

# From Molecules to Porous Materials: Integrating Discrete Electrocatalytic Active Sites into Extended Frameworks

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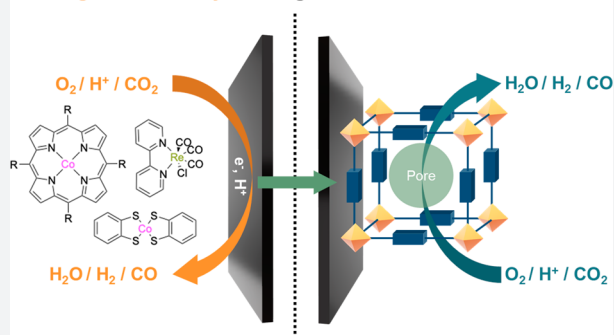
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**ABSTRACT:** Metal–organic and covalent–organic frameworks can serve as a bridge between the realms of homo- and heterogeneous catalytic systems. While there are numerous molecular complexes developed for electrocatalysis, homogeneous catalysts are hindered by slow catalyst diffusion, catalyst deactivation, and poor product yield. Heterogeneous catalysts can compensate for these shortcomings, yet they lack the synthetic and chemical tunability to promote rational design. To narrow this knowledge gap, there is a burgeoning field of framework-related research that incorporates molecular catalysts within porous architectures, resulting in an exceptional catalytic performance as compared to their molecular analogues. Framework materials provide structural stability to these catalysts, alter their electronic environments, and are easily tunable for increased catalytic activity. This Outlook compares molecular catalysts and corresponding framework materials to evaluate the effects of such integration on electrocatalytic performance. We describe several different classes of molecular motifs that have been included in framework materials and explore how framework design strategies improve on the catalytic behavior of their homogeneous counterparts. Finally, we will provide an outlook on new directions to drive fundamental research at the intersection of reticular and electrochemistry.

## Homogeneous Catalysts integrated into Framework Materials



## 1. INTRODUCTION

Electrocatalytic reaction pathways provide a method to store renewable energy within chemical bonds by synthesizing energy dense products.<sup>1,2</sup> Catalytic conversions of protons to molecular hydrogen (HER), molecular oxygen to water and vice versa (ORR and OER, respectively), and carbon dioxide to hydrocarbons and higher-order carbon species (CO<sub>2</sub>RR) are critical for solar energy storage. Both homogeneous and heterogeneous catalytic systems have been explored for the optimization of high product selectivity and activity.<sup>3–7</sup> Homogeneous systems, where freely diffusing species catalyze substrate conversion, have the benefit of synthetic tunability and relatively facile characterization for providing mechanistic insights. However, molecular systems suffer from under-utilization of the catalyst, catalyst deactivation, and sluggish electron transfer from the electrode.<sup>8–10</sup> In addition, the limited solubility of molecular complexes in common solvents, complicated product separation, and poor recyclability further hinder the practical applications of these systems. Heterogeneous systems, in which the catalyst is a solid-state material, overcome many of these issues yet lack similar synthetic versatility and simple characterization techniques to probe mechanistic details.

One way to bridge homogeneous and heterogeneous catalysis is to immobilize the molecular species directly onto the electrode. Heterogenizing molecular catalysts can enhance

both the activity and turnover number (TON), up to several orders of magnitude, by improving the electron transfer kinetics and overall catalyst utilization.<sup>11</sup> In addition, catalyst loading can be judiciously controlled to isolate active sites and prevent catalyst deactivation by inhibiting side reactions such as dimerization and catalyst poisoning. One of the earliest catalyst immobilization strategies involves noncovalent interactions (van der Waals,  $\pi$ – $\pi$  stacking, and electrostatic) between the molecular catalyst and the electrode material.<sup>12–14</sup> However, severe catalyst leaching still resulted in poor activity during long-term electrolysis. To overcome this pitfall, covalent immobilization techniques,<sup>15</sup> such as electropolymerization,<sup>16,17</sup> have also been developed. Molecular complexes have been directly attached to the electrode via self-assembled monolayers,<sup>18,19</sup> diazonium bonds,<sup>20</sup> click reactions,<sup>21,22</sup> and pyrazine linkages.<sup>23</sup> Despite these improvements, anchoring homogeneous catalysts is synthetically challenging, and the loading is often too low to

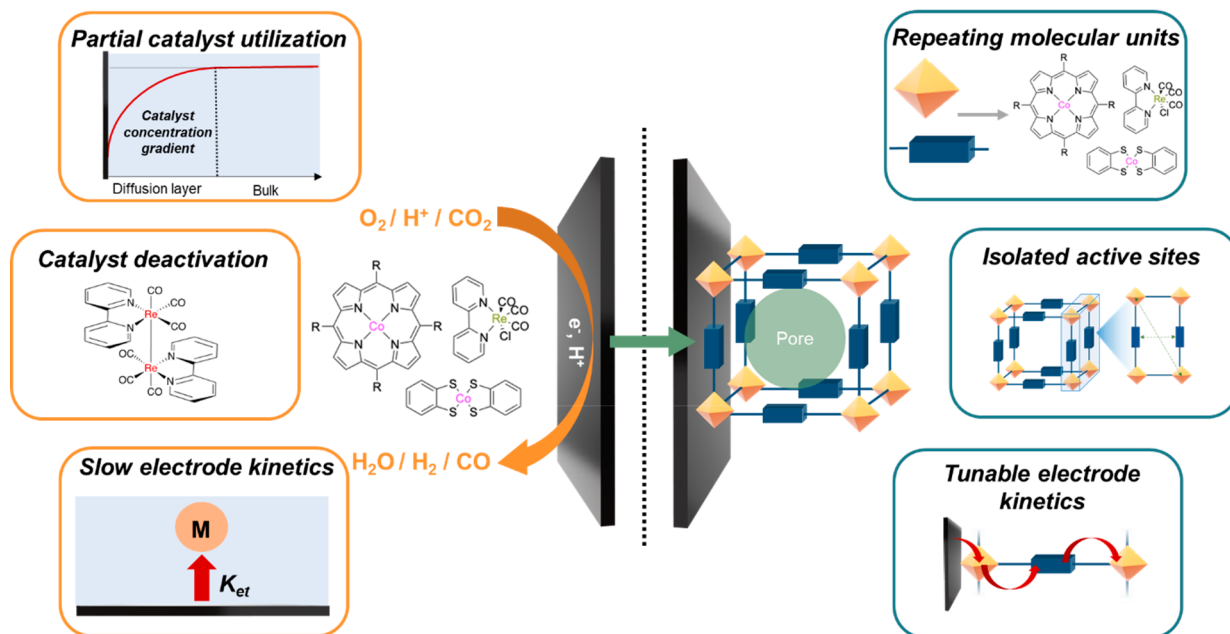
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**Scheme 1. Porous Framework Materials Are Well-Suited for the Incorporation of Molecular Active Sites with Modular Control over the Pore Environment, Charge Transport, and Electrode Integration**

### Homogeneous Catalysts integrated into Framework Materials



obtain significant geometric current densities. Furthermore, a majority of the catalytic centers are often buried within these densely packed films and therefore are not accessible by electrolyte or substrate.

Porous framework materials, with their atomically precise structures, synthetic versatility, and solid-state nature, offer a promising intermediary between homogeneous and heterogeneous catalysts (Scheme 1). In addition, the porous channels of framework materials render the buried molecular active sites more accessible as compared to other immobilized catalysts. Through incorporation of catalytic moieties in the metal nodes or organic struts, the active species can be site-isolated and uniformly distributed through the framework. Moreover, the secondary environment around the active site can be modulated by functionalizing the organic linkers surrounding the pores of the framework. As a solid-state material, the structural rigidity of framework materials increases the robustness of molecular active sites. High tunability of framework materials facilitates the incorporation of secondary coordination environments, distribution of active sites throughout the material, electronic and ionic conductivity, redox hopping, and various other parameters crucial for the catalytic performance of those complexes.

As there have been many reviews on the electrocatalytic application of framework materials,<sup>24–26</sup> the goal of this Outlook is to illustrate the unique ability of framework materials, namely, metal–organic frameworks (MOFs) and covalent–organic frameworks (COFs), to bridge between homogeneous and heterogeneous catalysis. Herein, we chose not to focus on a specific framework and will center our discussion on comparing the catalytic performance of framework materials and their molecular analogues for a variety of small-molecule transformations. We will first describe different design considerations for the incorporation of molecular active sites in framework materials. In the following sections, both catalytic performance and robustness of the framework materials will be compared with respect to the homogeneous molecular systems. Both

High tunability of framework materials facilitates the incorporation of secondary coordination environments, distribution of active sites throughout the material, electronic and ionic conductivity, redox hopping, and various other parameters crucial for the catalytic performance of those complexes.

advantages and disadvantages of molecular active sites in ordered porous framework materials will be critically evaluated. Finally, we will communicate some perspectives about strategies for further development.

## 2. FRAMEWORK DESIGN CONSIDERATIONS FOR ELECTROCATALYSIS

MOFs are a class of crystalline porous materials connected by discrete metal nodes and multitopic organic linkers, while COFs are ordered coordination networks consisting of purely organic linkages between node and linker. These framework materials are desirable candidates for electrocatalysis because they extend an electrocatalytic building block in a predictable, modular fashion to 2D or 3D porous networks. Their modularity and synthetic versatility allow for precise positioning and orientations of the components of the active site, immobilizing them for catalysis. When considering framework materials for electrocatalysis, five main aspects for modification and enhancement rise to the forefront: chemical design of the active site, the pore environment, charge transport, the suitability of the framework

to electrochemical systems, and stability under electrocatalytic conditions.<sup>25,27–31</sup>

**2.1. Tuning the Secondary Environment of Active Sites.** Catalytic active sites must be carefully designed to tune the relevant molecular orbitals for chemical reactivity.<sup>32</sup> A framework extends the chemical reactivity of an active site in a predictable fashion, often creating the conditions for enhanced performance. By manipulating the node and linker in tandem, new electrochemical behavior can be observed that is otherwise inaccessible from the component parts. In this Outlook, we compare how the chemical components of a molecular active site change upon incorporation into the framework. Catalytic framework design focuses on varying metals (whether at the node or the linker), using redox active linkers, and modifying defect sites, all of which provide modular avenues for activating the substrate.

By manipulating the node and linker in tandem, new electrochemical behavior can be observed that is otherwise inaccessible from the component parts.

Metals within a framework offer many opportunities to manipulate the electronics of the active site, and many studies have shown that metals with accessible oxidation states can house electrons to be used in catalysis. Copper, iron, titanium, and chromium<sup>29,33</sup> are prominent examples of metals that can be incorporated into the nodes and linkers to store multiple equivalents of electrons. In addition, bimetallic nodes can combine the chemical properties of each metal to lend better structural stability while also enhancing electronic transport abilities. PCN-415 is an example of such a MOF that contains Zr for its structural stability and Ti for its redox activity.<sup>34</sup>

Redox active linkers such as tetrathiafulvalene, quinones, and triphenylamines<sup>28,29</sup> can also provide additional sites of charge and ion storage, as seen in anthraquinone-based MOFs<sup>35,36</sup> and COFs,<sup>37</sup> which facilitate lithium redox chemistry in batteries. Additionally, frameworks hold linkers in conformations ideal for  $\pi$ – $\pi$  and  $\pi$ – $n$  stacking which then promotes charge transfer and electrocatalytic activity. In  $\text{Zn}_2(\text{TTFTB})$ , for example, the degree of  $\pi$ – $\pi$  stacking with tetrathiafulvalene-like linkers provides enhanced charge mobility to the active site.<sup>38</sup>

Framework materials are particularly advantageous because of their ability to be postsynthetically modified.<sup>39,40</sup> Postsynthetic modification includes metal exchange, ligand exchange, and functionalization at the linker or node. The UiO-66 class of MOFs has been well explored for postsynthetic modification because of their propensity for defect sites (missing linker sites) at the node and opportunities for functionalization on the aromatic ring. UiO-66 analogues with catechol and thiocatechol linkers have been studied for their ability to be postsynthetically metalated with Fe or Pd for newfound catalytic activity.<sup>41,42</sup> In framework materials, the active site can be manipulated through traditional chemical techniques with the added structural and chemical benefits of an extended system.

**2.2. Pore Features.** Akin to controlling the secondary environment of protein active sites, manipulation of the pore environment around catalytic centers is one of the great advantages of using framework materials for electrocatalysis. Pore functionality, hydrophobicity/hydrophilicity, electro-

statics, size, and shape offer novel methods to fine-tune the second coordination sphere of the active site and dictate the diffusion of the substrate and ions through the framework. For instance, hydrophobic pore environments have been shown to lower the catalytic ability of framework environments most likely because of hindered diffusion of polar ions through the framework.<sup>43–45</sup>

In addition to the secondary environment, pore morphology guides ion and electron diffusion through frameworks. The permanent porosity of framework materials allows for greater mass transport over molecular catalysts and is a significant advantage for incorporating them into electrocatalytic systems. Combining both mesopores and micropores<sup>43</sup> has also been shown to cooperatively improve catalytic performance by balancing the mass transport of the gaseous product and electrolyte through the large pores with active site accessibility. The combination of pore morphologies offers shorter ion diffusion pathways within the micropores. Commonly, iso-reticular frameworks are designed with ligands of various lengths to determine the effect of pore size on diffusion, catalysis, and accessibility. Increasing pore length has a dual effect on diffusion kinetics.<sup>46</sup> The increased distance reduces the possibility of electron hopping; however, large pore sizes can better accommodate ions and facilitate their movement through the framework. When comparing MOFs, such as MOF-808, NU-1000, and NU-1003, with similar morphologies but increasing pore widths, it was observed that the larger pores allowed for greater ion diffusion and decreased electron hopping.<sup>46</sup> When considered together, ion diffusion is typically the rate-limiting step, and pores that are 3–4 times larger than the counterion will have optimal charge transfer.

**2.3. Electron and Ion Transfer.** Improving electron and ion transfer within framework materials is essential to enhance framework catalytic activity and makes them viable for inclusion in electrochemical systems. Most framework materials are inherently insulating due to their highly stable metal-oxo bonds and/or organic components. While pore morphology can increase charge transfer, the insulating nature of frameworks poses a significant problem in moving electrons and ions to the active site for catalysis. To address this, significant work is being done to enhance charge transport through framework materials. Frameworks exhibit two main modes of electron transfer depending on the degree of orbital overlap: electron hopping and band transport.<sup>47–49</sup> Electron hopping can occur in frameworks when charge is delocalized across neighboring sites at discrete energy levels. Owing to the synthetic ease of tuning the proximity of these sites, electron hopping is the most common charge transfer pathway in frameworks. In band transport, electrons are delocalized across an entire axis of the material. Both types of transport can either occur through-space (such as through  $\pi$ – $\pi$  interactions) or through-bonds (by pairing electron donors and acceptors). For example, by pairing a Cu-based electron donating framework (HKUST-1) with an electron accepting guest molecule (7,7,8,8-tetracyanoquinodimethane), Talin et al. were able to obtain charge hopping conductivities at  $0.07 \text{ S cm}^{-1}$ .<sup>50</sup> Recently, in examining through-space band transport in framework materials, Aubrey et al. demonstrated band transport conductivity in the  $\text{Fe}(\text{BDP})_3$  MOF that capitalized on the significant  $\pi$ – $d$  delocalization along the iron-pyrazolate chain to offer a conductivity up to  $0.29 \text{ S cm}^{-1}$  upon incorporation of  $\text{K}^+$  as a counter charge.<sup>51</sup>

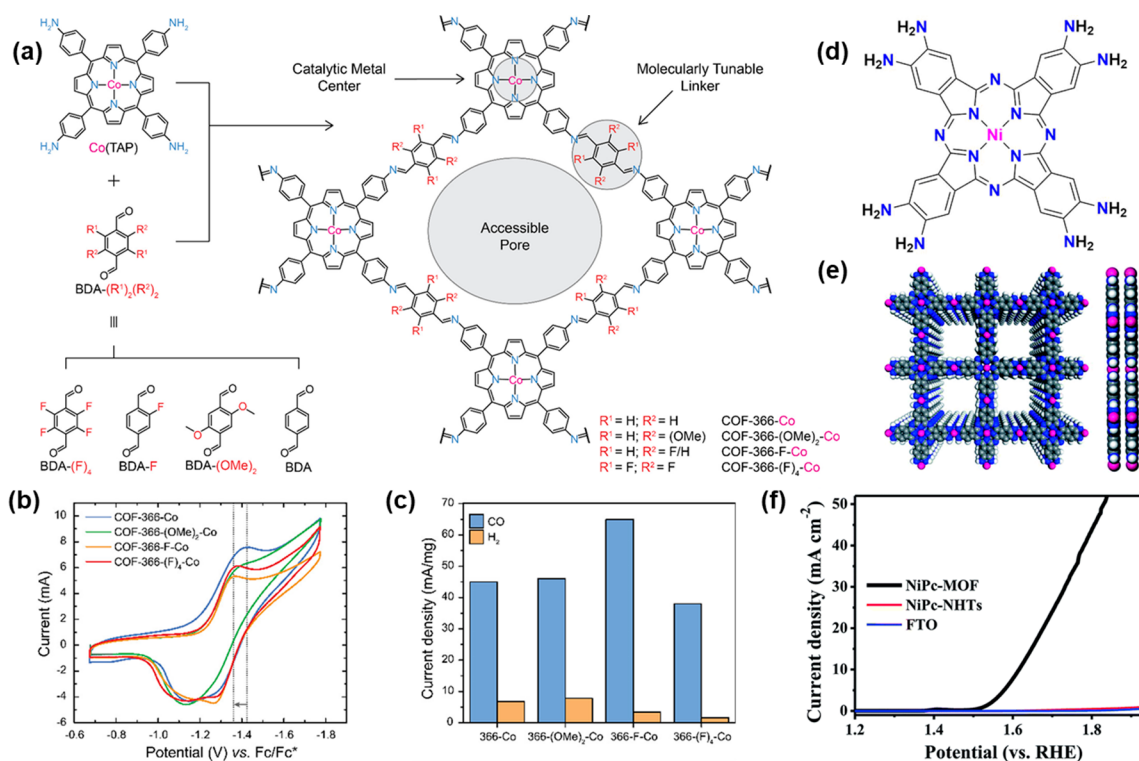
As hinted with the above study, the incorporation of ions is also important to improve charge mobility. For ionic

Table 1. Electrocatalytic Metrics for Framework Materials

molecular active site	framework	reaction	electrolyte	overpotential <sup>a</sup> (mV)	onset potential	current density	Faradaic efficiency (%)	TON <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )	ref
Co-TAP	COF-366-Co	CO <sub>2</sub> RR	0.5 M KHCO <sub>3</sub> (pH 7.3)	550		3 mA mg <sup>-1</sup>	90% CO (-0.67 V vs RHE)	1352 (-0.67 V vs RHE)	98 (-0.67 V vs RHE)	66
Co-TAP	COF-366-F-Co	CO <sub>2</sub> RR	0.5 M KHCO <sub>3</sub> (pH 7.3)	550		65 mA mg <sup>-1</sup>	87% CO (-0.67 V vs RHE)			66
Co-TAP	molecular analogue	CO <sub>2</sub> RR	0.5 M KHCO <sub>3</sub> (pH 7.3)	550		7 mA mg <sup>-1</sup>	80% CO	794 (-0.67 V vs RHE)	36 (-0.67 V vs RHE)	32
Fe-TAPPCl	FeDhaTph-COF	CO <sub>2</sub> RR	0.1 M TBAPF <sub>6</sub> in MeCN	200			80% CO (-2.1 V vs Ag/AgCl)		600 (-2.1 V vs Ag/AgCl)	57
Fe-TAPPCl	molecular analogue	CO <sub>2</sub> RR	0.1 M TBAPF <sub>6</sub> in MeCN				50% CO (-2.1 V vs Ag/AgCl)		1300 (-2.1 V vs Ag/AgCl)	57
Co-TEPP	Co-PDY COF	OER	1 M KOH	270		10 mA cm <sup>-2</sup>				67
Co-TEPP	molecular analogue	OER	1 M KOH	370						67
Ni-Pc	Ni-Pc MOF	OER	1 M KOH	270	1.48 V vs RHE	10 mA cm <sup>-2</sup>	94% O <sub>2</sub> (1.50 V vs RHE)		9000 (1.50 V vs RHE)	68
Ni-Pc	molecular analogue	OER	1 M KOH		1.65 V vs RHE					68
Re(Bipy) (CO) <sub>3</sub> Cl	Re-SURMOF	CO <sub>2</sub> RR	0.1 M TBAH in MeCN				93% CO (-1.6 V vs NHE)	580 (-1.6 V vs NHE)	690 (-1.6 V vs NHE)	69
Re(Bipy) (CO) <sub>3</sub> Cl	molecular analogue	CO <sub>2</sub> RR	0.1 M TBAH in MeCN			2.5 mA cm <sup>-2</sup>	65% CO (-1.6 V vs NHE)			69
Co-Bpy	Co-TpBpy COF	OER	0.1 M phosphate (pH 7.0)	400	1.63 V vs RHE	1 mA cm <sup>-2</sup>	95% O <sub>2</sub>		828 (1.63 V vs RHE)	70
Co-Bpy	molecular analogue	OER	0.1 M phosphate (pH 7.0)		~1.8 V vs RHE					70
[Co(dcpgh) (dcpgh) <sub>2</sub> ]Cl <sub>2</sub>	UU 100(Co) MOF	HER	0.1 M NaClO <sub>4</sub> /0.2 M acetate (pH 4.0)			1.7 mA cm <sup>-2</sup>	84% H <sub>2</sub> (-0.45 V vs RHE)	20 875 (-0.45 V vs RHE)	1171 (-0.45 V vs RHE)	71
[Co(dcpgh) (dcpgh) <sub>2</sub> ]Cl <sub>2</sub>	molecular analogue	HER	0.1 M NaClO <sub>4</sub> /0.1 M acetate (pH 5.3)		-0.43 V vs RHE			10 (-0.43 V vs RHE)		71
[Co(BDT) <sub>2</sub> ] <sup>-</sup>	MOS1	HER	H <sub>2</sub> SO <sub>4</sub> (pH 1.3)		-0.48 V vs RHE	4.3 × 10 <sup>4</sup> A mol <sub>Co</sub> <sup>-1</sup> (-0.63 V vs SHE)				72
[Co(BDT) <sub>2</sub> ] <sup>-</sup>	MOS2	HER	H <sub>2</sub> SO <sub>4</sub> (pH 1.3)			1.2 × 10 <sup>4</sup> A mol <sub>Co</sub> <sup>-1</sup> (-0.63 V vs SHE)				72
[Co(BDT) <sub>2</sub> ] <sup>-</sup> (0.3 mM)	molecular analogue	HER	1:1 H <sub>2</sub> SO <sub>4</sub> (pH 1.3):0.1 M KNO <sub>3</sub> in MeCN			1.4 × 10 <sup>2</sup> A mol <sub>Co</sub> <sup>-1</sup> (-0.63 V vs SHE)				72
[PMo <sup>V</sup> <sub>6</sub> Mo <sup>VI</sup> <sub>4</sub> O <sub>36</sub> (OH) <sub>4</sub> Zn <sub>4</sub> ]	ε(trim) <sub>4/3</sub> MOF	HER	1 M LiCl + HCl (pH 1)	200	20 mV vs RHE		95% H <sub>2</sub>	1.2 × 10 <sup>5</sup> (η = 0.2 V)	24 120	73
[TBA] <sub>3</sub> [ε-PMo <sup>V</sup> <sub>6</sub> Mo <sup>VI</sup> <sub>4</sub> O <sub>36</sub> (OH) <sub>4</sub> Zn <sub>4</sub> ]	NENU-500 MOF	HER	0.5 M H <sub>2</sub> SO <sub>4</sub>	237	180 mV vs RHE	10 mA cm <sup>-2</sup>				74

<sup>a</sup>Overpotential is defined as the excess applied potential compared to the equilibrium potential determined by the Nernst equation. <sup>b</sup>TON is the turnover number, defined as the number of moles of product per mole of individual active site. <sup>c</sup>TOF is the turnover frequency, defined as the TON per unit time.





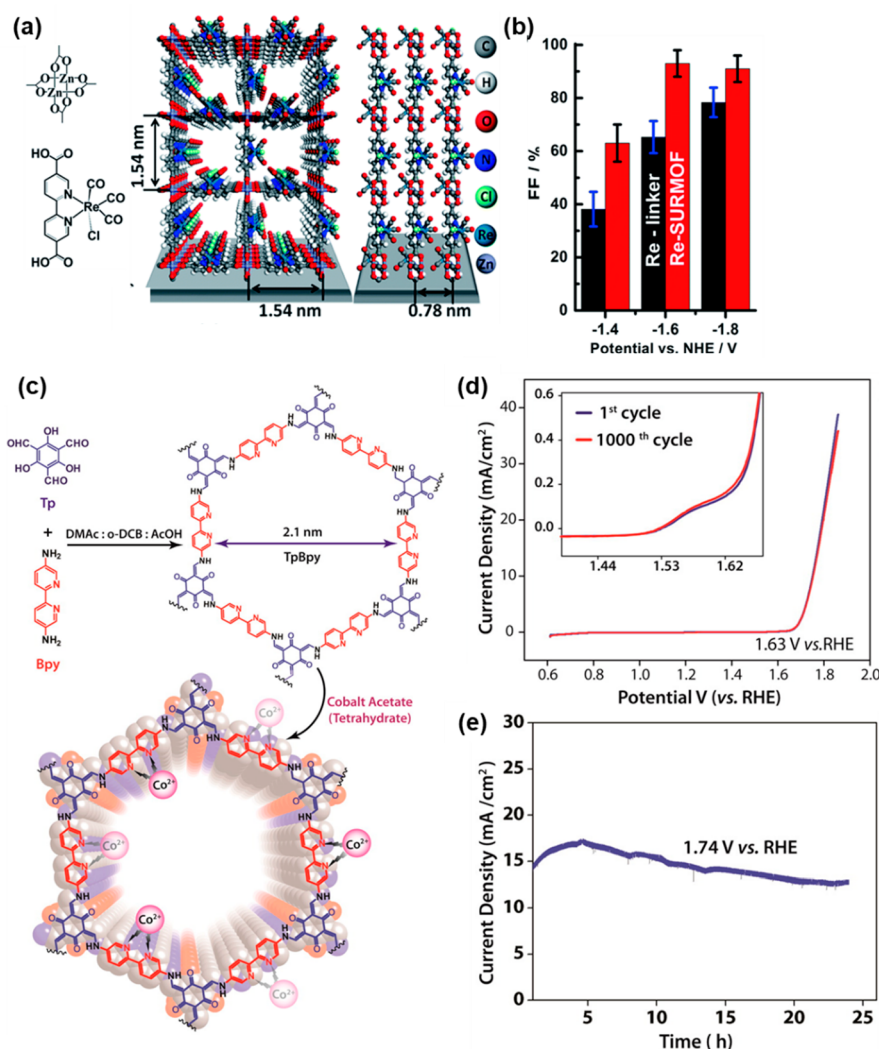
**Figure 1.** (a) Composition of cobalt-porphyrin-derived covalent organic frameworks. (b) Cyclic voltammograms of COF-366-Co, COF-366-(OMe)<sub>2</sub>-Co, COF-366-F-Co, and COF-366-(F)<sub>4</sub>-Co in *N,N*-dimethylformamide with tetrabutylammonium hexafluorophosphate as the electrolyte. (c) Current densities per milligram of cobalt in the different COF catalysts under an applied potential of  $-0.67$  V vs RHE in  $0.5$  M aqueous potassium bicarbonate buffer. Reproduced with permission from ref 32. Copyright 2018 American Chemical Society. (d) NiPc-NHTs monomer. (e) Crystal structure of NiPc-MOF. (f) LSV curves using the NiPc-MOF, NiPc-NHTs monomers, and blank FTO as catalysts for the OER. The scan rate was  $10$  mV s<sup>-1</sup>. Reprinted with permission from ref 68. Copyright 2018 Royal Society of Chemistry.

conductivity, studies have shown that functionalizing the framework with counterions allows the ion of interest to occupy the pores as a mobile phase. This phenomenon is observed in anionic frameworks like lithium-imidazole COFs and functionalized Zr-based MOFs that exhibit high Li-ion conductivity.<sup>52,53</sup> When considering proton mobility, a path of water molecules within the framework greatly promotes proton hopping via a Grotthuss-like mechanism with proton conductivities reaching up to  $10^{-2}$  S cm<sup>-1</sup>.<sup>54,55</sup> There is significant work still needed to bring conductivities to the level of Nafion, which has a proton conductivity up to  $0.3$  S cm<sup>-1</sup> upon incorporation into a zeolite.<sup>56</sup> Carefully tailoring the ionic properties of the framework can allow for more control over selective ion conductivity and mobility.

**2.4. Integration into Electrochemical Systems.** A significant factor that limits the utility of framework materials in electrochemical processes is inadequate contact between the framework and electrode surface, which increases interfacial resistance and limiting electron diffusion.<sup>29</sup> There are several methods to create a stronger framework-electrode interface. The most universally applied method is to make an ink containing the framework, a chemical binder (generally Nafion), and a conductive carbon material. The ink can be then drop-cast onto a substrate to form the electrode.<sup>57</sup> However, this technique has several drawbacks, including uneven deposition and poor interparticle and electrode contact. To overcome this issue, 2D framework materials have been synthesized directly on the electrode electrochemically or solvothermally upon the electrode as a thin film (typically in the range of  $100$ – $300$  nm),<sup>58,59</sup> increasing contact surface area. These surface-

anchored MOFs (or SURMOFs) form monolithic, highly crystalline domains that are intimately fixed to the electrode surface. Thin films of framework materials are also advantageous because they allow the substrate molecule to diffuse between the framework and the electrode, providing access to the catalytic active site. The electrochemical system can also be modified to better incorporate framework thin films for electrocatalysis. Frameworks have been designed to coat a porous electrode through which flowing substrate gas is continuously supplied at the surface of the catalyst, effectively preventing mass transport limitations.<sup>60</sup> More thoughtful electrode design will enable better catalytic outcomes for framework materials.

**2.5. Stability under Electrocatalytic Conditions.** Stability under electrolyzing conditions is another practical consideration when evaluating a molecular framework for electrocatalysts. Framework-based electrocatalysts mitigate the deactivation pathways for homogeneous active sites as described in previous sections of this Outlook. However, their stability is highly dependent on their local environment and the strength of coordination between metal-based nodes and organic struts. In a report by Zhang et al., a zeolitic imidazolate framework (ZIF-67) composed of cobalt-imidazole nodes was shown to undergo ligand replacements and phase transitions during electrochemical measurements to form a nonframework cobalt material that was found to be the catalytically active species.<sup>61</sup> It is therefore paramount to conduct careful controls to better understand the state of the electrocatalyst both throughout and following the experiment. A recent review by Ding et al. covers many different approaches toward stabilizing frameworks both synthetically and post synthetically.<sup>62</sup>



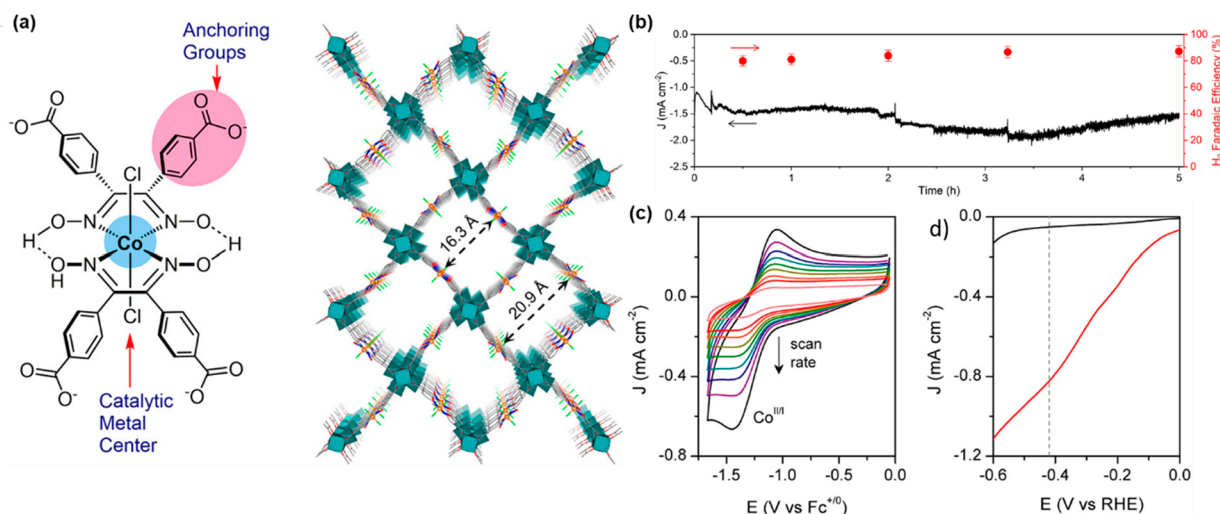
**Figure 2.** (a) Scheme of molecular Zn-carboxylate paddlewheels and Re-Bpy linkers and an atomic scale representation of the Re-SURMOF. (b) Carbon monoxide Faradaic efficiencies of the Re-SURMOF and Relinker (0.5 mM). Adapted with permission from ref 69. Copyright 2016 Royal Society of Chemistry. (c) Scheme of the synthesis and functionalization of TpBpy COF to form single Co active sites. (d) Linear sweep voltammogram profiles of the Co-modified COF before and after 1000 cycles. (e) Chronoamperometric stability profile of Co-TpBpy at 1.74 V (vs. RHE) for 24 h. Reprinted with permission from ref 70. Copyright 2016 American Chemical Society.

It is also important to consider the oxidation state of the metal centers and changes to the pore environment during electrocatalysis. Altering the oxidation state of a metal in a node may weaken the metal–linker bond and thereby compromise the overall structure of the framework. One way to stabilize redox active metal centers in frameworks is to shift the catalytic center to a scaffold in the pores, rather than the node or linker, which both increases connectivity and retains the framework structure during catalysis. Shen et al. incorporated a copper paddlewheel structure into the pore of an iron-based MOF, which greatly increased the paddlewheel's OER activity and prevented decomposition of the MOF.<sup>63</sup> In addition, frameworks are susceptible to decomposition upon exposure to acidic or alkaline conditions, resulting in an inevitable loss of structure.<sup>64</sup> Although many reports have discussed the decomposition of MOFs following electrolysis, we are unaware of any comprehensive studies on the factors for stabilizing a framework under electrochemical conditions.<sup>65</sup> More studies dedicated to determining what framework motifs contribute to electrochemical stability over a wide range of pH are essential to increasing the viability of frameworks in electrocatalytic systems.

### 3. EXTENDING MOLECULAR ACTIVE SITES INTO FRAMEWORK MATERIALS

In this section, we compare the activity of various electrocatalytic framework materials with that of the analogous molecular catalyst. Table 1 outlines important electrocatalytic metrics, when available, discussed in this Outlook.

**3.1. Pyrrole-Based Macrocycles.** Pyrrole-based macrocycles are prevalent active sites in numerous biocatalytic molecules,<sup>75</sup> including chlorophyll,<sup>76</sup> heme enzymes,<sup>77</sup> vitamin B12,<sup>78</sup> and in electrochemical applications.<sup>79,80</sup> These macrocycles exhibit high  $\pi$ -delocalization/conjugation and redox activity. Despite their importance in biology, molecular pyrrole-based macrocycles tend to have poor solubility and aggregate in solution, limiting their utility as homogeneous catalysts.<sup>81</sup> Immobilization of macrocycles within a framework solves these two problems by increasing their substrate accessibility and maintaining the activity of each catalytic site. To date, macrocycle-based frameworks<sup>82</sup> have been utilized for CO<sub>2</sub>RR,<sup>83</sup> HER,<sup>84</sup> OER,<sup>85</sup> and ORR.<sup>86</sup>



**Figure 3.** (a) Structure of the cobaloxime linker in the UU-100(Co) (left) structural model of UU-100(Co) MOF viewed along [001] plane (right). (b) Controlled potential electrolysis using UU-100(Co)/GCE at  $-0.45$  V (vs RHE) in acetate buffer (pH = 4). The black line represents geometric current density, and the red circles denote Faradaic efficiency for the HER. (c) Cyclic voltammograms of UU-100(Co)/GCE at different scan rates (0.2, 0.16, 0.14, 0.12, 0.1, 0.8, 0.06, 0.05, and 0.025 V s<sup>-1</sup>) in DMF. (d) Linear sweep voltammograms of UU-100(Co)/IGC (red) and blank GC (black) electrodes at pH 4 recorded at 20 mV s<sup>-1</sup> (the dashed line represents the potential that was selected for electrolysis). Reprinted with permission from ref 71. Copyright 2019 American Chemical Society.

Both MOFs and COFs have been derived from 5,10,15,20-tetrakis (4-aminophenyl) porphyrin (TAP).<sup>27</sup> In 2015, Lin et al. first synthesized COF-366-Co,<sup>66</sup> which was composed of TAP with a Co center and a 1,4-benzenedicarboxaldehyde, with 26 times the activity of the homogeneous catalyst toward CO<sub>2</sub>RR and a TON<sub>Co</sub> = 1352 compared to molecular Co(TAP) with a TON<sub>Co</sub> = 794 at the potential of  $-1.30$  V vs Ag/AgCl (note that the number of surface electroactive sites was determined by cyclic voltammetry). Extending pore size improved gas and ion diffusion which provides a TON<sub>Co</sub> = 3900 as a result. Adding electron withdrawing groups to the COF linker makes the Co(TAP) more amenable to electron acceptance in the catalytic mechanism and subsequently enhances selectivity toward CO production over H<sub>2</sub> (Figure 1a–c).<sup>32</sup> Cheung et al. incorporated a Fe-TAP-Cl with 2,5-dihydroxyterephthalaldehyde to observe its catalytic activity compared to the molecular Fe-TAP-Cl.<sup>57</sup> This COF was particularly advantageous in that it was synthesized directly on a carbon cloth electrode. This architecture provided the COF with better Faradaic efficiency (FE) than the molecular analogue, which can diffuse away from the electrode, toward CO production ( $\sim 80\%$  vs  $\sim 50\%$  over 3 h, respectively) at  $-2.1$  V vs Ag/AgCl. However, the COF also displayed decreased turnover frequency and compared to the molecular analogue (number of active sites was determined via cyclic voltammetry). Although, the COF thin film mitigated the leaching of the molecular catalyst, a drop of FE<sub>Co</sub> occurred within 3 h ( $\sim 90\%$  vs  $70\%$  over 3 h). The deactivation of catalytic activity was attributed to the decomposition of the porphyrin sites within the COF. These findings hint at the great potential for thin film porphyrin COFs to strengthen the catalytic abilities of metal porphyrins, although more research is needed to simultaneously improve selectivity and activity.

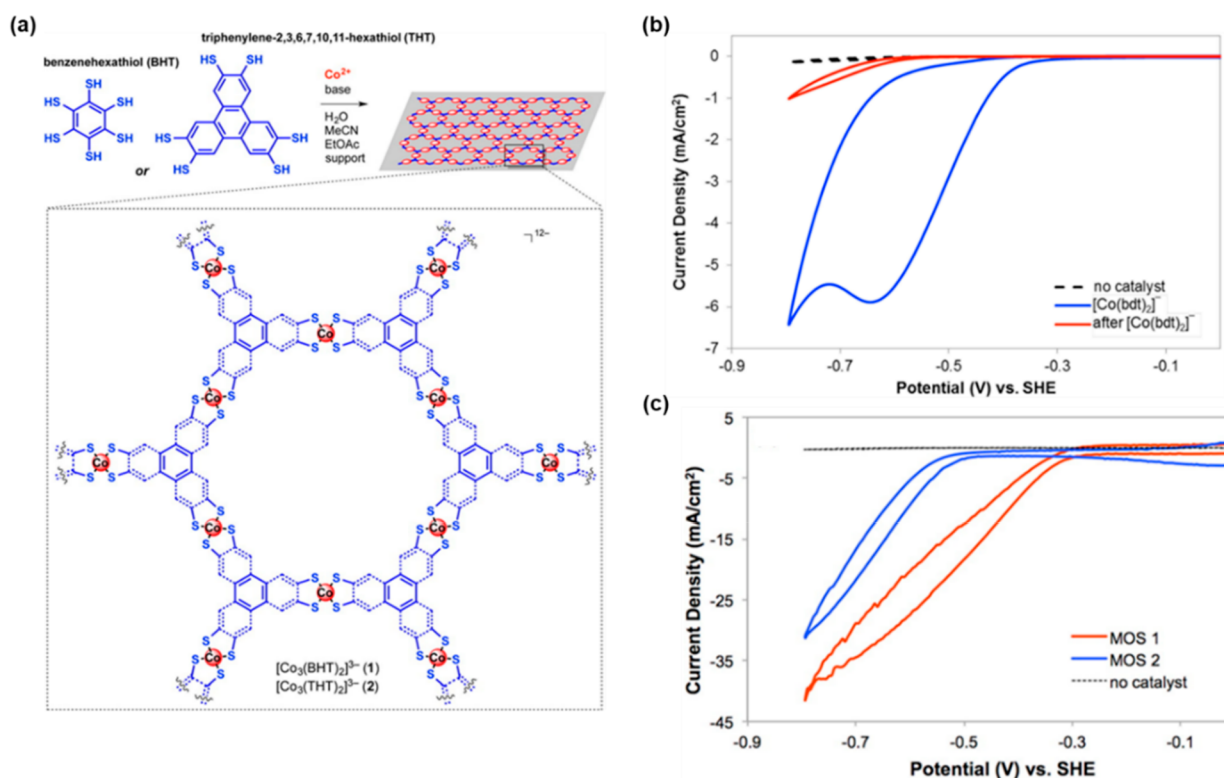
Recent work with pyrrole-based frameworks has also been evaluated for the electrocatalytic OER. In 2019, Huang et al. paired 5,10,15,20-(tetra-4-ethynylphenyl) porphyrin (Co-TEPP) with butadiyne linkages to form a robust COF which exhibited a 270 mV overpotential in the OER.<sup>67</sup> This overpotential is greatly improved from that of molecular

analogues, which are calculated at 370 mV.<sup>87</sup> The authors postulated that this improvement is due to the butadiyne linkers facilitating electron flow and the “expanded pore structure” enhancing mass transport. In addition, Jia et al. synthesized a 2D MOF composed of nickel nodes connected by nickel phthalocyanine linkers which can function as a catalyst for the OER (Figure 1d,e).<sup>68</sup> The framework displays an onset potential at 1.48 V vs Ag/AgCl compared to the molecular monomer, which is at 1.65 V vs Ag/AgCl as observed in Figure 1f. The catalyst also exhibits appreciable durability during long-term chronoamperometry ( $\sim 1.50$  V for 5 h) with no leaching of active material as evaluated by postelectrolysis UV–vis spectra of electrolyte. However, in postelectrolysis XPS, a slight increase of Ni 2p binding energy is observed, which is likely due to some structural rearrangement due to O binding with the Ni center. The enhanced catalytic behavior in this system was attributed to the structural motif of the framework that allowed for significant  $\pi$ -conjugation and conductivity (up to 0.2 S cm<sup>-1</sup>). The incorporation of macrocycles into frameworks provides new research directions with which to explore their electronic and chemical properties towards increased catalytic activity.

**3.2. Non-Macrocycle Coordination Compounds.** Many coordination complexes have been explored as homogeneous catalysts for a range of electrocatalytic transformations.<sup>65</sup> Unfortunately, inorganic complexes suffer from similar issues associated with other homogeneous analogues as described in the preface of this Outlook. Coordination complexes readily lend themselves toward incorporation in the linkers or nodes of extended frameworks. Several catalytic frameworks have been reported in the recent literature, with many of them relying on photoexcitation due to the largely insulating nature of MOFs.<sup>66</sup> However, several systems have been developed that utilize very specific synthetic designs to facilitate electron transfer between the electrode and the catalytic centers within the framework.

One recent system presented by Ye et al. used liquid phase epitaxy (LPE) to mount Zn-paddlewheel MOFs functionalized with Re complexes to fluorine-doped tin oxide (FTO) electrodes.<sup>69</sup> This surface-mounted rhenium MOF (or Re-





**Figure 4.** (a) Schematic diagram of MOS1 and MOS2 electrocatalytic film synthesis. (b) Cyclic voltammograms of 0.3 M  $[\text{Co}(\text{bdt})_2]^-$  soluble in 1:1 pH 1.3  $\text{H}_2\text{SO}_4$ :0.1 M  $\text{KNO}_3$  in acetonitrile (blue), after washing with  $5 \times 5$  mL of acetonitrile (red), scan rate  $100 \text{ mV s}^{-1}$ . (c) Cyclic voltammogram of MOS1 (red) and MOS2 (blue) in pH 1.3 aqueous  $\text{H}_2\text{SO}_4$ , scan rate  $100 \text{ mV s}^{-1}$ . Reprinted with permission from ref 72. Copyright 2015 American Chemical Society.

SURMOF), shown in Figure 2a, presented anisotropic charge migration that propagates perpendicular to the electrode surface following a redox hopping mechanism. The SURMOF exhibited an excellent capacity for  $\text{CO}_2\text{RR}$  as a result of the unique electrochemical integration of the MOF grafted on FTO. The authors compared the electrocatalytic performance of the framework to the free molecular complex. From Figure 2b, the framework material showed an enhanced current efficiency during controlled potential electrolysis with the highest  $\text{FE}_{\text{CO}}$  at 93.5% compared to the free molecule  $\text{FE}_{\text{CO}}$  65% at  $-1.6 \text{ V}$  vs NHE. The improved performance can be attributed to the increased concentration of active species at the electrode surface while maintaining a porous network for the free diffusion of the substrate. However, this SURMOF system is limited by short-range conductivity resulting from the insulating nature of electron deficient metal nodes. Additionally, a drop of overall current density was observed during bulk electrolysis in  $\text{CO}_2$  saturated electrolyte which was hypothesized to stem from the catalyst degradation.

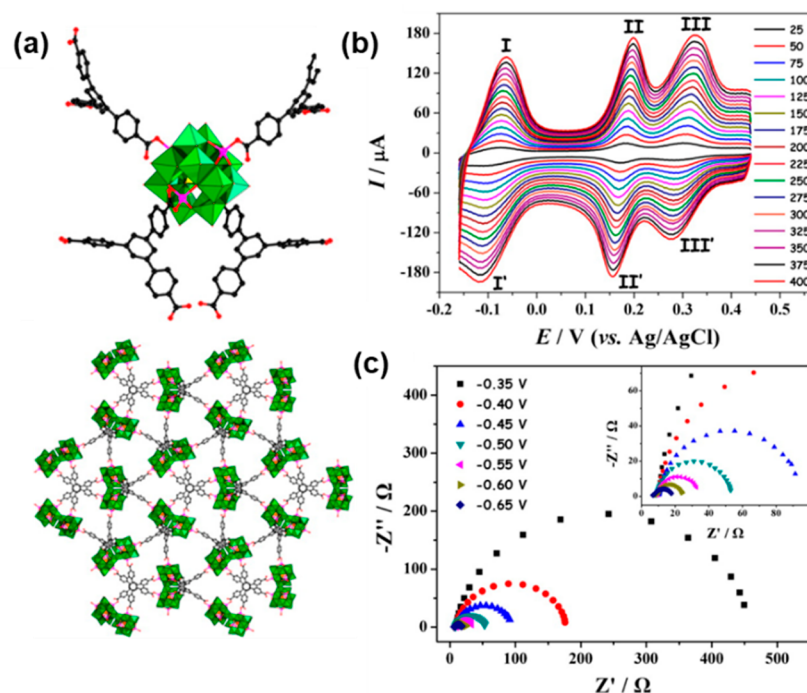
Unlike MOFs, covalent organic frameworks are formed exclusively by covalent bonds imparting great structural rigidity, chemical stability, and a higher degree of conductivity.<sup>27</sup> Aiyappa et al. presented Co-TpBpy, a COF system containing single Co-Bpy active sites, for the electrocatalytic OER (Figure 2c).<sup>70</sup> This system exhibited an excellent performance with an overpotential of 400 mV (at a current density of  $1 \text{ mA cm}^{-2}$ ) and a Tafel slope of  $59 \text{ mV dec}^{-1}$  (Figure 2d). Co-TpBpy demonstrated great catalytic stability following 1000 scans between 0.6 and 1.8 V vs RHE with a 94% retention of the current density during 24 h of controlled potential electrolysis at 1.74 V vs RHE (Figure 2d,e). A CV comparison study was

performed between the molecular starting material and the framework bound Co (II); the COF system demonstrated a prominent anodic wave at 1.6 V whereas the molecular species' catalytic onset was further anodically shifted by  $\sim 0.2 \text{ V}$  vs RHE.

Cobaloximes are a class of coordination complexes that have been widely applied as a hydrogen evolution catalyst.<sup>88</sup> Roy et al. demonstrated the growth of a novel 3D framework material (UU-100(Co)) thin film containing the cobaloxime active sites connected by Zr-oxo clusters grown over several conductive substrates and applied this system toward the HER (Figure 3a).<sup>71</sup> This thin film catalyst exhibited long-term stability during electrolysis ( $>18 \text{ h}$ ) with a  $\text{TON}_{\text{Co}}$  of 20 875, vastly outperforming the homogeneous catalyst ( $\text{TON}_{\text{Co}} = 10$ ), electropolymerized film ( $\text{TON}_{\text{Co}} = 420$ ), and carbon nanotube tethered analogue ( $\text{TON}_{\text{Co}} = 120$ ). The superior activity and robust nature of this catalytic system are attributed to rapid heterogeneous electron transfer kinetics throughout the framework and active site accessibility engendered by the porous nature of the framework.

Homogeneous square planar, redox active  $\text{MX}_4$  ( $\text{X} = \text{S}, \text{N}, \text{O}$ ) complexes have been actively studied for various electrocatalytic applications.<sup>89,90</sup> Among them, Co-dithiolene molecular systems have been widely reported for the photochemical and electrochemical HER.<sup>91–93</sup> Inspired by those molecular catalytic systems, Clough et al. incorporated the Co-dithiolene species to extended 2D metal organic surfaces (MOSs)  $[\text{Co}_3(\text{BHT})_2]^{3-}$  (MOS1, BHT = benzenehexathiophene) and  $[\text{Co}_3(\text{THT})_2]^{3-}$  (MOS2, THT = triphenylene-2,3,6,7,11,12-hexanethiol) (Figure 4a).<sup>72</sup> Both MOSs on glassy carbon substrates showed high activity for the HER in aqueous solution ( $J_{\text{MOS1}} = 4.3 \times 10^4 \text{ A mol}_{\text{Co}}^{-1}$ ,  $J_{\text{MOS2}} = 1.2 \times 10^4 \text{ A mol}_{\text{Co}}^{-1}$  at  $-0.63 \text{ V}$  vs SHE, pH 1.3, aqueous





**Figure 5.** (a) Connection mode between Zn- $\epsilon$ -Keggin and BTB3<sup>−</sup> molecular units and the 3D extended framework (NENU-500). (b) Cyclic voltammetry at different scan rates ( $\text{mV s}^{-1}$ ), measured in  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  aqueous solution. (c) Nyquist plots of NENU-500 examined at different potentials. (Inset denotes the magnified images of the high-frequency region.) Reprinted with permission from ref 74. Copyright 2015 American Chemical Society.

medium), which was an order of magnitude higher than the analogous molecular  $[\text{Co}(\text{bdt})_2]^-$  catalyst (bdt = benzene-1,2-dithiolene,  $J = 1.4 \times 10^2 \text{ A mol}_{\text{Co}}^{-1}$  at  $-0.63 \text{ V}$  vs RHE, 1:1  $\text{H}_2\text{O}$  (at pH 1.3):MeCN) (Figure 4b,c). Furthermore, a theoretical study by Tian et al. explored several metal bis-dithiolene nanosheets (Fe, Co, Ni, Rh, Ru) and predicted their  $\text{CO}_2\text{RR}$  activity and HER suppression. The Rh analogue was proposed to stabilize the  $\text{CHO}^*$  intermediate most effectively toward  $\text{CH}_4$  generation.<sup>94</sup>

The two-dimensionality of framework materials can also facilitate ligand-centered redox and charge transport. Miner et al. explored a similar metal diamine-based 2D framework,  $\text{Ni}_3(\text{HITP})_2$  (HITP = 2,3,6,7,10,11-hexaiminotriphenylene), for the ORR.<sup>95</sup> Their extensive investigation indicated that the catalytic activity arises from HITP.<sup>96</sup> Furthermore, significant ORR activity was observed when hexagonal crystal systems,  $\text{Cu}_3(\text{HITP})_2$ ,  $\text{Ni}_3(\text{HITP})_2$ , and  $\text{Co}_3(\text{HHTP})_2$  (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene), were used as the electrode material.<sup>97</sup> In contrast, minimal ORR activity in trigonal crystal systems in  $\text{Co}_3(\text{HHTP})_2$  and  $\text{Ni}_3(\text{HHTP})_2$  was attributed to the disruption of  $\pi$ - $\pi$  stacking interactions along the  $c$ -axis of the crystallographic plane. The  $\pi$ - $\pi$  stacking interactions and through-plane charge delocalization promoted charge transport that provides high catalytic activity in these frameworks. Additionally, Feng et al. developed a mixed ligand-based diamine-dithiolene ( $\text{MN}_2\text{S}_2$ ,  $\text{M} = \text{Co}, \text{Ni}$ ) framework nanosheet for the electrochemical HER and found an activity trend of  $\text{MN}_2\text{S}_2 > \text{MN}_4 > \text{MS}_4$ .<sup>98</sup> A metal-centered protonation and an M-N site assisted heterolytic elimination of  $\text{H}_2$  were proposed to be the reasons behind the unusually high HER activity. Overall, these studies paved the way to utilize unconventional coordination linkages and development of highly conductive framework materials for future catalytic applications.

**3.3. Polyoxometalates.** Polyoxometalates (POMs) are discrete transition metal clusters linked together by bridging oxygen atoms, resulting in highly accessible metal sites. POMs have been extensively used for applications in energy storage and conversion due to their incredible stability over a range of redox states.<sup>99</sup> They also possess intrinsic tunability by either varying heteroatoms or introducing vacancy sites. The application of POMs as molecular catalysts has been greatly hindered by many of the common limitations of traditional homogeneous systems including low stability over a range of pH conditions and low recyclability.<sup>100,101</sup> To circumvent these issues, recent work has been done to embed these clusters into the nodes of hybrid metal organic frameworks, referred to as POMOFs. The resulting materials are highly stable and porous and retain the unique redox features of POMs.

POMOFs can be formed by substituting heteroatoms of POMs with metal cations ( $\text{Zn}^{2+}$ ,  $\text{La}^{3+}$ , etc.) which can then be coordinated by organic linkers.<sup>102</sup> Frameworks prepared by this method have shown exceptional activity toward catalytic processes. Nohra et al. first presented a series of POMOF systems composed of redox active tetracoordinated molybdoxo clusters that exhibited variable activities for hydrogen evolution (Figure 5a,b).<sup>73</sup> The best performing of these frameworks consisted of trimetric acid linkers coordinated to Zn(II) capped phosphomolybdic acid (PMA) nodes (denoted as  $\epsilon(\text{trim})_{4/3}$ ), which exhibited an onset potential of +20 mV vs SCE, outperforming the benchmark Pt electrode (onset potential of  $-242 \text{ mV}$  vs SCE). Following this work, a similar POM-based framework was synthesized by Qin et al. with the goal of determining the chemical and electrocatalytic stability of POMOF catalysts for the HER.<sup>74</sup> The NENU-500 POMOF catalyst (Figure 5a) was composed of Zn(II) capped PMA coordinated by benzene tribenzoate linkers and displayed the best HER performance (onset potential = 180 mV and Tafel

slope = 96 mV dec<sup>-1</sup>) for these newly presented systems with a high chemical tolerance to various pH environments (pH = 1–12). The NENU-500 framework material maintained the characteristic redox features of POMs (Figure 5b) and exhibited admirable conductivity as shown by impedance measurements (Figure 5c). POMOF composite systems have also been exploited for the robust conductivity that is characteristic of POM-based systems. When Wang et al. combined Zn- $\epsilon$ -Keggin POMs with metalated tetrakis[4-carboxyphenyl]-porphyrin-M (M = Co, Fe, Ni, Zn), the POMOFs displayed a high CO<sub>2</sub>RR activity as a result of the strong electron donating capacity of the POM nodes to the catalytic active sites of the porphyrin linkers.<sup>103</sup> These composite systems open new avenues for robust, site-specific catalyst development, effectively coalescing MOF stability with POM functionality.

#### 4. CONCLUSION AND FUTURE DIRECTIONS

In summary, this Outlook demonstrates the benefits of covalent integration of homogeneous catalytic active sites into framework materials. We have discussed various properties of framework materials that are particularly attractive for electrocatalytic applications, such as their high surface area, porosity, and chemical tunability. These advantages are further highlighted by select molecular motifs, such as metal porphyrins and Re tricarbonyl complexes, that are commonly used in homogeneous catalysis. Conjugated 2D framework materials can facilitate charge transport and noninnocent ligand behavior. Taking advantage of molecular metal clusters, POMOFs can serve as a catalytic active site and a robust structural element and promote electron transport. The repeating units and porosity within a framework are crucial for maintaining active site utilization and substrate accessibility, a particular advance over homogeneous systems.

Despite significant progress over molecular systems, framework materials still face challenges compared to the state-of-the-art solid-state catalytic systems. While framework materials used for catalysis are chemically stable, most are electrically insulating, forcing redox hopping to be the only viable mechanism of electron transport between the electrode and the active site. To improve charge transport, greater clarity in how pore morphology and active site density impact the rate of electron transfer is necessary for further advancements.<sup>46,48,104,105</sup> Alternatively, unconventional coordination linkages such as those highlighted in this Outlook<sup>49,106–110</sup> can pave the way toward the development of more conductive framework materials. Furthermore, these linkages should be carefully chosen to improve both redox and chemical stability. More studies must be performed to determine how to strategically design frameworks that are stable under a range of pH values.

Moreover, thoughtful interfacial design between the electrode and framework can further improve charge mobility and electrochemical stability. Conventional methods of preparing ink slurries overlook the unique opportunity provided by framework materials that can be synthesized directly on the electrode. Perpendicular growth of the MOF/COF thin film can orient the crystallographic planes to maximize electron transport via anisotropic conduction pathways.<sup>111,112</sup> Furthermore, two different MOF films can be grown layer by layer via controlled liquid phase epitaxy to obtain a heterogeneous superstructure.<sup>113</sup> These heterogeneous SURMOFs can serve an interesting role in developing tandem electrochemical catalysis processes.

Another underexplored area in this field is modulating the secondary coordination environment of the active site by utilizing unique host–guest interactions. Molecular additives and ions trapped in the pores can influence both product selectivity and catalytic activity. In homogeneous chemistry, the electrostatic field of certain cationic species can impact the redox behavior of dissolved molecular complexes.<sup>114</sup> Interfacial chemistry in heterogeneous systems is commonly modulated by ionic additives<sup>115–117</sup> and electrolyte ions<sup>118–120</sup> in various electrocatalytic processes. Such strategies can be extrapolated to framework materials.<sup>121,122</sup> Future investigations into the role of trapped molecular additives and ions inside the pores of framework materials and their effects on the electrocatalytic behavior can provide new fundamental knowledge in catalyst design.

Taken together, incorporating molecular active sites into porous frameworks expands the experimental confines of traditional homogeneous catalysis. Framework materials can be specifically and rationally designed to incorporate molecular active sites, bridging the divide between homogeneous and heterogeneous catalysis. Although there are several challenges that need to be addressed in these integrated systems, framework materials offer a plethora of opportunities not only for elucidating catalytic mechanisms but also for advancing electrocatalytic conversions of small molecules to value-added products.

Framework materials can be specifically and rationally designed to incorporate molecular active sites, bridging the divide between homogeneous and heterogeneous catalysis.

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##### Notes

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