How Does Thickness Affect Magnetic Coupling on Ti-Based MXenes

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Table S1. Distance between metal and carbon atom, $d_{Ti–C}$, and lattice constant, a_0, both in Å, obtained for Ti_2C, Ti_3C_2, and Ti_4C_3 $p(1\times1)$ unit cells using PBE functional. For each optimized structure (FM and NM), the energy difference between the FM and NM solution, ΔE in meV, predicted by the PBE functional is reported. Negative values indicate that the FM configuration is more stable than the NM one, taken as zero.

MXene	Structure	ΔE_{FM-NM}^{PBE}
Ti_2C[a]	**NM**	-86
	FM	-135
Ti_3C_2	**NM**	-82
	FM	-85
Ti_4C_3	**NM**	-132
	FM	-130

[a] Values obtained from Ref. 19 of the main text.

Table S2. Energy of AFM1, AFM2, and AFM3 configurations relative to the FM one for $p(2\times1)$ Ti_2C, Ti_3C_2, and Ti_4C_3, ΔE in meV, using PBE functional and computed with the PBE optimized FM structures. Negative values indicate that the AFM_i (i = 1–3) configuration is more stable than the FM one and positive ones, and *vice versa*.

MXene	ΔE	**PBE**
Ti_2C[a]	**AFM1–FM**	-45
	AFM2–FM	172
	AFM3–FM	160
Ti_3C_2	**AFM1–FM**	-81
	AFM2–FM	109
	AFM3–FM	160
Ti_4C_3	**AFM1–FM**	-16
	AFM2–FM	189
	AFM3–FM	198

[a] Values obtained from Ref. 19 of the main text.

Table S3. Bader charges, Q, in a.u., of Ti and C atoms from Ti_2C, Ti_3C_2, and Ti_4C_3 obtained for all magnetic solutions with PBE functional.

MXene	**Ti_2C**	**Ti_3C_2**	**Ti_4C_3**
$Q_{surface\ Ti}^{FM}$	1.2	1.3	1.3
$Q_{inner\ Ti}^{FM}$	—	1.7	1.7
$Q_{inner\ C}^{FM}$	—	—	-1.9
$Q_{surface\ C}^{FM}$	-2.4	-2.1	-2.1
$Q_{surface\ Ti}^{AFM1}$	1.2	1.3	1.3
$Q_{inner\ Ti}^{AFM1}$	—	1.7	1.7
$Q_{inner\ C}^{AFM1}$	—	—	-1.9
$Q_{surface\ C}^{AFM1}$	-2.4	-2.1	-2.1
$Q_{surface\ Ti}^{AFM2}$	1.2	1.3	1.3
$Q_{inner\ Ti}^{AFM2}$	—	1.7	1.7
$Q_{inner\ C}^{AFM2}$	—	—	-1.9
$Q_{surface\ C}^{AFM2}$	-2.4	-2.1	-2.1
$Q_{surface\ Ti}^{AFM3}$	1.2	1.3	1.3
$Q_{inner\ Ti}^{AFM3}$	—	1.7	1.7
$Q_{inner\ C}^{AFM3}$	—	—	-1.9
$Q_{surface\ C}^{AFM3}$	-2.4	-2.1	-2.1

Table S4. Spin exchange parameters, J_{NN}^{inter}, J_{NN}^{intra}, and J_{NNN}^{inter}, given in meV, as obtained from DFT calculations for the PBE functional using the equations derived from the mapping of the broken symmetry solutions to the Heisenberg spin model Hamiltonian, see Eqs. (2–9), for Ti_3C_2 and Ti_4C_3 MXenes.

MXene	J_{NN}^{inter}	J_{NN}^{intra}	J_{NNN}^{inter}
Ti_2C[a]	-14.0	47.1	-0.9
Ti_3C_2	-7.4	43.7	-19.5
Ti_4C_3	3.2	50.4	-3.2

[a] Values obtained from Ref. 19 of the main text.

Table S5. Energy of AFM1, AFM2, and AFM3 configurations relative to the FM one for $p(2\times1)$ Ti_2C, Ti_3C_2, and Ti_4C_3, ΔE in meV, using PBE+U functional with U parameters within the range [1,8] eV and computed with the PBE optimized FM structures. Negative values indicate that the AFM_i (i = 1–3) configuration is more stable than the FM one and positive ones, and *vice versa*.

		***U* parameter**							
MXene	**ΔE**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Ti_2C	**AFM1–FM**	-49	-61	-77	-99	-132	-183	-254	669
	AFM2–FM	207	241	277	316	290	154	-84	590
	AFM3–FM	194	225	257	283	294	146	-24	574
Ti_3C_2	**AFM1–FM**	-92	-106	-127	-160	-200	-243	-277	-223
	AFM2–FM	137	170	200	225	239	220	158	120
	AFM3–FM	161	199	237	266	277	254	187	150
Ti_4C_3	**AFM1–FM**	-40	-70	-103	-131	-155	-172	-180	-174
	AFM2–FM	215	239	261	283	293	291	271	217
	AFM3–FM	223	245	265	284	284	282	268	220

Table S6. Magnetic coupling parameters, J_{NN}^{inter}, J_{NN}^{intra}, and J_{NNN}^{inter}, given in meV, as obtained from DFT calculations using PBE+*U* with *U* parameter within the range [1,8] eV and using the equations derived from the mapping of the broken symmetry solutions to the Heisenberg spin model Hamiltonian, see Eqs. (2–9), for Ti_2C, Ti_3C_2, and Ti_4C_3 MXenes.

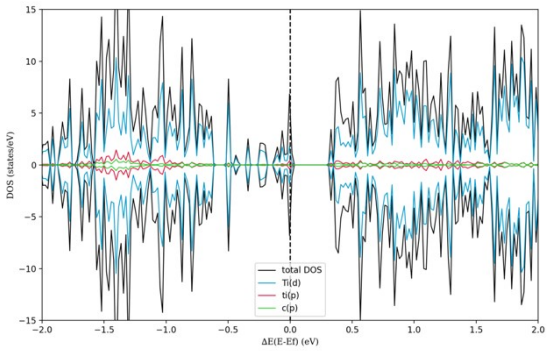
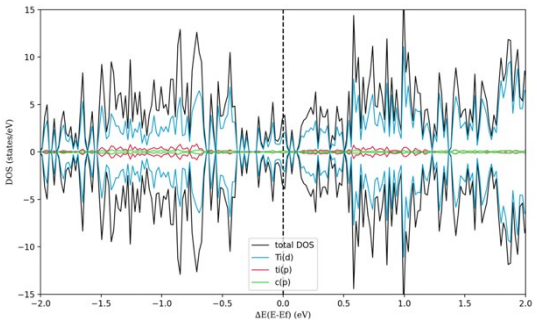
		***U* parameter**							
MXene		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Ti_2C	J_{NN}^{inter}	-15.4	-19.3	-24.4	-32.9	-31.9	-47.6	-48.5	163.2
	J_{NN}^{intra}	56.3	65.9	76.4	87.2	89.3	60.4	18.4	61.8
	J_{NNN}^{inter}	-1.0	-1.0	-1.4	-0.0	-12.0	-13.3	-36.3	59.8
Ti_3C_2	J_{NN}^{inter}	-16.9	-19.0	-22.5	-29.6	-40.4	-52.2	-62.2	-48.4
	J_{NN}^{intra}	48.8	59.4	70.5	81.4	89.5	89.6	77.8	61.6
	J_{NNN}^{inter}	-13.7	-16.3	-19.8	-23.6	-26.2	-28.7	-30.3	-26.1
Ti_4C_3	J_{NN}^{inter}	-3.9	-12.8	-22.1	-31.8	-46.0	-49.9	-46.7	-41.5
	J_{NN}^{intra}	59.7	69.3	78.6	87.2	91.5	93.1	89.9	76.4
	J_{NNN}^{inter}	-6.0	-9.6	-13.4	-16.6	-18.2	-20.4	-22.2	-22.1

Table S7. Total net spin densities of the *p*(2×1) Ti_2C, Ti_3C_2, and Ti_4C_3 supercells, S_{Tot}^{FM}, given in unpaired electrons per supercell, atomic spin densities of surface Ti, inner Ti and C atoms of FM configuration, and the atomic spin densities of Ti atoms in the different solution, $S_{atom}^{Solution}$, given in unpaired electrons per atom, in absolute value for the AFM ones, as predicted by PBE functional and using the projection on the atomic spheres approach. In the AFM solutions, the inner Ti atom spin densities are also coupled antiferromagnetically between them and, the values present in the table are absolute values of spin density.

	Ti_2C[a]	**Ti_3C_2**	**Ti_4C_3**
S_{Tot}^{FM}	3.85	3.40	3.92
$S_{surface\ Ti}^{FM}$	0.54	0.48	0.56
$S_{inner\ Ti}^{FM}$	—	0.03	0.03
S_{C}^{FM}	-0.04	-0.03	-0.04
$S_{surface\ Ti}^{AFM1}$	0.56	0.59	0.68
$S_{inner\ Ti}^{AFM1}$	—	0.00	0.08
$S_{surface\ Ti}^{AFM2}$	0.21	0.18	0.16
$S_{inner\ Ti}^{AFM2}$	—	0.00	0.01
$S_{surface\ Ti}^{AFM3}$	0.24	0.15	0.18
$S_{inner\ Ti}^{AFM3}$	—	0.00	0.02

[a] Values obtained from Ref. 19 of the main text.

Fig. S1. Density of states (DOS) computed with HSE06 for each $p(2\times1)$ Ti_2C magnetic solution.

<table>
<tr><td colspan="2">Ti_2C</td></tr>
<tr><td>AFM1
 
</td><td>AFM2
 
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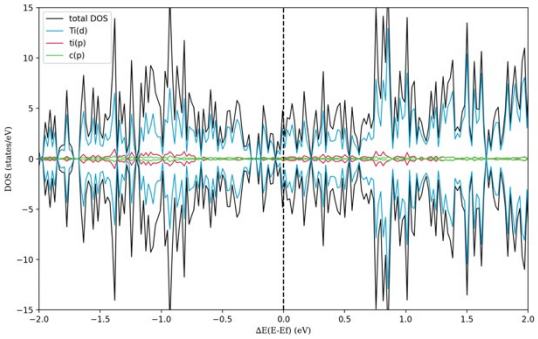
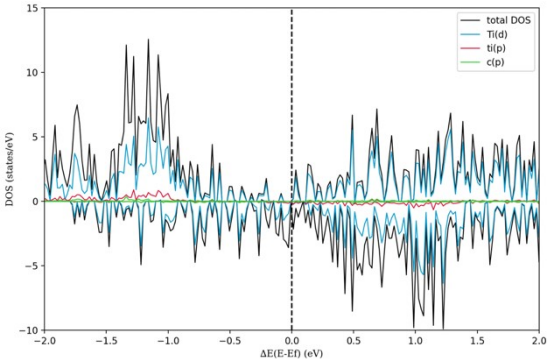
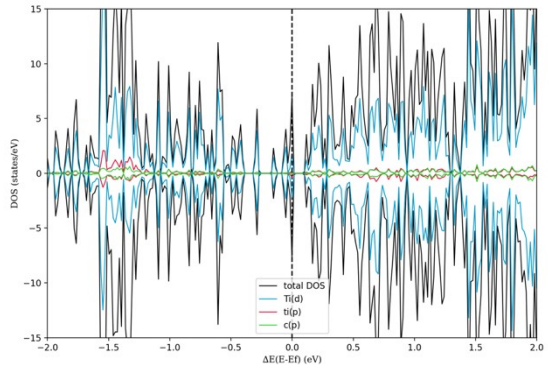
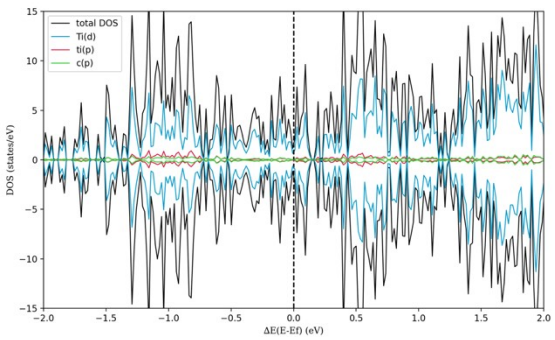
<tr><td>AFM3
 
</td><td>FM
 
</td></tr>
</table>

Fig. S2. Density of states (DOS) computed with HSE06 for each *p*(2×1) Ti_3C_2 magnetic solution.

<table>
<tr><td colspan="2">Ti_3C_2</td></tr>
<tr><td>AFM1
 
</td><td>AFM2
 
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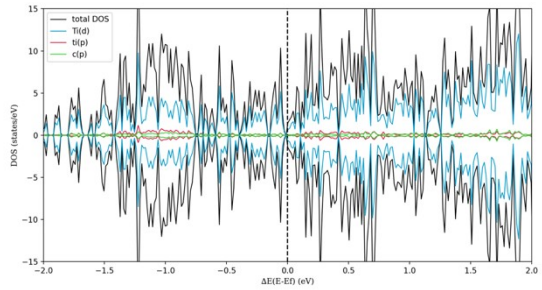
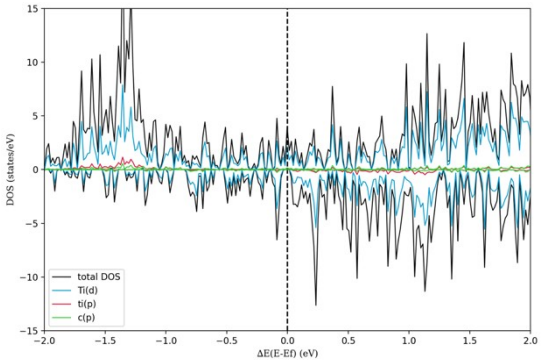
<tr><td>AFM3
 
</td><td>FM
 
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Fig. S3. Density of states (DOS) computed with HSE06 for each $p(2\times1)$ Ti_4C_3 magnetic solution.

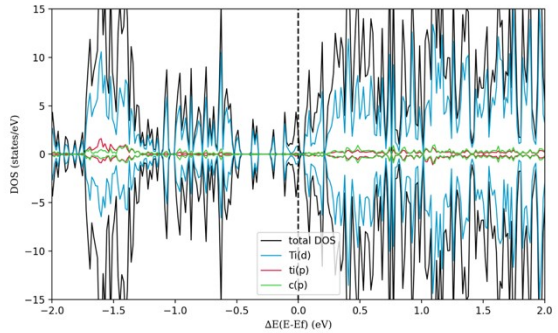
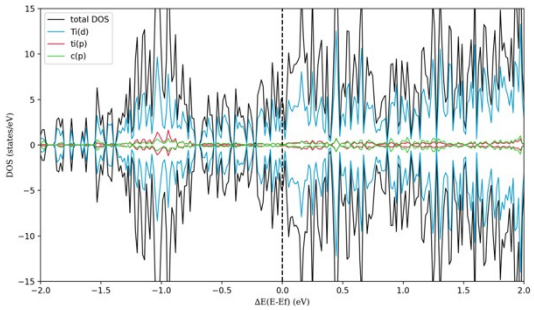
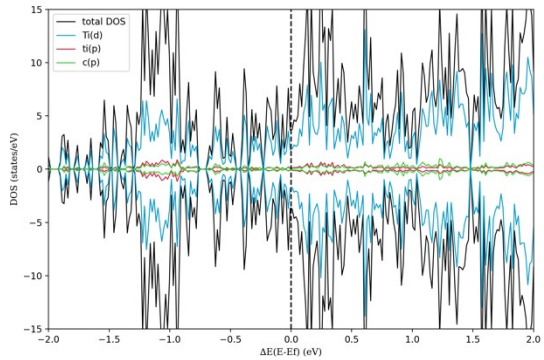
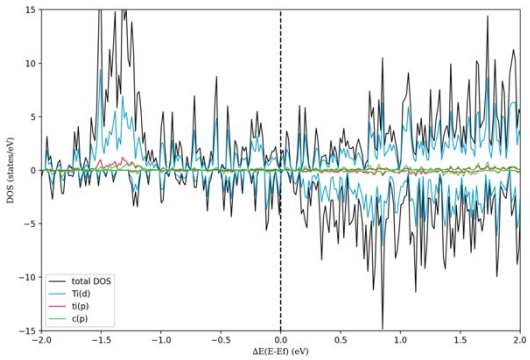
<table>
<tr><td colspan="2">Ti_4C_3</td></tr>
<tr><td>AFM1
 
</td><td>AFM2
 
</td></tr>
<tr><td>AFM3
 
</td><td>FM
 
</td></tr>
</table>

Fig. S4. Projected Density of states (PDOS) computed with HSE06 for each $p(2\times1)$ Ti_3C_2 magnetic solution for the surface and inner Ti atoms and C atoms.

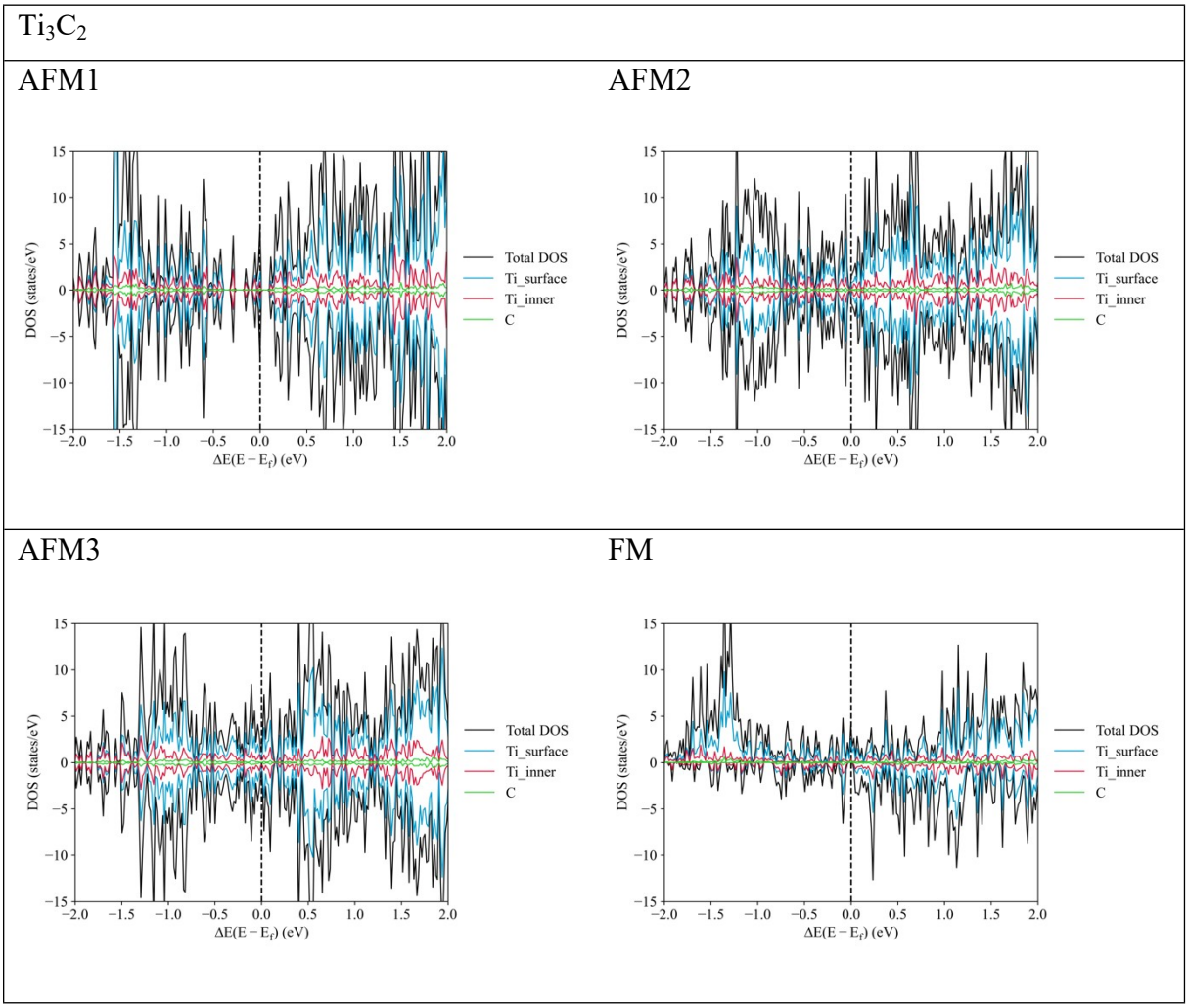


Fig. S5. Projected Density of states (PDOS) computed with HSE06 for each $p(2\times1)$ Ti_4C_3 magnetic solution for the surface and inner Ti atoms and C atoms.

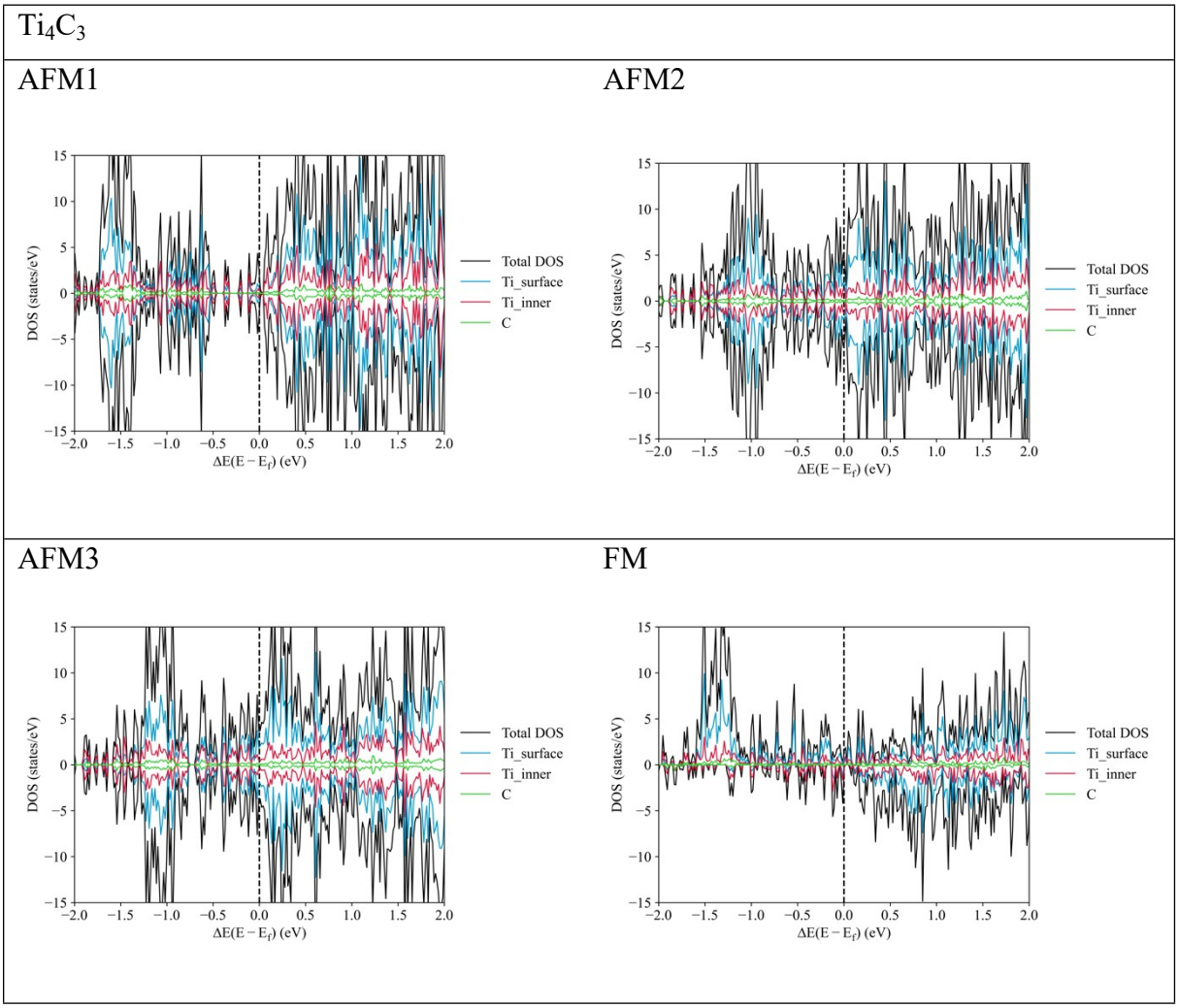
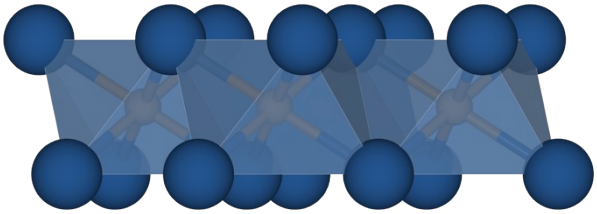
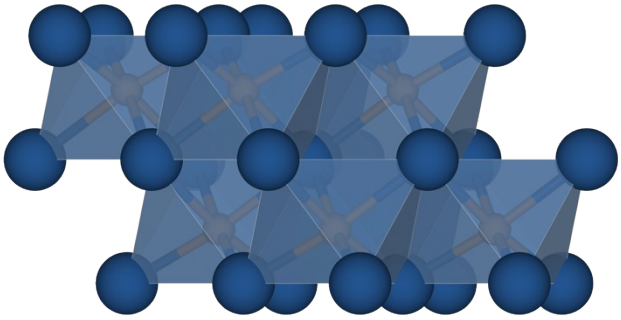


Fig. S6. Side view of fully relaxed of Ti_2C, Ti_3C_2, and Ti_4C_3, where the octahedral environment of the C atoms (orange) with the Ti atoms (blue) in vertices is shown.

Ti_2C



Ti_3C_2



Ti_4C_3

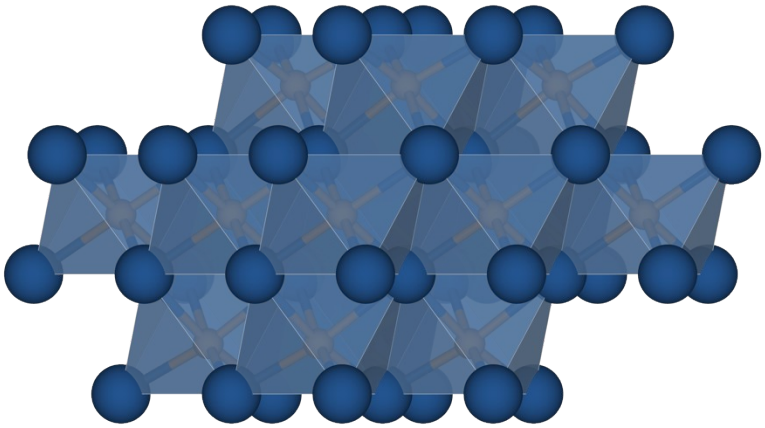


Fig. S7. Projected Density of states (PDOS) computed with HSE06 for Ti_2C and Ti_4C_3 FM solutions. Projections represented in the graphs include all equivalent atoms or atomic orbitals of the indicated type.

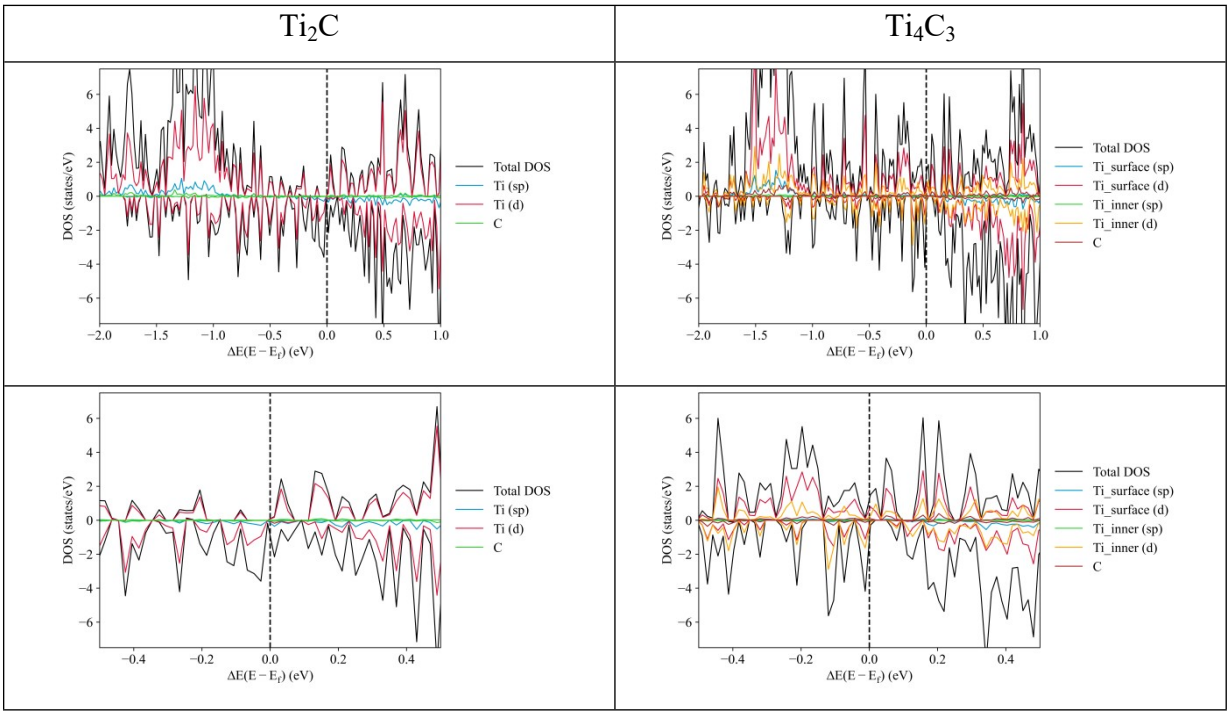
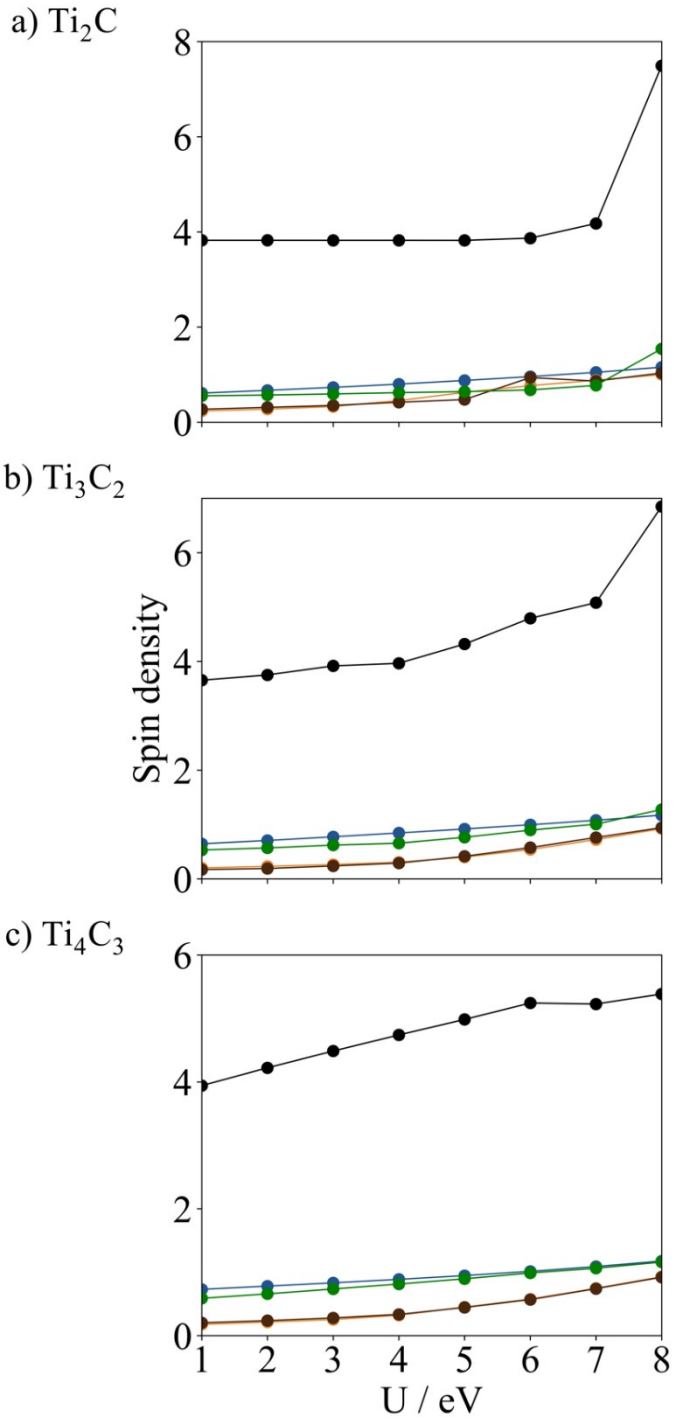


Fig. S8. Calculated PBE+*U* total spin density and atomic spin density of Ti surface atoms for the AFM1, AFM2, AFM3, and FM solutions of a $p(2\times1)$ for Ti_2C, Ti_3C_2, and Ti_4C_3 MXenes as a function of *U*. The black line corresponds to the total spin density and the blue/orange/brown/green, to the Ti surface atomic spin density of AFM1/AFM2/AFM3/FM solutions, respectively.



VASP input files used to compute the energy and electronic structure of each electronic state (NM, FM, AFM1, AFM2, and Neel-AFM) over the *p*(1×1) and *p*(2×1) FM structures optimized with PBE.

POSCAR input file for *p*(1×1) Ti_3C_2 FM structure:

```
Ti3C2
  1.00000000000000
    3.0994985104000001    0.0000000000000000    0.0000000000000000
    1.5497490764999999    2.6842445521000000    0.0000000000000000
    0.0000000000000000    0.0000000000000000   20.0000000000000000
  Ti   C
    3     2
Direct
  0.3333329855524383  0.3333329857370870  0.2573106706088458
  0.6666669844946185  0.6666659714741741  0.4900514968411537
 -0.0000000000000000  0.0000000000000000  0.3736792910000020
  0.6666659711048766  0.6666659714741741  0.3081208742262547
  0.3333329855524383  0.3333329857370870  0.4392446591737453
```

POSCAR input file for $p(2\times1)$ Ti_3C_2 FM structure:

```
Ti3C2
  1.00000000000000
    6.2007370931244745    0.0006881486060709    0.0000141131107424
    1.5504820716296204    2.6855141371907245   -0.0000000000005423
    0.0000455309005109   -0.0000262872776657   20.0054888077314565
   Ti   C
    6    4
Direct
  0.1666715442234961  0.3333279342898054  0.2572885630890843
  0.6666715441589719  0.3333279342898054  0.2572885630890843
  0.3333284408000251  0.6666710229214557  0.4900736035609152
  0.8333284407355006  0.6666710229214557  0.4900736035609152
  0.0000000000000000  0.0000000000000000  0.3736792803000029
  0.5000000000254445  0.9999999999627462  0.3736792803000029
  0.3333231983701982  0.6666757586564162  0.3081184337062845
  0.8333231984669883  0.6666757586564162  0.3081184337062845
  0.1666762799584557  0.3333231985548450  0.4392471005937174
  0.6666762798939313  0.3333231985548450  0.4392471005937174
```

POSCAR for $p(1\times1)$ Ti_4C_3 FM structure:

```
Ti4C3
  1.00000000000000
    3.1024822266952801    0.0000000026012869    0.0000000000000000
    1.5512409367414179    2.6868285250689410    0.0000000000000000
   -0.0000000000000001    0.0000000000000001   23.6991516497939365
   Ti   C
    4     3
Direct
  0.9999995828115473  0.0000008060463585  0.3193759194788868
  0.6666665673320509  0.6666668653784598  0.4197329240848049
  0.3333334327660964  0.3333331048184576  0.5196752207719371
  0.0000004028311409  0.9999991656241320  0.6200322533722229
  0.0000000000000000  0.0000000000000000  0.4697040864255513
  0.6666669247087995  0.6666660906456059  0.5779115789471234
  0.3333330453997121  0.3333338795513114  0.3614966218983469
```

POSCAR for $p(2\times1)$ Ti_4C_3 FM structure:

```
Ti4C3
  1.00000000000000
    6.2032337536958799   -0.0001864707480854    0.0003760983752760
    1.5507275154183058    2.6859392581726369   -0.0000000000144528
    0.0014364434275954   -0.0008293309995921   23.7092842510249326
   Ti   C
    8     6
Direct
 -0.0000292642035486  0.0000292642121889  0.3193157872262655
  0.4999707356514012  0.0000292642121889  0.3193157872262655
  0.3333476215616181  0.6666525276084305  0.4197230316790588
  0.8333476214165751  0.6666525276084305  0.4197230316790588
  0.1666523784748256  0.3333474429144411  0.5196850918168288
  0.6666523783297824  0.3333474429144411  0.5196850918168288
  0.0000292643697019  0.9999707356389382  0.6200923958498099
  0.5000292642246517  0.9999707356389382  0.6200923958498099
  0.0000000000830767  0.9999999999255635  0.4697040915380342
  0.4999999999380265  0.9999999999255635  0.4697040915380342
  0.3333164262166359  0.6666831267969446  0.5778819673991660
  0.8333164262327510  0.6666831267969446  0.5778819673991660
  0.1666835589248568  0.3333168433537376  0.3615262157191016
  0.6666835587798137  0.3333168433537376  0.3615262157191016
```

KPOINTS input file:

```
K-Points
0
Monkhorst Pack
 13  13  1
 0  0  0
```

INCAR for *p*(1×1) Ti_3C_2 and Ti_4C_3 FM structures and NM electronic state:

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IBRION =  -1
POTIM  =  0.5
EDIFFG =  -0.01
NSW    =  0

EDIFF  =  1E-06
ISPIN  =  1
LORBIT = 11
ISMEAR =  1
SIGMA  =  0.01

LREAL  =  .TRUE.

NWRITE =  2
NELM   =  101
NELMIN =  2
ENCUT  =  700
IALGO  =  58

ISTART =  0
INIWAV =  1

GGA    =  PE
```

INCAR for *p*(1×1) and *p*(2×1) Ti_3C_2 and Ti_4C_3 FM structures and FM electronic state:

```
IBRION =  -1
POTIM  =  0.5
EDIFFG =  -0.01
NSW    =  0

EDIFF  =  1E-06
ISPIN  =  2
LORBIT =  11
ISMEAR =  1
SIGMA  =  0.01

LREAL  =  .TRUE.

NWRITE =  2
NELM   =  101
NELMIN =  2
ENCUT  =  700
IALGO  =  58

ISTART =  0
INIWAV =  1

GGA    =  PE
```

INCAR for *p*(2×1) Ti_3C_2 FM structure and AFM1 electronic state:

```
IBRION =  -1
POTIM  =  0.5
EDIFFG =  -0.01
NSW    =  0

EDIFF  =  1E-06
ISPIN  =  2
MAGMOM =  -1.0 -1.0 1.0 1.0 2*0.0 4*0.0
NUPDOWN=  0.0
LORBIT = 11
ISMEAR =  1
SIGMA  =  0.01

LREAL  =  .TRUE

NWRITE =  2
NELM   =  101
NELMIN =  2
ENCUT  =  700
IALGO  =  58

ISTART =  0
INIWAV =  1

GGA    =  PE
```

INCAR for *p*(2×1) Ti_3C_2 FM structure and AFM2 electronic state:

```
IBRION =  -1
POTIM  =  0.5
EDIFFG =  -0.01
NSW    =  0

EDIFF  =  0.1E-05
ISPIN  =  2
MAGMOM =  -1.0 1.0 -1.0 1.0 2*0.0 4*0.0
NUPDOWN=  0.0
LORBIT = 11
ISMEAR =  1
SIGMA  =  0.01

LREAL  =  .TRUE.

NWRITE =  2
NELM   =  101
NELMIN =  2
ENCUT  =  700
IALGO  =  58

ISTART =  0
INIWAV =  1

GGA    =  PE
```

INCAR for *p*(2×1) Ti_3C_2 FM structure and Neel-AFM electronic state:

```
IBRION =  -1
POTIM  =  0.5
EDIFFG =  -0.01
NSW    =  0

EDIFF  =  0.1E-05
ISPIN  =  2
MAGMOM =  1.0 -1.0 -1.0 1.0 2*0.0 4*0.0
NUPDOWN=  0.0
LORBIT = 11
ISMEAR =  1
SIGMA  =  0.01

LREAL  =  .TRUE.

NWRITE =  2
NELM   =  101
NELMIN =  2
ENCUT  =  700
IALGO  =  58

ISTART =  0
INIWAV =  1

GGA    =  PE
```

INCAR for *p*(2×1) Ti_4C_3 FM structure and AFM1 electronic state:

```
IBRION =  -1
POTIM  =  0.5
EDIFFG =  -0.01
NSW    =  0

EDIFF  =  0.1E-05
ISPIN  =  2
MAGMOM =  -1.0 -1.0 4*0.0 1.0 1.0 6*0.0
NUPDOWN=  0.0
LORBIT = 11
ISMEAR =  1
SIGMA  =  0.01

LREAL  =  .TRUE.

NWRITE =  2
NELM   =  101
NELMIN =  2
ENCUT  =  700
IALGO  =  58

ISTART =  0
INIWAV =  1

GGA    =  PE
```

INCAR for *p*(2×1) Ti_4C_3 FM structure and AFM2 electronic state:

```
IBRION =  -1
POTIM  =  0.5
EDIFFG =  -0.01
NSW    =  0

EDIFF  =  0.1E-05
ISPIN  =  2
MAGMOM =  -1.0 1.0 4*0.0 -1.0 1.0 6*0.0
NUPDOWN=  0.0
LORBIT = 11
ISMEAR =  1
SIGMA  =  0.01

LREAL  =  .TRUE.

NWRITE =  2
NELM   =  101
NELMIN =  2
ENCUT  =  700
IALGO  =  58

ISTART =  0
INIWAV =  1

GGA    =  PE
```

INCAR for *p*(2×1) Ti_4C_3 FM structure and Neel-AFM electronic state:

```
IBRION =  -1
POTIM  =  0.5
EDIFFG =  -0.01
NSW    =  0

EDIFF  =  0.1E-05
ISPIN  =  2
MAGMOM =  1.0 -1.0 4*0.0 -1.0 1.0 6*0.0
NUPDOWN=  0.0
LORBIT = 11
ISMEAR =  1
SIGMA  =  0.01

LREAL  =  .TRUE.

NWRITE =  2
NELM   =  101
NELMIN =  2
ENCUT  =  700
IALGO  =  58

ISTART =  0
INIWAV =  1

GGA    =  PE
```