

Supplementary Information

Fullerene-like boron clusters stabilized by endohedrally doped iron atom: B_nFe with $n = 14, 16, 18$ and 20

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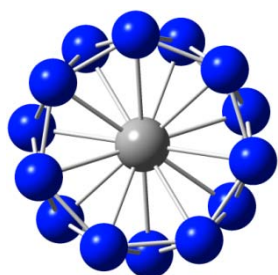
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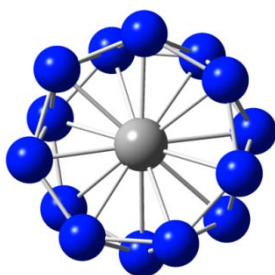
Computational Methods. Standard electronic structure calculations are carried out using the Gaussian 09 program.¹ Due to the relatively large number of structures involved, only DFT methods are employed in the searches for structures, and subsequent determination of relative energies. The searches for energy minima are conducted using first stochastic genetic algorithms to generate all possible structures.^{2,3} The equilibrium structures that are initially optimized using computations with small basis sets, are reoptimized using larger basis sets. Initial structures of a B_nFe cluster are also manually constructed by adding necessary B-atoms at all possible positions on surfaces of the $B_{n-2}Fe$ or smaller clusters. A combination of different search approaches allows new structures to be discovered and a consistent set of lower-energy structures to be obtained. While computations on initial guess geometries are carried out using the hybrid TPSSh functional in conjunction with the LAN2DZ basis set, all selected equilibrium geometries with relative energies up to ~3 eV are fully reoptimized using TPSSh functionals but with the larger 6-311+G(d) basis set. Their harmonic vibrational frequencies are also calculated at these levels. For the analysis of chemical bonding, we make use of canonical MOs, and electron localization function (ELF) maps.⁴

Figures S1, S2, S3 and S4 display for each size the shape, symmetry point group, electronic state and relative energies of the four lowest-lying isomers. As for a convention, the structures are

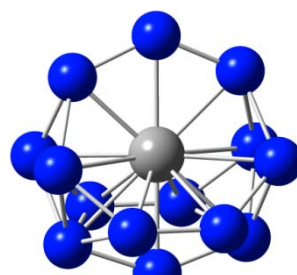
labeled as **S-n-X** with **S** stands for the size **S** = **14**, **16**, **18** and **20**, **n** stands for a neutral state, and **X** indicates the isomers **A**, **B**, **C** and **D**, in which **A** invariably represents the lowest-lying isomer.



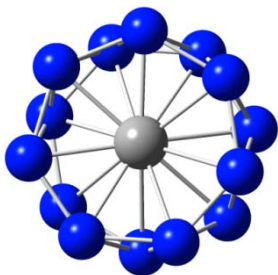
B14Fe.n.A $D_{7d}^3 A_{2u}$
0.00



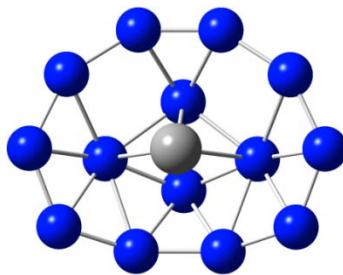
B14Fe.n.B $C_{7v}^1 A_1$
0.10



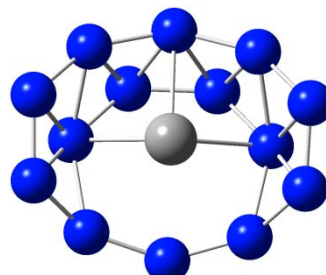
B14Fe.n.C $C_{2v}^1 A_1$
0.85



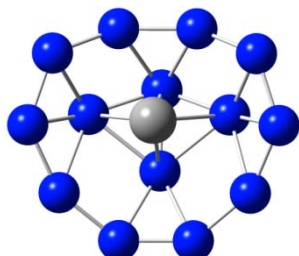
B14Fe.n.D $C_{7v}^5 A_{2u}$
1.03



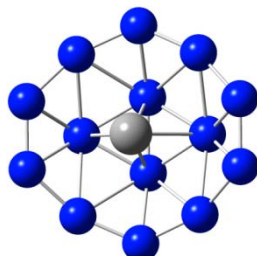
B14Fe.n.E $C_s^3 A''$
1.06



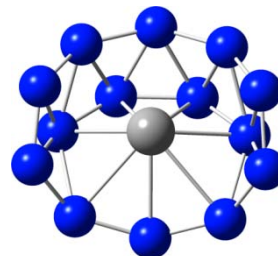
B14Fe.n.F $C_s^3 A''$
1.19



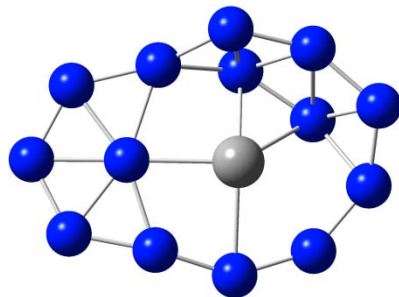
B14Fe.n.G $C_s^1 A'$
1.26



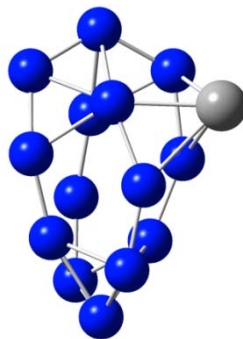
B14Fe.n.H $C_{2v}^1 A_1$
1.30



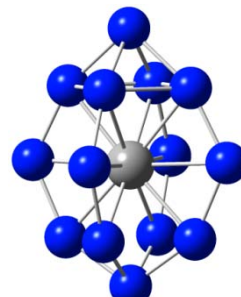
B14Fe.n.I $C_s^1 A'$
1.82



B14Fe.n.J $C_s^1 A'$
2.56



B14Fe.n.K $C_1^3 A$
2.91



B14Fe.n.L $C_{4v}^3 A_1$
4.01

Figure S1. Shapes, electronic states and relative energies (ΔE , eV) of the lower-lying neutral isomers $B_{14}Fe$. ΔE values are obtained at the TPSSH/6-311+G(d) + ZPE approach.

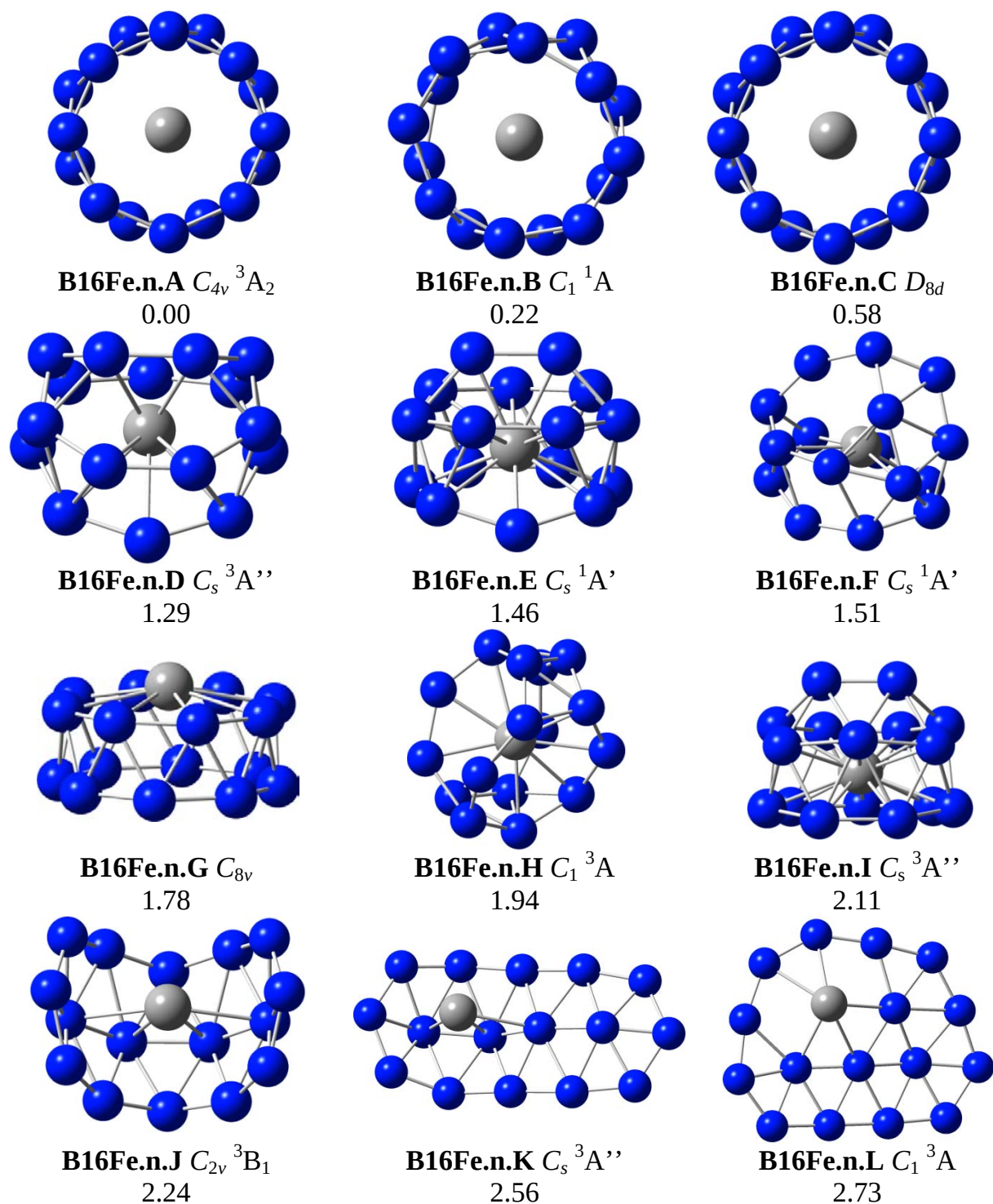


Figure S2. Shapes, electronic states and relative energies (ΔE , eV) of the lower -lying neutral isomers $B_{16}Fe$. ΔE values are obtained at the TPSSH/6-311+G(d) +ZPE approach.

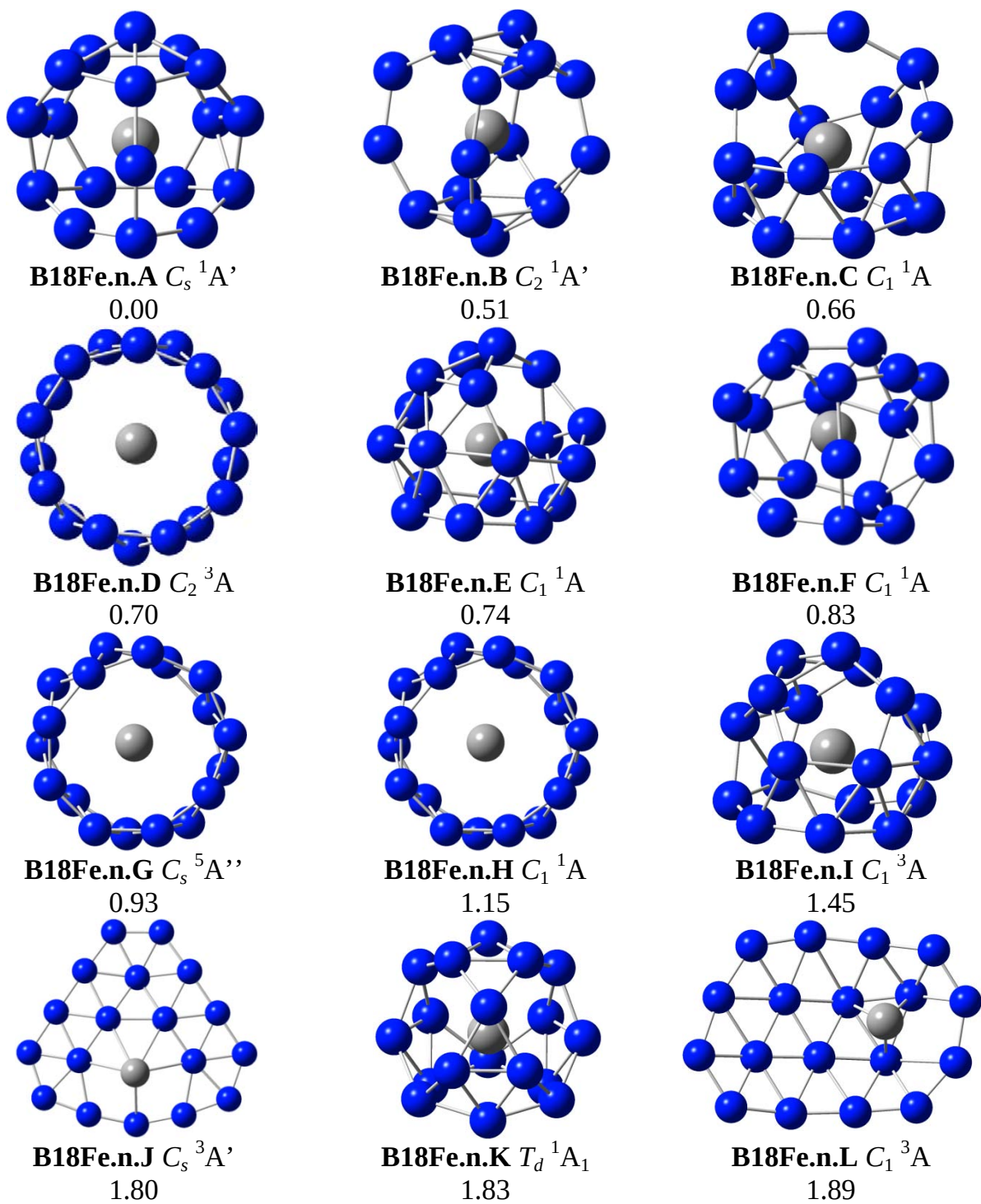
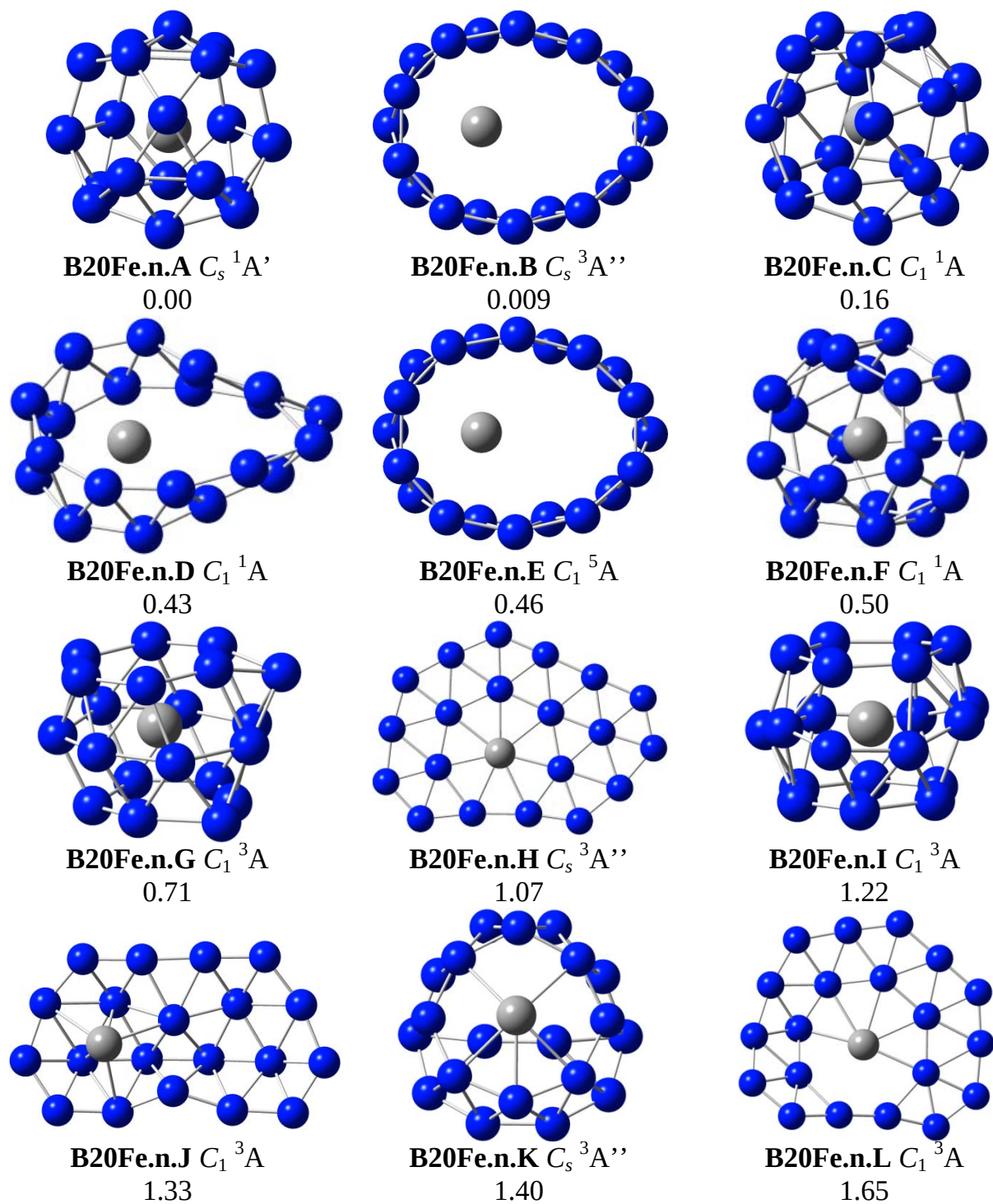


Figure S3. Shapes, electronic states and relative energies (ΔE , eV) of the lower -lying neutral isomers $B_{18}Fe$. ΔE values are obtained at the TPSSH/6-311+G(d) + ZPE approach.



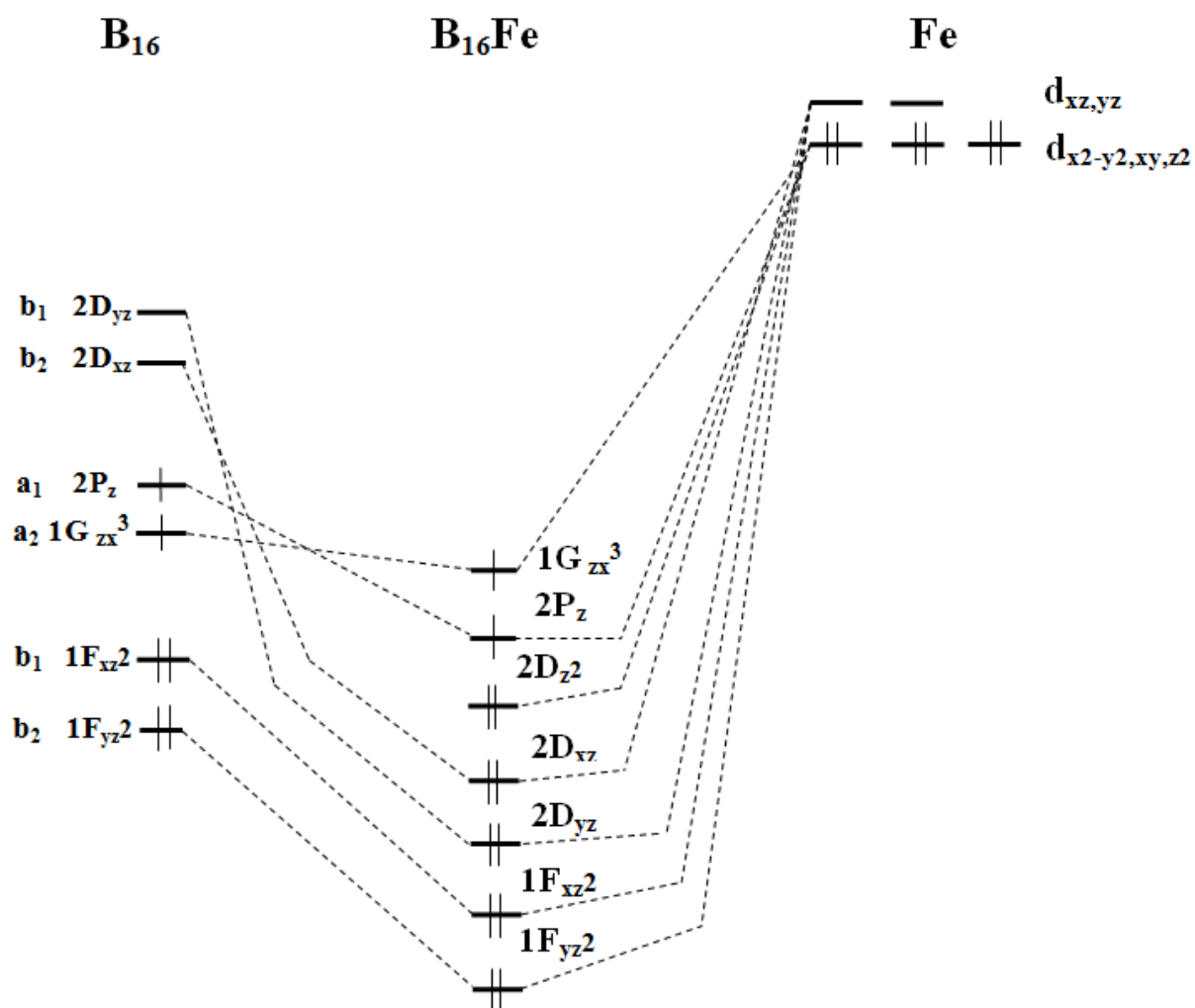


Figure S6. Orbital interaction diagram of the double-ring B_{16} cage and the Fe atom.

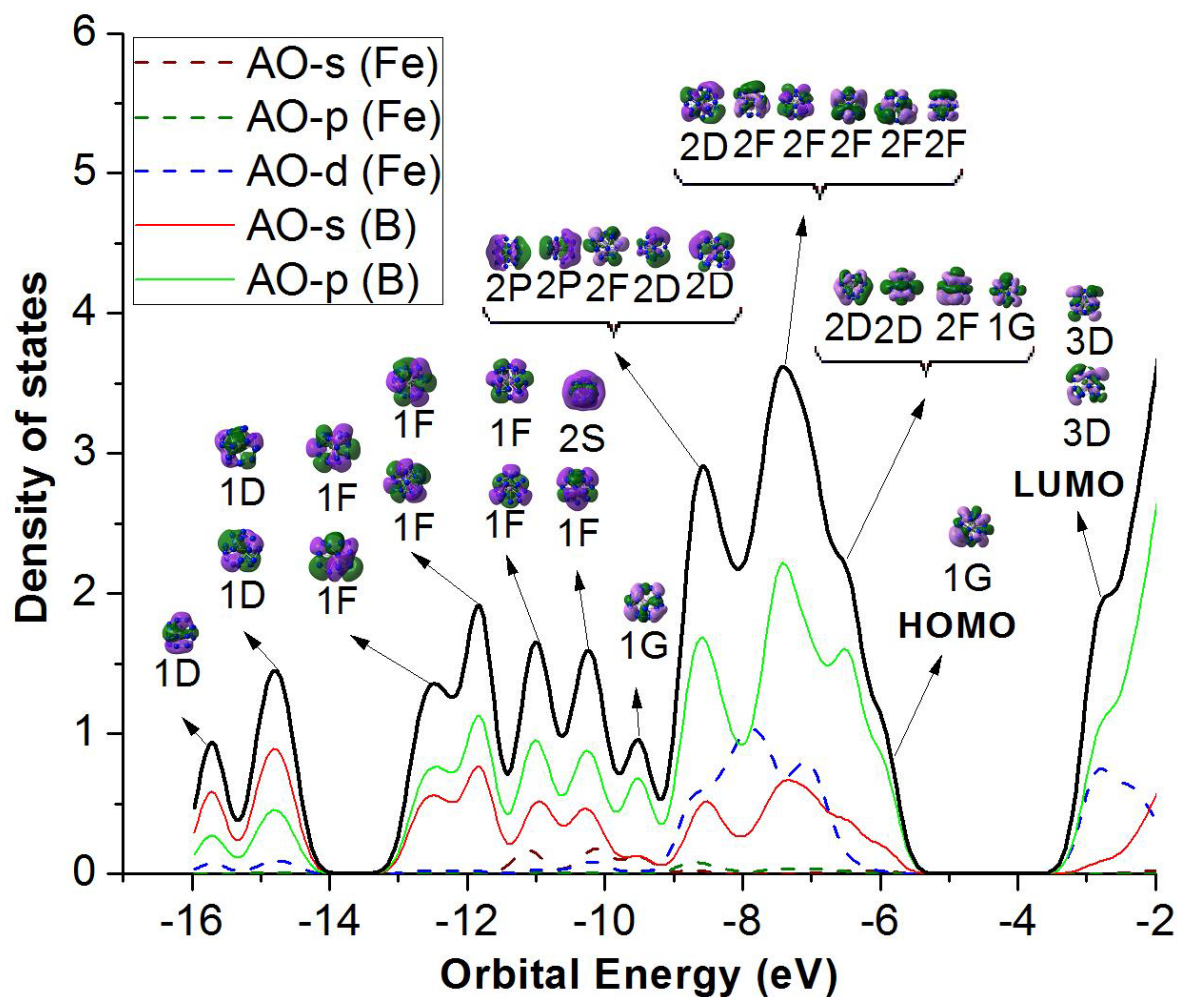


Figure S7. Total (DOS) and partial (pDOS) densities of state of $B_{20}Fe$.

References

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