Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Material for Easy axis rotation in ferromagnetic monolayer CrN induced by fluorine and chlorine functionalization

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I. STRUCTURAL PARAMETERS

TABLE SI: The Hubbard-U parameter (U), atomic distance and angles, buckling parameter (Δ), formation energy (E_f) and charge transfer between CrN monolayer and halide atom (Q_{CrN}).

	U (eV)	a (Å)	d_{Cr-N} (Å)	d_{Cr-X} (Å)	$\angle Cr-N$ (°)	$\angle Cr-X$ (°)	Δ (Å)	E_f (eV/atom)	Q_{CrN} (| e |)	Q_X(| e |)
CrN	4.10	3.29	1.90	–	120	–	0	–	–	–
F-CrN	3.50	3.10	1.89	1.76	110.55	108.37	0.59	-2.88	0.51	-0.51
Cl-CrN	4.10	3.22	1.92	2.22	114.10	104.32	0.47	-0.84	0.33	-0.33

II. ANISOTROPIC SPIN MODEL

A. In-plane easy axis

$$H = -\sum_{i,j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j - \sum_i A_i(\mathbf{S}_i \cdot \mathbf{z}_i)^2 - \sum_{i,j} \delta_{ij} S_i^z S_j^z - \sum_{i,j} \Gamma_{ij}(S_i^x S_j^x - S_i^y S_j^y)$$

where $J_{ij} \equiv J(\mathbf{R}_{ij})$ is the Heisenberg exchange interaction between spins $\mathbf{S}_i$ and $\mathbf{S}_j$, A_i is the single-ion magnetic anisotropy at spin $\mathbf{S}_i$, δ_{ij} is the anisotropic exchange interaction, Γ_{ij} describes the inter-site magnetic anisotropy within the xy-plane, and $\mathbf{z}_i$ is the unit vector pointing in the direction of the easy magnetization axis. The Holstein-Primakoff transformation can be applied to Eq. (S.1) which transforms the spin Hamiltonian to the bosonic Hamiltonian. In the linear Holstein-Primakoff approximation, spin operators are given as $S_i^+ \approx \sqrt{2S}a_i^\dagger$ and $S_i^- \approx \sqrt{2S}a_i$. After the Fourier transformation, the resulting Hamiltonian can be written as,

$$H = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \sum_{\mathbf{k}} \Delta_{\mathbf{k}}(a_{\mathbf{k}} a_{-\mathbf{k}} + a_{\mathbf{k}}^\dagger a_{-\mathbf{k}}^\dagger), \tag{S.1}$$

where

$$\hbar\omega_{\mathbf{k}} = 6S(2J + 2\Gamma - \frac{A}{6}) - S(4J - 2\Gamma + 2\delta)f(\mathbf{k})$$

and

$$\Delta_{\mathbf{k}} = -S\left[(\delta + \Gamma)f(\mathbf{k}) + \frac{A}{2}\right]$$

are diagonal and off diagonal parts of the bosonic Hamiltonian. In Eq. (S.1), $f(\mathbf{k}) = \cos k_x a + 2\cos(\frac{1}{2}k_x a)\cos(\frac{\sqrt{3}}{2}k_y a)$ is the structure factor of a hexagonal lattice. The total Hamiltonian given by Eq. (S.1) can be diagonalized by using the coupled oscillator type unitary transformation [1] to obtain spin-wave spectrum. Similar treatment is followed in Ref.2. Consequently, the spin-wave spectrum can be written as

$$E_{\mathbf{k}}^{in} = \sqrt{(\hbar\omega_{\mathbf{k}})^2 - 4(\Delta_{\mathbf{k}})^2}. \tag{S.2}$$

In the hexagonal lattice each Cr atom has six nearest neighbor Cr atoms. According to this model, the exchange coupling parameters can be expressed as

$$E_{FM_x} = -6JS^2 - 6\Gamma S^2$$

$$E_{FM_y} = -6JS^2 + 6\Gamma S^2$$

$$E_{FM_z} = -6JS^2 - AS^2 - 6\delta S^2$$

$$E_{AFM_x} = 2JS^2 + 2\Gamma S^2$$

$$E_{AFM_z} = 2JS^2 - AS^2 + 2\delta S^2$$

$$J = (3E_{AFM_z} - 2E_{FM_y} - E_{FM_x})/48S^2$$

$$A = (3E_{AFM_x} - 3E_{AFM_z} + E_{FM_x} - E_{FM_z})/4S^2$$

$$\delta = (3E_{AFM_x} - 3E_{AFM_z} - 3E_{FM_z} + E_{FM_x} + 2E_{FM_y})/48S^2 \tag{S.3}$$

$$\Gamma = (E_{FM_y} - E_{FM_x})/16S^2 \tag{S.4}$$

B. Out-of-plane easy axis

The DFT results can be mapped onto the anisotropic classical spin model,

$$H = -\sum_{i,j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j - \sum_i A_i(\mathbf{S}_i \cdot \mathbf{z}_i)^2 - \sum_{i,j} \delta_{ij} S_i^z S_j^z. \tag{S.5}$$

Similarly, the linear Holstein-Primakoff transformation is applied to the Hamiltonian. After the Fourier transformation, the resulting Hamiltonian can be written in a diagonal form as,

$$H = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}}, \tag{S.6}$$

where

$$\hbar\omega_{\mathbf{k}} = S(12J + 12\delta - 2A) - 4SJf(\mathbf{k}),$$

i.e, $\hbar\omega_{\mathbf{k}} = E_{\mathbf{k}}^{out}$. The spin-wave dispersion can be expanded in the vicinity of Γ point, $E_{\mathbf{k}}^{out/in}(\mathbf{k}) \simeq \epsilon_0 + \rho k^2$ where ϵ_0 and ρ are spin-wave gap and spin stiffness, respectively. Strictly speaking, Eq. (S.5) is justified for the atomic limit, i.e. when the Coulomb interaction between the Cr $3d$ electrons is larger compared to the $3d$ band width. Similarly, the exchange coupling parameters can be written as

$$E_{FM_x} = -6JS^2$$

$$E_{FM_z} = -6JS^2 - AS^2 - 6\delta S^2$$

$$E_{AFM_x} = 2JS^2$$

$$E_{AFM_z} = 2JS^2 - AS^2 + 2\delta S^2$$

$$J = (E_{AFM_x} - E_{FM_x})/16S^2$$

$$A = (3E_{AFM_x} - 3E_{AFM_z} + E_{FM_x} - E_{FM_z})/4S^2$$

$$\delta = (E_{AFM_x} - E_{AFM_z} - E_{FM_z} + E_{FM_x})/16S^2 \tag{S.7}$$

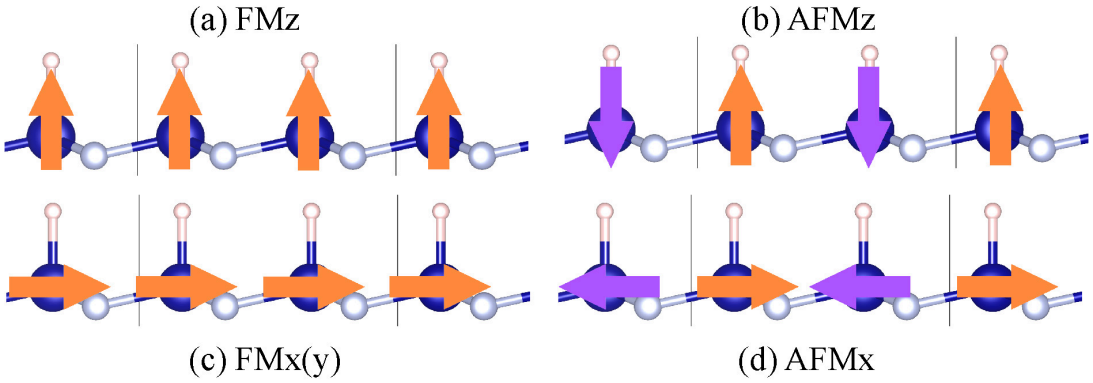

FIG. S1: The ferromagnetic (FM) configurations along (a) z and (c) x/y. The antiferromagnetic (AFM) configurations along (b) z and (d) x.

TABLE SII: The Hubbard parameter (U), net magnetic moment (M), spin stiffness (ρ), easy axis direction, magnetic exchange (J), site magnetic anisotropy (A), inter-site magnetic anisotropy (δ), inside the plane magnetic anisotropy (Γ) and Curie temperature T_C for pristine CrN monolayer and after adsorption of F and Cl atoms.

	U (eV)	M (μ_B)	ρ (meVÅ^2)	Easy Axis	J (meV)	A (meV)	δ (meV)	$\Gamma(\mu eV)$	T_C (K)
CrN	4.10	3.00	496	out-of-plane	10.73	0.25	0.03	-	910
F-CrN	3.50	2.00	510	in-plane	19.84	-0.07	-0.02	0.05	650
Cl-CrN	4.10	2.00	784	in-plane	26.08	-0.06	-0.01	0.01	800

III. CALCULATION OF THE CRITICAL TEMPERATURE

The critical temperature of magnetic ordering can be calculated within the random phase approximation (RPA) [3], which is a minimal approximation that takes long-range spin fluctuations into account. In case of a ferromagnet with one magnetic sublattice, the Curie temperature can be expressed as,

$$k_B T_c = \frac{2}{3}\frac{S(S+1)}{\langle S^z\rangle}\left\{\frac{1}{\Omega}\int d\mathbf{k}\left[\left(E^{out/in}(\mathbf{k})\right)^{-1}\right]\right\}^{-1}, \tag{S.8}$$

where $\Omega = 8\pi^2/\sqrt{3}a^2$ is the Brillouin zone area. $E^{out/in}(\mathbf{k})$ is the spin-wave dispersion for out-of-plane/in-plane easy axis. The thermal average of magnetization can be calculated within the random phase approximation and using magnon excited states [3].

IV. CALCULATION OF MAGNETIC MOMENT AS A FUNCTION OF TEMPERATURE

The thermal average of spin magnetic moment is calculated by using the following equation for the single sublattice of CrN monolayer [3].

$$< S >= \frac{(S-\lambda)(1+\lambda)^{2S+1} + (S+1+\lambda)\lambda^{2S+1}}{(1+\lambda)^{2S+1} - \lambda^{2S+1}} \tag{S.9}$$

where λ is a temperature dependent parameter defined as,

$$\lambda = -\frac{2\hbar}{\Omega}\int d\omega \int dk\, \mathrm{Im}(\left[\hbar\omega - E^{out/in}(\mathbf{k}) + i0^+\right]^{-1})(e^{\beta\hbar\omega}-1)^{-1}. \tag{S.10}$$

Here the expectation value of S in Eq. (S.9) and magnon energy spectrum in the whole Brillouin zone are solved self-consistently.

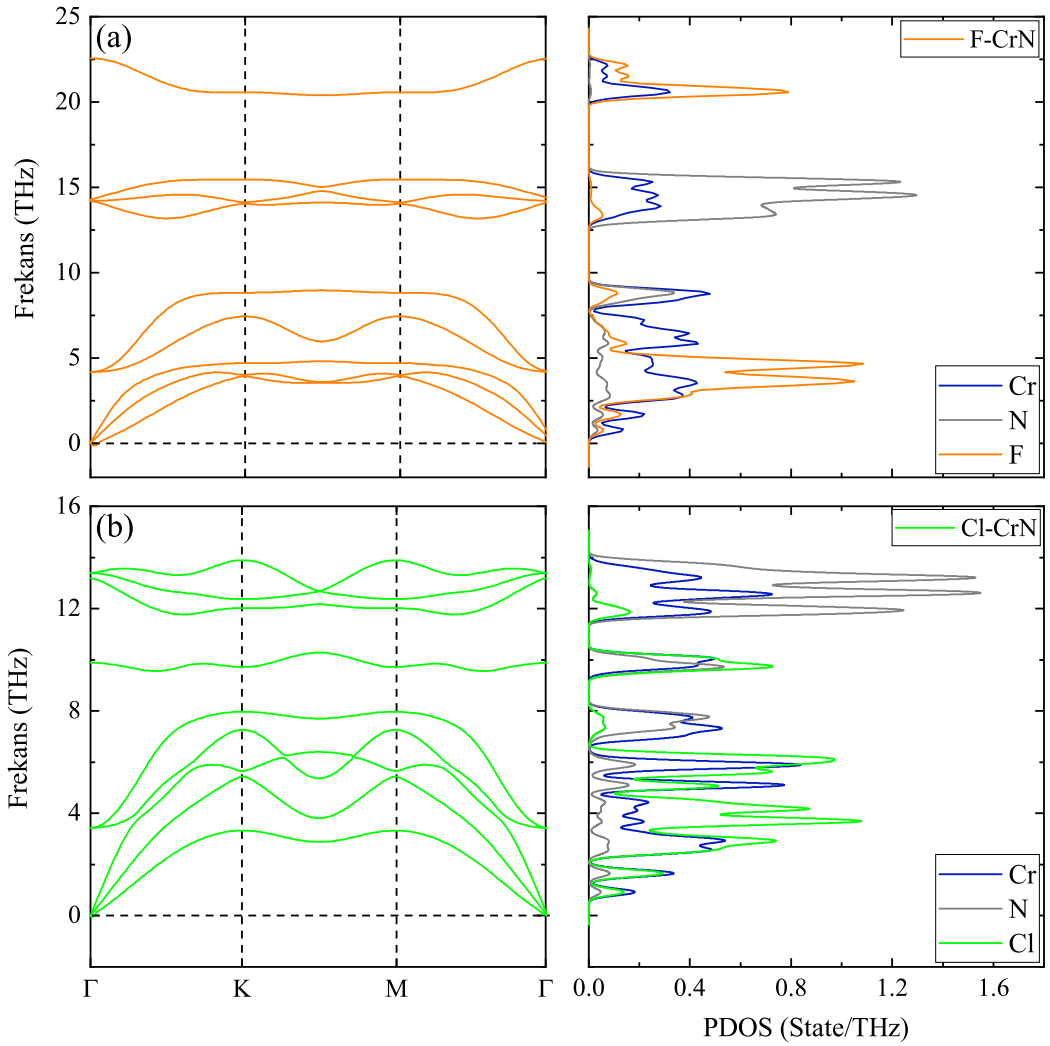

FIG. S2: The phonon spectra of (a) F-CrN (b) Cl-CrN with phonon projected density of states (right panel)

REFERENCES

[1] M. Wagner, *Unitary Transformations in Solid State Physics*, Modern problems in condensed matter sciences (North-Holland, 1986).
[2] S. Memarzadeh, M. R. Roknabadi, M. Modarresi, A. Mogulkoc, and A. N. Rudenko, 2D Mater. **8**, 035022 (2021).
[3] J. Rusz, I. Turek, and M. Diviš, Phys. Rev. B **71**, 174408 (2005).

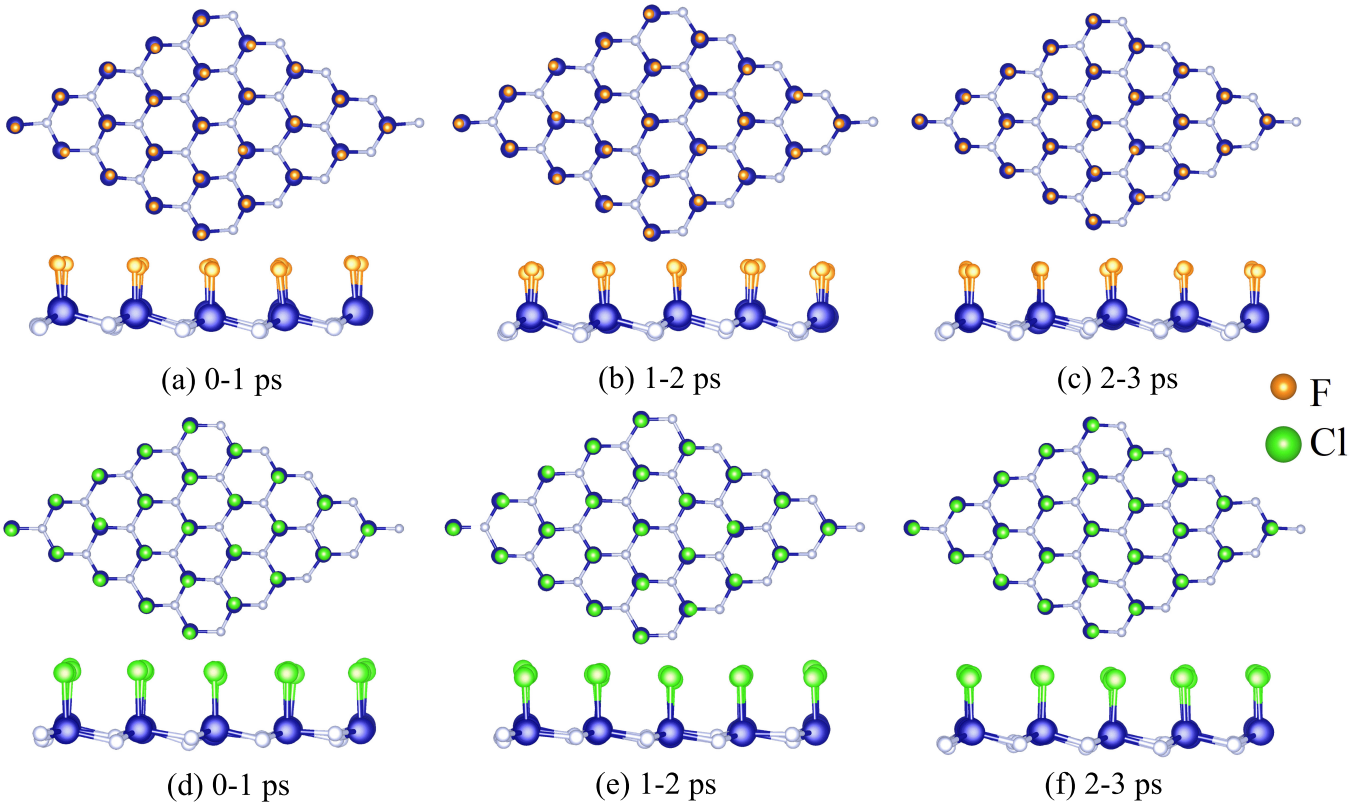

FIG. S3: The snapshots of AIMD simulations for (a)-(c) F-CrN and (d)-(f) Cl-CrN at 300 K with total simulation time of 3 ps.

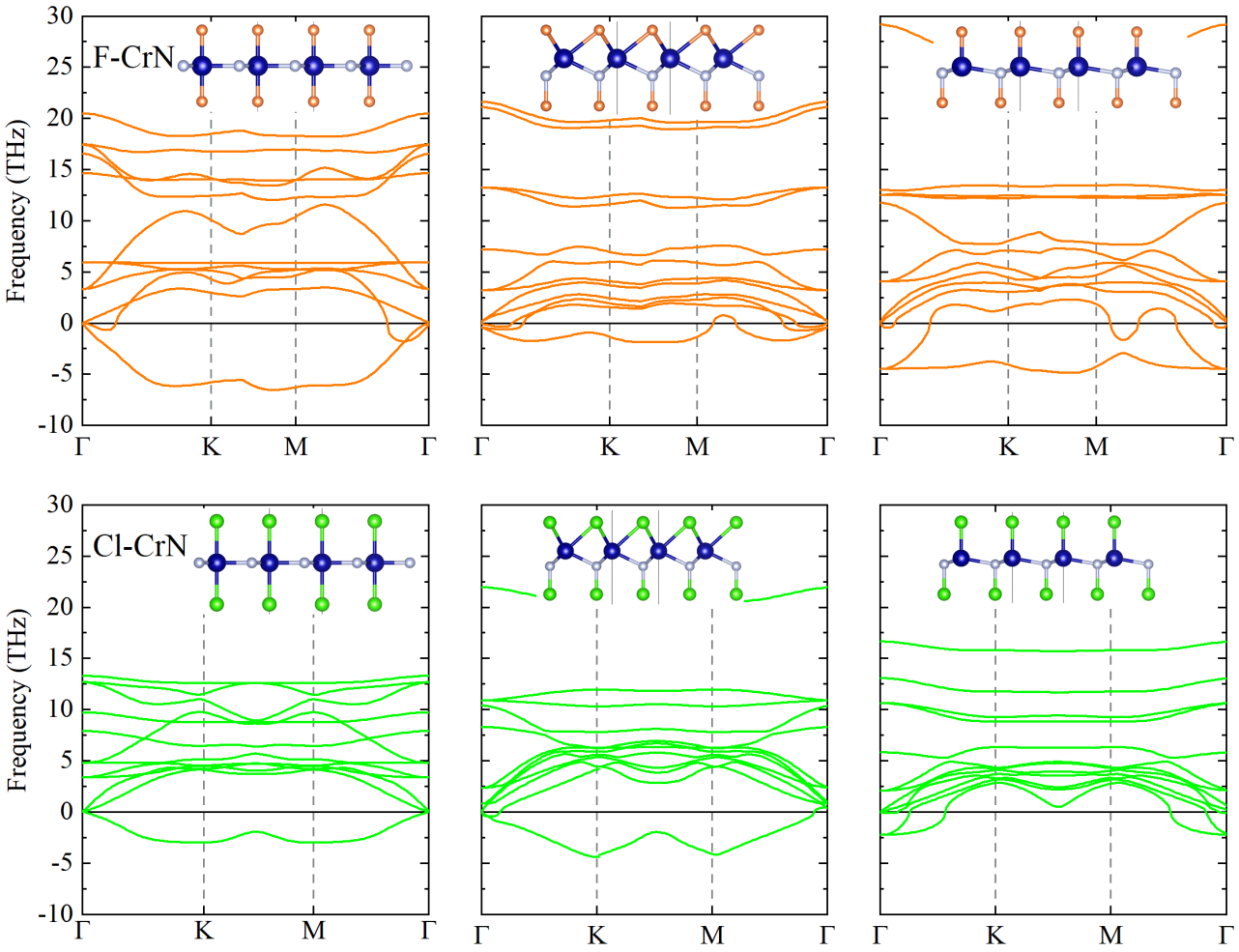

FIG. S4: Phonon spectra of the CrN monolayer functionalized by F and Cl atom on both sides, demonstrating dynamical instability of double-side functionalization.

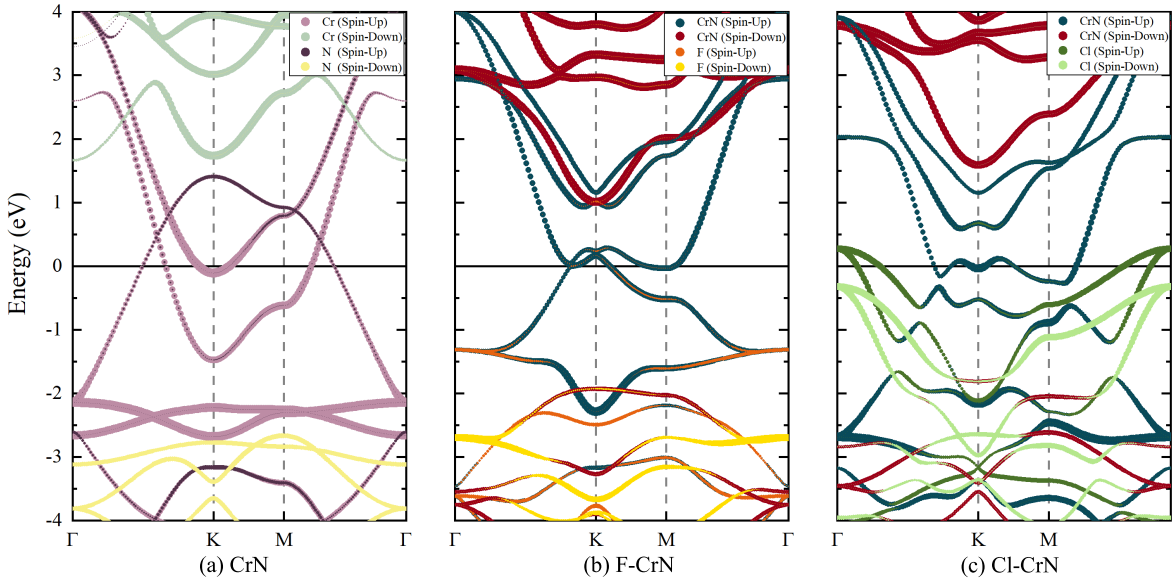

FIG. S5: The spin resolved partial bands of pristine CrN and F/Cl-CrN monolayers.

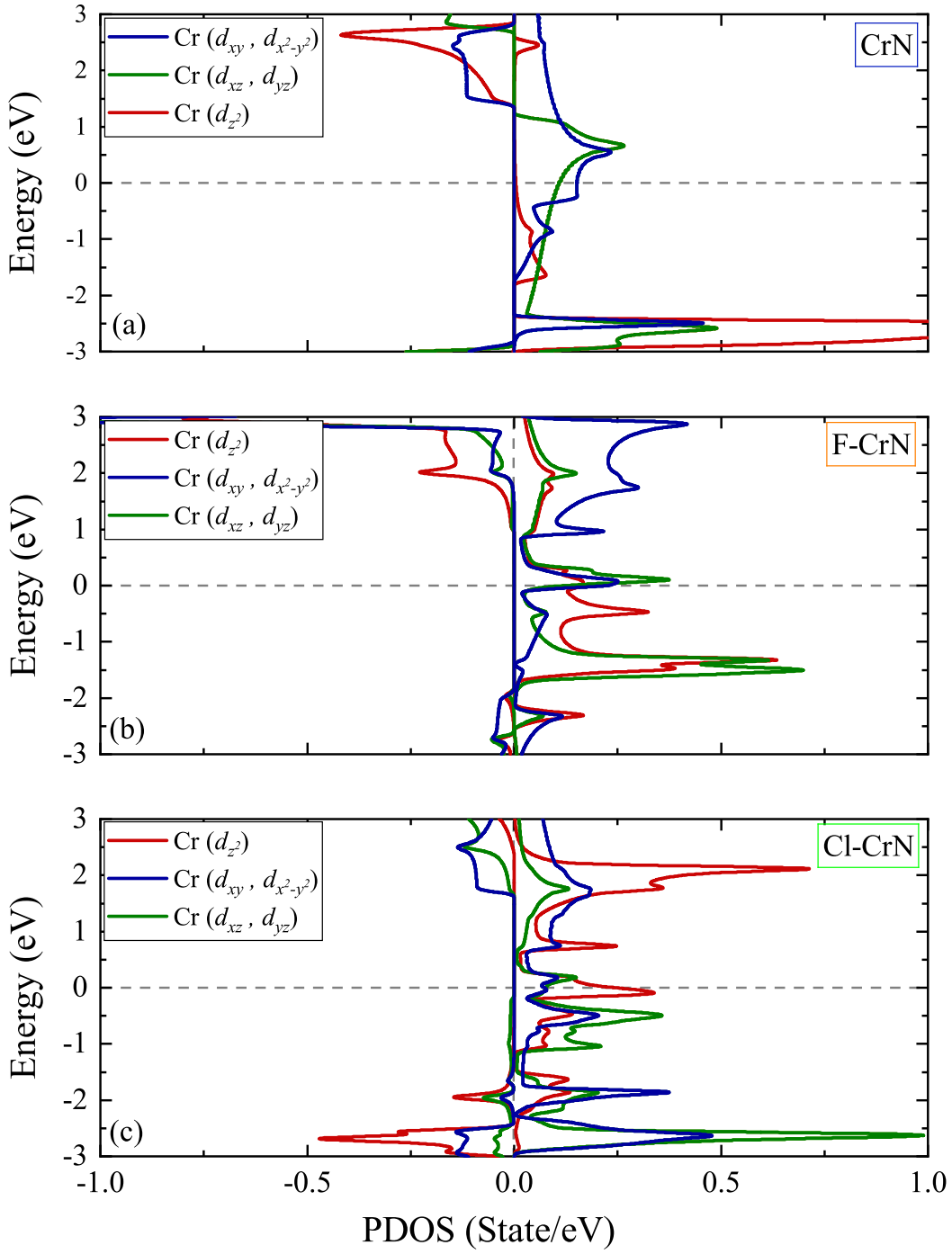

FIG. S6: Partial density of states (PDOS) of Cr d orbitals for (a) pristine CrN, (b) F-CrN and (c) Cl-CrN. The Fermi level is set to be zero