Supplementary Information (SI) for Journal of Materials Chemistry A.


SUPPLEMENTARY INFORMATION (SI)

# High-throughput screening of carbon nitride single-atom catalysts for nitrogen fixation based on machine learning

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**Table S1** $\Delta G_{*N_2-end}$, $\Delta G_{*N_2-side}$, $\Delta G_{*N_2-*N_2H}$, $\Delta E_{ad}[N_2H]$ and *N≡N* of 140 SACs.

| SACs | $\Delta G_{*N_2-en}$ (eV) | $\Delta G_{*N_2-side}$ (eV) | $\Delta G_{*N_2-*N_2}$ (eV) | $\Delta G_{*NH_2-*NH}$ (eV) | $\Delta E_{ad}[N_2H]$ (eV) | N≡N (Å) |
|---|---|---|---|---|---|---|
| Sc@g-$C_2N$ | -0.403 | -0.128 | 1.078 | 0.029 | 0.338 | 1.130 |
| Ti@g-$C_2N$ | -0.559 | -0.155 | 0.797 | -0.052 | -0.128 | 1.136 |
| V@g-$C_2N$ | -0.310 | 0.182 | 0.946 | -0.338 | 0.280 | 1.132 |
| Cr@g-$C_2N$ | -0.037 | -0.037 | 1.168 | -0.577 | 0.805 | 1.125 |
| Mn@g-$C_2N$ | -0.082 | 0.232 | 1.196 | -0.870 | 0.765 | 1.123 |
| Fe@g-$C_2N$ | -0.460 | 0.068 | 1.357 | -0.807 | 0.556 | 1.133 |
| Co@g-$C_2N$ | -0.595 | -0.048 | 1.269 | -0.993 | 0.282 | 1.132 |
| Ni@g-$C_2N$ | -0.283 | / | 1.258 | -1.203 | 0.580 | 1.129 |
| Cu@g-$C_2N$ | -0.347 | 0.116 | 1.906 | -1.526 | 1.221 | 1.123 |
| Zn@g-$C_2N$ | 0.005 | / | 1.516 | -1.182 | 1.190 | 1.116 |
| Y@g-$C_2N$ | -0.340 | -0.115 | 1.127 | 0.162 | 0.474 | 1.130 |
| Zr@g-$C_2N$ | -0.807 | -0.418 | 0.635 | 0.425 | -0.538 | 1.142 |
| Nb@g-$C_2N$ | -0.659 | -0.141 | 0.428 | 0.166 | -0.622 | 1.145 |
| Mo@g-$C_2N$ | 0.008 | 0.098 | 0.478 | 0.055 | 0.099 | 1.145 |
| Ru@g-$C_2N$ | -0.519 | 0.067 | 0.975 | -0.588 | 0.061 | 1.139 |
| Rh@g-$C_2N$ | -0.163 | / | 1.313 | -1.046 | 0.730 | 1.128 |
| Pd@g-$C_2N$ | 0.070 | / | 1.327 | -1.175 | 1.002 | 1.126 |
| Ag@g-$C_2N$ | 0.276 | / | 2.071 | -1.769 | 2.081 | 1.115 |

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| | | | | | | |
|---|---|---|---|---|---|---|
| Cd@g-$C_2N$ | 0.258 | / | 1.708 | -1.063 | 1.631 | 1.113 |
| Hf@g-$C_2N$ | -0.744 | -0.412 | 0.561 | 0.675 | -0.545 | 1.145 |
| Ta@g-$C_2N$ | -0.813 | -0.291 | 0.239 | 0.311 | -0.963 | 1.150 |
| W@g-$C_2N$ | -0.650 | -0.296 | 0.289 | -0.047 | -0.755 | 1.149 |
| Re@g-$C_2N$ | -0.952 | -0.521 | 0.496 | -0.214 | -0.847 | 1.146 |
| Os@g-$C_2N$ | -0.684 | 0.045 | 0.784 | -0.542 | -0.331 | 1.139 |
| Ir@g-$C_2N$ | -0.472 | / | 1.045 | -0.883 | 0.119 | 1.131 |
| Pt@g-$C_2N$ | -0.355 | / | 1.011 | -0.844 | 0.235 | 1.130 |
| Au@g-$C_2N$ | / | / | / | / | / | / |
| Hg@g-$C_2N$ | / | / | / | / | / | / |
| Sc@g-$C_3N_4$ | -0.473 | -0.257 | 1.061 | 0.400 | 0.265 | 1.135 |
| Ti@g-$C_3N_4$ | -0.570 | -0.050 | 0.747 | 0.085 | -0.187 | 1.140 |
| V@g-$C_3N_4$ | -0.208 | 0.292 | 0.811 | -0.146 | 0.232 | 1.137 |
| Cr@g-$C_3N_4$ | 0.101 | / | 1.181 | -0.471 | 0.922 | 1.123 |
| Mn@g-$C_3N_4$ | -0.005 | 0.251 | 1.270 | -0.559 | 0.935 | 1.127 |
| Fe@g-$C_3N_4$ | -0.535 | -0.060 | 1.340 | -0.359 | 0.431 | 1.137 |
| Co@g-$C_3N_4$ | -0.567 | -0.105 | 1.139 | -0.672 | 0.177 | 1.135 |
| Ni@g-$C_3N_4$ | -0.397 | -0.395 | 1.144 | -0.778 | 0.347 | 1.137 |
| Cu@g-$C_3N_4$ | -0.519 | / | 2.001 | -1.060 | 1.153 | 1.126 |
| Zn@g-$C_3N_4$ | 0.042 | / | 1.093 | -0.277 | 0.772 | 1.117 |
| Y@g-$C_3N_4$ | -0.329 | -0.106 | 1.111 | 0.246 | 0.494 | 1.133 |
| Zr@g-$C_3N_4$ | -0.607 | -0.267 | 0.538 | 0.727 | -0.425 | 1.147 |
| Nb@g-$C_3N_4$ | -0.505 | 0.088 | 0.300 | 0.422 | -0.581 | 1.153 |
| Mo@g-$C_3N_4$ | -0.631 | 0.348 | 0.819 | 0.053 | -0.200 | 1.149 |
| Ru@g-$C_3N_4$ | -0.404 | 0.057 | 0.387 | -0.388 | -0.412 | 1.138 |
| Rh@g-$C_3N_4$ | -0.950 | -0.950 | 1.306 | -0.960 | -0.034 | 1.132 |
| Pd@g-$C_3N_4$ | -0.288 | / | 1.400 | -1.069 | 0.719 | 1.133 |
| Ag@g-$C_3N_4$ | / | / | / | / | / | / |
| Cd@g-$C_3N_4$ | 0.242 | / | 1.778 | -0.567 | 1.628 | 1.113 |
| Hf@g-$C_3N_4$ | -0.612 | -0.290 | 0.456 | 0.880 | -0.512 | 1.154 |
| Ta@g-$C_3N_4$ | -0.654 | -0.121 | 0.134 | 0.687 | -0.895 | 1.157 |
| W@g-$C_3N_4$ | -0.926 | 0.030 | 0.551 | 0.422 | -0.769 | 1.155 |
| Re@g-$C_3N_4$ | -0.563 | -0.176 | 0.625 | 0.151 | -0.306 | 1.149 |
| Os@g-$C_3N_4$ | -0.726 | 0.004 | 0.817 | -0.255 | -0.340 | 1.143 |
| Ir@g-$C_3N_4$ | -0.467 | / | 1.512 | -0.688 | 0.623 | 1.135 |
| Pt@g-$C_3N_4$ | / | / | / | / | / | / |
| Au@g-$C_3N_4$ | / | / | / | / | / | / |
| Hg@g-$C_3N_4$ | / | / | / | / | / | / |
| Sc@g-$C_4N_3$ | -0.144 | / | 1.708 | -1.079 | 1.276 | 1.115 |
| Ti@g-$C_4N_3$ | -0.166 | 0.217 | 0.938 | -0.297 | 0.407 | 1.124 |
| V@g-$C_4N_3$ | -0.234 | 0.740 | 0.935 | -0.711 | 0.332 | 1.125 |
| Cr@g-$C_4N_3$ | 0.152 | / | 1.385 | -1.020 | 1.140 | 1.117 |
| Mn@g-$C_4N_3$ | 0.121 | / | 1.677 | -1.451 | 1.481 | 1.113 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Fe@g-$C_4N_3$ | -0.135 | / | 1.307 | -1.210 | 0.813 | 1.119 |
| Co@g-$C_4N_3$ | -0.156 | 0.311 | 1.248 | -1.317 | 0.683 | 1.124 |
| Ni@g-$C_4N_3$ | 0.050 | / | 1.442 | -1.456 | 1.102 | 1.121 |
| Cu@g-$C_4N_3$ | 0.290 | / | 1.615 | -1.575 | 1.500 | 1.120 |
| Zn@g-$C_4N_3$ | 0.310 | / | 2.155 | -1.815 | 2.051 | 1.113 |
| Y@g-$C_4N_3$ | -0.094 | / | 1.905 | -1.399 | 1.529 | 1.114 |
| Zr@g-$C_4N_3$ | -0.445 | 0.070 | 1.067 | -0.065 | 0.287 | 1.124 |
| Nb@g-$C_4N_3$ | -0.412 | 0.158 | 0.479 | 0.163 | -0.299 | 1.137 |
| Mo@g-$C_4N_3$ | -0.076 | 0.702 | 0.142 | 0.056 | -0.331 | 1.141 |
| Ru@g-$C_4N_3$ | -0.403 | / | 1.058 | -0.920 | 0.281 | 1.134 |
| Rh@g-$C_4N_3$ | 0.176 | / | 0.902 | -1.143 | 0.661 | 1.125 |
| Pd@g-$C_4N_3$ | / | / | / | / | / | / |
| Ag@g-$C_4N_3$ | / | / | / | / | / | / |
| Cd@g-$C_4N_3$ | 0.328 | / | 2.031 | -2.137 | 2.081 | 1.113 |
| Hf@g-$C_4N_3$ | -0.549 | -0.003 | 0.973 | 0.026 | 0.073 | 1.127 |
| Ta@g-$C_4N_3$ | -0.420 | 0.002 | 0.270 | 0.602 | -0.515 | 1.145 |
| W@g-$C_4N_3$ | -0.368 | 0.273 | -0.117 | 0.150 | -0.890 | 1.147 |
| Re@g-$C_4N_3$ | -0.712 | 0.585 | 0.485 | -0.148 | -0.629 | 1.143 |
| Os@g-$C_4N_3$ | -0.613 | -0.613 | 0.890 | -0.627 | -0.106 | 1.138 |
| Ir@g-$C_4N_3$ | -0.110 | / | 0.730 | -0.992 | 0.193 | 1.131 |
| Pt@g-$C_4N_3$ | / | / | / | / | / | / |
| Au@g-$C_4N_3$ | / | / | / | / | / | / |
| Hg@g-$C_4N_3$ | / | / | / | / | / | / |
| Sc@g-$C_6N_6$ | -0.362 | -0.069 | 1.088 | 0.032 | 0.391 | 1.130 |
| Ti@g-$C_6N_6$ | -0.556 | -0.152 | 0.818 | -0.044 | -0.103 | 1.136 |
| V@g-$C_6N_6$ | -0.329 | 0.289 | 0.910 | -0.309 | 0.228 | 1.132 |
| Cr@g-$C_6N_6$ | -0.035 | / | 1.094 | -0.717 | 0.680 | 1.125 |
| Mn@g-$C_6N_6$ | -0.014 | 0.305 | 1.226 | -0.779 | 0.859 | 1.124 |
| Fe@g-$C_6N_6$ | 0.181 | 0.161 | 0.777 | -1.116 | 0.579 | 1.136 |
| Co@g-$C_6N_6$ | -0.514 | 0.046 | 1.275 | -0.891 | 0.367 | 1.133 |
| Ni@g-$C_6N_6$ | -0.187 | / | 1.295 | -1.189 | 0.712 | 1.129 |
| Cu@g-$C_6N_6$ | -0.287 | / | 1.790 | -1.436 | 1.168 | 1.124 |
| Zn@g-$C_6N_6$ | 0.076 | / | 1.518 | -1.073 | 1.262 | 1.115 |
| Y@g-$C_6N_6$ | -0.298 | -0.051 | 1.130 | 0.092 | 0.543 | 1.130 |
| Zr@g-$C_6N_6$ | -0.820 | -0.447 | 0.637 | 0.334 | -0.541 | 1.140 |
| Nb@g-$C_6N_6$ | -0.795 | -0.118 | 0.422 | 0.315 | -0.770 | 1.145 |
| Mo@g-$C_6N_6$ | -0.436 | 0.047 | 0.540 | -0.195 | -0.286 | 1.142 |
| Ru@g-$C_6N_6$ | -0.610 | 0.079 | 1.054 | -0.671 | 0.037 | 1.136 |
| Rh@g-$C_6N_6$ | -0.249 | / | 1.372 | -1.168 | 0.699 | 1.127 |
| Pd@g-$C_6N_6$ | 0.046 | / | 1.414 | -1.313 | 1.066 | 1.127 |
| Ag@g-$C_6N_6$ | / | / | / | / | / | / |
| Cd@g-$C_6N_6$ | 0.221 | / | 1.779 | -1.023 | 1.673 | 1.113 |
| Hf@g-$C_6N_6$ | -0.783 | -0.452 | 0.588 | 0.564 | -0.556 | 1.144 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ta@g-$C_6N_6$ | -0.869 | -0.229 | 0.295 | 0.403 | -0.975 | 1.148 |
| W@g-$C_6N_6$ | -0.742 | -0.323 | 0.311 | 0.013 | -0.829 | 1.147 |
| Re@g-$C_6N_6$ | -0.872 | -0.370 | 0.507 | 0.020 | -0.756 | 1.145 |
| Os@g-$C_6N_6$ | -1.336 | -0.583 | 0.858 | -0.566 | -0.906 | 1.138 |
| Ir@g-$C_6N_6$ | -0.508 | / | 1.088 | -0.943 | 0.129 | 1.130 |
| Pt@g-$C_6N_6$ | / | / | / | / | / | / |
| Au@g-$C_6N_6$ | / | / | / | / | / | / |
| Hg@g-$C_6N_6$ | / | / | / | / | / | / |
| Sc@g-$C_9N_{10}$ | -0.378 | -0.205 | 1.047 | -0.253 | 0.333 | 1.129 |
| Ti@g-$C_9N_{10}$ | -0.539 | -0.093 | 0.727 | -0.375 | -0.191 | 1.136 |
| V@g-$C_9N_{10}$ | -0.524 | -0.017 | 0.895 | -0.701 | -0.011 | 1.126 |
| Cr@g-$C_9N_{10}$ | -0.524 | / | 0.835 | -0.946 | -0.074 | 1.120 |
| Mn@g-$C_9N_{10}$ | -0.26 | / | 0.685 | -0.978 | 0.008 | 1.119 |
| Fe@g-$C_9N_{10}$ | -0.488 | -0.069 | 0.551 | -0.908 | -0.311 | 1.131 |
| Co@g-$C_9N_{10}$ | -0.723 | -0.025 | 0.751 | -1.015 | -0.373 | 1.124 |
| Ni@g-$C_9N_{10}$ | -0.65 | / | 1.029 | -1.320 | -0.023 | 1.123 |
| Cu@g-$C_9N_{10}$ | -0.573 | / | / | / | / | / |
| Zn@g-$C_9N_{10}$ | -0.299 | / | 0.962 | -1.113 | 0.334 | 1.117 |
| Y@g-$C_9N_{10}$ | -0.346 | -0.189 | 1.096 | -0.158 | 0.431 | 1.130 |
| Zr@g-$C_9N_{10}$ | -0.532 | -0.289 | 0.422 | 0.066 | -0.487 | 1.144 |
| Nb@g-$C_9N_{10}$ | -0.587 | -0.344 | 0.410 | -0.186 | -0.569 | 1.144 |
| Mo@g-$C_9N_{10}$ | -0.243 | 0.177 | 0.390 | -1.057 | -0.241 | 1.145 |
| Ru@g-$C_9N_{10}$ | -0.941 | -0.250 | 0.849 | -0.948 | -0.495 | 1.128 |
| Rh@g-$C_9N_{10}$ | -0.879 | / | / | / | / | / |
| Pd@g-$C_9N_{10}$ | -0.438 | / | 1.338 | -1.368 | 0.537 | 1.119 |
| Ag@g-$C_9N_{10}$ | 0.011 | / | 2.054 | -1.973 | 1.753 | 1.115 |
| Cd@g-$C_9N_{10}$ | 0.027 | / | 1.765 | -1.396 | 1.486 | 1.113 |
| Hf@g-$C_9N_{10}$ | -0.430 | -0.243 | 0.367 | 0.058 | -0.434 | 1.151 |
| Ta@g-$C_9N_{10}$ | -0.673 | -0.513 | 0.204 | 0.031 | -0.857 | 1.150 |
| W@g-$C_9N_{10}$ | -0.974 | -0.335 | 0.273 | -0.397 | -1.138 | 1.132 |
| Re@g-$C_9N_{10}$ | -1.035 | -0.874 | 0.340 | -0.299 | -1.117 | 1.143 |
| Os@g-$C_9N_{10}$ | -1.182 | -0.596 | 0.597 | -0.802 | -0.999 | 1.132 |
| Ir@g-$C_9N_{10}$ | -1.270 | / | 0.631 | -0.845 | -1.084 | 1.127 |
| Pt@g-$C_9N_{10}$ | / | / | / | / | / | / |
| Au@g-$C_9N_{10}$ | / | / | / | / | / | / |
| Hg@g-$C_9N_{10}$ | / | / | / | / | / | / |

**Table S2** The $\Delta G_{*N_2}$ and $\Delta G_{*H}$ values of SACs considered in the competitive reactions of HER and NRR.

| SACs | $\Delta G_{*N_2}$ (eV) | $\Delta G_{*H}$ (eV) |
|---|---|---|
| Nb@g-$C_2N$ | -0.659 | -0.347 |
| Ta@ g-$C_2N$ | -0.813 | -0.671 |
| W@g-$C_2N$ | -0.650 | -0.540 |
| Re@g-$C_2N$ | -0.952 | -0.771 |
| Nb@g-$C_3N_4$ | -0.505 | -0.297 |
| Ru@g-$C_3N_4$ | -0.404 | -1.023 |
| Ta@g-$C_3N_4$ | -0.654 | -0.562 |
| Nb@g-$C_4N_3$ | -0.412 | -0.285 |
| Mo@g-$C_4N_3$ | -0.076 | -0.339 |
| Ta@g-$C_4N_3$ | -0.420 | -0.617 |
| W@g-$C_4N_3$ | -0.368 | -0.456 |
| Re@g-$C_4N_3$ | -0.712 | -0.563 |
| Nb@g-$C_6N_6$ | -0.795 | -0.448 |
| Mo@g-$C_6N_6$ | -0.436 | -0.226 |
| Ta@g-$C_6N_6$ | -0.869 | -0.690 |
| W@g-$C_6N_6$ | -0.742 | -0.698 |
| Re@g-$C_6N_6$ | -0.872 | -0.767 |
| Zr@g-$C_9N_{10}$ | -0.532 | -0.482 |
| Nb@g-$C_9N_{10}$ | -0.587 | -0.362 |
| Mo@g-$C_9N_{10}$ | -0.243 | -0.163 |
| Hf@g-$C_9N_{10}$ | -0.430 | -0.641 |
| Ta@g-$C_9N_{10}$ | -0.673 | -0.632 |
| W@g-$C_9N_{10}$ | -0.974 | -0.539 |
| Re@g-$C_9N_{10}$ | -1.035 | -0.651 |

**Table S3** Intrinsic properties of catalysts and adsorption intermediates.

| category | feature | symbol |
|---|---|---|
| center metals | 1st ionization energy | $I_1$ |
| | number of outermost d electrons | $N_d$ |
| | atomic number | $Z$ |
| | unpaired d-electron number | $N_{ie\text{-}d}$ |
| | Pauling electronegativity | $\chi$ |
| coordination environments | number of N atoms | $N_N$ |
| | number of C atoms | $N_C$ |
| | number of coordinative N atoms | $N_n$ |
| intermediates ($*N_2$) | N≡N bond length | *N≡N* |
| | TM-N bond length | *TM-N* |

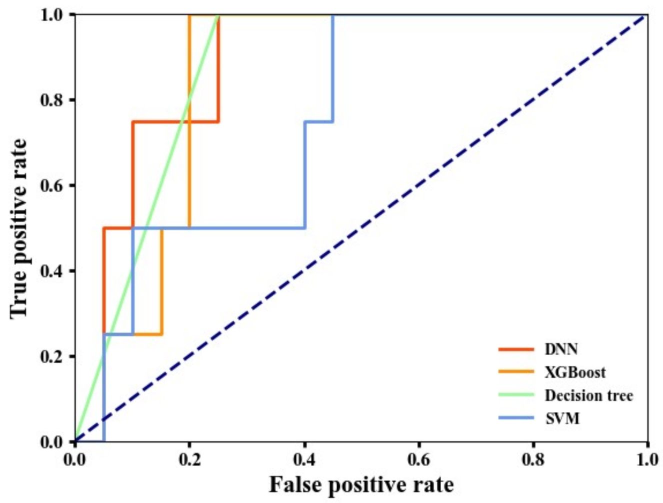



**Fig. S1** The ROC curves of the DNN, XGBoost, decision tree and SVM classification models.

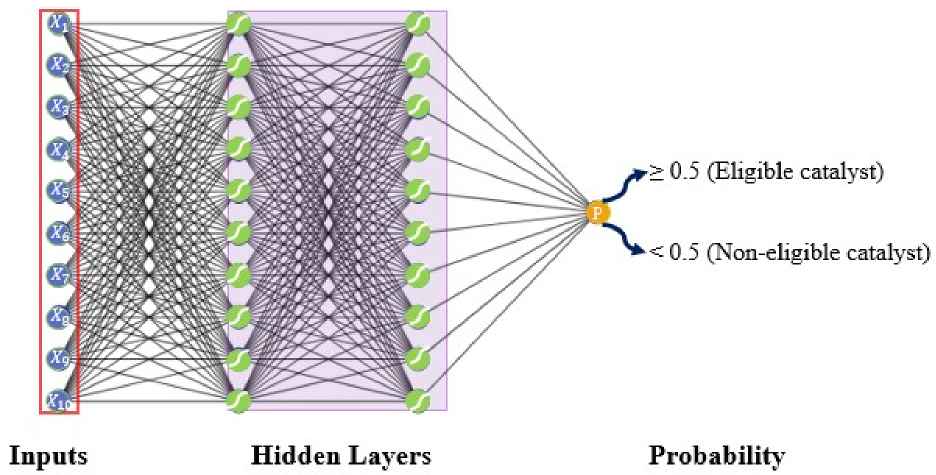



**Fig. S2** DNN classification model constructed in this study (each hidden layer has ten neurons), with input data consisting of optimized adsorbed nitrogen intermediates, each structure has ten features: $I_1$, $N_d$, $Z$, $\chi$, $N_{ie\text{-}d}$, $N_N$, $N_C$, $N_n$, $N{\equiv}N$, $TM\text{-}N$.

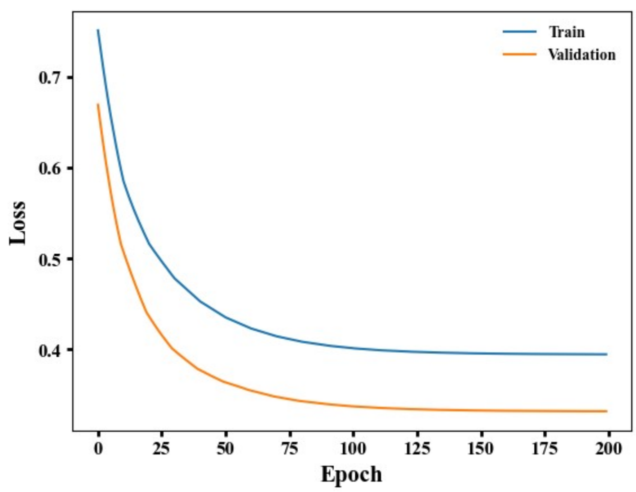



**Fig. S3** Changes in training loss and validation loss during the training epochs in the DNN model.

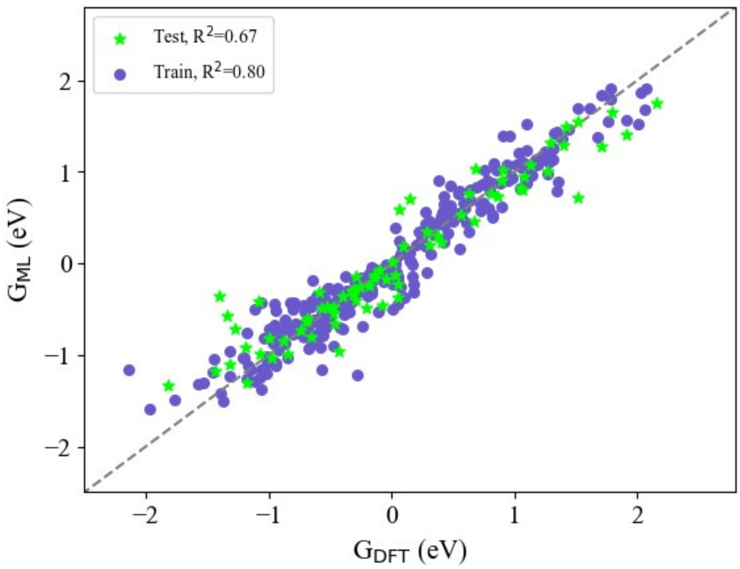



**Fig. S4** Comparison of prediction results between DFT calculations and linear regression model.

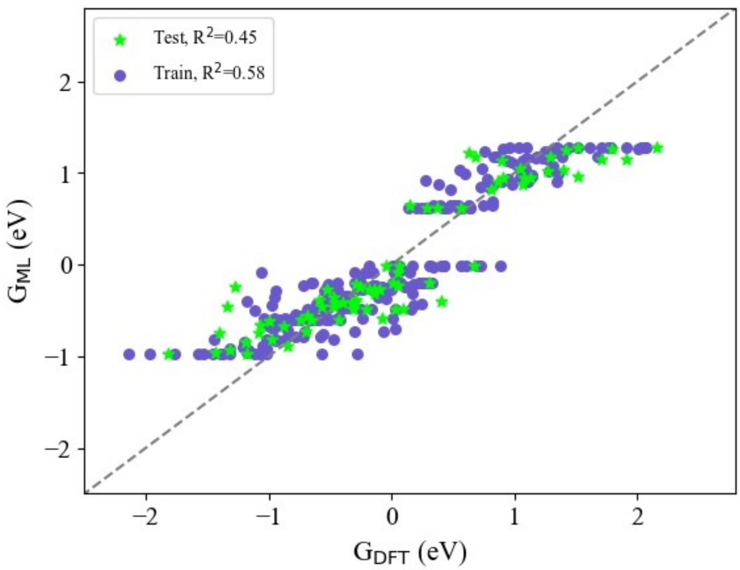



**Fig. S5** Comparison of prediction results between DFT calculations and random forest regression model.

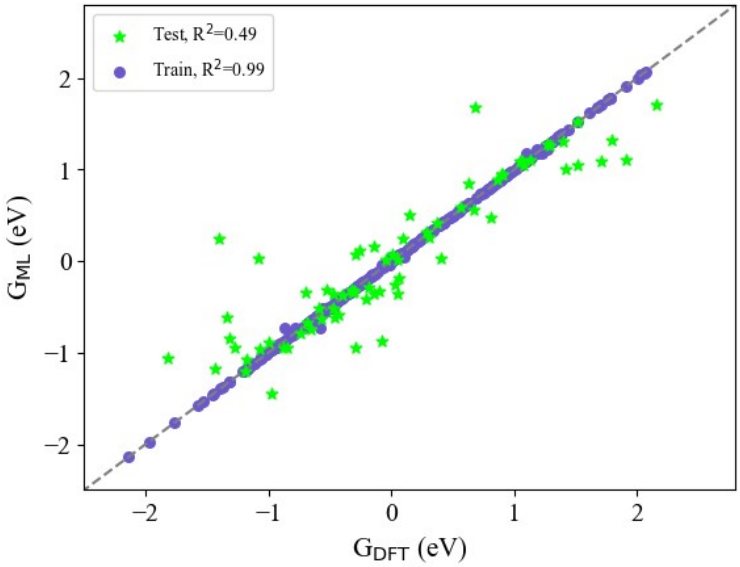



**Fig. S6** Comparison of prediction results between DFT calculations and decision tree regression model.

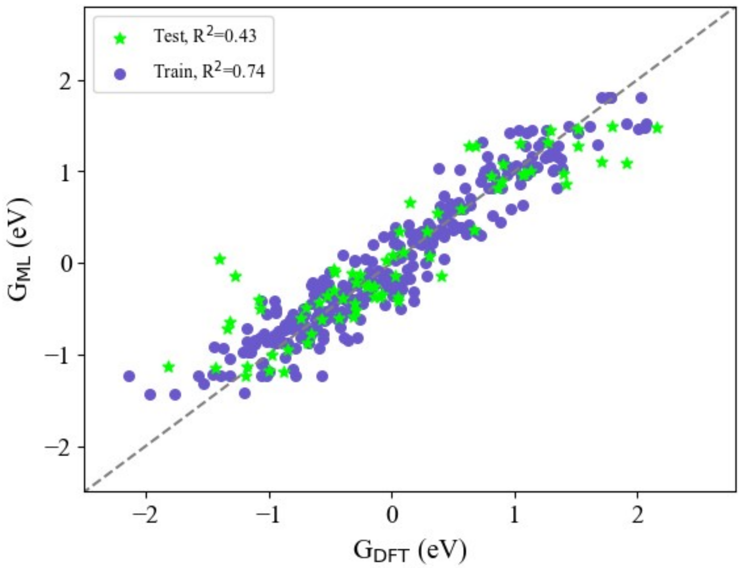



**Fig. S7** Comparison of prediction results between DFT calculations and K-Nearest neighbors regression model.

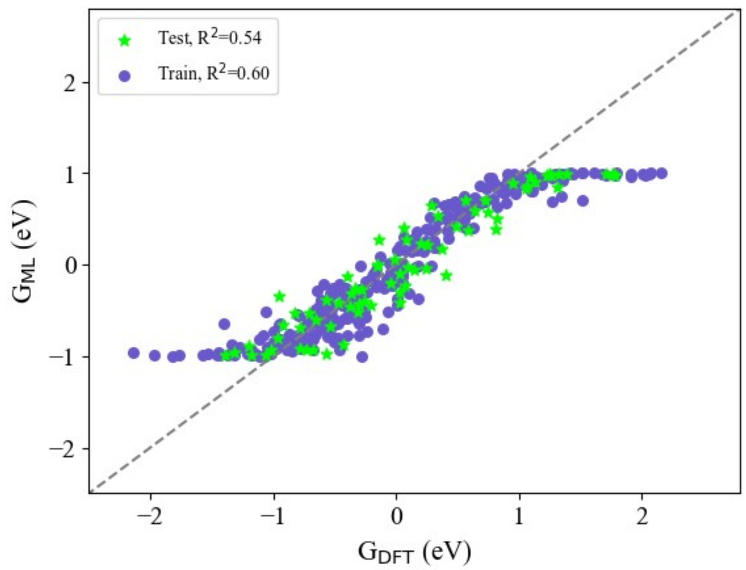
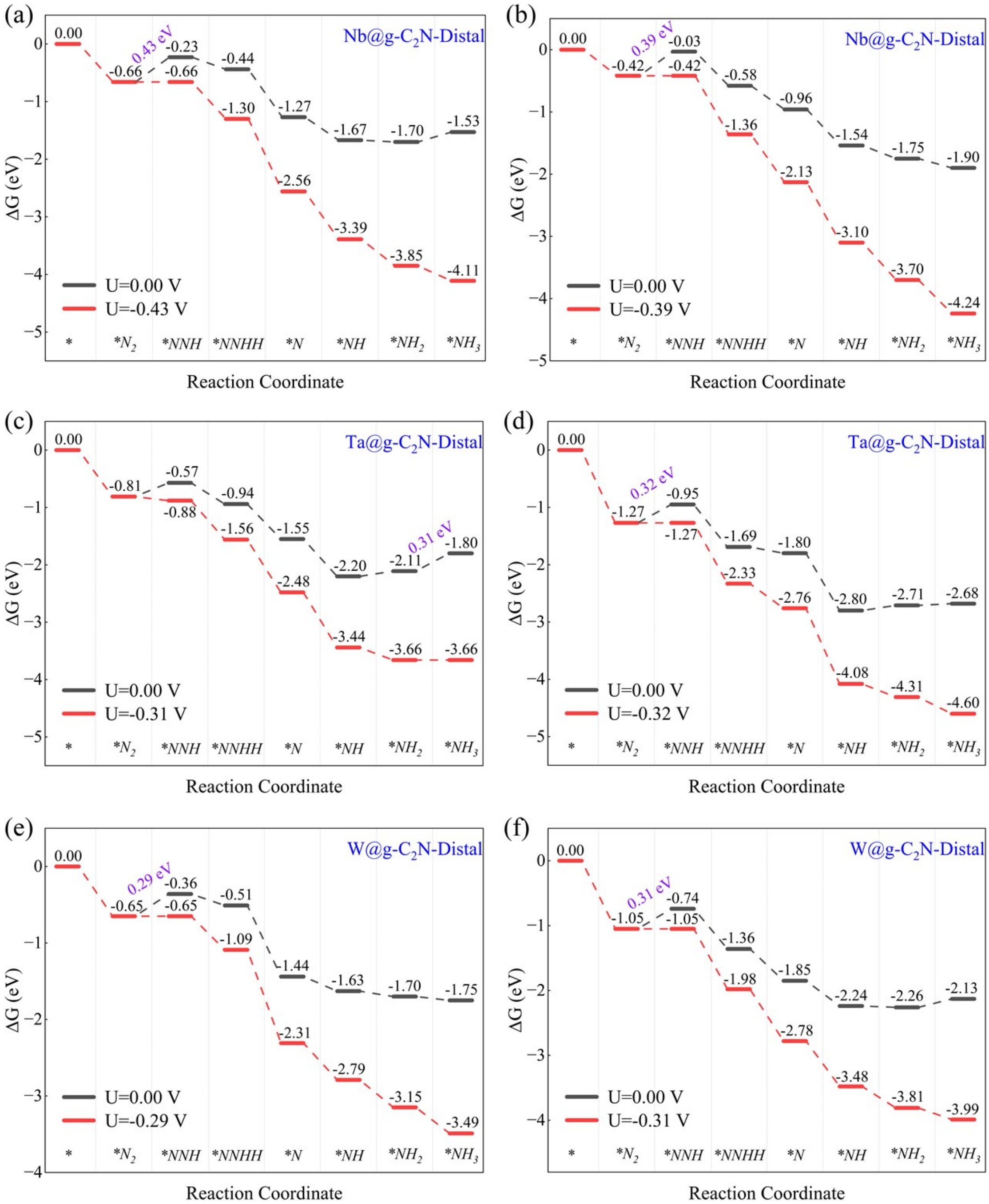



**Fig. S8** Comparison of prediction results between DFT calculations and DNN regression model.

**Table S4** 20 types of SACs that meet the screening criteria under the $*N_2$ configuration of N≡N, $\Delta E_{ad}[N_2H]$, $N_d$, PDS and $U_L$.

| SACs | N≡N (Å) | $\Delta E_{ad}[N_2H]$ (eV) | $N_d$ | PDS | $U_L$ (V) |
|---|---|---|---|---|---|
| Nb@g-$C_2N$ | 1.145 | -0.622 | 4 | $*N_2$+H→$*N_2H$ | 0.43 |
| Ta@g-$C_2N$ | 1.150 | -0.963 | 3 | $*NH_2$+H→$*NH_3$ | 0.31 |
| W@g-$C_2N$ | 1.149 | -0.755 | 4 | $*N_2$+H→$*N_2H$ | 0.29 |
| Re@g-$C_2N$ | 1.146 | -0.847 | 5 | $*N_2$+H→$*N_2H$ | 0.50 |
| Nb@g-$C_3N_4$ | 1.153 | -0.581 | 4 | $*NH_2$+H→$*NH_3$ | 0.42 |
| Ta@g-$C_3N_4$ | 1.157 | -0.895 | 3 | $*NH_2$+H→$*NH_3$ | 0.69 |
| Nb@g-$C_4N_3$ | 1.137 | -0.299 | 4 | $*N_2$+H→$*N_2H$ | 0.48 |
| Mo@g-$C_4N_3$ | 1.141 | -0.331 | 5 | *N+H→*NH | 0.34 |
| Re@g-$C_4N_3$ | 1.143 | -0.629 | 5 | *N+H→*NH | 0.61 |
| Nb@g-$C_6N_6$ | 1.145 | -0.770 | 4 | $*N_2$+H→$*N_2H$ | 0.42 |
| Mo@g-$C_6N_6$ | 1.142 | -0.286 | 5 | $*N_2$+H→$*N_2H$ | 0.54 |
| Ta@g-$C_6N_6$ | 1.148 | -0.975 | 3 | $*N_2$+H→$*N_2H$ | 0.40 |
| W@g-$C_6N_6$ | 1.147 | -0.829 | 4 | $*N_2$+H→$*N_2H$ | 0.31 |
| Re@g-$C_6N_6$ | 1.145 | -0.756 | 5 | $*N_2$+H→$*N_2H$ | 0.51 |

| | | | | | |
|---|---|---|---|---|---|
| Zr@g-$C_9N_{10}$ | 1.144 | -0.487 | 2 | $*N_2+H \rightarrow *N_2H$ | 0.43 |
| Nb@g-$C_9N_{10}$ | 1.144 | -0.569 | 4 | $*N_2+H \rightarrow *N_2H$ | 0.41 |
| Mo@g-$C_9N_{10}$ | 1.145 | -0.241 | 5 | $*N_2+H \rightarrow *N_2H$ | 0.39 |
| Ta@g-$C_9N_{10}$ | 1.150 | -0.857 | 3 | $*N_2+H \rightarrow *N_2H$ | 0.20 |
| W@g-$C_9N_{10}$ | 1.132 | -1.138 | 4 | $*N_2+H \rightarrow *N_2H$ | 0.27 |
| Re@g-$C_9N_{10}$ | 1.143 | -1.117 | 5 | $*N_2+H \rightarrow *N_2H$ | 0.34 |



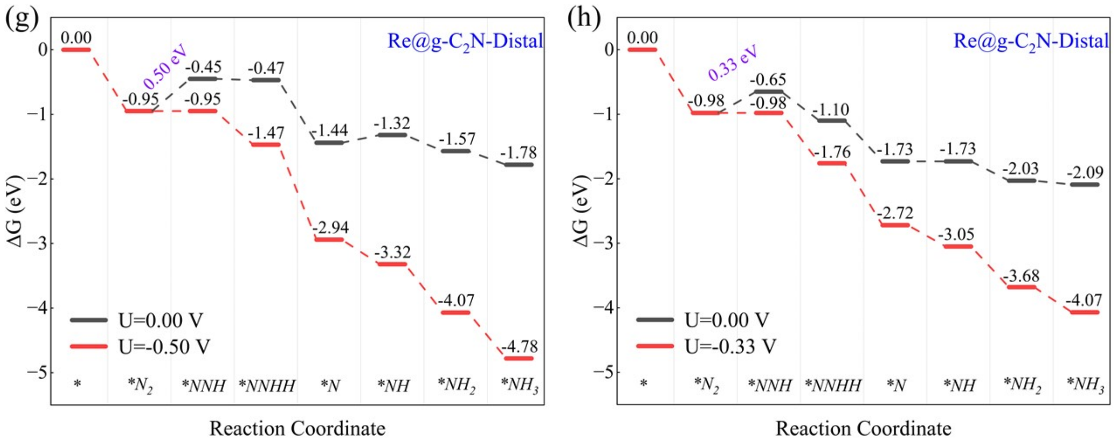



**Fig. S9** Gibbs free energy change diagram of Nb, Ta, W, Re@g-$C_2N$ along the distal pathway under (a, c, e, g) vacuum and (b, d, f, h) implicit solvation.

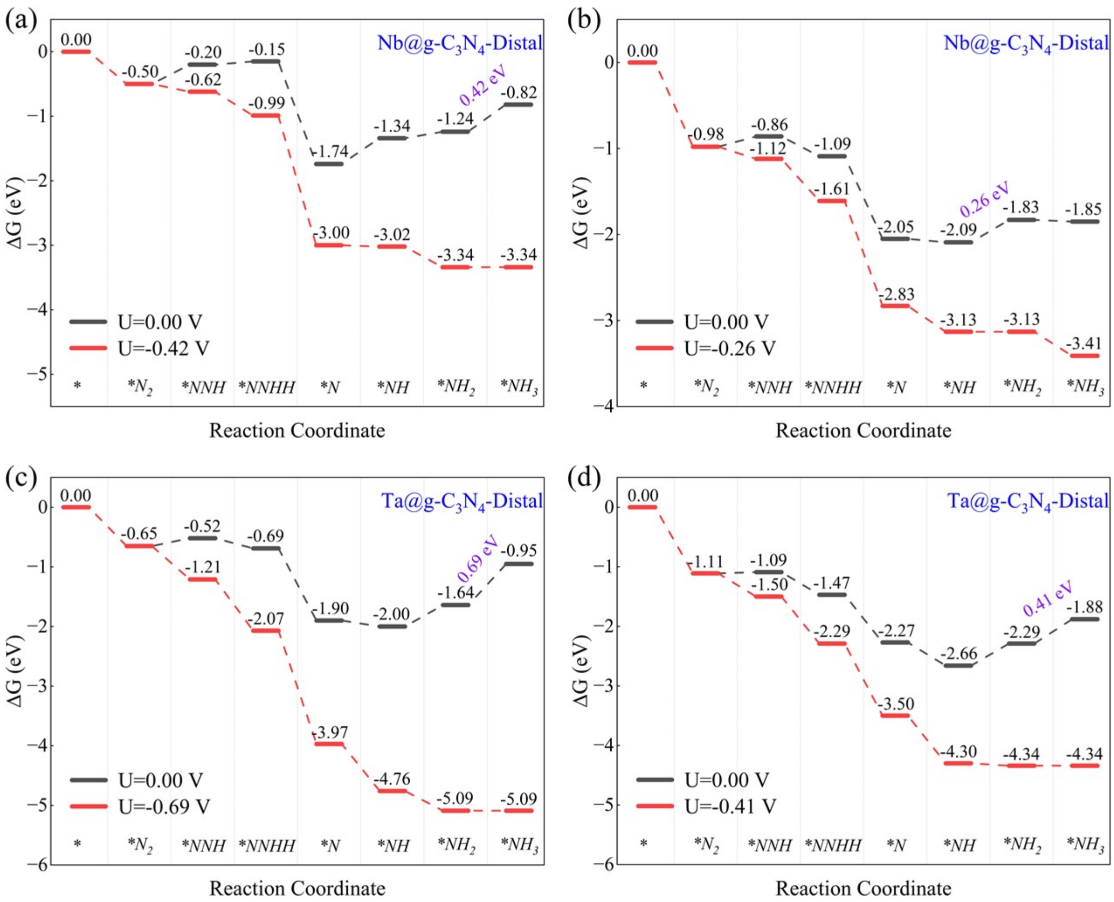



**Fig. S10** Gibbs free energy change diagram of Nb, Ta@g-$C_3N_4$ along distal pathway under (a, c) vacuum and (b, d) implicit solvation.

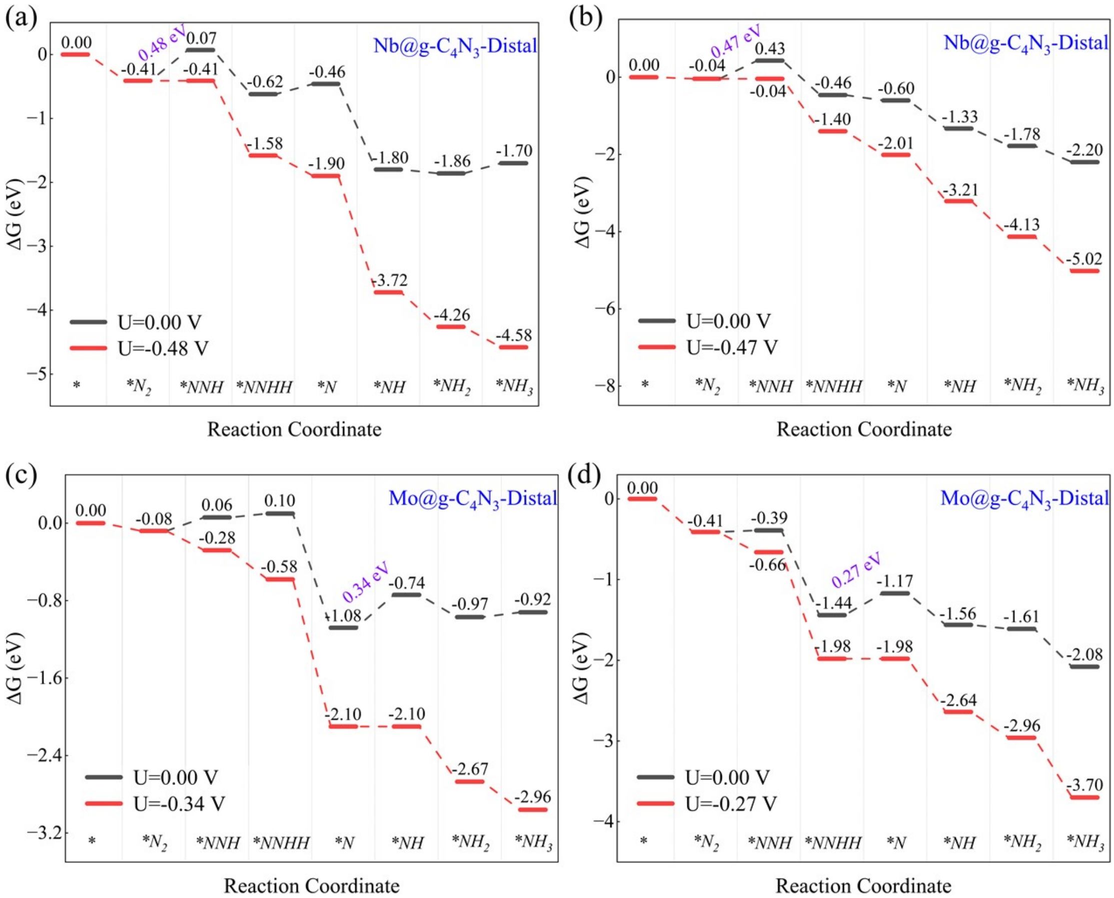
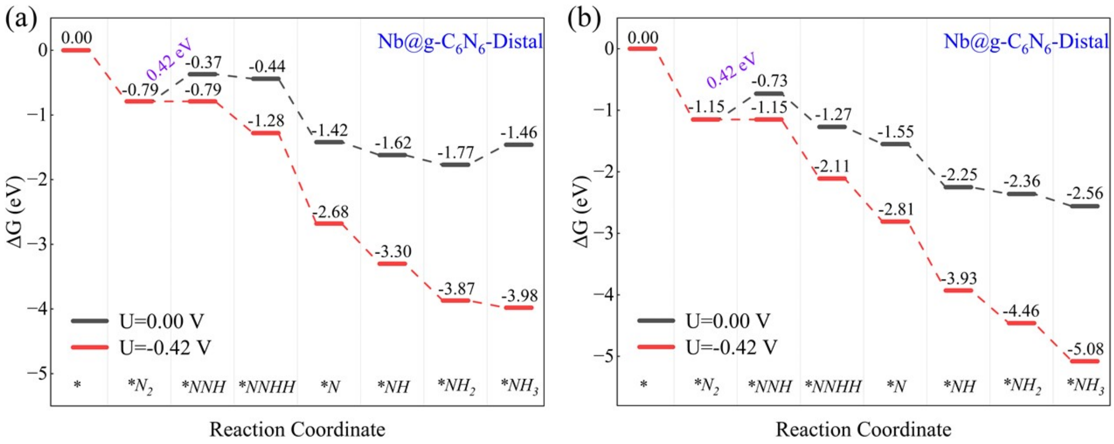
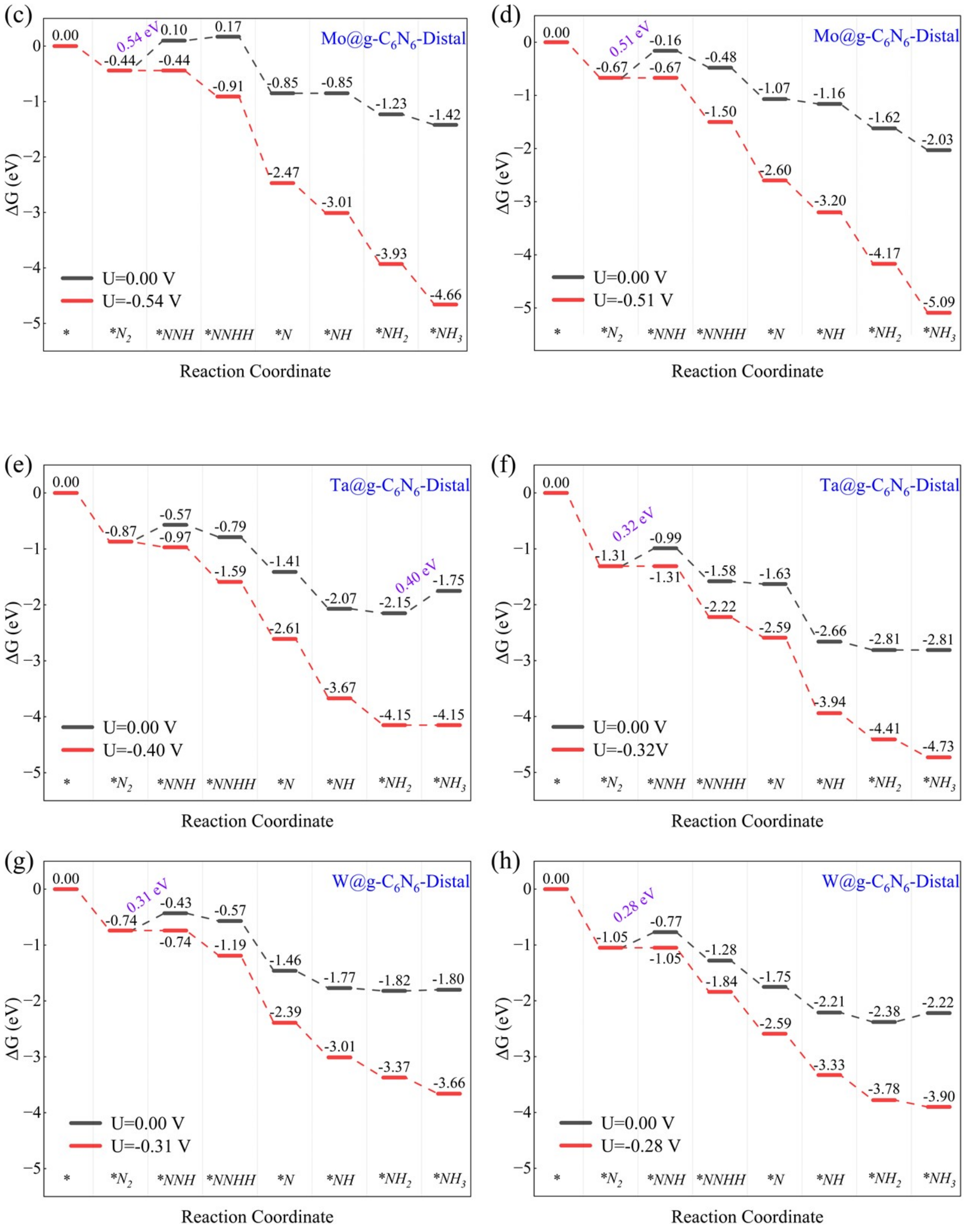



**Fig. S11** Gibbs free energy change diagram of Nb, Mo@g-$C_4N_3$ along the distal pathway under (a, c) vacuum and (b, d) implicit solvation.





(c)
Mo@g-C6N6-Distal
0.54 eV
0.00
-0.44
0.10
-0.44
0.17
-0.91
-0.85
-2.47
-0.85
-3.01
-1.23
-3.93
-1.42
-4.66
U=0.00 V
U=-0.54 V
(d)
Mo@g-C6N6-Distal
0.51 eV
0.00
-0.67
-0.16
-0.67
-0.48
-1.50
-1.07
-2.60
-1.16
-3.20
-1.62
-4.17
-2.03
-5.09
U=0.00 V
U=-0.51 V
(e)
Ta@g-C6N6-Distal
0.40 eV
0.00
-0.87
-0.57
-0.97
-0.79
-1.59
-1.41
-2.61
-2.07
-3.67
-2.15
-4.15
-1.75
-4.15
U=0.00 V
U=-0.40 V
(f)
Ta@g-C6N6-Distal
0.32 eV
0.00
-1.31
-0.99
-1.31
-1.58
-2.22
-1.63
-2.59
-2.66
-3.94
-2.81
-4.41
-2.81
-4.73
U=0.00 V
U=-0.32V
(g)
W@g-C6N6-Distal
0.31 eV
0.00
-0.74
-0.43
-0.74
-0.57
-1.19
-1.46
-2.39
-1.77
-3.01
-1.82
-3.37
-1.80
-3.66
U=0.00 V
U=-0.31 V
(h)
W@g-C6N6-Distal
0.28 eV
0.00
-1.05
-0.77
-1.05
-1.28
-1.84
-1.75
-2.59
-2.21
-3.33
-2.38
-3.78
-2.22
-3.90
U=0.00 V
U=-0.28 V
ΔG (eV)
Reaction Coordinate
* *N2 *NNH *NNHH *N *NH *NH2 *NH3

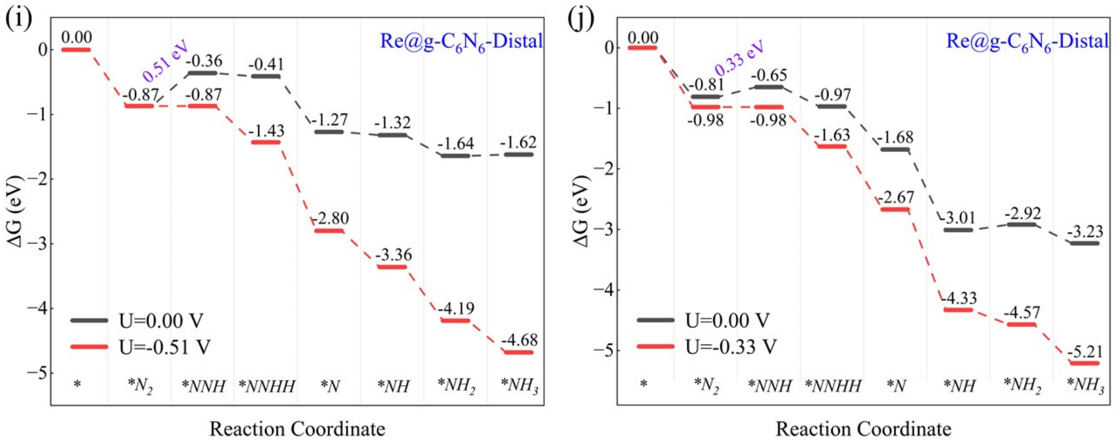
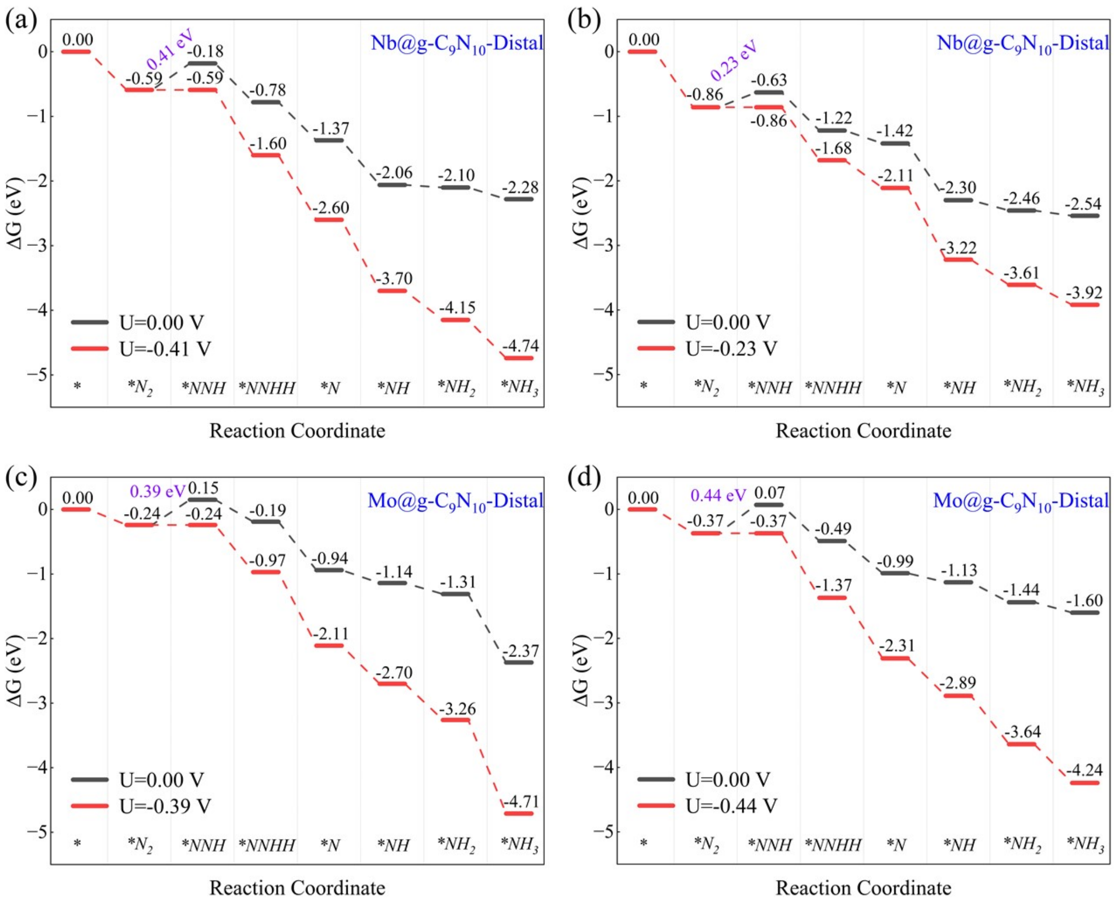



**Fig. S12** Gibbs free energy change diagram of Nb, Mo, Ta, W, Re@g-$C_6N_6$ along the distal pathway under (a, c, e, g, i) vacuum and (b, d, f, h, j) implicit solvation.



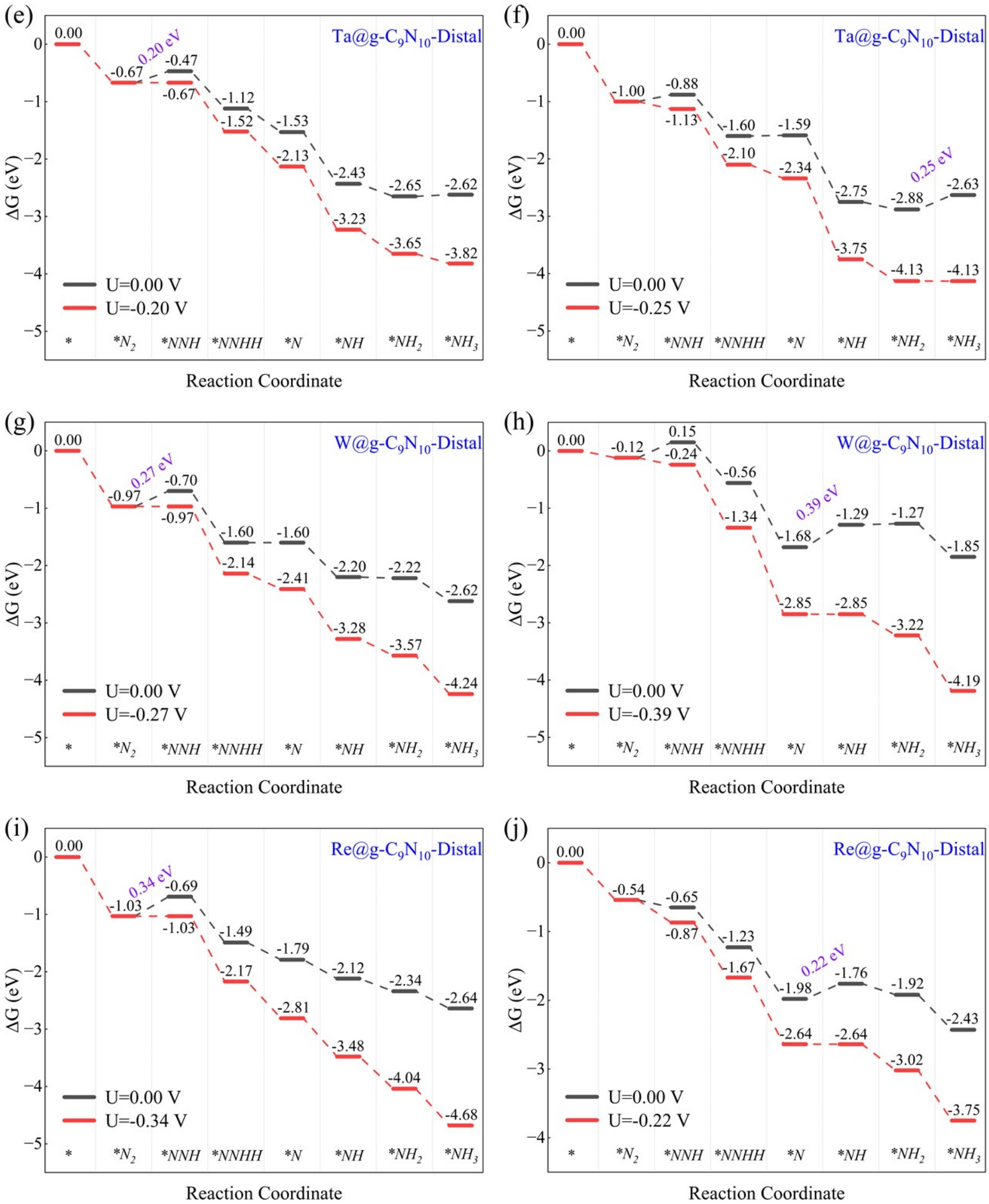



**Fig. S13** Gibbs free energy change diagram of Nb, Mo, Ta, W, Re@g-$C_9N_{10}$ along distal pathway under (a, c, e, g, i) vacuum and (b, d, f, h, j) implicit solvation.

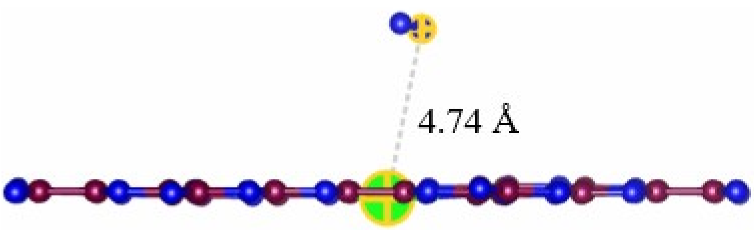



**Fig. S14** $N_2$ is physically adsorbed onto Zr@g-$C_9N_{10}$ under implicit solvation conditions.