Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Hypercoordinate Two-dimensional Transition-metal Borides for Spintronics and Catalyst Applications

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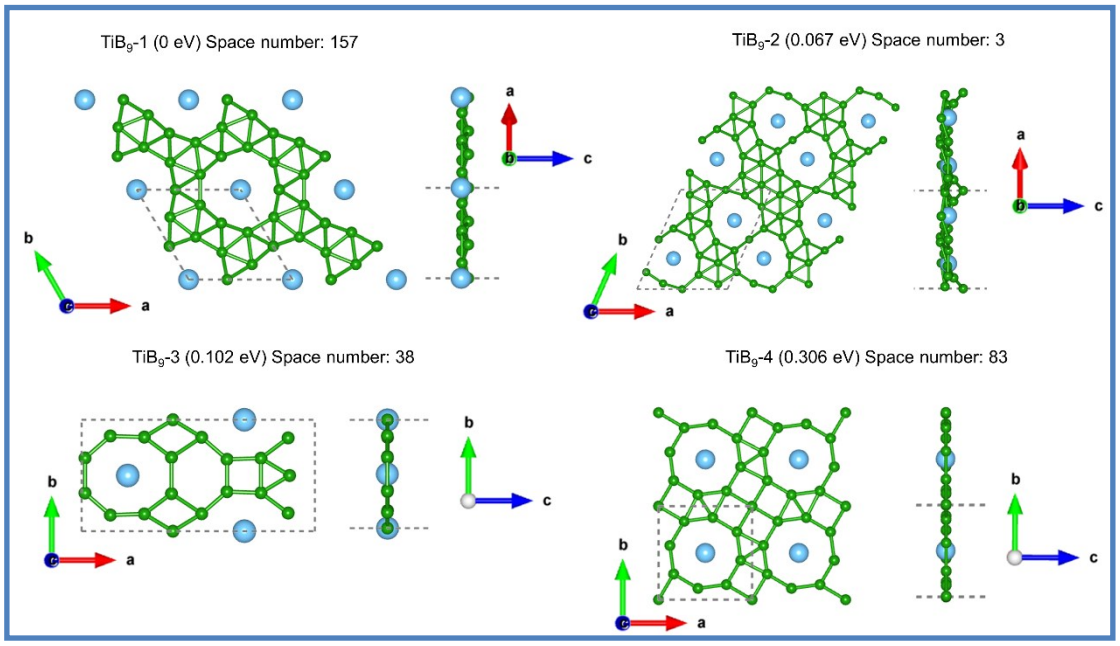

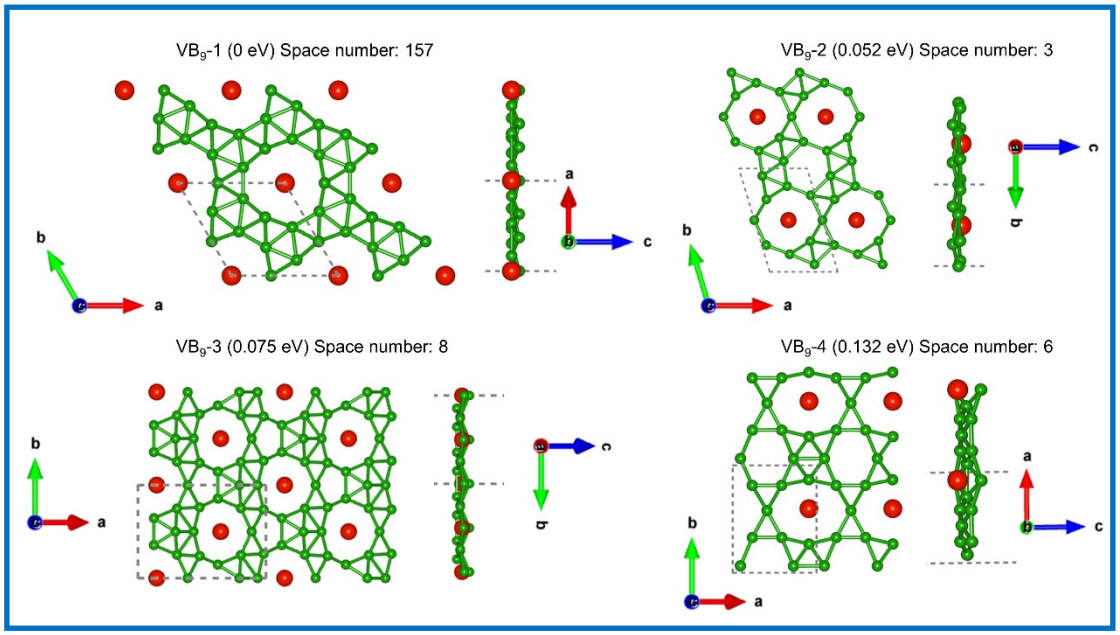

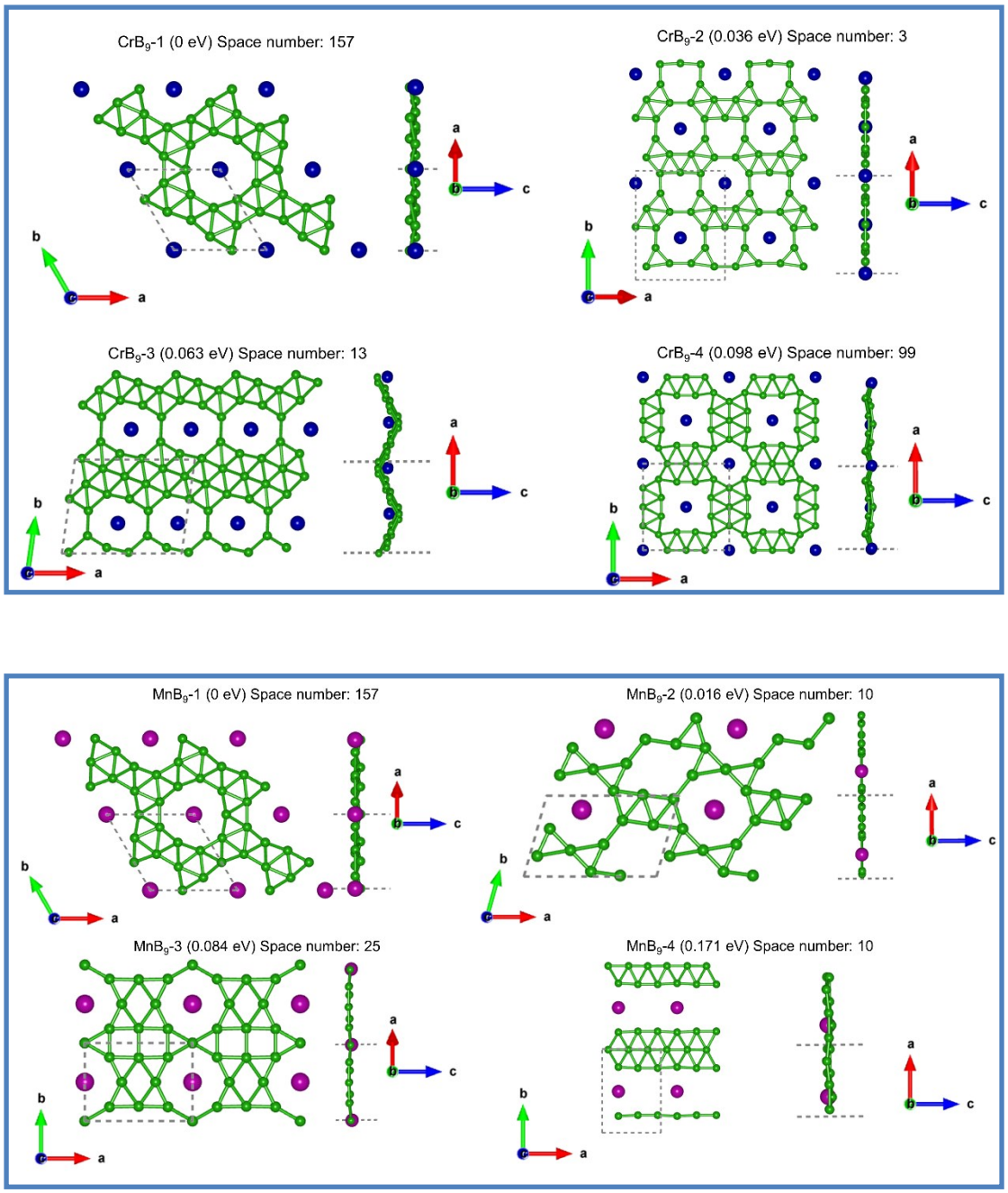

Fig. S1 The top and side views of predicted 2-D MB9 (M = Ti, V, Cr, Mn) with lower energy by USPEX code. The relative energy with respect to most stable one is calculated by the GGA method.

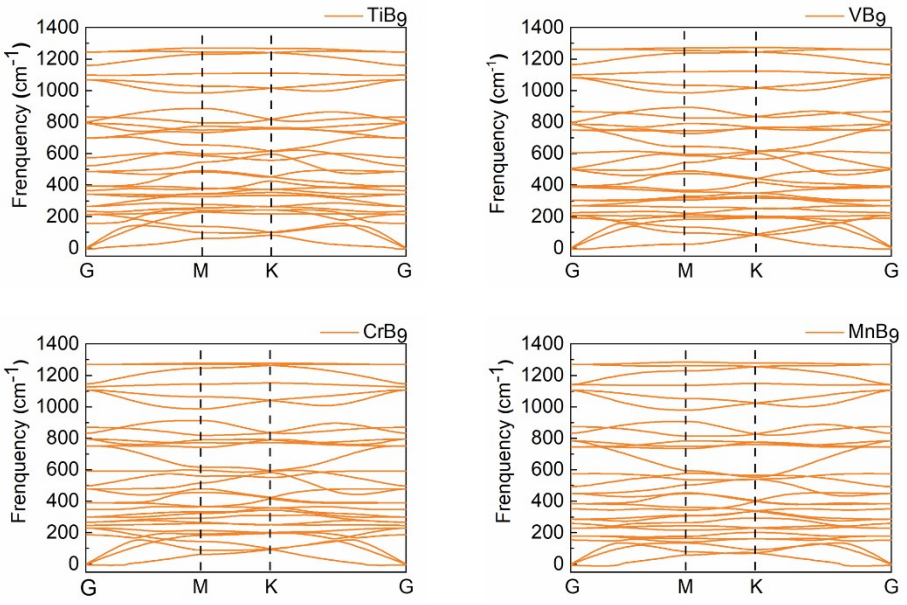

Fig. S2 Calculated phonon spectra of TiB_9, VB_9, CrB_9, and MnB_9 by employing PBE functional.

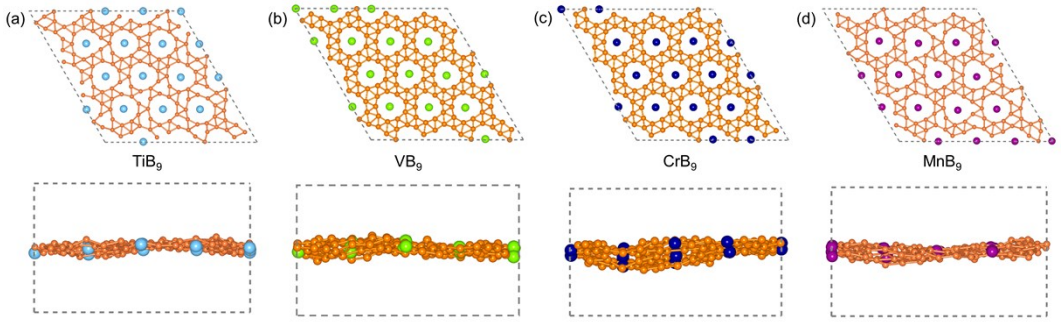

Fig. S3 Top and side views of snapshots of MB_9 equilibrium structures at 600 K after 12 ps AIMD simulations: a) TiB_9, b) VB_9, c) CrB_9, and d) MnB_9.

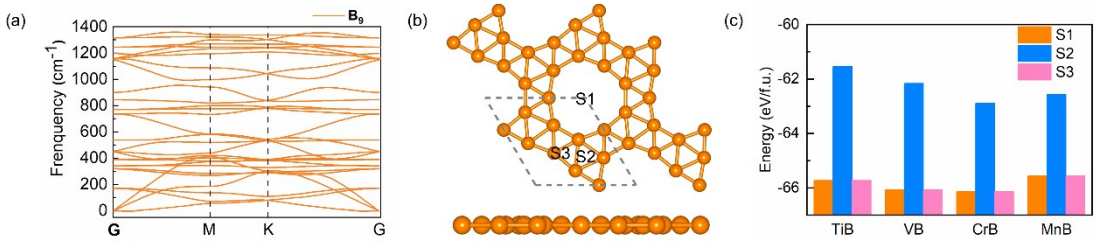

Fig. S4 a) Calculated phonon spectrum of B_9. b) Top and side views of predicted B_9 structure. S1, S2, and S3 are possible initial adsorption sites of transition-metal atoms on the surface of B_9. c) Total energy of each M adsorption configuration on the surface of B_9 (M = Ti, V, Cr, Mn).

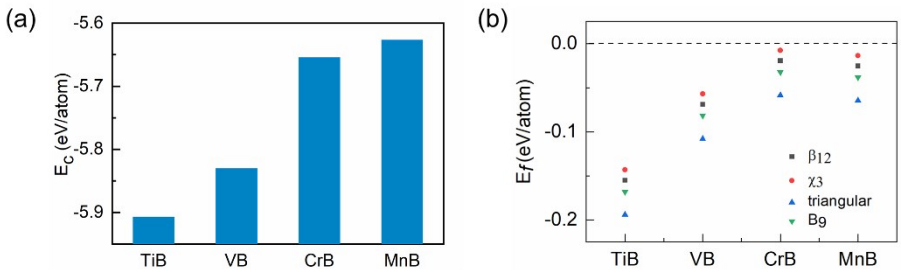

Fig. S5 a) Cohesive energy (E_{coh}) and b) Formation energy (E_f) of predicted 2-D MB_9 computed by using PBE functional. Four kinds of borophenes used as references including experimental β_{12}, χ_3, and triangular as well as predicted B_9.

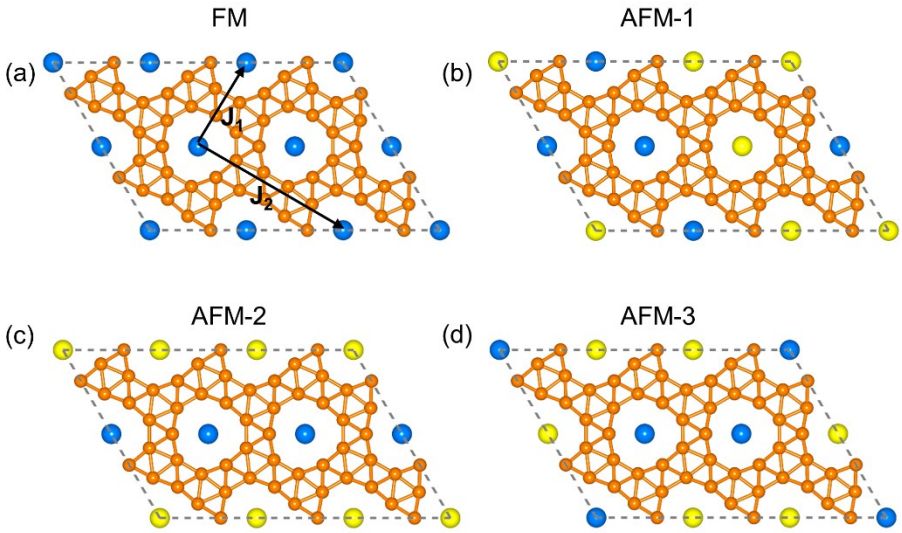

Fig. S6 Top views of four possible collinear magnetic configurations of MB_9. a) FM, b) AFM-1, c) AFM-2, and d) AFM-3 are ferromagnetic and three difference antiferromagnetic states, respectively. J_1 and J_2 are first nearest-neighboring (1^{st}) and second nearest-neighboring (2^{nd}) magnetic coupling parameters, respectively. The blue and yellow balls denote the spin-up and spin-down states of M atoms, respectively.

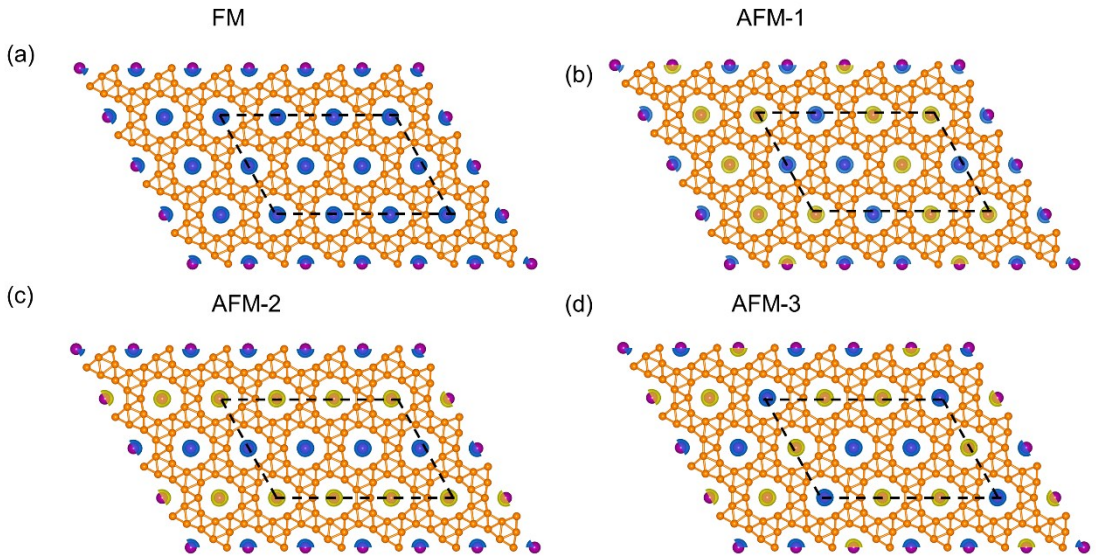

Fig. S7 Top views of spin density distributions of FM and AFM-i (i= 1, 2, 3) for 2-D MB_9. The blue and yellow colors indicate the spin-up and spin-down states (M= Mn, Cr, V), respectively. The isosurfaces of spin-up and spin-down densities were set as 0.02 e/a.u^3.

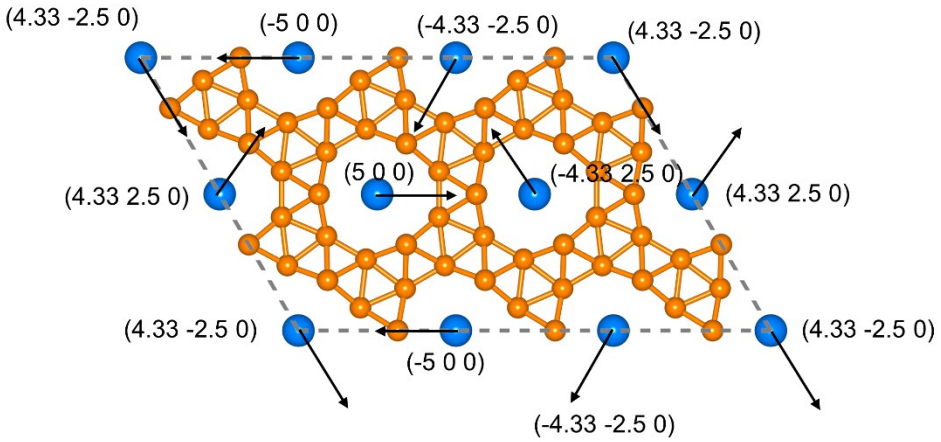

Fig. S8 Top views of noncollinear magnetic configuration of MB_9. The numbers are initial magnetic moments of M atoms in the calculation setting. The blue and orange balls indicate M (M= Mn, Cr, V) and B (B= boron) atoms, respectively.

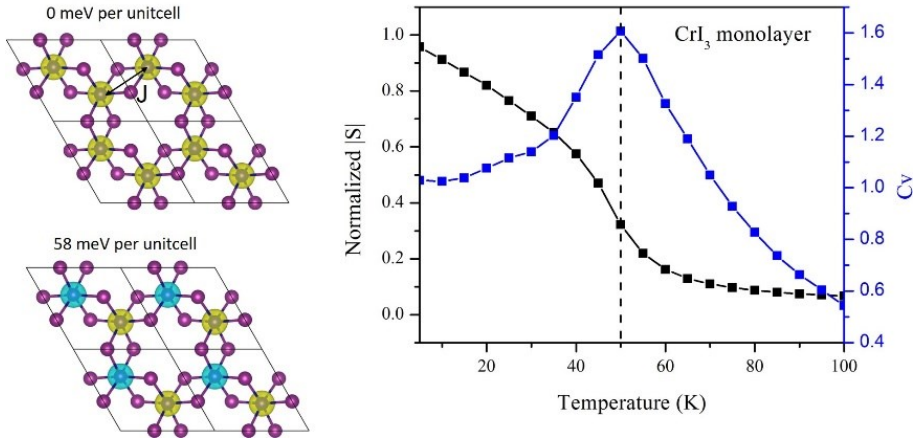

Fig. S9 Simulated normalized |S| (black data) and specific heat C_V (blue data) as a function of temperature for monolayer CrI_3.

For monolayer CrI_3, the energy difference between FM and AFM state per unit-cell is 58.0 meV. The J is obtained by $(E_{AFM}\text{-}E_{FM})/6S^2$, where **S** is the spin vector of each Cr atom. Using the normalized $|\mathbf{S}|=1$, J is 9.6 meV, which agrees with the value of 9.1 meV in same approach[S1]. The Curie temperature is about 50 K in Fig. S9.

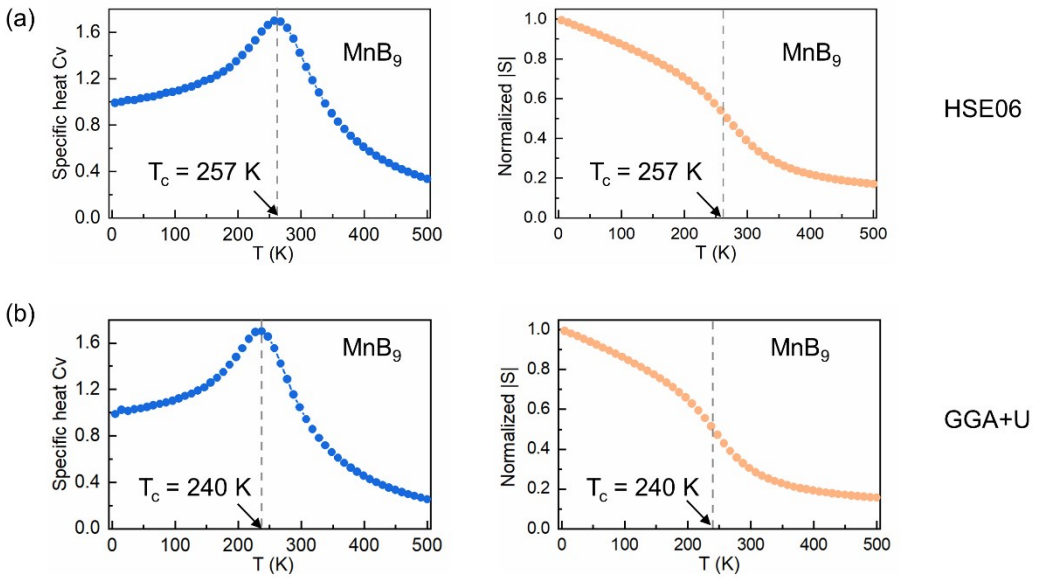

Fig. S10 Simulated specific heat C_V and simulated normalized |S| as a function of temperature for MnB_9 by employing the magnetic constant J_1 computed by a) HSE06 and b) GGA+U (U = 2.0 eV).

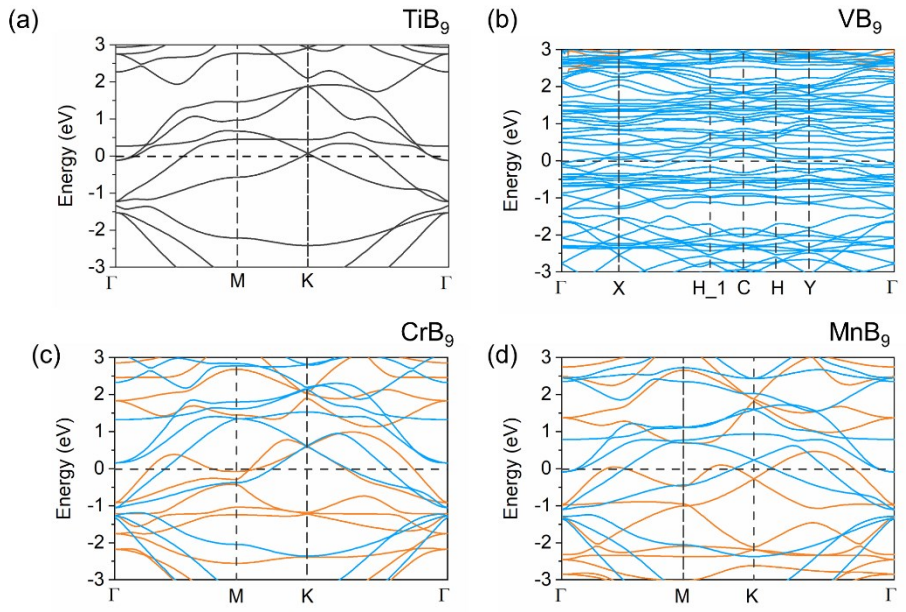

Fig. S11 Calculated band structure of a) TiB_9, b) VB_9, c) CrB_9, and d) MnB_9 in their magnetic ground state (respectively NM, AFM-3, FM, and FM) by employing PBE function. The Fermi level is set to zero. The orange and blue lines respectively stand for spin-up and spin-down channel.

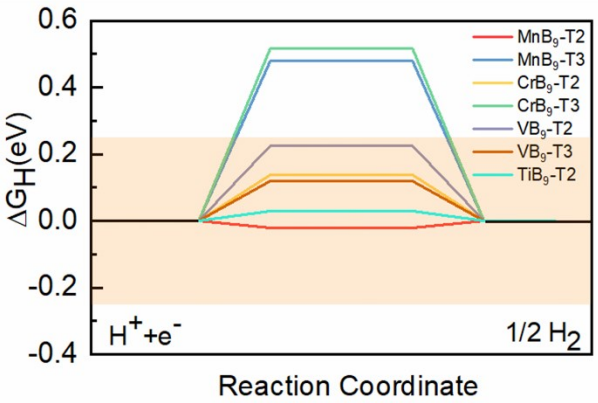

Fig. S12 Calculated Gibbs free energy (ΔG_H) of hydrogen adsorption for 2-D MB_9 monolayers at their relative stable adsorption sites.

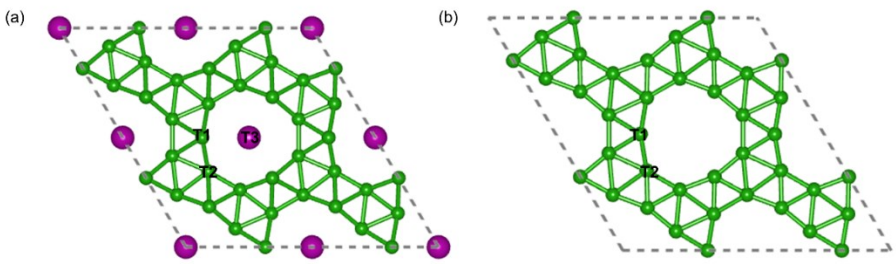

Fig. S13 The sites for calculating Bader charge in (a) MB_9; (b) B_9. (M= Ti, V, Cr and Mn)

Table S1 Structural parameters and calculated magnetic moments of 2-D MB_9. a (in Å) is lattice constant, SG is space group, l_1 and l_2 (in Å) are bond length between M and B_1 and B_2 atom, respectively, h (in Å) is layer height, M (in μB/f.u.) is the total magnetic moment per formula unit by using PBE method. ΔQ (in electron) is charge transfer from M to B atoms.

2-D	a	SG	l_1	l_2	h	M	ΔQ
MnB_9	5.801	P31m	2.182	2.433	0.366	3.27	1.48
CrB_9	5.802	P31m	2.177	2.428	0.365	2.82	1.20
VB_9	5.784	P31m	2.177	2.413	0.414	1.72	1.03
TiB_9	5.822	P31m	2.212	2.428	0.393	0.14	0.95

Table S2 Calculated elastic constants C (in GPa) of 2-D MB_9, graphene, MoS_2 and Ti_2C monolayers. The data from other calculations[S2, S3, S4] are listed in parentheses for comparison.

2-D	C_{11}	C_{22}	C_{44}	C_{12}
MnB_9	74.2	74.2	31.5	11.1
CrB_9	70.2	70.2	34.3	1.5
VB_9	81.2	81.2	38.9	3.2
TiB_9	78.1	78.1	40.2	-2.4
Graphene	351.6 (352.7)[2]	351.6 (352.7)[2]	145.4 (145.9)[2]	60.9 (60.9)[2]
MoS_2	131.1 (130)[3]	131.1 (130)[3]	49.3 (45)[3]	32.6 (40)[3]
Ti_2C	145.4 (137)[4]	145.4 (137)[4]	57.1 (53)[4]	31.2 (31.2)[4]

Table S3 Total energies (in eV) of nonmagnetic NM state, ferromagnetic FM state, three antiferromagnetic AFM-i states (i=1, 2, 3), and noncolinear antiferromagnetic state of MB_9 computed by GGA function. J_1 (in meV) is first nearest-neighboring (1^{st}) magnetic coupling constant. T_c (in K) is the magnetic critical temperature.

GGA	E_{NM}	E_{FM}	$E_{AFM\text{-}1}$	$E_{AFM\text{-}2}$	$E_{AFM\text{-}3}$	E_{ncl}	J_1	T_c
MnB_9	-388.216	**-393.371**	-392.875	-392.717	-392.715	-392.863	26.9	360
CrB_9	-391.605	**-396.734**	-396.696	-396.613	-396.625	-396.649	4.4	56
VB_9	-393.952	-396.351	-396.547	-396.531	**-396.577**	-396.550	-8.7	25
TiB_9	-394.357	-394.357	/	/	/	/	/	/

To obtain the magnetic coupling constant of monolayer MB_9 based on 2-D Heisenberg model, the energy in FM and three collinear AFM-i (i=1, 2, 3) states were used to compute J_1 using least-squares method. The corresponding Heisenberg Hamiltonian can be further written as:

$$E_{FM} = E_0 - 18J_1|S|^2 - A|S|^2$$

$$E_{AFM-1} = E_0 + 2J_1|S|^2 - A|S|^2$$

$$E_{AFM-2} = E_0 + 6J_1|S|^2 - A|S|^2$$

$$E_{AFM-3} = E_0 + 6J_1|S|^2 - A|S|^2$$

where E_0 is the energy of the nonmagnetic state, J_1 is the 1^{st} neighbor exchange coupling parameters. J_2 can be obtained by using a larger supercell, for example a 4x3x1, which was omitted in the present work, considering the second-nearest neighbor distance of these MB_9 is larger than 10 Å and its magnetic interaction is weak. A is anisotropy energy parameter, which is obtained by using the magnetic anisotropy energies as:

$$A = \frac{E_{hard}(axis) - E_{easy}(axis)}{|S|^2}$$

The calculation of least-square method is as follow. Here, 2-D MnB_9 is an example.

```
Y= [-393.371 -392.875 -392.717 -392.715]';

X= [1 18;1 -2;1 -6;1 -6];

B1_3 = pinv(X'*X)*X'*Y;

B2_3 = (X'*X)^-1*X'*Y;

B3_3 = [B1_3 B2_3]

Yp = X*B2_3;

err = [abs(Y-Yp)./Y]'

Ym = mean(Y);

SStot = sum((Y-Ym).^2);

SSreg = sum((Yp-Ym).^2);

SSres = sum((Yp-Y).^2);

R2 = 1-SSres/SStot

plot(Yp,Y,'o');

hold on

plot([min(Yp) max(Yp)],[min(Yp) max(Yp)])

hold off
```

The result of J_1 is as follow.

```
B3_3 = -392.8926 -392.8926
            -0.0269      -0.0269

err = 1.0e-04 *
       -0.1536      -0.9225      -0.3591      -0.4100

R2= 0.9937
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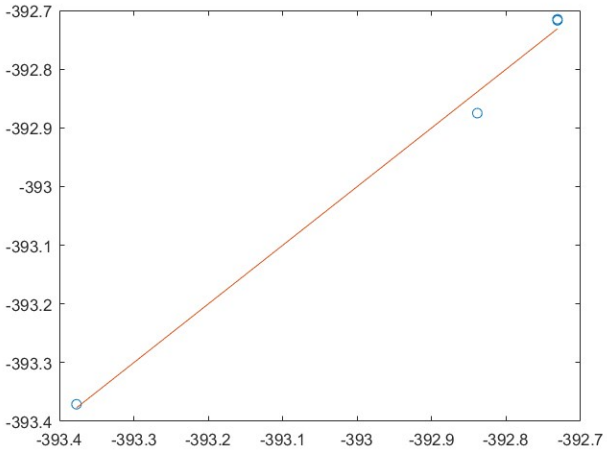

Table S4 Magnetic anisotropy energy MAE (in μeV) defined as the energy difference between the system with spin direction along the magnetic hard axis and the system with spin parallel to the magnetic easy axis. K_1 and K_2 (in μeV) anisotropy constants.

2-D	MAE	$K_{1(XZ)}$	$K_{2(XZ)}$	$K_{1(YZ)}$	$K_{2(YZ)}$	Easy axis
MnB_9	465.06	468.47	-4.04	468.47	-4.04	out-of-plane
CrB_9	332.80	332.99	-0.21	332.99	-0.21	out-of-plane
VB_9	58.47	55.69	-0.04	50.62	0.05	out-of-plane

Table S5 Total energies of FM and AFM states (in eV) of 2×1×1 MnB_9 computed by HSE06 and GGA+U function (U = 1.0, 2.0, 3.0, 4.0, 5.0 eV). M (in μB) is total magnetic moment of 2×1×1 MnB_9.

MnB_9	E_{FM}	E_{AFM}	M	J_1
GGA	-131.218	-131.019	6.58	24.8
U=1 eV	-129.797	-129.694	7.56	12.8
U=2 eV	-128.711	-128.578	8.00	16.6
U=3 eV	-127.747	-127.616	8.02	16.4
U=4 eV	-126.905	-126.768	8.14	17.2
U=5 eV	-126.147	-126.012	8.29	16.9
HSE06	-151.381	-151.233	8.00	18.5

Table S6 Calculated MAEs along different magnetic directions of MnB_9.

MnB_9	001	100	010	110	111	MAE	Easy axis
U=2	-64.326147	-64.325967	-64.325967	-64.325967	-64.326024	180	001

The corresponding Heisenberg Hamiltonian can be further written as:

$$E_{FM} = E_0 - 6J_1|S|^2 - A|S|^2$$

$$E_{AFM} = E_0 + 2J_1|S|^2 - A|S|^2$$

where E_0 is the energy of the nonmagnetic state, J_1 is the 1st neighbor exchange coupling parameters.

Table S7 Calculated total energies (in eV) of all possible H adsorption configurations on MB_9 after structural optimization.

	T1	T2	T3	B1	B2	B3	B4	B5	H1	H2	H3
TiB_9	-266.581	-266.569	-266.581	-266.569	-266.569	-266.581	-266.569	-266.569	-266.569	-266.569	-266.569
VB_9	-268.213	-267.785	-267.812	-268.213	-268.213	-268.213	-268.213	-268.213	-268.213	-268.213	-267.785
CrB_9	-268.363	-268.043	-267.588	-268.363	-268.363	-268.363	-268.363	-268.363	-268.363	-268.363	-268.043
MnB_9	-266.197	-265.981	-265.397	-266.197	-266.197	-266.197	-266.197	-266.197	-266.197	-266.197	-265.981

Table S8 Calculate results of Bader charge (in electron) on each atom for MB_9 and B_9 within 2×2×1 supercell (M= Ti, V, Cr, Mn). ΔQ (in electron) is the changed charge of boron atom after M atom embedding into B_9 monolayer.

	MnB_9	CrB_9	VB_9	TiB_9	B_9
T1	3.35	3.49	3.39	3.56	2.64
T2	2.95	2.87	3.01	2.95	3.21
T3	12.04	10.95	11.78	10.50	/
ΔQ1	0.71	0.85	0.75	0.92	/
ΔQ2	-0.26	-0.34	-0.20	-0.26	/
ΔQ3	0.96	0.95	1.22	1.50	/
electron	13.00	12.00	13.00	12.00	3.00

References

[S1] Y. Zhu, X. H. Kong, T. D. Rhone, H. Guo, *Phys. Rev. Mater*, 2018, **2**, 081001(R).

[S2] R. C. Andrew, R. E. Mapasha, A. M. Ukpong, N. Chetty, *Phys. Rev. B*, 2012, **85**, 125428.

[S3] R. C. Cooper, C. Lee, C. A. Marianetti, X. D. Wei, J. Hone, J. W. Kysar, *Phys. Rev. B*, 2013, **87**, 035423.

[S4] S. Wang, J. X. Li, Y. L. Du, C. Cui. *Comp. Mater. Sci*, 2014, **83**, 290.