



Self-assembled monolayer meets all-perovskite tandem solar cells

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Perovskite-based tandem solar cells with configuration of perovskite/Si or perovskite/perovskite (all-perovskite) have gained increasing attention, owing to their potential for achieving high efficiency beyond the Shockley–Queisser limit of single-junction cells. All-perovskite tandem solar cells, consisting of a wide-bandgap (1.7 ~ 1.9 eV) top subcell and a low-bandgap (1.2 ~ 1.3 eV) bottom subcell, are promising for achieving high power conversion efficiency (PCE) and low fabrication cost.¹

However, wide-bandgap perovskite top subcells suffer from the crucial issues of open-circuit voltage (V_{oc}) and fill factor (FF) losses, which limit the

performance of all-perovskite tandem solar cells, particularly for large-area devices. The main reasons of the considerable V_{oc} loss were ascribed to low photoluminescence quantum yields of absorber itself, energy level misalignment, and phase segregation.² In addition, film-formation quality, charge transport ability, and nonradiative interface recombination are key factors to modulate the FF values. Consequently, developing charge selective layers to synergistically modulate the surface morphology, energy level alignment as well as charge transport/collection capabilities for high-performance perovskite solar cells are highly desirable yet challenging.

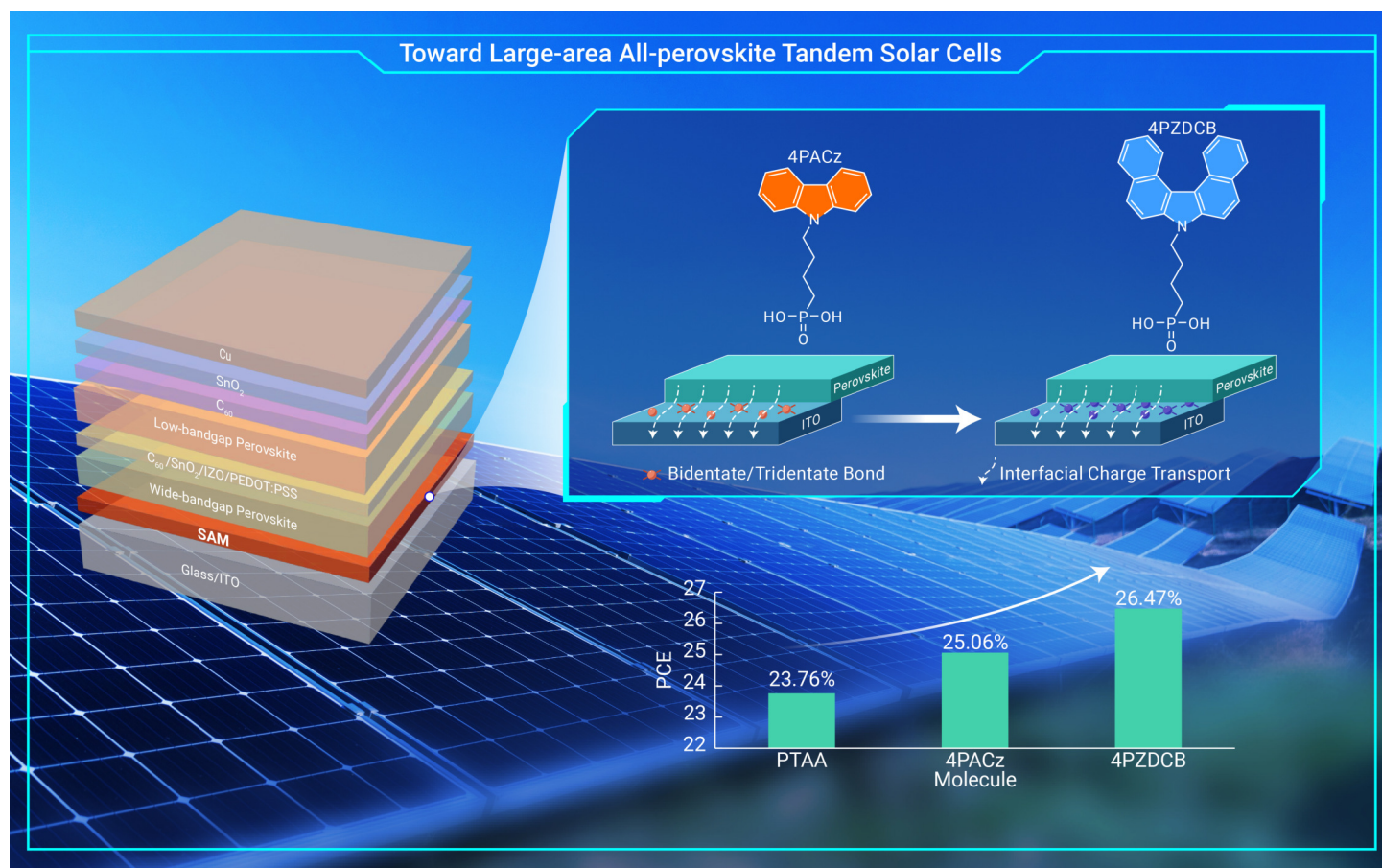


Figure 1. Development of hole interfacial layer for perovskite solar cells with a tandem structure

SELF-ASSEMBLED MONOLAYER

Phosphonic acid-based molecules possess the unique property of forming bidentate/tridentate bonds on the oxide surface. Moreover, SAMs typically acted as the chemically robust interlayers, which are inert to structural damage or ion accumulation. In 2018, Getautis et al. reported an efficient perovskite-based solar cell with a PCE of 17.8% and an FF close to 80% by using a newly developed hole-transport material (HTM) featuring a phosphonic acid anchoring group to form self-assembled monolayer (SAM) as the

dopant-free hole-selective contact.³ Since then, SAMs have become an appealing choice for efficient perovskite tandem devices due to their merits of fast extraction and efficient passivation at hole-selective contacts. The good film uniformity and well-matched energy levels at the interface of SAM/perovskite are indispensable for efficient hole extraction, which can be manipulated by molecular modification. For instance, it is known that regulating the type of the terminal substitution group in SAM is an effective way to control energy alignment with the perovskite valence band edge and thus

affect the charge extraction rate.² Apart from modulating substitution groups, tailoring conjugation range of the HTMs is also an ingenious strategy for fast and efficient hole extraction.

Recently, Tang and Zhao's groups developed a novel SAM, i.e., (4-(7H-dibenzo[c,g]carbazol-7-yl)butyl)phosphonic acid (4PADCB), for a wide-bandgap (1.77 eV) perovskite solar cell via replacing the carbazole group of the commercial 4PACz with the newly constructed terminal group of 7H-dibenzocarbazole (see Figure 1), which significantly improved the film coverage and surface wettability, enabling efficient hole extraction and suppressed interfacial non-radiative recombination.⁴ Compared with the previous reported SAM analogue (4PACz), the increased fused-phenyl groups of 4PADCB endowed the molecule with the more twisted conformation. On one hand, the terminal groups of 4PADCB played an important role in suppressing molecular aggregation due to the steric hindrance effect, leading to the more densely packed and homogeneous films. Consequently, the interfacial non-radiative recombination was significantly suppressed. On the other hand, the quasi-Fermi level splitting was manifested by photoluminescent quantum yield measurement to evidence the superiority of 4PADCB with the enhanced V_{OC} and FF. As schematically shown in Figure 1, a slightly extended conjugation induced by the fusing phenyl facilitated the more orderly π -stacking while the molecular orientation had a preference to be more parallel to the ITO substrate.

DEVICE APPLICATIONS

The impact of the extended fused ring conjugation on the electron density was proven by the electrostatic surface potential, which revealed that a relatively larger conjugated terminal of the HTM offered more interactions with perovskite materials, and promoted the interfacial charge transport. Besides, 4PADCB showed the better interfacial energy level alignment with perovskite absorber than 4PACz, determined by ultraviolet photoelectron spectroscopy. Due to these combined merits, the 4PADCB-based tandem device composed of a robust interconnection layer sandwiched between the wide- and low-bandgap perovskite solar subcells realized a certified PCE of 26.4% on an area of 1.044 cm² with a high V_{OC} (2.12 V) and an FF (82.6%), which demonstrated the most efficient all-perovskite tandem solar cells on 1 cm² scale and provided a solid approach to upscale perovskite photovoltaics. It is also worth noting that the operational lifetime T_{80} was 415 h, which was 1.6 times longer than that of the device with 4PACz.

CONCLUDING REMARKS

Based on molecular engineering, SAMs could alleviate the issue of poor conductivity of the conventional hole extraction layer with the nearly inevitable film inhomogeneity resulted from molecular aggregation due to the planar and π -conjugated groups. Introducing the appropriate SAMs provides an effective approach to facilitate the growth of wide-bandgap perovskite and accelerate hole extraction. Benefiting from the unique advantages of high PCE and low cost, all-perovskite tandem solar cells exhibit a great potential for the practical application.

Undoubtedly, as for the design of hole-selective molecule, it is essential to deliberately tailor molecular conjugation and substitution groups to synergistically manipulate molecular packing mode, energy level alignment, film-formation ability, and charge carrier transport/collection. In addition to molecular design, the device configuration should be elaboratively optimized, which dominates the growth and quality of perovskite films. From the perspective of mass production, inkjet printing technique as well as large-scale roll-to-roll manufacturing are promising to construct flexible and large-area all-perovskite tandem solar cells based on the SAMs. Further development of the versatile SAMs as well as process engineering, e.g., post-annealing strategies with high reproducibility,⁵ and management of optical transmission, would meet the requirements of the commercialization of the state-of-the-art perovskite photovoltaic technology.

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DECLARATION OF INTERESTS

The authors declare no competing interests.