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 ($E_{\text{coh}}$) 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 $\beta_{12}$, $\chi_3$, 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 different antiferromagnetic states, respectively. $J_1$ and $J_2$ are first nearest-neighboring (1$^{\text{st}}$) and second nearest-neighboring (2$^{\text{nd}}$) 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 MBs. 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 MBs. 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.
For monolayer CrI$_3$, the energy difference between FM and AFM state per unit-cell is 58.0 meV. The $J$ is obtained by $(E_{AFM} - E_{FM})/6S^2$, where $S$ is the spin vector of each Cr atom. Using the normalized $|S|=1$, $J$ is 9.6 meV, which agrees with the value of 9.1 meV in same approach$^{51}$. The Curie temperature is about 50 K in Fig. S9.

**Fig. S9** Simulated normalized $|S|$ (black data) and specific heat $C_V$ (blue data) as a function of temperature for monolayer CrI$_3$.

**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 ($\Delta G_{\text{H}}$) 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.

<table>
<thead>
<tr>
<th>2-D</th>
<th>$a$</th>
<th>SG</th>
<th>$l_1$</th>
<th>$l_2$</th>
<th>$h$</th>
<th>$M$</th>
<th>ΔQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnB$_9$</td>
<td>5.801</td>
<td>P31m</td>
<td>2.182</td>
<td>2.433</td>
<td>0.366</td>
<td>3.27</td>
<td>1.48</td>
</tr>
<tr>
<td>CrB$_9$</td>
<td>5.802</td>
<td>P31m</td>
<td>2.177</td>
<td>2.428</td>
<td>0.365</td>
<td>2.82</td>
<td>1.20</td>
</tr>
<tr>
<td>VB$_9$</td>
<td>5.784</td>
<td>P31m</td>
<td>2.177</td>
<td>2.413</td>
<td>0.414</td>
<td>1.72</td>
<td>1.03</td>
</tr>
<tr>
<td>TiB$_9$</td>
<td>5.822</td>
<td>P31m</td>
<td>2.212</td>
<td>2.428</td>
<td>0.393</td>
<td>0.14</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table S2  Calculated elastic constants C (in GPa) of 2-D MB$_9$, graphene, MoS$_2$ and Ti$_2$C monolayers. The data from other calculations$^{32,33,34}$ are listed in parentheses for comparison.

<table>
<thead>
<tr>
<th>2-D</th>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{44}$</th>
<th>$C_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnB$_9$</td>
<td>74.2</td>
<td>74.2</td>
<td>31.5</td>
<td>11.1</td>
</tr>
<tr>
<td>CrB$_9$</td>
<td>70.2</td>
<td>70.2</td>
<td>34.3</td>
<td>1.5</td>
</tr>
<tr>
<td>VB$_9$</td>
<td>81.2</td>
<td>81.2</td>
<td>38.9</td>
<td>3.2</td>
</tr>
<tr>
<td>TiB$_9$</td>
<td>78.1</td>
<td>78.1</td>
<td>40.2</td>
<td>-2.4</td>
</tr>
<tr>
<td>Graphene</td>
<td>351.6 (352.7)$^2$</td>
<td>351.6 (352.7)$^2$</td>
<td>145.4 (145.9)$^2$</td>
<td>60.9 (60.9)$^2$</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>131.1 (130)$^3$</td>
<td>131.1 (130)$^3$</td>
<td>49.3 (45)$^3$</td>
<td>32.6 (40)$^3$</td>
</tr>
<tr>
<td>Ti$_2$C</td>
<td>145.4 (137)$^4$</td>
<td>145.4 (137)$^4$</td>
<td>57.1 (53)$^4$</td>
<td>31.2 (31.2)$^4$</td>
</tr>
</tbody>
</table>
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 MB₉ computed by GGA function. $J_1$ (in meV) is first nearest-neighboring (1ˢᵗ) magnetic coupling constant. $T_c$ (in K) is the magnetic critical temperature.

<table>
<thead>
<tr>
<th>GGA</th>
<th>$E_{NM}$</th>
<th>$E_{FM}$</th>
<th>$E_{AFM-1}$</th>
<th>$E_{AFM-2}$</th>
<th>$E_{AFM-3}$</th>
<th>$E_{ncl}$</th>
<th>$J_1$</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrB₉</td>
<td>-391.605</td>
<td>-396.734</td>
<td>-396.696</td>
<td>-396.613</td>
<td>-396.649</td>
<td>4.4</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>VB₉</td>
<td>-393.952</td>
<td>-396.351</td>
<td>-396.547</td>
<td>-396.531</td>
<td>-396.577</td>
<td>-396.550</td>
<td>-8.7</td>
<td>25</td>
</tr>
<tr>
<td>TiB₉</td>
<td>-394.357</td>
<td>-394.357</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

To obtain the magnetic coupling constant of monolayer MB₉ 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:

$$E_{FM} = E_0 - 18J_1|S|^2 - A|S|^4$$
$$E_{AFM-1} = E_0 + 2J_1|S|^2 - A|S|^4$$
$$E_{AFM-2} = E_0 + 6J_1|S|^2 - A|S|^4$$
$$E_{AFM-3} = E_0 + 6J_1|S|^2 - A|S|^4$$

where $E_0$ is the energy of the nonmagnetic state, $J_1$ is the 1ˢᵗ 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 MB₉ 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.

\[
Y = [-393.371, -392.875, -392.717, -392.715]';
\]

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

\[
B1_3 = \text{pinv}(X'*X)*X'*Y;
\]

\[
B2_3 = (X'*X)^{-1}*X'*Y;
\]

\[
B3_3 = [B1_3 B2_3]
\]

\[
Yp = X*B2_3;
\]

\[
\text{err} = \lbrack \text{abs}(Y-Yp)./Y\rbrack'
\]

\[
Ym = \text{mean}(Y);
\]

\[
\text{SStot} = \text{sum}((Y-Ym).^2);
\]

\[
\text{SSreg} = \text{sum}((Yp-Ym).^2);
\]

\[
\text{SSres} = \text{sum}((Yp-Y).^2);
\]

\[
R2 = 1-\text{SSres}/\text{SStot}
\]

\[
\text{plot}(Yp,Y,'o');
\]

\[
\text{hold on}
\]

\[
\text{plot([min(Yp) max(Yp)], [min(Yp) max(Yp)])}
\]

\[
\text{hold off}
\]

The result of \(J_1\) is as follow.

\[
B3_3 = -392.8926 -392.8926
\]

\[
-0.0269 -0.0269
\]

\[
\text{err} = 1.0e-04 *
\]

\[
-0.1536 -0.9225 -0.3591 -0.4100
\]

\[
R2 = 0.9937
\]
**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.

<table>
<thead>
<tr>
<th>2-D</th>
<th>MAE</th>
<th>$K_{1(XZ)}$</th>
<th>$K_{2(XZ)}$</th>
<th>$K_{1(YZ)}$</th>
<th>$K_{2(YZ)}$</th>
<th>Easy axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnB$_9$</td>
<td>465.06</td>
<td>468.47</td>
<td>-4.04</td>
<td>468.47</td>
<td>-4.04</td>
<td>out-of-plane</td>
</tr>
<tr>
<td>CrB$_9$</td>
<td>332.80</td>
<td>332.99</td>
<td>-0.21</td>
<td>332.99</td>
<td>-0.21</td>
<td>out-of-plane</td>
</tr>
<tr>
<td>VB$_9$</td>
<td>58.47</td>
<td>55.69</td>
<td>-0.04</td>
<td>50.62</td>
<td>0.05</td>
<td>out-of-plane</td>
</tr>
</tbody>
</table>

**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$_9$.

<table>
<thead>
<tr>
<th>MnB$_9$</th>
<th>$E_{FM}$</th>
<th>$E_{AFM}$</th>
<th>$M$</th>
<th>$J_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>-131.218</td>
<td>-131.019</td>
<td>6.58</td>
<td>24.8</td>
</tr>
<tr>
<td>U=1 eV</td>
<td>-129.797</td>
<td>-129.694</td>
<td>7.56</td>
<td>12.8</td>
</tr>
<tr>
<td>U=2 eV</td>
<td>-128.711</td>
<td>-128.578</td>
<td>8.00</td>
<td>16.6</td>
</tr>
<tr>
<td>U=3 eV</td>
<td>-127.747</td>
<td>-127.616</td>
<td>8.02</td>
<td>16.4</td>
</tr>
<tr>
<td>U=4 eV</td>
<td>-126.905</td>
<td>-126.768</td>
<td>8.14</td>
<td>17.2</td>
</tr>
<tr>
<td>U=5 eV</td>
<td>-126.147</td>
<td>-126.012</td>
<td>8.29</td>
<td>16.9</td>
</tr>
<tr>
<td>HSE06</td>
<td>-151.381</td>
<td>-151.233</td>
<td>8.00</td>
<td>18.5</td>
</tr>
</tbody>
</table>
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 S6 Calculated MAEs along different magnetic directions of MnB9.

<table>
<thead>
<tr>
<th>MnB9</th>
<th>001</th>
<th>100</th>
<th>010</th>
<th>110</th>
<th>111</th>
<th>MAE</th>
<th>Easy axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>U=2</td>
<td>-64.326147</td>
<td>-64.325967</td>
<td>-64.325967</td>
<td>-64.325967</td>
<td>-64.326024</td>
<td>180</td>
<td>001</td>
</tr>
</tbody>
</table>

### Table S7 Calculated total energies (in eV) of all possible H adsorption configurations on MB9 after structural optimization.

<table>
<thead>
<tr>
<th></th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB9</td>
<td>-266.581</td>
<td>-266.569</td>
<td>-266.581</td>
<td>-266.569</td>
<td>-266.581</td>
<td>-266.569</td>
<td>-266.569</td>
<td>-266.569</td>
<td>-266.569</td>
<td>-266.569</td>
<td>-266.569</td>
</tr>
<tr>
<td>MnB9</td>
<td>-266.197</td>
<td>-265.981</td>
<td>-265.397</td>
<td>-266.197</td>
<td>-266.197</td>
<td>-266.197</td>
<td>-266.197</td>
<td>-266.197</td>
<td>-266.197</td>
<td>-266.197</td>
<td>-265.981</td>
</tr>
</tbody>
</table>

### Table S8 Calculate results of Bader charge (in electron) on each atom for MB9 and B9 within 2×2×1 supercell (M= Ti, V, Cr, Mn). \( \Delta Q \) (in electron) is the changed charge of boron atom after M atom embedding into B9 monolayer.

<table>
<thead>
<tr>
<th></th>
<th>MnB9</th>
<th>CrB9</th>
<th>VB9</th>
<th>TiB9</th>
<th>B9</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>3.35</td>
<td>3.49</td>
<td>3.39</td>
<td>3.56</td>
<td>2.64</td>
</tr>
<tr>
<td>T2</td>
<td>2.95</td>
<td>2.87</td>
<td>3.01</td>
<td>2.95</td>
<td>3.21</td>
</tr>
<tr>
<td>T3</td>
<td>12.04</td>
<td>10.95</td>
<td>11.78</td>
<td>10.50</td>
<td>/</td>
</tr>
<tr>
<td>( \Delta Q_1 )</td>
<td>0.71</td>
<td>0.85</td>
<td>0.75</td>
<td>0.92</td>
<td>/</td>
</tr>
<tr>
<td>( \Delta Q_2 )</td>
<td>-0.26</td>
<td>-0.34</td>
<td>-0.20</td>
<td>-0.26</td>
<td>/</td>
</tr>
<tr>
<td>( \Delta Q_3 )</td>
<td>0.96</td>
<td>0.95</td>
<td>1.22</td>
<td>1.50</td>
<td>/</td>
</tr>
<tr>
<td>electron</td>
<td>13.00</td>
<td>12.00</td>
<td>13.00</td>
<td>12.00</td>
<td>3.00</td>
</tr>
</tbody>
</table>
References


