Supplementary data for

Tailoring of the core structure towards promising small molecule hole-transporting materials for perovskite solar cells: a theoretical study

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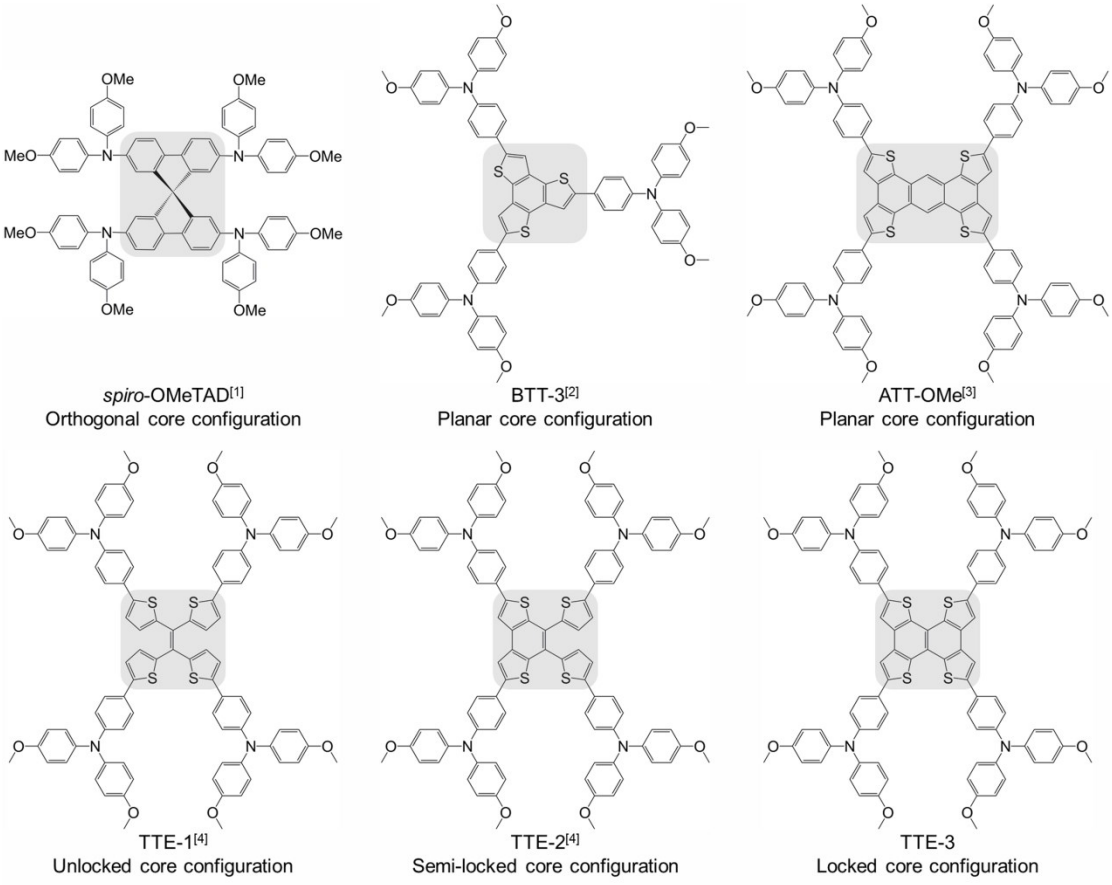

Fig. S1 The sample molecules are used to explain the terms of "orthogonal", "planar", "core structure", "unlocked", "semi-locked" and "locked", where the core structures are shown in the shaded areas. The references are listed as below.

[1] L. Calio, S. Kazim, M. Gräetzel and S. Ahmad, *Angew. Chem. Int. Ed.*, 2016, **55**, 14522-14545.

[2] A. Molina-Ontoria, I. Zimmermann, I. Garcia-Benito, P. Gratia, C. Roldan-Carmona, S. Aghazada, M. Gräetzel, M. K. Nazeeruddin, and N. Martin, Angew. Chem. Int. Ed., 2016, 55, 6270-6274

[3] I. Zimmermann, J. Urieta-Mora, P. Gratia, J. Arago, G. Grancini, A. Molina-Ontoria, E. Orti, N. Martin and M. K. Nazeeruddin, *Adv. Energ. Mater.*, 2017, **7**, 1601674.

[4] C. Shen, Y. Wu, H. Zhang, E. Li, W. Zhang, X. Xu, W. Wu, H. Tian and W.H. Zhu, *Angew. Chem. Int. Ed.*, 2019, **58**, 3784-3789.

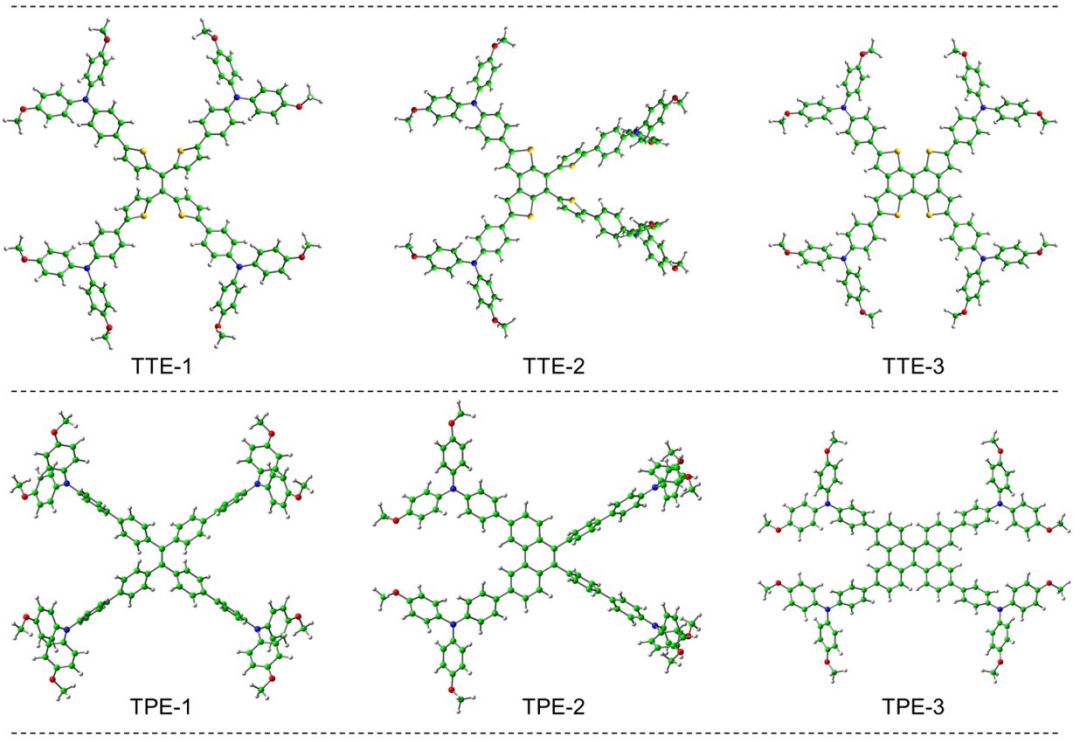

Fig. S2 Optimized molecular geometries of the investigated systems.

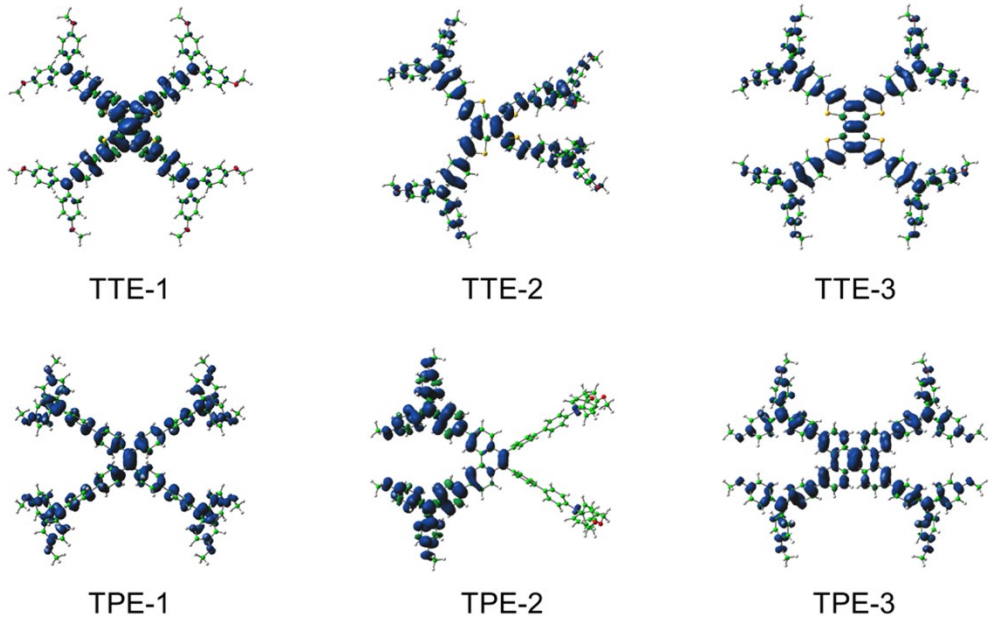

Fig. S3 Calculated electron spin density maps of the cationic state HTMs.

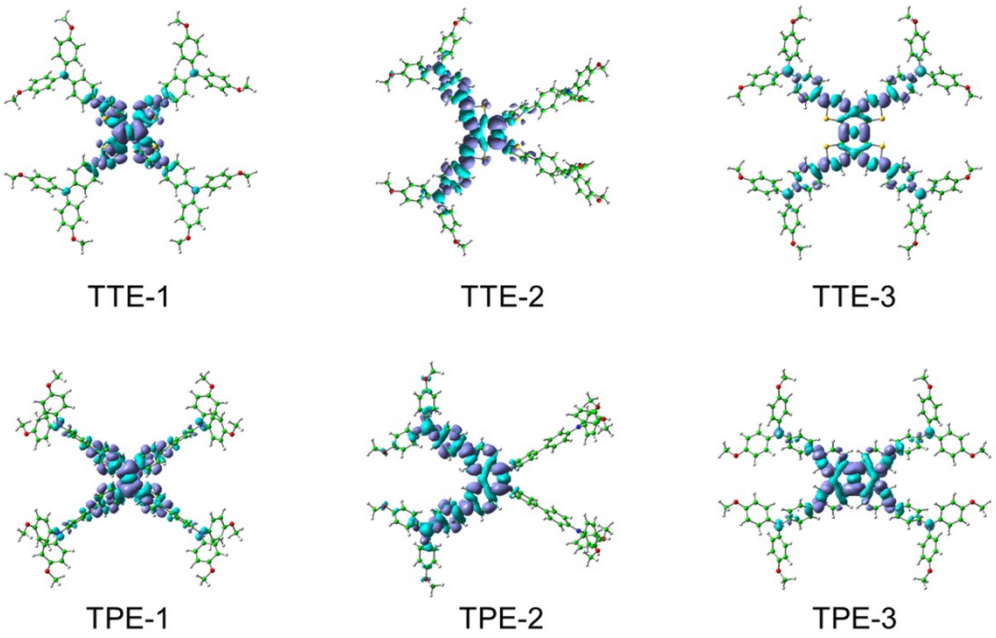

Fig. S4 Charge density difference maps of the investigated HTMs, the purple and the blue represent where the electrons are increased and reduced, respectively.

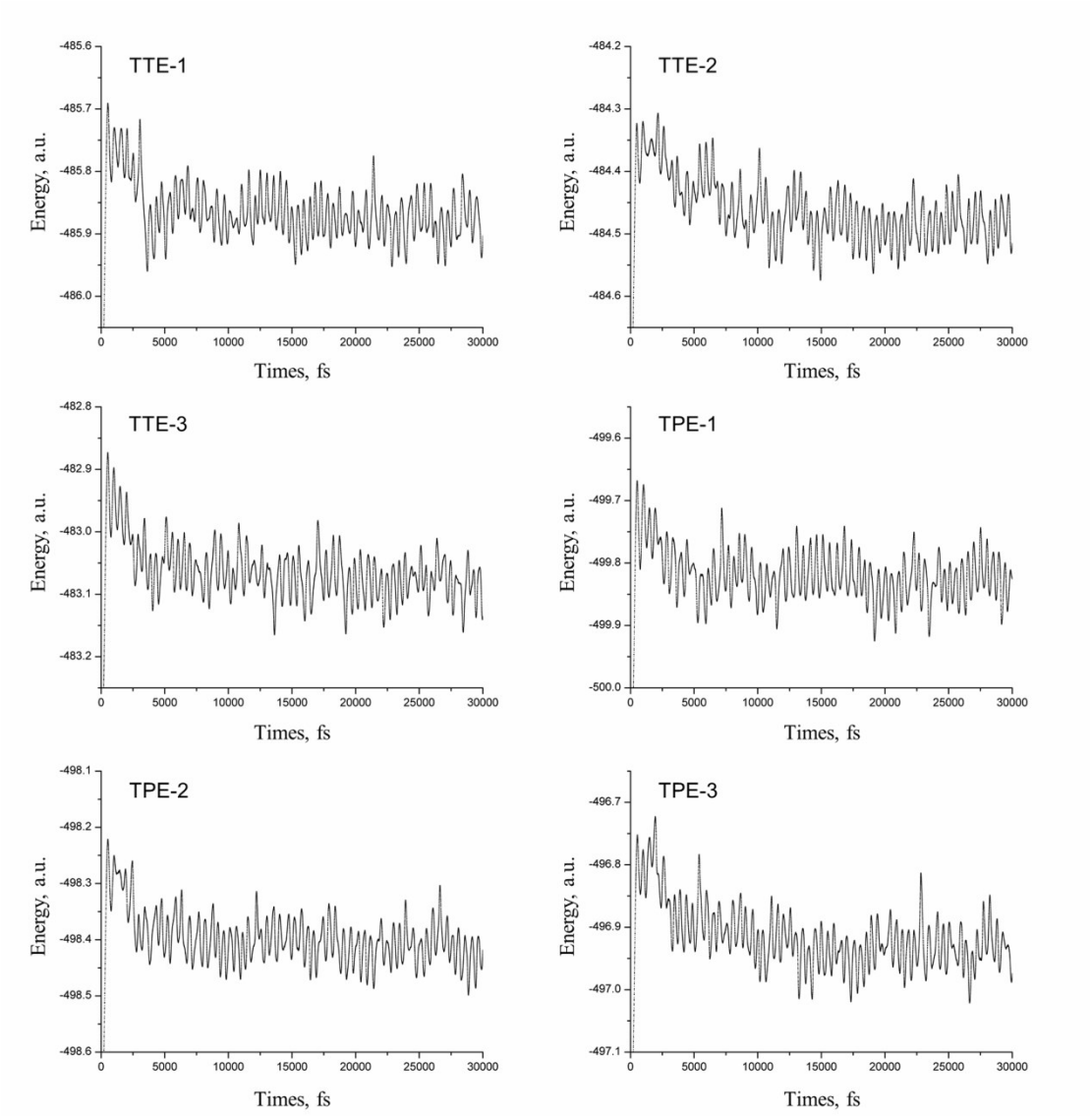

Fig. S5 Total electronic energy evolution of the investigated systems as a function of simulation time.