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Supporting information for article:

Revisiting stacking interactions in tetrathiafulvalene and selected derivatives using tight-binding quantum chemical calculations and local coupled-cluster method

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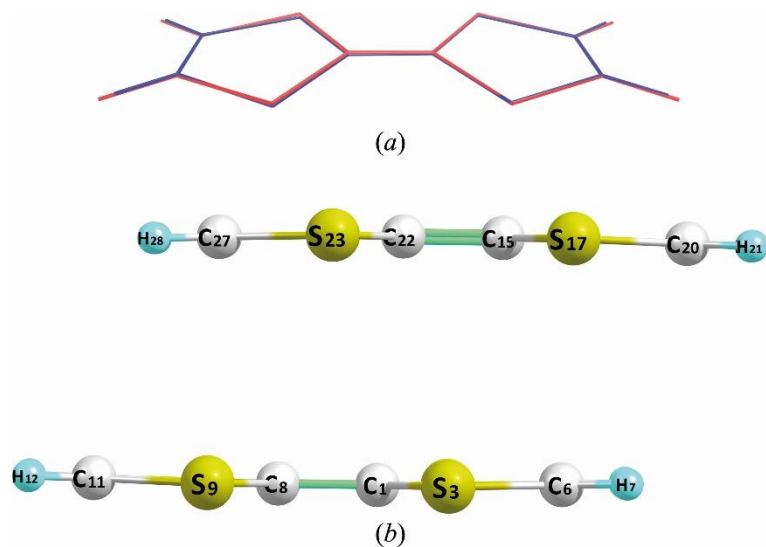


Figure S1 (a) An overlap analysis of the TTF molecule in crystal (blue) and in the TTF stacking dimer optimized by GFN2-xTB method (red). (b) Side view of the TTF stacking dimer optimized by GFN2-xTB method. The dihedral angles of C1—C8—S9—C11 and C8—C1—S3—C6 are 178.6° and -178.6° , respectively.

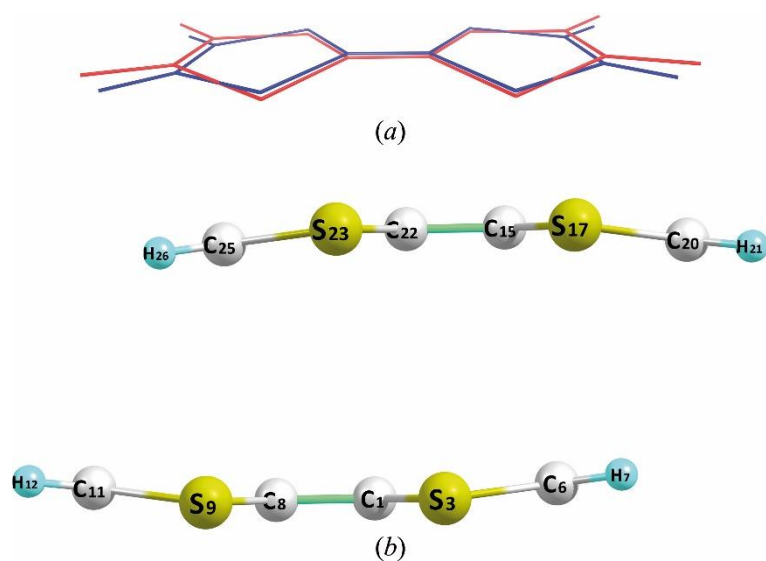


Figure S2 (a) An overlap analysis of the TTF molecule in crystal (blue) and in the TTF stacking dimer optimized by ω B97X-D3/def2-TZVPP (red). (b) Side view of the TTF stacking dimer optimized at ω B97X-D3/def2-TZVPP level of theory. The dihedral angles of C1—C8—S9—C11 and C8—C1—S3—C6 are 172.9° and -173.3° , respectively. The r.m.s. deviations between TTF molecules in optimized dimer and in the crystal structure are 0.160 \AA (including hydrogen atoms) and 0.100 \AA (without the hydrogen atoms).

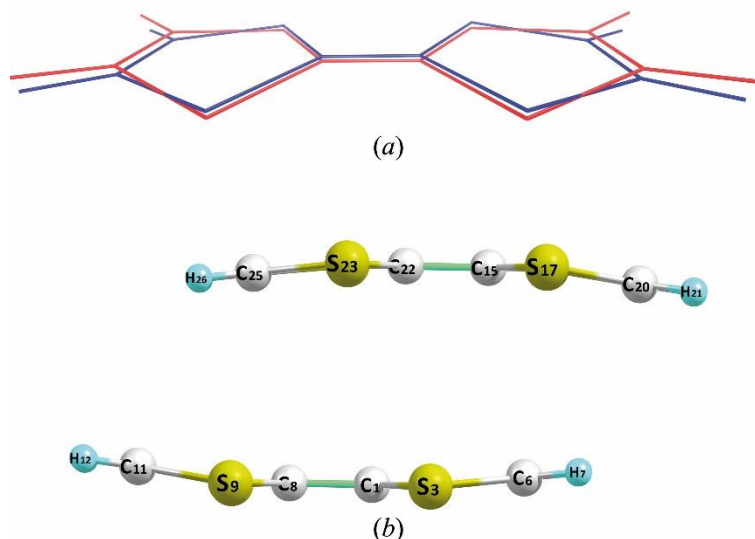


Figure S3 (a) An overlap analysis of the TTF molecule in crystal (blue) and in the TTF stacking dimer optimized by PBE0-D3(BJ)/def2-TZVPP (red). (b) Side view of the TTF stacking dimer optimized at PBE0-D3(BJ)/def2-TZVPP level of theory. The dihedral angles of C1—C8—S9—C11 and C8—C1—S3—C6 are 172.2° and -174.4° , respectively. The r.m.s. deviations between TTF molecules in optimized dimer and in the crystal structure are 0.164 \AA (including hydrogen atoms) and 0.104 \AA (without the hydrogen atoms).

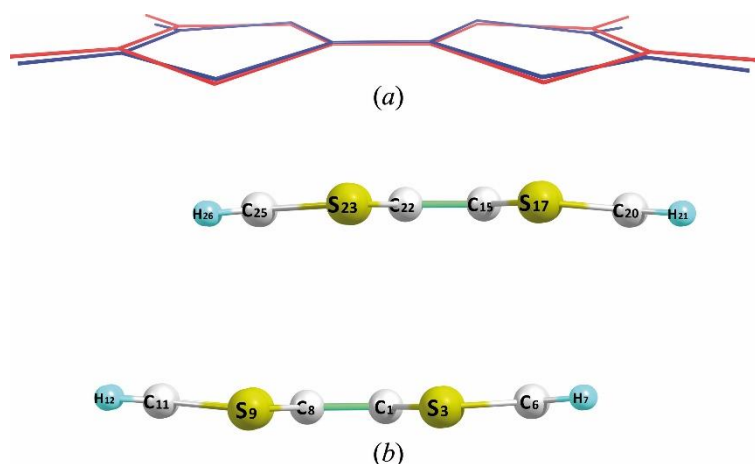


Figure S4 (a) An overlap analysis of the TTF molecule in crystal (blue) and in the TTF stacking dimer optimized by B3LYP-D3(BJ)/def2-TZVPP (red). (b) Side view of the TTF stacking dimer optimized at B3LYP-D3(BJ)/def2-TZVPP level of theory. The dihedral angles of C1—C8—S9—C11 and C8—C1—S3—C6 are 175.6° and -177.5° , respectively. The r.m.s. deviations between TTF molecules in optimized dimer and in the crystal structure are 0.130 \AA (including hydrogen atoms) and 0.062 \AA (without the hydrogen atoms).

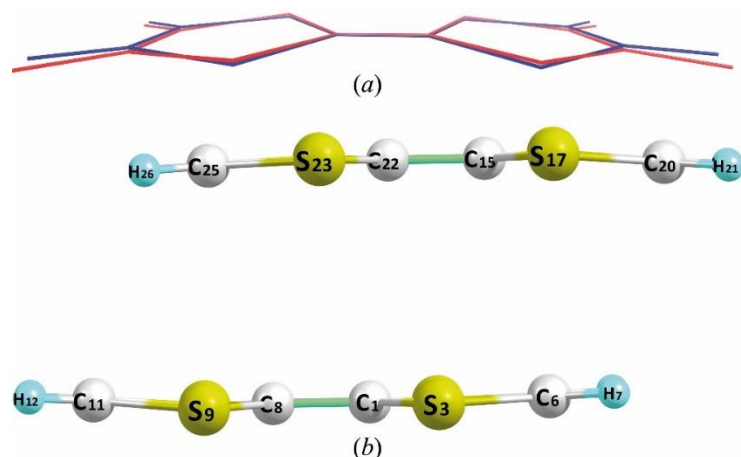


Figure S5 (a) An overlap analysis of the TTF molecule in crystal (blue) and in the TTF stacking dimer optimized by M06-2X-D3(zero)/def2-TZVPP (red). (b) Side view of the TTF stacking dimer optimized at M06-2X-D3(zero)/def2-TZVPP level of theory. The dihedral angles of C1—C8—S9—C11 and C8—C1—S3—C6 are 176.3° and -178.3° , respectively. The r.m.s. deviations between TTF molecules in optimized dimer and in the crystal structure are 0.118 \AA (including hydrogen atoms) and 0.054 \AA (without the hydrogen atoms).

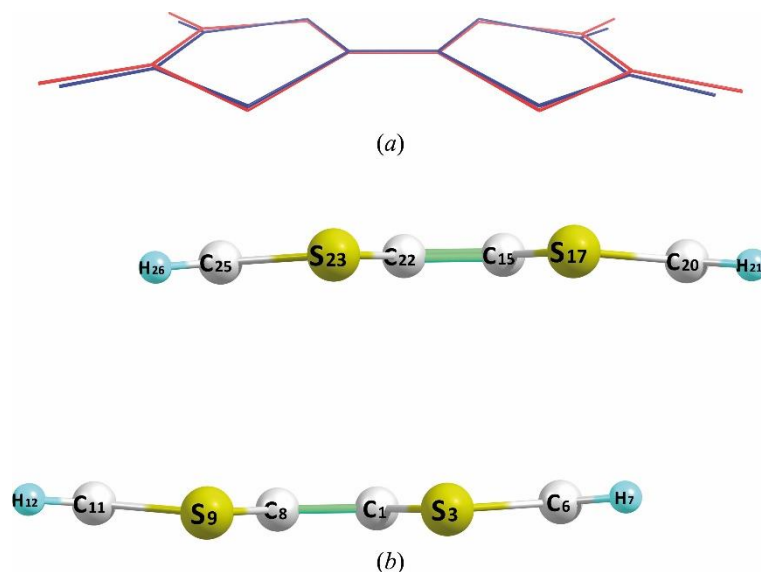


Figure S6 (a) An overlap analysis of the TTF molecule in crystal (blue) and in the TTF stacking dimer optimized by B2PLYP-D3(BJ)/def2-TZVPP (red). (b) Side view of the TTF stacking dimer optimized at B2PLYP-D3(BJ)/def2-TZVPP level of theory. The dihedral angles of C1—C8—S9—C11 and C8—C1—S3—C6 are 175.7° and -177.8° , respectively. The r.m.s. deviations between TTF molecules in optimized dimer and in the crystal structure are 0.203 \AA (including hydrogen atoms) and 0.139 \AA (without the hydrogen atoms).

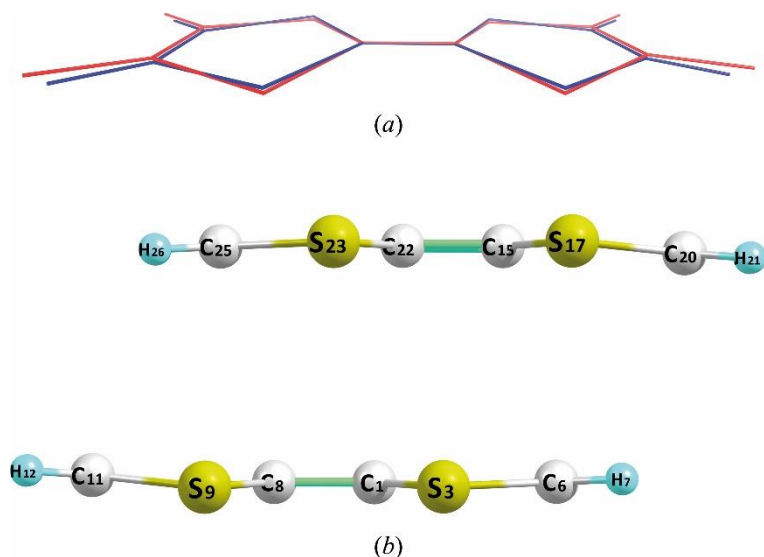


Figure S7 (a) An overlap analysis of the TTF molecule in crystal (blue) and in the TTF stacking dimer optimized by DLPNO-MP2/def2-TZVPP (red). (b) Side view of the TTF stacking dimer optimized at DLPNO-MP2/def2-TZVPP level of theory. The dihedral angles of C1—C8—S9—C11 and C8—C1—S3—C6 are 176.0° and -178.6° , respectively. The r.m.s. deviations between TTF molecules in optimized dimer and in the crystal structure are 0.255 \AA (including hydrogen atoms) and 0.204 \AA (without the hydrogen atoms).

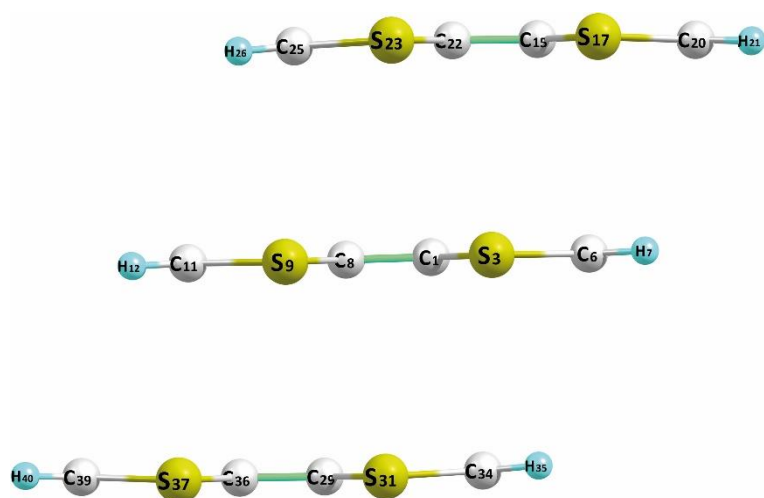


Figure S8 Side view of the TTF stacking trimer optimized at B3LYP-D3/def2-TZVPP level of theory. For the TTF molecule in the middle, the dihedral angles of C1—C8—S9—C11 and C8—C1—S3—C6 are 179.3° and 179.3° , respectively. The r.m.s. deviations between TTF molecules in optimized trimer and in the crystal structure are 0.229 \AA (including hydrogen atoms) and 0.178 \AA (without the hydrogen atoms).

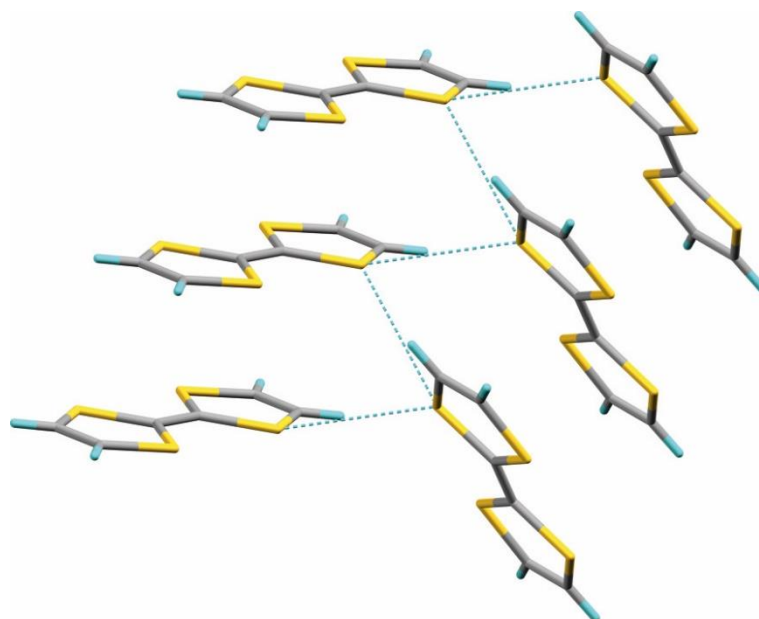


Figure S9 The “wedged” structure in the crystal packing of TTF (CSD refcode BDTOLE11).

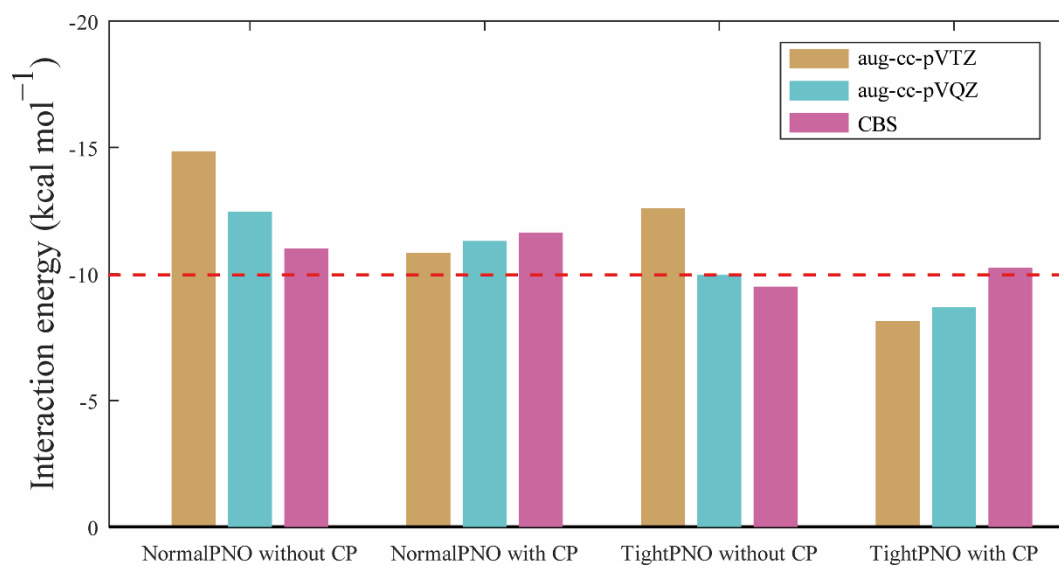


Figure S10 Comparison between the interaction energies calculated using triple/quadruple zeta basis sets, with and without counterpoise (CP) correction, and different PNO settings relative to the reference energy. The red dashed line indicates the reference energy.

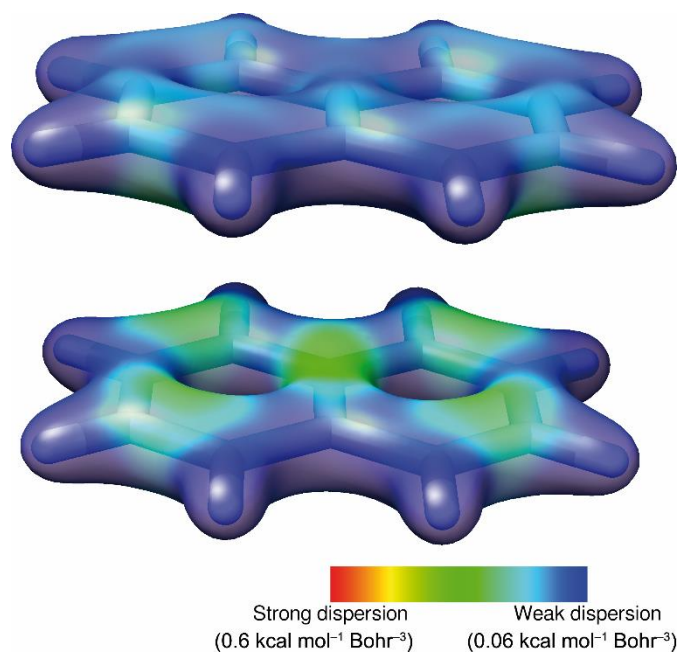


Figure S11 Dispersion interaction density plot of the stacking system of naphthalene dimer. The plot was based on the DLPNO-CCSD(T) calculations. The density isosurface was generated at a contour value of 0.1 a.u. The color scheme ranges from strong dispersion interaction (red) to zero interaction energy (blue).

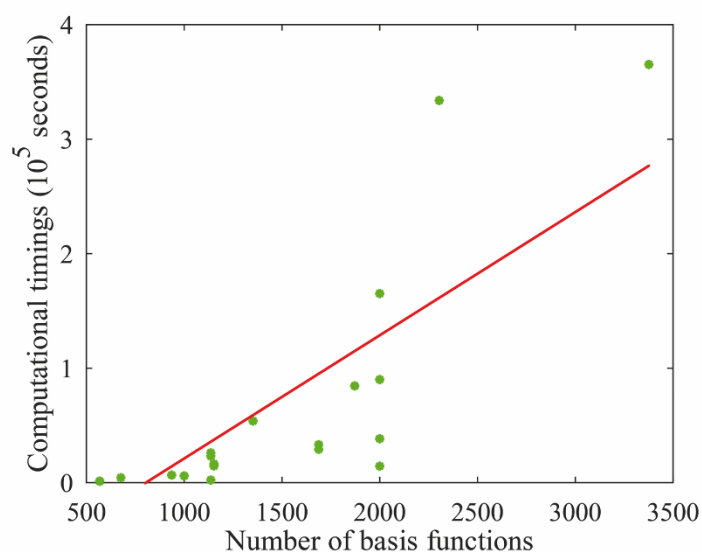


Figure S12 Representative computational timings of DLPNO-CCSD(T) with TightPNO settings for the studied systems. The calculations were completed using 36 CPU cores and 128 GB of memory on a single node.