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Editorial

Stabilizing inverted perovskite solar cells by phosphonic acid-based molecules

Inverted p-i-n perovskite solar cells (PSCs) exhibit compatibility with flexible substrates, low-temperature processing, and reduced hysteresis compared to conventional n-i-p architectures [1,2]. However, their long-term operational stability under realistic conditions remains a major commercialization hurdle, including UV radiation (280–400 nm, ~5% of solar irradiance), high temperature (up to 85 °C in outdoor environment), and high humidity (relative humidity ≥ 85%). A critical degradation mechanism stems from the buried interface between the transparent conductive oxide (TCO) and perovskite layers, where weak interfacial bonding, parasitic reaction, and inefficient charge transport accelerate performance degradation [3].

Phosphonic acid (PA)-based self-assembled monolayers (PA-SAMs) have emerged as pivotal interfacial modifiers in inverted PSCs, distinguished by their dual-function mechanism of phosphonic acid groups (-$PO(OH)_2$) [4]. This enables them to form robust covalent bonds with TCO surfaces (*e.g.*, ITO/FTO) *via* mono-, bi-, or tridentate coordination, while coordinating with under-coordinated Pb^{2+} in the perovskite lattice. This dual interaction optimizes energy-level alignment, mitigates ion migration, suppresses parasitic reactions, and enhances interfacial adhesion. Beyond the chemical structure, the intrinsic physical properties of PA molecules, including intrinsic conductivity, molecular size, functional group position, play a crucial role in PSC performance by shaping the interfacial microenvironment and charge transport behavior at the TCO/PA-SAM/perovskite interface. Recent studies have leveraged this characteristic to develop PA-based strategies, addressing specific stability challenges [5–7].

Building on the PA-SAM dual-function, a bifunctional aromatic phosphonic acid molecule, [2-(9-ethyl-9*H*-carbazol-3-yl)ethyl]phosphonic acid (EtCz3EPA), was designed to reinforce interfacial bonding for addressing UV-induced degradation (Figs. 1a and b) [5]. The phosphonic acid group in EtCz3EPA undergoes deprotonation, forming -PO_3^{2-} groups that establish strong M-O-P bonds (M = In, Sn) with hydroxyl groups (-OH) on TCO surfaces. Furthermore, the nitrogen atom in the carbazole ring coordinates with Pb^{2+} in the perovskite lattice *via* Lewis acid-base interactions, which enhance the perovskite-coordinating capability of the PA-SAM. This interaction strengthens the perovskite/hole-transporting material (HTM)/TCO interface. When the HTM layer contained a high hole-extraction polymer with a mass ratio of P3HT:EtCz3EPA of 10:1, the inverted p-i-n devices initially achieved a PCE of 23.2% for small-area devices (0.08 cm^2) and retained high efficiency during outdoor testing (average irradiance of 850 W/m^2 and ambient temperatures of 25–35 °C). Notably, a champion minimodule with an aperture area of 10 cm^2 retained more than 16% of its initial PCE of 20.1% after 29 weeks of continuous outdoor operation, representing a 2.5-fold improvement compared to devices without EtCz3EPA. This work demonstrates that PA-SAMs can effectively mitigate UV-induced degradation by reinforcing the perovskite/HTM/TCO interface and suppressing defect formation.

While the dual functionality of PA-SAMs ensures robust interfacial bonding, their charge transport efficiency is still limited by molecular packing disorders caused by steric hindrance. In inverted PSCs, where charge transport occurs perpendicular to the substrate, long-range ordered molecular stacking and a face-on orientation are critical for minimizing series resistance and non-radiative recombination. Rational molecular design, aimed at optimizing the self-assembly capability of PA-SAMs (a derivative of their structure), can mitigate steric hindrance, promoting uniform self-assembly and optimal π-π stacking for efficient charge carrier migration. In 2025, Zhu *et al.* synthesized an axially symmetric (2-(pyren-2-yl)ethyl)phosphonic acid (pPy) as PA-SAM, which retains the dual functionality of -$PO(OH)_2$ groups while addressing packing inefficiencies [6]. The symmetric pyrene minimizes intermolecular steric repulsion, thereby promoting face-on π-π stacking on ITO substrates and enhancing the ordered self-assembly of the monolayer. This ordered stacking, combined with the inherent TCO-binding and perovskite coordination of PA-SAMs, results in superior charge transport properties. The pPy-based inverted PSCs achieved a champion PCE of 26.6% (certified at 26.08%). Furthermore, the devices retained 94% of their initial PCE after 3000 h of continuous simulated solar illumination following the ISOS-L-1I protocol, due to reduced defect density and improved perovskite crystallinity. This study highlights that optimizing the structural design of PA-SAMs to enhance their self-assembly while preserving their dual functionality represents a robust strategy for improving charge transport and stability.

Another critical challenge in the application of PA-SAM bonding is their potential reactivity with perovskites under photothermal stress, including high temperatures and UV radiation. Fei *et al.* demonstrated that approximately 30% of the molecules in conventional PA-SAMs (*e.g.*, 2PACz, EtCz3EPA) bind to TCOs *via* weak hydrogen bonds rather than covalent bonds (Fig. 1c), which fails to fully utilize the bonding potential of PA-SAMs [7]. These weakly anchored PA molecules can desorb during device operation, exposing reactive -$PO(OH)_2$ groups that trigger three detrimental reactions: iodide (I^-) oxidation to I_2, FA^+ decomposition into NH_4^+

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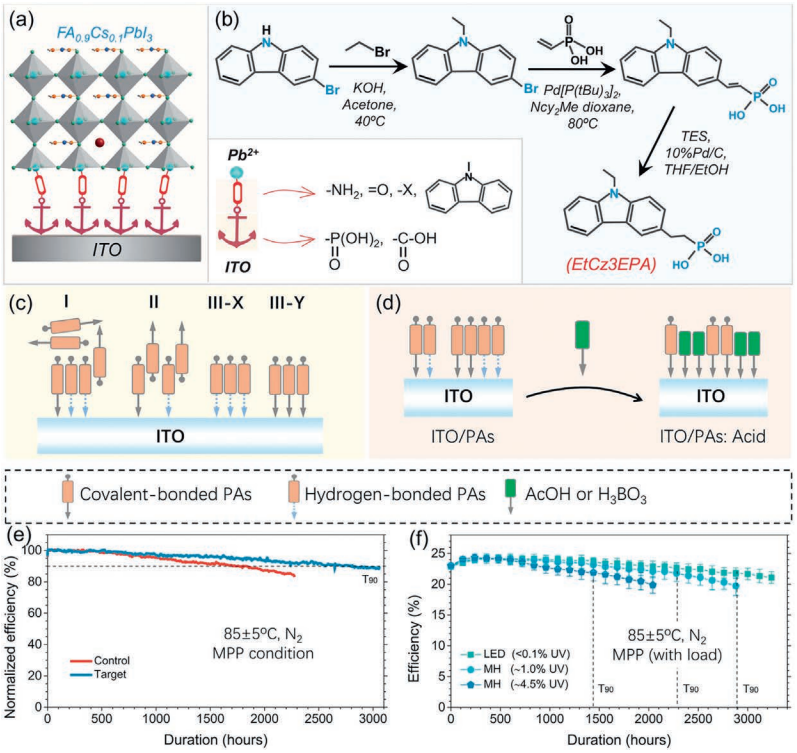


Fig. 1. (a) Schematic interfacial contact of perovskite, bifunctional molecular, and ITO substrate. (b) Synthesis route of EtCz3EPA. (c) Schematic illustration of different types of PA stacking modes on the ITO substrate. (d) Schematic of interfacial substitution of hydrogen-bonded PAs by acidic chemicals (AcOH or H_3BO_3). (e) Light-soaking stability of small-area devices (85 ± 5 °C) based on different HTM layers under the illumination of a MH lamp (100 mW/cm^2, 1.0 % UV). (f) Light-soaking stability of small-area devices (85 ± 5 °C) under different lamps. Copied with permission [7]. Copyright 2026, the Authors.

and HCN, and Pb^{2+} reduction to metallic Pb. These reactions are accelerated at elevated temperatures (≥85 °C) and under UV irradiation, emphasizing the need to optimize the covalent bonding efficiency of PA-SAMs, which is a key aspect of their functionality. To address this issue, a PA-SAM, (4-{4′-(diphenylamino)-(1,1′-biphenyl)-4-ylamino}benzyl)phosphonic acid (1PA-TPD), was designed to maximize the covalent bonding between PA groups and TCO substrates. The 1PA-TPD forms strong In-O bonds with ITO, reducing the fraction of weakly bound molecules to below 5 % (Fig. 1d). By optimizing a mixed PA-SAM system consisting of 60 wt% 1PA-TPD and 40 wt% EtCz3EPA, it is balanced that TCO binding strength (leveraging the enhanced covalent bonding of 1PA-TPD) and perovskite affinity (retaining the coordinating capability of EtCz3EPA) to synergize the dual functionality of both molecules (Fig. 1d). This mixed PA-SAM system achieves the modular integration of photothermal resilience and UV stability functions. It demonstrates the feasibility of designing multifunctional PA molecules by incorporating various functional modules onto a single molecular backbone. The inverted p-i-n devices achieved a PCE of 25.0 % and maintained 90 % of their initial efficiency (T_{90}) for nearly 3000 h under 85 °C full-spectrum illumination (including UV) (Figs. 1e and f). For minimodules with an aperture area of approximately 23.1 cm^2, the PCE exceeded 22 %, with a T_{90} of around 2200 h, setting a new benchmark for SAM-based module stability under harsh photothermal conditions. This study demonstrates that optimizing the covalent bonding efficiency of PA-SAMs while preserving their dual functionality effectively suppresses photothermal-induced reactivity, paving the way for high-temperature stable inverted PSCs.

In summary, the success of PA-based molecules in stabilizing inverted PSCs stems from the fundamental dual functionality of their -$PO(OH)_2$ groups, which enables covalent binding to TCOs and coordination with perovskites, coupled with their tunable structural and self-assembly properties and tailorable physical features (intrinsic conductivity, molecular size, functional group position). The strategies discussed target specific degradation pathways, EtCz3EPA for UV stability, pPy for charge transport, and 1PA-TPD for photothermal resilience. These three functional modules can be independently attached to the same PA molecular backbone to create a single multifunctional PA molecule. The trade-offs primarily involve balancing the degree of molecular conjugation, steric hindrance, UV-absorbing group content, and SAM packing density. These trade-offs can be effectively managed through precise structural regulation, such as introducing flexible alkyl linkers between the conjugated backbone and -$PO(OH)_2$ groups, and controlling the molar ratio of UV-absorbing groups. EtCz3EPA enhances interfacial bonding through direct utilization of its dual functionality, pPy optimizes molecular packing *via* structural tunability as a derivative, and 1PA-TPD strengthens covalent anchoring by refining TCO-binding capability. Thus, PA-SAMs serve as a versatile platform for interfacial engineering, addressing diverse stability challenges without compromising device efficiency. Notably, PA-based molecular strategies are highly compatible with industrial manufacturing. PA-SAM preparation is a non-vacuum, low-cost and easily scalable process, which can be directly integrated into existing R2R production lines. Solution coating methods enable uniform PA-SAM on large-area TCO substrates. In addition, PA-SAM does not alter the processing conditions of subsequent perovskite and HTL layers, and the PA-SAM with a thickness of ~1 nm can improve the uniformity of large-area perovskite films by passivating TCO surface defects. Future advancements in PA-based PSCs will likely focus on further optimizing these critical aspects, such as improving the uniformity of covalent bonding on rough TCO substrates, enhancing large-area self-assembly, and minimizing uncoordinated reactive groups, as well as the rational design and synthesis of single multifunctional PA molecules integrating UV stability, charge

transport and photothermal resilience, thus bringing inverted PSCs closer to commercialization.

CRediT authorship contribution statement

Wenbin Lai: Writing – original draft. **Jinrui Chang:** Writing – review & editing. **Gongqiang Li:** Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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