

Symmetry-breaking co-assembly of conjugated molecules boosts perovskite photovoltaics

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Chuanyao Luo^{1,10}, Zhongliang Yan^{2,3,10}, Tao Du^{1,10}, Zhiyuan Dai⁴, Tanghao Liu^{1,5}, Bosen Zou¹, Wenbin Yuan³, Yang Yang⁴, Yao Liu¹, Xicheng Tang¹, Biao Zhang¹, Jan Seidel⁶, Jae Sung Yun⁷, Ruihao Chen⁴, Renjun Guo^{8,9}, Jun Yin¹✉, Yang Bai^{2,3}✉ & Tom Wu¹✉

In perovskite photovoltaics, self-assembled molecules (SAMs) have demonstrated the ability to enhance interface quality, reduce charge recombination, and improve energy-level alignment. However, most symmetrical molecules for photovoltaic applications tend to self-aggregate, which hinders uniform film formation, reduces the active surface area, and limits interface contact and device efficiency. In this work, we propose a symmetry-breaking co-assembly (SBC) strategy to improve the performance of the widely employed SAM of 2-[3,6-Dimethoxy-9H-carbazol-9-yl]ethyl] phosphonic acid (MeO-2PACz) by coupling with another small conjugated molecule, dibenzo[b,d]thiophene-4-carboxylic acid (DTCA). The broken symmetry at the molecular level enables the synthesis of co-SAM layers with significantly improved uniformity and coverage. A quantitative protocol based on atomic force microscope-infrared spectroscopy (AFM-IR) has been developed to determine the surface coverage of SAM layers. When the surface coverage of co-SAM layers is maximized, the interfacial chemical reaction under electrical stress and the non-radiative recombination loss are effectively suppressed, resulting in power conversion efficiencies (PCEs) of 26.32% (certified as 25.67%) and 25.34% for areas of 0.08 cm² and 1 cm², respectively. The encapsulated device retains 93% of its initial PCE after operating at the maximum power point (MPP) for 1,150 hours, as evaluated following the ISOS-L-1 protocol. These results underscore the effectiveness of the SBC strategy in advancing perovskite photovoltaics, and the coverage-maximizing methodology may be generalized to other research domains involving SAMs.

Perovskite solar cells (PSCs) have attracted enormous interest from both academia and industry due to their exceptional photovoltaic performance, low-cost fabrication, and easy-to-tune optoelectronic properties, positioning them as a transformative technology for a new generation of solar energy-harvesting devices^{1,2}. The inverted *p-i-n* PSC is the prevailing architecture in the community and boasts the merits

of enhanced operational stability, reduced hysteresis effects, compatibility with flexible substrates, and simplified processing, producing record power conversion efficiencies (PCEs). In such devices, the buried interface is recognized for enhancing interfacial contacts and passivating defects, but it is elusive to characterize, which hampers optimal synthesis^{3–5}. Therefore, it remains a paramount task to boost

A full list of affiliations appears at the end of the paper. ✉ e-mail: jun.yin@polyu.edu.hk; baiyang@suat-sz.edu.cn; tom-tao.wu@polyu.edu.hk

the performance and stability of buried charge transport/blocking layers in PSCs.

Self-assembled molecules (SAMs), as next-generation hole-transporting layers (HTLs), have attracted widespread attention due to their low cost, tunable energy levels, and efficient hole extraction⁶. Compared to most metal oxide HTLs⁷, an organic interface made of SAMs offers much higher chemical and energetic versatility while circumventing parasitic chemical reactions at the heterointerfaces between HTLs and the perovskite absorber⁸. To obtain a comprehensive understanding of the impact of SAMs on PSCs, we utilized large language models (LLMs) to conduct a thorough literature review of existing publications from the past decade related to SAM applications in PSCs. Among the 34,015 abstracts of PSC publications (Scopus, as of January 30, 2026), there are 313 explicitly mentioning self-assembled molecules (the full list of extracted publications can be found in Supplementary Dataset T1). Although this dataset does not represent an

exhaustive record of all SAM-related publications in PSC research, its careful examination provides valuable insights for project design. Details on literature mining and LLM-assisted database extraction can be found in Supplementary Note 1. As shown in Fig. 1a, the advent of SAM molecules has propelled the research on single-junction PSCs in the last decade. In the list, the most commonly used SAMs are standard carbazole or benzene derivatives, particularly 2-[3,6-Dimethoxy-9H-carbazol-9-yl]ethyl] phosphonic acid (MeO-2PACz)⁹ and [4-(3,6-dimethyl-9H-carbazol-9-yl)butyl] phosphonic acid (Me-4PACz)¹⁰. They feature an electron-rich π -conjugated space unit and phosphonic acid anchoring groups, which guarantee the capacity of efficient hole transportation and strong anchoring on the indium tin oxide (ITO) substrate¹¹. However, these symmetrical, highly conjugated molecules suffer from an intense drive to form rigid face-to-face π - π stacks, leading to premature lateral crystallization or isolated macroscopic aggregates in solution before the molecules can cleanly bind to the

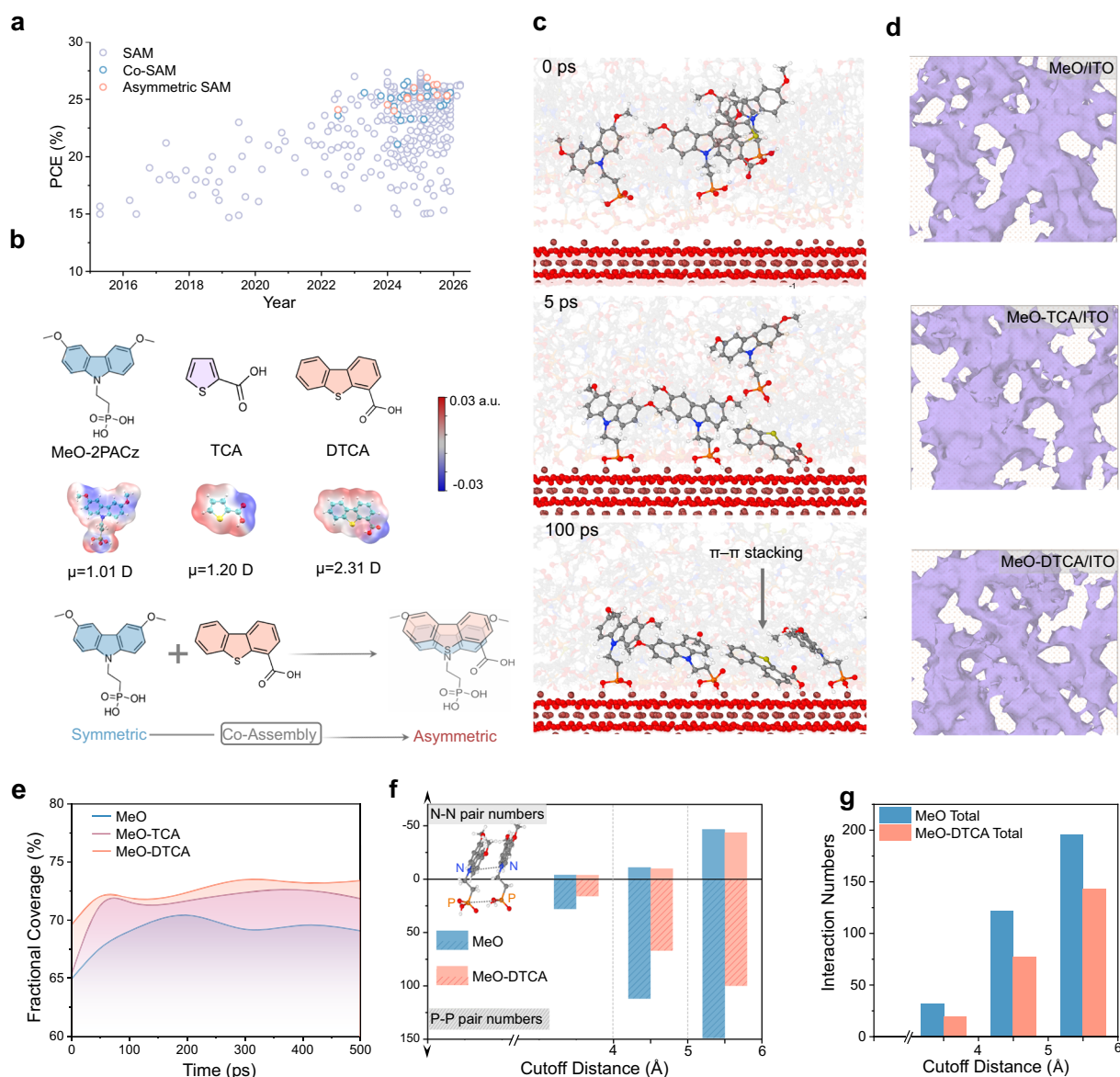


Fig. 1 | Design of asymmetric co-SAMs and adsorption dynamics. **a** Trend of PCE reported in the last decade on representative PSCs incorporating SAM or co-SAM, as obtained via LLM-assisted literature mining of 313 abstracts of representative publications. **b** Chemical structures, electrostatic potential maps, and calculated dipole moments of MeO, TCA, and DTCA molecules. **c** Snapshots of dynamic

adsorption of MeO-DTCA molecules on the ITO substrate. **d** Spatial distributions of MeO, MeO-TCA, and MeO-DTCA SAMs after 1 ns of MD simulations. **e** Surface coverage of SAMs on In_2O_3 substrates as a function of simulation time. **f,g** Variations of N-N and P-P pair numbers with cutoff distance within SAM molecules adsorbed on the In_2O_3 after equilibration for 500 ps.

substrate¹². As a result, the strong self-aggregation leads to inhomogeneous distribution and poor coverage (in most cases, 50–60%) with pinholes on the ITO substrate¹³. This drawback results in undesired incoherent buried contacts and unsatisfactory perovskite film deposition with poor wetting, hindering the device performance and the operational stability of inverted devices¹⁴. To address this issue, significant efforts have been devoted to improving the synthesis of SAMs in PSCs via strategies, such as engineering solvents¹⁵, designing less aggregated phosphonic acid molecules¹⁶, and exploring thermal evaporation¹⁷. It is noteworthy that there remains much room in terms of designing high-performance SAMs, reflected by the fact that symmetric molecules, in particular MeO-2PACz and Me-4PACz, are still the most frequently employed SAMs in the literature (Supplementary Fig. 1).

As shown in Fig. 1a, reports of PSCs incorporating co-SAMs emerged in 2022^{11,18}, and the chemical architectures of representative co-SAMs reported so far can be found in Supplementary Fig. 2. This strategy refers to molecular films consisting of two or more SAM molecules to introduce molecule-level dilution, thereby enhancing device performance¹¹. By tuning the co-SAM composition, both the molecular concentration and the intermolecular interaction strength can be precisely regulated. Consequently, the co-SAM approach offers significant advantages over conventional single SAM: it enables fine modulation of the work function by blending molecules with different dipole moments, and it promotes more uniform and complete substrate coverage, which reduces pinholes and improves contact quality. Systematic studies on diverse molecular combinations have demonstrated clear impacts on device efficiency and stability, establishing co-SAMs as an effective surface-modification method^{19,20}, and marking a new stage in interface engineering in the PSC research¹¹.

In parallel, the past three years have also seen notable progress in the development of asymmetric SAMs (Fig. 1a), which have generally delivered excellent PSC performance, with record efficiencies approaching 27%²¹, highlighting the important role of molecular symmetry in governing structure–property relationships. Molecular asymmetry has been recognized to be an important factor for influencing both the molecular assembly and the interfacial energy-level alignment with the perovskite layers^{22,23}. First, the spatial asymmetry modulates homo-molecular interactions (particularly π – π stacking) and keeps the molecules highly dispersed during the liquid deposition phase²⁴. Second, as these molecules approach the oxide surface during the film coating process, the lateral dipole moments of the asymmetric molecules guide them into tightly packed arrangements²⁵. Finally, an asymmetric configuration also minimizes steric hindrance directly around the anchoring sites. By opening physical clearance at the substrate interface, the kinetic barrier for neighboring anchors to attach is significantly lowered, leading to a higher density of robust bonds formed with the underlying lattice²⁶. Overall, the modulated intermolecular and SAM-substrate interactions can effectively help mitigate the self-aggregation of symmetric SAMs, thereby increasing the surface of asymmetric SAMs and improving the PSC performance¹⁵.

The structural asymmetry of SAM is typically achieved via planar asymmetric cores, asymmetric halogenation, or off-center backbone functionalization. As illustrated in Supplementary Fig. 3, the chemical architectures of representative asymmetric SAMs are considerably more complex than those of conventional symmetric analogs^{20,23,27}. One recent example is a highly asymmetric diradical SAM with pronounced steric hindrance, which demonstrated excellent assembly uniformity, enhanced stability, and processability for large-area PSC fabrication²³. However, the synthesis of asymmetric molecules often suffers from low yield and high cost, limiting their broad adoption at the current stage of PSC research. Therefore, developing a facile and effective strategy for engineering asymmetric SAMs remains a pressing priority for the field.

Furthermore, although SAM engineering has been recognized as critical for achieving homogeneous coverage of SAM/co-SAM layers, characterizations of such ultrathin molecular layers remain highly challenging. Prior studies have primarily relied on X-ray photoelectron spectroscopy (XPS) to determine coverage factors and surface atomic ratios²⁸, but the spectroscopic data are taken over macroscopic areas (on the scale of 10 μm), and, in addition, counting photoelectrons does not provide direct clues on the cluster formation²⁹. Recently, atomic force microscope-infrared spectroscopy (AFM-IR) has been used as a powerful tool to quantify the nanoscale distribution and surface coverage of SAMs in PSCs, but quantitative analysis of coverage remains underdeveloped^{30,31}. From a theoretical perspective, molecular dynamics (MD) simulations have enabled researchers to unravel the intricate assembly mechanisms of ultrathin SAMs, which can track dynamic evolution from picosecond-scale molecular vibrations to nanosecond-scale self-assembly processes¹⁴. Therefore, implementing both direct experimental analysis and simulation studies on surface coverage of SAM layers is crucial for uncovering molecular-level assembly mechanisms and improving the device stability and efficiency, but it remains a daunting task to accomplish.

In this work, we report a general methodology for enhancing SAM performance through a symmetry-breaking co-assembly (SBC) strategy, alongside the quantitative determination of SBC layer surface coverage using AFM-IR. The SBC of co-SAM was achieved by coupling MeO-2PACz (MeO) with thiophene-based carboxylic acid derivatives, namely, 2-thiophenecarboxylic acid (TCA) and dibenzo[b,d]thiophene-4-carboxylic acid (DTCA). MD simulations revealed that DTCA, with a significantly higher dipole moment, substantially reduces the cluster formation and improves the uniformity of the SBC layer by suppressing hydrogen bonding-driven aggregation of MeO molecules. The AFM-IR measurements confirmed that the SBC of MeO and DTCA (denoted as MeO-DTCA) increases the surface coverage by more than 35%. The improved interface resulted in PCE values of 26.32% (certified as 25.67%, area of 0.08 cm^2) and 25.34% (1 cm^2 area), and 93% of the original PCE was retained after operating at the maximum power point (MPP) for 1150 h. The SBC strategy is expected to be general and may inspire the design of a wide variety of artificial SAMs with tailored molecular symmetry and improved performance.

Results

Symmetry-breaking design of co-SAM

In this work, we hypothesize that the suppression of the SAM self-aggregation may be obtained by coupling widely used symmetric SAMs with another asymmetric small molecule, basically combining the merits of the aforementioned co-SAM and asymmetric SAM strategies (as illustrated schematically in Fig. 1b). We selected MeO-2PACz (denoted as MeO hereafter) as the host molecule, considering its well-recognized merits, such as reduced steric hindrance, tight packing, and proper energy levels⁹. Two guest molecules, 2-thiophenecarboxylic acid (TCA) and dibenzo[b,d]thiophene-4-carboxylic acid (DTCA), were chosen due to their different configurational asymmetry and dipole moments (Fig. 1b). It is well recognized that the symmetric configuration of the two MeO groups in MeO-2PACz, with opposite directions of dipole moments, resulted in a low molecular dipole moment. Nevertheless, the carbazole core and the phosphate group of MeO-2PACz allow strong interactions with other molecules, and if there is a large dipole disparity between the two molecules, the strong coupling is expected to render SBC configurations (Fig. 1b) and presumably can promote uniform surface coverage of SAM layers on substrates. As a proof of concept, we propose in this work two thiophene-based molecules to strongly interact with MeO molecules and to resolve the self-aggregation issue. The dipole moments of MeO, TCA, and DTCA were calculated to be 1.01 D, 1.20 D, and 2.31 D, respectively. Since both TCA and DTCA have the identical carboxyl ($-\text{COOH}$) group, the much larger

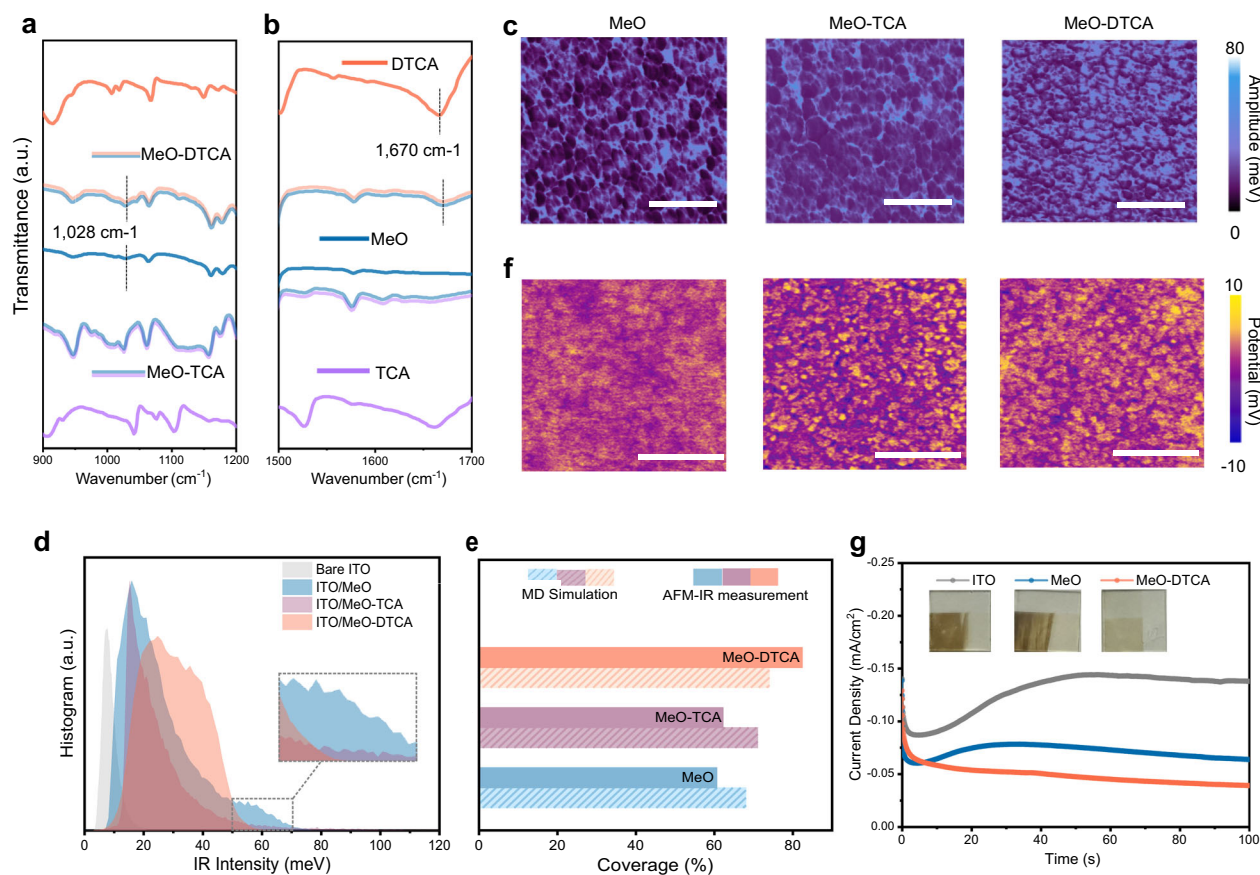


Fig. 2 | Surface Coverage of Buried SAM Layers. **a,b** FTIR spectra of MeO, TCA, DTCA, and MeO-hybrid sample. **c** AFM-IR intensity mapping of MeO, MeO-TCA, and MeO-DTCA at $1,028\text{ cm}^{-1}$ absorption; scale bar: $1\text{ }\mu\text{m}$. **d** AFM-IR intensity histograms of ITO, MeO, MeO-TCA, and MeO-DTCA from the 2D mapping data corresponding to the characteristic IR vibration wavenumber of 1028 cm^{-1} . **e** Comparative analysis of surface coverage derived from MD Simulations and

AFM-IR measurements. **f** KPFM images of MeO, MeO-TCA, and MeO-DTCA substrates; scale bar: $1\text{ }\mu\text{m}$. **g** Potentiostatic current density-time (j - t) plots for the indicated ITO/SAMs recorded at -1.0 V versus Ag/AgCl in a 0.1 M methylammonium chloride (MACl) aqueous electrolyte (the redox curves and film color indicate the chemical reaction, $\text{In}^{3+} \rightarrow \text{In}^0$).

dipole of the latter can be attributed to its higher molecular asymmetry (Supplementary Fig. 4).

To verify our hypothesis above and elucidate the adsorption behavior of the SBC strategy on transparent conductive oxide (TCO) substrate, we first performed molecular dynamics (MD) simulations using the LAMMPS package³². In this study, the ITO substrate was used instead of fluorine-doped tin oxide (FTO) due to its lower roughness³³. The ITO substrate was modeled as In_2O_3 with dimensions of $101\text{ }\text{\AA} \times 101\text{ }\text{\AA} \times 10\text{ }\text{\AA}$. Figure 1c shows the snapshots of the MD simulation for SBC surface absorption. Interfacial self-assembly of molecules on ITO progresses rapidly through three consecutive steps: (i) initial physisorption attachment, (ii) subsequent chemisorption-driven anchoring, and (iii) final reorganization into close-packed and long-range orientational domains²². DTCA molecules rapidly anchor to the In_2O_3 substrate within 5 ps, restricting the movement of MeO molecules through the formation of a MeO-DTCA π - π stacked framework (Fig. 1c), indicating the feasibility of the SBC strategy. This led to much more uniform distributions of MeO-TCA (Supplementary Fig. 5) and MeO-DTCA (Supplementary Fig. 6) layers than the MeO-only case (Supplementary Fig. 7). It is worth noting that the highly dynamic environment in the solution processing leads to the simultaneous existence of multiple co-SAM configurations, which break the symmetry of the MeO molecules. This trend was further confirmed by dynamic light scattering (DLS) experiments (Supplementary Fig. 8), where the reduced particle sizes of co-SAM indicate improved dispersity of SAM molecules in solution processing¹⁵.

As a theoretical tool, MD simulations can render a quantitative estimation of the surface coverage of SAM layers, although the theoretically extracted absolute values may deviate from the actual coverage since all realistic experimental parameters are not considered. The simulation result indicates that both MeO-TCA and MeO-DTCA achieve significantly higher coverage compared to the MeO-only system after the completion of the self-assembly process (Fig. 1d). Furthermore, the MD simulations reveal that the MeO-only interface suffers from rapid self-aggregation very soon after the initial small batch of molecules is dispersed and anchored on the substrate (Supplementary Fig. 9). In contrast, the surface coverage calculated from the equilibrated MD configurations at 500 ps increases from 68% for MeO only to 71% and 74% for MeO-TCA and MeO-DTCA, respectively, as shown in Fig. 1e. The estimated coverage of MeO-only system (68%) aligns with values reported for symmetric SAMs^{14,22}, and the progressive enhancement in co-SAM coverage validates our molecular design strategy.

To assess the uniformity of the SBC layer, two descriptors, i.e., the N-N and P-P pair numbers within specified cutoff distances, were used to characterize the spatial correlation of SAM clusters. A pair was counted when two N/P atoms fell within a given cutoff distance, enabling quantification of MeO aggregation via π - π stacking (N-N) or end-to-end dimer-like configurations (P-P). The variations in N-N and P-P pair numbers were statistically analyzed over cutoff distances of 4.0 – $6.0\text{ }\text{\AA}$ after 500 ps equilibration (Fig. 1f). Overall, the results indicate that hydrogen bonding among terminal groups serves as the

primary aggregation form for MeO molecules. When only the N–N pair is considered, the MeO-only system exhibits slightly higher cluster numbers than the MeO-DTCA case. More importantly, the analysis of P–P pair data demonstrates a significant reduction (35%) in pair number with DTCA addition compared to the MeO-only system. Figure 1g shows the total numbers of both N–N and P–P pairs, showing an overall 30% decrease in the number of MeO clusters upon DTCA incorporation. Taken together, the analysis of N–N and P–P pair patterns provides direct evidence that DTCA effectively suppresses the hydrogen bonding-driven aggregation propensity inherent to MeO, thereby modulating its self-assembly pathways.

We further analyzed the distribution of distances between the phosphorus (P) atoms of the SAM phosphate groups and the In_2O_3 surface to assess the degree of molecular aggregation. As shown in Supplementary Fig. 10, both MeO-TCA and MeO-DTCA systems exhibit a higher distribution intensity at an anchor distance of $1.63 \pm 0.31 \text{ \AA}$ than the MeO-only system, indicating a higher fraction of SAM molecules anchored at the ITO surface in the mixed-SAM cases. This result reflects an improved interfacial assembly behavior, where suppression of the intermolecular aggregation favors surface anchoring over molecular clustering. Such a modification of intermolecular interactions in co-SAM systems contributes to reduced aggregation-induced inhomogeneity and improved SAM coverage.

The mechanism underlying the success of SBC of MeO-DTCA, we hypothesize, is linked to the strong interactions between MeO and DTCA because of their similar topology of conjugation, as observed in the MD simulation (Supplementary Fig. 11). The π – π interaction between MeO-2PACz and DTCA was investigated through ultraviolet–visible absorption spectroscopy (Supplementary Fig. 12). Compared with the DTCA solution, the absorption peak of the MeO-DTCA solution shifts towards the longer wavelength direction. This could be attributed to the π – π stacking caused by forming SBC configurations, which reduced the $\pi \rightarrow \pi^*$ energy transition²². In such designed SBC co-SAM systems, the stacking between different kinds of SAMs suppresses the self-aggregation of MeO and presumably promotes the homogeneous dispersion of MeO molecules on the ITO substrate. Following the theoretical design of a suitable SBC system, we proceeded to experimentally verify that such an SBC strategy can facilitate the formation of compact and uniform SAM layers at the buried interface.

Experimental characterizations of SBC layers

To reveal the nature of the anchoring groups of the SAMs and their optical features, Fourier-transform infrared (FTIR) spectroscopy and ultraviolet–visible spectroscopy (UV–Vis) measurements were conducted. As shown in Fig. 2a, Supplementary Fig. 13, and Supplementary Fig. 14, MeO, MeO-TCA, and MeO-DTCA all exhibit phosphate-related P–OH stretching vibrations, consistent with previous reports²⁷. To further verify SAM anchoring on ITO, the FTIR spectra of the bulk SAM powders and the corresponding SAM-modified ITO substrates were compared (Supplementary Fig. 14). The phosphate-related vibration is observed in both cases, while its peak shift and intensity variation after surface modification indicate a changed local chemical environment caused by P–O–In bond formation, confirming chemical anchoring rather than the presence of free molecules. Therefore, the phosphate-related vibration can be used as a reliable marker for evaluating SAM anchoring and relative surface coverage. In addition, TCA and DTCA show characteristic C=O stretching peaks at 1660 and 1670 cm^{-1} , respectively (Fig. 2b)¹³. These FTIR results indicate that the phosphate-related stretching behavior of the co-SAMs is generally consistent with that of the MeO sample, providing a basis for the subsequent AFM-IR mapping measurements. In addition, UV–Vis absorption measurements (Supplementary Fig. 15) revealed that neither MeO-coated ITO nor co-SAM-coated ITO significantly affected the optical transparency

of the ITO-coated glass substrates, consistent with the ultrathin and wide-bandgap nature of these SAMs.

Then, we employed a complementary suite of techniques to investigate the surface properties of ITO/MeO, ITO/MeO-TCA, and ITO/MeO-DTCA samples. In this study, the AFM-IR technique played a pivotal role in analyzing the surface morphology and the spatial chemical properties of the SAM films. It offers the highest spatial resolution (as high as 5 nm) for chemical imaging³⁴, enabling monolayer-level measurement sensitivity, suitable to probe the chemical signatures of SAMs³⁵. In some prior studies, AFM-IR has been used to understand the distribution and homogeneity of the SAM layer, but quantitative analysis of coverage remains limited. In addition, to mitigate the interference caused by the irregular surface topography of transparent conducting oxides (TCOs) on the chemical information at buried interfaces³⁶, we consistently employed low-roughness ITO substrates for all samples synthesized in this work (Supplementary Fig. 16).

Subsequently, AFM-IR was utilized to map the distribution of SAMs and to assess their surface coverage by analyzing the characteristic P–OH vibrational mode at 1028 cm^{-1} (Fig. 2c and Supplementary Fig. 17). This mode was chosen because high-frequency IR-active modes (C–N, 1213 cm^{-1} or C=C, 1330 cm^{-1} , Supplementary Fig. 12) are more surface-sensitive and may introduce noise³⁶. Therefore, for the ultra-thin SAM layer, reliable AFM-IR measurements are required to consider the noise level from the substrates³⁶. These results confirm that the surface roughness does not affect the subsequent AFM-IR measurements or introduce additional noise. Therefore, despite the intrinsic limitations of AFM-IR in characterizing ultrathin layers, our experimental setup has successfully minimized extrinsic noise and topographical artifacts to the greatest extent possible. First, we performed AFM-IR testing on a bare ITO sample at 1028 cm^{-1} and noticed that bare ITO substrates without any SAM on top already exhibit a background noise level with an intensity lower than 19 meV (Supplementary Fig. 18). Then, we proceeded to measure SAM and co-SAM layers under the same measurement conditions, and to obtain consistent results, we measured more than three samples for each type and dozens of local areas for each sample. In the AFM-IR images, the bright blue and dark purple regions correspond to higher and lower molecule density, respectively. Intriguingly, localized high-intensity (between 50 meV and 70 meV) domains were observed in the MeO sample, which can be attributed to molecular aggregation, which is known to increase both the overall film thickness and the IR intensity³⁵. In the MeO-TCA sample, although some high-intensity domains are still visible, the average infrared (IR) intensity is noticeably higher than in the MeO-only case. In contrast, such exceptionally high-intensity regions were absent in the MeO-DTCA sample (inset of Fig. 2d), indicating that molecular aggregation was effectively suppressed by the co-assembly strategy. Furthermore, the analysis of the IR intensity mapping corresponding to the carboxylic acid (–COOH) stretching vibration at 1670 cm^{-1} (Supplementary Fig. 19) also revealed a well-defined distribution of SAM on the ITO substrate.

Different from the prior works on using AFM-IR technique to investigate SAM layer, in this work we established a protocol to quantitatively determine the surface coverage through histogram analysis (Fig. 2d). The coverage calculation protocol (Supplementary Method 1) involves: (1) acquiring IR intensity histograms through AFM-IR mapping, (2) systematically excluding data points with intensities below ITO- H_{th} (The H_{th} refers to the maximum IR response exhibited by bare ITO substrates in the IR intensity histograms), and (3) calculating effective coverage percentages through integration of residual high-intensity signals. Quantitative analysis revealed progressively enhanced surface coverage values of 60.6% (MeO), 62.2% (MeO-TCA), and 82.4% (MeO-DTCA) (Supplementary Fig. 20 and Supplementary Table 1), demonstrating a positive correlation between the significant dipole moment and surface coverage. These results are consistent with the fractional coverage calculated from MD simulations shown in

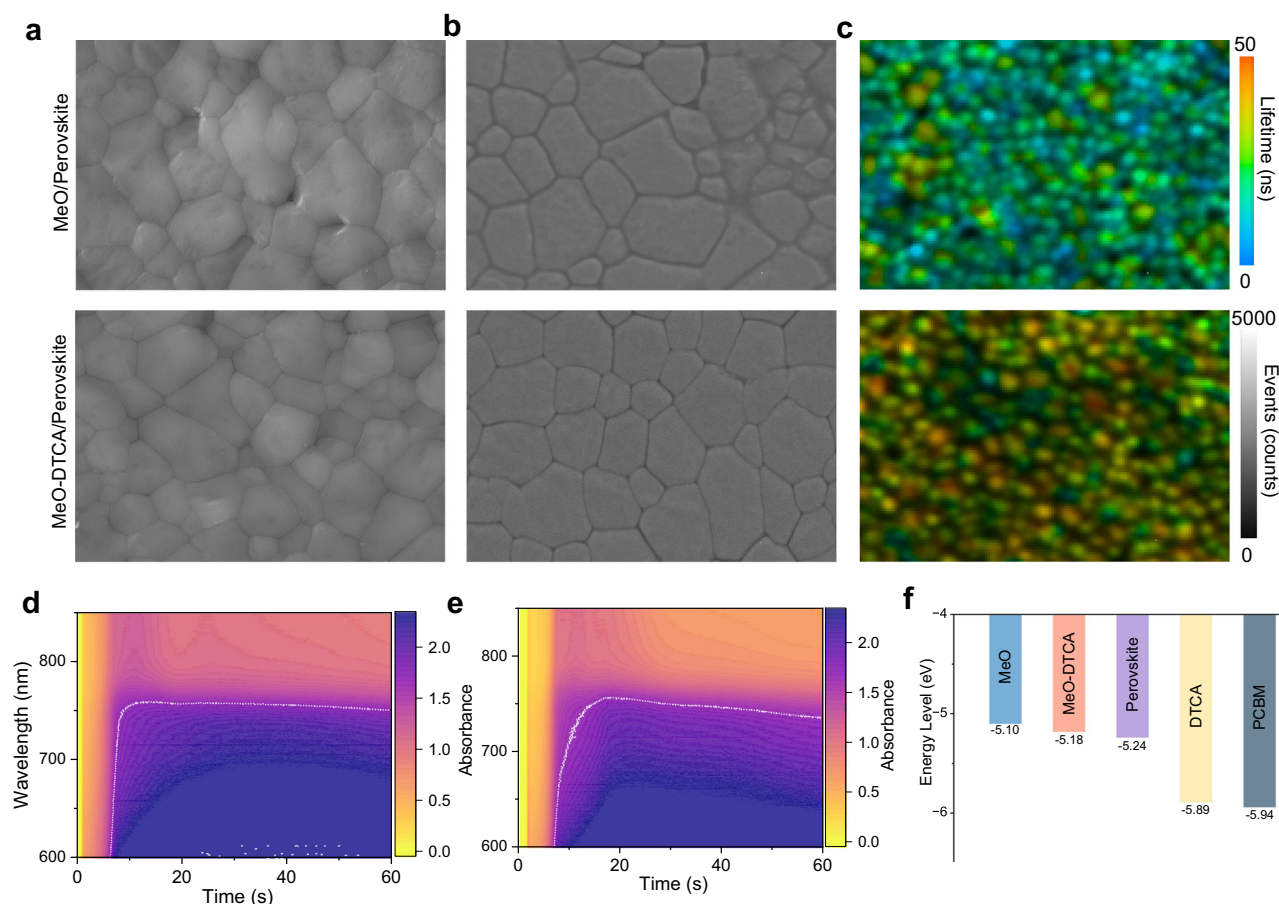


Fig. 3 | Characterization of perovskite films deposited on MeO and MeO-DTCA surfaces. SEM images of the top surface (a) and the buried interface (b) of MeO and MeO-DTCA-based perovskite films; scale bar: 1 μm. c Fluorescence lifetime imaging microscopy (FLIM) mapping of MeO/perovskite and MeO-DTCA/perovskite samples; scale bar: 3 μm. In-situ UV-vis spectra of perovskite films

deposited on the MeO (d) and MeO-DTCA (e) surfaces measured during the annealing process. The white dashed lines mark the wavelength where the films reach 80% of the maximum absorbance. f Energy levels of MeO, MeO-DTCA, DTCA, PCBM, and perovskite. The MeO-DTCA energy level of −5.18 eV is achieved at a molar ratio of 4:1.

Fig. 2e. In addition, XPS measurements were carried out, and a semi-quantitative analysis of the results was conducted by examining the area ratio of the P 2p peak associated with the SAM to the In 3d3/2 peak of the ITO substrate²². Both XPS and AFM-IR data confirmed that the surface coverage of the co-SAM layer always showed a higher coverage factor value compared with the MeO layer (Supplementary Figs. 21, 22 and Supplementary Table 2). However, the surface morphological features of the ITO substrate are known to alter the effective escape depth of photoelectrons during the XPS measurements, and the resultant shadowing effect is challenging to estimate. In comparison, AFM-IR provides simultaneous roughness data and IR intensity at the nanoscale, enabling more precise, quantifiable measurements.

To analyze the contact current distribution of the SAMs, conductive atomic force microscopy (c-AFM) measurements reveal that DTCA yields a more uniform current distribution compared to MeO. The broader distribution observed for MeO is attributed to molecular self-aggregation, which is effectively mitigated by the incorporation of DTCA (Supplementary Fig. 23). Then, we conducted Kelvin probe force microscopy (KPFM) measurements to investigate the potential distribution of MeO, MeO-TCA, and MeO-DTCA samples (Supplementary Note 2). These SAMs were deposited on ITO-coated substrates, and the corresponding surface topography images are presented in Supplementary Fig. 24. After SAM deposition, the surfaces became visibly porous, and similar root mean square (RMS) roughness values were observed across the samples. Figure 2f displays the corresponding contact potential difference (CPD) images. For the MeO sample, the

CPD image shows minimal nanoscale variation, with no apparent correlation to morphology. In contrast, the MeO-TCA and MeO-DTCA samples exhibit CPD images with distinct variations in surface potential. This behavior stems from the reduced self-aggregation of MeO-TCA and MeO-DTCA during film formation, which enables them to conformally coat the underlying morphological features. Such uniform adsorption orientation and conformal assembly could be facilitated by the dipole-induced electrostatic interactions between the molecules and the conductive oxide³⁷. Thus, besides the steric hindrance of DTCA, differences in molecular dipole moment between DTCA and TCA may contribute to the assembly behaviors.

It has recently been recognized that ITO can chemically interact with perovskites under thermal processing or applied electric fields³⁸, which constitutes a critical, yet often overlooked, factor compromising the PSC stability during operation. Under the influence of external stimuli, the mobile ions of the perovskite can cross the charge-transporting, e.g., SAM, layer to chemically etch the ITO, and the generated new ions may then migrate upwards into the perovskite film and produce detrimental effects on the operational stability. This interfacial electrochemical reaction may be suppressed if the SAM layer is uniform and capable of blocking the ionic exchange. Figure 2g shows the current density-time (*j*-*t*) plots of ITO and ITO/SAM samples biased at −1.0 V versus an Ag|AgCl reference electrode in a 0.1 M methylammonium chloride aqueous electrolyte (see the experimental setup in Supplementary Fig. 25). This potential is just above the threshold to induce acid-mediated cathodic reduction of ITO to metallic In⁰ via the

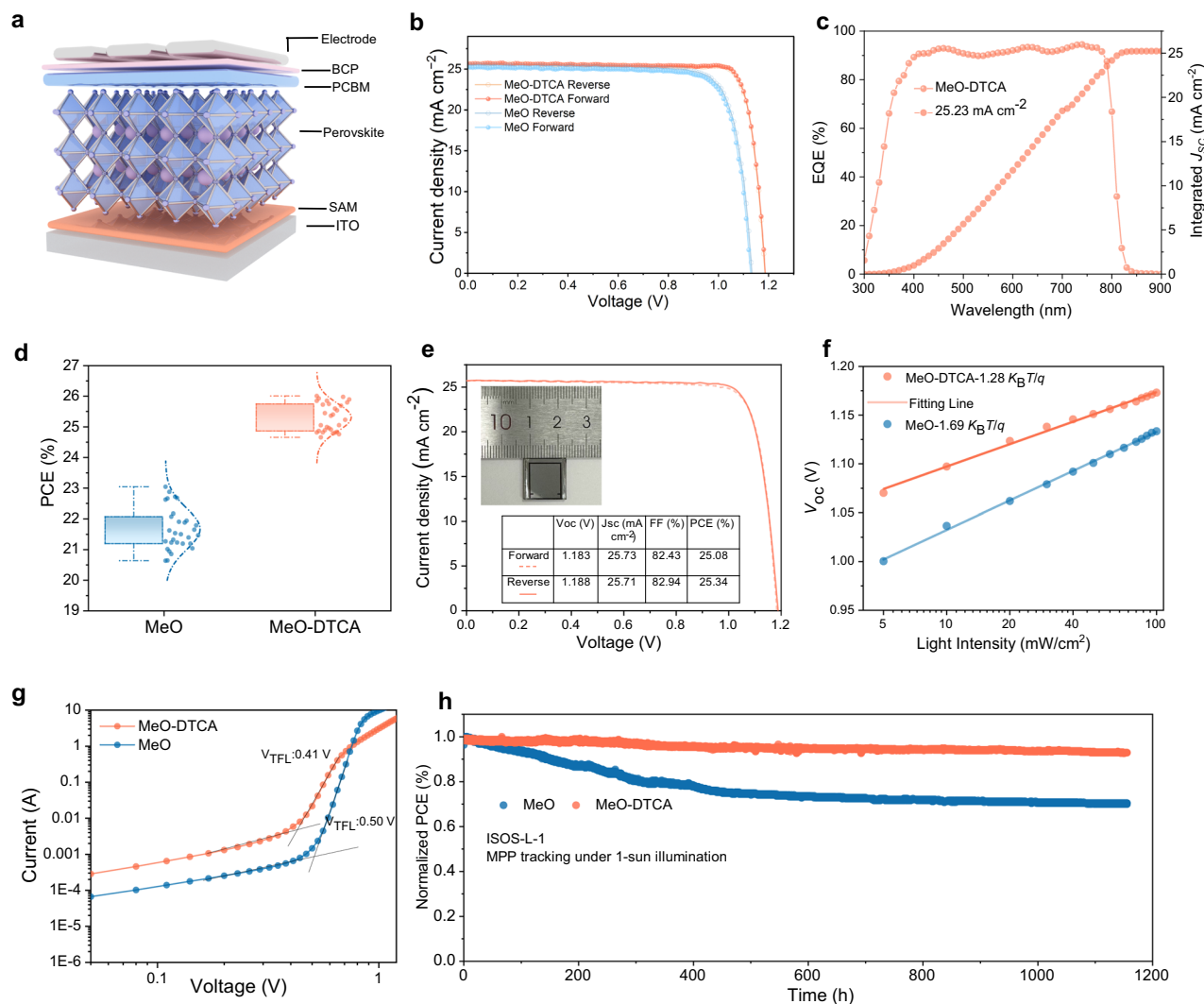
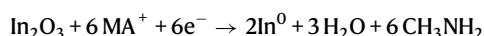


Fig. 4 | Device Efficiency and Stability. **a** Device structure **b** *J*-*V* curve of the PSCs based on MeO and MeO-DTCA. **c** EQE curve of the MeO-DTCA-based device. **d** Statistics of PCE values obtained from the *J*-*V* characteristics of PSCs based on MeO and MeO-DTCA, collected from 30 independent devices per condition (*n* = 30). **e** *J*-*V* characteristics of champion devices based on MeO-DTCA with

area=1 cm². **f** Light intensity dependence on *V*_{oc} plots for MeO and MeO-DTCA based devices. **g** The SCLC analysis of hole-only devices (ITO/SAMs/perovskite/PTAA/BCP/Ag) with the MeO and MeO-DTCA SAMs. **h** Maximum power point tracking (MPPT) of MeO-based and MeO-DTCA-based devices under 1-sun illumination.

following reaction³⁹:



As expected, after the reaction of merely two minutes, the ITO-alone substrate exhibits a brown color due to the generation of metallic In⁰ clusters (Fig. 2g), indicating a strong perovskite/ITO interface redox reaction under the electrical stress⁴⁰. The MeO-only SAM layer exhibits a much-reduced current density, but eventually the film still showed a brown color. In contrast, a further reduced current density was observed in the case of the MeO-DTCA co-SAM layer, and the sample remained transparent at the end of the experiment, indicating that the co-SAM layer possesses a much higher coverage and much better capacity at blocking the interfacial ionic transport to retard the reaction kinetics.

Characterizations of the SAM/perovskite interface

Guided by the theoretical simulations and experimental validation of the SBC strategy, we focused on investigating the perovskite films and PSCs coated on the MeO-DTCA co-SAM layers. As depicted in

Supplementary Fig. 26, all perovskite films fabricated on MeO-DTCA demonstrated complete coverage, with a perfect synthesis yield. However, on MeO-coated substrates, the average yield decreased to 83%. This result can be attributed to both improved SAM surface coverage and the more hydrophilic nature of the co-SAM surfaces, which facilitates the deposition of the perovskite precursor solution, in line with previous reports^{13,41}.

When other descriptors of molecules are similar, higher configurational asymmetry often leads to a larger electric dipole, which presumably improves the surface wettability⁴². Indeed, the incorporation of DTCA into the MeO layer significantly improved substrate wettability, with the contact angle being reduced from 24° to 16° (Supplementary Fig. 27), creating a favorable surface for uniform perovskite deposition³. The reduction in contact angles for the co-SAM-modified surface can be primarily attributed to the change in surface free energy, thereby promoting liquid spreading and resulting in a lower contact angle¹². In addition to the perovskite precursor solution, we also conducted water contact angle experiments (Supplementary Fig. 28). The contact angles of MeO-DTCA and DTCA samples are consistently lower than that of MeO, confirming the

modification effect associated with the large electric dipole of asymmetric DTCA.

As a benefit of the improved wettability of precursor solvents, the uniformity of perovskite layers is expected to be enhanced. To test this scenario, we used a previously established method to peel off the perovskite films from the ITO substrates (Supplementary Fig. 29) and examined the bottom surface of the perovskite films using scanning electron microscopy (SEM)⁴³. As shown in Fig. 3a–b, numerous nanovoids and pinholes were observed at the top and buried surfaces of the perovskite films grown on MeO because of its hydrophobicity and insufficient wetting. In contrast, the exposed top and buried surfaces of the perovskite films deposited on MeO-DTCA showed a more compact and smooth film morphology without obvious nanovoids. This improvement underscores SBC as a general strategy to increase the dipole moment and thereby provide a wetting underlayer and enhance the perovskite deposition. In addition, as shown in Supplementary Fig. 30, cross-section SEM images of perovskite films coated on MeO-DTCA reveal a more compact and smoother interface between the SAM and the perovskite. This is because high coverage and a dense buried interface facilitate the deposition and growth of the perovskite film, which is expected to reduce defect states and minimize interfacial carrier recombination at the SAM/perovskite interface.

We further used laser confocal fluorescence lifetime imaging microscopy (FLIM) to examine the buried perovskite films deposited on MeO-only and MeO-DTCA samples. It was observed that the average photoluminescence lifetimes of perovskite coated on MeO-DTCA in the mapping were longer than those of MeO (Fig. 3c and Supplementary Fig. 31), indicating that the perovskite coated on MeO-DTCA exhibits less non-radiative recombination and enhanced uniformity. In addition, it is worth noting that the DTCA containing sulfur atoms can passivate the uncoordinated Pb^{2+} at the buried interface of perovskite, which reduces non-radiative recombination and contributes to prolonged photoluminescence lifetimes⁴⁴. The Pb–S coordination was verified by XPS and FTIR characterization (Supplementary Figs. 32, 33 and Supplementary Note 3). The observed shift towards lower energy of the Pb 4*f* peaks in the corresponding perovskite films can be attributed to the enhanced electron density around Pb^{2+} at the buried surface⁴⁵. To verify the effect of the restructured buried interface on the quality of perovskite films, in-situ UV-vis absorption spectroscopy (Fig. 3d, e) was performed to study the crystallization kinetics of perovskite films with and without the DTCA modification. In the DTCA-modulated sample, the chemical interaction between the highly polarized DTCA and the perovskite precursors significantly reduced the nucleation rate during annealing, which ultimately led to the growth of high-quality perovskite films.

In addition, X-ray diffraction and UV-vis spectroscopy collectively demonstrate that the SBC strategy selectively optimizes interfacial charge dynamics without perturbing its light-harvesting capability (Supplementary Figs. 34–35). However, it is worth mentioning that XRD patterns reveal that the perovskite film on the MeO-DTCA substrate exhibits improved crystallographic purity compared to that on the MeO substrate, evidenced by the absence of secondary-phase peaks around 13° and 31°. This enhanced purity is attributed to the delayed crystallization kinetics on MeO-DTCA, which facilitates a more regulated growth process and suppresses the formation of impurity phases.

Besides improving perovskite quality, the combination of two SAMs enables continuous tuning of energy levels to optimize charge transport at the buried interface. Ultraviolet photoelectron spectroscopy (UPS) analysis (Fig. 3f, Supplementary Figs. 36, 37) further reveals that DTCA possesses the highest occupied molecular orbital (HOMO) energy (−5.89 eV) among the samples investigated. This intrinsically deep energy level indicates suboptimal energy alignment with the perovskite (−5.24 eV). By tuning the SBC ratio at 4:1 of

MeO:DTCA, a quantifiable 0.08 eV downshift in the valence band maximum (VBM) of modified ITO substrates was achieved (MeO-DTCA: −5.18 eV vs. pristine MeO: −5.10 eV), which benefits the hole extraction and transport from the perovskite layer to the HTLs. Meanwhile, the PCBM electron-transport layer provides selective electron extraction on the opposite side of the perovskite absorber, thereby promoting balanced charge transport and suppressing interfacial recombination⁴⁶. To further elucidate the impact of SBC strategy on charge transfer kinetics at the interface, we have conducted transient absorption spectroscopy (TAS) on perovskite with MeO and MeO-DTCA samples. The quenching kinetics of the ground-state bleaching (GSB) feature at 774 nm are directly indicative of hole transfer efficiency from the perovskite to the SAM. The co-SAM-treated sample exhibits a markedly faster GSB decay within 1 ns, suggesting more efficient hole extraction at the perovskite/SAM interface. The decay profiles (Supplementary Fig. 38) were fitted with a bi-exponential model to probe interfacial charge extraction kinetics. The fast decay component (t_1), which governs hole extraction efficiency, is significantly shorter for MeO-DTCA/perovskite (196.5 ± 24.3 ps) than for MeO/perovskite (217.1 ± 40.4 ps). This reduction indicates a faster extraction rate and effectively minimizes interfacial losses.

Photovoltaic performance and device stability

We further fabricated inverted PSCs with an architecture (Fig. 4a) of indium tin oxide (ITO)/SAM or SBC/perovskite/[6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/bathocuproine (BCP)/Ag, where perovskite with a composition of $\text{FA}_{0.85}\text{MA}_{0.10}\text{Cs}_{0.05}\text{PbI}_3$ was deposited by one-step coating to investigate the impact of SBC on its photovoltaic performance. The perovskite surface was passivated with phenethylammonium iodide (PEAI), which reduced contact-induced recombination at the top interface. As shown in current density versus voltage (*J*–*V*) curves in Fig. 4b, the champion device with MeO-only gave an inferior PCE of 23.18%, with an open-circuit voltage (V_{OC}) = 1.132 V, a short-circuit current density (J_{SC}) = 25.52 mA cm^{-2} , and a fill factor (FF) = 80.04% (steady-state PCE of 22.32%, Supplementary Fig. 39) under reverse scan. Meanwhile, the SBC device (MeO:DTCA = 4:1) achieved an optimal efficiency of 26.32% and a high V_{OC} of 1.186 V under reverse scan with low hysteresis and exhibited a steady-state PCE of 25.65% (Supplementary Fig. 40). The one of the best devices was sent for certification and achieved a certified PCE of 25.67% (Supplementary Fig. 41). We attributed the performance improvement to increased coverage as well as improved energy level alignment provided by MeO-DTCA, which was confirmed by a lower nonradiative recombination loss and a higher PL intensity (Supplementary Fig. 42) of SBC-based devices. The integrated short-circuit current density (J_{SC}) of 25.23 mA cm^{-2} derived from the external quantum efficiency (EQE) measurement matches well with that from the *J*–*V* sweep (Fig. 4c). Figure 4d and Supplementary Fig. 43 summarize the statistical photovoltaic performance of the devices. It was found that the SBC-based devices showed higher PCEs than the MeO-based case, and the narrow distribution in PCE across 20 devices confirmed device reproducibility. In addition, we also tested DTCA-only devices and the MeO:DTCA ratios of 3:1 and 5:1 (see Supplementary Figs. 44, 45 and Supplementary Table 3). Therefore, due to energy-level mismatch, the DTCA-only device achieved a PCE of 1.23%, which is consistent with the UPS data mentioned above. This indicates that the primary role of DTCA in this study is to effectively reduce MeO aggregation and improve coverage, while it cannot function as HTL individually. To assess the scalability and uniformity of MeO-DTCA as an SBC model for large-area applications, a device with an active area of 1 cm^2 was constructed as depicted in Fig. 4e. The large-area MeO-DTCA device achieved a PCE of 25.34% (with a V_{OC} of 1.188 V, J_{SC} of 25.73 mA cm^{-2} , and FF of 82.94%). To validate the structural origins of the enhanced performance, we introduced butanedioic acid (BA) as a comparative control with distinct symmetry and conjugation features.

Unlike the MeO-DTCA co-assembly, BA molecules failed to improve device performance, thereby confirming that symmetry-breaking co-assembly is the critical factor behind the enhanced performance (Supplementary Fig. 46 and Supplementary Discussion 1).

We further measured the V_{OC} -light intensity dependence of devices to determine the ideal factor, a critical parameter that reflects defect-assisted recombination within the device. As shown in Fig. 4f, the MeO-DTCA-based device exhibited a slope of 1.28 kT/q (where k is Boltzmann's constant, T denotes the temperature, and q is the elementary charge). In comparison, the MeO-only device displayed a larger slope of 1.69 kT/q . The ideal factor value of the MeO-DTCA device is closer to 1, indicating that the defect-assisted trap states at the buried interface have been suppressed. We further examined the improved FF for the MeO-DTCA-based device (Supplementary Note 4 and Supplementary Fig. 47). It reveals that the enhanced FF is primarily attributed to reduced non-radiative recombination and charge transport losses, which aligns well with the previous film characterization of SAM and perovskite.

Additionally, we numerically analyzed the trap density in the perovskite device with MeO-only or MeO-DTCA via the space-charge-limited-current (SCLC) method⁴⁷ on a device structure of ITO/SAM or SBC/perovskite/PTAA/BCP/Ag⁴⁸. As shown in Fig. 4g, the SCLC measurements revealed the trap-filled limit (V_{TFL}) voltages of 0.50 V for the MeO-only treated device and 0.41 V for the MeO-DTCA treated devices, respectively. These reduced V_{TFL} values correspond to trap densities of 3.2×10^{15} and $3.9 \times 10^{15}\text{ cm}^{-3}$, respectively (see Supplementary Note 5 and Supplementary Table 4). Finally, we investigated the operational stability of the encapsulated device under continuous AM 1.5G illumination at MPPT in ambient air (Fig. 4h). The MeO-DTCA-based device exhibited promising operational stability and maintained 93% of its initial PCE after 1150 hours of continuous operation. In contrast, the MeO-based device just maintained 70% of its original PCE after operation. In addition, the devices were subjected to thermal aging at 85 °C, and the results show that the optimized devices retained 97% of their initial PCE after 600 hours, whereas the MeO-only counterparts retained only 78% under identical conditions. (Supplementary Fig. 48). These results further demonstrate the robustness of the device architecture and provide additional support for the durability advantage associated with the SBC strategy.

Discussion

In summary, we have demonstrated that the SBC strategy effectively suppresses the strong self-aggregation of the primary SAM, leading to enhanced surface coverage, improved PSC efficiency, and long-term operational stability. The underlying mechanisms were elucidated through a comprehensive suite of techniques, including MD simulations and AFM-IR characterizations. Choosing secondary molecules with appropriate configurations, electronic structures, and energy levels is critical to prevent cluster formation. Incorporating asymmetric DTCA with a large electric dipole and passivation sites causes necessary steric hindrance and disrupts the MeO self-aggregation while maintaining anchoring to the ITO substrate. The SBC strategy guarantees a smooth, uniform co-SAM surface coating with improved wetting, subsequently leading to the growth of high-quality perovskite films. As a result, the SBC-modified devices achieved a certified PCE of 25.67% with robust operational stability (93% retention after 1150 h of MPP tracking). In comparison to other published works involving co-SAM, this approach demonstrates competitive performance in terms of both efficiency and stability (Supplementary Table 5). The significance of dipole-mediated anchoring underscores the need to systematically decouple its specific influence from other molecular features on surface coverage in future studies. The SBC strategy may be broadly applicable to other SAM-based devices and establish a versatile framework for advancing diverse, high-performance optoelectronic technologies.

Methods

Materials

Indium tin oxide (ITO) glass substrates (sheet resistance: $15\text{ }\Omega\text{ sq}^{-1}$) were purchased from Advanced Election Technology Co., Ltd. Methylammonium iodide (MAI, 99.5%), Formamidinium iodide (FAI, 99.5%), cesium iodide (CsI, 99.5%), and methylammonium chloride (MACl, 99.5%) were purchased from Xi'an Yuri Solar Co., Ltd. Lead iodide (PbI_2 , >99.99%) and (2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl) phosphonic acid (MeO-2PACz, 99.5%) were supplied by TCI America. 2-Thiophenecarboxylic acid (TCA) and dibenzo[b,d]thiophene-4-carboxylic acid (DTCA) were obtained from Leyan Co., Ltd. [6,6]-Phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were sourced from Vizuchem Co., Ltd. N, N'-Dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.8%), ethyl acetate (EA, 99.8%), isopropanol (IPA, 99.8%), and chlorobenzene (CB, 99.5%), were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Device fabrication

The ITO glass substrates were sequentially cleaned ultrasonically using detergent, deionized water, acetone, and ethanol, each for 25 min. After drying with nitrogen flow, the substrates were plasma-treated for 10 min and then transferred into a nitrogen-filled glovebox. The hole transport layer (HTL) was deposited by spin-coating a solution of MeO-2PACz or an SBC-based formulation (with TCA or DTCA) (0.7 mg mL^{-1} in IPA) onto the ITO substrate at 3000 rpm for 30 s using a spin coater from Wuhan Junwei Technology Co., Ltd. All SAM and SBC layers were deposited under these identical conditions, followed by annealing at 100 °C for 10 min. A 1.5 M perovskite precursor solution with a composition of $\text{FA}_{0.85}\text{MA}_{0.10}\text{Cs}_{0.05}\text{PbI}_3$ was prepared by dissolving MAI, FAI, CsI, PbI_2 , and excess MACl (10 mol%) in a mixed solvent of DMF and DMSO (volume ratio 4:1). Approximately 50 μL of the perovskite precursor was dropped onto the HTL and spin-coated at 5000 rpm for 30 s. Antisolvent treatment was performed by dripping 200 μL of ethyl acetate (EA) 5 s before the end of the spin-coating step. The resulting film was then annealed at 120 °C for 30 min. For the electron transport layer (ETL), PC_{61}BM (20 mg/mL in chlorobenzene) was spin-coated at 2000 rpm for 30 s, followed by spin-coating BCP (0.5 mg/mL in IPA) at 4000 rpm for 30 s, and thermal annealing at 70 °C for 5 min. Finally, a 100 nm Ag electrode was thermally evaporated at a deposition rate of 0.5 $\text{\AA/s}$ to complete the solar cell devices.

Characterizations

Top-view and cross-sectional scanning electron microscopy (SEM) images were obtained using a field emission SEM (Tescan MIRA). Ultraviolet-visible (UV-Vis) absorption spectra were recorded with a UV-Vis spectrometer (PerkinElmer). Atomic force microscopy-infrared (AFM-IR) spectroscopy was performed in tapping mode on a nanoIR2 system (Anasys Instruments). AFM-IR mapping was performed in fixed-wavenumber imaging mode with the IR source tuned to 1028 cm^{-1} . The laser power was set to 16.0 mW during the measurements. The stretching vibration of P-OH at 1028 cm^{-1} was used to identify MeO-2PACz within SBC layers deposited on ITO substrates. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a ULVAC-PHI PHI 5000 VersaProbe II system to determine the coverage of SBC layers, employing a non-monochromatic He I emission line (21.21 eV) as the ultraviolet light source. Ultraviolet photoelectron spectroscopy (UPS) spectra were acquired with an AXIS-ULTRA DLD-600 W Ultra spectrometer (Kratos) equipped with a non-monochromated He I α photon source ($h\nu = 21.21\text{ eV}$). Water contact angle measurements were performed using a Drop Shape Analyzer DSA100 (KRÜSS). Confocal fluorescence lifetime imaging microscopy (FLIM) was conducted on a TA100 system.

Kelvin probe force microscopy (KPFM) measurements were performed using an AIST-NT SmartSPM1000 atomic force microscope. A

platinum-coated probe (HQ: NSC35/Pt) with a nominal force constant of 5.4 N/m and a resonance frequency of approximately 150 kHz was employed. All KPFM measurements were carried out within a nitrogen-filled chamber to maintain a controlled environment. Prior to scanning, the sample surface was purged with nitrogen to remove surface contaminants. The amplitude modulation mode was used to simultaneously acquire surface topography and contact potential difference (CPD) maps. The tip-sample separation was maintained at approximately 30 nm to ensure reliable CPD sensitivity without compromising surface integrity. A scan rate of 1.0 Hz was applied to achieve high-resolution images.

The current density–voltage (J – V) characteristics of the fabricated devices were measured inside a glovebox using a Keysight B2901A source meter under simulated AM 1.5 G illumination (100 mW cm^{-2}) from an Enlitech SS-F7-3A solar simulator. Both the device contact area and the illuminated area were defined by a non-reflective metal mask (0.08 cm^2 with masked with a metal aperture to determine an active area of 0.05 cm^2). The J – V curves were recorded via both reverse scanning (from 1.3 V to -0.1 V) and forward scanning (from -0.1 to 1.3 V), with a voltage step of 0.02 V and a delay time of 10 ms. External quantum efficiency (EQE) spectra were acquired using a solar cell spectral response measurement system QE-R3011 (Enlitech Co., Ltd.) operating in AC mode, with light intensity calibrated at each wavelength using a standard monocrystalline Si photovoltaic cell. The long-term operational stability of encapsulated devices was monitored using a multi-channel solar cell stability testing system (91PVK Solar Technology Company) with automated data acquisition.

Classical molecular dynamics (MD) simulations

The dispersion behavior of SAM on ITO substrate was studied by classical molecular dynamics simulation using the LAMMPS package³². The ITO substrate was simplified as In_2O_3 with a dimension of $101 \times 101 \times 10 \text{ Å}$, which was first equilibrated using the Buckingham potential. The simulation box contained 180 MeO-2PACz molecules and 20 DTCA/TCA molecules (molar ratio 9:1) to qualitatively evaluate surface coverage. Notably, for the AFM-IR validation, a 9:1 molar ratio was adopted too. This specific ratio was selected because preliminary studies demonstrated that it offers an optimal balance between surface coverage. Following the method reported in refs. 13,14, the control and mixed systems were constructed by randomly placing the SAM molecules on top of the In_2O_3 substrate using the PACKMOL package⁴⁹. The interatomic interactions of SAM molecules were described using the OPLS-AA force field generated by the LigParGen software⁵⁰. The interactions within the phosphonic functional group were modified by a specially designed force field from ref. 51. The interactions between SAM molecules and the In_2O_3 substrates were simulated using the universal force field (UFF). The combined systems were equilibrated in the canonical (NVT) ensemble at 300 K for 1.0 ns, which is found to be long enough to converge the potential energy. During the equilibration process, the In_2O_3 substrate was fixed to avoid unexpected structural changes. The motion of atoms was described using the velocity-Verlet algorithm with a 1 fs time step. The coverage of SAM on In_2O_3 substrate was evaluated by constructing a surface mesh using the Ovito software⁵².

DFT calculations

The geometry optimization for MeO-2PACz, TCA, DTCA, and their clusters were performed using the B3LYP-D3 (BJ) functionals with def2-TZVP basis set implemented in the ORCA package⁵³. The partial charges and electrostatics of molecules were analyzed using the Multiwfn code. Specifically, for the dipole moment calculations, the molecular geometries were fully optimized prior to the calculations, and the dipole moments were obtained from the optimized isolated molecular structures in vacuum conditions.

Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability

The main data supporting the findings of this study are available within the article, its Supplementary Information, Supplementary Dataset, and Source Data files. Extra data generated or analyzed during this study are available from the corresponding author upon reasonable request. Source data are provided with this paper.

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Author contributions

T.W. supervised the project. C.L. and T.W. conceptualized the research idea and designed the experimental framework. C.L., Z.Y., J.S., J.Y., and T.W. analyzed the experimental data. C.L. and T.W. wrote the manuscript. Z.Y., T.D., T.L., B.Z., J.Y., and T.W. revised the manuscript. T.D. and J.Y. contributed to the DFT calculations and molecular dynamics simulations. X.T. conducted literature mining. Y.L. and B.Z. performed the electrochemical measurements. W.Y. contributed to the in-situ PL measurements. J.S.Y. performed the AFM measurements and analysis. Z.Y., Z.D., Y.Y., R.C., and R.G. contributed to the fabrication of inverted perovskite solar cells and conducted stability tests. All authors discussed and commented on the paper.

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Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Jun Yin, Yang Bai or Tom Wu.

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¹Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China. ²Faculty of Materials Science and Energy Engineering, Shenzhen University of Advanced Technology, Shenzhen, China. ³Shenzhen Institute of Advanced Technology (SIAT), Chinese Academy of Sciences, Shenzhen, China. ⁴School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, China. ⁵School of Physical Sciences, Great Bay University, Guangdong, China. ⁶School of Materials Science and Engineering, University of New South Wales, Sydney, NSW, Australia. ⁷School of Computer Science and Engineering, University of Surrey, Surrey, UK. ⁸Institute of Microstructure Technology (IMT), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany. ⁹Light Technology Institute (LTI), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. ¹⁰These authors contributed equally: Chuanyao Luo, Zhongliang Yan, Tao Du. ✉ e-mail: jun.yin@polyu.edu.hk; baiyang@suat-sz.edu.cn; tom-tao.wu@polyu.edu.hk