Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Multi-functional photocatalytic activity of transition-metal mtetraaza[14]annulene frameworks

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Fig. S1. The evolution of the total energies of the TM-TAA MOF monolayers at temperature of 300 K during the ab initio molecular dynamics simulations within 5000 fs. The insets are monolayers at the end of MD simulations.

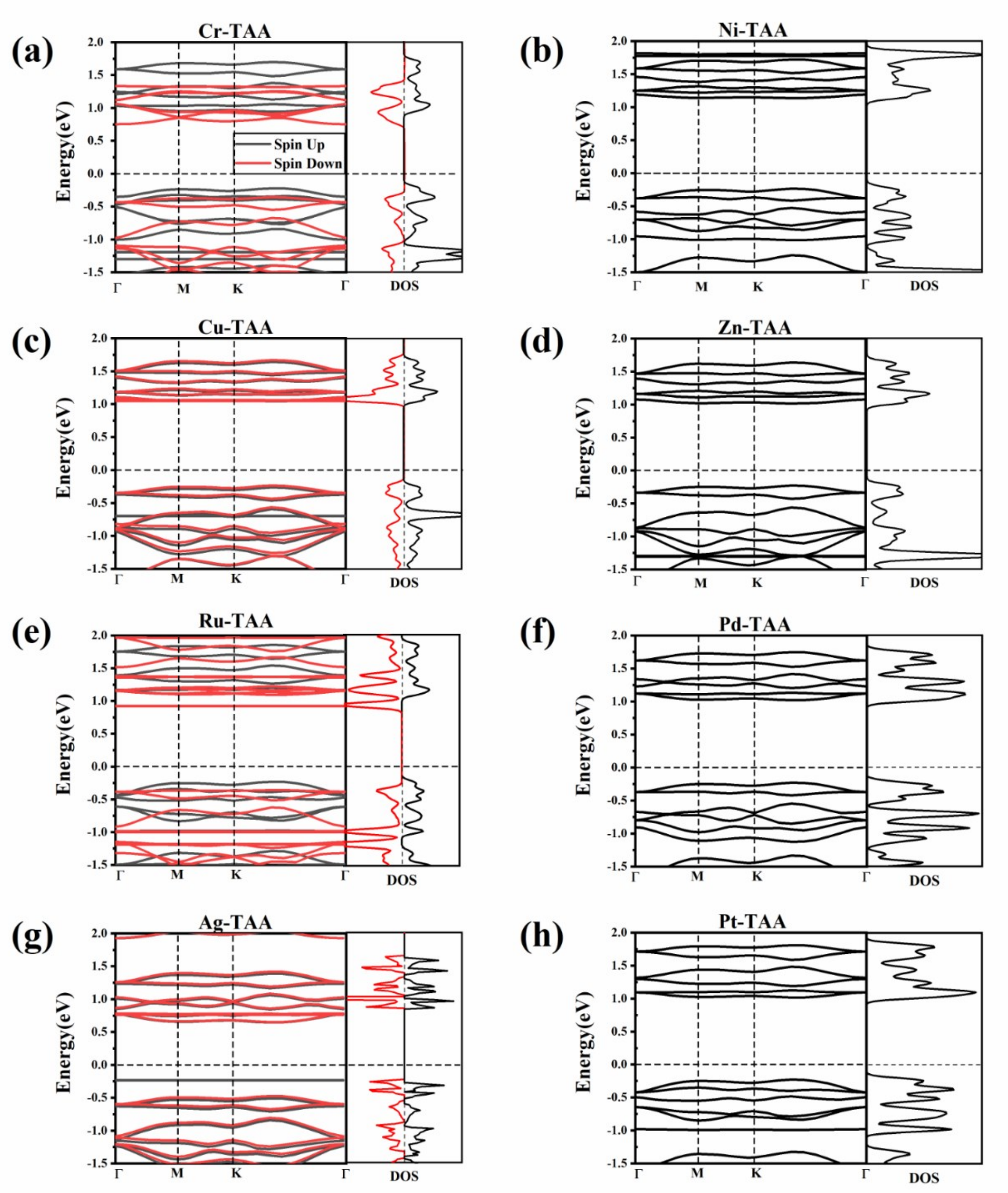

Fig. S2. Electronic band structures of the TM-TAA MOFs with TM = Ni, Cu, Zn, Ru, Rh, Pd, Cr, Pt. The energy at the Fermi level was set to zero.

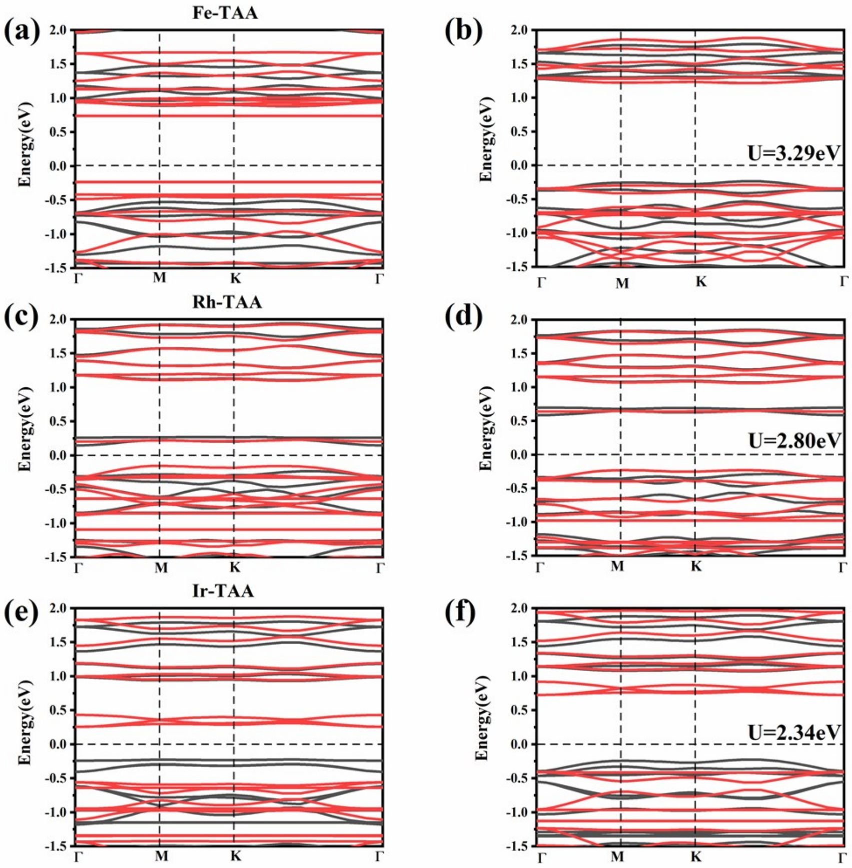

Fig.S3. The band structures with and without U of Fe-, Rh- and Ir-TAA MOF monolayers. The energy at the Fermi level was set to zero.

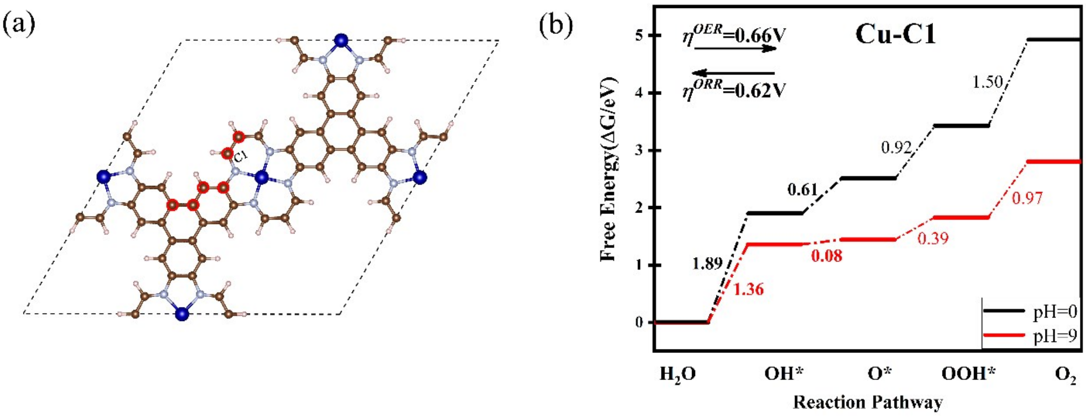

Fig. S4. (a) The different adsorption sites are labeled in TM-TAA MOF monolayer. (b) Free energy diagram for the OER and ORR pathway on C1 site of Cu-TAA MOF. The elementary reaction with ΔG in bold represent the potential-determining step for OER and ORR.

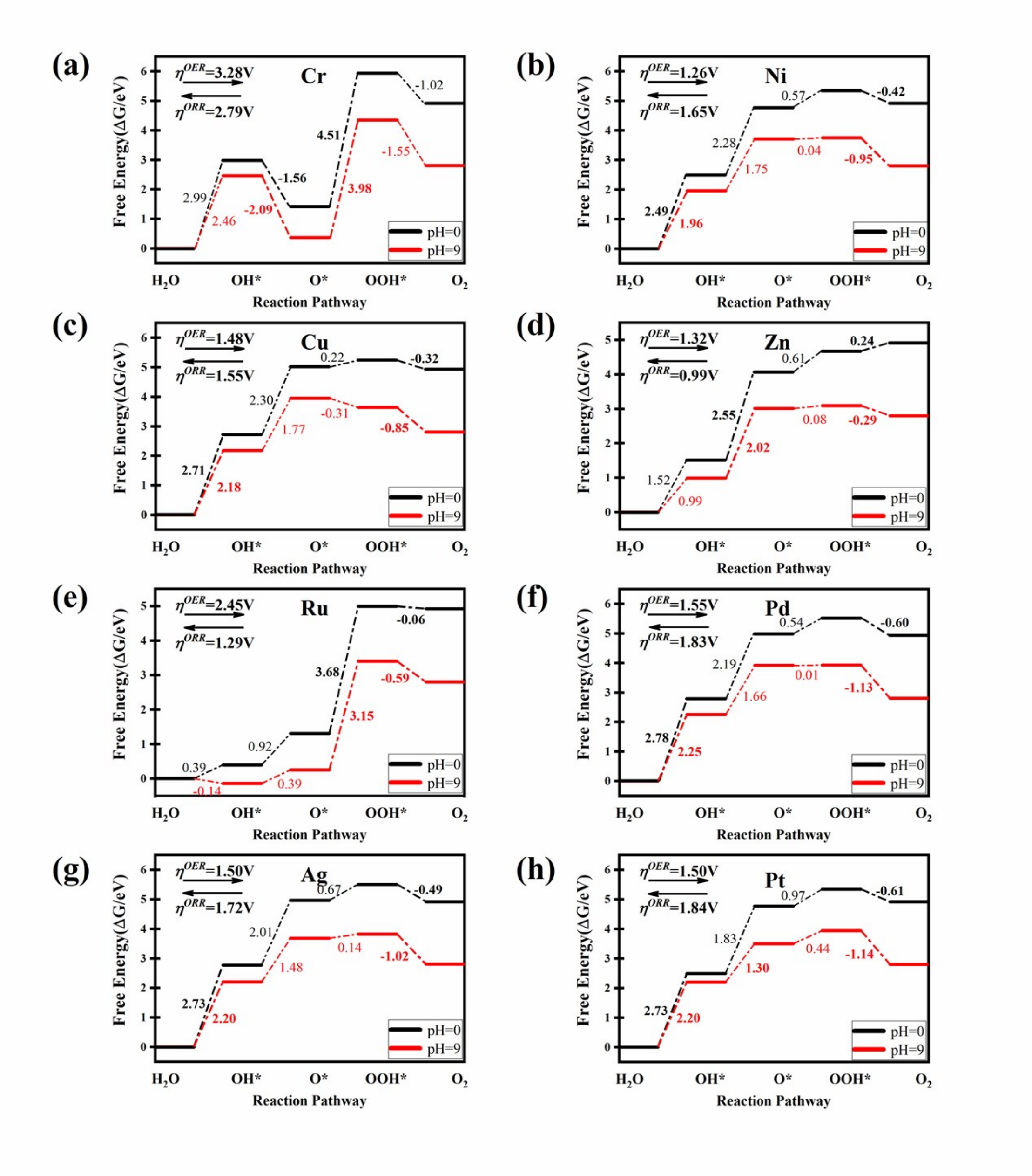

Fig. S5. Free energy figures for the OER and ORR process on TM site of (a) Cr-TAA, (b) Ni-TAA, (c) Cu-TAA, (d) Zn-TAA, (e) Ru-TAA, (f) Pd-TAA, (g) Ag-TAA and (h)Pt-TAA MOF at zero potential (U = 0), where the elementary reaction with ΔG in bold represent the potential-determining step for OER and ORR.

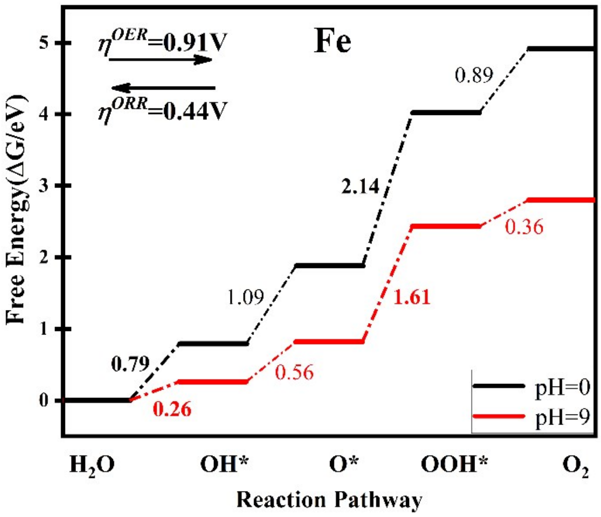

Fig. S6. Free energy diagram of Fe-TAA MOF obtained by involving solvent effect. The elementary reaction with ΔG in bold represent the potential-determining step for OER and ORR.

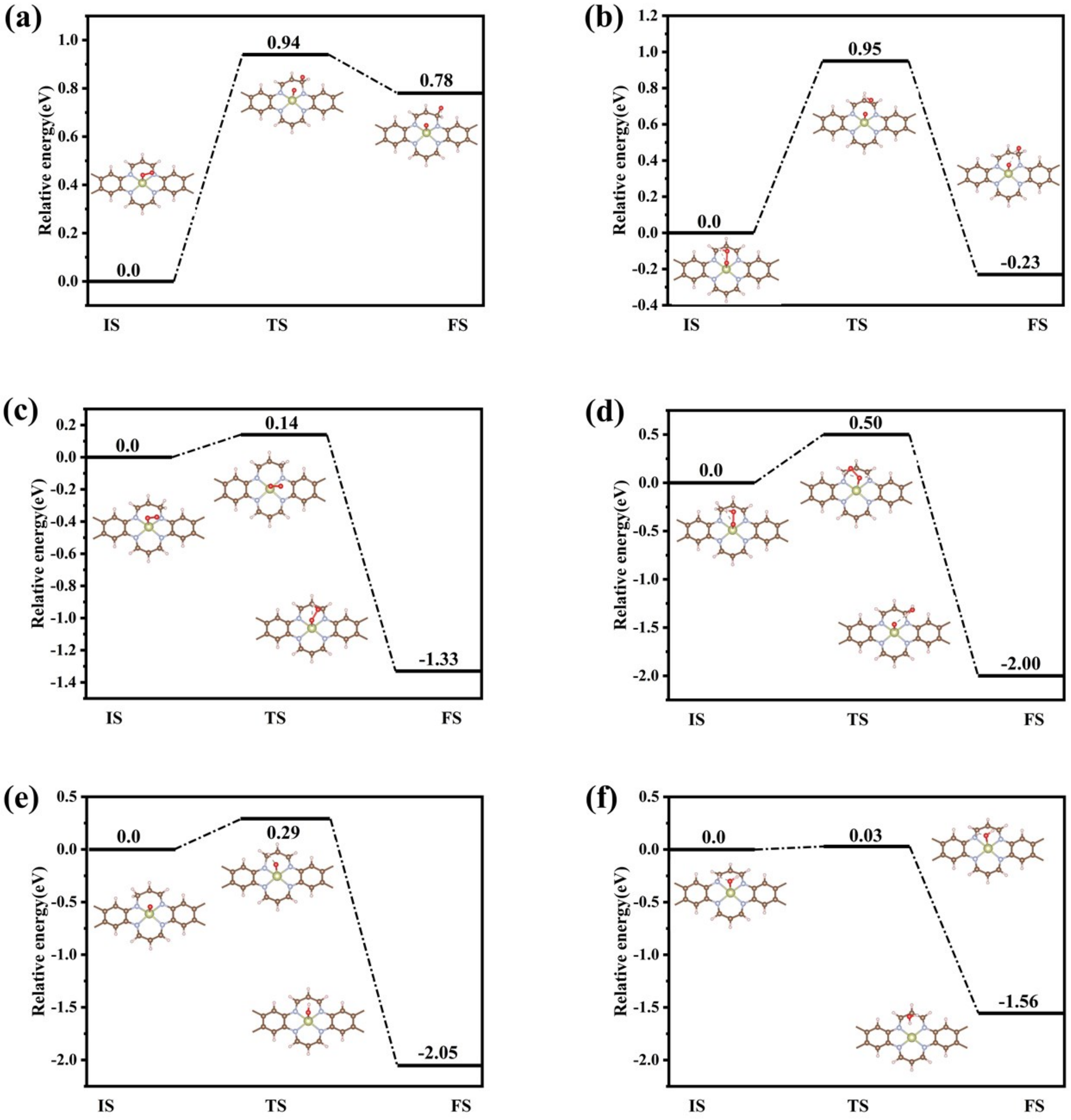

Fig.S7. The structures of the initial state (IS), transition state (TS), final state (FS) and potential energy profile for (a) $O_2* \rightarrow O* + O*$, (b) $OOH* \rightarrow OH* + O*$, (c) $O_2* + H^+ \rightarrow OOH*$, (d) $OOH*+H^+ \rightarrow O*+H_2O$, (e) $O*+H^+ \rightarrow OH*$ and (f) $OH*+H^+ \rightarrow H_2O*$ on Ir-TAA MOF.

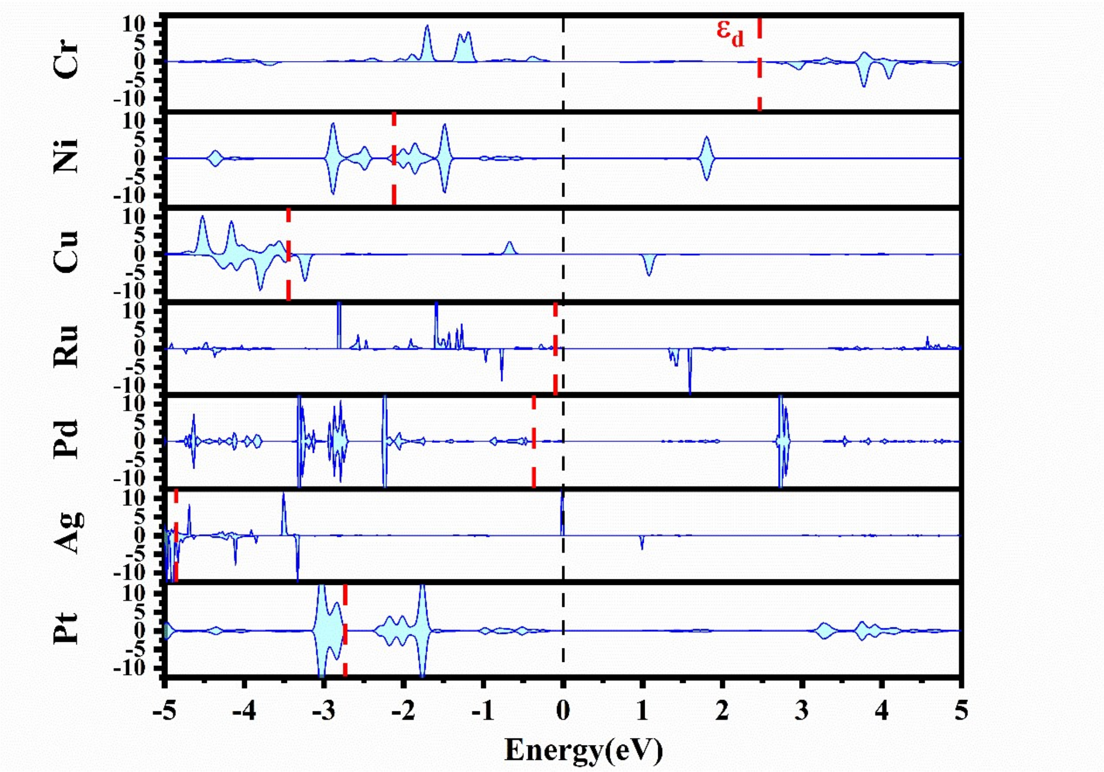

Fig. S8. Projected density of states (PDOS) for the d-orbital of single-TM-atom in 2D TM-TAA MOFs with M=Cr, Ni, Cu, Ru, Pd, Ag, Pt. The vertical dash dotted lines correspond to the Fermi level which is shifted to zero.

Table S1. The values of U-J parameters (eV) for DFT/PBE+U calculations

TM	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ru	Rh	Pd	Ag	Ir	Pt
U-J	2.79	3.06	3.29	3.42	3.40	3.87	4.12	2.79	2.80	3.35	2.79	2.34	2.41

Table S2. Energy difference (E_{diff}), experimental reversible potential U^0 for the metal redox reaction, number of electrons (n) involved in the dissolution for the pure metals, and computed dissolution potentials (U_{diss} / (V *v.s.* SHE)) of TM-TAA MOFs.

TM	E_{diss}	U^0	n	U_{diss}
Cr	-4.04	-0.19	2	1.83
Mn	1.84	-1.19	2	-1.89
Fe	-4.87	-0.45	2	1.99
Co	-4.44	-0.28	2	1.94
Ni	-4.87	-0.26	2	2.18
Cu	-0.92	0.34	2	0.80
Zn	-4.33	-0.76	2	1.41
Ru	-3.52	0.46	2	2.22
Rh	1.75	0.60	2	0.13
Pd	0.11	0.95	2	0.90
Ag	1.03	0.80	1	1.83
Ir	0.36	1.16	3	1.04
Pt	-0.53	1.18	2	1.45

Table S3. The values of *Ue*, *Uh*, $|\Delta G_{H*}|$, and largest free energy change of OER at pH =9.

System	ΔG_{max} of OER(eV)	U_h (eV)	$\lvert\Delta G_{H*}\rvert$ (eV)	*Ue* (eV)
Cr-TAA	3.98	1.00	1.40	1.08
Mn-TAA	2.17	0.35	0.68	0.90
Fe-TAA	1.15	1.08	1.42	1.24
Co-TAA	1.09	1.10	1.15	1.18
Ni-TAA	1.96	1.07	1.99	1.14
Cu-TAA	2.18	0.99	1.33	1.11
Zn-TAA	2.02	0.93	1.84	1.11
Ru-TAA	3.15	1.12	0.33	1.16
Rh-TAA	1.10	1.07	0.32	0.36
Pd-TAA	2.25	1.07	2.03	1.06
Ag-TAA	2.20	0.96	0.27	1.07
Ir-TAA	1.15	1.28	0.17	0.97
Pt-TAA	2.20	1.18	2.16	0.98

Table S4. The values of *Ue*, *Uh*, $|\Delta G_{H*}|$, and largest free energy change of OER at pH =12

System	ΔG_{max} of OER(eV)	U_h (eV)	$\lvert\Delta G_{H*}\rvert$ (eV)	*Ue* (eV)
Cr-TAA	3.80	1.18	1.58	0.90
Mn-TAA	1.99	0.53	0.86	0.72
Fe-TAA	0.97	1.26	1.60	1.06
Co-TAA	0.91	1.28	1.18	1.00
Ni-TAA	1.78	1.25	1.39	0.96
Cu-TAA	2.00	1.17	1.51	0.93
Zn-TAA	1.84	1.11	2.02	0.93
Ru-TAA	2.97	1.30	0.51	0.98
Rh-TAA	0.92	1.25	0.14	0.18
Pd-TAA	2.07	1.25	2.21	0.88
Ag-TAA	2.02	1.24	0.45	0.89
Ir-TAA	0.97	1.46	0.35	0.79
Pt-TAA	2.02	1.36	2.34	0.80

The strategy of free energy calculation for OER and HER

Considering the effect of electrode potential (U) and pH, the free energy change for OER electrochemical steps can be expressed as:

$$\Delta G_1 = G_{OH*}+1/2G_{H2} - G_{H2O} - G^* - eU - 0.059 \times pH \quad (S1)$$

$$\Delta G_2 = G_{O*}+1/2G_{H2} - G_{OH*} - eU - 0.059 \times pH \quad (S2)$$

$$\Delta G_3 = G_{OOH*}+1/2G_{H2} - G_{H2O} - G_{O*} - eU - 0.059 \times pH \quad (S3)$$

$$\Delta G_4 = G^*+1/2G_{H2} + G_{O2} - G_{OOH*} - eU - 0.059 \times pH \quad (S4)$$

The free energy change for HER electrochemical step can be expressed as:

$$\Delta G = G_{H*} - 1/2G_{H2} + G^* - eU + 0.059 \times pH \quad (S5)$$

The definition of the d band center of TM atoms

For the calculation of the band center of the d orbital of single-TM-atom in TM-TAA-MOFs, the following expression is used:

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} \left(E \times \rho_d(E)\right) dE}{\int_{-\infty}^{+\infty} \rho_d(E) dE}$$

where ρ_d is the density of states projected onto single-TM-atom d orbital.

The strategy of dual volcano plots

Based on the linear relationship between ΔG_{OOH*}, ΔG_{OH*}, ΔG_{O*}:

$$\Delta G_{OOH*} = 0.72 \times \Delta G_{OH*} + 2.26 \text{ eV} \quad (S6)$$

$$\Delta G_{O*} = 1.53 \times \Delta G_{OH*} + 0.52 \text{ eV} \quad (S7)$$

Therefore, the overpotential (η) for the ORR process in the dual volcano plot obeys the following equations:

η = -$\Delta G_{OH*}/e$ + 0.70 V (ΔG_{OH*} < 0.31eV) (S8)

η = 0.72×$\Delta G_{OH*}/e$ + 0.16 V (0.31eV < ΔG_{OH*} < 13.33eV) (S9)

η = 0.81×$\Delta G_{OH*}/e$ – 1.04 V (ΔG_{OH*} > 13.33eV) (S10)

The overpotential (η) for the OER process are:

η = -0.81×$\Delta G_{OH*}/e$ + 1.04 V (ΔG_{OH*} < 0.91eV) (S11)

η = 0.53×$\Delta G_{OH*}/e$ – 0.18eV (0.91eV < ΔG_{OH*} < 1.11eV) (S12)

η = $\Delta G_{OH*}/e$ – 0.70eV (ΔG_{OH*} > 1.11eV) (S13)

Computational method of absorption coefficient

To investigate the optical absorption properties of the Ir and Rh-TAA-MOF monolayers, we calculated the absorption spectra by converting the complex dielectric function to the absorption coefficient as follows:

$$\alpha_{abs} = \sqrt{2}\left(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)\right)^{\frac{1}{2}}$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the frequency-dependent complex dielectric function, respectively. Taking into account the tensor nature of the dielectric function, absorption coefficient was averaged over three polarization vectors (along x, y, and z directions). The complex dielectric function was obtained from the DFT calculations with the HSE06 functional.