Peer Review File

Manuscript Title: Regulating surface potential maximizes voltage in all-perovskite tandems

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

The reduction of open circuit voltage (Voc) deficit in perovskite solar cells is a common issue for the community, especially for wide-bandgap bromine-rich perovskite solar cells. In this work, Chen et al. report a diammonium molecule, 1,3-propylene diammonium (PDA), to regulate surface potential and improve open-circuit voltage of wide-bandgap perovskite solar cells. The authors demonstrate that the PDA molecule has a much better ability for surface passivation/treatment, compared to the common monoammonium molecules. Consequently, tandem solar cells using the PDA-treated wide-bandgap perovskite solar cells deliver a very impressive NREL-certified efficiency with a very high Voc. Overall, the results are well discussed and solid. This work presents a highly important advance for the perovskite photovoltaic field. Therefore, I would recommend publishing this work after some revisions.
Comments to the authors:
1) In Line 133, the authors claim no indication of reduced-dimensional perovskite formation nor of a perovskite polymorph. While I was wondering if the PDA cation can enter the perovskite lattices. The same or similar cation was reported to extend the unit cell and form a 3D “hollow” perovskite structure (ACS Energy Lett. 2018, 3, 1470−1476; Sci. Adv. 2017;3: e1701293). To confirm this, the authors can measure zoomed-in XRD patterns of the films and then check the change of the peak position and lattice parameters of the unit cell.
2) It is reasonable to use a diammonium molecule rather than a monoammonium molecule. While the authors should also comment on that why use this PDA molecule not other diammonium molecules with longer or shorter chains.
3) The efficiencies of the small-area solar cells reported in this work are very impressive. However, the large-area solar cells are also recommended to be included.
3) MPP tracking of single-junction wide-bandgap cells should be also provided.
4) I would recommend the authors change “BTA” to “BA” because the latter one is a more common abbreviation.
5) In Line 92, the authors claim that BA and PDA make the surface more p-type and n-type, respectively. This description is inaccurate because both of the films are still p-type. One should be a stronger p-type and the other one should be a weaker p-type.
6) In Figure S7, the right y-axis should be QFLS.
7) Figure S10, the title: Positive ions are tracked in (a,b) and negative ions in (c,d). The order is reversed. Please correct it.
8) J-V etc. should be italic.
9) Figures in Supplementary materials should be discussed sequentially.
10) The manuscript is overall well written but there are still some typos.

Referee #2 (Remarks to the Author):

Chen et al. present a passivation approach, using molecule PDA for efficient treatment at the perovskite/C60 interface. The results show significantly reduced losses, benefiting from improved energy alignment at the perovskite/C60 interface. This results in much improved single-junction device performance as well as one of the highest certified PCEs for all-perovskite tandem solar cell. The findings are well and clearly presented, and characterization techniques support the effectiveness of PDA layer, including statistics showing good reproducibility of the approach. The use of PDA is novel and with the benefits shown in this paper, I believe the manuscript will raise plenty of attention.

There are some minor things to be considered and further clarifications to be made before the manuscript can be accepted for publication.

1. Line 57: HTL should be stated
2. Line 93-94: by how much is the band offset reduced?
3. On page 7 (lines 116 to 140), the authors state that no reduced-dimensional perovskite formation is discovered, indicating that perovskite does not react with PDA. In what way does the PDA then improve the homogeneity of the surface and prevents the segregation?
4. Line 148, exact bandgap could be stated
5. Lines 167-168: What is the thickness of the PDA layer? Does it physically prevent ions to migrate into C60/metal electrode?
6. In Figure 4c, the sum of EQEs and reflection measurement could provide a lot of additional information about optical and parasitic losses in the device
7. How was stability testing of the tandem performed? Methods state white LED, which surely does not have a spectrum close to AM1.5 spectrum. How was the photogenerated current in both subcells determined for the stability test?
8. Lines 245-246: chosen concentration for PDA should be stated.

Author Rebuttals to Initial Comments:

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

We thank the editor and reviewers for their much-valued suggestions, which have enabled us to improve the manuscript. Following are the detailed actions taken in light of the editor's and reviewers' comments:

Editor's Comment to Author:

We find that adding XRD to confirm whether there is a lattice change and including results of large-area solar cells will be particularly useful to improve the impact of the work.

Response: In light of the Editor's feedback we now:

1) Provide XRD to ascertain whether there is a lattice change.
2) Provide results from large-area solar cells.

In more detail:

1) **Re: Provide XRD to ascertain whether there is a lattice change.** We now provide bulk and also surface-sensitive GIWAXS of control and PDA-treated films in **Figure R2**. These reveal that while the control film peaks are broadened, there is neither a peak shift nor the formation of additional peaks at lower q-values after PDA treatment; one would have expected such a shift/additional peaks if a "hollow" perovskite structure had been formed at the surface (J. Am. Chem. Soc. 2019, 141, 21, 8627–8637, J. Am. Chem. Soc. 2018, 140, 17, 5728–5742). We now discuss the fact that the concentration of PDA spin-coated onto the perovskite surface is low and thus, from our data, does not appear to result in appreciable diffusion into the bulk. We have added Figure R2 to the revised supplementary materials (Supplementary Fig. S12).
2) **Re: Provide results from large-area solar cells.** In light of the editor's feedback, we now report stabilized power output (SPO) data for a larger-area 1 cm^2 device (**Figure R1**). The device delivered an SPO PCE of 25.1% SPO. We have added Figure R1 to the revised supplementary materials (Supplementary Fig. S24), along with Supplementary Figure S17 showing the *J-V* curve and stabilized power output (SPO) data for a 1 cm^2 single junction wide bandgap device.

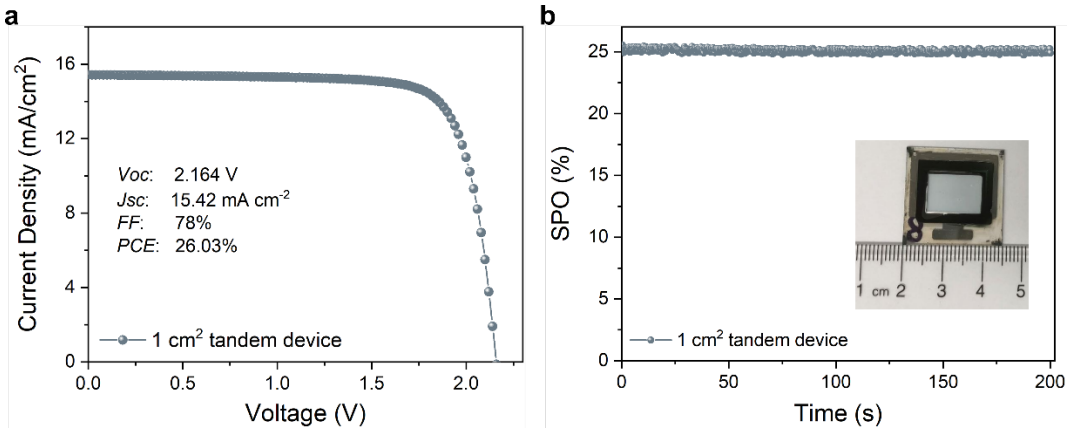

Figure R1. 1 cm^2 all-perovskite tandem device data. a) J-V curve and b) stabilized power output (SPO) for 200s of operation at the maximum power point. Inset is a picture of the 1 cm^2 tandem device.

Reviewers' Comments to Author:

Reviewer #1:

The reduction of open circuit voltage (Voc) deficit in perovskite solar cells is a common issue for the community, especially for wide-bandgap bromine-rich perovskite solar cells. In this work, Chen et al. report a diammonium molecule, 1,3-propylene diammonium (PDA), to regulate surface potential and improve open-circuit voltage of wide-bandgap perovskite solar cells. The authors demonstrate that the PDA molecule has a much better ability for surface passivation/treatment, compared to the common monoammonium molecules. Consequently, tandem solar cells using the PDA-treated wide-bandgap perovskite solar cells deliver a very impressive NREL-certified efficiency with a very high Voc. Overall, the results are well discussed and solid. This work presents a highly important advance for the perovskite photovoltaic field. Therefore, I would recommend publishing this work after some revisions.

1) In Line 133, the authors claim no indication of reduced-dimensional perovskite formation nor of a perovskite polymorph. While I was wondering if the PDA cation can enter the perovskite lattices. The same or similar cation was reported to extend the unit cell and form a 3D “hollow” perovskite structure (ACS Energy Lett. 2018, 3, 1470−1476; Sci. Adv. 2017;3: e1701293). To confirm this, the authors can measure zoomed-in XRD patterns of the films and then check the change of the peak position and lattice parameters of the unit cell.

1) Response: We now provide bulk and also surface-sensitive GIWAXS of control and PDA-treated films in **Figure R2**. These reveal that while the control film peaks are broadened, there is neither a peak shift nor the formation of additional peaks at lower q-values after PDA treatment; one would have expected such a shift/additional peaks if a "hollow” perovskite structure had been formed at the surface (J. Am. Chem. Soc. 2019, 141, 21, 8627–8637, J. Am. Chem. Soc. 2018, 140, 17, 5728–5742). We now discuss the fact that the concentration of PDA spin-coated onto the perovskite surface is low

and thus, from our data, does not appear to result in appreciable diffusion into the bulk. We have added Figure R2 to the revised supplementary materials (Supplementary Fig. S12).

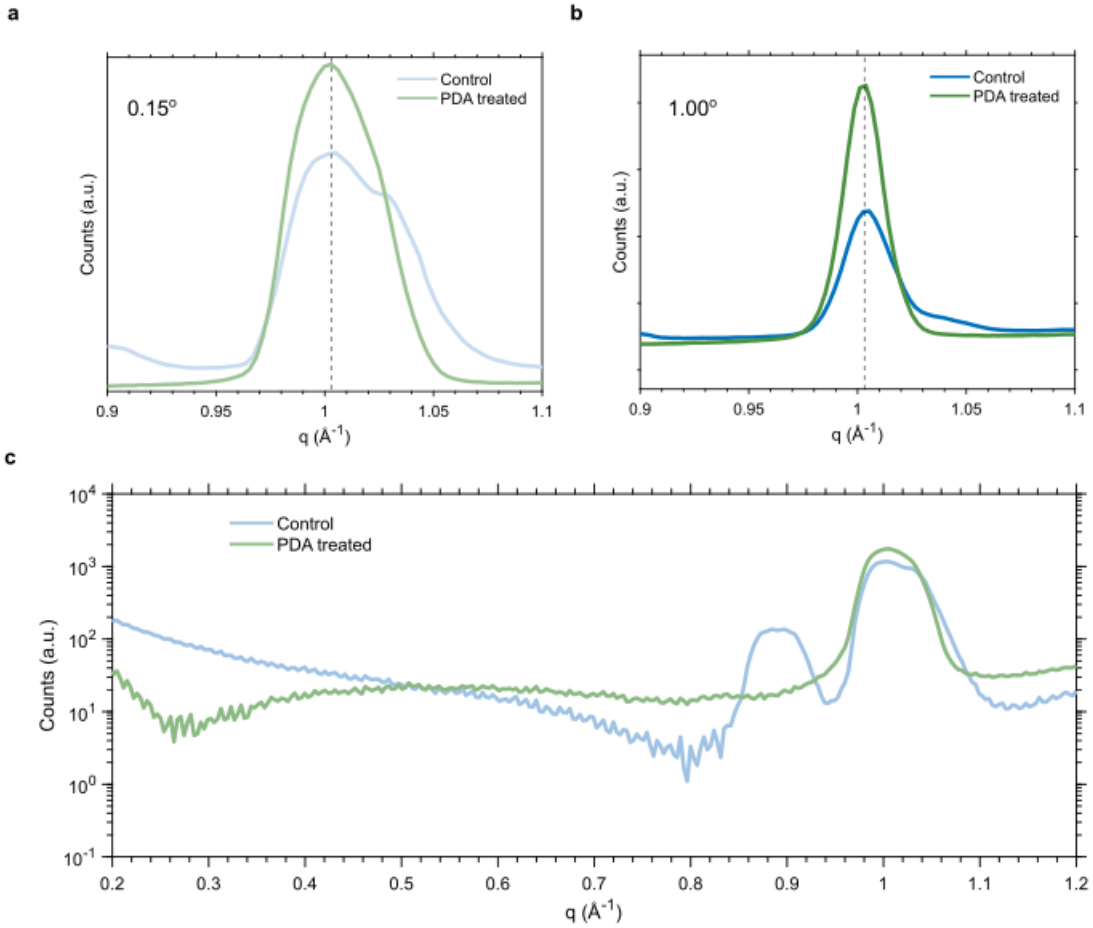

Figure R2. Summary of GIWAXS data. Surface sensitive a) and bulk b) GIWAXS spectra centered around the q = 1 Å^{-1} peak, demonstrating that though the control sample peaks are broadened, there is no overall peak shift between samples. c) Logarithmic plot demonstrating the lack of additional low q-value peaks at the surface of the treated sample.

2) It is reasonable to use a diammonium molecule rather than a monoammonium molecule. While the authors should also comment on that why use this PDA molecule not other diammonium molecules with longer or shorter chains.

Response: We now compare the effects of perovskite post-treatments with similar concentrations of 1,2-ethane-diammonium iodide (EDA) and 1,4-butane-diammonium iodide (BDA), diammonium ligands with a shorter and longer chain length, respectively. We now report the PLQY of the treated films on ITO/HTL substrates with and without a C_{60} layer deposited onto the perovskite.

Of these diammonium ligands, only PDA resulted in the retention of PLQY after the deposition of C_{60} (**Figure R3**).

We have added Figure R3 to the revised supplementary materials (Supplementary Fig. S3) and the above discussion to the revised manuscript as shown below:

"*We also compared the effects of perovskite post-treatments with similar concentrations of 1,2-ethane-diammonium iodide (EDA) and 1,4-butane-diammonium iodide (BDA), diammonium ligands with a shorter and longer chain length, respectively. Of these diammonium ligands, only PDA resulted in the retention of PLQY after the deposition of C60 (Supplementary Fig. S3).*" (Lines 75-79)

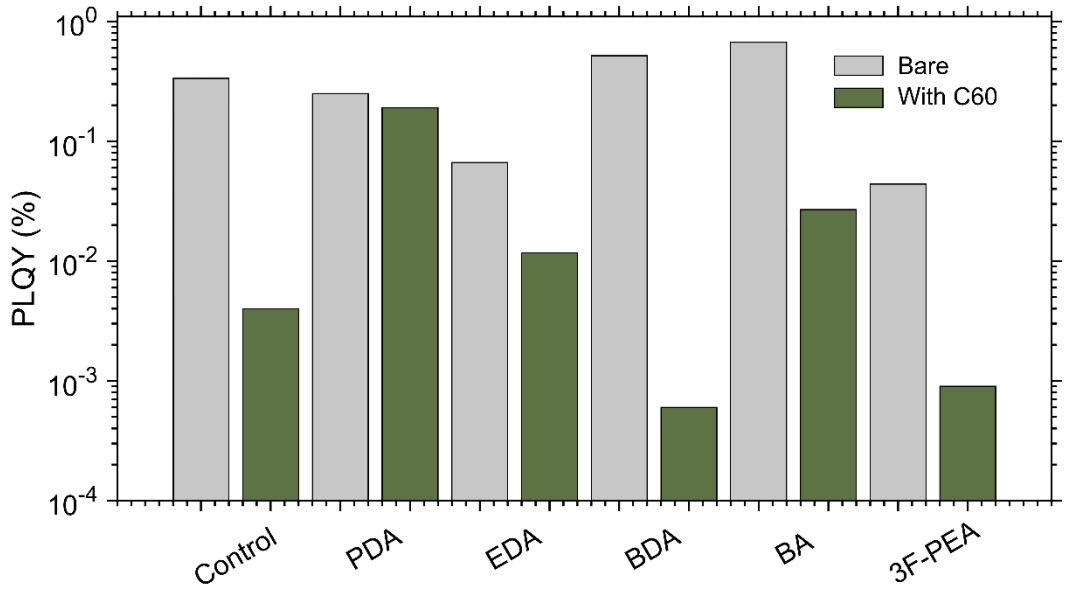

Figure R3. PLQY data from control, propane diammonium (PDA), ethane diammonium (EDA), butane diammonium (BDA), butylammonium (BA), and 3-fluoro phenethylammonium (3F-PEA) treated films with and without C60, on an ITO/HTL substrate.

3) The efficiencies of the small-area solar cells reported in this work are very impressive. However, the large-area solar cells are also recommended to be included.

Response: We have added the J-V curve and stabilized power output (SPO) data for a larger-area 1 cm^2 device (Figure R1 above). The device delivered a PCE of 26.0% (25.1% SPO). We have added Figure R1 to the revised supplementary materials (Supplementary Fig. S24), along with Supplementary Figure S17 showing the J-V curve and stabilized power output (SPO) data for a 1 cm^2 single junction wide bandgap device, which delivered a V_{OC} of 1.35 V and PCE of 19.0%.

4) MPP tracking of single-junction wide-bandgap cells should be also provided.

Response: We now provide MPP tracking under 1-sun illumination of the single-junction wide-bandgap cells in the revised supplementary materials (**Figure R4**, Supplementary Fig. S21). The following discussion was added to the revised manuscript:

"*We followed the output of a PDA-treated WBG cell operating for 700 hrs at the maximum power point (MPP) to determine the impact of PDA on device stability (Supplementary Fig. S21). After 700 hours of continuous operation under 1-sun illumination, the PDA-treated device exhibited no loss in PCE*." (Lines 146-148)

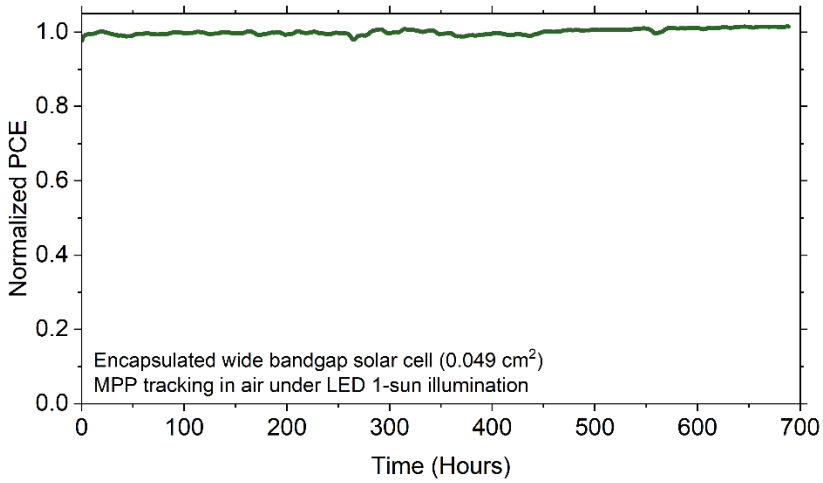

Figure R4. 700-hour MPP tracking of PDA-treated WBG device in ambient air under 1-sun illumination.

5) I would recommend the authors change "BTA" to "BA" because the latter one is a more common abbreviation.

Response: We thank the reviewer for this advice and have replaced BTA with BA in the revised manuscript.

6) In Line 92, the authors claim that BA and PDA make the surface more p-type and n-type, respectively. This description is inaccurate because both of the films are still p-type. One should be a stronger p-type and the other one should be a weaker p-type.

Response: We have updated our description in the revised manuscript as follows:

"*To understand how both treatments affect interface energetics we used ultra-violet photoelectron spectroscopy (UPS) and found that BA induces a Fermi level downshift, whereas PDA induces a Fermi level upshift, resulting in stronger and weaker surface p-type doping, respectively*." (Lines 80-82)

7) In Figure S7, the right y-axis should be QFLS.

Response: We added the axis label to the figure in the revised supplementary materials (now Supplementary Fig. S10).

8) Figure S10, the title: Positive ions are tracked in (a,b) and negative ions in (c,d). The order is reversed. Please correct it.

Response: We have corrected this error (Supplementary Fig. S5).

9) J-V etc. should be italic.

Response: We italicized *J-V*, V_{OC}, and J_{SC} in the revised manuscript.

10) Figures in Supplementary materials should be discussed sequentially.

Response: The figures in the revised supplementary materials are now discussed sequentially in the revised manuscript.

11) The manuscript is overall well written but there are still some typos.

Response: We have thoroughly reviewed the manuscript to correct any remaining typos.

Reviewer #2:

Chen et al. present a passivation approach, using molecule PDA for efficient treatment at the perovskite/C60 interface. The results show significantly reduced losses, benefiting from improved energy alignment at the perovskite/C60 interface. This results in much improved single-junction device performance as well as one of the highest certified PCEs for all-perovskite tandem solar cell.

The findings are well and clearly presented, and characterization techniques support the effectiveness of PDA layer, including statistics showing good reproducibility of the approach. The use of PDA is novel and with the benefits shown in this paper, I believe the manuscript will raise plenty of attention.

There are some minor things to be considered and further clarifications to be made before the manuscript can be accepted for publication.

1) Line 57: HTL should be stated

Response: We have now stated the HTL (NiOx/Me-4PACz) in the revised manuscript as follows:

"*We spin-coated WBG perovskite $Cs_{0.2}FA_{0.8}Pb(I_{0.6}Br0.4)_3$ films atop ITO/hole transport layer (HTL) substrates with a structure of ITO/NiOx/Me-4PACz and measured their PLQY with and*

without a C60 layer (Fig. 1b)." (Lines 58-60)

2) Line 93-94: by how much is the band offset reduced?

Response: The band offset is reduced by 60 meV. We now state this in the revised manuscript.

"*The latter change in the surface potential produces a lower minority carrier concentration at the interface and reduces the band offset between the perovskite and C60 by 60 meV. Drift-diffusion modelling suggests that this has the potential to increase QFLS by ~ 90 meV (Supplementary Fig. S4).*" (Lines 82-85)

3) On page 7 (lines 116 to 140), the authors state that no reduced-dimensional perovskite formation is discovered, indicating that perovskite does not react with PDA. In what way does the PDA then improve the homogeneity of the surface and prevents the segregation?

Response: XPS and GIWAXS spectra indicate that while no additional perovskite phase is formed after PDA treatment, the PDA does react with the surface of the perovskite to improve homogeneity, and it does so by removing PbI_2 (Figure R2c). Diammonium cations have been shown to have a templating-effect on perovskite crystal growth (Yan, N. et al. *Adv. Funct. Mater*. **32**, 2201384 (2022); Chiara, R. et al. *J. Mater. Chem. C.* **10**, 12367 (2022)). We have rewritten this discussion in the revised manuscript to include the following:

"*The suppression of surface phase segregation implies that while PDA does not induce the formation of a new crystal phase, it does react with the surface of the perovskite. This has been observed previously with diammoniums which template the growth of perovskite crystallization.*[36,37]" (Lines 121-124)

4) Line 148, exact bandgap could be stated

Response: We now state the exact bandgap (1.79 eV, measured by device EQE) in the revised manuscript. (Line 133)
We have also added **Figure R5** to the revised supplementary materials (Supplementary Fig. S15).

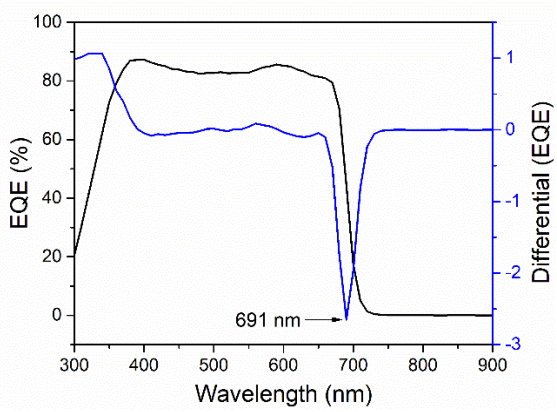

Figure R5. EQE curve of a PDA-treated WBG device, showing a bandgap of 1.79 eV.

5) Lines 167-168: What is the thickness of the PDA layer? Does it physically prevent ions to migrate into C60/metal electrode?

Response: Since the low-concentration post-treatment with PDA does not result in a peak-shift perceptible in the GIWAXS measurement, it is unlikely that the PDA molecules diffuse into the bulk perovskite. Additionally, the PDA signal in the TOF-SIMS results in Supplementary Fig. S5d rapidly decays, implying that PDA only resides as a very thin layer on the top surface of the perovskite.

We also investigated the possibility that PDA prevents ion migration into the C60/metal electrode by comparing TOF-SIMS results for control and PDA-treated devices after annealing on a hot plate at 100 °C for 20 hours (**Figure R6**). We found that PDA does slightly prevent ion migration, particularly the migration of Ag into the C60 and perovskite bulk. However, the effect is not significant.

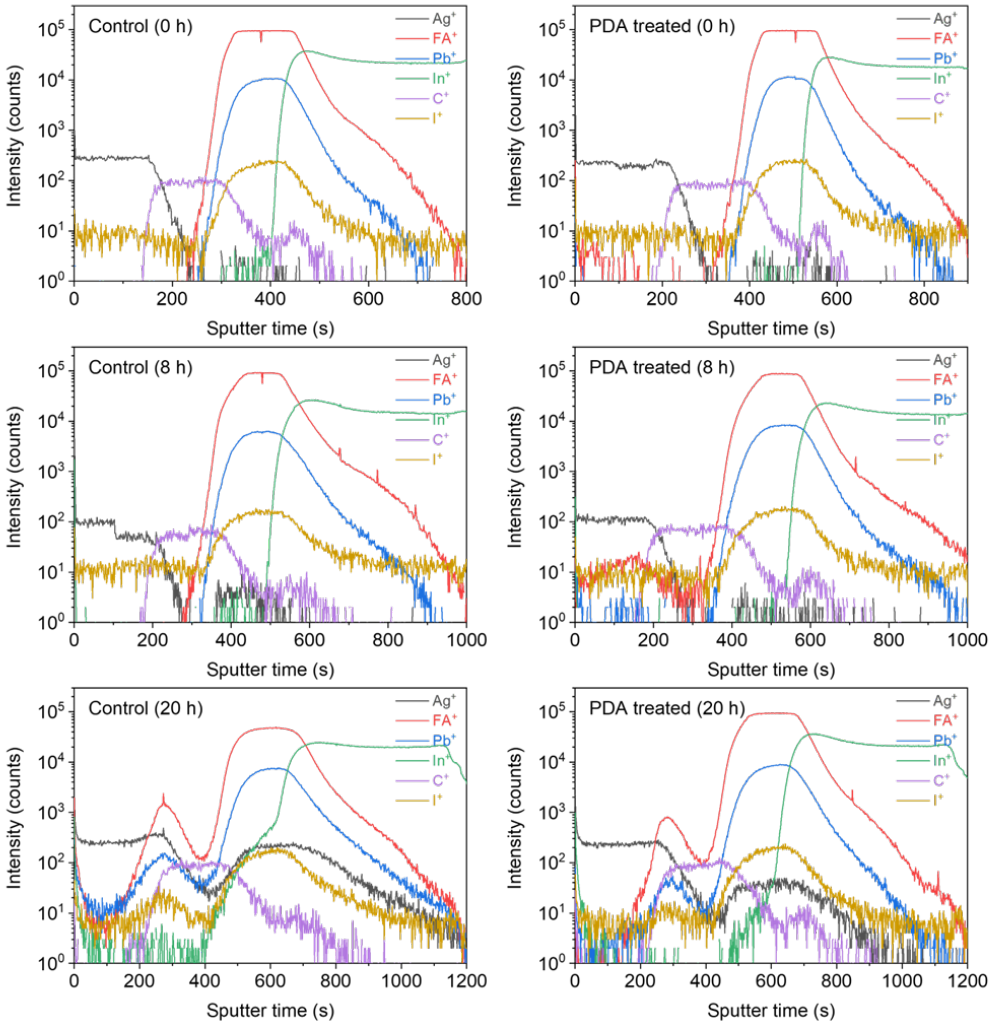

Figure R6. TOF-SIMS measurements of control and PDA treated devices before and after

annealing at 100 °C for 20 hours.

6) In Figure 4c, the sum of EQEs and reflection measurement could provide a lot of additional information about optical and parasitic losses in the device.

Response: We have replaced Figure 4c in the revised manuscript with **Figure R7** showing the optical losses due to reflection superimposed on the plot.

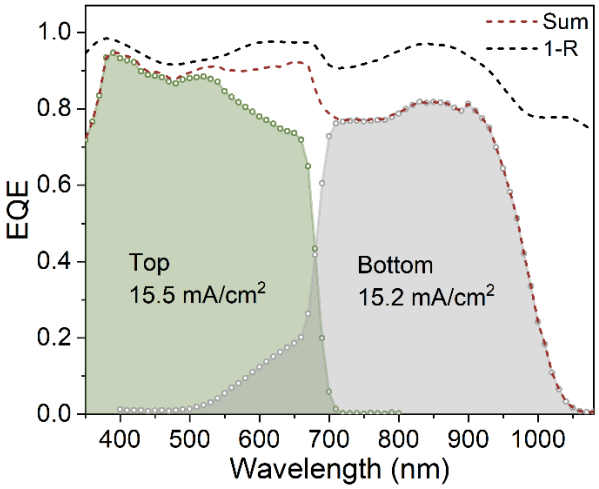

Figure R7. EQE curves of the WBG and NBG subcells in the tandem device, with the summed EQE and 1-R curves superimposed.

7) How was stability testing of the tandem performed? Methods state white LED, which surely does not have a spectrum close to AM1.5 spectrum. How was the photogenerated current in both subcells determined for the stability test?

Response: We accept the reviewer's advice that the spectrum of illumination for tandem stability is important. We now updated our MPP tracking data using an AM1.5G solar simulator (G2V sunbrick) for accurate current-matching under MPP conditions. We expect that the photogenerated current in this setup is equal to the EQE integrated Jsc (Figure R6). The new tandem stability testing result using this setup is attached below in **Figure R8** and replaces Figure 4f in the revised manuscript. The tandem solar cell, under AM1.5G illumination, retains 86% of its initial efficiency after 500 hours of continuous operation in ambient air at room temperature. We added the following text to the revised manuscript:

"*These tandems retain more than 86% of their initial PCE after 500 hrs operation*." (Abstract, Lines 37-38)

"*We tested operating stability using MPP tracking of an encapsulated tandem in ambient air (Fig. 4f). Under AM1.5G 1 sun illumination at the maximum power point, the device retained 86% of its initial PCE after 500 hours of continuous operation*." (Lines 179-181)

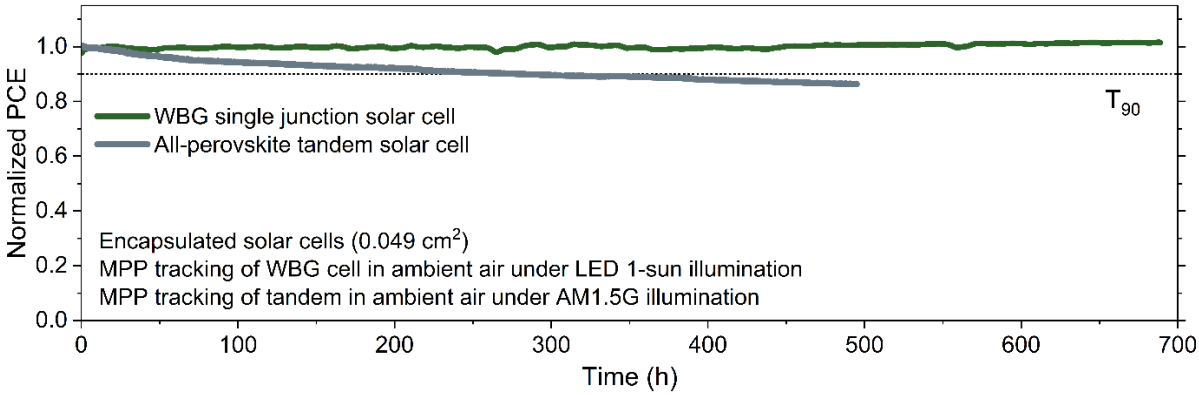

Figure R8. MPP tracking of WBG and all-perovskite tandem solar cell. An AM1.5G solar simulator was used for the stability tracking of the tandem cell to ensure current matching within subcells.

8) Lines 245-246: chosen concentration for PDA should be stated.

Response: In the revised manuscript, we now state the optimal PDA concentration used for devices (1 mg/ml). (Line 342)

Reviewer Reports on the First Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

I have carefully read the revised manuscript. The authors have well addressed the reviewers' concerns. I am very satisfied with the revisions and would recommend the publication of this work in Nature as soon as possible. Congratulations on this great work！
Two final suggestions: 1) Line 441 and Figure 4a, please change SAM to Me-4PACZ, which will be easily understandable. 2) Some Figures in Supplementary Materials are not too clear and could use high-resolution images.

Author Rebuttals to First Revision:

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

We thank the editor and reviewers for their much-valued suggestions, which have enabled us to improve the manuscript. Following are the detailed actions taken in light of the editor's and reviewers' comments:

Editor's Comment to Author:

The minor issue with the references is that the additional references 63-72, which are listed below the method, actually are not cited in the method section and are only cited in the Supplementary Information. In this case, the references 63-72 should be listed only in the SI (unless you move that part in the main text or Extended Data, but I think it is best to stay in SI). The SI also contains a list of all the references (cited in the main text, methods and SI), but it would be better to only list the references mentioned in the SI.

Response: In light of the Editor's feedback we now removed references 63-72 from the main text and instead listed them in the SI only, where they are referred to. We also only listed the references mentioned in the SI.

Reviewers' Comments to Author:

Reviewer #1:

1) Line 441 and Figure 4a, please change SAM to Me-4PACZ, which will be easily understandable.

1) Response: In both Line 441 and Figure 4a, we changed SAM to Me-4PACz as we agree with the reviewer's comment that it will be more understandable.

1) Some Figures in Supplementary Materials are not too clear and could use high-resolution images.

1) Response: We agree with the reviewer's comment. We have updated Figure S4, S5, S6, S10, S11, S12 and S14 to improve their resolution. We have now ensured that all Figures in the SI are displayed at a resolution of > 330 dpi.