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

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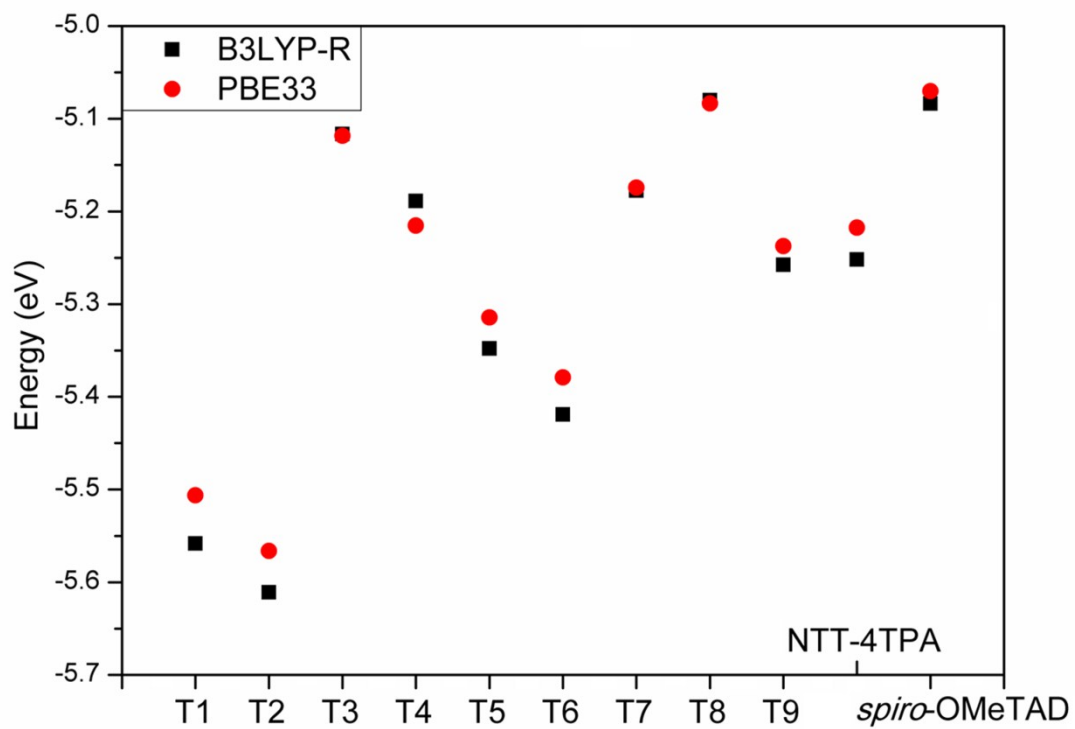
Fig. S1 Calculated HOMO levels of investigated molecules with the functional B3LYP and PBE33, and the B3LYP-R represents the data revised by a semi-rational formula.
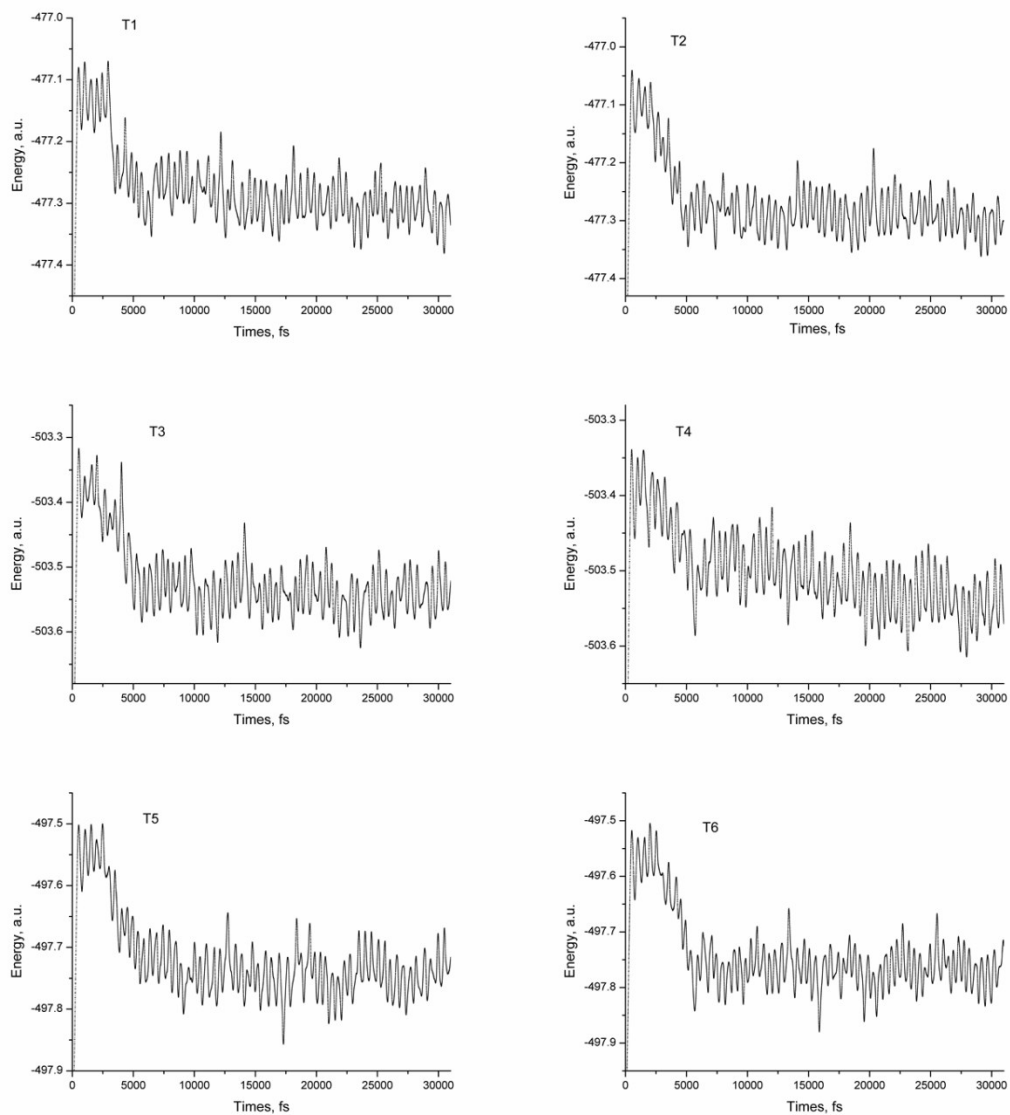
Fig. S2 Total electronic energy evolutions of the investigated dimers (T1~T6) as a function of simulation time.
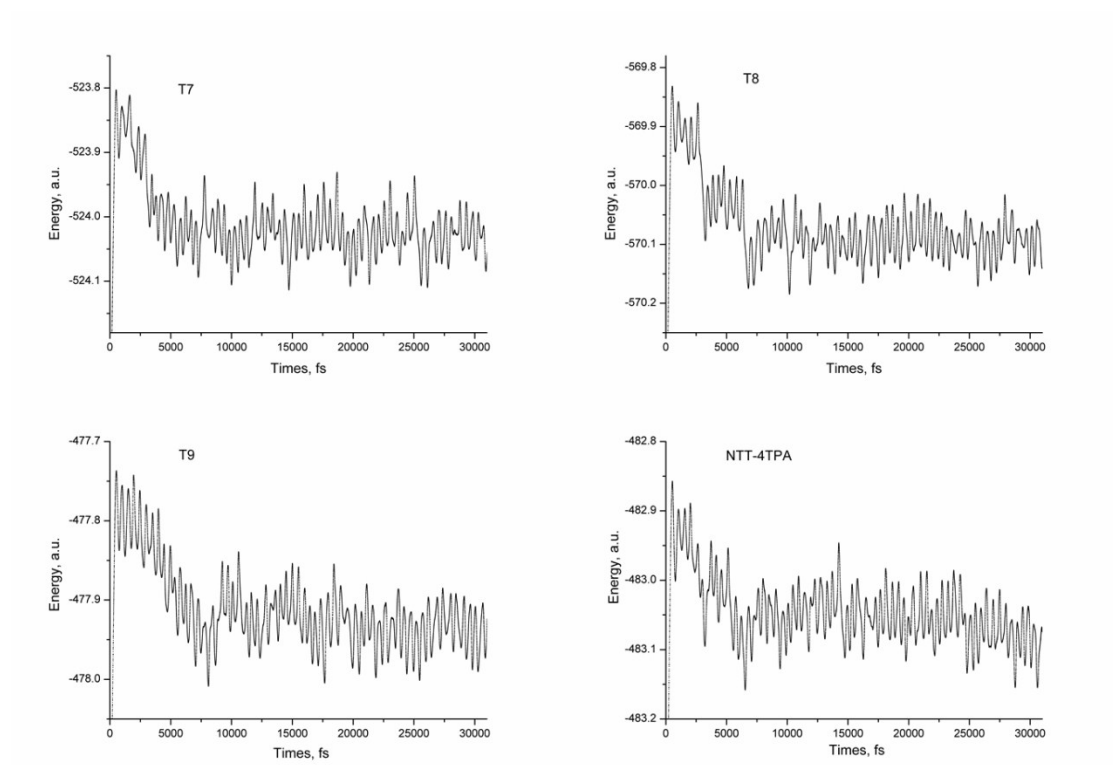
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Fig. S3 Total electronic energy evolutions of the investigated dimers (T7~T9) as a function of simulation time.
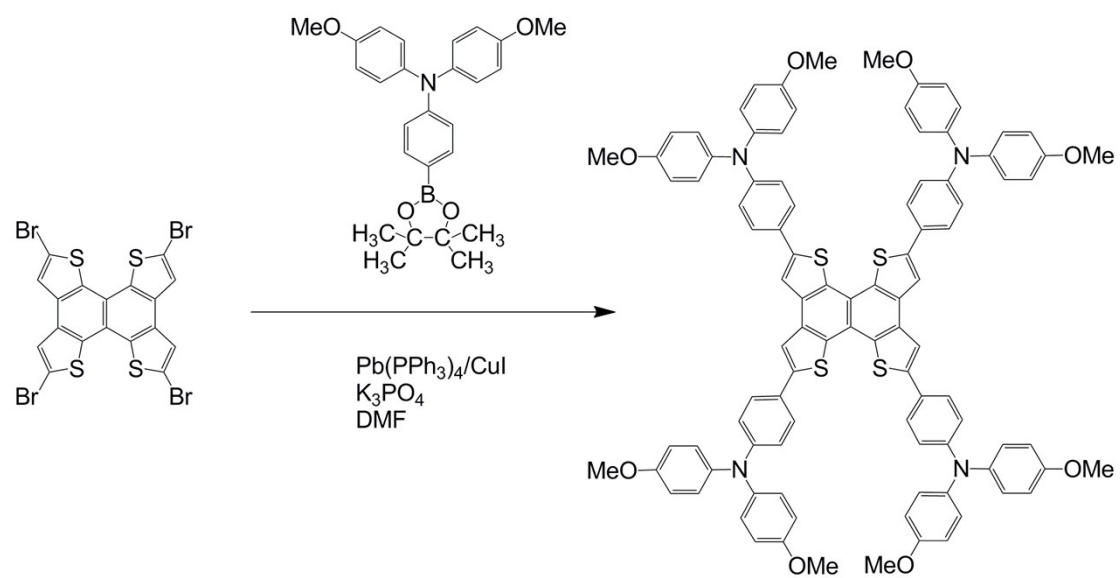
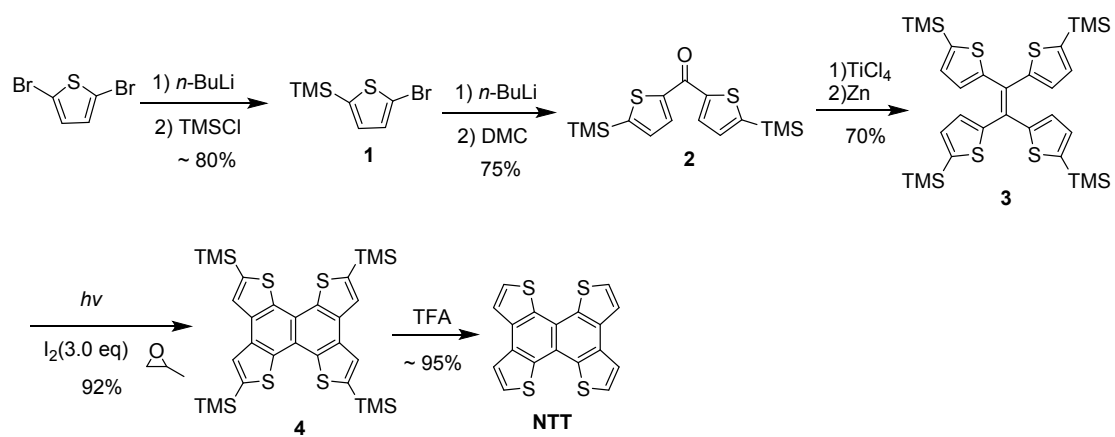**Fig. S4** Conjectural synthetic pathways for predicted molecules.

Fig. S5 Experimental synthetic pathways for the NTT core.
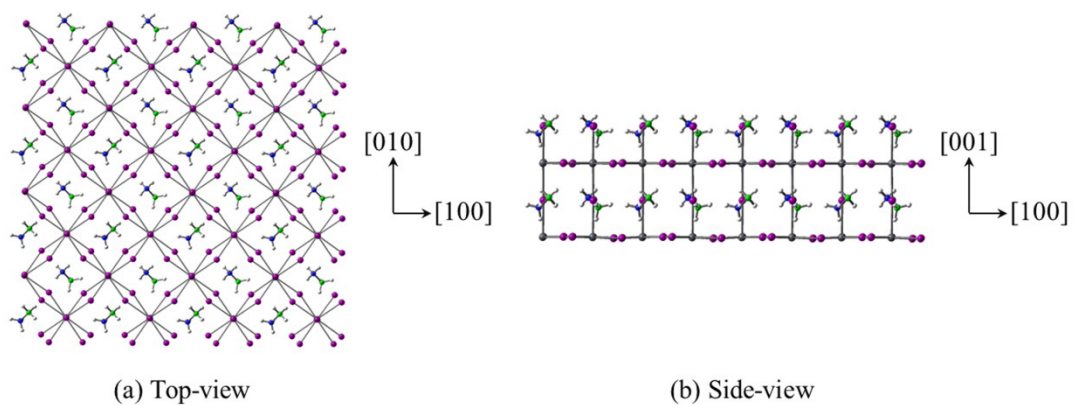
(a) Top-view   (b) Side-view

Fig. S6 Unrelaxed structure of the $(MAPbI_3)_{64}$ cluster with (001) surface exposed.
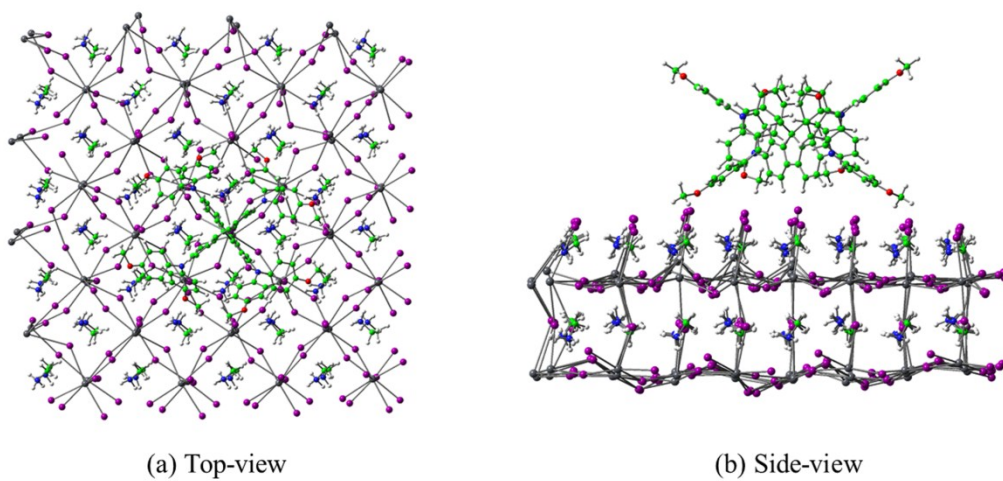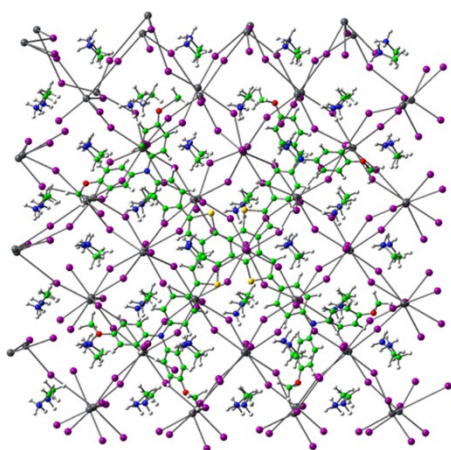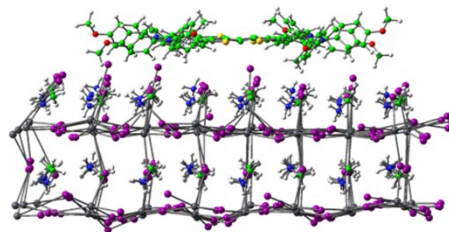
(a) Top-view (b) Side-view

Fig. S7 Optimized geometry of the Spiro-OMeTAD/(MAPbI$_3$)$_{64}$ complex.

(a) Top-view   (b) Side-view

Fig. S8 Optimized geometry of the NTT-4TPA/(MAPbI$_3$)$_{64}$ complex.