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Supporting Information

Two-dimensional metal-organic frameworks as efficient bifunctional electrocatalysts for oxygen evolution/reduction reactions

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Table S1. Formation energies (E_{form}) of $M_3(C_6S_6)_2$, the number of transferred electrons (N_e) during the process of dissolution, the standard dissolution potentials ($U_{diss\text{-}bulk}$) of M bulk, and the calculated dissolution potentials (U_{diss}) of M atoms on $M_3(C_6S_6)_2$.

$M_3(C_6S_6)_2$	E_{form}	N_e	$U_{diss\text{-}bulk}$	U_{diss}
V	-0.52	2	-1.18	-0.92
Cr	-2.96	2	-0.91	0.57
Mn	-2.07	2	-1.19	-0.15
Fe	-0.94	2	-0.45	0.02
Co	-1.08	2	-0.28	0.26
Ni	-1.86	2	-0.26	0.67
Cu	0.86	2	0.34	-0.09
Nb	1.96	3	-1.1	-1.75
Mo	1.94	3	-0.2	-0.85
Tc	3.68	2	0.400	-1.44
Ru	1.97	2	0.46	-0.52
Rh	-1.89	2	0.6	1.55
Pd	-1.39	2	0.95	1.64
Ir	-0.34	3	1.16	1.27
Pt	-3.00	2	1.18	2.68

Table S2. The bond lengths between TM atoms and the neighboring S atoms (d_{TM-S}) with a unit of Å and the charge transfer between TM atoms and the C_6S_6 (Q_{TM}) with a unit of *e*.

	d_{TM-S} (Å)	Q_{TM} (*e*)
$V_3(C_6S_6)_2$	2.28	-1.47
$Cr_3(C_6S_6)_2$	2.27	-1.20
$Mn_3(C_6S_6)_2$	2.25	-1.13
$Fe_3(C_6S_6)_2$	2.17	-0.82
$Co_3(C_6S_6)_2$	2.14	-0.61
$Ni_3(C_6S_6)_2$	2.14	-0.51
$Nb_3(C_6S_6)_2$	2.36	-1.53
$Mo_3(C_6S_6)_2$	2.36	-1.29
$Tc_3(C_6S_6)_2$	2.27	-0.86
$Ru_3(C_6S_6)_2$	2.17	-0.71
$Rh_3(C_6S_6)_2$	2.25	-0.40
$Pd_3(C_6S_6)_2$	2.28	-0.31
$Ir_3(C_6S_6)_2$	2.25	-0.39
$Pt_3(C_6S_6)_2$	2.27	-0.23

Table S3. Calculated zero-point energies and Gibbs free energies of *OH on $M_3(C_6S_6)_2$.

	E_{ZPE} (eV)	G (eV)
$V_3(C_6S_6)_2$	0.27	-197.00
$Cr_3(C_6S_6)_2$	0.30	-197.40
$Mn_3(C_6S_6)_2$	0.30	-196.36
$Fe_3(C_6S_6)_2$	0.29	-193.03
$Co_3(C_6S_6)_2$	0.31	-188.92
$Ni_3(C_6S_6)_2$	0.25	-184.38
$Nb_3(C_6S_6)_2$	0.28	-200.37
$Mo_3(C_6S_6)_2$	0.31	-199.59
$Tc_3(C_6S_6)_2$	0.31	-198.18
$Ru_3(C_6S_6)_2$	0.33	-193.81
$Rh_3(C_6S_6)_2$	0.30	-189.12
$Pd_3(C_6S_6)_2$	0.24	-182.87
$Ir_3(C_6S_6)_2$	0.31	-193.84
$Pt_3(C_6S_6)_2$	0.26	-187.09

* Only the adsorbed species are considered during the process of ZPE calculations, and $T\Delta S$ is specified as zero.

Table S4. Calculated zero-point energies and Gibbs free energies of *O on $M_3(C_6S_6)_2$.

	E_{ZPE} (eV)	G (eV)
$V_3(C_6S_6)_2$	0.05	-193.11
$Cr_3(C_6S_6)_2$	0.05	-194.02
$Mn_3(C_6S_6)_2$	0.06	-192.80
$Fe_3(C_6S_6)_2$	0.05	-188.60
$Co_3(C_6S_6)_2$	0.03	-184.31
$Ni_3(C_6S_6)_2$	0.01	-178.90
$Nb_3(C_6S_6)_2$	0.05	-196.43
$Mo_3(C_6S_6)_2$	0.06	-196.12
$Tc_3(C_6S_6)_2$	0.06	-194.86
$Ru_3(C_6S_6)_2$	0.06	-190.18
$Rh_3(C_6S_6)_2$	0.03	-184.43
$Pd_3(C_6S_6)_2$	0.01	-177.05
$Ir_3(C_6S_6)_2$	0.04	-189.49
$Pt_3(C_6S_6)_2$	0.01	-181.75

Table S5. Calculated zero-point energies and Gibbs free energies of *OOH on $M_3(C_6S_6)_2$.

	EZPE (eV)	G (eV)
$V_3(C_6S_6)_2$	0.37	-201.07
$Cr_3(C_6S_6)_2$	0.34	-201.61
$Mn_3(C_6S_6)_2$	0.35	-200.74
$Fe_3(C_6S_6)_2$	0.32	-197.40
$Co_3(C_6S_6)_2$	0.34	-193.33
$Ni_3(C_6S_6)_2$	0.33	-188.88
$Nb_3(C_6S_6)_2$	0.37	-204.35
$Mo_3(C_6S_6)_2$	0.33	-203.46
$Tc_3(C_6S_6)_2$	0.34	-202.32
$Ru_3(C_6S_6)_2$	0.34	-198.18
$Rh_3(C_6S_6)_2$	0.34	-193.59
$Pd_3(C_6S_6)_2$	0.27	-187.51
$Ir_3(C_6S_6)_2$	0.35	-198.32
$Pt_3(C_6S_6)_2$	0.29	-191.56

Table S6. The adsorption energies of *OH, *O and *OOH (ΔG_{*OH}, ΔG_{*O} and ΔG_{*OOH}).

	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)
$V_3(C_6S_6)_2$	-1.35	-0.86	2.00
$Cr_3(C_6S_6)_2$	-0.37	-0.39	2.85
$Mn_3(C_6S_6)_2$	0.69	0.85	3.73
$Fe_3(C_6S_6)_2$	0.79	1.82	3.84
$Co_3(C_6S_6)_2$	1.26	2.47	4.27
$Ni_3(C_6S_6)_2$	2.05	4.13	4.97
$Nb_3(C_6S_6)_2$	-1.86	-1.33	1.58
$Mo_3(C_6S_6)_2$	-0.58	-0.51	2.98
$Tc_3(C_6S_6)_2$	-1.00	-1.08	2.28
$Ru_3(C_6S_6)_2$	0.07	0.30	3.12
$Rh_3(C_6S_6)_2$	1.15	2.45	4.11
$Pd_3(C_6S_6)_2$	2.28	4.70	5.06
$Ir_3(C_6S_6)_2$	1.15	2.09	4.09
$Pt_3(C_6S_6)_2$	2.30	4.25	5.26

Table S7. The free energy changes of each elementary step (ΔG_1, ΔG_2, ΔG_3 and ΔG_4) and the overpotential of OER and ORR (η_{OER} and η_{ORR}).

	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η_{OER} (V)	η_{ORR} (V)
$V_3(C_6S_6)_2$	-1.35	0.49	2.86	2.92	1.69	2.58
$Cr_3(C_6S_6)_2$	-0.37	-0.02	3.24	2.07	2.01	1.60
$Mn_3(C_6S_6)_2$	0.69	0.16	2.88	1.19	1.65	1.07
$Fe_3(C_6S_6)_2$	0.79	1.03	2.02	1.08	0.79	0.44
$Co_3(C_6S_6)_2$	1.26	1.21	1.80	0.65	0.57	0.58
$Ni_3(C_6S_6)_2$	2.05	2.08	0.83	-0.05	0.85	1.28
$Nb_3(C_6S_6)_2$	-1.86	0.53	2.90	3.34	2.11	3.09
$Mo_3(C_6S_6)_2$	-0.58	0.07	3.48	1.94	2.25	1.81
$Tc_3(C_6S_6)_2$	-1.00	-0.08	3.36	2.64	2.13	2.23
$Ru_3(C_6S_6)_2$	0.07	0.23	2.82	1.80	1.59	1.16
$Rh_3(C_6S_6)_2$	1.15	1.30	1.66	0.81	0.43	0.42
$Pd_3(C_6S_6)_2$	2.28	2.42	0.36	-0.14	1.19	1.37
$Ir_3(C_6S_6)_2$	1.15	0.95	2.00	0.83	0.77	0.40
$Pt_3(C_6S_6)_2$	2.30	1.95	1.01	-0.34	1.07	1.57

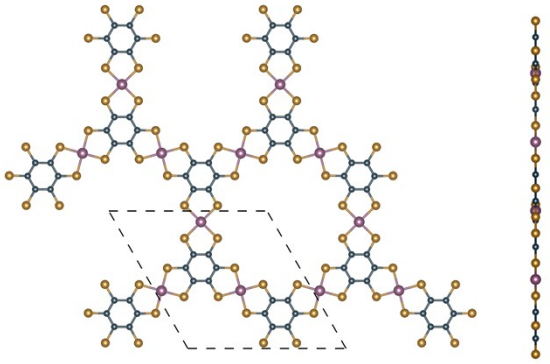

Fig. S1. Top and side views of $M_3(C_6S_6)_2$.

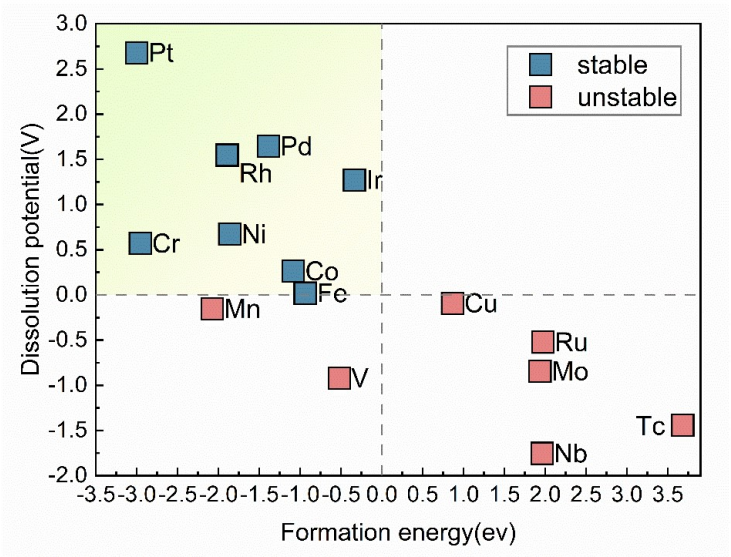

Fig. S2. The formation energy (E_{form}) and the dissolution potential (U_{diss}) of TM atoms. For a stable $M_3(C_6S_6)_2$ system, $E_{form} < 0$ eV and $U_{diss} > 0$ V should be satisfied.

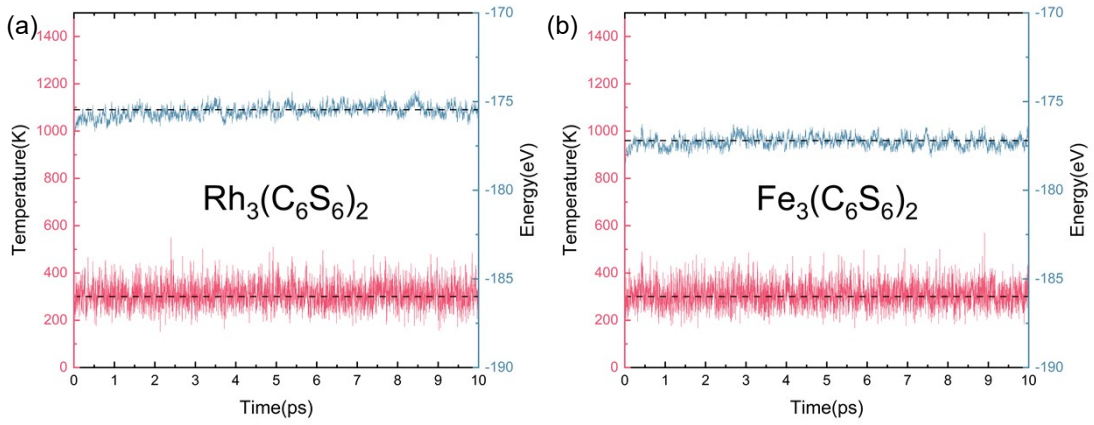

Fig. S3. Variations of energy and temperature versus the AIMD simulation time for (a) $Rh_3(C_6S_6)_2$ and (b) $Fe_3(C_6S_6)_2$, the simulation lasts for 10 ps at 300 K.

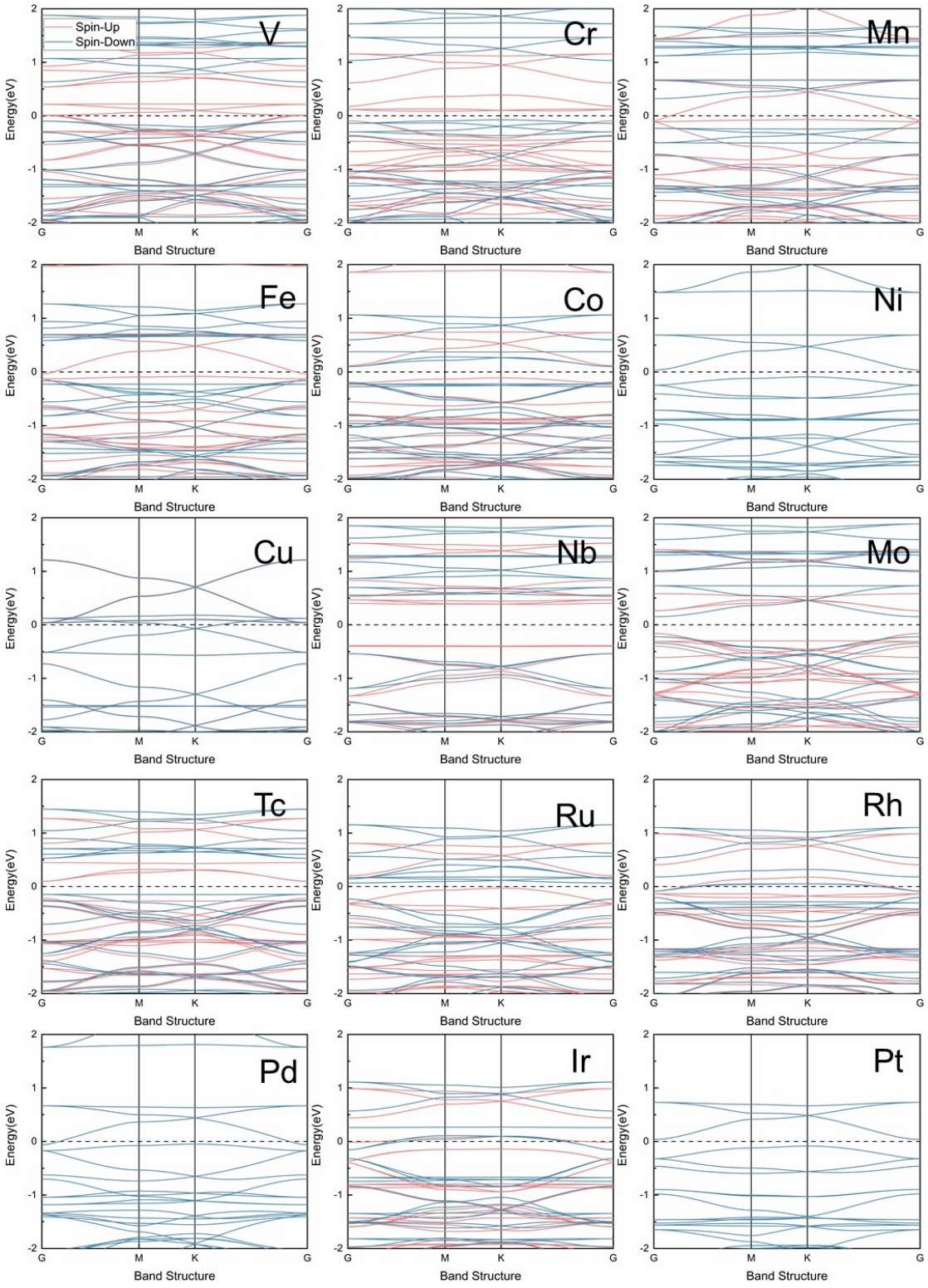

Fig. S4. Band structure of $M_3(C_6S_6)_2$.

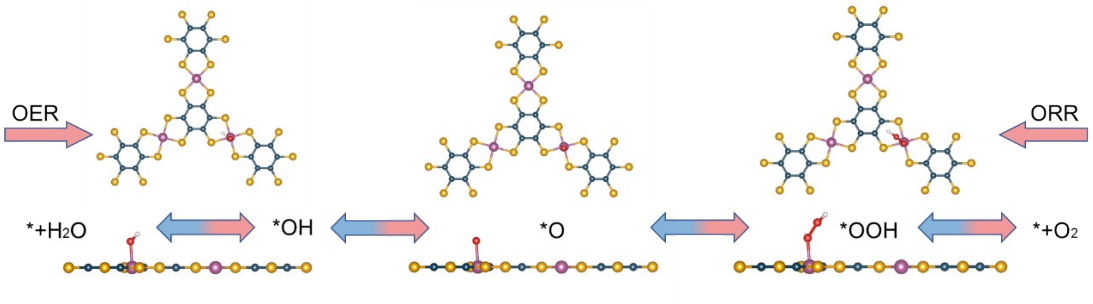

Fig. S5. The structures of intermediates (*OH, *O, and *OOH) of OER and ORR adsorbed on $M_3(C_6S_6)_2$.

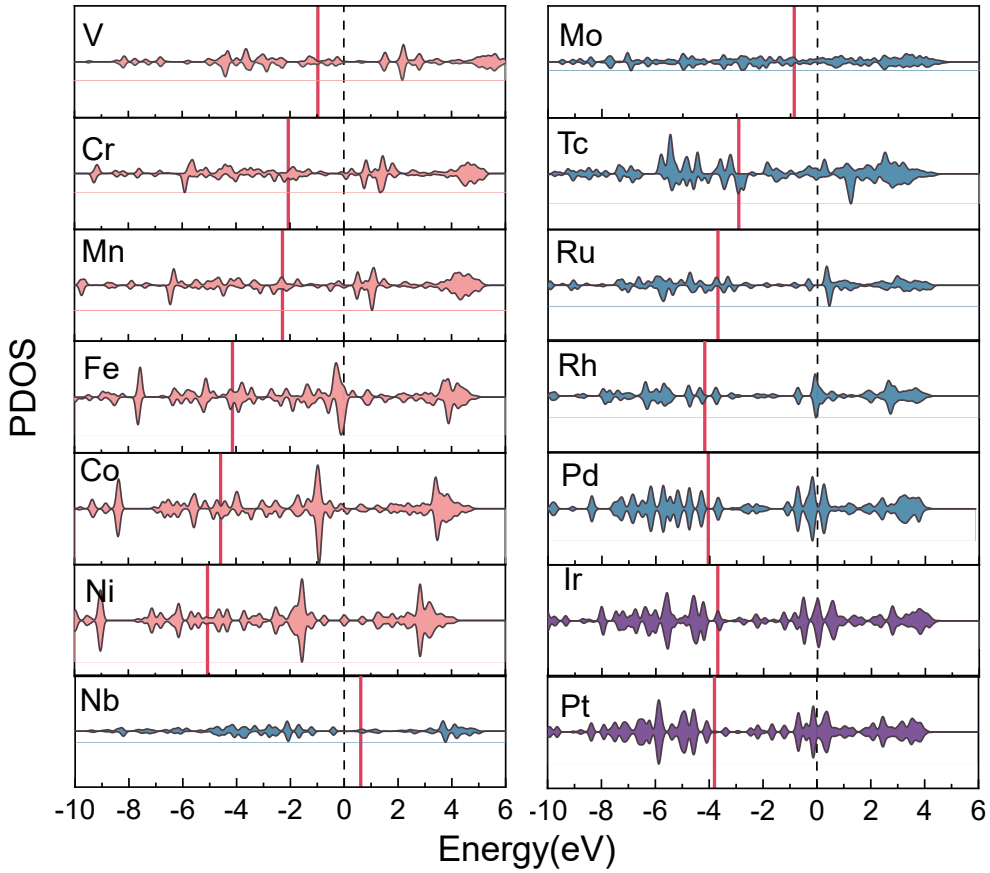

Fig. S6. The partial density of states (PDOS) of d orbitals for $M_3(C_6S_6)_2$. The *d*-band centers (ε_d) are also labeled for 3d TM, from V to Ni; 4d TM, from Nb to Pd; and 5d TM, from Ir to Pt. The Fermi level (E_F) is set to 0 eV. Different fill colors (red, blue, and purple) represent different periods (fourth, fifth and sixth periods).

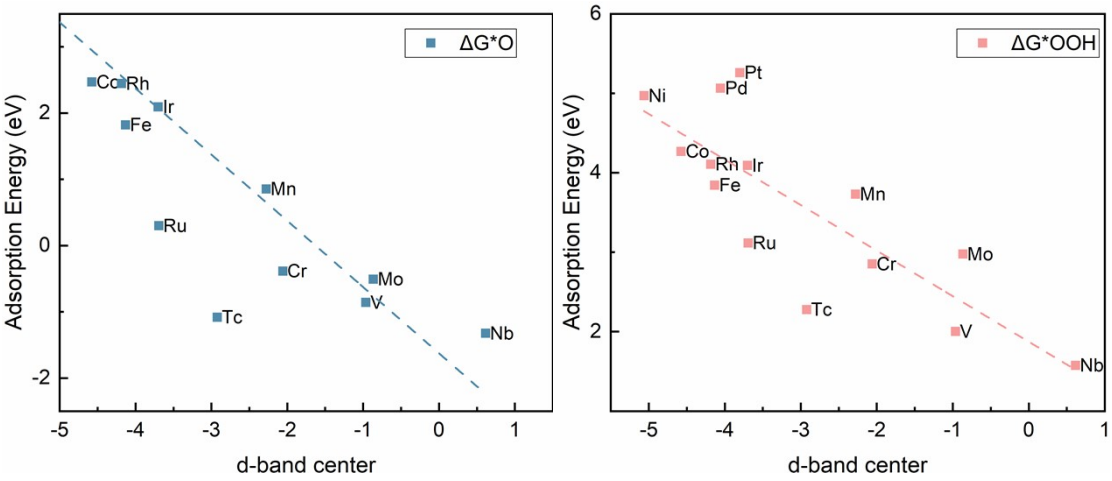

Fig. S7. The relationship between the d-band center and the adsorption energy of *O and *OOH.

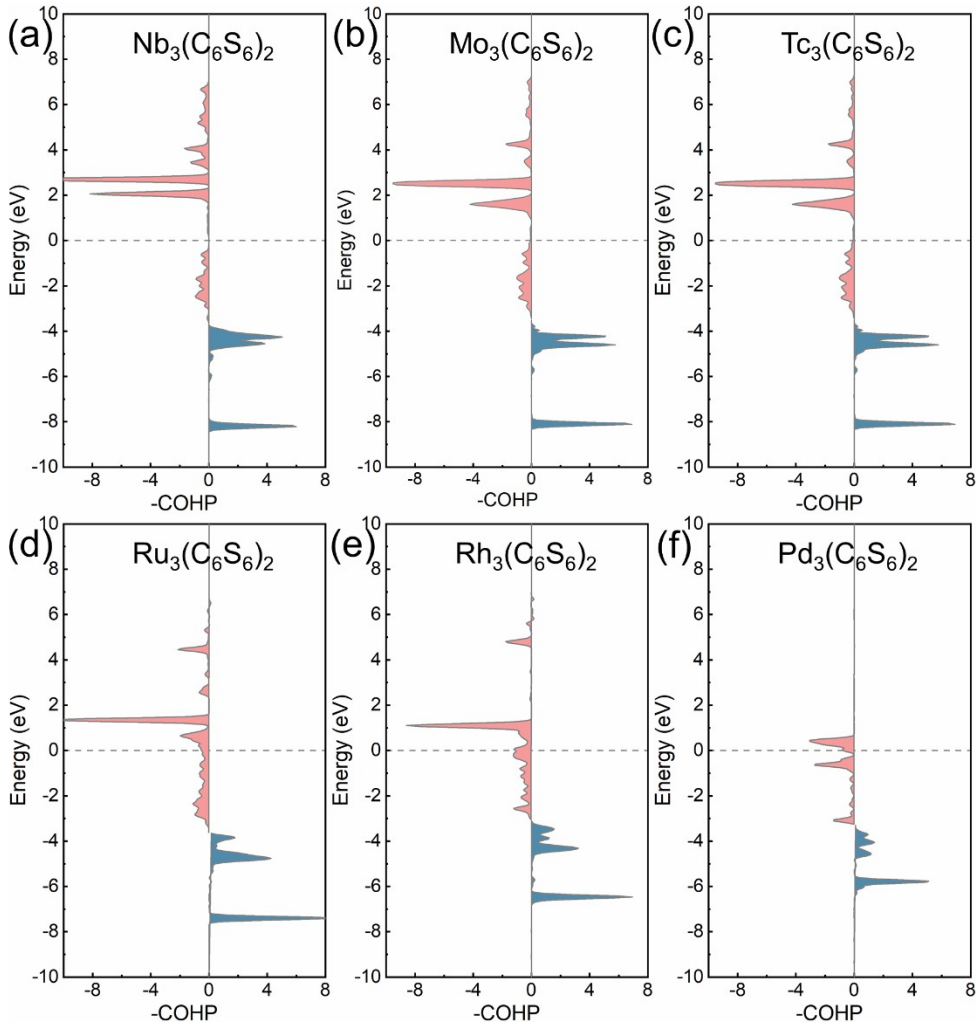

Fig. S8. (a)-(f) pCOHP between 4d TM centers (from Nb to Pd) and OH intermediate. The right and left sides represent the bonding and antibonding contributions, respectively.