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**Ru–Polyoxometalate as a Single-Atom Electrocatalyst for N<sub>2</sub> Reduction to NH<sub>3</sub>  
with High Selectivity under Applied Voltage: Perspective from DFT Studies**

Linghui Lin<sup>1</sup>, Liye Gao<sup>1</sup>, Ke Xie<sup>1</sup>, Rong Jiang<sup>2,\*</sup>, and Sen Lin<sup>1,\*</sup>

*<sup>1</sup>State Key Laboratory of Photocatalysis on Energy and Environment, College of  
Chemistry, Fuzhou University, Fuzhou 350002, China*

*<sup>2</sup>Institute of Advanced Energy Materials, Fuzhou University, Fuzhou 350002, China*

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\*Corresponding author. Email: [slin@fzu.edu.cn](mailto:slin@fzu.edu.cn) and [jiangrong@fzu.edu.cn](mailto:jiangrong@fzu.edu.cn)

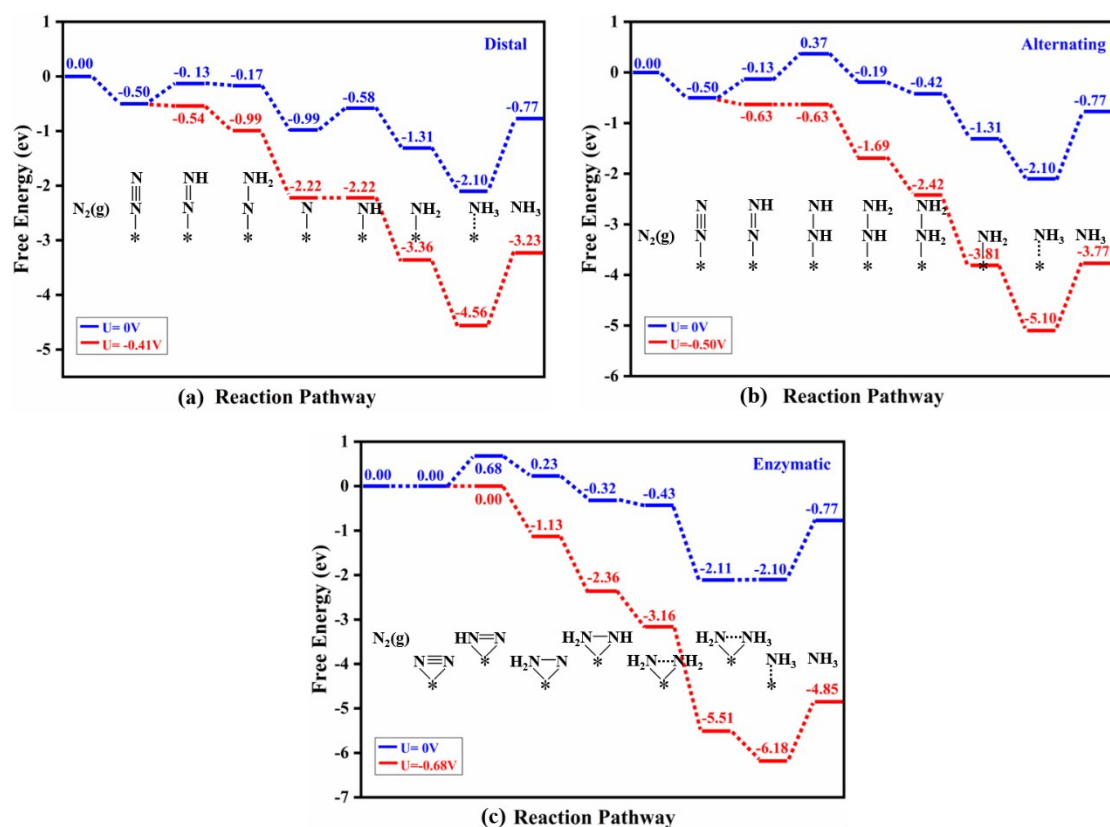


Figure S1. Free energy of  $N_2$  reduction on Ru-PMA through (a) distal, (b) alternating, and (c) enzymatic mechanisms at zero and applied potentials.

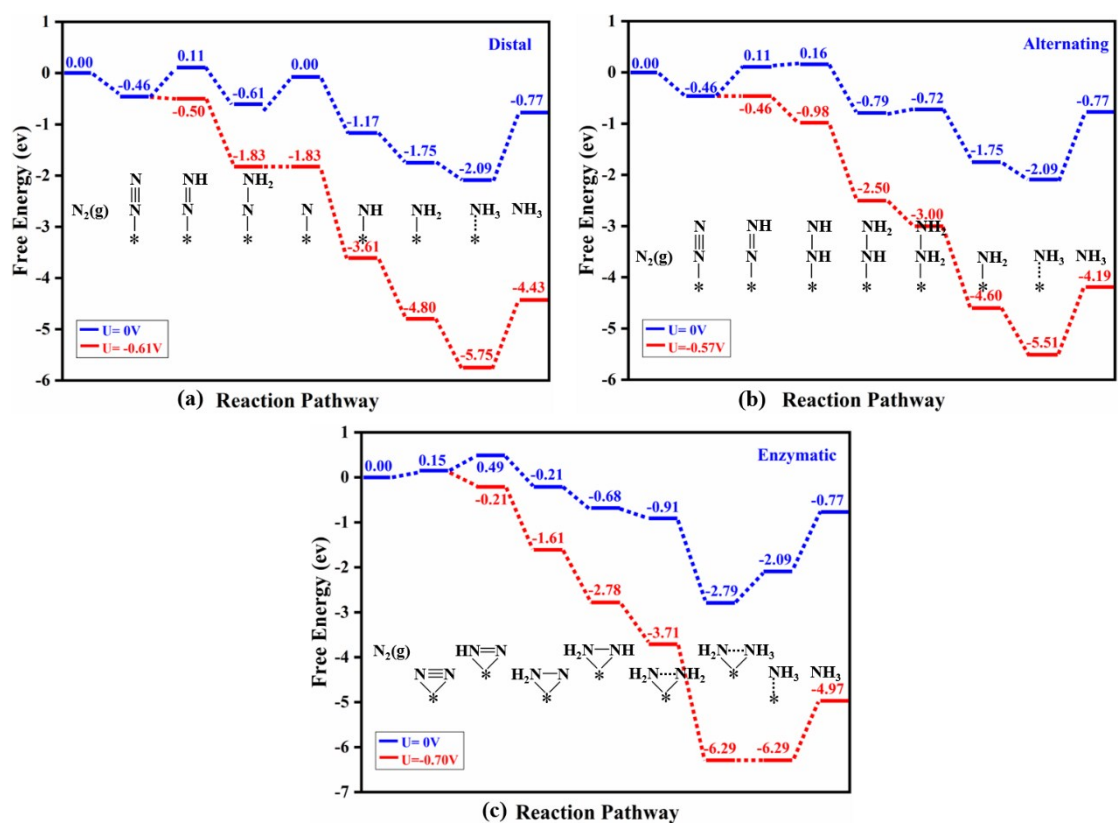


Figure S2. Free energy of  $N_2$  reduction on Ru-SiTA through (a) distal, (b) alternating, and (c) enzymatic mechanisms at zero and applied potentials.

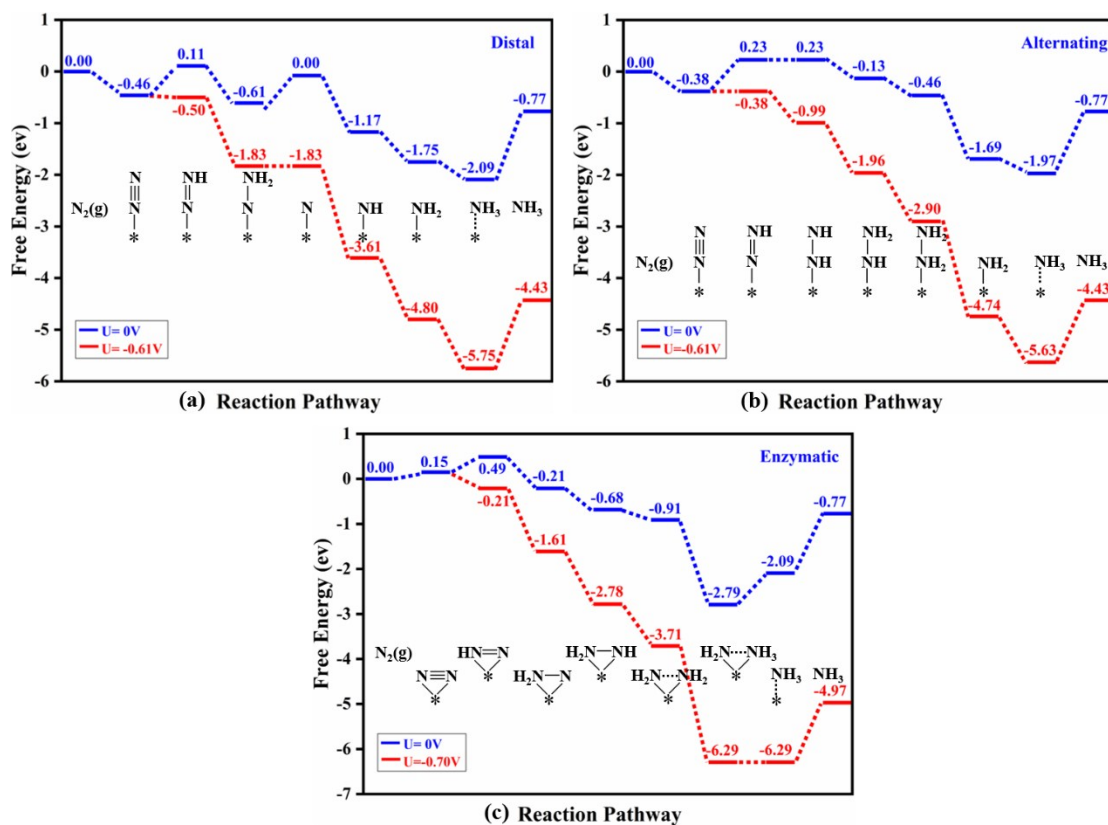


Figure S3. Free energy of  $N_2$  reduction on Ru-SiMA through (a) distal, (b) alternating, and (c) enzymatic mechanisms at zero and applied potentials.