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Electronic Supplementary Information

Bandgap Engineering of MXene Compounds for Water Splitting

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Table S1 Bandgap values, E_g, comparison, with and without vdW correction using PBE0 or PBE0 with Grimme D3, of selected O-terminated MXenes, with stacking and O adatoms positions specified. All values are given in eV.

	E_g (PBE0)	E_g (PBE0-D3)
Zr_2CO_2 ABC H_M	2.262	2.262
Hf_2CO_2 ABC H_M	2.744	2.744
Sc_2CO_2 ABC H_{MX}	3.786	3.786
Y_2NO_2 ABC H_{MX}	3.177	3.177
W_2NO_2 ABC H_M	0	0
Mo_2NO_2 ABC H_M	0	0

Table S2 Comparison of the relative energy of different O-termination positions when using PBE without or with Grimme D3 dispersive forces correction, taking ABC H_M structure as reference for the Zr_2CO_2 ABC and W_2NO_2 ABA structures.

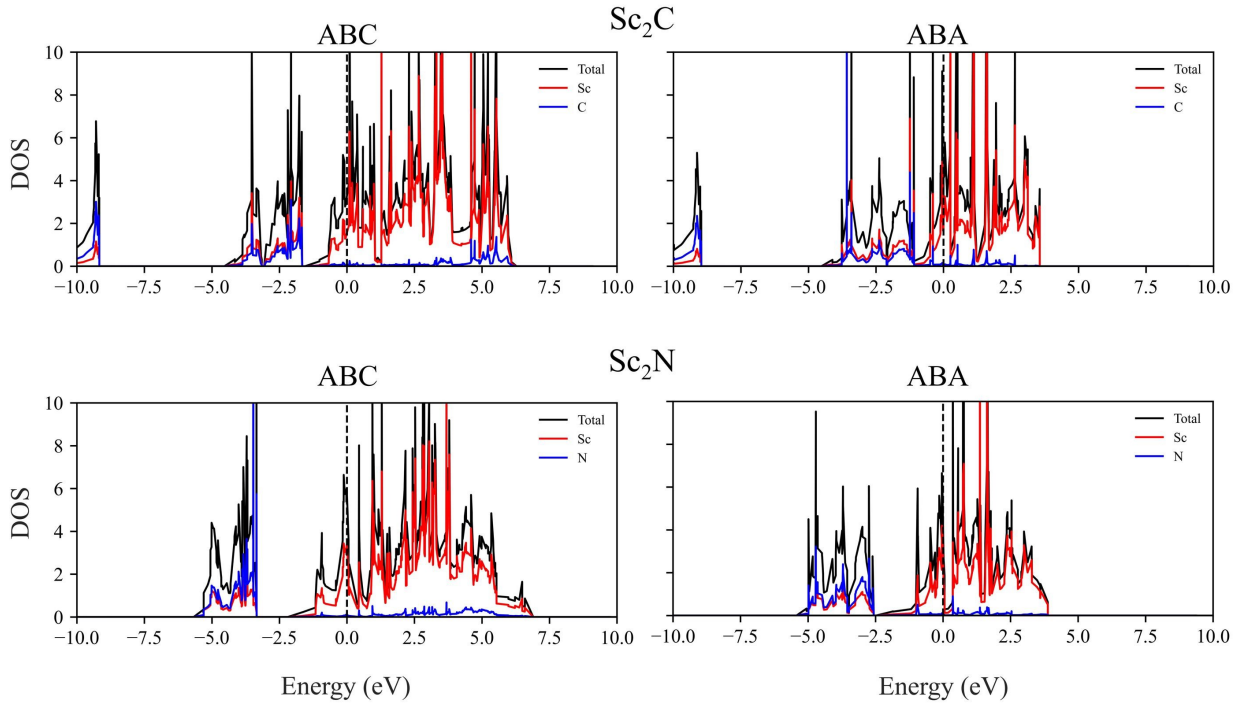
	Zr_2CO_2 ABC		
	H_M	**H_{MX}**	**H_X**
PBE	0	0.87	1.96
PBE-D3	0	0.86	1.94

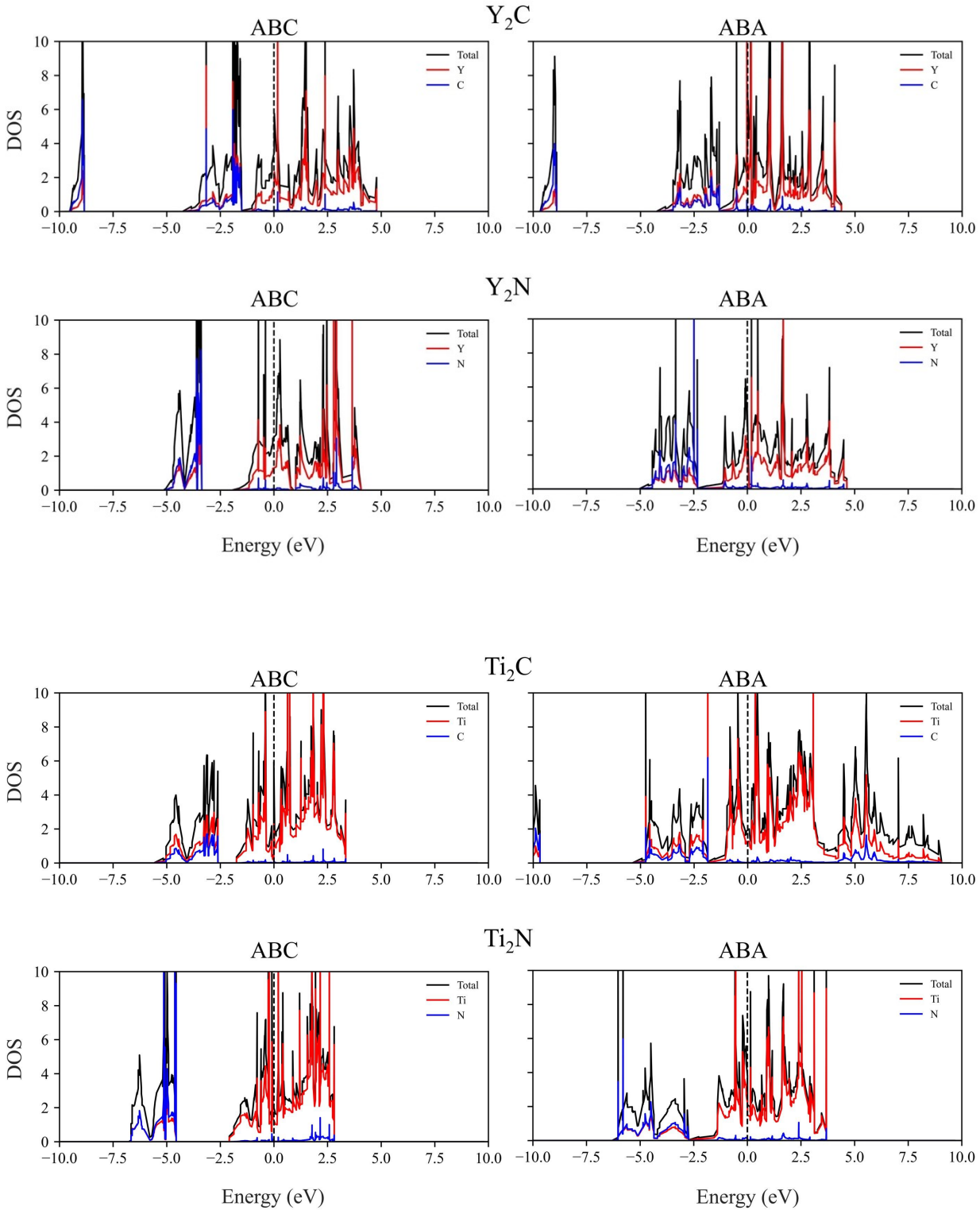
	W_2NO_2 ABA		
	H	**H_{MX}**	**H_X**
PBE	-0.96	-1.37	-1.64
PBE-D3	-0.93	-1.35	-1.54

Table S3 Calculated lattice parameters, *a*, and MXene widths, *d*, for the studied pristine M_2X MXenes with ABC or ABA stacking. All values are given in Å.

M	**C**				**N**			
	ABC		**ABA**		**ABC**		**ABA**	
	***a* (Å)**	***d* (Å)**	***a* (Å)**	***d* (Å)**	***a* (Å)**	***d* (Å)**	***a* (Å)**	***d* (Å)**
Sc	3.328	2.409	3.257	2.686	3.218	2.448	3.165	2.675
Y	3.588	2.661	3.535	2.910	3.481	2.681	3.361	3.015
Ti	3.075	2.250	3.041	2.498	2.978	2.287	2.878	2.652
Zr	3.274	2.544	3.240	2.808	3.230	2.519	3.092	2.935
Hf	3.212	2.544	3.168	2.809	3.163	2.523	3.050	2.909
V	2.900	2.174	2.765	2.563	2.867	2.125	2.690	2.598
Nb	3.130	2.388	2.975	2.819	3.131	2.308	2.913	2.875
Ta	3.084	2.436	2.965	2.811	3.082	2.363	2.888	2.905
Cr	2.807	2.112	2.638	2.521	2.821	2.066	2.606	2.498
Mo	2.925	2.512	2.850	2.742	2.804	2.815	2.817	2.773
W	2.889	2.625	2.847	2.788	2.785	2.906	2.789	2.902

Fig. S1 Total and projected DOS, calculated with PBE, for all M_2X systems, considering the two possible stackings, ABC and ABA. Energies corrected to E_F, indicated with a dashed black line. The particular M_2X compound and stacking are labelled on top of the image.

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ABA
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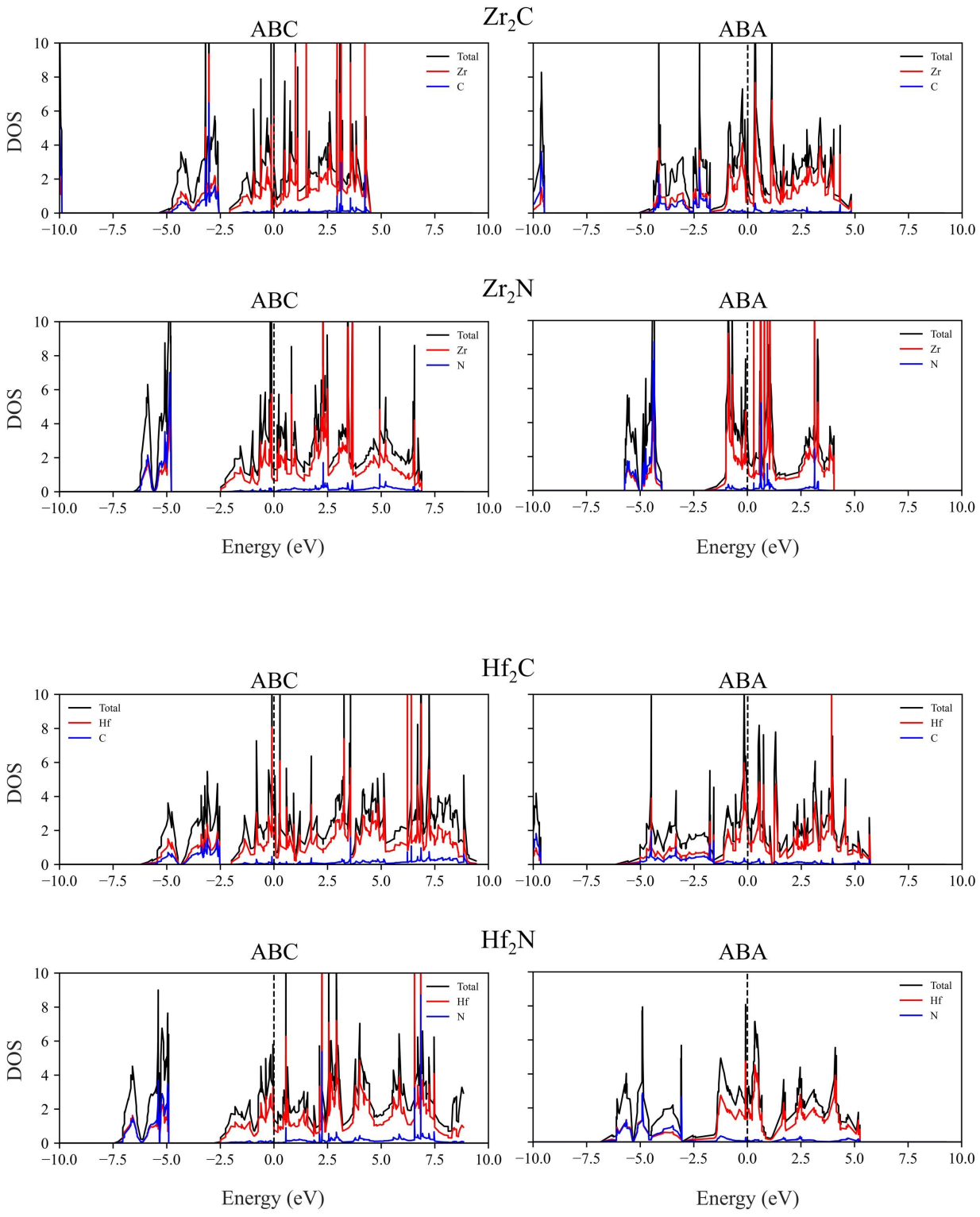
Y
C
Y2N
N
Ti2C
Ti
Ti2N
DOS
Energy (eV)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ABA
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Zr
C
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Hf2C
Hf
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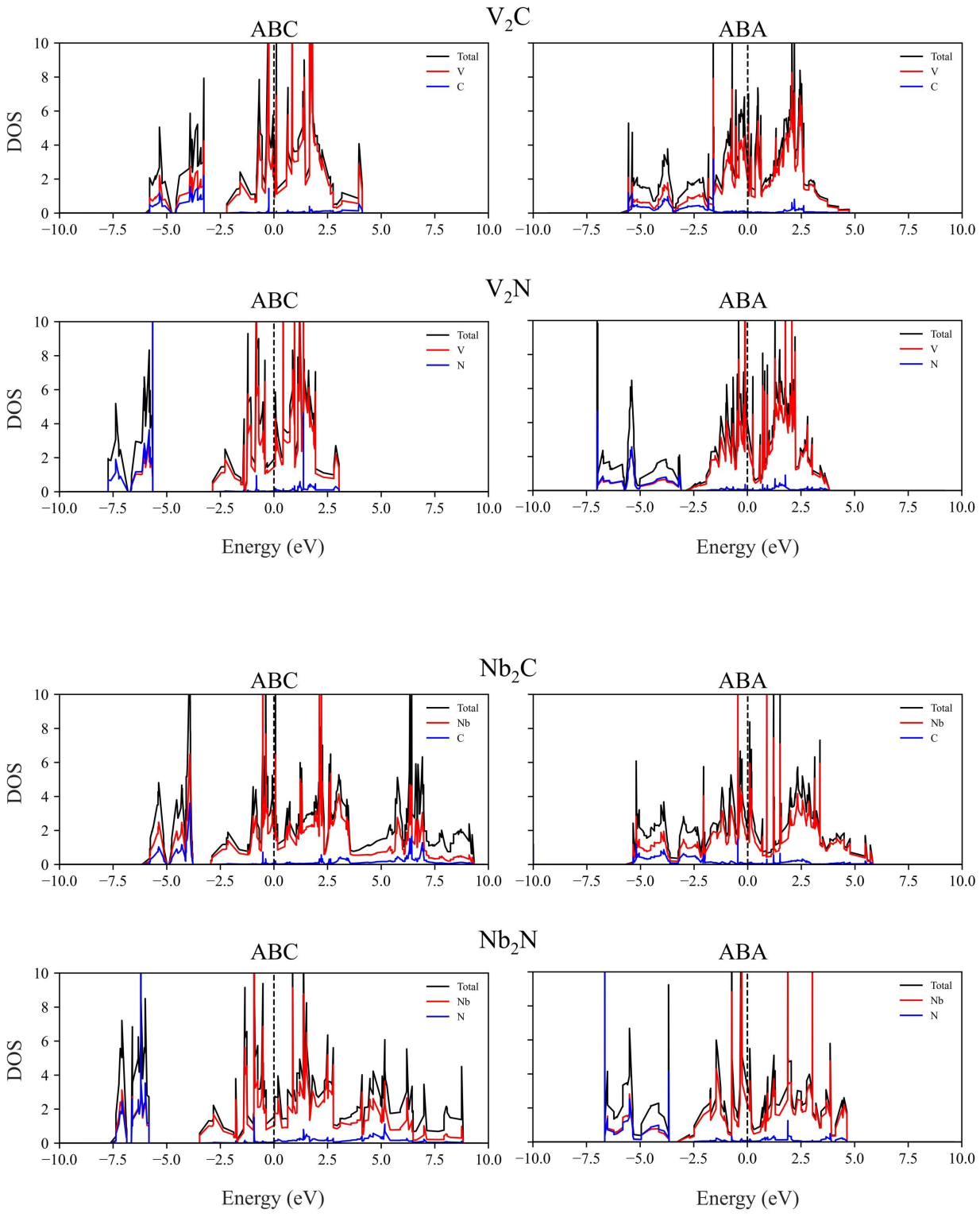
DOS
Energy (eV)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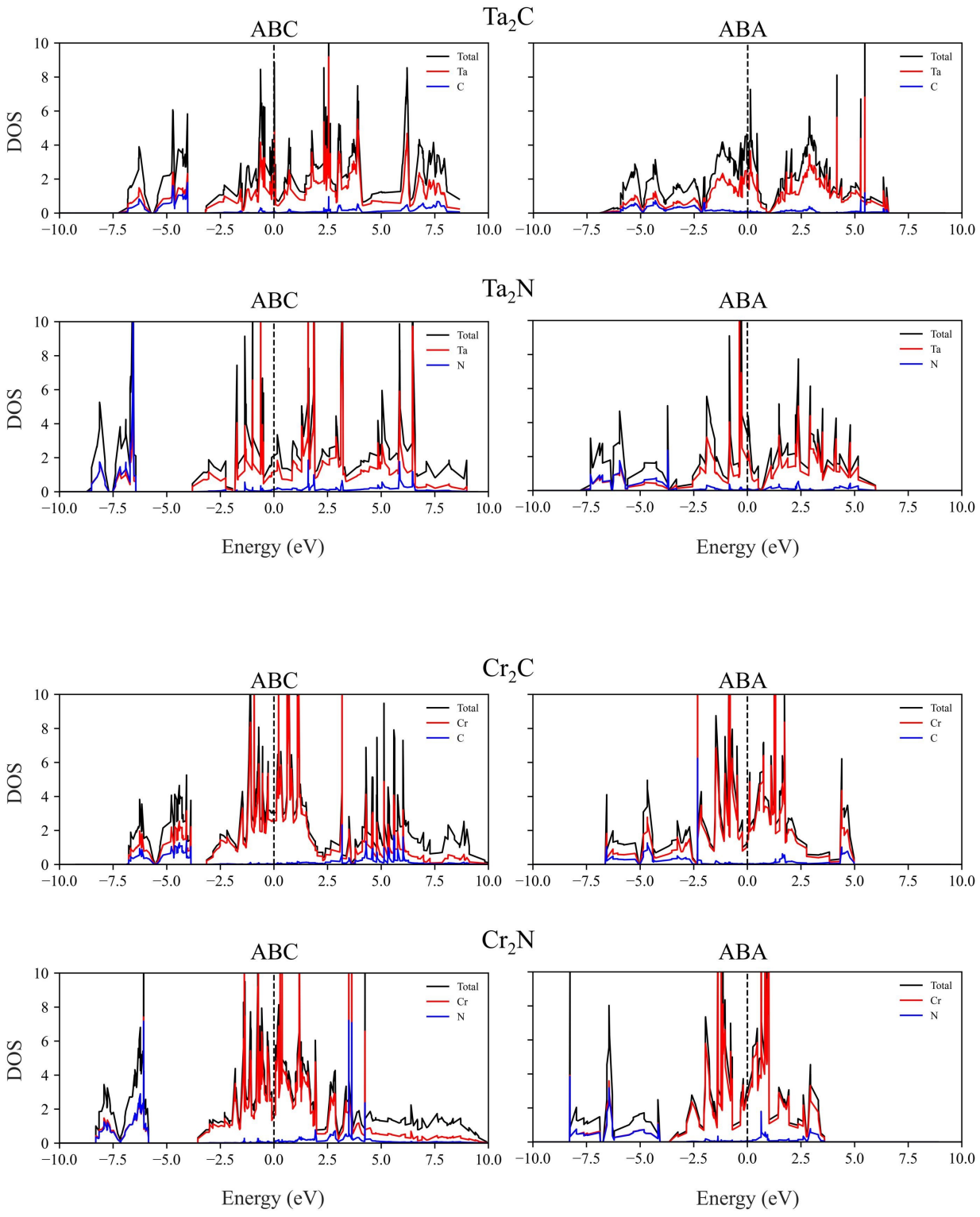
DOS
Energy (eV)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Cr
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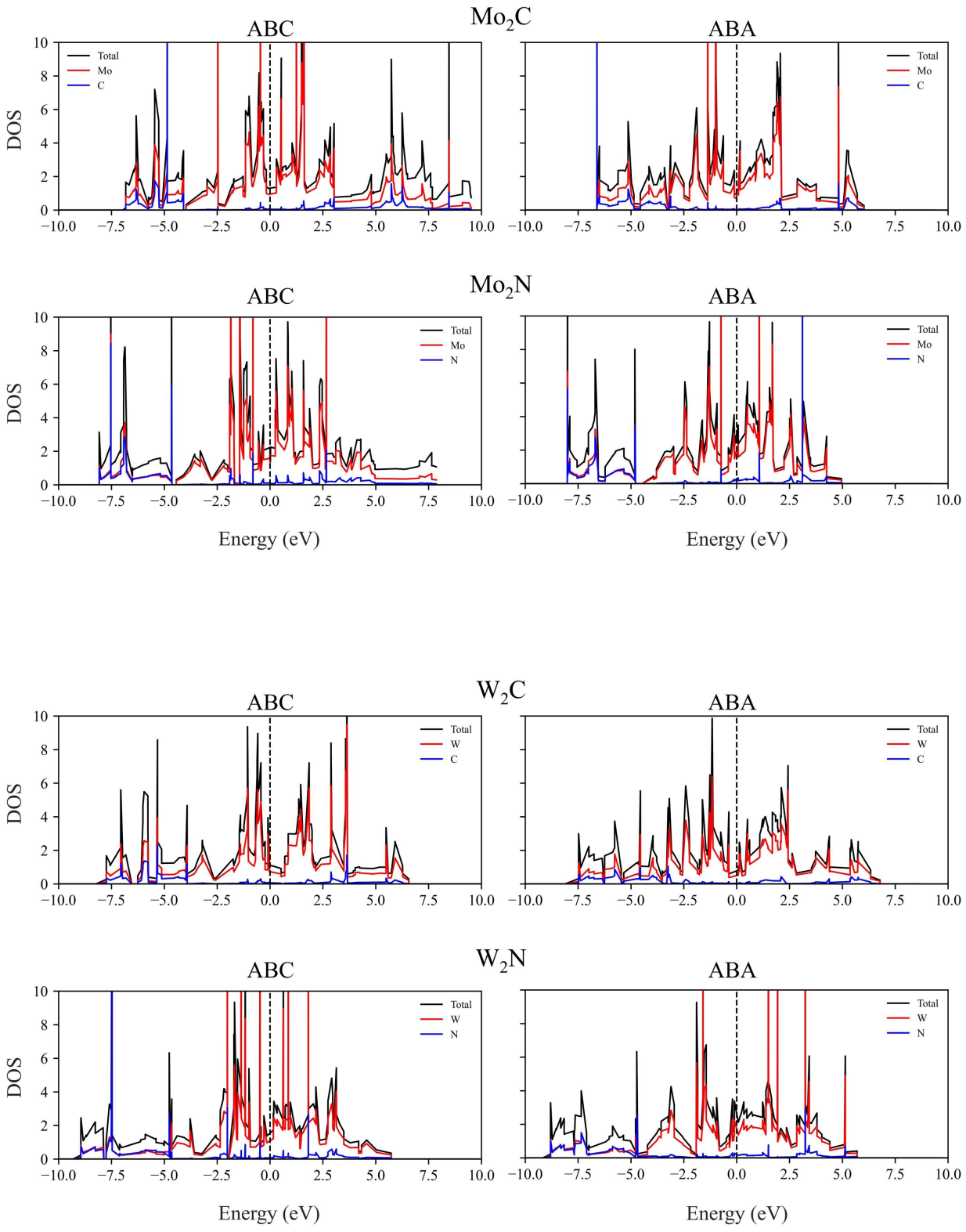
Energy (eV)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ABA
Total
Mo
C
Mo2N
N
W2C
W
W2N
DOS
Energy (eV)

Table S4 Calculated lattice parameters, *a*, and MXene widths, *d*, for the six studied M_2XO_2 MXenes with ABC or ABA stacking. All values are given in Å.

X	***M***	**ABC**						**ABA**					
		H_M		**H_{MX}**		**H_X**		**H**		**H_{MX}**		**H_X**	
		a **(Å)**	***d*** **(Å)**	***a*** **(Å)**	***d*** **(Å)**	***a*** **(Å)**	***d*** **(Å)**	***a*** **(Å)**	***d*** **(Å)**	***a*** **(Å)**	***d*** **(Å)**	***a*** **(Å)**	***d*** **(Å)**
	Sc	3.208	4.918	3.405	3.892	3.350	4.109	3.224	4.987	3.249	4.787	3.356	4.187
	Y	3.554	4.870	3.702	4.067	3.641	4.332	3.537	5.034	3.535	5.066	3.635	4.439
	Ti	3.011	4.467	2.986	4.616	2.941	4.850	3.041	4.494	3.012	4.659	2.965	4.896
	Zr	3.303	4.697	3.268	4.884	3.210	5.157	3.323	4.761	3.272	4.969	3.212	5.226
	Hf	3.372	4.379	3.212	4.828	3.170	5.089	3.258	4.708	3.228	4.897	3.172	5.157
C	**V**	2.875	4.456	2.840	4.591	2.802	4.742	2.852	4.692	2.818	4.802	2.770	4.937
	Nb	3.132	4.722	3.093	4.863	3.050	5.037	3.163	4.739	3.081	5.061	3.026	5.239
	Ta	3.113	4.700	3.077	4.835	3.044	5.010	3.149	4.703	3.050	5.072	3.008	5.239
	Cr	2.860	4.477	2.768	4.646	2.668	4.860	2.698	4.864	2.671	4.899	2.650	4.933
	Mo	3.082	4.539	2.917	5.149	2.876	5.217	2.899	5.260	2.886	5.260	2.870	5.274
	W	3.100	4.526	2.896	5.248	2.874	5.285	2.890	5.319	2.890	5.301	2.879	5.297
	Sc	3.218	4.464	3.230	4.455	3.190	4.658	3.197	4.669	3.242	4.538	3.208	4.713
	Y	3.510	4.758	3.520	4.697	3.476	4.913	3.489	4.971	3.516	4.821	3.484	4.983
	Ti	2.978	4.454	2.938	4.635	2.894	4.826	2.998	4.482	2.936	4.723	2.891	4.913
	Zr	3.248	4.740	3.221	4.880	3.187	5.083	3.271	4.771	3.231	4.974	3.161	5.217
	Hf	3.194	4.666	3.163	4.824	3.131	5.027	3.213	4.710	3.176	4.920	3.119	5.159
N	**V**	2.871	4.406	2.801	4.678	2.741	4.843	2.832	4.643	2.773	4.808	2.729	4.909
	Nb	3.132	4.618	3.025	5.045	2.989	5.150	3.011	5.188	3.003	5.219	2.978	5.250
	Ta	3.120	4.568	2.997	5.060	2.971	5.137	2.974	5.232	2.978	5.228	2.958	5.251
	Cr	2.926	4.305	2.752	4.759	2.670	4.866	2.690	4.782	2.659	4.868	2.642	4.887
	Mo	2.837	5.412	2.828	5.437	2.861	5.242	2.876	5.258	2.848	5.332	2.882	5.207
	W	2.820	5.554	2.817	5.581	2.866	5.303	2.857	5.363	2.847	5.405	2.881	5.252

Fig. S2 Evolution of the cell parameter, *a*, along *M* elements in the studied O-terminated C-MXenes (top) and N-MXenes (bottom) for ABC (left) and ABA (right) stackings, considering the different hollow positions.

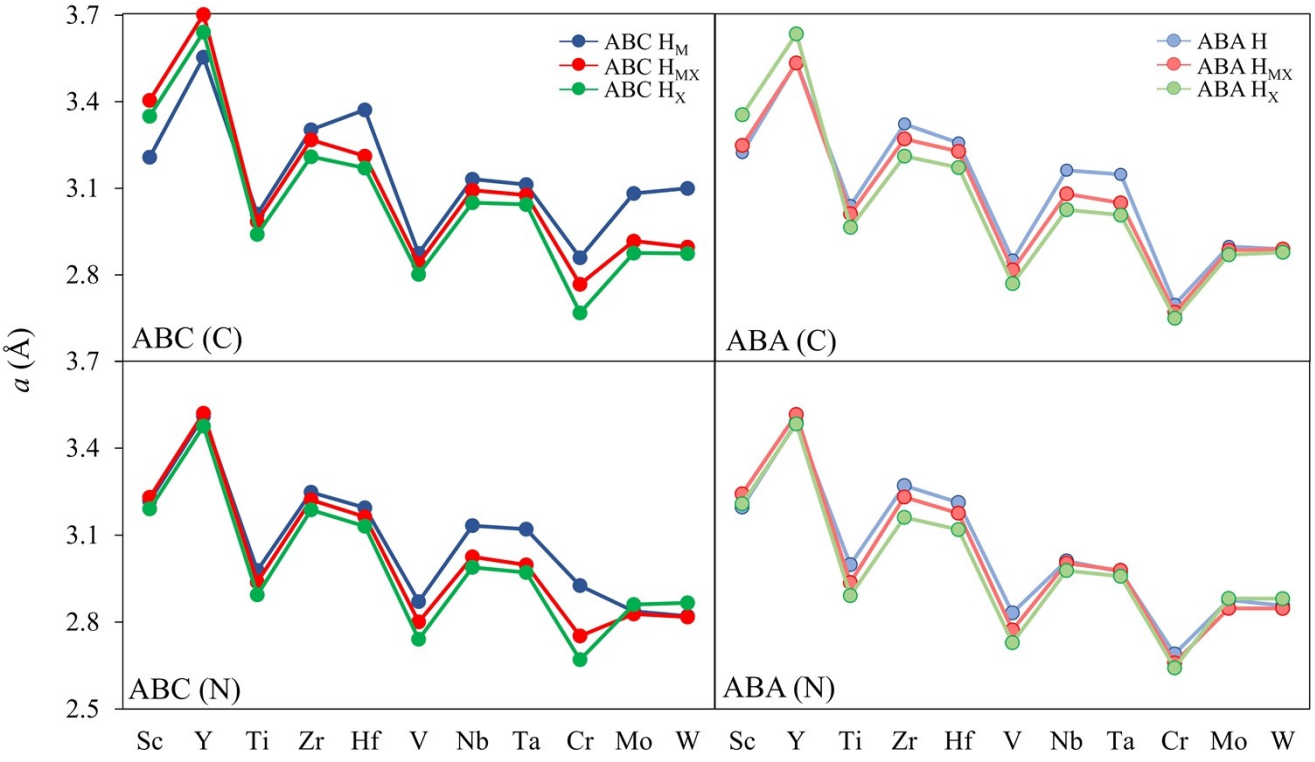


Fig. S3 Evolution of the MXene width, *d*, along *M* elements in the studied O-terminated C-MXenes (top) and N-MXenes (bottom) for ABC (left) and ABA (right) stackings, considering the different hollow positions.

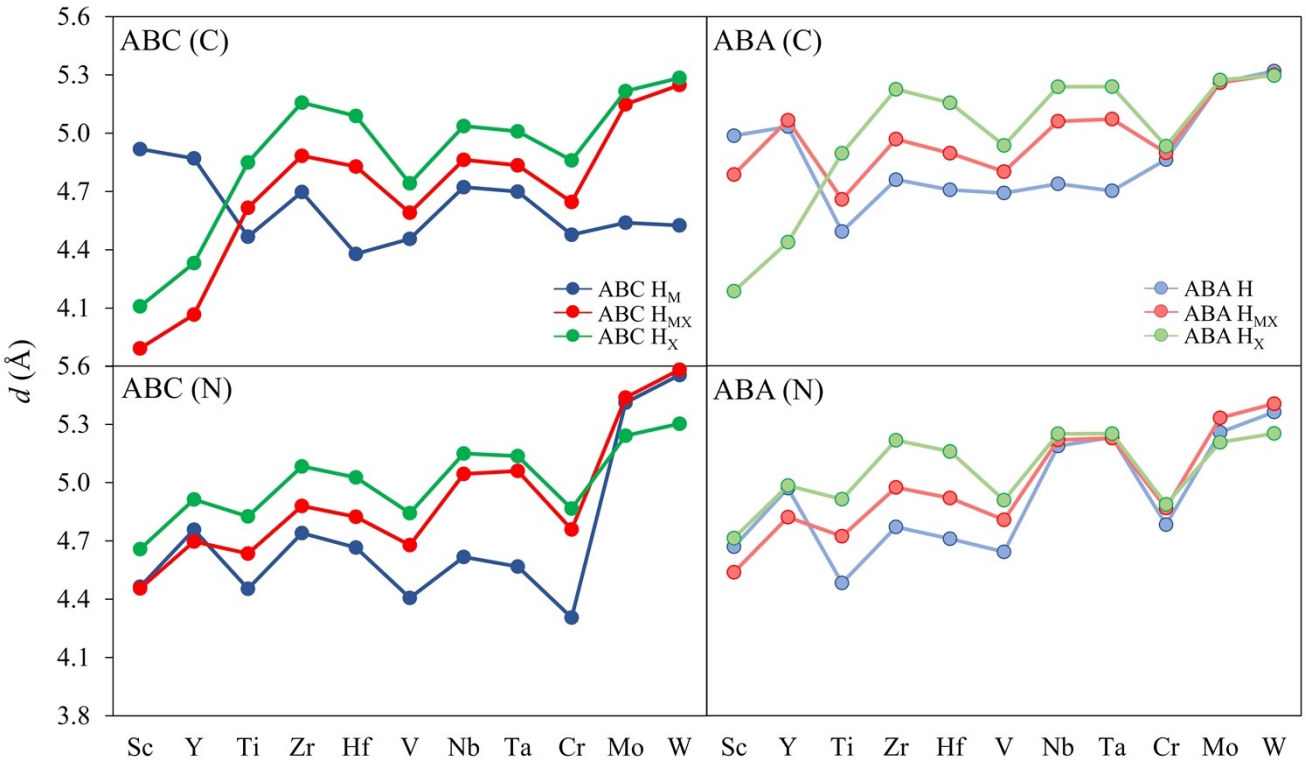


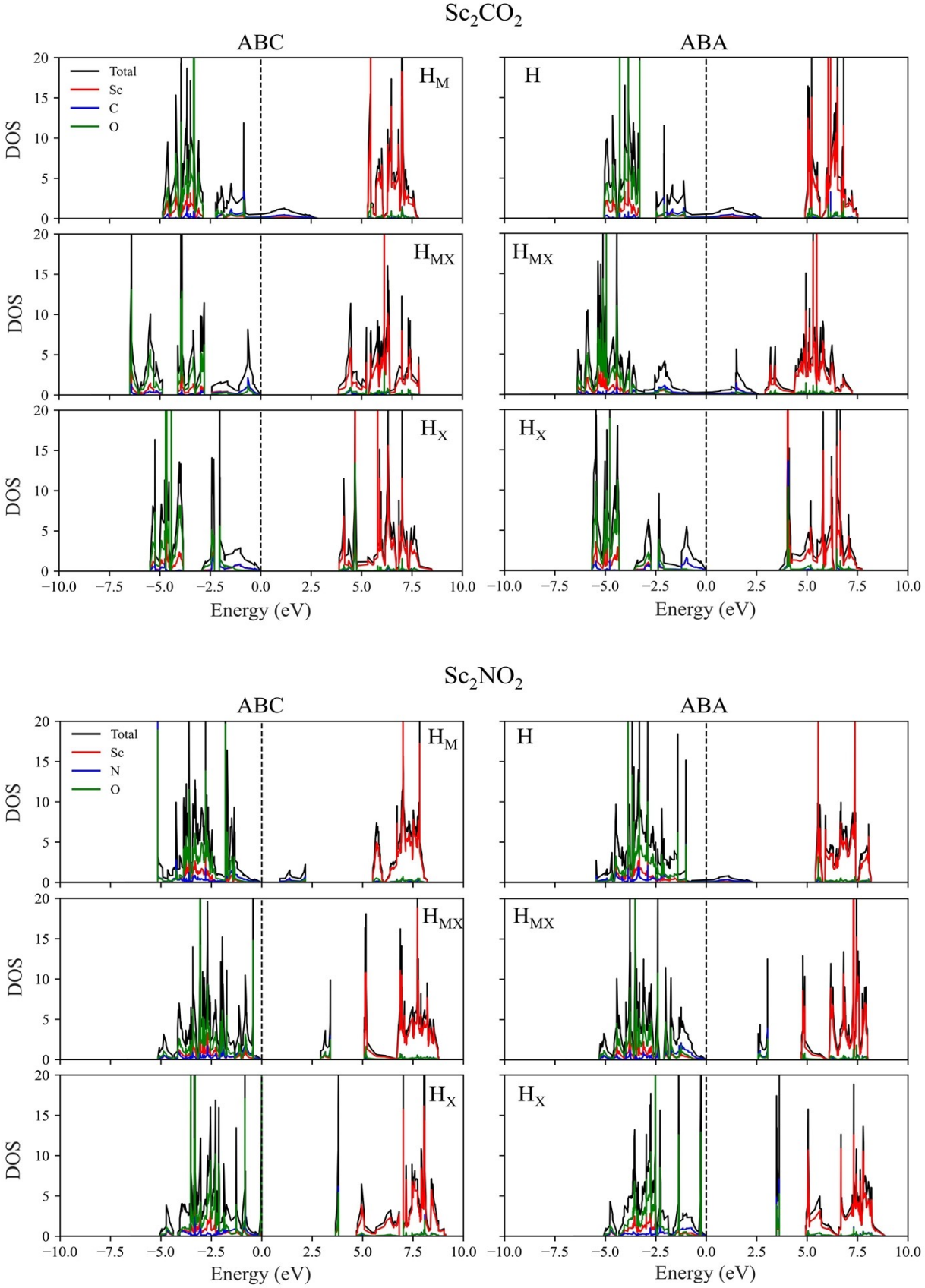
Table S5 Relative energy, ΔE, in eV, for each O-functionalized MXene, with respect the corresponding ABC H_M case, considering ABC/ABA stacking and different hollow positions. Values in bold indicate the most energetically stable structure.

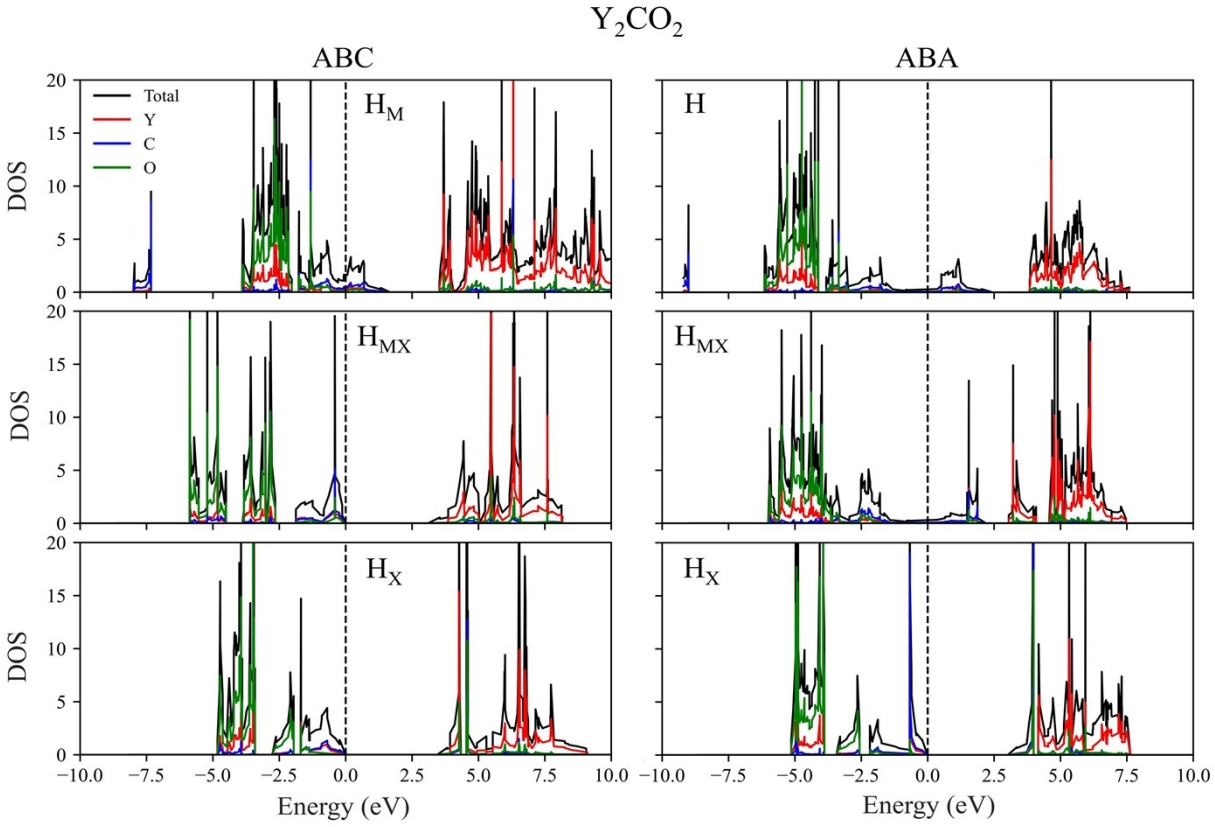
	C						N					
	ABC			ABA			ABC			ABA		
M	**H_M**	**H_{MX}**	**H_X**	**H**	**H_{MX}**	**H_X**	**H_M**	**H_{MX}**	**H_X**	**H**	**H_{MX}**	**H_X**
Sc	0.00	**-0.60**	-0.46	0.01	-0.33	0.13	**0.00**	0.30	0.77	0.23	0.66	1.06
Y	0.00	**-0.46**	-0.31	0.20	0.53	0.33	**0.00**	0.20	0.62	0.28	0.64	0.96
Ti	**0.00**	0.79	1.81	0.35	1.16	2.07	**0.00**	0.55	1.23	0.33	0.86	1.51
Zr	**0.00**	0.87	1.96	0.65	1.51	2.47	**0.00**	0.41	1.08	0.59	1.00	1.68
Hf	**0.00**	0.74	1.94	0.38	1.38	2.48	**0.00**	0.45	1.15	0.62	1.06	1.84
V	**0.00**	0.27	0.63	0.35	0.53	0.82	0.00	0.03	0.05	-0.04	-0.01	**-0.08**
Nb	**0.00**	0.16	0.52	0.69	0.94	1.19	0.00	0.24	**-0.11**	0.55	0.27	-0.06
Ta	**0.00**	0.16	0.56	0.71	1.01	1.31	0.00	0.27	**-0.16**	0.62	0.23	-0.13
Cr	0.00	-0.09	-0.21	-0.17	-0.31	**-0.59**	0.00	0.36	0.29	0.33	0.19	**-0.02**
Mo	0.00	-0.38	-1.06	-0.50	-0.93	**-1.46**	0.00	-1.34	-1.11	-0.86	-1.18	**-1.41**
W	0.00	-0.29	-1.16	-0.55	-1.02	**-1.79**	0.00	-0.76	-1.15	-0.96	-1.37	**-1.64**

Table S6 Calculated bandgap, E_g, in eV, as obtained using PBE or PBE0 functionals, for the O-terminated MXenes in the six different structures studied. Bold values indicate direct bandgap.

X	*M*	ABC						ABA					
		H_M		H_{MX}		H_X		H		H_{MX}		H_X	
		PBE	PBE0	PBE	PBE0	PBE	PBE0	PBE	PBE0	PBE	PBE0	PBE	PBE0
	Sc	—	—	2.00	3.79	2.12	3.89	—	—	—	—	**1.80**	**3.61**
	Y	—	—	**1.46**	**3.11**	**1.63**	**3.45**	—	—	—	—	**1.19**	**3.02**
	Ti	0.26	1.64	0.79	2.24	0.43	1.86	0.09	1.44	0.58	2.15	0.52	2.15
	Zr	0.87	2.26	1.06	2.43	0.62	2.01	0.56	1.90	0.80	2.18	0.93	2.38
	Hf	1.29	2.74	1.06	2.46	0.61	2.06	0.67	2.07	0.78	2.20	0.97	2.37
C	**V**	—	—	—	—	—	0.77	—	0.46	—	—	—	0.67
	Nb	—	—	—	0.63	—	0.12	—	0.56	—	0.97	—	—
	Ta	—	—	—	0.63	—	—	—	0.75	—	0.92	—	—
	Cr	—	1.27	—	—	**0.14**	**0.71**	—	0.57	—	1.65	—	0.66
	Mo	—	—	—	—	—	0.65	—	0.49	—	—	—	0.64
	W	—	—	—	—	—	0.66	—	0.66	—	—	—	0.63
	Sc	—	0.91	0.68	2.93	1.03	3.66	—	—	0.33	2.58	1.10	3.49
	Y	—	—	0.86	3.18	1.07	3.68	—	—	0.48	2.83	1.16	3.49
	Ti	—	0.37	—	—	—	—	—	1.66	—	0.85	—	—
	Zr	—	—	—	—	—	—	—	1.00	—	0.98	—	—
	Hf	—	—	—	—	—	—	—	0.64	—	0.82	—	—
N	**V**	—	—	—	1.17	—	0.16	—	—	—	—	—	—
	Nb	—	—	—	0.41	—	—	—	0.40	—	0.59	—	—
	Ta	—	—	—	—	—	—	—	—	—	—	—	—
	Cr	—	—	—	—	—	—	—	0.64	—	0.04	—	—
	Mo	—	—	—	—	—	—	—	—	—	—	—	—
	W	—	—	—	—	—	—	—	—	—	—	—	—

Fig. S4 Total and projected DOS, calculated with PBE0, for all M_2XO_2 cases, considering the six structures studied. Energies corrected to VBM or E_F, indicated with a dashed black line. The M_2XO_2 species, stacking and O position are specified in each plot.

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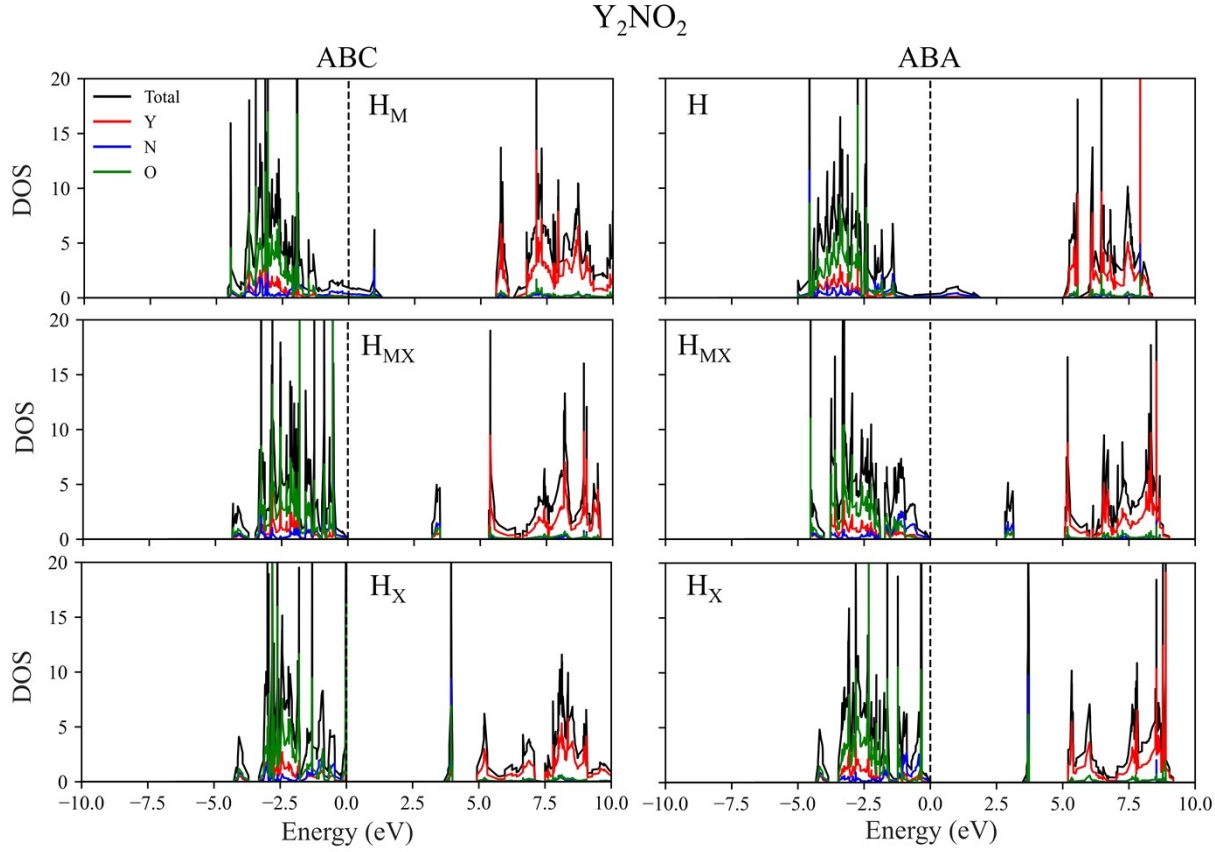
H
H_{MX}
H_X
DOS
Energy (eV)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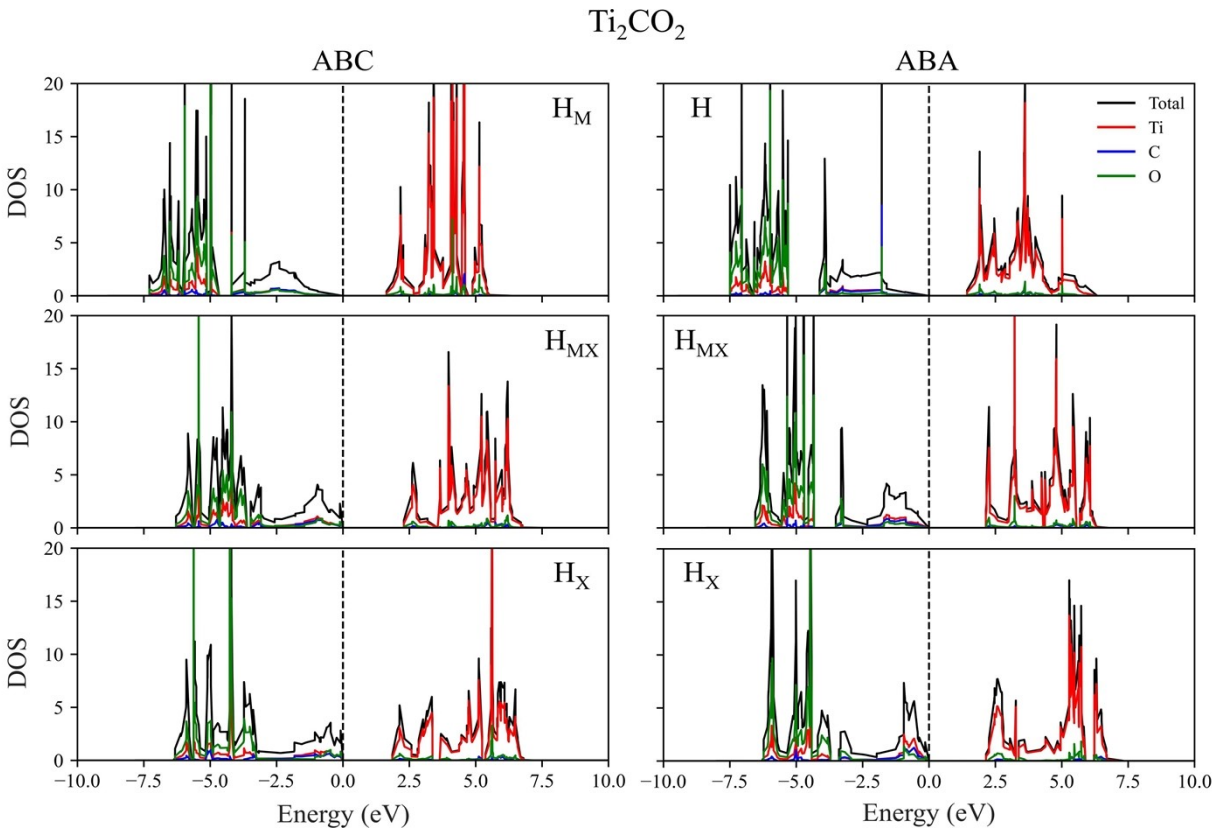
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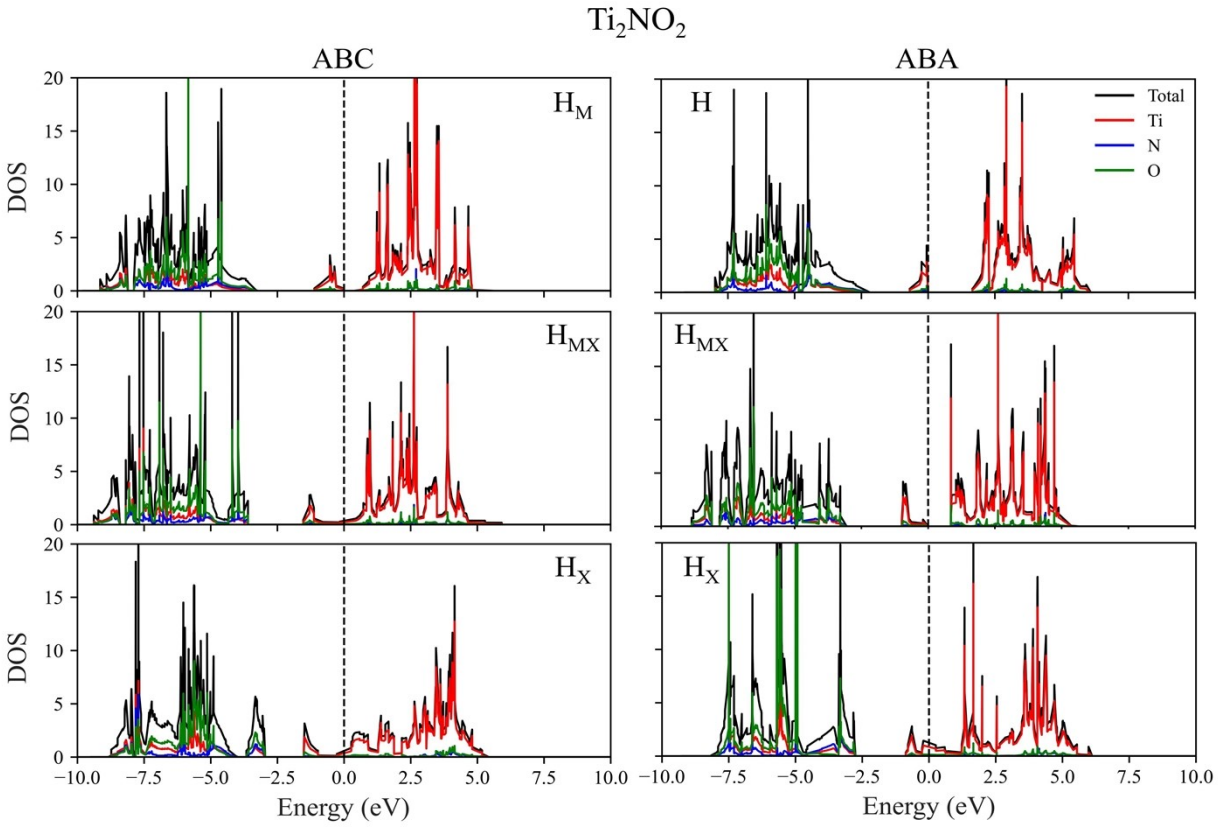
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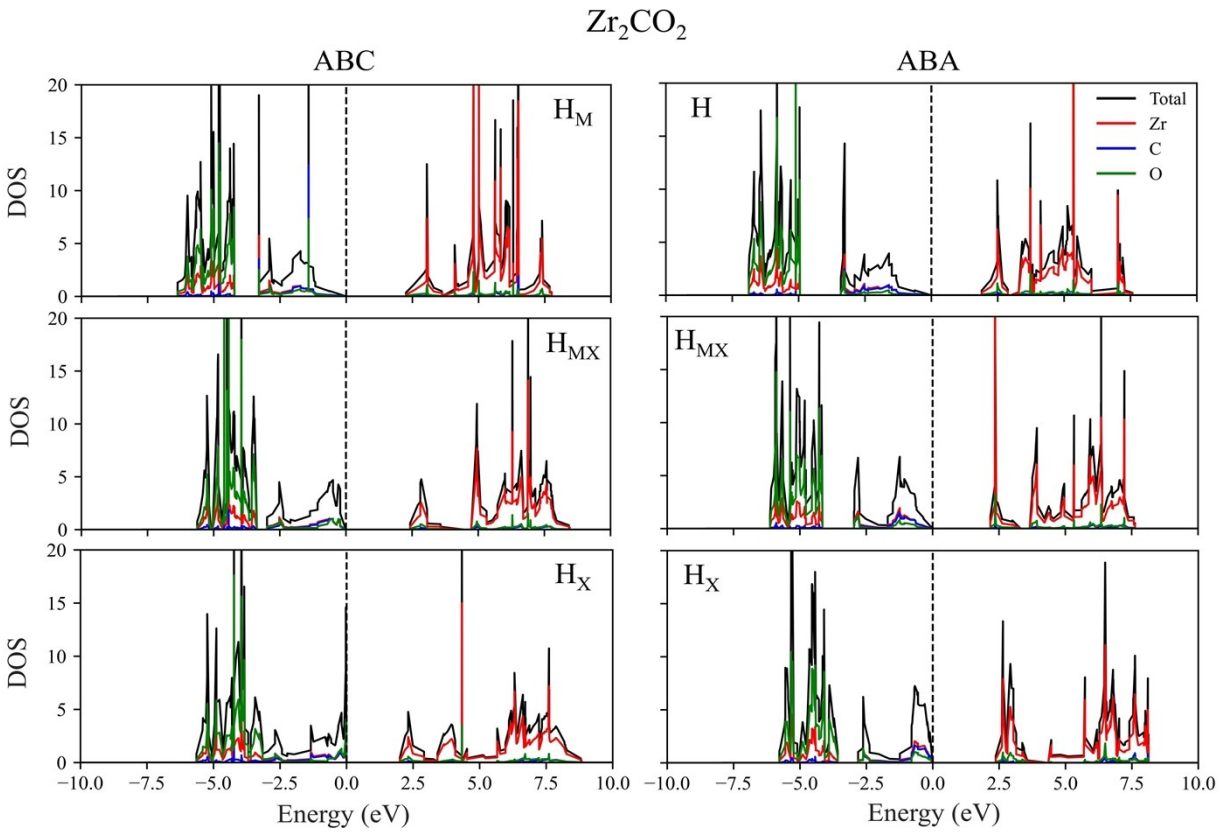
Energy (eV)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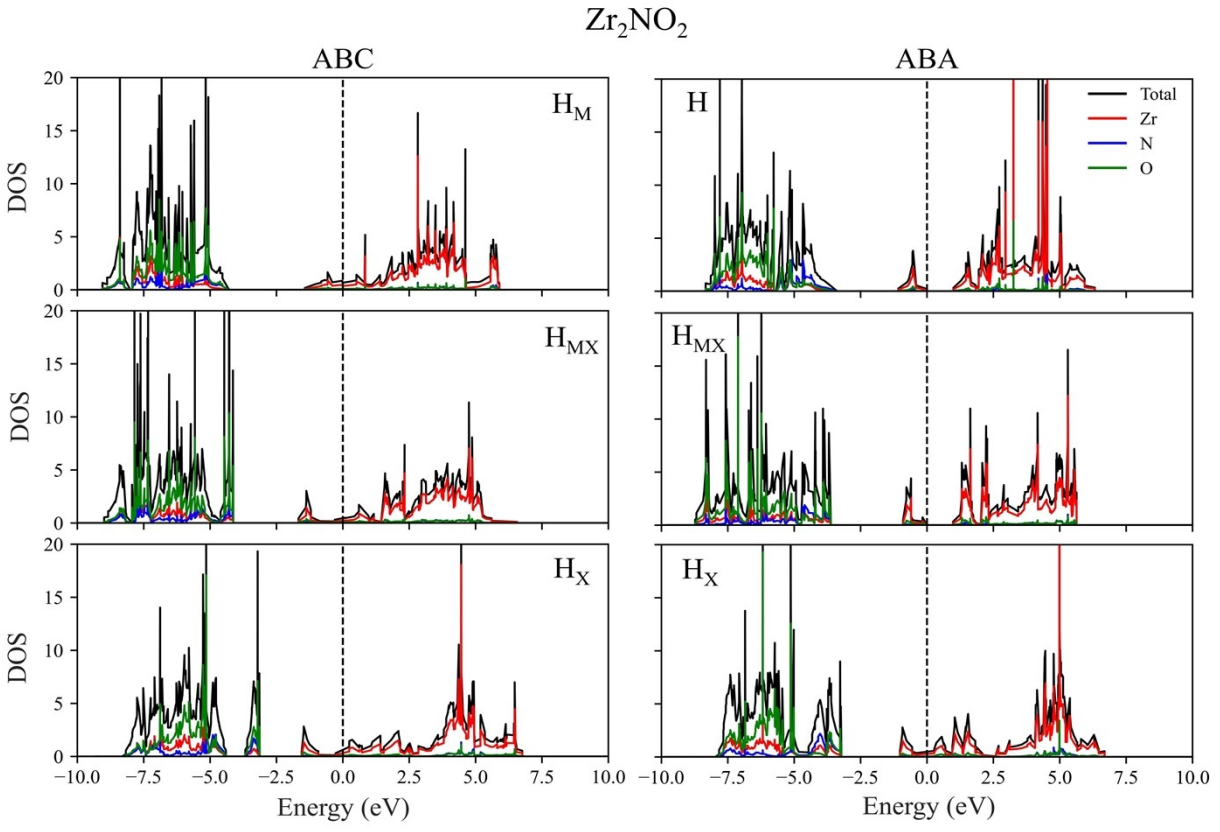
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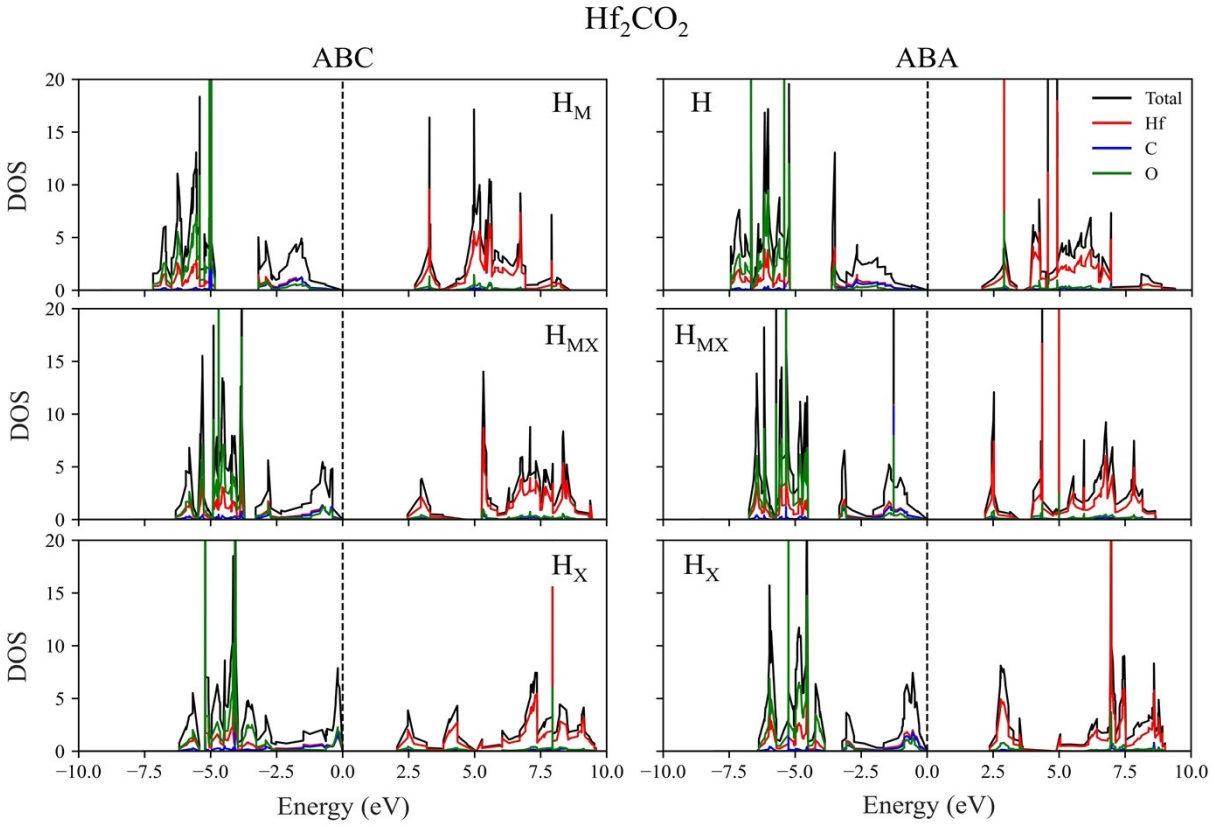
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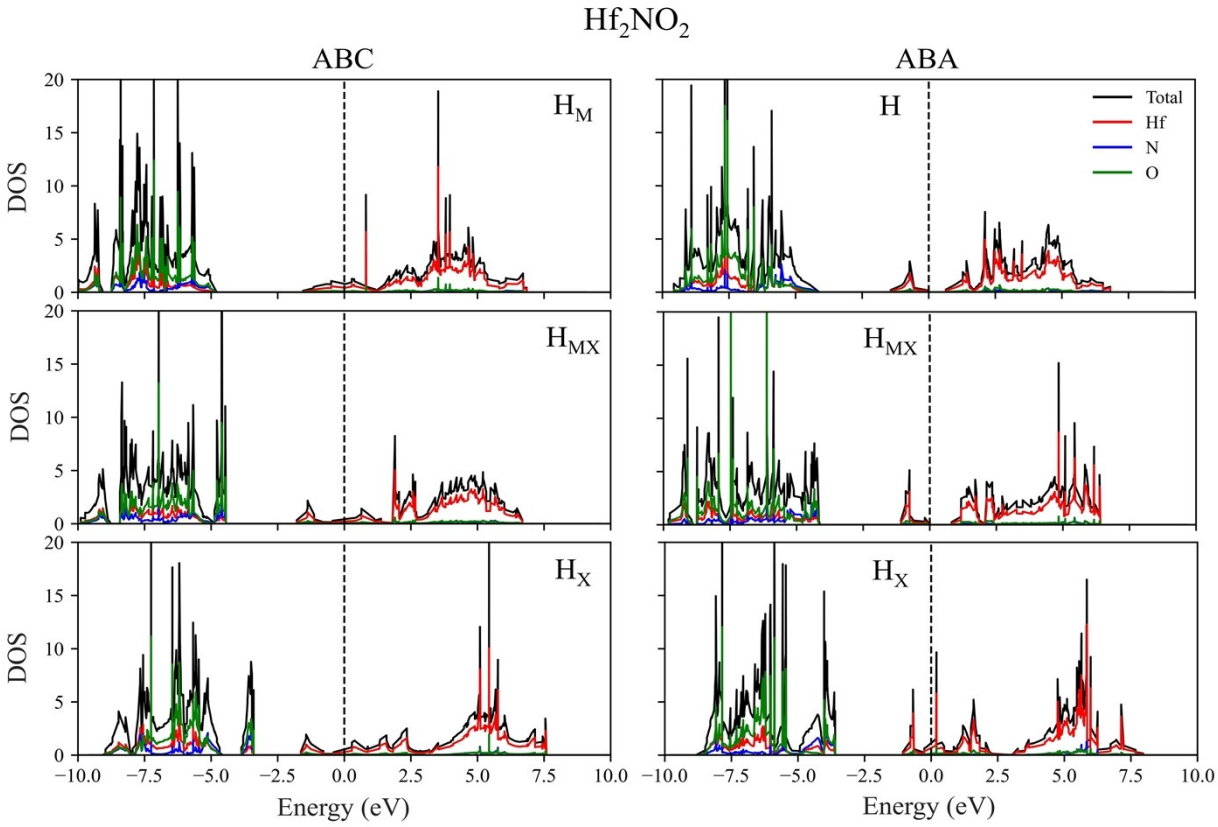
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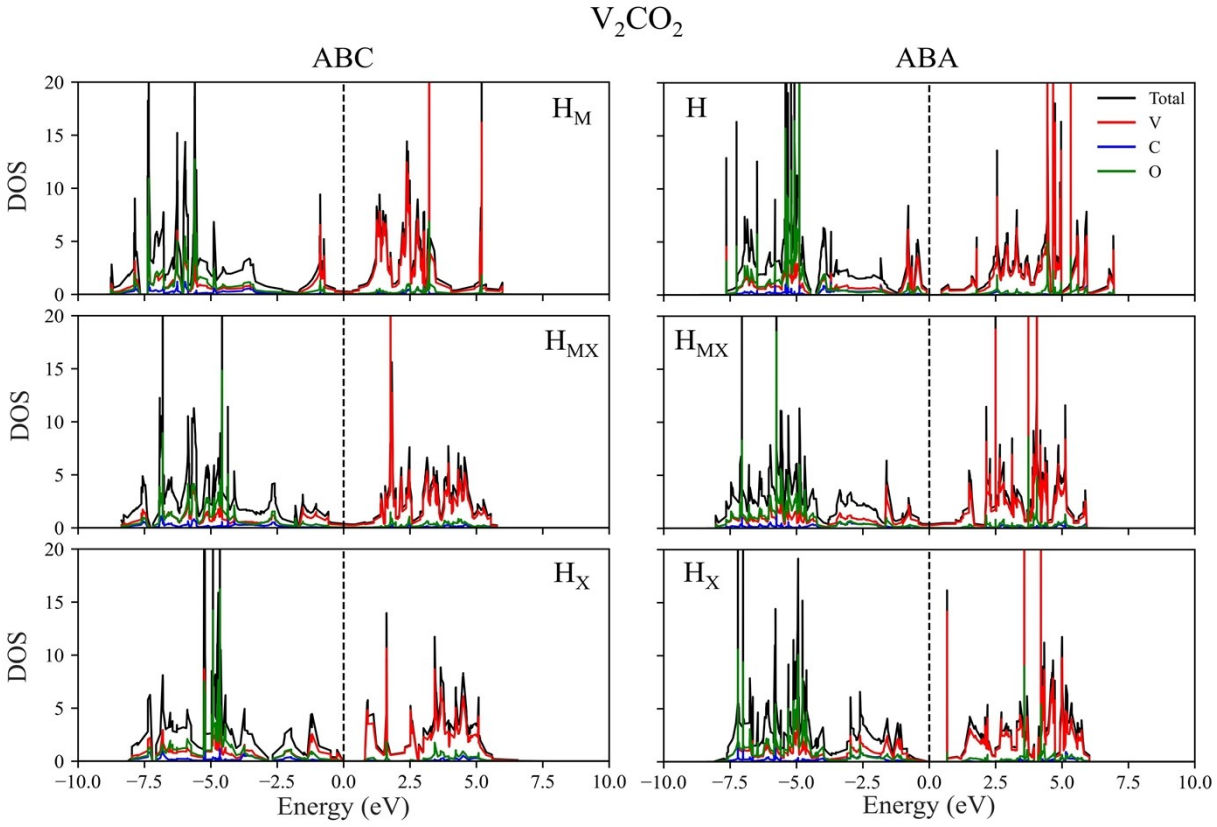
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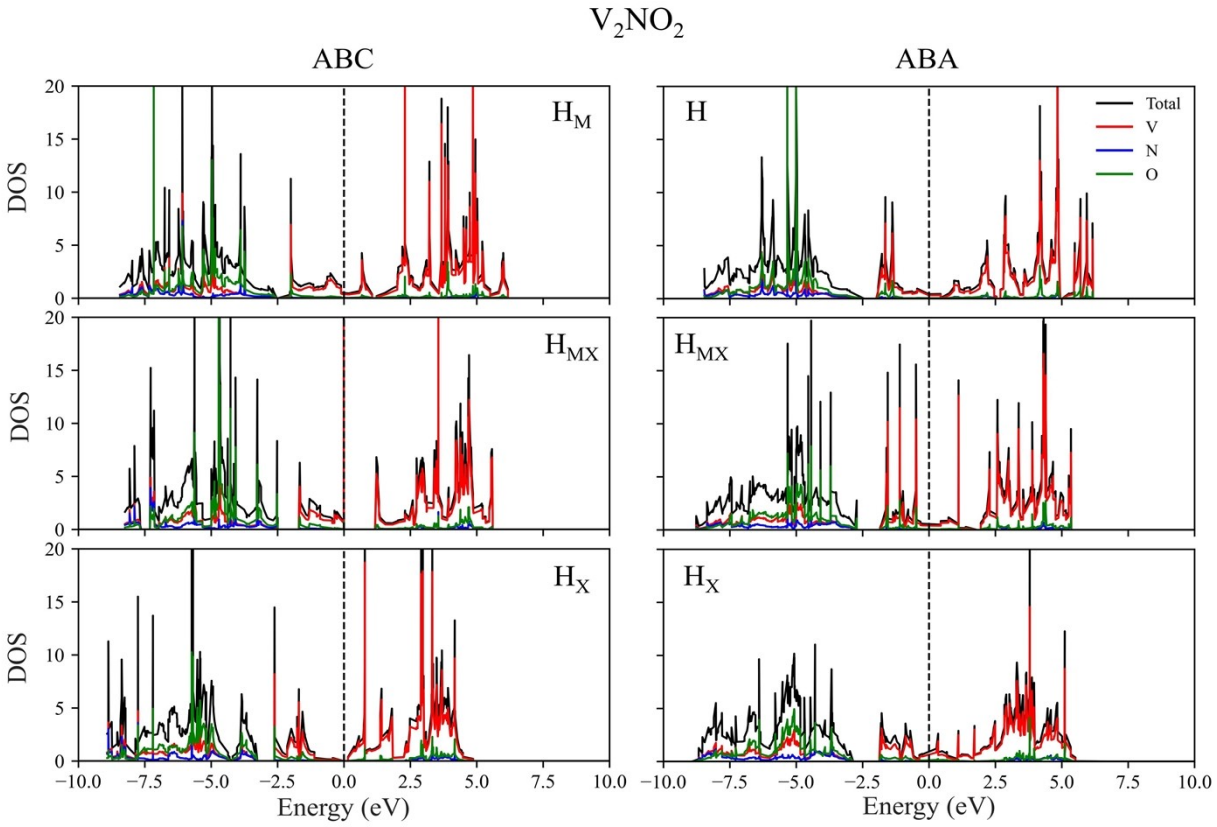
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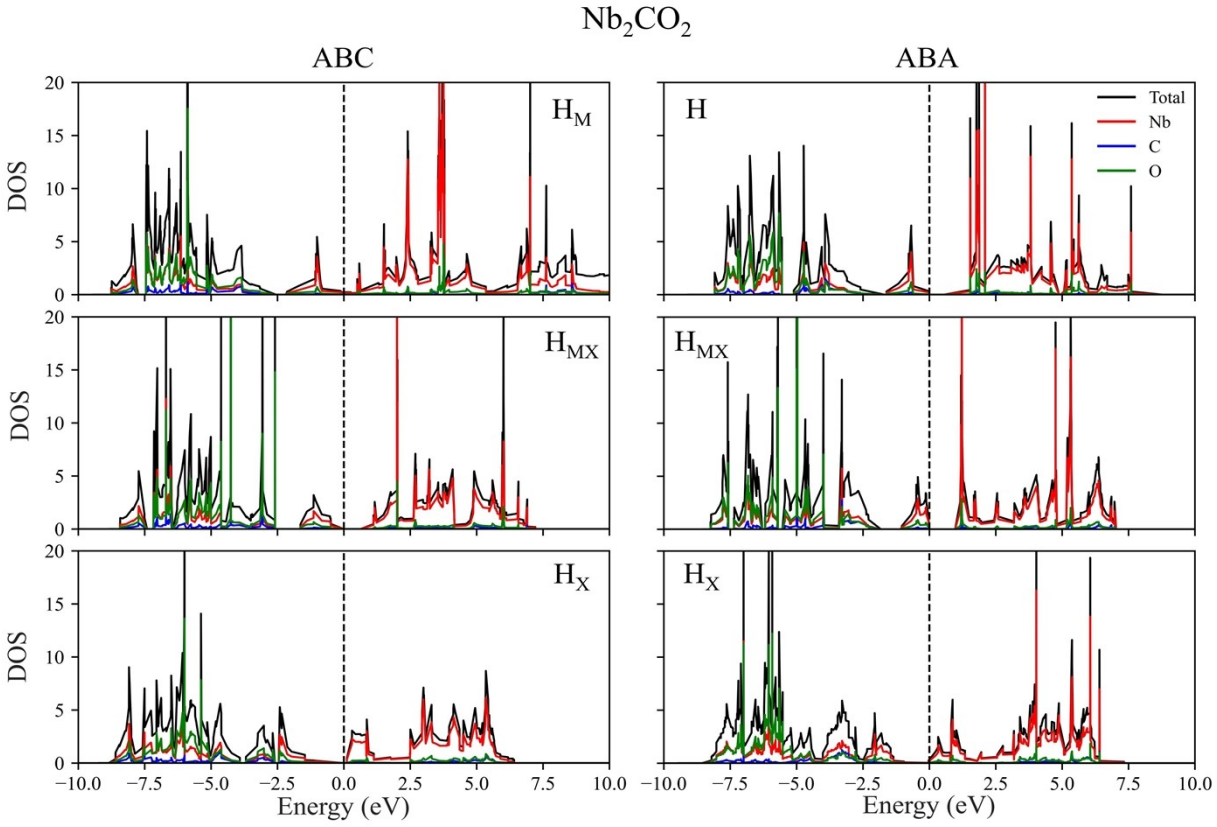
Energy (eV)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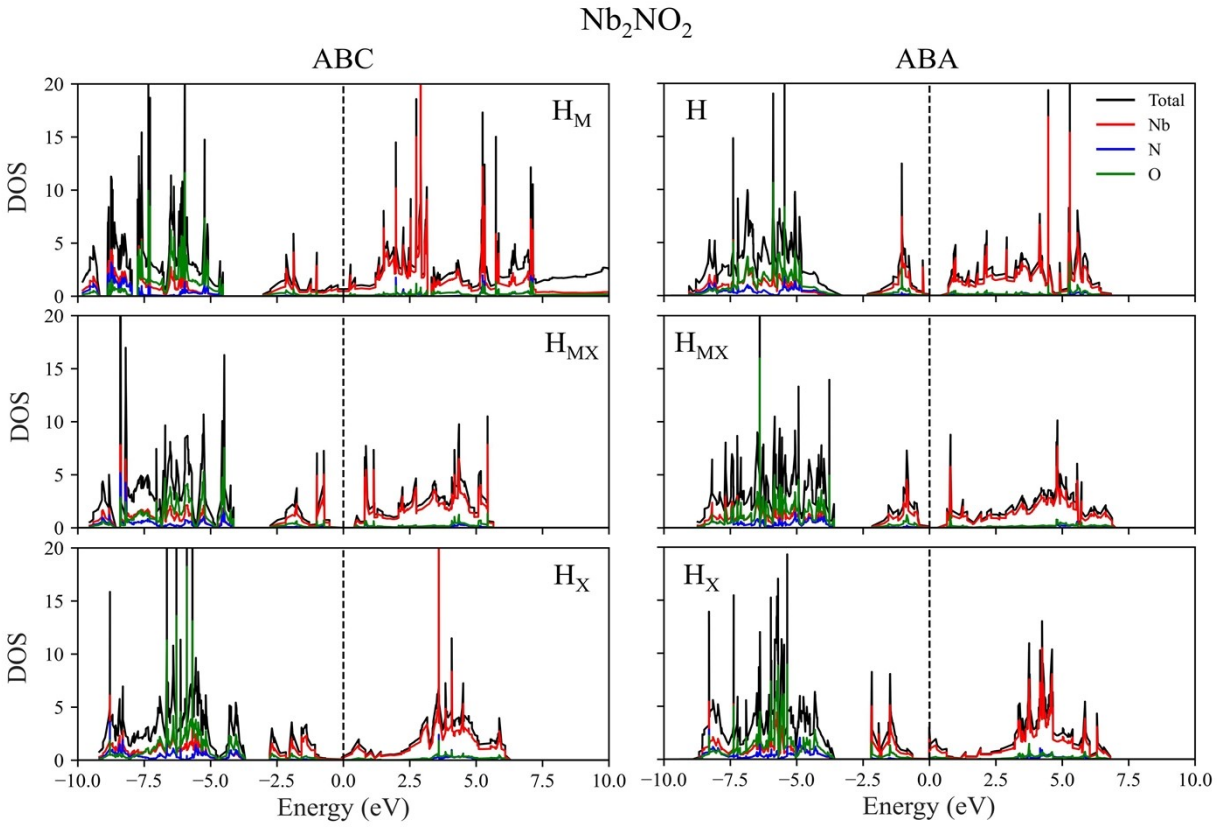
Energy (eV)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H_MX
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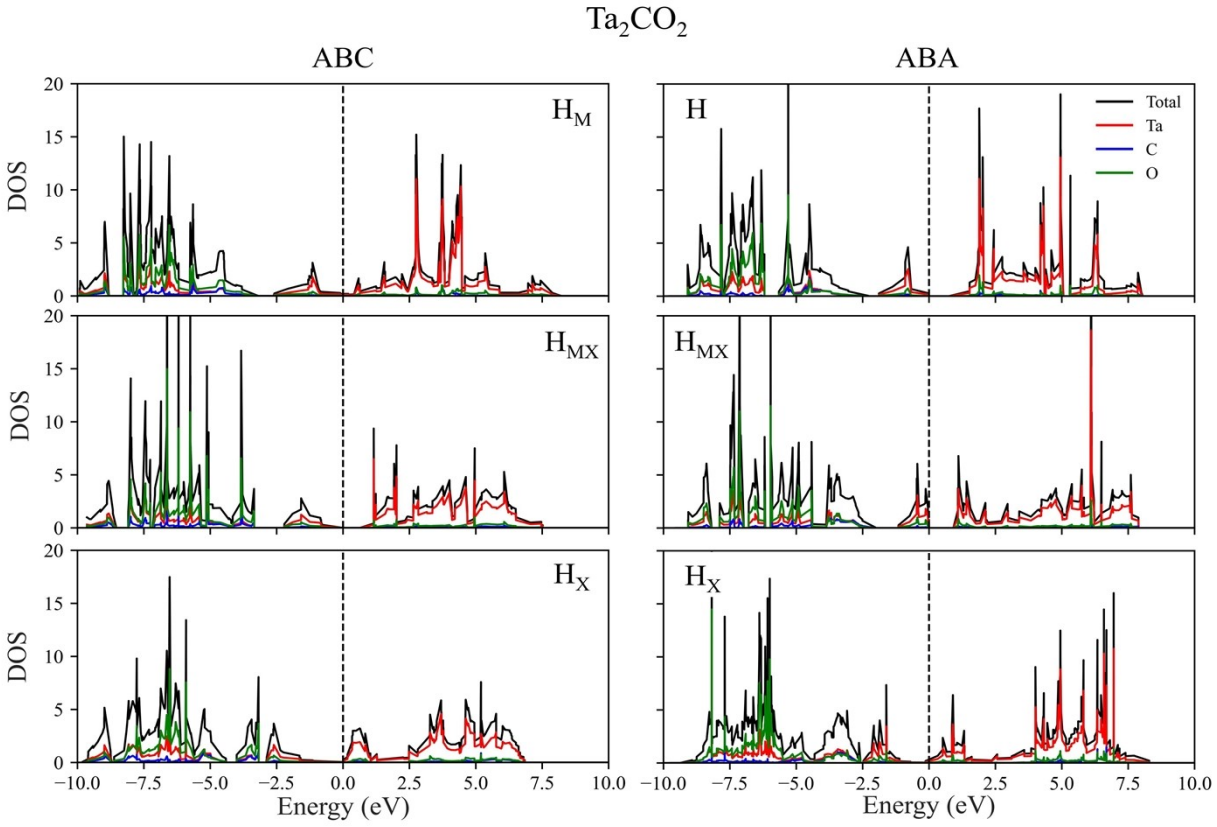
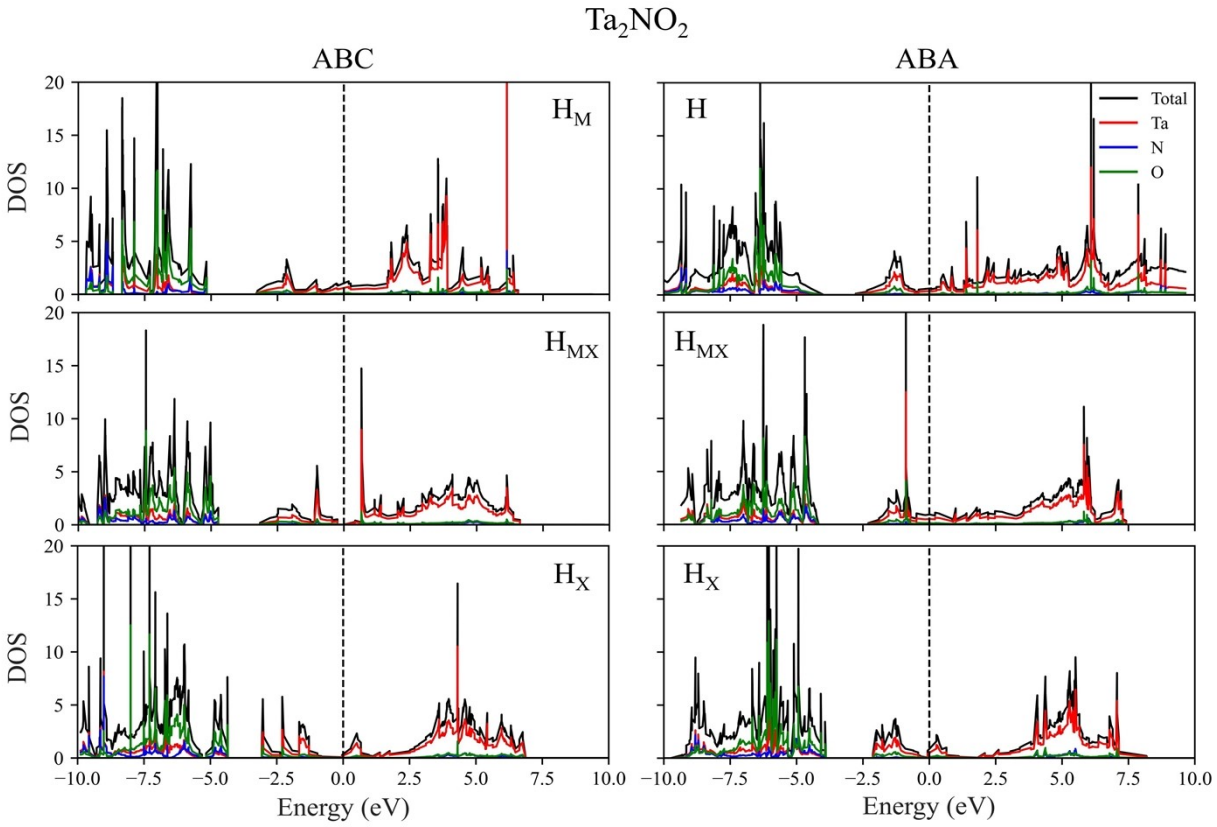
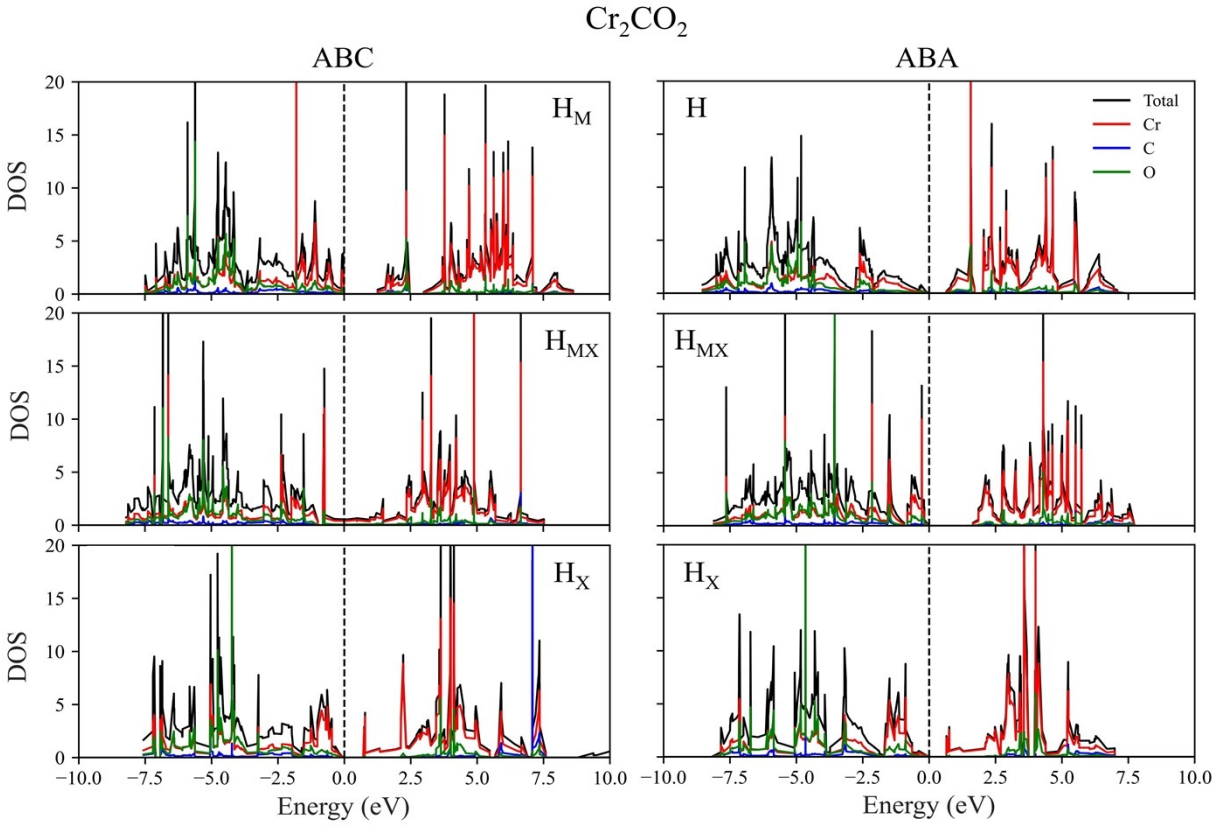
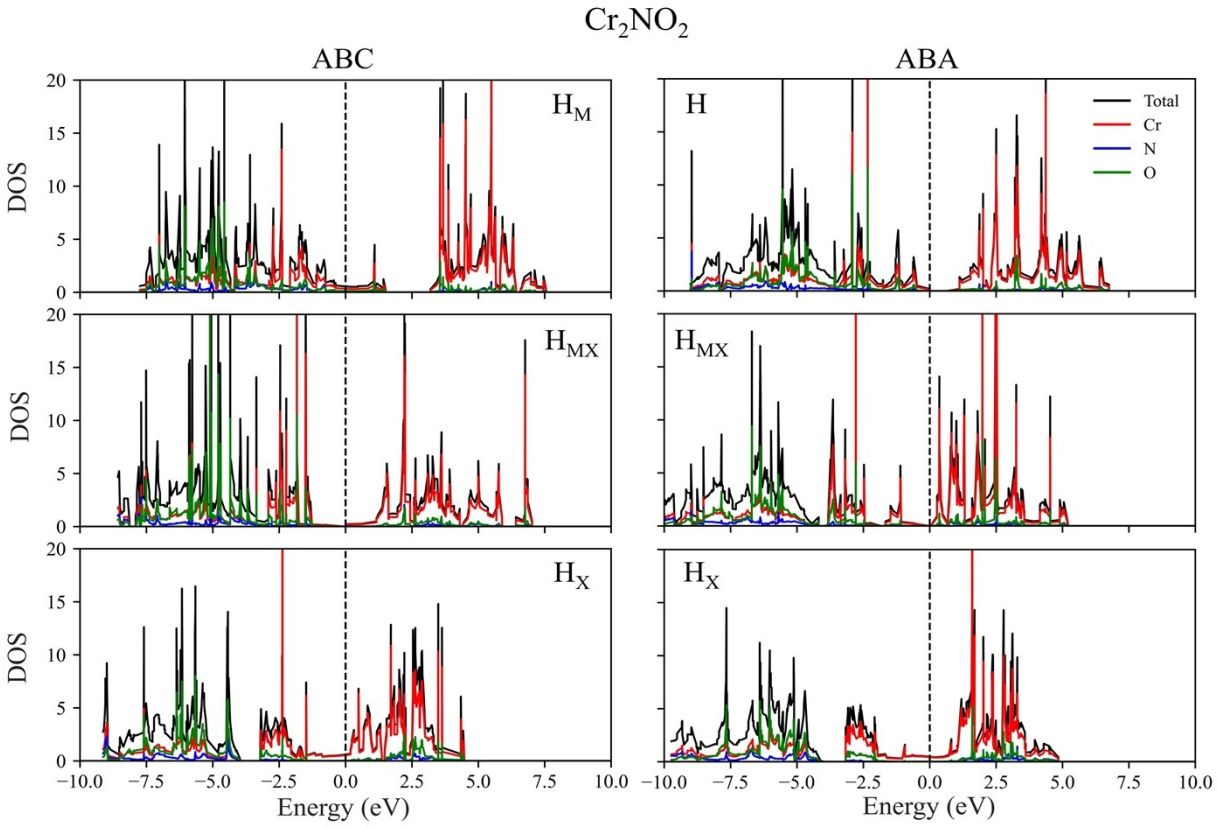
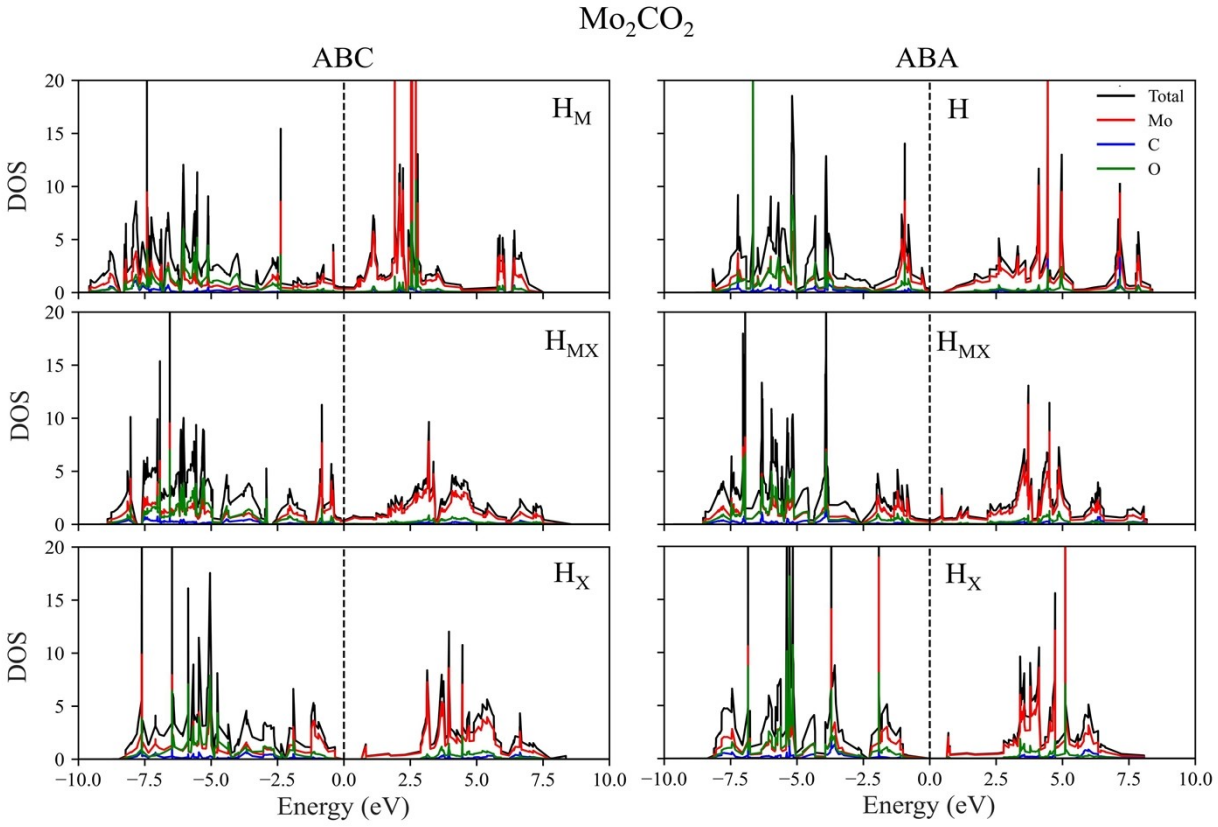
N
O
DOS
Energy (eV)

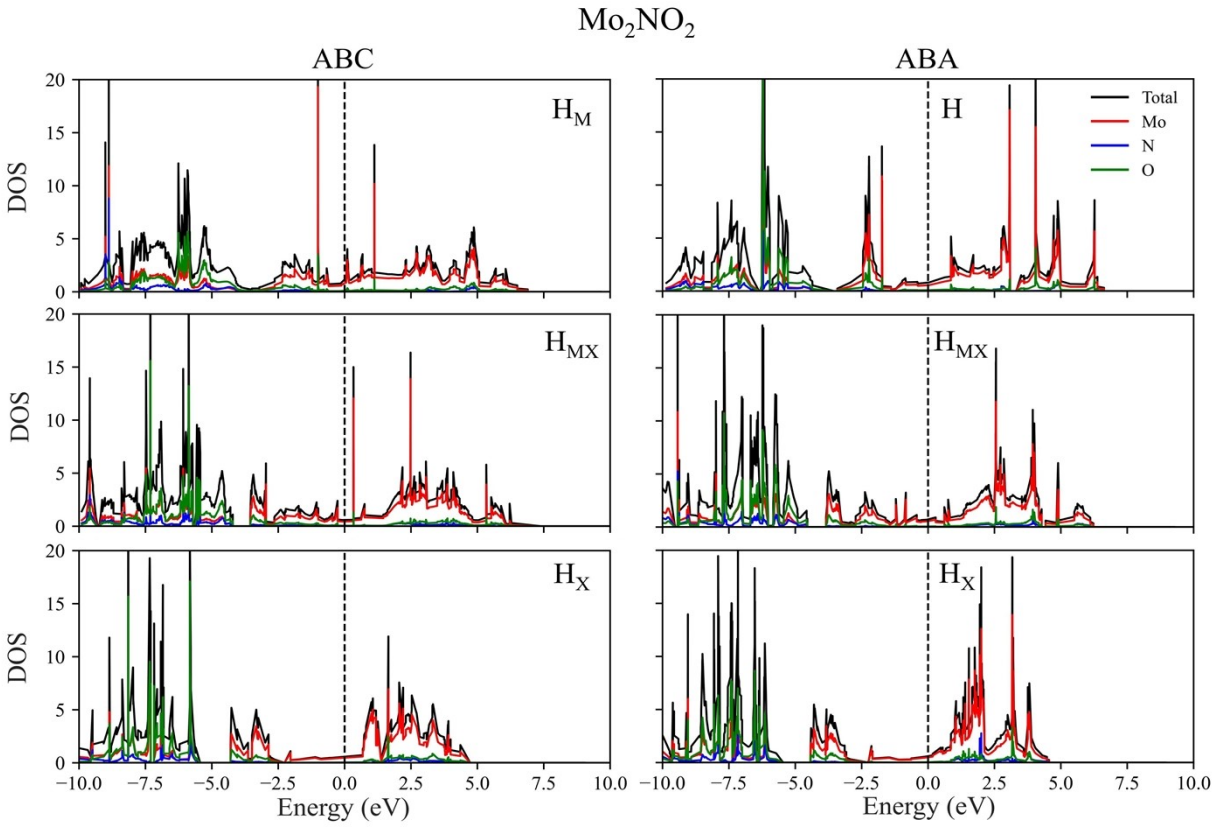

Ta2CO2
ABC
ABA
H_M
H_MX
H_X
H
Total
Ta
C
O
DOS
Energy (eV)

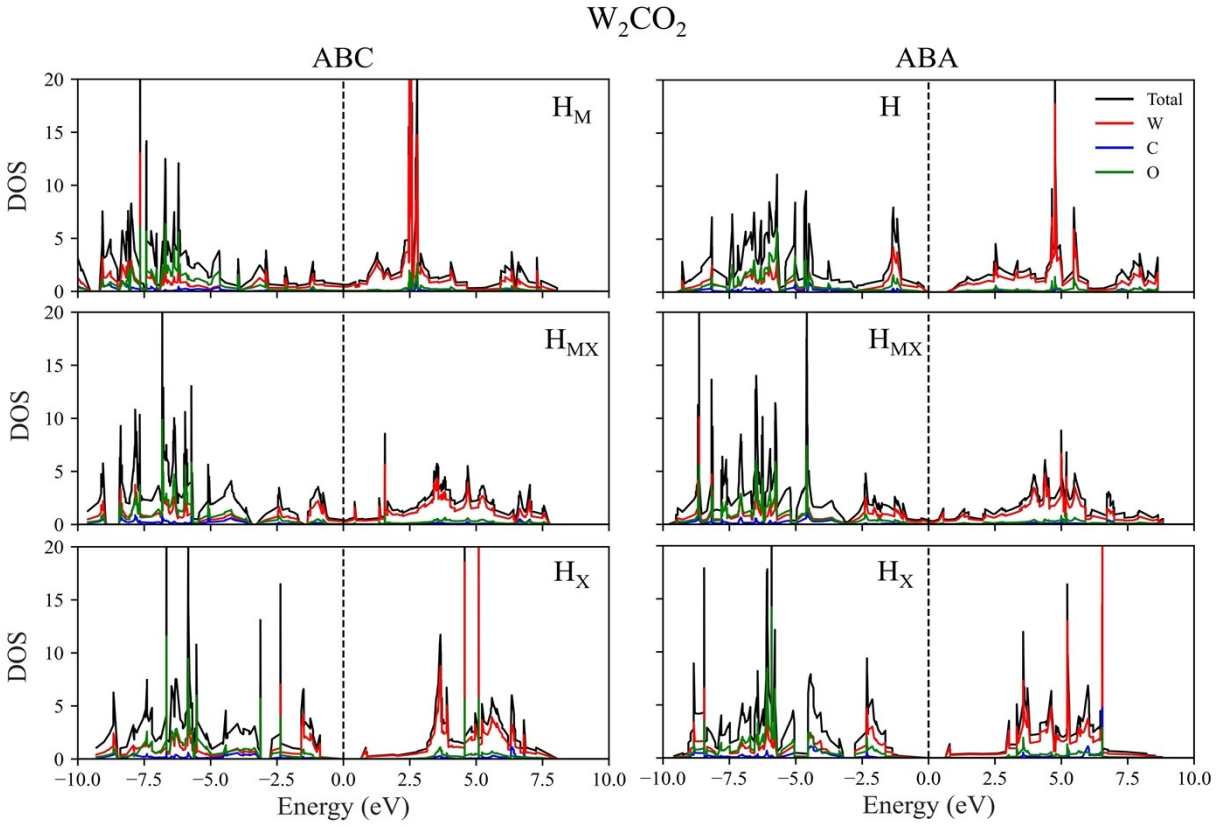

Ta2NO2
ABC
ABA
H_M
H_MX
H_X
H
Total
Ta
N
O
DOS
Energy (eV)


Cr2CO2
ABC
ABA
H_M
H
H_MX
H_X
Total
Cr
C
O
DOS
Energy (eV)


Cr2NO2
ABC
ABA
H_M
H
H_MX
H_X
Total
Cr
N
O
DOS
Energy (eV)


Mo2CO2
ABC
ABA
H_M
H
H_MX
H_X
Total
Mo
C
O
DOS
Energy (eV)


Mo2NO2
ABC
ABA
H_M
H
H_MX
H_X
Total
Mo
N
O
DOS
Energy (eV)


W2CO2
ABC
ABA
H_M
H
H_MX
H_X
Total
W
C
O
DOS
Energy (eV)

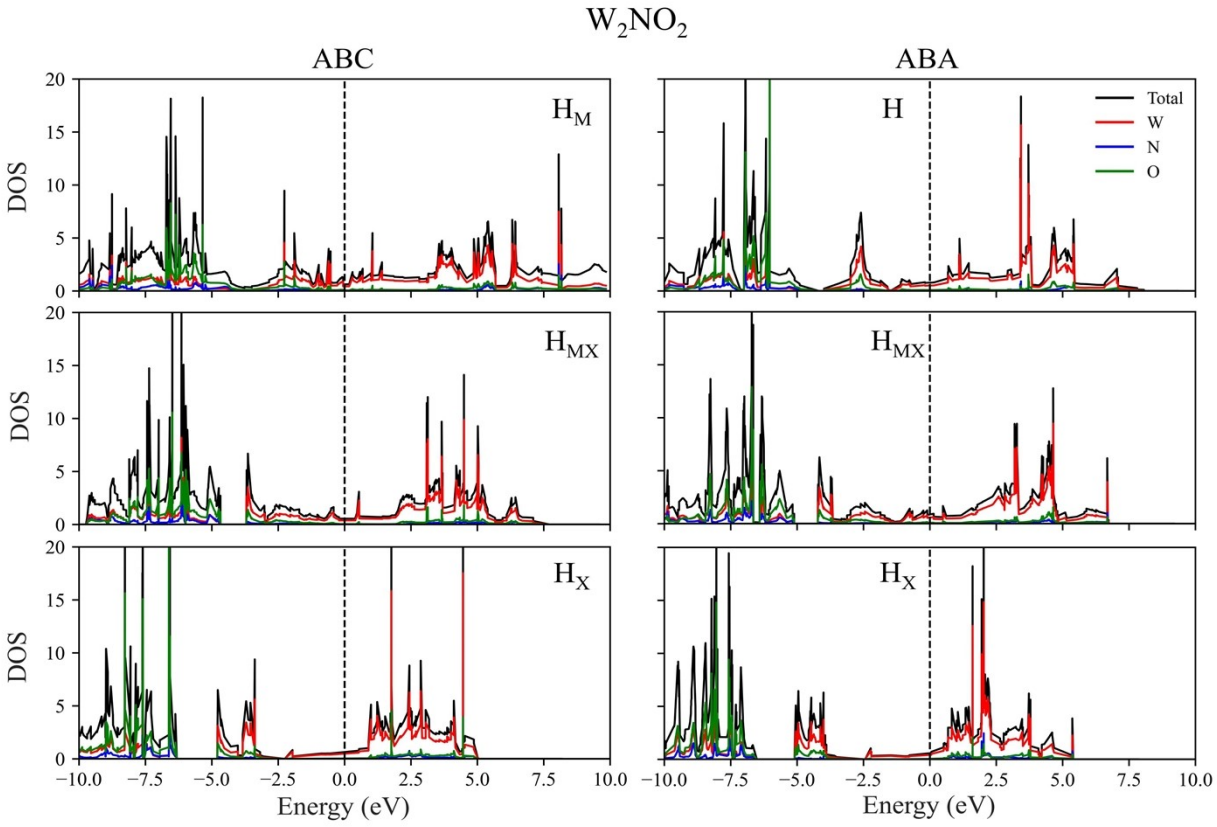

W2NO2
ABC
ABA
H_M
H
H_MX
H_X
Total
W
N
O
DOS
Energy (eV)

Fig. S5 Average electrostatic potential, V, in eV, as a function of *z* coordinate along the vacuum direction, in Å, for the Zr_2CO_2 ABC H_M system. The vacuum energy, V_v, is indicated as the red dashed line.

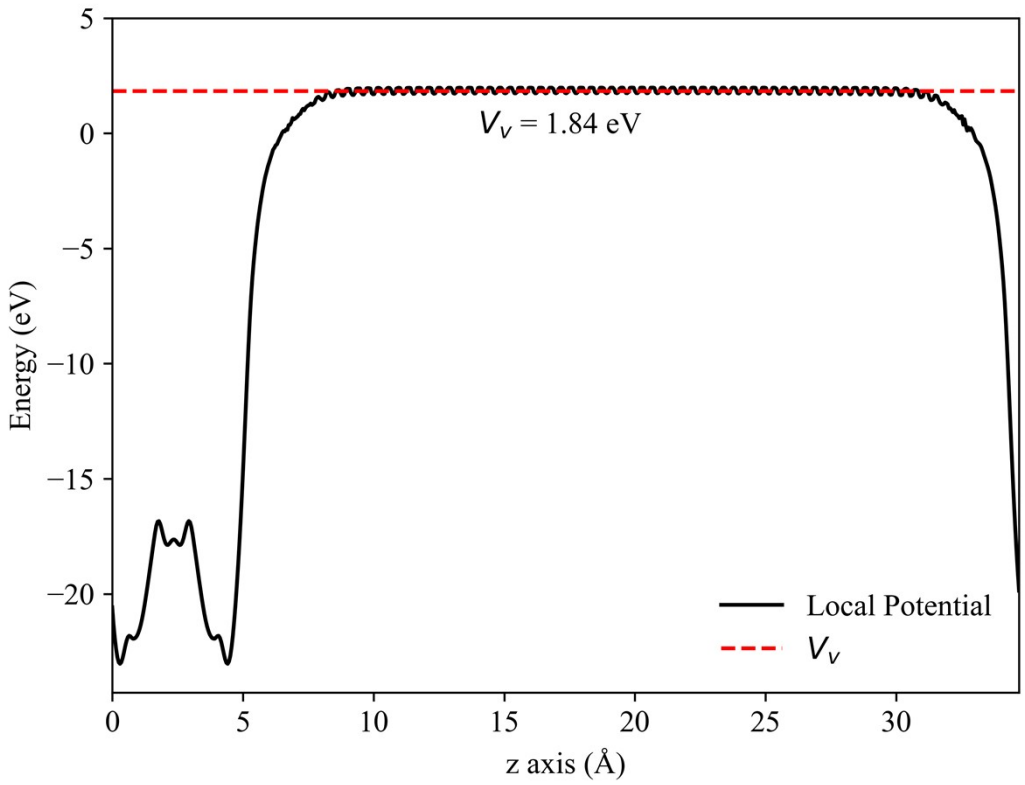


Fig. S6 Relation between the absolute surface dipole moment, *P*, and the workfunction, ϕ, for the Group III N-MXenes. On the right are present the colour coded linear regression equations.

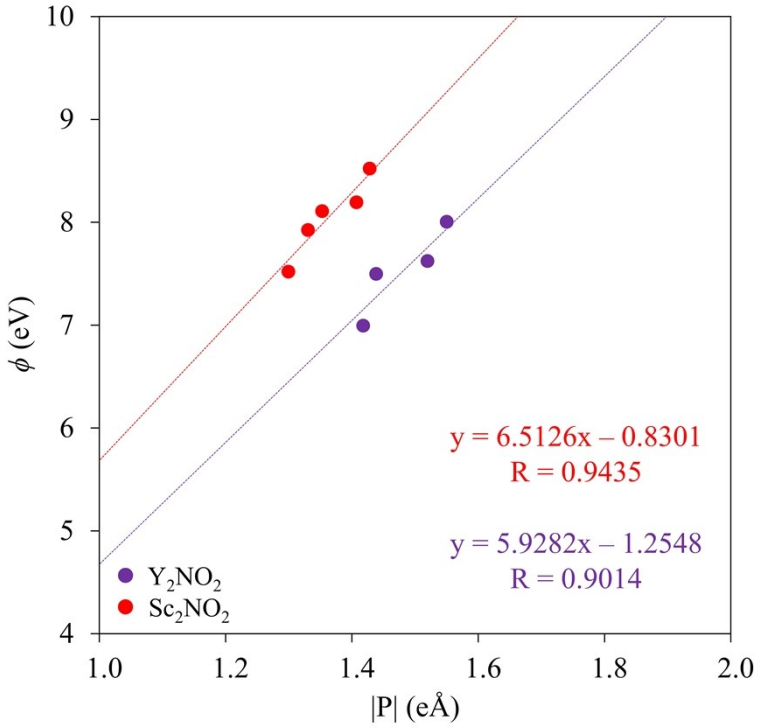


Fig. S7 Comparison of (a), (c) PBE and (b), (d) PBE0 bandstructures for Sc_2CO_2 and Y_2CO_2, respectively, computed on the most stable structure, ABC H_{MX}. Energy levels are referred to the VBM level.