Giant tunable Rashba Spin Splitting in Two-Dimensional Polar Perovskites $TlSnX_3$ (X=Cl, Br, I)

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I. STRUCTURE AND STABILITY

Table S1: Formation energy E_f (eV per f.u.) of 2D polar perovskites $TlSnX_3$ (X=Cl, Br, I)

structure	E_f（2D）
$TlSnCl_3$	-0.512
$TlSnBr_3$	-1.740
$TlSnI_3$	-1.859

In order to verify the stability of predicted two-dimensional (2D) polar perovskites $TlSnX_3$ (X=Cl, Br, I), we calculate the thermodynamic stability and dynamic stability of them. The formation energies of 2D $TlSnX_3$ (X=Cl, Br, I) are defined as follows:

$$E_f(2D) = E_{2D} - E_{AX} - E_{BX_2}$$

The calculation results show that the formation energy of 2D $TlSnX_3$ (X=Cl, Br, I) is negative, so they are stable in thermodynamics.

In order to further confirm the thermal stability, we calculate the molecular dynamics simulation of these materials. As shown in Figure s1, the supercell structure and total energy evolution of 2D $TlSnX_3$ (X=Cl, Br, I) calculated by 8ps molecular dynamics are given respectively. The results confirm the stability of these 2D polar perovskites at 300K and thermal fluctuation have little effect on the structures, so the physical properties such as electronic structure are not affected.

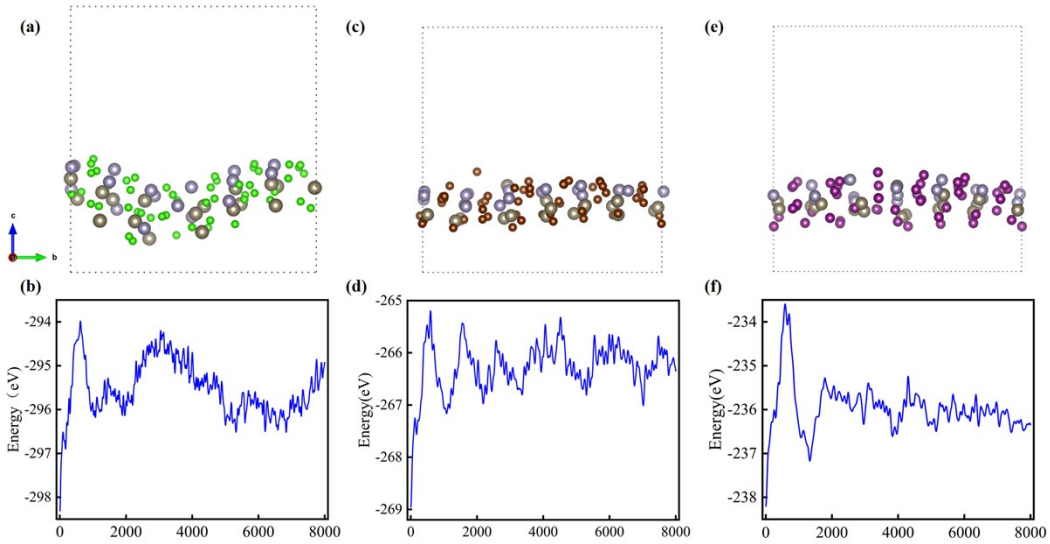

Fig. S1: Ab initio molecular dynamics simulation of 2D polar perovskites $TlSnX_3$ (X=Cl, Br, I) (T=300 K). (a) After 8ps molecular dynamics calculation, the supercell structure of $TlSnCl_3$ and the corresponding (b) total energy evolution were obtained. (c) After 8ps molecular dynamics calculation, the supercell structure of $TlSnBr_3$ and the corresponding (d) total energy evolution were obtained. (e) After 8ps molecular dynamics calculation, the supercell structure of $TlSnI_3$ and the corresponding (f) total energy evolution were obtained.

Secondly, we take $TlSnI_3$ as an example to further study the dynamic stability of these 2D polar perovskites by calculating the phonon spectra. As shown in Fig. s2, unfortunately, $TlSnI_3$ has an imaginary frequency of about 0.5 THz. We think this may be ascribed to the calculation accuracy, so we try to improve the accuracy and optimize the structure by adjusting the calculation parameters and expanding the size of the supercell. We find that the negative frequency is indeed reduced by improving the calculation accuracy, but it does take up more calculation resources. In fact, the imaginary frequency of perovskites has been mentioned in previous studies. For example, $LiOsO_3$ with $R^{-}3c$ room temperature phase have imaginary frequency around 5 THz; the tetragonal phase $RbPbI_3$ have imaginary frequency around 0.5 THz; In the research of perovskites $Cs_2AgInBr_{(6-x)}Cl_x$, it's also claimed that small imaginary frequency is acceptable errors in phonon calculations. Thus, through the analysis of binding energy, molecular dynamics and phonon spectrum, it can be considered that these 2D polar perovskites possess stable structures.

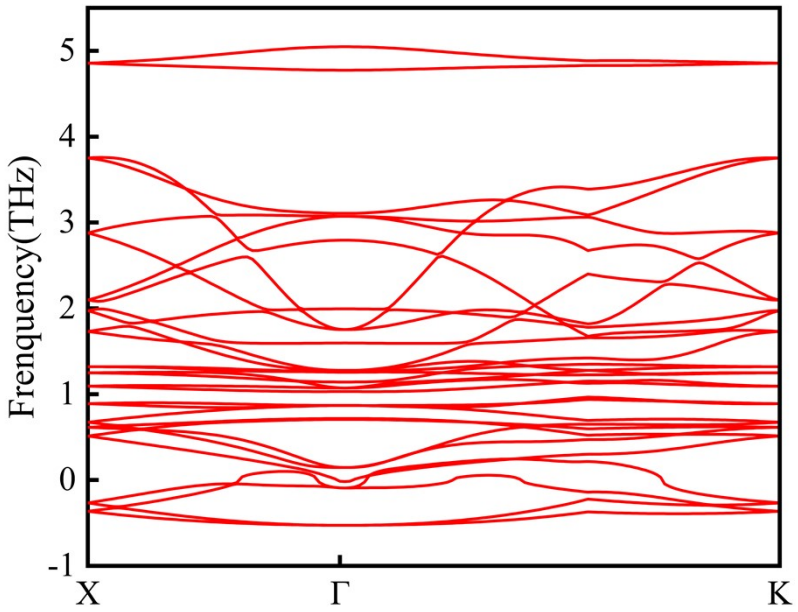

Fig. S2: Phonon spectra of $TlSnI_3$

II. MECHANISM ANALYSIS

Table S2: Bader charge analysis of 2D perovskites $TlSnX_3$ (X=Cl, Br, I). Q_B is the average charge of B site , and Q_X is the average charge of X site (Cl/Br/I).

	Q_B	Q_X
$TlSnCl_3$	0.829	-0.492
$TlSnBr_3$	1.051	-0.593
$TlSnI_3$	1.204	-0.654

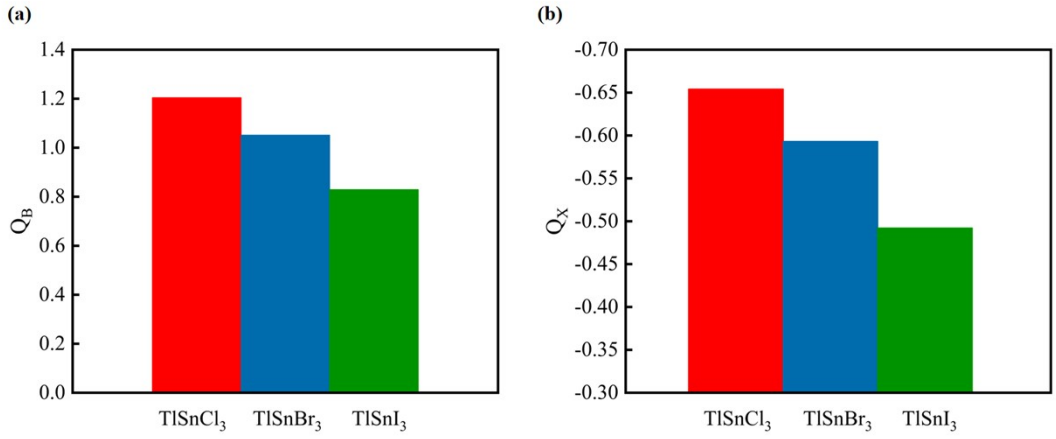

Fig. S3: (a) Q_B and (b) Q_X of 2D polarperovskites $TlSnX_3$ (X=Cl, Br, I).

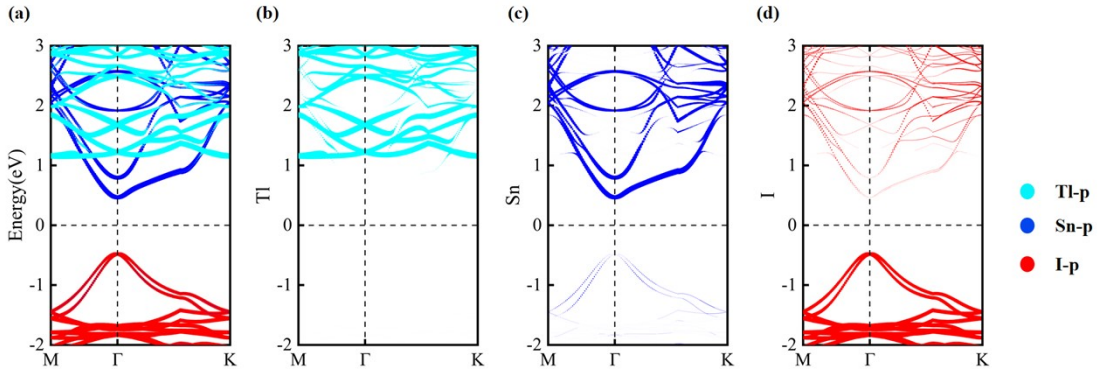

Fig. S4: The projected band structures of (a) $TlSnI_3$ with SOC for (b) Tl, (c) Sn and (d) I atoms. (The cyan, blue and red represent the P orbitals of Tl, Sn and I atoms, respectively)

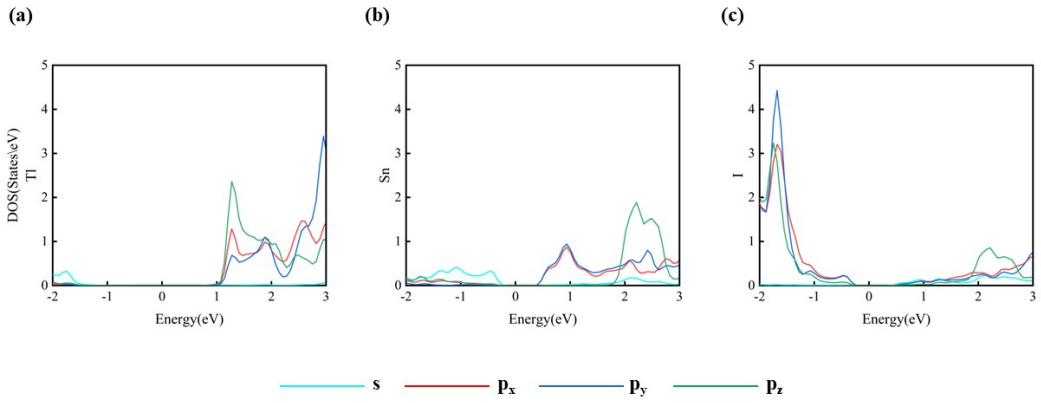

Fig. S5: The density of states of $TlSnI_3$ with SOC for (a) Tl, (b) Sn and (c) I atoms. (The green, red, blue and green lines represent s, p_x, p_y and p_z orbits respectively.)

III. ELECTRONIC PROPERTIES OF $TlSnI_3$ 3D BULK AND 2D NON-POLAR STRUCTURES

The electronic properties of 2D and 3D tetragonal $TlSnI_3$ were calculated by first principles. Two 2D nonpolar perovskites with TlI-terminated and SnI_2-terminated slabs will appear if the (001) plane is cut.

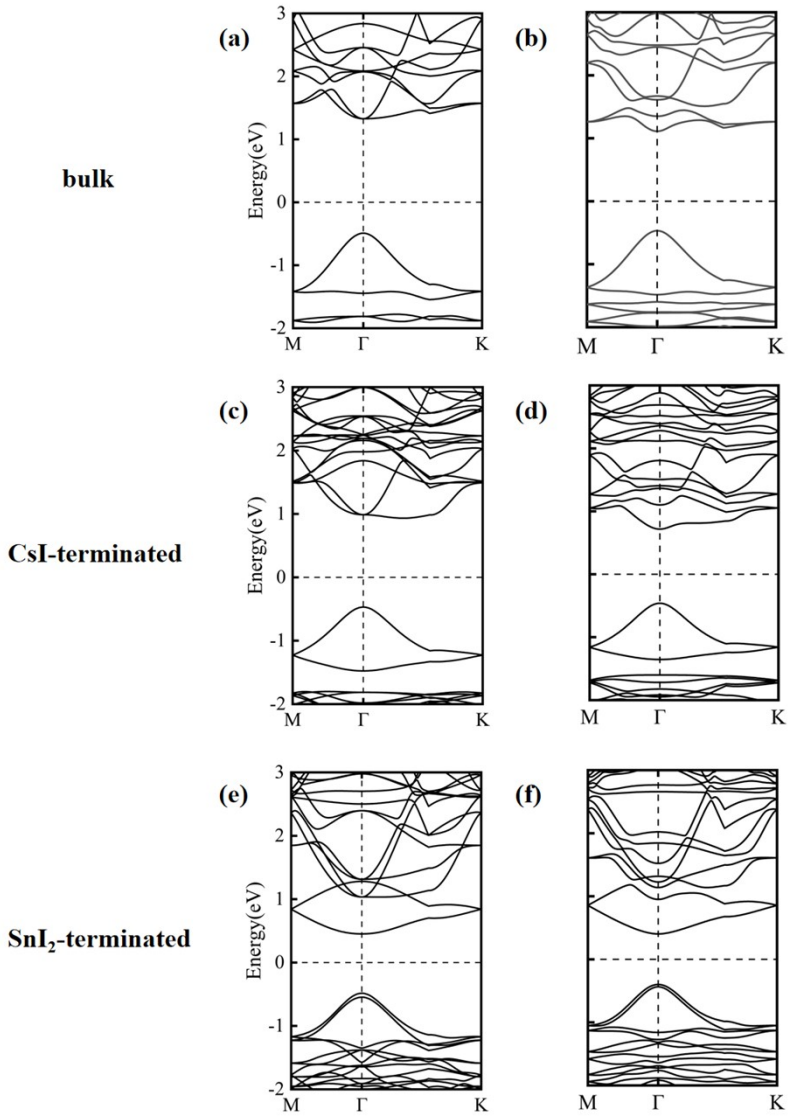

Fig. S6: Band structures of $TlSnI_3$ 3D bulk and 2D non-polar structures without (left) and SOC (right).

IV. ELECTRONIC STRUCTURES OF MULTILAYER 2D $TlSnI_3$ PEROVSKITES

The electronic structure of 2D multilayer $TlSnI_3$ is calculated by first principles, as shown in Fig. S7. The results show that the Rashba effect still exists near the Γ point of 2D multilayer perovskites, but the Rashba constant is much smaller.

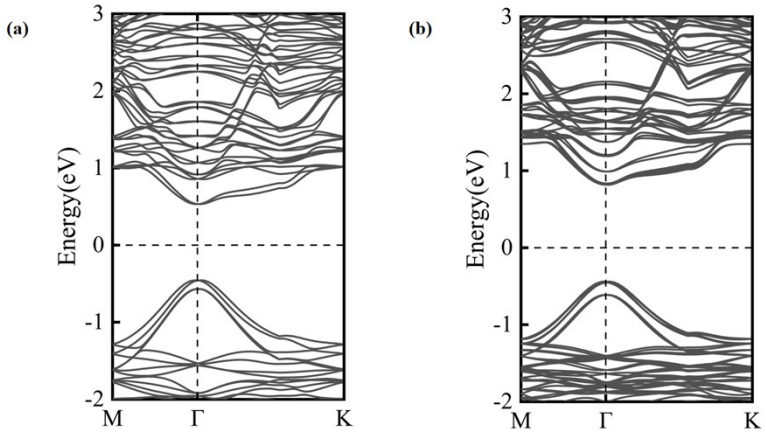

Fig. S7: Electronic structure of (a) 2L and (b) 3L of 2D polar perovskite $TlSnI_3$