Adsorbed cobalt porphyrins act like metal surfaces in electrocatalysis

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Electrodes chemically modified with molecular active sites are potent catalysts for energy conversion reactions. Such electrodes are typically presumed to operate by the same redox mediation mechanisms as the analogous soluble molecules, with electron transfer and substrate activation in separate elementary steps. Here we uncover solvent-dependent concerted reaction mechanisms for cobalt porphyrins attached to glassy carbon electrodes by flexible aliphatic linkages. In acetonitrile, outer-sphere Co^{III} reduction mediates H₂ evolution in a stepwise sequence. However, in aqueous media, outer-sphere reduction is not observed and H₂ evolution proceeds instead by concerted proton–electron transfer pathways typical of metal surfaces. Consequently, catalysis is not defined by the reduction potential of the parent molecule, but rather by the free energy of hydrogen binding. We attribute these mechanistic changes to electrostatic coupling between the molecule and the surface arising from adsorption. Our results motivate a re-examination of the reaction mechanisms of and design principles for molecularly modified electrodes.

An economy based on renewable energy requires efficient catalysts for interconverting between chemical and electrical energy. Molecular catalysts can be appended to inert electrodes to generate chemically modified electrodes (CMEs) that are potent catalysts for key reactions in next-generation energy conversion devices 1–9. While there are many strategies to prepare CMEs, a widely employed and convenient approach is the simple adsorption of the molecular component onto the electrode surface 10–13,15,17,19,22–27,32–34. This ease of preparation, along with the high degree of tuneability afforded by the molecular component and overall potent reactivity, make CMEs compelling catalyst materials. It is thus desirable to uncover the design principles for CMEs to enable rational optimization of this important class of catalysts 14,25–27.

The design of CMEs usually centres on the optimization of the molecular catalyst because the electrode support is generally viewed as an inert source or sink of electrons. The synthesis of active CMEs thus follows two general steps: the selection of a known, highly active molecular catalyst for the reaction of interest; and the development of a heterogenization method. This synthetic logic assumes that activity trends in homogeneous molecular catalysts will correspond to the same trends in electrode activity upon heterogenization. However, there are flaws in these implicit assumptions. For solubility reasons, most molecular electrocatalysts are evaluated and optimized in aprotic polar organic solvents, such as acetonitrile and dimethylformamide (DMF) with added proton donors. In contrast, catalysis by CMEs is typically evaluated in the aqueous medium relevant to device operation, which has starkly different solvation properties and proton conductivities, both of which are expected to dramatically impact the mechanisms of the proton-coupled electron transfer reactions. Further, in molecular electrocatalysis, substrate activation takes place in solution, far from the enormous electric fields native to the electrode surface 35–42. Since electric fields impact the reactivity of enzymes 43–45, surfaces 35–46,47 and molecules 48–53, there is every reason to expect that they may influence the reactivity of CMEs 28,35,41. An improved understanding of the mechanistic implications of the impact of solvation and local electric fields has the potential to expose design principles for the rational development of more active CMEs.

Recent observations lend credence to the notion that heterogenization does alter catalytic activity 1,4,8,10,17–31,35. For example, immobilization of an iron porphyrin results in a 26-fold rate enhancement versus the same species dissolved in the same reaction media 1. Other studies have shown that the reactivity of an appended catalyst is tuned by diverse factors, such as immobilization method 24,31, electrode surface chemistry 26,27 and polymer binder identity 16,27. Although these factors are as important as the catalyst structure in defining its reactivity, the origins of these effects remain unclear 16,24,26,27. In an extreme example, pyrazine linkages that engender strong electronic coupling between molecules and the surface prevent the immobilized catalyst from operating by the stepwise pathways characteristic of molecular catalysts, and instead enforce the concerted mechanisms unique to heterogeneous metallic catalysts 33,34,35. Clearly, the rational development of CMEs requires greater understanding of the molecule–surface interactions that play a key role in defining their reactivity.

In this study, we directly probe the impact of strong surface interactions on catalysis by adsorbed molecules. Counterintuitively, instead of directly adsorbing the molecular species to the surface, we anchored a cobalt tetraphenylporphyrin (CoTPP) to an oxidized glassy carbon electrode with a covalent aliphatic linkage. We chose this linkage to minimize convolution from multilayer adsorption (Supplementary Note 1), prevent dynamic aggregation on the surface 22 and permit the comparison of reactivity across diverse reaction media while maintaining a constant surface population of active sites. Importantly, this flexible cyclohexyl tether allows the appended CoTPP to adopt either an adsorbed or solvated configuration, depending on the solvating properties of the electrolyte. Thus, by examining catalytic trends across different reaction media, we isolate the critical role of surface interactions on catalysis by CMEs. We identify that surface adsorption of CoTPP confers
electrostatic coupling to the electrode surface, with dramatic implications for reaction mechanism and catalyst design. We identify these results by comparing the hydrogen evolution reaction (HER) activity of CoTPP covalently linked to a glassy carbon electrode in acetonitrile, aqueous and mixed aqueous–pyridine electrolytes. We further compare the surface-bound CoTPP to a water-soluble analogue in aqueous electrolyte. We demonstrate that the stepwise reaction pathways observed for soluble molecules occur for this CME in media in which CoTPP is soluble, but that the concerted reaction pathways typical of metallic electrodes occur for this CME in media in which CoTPP is insoluble. Finally, we provide a model to explain how this change in reaction mechanism could arise from adsorption onto the surface. These results have broad implications for the design of CMEs and suggest that the design criteria for optimizing soluble molecular catalysts may not apply upon adsorption to the electrode surface.

Results

Synthesis and characterization. The necessary surface functionalization precursor containing an insulating aliphatic linkage was accessed via treatment of 5-(p-aminophenyl)-10,15,20-triphenylporphyrin with trans-4-(BOC-amino)cyclohexanecarboxyl chloride followed by removal of the tert-butoxy carbonyl (BOC) group with trifluoroacetic acid to yield trans-4-amino-N-(4-(10,15,20-triphenylporphyrin-5-yl)phenyl) cyclohexane-1-carboxamide (H2PorNH2). The cobalt-coordinated species, CoPorNH2, was accessed via treatment of H2PorNH2 with cobalt (II) acetate tetrahydrate. Functionalization of the surface proceeded readily by modification of literature procedures11,56–58. Specifically, surface acyl chlorides were generated by treatment of oxidized glassy carbon electrodes with thionyl chloride. Subsequent treatment of the electrodes with either H2PorNH2 or CoPorNH2 in the presence of pyridine generated CH-MTPP (M = 2H, Co) (Fig. 1). Further details and characterization are provided in the Methods, Supplementary Methods and Supplementary Figs. 1–4.

X-ray photoelectron spectroscopy (XPS) evinces successful ligation of the molecular precursor to the graphitic support to form CH-CoTPP. Following functionalization, new features corresponding to N 1s and Co 2p transitions appear in the survey analysis (Supplementary Fig. 5). High-resolution scans of these features reveal an N 1s peak manifold that fits well with three peaks centred at 398.5, 399.7 and 401.4 eV, which we assign to porphyrin31, amide59 and pyridinium59,60 nitrogen environments, respectively (Fig. 2a). The porphyrin and amide features integrate in the expected 2:1 ratio, which is consistent with the structure of CH-CoTPP. The integration of the pyridinium feature varies from 1 to 1.5 with respect to the amide feature. The binding energy of this feature is inconsistent with metal-bound pyridinic nitrogen and the structural data are most consistent with square-planar cobalt (see below). Thus, we attribute this feature to the reaction of pyridine with reactive surface chlorides that result from the thionyl chloride treatment. Further, this feature is not observed, or is greatly attenuated, after electrochemistry in aqueous media, where such species would be expected to hydrolyse (Supplementary Fig. 6). The high-resolution spectrum of the Co 2p peak manifold reveals a single 2p doublet at 779.9 and 795.1 eV, indicative of only a single cobalt environment on the surface (Fig. 2b). The observed Co 2p binding energies are consistent with literature reports on cobalt porphyrins11,61. The relative integration of the amide and porphyrin N 1s features together against the Co 2p feature is not observed, or is greatly attenuated, after electrochemistry (Supplementary Fig. 7). Importantly, the charge passed in this feature scales linearly with scan rate, consistent with a surface-bound reaction (Supplementary Fig. 8). The origin of the changes to the pre-edge features remains undetermined. Together with the XPS data, the XAS data support the formation of the amide linkages and the presence of intact porphyrin units on the surface.

Outer-sphere electron transfer is observed in acetonitrile. In acetonitrile electrolyte, the cyclic voltammogram (CV) of CH-CoTPP exhibits a clear outer-sphere CoII/I feature, consistent with analogous systems64. In 0.1 M tetrabutylammonium hexafluorophosphate (TBAF6) in acetonitrile, this feature occurs at −0.76 V versus decamethylferrocene (Fc+/Fc0) (Fig. 3). The peak current density of this feature scales linearly with scan rate, consistent with a surface-bound species (Supplementary Fig. 7). Importantly, the charge passed in this feature correlates well to the amount of cobalt on the surface, as determined by inductively coupled plasma mass spectrometry (ICP-MS). We find a Co-to-electron ratio of 1.05 ± 0.07, which further supports our assignment of this feature as a CoII/I redox process. The observation
of this feature in electrolyte without strongly coordinating anions suggests that it is not ion coupled. Furthermore, this feature exhibits no dependence on chloride concentration, indicating that the feature is not tied to ion coordination or dissociation (Supplementary Fig. 8). Together, these data support that, in acetonitrile media, CH-CoTPP exhibits outer-sphere electron transfer (ET) behaviour.

Catalysis in acetonitrile operates by redox mediation. CH-CoTPP is a catalyst for HER in acetonitrile. CVs of CH-CoTPP were collected in acetonitrile containing 0.1 M TBAPF$_6$ and donors with defined proton activities. The proton activity was defined by addition of 25 mM each of proton donor and its conjugate base. In the presence of highly acidic donors, CH-CoTPP catalyses the HER but decomposes too rapidly for in-depth analysis. In the presence of a chloroacetic acid buffer ($pK_a = 15.3$; $\text{CH}_2\text{ClCO}_2\text{H}^+\text{TBA}^-$, $\text{CH}_2\text{ClCO}_2^-)$, CH-CoTPP catalyses the HER, with a sloping S-shaped wave observed at a scan rate of 5 mV s$^{-1}$ (Fig. 4a). The onset of this wave is tied to the CoII/I redox couple. Such behaviour indicates mediated catalysis that operates by stepwise outer-sphere pathways. At faster scan rates, which exceed the rate of the catalytic turnover, we observe the Co II/I redox wave. Integration of this wave in the chloroacetic acid buffer accounts for ~75% of the total loading of Co on the surface, indicating that CH-CoTPP does not substantially decompose under these reaction conditions (Supplementary Fig. 9).

To further support the assignment of a mediated stepwise mechanism, catalysis was evaluated in the presence of a less acidic donor. Redox-mediated reactions are pinned to an outer-sphere reduction potential, but $E_{\text{RHE}}$ shifts with the $pK_a$ of the proton donor, according to the Nernst equation. For a stepwise reaction, selection of a sufficiently basic donor can move $E_{\text{1/2}}$ to an underpotential of $E_{\text{RHE}}$ and catalysis will shut off. Such behaviour is diagnostic of a redox-mediated sequence proceeding by outer-sphere stepwise electron transfers. CVs of CH-CoTPP were collected in the presence of an acetic acid buffer ($pK_a = 22.3$; $\text{AcOH}^-\text{TBA}^+$, $\text{AcO}^-$), where $E_{\text{1/2}}$ of CoII lies at an estimated underpotential of ~100 mV (see Supplementary Note 2). In the acetic acid buffer, no catalysis was observed for the CuII couple and the redox feature was recovered (Fig. 4b). Importantly, the observation of clear CoII waves in the acetic acid buffer demonstrates that CH-CoTPP does not decompose under these more basic conditions. Together, the observation...
of a catalytic wave tied to the Co\textsuperscript{II} redox couple with chloroaacetate acid buffer and the lack of catalysis with the less acidic AcOH support a stepwise, redox-mediated sequence initiated by outer-sphere electron transfer.

**Electron transfer waves are not observed in aqueous media.** In contrast to its behaviour in acetonitrile, CH-CoTPP does not exhibit clear Co-based redox features in aqueous media. To aid interpretation of the aqueous electrochemistry of CH-CoTPP, we first examined the water-soluble cobalt meso-tetra (p-sulfonatophenyl)porphyrin chloride (CoClTSP). CVs of CoClTSP reveal an outer-sphere Co\textsuperscript{II} couple at −0.64 V versus the normal hydrogen electrode (NHE) in both 0.1 M sodium phosphate at pH 6.4 and in 0.1 M NaOH (Supplementary Figs. 10 and 11). In acidic media, CoClTSP mediates HER catalysts preventing observation of the Co\textsuperscript{II} wave (Supplementary Fig. 12). Consistent with our measured value for the $E_{\text{1/2}}$(Co\textsuperscript{II}) for CoClTSP, heterogenized cobalt protoporphyrin IX exhibits a Co\textsuperscript{II} couple at −0.6 V versus the standard hydrogen electrode when incorporated into a film on pyrolytic graphite.

Unlike for the soluble molecular analogue, voltammetry of CH-CoTPP does not reveal redox waves attributable to an outer-sphere Co\textsuperscript{II} redox process. The CV of CH-CoTPP in 0.1 M HClO\textsubscript{4} reveals one feature near 0.6 V versus the normal hydrogen electrode (NHE) in both 0.1 M sodium phosphate at pH 6.4 and in 0.1 M NaOH (Supplementary Figs. 10 and 11). In acidic media, CoClTSP mediates HER catalysts preventing observation of the Co\textsuperscript{II} wave (Supplementary Fig. 12). Consistent with our measured value for the $E_{\text{1/2}}$(Co\textsuperscript{II}) for CoClTSP, heterogenized cobalt protoporphyrin IX exhibits a Co\textsuperscript{II} couple at −0.6 V versus the standard hydrogen electrode when incorporated into a film on pyrolytic graphite.

**Catalysis operates by inner-sphere pathways in aqueous media.** In aqueous media, CH-CoTPP shows Nernstian scaling for the electrochemical response of CH-CoTPP.

**Fig. 4 | CH-CoTPP operates by redox mediation in acetonitrile.** Cyclic voltammograms of CH-CoTPP in acetonitrile containing 0.1 M TBAPF\textsubscript{6} (grey) and 25 mM each of proton donor and its conjugate base (black). Scans were recorded at 5 mV s\textsuperscript{-1}. a, The donor and conjugate base are CH\textsubscript{3}CICO\textsubscript{2}H and [TBA\textsuperscript{+}] [CH\textsubscript{3}CICO\textsubscript{2}]. respectively. b, The donor and conjugate base are AcOH and [TBA\textsuperscript{+}][AcO\textsuperscript{−}]. respectively.

Indicative of pyridine ligation to Co\textsuperscript{II}. Additionally, Co porphyrins have also been heterogenized via axial ligation to surface-bound pyridine units \cite{69–71}, suggesting that pyridine binds strongly to CoTPP in aqueous media. Thus, we collected CVs of CH-CoTPP in aqueous 0.1 M NaOH containing 0.1 M pyridine (Supplementary Fig. 16). In this media, no new waves were observed. However, further addition of pyridine to a final concentration of 3 M (−13% v/v) results in the appearance of a new redox feature (Fig. 5d). The new redox feature is centred at −0.91 V versus NHE and the charge integration accounts for approximately 90% of the surface Co. This potential is 0.27 V more negative than the $E_{\text{1/2}}$(Co\textsuperscript{II}) potential of water-soluble CoTSP, consistent with the more donating phenyl substituents and, perhaps, due to the interfacial solvation environment and/or pyridine coordination. Nonetheless, on the basis of the similarity in potentials and the correspondence in charge integration value, we assign this feature as a Co\textsuperscript{III} redox process. Importantly, the concentration of pyridine necessary to recover this wave in aqueous media is also enough to sparingly solvate the parent CoTPP molecule (Supplementary Fig. 17). Given the literature precedence and the high concentration necessary to reveal this Co\textsuperscript{III} wave, it is likely that both the solvation of the CoTPP unit by pyridine and axial ligation are responsible for the change in the electrochemical response of CH-CoTPP.

To investigate the mechanism of catalysis, we collected steady-state current–voltage (Tafel) data in buffers across a wide pH range. Control experiments establish that these data are not convoluted by mass transport artefacts or deactivation on the time scale of the measurement (Supplementary Figs. 18–23). These data therefore correspond to activation-controlled rates for CH-CoTPP-catalysed HER. Although high-resolution XPS scans of CH-CoTPP after catalysis at each pH reveal minor amounts of demetallation during catalysis, particularly in acidic media, they show no peaks for Co\textsuperscript{0} across all evaluated conditions (Supplementary Fig. 24). Since the post-catalysis XPS data indicate no detectable formation of Co nanoparticles during catalysis, we attribute the HER activity to intact CH-CoTPP.

Extraction of per-site turnover frequencies (TOFs) of 1 s\textsuperscript{-1} from the Tafel data reveal that CH-CoTPP catalyses HER with nearly constant overpotential across the pH range (Fig. 6d, red circles). Indeed, the potential required to sustain a TOF of 1 s\textsuperscript{-1} shifts 58 mV per pH unit (Fig. 6d, red dashed line), in line with the Nernstian scaling
were initiated by sweeping reductively. This upper bound value is 0.8 V more negative than the hypothetical \( E_{1/2}^{\text{CoII/I}} \) must lie more negatively than \(-1.4\) V versus NHE. This upper bound value is \(0.8\) V more negative than the \( E_{1/2}^{\text{CoII/I}} \) value of \(-0.64\) V versus NHE for the water-soluble CoClTSP analogue, and \(0.5\) V more negative than the \( E_{1/2}^{\text{CoII/I}} \) value of \(-0.91\) V versus NHE for CH-CoTPP in \(0.1\) M NaOH containing \(3\) M pyridine. While CH-CoTPP catalyses HER with a comparable overpotential across the pH range, the water-soluble CoClTSP only mediates HER via the \( E_{1/2}^{\text{CoII/I}} \) in acidic aqueous media (Fig. 6d, open blue square). Instead, Co\(^{III}\) waves are observed in neutral and basic media, where there is insufficient driving force for the \( E_{1/2}^{\text{CoII/I}} \) couple of CoClTSP to catalyse HER (Fig. 6d, blue squares). This starkly different pH scaling behaviour between CH-CoTPP and CoClTSP in aqueous media further suggests that CH-CoTPP does not operate by mediated sequences. While we acknowledge that CH-CoTPP could mediate HER, in principle, via different redox couples at varying pH values, the transition between these distinct mediating couples is unlikely to give rise to constant overpotential for catalysis. Furthermore, in this limit, we would expect to observe outer-sphere ET waves for the preceding redox couples that are unable to mediate catalysis in more basic media; yet, we do not observe any clear redox waves for CH-CoTPP in aqueous media without addition of a large concentration of pyridine. On the basis of the foregoing analysis, the observation that CH-CoTPP catalyses HER with similar overpotential across the pH range argues against a classical mediated redox sequence in water.

To gain further insight into the mechanism of HER catalysis by CH-CoTPP, we analysed the Tafel slope and measured the H/D isotope effect for HER. In aqueous \(0.5\) M HClO\(_4\) and \(0.1\) M NaOH, CH-CoTPP displays Tafel slopes of \(110\) and \(103\) mV dec\(^{-1}\), respectively. These values correspond to transfer coefficients of \(0.5\) and \(0.6\), which are consistent with a rate-limiting charge transfer step (Fig. 7a and Supplementary Fig. 22). Control experiments demonstrate no noticeable deactivation of the catalyst during these measurements, and that these values are not convoluted by mass transport limitations (Fig. 7a and Supplementary Fig. 23). Importantly, these values are inconsistent with mechanisms invoking pre-equilibrium reduction of the Co centre before rate-limiting proton transfer, which would yield a transfer coefficient of \(1.0\) and a Tafel slope of \(59\) mV dec\(^{-1}\) (refs. 72,73). Additionally, comparison of HER data collected in \(0.5\) M HClO\(_4\) in H\(_2\)O and D\(_2\)O reveals an H/D isotope effect of \(2.9\pm0.1\), indicative of a proton transfer involved in the rate-limiting step (Fig. 7b and Supplementary Fig. 25). Together, the Tafel and H/D isotope data are consistent with an HER mechanism by CH-CoTPP involving rate-limiting concerted proton–electron transfer (CPET). Although CPET reactions of water-soluble small molecules and coordination compounds can be driven by outer-sphere ET from an electrode, these mechanisms are generally restricted to a relatively narrow pH or potential range, over which both possible stepwise pathways are energetically disfavoured\(^{14,74-77}\). Thus, the Tafel and H/D isotope effect data, taken together with the observation of Nernstian scaling and similar mechanistic profiles across the entire pH range, lead us to invoke an inner-sphere, non-mediated concerted mechanism for HER by CH-CoTPP in water.

**Discussion**

The foregoing electrochemical data indicate distinct ET behaviours and HER mechanisms for CH-CoTPP in aqueous and acetonitrile media.
In acetonitrile, we observe a clear outer-sphere CoII/I redox process that is in quantitative agreement with the total cobalt population on the surface. That 1/2(CoII/I) couple mediates HER catalysis and the pKₐ dependence supports a stepwise mechanism initiated by outer-sphere reduction of the cobalt center. In water, clear Co-based surface redox waves are not observed but are recovered on addition of pyridine. Investigation of the mechanism of HER catalysis by CH-CoTPP in aqueous media supports a non-mediated mechanism in which proton transfer and electron flow are concerted. Additionally, we find that a water-soluble homogeneous CoTPP analogue operates via stepwise HER pathways in aqueous media, suggesting that the change in mechanism for CH-CoTPP requires surface interactions rather than simply resulting from the change in the reaction medium.

The non-mediated, concerted mechanism we observe for CH-CoTPP in aqueous media historically has been attributed solely to metal surfaces, and recently has been implicated for graphite-conjugated catalysts (GCCs), which are molecules conjugated to carbon through aromatic linkages. The ET behaviour of CH-CoTPP thus parallels the differences previously observed for GCCs and their soluble analogues but with the key distinction that the same surface-bound site displays mediated and non-mediated reaction mechanisms depending on the electrolyte environment. Given the parallels to GCCs, we rationalize the non-mediated reaction mechanisms depending on the electrostatic interactions that might be at play, we discuss how the electrochemical behaviour of CH-CoTPP in acetonitrile and aqueous electrolytes can be rationalized by distinct positioning of the Co centre within the electrochemical double layer. A cartoon schematic energy diagram of the double layer is presented in Fig. 8. In each panel, the rectangle represents the band states of the electrode, with filled states in grey and the Fermi level, E_F, marked in black. The position of E_F is sensed and directly modulated by the potentiostat during polarization. The red lines correspond to the electrostatic potential drop between E_F and the solution. The potential of zero free charge, E_PZFC, is the potential at which there is no electrostatic potential drop between the electrode and solution. In Fig. 8a,b, we denote a situation in which the Co centre does not interact with the electrode and is instead freely solvated, which places it outside the double layer electrostatic potential drop (red line) (see ref. 34, pages 771–894 and 1068–1070). Alternatively, in Fig. 8c,d, we depict a situation in which the Co centre is instead strongly adsorbed to the surface sufficiently strongly to reside within the electrochemical double layer (see ref. 34, pages 771–894 and 1068–1070).

The data for the CH-CoTPP in acetonitrile point to the model shown in Fig. 8a,b. This model details the classical behaviour expected for dissolved molecules and molecules appended to but not interacting with an electrode (see ref. 31, pages 1–28). In the left of Fig. 8b, the electrode is polarized at E_PZFC, where E_F lies at an underpotential of 1/2(CoII/I) and no ET occurs. Polarization of the electrode generates an interfacial electric field and raises the electronic levels of the electrode relative to those of the solution outside the EDL, which are fixed. When E_F approaches or shifts to more negative
across the EDL to the CoTPP unit and more electrons are provided catalysis and imposes a rate–overpotential scaling relationship\(^{29,82–88}\) to the ET behaviour shown in Fig. 8a,b. Further, the catalytic wave tied process (Fig. 2) that is not proton-coupled and is consistent with \(E^{1/2}_1\) values than the fixed \(E^{1/2}_{\text{red}}(\text{Co}^{2+/3+})\), electrons from the electrode tunnel across the EDL to the CoTPP unit and more electrons are provided by the external circuit to fill the resulting holes in the electrode band states (Fig. 8b)\(^8\). This is exactly the behaviour observed for dissolved molecules that lie outside the EDL\(^9\) (see also ref. \(^{63}\), pages 1-28). In acetonitrile, CH-CoTPP exhibits a clear outer-sphere Co\(^{2+/3+}\) redox process (Fig. 2) that is not proton-coupled and is consistent with the ET behaviour shown in Fig. 8a,b. Further, the catalytic wave tied to the \(E^{1/2}_{\text{red}}(\text{Co}^{2+/3+})\) redox couple and the pH-dependent changes to HER activity (Fig. 3) indicate that \(E^{1/2}_{\text{red}}(\text{Co}^{2+/3+})\) redox couple mediates catalysis and imposes a rate–overpotential scaling relationship\(^{85,86}\) for HER activity by CH-CoTPP, which causes catalysis to turn off under conditions in which \(E^{1/2}_1\) is close to or more negative than \(E^{1/2}_{\text{red}}(\text{Co}^{2+/3+})\). Importantly, applying a more negative potential cannot recover catalytic activity by CH-CoTPP in the presence of strongly basic donors because the free energy of the reaction of Co\(^2+\) with proton is pinned by \(E^{1/2}_{\text{red}}(\text{Co}^{2+/3+})\), regardless of the applied potential. Together, these data indicate that the energy levels of the Co centre are well isolated from those of the electrode in acetonitrile, and that ET proceeds by the tunnelling of electrons across the EDL in direct analogy to the ET mechanisms observed for dissolved molecules. Thus, the model in which the Co centre in CH-CoTPP resides outside the EDL potential drop is consistent with the experimental data in acetonitrile and implies that the Co centre behaves like a dissolved molecule in this medium.

In aqueous media, the data for CH-CoTPP points to the model shown in Fig. 8c,d. Surprisingly, this is the same model that is invoked for metallic surfaces, not molecular species. Here, any shifts in \(E_F\) also result in tandem movements of the energy levels of the CoTPP unit. As a result, there is insufficient driving force for outer-sphere ET from the electrode to the Co centre. Since this redox process is inaccessible, any mediated reaction pathways that proceed via outer-sphere ET steps are excluded. However, catalysis still occurs via inner-sphere mechanisms because there is a potential drop between the Co centre and the solution. Instead of the tunnelling of an electron, polarization drives the movement of an ion across the EDL to subsequently bind to the Co centre. Thus, unlike the redox-mediated mechanism described above, varying the strength of the proton donor across the pH range can be compensated for by polarization of the Co centre to a more negative potential, thereby maintaining HER catalysis across the entire pH range (Fig. 6). The charge of the proton brought to the Co centre is compensated by concerted electron flow from the external circuit to maintain the electrode potential. This CPET could be described as a one-electron, one-proton transfer to a Co\(^{2+}\) surface site to make a formally Co\(^{1+/2+}\)-H species. The catalytic cycle is completed when a soluble donor protonates this Co-H intermediate and an electron flows from the circuit to balance the charge of the proton that crossed the EDL, to result in the overall two-electron stoichiometry of the HER and regenerate a formally Co\(^3+\) state. This model (Fig. 8c,d) in which the Co centre in CH-CoTPP resides inside the EDL potential drop is consistent with the Tafel, H/D isotope effect and pH dependence data in water and requires that the CoTPP unit is interacting strongly with the electrode in this medium. We attribute the starkly divergent ET and catalytic behaviour in the above model to distinct positions of the CoTPP unit with respect to the EDL potential drop in each medium. This position defines whether there is a substantial electrostatic potential drop between the Co active sites and the electrode (Fig. 8a,b) or not (Fig. 8c,d). In acetonitrile, the data indicate that there are sufficient layers of solvent and ions between the surface and the CoTPP units to screen the Co centres from the charge on the electrode (Fig. 8a). These intervening layers comprise the EDL and the majority of the electrostatic potential drop occurs across these solvent and ion layers (see ref. \(^{38}\), pages 771–894 and 1068–1070). This model implies that, in acetonitrile the relative free energy of solvation of the molecular fragment and affinity of the solvent for the charged surface outcompete the free energy of adsorption of the molecule to the surface (see ref. \(^{44}\), pages 895–983). In line with this reasoning, the parent CoTPP complex is sparingly soluble in acetonitrile (Supplementary Fig. 17) and Co\(^{2+/3+}\) waves can be recovered in aqueous media on addition of 3 M pyridine (Fig. 5d), which sparingly solvates CoTPP (Supplementary Fig. 17).

In contrast, the aqueous data indicate that the catalytically active CoTPP units are not screened from the electrode charge in aqueous electrolyte and that there is no substantial electrostatic potential drop between the electrode and the Co centres. This lack of screening implies that there are insufficient layers of solvent and ions located between the electrode and the CoTPP units over the entire aqueous pH/potential window examined for HER (Fig. 8c). The majority of the electrostatic potential drop that occurs in the EDL thus lies between the Co active sites and the bulk solution. In short, the active CoTPP units are co-solvated with the electrode. In line with this reasoning, we note that the parent CoTPP complex is insoluble in water (Supplementary Fig. 17). We posit that interactions with the electrode surface, such as \(\pi-\pi\) interactions and/or axial coordination of the Co centres to oxidic edge terminations, stabilize the CoTPP fragment within the EDL (Fig. 8e). In addition to ensuring the

\[ E (V) \text{ versus } E^{1/2}_{\text{red}}(\text{Co}^{2+/3+}) \]

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strong electrostatic coupling between the CoTPP fragment and the electrode, these surface interactions also appear to afford sufficient quantum mechanical coupling to allow for concerted electron flow to the Co site on the time scale of proton transfer. Given the generality of these surface interactions for adsorbed porphyrins and phthalocyanines on graphitic carbons, the observation of non-mediated pathways for porphyrins heterogenized with alkyl tethers motivates a re-evaluation of the reaction mechanisms of a wide variety of electrochemical transformations by heterogenized macrocycles.

**Conclusion**

We report the ligation of CoTPP to a graphitic carbon electrode through an aliphatic tether and examined its electron transfer and catalytic behaviour in acetonitrile and aqueous electrolytes. We show that the ET behaviour follows a typical outer-sphere, redox-mediated, stepwise mechanism for the H₂ evolution reaction in acetonitrile but transitions to a non-mediated concerted reaction pathway in aqueous electrolytes. This concerted mechanism by CH-CoTPP in aqueous media is akin to those of metallic electrode...
surfaces and bypasses the redox intermediates that pin the reactivity of molecular electrocatalysts. The starkly disparate reaction mechanisms in the two media are attributed to the different solvating properties of acetonitrile and water for the CoTPP unit. The preference for solvation over surface adsorption of the porphyrin in acetonitrile causes it to reside outside the potential drop of the EDL, whereas poor solvation in water favors strong adsorption to the surface, causing the molecule to reside inside the EDL. Thus, in aqueous media, preferential surface interactions lead to strong electrostatic coupling of the CoTPP units to the electrode, which, in turn, drives inner-sphere, concerted reaction mechanisms.

Importantly, our model invokes nothing special about the covalent aliphatic amide linkage. While this covalent, flexible anchor was critical for us to expose distinct reaction mechanisms in aqueous and non-aqueous media, there is expected to be negligible electronic coupling between the surface and the appended molecule through this aliphatic tether. Thus, the linkage is not expected to contribute to the strong surface interactions that give rise to non-mediated concerted reaction mechanisms in water. Instead, the flexibility of the linkage permits other surface interactions to occur, if favourable. It is these other surface interactions that give rise to inner-sphere mechanisms in water and these native surface interactions are likely to exist for a wide variety of metallomacrocycles/carbon composite electrodes. Thus, these results motivate a re-examination of the electrochemical reaction mechanisms of adsorbed planar macrocycles.

Specifically, these findings suggest that chemically modified electrodes should not be presumed, a priori, to operate via stepwise mechanisms initiated by outer-sphere ET; the surface redox waves observed for CMEs may correspond to only a fraction of the surface-adsorbed and catalytic activity may not arise solely from those apparently electroactive surface sites; and molecular fragments with redox potentials misplaced relative to the thermodynamic potential of the target reaction may, nonetheless, be active as CMEs under electrolyte conditions that foster strong interactions with the electrode surface.

This last point suggests that the reduction potential, \( E_{1/2} \), is not as useful a descriptor for identifying the molecular constituents of high-performance CMEs, particularly for molecules that are expected to adsorb strongly to electrode surfaces. Despite the diminished role of the molecular redox potential, the metal identity and local structure\(^{11,12,20,22,89–94} \), as well as the local environment\(^{89-113} \) of the adsorbed molecule, remain effective handles for tuning catalysis. We posit that changing the structure influences the free energies of key intermediates\(^8 \), which are common descriptors used to optimize heterogeneous catalysts\(^{85-89} \). Thus, tuning catalyst structure to modulate the binding of key intermediates—instead of the redox potential—may be particularly valuable in identifying candidate molecules for high-performance CMEs. Given that the concerted reactivity observed here circumvents the redox intermediates endemic to mediated catalysis, our findings open the door to an expansion of the use of strong molecule/surface interactions to enhance electrocatalysis on chemically modified electrodes.

**Methods**

**Chemicals and materials.** All syntheses were performed in solvents of ACS grade or better. Chloroform and methanol were obtained from BDH; dichloromethane, hexanes, DMF and toluene were obtained from Macron Fine Chemicals; 200 proof ethanol was obtained from Koptec and pyridine was obtained from Acros Organics; and all were used as received unless otherwise noted. Dry dichloromethane and toluene were degassed and dried using a Glass Contour Solvent Purification System built by SG Water and were stored under an atmosphere of \( \text{N}_2 \) over 4 Å molecular sieves. Dry pyridine and dry dichloroethane were both obtained from DriSolv EMD Millipore. All aqueous synthetic manipulations used deionized water, while all aqueous electrochemical preparations and measurements used reagent-grade water (Millipore Type 1, 18.2 MΩ·cm resistivity). Sulfuric acid (OmniTrace, 95.5–96.5%) and hydrochloric acid (OmniTrace, 34–37%) were obtained from EMD Millipore and were used as received. Nitric acid (68–70%) was obtained from BDH and was used as received. Electrolytes were prepared from the following: perchloric acid (Suprapur, Sigma-Aldrich, 70%), sodium hydroxide (Sigma-Aldrich, 99.99%), sodium formate (Sigma BioUltra, >99%), sodium perchlorate monohydrate (Sigma-Aldrich, 99.99%), sodium chloride (Alfa Aesar, 99.99%), sodium tetraborate (Alfa Aesar, 99.95%), sodium perchlorate monohydrate (Sigma-Aldrich, 99.99%), tetrabutylammonium hexafluorophosphate (Sigma-Aldrich, >99.0%), tetrabutylammonium chloride (Sigma-Aldrich, >99.0%), dry acetonitrile (Sigma-Aldrich, 99.8%) and tetra(n-butyl)ammonium acetate (>99.0%). Cobalt meso-tetra(p-sulfonatophenyl)porphyrin chloride was obtained from Frontier Scientific and used as received. Glassy carbon disk electrodes were obtained from Pine Research Instrumentation. Hg/HgO and Hg/HgSO\(_4\) reference electrodes were obtained from CH Instruments. Non-aqueous Ag/AgCl reference electrodes with Vycor frits were assembled from kits purchased from BASi. Platinum wire (99.9%) and platinum mesh (99.9%) were obtained from Alfa Aesar. Sources and purities of other chemical reagents used in syntheses are included in the protocols below or in the Supplementary Methods.

**General electrochemical methods.** All electrochemical experiments were performed under ambient conditions (21 ± 1 °C) using a Biologic VSP 16-channel potentiostat and EC-Lab software (v.11.43). Rotation experiments were performed using a Metrohm Autolab RDE-2. A Hg/HgSO\(_4\) reference electrode (stored in 1 M NaOH, 99.999% semiconductor grade, Sigma-Aldrich) was used for all aqueous experiments in pH >10. All other aqueous experiments used a Hg/HgSO\(_4\) reference electrode (stored in saturated K\(_2\)SO\(_4\), 99.997% metals basis, Alfa Aesar). Both reference electrodes were periodically checked against pristine electrodes to ensure against potential drift. Electrode potentials for experiments performed in aqueous media were plotted versus the reversible hydrogen electrode (RHE, \( E_{\text{RHE}} = E_{\text{Hg/HgSO}_4} + 0.140 + \text{pH} \times 0.059 \text{ V} \) or \( E_{\text{RHE}} = E_{\text{Hg/HgSO}_4} + 0.640 + \text{pH} \times 0.059 \text{ V} \)). All non-aqueous measurements used a Ag/AgCl reference electrode that was filled with and stored in acetonitrile containing 0.1 M TBAPF\(_6\). At the end of each non-aqueous measurements a small portion of decamethylferrocene (obtained from Sigma-Aldrich) was added to the solution. All non-aqueous potentials were referenced to the Fe\(^{3+}/\text{Fe}^2+\) redox couple. A Pt mesh counter electrode was used for all experiments. All electrochemical measurements were recorded in a custom five-neck cell equipped with a sapphire tube and counter compartment separated by a glass frit. All glassware used for electrochemical measurements was soaked in aqua regia for at least 30 min and thoroughly washed with reagent-grade water before use. For non-aqueous measurements, the glassware was subsequently dried in an oven and then either brought immediately into an \( \text{N}_2 \)-filled glovebox or cooled while a stream of MeCN-saturated \( \text{N}_2 \) was passed through the cell. No iR correction was applied to any measurement.

**Preparation of CH-MTPP.** Electrode cleaning and pre-treatment. Glassy carbon (5 mm diameter, Pine Research Instruments) electrodes were soaked in freshly made aqua regia for 10 s to remove any trace metal impurities from previous functionalization treatments. Electrodes were polished using a Buehler MetaServ 250 Grinder/Polisher equipped with a Buehler Vector LC 250 rotating head. The electrodes were placed in custom-fabricated PTFE holders against a rotating (300 r.p.m.) Chemoto (HT Technologies) surface with an alumina slurry for two min with 2 lb applied force, followed by rinsing with reagent-grade water. This process was repeated in sequence using 1.0 μm, 0.3 μm and 0.05 μm alumina slurries, each on a different Chemoto plate. Finally, the electrodes were sonicated twice in reagent-grade water. To increase the surface area and bypass the redox intermediates that pin the reagent-grade water, the electrodes were sonicated twice in reagent-grade water. To increase the surface area, the electrodes were exposed to a stream of MeCN-saturated \( \text{N}_2 \) and was then purged with a stream of MeCN-saturated \( \text{N}_2 \) and then purged with a stream of MeCN-saturated \( \text{N}_2 \). The electrodes were subsequently washed with copious amounts of reagent-grade water and EtOH and dried in vacuo before electrochemical evaluation or further functionalization. Electrodes that were anodized in this way are referred to as GCox.

**Preparation of CH-MTPP electrodes.** This procedure modifies a literature protocol\(^{61-64} \). Inside a \( \text{N}_2 \)–filled glovebox, a septum-capped vial was charged with GCox electrodes and 12 ml of dry tolune. The vial was removed from the glovebox and, via syringe, 3 ml of SOC1 (TCI, -98.0%) was added and the vial heated to 120 °C for 1 h. Upon cooling to room temperature, the solution was removed via syringe (Caution: it is a cool liquid, so cool it slowly in an ice bath and then discard via a waste manifold). The vial was then brought back into the glovebox. The electrodes were washed by sequential submersion in two vials of dry tolune, and were then transferred to a clean vial. To the electrodes was added 8 ml of dry toluene and 4 ml of a 1:1 mixture of dry CH\(_2\)Cl\(_2\) and dry pyridine, which contained ~2.5 mg of either cobalt chloride (Alfa Aesar, 99%) and pyridine (Sigma-Aldrich, 99.8%) cyclohexane-1-carboxamide. The vial was sealed, removed from the glovebox and heated to 120 °C for 3 h. Upon cooling, the electrodes were washed with copious amounts of toluene, then DMF and then MeOH. The electrodes were dried in vacuo and stored in a vial under ambient conditions before electrochemical studies or surface characterization.

**Preparation of CH-MTPP on high-surface-area carbon.** Before use, Monarch 1300 powder (Cabot) was washed according to the literature\(^9 \). Under an inert atmosphere, Monarch 1300 powder was washed in a Soxhlet extractor with...
EtOH and o-dichlorobenzene for 24–72 h, each, then dried in vacuo. To a 40 mL scintillation vial charged with a stir bar, 200 mg of the washed Monarch 1300 was added. The vial was placed under an Ar atmosphere and 15 mL of dry toluene was added. The mixture was heated at 80 °C, was added via syringe and the vial was heated to 120 °C. The mixture was stirred for 1 h, then brought into a N₂-filled glovebox. The carbon powder was collected on a filter paper using a Hirsch funnel and washed with 4 x 5 mL of dry toluene. The carbon powder was dried by passing a gentle vacuum through the filtration apparatus and then was transferred to a clean vial charged with a stir bar. To the vial was added 12 mL of dry toluene and 3 mL of dry pyridine containing 10 mg of CoBr₂. The vial was sealed, removed from the glovebox and heated to 120 °C for 3 h. On cooling, the carbon was collected on a filter paper in a Hirsch funnel. The powder was washed with toluene, DMF and MeOH. The powder was transferred to a thimble and washed in a Soxhlet extractor with EtOH for 14 h then CH₂Cl₂ for 14 h. Elemental analysis: C, 89.95; H, 0.82; N, 1.02. The value for the carbon determination of Monarch 1300 yields a native nitrogen percentage of 0.25%. Controlling for the native nitrogen content yields a N-Co ratio of 27:1, consistent with excess incorporation of nitrogen by the SSCI treatment.

X-ray photoelectron spectroscopy. XPS spectra of CH-CoTPP were recorded using a Physical Electronics PHI Versaprobe II with a monochromatic Alkα X-ray source (1,486.6 eV) and a hemispherical energy analyser. Spectra were collected by fixing the glassy carbon button to the support plate with conductive carbon tape. Data were collected at a base pressure of 5 x 10⁻¹⁰ torr using a 200 μm, 50 W focused beam at a take-off angle of 45°. Survey spectra were collected using a pass energy of 187.85 eV and a step size of 0.8 eV. High energy resolution scans, which were used for peak fitting, were collected with a pass energy of 23.50 eV and a step size of 0.1 eV. All quantification was performed using MultiPak software (v9.6.3.3). Each spectrum was smoothed with a five-point Savitzky–Golay method before quantification. Peak fitting was performed in CasaXPS (v2.3.17PR1.1). All scans were smoothed with a five-point Savitzky–Golay method and referenced to the graphic C 1s peak (284.3 eV) of glassy carbon. The N 1s peak manifolds of all compounds were fitted with a Shirley-type background and fit with Gaussian/Lorentzian line shapes of 30% Gaussian shape. The Co 2p peak manifolds were fit with a linear background and an asymmetric peak shape comprising a Gellus profile convoluted with a Gaussian/Lorentzian obtained in CasaXPS by inputting A(0.35), 0.8(CH₄)(30) in the entry for Line Shape in the peak-fitting window. This procedure was used to produce the data in Fig. 2a,b and Supplementary Figures 5, 6 and 25. Summaries of surface atomic concentrations and peak binding energies are given in Supplementary Tables 1 and 2.

Determination of catalyst surface concentration. General methods for ICP-MS. Spectra were collected using an Agilent 7900 ICP-MS. A calibration curve was generated from aqueous 2% nitric acid solutions containing known concentrations of Co. Erbium (Ricca Chemical Company, 1,000 ppm in 3% HNO₃) was used as an internal standard in the calibration curve and samples. The calibration solution series were prepared by serial dilution of a Co standard solution (Fluka, TraceCERT 1,000 ppm in 2% HNO₃) with 2% nitric acid (EMD Millipore, OmniTraceUltra). All volumetric flasks were soaked in aqua regia and rinsed with copious amounts of reagent grade water before use. Solutions, if not used immediately, were stored in air-tight plastic containers and shielded from light.

Determination of the ratio of integrated charge to the surface Co concentration for CH-CoTPP. Before digestion for ICP-MS, cyclic voltammograms of CH-CoTPP modified glassy carbon electrodes were collected in 0.1 M TBAPF₆, in MeCN under N₂. Voltamograms were initiated at the open circuit potential and swept reversely, cycling three times. The third sweep was used for integration. The redox feature centred at ~0.76 V versus Fe⁺/Fe⁺ was assigned to the surface Co⁰ wave and was integrated to determine the charge passed. Following cyclic voltammetry, each electrode was left in the PTFE holder used for electrochemistry and carefully placed in a 15 mL plastic centrifuge tube containing approximately 1 mL HNO₃ (OmniTraceUltra, EMD Millipore) such that the acid only made contact with the holder and the face of the button electrode that had been exposed to electrolyte. This method ensured that only the surface of the button analysed electrochemically was digested. The electrodes were soaked overnight (~14 h) followed by dilution to a final volume of 25.00 mL by addition of reagent-grade water. The concentration of Co in the resulting solutions was measured by ICP-MS. The integrated charge in the Co⁰ wave was converted to moles of electrons by dividing by the Faraday constant. The measured cobalt surface concentration was divided by the integrated charge quantities for each electrode to obtain the Co/e⁻ ratio of 1.05 ± 0.07 reported in the main text.

Determination of Co surface concentration in CH-CoTPP. The above Co/e⁻ ratio, to the nearest integer value, was used along with the integrated charge in the non-aqueous Co⁰ wave to determine the Co surface concentration of all subsequently prepared CH-CoTPP electrodes using the following equation:

\[ \Gamma_C = \frac{Q_{Co^{0}}}{F \cdot e^{-}} \]

where \( \Gamma_C \) is the surface coverage of cobalt in mol, \( Q_{Co^{0}} \) is the integrated charge of the Co⁰ wave, \( F \cdot e^{-} \) is the experimentally determined ratio of cobalt to electrons rounded to the nearest integer and \( F \) is the Faraday constant.

Assessment of H₂ reduction activity. Evaluation of catalysis and lack thereof in non-aqueous media. Catalysts in non-aqueous media was evaluated by measurement of CVs. Electrolyte was prepared immediately before use in an N₂-filled glovebox. If experiments were not performed inside the glovebox, the electrochemical cell was purged with MeCN-saturated N₂ immediately following addition of electrolyte. During all measurements, MeCN-saturated gas was passed through the headspace to eliminate any traces of the electrolyte. Electrodes were cycled in MeCN electrolyte containing 0.1 M TRAPF₆, to establish the presence of the Co³⁺ surface feature. After these initial CVs, the relevant proton donor and conjugate base were dissolved using the electrolyte, and added via syringe to the electrochemical cell to yield a final concentration of 25 mM for both acid and conjugate base. Catalysis was then evaluated by recording CVs. In some cases, electrodes were initially cycled in 0.1 M NaOH before any evaluation in non-aqueous media, with no change to the observed catalytic activity but with cleaner baselines to the CV background charging current. After all voltammograms were recorded for a given solution, the CH-CoTPP electrode was replaced with a freshly polished Au electrode, a small portion of Fc⁺ was added, and a CV was recorded.

Evaluation of catalysis in aqueous media. Before recording electrochemical data in aqueous media, CVS on each electrode were recorded in MeCN electrolyte containing 0.1 M TRAPF₆, under N₂ to measure the Co⁰ redox couple. Integration of the charge passed in this wave was used to determine the surface cobalt concentration and TOFs for each electrode. After these CVSs, electrodes were rinsed with MeCN and dried in vacuo.

Measurement of electrochemistry in aqueous media. Steady-state data were collected via chronoamperometry across a series of potentials spanning the activation-controlled region. All measurements were recorded while the electrode was rotated at 2,000 r.p.m. unless otherwise noted. Chronoamperograms were collected in 25 mV increments from low to high potential (higher to lower overpotential) followed by the recollection of the lowest potential (highest overpotential). Each chronoamperogram was allowed to reach steady state (10 s) and the average current density over the last 5 s of data collection was used to determine the TOF at each potential. TOFs were calculated according to the following formula:

\[ \text{TOF} = \frac{i}{2.000 F \cdot \Gamma_C} \]

where \( i \) is the current in mA, \( \Gamma_C \) is the surface coverage of Co in mol and \( F \) is the Faraday constant.

H/D kinetic isotope effect. HClO₄, electrolytes (0.5 M) were prepared by adding 1.8 mL concentrated HClO₄, (EMD Millipore, Suprapur) to 38.0 mL H₂O or D₂O (Cambridge Isotope Laboratories, 99.9%). To clearly demonstrate the H/D kinetic isotope effect (KIE) for H₂ evolution at CH-CoTPP, we collected cyclic voltammograms at 25 mV s⁻¹ but quantified the KIE using Tafel data from steady-state measurements. At ~0.64 V versus NHE, we found KIEs of 3.0 and 2.8 for two separate electrodes, which averages to the value of 2.9 ± 0.1 reported in the main text. See Supplementary Note 3 for more details.
Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

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**Author contributions**
C.J.K. and Y.S. conceived the research and developed experiments. C.J.K. and S.W. conducted all experiments. J.W. processed and analysed X-ray absorption data. C.J.K. and Y.S. wrote the manuscript with input from all authors.

**Competing interests**
The authors declare no competing interests.

**Additional information**

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