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First-Principles Prediction of Polar Half-Metallicity and Out-of-Plane Piezoelectricity in Two-Dimensional Quintuple Layered Cobalt Selenide

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Computational Details

The structural search was performed with the population size being set to 30. For each step, the 60% of the generated structures were evolved into next generation by particle swarm optimization (PSO) methodology, while other 40% were randomly generated. In order to explore the quintuple layered structure, the structural search is performed as two separated layers with one layer containing 1 Se and 1 transition metal atoms and another layer containing 2 Se and 1 transition metal atoms. The initial distortion of each layer is set to be 0.2 Å, while the distance is set to zero. The magnetic transition temperature is estimated via Monte Carlo simulations in Vampire code. The Monte Carlo steps were set to be 1×10^5 followed by 1.5×10^5 steps for time averaging at each temperature. The simulated geometry is taken to be 15×15 nm for the structures. The thermal stability is examined by the *ab initio* molecular dynamic (AIMD) simulations at 200, 400 and 800 K for 10 ps with the time step of 1 fs. The temperature is controlled by the Nose-Hoover method.[1] The phonon spectrum is used to illustrate the dynamical stability of QL Co_2Se_3 monolayer, as implemented in Phonopy code within finite displacement method. Besides, the magnetic anisotropic is calculated by $E = E_{\perp} - E_{/\!/}$, where $E_{\perp}$ and $E_{/\!/}$ are the total energies with the initial magnetic moment along the *z* and *x* directions, respectively. The ferroelectric switching pathway is calculated by the nudged elastic band (NEB) method.[2] Additionally, the perpendicular (out-of-plane) polarization is estimated by the product of total number of valence charge (q) and the vector pointing from negative charge

centre (*NCC*) to the positive charge centre (*PCC*) along the *z* direction. The coordinate of *NCC* and *PCC* can be obtained from the integration of charge carrier density as following,

$$NCC = \frac{\iiint \rho z dx dy dz}{q}$$

$$PCC = \frac{\sum nz}{q}$$

where ρ is the charge density, while z is the coordinate along the out-of plane axis. n is the number of the valence charge of each ion in the unit cell. Based on this method, the obtained out-of-plane polarization of QL In_2Se_3 monolayer is 0.094 eÅ/unit cell., which is consistent with the previous report.[3]

U value for QL Co_2Se_3

The value of U is calculated based on the difference between non-selfconsistent (x_0) and selfconsistent (x_1) responds, which are described by $x_{IJ}^0 = \partial N_I^{NSCF}/\partial U_J$ and $x_{IJ}^1 = \partial N_I^{SCF}/\partial U_J$, respectively. Herein, the N and U represent the number of d-electrons and the additional potential U. Thus, the U parameter for Co_2Se_3 can be calculated through:

$$U = x_1^{-1} - x_0^{-1} \approx \left(\frac{\partial N_I^{SCF}}{\partial U_I}\right)^{-1} - \left(\frac{\partial N_I^{NSCF}}{\partial U_I}\right)^{-1}$$

Thus, the U is estimated to be 5.2 eV as shown in Fig. S1.

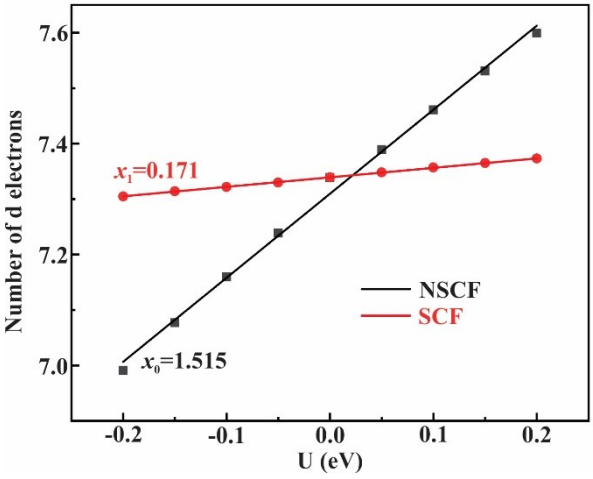

Fig. S1. The linear fit of the number of d-electrons on one Co atom as a function of the additional potential U. The x_0 and x_1 represent the slope for each line.

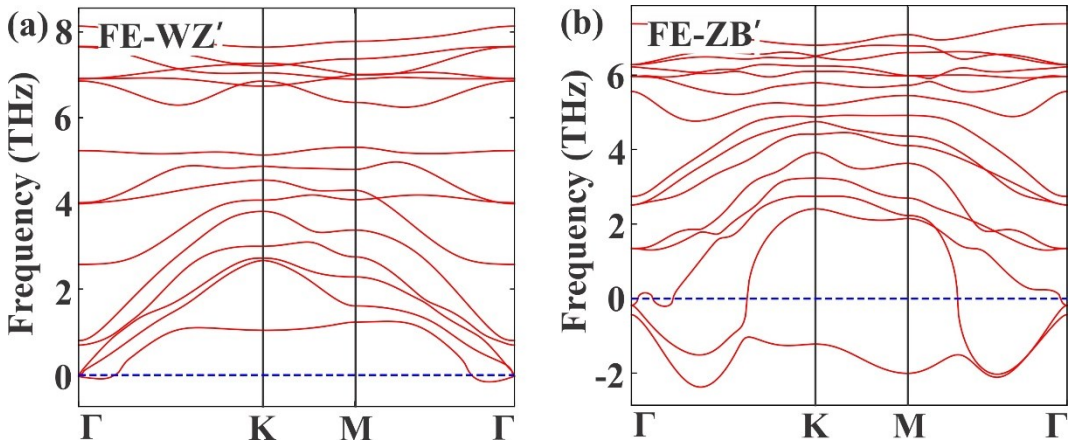

Fig. S2. Phonon spectra of (a) FE-WZ', (b) FE-ZB'and phase Co_2Se_3 monolayer. The negative frequency in (a) around Γ-point is attributed by the vertical vibration, which is exist in many 2D materials and can be stabilized by the substrate, as shown in pioneering works for 2D FeB_2 and Fe_3O_4.[4-5]

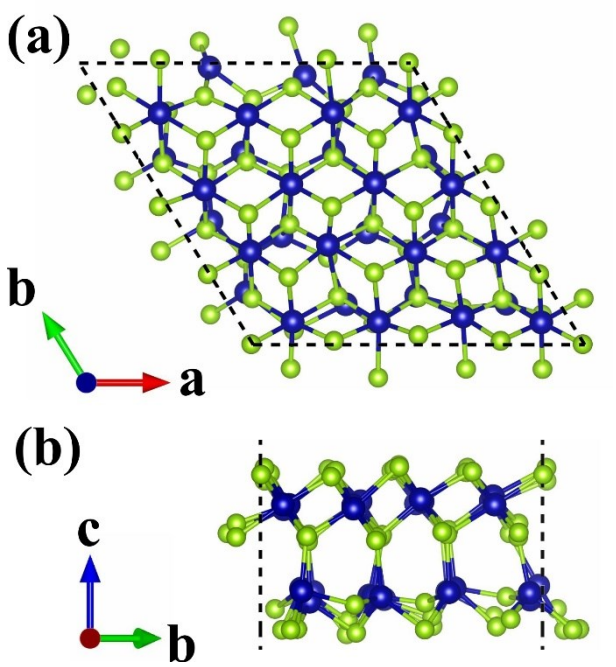

Fig. S3. The (a) top and (b) side views of final structures of AIMD simulations of FE-WZ' Co_2Se_3 monolayer at 400 K.

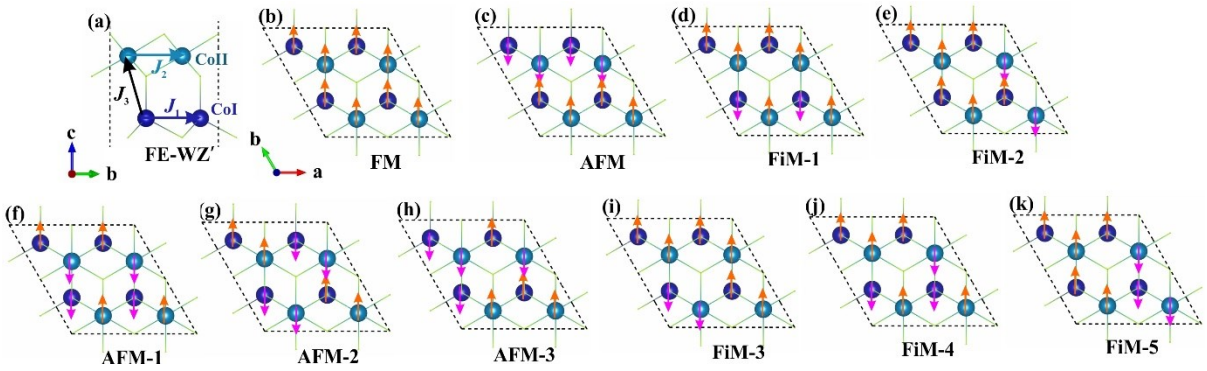

Fig. S4. (a) side view and the different (b-m) magnetic configurations of 2D Co_2Se_3 in FE-WZ' phase, including ferromagnetic (FM), ferrimagnetic (FiM) and antiferromagnetic (AFM) states. Blue and light blue spheres represent Co atoms in bottom (CoI) and top (CoII) layer, respectively. The J_1, J_2 and J_3 are the exchange parameters for the nearest-neighboring CoI-CoI, CoII-CoII and CoI-CoII hopping, respectively.

Table S1. Total energies (eV) of Co_2Se_3 monolayers in FE-WZ' phase under different magnetic configurations, including ferromagnetism (FM), ferrimagnetism (FiM), antiferromagnetism (AFM) and non-ferromagnetism (NM).

Configurations	Energy (eV)	Configurations	Energy (eV)
FM	**-79.345741**	FiM-3	-79.059803
AFM	-79.064367	FiM-4	-79.116200
FiM-1	-79.139989	FiM-5	-79.006027
FiM-2	-79.011703	NM	-72.460422
AFM-1	-79.046705		
AFM-2	-79.047033		
AFM-3	-79.037598		

Details for exchange parameters calculation

The magnetic exchange parameter, J, is estimated through Hamiltonian,

$$H = -J_1 \times \vec{S}_k \vec{S}_l - - J_2 \times \vec{S}_m \vec{S}_n - - J_3 \times \vec{S}_k \vec{S}_m + \sum_{k,m} K(\vec{S}^{\,z}_{k,m} \vec{A}_{k,m})^2$$

where, J_1, J_2 and J_3 are the exchange parameter between nearest neighboring CoI-CoI, CoII-CoII and CoI-CoII, respectively. (See Fig. S4) The $\vec{S}$ is the net magnetic moment of Co atoms. K and $\vec{A}$ represent the coefficient of anisotropy and magnetocrystalline axis. Accordingly, the total energies of Co_2Se_3 under different configurations can be expressed as

$$E_{FM} = E_0 - (12J_1 + 12J_2 + 12J_3) \times S^2$$

$$E_{AFM} = E_0 + (4J_1 + 4J_2 - 4J_3) \times S^2$$

$$E_{FiM-1} = E_0 - (-4J_1 + 12J_2) \times S^2$$

$$E_{FiM-2} = E_0 - (12J_1 - 4J_2) \times S^2$$

where S is the value of Co magnetic moment, which is fixed at 1 μ_B in our calculation. Therefore, the exchange parameter can be estimated based on the calculated total energies.

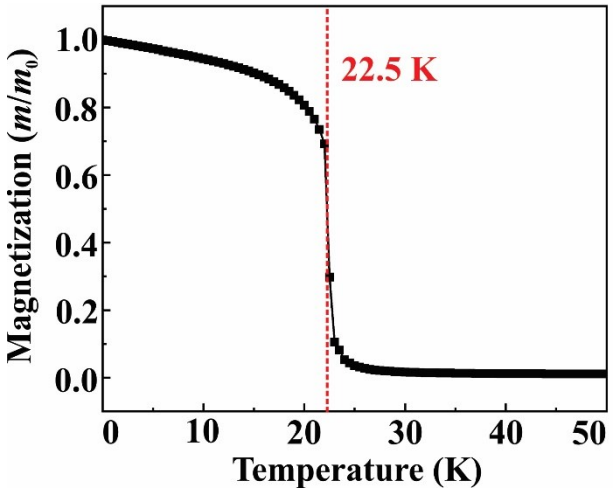

Fig. S5. Monte Carlo simulation for FM FE-WZ' Co_2Se_3 monolayer. The estimated Curie temperature is around 22.5 K.

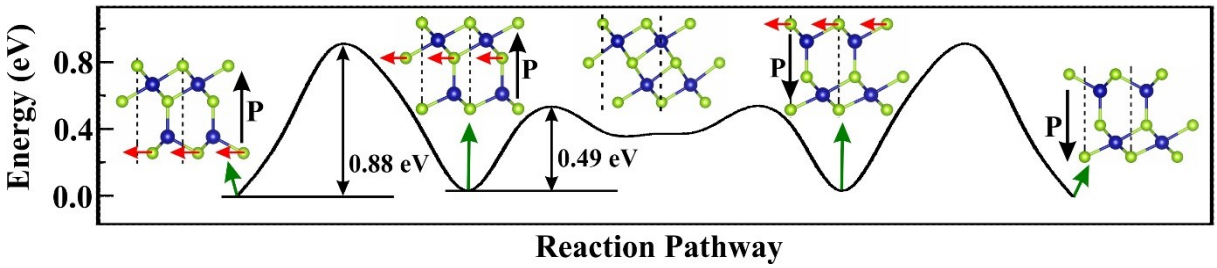

Fig. S6 Possible switching path for the electric polarization in QL Co_2Se_3 monolayer along FE-WZ'↑ – FE-ZB'↑ – fcc – FE-ZB'↓ – FE-WZ'↓.

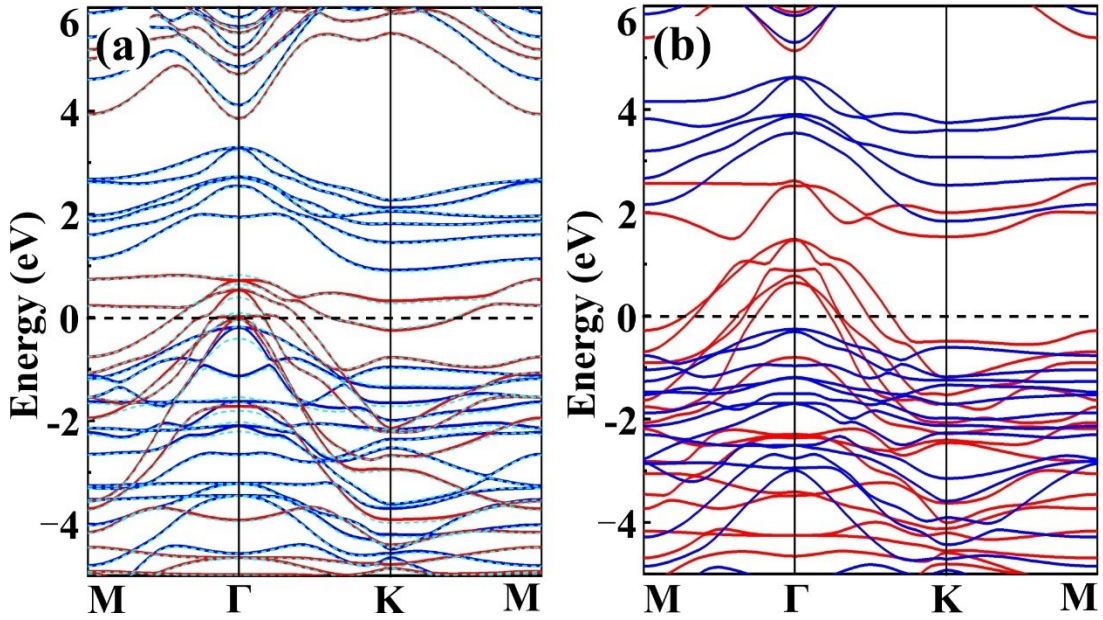

Fig. S7. (a) Calculated DFT+U band Structures without and with SOC effects (dashed line). (b) HSE band structure.

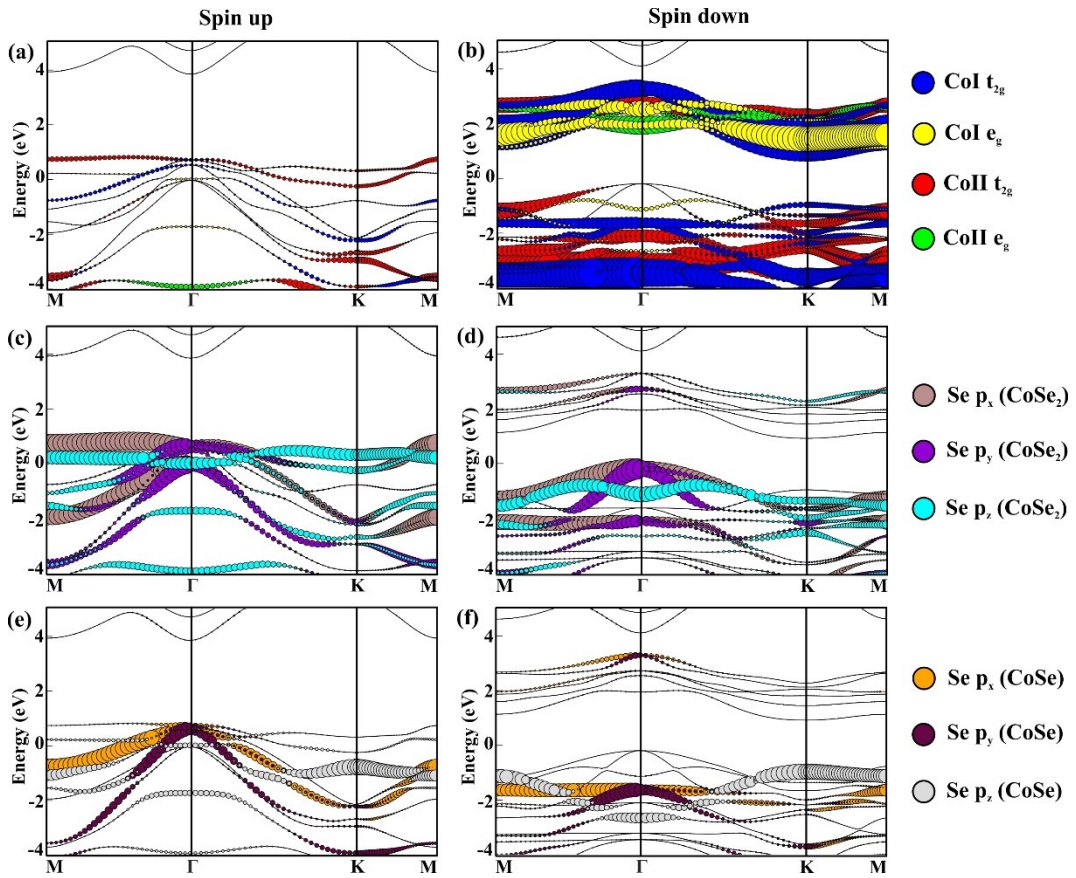

Fig. S8. Orbital-resolved spin-polarized band structure of FE-WZ' Co_2Se_3 monolayer. (a, b) d orbitals of CoI and CoII, (c, d) p orbitals of Se in octahedral $CoSe_2$ part and (e, f) p orbitals of Se in tetrahedral CoSe part.

Table S2. Total energies (eV) of strained FE-WZ' Co_2Se_3 monolayer under FM, AFM and FiM configurations and bandgaps (eV) for spin up and down channel.

	FM	AFM	FiM-1	FiM-2	Spin up	Spin down
-5%	**-79.2005**	-78.3120	-78.8794	-78.6276	0.00	0.00
-4%	**-79.2805**	-78.4979	-78.9197	-78.7974	0.00	0.00
-3%	**-79.3130**	-78.6435	-78.9524	-78.8507	0.00	0.00
-2%	**-79.3246**	-78.9016	-78.9968	-78.8852	0.00	1.18
-1%	**-79.3388**	-78.9664	-79.0267	-78.9019	0.00	1.18
0	**-79.3457**	-79.0644	-79.1400	-79.0117	0.00	1.11
1%	**-79.3364**	-79.0492	-79.1199	-78.9856	0.00	1.22
2%	**-79.3312**	-79.0394	-79.1079	-78.9207	0.00	1.18
3%	**-79.3051**	-79.0191	-79.0600	-78.6811	0.00	1.16
4%	**-79.2672**	-79.0087	-79.0223	-78.5927	0.00	1.33
5%	**-79.2049**	-78.8542	-78.9531	-78.4826	0.00	1.08

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