Supporting Information

Rational Design of Two-Dimensional Metal-Organic Framework with Transition Metal Support for High-Efficiency Bifunctional Oxygen Electrocatalysis

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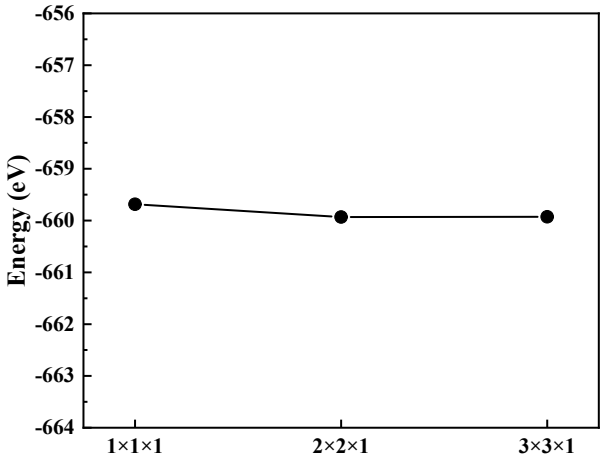


Fig.S1 KPOINTS convergence test for Fe-HITT

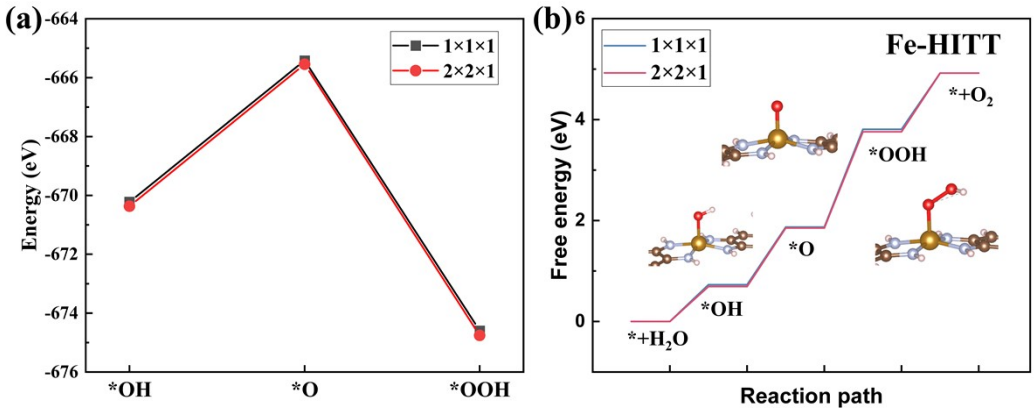


Fig. S2 (a) Comparison diagram of adsorption energy; (b) OER free energy diagram of Fe-MITT in 1×1×1 and 2×2×1 k-point grid for Brillouin zone sampling.

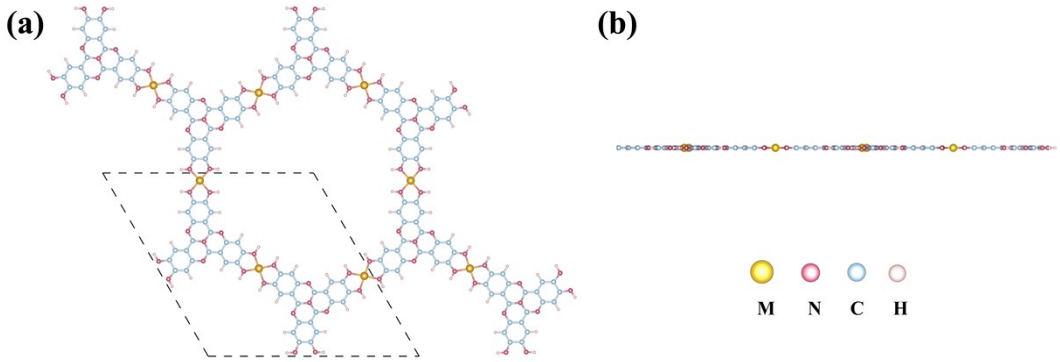


Fig. S3 (a) Top and (b) side views of M-HITT.

Table S1. The lattice constant, magnetic moment, and relative energy of M-HITT.

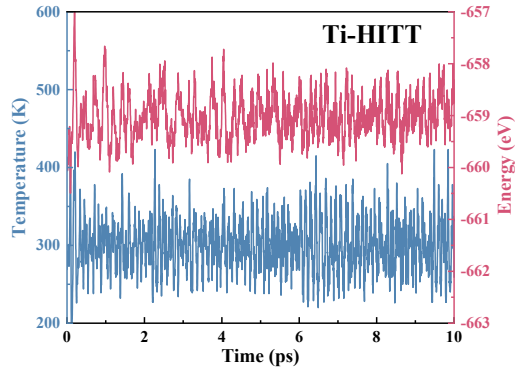
M-HITT	Magnetic moment (μB)	Lattice constant (Å)	Relative energy (eV)
Ti	0.30	26.58	-3.48
V	7.00	26.48	-4.34
Cr	10..00	26.41	-5.4
Mn	9.30	26.25	-4.29
Fe	6.66	26.14	0
Co	3.00	25.90	3.49
Ni	0.3	25.89	8.33
Cu	1.43	26.24	17.6
Zr	0.02	27.07	-5.12
Nb	3.68	26.88	-5.55
Mo	6.00	26.76	-5.27
Tc	8.93	26.68	-2.64
Ru	4.64	26.42	1.02
Rh	2.06	26.40	4.84
Pd	0	26.40	10.89
Ag	0.17	26.45	24.38
Hf	2.57	26.98	-9.49
Re	8.95	26.59	-6.86
Os	0	26.44	-5.05
Ir	2.84	26.44	-0.13
Pt	0	26.45	6.41
Au	0	26.45	19.73

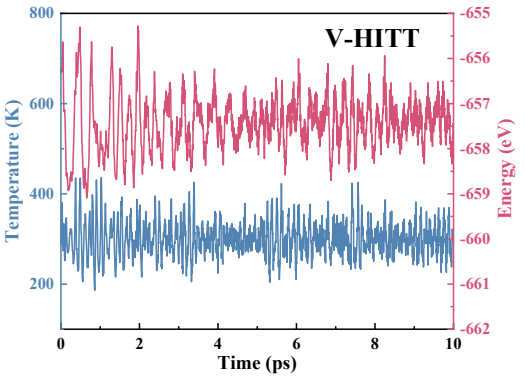
Table S2. The relevant data involved in the calculation of the formation energy.

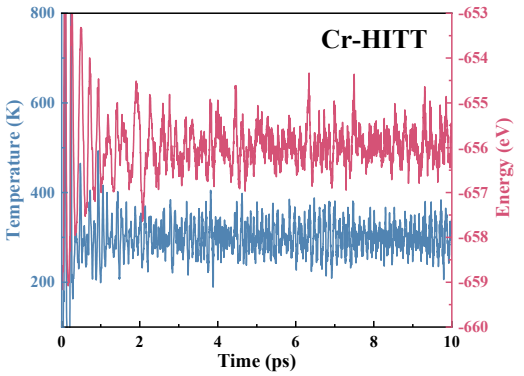
M-HITT	$E_{NTM/MOF}$ (eV)	E_{MOF} (eV)	$E_{TM\text{-}single}$ (eV)	E_{form} (eV)
Ti	-663.31	-620.87	-8.30	-5.85
V	-664.17	-620.87	-9.52	-4.91
Cr	-665.23	-620.87	-9.95	-4.85
Mn	-664.12	-620.87	-9.17	-5.25
Fe	-659.83	-620.87	-8.55	-2.40
Co	-656.34	-620.87	-7.38	-4.43
Ni	-651.5	-620.87	-5.87	-4.34
Cu	-642.23	-620.87	-4.24	-2.88
Zr	-664.95	-620.87	-8.95	-5.74
Nb	-665.38	-620.87	-10.78	-4.06
Mo	-665.1	-620.87	-11.46	-3.28
Tc	-662.47	-620.87	-10.89	-2.97
Ru	-658.81	-620.87	-9.79	-2.85
Rh	-654.99	-620.87	-7.83	-3.54
Pd	-648.94	-620.87	-5.80	-3.56
Ag	-635.45	-620.87	-3.21	-1.65
Hf	-669.32	-620.87	-10.33	-5.82
Re	-666.69	-620.87	-13.00	-2.27
Os	-664.88	-620.87	-11.84	-2.83
Ir	-659.96	-620.87	-9.56	-3.47
Pt	-653.42	-620.87	-6.86	-3.99
Au	-640.10	-620.87	-3.88	-2.53

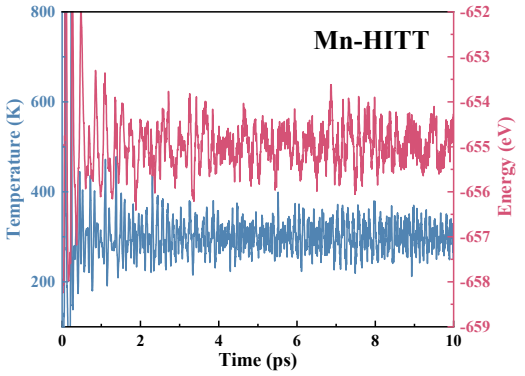
Table S3. The relevant data involved in the calculation of the dissolution potentials.

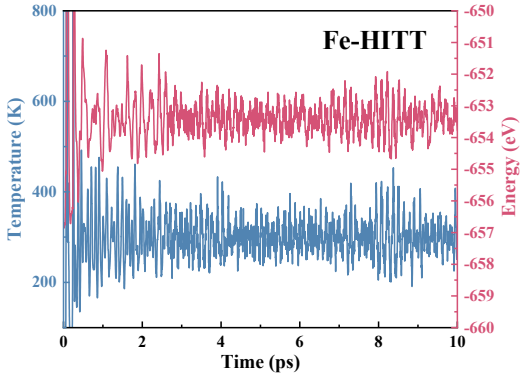
M-HITT	E_{form} (eV)	n	$U^{o}_{diss-bulk}$	U_{diss} (eV)
Ti	-5.85	2	-1.63	1.30
V	-4.91	2	-1.18	1.28
Cr	-4.85	2	-0.91	1.52
Mn	-5.25	2	-1.19	1.44
Fe	-2.4	2	-0.45	0.75
Co	-4.43	2	-0.28	1.94
Ni	-4.34	2	-0.26	1.91
Cu	-2.88	2	0.34	1.78
Zr	-5.74	4	-1.45	-0.02
Nb	-4.06	3	-1.10	0.25
Mo	-3.28	3	-0.20	0.89
Tc	-2.97	2	0.40	1.89
Ru	-2.85	2	0.46	1.89
Rh	-3.54	2	0.60	2.37
Pd	-3.56	2	0.95	2.73
Ag	-1.65	1	0.80	2.45
Hf	-5.82	4	-1.55	-0.10
Re	-2.27	3	0.30	1.06
Os	-2.83	8	0.84	1.19
Ir	-3.47	3	1.16	2.32
Pt	-3.99	2	1.18	3.18
Au	-2.53	3	1.50	2.34

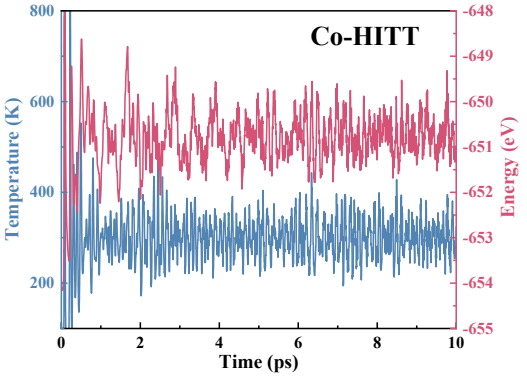

Ti-HITT
Temperature (K)
Energy (eV)
Time (ps)

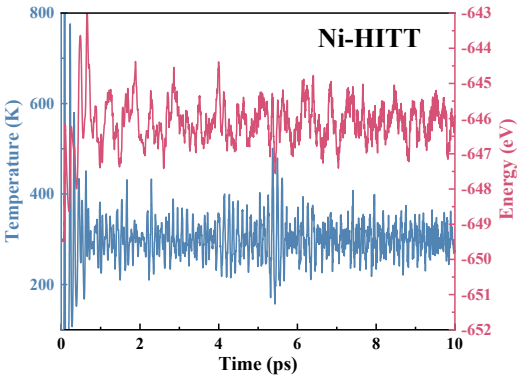

V-HITT
Temperature (K)
Energy (eV)
Time (ps)

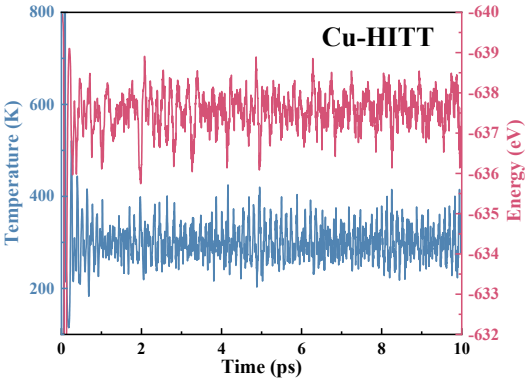

Cr-HITT
Temperature (K)
Energy (eV)
Time (ps)

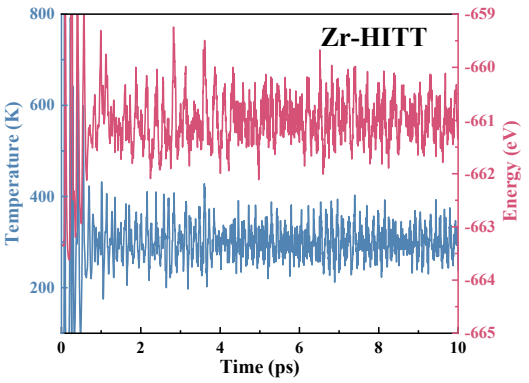

Mn-HITT
Temperature (K)
Energy (eV)
Time (ps)

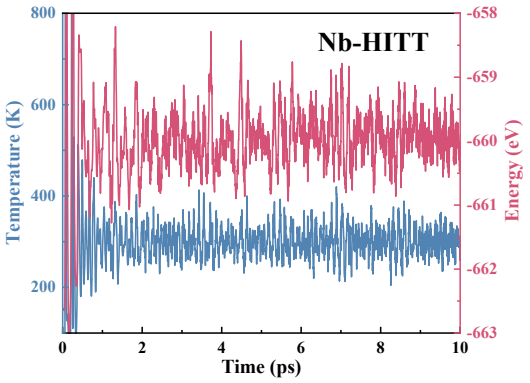

Fe-HITT
Temperature (K)
Energy (eV)
Time (ps)

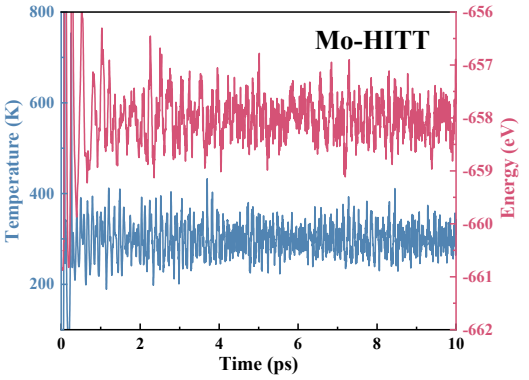

Co-HITT
Temperature (K)
Energy (eV)
Time (ps)

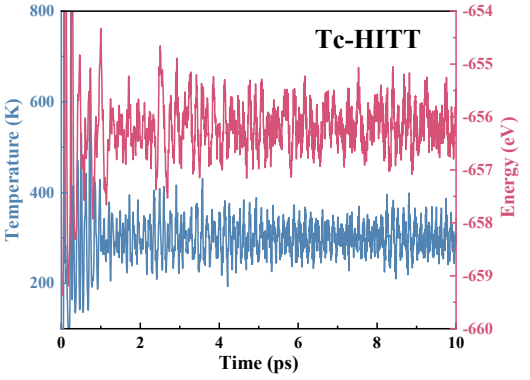

Ni-HITT
Temperature (K)
Energy (eV)
Time (ps)

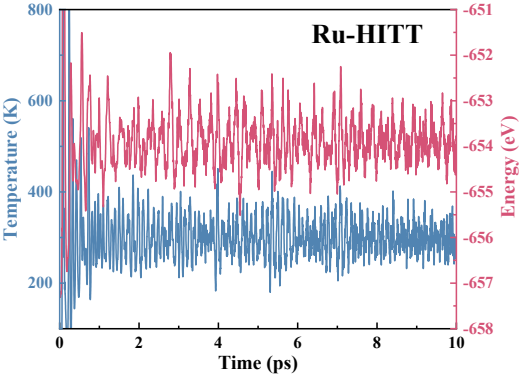

Cu-HITT
Temperature (K)
Energy (eV)
Time (ps)

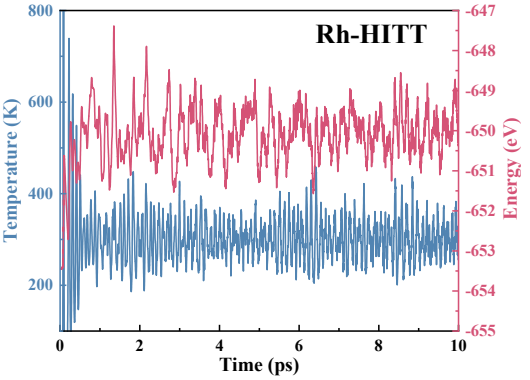

Zr-HITT
Temperature (K)
Energy (eV)
Time (ps)

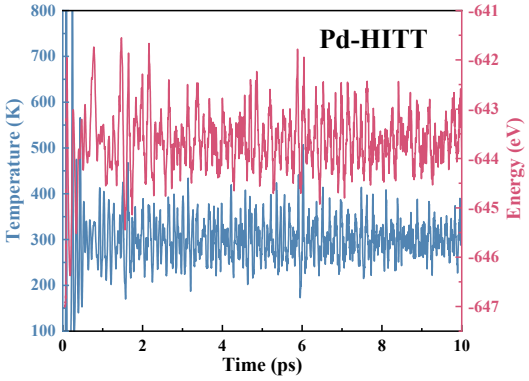

Nb-HITT
Temperature (K)
Energy (eV)
Time (ps)

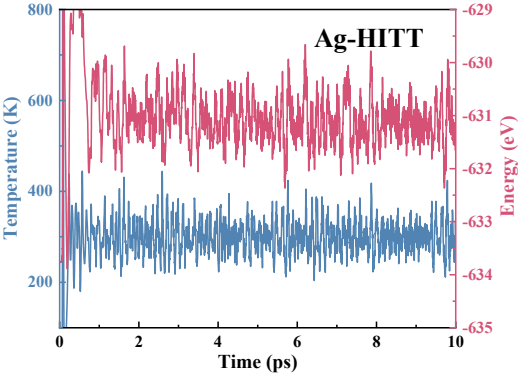

Mo-HITT
Temperature (K)
Energy (eV)
Time (ps)


Tc-HITT
Temperature (K)
Energy (eV)
Time (ps)


Ru-HITT
Temperature (K)
Energy (eV)
Time (ps)


Rh-HITT
Temperature (K)
Energy (eV)
Time (ps)


Pd-HITT
Temperature (K)
Energy (eV)
Time (ps)


Ag-HITT
Temperature (K)
Energy (eV)
Time (ps)

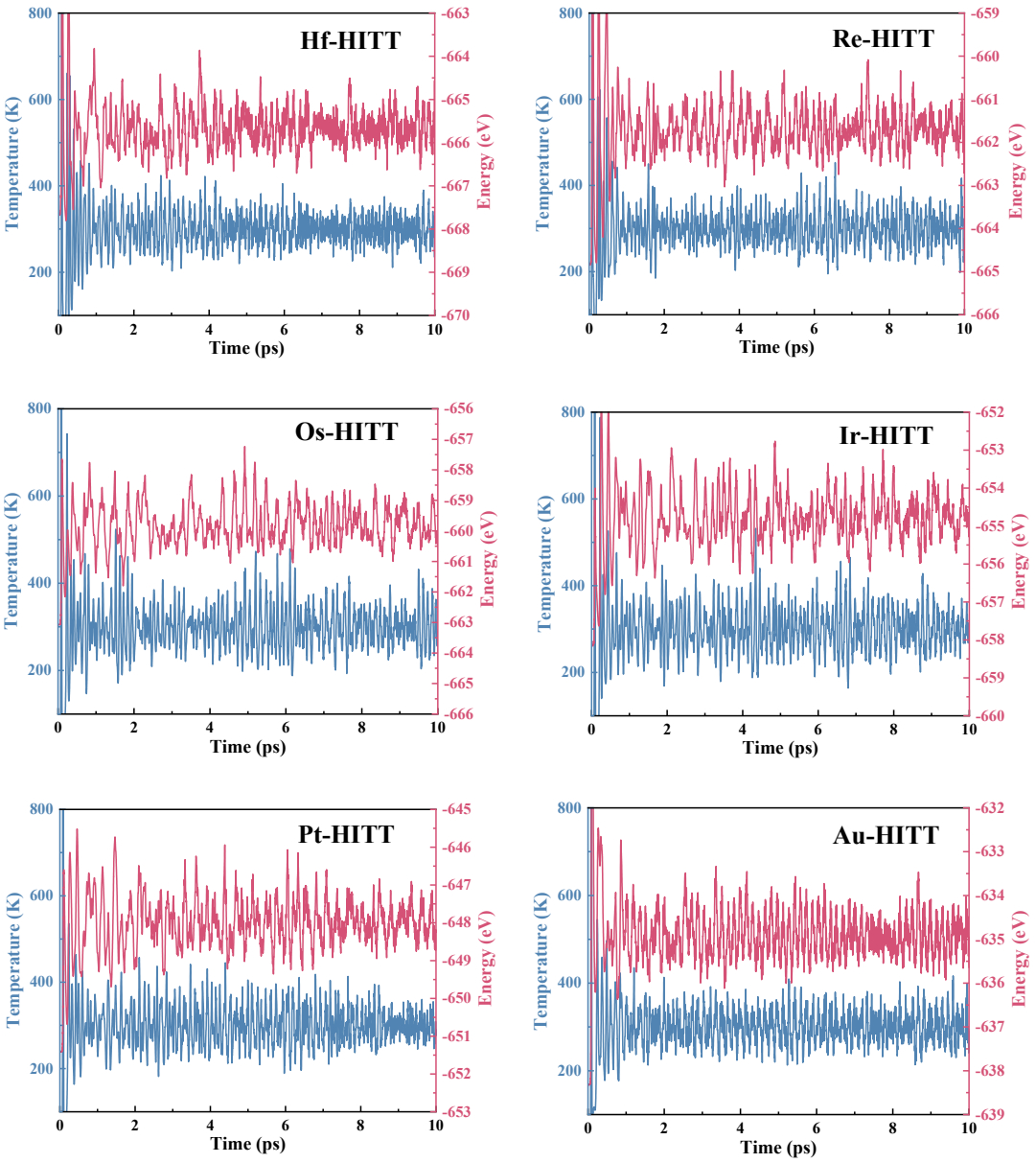


Fig. S4 Variations of energy and temperature versus the AIMD simulation time for M-HITT, the simulation lasts for 10 ps at 300 K.

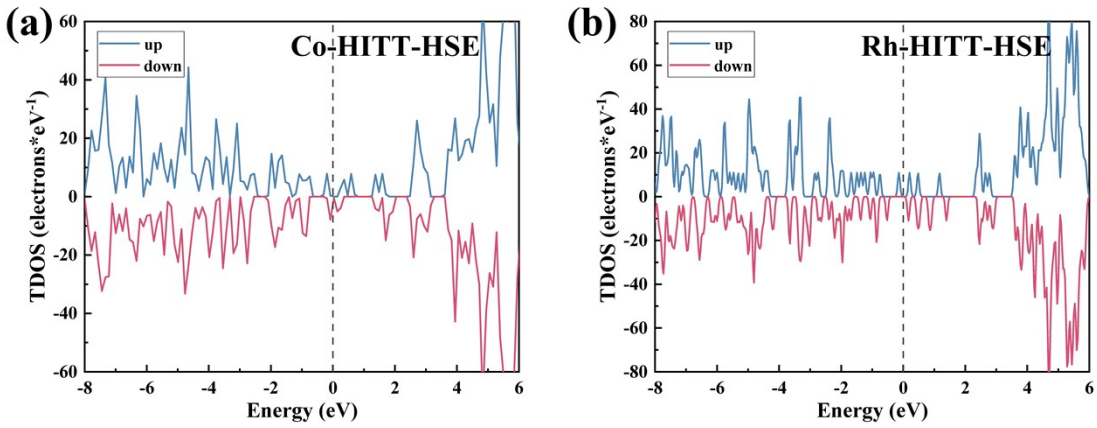
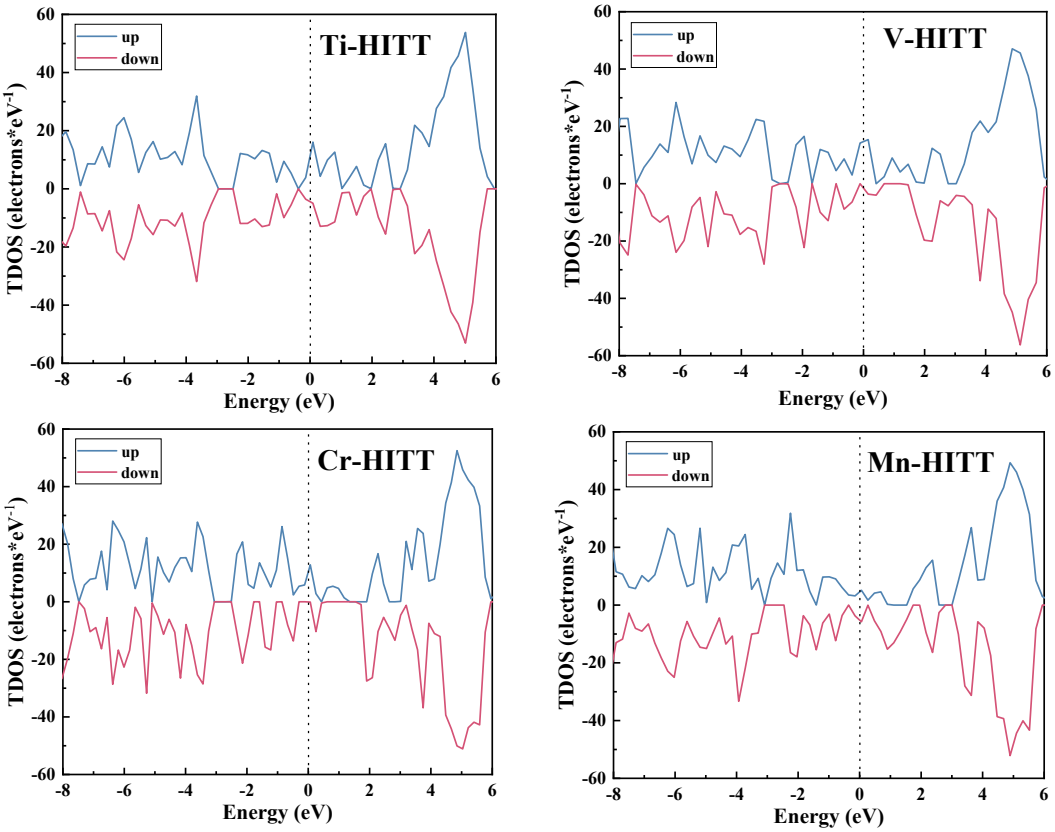
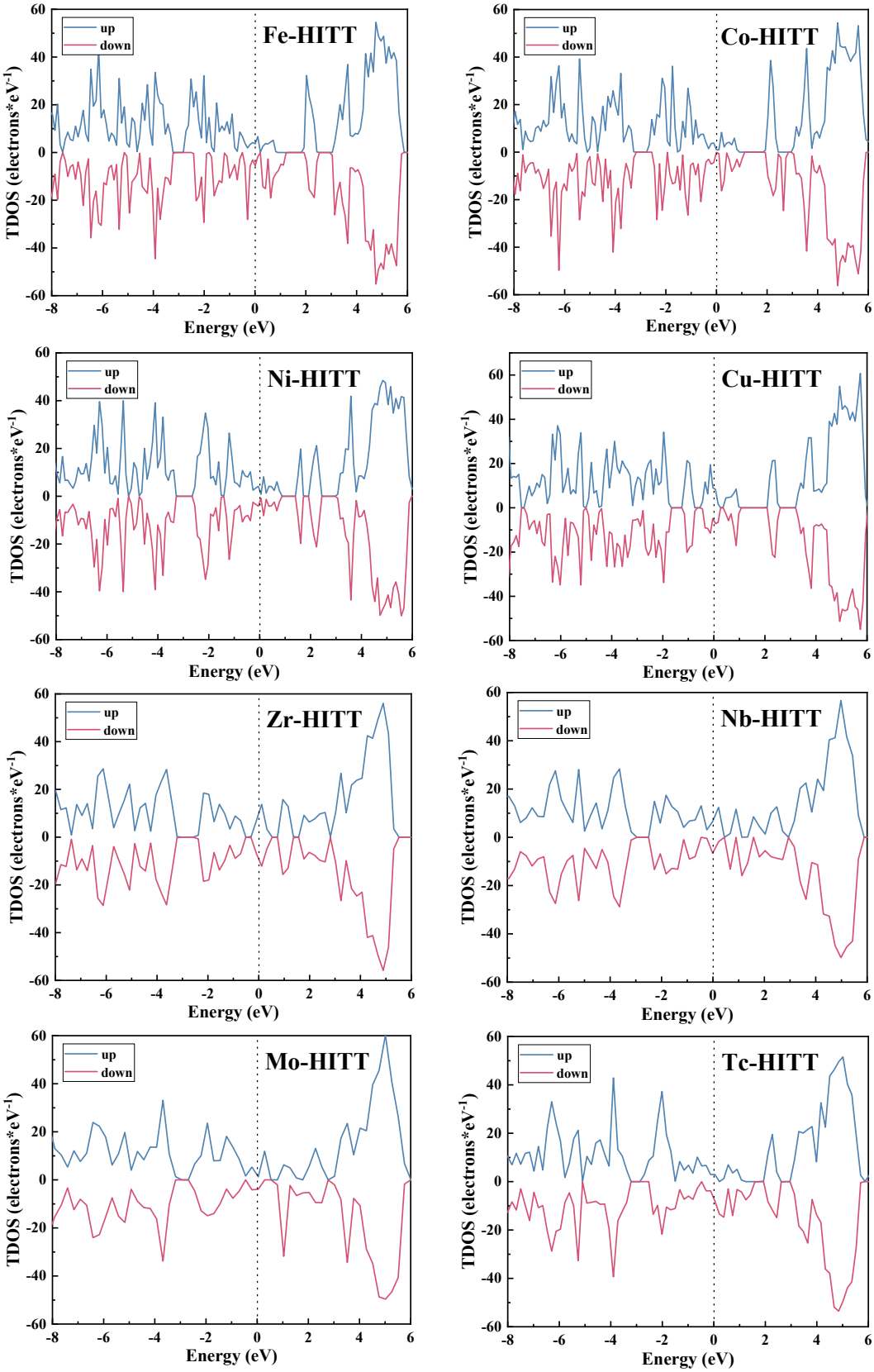
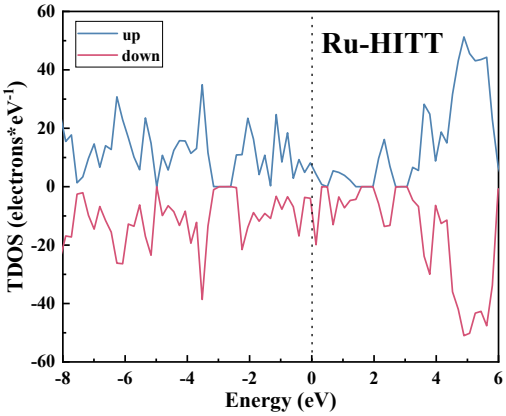
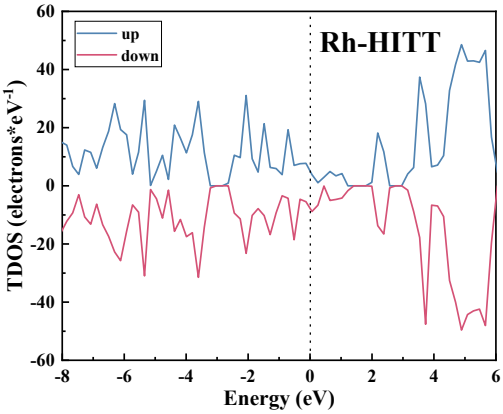


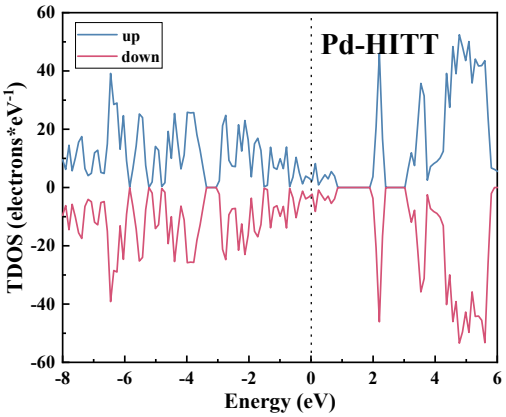
Fig.S5 Density of states of (a) Co-HITT and (b) Rh-HITT computed by HSE functional.

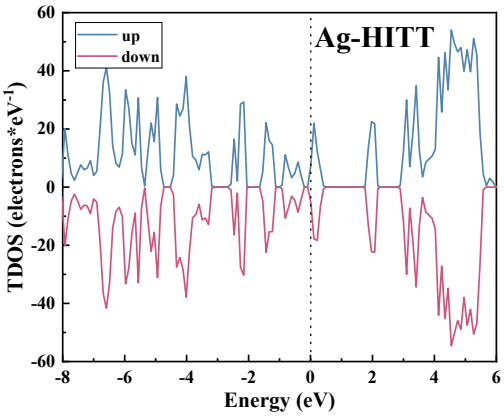


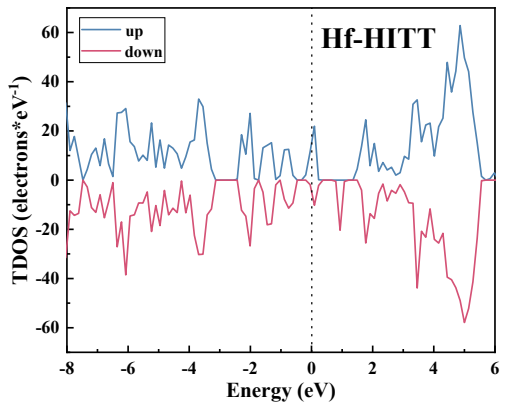

Fe-HITT
Co-HITT
Ni-HITT
Cu-HITT
Zr-HITT
Nb-HITT
Mo-HITT
Tc-HITT
up
down
TDOS (electrons*eV⁻¹)
Energy (eV)

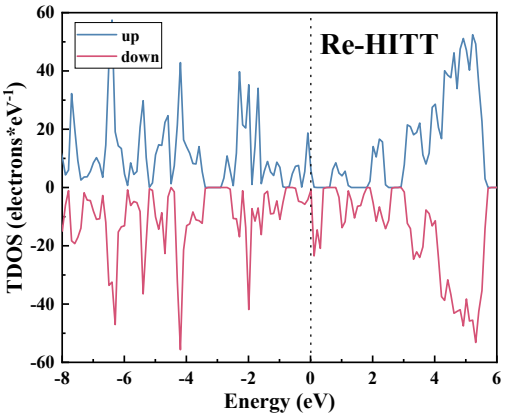

Ru-HITT
up
down
TDOS (electrons*eV^{-1})
Energy (eV)


Rh-HITT
up
down
TDOS (electrons*eV^{-1})
Energy (eV)


Pd-HITT
up
down
TDOS (electrons*eV^{-1})
Energy (eV)


Ag-HITT
up
down
TDOS (electrons*eV^{-1})
Energy (eV)


Hf-HITT
up
down
TDOS (electrons*eV^{-1})
Energy (eV)


Re-HITT
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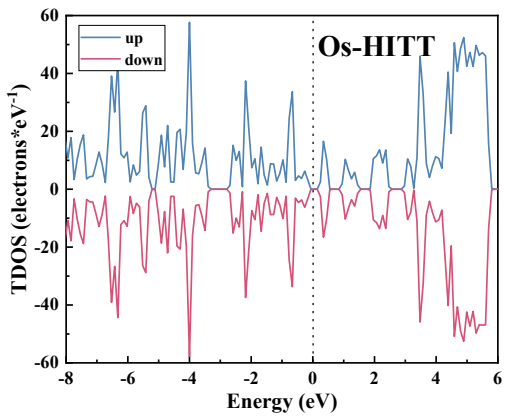
TDOS (electrons*eV^{-1})
Energy (eV)


Os-HITT
up
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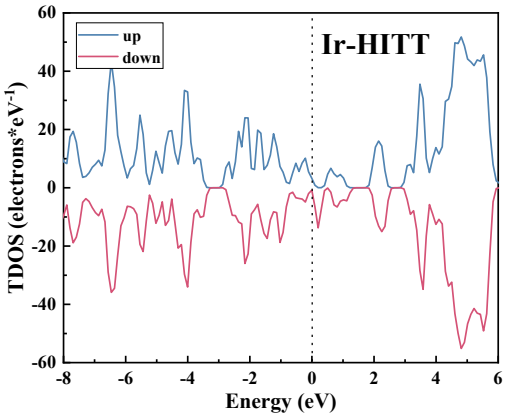
TDOS (electrons*eV^{-1})
Energy (eV)


Ir-HITT
up
down
TDOS (electrons*eV^{-1})
Energy (eV)

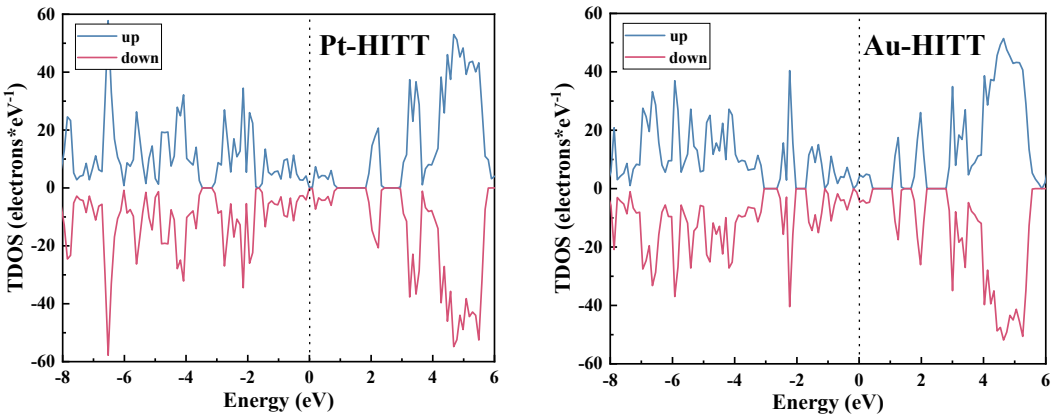


Fig. S6 Density of states of M-HITT.

Correspondingly, the free energy changes of the four elementary steps can be calculated using eqn (1)-(4).

$$\Delta G_A = G_{*OH} + \frac{1}{2}G_{H_2} - G_* - G_{H_2O} - \Delta_{pH} - eU \ \text{*MERGEFORMAT (1)}$$

$$\Delta G_B = G_{*O} + \frac{1}{2}G_{H_2} - G_{*OH} - \Delta_{pH} - eU \ \text{*MERGEFORMAT (2)}$$

$$G_C = G_{*OOH} + \frac{1}{2}G_{H_2} - G_{*O} - G_{H_2O} - \Delta_{pH} - eU \ \text{*MERGEFORMAT (3)}$$

$$\Delta G_D = G_{O_2} + \frac{1}{2}G_{H_2} - G_{*OOH} - \Delta_{pH} - eU \ \text{*MERGEFORMAT (4)}$$

where G_{H_2O} is to simulate liquid H_2O with gaseous H_2O at 0.035 bar pressure. In the above formula, considering that $1/2H_2 \leftrightarrow H^+ + e^-$ reaches equilibrium at standard atmospheric pressure, $G_{(H^+ + e^-)}$ is replaced by $1/2G_{H_2}$, and E is calculated at 1 bar. The electron structure of O_2 is relatively complex, and its free energy cannot be accurately calculated by DFT. The total free energy of the water-resolved hydrogen reaction is 4.92 eV, and the free energy of O_2 can be obtained indirectly from the equation of water-resolved hydrogen reaction.

The adsorption free energies of *OH, *O, and *OOH, respectively, which can be defined as eqn (5)-(7).

$$\Delta G_{*OH} = G_{*OH} - G_* - (G_{H_2O} - \frac{1}{2}G_{H_2}) \ \text{* MERGEFORMAT (5)}$$

$$\Delta G_{*O} = G_{*O} - G_* - (G_{H_2O} - G_{H_2}) \quad \text{* MERGEFORMAT (6)}$$

$$\Delta G_{*OOH} = G_{*OOH} - G_* - (2G_{H_2O} - \frac{3}{2}G_{H_2}) \ \text{* MERGEFORMAT (7)}$$

where * represents the catalyst, G* is the free energy of M-HITT when no species is adsorbed on the surface of the catalyst. ΔG_{*OH}, ΔG_{*O} and ΔG_{*OOH} are the free energy of *OH, *O and *OOH adsorbed on the surface, respectively. G_{H_2O} and G_{H_2} is the free energies of H_2O and H_2.

The standard free energy change in OER and ORR processes is -4.92 eV, and the reaction goes through four basic reaction steps. Under ideal conditions, the ORR output voltage for each step of electron transfer should be the average value 1.23 V.

Table S4. Calculated zero-point energies and Gibbs free energies of *O on M-HITT.

M-HITT	E_{ZPE} (eV)	G (eV)
Ti	0.04	-692.63
V	0.05	-693.52
Cr	0.05	-693.53
Mn	0.06	-691.34
Fe	0.05	-686.39
Co	0.09	-681.85
Ni	0.00	-675.54
Cu	-0.03	-666.30
Zr	0.03	-694.61
Nb	0.05	-696.01
Mo	0.06	-694.95
Tc	0.06	-691.96
Ru	0.06	-686.78
Rh	0.03	-680.94
Pd	-0.01	-672.71
Ag	-0.04	-659.87
Hf	0.03	-699.07
Re	0.06	-696.91
Os	0.06	-693.39
Ir	0.04	-686.18
Pt	0.02	-677.50
Au	-0.06	-663.76

Table S5. Calculated zero-point energies and Gibbs free energies of *OH on M-HITT.

M-HITT	E_{ZPE} (eV)	G (eV)
Ti	0.28	-693.16
V	0.30	-693.69
Cr	0.32	-693.67
Mn	0.29	-691.76
Fe	0.30	-687.54
Co	0.30	-683.27
Ni	0.25	-677.74
Cu	0.23	-668.71
Zr	0.27	-695.97
Nb	0.28	-696.09
Mo	0.30	-694.71
Tc	0.31	-691.66
Ru	0.31	-687.17
Rh	0.29	-682.39
Pd	0.23	-674.92
Ag	0.24	-662.32
Hf	0.26	-700.17
Re	0.32	-696.74
Os	0.33	-692.92
Ir	0.30	-687.16
Pt	0.25	-679.37
Au	0.21	-666.08

Table S6. Calculated zero-point energies and Gibbs free energies of *OOH on M-HITT.

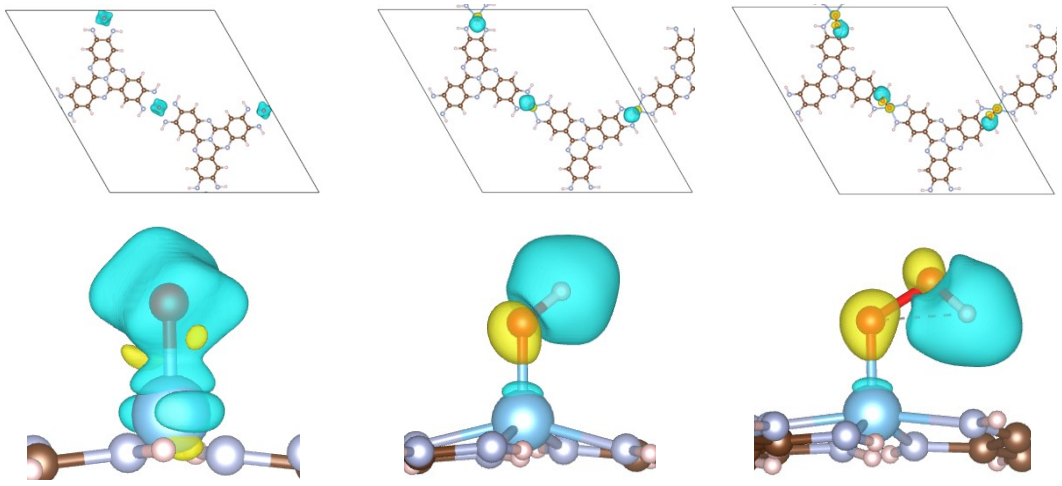
M-HITT	E_{ZPE} (eV)	G (eV)
Ti	0.35	-690.11
V	0.35	-690.30
Cr	0.35	-690.50
Mn	0.34	-688.74
Fe	0.34	-684.46
Co	0.38	-680.29
Ni	0.32	-674.81
Cu	0.26	-665.94
Zr	0.35	-691.83
Nb	0.32	-691.57
Mo	0.34	-691.36
Tc	0.39	-690.35
Ru	0.29	-684.34
Rh	0.34	-679.42
Pd	0.28	-672.05
Ag	0.26	-659.71
Hf	0.37	-697.54
Re	0.36	-695.73
Os	0.41	-691.85
Ir	0.34	-684.27
Pt	0.31	-676.55
Au	0.27	-663.62

Table S7. The adsorption energies of *OH, *O and *OOH (ΔG_{*OH}, ΔG_{*O} and ΔG_{*OOH}).

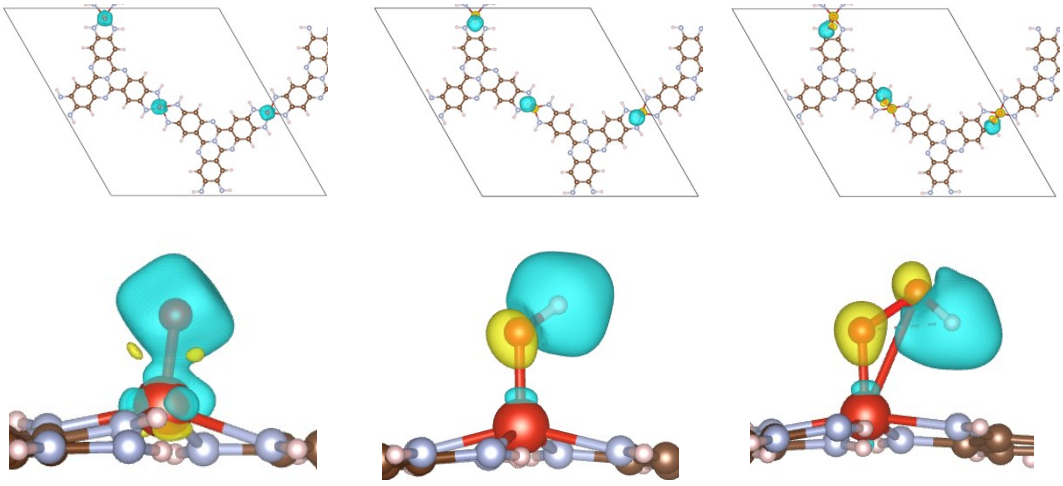
M-HITT	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)
Ti	-1.41	-0.88	1.64
V	-1.08	-0.91	2.30
Cr	-0.01	0.14	3.17
Mn	0.81	1.22	3.82
Fe	0.73	1.87	3.81
Co	1.51	2.94	4.49
Ni	2.20	4.40	5.13
Cu	1.96	4.37	4.73
Zr	-2.57	-1.22	1.56
Nb	-2.27	-2.18	2.26
Mo	-1.17	-1.42	2.18
Tc	-0.76	-1.05	0.56
Ru	0.08	0.47	2.91
Rh	1.04	2.49	4.00
Pd	2.47	4.67	5.33
Ag	1.57	4.02	4.10
Hf	-2.41	-1.31	0.22
Re	-1.61	-1.79	-0.61
Os	0.40	-0.07	1.47
Ir	1.24	2.22	4.13
Pt	2.49	4.36	5.30
Au	2.46	4.78	4.87

Table S8. The bond lengths of *O, *OH,*OOH on M-HITT.

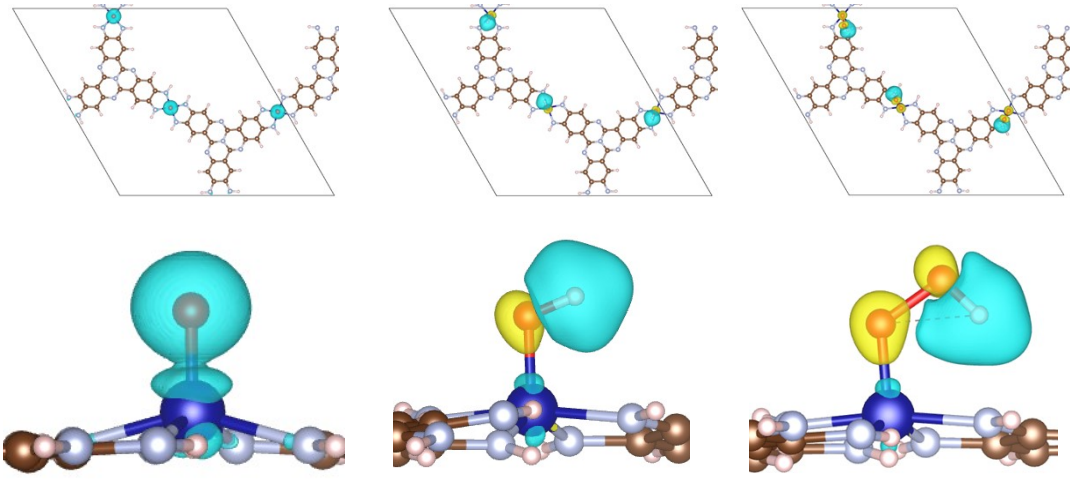
M-HITT	d_{TM-OH}(Å)	d_{TM-O}(Å)	d_{TM-OOH}(Å)
Ti	1.83	1.64	1.84
V	1.79	1.60	1.80
Cr	1.80	1.58	1.77
Mn	1.85	1.57	1.87
Fe	1.83	1.63	1.83
Co	1.87	1.68	1.86
Ni	1.94	1.83	2.03
Cu	1.96	1.93	2.96
Zr	1.95	1.78	1.98
Nb	1.91	1.72	1.91
Mo	1.89	1.69	1.87
Tc	1.87	1.66	1.68
Ru	1.91	1.71	1.74
Rh	1.96	1.80	1.95
Pd	2.12	1.94	2.27
Ag	2.25	2.23	3.01
Hf	1.92	1.79	2.02
Re	1.89	1.71	1.73
Os	1.91	1.73	1.72
Ir	1.97	1.81	1.94
Pt	2.11	1.91	2.92
Au	2.37	2.42	3.22



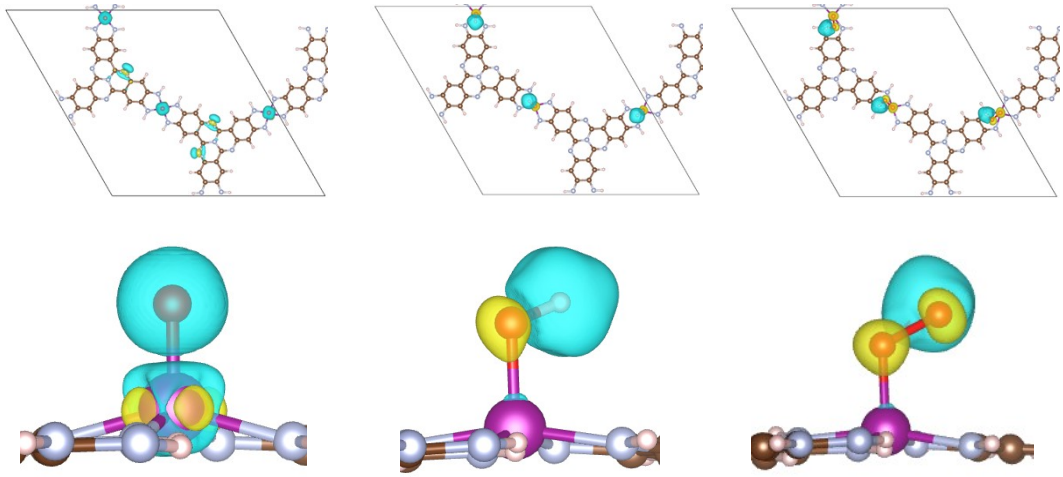
Ti-HITT



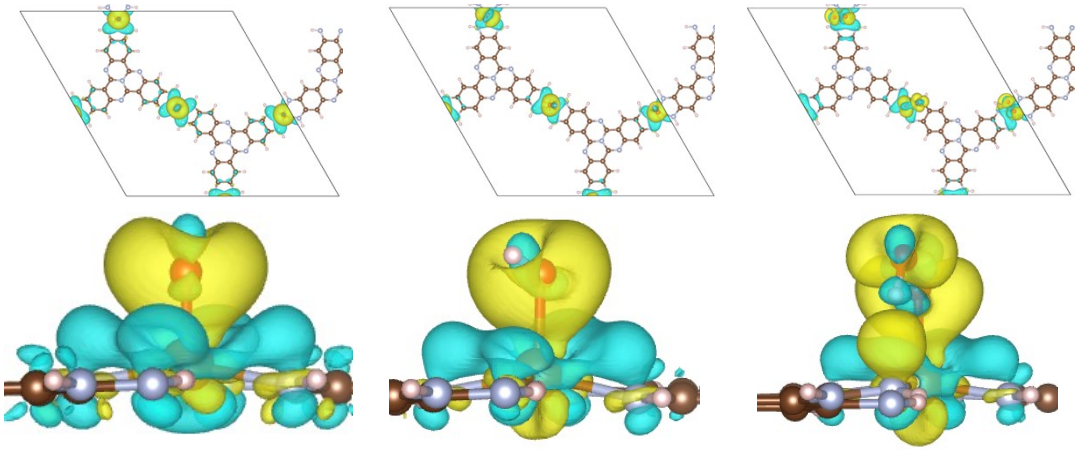
V-HITT



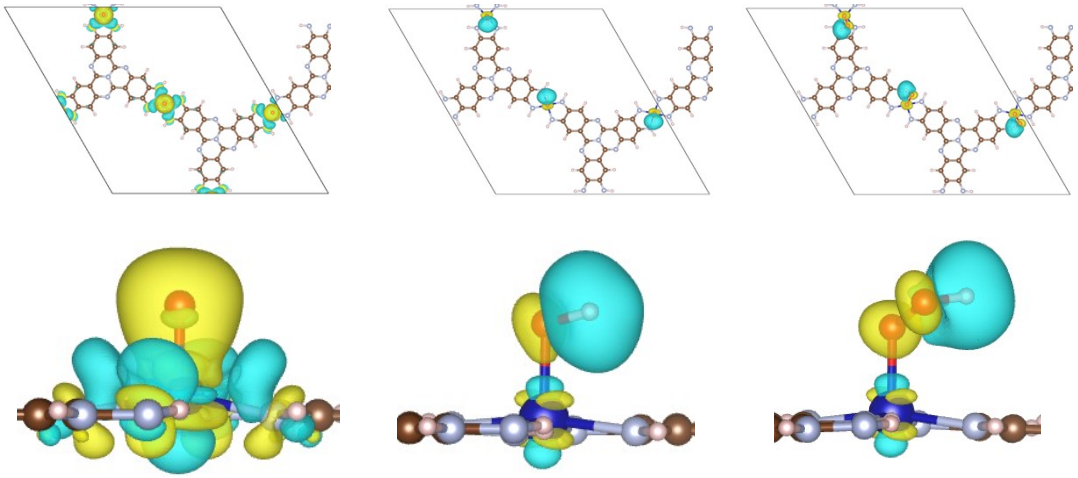
Cr-HITT



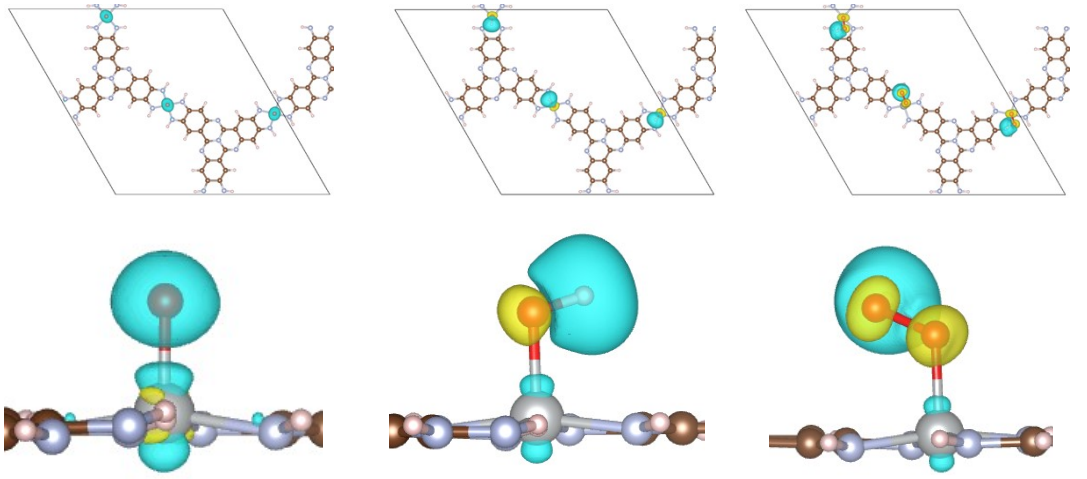
Mn-HITT



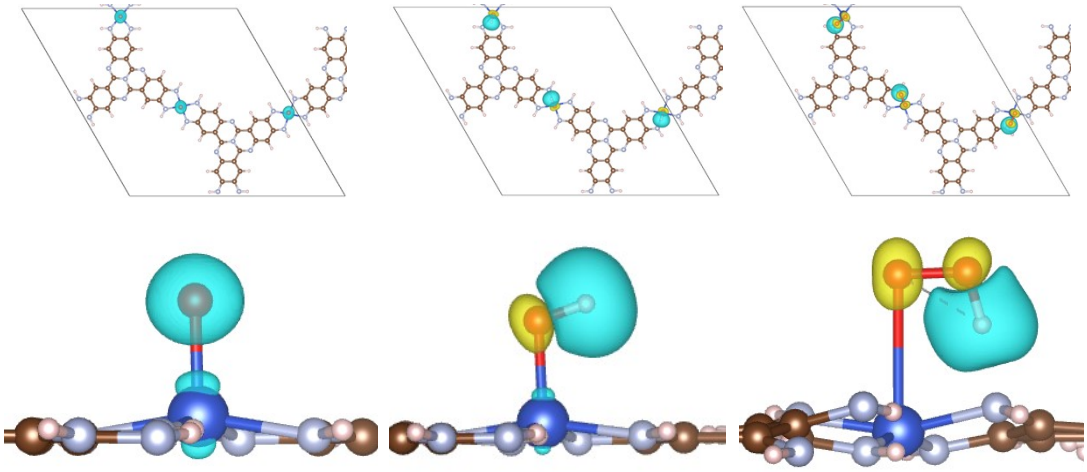
Fe-HITT



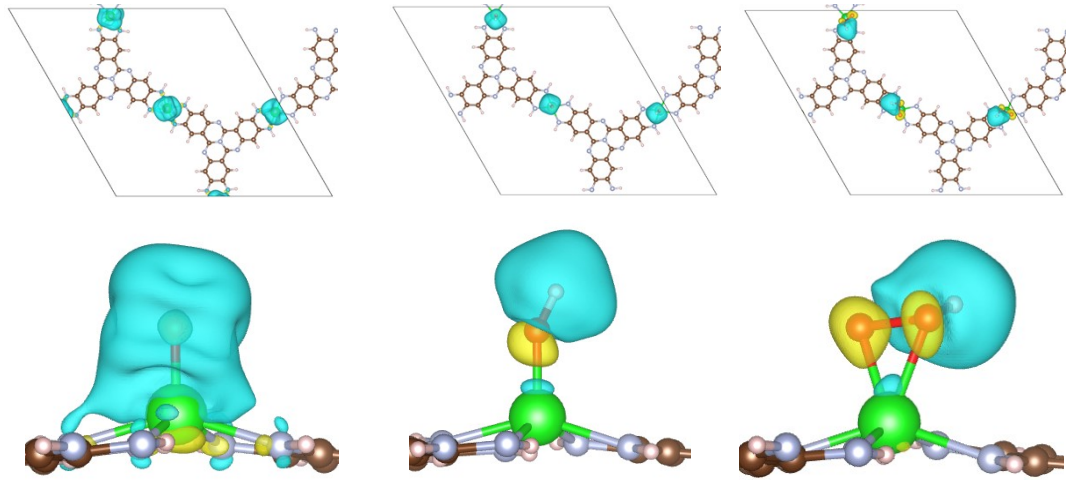
Co-HITT



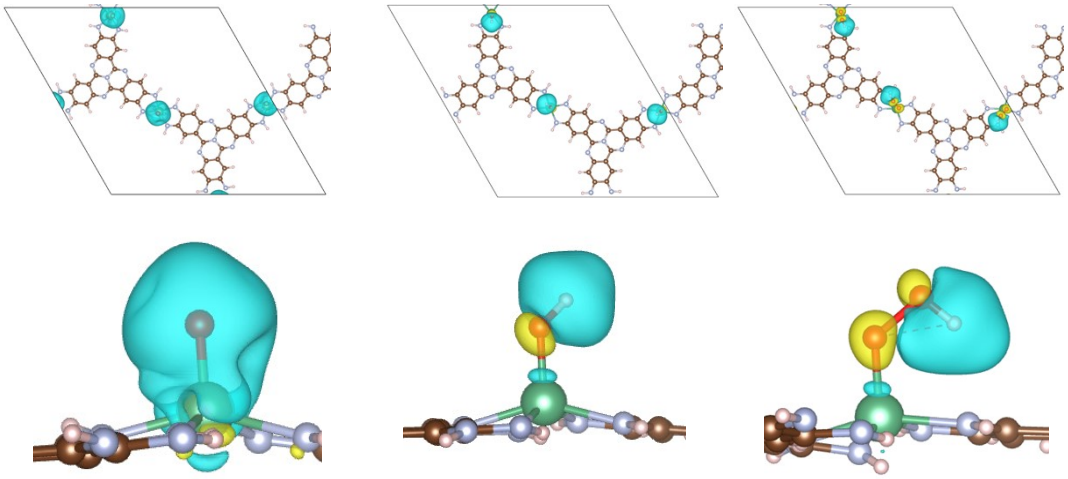
Ni-HITT



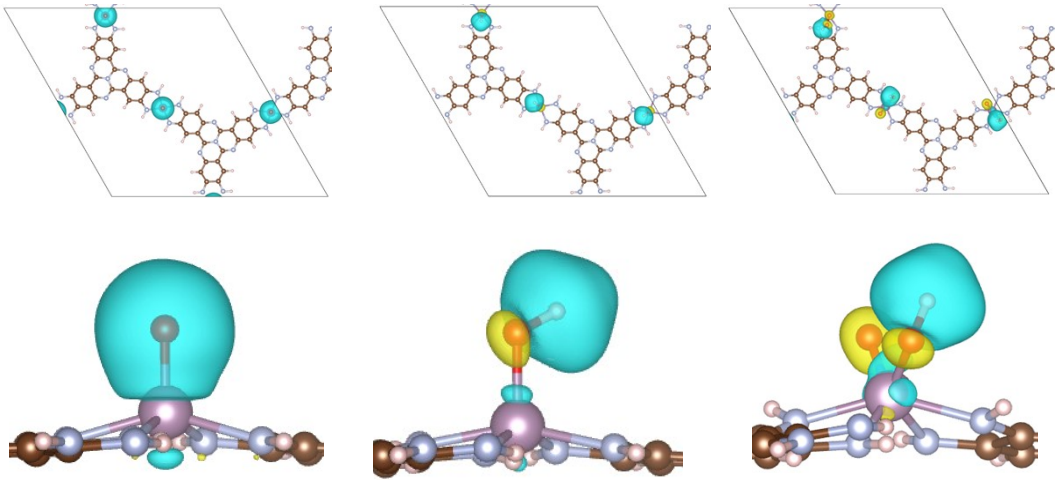
Cu-HITT



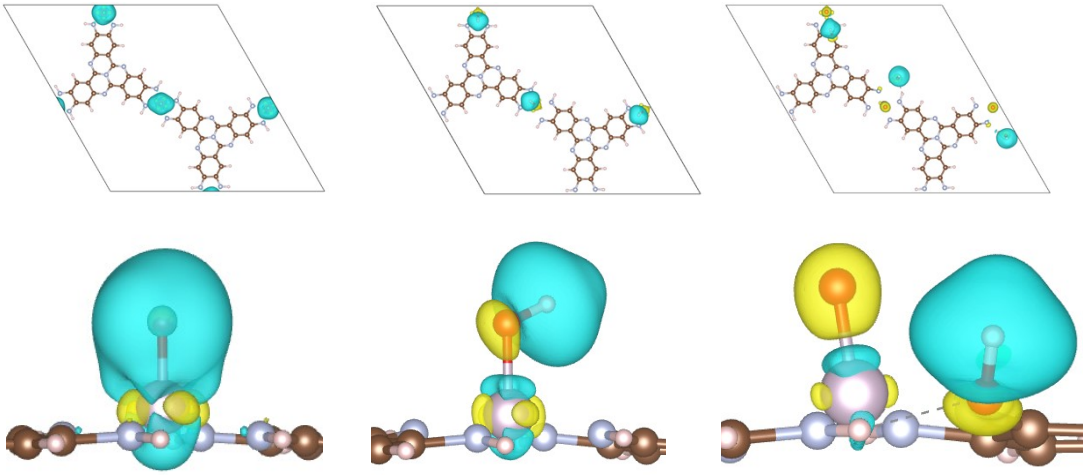
Zr-HITT



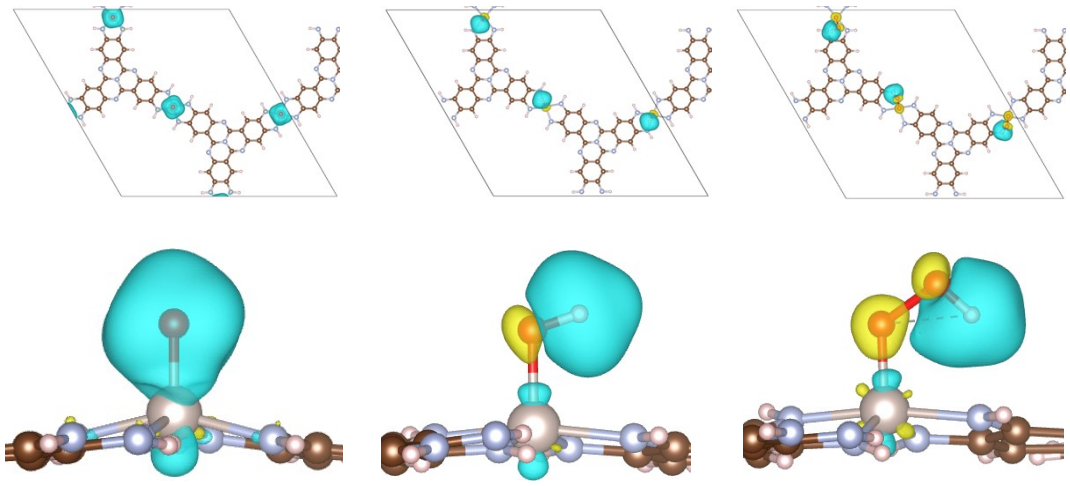
Nb-HITT



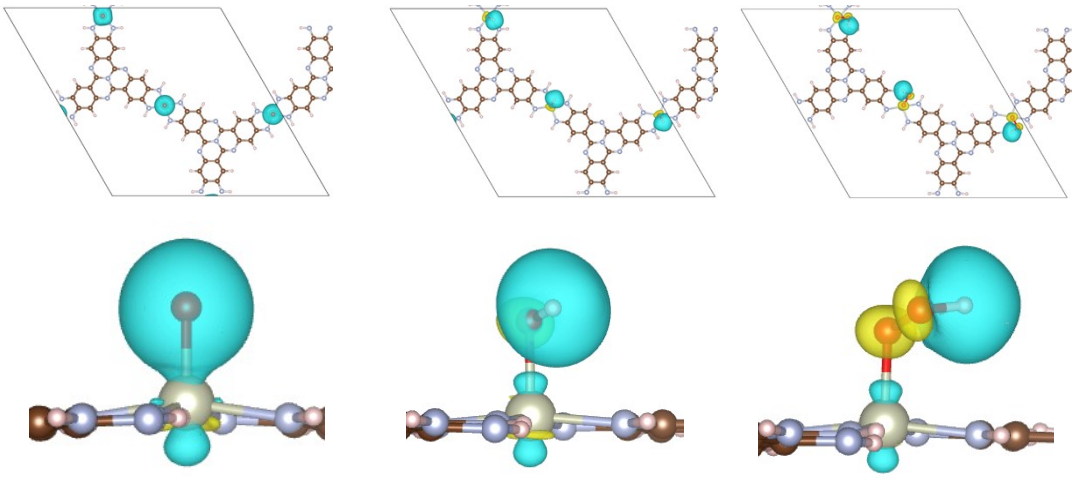
Mo-HITT



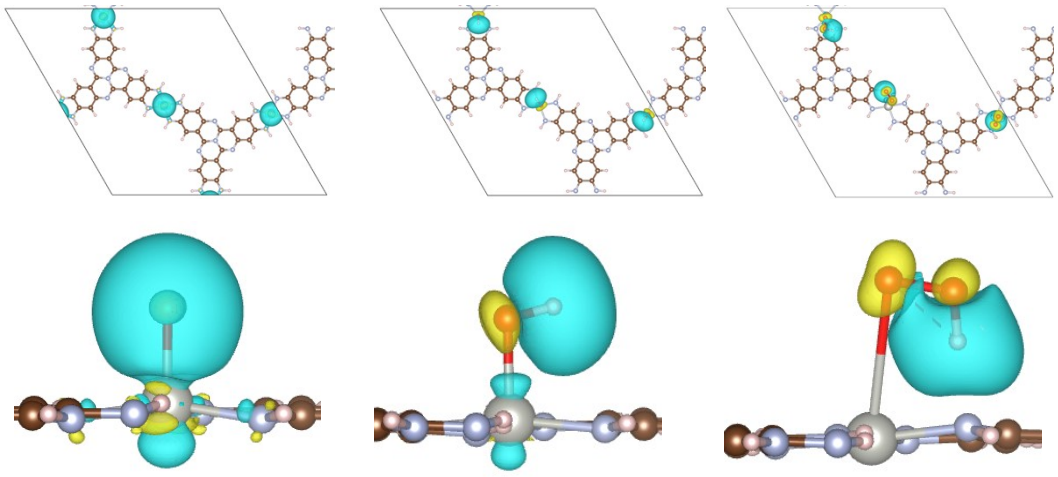
Tc-HITT



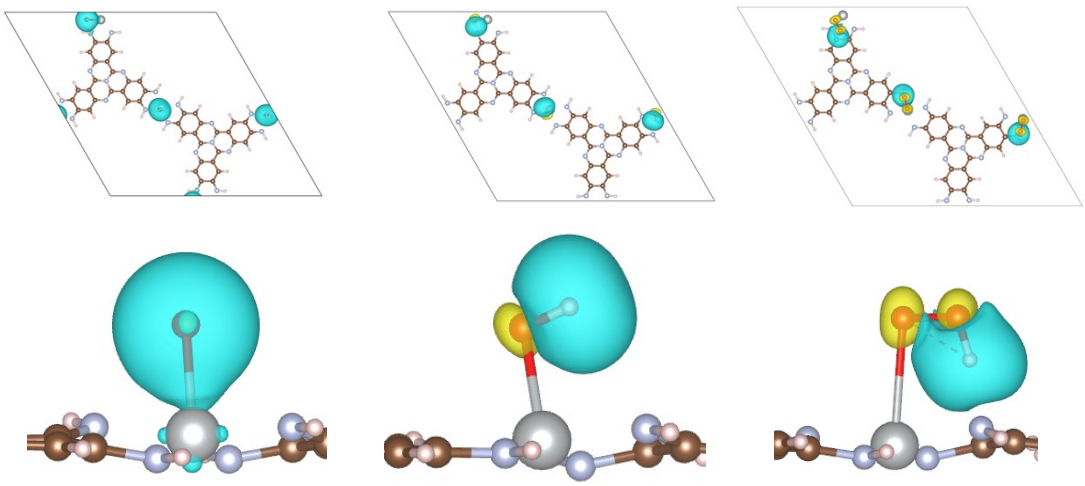
Ru-HITT



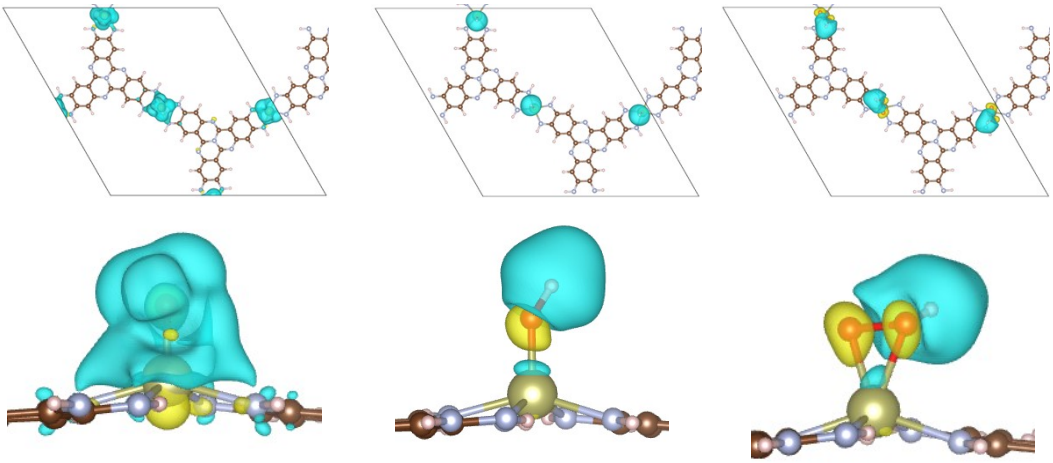
Rh-HITT



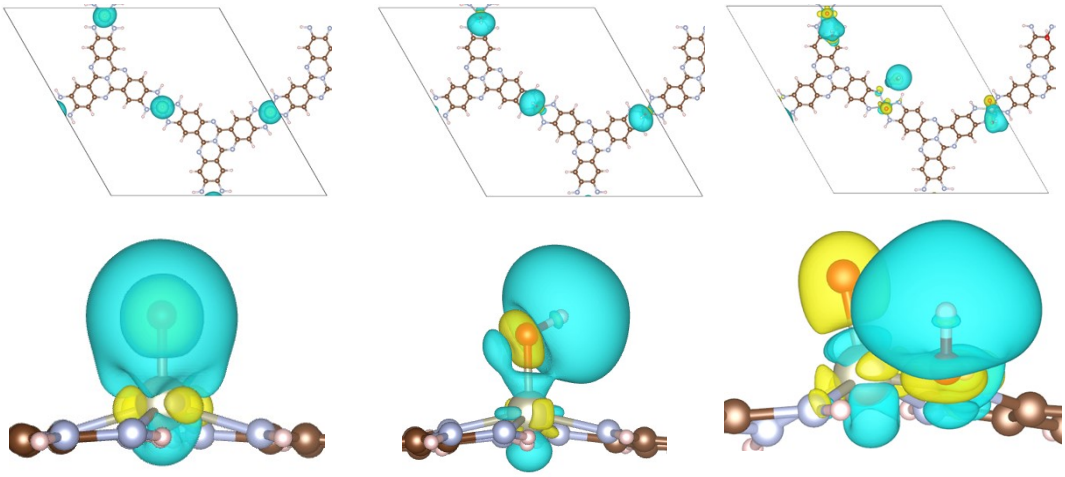
Pd-HITT



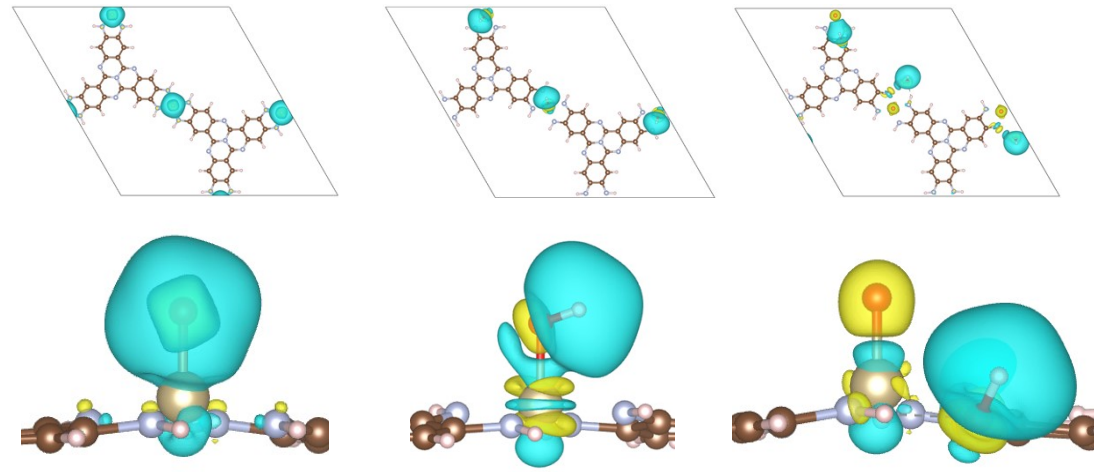
Ag-HITT



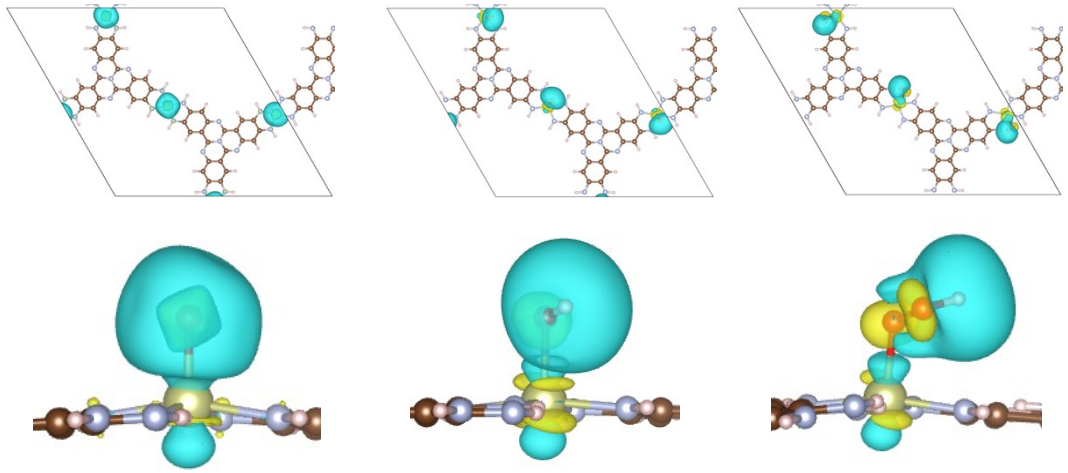
Hf-HITT



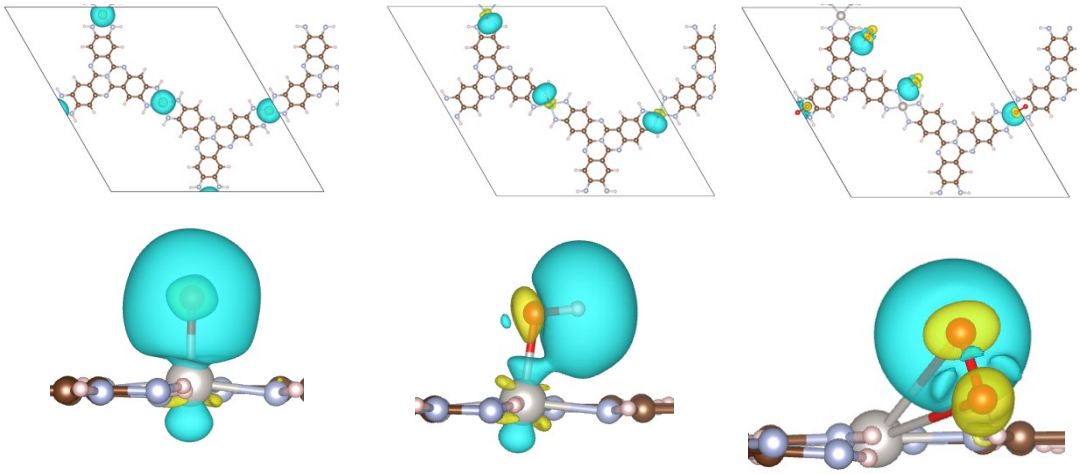
Re-HITT



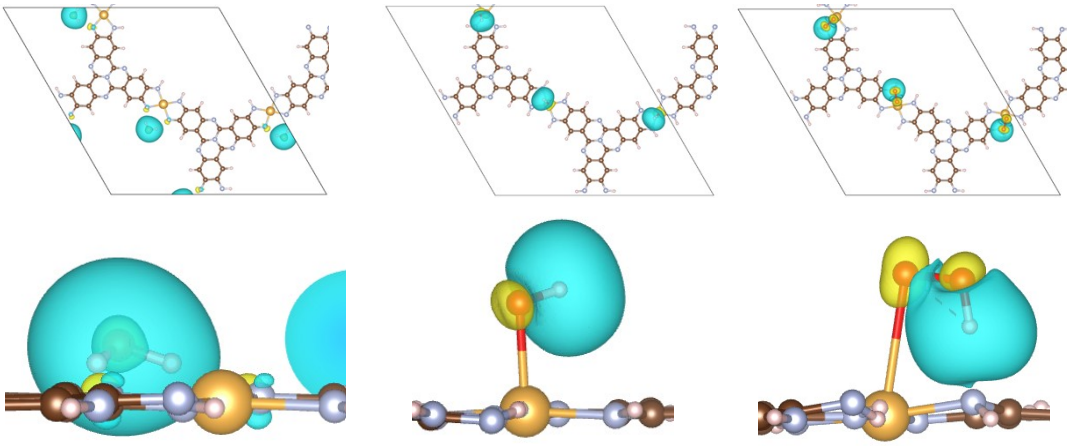
Os-HITT



Ir-HITT



Pt-HITT



Au-HITT

Fig. S7 Differential charge diagram of M-HITT adsorption intermediates (*O, *OH, *OOH from left to right).

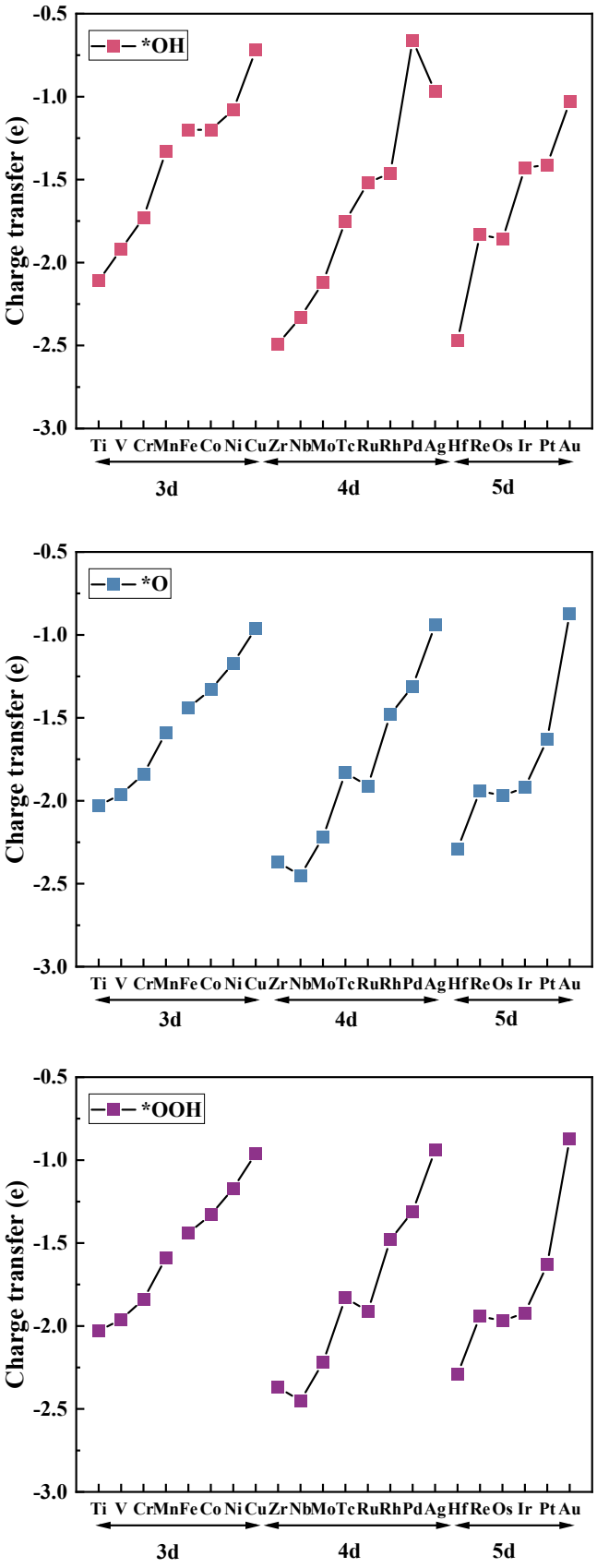


Fig. S8 Charge transfer on TM after adsorption of *OH, *O and *OOH by M-HITT.

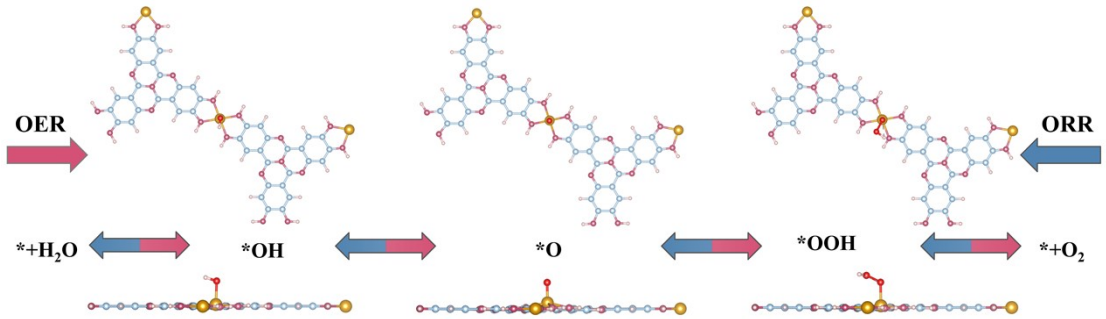
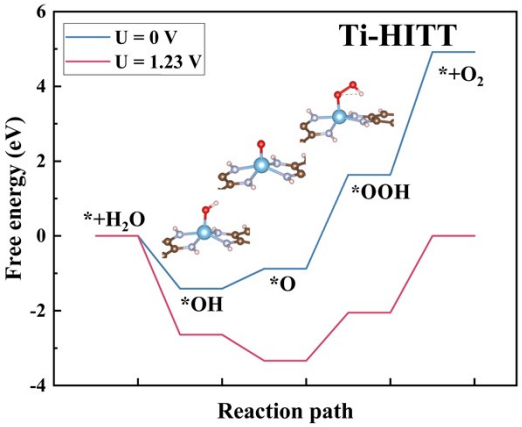
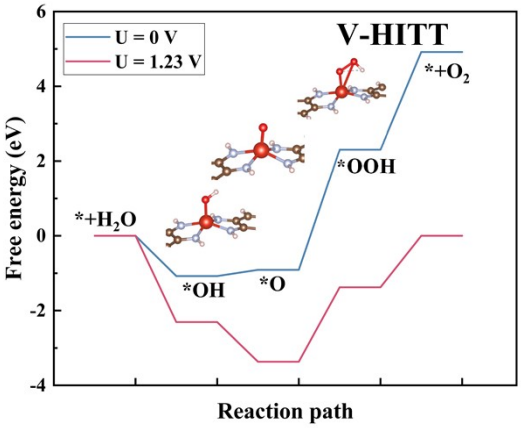


Fig. S9 The structures of intermediates (*OH, *O, and *OOH) of OER and ORR adsorbed on M-HITT.

Table S9. The free energy changes of each elementary step (ΔG_A, ΔG_B, ΔG_C and ΔG_D) and the overpotential of OER and ORR (η_{OER} and η_{ORR}).

	ΔG_A (eV)	ΔG_B (eV)	ΔG_C (eV)	ΔG_D (eV)	η_{OER} (V)	η_{ORR} (V)
Ti	-1.41	0.53	2.52	3.28	2.05	2.64
V	-1.08	0.17	3.22	2.61	1.99	2.31
Cr	-0.01	0.14	3.03	1.75	1.80	1.24
Mn	0.81	0.41	2.60	1.10	1.37	0.82
Fe	0.73	1.14	1.94	1.11	0.71	0.50
Co	1.51	1.42	1.55	0.43	0.32	0.80
Ni	2.20	2.20	0.72	-0.21	0.97	1.44
Cu	1.96	2.41	0.36	0.19	1.18	1.04
Zr	-2.57	1.35	2.78	3.36	2.13	3.80
Nb	-2.27	0.09	4.44	2.66	3.21	3.50
Mo	-1.17	-0.24	3.60	3.74	2.37	2.40
Tc	-0.76	-0.29	1.61	4.36	3.13	1.99
Ru	0.08	0.39	2.44	2.01	1.21	1.15
Rh	1.04	1.45	1.51	0.92	0.28	0.31
Pd	2.47	2.20	0.66	-0.41	1.24	1.64
Ag	1.57	2.46	0.16	0.74	1.23	0.49
Hf	-2.41	1.10	1.53	4.70	3.47	3.64
Re	-1.61	-0.18	1.18	5.53	4.30	2.84
Os	0.40	-0.47	1.54	3.45	2.22	1.70
Ir	1.24	0.98	1.91	0.79	1.24	0.44
Pt	2.49	1.87	0.94	-0.38	1.26	1.63
Au	2.46	2.32	0.09	0.05	1.23	1.18


Ti-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2


V-HITT
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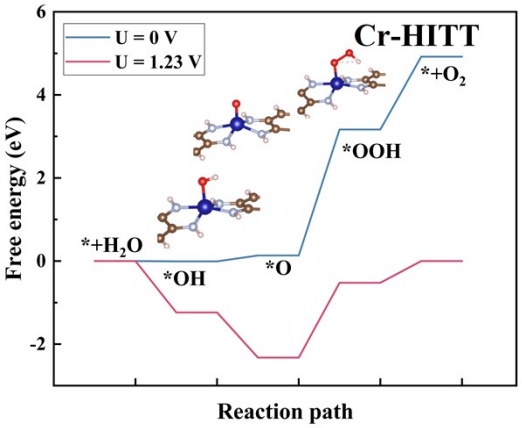
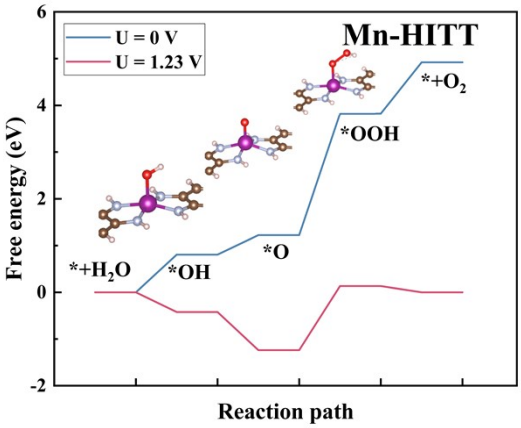
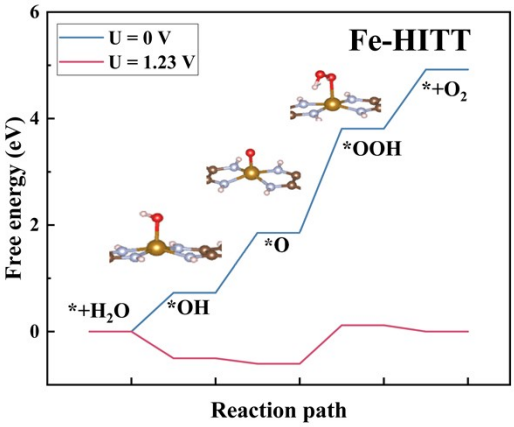
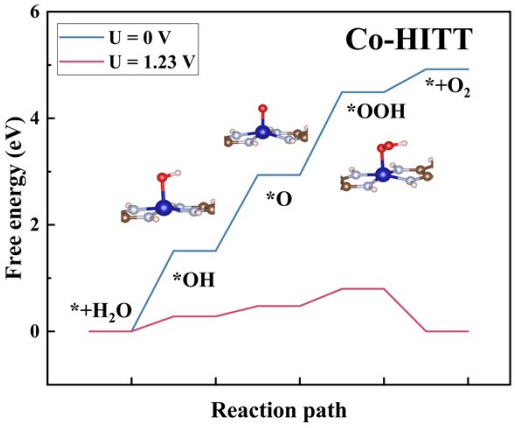
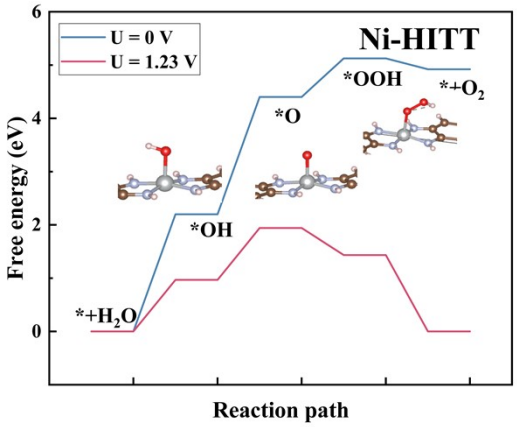
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

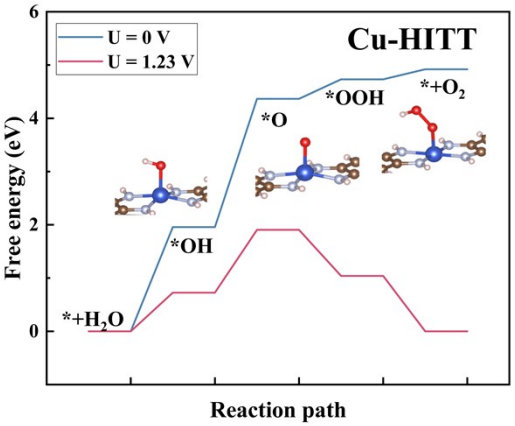

Cr-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

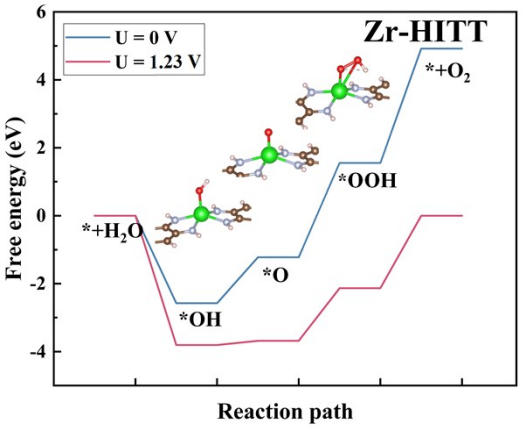

Mn-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

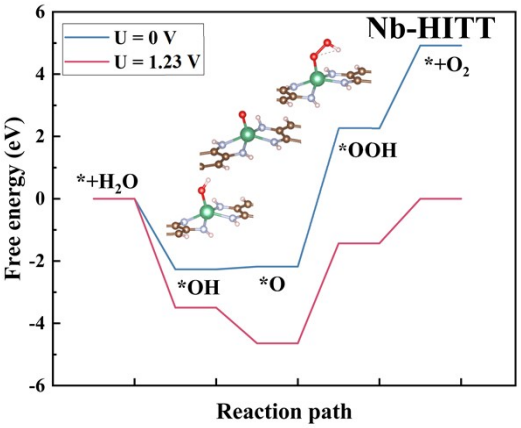

Fe-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

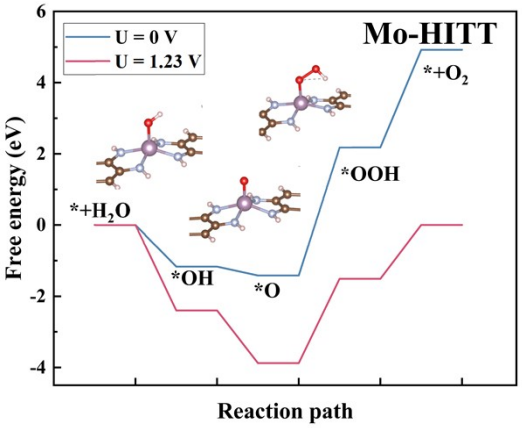

Co-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

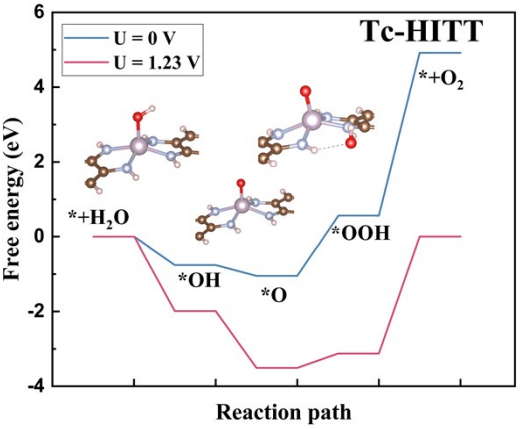

Ni-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

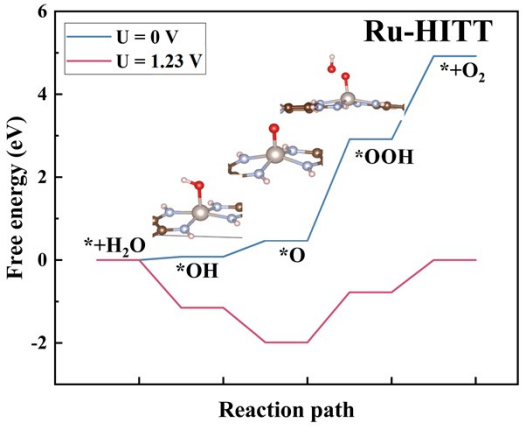

Cu-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

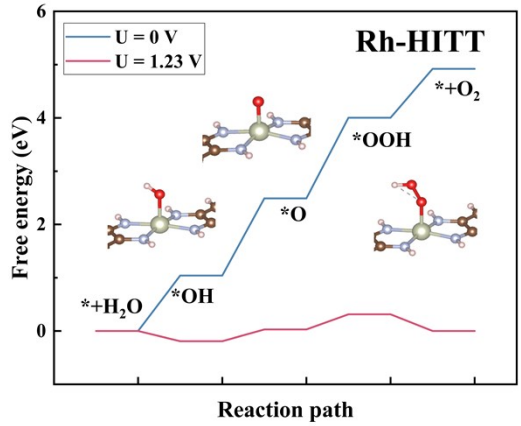

Zr-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

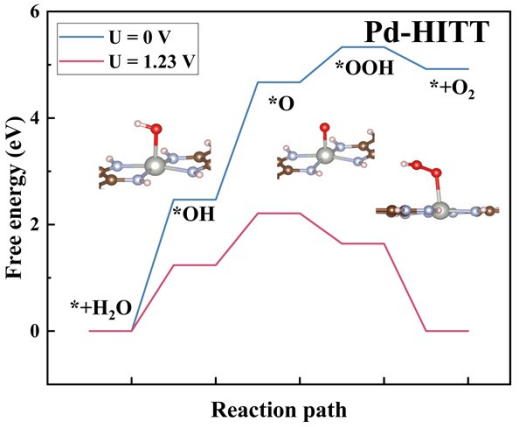

Nb-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

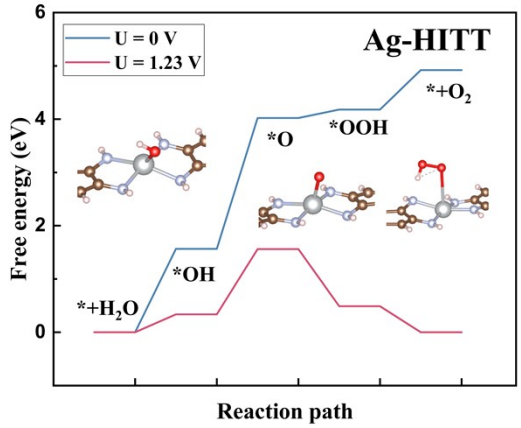

Mo-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2


Tc-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2


Ru-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2


Rh-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2


Pd-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2


Ag-HITT
U = 0 V
U = 1.23 V
Free energy (eV)
Reaction path
*+H2O
*OH
*O
*OOH
*+O2

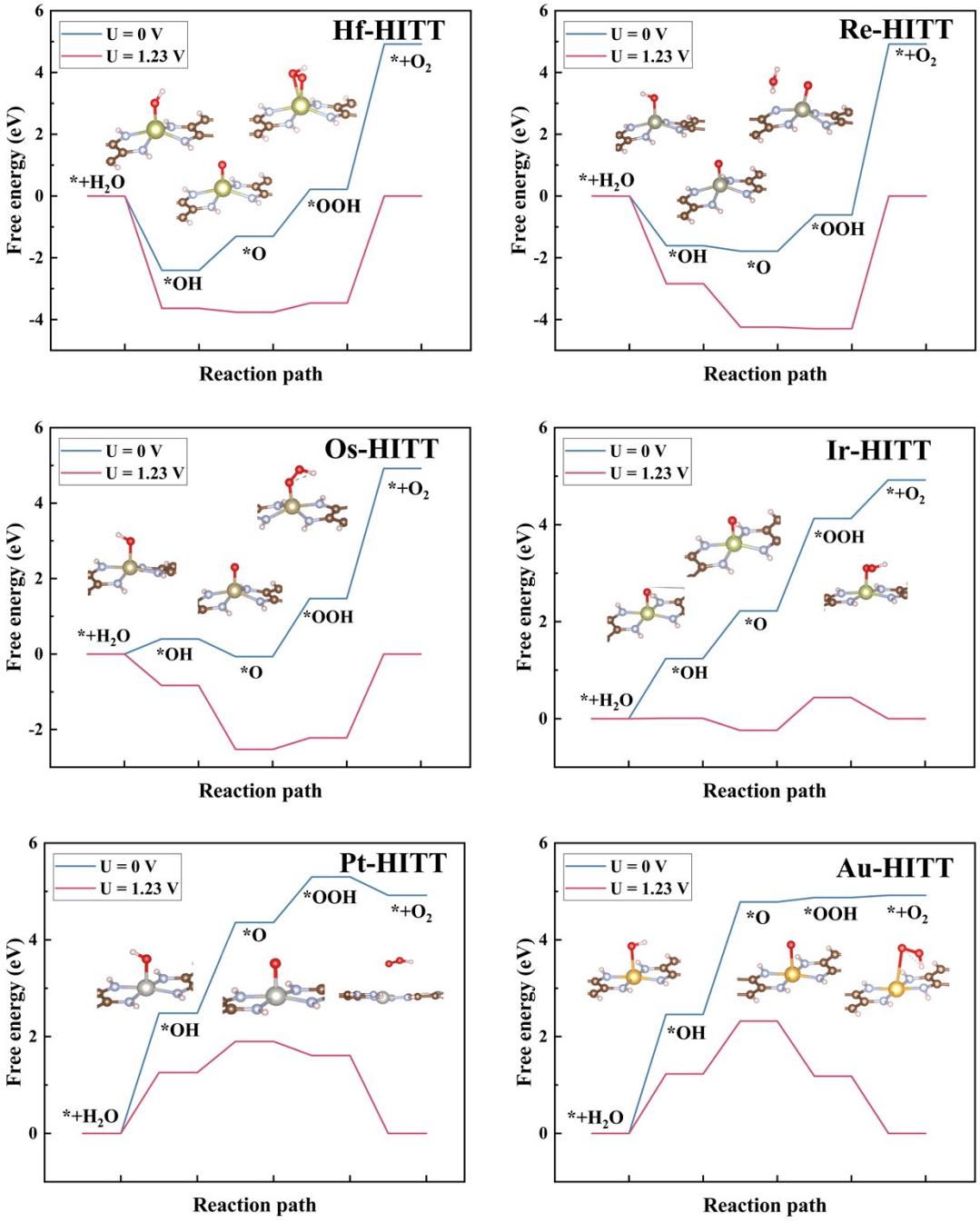
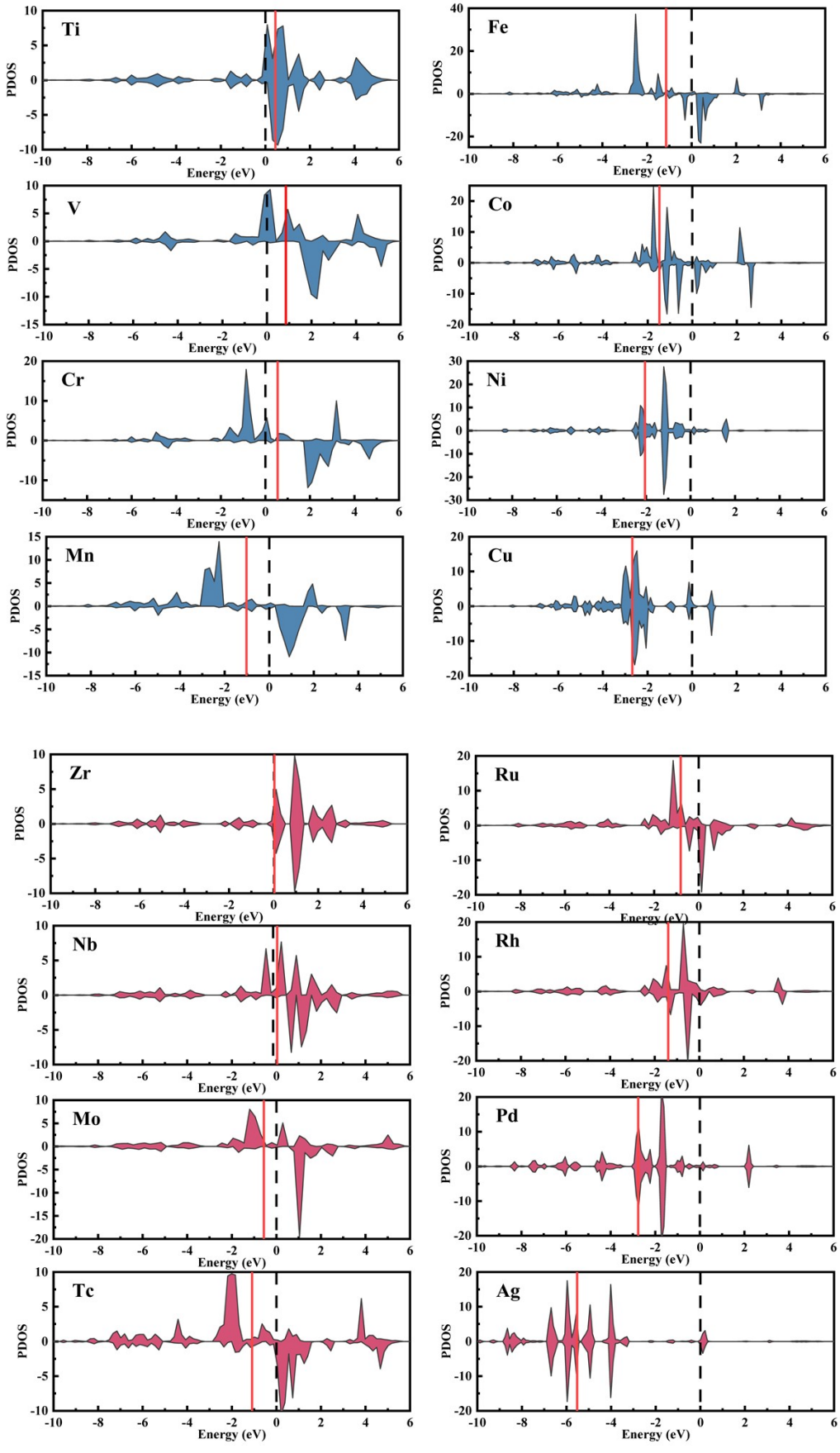


Fig. S10 The OER free energy diagrams of M-HITT.


Ti
Fe
V
Co
Cr
Ni
Mn
Cu
Zr
Ru
Nb
Rh
Mo
Pd
Tc
Ag
PDOS
Energy (eV)

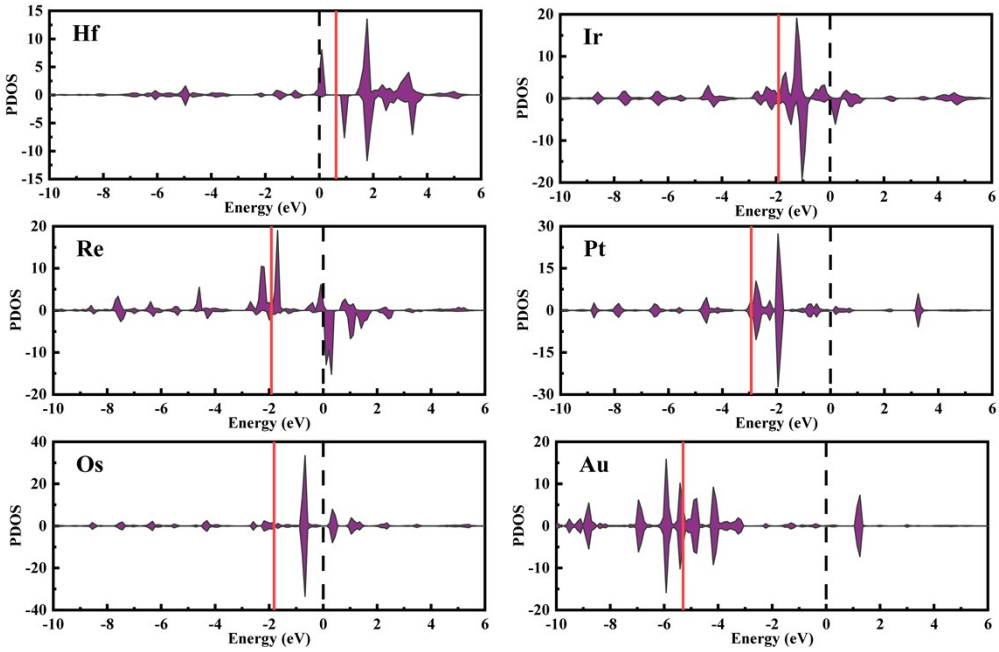
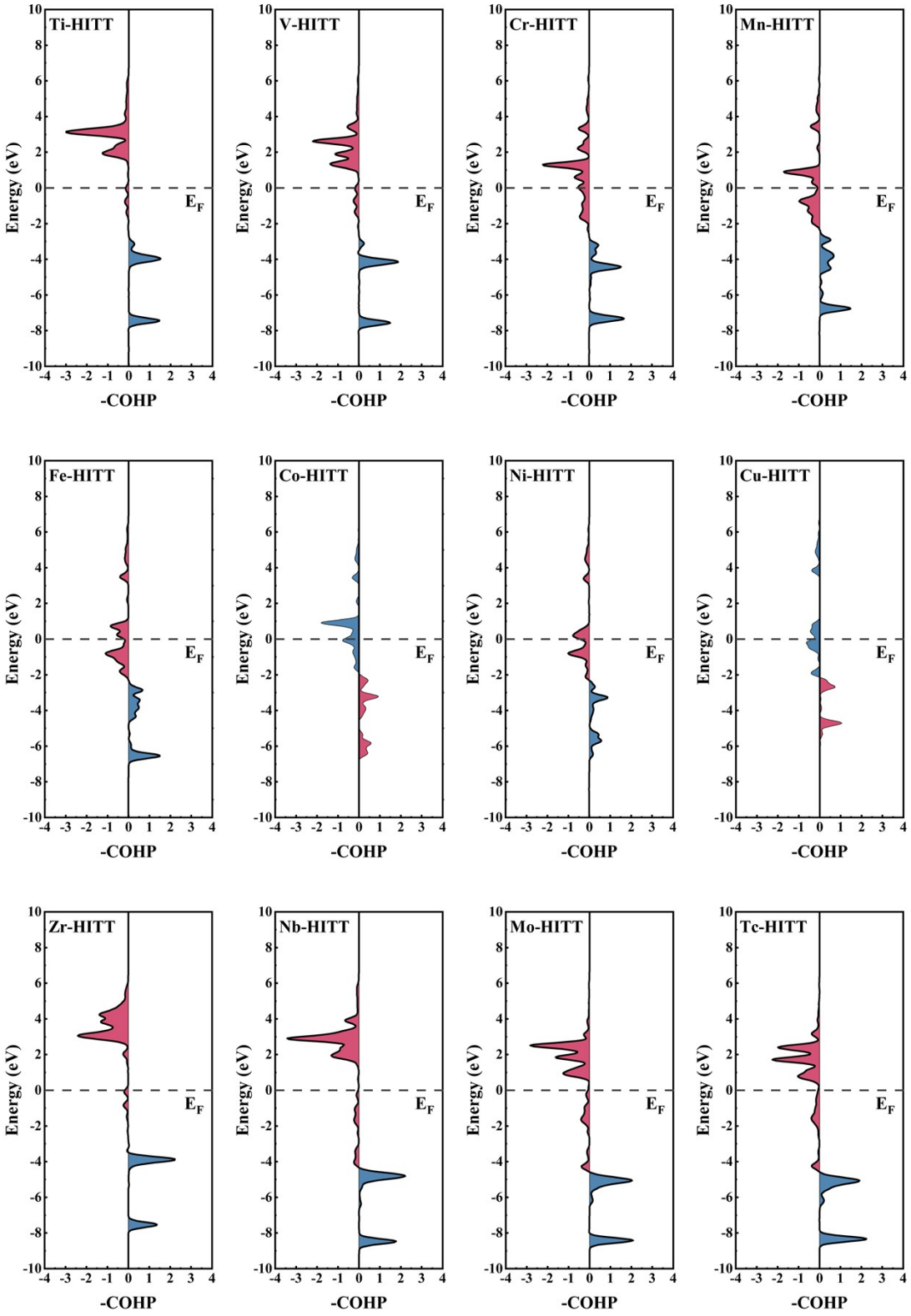


Fig. S11 The partial density of states (PDOS) of d orbitals for M-HITT. The d-band centers (ε_d) are also labeled for 3d TM, from Ti to Cu; 4d TM, from Zr to Ag; and 5d TM, from Hf to Au. The Fermi level (E_F) is set to 0 eV. Different fill colors (red, blue, and purple) represent different periods (fourth, fifth and sixth periods).


Ti-HITT
V-HITT
Cr-HITT
Mn-HITT
Fe-HITT
Co-HITT
Ni-HITT
Cu-HITT
Zr-HITT
Nb-HITT
Mo-HITT
Tc-HITT
Energy (eV)
-COHP
E_F

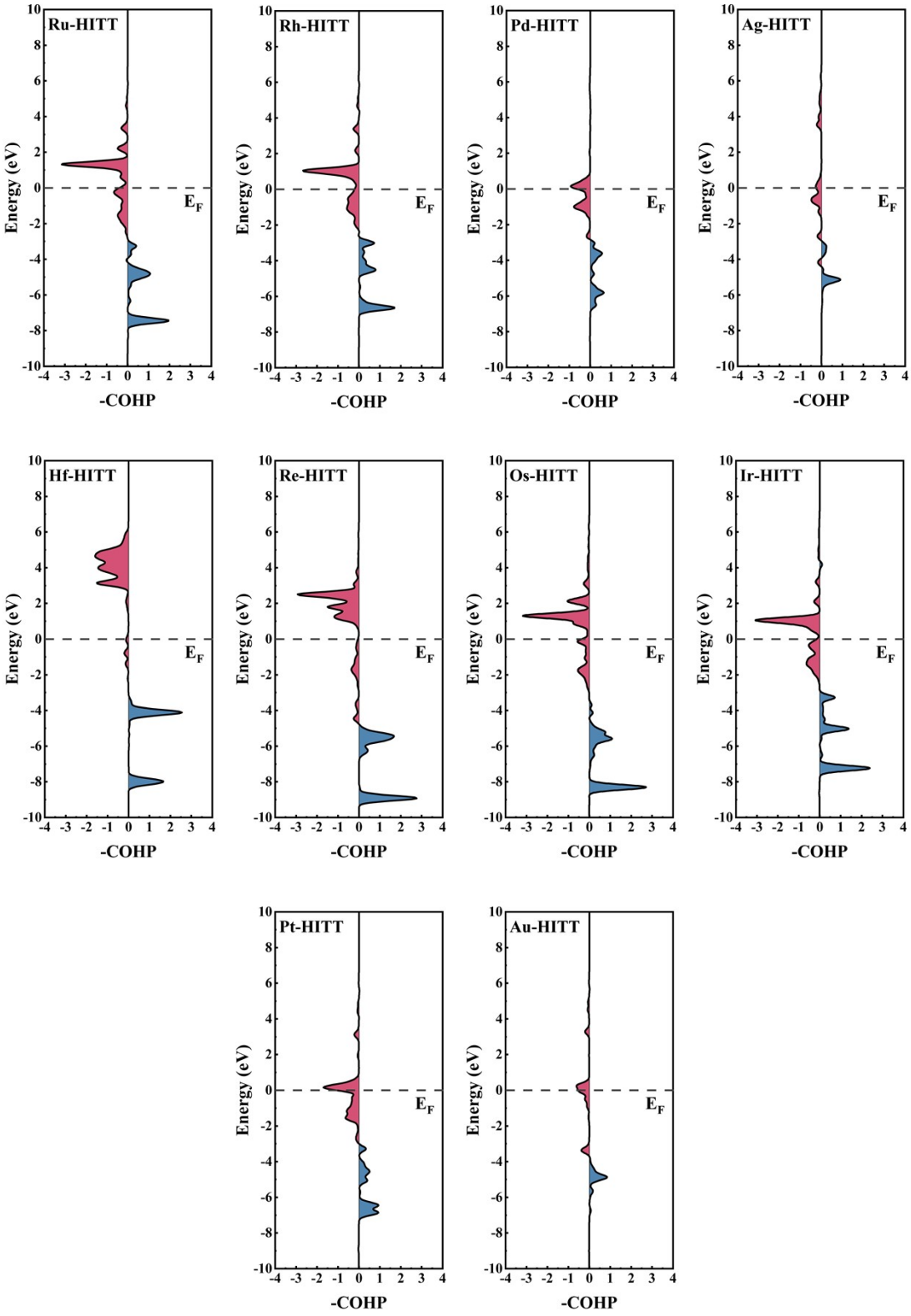


Fig. S12 -COHP between TM centers (from Ti to Au) and OH intermediate. The right and left sides represent the bonding and antibonding contributions, respectively.