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School of Science
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SCIENTIFIC REPORT

Melanin-Perovskite Composites for Photovoltaics

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Bauru

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Summary

1. Project Abstract

This project aims to explore the potential of perovskite solar cells (PSCs) with melanins as organic additives. PSCs represent a promising alternative to silicon solar cells due to their comparable efficiency and lower production cost. However, challenges such as long-term stability and efficiency persist. The goal is to investigate the influence of melanins on the stability, efficiency, and durability of PSCs, by exploring their defect passivation, metal chelation, and moisture resistance properties. The project includes establishing preparation procedures, structural, morphological, and electrical characterization, as well as manufacturing and device analysis. This project aims to contribute to significant advancements in solar energy technology, driving the transition to a renewable and sustainable energy matrix.

Keywords: Renewable energy; Melanin; Charge transfer; Photovoltaic devices; Perovskite solar cells.

2. Report Abstract

During the period covered by this scientific report, the following activities were achieved:

- Writing of the investigation of $PC_{60}DB$ aging effects in polymeric ETLs, comparing iodine- and bromine-terminated main-chain poly(fullerene)s;
- Investigation of sulfonated-eumelanin as an additive in the perovskite (PVK) layer;
- Investigation of solvent engineering for sulfonated-eumelanin passivation layer on top of PVK;
- Investigation of eumelanin deposition as an interfacial passivation between ETL and PVK using AISSP;
- Additional research activities, including the completion of ongoing studies and scientific collaborations that resulted in, or are expected to result in, publications in international peer-reviewed journals and a book chapter.

3. Activities & Achievements

3.1 $PC_{60}DB$ aging effect on the electron transport layer of PSC

During the first month, the analysis and discussion of a study comparing two materials were completed. The work focused on two main-chain poly(fullerene)s, $PC_{60}DB_{(IMP)}$ and $PC_{60}DB_{(ATRAP)}$, which differ only in their terminal halogen groups.[1] Prior to device fabrication, both materials were stored under nitrogen, in the dark, and at room temperature under three aging conditions: fresh (ca. 20 days old), mid-aged (ca. 6 months old), and aged (ca. 11 months old), enabling a consistent comparison of their behavior.

The current density-voltage (*J*-*V*) characteristics and the external quantum efficiency (EQE) spectra with their integrated current curves of the $PC_{60}DB$-based electron transport layer (ETL) of the PSC are exhibited in Figure 1(a, b) and Figure 1(c, d), respectively.

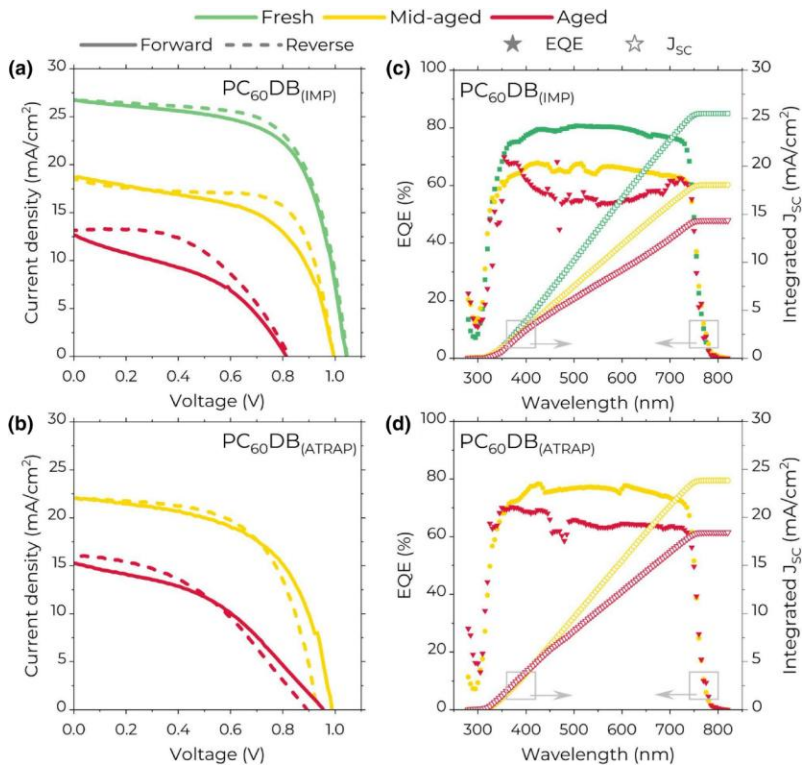

Figure 1. *J–V* characteristics of inverted PSCs and EQE spectra and corresponding integrated J_{SC} using (a, c) $PC_{60}DB_{(IMP)}$ and (b, d) $PC_{60}DB_{(ATRAP)}$ as ETL under different aging conditions.

Since the $PC_{60}DB$-based polymers were aged independently in the solid state under an inert atmosphere and in the dark, and both the PVK and the polymers were freshly processed for each device, the observed trends must originate from inherent changes within the polymers and how these changes affect interfacial interactions upon integration.

Devices containing the iodine-terminated polymer $PC_{60}DB_{(IMP)}$ exhibit a noticeable loss in efficiency and increased hysteresis as they age, likely due to instability of the carbon-iodine bond.[2] Because this bond is relatively weak, gradual chemical changes such as bond cleavage, molecular rearrangement, or crosslinking can occur over time, even in the solid state. These changes may negatively affect the interaction between the polymer and the PVK surface, increasing interfacial trap states that hinder charge extraction and favor recombination, possibly worsened by the aggregation of excess C_{60} domains.[3,4] In contrast, devices based on the bromine-terminated polymer $PC_{60}DB_{(ATRAP)}$ maintain more stable performance and show reduced hysteresis after aging. This behavior is attributed to the stronger and more stable carbon-bromine bond,[2] which better resists degradation and helps preserve a stable interface, potentially improving interfacial contact through mild structural reorganization over time.[5]

Although these changes may not be visible at the macroscopic level, they can still interfere with charge movement across the interface, ultimately affecting the photovoltaic efficiency. Taken together, the results show that even relatively small differences in halogen chemistry can have a meaningful impact on interfacial behavior, with bromine termination helping to create a more stable and reliable interface.

These observations point to the significant influence of end-group chemistry on the functional stability of polymeric ETLs. Although both materials share a similar backbone, the difference in halogen termination leads to distinct outcomes after storage. We hypothesize that, due to the very weak carbon-iodine bond, iodine promotes gradual degradation, whereas bromine helps preserve or even slightly improve the material's interfacial performance.[1]

A more in-depth discussion of the parameters and the methodology used is provided in the article “Impact of polymer aging on main-chain poly(fullerene)s with halide chain-ends for inverted perovskite solar cells” by João V. Paulin *et al.* (Article xviii, in section 4.2).

3.2 Sulfonated-eumelanin as an additive in PVK matrix

Although preliminary studies indicated that the use of eumelanin as an additive in the perovskite layer did not improve device performance, we hypothesized that this was due to the relatively high additive concentration initially employed. To test this assumption, the eumelanin concentration was reduced to one quarter of its original value, and a new set of devices was fabricated and electrically characterized. This approach allowed us to evaluate the impact of eumelanin, where interfacial stabilization could be achieved without strongly hindering charge transport.

We first examine the overall photovoltaic performance. Current-voltage measurements (Figure 2) show that devices treated with sulfonated-eumelanin (ST) display a moderate reduction in initial PCE compared to pristine cells. This decrease mainly arises from lower FF and J_{SC}, while the V_{OC} remains largely unchanged. The stable photovoltage indicates that the bulk properties of the perovskite absorber are preserved and that the initial performance loss is mainly linked to interfacial effects rather than bulk degradation.[6,7]

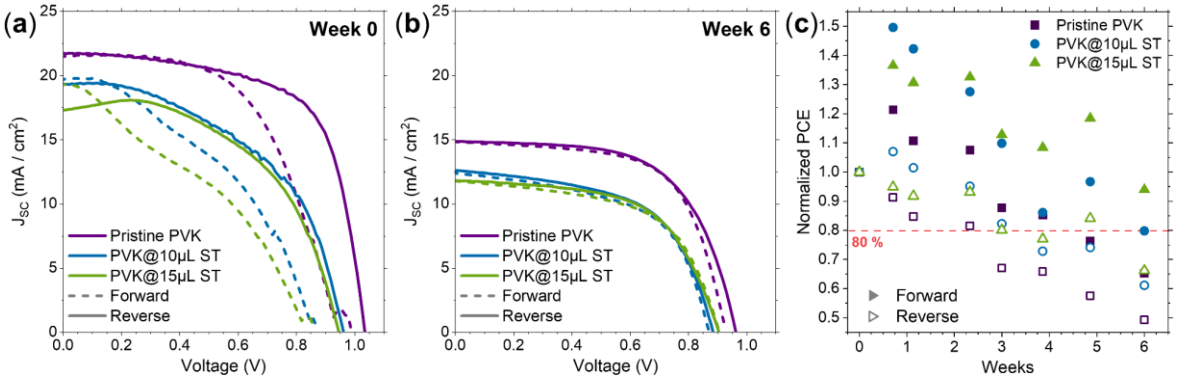

Figure 2. (a, b) Current-voltage (J-V) characteristics of pristine and ST-treated PSCs measured under forward and reverse scan directions at (a) Week 0 and (b) Week 6. (c) Normalized power conversion efficiency (PCE) as a function of aging time under forward and reverse scan directions.

To determine whether the reduced current originates from optical losses or electronic effects, we next analyze the EQE. ST-treated devices show a uniform decrease in EQE across the visible spectrum, without changes in spectral shape or absorption onset. This result rules

out changes in light absorption or bandgap energy and instead points to reduced charge-collection efficiency.[8] The close agreement between current densities obtained from EQE integration and J-V measurements confirms that the observed losses are electronic and interfacial in nature.

After establishing that charge extraction is affected, we investigate the devices' electronic properties using Mott-Schottky. ST-treated devices exhibit higher initial carrier densities than pristine cells, consistent with defect passivation at grain boundaries and crystal surfaces.[9,10] During aging, pristine devices show a gradual decrease in carrier density, whereas ST-treated devices retain higher carrier densities. This behavior indicates that ST helps stabilize the interfacial electronic environment as the devices age.[9,10]

To understand how these changes influence recombination, we analyze light-intensity-dependent measurements. At early stages, all devices exhibit nearly linear J_{SC} scaling with light intensity, indicating efficient charge extraction under short-circuit conditions. Differences become evident in the V_{OC} response. Pristine devices exhibit ideality factors slightly above 2, a characteristic of trap-assisted recombination.[6,11–13] ST-treated devices show a more complex initial response, suggesting temporary activation of interfacial states. With aging, pristine devices experience increased trap-assisted recombination, whereas ST-treated devices show a gradual reduction in ideality factor, indicating suppression of defect-related recombination and a shift toward more intrinsic recombination processes.[6,11–13]

These electronic trends are reflected in the stability of the devices. Aging tests reveal a clear difference between pristine and ST-treated PSCs. Pristine devices undergo strong performance degradation, retaining only about half of their initial efficiency. In contrast, ST-treated devices degrade more slowly, retain performance better, and exhibit reduced variability between devices. Although their absolute efficiency remains lower, ST-treated devices preserve a larger fraction of their initial performance, highlighting a clear trade-off between efficiency and stability.

To bring together the effects of charge transport, recombination, and interfacial processes, we finally perform EIS. At early stages, ST-treated devices show higher transport resistance, consistent with their lower fill factor and stronger hysteresis. Under illumination, impedance measurements reveal modified interfacial charge accumulation and relaxation

behavior.[14–17] With aging, pristine devices develop additional impedance features associated with interfacial degradation and ion migration. In contrast, ST-treated devices show a largely stable impedance response over time, indicating suppressed degradation and stabilized interfacial energetics.[14–17]

Overall, this study shows that ST initially impairs charge transport due to distributed grain-boundary modification, but progressively stabilizes the interfacial electronic structure during operation. By reducing defect-related recombination and limiting degradation, ST improves device stability at the cost of initial efficiency. These results demonstrate that bio-inspired interfacial modifiers can be used to intentionally tune the balance between efficiency and stability in PSCs, emphasizing that long-term durability is as important as peak performance when evaluating device optimization strategies.

A more in-depth discussion of the parameters and the methodology used is provided in the article "Defect Passivation-Stability Trade-Off in Perovskite Solar Cells Induced by Sulfonated-Eumelanin" by João V. Paulin *et al.* (Article i, Section 4.1).

3.3 Eumelanin as a passivation layer on top/on bottom of the PVK

Our first attempt at using eumelanin as a passivation layer for PSC followed the same procedure as in the preliminary results shown in the project. However, that procedure proved not be reproducible.

We observed that ST doesn't dissolve well in chlorobenzene (CB), leading to agglomerates that could degrade device performance. Since S-melanin is more soluble in DMSO and DMF, solvents that also dissolve PVK, we created a highly concentrated solution of S-melanin in DMSO or DMF and then diluted it in CB. The result was a stable and aggregate-free solution.

We then tested two things:

- Using the ST mixture as an anti-solvent during PVK deposition.
- Applying it as an additional layer on top of PVK.

Anti-solvent treatments are key in forming high-quality perovskite films. They speed up crystallization, reduce defects, and improve morphology.[18] For reference, Figure 1a shows the PVK film on glass without added eumelanin.

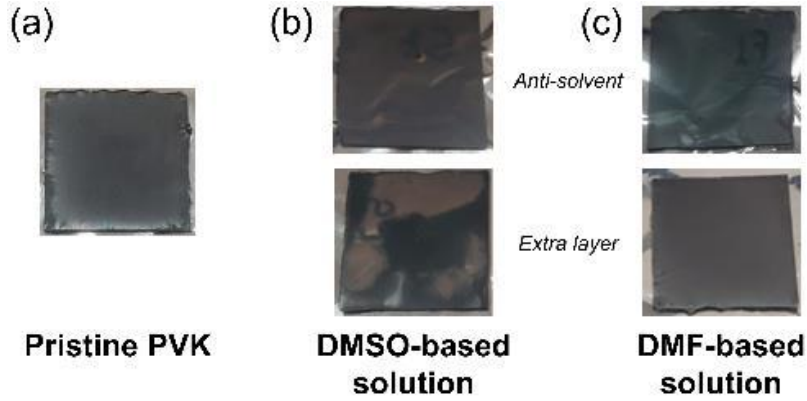

Figure 3. Comparison of PVK films processed with different S-melanin solvent mixtures: (a) pristine PVK, (b) DMSO-based, (c) DMF-based.

DMSO-based melanin mixtures didn't perform well, especially when used as a top layer. That's likely because the DMSO partially dissolved the PVK film (Figure 3b). DMF-based melanin solutions performed better, but the films appeared more transparent, possibly indicating slight PVK dissolution (Figure 3c). Additionally, they weren't as black as standard films. A possible explanation is increased reflection rather than material changes. In light of these changes in PVK, we move toward a passivation layer on the bottom of PVK.

To overcome the potential dissolution of the PVK layer during eumelanin deposition, a device featuring the configuration FTP/Nb_2O_5/TiO_2/eumelanin/PVK/Spiro-OMeTAD/Au was assembled. In this structure, eumelanin is introduced as a thin passivation interlayer between the ETL and the PVK following two different processing routes: 1) eumelanin without polymerization treatment (0h AISSP), and 2) eumelanin subjected to 3 hours of ammonia-induced solid-state polymerization (AISSP[19]).

The goal of introducing the AISSP processing strategy was to reduce eumelanin polymerization, as higher polymerization is associated with stronger optical absorption. By limiting polymer growth, the optical density of the eumelanin layer is lowered, reducing its ability to act as an optical filter. As a result, a larger fraction of incident light can reach the underlying PVK layer, which is expected to favor charge generation.

In addition to its optical role, controlling the polymerization state of eumelanin may also influence film morphology and interfacial properties. A less or moderately polymerized

eumelanin layer can form a thin, uniform interlayer, helping to passivate defects at the ETL/PVK interface while minimizing parasitic absorption. This balance between optical transparency and interfacial passivation is critical for achieving stable and reproducible device performance

Devices stored in the glove box exhibited more stable and consistent photovoltaic behavior across all configurations (Figure 4, top). Under these controlled conditions, device performance was reliable, and inter-measurement variability remained low, indicating good reproducibility.

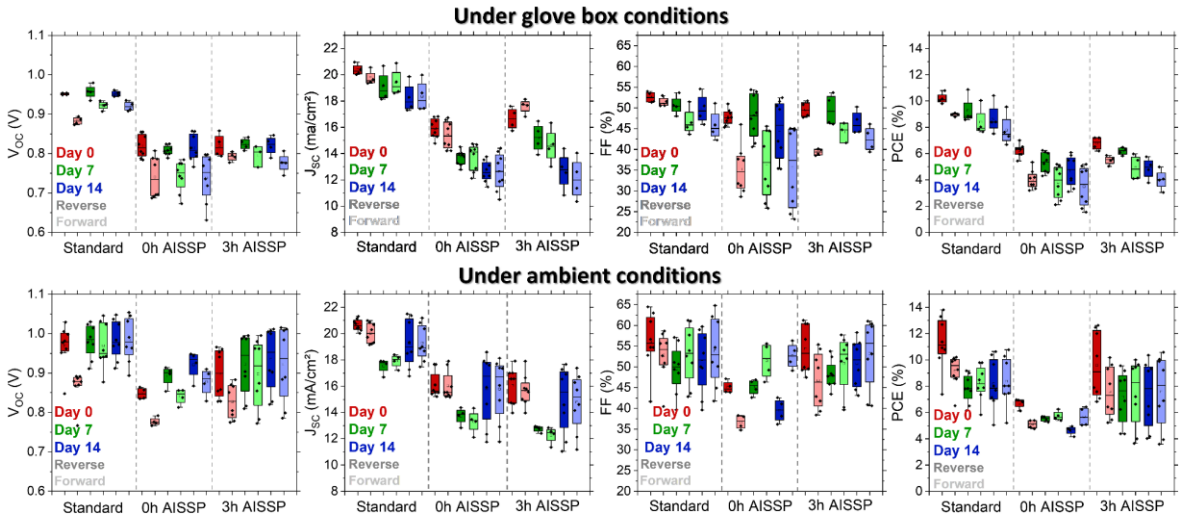

Figure 4. Photovoltaic parameters of devices measured under glove box (top row) and ambient (bottom row) conditions. The box plots summarize the distributions of open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and power conversion efficiency (PCE) for standard devices and devices incorporating eumelanin processed with 0 and 3 h of AISSP. Measurements were performed on Day 0, Day 7, and Day 14, with both forward and reverse J-V scans included.

When the devices were exposed to ambient humidity and oxygen, a clear degradation trend was observed (Figure 4, bottom). The photovoltaic parameters began to drift, and the performance became less predictable, particularly for devices incorporating eumelanin without AISSP treatment. In contrast, devices processed with 3 hours of AISSP showed

improved stability. Even under harsher environmental conditions, these devices maintained their performance more effectively than their untreated counterparts. This behavior suggests that AISSP provides meaningful protection against environmental stress, likely because polymerization promotes a denser and ordered eumelanin structure that is less permeable to moisture and oxygen and potentially more robust at the molecular level.

Notably, even under glovebox storage, where devices generally perform better, the AISSP-treated eumelanin devices continued to stand out. Their photovoltaic response was more consistent, and the distribution of measured parameters was narrower. This observation indicates that AISSP may improve not only environmental resistance but also intrinsic material properties, such as bulk morphology and interfacial quality.

The difference between forward and reverse J-V scans is commonly associated with device instability and charge trapping. In this study, hysteresis was reduced in devices treated with AISSP under both storage conditions (Figure 4). This result indicates improved charge transport and a lower trap-state density within the device.

Overall, these findings demonstrate that material engineering through AISSP is a promising strategy for enabling the use of bio-derived materials, such as eumelanin, in photovoltaic applications. Ongoing work focuses on optimizing both the AISSP process and the charge transport properties of eumelanin-based layers. By fine-tuning the conditions for ammonia-induced polymerization, we aim to further enhance film integrity while improving charge-transport efficiency.

3.5 Final considerations

During this period, I was also actively involved in the research activities of other group members, contributing to a broad range of projects on PSCs, bioelectronic devices, and energy storage systems. These collaborative efforts yielded several scientific outputs at various stages of publication, see Section 4 (*Scientific Contributions*).

In the field of photovoltaic devices, I'm contributing to studies on melanin-based dye-sensitized solar cells, focusing on optimizing the DHI/DHICA ratio and sulfonation to enhance device performance (Contribution ii). This work is conducted through an international collaboration among institutions in Brazil, South Korea, and Singapore.

Additional contributions include studies on solvent engineering of monoFAPA electron transport layers (Contribution iii), the synergistic role of aluminum and zinc oxides in Nb_2O_5-based ETLs (Contribution vii), and detailed analyses of recombination mechanisms and ideality factor extraction in PSCs using diode-based approaches (Contribution viii).

Beyond photovoltaics, I'm also participating in collaborative research on eumelanin-based materials for emerging technologies. This includes an international study employing quasi-elastic neutron scattering to probe hydrogen dynamics in hydrated eumelanins (Contribution iv), developed in collaboration with research groups in the United Kingdom, Russia, and Brazil. I also contributed to investigations of the paramagnetic properties of eumelanin with controlled DHI/DHICA composition (Contribution xviiii), in collaboration with partners in Brazil and Italy. In addition, I contributed to studies on the electrochemical behavior of non-functionalized and sulfonated melanins under different pH conditions (Contribution ix), providing further insight into charge transport and redox processes in these systems. I was also involved in the analysis and development of an organic electrochemical transistor with an eumelanin-based channel (Contribution xiv), which provides another piece of the puzzle regarding charge-carrier mechanisms in these materials. I also contributed to studies exploring melanin derived from black soldier fly as a material within a circular economy framework (Contribution xi).

My involvement further extended to energy storage and sustainable electronics applications. These efforts include studies on sulfur-functionalized melanin for enhanced charge storage in supercapacitor devices (Contribution xixii), developed through a collaboration between Brazilian and Canadian institutions, and on spray-coated melanin/PEDOT:PSS films for organic electrochemical transistors (Contribution xviii).

In addition to experimental research articles, I contributed to a book chapter on the role of eumelanin in bioelectronic interfaces and eco-friendly technologies (Contribution xxii). I was also invited to submit a review article to *npj Flexible Electronics* on eumelanin as a multifunctional platform for sustainable technologies (Contribution viii), with the article processing charge waived.

Complementing these research activities, I participated in the Young Voices in the Chemical Sciences for Sustainability Global Essay Competition, organized by the

International Organization for Chemical Sciences in Development (IOCD). My essay, entitled “Waste alchemy in the age of industry 5.0: rethinking sustainable electronics,” was selected as the Regional Winner for the Latin America & Caribbean region and was subsequently published in RSC Sustainability (Contribution ix).

Finally, during a technical visit to UNESP in Presidente Prudente, I was invited to serve as an evaluator for oral presentations at the POSMAT Technical Meeting held at the institution, contributing to the assessment of graduate research and to scientific exchange within the academic community. I also acted as a peer reviewer for scientific manuscripts submitted to international journals, including Process Biochemistry, Chemical Physics Impact, Materials Today Advances, International Journal of Biological Macromolecules, Progress in Biomedical Engineering, Journal of Materials Chemistry A, Industrial Crops & Products, reflecting recognition of my expertise in the field of eumelanin-based materials.

4. Scientific Contributions

4.1 Publications in preparation

i. Defect Passivation-Stability Trade-Off in Perovskite Solar Cells Induced by Sulfonated-Eumelanin. **João V. Paulin**, Vitor Pereira, Gabriel L. Nogueira, Carlos F. O. Graeff.

ii. Melanin-Based Dye Sensitized Solar Cells: Optimizing the DHI/DHICA Ratio and Sulfonation for Enhanced Photovoltaic Performance. Noah Al-Shamery, Eunyeong Song, **João V. Paulin**, Natan L. Nozella, Nayrim Brizuela Guerra, Thomas Bredow, Carlos F. O. Graeff, Jun-Hyeok Park, Pooi See Lee, Tae-Hyuk Kwon.

iii. Solvent Engineering of monoFAPA Electron Transport Layers for Efficient and Stable Perovskite Solar Cells. Silvia L. Fernandes, Hameed Ullah, Sherdil Khan, **João V. Paulin**, et al..

iv. Quasi-Elastic Neutron Scattering of Hydrated Eumelanins to Probe Hydrogen Motion. A. Bernardus Mostert, **João V. Paulin**, Carlos F.O. Graeff, Hamish Cavaye, Ian Silverwood, Konstantin A. Motovilov.

v. Synergistic Effects of Aluminum and Zinc Oxides in the Nb_2O_5 Electron Transport Layer of Perovskite Solar Cells. Inaiara L. Rodrigues, Gabriel L. Nogueira, **João V. Paulin**, Sergio S. Cava, Carlos F. O. Graeff.

vi. Ideality Factor Extraction and Recombination Mechanism in Perovskite Solar Cells Using Diode Analysis. Gabriel L. Nogueira, **João V. Paulin**, Inaiara L. Rodrigues, Sergio S. Cava, Carlos F. O. Graeff.

vii. Local reactivity and chemical softness analysis of Remdesivir and Favipiravir as RNA synthesis inhibitors of SARS-CoV-2. Alex P. Coleone, **João V. Paulin**, Augusto Batagin-Neto

viii. Eumelanin as a Flexible Platform for Sustainable and Biointegrated Technologies. Natan L. Nozella, João V. M. Lima, Nayrim B. Guerra, Vitor Pereira, Carlos F. O. Graeff, **João V. Paulin**.

4.2 Published studies in the period covered by this report duration

ix. Electrochemical behavior of non-functionalized and sulfonated melanins at different pH values. Nayrim B. Guerra, João V. M. Lima, **João V. Paulin**, Natan L. Nozella, Miguel H. Boratto, Gabriel L. Nogueira, Carlos C. B. Bufon, Carlos F. O. Graeff. Polymer International. v. 73, p. 992-1000, 2024. DOI: https://doi.org/10.1002/pi.6678.

x. Sustainable brain-inspired electronics: digging into natural biomaterials for healthcare applications. **João V. Paulin**, Carlos C. B. Bufon. RSC Sustainability. v. 2, p. 3235-3263, 2024. DOI: https://doi.org/10.1039/D4SU00459K.

xi. Exploring the chemistry of black soldier fly melanin, a material for a circular economy. A. B. Mostert, S. Mattiello, S. Li, G. Perna, et al.. Materials Advances, v. 5, p. 8986-8999, 2024. DOI: https://doi.org/10.1039/D4MA00825A.

xii. Synthesis of biochar and its metal oxide composites and application on next sustainable electrodes for energy storage devices. Bruna A. Bregadiolli, Glauco M. M. M. Lustosa, **João V. Paulin**, Waldir A. Bizzo, Lauro T. Kubota, Shuguang Deng, Talita Mazon. Next Materials. v. 7, p. 100444, 2025. DOI: https://doi.org/10.1016/j.nxmate.2024.100444.

xiii. Radical and Environmentally Friendly Route to Poly(fullerene)s Incorporating C_{60}, C_{70}, and PCBM. Eleftheria Batagianni, Olivier Doat, Nicolas Elissalt, Douvotsu E. M. Bouassa, et al.. Macromolecules. v. 58, p. 1686–1704, 2025. DOI: https://doi.org/10.1021/acs.macromol.4c02154.

xiv. Probing n-type Conduction in Eumelanin using Organic Electrochemical Transistors. ACS Applied Electronic Materials. Natan L. Nozella, **João V. Paulin**, Gabriel L. Nogueira, Nayrim B. Guerra, Rafael F. de Oliveira, Carlos F. O. Graeff. v. 7, p. 3176–3181, 2025. DOI: https://doi.org/10.1021/acsaelm.5c00293.

xv. Waste alchemy in the age of industry 5.0: rethinking sustainable electronics. **João Vitor Paulin**. *RSC Sustainability*. v. 3, p. 4878-4881, 2025. DOI: https://doi.org/10.1039/D5SU90048D.

xvi. Spray-Coated Melanin/PEDOT:PSS Films for Sustainable Organic Electrochemical Transistors. Natan L. Nozella, Gabriel L. Nogueira, **João V. Paulin**, Rafael F. de

Oliveira, Carlos F. O. Graeff. *J. Vis. Exp.*, v. 224, p. e69354, 2025. DOI: https://doi.org/10.3791/69354.

xvii. In-Depth Analysis of the Paramagnetic Properties in DHI/DHICA-Controlled Eumelanin. **João V. Paulin**, João P. Cachaneski-Lopes, Emanuele Carrella, Alessandro Pezzella, Augusto Batagin-Neto, Carlos F. O. Graeff. *ACS Omega*. v. 10, p. 54919-54928, 2025. DOI: https://doi.org/10.1021/acsomega.5c08896.

xviii. Impact of polymer aging on main-chain poly(fullerene)s with halide chain-ends for inverted perovskite solar cells. **João V. Paulin**, Gabriel L. Nogueira, Douglas H. N. Santos, Marco Antônio G. B. Gomes, Valdemiro P. Carvalho-Jr, Luiz C. Silva Filho, Roger C. Hiorns, Carlos F. O. Graeff. *Polymer International*. *Early View*, 2025. DOI: https://doi.org/10.1002/pi.70054.

xix. Enhancing Charge Storage in Melanin via Sulfur Functionalization for Supercapacitors Applications. João V. M. Lima, **João V. Paulin**, Pegah E. Moghaddam, Hadis Zarrin, Carlos F. O. Graeff. Journal of Energy Storage, v. 149, p. 120268, 2026. DOI: https://doi.org/10.1016/j.est.2025.120268.

xx. Eumelanin as a Key Material in Bioelectronic Interfaces and Eco-Friendly Technologies. Natan Luis Nozella, **João Vitor Paulin**, João Victor Morais Lima, Carlos Frederico de Oliveira Graeff. *In Press*, 2026, Springer Nature.

5. Supervisor Evaluation

I have carefully evaluated the activities and results presented in this final report and consider that the research was conducted in a highly satisfactory manner. The proposed objectives were successfully achieved, and the work demonstrates consistency, technical quality, and significant scientific progress throughout the fellowship period.

The report accurately documents the activities carried out and the results obtained, fully meeting the project's expectations. Based on this evaluation, I approve the present final report.

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