

Self-Assembled Monolayers for Stable Inverted Perovskite Solar Cells: Buried Interface Engineering and Degradation Challenges

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Abstract:

Inverted perovskite solar cells combine low-temperature processing with compatibility for flexible substrates and tandem architectures. Their performance, however, is strongly influenced by the buried contact between the bottom hole-selective layer and the perovskite absorber. This review examines how self-assembled monolayers (SAMs) modify that interface. Evidence is organised around molecular design, interface formation, degradation during fabrication and operation, and the additional constraints imposed by tandem devices. The most firmly established effects of SAMs are work-function adjustment, improved hole extraction, defect passivation, and control of perovskite nucleation. Their proposed role in limiting ion migration is promising but remains less directly demonstrated. Across the literature, performance depends as much on coverage, adsorption, wettability, and anchoring strength as on the molecular structure itself. These dependencies become more demanding in large-area and tandem cells, where local defects and processing damage are harder to tolerate. SAMs are therefore best treated as interface-forming materials whose value must be judged by reproducibility and durability, not by initial efficiency alone. Priorities for further work include stronger substrate binding, direct characterisation of buried interfaces, comparable stability protocols, and deposition methods that remain reliable on textured and large-area substrates.

Keywords:

Self-Assembled Monolayers, Inverted Perovskite Solar Cells, Buried Interface, Tandem Solar Cells, Operational Degradation, Stability

1. Introduction

Metal-halide perovskites combine strong optical absorption, tunable band gaps, and solution-processability, enabling rapid gains in photovoltaic efficiency. The remaining obstacle is not simply achieving a high initial power conversion efficiency, but retaining it under heat, illumination, moisture, and electrical bias.

Among different device structures, inverted p-i-n PSCs are especially important. In this architecture, the hole-selective contact is placed below the perovskite absorber, while the electron-selective contact is deposited above it. Inverted devices can be

fabricated at relatively low temperatures, often show reduced hysteresis, and are compatible with flexible and tandem solar cells [1] [2]. Their relevance is therefore not limited to single-junction devices. They are also central to perovskite/silicon and all-perovskite tandem photovoltaics, where interface quality strongly affects device performance.

The main materials challenge in the inverted structure is the buried interface between the bottom hole-selective contact and the perovskite absorber. This interface becomes hidden after perovskite deposition, but it strongly influences nucleation, crystallisation, film morphology, charge extraction, and interfacial recombination. Defects at this interface can create trap states where electrons and holes recombine, preventing the production of useful current. As a result, the buried interface can reduce open-circuit voltage, fill factor, and operational stability [1] [2].

Conventional hole-transport layers (HTLs), such as PEDOT:PSS, PTAA, and NiO_x , have enabled rapid development of inverted PSCs, but each has limitations. PEDOT:PSS can be acidic and hygroscopic, which may accelerate interfacial degradation. PTAA often requires relatively thick organic layers and can introduce parasitic absorption or increase processing costs. NiO_x is more robust, but surface defects and energy-level mismatch can still promote interfacial recombination. These limitations create a need for thinner and more chemically tunable contacts that can regulate the buried interface rather than transport holes [1] [2].

Self-assembled monolayers (SAMs) have therefore become important hole-selective contacts for inverted PSCs. A SAM is an ultrathin molecular layer, usually only one molecule thick, that forms through spontaneous adsorption and ordering on a substrate such as indium tin oxide (ITO) or NiO_x . Compared with conventional HTLs, SAMs can reduce material consumption and parasitic optical absorption while enabling molecular-level control over work function, surface chemistry, and interfacial dipoles [1]. However, their monolayer nature also makes them vulnerable. Small changes in coverage, anchoring strength, molecular packing, solvent compatibility, substrate pretreatment, or annealing conditions can strongly affect device performance.

Recent work has shifted attention from the nominal identity of the SAM molecule to the way the layer forms and survives processing. Tang et al. linked solvent resistance to anchoring chemistry [3], whereas Qu et al. showed that a conjugated linker can alter molecular ordering and charge extraction [4]. Ordered bilayers, mixed monolayers, and micelle-disassembly methods have been used to address wetting and coverage limitations [5] [6] [7]. Other studies have combined SAMs with NiO_x , varied heteroatoms, or exploited interfacial dipoles to modify defect chemistry and charge dynamics [8] [9] [10]. Together, these reports frame SAMs as active components of the buried interface rather than merely thinner substitutes for conventional HTLs.

This review considers two linked questions: how molecular and processing choices determine the buried interface formed by a SAM, and why the resulting devices still face unresolved stability and scale-up problems. The discussion moves from molecular structure to interface formation, then to degradation and tandem-cell requirements, before identifying the main limitations and priorities for future work.

2. Literature Review

2.1. SAM Molecular Engineering Design

SAM molecular engineering is based on a structure–property–interface–function relationship. A typical SAM molecule contains an anchoring group, a linker, and a terminal or conjugated functional group. The anchoring group binds the molecule to the substrate and largely determines assembly stability. The linker controls spacing, packing density, molecular tilt, and electronic communication. The terminal or conjugated unit affects dipole moment, interfacial interaction, energy-level alignment, and charge transport. Because a SAM is only one molecule thick, each part of the molecule can influence the final buried interface.

The anchoring group is especially important because the SAM must remain attached during perovskite precursor coating. Phosphonic acid-based molecules can bind to oxide substrates such as ITO and NiO_x, but binding strength and surface hydroxyl density strongly influence coverage and durability. Tang et al. showed that weakly anchored SAMs can be partially removed by strongly polar perovskite precursor solvents [3]. This means that anchoring chemistry is not only a matter of initial adsorption. It also determines whether the buried interface survives fabrication.

The linker is another active design variable rather than a passive spacer. Qu et al. replaced the flexible alkyl linker in a Me-4PACz-type molecule with a conjugated phenylene linker to form Me-PhpPACz [4]. This change improved molecular arrangement, hole extraction, and device performance. The significance of the work lies not only in the improved efficiency but also in the design logic. By changing the linker, the researchers altered molecular packing and interfacial electronic coupling, thereby affecting charge extraction. Linker design can therefore influence both structural order and electronic transport across the interface.

Heteroatom and terminal-group design provide another route for molecular control. Ullah et al. investigated SAM molecules containing O, S, and Se heteroatoms [9]. Their results showed that heteroatom selection changes molecular energetics and interaction strength with the perovskite absorber. The Se-containing SAM showed stronger interaction with the perovskite, reduced interfacial defect density, and improved carrier lifetime. However, this strategy also has limitations. Stronger interaction is not automatically better if it compromises molecular solubility, assembly uniformity, or compatibility with the perovskite precursor. Heteroatom engineering should therefore be evaluated together with adsorption behaviour, film formation, and long-term stability.

These examples reveal a causal chain rather than a list of independent molecular features. The anchor determines attachment to the oxide; the linker influences orientation, packing, and electronic coupling; and the terminal unit affects dipole, wetting, and interaction with the perovskite. Improving one element can compromise another. A more conjugated linker may support charge transfer but reduce solubility, while a strongly interacting terminal group may disrupt packing or shift the energy levels unfavourably. SAM design, therefore, requires simultaneous control of adsorption, assembly, energetics, and interfacial chemistry.

2.2. Physicochemical Regulation at Buried Interfaces

A favourable molecular energy level does not guarantee a favourable interface. During deposition, surface energy, solution-state aggregation, adsorption kinetics, substrate treatment, coverage, and perovskite nucleation act together. Failure at any one stage can offset the benefit of an otherwise well-designed molecule. Buried-

interface engineering is therefore a coupled processing problem, not a single-parameter optimisation.

Surface wettability is especially important because the perovskite precursor solution must spread evenly across the SAM-coated substrate. If the surface is poorly matched to the precursor ink, the film may develop pinholes, uneven grains, or defective regions. Qu et al. reported self-assembled materials that form an ordered hydrophilic bilayer through enhanced π - π interactions [5]. This bilayer improved buried-interface passivation and supported high-quality large-area perovskite preparation. The study is important because it challenges the simple assumption that a more hydrophobic SAM is always better. In practice, the surface must balance moisture resistance with sufficient wettability for coating.

Coverage control is another central issue. Since a SAM is only one molecule thick, incomplete coverage can expose the underlying substrate, creating leakage pathways or recombination centres. Zhang et al. addressed this problem using a mixed-SAM strategy [6]. By combining MeO-2PACz with FC-3283, they improved coverage, reduced molecular aggregation, and strengthened interfacial bonding. This provides direct evidence for one of the main challenges in SAM-based devices: interface quality depends not only on molecular energy levels but also on whether molecules form a continuous, uniform layer. However, mixed SAMs also introduce new variables, such as component ratio, phase distribution, and reproducibility. Better coverage may therefore come at the cost of greater processing complexity.

Processing conditions can be just as important as molecular structure. Liu et al. showed that many carbazole-based SAMs are amphiphilic and can form micelles in alcoholic solvents [7]. These micelles hinder compact adsorption on ITO because the anchoring groups are less available for binding. By introducing a co-solvent strategy to disassemble the micelles, the researchers improved molecular adsorption and SAM packing. This finding adds an important processing dimension to SAM research. A well-designed molecule may fail not because its molecular structure is unsuitable, but because its solution-state structure, adsorption pathway, substrate pretreatment, or annealing condition prevents proper assembly.

At chemically complex interfaces, multifunctional passivation may be needed. Cao et al. used a Co-SAM-modified NiO_x interface to improve stable inverted PSCs [8]. Their strategy combined Me-4PACz with phosphorylcholine chloride, allowing simultaneous passivation of NiO_x surface defects and perovskite-side vacancies. This reduced leakage current, suppressed non-radiative recombination, and improved device stability. The work shows that the buried interface is not a simple physical boundary between two layers. It is a chemically active region where substrate defects, perovskite vacancies, molecular dipoles, residual stress, and precursor chemistry can interact.

The four strategies discussed here address different stages of the same formation process. Wetting controls whether the precursor coats the surface; solution structure controls whether anchoring groups are available; adsorption and substrate preparation determine coverage; and passivating additives influence the chemistry on both sides of the interface. This explains why apparently similar SAM molecules can give different results under different deposition protocols. Meaningful comparison, therefore, requires reporting the complete preparation conditions, not only the molecular structure and final device efficiency.

2.3. Degradation Mechanisms and Long-Term Stability

Stability can be separated into three stages. Assembly stability concerns whether molecules adsorb densely and remain ordered before perovskite deposition. Fabrication stability concerns whether that layer survives contact with polar precursor solvents and subsequent thermal treatment. Operational stability concerns chemical and structural changes under illumination, heat, humidity, and electrical bias. These stages overlap, but failure at an early stage cannot be diagnosed reliably from a later ageing test alone.

Assembly stability is controlled by adsorption strength, molecular packing, substrate surface chemistry, and solution-state behaviour. Liu et al. showed that micelle formation can prevent compact adsorption of carbazole-based SAMs [7]. This means that poor device performance may begin before the perovskite layer is deposited. If the SAM is already incomplete or disordered after assembly, the buried interface formed later is likely to contain exposed substrate sites, non-uniform wetting, and recombination centres.

Fabrication stability is especially critical because the buried interface can be damaged before the device begins its ageing test. Tang et al. directly addressed this problem by showing that strongly polar perovskite precursor solvents can desorb weakly anchored SAMs [3]. To reduce this problem, the authors used atomic-layer deposition to create a more stable hydroxyl-covered ITO surface and designed a trimethoxysilane-based SAM with strong tridentate anchoring. Their devices showed improved stability under damp-heat testing and maximum-power-point tracking. This study provides a clear example of weak anchoring and solvent-induced desorption as practical degradation challenges. In this case, better stability came not from energy-level tuning alone, but from stronger interfacial bonding.

Operational stability is linked to ion migration, interfacial reactions, and molecular rearrangement under working conditions. Perovskite materials contain mobile ionic species, such as halide vacancies and organic cation vacancies. Under heat, illumination, and electric field, these species can migrate toward interfaces and cause recombination, phase instability, or interfacial reactions. Wang et al. investigated ion–dipole interactions at buried interfaces modified with SAMs [10]. Their work suggests that SAM dipoles can influence not only work-function tuning, but also interfacial ionic interactions and defect passivation. This expands the role of SAMs from electronic regulators to possible ionic stabilisers.

The buried location of the interface makes these degradation pathways difficult to verify. Longer carrier lifetime, stronger photoluminescence, or slower device decay are consistent with a better interface, but they do not identify the underlying cause: retained SAM coverage, reduced ion accumulation, altered crystallisation, or another effect. Claims about operational mechanisms should therefore be distinguished from correlations in device performance. In operation, depth-sensitive measurements are needed to monitor molecular desorption, ion redistribution, and interfacial reactions.

2.4. SAMs in Tandem Solar Cells

The appeal of SAMs in tandem cells is straightforward: an ultrathin contact introduces little optical loss and can be tuned electronically [1] [2]. The more important issue, however, is that tandem architectures offer less tolerance to imperfect SAMs. A defect at the bottom interface affects not only one junction but the current balance and voltage of the complete stack.

Perovskite/silicon tandems commonly use textured or rough substrates, so a monolayer that is continuous on planar ITO may leave exposed regions on the actual device surface. Coating uniformity must also be maintained over larger areas, and the SAM must withstand subsequent solvent, vacuum, and thermal steps. These requirements turn coverage, anchoring, and process compatibility from optimisation variables into reliability constraints.

All-perovskite tandems add further chemical complexity. Their interconnecting layers and multiple absorbers create more opportunities for solvent damage, interfacial recombination, and ion redistribution. A SAM may assist energy alignment or passivation, but it must do so without interfering with the deposition or stability of neighbouring layers.

Tandem relevance should therefore be demonstrated rather than inferred from a small planar cell. Convincing validation requires conformal coverage on representative substrates, low optical loss, compatibility with the full process sequence, and stable operation of the complete tandem stack. These criteria are stricter than those used for a conventional small-area single-junction device.

3. Discussion and Future Perspectives

3.1. Key Contradictions and Limitations

The literature no longer supports evaluating SAMs solely by peak efficiency. Device performance emerges from the molecular structure, the state of the coating solution, adsorption on the substrate, perovskite deposition, and subsequent ageing. A change that improves one step can make another less reliable. The central problem is therefore not whether SAMs can produce efficient devices—they clearly can—but whether the same interface can be formed reproducibly and preserved during fabrication and operation.

Initial efficiency and long-term stability are not interchangeable. A SAM can reduce interfacial recombination in a fresh device, but it remains vulnerable to solvent-induced desorption or gradual molecular rearrangement. Tang et al. showed that damage may begin during perovskite deposition, before any formal ageing test starts [3]. Stability claims should therefore be supported by evidence that the monolayer itself survives processing, rather than inferred only from the final device lifetime.

Wettability presents a second trade-off. Hydrophobic surfaces may limit water uptake, but poor wetting of the precursor can produce incomplete coating and non-uniform crystallisation. The ordered hydrophilic bilayer reported by Qu et al. illustrates why the most water-repellent surface is not necessarily the best processing surface [5]. The relevant target is controlled wetting that supports film formation without sacrificing interfacial stability.

Multicomponent approaches create a similar tension. Mixed SAMs, Co-SAMs, and bilayers can improve coverage or passivate several defect types at once [5] [6] [8]. They also introduce composition, mixing, phase distribution, and deposition variables that must be controlled from batch to batch. A strategy that performs well in a small research cell may therefore be harder to reproduce at the module scale.

Characterisation remains a limiting factor. Most measurements probe the completed device indirectly, whereas the relevant molecular layer is buried beneath the absorber.

Photoluminescence, electrical response, and ageing curves can indicate that an interface has improved, but they rarely show which molecular change persisted during operation. Stronger mechanistic claims will require measurements that resolve chemical state, coverage, and ion accumulation at the buried interface under realistic bias, light, and temperature.

3.2. Future Directions for Tandem and Scalable Devices

The most immediate priority is to make anchoring robust under realistic processing. Stronger or multidentate anchors, controlled hydroxylation of oxide surfaces, and crosslinked assemblies may reduce desorption, but they should be assessed for side effects on packing, energetics, and charge transfer. A stronger bond is useful only if the resulting layer still forms uniformly and remains electronically selective.

Assembly should also be reported as a processing outcome rather than assumed from the molecular structure. Solution concentration, solvent composition, aggregation, substrate cleaning, adsorption time, rinsing, and annealing can all change the final layer. Future studies would be more comparable if they included direct evidence of coverage and thickness together with these preparation details.

A second priority is direct observation of the buried interface. Depth-resolved spectroscopy, cross-sectional microscopy, and operando methods under illumination and bias could distinguish retained molecular coverage from secondary effects such as altered perovskite crystallisation. The aim should be to identify what changes first, not merely to record when device efficiency declines.

Stability tests also need to reflect the intended application. Short tests on encapsulated, small planar cells provide limited evidence for tandem or module use. More informative protocols would combine maximum-power-point tracking with controlled heat, illumination, and humidity, while reporting device area, encapsulation, atmosphere, and failure criterion. Tests on textured substrates and complete tandem stacks are particularly important.

Finally, efficiency, reproducibility, and durability should be reported together. A high-performing SAM is more persuasive when its coverage is verified, its processing window is defined, and the efficiency distribution across multiple devices is narrow. Linking molecular design to these practical metrics would make it easier to distinguish a genuinely transferable interface strategy from a result that depends on a narrow laboratory procedure.

4. Conclusions

SAMs influence inverted perovskite solar cells through several connected routes. Molecular dipoles can adjust the substrate work function; functional groups can passivate defects; surface chemistry can alter nucleation and wetting; and compact coverage can limit direct contact with the underlying electrode. These effects are well supported across the studies reviewed here. By contrast, the proposed suppression of ion migration is plausible but still relies more heavily on indirect evidence [10].

The same literature also shows why record efficiency is an incomplete measure of progress. Weak anchoring can lead to desorption during precursor coating [3]; aggregation in solution can prevent compact adsorption [7]; and improved coverage or multifunctional passivation can require more complex formulations [6] [8]. Tandem devices amplify these concerns because the SAM must coat nonideal surfaces,

withstand additional processing, and remain optically and electrically compatible with the full stack.

The practical criterion is therefore the quality of the interface after fabrication and during operation. A useful SAM must form reproducibly, remain attached, support uniform perovskite growth, and retain selectivity under realistic stress. No single molecular descriptor captures all of these requirements.

Progress will depend on combining molecular design with process control and direct interface measurements. Robust anchoring, verified coverage, operando characterisation, comparable ageing protocols, and validation on large-area or tandem-relevant substrates are more informative than a further increase in small-area PCE alone. Meeting these requirements would move SAM research from demonstrating possibility toward establishing reliability.

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this article.

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