Supporting Information

Two-Dimensional Metal-Organic TMTAP Monolayers as a Promising Class of Monoatomic Electrocatalysts for Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution Reactions

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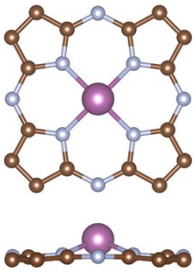
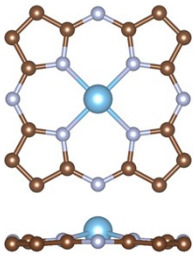
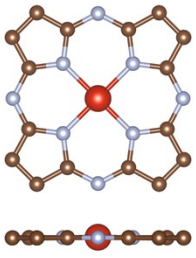
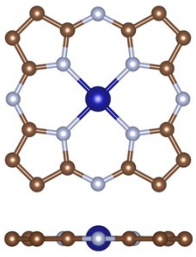
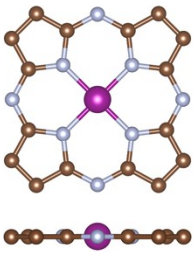
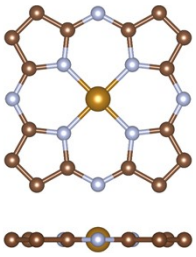
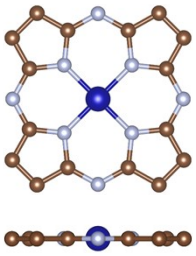
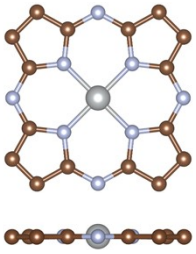
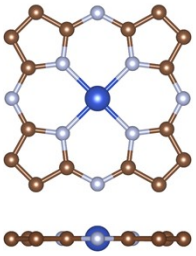
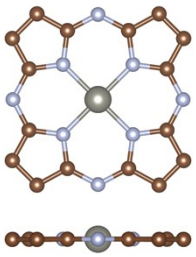
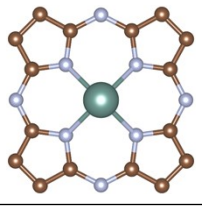
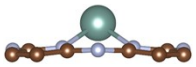
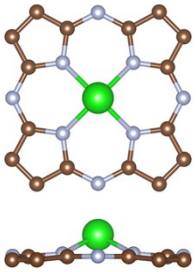
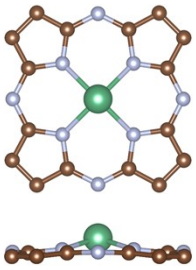
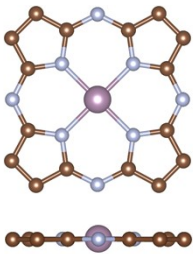
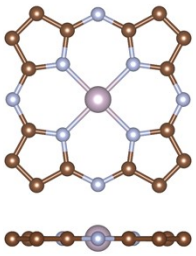
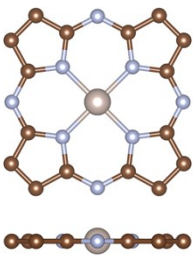
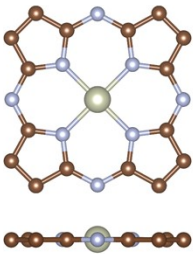
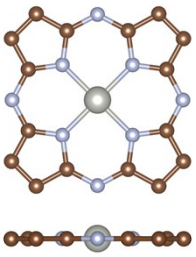
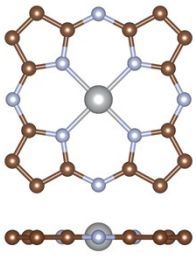
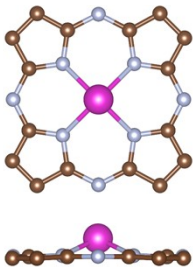
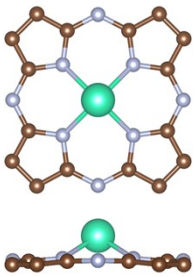
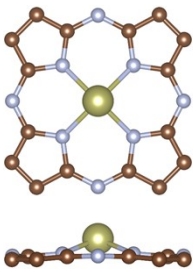
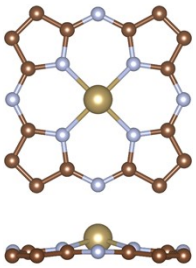
Table S1. The relaxed geometric structure, lattice parameter (Å), TM–N bond length (Å), magnetic moment of TM atom (μ_B), and total magnetic moment (μ_B) for 30 TMTAP monolayers.

TMTAP	Geometric structure	Lattice parameter	TM–N bond length	Magnetic moment of TM	Total magnetic moment
Sc		8.34	2.11	0.36	0.59
Ti		8.34	2.04	1.39	1.63
V		8.33	1.99	2.51	2.68
Cr		8.32	1.99	3.49	3.84

Mn		8.29	1.96	2.73	3.03
Fe		8.27	1.93	1.72	2.00
Co		8.24	1.91	0.55	0.63
Ni		8.26	1.93	0.16	0.21
Cu		8.30	1.98	0.43	0.68
Zn		8.33	2.00	0	0
Y		8.34	2.25	0.19	0.57

					
Zr		8.34	2.16	0.81	1.58
Nb		8.35	2.08	1.62	2.54
Mo		8.38	2.05	2.94	3.64
Tc		8.35	2.02	2.20	2.74
Ru		8.31	1.98	0.32	0.34
Rh		8.30	1.98	0	0

Pd		8.31	1.99	0	0
Ag		8.38	2.06	0.42	0.89
Cd		8.37	2.16	0	0
Lu		8.34	2.21	0.15	0.60
Hf		8.35	2.11	0.67	1.11
Ta		8.35	2.07	1.77	2.23

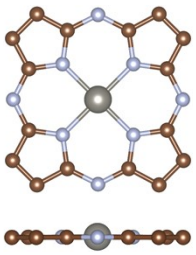
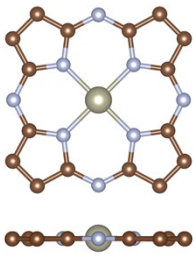
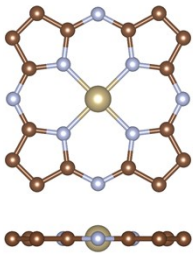
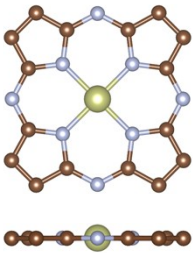
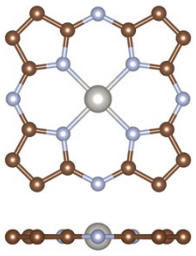
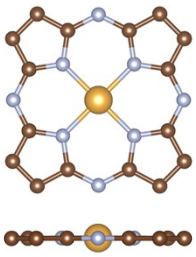
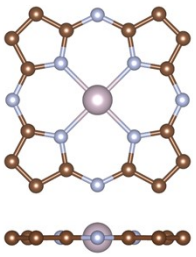
W		8.38	2.04	2.73	3.58
Re		8.36	2.02	1.94	2.64
Os		8.31	1.98	0	0
Ir		8.31	1.98	0	0
Pt		8.32	2.00	0	0
Au		8.37	2.05	0.31	0.64
Hg		8.45	2.13	0	0

Table S2. Calculated binding energies (E_b), cohesive energies ($E_c^{calc.}$), cluster energies ($E_{clus} = E_b + E_c$), and dissolution potentials of TM atoms (U_{diss}), number of transferred electrons during the dissolution (n). For comparison, the experimental cohesive energies ($E_c^{exp.}$) and standard dissolution potential (U_{diss}^{o}) of bulk metal are also listed.

TM	E_b (eV)	$E_c^{exp.}$ [a] (eV)	$E_c^{calc.}$ (eV)	E_{clus} (eV)	n	U_{diss}^{o} [b] (V)	U_{diss} (V)
Sc	–8.76	3.90	4.36	–4.40	3	–2.08	–0.61
Ti	–9.13	4.90	5.5	–3.63	2	–1.63	0.19
V	–8.50	5.30	5.4	–3.10	2	–1.18	0.37
Cr	–7.34	4.10	4.05	–3.29	2	–0.91	0.73
Mn	–6.82	2.90	3.29	–3.53	2	–1.19	0.57
Fe	–7.52	4.30	4.63	–2.89	2	–0.45	0.99
Co	–8.12	4.40	5.09	–3.03	2	–0.28	1.23
Ni	–7.44	4.40	4.74	–2.70	2	–0.26	1.09
Cu	–5.38	3.50	3.49	–1.89	2	0.34	1.29
Zn	–3.98	1.40	1.17	–2.81	2	–0.76	0.65
Y	–8.53	4.40	4.28	–4.25	3	–2.37	–0.95
Zr	–9.31	6.30	6.27	–3.04	4	–1.45	–0.69
Nb	–8.61	7.60	7.02	–1.59	3	–1.10	–0.57
Mo	–7.30	6.80	6.36	–0.94	3	–0.20	0.11
Tc	–8.06	6.90	7.07	–0.99	2	0.30	0.79
Ru	–8.47	6.70	7.03	–1.44	2	0.46	1.18
Rh	–8.33	5.80	5.98	–2.35	2	0.60	1.77
Pd	–6.12	3.90	3.74	–2.38	2	0.95	2.14
Ag	–3.08	3.00	2.82	–0.26	1	0.80	1.06
Cd	–2.21	1.20	0.94	–1.27	2	–0.40	0.23
Lu	–8.38	4.43	4.32	–4.06	3	–2.28	–0.93
Hf	–9.75	6.40	6.79	–2.96	4	–1.55	–0.81
Ta	–9.68	8.10	8.47	–1.21	3	-0.60	–0.20
W	–8.61	8.90	8.49	–0.12	3	0.10	0.14

Re	–7.76	8.00	7.82	0.06	3	0.30	0.28
Os	–9.06	8.20	8.43	–0.63	8	0.84	0.92
Ir	–9.42	6.90	7.56	–1.86	3	1.16	1.78
Pt	–8.20	5.80	5.72	–2.48	2	1.18	2.42
Au	–3.44	3.80	3.46	0.02	3	1.50	1.49
Hg	–0.26	0.70	0.58	0.32	2	0.85	0.69

[a)]Experimental cohesive energy values are taken from ref. 1 [1].

[b)]Standard dissolution potential values are taken from ref. 2 [2].

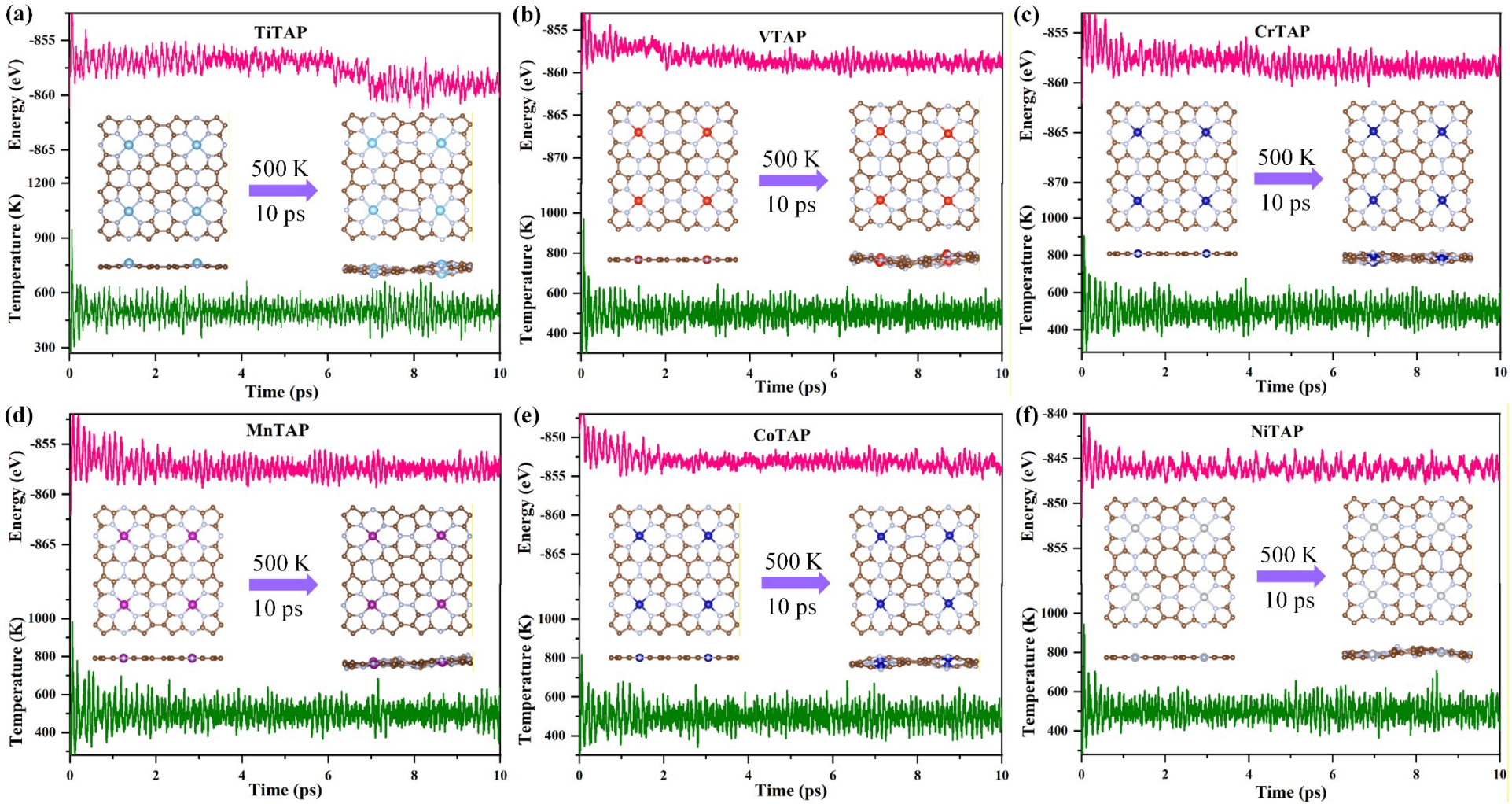


Figure S1. Evolution of the temperatures and total energies of AIMD simulations for (a) TiTAP, (b) VTAP, (c) CrTAP, (d) MnTAP, (e) CoTAP, and (f) NiTAP at 500 K for 10 ps with a time step of 2 fs. The illustrations are snapshots of the initial and final frame during AIMD simulations.

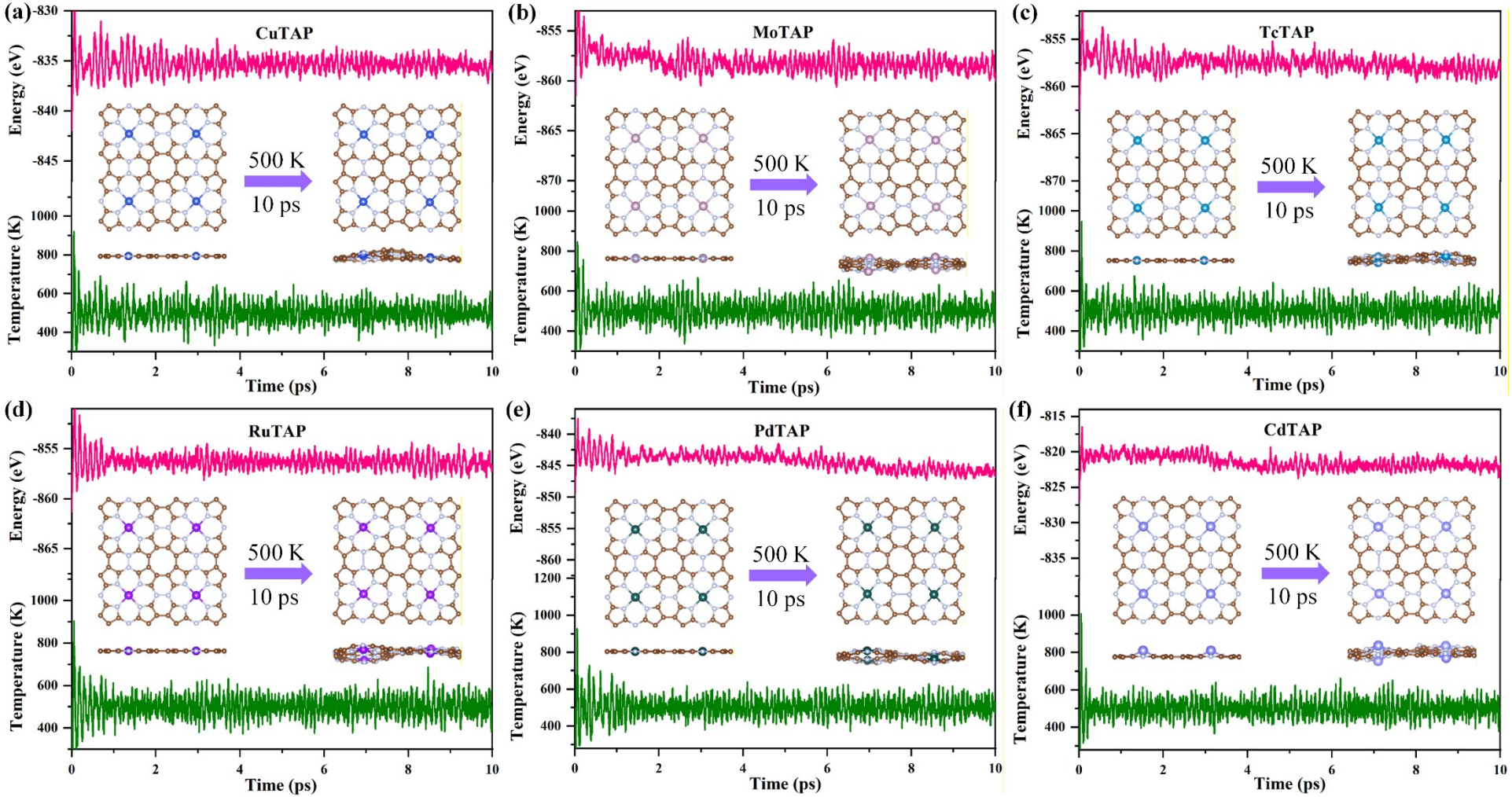


Figure S2. Evolution of the temperatures and total energies of AIMD simulations for(a) CuTAP, (b) MoTAP, (c) TcTAP, (d) RuTAP, (e) PdTAP, and (f) CdTAP at 500 K for 10 ps with a time step of 2 fs. The illustrations are snapshots of the initial and final frame during AIMD simulations.

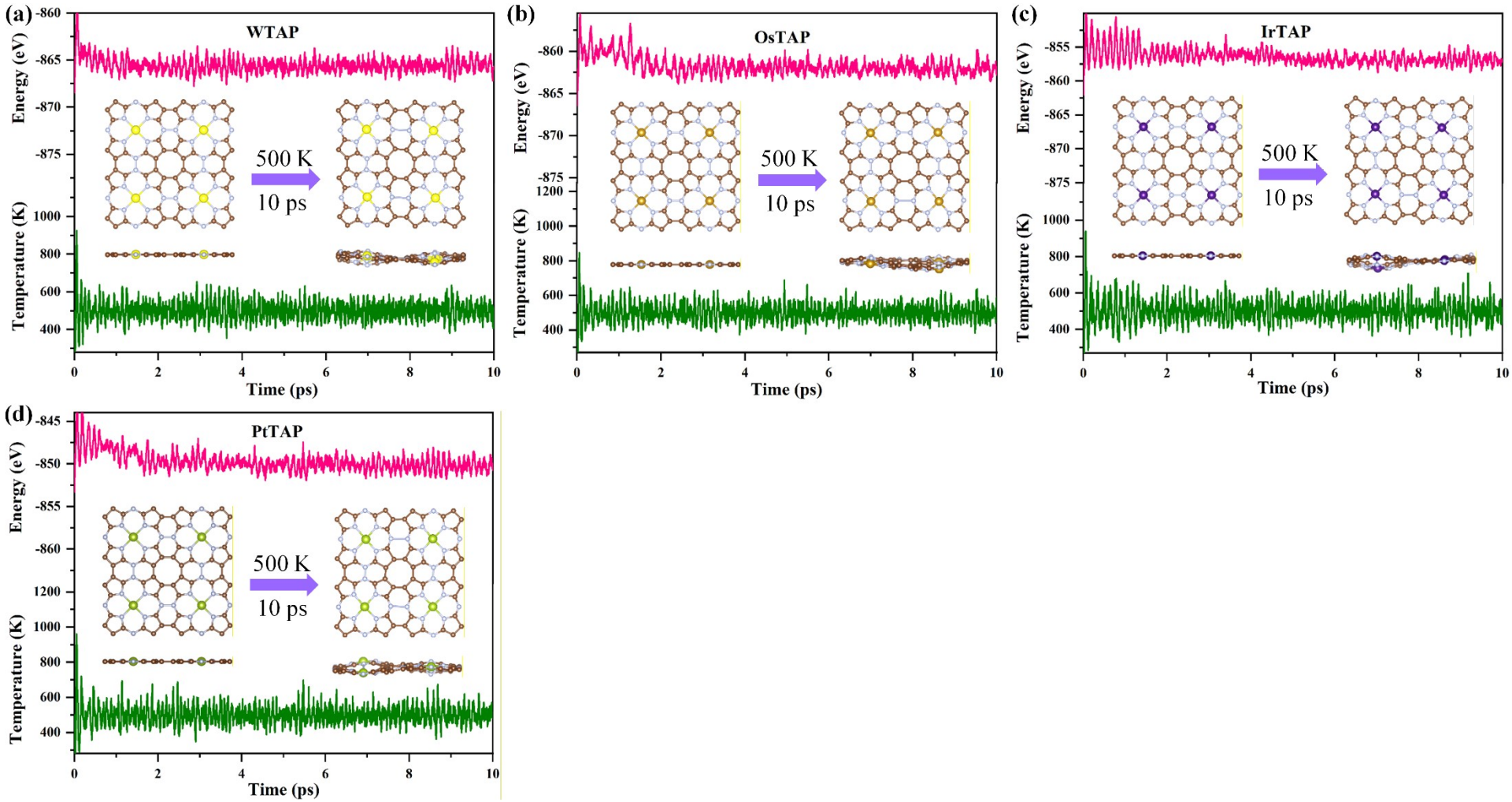


Figure S3. Evolution of the temperatures and total energies of AIMD simulations for(a) WTAP, (b) ReTAP, (c) OsTAP, (d) IrTAP, and (e) PtTAP at 500 K for 10 ps with a time step of 2 fs. The illustrations are snapshots of the initial and final frame during AIMD simulations.

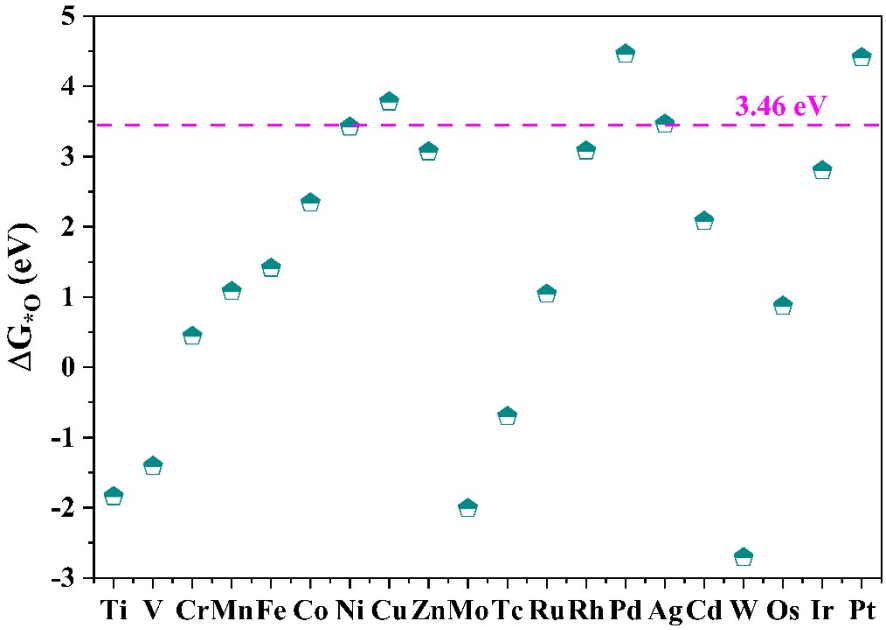


Figure S4. Calculated ΔG_{*O} values of the 20 stable SACs. The horizontal dotted line is $\Delta G_{*O} = \Delta G_{H_2O_2} - \Delta G_{H_2O} = 3.46$ eV.

Table S3. Summary Table of Benchmarking SACs.

Catalyst	Support	Reaction	Overpotential (V)	Literature
MnPor	metalloporphyrinoid (MPor)	ORR	0.56	*Rare Met.* 2025, *44*, 3920–3933
Fe-Pc	Phthalocyanine (Pc)	ORR	0.45	*Int. J. Hydrogen Energy* 2024, *88,* 850-857
$Mn_3(HHTP)_2$	2,3,6,7,10,11-hexahydroxytriphenylene (HHTP)	ORR/OER	0.44/0.53	*J. Phys. Chem. C* 2025, *129* (31), 14002–14010
$Rh_3(HADQ)_2$	2,3,6,7,10,11-hexamine ($C_{12}H_{12}N_{12}$) pyrazine quinoxaline (HADQ)	ORR/OER	0.31/0.31	*Langmuir* 2025, *41* (1), 745–754
Cu@g-C_4N_3	g-C_4N_3	ORR	0.70	*ACS Appl. Mater. Interfaces* 2024, *16* (14), 17617–17625
Co@C_3N_2	C_3N_2	HER	0.12	*New J. Chem.* 2025, *49,* 1672-1685
$Mn_{12}C_{12}$	carbon layer	HER	0.09	*Int. J. Hydrogen Energy* 2025, *144,* 1043-1050
ZnTAP	TAP	ORR	0.43	*This work*
RhTAP	TAP	OER	0.58	*This work*
CdTAP	TAP	HER	0.08	*This work*

Table S4. The adsorption free energies of *OOH (ΔG_{*OOH}), *O (ΔG_{*O}), and *OH (ΔG_{*OH}) on TMTAP.

TMTAP	ΔG_{*OOH} (eV)	ΔG_{*O} (eV)	ΔG_{*OH} (eV)
Ti	1.91	–1.84	–1.66
V	1.22	–1.41	–0.54
Cr	3.70	0.44	0.48
Mn	3.85	1.08	0.66
Fe	3.80	1.41	0.76
Co	4.40	2.34	1.50
Ni	4.94	3.42	1.95
Cu	4.85	3.78	2.00
Zn	4.02	3.07	0.80
Mo	–0.34	–2.01	–0.46
Tc	1.78	–0.70	–0.02
Ru	3.54	1.04	0.79
Rh	4.89	3.08	1.78
Pd	5.13	4.46	2.46
Ag	4.55	3.46	7.42
Cd	2.91	2.08	–0.36
W	–1.58	–2.71	–0.98
Re	0.84	–1.45	–0.30
Os	3.33	0.87	0.95
Ir	4.88	2.80	1.80
Pt	5.13	4.41	2.46

Table S5. The bond length of adsorbed O_2 molecule (Å), magnetic moment of TM atom (μ_B) before and after O_2 adsorption for Fe-, Zn-, Rh-, and AgTAP catalysts.

TMTAP	Bond length of adsorbed O_2 molecule	Magnetic moment of TM atom before O_2 adsorption	Magnetic moment of TM atom after O_2 adsorption
Fe	1.29	1.72	1.87
Zn	1.30	0	0.01
Rh	1.27	0	0.32
Ag	1.27	0.42	0.12

Table S6. Calculated Bader charges on TM and O atoms, magnetic moment of O atom (μ_B) after O_2 adsorption for Fe-, Zn-, Rh-, Ag-, Ti-, Mo-, and W-TAP catalysts.

TMTAP	TM	O	Magnetic moment of O
Fe	–1.13 |e|	+0.22 |e|	0.63
Zn	–1.26 |e|	+0.25 |e|	0.56
Rh	–0.77 |e|	+0.15 |e|	0.70
Ag	–0.69 |e|	+0.13 |e|	0.68
Ti	–1.65 |e|	+0.48 |e|	0.01
Mo	–1.54 |e|	+0.47 |e|	0
W	–1.76 |e|	+0.49 |e|	0.01

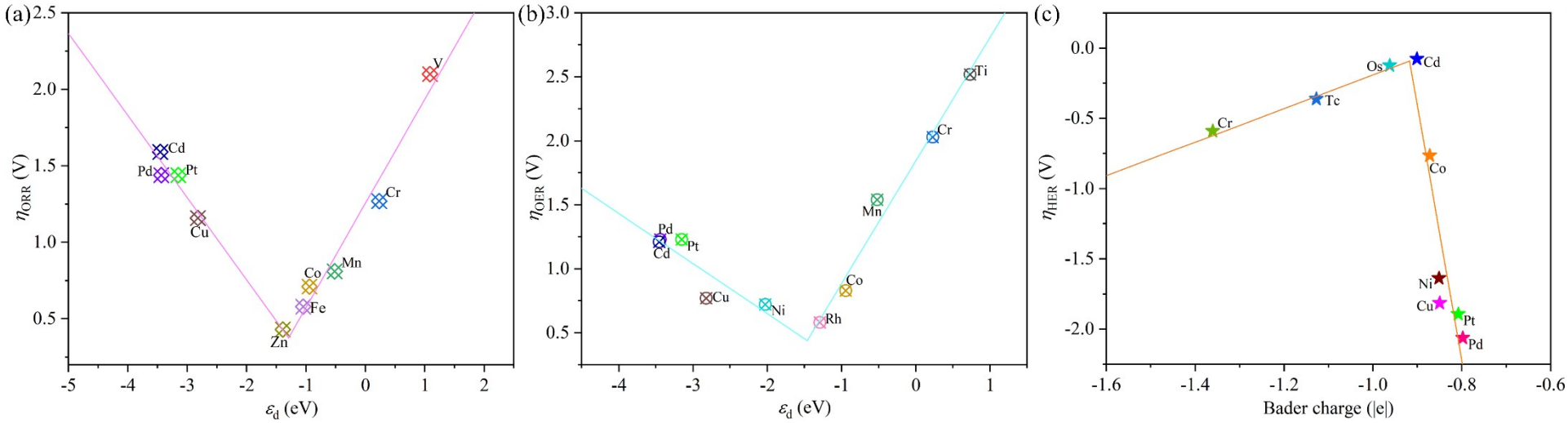


Figure S5. Volcano plot of the η_{ORR} as a function of the d-band center (ε_d). (b) Volcano plot of the η_{OER} as a function of the d-band center (ε_d). (c) Volcano plot of the η_{HER} as a function of the Bader charge.

References

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