Supporting Information

Electrochemical Ammonia Synthesis under Ambient Conditions using TM-embedded Porphine-Fused Sheets as Single-Atom Catalysts

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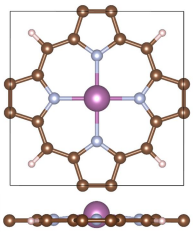
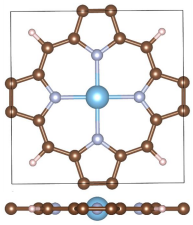
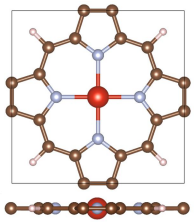
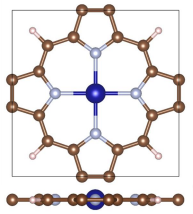
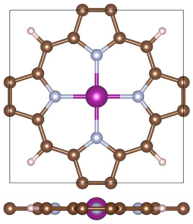
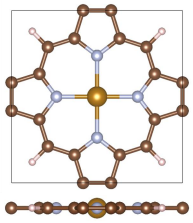
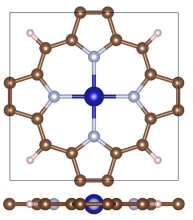
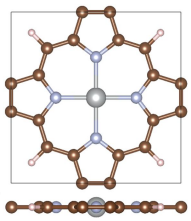
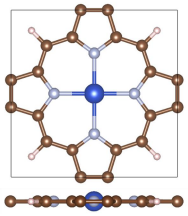
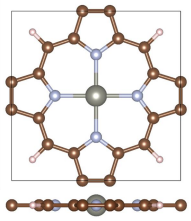
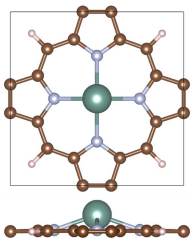
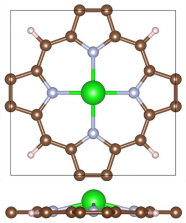
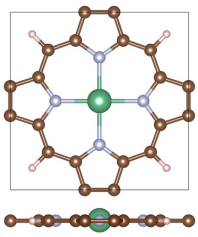
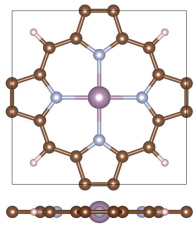
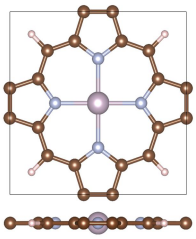
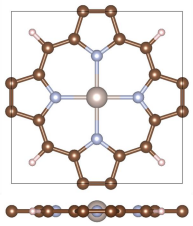
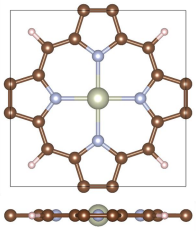
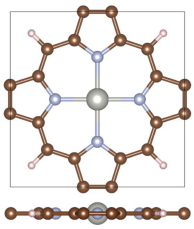
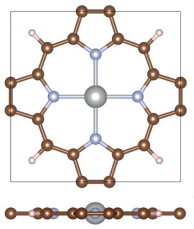
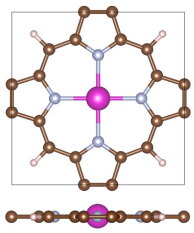
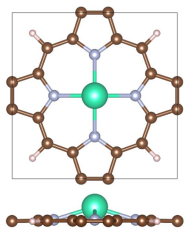
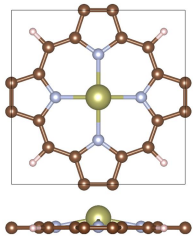
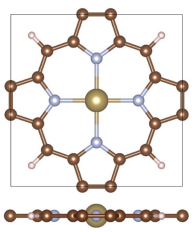
Table S1. Lattice constants, space groups, point groups, magnetic moments and energies of the TM-Por monolayers.

TM-Por	Crystal structure top (up) and side (down) views	Lattice constant (*a*, *b* and *c*)/Å	Space group	Point group	Magnetic moment	Energy/eV
Sc-Por		*a*=8.58245 *b*=8.58245 *c*=15.01112	P4/mm (#99)	C_{4v}	0	–201.37057
Ti-Por		*a*=8.53495 *b*=8.53495 *c*=15.17867	P4/mmm (#123)	D_{4h}	1.139	–201.56274
V-Por		*a*=8.51386 *b*=8.51386 *c*=15.25397	P4/mmm (#123)	D_{4h}	2.517	–202.14904
Cr-Por		*a*=8.50517 *b*=8.50517 *c*=15.28516	P4/mmm (#123)	D_{4h}	3.524	–202.99278
Mn-Por		*a*=8.45749 *b*=8.45749 *c*=15.45799	P4/mmm (#123)	D_{4h}	2.903	–202.05345
Fe-Por		*a*=8.43379 *b*=8.43379 *c*=15.54498	P4/mmm (#123)	D_{4h}	1.861	–200.57118
Co-Por		*a*=8.42270 *b*=8.42270 *c*=15.58595	P4/mmm (#123)	D_{4h}	0.839	–199.18339

Ni-Por		*a*=8.41060 *b*=8.41060 *c*=15.63081	P4/mmm（#123）	D_{4h}	–0.000	–197.88221
Cu-Por		*a*=8.48977 *b*=8.48977 *c*=15.34065	P4/mmm（#123）	D_{4h}	0.866	–195.62720
Zn-Por		*a*=8.53333 *b*=8.53333 *c*=15.18443	P4/mmm（#123）	D_{4h}	0.000	–194.18390
Y-Por		*a*=8.59311 *b*=8.59311 *c*=14.97388	P4/mm（#99）	C_{4v}	–0.000	–201.50627
Zr-Por		*a*=8.56910 *b*=8.56910 *c*=15.05793	P4/mm（#99）	C_{4v}	0.486	–202.12896
Nb-Por		*a*=8.57089 *b*=8.57089 *c*=15.05164	P4/mmm（#123）	D_{4h}	1.456	–202.29540
Mo-Por		*a*=8.56571 *b*=8.56571 *c*=15.06984	P4/mmm（#123）	D_{4h}	3.033	–202.46706
Tc-Por		*a*=8.52328 *b*=8.52328 *c*=15.22027	P4/mmm（#123）	D_{4h}	2.708	–201.86266

Ru-Por		*a*=8.49940 *b*=8.49940 *c*=15.30590	P4/mmm（#123）	D_{4h}	1.652	–200.71586
Rh-Por		*a*=8.47605 *b*=8.47605 *c*=15.39035	P4/mmm（#123）	D_{4h}	0.732	–199.48772
Pd-Por		*a*=8.48548 *b*=8.48548 *c*=15.35617	P4/mmm（#123）	D_{4h}	0.000	–197.98363
Ag-Por		*a*=8.58949 *b*=8.58949 *c*=14.98654	P4/mmm（#123）	D_{4h}	0.557	–193.73617
Cd-Por		*a*=8.65563 *b*=8.65563 *c*=14.75836	P4/mmm（#123）	D_{4h}	0.000	–192.86304
Lu-Por		*a*=8.58709 *b*=8.58709 *c*=14.99489	P4/mm（#99）	C_{4v}	0.000	–199.40190
Hf-Por		*a*=8.56650 *b*=8.56650 *c*=15.06707	P4/mm（#99）	C_{4v}	0.619	–203.69129
Ta-Por		*a*=8.54363 *b*=8.54363 *c*=15.14784	P4/mmm（#123）	D_{4h}	1.103	–203.85435

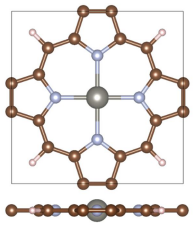
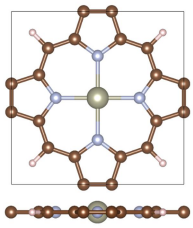
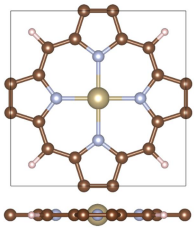
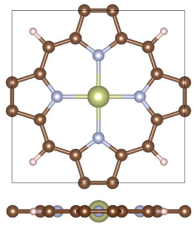
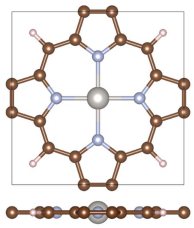
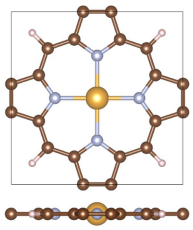
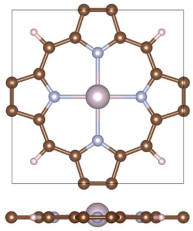
W-Por		*a*=8.53547 *b*=8.53547 *c*=15.17683	P4/mmm（#123）	D_{4h}	2.620	–203.97868
Re-Por		*a*=8.51623 *b*=8.51623 *c*=15.24545	P4/mmm（#123）	D_{4h}	2.592	–203.14203
Os-Por		*a*=8.46862 *b*=8.46862 *c*=15.41736	P4/mmm（#123）	D_{4h}	0.712	–202.04842
Ir-Por		*a*=8.45895 *b*=8.45895 *c*=15.45265	P4/mmm（#123）	D_{4h}	–0.000	–200.93570
Pt-Por		*a*=8.47533 *b*=8.47533 *c*=15.39297	P4/mmm（#123）	D_{4h}	0.000	–199.33241
Au-Por		*a*=8.47533 *b*=8.47533 *c*=15.39297	P4/mmm（#123）	D_{4h}	0.053	–194.39559
Hg-Por		*a*=8.47533 *b*=8.47533 *c*=15.39297	P4/mm（#99）	C_{4v}	–0.000	–190.68287

Table S2. ΔG_{*N_2} for end-on and side-on adsorptions and N≡N bond lengths of adsorbed N_2 molecule. The screening condition is $\Delta G_{*N_2} < 0$ eV.

TM-Por	End-on		Side-on	
	ΔG_{*N_2}/eV	R_{N-N}/Å	ΔG_{*N_2}/eV	R_{N-N}/Å
Sc	–0.210	1.125	0.090	—
Ti	–0.498	1.135	0.030	—
V	–0.354	1.135	0.276	—
Cr	/	/	1.321	—
Mn	/	/	/	/
Fe	0.227	—	/	/
Co	0.142	—	/	/
Ni	/	/	/	/
Cu	/	/	/	/
Zn	/	/	/	/
Y	–0.133	1.131	0.105	—
Zr	–0.607	1.140	–0.411	1.178
Nb	–0.619	1.144	–0.371	1.209
Mo	–0.334	1.142	0.328	—
Tc	–0.433	1.143	0.490	—
Ru	–0.631	1.139	0.512	—
Rh	0.368	—	/	/
Pd	/	/	/	/
Ag	/	/	/	/
Cd	/	/	/	/
Lu	–0.238	1.132	–0.006	1.152
Hf	–0.681	1.143	–0.460	1.186
Ta	–0.686	1.149	–0.361	1.226
W	–0.498	1.151	0.001	—
Re	–0.560	1.148	0.248	—
Os	–0.692	1.145	0.544	—
Ir	0.686	—	/	/
Pt	/	/	/	/
Au	/	/	/	/
Hg	/	/	/	/

"/" indicates that TM atom cannot be embedded in the substrate.
"—" indicates that the material is excluded because $\Delta G_{*N_2} \geq 0$ eV.

Table S3. $\Delta G_{*N_2 \rightarrow *N_2H}$ and $\Delta G_{*NH_2 \rightarrow *NH_3}$ in high throughput screening. The screening criteria is 0.8 eV.

Adsorption mode	TM-Por	$\Delta G_{*N_2 \rightarrow *N_2H}$/eV	$\Delta G_{*NH_2 \rightarrow *NH_3}$/eV
End-on	Sc	1.248	/
	Ti	0.809	/
	V	0.924	/
	Y	1.232	/
	Zr	0.623	0.945
	Nb	0.387	0.741
	Mo	0.359	0.040
	Tc	0.408	–0.105
	Ru	1.381	/
	Lu	1.237	/
	Hf	0.589	1.074
	Ta	0.285	0.950
	W	0.159	0.584
	Re	0.320	0.330
	Os	1.256	/
Side-on	Zr	0.216	0.945
	Nb	–0.029	0.741
	Lu	0.733	0.064
	Hf	0.146	1.074
	Ta	–0.161	0.950

Table S4. Comparisons between the nitrogen (ΔG_{*N_2}) and hydrogen adsorptions (ΔG_{*H}). The screening condition is $\Delta G_{*N_2} < \Delta G_{*H}$.

Adsorption mode	TM-Por	ΔG_{*N_2}/eV	ΔG_{*H}/eV
End-on	Nb	–0.619	–0.523
	Mo	–0.334	–0.329
	Tc	–0.433	–0.312
	W	–0.498	–0.588
	Re	–0.560	–0.660
Side-on	Nb	–0.371	–0.523
	Lu	–0.006	–0.108

Table S5. Thermal corrections (eV) of different adsorbed species. The temperature is set to 298.15 K.

*N_xH_y	Mo-Por			Tc-Por			Nb-Por		
	ZPE	$\int C_p dT$	TS	ZPE	$\int C_p dT$	TS	ZPE	$\int C_p dT$	TS
H_2[a]	0.27	0.09	0.40	0.27	0.09	0.40	0.14	0.05	0.20
N_2[a]	0.15	0.09	0.59	0.15	0.09	0.59	0.15	0.09	0.59
*N≡N	0.22	0.07	0.13	0.22	0.07	0.13	0.20	0.08	0.17
*N=NH	0.49	0.08	0.15	0.49	0.08	0.16	0.47	0.08	0.16
*N=NH_2	0.83	0.09	0.18	0.81	0.09	0.19	0.82	0.09	0.18
*N	0.09	0.03	0.05	0.09	0.03	0.05	0.08	0.03	0.06
*NH	0.36	0.05	0.08	0.33	0.06	0.10	0.36	0.05	0.08
*NH_2	0.68	0.06	0.10	0.69	0.05	0.09	0.65	0.07	0.12
*NH_3	1.04	0.07	0.15	1.05	0.07	0.13	1.04	0.07	0.13
*NH=NH	0.83	0.08	0.17	0.84	0.08	0.17	0.80	0.09	0.20
*NH–NH_2	1.15	0.09	0.18	1.15	0.09	0.18	1.13	0.11	0.23
*NH_2–NH_2	1.53	0.10	0.19	1.52	0.10	0.21	1.51	0.11	0.21
NH_3[a]	0.89	0.11	0.60	0.89	0.11	0.60	0.89	0.11	0.60

[a] from NIST database.

Table S6. ΔG (eV) for different protonation steps of eNRR along the end-on distal pathway on Mo-Por, Tc-Por, and Nb-Por. Red indicates the potential-determining step (PDS).

Protonation Steps	Mo-Por	Tc-Por	Nb-Por
$*N_2 + (H^+ + e^-) \rightarrow *N{=}NH$	0.36	0.41	0.39
$*N{=}NH + (H^+ + e^-) \rightarrow *N{-}NH_2$	0.07	0.53	–0.56
$*N{-}NH_2 + (H^+ + e^-) \rightarrow *N + NH_3(g)$	–1.23	–1.85	–0.42
$*N + (H^+ + e^-) \rightarrow *NH$	–0.09	0.69	–1.05
$*NH + (H^+ + e^-) \rightarrow *NH_2$	–0.27	–0.47	–0.12
$*NH_2 + (H^+ + e^-) \rightarrow *NH_3(g)$	0.12	–0.06	0.74

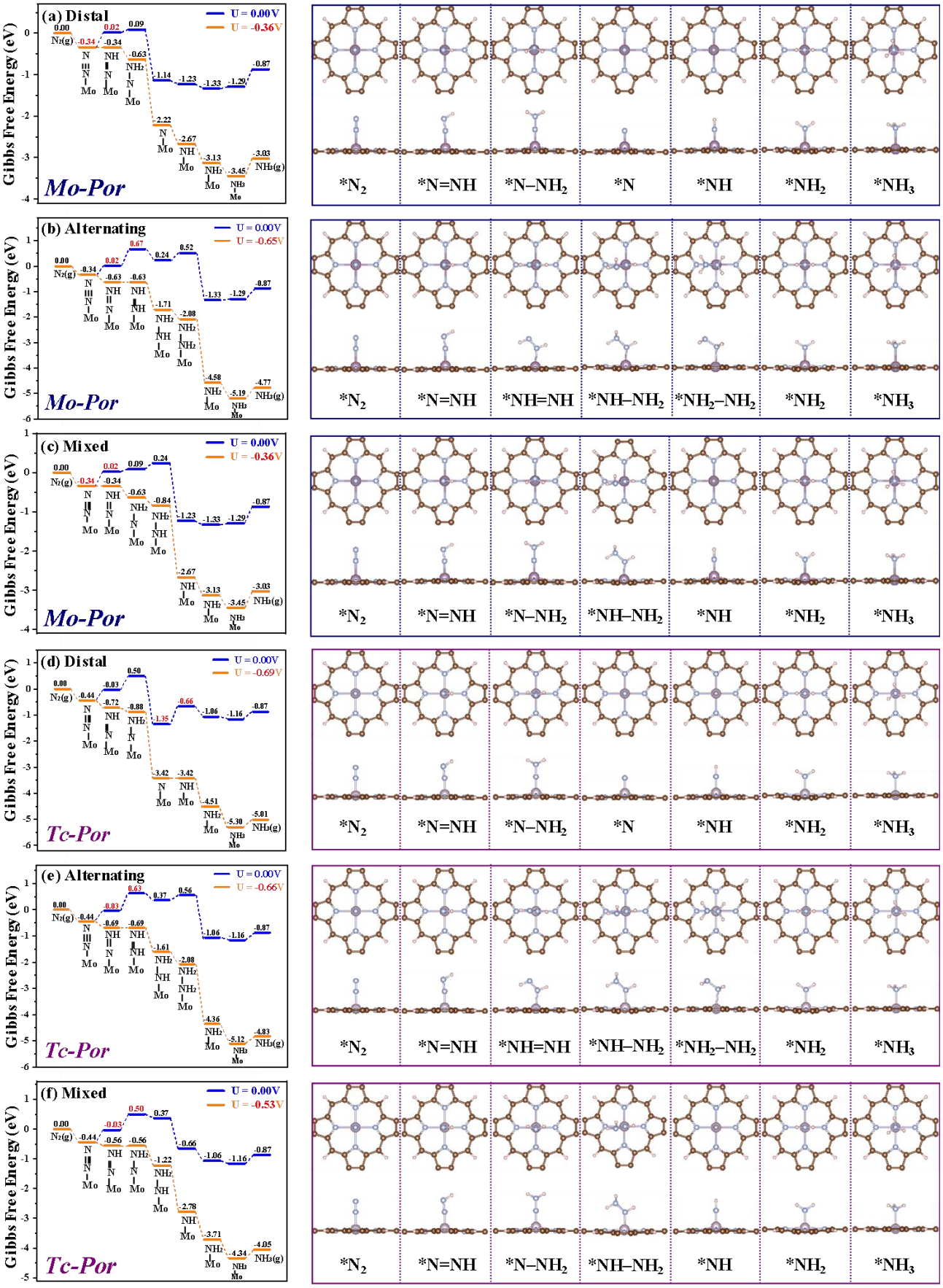


Fig. S1. Free energy profiles and relevant intermediates of N_xH_y-Mo-Por, N_xH_y-Tc-Por, and N_xH_y-Nb-Por in various eNRR pathways.

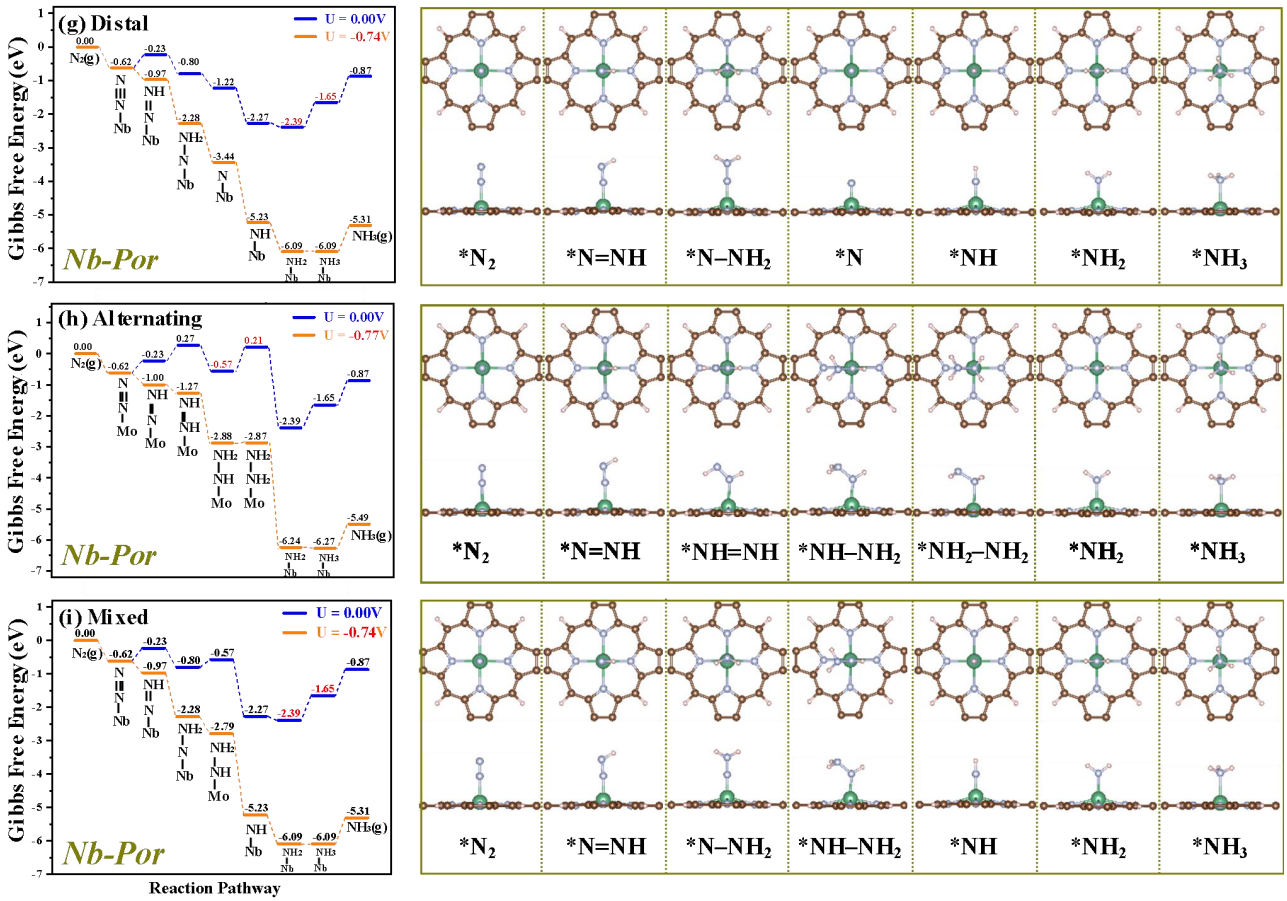


Fig. S1. *Continued*

Table S7. N-N bond lengths in N_xH_y-TM-Por (TM = Mo, Tc, Nb) along the distal pathway.

*N_xH_y-TM-Por	N_2(g)	*N≡N	*N=NH	*N–NH_2
***N_xH_y-Mo-Por**	1.115	1.142	1.235	1.335
***N_xH_y-Tc-Por**	1.115	1.143	1.230	1.317
***N_xH_y-Nb-Por**	1.115	1.144	1.244	1.355

Table S8. Charge transfers in N_xH_y-Mo-Por, N_xH_y-Tc-Por, and N_xH_y-Nb-Por.

*N_xH_y	Moieties	N_xH_y-Mo-Por	N_xH_y-Tc-Por	N_xH_y-Nb-Por
*N≡N	Por' (moiety1)	0.039	–0.112	0.060
	TM-N_4 (moiety2)	–0.321	–0.176	–0.448
	N≡N (moiety3)	0.282	0.288	0.388
*N=NH	Por' (moiety1)	–0.120	–0.115	–0.172
	TM-N_4 (moiety2)	–0.077	0.128	–0.001
	N=NH (moiety3)	0.198	–0.013	0.173
*N–NH_2	Por' (moiety1)	0.151	0.356	–0.045
	TM-N_4 (moiety2)	–0.063	–0.185	0.007
	N–NH_2 (moiety3)	–0.088	–0.171	0.038
*N	Por' (moiety1)	–0.394	–0.507	–0.319
	TM-N_4 (moiety2)	0.215	0.098	–0.030
	N (moiety3)	0.179	0.409	0.349
*NH	Por' (moiety1)	0.257	0.409	0.227
	TM-N_4 (moiety2)	–0.182	–0.269	0.029
	NH (moiety3)	–0.075	–0.140	–0.256
*NH_2	Por' (moiety1)	0.254	–0.027	0.240
	TM-N_4 (moiety2)	–0.052	0.245	0.091
	NH_2 (moiety3)	–0.201	–0.217	–0.332
*NH_3	Por' (moiety1)	0.235	0.269	0.338
	TM-N_4 (moiety2)	0.248	0.113	0.096
	NH_3 (moiety3)	–0.483	–0.382	–0.484
*NH=NH	Por' (moiety1)	0.192	0.248	0.115
	TM-N_4 (moiety2)	0.075	–0.102	0.146
	NH=NH (moiety3)	–0.266	–0.146	–0.261
*NH–NH_2	Por' (moiety1)	0.177	0.019	0.030
	TM-N_4 (moiety2)	–0.045	0.088	–0.111
	NH–NH_2 (moiety3)	–0.132	–0.107	0.080
*NH_2–NH_2	Por' (moiety1)	0.185	0.250	0.375
	TM-N_4 (moiety2)	0.138	0.032	0.137
	NH_2–NH_2 (moiety3)	–0.323	–0.282	–0.152

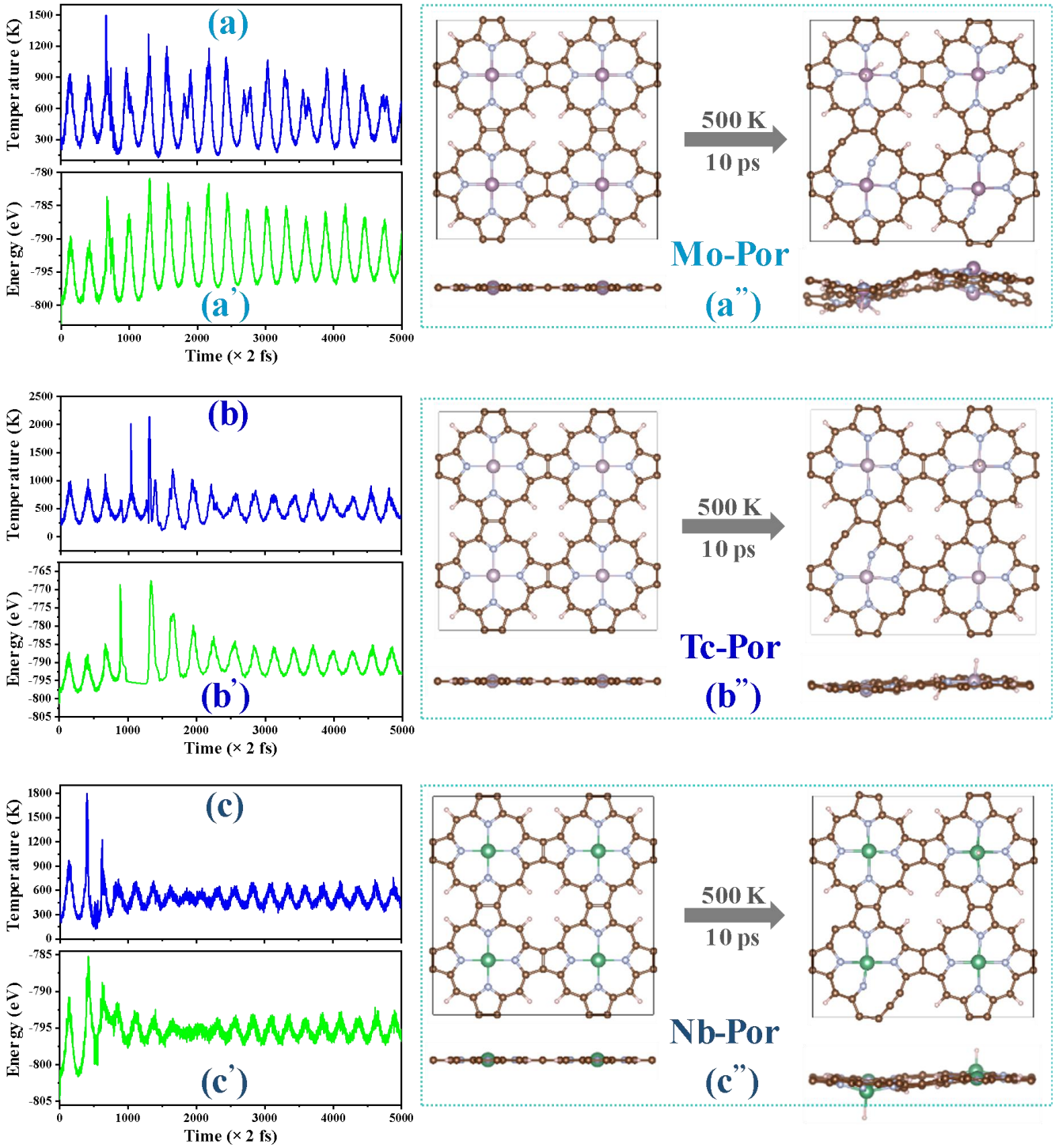


Fig. S2. AIMD simulation plots carried out at 500 K for 10 ps in 2 fs steps. (a), (b), and (c) are schematic representations of the temperature trends with time evolution for Mo-Por, Tc-Por, and Nb-Por, respectively, while (a'), (b'), and (c') represent corresponding energy trends. (a''), (b''), and (c'') in the right show the top and side views of the TM-Por (TM = Mo, Tc, Nb) structures before and after the AIMD simulation.