nature portfolio

Peer Review File

Interfacial Stability of Organic-Based Hole Transport Layers in Perovskite Photovoltaics for Space-like Thermal Environments

Corresponding Author: Professor Jaeki Jeong

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)
This work systematically investigates the impact of different organic hole transport layers (HTL) on the interfacial stability of inverted perovskite solar cells (PSCs) under simulated space-like thermal cycling environments. The study focuses on three HTL configurations, each with distinct advantages: the polymeric PTAA, the self-assembled monolayer MeO-2PACz, and a sequential PTAA/MeO-2PACz bilayer. Through comprehensive thermomechanical analysis, electrical characterization, thermal cycling tests, and structural evaluations, the authors elucidate the critical role of coefficient of thermal expansion (CTE) matching between the HTL and the perovskite layer. The findings demonstrate that the PTAA/MeO-2PACz bilayer structure effectively leverages the mechanical buffering effect of PTAA to mitigate thermal stress, thereby preserving the superior interfacial properties of MeO-2PACz. This strategy achieves a high-power conversion efficiency of 19.0% while maintaining approximately 73% of the initial performance after thermal cycling between -40°C and 90°C. The study provides an important interfacial engineering strategy for developing highly efficient and thermally stable perovskite solar cells intended for harsh space environments. However, this work may be published in this journal after undergoing the following minor revisions:
1. Compared to actual space conditions, the experimental parameters employed remain relatively moderate. For example, the synergistic effect of ultraviolet irradiation combined with thermal cycling in space may further accelerate interfacial degradation. Conducting multi-stress coupling aging studies that include UV irradiation and thermal cycling is therefore crucial.
2. The attribution of severe performance degradation for all devices after aging at 120°C (Figure 3) solely to the intrinsic decomposition of perovskite lacks sufficient rigor. It is recommended to support this claim more directly by incorporating control experiments or citing relevant literature. Additionally, the observed increase in water contact angle for the PTAA layer after thermal cycling is interpreted as "preferential orientation of hydrophobic phenyl groups". To provide more direct chemical-state evidence, supplementing this finding with XPS characterization is advised.
3. The discussion regarding the microscopic mechanism of thermal instability in the SAM layer is currently limited to the observation of molecular disordering in MeO-2PACz at elevated temperatures. This surface-level explanation hinders a thorough understanding of the SAM interface's thermal fragility. It is suggested that future work could integrate in situ spectroscopic characterization and molecular dynamics simulations to reveal the evolution of interactions between the anchoring groups and the substrate.
4. The study clearly demonstrates that CTE mismatch leads to an increase in defect state density, but a quantitative correlation is lacking. It would be beneficial to briefly discuss the challenges and potential pathways for establishing such a quantitative model.

Reviewer #3

(Remarks to the Author)
The manuscript presents an interesting and timely study on the thermal and interfacial stability of inverted PSCs employing PTAA, MeO-2PACz, and PTAA/MeO-2PACz HTLs under space-relevant conditions. The topic is valuable, and the results may be of interest to the photovoltaic and space-technology communities. However, several important aspects require clarification or additional data to support the conclusions. I therefore recommend Major Revision, with the following points to

be addressed:

1.Device fabrication details should be expanded.
A more complete description of film thicknesses, processing conditions, and deposition parameters would improve reproducibility and clarity.

2. Additional structural characterization is recommended.
Cross-sectional SEM/TEM showing the full device stack and individual layer thicknesses (before and after thermal cycling) would significantly strengthen the discussion on interfacial stability.

3. Electrical analysis requires further clarification.
Extracting and comparing the series resistance (Rs) for all HTL configurations, before and after thermal stress, would help identify the origin of the observed FF evolution.

4. Clarification regarding the exclusion of the BCP layer is needed.
As BCP commonly serves as an interfacial and diffusion-barrier layer in p–i–n PSCs, providing stability data for devices including BCP, or additional evidence excluding Ag-related degradation pathways, would help justify the chosen device architecture.

5. Recombination losses are not fully assessed.
A basic Voc vs light-intensity analysis for all HTL configurations, before and after thermal stress, would provide useful insight into changes in recombination mechanisms.

Overall, the manuscript is promising, and the requested additions would substantially strengthen the conclusions and enhance clarity. I look forward to reviewing a revised version.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed all the comments and suggestions from the two reviewers. I have no further comments and suggest to accept this article as it is.

Reviewer #3

(Remarks to the Author)
The authors have carefully addressed all comments raised in the previous round of review. The manuscript has been significantly improved, with additional experimental details, supporting data, and clarifications that strengthen the conclusions and overall quality of the work. The revisions adequately resolve the concerns raised by the reviewer. Therefore, I recommend the manuscript for publication in its current form without further changes.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This work systematically investigates the impact of different organic hole transport layers (HTL) on the interfacial stability of inverted perovskite solar cells (PSCs) under simulated space-like thermal cycling environments. The study focuses on three HTL configurations, each with distinct advantages: the polymeric PTAA, the self-assembled monolayer MeO-2PACz, and a sequential PTAA/MeO-2PACz bilayer. Through comprehensive thermomechanical analysis, electrical characterization, thermal cycling tests, and structural evaluations, the authors elucidate the critical role of coefficient of thermal expansion (CTE) matching between the HTL and the perovskite layer. The findings demonstrate that the PTAA/MeO-2PACz bilayer structure effectively leverages the mechanical buffering effect of PTAA to mitigate thermal stress, thereby preserving the superior interfacial properties of MeO-2PACz. This strategy achieves a high-power conversion efficiency of 19.0% while maintaining approximately 73% of the initial performance after thermal cycling between -40°C and 90°C. The study provides an important interfacial engineering strategy for developing highly efficient and thermally stable perovskite solar cells intended for harsh space environments. However, this work may be published in this journal after undergoing the following minor revisions:

- We appreciate the reviewer's positive and constructive comments.

1. Compared to actual space conditions, the experimental parameters employed remain relatively moderate. For example, the synergistic effect of ultraviolet irradiation combined with thermal cycling in space may further accelerate interfacial degradation. Conducting multi-stress coupling aging studies that include UV irradiation and thermal cycling is therefore crucial.

- Our response: Thank you for your considerable pointing out. We fully agree that the simultaneous exposure to multiple stress including UV irradiation, vacuum, and thermal cycling can further accelerate degradation under realistic space environments. In this study, our primary objective was to isolate and systematically investigate the effect of thermal stress for perovskite solar cells, particularly the influence of HTL thermomechanical properties and interfacial stability under space-like thermal cycling conditions. Therefore, we intentionally focused on vacuum thermal cycling, which represents one of the most critical tress factors experienced by satellites in low Earth orbit. In addition, UV-C radiation (100–280 nm), which is known to contribute strongly to photodegradation processes, is largely attenuated by the fluorine-doped tin oxide (FTO) layer used in this work. As shown in transmittance spectra of FTO substrate, the FTO substrate exhibits negligible-absorption below ~289 nm, thereby limiting the penetration of high energy UV photons into the device.

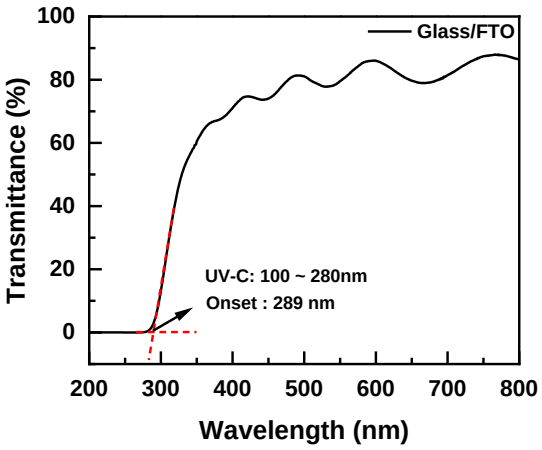

Figure R1. UV–vis spectrum of the FTO substrate used, showing no absorption in the UV-C region

related with significant performance degradation

➢ Following the reviewer's suggestion, we have added a discussion in the revised manuscript.

"In addition, evaluating device stability under multi-stress conditions, including combined UV irradiation and thermal cycling, will be important for realistic space applications."

2. The attribution of severe performance degradation for all devices after aging at 120°C (Figure 3) solely to the intrinsic decomposition of perovskite lacks sufficient rigor. It is recommended to support this claim more directly by incorporating control experiments or citing relevant literature. Additionally, the observed increase in water contact angle for the PTAA layer after thermal cycling is interpreted as "preferential orientation of hydrophobic phenyl groups". To provide more direct chemical-state evidence, supplementing this finding with XPS characterization is advised.

➢ Our response: Thank you for constructive point out. In air, hydrophobic moieties tend to preferentially segregate to the surface, while hydrophilic groups are buried within the bulk. As a result, polymer surfaces generally exhibit hydrophobic characteristics under ambient conditions. Especially, unstable state of materials based on phenyl ring side-chain facilitates reorientation. We have added the corresponding references in the manuscript for understanding.

68. Akhter, S., Fahlquist, L., White, J. M. & Hardegree, E. L. Preferential orientation of pendent groups at polymer surfaces: Phenyl ring distribution on polystyrene film surfaces. *Appl. Surf. Sci.* **37**, 406–418 (1989).

69. Wang, Y. *et al.* Effect of the phenyl ring orientation in the polystyrene buffer layer on the performance of pentacene thin-film transistors. *Organic Electronics* **11**, 1066–1073 (2010).

70. Narumi, H. & Oda, Y. Surface orientation of amphiphilic block copolymers via thermal annealing. *Polym. J.* **57**, 335–339 (2025).

➢ While XPS is a powerful tool for probing surface chemical composition, the thermally induced reorientation of PTAA is primarily associated with changes in molecular orientation rather than chemical bonding states. Furthermore, the information depth of XPS may lead to depth-averaging effects, which can obscure subtle rearrangements within the PTAA molecular layers. Therefore, we have further measured UV-Visible absorption spectra to suggest thermally induced changes in molecular packing or chain conformation of PTAA. Consequently, in this work, the increased water contact angle together with the red-shift in UV-vis absorption suggests structural reorganization of PTAA after thermal cycling.
We have added this result and updated the supporting information. And we have revised the manuscript.

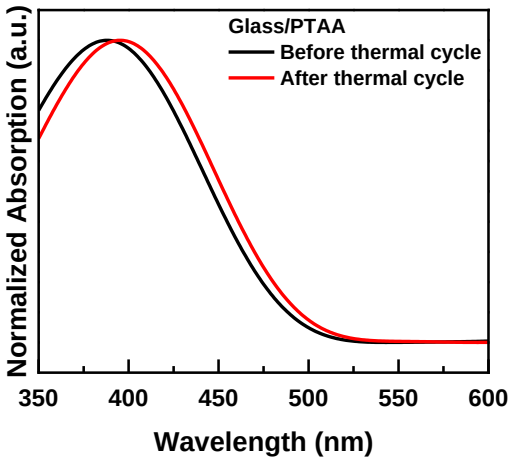

Figure S8. Absorption spectra and of PTAA film before and after thermal cycling.

- And we have revised the manuscript.

"This interpretation is further supported by the red-shift observed in the UV–Visible absorption spectra, suggesting enhanced π–π stacking and increased molecular packing order, and it is consistent with possible thermally surface reorientation of PTAA layer (see **Figure S8**)."

3. The discussion regarding the microscopic mechanism of thermal instability in the SAM layer is currently limited to the observation of molecular disordering in MeO-2PACz at elevated temperatures. This surface-level explanation hinders a thorough understanding of the SAM interface's thermal fragility. It is suggested that future work could integrate in situ spectroscopic characterization and molecular dynamics simulations to reveal the evolution of interactions between the anchoring groups and the substrate.

- Our response: We appreciate the reviewer's insightful suggestion. We agree that a deeper understanding of the microscopic mechanisms relating to the thermal stability of SAM-based HTLs is highly important. In this regard, we are currently investigating the thermal stability and post-thermal cycling test of various HTL SAM materials, including MeO-2PACz. This ongoing study is for interfacial changes under thermal stress using a broader range of SAM materials. This work is being pursued as part of our follow-up work, and the results will be reported in a future publication.

4. The study clearly demonstrates that CTE mismatch leads to an increase in defect state density, but a quantitative correlation is lacking. It would be beneficial to briefly discuss the challenges and potential pathways for establishing such a quantitative model.

- Our response: Thank you for your insightful comments. To address this point, we have added a short discussion in the revised manuscript highlighting the challenges and possible future approaches. (Page 17, Line 335-337)

"Beyond this work, further studies are needed to establish a quantitative link between CTE mismatch and defect formation, given the coupled effects of mechanical stress, interfacial adhesion, and ion migration."

Reviewer #3 (Remarks to the Author):

The manuscript presents an interesting and timely study on the thermal and interfacial stability of inverted PSCs employing PTAA, MeO-2PACz, and PTAA/MeO-2PACz HTLs under space-relevant conditions. The topic is valuable, and the results may be of interest to the photovoltaic and space-technology communities. However, several important aspects require clarification or additional data to support the conclusions. I therefore recommend Major Revision, with the following points to be addressed: Overall, the manuscript is promising, and the requested additions would substantially strengthen the conclusions and enhance clarity. I look forward to reviewing a revised version.

- We sincerely thank Reviewer #3 for the thoughtful and constructive evaluation of our manuscript. The reviewer's comments have helped us identify areas where additional clarity and experimental evidence were needed, and we believe the manuscript has been substantially strengthened as a result.

1. Device fabrication details should be expanded. A more complete description of film thicknesses,

processing conditions, and deposition parameters would improve reproducibility and clarity.

➢ Our response: Thank you for your constructive comments. We have revised and updated the experimental section including film thickness, details of processing condition.

"Materials

Lead(II) iodide (PbI_2, 99.99%), lead(II) bromide ($PbBr_2$, >98.0%), bathocuproine (BCP, >99.0%, sublimed), and [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz, >98.0%) were purchased from Tokyo Chemical Industry (TCI). Methylammonium chloride (MACl, >99.99%), methylammonium bromide (MABr, >99.99%), formamidinium iodide (FAI, >99.99%), and propane-1,3-diammonium iodide ($PDAI_2$) were purchased from Greatcell Solar Materials. Cesium iodide (CsI, 99.999%), N,N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), 2-propanol (IPA, 99.5%), and chlorobenzene (CB, 99.8%) were purchased from Sigma-Aldrich. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) was purchased from Ossila. C_{60} was purchased from Nichem. All chemicals were used as received without any other refinement.

Preparation of perovskite precursor

The 1.8 M triple-cation mixed-halide perovskite precursor($Cs_{0.05}FA_{0.90}MA_{0.05}Pb(I_{1-(x+y)}Br_xCl_y)_3$) solution was prepared in a mixed solvent of DMF: DMSO (4:1, v/v). The precursor solution was stirred for 1 hour before use.

Device Fabrication

FTO-coated glass substrates were sequentially cleaned by ultrasonication in deionized water, acetone, and IPA for 10 min each, followed by drying for at least 1 hour at 100 °C. The dried substrates were treated with UV–ozone for 20min. To investigate the role of the HTL, three HTL configurations were employed: MeO-2PACz, PTAA, and PTAA/MeO-2PACz. PTAA. PTAA (2mg ml^{-1} in toluene) was deposited by spin coating at 2000 rpm for 30 s. The MeO-2PACz (0.3 mg ml^{-1} in DMF) was deposited by spin coating at 5000rpm for 30s, annealing at 100 °C for 5 min. For the bilayer configuration, PTAA was first deposited, followed by the MeO-2PACz layer.

The perovskite precursor was deposited at 4000rpm for 50s, and CB(300 μL) was dripped on the perovskite film at 20s before the end of the spin coat process. After deposition of the perovskite layer, a surface passivation layer, $PDAI_2$ solution (1mg/ml in IPA), was deposited by spin coating at 5000 rpm for 30s, annealing at 100 °C for 5 min.

Subsequently, C60 layers (25 nm with a 5 nm BCP and 75 nm without BCP) were deposited by thermal evaporation. Finally, 100 nm Ag electrodes were deposited by thermal evaporation under high vacuum (~10^{-6} mtorr)."

2. Additional structural characterization is recommended.

Cross-sectional SEM/TEM showing the full device stack and individual layer thicknesses (before and after thermal cycling) would significantly strengthen the discussion on interfacial stability.

➢ Our response: We appreciate your positive pointing out. We have measured Cross-sectional TEM to confirm the changes of films in the devices before/after thermal cycling. As a result, no significant variation in film thickness was observed before and after thermal cycling. Therefore, it

can be concluded that the degradation of device performance after thermal cycling is dominantly determined by the interfacial stability of HTL and external thermal stress conditions.

- We have added the cross-section TEM image to support information (**Figure S11**).

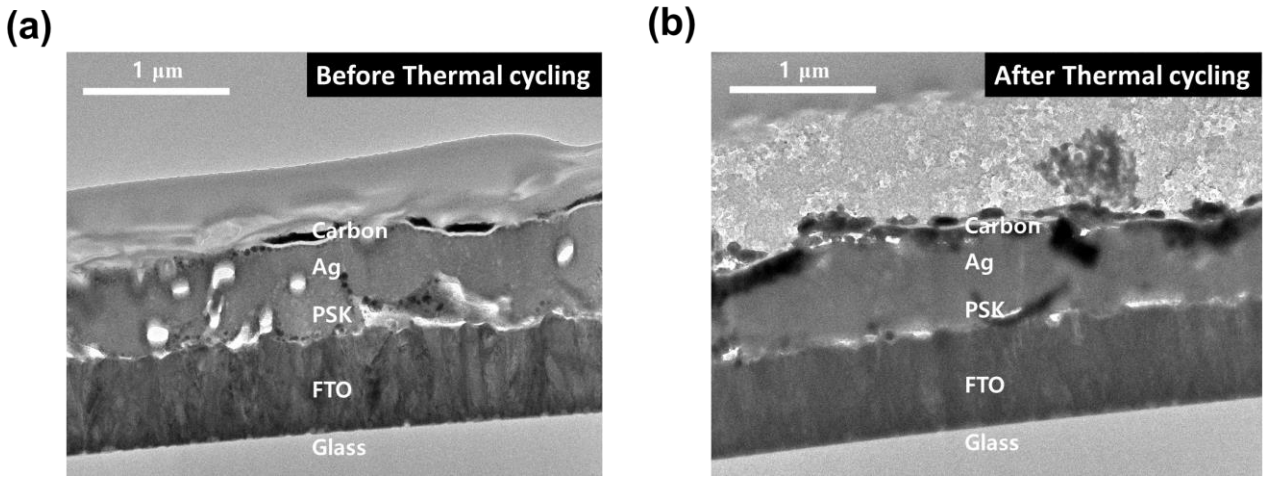

Figure S11. Cross-section TEM of devices (a) before and (b) after thermal cycling test.

- We have revised and updated the manuscript.

"The film thickness shows within the device shows negligible change before and after thermal cycling as shown in Figure S11."

3. Electrical analysis requires further clarification.

Extracting and comparing the series resistance (Rs) for all HTL configurations, before and after thermal stress, would help identify the origin of the observed FF evolution.

- Our response: Thank you for your helpful comments. We agree that confirming Rs and Rsh before and after thermal cycling would offer a more direct assessment of HTL performance degradation and film condition changes. As suggested, *J-V* characteristics were measured after thermal cycling to investigate the series resistance (Rs) and shunt resistance (Rsh), and the results have been provided in the supporting information as **Figure S5**. After thermal cycling, the thermal degradation of MeO-2PACz based device is dominated by a significant decrease in Rsh, whereas that of PTAA based device are mainly affected by the increased Rs.

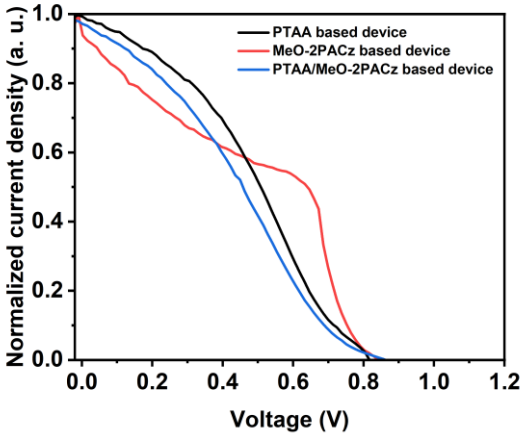

Figure S5. *J-V* characteristics of devices after thermal cycling test.

➢ We have revised and updated the manuscript.

"As shown in **Figure S5,** MeO-2PACz-based devices after thermal cycling test exhibit decreased shunt resistance, indicating that its film quality degraded severely under repeated thermal stress. Whereas the performance degradation of PTAA based devices is relatively affected by in increased series resistance."

4. Clarification regarding the exclusion of the BCP layer is needed.

As BCP commonly serves as an interfacial and diffusion-barrier layer in p–i–n PSCs, providing stability data for devices including BCP, or additional evidence excluding Ag-related degradation pathways, would help justify the chosen device architecture.

➢ Our response: We appreciate your pointing out. We have measured thermal stability for 30 hours at 90 °C in N_2 atmosphere conditions. As shown in the figure below, the PTAA/MeO-2PACz-based devices with BCP result in a more PCE decrease compared to the device without BCP layer.

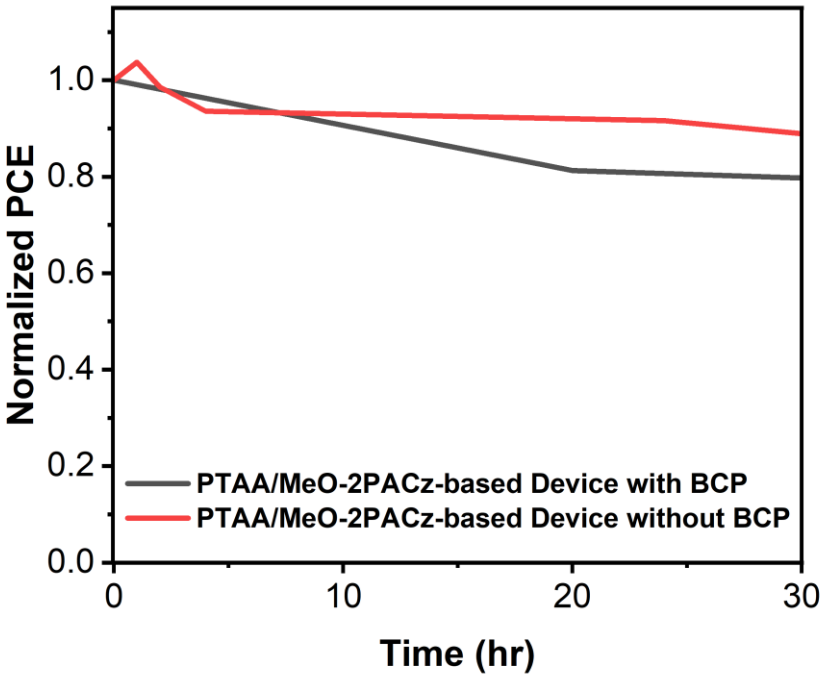

Figure S3. Thermal stability of PTAA/MeO-2PACz-based devices with and without BCP for 30 hours at 90 °C in N_2 atmosphere conditions.

➢ We have updated the manuscript

"BCP was intentionally excluded from the final architecture due to its poor thermal stability (See **Figure S3**)"

➢ Furthermore, we added a reference about the optimization of C60 layer and thermal instability of BCP layer.

55. Zheng, X. *et al.* Enhanced thermal stability of inverted perovskite solar cells by interface modification and additive strategy. *RSC Advances* **10**, 18400–18406 (2020).

5. Recombination losses are not fully assessed.

A basic Voc vs light-intensity analysis for all HTL configurations, before and after thermal stress, would provide useful insight into changes in recombination mechanisms.

➢ Our response: Thank you for your valuable suggestion. Voc-light intensity analysis was employed to probe trap-assisted recombination. For the MeO-2PACz based devices, the ideality factor increased from 1.03 to 1.10 (kT/q) after thermal cycling, indicating the increase of additional trap-assisted recombination pathways. In contrast, the PTAA based devices exhibited negligible changes in their ideality factors, suggesting stable recombination behavior. These results clearly demonstrated the pronounced degradation in MeO-2PACs device performance.

➢ We have added and updated supporting information.

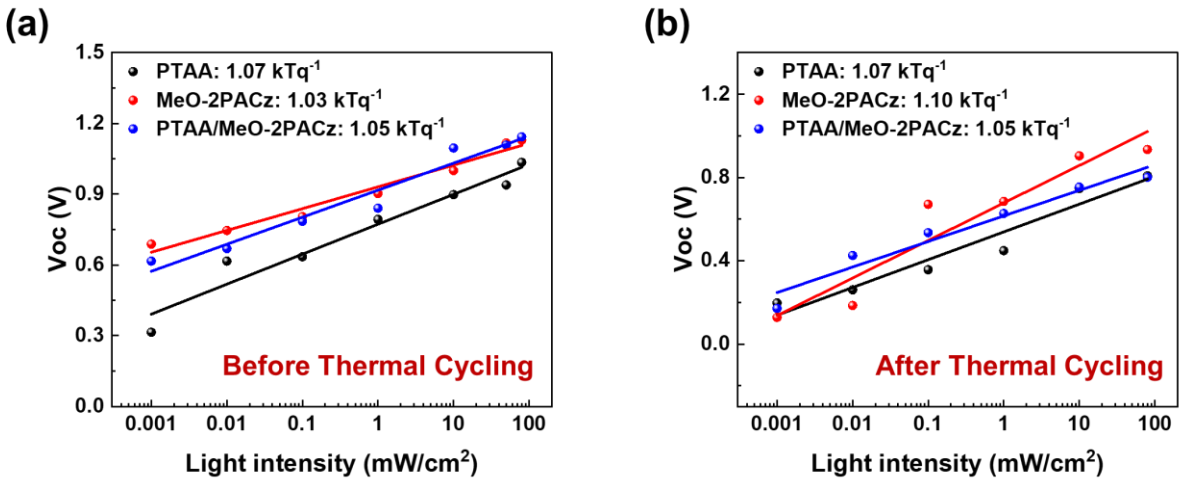

Figure S7. Voc vs light-intensity analysis for devices (a) before and (b) after thermal cycling.

➢ We have revised and updated our manuscript.

"Furthermore, **Figure S7** demonstrates that MeO-2PACz based devices exhibit an increased trap-assisted recombination after thermal cycling compared to the other devices, which is consistent with the result obtained from hole-only devices and TPC measurement."