EFFICIENT AND STABLE PEROVSKITE SOLAR CELLS USING LOW-COST ANILINE-BASED ENAMINE HOLE TRANSPORTING MATERIALS

Deimante Vaitukaityte[1], Zhiping Wang[2], Tadas Malinauskas[1], Artiom Magomedov[1], Giedre Bubniene[1], Vygintas Jankauskas[3], Egidijus Kamarauskas[3], Vytautas Getautis[1], Henry J. Snaith[2]

[1] Department of Organic Chemistry, Kaunas University of Technology, Lithuania
[2] Clarendon Laboratory, Department of Physics, University of Oxford, United Kingdom
[3] Department of Solid State Electronics, Vilnius University, Lithuania
deimante.vaitukaityte@ktu.edu

Over the last few years perovskite solar cell (PSC) technology has evolved from a scientific curiosity to a major research subject in the field of photovoltaics. In that short period of time they have gained recognition as one of the most promising photovoltaic technologies and managed to demonstrate remarkable achievements in the power conversion efficiency (PCE) exceeding 25% certified by the NREL [1]. Most of the high efficiency n-i-p structured perovskite solar cells are based on 2,2´,7,7´-tetrakis(*N*,*N*-di-*p*-methoxy-phenylamine)-9-9´-spirobifluorene (Spiro-OMeTAD) hole transporting material (HTM), which is very expensive [2]. The generated high cost is mainly due to the multi-step synthesis, complicated purification procedures and use of transition metal catalysts [3].

In this work, four low-cost enamines were functionalized *via* single-step synthetic procedure from commercially available aniline precursors without the use of expensive and problematic oraganometallic catalysts. Depending on the ration of the reagents enamines with two (**V1092**) or three (**V1091**) diphenylethenyl groups have been isolated. Additionally, aniline derivative with methoxy group in *para*-position (**V1056**) and 3,5-dimethyl substituted analogue (**V1102**) were also used for the synthesis.

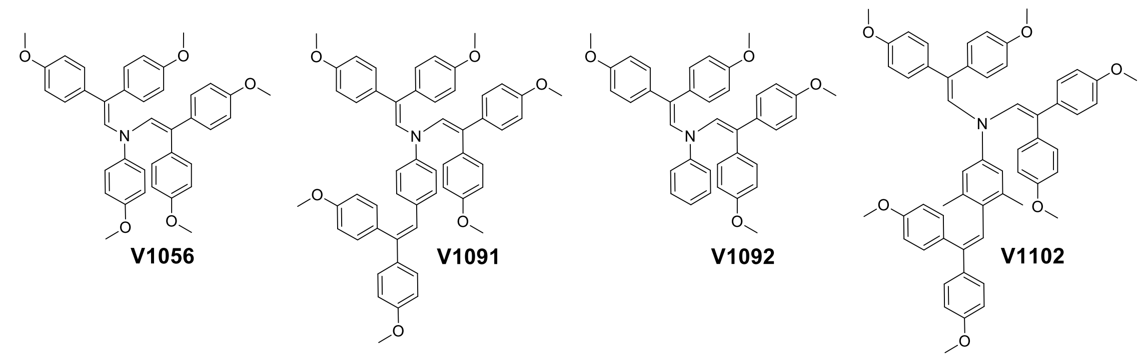

Fig. 1. Structures of aniline-based hole transporting materials **V1056**, **V1091**, **V1092** and **V1102**.

To investigate photoelectrical properties of synthesized HTMs hole drift mobility and ionization potential were measured. Photoelectron spectroscopy in air method was used to measure ionization potentials (I_p). Aniline derivative containing two diphenylethenyl groups (**V1092**) exhibits the highest ionization energy (5.3 eV). Additional electron donating diphenylethenyl (**V1091**) or methoxy (**V1056**) group lowers I_p of the HTM by ~0.1 eV. With the addition of methyl groups at 3,5-positions of the phenyl ring in **V1102**, negligible changes were observed in ionization energy. On the whole, the investigated HTMs show slightly higher ionization energy than Spiro-OMeTAD (5.0 eV), but still suitable for the hole extraction in PSCs. Charge transport properties of the investigated HTMs were measured using xerographic time-of-flight technique. **V1056** shows a similar hole mobility (7.8×10^{-4} cm^2/Vs) as compared to Spiro-OMeTAD (5.0×10^{-4} cm^2/Vs). In contrast, **V1091**, containing three diphenylethenyl moieties, displays significantly better hole drift mobilities (1.7×10^{-2} cm^2/Vs) at high electric fields. Addition of the methyl groups at 3,5-positions of the phenyl ring in **V1102** results in reduced charge mobility (1.5×10^{-4} cm^2/Vs).

The materials were tested as a HTM in planar heterojunction perovskite solar cells (with a device structure: fluorine doped tin oxide (FTO)/SnO_2/perovskite/HTM/Au). The device using **V1102** and **V1056** shows a champion efficiency of 17.6% and 18.7%, respectively, which is slightly lower than the PCE of 20.2% for the control device using Spiro-OMeTAD. In contrast, the PSC using **V1091** exhibits a high efficiency of 20.2%. To access device stability using the HTMs, non-encapsulated high efficiency devices were aged with **V1091** and Spiro-OMeTAD hole transporting layers in ambient air with a relative humidity of ~ 45% under dark conditions. **V1091** device showed superior stability sustaining 96% of its original efficiency after 820 h. In contrast, stabilized power output of the control device dropped to 42% after aging.

[1] https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20191106.pdf.
[2] K. Rakstys, C. Igci and M. K. Nazeeruddin, Efficiency *vs.* stability: dopant-free hole transporting materials towards stabilized perovskite solar cells, Chemical Science, **10**, 6748-6769 (2019). https://doi.org/10.1039/C9SC01184F.
[3] D. Vaitukaityte, Z. Wang, T. Malinauskas, et al., Efficient and Stable Perovskite Solar Cells Using Low-Cost Aniline-Based Enamine Hole-Transporting Materials, Advanced Materials, **30**, 45, 1803735 (2018). https://doi.org/10.1002/adma.201803735.