Supporting Information for

Screening Efficient Pt-based Dual-Metal Atomic-Level Catalysts for Oxygen Reduction Reaction

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Table S1. The crystal structure, lattice parameters (Å), space groups, point groups, magnetic moments (with order of Pt, TM and total/μ_B) and Pt-M bond length of optimized crystal structures of 30 PtM-N_6@Gra catalysts. "/" represents that the energy of the corresponding catalyst has not been obtained due to the fact that the structure of target catalyst cannot be obtained after structural relaxation.

Table S2. The crystal structure, lattice parameters (Å), space groups, point groups, magnetic moments (with order of Pt, TM and total/μ_B) and Pt-M bond length of optimized crystal structures of 30 PtM-C_6@Gra catalysts. "/" represents that the energy of the corresponding catalyst has not been obtained due to the fact that the structure of target catalyst cannot be obtained after structural relaxation.

Table S3. The crystal structure, lattice parameters (Å), space groups, point groups, magnetic moments (with order of Pt, TM and total/μ_B) and Pt-M bond length of optimized crystal structures of 30 PtM-B_6@Gra catalysts. "/" represents that the energy of the corresponding catalyst has not been obtained due to the fact that the structure of target catalyst cannot be obtained after structural relaxation.

Figure S1. The results from computer aided screening for PtM-C_6@Gra (a1-e1) and PtM-B_6@Gra (a2-e2). The red dashed lines refer to 0.00 eV. The blue and magenta dashed lines refer to 0.50 and 0.00 eV, respectively. In Figure e2, f2, the blue and magenta dashed lines refer to 1.00 and 0.25 eV, respectively.

Figure S2. Schematic illustration of different hydrogenation sites for the second protonation $\Delta G_{*O_2 \rightarrow *OOH}$ of PtM-L_6@Gra catalysts, named PtM.1-L_6@Gra and PtM.2-L_6@Gra, respectively.

Table S4. The Gibbs free energy profiles and the relevant intermediate species of different reaction pathways for 16 selected catalysts.

Table S5. Summary of the most favorable pathways of PtM-L_6@Gra catalysts under the acidic condition (pH=0), Gibbs free energy of the corresponding intermediates (eV), overpotentials (V), and potential-determining step (PDS) are listed.

Table S6. Summary of the most favorable pathways of PtM-L_6@Gra catalysts under the basic condition (pH=13), Gibbs free energy of the corresponding intermediates (eV), overpotentials (V), and PDS are listed.

Table S7. Thermal corrections (eV) of small molecule (H_2O, H_2) and the reaction intermediates (O_xH_y) along the most favorable pathways on PtM-L_6@Gra. Thermal corrections of the small molecules (H_2O, H_2) can be obtained from the NIST database.

Figure S3. Calculated PDOS of various intermediates (*OOH, *O, *OH) adsorption on the active site of (a1-a3) PtFe-N_6@Gra, (b1-b3) PtCo-N_6@Gra, (c1-c3) PtNi-N_6@Gra, (d1-d3) PtCo-C_6@Gra, (e1-e3) PtNi-C_6@Gra, (f1-f3) PtZn-C_6@Gra.

Table S8. The magnetic moment before and after O_2 adsorption. (*) and (*O_2) stand for before and after O_2 adsorption on the selected catalysts, respectively. The M represents the transition metal atom, the L_6 represents the six coordination atoms connected to the Pt and M atom, and the FV-Gra represents the rest part except the Pt, M and L_6 atoms. The positive and negative charge values represent gain and loss of electrons, respectively.

Figure S4. Schematic diagram of (a) the definition of the six coordination atoms connected to Pt and M (L1-L6), and absorbed O_2. O1 represents that O is close to the metal, O2 represents that O is far away from the metal, respectively. The Bader charge diagrams of each part (i.e., L1-L6, Pt, M, O1, O2) of the 21 catalysts (b) before and (c) after O_2 adsorption.

Table S9. Bader charge of each part of 21 catalysts before adsorbing O_2, the labels of different atoms following Figure S4a.

Table S10. Bader charge of each part of 21 catalysts after adsorbing O_2, the labels of different atoms following Figure S4a.

Figure S5. Schematic diagram of the definition of the three moieties for the intermediate species. Moiety 1, 2 and 3 represent the PtM-L_6@Gra excluding the PtM-L_6 part (the PtM-L_6 part represent the Pt, M atoms and six coordinated atoms) (moiety 1), the PtM-L_6 part (moiety 2), and the adsorbed O_xH_y intermediate species (moiety 3), respectively.

Table S11. Charge variation of the three moieties (PtM-L_6, O_xH_y and FV-Gra) along the most favorable reaction pathway on the 9 selected catalysts. The definition of moieties following Figure S5. The positive and negative charge values represent gain and loss of electrons, respectively.

Table S12. The d_{*}(Pt-M), d_{*O_2}(Pt-M), d_{*OOH}(Pt-M), d_{*O}(Pt-M), d_{*OH}(Pt-M) and avg[d_a(Pt-M)] of 21 catalysts were listed.

Figure S6. The diagrams of Pt-M bond length values of 21 catalysts substrates and various intermediates. (a) d_{*}(Pt-M), (b) d_{*O_2}(Pt-M), (c) d_{*OOH}(Pt-M), (d) d_{*O}(Pt-M), (e) d_{*OH}(Pt-M), and (f) avg[d_a(Pt-M)].

Figure S7. There is no clear structure-activity relationship between various descriptors and the limiting potential (U_L) after many tentative trial and error. $\Delta G_{*\rightarrow *O_2}$ and $\Delta G_{*O\rightarrow *OH}$ represent the Gibbs free energy change of O_2 adsorption, the second protonation step under basic condition, respectively. The d_{*}(Pt-M), d_{*O}(Pt-M), d_{*OH}(Pt-M) represent the distance between the active center metals Pt and M of the free substrate, substrate adsorbed O intermediate, substrate adsorbed OH intermediate, respectively. avg[d_a(Pt-M)] represents the average value of the distance of the active center metals Pt and M of the substrates and intermediates.

Table S13. The O-O bond length (Å) of free O_2 (g), *O_2 and *OOH on the 16 selected PtM-L_6@Gra catalysts.

Table S14. The calculated cohesive energies (E_c, eV/atom) of PtM bulk and the binding energies (E_b, eV/atom) of Pt and M atoms embedded in N_6@Gra substrate, and the binding energy along with the cohesive energy (E_b+E_c). "/" represents that the energy of the corresponding catalyst has not been obtained.

Table S15. The calculated cohesive energies (E_c, eV/atom) of PtM bulk and the binding energies (E_b, eV/atom) of Pt and M atoms embedded in C_6@Gra substrate, and the binding energy along with the

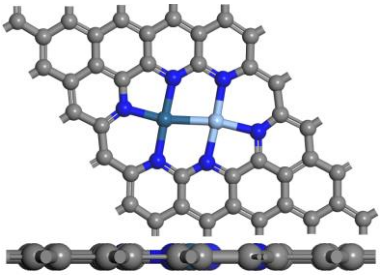
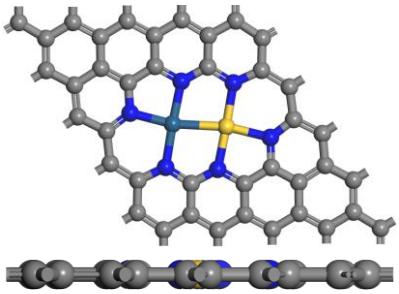
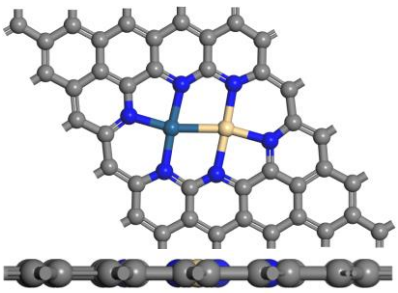
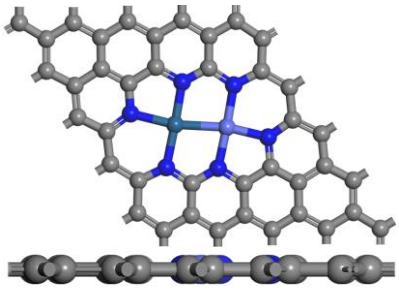
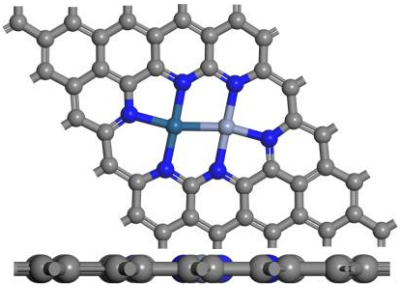
cohesive energy (E_b+E_c). "/" represents that the energy of the corresponding catalyst has not been obtained.

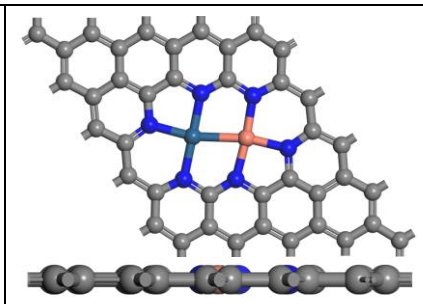
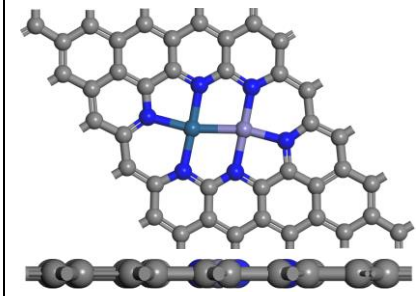
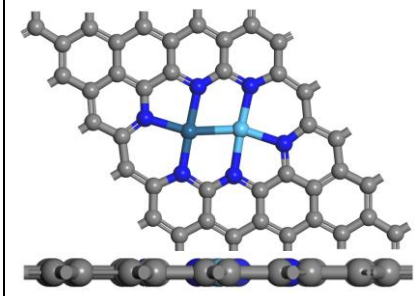
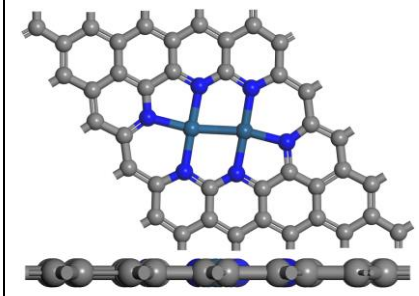
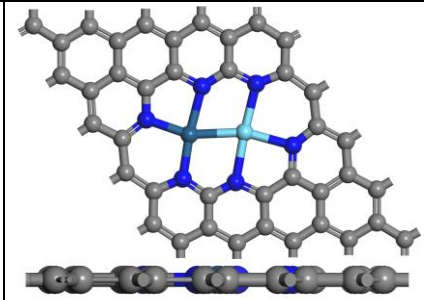
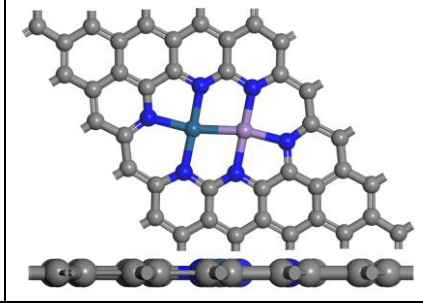
Table S16. The calculated cohesive energies (E_c, eV/atom) of PtM bulk and the binding energies (E_b, eV/atom) of Pt and M atoms embedded in B_6@Gra substrate, and the binding energy along with the cohesive energy (E_b+E_c). "/" represents that the energy of the corresponding catalyst has not been obtained.

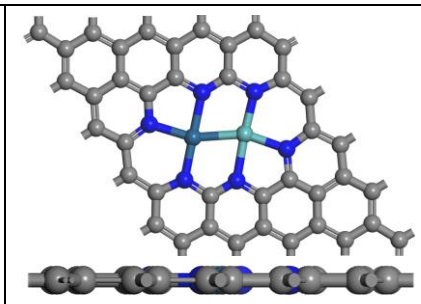
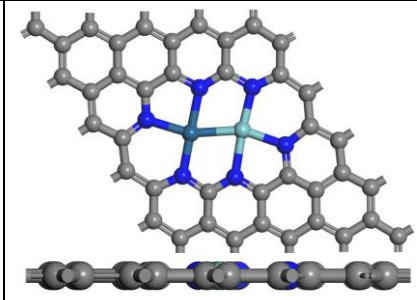
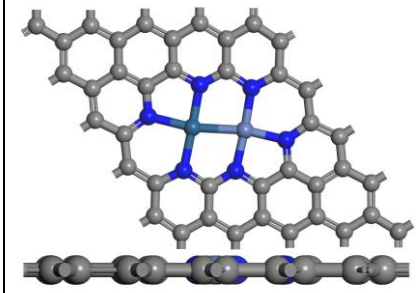
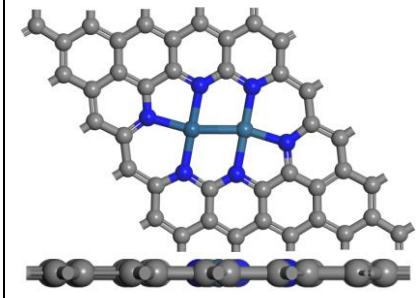
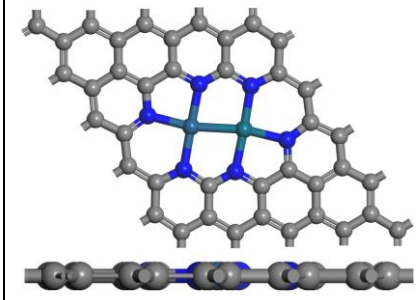
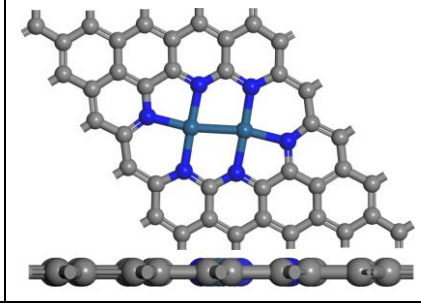
Table S17. The calculated binding energy of the Pt and M atoms embedded in PtM-L_6@Gra (E_b, eV), standard dissolution potentials (U_{diss}^{Θ}, pH = 0), number of electrons (N_e) involved in the dissolution for the pure metals, and computed dissolution potentials (U_{diss}^{Pt}, U_{diss}^{M}) for DACs. The minimum dissolution potential (U_{diss}^{min}) is taken to represent the dissolution potential of the whole system.

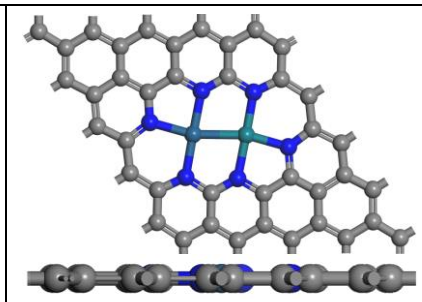
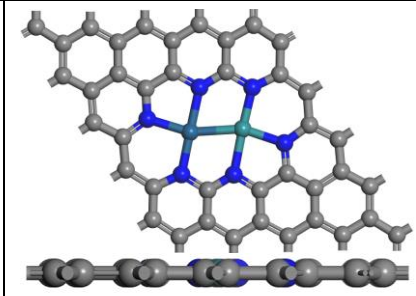
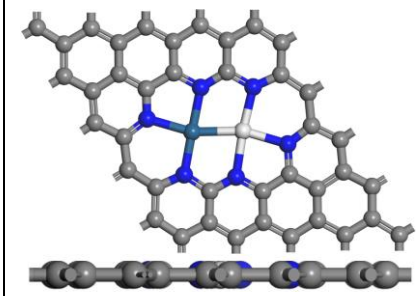
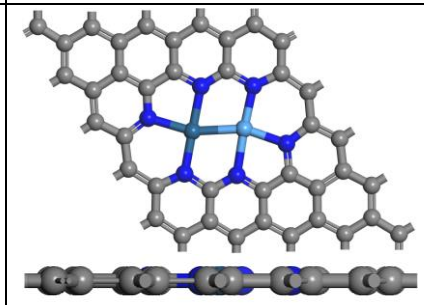
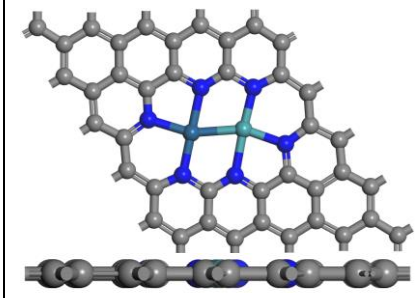
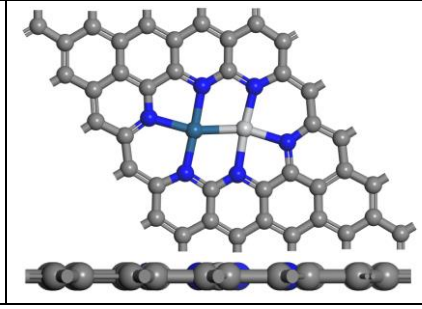
Figure S8. The variations of total energy and temperature during AIMD simulations of (a) PtCo-C_6@Gra, (b) PtNi-C_6@Gra, (c) PtZn-C_6@Gra, (d) PtFe-N_6@Gra, (e) PtNi-N_6@Gra, (f) PtCo-N_6@Gra catalysts under 500 K for 10 ps with a time step of 2 fs.

Table S1. The crystal structure, lattice parameters (Å), space groups, point groups, magnetic moments (with order of Pt, TM and total/μ_B) and Pt-M bond length of optimized crystal structures of 30 PtM-N_6@Gra catalysts. "/" represents that the energy of the corresponding catalyst has not been obtained due to the fact that the structure of target catalyst cannot be obtained after structural relaxation.

PtM-N_6 @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment	Pt-M Bond length
Ag		a = 12.26 b = 12.67 c = 15.37	Pm (#6)	C_s	0.00 0.00 0.00	2.436
Au		a = 12.27 b = 12.69 c = 15.36	Pm (#6)	C_s	0.00 0.00 0.00	2.440
Cd		a = 12.29 b = 12.71 c = 15.27	Pm (#6)	C_s	0.38 0.14 0.91	2.473
Co		a = 12.21 b = 12.62 c = 15.52	Pm (#6)	C_s	0.05 1.25 1.23	2.340
Cr		a = 12.19 b = 12.62 c = 15.48	Pm (#6)	C_s	0.01 3.05 2.82	2.312

Cu		a = 12.21 b = 12.56 c = 15.51	Pm (#6)	C_s	0.00 0.00 0.00	2.413
Fe		a = 12.21 b = 12.62 c = 15.50	Pm (#6)	C_s	0.12 2.55 2.65	2.327
Hf		a = 12.29 b = 12.75 c = 15.23	Pm (#6)	C_s	0.00 0.06 0.05	2.353
Ir		a = 12.26 b = 12.70 c = 15.38	Pm (#6)	C_s	0.04 0.12 0.17	2.403
La		a = 12.35 b = 12.80 c = 15.03	Pm (#6)	C_s	0.34 0.17 0.73	2.430
Mn		a = 12.20 b = 12.62 c = 15.45	Pm (#6)	C_s	0.07 3.44 3.35	2.319

Mo		a = 12.22 b = 12.67 c = 15.37	Pm (#6)	C_s	0.00 1.54 1.51	2.336
Nb		a = 12.25 b = 12.71 c = 15.30	Pm (#6)	C_s	0.01 0.72 0.58	2.329
Ni		a = 12.21 b = 12.61 c = 15.52	Pm (#6)	C_s	0.00 0.00 0.00	2.368
Os		a = 12.22 b = 12.68 c = 15.40	Pm (#6)	C_s	0.31 1.32 1.79	2.381
Pd		a = 12.26 b = 12.68 c = 15.37	Pm (#6)	C_s	0.00 0.00 0.00	2.410
Pt		a = 12.27 b = 12.70 c = 15.38	P2/m (#10)	C_{2h}	0.00 0.00 0.00	2.425

Rh		a = 12.24 b = 12.68 c = 15.40	Pm (#6)	C_s	0.26 0.49 0.86	2.406
Ru		a = 12.20 b = 12.63 c = 15.44	Pm (#6)	C_s	0.30 1.46 1.92	2.361
Sc		a = 12.29 b = 12.73 c = 15.25	Pm (#6)	C_s	0.00 0.00 0.00	2.301
Ta		a = 12.26 b = 12.73 c = 15.29	Pm (#6)	C_s	0.00 0.65 0.57	2.344
Tc		a = 12.20 b = 12.64 c = 15.42	Pm (#6)	C_s	0.07 1.58 1.66	2.348
Ti		a = 12.24 b = 12.68 c = 15.36	Pm (#6)	C_s	0.00 0.00 0.00	2.257

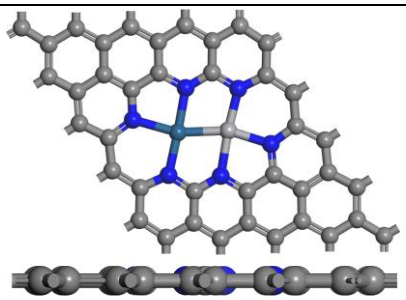
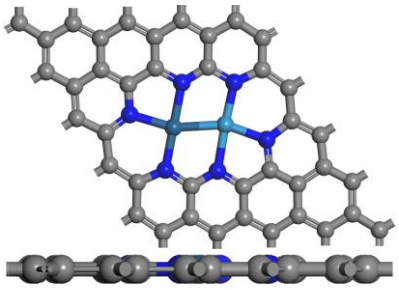
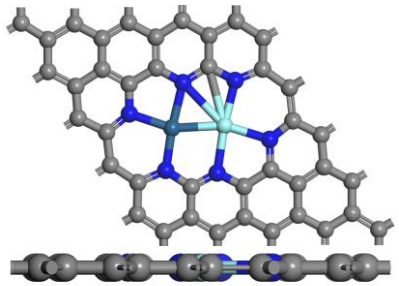
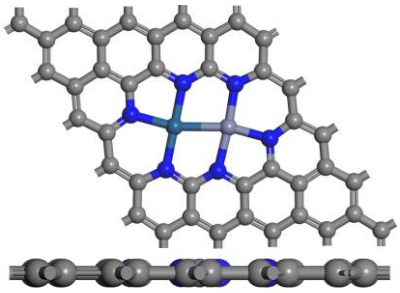
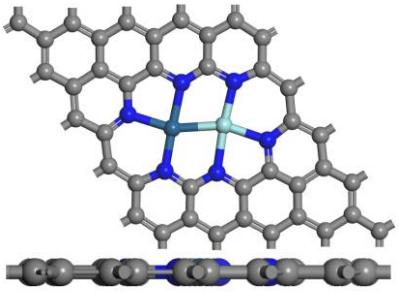
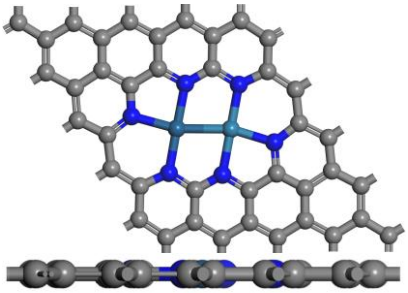
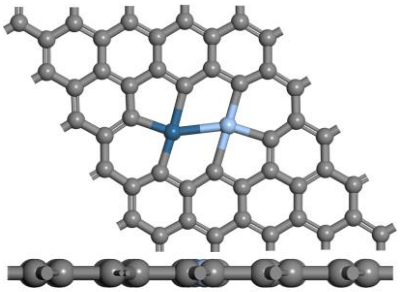
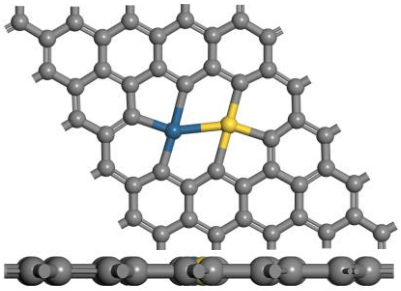
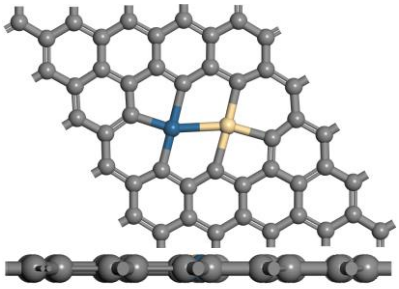
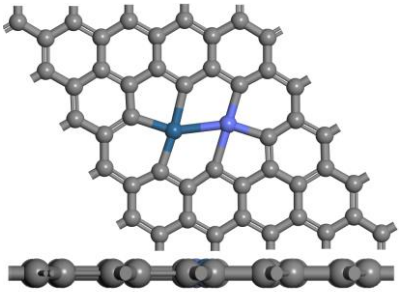
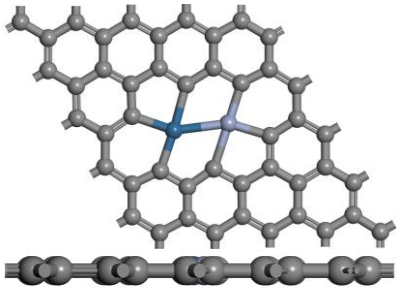
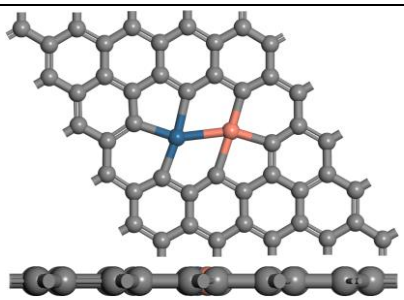
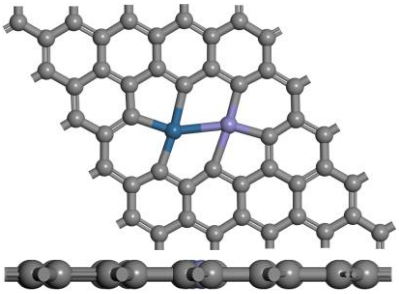
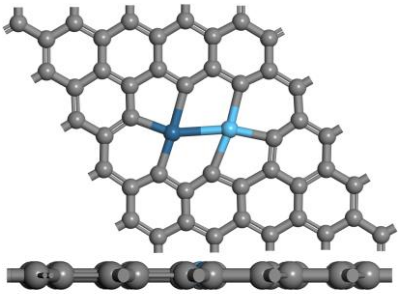
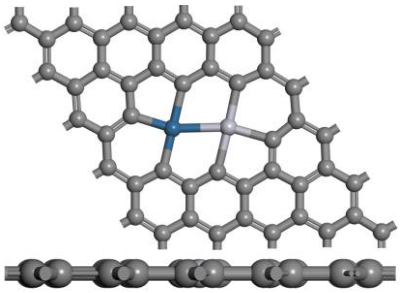
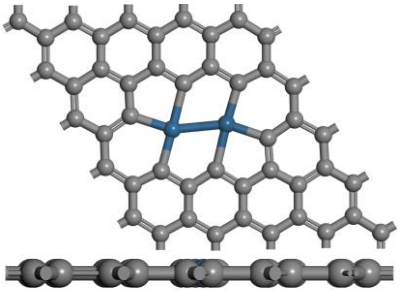
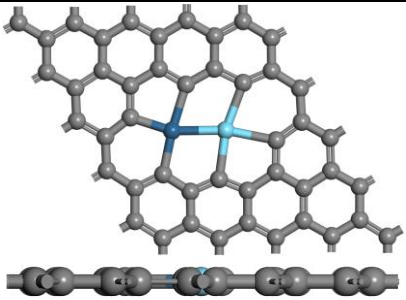
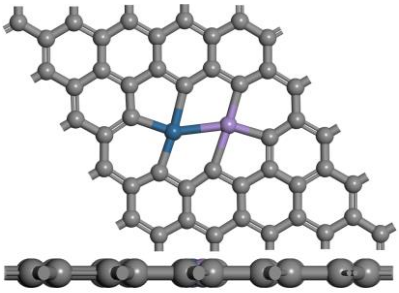
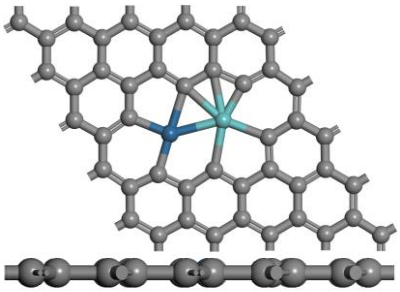
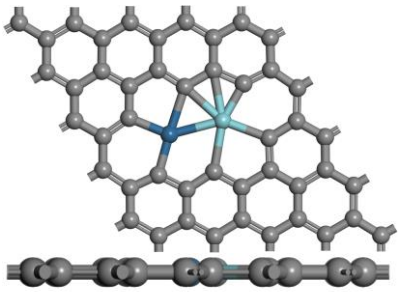
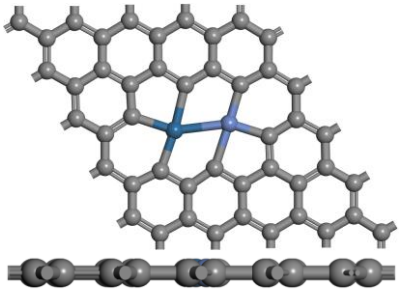
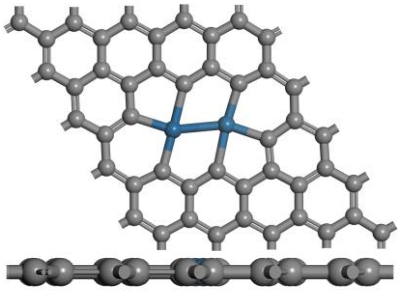
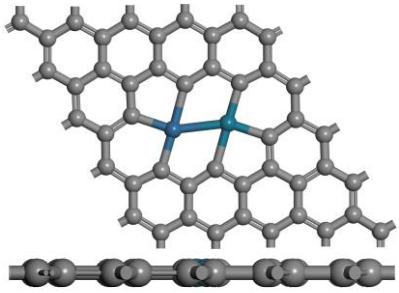
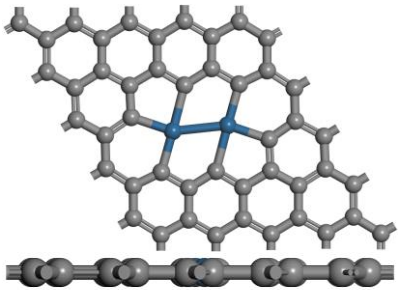
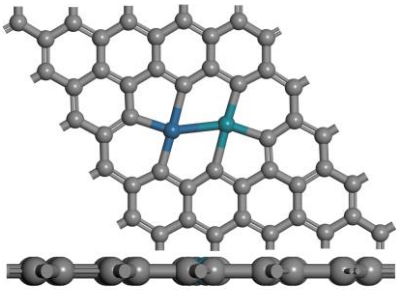
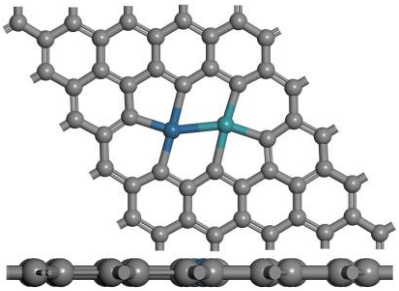
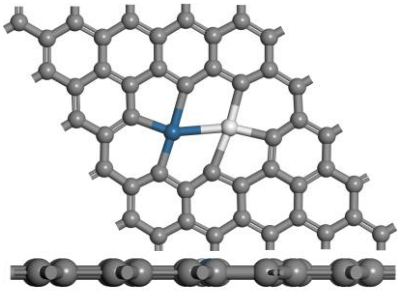
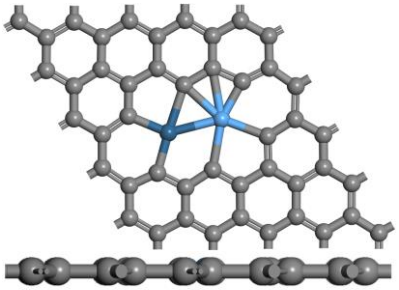
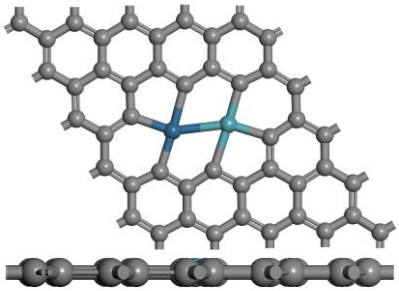
V		a = 12.21 b = 12.65 c = 15.42	Pm (#6)	C_s	0.13 1.54 1.20	2.260
W		a = 12.23 b = 12.70 c = 15.35	Pm (#6)	C_s	0.03 1.21 1.29	2.347
Y		a = 12.33 b = 12.78 c = 15.12	Pm (#6)	C_s	0.14 1.11 0.35	2.401
Zn		a = 12.23 b = 12.65 c = 15.40	Pm (#6)	C_s	0.40 0.13 0.91	2.4302.
Zr		a = 12.33 b = 12.78 c = 15.12	Pm (#6)	C_s	0.00 0.00 0.00	2.341
Re		a = 12.28 b = 12.75 c = 15.21	Pm (#6)	C_s	0.26 2.18 2.45	2.393
Hg	/	/	/	/	/	/

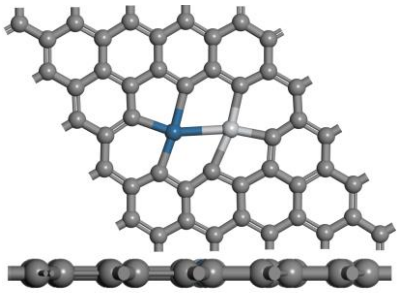
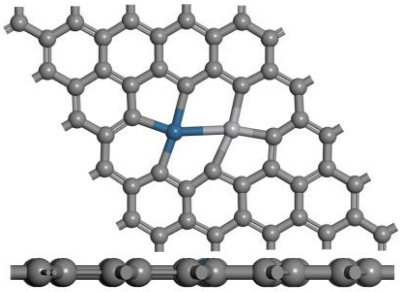
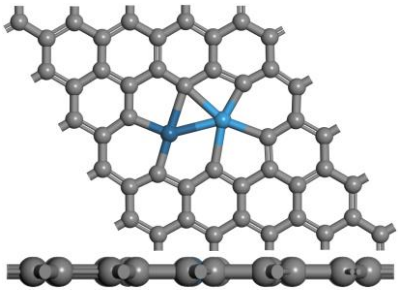
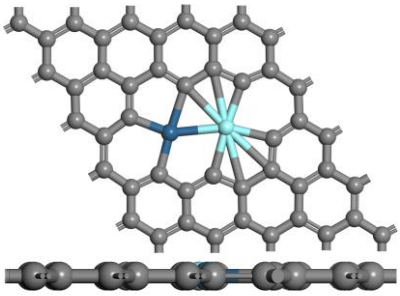
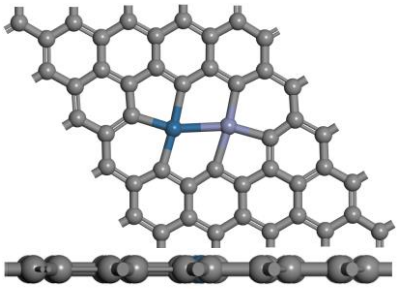
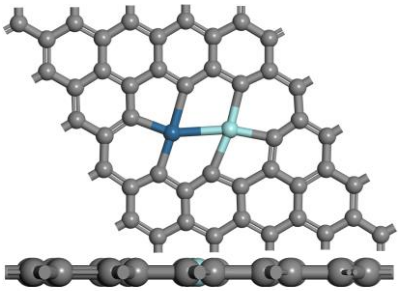
Table S2. The crystal structure, lattice parameters (Å), space groups, point groups, magnetic moments (with order of Pt, TM and total/μ_B) and Pt-M bond length of optimized crystal structures of 30 PtM-C_6@Gra catalysts. "/" represents that the energy of the corresponding catalyst has not been obtained due to the fact that the structure of target catalyst cannot be obtained after structural relaxation.

PtM-C_6 @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment	Pt-M Bond length
Ag		a = 12.33 b = 12.59 c = 15.21	Pm (#6)	C_s	0.00 0.00 0.00	2.492
Au		a = 12.33 b = 12.62 c = 15.20	Pm (#6)	C_s	0.00 0.00 0.00	2.494
Cd		a = 12.37 b = 12.68 c = 15.11	Pm (#6)	C_s	0.10 0.13 0.81	2.517
Co		a = 12.28 b = 12.53 c = 15.35	Pm (#6)	C_s	0.01 1.21 1.12	2.417
Cr		a = 12.34 b = 12.48 c = 15.32	Pm (#6)	C_s	0.04 2.95 2.97	2.459

Cu		a = 12.29 b = 12.50 c = 15.35	Pm (#6)	C_s	0.00 0.00 0.00	2.423
Fe		a = 12.29 b = 12.54 c = 15.33	Pm (#6)	C_s	0.02 2.57 2.56	2.469
Hf		a = 12.40 b = 12.60 c = 15.07	Pm (#6)	C_s	0.00 0.00 0.00	2.556
Hg		a = 12.37 b = 12.72 c = 15.10	Pm (#6)	C_s	0.15 0.16 0.81	2.525
Ir		a = 12.31 b = 12.64 c = 15.21	Pm (#6)	C_s	0.00 0.05 0.05	2.435
La		a = 12.46 b = 12.72 c = 15.95	Pm (#6)	C_s	0.00 0.15 0.50	2.384

Mn		a = 12.30 b = 12.53 c = 15.30	Pm (#6)	C_s	0.01 3.48 3.34	2.467
Mo		a = 12.38 b = 12.51 c = 15.22	Pm (#6)	C_s	0.02 1.50 1.52	2.435
Nb		a = 12.39 b = 12.54 c = 15.16	Pm (#6)	C_s	0.01 0.61 0.60	2.439
Ni		a = 12.29 b = 12.51 c = 15.36	Pm (#6)	C_s	0.00 0.00 0.00	2.441
Os		a = 12.32 b = 12.66 c = 15.18	Pm (#6)	C_s	0.08 1.10 1.11	2.399
Pd		a = 12.33 b = 12.59 c = 15.23	Pm (#6)	C_s	0.00 0.00 0.00	2.482

Pt		a = 12.32 b = 12.62 c = 15.22	P2/m (#10)	C_{2h}	0.00 0.00 0.00	2.476
Rh		a = 12.32 b = 12.61 c = 15.23	Pm (#6)	C_s	0.04 0.43 0.50	2.452
Ru		a = 12.32 b = 12.62 c = 15.21	Pm (#6)	C_s	0.06 1.09 1.10	2.415
Sc		a = 12.39 b = 12.59 c = 15.10	Pm (#6)	C_s	0.00 0.00 0.00	2.545
Ta		a = 12.38 b = 12.55 c = 15.14	Pm (#6)	C_s	0.02 0.63 0.61	2.445
Tc		a = 12.37 b = 12.56 c = 15.20	Pm (#6)	C_s	0.05 2.52 2.66	2.520

Ti		a = 12.36 b = 12.53 c = 15.21	Pm (#6)	C_s	0.00 0.00 0.00	2.548
V		a = 12.35 b = 12.51 c = 15.27	Pm (#6)	C_s	0.02 1.43 1.26	2.553
W		a = 12.38 b = 12.51 c = 15.21	Pm (#6)	C_s	0.03 1.23 1.33	2.439
Y		a = 12.44 b = 12.64 c = 15.97	Pm (#6)	C_s	0.03 0.19 0.76	2.515
Zn		a = 12.33 b = 12.64 c = 15.23	Pm (#6)	C_s	0.06 0.11 0.58	2.491
Zr		a = 12.41 b = 12.59 c = 15.06	Pm (#6)	C_s	0.00 0.00 0.00	2.579

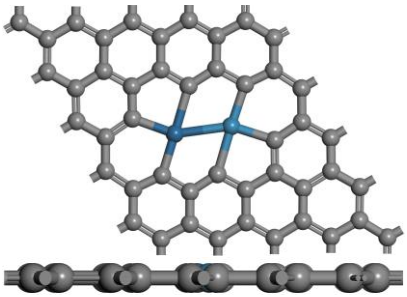
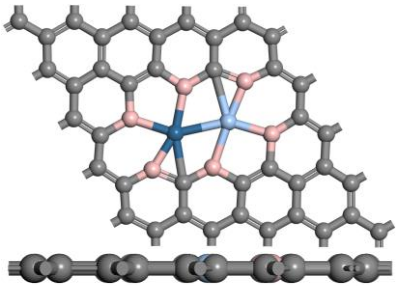
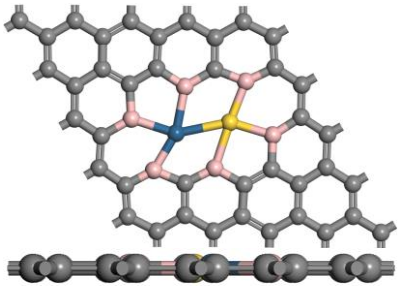
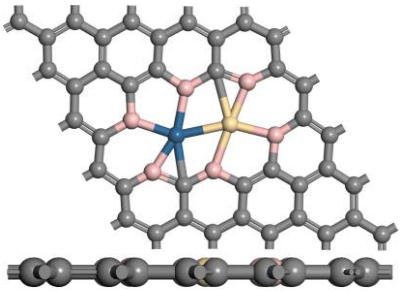
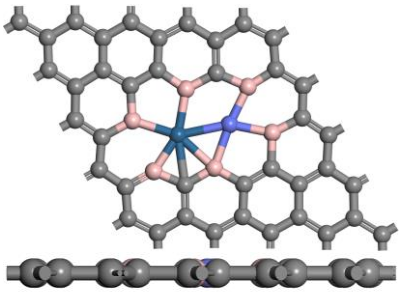
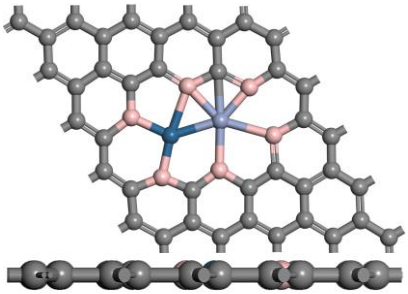
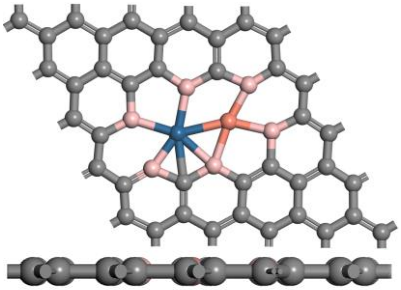
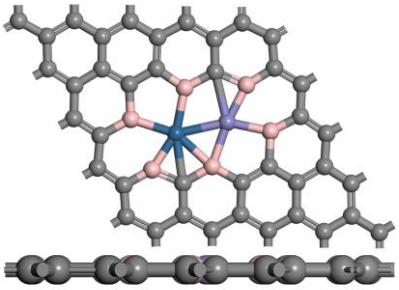
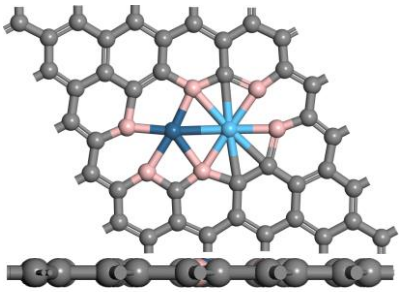
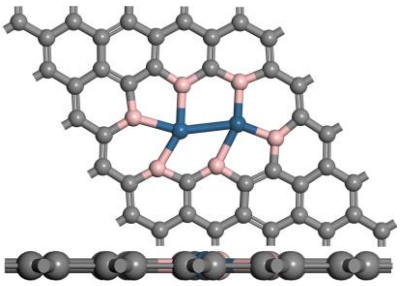
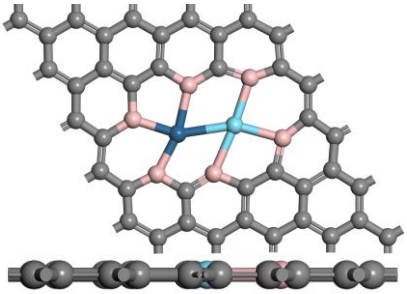
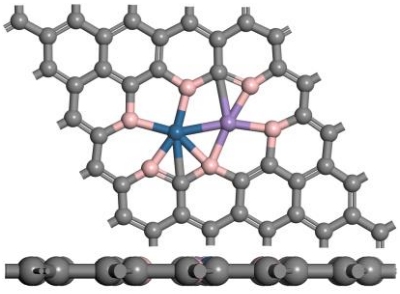
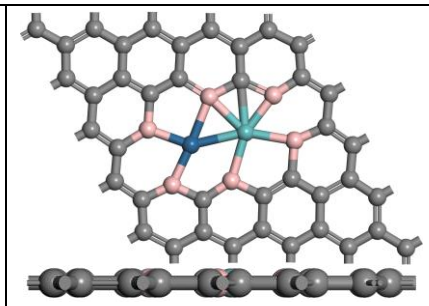
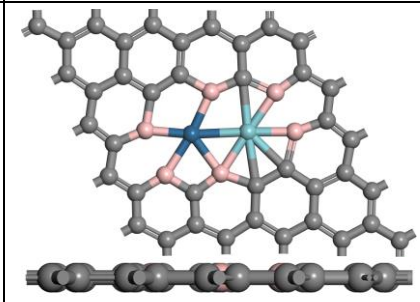
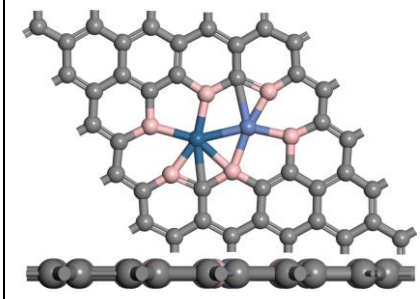
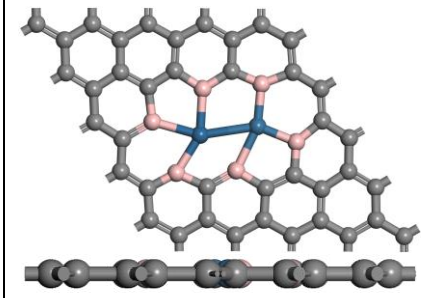
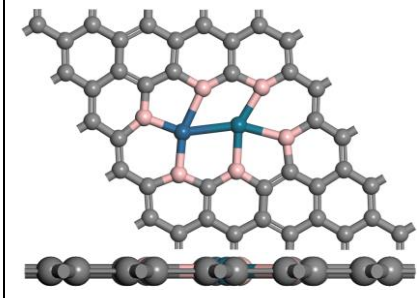
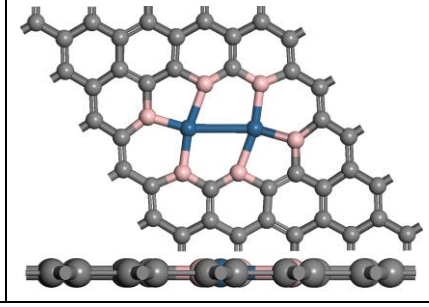
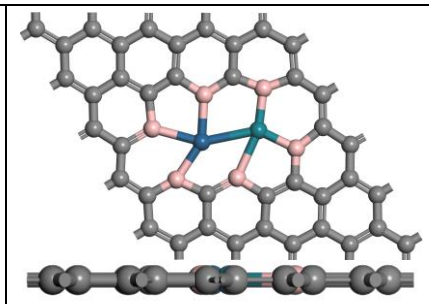
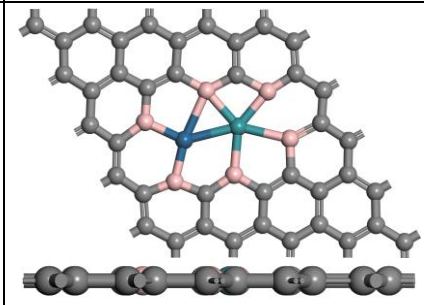
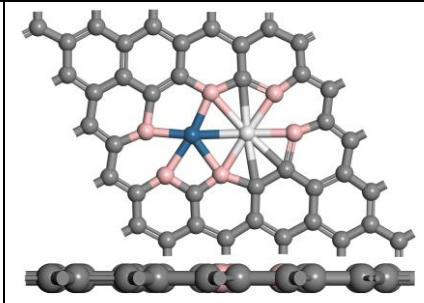
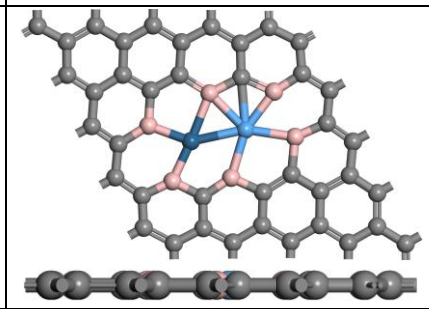
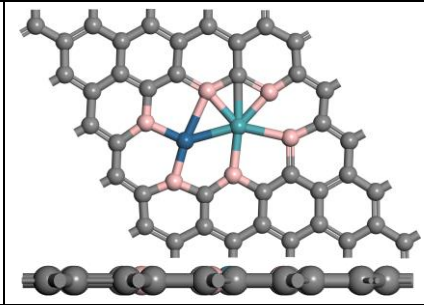
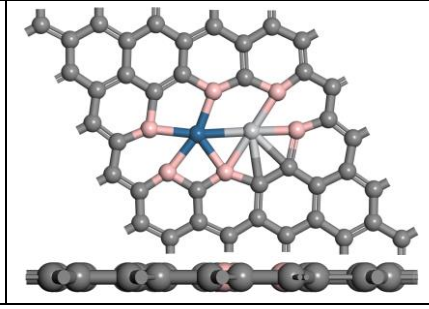
Re		a = 12.41 b = 12.59 c = 15.06	Pm (#6)	C_s	0.10 2.29 2.50	2.498

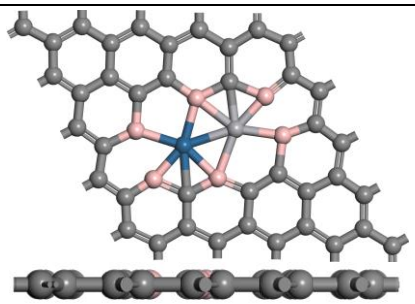
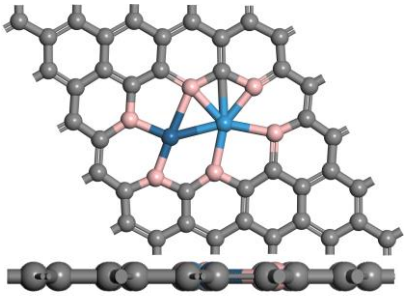
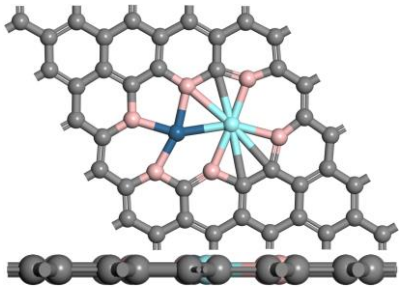
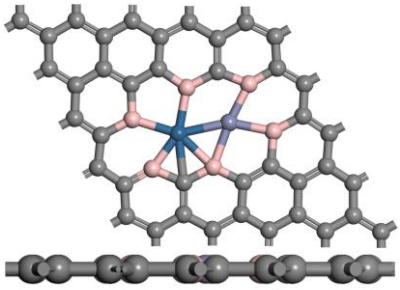
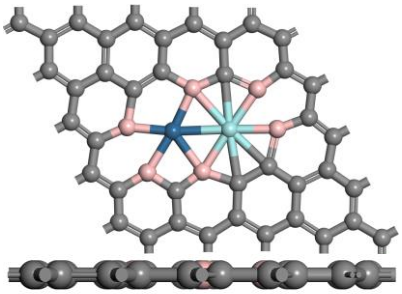
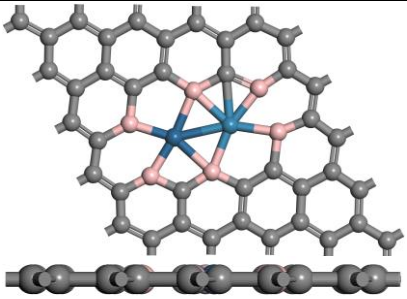
Table S3. The crystal structure, lattice parameters (Å), space groups, point groups, magnetic moments (with order of Pt, TM and total/μ_B) and Pt-M bond length of optimized crystal structures of 30 PtM-B_6@Gra catalysts. "/" represents that the energy of the corresponding catalyst has not been obtained due to the fact that the structure of target catalyst cannot be obtained after structural relaxation.

PtM-B_6 @Gra	Crystal structure (top and side views)	Lattice constant	Space group	Point group	Magnetic moment	Pt-M Bond length
Ag		a = 12.66 b = 12.50 c = 15.86	Pm (#6)	C_s	0.08 0.06 0.39	2.448
Au		a = 12.66 b = 12.54 c = 15.84	Pm (#6)	C_s	0.00 0.00 0.00	2.471
Cd		a = 12.69 b = 12.49 c = 15.83	Pm (#6)	C_s	0.00 0.00 0.00	2.453
Co		a = 12.58 b = 12.51 c = 15.98	P1 (#1)	C_1	0.07 1.81 2.14	2.436
Cr		a = 12.58 b = 12.75 c = 15.80	Pm (#6)	C_s	0.06 2.35 1.99	2.309

Cu		a = 12.63 b = 12.37 c = 15.03	Pm (#6)	C_s	0.00 0.00 0.00	2.326
Fe		a = 12.61 b = 12.47 c = 15.98	Pm (#6)	C_s	0.10 2.92 3.27	2.352
Hf		a = 12.74 b = 12.13 c = 15.96	Pm (#6)	C_s	0.00 0.00 0.00	2.462
Ir		a = 12.63 b = 12.67 c = 15.85	Pm (#6)	C_s	0.00 0.01 0.02	2.626
La		a = 12.69 b = 12.61 c = 15.65	Pm (#6)	C_s	0.00 0.00 0.00	2.531
Mn		a = 12.68 b = 12.28 c = 15.04	Pm (#6)	C_s	0.07 2.70 2.55	2.537

Mo		a = 12.66 b = 12.40 c = 15.88	Pm (#6)	C_s	0.11 0.97 0.57	2.426
Nb		a = 12.72 b = 12.11 c = 15.02	Pm (#6)	C_s	0.01 0.70 0.63	2.465
Ni		a = 12.64 b = 12.35 c = 15.05	Pm (#6)	C_s	0.11 0.66 1.10	2.322
Os		a = 12.64 b = 12.65 c = 15.84	Pm (#6)	C_s	0.04 1.23 1.47	2.599
Pd		a = 12.63 b = 12.66 c = 14.86	Pm (#6)	C_s	0.00 0.00 0.00	2.569
Pt		a = 12.65 b = 12.79 c = 15.73	P2/m (#10)	C_{2h}	0.00 0.00 0.00	2.974

Rh		a = 12.61 b = 12.61 c = 14.89	Pm (#6)	C_s	0.03 0.33 0.44	2.566
Ru		a = 12.63 b = 12.52 c = 14.88	Pm (#6)	C_s	0.07 1.08 1.29	2.441
Sc		a = 12.72 b = 12.13 c = 15.00	Pm (#6)	C_s	0.00 0.00 0.00	2.415
Ta		a = 12.69 b = 12.41 c = 14.82	Pm (#6)	C_s	0.00 0.27 0.40	2.435
Tc		a = 12.64 b = 12.48 c = 14.87	Pm (#6)	C_s	0.00 1.08 0.99	2.422
Ti		a = 12.71 b = 12.09 c = 15.09	Pm (#6)	C_s	0.00 0.00 0.00	2.374

V		a = 12.70 b = 12.18 c = 15.06	Pm (#6)	C_s	0.00 1.19 0.97	2.343
W		a = 12.65 b = 12.46 c = 14.83	Pm (#6)	C_s	0.09 1.05 1.25	2.432
Y		a = 12.68 b = 12.56 c = 14.73	Pm (#6)	C_s	0.00 0.00 0.00	2.480
Zn		a = 12.65 b = 12.37 c = 15.00	Pm (#6)	C_s	0.00 0.00 0.00	2.322
Zr		a = 12.74 b = 12.15 c = 14.94	Pm (#6)	C_s	0.00 0.00 0.00	2.474
Re		a = 12.74 b = 12.15 c = 14.94	Pm (#6)	C_s	0.00 1.04 0.96	2.466
Hg	/	/	/	/	/	/

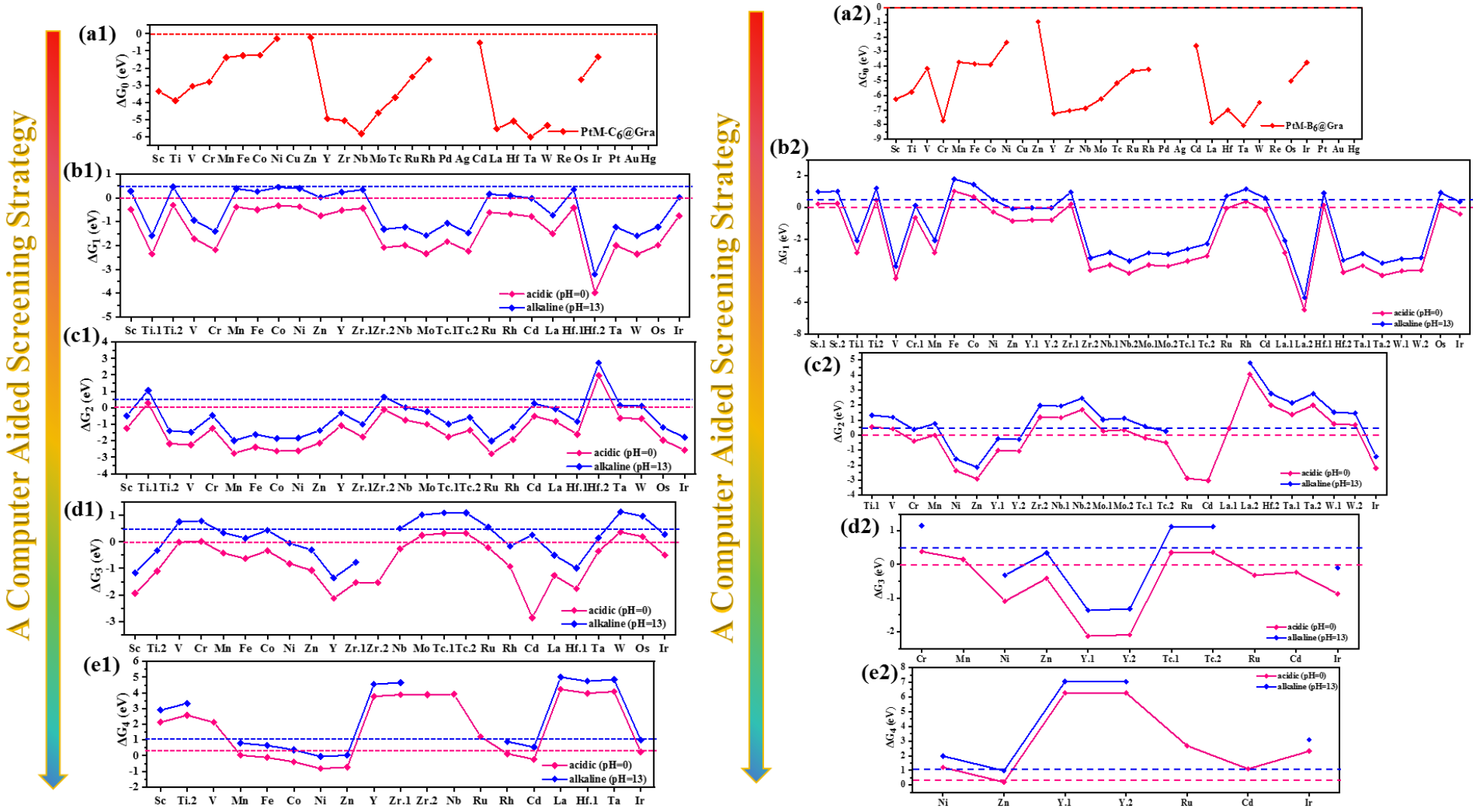


Figure S1. The results from computer aided screening for PtM-C_6@Gra (a1-e1) and PtM-B_6@Gra (a2-e2). The red dashed lines refer to 0.00 eV. The blue and magenta dashed lines refer to 0.50 and 0.00 eV, respectively. In Figure e2, f2, the blue and magenta dashed lines refer to 1.00 and 0.25 eV, respectively.

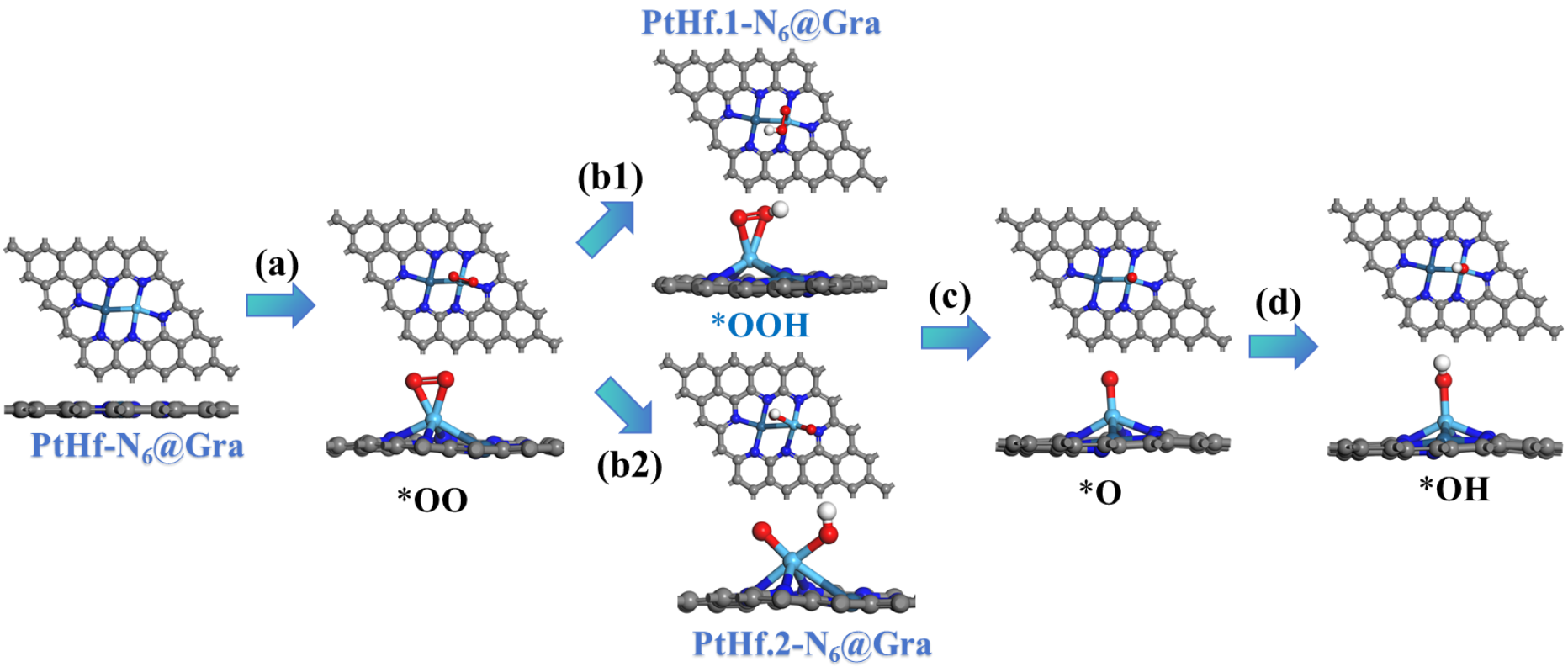
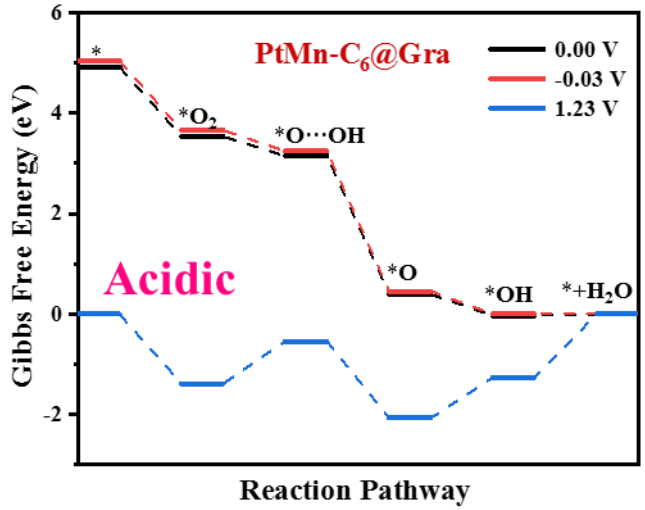
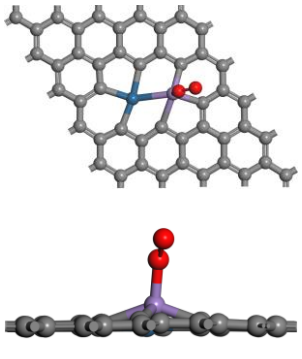
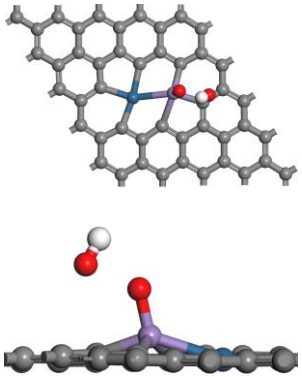
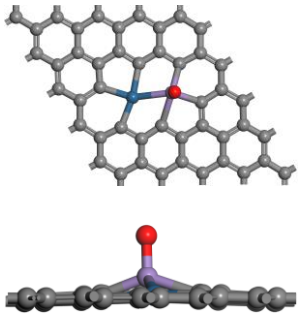
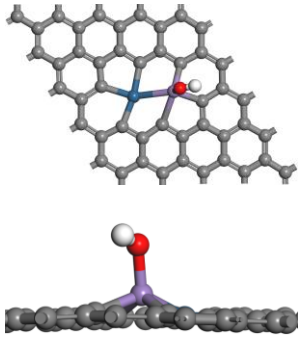
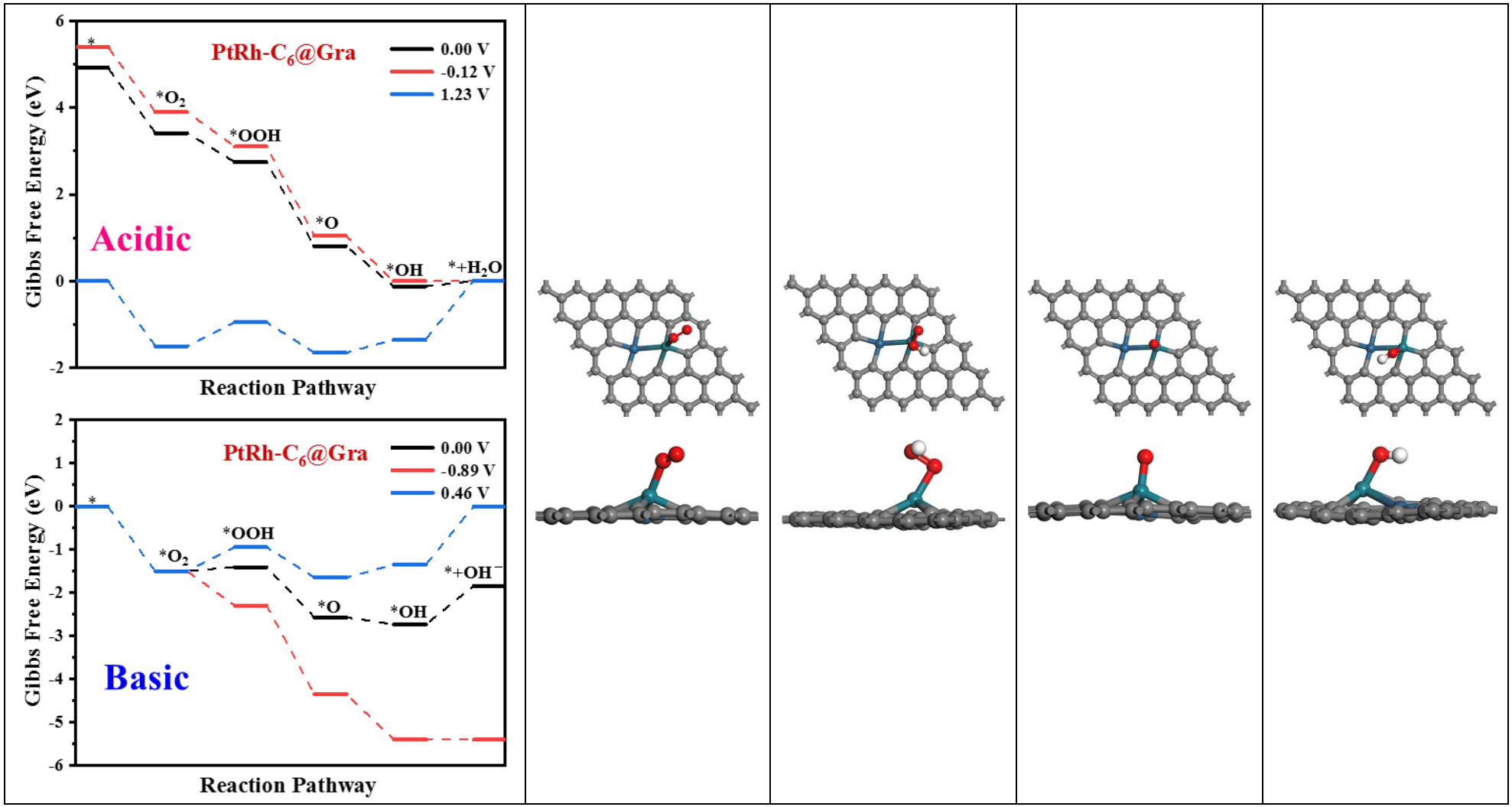
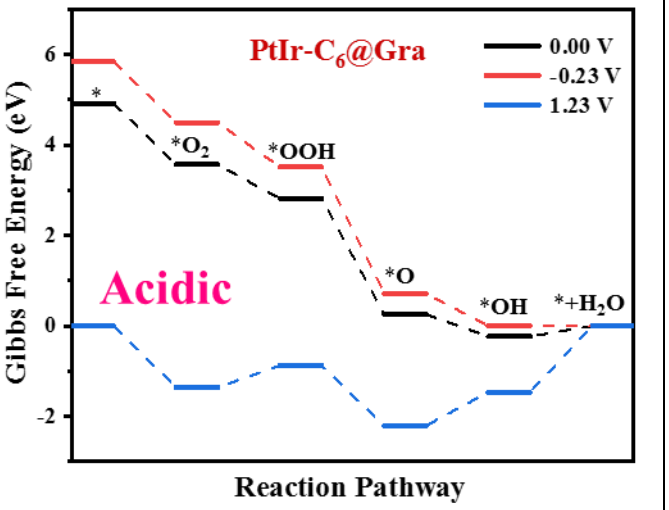


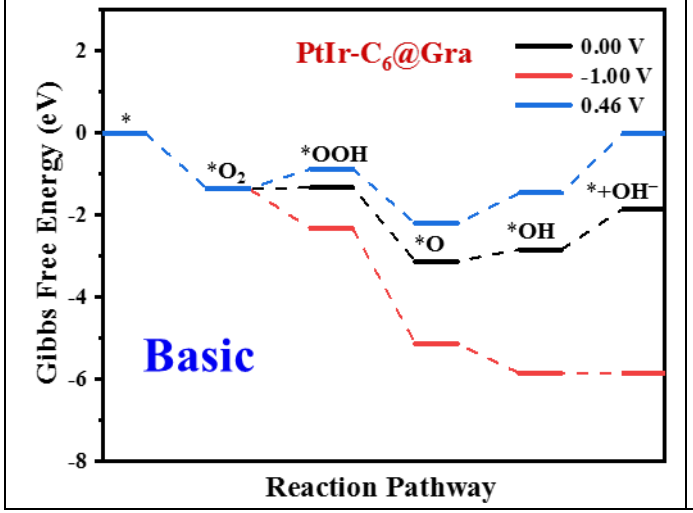
Figure S2. Schematic illustration of different hydrogenation sites for the second protonation $\Delta G_{*O_2 \rightarrow *OOH}$ of PtM-L_6@Gra catalysts, named PtM.1-L_6@Gra and PtM.2-L_6@Gra, respectively.

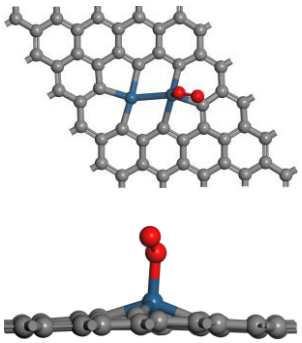
Table S4. The Gibbs free energy profiles and the relevant intermediate species of different reaction pathways for 16 selected catalysts.

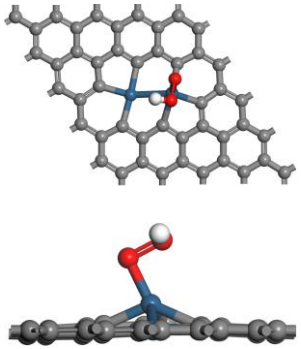
Gibbs free energy profiles	$*O_2$	*OOH or *O*OH	*O	*OH
				

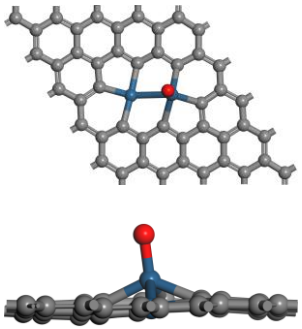

PtRh-C6@Gra
0.00 V
-0.12 V
1.23 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Reaction Pathway
PtRh-C6@Gra
0.00 V
-0.89 V
0.46 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Reaction Pathway

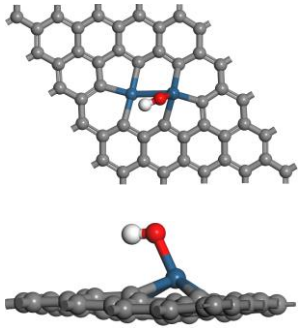

PtIr-C6@Gra
0.00 V
-0.23 V
1.23 V
Gibbs Free Energy (eV)
6
4
2
0
-2
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Reaction Pathway

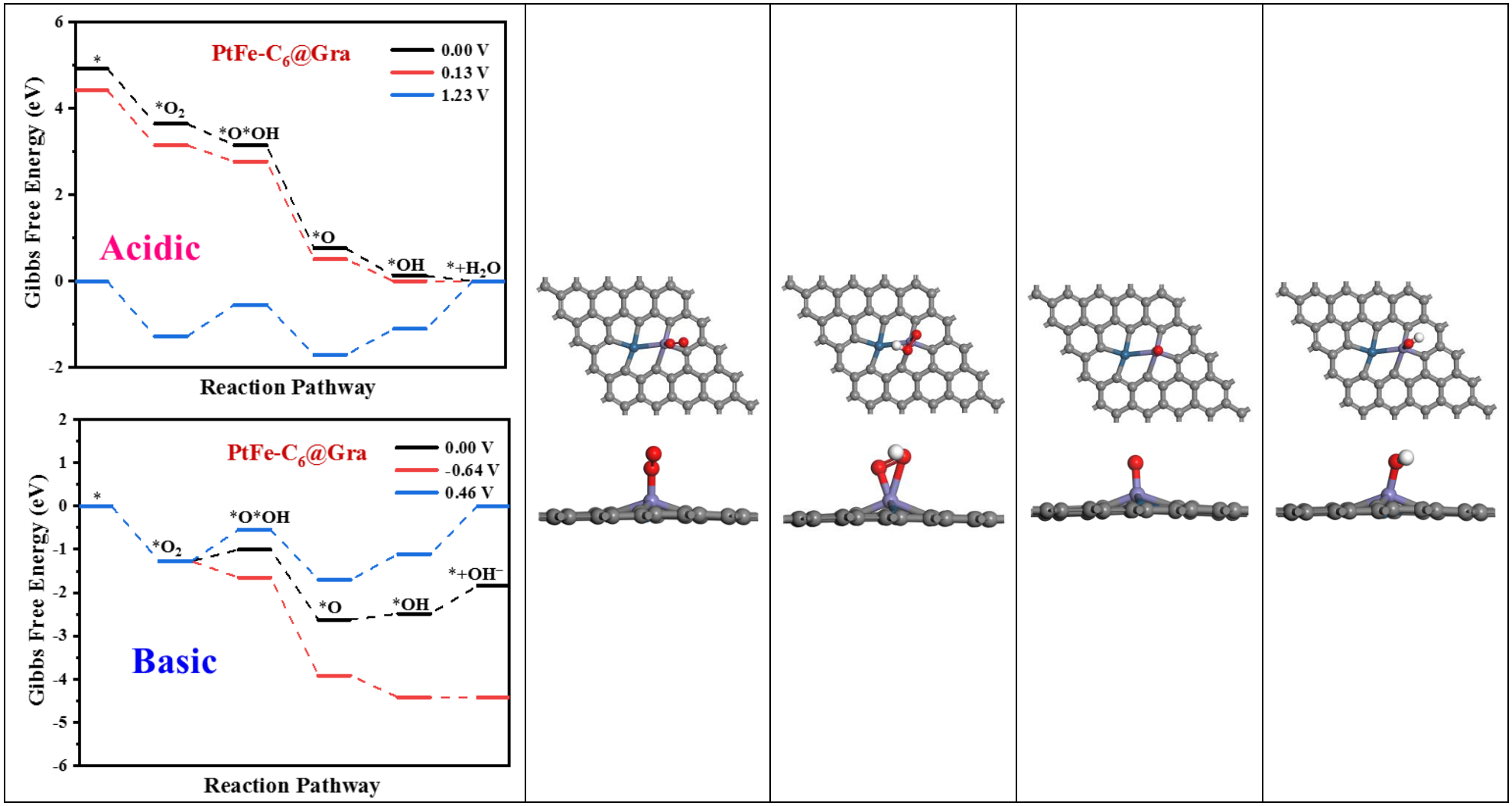

PtIr-C6@Gra
0.00 V
-1.00 V
0.46 V
Gibbs Free Energy (eV)
2
0
-2
-4
-6
-8
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Reaction Pathway

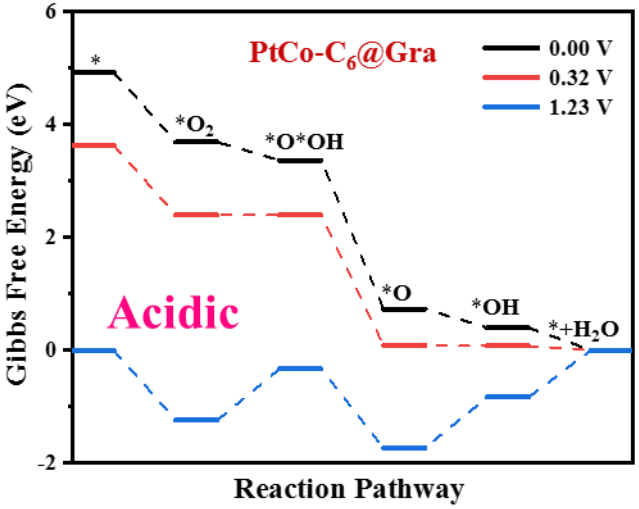


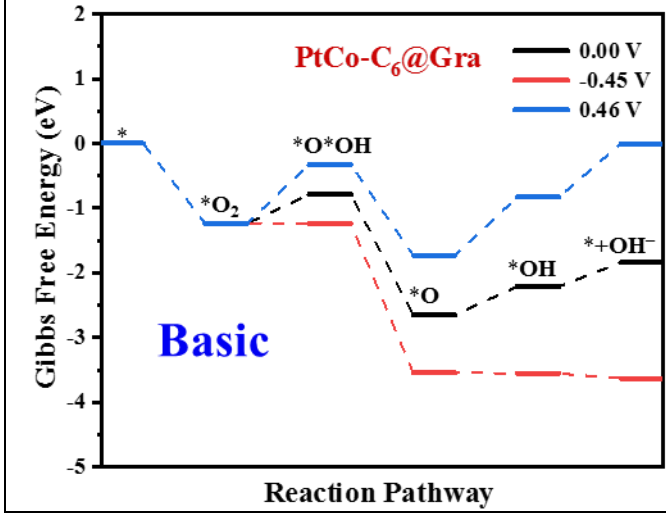


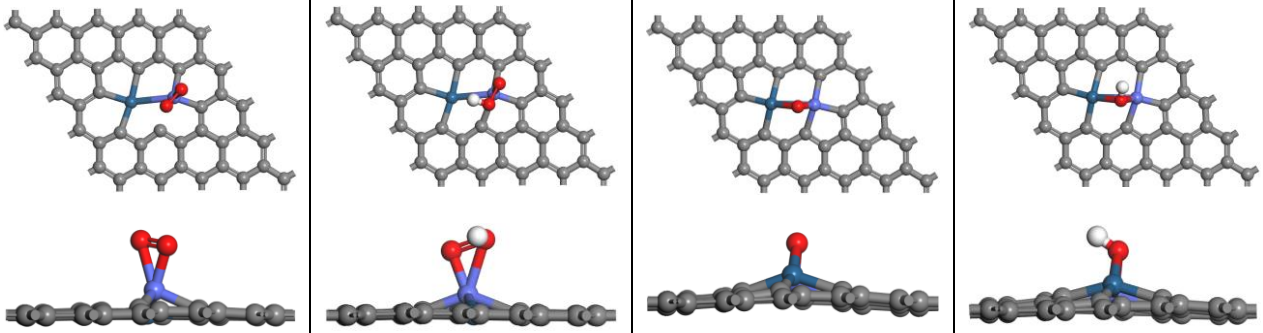


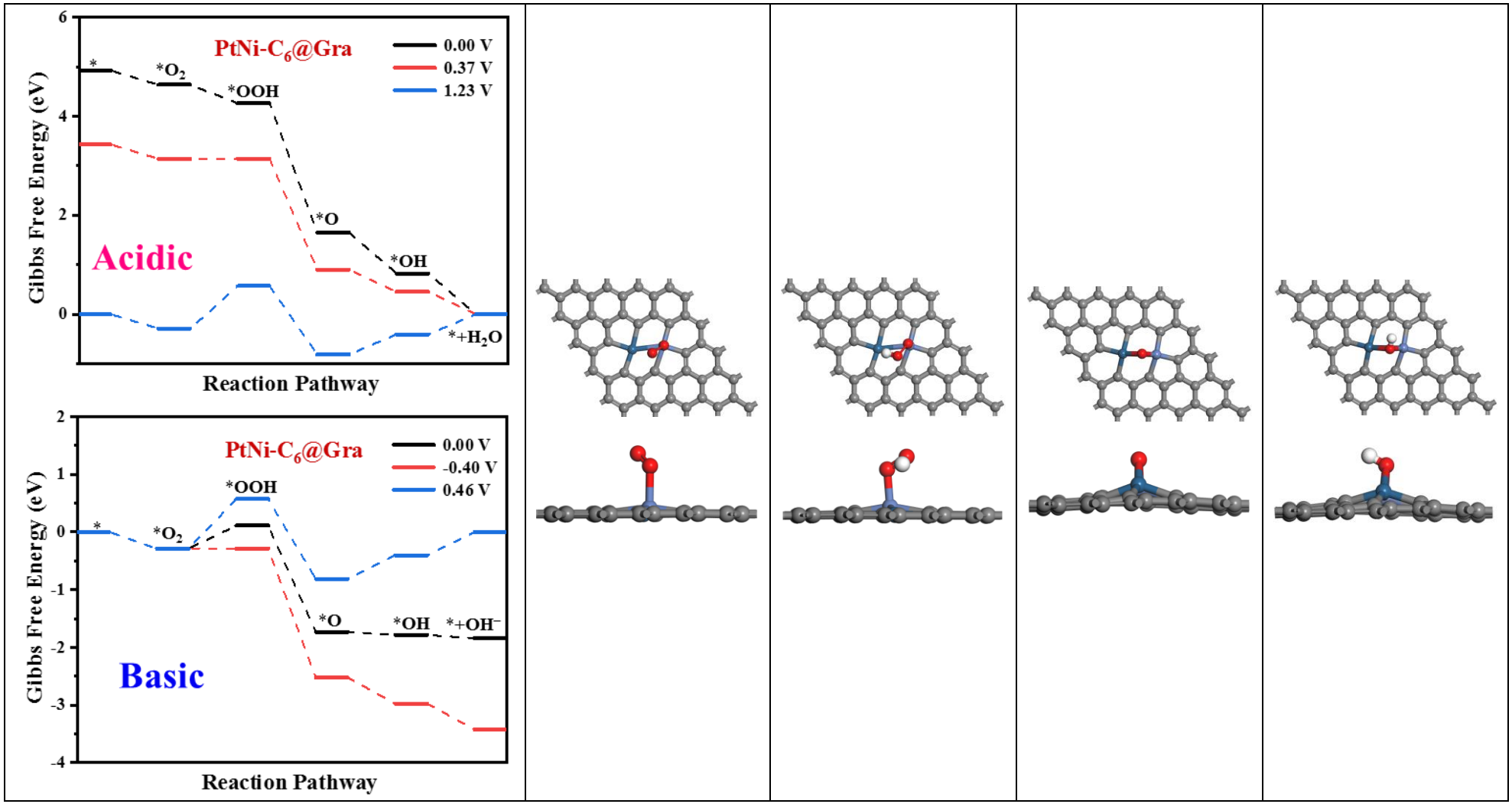


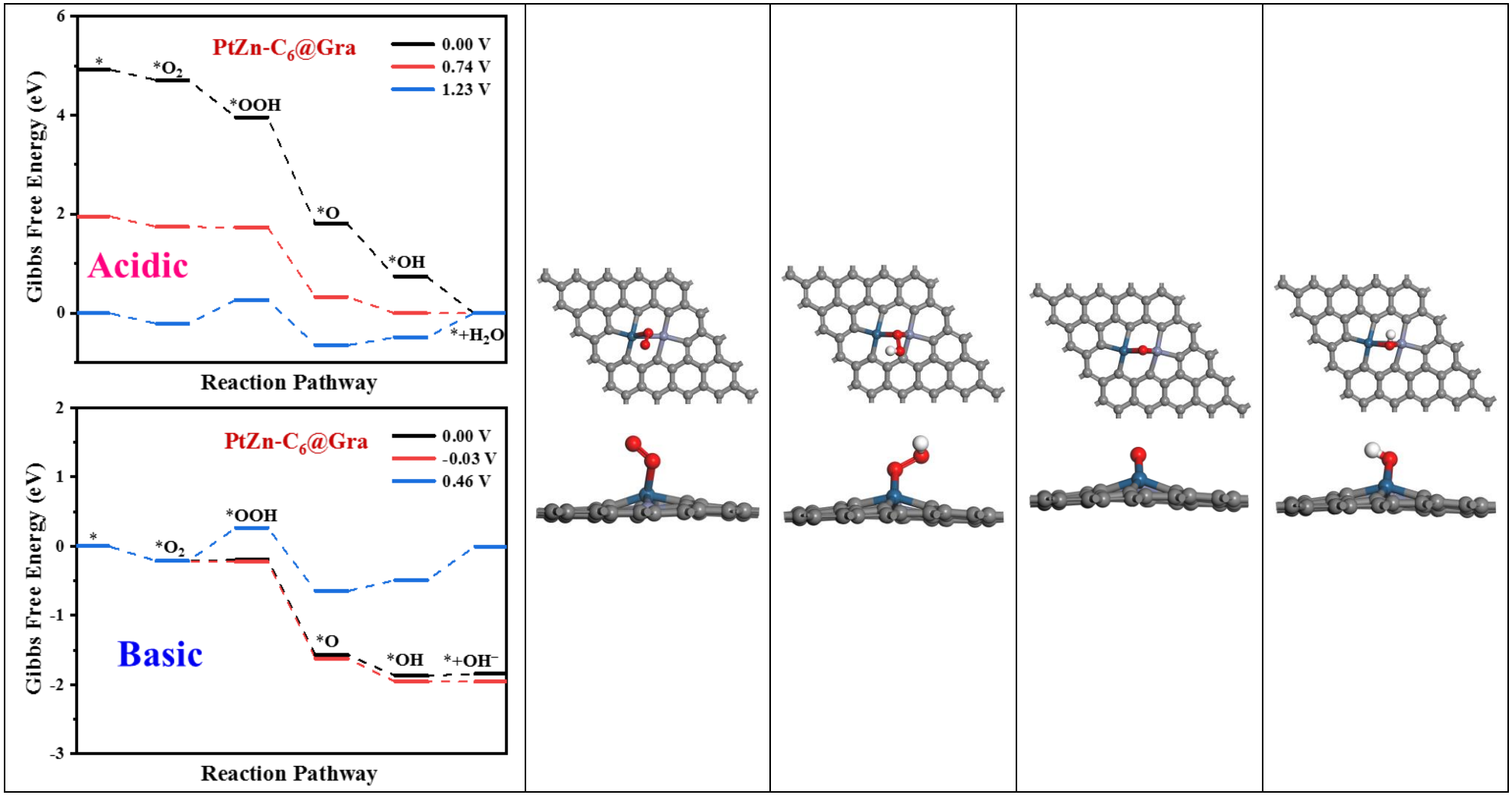

PtFe-C6@Gra
0.00 V
0.13 V
1.23 V
*
*O2
*O*OH
*O
*OH
*+H2O
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
PtFe-C6@Gra
0.00 V
-0.64 V
0.46 V
*
*O2
*O*OH
*O
*OH
*+OH−
Basic
Gibbs Free Energy (eV)
Reaction Pathway

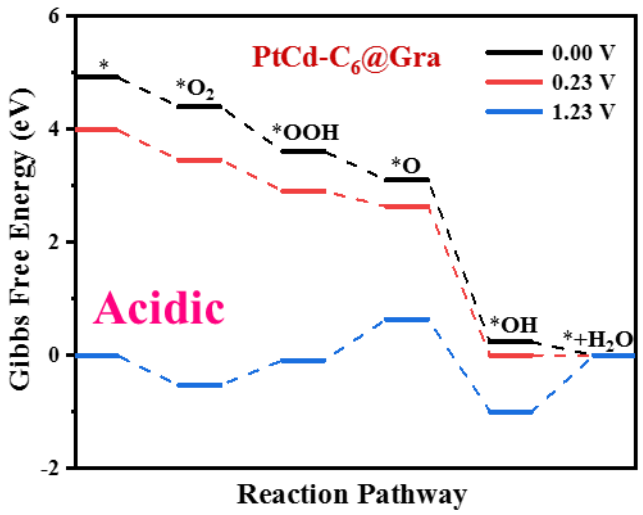

PtCo-C6@Gra
0.00 V
0.32 V
1.23 V
*
*O2
*O*OH
*O
*OH
*+H2O
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
6
4
2
0
-2

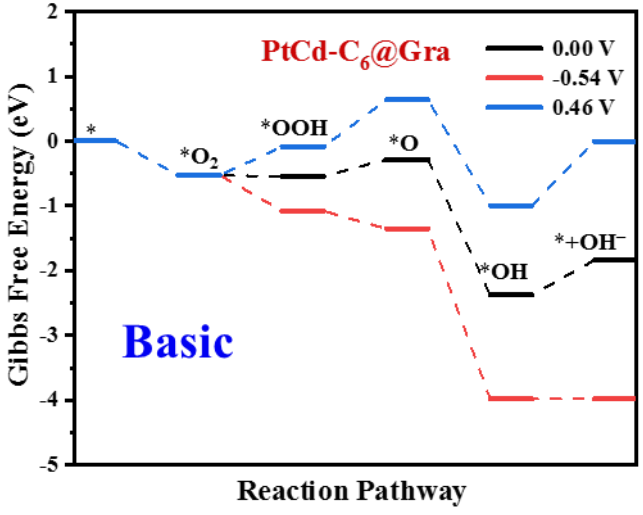

PtCo-C6@Gra
0.00 V
-0.45 V
0.46 V
*
*O2
*O*OH
*O
*OH
*+OH−
Basic
Gibbs Free Energy (eV)
Reaction Pathway
2
1
0
-1
-2
-3
-4
-5

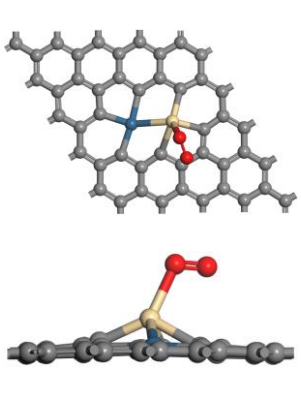


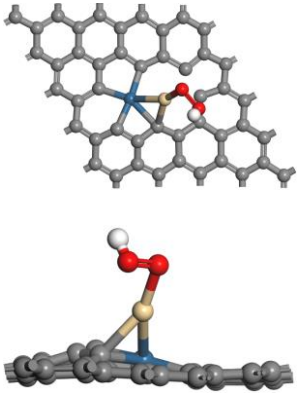

PtNi-C6@Gra
0.00 V
0.37 V
1.23 V
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
*
*O2
*OOH
*O
*OH
*+H2O
PtNi-C6@Gra
0.00 V
-0.40 V
0.46 V
Basic
Gibbs Free Energy (eV)
Reaction Pathway
*
*O2
*OOH
*O
*OH
*+OH−

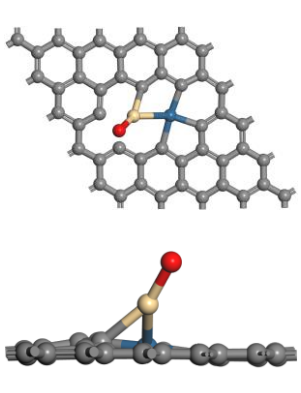

PtZn-C6@Gra
0.00 V
0.74 V
1.23 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Reaction Pathway
PtZn-C6@Gra
0.00 V
-0.03 V
0.46 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Reaction Pathway

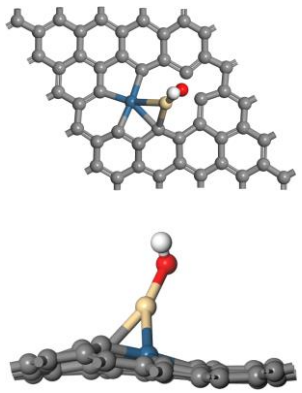

PtCd-C6@Gra
0.00 V
0.23 V
1.23 V
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
6
4
2
0
-2

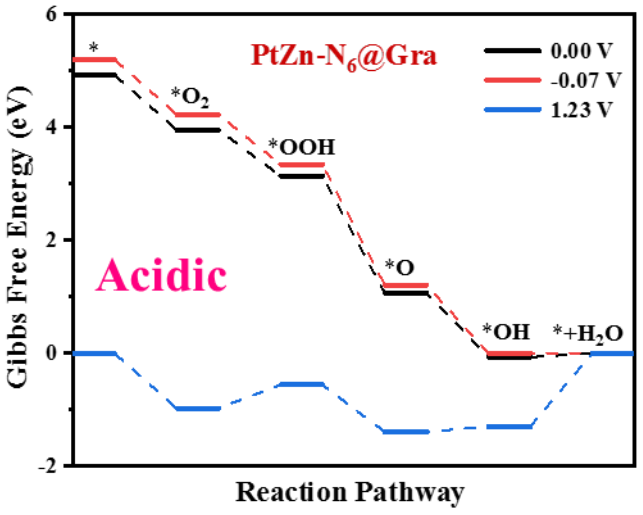

PtCd-C6@Gra
0.00 V
-0.54 V
0.46 V
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Gibbs Free Energy (eV)
Reaction Pathway
2
1
0
-1
-2
-3
-4
-5

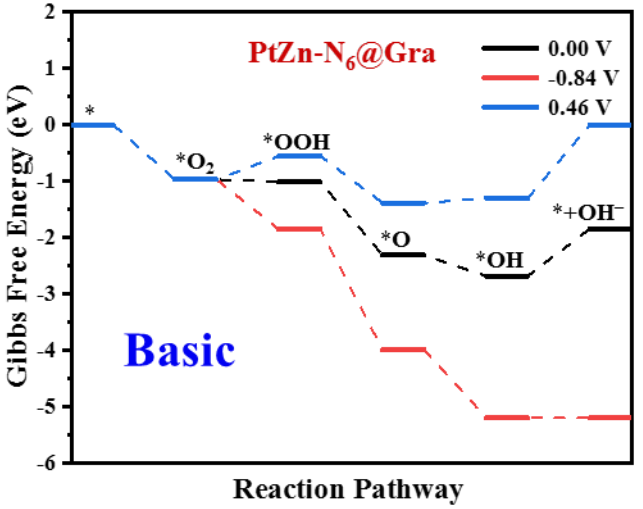


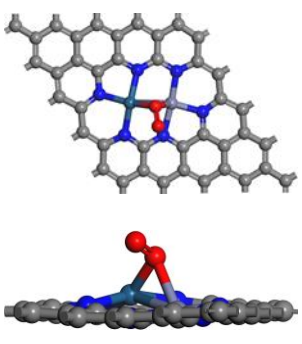


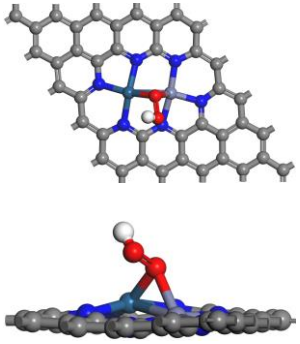


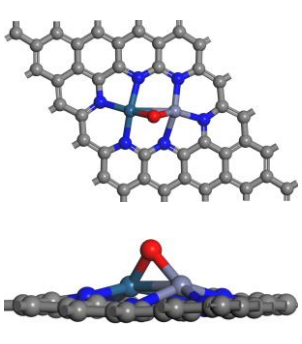


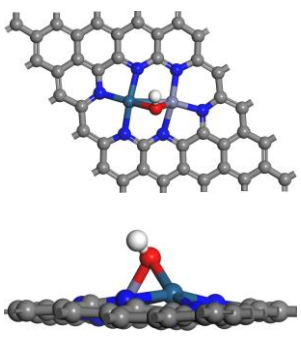

PtZn-N6@Gra
0.00 V
-0.07 V
1.23 V
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
6
4
2
0
-2

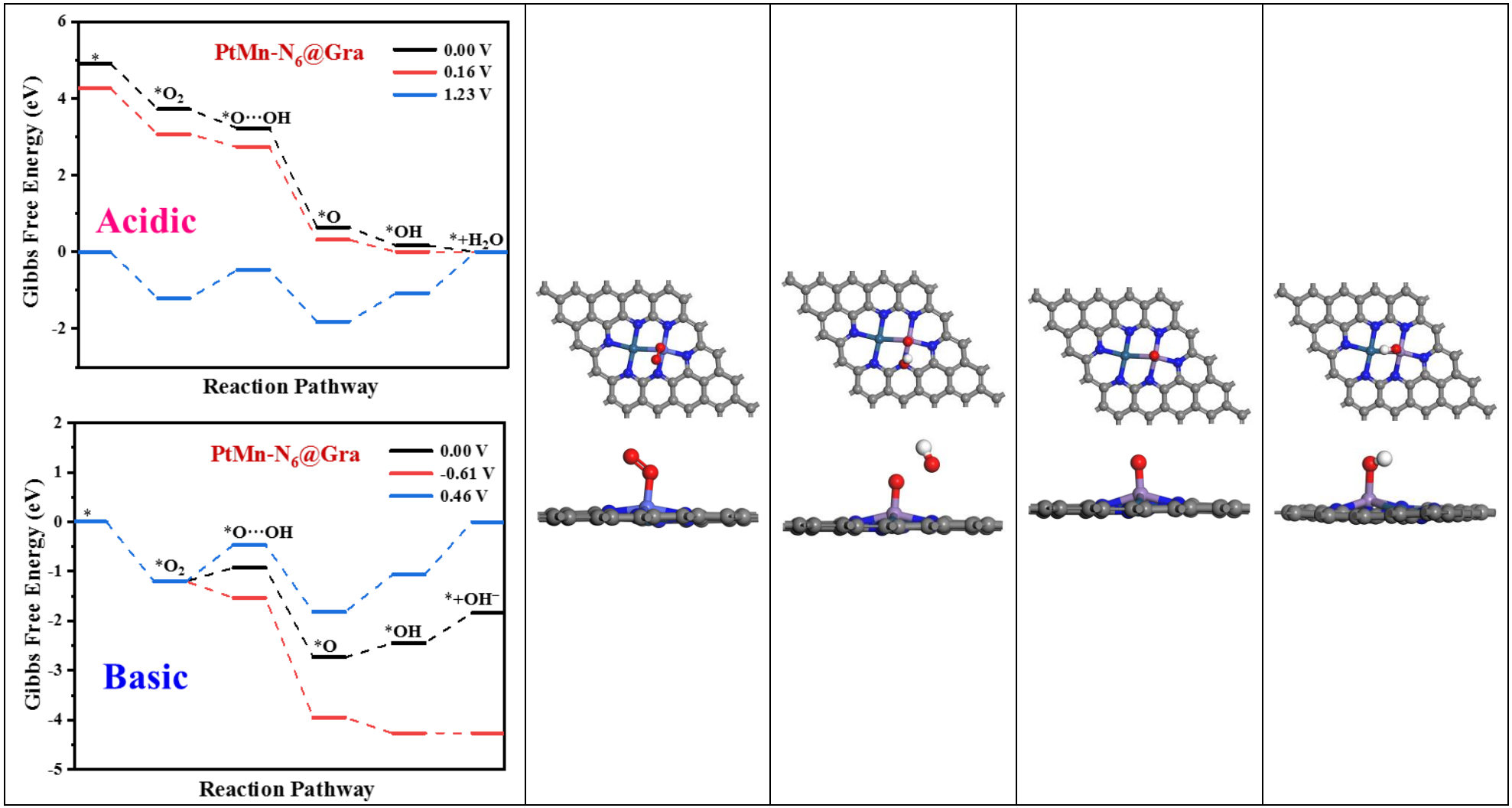

PtZn-N6@Gra
0.00 V
-0.84 V
0.46 V
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Gibbs Free Energy (eV)
Reaction Pathway
2
1
0
-1
-2
-3
-4
-5
-6










PtMn-N6@Gra
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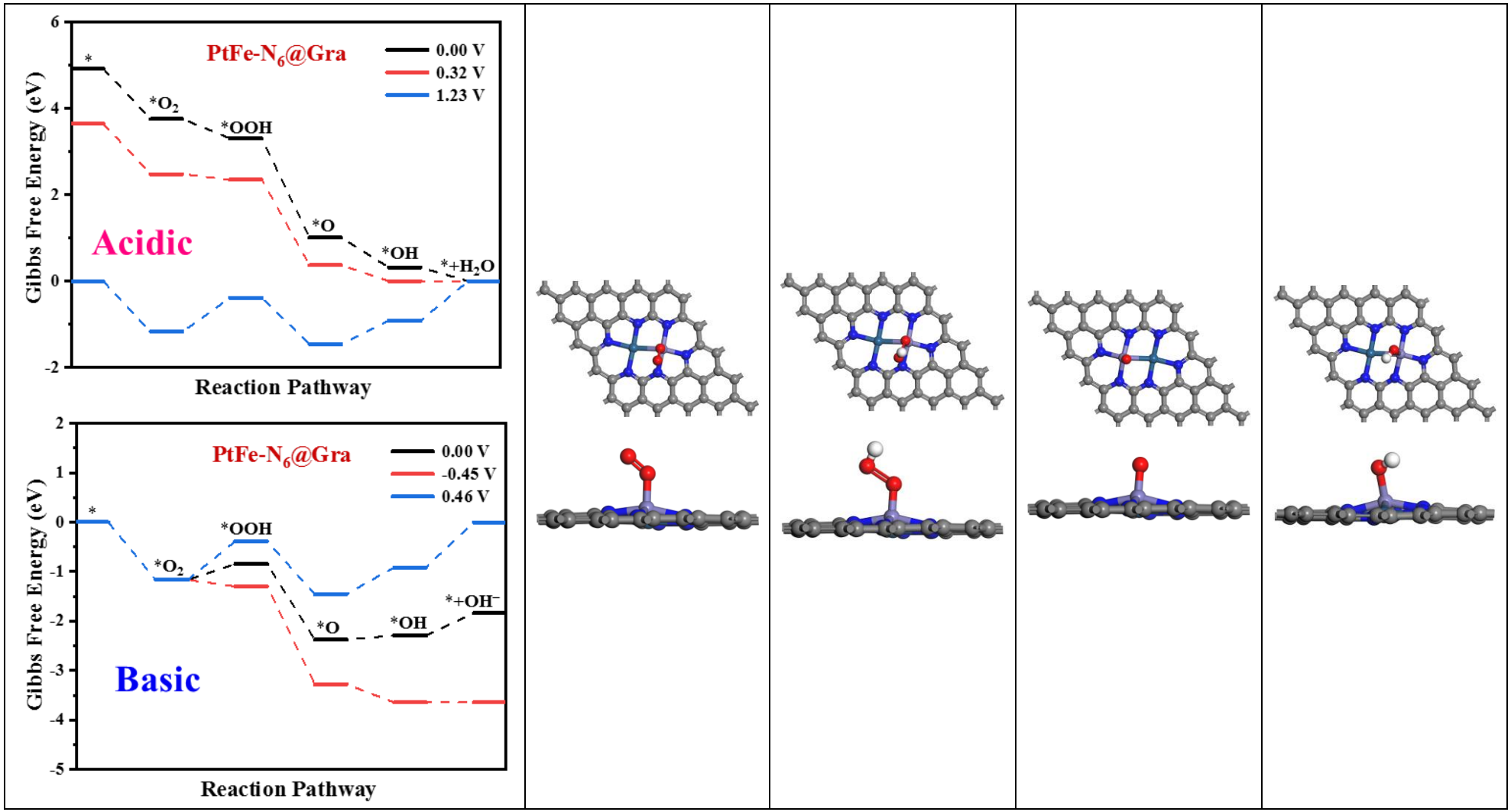
0.16 V
1.23 V
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
*
*O2
*O···OH
*O
*OH
*+H2O
PtMn-N6@Gra
0.00 V
-0.61 V
0.46 V
Basic
Gibbs Free Energy (eV)
Reaction Pathway
*
*O2
*O···OH
*O
*OH
*+OH−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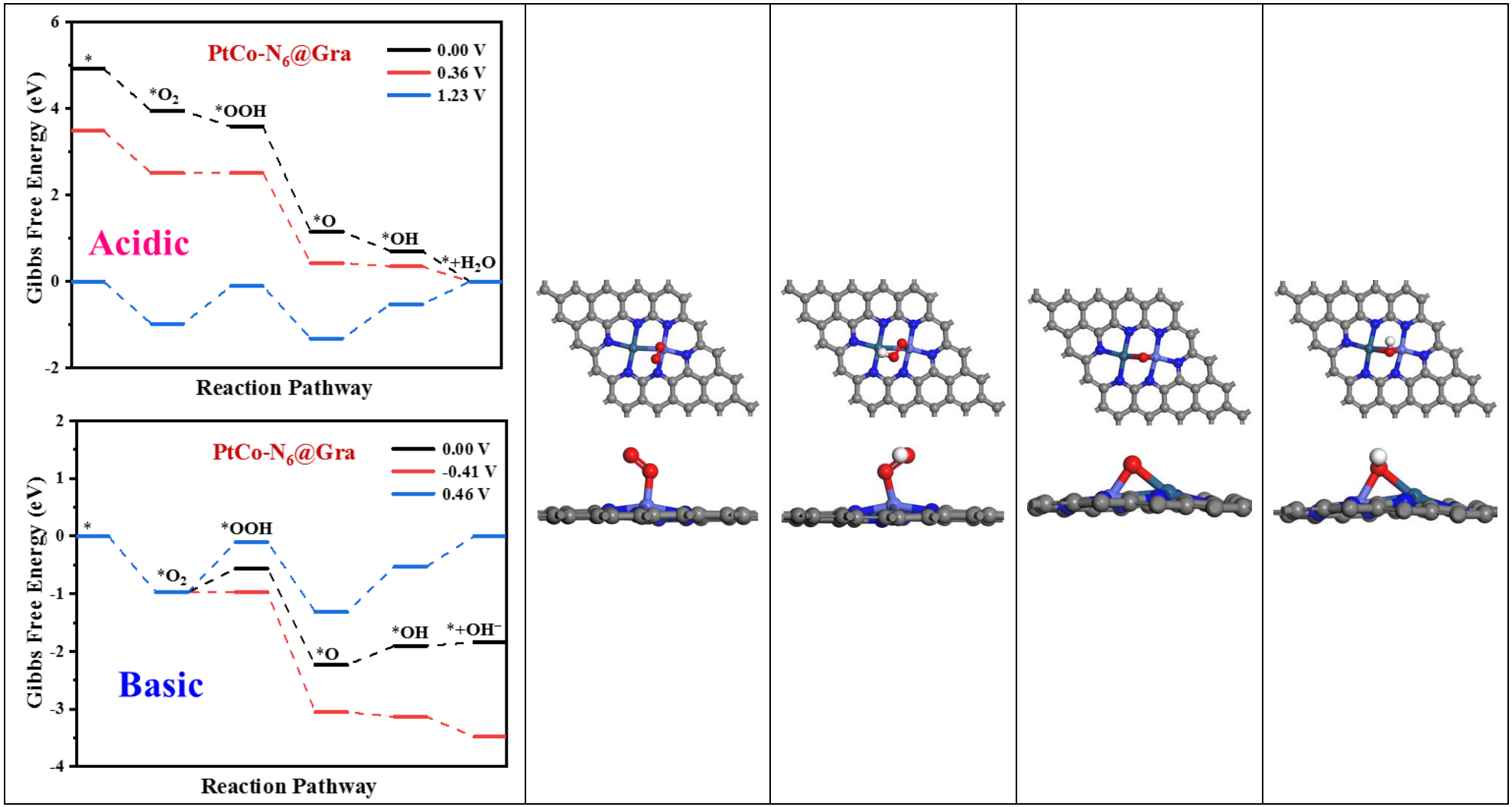
0.00 V
0.32 V
1.23 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Reaction Pathway
PtFe-N6@Gra
0.00 V
-0.45 V
0.46 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Reaction Pathway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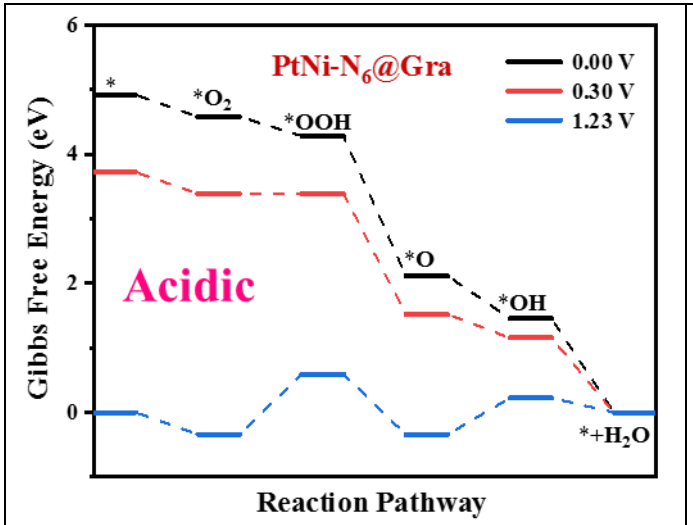
0.36 V
1.23 V
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
PtCo-N6@Gra
0.00 V
-0.41 V
0.46 V
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Gibbs Free Energy (eV)
Reaction Pathway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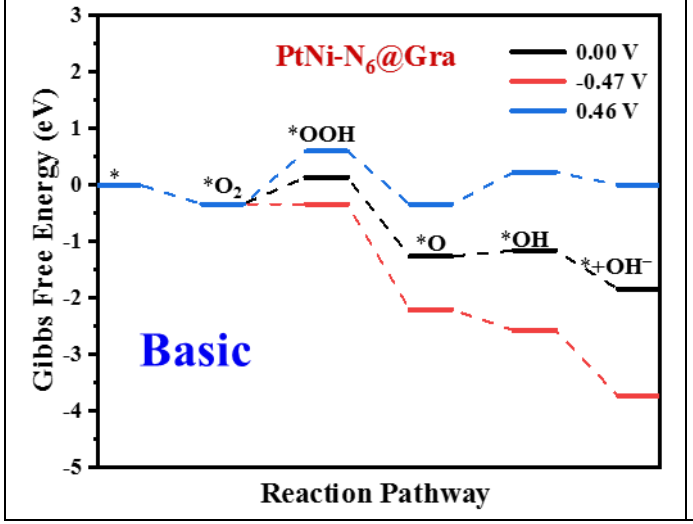
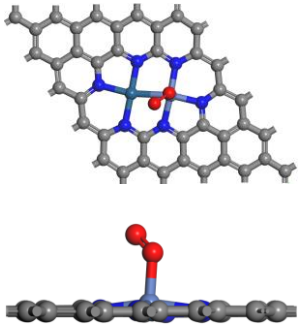
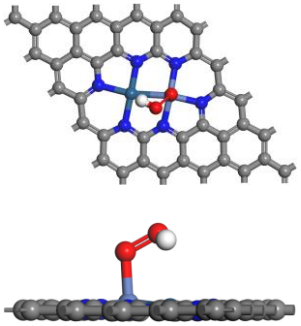
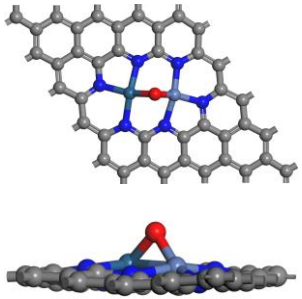
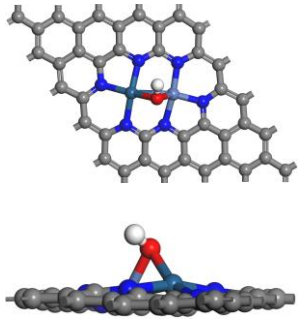
0.00 V
0.30 V
1.23 V
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
*
*O2
*OOH
*O
*OH
*+H2O

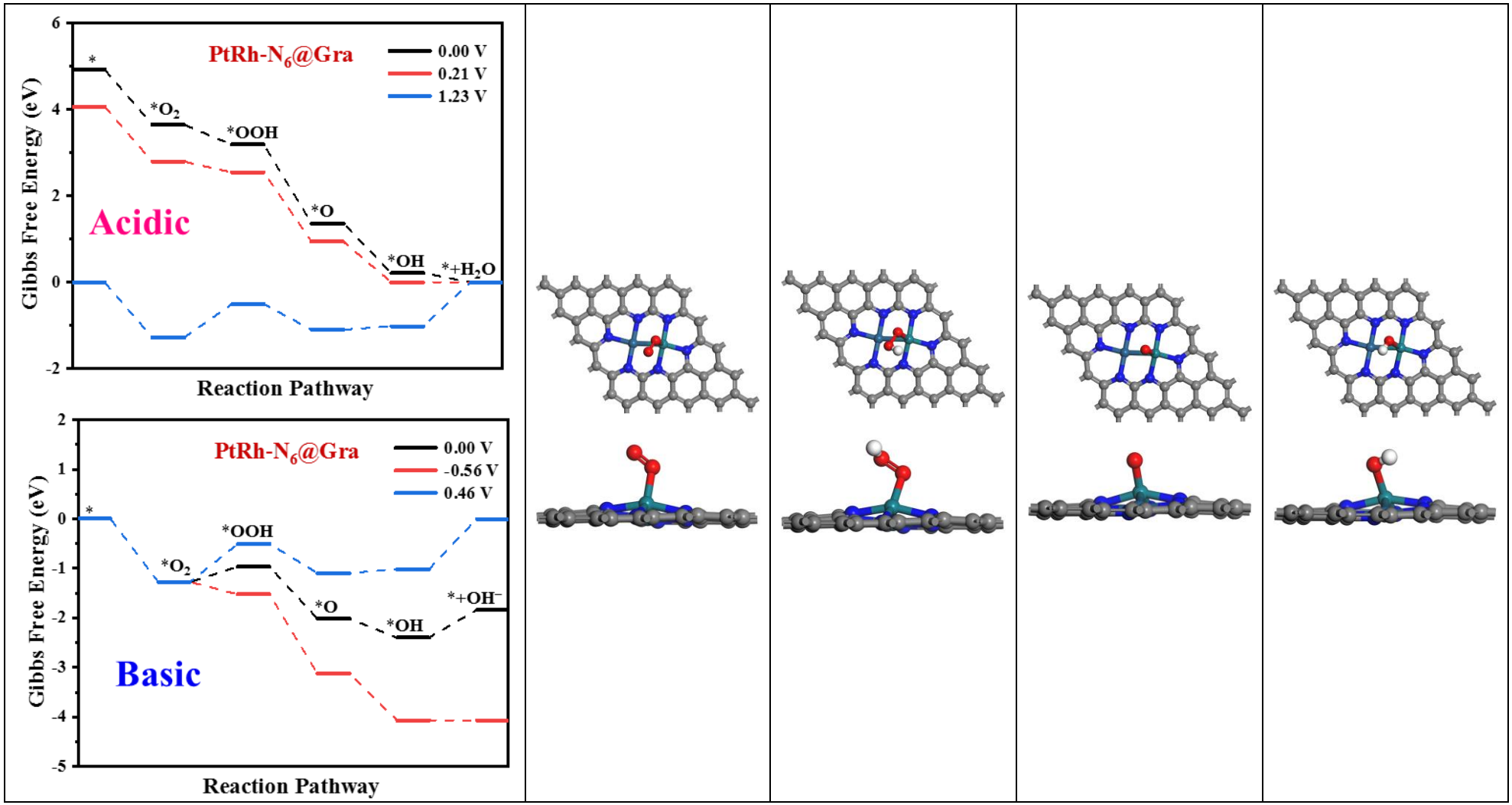

PtNi-N6@Gra
0.00 V
-0.47 V
0.46 V
Basic
Gibbs Free Energy (eV)
Reaction Pathway
*
*O2
*OOH
*O
*OH
*+OH−







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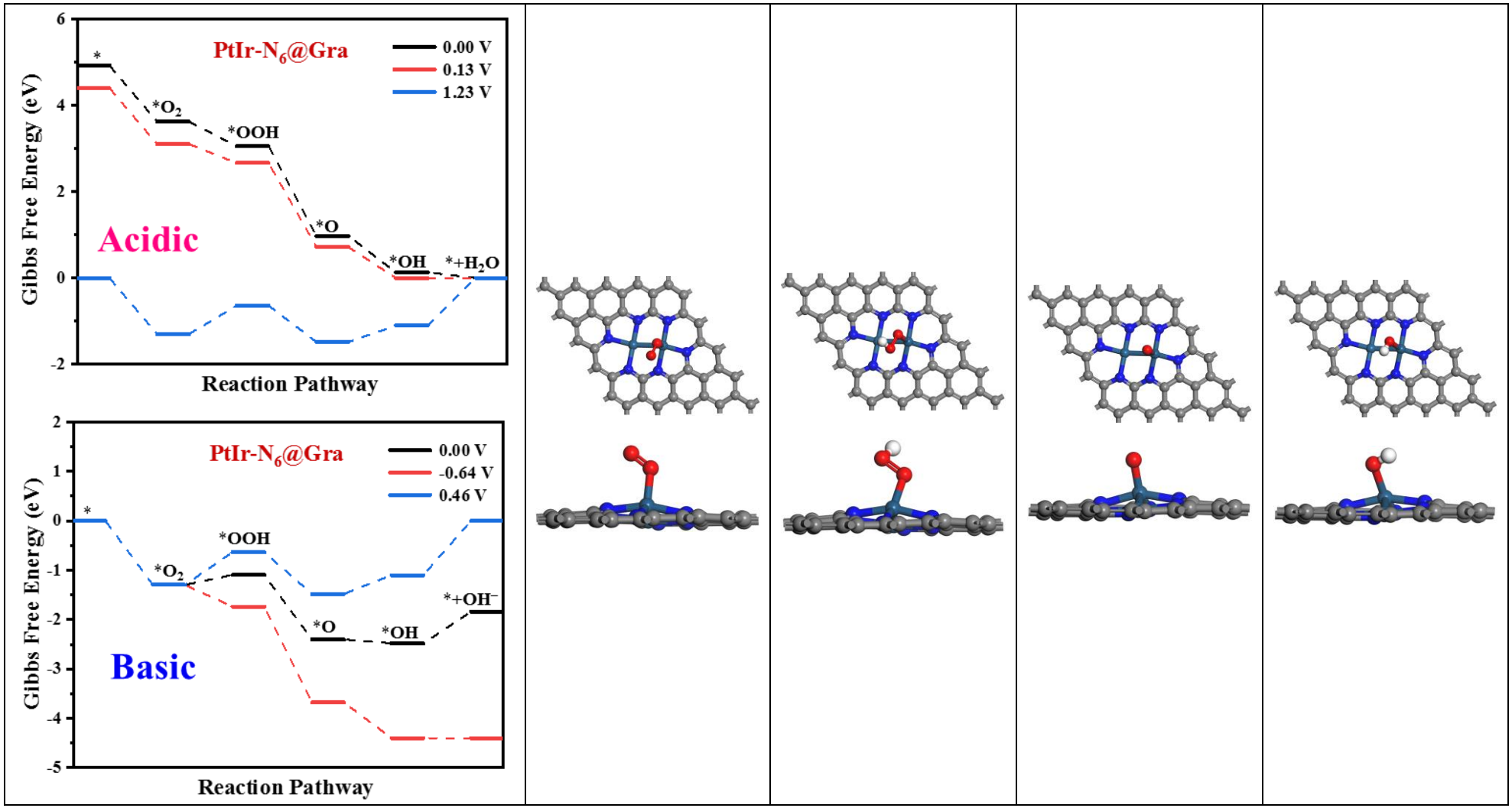
0.00 V
0.21 V
1.23 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Reaction Pathway
PtRh-N6@Gra
0.00 V
-0.56 V
0.46 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Reaction Pathway


PtIr-N6@Gra
0.00 V
0.13 V
1.23 V
Acidic
Gibbs Free Energy (eV)
Reaction Pathway
*
*O2
*OOH
*O
*OH
*+H2O
PtIr-N6@Gra
0.00 V
-0.64 V
0.46 V
Basic
Gibbs Free Energy (eV)
Reaction Pathway
*
*O2
*OOH
*O
*OH
*+OH−

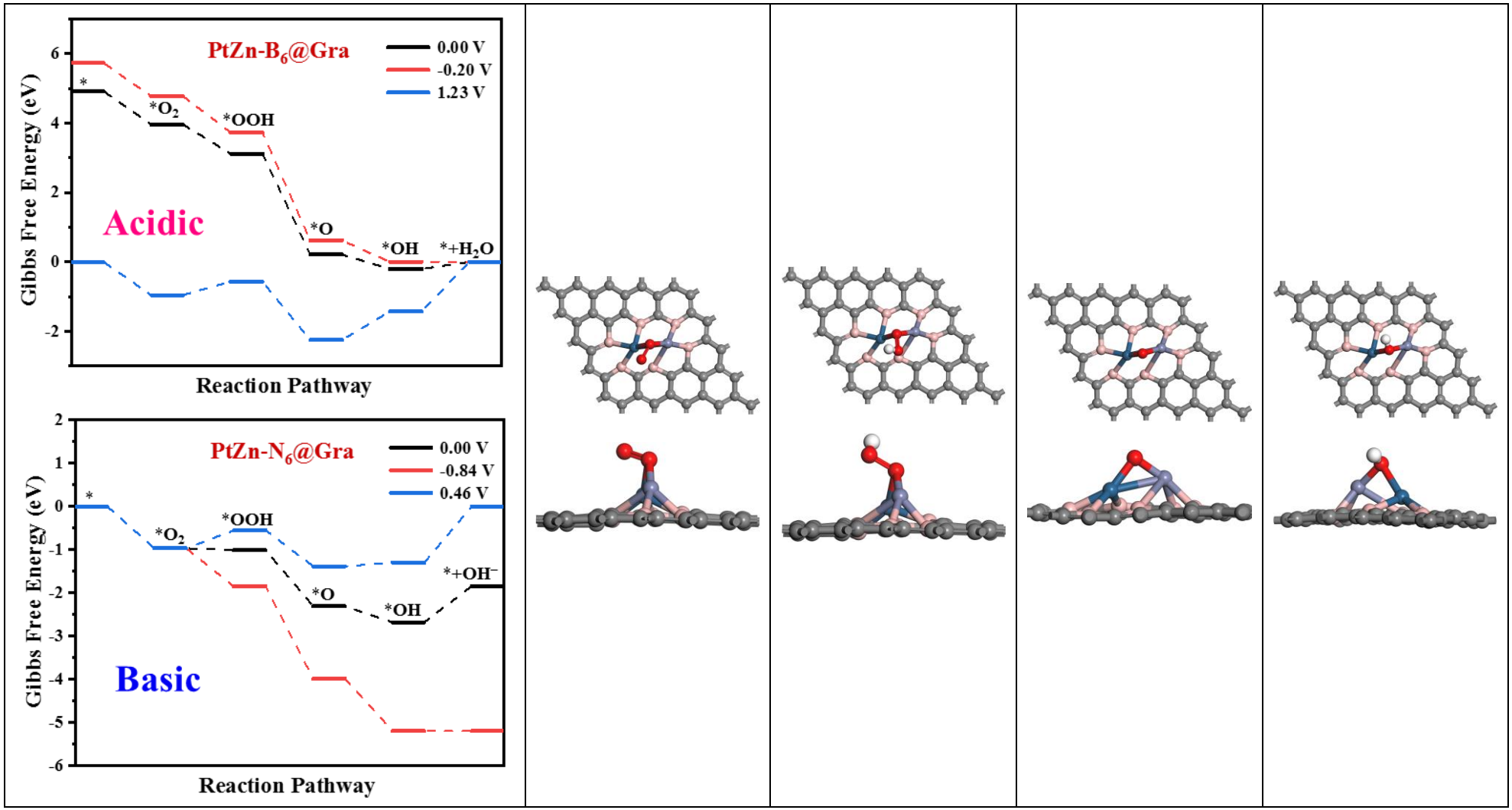

PtZn-B6@Gra
0.00 V
-0.20 V
1.23 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+H2O
Acidic
Reaction Pathway
PtZn-N6@Gra
0.00 V
-0.84 V
0.46 V
Gibbs Free Energy (eV)
*
*O2
*OOH
*O
*OH
*+OH−
Basic
Reaction Pathway

Table S5. Summary of the most favorable pathways of PtM-L_6@Gra catalysts under the acidic condition (pH=0), Gibbs free energy of the corresponding intermediates (eV), overpotentials (V), and potential-determining step (PDS) are listed.

Acidic	ΔG_0[a]	ΔG_1[a]	ΔG_2[a]	ΔG_3[a]	ΔG_4[a]	Overpotential	PDS
pH = 0	$O_2 \rightarrow *O_2$	$*O_2 \rightarrow *OOH$	$*OOH \rightarrow *O$	$*O \rightarrow *OH$	$*OH \rightarrow H_2O$		
PtCd-C_6@Gra	-0.53	-0.79	-0.51	-2.86	-0.23	1.00	ΔG_4[a]
PtCo-C_6@Gra	-1.24	-0.32	-2.63	-0.33	-0.40	0.91	ΔG_1[a]
PtFe-C_6@Gra	-1.27	-0.50	-2.39	-0.63	-0.13	1.10	ΔG_4[a]
PtIr-C_6@Gra	-1.36	-0.75	-2.56	-0.49	0.23	1.46	ΔG_4[a]
PtMn-C_6@Gra	-1.38	-0.38	-2.76	-0.42	0.03	1.26	ΔG_4[a]
PtRh-C_6@Gra	-1.50	-0.67	-1.93	-0.93	0.12	1.35	ΔG_4[a]
PtRu-C_6@Gra	-2.52	-0.61	-2.79	-0.21	1.21	2.44	ΔG_4[a]
PtZn-C_6@Gra	-0.21	-0.75	-2.14	-1.07	-0.74	0.49	ΔG_4[a]
PtNi-C_6@Gra	-0.29	-0.37	-2.61	-0.82	-0.83	0.86	ΔG_1[a]
PtCd-N_6@Gra	-1.59	-0.68	-0.97	-2.30	0.63	1.86	ΔG_4[a]
PtCo-N_6@Gra	-0.98	-0.36	-2.44	-0.44	-0.71	0.87	ΔG_1[a]
PtFe-N_6@Gra	-1.17	-0.45	-2.30	-0.69	-0.32	0.91	ΔG_4[a]
PtIr-N_6@Gra	-1.30	-0.57	-2.07	-0.85	-0.13	1.10	ΔG_4[a]
PtMn-N_6@Gra	-1.20	-0.49	-2.58	-0.48	-0.16	1.07	ΔG_4[a]
PtNi-N_6@Gra	-0.34	-0.30	-1.27	-0.66	-1.45	0.93	ΔG_1[a]
PtOs-N_6@Gra	-2.26	-1.13	-2.63	0.28	0.82	2.05	ΔG_4[a]
PtRh-N_6@Gra	-1.27	-0.46	-1.82	-1.15	-0.21	1.02	ΔG_4[a]
PtRu-N_6@Gra	-2.58	-0.08	-2.41	-0.17	1.04	2.27	ΔG_4[a]
PtZn-N_6@Gra	-0.97	-0.81	-2.06	-1.14	0.07	1.30	ΔG_4[a]
PtCd-B_6@Gra	-2.60	-0.17	-3.02	-0.23	1.10	2.33	ΔG_4[a]
PtNi-B_6@Gra	-2.40	-0.28	-2.36	-1.09	1.20	2.44	ΔG_4[a]
PtZn-B_6@Gra	-0.96	-0.85	-2.91	-0.41	0.20	1.43	ΔG_4[a]

Table S6. Summary of the most favorable pathways of PtM-L_6@Gra catalysts under the basic condition (pH=13), Gibbs free energy of the corresponding intermediates (eV), overpotentials (V), and PDS are listed.

Basic	$\Delta G_0{}^b$	$\Delta G_1{}^b$	$\Delta G_2{}^b$	$\Delta G_3{}^b$	$\Delta G_4{}^b$	Overpotential	PDS
pH = 13	$O_2 \rightarrow *O_2$	$*O_2 \rightarrow *OOH$	$*OOH \rightarrow *O$	$*O \rightarrow *OH$	$*OH \rightarrow OH^-$		
PtCd-C_6@Gra	-0.53	-0.02	0.26	-2.09	0.54	1.00	$\Delta G_4{}^b$
PtCo-C_6@Gra	-1.24	0.45	-1.86	0.44	0.37	0.91	$\Delta G_1{}^b$
PtFe-C_6@Gra	-1.27	0.27	-1.62	0.14	0.64	1.10	$\Delta G_4{}^b$
PtIr-C_6@Gra	-1.36	0.02	-1.79	0.28	1.00	1.46	$\Delta G_4{}^b$
PtMn-C_6@Gra	-1.38	0.39	-1.99	0.35	0.80	1.26	$\Delta G_4{}^b$
PtRh-C_6@Gra	-1.50	0.10	-1.16	-0.16	0.89	1.35	$\Delta G_4{}^b$
PtRu-C_6@Gra	-2.52	0.16	-2.02	0.56	1.98	2.44	$\Delta G_4{}^b$
PtZn-C_6@Gra	-0.21	0.02	-1.37	-0.30	0.03	0.49	$\Delta G_4{}^b$
PtNi-C_6@Gra	-0.29	0.40	-1.84	-0.05	-0.06	0.86	$\Delta G_1{}^b$
PtCd-N_6@Gra	-1.59	0.09	-0.20	-1.53	1.40	1.86	$\Delta G_4{}^b$
PtCo-N_6@Gra	-0.98	0.41	-1.67	0.33	0.06	0.87	$\Delta G_1{}^b$
PtFe-N_6@Gra	-1.17	0.32	-1.53	0.08	0.45	0.91	$\Delta G_4{}^b$
PtIr-N_6@Gra	-1.30	0.20	-1.31	-0.08	0.64	1.10	$\Delta G_4{}^b$
PtMn-N_6@Gra	-1.20	0.28	-1.81	0.29	0.61	1.07	$\Delta G_4{}^b$
PtNi-N_6@Gra	-0.34	0.47	-1.40	0.11	-0.68	0.93	$\Delta G_1{}^b$
PtOs-N_6@Gra	-2.26	-0.36	-1.86	1.05	1.59	2.05	$\Delta G_4{}^b$
PtRh-N_6@Gra	-1.27	0.31	-1.05	-0.38	0.56	1.02	$\Delta G_4{}^b$
PtRu-N_6@Gra	-2.58	-0.03	-1.64	0.60	1.81	2.27	$\Delta G_4{}^b$
PtZn-N_6@Gra	-0.97	-0.04	-1.29	-0.37	0.84	1.30	$\Delta G_4{}^b$
PtCd-B_6@Gra	-2.60	0.60	-2.25	0.54	1.87	2.33	$\Delta G_4{}^b$
PtNi-B_6@Gra	-2.40	0.49	-1.59	-0.32	1.98	2.44	$\Delta G_4{}^b$
PtZn-B_6@Gra	-0.96	-0.08	-2.14	0.35	0.97	1.43	$\Delta G_4{}^b$

Table S7. Thermal corrections (eV) of small molecule (H_2O, H_2) and the reaction intermediates (O_xH_y) along the most favorable pathways on PtM-L_6@Gra. Thermal corrections of the small molecules (H_2O, H_2) can be obtained from the NIST database.

molecule	ZPE	TS	∫CpdT
H_2O	0.56	0.58	0.10
H_2	0.27	0.40	0.09

O_xH_y	PtCd-C_6@Gra			PtCo-C_6@Gra			PtFe-C_6@Gra			PtZn-C_6@Gra			PtNi-C_6@Gra			PtZn-B_6@Gra		
	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT
*O_2	0.11	0.24	0.10	0.14	0.16	0.08	0.16	0.15	0.07	0.13	0.19	0.09	0.12	0.16	0.07	0.13	0.15	0.07
*OOH	0.42	0.24	0.11	0.45	0.17	0.09	0.47	0.17	0.08	0.43	0.20	0.10	0.43	0.20	0.10	0.44	0.17	0.09
*O	0.04	0.12	0.05	0.08	0.05	0.03	0.07	0.07	0.04	0.07	0.05	0.03	0.08	0.07	0.03	0.08	0.05	0.03
*OH	0.33	0.15	0.07	0.37	0.07	0.04	0.35	0.10	0.05	0.37	0.07	0.04	0.37	0.07	0.04	0.37	0.07	0.04

*O_xH_y	PtCo-N_6@Gra			PtFe-N_6@Gra			PtIr-N_6@Gra			PtMn-N_6@Gra			PtNi-N_6@Gra			PtRh-N_6@Gra		
	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT	ZPE	TS	∫CpdT
*O_2	0.15	0.16	0.08	0.15	0.15	0.07	0.15	0.16	0.08	0.13	0.19	0.09	0.12	0.20	0.09	0.14	0.18	0.08
*OOH	0.45	0.17	0.09	0.47	0.17	0.08	0.45	0.19	0.09	0.38	0.23	0.11	0.43	0.20	0.10	0.45	0.18	0.09
*O	0.09	0.04	0.02	0.07	0.07	0.04	0.07	0.07	0.04	0.08	0.06	0.03	0.09	0.03	0.02	0.06	0.07	0.04
*OH	0.39	0.05	0.03	0.35	0.10	0.05	0.36	0.09	0.05	0.33	0.12	0.06	0.38	0.07	0.04	0.35	0.10	0.05

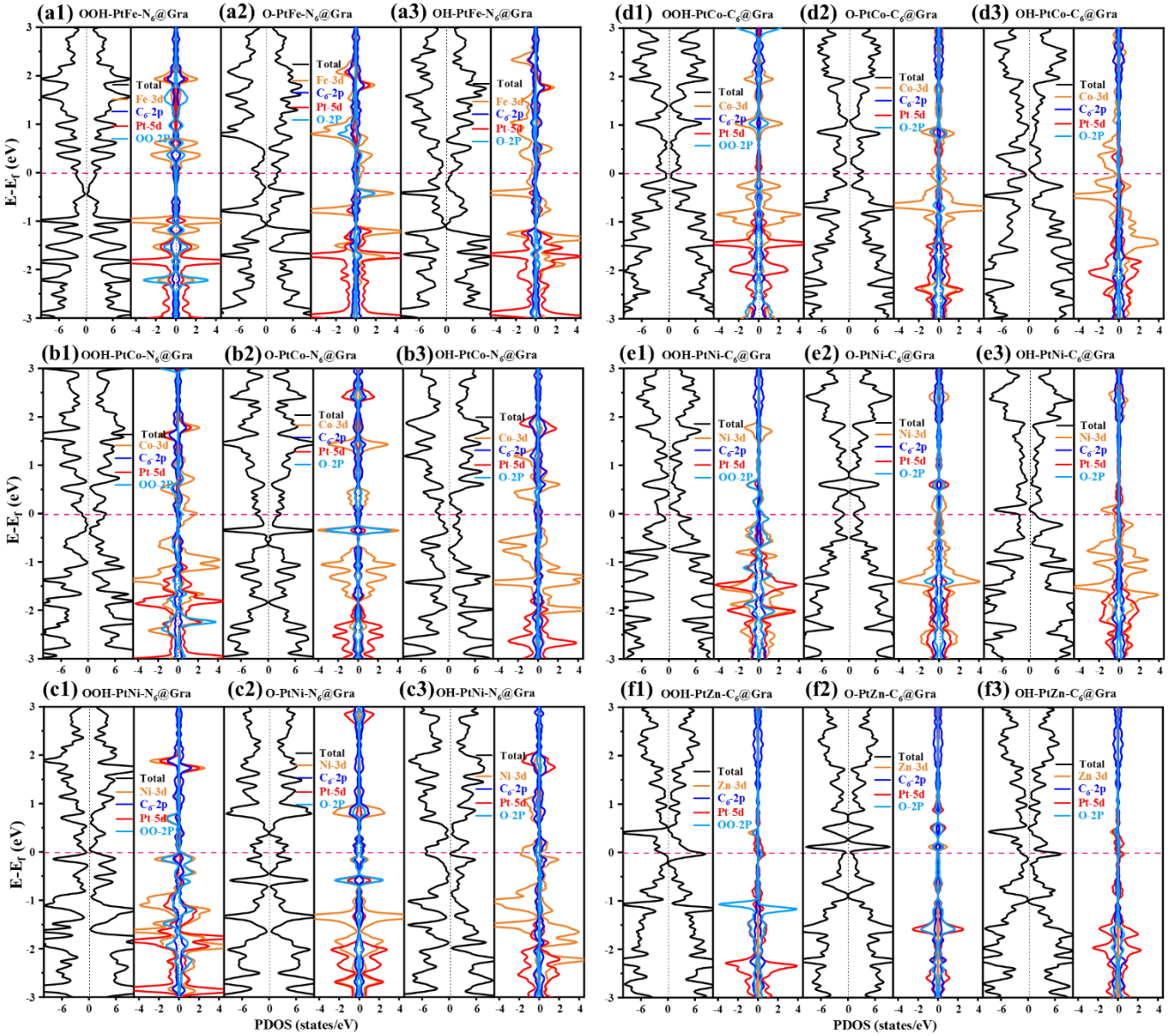


Figure S3. Calculated PDOS of various intermediates (*OOH, *O, *OH) adsorption on the active site of (a1-a3) PtFe-N_6@Gra, (b1-b3) PtCo-N_6@Gra, (c1-c3) PtNi-N_6@Gra, (d1-d3) PtCo-C_6@Gra, (e1-e3) PtNi-C_6@Gra, (f1-f3) PtZn-C_6@Gra.

Table S8. The magnetic moment before and after O_2 adsorption. (*) and (*O_2) stand for before and after O_2 adsorption on the selected catalysts, respectively. The M represents the transition metal atom, the L_6 represents the six coordination atoms connected to the Pt and M atom, and the FV-Gra represents the rest part except the Pt, M and L_6 atoms. The positive and negative charge values represent gain and loss of electrons, respectively.

PtM-L_6@Gra	Magnetic moment (*)/μ_B					Magnetic moment (*O_2)/μ_B				
	Pt	M	L_6	FV-Gra	total	Pt	M	L_6	FV-Gra	total
PtFe-C_6@Gra	0.02	2.57	-0.12	0.08	2.56	0.00	0.05	-0.01	0.00	-0.01
PtCo-C_6@Gra	0.01	1.22	-0.09	-0.01	1.12	-0.02	-0.34	0.02	0.00	-0.24
PtNi-C_6@Gra	0.00	0.00	0.00	0.00	0.00	0.01	0.21	0.01	0.02	0.68
PtZn-C_6@Gra	0.06	0.11	0.31	0.11	0.58	-0.06	-0.06	-0.19	-0.09	0.48
PtCd-C_6@Gra	0.10	0.13	0.45	0.14	0.81	0.00	0.06	0.39	0.08	0.68
PtMn-N_6@Gra	0.07	3.44	-0.15	-0.03	3.35	0.01	2.52	-0.09	-0.03	-0.40
PtFe-N_6@Gra	0.12	2.55	0.01	-0.02	2.65	0.00	0.00	0.00	0.00	0.00
PtCo-N_6@Gra	0.05	1.25	-0.03	-0.04	1.23	-0.02	0.15	0.00	0.00	0.17
PtNi-N_6@Gra	0.00	0.00	0.00	0.00	0.00	-0.01	0.38	0.02	0.02	0.58
PtRh-N_6@Gra	0.26	0.49	0.10	0.02	0.86	-0.04	-0.01	0.00	0.02	0.25
PtIr-N_6@Gra	0.04	0.12	0.01	0.01	0.17	0.00	0.00	0.00	0.00	0.00
PtZn-B_6@Gra	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

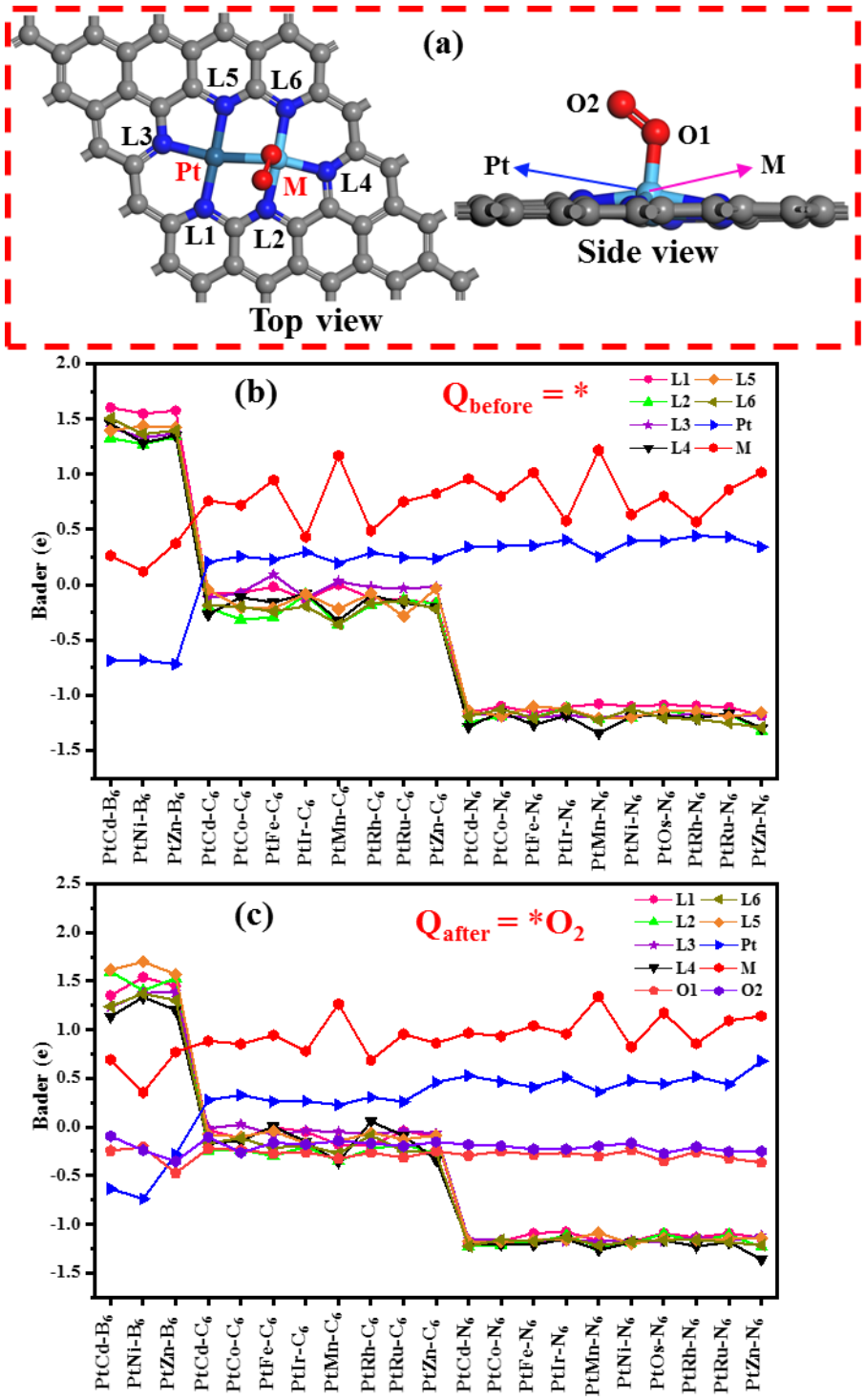


Figure S4. Schematic diagram of (a) the definition of the six coordination atoms connected to Pt and M (L1-L6), and absorbed O_2. O1 represents that O is close to the metal, O2 represents that O is far away from the metal, respectively. The Bader charge diagrams of each part (i.e., L1-L6, Pt, M, O1, O2) of the 21 catalysts (b) before and (c) after O_2 adsorption.

Table S9. Bader charge of each part of 21 catalysts before adsorbing O_2, the labels of different atoms following Figure S4a.

PtM-L_6@Gra	L1	L2	L3	L4	L5	L6	Pt	M
PtCd-B_6@Gra	1.60	1.33	1.42	1.46	1.40	1.51	-0.68	0.26
PtNi-B_6@Gra	1.55	1.27	1.33	1.28	1.44	1.36	-0.68	0.12
PtZn-B_6@Gra	1.58	1.34	1.37	1.35	1.43	1.39	-0.72	0.37
PtCd-C_6@Gra	-0.08	-0.21	-0.12	-0.27	-0.05	-0.19	0.21	0.76
PtCo-C_6@Gra	-0.08	-0.32	-0.07	-0.11	-0.21	-0.20	0.26	0.72
PtFe-C_6@Gra	-0.02	-0.29	0.09	-0.16	-0.21	-0.24	0.23	0.95
PtIr-C_6@Gra	-0.14	-0.09	-0.12	-0.08	-0.08	-0.19	0.30	0.43
PtMn-C_6@Gra	0.00	-0.36	0.03	-0.33	-0.22	-0.36	0.19	1.17
PtRh-C_6@Gra	-0.12	-0.19	-0.02	-0.10	-0.08	-0.17	0.29	0.49
PtRu-C_6@Gra	-0.14	-0.14	-0.03	-0.16	-0.29	-0.15	0.25	0.75
PtZn-C_6@Gra	-0.17	-0.17	-0.02	-0.21	-0.03	-0.22	0.24	0.82
PtCd-N_6@Gra	-1.16	-1.24	-1.15	-1.28	-1.14	-1.19	0.34	0.96
PtCo-N_6@Gra	-1.10	-1.19	-1.19	-1.15	-1.19	-1.13	0.35	0.80
PtFe-N_6@Gra	-1.16	-1.20	-1.20	-1.27	-1.10	-1.21	0.35	1.02
PtIr-N_6@Gra	-1.11	-1.12	-1.18	-1.19	-1.12	-1.12	0.41	0.58
PtMn-N_6@Gra	-1.08	-1.21	-1.20	-1.34	-1.21	-1.23	0.25	1.22
PtNi-N_6@Gra	-1.10	-1.20	-1.19	-1.19	-1.20	-1.12	0.40	0.64
PtOs-N_6@Gra	-1.09	-1.13	-1.19	-1.18	-1.14	-1.21	0.40	0.80
PtRh-N_6@Gra	-1.10	-1.19	-1.17	-1.21	-1.14	-1.22	0.44	0.57
PtRu-N_6@Gra	-1.11	-1.17	-1.18	-1.16	-1.20	-1.25	0.43	0.86
PtZn-N_6@Gra	-1.19	-1.32	-1.19	-1.30	-1.16	-1.29	0.34	1.02

Table S10. Bader charge of each part of 21 catalysts after adsorbing O_2, the labels of different atoms following Figure S4a.

PtM-L_6@Gra	L1	L2	L3	L4	L5	L6	Pt	M	O1	O2
PtCd-B_6@Gra	1.35	1.60	1.23	1.14	1.62	1.24	-0.63	0.69	-0.24	-0.09
PtNi-B_6@Gra	1.54	1.40	1.38	1.33	1.70	1.37	-0.74	0.36	-0.21	-0.24
PtZn-B_6@Gra	1.45	1.53	1.38	1.20	1.57	1.30	-0.28	0.77	-0.47	-0.35
PtCd-C_6@Gra	-0.03	-0.25	-0.01	-0.17	-0.08	-0.17	0.28	0.89	-0.22	-0.10
PtCo-C_6@Gra	-0.12	-0.23	0.03	-0.14	-0.10	-0.12	0.33	0.85	-0.24	-0.26
PtFe-C_6@Gra	0.00	-0.30	-0.08	0.01	-0.04	-0.21	0.26	0.94	-0.27	-0.16
PtIr-C_6@Gra	-0.05	-0.20	-0.04	-0.15	-0.17	-0.19	0.27	0.78	-0.26	-0.18
PtMn-C_6@Gra	-0.18	-0.35	-0.05	-0.36	-0.15	-0.27	0.23	1.27	-0.32	-0.14
PtRh-C_6@Gra	-0.19	-0.23	-0.07	0.06	-0.06	-0.09	0.31	0.69	-0.26	-0.17
PtRu-C_6@Gra	-0.04	-0.18	-0.04	-0.09	-0.13	-0.25	0.26	0.96	-0.31	-0.20
PtZn-C_6@Gra	-0.10	-0.27	-0.06	-0.34	-0.08	-0.26	0.46	0.86	-0.25	-0.15
PtCd-N_6@Gra	-1.20	-1.23	-1.15	-1.20	-1.17	-1.23	0.53	0.97	-0.29	-0.18
PtCo-N_6@Gra	-1.17	-1.21	-1.16	-1.21	-1.18	-1.16	0.47	0.93	-0.25	-0.19
PtFe-N_6@Gra	-1.09	-1.18	-1.16	-1.21	-1.16	-1.17	0.41	1.04	-0.28	-0.23
PtIr-N_6@Gra	-1.08	-1.12	-1.17	-1.15	-1.16	-1.13	0.51	0.96	-0.26	-0.23
PtMn-N_6@Gra	-1.17	-1.23	-1.18	-1.27	-1.09	-1.22	0.36	1.34	-0.30	-0.20
PtNi-N_6@Gra	-1.18	-1.20	-1.17	-1.19	-1.20	-1.18	0.48	0.82	-0.24	-0.16
PtOs-N_6@Gra	-1.09	-1.10	-1.18	-1.16	-1.15	-1.16	0.44	1.17	-0.35	-0.27
PtRh-N_6@Gra	-1.14	-1.18	-1.13	-1.23	-1.16	-1.16	0.52	0.86	-0.25	-0.20
PtRu-N_6@Gra	-1.09	-1.11	-1.17	-1.18	-1.15	-1.19	0.44	1.09	-0.32	-0.25
PtZn-N_6@Gra	-1.14	-1.23	-1.11	-1.36	-1.14	-1.22	0.68	1.14	-0.37	-0.25

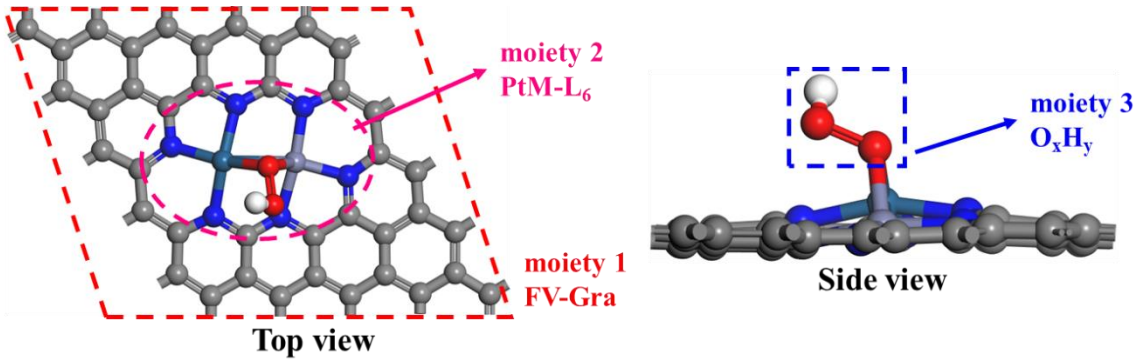


Figure S5. Schematic diagram of the definition of the three moieties for the intermediate species. Moiety 1, 2 and 3 represent the PtM-L_6@Gra excluding the PtM-L_6 part (the PtM-L_6 part represent the Pt, M atoms and six coordinated atoms) (moiety 1), the PtM-L_6 part (moiety 2), and the adsorbed O_xH_y intermediate species (moiety 3), respectively.

Table S11. Charge variation of the three moieties (PtM-L_6, O_xH_y and FV-Gra) along the most favorable reaction pathway on the 9 selected catalysts. The definition of moieties following Figure S5. The positive and negative charge values represent gain and loss of electrons, respectively.

*O_xH_y	Moiety	PtCo-C_6@Gra	PtZn-C_6@Gra	PtCd-C_6@Gra	PtFe-C_6@Gra	PtCo-N_6@Gra	PtFe-N_6@Gra	PtMn-N_6@Gra	PtIr-N_6@Gra	PtZn-B_6@Gra
*O_2	PtM-L_6	-0.51	0.04	-0.40	-0.24	-0.11	-0.24	-0.35	-0.52	-0.81
	FV-Gra	0.01	-0.44	0.08	-0.19	-0.33	-0.27	-0.14	0.03	-0.01
	O_2	0.50	0.40	0.33	0.43	0.45	0.51	0.50	0.49	0.83
*OOH	PtM-L_6	0.05	-0.30	-0.14	0.04	0.03	-0.12	0.02	-0.01	0.16
	FV-Gra	0.10	0.18	-0.10	0.02	-0.01	0.08	-0.34	0.05	0.16
	OOH	-0.15	0.12	0.24	-0.06	-0.03	0.04	0.32	-0.03	-0.32
*O	PtM-L_6	-0.30	-0.24	0.14	0.25	-0.53	0.01	-0.17	-0.04	-0.16
	FV-Gra	-0.09	-0.04	-0.19	-0.44	0.21	-0.07	0.39	-0.13	-0.22
	O	0.39	0.28	0.05	0.19	0.32	0.06	-0.23	0.16	0.38
*OH	PtM-L_6	-0.01	0.21	-0.11	-0.22	-0.01	-0.11	0.13	0.13	0.13
	FV-Gra	0.30	0.11	0.18	0.41	0.34	0.27	-0.05	0.07	0.28
	OH	-0.29	-0.32	-0.07	-0.18	-0.33	-0.16	-0.09	-0.20	-0..41

Table S12. The d_{*}(Pt-M), d_{*O_2}(Pt-M), d_{*OOH}(Pt-M), d_{*O}(Pt-M), d_{*OH}(Pt-M) and avg[d_a(Pt-M)] of 21 catalysts were listed.

PtM-L_6@Gra	d_{*}(Pt-M)	d_{*O_2}(Pt-M)	d_{*OOH}(Pt-M)	d_{*O}(Pt-M)	d_{*OH}(Pt-M)	avg[d_a(Pt-M)]
PtCd-B_6@Gra	2.45	2.62	2.99	3.02	3.04	2.83
PtNi-B_6@Gra	2.32	2.55	2.59	2.54	2.63	2.53
PtZn-B_6@Gra	2.32	2.62	2.79	2.74	2.79	2.65
PtCd-C_6@Gra	2.52	2.69	2.69	2.73	2.70	2.67
PtCo-C_6@Gra	2.42	2.73	2.66	2.63	2.70	2.63
PtFe-C_6@Gra	2.47	2.53	2.62	2.56	2.59	2.55
PtIr-C_6@Gra	2.43	2.57	2.68	2.68	2.72	2.62
PtMn-C_6@Gra	2.47	2.55	2.57	2.46	2.56	2.52
PtRh-C_6@Gra	2.45	2.71	2.74	2.71	2.72	2.67
PtRu-C_6@Gra	2.42	2.60	2.69	2.59	2.70	2.60
PtZn-C_6@Gra	2.49	2.61	2.63	2.66	2.64	2.60
PtCd-N_6@Gra	2.47	2.73	2.92	2.99	2.97	2.82
PtCo-N_6@Gra	2.34	2.41	2.46	2.51	2.56	2.46
PtFe-N_6@Gra	2.33	2.41	2.44	2.45	2.46	2.42
PtIr-N_6@Gra	2.40	2.47	2.51	2.50	2.51	2.48
PtMn-N_6@Gra	2.32	2.38	2.41	2.45	2.40	2.39
PtNi-N_6@Gra	2.37	2.39	2.38	2.67	2.55	2.47
PtOs-N_6@Gra	2.38	2.48	2.49	2.50	2.47	2.46
PtRh-N_6@Gra	2.41	2.47	2.51	2.51	2.51	2.48
PtRu-N_6@Gra	2.36	2.47	2.48	2.49	2.45	2.45
PtZn-N_6@Gra	2.43	2.54	2.58	2.65	2.60	2.56

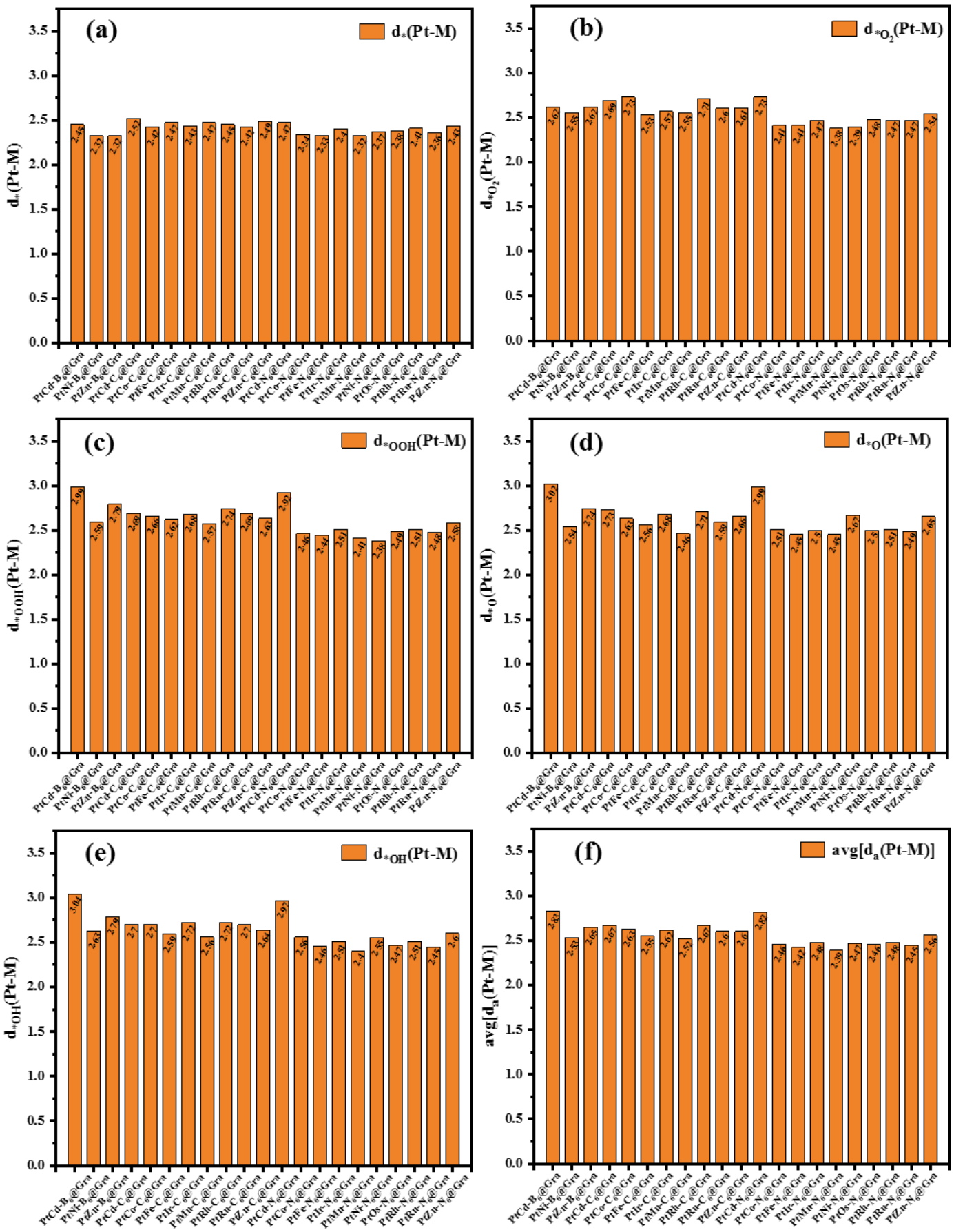
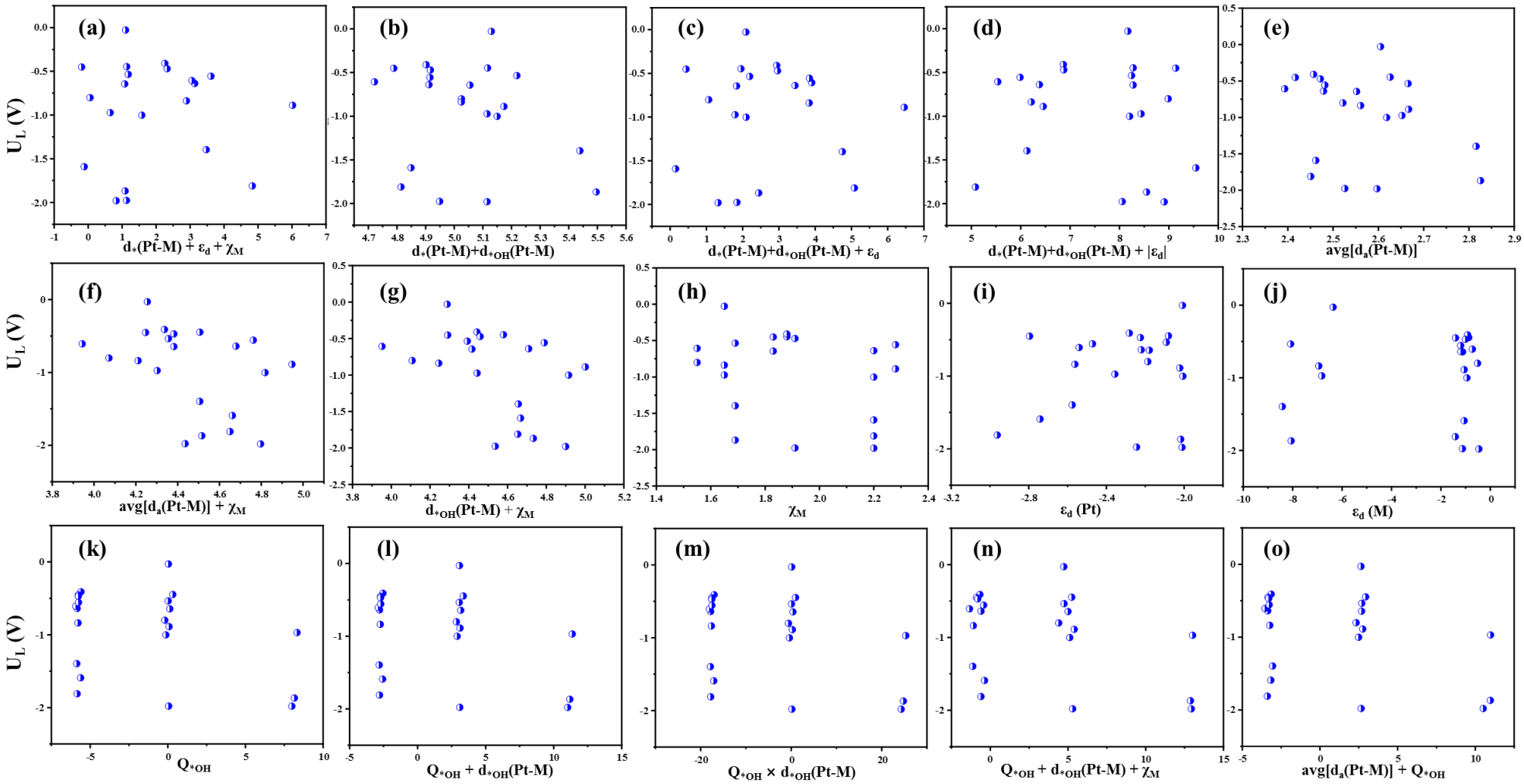


Figure S6. The diagrams of Pt-M bond length values of 21 catalysts substrates and various intermediates. (a) d_{*}(Pt-M), (b) d_{*O_2}(Pt-M), (c) d_{*OOH}(Pt-M), (d) d_{*O}(Pt-M), (e) d_{*OH}(Pt-M), and (f) avg[d_a(Pt-M)].


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
(m)
(n)
(o)
U_L (V)
d*(Pt-M) + εd + χM
d*(Pt-M)+d*OH(Pt-M)
d*(Pt-M)+d*OH(Pt-M) + εd
d*(Pt-M)+d*OH(Pt-M) + |εd|
avg[da(Pt-M)]
avg[da(Pt-M)] + χM
d*OH(Pt-M) + χM
χM
εd (Pt)
εd (M)
Q*OH
Q*OH + d*OH(Pt-M)
Q*OH × d*OH(Pt-M)
Q*OH + d*OH(Pt-M) + χM
avg[da(Pt-M)] + Q*OH

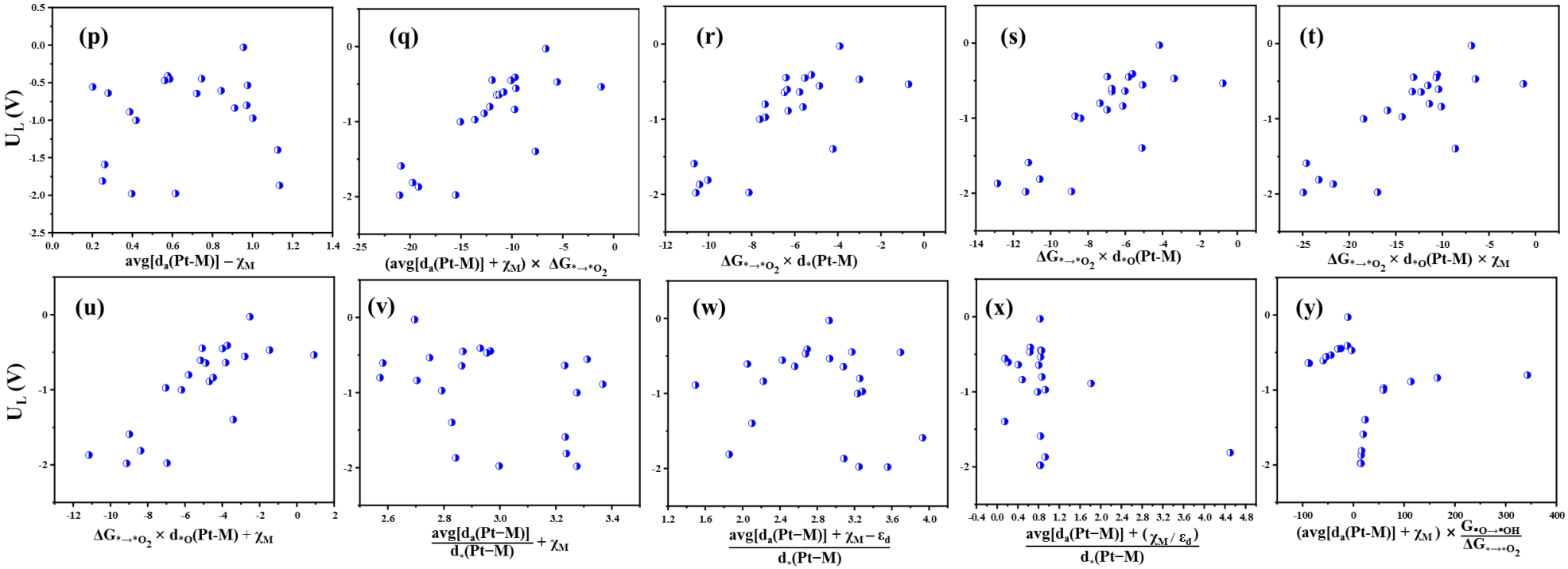


Figure S7. There is no clear structure-activity relationship between various descriptors and the limiting potential (U_L) after many tentative trial and error. $\Delta G_{*\rightarrow *O_2}$ and $\Delta G_{*O\rightarrow *OH}$ represent the Gibbs free energy change of O_2 adsorption, the second protonation step under basic condition, respectively. The d_*(Pt-M), d_{*O}(Pt-M), d_{*OH}(Pt-M) represent the distance between the active center metals Pt and M of the free substrate, substrate adsorbed O intermediate, substrate adsorbed OH intermediate, respectively. avg[d_a(Pt-M)] represents the average value of the distance of the active center metals Pt and M of the substrates and intermediates.

Table S13. The O-O bond length (Å) of free O_2 (g), $*O_2$ and *OOH on the 16 selected PtM-L_6@Gra catalysts.

PtM-L_6@Gra	O_2(g)	$*O_2$	*OOH
PtCd-C_6@Gra	1.21	1.28	1.49
PtCo-C_6@Gra	1.21	1.34	1.46
PtFe-C_6@Gra	1.21	1.27	1.48
PtZn-C_6@Gra	1.21	1.29	1.48
PtNi-C_6@Gra	1.21	1.26	1.46
PtMn-C_6@Gra	1.21	1.28	1.98
PtRh-C_6@Gra	1.21	1.29	1.46
PtIr-C_6@Gra	1.21	1.29	1.48
PtCo-N_6@Gra	1.21	1.28	1.46
PtFe-N_6@Gra	1.21	1.29	1.68
PtIr-N_6@Gra	1.21	1.30	1.50
PtMn-N_6@Gra	1.21	1.29	1.98
PtNi-N_6@Gra	1.21	1.28	1.42
PtRh-N_6@Gra	1.21	1.29	1.47
PtZn-N_6@Gra	1.21	1.33	1.48
PtZn-B_6@Gra	1.21	1.41	1.49

Table S14. The calculated cohesive energies (E_c, eV/atom) of PtM bulk and the binding energies (E_b, eV/atom) of Pt and M atoms embedded in N_6@Gra substrate, and the binding energy along with the cohesive energy (E_b+E_c). "/" represents that the energy of the corresponding catalyst has not been obtained.

metal	E_b	E_c	E_b+E_c
Sc	-15.96	5.52	-10.45
Ti	-16.94	6.22	-10.72
V	-16.01	6.14	-9.87
Cr	-14.40	5.41	-8.99
Mn	-14.95	5.19	-9.76
Fe	-15.55	5.88	-9.67
Co	-16.00	6.13	-9.87
Ni	-15.93	5.80	-10.13
Cu	-14.22	5.17	-9.05
Zn	-11.47	3.89	-7.57
Y	-14.22	5.49	-8.73
Zr	-16.49	6.64	-9.85
Nb	-16.33	6.92	-9.40
Mo	-14.83	6.62	-8.21
Tc	-15.52	7.00	-8.52
Ru	-15.35	7.06	-8.29
Rh	-15.51	6.50	-9.01
Pd	-14.04	5.33	-8.71
Ag	-11.91	4.67	-7.23
Cd	-9.36	3.70	-5.66
Lu	-13.18	5.48	-7.70
Hf	-16.75	6.77	-9.98
Ta	-17.55	7.70	-9.85
W	-16.29	7.72	-8.57
Re	-15.28	7.33	-7.95
Os	-16.22	7.64	-8.58
Ir	-16.65	7.34	-9.31
Pt	-16.02	6.34	-9.69
Ag	-12.82	5.01	-7.80
Hg	/	/	/

Table S15. The calculated cohesive energies (E_c, eV/atom) of PtM bulk and the binding energies (E_b, eV/atom) of Pt and M atoms embedded in C_6@Gra substrate, and the binding energy along with the cohesive energy (E_b+E_c). "/" represents that the energy of the corresponding catalyst has not been obtained.

metal	E_b	E_c	E_b+E_c
Sc	-18.16	5.52	-12.64
Ti	-19.43	6.22	-13.21
V	-18.48	6.14	-12.34
Cr	-17.11	5.41	-11.70
Mn	-17.94	5.19	-12.75
Fe	-18.68	5.88	-12.79
Co	-19.19	6.13	-13.06
Ni	-19.13	5.80	-13.33
Cu	-17.34	5.17	-12.17
Zn	-14.72	3.89	-10.83
Y	-16.52	5.49	-11.02
Zr	-19.09	6.64	-12.44
Nb	-18.74	6.92	-11.82
Mo	-17.71	6.62	-11.10
Tc	-18.74	7.00	-11.74
Ru	-19.25	7.06	-12.19
Rh	-19.16	6.50	-12.66
Pd	-17.62	5.33	-12.29
Ag	-15.39	4.67	-10.72
Cd	-12.97	3.70	-9.27
Lu	-16.49	5.48	-11.00
Hf	-19.39	6.77	-12.63
Ta	-20.07	7.70	-12.37
W	-19.43	7.72	-11.71
Re	-18.78	7.33	-11.45
Os	-19.97	7.64	-12.32
Ir	-20.74	7.34	-13.40
Pt	-20.13	6.34	-13.79
Ag	-16.95	5.01	-11.94
Hg	/	/	/

Table S16. The calculated cohesive energies (E_c, eV/atom) of PtM bulk and the binding energies (E_b, eV/atom) of Pt and M atoms embedded in B_6@Gra substrate, and the binding energy along with the cohesive energy (E_b+E_c). "/" represents that the energy of the corresponding catalyst has not been obtained.

metal	E_b	E_c	E_b+E_c
Sc	-11.52	5.52	-6.01
Ti	-12.70	6.22	-6.47
V	-11.42	6.14	-5.28
Cr	-8.68	5.41	-3.27
Mn	-10.21	5.19	-5.02
Fe	-11.59	5.88	-5.71
Co	-11.92	6.13	-5.79
Ni	-11.97	5.80	-6.17
Cu	-11.10	5.17	-5.94
Zn	-9.33	3.89	-5.43
Y	-9.48	5.49	-3.98
Zr	-12.25	6.64	-5.61
Nb	-11.96	6.92	-5.04
Mo	-10.23	6.62	-3.62
Tc	-11.56	7.00	-4.56
Ru	-12.17	7.06	-5.11
Rh	-12.01	6.50	-5.51
Pd	-10.16	5.33	-4.84
Ag	-8.54	4.67	-3.87
Cd	-7.16	3.70	-3.46
Lu	-9.57	5.48	-4.09
Hf	-12.49	6.77	-5.72
Ta	-12.16	7.70	-4.46
W	-11.89	7.72	-4.17
Re	-11.10	7.33	-3.77
Os	-12.35	7.64	-4.71
Ir	-13.22	7.34	-5.87
Pt	-11.74	6.34	-5.40
Ag	-9.96	5.01	-4.94
Hg	/	/	/

Table S17. The calculated binding energy of the Pt and M atoms embedded in PtM-L_6@Gra (E_b, eV), standard dissolution potentials ($U^{\ominus}_{diss}$, pH = 0), number of electrons (N_e) involved in the dissolution for the pure metals, and computed dissolution potentials (U^{Pt}_{diss}, U^{M}_{diss}) for DACs. The minimum dissolution potential (U^{min}_{diss}) is taken to represent the dissolution potential of the whole system.

PtM-L_6@Gra	E_b/2	Pt in PtM-L_6@Gra			M in PtM-L_6@Gra			U^{min}_{diss}
		$U^{\ominus}_{diss}$	N_e	U^{Pt}_{diss}	$U^{\ominus}_{diss}$	N_e	U^{M}_{diss}	
PtCo-C_6@Gra	-19.19	1.18	2	5.98	-0.28	2	4.52	4.52
PtNi-C_6@Gra	-19.13	1.18	2	5.96	-0.26	2	4.52	4.52
PtZn-C_6@Gra	-14.72	1.18	2	4.86	-0.76	2	2.92	2.92
PtFe-N_6@Gra	-15.55	1.18	2	5.07	-0.45	2	3.44	3.44
PtCo-N_6@Gra	-16.00	1.18	2	5.18	-0.28	2	3.72	3.72
PtNi-N_6@Gra	-15.93	1.18	2	5.16	-0.26	2	3.72	3.72

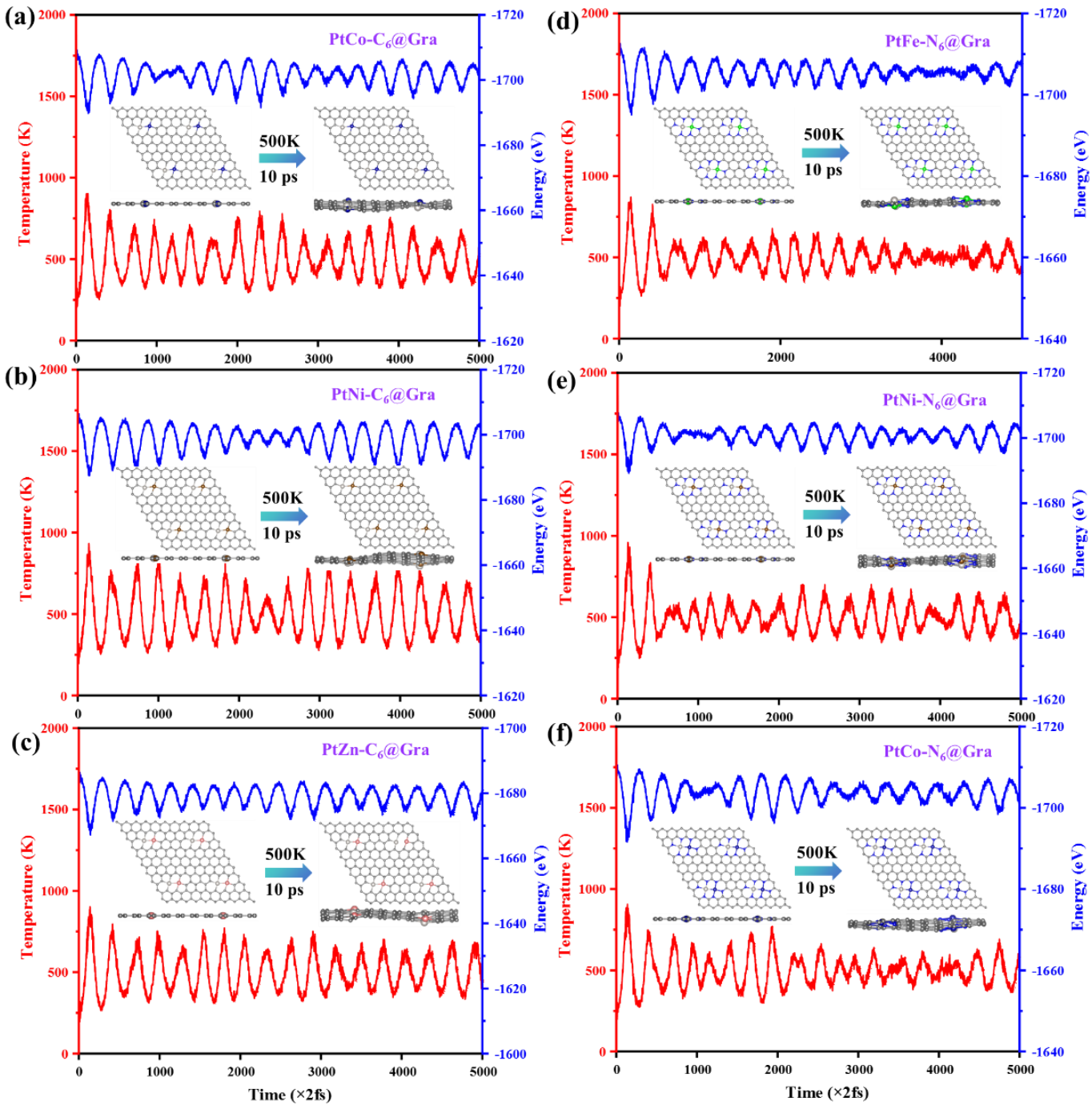


Figure S8. The variations of total energy and temperature during AIMD simulations of (a) PtCo-C_6@Gra, (b) PtNi-C_6@Gra, (c) PtZn-C_6@Gra, (d) PtFe-N_6@Gra, (e) PtNi-N_6@Gra, (f) PtCo-N_6@Gra catalysts under 500 K for 10 ps with a time step of 2 fs.