Supplementary Information: A First-Principles Study of Multilayer $Ti_3C_2T_x$ MXene Model

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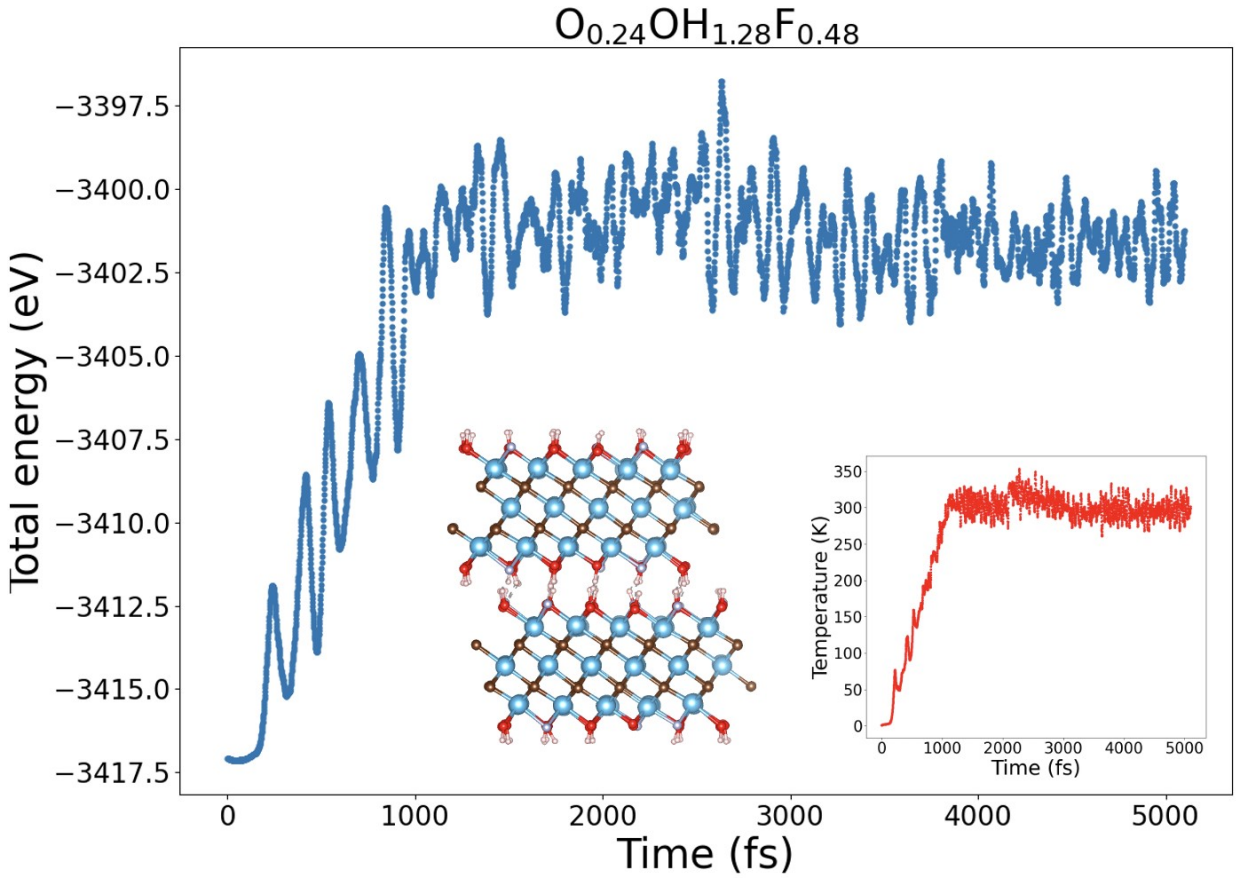

Figure S1. Thermal stability of the optimized $Ti_3C_2T_x$ (T_x = $O_{0.24}OH_{1.28}F_{0.48}$) multilayer structure at 300 K for 5 ps AIMD simulation. The inset shows the thermal equilibrated structure upon heating to 300 K.

Table S1. The total energy of multilayer $Ti_3C_2T_x$ with P-trigonal and P-octahedral stacking after full structural relaxation.

	Total energy (eV)	
T_x	P-trigonal	P-octahedral
F_2	-2963.65978	-2967.23103
O_2	-3225.48482*	-3225.45555
OH_2	-3562.73442	-3576.21684
H_2	-2781.17203*	-2779.38226
$O_{0.24}OH_{1.28}F_{0.48}$	-3392.74955	-3403.18012
$O_{0.24}OH_{0.64}F_{1.12}$	-3192.29390	-3203.63817

*The final optimized structure is P-octahedral stacking.

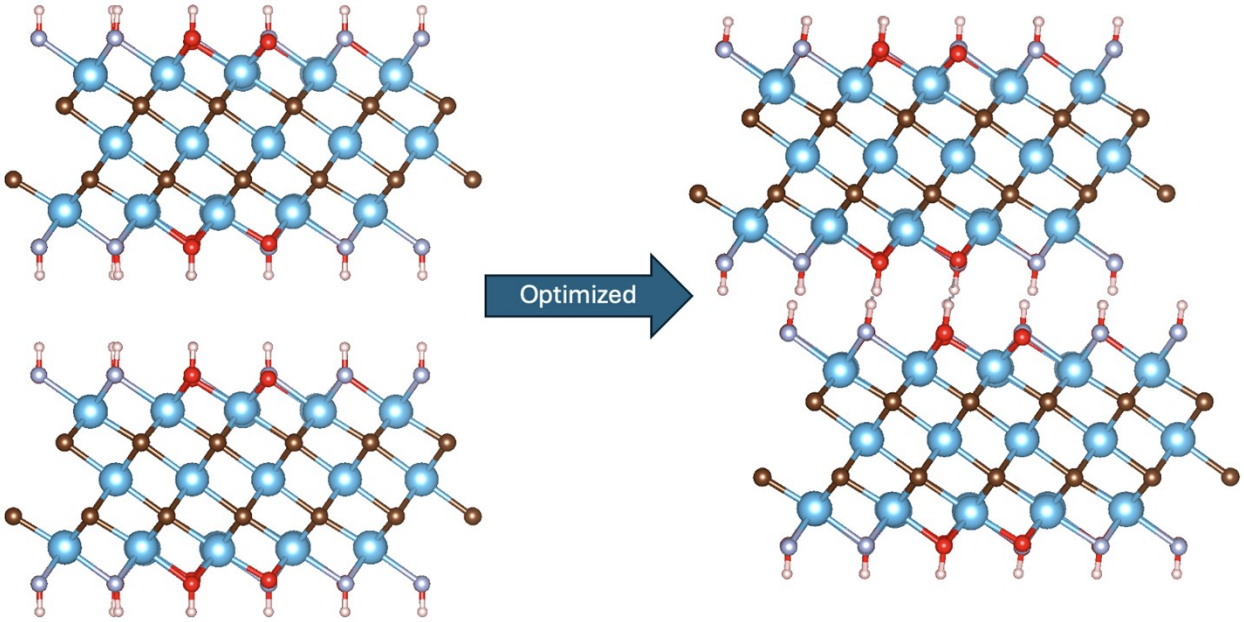

Figure S2. Initial and optimized structures of multilayer $Ti_3C_2T_x$. The initial configuration begins with P-trigonal stacking where the adjacent terminal groups face directly towards each other. Upon geometrical optimization, the final optimized structure resembles P-octahedral stacking.

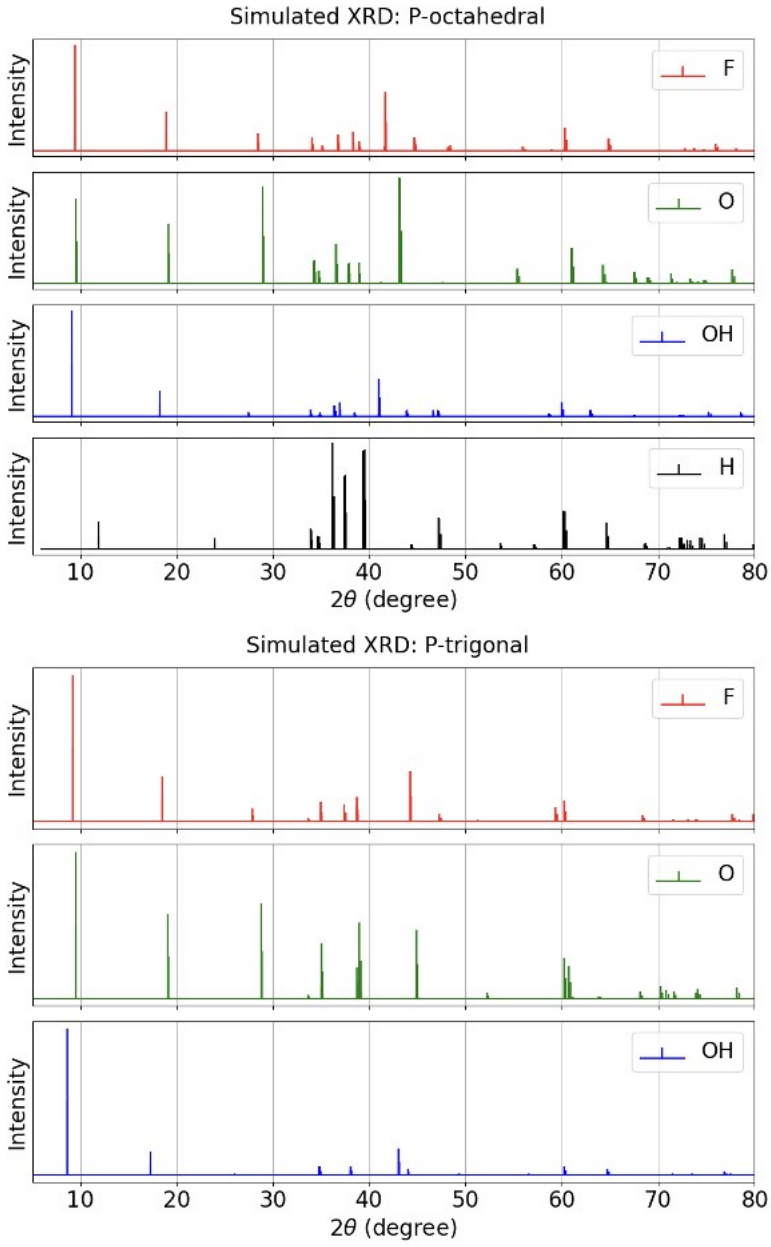

Figure S3. The simulated XRD of uniform F/O/OH/H terminated $Ti_3C_2T_x$ multilayers with P-octahedral and P-trigonal stacking.

Table S2. Calculated *d*-spacing of uniform O/OH/F/H and ternary/quaternary mixed O/OH/F/H-terminated $Ti_3C_2T_x$ multilayers.

T_x	*d*-spacing (Å)
O_2	9.24
OH_2	9.83
F_2	9.38
H_2	7.43
$O_{0.24}OH_{1.20}F_{0.48}H_{0.08}$	9.60
$O_{0.24}OH_{0.64}F_{0.48}H_{0.64}$	9.60
$O_{0.24}F_{0.48}H_{1.28}$	7.97

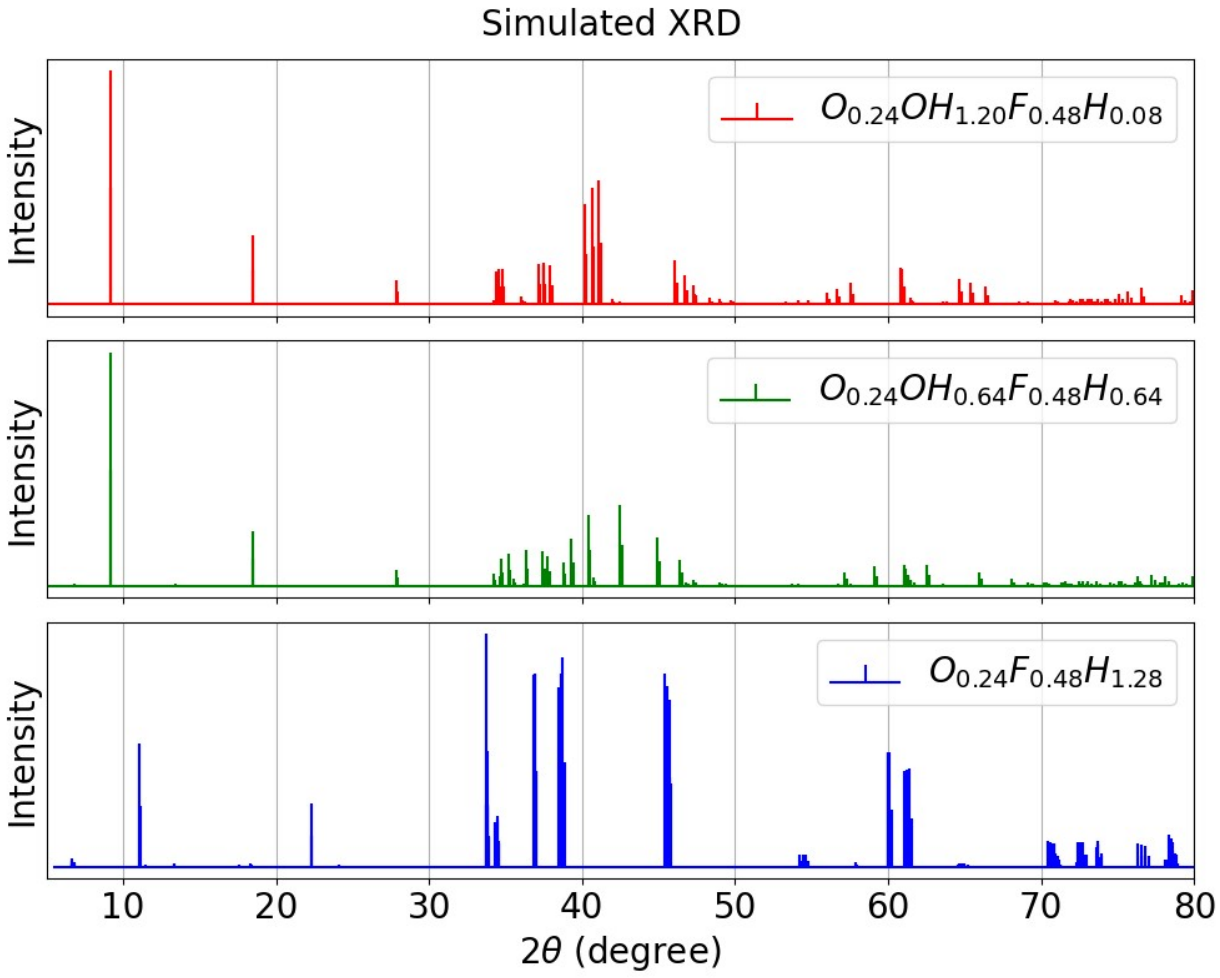

Figure S4. From the top to the bottom, the simulated XRD of quaternary/ternary mixed F/O/OH/H terminated $Ti_3C_2T_x$ multilayers with different stoichiometry etched with 5 wt. % HF.

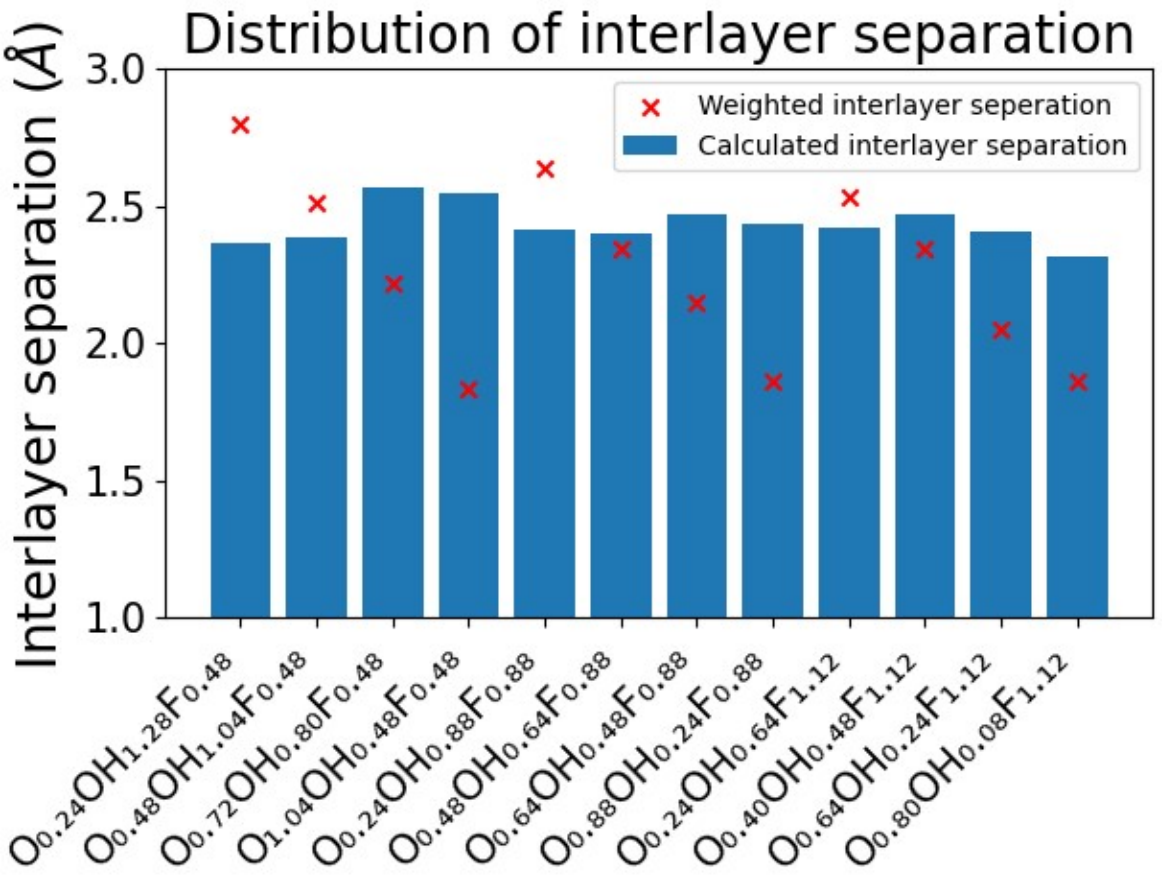

Figure S5. Distribution of interlayer separation with the fitting. The fitting function used the mean of the interlayer separation values of the uniform O-/OH-/F-terminated $Ti_3C_2T_x$ multilayer with P-trigonal and P-octahedral stacking. From the left to the right, the $Ti_3C_2T_x$ with different T_x stoichiometry is found by etching with 5, 10, and 48 wt. % HF.

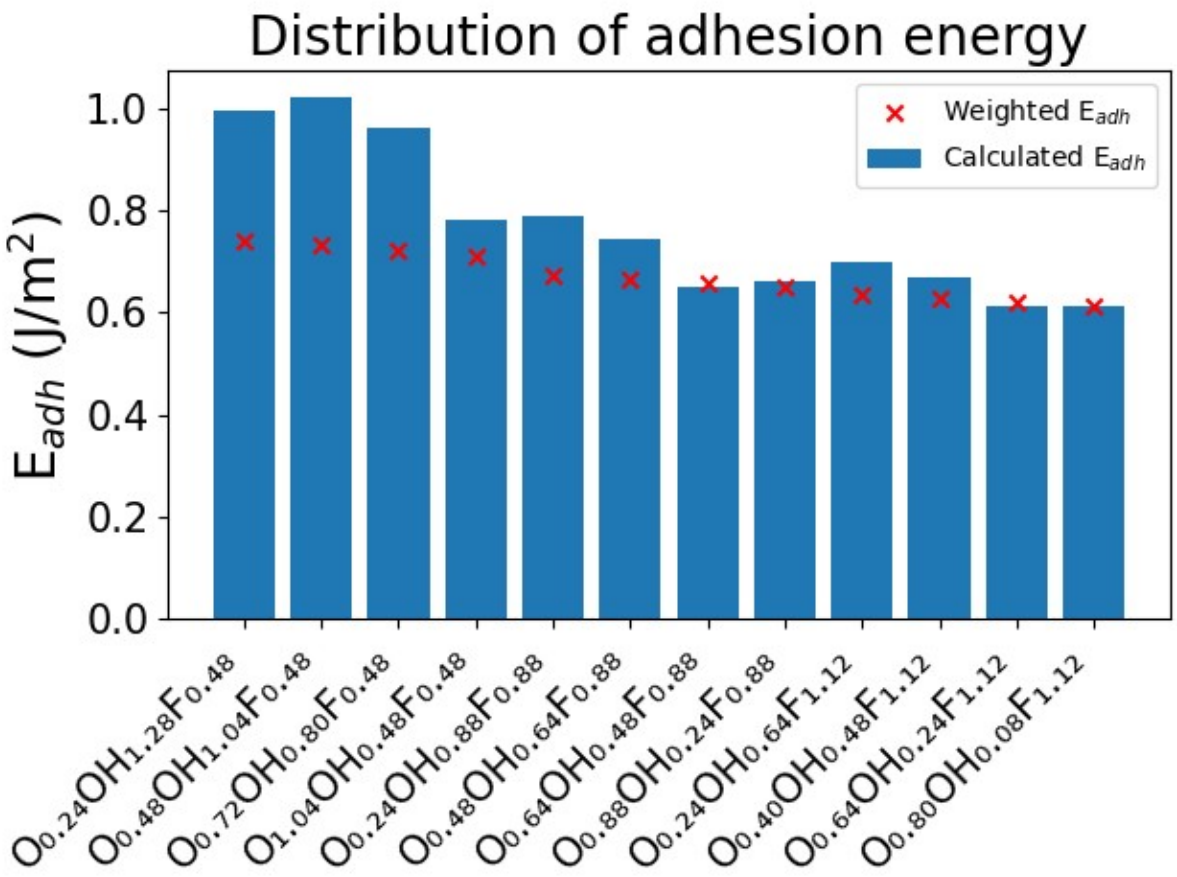

Figure S6. Distribution of adhesion energy with varying T_x stoichiometry. From the left to the right, the $Ti_3C_2T_x$ with different T_x stoichiometry is found by etching with 5, 10, and 48 wt. % HF.

The weighted interlayer separation is given as:

$$d_{weighted} = a \cdot \frac{\left(d_O^o + d_O^t\right)}{2} + b \cdot \frac{\left(d_{OH}^o + d_{OH}^t\right)}{2} + c \cdot \frac{\left(d_F^o + d_F^t\right)}{2} - b \cdot \frac{\left(d_{OH}^t - d_{OH}^o\right)}{2}$$

where d_x^o, d_x^t are the optimized interlayer separation of uniform terminated multilayer $Ti_3C_2T_x$ structures with x = O, OH, F, with P-octahedral and P-trigonal stacking respectively, and *a, b, c* are the O, OH, F percentage respectively.

The weighted adhesion energy is given as:

$$E_{adh}^{weighted} = a \cdot E_{adh}^{O} + b \cdot E_{adh}^{OH} + c \cdot E_{adh}^{F}$$

where E_{adh}^{x}, is the calculated adhesion energy of the uniform terminated multilayer $Ti_3C_2T_x$ structures with x = O, OH, F, *a, b, c* are the O, OH, F percentage respectively.

Table S3. Calculated adhesion energy of ternary and quaternary mixed H-terminated $Ti_3C_2T_x$.

T_x	E_{adh} (J/m^2)
$O_{0.24}OH_{1.20}F_{0.48}H_{0.08}$	0.95
$O_{0.24}OH_{0.64}F_{0.48}H_{0.64}$	0.79
$O_{0.24}F_{0.48}H_{1.28}$	1.09

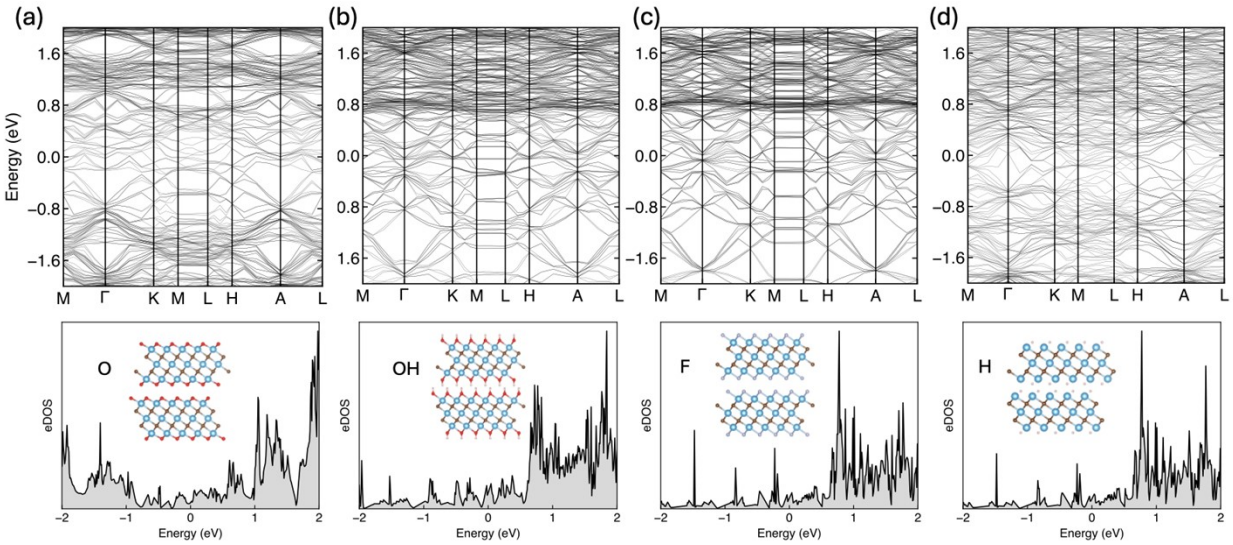

Figure S7. Electronic band structure and density of states of uniform O/OH/F/H-terminated multilayer $Ti_3C_2T_x$. All of the structures are found to be metallic.

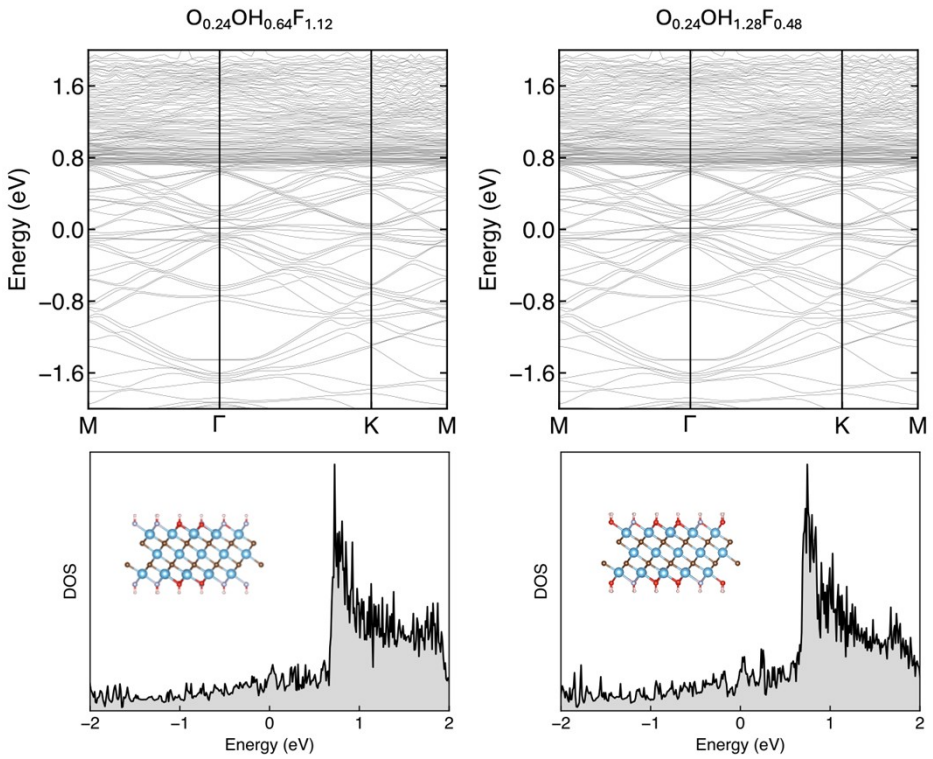

Figure S8. Electronic band structure and density of states of monolayer $Ti_3C_2T_x$ with T_x = $O_{0.24}OH_{0.64}F_{1.12}$ and $O_{0.24}OH_{1.28}F_{0.48}$, showing metallic characteristic.

Table S4. -ICOHP of the atomic pairs in different structures.

-ICOHP pairs	Pair distance (Å)	T_x/Structure	-ICOHP (eV)
F-F	2.85	F_2	0.003
O-O	2.9	O_2	0.02
O-H	2.26	OH_2	0.15
H-H	2.10	H_2	0.04
Ti-H	1.88-1.93	H_2	1.18-1.36
	1.87	TiH_2 crystal	1.21
	1.9	$T_x = O_{0.24}F_{0.48}H_{1.28}$	1.41
Ti-O	1.95-2.0	TiO_2 crystal	3.18-3.60
	1.97	$T_x = O_{0.24}F_{0.48}H_{1.28}$	3.4
Ti-F	2.0	$T_x = O_{0.24}F_{0.48}H_{1.28}$	2.4
	1.97	TiF_3 crystal	3.0
$O(H_2O)$-H(OH)	1.5-1.8	$Ti_3C_2T_x \cdot H_2O$	0.5-2.5
H(OH)-F	1.6	$Ti_3C_2T_x \cdot H_2O$	1.0-1.5