nature portfolio

Peer Review File

Ambient blade-coated perovskite solar cells with high reverse bias stability enabled by polymeric hole transporter design

Corresponding Author: Professor Shangshang Chen

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)
Reverse bias stability remains one of the most critical challenges in perovskite photovoltaics. Through high-resolution electroluminescence (EL) mapping, Zhao et al. demonstrated the significant impact of hole transport layer (HTL) heterogeneity on device performance under reverse bias, offering valuable guidance for future HTL development. Addressing the limitations of self-assembled monolayers (SAMs) and PTAA, the authors designed a novel polymeric HTL (Poly-PhPACz) that simultaneously delivers an exceptional reverse bias voltage (Vrb), a record efficiency of 26.1%, and outstanding operational stability. This work presents an innovative strategy for developing high-performance HTLs, with findings that will benefit the broader research community. Therefore, I recommend acceptance after addressing the following minor revisions:

1. While water contact angle measurements demonstrated improved wettability of Poly-PhPACz (suggesting better perovskite ink spreading), direct characterization using perovskite precursor solutions would provide more relevant interfacial information.
2. The consistently low Vrb values (~-4 V) observed for SAM-based HTLs compared to polymeric HTLs (Poly-PhPACz and PTAA) suggest a potential general advantage of polymeric architectures for reverse bias tolerance. The authors should discuss whether this represents a fundamental materials difference.
3. Although photo-CELIV measurements provide average mobility values, direct measurement of hole mobility in the HTL layer (e.g., through space-charge-limited current or field-effect transistor measurements) would more conclusively demonstrate the enhanced conductivity of Poly-PhPACz.
4. For comprehensive comparison, the forward scan J-V characteristics of SAM PhPACz devices should also be included alongside those of the champion Poly-PhPACz devices.
5. Additional fundamental characterization of Poly-PhPACz would strengthen the work, including: energy level alignment (via cyclic voltammetry or ultraviolet photoelectron spectroscopy). In addition, which method was used to fit the TRPL data?

Reviewer #2

(Remarks to the Author)
In this manuscript, Zhao et al. report a novel hole transport layer (HTL) in perovskite solar cells (i.e., Poly-PhPACz) as an alternative to commonly used PTAA and carbazole-based self-assembled monolayers. Specifically, authors find that this polymeric HTL provides superior reverse bias stability compared to its monomeric analogue, addressing a key limitation of self-assembled materials for use as hole-selective layers in perovskite solar cells. Poly-PhPACz is also shown to yield better wetting and to increase hole injection to perovskite (vs PTAA), as well as to improve the overall operational stability of the solar cell under illumination (vs PhPACz). Cr/Cu bilayer electrodes are also shown to increase the reverse bias stability of the device. In general the methodology and experiments in the paper are sound, and the performance and stability of the solar cells reported herein are excellent. However, there are crucial aspects in this manuscript that do not meet the high standards of Nature Communications. Mainly, the manuscript does not provide substantial conceptual advances relative to the existing literature on the topic of reverse bias stability. A major takeaway form this manuscript is that thicker Poly-PhPACz layers provide higher reverse bias stability, but a similar conclusion was reached in other papers for PTAA

(https://doi.org/10.1038/s41560-024-01600-z). Additionally, Poly-PhPACz does not yield a substantial increase in reverse bias stability (i.e., a more negative breakdown voltage) compared to PTAA. The literature cited in this manuscript is not fully up to date and does not capture some key advances in the field that already address some of the issues tackled herein. For example, the highest breakdown voltage values obtained in this paper were obtained via a strategy previously reported in the literature to increase reverse bias stability, i.e., using bilayer chromium/copper electrodes (https://doi.org/10.1021/acsenergylett.5c00727). For these reasons, I recommend the transfer of this manuscript to a more technical journal (e.g., Communications Materials) after the aforementioned issues are resolved. Additional comments that may help to improve the quality of the paper are also provided as follows:

1.Lines 116, 117: The polarity of the reverse bias application is described incorrectly (copper should be under positive bias (or grounded) and ITO should be under negative bias.

2.To test reverse bias stability of the various device architectures, authors scan devices from 2 V to -20 V. The initial bias (2 V) is considerable and, according to various reports (e.g., https://doi.org/10.1002/aenm.202000310, https://doi.org/10.1002/aenm.202403850, https://doi.org/10.1021/acsenergylett.5c00376), harsh to the perovskite device (2 V is almost twice the Voc of these solar cells. It is important that authors rule out any secondary effects from the applied forward bias (e.g., effect on ion redistribution). It would be interesting to carry out reverse bias stress tests at different scan ranges and/or dwell times.

3.A more accurate definition of breakdown voltage should be provided. Several breakdown regimes are known to affect perovskite solar cells, from milder Zener breakdown to irreversible junction destruction via thermal breakdown (e.g., https://doi.org/10.1002/solr.202300456).

4.The EL mapping technique employed herein operates under forward-biasing to acquire an image of the resulting EL. This implies that the solar cell HTL will act as a hole injection layer, being EL microscopy useful to verify the uniformity of this process. However, under reverse bias, the HTL will inject electrons to the perovskite as leakage current. The EL mapping used herein is therefore not fully convincing to verify the spatial uniformity of the electron blocking ability in the HTL, since it relies on HTL-to-perovskite hole injection rather than on HTL-to-perovskite electron leakage. Acknowledging that authors do mention that EL operates in different bias conditions compared to reverse bias, it is important that cross-checks with other techniques (e.g., leakage current analysis under reverse bias) are performed to corroborate the validity of the conclusions extracted from EL maps.

5.In Fig. 2a, authors determine that the optimal thickness of Poly-PhPACz is 63 nm. However, it is apparent in this figure that an increase in thickness is always followed by an improvement in Vrb, reaching no clear Vbr minimum. To increase the appeal of this new HTL as a reverse bias stability enhancer, it is advised that authors provide further details as to why 63 nm is the optimal thickness. Additionally, Fig. 2a shows that most gains in reverse bias stability occur by increasing the thickness up to 20 nm, being changes in Vrb from 20 to 63 nm more modest. This may suggest that, while a major part of current leakage pathways are suppressed with 20 nm Poly-PhPACz, increasing the thickness further does not result in clear improvements. Can authors explain the reason for this?

6.Authors mention that Poly-PhPACz possesses a superior processability window than PTAA (i.e., thick Poly-PhPACz layers yield higher PCE than thick PTAA layers). It is demonstrated that Poly-PhPACz leads to better wetting than PTAA and this is highlighted as a major advantage of the new HTL. However, it would also be interesting to verify whether differences in the conductivity of the HTLs also contributes to this superior processability window (e.g., as done for Poly-PhPACz and PhPACz in Supplementary Figure 6).

7.In Supplementary Figure 6, please compare the two existing images with a bare ITO control. This is to rule out if inhomogeneities present in both samples arise from conductivity differences between Poly-PhPACz and PhPACz or from coverage differences.

8. The use of chromium/copper bilayer contacts to enhance the reverse bias stability of p-i-n perovskite solar cells in this manuscript is not a novel contribution to the field. This has already been reported recently with very similar Vbr results (https://doi.org/10.1021/acsenergylett.5c00727). Before this, the use of chromium/copper contacts has been shown in multiple works to improve the operational stability perovskite solar cells (e.g., https://doi.org/10.1038/nmat4388, https://doi.org/10.1038/s41586-024-08546-y, https://doi.org/10.1021/acsnano.5b03687). No citations of previous works on chromium/copper contacts were added in this version of the paper. Authors should make sure the relevant literature on chromium/copper contacts is cited to keep the manuscript updated with the current state-of-the-art.

9.Further insights on the rationale behind the conceptual design of Poly-PhPACz would be useful, since this HTL is meant to bind onto the surface of ITO like a SAM but is instead deposited at comparatively high thickness.

Reviewer #3

(Remarks to the Author)
This study addresses the critical issue of reverse bias instability in perovskite solar cells (PSCs) by developing a novel polymeric hole transport layer (HTL) called Poly-PhPACz. Unlike conventional self-assembled monolayers (SAMs), which suffer from poor film uniformity and low breakdown voltage, Poly-PhPACz offers high conductivity, excellent wettability, and

robust interface adhesion. Devices incorporating this HTL achieved a high power conversion efficiency of 26.1% and a reverse breakdown voltage of up to -14.3 V, with over 92% performance retention after 1,800 hours of illumination. The high efficiency and stability are impressive, but I believe some major revisions and clarifications are necessary.

Question 01. In Fig. 1, Poly-PhPACz exhibited higher EL intensity and a narrower distribution compared to other SAMs and PTAA. However, the EL mapping images (Fig. 1c–f) and the corresponding intensity distribution graphs (Fig. 1g) do not appear to be fully consistent. For instance, the PhPACz EL mapping shows brighter intensity spots than Poly-PhPACz, but this is not reflected in the distribution graph. To improve clarity and reliability, it would be helpful to indicate the specific line cuts on the EL maps that were used to generate the distribution plots.

Question 02. The optimal thickness of Poly-PhPACz is 20 nm, indicating that it is not a monolayer. Typically, SAMs facilitate hole extraction by forming a well-ordered orientation and generating a dipole between the ITO and the perovskite. Therefore, a 20 nm-thick Poly-PhPACz layer may have a random molecular orientation, which could potentially hinder hole extraction. Given this, what is the precise mechanism by which Poly-PhPACz improves device performance compared to conventional SAMs, beyond the benefit of improved uniformity? In addition please suggest the energy level diagram of the whole device by measuring UV-Vis Absorbance and ultraviolet photoelectron spectroscopy (UPS).

Question 03. The authors attribute the enhancement in PL and TRPL performance to the passivation effect of Poly-PhPACz compared to PhPACz. (Fig. 2d) However, since both HTLs share the same basic molecular structure, it is unclear how this difference alone accounts for the observed passivation effect. It would be helpful to provide additional evidence or explanation to clarify the origin of the PL and TRPL enhancement. In addition show SEM images and XRD spectra of perovskite film, deposited on PhPACz and Poly-PhPACz please.

Question 04. The authors highlight the advantage of Poly-PhPACz for large-area PSC fabrication compared to PTAA; however, no data from large-area devices are currently presented. It would strengthen the manuscript to include J-V curves and EL mapping results for devices with an active area ≥ 1 cm^2.

Question 05. The authors successfully increased the Vrb by introducing a Cu/Cr bilayer, which is impressive as it demonstrates that reverse bias stability can be significantly enhanced simply by modifying the electrode. It would be interesting to see whether a similar effect can be observed with other commonly used electrodes, such as silver. Additionally, providing further insight or evidence into the specific role of Cr in improving reverse bias stability would help strengthen the discussion.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed the issues raised in my previous review. I suggest its publication without revisions.

Reviewer #2

(Remarks to the Author)
Authors have thoroughly addressed most of the points raised by the reviewers, which has improved the quality of the work. The role of Poly-PhPACz as a reverse bias stability enhancer next to commonly used PTAA or molecular SAMs is clear, since it offers i) a wider processing window owed to its higher conductivity and wetting, ii) interfacial anchoring and stabilisation owed to its phosphonic acid groups, iii) higher uniformity and lower chance of breakdown, and iv) non-compromised device efficiencies when employed at high thicknesses needed to obtain high reverse bias stability. This now makes the work of potential interest for publication in Nature Communications (further revisions indicated below).

I am still concerned about the novelty of the last part of the manuscript, i.e., the use of Cr/Cu double layer electrodes to enhance reverse bias stability. As I indicated in my previous report, Cr/Cu contacts have already been employed to enhance the reverse bias stability of p-i-n perovskite solar cells with very similar results (https://pubs.acs.org/doi/full/10.1021/acsenergylett.5c00727). While authors have correctly included citations to previous literature on Cr electrodes, currently the manuscript does not explicitly acknowledge that this approach has been used before for the same purpose. This is needed to give readers a clear notion of the state-of-the-art in this topic. Doing so would strengthen the paper and enhance the focus on the polymeric hole-transport layer presented herein (being the core finding of the manuscript). A clearer justification of the novelty in using Cr/Cu electrodes in Poly-PhPACz-based devices to enhance reverse-bias stability is also recommended to better align with the novelty and impact criteria of Nature Communications.

Reviewer #3

(Remarks to the Author)
The authors have adequately addressed the raised questions, and I recommend this work for publication in Nature

Communications.

In the following text, referee comments are in **black**, while our responses and the revisions made to the submitted files are in **blue** and **red**, respectively.

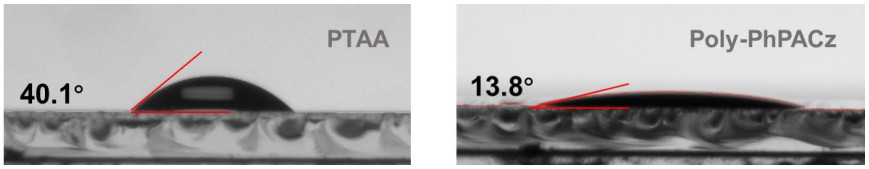
Reviewer #1

Reverse bias stability remains one of the most critical challenges in perovskite photovoltaics. Through high-resolution electroluminescence (EL) mapping, Zhao et al. demonstrated the significant impact of hole transport layer (HTL) heterogeneity on device performance under reverse bias, offering valuable guidance for future HTL development. Addressing the limitations of self-assembled monolayers (SAMs) and PTAA, the authors designed a novel polymeric HTL (Poly-PhPACz) that simultaneously delivers an exceptional reverse bias voltage (Vrb), a record efficiency of 26.1%, and outstanding operational stability. This work presents an innovative strategy for developing high-performance HTLs, with findings that will benefit the broader research community. Therefore, I recommend acceptance after addressing the following minor revisions:

Response: We thank the reviewer's recognition on our paper, and also the valuable comments that help us improve the quality of our paper.

1. While water contact angle measurements demonstrated improved wettability of Poly-PhPACz (suggesting better perovskite ink spreading), direct characterization using perovskite precursor solutions would provide more relevant interfacial information.

Response: Thanks for the good suggestion, following which we further measured the contact angles of the perovskite ink on the two HTLs. As shown in Supplementary Fig. 8, the contact angle of Poly-PhPACz (13.8°) is much smaller than that of PTAA (40.1°). The results follow the same trend as the water contact angles, confirming Poly-PhPACz's better wettability than PTAA.



Supplementary Fig. 8. Contact angles of the perovskite ink on the ITO substrates coated with PTAA and Poly-PhPACz.

2. The consistently low Vrb values (~-4 V) observed for SAM-based HTLs compared to polymeric HTLs (Poly-PhPACz and PTAA) suggest a potential general advantage of polymeric architectures for reverse bias tolerance. The authors should discuss whether this represents a fundamental materials difference.

Response: We thank the reviewer for the valuable comments.

The improvement of reverse-bias stability based on polymeric HTLs relies on both their better uniformity and higher conductivity compared to SAM counterparts. As our EL mapping shows, current SAM HTLs suffer from limited interface uniformity that generates spatial heterogeneity, which is not able to block electron injection and ultimately leads to device breakdown under reverse bias. On the contrary, conjugated polymers like PTAA and Poly-PhPACz can form relatively thicker HTLs with significantly improved uniformity and electron-blocking capacity. This shows the intrinsic advantages of conjugated HTL polymers over SAMs in terms of reverse bias stability.

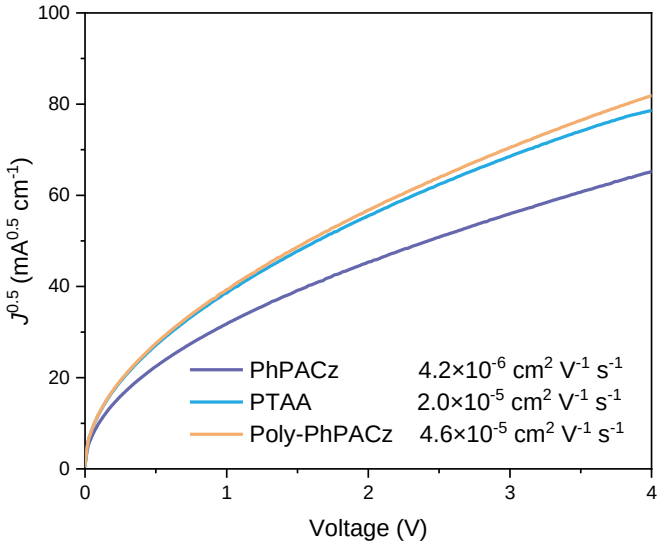
We further made additional discussion on this point in the revised manuscript: (page 10)

This indicates that the improvement of reverse bias stability based on polymeric HTLs relies on both their better uniformity and higher conductivity compared to SAM counterparts. Conjugated polymers like PTAA and Poly-PhPACz can form relatively thicker HTLs with significantly improved uniformity and electron-blocking capacity. This shows the intrinsic advantages of conjugated HTL polymers over SAMs in terms of reverse bias stability.

3. Although photo-CELIV measurements provide average mobility values, direct measurement of hole mobility in the HTL layer (e.g., through space-charge-limited current or field-effect transistor measurements) would more conclusively demonstrate the enhanced conductivity of Poly-PhPACz.

Response: We thank the reviewer for the constructive comments.

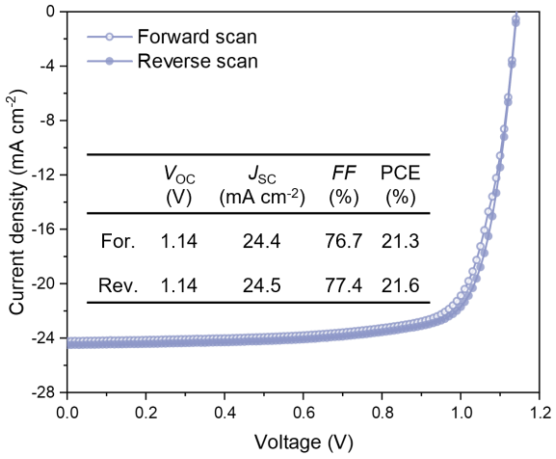
The hole mobilities of the HTLs were further investigated by the space-charge-limited current (SCLC) method with a hole-only structure of glass/ITO/PEDOT:PSS/HTL/MoO_x/Ag as shown in Supplementary Fig. 14 below. Poly-PhPACz shows the highest hole mobility of 4.6×10^{-5} cm^2 V^{-1} s^{-1} compared to PhPACz (4.2×10^{-6} cm^2 V^{-1} s^{-1}) and PTAA (2.0×10^{-5} cm^2 V^{-1} s^{-1}). This new result has been incorporated into the revised Supplementary Materials.



Supplementary Fig. 14. $J^{1/2}$ versus V characteristic curves of the hole-only devices based on three HTLs.

4. For comprehensive comparison, the forward scan J-V characteristics of SAM PhPACz devices should also be included alongside those of the champion Poly-PhPACz devices.

Response: We have provided the forward scan *J-V* characteristic curve and device parameters of PhPACz-based PSC in the revised Supplementary Materials accordingly.



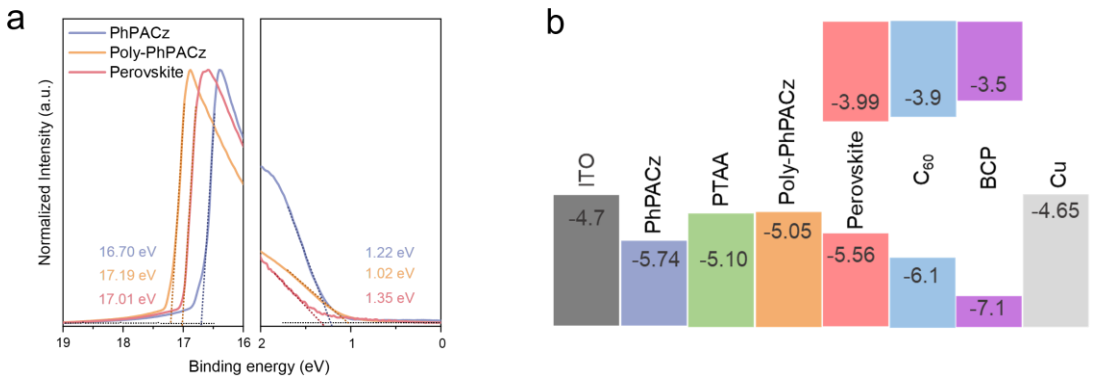
Supplementary Fig. 16. Reverse and forward *J-V* characteristic curves of the PSCs based on PhPACz. Inset shows the device parameters derived from the curves.

5. Additional fundamental characterization of Poly-PhPACz would strengthen the work, including: energy level alignment (via cyclic voltammetry or ultraviolet photoelectron spectroscopy). In addition, which method was used to fit the TRPL data?

Response: Thanks for an important comment.

Combining reviewer #3' request of measuring the energy alignment of complete devices, we studied the valance bands of PhPACz, Poly-PhPACz and the perovskite layer via UPS. The conductance bands are estimated based valence bands and optical bandgaps. The energy levels of each layer are summarized in Supplementary Fig. 10.

TRPL curves were fitted using the bi-exponential decay function of $y = y_0+A_1exp(-x/t_1)+A_2exp(-x/t_2)$, and the average PL lifetime is calculated based on $t_{avg} = (A_1t_1^2 + A_2t_2^2)/(A_1t_1 + A_2t_2)$ (Supplementary Table 2).



Supplementary Fig. 10. a, UPS spectra of PhPACz film, Poly-PhPACz film and perovskite film on ITO glass substrates. **b**, Summary for energy levels of each layer involved in the PSCs.

Supplementary Table 2. Summary of the fitting parameters for the TRPL spectra using the bi-exponential decay function $y = y_0+A_1exp(-x/t_1)+A_2exp(-x/t_2)$, $t_{ave} = (A_1t_1^2+A_2t_2^2)/(A_1t_1+A_2t_2)$.

Sample	A_1	t_1 (ns)	A_2	t_2 (ns)	t_{avg} (ns)
PhPACz/Perovskite	0.379	41.2	0.187	2130.8	2051.9
Poly-PhPACz/Perovskite	0.313	51.3	0.287	2708.8	2655.0

Reviewer #2

In this manuscript, Zhao et al. report a novel hole transport layer (HTL) in perovskite solar cells (i.e., Poly-PhPACz) as an alternative to commonly used PTAA and carbazole-based self-assembled monolayers. Specifically, authors find that this polymeric HTL provides superior reverse bias stability compared to its monomeric analogue, addressing a key limitation of self-assembled materials for use as hole-selective layers in perovskite solar cells. Poly-PhPACz is also shown to yield better wetting and to increase hole injection to perovskite (vs PTAA), as well as to improve the overall operational stability of the solar cell under illumination (vs PhPACz). Cr/Cu bilayer electrodes are also shown to increase the reverse bias stability of the device. In general, the methodology and experiments in the paper are sound, and the performance and stability of the solar cells reported herein are excellent. However, there are crucial aspects in this manuscript that do not meet the high standards of Nature Communications. Mainly, the manuscript does not provide substantial conceptual advances relative to the existing literature on the topic of reverse bias stability. A major takeaway form this manuscript is that thicker Poly-PhPACz layers provide higher reverse bias stability, but a similar conclusion was reached in other papers for PTAA (https://doi.org/10.1038/s41560-024-01600-z). Additionally, Poly-PhPACz does not yield a substantial increase in reverse bias stability (i.e., a more negative breakdown voltage) compared to PTAA. The literature cited in this manuscript is not fully up to date and does not capture some key advances in the field that already address some of the issues tackled herein. For example, the highest breakdown voltage values obtained in this paper were obtained via a strategy previously reported in the literature to increase reverse bias stability, i.e., using bilayer chromium/copper electrodes (https://doi.org/10.1021/acsenergylett.5c00727). For these reasons, I recommend the transfer of this manuscript to a more technical journal (e.g., Communications Materials) after the aforementioned issues are resolved.

Response: We thank the reviewer's time on reviewing our manuscript, and also the constructive comments that help us improve manuscript quality.

Here we would like to first illustrate the key findings of our work, before we give detailed response to the following comments.

(1) We use EL mapping to reveal the critical role of HTL uniformity in affecting device reverse-

bias stability, and poor uniformity of current HTLs causes spatial heterogeneity that is not able to block electron injection and leads to device breakdown under reverse bias. Ginger *et al.* also hypothesized that the spatial heterogeneity might affect the device reverse-bias break-down behavior, but failed to provide direct experimental evidence (*Nat. Energy* 2024, 9, 1275).

In addition, we also reveal that co-deposited SAMs exhibited further degradation in both EL intensity and spatial uniformity compared to sequentially deposited HTL/perovskite structures, although such a method simplifies the fabrication process. This provides important reference when evaluating the application of such a method in scalable manufacturing.

(2) Although previous work obtained high V_{rb} based on a thicker PTAA, these devices suffer from compromised PCEs (around 14%) due to the poor wettability of the thick PTAA layer. In our work, we develop a new polymeric hoe transporter (Poly-PhPACz) with both high wettability and hole-transporting capacity. The PSCs based on Poly-PhPACz realize high V_{rb} without compromising the solar cell efficiencies (over 22%), providing guidance for the development of new hole transporters.

Additional comments that may help to improve the quality of the paper are also provided as follows:

1. Lines 116, 117: The polarity of the reverse bias application is described incorrectly (copper should be under positive bias (or grounded) and ITO should be under negative bias.

Response: Thanks so much for the careful check and we have corrected this point in the revised manuscript.

2.To test reverse bias stability of the various device architectures, authors scan devices from 2 V to -20 V. The initial bias (2 V) is considerable and, according to various reports (e.g., https://doi.org/10.1002/aenm.202000310, https://doi.org/10.1002/aenm.202403850, https://doi.org/10.1021/acsenergylett.5c00376), harsh to the perovskite device (2 V is almost twice the Voc of these solar cells. It is important that authors rule out any secondary effects from the applied forward bias (e.g., effect on ion redistribution). It would be interesting to carry out reverse bias stress tests at different scan ranges and/or dwell times.

Response: Thank the reviewer for the insightful comments.

We further investigated the influence of both scan range and rate on the V_{rb} of devices based on Poly-PhPACz. Three different scan ranges were selected: 0 to −20 V, 1.2 to −20 V, and 2 to −20 V, along with two additional scan rates (0.05 V s^{-1} and 0.35 V s^{-1}). The corresponding V_{rb} values are summarized in Supplementary Fig. 2.

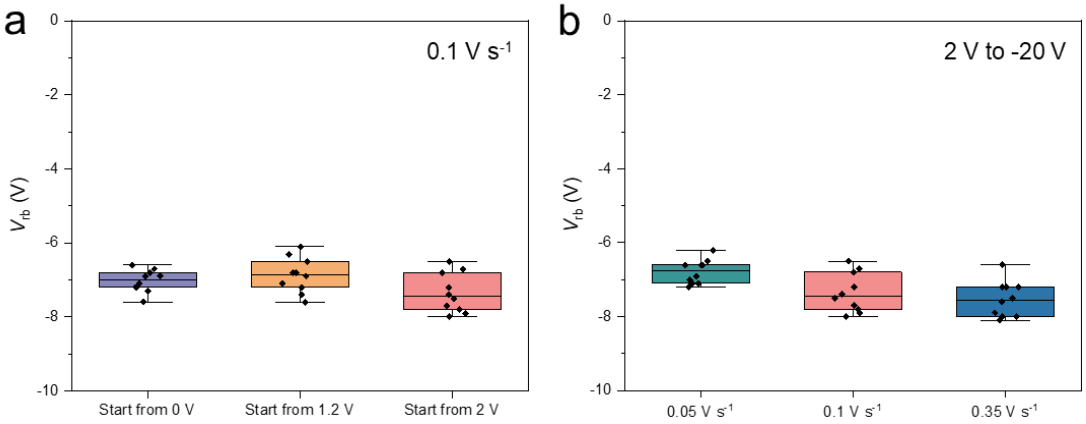
With respect to the bias scan range, we observed that a higher starting positive voltage had almost no detrimental effect on V_{rb}. We attribute this to the relatively short duration of applied forward bias in our experiments, unlike the prolonged (several hours) biasing conditions reported in other studies mentioned above.

Regarding the scan rate, we found that at 0.35 V s^{-1}, the V_{rb} values were comparable to those measured at 0.1 V s^{-1}. This result is consistent with the report by Ginger et al. (*Nat. Energy* 2024, 9, 1275; see page 23 of their Supporting Information), which indicated that within a reasonable range, the scan rate has limited impact on V_{rb}.

In the present study, as our primary goal is to evaluate and compare the reverse-bias stability of different HTLs, we adopted a consistent testing protocol (0.1 V s^{-1}, 2 V to −20 V) for all devices to ensure fair and direct comparison of their robustness.

We further made the following discussion in the Supplementary Materials:

To investigate the influence of the bias conditions (scan range and rate) on the V_{rb} of devices, three different scan ranges were selected: 0 to −20 V, 1.2 to −20 V, and 2 to −20 V, along with three scan rates including 0.05 V s^{-1}, 0.10 V s^{-1}, and 0.35 V s^{-1}. The corresponding V_{rb} values are summarized in Supplementary Fig. 24. With respect to the bias scan range, a higher starting positive voltage had almost no detrimental effect on V_{rb}, which is attributed to the relatively short duration of applied forward bias in this study. Regarding the scan rate, we found that at a high rate of 0.35 V s^{-1}, the V_{rb} values were comparable to those measured at 0.1 V s^{-1}. This result is consistent with the report by Ginger et al. (*Nat. Energy* 2024, 9, 1275), which indicated that within a reasonable range, the scan rate has limited impact on V_{rb}. As the focus of current work is to evaluate and compare the reverse-bias stability of different HTLs, we employed a bias condition adopted from a well-established protocol reported by Ginger *et al.*, and the scan rate is 0.10 V s^{-1} from 2 V to −20 V under dark to ensure fair and direct comparison of their robustness under reverse bias.



Supplementary Fig. 24. V_{rb} distribution of the Poly-PhPACz-based PSCs swept from different start voltage (**a**) and scan rate (**b**). Box plot elements in are defined as follows: center line: median; box limits: upper and lower quartiles; whiskers: 1.5× interquartile range.

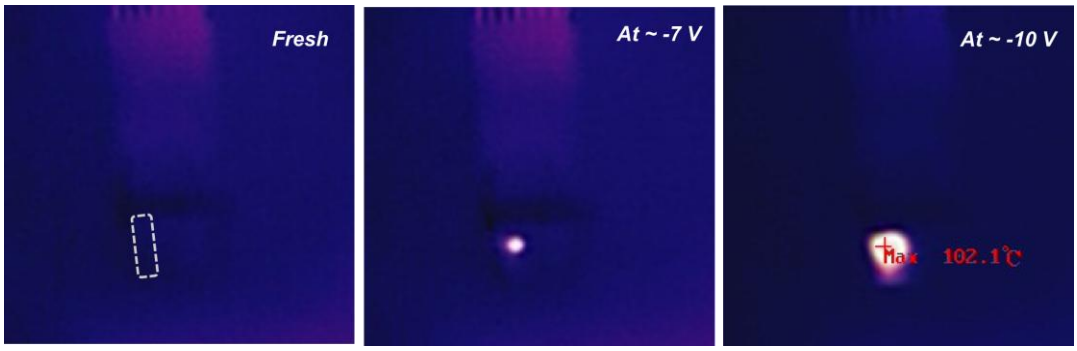
3.A more accurate definition of breakdown voltage should be provided. Several breakdown regimes are known to affect perovskite solar cells, from milder Zener breakdown to irreversible junction destruction via thermal breakdown (e.g., https://doi.org/10.1002/solr.202300456).

Response: We thank the reviewer for bringing this important reference to our attention, which has been cited as Ref. 42 in the revised manuscript.

In our initial submission, the breakdown voltage is defined as the reverse bias when the device exhibits obvious burnout behavior and the injected current density surged to 100 mA cm^{-2}.

In our case, since the breakdown of our devices is irreversible, we thus think the device breakdown should be thermal breakdown. To confirm this, we monitored the temperature change of the devices with increasing reverse bias. As presented below, the Poly-PhPACz-based device (Cu electrode) exhibited a gradual temperature increase and finally reached over 100°C when it broke down at −10 V, and the device breakdown is irreversible.

Following the reviewer's comments, we have clearly highlighted that the breakdown voltage is defined as the reverse bias when the device exhibits irreversible thermal breakdown and the injected current density surged to 100 mA cm^{-2} in the revised manuscript.



Supplementary Fig. 5. The temperature change of the Poly-PhPACz-based device under reverse bias sweeping monitored with an infrared radiometer.

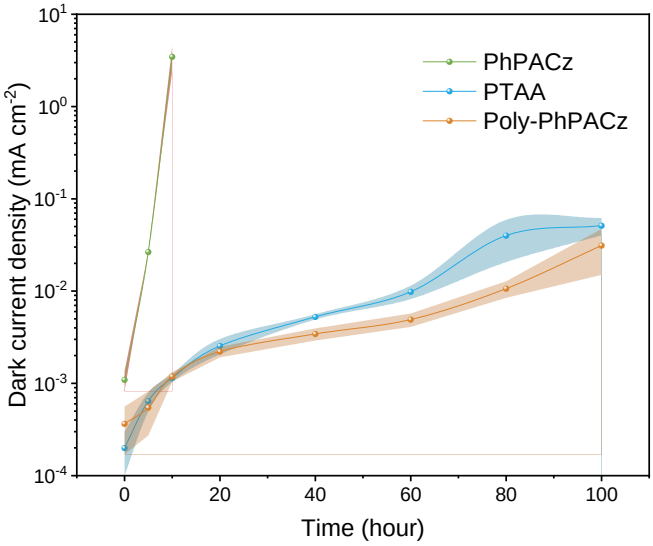
4.The EL mapping technique employed herein operates under forward-biasing to acquire an image of the resulting EL. This implies that the solar cell HTL will act as a hole injection layer, being EL microscopy useful to verify the uniformity of this process. However, under reverse bias, the HTL will inject electrons to the perovskite as leakage current. The EL mapping used herein is therefore not fully convincing to verify the spatial uniformity of the electron blocking ability in the HTL, since it relies on HTL-to-perovskite hole injection rather than on HTL-to-perovskite electron leakage. Acknowledging that authors do mention that EL operates in different bias conditions compared to reverse bias, it is important that cross-checks with other techniques (e.g., leakage current analysis under reverse bias) are performed to corroborate the validity of the conclusions extracted from EL maps.

Response: This is a very insightful comment.

In the EL mapping stimulated by the forward bias, we are able to visualize the significant difference in spatial heterogeneity that critically affects device reverse-bias stability. We think such observed spatial heterogeneity in EL mapping remains as localized change injection paths affecting device stability across different operational biases. Under the reverse bias condition, this spatial heterogeneity could not block electron injection and thus caused device breakdown. Following the reviewer's suggestion, we also carried out the leakage current analysis of the PSCs based on three HTLs. These devices were continuously biased at −2 V under dark, and current changes were continuously monitored (Supplementary Fig. 6). After 10 hours, the leakage current of the PhPACz device dramatically increased to around 10 mA cm^{-2}, indicating that the device had been permanently damaged, possibly due to thin and inhomogeneous

PhPACz layer. After 100 hours of bias application, both PTAA and Poly-PhPACz devices showed better resistance to reverse bias, indicating the advantages of polymeric HTLs over small-molecular SAMs in terms of reverse-bias stability.

We have included the new results in the revised Supplementary Materials:



Supplementary Fig. 6. The change of dark current for different PSCs when biased at -2 V (five devices for each group). Shadow areas represent the standard deviation among devices.

5.In Fig. 2a, authors determine that the optimal thickness of Poly-PhPACz is 63 nm. However, it is apparent in this figure that an increase in thickness is always followed by an improvement in Vrb, reaching no clear Vbr minimum. To increase the appeal of this new HTL as a reverse bias stability enhancer, it is advised that authors provide further details as to why 63 nm is the optimal thickness. Additionally, Fig. 2a shows that most gains in reverse bias stability occur by increasing the thickness up to 20 nm, being changes in Vrb from 20 to 63 nm more modest. This may suggest that, while a major part of current leakage pathways are suppressed with 20 nm Poly-PhPACz, increasing the thickness further does not result in clear improvements. Can authors explain the reason for this?

Response: Thanks for pointing out this issue.

First, we apologize that our previous description of "optimal thickness" is misleading, and "63 nm" is the maximum thickness that the resulting PSCs can still maintain a decent PCE of over 20%.

Second, further increasing Poly-PhPACz thickness from 20 to 63 nm does not show much improvement in V_{rb}, and this is because 20-nm Poly-PhPACz has already form highly uniform coverage on ITO, effectively blocking electron injection and enhancing device reverse-bias stability.

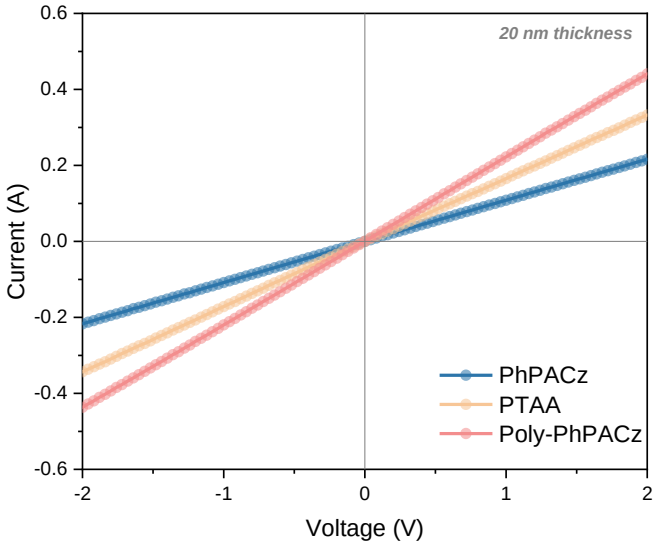
We realize our previous description of "optimal thickness of 63 nm" is misleading, so we have revised this point in the revised manuscript: (page 10)

As illustrated in Fig. 2a, increasing the Poly-PhPACz thickness leads to higher V_{rb} values, with the maximum V_{rb} reaching -8.4 V at a thickness of 63 nm at which the corresponding PSC can still maintain a decent PCE of over 20%.

6.Authors mention that Poly-PhPACz possesses a superior processability window than PTAA (i.e., thick Poly-PhPACz layers yield higher PCE than thick PTAA layers). It is demonstrated that Poly-PhPACz leads to better wetting than PTAA and this is highlighted as a major advantage of the new HTL. However, it would also be interesting to verify whether differences in the conductivity of the HTLs also contributes to this superior processability window (e.g., as done for Poly-PhPACz and PhPACz in Supplementary Figure 6).

Response: We sincerely appreciate the reviewer's insightful comments.

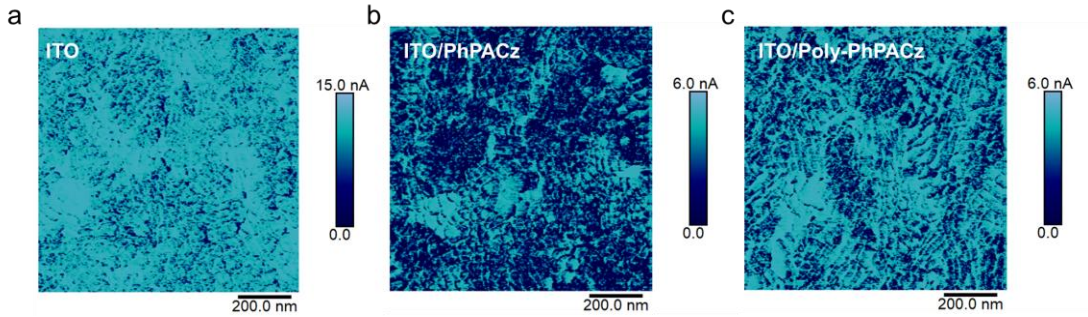
To evaluate the electrical conductivity of different HTLs, we fabricated the glass/ITO/HTL/Ag devices, and measured their *I-V* curves in dark as present in Supplementary Fig. 13. Compared to PhPACz and PTAA, Poly-PhPACz shows the highest conductance.



Supplementary Fig. 13. *I-V* curves of the glass/ITO/HTL/Ag devices for different HTLs (20 nm).

7.In Supplementary Figure 6, please compare the two existing images with a bare ITO control. This is to rule out if inhomogeneities present in both samples arise from conductivity differences between Poly-PhPACz and PhPACz or from coverage differences.

Response: Thanks for the insightful and constructive comments. The c-AFM image of bare ITO is also included with an average current of 8.81 nA.



Supplementary Fig. 12. c-AFM current images of bare ITO (**a**) and ITO substrates coated with PhPACz (**b**) and Poly-PhPACz (**c**).

8. The use of chromium/copper bilayer contacts to enhance the reverse bias stability of p-i-n perovskite solar cells in this manuscript is not a novel contribution to the field. This has already been reported recently with very similar Vbr results (https://doi.org/10.1021/acsenergylett.5c00727). Before this, the use of chromium/copper contacts has been shown in multiple works to improve the operational stability perovskite solar cells (e.g., https://doi.org/10.1038/nmat4388, https://doi.org/10.1038/s41586-024-08546-y, https://doi.org/10.1021/acsnano.5b03687). No citations of previous works on chromium/copper contacts were added in this version of the paper. Authors should make sure the relevant literature on chromium/copper contacts is cited to keep the manuscript updated with the current state-of-the-art.

Response: We sincerely thank the reviewer for bringing these important references to our attention, which have been cited as Refs. 47-50 in the revised manuscript.

The Cr/Cu bilayer electrode indeed plays a critical role in enhancing the resistance of back

electrode to positive bias in this work. In addition, the resistance of cathode to negative bias also has important effects on the reverse-bias stability of complete PSCs. Despite the successful application of SAMs in perovskite solar cells, these devices are found to suffer from much poorer reverse-bias stability. To address this issue, we develop Poly-PhPACz with high conductivity as well as uniformity, which significantly the cell reverse-bias tolerance without compromising device efficiency.

9.Further insights on the rationale behind the conceptual design of Poly-PhPACz would be useful, since this HTL is meant to bind onto the surface of ITO like a SAM but is instead deposited at comparatively high thickness.

Response: Thanks for a thoughtful comment.

The key design rationale of Poly-PhPACz is to construct a conjugated backbone by polymerizing carbazole monomers. Conventional SAMs are intrinsically insulating small molecules, and they have to form an ultra-thin monolayer to reduce charge-transport resistance. Once their layer thickness increases, the resistance increases significantly and deteriorate hole extraction efficiency. However, after polymerizing the carbazole monomers to conjugated Poly-PhPACz, the conjugation formed along the polymer backbone can significantly facilitate the intra- and inter-molecular charge transport as confirmed by its high conductivity. In addition, Poly-PhPACz also possesses phosphorous acid side-chains, enable it to bind to ITO like SAMs. We have included more discussion on the design rationale of Poly-PhPACz in the revised manuscript: (page 9)

The design of new HTLs should comprehensively address the limitations of current HTL materials while retaining their advantageous properties. Conventional SAMs are intrinsically insulating small molecules, and they have to form an ultra-thin monolayer to reduce charge-transport resistance. Once their layer thickness increases, the resistance increases significantly and deteriorate hole extraction efficiency[33]. To overcome these challenges, we developed a new conjugated polymer, Poly-PhPACz, synthesized through polymerization of a SAM molecule (Fig. 1a). The conjugation formed along the polymer backbone can significantly facilitate the intra- and inter-molecular charge transports, forming good coverage on ITO and reducing

current leakage. Meanwhile, Poly-PhPACz also possesses phosphorous acid side-chains, enabling it to bind to ITO like SAMs and stabilize the interface.

Reviewer #3

This study addresses the critical issue of reverse bias instability in perovskite solar cells (PSCs) by developing a novel polymeric hole transport layer (HTL) called Poly-PhPACz. Unlike conventional self-assembled monolayers (SAMs), which suffer from poor film uniformity and low breakdown voltage, Poly-PhPACz offers high conductivity, excellent wettability, and robust interface adhesion. Devices incorporating this HTL achieved a high-power conversion efficiency of 26.1% and a reverse breakdown voltage of up to -14.3 V, with over 92% performance retention after 1,800 hours of illumination. The high efficiency and stability are impressive, but I believe some major revisions and clarifications are necessary.

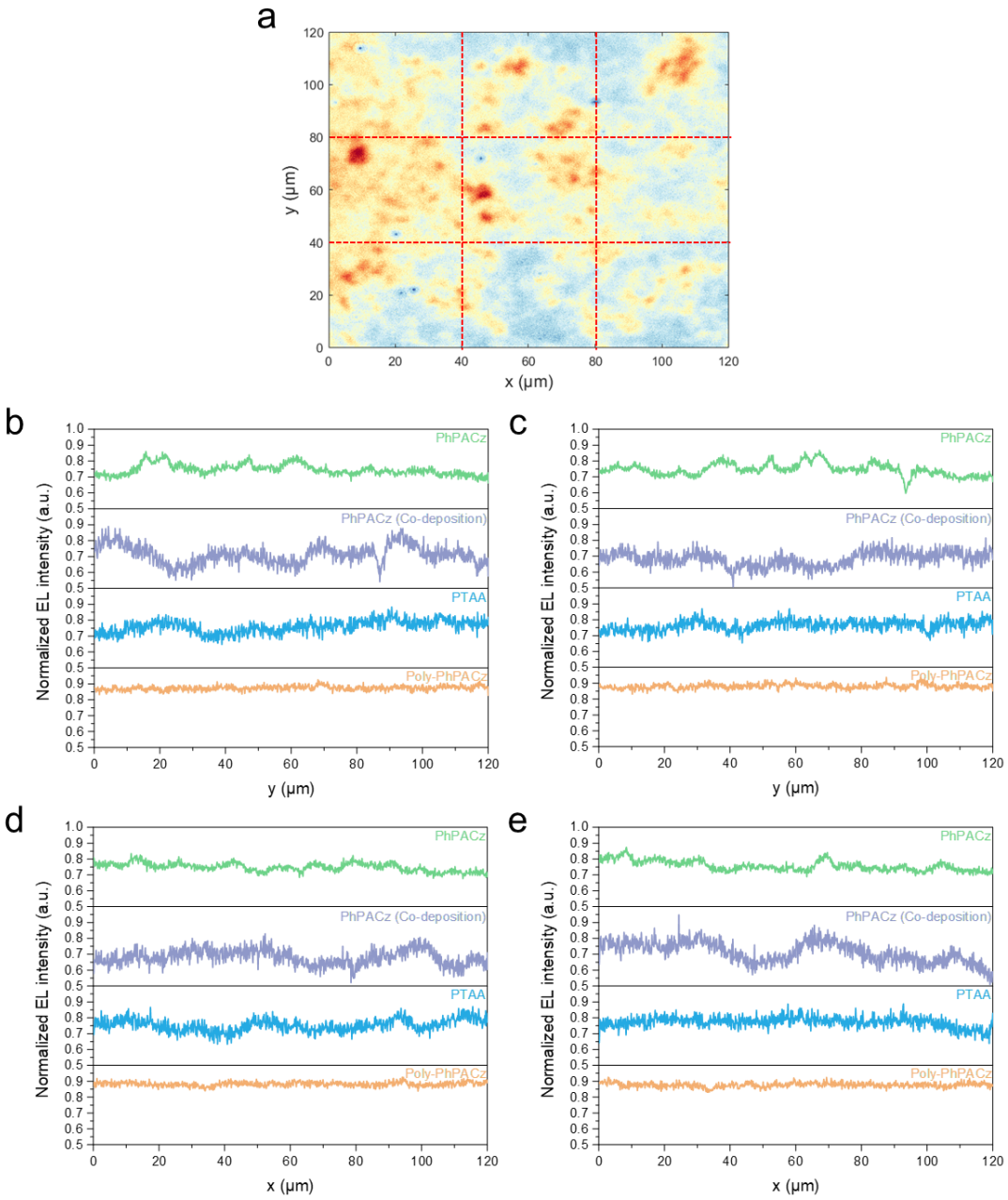
Response: We thank the reviewer for the positive comments on our work. We also appreciate the reviewer's valuable and constructive comments to help us significantly improve the manuscript quality.

Question 01. In Fig. 1, Poly-PhPACz exhibited higher EL intensity and a narrower distribution compared to other SAMs and PTAA. However, the EL mapping images (Fig. 1c–f) and the corresponding intensity distribution graphs (Fig. 1g) do not appear to be fully consistent. For instance, the PhPACz EL mapping shows brighter intensity spots than Poly-PhPACz, but this is not reflected in the distribution graph. To improve clarity and reliability, it would be helpful to indicate the specific line cuts on the EL maps that were used to generate the distribution plots.

Response: Thanks for an important comment and also a nice suggestion.

Following the reviewer's suggestion, we uniformly divided the EL maps (120 μm by 120 μm) into 9 identical regions using two horizontal lines (x = 40 μm and 80 μm) and two vertical lines (y = 40 μm and 80 μm), then extracted the EL intensity profiles along these four lines. As plotted in Supplementary Fig. 4, the EL intensity of Poly-PhPACz shows the smallest fluctuation, while the co-deposited PhPACz suffers from the largest variation.

We thank the reviewer again for this excellent suggestion, which makes the EL contrast among these four cases clearer.



Supplementary Fig. 4. a, Schematic illustration of extracted the EL intensity profiles from 2D EL maps along four lines: (**b**) x=40 μm, (**c**) x=80 μm, (**d**) y=40 μm, and (**e**) y=80 μm**.**

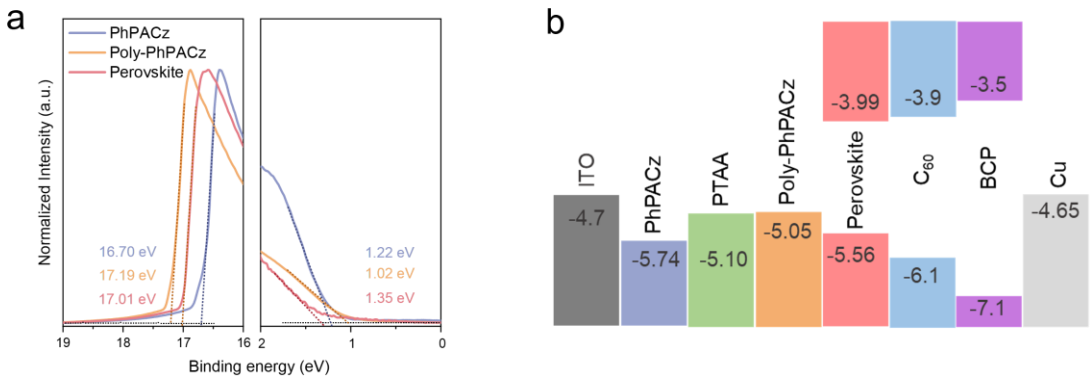
Question 02. The optimal thickness of Poly-PhPACz is 20 nm, indicating that it is not a monolayer. Typically, SAMs facilitate hole extraction by forming a well-ordered orientation and generating a dipole between the ITO and the perovskite. Therefore, a 20 nm-thick Poly-PhPACz layer may have a random molecular orientation, which could potentially hinder hole extraction. Given this, what is the precise mechanism by which Poly-PhPACz improves device

performance compared to conventional SAMs, beyond the benefit of improved uniformity? In addition please suggest the energy level diagram of the whole device by measuring UV-Vis Absorbance and ultraviolet photoelectron spectroscopy (UPS).

Response: Thanks for the constructive comment.

A key advantage of Poly-PhPACz over SAMs is its high conductivity contributed by its conjugated polymer backbone, facilitating the inter- and intra-molecular charge transports. As revealed by the SCLC results (Fig. S14), the hole mobility of Poly-PhPACz is one order of magnitude higher than that of PhPACz, enabling it to effectively transport holes even at a thicker layer.

Following the reviewer's comment, we further measured the energy levels of PhPACz, Poly-PhPACz and the perovskite layer via UPS, and summarized them in the energy level diagram of the whole device.



Supplementary Fig. 10. a, UPS spectra of PhPACz film, Poly-PhPACz film and perovskite film on ITO glass substrates. **b**, Summary for energy levels of each layer involved in the PSCs.

Question 03. The authors attribute the enhancement in PL and TRPL performance to the passivation effect of Poly-PhPACz compared to PhPACz. (Fig. 2d) However, since both HTLs share the same basic molecular structure, it is unclear how this difference alone accounts for the observed passivation effect. It would be helpful to provide additional evidence or explanation to clarify the origin of the PL and TRPL enhancement. In addition, show SEM images and XRD spectra of perovskite film, deposited on PhPACz and Poly-PhPACz please.

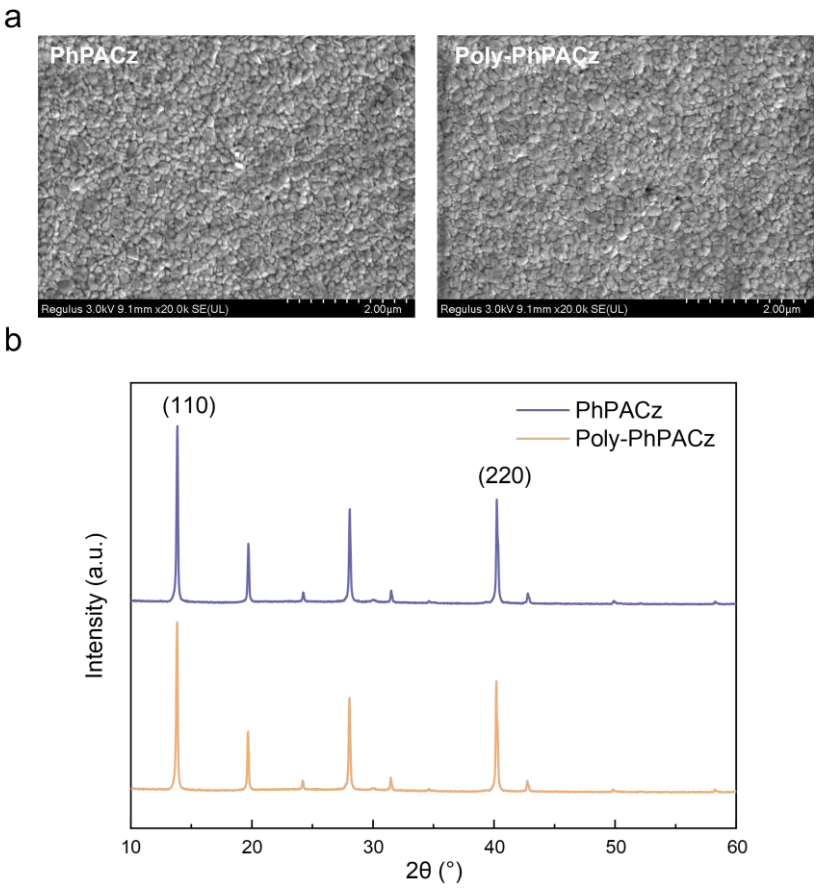
Response: Thank for the good suggestions.

The passivation effect is attributed to a much higher amount of phosphorous acid groups in the

thick Poly-PhPACz layer. Although PhPACz also has phosphorous acid group, most of them have to bind to ITO and self-assembly into an ultra-thin SAM layer. On the contrary, the thick Poly-PhPACz layer has more phosphorous acid groups. On the one hand, these high density of phosphorous acid groups bind to ITO and stabilizing the interface. On the other hand, the remain ones tune the HTL surface wettability and interact with perovskite layer, promoting ink spreading and passivating interface defects, respectively.

We have also provided the SEM images and XRD patterns of the perovskite films deposited on PhPACz and Poly-PhPACz, respectively. As shown below, we do not observe much difference in their grain size distribution or diffraction intensity. Therefore, the improvement in PL intensity should mainly come from the better passivation effect of Poly-PhPACz to perovskite interface.

The explanation above has been included in the revised manuscript (page 12).



Supplementary Fig. 11. Top-view SEM images (**a**) and XRD patterns (**b**) of the perovskite films deposited on PhPACz and Poly-PhPACz.

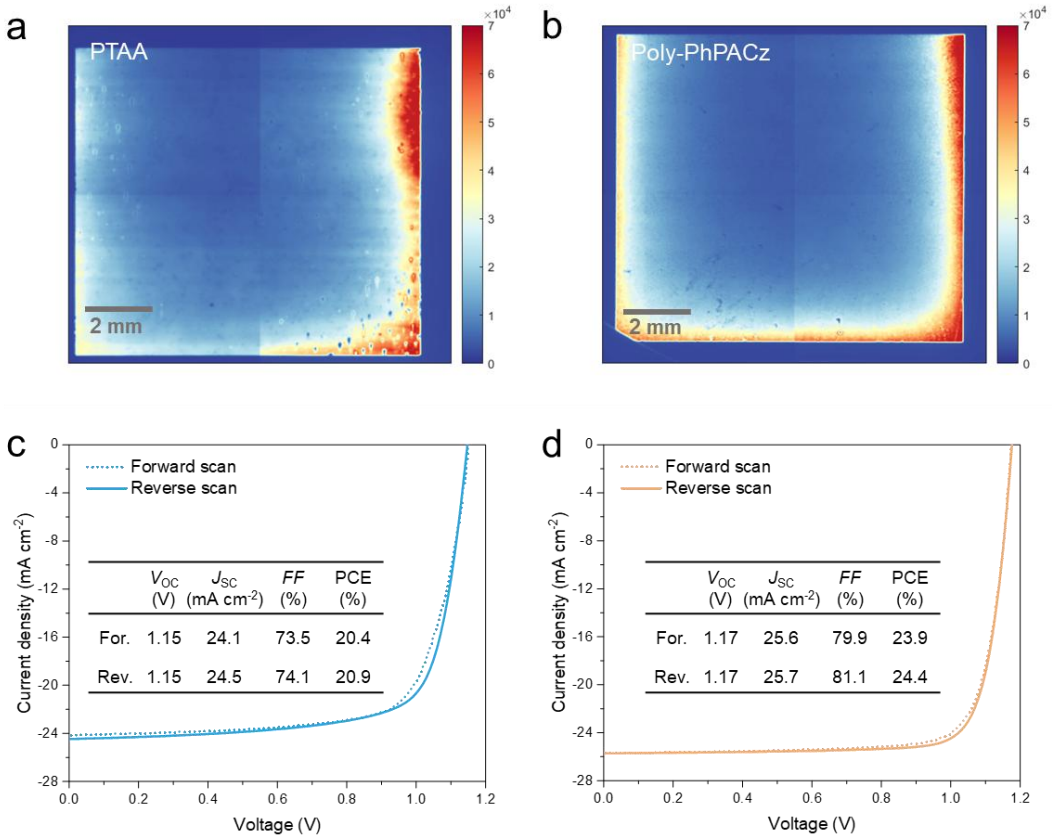
Question 04. The authors highlight the advantage of Poly-PhPACz for large-area PSC fabrication compared to PTAA; however, no data from large-area devices are currently presented. It would strengthen the manuscript to include J-V curves and EL mapping results for devices with an active area ≥ 1 cm^2.

Response: Thanks for the excellent suggestion.

We fabricated 1-cm^2 devices based on PTAA and Poly-PhPACz, and measured their EL mapping as shown below. Compared to PTAA, the EL emission of Poly-PhPACz devices was more uniform, while the PTAA device showed a few dispersed dark spots.

Regarding the efficiencies of 1-cm^2 devices, the Poly-PhPACz device delivered a higher PCE of 24.4% with less hysteresis than those of PTAA.

We have included these new results in the revised Supplementary Materials.



Supplementary Fig. 19. EL mapping (**a,b**) and *J-V* characteristic curves (**c,d**) of the1-cm^2 PSCs based on PTAA and Poly-PhPACz. Insets in (**c,d**) show the detailed photovoltaic parameters.

Question 05. The authors successfully increased the Vrb by introducing a Cu/Cr bilayer, which

is impressive as it demonstrates that reverse bias stability can be significantly enhanced simply by modifying the electrode. It would be interesting to see whether a similar effect can be observed with other commonly used electrodes, such as silver. Additionally, providing further insight or evidence into the specific role of Cr in improving reverse bias stability would help strengthen the discussion.

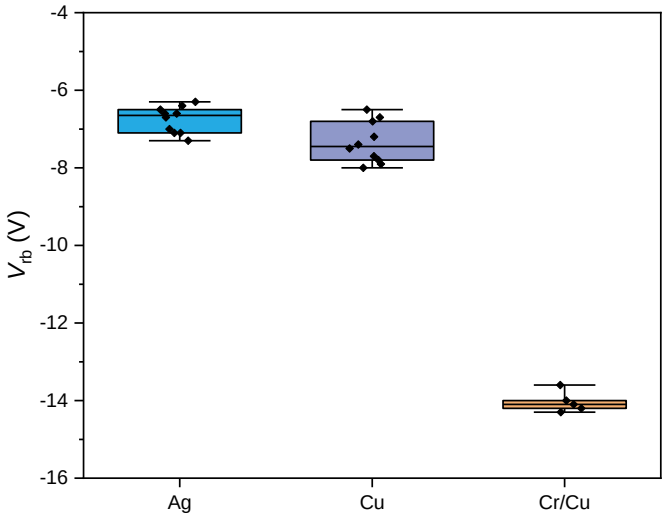
Response: We sincerely appreciate the reviewer's insightful comments.

We also tried Ag electrode, and the resultant devices suffered from lower V_{rb} values as plotted below. Ag electrode has been studied to diffuse to the perovskite layer and form AgI, which causes the device shunting and thus reduces V_{rb} (*Energy Environ. Sci.* 2016, 9, 3650). In addition, Ag electrode also tends to be oxidized when it is biased positively under the reverse bias condition.

Compared to neat Cu or Ag electrodes, the insertion of Cr can shield the diffusion of the top metal contact to perovskite, suppressing the formation of metal iodide species. In addition, Cr_2O_3 has also been reported to form with the trace amount of O_2 during the thermal evaporation of Cr layer. The enthalpies of formation of Cr_2O_3 ($H_f = -1{,}128\ kJ\ mol^{-1}$) versus CrI_3 ($H_f = -205\ kJ\ mol^{-1}$) explain the stability of the chromium oxide interlayer in contact with iodine/iodide (*Nat. Mater*. 2015, 14, 1032; *ACS Nano* 2016, 10, 218).

We have made more discussion on this point in the revised manuscript: (page 15)

We tried Ag electrode first and the resultant devices suffered from lower V_{rb} values as shown in Supplementary Fig. 21. Ag electrode has been studied to diffuse to the perovskite layer and form AgI, which causes the device shunting and thus reduces V_{rb}[46]. In addition, Ag electrode also tends to be oxidized when it is biased positively under the reverse bias condition. Compared to previous work using complicated fabrication procedures or expensive gold electrodes, we found that a double layer of Cr/Cu prepared by thermal evaporation can effectively improve device V_{rb}. The insertion of Cr can shield the diffusion of the top metal contact to perovskite and Cr_2O_3 has also been reported to form with the trace amount of O_2 during the thermal evaporation of Cr layer, thus suppressing the formation of metal iodide species[47, 48, 49, 50].



Supplementary Fig. 21. V_{rb} distribution of the PSCs based on Ag, Cu, and Cr/Cu electrodes. Box plot elements in are defined as follows: center line: median; box limits: upper and lower quartiles; whiskers: 1.5× interquartile range.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have addressed the issues raised in my previous review. I suggest its publication without revisions.
Response: We thank the reviewer again for the valuable comments that have significantly improved our manuscript.

Reviewer #2 (Remarks to the Author):

Authors have thoroughly addressed most of the points raised by the reviewers, which has improved the quality of the work. The role of Poly-PhPACz as a reverse bias stability enhancer next to commonly used PTAA or molecular SAMs is clear, since it offers i) a wider processing window owed to its higher conductivity and wetting, ii) interfacial anchoring and stabilisation owed to its phosphonic acid groups, iii) higher uniformity and lower chance of breakdown, and iv) non-compromised device efficiencies when employed at high thicknesses needed to obtain high reverse bias stability. This now makes the work of potential interest for publication in Nature Communications (further revisions indicated below).
Response: We thank the reviewer's recognition of our work.

I am still concerned about the novelty of the last part of the manuscript, i.e., the use of Cr/Cu double layer electrodes to enhance reverse bias stability. As I indicated in my previous report, Cr/Cu contacts have already been employed to enhance the reverse bias stability of p-i-n perovskite solar cells with very similar results (https://pubs.acs.org/doi/full/10.1021/acsenergylett.5c00727). While authors have correctly included citations to previous literature on Cr electrodes, currently the manuscript does not explicitly acknowledge that this approach has been used before for the same purpose. This is needed to give readers a clear notion of the state-of-the-art in this topic. Doing so would strengthen the paper and enhance the focus on the polymeric hole-transport layer presented herein (being the core finding of the manuscript). A clearer justification of the novelty in using Cr/Cu electrodes in Poly-PhPACz-based devices to enhance reverse-bias stability is also recommended to better align with the novelty and impact criteria of Nature Communications.
Response: We thank the reviewer for highlighting this important point. In the revised manuscript, we have revised our description to acknowledge the prior work on the use of Cr/Cu electrodes for improving device reverse-bias stability, as reflected in the following statement:
Instead of resorting to complex fabrication processes or costly gold electrodes, we **employed a previously reported approach involving a thermally evaporated Cr/Cu double layer** to further improve device V_{rb}[47, 48]. The insertion of Cr can shield the diffusion of the top metal contact to perovskite and Cr_2O_3 has also been

reported to form with the trace amount of O_2 during the thermal evaporation of Cr layer, thus suppressing the formation of metal iodide species[47, 48, 49, 50].

Reviewer #3 (Remarks to the Author):

The authors have adequately addressed the raised questions, and I recommend this work for publication in Nature Communications.

Response: We thank the reviewer again for the valuable comments that have significantly improved our manuscript.