Supplementary Information

# Photo-Assisted High Performance Single Atom Electrocatalysis of $N_2$ Reduction Reaction by Mo-embedded Covalent Organic Framework

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**Table S1.** The total energy, the zero-point energy (ZPE), entropy, and free energy of gaseous $N_2$, $H_2$ and $NH_3$.

| Species | Energy (eV) | ZPE (eV) | T*S (eV) | Free Energy (eV) |
|---|---|---|---|---|
| $N_2$ | -16.63 | 0.15 | 0.62 | -17.07 |
| $H_2$ | -6.78 | 0.27 | 0.40 | -6.90 |
| $NH_3$ | -19.54 | 0.91 | 0.59 | -19.22 |

**Table S2.** Thermal Corrections of zero-point energy ($E_{ZPE}$), enthalpy correction ($\int C_p dT$), and entropy correction (TS) of different adsorbed species. The entropy correction of the gas-phase molecules was obtained from the NIST database[a]

| Species | $E_{ZPE}$ | $\int C_p dT$ | T*S |
|---|---|---|---|
| $H_2$[a] | 0.27 | 0.09 | 0.40 |
| $N_2$[a] | 0.15 | 0.09 | 0.59 |
| $NH_3$[a] | 0.89 | 0.11 | 0.60 |
| *NN | 0.21 | 0.07 | 0.16 |
| *NNH | 0.48 | 0.08 | 0.17 |
| *NNHH | 0.80 | 0.08 | 0.17 |
| *N | 0.09 | 0.03 | 0.06 |
| *NH | 0.35 | 0.05 | 0.09 |
| *$NH_2$ | 0.68 | 0.06 | 0.10 |
| *$NH_3$ | 1.03 | 0.06 | 0.10 |
| *NHNH | 0.82 | 0.07 | 0.13 |
| *$NHNH_2$ | 1.14 | 0.10 | 0.21 |
| *$NH_2NH_2$ | 1.36 | 0.10 | 0.09 |
| *N*N | 0.20 | 0.06 | 0.11 |
| *N*NH | 0.49 | 0.07 | 0.12 |
| *NH*NH | 0.78 | 0.09 | 0.17 |
| *N*$NH_2$ | 0.85 | 0.07 | 0.14 |
| *NH*$NH_2$ | 1.13 | 0.10 | 0.21 |
| *$NH_2$*$NH_2$ | 1.36 | 0.10 | 0.16 |

$\Delta G = \Delta E + \Delta E_{ZPE} + \int C_p dT - T\Delta S - \Delta G_U + \Delta G_{pH}$

a. Computational Chemistry Comparison and Benchmark Database. http://cccbdb.nist.gov/.

**Table S3.** The Bader charge variation of three moieties along the distal pathway.

| Distal pathway | NmHn (moiety 1) | $MoN_4$ (moiety 2) | Pc-TFPN (moiety 3) |
|---|---|---|---|
| *+$N_2$—*NN | 0.28 | -0.19 | -0.09 |
| *+$N_2$+H—*NNH | 0.43 | -0.18 | -0.25 |
| *+$N_2$+2H—*NNHH | 0.37 | -0.14 | -0.23 |
| *+$N_2$+3H—*N+$NH_3$ | 0.74 | -0.20 | -0.54 |
| *+$N_2$+4H—*NH+$NH_3$ | 0.53 | -0.33 | -0.20 |
| *+$N_2$+5H—*$NH_2$+$NH_3$ | 0.24 | -0.29 | 0.06 |
| *+$N_2$+6H—*$NH_3$+$NH_3$ | -0.21 | -0.16 | 0.36 |

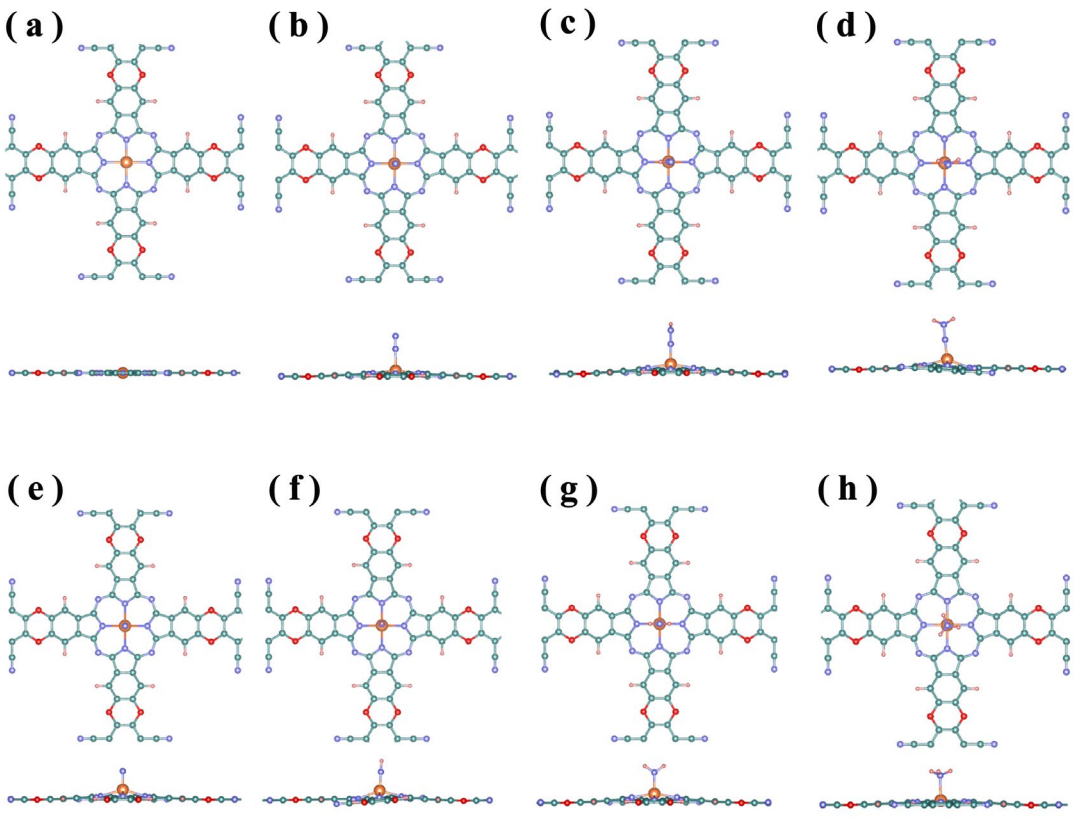


**Figure S1.** The optimized structures of intermediates along the distal pathway.

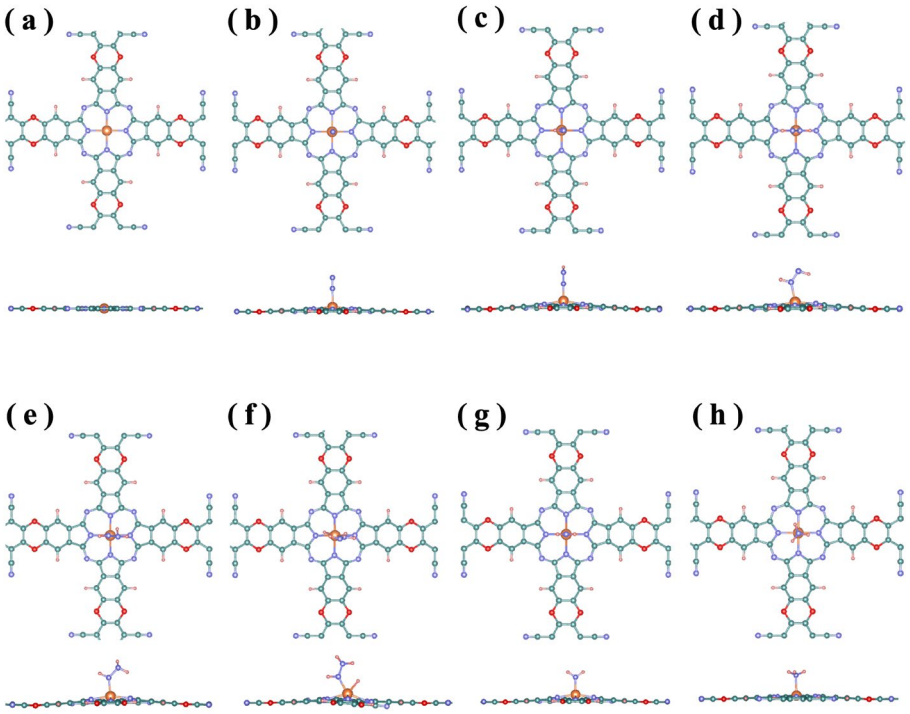


**Figure S2.** The optimized structures of intermediates along the alternating pathway.

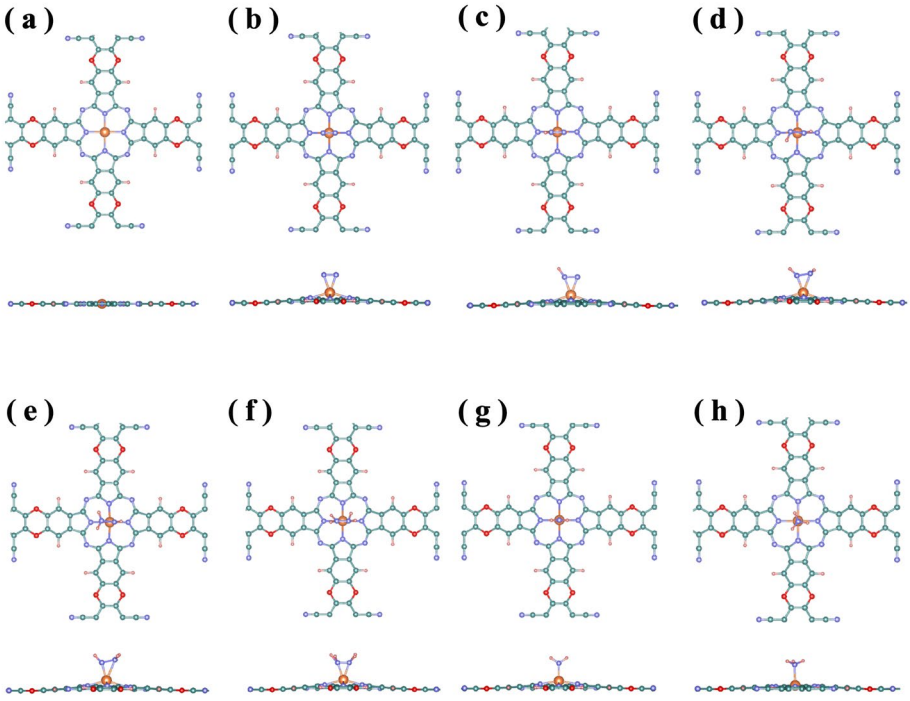


**Figure S3.** The optimized structures of intermediates along the enzymatic pathway.

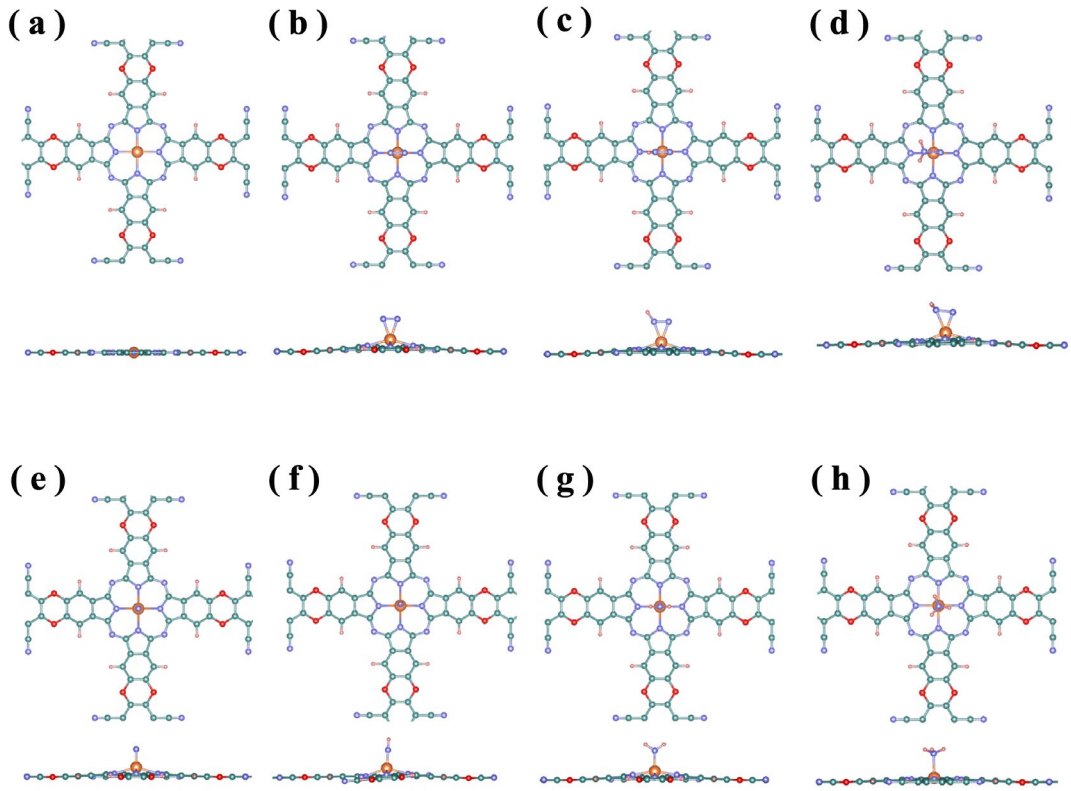


**Figure S4.** The optimized structures of intermediates along the consecutive pathway.

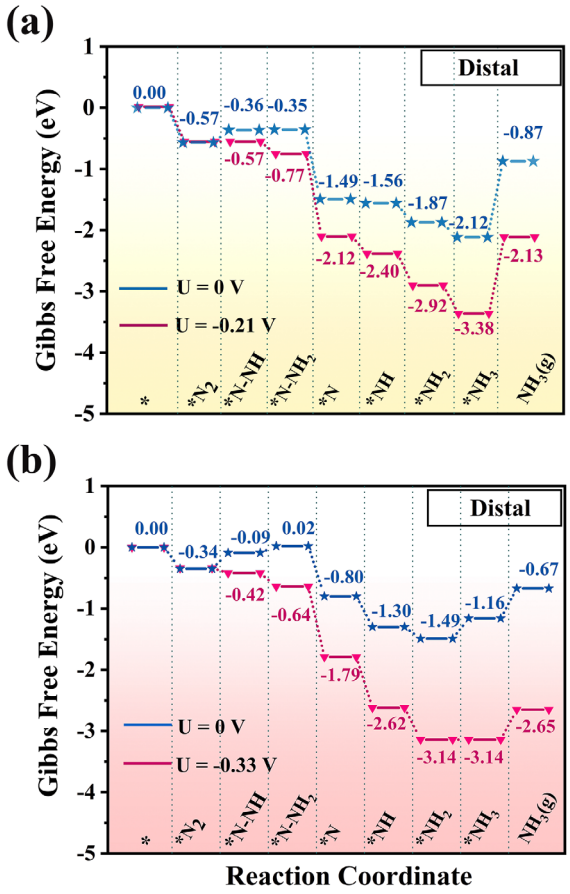


**Figure S5.** Gibbs free energy diagrams for NRR on MoPc-TFPN through distal way with (a) and without (b) correction (enthalpy correction + solvation model) calculations, respectively.