Supporting Information

Computational Screening of Single Transition−metal Atoms Anchored to g−C_9N_4 as Catalysts for N_2 Reduction to NH_3

Xuxin Kang[a], Junchao Huang[a] and Xiangmei Duan[a,b,*]

[a] School of Physical Science and Technology, Ningbo University, Ningbo 315211 P. R. China

[b] Laboratory of Clean Energy Storage and Conversion, Ningbo University, Ningbo, P.R. China

Table S1 The adsorption energy ($E^{ads}_{*N_2}$, in eV), the change of Gibbs free energy (ΔG_{*N_2}, in eV), and the bond length of N–N (d_{N-N}, Å) of N_2 adsorbed on TM@g–C_9N_4 in end–on and side–on modes.

TM atom	End–on			Side–on		
	$E^{ads}_{*N_2}$	ΔG_{*N_2}	d_{N-N}	$E^{ads}_{*N_2}$	ΔG_{*N_2}	d_{N-N}
Sc	–0.90	–0.46	1.13	–0.53	–0.13	1.15
Ti	–1.09	–0.48	1.14	**–0.57**	**0.09**	**1.18**
V	–0.93	–0.49	1.13	–0.34	0.07	1.15
Cr	–0.42	0.02	1.12	/	/	/
Mn	–0.47	–0.06	1.12	/	/	/
Fe	–0.90	–0.45	1.13	–0.36	0.05	1.15
Co	–0.93	–0.48	1.13	/	/	/
Ni	–0.54	–0.08	1.13	/	/	/
Cu	–0.92	–0.44	1.12	–0.42	0.04	1.14
Zn	–0.46	–0.02	1.12	/	/	/
Y	–0.80	–0.34	1.13	–0.44	–0.03	1.14
Zr	–1.15	–0.72	1.14	**–0.70**	**–0.27**	**1.18**
Nb	–1.24	–0.76	1.15	**–0.62**	**–0.16**	**1.19**
Mo	–0.83	–0.35	1.14	**–0.33**	**0.14**	**1.19**
Ru	–1.11	–0.64	1.14	/	/	/
Rh	–0.65	–0.14	1.13	/	/	/
Pd	–0.38	0.08	1.12	/	/	/
Ag	–0.15	0.19	1.12	/	/	/
Cd	–0.22	0.16	1.11	/	/	/
Hf	–1.13	–0.67	1.14	**–0.70**	**–0.27**	**1.20**
Ta	–1.31	–0.83	1.15	**–0.83**	**–0.36**	**1.21**
W	–1.17	–0.70	1.15	**–0.78**	**–0.29**	**1.21**
Re	–1.44	–0.94	1.15	**–0.89**	**–0.39**	**1.23**
Os	–1.21	–0.72	1.14	**–0.41**	**0.08**	**1.19**
Ir	–0.91	–0.39	1.13	/	/	/
Pt	–0.38	0.09	1.13	/	/	/
Au	–0.11	0.25	1.11	/	/	/

Table S2 Zero−point energy (ZPE) and entropy (TS, T = 298.15 K) for all reaction intermediates of Nb, W, Re@g−C_9N_4 via the enzymatic pathway and Ta@g−C_9N_4 via the distal pathway. * represent the catalyst.

Nb@g−C_9N_4	ZPE (eV)	TS (eV)
*N−*N	0.18	0.15
*N−*NH	0.47	0.13
*NH−*NH	0.79	0.14
NH−NH_2	1.13	0.15
NH_2−NH_2	1.36	0.17
*NH_2	0.66	0.12
*NH_3	1.02	0.11

W@g−C_9N_4	ZPE (eV)	TS (eV)
*N−*N	0.19	0.12
*N−*NH	0.48	0.12
*NH−*NH	0.8	0.14
NH−NH_2	1.13	0.12
NH_2−NH_2	1.35	0.16
*NH_2	0.65	0.13
*NH_3	1.01	0.09

Re@g−C_9N_4	ZPE (eV)	TS (eV)
*N−*N	0.2	0.11
*N−*NH	0.49	0.11
*NH−*NH	0.82	0.12
NH−NH_2	1.13	0.13
NH_2−NH_2	1.43	0.11
*NH_2	0.66	0.11
*NH_3	1.03	0.08

Ta@g−C_9N_4	ZPE (eV)	TS (eV)
*N−N	0.2	0.15
*N−NH	0.47	0.16
*N−NH_2	0.81	0.20
*N	0.09	0.05
*NH	0.36	0.08
*NH_2	0.66	0.12
*NH_3	1.01	0.10

Table S3 The adsorption energy (E_{*H}, in eV) of H on TM, C and N sites of SACs

	E_{*H} (TM site)	E_{*H} (C site)	E_{*H} (N site)
Zr@g−C_9N_4	**−0.70**	0.48	−0.20
Nb@g−C_9N_4	**−0.64**	0.46	−0.28
Ta@g−C_9N_4	**−0.90**	0.54	−0.24
W@g−C_9N_4	**−0.86**	0.77	−0.59
Re@g−C_9N_4	**−0.96**	0.91	−0.66
Ti@g−C_9N_4	**−0.27**	0.69	−0.17
Mo@g−C_9N_4	**−0.42**	0.71	−0.37

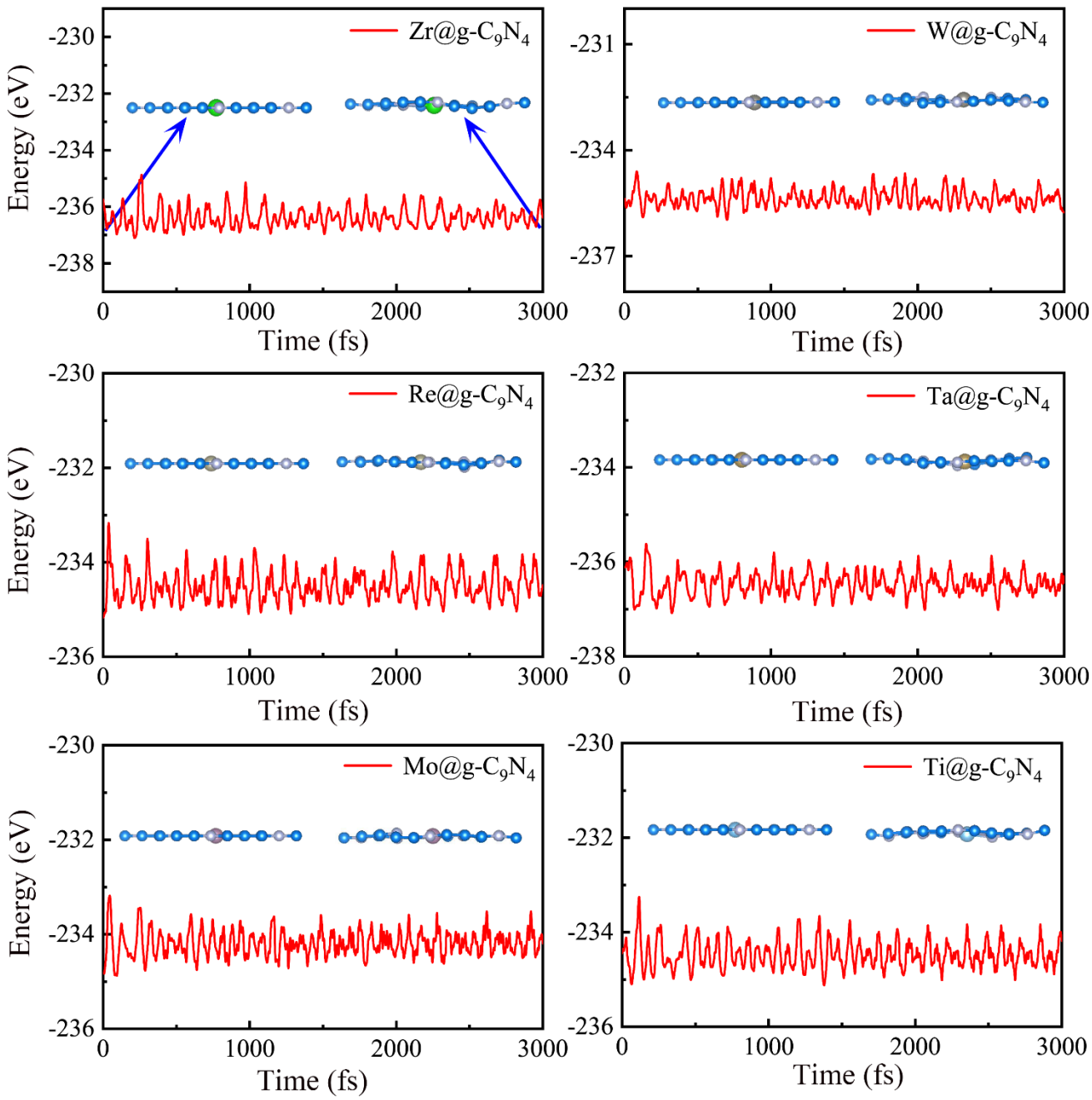
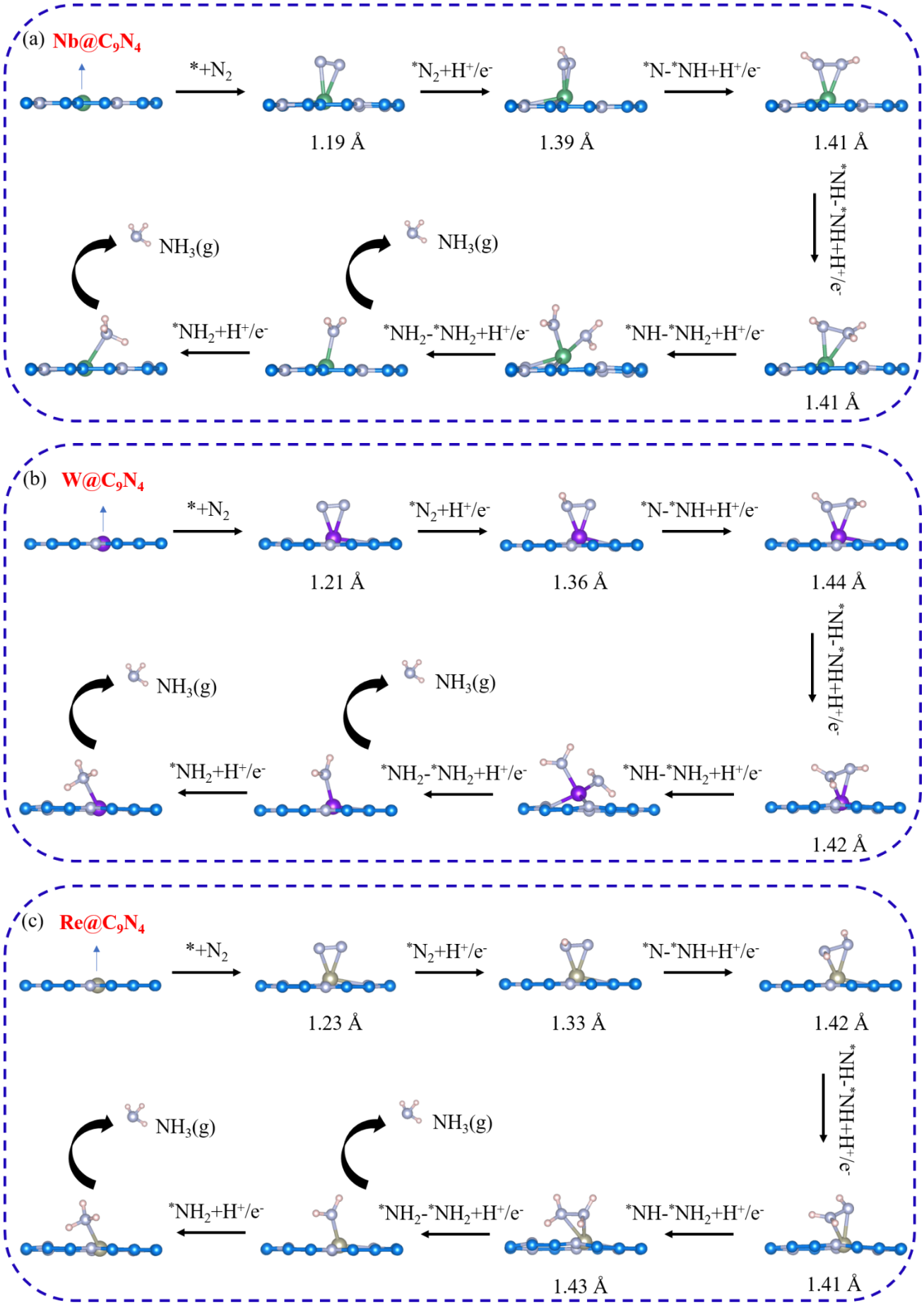


Fig. S1 The variation of energy after AIMD simulation for Zr, W, Re, Ta, Mo and Ti@g−C_9N_4. The insters display the initial and final structures of the catalysts at 500 K.


(a) Nb@C9N4
*+N2
*N2+H+/e-
*N-*NH+H+/e-
1.19 Å
1.39 Å
1.41 Å
*NH-*NH+H+/e-
NH3(g)
NH3(g)
*NH2+H+/e-
*NH2-*NH2+H+/e-
*NH-*NH2+H+/e-
1.41 Å
(b) W@C9N4
*+N2
*N2+H+/e-
*N-*NH+H+/e-
1.21 Å
1.36 Å
1.44 Å
*NH-*NH+H+/e-
NH3(g)
NH3(g)
*NH2+H+/e-
*NH2-*NH2+H+/e-
*NH-*NH2+H+/e-
1.42 Å
(c) Re@C9N4
*+N2
*N2+H+/e-
*N-*NH+H+/e-
1.23 Å
1.33 Å
1.42 Å
*NH-*NH+H+/e-
NH3(g)
NH3(g)
*NH2+H+/e-
*NH2-*NH2+H+/e-
*NH-*NH2+H+/e-
1.43 Å
1.41 Å

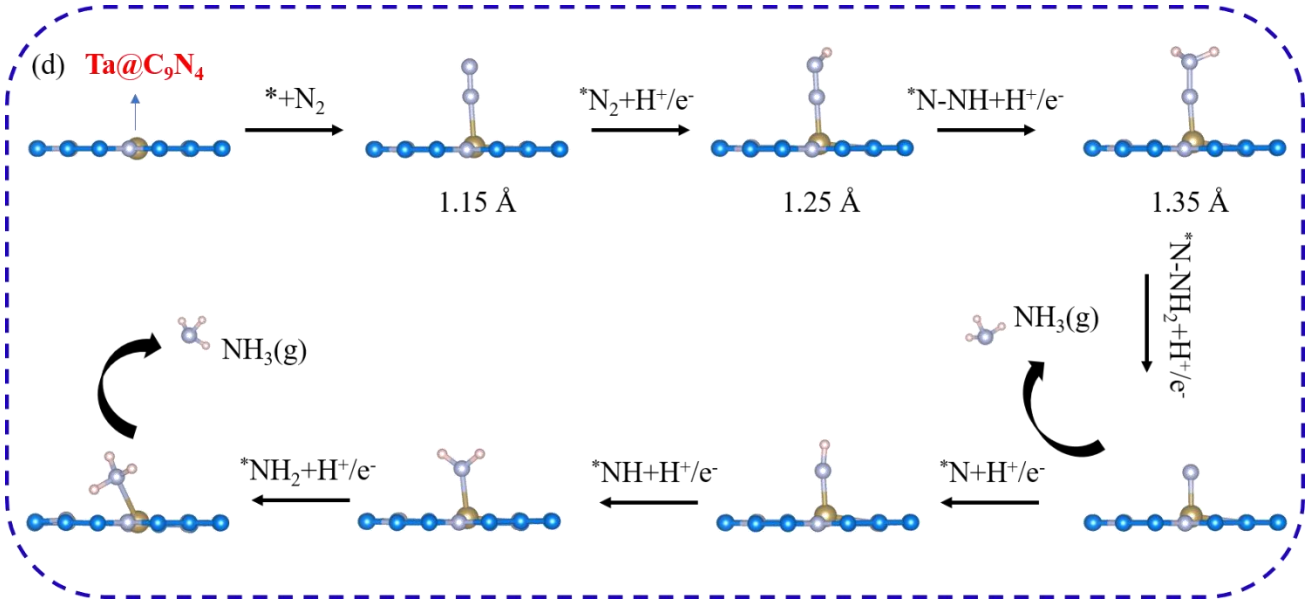


Fig. S2 Optimized structures of various reduction intermediates on (a) Nb@g−C_9N_4, (b) W@g−C_9N_4, (c) Re@g−C_9N_4 through the enzymatic pathway and (d) Ta@g−C_9N_4 through the distal pathway. N–N bond lengths are presented.

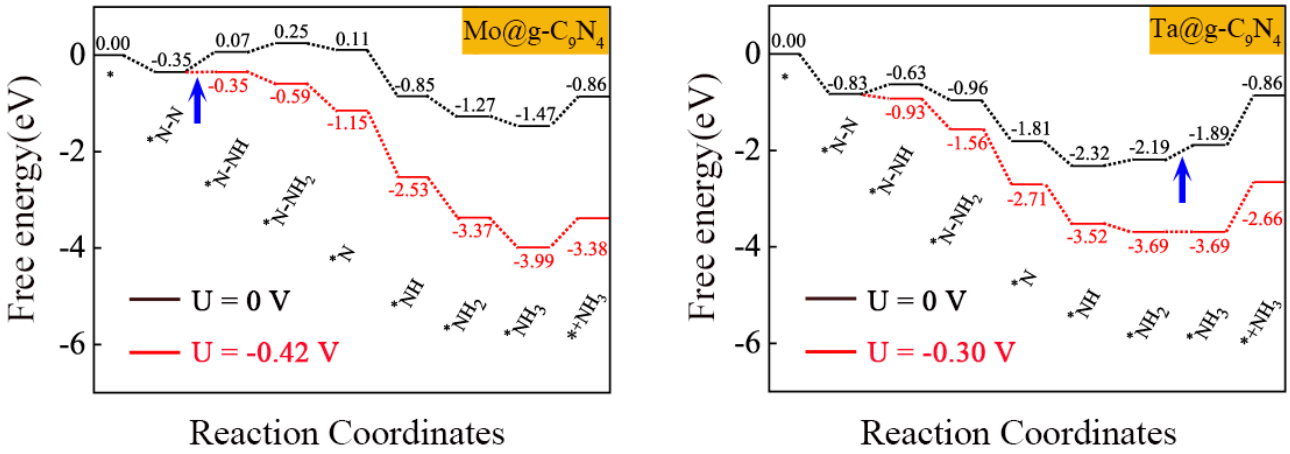


Fig. S3 Gibbs free energy diagrams of the NRR on Mo@g−C_9N_4 and Ta@g−C_9N_4 along distal pathway.

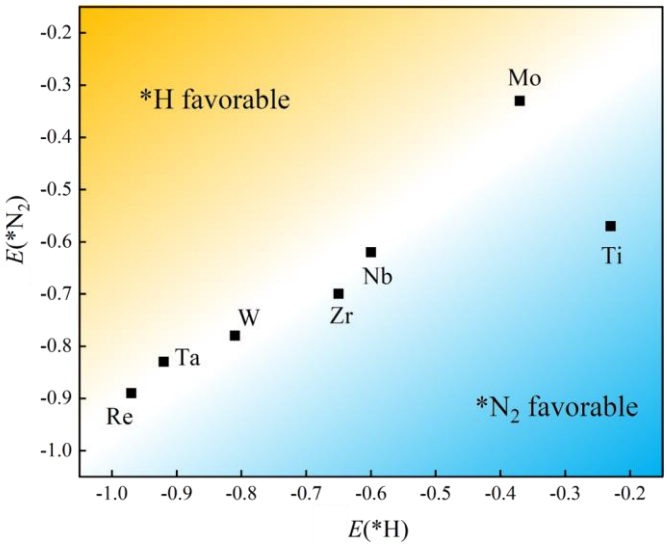


Fig. S4 The adsorption energy of $*N_2$ (E_{*N_2}) as a function of adsorption energy H atom (E_{*H}).

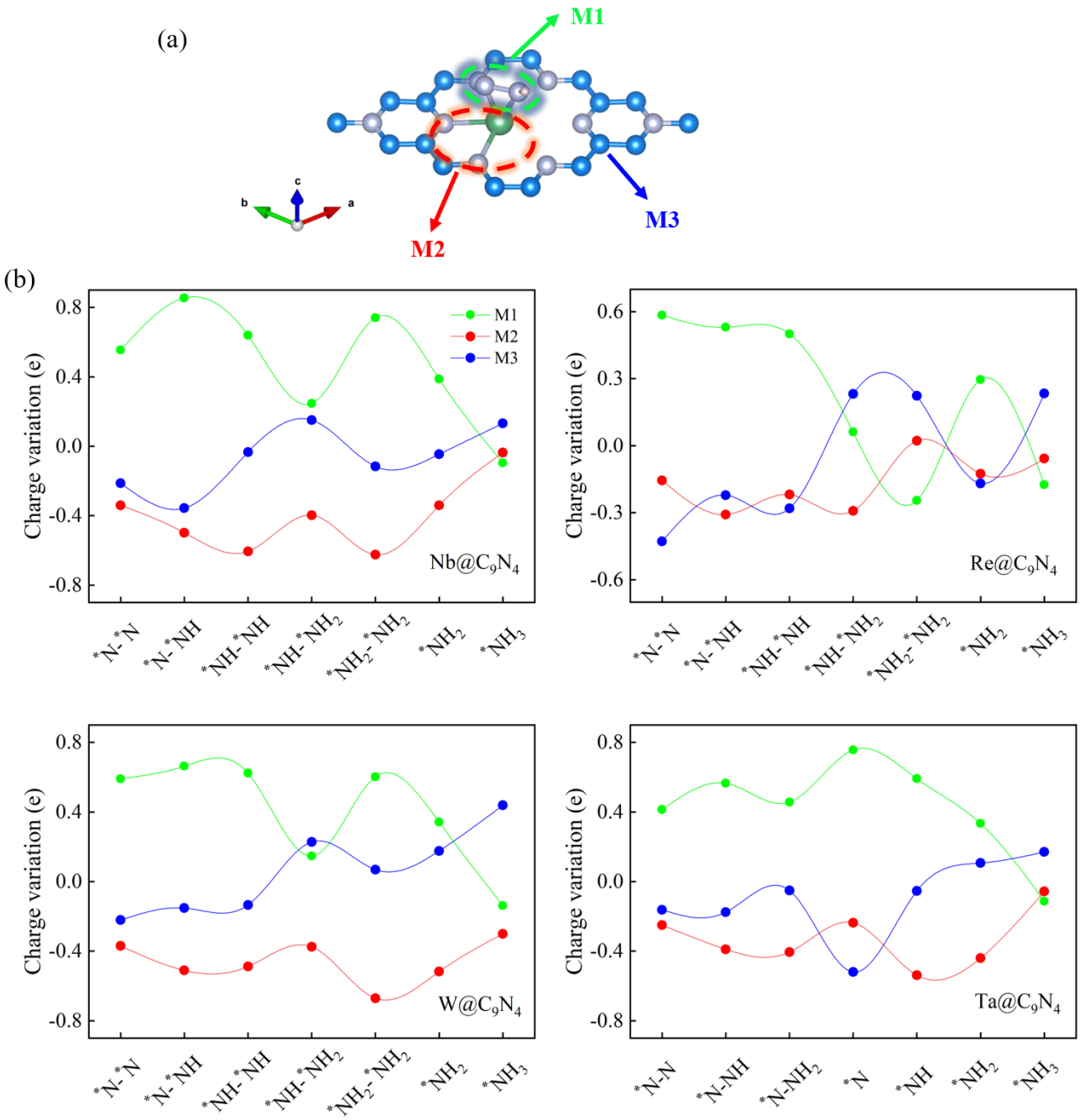


Fig. S5 (a) Defined three moieties in N_xH_y species adsorbed on TM@g−C_9N_4. (b) Charge variation of three moieties over Nb, Re, W@g−C_9N_4 via the enzymatic pathway and Ta@g−C_9N_4 via the distal pathway.

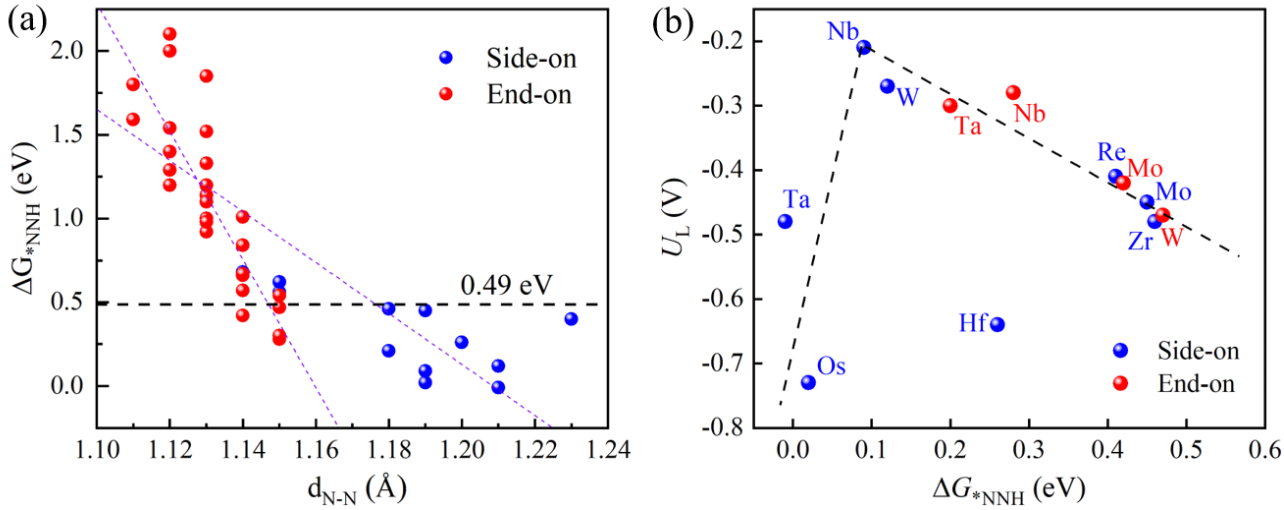


Fig. S6 (a) The free energy of *NNH species (ΔG_{*NNH}) as a function of N−N bond length (d_{N-N}). (b) The computed NRR limiting potential (U_L) as a function of the adsorption free energy of *NNH species (ΔG_{*NNH}), blue and red balls represent side–on and end–on configurations, respectively.