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# Dopant-free star-shaped hole-transport materials for efficient and stable perovskite solar cells

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ABSTRACT

Two star-shaped TPA-based small-molecule materials (Z1012 and Z1013) were designed and synthesized in this paper. These molecules show high hole mobility and suitable energy levels for $CH_3NH_3PbI_3$-based perovskite solar cells. Photovoltaic cells based on the Z1013 without any dopants or additives achieve an excellent power conversion efficiency (PCE) of 15.4%, which is comparable to devices based on state-of-art p-doped *spiro*-OMeTAD. Moreover, the devices based on these two HTMs show much better stability than that of devices based on *spiro*-OMeTAD when aging in ambient air both at room temperature and 80 °C. These results demonstrate that star-shape TPAs could be excellent dopant-free HTMs for perovskite solar cells and hold promise to replace the p-doped *spiro*-OMeTAD, which is important for the fabrication of cost-effective and stable devices.



## 1. Introduction

Organic–inorganic hybrid perovskite solar cells (e.g. $(RNH_3)PbX_3$ (R = alkyl, X = halogen)) have been recently receiving great attention owing to their outstanding features such as superb photovoltaic performance and low cost [1–4]. Since hybrid perovskite solar cells were first demonstrated by Kojima et al., cells based on such materials have shown an unprecedented increase of power conversion efficiency (PCE) to 22.1% in subsequent years [5–7].

The best performing device configuration of perovskite solar cell (PSC) is based on mesoporous $TiO_2$ scaffold, which is infiltrated with perovskite material and coated with the hole-transport materials (HTMs) [8]. Electrons and holes were produced in the perovskite absorber upon photo-excitation, the electrons were diffused to the $TiO_2$, and the holes were transferred to the HTMs. These photo-generated charge carriers are subsequently collected as photocurrent at the front and back contacts of the solar cell [2,9]. To date, a great number of HTMs have been developed and incorporated in PSCs, which are composed of organic and inorganic hole-conductors [9]. Among the organic semiconductors, triphenylamine (TPA) containing compounds 2,2′,7,7′-tetrakis (N,N′-di-*p*-methoxy-phenylamine)-9,9′-spirobifluorene (*spiro*-OMeTAD) along with poly-triarylamine (PTAA) have shown to be most effective. However, their relatively high cost of synthesis along with the need to use high levels of dopants present caveats for practical applications. The dopants and additives in the HTMs contribute to

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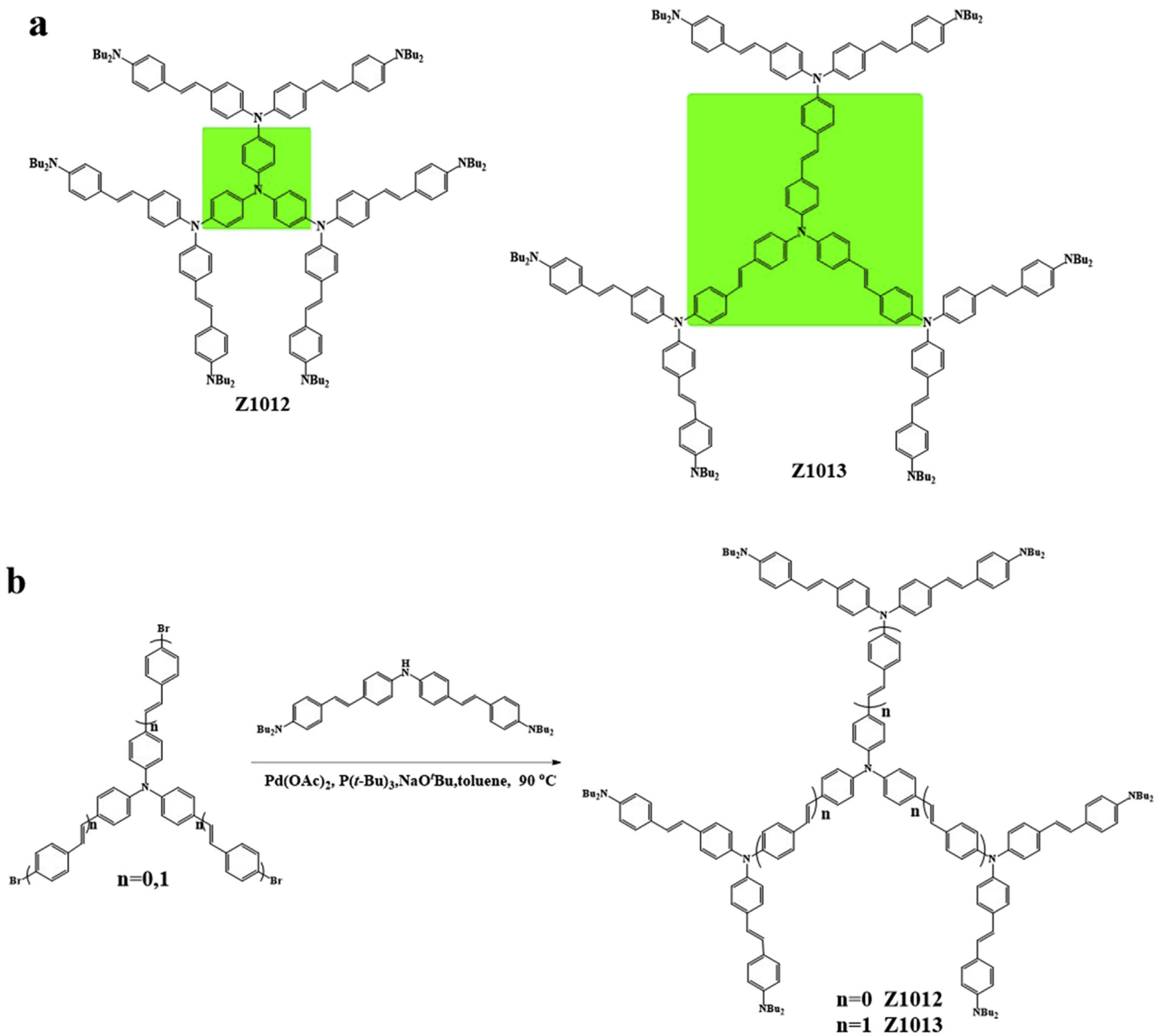


**Fig. 1.** (a) Molecular structures of Z1012 and Z1013; (b) Synthetic route for Z1012 and Z1013.

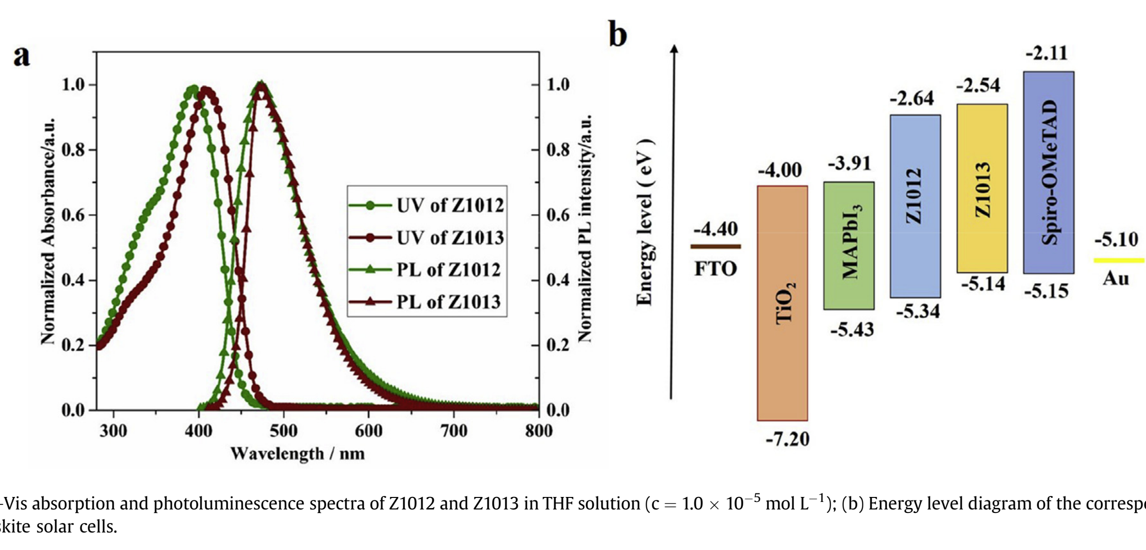


**Fig. 2.** (a) UV–Vis absorption and photoluminescence spectra of Z1012 and Z1013 in THF solution (c = $1.0 \times 10^{-5}$ mol $L^{-1}$); (b) Energy level diagram of the corresponding materials used in perovskite solar cells.