

Computational Insights into Two-Dimensional $M_3(\text{HHTP})_2$ Metal–Organic Frameworks as ORR/OER Electrocatalysts

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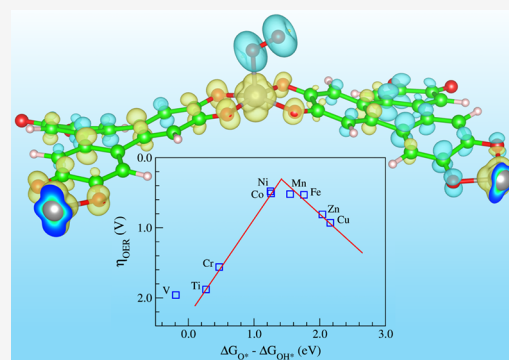


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ABSTRACT: Advancements in energy conversion technologies critically depend on the development of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) electrocatalysts that combine high activity, durability in acidic media, and cost-effectiveness. In this work, we employ first-principles calculations to investigate the mechanical strength, electrochemical stability, and catalytic performance of two-dimensional metal–organic frameworks (2D-MOFs), $M_3(\text{HHTP})_2$, with $M = \text{Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn}$, and $\text{HHTP} = 2,3,6,7,10,11\text{-hexahydroxytriphenylene}$. Our results show that these frameworks possess notable mechanical robustness, exhibiting both high thermal stability and structural flexibility. Furthermore, the electrochemical stability of $M_3(\text{HHTP})_2$ across the full pH range was analyzed using surface Pourbaix diagrams. The results indicate that only $\text{Mn}_3(\text{HHTP})_2$, $\text{Zn}_3(\text{HHTP})_2$, and $\text{Cu}_3(\text{HHTP})_2$ are predicted to be unstable under acidic conditions. Regarding catalytic activity, frameworks with $M = \text{Mn, Ni}$, and Zn exhibit ORR overpotentials ranging from 0.42 to 0.46 V. Similarly, frameworks with $M = \text{Mn, Fe, Co}$, and Ni show OER overpotentials between 0.48 and 0.53 V. These values outperform those theoretically obtained for state-of-the-art commercial electrocatalysts such as $\text{Pt}(111)$ for ORR and $\text{IrO}_2(110)$ for OER. Among the studied frameworks, $\text{Ni}_3(\text{HHTP})_2$ emerges as the most promising bifunctional electrocatalyst, offering a compelling combination of low overpotentials and high electrochemical stability. These findings suggest the viability of 2D-MOFs as effective bifunctional electrocatalysts for advanced energy conversion processes.



1. INTRODUCTION

Two-dimensional (2D) materials are receiving considerable attention as advanced electrocatalysts for key reactions involved in sustainable energy conversion and storage technologies.¹ Their atomically thin structures offer high surface-to-volume ratios and tunable electronic properties, enabling precise doping and defect engineering to introduce catalytically active sites. These features provide distinct advantages for promoting essential electrochemical processes such as the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER), which are integral to the operation of energy-conversion systems including fuel cells, metal-air batteries, and water electrolyzers.

Among the diverse range of 2D architectures, materials featuring metal cations coordinated by pyridinic nitrogen within a graphitic carbon matrix, denoted as G-MN_4 , have emerged as highly active bifunctional electrocatalysts for both ORR and OER.^{2,3} Within this category, G-FeN_4 ^{4–7} and G-MnN_4 ^{8–10} have demonstrated outstanding catalytic performance in O_2 and CO_2 reduction, achieving activity levels that rival those of platinum-based benchmarks such as Pt/C . Despite these promising attributes, G-MN_4 catalysts face key limitations, including low metal atom density and insufficient long-term durability.^{11,12} Notably, recent studies have high-

lighted issues such as carbon corrosion during ORR and the generation of reactive oxygen species, which can cause demetalation in Fe-N-C catalysts.¹³

On the other hand, two-dimensional metal–organic frameworks (2D-MOFs), assembled from metal ions and organic ligands, have shown significant potential as electrocatalysts.^{14–18} Their high chemical stability, accessible metal sites, and well-organized coordination structures enable the formation of uniformly distributed active centers with high density and adjustable electronic characteristics.¹⁹ The coordination modes between the metal and ligands are typically organized into three classes: metal-bis(dioxolane) (MO_4), metal-bis(diamine) (MN_4), and metal-bis(dithiolene) (MS_4).

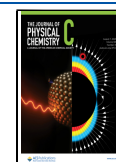
Some of the earliest reported catalytically active 2D-MOFs include nickel ions coordinated with 2,3,6,7,10,11-hexaiminotriphenylene (HITP) ligands $[\text{Ni}_3(\text{HITP})_2]$ ²⁰ and cobalt ions

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coordinated with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) ligands $[\text{Co}_3(\text{HHTP})_2]$.²¹ These materials exhibited high catalytic activity toward ORR and OER under alkaline conditions, respectively. Subsequent studies have further demonstrated the electrocatalytic potential of conductive 2D-MOFs,^{22–24} highlighting their promising applications across a wide range of electrochemical processes, including ORR,^{25,26} OER,^{27,28} HER,^{29,30} and the electroreduction of CO_2 ^{31,32} and N_2 .^{16,33}

In addition, numerous theoretical investigations have examined the stability, electronic structure, and catalytic activity of 2D-MOFs with various coordination environments, including MS_4 ,^{34–36} MN_4 ,^{37–42} MO_4 ,^{43–46} and mixed.^{47,48} These studies highlight that the nature of the metal–ligand coordination plays a critical role in modulating the electronic structure and adsorption energies of key reaction intermediates, which in turn governs the catalytic performance. Despite these advances, the electrochemical stability of 2D-MOFs under different operating conditions, an essential factor for practical catalytic applications, has received comparatively limited attention.

In this study, we employ density functional theory (DFT) calculations to investigate the electronic structure, electrochemical stability, and ORR/OER catalytic activity of 2D-MOFs $\text{M}_3(\text{HHTP})_2$, where $M = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$, and Zn . Particular emphasis is placed on the accuracy of the theoretical approach: a meta-GGA functional is used to capture a range of bonding scenarios, including both covalent and noncovalent interactions; the Hubbard correction is applied to address the self-interaction error of localized 3d electrons; and implicit solvation corrections are included to account for solvent effects on the reaction energetics. Electrochemical stability is evaluated through surface Pourbaix diagrams, while catalytic activity is assessed via the calculation of thermodynamic overpotentials. Our results reveal that frameworks incorporating metals with half-filled 3d orbitals exhibit significantly lower overpotentials compared to those of benchmark catalysts such as $\text{Pt}(111)$ and $\text{IrO}_2(110)$. Additionally, some $\text{M}_3(\text{HHTP})_2$ frameworks are found to be susceptible to degradation under acidic conditions.

2. COMPUTATIONAL DETAILS

Spin-polarized DFT calculations were carried out using the Vienna Ab initio Simulation Package (VASP 6.4).⁴⁹ The exchange-correlation energy was treated using the meta-GGA SCAN-rVV10 functional,⁵⁰ which accounts for intermediate-range van der Waals interactions and a more accurate varying electron density.⁵¹ To correct for self-interaction errors among the 3d electrons of transition metals, Hubbard (U) corrections were applied.⁵² The U values used for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn were 2.5, 2.5, 2.8, 3.1, 3.3, 3.3, 3.4, 3.5, and 3.5 eV, respectively, following a previous report.^{53,54} This correction plays a crucial role in accurately describing adsorbate-metal interactions, which are highly sensitive to the metal's d orbital.

The projector augmented wave (PAW) method was employed to describe the interaction between core and valence electrons.⁵⁵ All simulations were performed using a plane-wave energy cutoff of 400 eV, with Brillouin zone sampling conducted on a $2 \times 2 \times 1$ k-point mesh. Convergence tests for both the energy cutoff and k-point density were carried out to ensure the accuracy and reliability of the results, as demonstrated in Figure S1. The $\text{M}_3(\text{HHTP})_2$ crystalline

structure was modeled using a hexagonal unit cell containing 63 atoms, with a vacuum region of 15 Å along the z-direction. Full geometry optimization was carried out until the residual forces on all atoms were below 0.025 eV/Å. The electronic self-consistency criterion was set to a convergence threshold of 10^{-5} eV. Data analysis and visualization were performed using the VASPKIT⁵⁶ and VESTA⁵⁷ software packages, respectively.

The ORR/OER activity at the metal center of $\text{M}_3(\text{HHTP})_2$ was assessed through overpotential calculations based on the computational hydrogen electrode (CHE) approach developed by Nørskov et al.⁵⁸ This method evaluates the adsorption strength of key reaction intermediates (OH^* , O^* , and OOH^*) at the catalyst's active site by computing the adsorption free energy, given by $\Delta G = \Delta E_{\text{DFT}} + E_{\text{ZPE}} - T\Delta S$. Here, the zero-point energy (E_{ZPE}) and vibrational entropy term ($T\Delta S$) were obtained by calculating the vibrational frequencies of the adsorbed species, considering only their vibrational modes while keeping the catalyst surface fixed. Entropy values and vibrational data for gas-phase molecules were taken from the NIST database.⁵⁹

Corrections to the adsorbate binding energies were applied to account for solvent effects, particularly the hydrogen bonding interactions between the OH^* and OOH^* intermediates and surrounding H_2O molecules. These interactions typically weaken the adsorption strength by stabilizing the intermediates through solvation. The solvent influence on the binding energies of OH^* and OOH^* was evaluated individually for each $\text{M}_3(\text{HHTP})_2$ framework using a continuum dielectric model, as implemented in VASPsol.⁶⁰

The electrochemical stability of $\text{M}_3(\text{HHTP})_2$ was investigated under acidic and alkaline conditions using surface Pourbaix analysis. We employed the surface work function, defined as the energy required to remove an electron from the surface to the vacuum, as an estimate of the oxidation potential of the coordinated metal in the pristine structure. This approach provides detailed insight into the relationship between electrode potential and pH domains, offering a robust framework for evaluating electrochemical stability.⁴²

3. RESULTS AND DISCUSSIONS

3.1. Structural and Electronic Properties. Figure 1 presents the equilibrium geometry of $\text{M}_3(\text{HHTP})_2$ within a (2×2) surface unit cell, revealing a pore size of approximately 1.9 nm in diameter. This structure is formed by the metal centers each coordinated to four oxygen atoms from two HHTP ligands. The stability of the single-layer $\text{M}_3(\text{HHTP})_2$ was evaluated by calculating the formation energy, defined as the

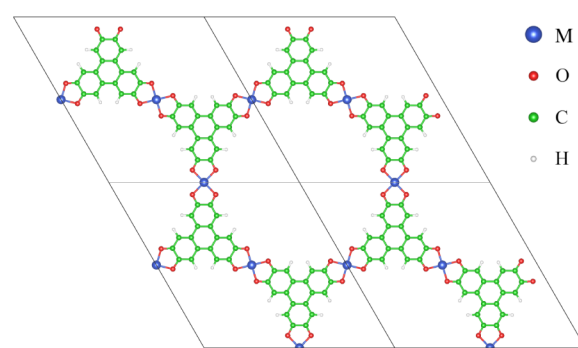


Figure 1. Atomic geometry of single-layer $\text{M}_3(\text{HHTP})_2$ in the hexagonal (2×2) surface unit-cell representation.

difference in total energy (E_t) between the pristine structure and one containing a metal vacancy, using the following equation:

$$E_f = E_t[M_3(\text{HHTP})_2] - E_t[M_2(\text{HHTP})_2] - \mu_M \quad (1)$$

where μ_M is the chemical potential of the metal, which is obtained from the energy per atom of the metal bulk phase. Our results indicate a strong metal–ligand interaction, with formation energy ranging from -5 to -10 eV. Additionally, we performed ab initio molecular dynamics (AIMD) simulations to further evaluate the thermal stability of the $M_3(\text{HHTP})_2$ structures. The simulations were conducted in the canonical ensemble (NVT) using the Nosé–Hoover thermostat at 400 K, over a total simulation time of 5 ps with a time step of 1 fs. Energy variation plots as a function of time for each $M_3(\text{HHTP})_2$ framework are shown in Figure S2, confirming that all structures remain stable at 400 K. This indicates a high degree of thermal stability and structural flexibility across the series. These results are consistent with thermogravimetric measurements of $\text{Cu}_3(\text{HHTP})_2$, which show stability up to 180 °C.⁶¹

To further probe thermal behavior, we also tested the stability of $\text{Ti}_3(\text{HHTP})_2$ and $\text{Zn}_3(\text{HHTP})_2$ structures with the highest and lowest calculated formation energies, respectively, by increasing the simulation temperature from 0 to 800 K. Our findings show that $\text{Zn}_3(\text{HHTP})_2$ begins to lose M–O bonds undergoing significant structural distortion at elevated temperatures, while $\text{Ti}_3(\text{HHTP})_2$ remains structurally intact throughout the simulation, as illustrated in Figure S3. These results confirm that the calculated formation energy provides reliable insight into the thermal stability of the MOFs.

In addition, we determined the work function (Φ), defined as the energy required to remove an electron from the surface of the framework to the vacuum, specifically from the metal center where unpaired electrons reside. This quantity is particularly relevant for evaluating the oxidation potential of the metal at the pristine surface, as discussed later. The calculated work functions of the $M_3(\text{HHTP})_2$ surface range from 4.9 to 5.4 eV across the 3d transition metal series.

Concerning the electronic properties, most $M_3(\text{HHTP})_2$ frameworks exhibit electrical conductivity, as shown the density of states in Figure S4. The exception is $\text{Cr}_3(\text{HHTP})_2$ which is a zero-bandgap semimetal, while $\text{V}_3(\text{HHTP})_2$ exhibits only one spin-up state crossing the Fermi level, as shown the band structures in Figure S5. These results were obtained using hybrid functional calculations.^{62,63} Additionally, transition metals with partially filled 3d orbitals (e.g., Cr, Mn, Fe, Co, and Ni) exhibit a high-spin ground states, with magnetic moment ranging from 6 to 10 μ_B in the unit cell. The structural and electronic properties of single-layer $M_3(\text{HHTP})_2$ for each metal are summarized in Table 1.

We also evaluated the stability and equilibrium properties of bulk $M_3(\text{HHTP})_2$, which consists of stacked multilayer structures, as summarized in Table S1. For all studied frameworks, the interplane distances are approximately 3.2 Å, indicating that the layers are held together by π - π stacking interactions. The interlayer binding energies range from -11.9 for $\text{Ti}_3(\text{HHTP})_2$ to -3.2 meV/Å² for $\text{V}_3(\text{HHTP})_2$. These values are significantly lower than that of graphite (-36.7 meV/Å²), as previously reported,⁶⁴ suggesting that multilayer $M_3(\text{HHTP})_2$ could be more easily exfoliated.

3.2. Electrochemical Stability. The development of efficient and robust electrocatalysts for ORR and OER is

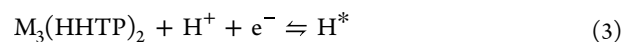
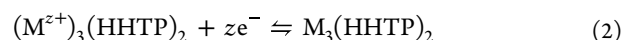
Table 1. Structural and Electronic Properties of Single-Layer $M_3(\text{HHTP})_2$ for Various Metal Centers^a

M	<i>a</i> (Å)	<i>d</i> _{M–O} (Å)	Φ (eV)	<i>E</i> _f (eV)	<i>m</i> (μ_B)
Ti	21.71	1.96	5.17	−10.19	0.0
V	21.73	1.92	4.92	−10.50	3.0
Cr	21.62	1.90	5.39	−8.18	8.0
Mn	21.43	1.86	5.11	−7.39	9.0
Fe	21.67	1.96	4.99	−8.75	10.0
Co	21.57	1.94	5.12	−6.48	7.0
Ni	21.16	1.81	5.37	−5.99	6.0
Cu	21.44	1.90	5.31	−6.45	1.0
Zn	21.52	1.96	5.21	−5.17	2.0

^aCalculated values include the lattice constant of the hexagonal unit cell (*a*), average metal–oxygen distance (*d*_{M–O}), work function (Φ), formation energy (*E*_f), and total magnetic moment per unit cell (*m*).

fundamental to the advancement of electrochemical energy conversion technologies. While catalytic activity has traditionally received the most attention, the long-term operational stability of these materials, particularly under harsh acidic and alkaline conditions, is equally essential for practical deployment.

To evaluate the electrochemical stability of single-layer $M_3(\text{HHTP})_2$ across the pH range we constructed surface Pourbaix diagrams, showing the electrode potential as a function of pH.⁶⁵ This analysis accounts for the redox reactions:



Here, *z* corresponds to the number of electrons transferred. Reaction 2 describes the oxidation of the coordinated metal in pristine $M_3(\text{HHTP})_2$, while reactions 3–5 describe the proton–electron transfer processes involved in H, OH, and O adsorption on the metal, respectively. Standard electrode potentials relative to the standard hydrogen electrode (SHE) were determined using the computational hydrogen electrode model,⁵⁸ which describes the electrochemical potential of the $2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$ half-cell reaction with that of molecular hydrogen at pH = 0.

The surface Pourbaix plots were constructed under standard conditions at 298 K using the Nernst equation, following the methodology described previously:⁶⁶

(i) Oxidation of the coordinated metal (reaction 2):

$$E(\text{M}^{z+}) = E^\circ(\text{M}^{z+}) - \frac{0.059}{z} \times \log a(\text{M}^{z+}) \quad (6)$$

(ii) Reduction via H adsorption (reaction 3):

$$E(\text{H}^*) = E^\circ(\text{H}^*) - 0.059 \times \text{pH} \quad (7)$$

(iii) Oxidation via OH adsorption (reaction 4):

$$E(\text{OH}^*) = E^\circ(\text{OH}^*) - 0.059 \times \text{pH} \quad (8)$$

(iv) Oxidation via O adsorption (reaction 5):

$$E(\text{O}^*) = E^\circ(\text{O}^*) - 0.059 \times \text{pH} \quad (9)$$

where E is the electrode potential of the galvanic cell, E° the standard electrode potential, and $a(\text{M}^{z+})$ the ionic activity. $E^\circ(\text{X}^*) = \Delta G_{\text{X}^*}/eF$, where ΔG_{X^*} is the adsorption free energy of the X adsorbates on the metal ($\text{X} = \text{H}, \text{O}$, and OH) and F is the Faraday constant. We consider $a(\text{M}^{z+}) = 1 \times 10^{-8} \text{ mol dm}^3$ and $z = 1$.

The standard oxidation potential of the coordinated metal, $E^\circ(\text{M}^{1+})$, was estimated based on the electronic work function (Φ) of the $\text{M}_3(\text{HHTP})_2$ surfaces, under the assumption that electron removal occurs primarily from the metal centers. This assumption is supported by spin density plots (Figure S6), which show that unpaired electrons are localized at the metal sites, suggesting that these sites are the most likely sources of oxidation. Accordingly, the estimation of $E^\circ(\text{M}^{1+})$ follows the established linear correlation between the work function and the standard potentials of various metals, as recently reported by Li et al.⁶⁷ Numerical values for the standard oxidation potentials of the metal and the adsorbates are provided in Table S2.

The effect of the solvent on the adsorption energies of the intermediates OH^* and OOH^* was included by applying an implicit solvent correction based on a continuum dielectric model.⁶⁰ This correction, along with the Bader charge analysis, were calculated independently for each metal in $\text{M}_3(\text{HHTP})_2$, and the results are presented in Table S3. We observe that the solvation corrections vary across metals and generally weaken the interaction between the metal and the adsorbate. This behavior can be attributed to charge transfer and the resulting change in polarization, consistent with previous results.⁶⁸

Figure 2 shows the Pourbaix plots for $\text{M}_3(\text{HHTP})_2$ with $\text{M} = \text{Mn}, \text{Ni}$, and Zn . The region enclosed by the black lines denotes the thermodynamic stability window of water, while the dashed line represents the metal oxidation potential. The green, blue, and red lines correspond to the equilibrium potentials associated with the adsorption of O^* , OH^* , and H^* , respectively. The position of the OH^* adsorption potential relative to the metal oxidation potential serves as a key indicator of electrochemical stability. When the OH^* potential falls below the metal oxidation potential, it implies that electron loss occurs upon OH adsorption, which destabilize the metal center within the framework. This can lead to metal dissolution or the binding of unwanted ionic species, reducing catalytic efficiency and durability. If the OH^* and metal oxidation potentials intersect, the system is expected to be electrochemically stable at pH values higher than the intersection point. Conversely, when the OH^* potential lies entirely above the metal oxidation potential, the catalyst remains electrochemically stable across the full pH range.^{42,69}

This analysis reveals that $\text{Mn}_3(\text{HHTP})_2$ and $\text{Zn}_3(\text{HHTP})_2$ are unstable under strong acidic conditions but become stable at $\text{pH} > 2$. In contrast, $\text{Ni}_3(\text{HHTP})_2$ remains stable across the entire pH range, as shown in Figure 2. Pourbaix plots for frameworks with other metals are provided in Figure S8, indicating that most of these materials are also stable throughout the full pH range. In summary, the Pourbaix analysis suggests that only the $\text{M}_3(\text{HHTP})_2$ structures with $\text{M} = \text{Mn}, \text{Zn}$, and Cu are prone to degradation in acidic environments, likely due to metal dissolution, whereas the other frameworks are expected to remain stable.

3.3. ORR and OER Catalytic Activity. The adsorption and activation of O_2 at the metal centers of 2D-MOFs

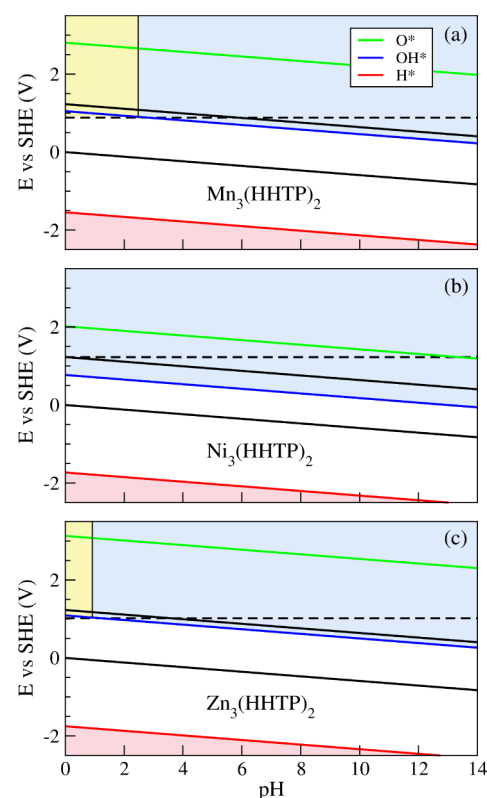


Figure 2. Surface Pourbaix plots displaying the electrode potential (E vs SHE) as a function of pH for $\text{M}_3(\text{HHTP})_2$, where M is (a) Mn, (b) Ni, and (c) Zn. The dashed line indicates the metal oxidation potential of the pristine surface, and the yellow region highlights the domain where the metal becomes unstable.

represents the initial step in the ORR process. To better understand this process, we first examine the stability and electronic properties of adsorbed dioxygen (O_2^*). Table 2

Table 2. Equilibrium Geometry and Stability of O_2 Adsorbed on the M Atom of $\text{M}_3(\text{HHTP})_2$ ^a

$\text{M}-\text{O}_2$	$d_{\text{M}-\text{O}}$ (Å)	$d_{\text{O}-\text{O}}$ (Å)	E_b (eV)	m (μ_B)
Ti- O_2	1.87	1.46	-2.34	2.0
V- O_2	1.98	1.33	-2.13	5.0
Cr- O_2	1.87	1.29	-0.81	8.0
Mn- O_2	2.08	1.28	-0.16	9.0
Fe- O_2	1.92	1.29	-0.92	12.0
Co- O_2	1.88	1.26	-0.23	3.0
Ni- O_2	2.05	1.25	-0.41	4.0
Cu- O_2	2.54	1.23	-0.17	1.0
Zn- O_2	2.25	1.25	-0.44	-2.0

^a E_b denotes the O_2 binding energy; d represents the relevant atomic distances, and m is the total magnetic moment per unit cell.

summarizes the equilibrium geometries, binding energies, and spin coupling of O_2 on $\text{M}_3(\text{HHTP})_2$. Our results show that O_2 binds strongly to $\text{M} = \text{Ti}$ and V , adopting a side-on adsorption geometry with binding energies around -2 eV , which suggests poor catalytic activity for these metals. In contrast, the other metals exhibit much weaker binding energies, ranging from -0.16 to -0.92 eV , with O_2^* favoring an end-on geometry.

We also observe changes in the ground-state magnetic moment of $\text{M}_3(\text{HHTP})_2$ upon O_2 adsorption, as shown in

Figure 3. Three distinct magnetic orders can be identified: (i) O_2^* adopts a singlet state, and the system's magnetic moment remains unchanged (for $M = \text{Cr, Mn, and Cu}$); (ii) O_2^* adopts a triplet state, leading to a change in magnetic moment of $\pm 2\mu_B$ (for $M = \text{Ti, V, Fe, and Ni}$); (iii) O_2^* adopts a triplet state, changing the magnetic moment by $-4\mu_B$ (for $M = \text{Co and Zn}$). These results indicate that triplet O_2 can significantly alter the spin polarization of the 2D MOF upon adsorption at the metal center. Its interaction induces spin transfer or a rearrangement of the local magnetic moments in nearby ligand atoms. Depending on the metal species and the strength of the coupling, this can either enhance or reduce the overall spin polarization.

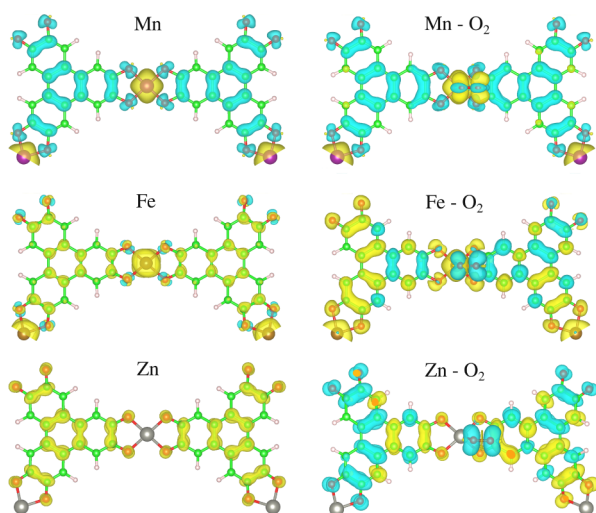
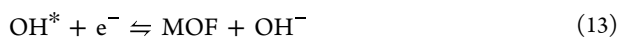
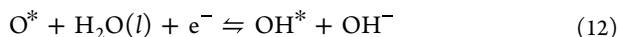
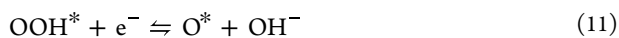
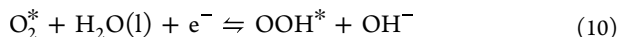


Figure 3. Top view of the spin-density plots for $M_3(\text{HHTP})_2$ with an adsorbed O_2 molecule, for $M = \text{Mn, Fe, and Zn}$. The right panel shows the layer with O_2 adsorbed on the metal center, while the left panel shows the pristine layer. Yellow and cyan regions represent spin-up and spin-down electron densities, respectively. The isosurface level is set to $\rho = 0.003a_0^{-3}$.

Once O_2 is adsorbed onto a metal site of $M_3(\text{HHTP})_2$, its catalytic activity toward the four-electron ORR is analyzed using the CHE model.⁵⁸ In an alkaline solution, water serves as the proton donor, and the reaction yields hydroxide ions as the final product through the overall reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.⁷⁰ Thus, the ORR proceeds by generating OH^- ions through four elementary steps:



For the OER, these reactions proceed in reverse. To assess the energetics of the ORR/OER reactions, we plotted adsorption free energy profiles for the reaction intermediates OOH^* , O^* , and OH^* , each bound to the metal cation of $M_3(\text{HHTP})_2$. We note a deformation of the structure after the intermediates adsorption mainly for O^* , as shown in Figure S7.

The reaction steps proceed spontaneously at zero applied potential with respect to the reversible hydrogen electrode (RHE) ($U = 0 \text{ V}$). At the standard thermodynamic equilibrium

potential ($U = 1.23 \text{ V}$), the free energy is lowered proportionally to the number of electrons transferred in each step. The applied potential at which all steps become thermodynamically favorable is known as the onset potential (U_{onset}). The theoretical overpotential (η), an indicator of ORR/OER electrocatalytic efficiency, is calculated as the difference between the equilibrium potential and the onset potential: $\eta_{\text{ORR}} = 1.23 \text{ V} - U_{\text{onset}}$ and $\eta_{\text{OER}} = U_{\text{onset}} - 1.23 \text{ V}$. A comprehensive explanation of the methodology used to compute the adsorption free energies of intermediates and the ORR/OER overpotentials is provided in the Supporting Information. Figure 4 presents the free energy diagrams for

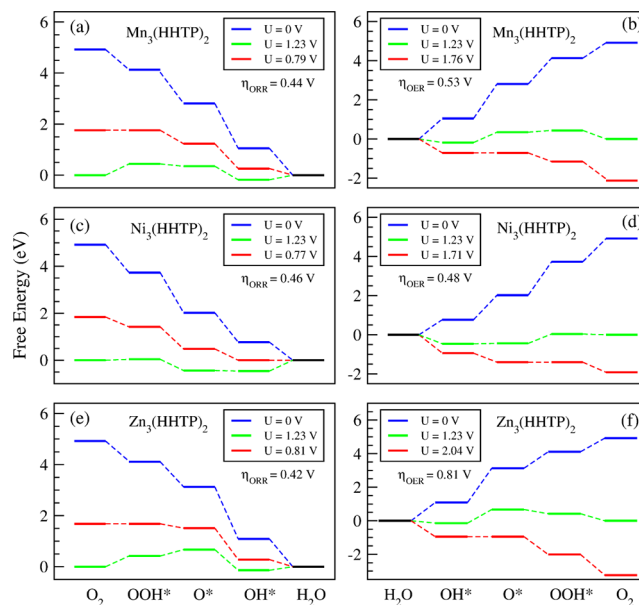


Figure 4. Reaction free energy diagrams for the elementary steps of ORR and OER at different electrode potential (U vs RHE) for (a,b) $Mn_3(\text{HHTP})_2$, (c,d) $Ni_3(\text{HHTP})_2$, (e,f) $Zn_3(\text{HHTP})_2$. The red diagrams represent the onset potential and η the thermodynamic overpotentials.

the elementary steps of the oxygen reactions at various electrode potentials on $M_3(\text{HHTP})_2$ ($M = \text{Mn, Ni, Zn}$). Our results reveal that $Mn_3(\text{HHTP})_2$ exhibits ORR and OER overpotentials of 0.44 and 0.53 V, respectively. Similar results are obtained for $Ni_3(\text{HHTP})_2$. In contrast, $Zn_3(\text{HHTP})_2$ shows slightly different overpotentials of 0.42 V for ORR and a much higher 0.81 V for OER. Free energy diagrams for the remaining frameworks are presented in Figures S9 and S10.

Table 3 summarizes the onset potentials and overpotentials of the $M_3(\text{HHTP})_2$ frameworks. To benchmark their catalytic performance, we compare these values with previously reported overpotentials for Pt(111) and $IrO_2(110)$ surfaces, obtained using the same theoretical approach.^{71,72} These surfaces are widely regarded as among the most effective commercial electrocatalysts for ORR and OER, respectively. For $M = \text{Ti, V, and Cr}$, both ORR and OER overpotentials are significantly higher, ruling them out as efficient electrocatalysts. In contrast, the remaining metals exhibit overpotentials below 0.9 V. Notably, for $M = \text{Mn, Ni, and Zn}$, the ORR overpotentials are lower than that of Pt(111), while for $M = \text{Mn, Fe, Co, and Ni}$, the OER overpotentials are lower than that of $IrO_2(110)$. Among these, $Mn_3(\text{HHTP})_2$ and $Ni_3(\text{HHTP})_2$ exhibit bifunctional behavior, with comparable

Table 3. Theoretical Results for ORR/OER Onset Potential (U_{onset} in V) and Overpotential (η in V) for $M_3(\text{HHTP})_2$ ^a

M	ORR		OER	
	U_{onset}	η	U_{onset}	η
Ti	−0.04	1.27	3.11	1.88
V	−0.19	1.42	3.19	1.96
Cr	−0.11	1.34	2.79	1.56
Mn	0.79	0.44	1.76	0.53
Fe	0.26	0.97	1.75	0.52
Co	0.51	0.72	1.74	0.51
Ni	0.77	0.46	1.71	0.48
Cu	0.32	0.91	2.16	0.93
Zn	0.81	0.42	2.04	0.81
Pt(111) ^b	0.75	0.48	−	−
IrO ₂ (110) ^c	−	−	1.88	0.65

^aPrevious theoretical results for ORR on Pt(111) and OER on IrO₂(110) are included for comparison. ^bReference 71. ^cReference 72.

overpotentials for both ORR and OER. Taking into account both catalytic activity and electrochemical stability, $\text{Ni}_3(\text{HHTP})_2$ emerges as the most promising bifunctional electrocatalyst within this series.

Currently, experimental evidence on the ORR/OER electrocatalytic activity of $M_3(\text{HHTP})_2$ MOFs remains limited. Yang et al.⁷³ reported OER activity for $\text{Co}_3(\text{HHTP})_2$, with an overpotential of 0.245 V at a current density of 10 mA cm^{−2} in alkaline solution, along with excellent durability. Dong et al.^{74,75} demonstrated outstanding OER performance for $\text{Ni}_3(\text{HHTP})_2$ by introducing high-valent metal species (Ni^{3+} and Ni^{2+}), achieving an overpotential of just 0.136 V at 10 mA cm^{−2} under alkaline conditions. These experimental results align well with our theoretical findings, which indicate that $\text{Co}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$ exhibit the lowest OER overpotentials. Interestingly, our calculations also suggest that Fe- and Mn-based MOFs display promising activity, offering alternative candidates for future experimental investigation. In the case of ORR, Miner et al.⁷⁶ reported that $\text{Cu}_3(\text{HHTP})_2$ exhibits catalytic activity in both neutral and alkaline media, in contrast to $\text{Co}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$, which show virtually no activity. In our study, however, we observe a clear discrepancy with these experimental results: $\text{Ni}_3(\text{HHTP})_2$ is predicted to exhibit ORR activity, while $\text{Cu}_3(\text{HHTP})_2$ appears inactive. Nevertheless, no other experimental studies were found to compare or validate these findings.

In the following analysis, we compare our results on the catalytic performance of $M_3(\text{HHTP})_2$ with predictions based on adsorption free-energy descriptors. Figure 5 presents the ORR overpotential as a function of ΔG_{OH^*} (adsorption free-energy of the OH* intermediate), and the OER overpotential as a function of $\Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*}$ (the universal OER descriptor).⁷⁷ The resulting volcano plots reveal that the lowest overpotentials are achieved for $\Delta G_{\text{OH}^*} \approx 0.9$ eV for ORR and $\Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*} \approx 1.4$ eV for OER. These results closely confirm that the selected free-energy descriptors effectively capture the ORR/OER catalytic performance trends of the $M_3(\text{HHTP})_2$ frameworks.

To investigate the intrinsic relationship between catalytic performance and electronic structure, we plotted the ORR and OER overpotentials as a function of the d-band center (ϵ_d), shown in Figure 6. The d-band center represents the average energy position of the metal's d-electron density of states

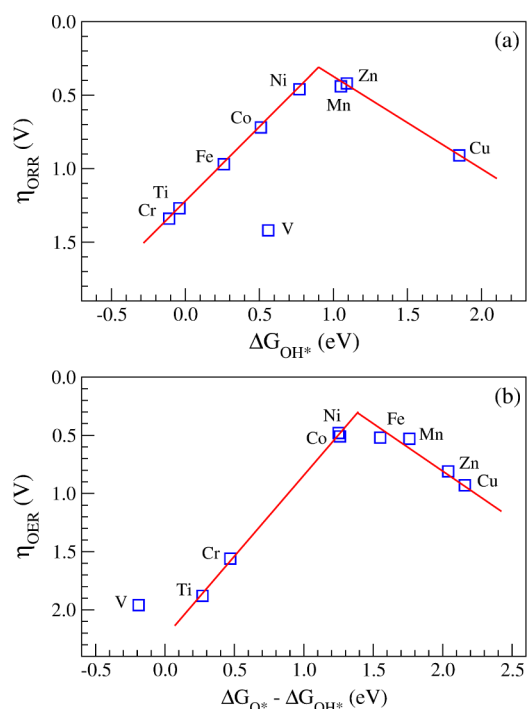


Figure 5. Volcano plots of $M_3(\text{HHTP})_2$ overpotentials (η) as a function of adsorption free energy descriptors, (a) for ORR and (b) for OER.

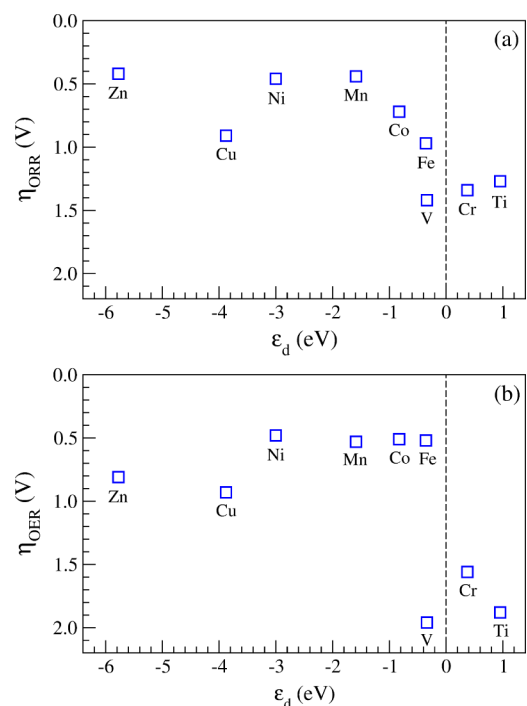


Figure 6. Overpotential (η) as a function of the d-band center (ϵ_d) of $M_3(\text{HHTP})_2$ for (a) ORR and (b) OER. The dashed line indicates the Fermi energy.

(DOS) relative to the Fermi level.^{78,79} Figure S11 shows the DOS of the M (3d) orbitals, highlighting the position of the d-band center. As shown in Figure 6, the $M_3(\text{HHTP})_2$ frameworks exhibiting the lowest overpotentials tend to have d-band centers positioned between −3 and −1 eV relative to the Fermi level. Therefore, this energy range for the d-band

center optimizes the binding strength of reaction intermediates, thereby enhancing catalytic activity. Notably, Zn deviates from this trend, although it exhibits favorable ORR and moderate OER overpotentials, its d states lie significantly lower in energy compared to the other metals studied. In this case, the occupation of antibonding states weakens the adsorption of intermediates.

4. SUMMARY AND CONCLUSIONS

In summary, we investigated the electronic properties, electrochemical stability, and ORR/OER catalytic activity of two-dimensional metal–organic frameworks, $M_3(\text{HHTP})_2$ ($M = \text{Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$), using spin-polarized DFT calculations. Most of these 2D-MOFs exhibit conductive behavior, with the exception of $\text{Cr}_3(\text{HHTP})_2$, which behaves as a zero-bandgap semimetal. The ground states typically display high-spin magnetization, especially for metals with partially filled 3d orbitals. Notably, O_2 adsorption at the metal center induces significant changes in magnetization, indicating strong magnetic coupling.

These frameworks demonstrate notable mechanical strength, flexibility, and thermal stability, with formation energies ranging from -5.2 to -10.5 eV, as confirmed by ab initio molecular dynamics simulations conducted up to 800 K. Additionally, their interlayer binding energies of bulk phase $M_3(\text{HHTP})_2$ are significantly lower than that of graphite, about one-third, suggesting facile exfoliation. Pourbaix diagrams indicate that single-layer $M_3(\text{HHTP})_2$ frameworks are electrochemically stable across the full pH range for $M = \text{Ti, V, Cr, Fe, Co, and Ni}$. In contrast, the Mn-, Zn-, and Cu-based frameworks become unstable under acidic conditions.

ORR and OER catalytic activities were evaluated using theoretical overpotentials derived from the computational hydrogen electrode method. Frameworks with $M = \text{Mn, Ni, and Zn}$ exhibit low ORR overpotentials ranging from 0.42 to 0.46 V, while those with $M = \text{Mn, Fe, Co, and Ni}$ perform well for OER, with overpotentials ranging from 0.48 to 0.53 eV. In contrast, frameworks with $M = \text{Ti, V, and Cr}$ show negligible activity for either reaction. Considering both catalytic performance and electrochemical stability, $\text{Ni}_3(\text{HHTP})_2$ emerges as the most promising bifunctional ORR/OER catalyst, with overpotentials around 0.47 eV. These findings enhance our understanding of structure–property relationships in 2D-MOFs and underscore their potential as cost-effective, sustainable alternatives to conventional noble-metal catalysts.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.5c03531>.

Here, we present convergence tests and details of the theoretical procedures, along with additional electronic and electrochemical characterizations (PDF)

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Notes

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