Supplementary data for

How to design more efficient hole-transporting materials for perovskite solar cells? Rational tailoring of the triphenylamine-based electron donor

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Computational details

The geometry optimizations of the HTM/MAPbI$_3$ complexes were performed by the CP2K/QUICKSTEP program$^{1-3}$ combined with a hybrid Gaussian and plane wave basis set. The generalized-gradient approximation(GGA)$^4$ of Perdew-Burke-Ernzerhof (PBE)$^5$ exchange correlation functional was employed together with norm-conserving Goedecker-Teter-Hutter (GTH)$^6$ pseudopotentials, and when forces were less than 45 meV Å$^{-1}$ (default value), the structures were considered as relaxed. Based on the optimized HTM/MAPbI$_3$ geometries, single-point DFT calculations were carried out with Gaussian 09 package to gain the electronic and energetic properties of HTM adsorbed systems at the theoretical level of B3LYP/6-31G*, coupled with the LANL2DZ potentials.$^7$ Herein, the (MAPbI$_3$)$_{64}$ cluster was obtained by appropriately cutting a tetragonal phase slab with the (001) surface exposed,$^8$ which was believed to favor the hole injection from MAPbI$_3$ to HTMs. Meanwhile, the parallel adsorption configuration$^9$ was reported to be energetic favorable for HTMs with big π-conjugated cores, and thus this adsorption model was employed for the new designed NTT-4TPA.

References


Fig. S1 Calculated HOMO levels of investigated molecules with the functional B3LYP and PBE33, and the B3LYP-R represents the data revised by a semi-rational formula.
Fig. S2 Total electronic energy evolutions of the investigated dimers (T1~T6) as a function of simulation time.
**Fig. S3** Total electronic energy evolutions of the investigated dimers (T7~T9) as a function of simulation time.
Fig. S4 Conjectural synthetic pathways for predicted molecules.
Fig. S5 Experimental synthetic pathways for the NTT core.
Fig. S6 Unrelaxed structure of the (MAPbI$_3$)$_{64}$ cluster with (001) surface exposed.
Fig. S7 Optimized geometry of the Spiro-OMeTAD/(MAPbI$_3$)$_{64}$ complex.
Fig. S8 Optimized geometry of the NTT-4TPA/(MAPbI$_3$)$_{64}$ complex.