

Nanocrystal-tailored recombination for all-perovskite tandem solar modules

Corresponding Author: Professor Hairen Tan

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)

This manuscript reports a comprehensive strategy, including designing a new tunnel recombination junction, tailoring the surface of In₂O₃ nanocrystals, and incorporating hole-selective materials into the narrow-bandgap perovskite, to optimize light absorption and reduce interfacial energy loss. A certified PCE of 26.2% on a 65-cm² all-perovskite tandem module is achieved, which is an impressive figure and suggests potential practical relevance. The manuscript is of very high quality, technically rigorous, and presents a compelling advance toward commercially viable perovskite tandem photovoltaics. However, the overall significance of the approach, particularly relative to existing mature device architectures, requires further evidence and more rigorous comparative analysis. The following issues should be addressed before the manuscript can be considered for publication. Detailed comments are as follows.

1. According to the Methods, both ITO and In₂O₃ nanocrystal layers are deposited using the same precursor concentration (2 mg mL⁻¹), yet their final thicknesses differ due to different density, particle size, and molecular weight. Because film thickness directly affects optics, conductivity, and tunneling behavior, comparing two layers with inherently different thicknesses cannot verify the superiority of In₂O₃. A thickness-matched or optical-density-matched comparison is required.
2. Given that the perovskite/C₆₀/SnO₂/sputtered ITO architecture is already mature and widely adopted, particularly in semi-transparent perovskite devices and perovskite tandems, it is critical for the authors to justify why a solution-processed In₂O₃ TRJ is necessary. The manuscript does not provide a clear comparison showing advantages of the proposed NC In₂O₃ layer over sputtered ITO, which in many cases may offer superior industrial scalability and reliability. At present, the work does not convincingly demonstrate that the NC In₂O₃ TRJ delivers performance, stability, or manufacturability benefits relative to conventional sputtered ITO. Without such a comparison, the practical and scientific significance of replacing established sputtered TCOs remains uncertain.
3. In Fig. 1f, Type II and III films exhibit significantly more uniform light absorption across the substrate. However, this improved optical uniformity does not lead to narrower J-V parameter distributions, especially J_{sc}, as shown in Fig. 1g. The authors should explain this inconsistency and clarify whether other variations, such as TRJ resistivity, perovskite crystallization, or series resistance, dominate the device-scale variations.
4. The work modifies the In₂O₃ nanocrystals using OAm, MMES, and MMPA. However, the functional group design of these materials is not given. In addition, the interactions between these materials and In₂O₃ are also not discussed when evaluating the surface tailoring of In₂O₃.
5. In Fig. 3a, the PbI₂ signal almost disappears for the target film, indicating suppressed PbI₂ formation. However, the authors use EDAl₂ for post-treatment, which typically reacts with residual PbI₂ for defect passivation. It is suggested to evaluate whether the extremely scarce amount of PbI₂ is sufficient to react with EDAl₂ and ensure the ideal passivation effect.
6. In Fig. 4b, although the target film exhibits smaller peak-position variations across the substrate, the FWHM at positions 3 and 4 is broader than in the control film, suggesting lower crystallinity. This apparent contradiction should be reconciled, including whether the broadening arises from microstrain, reduced grain size, or orientation distribution.
7. Although the MPP tracking tests and heat-damp stability tests all indicate the enhanced stability of the tandem photovoltaics, the in-depth mechanism is not given in this work. It is suggested to provide more experimental evidence and in-depth analysis.
8. Supplementary Fig. 3 contains an error: the TEM clearly shows larger ITO nanoparticles, whereas the label in panel c states that the In₂O₃ nanoparticles are larger.
9. Supplementary Fig. 7 only provides J-V curves for tandem devices based on ITO and In₂O₃ nanocrystals. For a complete comparison, the authors should also include tandem J-V data for the Type I structure.
10. Supplementary Fig. 14 presents statistics for Voc, J_{sc}, and FF but does not include the most important parameter, PCE.

This affects both completeness and the overall coherence of the figure.

11. If available, the authors could strengthen the manuscript by including evidence related to Sn oxidation suppression (e.g., XPS Sn²⁺/Sn⁴⁺ ratio), which is particularly relevant to long-term stability for Pb–Sn mixed perovskites.

12. For a module-focused work, a brief description of laser parameters, scribing width, and yield performance would help substantiate the high aperture efficiency and module uniformity.

All figure captions containing error bars should explicitly state what the error bars represent and specify the number of devices (n). For device and module statistics, the sample size should be listed. For stability data, the authors should indicate whether the plotted curve is representative or averaged from multiple modules.

Referee #2

(Remarks to the Author)

In this work, Ke et al. present a comprehensive approaches to enhance the overall performance of all-perovskite tandem solar modules. The key strategies employed in this research are summarized as follows: 1. The development of a novel recombination layer incorporating In₂O₃ nanoparticles, which replaces the conventional hygroscopic, acidic PEDOT:PSS layer and Au islands. This approach effectively minimizes parasitic absorption from Au islands and improves long-term stability, primarily by eliminating PEDOT:PSS. 2. The ligand for the In₂O₃ NCs was changed from OAm to MMPA to effectively modulate the energy levels and facilitate hole transport in the absence of a PEDOT:PSS layer. 3. The incorporation of HSM (MeO-2PACz) resulted in the improved device performance even without PEDOT:PSS layer. 4. The solvent system was changed from DMF:DMSO to a 2-ME:THF system to mitigate the issue of film thickness deviation across large-area substrates.

The resulting all-perovskite tandem solar modules demonstrated a power conversion efficiency of 26.6% (in-house) and a certified efficiency of 26.2% (by JET, for an area of 65 cm²), establishing the highest efficiency reported to date. Furthermore, the developed modules exhibited notable long-term stability, including retaining 82.5% of the initial efficiency after 1000 h (Maximum Power Point Tracking, 1 sun), ~80% after 120 h (65°C, 1 sun), 84% after 1000 h (Damp Heat), and 93% after 200 cycles (Thermal Cycling). This reviewer considers the results presented in this work to be a significant contribution toward the commercialization of all-perovskite tandem solar modules. Consequently, I recommend this work for publication in Nature, after the revision on the comments outlined below.

1. Previously, the authors' group demonstrated the improved performance of wide-bandgap and all-perovskite tandem solar modules using a green solvent system (ACN:EtOH:DMSO) (Nat. Energy 10, 318, 2025). However, in the current work, the WBG perovskite was fabricated using the conventional DMF:DMSO system. Is there a specific reason for selecting this solvent system? It would be valuable if the authors could provide a comparison or additional data utilizing the previously reported green solvent system to justify this choice.

2. Similarly, the authors' group previously reported the beneficial effects of adding aminoacetamide hydrochloride (AAH) to the perovskite precursor solution (Science 383, 855, 2024). Given its proven efficiency, could the authors comment on why AAH was not employed in this study, or provide additional results based on AAH?

3. In this work, the authors successfully replaced the Au/PEDOT:PSS system with In₂O₃ NPs. On Page 5, it is stated that the Type III (In₂O₃ NPs) system is advantageous over Type II (ITO NPs) due to improved smoothness and optimized electronic contact. However, there is a significant difference in particle size between the ITO NPs and In₂O₃ NPs used. Therefore, the observed performance difference might be influenced by the size effect rather than solely by the material properties. In order to improve the clarity, I suggest decoupling the size effect from the material comparison. Comparison data using ITO and In₂O₃ NPs of similar dimensions would be preferred to support this claim.

4. In Line 107, the authors that "In₂O₃ NCs-based TRJ exhibited the most ideal homoc contact behavior...". However, the results seem that resistance value extract from the measurement would be larger for In₂O₃ than ITO, which is detrimental to the device performance. Could the authors provide a more detailed explanation of this discrepancy and clarify how "ideal ohmic behavior" is defined in this context despite the apparent resistance values?

5. Replacing PEDOT:PSS with an In₂O₃ NP layer with tailored ligands is shown to be effective. However, other studies have suggested neutralizing PEDOT:PSS as an alternative strategy to minimize corrosion and degradation issues. To rigorously evaluate the superiority of the proposed strategy, could the authors compare the stability of the Type III (In₂O₃) system with that of a neutralized PEDOT:PSS-based control?

6. The ligand used for In₂O₃ differs significantly among themselves in terms of functional groups, quantity, and steric volume. While the authors explain the advantages from better energy alignment for MMPA, such a change in ligands may also alter charge transport characteristics. I recommend that the authors provide charge transport measurements, such as Space Charge Limited Current (SCLC) or Transient Photocurrent (TPC) analysis, to verify the carrier transport efficiency of the MMPA-capped In₂O₃ NPs.

7. In Page 9, the authors state that adding HSM results in the compensation for the deprotonation of FA⁺. If HSM molecules are utilized to prevent FA⁺ deprotonation, their ability to bind to the surface might be compromised or altered. Could the authors explain this mechanism? Additionally, a more detailed interpretation of the NMR spectra regarding the hydrogen bonding between the phosphonic acid and FAI would help clarify the interaction mode.

8. In Page 10, authors state that “... the interaction between HSMs and perovskite grains is significantly stronger than the binding affinity of the phosphonic acid anchoring group to the hydroxyl surface groups on the ITO.” If the statement is true, then the authors should compare the bare HSM film before and after washing by DMF. We believe that the MeO-2PACz molecules are easily washed by polar solvent, DMF, so this result does not support the author’s statement.

9. The authors significantly improved the quality of large-area films by changing the solvent system from DMF:DMSO to 2-ME:THF. The authors stated that “...DMF-based system requires a significantly slower coating speed of 5 mm/s...” and “This speed limitation becomes increasingly problematic during scale-up, while the optimized coating speed must be progressively reduced for larger substrates...”. However, slower coating speed can also be easily overcome by changing the concentration of solution for DMF:DMSO system. Therefore, I do not believe that this comparison is valid enough to support the superior properties of 2-ME:THF. At least, the device/module based on DMF:DMSO system should be optimized in terms of concentration, to compare the effectiveness of new solvent system. Could the authors explain in detail or provide additional experimental data on this aspect?

Referee #3

(Remarks to the Author)

The manuscript reports state-of-the-art performance for large-area perovskite/perovskite tandem modules. The authors achieve this primarily through: (i) introducing (functionalized) In₂O₃ nanoparticles in the tunnel recombination junction (TRJ), (ii) adding a self-assembled monolayer (SAM) molecule as an additive in the perovskite precursor, and (iii) demonstrating that the efficiency improvement arises from the synergistic combination of these two strategies rather than either approach alone. In addition, the authors introduce a new solvent system for Pb–Sn perovskites based on 2-methoxyethanol (2-ME) and THF. Using these approaches, they report 26.2% efficiency on a 65 cm² module. While the technological advance is clear and impressive, the scientific rationale and the manuscript’s narrative would benefit from further clarification and strengthening.

Major comments

Q1) Scalability claims attributed to the recombination junction require clearer substantiation.

The manuscript repeatedly states that performance loss upon scaling is predominantly due to the tunnel recombination junction (e.g., around line 51: “[...] This performance disparity stems predominantly from optical and energetic loss at the tunnel recombination junction (TRJ) [...]”). The introduction further argues that this configuration is fundamentally constrained in large-area fabrication because (a) ultrathin metal layers are difficult to deposit uniformly over large areas, and (b) PEDOT:PSS introduces parasitic absorption and instability due to acidity.

However, the first point appears specific to TRJs that rely on ultrathin metal films/metal nanoclusters. As acknowledged in the literature (including the manuscript’s Ref. 10), multiple TRJ implementations exist; metal nanoclusters are only one option, albeit often among the most efficient. Moreover, nanoparticle-based recombination layers have already been explored, including by some of the present authors. For example, H. Gao et al., *Solar RRL* 2021, 5, 2100814, and P. Wu et al., *Adv. Energy Mater.* 2022, 12, 2202948 demonstrated improved recombination junctions using conductive oxide nanoparticles; notably, the latter reported 26.3% tandem efficiency at small area using ITO nanoparticles.

The second point (PEDOT:PSS parasitic absorption and chemical instability) is primarily a stack/material-selection issue and is not inherently a scaling-specific limitation; it applies equally at small and large area.

The authors should therefore more clearly disentangle:

- what limitations are truly scaling-driven (e.g., thickness uniformity, sheet resistance, defect tolerance, patterning yield), versus
- what improvements reflect a better stack design irrespective of area.

A more quantitative discussion would help (e.g., physical simulations of optical/electrical loss budget attributable to the TRJ, sensitivity of PCE to thickness/roughness variations, and how nanoparticle TRJs mitigate these factors at module scale).

Q2) Novelty of SAM additives should be positioned accurately; the key novelty is the synergy with In₂O₃ nanoparticles.

The use of phosphonic-acid-based SAM molecules introduced directly in perovskite precursor solutions has increasingly become part of scalable processing since it was demonstrated in 2023 (Zheng et al., *Nat. Energy* 8, 462–472 (2023)). In this context, the general concept of SAM additives is not, by itself, fully novel.

What does appear distinctive here is the synergistic interaction between the functionalized In₂O₃ nanoparticles in the recombination layer and the SAM additive in the perovskite. This should be emphasized more explicitly in the Abstract and Introduction as the central conceptual contribution, alongside the large-area demonstration. Moreover, in order to clarify the mechanism, the description of SAM-In₂O₃ interactions should be supported by DFT calculations.

Q3) The late introduction of a new Pb–Sn solvent system (2-ME:THF) is conceptually disruptive.

A major source of confusion is the sudden introduction (Figure 4 and associated discussion) of the 2-ME:THF solvent system. The mechanistic arguments and process–property relationships developed earlier (based on the initial solvent system) cannot be assumed to transfer directly to a substantially different solvent chemistry. As a result, the final performance shown in Figure 4 cannot be straightforwardly connected to the preceding conclusions.

To improve coherence, the authors should either:

- introduce and use the 2-ME:THF system from the beginning, so that mechanistic conclusions and optimization steps consistently build toward the final module result; or
- provide a clear comparative bridge (e.g., direct head-to-head evidence showing that the same synergy/mechanism holds in both solvent systems, and which observations are solvent-specific versus universal).

Additional comments and requests for clarification

Q4. The introduction discusses PEDOT:PSS acidity (around line 65). Neutral or low-acidity PEDOT formulations/complexes are increasingly used and should be acknowledged as relevant alternatives.

Q5. The manuscript notes that PEDOT:PSS acidity is problematic for Sn-containing perovskites due to interfacial degradation, yet the work uses “phosphonic acid-assisted crystallization control.” The authors should discuss possible chemical interactions of these acidic functional groups in the precursor (e.g., with Sn powder or other reductants/additives) and whether they affect Sn²⁺/Sn⁴⁺ chemistry.

Q6. Lines 166–168: It remains unclear why MeO-2PACz provides the best performance among the phosphonic acids tested as additives, yet does not show a similar advantage when used as a conventional monolayer. A mechanistic explanation or supporting characterization would strengthen this point.

Q7. The experimental procedure for incorporating phosphonic-acid-based HTLs as additives is insufficiently described. Concentrations, dissolution conditions, mixing sequence, and aging/filtration steps should be explicitly reported.

Q8. Line 200: The meaning of “0.2%” must be specified (molar fraction, weight fraction, volume fraction) and referenced to the correct baseline (perovskite solids, total precursor, or solvent).

Q9. The distinction between “optimized” and “non-optimized” MeO-2PACz devices is unclear. What concentration was used in the non-optimized comparison set? Were solubility or solvent-compatibility differences across the additives a confounding factor? This should be discussed.

Q10. Prior work suggests that when phosphonic-acid-based molecules are used as additives, they may need to be removed or passivated at the perovskite surface (Zheng et al., Nat. Energy 2023). The manuscript should therefore clarify whether such removal/passivation is required here, and specify which solvent(s) were used during EDAI2 passivation. These details are currently missing.

Q11. Lines 229–230: The sentence should be rewritten for clarity, for example by splitting into two sentences and explicitly stating the causal link (loss of the hydroxy group; hydrogen bonding between phosphonic-acid functionalities and FAI).

Q12. If the manuscript mentions “three patents,” the patent/patent application identifiers should be provided.

Q13. The ITO and In₂O₃ nanoparticles have very different sizes. Can the authors comment on whether ITO nanoparticles of comparable size to the In₂O₃ particles can be synthesized using a similar approach, and whether size (rather than composition) could explain part of the observed differences?

Q14. The Supporting Information includes only two photographs of perovskite films. The effect of MeO-2PACz on Pb–Sn perovskite crystallization appears central, yet it is not shown comprehensively across both solvent systems (DMF–DMSO and 2-ME–THF). Additional photographs (and ideally complementary morphology/phase metrics) for all relevant films would be helpful.

Q15. The fabrication details for Pb–Sn perovskite films using DMF–DMSO are missing and should be added for reproducibility.

Q16. The volumes of perovskite solutions for blade-coating should be added in the SI.

Q17. The authors should comment on whether THF containing stabilizers/inhibitors could be used without compromising performance, and how sensitive the process is to THF grade and stabilizer content.

Q18. The authors must explicitly warn readers about the formation of highly reactive and potentially explosive peroxides in THF and other ethers, and clearly describe established measures to prevent explosions and fatalities during their handling and storage, supported by appropriate references. THF is a hazardous solvent that requires substantial practical experience and strict adherence to safety protocols; it cannot be considered safe for general use by non-expert practitioners. Publication of this article is likely to promote the use of this unusual and dangerous solvent, and without a clear and prominent safety discussion, it poses an unacceptable risk to inadequately prepared readers

Version 1:

Reviewer comments:

Referee #1

(Remarks to the Author)

This manuscript presents a well-executed and practically meaningful advance in all-perovskite tandem solar modules, addressing key challenges in recombination junction design, large-area uniformity, and module scalability. The authors have carefully addressed the concerns raised in the previous round of review, and I do not see any major outstanding issues. In my view, the work now meets the standard for publication in Nature and will be of broad interest to the photovoltaics and scalable device community.

I therefore recommend acceptance after minor revisions aimed at improving clarity and precision of presentation.

Minor comments:

1. The manuscript attributes the performance advantage primarily to the intrinsic properties of the In_2O_3 nanocrystal recombination layer. However, as also suggested by the rebuttal and supplementary data, ligand chemistry and nanocrystal morphology may also contribute. A slightly more balanced attribution would improve the accuracy of the discussion.
2. The phrase "improve interfacial recombination" could be clarified, as recombination is typically associated with loss. It would be more precise to describe improved recombination efficiency across the tunnel junction or enhanced carrier recombination at the interconnection layer.
3. The relatively low module-level current density ($\sim 1 \text{ mA cm}^{-2}$) is consistent with the series-connected architecture; however, it would be helpful to explicitly clarify its normalization and its relation to the subcell current ($\sim 15\text{-}16 \text{ mA cm}^{-2}$) to avoid potential confusion.
4. The suppression of lateral conductivity in the In_2O_3 nanocrystal layer is a key aspect of the proposed module-level advantage. While the device-level evidence is convincing, a brief clarification on whether lateral conductivity (or anisotropy) has been directly measured or estimated would further strengthen this point.
5. Given the emphasis on scalability, it would be helpful to briefly comment on the process tolerance (e.g., sensitivity to thickness, coating conditions, or nanocrystal coverage), as this is highly relevant for large-area manufacturing.

Junbo Gong

Foshan Xianhu Laboratory

Referee #2

(Remarks to the Author)

The authors have clearly responded to my previous comments, particularly regarding the size effect of NCs, the comparison with neutral PEDOT:PSS, and the utilization of an eco-friendly solvent system.

The current revision significantly improves the overall quality of the manuscript.

However, I have a few remaining minor points that require further clarification.

Minor Comments:

1. The authors mentioned that XPS spectra were collected from the opposite side of the sample, denoted as "target-bottom." Since the penetration depth of XPS is typically less than 10 nm, I am somewhat confused as to what the P 2p signal from the bottom side represents. Does it originate from the buried interface between the ITO and the SAM? If so, could the authors clearly describe the fabrication and measurement process for these "target-bottom" samples?
2. Could the authors provide more detailed insights into the possible causes of the incompatibility of the AAH additive in this system? For instance, is it due to a specific chemical reaction between the components, or simply a result of an excessive amount of the additive present in the perovskite film?
3. It remains a subject of debate whether the dynamic, weak interaction between HSM and FA can effectively inhibit the deprotonation of FA^+ thereby improving long-term stability. The authors are encouraged to provide further justification or discussion on this mechanism.

Referee #3

(Remarks to the Author)

The revision provided by the Authors addresses most of the comments and the manuscript is now more complete from scientific point of view. There however few major points to clarify before the paper could be published.

1) Reproducibility of the results (very important issue, a scientific result cannot be published without being reproducible)
Line 157: The manuscript states that supersaturation of the perovskite precursor solution was achieved by adding 20% THF. However, when we attempted to prepare the 1.4 M solution reported in the Supporting Information, the initial salt powders could not be fully dissolved. After stirring the solution for longer than 30 min, which is the recommended stirring time in the SI, we observed intense formation of a white precipitate, as described in the manuscript. We note that the experimental section has been revised to describe the preparation procedure as a sequence of steps ("first..., then..., then..."). However, it remains unclear why the solution preparation is described as the sequential addition of several components, while stirring appears to be applied only at the final stage. The main issue is that we were unable to reproduce the procedure already at the stage of perovskite precursor preparation. We mixed all components together and applied intensive stirring, as described, but still observed white precipitation before complete dissolution of the initial salts. Could the authors clarify why this precipitation occurs and how it can be avoided? In our experiments, complete dissolution was only possible up to a concentration of 1.2 M; however, this concentration did not yield the optimal film thickness. We therefore believe that some important experimental conditions may be missing from the current description. In addition, it will be nice to add a video related to this step.

2) On the use of THF.

Line 170: The statement "The incorporation of THF into the wide-bandgap perovskite..." is unclear in the context of the

experimental details, since the SI states that DMF and DMSO were used for the wide-bandgap perovskite precursor. The authors should clarify the role of THF in this case. In addition, the experimental details corresponding to Supplementary Figure 12 should be provided.

3) minor point

Line 218: In the sentence "...previously reported aminoacetamide hydrochloride (AAH) additive...", the relevant reference appears to be missing from the manuscript.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Point-to-point actions in response to the Reviewers' comments

Manuscript: 2025-11-30551

We sincerely thank the reviewers for their much-valued suggestions, which have enabled us to improve the manuscript. Following are the detailed actions taken in light of reviewers' comments: the comments appear in black, our responses appear in blue, and changes in the revised manuscript appear in boxes.

Referee #1:

This manuscript reports a comprehensive strategy, including designing a new tunnel recombination junction, tailoring the surface of In₂O₃ nanocrystals, and incorporating hole-selective materials into the narrow-bandgap perovskite, to optimize light absorption and reduce interfacial energy loss. A certified PCE of 26.2% on a 65-cm² all-perovskite tandem module is achieved, which is an impressive figure and suggests potential practical relevance. The manuscript is of very high quality, technically rigorous, and presents a compelling advance toward commercially viable perovskite tandem photovoltaics. However, the overall significance of the approach, particularly relative to existing mature device architectures, requires further evidence and more rigorous comparative analysis. The following issues should be addressed before the manuscript can be considered for publication. Detailed comments are as follows.

Response: We thank the reviewer for the appreciation of our work and the constructive suggestions to stimulate us to improve the manuscript. In light of the reviewers' and editor's suggestions, we have now substantially improved the manuscript and better clarified the significance and advancement of this work.

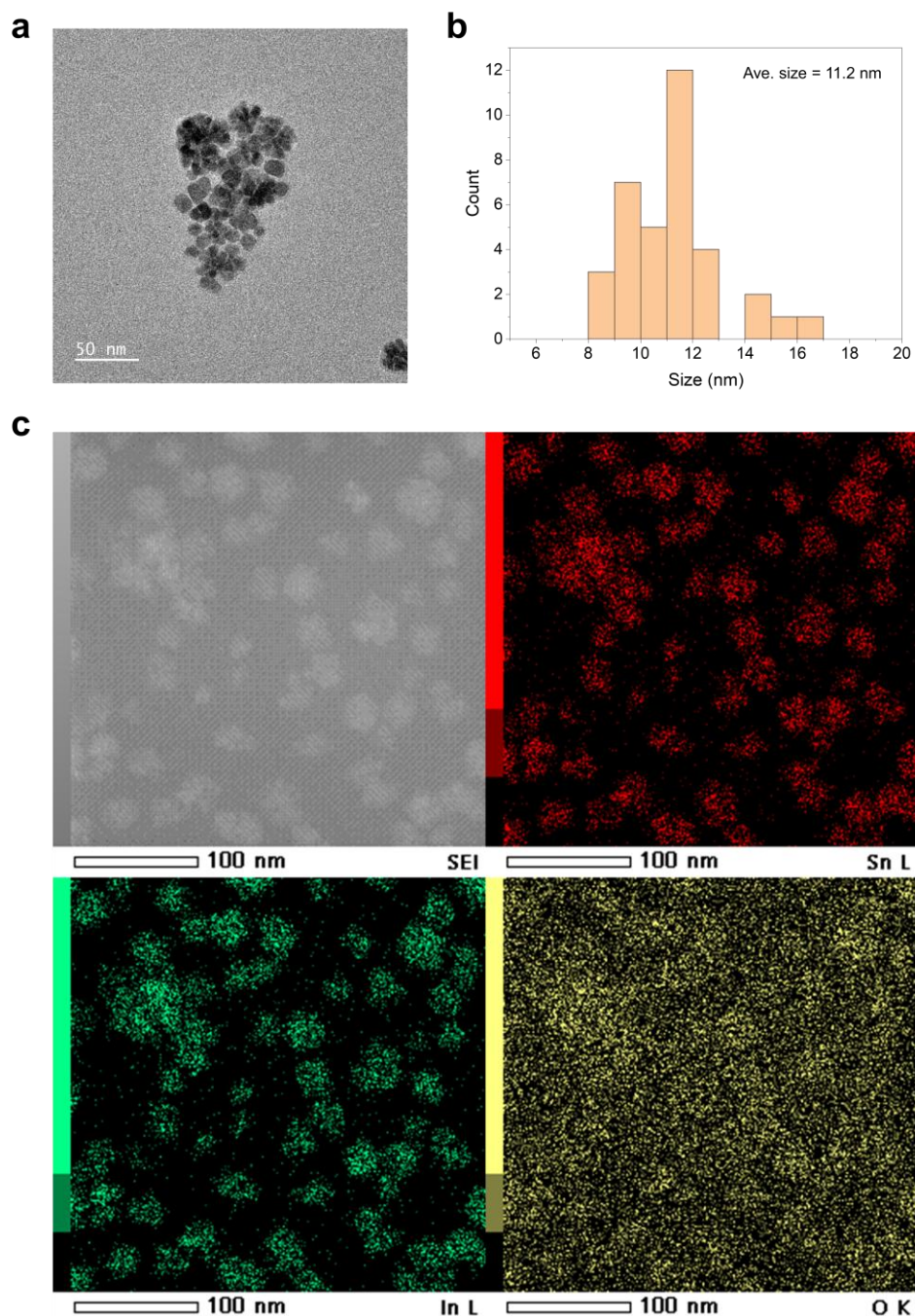
(1) According to the Methods, both ITO and In₂O₃ nanocrystal layers are deposited using the same precursor concentration (2 mg mL⁻¹), yet their final thicknesses differ due to different density, particle size, and molecular weight. Because film thickness directly affects optics, conductivity, and tunneling behavior, comparing two layers with inherently different thicknesses cannot verify the superiority of In₂O₃. A thickness-matched or optical-density-matched comparison is required.

Response: We thank the reviewer for raising this important point regarding the potential influence of film thickness on optical and electronic properties. To ensure a fair comparison independent of thickness variations, we synthesized ITO NCs with comparable size to In₂O₃ NCs using the same method and deposited them under identical conditions (Supplementary Fig. 16). Under these controlled conditions, In₂O₃ NC layers still exhibit superior optical transparency and device performance (Supplementary Fig. 17), confirming that the advantages originate from the intrinsic material properties of In₂O₃ rather than thickness differences.

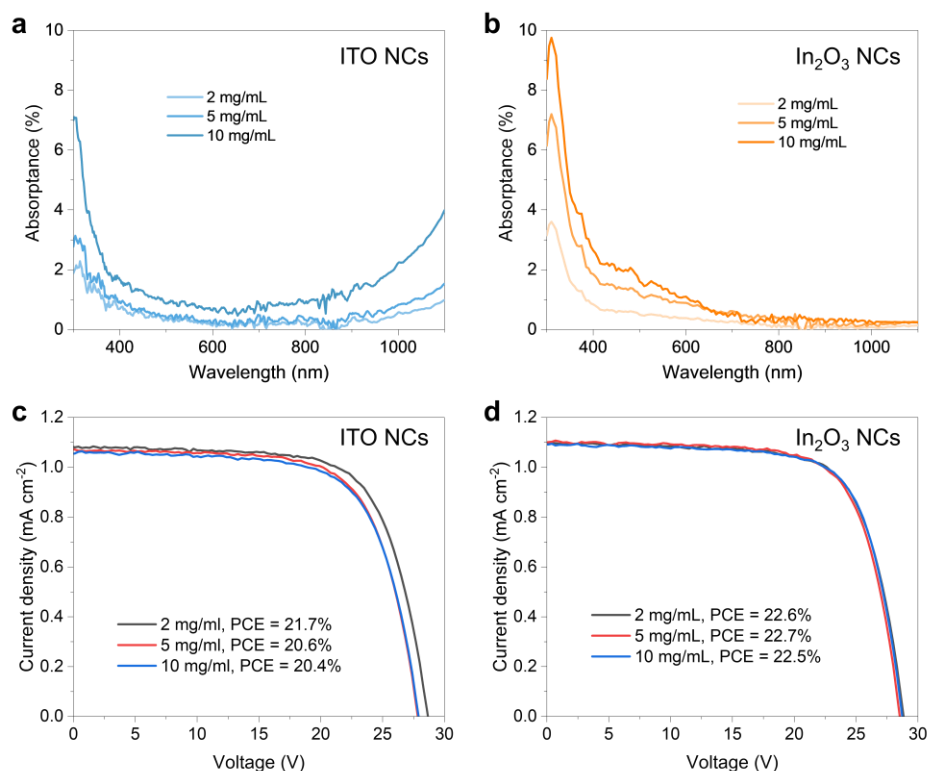
We have clarified this point and added the corresponding discussion in the revised manuscript:

"To verify that the superior performance of In₂O₃ NCs is intrinsic to the material rather than an artifact of thickness or morphological differences, we synthesized ITO NCs with comparable

particle size using the same synthetic route (**Supplementary Fig. 16**). When deposited under identical conditions, the size-matched ITO NCs still exhibited inferior optical transparency and device performance compared to In_2O_3 NCs (**Supplementary Fig. 17**), confirming that the advantages of In_2O_3 NCs originate from their intrinsic material properties."



Supplementary Figure 16 | Synthesis of ITO NCs. (a) TEM image of the self-synthesized ITO NCs. (b) Particle size statistics of ITO NCs. (c) HAADF-EDS of ITO NCs.



Supplementary Figure 17 | Optoelectrical property comparison. (a-b) Absorbance of different thickness of (a) ITO NCs and (b) In₂O₃ NCs using concentration from 2 mg/mL to 10 mg/mL. (c-d) Module performance comparison between ITO NCs and In₂O₃ NCs using concentration from 2 mg/mL to 10 mg/mL.

(2) Given that the perovskite/C₆₀/SnO₂/sputtered ITO architecture is already mature and widely adopted, particularly in semi-transparent perovskite devices and perovskite tandems, it is critical for the authors to justify why a solution-processed In₂O₃ TRJ is necessary. The manuscript does not provide a clear comparison showing advantages of the proposed NC In₂O₃ layer over sputtered ITO, which in many cases may offer superior industrial scalability and reliability. At present, the work does not convincingly demonstrate that the NC In₂O₃ TRJ delivers performance, stability, or manufacturability benefits relative to conventional sputtered ITO. Without such a comparison, the practical and scientific significance of replacing established sputtered TCOs remains uncertain.

Response: We thank the reviewer for raising this important point, which allows us to clarify the motivation for introducing a solution-processed In₂O₃ NC recombination layer in all-perovskite tandem solar modules.

Sputtered ITO and other TCOs such as IZO are indeed used in perovskite-based tandem solar cells. However, their application in monolithically interconnected tandem modules introduces an additional challenge related to the P2 interconnection structure. In series-connected tandem modules, the P2 channel directly exposes the recombination layer, creating a lateral electrical pathway between adjacent subcells. When the recombination layer exhibits high lateral conductivity, as is the case with sputtered ITO, this pathway can cause short-circuit between the

back electrode and conductive TCO layer in the TRJ, inducing leakage currents and reducing shunt resistance. This effect becomes increasingly pronounced as the module area increases, where longer P2 interconnection channels amplify lateral current leakage.

This module-level issue has previously motivated the use of low-conductivity Au clusters in tandem modules, as first demonstrated in our earlier work (Nature Energy, 2019, 14(10): 864–873) and subsequently adopted in several other high-efficiency tandem modules (e.g., Nature Energy, 2022, 7(7): 620–630; Nature Energy, 2022, 7(10): 923–931; Science 376, 762–767 (2022); Science 383, 855–859 (2024)). Despite these advances, the role of recombination-layer's lateral conductivity in governing module performance has yet been systematically investigated.

In this work, we address this issue by introducing a solution-processed In_2O_3 NC recombination layer designed to suppress lateral shunting while preserving excellent vertical charge recombination. Unlike sputtered ITO, which forms a continuous conductive film, the In_2O_3 NC-based layer forms a nanocrystal-interconnected network with limited lateral conductivity. This structural characteristic effectively suppresses P2-induced leakage pathways while preserving vertical charge recombination across the tunnel junction. In addition, the solution processability of In_2O_3 NCs enables low-temperature deposition without sputtering-induced damage and provides a scalable route compatible with large-area coating processes.

We have revised the manuscript and added a supplementary text as follow:

*"Although this structure enables efficient carrier recombination and suppresses lateral conductivity to prevent shunting (**Supplementary Fig. 1**), metal-based TRJ can introduce practical challenges during large-area fabrication."*

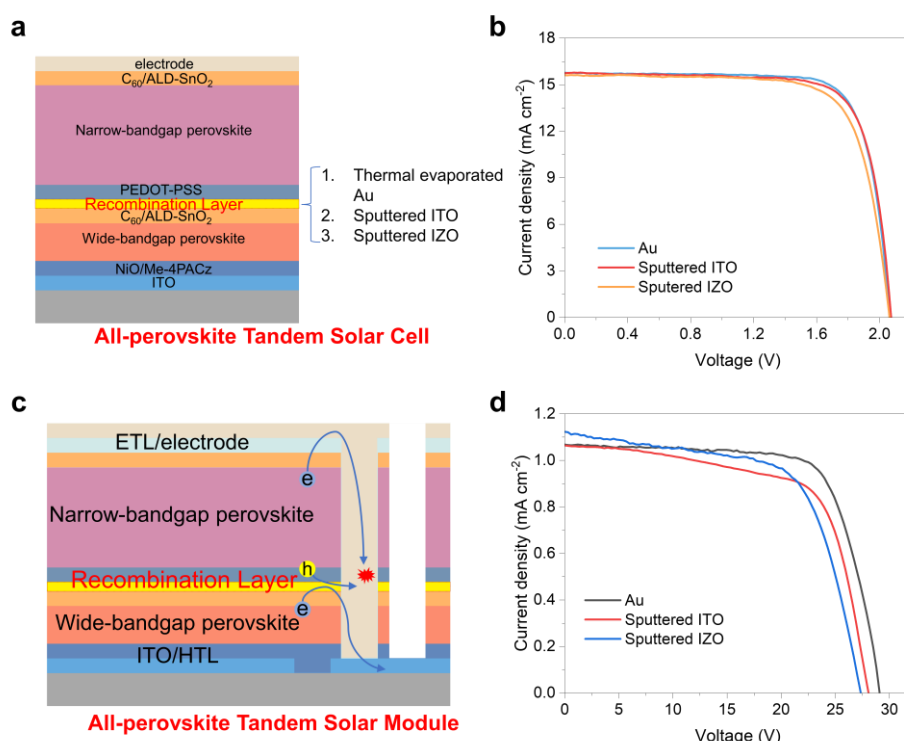
"Supplementary Text 1. Tunnel recombination junction for all-perovskite tandem solar modules

This note provides a comparative analysis between the proposed solution-processed In_2O_3 NC recombination layer and the conventionally used sputtered ITO, specifically addressing their applicability in monolithic all-perovskite tandem solar modules. While sputtered ITO is a mature and effective material for small-area tandem cells, its implementation in large-area interconnected modules introduces a critical challenge related to the P2 interconnection structure. In monolithically interconnected tandem modules, the P2 channel directly exposes the recombination layer, creating a lateral electrical pathway between adjacent subcells. When the recombination layer exhibits high lateral conductivity, as is the case with sputtered ITO, this pathway can cause short-circuit between subcells, inducing leakage currents and reducing shunt resistance. This effect becomes increasingly pronounced as the module area increases, where longer P2 interconnection channels amplify lateral current leakage.

The solution-processed In_2O_3 NC layer is specifically designed to address this module-level limitation. Unlike sputtered ITO, which forms a dense and continuous conductive film, the In_2O_3 NC-based layer forms a nanocrystal-interconnected network with inherently limited lateral conductivity while preserving excellent vertical charge recombination. This anisotropic conductivity effectively suppresses P2-induced leakage pathways without compromising the vertical charge recombination required across the tunnel junction. Additionally, the solution processability of In_2O_3

NCs enables low-temperature deposition without sputtering-induced damage and provides a scalable route compatible with large-area coating processes.

To verify these advantages, we provide a direct experimental comparison between different recombination layers at both the cell and module levels, as shown in Supplementary Fig. 1. Our results demonstrate that while sputtered ITO performs adequately in small-area tandem cells (0.049 cm^2 , Supplementary Fig. 1a and b), it leads to significant performance degradation in modules (65 cm^2) due to reduced shunt resistance and increased leakage current (Supplementary Fig. 1c). In contrast, the nanocrystal-based recombination layer effectively suppresses P2-induced shunting and maintains high module performance (Supplementary Fig. 1d). These results demonstrate that the In_2O_3 -based recombination layer addresses a module-specific limitation of conventional sputtered TCOs, establishing its practical and scientific significance for high-performance all-perovskite tandem solar modules."



Supplementary Figure 1 | Photovoltaic performance of all-perovskite tandem solar cells and modules using different recombination layers. (a) Configuration diagram of tandem structure using different recombination layers; (b) J-V curves of the all-perovskite tandem solar cells using different recombination layers; (c) Configuration diagram of the shunting in tandem solar modules while using sputtered TCO as recombination layers; (d) J-V curves of the all-perovskite tandem solar modules using different recombination layers.

(3) In Fig. 1f, Type II and III films exhibit significantly more uniform light absorption across the substrate. However, this improved optical uniformity does not lead to narrower J-V parameter distributions, especially J_{sc} , as shown in Fig. 1g. The authors should explain this inconsistency and clarify whether other variations, such as TRJ resistivity, perovskite crystallization, or series

resistance, dominate the device-scale variations.

Response: We thank the reviewer for this insightful observation regarding the relationship between optical uniformity and the distribution of device performance parameters.

In the tandem architecture used in this work, the optical influence of the TRJ primarily affects the average optical transmission toward the bottom Pb-Sn perovskite subcell, particularly in the 700-1100 nm wavelength range. Therefore, the improved optical uniformity observed in the Type II and Type III structures primarily increases the overall photocurrent generation, which is reflected in the higher average device performance.

However, the device-to-device variations in J_{sc} are governed predominantly by electrical rather than purely optical factors. In large-area tandem devices, the statistical distribution of J_{sc} is more strongly influenced by variations in charge transport and recombination processes. These include local variations in perovskite crystallization, interfacial non-radiative recombination, and spatial variations in series resistance. In addition, current matching between the top and bottom subcells further amplifies the impact of these electrical variations on the measured J_{sc} distribution. As a result, even when optical absorption becomes more spatially uniform, the overall distribution of J-V parameters can still be dominated by electrical and interfacial factors.

Therefore, the improved optical uniformity of the TRJ mainly enhances the average photocurrent, whereas the statistical spread of J_{sc} values is mainly determined by electrical variations and interfacial factors within the device.

(4) The work modifies the In_2O_3 nanocrystals using OAm, MMES, and MMPA. However, the functional group design of these materials is not given. In addition, the interactions between these materials and In_2O_3 are also not discussed when evaluating the surface tailoring of In_2O_3 .

Response: We thank the reviewer for raising important questions regarding the functional group design of the ligands used to modify the In_2O_3 nanocrystals and their interaction with the nanocrystal surface. The selection of OAm, MMES, and MMPA was not empirical but follows a stepwise ligand-engineering strategy guided by three design principles: (i) achieving stable surface anchoring, (ii) ensuring compatibility with industrial green-solvent processing, and (iii) enabling tunable interfacial energy-level alignment while preserving the nanocrystal size and crystal structure.

Oleylamine (OAm), a typical L-type amine ligand, was first employed during nanocrystal synthesis, enabling precise control over nanocrystal size, morphology, and crystallinity. However, the long hydrocarbon chain of OAm introduces a large tunneling distance between nanocrystals and limits compatibility with industrial green solvents. These limitations motivated the functional modification of surface ligands while maintaining the nanocrystal structural integrity.

To address solvent compatibility, ligand exchange was performed using mono-2-(methacryloyloxy)ethyl succinate (MMES), which contains a carboxylic acid anchoring group capable of coordinating with surface In^{3+} sites on In_2O_3 , together with polar ester functionalities that improve polarity matching and colloidal stability in the green solvent PGMEA. This carboxylate coordination replaces the weaker In-N interaction of OAm, forming stable In-O bonds while

significantly improving nanocrystal dispersibility in PGMEA without altering their size distribution or crystal structure. A direct manifestation of this ligand exchange is the drastic change in solubility: OAm-capped In_2O_3 nanocrystals are nearly insoluble in PGMEA (**Figure R1a, left**), whereas MMES- or MMPA-modified nanocrystals exhibit excellent dispersibility (**Figure R1a, right**). The successful surface modification was verified by ^1H NMR spectroscopy using MMES as a model ligand. Free MMES shows sharp proton signals at 5.6–6.1 ppm and 4.3 ppm in CDCl_3 (Fig. R1b). After ligand exchange, these peaks become significantly broadened and overlapped, consistent with restricted molecular motion upon surface binding. TEM and XRD analyses further confirm that the nanocrystal morphology and lattice structure remain unchanged after ligand exchange (**Fig. R1c–d**), indicating that the modification primarily alters the surface chemistry rather than the nanocrystal core structure.

To further tune the electronic structure, we designed the ligand MMPA by introducing a conjugated aromatic framework into the MMES structure. This modification alters the interfacial dipole and enables systematic tuning of the nanocrystal work function. Ultraviolet photoelectron spectroscopy (UPS) confirms that ligand modification shifts the Fermi level of In_2O_3 nanocrystals from -3.62 eV (OAm) to -4.49 eV (MMES) and -4.86 eV (MMPA) (corresponding to **Supplementary Figure 27** in the Supporting Information), enabling improved energy-level alignment with the perovskite layer.

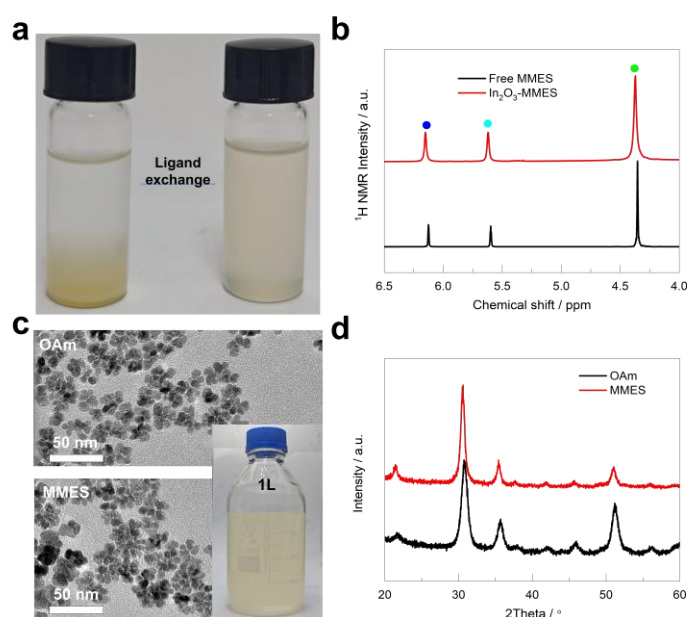


Figure R1. (a) MMES or MMPE capped In_2O_3 nanocrystals dissolve in PGMEA (right, after ligands exchange), while the same OAm capped In_2O_3 nanocrystals do not dissolve (light, before ligands exchange). (b) ^1H NMR of free MMES, and MMES-treated In_2O_3 nanocrystals in CDCl_3 . TEM (c, Inset: ≈ 30 mg/ml In_2O_3 nanocrystals dissolve in PGMEA) and XRD (d) images of In_2O_3 before and after ligand exchange.

We have revised the manuscript and added a supplementary text as follow:

"The choice of ligands was guided by a stepwise ligand-engineering strategy rather than empirical screening, aiming to achieve stable surface anchoring, compatibility with green-solvent processing, and tunable interfacial energy-level alignment while preserving the nanocrystal structure (Supplementary Text 2)."

"Supplementary Text 2. Ligand selection and surface engineering of In₂O₃ nanocrystals

Surface ligands for In₂O₃ nanocrystals were designed through a stepwise ligand-engineering strategy to achieve stable surface anchoring, compatibility with industrial green-solvent processing, and tunable interfacial energy-level alignment while preserving nanocrystal size and crystal structure.

Oleylamine (OAm) was used as the initial ligand during nanocrystal synthesis. As a typical L-type amine ligand, OAm coordinates with precursor species and regulates nucleation and growth kinetics, enabling precise control over nanocrystal size, morphology, and crystallinity. However, the long hydrocarbon chain of OAm increases interparticle tunneling distances and limits charge transport¹, and OAm-capped nanocrystals are typically dispersible only in nonpolar solvents such as toluene, which are incompatible with industrial green-solvent processing².

To enable green-solvent processing, mono-2-(methacryloyloxy)ethyl succinate (MMES) was introduced via ligand exchange. MMES contains a carboxylic acid anchoring group capable of coordinating with surface In³⁺ sites and polar functional groups compatible with the industrial solvent propylene glycol monomethyl ether acetate (PGMEA)^{3,4}. Replacement of OAm by MMES forms stable carboxylate-In coordination and enables stable nanocrystal dispersion in PGMEA without altering nanocrystal size or crystallinity. The surface binding of MMES was confirmed by broadened ¹H NMR signals after ligand exchange, while TEM and XRD measurements verify that the nanocrystal morphology and lattice structure remain unchanged.

To further tune the electronic structure, the ligand MMPA was designed by introducing a conjugated phenyl unit into the MMES framework. This modification increases molecular rigidity and modifies the molecular dipole, thereby modulating the interfacial electrostatic environment. Ultraviolet photoelectron spectroscopy (UPS) shows that ligand modification systematically shifts the Fermi level of In₂O₃ nanocrystals from -3.62 eV (OAm) to -4.49 eV (MMES) and -4.86 eV (MMPA), demonstrating that ligand-induced dipole engineering enables precise tuning of the nanocrystal work function and interfacial energy-level alignment."

(5) In Fig. 3a, the PbI₂ signal almost disappears for the target film, indicating suppressed PbI₂ formation. However, the authors use EDAl₂ for post-treatment, which typically reacts with residual PbI₂ for defect passivation. It is suggested to evaluate whether the extremely scarce amount of PbI₂ is sufficient to react with EDAl₂ and ensure the ideal passivation effect.

Response: We thank the reviewer for this insightful comment regarding the role of EDAl₂ post-treatment when the residual PbI₂ signal is significantly suppressed in the target film (Fig. 3a).

We agree that PbI₂ is commonly considered an important reactant for diammonium-based post-treatment. However, our analysis indicates that EDAl₂ passivation in our system proceeds through

two distinct pathways depending on the surface chemistry of the perovskite film.

In the control perovskite film, where residual PbI_2 is present, EDAI_2 primarily reacts with excess PbI_2 to form low-dimensional perovskite phases or coordination complexes that passivate grain-boundary defects. This mechanism is consistent with previous reports (Adv. Mater. 2024, 36, 2307701).

In contrast, for the target perovskite film (with minimal PbI_2), the dominant role of EDAI_2 is surface passivation rather than PbI_2 conversion. In this case, EDAI_2 can effectively passivate organic cation vacancies at the perovskite surface and form a favorable interfacial dipole, which improves energy-level alignment and facilitates electron transport. Similar passivation mechanisms for diammonium molecules have been reported in recent studies (Adv. Funct. Mater. 2025, 35, 2415797; Energy Environ. Sci. 2022, 15, 2096–2107).

Consistent with this interpretation, EDAI_2 post-treatment improves the device performance of both control and target devices (Fig. R2), indicating that effective passivation can be achieved even when residual PbI_2 is minimal.

Therefore, although the amount of residual PbI_2 in the target film is minimal, EDAI_2 post-treatment remains effective through surface-defect passivation and dipole formation, ensuring efficient interfacial passivation even in the absence of significant PbI_2 .

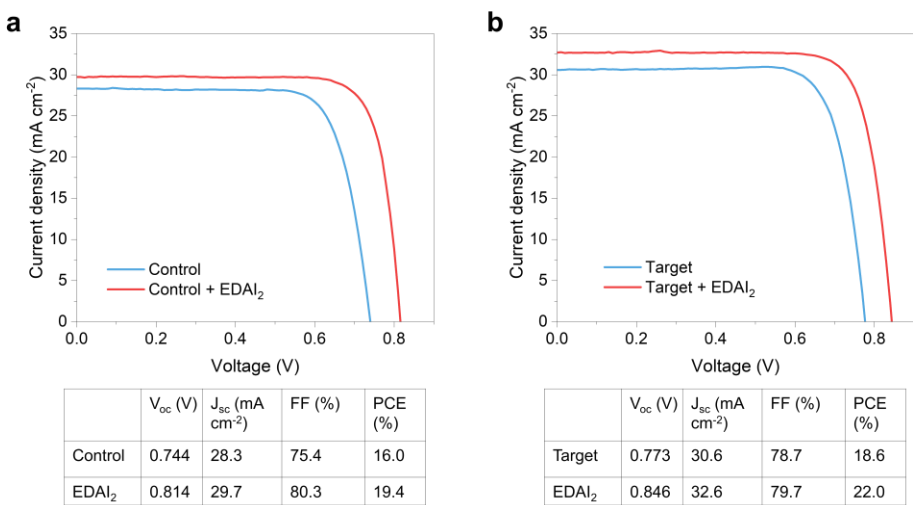


Figure R2. Performance of (a) control and (b) target Pb-Sn perovskite solar cells with and without EDAI_2 post treatment, respectively.

(6) In Fig. 4b, although the target film exhibits smaller peak-position variations across the substrate, the FWHM at positions 3 and 4 is broader than in the control film, suggesting lower crystallinity. This apparent contradiction should be reconciled, including whether the broadening arises from microstrain, reduced grain size, or orientation distribution.

Response: We appreciate the reviewer's insightful observation regarding the crystallinity in Fig. 4b. Our analysis suggests that the relevant structural unit in the target film is not the complete grain, but rather the domain (Joule, 2019, 3(12): 3048-3060). This domain structure is a result of grain

ripening facilitated by the incorporation of the HSM. These HSM-rich domains form at the interfaces between crystalline sub-units. Crucially, compared to typical grain boundaries, these domains exhibit a much lower defect density.

We also measured the FWHM of the 4 positions in both control and target perovskite films. As shown in Figure R3, the control film exhibited a gradually decreasing FWHM along the blade-coating direction, indicating inhomogeneous crystallization likely caused by localized rapid crystallization at the coating front. In contrast, the target film demonstrated superior spatial uniformity in crystallization. Consequently, the observed FWHM at positions 3 and 4 in the target film is broader than in the control film.

It is also worth noting that grain size alone does not play a decisive role in determining device performance, particularly in large-area modules. While the control film shows narrower FWHM at certain positions, this comes at the cost of spatial inhomogeneity. In contrast, the superior uniformity achieved in the target film is far more critical for the performance of large-area devices, as non-uniform crystallization can lead to localized shunts, voltage losses, and reduced reproducibility. Therefore, the slightly broader FWHM observed locally in the target film is an acceptable trade-off for achieving overall improved uniformity across the entire substrate.

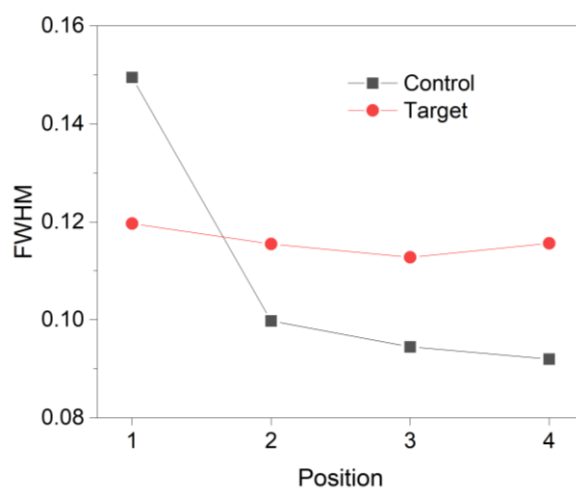


Figure R3. Corresponding FWHM from the XRD patterns in Fig. 4b of both control and target Pb-Sn perovskite films.

7. Although the MPP tracking tests and heat-damp stability tests all indicate the enhanced stability of the tandem photovoltaics, the in-depth mechanism is not given in this work. It is suggested to provide more experimental evidence and in-depth analysis.

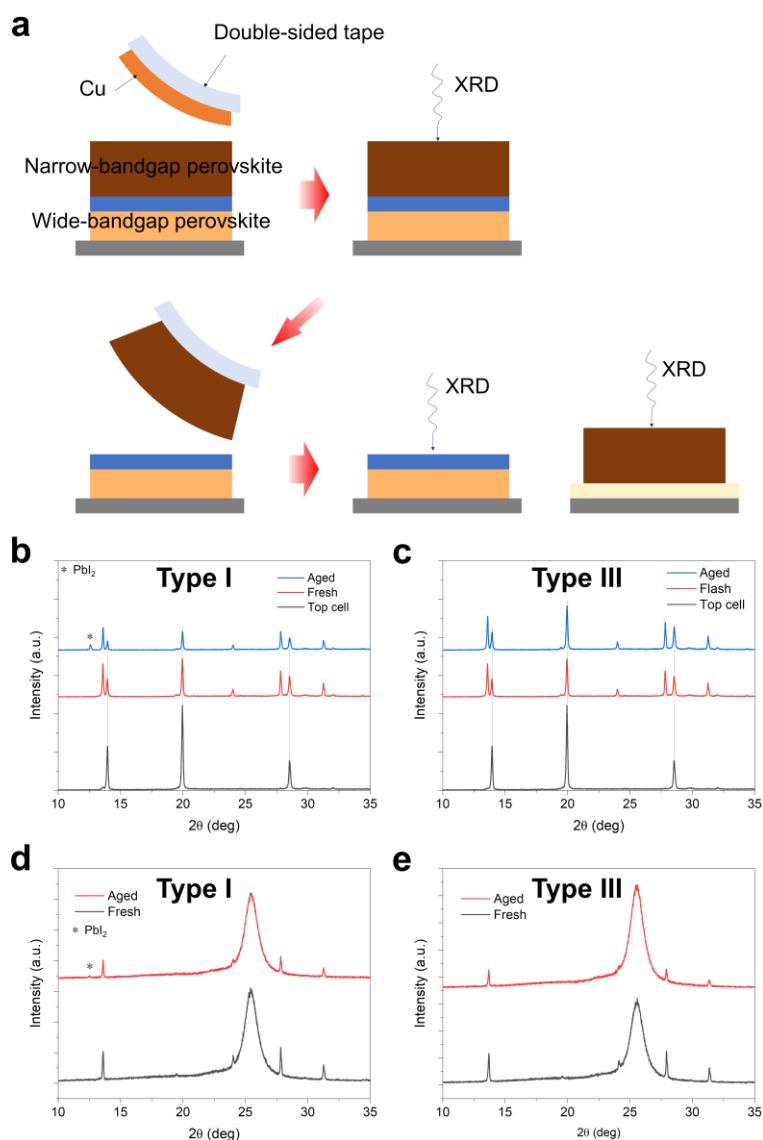
Response: We thank the reviewer for this important comment regarding the stability mechanism of the tandem devices. The thermal instability of the PEDOT-PSS/Pb-Sn perovskite interface is well-documented in prior literature (Nat. Energy 2019, 4, 939; ACS Energy Lett. 2020, 5, 1215; Solar RRL 2021, 5, 2100814; Adv. Energy Mater. 2022, 12, 2202948), with established degradation pathways involving Au diffusion and acidic PEDOT-PSS-induced decomposition. In this work, we further confirmed through XRD analysis (Supplementary Fig. 57) that degraded devices exhibit a PbI_2 peak, indicating that thermal stress during MPPT accelerates perovskite decomposition, consistent with

the acidic nature of PEDOT-PSS.

We have revised the manuscript as follow:

“Our analysis indicates that the significant performance degradation of the TSM is primarily attributable to the Type-I TRJ, which may induce the degradation of the Pb-Sn perovskite film from operating temperature and electrical bias (Supplementary Fig. 57).

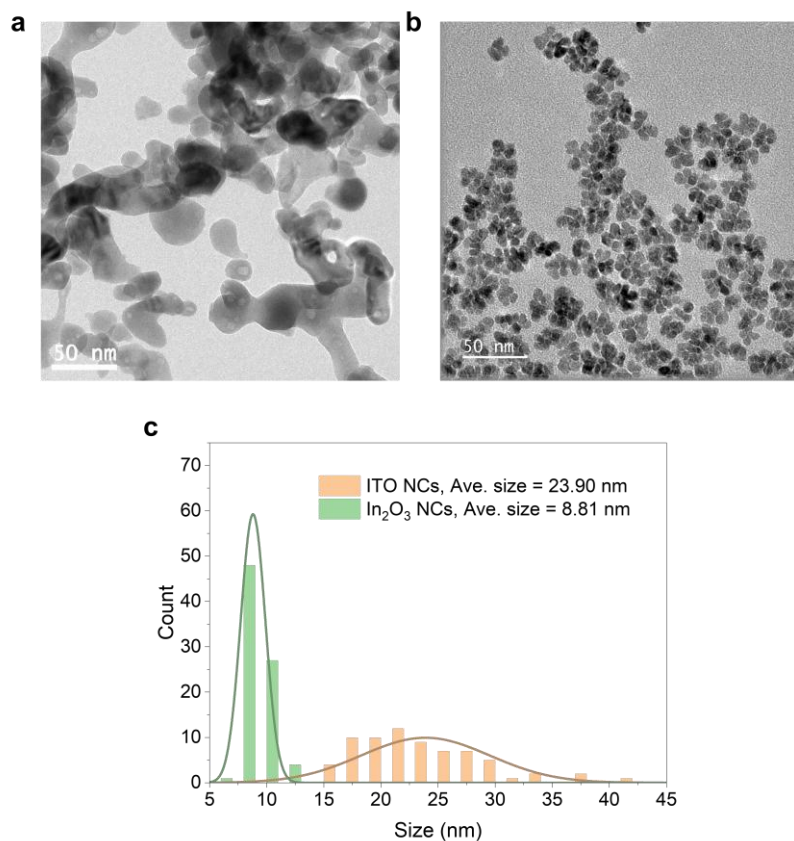
To assess performance under extreme conditions, we subjected devices to continuous illumination at open-circuit on a 65 °C hotplate (ISOS-L-3 protocol, Supplementary Fig. 58). The type-III TRJ module demonstrated exceptional stability throughout the 120-hour test. Furthermore, under damp heat testing (85 °C/85% RH, ISOS-D-3, Supplementary Fig. 59), the encapsulated type-III TRJ modules exhibited an average T84 lifetime of 1,000 hours, compared with a retention of below 40% for the type-I TRJ modules. We attribute the pronounced degradation of the type-I modules primarily to the thermal instability of the PEDOT-PSS layer, which is consistent with the thermal degradation trend observed in Fig. 1e. In contrast, the more gradual degradation of the type-III modules is mainly limited by the intrinsic instability of the MAFA perovskite composition, which is known to be less robust than MA-free or all-FA analogues.”



Supplementary Figure 57 | XRD patterns of different structures by peeling off the electrode and Pb–Sn perovskite layer in the TSMs after MPPT tracking. (a) Measured structure of tandem structure with peeled Cu, top cell with peeled Pb–Sn perovskite layer and peeled Pb–Sn perovskite layer attached to the glass substrate; (b and c) XRD patterns of type I (b) and type III (c) with peeled electrode and Pb–Sn perovskite layer before and after MPPT tracking aging; (d and e) XRD patterns of peeled Pb–Sn perovskite layers from type I (d) and type III (e) attached to the glass substrate before and after MPPT tracking aging. The widen peak arises from the attached tape.

8. Supplementary Fig. 3 contains an error: the TEM clearly shows larger ITO nanoparticles, whereas the label in panel c states that the In₂O₃ nanoparticles are larger.

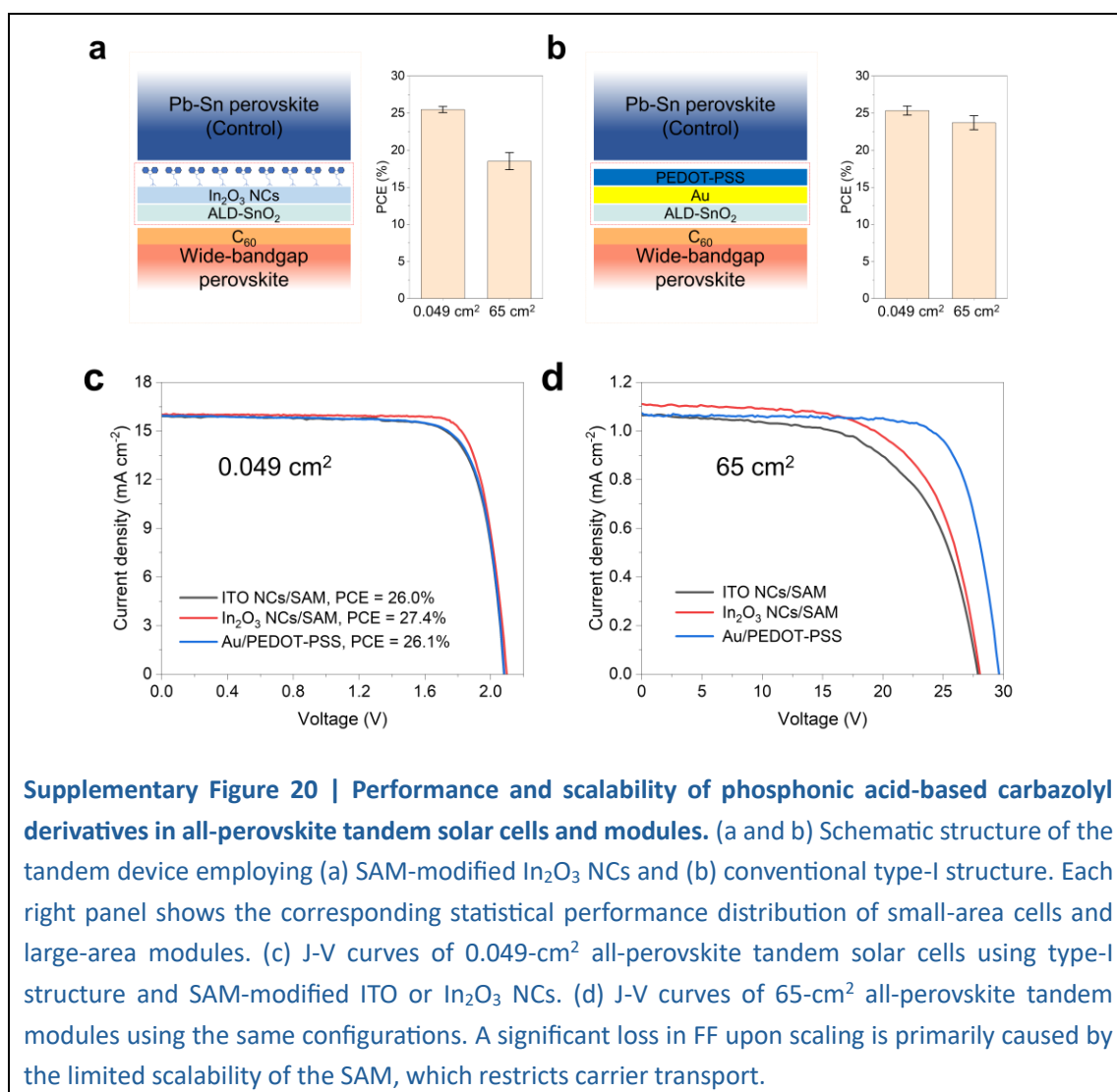
Response: We have corrected the figure in the revised manuscript.



Supplementary Figure 4 | Morphology comparison of ITO and In_2O_3 NCs. (a) TEM image of purchased commercial ITO NCs. (b) TEM image of self-synthesized In_2O_3 NCs. (c) Particle size statistics of ITO and In_2O_3 NCs.

9. Supplementary Fig. 7 only provides J-V curves for tandem devices based on ITO and In_2O_3 nanocrystals. For a complete comparison, the authors should also include tandem J-V data for the Type I structure.

Response: We now added the statistical performance and J-V curves of tandems using Type I structure in Supplementary Figure 20 (previously Supplementary Fig. 7)



10. Supplementary Fig. 14 presents statistics for V_{oc} , J_{sc} , and FF but does not include the most important parameter, PCE. This affects both completeness and the overall coherence of the figure.

Response: Figure 2e presents the PCE parameter of both control and target Pb-Sn PSCs fabricated using reduced PEDOT-PSS thicknesses. For clarity, the corresponding description in Supplementary Figure 31 (previously Supplementary Fig. 14) has also been revised accordingly:

Supplementary Figure 31 | Photovoltaic performance statistics of control and target Pb-Sn PSCs with reduced PEDOT-PSS thickness. (a) V_{oc} . (b) J_{sc} . (c) FF. The statistical PCE is shown in Fig. 2e. 10 devices for each type with aperture area of 0.049 cm^2 . The boxes and whiskers represent the standard deviation and the maximum and minimum of the distributions, respectively.

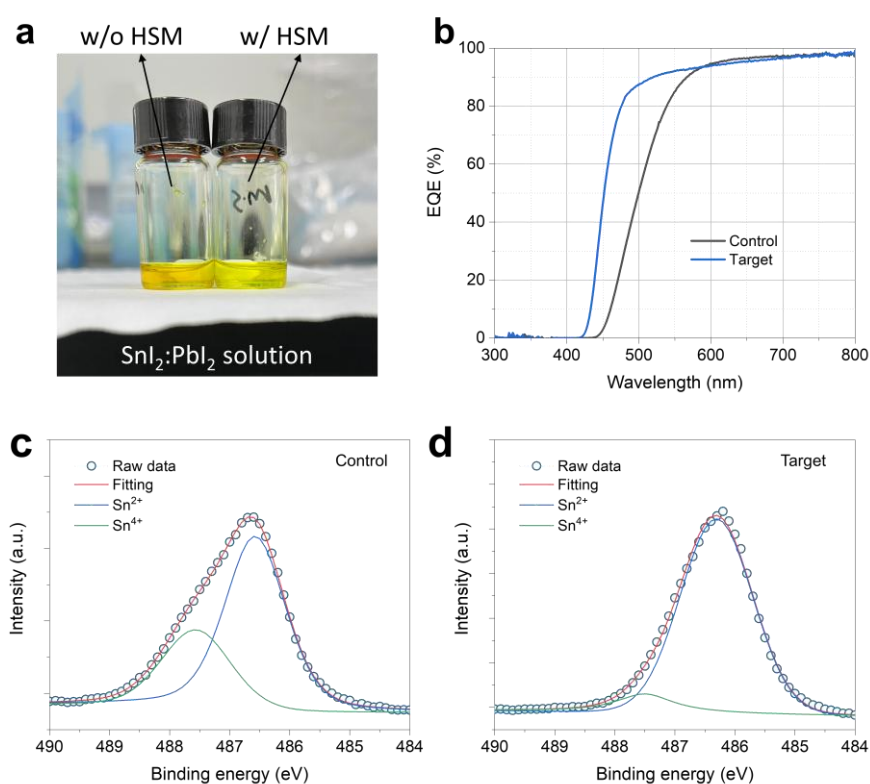
11. If available, the authors could strengthen the manuscript by including evidence related to Sn oxidation suppression (e.g., XPS $\text{Sn}^{2+}/\text{Sn}^{4+}$ ratio), which is particularly relevant to long-term stability for Pb-Sn mixed perovskites.

Response: We thank the reviewer for this valuable suggestion. We fully agree that evidence

regarding Sn^{2+} oxidation suppression is crucial for understanding the long-term stability of Pb-Sn mixed perovskites. In direct response to this comment, we have conducted additional optical and XPS analysis to distinguish the $\text{Sn}^{2+}/\text{Sn}^{4+}$ ratio.

The new data, now presented in Supplementary Figure 43, clearly demonstrates that the incorporation of HSM exhibits a significantly oxidation suppression of Sn^{2+} compared to the control sample after equivalent aging duration (e.g., under ambient exposure). The corresponding discussion has been added to the revised manuscript:

“The phosphonic acid anchor in the HSM also acts as an antioxidant barrier, significantly suppressing oxidation in the Pb-Sn perovskite. This protection is crucial for maintaining material integrity during transient air exposure, such as in the P2/P3 scribing steps or module measurement, which is essential for practical processing and operation (Supplementary Fig. 43).”



Supplementary Figure 43 | Oxidation suppression with HSM incorporation. (a) Digital photo of the $\text{SnI}_2:\text{PbI}_2$ mixed solution with and without HSM; (b) Corresponding optical absorption of the solution with and without HSM; (c and d) XPS spectra of Sn 3d for (c) control and (d) target Pb-Sn perovskite films.

12. For a module-focused work, a brief description of laser parameters, scribing width, and yield performance would help substantiate the high aperture efficiency and module uniformity.

Response: We thank the reviewer for the valuable suggestion. In response, we have added a detailed description of the optimized laser parameters, scribing geometry, and yield performance to the revised manuscript (see Supplementary Text 4). We believe this data provides transparent

and essential validation of the fabrication process used to achieve the reported high module performance.

Supplementary Text 4. Optimization of Laser Scribing Parameters for Module Fabrication

This note provides supplementary details on the optimization of the laser scribing processes (P1, P2, P3) used to fabricate the high-performance modules discussed in the main text. The optimization focused on three key aspects: wavelength selection, dead zone width, and P2 scribing energy.

1. Laser wavelength selection

To achieve clean and reliable pattern definition, three different laser wavelengths were evaluated for the P1, P2, and P3 scribing steps: infrared (1064 nm), green (532 nm), and ultraviolet (355 nm). The selection was based on the resulting scribe morphology, process stability, and material compatibility.

Based on these criteria, the optimal configuration was determined to be a 1064 nm laser for the P1 step and a 532 nm laser for both the P2 and P3 steps. It is noteworthy that the 355 nm laser produced ablation quality comparable to the 532 nm source, as illustrated in Supplementary Fig. 52. However, the 532 nm laser was ultimately adopted for the P2 and P3 processes due to its superior operational stability and higher throughput in our experimental setup.

2. Optimization of interconnection dead area width

The total interconnection dead area was optimized to balance aperture efficiency against manufacturing yield. This was achieved by systematically shifting the P2 and P3 scribes closer to the P1 scribe, as depicted in Supplementary Fig. 53.

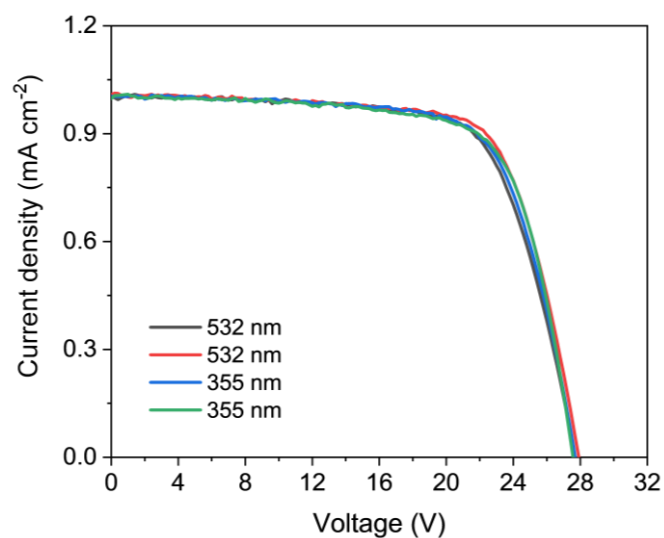
By adjusting the scribe positions, the dead zone width was successfully reduced from an initial value of 200 μm down to 160 μm and 155 μm . However, electrical characterization revealed that this reduction did not result in a significant improvement in the module's current density. Furthermore, reducing the dead zone to 155 μm increased the risk of electrical shunting due to undesirable contact or intersection between the P1 and P2 scribes, leading to a noticeable decrease in production yield. Consequently, a dead zone width of 160 μm was selected as the optimal compromise, ensuring both high aperture efficiency and robust process reliability.

3. Optimization of P2 Scribing Pulse Energy

The P2 process, which requires the precise removal of the absorber layer to expose the underlying transparent conductive oxide (TCO) without damaging it, was identified as the most critical step for series interconnection. To determine the optimal processing window, the laser pulse energy for the P2 scribe was varied systematically.

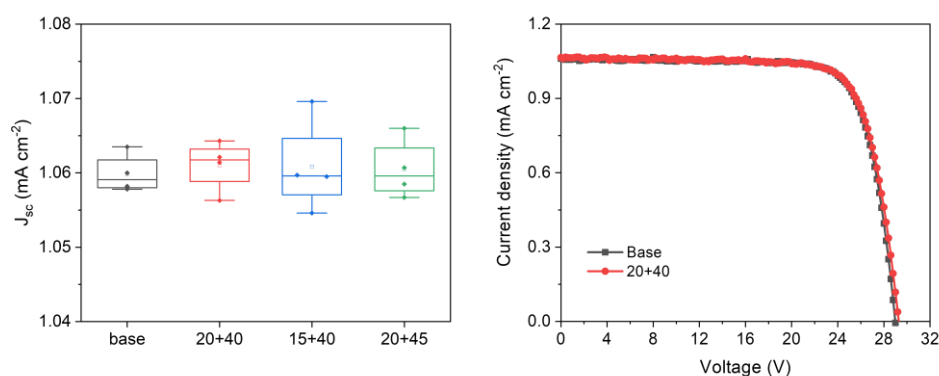
As shown in Supplementary Fig. 54, the pulse energy was increased from a regime of insufficient ablation (where residual absorber material remained, hindering conductivity) to a regime of excessive ablation (where the TCO layer was damaged). The optimal performance was achieved at a pulse energy of approximately 37 μJ . At this energy level, the absorber was cleanly ablated, leaving the TCO layer fully exposed and undamaged, which facilitates efficient series interconnection. Module performance was found to degrade at energies both below and above

this optimal point, confirming the importance of precise energy control for this step.



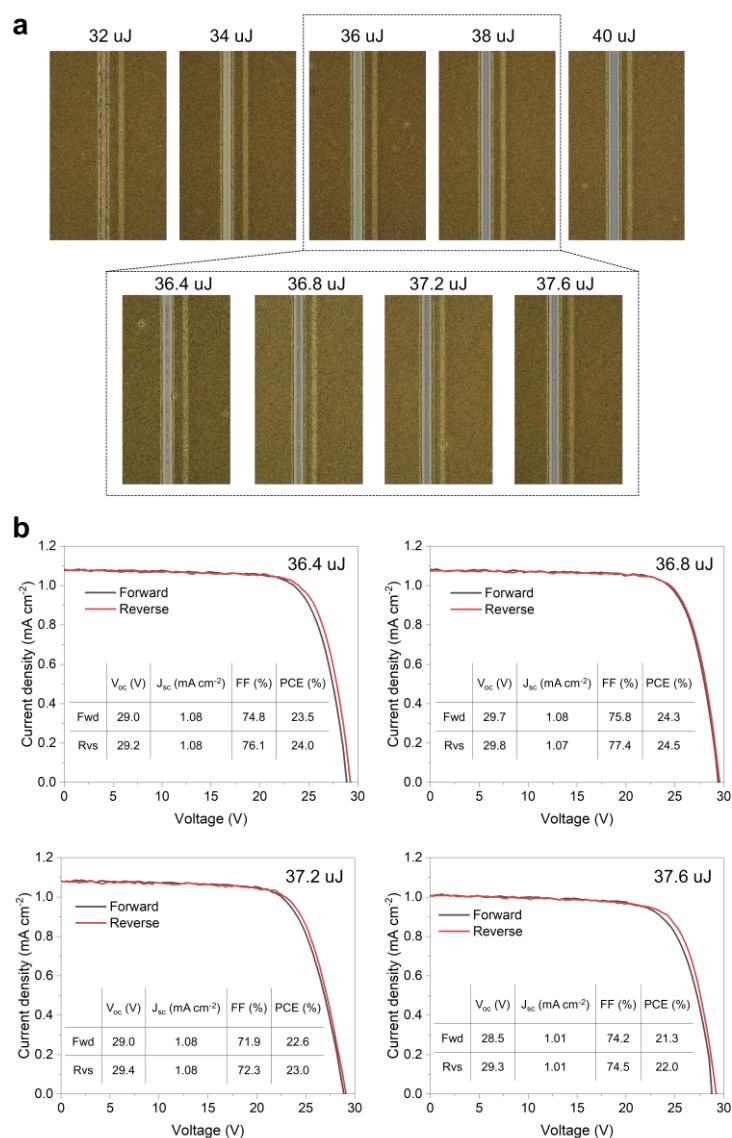
	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
532 nm	27.715	1.005	70.1	19.5
532 nm	27.886	1.009	71.8	20.2
355 nm	27.703	1.004	70.7	19.7
355 nm	27.260	0.997	72.3	19.8

Supplementary Figure 52 | J-V curves of all-perovskite TSMs using 532-nm or 355-nm scribing for P2 and P3.



	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
Base	28.813	1.063	78.0	23.8
20+40	29.310	1.065	76.9	24.0

Supplementary Figure 53 | Performance of all-perovskite TSMs with P2 and P3 patterning adjusted to reduce the dead area. The notation “20+40” indicates that P2 and P3 are shifted toward P1 by 20 μm and 40 μm , respectively, reducing the dead width from 200 μm to 160 μm . Similarly, “15+40” corresponds to shifts of 15 μm and 40 μm , also achieving a reduction from 200 μm to 160 μm . For “20+45”, shifts of 20 μm and 45 μm narrow the dead width from 200 μm to 155 μm .



Supplementary Figure 54 | Performance of all-perovskite TSMs with optimized P2 scribing power. (a) Digital photographs showing the effect of P2 laser power variation; (b) J-V characteristics of all-perovskite TSMs fabricated with different P2 scribing powers.

13. All figure captions containing error bars should explicitly state what the error bars represent and specify the number of devices (n). For device and module statistics, the sample size should be listed. For stability data, the authors should indicate whether the plotted curve is representative or averaged from multiple modules.

Response: We thank the reviewer for pointing out the need for greater clarity in our figure captions and statistical reporting. In accordance with the reviewer's suggestion, we have thoroughly revised the manuscript and the Supporting Information to ensure that all statistical information is explicitly stated.

The specific modifications are as follows:

Error bars and sample size: We have revised all relevant figure captions in the main text to explicitly

define the meaning of the error bars (e.g., standard deviation or min/max range). Additionally, the number of devices or modules (n) used for each set of statistics has been clearly specified. The same information has also been supplemented in the corresponding captions within the Supporting Information.

Stability Data: For the stability curves presented in the manuscript:

The representative curve (Figure 1e and 4f) is now clearly labeled as a “Representative module” in the caption, indicating it shows the typical performance evolution of a single device.

The statistical stability data (Supplementary Figure 59 and 60 which includes error bars, is now explicitly described in the caption as representing the “Average values obtained from multiple modules (n = 6)”, with the error bars indicating the standard deviation.

Fig. 1. Tunnel recombination junctions in all-perovskite TSMs. (A) Three types of TRJ in all-perovskite tandem structure. (B) Transmission electron microscope images of ITO NCs and In_2O_3 NCs. (C) Atomic force microscope images of ITO NCs and In_2O_3 NCs deposited on wide-bandgap subcells. (D) Absorption of the three types of TRJ deposited on quartz. The colored region is the response range of Pb-Sn perovskite subcell in tandem structure. (E) Thermal stability of encapsulated all-perovskite TSMs using different TRJs under 85°C ambient condition. (F) Optical absorption uniformity comparison among evaporated Au, blade-coated ITO NCs and In_2O_3 NCs within $10 \times 10 \text{ cm}^2$ substrates. (G) PV parameters of TSMs (aperture area: 65 cm^2 , 14 subcells in series) using three types of TRJ. 20 devices for type I and 12 devices for type II and III. The boxes and whiskers represent the standard deviation and the maximum and minimum of the distributions, respectively.

Fig. 2. Enhanced charge transport in Pb-Sn PSCs. (A) Schematic illustration of the co-optimization strategy: incorporating HSMs into the perovskite bulk and engineering the surface ligands of In_2O_3 NCs. (B) UPS spectra of the control and target perovskite films, as well as In_2O_3 NCs with different surface ligands, measured under an applied bias voltage. (C) Close-up of the Fermi edge region from the UPS spectra of the samples measured without an external bias voltage. (D) Energy level alignment diagram for the various In_2O_3 NCs, perovskite films, and C_{60} derived from the UPS results. (E) PV performance of control and target Pb-Sn PSCs fabricated with reduced PEDOT-PSS thicknesses. 10 devices for each type with aperture area of 0.049 cm^2 . The boxes and whiskers represent the standard deviation and the maximum and minimum of the distributions, respectively. (F) J-V curves of the champion target PSCs based on In_2O_3 NCs with different ligands (aperture area: 0.049 cm^2). (G) EQE curves of the corresponding best-performing PSCs shown in (F).

Referee #2 (Remarks to the Author):

In this work, Ke et al. present a comprehensive approaches to enhance the overall performance of all-perovskite tandem solar modules. The key strategies employed in this research are summarized as follows: 1. The development of a novel recombination layer incorporating In_2O_3 nanoparticles, which replaces the conventional hygroscopic, acidic PEDOT:PSS layer and Au islands. This approach effectively minimizes parasitic absorption from Au islands and improves long-term stability, primarily by eliminating PEDOT:PSS. 2. The ligand for the In_2O_3 NCs was changed from OAm to MMPA to effectively modulate the energy levels and facilitate hole transport in the absence of a PEDOT:PSS layer. 3. The incorporation of HSM (MeO-2PACz) resulted in the improved device performance even without PEDOT:PSS layer. 4. The solvent system was changed from DMF:DMSO to a 2-ME:THF system to mitigate the issue of film thickness deviation across large-area substrates. The resulting all-perovskite tandem solar modules demonstrated a power conversion efficiency of 26.6% (in-house) and a certified efficiency of 26.2% (by JET, for an area of 65 cm^2), establishing the highest efficiency reported to date. Furthermore, the developed modules exhibited notable long-term stability, including retaining 82.5% of the initial efficiency after 1000 h (Maximum Power Point Tracking, 1 sun), ~80% after 120 h (65°C , 1 sun), 84% after 1000 h (Damp Heat), and 93% after 200 cycles (Thermal Cycling). This reviewer considers the results presented in this work to be a significant contribution toward the commercialization of all-perovskite tandem solar modules. Consequently, I recommend this work for publication in Nature, after the revision on the comments outlined below.

Response: We thank the reviewer for the positive assessment and valuable comments on our work. We appreciate the reviewer's recommendation for publication in Nature and will carefully address all the comments outlined below to further strengthen the manuscript.

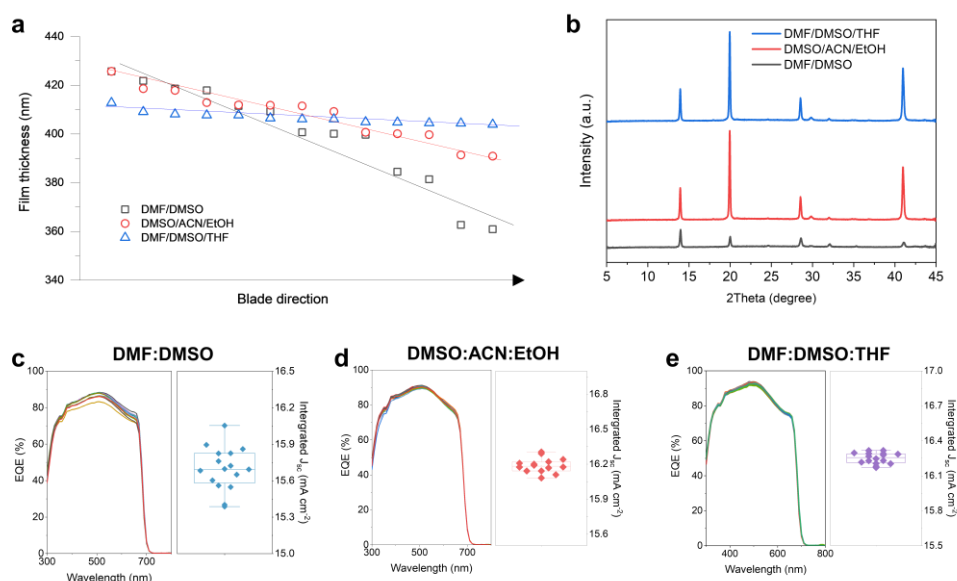
1. Previously, the authors' group demonstrated the improved performance of wide-bandgap and all-perovskite tandem solar modules using a green solvent system (ACN:EtOH:DMSO) (Nat. Energy 10, 318, 2025). However, in the current work, the WBG perovskite was fabricated using the conventional DMF:DMSO system. Is there a specific reason for selecting this solvent system? It would be valuable if the authors could provide a comparison or additional data utilizing the previously reported green solvent system to justify this choice.

Response: We thank the reviewer for this insightful question regarding the choice of solvent system for the WBG perovskite layer. While our previously reported ACN:EtOH:DMSO green solvent system performs well for small-area modules, it produced a significant thickness gradient when scaled to $10 \times 10\text{ cm}^2$ substrates due to its slow evaporation kinetics. We therefore developed a DMF:DMSO:THF ternary system with faster evaporation, which eliminated the thickness gradient and enabled more uniform film formation, as evidenced by the narrower EQE-integrated J_{sc} distribution across large-area modules.

We have revised the manuscript as follow:

"The incorporation of THF into the wide-bandgap perovskite can also improve coating speed and film uniformity, outperforming our previously reported green solvent system (Supplementary Fig. 12). This improvement enabled a 17.5% efficiency on a 65 cm^2 aperture area (Supplementary Fig.

13), highlighting its excellent scalability of this approach."



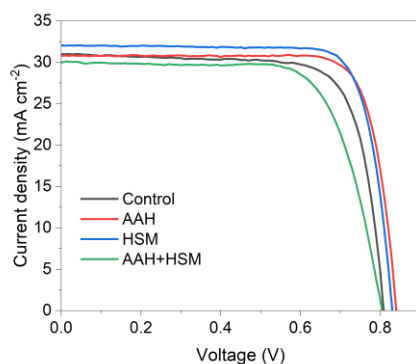
Supplementary Figure 12 | Comparison of different solvent systems. (a) Film thickness evolution along with the coating direction based on $10 \times 10 \text{ cm}^2$ substrates. (b) XRD patterns of $\text{Cs}_{0.35}\text{FA}_{0.65}\text{PbI}_{1.8}\text{Br}_{1.2}$ wide-bandgap perovskite using different solvent systems. (c-e) EQE spectra and corresponding integrated J_{sc} of wide-bandgap topcell fabricated using different solvent systems in tandem solar modules.

2. Similarly, the authors' group previously reported the beneficial effects of adding aminoacetamide hydrochloride (AAH) to the perovskite precursor solution (Science 383, 855, 2024). Given its proven efficiency, could the authors comment on why AAH was not employed in this study, or provide additional results based on AAH?

Response: We thank the reviewer for raising this important point regarding the use of aminoacetamide hydrochloride (AAH), which we previously reported as an effective additive for improving Pb–Sn perovskite solar cells (Science 383, 855, 2024). Our experiments revealed that the previously reported AAH additive is incompatible with the phosphonic-acid-based HSM used in this work, as devices containing both additives showed significantly lower performance (Supplementary Fig. 23).

We have revised the manuscript as follow:

"However, we found that HSM is incompatible with the previous reported aminoacetamide hydrochloride (AAH) additive (Supplementary Fig. 23). We attribute this mutual exclusivity to potential chemical interactions or competition between the amino-functionalized AAH and the phosphonic acid anchoring group of HSM at grain boundaries, which may disrupt passivation and charge extraction. This finding provides guidance for the selection and combination of additives in perovskite bulk."



Supplementary Figure 23 | Photovoltaic performance of Pb-Sn perovskite solar cells with different additives.

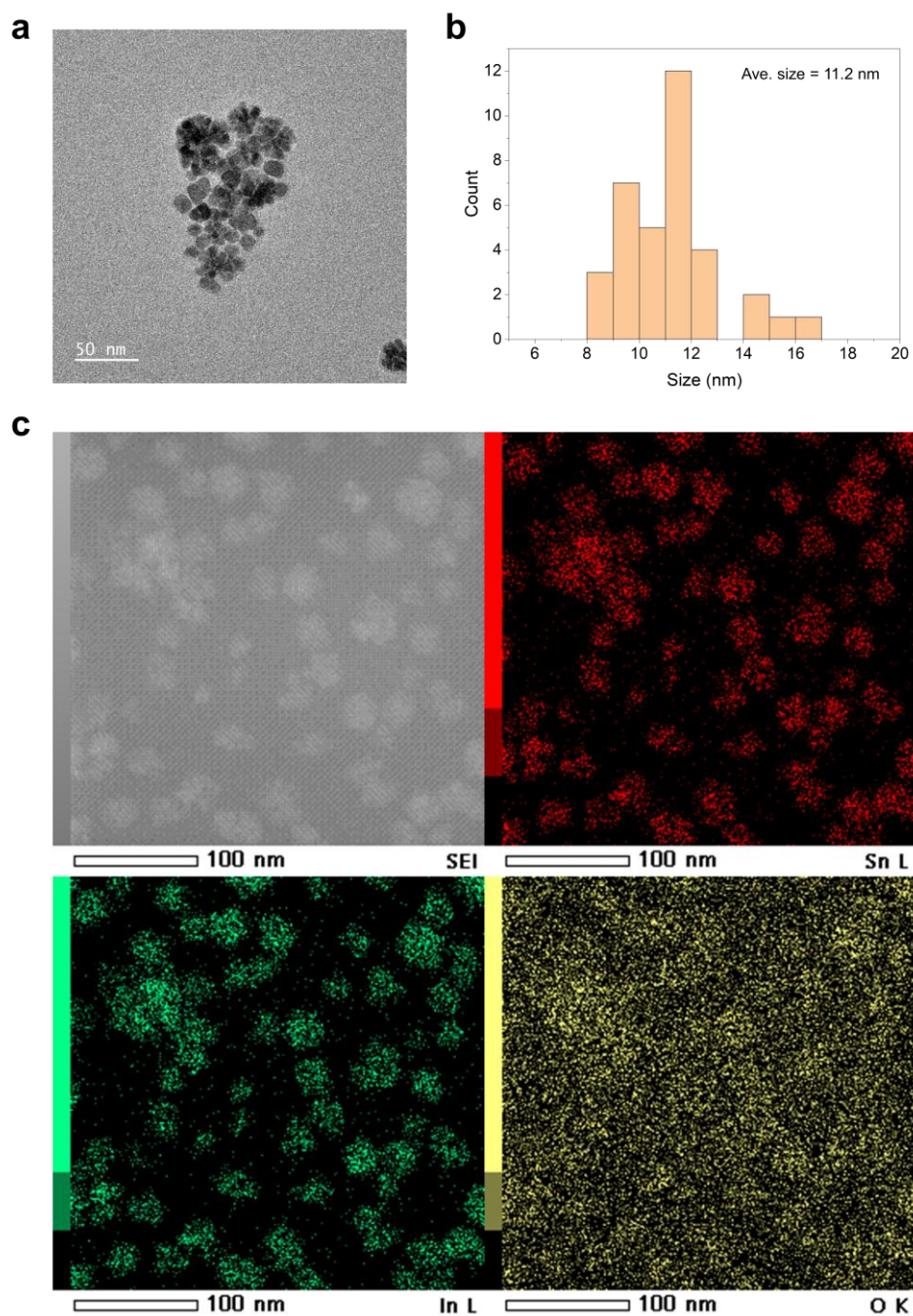
3. In this work, the authors successfully replaced the Au/PEDOT:PSS system with In_2O_3 NPs. On Page 5, it is stated that the Type III (In_2O_3 NPs) system is advantageous over Type II (ITO NPs) due to improved smoothness and optimized electronic contact. However, there is a significant difference in particle size between the ITO NPs and In_2O_3 NPs used. Therefore, the observed performance difference might be influenced by the size effect rather than solely by the material properties. In order to improve the clarity, I suggest decoupling the size effect from the material comparison. Comparison data using ITO and In_2O_3 NPs of similar dimensions would be preferred to support this claim.

Response: We thank the reviewer for this insightful suggestion regarding the possible influence of nanoparticle size on the comparison between ITO and In_2O_3 NC-based recombination layers.

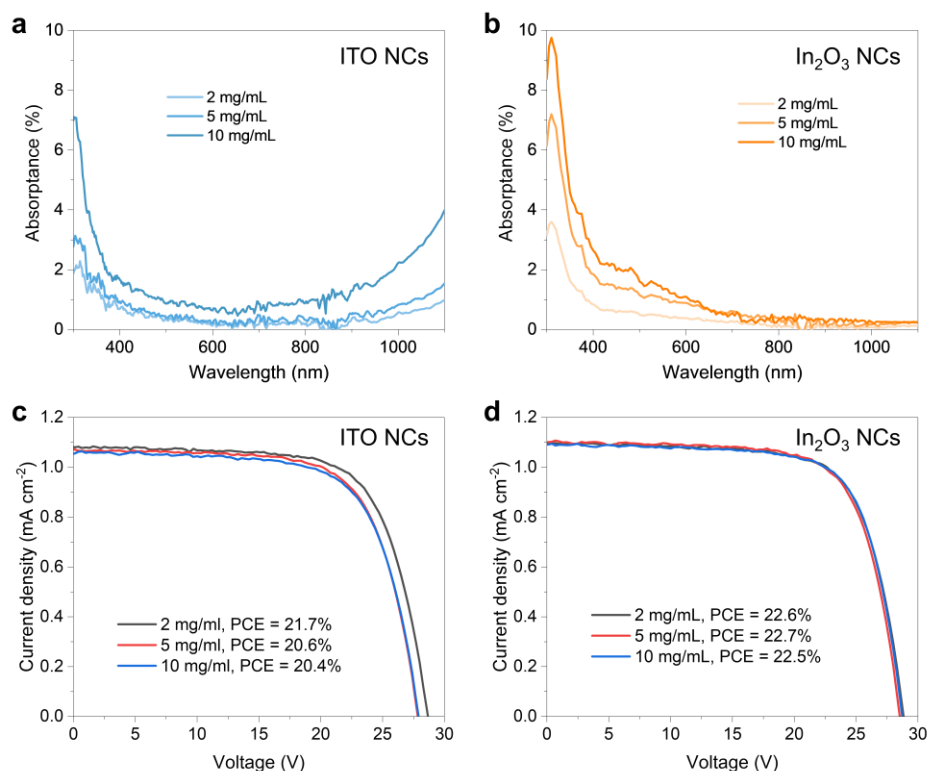
To decouple size effects from material properties, we synthesized ITO NCs with comparable size to In_2O_3 NCs using the same method (Supplementary Fig. 16). Under identical deposition conditions, the In_2O_3 NC layers still exhibited superior optical transparency and device performance (Supplementary Fig. 17), confirming that the advantages originate from the intrinsic properties of In_2O_3 rather than particle size differences.

We have revised the manuscript as follow:

“To verify that the superior performance of In_2O_3 NCs is intrinsic to the material rather than an artifact of thickness or morphological differences, we synthesized ITO NCs with comparable particle size using the same synthetic route (Supplementary Fig. 16). When deposited under identical conditions, the size-matched ITO NCs still exhibited inferior optical transparency and device performance compared to In_2O_3 NCs (Supplementary Fig. 17), confirming that the advantages of In_2O_3 NCs originate from their intrinsic material properties.”



Supplementary Figure 16 | Synthesis of ITO NCs. (a) TEM image of the self-synthesized ITO NCs. (b) Particle size statistics of ITO NCs. (c) HAADF-EDS of ITO nanocrystals.



Supplementary Figure 17 | Optoelectrical property comparison. (a-b) Absorbance of different thickness of (a) ITO NCs and (b) In₂O₃ NCs using concentration from 2 mg/mL to 10 mg/mL. (c-d) Module performance comparison between ITO NCs and In₂O₃ NCs using concentration from 2 mg/mL to 10 mg/mL.

4. In Line 107, the authors that “In₂O₃ NCs-based TRJ exhibited the most ideal homic contact behavior...”. However, the results seem that resistance value extract from the measurement would be larger for In₂O₃ than ITO, which is detrimental to the device performance. Could the authors provide a more detailed explanation of this discrepancy and clarify how "ideal ohmic behavior" is defined in this context despite the apparent resistance values?

Response: We thank the reviewer for this insightful comment. We agree that "the most ideal" in Line 107 is imprecise and have revised it accordingly. We have clarified that "ohmic behavior" refers specifically to the linearity of the I-V characteristics, indicating barrier-free contact, rather than the absolute resistance value.

We have revised the manuscript as follow:

“Electrical measurements of the three types of TRJ revealed that the In₂O₃ NCs-based TRJ exhibited the desired ohmic contact behavior, characterized by a linear I-V response that indicates the absence of a charge transport barrier (Supplementary Fig. 3).”

5. Replacing PEDOT:PSS with an In₂O₃ NP layer with tailored ligands is shown to be effective. However, other studies have suggested neutralizing PEDOT:PSS as an alternative strategy to

minimize corrosion and degradation issues. To rigorously evaluate the superiority of the proposed strategy, could the authors compare the stability of the Type III (In_2O_3) system with that of a neutralized PEDOT:PSS-based control?

Response: We thank the reviewer for this valuable suggestion. To address this point, we performed a direct comparison using commercial PEDOT:PSS as a control.

Our comparison as shown in Figure R4 shows that while neutral PEDOT:PSS improves thermal stability over standard PEDOT:PSS, it still underperforms relative to the In_2O_3 NC-based devices. More importantly, neutral PEDOT:PSS retains the strong parasitic absorption in the near-infrared region, which limits photocurrent in the narrow-bandgap bottom cell, whereas In_2O_3 NCs provide high transparency across the entire spectrum, offering a critical optical advantage for tandem architectures.

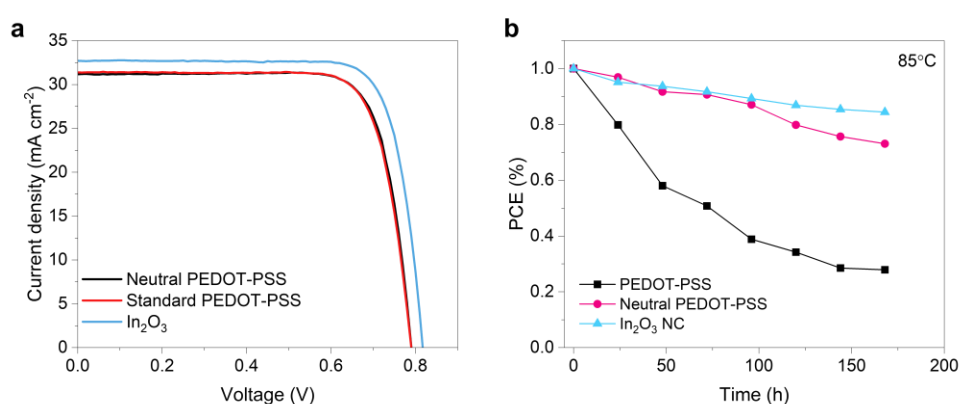


Figure R4. Performance comparison of Pb-Sn perovskite solar cells based on the standard PEDOT:PSS and neutral PEDOT:PSS. (a) Photovoltaic performance of Pb-Sn perovskite solar cells based on different HTLs. (b) Stability of the Pb-Sn perovskite solar cells based on different HTLs.

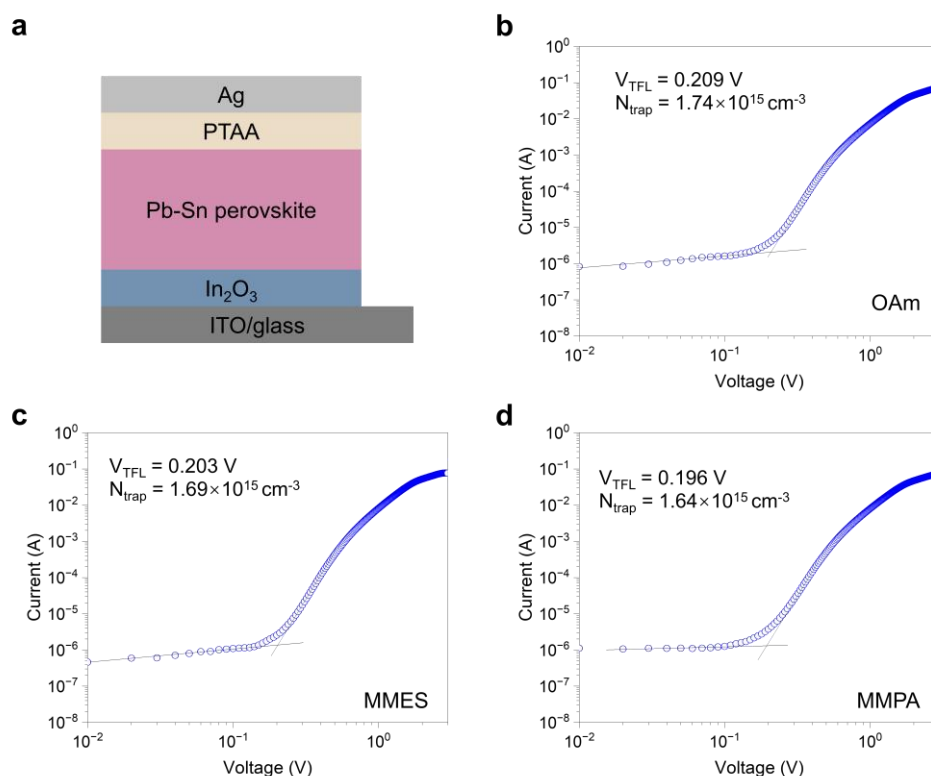
6. The ligand used for In_2O_3 differs significantly among themselves in terms of functional groups, quantity, and steric volume. While the authors explain the advantages from better energy alignment for MMPA, such a change in ligands may also alter charge transport characteristics. I recommend that the authors provide charge transport measurements, such as Space Charge Limited Current (SCLC) or Transient Photocurrent (TPC) analysis, to verify the carrier transport efficiency of the MMPA-capped In_2O_3 NPs.

Response: We thank the reviewer for this helpful suggestion regarding the possible influence of ligand chemistry on charge transport properties.

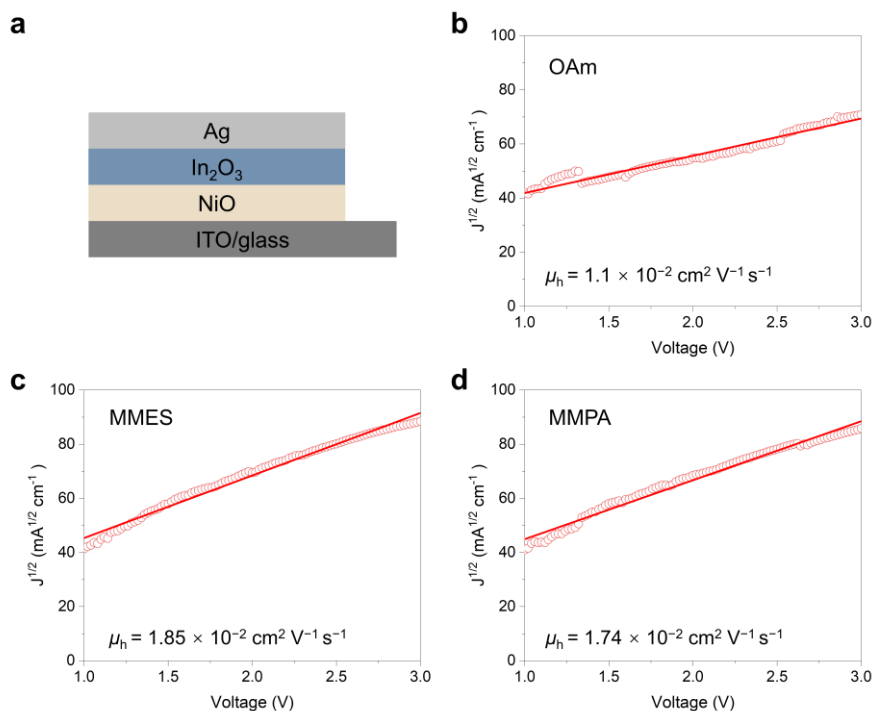
Following the recommendation, we performed SCLC measurements to evaluate trap density and hole mobility for In_2O_3 NCs capped with different ligands (OAm, MMES, and MMPA). The results show that all three ligands yield comparable trap densities ($\sim 1.7 \times 10^{15} \text{ cm}^{-3}$), and the MMES- and MMPA-capped films exhibit very similar hole mobilities, indicating that MMPA does not introduce additional transport limitations. Therefore, the improved device performance with MMPA-capped In_2O_3 NCs primarily originates from optimized interfacial energy alignment rather than enhanced charge transport.

We have revised the manuscript as follow:

*"To exclude the influence of the ligands on charge transport, we further characterized the interfacial defects and hole mobility via space-charge-limited current (SCLC) measurements (**Supplementary Fig. 28 and 29**). The results show negligible differences in trap density and mobility between MMES- and MMPA-capped In_2O_3 , confirming that the enhanced hole extraction primarily originates from the optimized energy band alignment rather than altered transport properties."*



Supplementary Figure 28 | Current-voltage traces and trap density of Pb-Sn perovskites as determined by the SCLC method. (a) Hole-only device structure constructed to obtain the hole trap density. The trap density N_{trap} is determined by the equation: $V_{\text{TFL}} = qN_{\text{trap}}L^2/(2\epsilon\epsilon_0)$, where V_{TFL} is trap-filled limit voltage, L is the thickness of perovskite film, ϵ is the relative dielectric constant of perovskite, and ϵ_0 is the vacuum permittivity. (b-d) I-V curves of the hole-only devices using In_2O_3 NCs with (b) OAm, (c) MMES and (d) MMPA.



Supplementary Figure 29 | Measurement of hole mobility by the SCLC model. (a) Device structure constructed to obtain the hole mobility. The hole mobility μ_h is determined by the Mott-Gurney law: $\mu_h = 8JL^3 / (9\varepsilon_0\varepsilon_r V^2)$, where J is the current density, L is the thickness of In_2O_3 NCs, ε_0 is the vacuum permittivity, and ε_r is the dielectric permittivity of In_2O_3 NCs. (b-d) $J^{1/2}$ - V curves of the hole-only devices using In_2O_3 NCs with (b) OAm, (c) MMES and (d) MMPA.

7. In Page 9, the authors state that adding HSM results in the compensation for the deprotonation of FA^+ . If HSM molecules are utilized to prevent FA^+ deprotonation, their ability to bind to the surface might be compromised or altered. Could the authors explain this mechanism? Additionally, a more detailed interpretation of the NMR spectra regarding the hydrogen bonding between the phosphonic acid and FAI would help clarify the interaction mode.

Response: We thank the reviewer for this helpful suggestion regarding the interpretation of the NMR spectra and the interaction mechanism between the phosphonic-acid-based HSM and FAI.

Following this comment, we carefully re-examined the NMR data in Fig. 3b to clarify how HSM regulates FA^+ deprotonation while still retaining its ability to anchor at the perovskite surface. We have revised the manuscript as follow:

"The natural deprotonation of FA^+ cations leads to A-site vacancies and unreacted PbI_2 accumulation⁴⁴. Liquid-phase ^1H NMR spectroscopy (Fig. 3b) reveals the role of HSM in mitigating this issue. Upon mixing HSM with FAI, the proton signal corresponding to the phosphonic acid group (P-OH) disappears completely, indicating deprotonation of the phosphonic acid functionality in the precursor solution. Concurrently, the FA^+ proton resonance evolves from a broad peak into a resolved multiplet with only a minor chemical-shift change. This spectral evolution suggests the presence of weak interactions between the deprotonated HSM species and FA^+ in solution. Such

interactions perturb the local environment of the FA⁺ ammonium protons and may partially break the symmetry of the FA⁺ cation, giving rise to the observed multiplet structure. The minimal shift in resonance indicates that the interaction remains relatively weak, consistent with a dynamic solution-phase association rather than the formation of a strongly bound complex. Such interactions modulate the precursor chemistry during crystallization and help stabilize the perovskite formation process."

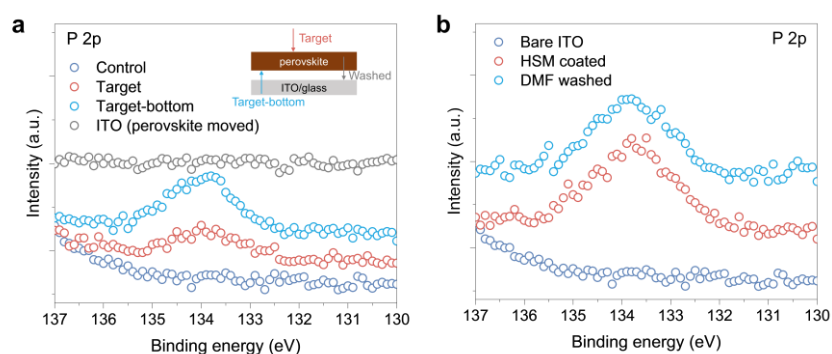
8. In Page 10, authors state that " ... the interaction between HSMs and perovskite grains is significantly stronger than the binding affinity of the phosphonic acid anchoring group to the hydroxyl surface groups on the ITO." If the statement is true, then the authors should compare the bare HSM film before and after washing by DMF. We believe that the MeO-2PACz molecules are easily washed by polar solvent, DMF, so this result does not support the author's statement.

Response: We thank the reviewer for raising this important point. We agree that our original phrasing was imprecise and have revised it accordingly. Rather than implying that the interaction between HSM and perovskite grains is intrinsically stronger than the phosphonic-acid binding to ITO, our intention was to indicate that HSM exhibits a preferential affinity toward the perovskite phase under the processing conditions used in this work.

Control experiments confirm that when HSM is pre-assembled as a SAM on ITO, it remains intact after DMF washing (Supplementary Fig. 40), indicating stable phosphonic-acid anchoring. However, in our fabrication process, HSM is dissolved in the perovskite precursor solution and preferentially interacts with perovskite components during crystallization rather than migrating to form a SAM on ITO. Therefore, HSM is removed together with the perovskite phase upon solvent washing, which is consistent with its incorporation at grain boundaries rather than indicating weak binding to ITO.

We have revised the manuscript as follow:

"However, upon removal of the target perovskite film, we noticed no residual HSMs on the ITO substrates (Supplementary Fig. 40). This observation suggests that, when incorporated into the perovskite precursor solution throughout the film formation process, HSMs exhibit a preferential affinity for perovskites over the ITO substrate."



Supplementary Figure 40 | The P 2p XPS spectra of different film surfaces. (a) Insert is a schematic

of the location of the XPS probe. It revealed that the distribution of HSM at the bottom interface of the perovskite film was higher than that at the top surface, while no HSM residue was found on the ITO surface after washing with DMF. (b) After DMF washing, the anchored self-assembled molecular still existed on the ITO substrates. The phosphorus signal persists after washing, confirming that the phosphonic acid anchoring group can form a stable bond with the ITO surface when directly deposited. These results collectively demonstrate that in our solution-processed architecture, HSM preferentially interacts with perovskite components during crystallization rather than forming a SAM on ITO, explaining its removal together with the perovskite phase upon solvent washing.

9. The authors significantly improved the quality of large-area films by changing the solvent system from DMF:DMSO to 2-ME:THF. The authors stated that "...DMF-based system requires a significantly slower coating speed of 5 mm/s..." and "This speed limitation becomes increasingly problematic during scale-up, while the optimized coating speed must be progressively reduced for larger substrates...". However, slower coating speed can also be easily overcome by changing the concentration of solution for DMF:DMSO system. Therefore, I do not believe that this comparison is valid enough to support the superior properties of 2-ME:THF. At least, the device/module based on DMF:DMSO system should be optimized in terms of concentration, to compare the effectiveness of new solvent system. Could the authors explain in detail or provide additional experimental data on this aspect?

Response: We thank the reviewer for the thoughtful comment regarding the possibility of compensating slower coating speeds in the DMF:DMSO system by increasing precursor concentration.

Following this suggestion, we attempted to increase the precursor concentration in the DMF:DMSO system during our optimization process. In practice, however, the DMF:DMSO system already operates close to the upper concentration range (~2.4 M) that can produce uniform films under blade-coating conditions. Further increasing the precursor concentration consistently resulted in severe film quality issues, including abnormal crystallization behavior and partial film delamination from the substrate during drying.

More importantly, adjusting the precursor concentration does not resolve the fundamental limitation associated with the solvent properties. DMF possesses a high boiling point (153 °C) and low vapor pressure, which leads to intrinsically slow solvent evaporation. As a result, even when the precursor concentration is increased, the wet film remains liquid for an extended period after gas-assisted drying. This slow drying kinetics prevents the film from crystallizing uniformly at higher coating speeds.

In contrast, the 2-ME:THF solvent system introduces significantly higher volatility through both components, enabling rapid solvent extraction and controlled nucleation during blade coating. This difference in solvent evaporation kinetics allows stable film formation at substantially higher coating speeds and enables more uniform large-area films.

Therefore, the advantage of the 2-ME:THF system originates from its fundamentally different solvent evaporation dynamics, which may not be compensated simply by adjusting the precursor concentration in the DMF:DMSO system.

Referee #3 (Remarks to the Author):

The manuscript reports state-of-the-art performance for large-area perovskite/perovskite tandem modules. The authors achieve this primarily through: (i) introducing (functionalized) In₂O₃ nanoparticles in the tunnel recombination junction (TRJ), (ii) adding a self-assembled monolayer (SAM) molecule as an additive in the perovskite precursor, and (iii) demonstrating that the efficiency improvement arises from the synergistic combination of these two strategies rather than either approach alone. In addition, the authors introduce a new solvent system for Pb–Sn perovskites based on 2-methoxyethanol (2-ME) and THF. Using these approaches, they report 26.2% efficiency on a 65 cm² module.

While the technological advance is clear and impressive, the scientific rationale and the manuscript's narrative would benefit from further clarification and strengthening.

Response: We thank the reviewer for the positive feedback and constructive suggestions. We will carefully address all comments to strengthen the scientific rationale and narrative of the manuscript.

Major comments

Q1) Scalability claims attributed to the recombination junction require clearer substantiation.

The manuscript repeatedly states that performance loss upon scaling is predominantly due to the tunnel recombination junction (e.g., around line 51: “[...] This performance disparity stems predominantly from optical and energetic loss at the tunnel recombination junction (TRJ) [...]”). The introduction further argues that this configuration is fundamentally constrained in large-area fabrication because (a) ultrathin metal layers are difficult to deposit uniformly over large areas, and (b) PEDOT:PSS introduces parasitic absorption and instability due to acidity.

However, the first point appears specific to TRJs that rely on ultrathin metal films/metal nanoclusters. As acknowledged in the literature (including the manuscript's Ref. 10), multiple TRJ implementations exist; metal nanoclusters are only one option, albeit often among the most efficient. Moreover, nanoparticle-based recombination layers have already been explored, including by some of the present authors. For example, H. Gao et al., Solar RRL 2021, 5, 2100814, and P. Wu et al., Adv. Energy Mater. 2022, 12, 2202948 demonstrated improved recombination junctions using conductive oxide nanoparticles; notably, the latter reported 26.3% tandem efficiency at small area using ITO nanoparticles.

Response: We agree that while the works by Gao et al. and Wu et al. successfully demonstrated the use of ITO NCs to improve stability, their primary focus was on stability rather than maximizing absolute efficiency. In our assessment, the performance of those devices remains below the state-of-the-art for all-perovskite tandems due to a critical materials compatibility issue: ITO nanoparticles require an additional NiO layer for effective hole extraction when integrated with

FACs-based narrow-bandgap perovskites.

In contrast, all-FA Pb-Sn perovskites possess a relatively high intrinsic hole concentration, enabling HTL-free device architectures. However, we have experimentally verified that this intrinsic property does not extend to the FAMA-based Pb-Sn perovskites used in this work, where an additional HTL is necessary to achieve high efficiency. While SAM-based HTLs can provide the required functionality, we found that they suffer from severe uniformity issues when scaled to large-area modules, as shown in Supplementary Fig. 20.

These combined challenges motivated the development of our In_2O_3 NC-based TRJ. This design simultaneously addresses both performance and scalability by offering: (i) efficient hole extraction without the need for an additional HSM or NiO layer, (ii) high optical transparency, and (iii) excellent uniformity over large areas. Furthermore, through rational ligand design, we systematically tune the surface chemistry and interfacial energy-level alignment of the In_2O_3 NCs, enabling optimized charge extraction and energy-level matching with the perovskite layer without compromising the nanocrystal core properties.

We have revised the Introduction in the manuscript as follow:

“This performance disparity is largely associated with optical and energetic losses at commonly used tunnel recombination junction (TRJ) architectures, and is further exacerbated by charge-transport limitations in large-area lead–tin (Pb–Sn) perovskite films during scalable deposition”⁸⁻¹⁰”

The second point (PEDOT:PSS parasitic absorption and chemical instability) is primarily a stack/material-selection issue and is not inherently a scaling-specific limitation; it applies equally at small and large area.

The authors should therefore more clearly disentangle:

- what limitations are truly scaling-driven (e.g., thickness uniformity, sheet resistance, defect tolerance, patterning yield), versus
- what improvements reflect a better stack design irrespective of area.

A more quantitative discussion would help (e.g., physical simulations of optical/electrical loss budget attributable to the TRJ, sensitivity of PCE to thickness/roughness variations, and how nanoparticle TRJs mitigate these factors at module scale).

Response: We thank the reviewer for this insightful and constructive comment, which helps us clarify the rationale behind our scalability claims. In response, we have refined our discussion and included supporting simulation data to better distinguish between scaling- and stack-driven limitations. Specifically, scaling-driven challenges, such as non-uniform thickness and charge extraction over large areas, are addressed by the thickness-insensitive properties of the In_2O_3 NC layer and the uniform crystallization of the perovskite. Stack-driven limitations, including parasitic absorption and chemical instability associated with conventional materials, are mitigated by the

design of the NC-based recombination layer. Optical and electrical simulations further confirm that this architecture maintains uniform performance across module scales and exhibits low sensitivity to thickness or roughness variations, as well as the inherent or interfacial defects of In_2O_3 NC layer.

We have revised the manuscript as follow:

"In conclusion, this work demonstrates a 26.2%-efficient all-perovskite tandem solar module with an aperture area of 65 cm^2 , achieved through a nanocrystal-based recombination layer that simultaneously addresses both scaling- and stack-driven limitations. The In_2O_3 NC layer mitigates stack-driven parasitic absorption and instability inherent to conventional architectures. Furthermore, its thickness-insensitive optoelectronic properties and favorable interfacial characteristics, combined with the uniform crystallization of Pb-Sn perovskite films achieved via HSM incorporation, effectively overcome key challenges associated with module scaling."

"To further quantify how these intrinsic advantages translate into scalable device performance, we performed optical and electrical simulations that account for key morphological factors. The simulations reveal that the In_2O_3 NC-based TRJ exhibits high tolerance to thickness variations and interfacial defects, which is critical for maintaining performance uniformity across large-area modules (Supplementary Fig. 18 and 19)."

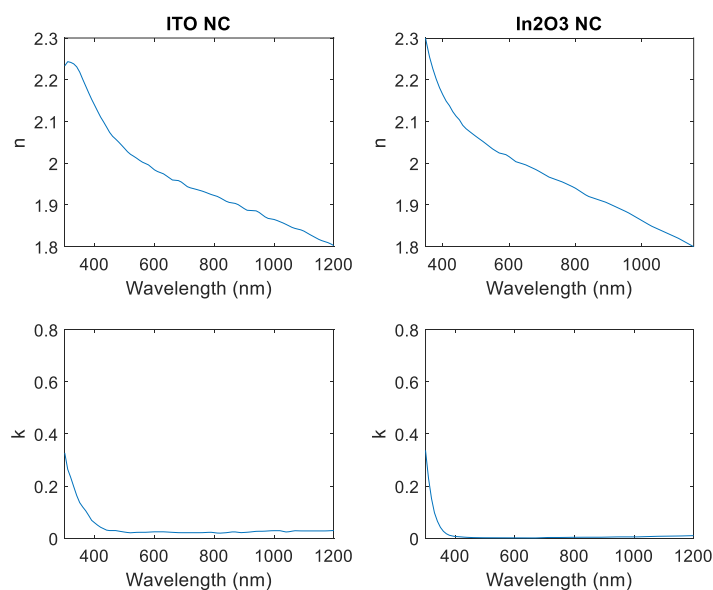
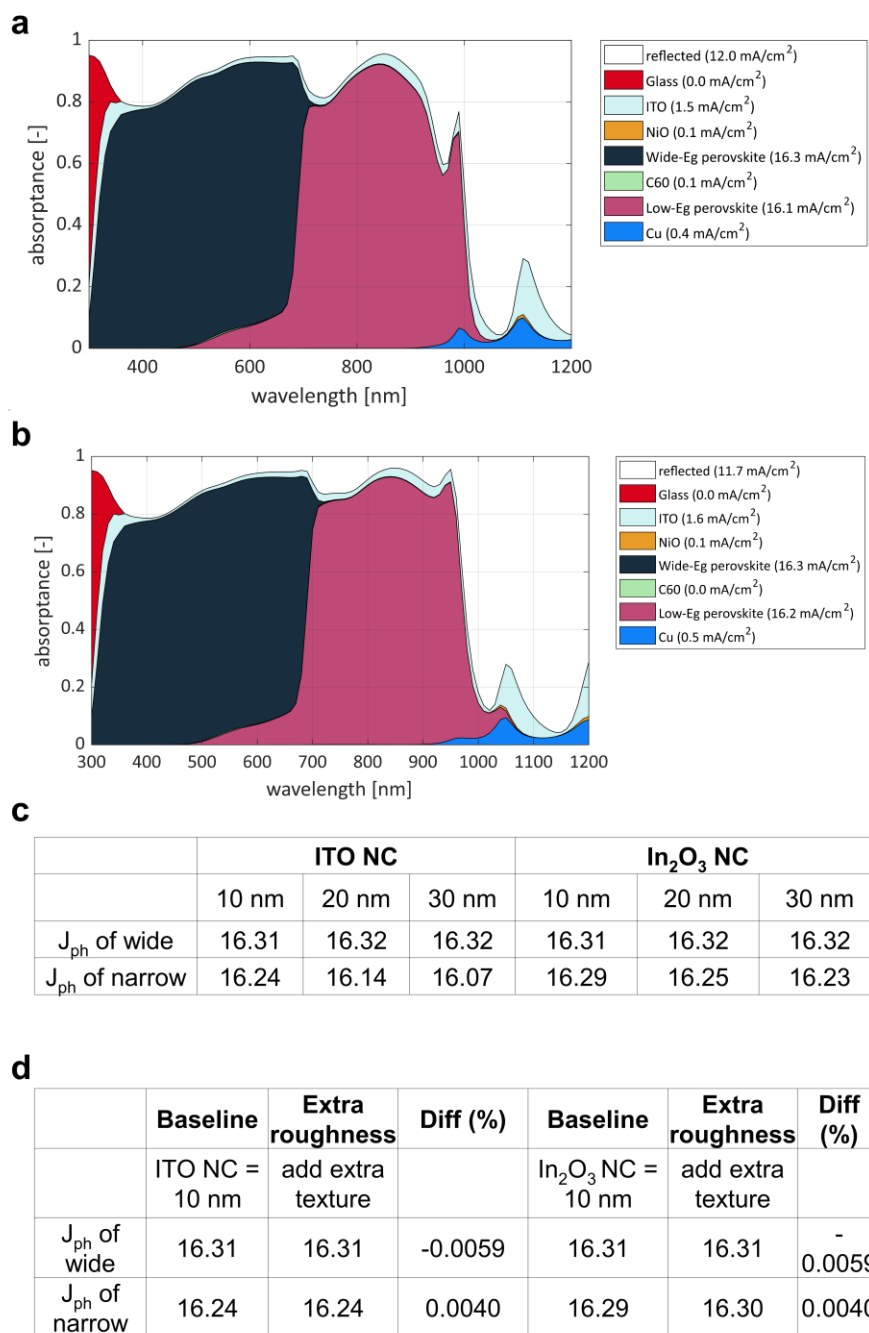
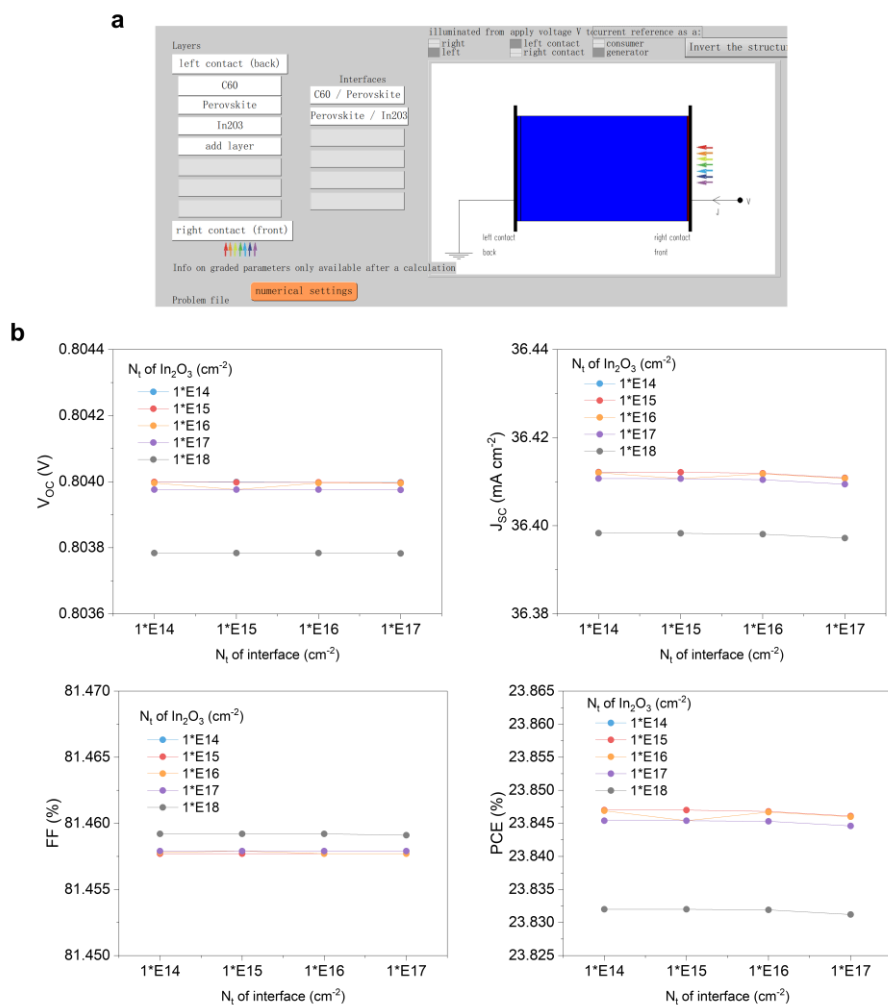


Figure R5. n, k data of ITO NCs and In_2O_3 NCs.



Supplementary Figure 18 | Optical simulations. Optical simulation of all-perovskite tandems using (a) 30-nm thickness of ITO NCs and (b) 10-nm thickness of In₂O₃ NCs. (c) Thickness sensitivity and (d) roughness sensitivity of all-perovskite tandems between ITO NCs and In₂O₃ NCs as recombination layer.



Supplementary Figure 19 | Electrical simulations. (a) Electrical simulation of Pb-Sn perovskite solar cell configuration. (b) Simulated performance of the Pb-Sn perovskite solar cells with changed total trap density of In_2O_3 NC and the interface of In_2O_3 /perovskite.

Q2) Novelty of SAM additives should be positioned accurately; the key novelty is the synergy with In_2O_3 nanoparticles.

The use of phosphonic-acid-based SAM molecules introduced directly in perovskite precursor solutions has increasingly become part of scalable processing since it was demonstrated in 2023 (Zheng et al., Nat. Energy 8, 462–472 (2023)). In this context, the general concept of SAM additives is not, by itself, fully novel.

What does appear distinctive here is the synergistic interaction between the functionalized In_2O_3 nanoparticles in the recombination layer and the SAM additive in the perovskite. This should be emphasized more explicitly in the Abstract and Introduction as the central conceptual contribution, alongside the large-area demonstration. Moreover, in order to clarify the mechanism, the description of SAM- In_2O_3 interactions should be supported by DFT calculations.

Response: We thank the reviewer for this insightful and constructive comment. We fully agree that the key novelty lies not in the HSM additive alone, but in its synergistic interaction with the

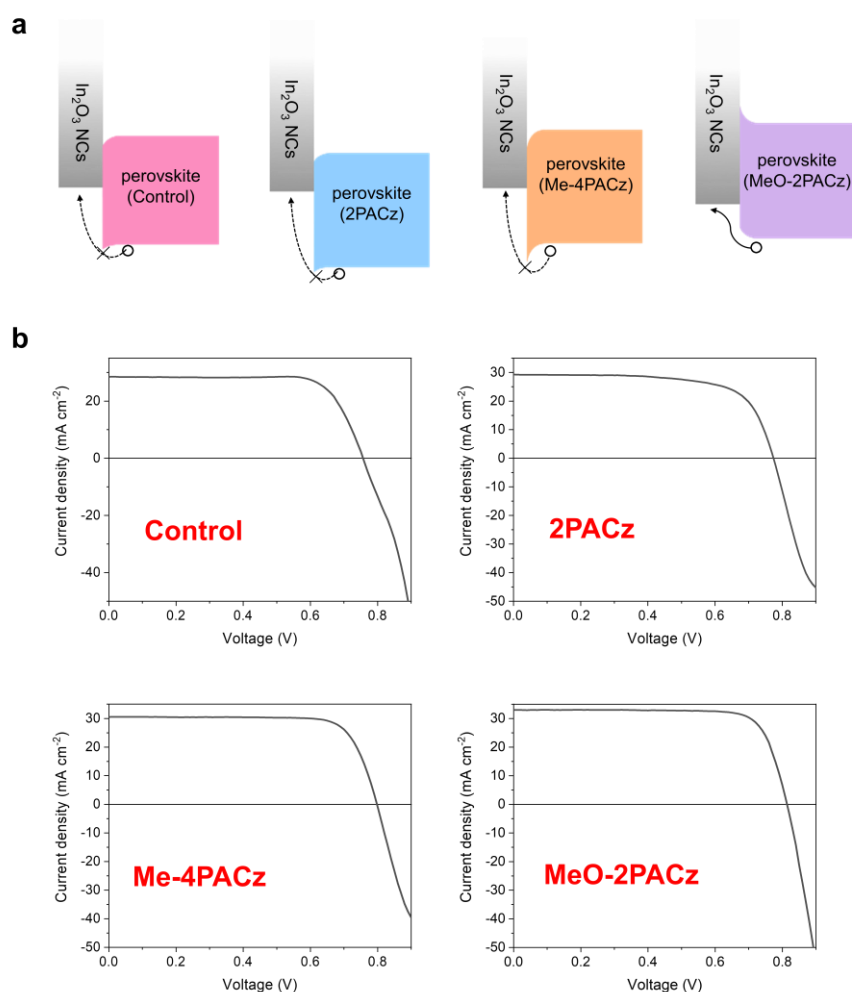
functionalized In_2O_3 NC recombination layer. Through stepwise ligand engineering, we systematically tuned the Fermi level of In_2O_3 NCs to align with the high HOMO level of the MeO-2PACz additive, enabling efficient hole extraction without additional HTLs while maintaining high optical transparency. This matched energy-level alignment, combined with the thickness-insensitive properties of the In_2O_3 NC layer, addresses both stack- and scaling-driven limitations in large-area modules. We have revised the Abstract and Introduction to emphasize this synergistic design as the central conceptual contribution, alongside the 65 cm^2 module demonstration. While DFT calculations were not included in this work, we have added discussion acknowledging this as a valuable direction for future mechanistic study.

Abstract: "... Critically, we introduce a phosphonic acid additive into the lead–tin (Pb–Sn) perovskite precursor, which synergistically improves the electronic contact with the In_2O_3 recombination layer, thereby enhancing hole extraction. In addition, the additive regulates perovskite crystallization to mitigate residual strain during film formation, ensuring high-quality large-area deposits. This coordinated interfacial and crystallization engineering strategy simultaneously improve interfacial recombination, carrier extraction, and large-area film uniformity in all-perovskite tandems. ..."

Introduction: "... For example, carbazole-based SAMs, exhibit low parasitic absorption and favorable hole selectivity, yet their poor energy-level alignment with Pb–Sn perovskites limits charge extraction^{27–29}. Recent studies show that SAM molecules can be introduced directly into perovskite precursors, where they self-assemble onto the substrate during film processing^{30–32}. However, this approach may introduce competing interactions, as SAM molecules either anchor to the substrate or coordinate with the perovskite bulk, leading to insufficient hole transport and influenced crystallization dynamics of perovskite formulation."

"... To ensure favorable band energy matching with the In_2O_3 NCs, we incorporate a phosphonic-acid-based HSM into the Pb–Sn perovskite precursor. This additive enhances hole transport and reduces defects by coordination, while its mediated crystallization control further enables scalable deposition by mitigating residual strain and sustaining uniform perovskite film quality across large areas. Through this synergistic interfacial and crystallization engineering strategy, ..."

Results and discussion: "This advantage arises from the electron-donating methoxy groups, which elevate the molecular energy levels and facilitate more efficient hole extraction, thereby enabling a better match with the energy level of the In_2O_3 NC layer⁴¹ (**Supplementary Fig. 24**)."



Supplementary Figure 24 | (a) Energy band alignment from UPS results between In_2O_3 NCs-MMPA and Pb-Sn perovskite with different HSMs. (b) J-V curves of the Pb-Sn perovskite solar cells with different HSMs.

Q3) The late introduction of a new Pb–Sn solvent system (2-ME:THF) is conceptually disruptive.

A major source of confusion is the sudden introduction (Figure 4 and associated discussion) of the 2-ME:THF solvent system. The mechanistic arguments and process–property relationships developed earlier (based on the initial solvent system) cannot be assumed to transfer directly to a substantially different solvent chemistry. As a result, the final performance shown in Figure 4 cannot be straightforwardly connected to the preceding conclusions.

To improve coherence, the authors should either:

- introduce and use the 2-ME:THF system from the beginning, so that mechanistic conclusions and optimization steps consistently build toward the final module result; or
- provide a clear comparative bridge (e.g., direct head-to-head evidence showing that the same synergy/mechanism holds in both solvent systems, and which observations are solvent-specific versus universal).

Response: We thank the reviewer for this insightful observation regarding the late introduction of

the 2-ME:THF solvent system. We agree that its initial placement in the manuscript may create the impression that the mechanistic discussion developed earlier was based on a different solvent system, which could disrupt the logical flow.

Specifically, we have moved the following statement to the first section before the all-perovskite tandem solar modules:

*“Building on the improved photon management achieved with the Type III TRJ, we therefore prioritized the large-scale fabrication of perovskite films as a critical preliminary step to developing all-perovskite TSMs. During the scale-up of Pb-Sn perovskite films, we identified that the reduced surface-to-volume ratio makes it particularly challenging to balance rapid solvent evaporation with required coating speeds during gas-assisted drying processes (**Supplementary Fig. 6**). Recognizing that the high boiling points and low evaporation rates of conventional solvents (DMF and DMSO) retard nucleation kinetics, we developed a binary cosolvent system with low boiling point and high evaporation rate of volatile coordinated 2-methoxyethanol (2-Me) and uncoordinated solvent of tetrahydrofuran (THF) to dissolve Pb-Sn perovskite precursors (**Supplementary Fig. 7 and Table S1**). We found that the perovskite precursor can reach critical supersaturation with 20 vol% THF incorporation in Pb-Sn perovskite precursor for rapid nucleation and improved large-scaled uniformity (**Supplementary Fig. 8**). The 2-Me-based Pb-Sn perovskite precursor enables high-speed blade coating at 30 mm/s, facilitated by its low boiling point and high vapor pressure. In contrast, the DMF-based system requires a significantly slower coating speed of 5 mm/s for small-area devices ($2.5 \times 2.5 \text{ cm}^2$, **Supplementary Fig. 9**). This speed limitation becomes increasingly problematic during scale-up, while the optimized coating speed must be progressively reduced for larger substrates, the DMF-based precursor fails to form uniform films even at $10 \times 10 \text{ cm}^2$ scale, with complete crystallization failure occurring at $22 \times 22 \text{ cm}^2$ dimensions. Then we characterized the uniformity of the perovskite films compared with DMF-based and 2-Me-based perovskite films deposited on $10 \times 10 \text{ cm}^2$ substrates (**Supplementary Fig. 10**). PL mapping revealed significantly enhanced homogeneity and greater intensity uniformity in the 2-Me-based films compared to their DMF-based counterparts, directly correlating with improved device performance consistency across the substrate area (**Supplementary Fig. 11**). The incorporation of THF into the wide-bandgap perovskite can also improve coating speed and film uniformity, outperforming our previously reported green solvent system (**Supplementary Fig. 12**). This improvement enabled a 17.5% efficiency on a 65 cm^2 aperture area (**Supplementary Fig. 13**), highlighting its excellent scalability of this approach.”*

Additional comments and requests for clarification

Q4. The introduction discusses PEDOT:PSS acidity (around line 65). Neutral or low-acidity PEDOT formulations/complexes are increasingly used and should be acknowledged as relevant alternatives.

Response: We thank the reviewer for pointing out the availability of neutral or low-acidity PEDOT formulations. We agree that these represent relevant alternatives and have revised the manuscript to acknowledge these developments. To further evaluate this point, we experimentally compared devices based on standard PEDOT-PSS, neutral PEDOT-PSS (Sigma-Aldrich, Product No. 739324) and the In_2O_3 NC recombination layer.

As shown in Figure R4, the initial device performances were comparable between standard and neutral PEDOT-PSS. However, under 85°C thermal stress, devices based on neutral PEDOT-PSS exhibited significantly improved stability compared to their standard counterparts, consistent with the expected benefit of mitigating acidity-related degradation. However, despite this improvement in stability, neutral PEDOT-PSS still introduces significant parasitic absorption in the near-infrared region, which directly limits the photocurrent generation of the narrow-bandgap Pb-Sn perovskite bottom cell in tandem configurations. In contrast, the high optical transparency of In₂O₃ NCs effectively minimizes these optical losses. This optical advantage makes In₂O₃ nanocrystals a more suitable recombination layer for simultaneously achieving high efficiency and stability in all-perovskite tandem devices.

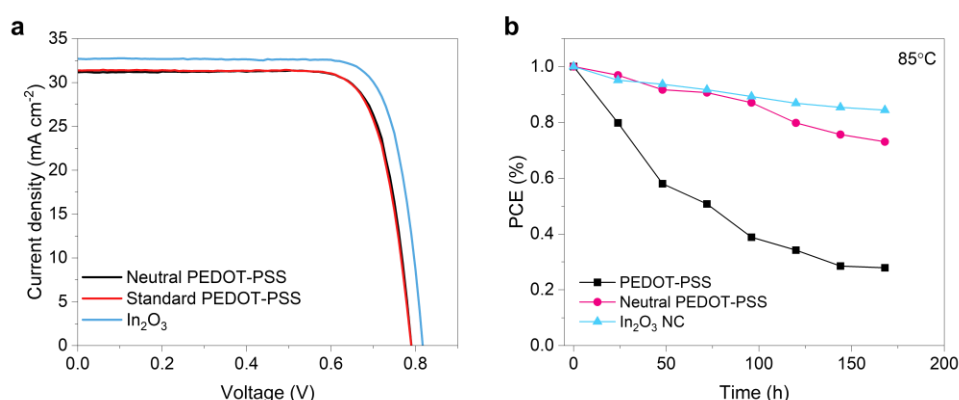


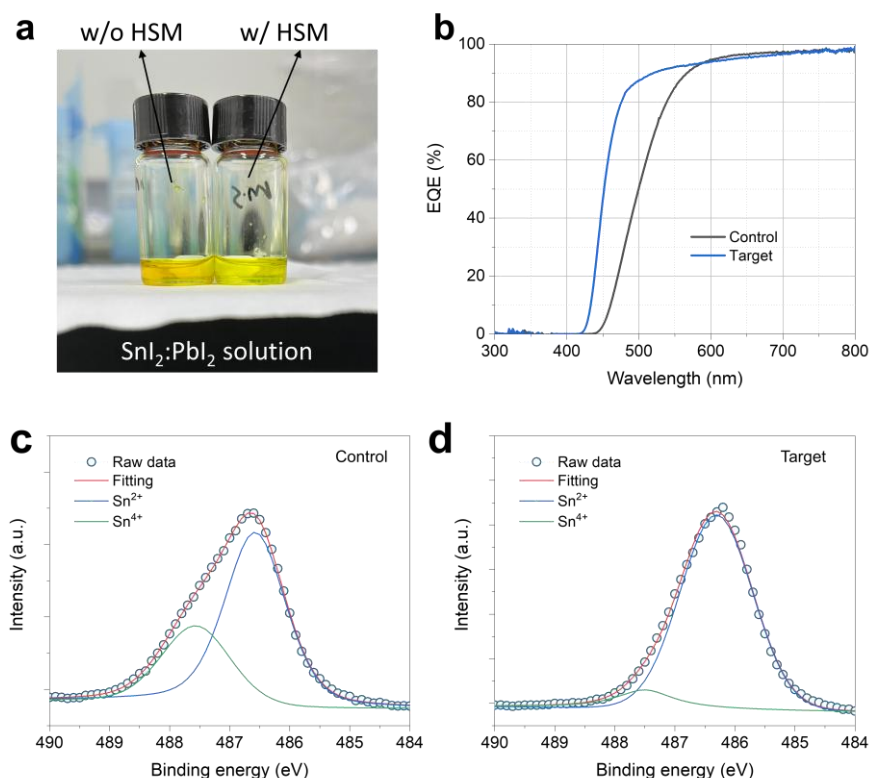
Figure R4. Performance comparison of Pb-Sn perovskite solar cells based on the standard PEDOT-PSS and neutral PEDOT-PSS. (a) Photovoltaic performance of Pb-Sn perovskite solar cells based on different HTLs. (b) Stability of the Pb-Sn perovskite solar cells based on different HTLs.

Q5. The manuscript notes that PEDOT:PSS acidity is problematic for Sn-containing perovskites due to interfacial degradation, yet the work uses “phosphonic acid-assisted crystallization control.” The authors should discuss possible chemical interactions of these acidic functional groups in the precursor (e.g., with Sn powder or other reductants/additives) and whether they affect Sn²⁺/Sn⁴⁺ chemistry.

Response: We thank the reviewer for this important comment. The key distinction is that the phosphonic acid groups in our HSM additive are introduced in dilute solution and largely consumed during film formation, unlike the fixed acidic interface of PEDOT-PSS. We verified that HSM incorporation does not compromise the reducing function of Sn powder, in fact, it suppresses Sn²⁺ oxidation (Supplementary Fig. 43). Thermal aging further confirms that devices with HSM exhibit stability comparable to neutral PEDOT-PSS, whereas acidic PEDOT-PSS accelerates degradation.

We have revised the manuscript as follow:

“The phosphonic acid anchor in the HSM also acts as an antioxidant barrier, significantly suppressing oxidation in the Pb-Sn perovskite. This protection is crucial for maintaining material integrity during transient air exposure, such as in the P2/P3 scribing steps or module measurement, which is essential for practical processing and operation (Supplementary Fig. 43).”



Supplementary Figure 43 | Oxidation suppression with HSM incorporation. (a) Digital photo of the SnI₂:PbI₂ mixed solution with and without HSM; (b) Corresponding optical absorption of the solution with and without HSM; (c and d) XPS spectra of Sn 3d for (c) control and (d) target Pb-Sn perovskite films.

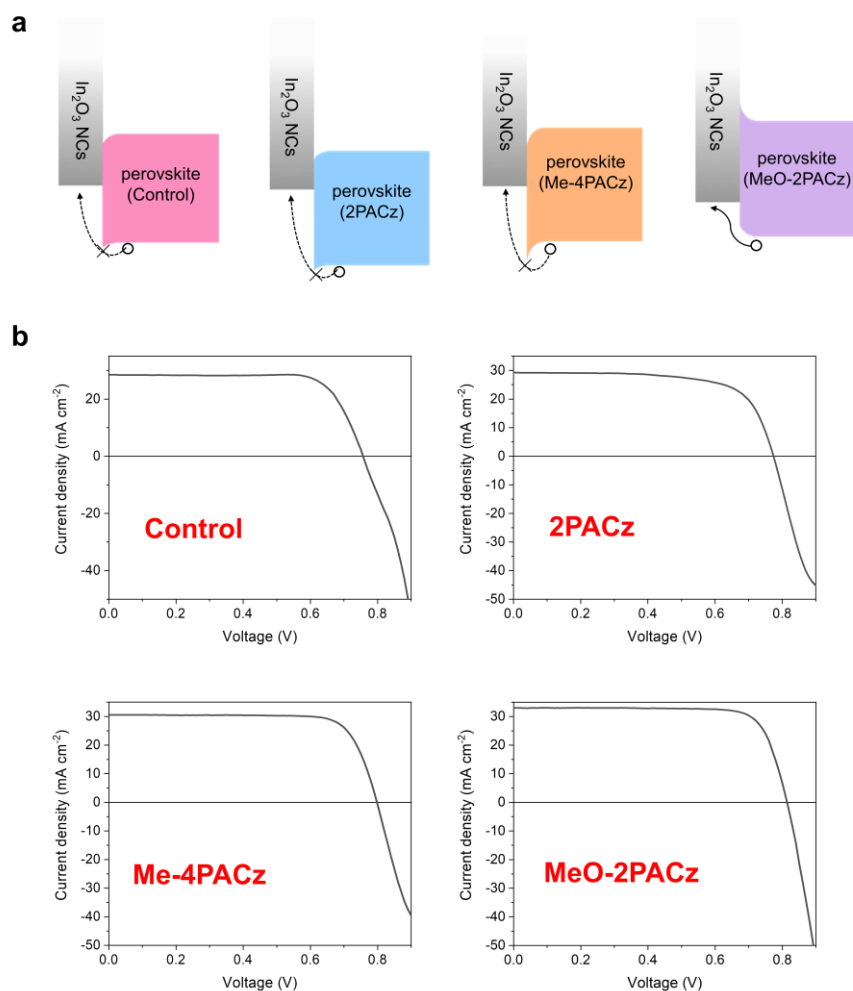
Q6. Lines 166–168: It remains unclear why MeO-2PACz provides the best performance among the phosphonic acids tested as additives, yet does not show a similar advantage when used as a conventional monolayer. A mechanistic explanation or supporting characterization would strengthen this point.

Response: We thank the reviewer for this helpful comment and for encouraging us to further clarify why MeO-2PACz provides the best performance among the phosphonic-acid molecules tested as additives.

We thank the reviewer for the insightful comment. MeO-2PACz outperforms other phosphonic acids as an additive because its methoxy group enhances precursor compatibility and raises the HOMO level (Angew. Chem. Int. Ed. 2025, 64, e202419375), enabling better hole extraction with In₂O₃ NCs. However, as a conventional monolayer, its long molecular backbone increases interfacial tunneling distance, and achieving uniform coverage over large areas is difficult, which limits hole transport (ACS Energy Lett. 2025, 10, 4983-4994). When used as an additive, MeO-2PACz distributes within the perovskite film and at grain boundaries, facilitating defect passivation and energy-level alignment without forming a continuous transport barrier.

We have revised the manuscript as follow:

"This advantage arises from the electron-donating methoxy groups, which elevate the molecular energy levels and facilitate more efficient hole extraction, thereby enabling a better match with the energy level of the In_2O_3 NC layer ⁴¹ (Supplementary Fig. 24). Furthermore, incorporating HSM directly into the perovskite precursor proves more favorable for scalable fabrication than conventional monolayer coating, as achieving uniform and complete monolayer coverage over large areas remains challenging to control ⁴²."



Supplementary Figure 24 | (a) Energy band alignment from UPS results between In_2O_3 NCs-MMPA and Pb-Sn perovskite with different HSMs. (b) J-V curves of the Pb-Sn perovskite solar cells with different HSMs.

Q7. The experimental procedure for incorporating phosphonic-acid-based HTLs as additives is insufficiently described. Concentrations, dissolution conditions, mixing sequence, and aging/filtration steps should be explicitly reported.

Response: we revised the experimental procedure section and clarified the details of precursor preparation:

"First, the molar ratios for FAI/MAI and $\text{PbI}_2/\text{SnI}_2$ were 0.7:0.3 and 0.5:0.5, respectively. The molar

ratio of (FAI + MAI)/(PbI₂ + SnI₂) was 1:1. HSM (optimized 0.2 mol% relative to PbI₂+SnI₂) and SnF₂ (10 mol% relative to SnI₂) was added into the precursor. The precursor solution (1.4 M) was prepared in mixed solvents of 2-methoxyethanol and tetrahydrofuran with a volume ratio of 4:1. Then tin powders (5mg mL⁻¹) as the antioxidant was added to the precursor solution. DMSO (0.1% mole ratio) as the additive was added to the precursor solution. After all the above additives have been added, the precursor solution was stirred at room temperature for 0.5 h. Prolonged stirring should be avoided, as it may lead to undesirable sedimentation. The precursor solution was filtered through a 0.22 μm PTFE membrane before using."

Q8. Line 200: The meaning of "0.2%" must be specified (molar fraction, weight fraction, volume fraction) and referenced to the correct baseline (perovskite solids, total precursor, or solvent).

Response: We have now specified that "0.2%" refers to the molar fraction relative to the total Pb–Sn perovskite solids (0.2 mol% relative to PbI₂+SnI₂), and have added this clarification to the Experimental Section and relevant figure captions.

Q9. The distinction between "optimized" and "non-optimized" MeO-2PACz devices is unclear. What concentration was used in the non-optimized comparison set? Were solubility or solvent-compatibility differences across the additives a confounding factor? This should be discussed.

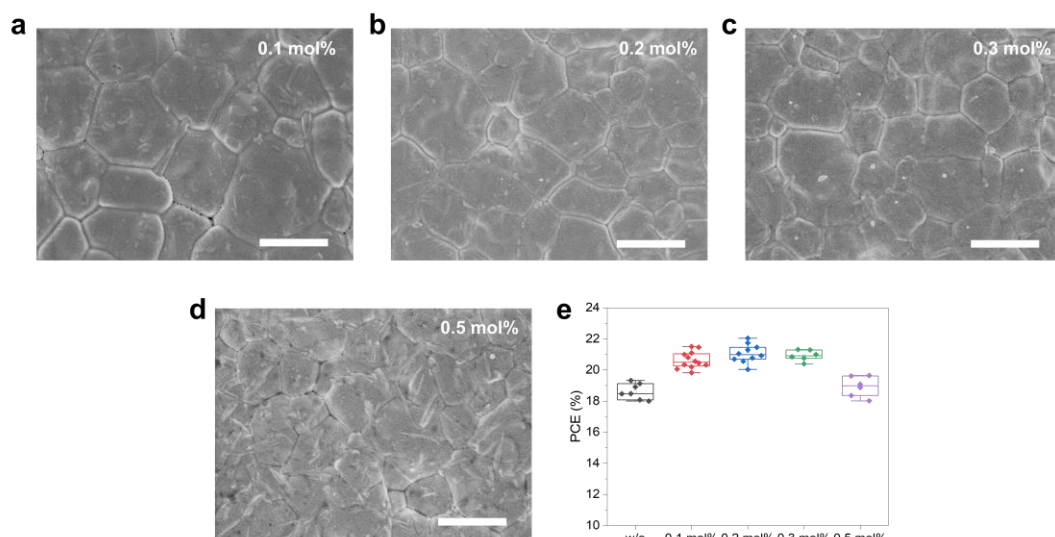
Response: We thank the reviewer for this valuable comment. The optimized MeO-2PACz devices were fabricated with a concentration of 0.2 mol% (relative to perovskite solids). Non-optimized devices were prepared with concentrations of 0.1, 0.3, and 0.5 mol% for comparison. As shown in Supplementary Figure 32, 0.1 mol% and 0.3 mol% films remain compact and uniform, while 0.5 mol% films exhibit visible surface impurities, indicating that excessive additive loading disrupts perovskite crystallization. This morphology-performance correlation justifies 0.2 mol% as the optimal condition.

To enable a controlled comparison of molecular structure effects, all phosphonic acid additives were initially tested at the same 0.2 mol% concentration. We recognize that each additive may have its own optimal concentration, but the current approach reveals clear trends: MeO-2PACz consistently outperforms others at this concentration, highlighting the advantages of its short carbon chain and methoxy groups. Importantly, with the exception of poly-4PACz, which showed limited solubility, all other additives dissolved readily in the 2-ME-based solvent system, confirming that solubility differences were not a confounding factor.

We have revised the manuscript as follow:

*"As summarized in **Supplementary Fig. 22**, all HSM candidates yielded PCEs exceeding 20% with a consistent concentration of 0.2 mol%, revealing clear trends despite the potential for further performance enhancement through newly synthesized materials, various combinations and individual concentration optimization."*

*"We optimized the concentration of the MeO-2PACz at 0.2 mol% to obtain a champion performance based on the HTL-free device (**Supplementary Fig. 32**)."*



Supplementary Figure 32 | Film morphology and device performance with different concentration of the incorporated HSM. SEM images of the perovskite films with different concentration of the incorporated HSM, (a) 0.1 mol%; (b) 0.2 mol%; (c) 0.3 mol%; (d) 0.5 mol%; (e) PCE statistics of the Pb-Sn PSCs, with different concentration of HSMs. The optimal condition is 0.2% mole ratio. The box plots show the PCE distributions for devices fabricated with 7, 12, 10, 6, and 6 individual cells at each concentration, respectively. All devices have an aperture area of 0.049 cm². The boxes represent the standard deviation, and the whiskers indicate the maximum and minimum values of each distribution.

Q10. Prior work suggests that when phosphonic-acid-based molecules are used as additives, they may need to be removed or passivated at the perovskite surface (Zheng et al., *Nat. Energy* 2023). The manuscript should therefore clarify whether such removal/passivation is required here, and specify which solvent(s) were used during EDAl₂ passivation. These details are currently missing.

Response: We thank the reviewer for raising this important point regarding the potential need to remove or passivate phosphonic-acid-based molecules when they are used as additives, as discussed in prior work (Zheng et al., *Nat. Energy*, 2023). We agree that clarifying the surface fate of these molecules is important.

To clarify the surface fate of phosphonic acid additives, we conducted XPS analysis and found that the phosphorus signal from MeO-2PACz is substantially reduced after IPA washing and becomes undetectable following EDAl₂ passivation (performed in IPA), indicating effective removal from the perovskite surface. Therefore, unlike prior reports, no additional removal or surface passivation step is required beyond our standard EDAl₂ treatment, and this detail has been added to the Experimental Section.

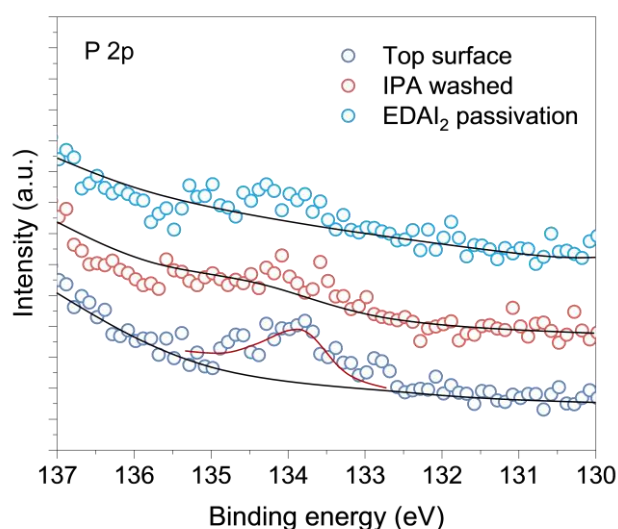


Figure R6. The P 2p XPS spectra of different perovskite film surfaces

Q11. Lines 229–230: The sentence should be rewritten for clarity, for example by splitting into two sentences and explicitly stating the causal link (loss of the hydroxy group; hydrogen bonding between phosphonic-acid functionalities and FAI).

Response: We thank the reviewer for this helpful suggestion to improve the clarity of the description of the NMR results. Following this comment, we carefully re-examined the liquid-phase NMR data shown in Fig. 3b and revised the corresponding sentence in the manuscript to better clarify the causal relationship between the observed spectral features and the proposed mechanism.

We have revised the manuscript as follow:

*“The natural deprotonation of FA^+ cations leads to A-site vacancies and unreacted PbI_2 accumulation⁴⁴. Liquid-phase ^1H NMR spectroscopy (**Fig. 3b**) reveals the role of HSM in mitigating this issue. Upon mixing HSM with FAI, the proton signal corresponding to the phosphonic acid group (P-OH) disappears completely, indicating deprotonation of the phosphonic acid functionality in the precursor solution. Concurrently, the FA^+ proton resonance evolves from a broad peak into a resolved multiplet with only a minor chemical-shift change. This spectral evolution suggests the presence of weak interactions between the deprotonated HSM species and FA^+ in solution. Such interactions perturb the local environment of the FA^+ ammonium protons and may partially break the symmetry of the FA^+ cation, giving rise to the observed multiplet structure. The minimal shift in resonance indicates that the interaction remains relatively weak, consistent with a dynamic solution-phase association rather than the formation of a strongly bound complex. Such interactions modulate the precursor chemistry during crystallization and help stabilize the perovskite formation process.”*

Q12. If the manuscript mentions “three patents,” the patent/patent application identifiers should

be provided.

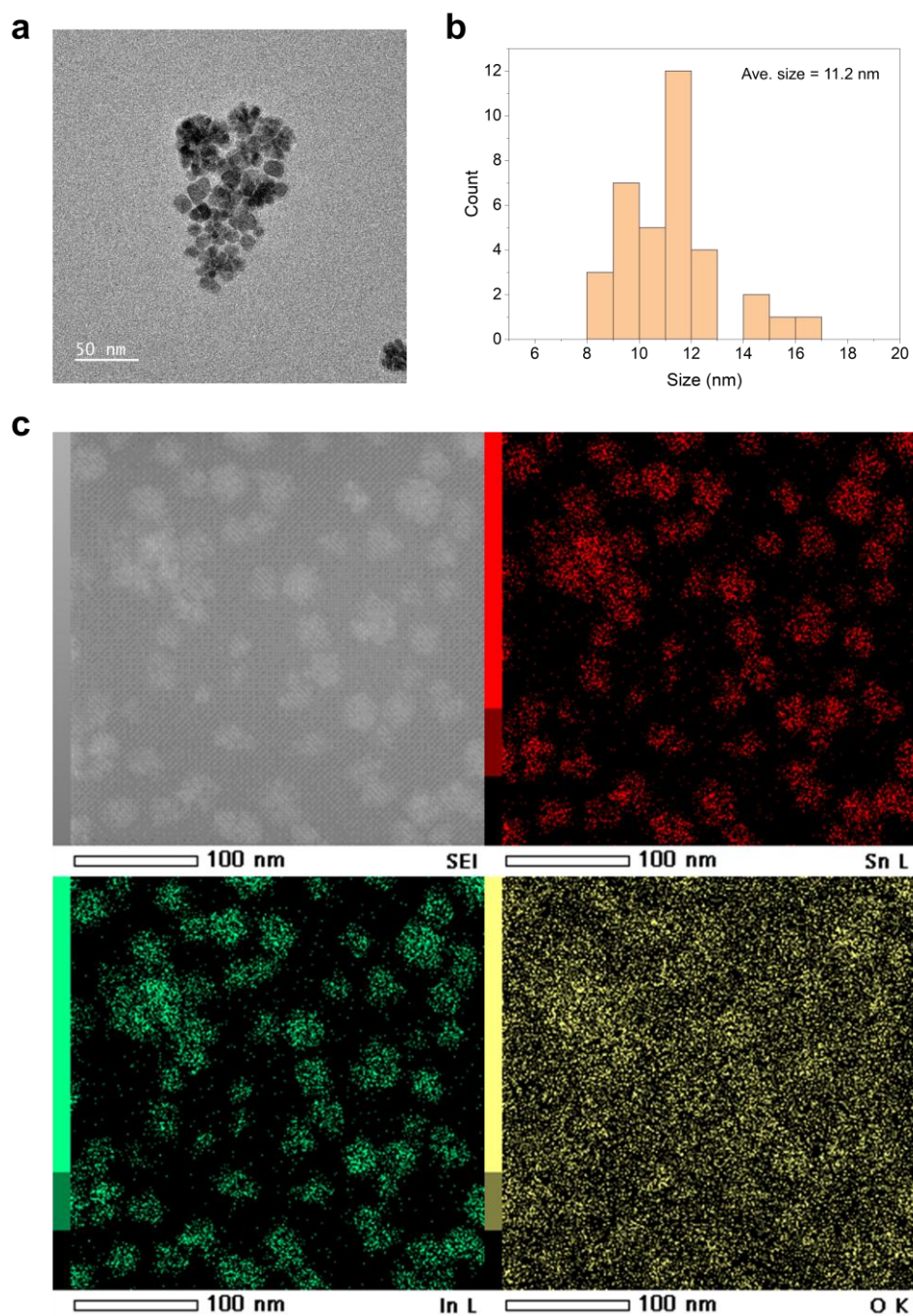
Response: We have now provided the patent application identifiers in the revised manuscript. Two patent applications (CN202411229410.3 and CN202411277886.4) have been filed by Nanjing University and Renshine Solar (Suzhou) Co., Ltd. The third patent application has been recently submitted, and its identifier will be provided once available. Correspondingly, we have revised the main text to state “two patents” instead of “three”.

Q13. The ITO and In₂O₃ nanoparticles have very different sizes. Can the authors comment on whether ITO nanoparticles of comparable size to the In₂O₃ particles can be synthesized using a similar approach, and whether size (rather than composition) could explain part of the observed differences?

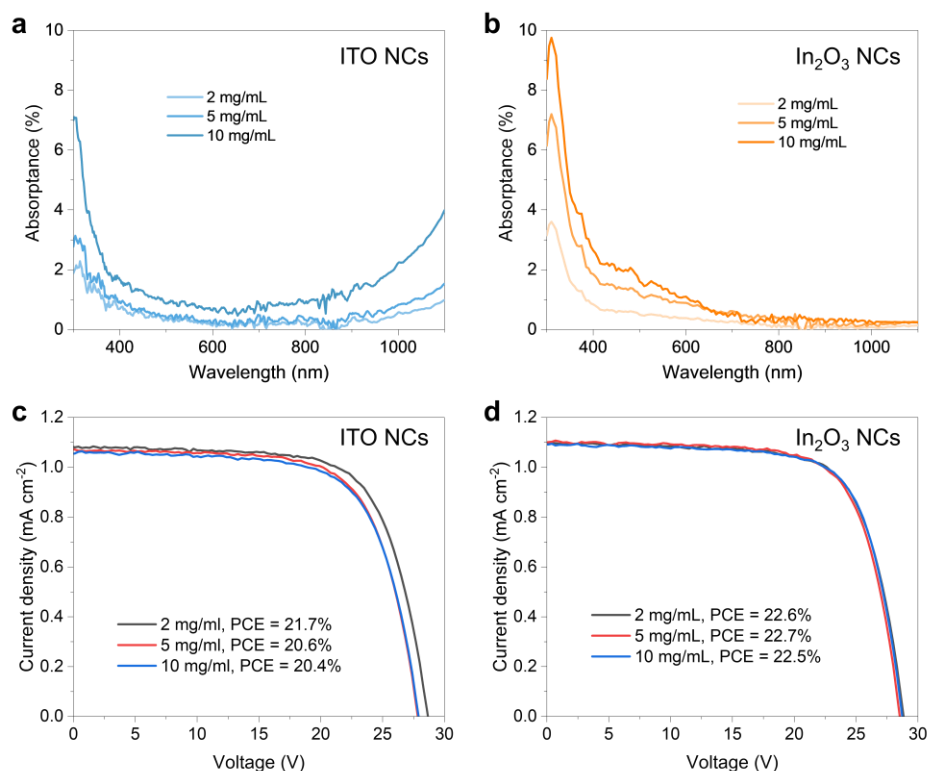
Response: We agree that decoupling the size effect from the material properties is important. To address this, we synthesized ITO NCs in-house using the same synthetic route as our In₂O₃ NCs, yielding nanoparticles with comparable size and surface properties (Supplementary Fig. 16). Accurate thickness measurement of the discontinuous films formed at low concentration is not feasible, so we used these size-matched nanoparticles deposited at the same concentration to ensure a meaningful comparison. Under identical conditions, In₂O₃ NCs still demonstrated superior optical transparency and device performance (Supplementary Fig. 17), confirming that the observed advantages are intrinsic to the material itself rather than artifacts of particle size or film thickness.

We have revised the manuscript as follow:

*“To verify that the superior performance of In₂O₃ NCs is intrinsic to the material rather than an artifact of thickness or morphological differences, we synthesized ITO NCs with comparable particle size using the same synthetic route (**Supplementary Fig. 16**). When deposited under identical conditions, the size-matched ITO NCs still exhibited inferior optical transparency and device performance compared to In₂O₃ NCs (**Supplementary Fig. 17**), confirming that the advantages of In₂O₃ NCs originate from their intrinsic material properties.”*



Supplementary Figure 16 | Synthesis of ITO NCs. (a) TEM image of the self-synthesized ITO NCs. (b) Particle size statistics of ITO NCs. (c) HAADF-EDS of ITO nanocrystals.



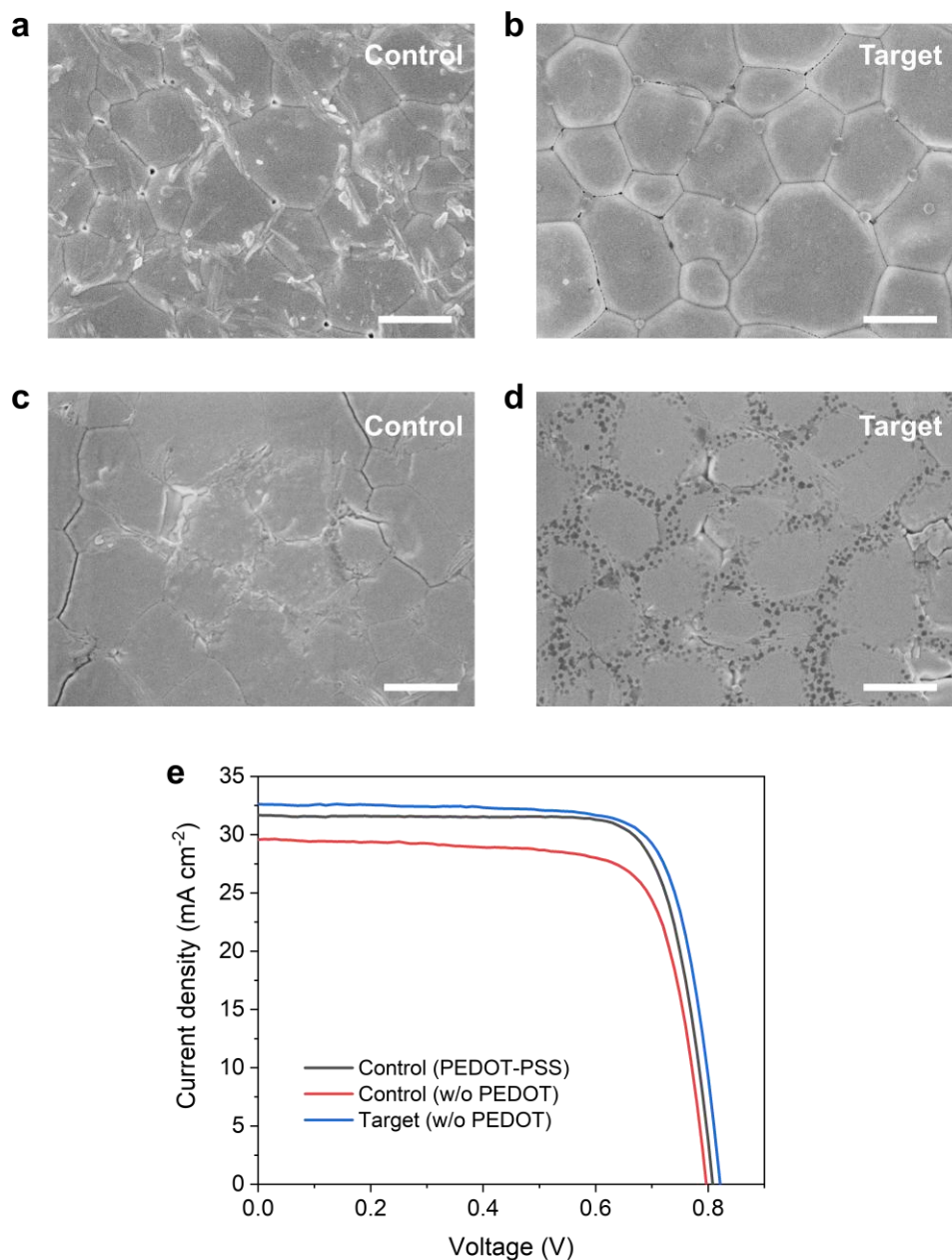
Supplementary Figure 17 | Optoelectrical property comparison. (a-b) Absorbance of different thickness of (a) ITO NCs and (b) In₂O₃ NCs using concentration from 2 mg/mL to 10 mg/mL. (c-d) Module performance comparison between ITO NCs and In₂O₃ NCs using concentration from 2 mg/mL to 10 mg/mL.

Q14. The Supporting Information includes only two photographs of perovskite films. The effect of MeO-2PACz on Pb–Sn perovskite crystallization appears central, yet it is not shown comprehensively across both solvent systems (DMF–DMSO and 2-ME–THF). Additional photographs (and ideally complementary morphology/phase metrics) for all relevant films would be helpful.

Response: We agree that the effect of HSM (e.g. MeO-2PACz) on Pb–Sn perovskite crystallization should be more comprehensively documented. In the revised Supporting Information, we have added photographs of perovskite films for DMF:DMSO solvent system with and without HSM, providing a complete visual comparison. Additionally, we also compared the device performance with and without HSM.

We have revised the manuscript as follow:

“Beyond the type of HSM used, we observed that Pb–Sn perovskite films fabricated using the DMF-based solvent system also exhibited the similar morphology (Supplementary Fig. 37).”



Supplementary Figure 37 | The surface morphology and performance of Pb-Sn perovskite fabricated using DMF-based solvent system. (a-b) Top- and (c-d) bottom-view SEM images of control and target perovskite films. (e) J-V curves of Pb-Sn perovskite solar cells.

Q15. The fabrication details for Pb–Sn perovskite films using DMF–DMSO are missing and should be added for reproducibility.

Response: We have now added the fabrication details for Pb–Sn perovskite films using the DMF-based solvent system in the revised Experimental Section. Both small-area and large-area fabrication details are included to ensure reproducibility.

We have revised the manuscript as follow:

“Narrow-bandgap perovskite solar cell fabrication (2.5×2.5 cm²)

... For 2-Me-based solution, the coating speed was 30 mm s⁻¹ with a coating gap of 300 μm. For DMF-based solution, the coating speed was 6 mm s⁻¹ with a coating gap of 300 μm. Both the N₂ knife worked at 60 psi during blade coating. ...

All-perovskite TSM fabrication (10×10 cm²)

... For 2-Me-based solution, the coating speed was 28 mm s⁻¹ with a coating gap of 300 μm. For DMF-based solution, the coating speed was 3 mm s⁻¹ with a coating gap of 300 μm. Both the N₂ knife worked at 60 psi during blade coating. ...”

Q16. The volumes of perovskite solutions for blade-coating should be added in the SI.

Response: We have now added the details for perovskites in the revised Experimental Section.

“Narrow-bandgap perovskite solar cell fabrication (2.5×2.5 cm²)

...10 uL of perovskite solution was dropped onto the blade coater, which filled the gaps under the influence of gravity and capillary action....

All-perovskite TSM fabrication (10×10 cm²)

...80 uL of perovskite solution was dropped onto the blade coater, which filled the gaps under the influence of gravity and capillary action. For 2-Me-based solution...”

Q17. The authors should comment on whether THF containing stabilizers/inhibitors could be used without compromising performance, and how sensitive the process is to THF grade and stabilizer content.

Response: The THF we purchased is inhibitor-free (Sigma-Aldrich, Product No. 401757, ≥99.9%, anhydrous, inhibitor-free).

Q18. The authors must explicitly warn readers about the formation of highly reactive and potentially explosive peroxides in THF and other ethers, and clearly describe established measures to prevent explosions and fatalities during their handling and storage, supported by appropriate references. THF is a hazardous solvent that requires substantial practical experience and strict adherence to safety protocols; it cannot be considered safe for general use by non-expert practitioners. Publication of this article is likely to promote the use of this unusual and dangerous solvent, and without a clear and prominent safety discussion, it poses an unacceptable risk to inadequately prepared readers

Response: we have added a prominent safety warning in the Experimental Section explicitly stating that THF can form explosive peroxides and must only be handled by trained personnel using

appropriate safety measures, including regular peroxide testing, storage under inert conditions with inhibitors, and avoidance of evaporation to dryness, supported by relevant safety references. We appreciate reviewer's guidance in ensuring the responsible communication of our work.

"Note: tetrahydrofuran (THF) is a hazardous solvent capable of forming explosive peroxides, and it should only be handled by trained personnel using appropriate safety protocols, including regular peroxide testing, storage under inert conditions, and avoidance of evaporation to dryness."

Point-to-point actions in response to the Reviewers' comments

Manuscript: 2025-11-30551A

We sincerely thank the reviewers again for their insightful comments and positive feedback, which have greatly helped us strengthen the manuscript. Below we provide a point-by-point response to the reviewers' remarks: the reviewers' comments are shown in black, our responses in blue, and the revised text in the manuscript is presented in boxes.

Referee #1 (Remarks to the Author):

This manuscript presents a well-executed and practically meaningful advance in all-perovskite tandem solar modules, addressing key challenges in recombination junction design, large-area uniformity, and module scalability. The authors have carefully addressed the concerns raised in the previous round of review, and I do not see any major outstanding issues. In my view, the work now meets the standard for publication in *Nature* and will be of broad interest to the photovoltaics and scalable device community.

I therefore recommend acceptance after minor revisions aimed at improving clarity and precision of presentation.

Response: We thank the reviewer for the positive and constructive feedback. We are truly grateful that the reviewer recognizes the significance of our work and find it suitable for publication in *Nature*. Following this suggestion, we have carefully revised the manuscript to further improve its clarity and precision of presentation.

Minor comments:

1. The manuscript attributes the performance advantage primarily to the intrinsic properties of the In_2O_3 nanocrystal recombination layer. However, as also suggested by the rebuttal and supplementary data, ligand chemistry and nanocrystal morphology may also contribute. A slightly more balanced attribution would improve the accuracy of the discussion.

Response: We thank the reviewer for this constructive suggestion. The reviewer notes that ligand chemistry and nanocrystal morphology may also contribute to the performance advantage, not only the intrinsic properties of In_2O_3 . We agree and have revised the discussion accordingly to provide a more balanced attribution. The changes are marked in the revised manuscript:

Abstract: *"Here, we develop a solution-processed interconnecting layer based on surface-engineered indium oxide (In_2O_3) nanocrystals featuring high optical transparency, wherein controlled nanocrystal morphology and tailored ligand chemistry enable smooth interfacial contact*

and favorable energy level alignment.”

Introduction: *“We introduce a fully solution-processed TRJ based on surface engineered indium oxide nanocrystals (In_2O_3 NCs) with nanoscale morphology, whose energy levels and solvent compatibility can be systematically tuned through ligand chemistry.”*

2.The phrase “improve interfacial recombination” could be clarified, as recombination is typically associated with loss. It would be more precise to describe improved recombination efficiency across the tunnel junction or enhanced carrier recombination at the interconnection layer.

Response: We thank the reviewer for this precise observation. We now revise the presentation in the revised abstract:

“This coordinated interfacial and crystallization engineering strategy simultaneously enhances carrier recombination efficiency at the interconnection layer, improves carrier extraction, and promotes large-area film uniformity in all-perovskite tandems.”

3.The relatively low module-level current density ($\sim 1 \text{ mA cm}^{-2}$) is consistent with the series-connected architecture; however, it would be helpful to explicitly clarify its normalization and its relation to the subcell current ($\sim 15\text{-}16 \text{ mA cm}^{-2}$) to avoid potential confusion.

Response: We thank the reviewer for helping to clarify the potential confusion. We now supplement the definition of subcell current in the revised abstract and introduction as follows:

Abstract: *“As a result, a 65-cm^2 all-perovskite tandem solar module achieves a certified power conversion efficiency of 26.2%, with an open-circuit voltage of 2.182 V, a fill factor of 77.4%, and a short-circuit current density of 15.6 mA cm^{-2} in terms of averaged subcell performance, measured by Japan Electrical Safety and Environment Technology Laboratories (JET).”*

Introduction: *“While record small-area all-perovskite tandem devices ($\sim 0.1 \text{ cm}^2$) have surpassed 30% efficiency⁵, their large-area modules (with area $\geq 20 \text{ cm}^2$) remain limited to 24.5%, primarily due to insufficient short-circuit current density ($J_{\text{SC}} < 15 \text{ mA cm}^{-2}$ per subcell, whereas the subcell current density is normalized by the area of a single subcell)^{3,6,7}.”*

4.The suppression of lateral conductivity in the In_2O_3 nanocrystal layer is a key aspect of the proposed module-level advantage. While the device-level evidence is convincing, a brief clarification on whether lateral conductivity (or anisotropy) has been directly measured or estimated would further strengthen this point.

Response: We thank the reviewer for this comment. To address this point, we have performed

direct lateral conductivity measurements using a two-probe device structure. As shown in Figure R1, the In_2O_3 NC film exhibits negligible lateral conductivity when the concentration is below 10 mg/mL (2 mg/mL is the optimized condition used in our champion modules). This confirms that lateral shunting is effectively suppressed, as the In_2O_3 NCs remain discontinuous at such low concentrations.

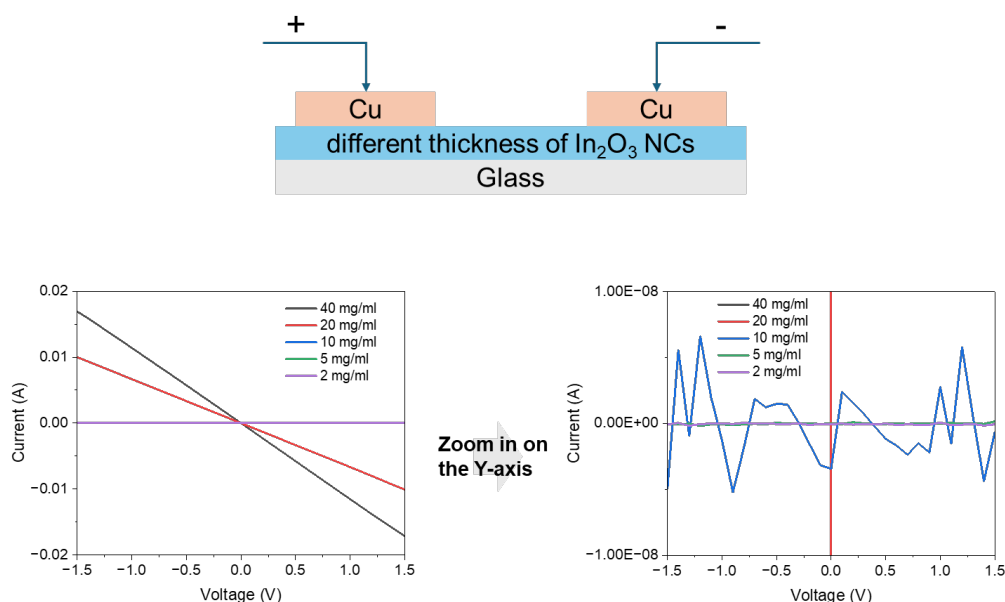


Figure R1. Lateral conductivity of In_2O_3 NCs. Top: Schematic of the device used to measure the lateral conductivity of In_2O_3 NCs. Bottom: I-V characteristics showing the lateral conductivity of In_2O_3 NCs at different thicknesses. In_2O_3 NC concentrations below 10 mg/mL resulted in negligible conductivity.

5. Given the emphasis on scalability, it would be helpful to briefly comment on the process tolerance (e.g., sensitivity to thickness, coating conditions, or nanocrystal coverage), as this is highly relevant for large-area manufacturing.

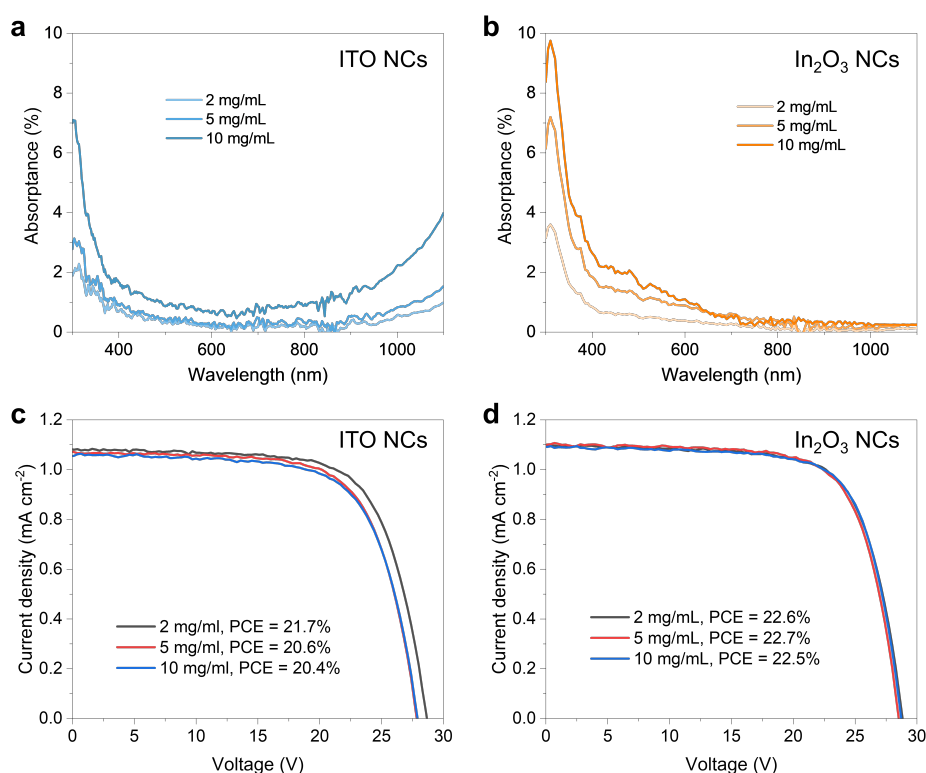
Response: We thank the reviewer for raising this practically important point. The reviewer notes that given the emphasis on scalability, it would be helpful to briefly comment on the process tolerance, such as sensitivity to thickness, coating conditions, or nanocrystal coverage, as this is highly relevant for large-area manufacturing.

- (1) Sensitivity to thickness: As shown in Supplementary Fig. 17, the tandem module performance remains virtually unchanged when the In_2O_3 NC concentration varies from 2 mg/mL to 10 mg/mL, demonstrating a broad processing window for scalable manufacturing.
- (2) Coating conditions: The In_2O_3 NC recombination layer can be processed entirely under ambient-air conditions without requiring an inert atmosphere or high-temperature treatment.

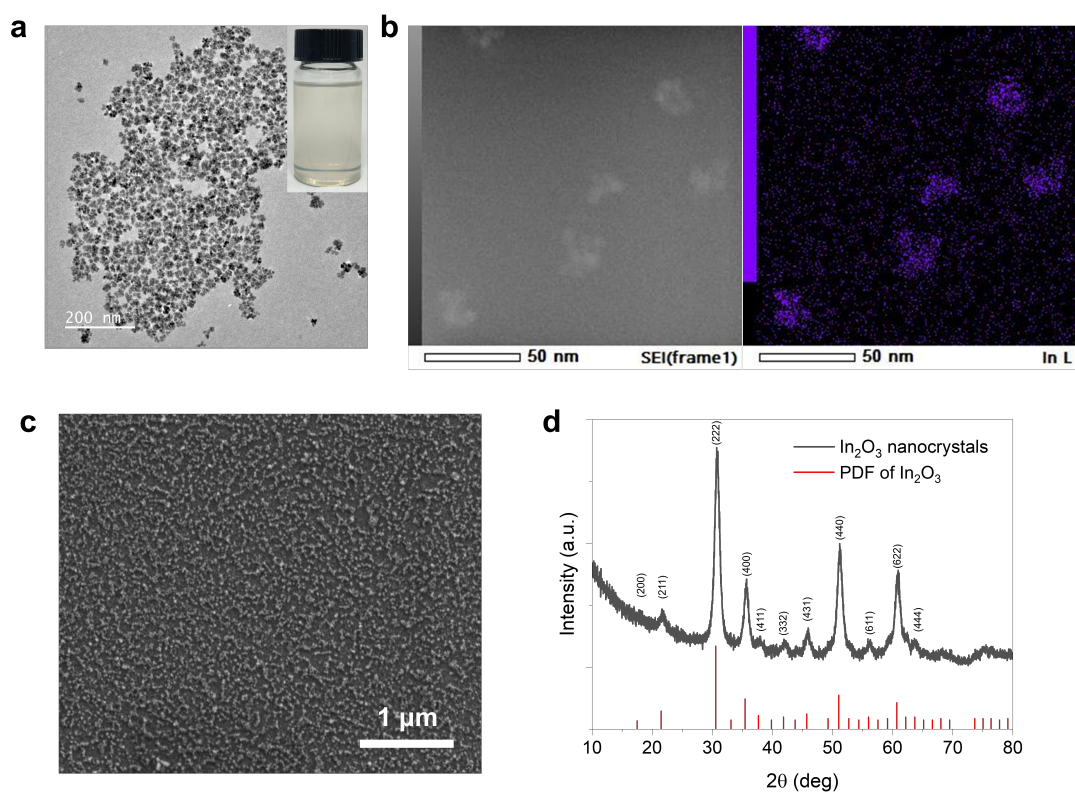
This process compatibility is advantageous for scalable manufacturing and has now been clarified in the revised manuscript.

- (3) Nanocrystal coverage: As shown in Supplementary Fig. 2c, the In_2O_3 NC film exhibits relatively uniform coverage under the optimized concentration and coating conditions employed in this work. Notably, efficient device operation does not require the nanocrystal layer to form a fully dense or continuous film. In practice, achieving such fully dense coverage uniformly over large areas would require substantially tighter control over coating and drying parameters during manufacturing. Instead, the nanocrystal network obtained here is already sufficient to enable effective interconnection in large-area tandem modules, as evidenced by the high module performance reported in this study. This result further demonstrates a broad processing tolerance with respect to nanocrystal coverage, which is highly advantageous for scalable manufacturing.

"After ALD deposition, ITO or In_2O_3 NC solution (2 mg mL⁻¹) was blade-coated with a coating gap of 300 μm , a speed of 10 mm s⁻¹ and the N₂ knife worked at 10 psi, followed by annealing at 100 °C for 10 min in air condition."



Supplementary Figure 17 | Optoelectrical property comparison. (a-b) Absorbance of different thickness of (a) ITO NCs and (b) In_2O_3 NCs using concentration from 2 mg/mL to 10 mg/mL. (c-d) Module performance comparison between ITO NCs and In_2O_3 NCs using concentration from 2 mg/mL to 10 mg/mL.



Supplementary Figure 2 | Synthesis of In_2O_3 nanocrystals. (a) TEM image of In_2O_3 nanocrystals. (b) HAADF-EDS of In_2O_3 nanocrystals. (c) SEM images of In_2O_3 nanocrystal films by blade-coated on the ITO substrate. (d) XRD pattern of In_2O_3 nanocrystals.

Referee #2 (Remarks to the Author):

The authors have clearly responded to my previous comments, particularly regarding the size effect of NCs, the comparison with neutral PEDOT:PSS, and the utilization of an eco-friendly solvent system.

The current revision significantly improves the overall quality of the manuscript.

However, I have a few remaining minor points that require further clarification.

Response: We thank the reviewer for the positive assessment and for acknowledging our previous responses. We are also grateful that the reviewer finds the current revision significantly improved in overall quality. We have addressed the remaining minor points as follows.

Minor Comments:

1. The authors mentioned that XPS spectra were collected from the opposite side of the sample, denoted as "target-bottom." Since the penetration depth of XPS is typically less than 10 nm, I am somewhat confused as to what the P 2p signal from the bottom side represents. Does it originate from the buried interface between the ITO and the SAM? If so, could the authors clearly describe the fabrication and measurement process for these "target-bottom" samples?

Response: We thank the reviewer for this question. The "target-bottom" spectra were intentionally collected from the exposed buried interface after mechanical delamination of the perovskite film from the ITO/glass substrate. Specifically, the sample preparation procedure is illustrated in Fig. R2. A UV-curable epoxy was first applied onto the perovskite surface and cured to mechanically support the perovskite layer. The perovskite film was then peeled away from the ITO/glass substrate, exposing the original buried ITO/perovskite interface. The exposed substrate side was subsequently placed facing upward for XPS and SEM characterization. Therefore, the detected P 2p signal originates from species remaining at the buried interfacial region rather than from the bulk perovskite film.

To further verify the effectiveness of the delamination process, we additionally measured the Pb 4f signal on the peeled ITO substrate. The negligible Pb signal confirms that minimal perovskite residue remained on the substrate after peeling, ensuring that the XPS measurements primarily probe the buried interface.

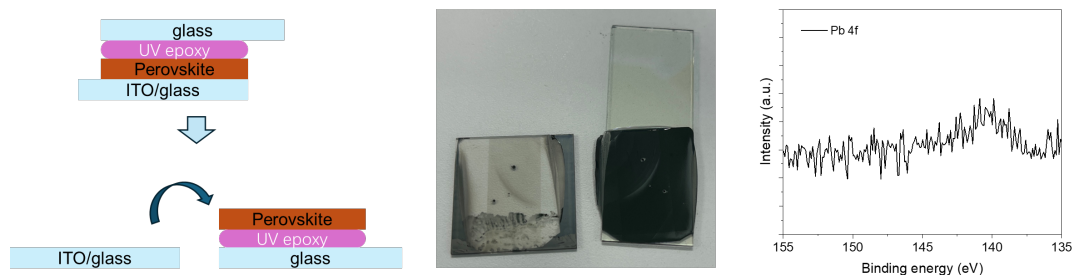


Figure R2. Sample preparation process for both XPS and SEM characteristics.

2. Could the authors provide more detailed insights into the possible causes of the incompatibility of the AAH additive in this system? For instance, is it due to a specific chemical reaction between the components, or simply a result of an excessive amount of the additive present in the perovskite film?

Response: We thank the reviewer for this question. Our key observation is that AAH and HSM individually improve device performance, but their co-addition causes degradation. This rules out a simple concentration effect and points to a specific interaction between the two additives. We speculate that a specific chemical interaction (e.g., hydrogen bonding or acid-base interaction) between the amino/ammonium groups of AAH and the phosphonic acid groups of HSM may lock their active sites, rendering both ineffective for defect passivation. Alternatively, competitive adsorption on perovskite defect sites could also play a role. We acknowledge that the exact mechanism requires further study, and we have provided this speculative discussion for the reviewer's reference.

3. It remains a subject of debate whether the dynamic, weak interaction between HSM and FA can effectively inhibit the deprotonation of FA⁺ thereby improving long-term stability. The authors are encouraged to provide further justification or discussion on this mechanism.

Response: We thank the reviewer for raising this mechanistic question. We agree that the interaction is relatively weak and dynamic rather than a strongly bound complex. However, such weak interactions can still significantly influence the local acid-base equilibrium and precursor coordination environment in perovskite inks.

Previous studies have shown that FA⁺ deprotonation can be promoted in mixed-cation Pb-Sn precursor systems, particularly in the presence of MA species (Chem. Mater. 2022, 34, 4394-4402), while appropriate solvent environments and molecular additives can suppress this process and stabilize the precursor solution (Nat. Energy 10, 318–328 (2025); Science 391, eadz7969 (2026)). In our system, we believe that the deprotonated phosphonic-acid species dynamically interact with FA⁺ and modulate the local chemical equilibrium, thereby reducing the tendency for irreversible

FA⁺ deprotonation during ink aging and crystallization.

More importantly, this interpretation is directly supported by the ink-aging experiments shown in Fig. R3. The HSM-containing precursor solution remained clear without observable precipitation after aging, and devices fabricated from aged HSM-containing inks exhibited performance comparable to those prepared from fresh inks. In contrast, the control precursor without HSM showed substantial precipitate formation and severe device-performance degradation after aging. These results collectively support that HSM incorporation effectively stabilizes the Pb-Sn precursor ink and suppresses the degradation pathways associated with FA⁺ deprotonation.

We have revised the manuscript as follow:

“Crucially, the preferential deprotonation of HSM consumes free acidic phosphonic acid groups that would otherwise directly acidify FA⁺ and induce its detrimental deprotonation. Instead, through these weak interactions, HSM effectively suppresses the deprotonation of FA⁺, thereby stabilizing the chemical environment of the precursor solution⁴.”

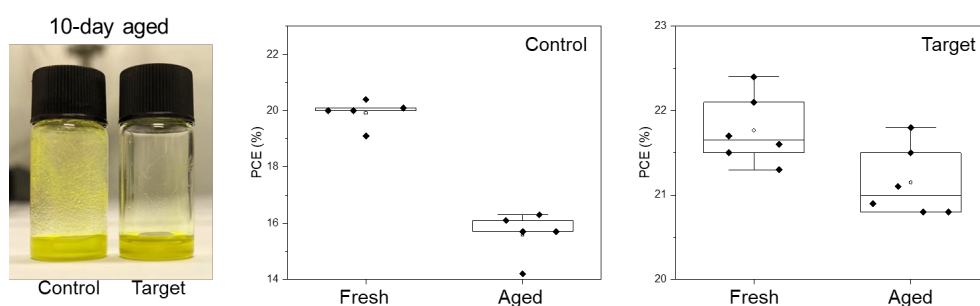


Figure R3. Picture and performance comparison of 10-day-aged control and target Pb-Sn perovskite solutions.

Referee #3 (Remarks to the Author):

The revision provided by the Authors addresses most of the comments and the manuscript is now more complete from scientific point of view. There however few major points to clarify before the paper could be published.

Response: We thank the reviewer for acknowledging that our revision has addressed most of the comments and improved the scientific completeness of the manuscript.

1) Reproducibility of the results (very important issue, a scientific result cannot be published without being reproducible)

Line 157: The manuscript states that supersaturation of the perovskite precursor solution was achieved by adding 20% THF. However, when we attempted to prepare the 1.4 M solution reported in the Supporting Information, the initial salt powders could not be fully dissolved. After stirring the solution for longer than 30 min, which is the recommended stirring time in the SI, we observed intense formation of a white precipitate, as described in the manuscript. We note that the experimental section has been revised to describe the preparation procedure as a sequence of steps ("first..., then..., then..."). However, it remains unclear why the solution preparation is described as the sequential addition of several components, while stirring appears to be applied only at the final stage. The main issue is that we were unable to reproduce the procedure already at the stage of perovskite precursor preparation. We mixed all components together and applied intensive stirring, as described, but still observed white precipitation before complete dissolution of the initial salts. Could the authors clarify why this precipitation occurs and how it can be avoided? In our experiments, complete dissolution was only possible up to a concentration of 1.2 M; however, this concentration did not yield the optimal film thickness. We therefore believe that some important experimental conditions may be missing from the current description. In addition, it will be nice to add a video related to this step.

Response: We thank the reviewer for this constructive and practically important comment regarding the reproducibility of the precursor preparation. The precipitation behavior described by the reviewer is fully consistent with our own observations when the precursor components are mixed improperly. In particular, introducing THF at the initial stage readily causes incomplete dissolution and precipitation formation.

We therefore emphasize that the precursor preparation critically relies on a sequential dissolution procedure rather than simultaneous mixing of all components. Specifically, all precursor salts must first be completely dissolved in 2-Me under stirring before THF is gradually introduced as the final component. Only after a fully clear precursor solution is obtained in 2-Me should THF be added. If THF is introduced at the beginning, or if all components are mixed simultaneously, white precipitation is indeed expected, especially at the high precursor concentration (1.4 M) used in this

work. For example, to prepare 1 mL of solution, 1.4 mol of salts were first dissolved completely in 0.8 mL of 2-Me, followed by the addition of 0.2 mL of THF into the 2-Me solution.

We have revised the Experimental Section to make this sequential order explicit as follow:

“The solvent ratio of 2-methoxyethanol and tetrahydrofuran to prepare precursor solution (1.4 M) is 4:1. For the precursor preparation (1 ml for example), 1.4 mol of abovementioned salts were first dissolved in 0.8 mL of 2-Me. Then tin powders (5mg ml⁻¹) as the antioxidant was added to the precursor solution. DMSO (0.1% mole ratio) as the additive was added to the precursor solution. After all the above additives have been added, the precursor solution was stirred at room temperature for 0.5 h. The precursor solution was filtered through a 0.22 μm PTFE membrane before using. Finally, 0.2 mL of THF was added to the filtered 2-Me-based solution, and the solution was mild shaken before using. Prolonged stirring of 2-Me-only solution and simultaneous mixing of all components (especially THF) should be avoided, as it may lead to undesirable sedimentation.”

2) On the use of THF.

Line 170: The statement “The incorporation of THF into the wide-bandgap perovskite...” is unclear in the context of the experimental details, since the SI states that DMF and DMSO were used for the wide-bandgap perovskite precursor. The authors should clarify the role of THF in this case. In addition, the experimental details corresponding to Supplementary Figure 12 should be provided.

Response: We thank the reviewer for pointing out these omissions. We have clarified the role of THF in the manuscript in the description of Supplementary Figure 12. Specifically, THF serves as a volatile co-solvent to accelerate solvent evaporation, thereby promoting rapid nucleation and improving large-area film uniformity. The wide-bandgap perovskite precursor solution actually contains a ternary solvent system of DMF/DMSO/THF. We have now added this information to the Experimental Section:

“All the salts were dissolved in mixed DMF:DMSO first. The precursor solution was stirred at 50 °C overnight, then filtered through a 0.22 μm polytetrafluoroethylene (PTFE) membrane before using. THF was then added to the filtered DMF:DMSO mixed solution, and the solution was mild shaken before using.”

3) minor point

Line 218: In the sentence “...previously reported aminoacetamide hydrochloride (AAH) additive...”, the relevant reference appears to be missing from the manuscript.

Response: We have added the citation.