Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

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Table S1. Formation energies (E_{form}) of $M_3(C_6Se_6)_2$, 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 $M_3(C_6Se_6)_2$.

$M_3(C_6Se_6)_2$	$E_{form\ (eV)}$	N_e	$U_{diss\text{-}bulk}$	U_{diss}
Ti	-4.14	2	-1.63	0.44
V	-1.18	2	-1.18	-0.59
Cr	-1.09	2	-0.91	-0.37
Mn	-2.61	2	-1.19	0.12
Fe	-1.43	2	-0.45	0.26
Co	-1.63	2	-0.28	0.53
Ni	-2.44	2	-0.26	0.96
Cu	-1.62	2	0.34	1.15
Zr	-4.69	4	-1.45	-0.28
Nb	-0.87	3	-1.1	-0.81
Mo	1.88	3	-0.2	-0.83
Ru	-0.44	2	0.46	0.68
Rh	-1.59	2	0.6	1.39
Pd	-2.82	2	0.95	2.36
Ir	-1.32	3	1.16	1.6
Pt	-3.52	2	1.18	2.94

Table S2. Optimized lattice constants, magnetic moments, and pore sizes (D_p) of the $M_3(C_6Se_6)_2$ systems.

$M_3(C_6Se_6)_2$	Lattice constant (Å)	magnetic moments of the MOFs (μ_B)	D_p (Å)
$Mn_3(C_6Se_6)_2$	15.69	9.0000	15.69
$Fe_3(C_6Se_6)_2$	15.52	6.1504	15.52
$Co_3(C_6Se_6)_2$	15.41	3.0007	15.41
$Ni_3(C_6Se_6)_2$	15.37	0.0000	15.37
$Cu_3(C_6Se_6)_2$	15.42	0.0000	15.42
$Ru_3(C_6Se_6)_2$	15.90	5.9992	15.90
$Rh_3(C_6Se_6)_2$	15.77	2.8837	15.77
$Pd_3(C_6Se_6)_2$	15.76	0.0000	15.76
$Ir_3(C_6Se_6)_2$	15.78	2.9270	15.78
$Pt_3(C_6Se_6)_2$	15.78	0.0000	15.78

Table S3. Calculated zero-point energies and Gibbs free energies of OH* on $M_3(C_6Se_6)_2$.

$M_3(C_6Se_6)_2$	E_{ZPE} (eV)	$T\Delta S$	G (eV)
$Mn_3(C_6Se_6)_2$	0.33	0.08	-202.55
$Fe_3(C_6Se_6)_2$	0.34	0.11	-199.55
$Co_3(C_6Se_6)_2$	0.35	0.10	-195.46
$Ni_3(C_6Se_6)_2$	0.32	0.10	-190.98
$Cu_3(C_6Se_6)_2$	0.31	0.17	-183.85
$Ru_3(C_6Se_6)_2$	0.36	0.09	-200.60
$Rh_3(C_6Se_6)_2$	0.36	0.10	-196.10
$Pd_3(C_6Se_6)_2$	0.32	0.11	-190.10
$Ir_3(C_6Se_6)_2$	0.37	0.09	-200.82
$Pt_3(C_6Se_6)_2$	0.33	0.15	-194.09

Table S4. Calculated zero-point energies and Gibbs free energies of O* on $M_3(C_6Se_6)_2$.

$M_3(C_6Se_6)_2$	E_{ZPE} (eV)	$T\Delta S$	G (eV)
$Mn_3(C_6Se_6)_2$	0.08	0.05	-202.70
$Fe_3(C_6Se_6)_2$	0.08	0.05	-198.65
$Co_3(C_6Se_6)_2$	0.06	0.08	-194.30
$Ni_3(C_6Se_6)_2$	0.08	0.04	-190.47
$Cu_3(C_6Se_6)_2$	0.02	0.02	-181.49
$Ru_3(C_6Se_6)_2$	0.08	0.05	-200.38
$Rh_3(C_6Se_6)_2$	0.06	0.07	-194.92
$Pd_3(C_6Se_6)_2$	0.05	0.10	-188.05
$Ir_3(C_6Se_6)_2$	0.07	0.07	-199.94
$Pt_3(C_6Se_6)_2$	0.05	0.09	-192.30

Table S5. Calculated zero-point energies and Gibbs free energies of OOH* on $M_3(C_6Se_6)_2$.

$M_3(C_6Se_6)_2$	E_{ZPE} (eV)	$T\Delta S$	G (eV)
$Mn_3(C_6Se_6)_2$	0.42	0.23	-199.89
$Fe_3(C_6Se_6)_2$	0.43	0.20	-195.99
$Co_3(C_6Se_6)_2$	0.42	0.17	-192.56
$Ni_3(C_6Se_6)_2$	0.42	0.17	-188.05
$Cu_3(C_6Se_6)_2$	0.43	0.21	-181.52
$Ru_3(C_6Se_6)_2$	0.42	0.20	-197.65
$Rh_3(C_6Se_6)_2$	0.43	0.18	-193.17
$Pd_3(C_6Se_6)_2$	0.39	0.20	-187.32
$Ir_3(C_6Se_6)_2$	0.43	0.18	-197.97
$Pt_3(C_6Se_6)_2$	0.39	0.20	-191.27

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

$M_3(C_6Se_6)_2$	ΔG_{OH*} (eV)	ΔG_{O*} (eV)	ΔG_{OOH*} (eV)
$Mn_3(C_6Se_6)_2$	0.90	0.74	3.55
$Fe_3(C_6Se_6)_2$	0.62	1.52	4.18
$Co_3(C_6Se_6)_2$	1.09	2.25	3.99
$Ni_3(C_6Se_6)_2$	1.77	2.27	4.70
$Cu_3(C_6Se_6)_2$	2.02	4.38	4.35
$Ru_3(C_6Se_6)_2$	-0.2	0.01	2.71
$Rh_3(C_6Se_6)_2$	0.94	2.11	3.87
$Pd_3(C_6Se_6)_2$	2.01	4.06	4.80
$Ir_3(C_6Se_6)_2$	0.91	1.80	3.77
$Pt_3(C_6Se_6)_2$	1.98	3.77	4.80

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}).

$M_3(C_6Se_6)_2$	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η^{OER} (V)	η^{ORR} (V)
$Mn_3(C_6Se_6)_2$	1.37	2.81	-0.15	-0.90	1.58	1.38
$Fe_3(C_6Se_6)_2$	0.74	2.66	0.90	0.62	1.43	0.61
$Co_3(C_6Se_6)_2$	0.93	1.74	1.16	1.09	0.51	0.30
$Ni_3(C_6Se_6)_2$	0.22	2.43	0.50	1.77	1.2	1.01
$Cu_3(C_6Se_6)_2$	0.57	-0.03	2.36	2.02	1.13	1.26
$Ru_3(C_6Se_6)_2$	2.18	2.73	0.22	-0.20	1.5	1.43
$Rh_3(C_6Se_6)_2$	1.05	1.76	1.18	0.94	0.53	0.29
$Pd_3(C_6Se_6)_2$	0.12	0.74	2.04	2.01	0.81	1.11
$Ir_3(C_6Se_6)_2$	1.15	1.97	0.89	0.91	0.74	0.34
$Pt_3(C_6Se_6)_2$	0.12	1.03	1.79	1.98	0.75	1.11

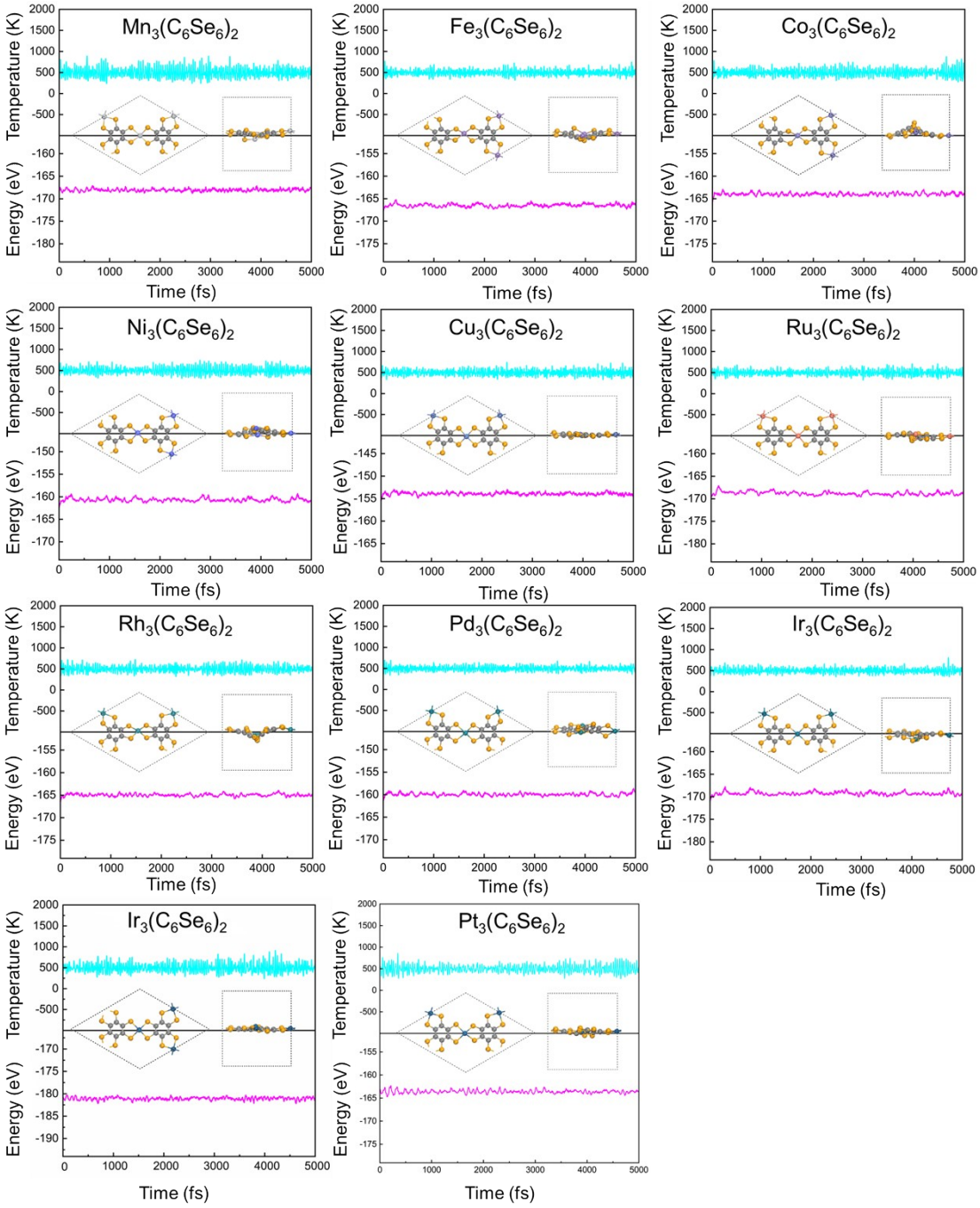

Figure S1. Energy and temperature variations of eleven 2D MOFs in AIMD simulations and their structural snapshots (top and side views) at 5ps.

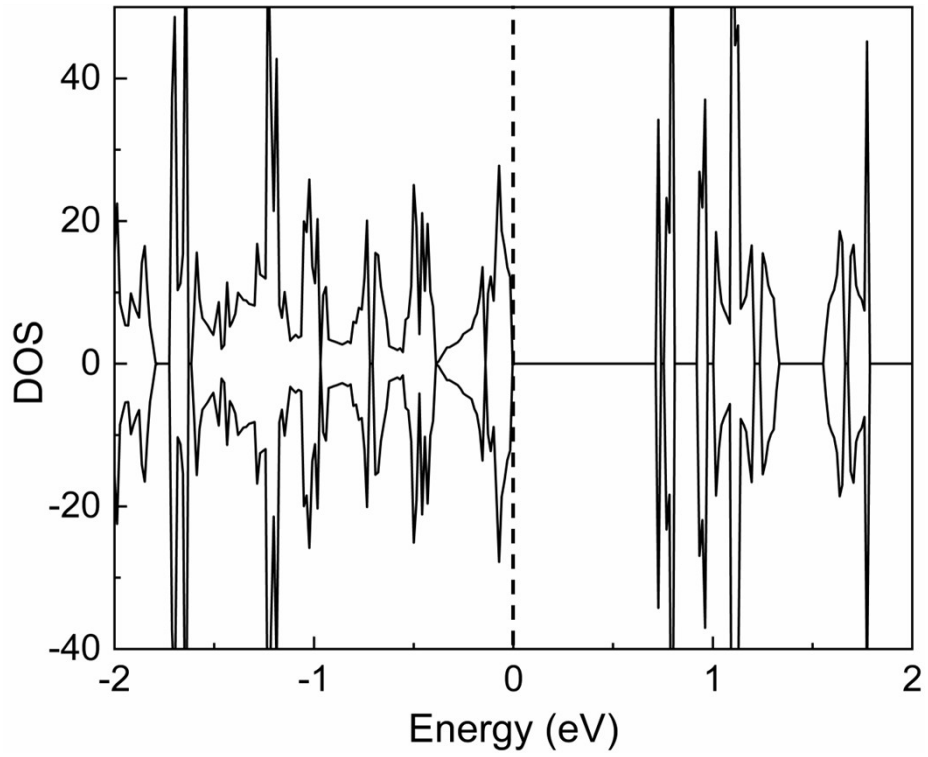

Figure S2. The density of states diagram for $Ti_3(C_6Se_6)_2$.

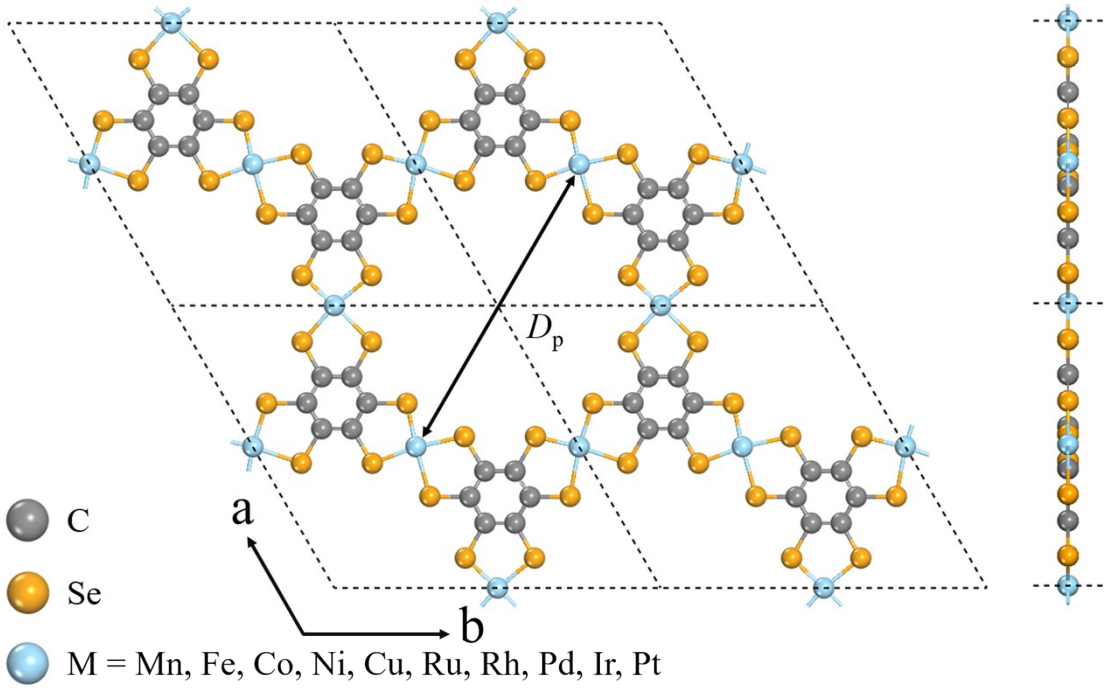

Figure S3. Top and side view of $M_3(C_6Se_6)_2$.

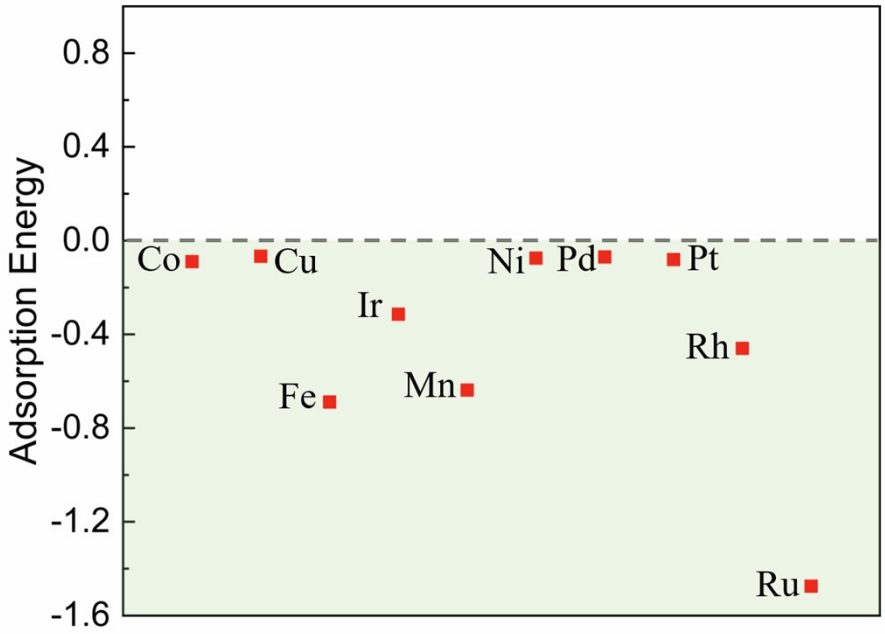

Figure S4. O_2 adsorption energy on 2D $M_3(C_6Se_6)_2$.

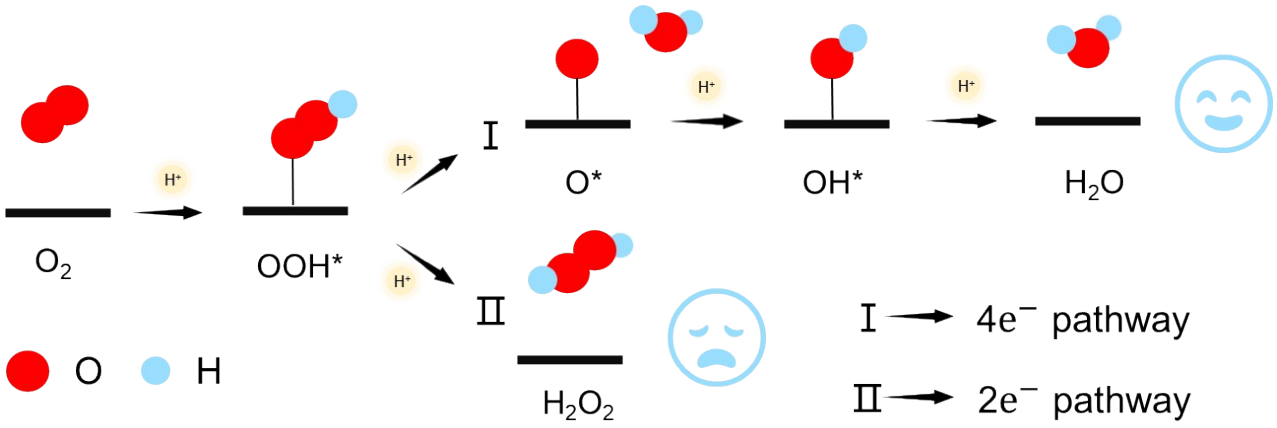

Fig S5. Schematic diagram of the reaction pathway for O_2 reduction.

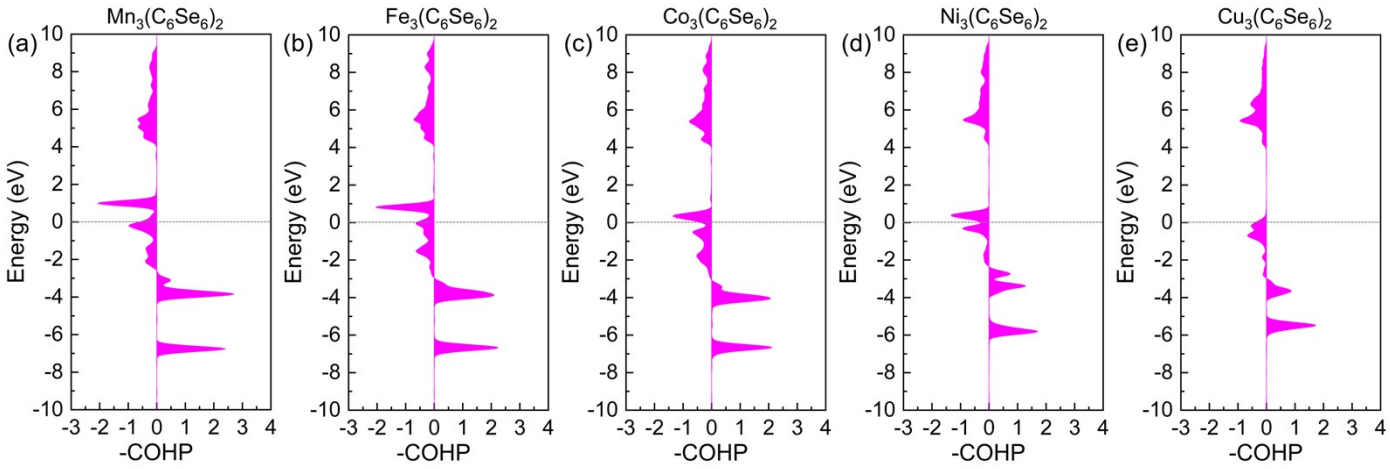

Figure S6. (a)-(e) pCOHP between 4d TM centers (from Mn to Cu) and OH intermediate. The right and left sides represent the bonding and antibonding contributions, respectively.