**ABSTRACT:** The development of noble-metal-free catalysts capable of electrochemically converting carbon dioxide (CO₂) selectively into value-added compounds remains one of the central challenges in catalysis research. Here, we present a systematic study of Fe(II) complexes of the functionalized ligands bpy²PY2Me (bpy²PY2Me = 6-[(1,1-bis(pyridin-2-yl)ethyl)-2,2'-bipyridine) in the pursuit of water-stable molecular Fe complexes that are selective for the catalytic formation of CO from CO₂. Taking advantage of the inherently high degree of tunability of this ligand manifold, we followed a bioinspired approach by installing protic functional groups of varying acidities (−H, −OH, −OMe, −NHEt, and −NEt₂) into the ligand framework to systematically modify the second coordination sphere of the Fe center. This family of [(bpy²PY2Me)FeII] complexes was characterized using single-crystal X-ray analysis, ¹H NMR spectroscopy, and mass spectrometry. Comparative catalytic evaluation of this set of compounds via voltammetry and electrolysis experiments identified [(bpy²NEt²PY2Me)Fe]⁺ in particular as an efficient, iron-based, non-heme CO₂ electroreduction catalyst that displays significant selectivity for the conversion of CO₂ to CO in acetonitrile solution with 11 M H₂O. We propose that the NH group acts as a local bifunctional catalyst that can promote nucleophilic attack by water and proton reduction. CO₂ reduction systems have been reported that utilize non-precious-metal surfaces, ¹¹–¹² molecularly inspired covalent¹³ and metal–organic frameworks, ¹⁴–¹⁶ and surface-attached molecular catalysts.¹⁷–²³ Designing electrocatalysts with high selectivities for the reduction of CO₂ to carbon monoxide (CO) over the energetically and kinetically more accessible reduction of protons is a major challenge for all CO₂ reduction catalyst systems in aqueous media. It is therefore not surprising that only very few molecular catalysts based on precious metals²⁴–²⁶ or base metals²⁷–⁴⁰ have been reported that are chemically compatible with aqueous conditions yet maintain high selectivities for the electrocatalytic production of CO from CO₂.

**INTRODUCTION**

Cost-effective solar-to-chemical conversion requires the identification of efficient electrocatalysts that are built solely from earth-abundant elements.¹–³ Powering the conversion of carbon dioxide (CO₂) via solar-derived potential energy would allow for the regeneration of carbon-based fuels and the utilization of CO₂ as an inexpensive C₁ feedstock molecule for industrial applications. Various heterogeneous electrocatalytic CO₂ reduction systems have been reported that utilize non-precious-metal surfaces,¹¹–¹² molecularly inspired covalent¹³ and metal–organic frameworks,¹⁴–¹⁶ and surface-attached molecular catalysts.¹⁷–²³ Designing electrocatalysts with high selectivities for the reduction of CO₂ to carbon monoxide (CO) over the energetically and kinetically more accessible reduction of protons is a major challenge for all CO₂ reduction catalyst systems in aqueous media. It is therefore not surprising that only very few molecular catalysts based on precious metals²⁴–²⁶ or base metals²⁷–⁴⁰ have been reported that are chemically compatible with aqueous conditions yet maintain high selectivities for the electrocatalytic production of CO from CO₂.

The identification of new design elements toward the development of next-generation molecular catalysts has recently involved the modulation of the second coordination sphere, with a particular focus on the incorporation of proton relays.²⁹,³⁰,⁴¹–⁵¹ These considerations are predominantly inspired by natural catalysts (enzymes), which are able to control substrate selectivity via a plethora of second and third coordination sphere functional groups with only a single cofactor. Specifically, functional and structural aspects of the active site of [FeFe]-hydrogenases⁵² have previously been exploited for the design of efficient synthetic molecular electrocatalysts for dihydrogen oxidation⁴¹,⁵³–⁵⁹ as well as proton reduction.⁴¹,⁵³,⁵⁶,⁵⁹–⁶⁸
We previously reported that the synergistic interplay between redox-active bipyrindine (bpy) ligand moieties and first-row transition-metal ions, stabilized by polydentate ligand platforms, results in increased electrocatalytic and photo-catalytic activity for proton reduction.40 Herein, we present a bioinspired expansion of this work to the systematic study of iron-based catalysts in the pursuit of systems for selective CO₂ reduction. The new catalysts feature three functional partitions (reactive metal, electron reservoir, and second coordination sphere Lewis acidic moiety; see Chart 1), which mimic some of the crucial components of the enzymatic active site in Nicotinamide dehydrogenase.5,7,14 We were especially interested in complexes of iron because, until very recently,7,3,5 selective electrocatalytic CO₂ reduction had only been observed for Fe-porphyrin molecules.

■ EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise noted, compounds were synthesized and manipulated under air-free conditions, using either a Vacuum Atmospheres drybox or standard Schlenk techniques under a dry nitrogen atmosphere. Anhydrous solvents were obtained using a commercial solvent purification system from JC Meyer Solvent Systems.

The compounds n-butyllithium, 2,6-dibromopyridine, ethylamine, diethylamine, NaObut, bis(1-adamantyl)-2-dimethylaminophenyl (EMD Millipore, OmniSolv Gradient grade) and water (18.2 M cm) were used to calculate the room-temperature solution magnetic moment. was used to calculate the room-temperature solution magnetic moment.

Magnetic susceptibility measurements were made using the Evans Microanalytical Laboratory at the University of California, Berkeley. Complexes were synthesized and manipulated under air-free conditions, using interested in complexes of iron because, until very recently,72,73 selective electrocatalytic CO₂ reduction had only been observed for Fe-porphyrin molecules.

EXPERIMENTAL SECTION

General Synthetic Procedure for Iron Complexes. Equimolar quantities of Fe(CF₃SO₃)₂ and ligand were vigorously stirred in anhydrous CH₃CN using a glassy-carbon disk (3.0 mm diameter) working electrode, a Ag/AgNO₃ (0.1 mM) reference electrode, and a graphite counter electrode with 0.1 M NBu₄PF₆ as the supporting electrolyte. A small amount of ferrocene was added after each cyclic voltammetry measurement of a compound. The potential scale was then referenced against the measured reversible ferrocenium/ferrocene couple (E[Fe(C₅H₅)₂]° = +0.16(1) V versus Ag/AgNO₃). iR (current through internal resistance) compensation was used in all CV experiments to account for the voltage drop between the reference and working electrodes using the EC-Lab software of the Bio-Logic SP-200 potentiostat.

Controlled-potential electrolyses were performed in a custom H-cell (Adams and Chittenden). The working electrode was a glassy-carbon plate (Tokai) with an area of ~6 cm², and the auxiliary electrode was a carbon cloth (Fuel Cell Earth) cut to ~225 cm². Electrical contacts between the electrodes and wires were made using silver epoxy (Chemtronics CW2400), which were then sealed into a borosilicate glass tube with epoxy (Agilent TorrSeal) to avoid exposure of the underlying conductive epoxy or bare wire. A Ag/AgNO₃ solution in a 4/1 (v/v) mixture of CH₃CN and water. The electrolyte was deaerated by sparging CO₂ (4.8 g, Praxair), after which a 2 mL aliquot of a stock solution of (8.5 mM) ferrocene catalyst was introduced via a gas-tight syringe to attain a final catalyst concentration of 240 μM. The cell was then sealed to allow a constant infusion of gaseous CO₂ into the liquid electrolyte. The headspace was permitted to flow into a mass-flow controller at 10 ± 0.1 scm and subsequently into an Agilent 490 MicroGC instrument for analysis. The MicroGC instrument was calibrated for simultaneous detection of H₂, CO, and CH₄. Each electrolysis at an applied potential of ~1.91 V was performed in quadruplicate. The electrolysis at an applied potential of ~2.20 V was performed once. iR (current times internal resistance) compensation was used in all CV experiments to account for the voltage drop between the reference and working electrodes using the EC-Lab software of the Bio-Logic SP-200 potentiostat.

Chart 1. Bioinspired Features in [(bpyPY2Me)Fe] Complexes

![Chart 1](image-url)

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N, C, O, S, F, and H atoms, respectively. H atoms, except those in the hydroxyl and aniline moieties, are omitted for clarity. Unbound solvent and ESI-MS crystals, which gave an orange powder after drying (282 mg, 96%).

2.82 (s, 3H). ESI-MS: m/z 211.0511, found 211.0501. Anal. Calcd for C29H26F6FeN6O7S2: C, 42.46; H, 3.16; N, 9.54. ESI-MS: m/z for [(bpyOMePY2Me)Fe(CH3CN)]+ requires 211.0511, found 211.0501. Anal. Calcd for C26H23F6FeN5O6S2: C, 42.46; H, 3.16; N, 9.49. ESI-MS: m/z for [(bpyNHEtPY2Me)Fe(CF3SO3)2] requires 218.0661, found 218.0659. Anal. Calcd for C26H23F6MnN5O6S2: C, 42.66; H, 3.16; N, 9.53. Found: C, 42.66; H, 2.86; N, 9.51. Yellow block-shaped crystals suitable for X-ray diffraction analysis were obtained after slow diffusion of EtO into a CH3CN solution of the title compound. Effective magnetic moment (CD3CN, 298 K): $\mu_{eff}$ = 5.8 MHz. UV–vis (CH3CN): $\lambda_{max}$ (ε50 M$^{-1}$ cm$^{-1}$) 263 (1.4 × 10$^3$), 367 (8600) nm.

**Crystal Structure Determinations.** Slow diffusion of diethyl ether into acetonitrile solutions of compounds 2–6 afforded single crystals suitable for X-ray diffraction analysis. Data collection was performed on single crystals coated with Paratone-N oil and mounted on Kapton loops. The crystals of 2–5 were cooled under a stream of N2 (100 K; Oxford Cryostream 700) during measurements. Data collection for 6 was performed at 250 K because its crystals fractured when they were cooled to 100 K. Data were collected using a Bruker APEX II QUAZAR diffractometer equipped with a Microfocus Sealed Source (Incoatec Iα15; Mo Kα λ = 0.71073 Å) and APEX-II detector. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker APEX2. Absorption corrections were applied using SADABS. Space group assignments were determined by examination of systematic absences, E statistics, and successive refinement of the structures. Structures were solved using SHELXT, and all non-hydrogen atoms were refined anisotropically by full-matrix least squares (SHELXL). Carbon-bound hydrogen atoms were inserted at idealized positions and refined isotropically using a riding model with the appropriate HFIX command in SHELXL.
In the structure of 5, the coordinated trifluoromethanesulfonate anion was found to be disordered over two orientations, with an occupancy ratio of 73/27. Bond distances of the trifluoromethanesulfonate were restrained with the SADI command. The anisotropic refinement of the disordered trifluoromethanesulfonate anions were restrained using the RIGU and SIMU commands. In addition, electron density was located near an edge of the unit cell. This was attributed to disordered solvent. Attempts to model the disorder were unsuccessful. As such, a solvent mask was applied to account for the unassigned electron density.87

In the structure of 6, the ethyl group of the complex was disordered over two positions, with an occupancy ratio of 64/36. Also, one of the coordinated trifluoromethanesulfonate anions was found to be disordered over two orientations, with an occupancy ratio of 75/25. The disorder was addressed in a fashion similar to that described above, using SADI, RIGU, and SIMU restraints. In addition, the higher collection temperature for 6 necessitated a RIGU restraint on the bipyridine ring.

The phenolic hydrogen atom in the structure of 2 was inserted with the HFIX 147 command. The nitrogen-bound hydrogen atoms in the structures of 4 and 6 were located in the Fourier difference map and refined freely.

## RESULTS AND DISCUSSION

**Design Elements and Synthesis of Functionalized Ligand Sets.** We previously demonstrated the utility of multidentate polypyridine ligand scaffolds in stabilizing highly active and water-compatible electrocatalysts for proton reduction using earth-abundant transition-metal elements such as molybdenum88−91 and cobalt.69,78,92−96 For the current study, we were particularly interested in the functionalization of complexes stabilized by the tetradentate ligand 6-(1,1-bis(pyridin-2-yl)ethyl)-2,2′-bipyridine (bpy-PY2Me), because of the reported favorable electrochemical potentials of metal-centered reduction events78 and the presence of the bpy-based redox reservoir. Indeed, a recent study of the iron complex with the bpyPY2Me ligand reported overlapping Fe- and ligand-based reduction events.81 To incorporate an acidic proton into the second coordination sphere, we synthesized the ligand bpyOHPY2Me, which features an OH group in the 6-position of the bipyridine moiety. Because the oxygen lone pair is partially delocalized into the bipyridine rings, this ligand is more electron rich than the bpyPY2Me parent ligand. Thus, to control electronic effects in the first coordination sphere, we also synthesized bpyOMePY2Me, which is devoid of the phenolic proton. Of relevance here are the Hammett constants, $\sigma_p$, of the OMe and OH groups, which are $-0.27$ and $-0.37$ versus $0.00$ for H.97 Finally, as a means of evaluating the effect of proton acidity on catalysis, we synthesized bpyNHEtPY2Me, which features a less...
acidic N–H proton in place of the O–H proton in bpy^{NH}PY2Me. For reference the pK_{a} values of 2-aminopyridine and 2-pyrindone in dimethyl sulfoxide are 27.7 and 17.0, respectively.98 For use in control experiments, we also synthesized the reference ligand bpyNEt2PY2Me, wherein the aniline proton of bpyNHEtPY2Me is replaced with a second ethyl group. Here, the \( \sigma_{p} \) constants for the shorter alkylamine derivatives NHMe and NMe_{2} are −0.70 and −0.83, respectively.97 Full details of the synthesis and characterization of these ligands are provided in the Supporting Information.

**Synthesis and Characterization of Tetrapyridyl Complexes.** Metalation of this series of ligands proceeded smoothly with the use of Fe(CF_{3}SO_{3})_{2} in acetonitrile (see Scheme 1). Adding it to solutions of ligands resulted in a rapid color change from pale yellow to dark red or orange. The resulting solutions were purified via filtration through a short Celite column and subsequently layered with diethyl ether. Diffusion of the ether into the acetonitrile solutions over the course of 1−2 days afforded crystalline forms of [(bpyPY2Me)Fe(CH_{3}CN)_{2}](CF_{3}SO_{3})_{2} (1), [(bpy^{O^{H}}PY2Me)Fe(CH_{3}CN)_{2}](CF_{3}SO_{3})_{2} (2), [(bpy^{OMe}PY2Me)Fe(CH_{3}CN)_{2}](CF_{3}SO_{3})_{2} (3), [bpy^{NH}PY2Me]Fe(CF_{3}SO_{3})_{2} (4), and [(bpy^{NEt}PY2Me)-Fe(CF_{3}SO_{3})_{2}] (5). To probe the critical role of the Fe center in 4 during catalysis (see below), while the same charge state was maintained for the overall complex, we also synthesized a crystalline form of [(bpyNHEtPY2Me)Mn(CF_{3}SO_{3})_{2}] (6) by following the same general preparation outlined in Scheme 1, starting from Mn(CF_{3}SO_{3})_{2}.

The solid-state structures of compounds 1−6 were established using single-crystal X-ray diffraction analyses (see Figure 1 and Figure S1 and Table S1 in the Supporting Information). The divalent metal centers in all six complexes display pseudo-octahedral coordination geometries, wherein four coordination sites are occupied by the tetrapyridyl ligand, thus leaving two open cis sites available for coordination by exogenous ligands. Notably, in the cases of 4 and 6, which bear the bpy^{NH}PY2Me ligand, two of the metal coordination sites are occupied by CF_{3}SO_{3}− anions. For both complexes, the NH protons were located in the Fourier difference map. Their positions suggest the presence of intramolecular hydrogen bonding between the ligand and the CF_{3}SO_{3}− anion occupying the L1 coordination site (see Scheme 1). This observation may showcase the ability of the bpy^{NH}PY2Me ligand to stabilize an axially coordinated anion. In contrast, complex 5, which

Scheme 2. Two Possible Competing Catalytic Pathways for the Catalytic Reduction of CO2 to CO or Water to H2 by Non-Heme Iron Complexes99

"Through hydrogen-bonding interactions, anilinic protons in the second coordination sphere stabilize CO2 binding to the reduced iron center. The more acidic phenol proton possibly favors a direct proton transfer to form a Fe−H intermediate and eventually H2."
features the bpy$^{\text{NEt}_2}$PY2Me ligand, bears one acetonitrile ligand at the L₁ coordination site and one CF₃SO₃⁻ ligand at the L₂ coordination site (see Figure 1). We ascribe the difference in exogenous ligand binding between complexes 4 and 5 to two factors. First, the bpy$^{\text{NEt}_2}$PY2Me ligand lacks a proton in the second coordination sphere, which decreases the ability of complex 5 to stabilize the coordination of both CF₃SO₃⁻ ligands. Second, the larger steric bulk of the NEt₂ motif in complex 5 destabilizes binding of the larger CF₃SO₃⁻ ligand at the L₁ site, as evidenced by the space-filling models of complexes 4 and 5 surrounding the L₁ coordination site (see Figure S2). For complexes 1–3, the similar Fe–ligand distances (ranging from 1.903(1) to 2.053(2) Å; see Table S2) indicate strong similarities of the first coordination spheres in these complexes. Notably, these metal–ligand distances lengthen in 4 and 5, ranging from 2.087(1) to 2.249(4) Å, perhaps due to the weaker ligand field imposed by the CF₃SO₃⁻ anions (versus the coordinated acetonitrile molecules in 1–3) and the steric bulk of the pendant alkyl aniline moieties.

To probe the electronic effect of the second coordination sphere functionality on the ferrous ion, we measured the room-temperature magnetic susceptibility of each complex in acetonitrile using the Evans method. While compounds 1–3 are diamagnetic in acetonitrile, the corresponding solution magnetic moment for 5 ($\mu_{\text{eff}}=5.1\mu_B$) is consistent with an $S=2$ ground state. Notably, a much lower value of $\mu_{\text{eff}}=1.4\mu_B$ was obtained for 4 and suggests a possible spin transition near room temperature. The solution magnetic moment of $\mu_{\text{eff}}=5.8\mu_B$ for 6 is consistent with an $S=5/2$ Mn(II) center.

**Cyclic Voltammetry in Acetonitrile.** Cyclic voltamograms (CVs) of compounds 1–6 were measured under an argon atmosphere in anhydrous acetonitrile to further probe the electronic effects of varying substituents on the bipyridine unit (see Figure 2). Due to the presence of Fe and a redox-active bipyridyl ligand, complexes 1–5 display a rich electrochemistry. For complex 1, which features the parent bipyridine moiety, three redox events are observed between +1.3 and −2.3 V versus Fe(C₆H₅)₂$^{\text{+/0}}$. These redox events are centered at $E_{1/2}=+0.81$, −1.71, and −1.86 V. For scan rates ($\nu$) of 50–1000 mV/s, the peak potentials ($E_p$) of these redox processes are invariant, and the peak-to-peak separation remains constant at 60 mV, near the ideal 57 mV for a reversible one-electron electron transfer (see Figure S3). Furthermore, the forward and reverse currents display a linear dependence on $\nu^{1/2}$, suggesting that these redox processes are reversible, diffusion-controlled processes. We attribute the oxidation feature to a metal-centered oxidation from Fe(II) to Fe(III), while the oxidation feature to a metal-centered oxidation from Fe(II) to Fe(III), while the first reductive process could tentatively be assigned to arise from a predominantly metal centered reduction, followed by a ligand-based reduction (see below).

The incorporation of electron-donating groups at the 6-position of the bipyridine introduces slight negative shifts to the potentials of the redox processes and substantially affects the electrochemical reversibility of those processes. Oxidation waves are observed at +0.78, +0.78, and +0.80 V versus Fe(C₆H₅)₂$^{\text{+/0}}$ for complexes 2–4 (see Figure 2). As with complex 1, the oxidation waves of complexes 2 and 3 appear to be reversible and diffusion-controlled across all measured scan rates (see Figures S4 and S5): $E_p$ does not vary with scan rate, $\Delta E_p=58$ mV for $\nu=50–1000$ mV/s, and the forward and reverse scans both vary linearly with $\nu^{1/2}$. The oxidation wave of complex 4 appears to be less reversible at slower scan rates, with the reverse sweep showing a peak shape only at $\nu \geq 100$ mV/s (see Figure S6). The forward peak current remains linear with $\nu^{1/2}$ (see Figure S6b, black squares), and the current ratio $i_{\text{pr}}/i_{\text{fr}}$ increases with increasing scan rate, where $r$ and $f$ denote the reverse and forward sweeps. As such, the oxidation of 4 appears to be a reversible electron transfer followed by an irreversible chemical reaction (ErCi). The effect of substitutions on the reductive processes in this family of compounds is more complex. For compound 3, which possesses an electron-donating OMe substituent ($\sigma_p=−0.27$) on the bpy moiety, the first reduction feature occurs at $E_{1/2}=−1.71$ V (see Figure 2 and Figure S4), at a potential similar to that of the first reduction in complex 1. This reduction is electrochemically reversible. A second reduction feature is not observed at potentials as low as −2.2 V. Complex 2, which bears an OH substituent ($\sigma_p=−0.37$), has a complicated reduction feature at $E_{1/2}=−1.72$ V (see Figure 2 and Figure S5). At slow scan rates, the forward scan shows several peak-shaped features. However, at $\nu \geq 5$ V/s the features appear to merge. Furthermore, with increasing scan rates, the reverse peak current is more pronounced. The trends in $E_p$ and $i_{\text{pr}}/\nu^{1/2}$ did not permit us to straightforwardly fit this feature to a single mechanism. An additional broad feature centered at −1.87 V is observable when CVs of 2 are swept at 250 mV/s $\leq \nu \leq 1000$ mV/s (see Figure S4). The peak current of this feature increases linearly with $\nu$, indicating an absorption event. In addition, the peak-to-peak separation increases at higher scan rates, suggesting that this process is coupled with slow/quasi-reversible electron transfer.

Like that of complex 1, the CV of 4 at $\nu = 0.1$ V/s exhibits two one-electron reduction events within a narrow 0.2 V window, at −1.79 and −1.87 V versus Fe(C₆H₅)₂$^{\text{+/0}}$ (see Figure 2). The first reduction event is irreversible, again highlighting the chemical liability of protic groups under reducing potentials. The second reduction process is reversible (see Figure S6) and occurs at a potential similar to the lone reversible reduction event at −1.85 V observed for 6 (see Figure 2 and Figure S8), which features the bpy$^{\text{NEt}_2}$PY2Me ligand and a Mn(II) ion. On this basis, we assign the reduction wave at −1.87/−1.85 V for complexes 4 and 6 as predominantly ligand based. At $\nu \geq 500$ mV/s, CVs of 4 show several small features between +0.5 and −0.5 V, which we attribute to possible electroactive intermediates arising from the irreversible oxidation and reduction of 4. In the CV of complex 5, a diffusion-controlled, irreversible oxidation feature is observed at $E_{1/2}=+0.87$ V. Return waves are observable at $\nu \geq 500$ mV/s and occur at $\sim+0.7$ and $\sim+0.5$ V (see Figure S7). Since the peak potentials of the forward and backward processes are insensitive to changes in scan rate, the irreversibility is chemical in nature. Similar to the case for 4, the first reduction feature of complex 5 is diffusion-controlled and irreversible, occurring at −1.71 V. A second irreversible reduction feature that occurs at $\sim−1.9$ V is apparent at $\nu \geq 500$ mV/s. Although the forward peak is prominent only at two measured scan rates, it increases with $\nu$ more rapidly than the reverse peak does, possibly implicating a quasi-reversible process where the transfer coefficient $\alpha$ is greater than 0.5.

**Electronic Absorption Spectroscopy in Acetonitrile/ Water Mixtures.** With the goal of using water as the proton source for C–O bond cleavage in CO₂ reduction, we therefore sought to evaluate the compatibility of all complexes in the presence of high concentrations of water. As a first step, we monitored the electronic absorption spectra of complexes 1–5.
as water was sequentially titrated, up to a final concentration of 11 M. The UV–vis spectra of the low-spin complexes 1 and 3 show minimal changes upon addition of water (see Figures S9 and 10), indicating that those d6 Fe(II) ions are kinetically inert to ligand substitution by water. Conversely, although complex 2 also has a S = 0 Fe(II) center, its UV–vis spectrum shows continuous changes with increasing concentrations of water, with isosbestic points at 336 and 380 nm (see Figure S11). Given the similar d-electron configurations and first coordination spheres across complexes 1–3, the unique sensitivity of 2 to water may implicate the second coordination sphere OH group in hydrogen-bonding interactions or acid–base chemistry. Finally, the UV–vis spectra of complexes 4 and 5, neither of which are low spin, suggest that those Fe(II) ions rapidly bind water (Figures S12–13).

**Cyclic Voltammetry in Acetonitrile/Water Mixtures.**

The base electrochemical responses of compounds 1–5 to water were evaluated by collecting CVs under a N2 atmosphere. Given the similar d-electron configurations and first coordination spheres across complexes 1–3, the unique sensitivity of 2 to water may implicate the second coordination sphere OH group in hydrogen-bonding interactions or acid–base chemistry. Finally, the UV–vis spectra of complexes 4 and 5, neither of which are low spin, suggest that those Fe(II) ions rapidly bind water (Figures S12–13).

The base electrochemical responses of compounds 1–5 to water were evaluated by collecting CVs under a N2 atmosphere using an 11 M solution of water in acetonitrile. The complexes exhibited little current increase at potentials as far negative as −2.2 V versus Fe(C5H5)2+/0 (see Figure S14), suggesting negligible background reactivity with water under a N2 atmosphere. The reductive features of complex 4 changes from two features in pure acetonitrile (see Figure 2, orange trace) to three (see Figure S14, orange trace). We ascribe this change to water displacing acetonitrile at one or both of the open coordination sites of the Fe(II) ion, resulting in a mixture of electroactive ions (e.g., [(bpyNHEtPY2Me)Fe(CH3CN)2]2+, [(bpyNHEtPY2Me)Fe(CH3CN)(H2O)]3+, [(bpyNHEtPY2Me)Fe(H2O)3]4+, etc.), as supported by following the UV–vis spectrum of 4 while titrating in water (see Figure S12). Conversely, the oxidation waves of complexes 1–4 now occur at E1/2 = +0.41, +0.21, +0.35, and +0.12 V versus Fe(C5H5)2+/0, which are shifted negatively by 0.4–0.7 V relative to those in pure acetonitrile. Additionally, the transition from pure acetonitrile to acetonitrile/water mixtures significantly affects the the electrochemical reversibility of the Fe(III/II) redox couples in complexes 1 and 2 (compare Figures 2 and Figure S14). While the inherent reactivity of complex 2 with water could explain the electrochemical changes, the UV–vis spectra of 1 suggested compound 1 to be inert to water. A possible but untested explanation is that oxidation of I affords an electrogenerated Fe(III) species where ligand substitution is facile.

To probe the reactivity toward CO2, CVs were subsequently recorded after saturating electrolyte solutions with 1 atm of CO2. For complexes 1 and 3, which lack acidic protons, reductive current enhancements are observed at onset potentials of approximately −1.6 V versus Fe(C5H5)2+/0 (see Figures S15 and S16, red traces). The resulting peak currents are approximately 5-fold greater than the corresponding one-electron events (see Figures S15 and S16, black traces), suggesting a multielectron process and possibly CO2 reduction catalysis. Curve crossing occurs in the CVs of complexes 1 and 3 (see Figures S15 and S16, red traces), indicating the formation of a new, more electroactive species on the reverse sweep. Given that complexes 1 and 3 are both active for CO2 reduction but their Faradaic efficiencies are less than 100% (see below), we cannot definitively assign the curve-crossing event to catalysis or complex reactions such as dimerization, adsorption reactivity, and electrode fouling. Notably, the presence of CO2 induces an even greater 12-fold current enhancement for 4 at −1.91 V versus Fe(C5H5)2+/0 (see Figure 3). The rise in reductive current that occurs for these complexes upon introduction of CO2 suggests the onset of an electrocatalytic reaction, while the greater current exhibited by 4 suggests that the corresponding reaction rate is greater than that of 1 or 3. To confirm that 4 participates in catalysis, the scan rates were systematically decreased (see Figure S17). Although the limiting S-like response has yet to be achieved at a scan rate of 10 mV/s, the forward sweep becomes progressively less peak shaped with decreasing scan rate, indicative that 4 is catalytically regenerated.99 Likewise, the current function (i(t)/t1/2) rapidly increases with decreasing scan rate, without reaching the expected scan-rate-independent limit (Figure S18).99 Upon sweeping to more negative potentials, a separate multielectron wave is observed for complexes 1, 3, and 4, likely due to competing side reactions. In stark contrast to these results, the CV of 2 reveals little sensitivity to the presence of CO2 (see Figure S19). Although there is a catalytic wave, it strongly overlaps with the multielectron feature already observed under N2, suggesting that the complex may be participating in the reduction of water acidified by CO2 gas100 where the apparent pK of H2O + CO2 is 11.2 in acetonitrile with 11 M H2O.101 Curve crossing also takes place in the CV of 2 under CO2 (see Figure S19, red trace). Notably, the CV of the tertiary amine functionalized complex 5 exhibits no apparent electrocatalytic activity (see Figure S20), further highlighting the importance of the N–H moiety in 4 during catalysis.

**Controlled-Potential Electrolyses in CO2-Saturated Wet Acetonitrile.** To establish whether the observed current enhancements for 1, 3, and 4 could be sustained over multiple catalytic cycles, we next performed controlled-potential electrolysis. Over the course of these experiments, we also used gas chromatography via a flow-cell setup to continuously monitor the composition of the reaction vessel headspace for electrocatalysis products. During catalysis, the cathodic chamber of the two-compartment electrolysis cell was purged with a constant stream of CO2 and the chamber headspace was directly plumbed into a gas chromatograph and sampled at 10 min intervals. To avoid interference from the second reductive wave while maximizing current densities, electrolyses were performed at a constant potential of −1.91 V versus Fe(C5H5)2+/0 for 3 h, corresponding to the peak of the first multielectron feature of 4. Using a 240 μM solution of 4 in acetonitrile, with 11 M of added water, a sustained charge buildup of 37 ± 7 C was observed in excess of the background reaction from the glassy-carbon electrode (see Figure 4). In contrast, electrolyses in the presence of 1 and 3 under identical experimental conditions only passed 14.17 ± 0.04 and 7 ± 1 C, respectively. Furthermore, over the course of the 3 h experiment, the charge accumulation for the last two complexes slowed dramatically. These findings are in contrast with the CO2-induced reactivity observed previously on the shorter voltammetry time scale and underscore the importance of preparative electrolytic data. Unsurprisingly, electrolysis of 2, which did not display CO2 reduction activity in its CV, accumulated only 5 ± 2 C. The foregoing results demonstrate that the N–H-functionalized complex in 4 alone can sustain reductive currents at high rates. Complexes lacking an acidic proton, such as in 1 and 3, or with a proton that is too acidic, such as in 2, do not catalyze the reduction of CO2.

Importantly, the electrolytic performance of 4 is also superior in comparison to several control experiments. Compound 5, in which the bipyridine unit of the ligand
bears the dialkyl aniline motif, passes only 5 ± 2 C over 3 h. This observation also eliminates the possibility that CO₂ reduction is catalyzed by a protonated anilinium complex of 4. Electrolysis of a solution containing the simple salt Fe(CF₃SO₃)₂ under identical conditions displays no charge buildup, indicating that solvated Fe(II) centers without the ligand scaffold are incapable of catalyzing CO₂ reduction under these conditions (see Figure S21). Furthermore, electrolysis of the Mn(II) complex in 6, which possesses the same ligand as 4 and similar bpy⁷⁺⁻⁺⁺ redox potentials but lacks the metal-based redox activity, reveals no catalytic activity. Altogether, these results indicate that a confluence of at least two factors is required for catalysis—the redox-active Fe center, ligated by the tetradentate ligand, and the second coordination sphere N–H functional group.

Notably, the electrocatalytic activity of 4 could be reproducibly sustained for at least 12 h, and the average charge passed over four trials was found to be 130 ± 21 C (see Figure 4, bottom).¹⁰⁹ During this period, H₂ and CO were the only gaseous products observed by chromatography, with total Faradaic efficiencies of 11 ± 3% and 81 ± 11%, respectively, as determined from the four trials. Over the course of catalysis, the Faradaic efficiency of the two gases combined is 92 ± 11% (see Tables S3 and S4 for the full electrolysis data).¹¹¹ H NMR spectra of the electrolyte solution after acidic workup showed no detectable traces of formic acid, formaldehyde, or methanol. For this family of iron complexes, complex 4 is the most selective for CO₂ reduction to CO (see Figure S5). Notably, for compound 2, in which the iron complex possesses the more acidic phenol proton in the second coordination sphere, more of the consumed charge is directed toward hydrogen evolution (see Figure S5).

As there is a faster electrocatalytic event occurring at more negative potentials with complex 4 (see the red trace of Figure 3), a separate electrolysis experiment was conducted at E = −2.2 V (i.e., at the peak of the second reductive wave) for 1 h. Concurrent analysis of the headspace indicated that H₂ was the major product at 80% yield, with CO formation at 13% yield, suggesting a distinct catalytic pathway takes place at more negative potentials that favors reduction of water over carbon dioxide.

To date, 4 is the non-heme electrocatalyst that displays the highest selectivity for the reduction of CO₂ to CO. The Faradaic efficiencies of various Fe-containing electrocatalysts for CO₂ reduction are summarized in Table S5. The few reported examples of non-heme electrocatalysts for CO₂ reduction typically favor the production of formate (rather than CO). A phenanthroline-based Fe complex was reported to electrocatalytically reduce CO₂ in organic solvents in the presence of weak Bronsted acids in dimethylformamide and dimethyl sulfoxide solutions.¹⁰² These systems yield mixtures of CO and formate in a ~1:2 ratio. Two recently reported non-heme Fe electrocatalysts display higher selectivities for producing formate.²⁷,⁷⁵ An Fe complex supported by a macrocyclic pyridine-dimine ligand was reported to produce only formate under electrocatalytic conditions in dimethylformamide, albeit in the absence of a proton source.⁷⁵ A tetrairon carbonyl cluster produces formate with Faradaic efficiencies of up to 96% in aqueous solutions at near-neutral pH.⁷² In contrast to these non-heme examples, the preference of 4 for the production of CO (rather than formate) resembles the reactivities reported for Fe porphyrin electrocatalysts.³⁰⁻⁻³³,⁴⁴ Notably, the CO/H₂ selectivity of 4 in the presence of a high water content/proton activity compares favorably with those reported for most Fe porphyrin catalysts (see Table S5). The potential at which electrolyses were carried out with complex 4 (−1.91 V) also compares favorably to some of the catalysts in Table S3, though we note that the thermodynamic potential for CO₂ reduction has not been determined in acetonitrile with 11 M (i.e., 20% v/v) water, making direct comparisons of electrolytic performance difficult.

We performed further experiments to ascertain whether CO₂ reduction catalysis arises from a molecular species or a heterogeneous adsorbate. After a 12 h electrolysis was performed of a solution of 4 under CO₂, the glassy-carbon electrode was rinsed with anhydrous, deaerated acetonitrile under an atmosphere of Ar. Electrolysis was subsequently performed using a fresh, iron-free electrolyte, after which the rinsed electrode displayed electrochemical characteristics identical with those of a freshly polished glassy-carbon electrode (see Figure S22). After the 12 h electrolysis with 4, the resulting electrode was also characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). SEM revealed that the electrode surface is slightly roughened following electrolysis (see Figure S23). The absence of Fe Kα or Feβ features in the EDX spectrum suggests that the active catalyst does not decompose into iron-containing adsorbates on the electrode surface (see Figure S23). We note that these rinse tests and postelectrolysis analyses cannot preclude nondestructive adsorption onto the electrode.

**Kinetic Interrogation by Foot-of-the-Wave Analysis.** If it is assumed that every complex in the bulk solution participates in catalysis, it is only possible to establish a lower bound for turnover number (TON) and turnover frequency (TOF). However, as has been previously noted, using electrocyclic data leads to an underestimation of TON and TOF, as the participation of every catalyst molecule in the electrolyte solution during catalysis is not guaranteed.¹⁰³⁻¹⁰⁵ Instead, cyclic voltammetry data can be used to give complementary estimates for catalytic rates, and utilizing the foot-of-the-wave analyses developed by Savéant and co-workers, we estimated TOF—potential relationships for this family of complexes.¹⁰⁴ The logarithmic TOF versus potential curves derived for solutions of compounds 1–4 (Figures S24–S28) were calculated with slopes of 59 mV/dec, a value that is consistent with fast Nernstian electron transfer followed by a slow, rate-limiting chemical step. From foot-of-the-wave analysis, we derived the rate constant of the first chemical step, k₁. For this family of iron complexes, 4 not only is the most selective for CO production, but also exhibits the fastest k₁ value (2067 s⁻¹, Table 1). Further mechanistic and kinetic studies are required to corroborate these k₁ rate constants with the apparent rate constant kₐp.

**Divergent Catalytic Roles by the Second Coordination Sphere.** The voltammetric and electrolytic data of complexes 2 and 4 constitute rare examples of electrocatalysts wherein the acidity of the second coordination sphere can direct substrate selectivity between CO₂ reduction and water reduction. We postulate that the N–H proton in complex 4 behaves as a local hydrogen bond donor, which stabilizes transition states with significant metallacarboxylate character and assists in CO₂ binding or C–O bond cleavage (Scheme 2, left). This type of role by second coordination sphere protic groups or water channels has been invoked in iron porphyrin,⁵⁰,⁵³,⁹²–⁹⁴ macrocyclic nickel,⁶⁰ and bipyridyl–Mn/
The selectivity of complex 2 for producing hydrogen may be rationalized by the increased acidity of the second coordination sphere (estimated \( \sim 11 \) pK\textsubscript{a} units versus the aniline of complex 4, see above), which promotes the formation of a Fe hydride and is protonated more quickly than CO\textsubscript{2} can bind and be reduced (Scheme 2, right). Ongoing computational studies are aimed at elucidating the catalytic mechanism of CO\textsubscript{2} reduction by complex 4 and the precise roles of both the redox noninnocence and second coordination sphere in the ligand scaffold.

## CONCLUSIONS

We have designed and synthesized a new family of nonheme iron complexes and shown that the incorporation of functional groups featuring protic groups of varying acidity can enhance electrocatalytic activity toward CO\textsubscript{2}. With the appropriate protic group in the second coordination sphere, the \([\text{bpyNH}_{2}\text{PY2Me}]_{2}\text{Fe}^{2+}\) complex in compound 4 is able to utilize water as the proton source for CO\textsubscript{2} to CO conversion with high activity, selectivity, and stability. Notably, catalyst 4 represents a rare example of a non-heme iron CO\textsubscript{2} electro-reduction catalyst and is the first example that selectively generates CO. Furthermore, 4 is devoid of strongly light absorbing moieties such as porphyrins, rendering it a potentially attractive new candidate for the functionalization of semiconductor surfaces for photocatalytic CO\textsubscript{2} reduction. Finally, the foregoing results suggest the myriad of still untapped areas wherein fine synthetic molecular control can be harnessed in the design of improved molecular electrocatalysts.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00455.

Materials and methods, synthetic details and characterization of ligands, molecular structure of 6, crystallographic information and bond lengths, additional electrochemical details and characterization, and SEM and EDX characterization of electrode postelectrolysis (PDF)

### Accession Codes

CCDC 1583538–1583542 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

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(109) Although the performance of 4 was quite good after 12 h, we did not run electrolyses for longer than 12 h because of experimental difficulties with continuous sparging of CO2 in our flow cell setup. By this stage, most of the CH3CN in the bubblers (used to help maintain solvent composition and volume) had evaporated. Longer electrolyses resulted in substantial solvent evaporation from the cell, and the working electrode would no longer be immersed in the electrolyte.