Optimizing the Processability of Phenothiazine-Modified PTAA Hole Transporting Materials in Green Solvents: a Step Toward Sustainable Flexible Perovskite Solar Cells.

Daniel Alencar [a, f], Francesca De Rossi [b], Giuseppe Ferraro [c], Matteo Bonomo [a], Barbara Paci [d], Amanda Generosi [d], Pierluigi Quagliotto [a], Claudia Barolo [a, e], Francesca Brunetti [b], Giulio Koch [b]

[a] *Dipartimento di Chimica, NIS Interdepartmental and INSTM Reference Centre, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 Torino, Italy*

[b] *Chose- Centre for Hybrid and Organic Solar Energy, Department of Electronic Engineering, University of Rome 'Tor vergata', via del Politecnico 1, 00133 Roma, Italy*

[c] *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129-Turin*

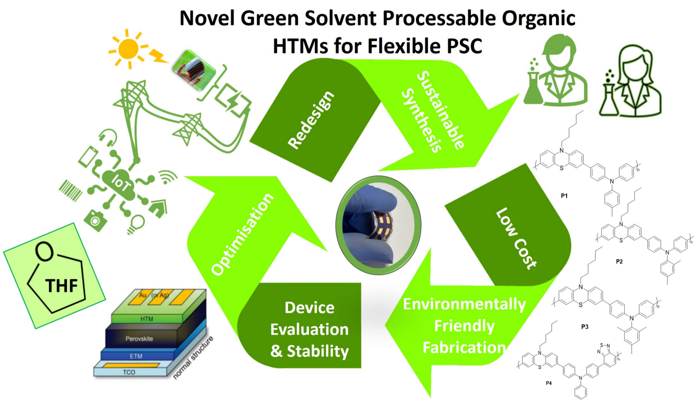
[d] *Istituto di Struttura della Materia - CNR (ISM-CNR), Via del Fosso del Cavaliere 100, 00133 Rome, Italy*

[e] *ICxT Interdepartmental Centre Università degli Studi di Torino, Lungo Dora Siena, 100, Torino, Italy*

[f] *IUSS Pavia, Palazzo del Broletto, Piazza della Vittoria, 15, 27100 Pavia PV*

Materials for Sustainable Development Conference (MATSUS) (/Materials-for-Sustainable-Development-Conference)
Proceedings of MATSUS Spring 2024 Conference (MATSUS24)
#SusPer - Sustainability of halide perovskites
Barcelona, Spain, 2024 March 4th - 8th
Organizers: Francesca Brunetti and Iris Visoly-Fisher

Oral, Daniel Alencar, presentation 396
DOI: https://doi.org/10.29363/nanoge.matsus.2024.396 (https://doi.org/10.29363/nanoge.matsus.2024.396)
Publication date: 18th December 2023



Recently, flexible Perovskite Solar Cells (f-PSC) have been a growing niche within the research on PSC with the aim of broadening its range of applications toward light-weight Building Integrated Photovoltaics (BIPV), Internet of Things (IoT), portable electronics and even space applications. [1] This is mainly related to the higher power-to-weight (PWR) ratio of flexible devices compared to glass-based counterparts. [2] However, to unlock f-PSC full potential, research must focus on boosting the sustainability of the cell, besides its performance and stability. Sustainability concerns mainly deal with the use of organic Hole Transport Materials, whose synthesis has a huge impact on the overall score of the final device, especially when polymeric HTMs are considered.

Indeed, state of the art polymeric HTMs, such as poly(triarylamine) (PTAA), are still processed with toxic solvents such as chlorobenzene (CB), dichlorobenzene (DCB) or toluene, [3] which pose an obvious barrier to the upscaling of this technology. As the literature in green-solvent-deposition charge transport layers is still scarce, we present a new set of HTMs processed using Tetrahydrofuran (THF) that is a non-aromatic, non-halogenated, cheap low environmental risk solvent and has low human health toxicity. [4] We find that the choice of green solvent processable HTM's is a defining parameter for polymers when compared to small molecules, due to their limited solubility resulting from prioritising extended π-π conjugation frameworks, [5] yielding this study even more promising to the sustainable upscaling of f-PSCs.

Throughout this work, the four newly synthetized HTMs incorporate additional scaffolds to modify the conventional triphenylamine moiety characterizing the PTAA, with the scope of improving their solubility in THF. Aiming at this, the phenothiazine moiety was opted due to its good solubility in common organic solvents, high chemical stability, high tunability, high hole mobilities and extremely low cost. [6] The methyl substitution of the TPA phenyl unit was also altered to evaluate the trade-off effect on solubility and polymeric chain packing. As an alternative to PTZ-PTAA polymers, we also considered the benzothiadiazole unit due to its electron deficient system, [7] giving rise to the ability to tune the electronic properties of the final HTM. To the best of our knowledge, the coupling of these three scaffolds in a polymeric system has never been reported.

The novel polymers P1-4 were successfully synthesized using specially optimized protocols, adhering to Green Chemistry Principles, [8] and thoroughly characterized in terms of structural, optoelectronic, and thermal properties. All the polymers have appropriate band gaps and a HOMO energy levels aligned with the valence band of the active layer, assuring fast and efficient charge extraction. Additionally, they are thermally stable well above operating standard temperatures and could withstand high annealing temperatures.

After their characterization, P1-4 were implemented as HTMs on flexible n-i-p devices using PTAA as the reference. Results reveal that P1-4 can achieve competitive efficiencies compared to PTAA when the latter is processed with toluene, and even outperform the reference processed with THF.

This work will serve as a baseline for the pursuit of increasing environmentally friendly, solution processable materials (e.g BioRenewable sources, 2-MeTHF), paving the way toward highly efficient, stable, and sustainable f-PSCs to enter the market.

References:

[1] De Rossi, F.; Renno, G.; Taheri, B.; Yaghoobi Nia, N.; Ilieva, V.; Fin, A.; Di Carlo, A.; Bonomo, M.; Barolo, C.; Brunetti, F., Modified P3HT materials as hole transport layers for flexible perovskite solar cells. Journal of Power Sources 2021, 494. (https://doi.org/10.1016/j.jpowsour.2021.229735)

[2] Mishra, S.; Ghosh, S.; Singh, T., Progress in Materials Development for Flexible Perovskite Solar Cells and Future Prospects. ChemSusChem 2021, 14 (2), 512-538. (https://doi.org/10.1002/cssc.202002095)

[3] Zhang, M.; Xin, D.; Zheng, X.; Chen, Q.; Zhang, W.-H., Toward Greener Solution Processing of Perovskite Solar Cells. ACS Sustainable Chemistry & Engineering 2020, 8 (35), 13126-13138. (https://doi.org/10.1021/acssuschemeng.0c04289)

[4] Vidal, R.; Alberola-Borràs, J.-A.; Habisreutinger, S. N.; Gimeno-Molina, J.-L.; Moore, D. T.; Schloemer, T. H.; Mora-Seró, I.; Berry, J. J.; Luther, J. M., Assessing health and environmental impacts of solvents for producing perovskite solar cells. Nature Sustainability 2020, 4 (3), 277-285. (https://doi.org/10.1038/s41893-020-00645-8)

[5] Li, Y.; Scheel, K. R.; Clevenger, R. G.; Shou, W.; Pan, H.; Kilway, K. V.; Peng, Z., Highly Efficient and Stable Perovskite Solar Cells Using a Dopant-Free Inexpensive Small Molecule as the Hole-Transporting Material. Advanced Energy Materials 2018, 8 (23). (https://doi.org/10.1002/aenm.201801248)

[6] Salunke, J.; Guo, X.; Lin, Z.; Vale, J. R.; Candeias, N. R.; Nyman, M.; Dahlström, S.; Österbacka, R.; Priimagi, A.; Chang, J.; Vivo, P., Phenothiazine-Based Hole-Transporting Materials toward Eco-friendly Perovskite Solar Cells. ACS Applied Energy Materials 2019, 2 (5), 3021-3027. (https://doi.org/10.1021/acsaem.9b00408)

[7] Fu, H.; Li, Y.; Yu, J.; Wu, Z.; Fan, Q.; Lin, F.; Woo, H. Y.; Gao, F.; Zhu, Z.; Jen, A. K., High Efficiency (15.8%) All-Polymer Solar Cells Enabled by a Regioregular Narrow Bandgap Polymer Acceptor. J Am Chem Soc 2021, 143 (7), 2665-2670. (https://doi.org/10.1021/jacs.0c12527)

[8] Maluenda, I.; Navarro, O., Recent developments in the Suzuki-Miyaura reaction: 2010-2014. Molecules 2015, 20 (5), 7528-57. (https://doi.org/10.3390/molecules20057528)

nanoGe (/)

nanoGe is a prestigious brand of successful science conferences that are developed along the year in different areas of the world since 2009. Our worldwide conferences cover cutting-edge materials topics like perovskite solar cells, photovoltaics, optoelectronics, solar fuel conversion, surface science, catalysis and two-dimensional materials, among many others.

(/advanced-materials-2dimensions-quantum-dots-renewable-energy-conference)**nanoGe Fall Meeting (/advanced-materials-2dimensions-quantum-dots-renewable-energy-conference)**

nanoGe Fall Meeting (NFM) is a multiple symposia conference celebrated yearly and focused on a broad set of topics of advanced materials preparation, their fundamental properties, and their applications, in fields such as renewable energy, photovoltaics, lighting, semiconductor quantum dots, 2-D materials synthesis, charge carriers dynamics, microscopy and spectroscopy semiconductors fundamentals, etc.

(/nanoge-spring-meeting)**nanoGe Spring Meeting (/nanoge-spring-meeting)**

This conference is a unique series of symposia focused on advanced materials preparation and fundamental properties and their applications, in fields such as renewable energy (photovoltaics, batteries), lighting, semiconductor quantum dots, 2-D materials synthesis and semiconductors fundamentals, bioimaging, etc.

(/hybrid-and-organic-photovoltaics-international-conference)**International Conference on Hybrid and Organic Photovoltaics (/hybrid-and-organic-photovoltaics-international-conference)**

International Conference on Hybrid and Organic Photovoltaics (HOPV) is celebrated yearly in May. The main topics are the development, function and modeling of materials and devices for hybrid and organic solar cells. The field is now dominated by perovskite solar cells but also other hybrid technologies, as organic solar cells, quantum dot solar cells, and dye-sensitized solar cells and their integration into devices for photoelectrochemical solar fuel production.

(/international-perovskite-and-organic-photovoltaics-and-optoelectronics-conferenc)**Asia-Pacific International Conference on Perovskite, Organic Photovoltaics and Optoelectronics (/international-perovskite-and-organic-photovoltaics-and-optoelectronics-conferenc)**

The main topics of the Asia-Pacific International Conference on Perovskite, Organic Photovoltaics and Optoelectronics (IPEROP) are discussed every year in Asia-Pacific for gathering the recent advances in the fields of material preparation, modeling and fabrication of perovskite and hybrid and organic materials. Photovoltaic devices are analyzed from fundamental physics and materials properties to a broad set of applications. The conference also covers the developments of perovskite optoelectronics, including light-emitting diodes, lasers, optical devices, nanophotonics, nonlinear optical properties, colloidal nanostructures, photophysics and light-matter coupling.

(/perovskite-thin-film-photovoltaics-perovskite-photonics-and-optoelectronics)**International Conference on Perovskite Thin Film Photovoltaics Perovskite Photonics and Optoelectronics (/perovskite-thin-film-photovoltaics-perovskite-photonics-and-optoelectronics)**

The International Conference on Perovskite Thin Film Photovoltaics Perovskite Photonics and Optoelectronics (NIPHO) is the best place to hear the latest developments in perovskite solar cells as well as on recent advances in the fields of perovskite light-emitting diodes, lasers, optical devices, nanophotonics, nonlinear optical properties, colloidal nanostructures, photophysics and light-matter coupling.