

Supporting Information

Theoretical insight into the unique dual roles of Li doping in switching magnetic anisotropy and enhancing curie temperature in CoCl_3 monolayers

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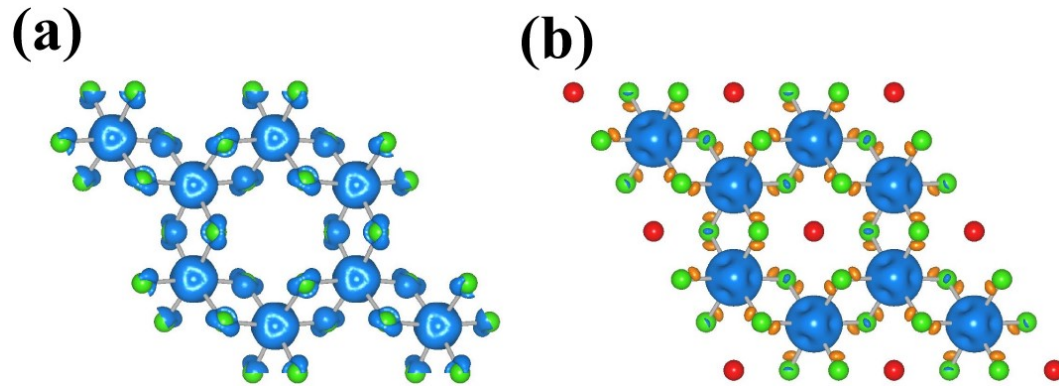


Fig. S1 The illustration of the magnetic distribution at the iso-value of $0.01 \mu_B/\text{\AA}^3$. (a) for the pristine CoCl_3 monolayer and (b) for the LiCo_2Cl_6 . The blue isosurfaces correspond to excess of spin-up electrons, and the yellow isosurfaces correspond to excess of spin-down electrons.

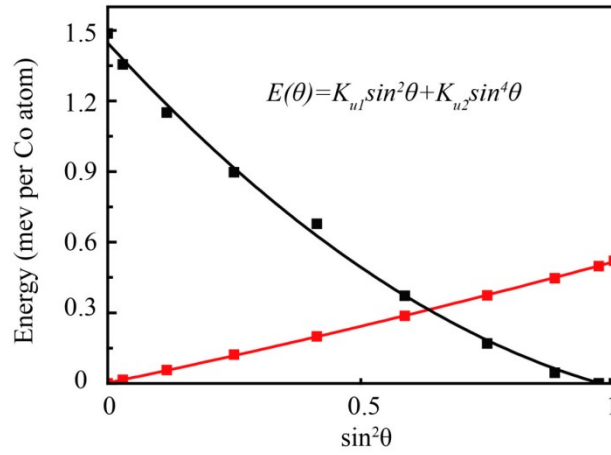


Fig. S2 Relative total energy as a function of $\sin^2\theta$ for pristine CoCl_3 and LiCo_2Cl_6 monolayers. The black squares and fitting curve represent CoCl_3 , while the red squares and fitting curve represent LiCo_2Cl_6 .

To further verify the magnetic easy-axis direction, we calculated the relative total energy at different magnetization angles. The angle θ is defined with respect to the out-of-plane direction. Therefore, $\sin^2\theta=0$ corresponds to the out-of-plane magnetization direction, while $\sin^2\theta=1$ corresponds to the in-plane magnetization direction. For each system, the lowest total energy in the angular scan was taken as the reference.

The calculated angular-dependent energies were fitted using $E(\theta)=K_{u1}\sin^2\theta+K_{u2}\sin^4\theta$. In this expression, the energy difference between the in-plane and out-of-plane directions can be estimated as $\text{MAE}=E(90 \text{ degrees})-E(0 \text{ degrees})=K_{u1}+K_{u2}$. Thus, the sign of $K_{u1}+K_{u2}$ provides a direct check of the magnetic easy axis: a negative value indicates that the in-plane direction is lower in energy, while a positive value indicates that the out-of-plane direction is lower in energy. For the pristine CoCl_3 monolayer, the black fitting curve gives $K_{u1}=-2.35$ and $K_{u2}=0.89$. Thus, $K_{u1}+K_{u2}$ is negative, and the energy minimum occurs at $\sin^2\theta=1$, corresponding to $\theta=90$ degrees. This confirms the in-plane magnetic easy axis. For the LiCo_2Cl_6 monolayer, the red fitting curve gives $K_{u1}=0.48$ and $K_{u2}=0.07$. In this case, $K_{u1}+K_{u2}$ is positive, and the energy minimum appears at $\sin^2\theta=0$, corresponding to the out-of-plane direction.

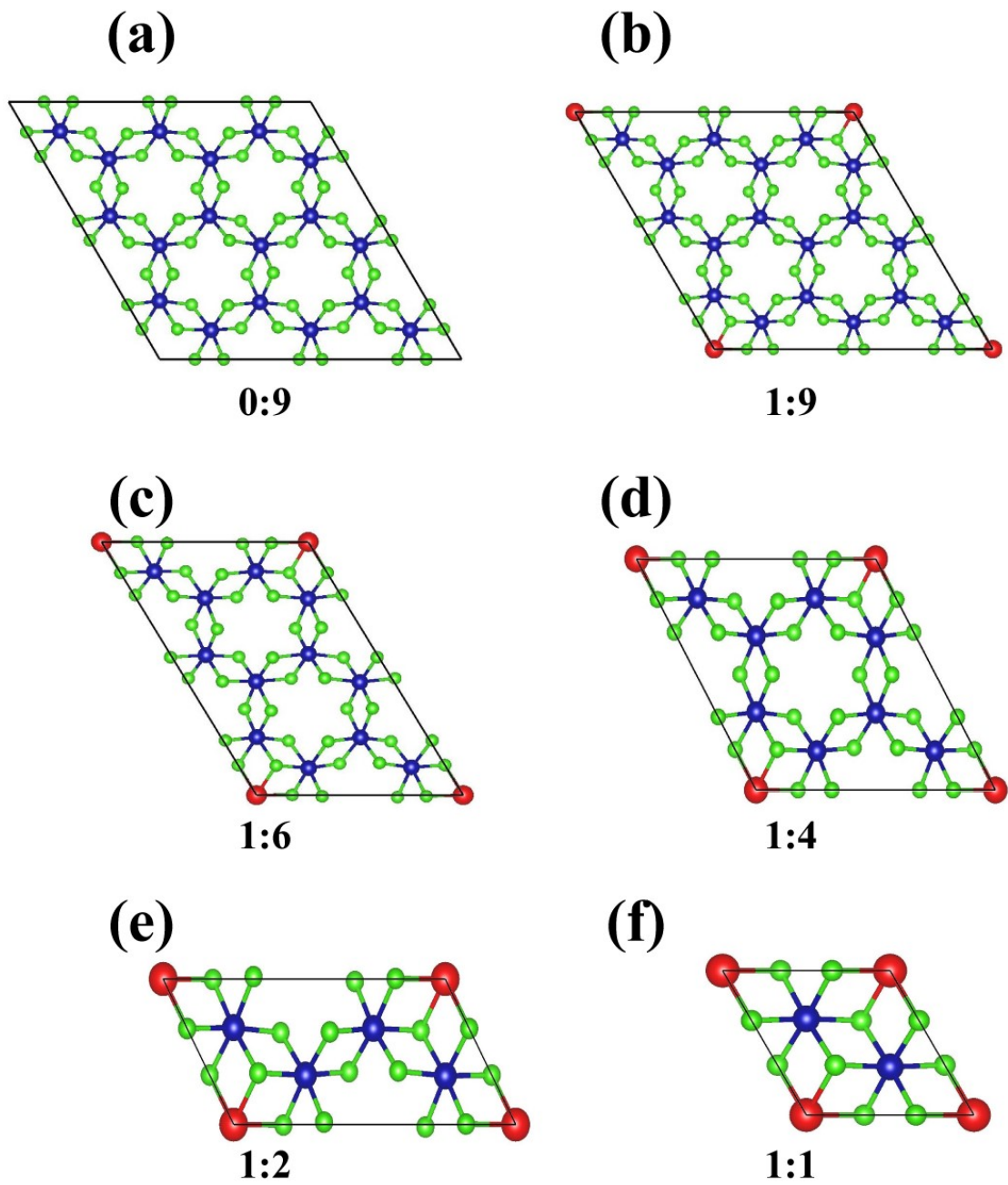


Fig. S3 The configurations of CoCl_3 monolayer at different Li doping concentration.

The bottom numbers are the ratios between the Li ions and the Co_2Cl_6 units.

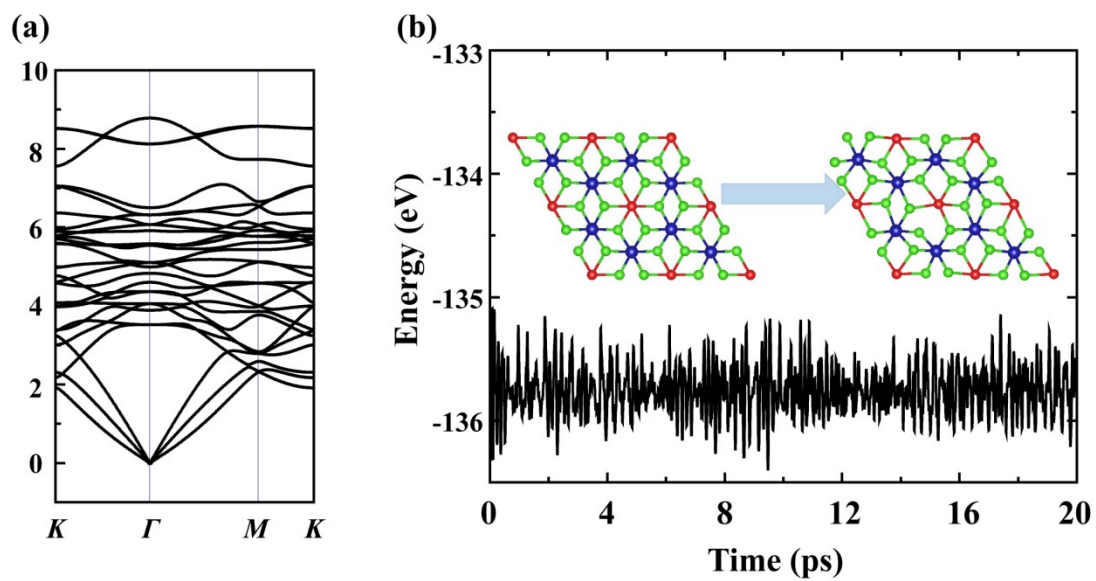


Fig. S4 (a) Phonon spectrum LiCo₂Cl₆ monolayer. (b) Potential energy versus time of the simulation performed at 300 K of the LiCo₂Cl₆ monolayer and the corresponding structures obtained at the beginning and the end of the simulation.

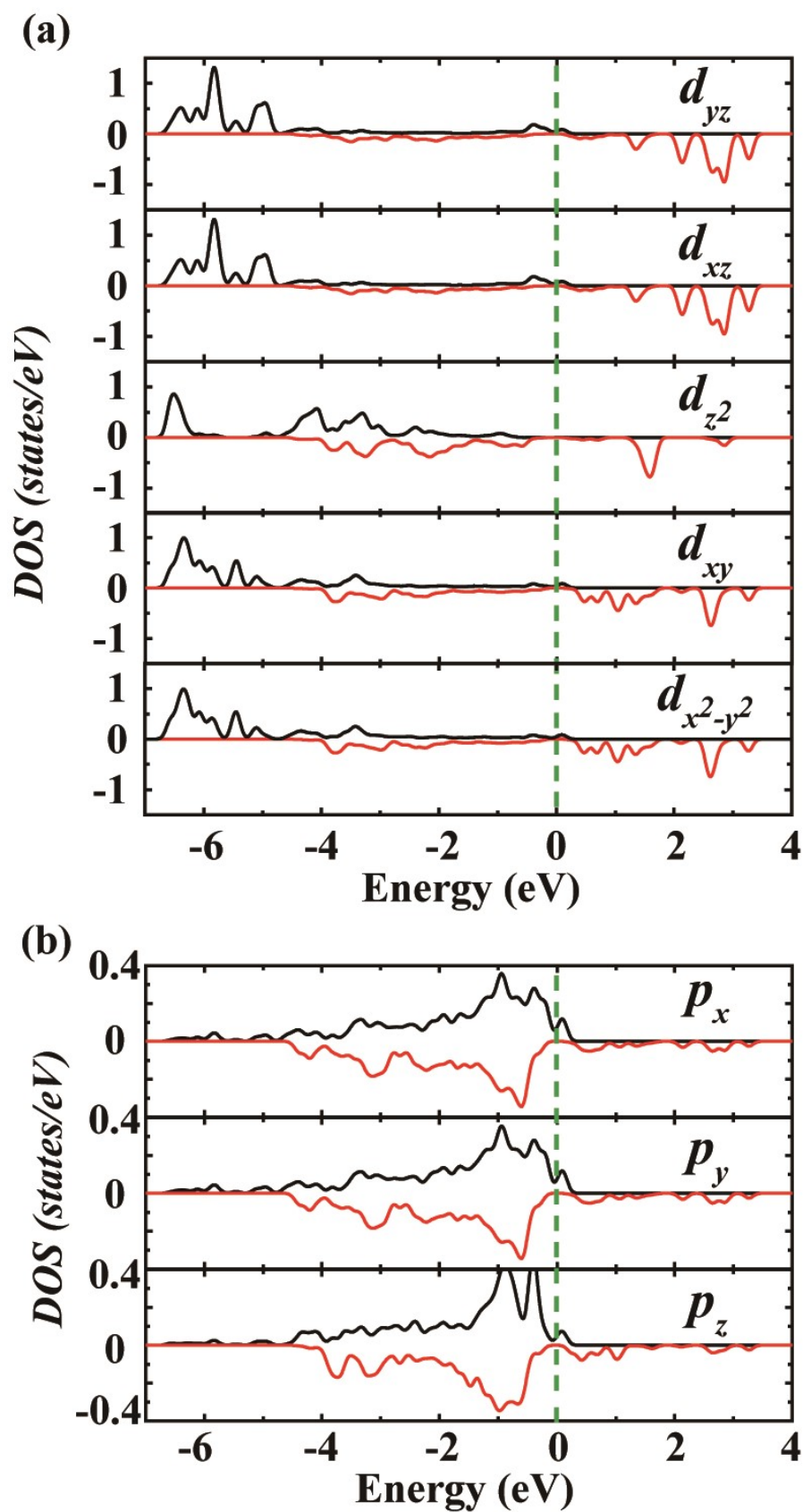


Fig. S5 (a) and (b) Orbitally resolved DOS of Co and Cl atom in $\text{Li}(\text{Co}_2\text{Cl}_6)_9$ monolayer which is shown in Fig. S3(b), respectively.

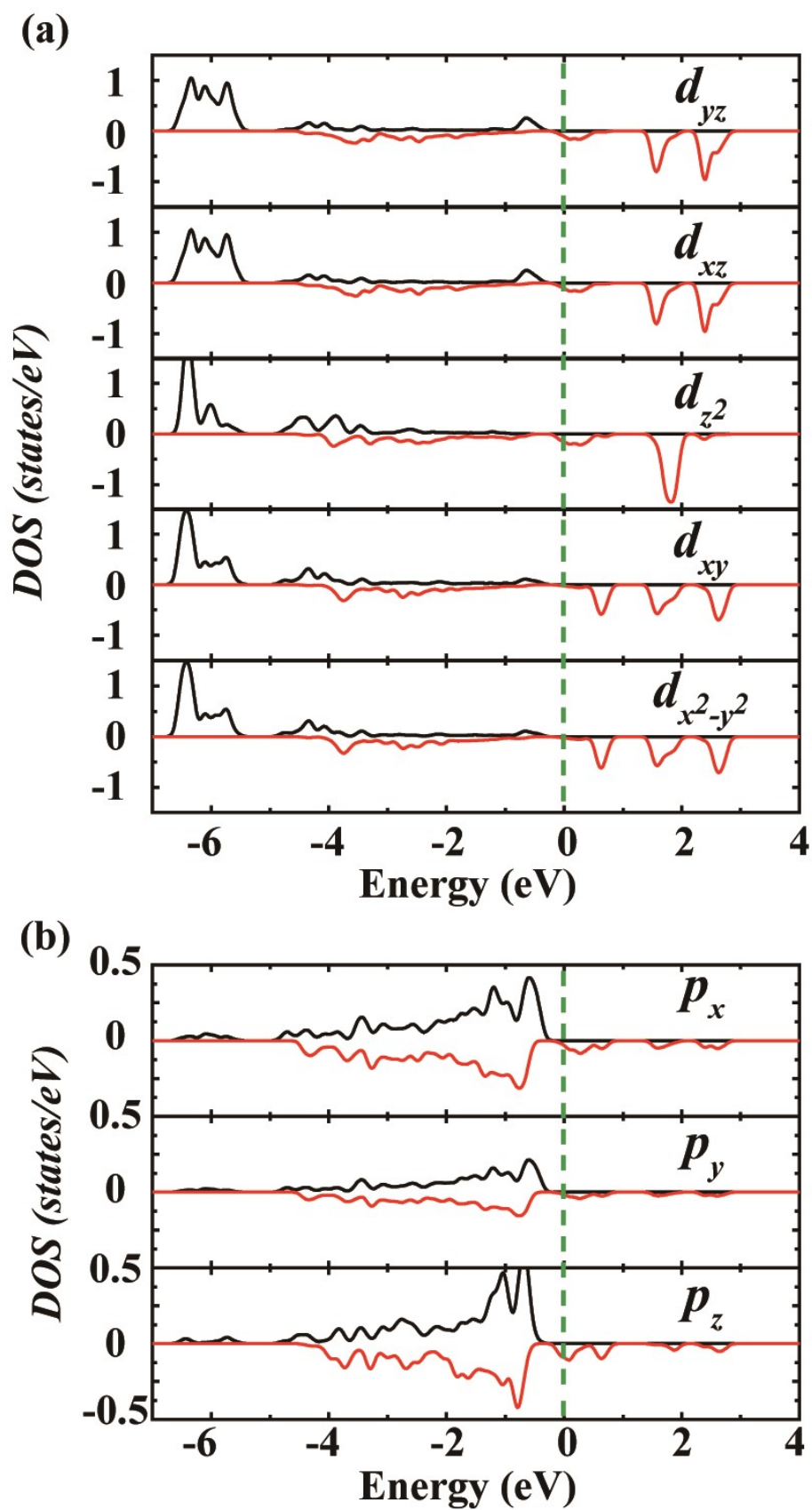


Fig. S6 (a) and (b) Orbitally resolved DOS of Co and Cl atom in $\text{Li}(\text{Co}_2\text{Cl}_6)_4$ monolayer which is shown in Fig. S3(d), respectively.

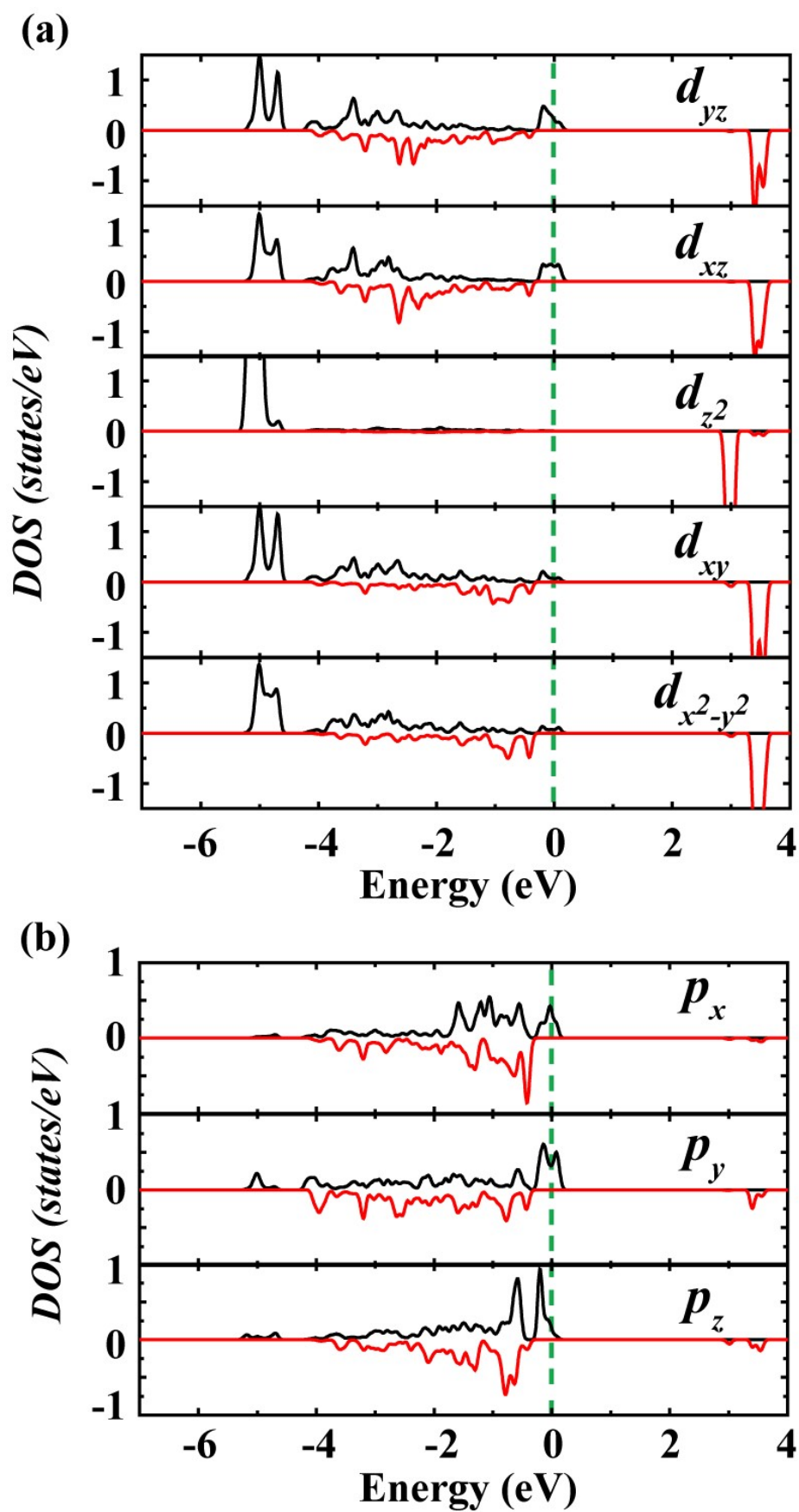


Fig. S7 (a) and (b) Orbitally resolved DOS of Co and Cl atom in LiCo₂Cl₆ monolayer, respectively.

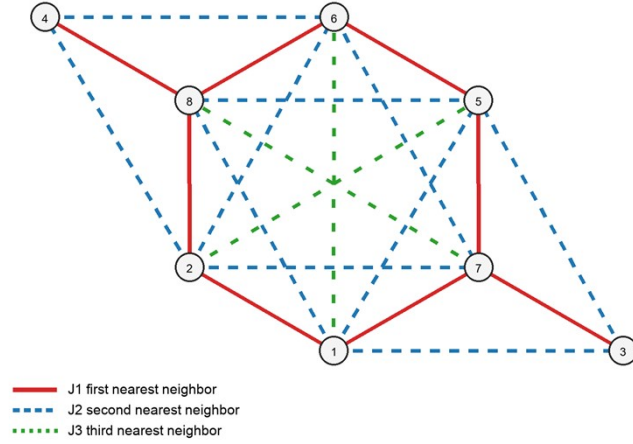


Fig. S8 Schematic illustration of the first-, second-, and third-nearest-neighbor exchange paths in the 2×2 CoCl_3 supercell. The red solid, blue dashed, and green dotted lines represent J_1 , J_2 , and J_3 , respectively.

For the exchange parameters, we provide the detailed energy-mapping procedure used to extract the magnetic exchange interactions. The first-, second-, and third-nearest-neighbor Co-Co exchange paths in a 2×2 CoCl_3 supercell are denoted as J_1 , J_2 , and J_3 , respectively. By fitting the total energies of different magnetic configurations, J_1 , J_2 , and J_3 can be extracted independently. The obtained values are $J_1 = 1.14$ meV, $J_2 = -0.27$ meV, and $J_3 = -0.26$ meV. Since the magnitudes of J_2 and J_3 are much smaller than that of J_1 , the nearest-neighbor exchange interaction dominates the magnetic coupling.