# Supporting Information

## Boosting electrochemical nitrogen reduction reaction performance of two-dimensional Mo Porphyrin monolayer via turning the coordination environment

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## Content

**Thermochemistry**

When we calculate the Gibbs free energy difference (ΔG) between two neighboring intermediates, which can be named as 1 and 2, ΔG can be calculated as:

$$\Delta G_{21} = G_2 - G_1 \quad (1)$$

Such as: in the reaction $N_2$*→$N_2H$*, where '*' denotes the substrate, the Gibbs free energy ΔG will result in the following equation:

$$G = G(N_2H*) - G(N_2*) - G(H^+/e^-) \quad (2)$$

For this equation, the chemical potential of the $H^+/e^-$ pair equals to the half value of the chemical potential of the dihydrogen molecule. Given the standard hydrogen electrode conditions, the $G(H^+/e^-)$ equals to $1/2G(H_2)$. [1, 2]

Adsorbed intermediates species were only taken vibrational entropy (S) into account, which the corresponding function is showed in the (3) formula.

$$S = -R\sum_i \ln\left(1 - e^{-h\nu_i/kT}\right) + R\sum_i \frac{h\nu_i \; e^{-h\nu_i/kT}}{kT\left(1 - e^{-h\nu_i/kT}\right)} \quad (3)$$

among which $R=8.314 J\cdot mol^{-1}K^{-1}$, $k_B=1.38*10^{-23}J\cdot K^{-1}$ $h=6.63*10^{-34}J\cdot s$, T=298.15K, i is the frequency number，$\nu_i$ is the vibrational frequency.

**Table S1.** $N_2$ absorption energy in end-on and side-on configuration, the geometric structures and electronic structures of pure 2D Mo-Pp monolayer and 2D Mo-Pp monolayers modified by heteroatoms.

| | B | C | $N^3$ | O | P | S |
|---|---|---|---|---|---|---|
| Side-on | -1.43 | -0.67 | -0.08 | -0.24 | -0.38 | -0.60 |
| End-on | -1.92 | -1.33 | -0.77 | -0.63 | -0.99 | -0.90 |
| Mo charge | 1.48 | 1.53 | 1.44 | 1.37 | 1.33 | 1.24 |
| electronegativity | 2.04 | 2.55 | 3.04 | 3.44 | 2.19 | 2.58 |
| electronegativity of $N_3X$ | 2.79 | 2.9175 | 3.04 | 3.14 | 2.8275 | 2.925 |
| X $P_z$ filling | 0.221 | 0.386 | 0.782 | 1.376 | 0.491 | 0.803 |
| $N_3X$ $P_x$ filling | 3.151 | 3.476 | 3.759 | 4.028 | 3.228 | 3.470 |
| $N_3X$ $P_y$ filling | 3.151 | 3.476 | 3.756 | 4.028 | 3.228 | 3.469 |
| $N_3X$ $P_z$ filling | 2.734 | 2.856 | 3.127 | 3.856 | 3.028 | 3.198 |
| optimized lattice parameters | 8.444 | 8.416 | 8.437 | 8.403 | 8.390 | 8.365 |

**Table S2.** Regression models for calculating of those 2D Mo-Pp monolayers

| | **Model** | $R^2$ | **SD** | **F** | **sig.** |
|---|---|---|---|---|---|
| 1 | $E(s) = 0.794\varepsilon_X - 1.105$ | 0.682 | 0.392 | 3.473 | 0.136 |
| 2 | $E(s) = 0.761\varepsilon_{N3X} - 2.954$ | 0.392 | 0.417 | 2.577 | 0.184 |
| 3 | $E(e) = 0.953\varepsilon_X - 1.734$ | 0.697 | 0.288 | 9.210 | 0.039 |
| 4 | $E(e) = 0.936\varepsilon_{N3X} - 4.023$ | 0.618 | 0.324 | 6.466 | 0.064 |
| 5 | $E(s) = 2.840\varphi + 0.498\varepsilon_X - 4.876$ | 0.796 | 0.279 | 5.861 | 0.092 |
| 6 | $E(s) = 0.162\varepsilon_X + 0.546\lambda - 2.118$ | 0.527 | 0.425 | 1.673 | 0.325 |
| 7 | $E(e) = 1.553\varphi + 0.790\varepsilon_X - 3.796$ | 0.801 | 0.270 | 6.023 | 0.089 |
| 8 | $E(e) = 0.851\varepsilon_X + 0.088\lambda - 1.897$ | 0.699 | 0.332 | 3.482 | 0.165 |

**Table S3.** Correlation coefficient between absorption energy and $\varepsilon_X$ , φ and N

| | $\varepsilon_X$ | φ | N |
|---|---|---|---|
| E(s) | 0.682 | 0.802 | 0.293 |
| E(e) | 0.835 | 0.632 | 0.436 |

**Table S4.** Thermodynamic quantities for the isolated $N_2$, $H_2$, $NH_3$ species in the gas phase, in eV (Mild conditions, T= 298.15 K and *f* = 101 325 Pa).

| | **ZPE** | **TS** | **E** | **Gibbs free energy** |
|---|---|---|---|---|
| **$H_2$** | 0.32 | 0.39[4] | -6.77 | -6.84 |
| **$N_2$** | 0.15 | 0.58[4] | -16.63 | -17.05 |
| **$NH_3$** | 0.94 | 0.60[4] | -19.53 | -19.19 |

**Table S5.** Gibbs free energy for the chemisorbed intermediates species on 2D Mo-Pp monolayer modified by B, in eV (Mild conditions, T= 298.15 K and *f* = 101 325 Pa).

| | **Gibbs free energy** | | **Gibbs free energy** |
|---|---|---|---|
| **$N_2$ end-on** | -239.60 | **NNH*(e)** | -242.67 |
| **$NNH_2$*** | -246.48 | **N*** | -231.32 |
| **NH*** | -235.27 | **$NH_2$*** | -238.84 |
| **$NH_3$*** | -241.98 | **NHNH*(e)** | -245.30 |
| **$NHNH_2$*(e)** | -249.56 | **$NH_2NH_2$*(e)** | -252.51 |
| **$N_2$ side-on** | -239.11 | **NNH*(s)** | -242.43 |
| **NHNH*(s)** | -245.83 | **$NHNH_2$*(s)** | -249.49 |
| **$NH_2NH_2$*(s)** | -252.26 | **Mo-Pp-B** | -221.10 |

**Table S6.** Charge population of three parts along the alternating, distal and enzymatic pathway.

| species | species | Mo-Pp | $N_2$* | NNH* | NHNH* | $NHNH_2$* | $NH_2NH_2$* | $NH_2$* | $NH_3$* |
|---|---|---|---|---|---|---|---|---|---|
| alternating | $N_xH_x$ | | 0.31 | 0.41 | 0.23 | 0.20 | 0.14 | 0.34 | -0.13 |
| | $Mo@N_3B$ | 1.18 | 0.87 | 0.91 | 0.93 | 0.76 | 0.00 | 0.74 | 1.06 |
| | carbon substrate | -1.18 | -1.18 | -1.32 | -1.17 | -0.96 | 0.14 | -1.08 | -0.92 |
| **species** | **species** | **Mo-Pp** | **$N_2$*** | **NNH*** | **$NNH_2$*** | **N*** | **NH*** | **$NH_2$*** | **$NH_3$*** |
| distal | $N_xH_x$ | | 0.31 | 0.41 | 0.39 | 1.26 | 0.59 | 0.34 | -0.13 |
| | $Mo@N_3B$ | 1.18 | 0.87 | 0.91 | 0.81 | 0.06 | 0.72 | 0.74 | 1.06 |
| | carbon substrate | -1.18 | -1.18 | -1.32 | -1.19 | -1.33 | -1.31 | -1.08 | -1.19 |
| **species** | **species** | **Mo-Pp** | **$N_2$*** | **NNH*** | **NHNH*** | **$NHNH_2$*** | **$NH_2NH_2$*** | **$NH_2$*** | **$NH_3$*** |
| enzymatic | $N_xH_x$ | | 0.52 | 0.63 | 0.57 | 0.23 | -0.21 | 0.34 | -0.13 |
| | $Mo@N_3B$ | 1.18 | 0.81 | 0.84 | 0.65 | 0.78 | 0.99 | 0.74 | 1.06 |
| | carbon substrate | -1.18 | -1.33 | -1.47 | -1.22 | -1.01 | -0.78 | -1.08 | -0.92 |

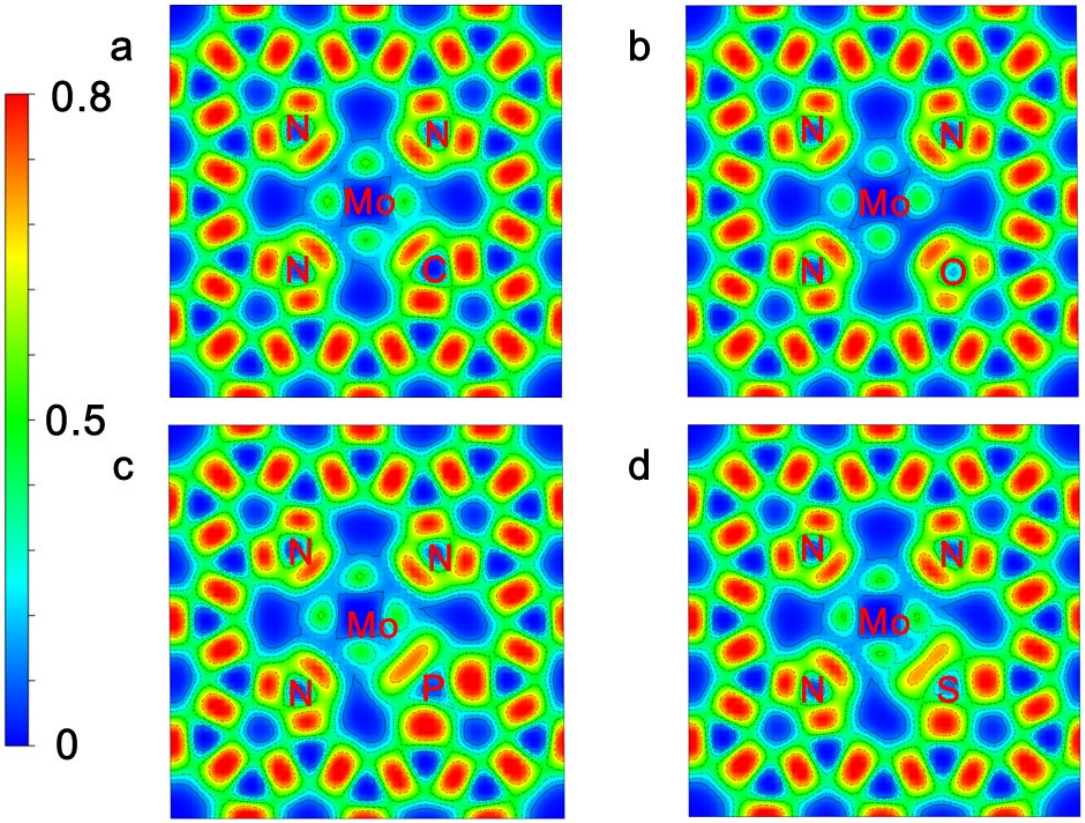


**Figure S1.** The electron localization function (ELF) of 2D Mo-Pp monolayers modified by C, O, P and S, corresponding to a, b, c, d, respectively. Note: the lack (0) or abundance (0.8) of electron.

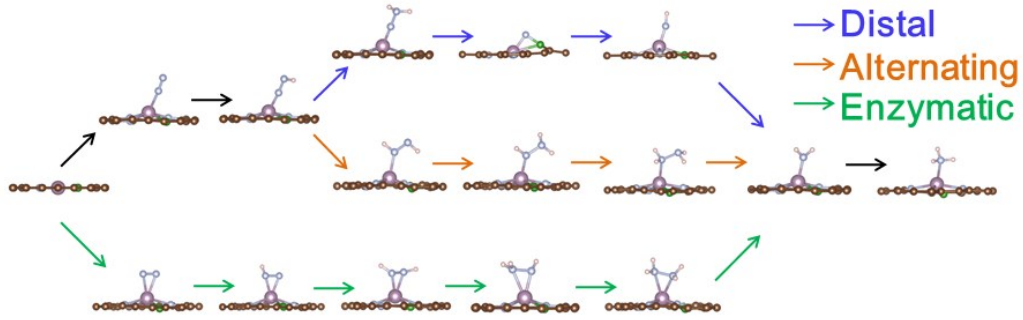


**Figure S2.** Optimized structures of various intermediates on 2D Mo-Pp modified by B along the Distal, Alternating and Enzymatic pathway.

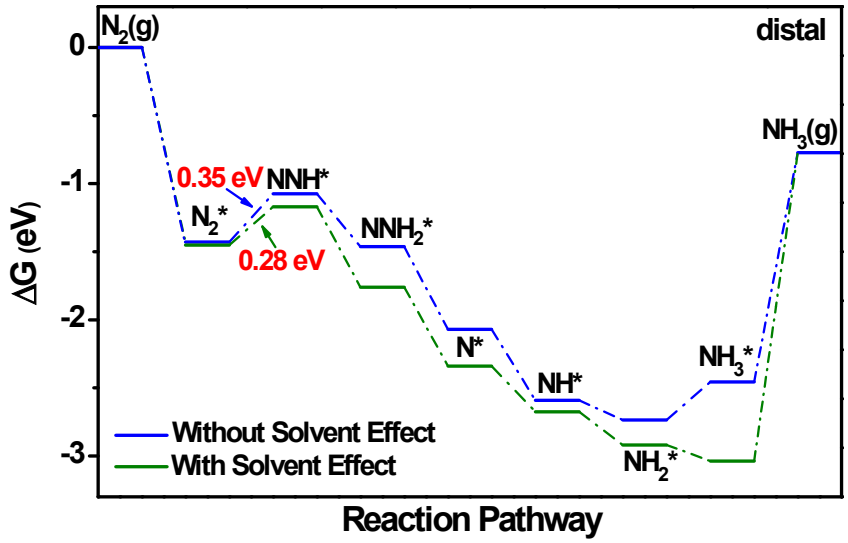


**Figure S3**. The Gibbs free energy profiles of the NRR on 2D Mo-Pp monolayers modified by B at zero through distal pathway without and with solvent effect.

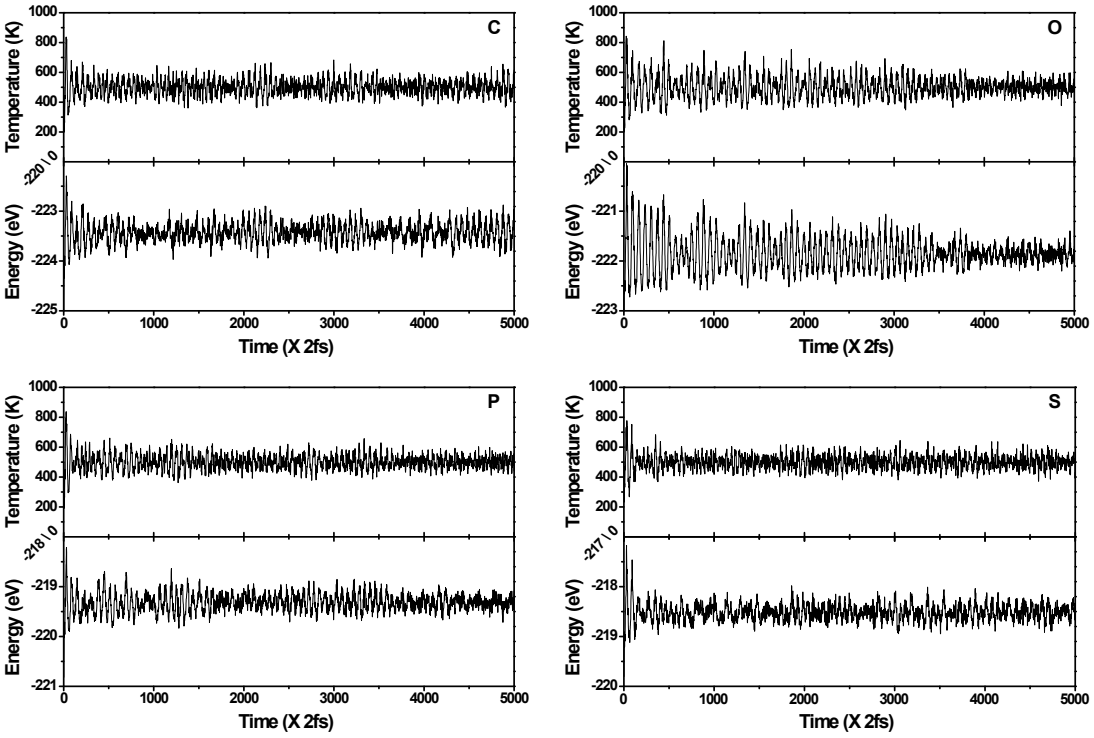


**Figure S4** Variations of temperature and energy against the time for AIMD simulations of 2D Mo-Pp monolayer modified by C, O, P and S heteroatoms. The simulation is run at 500 K for 10 ps with a time step of 2 fs.

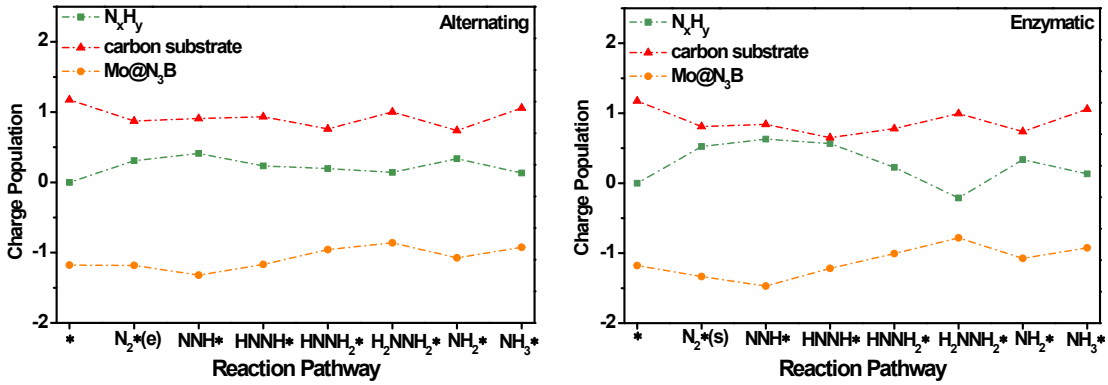


**Figure S5** Charge population of three moieties along the alternating pathway and enzymatic pathway of NRR on 2D Mo-Pp monolayer modified by B.

## References

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2. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, *The Journal of Physical Chemistry B*, 2004, 108, 17886-17892.
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