Stabilization of reactive Co_4O_4 cubane oxygen-evolution catalysts within porous frameworks

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A major challenge to the implementation of artificial photosynthesis (AP), in which fuels are produced from abundant materials (water and carbon dioxide) in an electrochemical cell through the action of sunlight, is the discovery of active, inexpensive, safe, and stable catalysts for the oxygen evolution reaction (OER). Multimetallc molecular catalysts, inspired by the natural photosynthetic enzyme, can provide important guidance for catalyst design, but the necessary mechanistic understanding has been elusive. In particular, fundamental transformations for reactive intermediates are difficult to observe, and well-defined molecular models of such species are highly prone to decomposition by intermolecular aggregation. Here, we present a general strategy for stabilization of the molecular cobalt-oxo cubane core (Co_4O_4) by immobilizing it as part of metal-organic frameworks, thus preventing intermolecular pathways of catalyst decomposition. These materials retain the OER activity and mechanism of the molecular Co_4O_4 analog yet demonstrate unprecedented long-term stability at pH 14. The organic linkers of the framework allow for chemical fine-tuning of activity and stability and, perhaps most importantly, provide “matrix isolation” that allows for observation and stabilization of intermediates in the water-splitting pathway.

artificial photosynthesis | mechanism | OER | cubane | MOF

One of the barriers to efficient conversion of sunlight into chemical fuels [artificial photosynthesis (AP)] is the lack of mechanistic understanding derived from functional yet stable molecularly designed catalysts (1). This barrier is especially relevant for the most challenging step of AP, the oxidation of water [the oxygen-evolution reaction (OER)] to provide protons and electrons for fuel production. The OER requires precise management of multiple reacting species and high-energy intermediates, with coordinated removal of four protons and four electrons per evolved dioxygen molecule, to achieve the efficiency needed for practical AP. In nature, this mechanistically challenging transformation is accomplished with a discrete cluster containing four manganese atoms known as the oxygen-evolving complex (OEC) (2–5). The cooperative action of these manganese centers provides fast and efficient water splitting and has inspired the design and synthesis of a large number of multimetallic molecular models (3, 6–9). However, despite this progress in mimicking the structure of the natural OER catalyst, synthetic molecular OER catalysts that correlate structure and function remain rare, particularly due to the known instability of many molecular complexes under OER conditions (10–16). Even rarer are catalysts that are made from earth-abundant elements, a requirement for large-scale implementation of AP. A notable exception is the cobalt(III)-oxo “cubane” cluster $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ (1), which emulates the OEC’s oxo-bridged arrangement of four metal centers and is unique among tetrametallic clusters in being demonstrated, in thorough mechanistic detail, as a functional OER catalyst (17,

18). The Co(III) centers in this cubane impart short-term stability, and the cluster is highly tunable by synthetic manipulation, making it an attractive starting point for mechanistic and structure–function relationship studies (19–21). Since the carboxylate ligand lability that is required for its water oxidation activity also causes eventual aggregation (and deactivation) of the cluster units (Scheme 1A) (17), a critical goal is the stabilization of the catalytic $[\text{Co}_4\text{O}_4]$ core to allow for more in-depth studies of its reactivity over a broader range of potentials, pHs, and timescales. This instability has prevented isolation or observation of reactive intermediates during the OER catalytic cycle and long-term electrocatalytic studies.

Nature elegantly addresses the stability problem for its tetramanganese OER catalyst with the highly tailored protein environment of photosystem II (Scheme 1B). This protein support encapsulates the OEC, stabilizing it against aggregation and degradation, while providing an electronic environment precisely tuned for the multiple redox steps of the OER. These two key elements of the natural system for OER, a molecular cluster and a tailored, stabilizing support, provide an essential blueprint

Significance

A long-standing goal in science seeks to understand and mimic photosynthesis. The water oxidation half-reaction of photosynthesis can be mimicked with bulk metal oxide catalysts, although with only modest efficiencies. Thus, there is immense effort to learn how bulk oxides operate and to identify critical mechanistic principles that can guide the design of improved catalysts. A functional molecular analogue of cobalt oxide water oxidation catalysts, the Co_4O_4 cubane, has provided a plethora of mechanistic information, although its instability in solution has prevented thorough characterization of key catalytic intermediates. We now show that a rigid coordination network greatly stabilizes this Co_4O_4 catalyst by providing a supporting “matrix,” immobilizing and preserving the key reactive intermediate to enable structural and catalytic characterization.

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A General reactivity pathways for molecular catalysts

B Site-isolation strategies that prevent catalyst deactivation via aggregation

Scheme 1. Factors affecting catalyst stability: Achieving catalytic turnover while limiting aggregation. (A) General reactivity pathways for molecular catalysts. (B) Site-isolation strategies that prevent catalyst deactivation via aggregation.

for new generations of catalysts that meet the stringent demands of practical AP. These themes have recently been applied in the incorporation of a $[\text{Co}_4\text{O}_4]$ cluster into the mutated pocket of a metalloprotein, which allowed stabilization of this active site against condensation, and manipulation of secondary sphere interactions in mediating multielectron, multiproton reactivity (22). Here, we report the greatly improved stability of a $[\text{Co}_4\text{O}_4]$ molecular cluster by covalent immobilization in a porous metal–organic framework. This strategy has allowed (i) significantly improved stability for a molecular OER catalyst (under practical, high pH conditions), and (ii) observation of a reactive, proposed (and otherwise unstable) intermediate in the OER mechanism (23–31). The organic linkers of these frameworks were optimized both for protection of the $[\text{Co}_4\text{O}_4]$ units from aggregation, and to provide electronic and structural tuning of reactivity (32–34). Reactivity and mechanistic experiments show that this immobilization strategy preserves the $[\text{Co}_4\text{O}_4]$ core throughout catalysis under the harsh conditions of OER.

Results and Discussion

Synthesis. The coordination networks were readily synthesized in a single-step ligand substitution reaction, whereby the parent

cubane $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ (**1**) was heated with an appropriate linker (as shown in Scheme 2). The Co_4O_4 -based materials were synthesized with five different organic linkers: 1,3,5-benzene tricarboxylate (BTC^{3-}), 1,3,5-tris(4-carboxylatophenyl)benzene (BTB^{3-}), tris(4-pyridyl)triazine (TPT), tris(4-pyridyl)pyridine (TPP), and tris(4-pyridyl)benzene (TPB). The resulting products are **Co₄-BTC**, **Co₄-BTB**, **Co₄-TPT**, **Co₄-TPP**, and **Co₄-TPB**. The **Co₄-TPT** product is a brick-red solid; **Co₄-TPP** is brown; **Co₄-TPB** is dark green; **Co₄-BTC** and **Co₄-BTB** are dark green (see *SI Appendix*, Fig. S19, for electronic absorbance spectra). The syntheses are done in one reaction vessel, with the longest reaction requiring 2 d, and are easily scaled to produce grams of material.

The empirical formulae for these solids, which contain stoichiometric excesses of ligand as determined by combustion analysis and NMR spectroscopy on digested solids (*SI Appendix*), suggest that the as-synthesized solids contain small framework domains capped by extrastochiometric linker ligands. This hypothesis is supported by spectroscopic analysis of the materials' structures (see below).

For any investigation into the inherent OER activity of a new Co OER catalyst, the known tendency of Co(II) ions to convert to Co oxides under OER conditions must be addressed (14, 35).

Scheme 2. Two routes for synthesis of cubane-derived framework materials.

On the other hand, Co(III) is inherently more stable than Co(II) toward ligand dissociation because of its intrinsically lower lability (36). While Co(II)-based framework materials have been studied for OER (37–42), no example of OER by a Co(III) framework has been reported before this work. Although the framework materials reported herein are based on Co(III), it is still essential to remove all traces of Co(II) that may be present as an impurity to accurately characterize the OER activity of the new materials. To remove any Co(II) formed during the synthesis, the networks were stirred in water with a chelating membrane (*SI Appendix*). An alternative method found to provide material of similar purity was Soxhlet extraction of the materials with boiling methanol over 16 h. This method is significantly faster than the chelation method and also produces material that is free of Co(II), as evidenced by the absence of any pink color in a chelating membrane when the Soxhlet-treated solids were stirred for 5 d together with the membrane.

Structural Characterization. The first indication that oxo cubane clusters are present in the networks came from spectroscopic observation of $[\text{Co}_4\text{O}_4]^{5+}$ derivatives, accessible by oxidation of the network materials. The analogous molecular cubane **1** can be oxidized to the isolable $[\text{Co}_4\text{O}_4]^{5+}$ species $\mathbf{1}^+$ (17, 19, 22), which has a characteristic electron paramagnetic resonance (EPR) signal at $g = 2.33$ (43). After oxidation with aqueous ceric ammonium nitrate for 1 h (*SI Appendix, Scheme S1*), each of the networks exhibited an EPR spectrum that is consistent with that reported for $\mathbf{1}^+$ (*SI Appendix, Fig. S18*) (43). Furthermore, the local environment and charge state of the cobalt for the $[\text{Co}_4\text{O}_4]$ building units are the same in all of the materials under study, as indicated by the X-ray absorption near edge structure (XANES). This technique has been used for the photosystem II active site (44–48), the cobalt oxide water-oxidation catalyst (49, 50), and Mn-oxo cubanes (9, 51–53). The XANES spectra from all of the compounds are highly similar to each other, indicating that the local charge state is the same in all of the compounds, and to the $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ (**1**) molecular species, which contains the Co(III)-oxo cubane structure (Fig. 1A). Based on these initial observations, the proposed local structures are shown in Fig. 2.

The as-synthesized networks lack long-range periodicity, as evidenced by the absence of sharp Bragg diffraction peaks in the powder X-ray diffraction pattern. It is important to note that crystallinity is not needed for the purpose of obtaining a tunable, porous

material that immobilizes the $[\text{Co}_4\text{O}_4]$ unit (54–59). To confirm that the cubane clusters survived the synthesis process and were incorporated into the coordination compounds we turned to two local structural methods, atomic pair distribution function (PDF) analysis of X-ray diffraction and Fourier-transform extended X-ray absorption fine structure (FT-EXAFS) analysis, that give structural information in the absence of crystalline long-range order (54). The low- r regions of both the FT-EXAFS (Fig. 1B) and PDF (Fig. 1C) patterns from all of the compounds are highly similar to each other and, in the EXAFS case, highly similar to that of the cubane-containing $\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4$ (**1**) compound (this compound was not studied by PDF). This evidence strongly supports the preservation of the cubane local structure in the network materials.

The presence of the $[\text{Co}_4\text{O}_4]$ cubane in the framework materials is further established by fitting structural models to the data. For EXAFS fits (Fig. 1B, shown in black), scattering paths and parameters determined from the crystal structure of **1** were used as a starting point and refined individually to each network spectrum (*SI Appendix*). In the PDF case, the local structures, including atomic coordinates, were generated for each compound using known network structure types with cubanes at the nodes joined by the relevant organic linker. These structures were then relaxed to an energy minimum using density functional theory (DFT) (see *SI Appendix* and below), and the resulting optimized structures were used as the starting models for PDF refinement (Fig. 1C, shown in black). The presence of interatomic scattering pairs from within the $[\text{Co}_4\text{O}_4]$ cubane, within the linkers, and between the cubane and the linkers, were confirmed in the data (*SI Appendix, Fig. S37*), establishing that the cubane survives and is incorporated into the network.

We now turn our attention to the higher-order network and pore structure. Framework porosity is important to provide access of reagents to the cubane linkers throughout the material, and therefore critical for catalytic efficiency. Although porosity is essential, the preservation of pore structure when solvent is not present (permanent porosity) is not needed for OER applications that are carried out in liquid solution, unlike other framework applications such as gas sorption and storage. We nonetheless estimated the permanent porosity using Brunauer–Emmett–Teller (BET) analysis of the N_2 adsorption isotherms of the solvent-free materials. First, thermogravimetric analysis was performed to measure the temperatures and amounts of thermal solvent elimination. All of the solids exhibited a significant mass loss (12–22%; *SI Appendix, Fig. S20*) at low temperature (60–100 °C), consistent with a large amount of unbound methanol solvent

Fig. 1. (A) Co K-edge absorption spectra, comparing framework materials (colored) to complex **1** (gray). (B) Fourier-transformed (FT) EXAFS spectra and (C) PDFs for the networks (colored) compared with simulated data (black) based on structural models. The colors of the curves are consistent between the panels. The spectra are offset vertically for clarity. See text and *SI Appendix* for details of model construction and fitting.

Fig. 2. Proposed local coordination environment of framework materials synthesized by (A) carboxylate exchange and (B) pyridine exchange.

within the pores of the as-synthesized materials (4–9 mol MeOH per mol [Co₄O₄]; *SI Appendix*) (60). After solvent removal, all of the solids are stable up to 200–250 °C. The BET results varied significantly between the different linker solids (*SI Appendix*, Figs. S21–S31). Two materials, Co₄-BTC and Co₄-TPB, showed no permanent porosity, suggesting pore collapse. On the other hand, Co₄-TPT and Co₄-TPP had high surface areas of 628 (2) m²/g and 527 (2) m²/g, respectively. Co₄-BTB exhibited a moderate surface area [*S*_{BET} = 191 (1) m²/g]. However, the permanent porosity as observed by gas adsorption and BET analysis does not necessarily reflect the surface area of a solvent-filled pore, and was not a strong indicator for OER activity, as we show later. It is therefore important to get information about the structure of the pores, collapsed or open, in the presence of solvent, which can be provided by the measured PDFs of the solvated products on longer length-scales. Sharp peaks are visible in the PDF to higher *r* values (*SI Appendix*, Fig. S38), up to 2 nm in some cases, indicating that the local geometry of the frameworks is quite rigid and well-defined, allowing the observation of scattering between rather distant atoms. The absence of bulk crystallinity observable by X-ray diffraction can then be understood to result from the framework structure not being rigidly arranged on a lattice, i.e., there is short-range ordering of relatively well-defined repeat units, but no long-range order.

To explore this hypothesis in greater detail, we searched for features in the PDF signal that yield direct information on long-range ordering of the framework structures. For a porous crystalline structure, long-wavelength oscillations in the PDF would be expected to appear superimposed on the shorter-wavelength features arising from within the constituent clusters and their linkers. These oscillations indicate the presence of both an ordered, crystalline framework and pores that are empty or filled with disordered solvent, and result from coherence between framework elements across one or more pores. This information would appear in the PDF on length-scales corresponding to the

pore–pore separation distance, ~1 nm or greater depending on the pore size. This region of the PDF is shown in *SI Appendix*, Fig. S38 for each of the materials. As presented in detail in *SI Appendix*, such an oscillation is evident in all of the samples at around 10 Å, but there is no long-wavelength oscillation in any of the compounds beyond ~30 Å. This suggests that all of the materials have well-defined local structures including pores with a separation of ~1.0–1.5 nm, but the rigidity is low, and pore–pore correlations are rapidly lost with increasing *r*. The combined evidence of the empirical formulae (from elemental analysis by combustion and NMR spectroscopy of digested solids; *SI Appendix*) with the lack of long-range order confirmed by PDF analysis suggests that the average framework domain sizes are small, with surfaces capped by extrastochiometric linker ligands.

Finally, to supplement the empirical observations from PDF of a well-defined, porous material lacking long-range order, atomic structural models were constructed and optimized by DFT. These models represent the idealized structure if long-range order were present and PDFs calculated from them (black lines in Fig. 1 and *SI Appendix*, Figs. S37 and S38) are consistent with the measured PDFs on shorter length scales (<6 Å). The models were constructed by placing the molecular units for the cubane and relevant linker on appropriate sites of candidate framework structures from the Reticular Chemistry Structure Resource (RCSR) (61). Details of their construction and optimization are presented in *SI Appendix*. Three of the proposed, DFT-optimized extended structures are shown in Fig. 3, and all are available in CIF format as *SI Appendix* for this paper.

Isolation and Characterization of a Hydroxide-Ligated Cobalt-Oxo Cubane. Oxygen evolution by the [Co₄O₄] cubane (**1**) and most cobalt oxides proceeds with greater efficiency at high pH. At high pH, hydroxide ions displace the acetate ligands of cubane **1** to generate the active form of the OER catalyst, [Co₄O₄(OAc)₃(OH)₂(py)₄][−] (**2**),

Scheme 3. Evidence for O–O bond formation via a cofacial hydroxo-oxo species. (A) Mechanism previously proposed: cofacial dioxo coupling. (B) Mechanism proposed herein: cofacial oxo-hydroxo coupling.

which contains a cofacial dihydroxide motif (17). Note that while some authors have proposed a geminal di-hydroxide mechanism for this process, our previous findings of a zero-order dependence in pyridine concentration for water oxidation by **1** lead to the conclusion that the cofacial dihydroxide intermediate **2** is active (17). This same cofacial dihydroxide motif is present at the catalytically active edge sites of cobalt oxide (62). However, molecular complexes **1** and **2** are unstable for long periods at high pH, since extra hydroxide ligands engage in further acetate displacement and condensation reactions that result in precipitation of CoO_x over the course of 1 h. This instability prevents use of the molecular system for long-term OER.

The rigid frameworks of these materials offer a strategy to stabilize the $[\text{Co}_4\text{O}_4]$ units under basic conditions. The framework structure spatially isolates the cubane units to prevent unwanted $[\text{Co}_4\text{O}_4]$ aggregation, thereby stabilizing the desired, cofacial dihydroxide active site. Indeed, ^1H NMR spectroscopy shows that **Co₄-TPT**, **Co₄-TPP**, and **Co₄-TPB** release acetate into solution via substitution by hydroxide during treatment at pH 14 (1.0 M NaOH) for at least 5 h (see *SI Appendix* for details). After hydroxide treatment, the materials were washed and soaked in water to achieve a final pH of 7–8. Analysis of the isolated solids by acid digestion and subsequent ^1H NMR spectroscopy indicates between 74% and 88% replacement of acetate relative to the starting composition (*SI Appendix*, Figs. S15–S17). The X-ray absorption spectroscopy (XAS) data indicate that the $[\text{Co}_4\text{O}_4]$ units are preserved with no evidence of CoO_x formation (Fig. 4A). Notably, sodium was not detected in the hydroxide-exchanged materials (by X-ray photoelectron spectroscopy; *SI Appendix*, Fig. S14), suggesting an overall neutral cluster (otherwise, Na^+ would be required for charge balance). The EXAFS data for these hydroxide-exchanged materials fit well to a DFT-optimized molecular model of $\text{Co}_4\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{py})_4$ (Fig. 4B; black traces in Fig. 4A). These materials are abbreviated hereafter as **Co₄-TPT-OH**, **Co₄-TPP-OH**, and **Co₄-TPB-OH**, and represent structural evidence (17, 19) of the proposed active form of the $[\text{Co}_4\text{O}_4]$ OER catalyst.

Importantly, the carboxylate-linked materials **Co₄-BTC** and **Co₄-BTB** are quite unstable in alkaline water, making them un-

suitable for studies over extended time periods under OER conditions. **Co₄-BTC** and **Co₄-BTB** completely decompose into CoOOH within an hour, as shown by EXAFS (*SI Appendix*, Fig. S34) and Raman spectroscopy (*SI Appendix*, Fig. S13). These results are consistent with the previous observation that hydroxide ions displace the carboxylate ligands in preference to the pyridyl ligands of **1** (17), which explains the rapid decomposition of the **Co₄-BTC** and **Co₄-BTB** frameworks at pH 14.

It is notable that the overall charge of the clusters in the isolated hydroxide-exchanged materials is neutral at pH ~ 8 (see below), resulting in $[\text{Co}^{\text{III}}_2(\text{H}_2\text{O})(\text{OH})]$ rather than $[\text{Co}^{\text{III}}_2(\text{OH})_2]$ structures on each of the four faces of the cube not ligated by the pyridyl backbone (Fig. 4B). This arrangement gives a total of one hydroxide and one water ligating each cobalt(III) center. While molecular cationic dicobalt complexes containing cofacial $[\text{Co}^{\text{III}}_2(\text{H}_2\text{O})_2]$ units in a naphthyridine ligand platform (62) exhibit pK_a values of 5.08 and 6.75, measurements of a $[\text{Co}_4\text{O}_4]$ artificial metalloprotein (22) determined that $\text{Co}^{\text{III}}\text{--OH}_2$ sites in a more electron-rich cubane environment had a pK_a value of 8.0. The latter pK_a value is consistent with the observed 1:1 ratio of $\text{Co}^{\text{III}}\text{--OH}_2$: $\text{Co}^{\text{III}}\text{--OH}$ moieties at pH 8 in **Co₄-TPT-OH**, **Co₄-TPP-OH**, and **Co₄-TPB-OH**. Additionally, the pK_a of $\text{Co}^{\text{III}}\text{--OH}_2$ in CoO_x has been estimated as ~7.5 (63).

The starting protonation state of a cobalt oxide catalyst has significant implications for the intermediate structures and mechanism of the crucial O–O bond-forming step in OER. Some studies (62, 64) with cobalt oxide at pH 7–8 have proposed that the O–O bond is formed at a cofacial di-oxo state, $[\text{Co}^{\text{IV}}_2(\text{O})_2]$, itself formed by a $2\text{H}^+/2e^-$ proton-coupled electron transfer (PCET) from a $[\text{Co}^{\text{III}}_2(\text{OH})_2]$ state. Our results, conversely, suggest that $[\text{Co}^{\text{III}}_2(\text{H}_2\text{O})(\text{OH})]$ is the starting protonation state, and thus a $2\text{H}^+/2e^-$ PCET would generate a cofacial oxo-hydroxo $[\text{Co}^{\text{IV}}_2(\text{OH})(\text{O})]$ unit as the immediate precursor to O–O bond formation (Scheme 3). Along with previous studies (17, 63) of cobalt oxide and the molecular cluster, **1**, which demonstrate that oxidation to Co^{IV} is a H^+/e^- PCET, our results suggest that the Co_4O_4 cluster accesses the cofacial dihydroxide state, $[\text{Co}^{\text{IV}}\text{Co}^{\text{III}}(\text{OH})_2]$, upon oxidation of the cluster to $[\text{Co}^{\text{IV}}\text{Co}^{\text{III}}_3\text{O}_4]$. Then, a second proton-coupled oxidation of the cluster to a formal $[\text{Co}^{\text{IV}}_2\text{Co}^{\text{III}}_2\text{O}_4]$

Fig. 3. Proposed extended structures of framework materials if long-range crystallinity were present. These extended structures were used to model the PDF data. Representative segments of the DFT-relaxed model structures of (A) $\text{Co}_4\text{-BTC}$ (pseudotbo topology), (B) $\text{Co}_4\text{-BTB}$ (pseudotbo topology), and (C) $\text{Co}_4\text{-TPT}$ (srs-c topology). Building units of (D) $\text{Co}_4\text{-BTC}$, (E) $\text{Co}_4\text{-BTB}$, and (F) $\text{Co}_4\text{-TPT}$.

or $[\text{Co}^{\text{V}}\text{Co}^{\text{III}}_3\text{O}_4]$ oxidation state, which has been supported by kinetics and electrochemical studies (17, 19, 65, 66), generates a cofacial $[\text{Co}^{\text{IV}}_2(\text{OH})(\text{O})]$ moiety that forms the O–O bond. These experimental results provide strong support of our previous linear free-energy analysis-based prediction (19) that an oxo-hydroxo ligated cubane is thermodynamically accessible during the OER catalytic cycle. Interestingly, a mechanistic study of CoO_x thin films by Nocera and coworkers (63) also inferred via electrochemical arguments that a $[\text{Co}^{\text{IV}}_2(\text{OH})(\text{O})]$ is likely formed after PCET events. While a cofacial di-oxo intermediate would suggest that O–O bond formation occurs via a symmetric radical coupling mechanism, the cofacial oxo-hydroxo intermediate consistent with our observations allows for the possibility of a nucleophilic attack mechanism. Additionally, the less symmetric cofacial oxo-hydroxo intermediate could permit a more localized valence tautomer involving a formal $\text{Co}^{\text{V}}\text{-oxo}/\text{Co}^{\text{IV}}\text{-oxyl}$ species, which has been proposed in some DFT calculations (64, 67, 68) of cobalt-catalyzed OER.

Stoichiometric Water Oxidation by Framework Materials. In the molecular species, the OER is initiated by oxidation to 1^+ by an electrode or chemical oxidant. Analogously, $\text{Co}_4\text{-TPT}$, $\text{Co}_4\text{-TPP}$, and $\text{Co}_4\text{-TPB}$ were oxidized by excess ceric ammonium nitrate to form the isolable species $[\text{Co}_4\text{-TPT}]^+$, $[\text{Co}_4\text{-TPP}]^+$, and $[\text{Co}_4\text{-TPB}]^+$ (see above). Notably, subsequent addition of one equivalent of NaOH to $[\text{Co}_4\text{-TPT}]^+$, $[\text{Co}_4\text{-TPP}]^+$, and $[\text{Co}_4\text{-TPB}]^+$ produced O_2 (Movie S1), in yields of 12%, 44%, and 30%, respectively, on the basis of $[\text{Co}_4\text{O}_4]$ units (Fig. 5A). Yields of O_2 lower than 100% and varying between the materials could result from incomplete oxidation by Ce(IV) , clogging of pores by residual Ce species (see above), or partial adventitious reduction of the oxidized networks

during workup before hydroxide addition (SI Appendix, Fig. S39). Nonetheless, these stoichiometric (i.e., nuncatalytic) OER experiments demonstrate the retention of molecular reactivity in the heterogeneous, porous solids. Presumably, the mechanism of these OERs is analogous to that determined for **1** and involves

Fig. 4. (A) Co-K edge EXAFS spectra of hydroxide-exchanged materials, $\text{Co}_4\text{-TPT-OH}$, $\text{Co}_4\text{-TPP-OH}$, and $\text{Co}_4\text{-TPB-OH}$. Experimental data are shown as colored lines, and the black lines are the fit to the DFT-optimized molecular model, $\text{Co}_4\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{py})_4$, shown in B.

Fig. 5. (A) Quantification of O₂ as percentage yield on the basis of [Co₄O₄] units, evolved from oxidized networks upon addition of 1 M NaOH. (B) Photograph showing bubbles of O₂ upon addition of 1 M NaOH to [Co₄-TPP]⁺ (Movie S1). (C) Comparison of Raman spectra for materials before and after OER; treatment at pH 14 for 5 h. Notably, peaks corresponding to cobalt oxide are absent from the spectra (69, 70).

electron-transfer redox disproportionation between oxidized cubane sites of the lattice, perhaps via a redox hopping mechanism such as that proposed in Fig. 6. The conservation of reactivity from **1** in the frameworks would then provide further evidence for the previously proposed cofacial dihydroxide mechanism (17). The Co₄-TPT, Co₄-TPP, and Co₄-TPB frameworks do not substantially change upon redox cycling (oxidation by Ce⁴⁺ followed

by reduction with OH⁻), as indicated by Raman spectra taken after the OERs described above (Fig. 5C). The spectra are largely the same as those of the pre-OER materials, but with some changes in intensities that may correspond to the partial replacement of acetate ligands with hydroxide. The stoichiometric OER demonstrates that these materials oxidize water by a well-defined mechanism that is a consequence of their molecular active site.

Fig. 6. Proposed redox-hopping mechanism to achieve a [Co(III)₂Co(IV)₂] or [Co(III)₃Co(V)] intermediate by redox disproportionation of two [Co(III)₃Co(IV)] clusters in Co₄-TPT.

Table 1. Redox potentials determined for Co₄-TPT, Co₄-TPP, and Co₄-TPB by CV

Compound	$E_{1/2}$ in MeCN, V vs. Fc/Fc ⁺	$E_{1/2}$ in H ₂ O, V vs. Ag/AgCl
1	0.280	1.008
Co₄-TPT	0.438	—
Co₄-TPP	0.351	1.052
Co₄-TPB	0.346	1.036

Prolonged Stability Under Electrochemical OER Conditions. For investigation of the electrochemical OER, we fabricated working electrodes modified with the pyridyl-linked networks **Co₄-TPT**, **Co₄-TPP**, and **Co₄-TPB**. These networks show reversible Co(III)/Co(IV) waves analogous to that of **1** in acetonitrile. This redox couple shifts toward more positive potentials moving from **Co₄-TPB** to **Co₄-TPP** to **Co₄-TPT**, following the trend of decreasing electron donation from the pyridyl linker (Table 1 and *SI Appendix*, Fig. S41). Importantly, these redox waves display scan rate-dependent currents characteristic of diffusion-controlled electron transfer (Randles-Sevcik behavior; *SI Appendix*, Fig. S42) (71); this behavior is suggestive of an electron-hopping charge transport mechanism within the material under the applied potential (72, 73). These materials are poorly conductive, as shown by the electroactive fraction during a cyclic voltammetry (CV) sweep at 100 mV/s: 4.0% for **Co₄-TPT**, 5.7% for **Co₄-TPP**, and 3.2% for **Co₄-TPB** (see *SI Appendix* for calculation). The materials show similar behavior in aqueous solution (pH 7; 0.1 M KPi buffer); however, the peaks for **Co₄-TPT** were too broad to observe. The CVs of **Co₄-TPP** and **Co₄-TPB** with well-defined redox waves and low current at 1,300 mV vs. Ag/AgCl are also consistent with pure material (Fig. 7, green curves; Table 1), free of Co(II)-containing impurities as determined by the method of Nocera and coworkers (14). Increasing the pH of the solutions to 11 and 12 (Fig. 7, blue and red curves) led to an OER electrocatalytic current originating from the Co(III)/Co(IV) redox couple. The potential of this electrocatalytic wave is comparable to that of molecular cubane **1** (17). There is a small but clear reduction in overpotential for **Co₄-TPB** relative to **Co₄-TPP**, reflecting the intrinsic electronic differences of these materials and demonstrating the potential to tune electronic properties via modifications of the ancillary ligands (19).

The hydroxide-exchanged materials **Co₄-TPP-OH** and **Co₄-TPB-OH** are highly active OER catalysts. The overpotentials required to reach a current density of 10 mA/cm² during CV in pH 14 water were 464 mV for **Co₄-TPP-OH** and 430 mV for **Co₄-TPB-OH**, which are comparable to those observed for cobalt oxide (Fig. 7) (74). The applied potential required to reach a current density of 10 mA/cm² in a controlled-current electrolysis was found to be steady (<10% decrease in overpotential after an initiation period of ~30 s) for at least 5 h (*SI Appendix*, Fig. S43), demonstrating a dramatic stabilizing effect of [Co₄O₄] immobilization. The product was confirmed to be oxygen with faradaic efficiencies of 87–99% (*SI Appendix*). While electrochemistry alone cannot distinguish whether the active OER catalyst is cobalt oxide or the intact framework materials, structural evidence from EXAFS and Raman spectroscopy, which shows the presence of the *syn*-dihydroxide, supports [Co₄O₄]-based OER. Again, the differences in overpotentials are correlated with the basicity of the pyridyl linker, reinforcing the concept of molecular-level tunability. The Tafel slopes for **Co₄-TPP** and **Co₄-TPB** were 69 and 64 mV/dec, respectively, indicating a catalytic mechanism that involves an electron-transfer pre-equilibrium before a rate-determining chemical step. This mechanism is consistent with that proposed for OER by **1** and cobalt oxide catalysts (17, 75).

Conclusions

Porous, solid-state materials derived from a [Co₄O₄] cubane, one of the most intriguing molecular structures capable of water oxidation, have been prepared. Despite lacking long-range crystallinity, the materials fulfill the key criterion of immobilizing a molecular [Co₄O₄] unit inside a porous metal–organic framework. As demonstrated here, this allows for a “matrix isolation” approach to observation of reactive intermediates in the catalytic cycle. An ensemble of techniques, including UV-visible absorption, EPR, PDF, and X-ray absorption spectroscopies, confirmed the preservation of [Co₄O₄] units in the resulting coordination networks. Nitrogen adsorption and PDF analysis provide experimental evidence for particular DFT-refined structural models for all of these porous materials, despite the absence of long-range crystallographic order. Favorable properties attained by the coordination networks, relative to those of the parent cubane complex **1**, include high porosity, good thermal stability, and resistance to the deactivating condensation processes associated with water-oxidizing conditions. Most significantly, the “matrix isolation” strategy described here enabled isolation and characterization of a key hydroxide-ligated

Fig. 7. (A) CV traces in 0.1 M KPi (aq.) at pH 7, 11, and 12 and 100 mV/s scan rate for **Co₄-TPP** (solid lines) and **Co₄-TPB** (dashed lines). The currents (*i*) were normalized to the peak current under noncatalytic conditions (*i_p*). (B) Linear sweep voltammogram (LSV) of **Co₄-TPP-OH** and **Co₄-TPB-OH** in pH 14 (1 M NaOH) solution. Inset shows the Tafel slopes.

cubane complex, which is central to proposed mechanisms of cobalt-catalyzed OER. While there is strong evidence that the O–O bond formation occurs at a cofacial edge site of CoO_x , the exact details about the identity of the Co–O species and the manner in which the bond is formed remain uncertain. The two prevailing hypotheses invoke either a symmetrical radical coupling of two cofacial Co^{IV} –oxo moieties or an asymmetric nucleophilic attack of hydroxide onto a high-valent Co–oxo unit. The characterization of this isolated intermediate identifies a protonation state of the oxygen-type ligands that lends support for a cofacial oxo-hydroxo species compatible with an intramolecular nucleophilic attack mechanism. Stoichiometric oxidation with Ce(IV) provides further evidence that these networks operate via a well-defined OER mechanism analogous to that of **1** (17), and electrocatalytic experiments demonstrate rational activity trends and the suitability of such materials in heterogeneous catalysis. However, these materials are nonconductive and only small fractions of the materials are electrochemically active. Thus, future catalyst designs should incorporate features, such as redox-active linker ligands, that promote charge transport. The results presented in this work provide the basic design and synthesis of new metal-organic networks for OER catalysis and illustrate the potential of applying molecular design principles to heterogeneous catalysis.

Materials and Methods

General Procedures. Solvents were purchased from commercial sources and used without any further purification. Water was deionized using a MilliQ system. All manipulations were performed in air unless noted. Details of all procedures are provided in *SI Appendix*.

Synthesis. Cubane **1** (17, 20), 1,3,5-tris(4-pyridyl)triazine (76), 2,4,6-tris(4-pyridyl)pyridine (77), and 1,3,5-tris(4-pyridyl)benzene (78) were synthesized according to published procedures. For carboxylate linked materials, cubane **1** and the tricarboxylic acid were stirred in methanol at 60 °C for 2 h. The resulting dark green solid was collected by filtration and washed with methanol. A section of Empore SPE chelating membrane was stirred with each material for 5 d at a time, after which the chelating membrane was checked for pink color. For pyridyl linked materials, cubane **1** and the tripyridyl ligand were suspended in benzonitrile in a Schlenk tube. An active vacuum was applied, and the vessel was heated to 90 °C for 2 d. The dark solid was collected by filtration, transferred to a Soxhlet apparatus, and extracted with methanol for 24 h. To exchange the labile ligands for hydroxide, each sample was sus-

pended in 1 M NaOH solution and stirred gently for 5 h, then collected by filtration and washed with water, and then soaked in water for 12 h.

Structural Characterization. XAS measurements were performed on powdered samples at –20 °C, under the threshold of X-ray damage as monitored by the XANES edge shift. Energy was calibrated using a Co foil. Fitting of the experimental data was performed using initial Co nearest-neighbor paths from the crystal structure of **1**. X-ray total scattering and pair-distribution function measurements were collected on powdered samples at 100 K using an X-ray wavelength of 0.1827 Å. The experimental setup was calibrated using a Ni standard. The experimental PDF data were fit using structural models assembled using the symmetry of known network structures compatible with the linker and cubane bonding, the models having been optimized by DFT before their use in fitting the PDF.

Chemical and Electrochemical OER. The chemical OER experiments were performed with oxidized frameworks, which were produced by stirring with Ce(IV) . Under a N_2 atmosphere, a solution of 1 M NaOH was added, and O_2 production was measured using an Ocean Optics Multi-Frequency Phase Fluorimeter (MFPF-100) with a FOSPOR-R probe. For electrode fabrication, suspensions of the materials were drop-cast onto polished, glassy carbon electrodes. Electrochemical measurements were performed with a three-electrode setup.

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1. N. S. Lewis, D. G. Nocera, Powering the planet: Chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U.S.A.* **103**, 15729–15735 (2006).
2. J. P. McEvoy, G. W. Brudvig, Water-splitting chemistry of photosystem II. *Chem. Rev.* **106**, 4455–4483 (2006).
3. G. C. Dismukes *et al.*, Development of bioinspired Mn_4O_4 -cubane water oxidation catalysts: Lessons from photosynthesis. *Acc. Chem. Res.* **42**, 1935–1943 (2009).
4. M. Suga *et al.*, Native structure of photosystem II at 1.95 Å resolution viewed by femtosecond X-ray pulses. *Nature* **517**, 99–103 (2015).
5. M. M. Najafpour, M. Z. Ghobadi, A. W. Larkum, J.-R. Shen, S. I. Allakhverdiev, The biological water-oxidizing complex at the nano-bio interface. *Trends Plant Sci.* **20**, 559–568 (2015).
6. K. Meelich, C. M. Zaleski, V. L. Pecoraro, Using small molecule complexes to elucidate features of photosynthetic water oxidation. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* **363**, 1271–1279, discussion 1279–1281 (2008).
7. J. S. Kanady, E. Y. Tsui, M. W. Day, T. Agapie, A synthetic model of the Mn_3Ca subsite of the oxygen-evolving complex in photosystem II. *Science* **333**, 733–736 (2011).
8. J. S. Kanady *et al.*, Oxygen atom transfer and oxidative water incorporation in cuboidal Mn_3MO_4 complexes based on synthetic, isotopic labeling, and computational studies. *J. Am. Chem. Soc.* **135**, 1073–1082 (2013).
9. E. Y. Tsui, R. Tran, J. Yano, T. Agapie, Redox-inactive metals modulate the reduction potential in heterometallic manganese-oxido clusters. *Nat. Chem.* **5**, 293–299 (2013).
10. R. H. Crabtree Resolving heterogeneity problems and impurity artifacts in operationally homogeneous transition metal catalysts. *Chem. Rev.* **112**, 1536–1554 (2012).
11. R. H. Crabtree, Deactivation in homogeneous transition metal catalysis: Causes, avoidance, and cure. *Chem. Rev.* **115**, 127–150 (2015).
12. R. K. Hocking *et al.*, Water-oxidation catalysis by manganese in a geochemical-like cycle. *Nat. Chem.* **3**, 461–466 (2011).
13. M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark, Artificial photosynthesis: Molecular systems for catalytic water oxidation. *Chem. Rev.* **114**, 11863–12001 (2014).
14. A. M. Ullman *et al.*, Water oxidation catalysis by Co(II) impurities in $\text{Co(III)}_4\text{O}_4$ cubanes. *J. Am. Chem. Soc.* **136**, 17681–17688 (2014).
15. J. J. Stracke, R. G. Finke, Distinguishing homogeneous from heterogeneous water oxidation catalysis when beginning with polyoxometalates. *ACS Catal.* **4**, 909–933 (2014).
16. B. M. Hunter, H. B. Gray, A. M. Müller, Earth-abundant heterogeneous water oxidation catalysts. *Chem. Rev.* **116**, 14120–14136 (2016).
17. A. I. Nguyen *et al.*, Mechanistic investigations of water oxidation by a molecular cobalt oxide analogue: Evidence for a highly oxidized intermediate and exclusive terminal oxo participation. *J. Am. Chem. Soc.* **137**, 12865–12872 (2015).
18. P. F. Smith *et al.*, Water oxidation by the $[\text{Co}_4\text{O}_4(\text{OAc})_4(\text{py})_4]^+$ cubium is initiated by OH^- addition. *J. Am. Chem. Soc.* **137**, 15460–15468 (2015).
19. A. I. Nguyen, J. Wang, D. S. Levine, M. S. Ziegler, T. D. Tilley, Synthetic control and empirical prediction of redox potentials for Co_4O_4 cubanes over a 1.4 V range: Implications for catalyst design and evaluation of high-valent intermediates in water oxidation. *Chem. Sci.* **8**, 4274–4284 (2017).
20. R. Chakrabarty, S. J. Bora, B. K. Das, Synthesis, structure, spectral and electrochemical properties, and catalytic use of cobalt(III)-oxo cubane clusters. *Inorg. Chem.* **46**, 9450–9462 (2007).
21. S. Berardi *et al.*, Photocatalytic water oxidation: Tuning light-induced electron transfer by molecular Co_4O_4 cores. *J. Am. Chem. Soc.* **134**, 11104–11107 (2012).
22. L. Olshansky *et al.*, Artificial metalloproteins containing Co_4O_4 cubane active sites. *J. Am. Chem. Soc.* **140**, 2739–2742 (2018).
23. S. M. J. Rogge *et al.*, Metal-organic and covalent organic frameworks as single-site catalysts. *Chem. Soc. Rev.* **46**, 3134–3184 (2017).
24. G. Cai, W. Zhang, L. Jiao, S.-H. Yu, H.-L. Jiang, Template-directed growth of well-aligned MOF arrays and derived self-supporting electrodes for water splitting. *Chem* **2**, 791–802 (2017).
25. H.-C. Zhou, J. R. Long, O. M. Yaghi, Introduction to metal-organic frameworks. *Chem. Rev.* **112**, 673–674 (2012).
26. C. Wang, Z. Xie, K. E. deKrafft, W. Lin, Doping metal-organic frameworks for water oxidation, carbon dioxide reduction, and organic photocatalysis. *J. Am. Chem. Soc.* **133**, 13445–13454 (2011).

27. C. Wang, J.-L. Wang, W. Lin, Elucidating molecular iridium water oxidation catalysts using metal-organic frameworks: A comprehensive structural, catalytic, spectroscopic, and kinetic study. *J. Am. Chem. Soc.* **134**, 19895–19908 (2012).
28. H. Fei, M. D. Sampson, Y. Lee, C. P. Kubiak, S. M. Cohen, Photocatalytic CO₂ reduction to formate using a Mn(II) molecular catalyst in a robust metal-organic framework. *Inorg. Chem.* **54**, 6821–6828 (2015).
29. E. D. Metzger, C. K. Brozek, R. J. Comito, M. Dincă, Selective dimerization of ethylene to 1-butene with a porous catalyst. *ACS Cent. Sci.* **2**, 148–153 (2016).
30. J. He et al., A PCP pincer ligand for coordination polymers with versatile chemical reactivity: Selective activation of CO₂ gas over CO gas in the solid state. *Angew. Chem. Int. Ed. Engl.* **55**, 12351–12355 (2016).
31. B. L. Wadsworth, D. Khusnutdinova, G. F. Moore, Polymeric coatings for applications in electrocatalytic and photoelectrosynthetic fuel production. *J. Mater. Chem. A* **6**, 21654–21665 (2018).
32. K. Meyer, M. Ranocchiari, J. A. van Bokhoven, Metal organic frameworks for photocatalytic water splitting. *Energy Environ. Sci.* **8**, 1923–1937 (2015).
33. S. Lin et al., Covalent organic frameworks comprising cobalt porphyrins for catalytic CO₂ reduction in water. *Science* **349**, 1208–1213 (2015).
34. N. Kornienko et al., Metal-organic frameworks for electrocatalytic reduction of carbon dioxide. *J. Am. Chem. Soc.* **137**, 14129–14135 (2015).
35. J. J. Stracke, R. G. Finke, Water oxidation catalysis beginning with 2.5 μM [Co₄(H₂O)₂(PW₆O₃₄)₂]¹⁰⁻: Investigation of the true electrochemically driven catalyst at ≥600 mV overpotential at a glassy carbon electrode. *ACS Catal.* **3**, 1209–1219 (2013).
36. C. H. Langford, H. B. Gray, *Ligand Substitution Processes* (W. A. Benjamin, Inc., New York, 1966).
37. H. B. Aiyappa, J. Thote, D. B. Shinde, R. Banerjee, S. Kurungot, Cobalt-modified covalent organic framework as a robust water oxidation electrocatalyst. *Chem. Mater.* **28**, 4375–4379 (2016).
38. X.-F. Lu et al., An alkaline-stable, metal hydroxide mimicking metal-organic framework for efficient electrocatalytic oxygen evolution. *J. Am. Chem. Soc.* **138**, 8336–8339 (2016).
39. S. Zhao et al., Ultrathin metal-organic framework nanosheets for electrocatalytic oxygen evolution. *Nat. Energy* **1**, 16184 (2016).
40. S. Xiang et al., A 3D canted antiferromagnetic porous metal-organic framework with anatase topology through assembly of an analogue of polyoxometalate. *J. Am. Chem. Soc.* **127**, 16352–16353 (2005).
41. J. Jiang, L. Huang, X. Liu, L. Ai, Bioinspired cobalt-citrate metal-organic framework as an efficient electrocatalyst for water oxidation. *ACS Appl. Mater. Interfaces* **9**, 7193–7201 (2017).
42. J.-Q. Shen et al., Modular and stepwise synthesis of a hybrid metal-organic framework for efficient electrocatalytic oxygen evolution. *J. Am. Chem. Soc.* **139**, 1778–1781 (2017).
43. J. G. McAlpin et al., Electronic structure description of a [Co(III)₃Co(IV)O₄] cluster: A model for the paramagnetic intermediate in cobalt-catalyzed water oxidation. *J. Am. Chem. Soc.* **133**, 15444–15452 (2011).
44. T.-A. Ono et al., X-ray detection of the period-four cycling of the manganese cluster in photosynthetic water oxidizing enzyme. *Science* **258**, 1335–1337 (1992).
45. V. K. Yachandra, K. Sauer, M. P. Klein, Manganese cluster in photosynthesis: Where plants oxidize water to dioxygen. *Chem. Rev.* **96**, 2927–2950 (1996).
46. L. Iuzzolino, J. Dittmer, W. Dörner, W. Meyer-Klaucke, H. Dau, X-ray absorption spectroscopy on layered photosystem II membrane particles suggests manganese-centered oxidation of the oxygen-evolving complex for the S0-S1, S1-S2, and S2-S3 transitions of the water oxidation cycle. *Biochemistry* **37**, 17112–17119 (1998).
47. J. Messinger et al., Absence of Mn-centered oxidation in the S(2) → S(3) transition: Implications for the mechanism of photosynthetic water oxidation. *J. Am. Chem. Soc.* **123**, 7804–7820 (2001).
48. J. Yano, V. K. Yachandra, Oxidation state changes of the Mn₄Ca cluster in photosystem II. *Photosynth. Res.* **92**, 289–303 (2007).
49. M. Risch et al., Cobalt-oxo core of a water-oxidizing catalyst film. *J. Am. Chem. Soc.* **131**, 6936–6937 (2009).
50. M. W. Kanan et al., Structure and valency of a cobalt-phosphate water oxidation catalyst determined by in situ X-ray spectroscopy. *J. Am. Chem. Soc.* **132**, 13692–13701 (2010).
51. J. S. Kanady et al., Role of oxido incorporation and ligand lability in expanding redox accessibility of structurally related Mn₄ clusters. *Chem. Sci.* **4**, 3986–3996 (2013).
52. S. Suseno et al., Molecular mixed-metal manganese oxido cubanes as precursors to heterogeneous oxygen evolution catalysts. *Chemistry* **21**, 13420–13430 (2015).
53. K. M. Van Allsburg, E. Anzenberg, W. S. Drisdell, J. Yano, T. D. Tilley, Oxygen-atom transfer chemistry and thermolytic properties of a di-tert-butylphosphate-ligated Mn₄O₄ cubane. *Chemistry* **21**, 4646–4654 (2015).
54. T. D. Bennett, A. K. Cheetham, Amorphous metal-organic frameworks. *Acc. Chem. Res.* **47**, 1555–1562 (2014).
55. S. J. Kraft, R. H. Sánchez, A. S. Hock, A remarkably active iron catecholate catalyst immobilized in a porous organic polymer. *ACS Catal.* **3**, 826–830 (2013).
56. S. J. Kraft et al., Rhodium catechol containing porous organic polymers: Defined catalysis for single-site and supported nanoparticle materials. *Organometallics* **33**, 2517–2522 (2014).
57. K. K. Tanabe et al., Discovery of highly selective alkyne semihydrogenation catalysts based on first-row transition-metallated porous organic polymers. *Angew. Chem. Int. Ed. Engl.* **53**, 12055–12058 (2014).
58. J. Camacho-Bunquin et al., Synthesis and catalytic hydrogenation reactivity of a chromium catecholate porous organic polymer. *Organometallics* **34**, 947–952 (2015).
59. J. Camacho-Bunquin et al., Supported aluminum catalysts for olefin hydrogenation. *ACS Catal.* **7**, 689–694 (2016).
60. T. M. McDonald, E. D. Bloch, J. R. Long, Rapidly assessing the activation conditions and porosity of metal-organic frameworks using thermogravimetric analysis. *Chem. Commun. (Camb.)* **51**, 4985–4988 (2015).
61. M. O’Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, The Reticular Chemistry Structure Resource (RCSR) database of, and symbols for, crystal nets. *Acc. Chem. Res.* **41**, 1782–1789 (2008).
62. A. M. Ullman, C. N. Brodsky, N. Li, S.-L. Zheng, D. G. Nocera, Probing edge site reactivity of oxidic cobalt water oxidation catalysts. *J. Am. Chem. Soc.* **138**, 4229–4236 (2016).
63. Y. Surendranath, M. W. Kanan, D. G. Nocera, Mechanistic studies of the oxygen evolution reaction by a cobalt-phosphate catalyst at neutral pH. *J. Am. Chem. Soc.* **132**, 16501–16509 (2010).
64. L.-P. Wang, T. van Voorhis, Direct-coupling O₂ bond forming a pathway in cobalt oxide water oxidation catalysts. *J. Phys. Chem. Lett.* **2**, 2200–2204 (2011).
65. C. N. Brodsky et al., In situ characterization of cofacial Co(IV) centers in Co₄O₄ cubane: Modeling the high-valent active site in oxygen-evolving catalysts. *Proc. Natl. Acad. Sci. U.S.A.* **114**, 3855–3860 (2017).
66. C. Costentin, T. R. Porter, J. M. Savéant, Conduction and reactivity in heterogeneous-molecular catalysis: New insights in water oxidation catalysis by phosphate cobalt oxide films. *J. Am. Chem. Soc.* **138**, 5615–5622 (2016).
67. A. Fernando, C. M. Aikens, Reaction pathways for water oxidation to molecular oxygen mediated by model cobalt oxide dimer and cubane catalysts. *J. Phys. Chem. C* **119**, 11072–11085 (2015).
68. G. Mattioli, P. Giannozzi, A. Amore Bonapasta, L. Guidoni, Reaction pathways for oxygen evolution promoted by cobalt catalyst. *J. Am. Chem. Soc.* **135**, 15353–15363 (2013).
69. Y. Li et al., Identification of cobalt oxides with Raman scattering and fourier transform infrared spectroscopy. *J. Phys. Chem. C* **120**, 4511–4516 (2016).
70. B. Rivas-Murias, V. Salgueiríño, Thermodynamic CoO-Co₃O₄ crossover using Raman spectroscopy in magnetic octahedron-shaped nanocrystals. *J. Raman Spectrosc.* **48**, 837–841 (2017).
71. A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications* (Wiley, ed. 2, 2001).
72. S. R. Ahrenholtz, C. C. Epley, A. J. Morris, Solvothermal preparation of an electrocatalytic metalloporphyrin MOF thin film and its redox hopping charge-transfer mechanism. *J. Am. Chem. Soc.* **136**, 2464–2472 (2014).
73. S. Lin, P. M. Usov, A. J. Morris, The role of redox hopping in metal-organic framework electrocatalysis. *Chem. Commun. (Camb.)* **54**, 6965–6974 (2018).
74. C. C. L. McCrory et al., Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices. *J. Am. Chem. Soc.* **137**, 4347–4357 (2015).
75. J. B. Gerken et al., Electrochemical water oxidation with cobalt-based electrocatalysts from pH 0–14: The thermodynamic basis for catalyst structure, stability, and activity. *J. Am. Chem. Soc.* **133**, 14431–14442 (2011).
76. H. L. Anderson, S. Anderson, J. K. M. Sanders, Ligand binding by butadiyne-linked porphyrin dimers, trimers and tetramers. *J. Chem. Soc. Perkin Trans. 1*, 2231–2245 (1995).
77. E. C. Constable, G. Zhang, C. E. Housecroft, J. A. Zampese, Zinc(II) coordination polymers, metallohexacycles and metallocapsules—do we understand self-assembly in metallosupramolecular chemistry: Algorithms or serendipity? *CrystEngComm* **13**, 6864–6870 (2011).
78. M. Schmittel, B. He, P. Mal, Supramolecular multicomponent self-assembly of shape-adaptive nanoprisms: Wrapping up C₆₀ with three porphyrin units. *Org. Lett.* **10**, 2513–2516 (2008).
79. A. I. Nguyen, “A molecular approach for deciphering and designing cobalt water oxidation catalysts,” PhD dissertation, University of California, Berkeley, CA (2016).
80. K. M. Van Allsburg, “Molecular and materials investigations of Mn₄O₄ and Co₄O₄ cubanes in pursuit of artificial photosynthesis,” PhD dissertation, University of California, Berkeley, CA (2016).