Supporting Information

The Nearby Atomic Environment Effect on Fe-N-C Catalyst for Oxygen Reduction Reaction Studied by Density Functional Theory

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Constant-Potential Calculations

The electric potential of electrochemical interface is changed by adjusting the work function. It could be calculated by:

$$U = (Wf - 4.60) + 0.0592 \times pH \quad (S1)$$

where U is electrode potential referenced to SHE, Wf is the work function and 4.60 is the work function of H2/H+ at standard conditions.[1-3] The work function could be controlled by adjusting the numbers of charges. When electrode potential at a fixed potential on the RHE scale, electric potential referenced to SHE scale is also changed by changing the pH values. It was given by:

$$U_{RHE} = U_{SHE} + 0.0592 \times pH \quad (S2)$$

According to Neurock methods,[4] the potential-dependent energy can be calculated by:

$$\mathrm{E_{free}}(U) = E_{DFT} + \int_{-q}^{q} \langle \overline{V_{tot}} \rangle \, dQ + q \, W_f \quad (S3)$$

The electrode potential (U) and energy (E) can be fitted to a function of quadratic form, and this quadratic form is consistent with a capacitor created by charged-slab and background-charge system, which could be written as:

$$\mathrm{E(U)} = -\frac{1}{2} C \, (U - U_{PZC})^2 + E_0 \quad (S4)$$

(1) Duan, Z.; Henkelman, G. Theoretical Resolution of the Exceptional Oxygen Reduction Activity of Au (100) in Alkaline Media. ACS Catal. 2019, 9, 5567−5573.

(2) Duan, Z.; Henkelman, G. Identification of Active Sites of Pure and Nitrogen-

Doped Carbon Materials for Oxygen Reduction Reaction Using Constant-Potential Calculations. J. Phys. Chem. C 2020, 124, 12016−12023.

(3) Duan, Z.; Henkelman, G. Surface Charge and Electrostatic Spin Crossover Effects in CoN4 Electrocatalysts. ACS Catal. 2020, 10, 12148−12155.

(4) Filhol, J. S.; Neurock, M. Elucidation of the Electrochemical Activation of Water Over Pd by First Principles. Angew. Chem. Int. Ed. 2006, 118, 416−420.

Microkinetic Simulations

Following the kinetic model developed by Hansen et al. [(1)], we simulated the polarization curves of str-11. Here, we only consider the dominating associative mechanism pathway. The O_2 molecule diffusion, adsorption, and electrochemical reduction steps are listed by the following equations:

$$O_2(\mathrm{aq}) \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} O_2\,(dl) \quad \text{(S1)}$$

$$O_2(\mathrm{dl}) + * \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} *O_2 \quad \text{(S2)}$$

$$*O_2 + H^+ + e^- \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} *OOH \quad \text{(S3)}$$

$$*\mathrm{OOH} + H^+ + e^- \underset{k_{-4}}{\overset{k_4}{\leftrightarrow}} *O + H_2O \quad \text{(S4)}$$

$$*O + H^+ + e^- \underset{k_{-5}}{\overset{k_5}{\leftrightarrow}} *OH \quad \text{(S5)}$$

$$*\mathrm{OH} + H^+ + e^- \underset{k_{-6}}{\overset{k_6}{\leftrightarrow}} * + H_2O \quad \text{(S6)}$$

Where k_i and k_{-i} are the rate constants of reaction and reverse reaction, O_2 (aq) and O_2 (dl) represent O_2 in the electrolyte and catalyst-electrolyte interface, respectively. Based on steady-state approximations, the ORR dynamical coverage rate of str-11, O_2 (dl), O_2*, OOH*, O* and OH* could be written as:

$$\frac{\partial \theta_{O2(dl)}}{\partial t} = \mathrm{k}_1 X_{O_2} - k_{-1}\theta_{O2(dl)} - k_2\theta_{O2(dl)}\theta_* + k_{-2}X_{*O2} \quad \text{(S7)}$$

$$\frac{\partial \theta_*}{\partial t} = \mathrm{k}_6\theta_{*OH} - k_{-6}X_{H2O}\theta_* - k_2\theta_{O2(dl)}\theta_* + k_{-2}X_{*O2} \quad \text{(S8)}$$

$$\frac{\partial \theta_{*O2}}{\partial t} = -\mathrm{k}_3\theta_{*O2} + k_{-3}\theta_{*OOH} + k_2\theta_{O2(dl)}\theta_* - k_{-2}\theta_{*O2} \quad \text{(S9)}$$

$$\frac{\partial\theta_{*OOH}}{\partial t} = -\mathrm{k}_4\theta_{*OOH} + k_{-4}\theta_{*O}X_{H2O} + k_3\theta_{*O2} - k_{-3}\theta_{*OOH} \text{ (S10)}$$

$$\frac{\partial\theta_{*O}}{\partial t} = -\mathrm{k}_5\theta_{*O} + k_{-5}\theta_{*OH} + k_4\theta_{*OOH} - k_{-4}\theta_{*O}X_{H2O} \text{ (S11)}$$

$$\frac{\partial\theta_{*OH}}{\partial t} = -\mathrm{k}_6\theta_{*OH} + k_{-6}\theta_{*}X_{H2O} + k_5\theta_{*O} - k_{-5}\theta_{*OH} \text{ (S12)}$$

Where θ is defined as the coverage of the intermediate species, t is the reaction time. The coverage of each species should satisfy the relationship:

$$\theta_* + \theta_{*O2} + \theta_{*O} + \theta_{*OOH} + \theta_{*OH} = 1 \text{ (S13)}$$

The value of X_{H2O} was taken as 1, and X_{O2} was taken as 2.34×10^{-5}, representing O_2 (g) in equilibrium with O_2 (aq) at 1 atm.[1] For non-electrochemical reaction steps, the equilibrium constant (Ki) can be expressed as:

$$\mathrm{K_i} = \exp\left(-\frac{\Delta G_i}{K_bT}\right) \text{ (S14)}$$

While for electrochemical steps, the rate constant is calculated by:

$$k_\mathrm{i} = \exp\left(-\frac{e(U-U_i)}{K_bT}\right) \text{ (S15)}$$

Where Ui is the reversible potential of electrochemical step, and ki is written as:

$$\mathrm{k_i} = A_i \exp\left(-\frac{E_{a,i}}{K_bT}\right)\exp\left(-\frac{e\beta_i(U-U_i)}{K_bT}\right) \text{ (S16)}$$

The per-factor A_i is set to 1×10^9, the temperature is set to be 300 K and the β_i is 0.5. Since the $E_{a,i}$ of electrochemical ORR steps are generally small, we adopted to 0.26 eV to represent the proton transfer energy barrier, and this approach has been adopted by many theoretical studies.[2-5] These rate equations are solved at steady state.

(1) Hansen, H. A.; Viswanathan, V.; Nørskov, J. K. Unifying Kinetic and

Thermodynamic Analysis of 2e- and 4e- Reduction of Oxygen on Metal Surfaces. J. Phys. Chem C 2014, 118, 6706−6718.

(2) Tripkovic, V.; Skulason, E.; Siahrostami, S.; Nørskov, J. K.; Rossmeisl, J. The Oxygen Reduction Reaction Mechanism on Pt (111) from Density Functional Theory Calculations. J. Electrochim. Acta 2010, 55, 79757981.

(3) Li, Y.; Zhang, S.; Yu, J.; Wang, Q.; Sun, Q.; Jena, P. A new C = C embedded porphyrin sheet with superior oxygen reduction performance. Nano Res. 2015, 8, 2901−2912.

(4) Rebarchik, M.; Bhandari, S.; Kropp, T.; Mavrikakis, M. How Noninnocent Spectator Species Improve the Oxygen Reduction Activity of Single-Atom Catalysts: Microkinetic Models from First-Principles Calculations. ACS Catal. 2020, 10, 9129–9135.

(5) Huang, X.; Gan, L.-Y.; Wang, J.; Ali, S.; He, C.-C.; Xu, H. Developing Proton-Conductive Metal Coordination Polymer as Highly Efficient Electrocatalyst toward Oxygen Reduction. J. Phys. Chem. Lett. 2021, 12, 9197−9204.

Table S1. The calculated total energy (eV) and corresponding ZPE-TS (eV) used in the Gibbs free energy calculations.

	Total energy	ZPE-TS (T=300K)	Free energy (eV)
H_2O	-14.2244	-0.0662	-14.2906
H_2	-6.75924	-0.1335	-6.89276
OH^-			-10.8442
*OOH		0.2215	
*O		-0.0145	
*OH		0.2588	

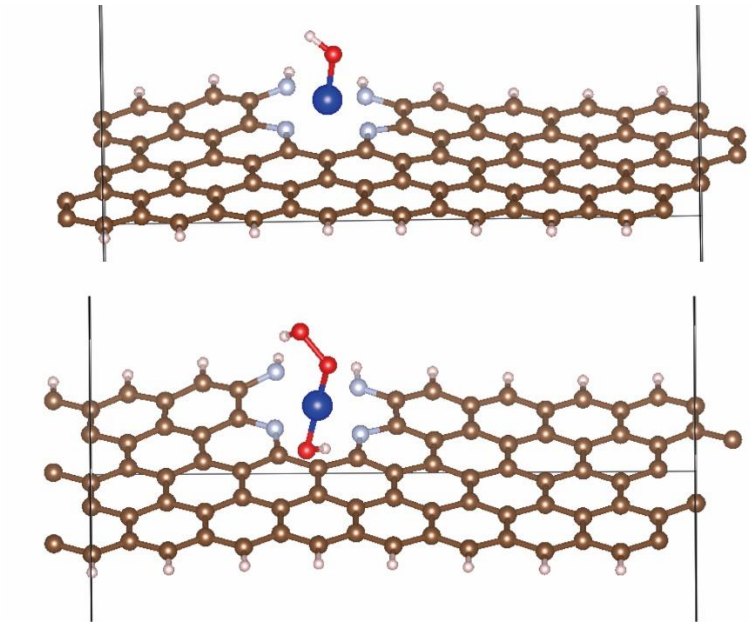
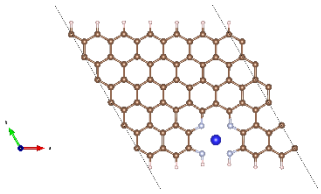
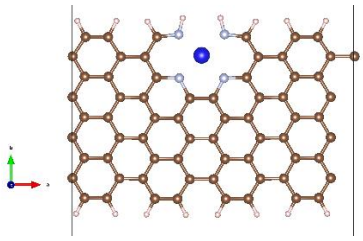


Figure S1. The structure of OH ligand modified zig-zag-hosted Fe-N_4, and with OOH adsorption. The two structured are drawn by the data in reference below, which is Ref. 3 in the main text.

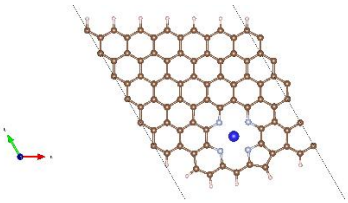
Hoon, T. C.; David, A. C.; Drew, H.; Brian, T. S.; Edward, F. H.; Karren, L. M.; Piotr, Z. Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst. Science 2017, 357, 479-484.



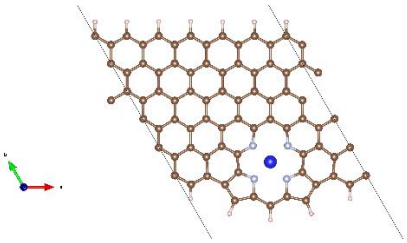
str-1



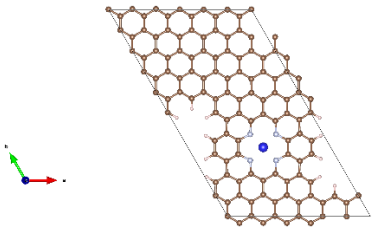
str-2



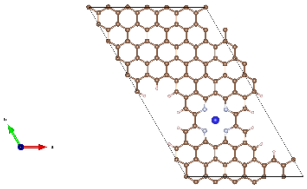
str-3



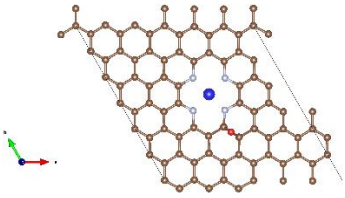
str-4



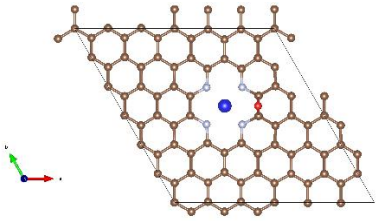
str-5



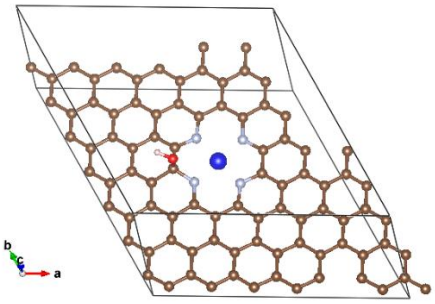
str-6



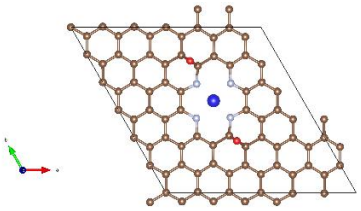
str-7



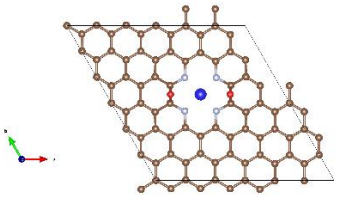
str-8



str-9

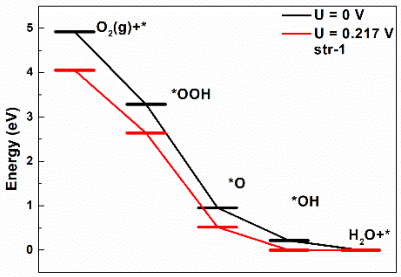


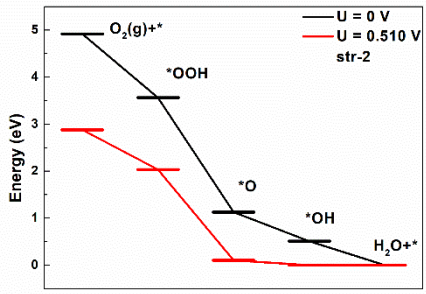
str-10

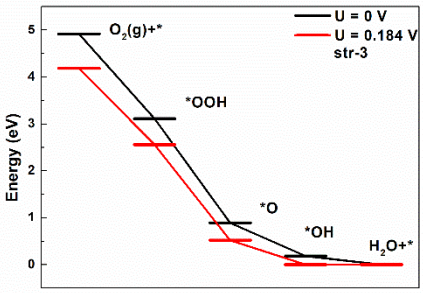


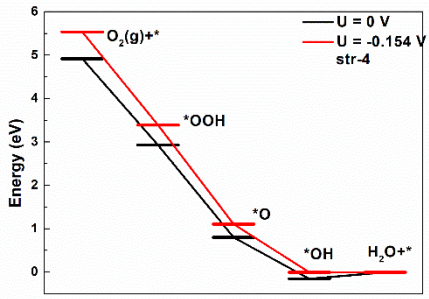
str-11

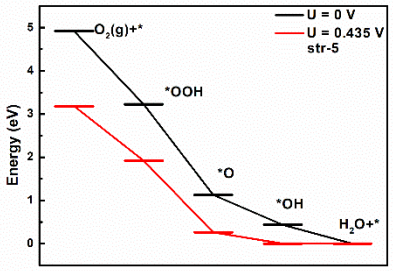
Figure S2. The original figure of structures used in this manuscript: str-1 to str-11.

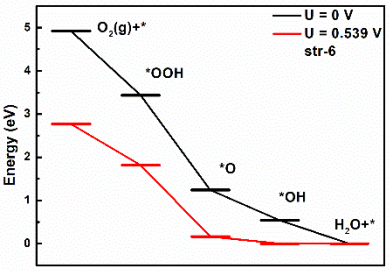

U = 0 V
U = 0.217 V
str-1
O2(g)+*
*OOH
*O
*OH
H2O+*
Energy (eV)

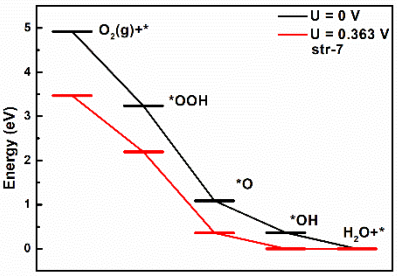

U = 0 V
U = 0.510 V
str-2
O2(g)+*
*OOH
*O
*OH
H2O+*
Energy (eV)


U = 0 V
U = 0.184 V
str-3
O2(g)+*
*OOH
*O
*OH
H2O+*
Energy (eV)


U = 0 V
U = -0.154 V
str-4
O2(g)+*
*OOH
*O
*OH
H2O+*
Energy (eV)


U = 0 V
U = 0.435 V
str-5
O2(g)+*
*OOH
*O
*OH
H2O+*
Energy (eV)


U = 0 V
U = 0.539 V
str-6
O2(g)+*
*OOH
*O
*OH
H2O+*
Energy (eV)


U = 0 V
U = 0.363 V
str-7
O2(g)+*
*OOH
*O
*OH
H2O+*
Energy (eV)

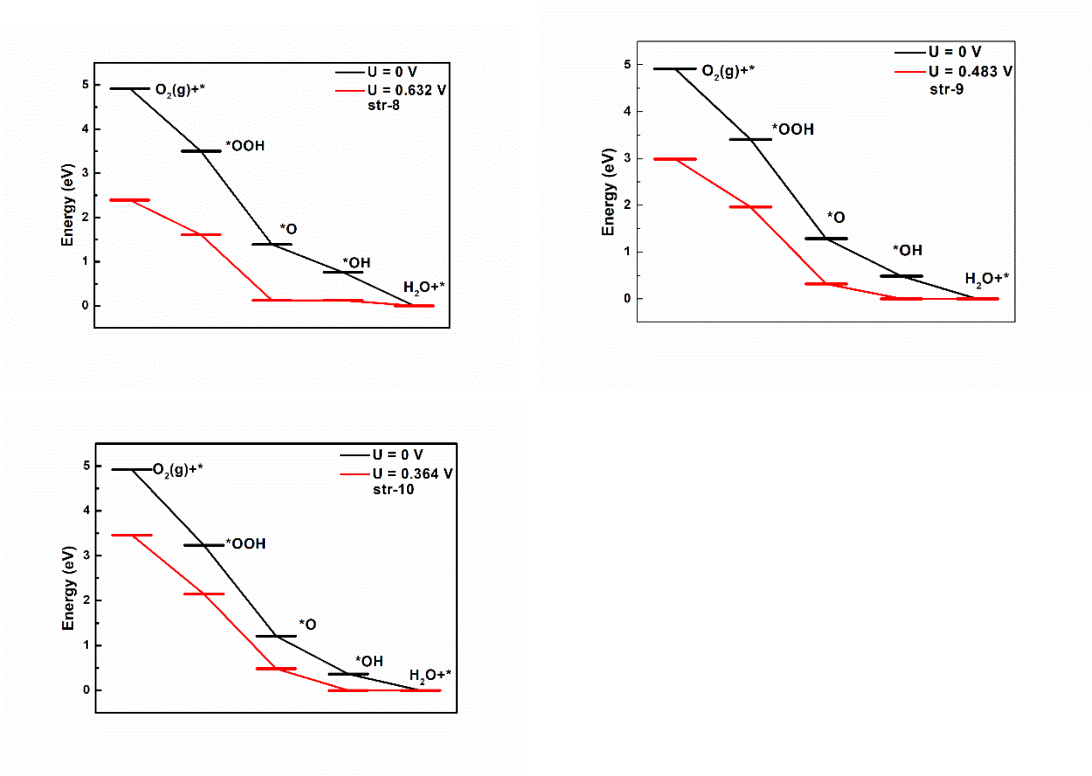
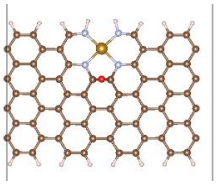
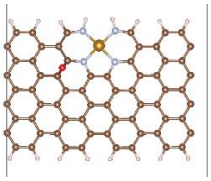


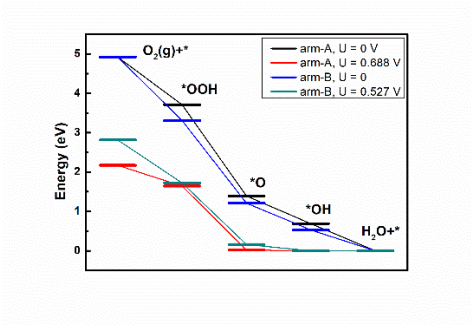
Figure S3. The calculated reaction Gibbs free energy for str-1 to str-10.

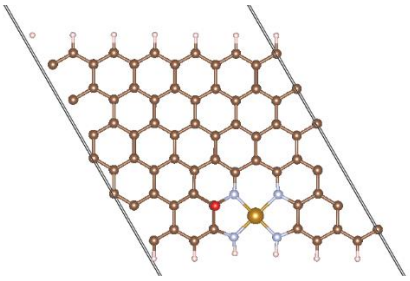


arm-typeA

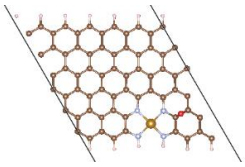


arm-typeB





zig-typeA



zig-typeB

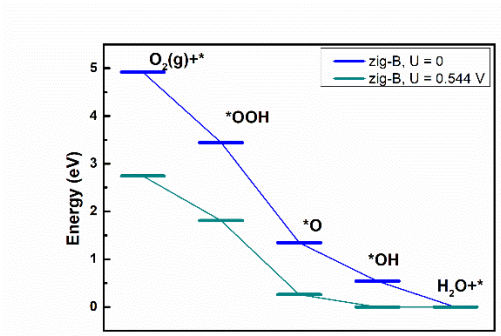


Figure S4. The structure of O adsorbed on str-1 and str-2 with type A and type B carbon atoms. The calculated reaction Gibbs free energy on these structures.

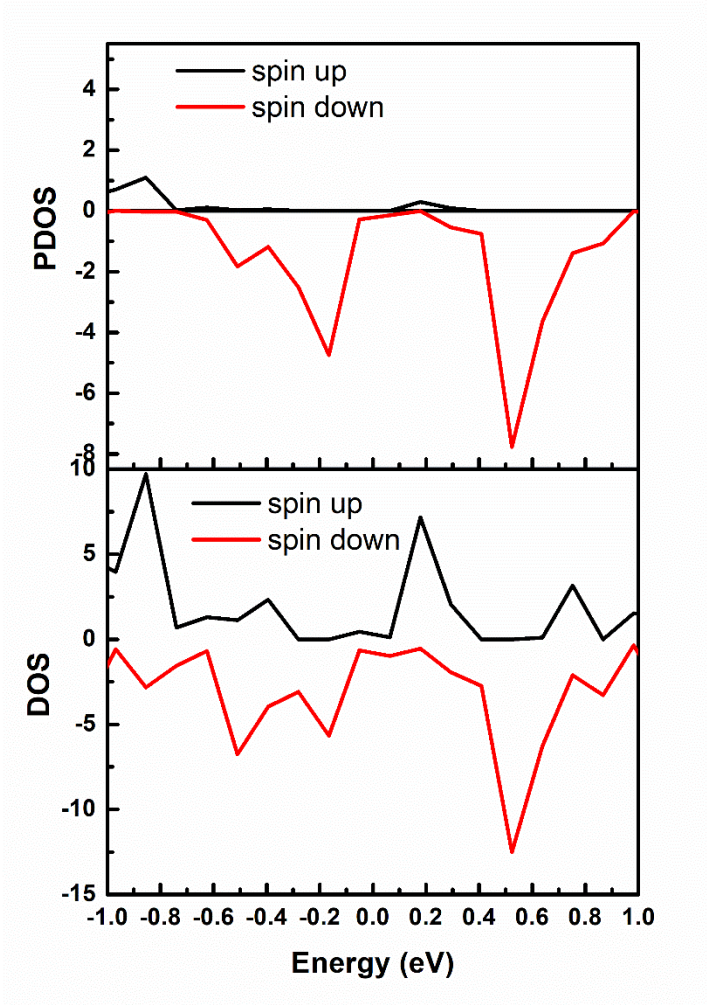


Figure S5. The calculated total DOS and PDOS of Fe of str-11. Fermi level is set to zero.

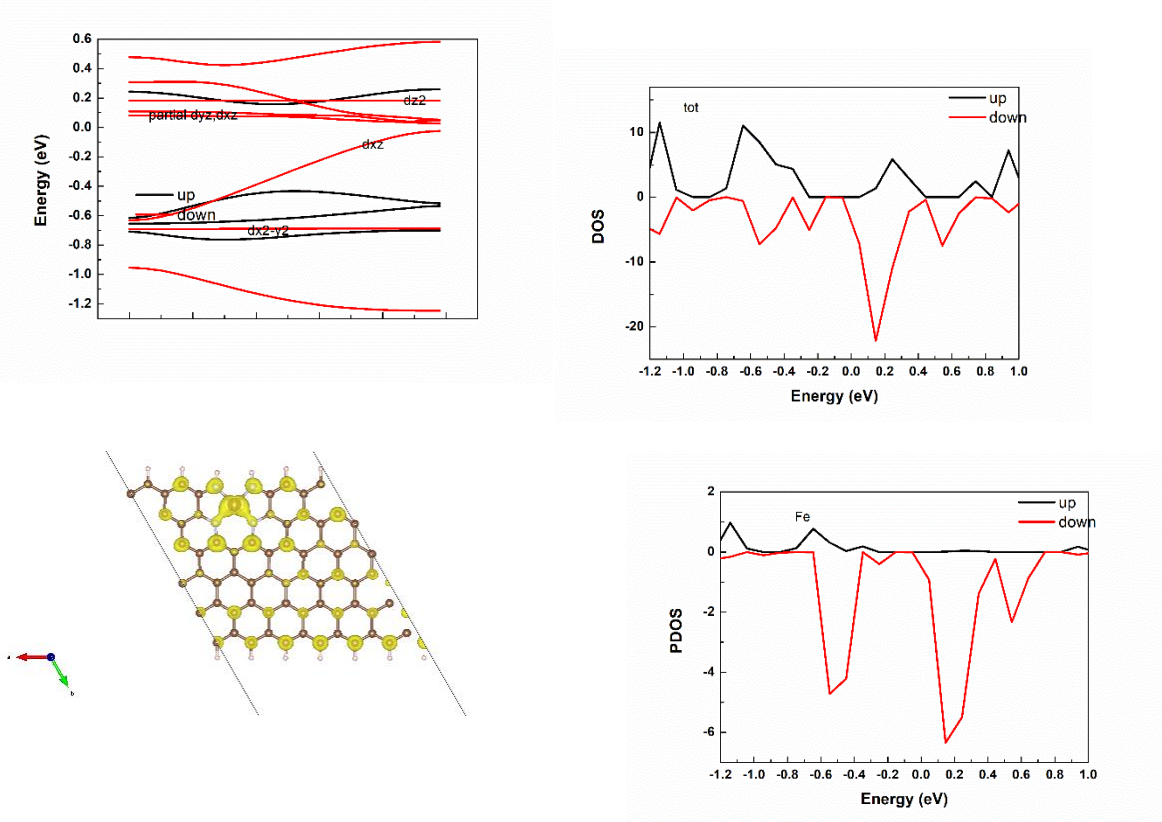


Figure S6. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-1. Fermi level is set to zero.

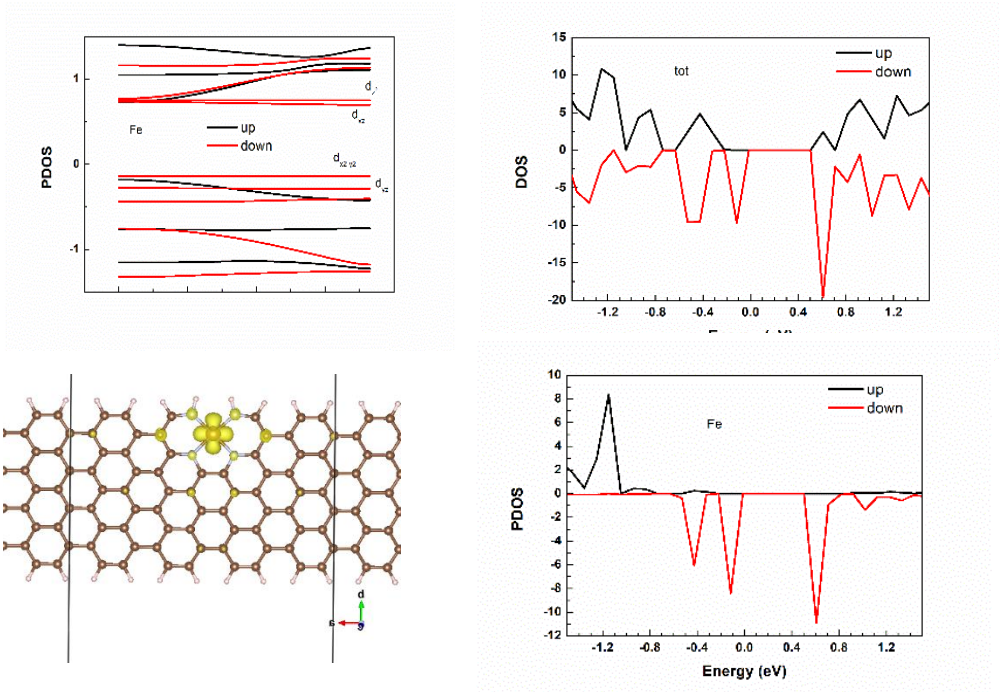


Figure S7. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-2. Fermi level is set to zero.

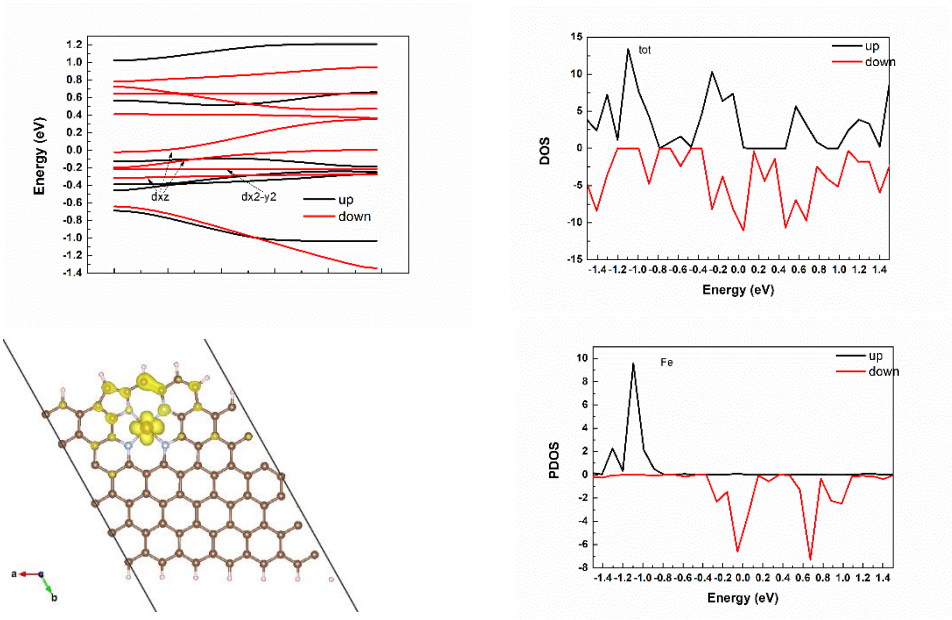


Figure S8. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-3. Fermi level is set to zero.

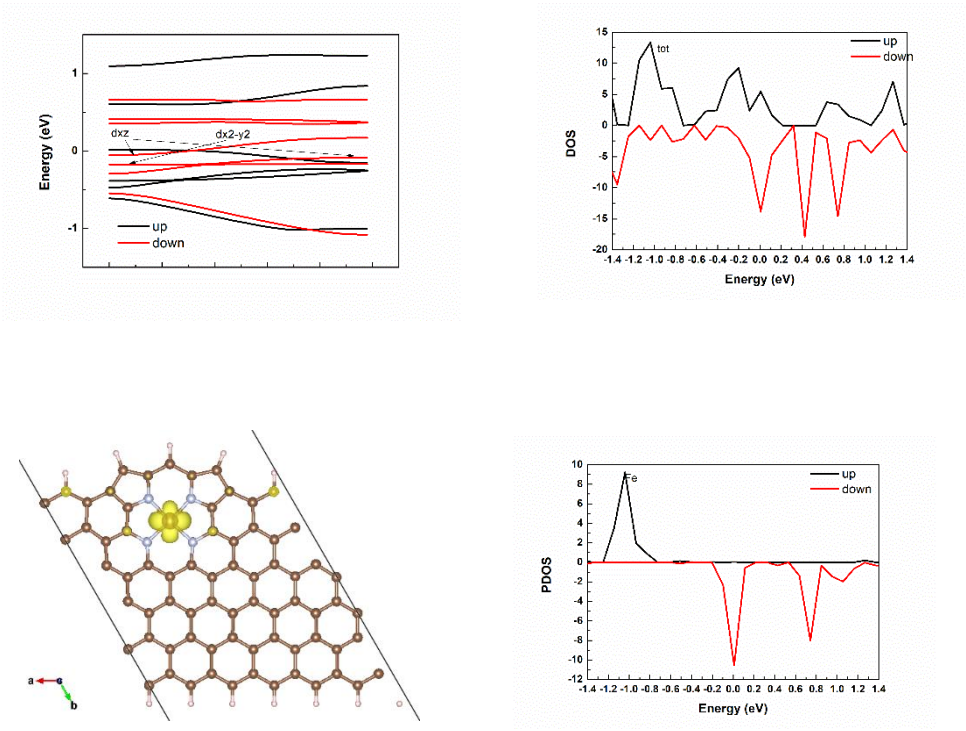


Figure S9. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-4. Fermi level is set to zero.

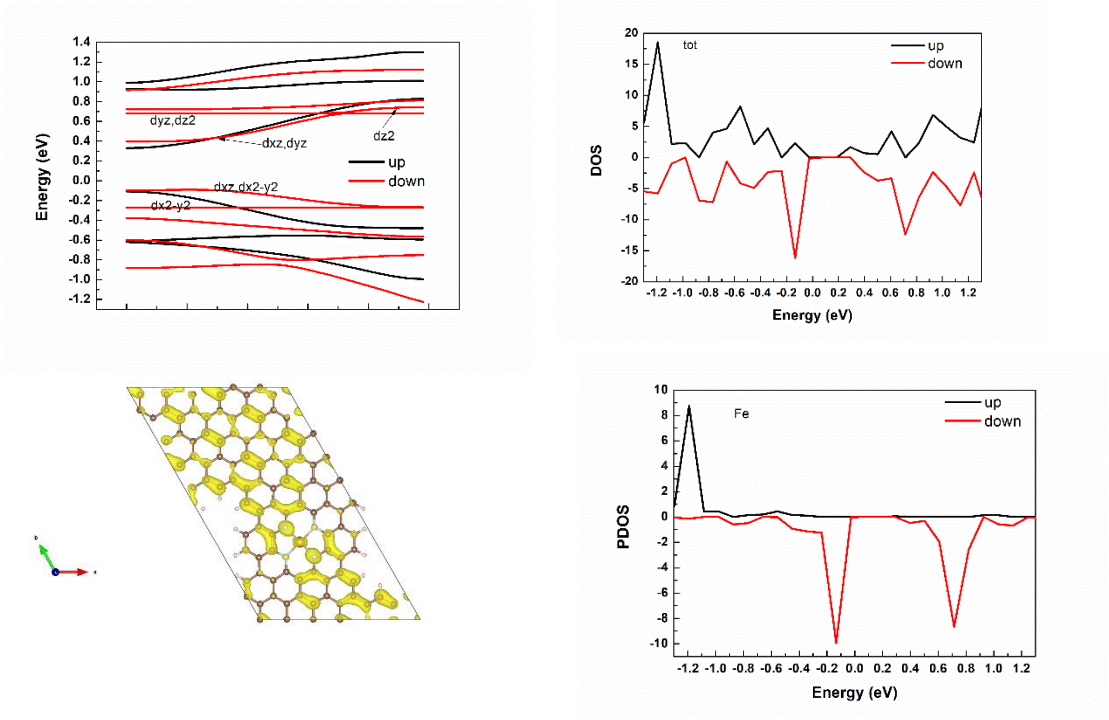


Figure S10. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-5. Fermi level is set to zero.

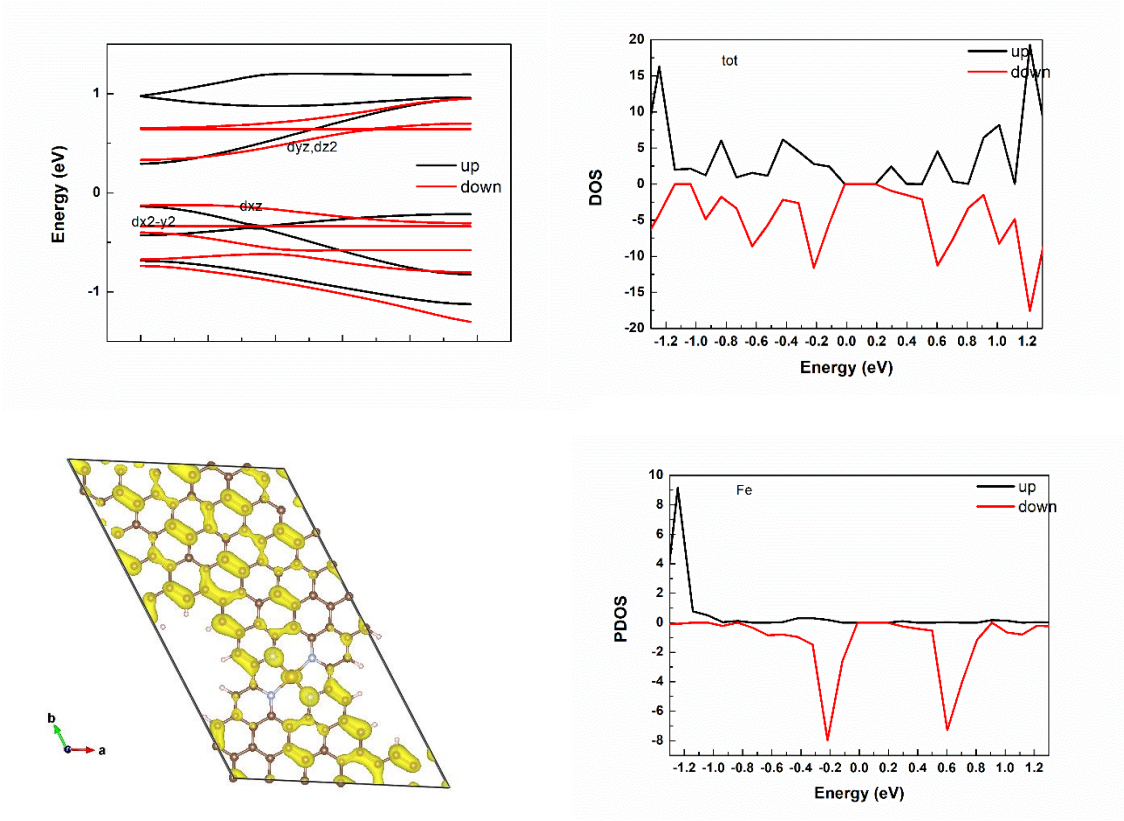


Figure S11. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-6. Fermi level is set to zero. Fermi level is set to zero.

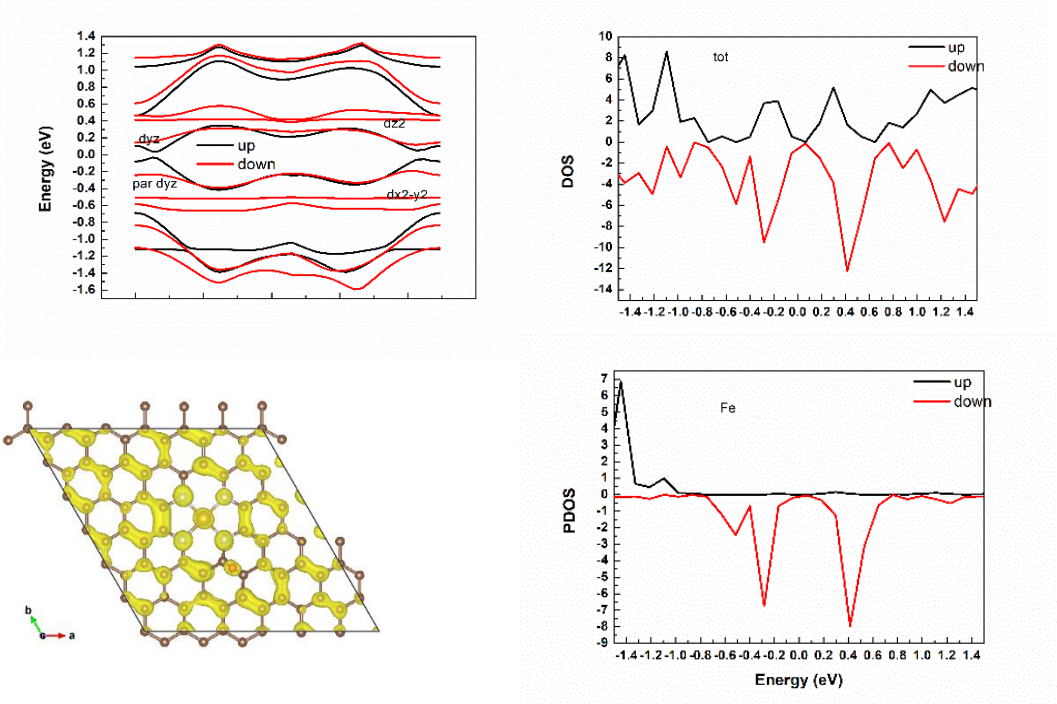


Figure S12. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-7. Fermi level is set to zero.

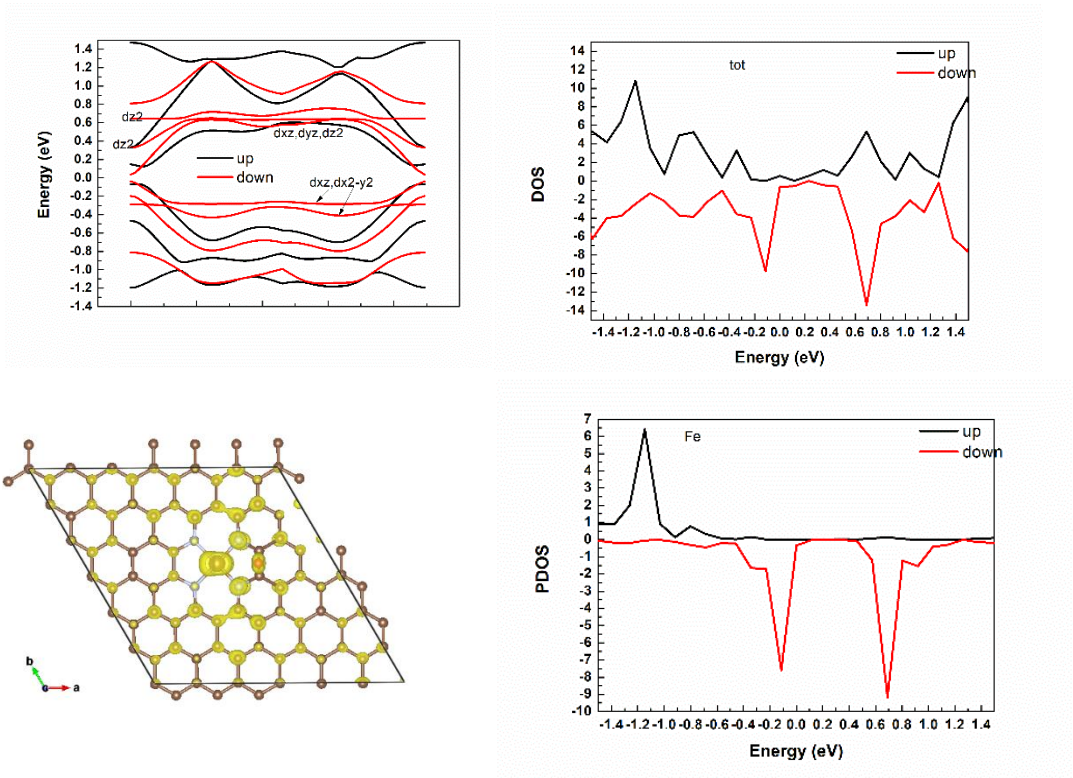


Figure S13. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-8. Fermi level is set to zero.

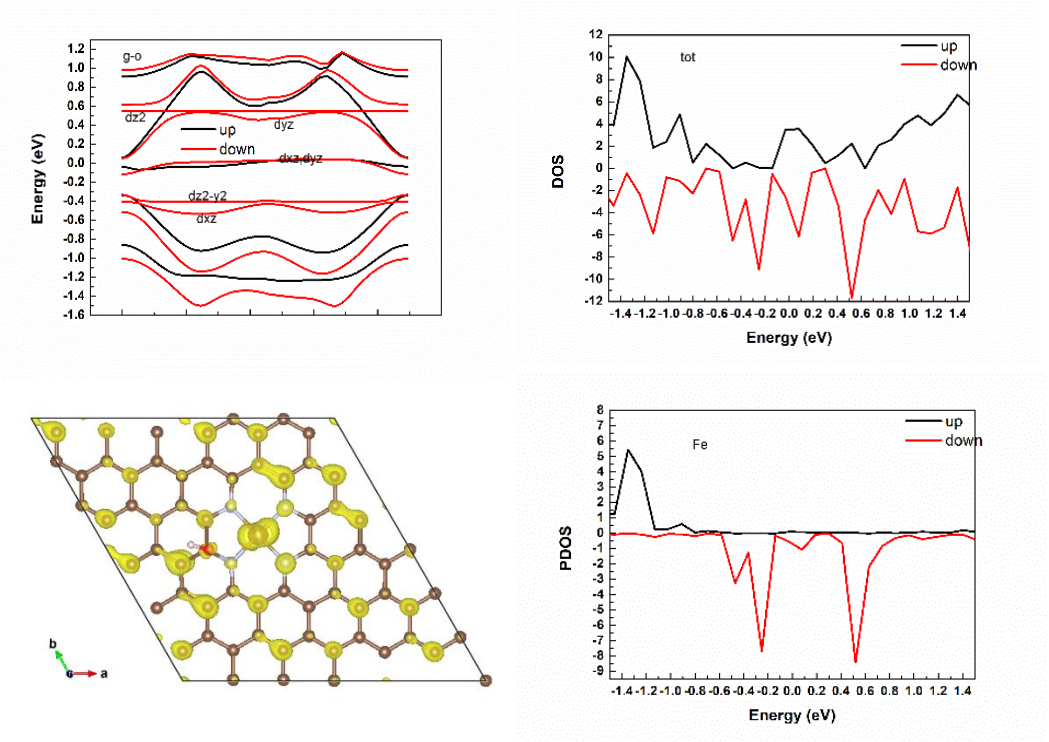


Figure S14. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-9. Fermi level is set to zero.

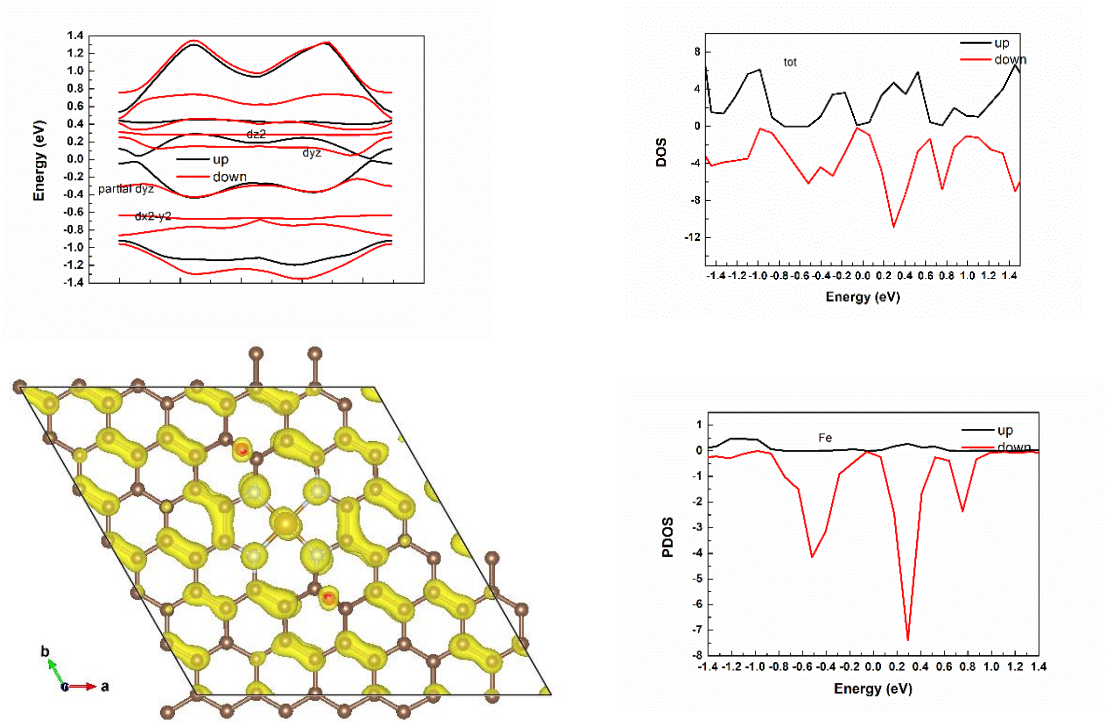


Figure S15. The calculated band structure, partial charge density, total density of states (DOS) and the partial DOS (PDOS) of Fe atom in str-10. Fermi level is set to zero.