

Editorial

The Role of Organic Compounds in Dye-Sensitized and Perovskite Solar Cells

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Developing solar energy conversion devices is one key driver of the energy transition pathway [1]. Currently, crystalline silicon-based solar cells are the dominant technology for PV modules, with over 95% market share. Still, in the last years, widespread interest has also been dedicated to emerging technologies, such as dye-sensitized solar cells (DSSCs) and perovskite solar cells (PSCs) [2]. DSSCs are characterized by simple manufacturing processes based on low-cost and scalable raw materials. They have the great advantage of working well under ambient and diffused light, which allows their implementation as smart objects for indoor applications [3]. On the other hand, PSCs rival silicon-based solar cells for their high-power conversion efficiency (PCE up to 25% in 2022) and are characterized by simple fabrication processes [4]. However, driving DSSCs and PSCs from the research lab to their exploitation at the industrial level requires further improvements in efficiency, stability, and scalability [2–4]. In this context, the rational design of novel materials can be considered a viable approach for achieving enhanced performance. In particular, organic compounds are often presented as the best candidates as photosensitizers (solar energy absorbers) in DSSCs, and as hole transport materials -HTMs- (responsible for the charge extraction and transport) in PSCs because they possess many advantages over their inorganic counterparts [3–6]. Indeed, they can be easily synthesized and purified, and their optoelectronic properties can be adjusted with appropriate design rules, allowing fine-tuning interfacial contact with the other cells' components [5–8]. This Editorial paper intends to provide some examples of the active role of organic compounds in the DSSCs and PSCs research fields. Communication, Research, and Review papers recently published in *Energies* have been selected for this aim.

Organic dyes are generally characterized by the peculiar donor group- π spacer-acceptor group (D- π -A) structure, which helps to promote a rapid injection of the absorbed photons into the semiconductor, thanks to an intramolecular charge transfer transition (ICT) from the donor to the acceptor moiety [9]. How the organic photosensitizers' molecular structures can affect the photovoltaic performances of DSSCs devices has been emphasized in the work of Kim et al. [10]. Here, three novel pyrazine-based organic photosensitizers (TPP, TPPS, and TPPF) have been presented. They all bear two triphenylamine as donor groups, while the acceptor unit is represented by a benzopyrazine, a pyrido[3,4-b]pyrazine, and a trifluoromethylbenzopyrazine in TPP, TPPS, and TPPF, respectively. Additionally, while TTP is characterized by a D- π -A structure, in TPPS and TPPF the presence of an additional thiophene-cyanoacrylic group gives rise to D- π -A- π' -A' structures. The authors found that the TPPF-based DSSC device shows superior photovoltaic parameters and overall PCE. Indeed, the bulky trifluoromethylbenzopyrazine-based structure of TPPF can help to prevent intermolecular aggregations, resulting in improved molecular adsorption



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on the TiO₂ semiconductor and reduced interfacial TiO₂/photosensitizer/electrolyte charge transfer resistance.

New insights into the adsorption mechanism at the dye/semiconductor interface have been provided in the work of Holliman et al. [11], where two novel triarylamine-based organic dyes have been presented and taken as references for such a purpose. The two dyes are endowed with either two carboxylic (**10**) or two cyanoacrylic (**8**) acids as anchoring groups, and the double linkers' influence on the adsorption mechanism on TiO₂ anatase (101) surfaces has been investigated by using three atomistic modeling methods. The single-dye simulations reveal that (**8**) and (**10**) dyes preferentially adopt horizontal orientations on the TiO₂ surface, which are stabilized by covalent, van der Waals, hydrogen-bonding, and electrostatic interactions, that can influence where the electron injection occurs. Additionally, the presence of two cyanoacrylic acids in (**8**) results in a more red-shifted absorption for this molecule than that of dye (**10**), which contributes to enhancing the PCE of (**8**)-based DSSCs devices.

Organic dyes have also been proven to be the ideal candidates to make DSSCs good competitors to other PV technologies for niche applications, such as the so-called "agri-voltaics" (photovoltaics for agriculture). Chalkias et al. [12] have proposed for the first time the application of a di-carbazole-based dye (**Cz-2**) for the development of a semi-transparent DSSC for greenhouses-oriented applications. They demonstrated that the blue-light absorption of **Cz-2** and its absorption onset below 500 nm could guarantee good transparency in the red region of the spectrum where chlorophyll absorbs, even after adsorption on the semiconductor. Then, **Cz-2** dye was tested in DSSCs devices using an I₂-based electrolyte and a transparent I₂-free electrolyte. Both devices resulted suitable for a greenhouses-oriented application, as they show high transparency (up to 50%) in the red region, external quantum efficiency over 70% in the blue-green region, a crop growth factor higher than 30%, and overall efficiency higher than 3%.

Towards the commercialization of PSCs, HTMs can largely contribute to enhanced stability, as they are responsible for charge extraction and transport at the perovskite/HTM/electrode interface. Recently, the design of efficient and cost-effective small conductive organic HTMs has become a thrilling topic, hence a deep understanding of their structure-property relationships appears pivotal. In this context, additional knowledge on how the HTMs' structure can influence the ultimate PSCs performances is given in the review of Desoky et al. [13]. Here, all the relevant dopant-free organic HTMs developed in the 2014–2020 period have been collected, focusing the attention on those whose application in PSCs devices allowed reaching at least 15% of efficiency. The selected dopant-free HTMs have been grouped and discussed according to their morphology: linear 1D, two-dimensional star-shaped, or three-dimensional spiro-orthogonal structures. The analysis highlights that all the elements promoting the molecular planarity, the fine-tuning of the alkyl chains, and the HTMs' face-on arrangement on the perovskite surface can allow effective contact of the HTM molecules in the solid-state film. For this reason, the hole mobility across the molecular planes improves, and consequently, PSCs' performances can be enhanced.

The possibility of realizing stable HTM thin films by employing organic-based molecules has also been explored in the work of Magaldi et al. [14]. The authors have designed a novel polymerizable carbazole-based compound (**iDM1**) having glass-forming properties. They found that **iDM1** possesses suitable thermal, optical, and electrochemical properties to be employed as HTM, and its implementation in three PSCs' devices with different perovskite compositions provides PCE higher than 14%. Even if the photovoltaic performances of **iDM1**-based PSCs cannot rival PSCs with the well-established but unstable Spiro-OMeTAD, this work adds another brick to the organic-based HTMs knowledge, and it could inspire researchers in the discovery of more efficient carbazole-based structures.

Vesce et al. [15] stressed the importance of having good film-forming organic-based HTMs in the upscaling from small to large area cells. For the first time in their work, the already known low-cost spiro[fluorene-9,9'-xanthene]-based X55 HTM [16] has been tested and compared to Spiro-OMeTAD on small (0.09 cm²) and large (1.01 cm²) area PSCs. X55-based small area PSCs have higher efficiency than Spiro-OMeTAD-based ones (17% vs. 16%), and the trend is confirmed when upscaling to the large area cells, showing 16.05% and 14.9% of PCE, respectively. Additionally, the stability tests performed for more than 1000 h in an ambient condition (ISOS-D-1, c.a. 50% of relative humidity) support the best performance of X55-based PSCs, as they show c.a. 15% of efficiency drop, while c.a. 30% is that measured for Spiro-OMeTAD-based devices. These results are explained considering the molecular structure of X55: the presence of three spiro[fluorene-9,9'-xanthene] units allows the formation of a homogeneous and uniform film on the perovskite layer. Moreover, X55 is characterized by a low charge recombination rate and lower hydrophobicity features than Spiro-OMeTAD.

In conclusion, the works presented in this Editorial contribute to sharing the knowledge of organic-based compounds' behavior in DSSCs and PSCs, while suggesting also that there is still room for developing more efficient materials to push the commercialization of such devices and success in the decarbonization process expected by 2050.

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References

1. Kyriakopoulos, G.L.; Streimikiene, D.; Baležentis, T. Addressing Challenges of Low-Carbon Energy Transition. *Energies* **2022**, *15*, 5718. [[CrossRef](#)]
2. Ghosh, S.; Yadav, R. Future of photovoltaic technologies: A comprehensive review. *Sustain. Energy Technol. Assess.* **2021**, *47*, 101410. [[CrossRef](#)]
3. Muñoz-García, A.B.; Benesperi, I.; Boschloo, G.; Concepcion, J.J.; Delcamp, J.H.; Gibson, E.A.; Meyer, G.J.; Pavone, M.; Pettersson, H.; Hagfeldt, A.; et al. Dye-sensitized solar cells strike back. *Chem. Soc. Rev.* **2021**, *50*, 12450–12550. [[CrossRef](#)] [[PubMed](#)]
4. Kim, J.Y.; Lee, J.-W.; Jung, H.S.; Shin, H.; Park, N.-G. High-Efficiency Perovskite Solar Cells. *Chem. Rev.* **2020**, *120*, 7867–7918. [[CrossRef](#)] [[PubMed](#)]
5. Lee, C.-P.; Li, C.-T.; Ho, K.-C. Use of organic materials in dye-sensitized solar cells. *Mater. Today* **2017**, *20*, 267–283. [[CrossRef](#)]
6. Sheibani, E.; Yang, L.; Zhang, J. Recent advances in organic hole transporting materials for perovskite solar cells. *Sol. RRL.* **2020**, *4*, 2000461. [[CrossRef](#)]
7. Mohammadpourasl, S.; Fabrizi de Biani, F.; Coppola, C.; Parisi, M.L.; Zani, L.; Dessi, A.; Calamante, M.; Reginato, G.; Basosi, R.; Sinicropi, A. Ground-State Redox Potentials Calculations of D- π -A and D-A- π -A Organic Dyes for DSSC and Visible-Light-Driven Hydrogen Production. *Energies* **2020**, *13*, 2032. [[CrossRef](#)]
8. Coppola, C.; Infantino, R.; Dessi, A.; Zani, L.; Parisi, M.L.; Mordini, A.; Reginato, G.; Basosi, R.; Sinicropi, A. DFT and TDDFT investigation of four triphenylamine/phenothiazine-based molecules as potential novel organic hole transport materials for perovskite solar cells. *Mater. Chem. Phys.* **2022**, *278*, 125603. [[CrossRef](#)]
9. Coppola, C.; D'Ettoire, A.; Parisi, M.L.; Zani, L.; Reginato, G.; Calamante, M.; Mordini, A.; Taddei, M.; Basosi, R.; Sinicropi, A. In silico investigation of catechol-based sensitizers for type II dye sensitized solar cells (DSSCs). *Inorg. Chim. Acta* **2021**, *518*, 120233. [[CrossRef](#)]
10. Kim, M.-R.; Pham, T.C.; Choi, Y.; Yang, S.; Yang, H.-S.; Park, S.H.; Kang, M.; Lee, S. Syntheses and Photovoltaic Properties of New Pyrazine-Based Organic Photosensitizers for Dye-Sensitized Solar Cells. *Energies* **2022**, *15*, 5938. [[CrossRef](#)]
11. Holliman, P.J.; Mohsen, M.; Connell, A.; Kershaw, C.P.; Meza-Rojas, D.; Jones, E.W.; Geatches, D.; Sen, K.; Hsiao, Y.-W. Double Linker Triphenylamine Dyes for Dye-Sensitized Solar Cells. *Energies* **2020**, *13*, 4637. [[CrossRef](#)]
12. Chalkias, D.A.; Charalampopoulos, C.; Aivali, S.; Andreopoulou, A.K.; Karavioti, A.; Stathatos, E. A Di-Carbazole-Based Dye as a Potential Sensitizer for Greenhouse-Integrated Dye-Sensitized Solar Cells. *Energies* **2021**, *14*, 1159. [[CrossRef](#)]
13. Desoky, M.M.H.; Bonomo, M.; Buscaino, R.; Fin, A.; Viscardi, G.; Barolo, C.; Quagliotto, P. Dopant-Free All-Organic Small-Molecule HTMs for Perovskite Solar Cells: Concepts and Structure-Property Relationships. *Energies* **2021**, *14*, 2279. [[CrossRef](#)]
14. Magaldi, D.; Ulfa, M.; Peralta, S.; Goubard, F.; Pauporté, T.; Bui, T.-T. Carbazole Electroactive Amorphous Molecular Material: Molecular Design, Synthesis, Characterization and Application in Perovskite Solar Cells. *Energies* **2020**, *13*, 2897. [[CrossRef](#)]

15. Vesce, L.; Stefanelli, M.; Di Carlo, A. Efficient and Stable Perovskite Large Area Cells by Low-Cost Fluorene-Xantene-Based Hole Transporting Layer. *Energies* **2021**, *14*, 6081. [[CrossRef](#)]
16. Xu, B.; Zhang, J.; Hua, Y.; Liu, P.; Wang, L.; Ruan, C.; Li, Y.; Boschloo, G.; Johansson, E.M.J.; Kloo, L.; et al. Tailor-Making Low-Cost Spiro[fluorene-9,9'-xanthene]-Based 3D Oligomers for Perovskite Solar Cells. *Chem* **2017**, *2*, 676–687. [[CrossRef](#)]

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