Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Electronic Supplementary Information

MBenes: emerging 2D materials as efficient electrocatalysts for nitrogen reduction reaction

Xiaowei Yang, Chanjuan Shang, Si Zhou*, Jijun Zhao

Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China

*Corresponding author. Tel: 86-0411-84706100 E-mail: sizhou@dlut.edu.cn (Si Zhou)

Table S1. Zero-point energy (ZPE) and entropic correction (*TS*) of H_2, N_2, and NH_3 gas molecules (T = 298.15 K) taken from the NIST-JANAF thermodynamics table.[1]

Molecule	ZPE (eV)	*TS* (eV)	ZPE − *TS* (eV)
H_2	0.27	0.44	−0.15
N_2	0.16	0.60	−0.44
NH_3	0.94	0.60	0.34

Table S2. Zero-point energy (ZPE, in eV) of all the reaction intermediates involved in NRR under the distal, alternating and enzymatic pathways for various MBenes.

ZPE	Distal pathway									
	FeB_2	RuB_2	OsB_2	V_3B_4	Nb_3B_4	Ta_3B_4	CrB	MnB	ZrB	HfB
*N≡N	0.23	0.23	0.23	0.20	0.19	0.19	0.21	0.21	0.19	0.19
*N−NH	0.48	0.48	0.45	0.43	0.43	0.46	0.45	0.47	0.44	0.45
*N−NH_2	0.82	0.83	0.84	0.80	0.80	0.80	0.81	0.79	0.79	0.78
*N−NH_3	1.15	1.16	1.16	1.14	1.16	1.16	1.11	1.12	1.10	1.15
*N	0.12	0.11	0.05	0.05	0.06	0.05	0.07	0.08	0.09	0.09
*NH	0.34	0.42	0.35	0.34	0.36	0.36	0.35	0.37	0.35	0.36
*NH_2	0.70	0.71	0.71	0.63	0.69	0.63	0.65	0.71	0.67	0.69
*NH_3	1.08	1.09	1.09	1.01	1.00	1.01	0.98	1.03	1.00	1.00

ZPE	Alternating pathway									
	FeB_2	RuB_2	OsB_2	V_3B_4	Nb_3B_4	Ta_3B_4	CrB	MnB	ZrB	HfB
*N≡N	0.23	0.23	0.23	0.20	0.19	0.19	0.21	0.21	0.19	0.19
*N−NH	0.48	0.48	0.45	0.43	0.43	0.46	0.45	0.47	0.44	0.45
*NH−NH	0.84	0.85	0.86	0.77	0.73	0.76	0.80	0.82	0.77	0.78
*NH−NH_2	1.16	1.16	1.17	1.11	1.12	1.11	1.12	1.13	1.10	1.14
*NH_2−NH_2	1.54	1.53	1.55	1.48	1.48	1.47	1.50	1.49	1.47	1.48
*NH_2−NH_3	1.80	1.79	1.80	1.71	1.63	1.71	1.72	1.74	1.67	1.69
*NH_2	0.70	0.71	0.69	0.69	0.70	0.70	0.70	0.71	0.68	0.69
*NH_3	1.08	1.09	1.09	1.01	1.00	1.01	0.98	1.03	1.00	1.00

ZPE	Enzymatic pathway									
	FeB_2	RuB_2	OsB_2	V_3B_4	Nb_3B_4	Ta_3B_4	CrB	MnB	ZrB	HfB
*N≡N	0.21	0.25	0.21	0.19	0.19	0.20	0.21	0.21	0.19	0.19
*N−NH	0.57	0.57	0.57	0.49	0.49	0.50	0.50	0.50	0.46	0.48

*NH−NH	0.88	0.87	0.86	0.80	0.81	0.82	0.82	0.84	0.81	0.78
*NH−NH_2	1.22	1.22	1.23	1.13	1.14	1.15	1.14	1.14	1.13	1.14
*NH_2−NH_2	1.40	1.41	1.42	1.49	1.48	1.49	1.50	1.51	1.47	1.48
*NH_2−NH_3	1.79	1.79	1.80	1.71	1.70	1.71	1.72	1.70	1.67	1.69
*NH_2	0.70	0.71	0.71	0.69	0.69	0.71	0.70	0.71	0.68	0.69
*NH_3	1.08	1.09	1.09	1.01	1.00	1.01	0.98	1.03	1.00	1.00

Table S3. Entropic contribution *TS* (eV, with $T = 298.15$ K) to Gibbs free energy of all the reaction intermediates involved in NRR under the distal, alternating and enzymatic pathways for various MBenes.

TS	Distal pathway									
	FeB_2	RuB_2	OsB_2	V_3B_4	Nb_3B_4	Ta_3B_4	CrB	MnB	ZrB	HfB
*N≡N	0.09	0.07	0.07	0.08	0.05	0.06	0.07	0.08	0.16	0.10
*N−NH	0.20	0.11	0.11	0.04	0.05	0.12	0.03	0.05	0.13	0.13
*N−NH_2	0.16	0.18	0.13	0.14	0.13	0.15	0.12	0.14	0.17	0.15
*N−NH_3	0.12	0.16	0.15	0.11	0.16	0.19	0.16	0.19	0.18	0.24
*N	0.02	0.03	0.00	0.00	0.05	0.00	0.09	0.04	0.03	0.03
*NH	0.10	0.04	0.09	0.01	0.10	0.12	0.11	0.05	0.06	0.06
*NH_2	0.11	0.09	0.09	0.05	0.08	0.14	0.07	0.08	0.09	0.08
*NH_3	0.11	0.11	0.10	0.16	0.12	0.17	0.05	0.10	0.18	0.19

TS	Alternating pathway									
	FeB_2	RuB_2	OsB_2	V_3B_4	Nb_3B_4	Ta_3B_4	CrB	MnB	ZrB	HfB
*N≡N	0.09	0.07	0.07	0.08	0.05	0.06	0.07	0.08	0.16	0.10
*N−NH	0.20	0.11	0.11	0.04	0.05	0.12	0.03	0.05	0.13	0.13
*NH−NH	0.13	0.16	0.14	0.13	0.16	0.18	0.13	0.13	0.18	0.11
*NH−NH_2	0.13	0.12	0.16	0.10	0.18	0.16	0.15	0.14	0.17	0.09
*NH_2−NH_2	0.14	0.19	0.17	0.18	0.16	0.16	0.16	0.16	0.18	0.17
*NH_2−NH_3	0.06	0.10	0.06	0.10	0.12	0.11	0.13	0.11	0.11	0.11
*NH_2	0.06	0.04	0.07	0.04	0.03	0.03	0.03	0.03	0.04	0.03
*NH_3	0.07	0.06	0.05	0.16	0.12	0.13	0.05	0.07	0.18	0.19

TS	Enzymatic pathway									
	FeB_2	RuB_2	OsB_2	V_3B_4	Nb_3B_4	Ta_3B_4	CrB	MnB	ZrB	HfB
*N≡N	0.08	0.06	0.08	0.13	0.11	0.10	0.04	0.11	0.11	0.12

*N−NH	0.07	0.07	0.07	0.12	0.13	0.11	0.11	0.11	0.09	0.13
*NH−NH	0.09	0.09	0.10	0.14	0.12	0.12	0.11	0.11	0.13	0.16
*NH−NH_2	0.12	0.10	0.10	0.18	0.16	0.15	0.16	0.17	0.13	0.18
*NH_2−NH_2	0.20	0.18	0.18	0.18	0.19	0.14	0.17	0.15	0.19	0.16
*NH_2−NH_3	0.09	0.07	0.06	0.10	0.12	0.12	0.12	0.16	0.11	0.11
*NH_2	0.05	0.04	0.04	0.04	0.03	0.03	0.03	0.04	0.04	0.03
*NH_3	0.06	0.05	0.06	0.16	0.12	0.17	0.05	0.08	0.18	0.19

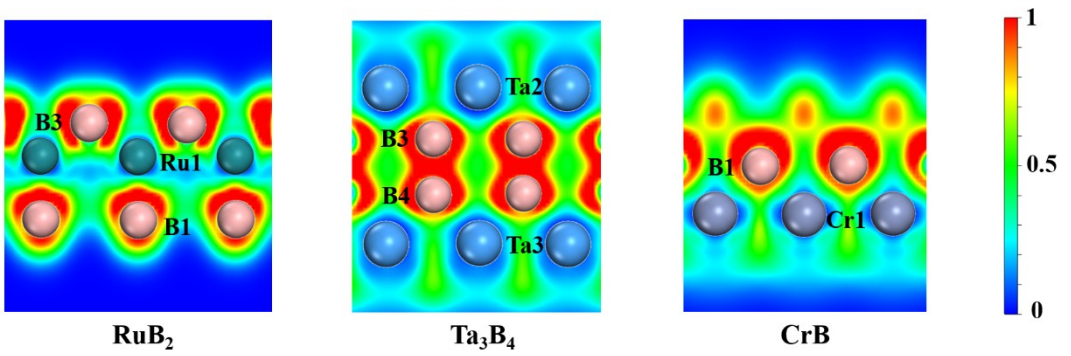

Figure S1. Electron localization function of RuB_2, Ta_3B_4 and CrB from side views. The red (blue) color shows maximum (minimum) of electron localization. The positions of atoms are also given for reference.

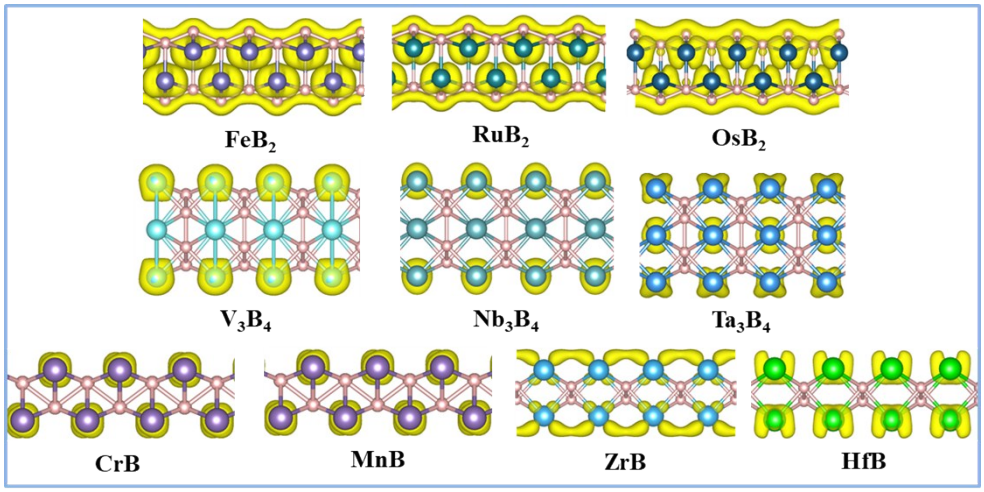

Figure S2. Band-decomposed charge density of various MBenes for the energy bands in the vicinity of the Fermi level (±0.5 eV), with an isosurface value of 0.01 e/Å^3.

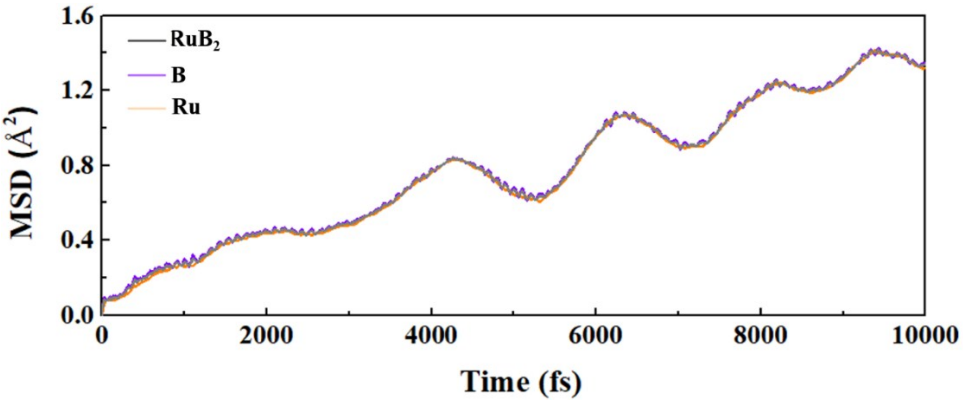

Figure S3. Variations of mean square displacement (MSD) with AIMD simulation time for RuB_2 in water environment. The MSD is defined as: $MSD = \frac{1}{N}\sum_{i=1}^{N}|r_i(t) - r_i(0)|^2$, where $r_i(t)$ is the atom position of atom i at time t, and N is the total number of atoms.[2]

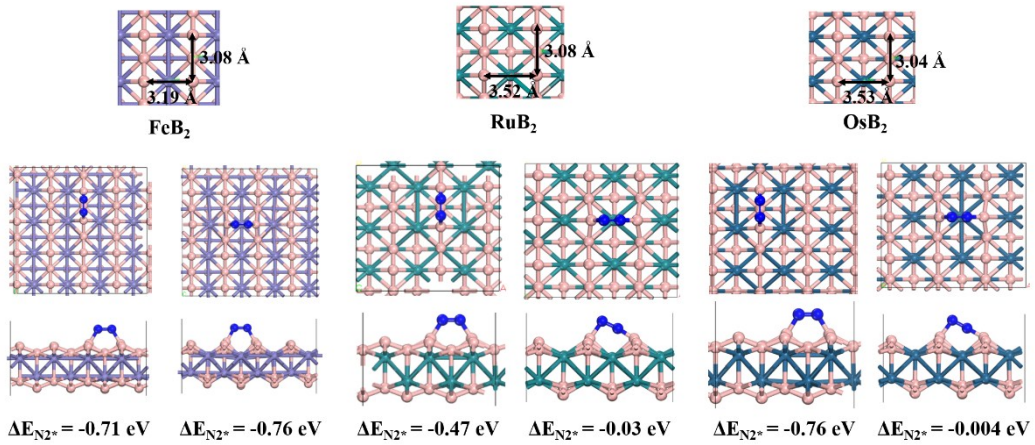

Figure S4. Structures and adsorption energies of N_2 adsorbed in the side-on configuration on the B-exposed surfaces of FeB_2, RuB_2 and OsB_2, along the armchair (left panel) and zigzag (right panel) directions, respectively.

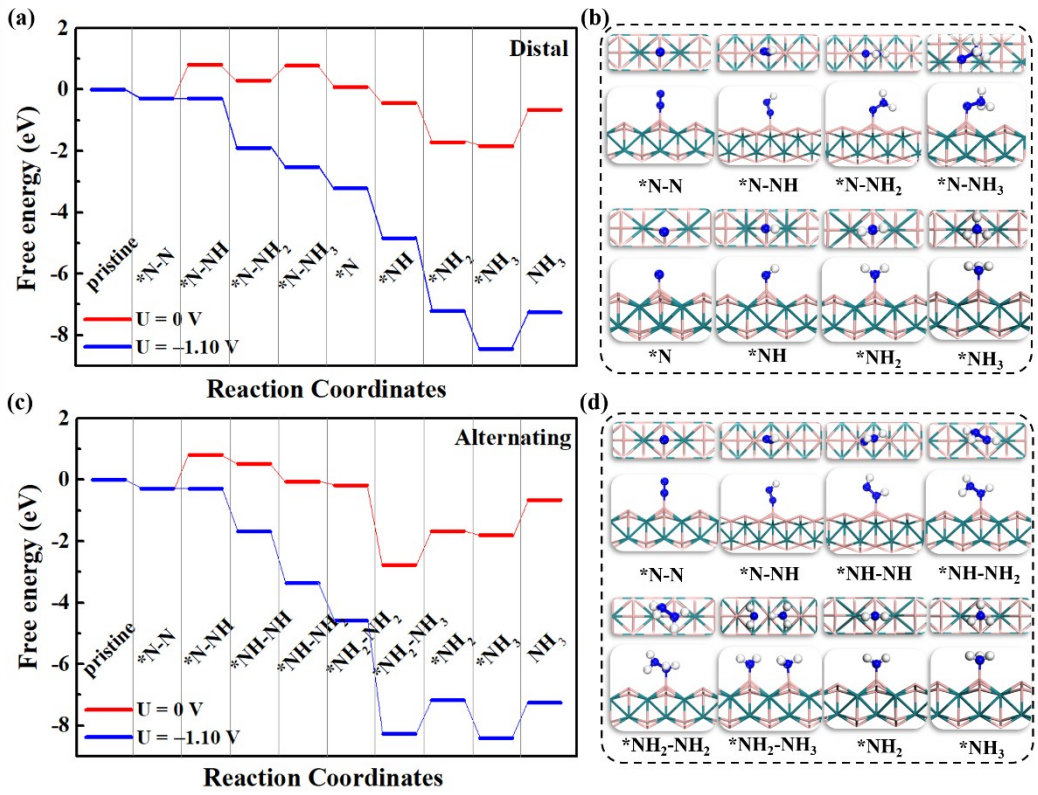

Figure S5. Free energy diagrams of N_2 reduction reaction on RuB_2 via the distal (a) and alternating (c) mechanisms at different applied potentials. The corresponding structures (top view and side view) of the reaction intermediates are displayed in (b) and (d), respectively. The H, B, N and Ru atoms are shown in white, pink, blue and turquoise colors, respectively.

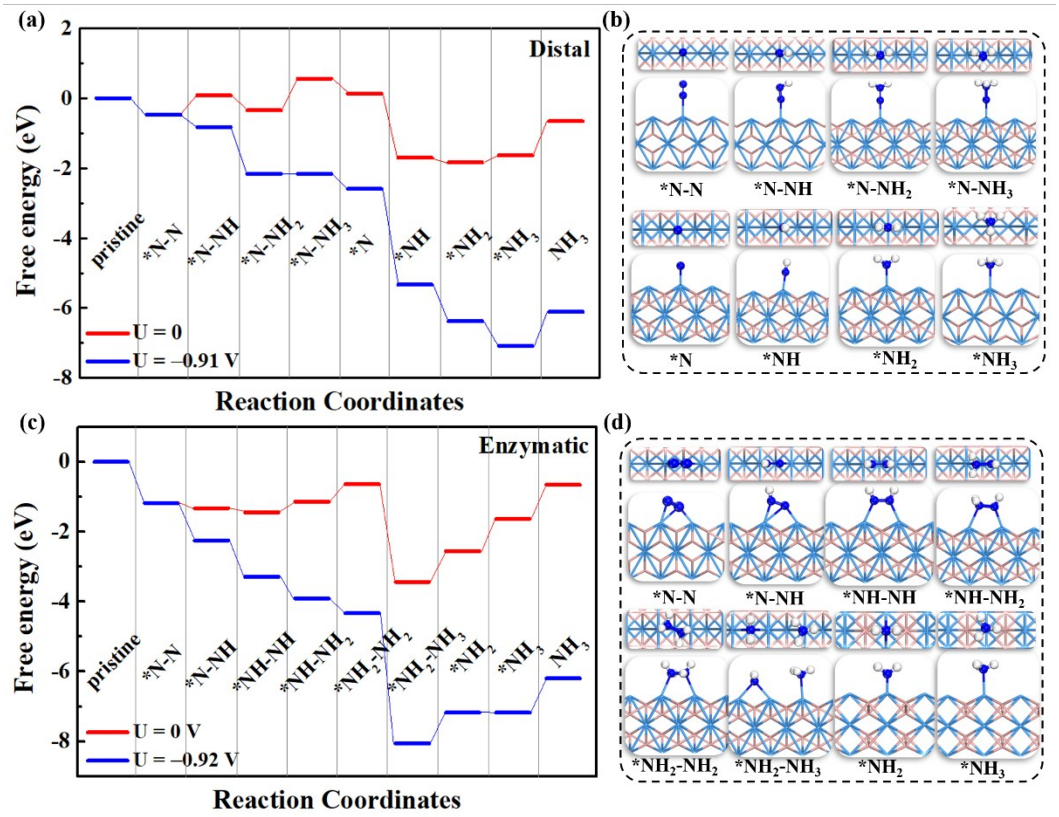

Figure S6. Free energy diagrams of N_2 reduction reaction on Ta_3B_4 via the distal (a) and enzymatic (c) mechanisms at different applied potentials. The corresponding structures (top view and side view) of the reaction intermediates are displayed in (b) and (d), respectively. The H, B, N and Ta atoms are shown in white, pink, blue and light blue colors, respectively.

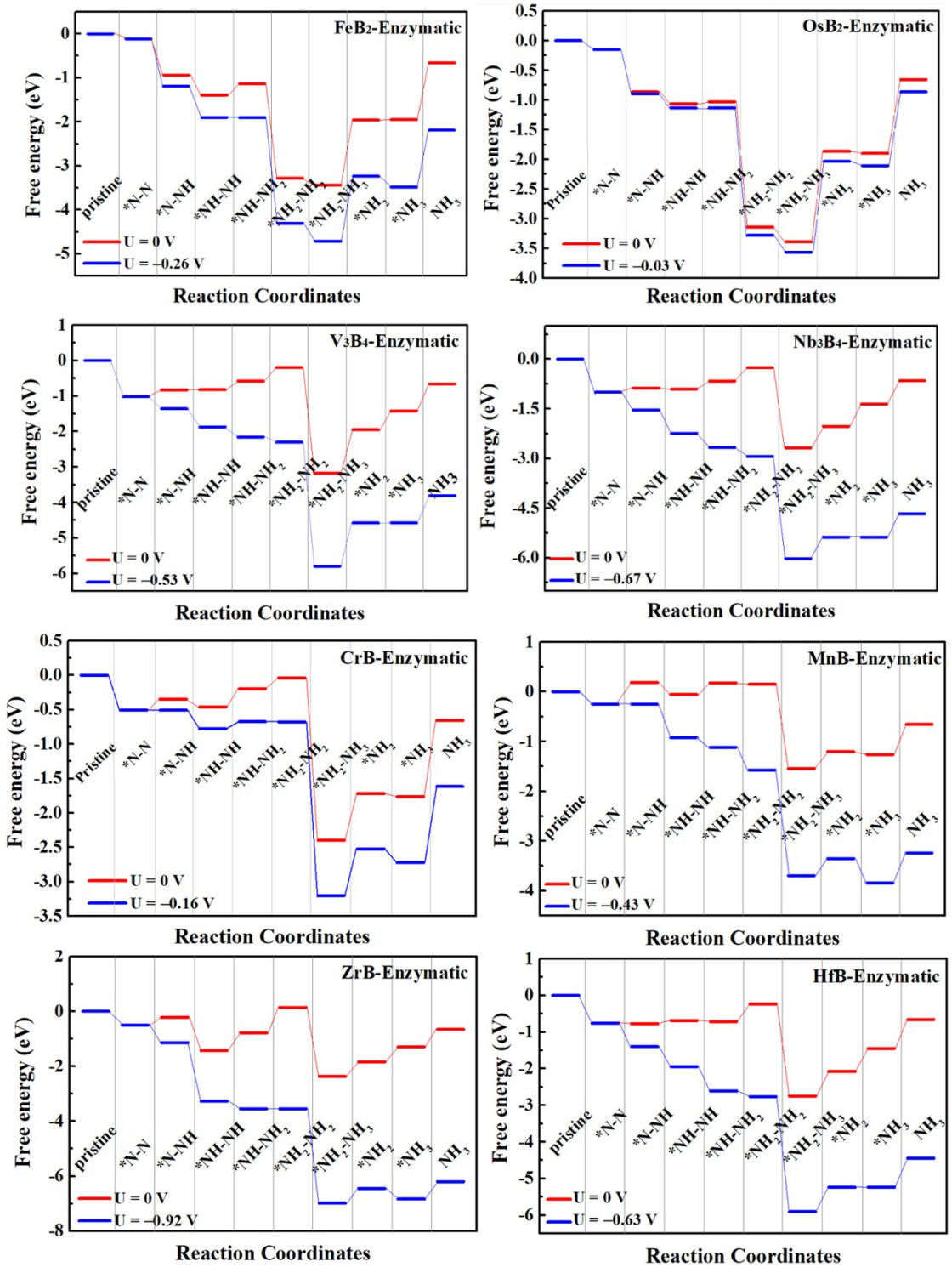

Figure S7. Free energy diagrams of the most efficient pathway of NRR for various MBenes. The finite potential (blue line), at which all the elementary steps become downhill in free energy, is given for each system.

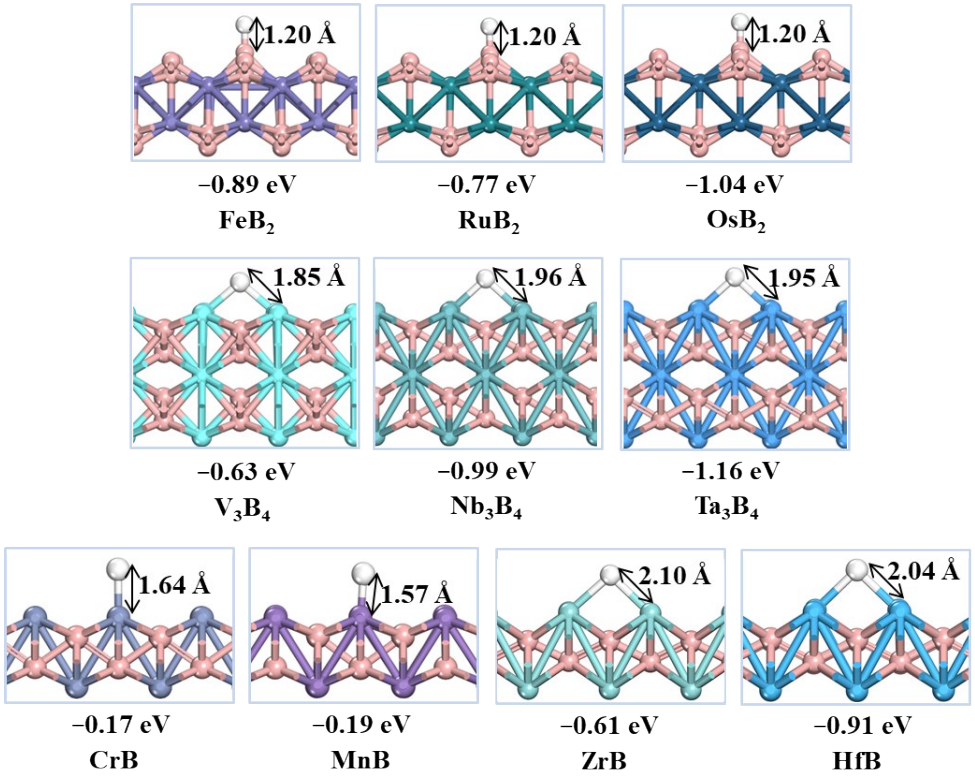

Figure S8. Structures of H* species adsorbed on various MBenes. The bond length between the active-site atom and H atom, and H* adsorption energy are given for each system.

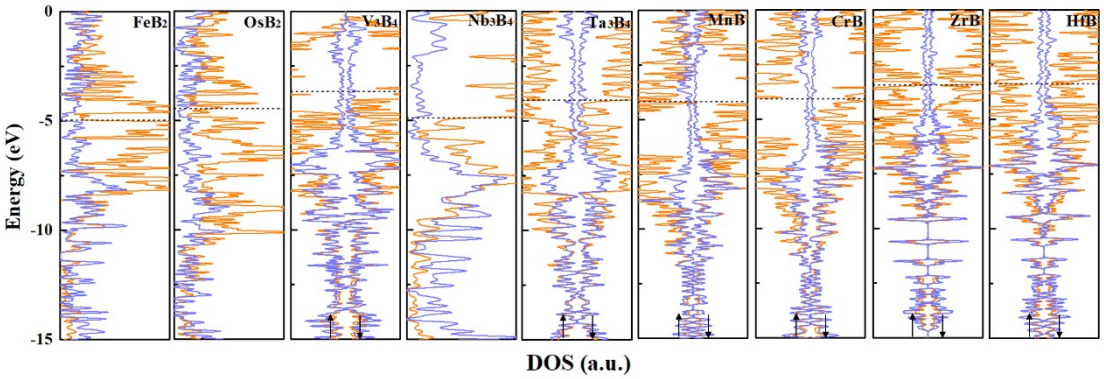

Figure S9. Density of states (DOS) of various MBenes. The color indicates the contribution of DOS from B and metal atoms. The energy is relative to vacuum, and the dashed lines indicate the Fermi level.

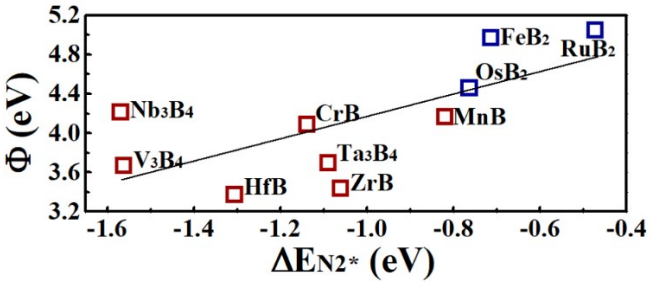

Figure S10. Work function vs. N_2 adsorption energy for MBenes.

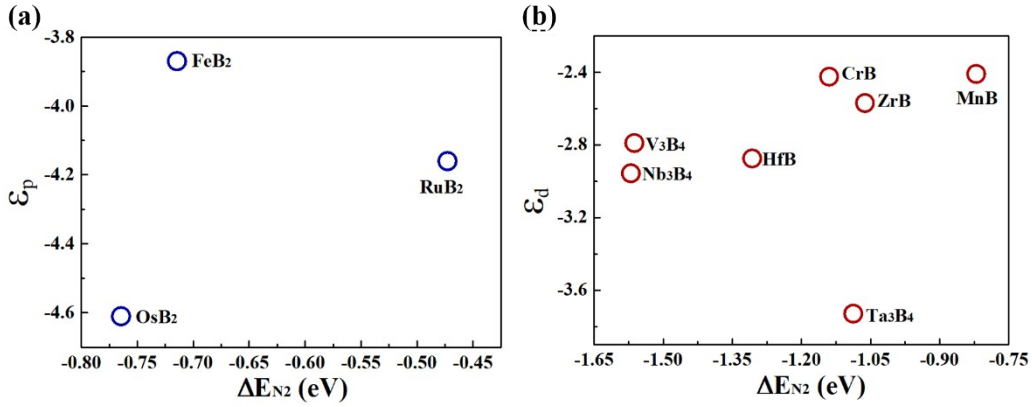

Figure S11. Correlation between the (a) *p* band center (ε_p), or (b) *d* band center (ε_d) and ΔE_{N2*} for various MBenes with (a) boron exposed surface or (b) metal exposed surface.

References

1 M. W. Chase, *NIST-JANAF Thermochemical Tables*, American Chemical Society, New York, **1998**.

2 V. Wang, N. Xu, J. Liu, G. Tang and W. Geng, *arXiv preprint arXiv:* 1908.08269.[online 2019]