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Thesis Changes Log

Name of Candidate: Mayuribala Mangrulkar

PhD Program: Materials Science and Engineering

Title of Thesis: Additives for improving the intrinsic stability of hybrid perovskite solar cells

Supervisor: Prof. Keith Stevenson

The thesis document includes the following changes in answer to the external review process.

Dear Jury Members,

I express my gratitude for your valuable comments and suggestions. I found all of them highly important since they resulted in a significant improvement of the thesis quality. I carefully addressed all issues and answered below, point-by-point, with your comments in italic.

Reviewer Prof. Aditya Sadhanala

There are many grammatical mistakes that need to be looked at and I suggest Mayuribala to have a keen read and correct these and at one odd place there is a figure missing as well.

Response: Thank you for evaluating the thesis quite extensively. As suggested, the thesis have been proofread again and grammatical errors have been corrected throughout the thesis. Also the missing figure is updated in the thesis as Figure 11 (a-d). Please see the revised thesis.

Furthermore, I have few minor but optional suggestions/comments:
1) Can you comment if these additives help alter the electronic property locally?

Response: Thank you for your suggestions. Monitoring the influence of additive incorporation on the electronic properties such as band structures, the density of states would require further investigation. The expansion of the current work involves using density functional theory (DFT) for theoretical studies and further comparing the results with experimental investigation of electronic properties. Experimental results can be obtained by using either of the techniques, such as angle-resolved photoemission spectroscopy (ARPES), electron energy loss spectroscopy (EELS), ultraviolet photoelectron spectroscopy (UPS) and/or scanning tunnelling spectroscopy (STS). The above has been updated under the "Conclusion and prospects" section. Please see the revised thesis.

2) Do these additives dope the perovskite in some way and change their semiconducting nature in terms of being p-type, n-type or intrinsic?

Response: Thank you for your suggestion. In the absence of data related to charge transport measurement, it is difficult to comment on the influence of additive doping on the semiconducting nature of the perovskite layer. Therefore, an expansion of this is proposed to study charge transport phenomena using a space charge limited current model (SCLC). Please see the revised thesis.

3) I would have liked to see a expanded future work section for such promising work.

Response: Thank you for your suggestion/advice. The future work has been updated in the revised thesis. Please see the section "Conclusion and Prospects".

Reviewer Prof. Ajay Kumar Jena

I have posted many such comments at the right places in the pdf file. In addition, in general, I feel
1. The title needs to be modified a little. It should be changed to a more appropriate one reflecting the main aim/objectives and findings of the work.

Response: As advised, the thesis title is changed and updated thesis title appears as "ADDITIVES FOR IMPROVING THE INTRINSIC STABILITY OF HYBRID PEROVSKITE SOLAR CELLS".

2. The writing needs to be improved in many places (some have been highlighted in the file, as examples). Grammatical errors and inappropriate Eng expressions should be corrected throughout the file.

Response: Thank you for the thorough revision of the thesis that allowed me significantly increasing the text quality. I accepted all your text correction recommendations and provided answers to several comments that required my responses below, point-by-point. Please, see them.

- *"Design" sounds like molecules are designed and synthesized for the purpose while they have been picked up /selected. The title needs to be modified to reflect the main objectives and findings.*

  Response: Thank you for your advice. As mentioned earlier, the thesis title is updated and now in line with the main objective and findings.

- *"hybrid" is better.*

  Response: The mentioned has been modified as per suggestion.

- *"Hence the objective of this work is to design and engineer additives for improving the stability of hybrid organic-inorganic perovskite solar cells based on methylammonium lead iodide based active layer." This sentence should follow the sentence coming after this for better sequence.*

  Response: Thank you for the comment. The mentioned has been amended in the revised thesis and appears as "The poor stability of the perovskite layer often disintegrates perovskite into either PbI_2, metallic lead, or some volatile species, creating defects at the surface, grain boundaries, causing irreversible damage to the perovskite layer. Hence, this work aims to investigate additives for improving the stability of hybrid organic-inorganic perovskite solar cells based on methylammonium lead iodide-based active layer."

- *"Opted"- sounds inappropriate/incomplete*

  Response: Thank you for the comment. The sentence has been reframed and appears in the revised thesis as "To achieve the aim, additives were mixed into the perovskite precursor, first screened by a thin-film photostability test, and then investigated in the complete solar cell devices to further examine their operational stability under illumination."

- *"The highest operational stability of solar cells achieved in this work was 4400 h due to HAI incorporation in $MAPbI_3$ film, followed by 1500 h due to NMP cosolvent present with excess PbI_2 in $MAPbI_3$." I think it's necessary to mention what was the PCE (or percent of initial PCE) retained.*

  Response: Thank you for your comment. The suggested has been amended in the thesis abstract. Now the revised text appears as "The highest operational stability of solar cells achieved in this work was 4400 h (which is ~80% PCE of the initial stage) due to N_2H_5I (hydrazinium iodide/HAI)

incorporation in $MAPbI_3$ film, followed by 1500 h (which is more than 95% of the initial stage) due to N-Methyl-2-pyrrolidone (NMP) cosolvent present with excess PbI_2 in $MAPbI_3$."

- *Thus solar cells are a great tool to utilize solar energy. Correct the English.*

  Response: Thank you for the comment. The mentioned has been corrected.

- *"In practical terms, this Voc depends on effective bandgap potential (Eg/q – Voc)." Should it be called effective bandgap potential or "bandgap potential loss"?*

  Response: Thank you for the comment. The suggested has been modified and now appears in revised thesis as "In practical terms, this V_{oc} depends on effective bandgap potential loss ($E_g/q - V_{oc}$)."

- *"Because of this energy-intensive purifying and extraction process of Si technology, the quantity of Silicon required to produce one year of production is almost double that of perovskite light absorber materials (Figure 7) [18]." The meaning of this line is not clear. ….the quantity of Silicon required to produce one year of production of what?*

  Response: Thank you for your comment. As suggested, the sentence is reframed and appears in the revised thesis as "Because of the energy-intensive silicon purifying and extraction process, the cost required to produce silicon PV is almost double that of perovskite light absorber materials (Figure 7a). Furthermore, it is projected that three years of silicon will be required to cover 12.5 TWh usage at the current production capacity. On the other hand, perovskites would just take a few days to produce with the current lead manufacturing technology (Figure 7b) [19]."

- *"Thus faces serious stability issues compared to already available PV technology in the market" This sentence is missing the subject. Should it be –"Thus, it faces……."*

  Response: Thank you for the comment. The sentence has been corrected.

- *Regarding "1.6 Aim"- Can be improved by including answers to questions like, why did you choose this topic? or What was the gap /unresolved issue (as additive engineering is well reported), but what is new being done here. As I understand, the photostability test is new/not often done by others. It is better to move this section to "after the Literature review." In that case, you can state the problems/gaps present in literature. And, then it can connect to/justify easily what you aim to do here.*

  Response: Thank you for your suggestion. As recommended, the section has been moved after "the Literature review". In the revised thesis, the section appears as "2.4 Aim". Please see the revised thesis.

- *"Thus this research project aims to improve the intrinsic stability challenge of $MAPbI_3$ perovskite-based light-absorbing layer" Should it be intrinsic stability, not intrinsic stability challenge?*

  Response: Thank you for your comment. The above is corrected.

- *"Thus this research project aims to improve the intrinsic stability challenge of $MAPbI_3$ perovskite-based light-absorbing layer using additive engineering." should it be using additives or by additive engineering?*

  Response: Thank you for your comment. The above is corrected. Further, using "additive engineering" is changed to "additives" throughout the text.

- *"Thus, this thesis is dedicated to additive engineering for $CH_3NH_3PbI_3$ photo-active layer for photovoltaic application." I think this line is not necessary. This is understood from the above lines.*

Response: Thank you for your comment. As per suggestion, the above line is deleted.

- *"It was reported that FAAc controls the film morphology and improved fill-factor over 80%, improving PCE to 16.59%." Controls (in present form) but improved (past form). It is better to write both in one form, at least in the same sentence. Also, it is necessary to mention FAAc was used in which perovskite system, otherwise, it sounds like it's a universal additive, used in all/most of the perovskites.*

  Response: Thank you for your comment. The above has been modified. The revised text appears as "It is reported that FAAc controls the film morphology of $MAPbI_3$ film and improves fill-factor over 80%, improving PCE to 16.59%." In addition to it, I would like to kindly bring it yo your attention the entire literature review section is devoted to $MAPbI_3$ perovskite only, which is also pointed in the beginning of the literature review section.

- *"MAAC"- subscript?*

  Response: Thank you for the comment. As per suggestion, above has been corrected.

- *"Sadly"- I think it's inappropriate in technical writings.*

  Response: Thank you for your comment. The above has been corrected.

- *"Rh"- defined before? Should it be RH (not Rh)*

  Response: Thank you for the comment. The above has been corrected to "RH". Yes, RH has been defined before.

- *"While compared to Zinc-acetate ($ZnAc_2$) additive, devices with $ZnAc_2$ demonstrated improved fill factor" "both $ZnAc_2$?"*

  Response: Thank you for the comment. The above has been corrected. "While compared to Zinc-acetate ($ZnAc_2$) additive, (devices with $ZnAc_2$) demonstrated improved fill factor"

- *"It was further demonstrated that incorporation of $PbAc_2$ in precursor creates an intermediate phase by forming hydrogen bonding due to interaction with MA^+ and O from acetate. Thus, this hydrogen bonding acts as a crossing linking agent for the intermediate phase, which later causes to improve intrinsic stability of devices that maintained almost 95% of initial PCE till 20 days 100 ." - "bond"," between H from MA^+ and O from acetate?" "cross-linking", "causes improvement in intrinsic stability of ....."*

  Response: Thank you for the comments. Corrections are made as per the suggestion. Now the revised text appears as "It was further demonstrated that incorporating $PbAc_2$ in precursor creates an intermediate phase by forming hydrogen bond due to the interaction between hydrogen from MA^+ and O from acetate. Thus, this hydrogen bonding acts as a crosslinking agent for the intermediate phase, which later causes improvement in intrinsic stability of devices that maintained almost 95% of initial PCE till 20 days [101]."

- *"Further, the acetate-based additives are summarized in Table 4, as shown below." Further -not necessary, The sentence can be modified to "Some/most of the aacetate-based additives reported in literature are summarized in Table 4, as shown below."*

  Response: Thank you for the comment. The above has been modified as per the suggestion.

- *"2.3 Summary of literature review"- Should be improved by bringing up some general thoughts/insights into the mechanism how different families of additives work. why some work better than others? and finally, bring out what is needed to be done.*

Response: Thank you for the suggestions. As advised the "2.3 Summary of literature review" is modified. The see the revised thesis.

- *"Furthermore, it has been observed that additives showing stabilization effect typically resulted in improved nucleation growth, film morphology.."- nucleation or growth? Nucleation and growth generally stand for two different steps in crystallization of any material*

  Response: Thank you for the comment. I mean nucleation and growth. The mentioned has been updated in the thesis. See the revised thesis, section 2.4.

- *"PbI_2 as an additive is one of the controversial additive…." –"additives"*

  Response: Thank you for the comment. The above has been corrected.

- *"Many groups most widely investigate the non-stoichiometric usage of PbI_2"-English*

  Response: Thank you for the comment. The above has been corrected.

- *"Next, I prepared films with these two solution formulations" - This expression is not usually used for technical writing. It's appropriate to use " Then, films were prepared..."*

  Response: Thank you for the comment. The above has been corrected.

- *"UV-Vis tests revealed that all fresh films (independent of solvent formulation or excess PbI_2 content) had an absorbance characteristic at 750 nm, indicating that perovskite production had occurred.."- I think it is necessary to begin the discussion with comparison of the initial conditions of all four cases, such as XRD patterns and morphology (SEM images).*

  Response: Thank you for the comment. As per the suggestion, necessary information has been added. Also XRD patterns of all four cases and SEM images has been added and appear as Figure A2.2a, Appendix 2 and Figure A2.2 (b-e), Appendix 2, respectively. Please see the revised thesis.

- *"Figure 10"- improve the quality of the figure, make it more legible, enlarge it a bit*

  Response: Thank you for the comment. As suggested, figure is enlarged.

- *"PbI_2 peaks were located at 12.68˚, 25.69˚, 38.65˚, 39.60˚"- "inappropriate usage. PbI2 is not located at these 2theta values."*

  Response: Thank you for the comment. The values have been corrected.

- *"Furthermore, the PbI_2 peak was observed to be slightly displaced to 12.76°,"- inappropriate.*

  Response: Thank you for the comment. The above has been corrected.

- *"accompanied by the additions peaks at 8.3° and 11.10°, belonging to NMP-PbI_2 adduct 195,196."- can not be seen in the figure 11. XRD patterns zoomed-in the range should be provided.*

  Response: Thank you for the comment. The above has been amended. The Figure 11(c) and Figure 11(d) shows the zoomed in range of XRD spectra and adduct formation. Please see the revised thesis.

- *"Furthermore, the PbI_2 peak was observed to be slightly displaced to 12.76°, with only a minimal peak corresponding to Pb at 31.31°, implying that when formulated from DMF/NMP combination, conversion of PbI_2 into Pb is slowed, resulting in visible, stable peaks corresponding to perovskite*

(Figure 11b)"- This suggests that PbI2, not the PbI2-NMP complex, is responsible for the photodegradation It is reasonable, PbI2 is photosensitive but PbI2-NMP complex may not be so. Few lines with such discussion should be added. Besides, it will be good if you can discuss the PbI2 existence quantitatively, like how much is remaining in what form (comparing the XED peak area).

Response: Thank you for the comment. The requested information has been amended in the revised thesis. Further, XRD qualitative analysis of remaining product upon photoaging has been presented in Figure A 2.3, Appendix 2. Please see the revised thesis.

- *"Proposed mechanism of improved stability with $MAPbI_3$+PbI_2.NMP" - although the title says "proposed mechanism" there is no such mechanism discussed/clear from the discussion. The discussion essentially reveals more about the characterization/XPS results.*

  Response: Thank you for the comment. Information is updated to match with the section heading. Please see the revised thesis. The main mechanism of stability is the adduct formation between PbI_2-NMP. The discussion primarily describes XPS, EDX, AFM insitu degradation results, all of which validate the adduct formation and stability due to adduct against illumination in co-relation with NMP chemical structures and Pb coordination. Therefore, the section heading is not changed. I am hoping for your understanding.

- *"Figure 13"- this figure can be still enlarged.*

  Response: Thank you for the comment. As suggested, the figure is enlarged. Note: in the revised thesis the figure number is updated and now appears as Figure 14.

- *"Evolution of the UV-Vis spectra of $MAPbI_3$ films (a) reference film with 0 % HAI.(b) $MAPbI_3$+HAI film"- Enlarge the figure, also mention the aging condition in the caption*

  Response: Thank you for the comment. As suggested, the figure is enlarged and aging conditions are updated in the caption. Please see Figure 15 in the revised thesis.

- *"Simultaneously, the XRD patterns for fresh, pristine $MAPbI_3$ revealed less crystalline nature of the film with peaks located"- Is this different from the 0%PbI2 DMF sample (earlier section)? If so, it is necessary to mention that in the discussion. Else, it raises the question why the XRD pattern and UV-Vis spectra evolution (photo-aging) look different.*

  Response: Thank you for the comment. Yes, it is different from earlier section. A section heading as "4.2 Enhanced intrinsic photostability of $MAPbI_3$ thin films and solar cells with hydrazinium iodide" is already used that separates these two sections from each other.

- *"XRD patterns of fresh and aged $MAPbI_3$ and $MAPbI_3$+HAI films. * represents perovskite peaks."- mention the percent of HAI added in the caption*

  Response: Thank you for the comment. The requested information is added. See revised thesis Figure 16. Also, I would like to kindly bring it to your attention that thesis text already contained information that "The pristine $MAPbI_3$ film is defined as a reference $MAPbI_3$ film with 0% HAI. Similarly, $MAPbI_3$ film with 15% HAI is referred to as $MAPbI_3$+HAI.", which appears in the beginning of section 4.2.1.

- *"4.2.2. Proposed mechanism of improved stability with HAI salt"- Again, this heading is misleading. In the discussion, there is no proposed mechanism.*

  Response: Thank you for the comment. The section describes that the intermediate formation between PbI_2 and HAI salt, improves crystallinity and grain size of film, further resulting in smooth morphology, resulting in grain boundary passivation that is perceived to be the cause of improved photostability due to PbI_2-HAI intermediate formation which was also validated using FTIR. Therefore, the section heading is not changed. I am hoping for your understanding.

- *"Table 16 HAI concentration vs IV parameters"- are these the best cell parameters? It is better to include the average values. Also, enlarge the table*

  Response: Thank you for the comment. As suggested, average values are also included in the table. Also, table is enlarged. Please see the revised thesis.

- *"Hence, reduced hysteresis is attributed to reduced recombination centres at the grain borders.."- use "boundaries"*

  Response: Thank you for the comment. The suggested has been modified.

- *"PCBA"- expansion?*

  Response: Thank you for the comment. Expansion is updated as "Phenyl-C_{61}-butyric acid (PCBA)". Please see the revised thesis. Also, I would like to kindly bring it to your that full form of PCBA is already defined in Table 15 under section 3.1.

- *"Figure 18 Normalised IV parameters with HAI additive."- inadequate information in the caption.*

  Response: Thank you for the comment. The requested is updated and appears in the revised thesis as "Figure 19 Operational stability of $MAPbI_3$ solar cells due to HAI additive"

- *"The UV-vis results of fresh $MAPbI_3$ films illustrated that incorporation of additives in $MAPbI_3$ precursor resulted in the blue shift of the absorbance edge, altering the bandgap of the perovskite layer 238."- which figure?*

  Response: Thank you for the comment. The Figure number is added - Figure 20. Please see the revised thesis.

- *"(a) UV-vis results"- replace with "absorption" in the caption*

  Response: Thank you for the comment. The requested is updated. Please see Figure 20 caption in the revised thesis.

- *"Further, the XRD analysis was done. The XRD of fresh, pristine $MAPbI_3$ film showed patterns consistent with the cubic structure/phase of $MAPbI_3$ 239."- Figure number?*

  Response: Thank you for the comment. The requested information is updated in the revised thesis and appears as "Figure A2.13, Appendix A2".

- *"while the pristine film died/degraded."- Delete died.*

  Response: Thank you for the comment. The requested information is deleted.

- *"Likewise, oxiphenanthroline (N3) was omitted …."- inappropriate.*

- Response: Thank you for the comment. The requested information is updated and appears as "Likewise, 4-hydroxy-1,10-phenanthroline (N3**)** was not considered as well."

- *"Figure 20"- Enlarge the figures, nothing can be read, the letters are so small. The XRD patterns need background subtraction.*

  Response: Thank you for the comment. As suggested, the figure is enlarged for better readability. Since, XRD patterns of $MAPbI_3$+N1, $MAPbI_3$+N3, $MAPbI_3$+N4, show loss of crystalline nature of the film over pristine film. Subtracting background from XRD patterns, will take

away this important information. Therefore, the XRD patterns are plotted as obtained and presented without background structuration.

- *"yet the R_{MS} roughness"- not right expression, MS as subscript?*

  Response: Thank you for the comment. The above is corrected.

- *"growth of needle-like structure"- can not be seen in the figure*

  Response: Thank you for the comment. The figure is updated with highlighting new structures. Please revised thesis, Figure 22.

- *"However, the device stability test is a further prospect of investigation in this case."- has not been carried out?*

  Response: Thank you for the comment. Yes, the operational stability test with $MAPbI_3$+N2 has not been carried out.

- *A summary from comparison of all the N-additives used is needed. A discussion (likely based on molecular structure and size) relating to why some (N2) worked and while others should be included.*

  Response: Thank you for the comment. As suggested, above discussion is added under the section 4.3.2. Please see the revised thesis.

- *"illumination in inert"- inert atmosphere?*

  Response: Thank you for the comment. The mentioned is corrected.

- *"Further, it should be noticed that.."- "noted"*

  Response: Thank you for the comment. The mentioned is corrected.

- *"Although NMP does contain the carbonyl group."- incomplete sentence*

  Response: Thank you for the comment. The sentence is rephrased. Please see the revised thesis.

Reviewer Prof. Juan-Pablo Correa-Baena

- *However, there is a lack of depth on the conclusions drawn from the studies presented.*

  Response: Thank you for the comment. Similar comments were made by other jury members. Necessary changes are made. Please see the revised thesis.

- *"I made solar cells with additives.."*

  Response: Thank you for the comment. The thesis is proofread again and corrections are made.

- *"The thesis, lack in depth fundamental understanding of materials science questions such as structure-property relationships"*

  Response: Thank you for the comment. I would like to kindly bring it to your attention that in the scope of thesis work, state of art techniques are used to monitor improvement in intrinsic photostability due to additive incorporation, additive influence on morphology and operational stability. Thus, screening the additives with better stabilization effect. Therefore, studying structure-

property relationships of the additives showing stabilization effect has been a future goal as the expansion of the current research work. This has been also updated under "conclusion and prospect" section in the revised thesis. Besides, for the literature review section, the chemical structures of reported/discussed additives are added in Appendix 0 so that the discussion under literature review can be correlated with additive structure. The chemical structure in appendix 0 follows the same classification as per literature review. Please see Figure A0.1- Figure A0.18, Appendix 0 in the revised thesis.

Reviewer Prof. Alexei Buchachenko

- *First, I would like to acknowledge the composition and logic of the thesis. It starts with the well-written introductory Sec. 1, which channels a broad perovskite PV landscape into the extrinsic and intrinsic stability issues and use of additives as a particular remedy (I do not like the term «additive engineering» in this context as it sounds misleading for additive manufacturing and additive technology). The aim of the thesis formulated in Sec. 1.6 looks a bit vague, but clear enough to justify the literature review that follows.*

  Response: Thank you for the comment. As suggested, the thesis title is modified. The updated title is "additives for improving the intrinsic stability of hybrid perovskite solar cells". Also, the aim of the thesis is moved to after literature review section (section 2.4 now) to give better flow and connection with gap in literature and investigations presented in the thesis. Please see the revised thesis.

- *Sec. 3 describes experimental approaches, methodology, materials and characterization techniques. Everything is on the up-to-date level and suits the aims of the thesis. However, I found it strange that the protocols for stability testing of the films and cells are not explicitly given in this section. Moreover, I did not see a reference on the recently published consensus statement on the perovskite stability assessment [M. V. Khenkin et al. Consensus statement for stability assessment and reporting for perovskite photovoltaics based on ISOS procedures, Nature Energy, 5, 35 (2020)]. Such statements help to reduce the dimensionality of the problem, so I think that the relation of the conducted stability test to the consensus protocol should at least be commented. Less important comment is that the preselection of additives for in-depth study, well justified and illustrated by Table 15, could be better placed in the very beginning of Sec. 3 for clear connection with the lessons of literature review and reiteration of the thesis aim at an elevated level.*

  Response: Thank you for the comment. As suggested, the above information is added under section 3.2 methodology. Also the above citation is added to thesis and appears as reference number 183 in the updated thesis. In addition, Table 15 in combination with Figure showing chemical structures of investigated additives are moved in the beginning of section 3 and now appears under the section 3.1. Please see the revised thesis.

- *My questions actually address the lessons that one can take away of this work rather than to the work itself.*
- *How general the conclusions are? For instance, a unified typical cell architecture is used for stability tests - n-i-p Glass/TCO/ETL/Passivation layer/MAPbI3+additive/HTL/electrode with ETL = SnO2, Passivation layer = PCBM /PCBA, HTL = PTA or PTAA. To what extent the present results can be used to predict the effect of the additive in a cell with different configuration and CT layer compositions? Would the mechanisms proposed be helpful for such predictions?*

  Response: Thank you for the comment. n-i-p configuration is chosen because, it give slightly better efficiency and high reproducibility. Moreover, SnO_2 as ETL, PCBM /PCBA as passivation layers, and PTA or PTAA as HTL, these materials are standard in the perovskite fabrication procedure for n-i-p configuration, with an effect known on the performance and stability of $MAPbI_3$ PSC. Therefore, it can be predicted that if p-i-n configuration is used with standard materials used, the efficiency might be slightly lower. The stability of the perovskite layer associated with additive incorporation would be similar to the thin-film stability tests. However, a change of charge transport layer might affect stability. This is because charge transport layers

play a vital role in the completed solar cell devices. For example, it was found that stability of PEDOT:PSS based solar cells exhibited poor stability over PTAA based solar cells as HTL when used pristine perovskite layer without any additives. Therefore, new charge transport layers might be further tested to investigate their impact on stability in the presence of an additive, which would require a separate investigation, following the similar approach as mentioned in this thesis. The relevant discussion is also amended in the thesis. Please see the revised thesis.

- *The author sees this main future prospect for using additives for perovskite stability improvement in the «developing an artificial intelligence-based system/ machine learning/ depository» because «there was no proper rule to select the correct/suitable material to achieve stabilization effect until now». On the one hand, artificial intelligence is indeed a proper means for solving multidimensional problem. On the other, does this statement mean that efforts based on the human chemical knowledge and intuition are hopeless? The question is not solely philosophical, as the answer determines experimental strategy: artificial intelligence would prefer wide screening for a few target parameters, human one – deep comprehensive exploration of the physical and chemical phenomena in a limited number of examples. As the thesis under review certainly belongs to a latter case, it is interesting to learn why this experience turned to be so disappointing for the author.*

  Response: Thank you for the comment. The artificial intelligence –based system will be useful to have "at a glance" information about the chemical structure, related properties, and influence on stability. Thus, it will be helpful to make a more rational design of additives by having at a glance information. At the same time, it must be noted that the enumeration approach (i.e. thin film and device stability test) will still be the key to verifying additive influence on the stability of the perovskite layer. When I proposed using artificial intelligence based system, I do not mean to replace it with experimental investigation. I mean to combine it with experimental investigation. Information from the artificial intelligence-based system can be used to design new additives and experimental investigation of newly designed additives should be followed in the sequence as shown in Figure 26 in the updated thesis. An internationally recognised depository should be created for the research community to follow such steps shown in Figure 26, which would provide at a glance updated information to researchers and scientists for a deep, comprehensive exploration of the physical and chemical phenomena associated with additive influence. Because, certainly the artificially intelligent system would be limited to only widely screen for a few defined parameters. Therefore, artificial intelligence systems should be limited to collecting information for material structure properties and their effect on stability, which should be available for human comprehension that will ultimately lead to a more rational design of additives. Relevant information is also updated under the conclusion section. Please see revised thesis.

- *Unfortunately, the thesis text suffers from many misprints, stylistic problems (broken sentences, missing or excessive punctuation marks) and formatting inaccuracies.*

  Response: Thank you for the comment. The thesis has been proofread and grammatical errors are corrected. Please see the revised thesis.

Reviewer Prof. Andriy Zhugayevych

- *However, there are some comments to the thesis itself. I will start with quality of scholarly presentation. Results and Discussion session is only 28 pages long and has no explicit connection to thesis publications. Also, there are some important figures discussed in that session (e.g. XPS results) but moved to Supporting Information which is inconvenient for reading. Formula 1 (Goldschmidt tolerance factor) is mistyped. There are multiple minor grammatical errors/mistypes or text requiring clarity improvement, already at the beginning of the thesis, for example:*

Response: Thank you for the comments. Further information is added in relevant places under the section of "Results and discussions". XPS related figure is now moved in the main text and appears as Figure 12 in the revised thesis. The mistyped Formula 1 (Goldschmidt tolerance factor) is corrected. Further, I accepted all your text correction recommendations and provided answers to several comments that required my responses below, point-by-point. Please, see them.

1) Improper punctuation in Figure 2 caption.

Response: Thank you for the comment. The above is updated.

2) In sentence "Thus, destabilize the solar cells" (p.31) it is unclear what does destabilize the cells.

Response: Thank you for the comment. The above is updated and appears in the revised text as "Thus, the formation of PbI_2, I_2 and water results in the destabilization of the solar cells."

3) The same page, grammar/mistype in "This reactive O2− species".

Response: Thank you for the comment. Corrections are made as suggested. The revised text appears as "This reactive O_2^- species".

4) Unclear meaning of the phrase "to improve the intrinsic stability challenge of MAPbI" in p.33.

Response: Thank you for the comment. The sentence is rephrased and revise text appears as "Thus, this research project aims to improve the intrinsic stability of the $MAPbI_3$ perovskite-based light-absorbing layer using additives." Note this section is moved to "2.4" in the revised thesis.

At the end of the thesis, the writing style of "Results and Discussion" session requires improvement to meet common requirements of scientific publications, e.g. in p.101 what is "absorbance characteristic", what is meant by "perovskite production had occurred". Also, in Fig.12 the caption is split across pages.

Response: Thank you for the comments. Several proof readings are performed to essentially enhance the language quality. The above sentence is rephrased and appears as "UV-Vis tests revealed that all fresh films (independent of solvent formulation or excess PbI_2 content) had an absorbance feature/characteristic at 750 nm, corresponding to perovskite formation"

- *Considering scientific aspects of the thesis, I have the following questions and comments to be discussed before or on the Defense:*

- *The selection of additives for the investigation is not explained. Is there some rationale behind Table 15? This is also related to the literature review – it ends with too short summary, not providing useful keys for rationalization of additives.*

Response: Thank you for the comment. The selection of additives is based on the literature review analysis. The Table 15 further mentions the details of functional groups associated with the additives, which later helped to understand and classify the influence of additives on photostability accordingly. The summary of literature review is expanded in the same context. Please see the revised thesis section 2.3 and 2.4.

- *2) The strategy of the thesis work is unclear: from the presentation it looks like the candidate studied additives sequentially for the entire duration of the thesis work. Given a huge number of possible additives, such "enumeration" approach seems to be inefficient. Is it possible to make a more rational design of additives?*

Response: Thank you for the comment. To make a more rational design of additives, inclusion of an artificial intelligence –based system should be adopted in combination with the "enumeration approach". The artificial intelligence–based system will be useful to have "at a glance" information

about the chemical structure, related properties, and influence on stability. Thus, it will be helpful to make a more rational design of additives by having at a glance information. At the same time, it must be noted that the enumeration approach (i.e. thin film and device stability test) will still be the key to verify additive influence on the stability of the perovskite layer in practical terms. The similar is shown in Figure 26 in the updated thesis, under conclusion and prospects section. A relevant discussion is also added. Please see the revised thesis.

- *3) Why does hydrazinium iodide additive produce the most stable device among studied additives?*

  Response: Thank you for the comment. The higher operational stability due to N_2H_5I over NMP+PbI_2 could be because of the intermediate formation between N_2H_5I and PbI_2, which disappears upon photoaging and perovskite degradation. Another possible reason could be that the formed adduct between NMP and PbI_2 is weak compared to the adduct/intermediate phase of PbI_2 with N_2H_5I against illumination. However, a further experimental investigation would require comparing adducts with PbI_2 and NMP to intermediate between PbI_2 and N_2H_5I. The similar discussion is added in the revised thesis under the conclusion section.

- *4) How the achieved stability of 4400 hours compares to current state of the art for the studied materials and overall for PSCs?*

  Response: Thank you for the comment. When compared to the current state of the art, the highest reported stability of perovskite solar cells was more than 10000 h (~ 1 year) due to 2D/3D aminovaleric acid iodide ($HOOC(CH_2)_4NH_3)_2PbI_4$)/$CH_3NH_3PbI_3$ perovskite junction. (2D/3D perovskite junction results in a mixed cation perovskite layer, which is not pure $MAPbI_3$). The configuration used was FTO/c-TiO_2/mp-TiO_2/ZrO_2(5-AVA)$_x$(MA)$_{1-x}$$PbI_3$/Carbon. However, compared to a pure $CH_3NH_3PbI_3$ based active layer, the obtained result of 4400 h with N_2H_5I addition stands at the highest position to improve intrinsic photostability and the highest number of days of operational solar cells, as shown in Figure A0.18, non-metal additives, Appendix 0.

Reviewer Prof. Sergey Levchenko

- *Please explain from very beginning what is meant by additives. At which stage of synthesis are they added?*

  Response: Thank you for the comment. I mean by "additive"- a compound which is added into the perovskite precursor solution. The mentioned above is also amended in the thesis under section 1.5.2. Please see the revised thesis.

- *"The poor stability of the perovskite layer often disintegrates perovskite into either PbI2, metallic lead or some volatile species, creating defects at the surface, grain boundaries." – clarify why this is bad?*

  Response: Thank you for the comment. "The formation of metallic lead or some volatile species results in permanent damage to perovskite structure creating defects at the surface and grain boundaries." The same has been updated in the thesis. Please see the revised thesis abstract.

- *"due to HAI incorporation" – explain abbreviation HAI.*

  Response: Thank you for the comment. The HAI represents hydrazinium iodide/ N_2H_5I. The relevant information is amended in the thesis abstract.

- *"The author prepared sampled" - ... samples*

  Response: Thank you for the comment. The correction is done.

- *"Besides, their application became limited to powering satellites and some other space applications." – why "besides"? in this context, "Therefore, ..." would be better*

  Response: Thank you for the comment. The correction is done.
- *"These choices are of the cation and anion relies on Goldschmidt tolerance factor (t), which predicts a stable crystal structure of perovskite." -> "The choices of the cation and anion rely on Goldschmidt tolerance factor (t), which predicts a stable crystal structure of perovskite."*

  Response: Thank you for the comment. The correction is done.

- *"long diffusion lengths of charge carriers >1 um" – μm?*

  Response: Thank you for the comment. The correction is done.

- *"Further, low trap states" – do you mean "low density of trap states"?*

  Response: Thank you for the comment. Yes, I mean the low density of trap states. The mentioned is also updated in the thesis text.

- *"Since perovskite solar cells showed rapid progress of improvement in the efficiencies within a decade, it has emerged as future generation PV technology" – "...they have emerged ..."*

  Response: Thank you for the comment. The correction is done.

- *"On the contrary, perovskite solar cells are reported to be stable only for a few hundred hours to a maximum of one year 5. Thus faces serious stability issues..." -> "On the contrary, perovskite solar cells are reported to be stable only for a few hundred hours to a maximum of one year 5, thus facing serious stability issues..."*

  Response: Thank you for the comment. The correction is done.

- *"Reports have shown that upon exposure to these external factors, PSCs degrades and loses their operational stability." -> "Reports have shown that upon exposure to these external factors, PSCs degrade and lose their operational stability."*

  Response: Thank you for the comment. The mentioned is corrected.

- "In the presence of light and heat, PbI2 is further decomposed and results in the formation of metallic lead and ionic iodine" – what do you mean by "ionic iodine"? how is this possible when lead is metallic?

  Response: Thank you for the comment. I mean "molecular iodine" as one of the by-products. The errors has been corrected and appears in thesis text as "In the presence of light and heat, PbI_2 is further decomposed and results in metallic lead and molecular iodine formation, as mentioned above [20,26]."

- *"Majorly the additives have opted" – "Majority of the additives"*

  Response: Thank you for the comment. It is updated as per the suggestion..

- *"Majorly the additives have opted from already available literature or experimental data related to dye-sensitized solar cells (DSSC)" – DSSC abbreviation was used before but not explained; explain it above"*

  Response: Thank you for the comment. It is updated as per the suggestion.

- "Majorly the additives have opted from already available literature or experimental data related to dye-sensitized solar cells (DSSC). For which additives are often categorized..." -> "Majorly the additives have opted from already available literature or experimental data related to dye-sensitized solar cells (DSSC), for which additives are often categorized..."

  Response: Thank you for the comment. The sentence is rephrased as per the suggestion.

- *"Unfortunately, the addition of MACl was reported to form mixed halide perovskite CH3NH3PbI3-xClx" – explain why this is bad*

  Response: Thank you for the comment. Because the literature research is primarily concerned with the $CH_3NH_3PbI_3$ active layer, additives that alter perovskite composition are not addressed when comparing further attributes. Because comparing one perovskite layer to another is a completely different matter.

- *"For instance, the introduction of 4, 4'-bipyridine in MAPbI3 demonstrated complex formation with PbI2" – explain what it means "demonstrated complex formation with PbI" and why this is good?*

  Response: Thank you for the comment. The complex formation with PbI_2 is good because it implies tslowing down the metallic lead formation, thus improved intrinsic stability against illumination. The relevant information is also amended in the thesis text. Please see the revised thesis.

- *"Additionally, it has been shown that the presence of N atoms prevents the loss of volatile species..." – I guess you do not really mean free N atoms, but it sounds like this; please re-write to clarify this.*

  Response: Thank you for the comment. As suggested, the sentence is rephrased and appears as "Additionally, it has been shown that the presence of reduced N atoms prevents the loss of volatile species by reacting with Pb^{2+} from the perovskite film and acts in a similar way as polymeric passivation coating."

- *"eliminated ion migration. While the hydrophobic C60 unit does not let moisture directly affect the film" – "eliminated ion migration, while the hydrophobic"; as you can see from previous similar comments, this is a common mistake in the text: you use part of a sentence as a separate sentence, which is strange to read; please revise your writing.*

  Response: Thank you for the comment. The mentioned is corrected. Also, additional attention is given to enhance text quality while proof reading.

- *"In an investigation, Zhang and co-workers demonstrated that NMP as a solvent additive (when added in DMF) – explain abbreviation NMP, DMF; also further on, please introduce abbreviations first time they appear in the text*

  Response: Thank you for the comment. The abbreviations are added as suggested. Further, text is proofread and abbreviations are added as required.

- *"when the intermediate phase was found to be vanished with CHP solvent additive" – "to vanish"*

  Response: Thank you for the comment. The correction is done as suggested.

- *"and ambient stability due to hydrophobicity of N atoms with ring like structure" – "N atoms within ring-like structure"?*

  Response: Thank you for the comment. Yes, I mean N atoms with in ring-like structure. The correction is done as suggested.

- *"The oxygen atoms act as Lewis base. Whereas Pb2+ acts as Lewis acid" – this is ONE sentence: "The oxygen atoms act as Lewis base, whereas Pb2+ acts as Lewis acid"*

  Response: Thank you for the comment. The correction is done as suggested.
- *"This adduct formation further results in large, flat grains" – explain why this is important*

  Response: Thank you for the comment. This adduct formation further results in large, flat grains resulting in a smooth film morphology, which results defect passivation at grain boundaries.

- *"Moreover, it was shown that incorporating amides in MAPbI3 reduces the Fermi level by interacting I- defect vacancy and reducing the trap sites and increasing the work function of MAPbI3 perovskite." – very unclear sentence; what does it mean "reduces the Fermi level", "I-defect vacancy", "reducing the trap sites"? Also, why is it good to increase the work function of MAPbI3 perovskite?*

  Response: Thank you for the comment. "reduces the fermi level" refers to the shift in value of fermi level.(For example-An amide additive shifted the Fermi level of the $MAPbI_3$ perovskite from −4.36 eV to −4.65). The shift/tuning of fermi level allows band structure alignment for better charge transport. Thus, increasing work function is good, because, it helps to attain voltage gain and better charge transport properties, which, in turn helps to boost power conversion efficiency. "I-defect vacancy" refers to Iodine defect site. "reducing the trap sites" refers to interaction with defect sites (i.e. interaction with Iodine defect site/vacancy).

- *"Recently, a variant of urea, biuret incorporation in MAPbI3 precursor attributed the intermediate formation with PbI2 to the electron delocalization in the N-C=O-N system in the presence of carbonyl group and explained this is why the peak shift for C=O vibration is noticed in FTIR spectra. (in the case of biuret-modified MAPbI3 film from 1722 to 1713 cm-1) 68" -> revise this sentence, it is impossible to understand.*

  Response: Thank you for the comment. As suggested, the sentence is rephrased and appears as "Recently, the addition of biuret (a variant of urea) in $MAPbI_3$ precursor ascribed the intermediate formation with PbI_2 to the electron delocalization in the N-C=O-N system in the presence of carbonyl group and explained the cause of peak shift for C=O vibration in FTIR spectra. (in the case of biuret-modified $MAPbI_3$ film from 1722 to 1713 cm-1) [69]."

- *"This further reflected improvements in the contact angles of the film (so that the hydrophobicity of the films)" – the phrase in parentheses looks unfinished*

  Response: Thank you for the comment. As suggested, the sentence is corrected.
  "This further reflected improvements in the contact angles of the film (which signifies improvement in hydrophobicity of the films)."

- *"could inhibit the raid of moisture to MAPbI3 films" – what is "raid of moisture"?*

  Response: Thank you for the comment. I mean, "penetration of moisture" to perovskite structure.

- *"However, both IDIC-Th and IDIS-Th are known for their hydrophobic nature." – Why "however"? In the previous sentence you wrote that hydrophobic is good*

  Response: Thank you for the comment. Yes, in previous sentence I wrote that hydrophobicity is good. What I mean here is both IDIC-Th and IDIS-Th already have hydrophobic nature and increasing their hydrophobicity, enhances ambient stability. I hope it is clear now.

- *"Although the purpose of using the azo group was to reduce the stiffness of the perovskite film 91. However, due to the hydrophobic nature of attached cation in the acid-containing additive, most of*

them increase ambient stability." -> "Although the purpose of using the azo group was to reduce the stiffness of the perovskite film 91, due to the hydrophobic nature of attached cation in the acid-containing additives, most of them also increase ambient stability."

Response: Thank you for the comment. As suggested, the sentence is rephrased.

- *"Further, cyclic ether compound THF (Tetrahydrofuran) also reported improving stability in ambient air" -> "Further, cyclic ether compound THF (Tetrahydrofuran) was also reported to improve stability in ambient air"*

  Response: Thank you for the comment. Correction is done as per the suggestion.

- *"which was used to achieve fast electron transport rates toward the anode, including the growth of large, uniform, smooth and crystalline perovskite film" -> "which was used to achieve fast electron transport rates toward the anode and growth of large, uniform, smooth and crystalline perovskite film"*

  Response: Thank you for the comment. Correction is done as per the suggestion.

- *"At the same time, quantum dot improves the crystallinity of film due to the quantum confinement effect" – are you sure? how can quantum confinement effect improve crystallinity? please explain the mechanism of this effect*

  Response: Thank you for the comment. Please see below the rephrased sentence, conveying the proper information. The complete sentence appears as "At the same time, quantum dot reduces non-radiative recombination centers (due to the quantum confinement effect), while the chelating functional groups attached to quantum dot help co-ordinate with defect sites, improving the crystallinity of the film, thus passivating defects at grain boundaries." The same has been revised in the thesis text as well.

- *"However, as the size of nuclei increases, the perovskite shows partial replacement" – do you mean weight of nuclei?*

  Response: Thank you for the comment. I mean both. The revised text appears as "However, as the nuclei weight and radius increase, the A site cation is partially replaced, and a mixed perovskite with a double cation is formed"

- *"Further, the transitional metal halides," – "transition metal halides"*

  Response: Thank you for the comment. Correction is done as per the suggestion.

- *"over stoichiometric PbI2" – explain what this means?*

  Response: Thank you for the comment. Over stoichiometric PbI_2 refers to excess amount of PbI_2 in the precursor compared to standard recipe.

- *"Whereas Pb2+ defects sites that act as Lewis acid." – this is not a complete sentence?*

  Response: Thank you for the comment. The sentence is rephrased and appears as "Furthermore, The N atom in pyridine derivatives has been demonstrated to be capable of interacting with Pb^{2+} defect sites as Lewis base [27], while Pb^{2+} defects sites act as Lewis acid [236].

- *"In the scope of this thesis, selection criteria for choosing additives for the MAPbI3 active layer have been presented, which was absent otherwise." – The state-of-the-art overview pointed out several selection criteria for choosing one or another additive. In what sense was this absent? Or was the literature reviewed in the light of the knowledge obtained in this thesis? It is very important to make this very clear.*

Response: Thank you for the comment. It was absent it the sense that earlier there was no selection criteria for choosing and classifying additive for $MAPbI_3$ perovskite layer. Therefore, the literature review was obtained to shed light on the gap of knowledge in literature. Later this literature review was also published (https://doi.org/10.3390/cryst11070814)

- *"The organic additives were later subcategorised based on N donor atom, O donor atom and S donor atom mainly with the associated functional group. Inorganic additives were subcategorised based on the group in the periodic table." – related to the previous question; is this kind of classification your idea, based on your research, or not?*
- Response: Thank you for the comment. Yes, such idea of classification of additives for $MAPbI_3$ perovskite is based on my research.

Reviewer Prof. Stanislav Fedotov

- *The detailed reading of the thesis provoked some comments listed in the attached file.*

  Response: Thank you for the thorough revision of the thesis. I accepted all your text correction recommendations and provided answers to several comments that required my responses below, point-by-point. Please, see them

- *Figure 4 (a) crystal structure of perovskite materials, (b) suitable A cations for perovskite solar cells.8*

  Response: Thank you for the comment. The mentioned above is corrected.

- *"External radiative efficiency"- What is it?*

  Response: Thank you for the comment. The mentioned is amended in the thesis. The revised text appears as "Further, the improvement in external radiative efficiency allows measuring the improvement in non-radiative losses quantitatively (Figure 5c), providing the benefit of additional gain in V_{oc} and fill factor"

- *Table?*

  Response: Thank you for the comment. Figure 5 has been updated. Please see the revised thesis.

- *"1.4.3. Easy and low cost of manufacturing"- Ease*

  Response: Thank you for the comment. As suggested, the subheading is updated.

- *"Si PV is expensive because of the high cost of manufacturing"- What is the cost of manufacturing a Si wafer in comparison to that of a perovskite PV cell?*

  Response: Thank you for the comment. The cost comparison of Si PV vs PSC (perovskite solar cells) is illustrated in Figure 7a. Please see the revised thesis.

- *Citation 17- This paper does not exist.*

  Response: Thank you for the comment. The corrected citation is updated as reference 5, 18 in the revised thesis.

- *"the quantity of Silicon required to produce one year of production is almost double that of perovskite light absorber materials (Figure 7)- Did not get what it means.*

- *In the original paper they discuss the production of element needed to cover 12.5 TWh consumption and for Si 3 years of current production capacity is needed, for Pb - much less.*

  Response: Thank you for the comment. The sentence is rephrased and now appears as "Furthermore, it is projected that to cover 12.5 TWh consumption, three years of current production capacity is needed for silicon. On the other hand, perovskites would just take a few days to produce with the current lead manufacturing technology (Figure 7b) [19]."

- *"additive engineering"- It is better to write "engineering of additives" rather than "additive engineering" because it sounds like "additive technologies" (additive is an attr.) which is a completely different field*
  Response: Thank you for the comment. Similar comments are received from other jury members. Instead of "additive engineering" the term "additive" is used in the thesis. Please see the revised thesis section 2.4.

- *"categorized based on N donor, O donor and S donor atoms"- N, O, S atoms serving as electron donors*

  Response: Thank you for the comment. Text is updated as per the suggestion.

- *Amides- Why is it not an N-donor?*

  Response: Thank you for the comment. Since, amides can be viewed as a derivative of a carboxylic acid. Therefore, it is classified under O donor atom.

- *"It was established that adding excess MAI reduces tap density,"- Defect traps density or Tap density?*

  Response: Thank you for the comment. As suggested, it is corrected to "Defect traps density".

- *"improving the stability in ambient condition"- conditions*

  Response: Thank you for the comment. As suggested, the text is corrected.

- *"Thus, grain boundaries are passivated by assisting coordination interactions with the Pb2+ ion of MAPbI3 and PyP unit that further improved short circuit current density Jsc and eliminated ion migration. While the hydrophobic C60 unit does not let moisture directly affect the film 45."- Should be one sentence, not two.*

  Response: Thank you for the comment. The corrections are made as suggested.

- *"additives were employed in MAPbI3 precursor"- a MAPbI3 precursor*

  Response: Thank you for the comment. The above is corrected.

- *"resulted in high quality of perovskite film due to Lewis acid-base reaction with Pb atom"- " resulted in a high quality of perovskite film due to a Lewis acid-base reaction with the Pb atom."*

  Response: Thank you for the comment. The above is corrected.

- "KIM and co-workers"- "Kim and co-workers"

  Response: Thank you for the comment. The above is corrected.

- *"compared them with commonly used DMF…"-" compared them with a commonly used DMF.."*

Response: Thank you for the comment. The above is corrected.

- *"N-methyl-2-pyrrolidone (NMP), N-ethyl-2-pyrrolidone (NEP), N-cyclohexyl-2-pyrrolidone (CHP), and N-octyl-2-pyrrolidone (NOP) was"- "were"*

  Response: Thank you for the comment. The above is corrected.

- *"it was observed that solvent additive containing pyrrolidone structure with higher boiling point results in lower vapour pressure over pristine DMF based precursor."- "it was observed that a solvent additive containing the pyrrolidone structure with a higher boiling point results in a lower vapour pressure over the pristine DMF based precursor."*
  Response: Thank you for the comment. The above is corrected.

- *"in the morphology of perovskite film since"-" in the morphology of the perovskite film"*

  Response: Thank you for the comment. The above is corrected.

- *"Furthermore, it was discovered that the strength of coordination of solvent component influenced intermediate formation with PbI2,"- "Furthermore, it was discovered that the strength of coordination of a solvent component influenced the intermediate formation with PbI2". Also, what does it mean- "the strength of coordination"*

  Response: Thank you for the comment. The above is corrected. By "the strength of coordination", I mean how strongly a solvent substituent binds with PbI_2.

- *"with CHP solvent additive"- "with a CHP solvent additive" and "whereas pure DMF solvent"-" whereas the pure DMF solvent"*

  Response: Thank you for the comment. The above is corrected.

- *"suppress DMF: PbI2 solvate formation"- "suppress the DMF: PbI2 solvate formation"*

  Response: Thank you for the comment. The above is corrected.

- *"Some other derivative such as"- derivatives*

  Response: Thank you for the comment. The above is corrected.

- *"It was suggested that balanced charge distribution in the C=N bond in the triazine ring promotes stronger interaction with Pb2+, resulting in very tight contact between these two materials."- "It was suggested that a balanced charge distribution in the C=N bond in the triazine ring promotes stronger interaction with Pb2+, resulting in a very tight contact between these two materials.*

  Response: Thank you for the comment. The above is corrected.

- *"power conversion efficiencies (PCEs)"- The abbreviation PCE was used several times above without description.*

  Response: Thank you for the comment. The above is corrected. The abbreviation PCE is first defined under section 1.4.2. Please see the revised thesis.

- *"when added in DMF based precursor"-" when added in a DMF based precursor"*

  Response: Thank you for the comment. The above is corrected.

- *"Additives containing O atom"- "Additives containing an O atom"*

Response: Thank you for the comment. The above is corrected.

- *"The oxygen atoms act as Lewis base. Whereas Pb2+ acts as Lewis acid, resulting in the formation of Lewis acid-base adduct."*- "*The oxygen atoms act as a Lewis base, whereas Pb2+ acts as a Lewis acid, resulting in the formation of a Lewis acid-base adduct."*

  Response: Thank you for the comment. The above is corrected.

- *"Recently, a variant of urea, biuret incorporation in MAPbI3 precursor attributed the intermediate formation with PbI2 to the electron delocalization in the N-C=O-N system in the presence of carbonyl group and explained this is why the peak shift for C=O vibration is noticed in FTIR spectra."- This sentence is too heavy and long. Split or rephrase.*

  Response: Thank you for the comment. The above is rephrased and appears in revised thesis as "Recently, the addition of biuret (a variant of urea) in $MAPbI_3$ precursor ascribed the intermediate formation with PbI_2 to the electron delocalization in the N-C=O-N system in the presence of carbonyl group and explained the cause of peak shift for C=O vibration in FTIR spectra."

- *"have shown similar properties 73. Similarly, it was also shown that"- rewrite*

  Response: Thank you for the comment. The above is rephrased and appears in revised thesis as "have revealed similar properties [70–74]. Likewise, it was also presented that"

- *"carbonyl with sulfonyl group"- "carbonyl with a sulfonyl group"*

  Response: Thank you for the comment. The above is corrected.

- *"Pb-O"-"the Pb-O"*

  Response: Thank you for the comment. The above is corrected.

- *"(The boiling point of the DMF, NMP, DMSO, and HMPA are 152, 202, 189, 235 °C, respectively) 79,80"- "(The boiling point of DMF, NMP, DMSO, and HMPA are 152, 202, 189, 235 °C, respectively) 80,81"*

  Response: Thank you for the comment. The above is corrected.

- *"over pristine (DMF)"- remove the brackets*

  Response: Thank you for the comment. The above is corrected.