Novel hole-transporting materials for durable and efficient perovskite solar cells: insights from theory and computations

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Perovskite solar cells (PSCs) have attracted a lot of attention as an inexpensive solar energy harvesting technology. Though, the challenges related to achieving their long-term stability at a reasonable cost while preserving the optimal power conversion efficiency (PCE) prevent the large-scale implementation of PSCs [1,2]. Selecting an appropriate hole-transporting material (HTM) is among possible routes to improve both the durability of the PSC and maintain its performance, since the HTM layer can serve to stabilize the metastable perovskite phases, protect them from external environmental agents, passivate the defects and restrain the ionic migration, enhance the interfacial charge injection and carrier transport [1-3]. With this strategy in mind, a substantial effort has been recently dedicated to find a cost-effective alternative to the benchmark spiro-OMeTAD hole-transporter [1-3]. The target compound has to satisfy multiple criteria, among which an appropriate band alignment, optical properties, high hole mobility and conductivity, efficient carrier injection characteristics at the perovskite interface. The knowledge about atomistic-scale leverages for modifying those characteristics, which can be extracted from the theoretical analysis along with the computational modeling, greatly accelerates the experimental quest for optimal system and reduces corresponding expenses. In this work, the influence of the HTM building blocks (donor-acceptor units, conjugated *π*-bridges, side group anchors) on the structure of the perovskite-HTM interface and molecular stacking ability is investigated by first-principles simulations. The flexible oligothiophene [1] and rigid carbazole [2] cores are considered. While rigid carbazole-like cores are favoring planar orientation [2] of the HTM on the perovskite surface, the presence of sulfur heteroatoms is essential for a good contact at the perovskite-HTM interface [1], which ultimately translates into an improved conductivity and hole extraction parameters, resulting in an increased durability and efficiency. The conformational freedom of the TPA-like branches governed by its spatial distribution in the donor-*π*-bridge systems is another structural factor to be controlled [1]. Besides, an inclusion of side-group anchors ensuring directional site-specific interactions additionally improves the perovskite coating by HTM. Accounting for these findings, a planar-core donor-*π*-bridge-acceptor heteroatomic molecular system is suggested as a hole-transporter, defect state passivator and perovskite protector, enabling the fabrication of durable and efficient all-inorganic PSC [3].

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