Supporting Information

FeB$_6$ Monolayers: The Graphene-like Material with Hypercoordinate Transition Metal

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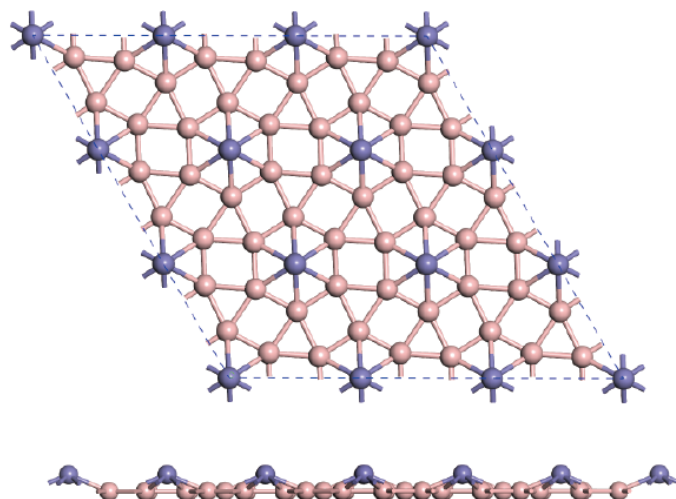
Fig. S1 Snapshot of final β-FeB$_6$ sheet at 3000 K after 10 *ps* AIMD simulations.
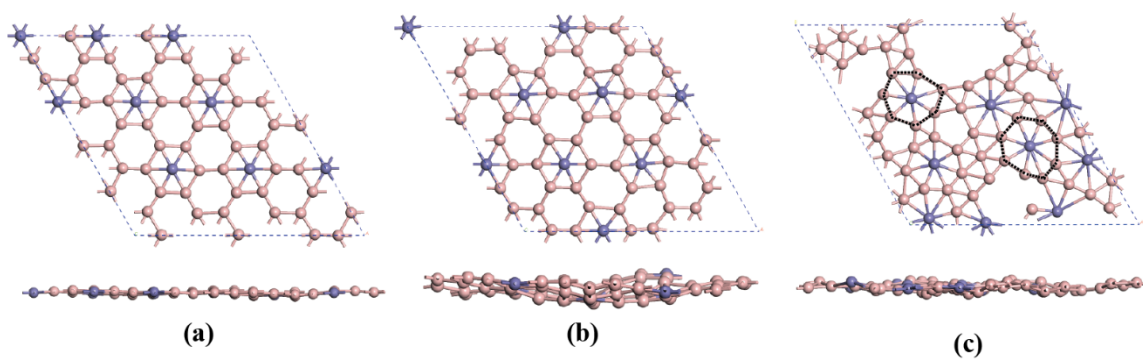

(a)　　　　　　　　(b)　　　　　　　　(c)

Fig. S2 Snapshot of final γ-FeB$_6$ monolayers at (a) 300 K, (b) 500 K and (c) 1000 K, at the end of 10 *ps* AIMD simulations. Black dashed lines are guide lines for emphasizing the Fe©B$_7$ and Fe©B$_8$ units.

Legend:
- Upper-Layer Fe Atoms
- Upper-Layer B Atoms
- Sublayer Fe Atoms
- Sublayer B Atoms

(a) AA Stacking
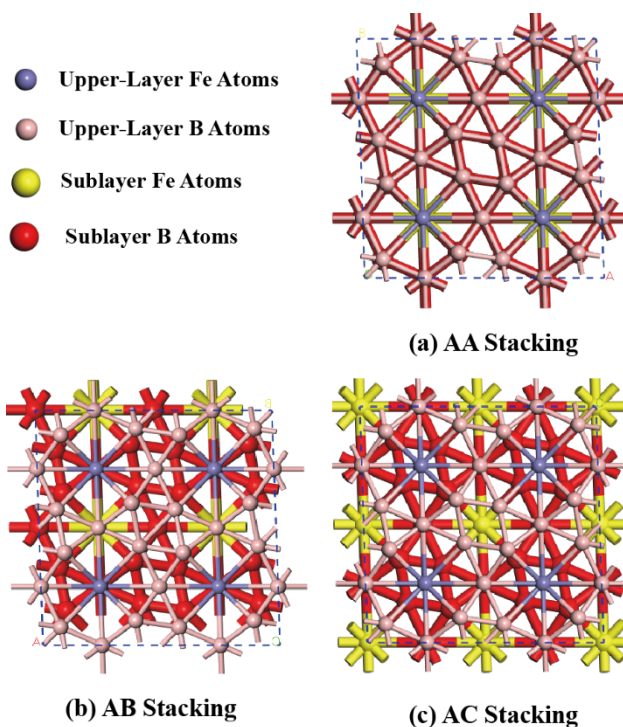
(b) AB Stacking

(c) AC Stacking

Fig. S3 The optimized structures of the α-FeB$_6$ bilayer systems with different stacking patterns. In AA (a) and AB (b) stacking bilayers, the Fe atoms in the upper layers are directly located above the Fe (AA stacking) and B (AB stacking) atoms in the sublayers, respectively. In AC (c) stacking pattern, the Fe atoms in the upper layer are above the center of B$_4$ rings in the lower layer.
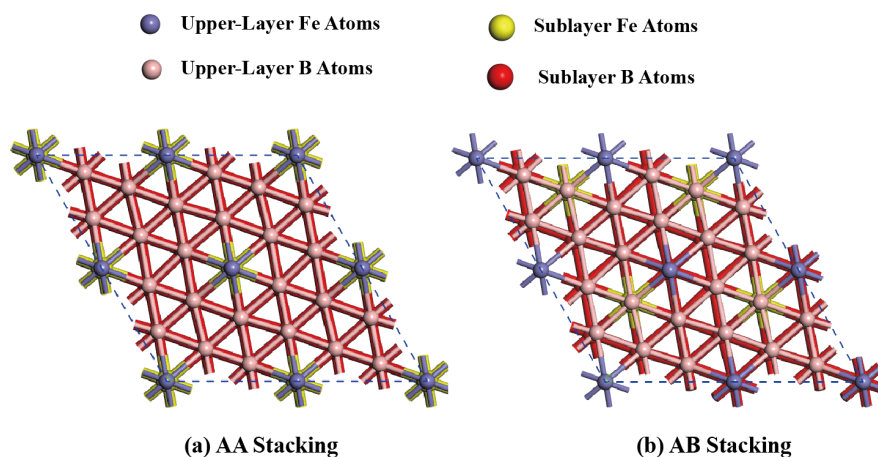

Legend:
- Upper-Layer Fe Atoms
- Sublayer Fe Atoms
- Upper-Layer B Atoms
- Sublayer B Atoms

(a) AA Stacking

(b) AB Stacking

Fig. S4 The optimized structures of the β-FeB$_6$ bilayer systems with different stacking patterns. In AA (a) and AB (b) stacking bilayers, the Fe atoms in the upper layer directly locate above the Fe (AA stacking) and B (AB stacking) atoms in the sublayers, respectively. Because of the high density of boron atoms, there are only B$_3$ rings in the β-FeB$_6$ sheet, and it's impossible to establish a geometry with the upper-layer Fe atoms locating above the center of B$_3$ rings in the sublayer. Accordingly, the AC stacking is not available in the β-FeB$_6$ bilayer system.
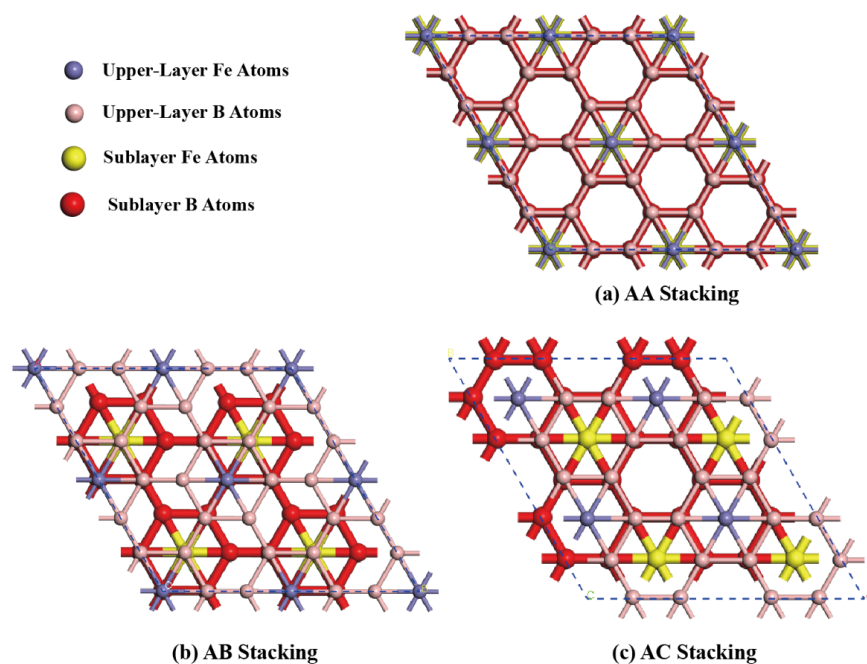
(a) AA Stacking

(b) AB Stacking

(c) AC Stacking

Legend:
- Upper-Layer Fe Atoms
- Upper-Layer B Atoms
- Sublayer Fe Atoms
- Sublayer B Atoms

Fig. S5 The optimized structures of the γ-FeB$_6$ bilayer systems with different stacking patterns. In AA (a) and AB (b) stacking bilayers, the Fe atoms in the upper layer directly locate above the Fe (AA stacking) and B (AB stacking) atoms in the sublayers, respectively. In AC (c) stacking pattern, the Fe atoms in the upper layer are above the center of B$_6$ rings in the lower layer
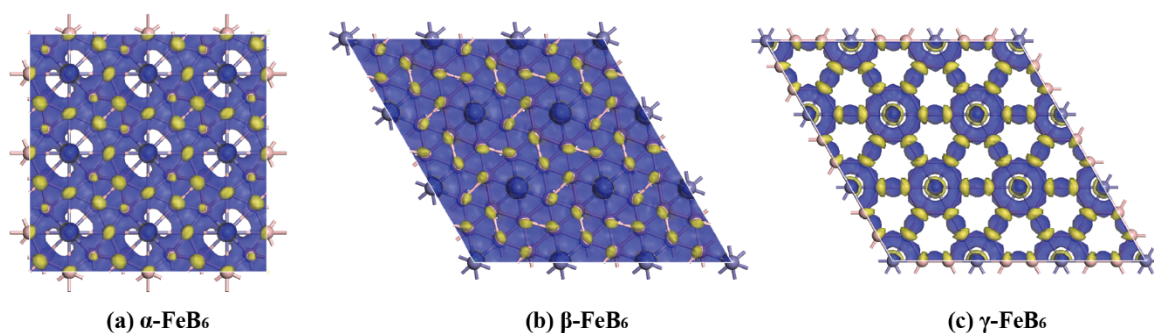

(a) α-FeB$_6$ **(b) β-FeB$_6$** **(c) γ-FeB$_6$**

Fig. S6 Deformation electronic density plotted with iso-surface value of 0.05 e/au, for the (a) α-FeB$_6$, (b) β-FeB$_6$ and (c) γ-FeB$_6$ monolayers. Blue and yellow refer to the accumulation and depletion of electrons, respectively.
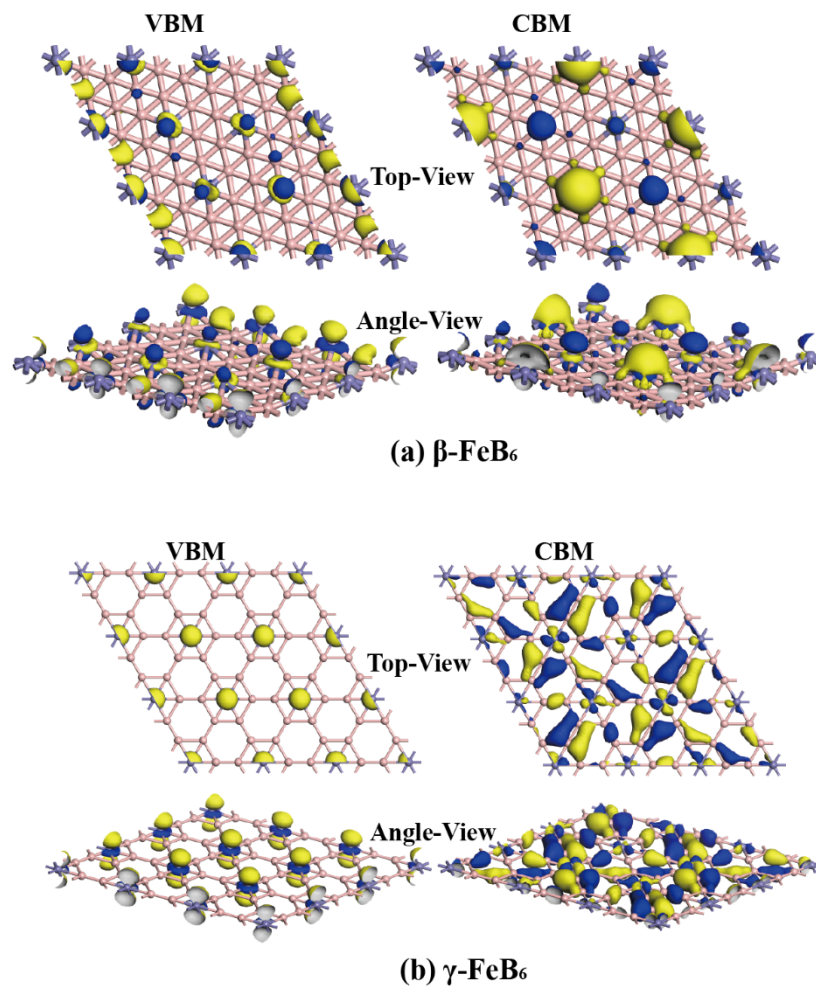
Fig. S7 Charge distributions of valence band maximum (VBM) and conduction band minimum (CBM) at Γ point for the semiconducting (a) β-FeB$_6$ and (b) γ-FeB$_6$ monolayers. The isovalue is 0.02 e·Å^{-3}

8 × 3c-2e, ON= 1.87 **4 × 3c-2e, ON= 1.93** **9c-2e, ON= 1.89**
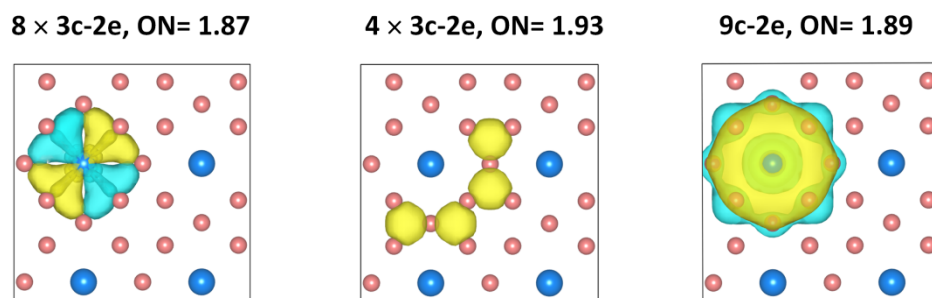
Figure S8. Schematic of SSAdNDP chemical bonding pattern for α-FeB$_6$ monolayer.

6 × 3c-2e, ON= 1.89 **2× 3c-2e, ON= 1.88** **3× 4c-2e, ON= 1.62**

7c-2e, ON= 1.90 **7c-2e, ON= 1.65**
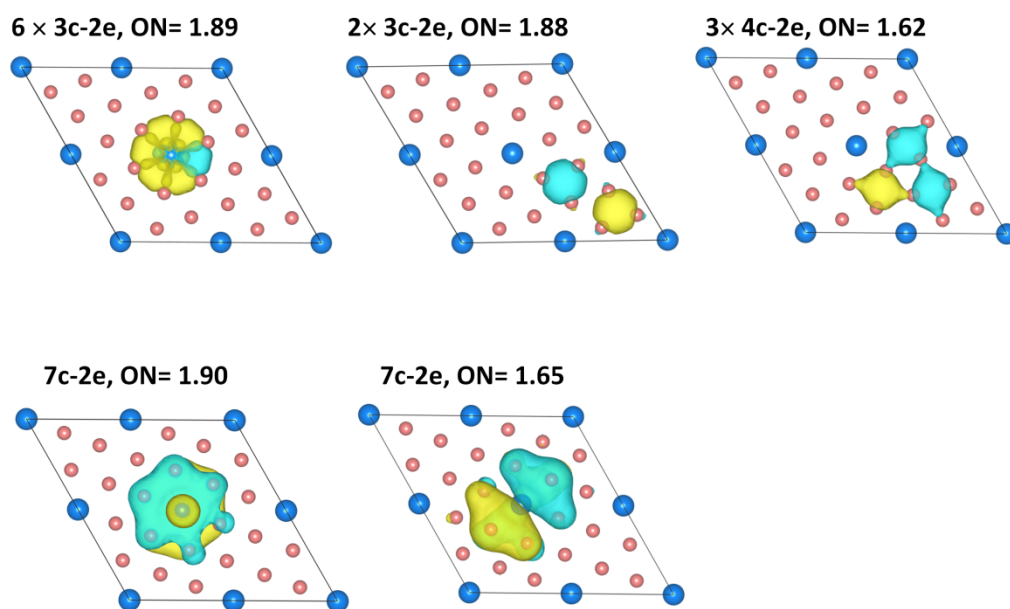
Figure S9. Schematic of SSAdNDP chemical bonding pattern for β-FeB$_6$ monolayer.

1c-2e, ON= 1.90   **3 × 2c-2e, ON= 1.88**   **6 × 3c-2e, ON= 1.96**

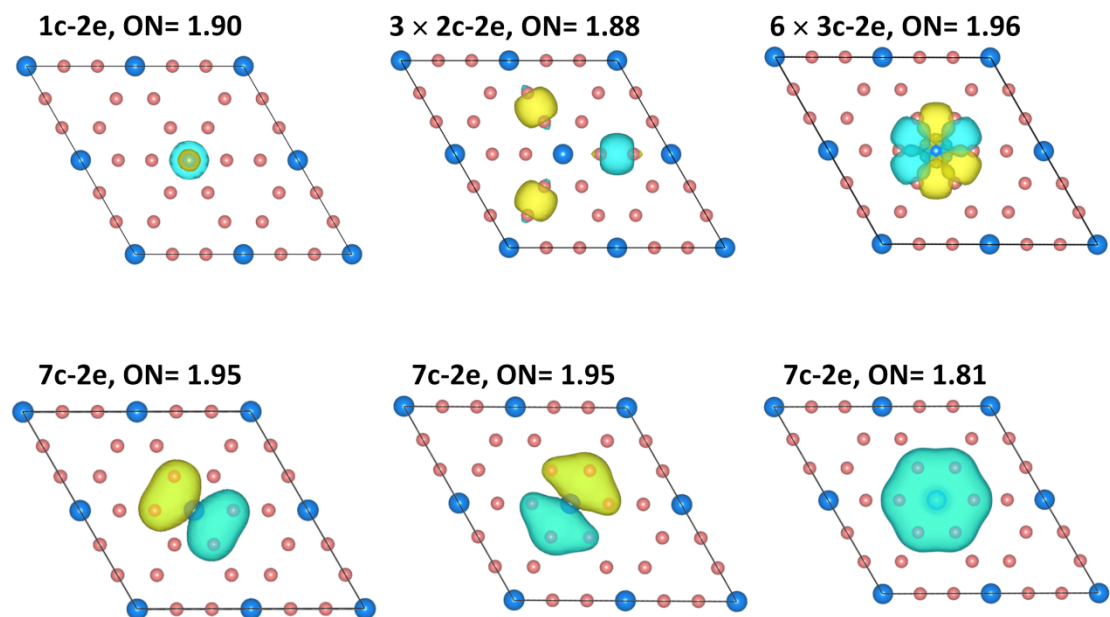**7c-2e, ON= 1.95**   **7c-2e, ON= 1.95**   **7c-2e, ON= 1.81**

Figure S10. Schematic of SSAdNDP chemical bonding pattern for γ-FeB$_6$ monolayer.

Table S1 The interlayer distances (d in Å) and binding energies (E_B in meV/atom) of the α-FeB$_6$, β-FeB$_6$ and γ-FeB$_6$ bilayer systems with different stacking patterns computed at the PBE+D2 level of theory. The E_B is defined as the total energies of the two corresponding constituent FeB$_6$ monolayers minus the total energy of the fully relaxed FeB$_6$ bilayer systems.

	AA Stacking		AB Stacking		AC Stacking	
	d	E_B	d	E_B	d	E_B
α-FeB$_6$	3.00	32	2.81	68	2.69	88
β-FeB$_6$	3.01	36	2.95	58	none	none
γ-FeB$_6$	2.89	14	2.49	102	3.55	0