

## Supporting Information

### Charge Disproportionation Induced Multiferroics and Electric Field

#### Control of Magnetism in 2D MXene $\text{Mo}_2\text{NCl}_2$

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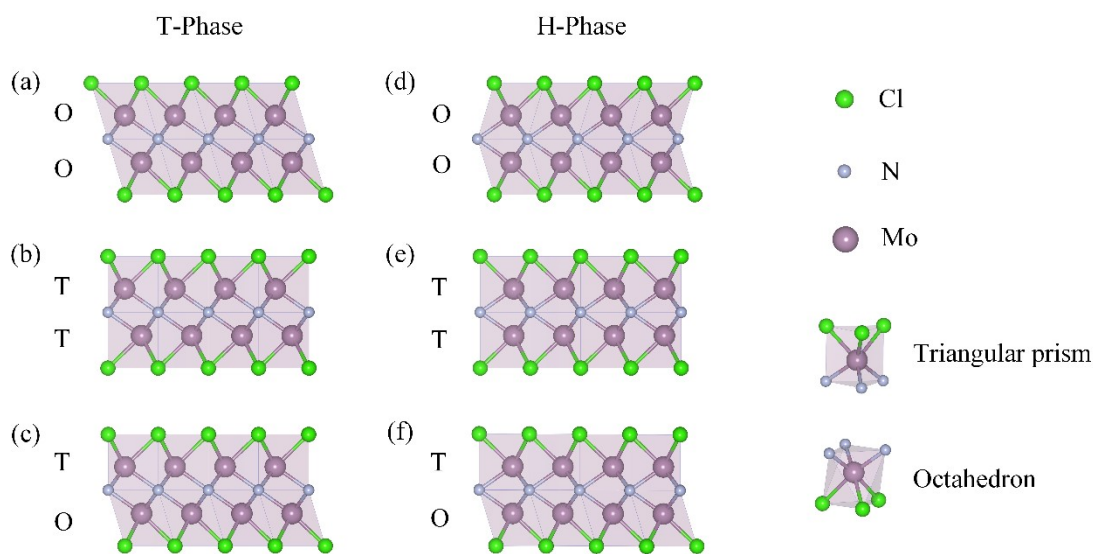
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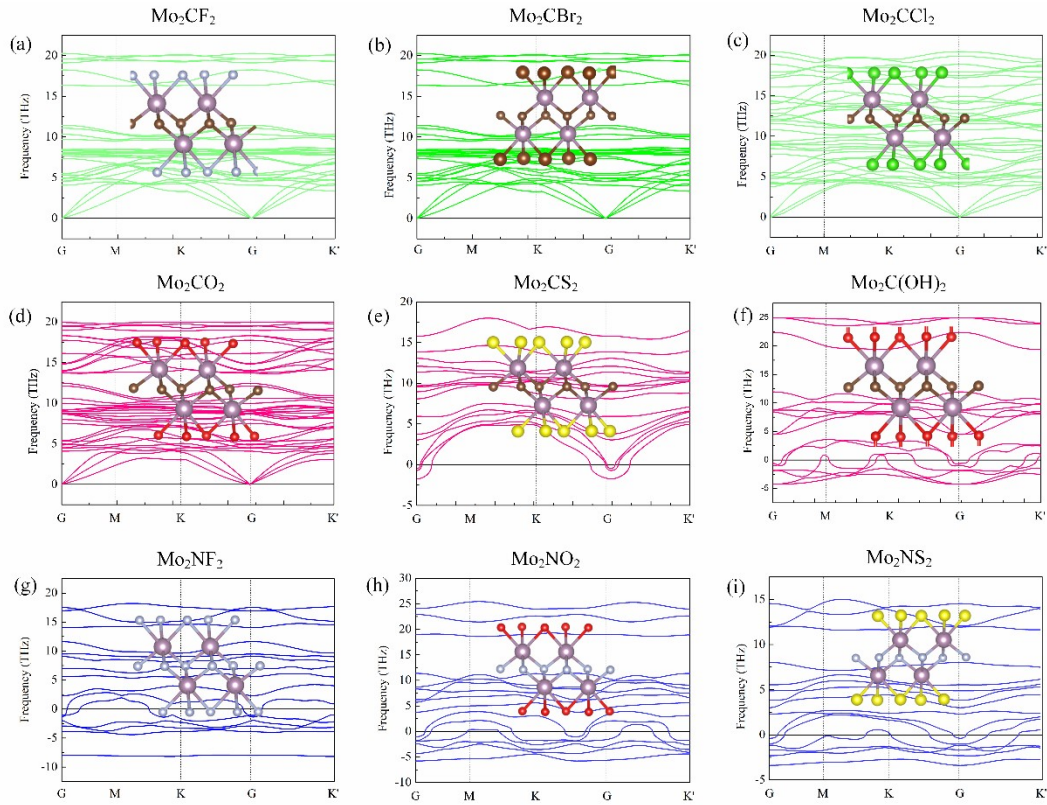
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#### Figures:



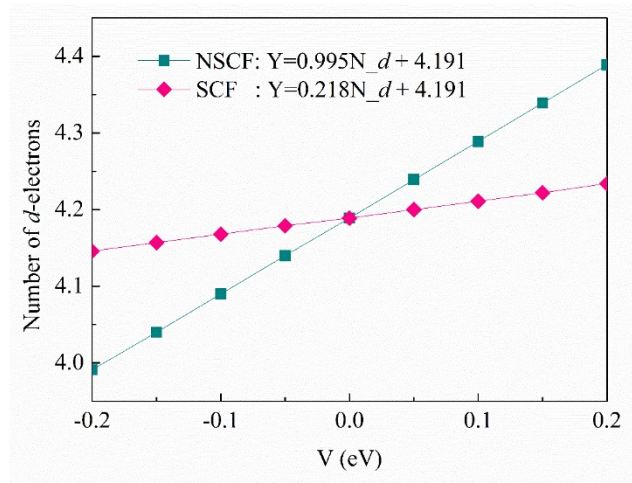
**Fig. S1.** Side view of (a) TOO (b) TTT (c) TTO (d) HOO (e) HTT and (f) HTO atomic structures. Surface terminations Cl, Mo and N atoms are indicated by the green, purple and grey circles, respectively. T and H refer to the octahedral and trigonal prismatic geometries, respectively.

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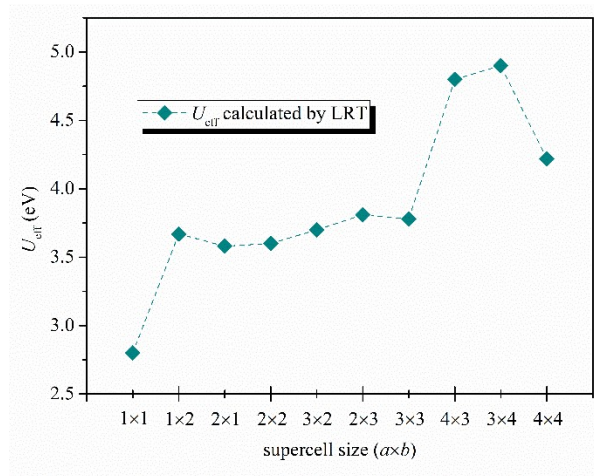
**Fig. S2.** Calculated phonon band structures of (a)  $\text{Mo}_2\text{CF}_2$ ; (b)  $\text{Mo}_2\text{CBr}_2$ ; (c)  $\text{Mo}_2\text{CCl}_2$ ; (d)  $\text{Mo}_2\text{CO}_2$ ; (e)  $\text{Mo}_2\text{CS}_2$ ; (f)  $\text{Mo}_2\text{C}(\text{OH})_2$ ; (g)  $\text{Mo}_2\text{NF}_2$ ; (h)  $\text{Mo}_2\text{NO}_2$ ; (i)  $\text{Mo}_2\text{NS}_2$ .

we have adopted the linear response theory to calculate the  $U$  value for Mo. The table below lists the parameters used in the calculation process and Figure 1 shows the variation of the number of  $d$  orbital electrons as  $V$  changes. By performing a linear fit to the two curves, we can obtain the slope, and then use Equation 1 to calculate the effective  $U$  value, which is determined to be 3.582 eV.

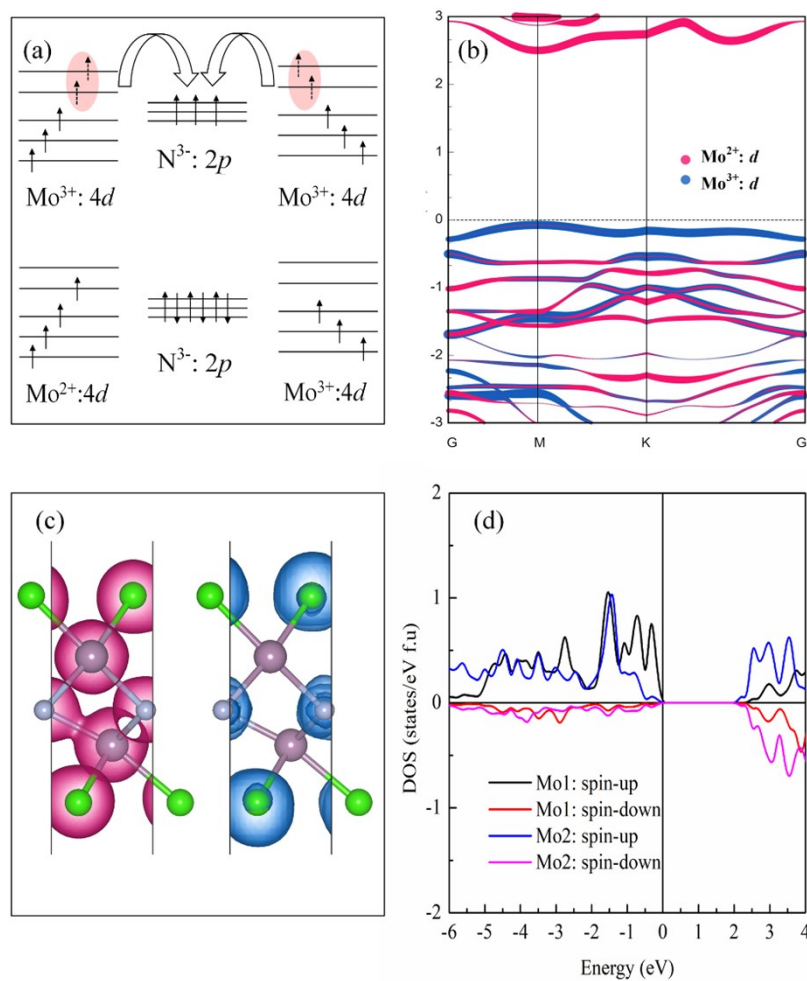


**Fig. S3.** Linear fitting of  $d$ -orbital electron numbers.

$$U = \chi^{-1} - \chi_0^{-1} \approx \left( \frac{\partial N^{SCF}}{\partial V_I} \right)^{-1} - \left( \frac{\partial N^{NSCF}}{\partial V_I} \right)^{-1} = \frac{1}{0.218} - \frac{1}{0.995} = 3.582 \text{ eV} \quad \dots(S1)$$

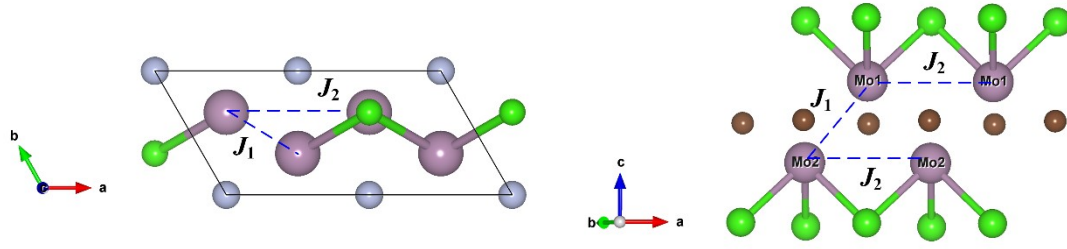


**Fig. S4.** (a) The variation of  $U_{\text{eff}}$ -value with the change of supercell size ( $a \times b$ ) is calculated using linear response theory (LRT).

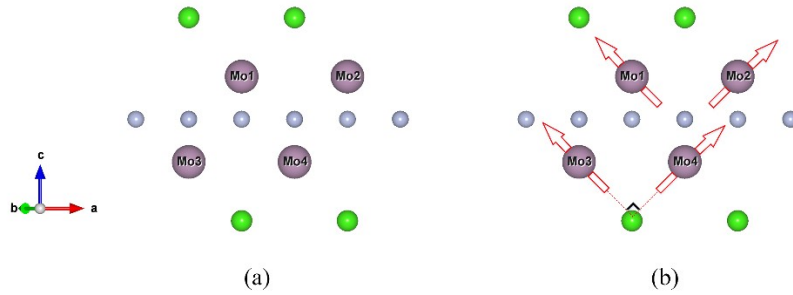


**Fig. S5.** (a) Schematic illustration of splitting  $d$  orbitals and the exchange interactions between the electrons of Mo ions. (b) The  $d$  orbital projected band structure of  $\text{Mo}^{2+}$  and  $\text{Mo}^{3+}$  ions. (c) Charge density and ELF for  $\text{Mo}_2\text{NCl}_2$  monolayer. (d) Projected density of states for  $\text{Mo}_1$  and  $\text{Mo}_2$  ion in  $\text{Mo}_2\text{NCl}_2$

monolayer, respectively.

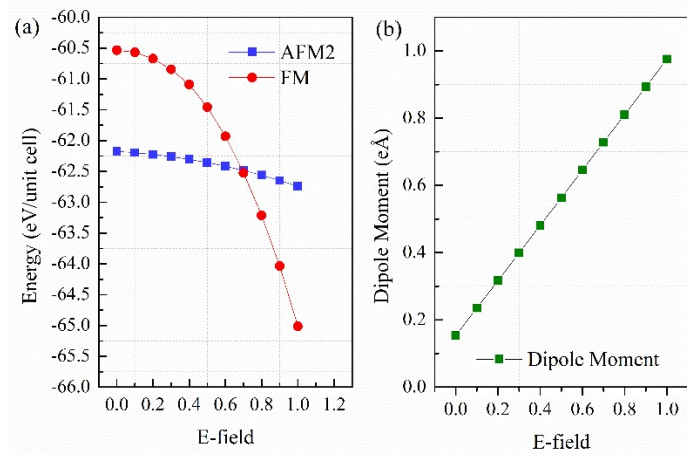


**Fig. S6.** The  $2 \times 1 \times 1$  super cell of  $\text{Mo}_2\text{NCl}_2$ . (left) top view, (right) side view. The  $J_1$  and  $J_2$  denote the nearest-neighbor and next-nearest-neighbor spins exchange paths.

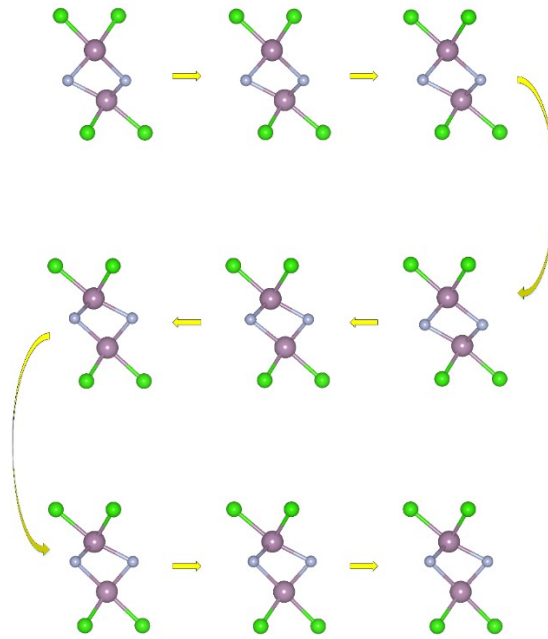


**Fig. S7.** The structure of  $\text{Mo}_2\text{NCl}$  monolayer. (a)  $2 \times 1 \times 1$  supercell; (b) Non collinear spin configuration. The red arrow represents the direction of spin.

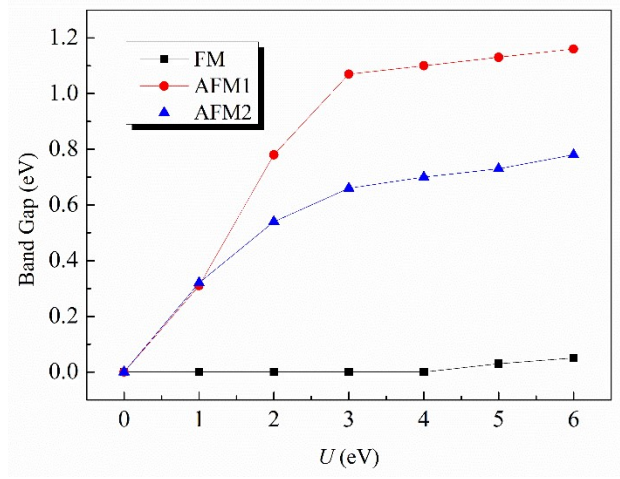
In our work, an external electric field was applied to both the AFM2 and FM magnetic structures. During the execution, to ensure that the applied electric field does not cause structural collapse, we initially selected a relatively small field value of  $0.1 \text{ V/\AA}$ . The structure was then sufficiently relaxed, and the total energy of the system was calculated. When applying a larger electric field, the charge density from the previous field was used, and this process was repeated to observe the energy variation with the applied electric field. Due to the different energy change rates between AFM2 and FM configurations, there is an intersection where the energy curves cross. This intersection corresponds to the critical electric field for the magnetic phase transition of the ground state magnetic structure. The curves depicting the variations of energy and dipole moment with electric field are shown in the following figure.



**Fig. S8.** The tuning of the electric field for  $\text{Mo}_2\text{NCl}_2$  monolayer in AFM2 and FM (a) the total energy of per unit cell, (b) Linear relationship between dipole moment ( $\text{e}\text{\AA}$ ) and electric field ( $\text{V}/\text{\AA}$ ).



**Fig. S9.** The NEB ferroelectric polarization reversal path.



**Fig. S10.** Calculated band gap with different  $U_{\text{eff}}$  values of Mo ion for three magnetic structures (FM, AFM1, AFM2).

## Tables

Table S1. Calculated total energy for non-spin-polarization (No-SP) and three magnetic orders (FM, AFM1, AFM2) with different hubbard  $U$  values of Mo ion.

	$U=0$	$U=1$	$U=2$	$U=3$	$U=4$	$U=5$	$U=6$
No-SP	-75.9791	-70.9158	-65.1160	-60.8813	-57.2247	-52.6223	-50.8382
FM	-76.1212	-71.3159	-66.5802	-61.8366	-59.8354	-57.1061	-54.5326
AFM1	-76.1211	-71.3159	-66.6366	-64.4913	-60.9911	-58.3806	-56.1012
AFM2	-76.1211	-71.3158	-66.5802	-63.9404	-61.0932	-58.4324	-56.1825

Table S2. Calculated magnetic moments for three magnetic orders (FM, AFM1, AFM2) with different hubbard  $U$  values of Mo ion.

	$U=0$	$U=1$	$U=2$	$U=3$	$U=4$	$U=5$	$U=6$
$(\text{Mo1}/\text{Mo2})_{\text{FM}}$	0/0	0/0	0.22/0.22	0.49/0.49	2.37/2.37	2.42/2.42	2.53/2.53
$(\text{Mo1}/\text{Mo2})_{\text{AFM1}}$	0/0	0/0	0/0	2.27/-1.39	2.99/-2.16	3.36/-2.55	2.76/-3.56
$(\text{Mo1}/\text{Mo2})_{\text{AFM2}}$	0/0	0/0	0.8/-0.8	2.12/-2.78	3.15/-2.43	2.63/-3.38	3.54/-2.77

Table S3. Four methods for calculating the band gaps

Approach	Band Gap (eV)
HSE06 ( $AEXX = 1.8$ )	1.18

MBJ	1.28
SCAN	1.23
DFT+ $U$ ( $U = 4$ eV)	1.12

Table S4. Parameters used in the calculation process of linear response theory.

$U$	DFT	NSCF	SCF
-0.2	4.189	3.991	4.146
-0.15	4.189	4.04	4.157
-0.1	4.189	4.09	4.168
-0.05	4.189	4.14	4.179
0	4.189	4.189	4.189
0.05	4.189	4.239	4.2
0.1	4.189	4.289	4.211
0.15	4.189	4.339	4.222
0.2	4.189	4.389	4.234

Table S5. Total energy of different phases (T, H- phase) and magnetic orderings (FM, AFM1, AFM2) of  $\text{Mo}_2\text{CT}_2$  calculated by DFT+ $U$  ( $U = 3.6$  eV).

T-Phase	TOO			TTO			TTT		
Ordering	FM	AFM1	AFM2	FM	AFM1	AFM2	FM	AFM1	AFM2
$\text{Mo}_2\text{C-F}_2$	-61.0497	-62.0925	<b>-62.6294</b>	-59.1725	-62.6234	-62.0935	-61.0318	-62.6256	-58.8600
$\text{Mo}_2\text{C-Cl}_2$	-53.9074	<b>-55.8544</b>	-54.9663	-52.9336	54.1322	-53.5741	-52.0053	-52.4295	-52.2084
$\text{Mo}_2\text{C-Br}_2$	-51.0748	-51.9693	<b>-53.0706</b>	-50.1883	-51.4951	-50.6677	-49.3556	-49.9195	-49.3129
$\text{Mo}_2\text{C-O}_2$	-70.8648	-71.1237	-71.0572	-70.2190	-69.9038	-70.5089	-69.7218	-69.7218	-69.8774
$\text{Mo}_2\text{C-S}_2$	-60.5564	-60.7627	-60.7880	-60.5067	-60.5566	<b>-60.8910</b>	-60.2644	-60.2675	-60.5800
$\text{Mo}_2\text{C(OH)}_2$	-85.1387	<b>-86.7101</b>	-86.2411	-83.7262	-84.7683	-84.7009	-82.6926	-86.7091	-83.2592
H-Phase	HOO			HTO			HTT		
Ordering	FM	AFM1	AFM2	FM	AFM1	AFM2	FM	AFM1	AFM2
$\text{Mo}_2\text{C-F}_2$	-56.5264	-56.7580	-58.0338	-60.1071	-61.2655	-60.7389	-58.5775	-59.1817	-59.2744
$\text{Mo}_2\text{C-Cl}_2$	-52.8974	-53.0822	-52.8663	-53.2336	54.0322	-53.8893	-51.8751	-51.0101	-52.0099
$\text{Mo}_2\text{C-Br}_2$	-47.5245	-48.3254	-47.6103	-49.7663	-51.1061	-49.7205	-48.9814	-49.7273	-48.9700
$\text{Mo}_2\text{C-O}_2$	-70.4478	-70.4478	-70.4478	-70.6332	-70.6369	<b>-71.1395</b>	-70.6407	-70.6407	-70.9323
$\text{Mo}_2\text{C-S}_2$	-58.4561	-58.7327	-57.9888	-59.1061	-58.9964	-58.8974	-57.9231	-57.2683	-57.5800
$\text{Mo}_2\text{C(OH)}_2$	-81.2594	-81.5616	-82.5644	-85.2643	-84.9477	-82.9873	-83.4758	-83.6502	-83.9271

Table S6. Total energy of different phases (T, H- phase) and magnetic orderings (FM, AFM1, AFM2) of  $\text{Mo}_2\text{NT}_2$  calculated by DFT+ $U$  ( $U = 3.6$  eV).

T-Phase	TOO			TTO			TTT		
Ordering	FM	AFM1	AFM2	FM	AFM1	AFM2	FM	AFM1	AFM2
$\text{Mo}_2\text{N-F}_2$	-62.6829	-63.5958	-63.4661	-62.5029	-63.2703	-63.4652	-62.5017	<b>-63.8128</b>	-63.4484
$\text{Mo}_2\text{N-Cl}_2$	-54.5324	-56.1012	<b>-56.4405</b>	-55.1215	-55.6040	-56.1125	-51.6459	-56.1012	-56.1820
$\text{Mo}_2\text{N-Br}_2$	-51.5032	-53.2778	-53.8175	-51.7643	-52.8157	-53.1131	-48.8261	-53.6794	-53.1452
$\text{Mo}_2\text{N-O}_2$	-73.4027	<b>-73.9538</b>	-73.7762	-71.2098	-71.3858	-71.6712	-69.1503	-69.6826	-70.1411
$\text{Mo}_2\text{N-S}_2$	-61.6276	-62.2734	-62.5157	-60.6958	-60.7161	-61.6272	-59.3188	-59.3418	-60.5569
$\text{Mo}_2\text{N(OH)}_2$	-86.3585	-87.6693	-86.8769	-86.5693	-86.6612	<b>-87.6810</b>	-82.4679	-87.2588	-86.7018
H-Phase	HOO			HTO			HTT		
Ordering	FM	AFM1	AFM2	FM	AFM1	AFM2	FM	AFM1	AFM2
$\text{Mo}_2\text{N-F}_2$	-56.5877	-57.6262	-58.6562	-60.9752	-60.4037	-60.7166	-62.4981	-61.4029	-62.9906
$\text{Mo}_2\text{N-Cl}_2$	-50.9003	-50.9992	-52.8255	-53.8098	-53.5281	-53.9312	-55.1222	-52.7038	-55.6983
$\text{Mo}_2\text{N-Br}_2$	-50.4624	-50.6452	-50.5438	-50.6393	-50.2334	-50.7292	-51.4410	<b>-53.8783</b>	-52.7853
$\text{Mo}_2\text{N-O}_2$	-69.7787	-69.7916	-70.0701	-72.7154	-72.6699	-73.2109	-70.9064	-71.1869	-71.4173
$\text{Mo}_2\text{N-S}_2$	-62.6876	-62.7734	<b>-63.7149</b>	-61.0951	-61.7254	-61.8272	-62.1186	-62.2418	-61.9968
$\text{Mo}_2\text{N(OH)}_2$	-81.3847	-82.2459	-85.9088	-85.5908	-85.4455	-85.9311	-83.6213	-85.6103	-87.2089

[S1] Matteo Cococcioni and Stefano de Gironcoli. Linear response approach to the calculation of the effective interaction parameters in the LDA+ $U$  method. *Phys. Rev. B* **71**, 035105 (2005).

[S2] Ceder. G. et al. Formation enthalpies by mixing GGA and GGA +  $U$  calculations. *Phys. Rev. B* **84**, 045115 (2005).