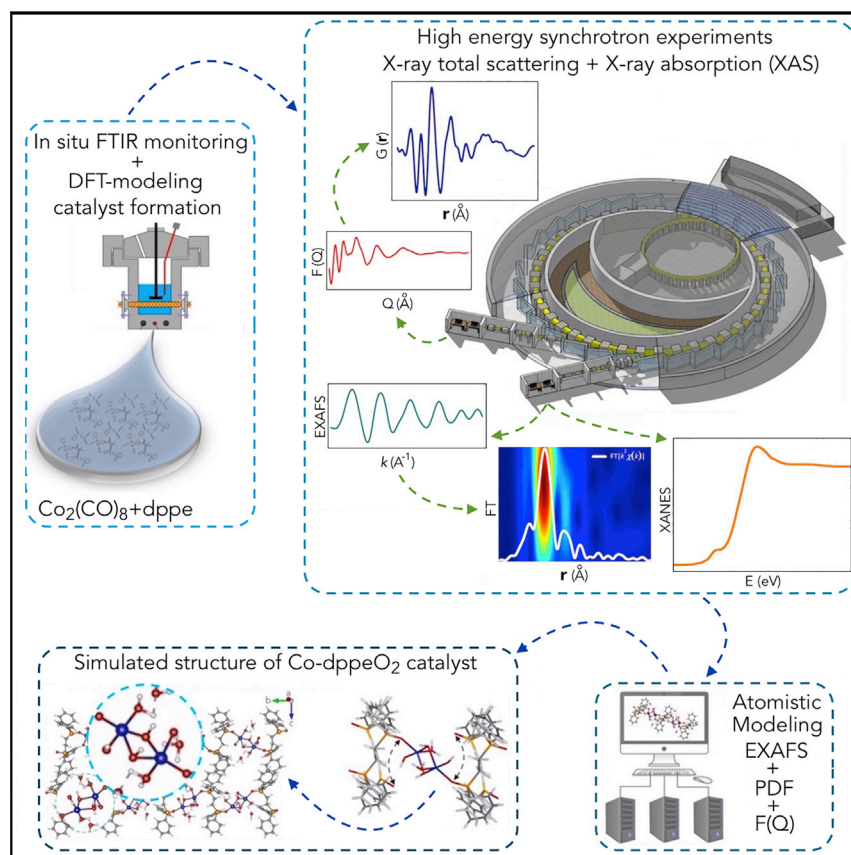


Article

Soft Templating and Disorder in an Applied 1D Cobalt Coordination Polymer Electrocatalyst



Designing hybrid organic-inorganic catalysts with bioinspired principles inspires applied catalyst development. We monitor the formation *in situ* and unravel the structure of a high-performance disordered hybrid cobalt oxidation catalyst. Atomistic modeling of X-ray scattering and absorption spectra identifies the catalyst as an unconventional cobalt coordination polymer of hydrated $\{H_2O-Co_2(OH)_2-OH_2\}$ edge-site motifs connected by bridging hydrophobic bis-phosphine oxide ligands. The flexibility of this structural topology opens up new roads for rational design of disordered catalysts beyond molecules and solids.

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HIGHLIGHTS

Structure of a soft-templated disordered 1D cobalt coordination polymer catalyst

Discerning the active catalytic site for high performance in alkaline electrolysis

In situ monitoring of catalyst formation to track the synthetic structural evolution

Understanding hydrated $\{H_2O-Co_2(OH)_2-OH_2\}$ motifs within a flexible organic matrix

3

Understanding

Dependency and conditional studies on material behavior

Article

Soft Templating and Disorder in an Applied 1D Cobalt Coordination Polymer Electrocatalyst

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SUMMARY

Disordered materials with resilient and soft-templated functional units bear the potential to fill the pipeline of robust catalysts for renewable energy storage. However, for novel materials lacking long-range order, the ability to discern local structure with atomic resolution still pushes the boundaries of current analytical and modeling approaches. We introduce a two-pillar strategy to monitor the formation and unravel the structure of the first disordered one-dimensional cobalt coordination polymer catalyst, Co-dppeO₂. This target material excels through proven high performance in commercial alkaline electrolyzers and organic transformations. We demonstrate that the key architecture behind this activity is the unconventional embedding of hydrated {H₂O-Co₂(OH)₂-OH₂} edge-site motifs, nested into a flexible organic matrix of highly oxidized and bridging hydrophobic dppeO₂ ligands. Our combination of *in situ* spectroscopy and computational modeling of X-ray scattering and absorption spectra, backed with complementary experimental techniques, holds the key to understanding the atomic-range structure of important disordered materials.

INTRODUCTION

The growing worldwide need for storable fuels from sustainable energy sources has triggered an intense search for low-cost, robust, and flexible catalysts with extended durability under harsh conditions.^{1–10} The tremendous influence of disorder on catalytic activity and resilience^{11–15} has yet to be fully grasped, and most catalyst development is still based on classic and ordered structure-activity relationships. This contrast between catalytic reality and synthetic strategy is due to considerable difficulties that are still associated with the structural understanding of disordered materials.

Even the analysis of prominent disordered high-performance materials with known catalytic motifs, such as the “CoPi” water oxidation catalyst, “black TiO₂,” and manganese- or vanadium oxide-based oxidation catalysts took time and intense analytical effort.^{16–21} While modeling techniques, such as reverse Monte Carlo (RMC) simulations, are now available, access to the required high-end analytical techniques, such as X-ray absorption spectroscopy (XAS) or *in situ* high-resolution transmission electron microscopy (HRTEM), is still restricted to beamlines and larger facilities. In short, we are not yet fully equipped to explore an emerging new generation of unconventional and disordered catalysts beyond familiar structural

Progress and Potential

The growing need for multifunctional and low-cost catalysts to store renewable energy resources has triggered great interest in new design concepts embracing their dynamic, and often disordered, features. This stands in sharp contrast to the challenges to reveal their atomic-range order, where major effort is still required to fully understand disordered catalysts. To date, few studies have focused on the almost unlimited combinations of metal centers and soft templating ligands that can create disordered hybrid catalysts. Our innovative, two-pillar strategy based on *in situ* monitoring and modeling of cutting-edge analytical data pushes these boundaries and explores a new disordered one-dimensional cobalt coordination polymer catalyst that outperforms conventional materials. Our results show the potential of soft templating of active moieties with flexible ligand environments and outline much-needed strategies to understand the functionalities of disordered catalysts.

motifs, such as disordered hybrid materials. New methodologies are, therefore, required to fully explore the unconventional potential of these catalyst types.^{22–27} Physical chemists are constantly advancing toward bringing XAS equipment and related beamline technologies to benchtop scales.^{28,29} However, even with such instrumentation available, understanding completely new disordered compounds remains challenging terra incognita, when no X-ray scattering or detailed nuclear magnetic resonance (NMR) data are at hand.

With our discovery of the unconventional structural features of a disordered high-performance catalyst, we demonstrate analytical concepts that extend beyond empirical performance characterizations. Our representative target material, referred to as Co-dppeO₂, was selected due to its proven and leading performance in oxidation catalysis.³⁰ First and foremost, it shows high performance as a water oxidation catalyst, outperforming electrodeposited amorphous cobalt oxide (CoO_x) in both clean and contaminated water sources.³¹ Co-dppeO₂ demonstrates operational stability on stainless-steel electrodes in alkaline electrolyzers for over 60 days without performance reduction.³⁰ Consequently, facile decagram-scale synthesis of Co-dppeO₂ and its simple incorporation into coatings has furthered its commercial application.³¹ Furthermore, Co-dppeO₂ displays cutting-edge multifunctional properties for the electrocatalytic upgrading of organic feedstock when compared with conventional cobalt oxide-based catalysts.^{32,33}

Notably, this material emerged from an unconventional crossover synthetic screening strategy of organic ligands for highest catalytic activity in a synthetic system starting from dicobalt octacarbonyl Co₂(CO)₈.³¹ However, the strongly disordered nature of Co-dppeO₂, i.e., its complete lack of long-range order, forestalled all analytical options to elucidate the underlying structural features with conventional approaches.

Therefore, we developed a state-of-the-art and generally applicable approach based on two complementary pillars, namely *in situ* formation monitoring of Co-dppeO₂ together with computational modeling of X-ray scattering and absorption spectra. To this end, we applied a combination of *in situ* infrared spectroscopy and density functional theory (DFT) to monitor and determine the structure of synthetic intermediate species toward formation of the active site. The structure of the final purified Co-dppeO₂ solid catalyst was elucidated by simultaneous atomistic RMC modeling of the experimental X-ray structure factor $F(\mathbf{Q})$, the pair distribution function (PDF) $G(r)$, and the extended X-ray absorption fine structure (EXAFS) spectra, all backed up by a comprehensive set of complementary analytical and experimental *in situ/ex situ* data.

In addition to the methodological progress presented here, we discovered that Co-dppeO₂ represents the first Co-based disordered one-dimensional (1D) transition metal coordination polymer, based on flexible templating of cobalt centers by oxidized 1,2-bis(diphenylphosphino)ethane (dppeO₂) ligands.^{30,31} Our study introduces 1D transition metal coordination polymers as a versatile, soft-templated^{34–36} catalyst type that complements metal-organic frameworks^{37–39} and modern hybrid materials.^{40–44}

In the following, we unravel how the formation process of Co-dppeO₂ generates unique polymer architecture of hydrophobic organic linkers connecting hydrophilic Co-hydroxide clusters, which are themselves surrounded by a network of hydrogen-bound H₂O molecules. This unexpected embedding of {H₂O-Co₂(OH)₂-OH₂}

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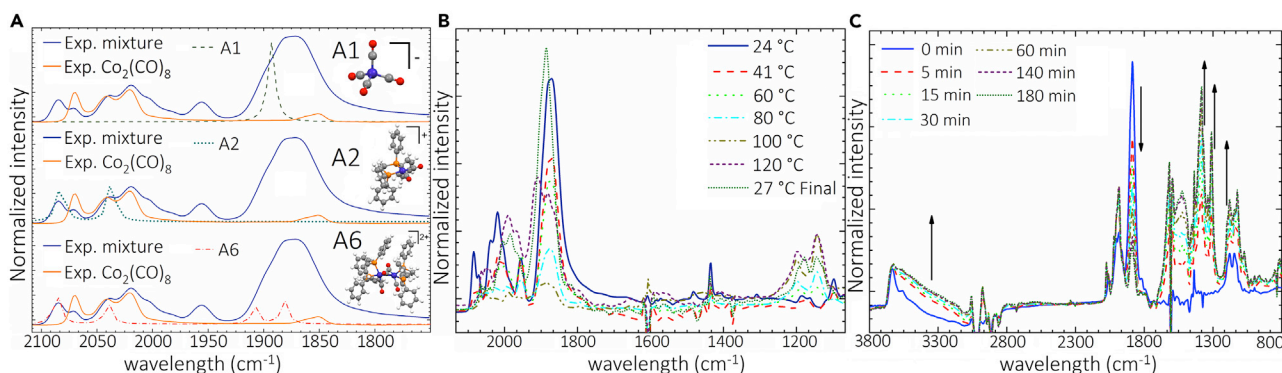


Figure 1. *In Situ* and DFT Calculated IR Spectra for Potential Co-CO-dppe Intermediates

(A) *In situ* IR spectra at the start of the reaction at 24°C with the DFT calculated IR spectra for candidate molecules A1, A2, A6; IR spectra were calculated with ω B97XD/def2svp level of theory in mesitylene.

(B) *In situ* IR spectra at increasing temperatures.

(C) *In situ* IR spectra for the oxidation time course.

sites^{45–49} is among the first examples of soft matter templating along the lines of photosystem II⁵⁰ that resulted in durable heterogeneous catalysts.

RESULTS

Analysis of Intermediate Species: *In Situ* FTIR Spectroscopy and DFT Simulations

In an effort to identify the relevant species involved in the formation of Co-dppeO₂, the three phases of the synthesis, i.e., the initial reaction at ambient temperature, thermolysis, and oxidation, were followed using *in situ* Fourier-transform infrared (FTIR) spectroscopy. Spectral peaks were then compared with computed spectra from an ensemble of optimized candidate molecules. Potential cobalt-CO-dppe complexes were modeled by DFT at the ω B97XD/def2SVP level of theory and with solvation in mesitylene using a continuum dielectric method (for details of calculations, see [Supplemental Experimental Procedures](#)). The ω B97XD density functional was chosen as it contains long-range exchange and dispersion corrections and has been successfully used in the studies of transition metal compounds.

In the initial mixture, dppe reacted rapidly with a slight excess of Co₂(CO)₈ in deoxygenated mesitylene at 24°C under 50 psi of CO, converging to a complex but stable mixture of cobalt carbonyl species, and a modest elevation of pressure in the system. In addition to some remaining Co₂(CO)₈, the major species in this mixture appear to be A1 ([CoCO₄]⁺), A2 ([Co(dppe)(CO)₂]⁺), and possibly A6 ([Co(dppe)(μ -CO)(CO)₂]²⁺).

As shown in [Figure 1A](#), the broad peak observed at $\approx 1,920$ – $1,820$ cm⁻¹ matches the asymmetric metal-bound C–O stretching vibration of A1 at $\approx 1,900$ cm⁻¹ and both asymmetric and symmetric C–O stretching vibrations for carbonyls bridging the Co centers of A6 at $\approx 1,905$ and $\approx 1,882$ cm⁻¹, as well as residual Co₂(CO)₈. The peak seen at $\approx 2,085$ cm⁻¹ matches very well with the symmetric C–O stretching vibration of terminal carbonyls for both A2 and A6, while the peak at $\approx 2,036$ cm⁻¹ matches the asymmetric C–O stretching vibration for both A2 and A6. Together, these species account for all observed carbonyl peaks in the spectrum, except for the peak at $\approx 1,950$ cm⁻¹, which may indicate presence of a μ -CO, but all calculated structures with excellent overlap in this region have significant deviations in other areas (see [Supplemental Information](#) for details).

Thermolysis of the reaction followed. The reactor was heated by 20°C increments, allowing 20–120 min for the spectrum to stabilize after each temperature change. From 24°C until 100°C only minor changes were observed, but at 120°C there was an evident increase in complexity of the spectrum, including new strong peaks at $\approx 1,990$ and $\approx 1,905$ cm^{-1} and nearly complete disappearance of peaks ascribed to terminal carbonyls in **A2** and/or **A6** (Figure 1B). This is particularly interesting because previous studies^{30,32} found material produced in refluxing toluene (boiling point [bp] 110°C) to be chemically distinct and catalytically inferior to material produced in refluxing xylenes (bp 142°C). Because toluene, xylenes, and mesitylene all have properties similar to those of solvents, it is likely that reactions occurring above the boiling point of toluene are crucial to the formation of active catalyst. After cooling back to 27°C, the IR spectrum was noticeably different from that observed before thermolysis, lacking peaks ascribed to terminal carbonyls in **A2** and/or **A6**.

At this point, the CO atmosphere was vented, and replaced with 25 psi of dry O₂, to oxidize the intermediate product. This resulted in an increase in vibrations assigned to phosphine oxides ($\approx 1,200$ – $1,000$ cm^{-1}) (Figure 1C), and the appearance of peaks attributed to O–H stretching and bending modes ($\approx 3,685$ – $3,150$ and $\approx 1,700$ – $1,260$ cm^{-1}), as well as a marked overall decrease in carbonyl signal intensity (Figure 1C). There are multiple documented examples of cobalt-tertiary phosphine complexes reacting selectively with dioxygen to produce the corresponding cobalt-tertiary phosphine oxide complexes with high selectivity.^{51–54} Both PO and residual CO signals appear to match well with calculated spectra for Co(CO)₂ centers with phosphine oxide ligands (see Supplemental Information for computed structures and spectra). After 3 h under 25 psi O₂ and then 70 h under air at ambient pressure, the precipitate was purified using the same method employed in preparative synthesis, and the IR spectrum of the resulting material matched the spectra found for the final purified Co-dppeO₂ complex used in all *ex situ* studies (Figure S1).

Structure of the Final Purified Co-dppeO₂ Solid Catalyst

Understanding the topologically disordered structure of Co-dppeO₂ sets an essential example for future rationalization and exploitation of the structure-activity relationships involved in electrochemical reactions of disordered hybrid organic-inorganic coordination systems. However, the absence of systematic and well-established methods to accomplish such complex tasks still poses great challenges.

An earlier study³¹ has shown that the structure of Co-dppeO₂ cannot be resolved from standard X-ray diffraction refinement, because the diffraction pattern only exhibits broad and low-intensity diffraction signals arising from the dppeO₂ ligand. This renders the determination of the structure of Co-dppeO₂ quite difficult, beyond the qualitative suggestion that it represents a disordered catalyst containing traces of crystalline dppeO₂. Here, the topological atomic short-range order of Co-dppeO₂ is deciphered from RMC modeling using an input model structure to simultaneously fit the structure factor $F(\mathbf{Q})$, the pair distribution function $G(r)$, and the EXAFS spectra extracted from measured high-energy synchrotron X-ray total scattering and XAS data.

The local structure of the hydrophobic bis-phosphine oxide bridging the cobalt clusters is obtained from fitting the $F(\mathbf{Q})$ and $G(r)$ functions. The statistics of many-body correlations in the nearest coordination shells around catalytically active cobalt centers is more precisely extracted from fitting the EXAFS spectra. This unified approach allows a seamless correlation between different experimental data offering structural insights at multiple atomic length scales, thus providing a

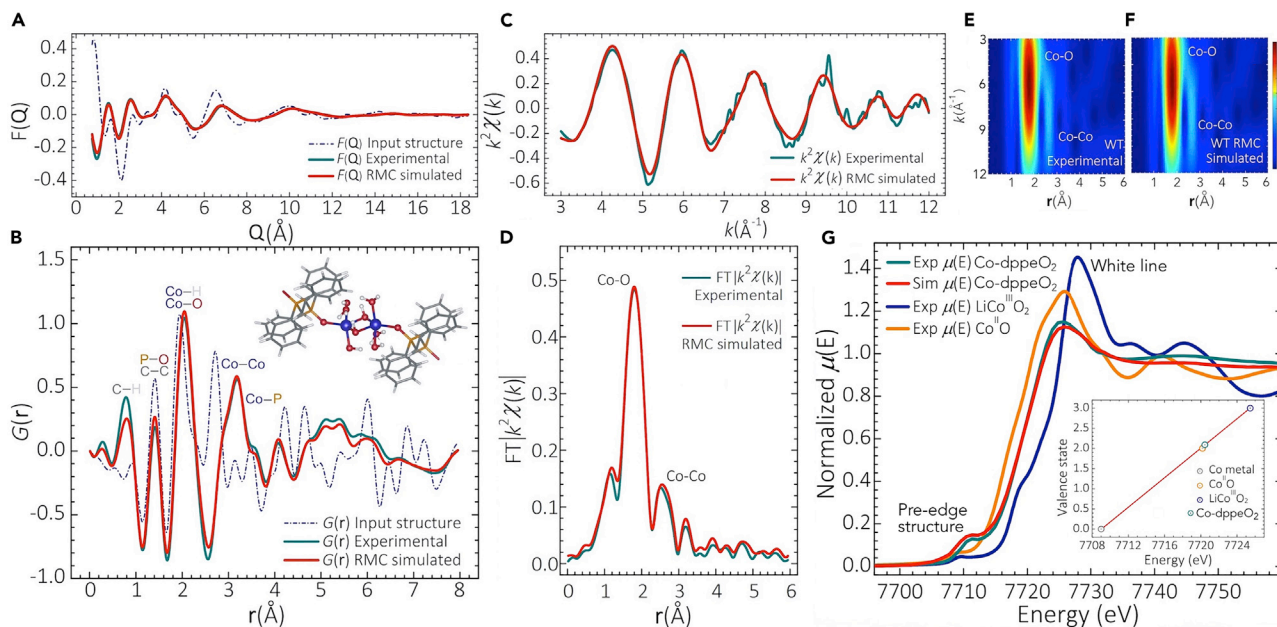


Figure 2. RMC Modeling of the Structure of the Final Purified Co-dppeO₂ Solid Catalyst

(A and B) RMC simulations (red line) of the experimental $F(Q)$ (A) and $G(r)$ (B) spectra of Co-dppeO₂ (green line). The dotted curves correspond to the calculated $F(Q)$, $G(r)$ functions of the input model structure.

(C and D) RMC simulations (red line) of the experimental $k^2\chi(k)$ (C) and $FT|k^2\chi(k)|$ (D) spectra of Co-dppeO₂ (green line, phase-uncorrected).

(E and F) 2D-contour plots of the experimental (E) and RMC simulated (F) WT of the $k^2\chi(k)$ spectra.

(G) Experimental XANES spectra (green line) and the calculated one from the RMC optimized structure of Co-dppeO₂ by *ab initio* methods (red line). The XANES spectra of reference compounds LiCo^{III}O₂ and Co^{II}O are also shown and used for estimation of the Co^{II} valence state in the inset.

realistic 3D model of the disordered structure of Co-dppeO₂, which cannot be achieved from conventional crystallographic analysis.

For RMC modeling, the input model motif was built in line with structural insights acquired from the comprehensive analyses of complementary *ex situ* X-ray photoelectron spectroscopy (XPS), NMR, thermogravimetric analysis, IR, and Raman characterizations of the synthesized Co-dppeO₂ catalyst (for details see [Supplemental Information](#)). First, measured *ex situ* XPS C 1s spectra (Figure S5) display the C–C, C–H, and C–P bonds of the dppe ligand, and exclude the presence of carbonates. XPS P 2p spectra suggest P–O bonding most consistent with tertiary phosphine oxide functionality,⁵⁵ and the O 1s spectra indicate the chemical state of oxygen involving OH groups. Furthermore, *ex situ* ³¹P NMR spectra show two isotropic signals at ≈ 33.4 and ≈ 34.9 ppm, consistent with having one molecule of oxidized dppeO₂ ligand. The dppeO₂ ligands are coordinated via their O atoms to two Co centers (Figure S6). Elemental analysis suggested the presence of 15 wt % of water (confirmed by Karl Fischer titration), and a stoichiometry of two cobalt atoms per molecule of dppeO₂ ligand (Figure S7 and Table S5). Direct comparison of the absorption-edge energy position in the X-ray absorption near-edge structure (XANES) spectra of Co-dppeO₂ with that of reference compounds (Co-metal, LiCo^{III}O₂, and Co^{II}O) indicates that most Co sites hold the Co^{II} valence state (see inset of Figure 2G).

Taking this structural information into account, an input model motif of Co-dppeO₂ was established, consisting of oxidized dppeO₂ ligands linking {Co₂(μ-OH)₂(OH)₂(H₂O)₂} clusters enclosed by hydrogen-bonded water molecules (see

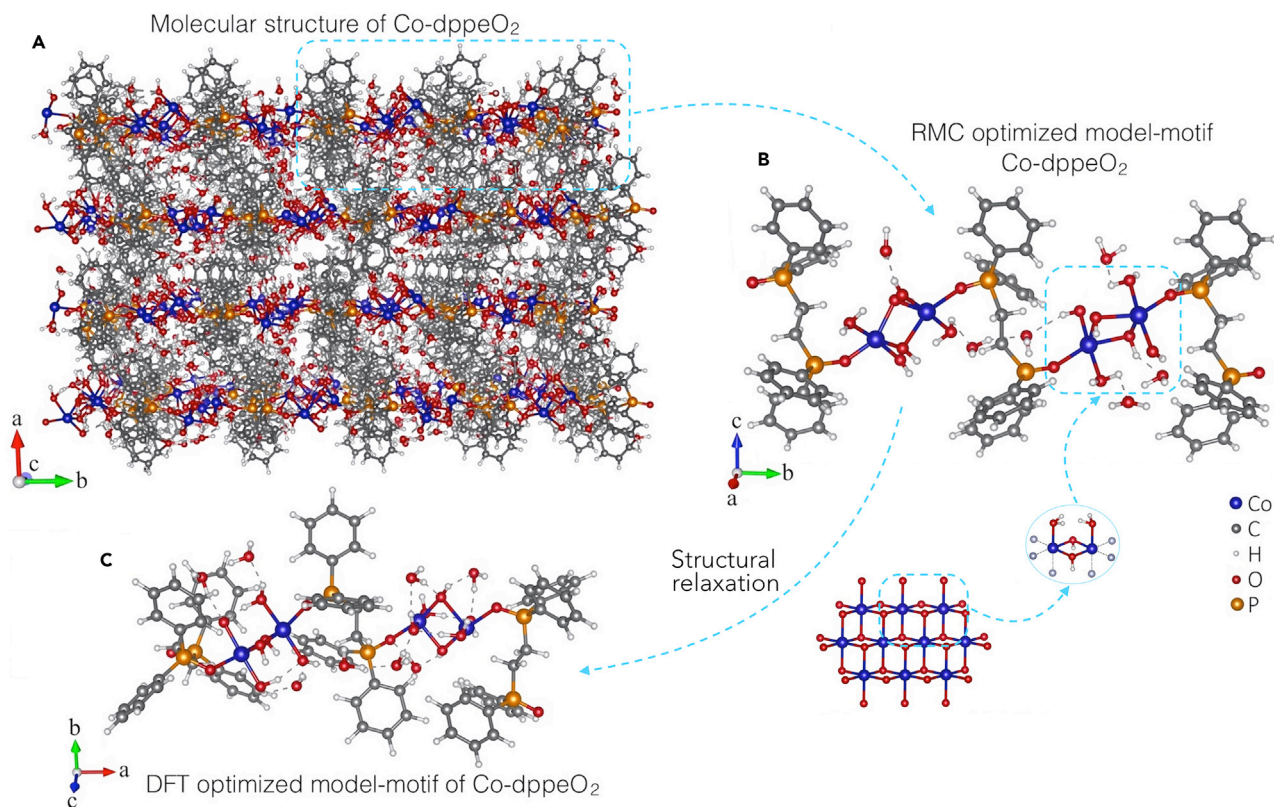


Figure 3. RMC Optimized Structure of Co-dppeO₂

(A and B) RMC optimized structure of final purified Co-dppeO₂ solid catalyst comprising a coordination polymer consisting of hydrophobic bis-phosphine oxide dppeO₂ ligands linked by bridging distorted hydrophilic oxocluster motifs {Co₂(μ-OH)₂(OH)₂(H₂O)₂} surrounded by H-bound H₂O molecules.

(C) DFT optimized structure showing the molecular stability of Co-dppeO₂ upon structural relaxation.

inset of Figure 2B). From this model motif an extended-input 3D-model structure of Co-dppeO₂ was built by linking different dppeO₂-{Co₂(μ-OH)₂(OH)₂(H₂O)₂}-dppeO₂ clusters. Figures 2A and 2B contrast the $F(Q)$ and $G(r)$ functions as calculated from the input model structure against the experimental spectra, showing that the input Co-dppeO₂ model structure nearly reproduces the measured spectral features of the experimental data.

Results from RMC optimization of the input Co-dppeO₂ model structure attain good fit to the measured $F(Q)$ and $G(r)$ spectra, replicating all relevant spectral features of the experimental data (Figures 2A and 2B). Main interatomic distances are given in Table S6. The RMC simulated EXAFS $k^2\chi(k)$ and $FT|k^2\chi(k)|$ spectra and its wavelength transform (WT) reproduce the experimental k - and real-space position at $r \approx 1.82 \text{ \AA}$ [$k \approx 6.2 \text{ \AA}^{-1}$] and $r \approx 2.54 \text{ \AA}$ [$k \approx 7.3 \text{ \AA}^{-1}$] arising from backscattering by neighboring O and Co atoms sited at the first-second coordination shells from the photo-absorbing Co centers (Figures 2C–2F).

The RMC optimized structure shows that the atomic short-range topology of Co-dppeO₂ comprises a coordination polymer consisting of hydrophobic bis-phosphine oxide dppeO₂ ligands connected to each other by bridging hydrophilic {Co₂(μ-OH)₂(OH)₂(H₂O)₂} clusters surrounded by H-bound H₂O molecules (Figures 3A and 3B). The Co atoms adopt a distorted square pyramidal

pentacoordinate environment consisting of neighboring O atoms, one of which belongs to the dppeO₂ ligand. While the structure of Co-dppeO₂ appears to hold a well-defined atomic short-range topology into the metal-to-ligand environment, the molecular structure of the dppeO₂ ligands is disordered between two relative molecular orientations (Figures 3B and 5). This finding is consistent with the ¹³C NMR spectra, which show two signals at ≈22.6 and ≈24.9 ppm, assigned to the CH₂ groups of the phosphine dppeO₂ ligands. The low number of phenyl ring resonances is evidence for disordered and still mobile aromatic carbon sites, as expected for such types of terminal groups (Figure S6). While these two disordered dppeO₂ molecular orientations are uniformly distributed in the topological structure of Co-dppeO₂, the (CH₂)₂ chain displays anti-conformation, with the P=O groups in a given molecule oriented antiparallel to each other, so that—independent of the relative molecular orientation of the dppeO₂ ligands—they are bridged by rotated and distorted {Co₂(μ-OH)₂(OH)₂(H₂O)₂} clusters.

Structural stability of the key structural motif of Co-dppeO₂ was further evaluated by DFT optimization (Figure 3C). Structural relaxation the Co-dppeO₂ motif conserves its atomic short-range topology, with dppeO₂ ligands linked to each other by bridging hydrophilic distorted {Co₂(μ-OH)₂(OH)₂(H₂O)₂} clusters surrounded by H-bonded H₂O molecules. While additional rotations of the dppeO₂ ligands are observed, their occurrence will depend largely on structural packing, as they are more likely to arise *in silico* due to the degrees of freedom of the single molecule used during DFT optimization. Additionally, the distorted CoO₅ units give rise to the pre-edge structure observed in the Co K-edge XANES spectra of Co-dppeO₂ (Figure 2G), whose relative energy position and intensity are well reproduced from *ab initio* simulations from the RMC optimized structure of Co-dppeO₂. Since XANES spectra are sensitive to interatomic distances/angles and atomic coordination environments, these findings further support the simulated atomic-range order around the photoabsorbing Co atoms to properly reflect those present in the structure of the final purified Co-dppeO₂ solid catalyst.

The hydrogen-bonded network of water molecules in Co-dppeO₂, enabled by the dppeO₂ soft template, is a key differentiator between the active site in this catalyst and cobalt oxide. Cobalt oxide is less active than many amorphous catalysts,¹² but we show that in this case both possess a substantially similar active site. Just as delivery of water and egress of protons to the active site of photosystem II is facilitated by a proton relay that involves an adjacent tyrosine proton acceptor with a long-range water hydrogen-bonded network,⁵⁶ which has been shown to be a critical factor in the high activity of the oxygen evolution reaction (OER) in photosystem II,⁵⁷ in this system we suggest that hydrophobic ligands in Co-dppeO₂ serve to channel water (and protons) to (and from) the hydrophilic active sites. Additional structural flexibility allows for efficient binding of substrate waters and rapid catalysis concomitant with rapid transport of substrate water, product protons, and O₂ gas. Under longer operational periods, or in harsh environments, the hydrophobic dppeO₂ ligands can act as a soft template to optimize distribution of degradation products (such as CoO_x). This can explain the observed operational stability,³⁰ regardless of the structural stability of the ligand configuration over long periods of time.

Vibrational Properties of Co-dppeO₂

The experimental FTIR spectrum of Co-dppeO₂ was compared with simulated IR spectra calculated using the ωB97XD/def2SVP level of theory with solvation in mesitylene (Figures 4A and 4B) from model structures generated *de novo* A27

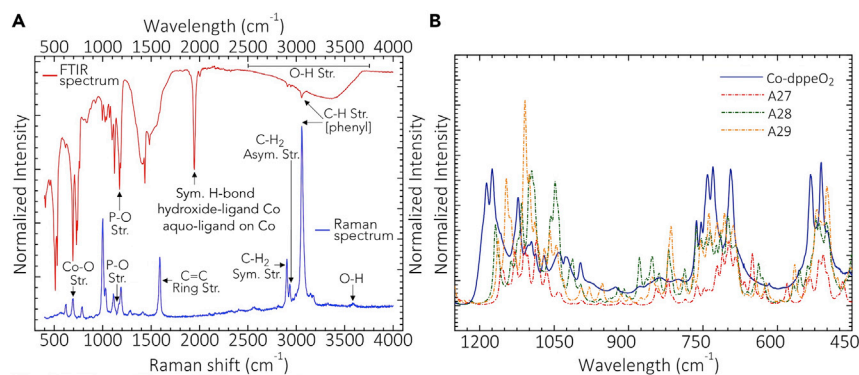


Figure 4. Ex Situ FTIR and Raman Spectra of Co-dppeO₂

(A) Ex situ FTIR and Raman spectra of Co-dppeO₂ showing transitions mainly from the dppeO₂ ligand.

(B) Fingerprint region of the FTIR spectra of Co-dppeO₂ versus the ωB97XD/def2svp calculated IR spectra from A27, A28, and A29 model structures.

and using RMC-derived model motifs A28 and A29 (Figure S8). Comparison of the vibrational modes computed directly from complexes A27, A28, and A29 with the experimental spectra of Co-dppeO₂ are given in Table S7. The fingerprint portion of the IR spectra in the range $\approx 1,200\text{--}400\text{ cm}^{-1}$ is very complicated to assign, as several vibrational modes from the C–C, C–H, and O–H stretching and bending motions are overlapping. However, the simulated and experimental spectra appear to be in general agreement, showing analogous line-shape features (Figure 4B). The IR spectra calculated from model structures A27, A28, and A29 partially match the P–O stretching vibrational modes observed in the experimental spectra at $\approx 1,175$, $\approx 1,069$, and $\approx 1,040\text{ cm}^{-1}$ (Table S7). The simulated Co–O stretching vibrations at $\approx 510\text{--}530\text{ cm}^{-1}$ from the A28 and A29 model motifs match the two peaks of the Co-dppeO₂ IR spectra in this region (Figure S9). However, these calculated vibrations are lower in intensity and closely overlap with the C–C, C–H, and O–H vibrations. It should be noted, however, that the A27, A28, and A29 model motifs only represent discrete snapshots of the multiple distorted units having different bond lengths and bond angles in the final Co-dppeO₂ product. Since the structures of these model motifs are different due to the various conformational arrangements of the ligands around the Co centers, shifts in vibrational modes are reflected on the calculated spectra for each model A27–A29 (Figure 4B).

Therefore, while similarities between the IR spectra calculated from A27, A28, and A29 model motifs and the experimental IR spectrum of the final Co-dppeO₂ complex in these fingerprint regions can be observed, its IR spectrum should be an average of all possible combinations of the aqua, hydroxy, and dppeO₂ ligand environments around the Co centers. Although the broad feature observed at $\approx 1,950\text{ cm}^{-1}$ in the experimental IR spectrum (Figure 4A) appears to be in the proper region for a cobalt-bound carbonyl stretching vibration, ¹³C NMR spectra did not offer any evidence of carbonyls (Figure S6). Additionally, the peak survived light-driven water oxidation under strongly alkaline conditions in a parallel study (Figure S10), which would be highly unusual for the easily oxidized carbonyl moiety. Interestingly, the peak disappears within hours when the catalyst is stored in the presence of a desiccant, but is stable under a humid atmosphere for weeks, suggesting the involvement of water (unfortunately, disappearance of this peak is irreversible, and treatment with H₂O or D₂O does not change this region of the IR spectrum further). A possible assignment for this vibration could be ascribed to a symmetrical

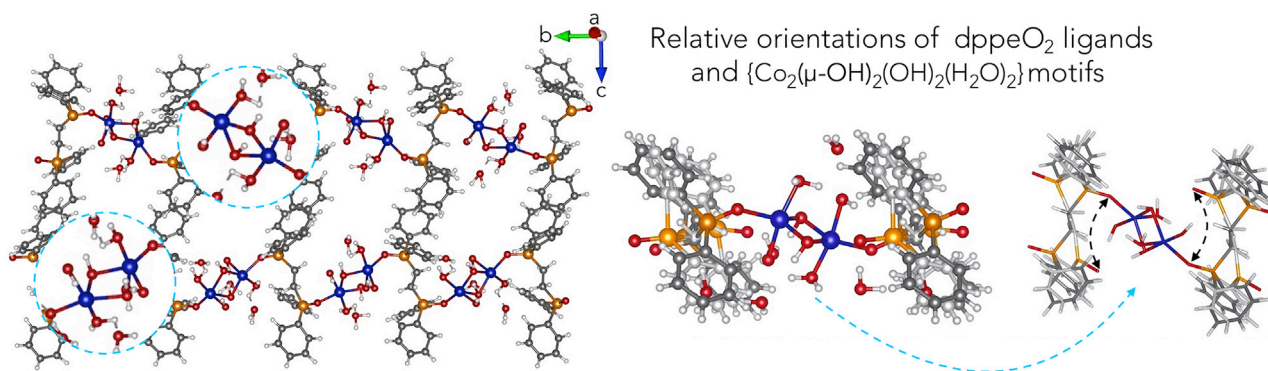


Figure 5. Rotational Disordered Moieties of Co-dppeO₂ and {H₂O-Co₂(OH)₂-OH₂} Edge Site

Molecular structure of the final purified Co-dppeO₂ solid catalyst showing the two relative orientations of the dppeO₂ ligands with the bridging distorted hydrophilic oxocluster motifs {Co₂(μ-OH)₂(OH)₂(H₂O)₂}.

hydrogen bond between a cobalt-bound water molecule (H donor) and a hydroxide ion bound to the neighboring cobalt center (H acceptor). This motif appears in several computed models, and in the case of structure A27, DFT calculations predict a stretching frequency of ca. $\approx 1,930\text{ cm}^{-1}$ for this O-H...O bond (Figure S11).

Ex situ Raman spectra of Co-dppeO₂ show transitions mainly arising from the organic dppeO₂ ligand (Figure 4A). Characterization of the vibrational modes is presented in Table S8. Comparing the Raman spectra of Co-dppeO₂ with that of reference compounds (CoOOH, Co(OH)₂, Ph₃PO, Co₃O₄, CoO) (Figures S12 and S13) ruled out the presence of adventitious cobalt oxide particles in the dppeO₂ organic ligand matrix, because the oxide peaks are absent in the Raman spectra of Co-dppeO₂.

This agrees with HRTEM images, which show a disordered microstructure without traces of cobalt oxide particles (Figure S14). The vibrational band at $\approx 692\text{ cm}^{-1}$ in the Raman spectra of Co-dppeO₂ is due to overlapping of Co-O stretching modes of distorted {Co₂(μ-OH)₂(OH)₂(H₂O)₂} units and out-of-plane sextant ring deformation modes of the dppeO₂ ligand. The vibrational bands at $\approx 1,169\text{ cm}^{-1}$ and $\approx 3,587\text{ cm}^{-1}$ arise from P-O stretching and OH vibrational modes, respectively (Figure 4A). Based on the FTIR Raman spectra, the C-H and C-C bond lengths were estimated from bond length stretching frequency correlations. Thus, the stretching frequencies at $\approx 3,057\text{--}3,059\text{ cm}^{-1}$ and $\approx 1,590\text{ cm}^{-1}$ relate to bond lengths of C-H $\approx 0.98 \pm 0.02\text{ \AA}$ and C-C $\approx 1.40 \pm 0.02\text{ \AA}$, respectively, which agree with those calculated from RMC modeling of the experimental $F(Q)$ and $G(r)$ functions (Table S6).

DISCUSSION

The compositional and structural properties of Co-dppeO₂ clearly indicate that its structural features differ fundamentally from cobalt oxide catalysts. In general terms, the structural elucidation of Co-dppeO₂ demonstrates the great potential of disordered hybrid materials to combine critical motifs of inorganic materials with hydrogen-bonded organic environments. Our cohesive methods that unify experimental *in situ/ex situ* spectroscopic data and theoretical modeling reveal the presence of a complex and disordered 1D-coordination polymer architecture in Co-dppeO₂ (Figures 3 and 5).

The key structural motif of Co-dppeO₂, namely hydrophobic dppeO₂ ligands bridging hydrophilic distorted edge-site {Co₂(μ-OH)₂(OH)₂(H₂O)₂} clusters (Figure 3),^{43,46,58} each surrounded by a network of hydrogen-bonded water molecules, emerged as the highest-performing catalyst after screening >20 ligands with Co₂(CO)₈ as a cobalt source (Figure 5).³⁰ Most importantly, the embedding of the dicobalt units into the flexible and preoxidized dppeO₂ environment bears a striking functional resemblance to the oxygen-evolving complex and related biological systems.^{50,59} Therein, active hydrophilic metal-oxo cluster sites are embedded within a flexible scaffold allowing for transport of substrate water molecules to the cluster, while acting as a soft template for structural evolution. In addition, the flexibility of the organic ligands holding the {Co₂(μ-OH)₂(OH)₂(H₂O)₂} active sites in place enable adaptable Co–O bond lengths and atom efficiency that are not provided by the more rigid cobalt oxide lattice.

Since the local conformation of the polymer, the distribution of water molecules, and the potential stereoisomerism at cobalt have a significant number of degrees of freedom, disordered Co-dppeO₂ must be treated as an ensemble of closely related, but non-identical, monomers. Bottom-up DFT models converge to discrete examples of these possible monomeric units, while longer-range order RMC simulations converge to their “average” structures. Given the agreement found between the results from computational modeling and experimental data on multiple aspects, including the complex distribution of interatomic distances (PDF, EXAFS), vibrational frequencies (FTIR, Raman), and the electronic structure (XPS, XANES), we are quite confident in our structural assignments in Co-dppeO₂ and in the validity and consistency of the methods herein.

It has been shown previously that the mode of action and relative activity of Co-dppeO₂ in phosphate and borate electrolytes is different from CoO_x and Co₃O₄.^{30,31} The performance durability³⁰ of Co-dppeO₂ leads us to propose hypotheses pertaining to the structurally adaptive and preoxidized dppeO₂ ligand environment: (1) that it lends high efficiency to the hydrophilic active di-μ-oxo bridged cobalt site through assisting substrate H₂O transport, and (2) that hydrophobic dppeO₂ ligands act as a soft matrix template to optimize the distribution of highly active possible structural degradation products. Hence, even if smaller amounts of cobalt oxides CoO_x and Co₃O₄ are formed during catalysis, the hydrophobic dppeO₂ ligands are likely to prevent their aggregation, thus avoiding electrode deactivation and sustaining the observed high catalytic activity over longer operational periods. Importantly, the number of low-nuclear molecular cobalt complexes explored as water oxidation catalysts remain rather limited to date compared with their extensively studied heterogeneous Co-containing counterparts. Although pentacoordinate binuclear Co(II) complexes containing Co₂O₃N₂ motifs have been reported in previous studies,^{60–63} to the best of our knowledge none of these materials have been investigated for their water oxidation catalytic activity. In contrast, pentacoordinate Co-species in solid-state water oxidation catalysts offer unsaturated and accessible edge sites with high affinity for OH[–] species in alkaline electrolytes, which strengthens interaction with water molecules and improves electrochemical OER performance.^{64,65} In the present case, the pentacoordinate Co(II) ions in our inorganic-organic hybrid material do indeed enable strategies to improve catalytic reactivity. Identifying these key structural motifs for Co-dppeO₂ furthermore enables us to study their effect on the way O₂ is formed and subsequently removed from the system, which we will pursue by analyzing kinetics and thermodynamics of this reaction using DFT in our future studies.

With such new structural insight into the key functional components of a flexible hybrid catalyst class at hand, we believe that this work will stimulate the informed exploration of this unlimited toolbox of disordered systems for water oxidation catalysis and beyond. Tailored geometry and hydrophobicity of the linking ligands hold the key to controlling the water networks, while the electronic properties of the clusters can be fine-tuned through appropriate metal-binding termini. This concept opens the door to new 1D, 2D, or 3D coordination polymers, exploiting the role of disorder and flexibility in material resilience.

Unveiling the atomic-range structure of disordered and dynamic materials has been a challenging and long-standing task in fundamental and applied research. Modern catalysis now requires creative approaches to resolve the detailed topological structure of their active centers to close the widening gap between empirical catalyst development and conceptual understanding. To this end, the comprehensive computational modeling and analytical *in situ/ex situ* characterizations used in this work can be further extrapolated to any disordered material to unravel its complex atomic-range structure from the bottom up. Such insight is vital for unleashing the unlimited application potential of robust and low-cost disordered catalysts for a sustainable economy.

EXPERIMENTAL PROCEDURES

Materials Synthesis

Synthesis of the Co-dppeO₂ catalyst was carried out following the protocol previously described in Lam et al.,³² using as reagents dicobalt octacarbonyl, Co₂(CO)₈ (345 mg, 1.01 mmol), and 1,2-bis(diphenylphosphino)ethane, denoted dppe (399 mg, 1.00 mmol). Further details on the synthetic procedures of reference compounds can be found in [Supplemental Information](#).

FTIR and Raman Spectroscopy

FTIR spectroscopy was performed using a Bruker Vertex 70 spectrometer equipped with a Pt attenuated total reflection (ATR), in transmittance mode. Raman spectra were recorded using a Renishaw Ramascope 1000 spectrometer equipped with a 780-nm diode laser from Renishaw with 50 mW capacity. To improve the signal-to-noise ratio, we used detection times of about 120 s.

In Situ FTIR Spectroscopy

The FTIR instrument used for the *in situ* study is a Bruker Tensor 27 equipped with a mid-IR source, swappable room-temperature deuterated triglycine sulfate detector, and liquid nitrogen-cooled narrow-band mercury-cadmium-telluride (MCT) detectors. The MCT detector was used with the SpectraTech high-pressure IR cell. The Bruker OPUS program (version 7.2.139.1294) was used for data collection and data analysis on a Windows 7 computer system. The higher IR throughput of the ZnSe crystal led us to use a 2-mm aperture setting to avoid oversaturating the MCT detector. Background spectra with mesitylene solvent were collected and stored at the various temperatures planned for the sample spectra. Solvent backgrounds were then loaded and automatically subtracted from sample spectra at the corresponding temperatures. FTIR spectra were collected with the following parameters: 128 scans (background and sample), 4 cm⁻¹ resolution, Blackman-Harris 3-term apodization, Mertz phase correction, zero filling factor = 2, and ATR intensity correction. Further details on the FTIR SpectraTech High-Pressure IR Cell spectrometer and experimental method can be found in [Supplemental Information](#).

Synchrotron X-Ray Total Scattering

The high-energy X-ray total scattering experiments were conducted at the beamline ID15A at the European Synchrotron Radiation Facility, Grenoble. Data were collected at room temperature using high-energy photons of 75 keV ($\lambda = 0.164 \text{ \AA}$), with appropriate statistics to achieve high momentum transfer values Q ($Q_{\text{max}} = 4\pi\sin\theta/\lambda$). Solid samples were packed into Kapton tubes with inner diameter of 1.5 mm and mounted in transmission geometry. The intensity scattered from the unfilled Kapton tubes was measured separately for background subtraction. Intensities were recorded using a PILATUS3X CdTe 2M solid-state detector with sample-to-detector distance of ≈ 200 mm. The experimental 2D images were processed using the pyFAI program⁶⁶ to yield 1D (Q , I) diffraction patterns. The PDFgetX3 program⁶⁷ was used to subtract the background (empty Kapton tube), to perform instrument and sample corrections, and to obtain the corrected-normalized diffraction intensity of the total scattering structure factor $S(Q)$ and the X-ray structure factor $F(Q)$. The $S(Q)$ was converted into the pair distribution function (PDF), $G(r)$, through the sine-Fourier transform according to

$$G(r) = \frac{2}{\pi} \int_{Q_{\text{min}}}^{Q_{\text{max}}} Q[S(Q) - 1] \sin Qr dQ,$$

$G(r)$ represents the probability of finding an atom i at a given distance r from another atom j . The relative intensity in $G(r)$ relates directly to the number of these pairs and their scattering power. For amorphous materials, the intensity in $G(r)$ peaks diminish as r increases due to the finite range of structural correlations, and defines the atomic-range order in the material.

X-Ray Absorption Spectroscopy

Experiments were performed at the SuperXAS beamline of the Swiss Light Source, Villigen, Switzerland, on solid samples dispersed in cellulose at room temperature. The storage ring was run in the top-up mode with an average current of 400 mA. The X-ray beam was collimated by a Si-coated mirror and the energy was scanned by a channel-cut Si[111] monochromator. Energy calibration was performed using metal Co foil (with the maximum of the first derivative of the spectrum at 7,709 eV). A toroidal mirror with Rh coating was employed after the monochromator to focus the incident X-rays with a spot size of $140 \times 120 \mu\text{m}^2$ on the sample. Measurements on Co-dppeO₂ tablet-shaped samples were performed in transmission mode. Absorption-edge-energy calibration, background subtraction, data reduction, and analyses of the extracted EXAFS ($k^2\chi(k)$) and Fourier transform (FT $|k^2\chi(k)|$) spectra were performed using the Athena and Artemis programs as implemented into the IFEFFIT software package.⁶⁸

Density Functional Theory Calculations

All calculations were performed using the Gaussian 09 (revision D.01)⁶⁹ suite programs. Ground-state geometries were optimized in mesitylene employing the self-consistent reaction field method via the polarized continuum solvation model⁷⁰ with the ω B97XD⁷¹ density functional and the def2SVP^{72,73} basis set. The optimized geometries were then used in vibrational frequency calculations. Obtained frequencies were then subsequently scaled by a factor of 0.9394. A pruned integration grid with 75 radial shells and 302 angular points per shell (the G09 default fine grid) was used for all calculations. Further details on the calculations can be found in [Supplemental Information](#).

Atomistic Reverse Monte Carlo Modeling

To simulate the atomic short-range topology in the molecular structure of Co-dppeO₂, we fitted an extended-input 3D-model structure of Co-dppeO₂ consisting of dppeO₂-{Co₂(μ-OH)₂(OH)₂(H₂O)₂}-dppeO₂ clusters to the experimental $F(Q)$ [$\Delta Q \approx 1\text{--}18 \text{ \AA}^{-1}$], $G(r)$ [$\Delta r \approx 0\text{--}8 \text{ \AA}$] and $k^2\chi(k)$ [$\Delta k \approx 3\text{--}12 \text{ \AA}^{-1}$], $FT|k^2\chi(k)|$ [$\Delta r \approx 0\text{--}6 \text{ \AA}$] spectra by RMC simulations, as implemented in RMCProfile.⁷⁴ From prior EXAFS fitting by Artemis⁶⁸ the threshold energy shift was set to $\Delta E_0 \approx -0.59 \text{ eV}$ and $S_0^2 \approx 0.9$. The atoms were constrained to move into cutoff distances C–C $\approx 1.38\text{--}1.46 \text{ \AA}$, C–H $\approx 0.96\text{--}1.02 \text{ \AA}$, Co–O $\approx 2.0\text{--}2.4 \text{ \AA}$, Co–Co $\approx 2.9\text{--}3.4 \text{ \AA}$, Co–P $\approx 3.0\text{--}3.4 \text{ \AA}$, O–P $\approx 1.52\text{--}1.72 \text{ \AA}$, and O–H $\approx 0.96\text{--}0.99 \text{ \AA}$. To conserve the bonding of aromatic C–H rings and H₂O molecules, we used the stretching potentials C–C 4.08 eV (1.42 Å), C–H 3.66 eV (0.96 Å), and O–H 3.43 eV (0.98 Å), and optimized their weightings at each RMC cycle. The input model structure of Co-dppeO₂ was then optimized by RMC modeling by allowing 1%–3% of atoms to undergo displacements of $\approx 0.01\text{--}0.08 \text{ \AA}$ at each RMC cycle. Total $k^2\chi(k)$, $FT|k^2\chi(k)|$ RMC functions equal to the averaged single spectrum of each photoabsorbing Co atom were recalculated at each RMC run. Convergence to a minimum residual was attained by running $\approx 1 \times 10^6$ RMC cycles. Each atomic movement was tested according to the degree of consistency R^2 between the experimental and refined spectral data points as described in detail previously.^{75–78}

Ab Initio Calculations of XANES Spectra

Ab initio simulations of the Co *K*-edge XANES spectra for the RMC optimized molecular structure of Co-dppeO₂ were done self-consistently by finite difference method as implemented in the near-edge structure FDMNES code.⁷⁹ The real self-energy-dependent exchange potential by Hedin-Lundqvist was used. The final excited state was approached by relaxed configurations with a core hole at the 1s level and an extra electron at the 4p level. Single Co *K*-edge signals were computed on a grid of 7 Å centered at each Co center and averaged to total XANES spectra.

Further details on the complementary analytical characterization can be found in [Supplemental Information](#).

DATA AND CODE AVAILABILITY

The authors declare that data supporting the findings of this study are available within the paper, the [Supplemental Information](#), and the [Experimental Procedures](#). All other data are available from the Lead Contact upon reasonable request.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.matt.2019.06.021>.

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AUTHOR CONTRIBUTIONS

G.R.P., S.W.S., A.J.B., and P.T.A. conceived the research. C.A.T., P.V.P., E.N.B., and S.D.Z. performed the theoretical studies. A.J.B. and G.S. collected *in situ* monitoring data. R.M., T.F., and S.G.F. performed structural and analytical characterizations. G.R.P., C.A.T., S.W.S., P.V.P., and A.J.B. wrote the manuscript. All authors analyzed the data and commented on the manuscript.

DECLARATION OF INTERESTS

US Patent No. 10,081,650B2, by A.J.B., S.W.S., and P.T.A., contains intellectual property described in the article. The other authors declare no competing interests.

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