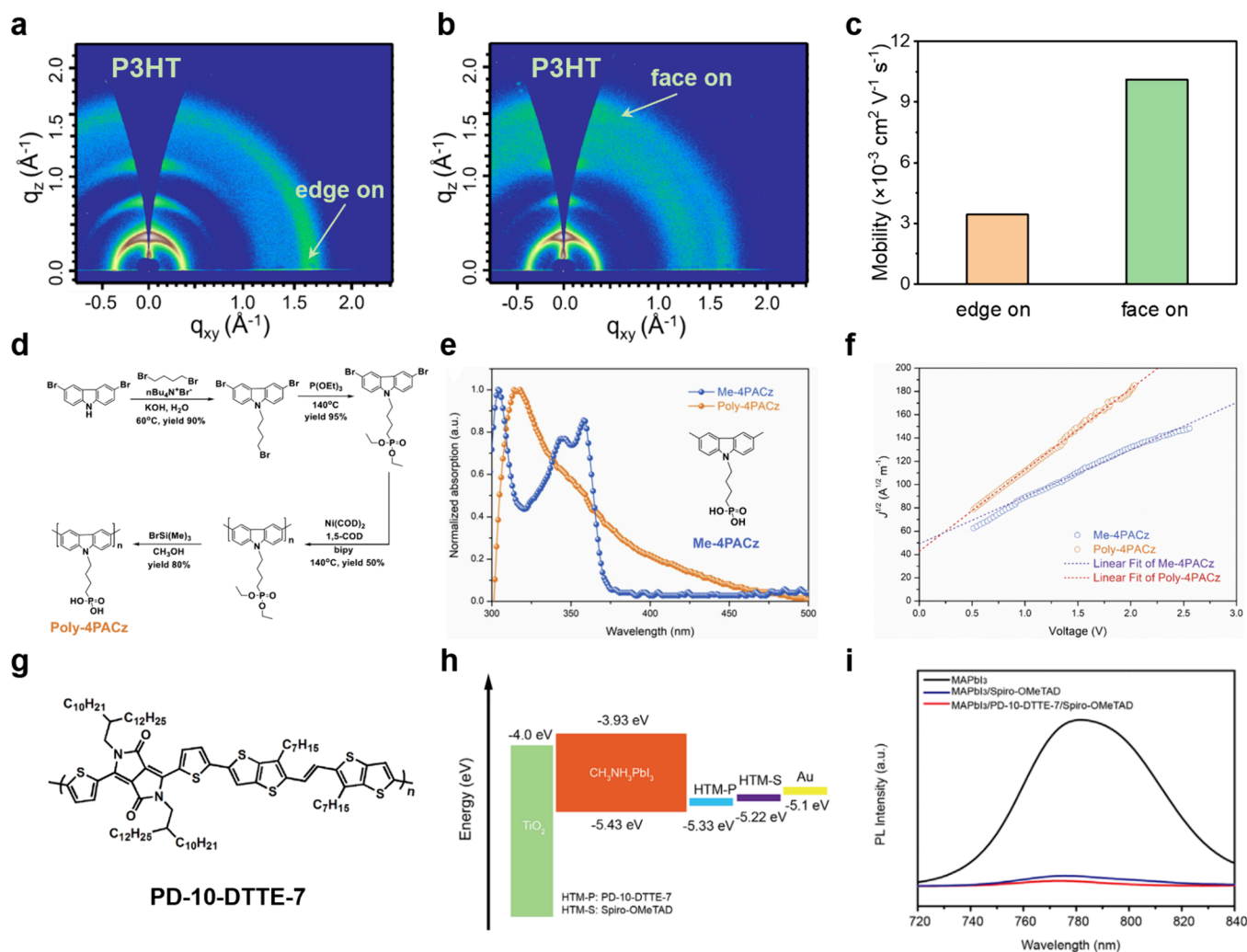


Figure 3. Carrier transport manipulation. GIWAXS mapping of control (a) “edge on” and (b) “face on” stacked P3HT films. (c) Mobility results. Reproduced with permission from ref 20. Copyright 2021 Wiley-VCH. (d) Synthesis route of Poly-4PACz. (e) UV-vis spectra and chemical structure of Me-4PACz and Poly-4PACz thin films. (f) $J^{1/2}$ vs V characteristics of hole-only devices with a structure of glass/ITO/PEDOT:PSS/HTM/MoO₃/Ag. Dash lines are linear fitting curves. Reproduced with permission from ref 34. Copyright 2023 Cell Press. (g) Molecular structure of PD-10-DTTE-7. (h) Schematic energy level alignment. (i) Steady-state photoluminescence spectra. Reproduced with permission from ref 35. Copyright 2019 Wiley-VCH.

complex intermediate phase and facilitated directional crystallization of α -phase perovskite.³¹ The hydrogen bonding between FTPA and perovskite promotes the formation of the FTPA- δ -FAPbI₃ intermediate phase, effectively inhibits the formation of other complex intermediate phases, and delays the crystallization kinetics of perovskite (Figure 2b, c). Benefiting from the promoted orientated crystallization of perovskite films, the unencapsulated devices achieve 24.10% PCE and maintain >95% of the initial efficiency for 1000 h under continuous sunlight soaking. In the two-step method, Zhao et al. introduced a polymerization-assisted grain growth (PAGG) strategy to enhance the film quality of $\text{FA}_{1-x}\text{MA}_x\text{PbI}_3$ perovskite.³³ The bulk polymer would adhere to the grain boundaries of PbI₂ through previously established interactions during the PbI₂ annealing process, and the energy barrier for the formation of perovskite crystals is higher than before due to the sufficient interaction between the polymer and PbI₂. PAGG slows the crystallization rate, increases the grain size of perovskite, and improves the crystallinity and orientation of the films. By further leveraging the advantages of polymer cross-linking, a telechelic silicone polymer, poly(dimethylsiloxane-co-methylsiloxane

acrylate (PDMA) (Figure 2d), was introduced to realize functions of crystallization regulation and defect healing.³² PDMA additives tightly anchor at the grain boundaries (GBs) and bridged perovskite grains through a condensation reaction, thereby retarding the rapid crystallization kinetics and reducing the film defects (Figure 2e, f).³² Based on similar research considerations, Xu et al. developed a multifunctional polymer additive PPG-mUPy-APDS, rich in hydrogen bonds and carbonyl groups.⁷⁹ The O and N in PPG-mUPy-APDS form hydrogen bonds with methylamine (MA⁺), formamidinium (FA⁺) and halide ions in perovskite, respectively, which slow down the growth of perovskite crystals and improve the quality of perovskite films. The strong interaction between C=O and Pb²⁺ can also passivate uncoordinated Pb²⁺, leading to reduced nonradiative recombination loss.

Furthermore, to address the challenge of achieving high-quality inorganic perovskite films, Hu and co-workers developed a universal hydrogen-bonding-facilitated dimethylammonium extraction strategy to control the CsPbI₃ crystallization kinetics (Figure 2g).³⁰ Theoretical and experimental findings revealed that the introduced poly(acrylic acid) (PAA) could effectively

coordinate with DMAbPbI_3 , decreasing the escape energy barrier (E_b) of DMA by forming hydrogen bonds ($\text{N-H}\cdots\text{O}$) (Figure 2h, i). This interaction accelerated the decomposition of DMAbPbI_3 and promoted the crystallization of CsPbI_3 . With improved control over crystallization, the resulting CsPbI_3 films present uniform morphology, high crystallinity, and low defects. Thus, effective modulation of the polymer–perovskite interaction represents a promising approach to manipulate crystallization kinetics and enhance perovskite film quality.

2.2. Carrier Transport Manipulation

The photoelectrical properties of the CTLs significantly influence carrier separation, transfer and nonradiative recombination in PSCs, thereby crucially impacting photovoltaic performance and stability of PSCs.^{36,37} To address the low-efficiency carrier transport, new polymeric CTLs and interface modifiers have been developed to enhance the carrier transport ability, optimize energy level alignment and reduce interface recombination loss.^{38,39}

P3HT stands out as one of the most classical and commercially viable polymeric hole transport layers (HTLs) due to its excellent carrier mobility, suitable energy levels, hydrophobic property and favorable thermal stability, making it highly promising for PSCs.^{40–44} However, P3HT typically presents an “edge on” stacking configuration, which restricts the effective carrier transport in the vertical direction (Figure 3a).^{45–48} To overcome this challenge, Hu et al. engineered a “face on” stacked P3HT by controlling the intermolecular interaction (Figure 3b), resulting in nearly 3-fold enhanced carrier mobility in the vertical direction (Figure 3c).²⁰ This advancement enabled the achievement of record-efficiency CsPbI_2Br PSCs with dopant-free HTLs. To overcome the poor wettability and substrate roughness, Ren et al. synthesized a novel polymer HTL called polycarbazole phosphonic acid (Poly-4PACz, Figure 3d), which exhibits superior hole mobility and conductivity compared to traditional self-assembled monomolecules (Figure 3e,f).³⁴ In addition, in the scalable manufacturing of perovskite components, the wettability, densification, and uniformity of HTMs on TCO crucially impact the perovskite film quality and device performance. The newly synthesized polymeric HTL presents insensitivity to layer thickness on underlying substrates like ITO and FTO, offering excellent wetting and compactness, which delivers promising potential for the scalable deposition of perovskite films. These superiorities benefit the achievement of large-area PSCs with a notable 20.7% PCE at the 25 mm² area.

Polymers have been widely used as interfacial modifiers between perovskite and CTL to improve the interface contact quality, passivate defects, and manage carrier transfer. Addressing the significant energy level mismatch between perovskite and spiro-OMeTAD, Gao et al. developed a high-mobility conjugated polymer (PD-10-DTTE-7, Figure 3g) as an interlayer to markedly reduce the interface recombination.³⁵ The PD-10-DTTE-7 polymer exhibits an extremely high mobility of 9.54 cm² V⁻¹ s⁻¹ compared to spiro-OMeTAD (10⁻³ cm² V⁻¹ s⁻¹), with a HOMO level at -5.33 eV, slightly lower than spiro-OMeTAD (-5.22 eV), resulting in interface energy level matching (Figure 3h). These electronic properties ensure an effective hole injection at the interface (Figure 3i). Dai et al. utilized an iodine-terminated self-assembled monolayer (I-SAM) between perovskite and SnO_2 ETL, enhancing adhesion toughness by 50% and mechanical reliability.⁴⁹ This modification increased PCE from 20.2% to 21.4% and the T_{80} operational

stability from ~700 to 4000 h under 1-sun illumination and with continuous maximum power point tracking (MPP). Hu et al. modified the poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) HTL with poly(methyl methacrylate) (PMMA):2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ).⁵⁰ The results reveal that PMMA molecules on PTAA induce an interface dipole at the PTAA/perovskite interface caused by the electrostatic interaction between the ester groups in the PMMA molecules and the electron-deficient N⁺ free radicals in the PTAA molecules. Physical adsorption results in an increase of 60 mV V_{oc} and achieves a PCE of more than 20%, with ideal stability.

In addition to their carrier transport function, polymers with defect passivation groups have been designed to reduce the interface recombination loss for further strengthening the carrier transport efficiency.^{51,52} To address the largely nonradiative recombination loss at interfaces, Sun et al. developed a new pyridine-based polymer HTL to extract photogenerated holes and passivate uncoordinated Pb^{2+} and iodide defects.⁵³ The interaction mechanism involves pyridine acting as a Lewis base and coordinating with lead ions to regulate the highest occupied molecular orbital (HOMO) levels and mobility of HTLs. These advancements led to PSCs with the newly synthesized dopant-free HTLs achieving an impressive PCE up to 22.41%. Similarly, Bai et al. synthesized two donor–acceptor (D-A) conjugated polymers, PBTI and PFBTI, which incorporate benzene dithiophene (BDT) and thiopheneimine (BTI) units. These polymers present high mobility and suitable energy levels. Due to the strong electronegative potential of the oxygen and fluorine atoms, the Lewis base is coordinated with uncoordinated Pb^{2+} in the perovskite. As a result, PSCs employing dopant-free PBTI- and PFBTI-HTLs achieved promising PCEs of 23.1% and 22.6%, respectively, surpassing conventional doped spiro-OMeTAD HTL devices (21.4%) due to synergetic carrier transport ability and surface passivation effect.⁵⁴

Sun et al. demonstrated that introducing the n-type polymer N2200 into PCBM can improve the electrical properties of PCBM and passivate the defects distributed on the surface of the perovskite, resulting in the improvement of band alignment and electron mobility. They obtained a high V_{oc} of 1.20 V and a PCE of 24.53% based on the PCBM@N2200 CTL.⁵⁵ Chen et al. employed two n-type polymers, PBTI and PDTzTI, both of which were synthesized based on thienyl imine and thiazolyl imine, respectively, to fabricate inverted perovskite solar cells (PSCs) as electron transport layers (ETLs). The PDTzTI ETL exhibited higher power conversion efficiency than PBTI and PCBM ETLs, attributed to its superior electron mobility, well-matched energy level alignment, and passivation of interfacial defects. A comparative analysis of the HOMO and LUMO levels of these two polymers revealed that the incorporation of thiazole significantly reduced the HOMO (~-5.8 eV) and LUMO (~-3.8 eV) energy levels. Consequently, the energy offset between the LUMO of PDTzTI and the conduction band of the perovskite could be greatly minimized following modification of the polymer structure, facilitating efficient extraction of electrons from the perovskite to the ETL. This study demonstrates that the energy level alignment between the perovskite and the ETL is crucial for electron extraction and interfacial contact. Moreover, due to the high hydrophobicity of the polymer and its ability to block mobile ions, devices utilizing PDTzTI ETL exhibited excellent long-term stability and operational stability compared to those utilizing PCBM.⁵⁶

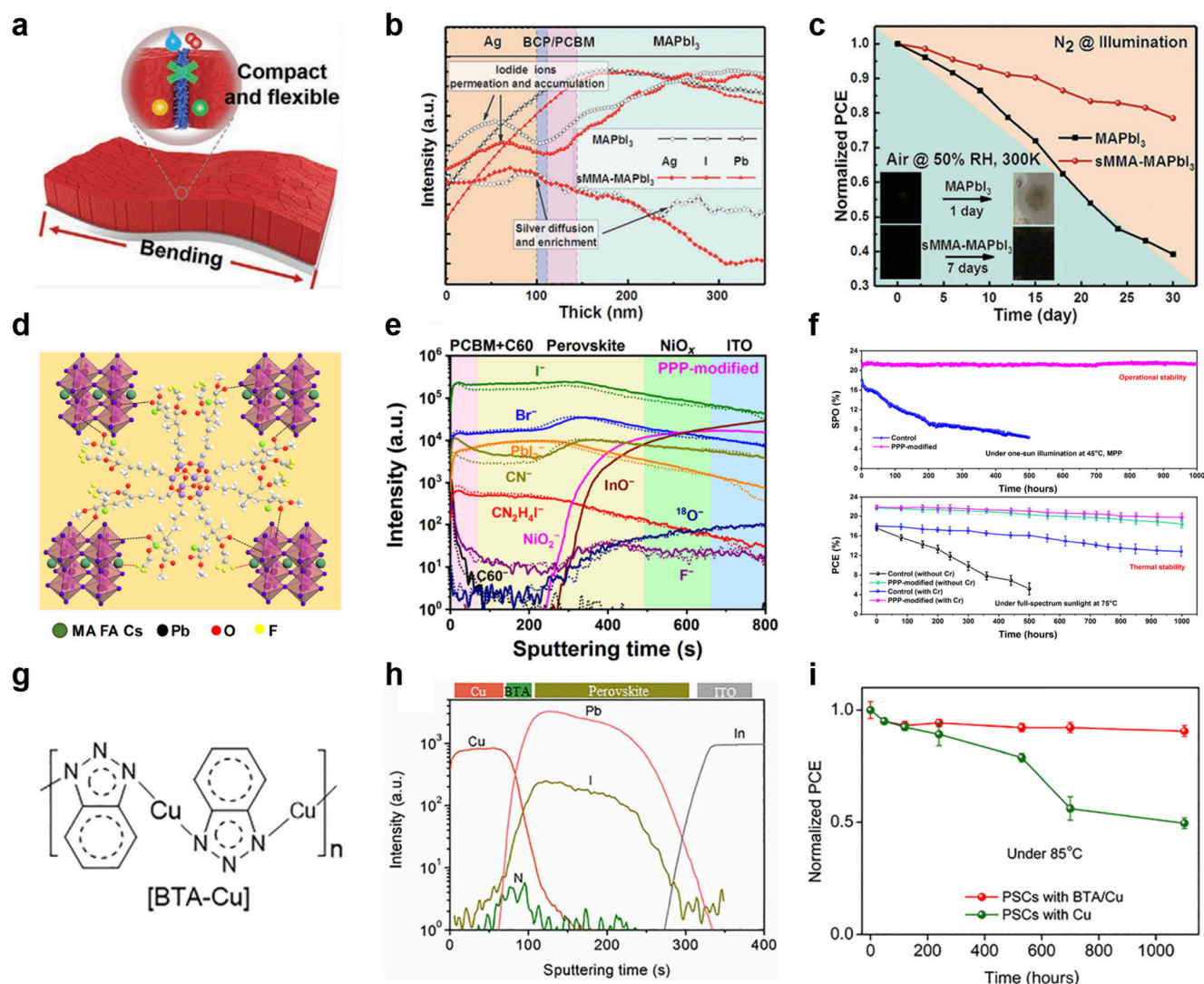


Figure 4. Ion migration suppression. (a) The mesoporous sMMA-PbI₂ membrane contains residual MMA monomers that can form a polymer network. (b) Linear energy dispersive spectrometer (I-EDS) patterns tested in the cross section. (c) Long-term stability of the corresponding PSCs under nitrogen and illumination. Reproduced with permission from ref 66. Copyright 2020 Wiley-VCH. (d) Schematic diagram of the interaction between the PPP polymer (partial 3D structure) and perovskite, including chelation between C=O and Pb and hydrogen bonding between -CF₃ and FA⁺ and MA⁺. (e) ToF-SIMS depth profiles of PPP-modified PSCs before (solid line) and after (short dashed line) thermal aging at 75 °C and full-spectrum sunlight for 300 h in N₂ atmosphere. (f) Maximum power point (MPP) illumination at 45 °C and thermal stability of encapsulated control and PPP-modified devices. Reproduced with permission from ref 67. Copyright 2021 American Association for the Advancement of Science. (g) The schematic diagram of BTA anticorrosion. (h) ToF-SIMS for depth profiling in aged PSCs with BTA/Cu after aging at 85 °C for 500 h in a glovebox. (i) Thermal stability of unencapsulated PSCs aged at 85 °C in a glovebox. Reproduced with permission from ref 68. Copyright 2020 American Association for the Advancement of Science.

2.3. Ion Migration Suppression

Perovskite materials, characterized by their soft lattice and relatively weak bonds as ionic crystals, exhibit a low defect formation energy. This makes them susceptible to ion defects induced by heat and light, exacerbated by electric fields that promote ion migration within the perovskite lattice.^{57–59} Such ion migration leads to local crystal deformation and electrode erosion, contributing to detrimental phenomena like current density–voltage hysteresis and phase segregation.^{60,61} These issues significantly curtail the stability and performance of PSCs, thereby impeding their path to commercial viability. Organic molecules have emerged as effective agents to mitigate these challenges by passivating defects and suppressing ion migration in PSCs. Polymers, in particular, offer superior passivation

capabilities and stronger barriers compared to small molecules.^{62–65}

Duan et al. introduced self-polymerized methyl methacrylate (sMMA) as an innovative approach to suppress ion migration and enhance PSCs' durability (Figure 4a).⁶⁶ The introduced sMMA effectively blocks ion diffusion channels and immobilizes Pb²⁺ ions, significantly hindering their migration toward the Ag electrode and the diffusion of Ag (Figure 4b). This intervention notably enhances operation stability (Figure 4c), presenting a promising avenue for advancing PSCs toward commercialization. Cao et al. developed a 3D star-shaped polymer, silsesquioxane-poly(trifluoroethyl methacrylate)-*b*-poly(methyl methacrylate) (PPP), aimed at mitigating ion migration and improving charge transport at the perovskite interface (Figure 4d).⁶⁷ The polymeric PPP forms a protective core–shell

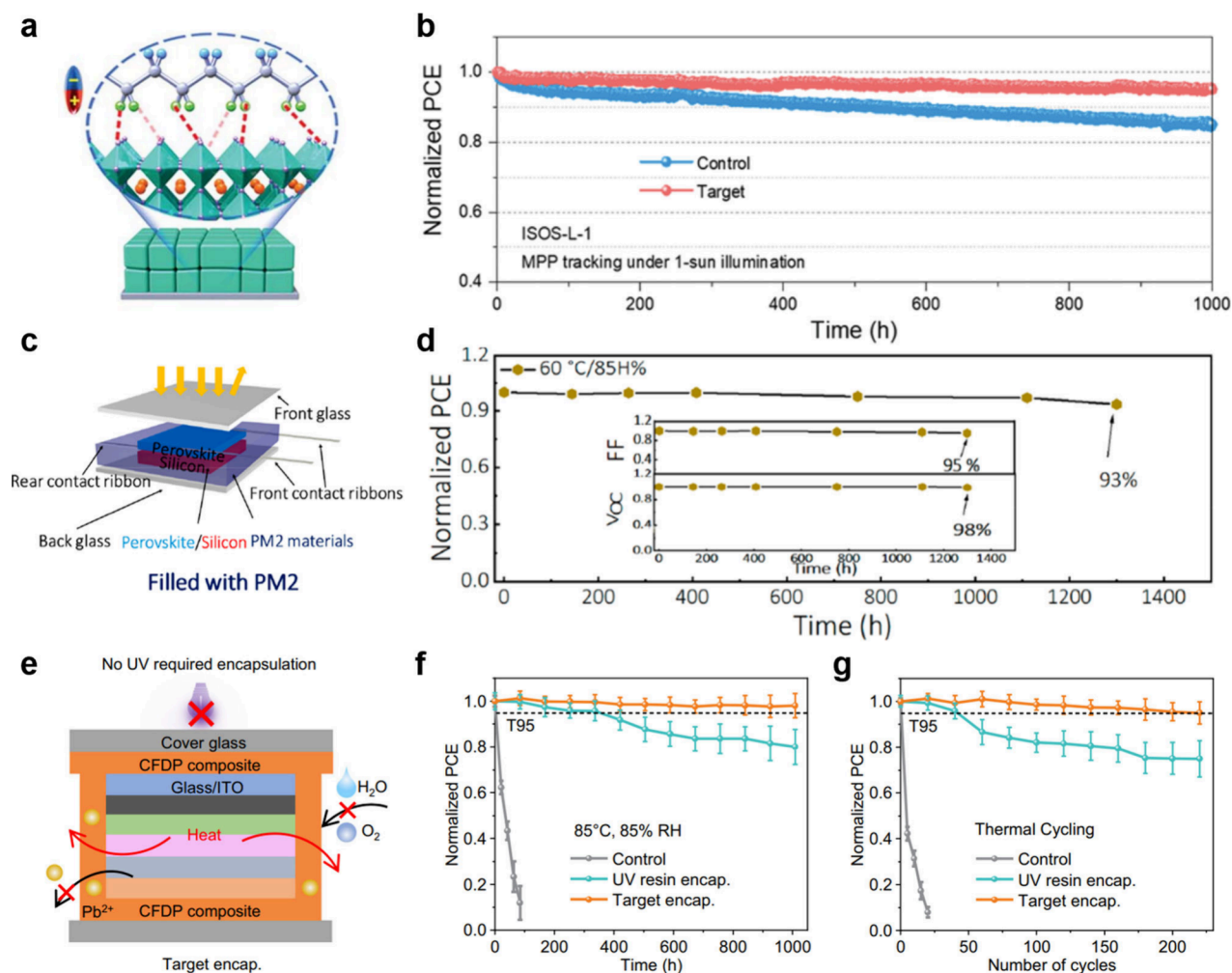


Figure 5. Device stability improvement. (a) Schematic diagram of the interaction between perovskite and 1,1-difluoroethylene. (b) Long-term stability at maximum power point tracking under room-temperature continuous illumination in a N_2 atmosphere for unencapsulated PSCs (ISOS-L-1 procedure). Reproduced with permission from ref 79. Copyright 2023 American Association for the Advancement of Science. (c) Novel encapsulating method using PM2 for monolithic PSTs. (d) Stability of encapsulated PSTs under the condition of 60 °C/85% RH. Reproduced with permission from ref 82. Copyright 2023 American Chemical Society. (e) Scheme of the PSCs with target encapsulation. Efficiency evolution of PSCs under (f) damp heat test at 85 °C and 85% relative humidity and (g) thermal cycling test from -40 and 85 °C. Reproduced with permission from ref 83. Copyright 2023 Spring Nature.

structure around the perovskite crystals, imparting robust resistance to ion migration and humidity (Figure 4e). PSCs with PPP incorporation demonstrated exceptional stability, maintaining high efficiency at the maximum power point for 1000 h at elevated temperature under continuous one-sun illumination (Figure 4f). Li et al. proposed a chemical anticorrosion strategy to enhance the PSC stability by incorporating benzotriazole (BTA) before the Cu electrode (Figure 4g). BTA chemically coordinated with the Cu, forming a polymeric [BTA-Cu] film that effectively suppresses ion migration of I^- and corrosion of the Cu electrode (Figure 4h). The modified device with this chemical anticorrosion strategy demonstrated excellent durability, maintaining over 90% of its initial efficiency even after undergoing 1000 h of aging at 85 °C (Figure 4i).⁶⁸

Besides, a copolymer strategy by Ma et al. was innovatively developed using a poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-)-2-carboxylate-2-6-diyl)] (PCE10) and monopolymer polystyrene (PS) to create a barrier at the perovskite boundary, effectively hindering ion migration

across grain boundaries.⁶⁹ The barrier prevents ions from diffusing freely, thereby stabilizing the devices. Liu et al. developed hydrophobic hydrogen-bonded polymer networks (HHPN) using poly(ionic liquid)s (PILs), which passivate the perovskite/ETL interface.⁷⁰ These networks not only inhibit ion migration but also act as barriers against water and oxygen intrusion, thereby enhancing the device stability. Furthermore, Zhang et al. integrated a polymerizable organic small molecule monomer, *n*-carbamoyl-2-propen-2-yl-4-enamide (Apronal), into perovskite films to form a cross-linked polymer (P-Apronal) by thermal cross-linking.⁷¹ The approach effectively fixes ion positions through multiple hydrogen bonds, thereby preventing thermally active ion migration and improving long-term stability.

2.4. Device Stability Improvement

Obtaining satisfactory lifetime for PSCs remains challenging compared to commercial silicon solar cells.^{72,33} Perovskite materials have a soft ionic lattice feature and include unstable components with weak interactions, such as hydrogen bonds or van der Waals interactions. Defects like halide vacancy usually

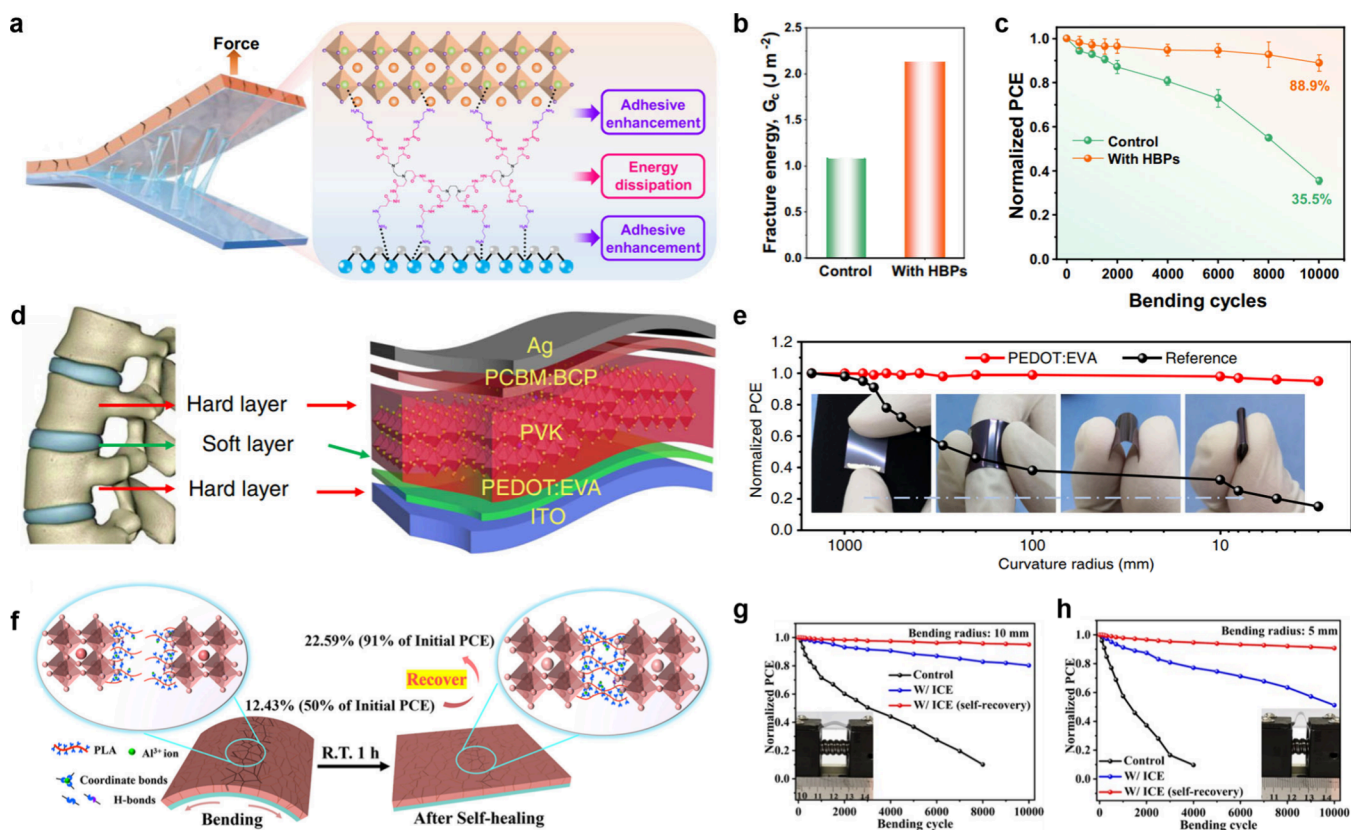


Figure 6. Film flexibility improvement. (a) Schematics of the HBPs bonding between SnO_2 and the perovskite interface. (b) Fracture energy of the interface with and without HBPs modification. (c) Normalized PCE for flexible PSCs after bending at different curvature radii for 1000 cycles. Reproduced with permission from ref 86. Copyright 2023 Spring Nature. (d) Biomimetic mechanisms of the vertebrae and PSCs. (e) Normalized averaged PCE value for the flexible PSCs after bending 500 cycles with different bending radius. Reproduced with permission from ref 87. Copyright 2020 Spring Nature. (f) Self-healing diagram of perovskite film with ICE. Normalized average PCE of PSCs as a function of bending cycles with bending radius of (g) 10 mm and (h) 5 mm. Reproduced with permission from ref 88. Copyright 2024 Royal Society of Chemistry.

serve as initial decomposition sites or channels for ion migration, contributing to phase separation and film decomposition.^{73–75} Besides, CTLs are sensitive to light and heat. In organic semiconductors, illumination can generate free radicals that result in cross-linking to form new separated phases or increased disorder within CTLs.⁷⁶ To enhance device stability, various polymer design strategies were developed to enhance the inherent perovskite stability and establish in situ device self-encapsulation networks within devices.^{77,78}

Internally, defects in the bulk, grain boundaries, and surfaces of perovskite crystals make them susceptible to degradation by oxygen and moisture in the environment. Many polymers can effectively passivate these defects by coordinating with uncoordinated Pb^{2+} ions. For instance, Li et al. utilized the ordered dipolar structure polymer, b-poly(1,1-difluoroethylene), to stabilize perovskite films (Figure 5a), achieving 96% retention of the initial efficiency after 1000 h of 1-sun maximum power point tracking (Figure 5b).⁷⁹ Additionally, Li et al. improved humidity stability using polymeric 3-fluoro-4-methoxy-4',4''-bis((4-vinyl benzyl ether) methyl)-triphenylamine (FTPA), attributing its effectiveness to the hydrophobic properties of fluorine-based polymeric FTPA on grain boundaries and perovskite surfaces, maintaining over 95% of initial PCE after 1000 h of exposure to sunlight and 50% humidity.³¹ Xu et al. developed a self-repairing polymer PPG-mUPy-APDS, rich in hydrogen bonds and carbonyl groups, which enhanced stability by forming chemical interactions with

perovskite and coordinating with Pb^{2+} ions. The resulting device remained 89% of its initial efficiency after 2000 h stability test in ambient air ($23 \pm 2^\circ\text{C}$ and $30 \pm 10\%$ relative humidity (RH)).⁸⁰ Zhao et al. proposed using hygroscopic polymer PEG, which demonstrated improved water stability and self-healing capabilities by attracting MA^+ through hydrogen bonding and preventing its escape.⁸¹

Another effective strategy to enhance thermal and humidity stability involves employing encapsulation techniques to prevent the ingress of humidity and oxygen from the environment, thereby suppressing the gaseous decomposition of perovskite materials. Li et al. developed an ultraviolet-curable block polymer (PM2) for encapsulating monolithic perovskite-silicon tandem solar cells (Figure 5c). PM2 material is eco-friendly and solidifies under UV light in just 1 min. Stability test conducted at 60°C and 85% relative humidity (RH) demonstrated that the device retained over 90% of its initial efficiency after 1000 h (Figure 5d).⁸² Moreover, Wang et al. designed a self-cross-linked fluorosilicone polymer gel (CFDP) for room-temperature, encapsulation. This approach effectively enhances heat dissipation, mitigates thermal stress, and blocks humidity and oxygen ingress (Figure 5e). Encapsulated devices maintained 98% of their initial PCE after 1000 h under 85% RH and 85°C conditions (Figure 5f). Moreover, 220 thermal cycles, the devices retained 95% of their initial PCE (Figure 5g).⁸³ These strategies highlight the potential of polymers for enhancing the stability of PSCs through both internal modification and external

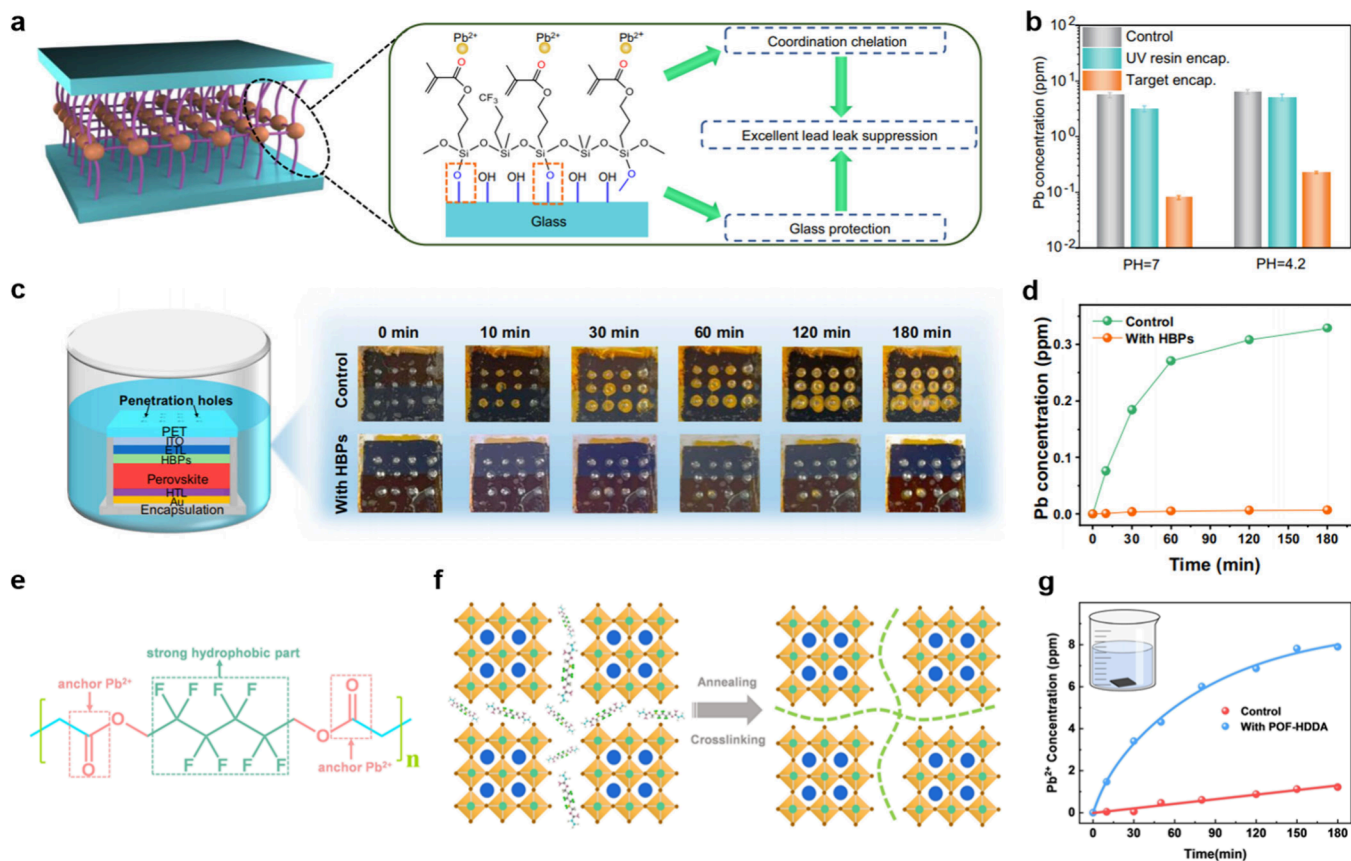


Figure 7. Immobilizing Pb to enhance use safety. (a) Illustration of lead leakage suppression via excellent glass protection and the strong coordination interaction between C=O groups and Pb²⁺. (b) Water-dripping test results for the damaged PSCs without encapsulation, with UV-resin encapsulation, and with target encapsulation. Reproduced with permission from ref 83. Copyright 2023 Springer Nature. (c) Schematics and photos of damaged flexible PSCs immersed in water for lead leakage test. (d) Pb concentration in the contaminated water measured by ICP-MS. Reproduced with permission from ref 86. Copyright 2023 Springer Nature. (e) Chemical structure of POF-HDDA. (f) Schematic diagram of in situ cross-linking of OF-HDDA. (g) Time variation of lead concentration in water immersed in perovskite films with/without POF-HDDA at 35 °C. Reproduced with permission from ref 100. Copyright 2023 Wiley-VCH.

encapsulation approaches, paving the way for their further development and application in renewable energy technologies.

2.5. Film Flexibility Improvement

The rapid growth of portable electronic products has made research into flexible solar cells increasingly attractive. Perovskite materials are recognized as promising candidates due to their excellent photovoltaic performance, low-temperature film processing, and low cost. However, the tendency to generate cracks during bending restricts their widespread application in devices such as wearables and portables.⁸⁰ To address this challenge, polymers or polymeric networks are commonly used to bridge grain boundaries or adhere the perovskite to adjacent functional layers, which effectively mitigates film strain and enhances mechanical properties.^{84,85}

Given to strengthen the interface adhesion between perovskite and charge transport layer (CTL), Li et al. developed dendritic hyperbranched molecules (HBPs) integrated into the SnO₂/perovskite interface to improve the film adhesion and mechanical stability in flexible PSCs (Figure 6a).⁸⁶ These HBPs contained amine and carbonyl functional groups that anchor with perovskite and SnO₂, respectively, creating a binding effect. Moreover, the hydrogen bond network within HBPs dissipated the mechanical energy through reversible association, increasing fracture energy and enabling self-healing of microcracks while inhibiting crack formation (Figure 6b). Flexible PSCs with

HBPs exhibited exceptional bending resistance even after 10000 bends at a radius of 3 mm (Figure 6c). Meng et al. employed a conductive and glued polymer, Poly(3,4-ethylenedioxythiophene):poly(ethylene-co-vinyl acetate) (PEDOT:EVA), between indium tin oxide (ITO) and perovskite layers to promote oriented crystallization and device adhesion (Figure 6d).⁸⁷

On the one hand, PEDOT:EVA can interact with perovskite precursor solution and ITO film to produce fewer perovskite nuclei, thus optimizing the growth of perovskite film and improving the interfacial contact with ITO. On the other hand, PEDOT:EVA has better cohesion and mechanical stability due to the adsorption interaction in PEDOT:EVA ink. Benefiting from the strengthened interface contact, the flexible device maintained approximately 96% of its initial PCE After 7000 cycles at a 10 mm bending radius (Figure 6e).

Considering the intrinsic flexible improvement, Xue et al. explored the benefits of a self-healing ionic conductive elastomer (ICE) in flexible PSCs, demonstrating its capability to repair grain boundary cracks and reduce the potential difference between grains and grain boundaries (Figure 6f).⁸⁸ The self-healing ICE was added to the perovskite precursor, leading to the formation of the cross-linked network structure of ICE at the grain boundary of the perovskite. The adhesive ICE on the separated particles at the bending cycle fracture of the film can

be rapidly connected by dynamic covalent disulfide bonds and noncovalent hydrogen bonds, thereby repairing micro- and macrocracks in perovskite films. This self-repairing ability significantly improved device performance and bending stability over 10 000 cycles at bending radii of both 10 mm and 5 mm (Figure 6g, h). Xiong et al. investigated the incorporation of polymer polyvinylpyrrolidone (PVP) into perovskite films through hydrogen bonding interactions, which not only slowed perovskite film degradation in a humid environment but also enhanced the film mechanical strength.⁸⁹ Huang et al. found that elastomer polyurethane (PU) additives cross-linked the grain boundaries between adjacent perovskite crystals, forming a PU network that effectively enhanced film flexibility.⁹⁰ Comparative mechanical bending tests showed perovskite films with PU maintained uniform morphology without cracks, highlighting PU's role in improving film flexibility.

2.6. Pb Immobilization for Use Safety

In the process of commercializing PSCs, they are inevitably exposed to environmental factors, such as rain and high temperatures. These conditions can lead to significant lead leakage from the devices, posing serious health and environmental risk due to the toxicity of lead accumulation.^{91,92} To address this issue, strategies focus on converting water-soluble Pb^{2+} into insoluble forms to prevent their transfer from damaged equipment.^{93,94}

One effective approach involves the use of interpenetrating polymer networks within the perovskite structure. These networks utilize abundant functional groups that interact strongly with Pb^{2+} ions, thereby effectively limiting lead leakage.^{95–97} For instance, Wang et al. developed a self-cross-linked fluorosilicone polymer gel, CFDP, which achieves nondestructive encapsulation at room temperature (Figure 7a). Devices encapsulated with CFDP exhibited excellent inhibition of lead leakage under the water-dripping test (Figure 7b).⁸³ This polymer not only addresses the lead leakage issue effectively but also offers excellent processability at low temperatures, thereby mitigating the impact of high temperatures on unstable perovskite materials. Similarly, Li et al. utilized a highly adhesive polyamide-amine-based hyperbranched polymer to enhance the interface integrity and effectively suppress lead leakage. The polymers contain abundant intramolecular cavities that provide numerous sites ($-\text{C}=\text{O}$, $-\text{NH}-$ and $-\text{NH}_2$ groups) for Pb^{2+} adsorption sites to capture Pb^{2+} , significantly reducing lateral water permeation and maintaining 98% lead retention efficiency compared to control devices (Figure 7c, d).⁹⁸

Additionally, Dong et al. implemented a poly(vinyl butyraldehyde) (PVB) layer as an internal encapsulation barrier between the perovskite and ETLs. This internal layer effectively suppresses lead leakage and enhances the overall stability of PSCs.⁹⁹ Another innovative method introduced by Zhang et al. involves incorporating the introduced organic monomer octafluoro-1,6-hexanediol diacrylate (POF-HDDA) into the perovskite film.¹⁰⁰ This forms a protective polymer POF-HDDA through in situ cross-linking, where the hydrophobic $-\text{C}-\text{F}$ groups shield Pb^{2+} from water infiltration and anchor non-coordinating Pb^{2+} ions (Figure 7e, f). Testing shows that POF-HDDA significantly reduces lead leaching compared to control films, with an 85% inhibition rate observed after 180 min (Figure 7g).

3. CONCLUSION AND OUTLOOK

High-efficiency and stable PSCs have long been the focus of research efforts. While significant strides have been made in improving their efficiency, ensuring long-term stability remains a critical challenge for their commercial viability. Researchers have explored various approaches to achieve efficient, stable, and hysteresis-free perovskite solar cells. Among these, polymers have emerged as promising partners due to their unique chemical and physical properties. Polymers have been extensively studied as additives in various components of PSCs, including the light-absorbing layers, charge transport layers, and interfacial buffer layers. This strategy harnesses polymers' potential to enhance stability and overall performance. This review summarizes recent advancements in polymer applications for enhancing charge transport, controlling perovskite crystallization kinetics, inhibiting ion migration, improving device flexibility, ensuring stability, and preventing lead leakage in PSCs.

While polymer strategies demonstrate significant potential, several challenges remain unresolved. These include identifying optimal types of functional groups, chemical interaction strength, optical properties and physical properties of polymers (Figure 8). Addressing these challenges is crucial for further

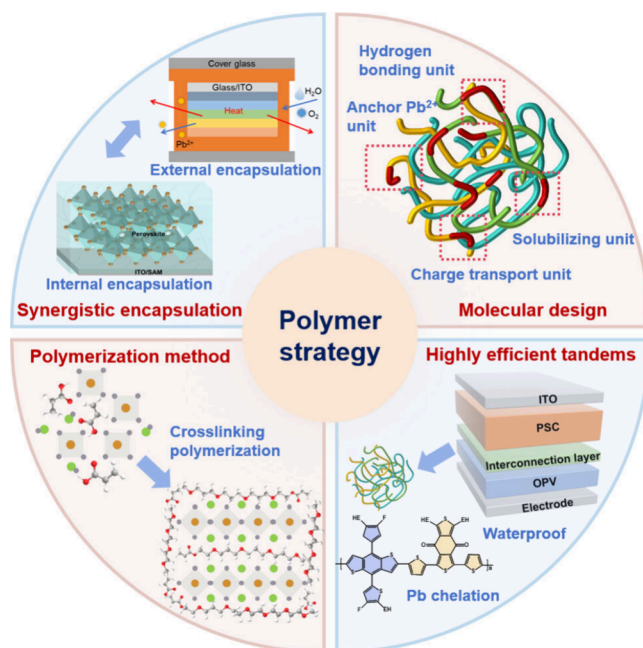


Figure 8. Perspectives for the advancement of polymer strategy in PSCs.

advancing polymer applications in perovskite films and devices. To tackle these issues, the following strategies are proposed

- I. Tailoring polymer structure to enhance intrinsic stability of perovskite materials: Improving the intrinsic stability of perovskite materials is crucial for addressing the device stability issues. Thus, the most effective and urgent strategy involves customizing the polymer structures to meet the perovskite requirements. Designing novel polymers with specific functional groups that interact favorably with perovskite materials is essential. These polymers should effectively passivate defects, regulate perovskite crystallization, inhibit ion migration, and facilitate high charge transfer rates with high selectivity

for either holes or electrons. For example, polymers with multiple active sites can support the coexistence of various interactions to enhance the passivation effectiveness. Additionally, incorporating a cross-linked network with a high elastic modulus improves the mechanical properties of perovskite films, thereby enhancing their resistance to environmental stress and prolonging their operational stability.

- II. Simultaneous external and internal polymer encapsulation: Implementing both external polymer encapsulation and internal polymer encapsulation integration within the device concurrently can comprehensively enhance the performance and stability of PSCs. The encapsulation materials should meet the following criteria: a suitable refractive index to minimize optical losses; resistance to heat, oxygen, and ultraviolet radiation; an appropriate coefficient of thermal expansion compatible with the perovskite layer to prevent delamination; low-temperature processing to avoid damaging the perovskite; and enhanced capability to absorb lead ions from damaged perovskite modules, thereby reducing environmental contamination.
- III. Optimizing polymer integration method: Practical application of polymer strategy in PSCs faces several challenges. For example, phase separation between polymer and main material may occur, reducing the efficiency and stability of the device due to the poor compatibility of polymer and perovskite. Additionally, some polymers exhibit low charge mobility or electrical insulation, making device performance highly sensitive to the polymer concentration or thickness. To address these issues, we propose that employing suitable methods such as *in situ* or *ex situ* polymerization for chemical blending and determining appropriate molecular weights or doping levels based on specific integration methods and experimental conditions.
- IV. Establishing perovskite/organic tandem devices: Utilizing organic active layers as an effective encapsulation layer or protective barrier for underlying PSCs on the consideration of their robust hydrophobic properties. Incorporating chelation groups for Pb^{2+} can suppress lead leakage and enhance operational safety. Besides, PSCs serve as high-energy photon filter to effectively enhance the photostability of organic solar cells. Thus, tandem devices combining perovskite and organic solar cells can improve overall device efficiency and stability.

In wide-bandgap perovskite subcells of tandem devices, polymers containing various functional groups can be engineered as additives or interfacial layers to facilitate multiple interactions with perovskites. Designing confined polymer networks can effectively suppress ion migration and passivate defects while serving as a barrier against water and oxygen intrusion, thereby enhancing device stability and photovoltaic conversion efficiency.

Apart from the active layer, the interconnective layer (ICL) in tandem devices is crucial to the overall device performance. Factors such as parasitic absorption, interfacial contact properties, and material mobility of ICLs significantly affect light absorption in the active layer and carrier transport efficiency. While ultrathin metal materials are commonly used for ICLs, their poor light transmission often results in inferior performance. Additionally, the vacuum deposition process used to

prepare metal-based ICLs can cause perovskite film damage. By molecularly designing polymeric ICLs with high mobility and high transparency, it is possible to improve carrier transport and light absorption in the active layer, as well as reduce voltage loss and nonradiative recombination, thereby enhancing the performance of tandem devices.

By pursuing these strategies, researchers aim to unlock the full potential of polymers in improving the stability and efficiency of PSCs, paving the way for their broader application in renewable energy technologies.

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Notes

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