Supplementary Material

Pt_2 dimer anchored vertically in defective BN monolayer as an efficient catalyst for N_2 reduction: A DFT study

Linke Yu and Fengyu Li *

Physical School of Science and Technology, Inner Mongolia University, Hohhot 010021, China

* Correspondence: fengyuli@imu.edu.cn

Table S1. The distance between metal atoms (D, in Å), the binding energies (E_b) of metal atoms in 10 species, the cohesive energy (E_{coh}) of bulk M (in eV), and the $E_b - E_{coh}$ (in eV).

system	D	E_b	E_{coh}	$E_b - E_{coh}$
Co_2⊥vb-BN	2.40	−5.49	−5.04	−0.45
Ni_2⊥vb-BN	2.37	−5.62	−5.04	−0.58
Rh_2⊥vb-BN	2.78	−5.60	−5.93	0.33
Ir_2⊥vb-BN	2.85	−5.80	−7.59	1.79
Pt_2⊥vb-BN	2.92	−4.53	−5.52	0.99
Co_2⊥vn-BN	2.30	−4.30	−5.04	0.74
Ni_2⊥vn-BN	2.48	−5.11	−5.04	−0.07
Rh_2⊥vn-BN	2.76	−5.63	−5.93	0.30
Ir_2⊥vn-BN	3.24	−6.04	−7.59	1.55
Pt_2⊥vn-BN	2.99	−6.31	−5.52	−0.79

Table S2. The Bader charge (*Q*, in |*e*|) on the M atoms, the magnetic order (*MO*) and the magnetic moment on M atoms (*M*, in μ_B) of the stable catalyst structures.

system	*Q* (M/M′)	*MO*	*M* (M_1/M_2)
Co_2⊥vb-BN	+0.84/+0.84	AFM	1.97/−1.14
Ni_2⊥vb-BN	+0.76/+0.76	FM	0.40/0.40
Rh_2⊥vb-BN	+0.50/+0.50	FM	0.36/0.36
Pt_2⊥vb-BN	+0.44/+0.44	FM	0.26/0.26
Co_2⊥vn-BN	+0.15/+0.15	FM	0.61/0.61
Ni_2⊥vn-BN	−0.05/−0.05	NM	0.00/0.00
Rh_2⊥vn-BN	−0.25/−0.25	FM	0.45/0.45
Pt_2⊥vn-BN	−0.48/−0.48	FM	0.14/0.14

Table S3. The adsorption energy (E_{ad}, in eV), the charge transferred from the stable DACs to the adsorbed N_2 (ΔQ, in |e|), the shortest distance between the N_2 and M (*d*, in Å), the distance between the N atom and N atom in N_2 (d_{N-N}, in Å) of the N_2 molecule adsorbed on the stable catalyst structures.

system	E_{ad}	ΔQ	*d*	d_{N-N}
Co_2⊥vb-BN	−1.26	−0.43	1.92/2.00	1.17
Rh_2⊥vb-BN	−0.89	−0.35	2.07/2.23	1.16
Pt_2⊥vb-BN	−1.11	−0.35	2.11/2.11	1.17
Rh_2⊥vn-BN	−1.26	−0.30	2.13/2.22	1.15

Table S4. The $E_{zpe} - TS$ of the free gas molecules.

	$E_{zpe} - TS\ (eV)$
NH_3	0.42
H_2O (l)	0.00
H_2	−0.05
N_2	−0.35

Table S5. Free energy correction ($E_{zpe} - TS$) (in eV) for each adsorbed species in the NRR reaction path on Co_2⊥vb-BN, Rh_2⊥vb-BN, Pt_2⊥vb-BN and Rh_2⊥vn-BN.

	$*N_2$	*NNH	*NHNH	$*NHNH_2$	$*NH_2NH_2$	$*NH_2…NH_3$	$*NH_3$
Co_2⊥vb-BN	0.09	0.36	0.69	1.04	1.33	1.42	0.96
	$*N_2$	*NNH	*NHNH	$*NHNH_2$	$*NH_2NH_2$	$*NH_2…NH_3$	$*NH_3$
Rh_2⊥vb-BN	0.09	0.35	0.72	1.07	1.34	1.47	0.94
	$*N_2$	*NNH	*NHNH	$*NHNH_2$	$*NH_2NH_2$	$*NH_2…NH_3$	$*NH_3$
Pt_2⊥vb-BN	0.09	0.41	0.72	1.10	1.42	1.48	0.97
	$*N_2$	*NNH	*NHNH	$*NHNH_2$	$*NH_2NH_2$	$*NH_2…NH_3$	$*NH_3$
Rh_2⊥vn-BN	0.09	0.40	0.69	1.09	1.37	1.42	0.96

Table S6. The potential-determining steps, and limiting potentials (U_L) for the NRR on the stable catalyst structures.

System	Potential-determining step	U_L (in V)
Co_2⊥vb-BN	*$NHNH_2$ → *NH_2NH_2	−0.69
Rh_2⊥vb-BN	*NN → *NNH	−0.50
Pt_2⊥vb-BN	*NN → *NNH	−0.06
Rh_2⊥vn-BN	*NN → *NNH	−0.49
Rh@vb-BN	*NN → *NNH	−1.25
Pt@vb-BN	*NN → *NNH	−0.35
Rh@vn-BN	*NN → *NNH	−1.48

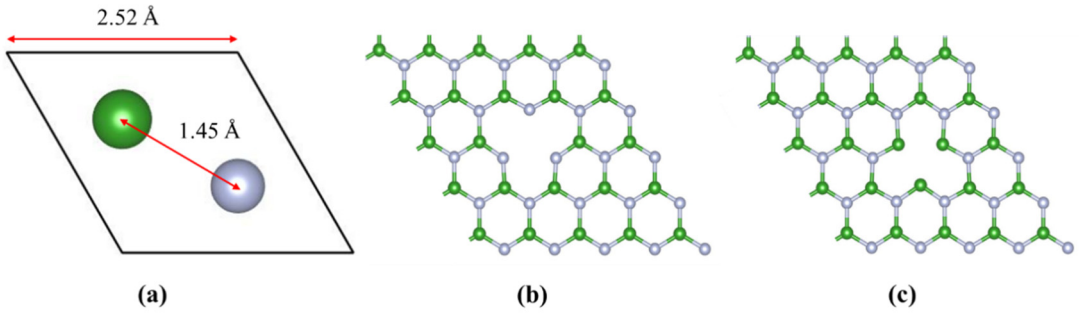

Figure S1. Structural diagram of the single-cell structure of (a) *h*-BN, (b) vb-BN and (c) vn-BN model. Colour scheme: B, green and N, silver.

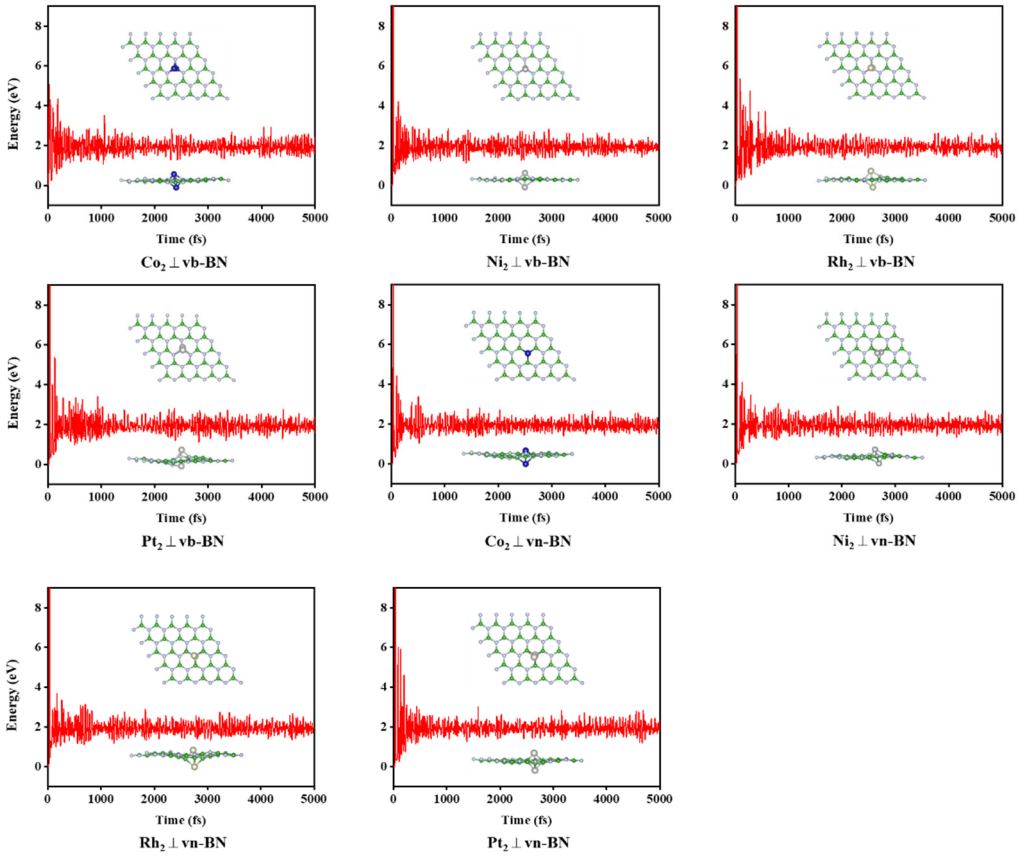

Figure S2. The energy evolution of 8 catalysts during 5 ps FPMD simulations at 300 K, the insets are the final annealed structures.

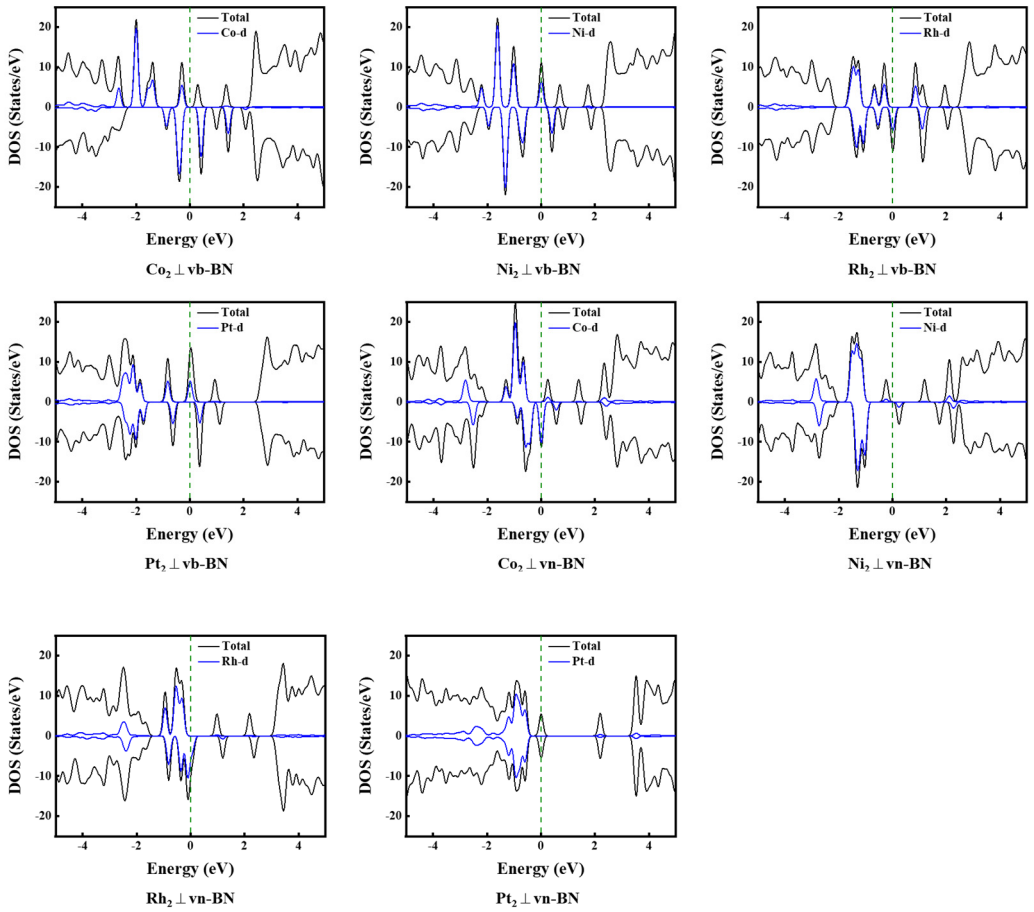

Figure S3. Density of states (DOS) of 8 DACs. The green dashed lines indicate the Fermi energy level.

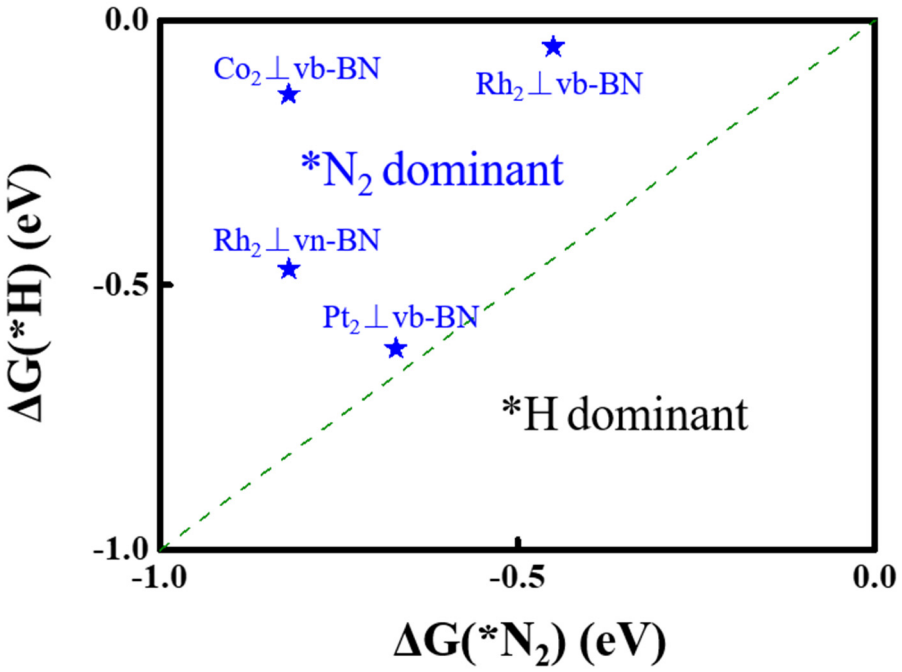

Figure S4. Calculated ΔG(*N_2) and ΔG(*H) on 4 DACs.

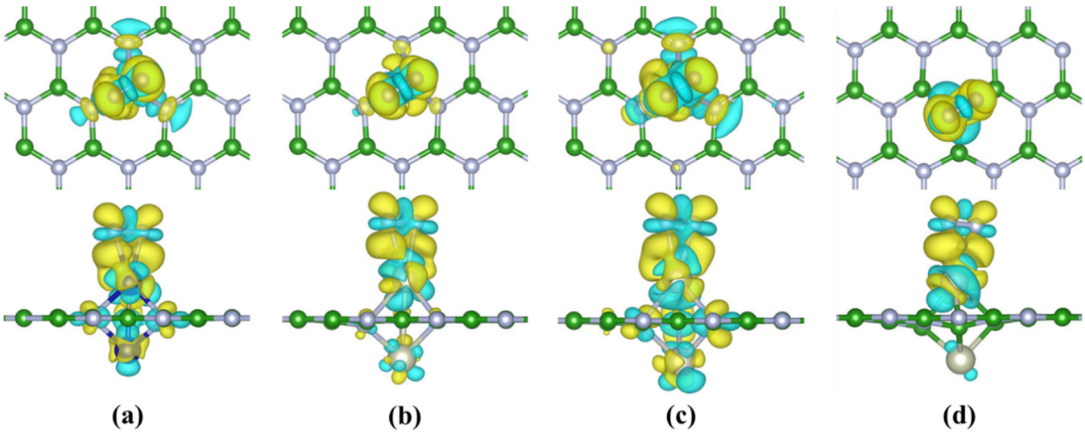

Figure S5. Differential charge diagram of N_2-adsorbed on (a) Co_2 ⊥ vb-BN, (b) Rh_2 ⊥ vb-BN, (c) Pt_2 ⊥ vb-BN and (d) Rh_2 ⊥ vn-BN. Yellow is positively charged, blue is negatively charged. The isosurface value was set as 0.003 e/Å^{-3}.

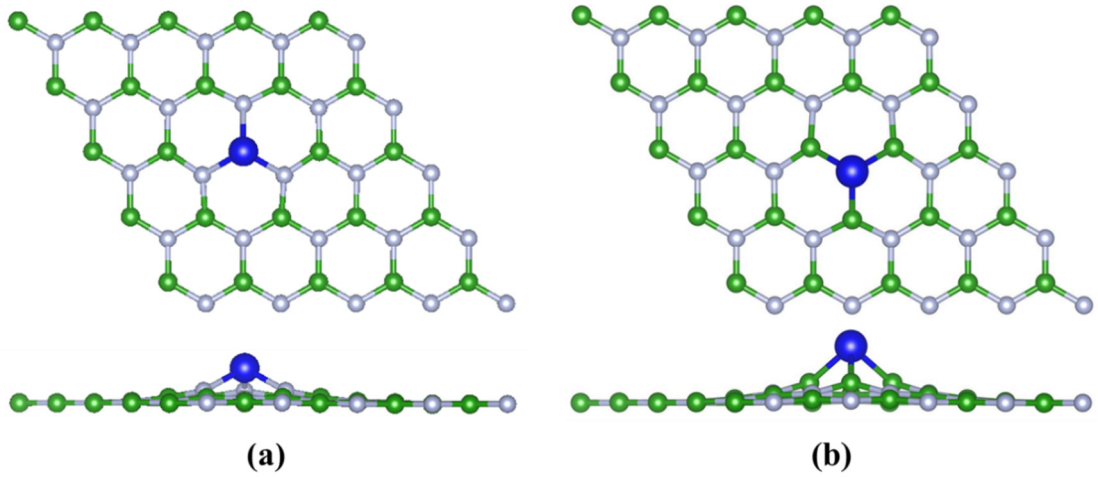

Figure S6. Structural diagram of the (a) M@vb-BN and (b) M@vn-BN model. Colour scheme: B, green; N, silver; M, blue.

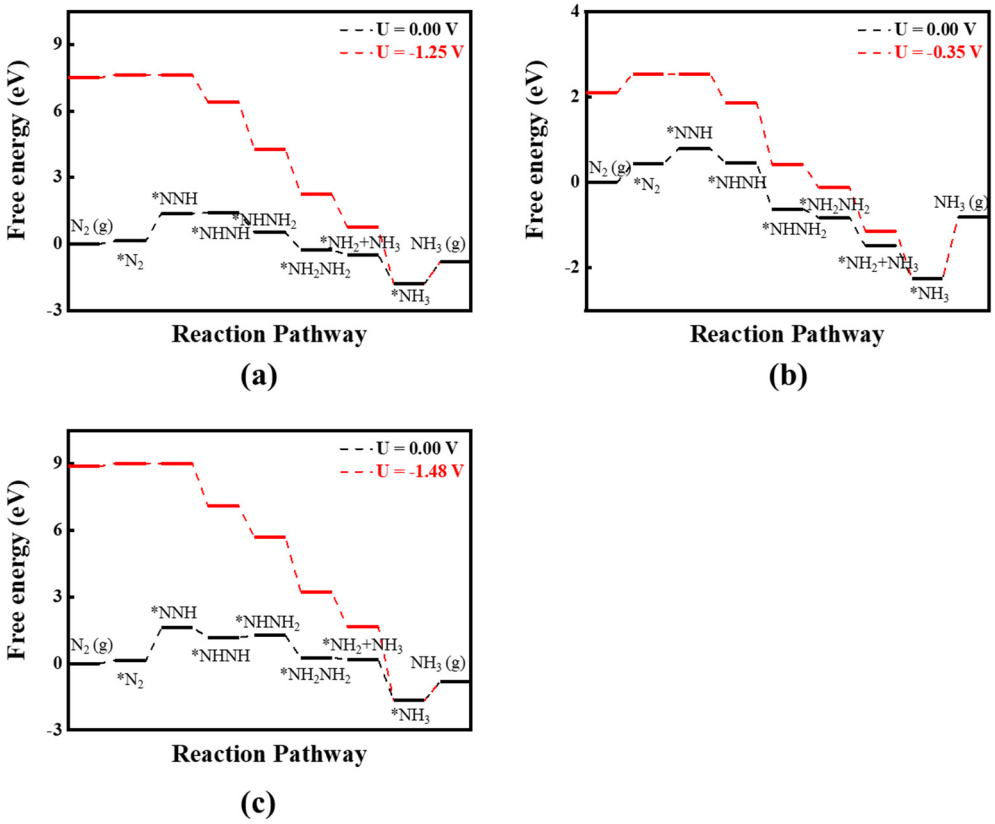

Figure S7. Free energy diagram of NRR on (a) Rh@vb-BN, (b) Pt@vb-BN and (c) Rh@vn-BN catalyst at zero and applied potential (limiting potential) through the enzymatic mechanism.

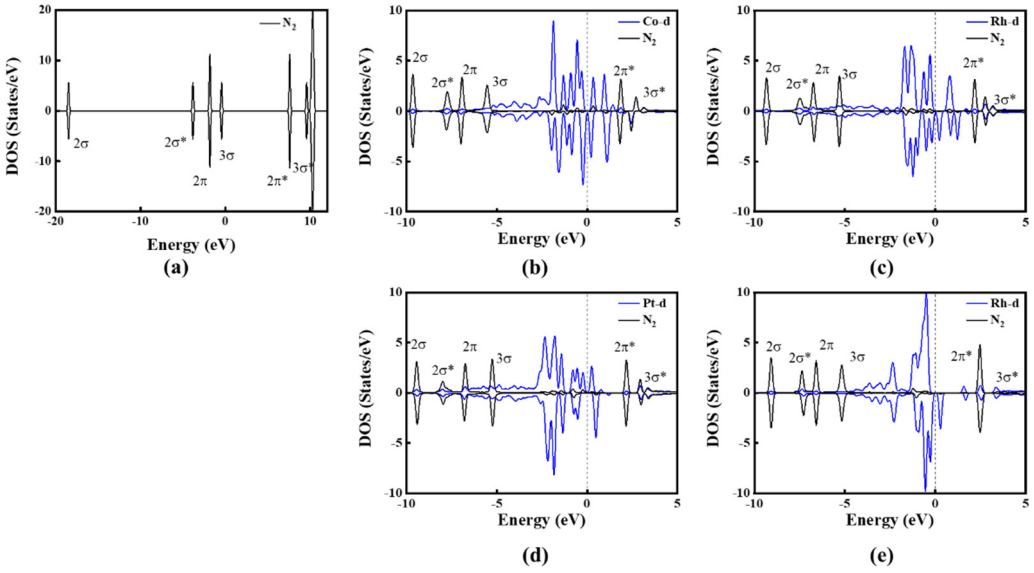

Figure S8. (a) Molecular orbitals of free N_2. The projected density of states (PDOS) of (b) $Co_2 \perp$ vb-BN, (c) $Rh_2 \perp$ vb-BN, (d) $Pt_2 \perp$ vb-BN and (e) $Rh_2 \perp$ vn-BN.

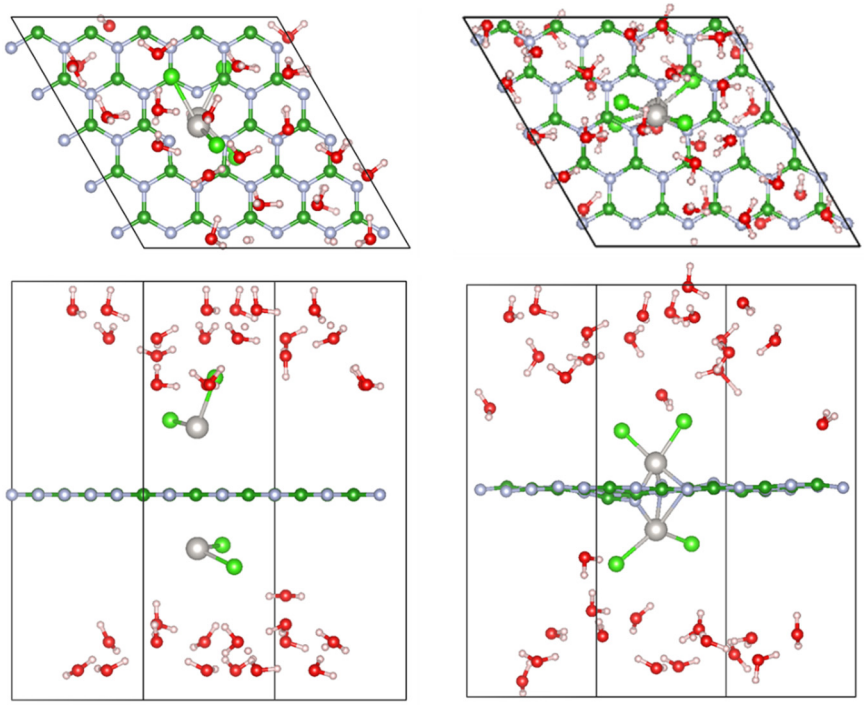

Figure S9. Top and side views of the snapshots of atomic configurations of FAMD simulations for the synthetic process of $Pt_2 \perp$ vb-BN (a,b). The model consists of a 5×5×1 supercell of BN with a boron vacancy, two $PtCl_2$ molecules and 34 water molecules. Pt, N, B, H, O and Cl are indicated by gray, silver, dark green, white, red and light green, respectively.