High current density microkinetic and electronic structure analysis of CO$_2$ reduction using Co and Fe complexes on gas diffusion electrode

The reactivity and energetics at each elementary step of immobilized Co and Fe complexes on gas diffusion electrode for the electrocatalytic CO$_2$ reduction reaction were examined through a combination of microkinetic assessment and theoretical DFT calculations. The experimental and theoretical calculation results disclosed distinctive performance between Co and Fe complexes resulting from their electronic structure and CO or CO$_2$ adsorption free energies on the metal center.

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Highlights
- Microkinetic analysis was performed at high current densities
- The redox non-innocent TPP and Pc were disclosed by electronic structure analysis
- The distinctive performance between Co and Fe complexes was interpreted

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High current density microkinetic and electronic structure analysis of CO₂ reduction using Co and Fe complexes on gas diffusion electrode

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SUMMARY
Reaction mechanisms of electrocatalytic CO₂ reduction into CO over Co or Fe complexes were examined using gas diffusion electrodes to meet the requirement of high current densities for industrial deployment. Our experimental and theoretical calculation results consistently revealed that the Fe-based molecular catalysts exhibited more positive redox potentials relevant to CO₂ electrocatalysis but disfavored the desorption of generated CO, especially at high overpotentials, failing to achieve appreciable reaction rates. Distinctively, the heterogenized Co-based molecular complexes were found to be tolerant to the high coverage of CO at steady state on the active site and achieved rates exceeding 100 mA cm⁻² toward exclusive CO evolution. Density-functional theory calculations not only disclosed the redox non-innocent tetraphenylporphyrins and phthalocyanines during electrocatalytic CO₂ reduction but also corroborated the energetics, especially for CO₂ and CO adsorption, accounting for distinctive reaction pathways between Co and Fe complexes.

INTRODUCTION
Valorization of CO₂ is a prerequisite for modern society to achieve sustainability.¹ Electrocatalytically converting CO₂ into value-added and energy-dense chemicals powered by renewable electricity stands out as a route well compatible with the need to decarbonize the economy. Accordingly, recent decades have witnessed intensive research efforts dedicated to electrocatalytic CO₂ reduction to CO, formic acid, methanol, or hydrocarbons.² Notably, CO is a useful and versatile feedstock for the chemical industry, which requires less overpotential via the electrocatalytic CO₂ reduction than the other products.³,⁴ Silver and gold metal electrocatalysts in a zero-gap cell direct the reaction toward the CO route selectively, achieving a Faradaic efficiency toward CO (FE_CO) larger than 90% and stable long-term performance (200–500 mA cm⁻², >1,000 h), which is closest to commercialization.⁵,⁶ Nevertheless, their scarcity and high costs affect the economic benefits of industrial application. Some non-precious metal electrocatalysts, such as p-block element-modified Cu, could also selectively produce CO at reasonable currents, but stability still needs to be improved,⁷–⁹ necessitating the development of an alternative and scalable candidate. Molecular complexes, such as metallophthalocyanines (MPc) and metallotetraphenylporphyrins (MTPP), have recently received increasing attention for the electrocatalytic CO₂ reduction into CO because of their chemical and geometrical tunability.
as well as their industrial merits.\textsuperscript{10,11} The ligand environment enables the earth-abundant metals (Co, Fe, and Ni) to electro-catalyze CO\textsubscript{2} reduction to CO, which could be precisely designed to tailor the electronic structure of central metal and optimize the geometric structure (steric effects and the secondary coordination sphere) to improve catalytic performance.\textsuperscript{12–17} Adding further motivation to this field is its versatility in fabricating electrodes. The molecular catalysts could be immobilized on the high surface area and conductive support, including carbon nanotubes,\textsuperscript{18} carbon cloth,\textsuperscript{19} carbon black,\textsuperscript{20} and graphene\textsuperscript{13,21} by non-covalent interaction, covalent grafting,\textsuperscript{22} embedding into metal-organic frameworks (MOFs) or covalent organic frameworks (COFs),\textsuperscript{23} and polymer encapsulation.\textsuperscript{24} Furthermore, functionalized CoPc and NiPc deposited on the gas diffusion layer (GDL) in a gas-fed flow cell have demonstrated industrially relevant current densities of >100 mA cm\textsuperscript{-2} with >90% FE\textsubscript{CO\textsubscript{2}}, where a three-phase interface was created to reduce mass-transfer limitation.\textsuperscript{25–28} The mechanistic insights interpreted by well-defined molecular catalysts supported on GDL could, in turn, facilitate developing clear structure-activity relationships for rational catalyst design. The rational design of molecular catalysts together with the use of GDL improves their activity and stability,\textsuperscript{25,27,28} which hold promise to close the gap between molecular and metal catalysts.

Identifying the catalytically active sites and clear interpretation of reaction mechanisms are imperative to establish the robust design principles of molecular catalysts. The catalytic site of the molecular catalyst has been presented on the basis of spectroscopic measurements and density-functional theory (DFT) calculations. In situ UV-vis was used to probe the active sites of CoTPP and CoPc under reaction conditions to reveal that the Co(II) center was reduced to Co(I).\textsuperscript{19,23,29} Operando X-ray absorption spectroscopy (XAS) revealed a change in the oxidation state of CoTPP installed in COF from +2 to +1 upon cathodic polarization, which was in agreement with the UV-vis results.\textsuperscript{23} However, the oxidation state of CoPc immobilized on carbon fiber paper remained identical at CO\textsubscript{2}-reducing potentials in another study.\textsuperscript{30} Recently, operando UV-vis and XAS results indicated the reduction of Fe(III) into Fe(II) state in fluoridized FeTPP, which persisted at −0.6 V compared with a reversible hydrogen electrode (RHE) in CO\textsubscript{2}-saturated aqueous solution of 0.5 M NaHCO\textsubscript{3} at pH 7.2.\textsuperscript{31} Several attempts have been conducted to resolve disputes related to the electronic structures using DFT calculation.\textsuperscript{32,33} It is generally accepted that the metal center of Fe- or Co-based molecular catalysts was reduced to +1 state, which could adsorb and activate CO\textsubscript{2} under reaction conditions.\textsuperscript{32,33} In contrast, some computational studies pointed to the electron localization not on the metal center but the porphyrin macrocycles, especially for Fe-based molecular complex.\textsuperscript{34–36} The previous studies exhibit a lack of agreement regarding the redox state of the metal center, impeding the rational catalyst design.

Microkinetic analysis is a powerful tool to gain insights into catalytic pathways over molecular catalysts. For example, previous studies showed that CoPc and CoTPP are highly sensitive to pH during electrochemical CO\textsubscript{2} reduction to CO in the H-cell configuration.\textsuperscript{37,38} The aminopyridyl groups bridging Co-based molecular catalysts acted as a Lewis base, enhanced the proton transfer, and increased the local concentration of CO\textsubscript{2} in the catalyst layer to accelerate electrocatalytic CO\textsubscript{2} reduction to CO.\textsuperscript{37,38} In contrast, a study based on online electrochemical mass spectrometry revealed that the CO evolution rate on Co protoporphyrin was insensitive to the pH values (≥2), which indicated that a decoupled proton-electron transfer mechanism occurred.\textsuperscript{39} Moreover, the experimental studies on immobilized CoPc at low loading suggested the reaction mechanism was shifted from “concerted proton-electron
transfer step limited and H₂O as the proton donor” to “electron transfer limited and bicarbonate as the proton donor” upon going from low to high overpotential by integrating the Tafel slope, bicarbonate, and CO₂ order dependences and catalysts poisoning via bicarbonate electrosorption.⁴⁰,⁴¹ Some other electrokinetic measurements indicated that the rate-determining step over CoPc and CoTPP involved the first electron transfer and a zeroth order existed on the concentration of bicarbonate.⁴²,⁴³ Notwithstanding these insights provided by microkinetic analysis, all these studies were performed using a conventional aqueous H-cell, which fails to achieve an industrially relevant reaction rate because of the mass-transport limitations. Therefore, it is essential to perform a microkinetic assessment in a cell configuration with improved mass transfer flux to understand and design active molecular catalysts.

In this contribution, we examine the electrocatalytic CO₂ reduction into CO over molecular catalysts supported on GDL with gaseous CO₂ supply to shed light on their reaction mechanisms, conjugated with theoretical calculations. The molecular complexes including FePc, FeTPP, CoPc, and CoTPP were immobilized on the carbon nanotube (CNT) and then spray coated on the GDL, which were proved successful by our characterization. The revaluations using a gas-fed flow cell in CO₂-saturated aqueous solution of 1 M NaHCO₃ disclosed that the Fe-based molecular catalysts are sensitive to generated CO, especially at high overpotential. Distinctively, the heterogenized Co-based molecular complexes were found to be active toward CO evolution catalysts at rates above 100 mA cm⁻², consistent with the literature.²⁵ The electrokinetic data over Co-based molecular catalysts suggested a decoupled proton-electron transfer reaction mechanism for CO evolution over these Co-based catalysts, which was thoroughly supported by the thermochemical values of each elementary step during CO₂ electrochemical reduction obtained by our theoretical calculations. The microkinetic assessments and theoretical studies provide a fundamental perspective for the community, paving the way for CO₂ valorization using electrocatalytic CO₂ reduction over heterogenized molecular catalysts using pure or diluted CO₂ streams.

RESULTS

Electronic structure of porphyrin or phthalocyanine complexes with embedded iron or cobalt center

To understand the roles of metal and the ligand in the electrocatalytic reduction of CO₂ to CO with the two-electron transfer, we initially scrutinized the electronic structure of Fe- and Co-based molecular complexes with both Pc and TPP ligands. The spin density distributions for molecular structures with all metal-ligand combinations comprising +3, +2, +1, and 0 formal oxidation states are detailed (see supplemental information for full details; Figures S1 and S2; Tables S1–S3), and the most stable ground state structures for each complex are presented in Figures 1 and S1. The quotation marks used for M(I) and M(0) (M = Fe, Co) emphasize that these are formal assignments of oxidation states, thus independent from any implication of either metal- or ligand-centered reduction. M(III) complexes are well-described catalyst precursors in catalytic CO₂ reduction reactions, and therefore they are also included in our electronic structure characterization. Notably, Fe(III) and Co(III) complexes display different spin coupling features, shown in Figure S1. Fe(III) unpaired electrons couple with the ligand unpaired electrons ferromagnetically, while Co(III) complexes show antiferromagnetic coupling resulting in open-shell singlet states. Thus, a high-spin state is assigned to Fe(III) complexes, whereas a low-spin state is predicted for the Co counterparts. One electron injection to M(III) generates M(II) with a metal-centered reduction for both metals, giving rise to a triplet Fe(II) and a
doublet Co(II), also shown in Figure S1. However, the second and third electron injections lead to the flow of electrons through the ligands preserving the metal oxidation state at +2. Therefore, “Fe(I)” and “Co(I)” in Figure 1 can be denoted as [Fe(II)L]$^-$ and [Co(II)L]$^-$ (L = TPP, Pc) with doublet and open-shell singlet ground states, respectively. Similarly, “Fe(0)” and “Co(0)” can be denoted as [Fe(II)L$_2$] and [Co(II)L$_2$], implying a doubly reduced ligand. [Fe(II)L$_2$]$^-$ is predicted to be an open-shell singlet with both ligands, while [Co(II)L$_2$]$^-$ is found to be doublet with the TPP and Pc ligands. By and large, the two metal systems exhibit similar electronic structures in the sense of where the injected electrons will be located, either the metal or the ligand. Also, the two ligands have quite similar behavior, both facilitating the reduction of the catalyst by their direct participation in the electron transfer step.

Next, we calculated the reduction potentials for catalytically relevant complexes, including [M(II)L]/[M(II)L$^-$] and [M(II)L$^-$]/[M(III)L$^{2-}$] redox couples. The predicted redox potentials are given in Table 1. Predicted redox potentials for FeTPP and CoTPP systems are similar, with Co complexes having slightly less negative potentials than the Fe counterpart. In contrast, there is a clear difference in the redox potentials of Pc complexes, with FePc having a less negative potential than CoPc by approximately 0.1–0.3 V. Of all the four complexes, FePc is anticipated to more readily undergo one-electron reduction because of its less negative reduction potential. Additionally, Pc complexes facilitate one-electron reduction more easily than TPP complexes do. Predicted reduction potentials for molecular complexes are consistent with the experimental values (see Section S2; Figures S3 and S4; and Table S4 for electrochemical characterizations of four molecular catalysts). These findings suggested that the ability of electron transfer in molecular complexes could enable us to investigate and examine their catalytic performance, especially the onset potential during electrocatalytic CO$_2$ reduction.
Given the onset potentials obtained by experiments, active catalysts appear to be \([\text{M(II)L}]^{\text{a}}/\text{M(II)L}^{\text{b}}\) at a potential range from \(-0.6\) to \(-0.9\) V, because \(E_2\) reduction potentials associated with \([\text{M(II)L}]^{\text{a}}/[\text{M(II)L}^{\text{b}}]_2^{\text{a}}\) redox couples are at far more negative values, which are more than the typical accuracy of DFT for predicting redox potentials (0.2–0.3 V). To obtain additional insight into the electronic structure of the activated CO2 moieties in the metal-carboxylate complexes, \([\text{M(II)(L'COO)}]^{\text{a}}\), several descriptors were determined for a quantitative description of essential physical properties including complexation energies, structural differences, and charge densities, as presented in Table 2. Apparently, coordination of CO2 to the Co center is stronger for both TPP and Pc ligands than the Fe center. The stronger M-CO2 interaction is reflected in shorter M-C bond lengths. There is no significant difference in OCO angle that CO2 molecule has a bent structure in all cases, albeit slightly more distortion from linearity in TPP systems because of stronger interaction.

Considering the charge transfer behavior of complexes in Table 2, TPP systems either with Fe or Co display a larger charge transfer from the ML moiety to the CO2 molecule. Although the \(\text{q(CO2)}\) amounts to \(-0.69\) and \(-0.65\) for FeTPP and CoTPP systems, respectively, it is \(-0.58\) and \(-0.56\) for the Pc systems. Similarly, \(\Delta\text{q(ML)}\) manifests the larger charge transfer from ML to CO2 in TPP systems given by \(\Delta\text{q(ML)}\) values of 0.76 and 0.79 in contrast to 0.60 and 0.59 predicted for Pc derivatives. The weaker affinity of Pc ligand to donate its electrons to the bound CO2 molecule can rationalize the weaker binding of CO2 in \([\text{Fe(II)(Pc')COO]}^{\text{a}}\) and \([\text{Co(II)(Pc')COO]}^{\text{a}}\) complexes.

The molecular orbitals (MOs) relevant to CO2 activation reveal the nature of charge transfer upon CO2 coordination as illustrated in Figures 2 and S5. When CO2 actively coordinates to the metal center in \([\text{M(II)L}^{\text{a}}]^{\text{b}}\), it takes up electrons from the ligand via the metal center and generates \([\text{M(II)L'}^{\text{a}}\text{COO}]^{\text{a}}\) species. The electron density is localized mainly on the TPP and Pc ligands for Fe complexes, as shown in Figure S2. In Figures 2A and 2B, there seems accumulation of electron density toward the metal center and CO2 moiety in \([\text{Fe(II)(L'COO)}]^{\text{a}}\) complexes, pointing out the reduction of CO2 molecule. Very similar behavior is predicted for \([\text{Co(II)(L')}\text{COO}]^{\text{a}}\) complexes in Figures 2C and 2D, though larger electron density is localized over the metal center in CO2 free complexes that can be attributed to the existence of more valence electrons in Co d orbitals. Consequently, higher electron density on the Co center can more readily facilitate the CO2 reduction, giving rise to stronger Co-CO2 interactions that can be translated into more favorable complexation free energies.

**Immobilized molecular catalysts for exclusive CO evolution**

Following the molecular-level understanding of the molecular catalysts provided by theoretical calculations, this section discusses the results of catalytic testing. The supporting materials and dispersion of molecular complexes play a significant role in catalytic performance. The proximity of molecular complexes on the high surface area and conductive support could efficiently deliver electrons to each active
site, which enhanced the catalytic performance. Additionally, maintaining a high degree of porosity in the catalysts layer is critical to managing the transport of gaseous products through the GDL when reaching high current densities. To achieve the high dispersion of molecular complexes and minimal gas-bubble accumulation, the CNT and carbon fiber (CF) were selected to construct a three-dimensional network of the carbon electrode, which were finally spray-coated on GDL, denoted as MPc or MTPP/CNT-CF/GDL (M refers to Fe or Co). The mixture of ethanol and dimethylformamide (DMF) was found to act as a good solvent to dissolve the molecular catalysts, allowing effective anchoring via \( p-p \) interactions and rapid evaporation in the spray-coating procedure. Scanning electron microscopy (SEM) was used to reveal the morphology of the working electrodes. Figure 3A displays a representative SEM image of as-prepared CoPc/CNT-CF/GDL, where the CNT and CF (>5 \( \mu \)m) were well mixed on GDL. Figure 3B shows the cross-sectional field of the working electrode, where the CF was embedded in the catalyst layer to generate the porosity of the electrode. The high-resolution SEM image and the corresponding energy dispersive spectroscopy maps in Figure 3C reveal that the distribution of C and N elements overlapped without any clear aggregated Co areas, suggestive of high dispersion of the CoPc molecules on the support.

Spectroscopic tools help identify the chemical specification of the prepared electrode. Figure 3D shows Raman spectra of CoPc/CNT-CF composite, together with some standard references (pure CNT, CF, and CoPc), which exhibited the characteristic peaks of CoPc and supports. More specifically, the composite displayed a defect (D) band at 1360 cm\(^{-1}\) and a graphite (G) band at 1580 cm\(^{-1}\) assigned to the carbon supports, accompanying the apparent peaks at about 500 and 650 nm coming from macrocyclic vibration. The strong molecular complex and support interactions likely resulted in the disappearance of some of the vibrational peaks of CoPc, in agreement with previous spectroscopic characterization. Additionally, the \( \text{ex situ} \) UV-vis measurements were conducted to assess the molecular structure and properties after immobilization. Figure S6 shows the UV-vis spectrum of immobilized CoPc extracted from as-prepared electrode using DMF as solvent. The persistence of characteristic absorption at approximately 665 nm due to Q-bands and additional excitation at about 330–340 nm ascribable to B-band of phthalocyanine indicates that the structural and chemical properties of the molecular catalysts were preserved. Characterizations of CoTPP, FePc, and FeTPP were also conducted and detailed in Section S3 (Figures S7–S9). These all data indicated the successful immobilizations of the molecular complexes on the conductive support, allowing the use of the thus fabricated electrode in further study.

We move on to the electrocatalytic testing of the immobilized molecular complexes supported on GDL in a gas-fed flow cell (the scheme is shown in Figure S10). Our

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \Delta G_{\text{complexation}} ) (eV)</th>
<th>( d(M-C) ) (( \text{Å} ))</th>
<th>( &lt;(OCO) &gt; )</th>
<th>( q(CO_2) )</th>
<th>( \Delta q(ML) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(TPP)</td>
<td>0.06</td>
<td>1.978</td>
<td>129.599</td>
<td>-0.69</td>
<td>0.76</td>
</tr>
<tr>
<td>FePc</td>
<td>0.42</td>
<td>1.992</td>
<td>132.588</td>
<td>-0.58</td>
<td>0.60</td>
</tr>
<tr>
<td>Co(TPP)</td>
<td>-0.16</td>
<td>1.951</td>
<td>129.746</td>
<td>-0.65</td>
<td>0.79</td>
</tr>
<tr>
<td>CoPc</td>
<td>0.11</td>
<td>1.978</td>
<td>132.507</td>
<td>-0.56</td>
<td>0.59</td>
</tr>
</tbody>
</table>

M = Fe, Co; L = TPP, Pc.

\(^a\)Bond distance between the metal and C atom of the coordinated CO\(_2\) molecule.

\(^b\)Partial NPA charge on CO\(_2\) moiety of [M(II)(L\(^d\))COO]\(^-\) complex.

\(^c\)Change in metal partial charge upon CO\(_2\) coordination: \( \Delta q(ML) = q(ML\text{CO}_2) - q(ML) \).
control experiment using pure CNT-CF/GDL recorded a FEH₂ of nearly 100% (Figure S11), validating the CNT-CF as a suitable catalyst support for testing the CO₂ reduction reaction. Also, the loading of the catalysts was optimized to be 10% for Co-based molecular catalysts (see Figure S12), to maximize the CO evolution occurring on the CNT-CF/GDL substrate. With the area of each molecular complex (~1-1.25 nm²), the loading of molecular complexes fully covering CNT/CF (Brunauer-Emmett-Teller [BET] area ~200 m² g⁻¹ for CNT and 20 m² g⁻¹ for CF) was calculated to be about 9%, provided that the molecular complexes preferred laying flat on the graphite according to the previous results from in situ electrochemical scanning tunneling microscopy and atomic force microscopy. The quantitative similarity between these numbers indicated that the quantity to maximize the catalytic performance shown in Figure S12 coincided with that equivalent to a monolayer of the complex on the carbon support.

Chronoamperometric (CA) measurements were conducted for 30 min at various potentials in a CO₂-saturated aqueous solution of 1 M NaHCO₃. Figure 4 summarizes the CO partial current density (jCO) and FECO of FePc/CNT-CF/GDL, FeTPP/CNT-CF/GDL, CoPc/CNT-CF/GDL, and CoTPP/CNT-CF/GDL (see Section S5; Figures S13–S16 for total current densities and product distributions of four molecular catalysts, as well as raw representative CA profiles of FePc/CNT-CF/GDL and CoPc/CNT-CF/GDL). The current-potential relationships were disclosed to be distinct between the Fe- and Co-based molecular catalysts. The Fe-based molecular catalysts, namely FePc/CNT-CF/GDL and FeTPP/CNT-CF/GDL, catalyzed CO₂ reduction to CO selectively only when the potential was more positive than ~0.6 V compared with RHE, followed by a decrease of jCO and FE CO at more negative potentials. In contrast, the Co-based catalysts exhibited exponentially increasing jCO at more cathodic potentials, with FE CO higher than 90% throughout most potentials ranging from ~0.6 to ~0.9 V compared with RHE.

The electrocatalytic performance of four kinds of molecular catalysts was detailed. First, the Fe-based catalysts produced CO at about ~0.31 and ~0.41 V compared to
with RHE over FePc/CNT-CF/GDL and FeTPP/CNT-CF/GDL, respectively. Over FePc/CNT/GDL, a FECO of about 80% was observed at $-0.36 \text{ V compared with RHE}$ that increased with the overpotential to reach the maximum of FECO 93% with a $j_{\text{CO}}$ of about 9 mA cm$^{-2}$ at $-0.6 \text{ V compared with RHE}$. Beyond this potential range, the current decreased quickly with time to a value of about 10 mA cm$^{-2}$ within 30 min (Figure S14). The FEH$_2$ increased to 55% as the main product, and a trace amount of methane (2%) was detected at about $-0.75 \text{ V compared with RHE}$. The FeTPP/CNT-CF/GDL shared a similar trend with FePc/CNT-CF/GDL. The fast deactivation of these Fe-based molecular catalysts does not likely originate from the de metallation, which was proved by the consistent ex situ UV-vis spectra of the samples before and after the catalysis, as shown in Figures S8B and S9B. With cobalt being the metal center, the onset potentials of CO evolution over CoPc and CoTPP were found to be $-0.44$ and $-0.48 \text{ V compared with RHE}$, respectively. Their $j_{\text{CO}}$ reached about 155 and 105 mA cm$^{-2}$, respectively, with FECO as high as 90% at about $-0.9 \text{ V compared with RHE}$, which benefit from the improved mass transfer under reaction.

**Figure 3. Ex situ characterization of samples**

Top (A) and cross-sectional (B) scanning electron microscopy (SEM) images of carbon nanotube (CNT) and carbon fiber (CF) modified by cobalt phthalocyanine (Co-Pc) supported on gas diffusion layer (GDL). (C) High-resolution SEM image of the CoPc/CNT-CF composite and the corresponding energy dispersive spectroscopy (EDS) maps of C, N, and Co. (D) Raman spectra of pure CNT, CF, CoPc, and the hybrid CoPc/CNT-CF.
conditions. CO was the only gaseous product from CO2 reduction for Co-based molecular catalysts, along with H2 as the side product from hydrogen evolution reaction, whose FE was maintained below 10% throughout the potential range (shown in Figure S15). Notably, the CoPc/CNT-CF/GDL retained its exclusive CO evolution throughout on-off testing for about 30 h (Figure S17), and the small decreases in jCO and FECO likely resulted from two aspects: (1) the electrolyte flooding, evidenced by the morphology change and loss of hydrophobicity of electrode in Figure S18, and (2) detachment of CoPc from the electrode after electrocatalysis, not CoPc demetalation, as supported by the surviving molecular structure assessed by ex situ X-ray photoelectron spectroscopy (XPS), UV-vis spectra, and inductively coupled plasma (ICP) in Figure S19. Detailed discussion can be found in Section S5.

Overall, molecular catalysts with Fe being the metal center irrespective of ligand (Pc or TPP) afforded a positive shift in the onset potential and improved electrocatalytic CO2 reduction into CO activities at >−0.5 V compared with RHE in comparison with those of Co-based catalysts. The Pc-based molecular complexes regardless of metal center (Fe or Co) delivered higher activities for CO evolution than those of TPP-based ones. This finding was consistent with the redox potentials of molecular complexes obtained by DFT calculations. All molecular complexes directed CO2 reduction to CO selectively at low overpotentials (>−0.6 V versus RHE), but Co-based ones showed higher FE for CO productions than Fe-based molecular counterparts at higher overpotentials. These results demonstrate that CO formation via electrocatalytic CO2 reduction over the immobilized Co-based and Fe-based molecular catalysts was limited by different steps. We address their elementary steps in the subsequent sections by electrokinetic measurements and theoretical calculations.

**Reaction pathways were examined by electrokinetic measurements**

The relative binding energies of adsorbed CO and H on catalyst surfaces are generally accepted as the descriptors to explain the different catalytic performances for electrochemical CO2 reduction.54,55 The relatively weak binding energy of CO on the active site prefers CO desorption, making CO the major product; otherwise, the adsorbed CO is further reduced at more negative potentials, where the competing H2 evolution reaction likely prevails, such as over flat metallic Fe

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**Figure 4. Electrocatalytic CO2 reduction reaction over molecular-based electrocatalysts**

(A) current densities and (B) Faradaic efficiencies of electrocatalytic CO2 reduction reaction into CO over 10 wt % metallophthalocyanines (MPc) and metallotetraphenylporphyrins (MTPP) supported on CNT-CF/GDL, including FePc/CNT-CF/GDL, FeTPP/CNT-CF/GDL, CoPc/CNT-CF/GDL, and CoTPP/CNT-CF/GDL assessed by chronoamperometry (CA) using gas-fed flow cell at the denoted potential for 30 min in CO2-saturated aqueous solution of 1 M NaHCO3 at pH 7.5 at 25°C.
This rationale points to a scenario in which CO evolution rates on Co- and Fe-based molecular catalysts would result from their different CO binding energies, especially given the large amount of generated CO under relatively high overpotential. $j_{\text{CO}}$ was thus assessed at varying CO partial pressure ($P_{\text{CO}}$) in feeding gas, and the obtained data are presented in Figure 5. During this testing, H$_2$, CO, and CH$_4$ were the only products observed whose total FE closed at almost 100% for molecular catalysts. This condition allowed the determination of $j_{\text{CO}}$ by subtracting the H$_2$ and CH$_4$ partial current densities from the total obtained current densities. To maintain the pH of the electrolyte, the partial pressure of CO$_2$ ($P_{\text{CO}_2}$) was kept constant at 70.7 kPa, and $P_{\text{CO}}$ was varied by balancing the total pressure with Ar.

In Figures 5A and 5B, even a small amount of added CO (~5.1 kPa) was sufficient to cause a significant decrease in $j_{\text{CO}}$ over Fe-based molecular catalysts. Over FePc/CNT-CF/GDL in Figure 5A, the $j_{\text{CO}}$ was 7.4 mA cm$^{-2}$ at ~0.94 V compared with SHE without CO feeding. With CO at 5.1 kPa in feeding gas, the $j_{\text{CO}}$ decreased to about 5 mA cm$^{-2}$, which was only about 65% of its initial catalytic activity at $P_{\text{CO}}$ = 0. With increasing $P_{\text{CO}}$ to 20.2 kPa, the $j_{\text{CO}}$ continued to decrease to about 4 mA cm$^{-2}$. Likewise, $j_{\text{CO}}$ decreased with $P_{\text{CO}}$ over FeTPP/CNT-CF/GDL, as shown in Figure 5B. These results demonstrated that the generated CO on FePc and FeTPP could inhibit its production, especially under higher overpotential. The drop of $j_{\text{CO}}$ under high overpotential has been previously observed on other electrocatalysts, such as...
atomically dispersed Fe-N₄-C based catalysts. The high coverage of CO at steady state on the active site over Fe-based molecular catalysts likely relates to the Fe(II)-CO adduct, which was proposed and captured by operando experiments and theoretical calculations. The slow dissociation rate of CO from Fe(II) species seems to result in the irreversible CO binding, inhibiting CO₂ reduction, which will be detailed by the following DFT calculation.

In contrast to the irreversible CO binding on Fe-based molecular catalysts, Co-based molecular catalysts were tolerant to this issue. Figure 5C revealed the relationship of jₐ CO and P CO on CoPc/CNT-CF/GDL, where the jₐ CO maintained about 12.5 mA cm⁻² at -1.07 V compared with SHE and about 35 mA cm⁻² at -1.14 V compared with SHE at various P CO from 0 to 20.2 kPa. Figure 5D shows the jₐ CO versus P CO for CoTPP/CNT-CF/GDL, which could reach comparable jₐ CO to Co-Pc/CNT-CF/GDL at higher overpotential. With these kinetic data, the kinetic order of CO evolution to P CO was determined to be zero over both CoTPP/CNT-CF/GDL and CoPc/CNT-CF/GDL at least at P CO₂ = 70.7 kPa.

Various effectively buffered pH electrolytes, including 1 M NaHCO₃ (pH ~ 7.5), 0.5 M Na₂CO₃ (pH ~ 11.2), and 1 M NaOH (pH ~ 13.6), were used to examine the pH effect on electrochemical CO₂ reduction into CO using gas diffusion electrodes. Figures 6A, 6D, and S20 provide the order dependences of jₐ CO on pH at various applied potentials over CoPc/CNT-CF/GDL and CoTPP/CNT-CF/GDL, respectively. These figures show that jₐ CO did not change with pH at P CO₂ = 101 kPa, consistent with previous reports over Co protoporphyrin and graphene-embedded Fe-N-C. The rate was insensitive to pH and the existence of (bi)carbonate ions at lower P CO₂ of 10.1 kPa (Figure S21A), revealing that electrocatalytic CO₂ reduction over these Co complexes exhibits zeroth orders kinetics on H⁺ and OH⁻ irrespective of P CO₂.

As to the effect of bicarbonate concentration (c HCO₃⁻) on jₐ CO, there are conflicting reports in the literature on whether bicarbonate could be used as a proton source and CO₂ source. The existing kinetic studies examining the bicarbonate order dependence on Co-based molecular catalysts were conducted in electrolytes containing different concentrations of bicarbonate with different ionic strength. It is acknowledged that the ionic strengths of the solution could alter the interface electric field and reaction intermediate stabilization, which affect the catalytic performance of CO₂ reduction, especially alkali cations. In this context, the same ionic strength of electrolytes containing different c HCO₃⁻ was prepared by tuning the sodium bicarbonate and sodium perchlorate ratio. In our study, the concentration of Na⁺ was maintained at 1 M, and the c HCO₃⁻ was increased from 0 to 1 M. Figures 6B and 6E plot jₐ CO as a function of c HCO₃⁻ over CoPc/CNT-CF/GDL and CoTPP/CNT-CF/GDL. jₐ CO was found to remain constant with varied c HCO₃⁻ at P CO₂ = 101 kPa (in Figures 6B and 6E) and also P CO₂ = 10.1 kPa (Figure S21B) disclosing that the CO evolution via electrocatalytic CO₂ reduction rate was zeroth orders on the concentration of bicarbonate. These results suggested that HCO₃⁻ was not involved at the rate-determining step as a reactant or a proton source over these Co complexes.

In contrast to pH and c HCO₃⁻, the partial pressure of CO₂, P CO₂, varied the CO evolution rate. jₐ CO is compiled with respect to P CO₂ over CoPc/CNT/GDL and CoTPP/CNT/GDL in Figures 6C and 6F, respectively. In both cases, the jₐ CO increased with P CO₂ below about 20.2 kPa with a slope of about 0.9 (see Table S5), while above this partial threshold pressure, the rate remained unchanged. This order
dependence was distinct from the previous studies over Co-based molecular catalysts in aqueous CO2-saturated solution that reported first order dependence in 0.1 M NaHCO3 and positive \((1/2.40)\) order dependence in 1.0 M NaHCO3 over \(P_{CO2}\) range from 0 to 1 kPa.40 The present study disclosed that the CO2 was not involved at the rate-determining step of electrocatalytic CO2 reduction reaction at higher partial pressure (>20.2 kPa) for the gas-fed electrochemical cell. Finally, the relationships between overpotential and \(j_{CO}\) over CoPc and CoTPP are plotted in Figures S22A and S22B respectively, where \(j_{CO}\) was proportional to the overpotential when the current density was lower than 50 mA cm\(^{-2}\), giving a Tafel slope of 138\(\pm\)9 and 124\(\pm\)7 mV/dec for CoPc and CoTPP, respectively. However, the relationships deviated from linearity when the current densities were high. The deviation likely resulted from the bubble accumulation in the catalyst layer and electrolyte flooding under high current densities.48 These Tafel slope values indicate that the rate-determining step of electrocatalytic CO2 reduction to CO over Co-based molecular catalysts likely involved the electron transfer with the surface covered by the species formed at the immediately prior step.66

Thus far, these electrokinetic results integrating reaction orders concerning \(P_{CO2}\), pH, \(c_{HCO3}\), \(P_{CO2}\), and Tafel slopes provide the basis for mechanistic interpretation of

![Figure 6. Electrokinetic data for electrochemical CO2 reduction](A–C) CoPc/CNT-CF/GDL and (D and E) CoTPP/CNT-CF/GDL. (A and D) pH dependence of the CO partial current density \((j_{CO})\) at constant potentials recorded in 1 M NaHCO3, 0.5 M Na2CO3, and 1 M NaOH. (B and E) bicarbonate concentration dependence of \(j_{CO}\) at constant potentials recorded in NaClO4/NaHCO3 \((c_{K^+} = 1\) M) mixed electrolytes. (C and F) \(P_{CO2}\) dependence of \(j_{CO}\) at constant potentials recorded in 1 M NaClO4 electrolyte.

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CO evolution catalyzed by Co-based molecular catalysts: the rate-determining step is most likely a decoupled electron transfer on the surface covered with species formed at the immediately prior step, with and without CO2 involved below and above $P_{\text{CO2}} = 20.2 \text{ kPa}$, respectively. The step also did not involve CO (at least above $P_{\text{CO2}} = 20.2 \text{ kPa}$). To elucidate the complicated two-electron two-proton reaction and map the catalytic sequences over molecular catalysts, DFT calculations were performed in the next section to complement the main existing intermediates and reaction pathways under reaction conditions.

**Reaction pathways examined by DFT calculations**

We inspected the reaction mechanism for all TPP and Pc systems and tried to understand the role of each individual PT and ET step in the formation of key intermediate species (Figure S7). Figure 7 shows the initial CO2 binding to the $[\text{M(II)}(\text{L}^\text{d})\text{COO}]^-$ complex, which is proposed to be the active catalyst facilitating CO2 activation through electron transfer from the singly reduced ligand to the CO2.
moiety. One-electron reduction of [M(II)(L')COO]^− complexes are more facile with Pc ligands amounting to −0.72 and −0.67 V for FePc and CoPc species, respectively, while the TPP counterparts have $E_0^\circ = -1.13$ V and $E_0^\circ = -1.04$ V, respectively. Moreover, reduction of [M(II)(L')COO]^− to [M(II)(L')COO]^2− takes place more readily compared with the [M(II)L']^−/[M(II)L']^2− redox couple, suggesting that CO2 takes up electrons from the metal complex rendering the catalyst more prone to a subsequent electron reduction upon CO2 binding. Alternative to an initial ET, [M(II)(L')COO]^− complexes can undergo PT, generating a neutral [M(II)(L')COOH] intermediate with surmountable barriers at 0.5 and 0.7 eV for FeTPP and CoTPP systems, respectively. However, an initial PT step is difficult for Pcs complexes at room temperature because the respective barriers amount to 1.1 eV for both FePc and CoPc. Thus, operative mechanisms for Fe and Co systems seem to be different on the basis of the choice of ligand rather than the metal atom. The red pathways stand for the most likely reaction path in Figure 7, which is detailed in Figures S23–S27.

Herein, our analysis indicates that the electronic features of the ligand dictate the propensity toward an initial ET or PT. The Pc ligand provides a less electron donating nature feature to the complex (Table 2), which leads to a diminished extent of electron transfer to the CO2 substrate compared with the TPP ligand, favoring an ET step at first. Overall, the protonated [M(II)(L')COOH]^− carboxylate adduct is formed as a key intermediate, as the reduction of [M(II)(L')COO]^− to the corresponding [M(II)(L')COO]^− occurs at high overpotentials and protonation of [M(II)(L')COO]^− to [M(II)(L')COOH] is too endergonic (see supplemental information for full details).

For more insights, we also calculated pK_a values of [M(II)(L')COO]^−/[M(II)(L')COOH] acid-base pairs that can in principle play a role in the operative mechanisms. We applied an isodesmic proton-exchange reaction scheme as applied in our previous report.31 Accordingly, we took the associated CoTPP species as the reference acid-base pair with a reference pK_a value of 3.5, as reported by Göttele et al.67 The predicted pK_a values are 7.1 and −1.2 for FeTPP and FePc systems, respectively, supporting that an initial PT is not an operative mechanism for the highly acidic FePc carboxylate adduct. Nonetheless, FeTPP can undergo either an initial PT or an initial ET regarding its neutral pK_a and the reaction medium with pH 7.5. As for the CoPc system, the associated pK_a is predicted to be −2.3, which is consistent with a high barrier for the protonation of [M(II)(L')COO]^− to [M(II)(L')COOH] found at 1.1 eV. Given the pK_a of 3.5 for CoTPP, it is more likely that CoTPP species proceeds via an initial ET as the [Co(II)(TPP')COOH] is more acidic than the reaction medium (pH 7.5). Formation of [M(II)(L')COOH]^− intermediate is followed by a second protonation giving rise to the [M(II)L'] complexes, as indicated in Figure 7. The release of CO regenerates the active catalyst to re-enter the catalytic cycle. The salient question herein is whether M(II)L-CO dissociation is thermodynamically favorable or not to accomplish high turnover numbers, in agreement with previous work by Dey's group using operando spectroscopies (FTIR, resonance Raman, and Mössbauer).59–61

Of all four complexes in Figure 7, dissociation of M(II)L-CO is endergonic except that for CoPc, which is nearly thermoneutral. This is in line with experimental results that also confirm a facile M(II)L-CO dissociation for CoPc, while Fe poisoning can be explained by thermodynamically disfavored CO release from FePc and FeTPP complexes.

CoPc exhibits the highest FE for CO2 to CO reduction (see experimental procedures for details) among all four complexes. DFT analysis permits us to gain insights into the superior reactivity of CoPc through closer inspection of PCET cycles. Although CO2 binding affinity varies, all four systems can essentially activate CO2 with slightly
endergonic complexation energies. However, the distinct features of mechanistic pathways are evident in the following ET and PT steps. One-electron reduction of $[\text{M(II)}(\text{L}^-)\text{COO}]^{-}$ adduct for CoPc takes place at $E^0 = -0.67 \text{ V}$, which is less negative than the respective reduction potential of the other three complexes. Thus, the formation of a doubly reduced ligand, which is key to the reactivity, especially for Pc complexes in which an initial ET is preferred over a PT (Figure 7), is most facile for CoPc species. The subsequent reaction steps generating $[\text{M(II)}(\text{L}^-)\text{COOH}]^{-}$ and $[\text{M(II)}(\text{L}^-)\text{CO}]$ reveal more or less similar trends for all four complexes. Nevertheless, dissociation of $\text{M(II)}\text{-CO}$ is thermodynamically unfavorable for all the complexes, except for CoPc that can facilitate the ready formation of active catalyst thereby contributing to its higher reactivity.

Conclusions
In this contribution we examined the reactivity and energetics at each elementary step of immobilized molecular catalysts loaded on GDL for the electrocatalytic CO$_2$ reduction reaction through a combination of microkinetic assessment and theoretical DFT calculations. First, the electronic structure of four kinds of molecular catalysts (FePc, FeTPP, CoPc, and CoTPP) and their activated CO$_2$ moieties in the metal-carboxylate complexes were detailed, revealing that the Pc and TPP were redox non-innocent ligands during electrocatalytic CO$_2$ reduction. The highly dispersed molecular catalysts immobilized on CNT-CF-GDL exhibited that as-prepared Fe-based molecular catalysts only catalyzed CO$_2$ reduction to CO efficiently at low overpotential ($\leq -0.6 \text{ V}$ versus RHE) in CO$_2$-saturated aqueous solution of 1 M NaHCO$_3$ at pH 7.5, and their maximum $j_{\text{CO}}$ were limited to below 10 mA cm$^{-2}$, likely because of the high coverage of CO at steady state on the active site confirmed by DFT calculation. In contrast, the CoPc/CNT-CF/GDL electrode catalyzed CO$_2$ reduction to CO at current densities of about 155 mA cm$^{-2}$ with 92% FE$_{\text{CO}}$ at $-0.9 \text{ V}$ compared with RHE. At comparable potential, the $j_{\text{CO}}$ of CoTPP/CNT-CF/GDL reached 103 mA cm$^{-2}$ with 90% FE$_{\text{CO}}$. The electrokinetic data over Co-based catalysts revealed that the $j_{\text{CO}}$ exhibited a positive order dependence on $P_{\text{CO}_2}$ ranging from 2.53 to 20.2 kPa, while it did not depend on pH and $c_{\text{HCO}_3}$.. The reaction order to CO was also found to be zeroth at least at $P_{\text{CO}_2} = 70.7 \text{ kPa}$. DFT calculations demonstrated that the ligand participation in ET cycles is crucial where less electron-donating nature predicted for Ppc ligand enables ET step at more positive potentials for those complexes. More facile CO dissociation from CoPc renders it the most active catalyst without the irreversible CO binding. Ultimately, the findings given by this study aid in the prospect of using the rational design of immobilized molecular electrocatalysts and optimization of reactor configuration to drive electrochemical CO$_2$ conversion chemistry at meaningful rates of production, even under dilute CO$_2$ streams as the feed.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Kazuhiro Takanabe (takanabe@chemsys.t.u-tokyo.ac.jp).

Materials availability
This study did not generate new materials.

Data and code availability
All Cartesian coordinates are available at Zenodo: 10.5281/zenodo.6076110.
Materials
The reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. Multiwall carbon nanotubes (CNT; >98%), carbon fiber (CF; iron-free), CoPc (>97%), FeTPP (>94%), ferrocene (98%), ethanol (99.5%), hydrochloric acid (ACS reagent; 37%), Nafion 117 solution (5 wt %), and N, N dimethylformamide were ordered from Sigma-Aldrich. The CoPc (>85%) and Fe(II)Pc (>95%) were purchased from Tokyo Chemical Industry. Iridium carbon (40 wt %), carbon black (Vulcan XC 72), gas diffusion layer (Sigracet 39BC), and glassy carbon (GC; D = 6 mm) were bought from FuelCellStore. The CNTs were purified by soaking in a 6 M HCl solution overnight (>12 h) as the support.

Electrode preparation
A three-dimensional network of the carbon substrate was constructed using a mixture of CNTs and CF as additional carbon supports, which were finally spray-casted on a gas diffusion layer. So that all molecular catalysts are supported by the carbon substrate with little substrate exposed and with little amounts of molecular catalysts stacked to each other, the loading of molecular complexes was optimized. For the fabrication of a working electrode modified by CoPc as an example, a calculated amount of CoPc was dissolved in 10 mL of ethanol/DMF mixture (9/1, V/V) and was sonicated for 30 min. Then, 24 mg CNT and 6 mg CF were added to the solution, and the suspension was sonicated for 30 min again. The mixed suspension was further stirred at 80°C for 24 h. Afterward, 200 µL Nafion solution was introduced to the resulting suspension, which was sonicated for another 30 min. Finally, this catalyst ink was spray-coated onto a GDL using an airbrush (Iwata Eclipse HP-SBS) with dimensions of 3 x 1 cm mounted on an 80°C hot plate. A total powder loading of 0.5–0.7 mg cm⁻² was typically achieved for each electrode, and the working area was always 1 x 1 cm. For the counter electrode, Ir/C was used as the catalyst, pure ethanol was used as the solvent, and the rest of the procedure remained identical. For electrochemical characterization, carbon black was used as the support to replace CNT to exclude adventitious peaks. Instead of GDL, GC was used as a substrate, onto which 10 µL of the suspension was dropped and allowed to dry under ambient conditions.

Electrochemical measurements
A BioLogic potentiostat electrochemical workstation was used for all electrochemical measurements. The catalytic performance of the fabricated electrodes was investigated by chronoamperometry in a gas-fed flow cell. A three-compartment cell configuration consists of three chambers (gas, cathodic, and anodic) and an anion-exchange membrane (Selemion) separating the cathodic and anodic chamber. A reference electrode (Ag/AgCl filled with saturated KCl solution) was integrated into the cell to ensure the potential control, which is close to the working electrode. Two pieces of copper tapes were used as current collectors for cathode and anode. An aqueous solution containing various solutes in the given catholyte and anolyte reservoirs was circulated using a peristaltic pump at 5 mL min⁻¹ and a gas-liquid mixed pump at 10 mL min⁻¹, respectively. The gaseous CO₂ was supplied at a flow rate of 20 mL min⁻¹ in a gas chamber and passed behind the gas diffusion layer to diffuse into the interface between catalyst and electrolyte. The gaseous Ar was used to dilute the CO/CO₂ or CO₂ feeding gases, which were supplied together at a total flow rate of 20 mL min⁻¹ when the dependence of CO or CO₂ partial pressure on CO evolution rate was examined.

The heterogeneous cyclic voltammetry (CV) in an aqueous solution was collected in a single-compartment custom-made cell equipped with two chambers...
separated by an embedded quartz-frit. A Pt coil and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Homogeneous CVs in the organic phase were recorded in a single-compartment glass cell. A solution with DMF solvent was used, which contained 10 mL of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) and 1 mM of CoTPP and FeTPP. For CoPc and FePc, we used DMSO containing 0.1 M tetrabutylammonium perchlorate (TBAP) because of their relatively low solubility in DMF, while the rest of the recipe remained identical. An Ag+/Ag (0.1 M TBAP in CH3CN) electrode was used as the reference electrode, which was calibrated with respect to ferrocene/ferroocene.

Products detection

Gaseous products were monitored using an online gas chromatograph (GC) system (Shimadzu GC-2014). The outlet of the cell was connected to a sampling loop with a volume of 3 mL, which was injected into the GC every 14 min. The GC system was equipped with two detectors: a thermal conductivity detector (TCD) with a Shimadzu column (for H2, CO, and CO2) and a flame ionization detector (FID) with a GS-Gaspro column (for hydrocarbon products). The partial current density (j) and Faradaic efficiency (FEj) were calculated using the following equation:

\[
FE_j = \frac{\text{Gas flow through the cell} \times \text{Concentration of the product}(i)}{\text{Electric current at sampling time}/nF} \times 100
\]

(Equation 1)

Gas flow through the cell in this study was 20 mL min\(^{-1}\), concentration of the product (i) was determined by GC peak area, F = Faradaic constant = 9.65 \times 10^4 A s mol\(^{-1}\), and n is the number of electron transfers where n is 8 for CH4, and 2 for both CO and H2 generation.

Material characterization

Scanning electron microscopy images were obtained using a Hitachi 8500 microscope. Transmission electron microscope (TEM) image was collected using a JEM 2000 EX II. X-ray photoelectron spectroscopy analysis was performed on an JPS-9010MC. Inductively coupled plasma analysis was carried out to quantify the Co amount in the electrolyte after durability test using iCAP PRO ICP-OES. UV-vis spectra were recorded using JASCO V-670. The absorbance was recorded in a wavelength range from 300 to 800 nm with data intervals of 1 nm at room temperature. Raman spectra were collected using JASCO RMP-510. Water contact angle was captured using a high-speed video camera by a water drop (4 \muL).

Density-functional theory calculations

All molecular structures were fully optimized at the density-functional level of theory using the hybrid functional B3LYP\(^{68,69}\) corrected for medium-range correlation and dispersion effects using the D3\(^{70}\) correction of Grimme with Becke-Johnson damping in Gaussian 09.\(^\text{71}\) For geometry optimizations, the def2-SVP\(^\text{72}\) basis set was used for light elements, and the def2-TZVP\(^\text{69}\) basis set was used for Fe and Co atoms. Optimizations were performed in condensed phase to incorporate the solvation effect via the SMD\(^\text{73}\) continuum solvation model with the solvent parameters for water (\(\epsilon = 80\)). The natures of all stationary points were determined by the calculation of the analytical vibrational frequencies. These were also used to compute the molecular partition functions (298 K, 101 kPa) with the conventional particle-in-a-box, rigid-rotator, quantum-mechanical harmonic oscillator approximation, except that all vibrational frequencies below 50 cm\(^{-1}\) were replaced with values of 50 cm\(^{-1}\) (the quasi-harmonic-oscillator approximation).
In our previous work we evaluated several functionals to assess the sensitivity of spin-state energies to the choice of functional for iron porphyrin complexes. For computational expediency, we chose B3LYP-D3 as the common level of theory because of its reasonable accuracy to predict the spin-state energies and broken symmetry character of the transition-metal complexes as well as its relatively low computational cost. Test calculations using a graphene layer to model the carbon support indicated minor impact of the support on the electronic structure of the phthalocyanine, and thus all calculations were performed on the Co and Fe complexes only. This allowed us to perform extensive calculations within the broken symmetry methodology (see supplemental information for full details; Figures S2; Tables S2 and S3).

The reversible hydrogen electrode was taken into account by incorporating pH effects (pH 7.5) for calculating the reduction potentials of all redox couples in an aqueous solution. For CO2 adducts, we included one explicit water molecule to stabilize CO2 binding to a metal center, which is proved to bring computed redox potentials into better agreement with the experimental potentials in our previous literature report.

In protonation reactions, bicarbonate ($\text{HCO}_3^-$) evolving from the NaHCO3 electrolyte was used as the proton source because pKa [$\text{HCO}_3^-$] (10.3) is smaller than pKa [H2O] (14.0). Consistently, we used a correction term of 0.64 eV (for full details, see Lu et al.) to adjust the reaction free energies for each $\text{HCO}_3^-$/CO3$^{2-}$ pair involved in the catalytic cycle. For all species a factor of $\text{RT} \times \ln(24.46)$ was added to account for the 101 kPa to 1 M standard-state change at 298.15 K. The natural population analysis (NPA) was carried out on the basis of the natural bond orbital (NBO) method to obtain the charge distributions of key stationary points.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.checat.2022.03.010.

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AUTHOR CONTRIBUTIONS
X.L. prepared the electrodes and performed catalytic tests and characterization. B.D. performed DFT calculations. T.S., M.E., L.C., and K.T. contributed to data analysis. All authors contributed to the writing of the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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