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A Study of the Life-span approximation of Organic Photovoltaic Cells through Accelerated Thermal Aging

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ABSTRACT

Organic Photovoltaics (OPVs) are cheaper, more sustainable and easier to fabricate alternatives to traditional silicon-based photovoltaics. Regardless of significant strides in OPV research, major barriers to commercialization exist. A significant barrier is their sensitivity to environmental conditions causing smaller lifespans and decreased usability in domestic and commercial energy production when compared to silicon-based cells. This aging can be majorly attributed to the thermal degradation that is caused by morphological changes within the donor-acceptor material inside the cell, which is an integral part of its energy production mechanism. Techniques like T70 or T80 are traditionally used to calculate lifespans. These are reliable and accurate methods; however, they are also slow and costly. A quicker alternative is accelerated aging, which is reviewed and empirically evaluated for its effectiveness in determining the lifespan of an OPV through heating at 353K. It was hypothesized that the characteristics of the device will show degradation as the time of heating is increased at constant temperature. Several characteristics were tested at prolonged heating periods: Open circuit voltage (OCV), short-circuit current density (SCCD), fill factor (FF) and efficiency. FF and efficiency showed clear negative correlations and were used in extrapolation to evaluate the Equivalent Thermal Aging Time (ETAT): a comparative measure of thermal endurance. Using the prescribed methodology, $ETAT_{70}$ values were calculated. Further research should focus on validating the methodology using long term operational aging. If validated, the methodology could prove useful in faster quality control, device optimization, materials screening etc., resulting in quicker development and industrialization.

Index Terms **-** Power conversion efficiency or efficiency, Thermal degradation, accelerated thermal aging, Organic Photovoltaics (OPVs), Fill factor (FF), open circuit voltage (OCV), short circuit current density (SCCD).

INTRODUCTION

The global shift toward sustainable energy systems due to the environmentally detrimental effects of fossil fuels, has accelerated the development and deployment of photovoltaic technologies as viable alternatives. Amongst these, the most prominently commercialized form of photovoltaic are crystalline silicon solar cells due to their high efficiencies and relatively long lifetimes. However, their rigidity and their expensive and complicated fabrication process motivate the exploration of next-generation photovoltaic technologies[1]. Organic photovoltaic (OPV) cells have emerged as promising alternatives due to their lightweight structure, relatively easier fabrication methods, large area production and their abundant raw materials[2]. These advantages make OPVs attractive for building-integrated photovoltaics, wearable electronics, and portable power generation[3], making the technology even more relevant.

OPV cells generate energy by relying on the generation of excitons due to photon absorption. This is accomplished using various layers that the cells are composed of. Firstly, there is the top transparent electrode, followed by the electron transport layer (ETL), then the donor, the acceptor, followed by the hole transport layer (HTL), and finally the bottom electrode. The architecture of an OPV is represented in the format shown below, where a "/" represents layer separation, and ":" represents a blend.

"Top electrode" / "ETL" / "donor" : "acceptor" / "HTL" / "Bottom electrode"

For electricity to be generated, light that enters the transparent electrode is absorbed by the donor, causing it to absorb energy and create a bound electron-hole pair also known as the exciton. At the interface, which is a blend of the donor and acceptor materials, the exciton splits as the electron transfers from the donor to the acceptor. The electron then travels to the ETL and collects at the top electrode, and the hole travels through the HTL and collects at the bottom electrode. This causes the electrons to flow through the external circuit allowing for the generation of usable power[6].

A major challenge limiting the commercialization of OPVs is their operational stability under environmental stressors such as heat, oxygen, moisture, and prolonged illumination[7]. Thermal stress is particularly critical, as elevated temperatures can cause changes within the active layer that result in higher recombination losses and reduce charge transport efficiency[4]. These forms of degradation result in reductions in power conversion efficiency (PCE), fill factor, and short-circuit current density and other relevant characteristics over time[7].

A factor contributing to the delay in research and commercialization, is the difficulty in predicting the operational lifetime of OPV devices due to multiple degradation mechanisms. To predict lifespans, accelerated aging methods, including thermal stress testing, are used to simulate long-term degradation and estimate device lifetimes using extrapolation. By monitoring efficiency decay under controlled thermal conditions, it is possible to extrapolate performance trends and approximate operational lifespan.

Fill factor (FF) measures the squareness of the J-V curve and decreases due to resistive losses, recombination and interfacial defects. Power conversion efficiency represents total energy conversion efficiency and declines as it captures all the degradation effects in the device. Short circuit current density indicates maximum photocurrent and is reduced due to UV-induced material degradation, especially at interfaces like ZnO. Open-circuit voltage reflects the maximum voltage and drops due to trap formation and increase non-radiative recombination.[8]

A significant literature gap is the testing of organic photovoltaics through heating at high temperatures for slower time frames to provide a relatively quicker approximation of the device's lifespan. Current life-span prediction methods[4,5], include T80 or T70 which involve degrading the device to approximately 70-80% of degradation parameters. These are longer and more expensive processes, which are accurate, however they do require more time and resources to undertake. This results in research pertaining to OPVs to slow down. A significant disadvantage to accelerated aging, is the high amount of uncertainty that it gives, meaning that the results are not accurate and require further corroboration[4,5].

In this study, an organic photovoltaic cell was subjected to thermal aging at 353K for varying durations. Device performance parameters were characterized at defined intervals, with special emphasis on efficiency degradation as it is a key indicator of degradation. The objectives of this paper are:

1. To Evaluate the rate at which an OPV cell degrades under thermal stress at 353 K
2. To estimate degradation parameters for OPV cells such as short circuit current density, open circuit voltage, fill factor & efficiency.
3. To estimate the lifespan of the OPV cell using degradation curves.

METHOD

Device architecture plays a critical role in determining both performance and operational stability. The architecture for the device used in these experiments is:

ITO/ ZnO / PTB7-Th : PC71BM / MoO_3 / Ag

The architecture is pictorially represented in Figure 1. In this configuration, indium tin oxide (ITO) serves as a transparent electrode, ZnO functions as the electron transport layer facilitating electron extraction and blocking holes, and MoO_3 acts as a hole transport layer that enhances hole extraction and energy level alignment. The silver top electrode completes the device while providing efficient charge collection. However, degradation processes can occur at interfaces, including metal diffusion, interfacial reactions, and transport layer instability, all of which may contribute to performance loss[7].

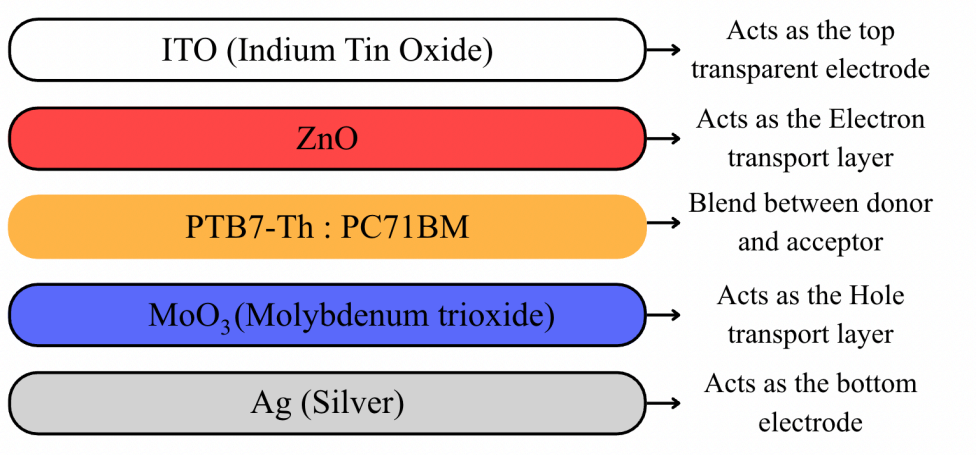

Figure 1: Architecture of the layers of the OPV used in the study

First, a single photovoltaic cell is fabricated. To do this the following steps are taken: First the ITO glass is thoroughly cleaned and treated with UV-ozone to remove impurities and improve its ability to collect electrons. Next, a thin ZnO layer is spin-coated and heated to form a smooth film that helps transport electrons efficiently. Then, the active layer is spin coated in a controlled environment to create a uniform light absorbing layer that generates charge. After that, a thin MoO_3 layer is deposited under vacuum to help extract holes and block unwanted electrons. Finally, a silver (Ag) electrode is added on top to complete the device and allow current to flow. This process can take up to 3 days to complete[9].

Figure 1: OPV being characterized using a solar simulator

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Post fabrication, its initial characterization is conducted using a solar simulator. This is necessary to get an initial reading to compare the final readings with. To do this the following steps are taken: The efficiency of an organic solar cell is measured through a series of simple testing steps under controlled conditions. First, the solar simulator is calibrated to standard sunlight to ensure accurate light intensity.

Next, the device is placed under illumination and connected to a measuring unit, where voltage is swept and the current is recorded to obtain the J-V curve. From this curve, key parameters mentioned above are calculated. Finally, an additional step that was not taken during this investigation can be taken: an EQE measurement is performed by shining different wavelengths of light on the device to check how efficiently it converts photons into current across the spectrum, confirming the accuracy of the results[10].

Next the cell is placed on an electric hotplate at 353 K and a stopwatch is started. Once the required time has lapsed, the cell is removed from the hot-plate and cooled to room temperature. It is then characterized at the same intensity using a solar simulator to calculate and compare the degradation parameters. For parameter measurements, to ensure precision, the digital characterization instrument recorded all measurements up to 5 significant figures, allowing for a lower percentage uncertainty for measurement values. . The parameters considered are explained in Table 1.

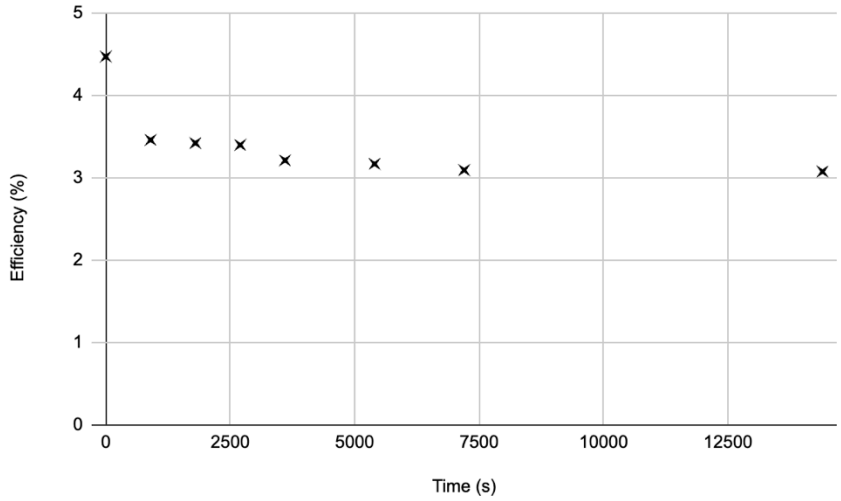
Independent Variable(s)	
1.	Time of heating (s): 900, 1800, 2700, 3600, 5400, 7200,14400
Dependent Variable(s)	
1.	Final efficiency (%)
2.	Short circuit current density (A/cm^2)
3.	FF (Fill factor) (%)
4.	Open circuit voltage (V)
Control Variable(s)	
1.	Initial Temperature (K)
2.	Heating temperature: 353 K
3.	Area of solar cells: 0.09 cm^2
4.	Intensity: 100 mW/cm^2

Table 1: Variables considered in the experiment categorized as Independent, Dependent & Control

RESULTS & DISCUSSION

Table 3.1: Experimental results of the characterization at different time intervals.

Time (s)	Efficiency (%)	Fill Factor (%)	Short circuit density (A/cm^2)	Open Circuit Voltage
0	4.47283	58.0003	-9.34779	0.824979
900	3.46108	50.3084	-8.102	0.784995
1800	3.42265	48.2892	-8.6668	0.78499
2700	3.39973	48.6067	-8.79807	0.814986
3600	3.21263	48.2032	-8.47011	0.794987
5400	3.17023	46.5388	-8.15552	0.804988
7200	3.09458	47.2138	-8.04235	0.814985
14400	3.07707	44.5106	-8.80658	0.814997



Graph 1:Scatter plot of the results obtained from table 3.1 of heating time (s) against efficiency in (%), showing a clear moderate negative co-relation between efficiency and time of heating

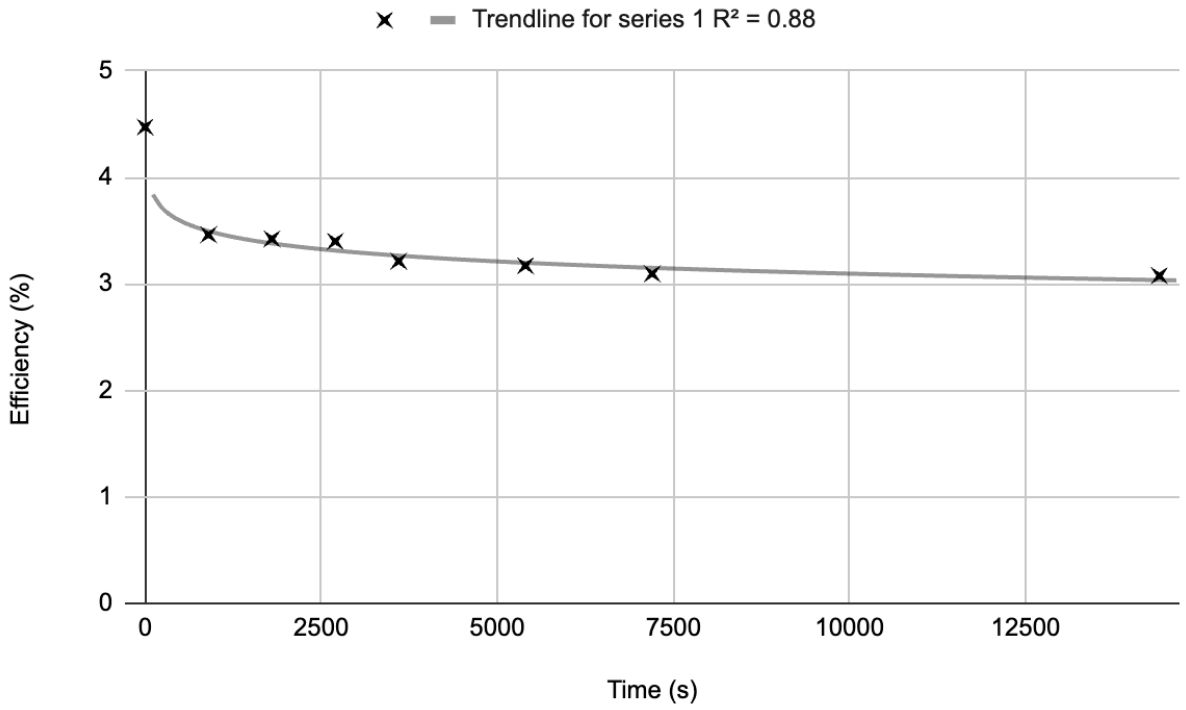
Graph 1.1 plots efficiency against time. The correlation between efficiency and time of heating, shows a clear negative correlation, corroborating the hypothesis of the results as described in section 2. Observing the data, it should be noted that there is a sudden initial drop in the efficiency that slows down as the device is further heated. In the first 900 seconds, the efficiency drops from 4.47 to 3.46, which is a 22.6% drop. Further the efficiency only dropped from 3.46 to 3.08, which is only a 11.1% drop. This non-uniform degradation rate suggests a more non-linear relationship.

Time (s)	Degradation (%)
900	22.6
1800	2.75
2700	1.64
3600	13.41
5400	3.04
7200	5.42
14400	1.25

As shown in table 2, the initial rapid degradation was the result of an initial burn in period. This cannot be directly proven using the available data, however the rapid initial decline in the efficiency is consistent with the burn-in degradation commonly reported in OPV cells. Following this initial phase, the degradation rate decreases, indicating a transition to a slower more stable degradation regime[11]. Burn in

degradation generally occurs due to rapid molecular rearrangement, donor-acceptor phase separation, interfacial relaxation or initial oxidation[12].

Graph 1.2 shows a logarithmic model of the degradation which shows the highest R^2 value of 0.88 when compared to linear and exponential models.



Graph 1.2: Exponential model of the rate of degradation of efficiency showing a gradually decreasing rate of degradation.

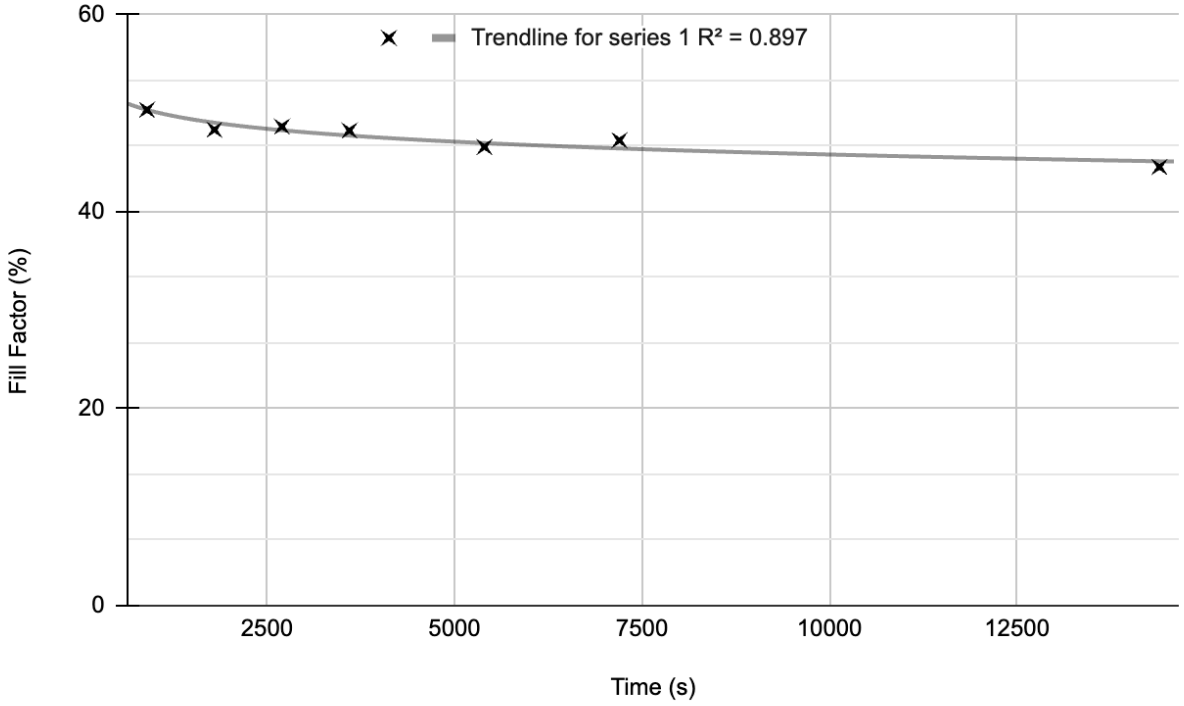
The curve can be expressed using the following equation where x is time in seconds.

$$\mathbf{1.62 + -0.166 \ln x}$$

A similar result is shown by the fill factor as well in Graph 2, which also displays a clear negative correlation. Fill factor degradation also shows the highest R^2 value when expressed using a logarithmic model, further corroborating its selection.

Time (s)	Degradation (%)
0	—
900	−13.27
1800	−4.01
2700	0.66
3600	−0.83
5400	−3.45
7200	1.45
14400	−5.72

The fill factor dropped from 58% to 44.51% over 14,400 seconds of heating, which amounts to a total loss of about 23%. Most of this loss happened within the first 900 seconds, after which the rate slowed considerably. This stage behavior is consistent with what is commonly observed as stated earlier in the analysis of the efficiency. The early rapid drop for FF is likely caused by damage at the device interfaces. At 353 K, metal contacts can begin to diffuse into the organic layer beneath them, and the hole transport layer can degrade its contact with the ITO electrode. Both effects increase the device's internal resistance, which directly reduces FF. The slower degradation that follows is typical of bulk processes: once the interfaces are damaged, further losses are driven by gradual changes in the internal structure of the active layer, which proceed more slowly and produce the flatter tail seen in the data. The small positive values at 2700 and 7200 seconds are within normal instrument measurement noise and do not indicate genuine recovery[13].



Graph 2: Logarithmic model of the rate of degradation of efficiency showing a gradually decreasing rate of degradation.

The curve can be expressed using the following equation where x is time in seconds.

63.1 + -1.88 ln x

For the above mentioned graphs (1.1,1.2, and 2), the values represent single measurements and not averaged replicates.

A point of concern in the study is the short circuit current density that shows almost no correlation with a surprising R^2 value of just 0.06. The varied results could be attributed to experimental inaccuracies and need to be tested using repeated trials in future iterations to ratify this concern,

Similarly, a weak slightly positive correlation was also observed between open circuit voltage and time of heating The line of best fit has a near zero gradient of 8.27×10^{-7}, meaning thermal degradation does not occur for that characteristic which is consistent with the literature defined cause for its degradation. Since UV exposure primarily causes OCV degradation, heating did not have an effect, further corroborating the cause of degradation within the experiment. The fact that the results showed a slightly positive correlation can be attributed to experimental inaccuracies, as the values obtained have very small differences, and

show a near zero rate of change with increase in time. The data should not be interpreted as an indicator that OCV increases when an OPV is heated.

Due to these reasons, these two characteristics were not used in predicting the lifespan of the cell for this specific study.

To extend the comparative analysis of thermal degradation, an Equivalent Thermal Aging Time(ETAT) metric is proposed. Unlike conventional lifetime metrics such as T80, which estimate operational lifetime under standard operating conditions, ETAT represents the projected exposure duration required for a photovoltaic parameter to reach a specified fraction of its initial value under the degradation kinetics observed during accelerated thermal aging. Consequently, ETAT should be interpreted as a standardized comparative measure of thermal endurance rather than a prediction for a real-world device lifetime.

For the present study, ETAT corresponding to a reduction to 70% of the initial parameter value was selected as the comparative threshold. This was chosen because the commonly used T80 criterion is reached during the initial burn-in period of the investigated device, limiting its usefulness for comparing longer-term degradation behavior, whereas lower thresholds require excessive extrapolation beyond the experimental data.

Using the logarithmic degradation model for PCE described in equation 1, the time required for PCE to degrade to 70% of its original value would be 7.0×10^3 seconds, or roughly 2.2 hours.

In comparison, the degradation model for FF showed a much higher endurance, giving a figure of 1.57×10^5 seconds, amounting to about 43.78 hours. However, this approximation is an extrapolation which is much further from the measured values. This results in the approximation for FF to be limited in reliability.

The proposed ETAT metric is not intended to predict operational lifetime. Instead, it provides a standardized means of comparing the relative thermal endurance of OPV devices under identical accelerated aging conditions. Because ETAT is calculated directly from experimentally obtained degradation equations, it can be readily applied to different materials, fabrication methods, and device architectures, enabling rapid comparative assessment without requiring prolonged real-time aging experiments. Future studies involving multiple OPV systems may establish whether ETAT correlates with operational lifetime under standard environmental conditions, thereby extending its applicability beyond comparative thermal stability analysis.

CONCLUSION

In this study, a single solar cell was fabricated to test the hypothesis that it will display accelerated thermal aging when exposed to a temperature of 353 K for a prolonged period. The experiments included

a characterization of the power conversion efficiency, fill factor, open circuit voltage and short-circuit current density.

Circling back to the initial hypothesis, it was predicted that the results will show a negative correlation in the characteristics that are assessed. However, the study showed that this was only true for 2 of the 4 characteristics that we examined. Due to the weakness in the correlations in the ones that didn't show the expected correlation, they were discarded from extrapolation.

In addition to evaluating degradation behavior, this study introduces the Equivalent Thermal Aging Time (ETAT**)** as a standardized comparative metric for accelerated thermal aging studies. Rather than representing the operational lifespan of an organic photovoltaic device, ETAT quantifies the projected thermal exposure duration required for a device parameter to reach a predefined degradation threshold under accelerated aging conditions. By providing a simple, reproducible metric derived directly from experimentally obtained degradation trends, ETAT enables rapid comparison of the relative thermal endurance of different OPV materials, fabrication techniques, and device architectures. While further validation across multiple devices and correlation with long-term operational aging are required, the proposed metric offers a practical framework for preliminary material screening, quality assessment, and accelerated device optimization.

A major limitation of this experiment was that a single fabricated cell was used. This results in there being limited weight towards the obtained ETAT approximations and R^2 values. In the scope that this study was conducted, only a single fabricated device could be obtained, thus not allowing for repeated trials. However, the results from the trial conducted were validated using mechanistic analysis which allowed for the correlation observed to be backed by literature. This is why to a certain extent the experiment can be used as a proof of concept, motivating further research regarding the comparative ETAT metric.

Future research should focus on validating the proposed Equivalent Thermal Aging Time (ETAT) metric across multiple OPV material systems and device architectures to determine its effectiveness as a comparative indicator of thermal stability, and eliminating the single trial limitation mentioned earlier. Fabricating identical devices and subjecting one set to accelerated thermal aging while monitoring another under standard operating conditions would enable the relationship between ETAT and actual operational lifetime to be established. Such validation would determine whether accelerated thermal degradation can serve as a reliable surrogate for long-term stability testing. Comparison with T80 and T70 lifespans and ETAT approximations could also allow for evaluation of the accuracy of extrapolations. If successfully correlated, the methodology could provide researchers and manufacturers with a rapid, standardized tool for comparative material screening, optimization of fabrication processes, and preliminary quality control, substantially reducing the time required to evaluate the thermal stability of emerging OPV technologies.

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