Molecular Engineering of Chalcogen-Containing Hole Transport Materials

Ehsan Ullah Rashid[1], Mariia Stanitska[1], Svetlana Sargsyan[1], Oleksandr Bezvikonnyi[1,2], Dmytro Volyniuk[1], Juozas Vidas Grazulevicius[1]

[1] *Department of Polymer Chemistry and Technology, Faculty of Chemical Technology, Kaunas University of Technology, K. Baršausko g. 59, LT-51423, Kaunas, Lithuania*

[2] *Institute of Solid State Physics, University of Latvia, Kengaraga 8, LV-1063, Riga, Latvia*

Efficient hole-transporting materials (HTMs) require a delicate balance between frontier orbital alignment, small structural relaxation upon charge exchange, and sufficient solid-state hole mobility to sustain efficient charge injection and stable device operation. In organic HTMs, these parameters are strongly governed by molecular topology, heteroatom incorporation, and the extent of π-conjugation [1]. Here, we investigate a series of phenylenediamine-derived HTMs designed to resolve how sulphur-containing fragments modulate hole-transport characteristics through a structure-to-property relationship. This design enables a direct comparison of how sulphur alters electronic delocalization, frontier orbital energetics, and intramolecular reorganization associated with hole transfer. The target materials were synthesized in high yield via Buchwald-Hartwig cross-coupling. The properties are evaluated using a combined theoretical and experimental workflow. Quantum-chemical calculations reveal that the nature and placement of sulphur-containing moieties govern frontier-orbital distribution and the energetic for hole hopping, thereby providing a molecular-level explanation for the observed hole transport trends. Time-of-flight measurements on solid-state samples confirm efficient hole transport and show that the mobility is not dictated by sulphur incorporation alone, but by how sulphur-containing fragments reshape molecular rigidity, conjugation pathway, and charge delocalization. These results signifies that sulphur is effective when embedded in frameworks that simultaneously lower ionization energy and reduce reorganization energy without disrupting charge mobility. HTMs with such properties are not only efficient for light emitting diodes and perovskite solar cells but may also be relevant to quantum-light emitters, where controlled carrier injection and suppression of background recombination are important for isolating emission from localized single-photon emitters [2].

Funding acknowledgement

This project has received funding from the Research Council of Lithuania (LMTLT), agreement No S-MIP-24-6.

References

[1] Schloemer, T. H. *et al.* Chemi. Sci. 10(7), 1904-1935 (2019).

[2] Lin, X., Dai, *et al. Nat. Commun. 8, 1132 (2017).*