

Electronic Supporting Information:

**MXene's Surface Functionalization Patterns and Their Impacts on Magnetism**

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To ascertain the stability of bare and functionalized MXenes we calculated cohesive energies by the relation

$$E_{\text{coh}} = [E_{\text{MX}} - (n_{\text{Ti}}E_{\text{Ti}} + n_{\text{C}}E_{\text{C}} + n_{\text{T}}E_{\text{T}})] / (n_{\text{Ti}} + n_{\text{C}} + n_{\text{T}}), \quad (1)$$

where  $E_{\text{MX}}$  denotes the total energy of supercell of  $\text{Ti}_2\text{C} - n \cdot \text{T}$  monolayer MXene,  $E_{\text{Ti}}$ ,  $E_{\text{C}}$ , and  $E_{\text{T}}$  are total energies of isolated single atoms T (T = O, F or O+H) obtained from a supercell, respectively. The alphabet  $n$  represents the number of Ti, C, and T atoms in the  $\text{Ti}_2\text{C} - n \cdot \text{T}$  MXene.

Table S1: Cohesive energies per atom ( $E_{\text{coh}}$  in eV), total magnetic moments ( $m$  in  $\mu_B$ ), bonding distance between Ti and Ti ( $d_{\text{Ti-Ti}}$  in Å), C and Ti ( $d_{\text{C-Ti}}$  in Å), bonding distance between Ti and terminal atoms ( $d_{\text{Ti-T}}$  in Å) and Bader charge of Ti, O atoms and OH group in e for  $\text{Ti}_2\text{CT}_2$  MXenes (T = O, F, and OH).

	$E_{\text{coh}}$	$m$	$d_{\text{Ti-Ti}}$	$d_{\text{C-Ti}}$	$d_{\text{Ti-T}}$	$Q_{\text{Ti}}$	$Q_{\text{C}}$	$Q_{\text{T}}$
$\text{Ti}_2\text{CO}_2$	-5.91	0.00	3.18	2.22	2.00	2.11	-1.85	-1.19
$\text{Ti}_2\text{CF}_2$	-5.21	0.00	2.91	2.12	2.20	1.85	-2.11	-0.79
$\text{Ti}_2\text{C}(\text{OH})_2$	-4.73	0.00	2.93	2.13	2.20	1.85	-2.11	-0.80

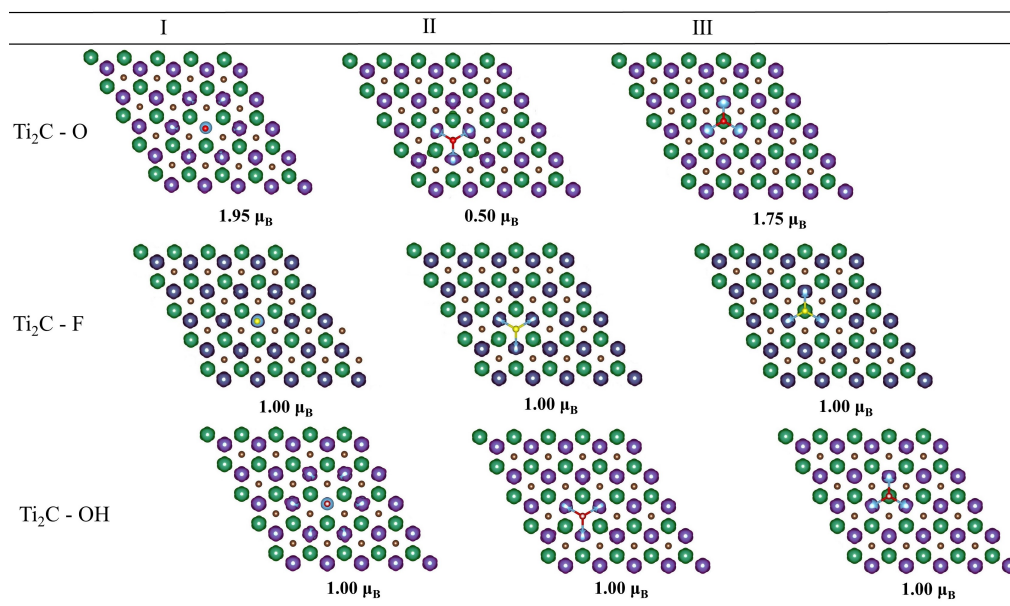


Figure S1: Spin density distribution of Ti<sub>2</sub>C- 1T MXenes, where T represents O, F, and/or OH. Titanium, carbon, oxygen, fluorine, and hydrogen atoms are represented in blue, brown, red, yellow, and white. The isosurface values are 0.02 e/Å<sup>3</sup> (green and purple colors represent positive and negative spin densities, respectively).

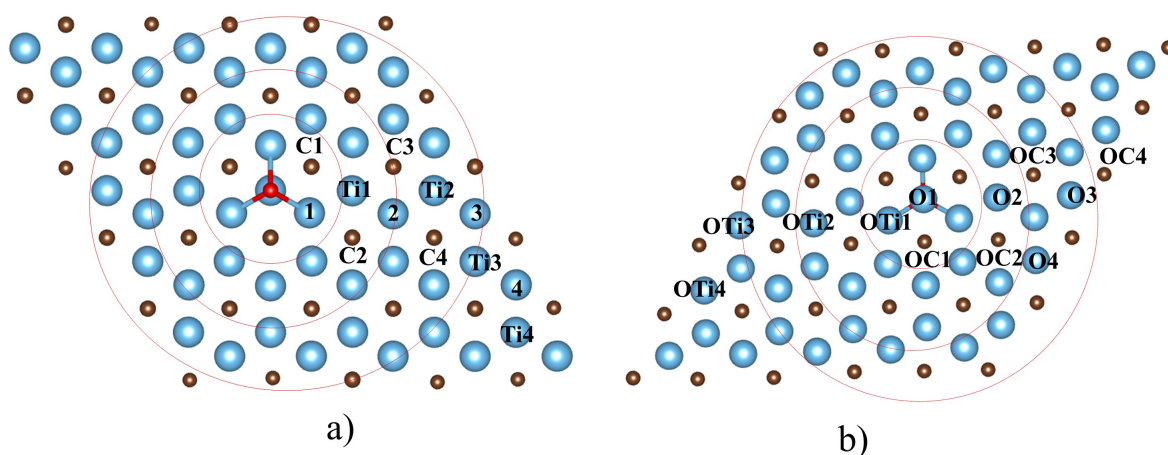


Figure S2: Structure of the  $\text{Ti}_2\text{C} - 1\text{T}$  ( $\text{T} = \text{O}$  and  $\text{F}$ ) MXenes in a  $5 \times 5$  supercell with the position marking for the addition of the second atom in the case of structure III. Where the number expresses the position of the added atom relative to the first atom. The symbols represent the position of the second atom before optimization: only the number represents position I, label C represents position II, label Ti represents position III, and O represents the atoms on the opposite layer of titans with respect to the first atom. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red. The notation is also the same for atoms of fluorine.

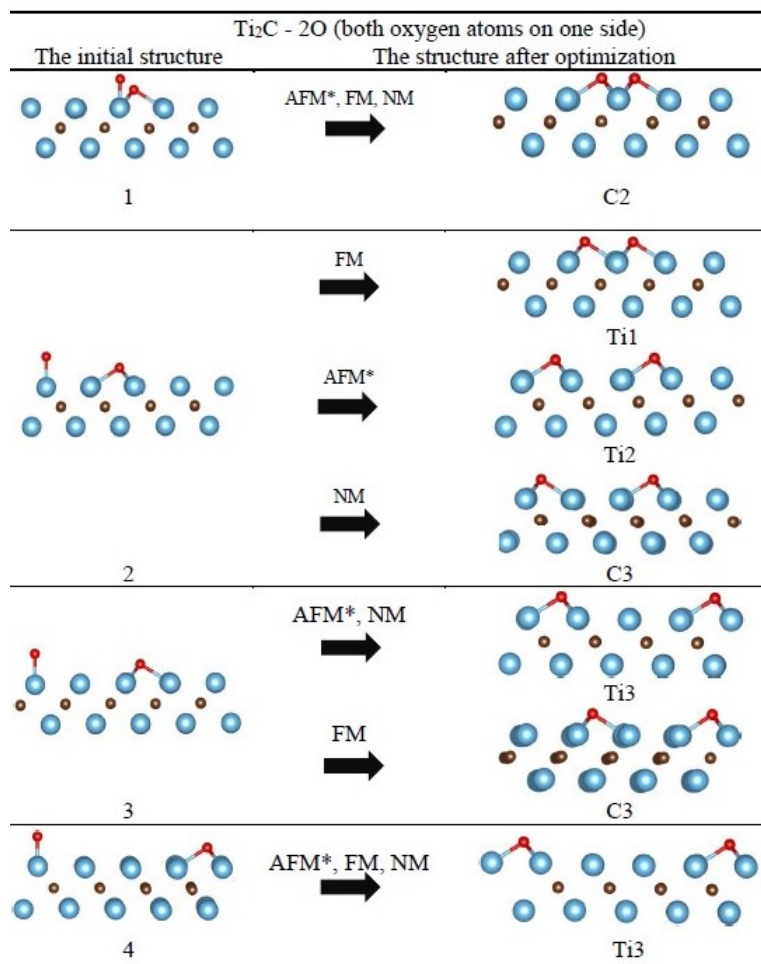


Figure S3: Structure of the MXene Ti<sub>2</sub>C - 2O in a 5 × 5 supercell with the position marking for the addition of the second atom to position I (marking according to picture S2). Where the number expresses the position of the added atom relative to the first atom. The labels on the right represent the position of the second atom after optimization (Ti represents position III and C represents position II), and the magnetic states shown in parentheses represent the initial magnetic states. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red.

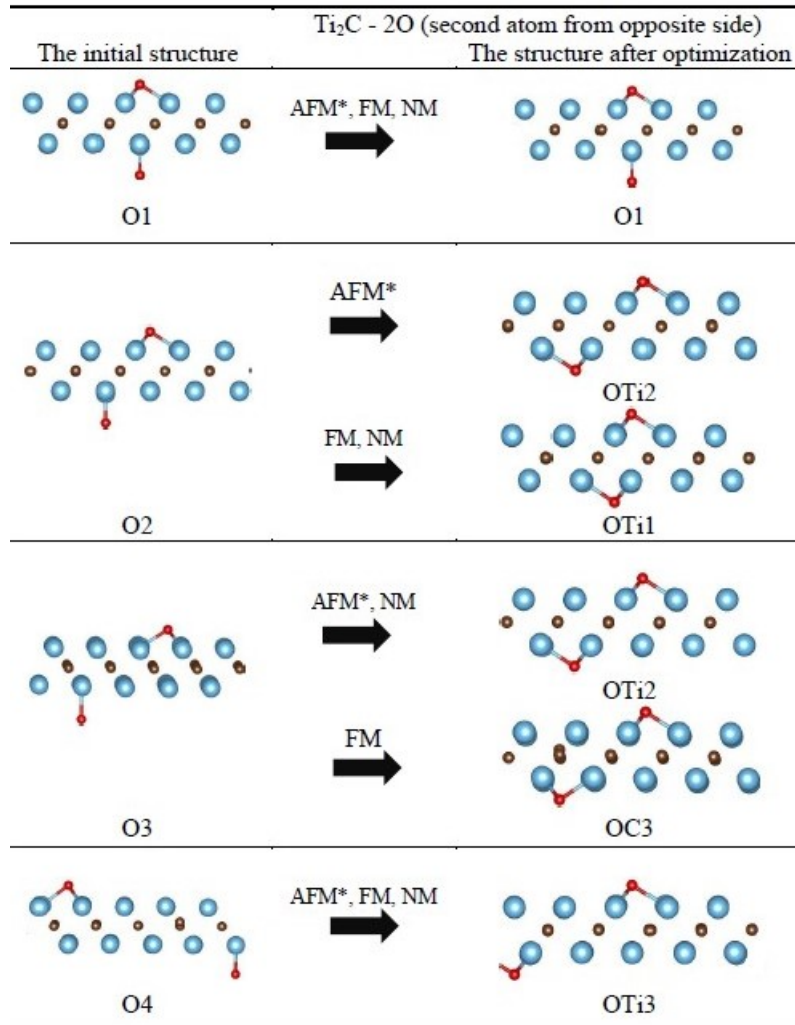


Figure S4: Structure of the MXene  $Ti_2C - 2O$  in a  $5 \times 5$  supercell with the position marking for the addition of the second atom to the opposite position I (marking according to picture S2). Where label O represents the addition of an atom to the opposite layer of Ti atoms and the number represents the position of the added atom relative to the first atom. The labels on the right represent the position of the second atom after optimization (Ti represents position III and C represents position II), and the magnetic states shown in parentheses represent the initial magnetic states. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red.

Table S2: Magnetic states (NM = nonmagnetic, FM = ferromagnetic and AFM = antiferromagnetic), relative energies ( $\Delta E$  in eV/supercell  $5 \times 5$ ), adsorption energy ( $E_{Ad}$  in eV/atom) relative energies ( $\Delta E$  in eV/supercell  $5 \times 5$ ), total magnetic moments in supercell ( $m$  in  $\mu_B$ ) of the  $Ti_2C - 2O$  MXenes (marking according to picture S2). The most stable geometry is highlighted in bold and the energy diagram for the ground states (AFM\*) for the adsorption energies is plotted in Figure 2 in the main text.

	$\Delta E$			$E_{Ad}$			$m$	
	AFM*	FM	NM	AFM*	FM	NM	AFM*	FM
1	0.50	1.68	6.79	-7.955	-6.777	-1.669	3.50	47.00
2	0.12	1.09	6.60	-8.337	-7.371	-1.855	3.90	47.50
3	0.14	1.58	6.22	-8.317	-6.878	-2.237	3.70	47.50
4	0.15	1.00	6.22	-8.308	-7.454	-2.236	3.00	47.00
<b>Ti1</b>	0.01	1.09	6.39	<b>-8.448</b>	-7.371	-2.069	4.00	47.50
Ti2	0.13	0.99	6.25	-8.328	-7.469	-2.206	2.50	47.50
Ti3	0.15	1.15	6.22	-8.307	-7.303	-2.237	2.50	47.50
C1	1.60	2.75	8.02	-6.857	-5.707	-0.434	2.50	46.10
C2	0.50	1.64	6.79	-7.955	-6.812	-1.669	2.50	47.00
C3	0.53	1.58	6.60	-7.923	-6.878	-1.855	3.50	47.02
C4	0.57	1.36	6.57	-7.887	-7.093	-1.882	3.00	47.00
O	2.31	3.51	8.70	-6.144	-4.951	0.241	-0.50	46.00
O2	0.14	1.03	6.09	-8.314	-7.430	-2.370	0.00	47.00
O3	0.11	1.58	6.61	-8.344	-6.878	-1.843	0.00	47.00
O4	0.15	1.01	6.25	-8.308	-7.444	-2.208	0.00	47.50
<b>OTi1</b>	<b>0.00</b>	1.03	6.08	<b>-8.456</b>	-7.430	-2.372	0.00	47.00
OTi2	0.11	1.05	6.23	-8.347	-7.411	-2.225	0.00	47.00
OTi3	0.11	1.02	6.22	-8.344	-7.433	-2.237	0.00	47.50
OTi4	0.13	1.18	6.33	-8.329	-7.278	-2.123	0.00	47.50
OC1	0.46	1.65	6.66	-7.996	-6.806	-1.791	1.20	46.12
OC2	0.46	1.84	6.61	-8.000	-6.614	-1.843	1.03	47.22
OC3	0.52	1.58	6.61	-7.937	-6.872	-1.849	1.46	47.12
OC4	0.51	1.54	6.64	-7.944	-6.913	-1.814	1.46	48.16

\*the label represents the initial magnetic state before optimization

Table S3: Magnetic states (NM = nonmagnetic, FM = ferromagnetic and AFM = antiferromagnetic), relative energies ( $\Delta E$  in eV/supercell  $5 \times 5$ ), adsorption energy ( $E_{Ad}$  in eV/atom) relative energies ( $\Delta E$  in eV/supercell  $5 \times 5$ ), total magnetic moments in supercell ( $m$  in  $\mu_B$ ) of the  $Ti_2C$  - 2F MXenes (marking according to picture S2). The most stable geometry is highlighted in bold and the energy diagram for the ground states (AFM\*) for the adsorption energies is plotted in Figure 2 in the main text.

	$\Delta E$			$E_{Ad}$			$m$	
	AFM	FM	NM	AFM	FM	NM	AFM	FM
1	0.29	1.63	6.92	-6.166	-4.821	0.466	2.00	46.50
2	0.29	1.21	6.55	-6.166	-5.238	0.101	2.00	48.00
3	0.06	1.21	6.79	-6.397	-5.238	0.340	2.00	48.00
4	0.06	2.15	6.57	-6.397	-4.307	0.118	2.00	48.00
<b>Ti1</b>	<b>0.00</b>	1.18	6.48	<b>-6.452</b>	-5.269	0.029	2.00	46.50
Ti2	0.06	1.21	6.48	-6.396	-5.238	0.026	2.00	46.50
Ti3	0.06	1.21	6.46	-6.397	-5.238	0.003	2.00	46.50
C1	0.58	2.07	7.15	-5.868	-4.383	0.700	2.00	47.00
C2	0.29	1.63	6.92	-6.166	-4.820	0.466	2.00	46.50
C3	0.66	1.57	6.80	-5.797	-4.883	0.344	6.00	47.00
C4	0.23	1.56	6.80	-6.221	-4.888	0.351	2.00	47.00
O	1.12	2.21	7.49	-5.335	-4.241	1.033	1.50	47.50
O2	0.25	2.35	6.84	-6.198	-4.105	0.386	0.00	52.00
O3	0.24	2.15	6.82	-6.211	-4.304	0.371	0.00	48.00
O4	0.23	2.15	6.50	-6.222	-4.304	0.046	0.00	48.00
<b>OTi1</b>	0.06	1.25	6.48	<b>-6.392</b>	-5.201	0.028	0.00	46.50
OTi2	0.05	1.23	6.46	-6.401	-5.225	0.006	0.00	46.50
OTi3	0.06	1.24	6.48	-6.393	-5.209	0.023	0.00	46.50
OTi4	0.05	1.24	6.50	-6.398	-5.212	0.046	0.00	47.00
OC1	0.23	1.56	6.80	-6.218	-4.889	0.346	0.00	47.00
OC2	0.24	1.57	6.82	-6.212	-4.877	0.370	0.00	47.00
OC3	0.23	1.56	6.81	-6.225	-4.890	0.355	0.00	47.00
OC4	0.22	1.73	6.80	-6.231	-4.726	0.346	0.00	46.58

\*the label represents the initial magnetic state before optimization

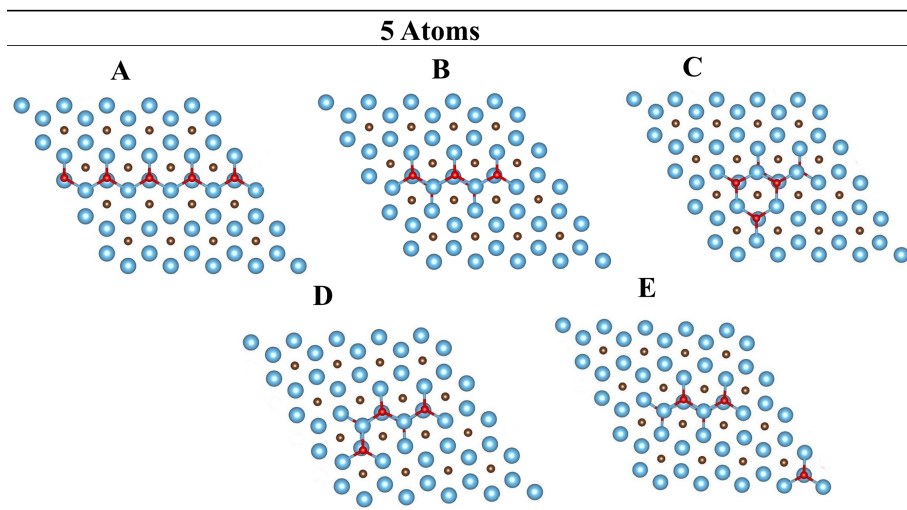


Figure S5: Optimized structures of  $Ti_2C$  after adsorption of five oxygen atoms for various adsorption patterns. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red, respectively.

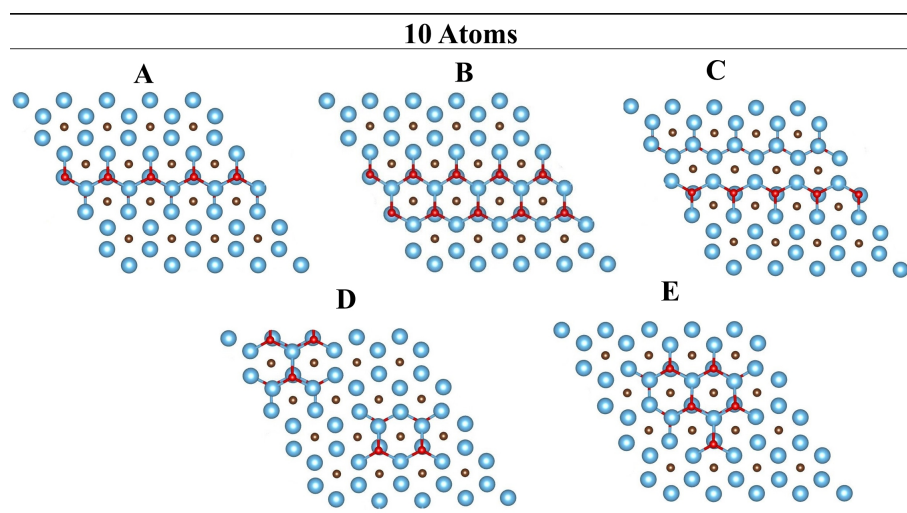


Figure S6: Optimized structures of  $Ti_2C$  after adsorption of ten oxygen atoms for various adsorption patterns. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red, respectively.



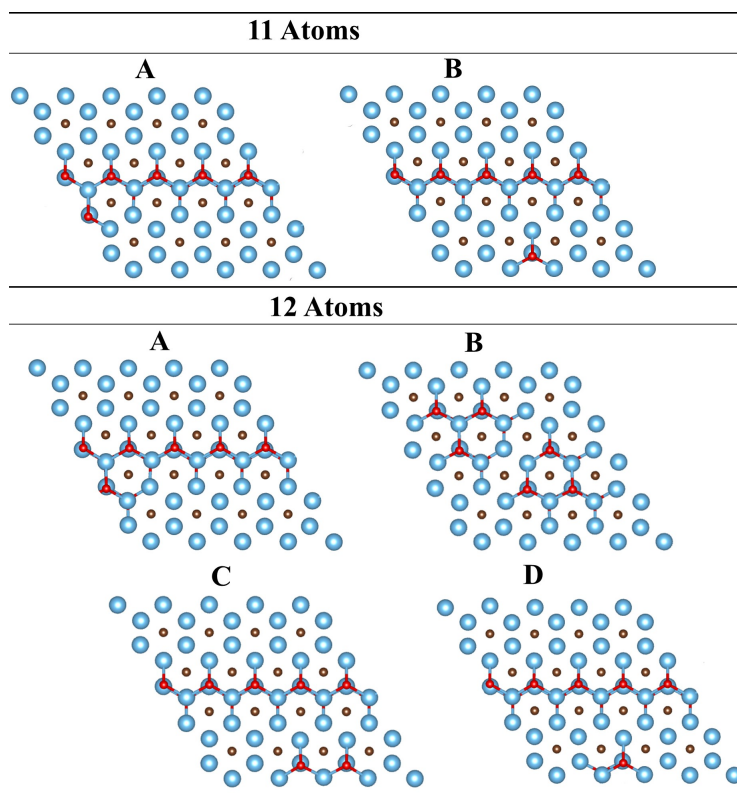


Figure S7: Optimized structures of  $\text{Ti}_2\text{C}$  after adsorption of eleven and twelve oxygen atoms for various adsorption patterns. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red, respectively.

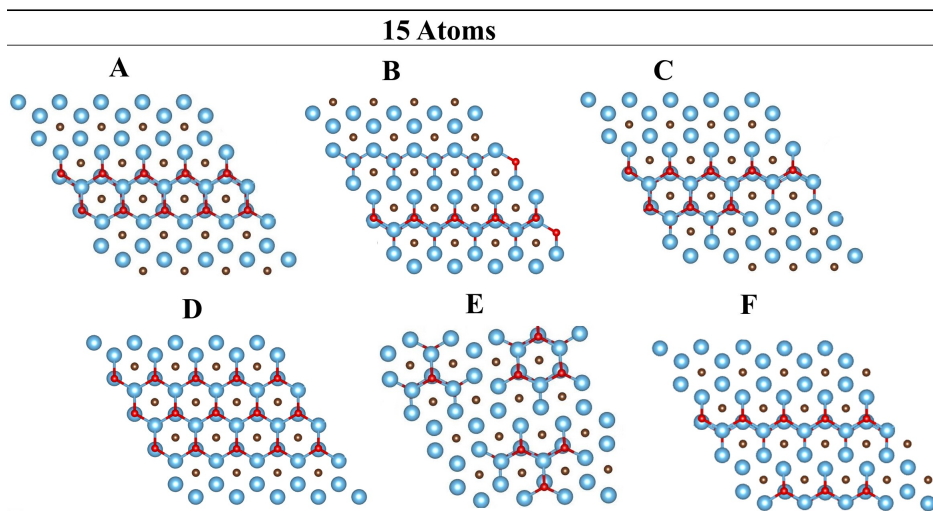


Figure S8: Optimized structures of  $\text{Ti}_2\text{C}$  after adsorption of fifteen oxygen atoms for various adsorption patterns. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red, respectively.

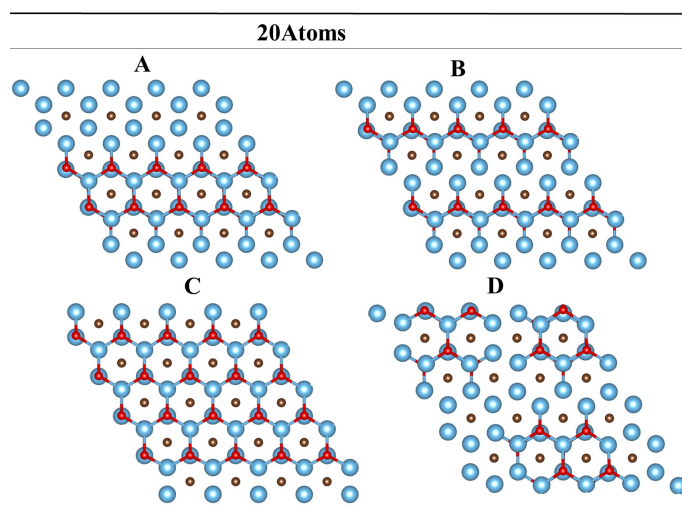


Figure S9: Optimized structures of  $\text{Ti}_2\text{C}$  after adsorption of twenty oxygen atoms for various adsorption patterns. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red, respectively.

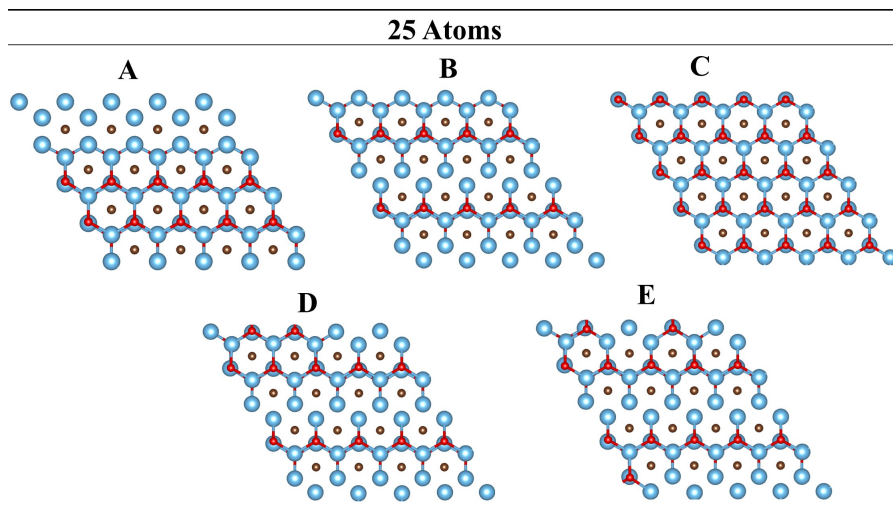


Figure S10: Optimized structures of  $\text{Ti}_2\text{C}$  after adsorption of twenty-five oxygen atoms for various adsorption patterns. Titanium, carbon, and oxygen atoms are represented in blue, brown, and red, respectively.

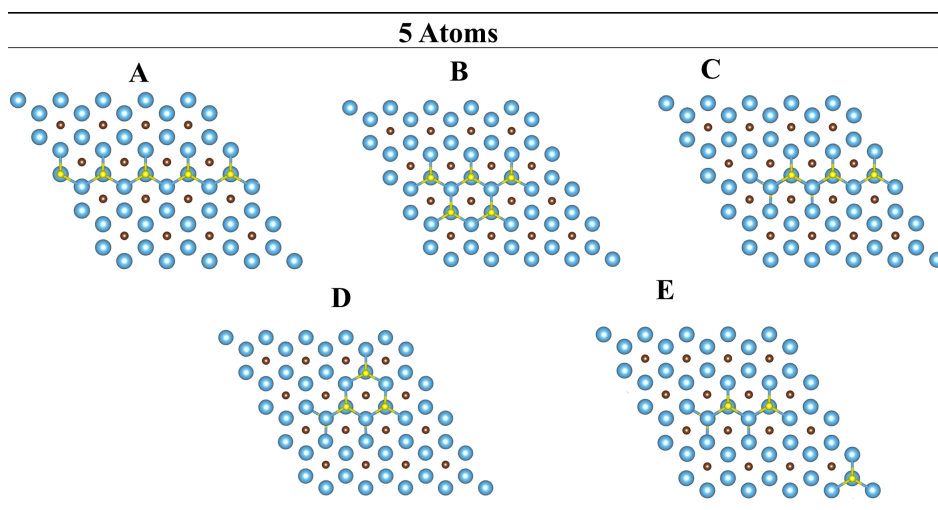


Figure S11: Optimized structures of  $\text{Ti}_2\text{C}$  after adsorption of five fluorine atoms for various adsorption patterns. Titanium, carbon, and fluorine atoms are represented in blue, brown, and yellow, respectively.

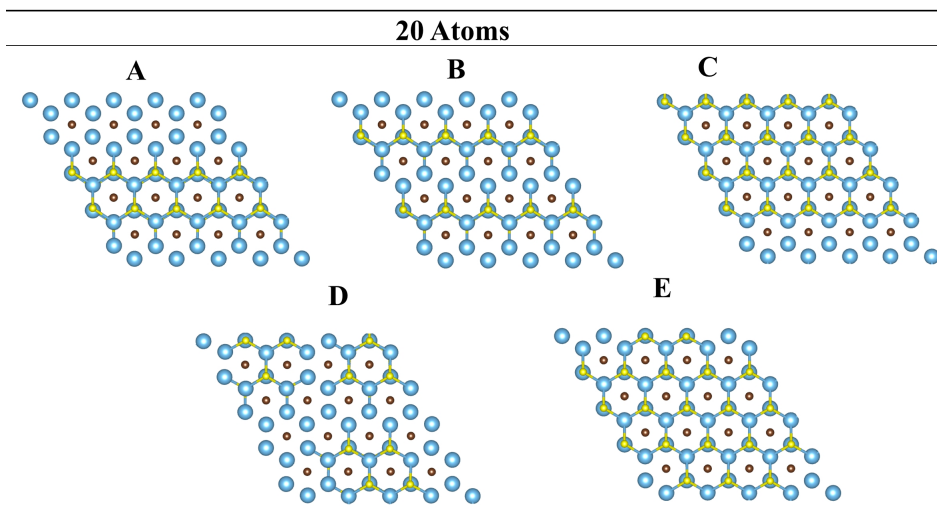


Figure S12: Optimized structures of  $\text{Ti}_2\text{C}$  after adsorption of twenty fluorine atoms for various adsorption patterns. Titanium, carbon, and fluorine atoms are represented in blue, brown, and yellow, respectively.

Table S4: Magnetic states (NM = nonmagnetic, FM = ferromagnetic and AFM = antiferromagnetic), relative energies ( $\Delta E$  in eV/supercell  $5 \times 5$ ), total magnetic moments in supercell ( $m$  in  $\mu_B$ ) of  $\text{Ti}_2\text{C}$  MXene with different concentrations of terminal oxygen atoms in various patterns. The most stable geometry is highlighted in bold.

	$\Delta E$			$m$	
	AFM*	FM	NM	AFM*	FM
<b>10A</b>	<b>0.00</b>	0.41	3.70	0.00	32.49
10B	1.76	2.12	6.38	21.00	46.59
10C	0.53	1.19	8.63	0.00	30.74
10D	0.50	0.76	3.73	1.50	33.50
10E	0.84	1.25	4.76	0.00	34.89
11A	0.18	0.23	0.41	1.00	33.00
<b>11B</b>	<b>0.00</b>	0.21	3.22	2.00	33.00
12A	0.32	0.52	3.51	-2.00	31.50
12B	0.70	0.84	3.47	0.00	33.50
12C	0.12	0.19	2.97	4.00	33.50
<b>12D</b>	<b>0.00</b>	0.13	2.61	0.00	32.50
15A	2.05	1.96	4.83	8.00	32.00
15B	0.39	0.43	2.53	-10.00	23.50
15C	3.57	3.52	7.24	-29.50	46.50
15D	1.31	1.38	4.07	-2.50	29.50
15E	0.66	0.65	2.23	0.00	23.27
<b>15F</b>	<b>0.00</b>	0.10	1.86	2.00	26.50
25A	3.98	3.82	5.76	-1.00	19.50
25B	0.99	0.80	1.36	-3.00	9.00
25C	7.37	7.37	11.12	46.50	46.50
25D	0.11	0.38	0.57	1.00	11.00
<b>25E</b>	0.01	<b>0.00</b>	0.14	0.10	7.00

\*the label represents the initial magnetic state before optimization

Table S5: Magnetic states (NM = nonmagnetic, FM = ferromagnetic and AFM = antiferromagnetic), relative energies ( $\Delta E$  in eV/supercell  $5 \times 5$ ), total magnetic moments in supercell ( $m$  in  $\mu_B$ ) of  $\text{Ti}_2\text{C}$  MXene with different concentrations of terminal fluorine atoms in various patterns. The most stable geometry is highlighted in bold.

	$\Delta E$			$m$	
	AFM*	FM*	NM	AFM	FM
10A	0.56, 0.26 <sup>a</sup>	0.84	4.54	0.00, 0.50 <sup>a</sup>	36.50
<b>10B</b>	<b>0.00</b> , 0.00 <sup>a</sup>	0.39	4.65	12.00, 9.00 <sup>a</sup>	36.50
10C	0.70	0.98	4.63	0.00	36.50
10D	0.71	-*	-*	-0.50	-*
10E	0.42	-*	-*	-0.50	-*
10F	0.66	1.02	3.90	12.00	36.50
15A	0.66	1.02	3.90	3.00	29.50
15B	0.87	0.65	3.47	-18.06	31.50
<b>15C</b>	<b>0.00</b>	0.13	3.69	15.00	32.00
15D	1.36	-*	-*	0.50	-*
15E	0.18	0.13	3.69	15.50	31.50
25A	1.34	1.65	3.98	-4.00	24.00
25B	1.54	1.55	3.27	-12.50	14.50
<b>25C</b>	<b>0.00</b>	<b>0.00</b>	2.65	24.50	24.50

<sup>a</sup> SCAN functionals used, \*the label represents the initial magnetic state before optimization

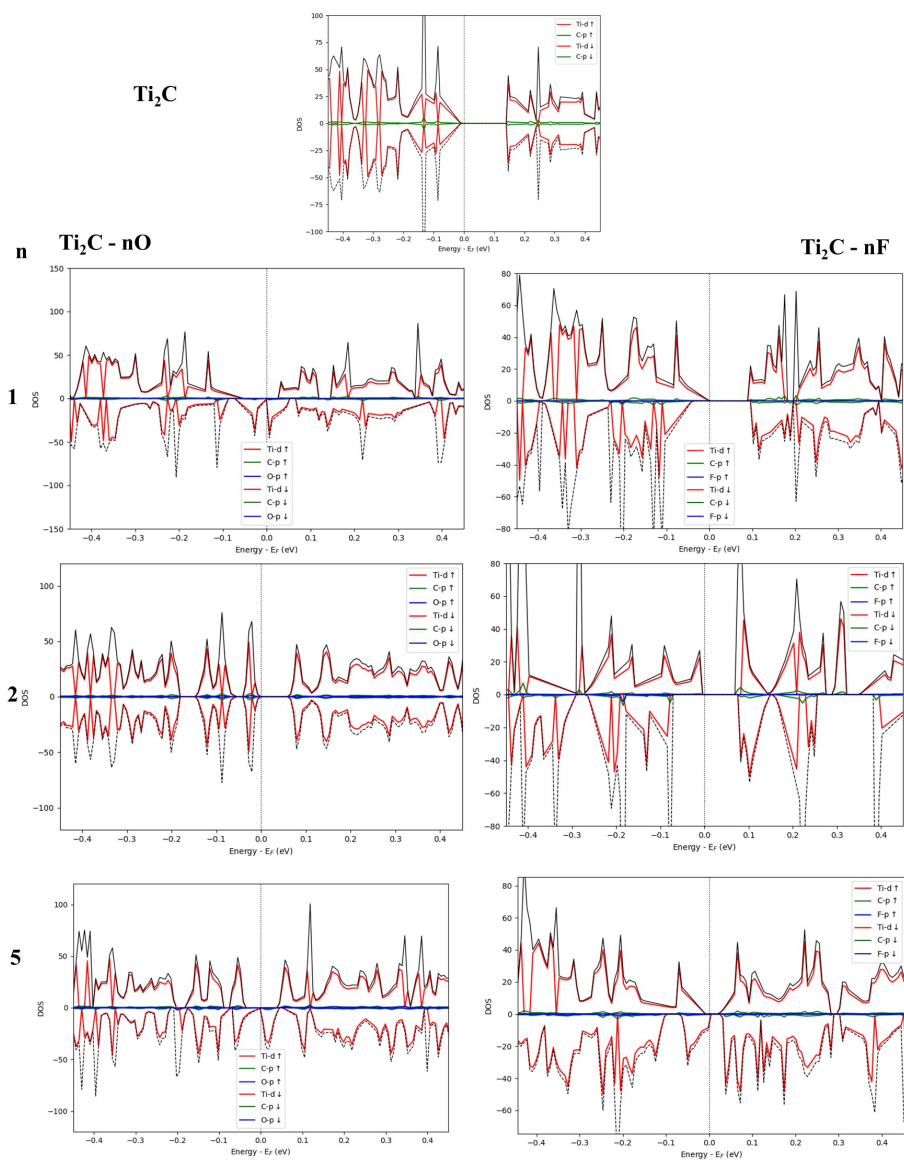


Figure S13: Projected densities of states of the selected  $\text{Ti}_2\text{C-nO}$  and  $\text{Ti}_2\text{C-nF}$  mono-layers.  $n$  represents the number of terminal atoms on the surface. The black line represents the total densities of states.

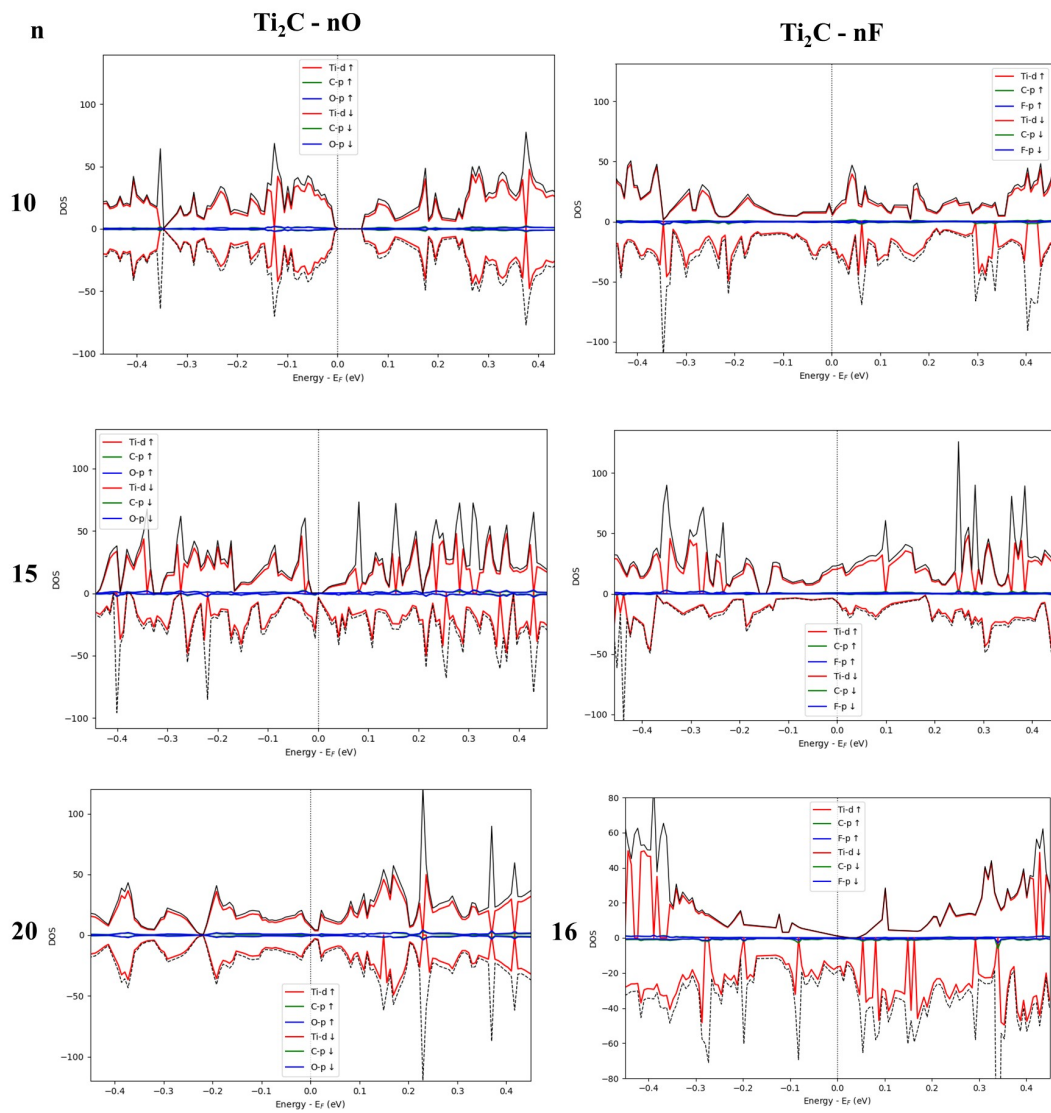


Figure S14: Projected densities of states of the selected  $\text{Ti}_2\text{C-nO}$  and  $\text{Ti}_2\text{C-nF}$  mono-layers.  $n$  represents the number of terminal atoms on the surface. The black line represents the total densities of states.



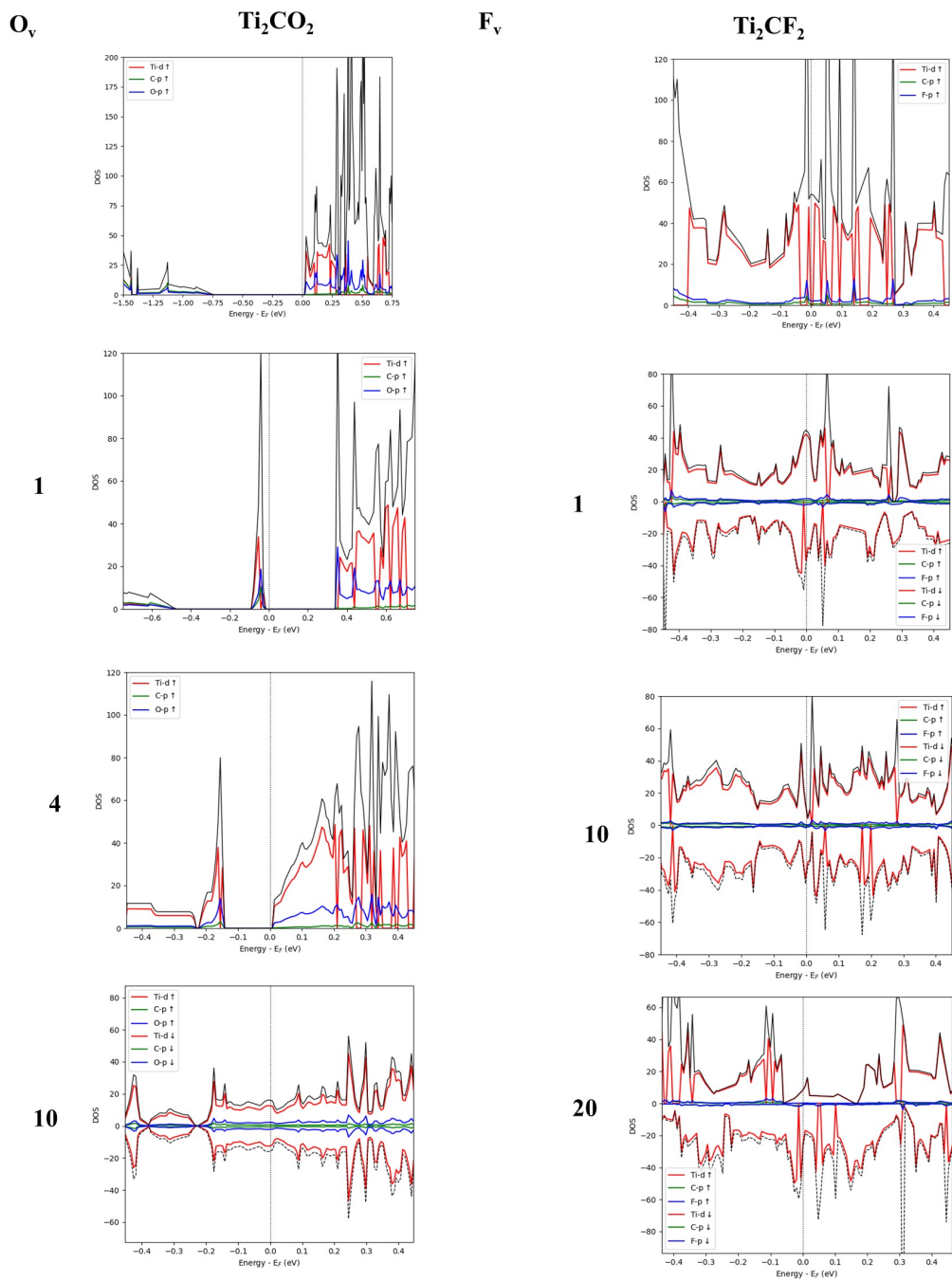


Figure S15: Projected densities of states of selected defect monolayers  $\text{Ti}_2\text{C-nO}$  and  $\text{Ti}_2\text{C-nF}$ .  $\text{O}_v$  and  $\text{F}_v$  represent the number of vacancies on the surface. The black line represents the total densities of states.

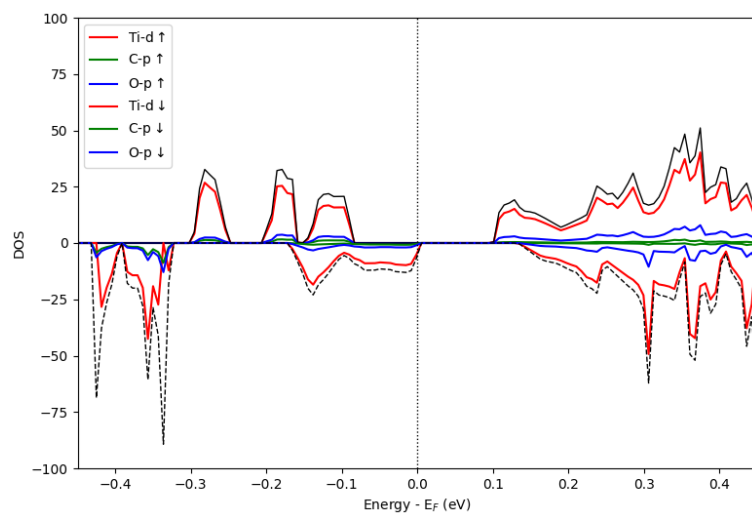


Figure S16: Projected densities of states of the defective  $\text{Ti}_2\text{CO}_2$  monolayer with 5 local O - vacancies. The black line represents the total densities of states.

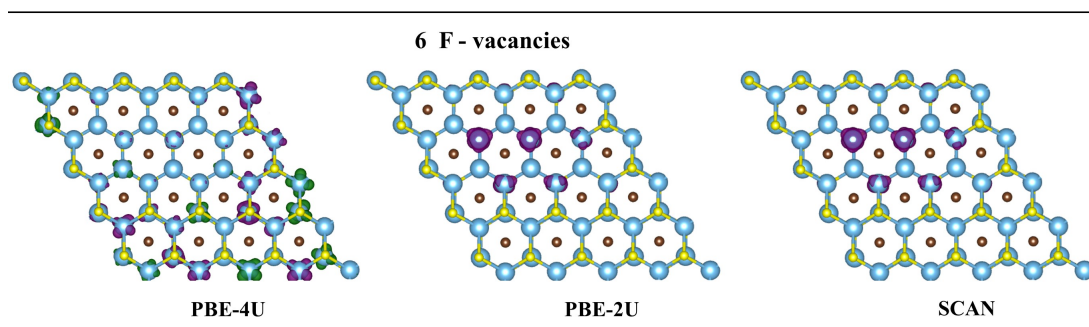


Figure S17: Spin density distribution for  $\text{Ti}_2\text{CF}_2$  monolayer with 6F - vacancies for different functionals. The isosurface values are  $0.01 \text{ e}/\text{\AA}^3$  (green and purple colors represent positive and negative spin densities, respectively). Titanium, carbon, and fluorine atoms are represented in blue, brown, and yellow, respectively.

Table S6: Magnetic states (NM = nonmagnetic, FM = ferromagnetic and AFM = antiferromagnetic), relative energies ( $\Delta E$  in eV/supercell  $5 \times 5$ ), total magnetic moments in supercell ( $m$  in  $\mu_B$ ) of the  $\text{Ti}_2\text{CO}_2$  MXenes with different concentrations of O - vacancies with various patterns The most stable geometry is highlighted in bold.

	$\Delta E$			$m$	
	AFM*	FM*	NM	AFM*	FM*
45A	1.29	1.30	1.34	1.00	3.00
45B	0.61	**	**	0.00	**
45C	0.22	0.22	0.22	0.00	0.00
<b>45D</b>	0.00	0.00	0.00	0.00	0.00
45E	0.38	**	**	0.00	**
45F	1.34	**	**	4.00	**
45G	0.14	**	**	0.00	**
45H	0.17	0.17	0.17	0.00	0.00
46A	0.49	0.49	0.49	0.00	0.00
<b>46B</b>	0.00	0.00	0.00	0.00	0.00
46C	0.91	**	**	0.00	**
46D	0.30	**	**	0.00	0.00
46E	0.12	0.15	0.15	0.00	0.00
46F	0.15	**	**	2.00	-
47A	0.31	0.35	0.36	1.00	2.00
47B	0.61	0.61	0.60	2.00	2.00
47C	0.08	0.07	0.07	0.00	0.00
47D	0.29	**	**	0.00	**
47E	0.28	**	**	0.00	**
<b>47F</b>	0.00	0.00	0.00	0.00	0.00
47 G	0.11	**	**	0.00	**
48A	0.27	0.27	0.27	0.00	0.00
48B	0.08	0.08	0.08	0.00	0.00
48C	0.09	0.09	0.09	0.00	0.00
48D	0.08	0.07	0.07	0.00	0.00
48E	0.09	0.09	0.09	0.00	0.00
<b>48F</b>	0.00	0.00	0.00	0.00	0.00

\*the label represents the initial magnetic state before optimization, \*\*NM and FM magnetic states have not been calculated for the least stable structures

Table S7: Magnetic states (NM = nonmagnetic, FM = ferromagnetic and AFM = antiferromagnetic), relative energies ( $\Delta E$  in eV/supercell  $5 \times 5$ ), total magnetic moments in supercell ( $m$  in  $\mu_B$ ) of  $Ti_2CF_2$  MXene with different concentrations of F vacancies in various patterns. The most stable geometry is highlighted in bold.

	$\Delta E$			$m$	
	AFM*	FM*	NM	AFM	FM
44A	0.20	0.23	0.31	3.00	14.50
44B	0.10	0.15	0.29	3.50	14.50
44C	0.02, 0.06 <sup>a,b</sup>	0.08	0.32	2.00, 0.00 <sup>a,b</sup>	11.50, 6.80 <sup>a</sup>
<b>44D</b>	0.00, 0.00 <sup>a,b</sup>	0.11, 0.00 <sup>a</sup>	0.34	3.50, 5.00 <sup>a,b</sup>	8.50, 5.08 <sup>a</sup>
44E	0.04, 0.08 <sup>a,b</sup>	0.20, 0.06 <sup>a</sup>	0.32	0.50, 1.47 <sup>a</sup>	12.00, 6.45 <sup>a</sup>
45A	0.01, 0.15 <sup>a</sup>	0.13, 0.15 <sup>a</sup>	0.24	- 4.00, -4.06 <sup>a</sup>	14.00, -4.06 <sup>a</sup>
45B	0.14	0.14	0.34	-2.50	12.00
<b>45C</b>	0.00, 0.00 <sup>a,b</sup>	0.17, 0.00 <sup>a,b</sup>	0.29	3.00, 3.50 <sup>a,b</sup>	9.50, 3.50 <sup>a,b</sup>
45D	0.05, 0.07 <sup>a,b</sup>	0.09, 0.07 <sup>a,b</sup>	0.29	0.50, 1.00 <sup>a</sup>	7.50, 6.50 <sup>a,b</sup>
46A	0.01, 0.02 <sup>a</sup>	0.18, 0.01 <sup>a</sup>	0.25	0.50	11.50, 4.35 <sup>a</sup>
46B	0.07	-**	-**	-1.00	-**
<b>46C</b>	0.00, 0.00 <sup>a,b</sup>	0.16, 0.00 <sup>a,b</sup>	0.25	1.50, 3.00 <sup>a,b</sup>	8.00, 3.00 <sup>a,b</sup>
46D	0.08, 0.03 <sup>a,b</sup>	0.12, 0.02 <sup>a,b</sup>	0.24	0.50	8.50, 4.52 <sup>a,b</sup>
46E	0.14	-**	-**	2.50	-**
47A	0.07, 0.04 <sup>a</sup>	0.28, 0.04 <sup>a</sup>	0.23	1.00, 3.44 <sup>a</sup>	11.50, 3.51 <sup>a</sup>
47B	0.12	0.27	0.21	3.50	10.50
47C	0.09	0.17	0.22	0.50	6.50
47D	0.04, 0.04 <sup>a</sup>	0.09, 0.01 <sup>a</sup>	0.20	0.50, 1.00 <sup>a</sup>	6.50, 3.51 <sup>a</sup>
47E	0.10	0.32	0.22	-0.50	-11.50
<b>47F</b>	0.00, 0.00 <sup>a</sup>	0.15, 0.00 <sup>a</sup>	-**	2.00, 3.06 <sup>a</sup>	8.5, 3.13 <sup>a</sup>
<b>48A</b>	0.00, 0.00 <sup>a</sup>	0.10, 0.00 <sup>a</sup>	0.13, 0.12 <sup>a</sup>	1.00, 1.50 <sup>a</sup>	7.50
48B	0.01, 0.01 <sup>a</sup>	0.09, 0.00 <sup>a</sup>	0.13, 0.10 <sup>a</sup>	0.50, 0.00 <sup>a</sup>	7.50, 2.5 <sup>a</sup>
48C	7.14	0.15	0.13	-7.00	8.00
48D	0.11	0.22	0.14	0.50	9.50
48E	0.09	0.12	0.14	-0.50	6.00
48F	0.05	0.04	0.13	0.00	0.00

<sup>a</sup> SCAN and <sup>b</sup> PBE-U(2eV) functionals used, \*the label represents the initial magnetic state before optimization, \*\*NM and FM magnetic states have not been calculated for the least stable structures

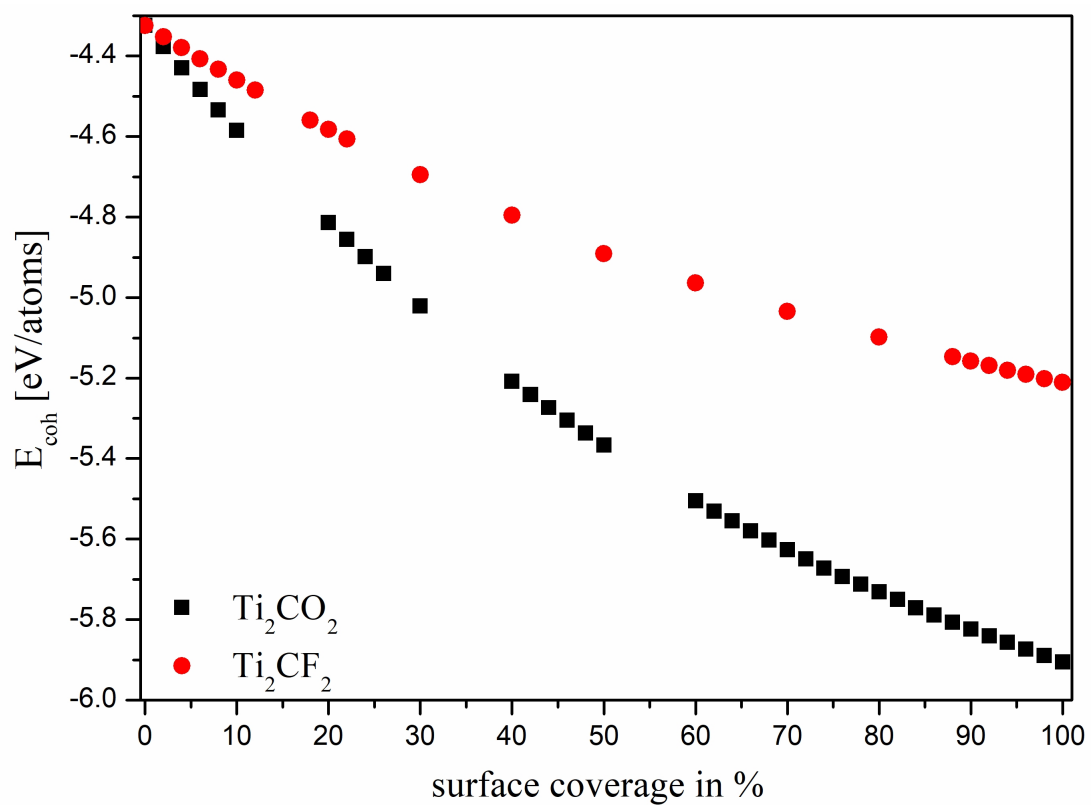


Figure S18: Dependence of the cohesive energy on the type of terminal atoms on the  $\text{Ti}_2\text{C-}n\text{T}$  surface ( $\text{T} = \text{O}$ , and  $\text{F}$ ,  $n = 1 - 50$ ).