Electronic Supplementary Material (ESI) for RSC Advances.

Structures, electronic and spectral properties of single-atom transition metal-doped boron clusters MB_{24}^- (M=Sc, Ti, V, Cr, Mn, Fe, Co, and Ni)

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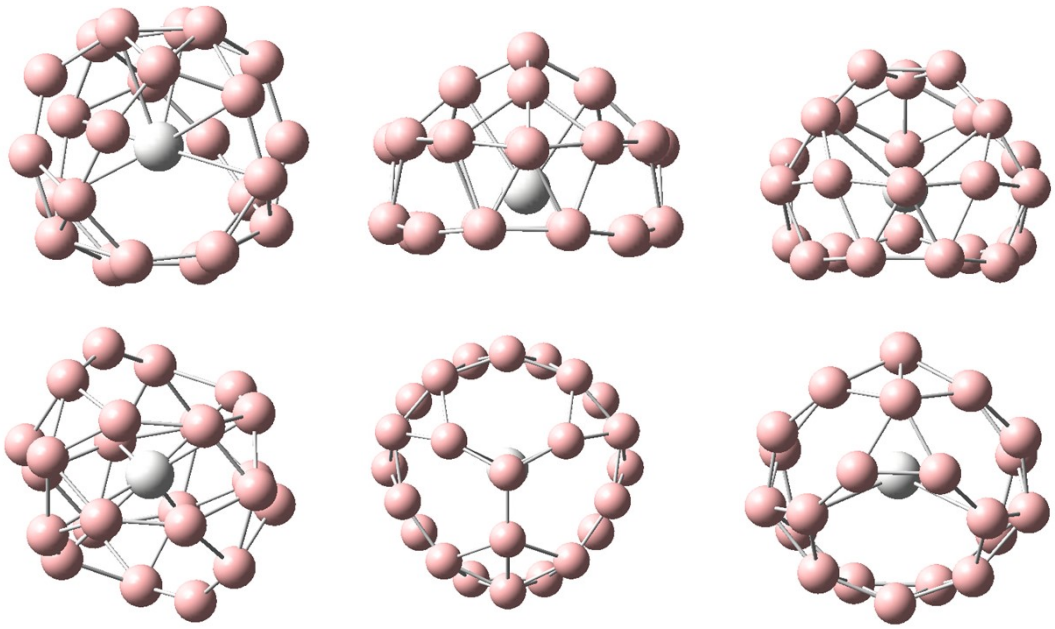

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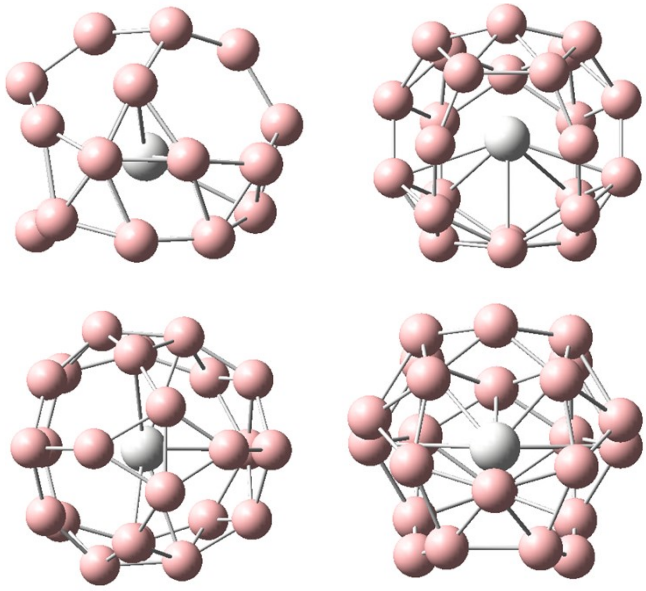
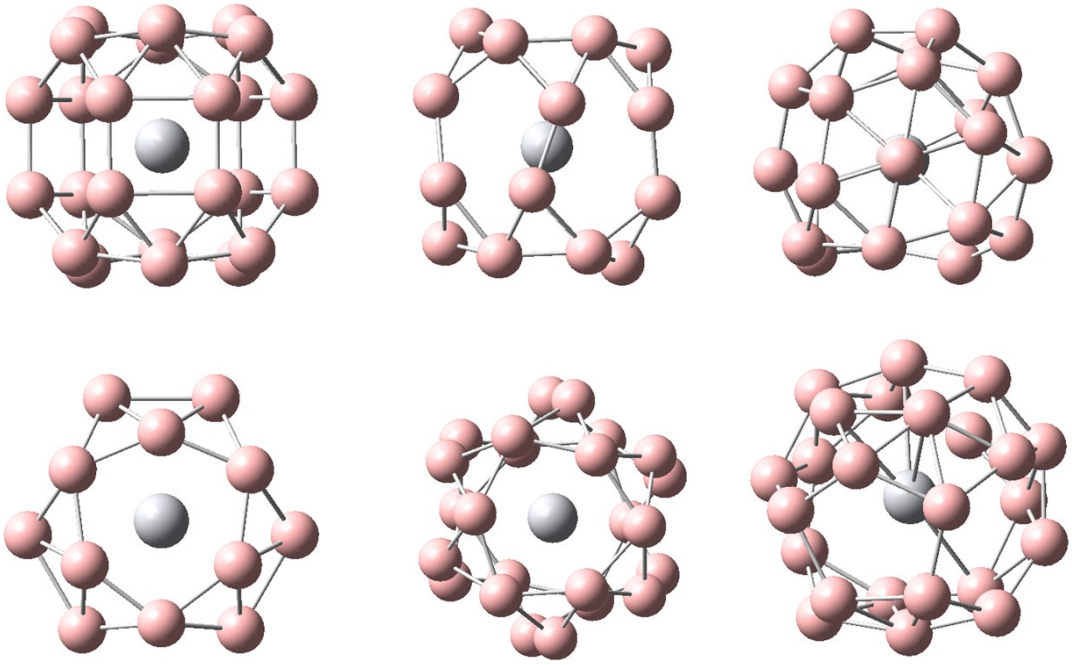
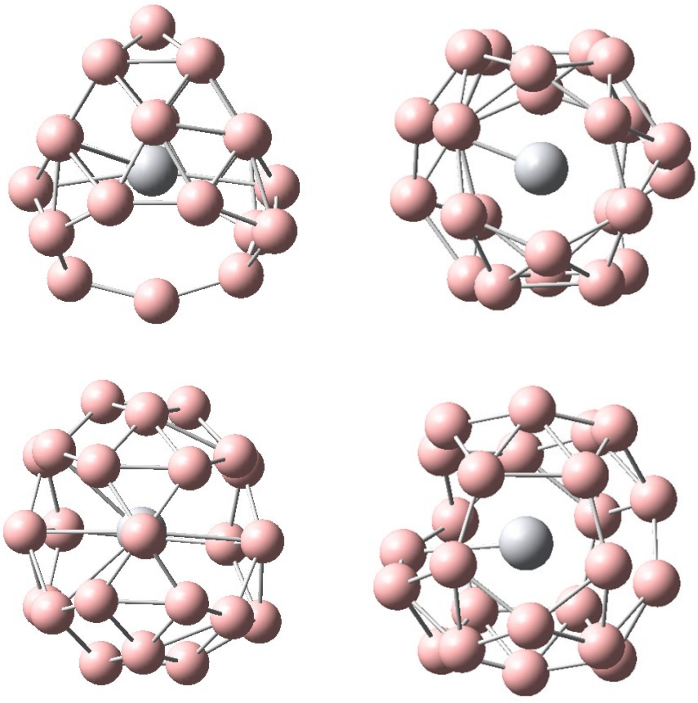


(d) (0.50)[0.48]{0.52}　　(e) (0.85)[0.86]{ 0.83}

Figure. S1 Low-lying isomers of doped boron clusters ScB_{24}^-. Values in parentheses are the relative energies (eV) of the five low-energy isomers for ScB_{24}^- at the PBE0/6-311+G* level. Values in square brackets are the relative energies (eV) of the five low-energy isomers for ScB_{24}^- at the TPSSH/6-311+G* level. Values in curly brackets are the relative energies (eV) of the five low-energy isomers for ScB_{24}^- at the PBE0-D3/6-311+G* level. The upper row is side view and the bottom row is top view.

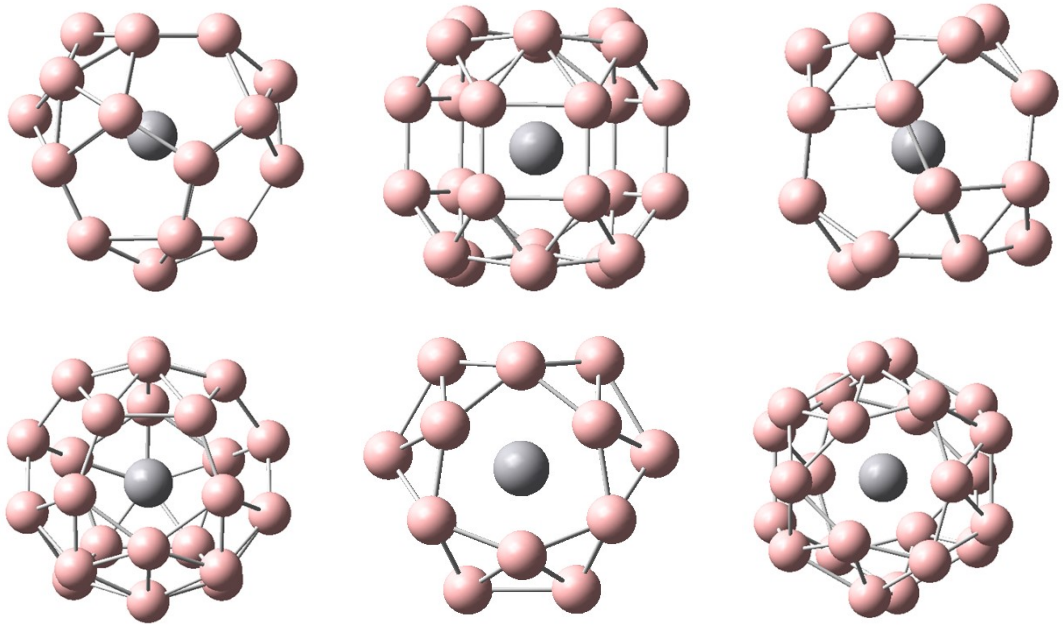


(a) (0.00)[0.00]{0.00}　(b) (0.37)[0.36]{0.36}　(c) (0.55)[0.39]{0.52}

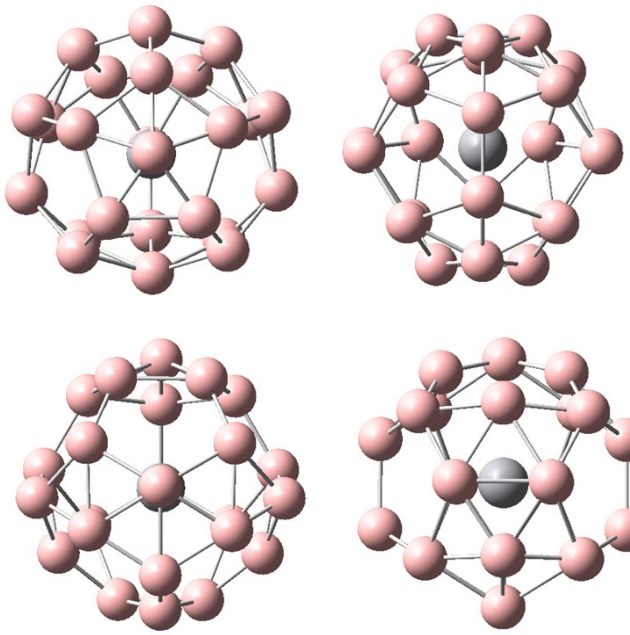


(d) (0.57)[0.49]{0.56}　(e) (0.61)[0.47]{0.59}

Figure.S2 Low-lying isomers of doped boron clusters TiB_{24}^-. Values in parentheses are the relative energies (eV) of the five low-energy isomers for TiB_{24}^- at the PBE0/6-311+G* level. Values in square brackets are the relative energies (eV) of the five low-energy isomers for TiB_{24}^- at the TPSSH/6-311+G* level. Values in curly brackets are the relative energies (eV) of the five low-energy isomers for TiB_{24}^- at the PBE0-D3/6-311+G* level. The upper row is side view and the bottom row is top view.

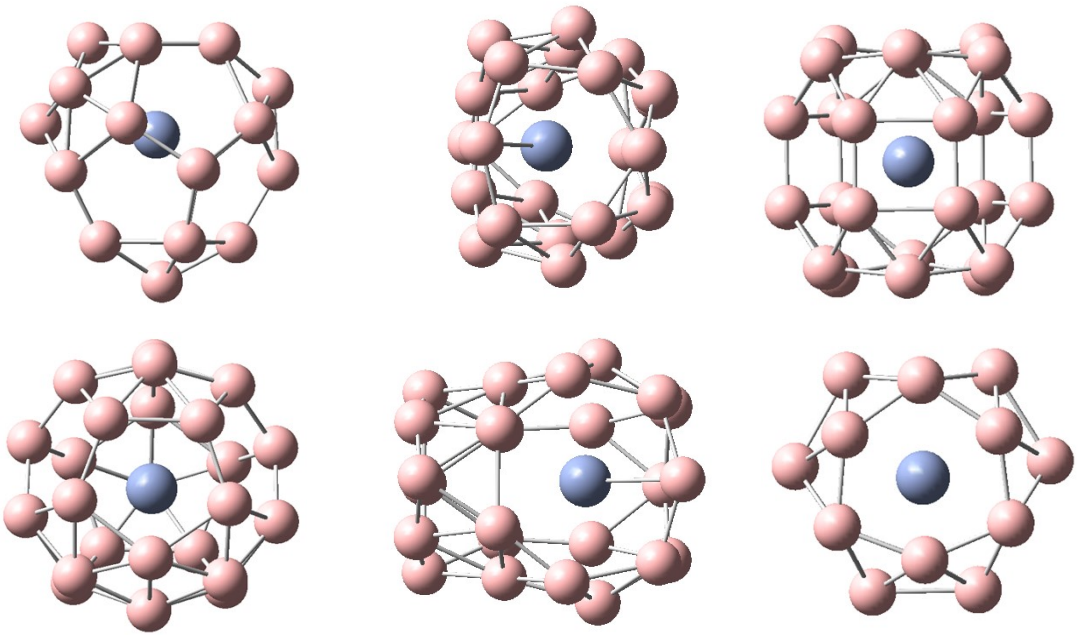


(a) (0.00)[0.00]{0.00}　　(b) (0.25)[0.27]{0.28}　　(c) (0.38)[0.38]{0.38}



(d) (0.47)[0.44]{0.47}　　(e) (0.49)[0.45]{0.49}

Figure. S3 Low-lying isomers of doped boron clusters VB_{24}^-. Values in parentheses are the relative energies (eV) of the five low-energy isomers for VB_{24}^- at the PBE0/6-311+G* level. Values in square brackets are the relative energies (eV) of the five low-energy isomers for VB_{24}^- at the TPSSH/6-311+G* level. Values in curly brackets are the relative energies (eV) of the five low-energy isomers for VB_{24}^- at the PBE0-D3/6-311+G* level. The upper row is side view and the bottom row is top view.



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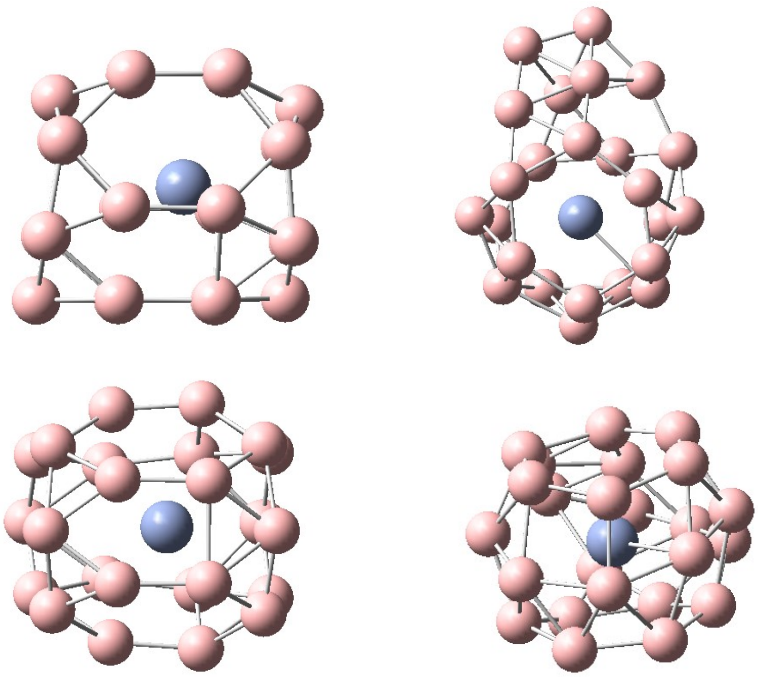
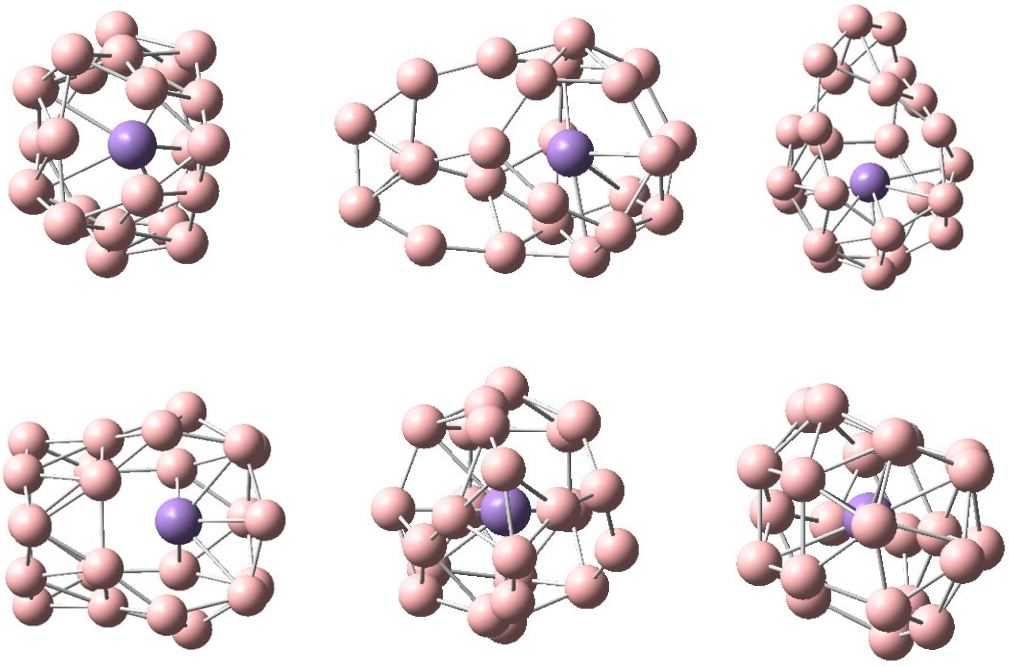
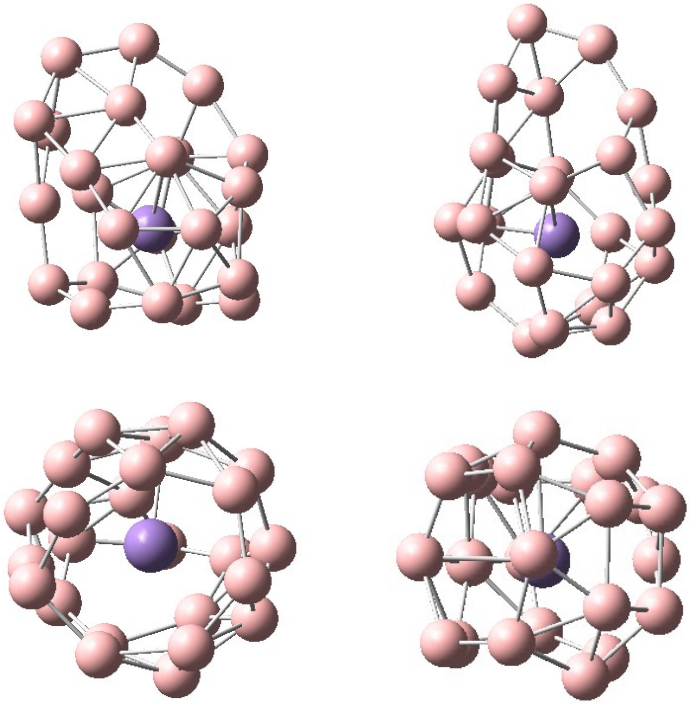


(d) (0.08)[0.07]{0.11}　　(e) (0.25)[0.17]{0.30}

Figure. S4 Low-lying isomers of doped boron clusters CrB_{24}^-. Values in parentheses are the relative energies (eV) of the five low-energy isomers for CrB_{24}^- at the PBE0/6-311+G* level. Values in square brackets are the relative energies (eV) of the five low-energy isomers for CrB_{24}^- at the TPSSH/6-311+G* level. Values in curly brackets are the relative energies (eV) of the five low-energy isomers for CrB_{24}^- at the PBE0-D3/6-311+G* level. The upper row is side view and the bottom row is top view.

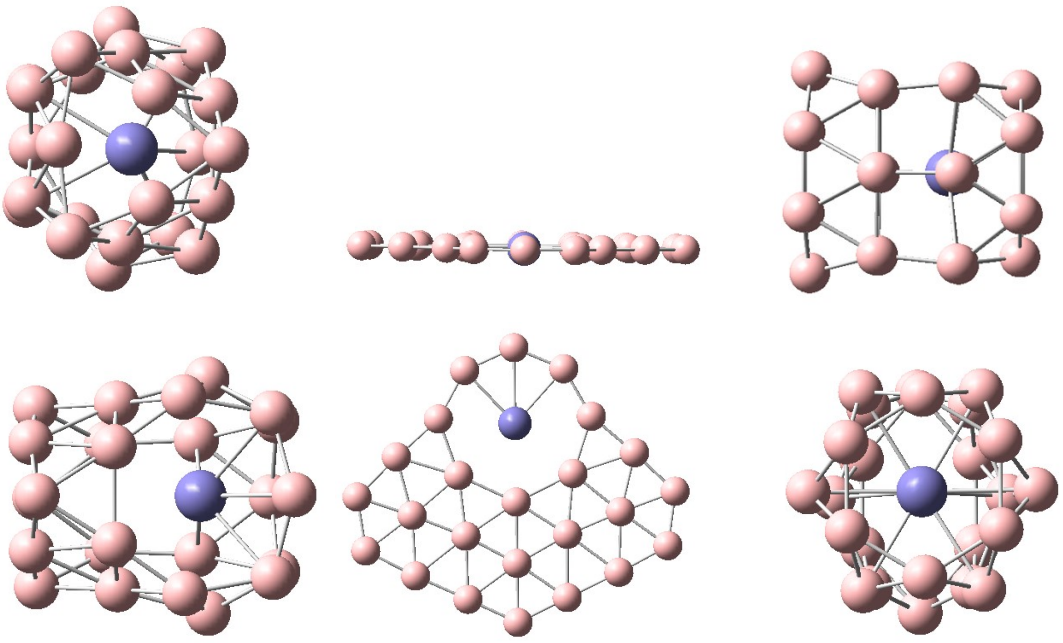


(a) (0.00)[0.00]{0.00}　　(b) (0.18)[0.07]{0.25}　　(c) (0.21)[0.07]{0.21}

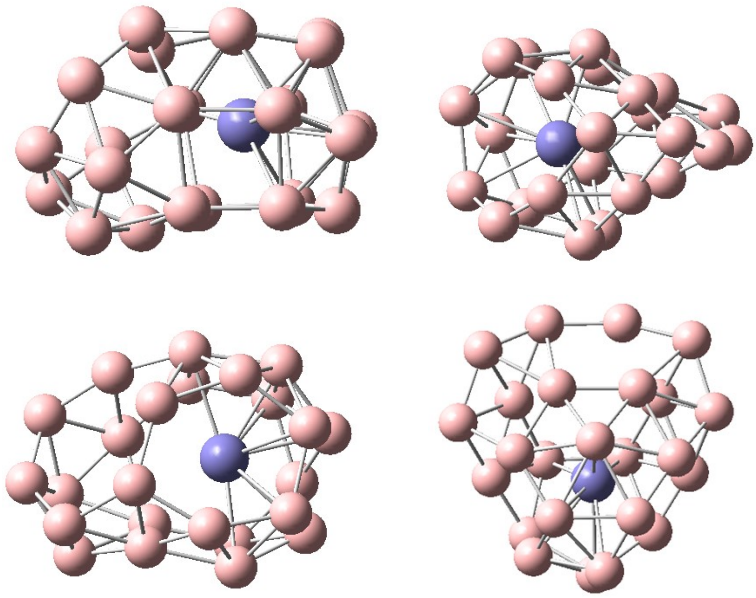


(d) (0.47)[0.30]{0.47}　　(e) (0.61)[0.43]{0.65}

Figure. S5 Low-lying isomers of doped boron clusters MnB_{24}^-. Values in parentheses are the relative energies (eV) of the five low-energy isomers for MnB_{24}^- at the PBE0/6-311+G* level. Values in square brackets are relative energies (eV) of the five low-energy isomers for MnB_{24}^- at the TPSSH/6-311+G* level. Values in curly brackets are the relative energies (eV) of the five low-energy isomers for MnB_{24}^- at the PBE0-D3/6-311+G* level. The upper row is side view and the bottom row is top view.

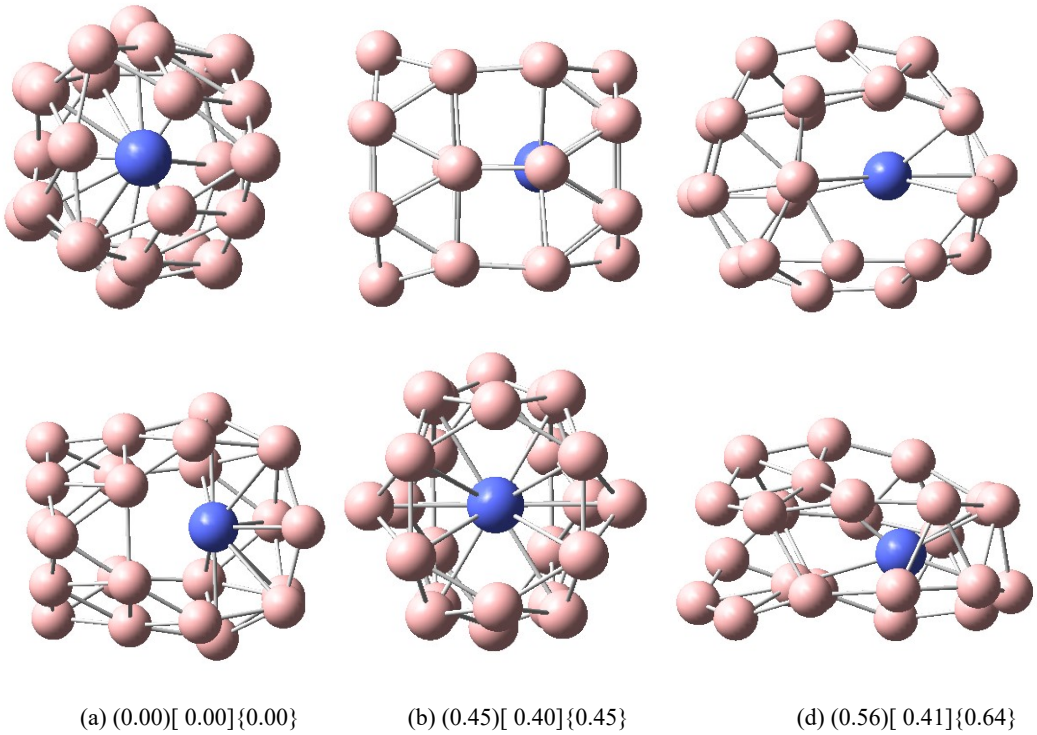


(a) (0.00)[0.00]{0.00}　　(b) (0.65)[1.19]{1.17}　　(c) (0.90)[0.93]{0.91}

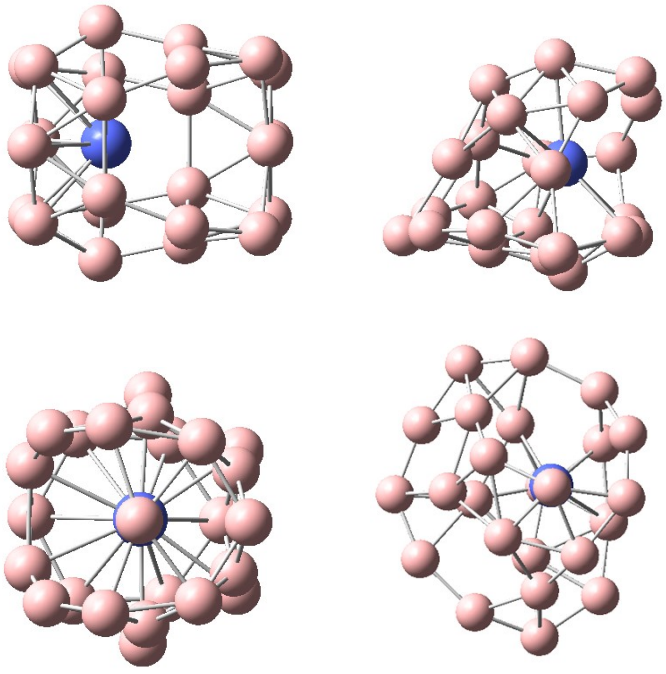


(d) (0.91)[0.86]{0.94}　　(e) (1.01)[0.79]{1.03}

Figure. S6 Low-lying isomers of doped boron clusters FeB_{24}^-. Values in parentheses are the relative energies (eV) of the five low-energy isomers for FeB_{24}^- at the PBE0/6-311+G* level. Values in square brackets are relative energies (eV) of the five low-energy isomers for FeB_{24}^- at the TPSSH/6-311+G* level. Values in curly brackets are the relative energies (eV) of the five low-energy isomers for FeB_{24}^- at the PBE0-D3/6-311+G* level. The upper row is side view and the bottom row is top view.

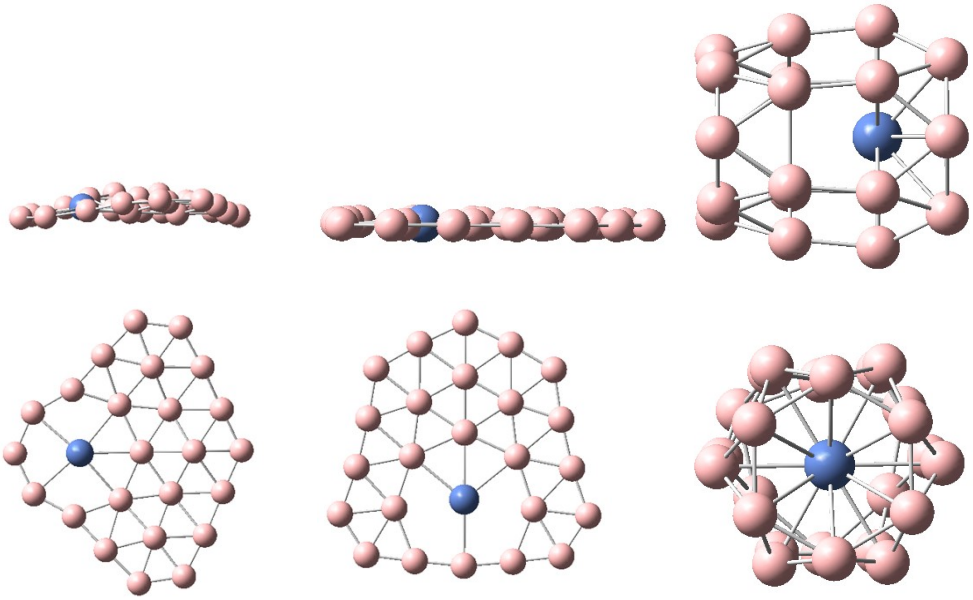


(a) (0.00)[0.00]{0.00}　　(b) (0.45)[0.40]{0.45}　　(d) (0.56)[0.41]{0.64}

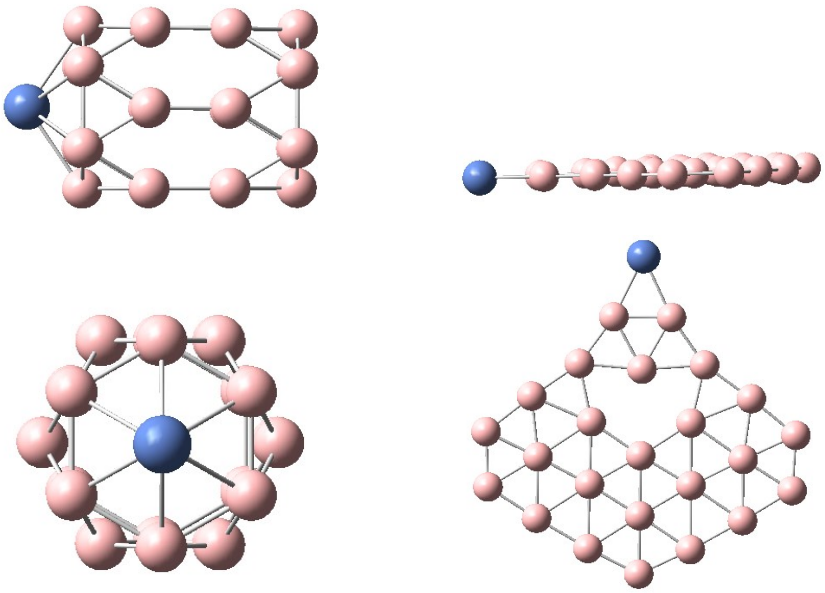


(c) (0.76)[0.68]{0.77}　　(e) (0.77)[0.55]{0.78}

Figure. S7 Low-lying isomers of doped boron clusters CoB_{24}^-. Values in parentheses are the relative energies (eV) of the five low-energy isomers for CoB_{24}^- at the PBE0/6-311+G* level. Values in square brackets are relative energies (eV) of the five low-energy isomers for CoB_{24}^- at the TPSSH/6-311+G* level. Values in curly brackets are the relative energies (eV) of the five low-energy isomers for CoB_{24}^- at the PBE0-D3/6-311+G* level. The upper row is side view and the bottom row is top view.

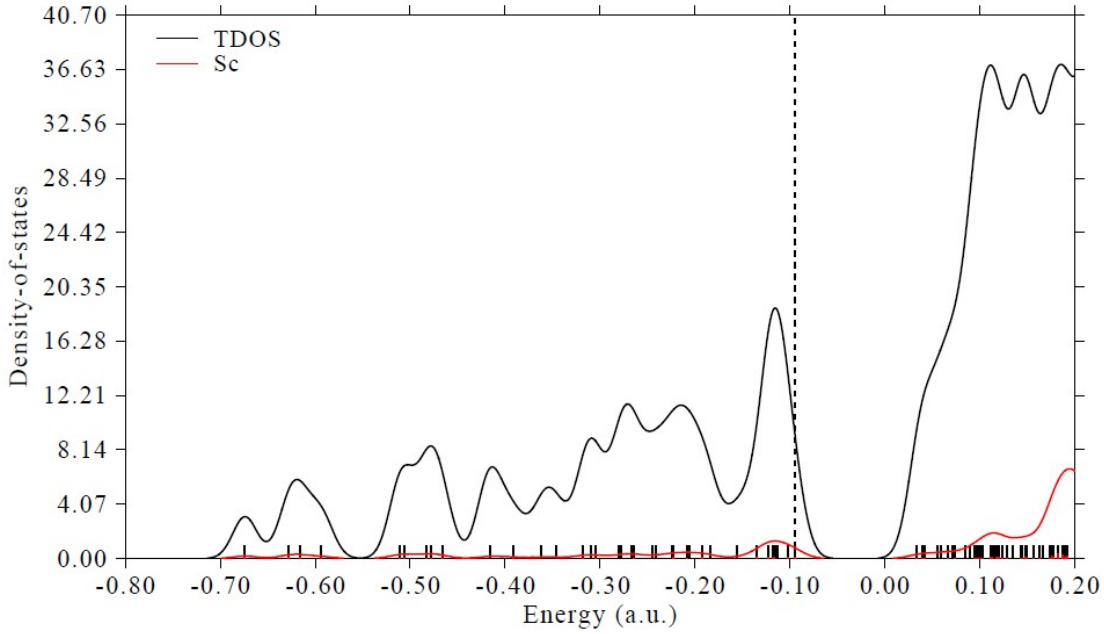


(a) (0.00)[0.00]{0.00}　　(b) (0.52)[0.66]{0.53}　　(c) (0.84)[0.84]{0.35}

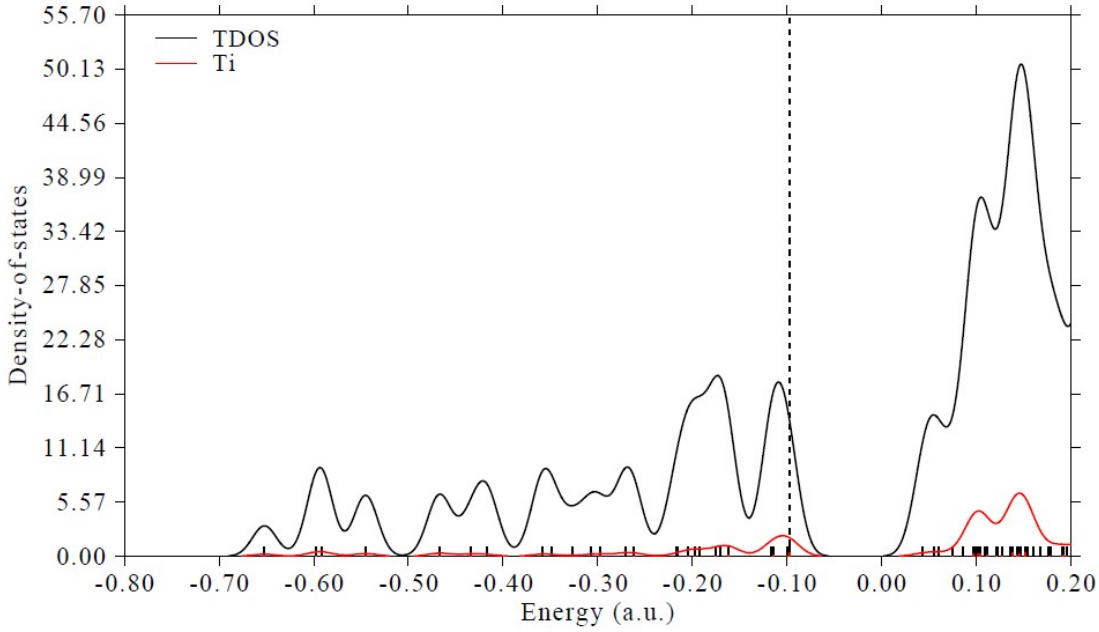


(d) (0.85)[1.36]{0.42}　　(e) (0.86)[1.37]{0.90}

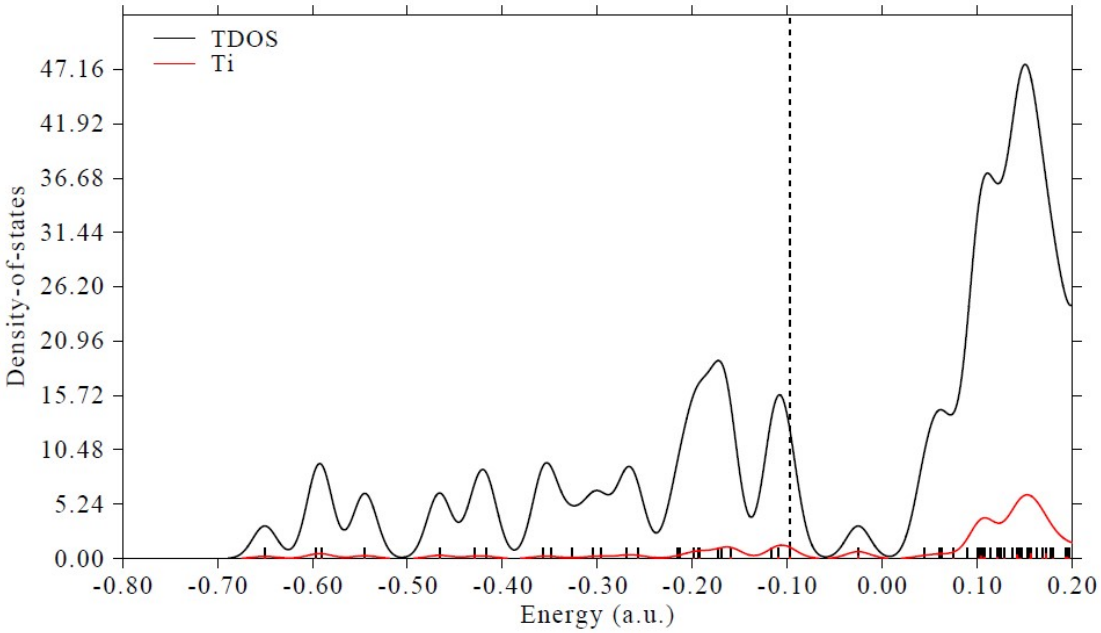
Figure. S8 Low-lying isomers of doped boron clusters NiB_{24}^-. Values in parentheses are the relative energies (eV) of the five low-energy isomers for NiB_{24}^- at the PBE0/6-311+G* level. Values in square brackets are relative energies (eV) of the five low-energy isomers for NiB_{24}^- at the TPSSH/6-311+G* level. Values in curly brackets are the relative energies (eV) of the five low-energy isomers for NiB_{24}^- at the PBE0-D3/6-311+G* level. The upper row is side view and the bottom row is top view.


TDOS
Sc
Density-of-states
40.70
36.63
32.56
28.49
24.42
20.35
16.28
12.21
8.14
4.07
0.00
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

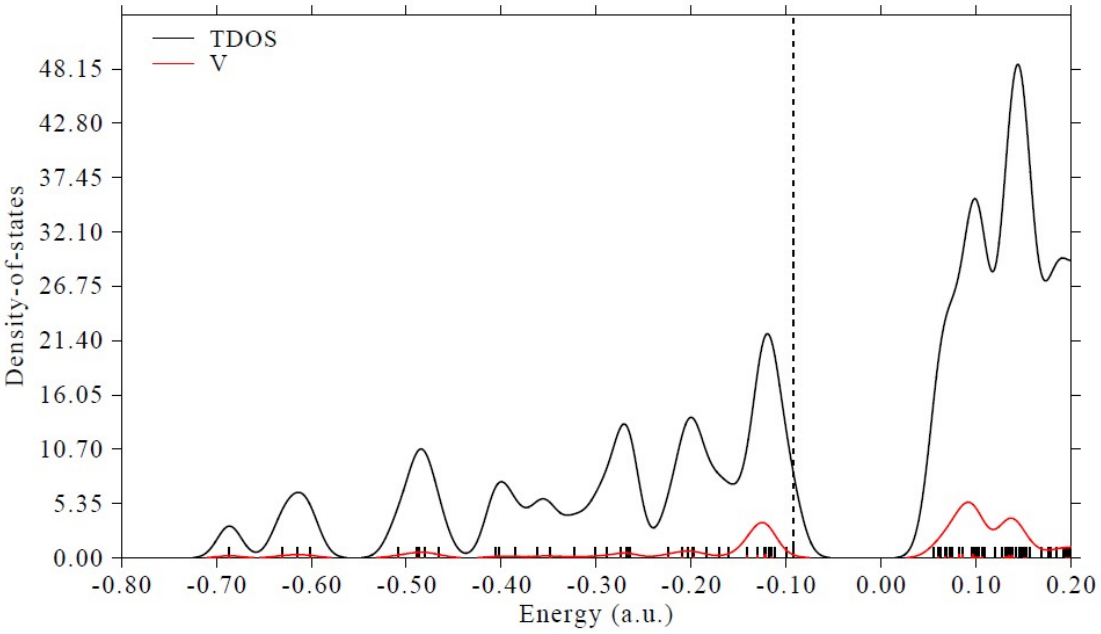
(a)


TDOS
Ti
Density-of-states
55.70
50.13
44.56
38.99
33.42
27.85
22.28
16.71
11.14
5.57
0.00
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

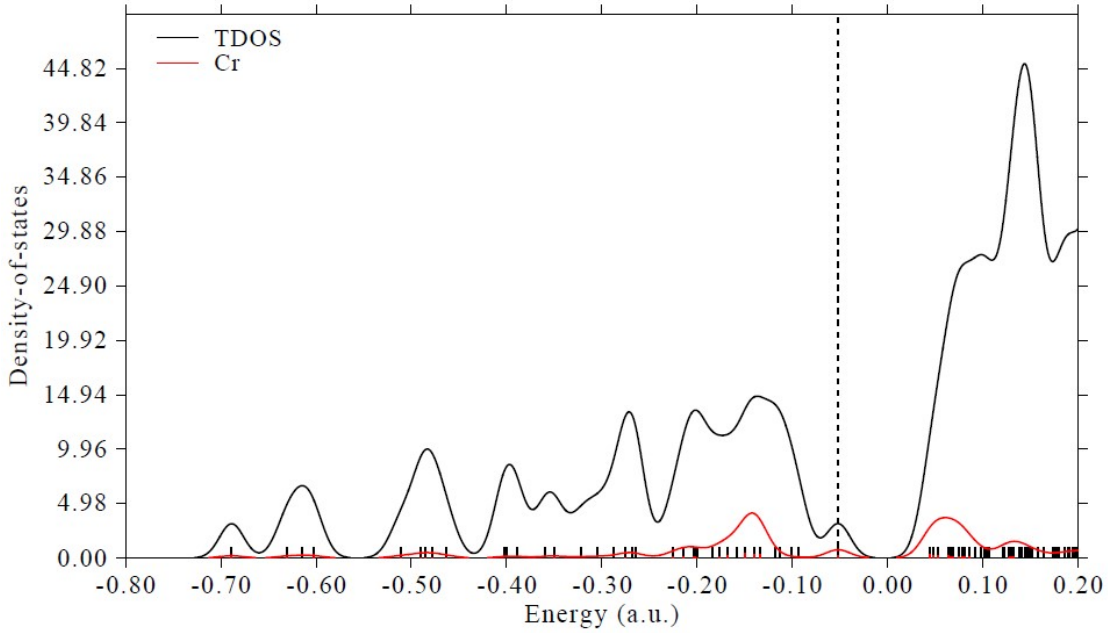
(b)


TDOS
Ti
47.16
41.92
36.68
31.44
26.20
20.96
15.72
10.48
5.24
0.00
Density-of-states
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

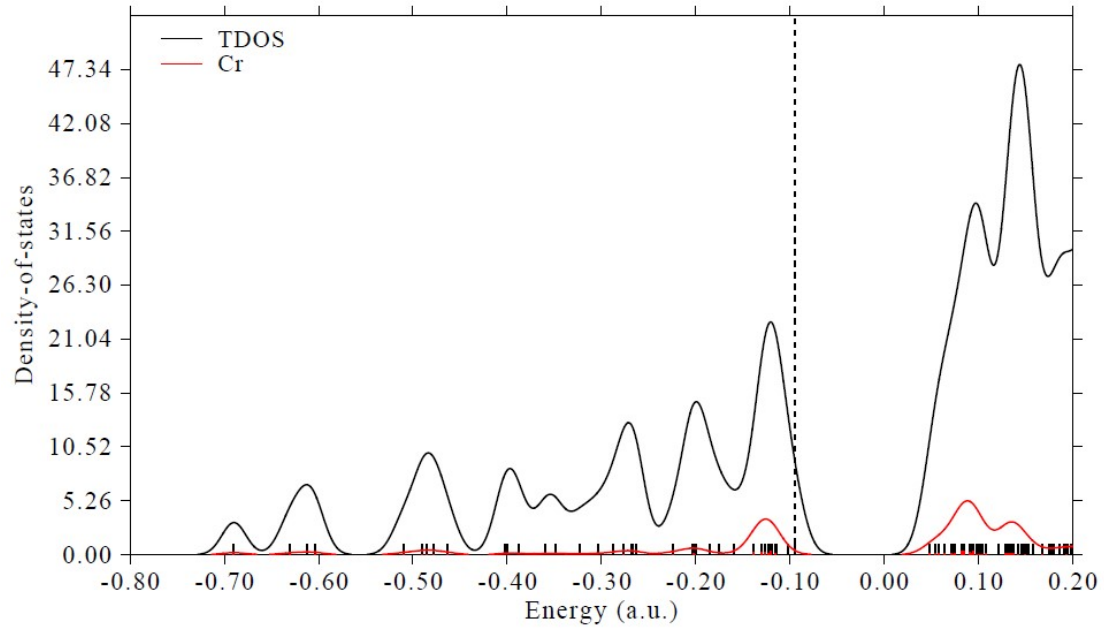
(c)


TDOS
V
48.15
42.80
37.45
32.10
26.75
21.40
16.05
10.70
5.35
0.00
Density-of-states
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

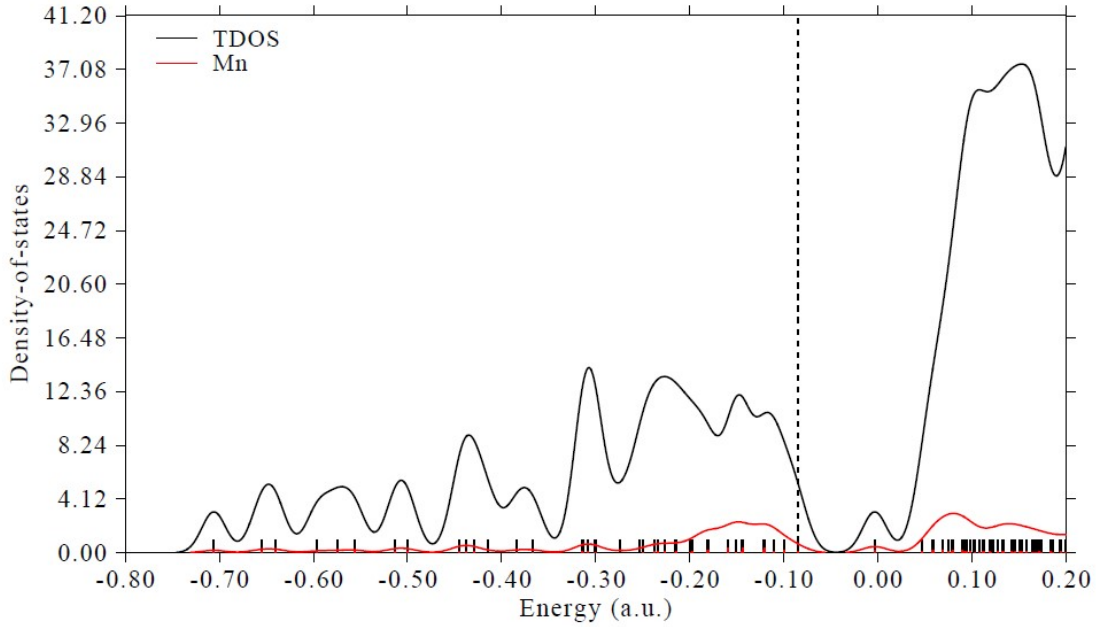
(d)


TDOS
Cr
44.82
39.84
34.86
29.88
24.90
19.92
14.94
9.96
4.98
0.00
Density-of-states
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

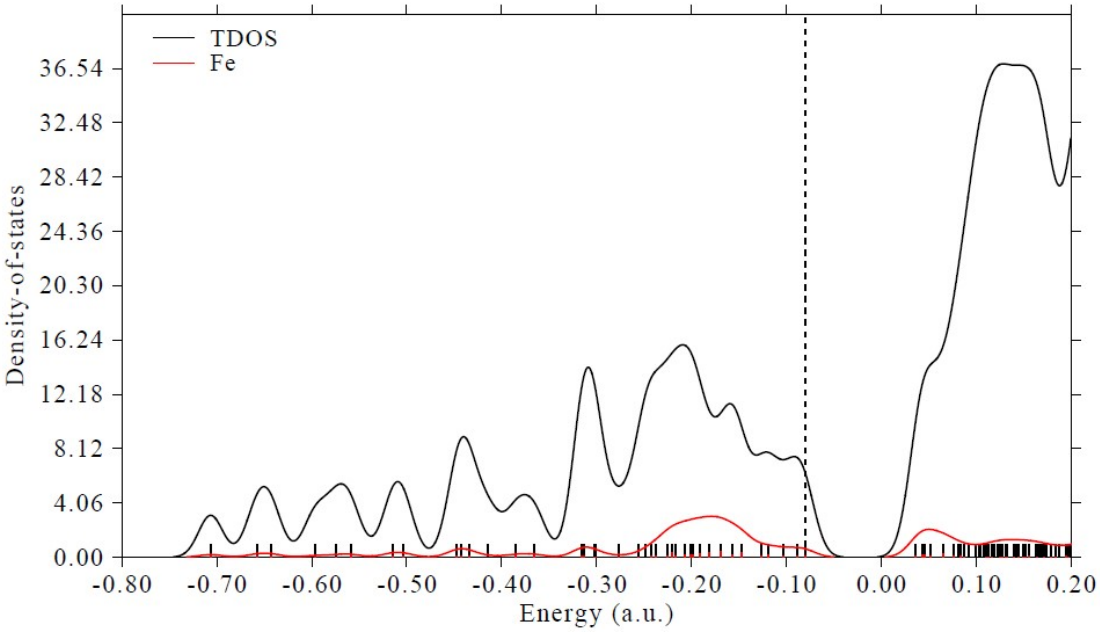
(e)


TDOS
Cr
47.34
42.08
36.82
31.56
26.30
21.04
15.78
10.52
5.26
0.00
Density-of-states
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

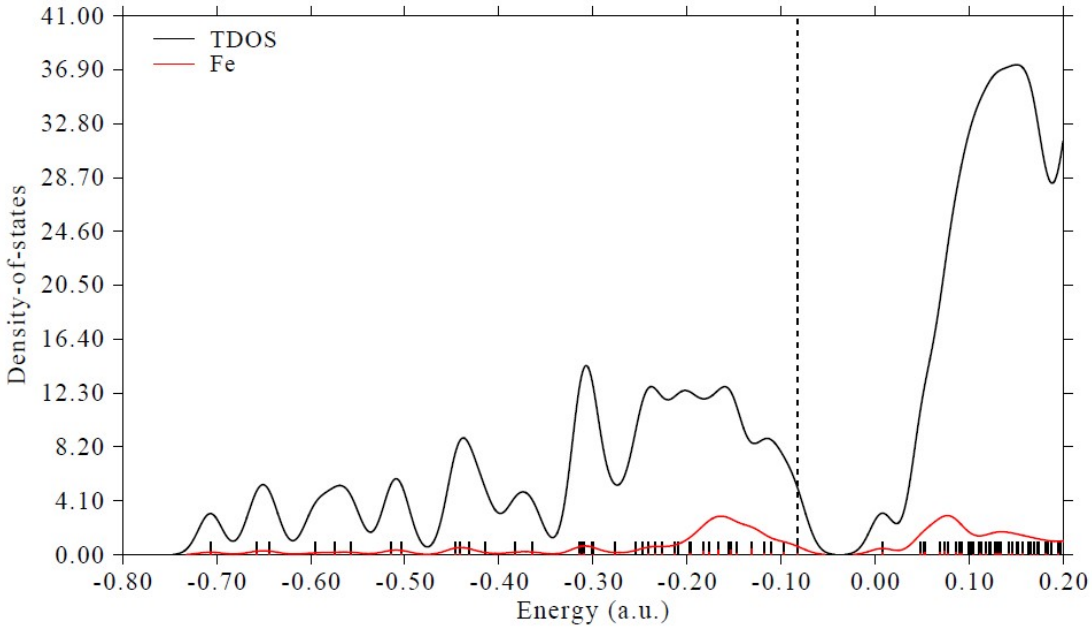
(f)


TDOS
Mn
Density-of-states
41.20
37.08
32.96
28.84
24.72
20.60
16.48
12.36
8.24
4.12
0.00
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

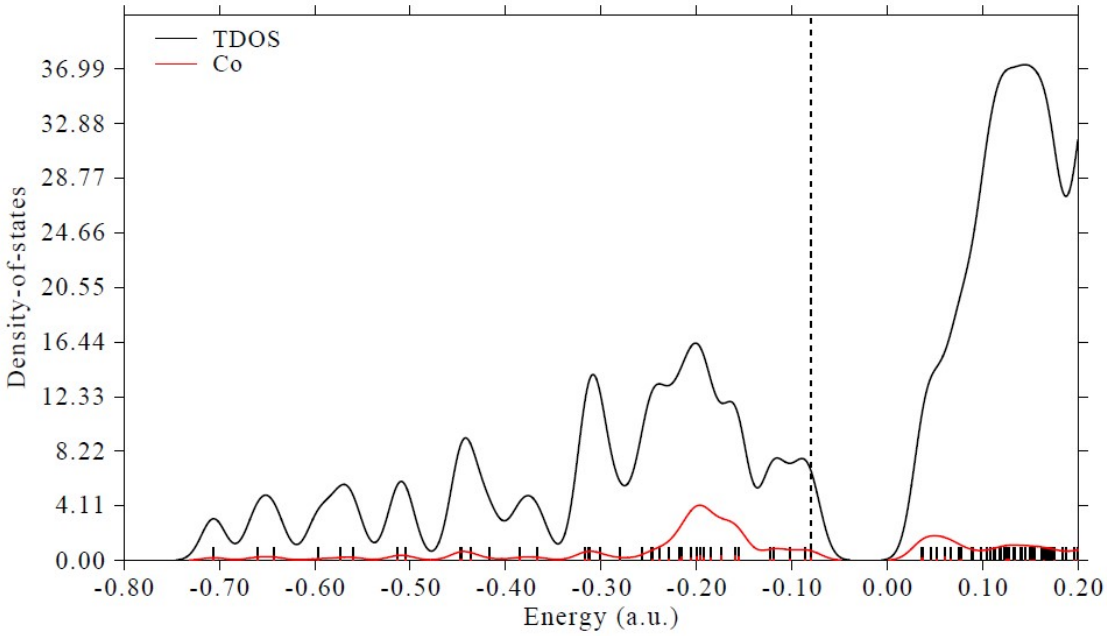
(g)


TDOS
Fe
Density-of-states
36.54
32.48
28.42
24.36
20.30
16.24
12.18
8.12
4.06
0.00
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

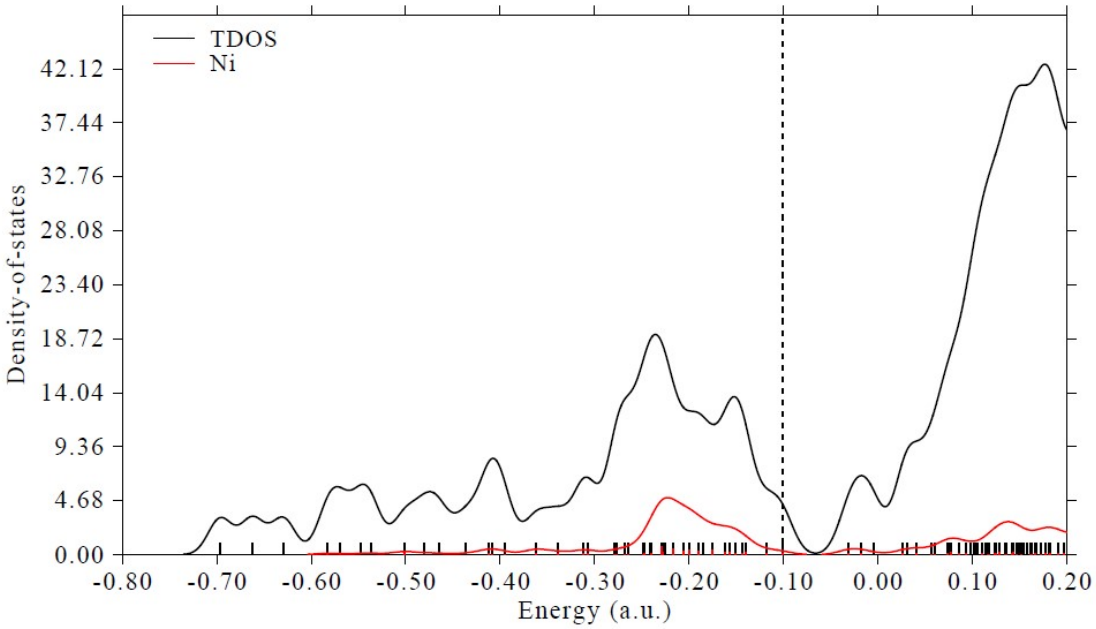
(h)


TDOS
Fe
Density-of-states
41.00
36.90
32.80
28.70
24.60
20.50
16.40
12.30
8.20
4.10
0.00
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

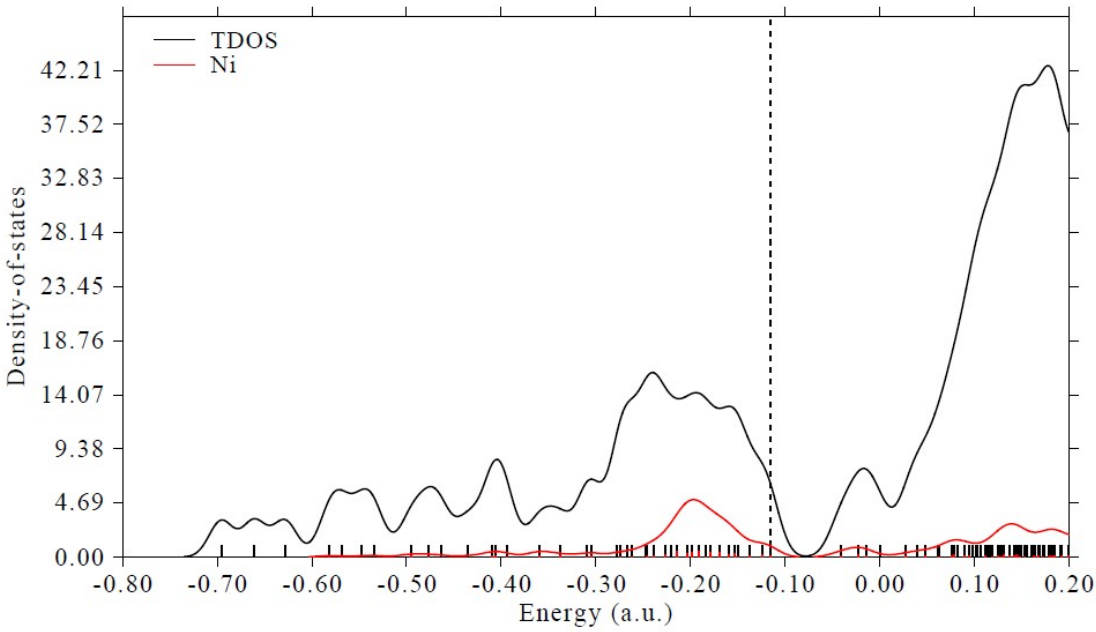
(i)


TDOS
Co
Density-of-states
36.99
32.88
28.77
24.66
20.55
16.44
12.33
8.22
4.11
0.00
-0.80
-0.70
-0.60
-0.50
-0.40
-0.30
-0.20
-0.10
0.00
0.10
0.20
Energy (a.u.)

(j)



(k)



(l)

Figure. S9 Total density of states (TDOS) of each cluster and partial density of states (PDOS) of the transition metal atom. (a) ScB_{24}^-; (b) alpha spin for TiB_{24}^-; (c) beta spin for TiB_{24}^-; (d) VB_{24}^-; (e) alpha spin for CrB_{24}^-; (f) beta spin for CrB_{24}^-; (g) MnB_{24}^-; (h) alpha spin for FeB_{24}^-; (i) beta spin for FeB_{24}^-; (g) CoB_{24}^-;(k) alpha spin for NiB_{24}^-;(l) beta spin for NiB_{24}^-. The dashed line highlights the position of HOMO (alpha HOMO or beta HOMO). The energy unit a.u. represent hartree and one hartree is 27.21 eV.

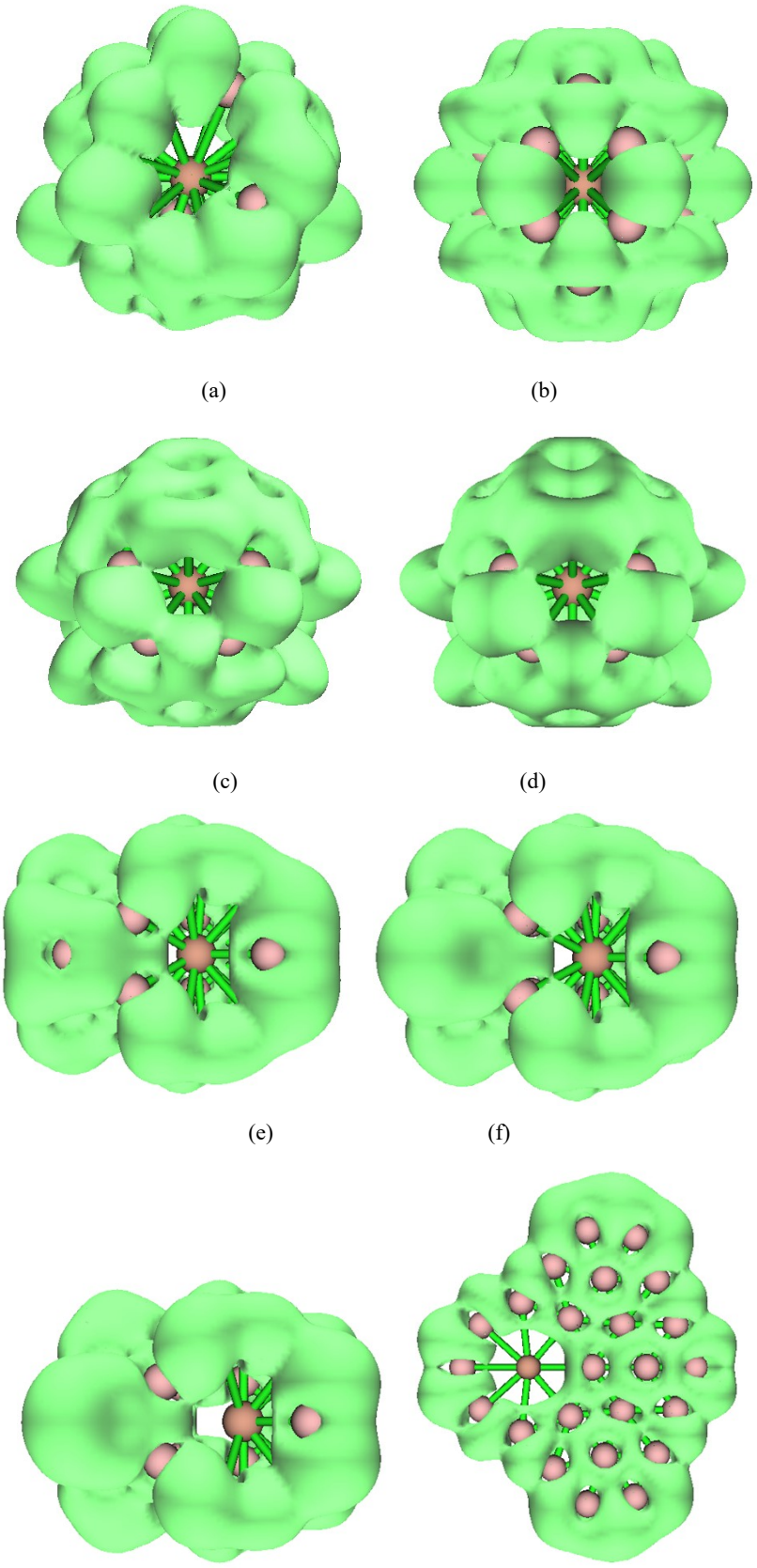
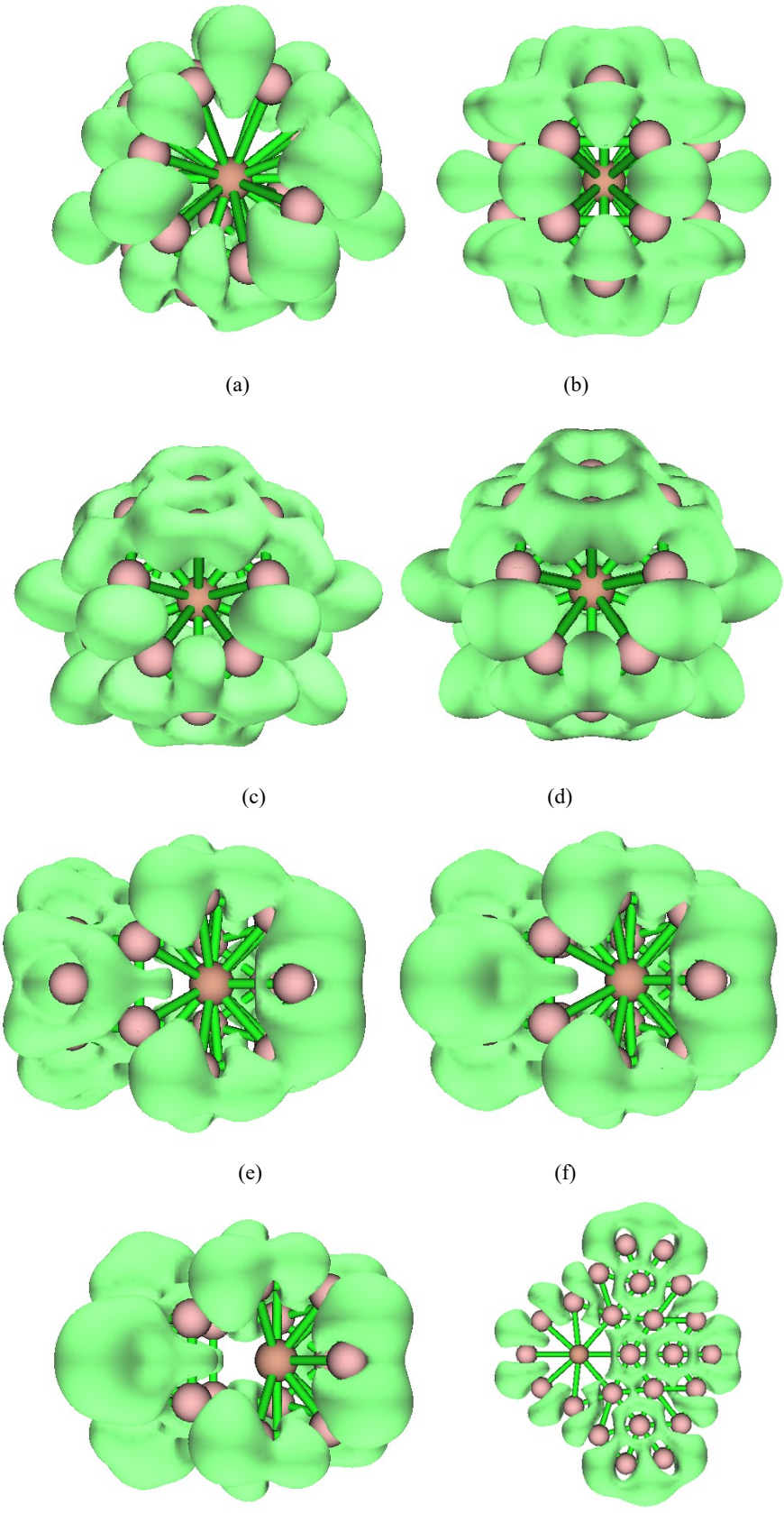


Figure. S10 Electron localization function (ELF) with the isovalue set to 0.60. (a) ScB_{24}^-; (b) TiB_{24}^-; (c) VB_{24}^-; (d) CrB_{24}^-; (e) MnB_{24}^-; (f) FeB_{24}^-; (g) CoB_{24}^-;(h) NiB_{24}^-.



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure. S11 Electron localization function (ELF) with the isovalue set to 0.7. (a) ScB_{24}^-; (b) TiB_{24}^-; (c) VB_{24}^-; (d) CrB_{24}^-; (e) MnB_{24}^-; (f) FeB_{24}^-; (g) CoB_{24}^-;(h) NiB_{24}^-.

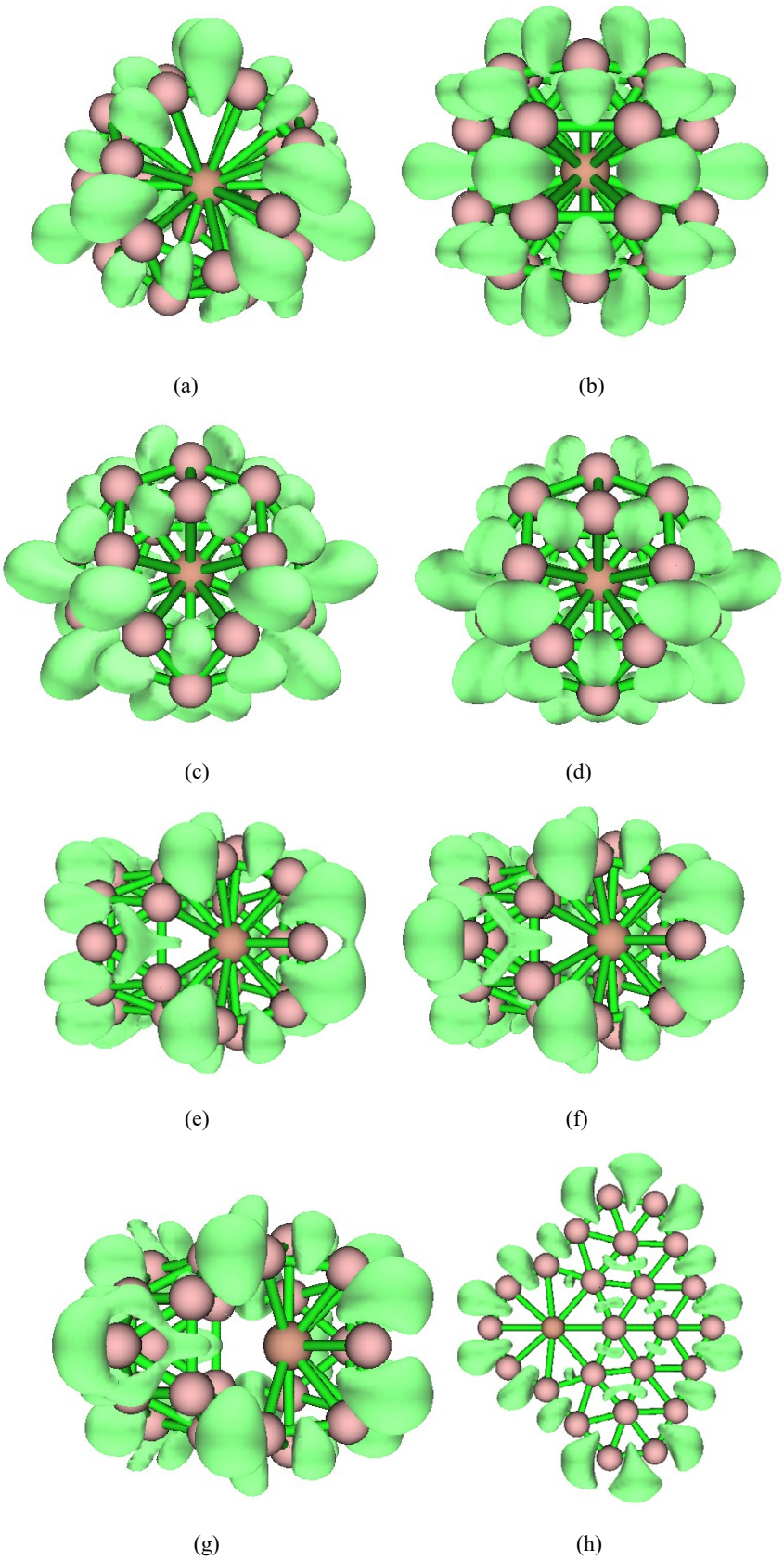


Figure. S12 Electron localization function (ELF) with the isovalue set to 0.80. (a) ScB_{24}^-; (b) TiB_{24}^-; (c) VB_{24}^-; (d) CrB_{24}^-; (e) MnB_{24}^-; (f) FeB_{24}^-; (g) CoB_{24}^-;(h) NiB_{24}^-.

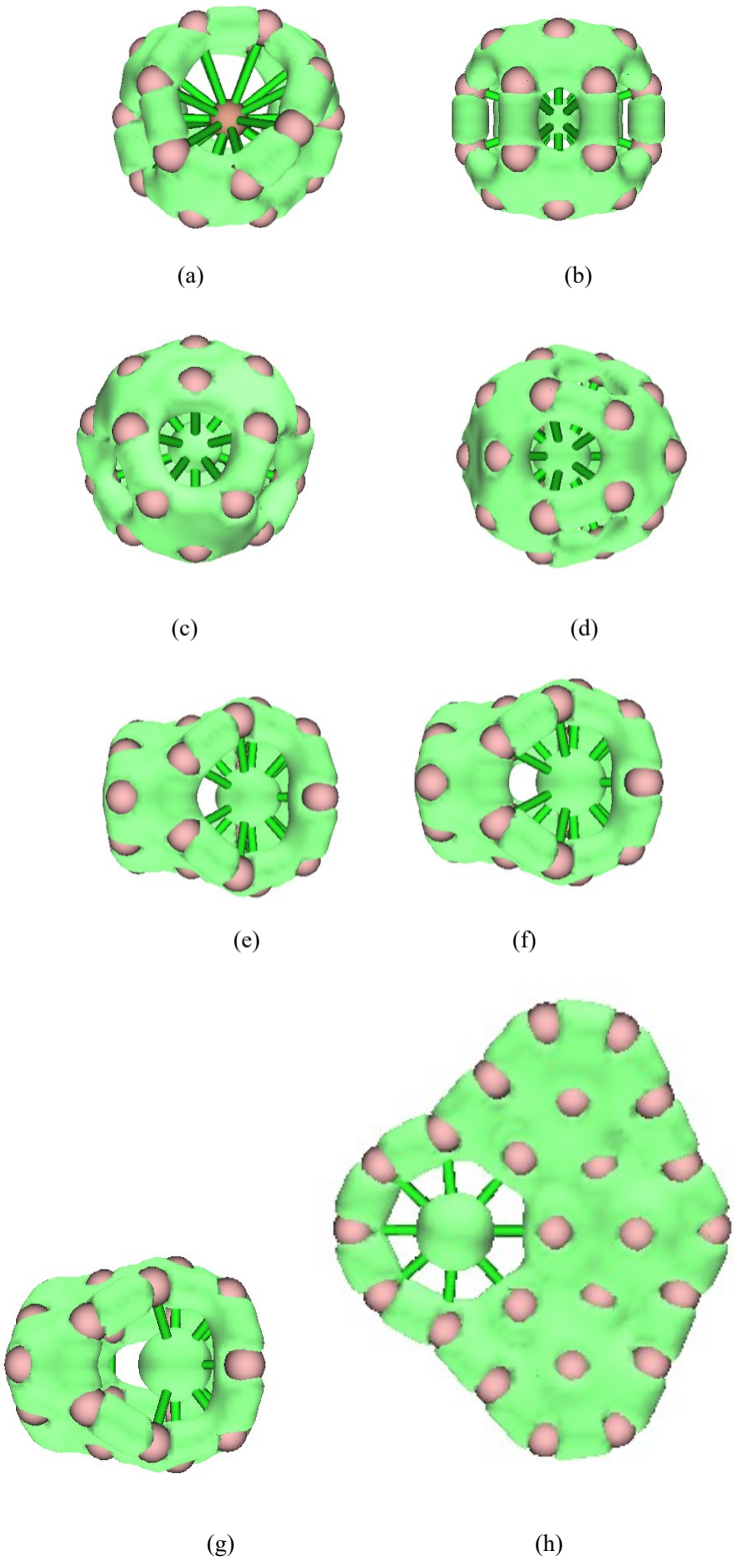


Figure. S13 Valence electron density with the isovalue set to 0.1. (a) ScB_{24}^-; (b) TiB_{24}^-; (c) VB_{24}^-; (d) CrB_{24}^-; (e) MnB_{24}^-; (f) FeB_{24}^-; (g) CoB_{24}^-;(g) NiB_{24}^-.

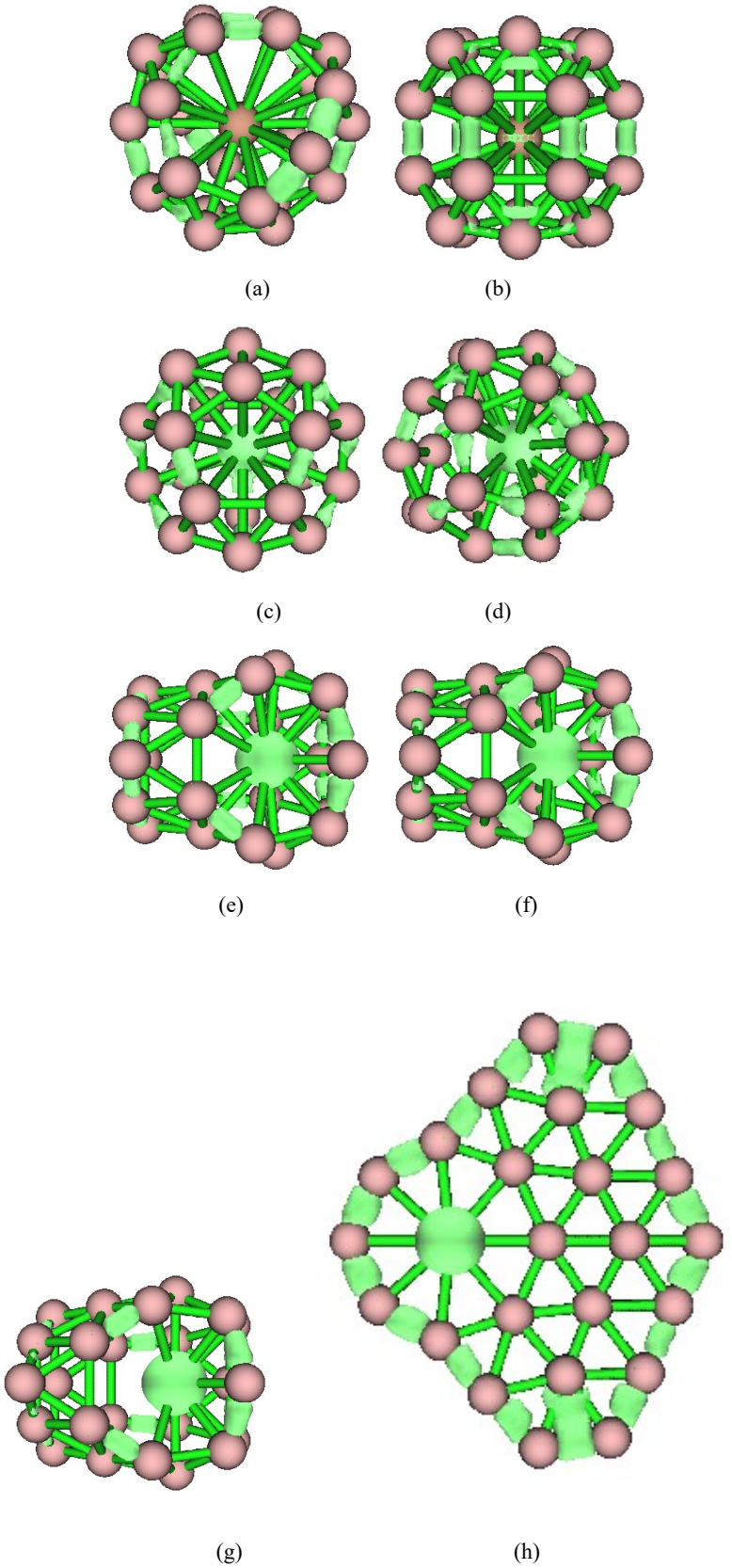


Figure. S14 Valence electron density with the isovalue set to 0.14. (a) ScB_{24}^-; (b) TiB_{24}^-; (c) VB_{24}^-; (d) CrB_{24}^-; (e) MnB_{24}^-; (f) FeB_{24}^-; (g) CoB_{24}^-;(g) NiB_{24}^-.

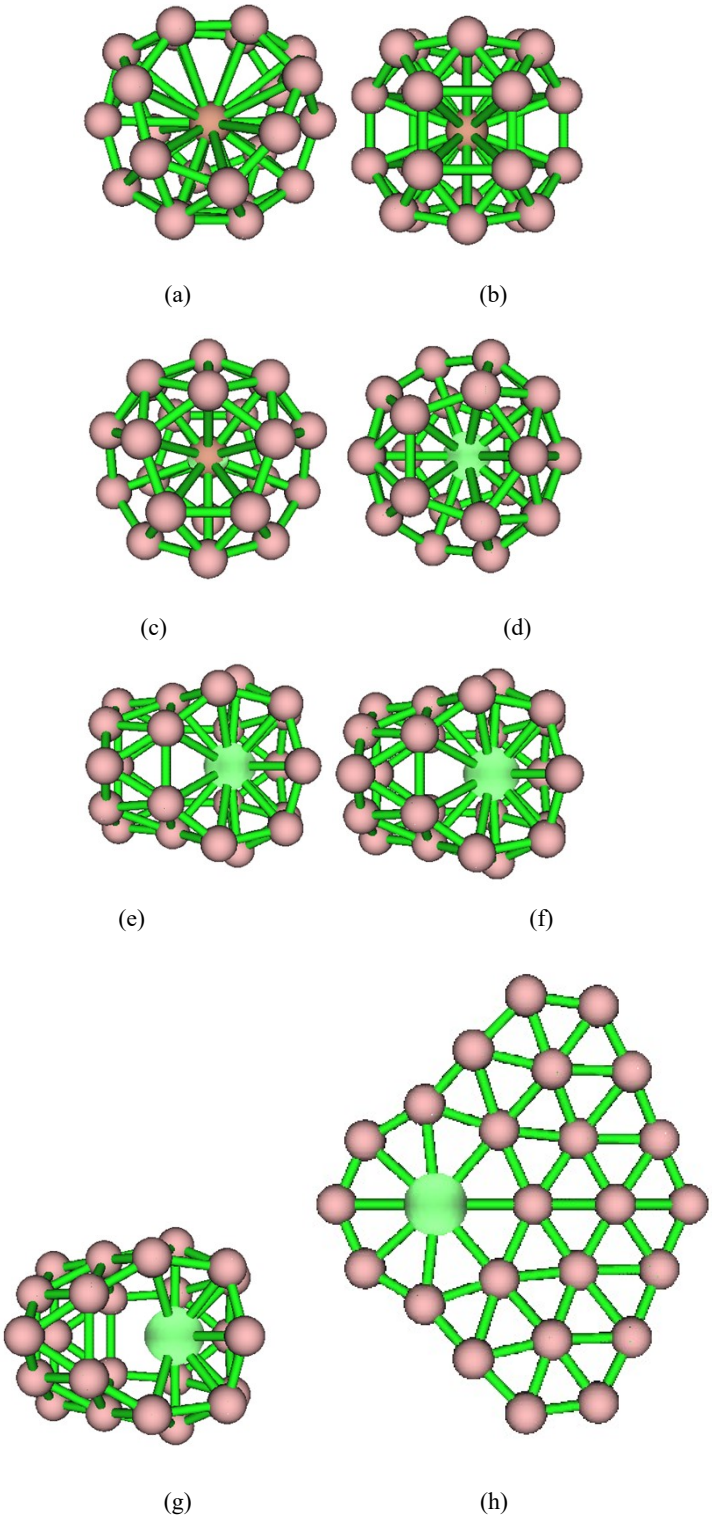


Figure. S15 Valence electron density with the isovalue set to 0.20. (a) ScB_{24}^-; (b) TiB_{24}^-; (c) VB_{24}^-; (d) CrB_{24}^-; (e) MnB_{24}^-; (f) FeB_{24}^-; (g) CoB_{24}^-;(g) NiB_{24}^-.

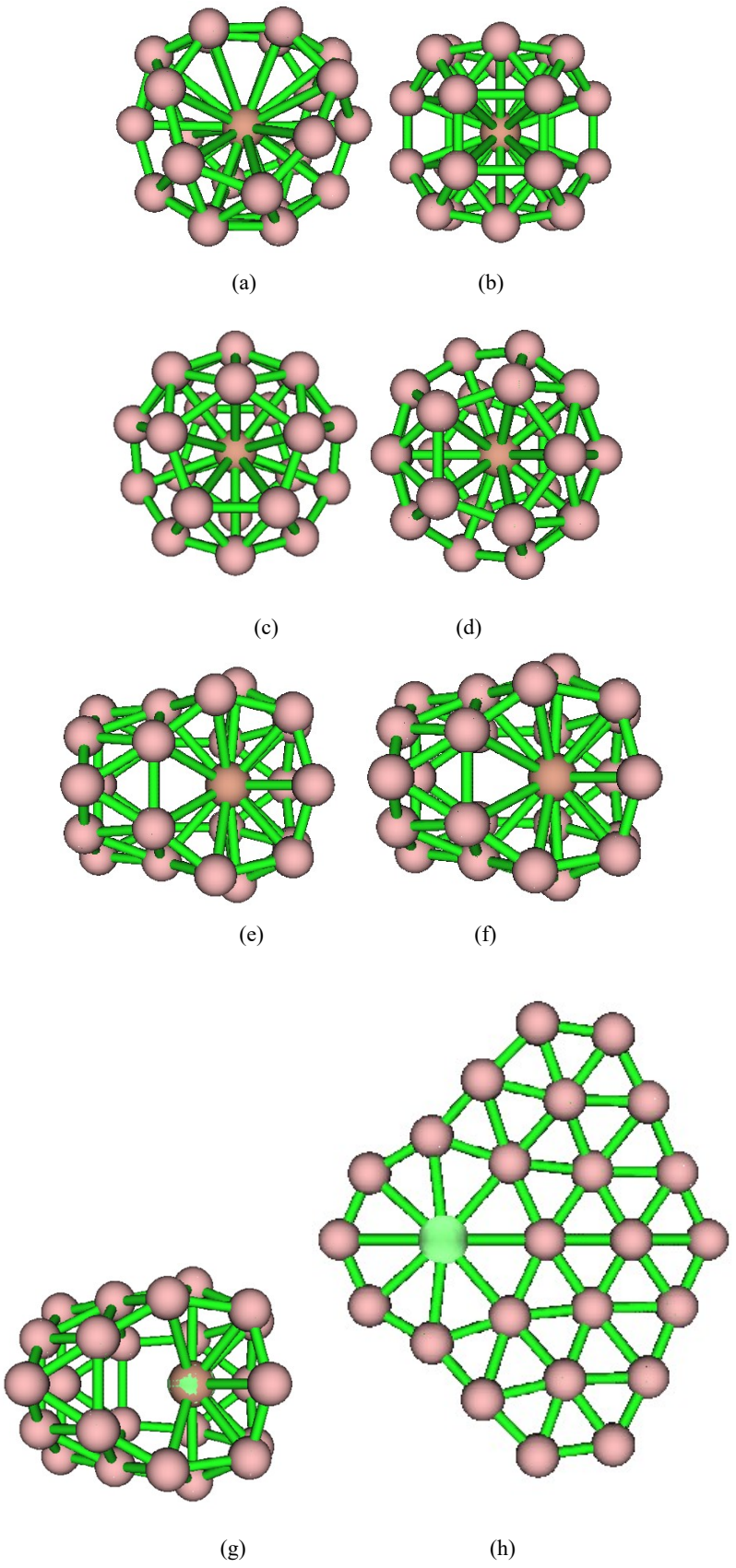


Figure. S16 Valence electron density with the isovalue set to 0.52. (a) ScB_{24}^-; (b) TiB_{24}^-; (c) VB_{24}^-; (d) CrB_{24}^-; (e) MnB_{24}^-; (f) FeB_{24}^-; (g) CoB_{24}^-;(g) NiB_{24}^-.