nature catalysis

SUPPLEMENTARY INFORMATION

https://doi.org/10.1038/s41929-018-0063-z

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A universal principle for a rational design of single-atom electrocatalysts

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Supplementary Information

A universal principle for a rational design of single-atom electrocatalysts

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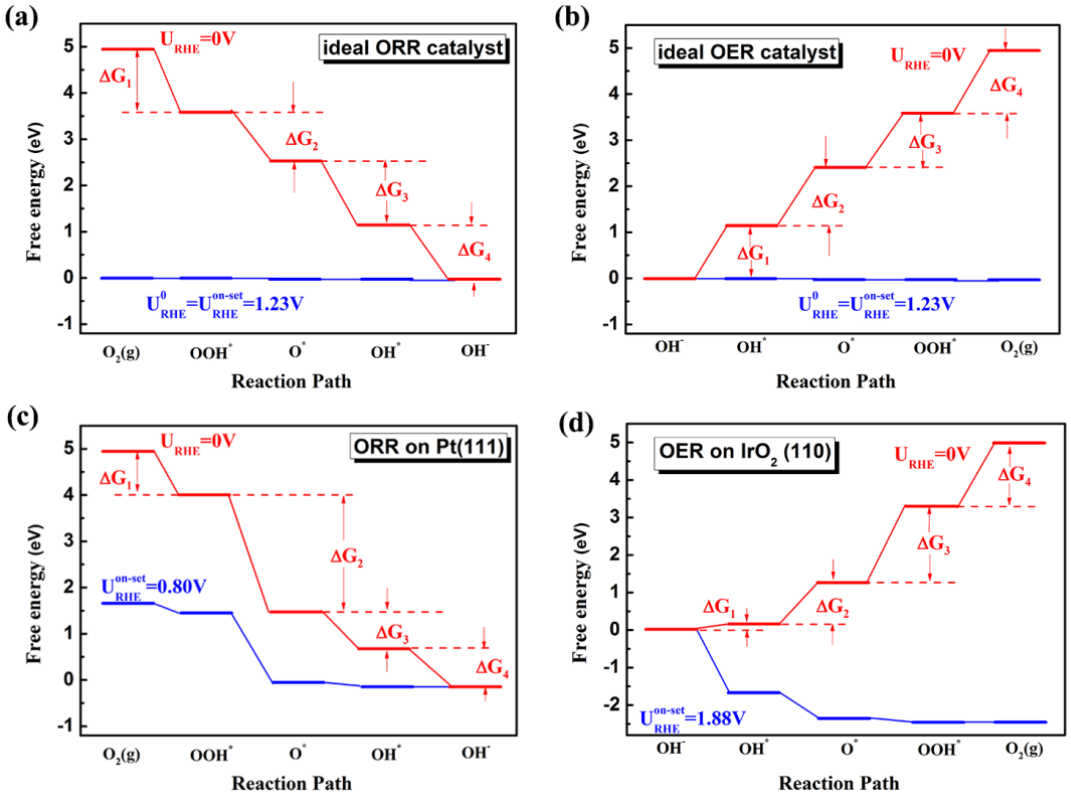

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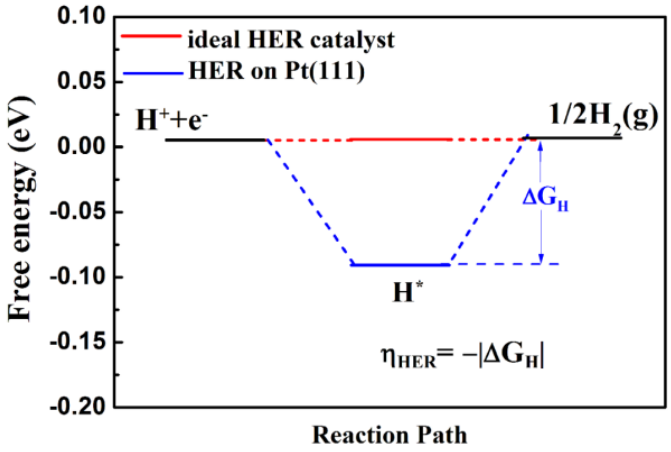

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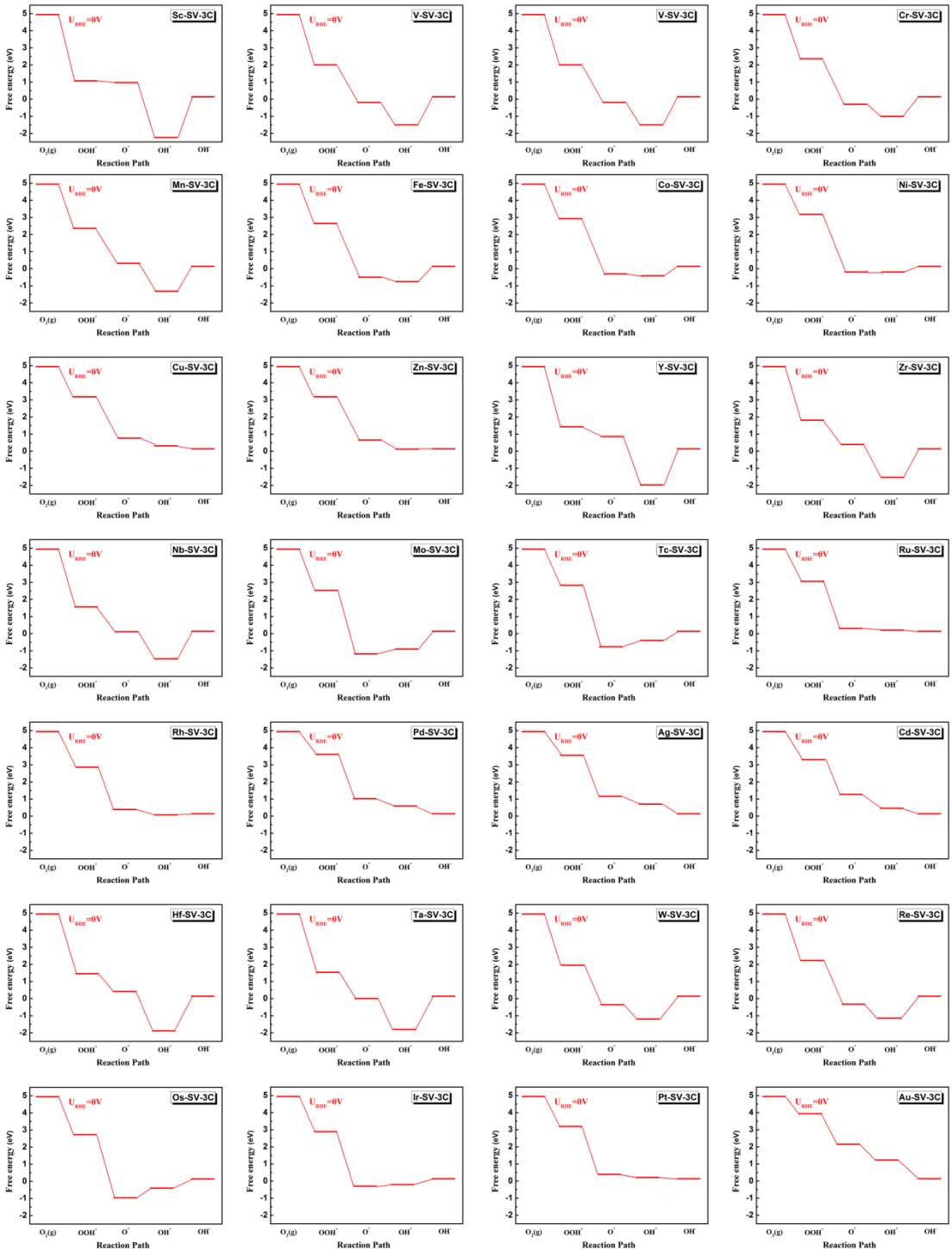

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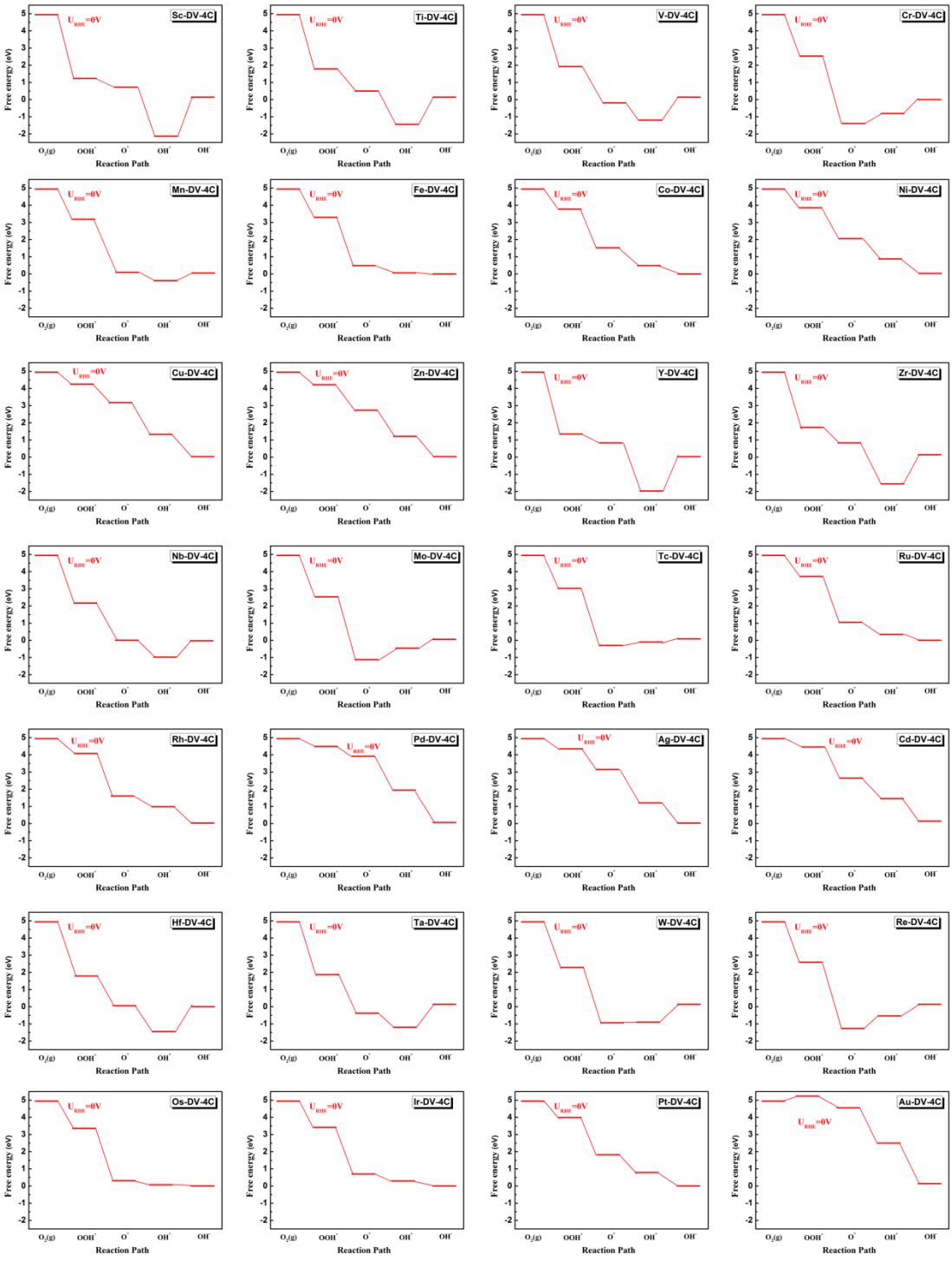

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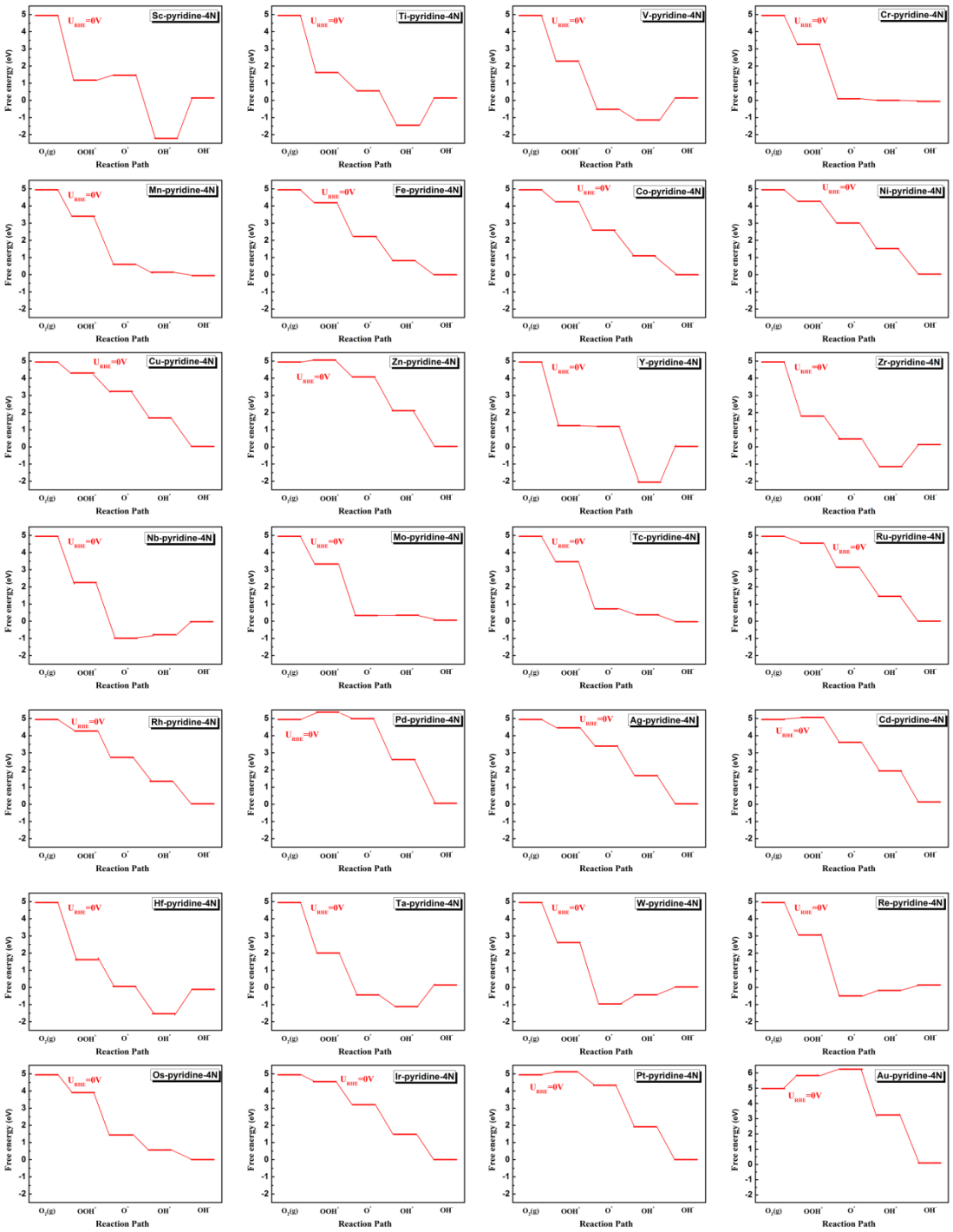

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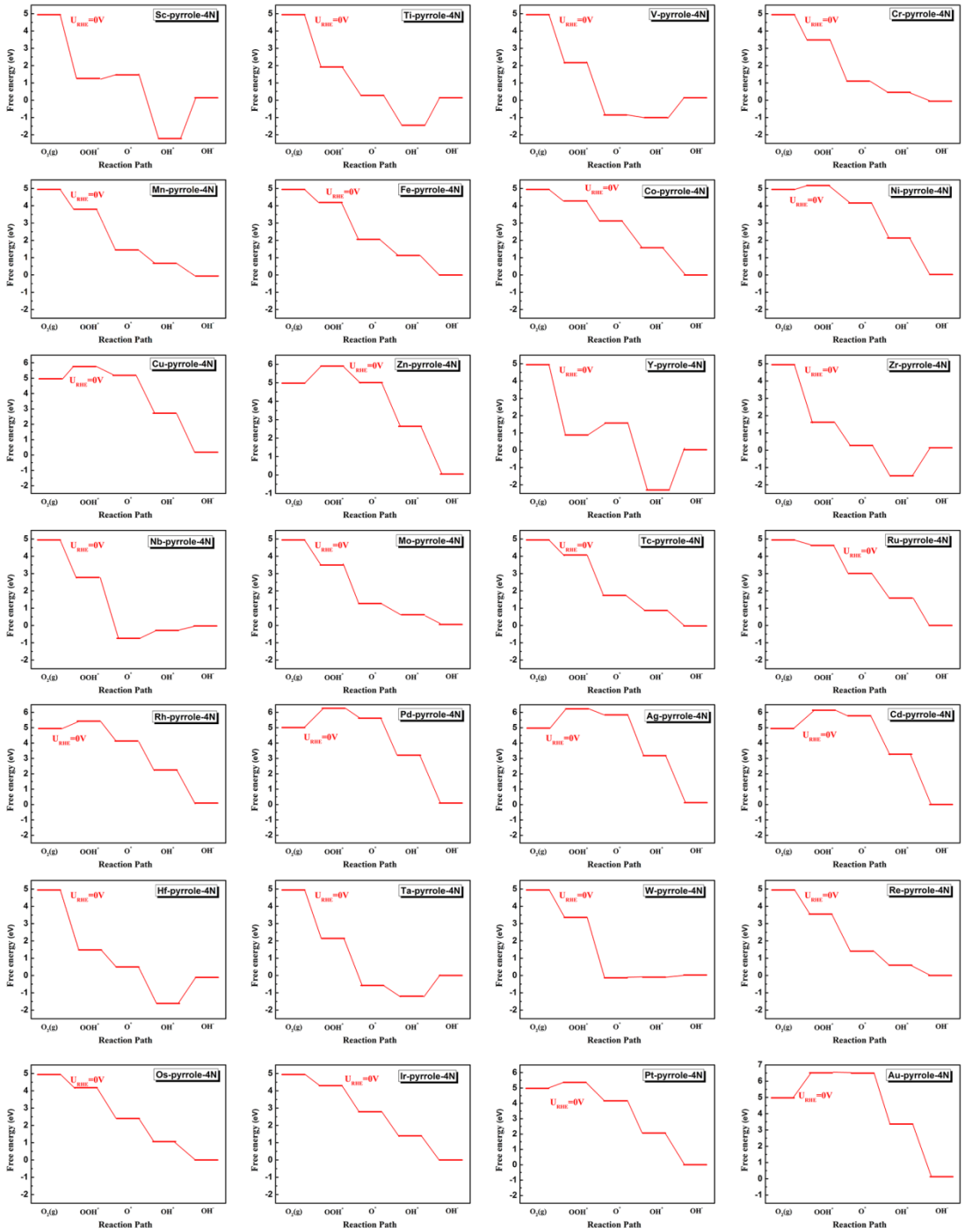

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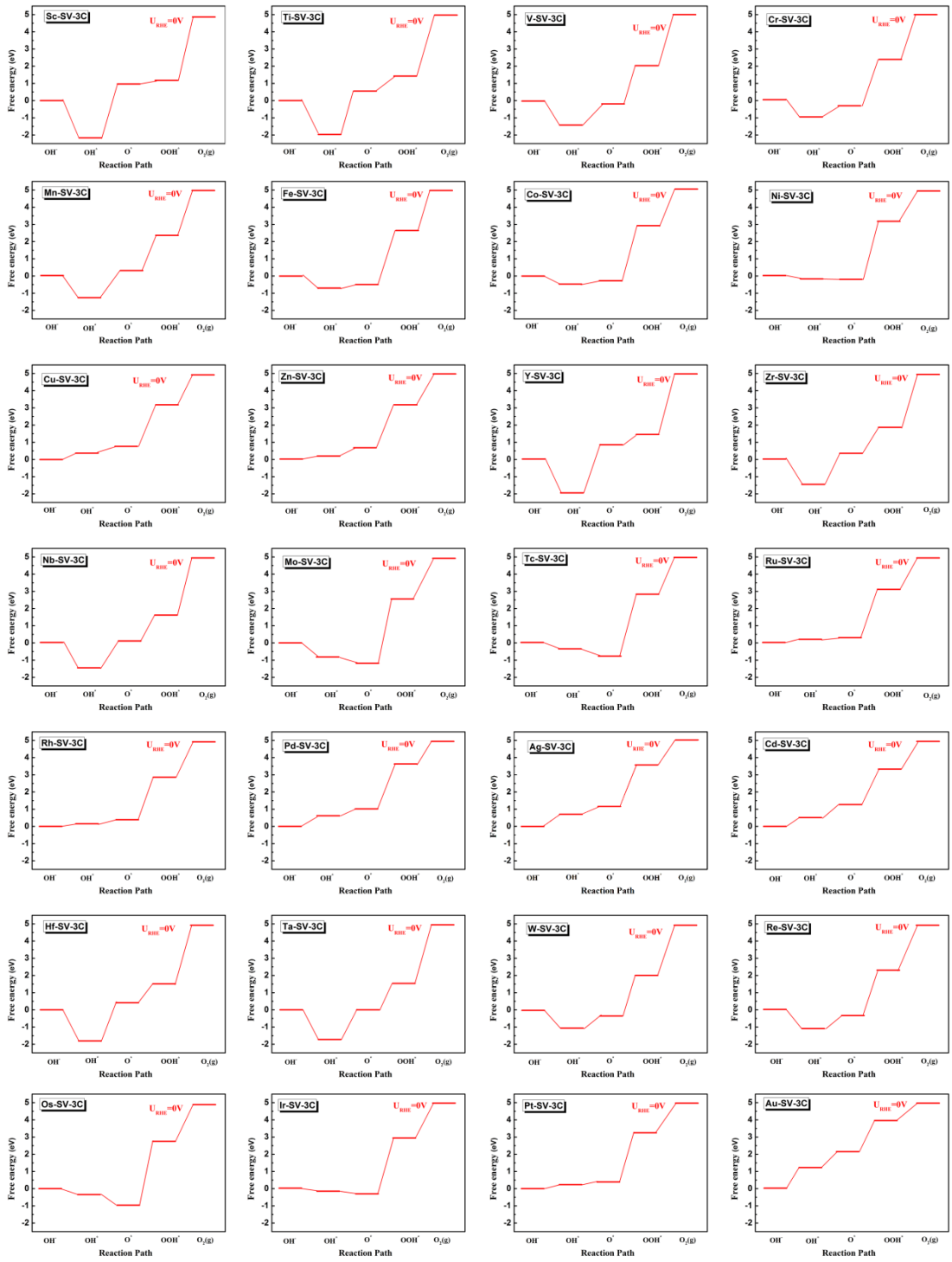

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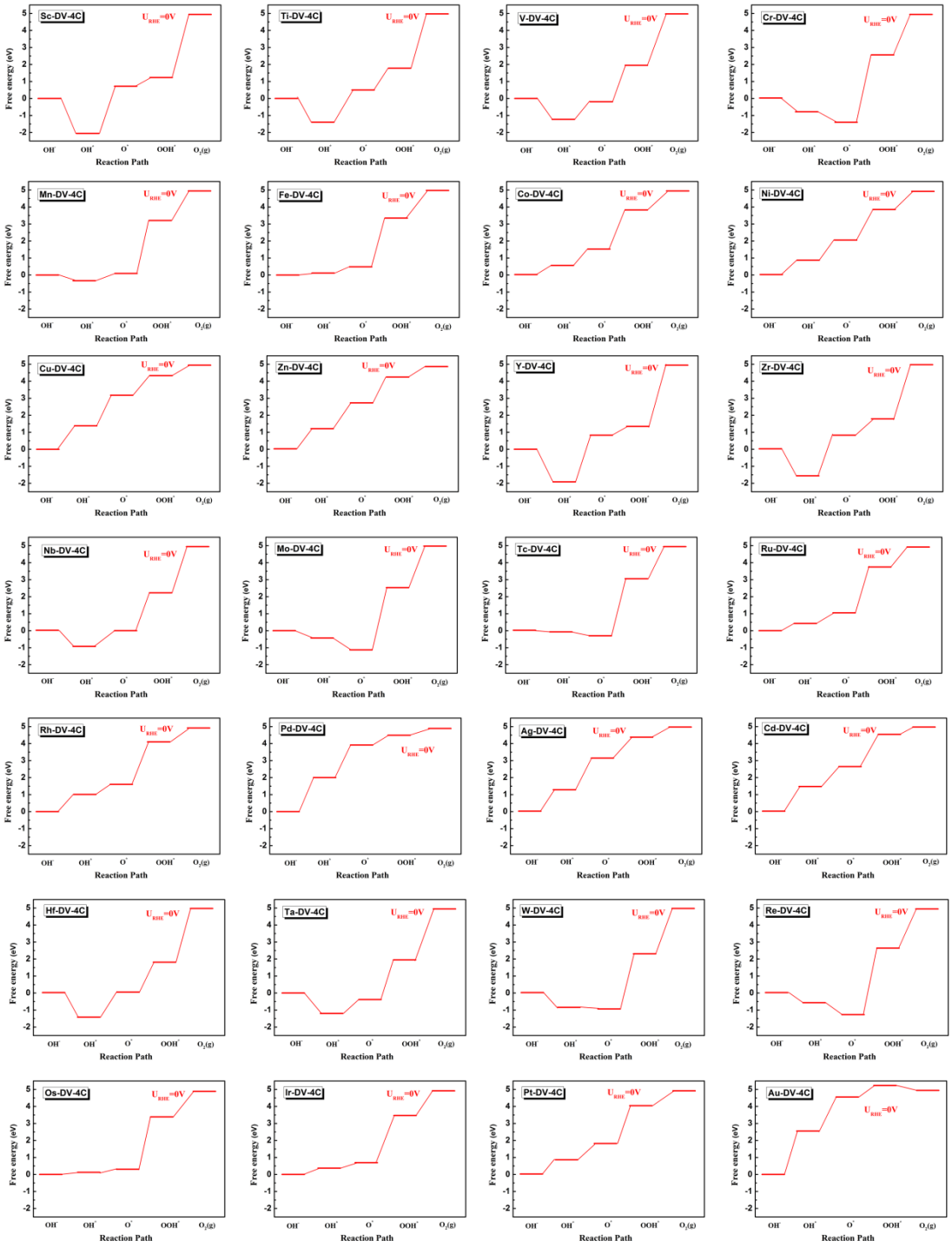

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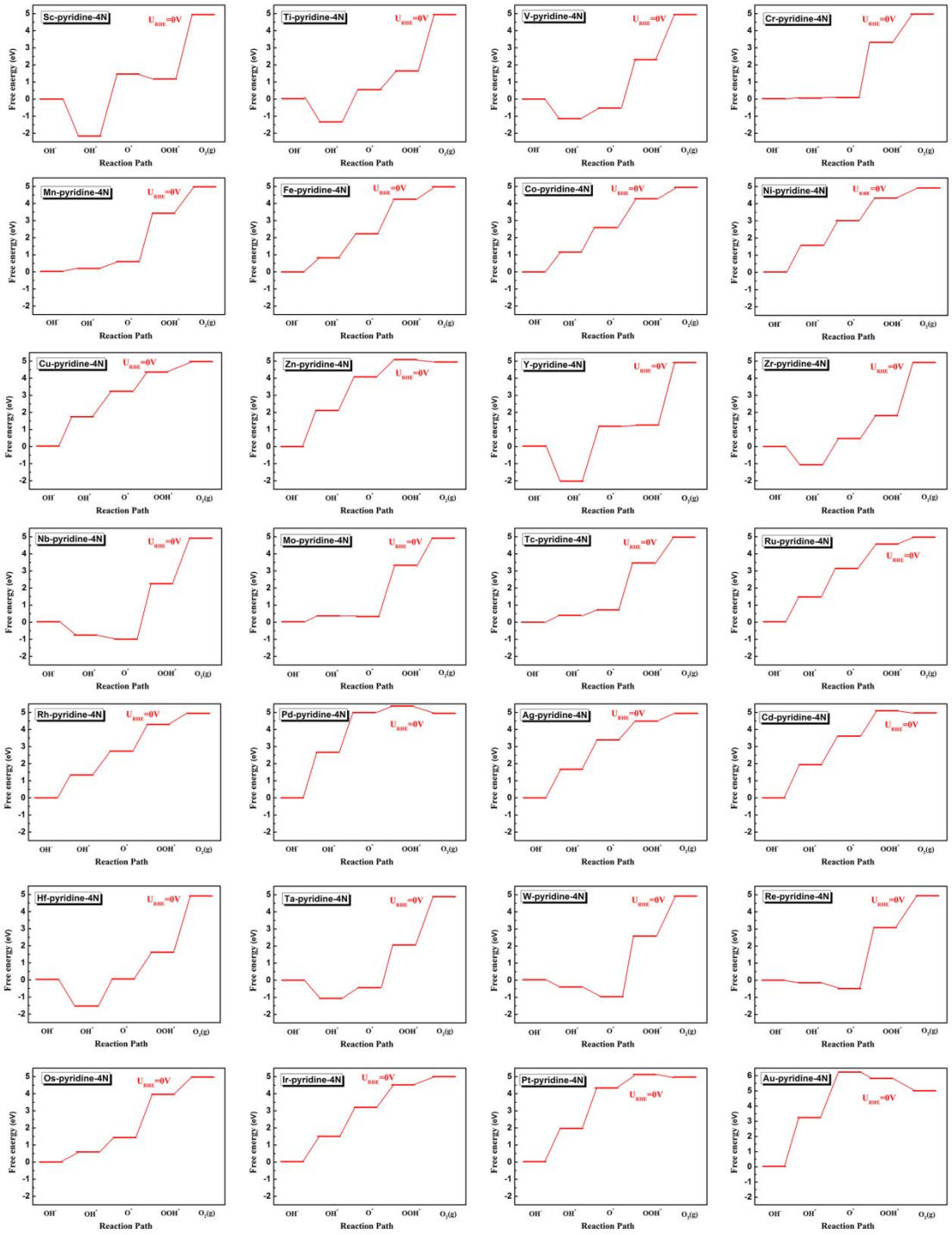

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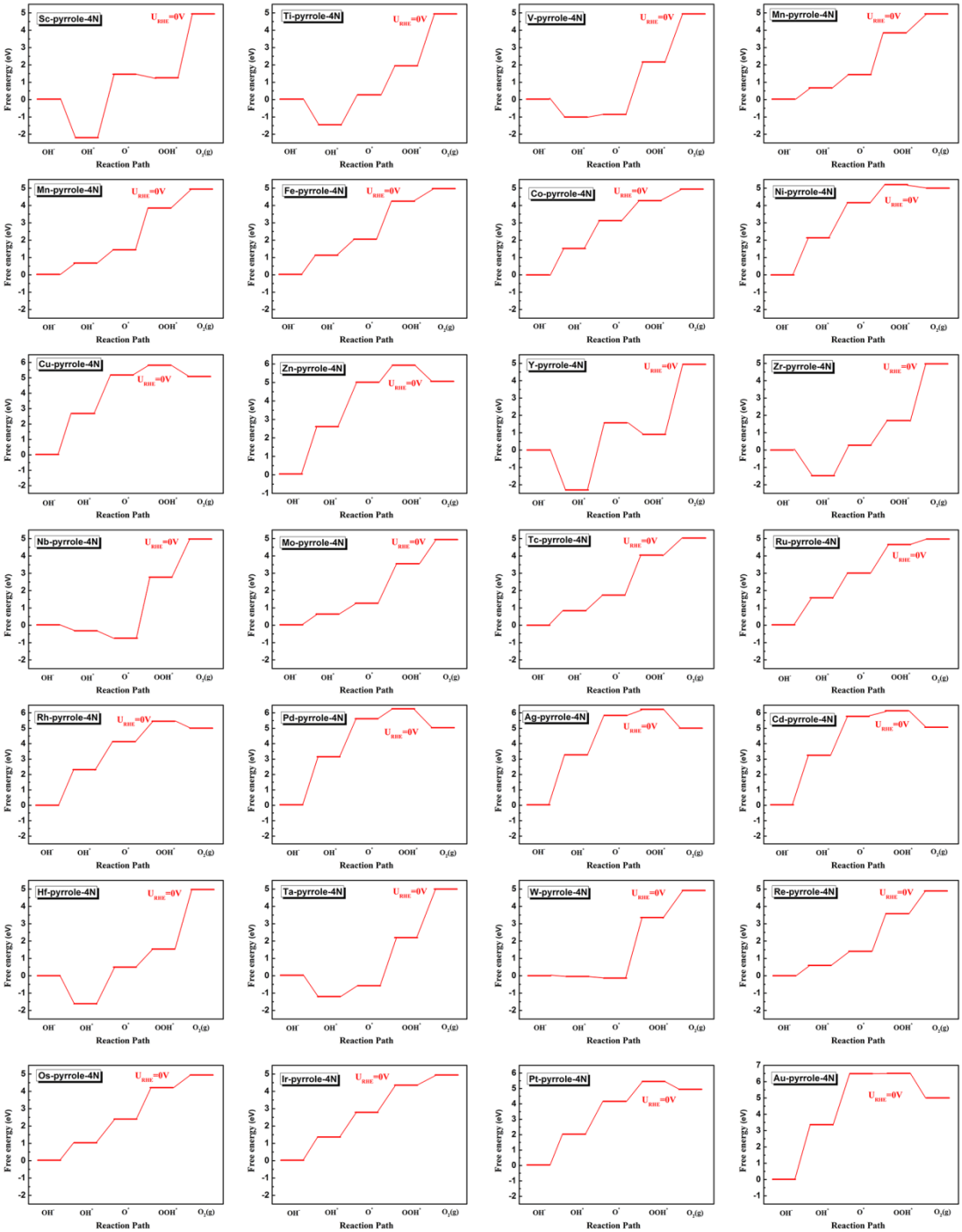

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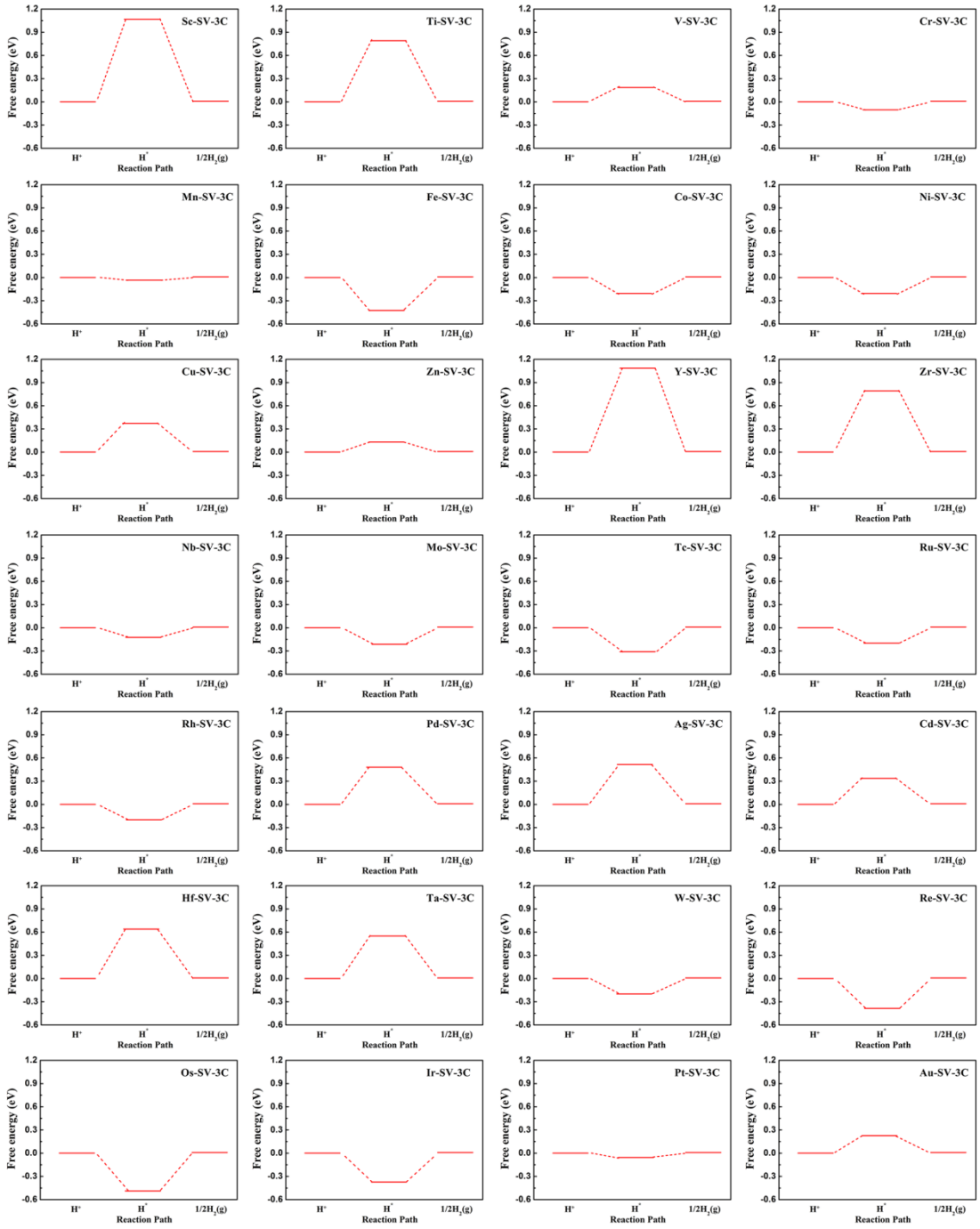

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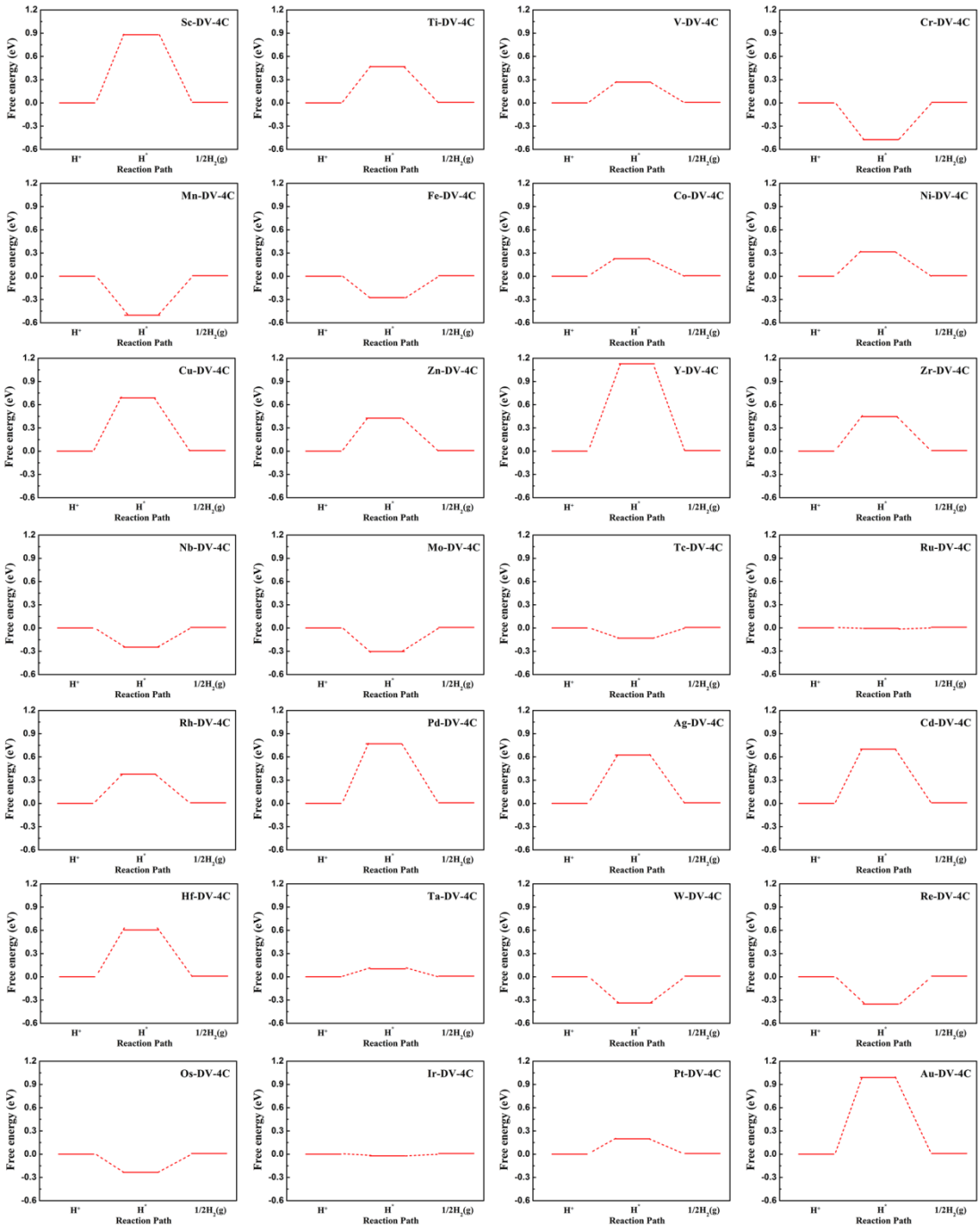

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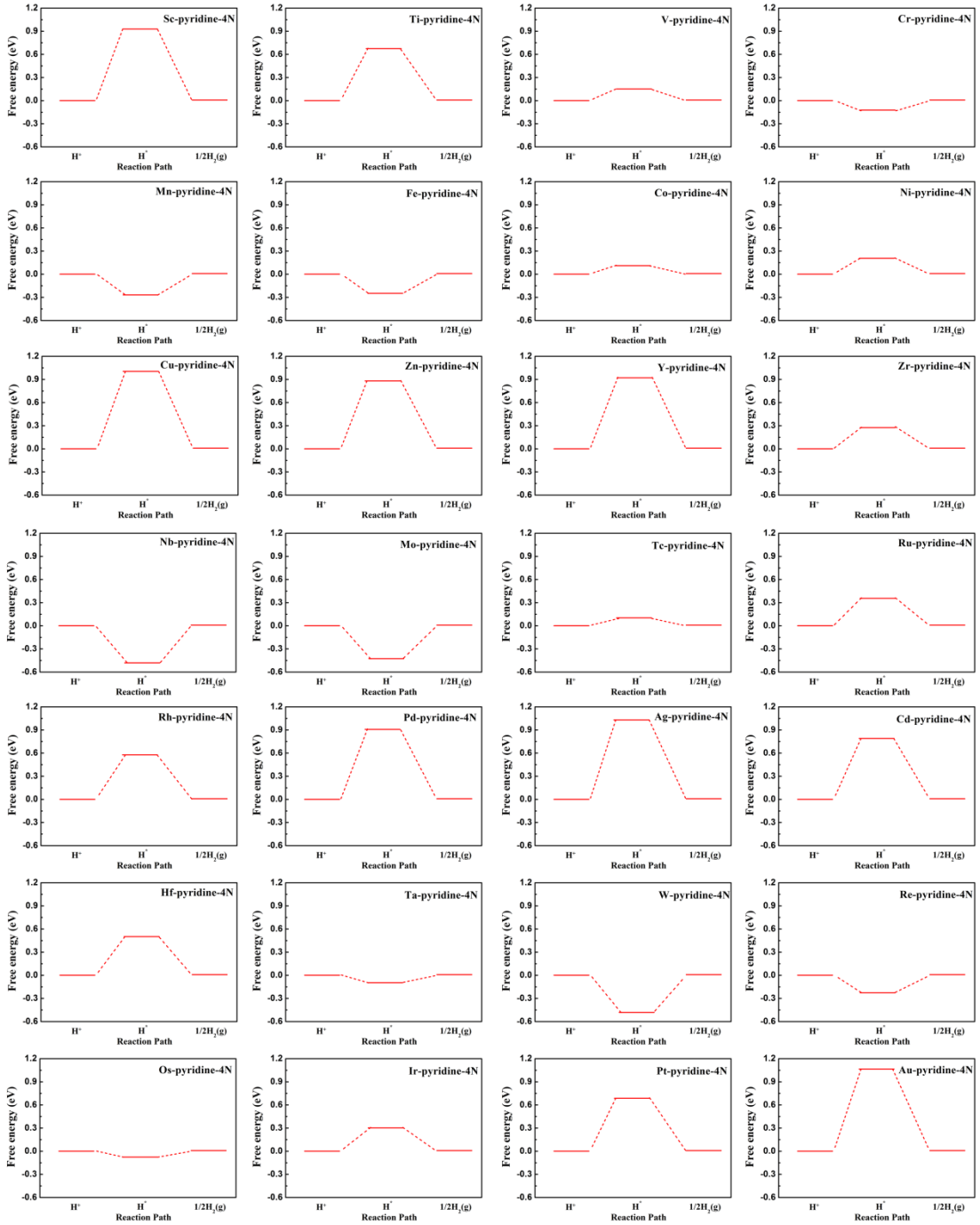

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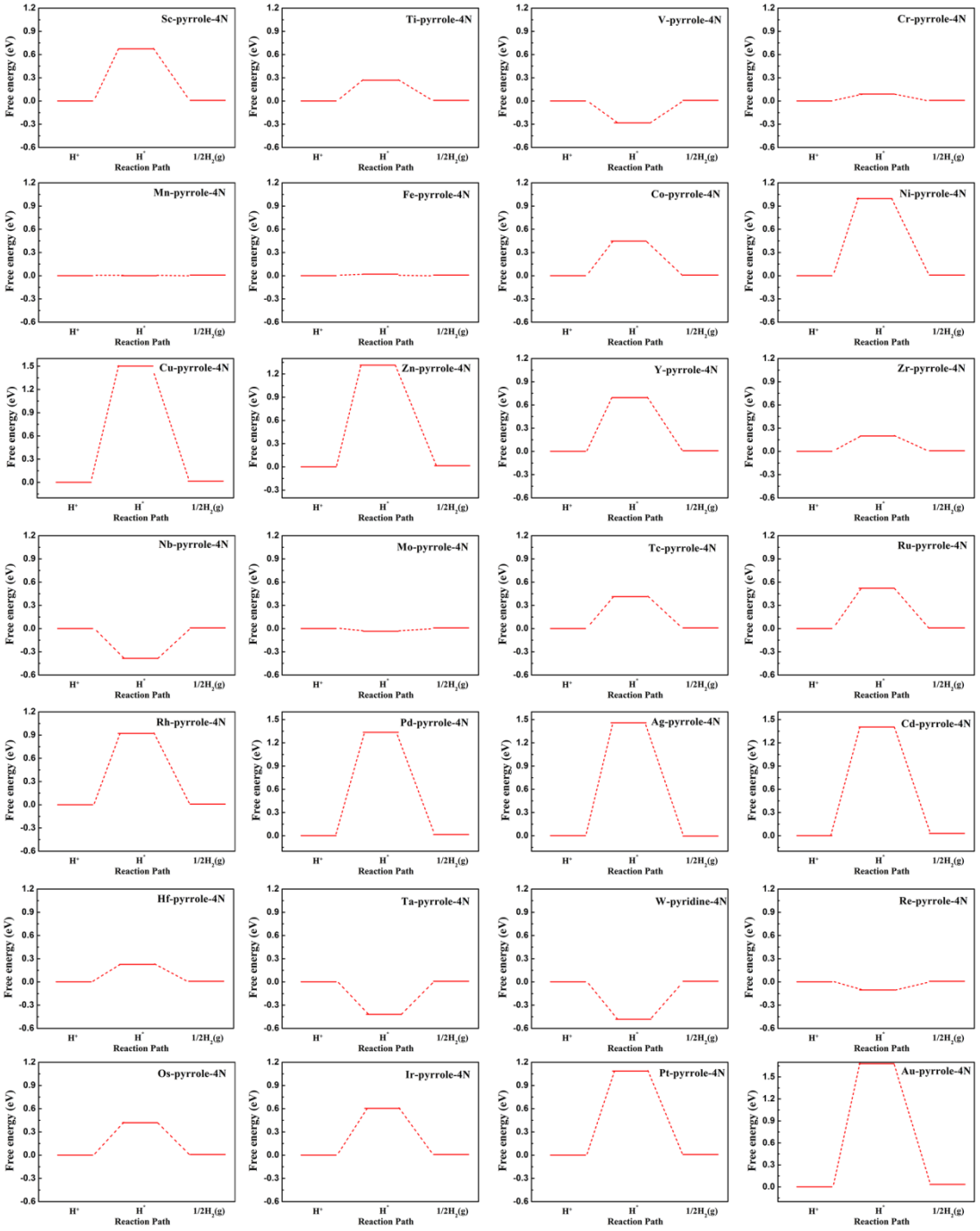

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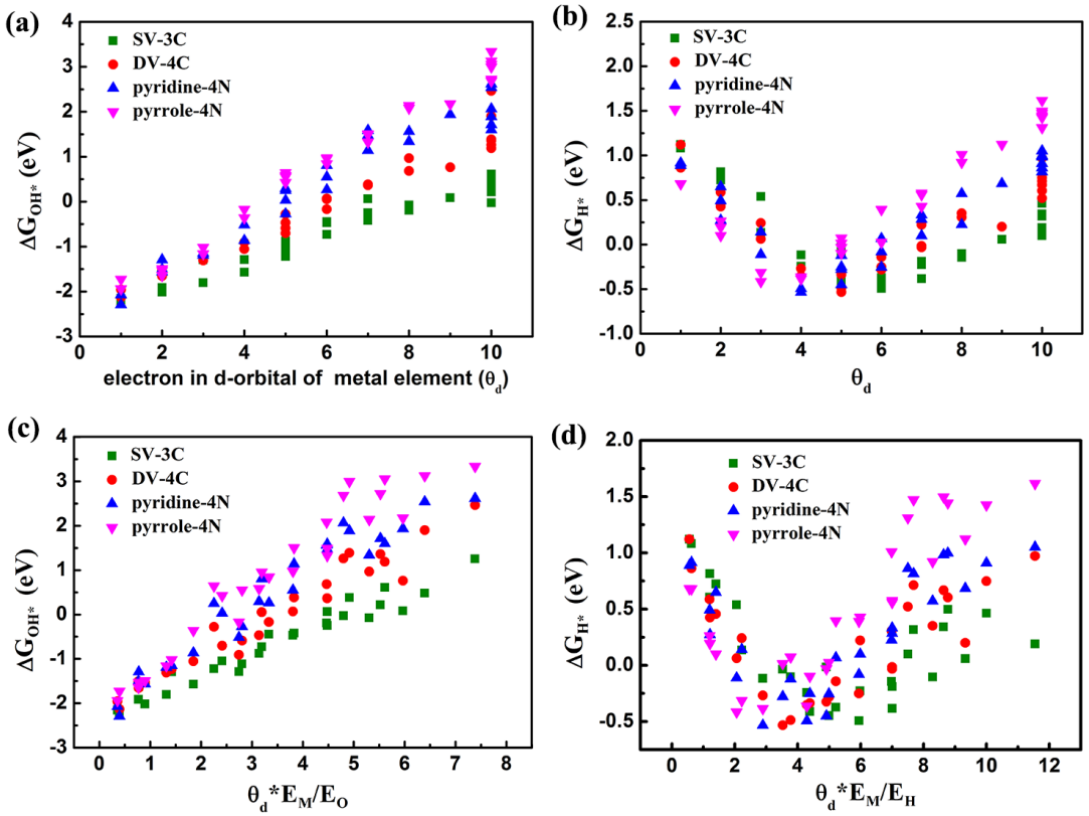

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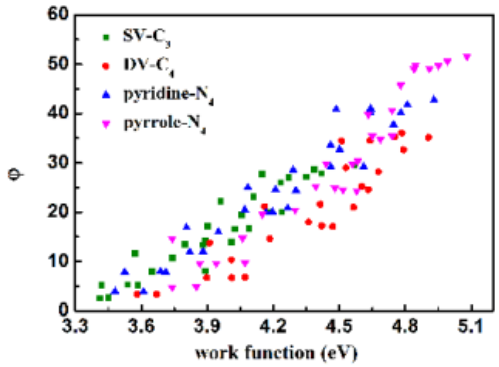

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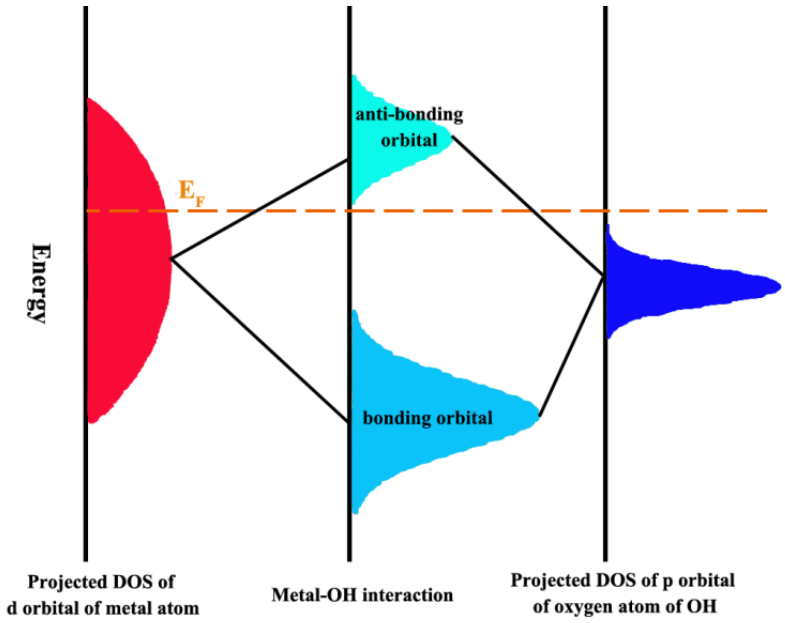

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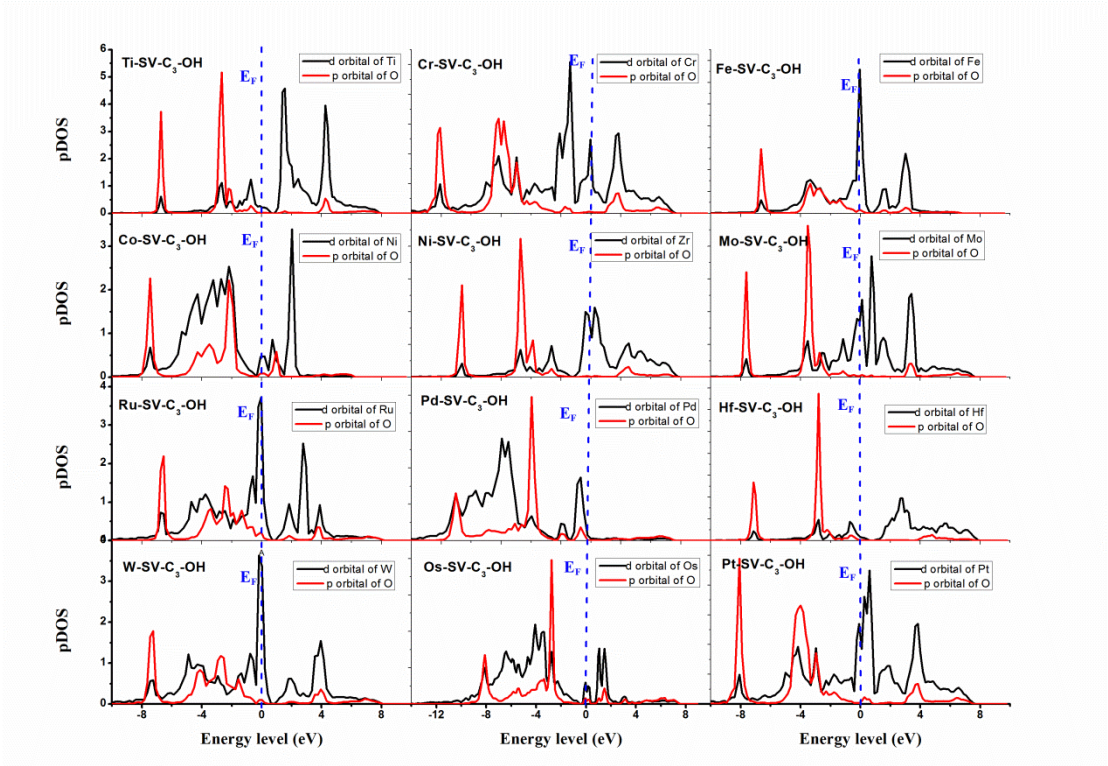

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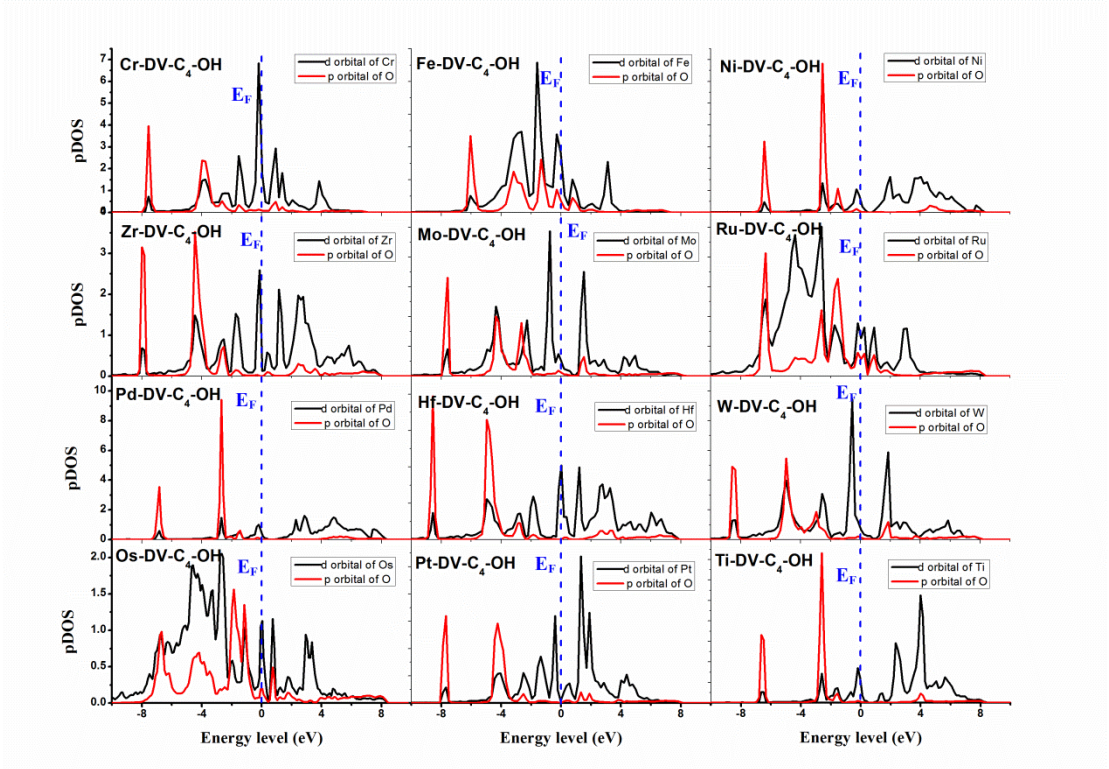

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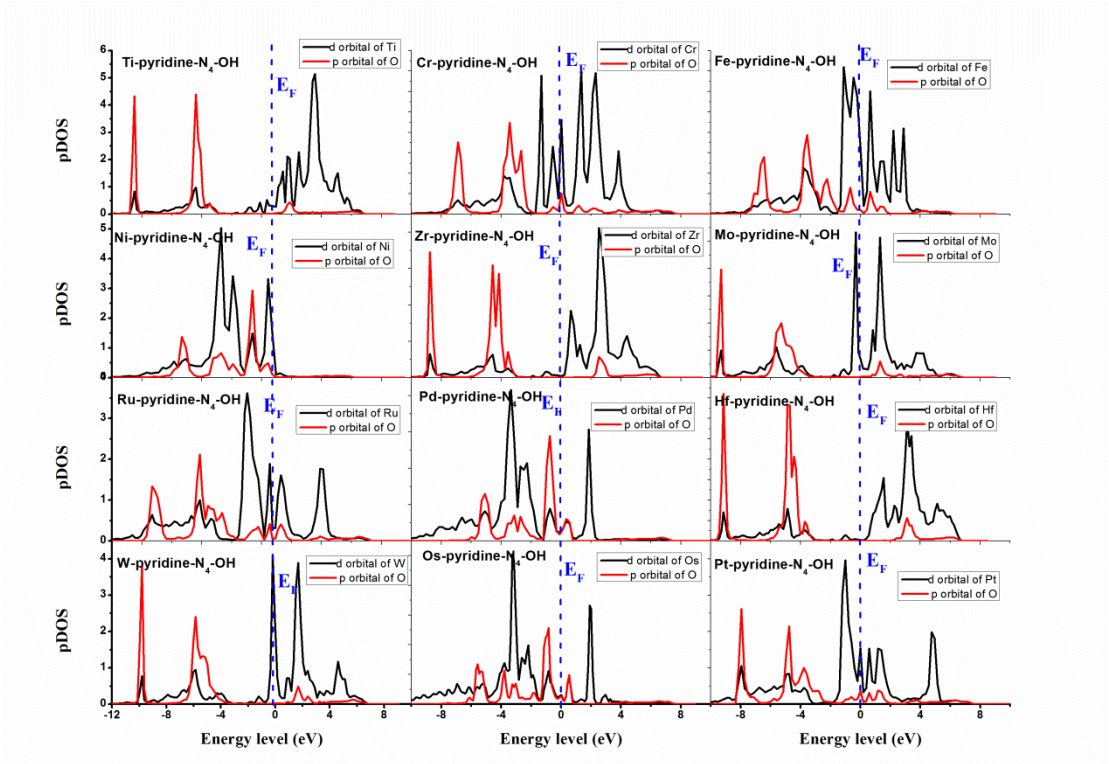

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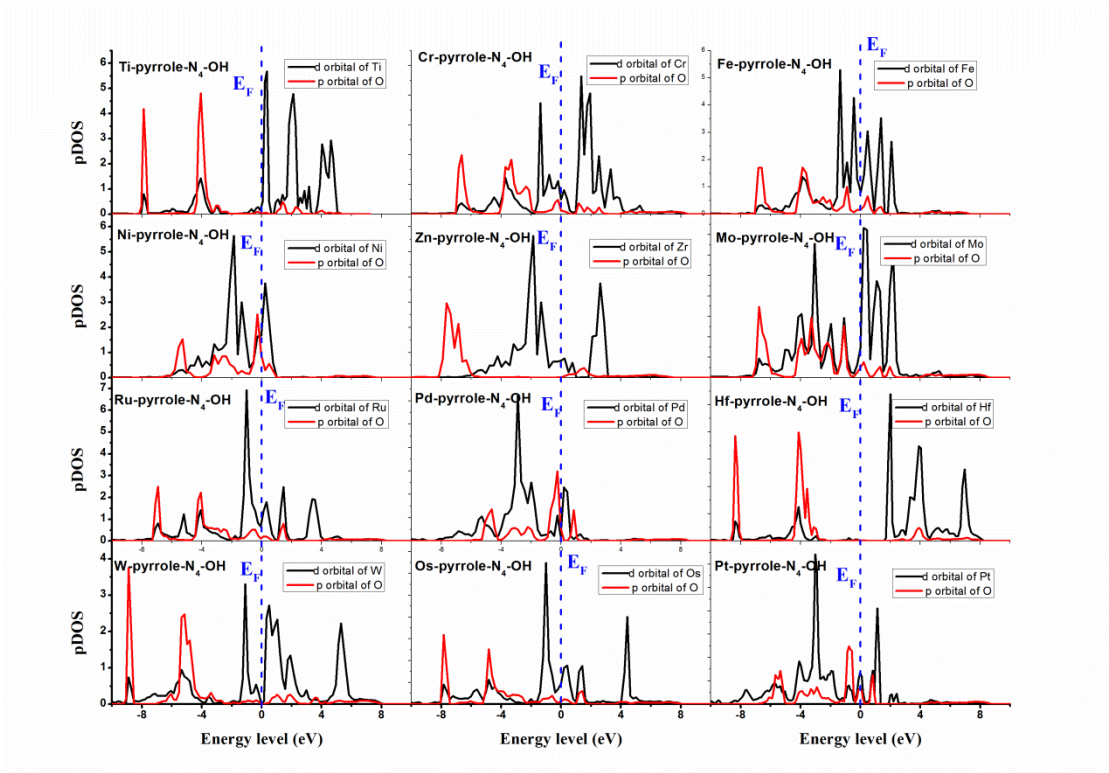

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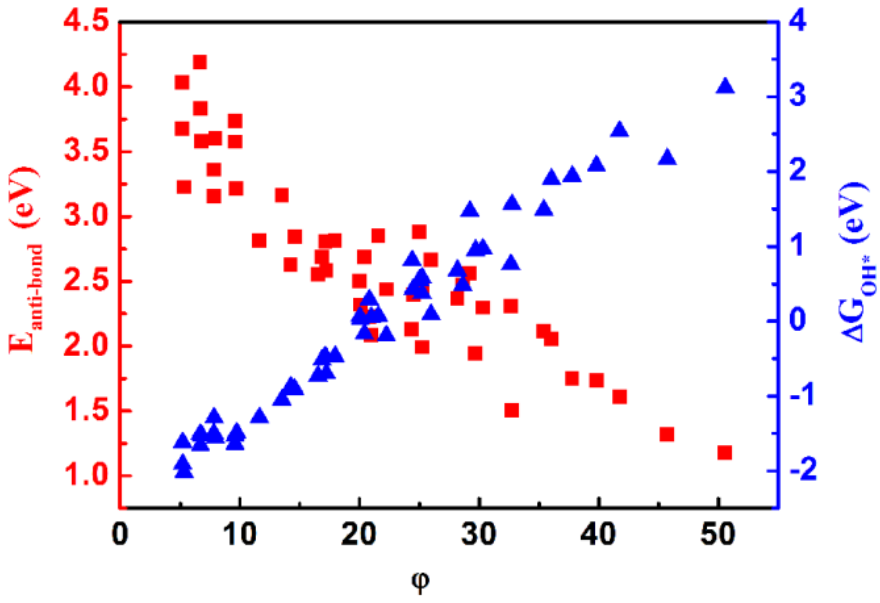

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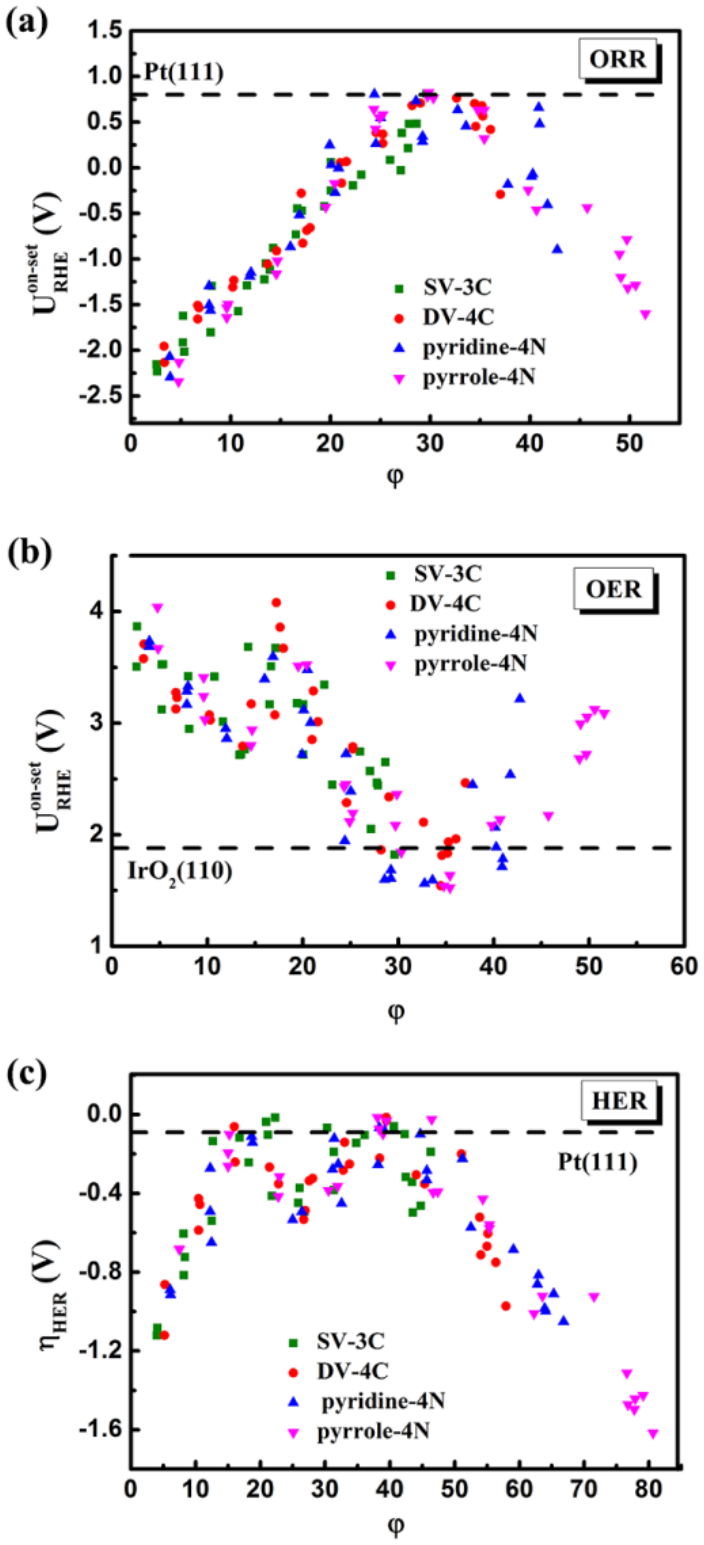

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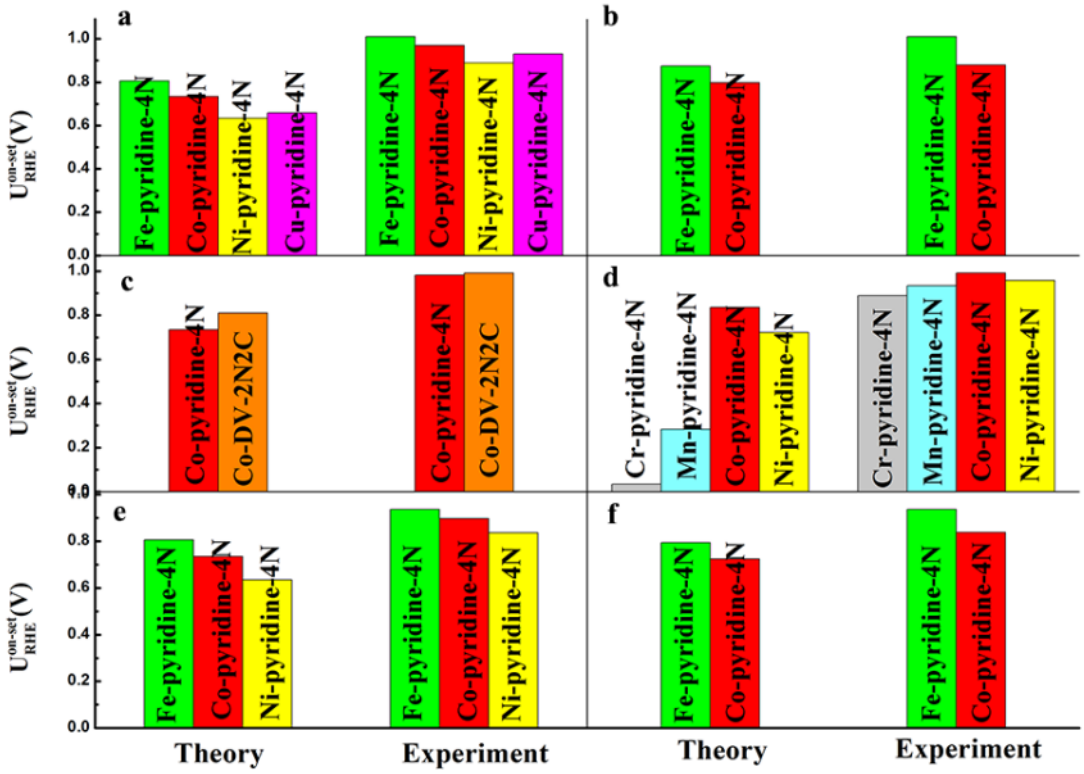

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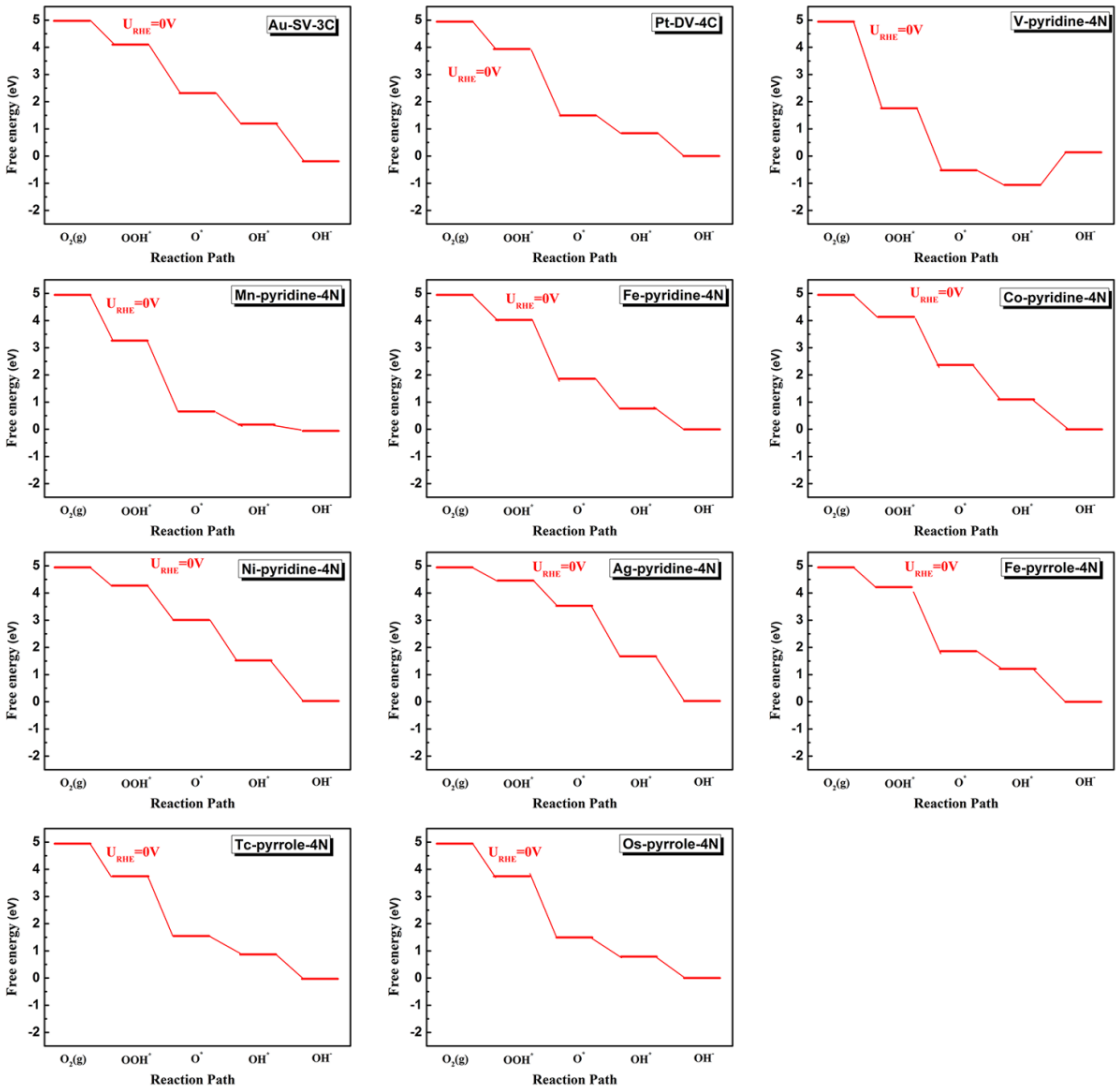
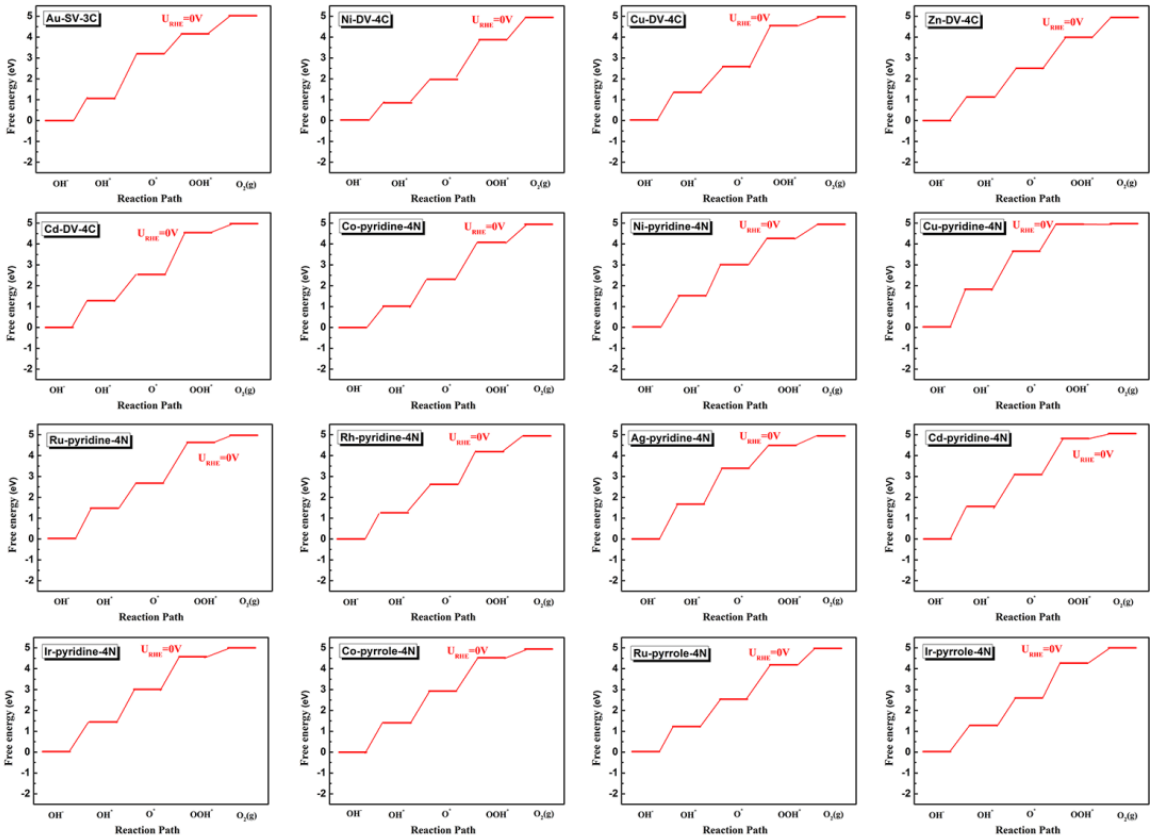


Supplementary Figure 25. Free energy diagram for **ORR** on single TM atom supported on **macrocyclic molecule**, at zero electrode potential.



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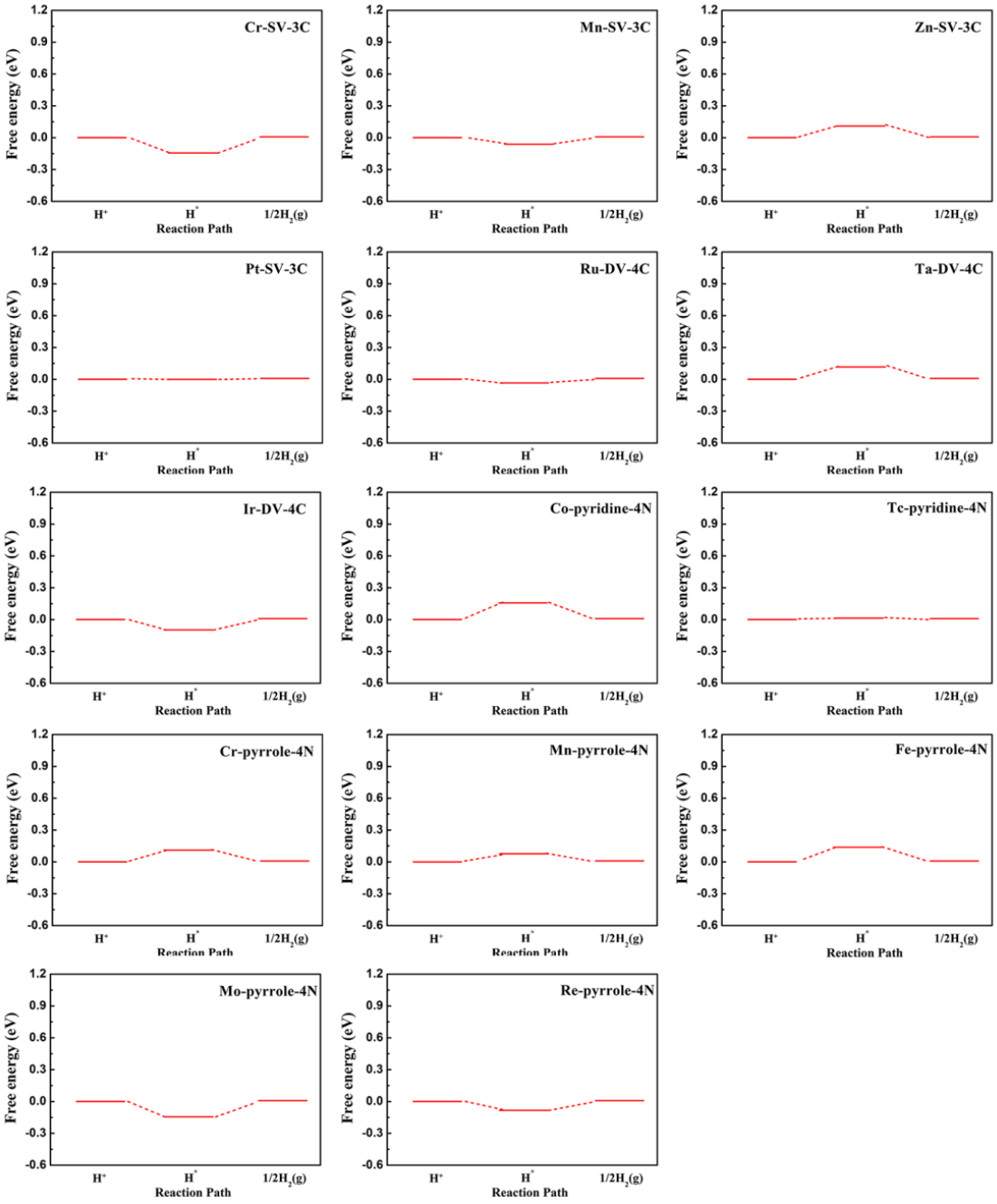
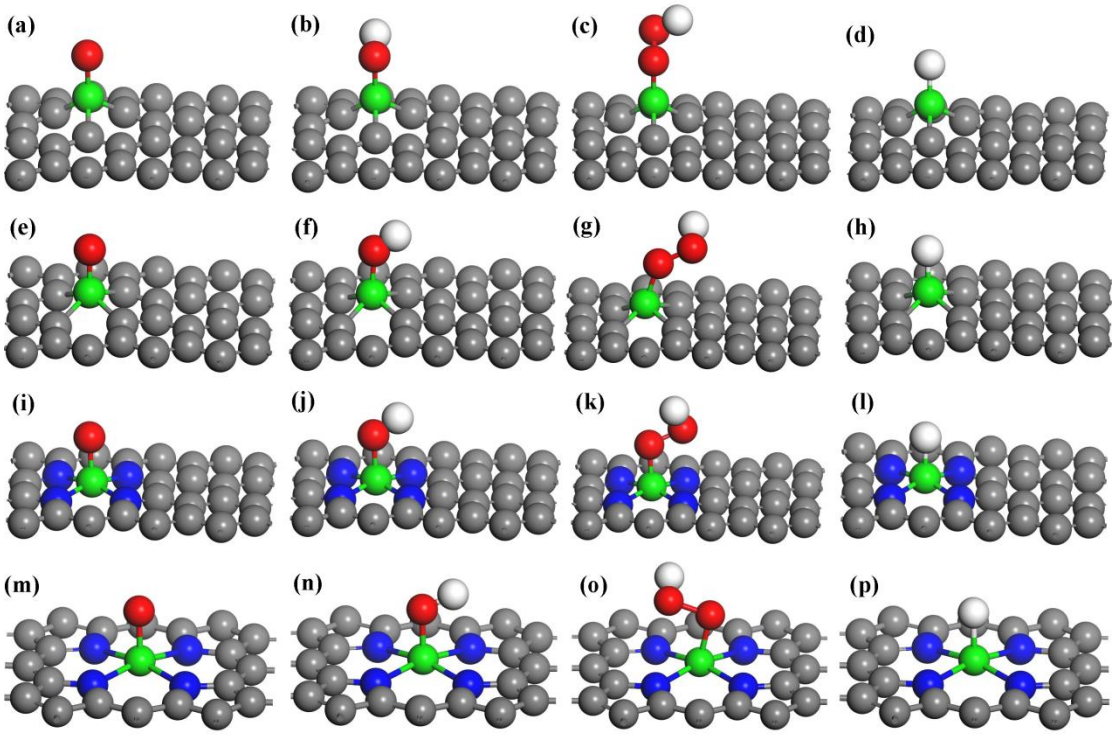


Supplementary Figure 27. Free-energy diagram for **HER** on single TM atom supported on **macrocyclic molecule**, at zero electrode potential.



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Supplementary Tables

Supplementary Table 1. Values used for the entropy and zero-point energy corrections in determining the free energy of reactants, products, and intermediate species adsorbed on catalysts. For the adsorbates, the ZPE values are averaged over all single atom catalyst systems since they have rather close value.

Species	T×S (eV) (298K)	ZPE (eV)
H^*	0	0.17
O^*	0	0.07
OH^*	0	0.33
OOH^*	0	0.43
H_2(g)	0.41	0.27
H_2O(g)	0.58	0.57

Supplementary Table 2. Adsorption free energies of OH, O, OOH and H (eV) on Pt(111) and IrO_2(110).

Active site	ΔG_{OH}^*	ΔG_O^*	ΔG_{OOH}^*	ΔG_H^*
Pt(111)	0.80	1.62	4.10	-0.09
IrO_2(110)	0.11	1.36	3.24	/

Supplementary Table 3. Adsorption free energies of OH, O, OOH and H (eV) on single TM atom supported on **functional graphite materials with SV-3C coordination**.

single TM atom	ΔG_{OH}^*	ΔG_O^*	ΔG_{OOH}^*	ΔG_H^*
Sc	-2.23	0.93	1.05	1.08
Ti	-2.02	0.58	1.39	0.72
V	-1.29	-0.16	1.97	0.13
Cr	-1.05	-0.51	2.20	-0.10
Mn	-1.22	0.14	2.20	-0.04
Fe	-0.73	-1.15	2.62	-0.45
Co	-0.42	-0.30	2.87	-0.23
Ni	-0.19	-0.19	3.16	-0.14
Cu	0.22	0.71	3.17	0.34
Zn	-0.03	0.63	3.20	0.10
Y	-2.15	0.84	1.41	1.12
Zr	-1.62	0.44	1.80	0.82
Nb	-1.57	0.10	1.50	-0.12
Mo	-0.88	-1.21	2.47	-0.22
Tc	-0.45	-0.71	2.80	-0.37
Ru	0.06	0.28	2.99	-0.19
Rh	-0.08	0.37	2.82	-0.20
Pd	0.48	0.97	3.62	0.46
Ag	0.61	1.09	3.53	0.50

Cd	0.38	1.27	3.32	0.32
Hf	-1.91	0.36	1.40	0.61
Ta	-1.80	-0.10	1.50	0.54
W	-1.29	-0.31	1.91	-0.24
Re	-1.12	-0.36	2.15	-0.41
Os	-0.47	-0.97	2.70	-0.49
Ir	-0.25	-0.32	2.85	-0.38
Pt	0.09	0.37	3.12	0.06
Au	1.25	2.06	3.89	0.19

Supplementary Table **4.** Adsorption free energies of OH, O, OOH and H (eV) on single TM atom supported on **functional graphite materials with DV-4C coordination**.

single TM atom	ΔG_{OH}^*	ΔG_O^*	ΔG_{OOH}^*	ΔG_H^*
Sc	-2.13	0.76	1.21	0.86
Ti	-1.53	0.45	1.69	0.46
V	-1.23	-0.25	1.89	0.24
Cr	-0.70	-1.53	2.55	-0.49
Mn	-0.28	0.02	3.09	-0.53
Fe	0.05	0.41	3.27	-0.28
Co	0.39	1.52	3.80	0.22
Ni	0.68	1.94	3.81	0.31
Cu	1.36	3.20	4.24	0.67
Zn	1.26	2.67	4.22	0.52
Y	-1.96	0.94	1.34	1.12
Zr	-1.66	0.79	1.65	0.43
Nb	-1.06	-0.63	2.13	-0.27
Mo	-0.47	-1.13	2.54	-0.32
Tc	-0.17	-0.33	2.96	-0.14
Ru	0.37	0.97	3.74	-0.02
Rh	0.97	1.68	4.02	0.35
Pd	1.90	3.86	4.50	0.75
Ag	1.19	3.12	4.35	0.60
Cd	1.39	2.65	4.47	0.71
Hf	-1.51	0.05	1.79	0.59
Ta	-1.31	-0.43	1.85	0.06
W	-0.91	-0.96	2.22	-0.35
Re	-0.59	-1.27	2.58	-0.34
Os	0.07	0.25	3.26	-0.25
Ir	0.36	0.63	3.42	-0.03
Pt	0.76	1.80	3.91	0.20
Au	2.46	4.51	5.21	0.97

Supplementary Table 5. Adsorption free energies of OH, O, OOH and H (eV) on single TM atom supported on **functional graphite materials with pyridine-4N coordination**.

single TM atom	ΔG_{OH}^*	ΔG_O^*	ΔG_{OOH}^*	ΔG_H^*
Sc	-2.29	1.44	1.19	0.92
Ti	-1.56	0.62	1.59	0.65
V	-1.15	-0.62	2.25	0.14
Cr	0.03	0.10	3.22	-0.12
Mn	0.15	0.63	3.35	-0.28
Fe	0.81	1.90	3.85	-0.25
Co	1.14	2.59	4.19	0.10
Ni	1.56	2.99	4.29	0.22
Cu	1.71	3.40	4.26	0.98
Zn	2.06	4.13	5.02	0.86
Y	-2.07	1.14	1.23	0.89
Zr	-1.29	0.44	1.75	0.27
Nb	-0.86	-1.14	2.25	-0.53
Mo	0.29	0.29	3.30	-0.45
Tc	0.26	0.70	3.42	0.07
Ru	1.47	3.15	4.58	0.33
Rh	1.34	2.93	4.46	0.57
Pd	2.54	4.97	5.33	0.91
Ag	1.60	3.38	4.44	1.00
Cd	1.89	3.72	4.99	0.82
Hf	-1.50	0.10	1.64	0.49
Ta	-1.19	-0.42	1.97	-0.11
W	-0.52	-1.02	2.57	-0.49
Re	-0.27	-0.46	3.02	-0.25
Os	0.55	1.40	3.79	-0.08
Ir	1.59	3.19	4.63	0.28
Pt	1.94	4.38	5.10	0.68
Au	3.22	6.21	5.82	1.05

Supplementary Table 6. Adsorption free energies of OH, O, OOH and H (eV) on single TM atom supported on f**unctional graphite materials with pyrrole-4N coordination**.

single TM atom	ΔG_{OH}^*	ΔG_O^*	ΔG_{OOH}^*	ΔG_H^*
Sc	-2.13	1.45	1.25	0.68
Ti	-1.49	0.33	1.89	0.25
V	-1.02	-0.88	2.06	-0.31
Cr	0.43	0.96	3.41	0.07
Mn	0.64	1.29	3.72	0.01
Fe	0.95	2.05	4.14	0.02
Co	1.50	3.05	4.29	0.43
Ni	2.08	4.16	5.16	1.01

Cu	2.72	5.18	5.70	1.50
Zn	2.68	4.95	5.87	1.31
Y	-2.34	1.54	0.88	0.68
Zr	-1.53	0.24	1.68	0.19
Nb	-0.36	-0.79	2.72	-0.39
Mo	0.58	1.27	3.46	-0.03
Tc	0.84	1.73	4.09	0.40
Ru	1.49	2.96	4.60	0.56
Rh	2.14	4.16	5.38	0.92
Pd	3.12	5.58	6.21	1.43
Ag	3.05	5.82	6.24	1.44
Cd	3.00	5.78	6.12	1.47
Hf	-1.64	0.42	1.51	0.26
Ta	-1.16	-0.63	2.12	-0.42
W	-0.17	-0.21	3.31	-0.36
Re	0.55	1.42	3.53	-0.10
Os	0.97	2.31	4.16	0.39
Ir	1.33	2.85	4.29	0.58
Pt	2.17	4.11	5.36	1.12
Au	3.34	6.42	6.52	1.62

Supplementary Table 7. Reaction free energy (eV vs RHE) of elementary step for ORR and OER at U_{RHE} = 0V on Pt(111) and IrO_2(110).

Model	ORR				OER			
	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6	ΔG_7	ΔG_8
Pt(111)	-0.82	-2.48	-0.82	-0.80	/	/	/	/
IrO_2(110)	/	/	/	/	0.11	1.25	1.88	1.68

Supplementary Table 8. Theoretical onset potential for ORR and OER(U^{onset}, V vs RHE), theoretical overpotential (η^{HER}, V vs RHE) for HER on Pt(111) and IrO_2(110).

Active site	U^{onset}ORR	U^{onset}OER	η^{HER}
Pt(111)	0.80	/	0.09
IrO_2(110)	/	1.88	/

Supplementary Table 9. Reaction free energy (eV vs RHE) of elementary step for ORR and OER at U_{RHE} = 0V on single TM atom supported on **functional graphite materials with SV-3C coordination**.

	ORR				OER			
single TM atom	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6	ΔG_7	ΔG_8
Sc	-3.87	-0.12	-3.16	2.23	-2.23	3.16	0.12	3.87
Ti	-3.53	-0.82	-2.59	2.02	-2.02	2.59	0.82	3.53

V	-2.95	-2.13	-1.14	1.29	-1.29	1.14	2.13	2.95
Cr	-2.72	-2.71	-0.53	1.05	-1.05	0.53	2.71	2.72
Mn	-2.72	-2.07	-1.36	1.22	-1.22	1.36	2.07	2.72
Fe	-2.30	-3.17	-0.18	0.73	-0.73	0.18	3.17	2.30
Co	-2.05	-3.18	-0.12	0.42	-0.42	0.12	3.18	2.05
Ni	-1.76	-3.34	-0.01	0.19	-0.19	0.01	3.34	1.76
Cu	-1.75	-2.47	-0.49	-0.22	0.22	0.49	2.47	1.75
Zn	-1.72	-2.57	-0.66	0.03	-0.03	0.66	2.57	1.72
Y	-3.51	-0.57	-2.99	2.15	-2.15	2.99	0.57	3.51
Zr	-3.12	-1.36	-2.07	1.62	-1.62	2.07	1.36	3.12
Nb	-3.42	-1.41	-1.67	1.57	-1.57	1.67	1.41	3.42
Mo	-2.45	-3.68	0.33	0.88	-0.88	-0.33	3.68	2.45
Tc	-2.12	-3.51	0.26	0.45	-0.45	-0.26	3.51	2.12
Ru	-1.93	-2.72	-0.21	-0.06	0.06	0.21	2.72	1.93
Rh	-2.10	-2.45	-0.44	0.08	-0.08	0.44	2.45	2.10
Pd	-1.30	-2.65	-0.49	-0.48	0.48	0.49	2.65	1.30
Ag	-1.39	-2.44	-0.48	-0.61	0.61	0.48	2.44	1.39
Cd	-1.60	-2.05	-0.89	-0.38	0.38	0.89	2.05	1.60
Hf	-3.52	-1.04	-2.27	1.91	-1.91	2.27	1.04	3.52
Ta	-3.42	-1.60	-1.71	1.80	-1.80	1.71	1.60	3.42
W	-3.01	-2.22	-0.98	1.29	-1.29	0.98	2.22	3.01
Re	-2.77	-2.52	-0.75	1.12	-1.12	0.75	2.52	2.77
Os	-2.22	-3.67	0.50	0.47	-0.47	-0.50	3.67	2.22
Ir	-2.07	-3.17	0.07	0.25	-0.25	-0.07	3.17	2.07
Pt	-1.80	-2.75	-0.29	-0.09	0.09	0.29	2.75	1.80
Au	-1.03	-1.82	-0.81	-1.25	1.25	0.81	1.82	1.03

Supplementary Table **10** Reaction free energy (eV vs RHE) of elementary step for ORR and OER at U_{RHE}=0V on single TM atom supported on **functional graphite materials with DV-4C coordination**.

	ORR				OER			
single TM atom	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6	ΔG_7	ΔG_8
Sc	-3.71	-0.45	-2.90	2.13	-2.13	2.90	0.45	3.71
Ti	-3.23	-1.24	-1.98	1.53	-1.53	1.98	1.24	3.23
V	-3.03	-2.14	-0.99	1.23	-1.23	0.99	2.14	3.03
Cr	-2.37	-4.08	0.83	0.70	-0.70	-0.83	4.08	2.37
Mn	-1.83	-3.07	-0.30	0.28	-0.28	0.30	3.07	1.83
Fe	-1.65	-2.85	-0.36	-0.05	0.05	0.36	2.85	1.65
Co	-1.12	-2.29	-1.13	-0.39	0.39	1.13	2.29	1.12
Ni	-1.11	-1.86	-1.26	-0.68	0.68	1.26	1.86	1.11
Cu	-0.68	-1.05	-1.83	-1.36	1.36	1.83	1.05	0.68
Zn	-0.70	-1.54	-1.41	-1.26	1.26	1.41	1.54	0.70
Y	-3.58	-0.41	-2.89	1.96	-1.96	2.89	0.41	3.58

Zr	-3.27	-0.86	-2.44	1.66	-1.66	2.44	0.86	3.27
Nb	-2.79	-2.75	-0.43	1.06	-1.06	0.43	2.75	2.79
Mo	-2.38	-3.67	0.66	0.47	-0.47	-0.66	3.67	2.38
Tc	-1.96	-3.29	0.16	0.17	-0.17	-0.16	3.29	1.96
Ru	-1.18	-2.77	-0.61	-0.37	0.37	0.61	2.77	1.18
Rh	-0.90	-2.34	-0.71	-0.97	0.97	0.71	2.34	0.90
Pd	-0.42	-0.64	-1.96	-1.90	1.90	1.96	0.64	0.42
Ag	-0.57	-1.23	-1.94	-1.19	1.19	1.94	1.23	0.57
Cd	-0.45	-1.81	-1.26	-1.39	1.39	1.26	1.81	0.45
Hf	-3.13	-1.74	-1.56	1.51	-1.51	1.56	1.74	3.13
Ta	-3.07	-2.28	-0.88	1.31	-1.31	0.88	2.28	3.07
W	-2.70	-3.17	0.05	0.91	-0.91	-0.05	3.17	2.70
Re	-2.34	-3.86	0.68	0.59	-0.59	-0.68	3.86	2.34
Os	-1.66	-3.01	-0.18	-0.07	0.07	0.18	3.01	1.66
Ir	-1.50	-2.79	-0.27	-0.36	0.36	0.27	2.79	1.50
Pt	-1.01	-2.11	-1.03	-0.76	0.76	1.03	2.11	1.01
Au	0.29	-0.70	-2.05	-2.46	2.46	2.05	0.70	-0.29

Supplementary Table **11** Reaction free energy (eV vs RHE) of elementary step for ORR and OER at U_{RHE} = 0V on single TM atom supported on **functional graphite materials with pyridine-4N coordination**.

	ORR				OER			
single TM atom	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6	ΔG_7	ΔG_8
Sc	-3.73	0.25	-3.73	2.29	-2.29	3.73	-0.25	3.73
Ti	-3.33	-0.97	-2.18	1.56	-1.56	2.18	0.97	3.33
V	-2.67	-2.86	-0.53	1.15	-1.15	0.53	2.86	2.67
Cr	-1.70	-3.12	-0.07	-0.03	0.03	0.07	3.12	1.70
Mn	-1.57	-2.72	-0.38	-0.25	0.25	0.38	2.72	1.57
Fe	-1.07	-1.95	-1.10	-0.81	0.81	1.10	1.95	1.07
Co	-0.73	-1.60	-1.45	-1.14	1.14	1.45	1.60	0.73
Ni	-0.63	-1.29	-1.43	-1.56	1.56	1.43	1.29	0.63
Cu	-0.66	-0.87	-1.68	-1.71	1.71	1.68	0.87	0.66
Zn	0.10	-0.88	-2.07	-2.06	2.06	2.07	0.88	-0.10
Y	-3.69	-0.10	-3.21	2.07	-2.07	3.21	0.10	3.69
Zr	-3.17	-1.32	-1.73	1.29	-1.29	1.73	1.32	3.17
Nb	-2.67	-3.40	0.28	0.86	-0.86	-0.28	3.40	2.67
Mo	-1.62	-3.01	0.00	-0.29	0.29	-0.00	3.01	1.62
Tc	-1.50	-2.73	-0.43	-0.26	0.26	0.43	2.73	1.50
Ru	-0.34	-1.42	-1.68	-1.47	1.47	1.68	1.42	0.34
Rh	-0.46	-1.53	-1.59	-1.34	1.34	1.59	1.53	0.46
Pd	0.41	-0.36	-2.43	-2.54	2.54	2.43	0.36	-0.41
Ag	-0.48	-1.06	-1.78	-1.60	1.60	1.78	1.06	0.48
Cd	0.07	-1.26	-1.84	-1.89	1.89	1.84	1.26	-0.07

Hf	-3.28	-1.54	-1.60	1.50	-1.50	1.60	1.54	3.28
Ta	-2.95	-2.39	-0.76	1.19	-1.19	0.76	2.39	2.95
W	-2.35	-3.60	0.51	0.52	-0.52	-0.51	3.60	2.35
Re	-1.90	-3.48	0.19	0.27	-0.27	-0.19	3.48	1.90
Os	-1.13	-2.39	-0.85	-0.55	0.55	0.85	2.39	1.13
Ir	-0.29	-1.44	-1.61	-1.59	1.59	1.61	1.44	0.29
Pt	0.18	-0.72	-2.45	-1.94	1.94	2.45	0.72	-0.18
Au	0.90	0.40	-3.00	-3.22	3.22	3.00	-0.40	-0.90

Supplementary Table 12. Reaction free energy (eV vs RHE) of elementary step for ORR and OER at U_{RHE} = 0V on single TM atom supported on **functional graphite materials with pyrrole-4N coordination**.

	ORR				OER			
single TM atom	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6	ΔG_7	ΔG_8
Sc	-3.67	0.20	-3.58	2.13	-2.13	3.58	-0.20	3.67
Ti	-3.03	-1.56	-1.82	1.49	-1.49	1.82	1.56	3.03
V	-2.86	-2.94	-0.14	1.02	-1.02	0.14	2.94	2.86
Cr	-1.51	-2.45	-0.53	-0.43	0.43	0.53	2.45	1.51
Mn	-1.20	-2.43	-0.65	-0.64	0.64	0.65	2.43	1.20
Fe	-0.78	-2.08	-1.10	-0.95	0.95	1.10	2.08	0.78
Co	-0.63	-1.24	-1.54	-1.50	1.50	1.54	1.24	0.63
Ni	0.24	-1.00	-2.08	-2.08	2.08	2.08	1.00	-0.24
Cu	0.78	-0.52	-2.46	-2.72	2.72	2.46	0.52	-0.78
Zn	0.95	-0.91	-2.27	-2.68	2.68	2.27	0.91	-0.95
Y	-4.04	0.65	-3.88	2.34	-2.34	3.88	-0.65	4.04
Zr	-3.24	-1.44	-1.77	1.53	-1.53	1.77	1.44	3.24
Nb	-2.20	-3.51	0.43	0.36	-0.36	-0.43	3.51	2.20
Mo	-1.46	-2.19	-0.69	-0.58	0.58	0.69	2.19	1.46
Tc	-0.83	-2.36	-0.89	-0.84	0.84	0.89	2.36	0.83
Ru	-0.32	-1.64	-1.48	-1.49	1.49	1.48	1.64	0.32
Rh	0.46	-1.22	-2.03	-2.14	2.14	2.03	1.22	-0.46
Pd	1.29	-0.63	-2.45	-3.12	3.12	2.45	0.63	-1.29
Ag	1.32	-0.42	-2.76	-3.05	3.05	2.76	0.42	-1.32
Cd	1.20	-0.34	-2.78	-3.00	3.00	2.78	0.34	-1.20
Hf	-3.41	-1.09	-2.06	1.64	-1.64	2.06	1.09	3.41
Ta	-2.80	-2.75	-0.53	1.16	-1.16	0.53	2.75	2.80
W	-1.61	-3.52	0.04	0.17	-0.17	-0.04	3.52	1.61
Re	-1.39	-2.12	-0.86	-0.55	0.55	0.86	2.12	1.39
Os	-0.76	-1.84	-1.34	-0.97	0.97	1.34	1.84	0.76
Ir	-0.63	-1.44	-1.53	-1.33	1.33	1.53	1.44	0.63
Pt	0.44	-1.24	-1.94	-2.17	2.17	1.94	1.24	-0.44
Au	1.60	-0.09	-3.09	-3.34	3.34	3.09	0.09	-1.60

Supplementary Table 13. Theoretical onset potential for ORR and OER(U^{onset}, V vs RHE), theoretical overpotential (η^{HER}, V vs RHE) for HER on single TM atom supported on **functional graphite materials with SV-3C coordination**. The catalytic performance better than or comparable to Pt(111) or IrO_2 is marked with red.

single TM atom	U^{onset}ORR	U^{onset}OER	η^{HER}
Sc	-2.23	3.87	-1.08
Ti	-2.02	3.53	-0.72
V	-1.29	2.95	-0.13
Cr	-1.05	2.72	-0.10
Mn	-1.22	2.72	-0.04
Fe	-0.73	3.17	-0.45
Co	-0.42	3.18	-0.23
Ni	-0.19	3.34	-0.14
Cu	0.22	2.47	-0.34
Zn	-0.03	2.57	-0.10
Y	-2.15	3.51	-1.12
Zr	-1.62	3.12	-0.82
Nb	-1.57	3.42	-0.12
Mo	-0.88	3.68	-0.22
Tc	-0.45	3.51	-0.37
Ru	0.06	2.72	-0.19
Rh	-0.08	2.45	-0.20
Pd	0.48	2.65	-0.46
Ag	0.48	2.44	-0.50
Cd	0.38	2.05	-0.32
Hf	-1.91	3.52	-0.61
Ta	-1.80	3.42	-0.54
W	-1.29	3.01	-0.24
Re	-1.12	2.77	-0.41
Os	-0.47	3.67	-0.49
Ir	-0.25	3.17	-0.38
Pt	0.09	2.75	-0.06
Au	0.81	1.82	-0.19

Supplementary Table 14. Theoretical onset potential for ORR and OER(U^{onset}, V vs RHE), theoretical overpotential (η^{HER}, V vs RHE) for HER on single TM atom supported on **functional graphite materials with DV-4C coordination**. The catalytic performance better than or comparable to Pt(111) or IrO_2 is marked with red.

single TM atom	U^{onset}ORR	U^{onset}OER	η^{HER}
Sc	-2.13	3.71	-0.86
Ti	-1.53	3.23	-0.46
V	-1.23	3.03	-0.24
Cr	-0.83	4.08	-0.49
Mn	-0.28	3.07	-0.53

Fe	0.05	2.85	-0.28
Co	0.39	2.29	-0.22
Ni	0.68	1.86	-0.31
Cu	0.68	1.83	-0.67
Zn	0.70	1.54	-0.52
Y	-1.96	3.58	-1.12
Zr	-1.66	3.27	-0.43
Nb	-1.06	2.79	-0.27
Mo	-0.66	3.67	-0.32
Tc	-0.17	3.29	-0.14
Ru	0.37	2.77	-0.02
Rh	0.71	2.34	-0.35
Pd	0.42	1.96	-0.75
Ag	0.57	1.94	-0.60
Cd	0.45	1.81	-0.71
Hf	-1.51	3.13	-0.59
Ta	-1.31	3.07	-0.06
W	-0.91	3.17	-0.35
Re	-0.68	3.86	-0.34
Os	0.07	3.01	-0.25
Ir	0.27	2.79	-0.03
Pt	0.76	2.11	-0.20
Au	-0.29	2.46	-0.97

Supplementary Table 15. Theoretical onset potential for ORR and OER(U^{onset}, V vs RHE), theoretical overpotential (η^{HER}, V vs RHE) for HER on single TM atom supported on **functional graphite materials with pyridine-4N coordination.** The catalytic performance better than or comparable to Pt(111) or IrO_2 is marked with red.

single TM atom	U^{onset}ORR	U^{onset}OER	η^{HER}
Sc	-2.29	3.73	-0.92
Ti	-1.56	3.33	-0.65
V	-1.15	2.86	-0.14
Cr	0.03	3.12	-0.12
Mn	0.25	2.72	-0.28
Fe	0.81	1.95	-0.25
Co	0.73	1.60	-0.10
Ni	0.63	1.56	-0.22
Cu	0.66	1.71	-0.98
Zn	-0.10	2.07	-0.86
Y	-2.07	3.69	-0.89
Zr	-1.29	3.17	-0.27
Nb	-0.86	3.40	-0.53
Mo	-0.00	3.01	-0.45

Tc	0.26	2.73	-0.07
Ru	0.34	1.68	-0.33
Rh	0.46	1.59	-0.57
Pd	-0.41	2.54	-0.91
Ag	0.48	1.78	-1.00
Cd	-0.07	1.89	-0.82
Hf	-1.50	3.28	-0.49
Ta	-1.19	2.95	-0.11
W	-0.52	3.60	-0.49
Re	-0.27	3.48	-0.25
Os	0.55	2.39	-0.08
Ir	0.29	1.61	-0.28
Pt	-0.18	2.45	-0.68
Au	-0.90	3.22	-1.05

Supplementary Table 16. Theoretical onset potential for ORR and OER(U^{onset}, V vs RHE), theoretical overpotential (η^{HER}, V vs RHE) for HER on single TM atom supported on **functional graphite materials with pyrrole-4N coordination**. The catalytic performance better than or comparable to Pt(111) or IrO_2 is marked with red.

single TM atom	U^{onset}ORR	U^{onset}OER	η^{HER}
Sc	-2.13	3.67	-0.68
Ti	-1.49	3.03	-0.25
V	-1.02	2.94	-0.31
Cr	0.43	2.45	-0.07
Mn	0.64	2.43	-0.01
Fe	0.78	2.08	-0.02
Co	0.63	1.54	-0.43
Ni	-0.24	2.08	-1.01
Cu	-0.78	2.72	-1.50
Zn	-0.95	2.68	-1.31
Y	-2.34	4.04	-0.68
Zr	-1.53	3.24	-0.19
Nb	-0.43	3.51	-0.39
Mo	0.58	2.19	-0.03
Tc	0.83	2.36	-0.40
Ru	0.32	1.64	-0.56
Rh	-0.46	2.14	-0.92
Pd	-1.29	3.12	-1.43
Ag	-1.32	3.05	-1.44
Cd	-1.20	3.00	-1.47
Hf	-1.64	3.41	-0.26
Ta	-1.16	2.80	-0.42
W	-0.17	3.52	-0.36

Re	0.55	2.12	-0.10
Os	0.76	1.84	-0.39
Ir	0.63	1.53	-0.58
Pt	-0.44	2.17	-0.92
Au	-1.60	3.09	-1.62

Supplementary Table 17. The difference between adsorption energy and cohesive energy (eV) of various single metal atoms ($E_{ad} - E_{coh}$), as well as E_{ad} (in parentheses). Negative values mean that embedding is stable against metal clustering or being leached.

	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
3C	-2.31	-2.66	-1.76	-1.89	-2.14	-2.31	-2.66	-1.81	-0.17	-0.15
	(-8.53)	(-8.67)	(-6.16)	(-6.10)	(-6.10)	(-7.63)	(-8.03)	(-6.85)	(-3.60)	(-3.34)
4C	-2.52	-2.80	-0.86	-1.60	-2.09	-1.59	-2.08	-1.99	-2.30	-1.88
	(-8.42)	(-8.81)	(-5.07)	(-5.90)	(-6.04)	(-6.89)	(-7.45)	(-7.03)	(-5.95)	(-6.16)
4-pyridine N	-4.36	-2.96	-2.25	-2.33	-2.45	-2.52	-2.36	-2.53	-1.34	-2.32
	(-9.44)	(-8.97)	(-6.74)	(-6.53)	(-6.40)	(-6.92)	(-7.77)	(-7.56)	(-4.98)	(-6.95)
4-pyrrole-N	-7.35	-6.04	-4.76	-4.88	-4.63	-3.88	-3.66	-3.39	-2.93	-3.59
	(-13.74)	(-12.10)	(-8.95)	(-9.08)	(-8.58)	(-9.91)	(-9.04)	(-8.43)	(-6.58)	(-8.69)
	Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
3C	-2.08	-2.19	-1.29	-0.86	-1.35	-2.05	-2.55	-1.31	1.05	0.95
	(-8.17)	(-8.34)	(-8.58)	(-9.28)	(-9.15)	(-9.53)	(-7.36)	(-5.08)	(-1.62)	(-1.05)
4C	-1.87	-2.69	-0.99	-1.19	-0.57	-1.76	-0.83	-1.44	-0.04	0.42
	(-9.03)	(-8.85)	(-5.03)	(-9.68)	(-9.42)	(-9.25)	(-4.88)	(-5.22)	(-3.11)	(-2.04)
4-pyridine N	-4.11	-2.48	-1.08	0.36	0.07	-0.07	-0.34	-1.51	0.99	0.17
	(-9.31)	(-8.64)	(-8.35)	(-8.12)	(-7.37)	(-6.55)	(-5.74)	(-5.28)	(-1.67)	(-0.46)
4-pyrrole-N	7.66	-5.83	-3.89	-3.42	-3.25	-3.11	-3.48	-3.79	-2.10	-2.98
	(-13.22)	(-12.00)	(-11.64)	(-11.90)	(-10.06)	(-10.60)	(-8.84)	(-7.56)	(-4.76)	(-2.57)
		Hf	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	
3C		-2.52	-1.16	-0.47	-0.69	-1.46	-2.22	-1.50	0.45	
		(-8.53)	(-8.46)	(-9.06)	(-9.42)	(-8.04)	(-7.57)	(-7.17)	(-2.06)	
4C		-1.82	-1.09	-0.25	-0.395	-0.71	-1.15	-2.08	-1.26	
		(-9.24)	(-8.85)	(-8.25)	(-9.68)	(-8.42)	(-8.07)	(-7.75)	(-2.63)	
4-pyridine N		-2.60	-0.52	1.20	0.73	0.35	-1.05	-1.75	-0.07	
		(-9.68)	(-8.93)	(-8.47)	(-8.15)	(-7.94)	(-7.59)	(-7.41)	(-1.75)	
4-pyrrole-N		-5.93	-3.35	-2.29	-1.94	-2.78	-3.56	-4.22	-3.73	
		(-12.93)	(-11.85)	(-11.36)	(-10.94)	(-10.55)	(-10.36)	(-9.88)	(-5.05)	

Supplementary Table 18. Valance electron in d-orbital (θ_d), electronegativity of single TM atom.

Atom	E	**single TM atom**	Θ_d	E_M	**single TM atom**	Θ_d	E_M	**single TM atom**	Θ_d	E_M

H	2.2	**Sc**	1	1.36	**Y**	1	1.22			
O	3.44	**Ti**	2	1.54	**Zr**	2	1.33	**Hf**	2	1.32
C	2.55	**V**	3	1.63	**Nb**	4	1.59	**Ta**	3	1.51
N	3.04	**Cr**	5	1.66	**Mo**	5	2.16	**W**	4	2.36
		Mn	5	1.55	**Tc**	6	1.91	**Re**	5	1.93
		Fe	6	1.83	**Ru**	7	2.2	**Os**	6	2.18
		Co	7	1.88	**Rh**	8	2.28	**Ir**	7	2.2
		Ni	8	1.92	**Pd**	10	2.2	**Pt**	9	2.28
		Cu	10	1.9	**Ag**	10	1.93	**Au**	10	2.54
		Zn	10	1.65	**Cd**	10	1.69			

Supplementary Table 19. Descriptor φ of single TM atom with SV-3C coordination. φ(O) is correlated with attachment between single TM atom and O atom. φ(H) is correlated with attachment between single TM atom and H atom.

single TM atom	φ(O)	φ(H)	**single TM atom**	φ(O)	φ(H)	**single TM atom**	φ(O)	φ(H)
Sc	2.62	4.10	Y	2.58	4.03			
Ti	5.34	8.35	Zr	5.22	8.16	Hf	5.22	8.15
V	8.09	12.65	Nb	10.74	16.80	Ta	7.99	12.49
Cr	13.53	21.16	Mo	14.26	22.30	W	11.64	18.20
Mn	13.37	20.91	Tc	16.67	26.07	Re	13.92	21.77
Fe	16.53	25.85	Ru	20.04	31.34	Os	17.15	26.81
Co	19.39	30.32	Rh	23.09	36.11	Ir	20.04	31.34
Ni	22.26	34.80	Pd	28.63	44.77	Pt	25.98	40.62
Cu	27.76	43.41	Ag	27.85	43.55	Au	29.62	46.32
Zn	27.03	42.27	Cd	27.15	42.45			

Supplementary Table 20. Descriptor φ of single TM atom with DV-4C coordination. φ(O) is correlated with attachment between single TM atom and O atom. φ(H) is correlated with attachment between single TM atom and H atom.

single TM atom	φ(O)	φ(H)	**single TM atom**	φ(O)	φ(H)	**single TM atom**	φ(O)	φ(H)
Sc	3.36	5.25	Y	3.36	5.19			

Ti	6.83	10.67	Zr	6.83	10.48	Hf	6.70	10.47
V	10.32	16.13	Nb	10.32	21.44	Ta	10.21	15.97
Cr	17.24	26.95	Mo	17.24	28.09	W	14.60	22.84
Mn	17.08	26.70	Tc	17.08	33.03	Re	17.63	27.57
Fe	20.98	32.81	Ru	20.98	39.45	Os	21.59	33.76
Co	24.58	38.44	Rh	24.58	45.38	Ir	25.23	39.45
Ni	28.19	44.07	Pd	28.19	56.36	Pt	32.65	51.05
Cu	35.17	55.00	Ag	35.17	55.14	Au	37.03	57.91
Zn	34.45	53.86	Cd	34.45	54.05			

Supplementary Table 21. Descriptor φ of single TM atom with pyridine-4N coordination. φ(O) is correlated with attachment between single TM atom and O atom. φ(H) is correlated with attachment between single TM atom and H atom.

single TM atom	φ(O)	φ(H)	**single TM atom**	φ(O)	φ(H)	**single TM atom**	φ(O)	φ(H)
Sc	3.93	6.15	Y	3.89	6.08			
Ti	7.97	12.45	Zr	7.84	12.26	Hf	7.84	12.25
V	12.03	18.80	Nb	15.99	25.00	Ta	11.92	18.64
Cr	20.09	31.41	Mo	20.81	32.55	W	16.88	26.40
Mn	19.93	31.16	Tc	24.54	38.37	Re	20.48	32.02
Fe	24.40	38.15	Ru	29.22	45.69	Os	25.01	39.11
Co	28.57	44.67	Rh	33.58	52.51	Ir	29.22	45.69
Ni	32.74	51.20	Pd	41.74	65.27	Pt	37.78	59.07
Cu	40.87	63.91	Ag	40.96	64.05	Au	42.73	66.82
Zn	40.15	62.77	Cd	40.26	62.95			

Supplementary Table 22. Descriptor φ of single TM atom with pyrrole-4N coordination. φ(O) is correlated with attachment between single TM atom and O atom. φ(H) is correlated with attachment between single TM atom and H atom.

single TM atom	φ(O)	φ(H)	**single TM atom**	φ(O)	φ(H)	**single TM atom**	φ(O)	φ(H)
Sc	4.81	7.53	Y	4.77	7.46			

Ti	9.73	15.22	Zr	9.61	15.03	Hf	9.60	15.02
V	14.68	22.95	Nb	19.52	30.53	Ta	14.57	22.79
Cr	24.51	38.32	Mo	25.23	39.45	W	20.42	31.93
Mn	24.35	38.07	Tc	29.84	46.66	Re	24.90	38.93
Fe	29.70	46.45	Ru	35.41	55.36	Os	30.31	47.40
Co	34.76	54.35	Rh	40.65	63.56	Ir	35.41	55.36
Ni	39.81	62.25	Pd	50.58	79.09	Pt	45.73	71.51
Cu	49.71	77.73	Ag	49.80	77.86	Au	51.57	80.64
Zn	48.98	76.59	Cd	49.10	76.77			

Supplementary Table 23. The adsorption free energies of adsorbates (eV), reaction energy of each elementary steps (eV) on Pt(111), IrO_2(110) and promising SACs candidates marked with red in Supplementary Table 13-16 after solvation corrections.

	ΔG_{OH^*}	ΔG_{OOH^*}	ORR				OER			
			ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6	ΔG_7	ΔG_8
Pt(111)	0.5	3.8	-1.12	-2.18	-1.12	-0.50	/	/	/	/
IrO_2(110)	-0.19	2.94	/	/	/	/	-0.19	1.55	1.58	1.98
Au-SV-3C	0.95	3.59	-1.33	-1.53	-1.11	-0.95	0.95	1.11	1.53	1.33
Pt-DV-4C	0.46	3.61	-1.31	-1.81	-1.34	-0.46	/	/	/	/
Fe-pyridine-4N	0.51	3.55	-1.37	-1.65	-1.39	-0.51	/	/	/	/
Co-pyridine-4N	0.84	3.89	-1.03	-1.30	-1.75	-0.84	/	/	/	/
Fe-pyrrole-4N	0.65	3.84	-1.08	-1.79	-1.40	-0.65	/	/	/	/
Tc-pyrrole-4N	0.54	3.79	-1.13	-2.06	-1.19	-0.54	/	/	/	/
Os-pyrrole-4N	0.67	3.86	-1.06	-1.55	-1.64	-0.67	/	/	/	/
Ni-DV-4C	0.38	3.51	/	/	/	/	0.38	1.56	1.57	1.41
Zn-DV-4C	0.96	3.92	/	/	/	/	0.96	1.71	1.25	1.00
Cd-DV-4C	1.09	4.17	/	/	/	/	1.09	1.56	1.52	0.75
Co-pyridine-4N	0.84	3.89	/	/	/	/	0.84	1.75	1.30	1.03
Ni-pyridine-4N	1.26	3.99	/	/	/	/	1.26	1.73	1.00	0.93
Cu-pyridine-4N	1.41	3.96	/	/	/	/	1.41	1.99	0.56	0.96
Ru-pyridine-4N	1.17	4.28	/	/	/	/	1.17	1.98	1.13	0.64
Rh-pyridine-4N	1.04	4.16	/	/	/	/	1.04	1.89	1.23	0.76
Ir-pyridine-4N	1.29	4.33	/	/	/	/	1.29	1.90	1.14	0.59
Co-pyrrole-4N	1.2	3.99	/	/	/	/	1.20	1.85	0.94	0.93
Ru-pyrrole-4N	1.19	4.3	/	/	/	/	1.19	1.77	1.34	0.62
Ir-pyrrole-4N	1.03	3.99	/	/	/	/	1.03	1.82	1.14	0.93

Supplementary Table 24. The electrocatalytic activity (V vs RHE) on promising SACs candidates marked with red in Supplementary Table 13-16 after solvation corrections.

	$U^{onset}ORR$	$U^{onset}OER$
Pt(111)	-0.50	
IrO_2(110)		1.98
Au-SV-3C	-0.95	1.53
Pt-DV-4C	-0.46	
Fe-pyridine-4N	-0.51	
Co-pyridine-4N	-0.84	
Fe-pyrrole-4N	-0.65	
Tc-pyrrole-4N	-0.54	
Os-pyrrole-4N	-0.67	
Ni-DV-4C		1.57
Zn-DV-4C		1.71
Cd-DV-4C		1.56
Co-pyridine-4N		1.75
Ni-pyridine-4N		1.73
Cu-pyridine-4N		1.99
Ru-pyridine-4N		1.98
Rh-pyridine-4N		1.89
Ir-pyridine-4N		1.90
Co-pyrrole-4N		1.85
Ru-pyrrole-4N		1.77
Ir-pyrrole-4N		1.82

Supplementary Table 25. Experimental U^{onset}_{ORR} in alkaline electrolyte and η^{HER} in acidic electrolyte (V) vs RHE on single TM atom supported on function graphene materials with different active centers in reference.

Active center	Experimental Activity (U^{onset}_{ORR} and η^{HER})	Reference
	ORR	
V-pyridine-4N	0.79	4
Mn-pyridine-4N	0.82	4
Fe-pyridine-4N	0.965	7
Co-pyridine-4N	0.92	8
Ni-pyridine-4N	0.89	1
Ag-pyridine-4N	0.87	9
Fe-pyrrole-4N	0.927	10
Ni-SV-3N	1.01	11
Co-DV-2C2N	0.991	3
Pt-SV-2C1N	0.93	12
	HER	
Mn-pyridine-4N	-0.275	13
Co-pyridine-4N	-0.069	13
Ni-pyridine-4N	-0.22	13
Co-DV-4C	-0.2	14

Co-DV-3C1N	-0.05	15
Pt-SV-2C1N	-0.015	16

Supplementary Table 26. Descriptor φ, theoretical results for ORR/HER of single TM atom with C/N hybrid coordination

Active center	**ORR**									**HER**		
	φ(O)	ΔG_{OH}^*	ΔG_O^*	ΔG_{OOH}^*	ΔG_1	ΔG_2	ΔG_3	ΔG_4	U^{onset}	φ(H)	ΔG_H^*	η
Ni-SV-3N	25.67	0.81	1.79	3.85	-1.07	-2.06	-0.98	-0.81	0.81	/	/	/
Co-DV-2C2N	26.58	0.82	1.82	3.94	-0.98	-2.12	-1.00	-0.82	0.82	/	/	/
Pt-SV-2C1N	27.26	0.77	1.89	3.91	-1.01	-2.02	-1.12	-0.77	0.77	42.63	0.015	-0.015
Co-DV-3C1N	/	/	/	/	/	/	/	/	/	40.00	-0.04	-0.04

Supplementary Table 27. Adsorption free energies of OH and H (eV) on single TM atom supported on macrocyclic molecule with SV-3C coordination.

Active center	ΔG_{OH}^*	ΔG_H^*
Sc	-2.42	0.84
Ti	-2.21	0.56
V	-1.77	0.28
Cr	-0.81	-0.14
Mn	-1.06	-0.06
Fe	-0.86	-0.34
Co	-0.60	-0.24
Ni	-0.22	-0.25
Cu	0.36	0.37
Zn	0.16	0.10
Y	-1.79	1.05
Zr	-1.79	0.96
Nb	-1.48	-0.06
Mo	-0.75	-0.11
Tc	-0.47	-0.59
Ru	-0.13	-0.39
Rh	-0.20	-0.25
Pd	0.61	0.44
Ag	0.69	0.46
Cd	0.52	0.20
Hf	-1.99	0.78
Ta	-1.75	0.42
W	-1.38	0.07
Re	-1.12	-0.24
Os	-0.58	-0.52

Ir	-0.44	-0.37
Pt	0.20	-0.01
Au	1.09	0.28

Supplementary Table 28. Adsorption free energies of OH and H (eV) on single TM atom supported on macrocyclic molecule with DV-4C coordination.

Active center	ΔG_{OH}^*	ΔG_H^*
Sc	-2.05	0.99
Ti	-1.40	0.55
V	-1.18	0.27
Cr	-0.67	-0.50
Mn	-0.29	-0.49
Fe	0.06	-0.34
Co	0.45	-0.28
Ni	0.88	0.22
Cu	1.35	0.84
Zn	1.16	0.54
Y	-2.13	0.97
Zr	-1.66	0.57
Nb	-1.18	-0.18
Mo	-0.31	-0.35
Tc	-0.35	-0.25
Ru	0.43	-0.04
Rh	0.72	0.29
Pd	1.76	0.80
Ag	1.26	0.62
Cd	1.29	0.51
Hf	-1.66	0.54
Ta	-1.26	0.09
W	-1.01	-0.21
Re	-0.72	-0.51
Os	-0.18	-0.36
Ir	0.24	-0.09
Pt	0.71	0.40
Au	2.09	0.85

Supplementary Table 29. Adsorption free energies of OH and H (eV) on single TM atom supported on macrocyclic molecule with pyridine-4N coordination.

Active center	ΔG_{OH}^*	ΔG_H^*
Sc	-2.02	0.78
Ti	-1.78	0.49
V	-1.02	0.12

Cr	0.11	-0.13
Mn	0.22	-0.19
Fe	0.76	-0.04
Co	0.97	0.14
Ni	1.40	0.50
Cu	1.88	1.00
Zn	1.91	0.73
Y	-2.22	0.80
Zr	-1.21	0.14
Nb	-0.60	-0.52
Mo	0.12	-0.36
Tc	-0.06	0.01
Ru	1.42	0.42
Rh	1.22	0.47
Pd	2.15	0.96
Ag	1.59	1.09
Cd	1.56	0.76
Hf	-1.79	0.43
Ta	-1.36	0.07
W	-0.76	-0.47
Re	-0.41	-0.38
Os	0.36	-0.12
Ir	1.44	0.26
Pt	2.02	0.67
Au	2.28	1.04

Supplementary Table 30. Adsorption free energies of OH and H (eV) on single TM atom supported on macrocyclic molecule with pyrrole-4N coordination.

Active center	ΔG_{OH}^{*}	ΔG_{H}^{*}
Sc	-1.97	0.76
Ti	-1.61	0.09
V	-1.27	-0.20
Cr	0.31	0.09
Mn	0.46	0.05
Fe	1.13	0.12
Co	1.41	0.41
Ni	2.29	0.83
Cu	3.03	1.23
Zn	2.68	1.28
Y	-2.25	0.69
Zr	-1.52	0.23
Nb	-0.50	-0.23
Mo	0.48	-0.13

Tc	0.72	0.30
Ru	1.26	0.55
Rh	1.82	0.89
Pd	3.04	1.62
Ag	2.92	1.27
Cd	2.56	1.31
Hf	-1.42	0.08
Ta	-1.06	-0.26
W	-0.39	-0.24
Re	0.40	-0.08
Os	0.74	0.27
Ir	1.27	0.73
Pt	2.68	1.32
Au	3.16	1.39

Supplementary Table 31. Reaction free energy (eV vs RHE) of elementary step for ORR at U_{RHE}=0V on single TM atom supported on macrocyclic molecule.

Active site	ORR			
	ΔG_1	ΔG_2	ΔG_3	ΔG_4
Au-SV-3C	-0.79	-1.97	-1.07	-1.09
Pt-DV-4C	-1.04	-2.47	-0.70	-0.71
V-pyridine-4N	-3.14	-2.56	-0.24	1.02
Mn-pyridine-4N	-1.75	-2.68	-0.27	-0.22
Fe-pyridine-4N	-0.99	-2.08	-1.09	-0.76
Co-pyridine-4N	-0.83	-1.73	-1.39	-0.97
Ni-pyridine-4N	-0.67	-1.33	-1.52	-1.40
Ag-pyridine-4N	-0.55	-0.91	-1.87	-1.59
Fe-pyrrole-4N	-0.73	-2.35	-0.71	-1.13
Tc-pyrrole-4N	-1.15	-2.31	-0.74	-0.72
Os-pyrrole-4N	-1.20	-2.24	-0.74	-0.74

Supplementary Table 32. Reaction free energy (eV vs RHE) of elementary step for OER at U_{RHE} = 0V on single TM atom supported on macrocyclic molecule.

Active site	OER			
	ΔG_5	ΔG_6	ΔG_7	ΔG_8
Au-SV-3C	1.09	1.07	1.97	0.79
Ni-DV-4C	0.88	0.97	1.98	1.09
Cu-DV-4C	1.35	1.24	1.88	0.46
Zn-DV-4C	1.16	1.23	1.58	0.96
Cd-DV-4C	1.29	1.39	1.77	0.47
Co-pyridine-4N	0.97	1.39	1.73	0.83
Ni-pyridine-4N	1.40	1.52	1.33	0.67

Cu-pyridine-4N	1.88	1.76	1.27	0.00
Ru-pyridine-4N	1.42	1.32	1.83	0.35
Rh-pyridine-4N	1.22	1.35	1.70	0.66
Ag-pyridine-4N	1.59	1.87	0.91	0.55
Cd-pyridine-4N	1.56	1.45	1.72	0.19
Ir-pyridine-4N	1.44	1.51	1.57	0.40
Co-pyrrole-4N	1.41	1.44	1.62	0.44
Ru-pyrrole-4N	1.26	1.29	1.63	0.74
Ir-pyrrole-4N	1.27	1.39	1.55	0.70

Supplementary Table 33. The values of U-J parameters for DFT/PBE+U calculations

3d	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
U-J	2.11	2.58	2.72	2.79	3.06	3.29	3.42	3.4	3.87	4.12

Supplementary Table 34. The spin states of single TM atom supported on functional graphite materials **with SV-3C coordination** without adsorbates as well as with O^*, OH^*, OOH^*, H^* adsorption.

	Without adsorbate	**O^***	**OH^***	**OOH^***	**H^***
Sc	1	1.58	1.49	2.09	2.21
Ti	1	1.44	1	1	1
V	1.98	1	1	1	1
Cr	3	1.72	2.40	2.36	4.01
Mn	3.97	3.06	3	3	2.96
Fe	1	2.55	1.89	1.70	1.63
Co	1.90	1.21	1	1	1
Ni	1	1	1.96	1.94	2
Cu	1.95	2.01	1.15	1.35	2.50
Zn	2.34	3.03	2.34	2.17	3.50
Y	1	2.46	1	1	1
Zr	1	2.05	1	1	1
Nb	1.97	1	1	1	2.97
Mo	3	2	2.04	2	2
Tc	1.99	2	1.93	1.75	2
Ru	1	1.22	1	1	1
Rh	1.83	1.42	1	1	1
Pd	1	1.62	1.95	1.69	1.89
Ag	2	1.86	1.27	1.05	2.20
Cd	3	1.86	2.18	1.90	2.34
Hf	1	1	1	1	1
Ta	1.88	1	1	1	1
W	3	1	2	2	2
Re	2	1.80	2.97	2.92	2.96

Os	1	1.83	1	1.39	1.51
Ir	1.94	1	1	1	1
Pt	1	1	1.90	1.97	1.59
Au	1.07	1.87	1	1	1.66

Supplementary Table 35. The spin states of single TM atom supported on functional graphite materials **with DV-4C coordination** without adsorbates as well as with O^*, OH^*, OOH^*, H^* adsorption.

	Without adsorbate	**O^***	**OH^***	**OOH^***	**H^***
Sc	1	1.38	1.09	1.03	1.21
Ti	1	1	1	1	1
V	1.18	1	1	1	1
Cr	1.92	1.70	2.02	2.11	2.10
Mn	1.70	1.98	2.87	2.82	3.10
Fe	1.12	1	1	1.54	2.39
Co	2.02	2.16	1.17	1	2.37
Ni	2.18	2.46	1	1	1
Cu	1	1.92	1	1.26	2
Zn	1	2.01	1.25	1.12	2.17
Y	1	2.04	1	1	2
Zr	1	1.69	1	1	2
Nb	1.66	1	1	1	1
Mo	1.60	1	2	1.53	1.99
Tc	1	1	1.05	1.25	1
Ru	1	1	1	1	1
Rh	1.94	1.07	1	1	1
Pd	1	1	1.74	1.66	2
Ag	1	2.15	1	1	1
Cd	2	2.03	2	2	1.14
Hf	1	1.56	1	1	1
Ta	1	1	1	1	1
W	1.03	1	1.99	2	1.28
Re	1	1.77	3.03	3.12	1.99
Os	1	1	1	1	1
Ir	2	1	1	1	1
Pt	1.38	1	1	1	1.99
Au	1.07	1.17	1	1	1.96

Supplementary Table 36. The spin states of single TM atom supported on functional graphite materials **with pyridine-4N coordination** without adsorbates as well as with O^*, OH^*, OOH^*, H^* adsorption.

	Without adsorbate	**O^***	**OH^***	**OOH^***	**H^***
Sc	2	1.08	1.19	1.11	1.05

Ti	2.10	1	1.35	1.44	1
V	3.08	1	3.14	3.07	1
Cr	4.99	1.30	3.87	3.97	2.92
Mn	4.02	1.71	3.42	3.38	3
Fe	1.18	3	2.06	2	1.99
Co	1.01	3.94	1	1	1
Ni	1	4.37	1.56	1.98	1.75
Cu	2	2.89	1.92	2.53	1.75
Zn	2	3.01	2.05	2.12	2.02
Y	1	2.14	1	1	1
Zr	1.83	1	1	1	1
Nb	3.96	1.53	1	1	2.05
Mo	4.12	1.46	1	1	2.42
Tc	2.89	1	2.01	2.17	1.47
Ru	2.68	1.16	2	2.04	1.51
Rh	1.03	1.07	1	1	1
Pd	1	2.64	1.97	2	1.10
Ag	1.62	2.64	1.34	1.48	1
Cd	2.58	2.84	2.12	2.08	1.14
Hf	1.92	1	1	1	1
Ta	2	1	1	1	1
W	3.17	1.67	1	1	2.08
Re	3.03	2.21	2.04	2.11	3
Os	3.06	1.66	1.96	2	1.78
Ir	4	1.70	2	2	2
Pt	1	1.40	1	1	1
Au	1.07	1.17	1	1	1.06

Supplementary Table 37. The spin states of single TM atom supported on functional graphite materials **with pyrrole-4N coordination** without adsorbates as well as with O^*, OH^*, OOH^*, H^* adsorption.

	Without adsorbate	**O^***	**OH^***	**OOH^***	**H^***
Sc	1	1.88	2	1	1
Ti	1	1.72	1.03	1.07	1
V	2.02	2	2.07	2.07	3
Cr	4.06	1.77	3.10	3.22	3
Mn	4.34	1.24	4.10	3.80	3.10
Fe	3.03	1.01	2.45	2.23	2.02
Co	2	3.18	1.55	1.59	1.33
Ni	1.62	4.04	1.27	3.07	2.46
Cu	2.88	4.48	3.80	3.94	1.70
Zn	3	4.02	3.15	3.14	1.92
Y	1	1.11	1	1	1

Zr	1	1.76	1	1	1
Nb	2.91	2.13	3.09	3.04	2
Mo	3.02	1.95	4.10	4.02	2
Tc	2.07	2	3.07	3.11	2.27
Ru	2.67	1	1.32	1.26	1
Rh	1	1	1	1	1
Pd	1.12	1.58	2.62	2.58	1
Ag	2.52	4.27	2.53	2.25	1.10
Cd	3.53	1.94	3.12	3.09	1.04
Hf	1.02	1.72	1	1	1
Ta	1	2	1	1	1
W	3	2.02	2	2	2
Re	3	3.11	3.06	3.17	3
Os	3.29	1	1.32	1.18	1
Ir	4	1.05	1.09	1.12	1
Pt	1	1.83	1.77	2.10	1
Au	1.07	2.14	2.04	2.06	1.01

Supplementary Table 38. The thermodynamic corrections to gas phase molecule and adsorbates derived from solvent effect (G_{solv}).

Species	**G_{solv} (eV)**
O^*	0
OH^*	-0.30
OOH^*	-0.30
H_2(g)	0
H_2O(g)	0

Supplementary Table 39. DFT adsorption energies of O (ΔE_{O^*}, eV), bond length of metal-oxygen (d(M-O), Å), harmonic vibrational frequencies of adsorbed O ($v(O^*)$, cm^{-1}) on single TM atom supported on functional graphite materials **with SV-3C coordination**.

single TM atom	**ΔGo^***	**d(M-O)**	**$v(O^*)$**
Sc	0.89	1.680	836
Ti	0.54	1.620	1031
V	-0.20	1.651	974
Cr	-0.55	1.580	1126
Mn	0.10	1.620	1049
Fe	-1.19	1.618	1020
Co	-0.34	1.607	1085
Ni	-0.23	1.621	1026
Cu	0.67	1.669	1046
Zn	0.59	1.722	829

Y	0.80	1.745	821
Zr	0.40	1.678	962
Nb	0.06	1.711	906
Mo	-1.25	1.649	1044
Tc	-0.75	1.676	985
Ru	0.24	1.668	1005
Rh	0.33	1.662	998
Pd	0.93	1.687	963
Ag	1.05	1.669	1015
Cd	1.23	1.722	925
Hf	0.32	1.798	736
Ta	-0.14	1.800	729
W	-0.35	1.789	768
Re	-0.40	1.773	903
Os	-1.01	1.768	890
Ir	-0.36	1.760	901
Pt	0.33	1.781	867
Au	2.02	1.831	758

Supplementary Table 40. DFT adsorption energies of OH (ΔE_{OH}^{*}, eV), bond length of metal-oxygen (d(M-O), Å) and oxygen-hydrogen (d(O-H), Å), harmonic vibrational frequencies of adsorbed OH (v(O-H), cm^{-1}) on single TM atom supported on functional graphite materials **with SV-3C coordination**.

single TM atom	ΔE_{OH}^{*}	**d(M-O)**	**d(O-H)**	**v(O-H)**
Sc	-2.57	1.910	0.975	3714
Ti	-2.36	1.870	0.972	3774
V	-1.63	1.970	0.967	3752
Cr	-1.39	1.810	0.969	3796
Mn	-1.56	1.770	0.963	3819
Fe	-1.07	1.779	0.974	3735
Co	-0.76	1.770	0.974	3776
Ni	-0.53	1.775	0.969	3772
Cu	-0.12	1.793	0.969	3815
Zn	-0.37	3.200	0.963	3862
Y	-2.49	2.054	0.965	3813
Zr	-1.96	2.038	0.967	3795
Nb	-1.91	1.972	0.964	3784
Mo	-1.22	1.705	0.967	3831
Tc	-0.79	1.920	0.963	3753
Ru	-0.28	1.941	0.972	3889
Rh	-0.42	1.906	0.964	3758
Pd	0.14	1.991	0.973	3758
Ag	0.27	1.960	0.960	3891
Cd	0.04	1.967	0.961	3863

Hf	-2.25	1.990	0.963	3799
Ta	-2.14	1.981	0.967	3805
W	-1.63	1.957	0.970	3852
Re	-1.46	1.921	0.962	3817
Os	-0.81	1.940	0.974	3763
Ir	-0.59	1.939	0.975	3852
Pt	-0.25	1.976	0.975	3749
Au	0.91	1.956	0.966	3747

Supplementary Table 41. DFT adsorption energies of OOH (ΔE_{OOH}^*, eV), bond length of metal-oxygen (d(M-O), Å), oxygen-hydrogen (d(O-H), Å) and oxygen- oxygen (d(O-O), Å), harmonic vibrational frequencies of adsorbed OOH (v(O-H), v(O-O), cm^{-1}) on single TM atom supported on functional graphite materials **with SV-3C coordination**.

single TM atom	ΔE_{OOH}^*	**d(M-O)**	**d(O-H)**	**v(O-H)**	**d(O-O)**	**v(O-O)**
Sc	0.60	1.970	0.985	3636	1.498	1221
Ti	0.94	1.940	0.983	3641	1.483	1229
V	1.52	1.910	0.982	3637	1.485	1252
Cr	1.75	1.880	0.981	3651	1.479	1258
Mn	1.75	1.840	0.980	3656	1.490	1266
Fe	2.17	1.785	0.981	3656	1.484	1265
Co	2.42	1.787	0.982	3627	1.480	1257
Ni	2.71	1.830	0.982	3635	1.487	1224
Cu	2.72	1.832	0.983	3626	1.495	1222
Zn	2.75	1.838	0.982	3652	1.491	1231
Y	0.96	2.175	0.978	3661	1.501	1210
Zr	1.35	2.038	0.980	3626	1.458	1267
Nb	1.05	1.961	0.980	3647	1.453	1267
Mo	2.02	2.076	0.980	3626	1.450	1273
Tc	2.35	1.968	0.981	3649	1.482	1225
Ru	2.54	1.941	0.981	3632	1.477	1238
Rh	2.37	1.968	0.982	3641	1.471	1230
Pd	3.17	1.984	0.980	3628	1.459	1263
Ag	3.08	2.035	0.980	3649	1.451	1259
Cd	2.87	2.047	0.978	3663	1.487	1226
Hf	0.95	2.118	0.979	3657	1.499	1217
Ta	1.05	2.097	0.982	3647	1.492	1225
W	1.46	2.045	0.981	3626	1.494	1225
Re	1.70	1.964	0.981	3636	1.506	1208
Os	2.25	1.941	0.981	3613	1.505	1211
Ir	2.40	1.953	0.981	3674	1.493	1202
Pt	2.67	1.976	0.980	3621	1.485	1232
Au	3.44	1.997	0.979	3638	1.467	1273

Supplementary Table 42. DFT adsorption energies of H (ΔE_H^*, eV), bond length of metal-hydrogen (d(M-H), Å), harmonic vibrational frequencies of adsorbed H ($v(H^*)$, cm^{-1}) on single TM atom supported on functional graphite materials **with SV-3C coordination**.

single TM atom	ΔE_H^*	d(M-H)	$v(H^*)$
Sc	0.84	2.015	927
Ti	0.48	1.986	982
V	-0.11	1.652	1537
Cr	-0.34	1.626	1686
Mn	-0.28	1.621	1707
Fe	-0.69	1.574	1777
Co	-0.47	1.556	1805
Ni	-0.38	1.583	1648
Cu	0.10	1.656	1621
Zn	-0.14	1.659	1639
Y	0.88	1.997	1031
Zr	0.58	1.970	1084
Nb	-0.36	1.637	1682
Mo	-0.46	1.797	1363
Tc	-0.61	1.583	1721
Ru	-0.43	1.602	1653
Rh	-0.44	1.596	1685
Pd	0.22	1.723	1426
Ag	0.26	1.698	1479
Cd	0.08	1.643	1604
Hf	0.37	1.950	1016
Ta	0.30	1.867	1269
W	-0.48	1.804	1417
Re	-0.65	1.752	1570
Os	-0.73	1.707	1695
Ir	-0.62	1.685	1748
Pt	-0.18	1.698	1704
Au	-0.05	1.669	1783

Supplementary Table 43. DFT adsorption energies of O (ΔE_O^*, eV), bond length of metal-oxygen (d(M-O), Å), harmonic vibrational frequencies of adsorbed O ($v(O^*)$, cm^{-1}) on single TM atom supported on functional graphite materials **with DV-4C coordination**.

single TM atom	ΔG_O^*	d(M-O)	$v(O^*)$
Sc	0.72	1.689	990
Ti	0.41	1.661	1031
V	-0.29	1.612	1104
Cr	-1.57	1.588	1159

Mn	-0.02	1.578	1187
Fe	0.37	1.564	1125
Co	1.48	1.614	1031
Ni	1.90	1.670	960
Cu	3.16	1.794	728
Zn	2.63	1.762	780
Y	0.90	1.692	921
Zr	0.75	1.825	1153
Nb	-0.67	1.635	819
Mo	-1.17	1.712	780
Tc	-0.37	1.605	865
Ru	0.93	1.654	793
Rh	1.64	1.703	728
Pd	3.82	1.828	603
Ag	3.08	1.992	495
Cd	2.61	1.793	647
Hf	0.01	1.583	1067
Ta	-0.47	1.573	1126
W	-1.00	1.581	1136
Re	-1.31	1.590	1097
Os	0.21	1.636	1036
Ir	0.59	1.651	1004
Pt	1.76	1.827	806
Au	4.47	2.015	479

Supplementary Table 44. DFT adsorption energies of OH (ΔE_{OH}^*, eV), bond length of metal-oxygen (d(M-O), Å) and oxygen-hydrogen (d(O-H), Å), harmonic vibrational frequencies of adsorbed OH (v(O-H), cm^{-1}) on single TM atom supported on functional graphite materials **with DV-4C coordination**.

single TM atom	**ΔE_{OH}^***	**d(M-O)**	**d(O-H)**	**v(O-H)**
Sc	-2.47	1.863	0.971	3815
Ti	-1.87	1.835	0.968	3829
V	-1.57	1.785	0.974	3796
Cr	-1.04	1.754	0.977	3784
Mn	-0.62	1.772	0.974	3721
Fe	-0.29	1.739	0.975	3715
Co	0.05	1.759	0.977	3711
Ni	0.34	1.827	0.976	3715
Cu	1.02	1.879	0.975	3726
Zn	0.92	1.881	0.973	3721
Y	-2.30	2.012	0.965	3846
Zr	-2.00	2.001	0.966	3815
Nb	-1.40	1.953	0.969	3792
Mo	-0.81	1.899	0.975	3790

Tc	-0.51	1.895	0.972	3761
Ru	0.03	1.896	0.974	3744
Rh	0.63	1.963	0.974	3758
Pd	1.56	2.011	0.975	3731
Ag	0.85	2.069	0.975	3748
Cd	1.05	2.053	0.974	3715
Hf	-1.85	1.954	0.964	3826
Ta	-1.65	1.926	0.970	3818
W	-1.25	1.895	0.973	3783
Re	-0.93	1.896	0.972	3777
Os	-0.27	1.893	0.975	3725
Ir	0.02	1.962	0.982	3735
Pt	0.42	2.044	0.977	3745
Au	2.12	2.063	0.975	3725

Supplementary Table 45. DFT adsorption energies of OOH (ΔE_{OOH^*}, eV), bond length of metal-oxygen (d(M-O), Å), oxygen-hydrogen (d(O-H), Å) and oxygen- oxygen (d(O-O), Å), harmonic vibrational frequencies of adsorbed OOH (v(O-H), v(O-O), cm^{-1}) on single TM atom supported on functional graphite materials **with DV-4C coordination**.

single TM atom	**ΔE_{OOH^*}**	**d(M-O)**	**d(O-H)**	**v(O-H)**	**d(O-O)**	**v(O-O)**
Sc	0.76	1.897	0.983	3641	1.491	1318
Ti	1.24	1.911	0.981	3630	1.480	1249
V	1.44	1.864	0.983	3658	1.473	1283
Cr	2.10	1.769	0.981	3643	1.467	1261
Mn	2.64	1.755	0.982	3627	1.458	1296
Fe	2.82	1.693	0.981	3651	1.512	1315
Co	3.35	1.746	0.983	3667	1.451	1327
Ni	3.36	1.830	0.981	3636	1.442	1293
Cu	3.79	1.948	0.982	3645	1.416	1327
Zn	3.77	1.973	0.981	3627	1.436	1336
Y	0.89	2.093	0.983	3654	1.487	1281
Zr	1.20	2.085	0.980	3638	1.491	1267
Nb	1.68	2.012	0.982	3635	1.489	1263
Mo	2.09	1.961	0.984	3647	1.477	1273
Tc	2.51	1.928	0.983	3621	1.441	1259
Ru	3.29	1.896	0.981	3658	1.436	1323
Rh	3.57	1.943	0.984	3641	1.415	1334
Pd	4.05	2.061	0.981	3634	1.428	1307
Ag	3.90	2.120	0.982	3626	1.425	1339
Cd	4.02	2.153	0.983	3646	1.448	1296
Hf	1.34	2.053	0.980	3657	1.496	1252
Ta	1.40	2.015	0.984	3631	1.492	1276

W	1.77	1.976	0.983	3657	1.474	1253
Re	2.13	1.953	0.981	3643	1.433	1298
Os	2.81	1.932	0.982	3649	1.419	1311
Ir	2.97	1.983	0.983	3638	1.438	1302
Pt	3.46	2.068	0.984	3647	1.448	1284
Au	4.76	2.164	0.984	3626	1.484	1279

Supplementary Table 46. DFT adsorption energies of H (ΔE_H^*, eV), bond length of metal-hydrogen (d(M-H), Å), harmonic vibrational frequencies of adsorbed H ($v(H^*)$, cm^{-1}) on single TM atom supported on functional graphite materials **with DV-4C coordination**.

single TM atom	ΔE_H^*	**d(M-H)**	**$v(H^*)$**
Sc	0.62	1.776	1553
Ti	0.22	1.757	1603
V	0.00	1.689	1724
Cr	-0.73	1.611	1847
Mn	-0.77	1.568	1904
Fe	-0.52	1.527	1861
Co	-0.02	1.441	2063
Ni	0.07	1.441	2094
Cu	0.43	1.504	1942
Zn	0.28	1.567	1806
Y	0.88	1.904	1463
Zr	0.19	1.917	1431
Nb	-0.51	1.863	1573
Mo	-0.56	1.740	1752
Tc	-0.38	1.703	1844
Ru	-0.26	1.652	1745
Rh	0.11	1.579	1906
Pd	0.51	1.521	2052
Ag	0.36	1.639	1805
Cd	0.47	1.696	1742
Hf	0.35	1.896	1483
Ta	-0.18	1.843	1531
W	-0.59	1.785	1689
Re	-0.58	1.687	1906
Os	-0.49	1.590	2023
Ir	-0.27	1.553	2156
Pt	-0.04	1.594	1963
Au	0.73	1.642	1826

Supplementary Table 47. DFT adsorption energies of O (ΔE_O^*, eV), bond length of metal-oxygen (d(M-O), Å), harmonic vibrational frequencies of adsorbed O ($v(O^*)$, cm^{-1}) on single TM atom supported on functional graphite

materials **with pyridine-4N coordination**.

single TM atom	ΔG_{O^*}	d(M-O)	v(O^*)
Sc	1.40	1.672	1026
Ti	0.58	1.648	1083
V	-0.66	1.525	1193
Cr	0.06	1.580	1074
Mn	0.59	1.596	1173
Fe	1.86	1.653	1063
Co	2.55	1.662	1045
Ni	2.95	1.725	791
Cu	3.36	1.789	703
Zn	4.09	1.853	590
Y	1.10	1.641	1002
Zr	0.40	1.803	614
Nb	-1.18	1.502	1252
Mo	0.25	1.705	862
Tc	0.66	1.683	906
Ru	3.11	1.815	715
Rh	2.89	1.742	803
Pd	4.93	1.829	726
Ag	3.34	1.982	552
Cd	3.68	1.873	736
Hf	0.06	1.585	1067
Ta	-0.46	1.536	1184
W	-1.06	1.503	1241
Re	-0.50	1.528	1195
Os	1.36	1.663	1027
Ir	3.15	1.817	754
Pt	4.34	1.800	763
Au	6.17	1.853	689

Supplementary Table 48. DFT adsorption energies of OH (ΔE_{OH^*}, eV), bond length of metal-oxygen (d(M-O), Å) and oxygen-hydrogen (d(O-H), Å), harmonic vibrational frequencies of adsorbed OH (v(O-H), cm^{-1}) on single TM atom supported on functional graphite materials **with pyridine-4N coordination**.

single TM atom	ΔE_{OH^*}	d(M-O)	d(O-H)	v(O-H)
Sc	-2.63	1.823	0.968	3845
Ti	-1.90	1.811	0.967	3858
V	-1.49	1.935	0.972	3791
Cr	-0.31	1.841	0.974	3763
Mn	-0.19	1.840	0.975	3719
Fe	0.47	1.822	0.978	3721
Co	0.80	1.875	0.976	3714

Ni	1.22	1.990	0.975	3713
Cu	1.37	1.941	0.973	3719
Zn	1.72	1.953	0.975	3715
Y	-2.41	1.957	0.966	3852
Zr	-1.63	1.964	0.965	3814
Nb	-1.20	1.923	0.970	3789
Mo	-0.05	1.876	0.971	3791
Tc	-0.08	1.858	0.974	3763
Ru	1.13	1.943	0.977	3725
Rh	1.00	2.014	0.975	3727
Pd	2.20	2.242	0.978	3718
Ag	1.26	2.062	0.978	3702
Cd	1.55	1.946	0.977	3709
Hf	-1.84	1.922	0.963	3843
Ta	-1.53	1.898	0.967	3816
W	-0.86	1.875	0.971	3795
Re	-0.61	1.926	0.974	3775
Os	0.21	1.943	0.977	3714
Ir	1.25	2.126	0.974	3729
Pt	1.60	2.258	0.978	3711
Au	2.88	2.279	0.977	3718

Supplementary Table 49. DFT adsorption energies of OOH (ΔE_{OOH}^{*}, eV), bond length of metal-oxygen (d(M-O), Å), oxygen-hydrogen (d(O-H), Å) and oxygen- oxygen (d(O-O), Å), harmonic vibrational frequencies of adsorbed OOH (v(O-H), v(O-O), cm^{-1}) on single TM atom supported on functional graphite materials **with pyridine-4N coordination**.

single TM atom	ΔE_{OOH}^{*}	**d(M-O)**	**d(O-H)**	**v(O-H)**	**d(O-O)**	**v(O-O)**
Sc	0.74	1.915	0.985	3641	1.501	1163
Ti	1.14	1.907	0.981	3635	1.493	1188
V	1.8	1.851	0.984	3631	1.485	1205
Cr	2.77	1.843	0.982	3629	1.489	1199
Mn	2.9	1.840	0.981	3619	1.492	1196
Fe	3.4	1.765	0.979	3621	1.508	1167
Co	3.74	1.890	0.982	3596	1.430	1267
Ni	3.84	2.132	0.982	3590	1.410	1292
Cu	3.81	2.173	0.984	3603	1.434	1268
Zn	4.57	2.195	0.981	3615	1.457	1226
Y	0.78	2.086	0.980	3625	1.486	1193
Zr	1.3	2.012	0.979	3636	1.466	1226
Nb	1.8	1.952	0.985	3596	1.452	1249
Mo	2.85	1.876	0.983	3592	1.416	1291
Tc	2.97	1.941	0.984	3590	1.396	1316

Ru	4.13	1.952	0.979	3585	1.373	1343
Rh	4.01	2.056	0.980	3599	1.356	1366
Pd	4.88	2.399	0.985	3592	1.384	1323
Ag	3.99	2.103	0.983	3607	1.430	1241
Cd	4.54	2.256	0.981	3621	1.479	1194
Hf	1.19	2.105	0.984	3632	1.512	1142
Ta	1.52	2.063	0.983	3628	1.496	1179
W	2.12	1.983	0.981	3625	1.437	1247
Re	2.57	1.935	0.980	3611	1.375	1316
Os	3.34	1.895	0.981	3596	1.383	1302
Ir	4.18	1.842	0.984	3617	1.402	1273
Pt	4.65	1.900	0.982	3607	1.459	1216
Au	5.37	2.053	0.985	3592	1.495	1171

Supplementary Table 50. DFT adsorption energies of H (ΔE_H^*, eV), bond length of metal-hydrogen (d(M-H), Å), harmonic vibrational frequencies of adsorbed H ($v(H^*)$, cm^{-1}) on single TM atom supported on functional graphite materials **with pyridine-4N coordination**.

single TM atom	ΔE_H^*	**d(M-H)**	**$v(H^*)$**
Sc	0.68	1.784	1486
Ti	0.41	1.736	1522
V	-0.1	1.635	1727
Cr	-0.36	1.598	1798
Mn	-0.52	1.482	1915
Fe	-0.49	1.492	1899
Co	-0.14	1.445	2035
Ni	-0.02	1.477	1958
Cu	0.74	1.547	1835
Zn	0.62	1.631	1672
Y	0.65	1.895	1294
Zr	0.03	1.902	1268
Nb	-0.77	1.853	1368
Mo	-0.69	1.717	1552
Tc	-0.17	1.652	1642
Ru	0.09	1.573	1746
Rh	0.33	1.547	1789
Pd	0.67	1.623	1693
Ag	0.76	1.694	1607
Cd	0.58	1.703	1598
Hf	0.25	1.794	1519
Ta	-0.35	1.736	1577
W	-0.73	1.674	1613
Re	-0.49	1.621	1657
Os	-0.32	1.579	1702

Ir	0.04	1.542	1753
Pt	0.44	1.587	1716
Au	0.81	1.683	1614

Supplementary Table 51. DFT adsorption energies of O (ΔE_{O^*}, eV), bond length of metal-oxygen (d(M-O), Å), harmonic vibrational frequencies of adsorbed O (v(O^*), cm^{-1}) on single TM atom supported on functional graphite materials **with pyrrole-4N coordination**.

single TM atom	ΔG_{O^*}	d(M-O)	v(O^*)
Sc	1.41	1.610	1162
Ti	0.29	1.637	1131
V	-0.92	1.527	1263
Cr	0.92	1.642	1067
Mn	1.25	1.579	1190
Fe	2.01	1.629	1094
Co	3.01	1.646	1053
Ni	4.12	1.720	929
Cu	5.14	1.869	705
Zn	4.91	1.753	916
Y	1.50	1.636	1142
Zr	0.20	1.797	835
Nb	-0.83	1.558	1263
Mo	1.23	1.605	1173
Tc	1.69	1.596	1184
Ru	2.92	1.662	1079
Rh	4.12	1.703	995
Pd	5.54	1.922	607
Ag	5.78	2.039	478
Cd	5.74	1.996	599
Hf	0.38	1.642	1136
Ta	-0.67	1.553	1283
W	-0.25	1.573	1252
Re	1.38	1.617	1190
Os	2.27	1.683	1053
Ir	2.81	1.663	1083
Pt	4.07	1.913	635
Au	6.38	2.094	495

Supplementary Table 52. DFT adsorption energies of OH (ΔE_{OH^*}, eV), bond length of metal-oxygen (d(M-O), Å) and oxygen-hydrogen (d(O-H), Å), harmonic vibrational frequencies of adsorbed OH (v(O-H), cm^{-1}) on single TM atom supported on functional graphite materials **with pyrrole-4N coordination**.

single TM atom	ΔE_{OH^*}	d(M-O)	d(O-H)	v(O-H)

Sc	-2.47	1.832	0.969	3852
Ti	-1.83	1.799	0.972	3814
V	-1.36	1.834	0.973	3804
Cr	0.09	1.816	0.976	3784
Mn	0.30	1.839	0.976	3774
Fe	0.61	1.804	0.978	3722
Co	1.16	1.835	0.978	3725
Ni	1.74	1.886	0.978	3721
Cu	2.38	1.864	0.978	3715
Zn	2.34	1.874	0.979	3719
Y	-2.68	1.942	0.964	3846
Zr	-1.87	1.936	0.966	3810
Nb	-0.7	1.863	0.974	3778
Mo	0.24	1.838	0.976	3753
Tc	0.50	1.894	0.977	3742
Ru	1.15	1.922	0.979	3721
Rh	1.80	1.982	0.978	3712
Pd	2.78	2.223	0.979	3718
Ag	2.71	2.235	0.976	3722
Cd	2.66	2.215	0.978	3717
Hf	-1.98	1.896	0.963	3863
Ta	-1.50	1.892	0.968	3826
W	-0.51	1.887	0.976	3793
Re	0.21	1.874	0.977	3763
Os	0.63	1.920	0.979	3735
Ir	0.99	2.053	0.979	3725
Pt	1.83	2.162	0.979	3715
Au	3.00	2.126	0.980	3707

Supplementary Table 53. DFT adsorption energies of OOH (ΔE_{OOH}^*, eV), bond length of metal-oxygen (d(M-O), Å), oxygen-hydrogen (d(O-H), Å) and oxygen- oxygen (d(O-O), Å), harmonic vibrational frequencies of adsorbed OOH (v(O-H), v(O-O), cm^{-1}) on single TM atom supported on functional graphite materials **with pyrrole-4N coordination**.

single TM atom	ΔE_{OOH}^*	**d(M-O)**	**d(O-H)**	**v(O-H)**	**d(O-O)**	**v(O-O)**
Sc	0.80	1.953	0.984	3641	1.514	1138
Ti	1.44	1.876	0.984	3635	1.479	1204
V	1.61	1.860	0.980	3631	1.456	1263
Cr	2.96	1.824	0.982	3629	1.451	1253
Mn	3.27	1.853	0.981	3619	1.445	1267
Fe	3.69	1.791	0.983	3621	1.440	1269
Co	3.84	1.791	0.984	3596	1.411	1325
Ni	4.71	1.937	0.983	3590	1.410	1337

Cu	5.25	1.953	0.986	3603	1.405	1357
Zn	5.42	1.974	0.984	3615	1.409	1363
Y	0.43	2.242	0.983	3625	1.507	117
Zr	1.23	2.050	0.982	3636	1.495	1195
Nb	2.27	1.993	0.985	3596	1.475	1226
Mo	3.01	1.973	0.986	3592	1.452	1269
Tc	3.64	2.041	0.982	3590	1.436	1295
Ru	4.15	2.124	0.985	3585	1.415	1315
Rh	4.93	2.346	0.981	3599	1.398	1365
Pd	5.76	2.537	0.987	3592	1.372	1405
Ag	5.79	2.498	0.985	3607	1.388	1385
Cd	5.67	2.473	0.986	3621	1.373	1409
Hf	1.06	2.363	0.983	3632	1.489	1205
Ta	1.67	2.126	0.980	3628	1.463	1257
W	2.86	2.063	0.982	3625	1.421	1325
Re	3.08	1.983	0.984	3611	1.405	1369
Os	3.71	2.115	0.986	3596	1.394	1380
Ir	3.84	2.357	0.985	3617	1.387	1379
Pt	4.91	2.594	0.986	3607	1.375	1393
Au	6.07	2.582	0.983	3592	1.363	1415

Supplementary Table 54. DFT adsorption energies of H (ΔE_H^*, eV), bond length of metal-hydrogen (d(M-H), Å), harmonic vibrational frequencies of adsorbed H ($v(H^*)$, cm^{-1}) on single TM atom supported on functional graphite materials **with pyrrole-4N coordination**.

single TM atom	**ΔE_H^***	**d(M-H)**	**$v(H^*)$**
Sc	0.44	1.731	1665
Ti	0.01	1.685	1724
V	-0.55	1.632	1789
Cr	-0.17	1.583	1842
Mn	-0.23	1.524	1925
Fe	-0.22	1.480	1983
Co	0.19	1.434	2053
Ni	0.77	1.433	2038
Cu	1.26	1.536	1885
Zn	1.07	1.478	1940
Y	0.44	1.829	1542
Zr	-0.05	1.841	1504
Nb	-0.63	1.751	1631
Mo	-0.27	1.778	1608
Tc	0.16	1.687	1729
Ru	0.32	1.633	1795
Rh	0.68	1.578	1873
Pd	1.19	1.530	1906

Ag	1.20	1.728	1695
Cd	1.23	1.783	1627
Hf	0.02	1.804	1576
Ta	-0.66	1.757	1639
W	-0.60	1.673	1725
Re	-0.34	1.605	1707
Os	0.15	1.573	1832
Ir	0.34	1.551	1866
Pt	0.88	1.539	1882
Au	1.38	1.637	1779

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