nature portfolio

Peer Review File

Resonance-Induced Electron Delocalization for Efficient Lead-Free Perovskite Solar Cells

Corresponding Author: Professor Ligang Xu

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Here, authors report a resonance-induced electron delocalization strategy to fundamentally stabilize tin perovskite by enhancing Sn-centered interactions using trithiocyanuric acid (Cy-SH) and cyanuric acid (Cy-OH) molecules as interfacial layer. Results further demonstrate the electron delocalization between the N–C=O and N=C–OH tautomeric configurations of Cy-OH at the perovskite buried interface, which strengthens its interaction with uncoordinated Sn atoms, thereby significantly suppressing non-radiative recombination and enhancing carrier extraction and transport. The manuscript has sufficient data and reasonable analysis. But there are still some issues in the manuscript that need to be addressed and supplemented.
1.Keywords: Device performance, Stability. These two words are a bit repetitive.
2.The device performance in the manuscript should be listed in a table, which can directly show the performance of the devices.3.Based on the interaction between N-C=O and N-C=S groups and Pb and iodide ions in perovskite, some articles have reported it. If the author can analyze the impact of N-C=O and N-C=S on the nucleation and crystallization of perovskite, the quality of the manuscript will be higher. The author should explain the effect of modifiers on the nucleation and crystallization of perovskite.
4.Since the author used two types of modifiers to modify the buried interface, the author can also compare the advantages and disadvantages of these two modifiers on the modification effect of perovskite. This system will attract more attention.
5.Some relevant references can be cited, which may improve the quality of the manuscript. For example: Advanced Materials, 2025, 37，2500708; Advanced Energy Materials, 2025, 15, 2405571; Angewandte Chemie International Edition, 2024, 63, e202404385.
6.The two vertical lines in Figure 1d and e should be dashed lines, they are only auxiliary lines, not the actual lines in the figure.

Reviewer #2

(Remarks to the Author)
The authors report a resonance-induced electron delocalization strategy to fundamentally stabilize lead-free tin perovskite solar cells (TPSCs). They employed tautomeric molecules, specifically trithiocyanuric acid (Cy-SH) and cyanuric acid (Cy-OH), as an interfacial layer to enhance interactions with uncoordinated Sn atoms. The study demonstrates that these molecules undergo a structural transformation from the enol form to the keto form upon interaction with the perovskite surface, creating strong electron-donating groups (C=O or C=S) that effectively coordinate with Sn2+ sites. This mechanism significantly suppresses non-radiative recombination, regulates perovskite crystallization, and enhances carrier extraction and transport. Consequently, the best-performing device achieved a power conversion efficiency (PCE) of 12.1% and exhibited excellent long-term stability, maintaining 86% of its initial efficiency after 1000 hours of aging. In summary, this work provides a rational design guideline for utilizing tautomeric molecules to develop high-performance and stable lead-free photovoltaics. However, several issues should be addressed before publication.

1. Although both Cy-OH and Cy-SH are introduced as interfacial molecules, the subsequent figures and discussions present a somewhat confusing comparison between the two. The authors are encouraged to clearly clarify the role and positioning of Cy-SH in this work (e.g., as a control or a supplementary reference) in this section to improve clarity and coherence.
2. To elucidate the modification and coordination effects on the perovskite films, the authors should compare the pristine perovskite film with the Cy-OH-modified perovskite film, rather than comparing the Cy-OH-modified perovskite film with the

Cy-OH film.
3. The authors are requested to explain why a photoluminescence (PL) peak appears at around 790 nm in Figure 2d. According to Figure 4c, the VTFL of Cy-OH is shown to be 0.94 V; however, the manuscript states that the VTFL of Cy-OH is 0.92 V. Please check and clarify whether these values are consistent.
4. It is recommended to supplement AFM or KPFM images to compare the uniformity of interfacial supramolecular assembly and work function before and after modification. Also, it is recommended to supplement UPS characterization for quantitative calculation of whether energy level offset occurs at the interface.
5. In order to demonstrate the coordination of Cy-OH/Cy-SH and their defect passivation ability at the Fermi level, the authors hope to add a DFT calculation of adsorption energy and density of states (DOS).
6. Adding at least one MPPT light-soaking (or bias-illumination) stability test, together with aging-dependent tracking of Sn^{2+}/Sn^{4+} and interfacial chemistry, would make the stability claim more convincing and closer to real operation.
7. In this manuscript, some figures are displayed in bold while others are not. It is recommended that the author standardize the format.
8. Some related references (https://doi.org/10.1002/cey2.70123; https://doi.org/10.1002/cey2.710) should be cited.

Reviewer #3

(Remarks to the Author)
In this manuscript, Xu et al. report a resonance-induced electron delocalization strategy 19 to fundamentally stabilize tin perovskite by enhancing Sn-centered interactions using trithiocyanuric acid (Cy-SH) and cyanuric acid (Cy-OH) molecules as interfacial layer. The optimized devices achieved a power conversion efficiency (PCE) of 12.1% with improved stability (86% retention after 1000 h in N2). However, the manuscript has some major technical flaws and critical validations (the uniqueness and mechanism of the proposed strategy) that need to be addressed, and detailed discussions of some analytical approaches are needed to justify interpretations and better comprehend the results. Addressing the following refinements would further enhance the paper's clarity and impact:

1、The existing data (FTIR, XPS, NMR) only confirm coordination and tautomeric isomerism: these results merely indicate that the molecule has undergone chemical interaction with Sn2+ and that its own structure has changed. It cannot directly prove the occurrence of the key physical process of "electron delocalization", much less demonstrate that this process is the primary reason for the performance enhancement. More evidence should supplement to visualize and quantify the degree of electron delocalization.

2、The author selected Cy-OH and Cy-SH as representative molecules for the "resonance-induced electron delocalization" strategy because they are tautomers. Compared to molecules lacking resonance tautomerism but possessing similar coordinating groups (such as C=O or C=S), what are the unique advantages of this strategy? Is the performance enhancement attributable to the coordination of the C=O or C=S?

3、Figure 3d requires additional parameter information (Jsc, Voc, FF) beyond PCE comparisons along with specific JV data supplementation.

4、According to Figure 3a, the short-circuit current density (JSC) increased from 17.10 mA cm-2 to 19.29 mA cm-2, raising the average short-circuit current density. What is the reason? The authors should support more evidences and explain in details.

5、This manuscript focuses on the intrinsic instability of Sn2+, but its characterization of stability is insufficient, which suggest that the authors should conduct more stability characterization studies on perovskite films.

Reviewer #4

(Remarks to the Author)
Dear Editor,
The manuscript (manuscript number: COMMSMAT-25-1297) uses cyanuric acid (Cy-OH) and trithiocyanuric acid (Cy-SH) as interfacial layers in tin-based PSCs reporting increased PCE and Voc, reduced hysteresis, longer PL lifetimes, and 86% retention after 1000 h. However the data and interpretation are not convincing due to clear gaps in the data and methodology and limited novelty since interfacial passivation strategies have been widely reported. These concerns are fundamental so I recommend rejection of this manuscript.
The main idea using an interfacial molecule to bind/coordinate Sn and reduce defects is already common in perovskite research. Many previous studies have used similar passivation or coordination strategies including molecules with conjugation resonance effects. So using cyanuric-acid-type molecules here looks like an incremental variation of known approaches not a clearly new breakthrough. The performance is also not state of the art. The best device is 12.1%, while tin-based perovskite solar cells in the literature have already reported >12% .
(DOI: 10.1002/advs.202309668, DOI: 10.1039/D3EE03359G, DOI: 10.1002/adma.202410248, DOI: 10.1021/acs.nanolett.4c00474, DOI: 10.1002/aenm.202406024, DOI: 10.1016/j.matt.2021.12.013, DOI: 10.1016/j.nanoen.2022.107818, DOI: 10.1021/acsenergylett.2c00776, DOI: 10.1002/adfm.202413281, DOI: 10.1002/adma.202410248, DOI: 10.1038/s41566-024-01381-7, DOI: 10.1002/anie.202420150, DOI: 10.1021/acsenergylett.4c03172, DOI: 10.1002/anie.202415681, DOI: 10.1021/jacs.1c03032, DOI: 10.1002/adma.202402947, DOI: 10.1002/eom2.12500, DOI: 10.1021/acs.nanolett.4c00646, DOI:

10.1021/acsenergylett.3c02795, DOI: 10.1002/anie.202318133, DOI: 10.1021/acs.nanolett.5c01498, DOI: 10.1021/acsenergylett.5c00034, doi.org/10.1021/acs.nanolett.5c02305).
The mechanism the authors propose is not clearly proven. They repeatedly claim that a special resonance-induced electron delocalization and tautomerism at the interface fundamentally stabilizes the tin perovskite. But the evidence they show mostly looks like what we normally see from standard interfacial passivation. Such as they report sharper XRD peaks and longer PL lifetimes but these improvements can happen with many ordinary (non-tautomeric) additives simply because they passivate traps or change crystallization. They do not isolate what is unique about tautomerism. There is no control molecule that is similar but cannot tautomerize. Without that control it is just as likely that the benefit comes from common features like multiple H-bonding groups or Lewis-basic sites that bind to Sn/I defects.
The paper suggests the interfacial molecular network changes the perovskite electronic structure even in regions not directly interacting. If the molecules sit only at the interface their effect should be limited to a very thin region unless the authors show evidence of bulk changes, for example clear band shifts, doping changes, depth-dependent measurements this evidence is not provided.
The authors present stability data but the storage test was done in a very mild N2 glovebox (trace O2) yet the best Cy-OH device still lost 14% PCE in 6 weeks and the control is described as degrading rapidly without clear numbers. More importantly under continuous light at 60oC the Cy-OH device drops to 60% of its initial PCE within 250 hours (40% loss) which is not convincing long-term stability. No humidity, ambient air, thermal-cycling, or outdoor tests are provided, so the stability evaluation is too limited to support claims of durable and practical performance. The authors claim the benefit comes from the tautomeric/resonance nature of Cy-OH and Cy-SH but they do not test a similar molecule that cannot tautomerize. A good control would be an analog molecule where tautomerism is not possible for example a monofunctional version or a structure with the enol/keto form locked. Without this comparison it is unclear whether the improvement is truly due to tautomeric resonance or simply normal surface passivation.
The study also does not compare the Cy-OH interlayer to common and simpler passivation strategies including widely reported molecules in the literature. Since SnF2 is already used in the precursor the authors didn't show how much extra benefit Cy-OH adds compared with standard approaches. The authors say they made 15 devices but they only show the average PCE. They didn't show how Jsc, Voc, FF vary across those devices not just the average, because the treatment might improve one parameter more than the others.
In the EQE plot the response is strangely high at short wavelengths but abnormally low in the 400–500 nm range. The authors claim the treated device has higher EQE across the whole spectrum but the curve itself shows a clear dip in that region which contradicts. This unusual spectral shape may indicate issues with the measurement setup or calibration uncertainty.
Given these issues along with limited novelty and the insufficient scientific merit of this work I recommend complete rejection.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The author has made revisions to the manuscript based on the review comments, and I recommend that the revised manuscript can be accepted by the communications materials journal.

Reviewer #2

(Remarks to the Author)
The quality of the revised manuscript has been improved and I recommend accept it.

Reviewer #3

(Remarks to the Author)
The authors have modified their manuscript according to the reviewer's comments, I recommend the acceptance of this manuscript for publication in Communications Materials.

Reviewer #4

(Remarks to the Author)
After carefully reading the author's response I still do not think the manuscript is suitable for publication and I still recommend rejection of this manuscript. Although the authors have added some supplementary data including AHP control devices AFM/UPS, light dark cycling stability and repeated EQE measurements these additions do not satisfactorily address the fundamental concerns regarding novelty, mechanism, stability and data reliability. The novelty remains limited. The work is still mainly based on interfacial molecular passivation coordination of Sn-related defects which is already a widely reported strategy in tin-based perovskite solar cells. The authors try to distinguish their work by claiming resonance induced electron delocalization and ordered supramolecular interfacial assembly but the experimental evidence does not convincingly prove that this is fundamentally different from ordinary passivation or crystallization control. The direct proof of electron delocalization is important but their response mainly relies on a previous Science report and indirect evidence such as XPS shifts FTIR changes, PL lifetime and crystallinity. The stability evidence is still weak. EQE correction raises reliability concerns. The initial EQE data had an abnormal dip and repeated the measurement which suggests the data were

not well calibrated that raise concerns about the consistency of the measurement. This performance is not strong enough to support the broad claims. The best PCE is only 12.10% and the improvement over AHP and Cy-SH is limited so the paper remains more like an incremental passivation study.

Version 2:

Reviewer comments:

Reviewer #4

(Remarks to the Author)
The modifications are done, and they have reached an acceptable level.

南京郵電大學
Nanjing University of Posts and Telecommunications

April 15, 2026

Doctor Meltem Yanilmaz

Associate Editor, Communications Materials

Email: commsmat@nature.com

Dear Doctor Meltem Yanilmaz,

Re: Decision on manuscript COMMSMAT-25-1297

Thank you so much for your letter dated February 5, 2026 regarding our manuscript entitled: **"Resonance-Induced Electron Delocalization for Efficient Lead-Free Perovskite Solar Cells" (Research Article, Manuscript ID: COMMSMAT-25-1297A)** (Authors: Ao Shen, Chensi Gong, Zhiheng Dong, Mingtai Chen, Wenzhen Lv, Runfeng Chen*, Ligang Xu*).

We have carefully gone through the comments of the reviewers/editor and made necessary changes to the manuscript. These changes have been highlighted in red in the revised manuscript. The details are as follows.

The reply is indicated by black letters, while the comments by the editor/reviewers are indicated by *blue italic* letters. We have documented any changes that we have made to the original manuscript.

Reviewer #1

Comment: *Here, authors report a resonance-induced electron delocalization strategy to fundamentally stabilize tin perovskite by enhancing Sn-centered interactions using trithiocyanuric acid (Cy-SH) and cyanuric acid (Cy-OH) molecules as interfacial layer. Results further demonstrate the electron delocalization between the N–C=O and N=C–OH tautomeric configurations of Cy-OH at the perovskite buried interface, which strengthens its interaction with uncoordinated Sn atoms, thereby significantly suppressing non-radiative recombination and enhancing carrier extraction and transport. The manuscript has sufficient data and reasonable analysis. But there are still some issues in the manuscript that need to be addressed and supplemented.*

Response: Many thanks for the professional comments and kind recommendation of our work.

1. Keywords: Device performance, Stability. These two words are a bit repetitive.

Response: Thanks for the kind reminding. We have replaced these two words by "Efficiency; Stability". Many thanks.

Revised text:

Page 2 of the revised manuscript:

Lead-free perovskite solar cells; Resonance-induced electron delocalization strategy; Tautomeric configurations; Power conversion efficiency; Stability

2. The device performance in the manuscript should be listed in a table, which can directly show the performance of the devices.

Response: We thank the reviewer for this constructive suggestion. We have provided the device performance parameters in the Table S1 in the revised manuscript.

Table S1. Device performance of the devices based on different interfacial materials.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Control	0.80	17.10	72.05	9.9
Cy-OH	0.86	19.29	72.80	12.10
Cy-SH	0.80	18.83	71.20	10.73
AHP	0.86	18.36	64.45	10.22

3. Based on the interaction between N-C=O and N-C=S groups and Pb and iodide ions in perovskite, some articles have reported it. If the author can analyze the impact of N-C=O and N-C=S on the nucleation and crystallization of perovskite, the quality of the manuscript will be higher. The author should explain the effect of modifiers on the nucleation and crystallization of perovskite.

Response: We thank the reviewer for this insightful suggestion. As suggested, we employed *in situ* UV-vis absorption spectroscopy and *in situ* photoluminescence (PL) measurements to further elucidate the influence of these functional groups on the nucleation and crystallization kinetics of perovskite (**Figure S6**). From the results, the Cy-OH–based films exhibit an earlier onset of absorption, indicating accelerated nucleation. Furthermore, the time evolution of the PL intensity reveals a slower crystal growth rate in the treated films compared to the control, suggesting that the strong coordination between the tautomeric molecules and Sn^{2+} effectively retards the rapid and uncontrolled crystallization of tin perovskites. Consequently, this results in a reduced defect density and enhanced film crystallinity, which aligns well with the improved device performance and stability observed in our study. We have updated these related discussions in the revised manuscript.

Revised text:

Page 12 of the revised manuscript:

To investigate the real-time crystallization process of tin-based perovskite films during annealing, in-situ photoluminescence (Figure S6) and in-situ UV-vis absorption spectra (Figure S7) were employed. The Cy-OH-based film showed much higher PL intensity than the control, indicating improved crystalline quality. From the first 100 s before annealing (Figure S6c, d), the control film's PL intensity began to rise at around 30 s, marking the onset of recrystallization, whereas the Cy-OH-treated film showed signal emergence earlier (25 s), indicating accelerated nucleation. Furthermore, in-situ UV-vis spectroscopy revealed that the Cy-OH-containing film exhibited a slow increase in absorption intensity after 10 s, while the control film showed a rapid increase within 5 s, confirming that Cy-OH significantly retards the crystallization growth rate of tin-based perovskites.

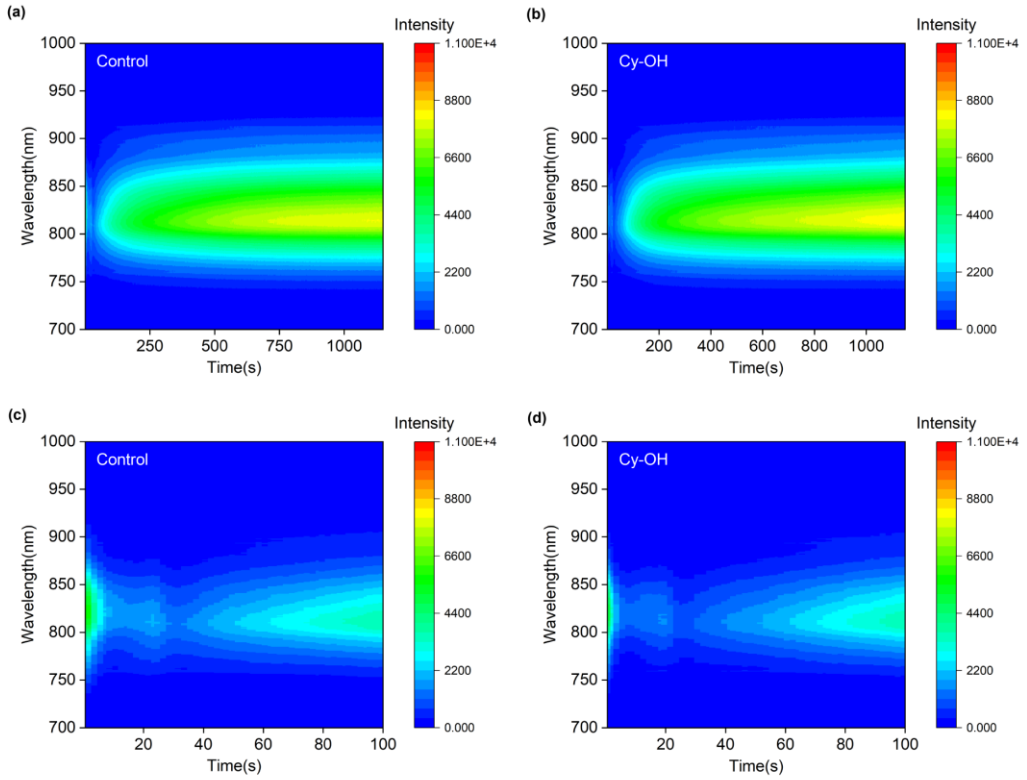


Figure S6. In situ PL spectroscopy of the (a) control and (b) Cy-OH–based perovskite films. (c, d) The initial annealing phase for 100 s.

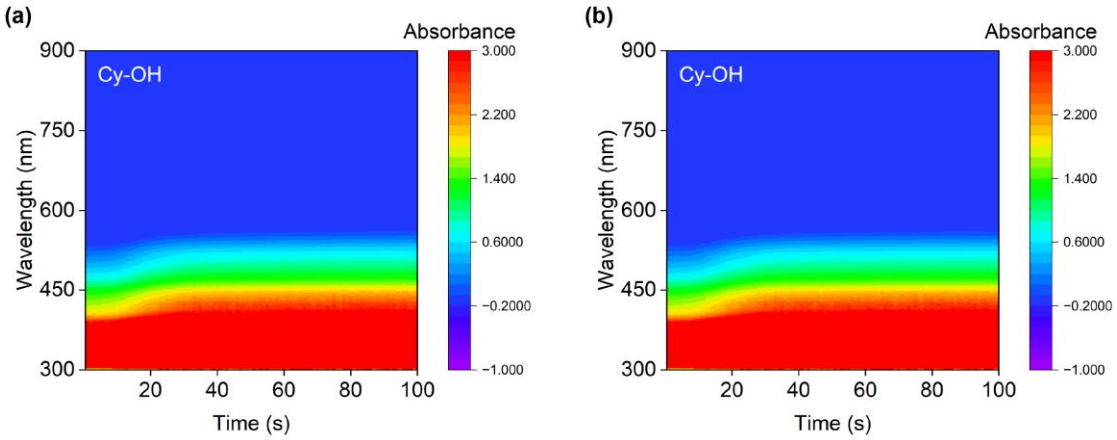


Figure S7. *In situ* UV-vis absorption spectra of the control and target samples.

4. Since the author used two types of modifiers to modify the buried interface, the author can also compare the advantages and disadvantages of these two modifiers on the modification effect of perovskite. This system will attract more attention.

Response: Thanks for the reviewer's insightful comments and constructive suggestions. We fully agree with this perspective. However, due to the specific solubility requirements of these

organic molecules, we encountered technical difficulties when attempting deposition onto perovskite surface. Specifically, Cy-OH and Cy-SH are readily soluble only in polar solvents (DMF and DMSO), which would damage the perovskite film during the spin-coating. Meanwhile, they are insoluble in common anti-solvents (e.g., toluene or chlorobenzene), making it impossible to deposit them via conventional spin-coating methods. We also attempted to introduce a template method for processing, but these efforts were unsuccessful. We hope the reviewer can understand and agree with us.

5. Some relevant references can be cited, which may improve the quality of the manuscript. For example: Advanced Materials, 2025, 37，2500708; Advanced Energy Materials, 2025, 15, 2405571; Angewandte Chemie International Edition, 2024, 63, e202404385.

Response: As suggested, we have cited these references into the revised manuscript. Many Thanks.

6. The two vertical lines in Figure 1d and e should be dashed lines, they are only auxiliary lines, not the actual lines in the figure.

Response: Thanks for the kind reminding. We have revised the figures accordingly in the revised manuscript.

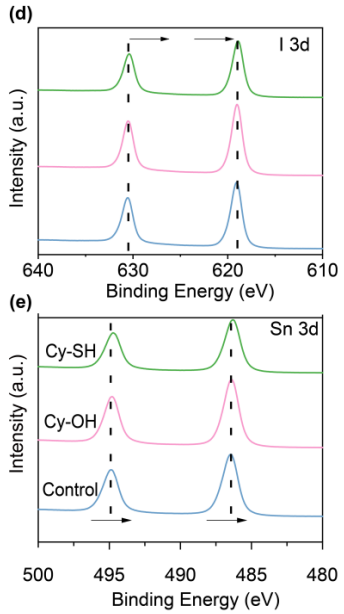


Figure 1 (d, e) XPS measurements of (d) I 3d and (e) Sn 3d based on control and target perovskite samples.

Reviewer #2

Comment: *The authors report a resonance-induced electron delocalization strategy to fundamentally stabilize lead-free tin perovskite solar cells (TPSCs). They employed tautomeric molecules, specifically trithiocyanuric acid (Cy-SH) and cyanuric acid (Cy-OH), as an interfacial layer to enhance interactions with uncoordinated Sn atoms. The study demonstrates that these molecules undergo a structural transformation from the enol form to the keto form upon interaction with the perovskite surface, creating strong electron-donating groups (C=O or C=S) that effectively coordinate with Sn^{2+} sites. This mechanism significantly suppresses non-radiative recombination, regulates perovskite crystallization, and enhances carrier extraction and transport. Consequently, the best-performing device achieved a power conversion efficiency (PCE) of 12.1% and exhibited excellent long-term stability, maintaining 86% of its initial efficiency after 1000 hours of aging. In summary, this work provides a rational design guideline for utilizing tautomeric molecules to develop high-performance and stable lead-free photovoltaics. However, several issues should be addressed before publication.*

Response: Thank you very much for your positive and insightful comments on our work.

1. Although both Cy-OH and Cy-SH are introduced as interfacial molecules, the subsequent figures and discussions present a somewhat confusing comparison between the two. The authors are encouraged to clearly clarify the role and positioning of Cy-SH in this work (e.g., as a control or a supplementary reference) in this section to improve clarity and coherence.

Response: Thank you for your valuable comments. We have clarified in the revised manuscript that Cy-SH is included as a supplementary reference, while Cy-OH constitutes the primary focus of our investigation. This distinction has been explicitly stated in the *Results and Discussion* section. Many thanks.

Revised text:

Page 6 of the revised manuscript:

To determine the optimal concentration for buried interface modification, we conducted a series of concentration-dependent experiments (Table S1-S2). And the device treated by Cy-OH at 2 mg/mL exhibited the highest PCE. Consequently, all subsequent characterizations and discussions in this study are primarily focused on devices fabricated under this optimal

condition, with Cy-SH treated devices included as a supplementary reference.

2. To elucidate the modification and coordination effects on the perovskite films, the authors should compare the pristine perovskite film with the Cy-OH-modified perovskite film, rather than comparing the Cy-OH-modified perovskite film with the Cy-OH film.

Response: Thanks for the kind reminding. We have provided the XPS spectra of the pristine perovskite film and the Cy-OH-treated film (**Figure 1d, e**).

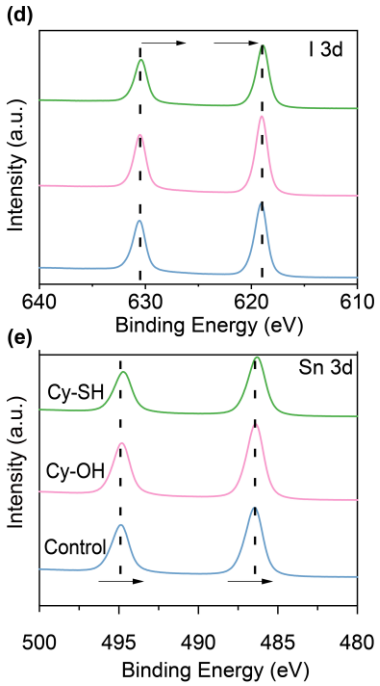


Figure1. (d, e) XPS measurements of (d) I 3d and (e) Sn 3d based on control and target perovskite samples.

3. The authors are requested to explain why a photoluminescence (PL) peak appears at around 790 nm in Figure 2d. According to Figure 4c, the V_{TFL} of Cy-OH is shown to be 0.94 V; however, the manuscript states that the V_{TFL} of Cy-OH is 0.92 V. Please check and clarify whether these values are consistent.

Response: Many thanks for the reviewer's comments. From the previous report (J. Energy Chem, 2024, 98, 556-561; Nature 2024, 628, 93-98), we believe that the fluorescence peak at 750-820nm is attributed to the two-dimensional phase in the perovskite film, which could be detected by PL. We also thank the reviewer for pointing out the inconsistency in the reported V_{TFL} values of the Cy-OH–treated device. As suggested, we have revised the manuscript

accordingly.

4. It is recommended to supplement AFM or KPFM images to compare the uniformity of interfacial supramolecular assembly and work function before and after modification. Also, it is recommended to supplement UPS characterization for quantitative calculation of whether energy level offset occurs at the interface.

Response: We have obtained AFM and UPS characterizations. The results show that the film treated with Cy-OH exhibits lower roughness and better film quality (**Figure S5**). Moreover, UPS reveals that the treated device has a smaller energy level barrier, which is relatively more favorable for hole transport(**Figure S13**). We have updated these related discussions in the revised manuscript. Many thanks

Revised text:

Page 12 of the revised manuscript:

In addition, atomic force microscopy (AFM) revealed that the Cy-OH-treated perovskite film exhibits a smoother surface（the RMS roughness reduced from 20.02 nm to 11.2 nm), further confirming the positive role of tautomeric molecules in optimizing film quality（Figure S5）

Ultraviolet photoelectron spectroscopy (UPS) (FigureS13) measurements reveal that the treated device exhibits a smaller energy level barrier, which is relatively more favorable for hole transport[34].

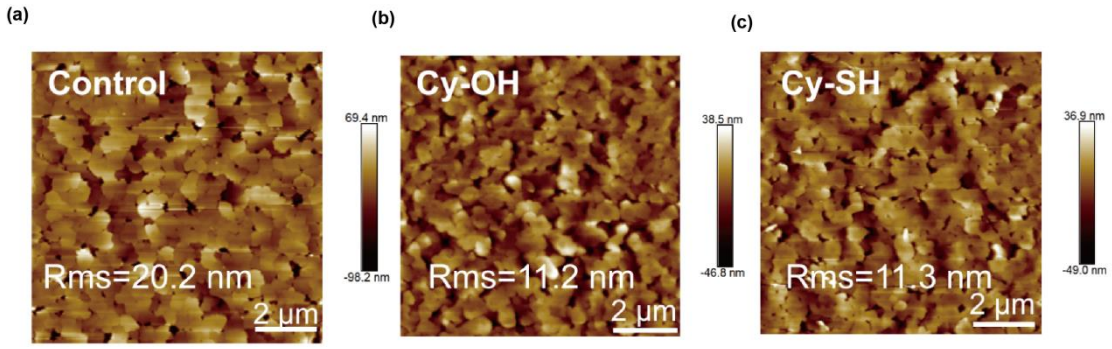


Figure S5. AFM images of (a) the control, (b) Cy-OH-treated, and (c) Cy-SH-treated perovskite films.

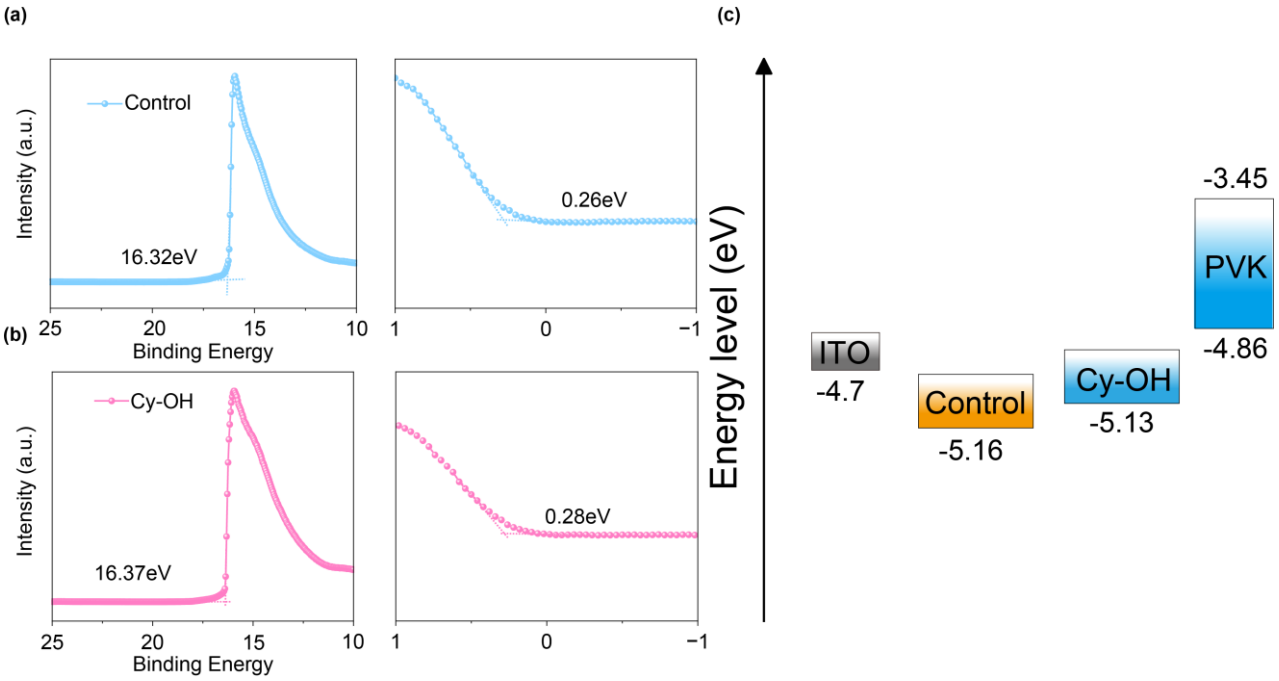
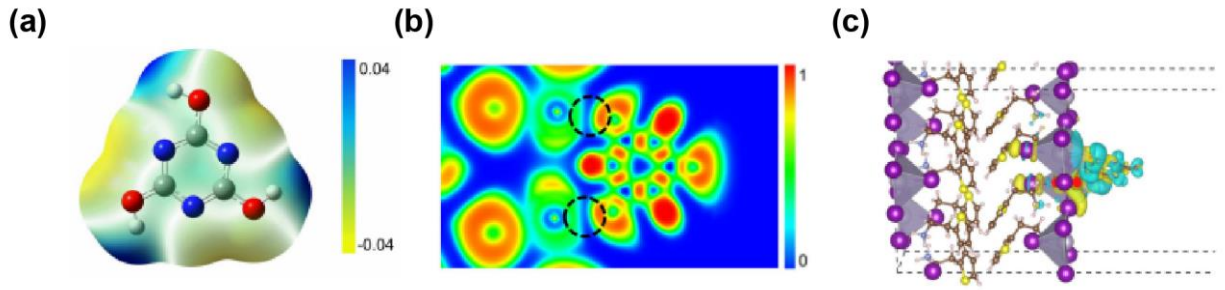


Figure S13. (a, b) UPS spectra of the control and Cy-OH-treated HTLs, (c) corresponding energy level diagram.

5. In order to demonstrate the coordination of Cy-OH/Cy-SH and their defect passivation ability at the Fermi level, the authors hope to add a DFT calculation of adsorption energy and density of states (DOS).

Response: We thank the reviewer for highlighting the importance of theoretical calculations to verify the coordination effects and defect passivation at the Fermi level for Cy-OH and Cy-SH. We agree that DFT analysis would provide valuable support for the proposed mechanisms. In this regard, we noted that a previous study by Wang *et al.* (Science, 2023, 622, 493-498.) has already performed comprehensive DFT calculations on similar tautomeric molecules interacting with tin perovskites, including adsorption configurations and density of states analysis. Their results clearly demonstrate interfacial coordination and electronic modulation, which strongly support our proposed mechanism. We have now cited this work in the revised manuscript to provide relevant theoretical support and strengthen our discussion.



Supplemental Figure S1. (a) Calculated electrostatic potential distribution map for the enol form of the Cy-OH molecule. (b) Electron localization function (ELF) image of the perovskite treated with Cy-OH. (c) Charge density difference between the tin-based perovskite and Cy-OH, obtained in a system with an iodide vacancy.

6. Adding at least one MPPT light-soaking (or bias-illumination) stability test, together with aging-dependent tracking of Sn^{2+}/Sn^{4+} and interfacial chemistry, would make the stability claim more convincing and closer to real operation.

Response: We appreciate the professional suggestion from the reviewer. As suggested, we have provided a light-dark cycling stability test (bias-illumination) in the revised manuscript which effectively simulates device operation under intermittent illumination. The results show that after 700 hours, the PCE of the control device dropped to 65% of its original value, while the target device still remained over 85%. We analyzed the evolution of the Sn^{2+}/Sn^{4+} ratio during aging by monitoring the color changes of SnI_2 and Cy-OH–treated SnI_2 solutions exposed to air. The results show that the color of the pure SnI_2 solution changes significantly after 25 minutes of exposure to air, indicating increased oxidation, while the solution with Cy-OH exhibits weaker color change, suggesting better oxidation resistance. We have updated these related discussions in the revised manuscript. Many thanks.

Revised text:

Page 16 of the revised manuscript:

Meanwhile, day–night cycling stability tests were conducted in N_2 containing 100-200 ppm O_2 with a 12-hour light–dark alternation. After 30 consecutive cycles (approximately 700 hours) in a nitrogen environment, the target device retained 85% of its initial efficiency, whereas the control device dropped significantly to 66%. To evaluate the effect of Cy-OH on the ambient

stability of SnI_2, the color evolution of pristine SnI_2 and SnI_2 with Cy-OH was monitored upon air exposure for different time (Figure S10). The pristine SnI_2 film rapidly changed from yellow to dark brown within 15 min, indicating severe oxidation of Sn^{2+} to Sn^{4+}. In contrast, the Cy-OH-modified SnI_2 film showed significantly retarded darkening, with only a slight change even after 25 min of air exposure. These results demonstrate that Cy-OH effectively suppresses oxidation and enhances the stability of SnI_2 under ambient conditions.

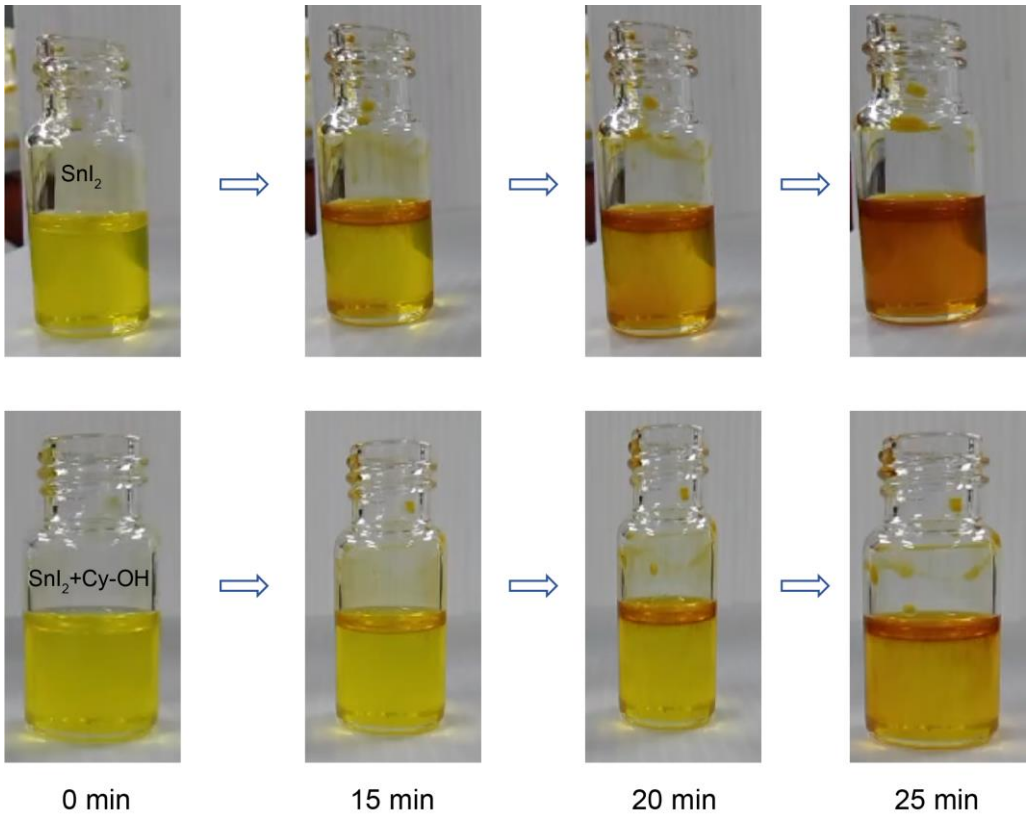


Figure S10. Color changes of pristine SnI_2 and SnI_2 with Cy-OH additive upon exposure to air for different time.

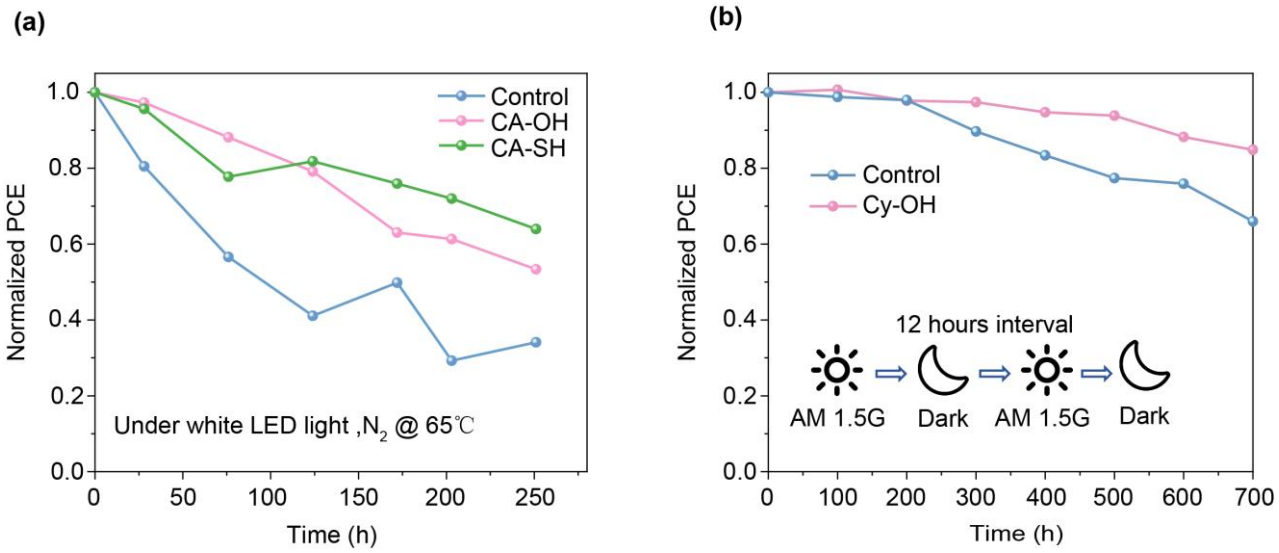


Figure S9. (a) The light stability of different devices in a N_2 glovebox. (b) Light-dark cycling stability of different devices in N_2..

7. In this manuscript, some figures are displayed in bold while others are not. It is recommended that the author standardize the format.

Response: Thanks for the kind reminding. We have thoroughly checked all figures and ensured that all numbers are consistently presented in bold format throughout the manuscript. Many thanks.

8. Some related references (https://doi.org/10.1002/cey2.70123; https://doi.org/10.1002/cey2.710) should be cited.

Response: We have cited these references in the revised manuscript. Many thanks.

Reviewer #3

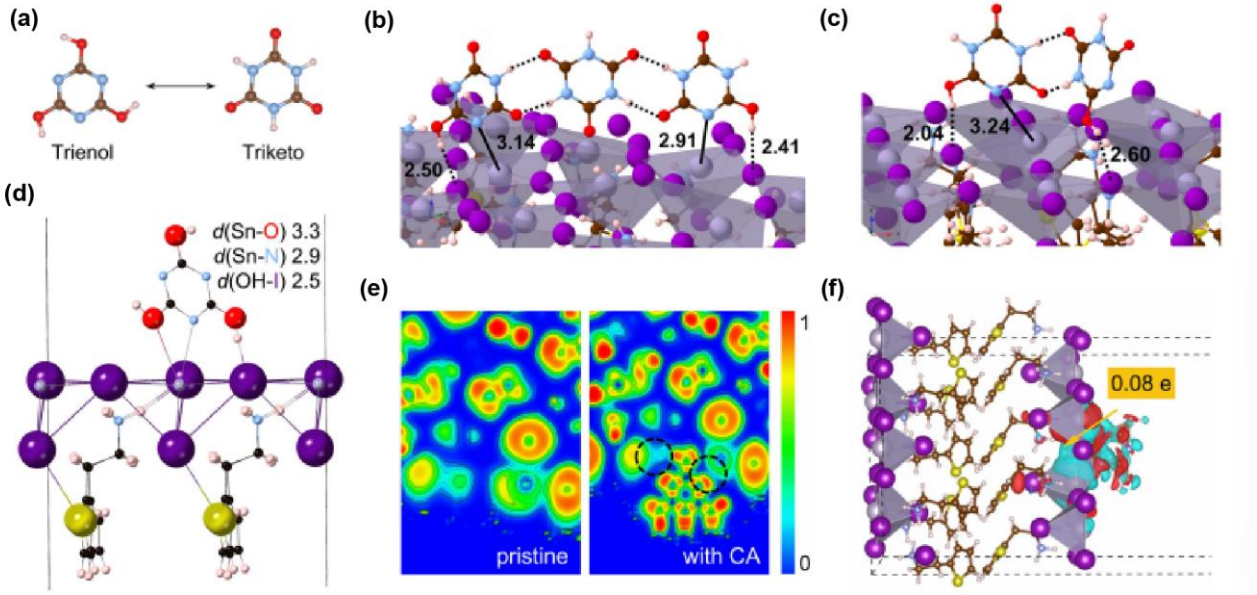
Comment: *In this manuscript, Xu et al. report a resonance-induced electron delocalization strategy to fundamentally stabilize tin perovskite by enhancing Sn-centered interactions using trithiocyanuric acid (Cy-SH) and cyanuric acid (Cy-OH) molecules as interfacial layer. The optimized devices achieved a power conversion efficiency (PCE) of 12.1% with improved stability (86% retention after 1000 h in N_2). However, the manuscript has some major technical flaws and critical validations (the uniqueness and mechanism of the proposed strategy) that need to be addressed,*

and detailed discussions of some analytical approaches are needed to justify interpretations and better comprehend the results. Addressing the following refinements would further enhance the paper's clarity and impact.

Response: We sincerely thank the reviewer for the thorough evaluation and constructive comments on our manuscript.

1. The existing data (FTIR, XPS, NMR) only confirm coordination and tautomeric isomerism: these results merely indicate that the molecule has undergone chemical interaction with Sn^{2+} and that its own structure has changed. It cannot directly prove the occurrence of the key physical process of "electron delocalization", much less demonstrate that this process is the primary reason for the performance enhancement. More evidence should supplement to visualize and quantify the degree of electron delocalization.

Response: Thank you for the reviewer's thoughtful comment. We totally agree that directly proving the occurrence of the key physical process of "electron delocalization" is crucial. From the previous report (Science,2023,622, 493-498), Wang et al. used ab initio molecular dynamics (AIMD) and DFT calculations to analyze the interaction between Cy-OH and the perovskite. They also proved that these tautomeric molecules induce electron delocalization and suppress Anderson localization of electrons around Sn atoms (**Supplemental Figure S2**). Their key findings directly support our statement. Besides, the XPS data (**Figures 1d-e** and **Figure S4**) show a significant increase in the Sn^{2+}/Sn^{4+} ratio and a shift in binding energy. This is in strong agreement with the DFT-predicted increase in local electron density and the enhanced stability of Sn^{2+} resulting from electron localization. Furthermore, our FTIR measurements confirmed the formation of hydrogen bonds, which also supports the generation of dimers and trimers. The improved crystallinity and preferred orientation shown in Figure 2a suggest that electron delocalization mitigates the "Anderson localization" effect, promoting an ordered lattice arrangement. Many thanks.



Supplemental Figure S2. (a) Trienol and triketo forms of Cy-OH. (b, c) The most stable configurations for the tautomeric Cy-OH dimer (b) and trimer (c) bonded to the Sn perovskite surface. The distances are in Å. (d) Configuration and characteristic interactions of Cy-OH on the perovskite surface. (e) ELF images of the pristine and the perovskite with Cy-OH, which were obtained in systems with an iodide vacancy. (f) Charge density difference between the Sn perovskite and Cy-OH.

2. The author selected Cy-OH and Cy-SH as representative molecules for the "resonance-induced electron delocalization" strategy because they are tautomers. Compared to molecules lacking resonance tautomerism but possessing similar coordinating groups (such as C=O or C=S), what are the unique advantages of this strategy? Is the performance enhancement attributable to the coordination of the C=O or C=S?

Response: We sincerely thank the reviewer for raising this insightful question. As suggested, we have utilized a molecule containing only a C=N coordination group of 5-amino-1(2-hydroxyethyl)pyrazole (AHP) for TPSCs.(**Table S1, FigureS1**) However, the devices showing significantly inferior performance compared to those modified with Cy-OH or Cy-SH molecules. AIMD simulations (**Supplemental Figure S2**) show that tautomeric molecules (Cy-OH) do not exist as monomers on the tin perovskite surface; instead, they spontaneously form stable, ordered hydrogen-bonded dimers and trimers (**Figure 1b**). Their lattice constant closely matches the Sn–Sn next-nearest neighbor distance, enabling full interfacial coverage, whereas

non-tautomeric molecules form only isolated point-like coordination. We have updated these discussions in the revised manuscript. Furthermore, Cy-OH undergoes a structural transformation from N=C-OH to N-C=O upon interaction with SnI_2, providing direct spectroscopic evidence that the Lewis acidic SnI_2 induces tautomerization of Cy-OH. In stark contrast, 5-amino-1-(2-hydroxyethyl)pyrazole (AHP) does not undergo any similar structural changes upon interaction with SnI_2.(**Figure1b, Figure S1**)

Table S1. Device performance of the devices based on different interfacial materials.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Control	0.80	17.10	72.05	9.9
Cy-OH	0.86	19.29	72.80	12.10
Cy-SH	0.80	18.83	71.20	10.73
AHP	0.86	18.36	64.45	10.22

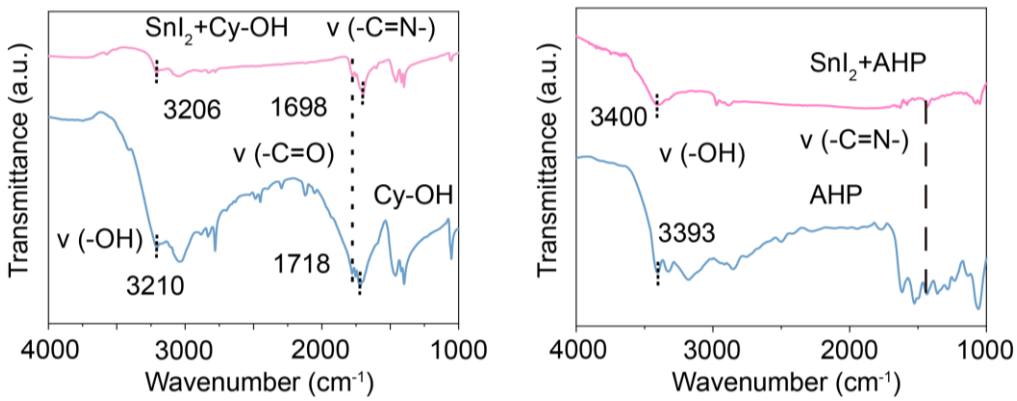


Figure S1. FTIR spectra of pristine Cy-OH and AHP-SnI2 samples.

3. Figure 3d requires additional parameter information (Jsc, Voc, FF) beyond PCE comparisons along with specific JV data supplementation.

Response: Thank you for your valuable suggestion. We have provided other parameters (J_{SC}, V_{OC}, and FF) in the Figure S8 Many thanks

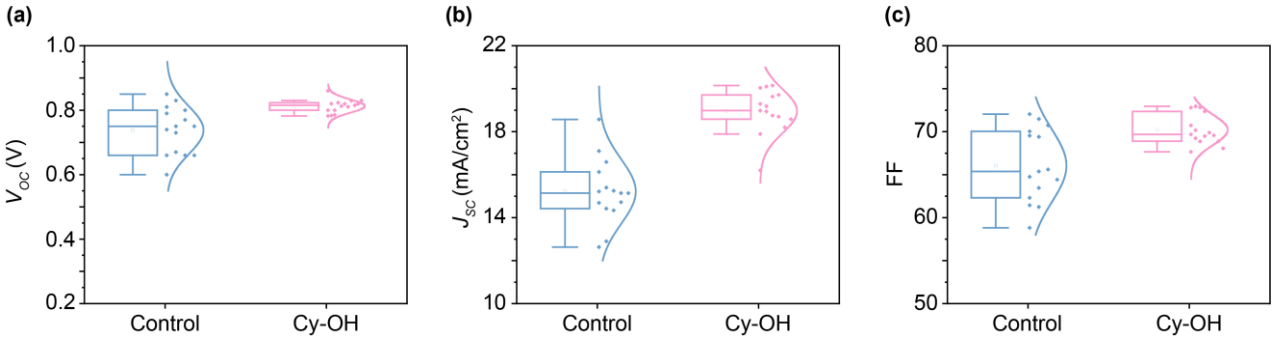


Figure S8. Photovoltaic performance parameters of the control and Cy-OH based devices.

4. According to Figure 3a, the short-circuit current density (J_{SC}) increased from 17.10 mA cm^{-2} to 19.29 mA cm^{-2}, raising the average short-circuit current density. What is the reason? The authors should support more evidences and explain in details.

Response: We thank the reviewer for very professional comment. The enhanced J_{SC} in the Cy-OH-treated devices is attributed to improved perovskite film quality via bulk defect passivation (**Figure 4c**) and regulated crystallinity (**Figure 2a**), as well as enhanced interfacial carrier extraction (**Figure 2d-e**). We have updated these discussions in the revised manuscript.

5. This manuscript focuses on the intrinsic instability of Sn^{2+}, but its characterization of stability is insufficient, which suggest that the authors should conduct more stability characterization studies on perovskite films.

Response: Thank you for your valuable comment. As suggested, we have provided light-dark cycling stability measurements to evaluate device performance. These results show that after 700 hours, the PCE of the control device dropped to 65% of its original value, while the target device still remained over 85%. We analyzed the evolution of the Sn^{2+}/Sn^{4+} ratio during aging by monitoring the color changes of SnI_2 and Cy-OH treated SnI_2 solutions exposed to air. The results show that the color of the pure SnI_2 solution changes significantly after 25 minutes of exposure to air, indicating increased oxidation, while the solution with Cy-OH exhibits weaker color change, suggesting better oxidation resistance. We have updated these related discussions in the revised manuscript. Many thanks.

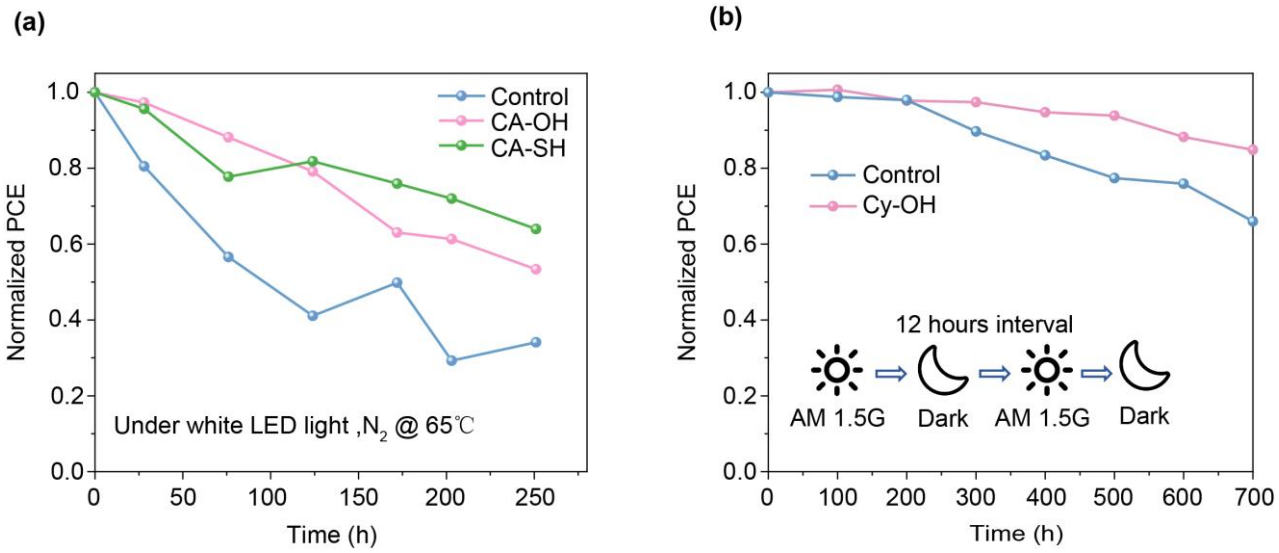


Figure S9. (a) The light stability of different devices in a N_2 glovebox. (b) Light-dark cycling stability of different devices in N_2.

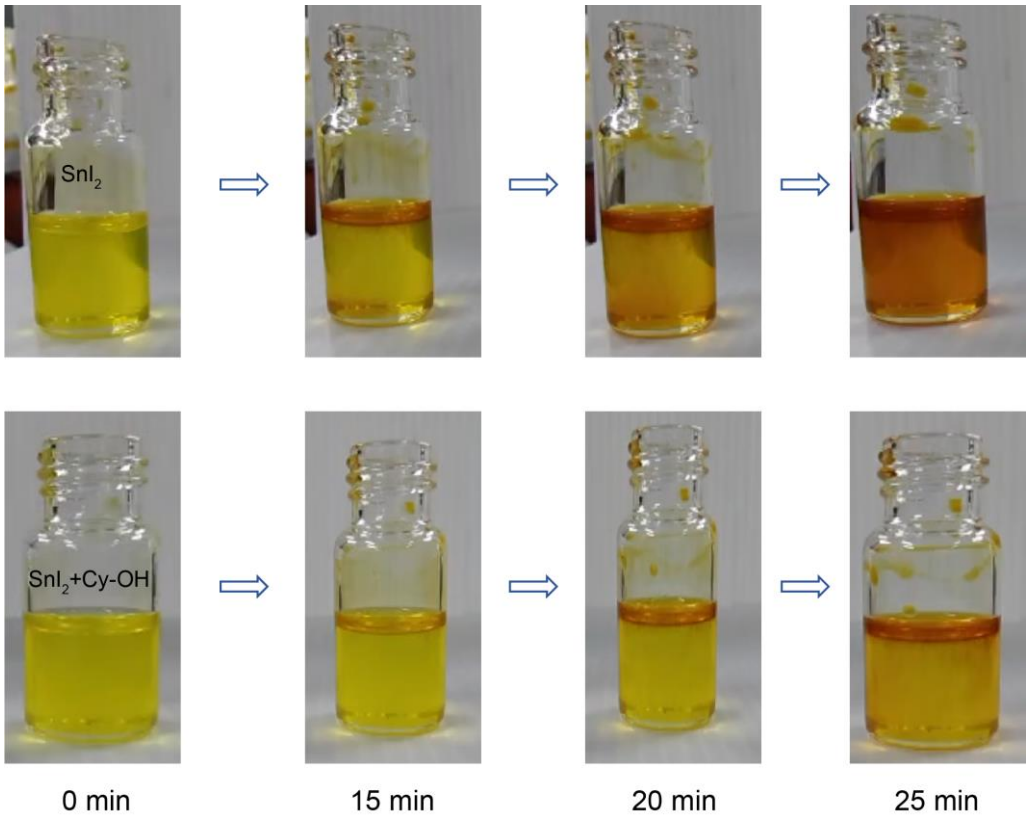


Figure S10. Color changes of pristine SnI_2 and SnI_2 with Cy-OH additive upon exposure to air for different time.

Reviewer #4

Comment:*The manuscript (manuscript number: COMMSMAT-25-1297) uses cyanuric acid (Cy-OH)*

and trithiocyanuric acid (Cy-SH) as interfacial layers in tin-based PSCs reporting increased PCE and Voc, reduced hysteresis, longer PL lifetimes, and 86% retention after 1000 h. However the data and interpretation are not convincing due to clear gaps in the data and methodology and limited novelty since interfacial passivation strategies have been widely reported. These concerns are fundamental so I recommend rejection of this manuscript.

Response: Thank you for taking the time to review our manuscript (COMMSMAT-25-1297) and for providing your detailed feedback. We sincerely appreciate your critical assessment and the effort you have invested in evaluating our work.

1. The main idea using an interfacial molecule to bind/coordinate Sn and reduce defects is already common in perovskite research. Many previous studies have used similar passivation or coordination strategies including molecules with conjugation resonance effects. So using cyanuric-acid-type molecules here looks like an incremental variation of known approaches not a clearly new breakthrough. The performance is also not state of the art. The best device is 12.1%, while tin-based perovskite solar cells in the literature have already reported >12% .

Response: Thank you for this insightful comment. We fully agree that interfacial passivation and coordination strategies have been extensively explored in tin-based perovskite solar cells, including the use of conjugated molecules and functional groups such as C=O or C=S. However, the key distinction of our work lies not in the use of these functional groups, but in the resonance-induced electron delocalization behavior of the molecules, which drives a fundamentally different interfacial organization. Specifically, trithiocyanuric acid (Cy-SH, N–C=S) and cyanuric acid (Cy-OH, N–C=O) exhibit tautomerism that promotes the formation of ordered supramolecular assemblies (e.g., dimers/trimers) at the buried interface, rather than acting as isolated coordination sites as commonly reported. Supported by AIMD simulations (Science, 2023, 622, 493-498) together with our FTIR and XPS analysis, we find that Cy-OH forms a hydrogen-bonded network with a characteristic periodicity (~1.1 nm), which closely matches the Sn–Sn next-nearest neighbor distance (~1.05 nm) on the perovskite surface.

This structural matching enables **quasi-periodic and full-coverage interfacial modulation**, in contrast to the localized and random distribution typically observed in conventional passivation approaches. Importantly, such an ordered and lattice-matched supramolecular structure

facilitates **more uniform defect passivation and enhanced electronic coupling at the interface**, thereby effectively suppressing trap states and improving charge transport. We therefore emphasize that the novelty of this work lies in introducing a **collective and structurally matched interfacial regulation mechanism**, rather than a simple extension of conventional molecular passivation strategies. While related concepts such as coordination or hydrogen bonding have been individually explored, their integration into an ordered, lattice-matched supramolecular interfacial structure remains **less explored** in tin-based perovskites.

Regarding device performance, we acknowledge that the champion efficiency (12.1%) is comparable to the current state-of-the-art. However, we note that our system is based on resonance-induced electron delocalization strategy with unoptimized device architecture, and the improvement is achieved primarily through interfacial regulation without extensive compositional or device engineering. More importantly, the proposed mechanism provides a **generalizable design principle** for interface engineering, which we believe is of broader significance for advancing tin-based perovskite photovoltaics.

2. The mechanism the authors propose is not clearly proven. They repeatedly claim that a special resonance-induced electron delocalization and tautomerism at the interface fundamentally stabilizes the tin perovskite. But the evidence they show mostly looks like what we normally see from standard interfacial passivation. Such as they report sharper XRD peaks and longer PL lifetimes but these improvements can happen with many ordinary (non-tautomeric) additives simply because they passivate traps or change crystallization. They do not isolate what is unique about tautomerism. There is no control molecule that is similar but cannot tautomerize. Without that control it is just as likely that the benefit comes from common features like multiple H-bonding groups or Lewis-basic sites that bind to Sn/I defects.

Response: Thank you for your insightful comment. We fully agree that commonly observed improvements such as enhanced crystallinity (XRD) and prolonged carrier lifetime (PL) can also arise from conventional interfacial passivation effects. Therefore, distinguishing the specific role of tautomerism is indeed critical. To address this point, we introduced a control molecule (AHP), which contains similar C=N functional groups but lacks tautomerization capability. Under identical processing conditions, the AHP-treated devices exhibit clearly inferior performance

compared to Cy-OH and Cy-SH (**Table S1**). This comparison suggests that the presence of similar functional groups alone is insufficient to reproduce the observed effects.

More importantly, the key difference lies in the collective interfacial organization enabled by tautomerism. As supported by prior AIMD/DFT studies (Science, 2023, 622, 493-498.) and further corroborated by our FTIR and XPS analysis, Cy-OH does not behave as an isolated ligand. Instead, its tautomeric nature promotes the formation of ordered hydrogen-bonded supramolecular assemblies (e.g., dimers/trimers), which facilitates more uniform electronic coupling and resonance-assisted electron delocalization across the interface, rather than isolated and random defect passivation.

Taken together, the control experiment and combined experimental–theoretical evidence support that the observed improvements cannot be solely attributed to generic functional groups or Lewis basicity, but are closely associated with the tautomerism-enabled supramolecular interfacial structure. Many thanks.

Table S1. Device performance of the devices based on different interfacial materials.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Control	0.80	17.10	72.05	9.9
Cy-OH	0.86	19.29	72.80	12.10
Cy-SH	0.80	18.83	71.20	10.73
AHP	0.86	18.36	64.45	10.22

3. The paper suggests the interfacial molecular network changes the perovskite electronic structure even in regions not directly interacting. If the molecules sit only at the interface their effect should be limited to a very thin region unless the authors show evidence of bulk changes, for example clear band shifts, doping changes, depth-dependent measurements this evidence is not provided.

Response: As suggested, we performed UPS characterization, and the results show that the treated device exhibits a smaller energy level barrier, which is relatively more favorable for hole transport.

Revised text:

Page 12 of the revised manuscript:

UPS (FigureS12) measurements reveal that the treated device exhibits a smaller energy level barrier, which is relatively more favorable for hole transport[34].

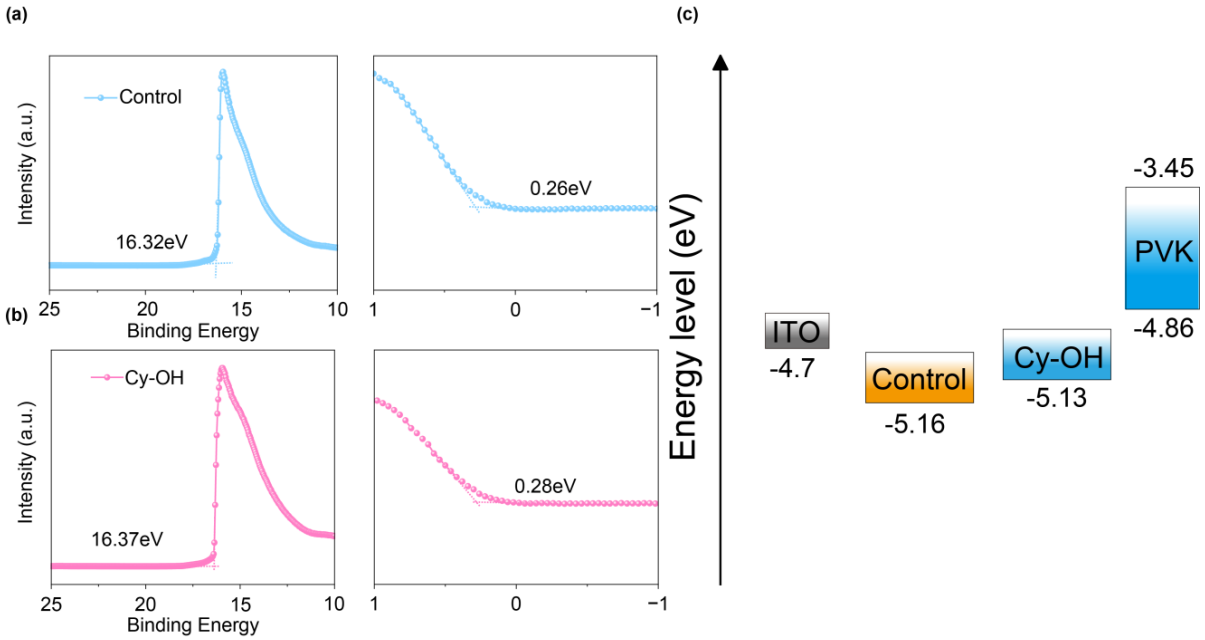


Figure S13. (a, b) UPS spectra of the control and Cy-OH-treated HTLs, (c) corresponding energy level diagram.

4. The authors present stability data but the storage test was done in a very mild N_2 glovebox (trace O_2) yet the best Cy-OH device still lost 14% PCE in 6 weeks and the control is described as degrading rapidly without clear numbers. More importantly under continuous light at 60oC the Cy-OH device drops to 60% of its initial PCE within 250 hours (40% loss) which is not convincing long-term stability. No humidity, ambient air, thermal-cycling, or outdoor tests are provided, so the stability evaluation is too limited to support claims of durable and practical performance. The authors claim the benefit comes from the tautomeric/resonance nature of Cy-OH and Cy-SH but they do not test a similar molecule that cannot tautomerize. A good control would be an analog molecule where tautomerism is not possible for example a monofunctional version or a structure with the enol/keto form locked. Without this comparison it is unclear whether the improvement is truly due to tautomeric resonance or simply normal surface passivation.

Response: Thank you for this important comment. We fully agree that a comprehensive stability evaluation for practical applications should include humidity, ambient air exposure, thermal

cycling, and outdoor testing. In the present work, our primary objective is to elucidate the molecular-level interfacial mechanism, and therefore we employed controlled environments (N_2 with trace O_2) together with accelerated aging conditions (continuous illumination at 60 °C) as an initial and reproducible platform for comparison. Regarding the device stability, we acknowledge that a ~40% efficiency loss after 250 h under 60°C illumination does not yet represent long-term operational stability. However, considering the well-known instability of tin-based perovskites, the retention of ~60% of the initial PCE under simultaneous thermal and light is comparable to or better than many reported Sn-based systems under similar conditions, as now discussed in the revised manuscript (Figure S9). In the revised version, we now provide explicit quantitative comparison: under identical conditions, the control device shows significantly faster degradation (retaining only ~30% of its initial PCE after 250 h), whereas the Cy-OH device maintains ~60%, demonstrating a clear improvement in operational stability. More importantly, to directly address the role of tautomerism, we have introduced an additional control molecule (AHP), which contains similar functional groups (e.g., carbonyl/hydroxyl) but lacks tautomerization capability (Table S1-S2, FigureS1b). The AHP-treated devices show substantially weaker improvements in both performance and stability, and fail to reproduce the spectroscopic signatures associated with ordered interfacial organization observed for Cy-OH. This indicates that the observed stabilization cannot be attributed solely to generic functional groups or conventional surface passivation, but is closely related to the tautomerism-enabled interfacial structure. Taken together, while further extended stability tests under practical conditions are indeed valuable and will be pursued in future work, the current results already demonstrate a **clear and mechanistically meaningful improvement** in tin perovskite stability arising from the proposed interfacial design.

Table S1. Device performance of the devices based on different interfacial materials.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Control	0.80	17.10	72.05	9.9
Cy-OH	0.86	19.29	72.80	12.10
Cy-SH	0.80	18.83	71.20	10.73
AHP	0.86	18.36	64.45	10.22

Table S2. Summary on the photovoltaic parameters of the devices based on different Cy-OH

concentration.

Concentration	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
1mg/ml	0.80	18.98	72.95	11.12
2mg/ml	0.86	19.29	72.80	12.10
3mg/ml	0.82	17.89	72.35	10.64

5. The study also does not compare the Cy-OH interlayer to common and simpler passivation strategies including widely reported molecules in the literature. Since SnF2 is already used in the precursor the authors didn't show how much extra benefit Cy-OH adds compared with standard approaches. The authors say they made 15 devices but they only show the average PCE. They didn´t show how Jsc, Voc, FF vary across those devices not just the average, because the treatment might improve one parameter more than the others.

Response: We thank the reviewer for these constructive comments. We have introduced an additional control molecule (AHP), which contains similar functional groups (e.g., carbonyl/hydroxyl) but lacks tautomerization capability (Table S1, FigureS1b). The AHP-treated devices show substantially weaker improvements in both performance and stability, and fail to reproduce the spectroscopic signatures associated with ordered interfacial organization observed for Cy-OH. This indicates that the observed stabilization cannot be attributed solely to generic functional groups or conventional surface passivation, but is closely related to the tautomerism-enabled interfacial structure. As suggested,, we have now provided a comprehensive statistical analysis of the key photovoltaic parameters. It can be seen that the Cy-OH treated devices exhibit a generally significant improvement in both V_{OC} and J_{SC}.

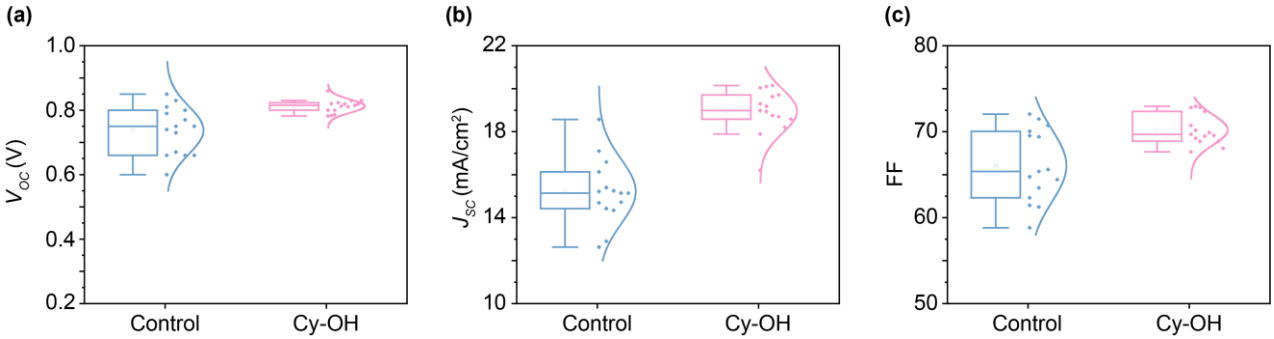


Figure S8. Photovoltaic performance parameters of the control and Cy-OH based devices.

6. In the EQE plot the response is strangely high at short wavelengths but abnormally low in the 400-500 nm range. The authors claim the treated device has higher EQE across the whole spectrum but the curve itself shows a clear dip in that region which contradicts. This unusual spectral shape may indicate issues with the measurement setup or calibration uncertainty.

Response: Thanks for the review's kind reminding. We totally agree that the previously reported EQE spectrum exhibited an unusual dip in the 400 – 500 nm range, which indeed contradicted our claim of enhanced EQE across the entire spectral range. To address this concern, we have repeated the EQE measurements using carefully calibrated equipment. The revised EQE spectra are now presented in Figure 3e. And the re-measured EQE exhibited normal signal fluctuations.

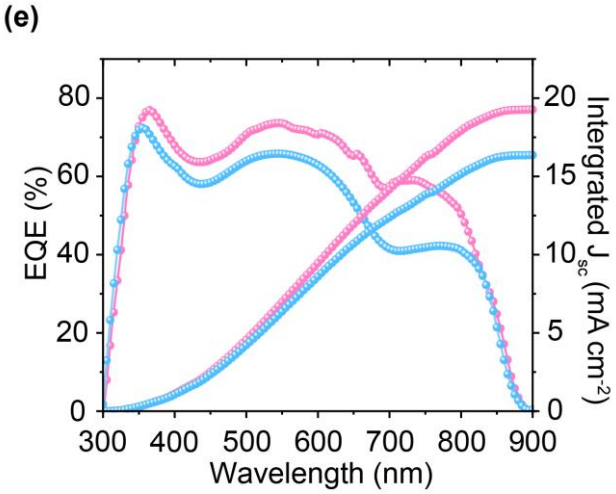


Figure 3e. EQE spectra and the integrated J_{SC}.

A list of changes made:

(1) The keywords in the abstract have been revised.

(2) The device performance (**Table S1**) has been provided.

(3) The corresponding references have been cited.

(4) The auxiliary lines in Figures 1d and 1e have been modified to dashed lines.

(5) The supplementary information regarding stability has been incorporated into the manuscript (**Figures S9-S10**).

(6) AFM data have been provided (**Figure S5**).

(7) An explanation has been provided for the photoluminescence peak in Figure 2d.

(8) Additional device performance data have been supplied (**Figure S8**).

(9) UPS data have been added (**Figure S12**)

If there are any further queries, please feel free to contact me. I can be reached by E-mail: iamlgxu@njupt.edu.cn or by Fax: (+86) 25 8586 6396.

Thank you very much.

Yours sincerely,

Ligang Xu

Professor

Ligang Xu

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南京郵電大學
Nanjing University of Posts and Telecommunications

May 15, 2026

Doctor Meltem Yanilmaz

Associate Editor, Communications Materials

Email: commsmat@nature.com

Dear Doctor Meltem Yanilmaz,

Re: Decision on manuscript COMMSMAT-25-1297

Thank you so much for your letter dated May 13, 2026 regarding our manuscript entitled: **"Resonance-Induced Electron Delocalization for Efficient Lead-Free Perovskite Solar Cells" (Research Article, Manuscript ID: COMMSMAT-25-1297A)** (Authors: Ao Shen, Chensi Gong, Zhiheng Dong, Mingtai Chen, Wenzhen Lv, Runfeng Chen*, Ligang Xu*).

We have carefully gone through the comments of the reviewers/editor and made necessary changes to the manuscript.

The reply is indicated by black letters, while the comments by the editor/reviewers are indicated by *blue italic* letters. We have documented any changes that we have made to the original manuscript.

Reviewer #1

***Comment**: The author has made revisions to the manuscript based on the review comments, and I recommend that the revised manuscript can be accepted by the communications materials journal.*

Response: We sincerely thank you for your affirmation and recommendation of our revised work.

Reviewer #2

***Comment**: The quality of the revised manuscript has been improved and I recommend accept it.*

Response: Thank you very much for your recognition of our improved manuscript. Your encouragement is a great support to our work.

Reviewer #3

***Comment**: The authors have modified their manuscript according to the reviewer's comments, I recommend the acceptance of this manuscript for publication in Communications Materials.*

Response: Thank you for your satisfaction with and recommendation of our revisions. We are truly honored.

Reviewer #4

***Comment:** After carefully reading the author's response I still do not think the manuscript is suitable for publication and I still recommend rejection of this manuscript. Although the authors have added some supplementary data including AHP control devices AFM/UPS, light dark cycling stability and repeated EQE measurements these additions do not satisfactorily address the fundamental concerns regarding novelty, mechanism, stability and data reliability. The novelty remains limited.*

Response: We sincerely thank the reviewer for the continued careful evaluation of our manuscript and for the constructive comments provided throughout the review process. We have carefully considered all concerns raised and performed additional experiments and analyses to further strengthen the manuscript. While we fully respect the reviewer's assessment, we respectfully believe that the revised manuscript and newly added data sufficiently address the concerns regarding novelty, mechanism, stability, and data reliability. Specifically, we have included additional control experiments, AFM/UPS characterizations,

repeated EQE measurements, and extended operational stability evaluations to further support the reproducibility and validity of our conclusions.

In addition, we have substantially clarified the mechanistic discussion and further highlighted the distinction between our work and previously reported studies. We believe these revisions significantly improve the scientific rigor and overall quality of the manuscript.

We therefore respectfully hope that the reviewer and editor will reconsider the suitability of the revised manuscript for publication.

1. The work is still mainly based on interfacial molecular passivation coordination of Sn-related defects which is already a widely reported strategy in tin-based perovskite solar cells. The authors try to distinguish their work by claiming resonance induced electron delocalization and ordered supramolecular interfacial assembly but the experimental evidence does not convincingly prove that this is fundamentally different from ordinary passivation or crystallization control. The direct proof of electron delocalization is important but their response mainly relies on a previous Science report and indirect evidence such as XPS shifts FTIR changes, PL lifetime and crystallinity.

Response: We thank the reviewer for this important comment. We agree that interfacial coordination/passivation is a widely adopted strategy in TPSCs. However, the central point of our work is not merely defect passivation itself, but the resonance-assisted interfacial electronic delocalization and supramolecular assembly behavior induced by Cy-OH molecules at the hybrid interface. We acknowledge that direct visualization of electron delocalization at buried molecular–perovskite interfaces remains experimentally challenging. Therefore, in this work, we employed multiple complementary characterizations together with theoretical analysis to support this mechanism. Specifically, the XPS results (Figure 1) show that after Cy-OH treatment, the relative area ratio of the N–C=O component increases significantly from 57.7% to 75.6%, while the relative area ratio of the N=C–OH component decreases from 42.3% to 24.4%. The pronounced variation in the relative proportion of these resonance-associated configurations indicates substantial interfacial electron redistribution after coordination between Cy-OH and the perovskite surface, providing direct spectroscopic evidence for electron rearrangement at the molecular–perovskite interface.

In addition, single-crystal X-ray diffraction analysis reported in the literature (Chin. J. Struct.

Chem., 1995, 14(4): 241–244) further supports the existence of strong resonance characteristics in Cy-OH. The measured C=O bond length (1.214 Å) is longer than that of a typical C=O double bond (1.200 Å), while the C–N bond length (1.336 Å) is significantly shorter than a standard C–N single bond (1.445 Å). These abnormal bond-length characteristics indicate partial electron delocalization within the molecular backbone and confirm the coexistence of the N–C=O and N=C–OH resonance forms. Therefore, unlike conventional localized defect coordination, Cy-OH exhibits intrinsic resonance-assisted electronic redistribution capability, which facilitates more spatially extended interfacial electronic coupling at the molecular–perovskite interface.

In addition, the ELF and charge-density-difference analyses shown in Supplementary Figure S2 further support the formation of intermolecular electronic coupling between Cy-OH and the tin perovskite surface through carbonyl/hydroxyl coordination with Sn-related defect sites or iodine vacancies. Compared with conventional localized defect passivation, the calculated electron-density distribution exhibits a more spatially extended interfacial electron cloud, suggesting enhanced electronic delocalization across the molecular–inorganic interface. To avoid overstatement, we have further revised the manuscript to clarify that the proposed mechanism is supported by the collective experimental observations and theoretical calculations rather than by a single direct experimental visualization.

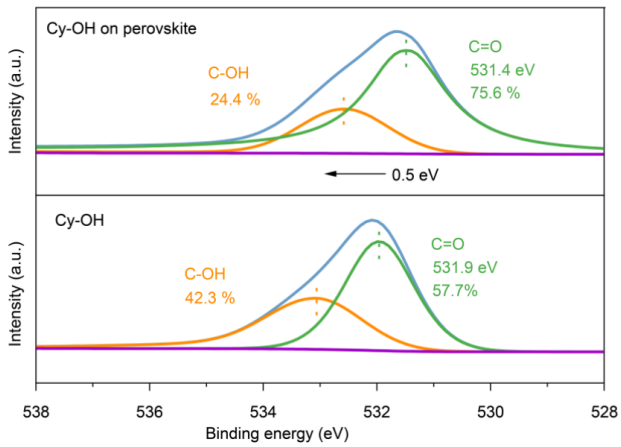
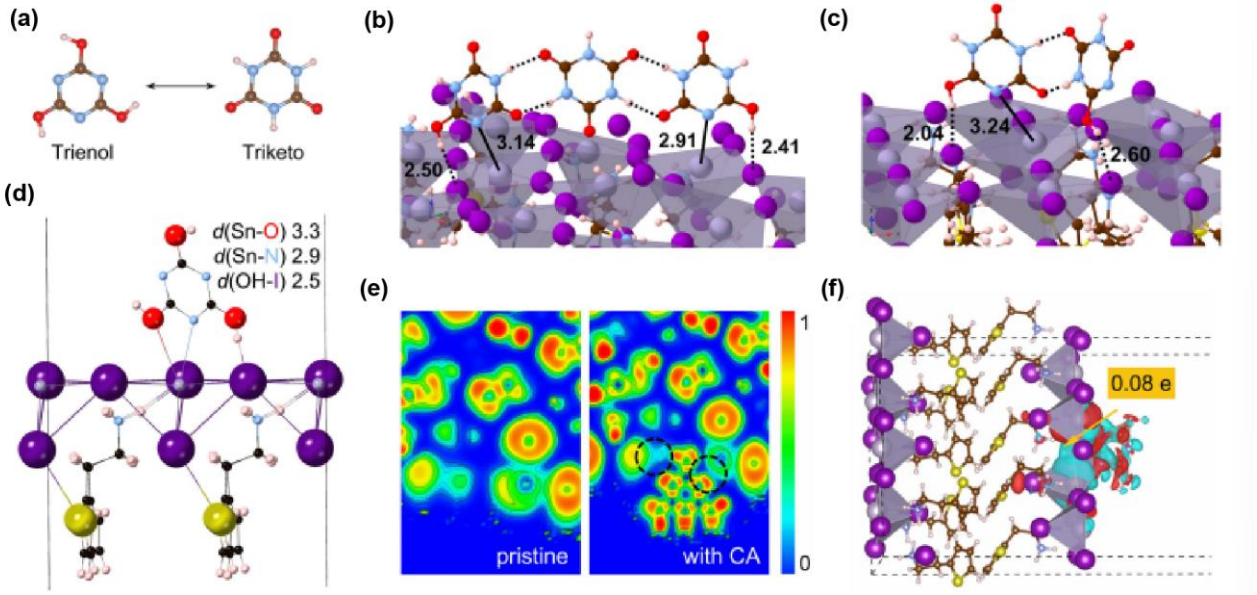


Figure 1. XPS of Cy-OH film and Cy-OH deposited on the tin perovskite.



Supplemental Figure S2: (a) Trienol and triketo forms of Cy-OH. (b, c) The most stable configurations for the tautomeric Cy-OH dimer (b) and trimer (c) bonded to the Sn perovskite surface. The distances are in Å. (d) Configuration and characteristic interactions of Cy-OH on the perovskite surface. (e) ELF images of the pristine and the perovskite with Cy-OH, which were obtained in systems with an iodide vacancy. (f) Charge density difference between the Sn perovskite and Cy-OH.

2. The stability evidence is still weak. EQE correction raises reliability concerns. The initial EQE data had an abnormal dip and repeated the measurement which suggests the data were not well calibrated that raise concerns about the consistency of the measurement. This performance is not strong enough to support the broad claims. The best PCE is only 12.10% and the improvement over AHP and Cy-SH is limited so the paper remains more like an incremental passivation study.

Response: We thank the reviewer for the careful evaluation of the stability and device-performance data. Regarding the stability characterization, we respectfully note that TPSCs are intrinsically far more vulnerable to oxidation than lead-based systems due to the rapid oxidation of Sn^{2+} under simultaneous oxygen and moisture exposure. Unencapsulated tin-based perovskite films typically degrade very rapidly under ambient air conditions, making reliable photovoltaic characterization under such conditions highly challenging and not fully representative of intrinsic device stability. Therefore, in this work, we focused on controlled operational stability measurements under well-defined illumination and environmental

conditions to more accurately evaluate the stabilizing effect of Cy-OH at the molecular interface. We also acknowledge that the initially submitted EQE spectrum exhibited an abnormal dip caused by calibration drift during measurement, and we sincerely appreciate the reviewer for identifying this issue. To address this concern, we repeated the EQE measurements using recalibrated equipment and independently verified the integrated current density. The updated EQE spectra now display smooth and consistent photoresponse behavior across the entire wavelength range (300–900 nm), confirming the reliability and reproducibility of the photovoltaic measurements.

Regarding the reviewer's concern that the efficiency enhancement appears limited, we respectfully believe that the comparison with the control molecules provides important mechanistic insight. In particular, the Cy-OH-treated device achieved a PCE of 12.10%, compared with approximately 9.9% for the control device and ~10.22% for the non-tautomeric/passivation analogue AHP. Importantly, both Cy-OH and AHP possess coordination capability, whereas Cy-OH additionally exhibits resonance-assisted tautomerization behavior. Therefore, the improved performance relative to AHP suggests that the enhancement does not arise solely from conventional defect passivation, but is also associated with the proposed resonance-assisted interfacial electronic regulation. Furthermore, for TPSCs, an absolute efficiency improvement of more than 2 percentage points together with enhanced operational stability is meaningful considering the severe non-radiative recombination and intrinsic instability challenges of Sn-based systems. To avoid overstatement, we have further revised the manuscript to more clearly position this work as a mechanistic study on resonance-assisted interfacial regulation rather than a record-efficiency report.

南京郵電大學
Nanjing University of Posts and Telecommunications

June 11, 2026

Doctor Meltem Yanilmaz

Associate Editor, Communications Materials

Email: commsmat@nature.com

Dear Doctor Meltem Yanilmaz,

Re: Decision on manuscript COMMSMAT-25-1297

Thank you so much for your letter dated June 10, 2026 regarding our manuscript entitled: **"Resonance-Induced Electron Delocalization for Efficient Lead-Free Perovskite Solar Cells" (Research Article, Manuscript ID: COMMSMAT-25-1297A)** (Authors: Ao Shen, Chensi Gong, Zhiheng Dong, Mingtai Chen, Wenzhen Lv, Runfeng Chen*, Ligang Xu*).

We have carefully gone through the comments of the reviewers/editor and made necessary changes to the manuscript.

The reply is indicated by black letters, while the comments by the editor/reviewers are indicated by *blue italic* letters. We have documented any changes that we have made to the original manuscript.

Associate Editor

Comment：Thank you once again for submitting your revised manuscript, "Resonance-Induced Electron Delocalization for Efficient Lead-Free Perovskite Solar Cells," to Communications Materials. Your manuscript has been seen again by the referees, whose comments are appended below. I am happy to say that the concerns of our reviewers have now been addressed, and that we only require some minor amendments before we can accept your paper.

Response: Thank you for your encouraging decision. We have revised these parts as you suggested.

1. "Results and Discussion" section should have sub-headings.

Response: We have provided the sub-heading in the "Results and Discussion" section.

2. A "Method" section should be after the Conclusions.

Response: As suggested, the "Method" section has been provided in the revised manuscript.

3. We notice that there are authors missing from your Author Contributions statement [You have mentioned Chensi Gong as SG in author contribution please correct it to CG or change the initials on system]. Please ensure that all authors are included. Where multiple authors possess identical initials, they must be clearly disambiguated from one another.

Response: The author contributions section has been revised accordingly.

Reviewer #4

Comment: *The modifications are done, and they have reached an acceptable level.*

Response: Thank you very much for your affirmation and recognition of our revisions. Your valuable comments have helped us significantly improve the quality of our paper.