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Efficient and stable industrial-size perovskite/silicon tandems with long-span bisphosphonic self-assembled molecules

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1 **Abstract:** With the blessing of self-assembled molecules (SAMs), the power
2 conversion efficiency (PCE) of perovskite/silicon tandem solar cells (TSC) ($\sim 1\text{ cm}^2$)
3 has exceeded the Shockley-Queisser limit. However, achieving uniform SAM
4 deposition on industrial-scale textured silicon remains challenging. At present, mono-
5 phosphonic SAMs fail to fully cover the silicon pyramid, whereas polymeric SAMs are
6 prone to aggregation, resulting in inhomogeneous film formation. To overcome this,
7 we designed a long-span bisphosphonic SAM (**S2**) featuring an extended π -conjugated
8 framework and flexible C-C bonds that enable conformal coverage over industrial-size-
9 pyramid-textured silicon surfaces. Furthermore, its bisphosphonic anchors provide
10 stronger interfacial bonding to across the pyramid-tips and ridges, while a higher dipole
11 moment further enhances charge transport and energy-level alignment. S2-based lab-
12 scale TSCs deliver 34.3% efficiency (0.98 cm^2 , certified 33.8%) and a certified 32.6%
13 for 210 mm-half wafer TSC (196.97 cm^2). Encapsulated large-size TSCs retain 91%
14 and 93% of initial efficiency after 1000 h damp heat and 200 thermal cycles,
15 respectively. A four-subcell integrated module maintains $\sim 95\%$ of its initial power after
16 one month of outdoor operation.

1 Thanks to the fast hole transport capability and low parasitic absorption, self-assembled
2 molecules (SAMs) can greatly reduce energy loss at the interface of perovskite
3 (PVK)/silicon tandem solar cells (TSCs), which have demonstrated great potential for
4 breaking the Shockley-Queisser limit in small-area ($\sim 1 \text{ cm}^2$) PVK/silicon TSCs¹⁻⁶.
5 Nevertheless, conventional monophosphonic SAMs face severe challenges when
6 extended to industrial-scale TSC fabrication^{7,8}. On textured silicon with $\sim 1 \text{ }\mu\text{m}$ range
7 of pyramid features, conventional SAMs only possess single-site anchoring capability
8 due to its monophosphonic group, while their limited molecular span makes it difficult
9 to bridge adjacent facets across the pyramid tips and ridges, resulting in discontinuous
10 coverage. Moreover, their small molecular volume further hinders the construction of
11 dense, uniform interfacial films on pyramid-textured silicon^{9,10}.

12 To address these challenges, previous studies have primarily focused on three
13 strategies: (i) improving substrate wettability via the introduction of co-deposited
14 molecules that suppress molecular aggregation, such as carboxylic acid derivatives (e.g.,
15 3-MPA)^{8,11}; (ii) designing asymmetric molecular architectures to strengthen interfacial
16 dipoles and promote charge transport, such as asymmetrically functionalized
17 phenoxazine- or carbazole-based SAMs^{12,13}; and (iii) developing bisphosphonic and
18 triphosphonic SAMs to enhance interfacial bonding strength, such as multipodal
19 anchoring molecules^{14,15}. However, these existing designs still suffer from fundamental
20 drawbacks. Most reported multi-phosphonic SAMs lack sufficient molecular span to
21 fully cover the sharp pyramid tips and ridges of textured silicon. Although polymeric
22 SAMs can realize large-area surface coverage, they are prone to severe molecular
23 aggregation, and in-situ polymerization fails to optimize surface bonding
24 configurations either as the monophosphonic SAMs^{16,17}. To date, no available SAM
25 system can achieve fully continuous and uniform coverage on industrial-scale textured
26 silicon substrates, which has become a critical bottleneck restricting the
27 commercialization of high-efficiency TSCs.

28 Herein, we rationally designed a long-span bisphosphonic SAM **S2** that achieves
29 truly conformal coverage on industrial-scale textured silicon. The extended π -
30 conjugated framework increases molecular span, while flexible C-C bonds act as
31 molecular hinges, enabling the SAM molecules to fully span and cover the pyramid tips
32 and ridges. Meanwhile, sp^3 -hybridized gem-dimethyl moieties suppress molecular
33 aggregation. Collectively, these design features ensure highly uniform SAM coverage

across textured surfaces. Moreover, the extended conjugation imparts outstanding thermal stability and charge transport capability, while the bisphosphonic anchors enhance interfacial bonding strength and provide a higher dipole moment for optimized energy-level alignment. Benefiting from this molecular design, highly uniform SAM coverage can be realized on industrially sized textured silicon substrates, accompanied by simultaneous improvements in charge transport, energy level alignment and thermal stability. By integrating **S2**, we obtain a lab-scale TSC with a power conversion efficiency (PCE) of 34.3% (certified 33.8%, 0.98 cm²) and a certified 32.6% @196.97 cm² for 210 mm-half wafer TSC, which is the highest PCE for industrial-size PVK/silicon TSCs (Supplementary Table 6). Moreover, the **S2**-based devices exhibit outstanding resilience under photo-thermal, damp-heat, thermal cycling, and outdoor conditions, underscoring the critical role of interfacial anchoring and energy-level alignment in facilitating the translation from lab-scale cells to industrial-grade tandem modules.

Design of SAM

Conventional benchmark SAM, i.e., Me-4PACz, fails to form high-quality molecular layers on large-area pyramid-textured crystalline silicon. Guided by density functional theory (DFT) screening, we first adopted a π -extension strategy and further replaced carbazole with indeno[2,1-b]carbazole to break molecular symmetry and enhance its dipole moment (Fig. 1a and Supplementary Figs. 1-2), yielding the asymmetric **SC** molecule (Fig. 1b)¹⁸. Nevertheless, molecular dynamics (MD) simulations reveal that both Me-4PACz and asymmetric **SC** suffer from severe film inhomogeneity and abundant interfacial voids, failing to satisfy large-area device requirements (Fig. 1c). To further enlarge molecular span, we introduced flexible fluorene units as π -bridges to connect two asymmetric **SC** fragments and constructed a bisphosphonic-anchored SAM of **S2** (Supplementary Fig. 2 Step2). The synthetic details of **S2** are provided in Supplementary Note 1, Supplementary Scheme 1, and Supplementary Figs 3-9. The optimized molecular span of **S2** exceeds that of most previously reported SAM molecules, making it possible to cover the pyramid tips and ridges of textured silicon to achieve conformational coverage. MD simulations validate that **S2** dynamically preserves a high spatial span and dense uniform arrangement in the assembled state (Fig. 1c).

To clarify the physical origin of its superior film-forming performance, we systematically investigated the intermolecular topological structures and noncovalent

interactions of **S2**, and the conventional benchmark Me-4PACz, alongside molecule **SC** which bears solely the indeno[2,1-*b*]carbazole terminal group without further π -extension, was introduced as references (Supplementary Fig. 10). Hirshfeld independent gradient model (IGMH) and reduced density gradient (RDG) analyses demonstrate that molecular stretching significantly expands intermolecular interaction regions (Supplementary Fig. 11)^{19,20}. **S2** possesses the largest interaction domain, strongest intermolecular coupling, and shortest intermolecular distance, which collectively facilitate dense film packing. Notably, despite enhanced intermolecular interactions, MD simulations indicate that **S2** effectively suppresses molecular aggregation compared with rigid analogs (Supplementary Note 2 and Supplementary Figs. 12-13). This unique behavior originates from the steric hindrance of gem-dimethyl substituents on the fluorene backbone, together with the conformational flexibility of side alkyl chains and C-C linkages.

Characterization of SAMs

To quantitatively evaluate surface coverage and anchoring stability, X-ray photoelectron spectroscopy (XPS) was performed and a semi-quantitative analysis of the coverage factor was conducted by examining the P 2*p* to In 3*d*_{3/2} peak area ratio (Supplementary Fig. 14 and Supplementary Table 1). XPS analysis (Fig. 1d) showed that **S2** retains 86% of its signal after three washing cycles, which outperformed **SC** (67%) and Me-4PACz (62%). Notably, the post-washing P/In ratio of **S2** even exceeds the initial ratios of both references, confirming its superior resistance to desorption¹². DFT calculations further confirmed this robust binding, revealing a higher adsorption energy for **S2** (-1.67 eV) compared to **SC** (-0.89 eV) and Me-4PACz (-0.81 eV) on the indium tin oxide (ITO) substrate (Supplementary Fig. 15). To bridge this microscopic stability with nanoscale morphology, atomic force microscopy-infrared spectroscopy (AFM-IR) was deployed to visualize the SAM distribution on textured substrates (Fig. 1e)^{21,22}. The Me-4PACz-coated substrate exhibits pronounced heterogeneity, characterized by bright clusters of aggregation and dark exposed ITO areas. **SC** shows modestly improved but still non-uniform coverage. In sharp contrast, **S2** displays a remarkably homogeneous signal distribution across the entire scanned area, experimentally verifying a truly conformal, aggregation-suppressed interfacial template.

To elucidate the molecular packing behavior of **S2**, grazing-incidence wide-angle X-ray scattering (GIWAXS) was performed on SAM-coated ITO substrates using identical conditions as device fabrication (Fig. 1f). Me-4PACz exhibits a diffraction spot at $q_z = 0.22 \text{ \AA}^{-1}$ without higher-order reflections, whereas **SC** shows out-of-plane diffraction with arcs. In contrast, **S2** displays intense diffraction spots at $q_z = 0.22 \text{ \AA}^{-1}$ and $0.35 \text{ \AA}^{-1}$ (Supplementary Fig. 16), indicative of long-range molecular periodicity^{23,24}. The substantially stronger and higher-order reflections of **S2** reveal markedly enhanced intermolecular packing order. This progressive ordering, driven by the expanded conjugated framework, accounts for the dense and uniform coverage corroborated by XPS and MD simulations. The conductive atomic force microscopy results further confirmed that **S2** demonstrates the highest conductivity, with an average current of 72.3 nA, versus 54.7 nA for Me-4PACz and 62.5 nA for **SC** (Supplementary Fig. 17), respectively. This superior conductivity arises from the dense molecular packing enabled by the long-span configuration, which facilitates efficient intermolecular charge transfer^{25,26}.

To evaluate the operational endurance of the modifying layers, the intrinsic electrochemical and thermal stabilities of the SAMs were characterized. Long-term cyclic voltammetry (CV) over 50 cycles (Figs. 2a-c) reveals that Me-4PACz exhibits a gradual decline in redox peak current starting from the 10th cycle, indicating a progressive electrochemical degradation¹². **SC** shows an initial decrease followed by an anomalous increase, suggesting complex degradation pathways or side reactions. In sharp contrast, **S2** maintains a nearly constant peak current throughout all 50 cycles, demonstrating exceptional electrochemical robustness. Furthermore, thermogravimetric analysis (TGA) was utilized to quantify thermal endurance under elevated regimes (Supplementary Fig. 18). **S2** delivers an outstanding decomposition temperature (T_d , 5% weight loss) of 398 °C, ensuring exceptional stability under the practical operating conditions of the devices (~100 °C). MD simulations were further performed to track the structural evolution of SAM under thermal stress (Supplementary Fig. 19). Our results reveal that the indenocarbazole terminal group in **S2** exhibits a dramatically larger thermally-driven torsion angle variation within the 300-420 K range (average $\Delta\alpha = 44.7^\circ$) compared to the reported phenyl-based systems ($\Delta\alpha = 19.0^\circ$)²⁷. The superior dynamic conformational adaptability enables **S2** to function as a highly efficient “molecular buffer” to accommodate and release the

residual strain at the PVK/SAM interface, which is beneficial to prevent molecular aggregation and enhance the long-term durability of devices.

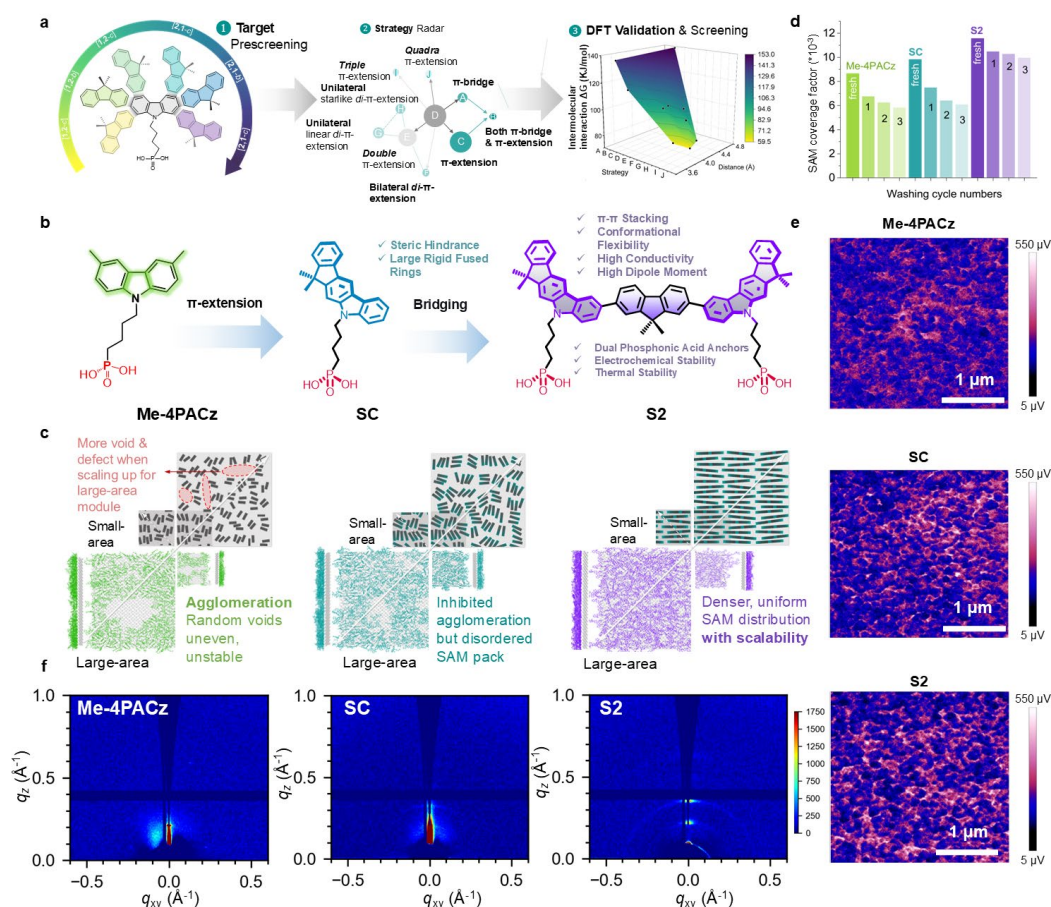


Fig. 1. Designing and characterization of long-span bisphosphonic SAM. (a) DFT-driven screening workflow for identifying optimal SAM building blocks and design strategies that maximize intermolecular π - π interactions and minimize aggregation. (b) Chemical structures of Me-4PACz, SC, and S2. (c) MD-simulated substrate coverage images (top-view and side-view) of Me-4PACz, SC, and S2. (d) XPS-derived coverage factors (P 2p to In 3d peak area ratio) for as-deposited and ethanol-washed SAMs. (e) AFM-IR characterization of SAMs on ITO substrates. (f) GIWAXS profiles of different SAMs on ITO substrates. All SAMs were deposited from 0.5 mg mL⁻¹ ethanol solutions via spin-coating followed by annealing.

To gain deeper insights to the interfacial electronic structure, theoretical calculations and ultraviolet photoelectron spectroscopy (UPS) were conducted. DFT calculations reveal that S2 possesses a significantly higher dipole moment (3.34 D) compared to SC (1.79 D) and Me-4PACz (1.21 D) (Supplementary Fig.20). Benefiting from the highly ordered perpendicular orientations proved by GIWAXS, such a large molecular dipole can effectively align at the interface, thereby playing a vital role in modulating the

1 interfacial electric field to suppress charge recombination and facilitate efficient hole
2 extraction^{28,29}. Three-dimensional differential charge density profiles and adsorption
3 energies between SAMs and perovskite corroborate this interfacial electronic coupling,
4 providing atomistic evidence for the enhanced interaction (Supplementary Fig. 21). In
5 contrast to the localized and confined regions observed in Me-4PACz/PVK and
6 SC/PVK, **S2**/PVK interface delivers intensified and prominent polarization clusters at
7 the symmetrical conjugated termini of SAM, yielding a higher adsorption energy of -
8 0.14 eV. Consequently, this alignment of dipoles and enhanced interaction between **S2**
9 and perovskite manifest construct an idealized energetic corridor for hole-extraction.
10 As shown in Fig. 2d and Supplementary Figs. 22-25, a substantial vacuum level shift
11 in the UPS yields a lowered work function for **S2** (4.52 eV vs. 4.80 eV for Me-4PACz
12 and 4.85 eV for SC, respectively) alongside a shallower valence band maximum (VBM)
13 of -5.37 eV (vs. -5.42 eV for Me-4PACz and -5.53 eV for SC, respectively). This
14 experimentally observed energy level realignment is further corroborated by the highest
15 occupied molecular orbital (HOMO) level obtained by calculations (Supplementary
16 Fig. 26).

17 The conformal coverage enabled by the synergistic design, together with the high
18 thermal stability and idealized energetic alignment of **S2**, is expected to serve as an
19 optimal growth template and facilitate charge extraction by minimizing interfacial non-
20 radiative recombination. The photoluminescence quantum yield (PLQY) of perovskite
21 films on different SAMs was measured to evaluate interfacial non-radiative
22 recombination losses (Fig. 2e). The **S2**-based perovskite film exhibits a PLQY of 2.70%,
23 significantly higher than SC (0.97%) and Me-4PACz (0.54%) —nearly 5-fold higher
24 than the conventional SAM. The corresponding quasi-Fermi level splitting (QFLS)
25 values increase from 1.27 eV (Me-4PACz) and 1.28 eV (SC) to 1.31 eV for **S2**,
26 confirming the suppression of non-radiative recombination³⁰. Time-resolved
27 photoluminescence (TRPL) measurements (Fig. 2f) reveal a clear trend in charge carrier
28 dynamics. The reference perovskite film (no SAM) exhibits the fastest decay (532 ns).
29 Among SAM-modified samples, **S2** exhibits the longest carrier lifetime (943 ns),
30 compared to Me-4PACz (761 ns) and SC (725 ns). Steady-state PL measurements
31 (Supplementary Fig. 27) also show that **S2**-based perovskite films exhibit the highest
32 PL intensity. These optical measurements confirm the suppressed non-radiative
33 recombination of perovskite films deposited on **S2**³¹. Additionally, scanning electron

1 microscope (SEM) and X-ray diffraction results further establish the morphology and
2 structural origin of the alleviated non-radiative recombination. The perovskite film
3 deposited on **S2** exhibits a substantially enlarged average grain size and weaker PbI₂
4 signal (Supplementary Figs. 28-29).

5 PL mapping (Fig. 2g) tracked the active area after sequential deposition of
6 passivation layer, C₆₀, SnO_x, and indium zinc oxide (IZO) onto PVK/SAM stacks on
7 silicon bottom cells. Samples based on **S2** exhibited the highest PL intensity throughout
8 all processing steps, indicating the lowest non-radiative recombination loss at the
9 perovskite bottom interface, as well as the least degradation from subsequent layers.
10 Consistently, full devices incorporating **S2** showed superior performance, particularly
11 in open-circuit voltage (V_{OC}). This is reflected in the performance of single-junction
12 perovskite solar cells on n-i-n substrates (Figs. 2h, Supplementary Fig. 30 and
13 Supplementary Table 2). The current density-voltage ($J-V$) curves show that **S2**-based
14 devices achieve the highest PCE of 22.54% (reverse scan), versus 21.18% for **SC** and
15 20.72% for Me-4PACz. This gain primarily comes from improved V_{OC} (average of
16 ~1.27 V for **S2** versus ~1.24 V for Me-4PACz and ~1.25 V for **SC** (Supplementary
17 Fig. 31 and Supplementary Table 3), consistent with the reduced non-radiative
18 recombination and higher QFLS observed²⁹. Light-intensity-dependent V_{OC} test derived
19 from corresponding $J-V$ measurements on n-i-n devices were further carried out (Fig.
20 2i). The **S2**-based device exhibits a reduced ideality factor (n) of 1.59, compared to
21 those of **SC** (1.72) and Me-4PACz (1.90), which quantitatively substantiates the
22 suppressed trap-assisted recombination at the **S2**-templated buried interface.

23 Therefore, the extended π -conjugated skeleton increases the molecular span, while
24 endowing the molecule with excellent thermal stability and charge transfer ability. In
25 addition, the bisphosphonate anchoring groups enhance the interfacial bonding strength.
26 Under this combinational molecular design strategy, **S2** achieves the optimal balance
27 between favorable intermolecular coupling and suppression of excessive aggregation,
28 achieving excellent conformal coverage on industrial scale textured substrates while
29 improving charge transfer, energy level alignment, and thermal stability, and meeting
30 the strict interface requirements of high-performance TSC.

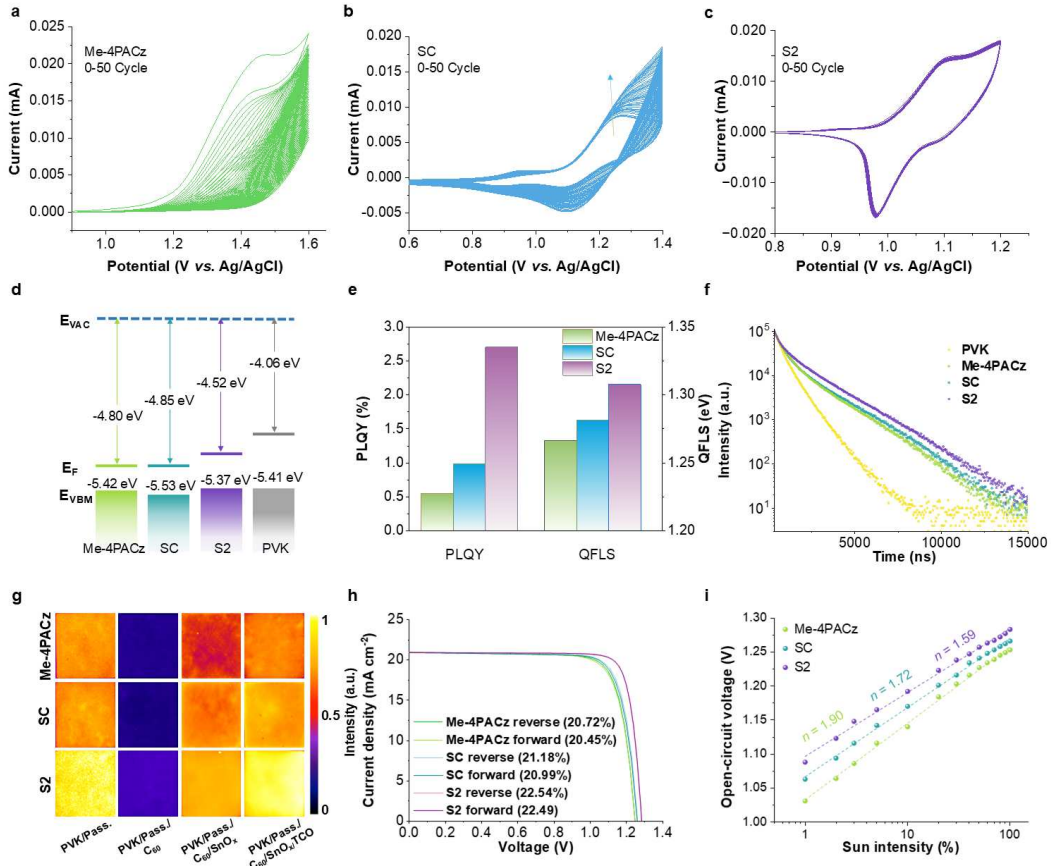


Fig. 2. Molecular stability and small size device performance of SAMs. Repeated CV trace (50 cycles) of (a) Me-4PACz, (b) SC, and (c) S2. (d) Energy level diagrams of ITO-SAMs and the perovskite film acquired via UPS tests. (e) PLQY/QFLS and (f) TRPL decay curves of different SAM-based perovskite films. The incident light was directed from the perovskite side. (g) PL mapping for different configuration of PVK/pass., PVK/pass./C₆₀, PVK/pass./C₆₀/SnO_x, and PVK/pass./C₆₀/SnO_x/TCO, the active area is around 10 mm×10 mm. (h) *J-V* curves and (i) light-intensity-dependent *V*_{OC} measurements of single-junction n-i-n devices.

Photovoltaic performances of tandems

Different SAM materials were utilized as hole selective layers in the integration of both lab-scale and wafer-size perovskite/crystalline silicon monolithic TSCs. The device structure (Fig. 3a) was based on a double-side textured silicon heterojunction bottom cell (Supplementary Fig. 32), employing a thin ITO layer as the recombination layer. Subsequently, SAM/PVK/C₆₀/SnO_x/TCO/Ag/MgF_x layers were sequentially deposited. Cross-sectional SEM images (Figs. 3b, 3c) show uniform perovskite coverage on textured pyramids, with slot-die-coated films being thicker than spin-coated ones. The in-house measured *J-V* curves for lab-scale champion TSCs based on different SAMs

1 under AM1.5G illumination were shown in Fig. 3d, the **S2**-bearing devices achieved a
2 champion efficiency of 34.29% under reverse scan ($J_{SC} = 20.30 \text{ mA cm}^{-2}$, $V_{OC} = 1.994$
3 V, FF = 84.71%; stabilized efficiency of 34.29%, Supplementary Table 4 and
4 Supplementary Fig. 33), with substantially higher V_{OC} and FF than other groups,
5 attributed to improved energy level alignment and suppressed interfacial nonradiative
6 recombination resulted from the conformal coverage by **S2**. Certified by Shanghai
7 Institute of Microsystem and Information Technology (SIMIT), the device delivered a
8 reverse-scan efficiency of 34.13% and a stabilized efficiency of 33.84%
9 (Supplementary Fig. 34), respectively. The integrated photogenerated current densities
10 according to the external quantum efficiency (EQE) spectrum of **S2**-based TSC (Fig.
11 3e) are determined to be 20.91 and 20.62 mA cm^{-2} for perovskite and silicon sub-cells,
12 respectively, corresponding well with the measured J_{SC} value under J - V scan.

13 **S2** was further incorporated into wafer-size TSCs based on 210 mm-half wafers
14 ($210 \times 105 \text{ mm}^2$) via slot-die coating. The champion device (active area of $\sim 197.5 \text{ cm}^2$)
15 delivered reverse-/forward-scan efficiencies of 32.81%/32.63%, respectively (Fig. 3f
16 and Supplementary Table 5), and a steady-state output of 32.79% over 5 min at the
17 maximum power point, substantially outperforming the Me-4PACz-based counterpart
18 (Supplementary Fig. 35). One **S2**-based tandem cell was sent to Fraunhofer ISE Callab
19 for independent certification, which confirmed a PCE of 32.6% (the corresponding
20 certified J - V curve and stabilized efficiency output are provided in Fig. 3g and
21 Supplementary Fig. 36). To the best of our knowledge, this result establishes the highest
22 efficiency for tandem solar cells on 210 mm-half wafer-size substrates (Supplementary
23 Table 6).

24 Fig. 3h presents the photoelectric parameter distributions of different SAMs applied
25 in lab-scale and wafer-size tandem solar cells, detailed parameters are provided in
26 Supplementary Table 7 and 8. **S2** yields consistently enhanced performance in terms of
27 V_{OC} and FF parameters for both large- and small-area devices compared to other
28 materials, along with better convergence, which is attributed to its stronger and more
29 uniform anchoring properties. As shown in Fig. 3i, to evaluate the uniformity across
30 large areas, the 210 mm-half TSC was uniformly diced into 32 individual small-area
31 cells for separate measurement (Photographs and schematic diagrams of the devices as
32 shown in Supplementary Fig. 37). The efficiencies of the **S2**-based small-area cells

were uniformly distributed between 31.12% and 32.07%, whereas those of the Me-4PACz-based cells ranged from 22.92% to 30.84%, with many devices suffering from poor integration between the top and bottom sub-cells. Benefiting from the synergistic effect of its large-area anchoring capability and hydrophilicity, the perovskite top cell based on **S2** exhibited excellent uniformity. The optical bandgaps and implied V_{OC} (iV_{OC}) across the active area, as determined by PL mapping spectrum (Figs. 3j-k and Supplementary Fig. 38), fall within narrow ranges of 1.68-1.69 eV and 1.27-1.28 V, respectively.

Furthermore, photo-thermal stability of encapsulated TSCs using different group of SAMs were compared, seen in Fig. 4a, following the ISOS-L-2 protocol, under 1-sun illumination (Supplementary Fig. 39) and 65 °C, the **S2**-based lab-scale TSC showed outstanding stability, maintaining 92% of its initial efficiency after 1200 h of maximum power point tracking (MPP) tracking. Accelerated stress testing was also performed on encapsulated wafer-size TSCs in accordance with IEC 61215-2 standards, including damp heat and thermal cycling, respectively. Encapsulation resulted in a minor loss of absolute PCE of 1.5-2% for the TSCs. Encapsulated devices employing the **S2** material exhibited remarkable operational stability. Specifically, after 1000 hours of “double 85” aging (85 °C/ 85% relative humidity), the device retained 91.0% of its initial output (Fig. 4b). Similarly, a 93.5% retention rate was achieved after 200 thermal cycles (Fig. 4c). Outdoor operational stability was assessed by deploying the encapsulated series of four 210 mm-half TSCs in Changzhou, where it operated at its maximum power point while daily energy yield was monitored. Over one month of testing, the module maintained consistent energy yield under comparable irradiance conditions (Fig. 4d). Reverse and forward scan I - V curves of tandem modules before and after outdoor aging are shown in Fig. 4e. Maximum output powers decreased from 23.88/23.57 W to 23.03/22.63 W after aging, with a relative degradation of <5%. Collectively, these results confirm the excellent stability of tandem devices incorporating the **S2** material under accelerated photo-thermal aging, humidity, thermal stress, and real-world operating conditions.

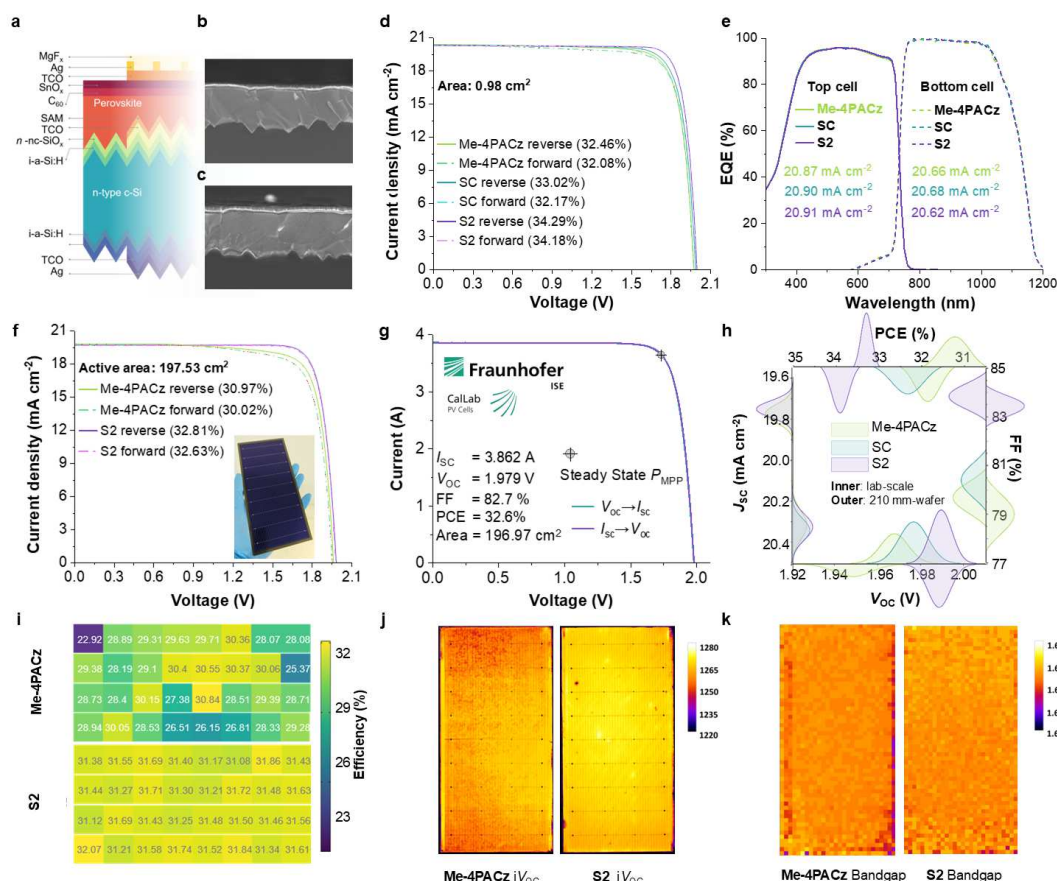
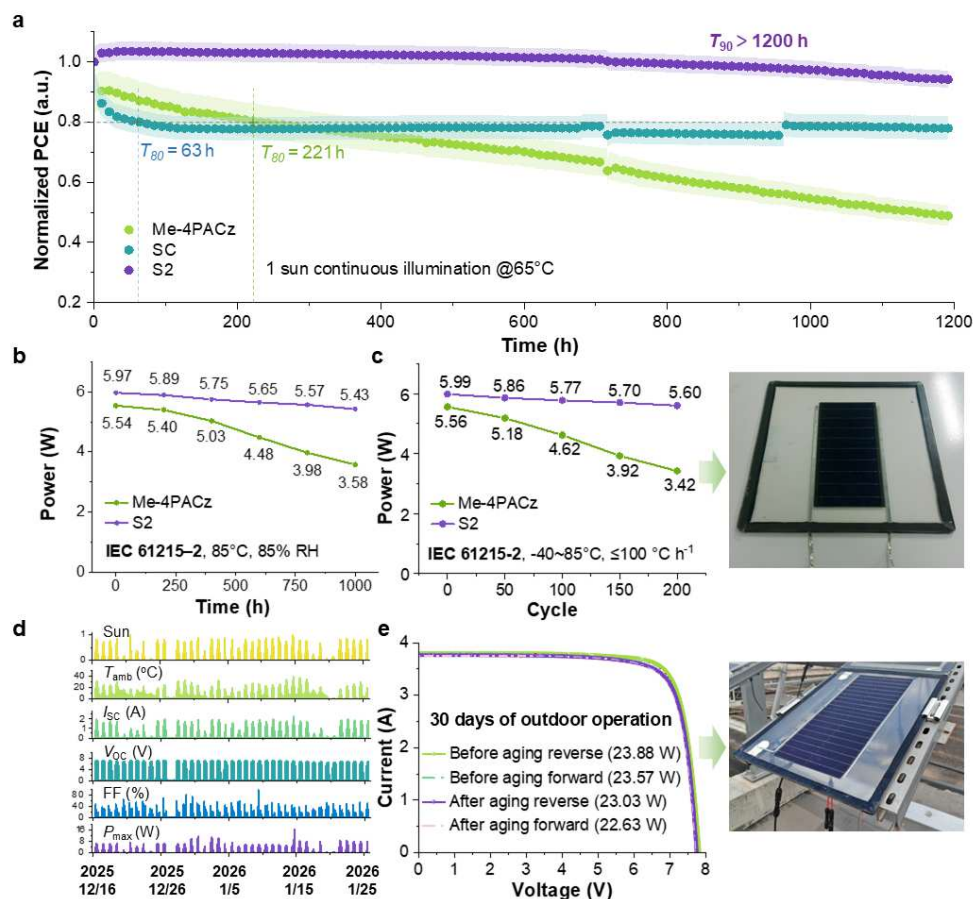


Fig. 3. Photovoltaic performance of S2-based PVK/silicon TSCs from lab-scale to industrial modules. (a) Schematic illustration of the TSC. Cross-sectional SEM images of the perovskite top cell in lab-scale (b) and wafer-size (c) TSCs, respectively. (d) In-house measured $J-V$ curves of lab-scale TSCs fabricated with different SAMs, the inset shows the photograph of the device. (e) EQE spectrum of the lab-scale TSCs based on different SAMs. (f) In-house measured $J-V$ curves of wafer-size TSCs with different SAMs. Right: corresponding photograph of the device. (g) $I-V$ and steady-state curves of the wafer-size TSC independently certified by Fraunhofer ISE Callab. (h) Statistical distribution of photovoltaic parameters for lab-scale and wafer-size TSCs. (i) Efficiency distribution within wafer-size TSCs fabricated with S2 and Me-4PACz SAMs, measured after dicing the wafer-size into individual lab-scale cells. (j) iV_{OC} and (k) bandgap mappings derived from photoluminescence spectrum of wafer-size TSCs.

Conclusions

Our findings reveal that the primary limitation of conventional SAMs in large-area tandems is their inability to simultaneously achieve conformal coverage and robust performance on textured surfaces. Small-molecule SAMs with monoposphonic even multi-phosphonic aggregate on micron-scale pyramids, leaving exposed substrate that creates shunting pathways. Polymerization of SAMs has been explored to address this

1 issue, which is prone to aggregation, resulting in uneven film formation. We rationally
 2 designed a long-span SAM featuring a synergistic strategy to resolve this dilemma: long
 3 span with extended conjugation enable to cross the pyramid tips and ridges on
 4 industrial-scale textured silicon and delivers dense packing and stability for the SAMs,
 5 while conformational flexibility with dual anchors ensures uniform spreading and
 6 robust binding. This design achieves certified efficiencies of 33.8% on a 0.98 cm² lab-
 7 scale cell and 32.6% on a 210 mm-half wafer TSC (196.97 cm²). Moreover, outstanding
 8 resilience under photo-thermal, damp-heat, thermal cycling, and outdoor conditions has
 9 been achieved, establishing molecular span engineering as a generalizable strategy for
 10 industrial-scale perovskite photovoltaics.



11

12 **Fig. 4. Stability evaluation of S2-based tandems.** (a) Operational stability of lab-scale
 13 TSCs with different SAMs under 1-sun illumination at 65 °C at the maximum power
 14 point. Damp-heat (b) and thermal-cycling (c) aging of encapsulated 210 mm-half
 15 wafer-size TSCs with different SAMs. Right: corresponding device photograph. (d)
 16 Evolution of photovoltaic parameters of a four-subcell integrated tandem module
 17 during one month of outdoor operation. (e) Comparison of J - V curves before and after
 18 outdoor aging. Right: corresponding device photograph.

1 **Methods**

2 **Materials**

3 The reagents and starting materials are commercially available and can be used without
4 further purification. Cesium iodide (CsI), methylammonium bromide (MABr), lead
5 iodide (PbI₂, 99.99%), formamidinium iodide (FAI, 99%), methylammonium chloride
6 (MACl, 99.9%), 1,3-diaminopropane dihydroiodide (PDAI₂), and RbSCN were
7 purchased from Suzhou LiWei Tech Co., Ltd. (China). Lead bromide (PbBr₂) was
8 obtained from Tokyo Chemical Industry (TCI). C₆₀ and bathocuproine (BCP) (99.9%)
9 were procured from Xian p-OLED (China). All solvents used in the experiments,
10 including methanol, isopropanol (IPA, 99%), toluene (99.9% anhydrous), *N,N*-
11 dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.7%), and
12 chlorobenzene (CB, 99.8%), were acquired from Sigma-Aldrich.

13 **Fabrication of silicon bottom cell**

14 Pre-cleaning of Czochralski silicon wafers (resistivity: 1–3 Ω·cm, thickness: 300 μm)
15 was performed using a mixed solution of hydrogen peroxide (H₂O₂) and potassium
16 hydroxide (KOH), followed by polishing to remove surface damage. An alkaline
17 solution with additives is used to texture the wafers, forming a double-sided pyramidal
18 structure with a height of approximately 0.8 μm. RCA cleaning is then conducted to
19 eliminate residual additives and impurities.

20 A double-sided intrinsic amorphous silicon (i-a-Si:H) layer with a thickness of 7 nm
21 is deposited by PECVD at a temperature of 180 °C. Subsequently, a phosphorus-doped
22 microcrystalline silicon layer (n-μc-Si:H, 17 nm, doped concentration of 2×10²⁰ cm⁻³)
23 and a boron-doped microcrystalline silicon layer (p-μc-Si:H, 25 nm, doped
24 concentration of 5×10¹⁹ cm⁻³) is grown on the rear side and the front side via PECVD,
25 respectively. Then, a 100 nm of indium tin oxide (ITO) is patterned deposited on the
26 rear side by PVD method followed Ag deposition through screen-printing, and a 10 nm
27 of ITO layer is patterned deposited on the front side. For lab-scale tandem solar cells
28 (TSCs) fabrication, the silicon bottom cells are laser cut to 2.5×2.5 cm² substrate. The
29 resulting bottom-cell architecture is denoted as N-i-P. Replacing p-μc-Si:H with
30 PECVD-grown n-μc-Si:H, while keeping all other layers unchanged, yields the N-i-N
31 configuration.

32 **Lab-scale tandem fabrication**

The silicon bottom cell is treated with ultraviolet-visible (UV)/O₃ for 5 minutes to improve wettability and interface properties. Different self-assembled molecules (SAMs) are served and compared as hole transport layer, the concentration of SC, S2, and ME-4PACz precursor solution has been optimized to 0.5 mg mL⁻¹ in ethanol. After filtration, 70 μL of SAM precursor is spin-coated on Si bottom cell at 4000 rpm for 15 s in glovebox, followed by heat treatment at 100 °C for 10 min. For wide-bandgap perovskite layer deposition, 1.8 M of FA_{0.8}MA_{0.15}Cs_{0.05}Pb(I_{0.75}Br_{0.25})₃ precursor solution is prepared by dissolving 116.9 mg CsI, 151.2 mg MABr, 1238.2 mg FAI, 2904.4 mg PbI₂, and 991.0 mg PbBr₂ in mixed anhydrous solvent of DMF: DMSO (v:v = 4:1), the concentration of RbSCN as an additive is 1 mg mL⁻¹, the precursor is then stirred for 10 h and filtered via a 0.22 μm polytetrafluoroethylene membrane. A 100 μL of the perovskite precursor solution is spin-coated by a triple-step program in N₂ atmosphere: 600 rpm for 10 s, 2500 rpm for 50 s, and then 6000 rpm for 15 s. 300 μL of Chlorobenzene is dropped onto the substrate 12 s before the end of spin-coating procedure. Then, the substrate is immediately annealed at 120 °C for 10 min. For the interface passivation, a 1 mg mL⁻¹ of PDAI₂ in IPA is dynamically spin-coated onto the perovskite film at 4000 rpm for 15 s followed by thermal treatment at 100 °C for 5 min. Subsequently, 10 nm C₆₀ is thermally evaporated at 0.1 Å s⁻¹. Then, 15 nm SnO_x buffer layer is prepared at 90 °C by atomic-layer deposition using tetrakis(dimethylamino)tin(IV) (99.9%, Jiangxi Jiayin Optoelectronic Material Co., Ltd) and water as precursors. A 40-nm-thick indium zinc oxide (IZO) layer (sheet resistance ≈140 Ω/sq) is patterned sputtered by radio-frequency magnetron sputtering method via an IZO target (Enam Optoelectronic Material Co., Ltd. In₂O₃: ZnO = 90: 10 wt%). Finally, a 500-nm-thick Ag metal electrode and a 110-nm-thick MgFx anti-reflection layer are sequentially deposited using customized mask by thermal evaporation. The active area is determined to be ~0.98 cm².

210 mm-half tandem fabrication

The fabrication process of 210 mm-half TSCs is similar to lab-scale TSCs, the Si bottom cells (210 × 105 mm²) are first UV-ozone cleaned for 15 min. For the SAM deposition, SAM solution (0.5 mg/mL in IPA) is slot-die coated onto the substrate with coating speed of 15 mm s⁻¹ followed by annealing at 100 °C for 10 min (Manst, tandem-2024). For the perovskite layer, the same precursor composition is applied, while the solvent is changed to a mixture of DMF and NMP in a volume ratio of 6: 1, and the

1 concentration is adjusted to 2 M. Slot-die coating (Manst, tandem-2024) was performed
2 in ambient air (RH of 10-20% (RH) and temperature of 20-25 °C) at a substrate speed
3 of 15 mm s⁻¹ and an ink flow rate of 20 µL s⁻¹, followed by nitrogen knife blow-drying
4 and annealing at 120 °C for 20 min. For the interface passivation, 1 nm of PDAI₂ is
5 deposited via thermal evaporation at 0.1 Å s⁻¹. The deposition processes for the C₆₀ and
6 SnO_x buffer layer are identical to those established for the lab-scale TSCs. For the
7 metallization, silver grid electrodes are patterned screen-printed with 9 busbars (width:
8 60 µm) and 38 finger lines (width: 30 µm) followed by sintering at 120 °C for 10 min.
9 Finally, 120 nm of MgF_x layer is deposited via thermal evaporation. Through patterning,
10 the active area is determined to be ~197.53 cm².

11 **Characterizations**

12 The surface morphology of the perovskite films was characterized using a Hitachi S-
13 4800 field-emission scanning electron microscope (SEM). Photoluminescence (PL)
14 mapping was performed on a Lumikon Max system (Open Instrument) with excitation
15 wavelength of 445 and 915 nm for top and bottom subcell, respectively. According to
16 the simplified Planck's law^{32,33}, the photoluminescence (PL) signal at each pixel was
17 calibrated to yield the absolute implied open-circuit voltage (*iV*_{OC}) signal. Steady-state
18 photoluminescence quantum yield (PLQY) was measured using an Ocean Optics
19 system with an excitation wavelength of 450 nm for the perovskite layer. A perovskite
20 solar cell was used to calibrate the laser intensity to 1-sun equivalent, ensuring the
21 current density at 0 V matched the short-circuit current density (*J*_{SC}) measured under
22 standard solar simulator conditions. Current density-voltage (*J-V*) characteristics and
23 Suns-*V*_{OC} tests were measured using a Keithley 2400 semiconductor parameter analyzer
24 and a Wavelabs LED-based solar simulator under simulated AM1.5G illumination at
25 100 mW cm⁻². The spectral output of the solar simulator was calibrated with a
26 spectrometer to determine the spectral mismatch factor³⁴, which was maintained
27 between 0.99 and 1.01 for both top and bottom subcells. All devices were scanned at a
28 step size of 0.02 V with a dwell time of 30 ms in both forward and reverse directions.
29 External quantum efficiency (EQE) spectra were acquired using QE system (EnliTech)
30 with monochromatic light focused on the active area of devices, EQE was measured
31 individually for each subcell, to maintain short-circuit conditions, the perovskite subcell
32 was saturated under 850 nm NIR LED illumination with a 0.7 V bias, while the silicon
33 subcell was saturated under 450 nm blue LED illumination with 0 V bias.

Stability tests

For outdoor test, the encapsulated modules were installed outdoors on fixed racks in Changzhou, China, oriented due south with a tilt angle of 23°. Real-time power generation was monitored via APsystems micro-inverters with maximum power point tracking (MPPT). In-situ solar irradiance and ambient temperature were recorded synchronously using a micro-meteorological station. MPPT test was conducted under simulated 1 Sun illumination (AM1.5G, 100 mW cm⁻²) generated by a multi-color LED simulator. The measurements were performed in ambient air with a relative humidity of 30-50%, and the device temperature during operation was maintained at approximately 65 °C, the spectrum of the simulator was provided in the Supplementary Fig. 39. For thermal cycling (TC) and damp heat (DH) tests, encapsulated modules were subjected to aging testing according to IEC 61215-2 qualification standards in an environmental chamber. For TC tests, modules were cycled 200 times between -40 °C and 85 °C with a ramp rate ≤ 100 °C h⁻¹ and a dwell time of at least 10 min at each temperature extreme. For DH tests, modules were aged at 85 °C and 85% relative humidity for 1000 h. Module appearance and electrical performance were evaluated before and after aging to assess long-term stability under thermal-mechanical and humidity-related stress.

Density functional theory (DFT) calculations

The geometry optimization of all investigated single molecules was performed at the B3LYP/6-31G* level, without any symmetry constraints. The molecule stable dimers were pre-optimized by using the XTB 6.7.0 package to get rough dimeric structures, and then the rough dimers with the lowest energies were selected to be optimized to their potential energy minimum at B3LYP-D3(BJ)/6-31G* level by Gaussian 16. The dipole moment was calculated using the B3LYP/6-31G (d) functional and basis set optimized ground state geometry of the studied molecule in the Gaussian 09 program³⁵. The perovskite (FAPbI₃)/SAM interface system was optimized using the generalized gradient approximation (GGA) and Perdew Burke Ernzerhof (PBE) exchange correlation functions from the Vienna ab initio simulation program (VASP). A 3 × 3 × 2 FAPbI₃ perovskite crystal cell was constructed. The cutoff energy of the level surface wave is 400 eV. For *k*-point sampling, apply a 1 × 1 × 1 Monkhorst Pack grid in the irreducible Brillouin zone. Embed a 25 Å vacuum region on the outer surface of PbI₂ to avoid unnecessary interactions. In order to unify the initial configuration, we placed

each molecule horizontally at the same distance on the surface of the perovskite layer and aligned the O atom with the Pb atom below. The convergence threshold for self-consistent iteration is set at 1.0×10^{-4} eV/atom, with the atomic positions completely relaxed until the maximum force on each atom is less than $0.05 \text{ eV } \text{\AA}^{-1}$. Then perform non-self-consistent calculations and process the charge density file into charge difference density map, density of states (DOS) map, and electron local function (ELF) map, and obtain the adsorption energy.

The ITO surface model was constructed based on the cubic In_2O_3 bulk structure obtained from the Materials Project database. The (111) crystal plane was cleaved from the fully relaxed bulk structure, and one In atom in the topmost surface layer was substituted by a Sn atom to mimic the Sn-doped ITO substrate. A clean non-hydroxylated surface termination with exposed In and O atoms was adopted in all calculations. For molecular dynamics (MD) simulations, the surface model was expanded to a large supercell with a lateral size of $\sim 80 \text{ \AA} \times 80 \text{ \AA}$ to ensure sufficient simulation scale and avoid artificial periodic interference. Density functional theory (DFT) calculations, as implemented in VASP, were used to carry out geometric optimizations and electronic structure calculation. The projector augmented wave (PAW) method was adopted to describe the interaction between core electrons, atomic nuclei and valence electrons. The GGA with the PBE functional was employed to handle the exchange-correlation energy of electrons. To properly account for the long-range van der Waals (vdW) dispersion interactions that are insufficiently described by the standard PBE functional, the DFT-D3 empirical dispersion correction method developed by Grimme was applied throughout all structural relaxations and energy calculations. A high plane-wave cutoff energy of 600 eV was set for all calculations to ensure sufficient basis set accuracy. The Brillouin zone integration was performed via the Monkhorst-Pack scheme, and only the Gamma point was sampled for k -point mesh in consideration of the large supercell model. During structural relaxation, all atomic positions were fully optimized until the residual force on each atom was less than $0.02 \text{ eV } \text{\AA}^{-1}$, and the self-consistent field (SCF) convergence threshold for electronic iterations was set to 10^{-5} eV to guarantee the precision of electronic structure calculation results. Then, the binding energy was calculated to quantify the intrinsic bonding interaction and structural stability between different components of the composite system. The calculation formula is defined as follows: $E_{\text{bind}} = E_{\text{A+B}} - E_{\text{A}} - E_{\text{B}}$, where $E_{\text{A+B}}$ stands for the total energy of the integrated composite structure, while E_{A} and

E_B are the total energies of two independent constituent components after respective structural optimization. Negative binding energy confirms that the composite structure can form stably, and the magnitude of the value directly reflects the strength of interfacial bonding interaction.

Molecular dynamics simulations

MD simulations are carried out to investigate the distribution behaviors of Me-4PACz, SC and S2 on the substrate of ITO at the molecular level. To this end, two MD boxes with dimensions of $84 \times 84 \times 90 \text{ \AA}^3$ are created, in which ITO substrate with thickness of around $6 \text{ \AA}$ is placed in the bottom region, whereas the Me-4PACz, SC, and S2 molecules are placed in the top region. To describe the atomic interactions between the SAM molecules and the ITO substrate, the PCFF force field is utilized. For the non-bonded interactions in the system, the 12-6 Lennard-Jones potential with cutoff distance of $10 \text{ \AA}$ is applied to describe the vdW forces between atoms, while the standard Coulomb potential is utilized to mimic the atomic electrostatic interactions that is evaluated by the particle–particle particle–mesh (PPPM) algorithm. Prior to MD simulations, an energy minimization is initially performed to relax the configurations of Me-4PACz, SC and S2 on the ITO substrate. Soon afterwards, MD simulations with 1,000,000 timesteps are performed to explore the spatial distribution of Me-4PACz, SC and S2 on the ITO substrate at temperature of 300 K under canonical (NVT) ensemble. During the MD simulations, the temperature is controlled by Nose-Hoover thermostat technique, and the ITO substrate is fixed. The dynamics of atoms in the systems are described by the classical Newton's motion equation that is solved by the velocity-Verlet algorithm with timestep of 1.0 fs. All the simulations are implemented using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package.

Other characterizations

Molecular structure characterization: ^1H NMR and ^{13}C NMR spectra were acquired on a Bruker AV400 spectrometer at operating frequencies of 400 MHz and 100 MHz, respectively. High-resolution mass spectra (HRMS) were recorded using a Micromass GCT-TOF mass spectrometer.

Thermal, photophysical, and electrochemical characterization: Thermogravimetric analysis (TGA) was conducted on a Netzsch TG 209 F3 instrument under a nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Cyclic voltammetry (CV) was performed

on a CHI 660D electrochemical workstation at ambient temperature using a standard three-electrode configuration, comprising a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl (saturated KCl) reference electrode.

Electrochemical measurements: A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in dichloromethane served as the supporting electrolyte, with all voltammograms recorded at a scan rate of 0.1 V s^{-1} . The ferrocene/ferrocenium (Fc/Fc^+) redox couple was measured under identical experimental conditions for internal potential calibration. The oxidation potential (E_{ox}) was identified from the anodic peak in the cyclic voltammogram, corresponding to the onset of electron abstraction from the molecule. The highest occupied molecular orbital (HOMO) energy level was subsequently derived from E_{ox} according to the equation: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.44) \text{ eV}$, where 4.44 eV is the absolute potential of the standard hydrogen electrode (SHE) versus the vacuum level.

Ultraviolet photoelectron spectroscopy (UPS): UPS measurements were employed to probe the energy band structure variations across the different samples. The work function (WF) was extracted from the UPS spectrum by determining the kinetic energy of photoelectrons emitted at the vacuum level cutoff, calculated as $\text{WF} = E_{\text{photon}} - E_{\text{kinetic}}$, where E_{photon} denotes the incident photon energy (e.g., He I excitation at 21.22 eV) and E_{kinetic} represents the maximum kinetic energy of the emitted photoelectrons, identified from the high-energy edge of the spectrum. The HOMO energy level was then obtained by combining the work function with the valence band onset: $E_{\text{HOMO}} = -(\text{WF} + E_{\text{cut-off}})$, where $E_{\text{cut-off}}$ is the energy separation between the valence band maximum and the Fermi level.

Surface coverage and work function characterization: The elemental composition of the SAM-modified thin films was investigated by X-ray Photoelectron Spectroscopy (XPS) on a Thermo Scientific Nexsa system, which was outfitted with a monochromatic Al K α X-ray source (1486.6 eV). The SAM samples were deposited onto ITO substrates following an identical protocol to that employed in device fabrication. Binding energy calibration was performed by referencing the C 1s peak of adventitious hydrocarbon carbon to 284.8 eV.

SAM distribution on textured IZO substrates was characterized by atomic force microscopy-infrared spectroscopy (AFM-IR). AFM-IR was characterized by NanoIR3s (Bruker, CA, USA) and the stretching vibration of P=O at 1230 cm^{-1} was used to define SAMs. Grazing-incidence wide-angle X-ray scattering (GIWAXS) was performed to

test the high coverage of SAMs on ITO-substrates. GIWAXS measurements were performed at the BL17UM in Shanghai Synchrotron Radiation Facility (SSRF).

Characterization of perovskite film morphology and photophysical property: The structure and morphology of the perovskite thin films were studied using a Scanning Electron Microscope (SEM, FEI Inspect F50). Conductive Atomic Force Microscopy (C-AFM) images of the deposited thin films were obtained using a Keysight Technologies 7500 scanning probe microscopes. X-ray Diffraction (XRD) patterns for crystallographic analysis of the perovskite thin films were measured using a Bruker D2 phaser and Cu K α radiation.

Charge carrier dynamics characterization: Steady-state photoluminescence (SSPL) spectra were recorded on an FLS 980 fluorescence spectrophotometer (Edinburgh Instruments, FLSP980) under continuous-wave excitation, while time-resolved photoluminescence (TRPL) measurements were performed using the same instrument equipped with a pulsed laser source. The dynamics of charge extraction and transport within the perovskite solar cells were investigated through TRPL decay analysis. The acquired TRPL transients were fitted to a bi-exponential decay model, from which the average carrier lifetime (τ_{avg}) was calculated according to the following equation³⁶:

$$\tau_{\text{ave}} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

The rapid initial decay represents the combination of charge extraction (quenching) and non-radiative recombination process (τ_1). Although the slower decay lifetime (τ_2) is mainly related to bulk and surface trap assisted recombination, it is widely considered as a reliable indicator of high-quality perovskite.

Data availability

All data are available in the main text or the supplementary materials. Further data are available from the corresponding author on reasonable request.

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Author contributions

Conceptualization: M.L., L.X., and R.X.; funding acquisition: M.L., D.Z., X.Zong., R.X., and J.Gao; writing: M.L., L.G., R.X., J.Gu., Z.Y., L.Y., and X.Zong.; designed and synthesized the SAMs: M.L., J.Gu, T.G., and Z.M.; methods: R.X., H.L., J.Gu, Z.Y., C.Zhao, C.Zhu, H.M., Q.C., C.Zhang., and Y.L.; investigation: R.X., Y.X., J.Gu, Z.Y., L.G., H.W., B.C., Y.W., Z.W., X. Zong., W.T., X.Zhu., Zhou Liu., R.H., H.Z., Y.M., Z.Liu., D.Y., X.Zhang., Y.C., C.W., T.T., G.Y., Z.X., and S.H.; visualization: M.L., L.G., R.X., J.Gu, and Z.Y. All authors reviewed and commented on the manuscript.

Competing interests

A Chinese patent application (CN 202610118960.0) was submitted by M.L., L.X., D.Z., R.X., L.G., Z. M., H.W., Y.W., and Z. C., which covers the molecules for PSCs. All other authors declare no competing interests.

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