

Supporting information for “Regulate the Thermoelectric Power Factor of Donor-
Acceptor Copolymers by Heavy Chalcogens Substitution: A First-principles
Study”

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1. Geometrical and electronic structure calculations

To determine the most stable conformation of conjugated backbone, the torsional potentials between the A and D units are calculated at B3LYP level firstly using Gaussian 09 code, while the pseudopotential basis set SDD is employed for Te atom and 6-31G (d, p) is used for other atoms. The alkyl side chain of the acceptor unit is replaced by methyl group to reduce the computational cost. Then, the isolated copolymer chains with 1D periodicity are constructed employing the most stable monomer conformation as the repeating unit, and then are optimized at the PBE-D3 level in Vienna Ab initio Simulation Package (VASP) 5.3 code.^[1] The copolymer chains are placed along the *a*-axis with a vacuum layer of 20 Å in the in-plane *b* and out-of-plane *c* axes. The GGA-PBE exchange-correlation functional^[2] with D3 dispersion correction^[2] and the Projector-Augmented Wave (PAW) potential^[3] are employed to optimize the chain length as well as the atomic positions. The cutoff energy for the plane-wave basis set is 500 eV, and the convergence threshold of ionic relaxation is 0.02 eV/Å. The Monkhorst-Pack *k*-meshes of 6×1×1 and 18×1×1 are used for geometry optimization and exact single-point energy calculations, respectively. Then, the band structures along the direction of high symmetry points Γ to X and density of states (DOS) structures are performed at PBE-D3 level employing the optimized 1D periodic isolated chains. Even though the PBE functional will underestimate the bandgap, it has been verified that different functionals have no significant effects on the band profile, especially on the band edge. Hence, almost identical *ZT* and *PF* values can be obtained using PBE functional compared with HSE06 functional in the case of semiconductors with relatively large bandgap. ^[4-7]

The effective mass m^* along the backbone direction is calculated by a parabolic fitting method according to equation (1), where $E(k)$ is band energy at wave vector k , \hbar is reduced Planck constant.

$$\frac{1}{m^*} = \frac{\partial^2 E(k)}{\hbar \partial k^2} \quad (1)$$

2. SE coupling calculations

In D-A copolymers, effective electronic coupling occurs between two adjacent D (or A) units through a SE coupling mechanism mediated by the in-between A (or D) as the bridge, which endows the copolymer with excellent TE transport properties along the intra-chain direction.^[6, 8-11] Here, the SE coupling is calculated using Larsson partition method^[8, 12] based on the triad oligomer ADA or DAD that is saturated by hydrogen atoms. The Hamiltonian and the overlap matrix of the triad oligomer are defined as H and S , respectively. The molecular orbitals of the oligomer and the fragments (hydrogen saturated D, A, and Bridge molecules) are first calculated, and then H and S of the triad oligomer can be projected to the fragment molecular orbitals as follows:

$$H = \begin{pmatrix} \varepsilon_1 & V_{12} & V_{1B} \\ V_{21} & \varepsilon_2 & V_{2B} \\ V_{B1} & V_{B2} & \varepsilon_B \end{pmatrix} \quad (2)$$

$$S = \begin{pmatrix} 1 & S_{12} & S_{1B} \\ S_{21} & 1 & S_{2B} \\ S_{B1} & S_{B2} & 1 \end{pmatrix} \quad (3)$$

The matrix elements are $\varepsilon_i = \langle \psi_i | \hat{H} | \psi_i \rangle$, $V_{ij} = V_{ji} = \langle \psi_i | \hat{H} | \psi_j \rangle$, and $S_{ij} = S_{ji} = \langle \psi_i | \psi_j \rangle$, respectively, where ψ is the the triad oligomer orbitals localized on fragment molecular orbitals. Take ADA triad as an example, ψ_1 and ψ_2 are the LUMOs of isolated A₁ and A₂ molecules, and ψ_B denotes the molecular orbitals of the bridge, that is isolated D molecule. After the Löwdin symmetric transformation, the Hamiltonian matrix can be represented by an orthogonalized basis set:

$$H = S^{-1/2}HS^{-1/2} = \begin{pmatrix} \tilde{\varepsilon}_1 & V_{12} & V_{1B} \\ \tilde{V}_{21} & \tilde{\varepsilon}_2 & \tilde{V}_{2B} \\ V_{B1} & V_{B2} & \tilde{\varepsilon}_B \end{pmatrix} \quad (4)$$

This orthogonalized basis set can take into account the polarization effect of the site energy, and then based on the Larsson partition method, we have

$$H^{eff} = \begin{pmatrix} \varepsilon_1^{eff} & V_{12}^{eff} \\ V_{21}^{eff} & \varepsilon_2^{eff} \end{pmatrix} = \begin{pmatrix} \tilde{\varepsilon}_1 & V_{12} \\ \tilde{V}_{21} & \tilde{\varepsilon}_2 \end{pmatrix} + \begin{pmatrix} V_{1B} \\ \tilde{V}_{2B} \end{pmatrix} \frac{1}{E - \tilde{\varepsilon}_B} (V_{B1} V_{B2}) \quad (5)$$

Here, V_{12}^{eff} is the SE coupling, which can be expressed as

$$V_{12}^{eff} = \tilde{V}_{12} + \sum_{b \in B} \frac{V_{1b} V_{b2}}{E - \tilde{\varepsilon}_b} \quad (6)$$

Where E represents the adiabatic energy of the triad oligomer, $\tilde{\varepsilon}_b$ is the energy levels of bridge orbitals, V_{1b} and V_{b2} are the couplings between each molecular orbital of the bridge and the frontier molecular orbitals (FMOs) of two adjacent fragments. According to equation (6), the contribution of all molecular orbitals of the bridge to the SE coupling can be considered. Besides, in

copolymers, the \tilde{V}_{12} term is much smaller than the $\sum_{b \in B} \frac{V_{1b} V_{b2}}{E - \tilde{\varepsilon}_b}$ term. Therefore, the SE coupling principally depends on the contribution of bridge orbitals.

The calculation of SE coupling is carried out at the B3LYP level in the Gaussian 09 code. And the def2-SV basis set is adopted, which is used as a pseudopotential basis set for Te element and an all-electron basis set for other elements.

3. TE transport parameters calculations

Based on the Boltzmann transport equation, deformation potential (DP) theory, and first-principles band structures, the TE transport parameters of the copolymers along the backbone direction can

be calculated. According to Boltzmann transport equation, the transport tensors, electrical conductivity σ and Seebeck coefficient S , are defined as

$$\sigma = \frac{e^2}{V} \sum_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) v_k v_k \tau_k \quad (7)$$

$$S = \frac{e}{V \sigma T} \sum_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) (\varepsilon_k - \varepsilon_F) v_k v_k \tau_k \quad (8)$$

Where e is the electron charge, V is the volume of the unit cell, $f_0 = \frac{1}{\exp\left(\frac{\varepsilon_k - \varepsilon_F}{k_B T}\right) + 1}$ is Fermi-Dirac distribution function, k_B is Boltzmann constant, ε_F is Fermi energy, T is temperature, and

$v_k v_k \tau_k$ is transport distribution tensor. $v_k = \frac{1}{\hbar} \frac{\partial \varepsilon_k}{\partial k}$ is group velocity, which can be calculated from the band structure. τ_k is relaxation time. Here, the DP theory^[12] is employed to calculate the relaxation time, which is widely applied in TE transport parameters calculations of conjugated polymers based on the assumption that carriers are mainly scattered by longitudinal acoustic phonon with long wavelength.^[6, 13-15] In the DP theory, the relaxation time is defined as

$$\frac{1}{\tau_k} = \frac{2\pi k_B T E_1^2}{V \hbar C_{ii}} \sum_{k \in BZ} \left\{ \delta(\varepsilon_k - \varepsilon_{k'}) (1 - \cos \theta) \right\} \quad (9)$$

Where $\delta(\varepsilon_k - \varepsilon_{k'})$ is Dirac delta function used to ensure energy conservation under the assumption of elastic scattering, θ is scattering angle between wave vectors κ and k' . C_{ii} and E_1 is elastic constant and DP constant, respectively, which can be calculated according to the formulas listed below

$$C_{ii} = \frac{\partial^2 E_{total}}{\partial (\Delta a / a_0)^2} / a_0 \quad (10)$$

$$E_1 = \frac{dE_{VBM/CBM}}{d(\Delta a / a_0)} \quad (11)$$

Where a_0 the lattice constant along the backbone direction at the equilibrium, $\Delta a/a_0$ is deformation rate, E_{total} is the total energy of the unit cell, $E_{VBM/CBM}$ is the energy at valence band maximum (VBM) for the hole DP constant calculation or conduction band minimum (CBM) for the electron DP constant calculation. Based on calculated C_{ii} and E_1 , the intra-chain carrier mobility of quasi 1D systems can be evaluated by effective mass approximate:

$$\mu^{1D} = \frac{e\hbar^2 C_{ii}}{(2\pi k_B T m^*)^{1/2} E_1^2} \quad (12)$$

In view of the inherently low thermal conductivity of organic materials, especially conjugated polymers,^[16, 17] the power factor is used here to simplify the evaluation index of D-A copolymers, which is calculated by the formula $PF = S^2 \sigma$.

TE parameters calculations should be performed based on the band energies with denser k -meshes obtained by smoothed Fourier interpolation method. Here, the original k -meshes $45 \times 1 \times 1$ are interpolated on a mesh twenty times denser. Calculations of σ and S are performed in the program BoltzTraP.^[18]

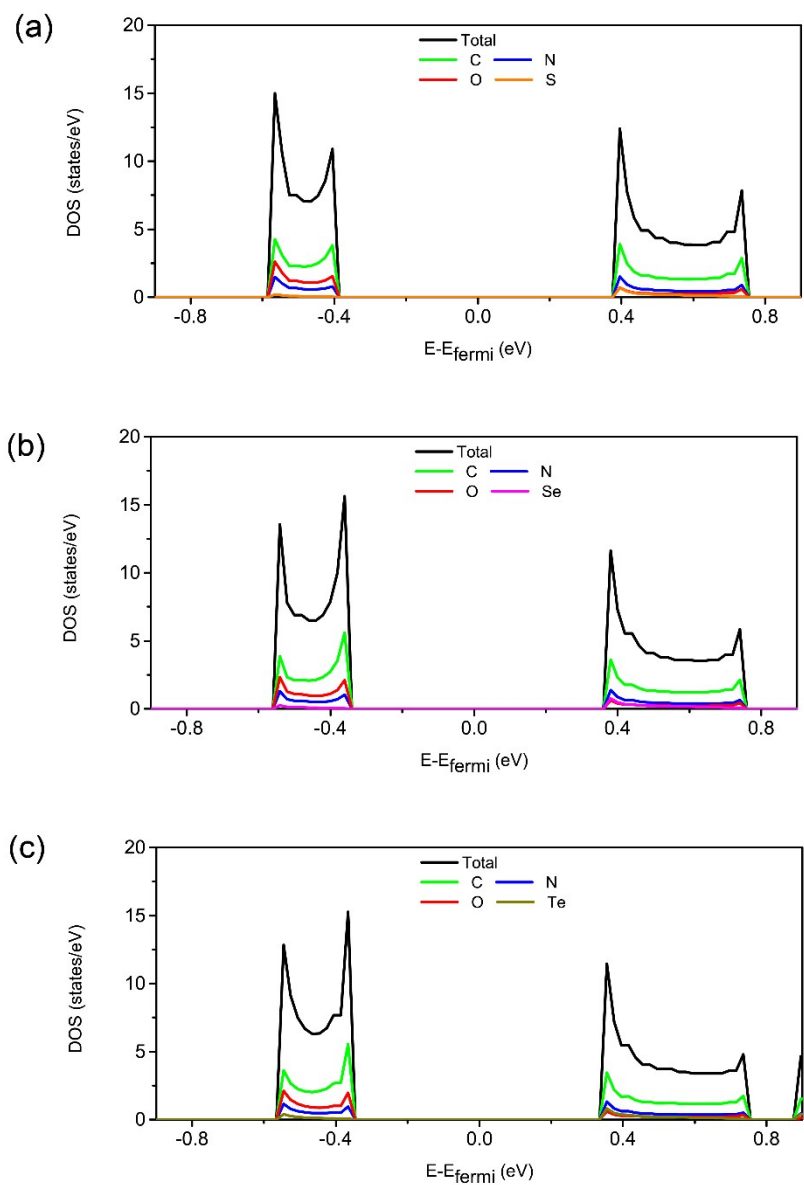


Fig. S1 Total DOS and projected DOS of (a) PzDPP-CT2 (b) PzDPP-CSe2 (c) PzDPP-CTe2.

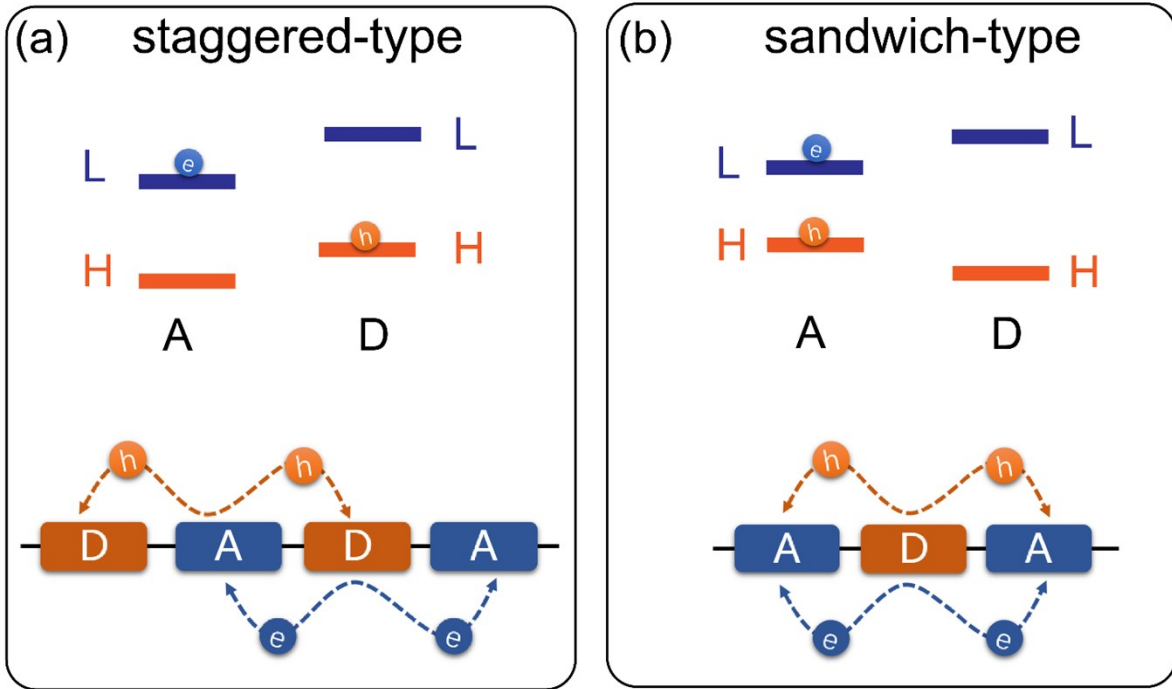


Fig. S2 Two types of SE coupling models and corresponding energy alignment: (a) staggered-type; (b) sandwich-type.

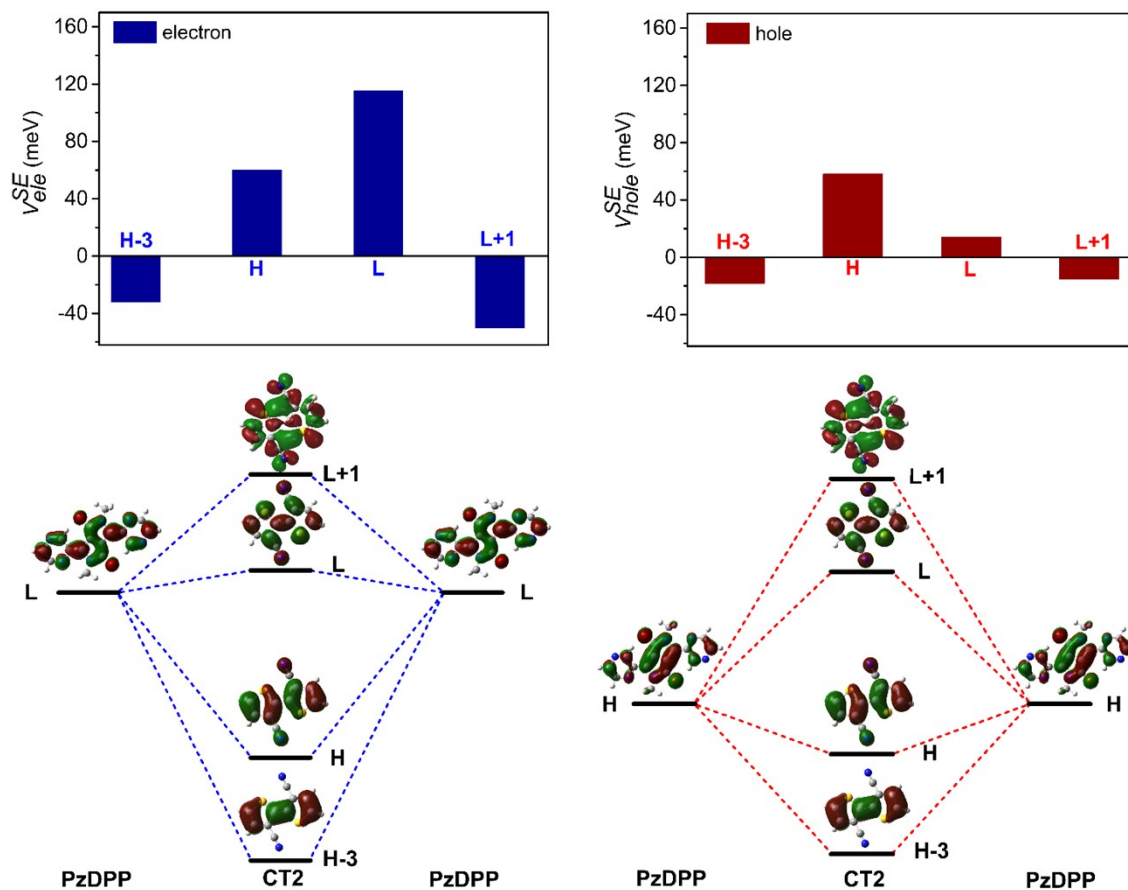


Fig. S3 The energy decomposition of electron and hole SE coupling contributed from the bridge orbitals, as well as energy alignment and wave functions for molecular orbitals of PzDPP and CT2.

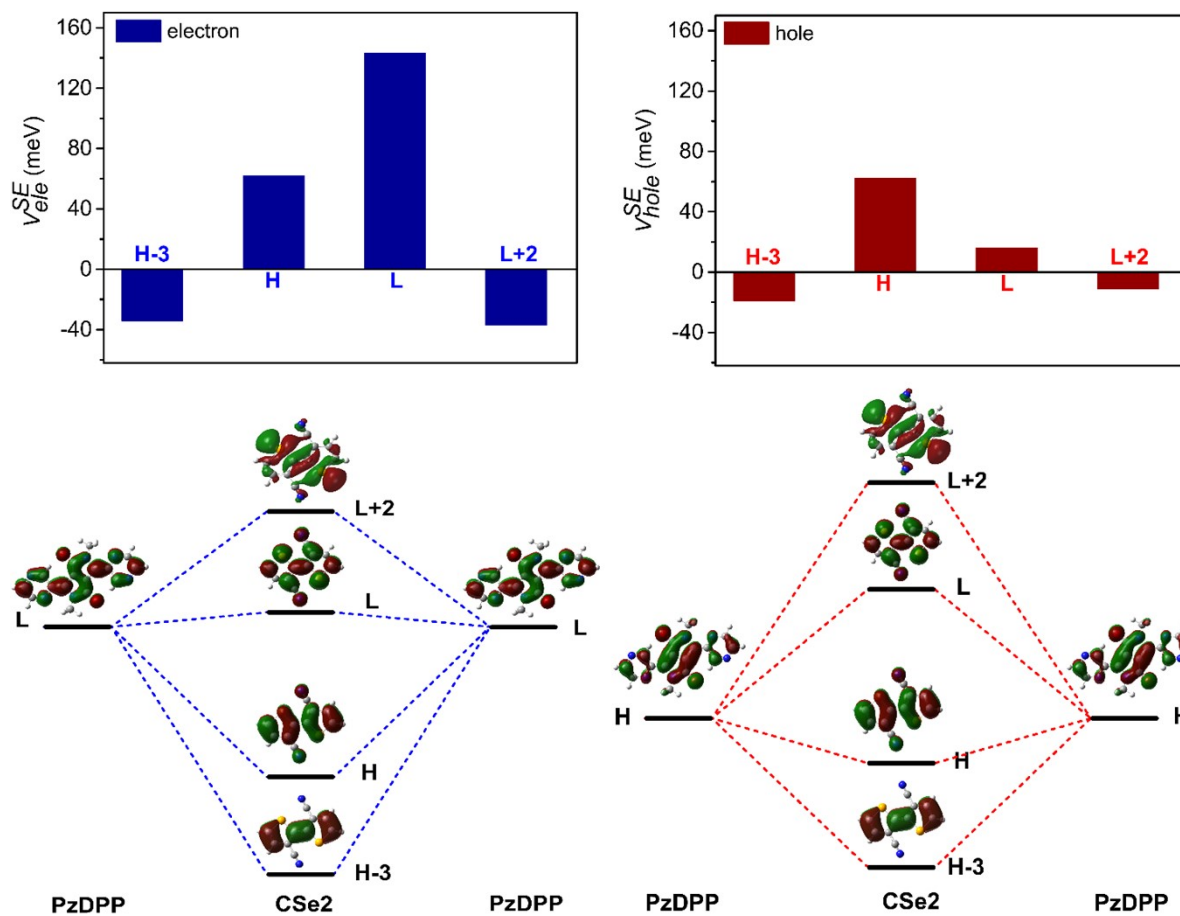


Fig. S4 The energy decomposition of electron and hole SE coupling contributed from the bridge orbitals, as well as energy alignment and wave functions for molecular orbitals of PzDPP and CSe2.

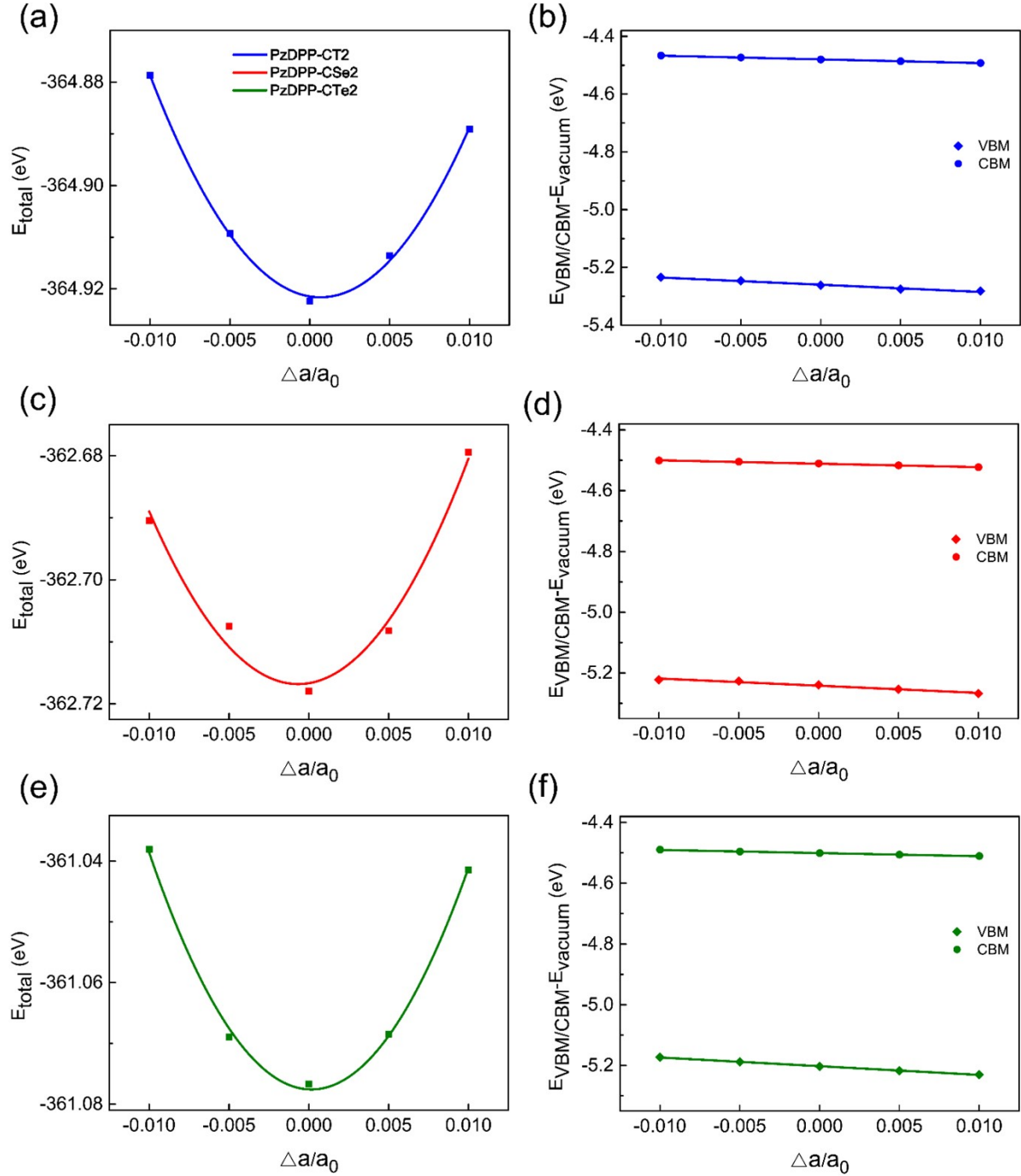


Fig. S5 The parabolic relationship between the total energy of the unit cell E_{total} and the linear relationship between the band edge energy $E_{\text{VBM/CBM}}$ with respect to the lattice dilation along a -axis ($\Delta a/a_0$). $E_{\text{VBM/CBM}}$ takes the vacuum level E_{vacuum} as the energy reference.

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