Electronic Supplementary Information (ESI)

Adjustable uniaxial zero thermal expansion and zero linear compressibility in unique hybrid semiconductors: the role of organic chain

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1. Thermodynamic properties of [ZnTe(L)$_{0.5}$]

In QHA, vibrational energy F_{vib} is given by

$$F_{vib} = U - E_{stat} - TS = k_B T \sum_{q\lambda} \ln \left\{ 2\sinh\left(\frac{\hbar\omega_{q\lambda}(a)}{2k_B T} \right) \right\}, \tag{1}$$

where U is the internal energy.

The heat capacity C_V at a constant volume is obtained from

$$C_V = k_B \sum_{q\lambda} \left(\frac{\hbar\omega_{q\lambda}(q)}{2k_B T} \right)^2 \frac{1}{\sinh^2\left(\hbar\omega_{q\lambda}(q) / 2k_B T \right)}. \tag{2}$$

For a constant volume process, the entropy S is established by

$$S - S_0 = vC_V \ln \frac{T}{T_0}, \tag{3}$$

where v represents the amount of substance.

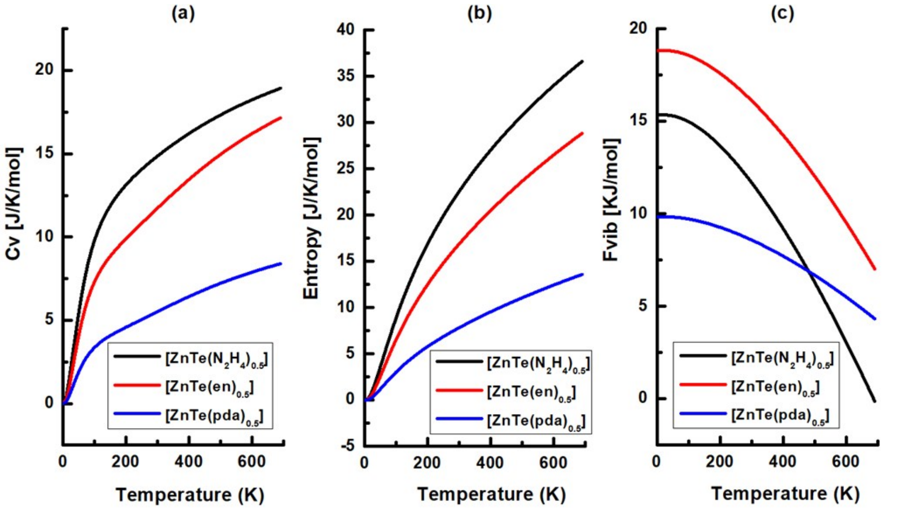
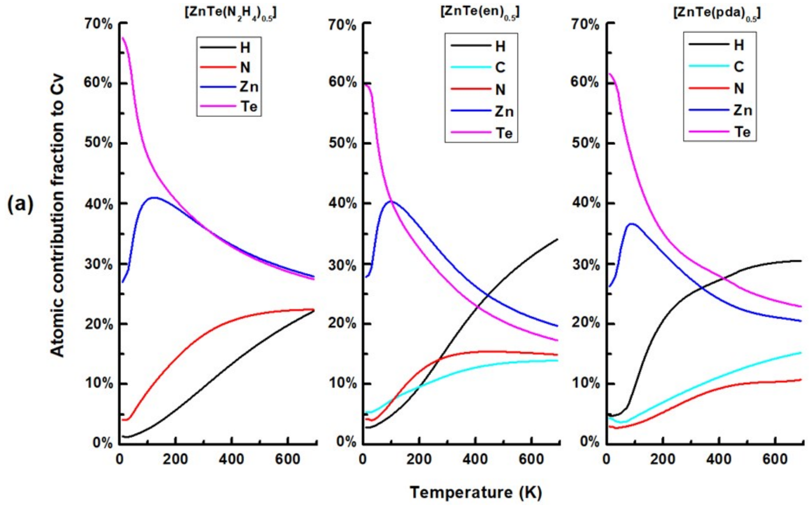
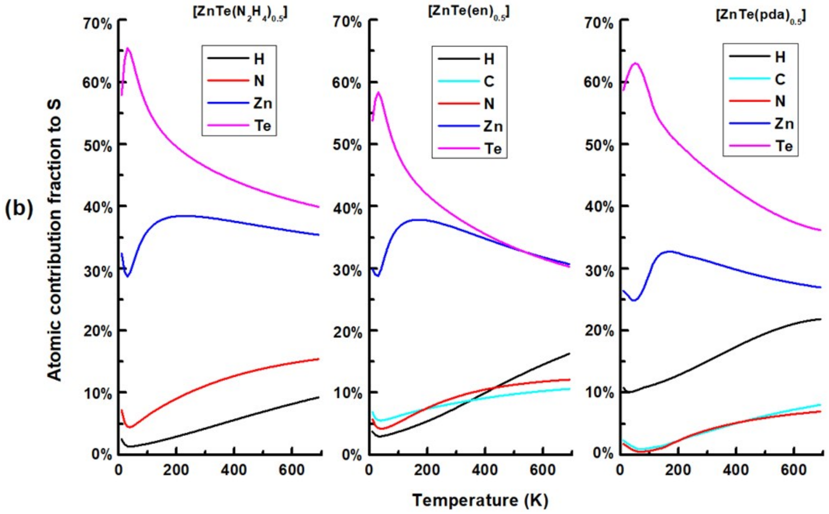


Figure S1: (Color online) Variations of (a) heat capacity C_V, (b) entropy and (c) vibrational free energy F_{vib} of [ZnTe(N_2H_4)$_{0.5}$], [ZnTe(en)$_{0.5}$] and [ZnTe(pda)$_{0.5}$] with temperature.

The calculated isochoric heat capacity C_V, entropy S and vibrational energy F_{vib} of [ZnTe(L)$_{0.5}$] are displayed in Fig. S1. Temperatures higher than 700 K are not considered here, owing to the appearance of high-order anharmonicity not included in QHA. When heated, the frequency of lattice vibration increases gradually, so the C_V attributed from the lattice vibration will increase accordingly and follow the Debye T^3 law at low temperature (< 100 K). After reaching a certain temperature, all phonons have been excited, the heat capacity will stabilize and reach a fixed value, following the Dulong-Petit law. The S increases as the temperature rises due to the increase of disorder degree. On the contrary, F_{vib} will show a decreasing trend with the increase of temperature T and entropy S, based on formula (1). At a given temperature, the C_V and S of [ZnTe(L)$_{0.5}$] decrease gradually as the length of organic chain increases from N_2H_4 to pda. Whereas the rate of decline of F_{vib} of [ZnTe(pda)$_{0.5}$] is quite different from other two compounds. The F_{vib} follows $F_{vib}[\mathrm{ZnTe(en)}_{0.5}] > F_{vib}[\mathrm{ZnTe(N_2H_4)}_{0.5}] > F_{vib}[\mathrm{ZnTe(pda)}_{0.5}]$ below 480 K and thereafter $F_{vib}[\mathrm{ZnTe(en)}_{0.5}] > F_{vib}[\mathrm{ZnTe(pda)}_{0.5}] > F_{vib}[\mathrm{ZnTe(N_2H_4)}_{0.5}]$.





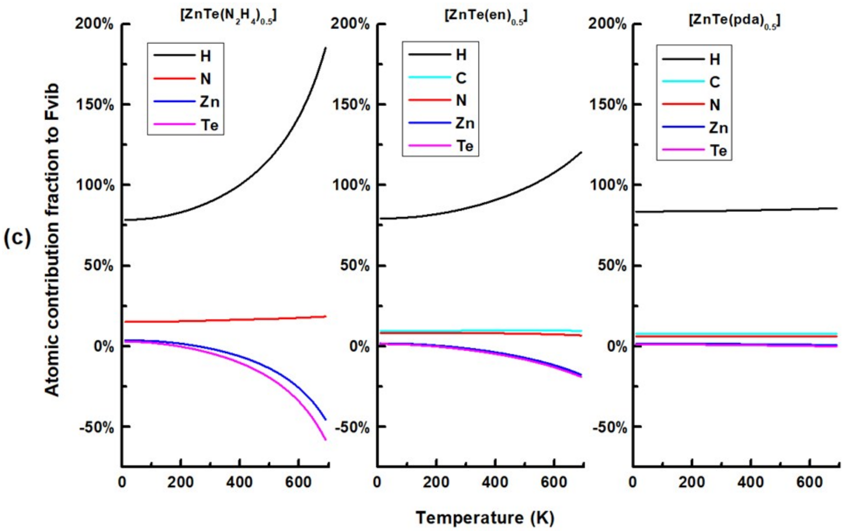


Figure S2: (Color online) Temperature dependence of atomic contribution fraction to (a) heat capacity C_V, (b) entropy S and (c) vibrational free energy F_{vib} of [ZnTe(N$_2$H$_4$)$_{0.5}$], [ZnTe(en)$_{0.5}$] and [ZnTe(pda)$_{0.5}$].

Moreover, we estimate the weight of atomic contribution to the above thermodynamic parameters in [ZnTe(L)$_{0.5}$], as shown in Fig. S2. It is found in Fig. S2(a) and Fig. S2(b) that on the whole Zn and Te atoms have larger weights to C_V and S compared with H, C and N atoms. Heavier atoms have lower vibrational frequencies, hence they are easier to be excited. Here it is manifest that the contributions from Zn and Te prevail in these thermodynamic parameters. The contribution weight of Te to C_V is gradually decreasing with increasing temperature, while that of Zn first increases and then decreases with the change in temperature. The transition temperature of contribution weight of Zn is also gradually decreasing from ~120 K for [ZnTe(N$_2$H$_4$)$_{0.5}$] to ~100 K for [ZnTe(en)$_{0.5}$], then to ~90 K for [ZnTe(pda)$_{0.5}$]. On the contrary, the contribution weights of H, N and C atoms to C_V increase as temperature rises. Specially, in [ZnTe(en)$_{0.5}$] and [ZnTe(pda)$_{0.5}$], the contribution of H atom to C_V exceeds that of Zn and Te atoms when a certain temperature is reached. As for the atomic contribution weight to entropy, at low temperatures, the contribution of Te atom to entropy decreases after an initial increases, but that of H, N and C atoms show an opposite trend. The contribution of Zn to entropy experiences a complex change in the studied range of temperature from initial decrease to increase, then to final decrease. In the case of F_{vib} (Fig. S2(c)), we find that nonmetallic atoms including H, C and N have positive contribution to F_{vib}, especially the contribution from the H atom is overwhelming and will increase with the increasing temperature. By contrast, the metallic atoms, i.e. Zn and Te, contribute negatively to F_{vib}. The negative contributions from metal atoms are growing stronger with the rise of temperature. Overall, the absolute value of atomic contribution to F_{vib} at any given temperature decreases as the length of organic chain increases, and the contribution weights are also gradually weakened.

2. Phonon dispersion

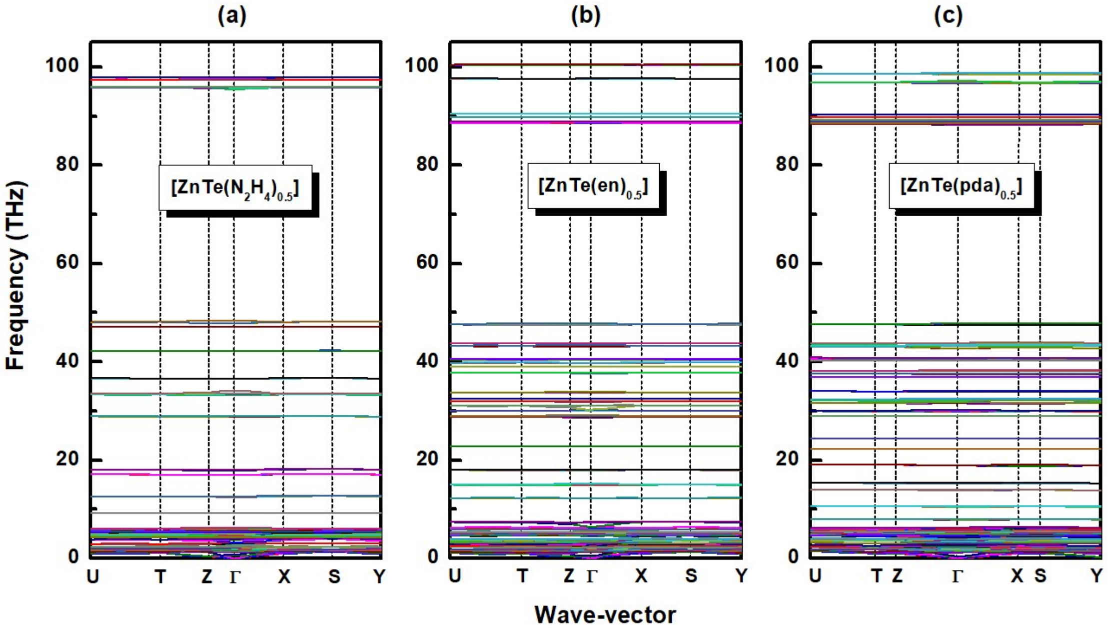


Figure S3: Calculated phonon dispersion curves along high-symmetry direction in Brillouin zone of (a) [ZnTe(N_2H_4)$_{0.5}$], (b) [ZnTe(en)$_{0.5}$] and (c) [ZnTe(pda)$_{0.5}$].

As shown in Fig. S3, the dispersion relations are found to be quite similar in the studied [ZnTe(L)$_{0.5}$], whereas the gap between mid-energy (< 50 THz) and high-energy (> 50 THz) phonons decreases gradually as the length of organic chain increases.

The total phonons of the three compounds can be described using the method of factor group analysis. The irreducible representations for the vibrational modes of three compounds are

$$\Gamma_{total}[\mathrm{ZnTe(N_2H_4)_{0.5}}] = 15A_g(\mathrm{R}) + 15B_{1g}(\mathrm{R}) + 15B_{2g}(\mathrm{R}) + 15B_{3g}(\mathrm{R}) + 15A_u + 15B_{1u}(\mathrm{ir}) + 15B_{2u}(\mathrm{ir}) + 15B_{3u}(\mathrm{ir}),$$
$$\Gamma_{acoustic}[\mathrm{ZnTe(N_2H_4)_{0.5}}] = B_{1u} + B_{2u} + B_{3u};$$

$$\Gamma_{total}[\mathrm{ZnTe(en)_{0.5}}] = 24A_g(\mathrm{R}) + 24B_{1g}(\mathrm{R}) + 24B_{2g}(\mathrm{R}) + 24B_{3g}(\mathrm{R}) + 24A_u + 24B_{1u}(\mathrm{ir}) + 24B_{2u}(\mathrm{ir}) + 24B_{3u}(\mathrm{ir}),$$
$$\Gamma_{acoustic}[\mathrm{ZnTe(en)_{0.5}}] = B_{1u} + B_{2u} + B_{3u};$$

$$\Gamma_{total}[\mathrm{ZnTe(pda)_{0.5}}] = 30A_1(\mathrm{R,ir}) + 27A_2(\mathrm{R}) + 27B_1(\mathrm{R,ir}) + 30B_2(\mathrm{R,ir}),$$
$$\Gamma_{acoustic}[\mathrm{ZnTe(pda)_{0.5}}] = A_1 + B_1 + B_2.$$

R(ir) denotes Raman (infrared) activity and the remaining modes are silent. [ZnTe(N$_2$H$_4$)$_{0.5}$] and [ZnTe(en)$_{0.5}$] have the same mode symmetry classification because of the same space group. It is only the difference in the number of atoms in primitive cells of the two compounds that leads to the difference in the number of mode symmetries. Whereas, increasing the length of organic chains subtly changes the space group of [ZnTe(pda)$_{0.5}$], so the mode symmetry has also changed accordingly.