Supporting Information for:

Regulating the spin state of single Fe Atom enhances photocatalytic nitrogen reduction in Fe-doped BiOBr: insights from theoretical studies

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Theoretical Calculation Details

The nitrogen reduction reaction (NRR) pathways were calculated according the following equations (2)–(15), the * denotes the surface of catalysts.[1]

Enzymatic mechanism:

$$* + N_2 + H^+ + e^- \rightarrow *NNH \text{.....} \quad (2)$$

$$*NNH + H^+ + e^- \rightarrow *NNH_2 \quad (3)$$

$$*NNH_2 + H^+ + e^- \rightarrow *NHNH_2 \quad (4)$$

$$*NHNH_2 + H^+ + e^- \rightarrow *NH_2NH_2 \quad (5)$$

$$*NH_2NH_2 + H^+ + e^- \rightarrow *NH_2NH_3 \quad (6)$$

$$*NH_2NH_3 + H^+ + e^- \rightarrow *NH_3 + NH_3 \quad (7)$$

$$*NH_3 + NH_3 \rightarrow * + 2NH_3 \quad (8)$$

Alternating mechanism:

$$* + N_2 + H^+ + e^- \rightarrow *NNH \quad (9)$$

$$*NNH + H^+ + e^- \rightarrow *NHNH \quad (10)$$

$$*NHNH + H^+ + e^- \rightarrow *NHNH_2 \quad (11)$$

$$*NHNH_2 + H^+ + e^- \rightarrow *NH_2NH_2 \quad (12)$$

$$*NH_2NH_2 + H^+ + e^- \rightarrow *NH_2 + NH_3 \quad (13)$$

$$*NH_2 + NH_3 + H^+ + e^- \rightarrow *NH_3 + NH_3 \ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

$$*NH_3 + NH_3 \rightarrow * + 2NH_3 \quad (15)$$

Distal mechanism:

$$* + N_2 + H^+ + e^- \rightarrow *NNH \quad (16)$$

$$*NNH + H^+ + e^- \rightarrow *NNH_2 \quad (17)$$

$$*NNH_2 + H^+ + e^- \rightarrow *N + NH_3 \quad (18)$$

$$*N + H^+ + e^- \rightarrow *NH \quad (19)$$

$$*NH + H^+ + e^- \rightarrow *NH_2 \quad (20)$$

$$*NH_2 + H^+ + e^- \rightarrow *NH_3 \quad (21)$$

$$*NH_3 + NH_3 \rightarrow * + 2NH_3 \quad (22)$$

The Gibbs free energy, G, was computed according to the equation (8) as follows:[2]

$$G = E + E_{ZPE} - TS - eU \quad (23)$$

In the above equation, E, E_{ZPE}, and S represents the single point energy, zero point energy and entropy of intermediates for NRR, respectively. The U is the potential versus standard hydrogen electrode. The temperature is set to 298.15 K.

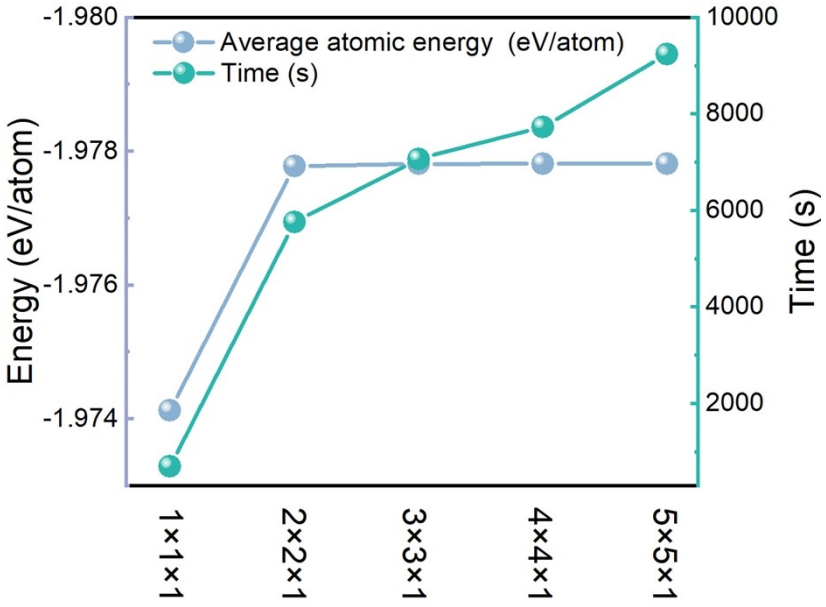

Fig. S1. Convergence test of k-points meshes.

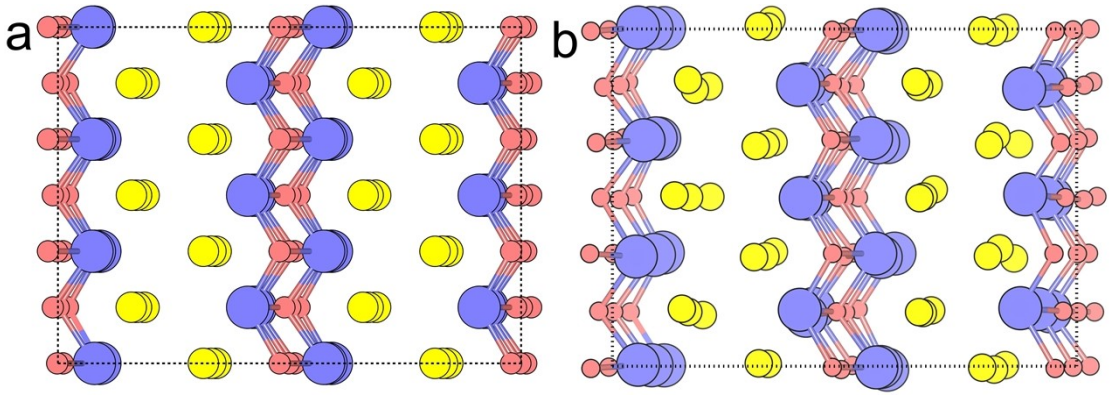

Fig. S2. Geometries of pristine BiOBr system at (a) 0 K and (b) 300K. The blue, light red, and yellow spheres denote Bi, O, and Br atoms, respectively.

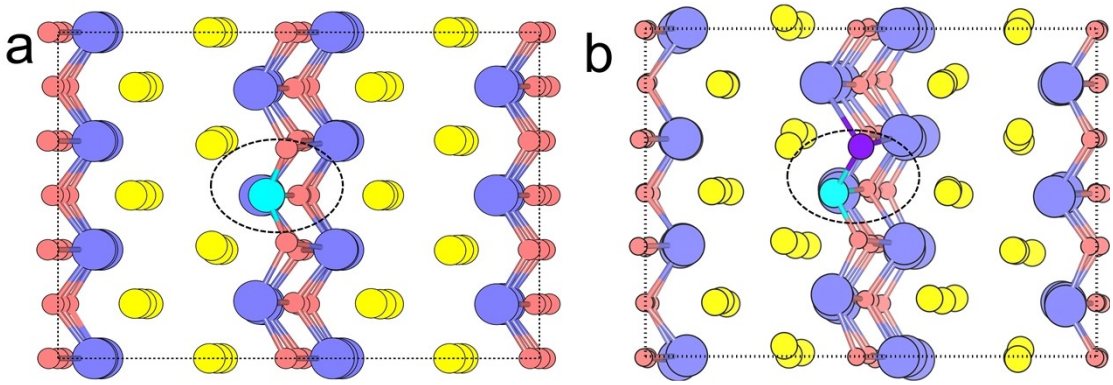

Fig. S3. Representative geometries of MD trajectories for (a) Fe-doped and (b) FeP-doped BiOBr systems. The blue, light red, yellow, cyan and purple balls represent Bi, O, Br, Fe and P atoms, respectively.

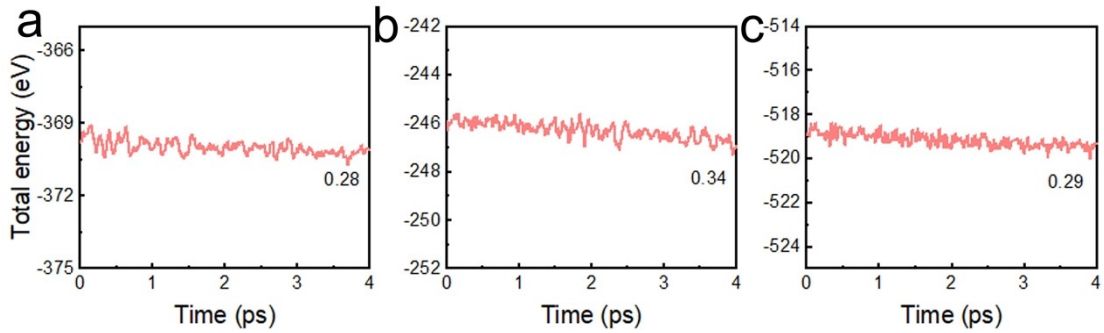

Fig. S4. Evolution of total energies during the MD in (a) pristine BiOBr, (a) Fe-doped, and (b) FeP-doped BiOBr systems. The data represent the canonically averaged standard deviations of the total energies.

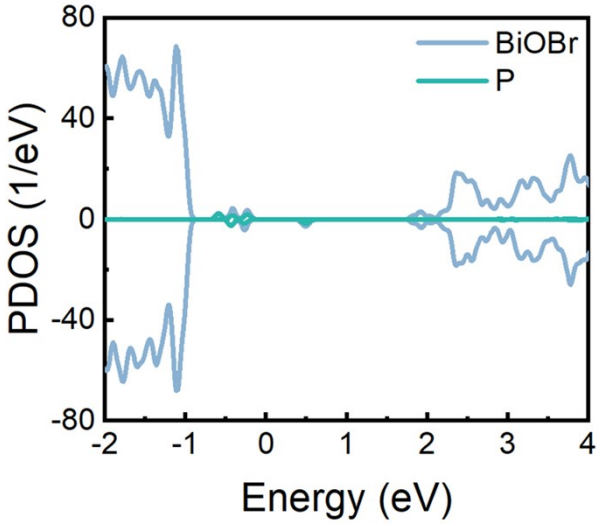

Fig. S5. Projected density of states (PDOS) of P doped BiOBr. The Fermi level is set to zero.

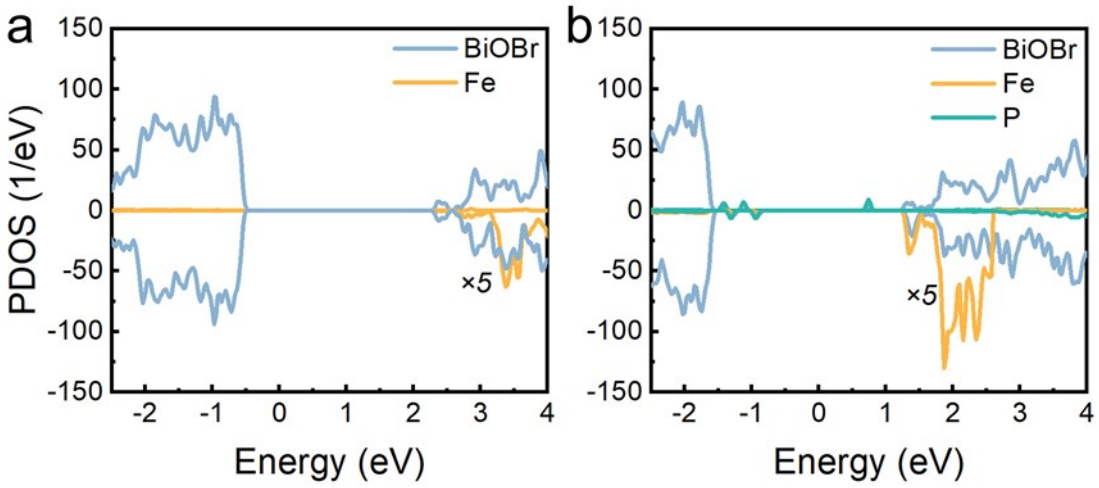

Fig. S6. Projected density of states (PDOS) (a) Fe-doped and (b) FeP-doped BiOBr systems calculated using the HSE06 functional. The Fermi level is set to zero.

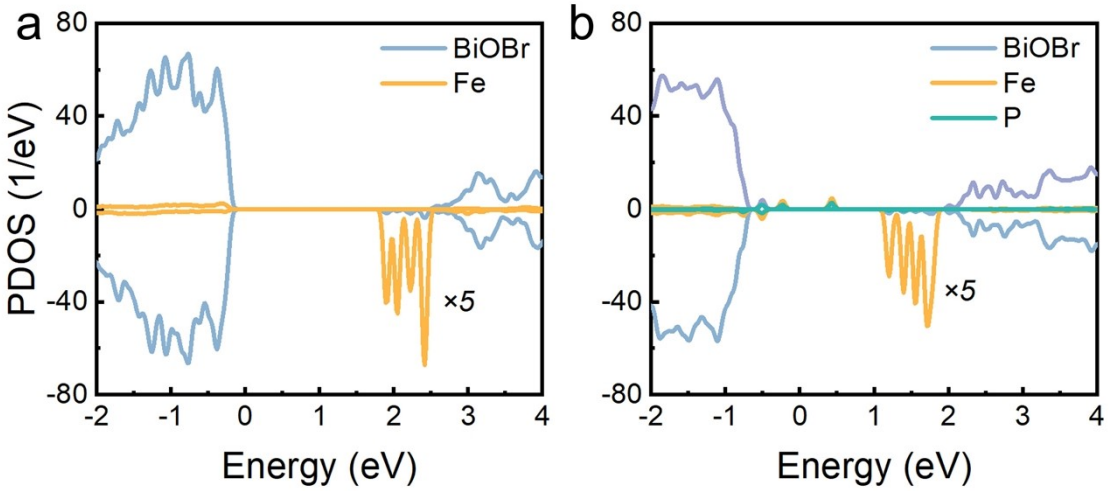

Fig. S7. Projected density of states (PDOS) of (a) Fe-doped and (b) FeP-doped BiOBr systems calculated using 3×3×1 k-points. The Fermi level is set to zero.

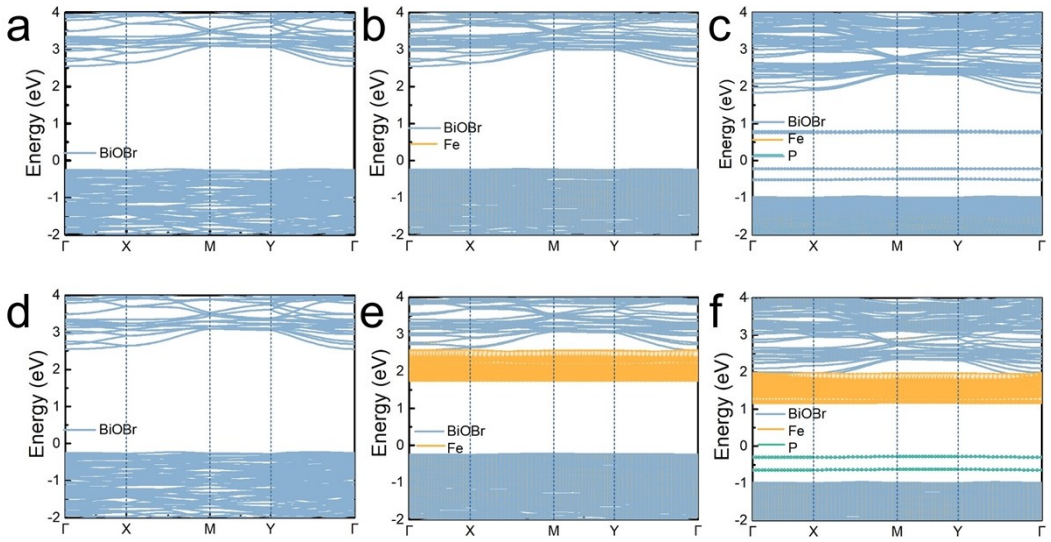

Fig. S8. Spin-up (top panel) and spin-down (bottom panel) band structures of (a, d) pristine, (b, e) Fe-doped, and (c, f) FeP-doped BiOBr systems. The Fermi level is set to zero.

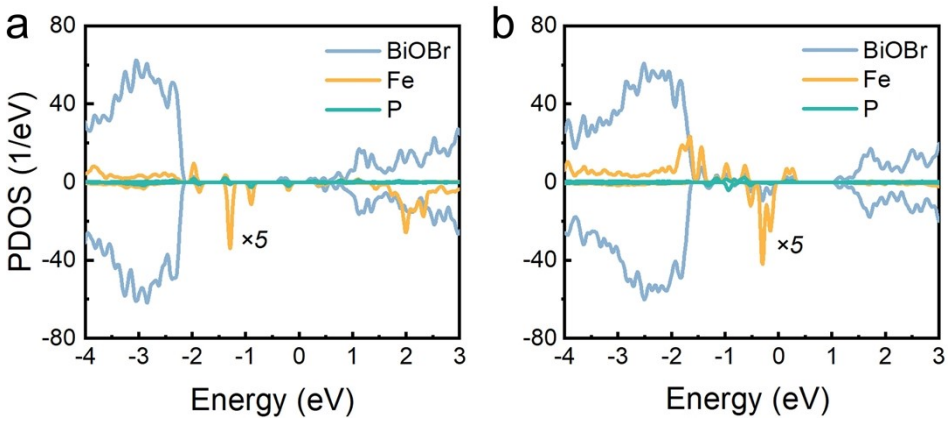

Fig. S9. Projected density of states (PDOS) of (a) FeP_2 and (b) FeP_3 doped BiOBr systems. The Fermi level is set to zero.

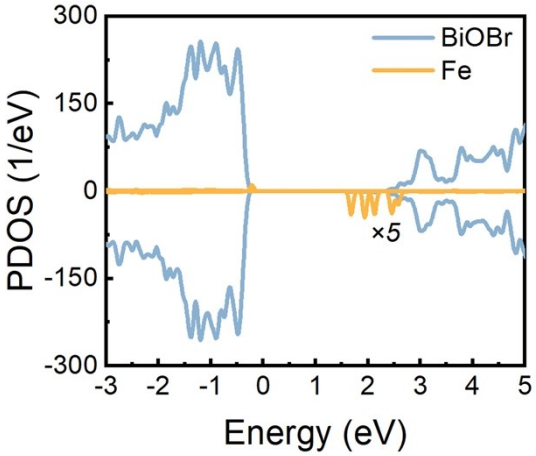

Fig. S10. Projected density of states (PDOS) of Fe-doped 4×4×1BiOBr supercell. The Fermi level is set to zero.

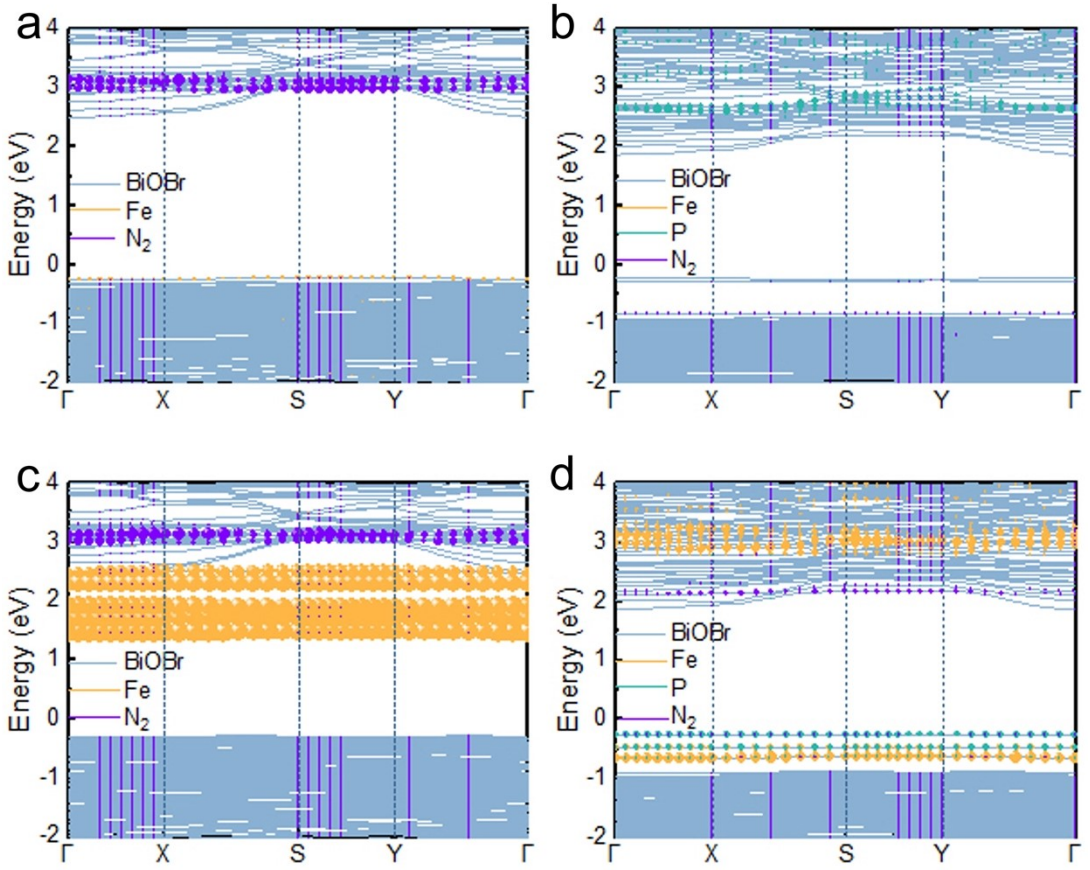

Fig. S11. Spin-up (top panel) and spin-down (bottom panel) band structures of nitrogen adsorbed (a, b) Fe-doped and (c, d) FeP-doped BiOBr systems The Fermi level is set to zero.

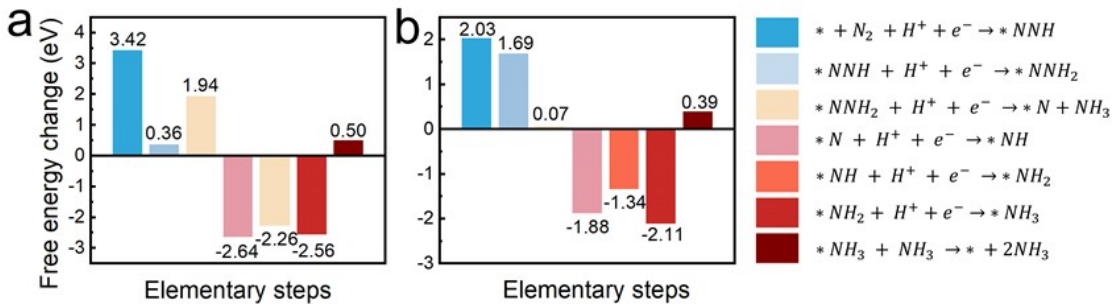

Fig. S12. Free energy change for elementary steps along the distal pathways for NRR in (a) Fe-doped and (b) FeP-doped BiOBr systems.

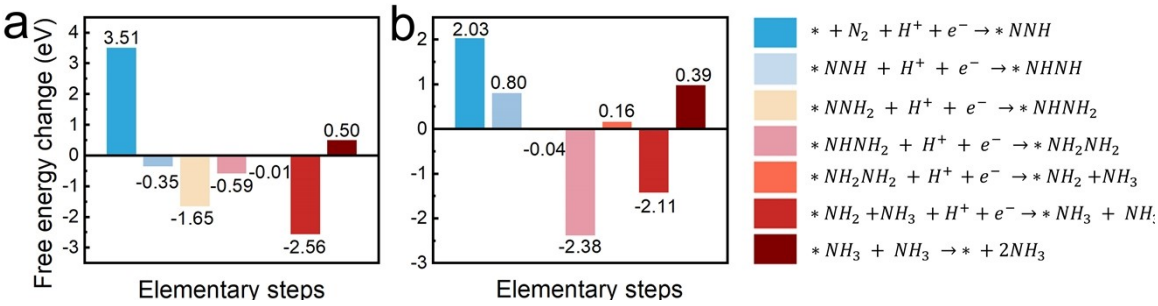

Fig. S13. Free energy change for elementary steps along the alternating pathways for NRR in (a) Fe-doped and (b) FeP-doped BiOBr systems.

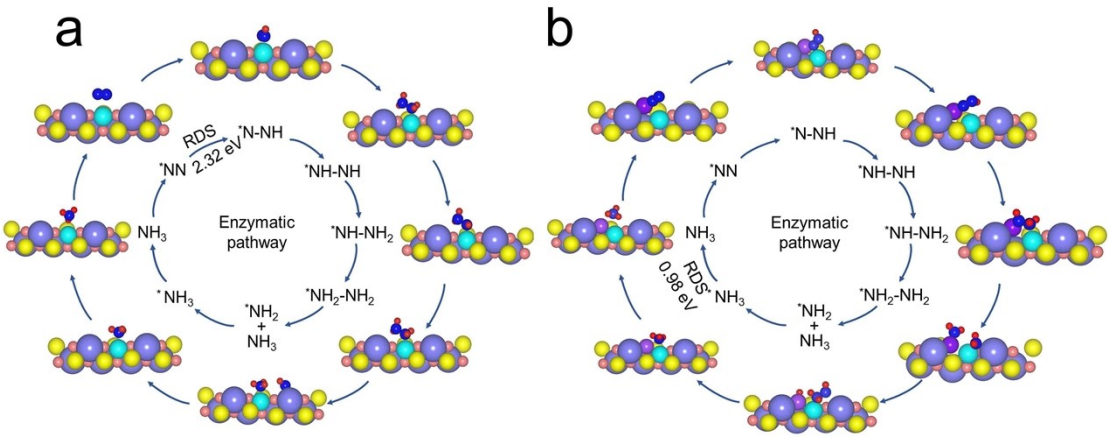

Fig. S14. Configurations of the intermediate in the enzymatic pathway for NRR in (a) Fe-doped and (b) FeP-doped BiOBr systems.

References

1 H. D. Shen, M. M. Yang, L. D. Hao, J. R. Wang, J. Strunk and Z. Y. Sun, *Nano Res.*, 2022, **15**, 2773-2809.

2 K. Gao, C. Zhang, H. Zhu, J. Xia, J. Chen, F. Xie, X. Zhao, Z. Tang and X. Wang, *Chem. Eur. J.*, 2023, **29**, e202300616.