A pyridinic Fe-N₄ macrocycle models the active sites in Fe/N-doped carbon electrocatalysts

Travis Marshall-Roth, Nicole J. Libretto, Alexandra T. Wrobel, Kevin J. Anderton, Michael L. Pegis, Nathan D. Ricke, Troy Van Voorhis, Jeffrey T. Miller & Yogesh Surendranath

Iron- and nitrogen-doped carbon (Fe-N-C) materials are leading candidates to replace platinum catalysts for the oxygen reduction reaction (ORR) in fuel cells; however, their active site structures remain poorly understood. A leading postulate is that the iron-containing active sites exist primarily in a pyridinic Fe-N₄ ligation environment, yet, molecular model catalysts generally feature pyrrolic coordination. Herein, we report a molecular pyridinic hexaazacyclononane macrocycle, (phen₂N₂)Fe, and compare its spectroscopic, electrochemical, and catalytic properties for ORR to a typical Fe-N-C material and prototypical pyrrolic iron macrocycles. N 1s XPS and XAS signatures for (phen₂N₂)Fe are remarkably similar to those of Fe-N-C. Electrochemical studies reveal that (phen₂N₂)Fe has a relatively high Fe(III/II) potential with a correlated ORR onset potential within 150 mV of Fe-N-C. Unlike the pyrrolic macrocycles, (phen₂N₂)Fe displays excellent selectivity for four-electron ORR, comparable to Fe-N-C materials. The aggregate spectroscopic and electrochemical data demonstrate that (phen₂N₂)Fe is a more effective model of Fe-N-C active sites relative to the pyrrolic iron macrocycles, thereby establishing a new molecular platform that can aid understanding of this important class of catalytic materials.

1 Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA. 2 Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47097, USA. 3 Chemical Science and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, USA. 4 Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA. Email: yogi@mit.edu

https://doi.org/10.1038/s41467-020-18969-6
The four-electron, four-proton reduction of molecular oxygen to water is the efficiency-limiting half reaction in low-temperature fuel cells. Regardless of the fuel source used, the current density output is primarily limited by the slow electron transfer kinetics of the oxygen reduction reaction (ORR) taking place at the cathode. The prototypical material for catalyzing this reaction in commercial fuel cells is platinum metal (Pt) supported on carbon. However, the high cost and scarcity of Pt impedes the large-scale deployment of fuel cell devices and motivates the development of Earth-abundant electrocatalysts for oxygen reduction. These catalysts must operate at low overpotentials and with high selectivity for the four-electron reduction of oxygen to water instead of the two-electron reduction process to generate hydrogen peroxide. Since early reports of oxygen reduction catalyzed by macrocyclic first-row transition metal complexes, numerous recent studies have provided significant improvements in their performance, however systematic development of these materials is hampered by limited molecular-level understanding or control of the iron active sites. Fe-N-C materials are typically prepared by pyrolyzing iron- and nitrogen-doped materials. This poor control, combined with the high temperature of pyrolysis of finely dispersed iron salts, porphyrins, or phthalocyanines, along with a metal-organic framework (MOF) or carbon-based support. The uncontrolled nature of pyrolysis leads to a wide diversity of iron environments as well as extended solid iron phases in the resulting Fe-N-C materials. This poor control, combined with the wide variability in preparative procedures, has led to longstanding uncertainty about the local structure of the iron active sites responsible for ORR, thereby impeding systematic enhancements to catalytic performance.

Numerous recent studies have provided significant insight into possible Fe-N-C active site structures. While metallic iron active sites have been postulated, mononuclear Fe-N active sites are more commonly invoked to explain correlations between X-ray absorption spectroscopy (XAS) or 57Fe Mössbauer spectroscopy with ORR activity. Despite the growing consensus that Fe-N4 sites are essential for ORR, the ligation environment of these iron sites remains uncertain. Indeed, even though iron porphyrin and phthalocyanine complexes can be used as precursors to Fe-N-C materials, there is evidence that the core pyrrolic ligation environment of these precursors changes substantially upon pyrolysis. In particular, the first shell Fe-N bond lengths in Fe-N-C materials have been reported to be shorter than the macrocyclic iron complex precursor used in the material synthesis. X-ray photoelectron spectroscopy (XPS) results have pointed to the presence of metal-coordinated pyridinic nitrogen moieties as opposed to metal-bound pyrrolic nitrogen in Fe-N-C materials.

57Fe Mössbauer spectra of many iron porphyrin and phthalocyanine complexes differ dramatically from the main 57Fe Mössbauer doublets assigned to the putative Fe-N4 active sites in Fe-N-C materials. In addition, atomic-resolution electron microscopy data indicate the presence of mono-dispersed iron atoms bound within the plane of graphitic carbon, suggesting that the ligating groups are six-membered heterocycles rather than the five-membered rings found in pyrrolic macrocycles. Based on these spectroscopic and imaging results, there is a growing body of evidence that the Fe-N4 sites in Fe-N-C materials are ligated by pyridinic moieties fused within graphitic sheets (Fig. 1a).

Despite substantial evidence for pyridinic Fe-N4 sites in Fe-N-C materials, nearly all molecular Fe-based ORR catalysts that are used to model the iron-containing active sites of Fe-N-C are macrocyclic complexes that feature pyrrolic coordination environments (Fig. 1b). Notwithstanding evident differences between the spectroscopic features of Fe-N-C and pyrrolic-type macrocycles, such macrocyclic complexes are routinely used as models during the analysis of X-ray absorption data to build computational fits to the experimental Fe-N-C data in order to construct toy models of the apparent Fe-N4 sites. Such an approach could be strengthened by the creation of a pyridinic Fe-N4 model architecture that is better able to model the average Fe-N4 sites in Fe-N-C relative to pyrrolic iron complexes. Owing to the inherent multiscale complexity of Fe-N-C materials, no molecular complex will ever be able to perfectly reproduce their spectroscopic signatures or catalytic function. Pyrrolic model compounds have offered valuable spectroscopic and mechanistic insights and such molecular-level studies would benefit from new model complexes that feature the pyridinic ligation motifs that are now thought to exist in Fe-N-C materials.

Based on the aggregate spectroscopic evidence on Fe-N-C materials, we envisioned that an improved model complex would feature (a) a tetrapyrrolic coordination environment, (b) relatively short Fe-N bond lengths, (c) an extended ligand π system, and (d) a relatively high Fe(III)-OH/Fe(II)-OH2 redox potential. Towards realizing the above goal of synthesizing a pyridinic Fe-N4 model complex, we searched the literature for pyridinic N4 macrocyclic ligands. Notably, the aza-bridged bis-1,10-phenanthroline hexaazamacrocycle, (phen2N2)H2, (phen2N2 = 1,14:7,8-diethenotetrayrido[2,1,6-de:2′,1′,6′-gzh:1″,6″-kl2″:1′″,6″′-na]1,3,5,8,10,12-hexaazacyclotetradecine), as well as its cobalt(II), nickel(II) and copper(II) complexes have been reported and applied to DNA binding studies and carbon dioxide reduction catalysis. Despite this precedent, the synthesis and ORR activity of the corresponding (phen2N2)Fe fragment has to the best of our knowledge, remained unexplored.

Herein, we report the synthesis and characterization of this pyridinic Fe-N4 macrocyclic fragment (Fig. 1c) and compare its 57Fe Mössbauer, XPS, and XAS features and ORR performance to those of prototypical Fe-N-C, iron octaethylporphyrin, (OEP)Fe, and iron phthalocyanine, (Pc)Fe, catalysts. Through these studies, we demonstrate that the iron coordination environment in [(phen2N2)Fe]2O displays greater spectroscopic similarity to Fe-N-C materials than [(OEP)Fe]2O and [(Pc)Fe]2O. Furthermore, we find that (phen2N2)FeCl displays superior catalytic activity and selectivity relative to (OEP)FeCl and (Pc)FeCl, approaching the performance metrics of Fe-N-C materials. These studies establish (phen2N2)Fe complexes as better structural and functional mimics of Fe-N4 active sites in Fe-N-C materials than legacy pyrrolic macrocycles.

**Results and discussion**

**Synthesis of Fe-N-C and (phen2N2)Fe complexes.** A prototypical Fe-N-C material was synthesized by a combination of literature methods. In brief, Fe-N-C was prepared by pyrolysis of a mixture of iron(II) acetate, 1,10-phenanthroline, and a zinc imidazolate MOF (ZIF-8) under a reducing atmosphere (5% H2 in Ar). After pyrolysis, the sample was washed with 0.1 M H2SO4 to remove trace Fe(0). The 57Fe Mössbauer spectrum of this material (Supplementary Fig. 1, top and Supplementary Table 1) displays two quadrupole doublets in line with previously reported Fe-N-C materials.

The bis-phenanthroline macrocycle, (phen2N2)H2, was prepared by exposure of 2,9-dichlorophenanthroline (Supplementary Fig. 2) to anhydrous ammonia in a Parr reactor that was held at 280°C for 24 h and then ramped to 300°C for 12 h (Fig. 2).
Metalation with iron was achieved by treating (phen2N2)H2 with anhydrous FeCl3 in DMF or HMPA in the presence of excess tributylamine under an N2 atmosphere. To remove unreacted FeCl3 and other reaction byproducts, the crude reaction mixture was washed with copious amounts of diethyl ether and dichloromethane. Due to the extremely low solubility of the (phen2N2)FeCl complex, we found that residual Fe2Cl6•(DMF)3 (~16%) remained in the sample despite exhaustive washing with anhydrous solvents. HR-MS analysis of the material reveals a prominent peak at 440.1061 m/z and a smaller peak at 475.1023 m/z, in line with the expected masses of [(phen2N2)Fe]+ (440.0473 m/z) and [(phen2N2)FeCl]+ (475.0161 m/z), respectively. UV–Vis data also support formation of the metalated complex with a bathochromic shift of the ligand π→π* transitions and the appearance of shoulders on the main π→π* peak (Supplementary Fig. 3). The 57Fe Mössbauer spectrum of (phen2N2)FeCl (Supplementary Fig. 1, middle and Supplementary Table 2) reveals a broad quadrupole doublet assigned to (phen2N2)FeCl in the S = 3/2 state, which differs dramatically from the parameters for (OEP)FeCl and (Pc)FeCl (Supplementary Figs. 4 and 5 and Supplementary Table 2). This assignment is consistent with our calculations on (phen2N2)FeCl, which predict an intermediate-spin ground state and is consistent with a compressed N4-binding pocket that stabilizes the S = 3/2 spin state (see Supplementary Note 1 for calculated energies and geometries).

To better mimic the axial O-ligation present in the material, we Soxhleted the (phen2N2)FeCl sample with ethanol. This served to generate the μ-oxo [(phen2N2)Fe]2O via reaction with adventitious water and base. Similar conversions are precedented for sterically unprotected porphyrin complexes. While this species is catalytically inactive in the acidic electrolyte (Supplementary Fig. 6), it provides a good spectroscopic model for Fe-N-C materials and the analogous [(OEP)Fe]2O and [(Pc)Fe]2O were synthesized for comparison. The 57Fe Mössbauer spectrum of the [(phen2N2)Fe]2O complex is a narrow doublet (Supplementary Fig. 1, bottom and Supplementary Table 2), distinct from the spectra of [(OEP)Fe]2O and [(Pc)Fe]2O (Supplementary Figs. 7 and 8 and Supplementary Table 2). The vast differences in the 57Fe Mössbauer spectra of (phen2N2)Fe, (OEP)Fe, and (Pc)Fe upon exchange of the axial ligand suggest that 57Fe Mössbauer spectroscopy alone may be insufficient to distinguish pyrrolic from pyridinic ligation at putative Fe-N 4 sites in Fe-N-C materials.

XPS reveals nitrogen and iron environments similar to Fe-N-C. The nitrogen environments present in Fe-N-C, [(phen2N2)Fe]2O, (phen2N2)H2, [(Pc)Fe]2O, and [(OEP)Fe]2O were synthesized for comparison. XPS reveals nitrogen and iron environments similar to Fe-N-C.
all samples, component decomposition of the N 1s manifold for Fe-N-C, and N 1s peaks, assignments, and parameters for all samples). For Fe-N-C, we observed a broad N 1s XPS signal similar to that reported for other Fe-N-C materials (Fig. 3a). The N peak envelope for Fe-N-C spans 396–407 eV and can be deconvoluted into four peaks, previously assigned to oxidized (404.0 eV), graphitic/pyrrolic (401.3 eV), metal-coordinated (399.9 eV), and pyridinic nitrogen (398.3 eV). We note that since this sample was prepared by the pyrolysis of ZIF-8, we expect the metal-coordinated N peak to result from both iron and zinc coordination. Notably, comparing N 1s XPS binding energies for ZnII porphyrins and FeII porphyrins (Fig. 3d and Supplementary Fig. 11) reveal N XPS peaks within 0.2 eV, suggesting that residual Zn does not dramatically convolute the N XPS envelope of this Fe-N-C preparation.

The broad peak envelope for Fe-N-C contrasts with the well-defined nitrogen environments in [(Pc)Fe]2O, [(OEP)Fe]2O, and [(phen2N2)Fe]2O. For [(phen2N2)Fe]2O, high-resolution N 1s spectra (Fig. 3b) reveal a single peak centered at 399.3 eV that can be deconvoluted into two components centered at 398.3 and 399.6 eV with a ratio of peak area values of 1:2. Based on the integration ratio and the symmetry of the (phen2N2)Fe subunits in [(phen2N2)Fe]2O, we assign the 398.3 eV peak to the bridgehead nitrogens and the 399.6 peak to the coordinated pyridinic nitrogens. In comparison, the N 1s XPS spectrum (Supplementary Fig. 12, bottom) of (phen2N2)H2 is dominated by two peaks corresponding to bridging and pyridinic nitrogen atoms at 397.9 and 399.5 eV, respectively, in a 1:2 ratio. This indicates that both bridging and pyridinic nitrogen atoms shift to higher binding energies upon metalation with iron. Similar changes in the N 1s spectrum have been reported for free-base porphyrins upon metalation. In contrast, the N 1s XPS spectra of [(Pc)Fe]2O and [(OEP)Fe]2O differ markedly from that of [(phen2N2)Fe]2O. The spectrum of [(Pc)Fe]2O is composed of a sharp peak at 398.4 eV with a satellite peak centered at 400.1 eV (Fig. 3c). Analogously, [(OEP)Fe]2O consists of a sharp peak at 397.6 eV with a broad satellite peak centered at 399.9 eV (Fig. 3d). While the main peak in [(Pc)Fe]2O appears in the region assigned to Npyrrolic for Fe-N-C, it is best fit with a single component, indicating that the coordinating and non-coordinating N atoms have comparable binding energies. Thus, the exclusive presence of phthalocyanine environments in Fe-N-C would be insufficient to account for the large metal-Nx peak in Fe-N-C. Notably, N 1s peaks for (phen2N2)FeCl, (Pc)FeCl, and (OEP)FeCl (Supplementary Fig. 11) appear within 0.1–0.4 eV of the corresponding peaks for the μ-oxo compounds, indicating that the identity of the axial ligand does not impact the N 1s binding energy to the same extent as does changing the metal-coordinated nitrogen atoms from pyrrolic to pyridinic. Importantly, the N 1s peaks for the coordinated pyridinic nitrogens in the (phen2N2)Fe complexes match well with the peak corresponding to the metal-coordinated pyridinic nitrogen component (399.9 eV) of Fe-N-C, whereas the N 1s peaks of the coordinated pyrrolic nitrogens in (Pc)Fe and (OEP)Fe complexes appear at significantly lower binding energies. Together, the XPS data indicate that the iron-coordinated N environment in [(phen2N2)Fe]2O species are electronically very similar to the metal-coordinated N environments in Fe-N-C materials.

The iron environments present in Fe-N-C, [(phen2N2)Fe]2O, [(Pc)Fe]2O, and [(OEP)Fe]2O were also examined by XPS (Supplementary Table 6). Consistent with previously reported data for Fe-N-C materials, we observe Fe 2p3/2 peaks at 705.5 and 713.9 eV (Fig. 3e) assigned to Fe(II) and Fe(III) formal oxidation states, respectively (Supplementary Table 7). In contrast, [(Pc)Fe]2O (Fig. 3g) exhibits Fe 2p3/2 and 2p1/2 peaks at 708.9 and 722.0 eV, respectively, and [(OEP)Fe]2O (Fig. 3h) displays Fe 2p3/2 and 2p1/2 peaks at 709.2 and 723.2 eV, respectively. As reported for iron porphyrin and phthalocyanine complexes, the Fe 2p spectra of Fe-N-C, [(Pc)Fe]2O, and [(OEP)Fe]2O display small Fe 2p3/2 and 2p1/2 peaks at 712.4 and 725.6 eV, respectively.
samples, we also observe significant asymmetry on the main Fe 2p_{3/2} peak for both [(OEP)Fe]_2O and [(Pc)Fe]_2O compounds that is attributed to multiplet splitting arising from core-hole interactions with the open-shell electronic structure of the high-spin ferric centers. Similar features are observed for (OEP)FeCl and (Pc)FeCl, albeit with a ~0.5–1.9 eV shift to higher binding energy (Supplementary Figs. 13 and 14). These XPS features are distinct from those observed for [(phen2N2)Fe]_2O (Fig. 3f) which displays Fe 2p_{3/2} and 2p_{1/2} peaks at 710.8 and 724.3 eV. We note that (phen2N2)FeCl shows Fe 2p_{3/2} and 2p_{1/2} peaks at similar binding energies, 710.5 and 723.9 eV, respectively (Supplementary Fig. 15), and that residual FeCl3 salts are likely subsumed into these peaks. As with [(OEP)Fe]_2O and [(Pc)Fe]_2O, we also observe significant asymmetry in the Fe 2p_{3/2} and Fe 2p_{1/2} peaks of [(phen2N2)Fe]_2O that we also attribute to core-hole interactions. Importantly, we observe a ~1.5–1.9 eV shift to higher binding energy for the main Fe 2p_{3/2} peak for [(phen2N2)Fe]_2O relative to both [(OEP)Fe]_2O and [(Pc)Fe]_2O. This observation is consistent with increased π-acidity of the pyridinic macrocycle in [(phen2N2)Fe]_2O which withdraws electron density from the iron center and is mirrored by the positions of the Fe–O–Fe peaks evident in the high-resolution O 1s spectra of the μ-oxo complexes (Supplementary Fig. 16 and Supplementary Table 8). Notably, the peak in Fe-N-C assigned to Fe(III) is 2.7 eV positive of the corresponding Fe(III) peak for [(phen2N2)Fe]_2O but even more positive than the same peak in [(OEP)Fe]_2O and [(Pc)Fe]_2O. These data suggest that while the Fe(III) centers in Fe-N-C may exist in an even more withdrawing ligand environment, a pyridinic macrocycle complex such as [(phen2N2)Fe]_2O provides a better structural model for Fe-N-C than pyrrolic macrocycles such as [(OEP)Fe]_2O and [(Pc)Fe]_2O. Indeed, the strongly electron-withdrawing environment in the material helps explain the positive shift of the putative Fe(II) component of Fe-N-C, which makes it appear close in energy to the main Fe 2p_{3/2} peaks of the Fe(III) complexes. Overall, the XPS data are consistent with nitrogen and iron environments in [(phen2N2)Fe]_2O that are more electropositive than the pyrrolic macrocycles and more similar to the metal-Nx sites in Fe-N-C.

**Fig. 4 X-ray absorption spectroscopy data.** XANES spectra (a) and expanded main-edge region (inset), k^2-weighted Fe k-edge EXAFS spectra (b) and k^2-weighted Fourier transform Fe EXAFS spectra (c). The energy values of the vertical lines and the alphabetical labels in (a) are taken from reference. Fe-N-C is shown in black, [(phen2N2)Fe]_2O in blue, [(OEP)Fe]_2O in orange and [(Pc)Fe]_2O in aqua.

XAS results demonstrate a strong similarity with Fe-N-C. We next examined the electronic structure and coordination environment of the iron centers in Fe-N-C, [(phen2N2)Fe]_2O, [(OEP)Fe]_2O, and [(Pc)Fe]_2O by XAS. The XANES spectrum of our Fe-N-C preparation (Fig. 4a, black) matches those reported in the literature. While a rigorous analysis of the X-ray absorption near edge structure (XANES) spectra for Fe-N-C materials is challenging due to the presumed presence of a mixture of Fe(II) and Fe(III) (Supplementary Table 7) as well as an unknown degree of heterogeneity in the local coordination environment of each iron, the XANES line shapes have been examined for a wide variety of pyrolyzed Fe-N-C catalysts, including Fe-N-C derived from iron pyrrolic macrocycles, and features of the XANES have been correlated to pyrolysis temperature and ORR activity. In particular, the intensity of the first main-edge peak, C, has been found to positively correlate with increased pyrolysis temperature as well as improved ORR activity, whereas the intensities of the main-edge shoulder, B, and the higher energy main-edge peak, D, have been shown to anticorrelate with both pyrolysis temperature and ORR activity (Fig. 4a, dotted vertical lines). Notably, the XANES spectra of [(OEP)Fe]_2O (Fig. 4a, orange) and [(Pc)Fe]_2O (Fig. 4a, aqua) show enhanced intensity for D with [(OEP)Fe]_2O also showing enhanced intensity for B. These features contrast with the XANES spectrum of [(phen2N2)Fe]_2O (Fig. 4a, blue), which shows a higher intensity for C, and lower intensities for B and D. The intensity of pre-edge peak, A, has also been shown to positively correlate with ORR activity. We find that the pre-edge peak line shape for [(phen2N2)Fe]_2O matches closely with that of Fe-N-C, but that the peak intensity for both is lower than that for [(OEP)Fe]_2O and dramatically lower than the sharp pre-edge feature observed for [(Pc)Fe]_2O (Supplementary Fig. 17). Given the high sensitivity of the pre-edge peak to the identity of the axial ligand in similar tetrapyrrolic complexes as well as distortions in the Fe-Nx plane resulting from variation of the Fe-O-Fe angle in [(OEP)Fe]_2O and [(Pc)Fe]_2O, we refrain from overinterpreting the pre-edge peak shapes or intensities. Nonetheless, the suppressed intensity at B and D and increased intensity at C for [(phen2N2)Fe]_2O suggest that the (phen2N2)Fe molecular analogue is a superior model for the active sites in Fe-N-C materials relative to pyrrolic macrocycles.
Extended X-ray absorption fine structure (EXAFS) data provide further evidence in support of the structural similarity between the iron coordination environments in [(phen2N2)Fe]2O and Fe-N-C. The k²-weighted EXAFS oscillations for Fe-N-C (Fig. 4b, black) exhibit remarkably similar amplitudes and periods to the EXAFS of [(phen2N2)Fe]2O (Fig. 4b, blue) out to ~10 Å⁻¹ with only a small phase shift beyond ~6 Å⁻¹. In contrast, the k²-weighted EXAFS for [(OEP)Fe]2O (Fig. 4b, orange) and [(Pc)Fe]2O (Fig. 4b, aqua) display amplitudes and periods that differ dramatically from the EXAFS of [(phen2N2)Fe]2O and Fe-N-C beyond ~3.5 Å⁻¹. For example, whereas traces for both Fe-N-C and [(phen2N2)Fe]2O pass through χ(k)² = 0 at eight different points between 2.5 and 10 Å⁻¹, [(OEP)Fe]2O and [(Pc)Fe]2O do so nine and eleven times, respectively. Furthermore, the similarity between Fe-N-C and [(phen2N2)Fe]2O is also reflected in the k²-weighted Fourier transform EXAFS radial distribution spectra (Fig. 4c). The [(phen2N2)Fe]2O complex displays a broad primary coordination shell scattering peak at 1.36 Å apparent distance, similar to the first shell peak for Fe-N-C at 1.46 Å apparent distance. In contrast, the first shell scattering peaks for [(OEP)Fe]2O and [(Pc)Fe]2O appear at 1.62 and 1.47 Å apparent distance and display prominent shoulders at lower apparent distances that are not observed in Fe-N-C or [(phen2N2)Fe]2O. Likewise, both [(phen2N2)Fe]2O and Fe-N-C have no prominent scattering interactions beyond 2.25 Å, whereas significant higher-order scattering is observed for [(OEP)Fe]2O and [(Pc)Fe]2O. Taken together, the raw EXAFS data for Fe-N-C mostly match the spectra of [(phen2N2)Fe]2O and are quite distinct from those of either [(OEP)Fe]2O or [(Pc)Fe]2O.

The EXAFS peaks for all four materials are well modeled with a five-coordinate Fe center bearing four equatorial Fe-N scatterers and one axial Fe-O scatterer (Supplementary Table 9). The fits (Supplementary Figs. 18 and 19) from modeling the data return Fe-N scattering paths of 1.94, 1.97, 2.06, and 1.94 Å for Fe-N-C, [(phen2N2)Fe]2O, [(OEP)Fe]2O, and [(Pc)Fe]2O, respectively. The Fe-N distances for both [(OEP)Fe]2O and [(Pc)Fe]2O agree with the corresponding distances extracted from crystal structures. Importantly, these Fe–N bond lengths reflect not only the N–N separation in the ligand, but also the degree of pucker of the iron center out of the equatorial plane. Thus, this distance alone cannot distinguish pyridinic from pyrrolic ligation and, indeed, we see similar Fe–N vectors for [(phen2N2)Fe]2O and [(Pc)Fe]2O. Furthermore, for [(phen2N2)Fe]2O, the 1.97 Å Fe-N distance extracted from EXAFS modeling is substantially higher than the 1.86 Å distance predicted from the calculation if the iron were to reside in the N4 plane for the phen2N2 ligand (Supplementary Fig. 20), further evincing that the iron center is puckered. This reasoning is also in line with a computational XAS study that showed an enhancement of the main-edge peak C (Fig. 4b, blue) as the displacement of iron from the N4 plane was increased. Consistent with the Fe-N-C material having a putative OH₄ axial ligand, the EXAFS fits return an Fe–O scattering path of 2.04 Å, slightly larger than the range of Fe–O scattering paths, 1.73–1.79 Å, extracted for the molecular μ-oxo complexes.

Taking the raw k²-weighted EXAFS oscillations, the FT-EXAFS spectra, and the degree of iron puckering into account, the XAS data highlight that, relative to (Pc)Fe and (OEP)Fe, (phen2N2)Fe is an improved model of the iron sites in Fe-N-C catalysts. We stress that the similarity in the k-space EXAFS data should not be taken to mean that (phen2N2)Fe has an identical structure to Fe-N-C, but that the aggregate scattering environment of the iron centers in (phen2N2)Fe is qualitatively similar to the average cumulative scattering environment of the iron centers in Fe-N-C. We acknowledge this resemblance could be coincidental and introduced by countervailing changes in axial and equatorial scattering interactions. Nonetheless, the data indicate that the iron centers in (phen2N2)Fe exist in a qualitatively similar average environment to the iron centers in Fe-N-C.

**Fe(III/II) potentials are defined by ligating and proximal N atoms.** All three model compounds as well as the Fe-N-C material were evaluated electrochemically as thin films supported on glassy carbon electrodes. In a typical preparation, Fe-N-C powders were dispersed in a 7:2:1 combination of CH₃Cl₂, ethanol, and 5 wt% Nafion solution (75 wt% ethanol and 20 wt% water), respectively. The resulting inks were dropcast onto electrodes and allowed to dry in air to generate a well-adhered catalyst film. A similar procedure was used for (phen2N2)FeCl, (OEP)FeCl, and (Pc)FeCl with inclusion of Vulcan carbon powder to enhance film conductivity. We expect that any residual FeCl₃ salts present in the (phen2N2)FeCl sample will readily dissolve into the acidic electrolyte and will not impact the electrochemical results. In line with this expectation, we find that FeCl₃/Vulcan inks are inactive for ORR (Supplementary Fig. 21).

Cyclic voltammograms of Fe-N-C, (phen2N2)FeCl, (OEP)FeCl, and (Pc)FeCl recorded in the absence of O₂ provide insight into the redox potential of the metal center. For (OEP)FeCl (Fig. 5, orange), we observe a redox feature with E₁/₂ = 0.27 V (all potentials are reported vs the reversible hydrogen electrode, RHE). We note that the Fe(III/II) redox couple of (OEP)FeCl is quite broad with a peak-to-peak separation of 315 mV. We attribute this to sluggish Fe(III/II) redox self-exchange through the film, but nonetheless, we note that the observed E₁/₂ value is comparable to other carbon-adsorbed iron porphyrin compounds. For (Pc)FeCl (Fig. 5, blue), we observe a broad redox feature with E₁/₂ = 0.61 V (Supplementary Fig. 22), similar to reported values for carbon-supported iron phthalocyanine complexes. For (phen2N2)FeCl (Fig. 5, blue), we observe a reversible redox wave at 0.59 V. Based on the known Nernstian pH dependence of Fe(III/II) couples for adsorbed porphyrin complexes as well as the quasi-Nernstian behavior of the redox wave for (phen2N2)Fe (Supplementary Fig. 23), we assign this redox process to the one-electron, one-proton reduction of Fe(III)/OH to Fe(II)-OH₂.

For Fe-N-C (Fig. 5, black), we observe a large double-layer capacitance, consistent with the high surface area of the material, and a pronounced redox wave at 0.63 V (Fig. 5). Although in situ spectroscopic data are required for an unambiguous assignment, we tentatively attribute this redox wave to proton-coupled
electron transfer (PCET) reactions of edge-localized quinone and hydroxyl moieties, rather than to an Fe(III/II) redox process. Although this assignment may seem counterintuitive, we favor it for several reasons. First, quinone and hydroxyl PCET reactions are known to occur in the ~0.6 V potential region on carbon powders. Second, integrating the observed 0.6 V redox wave yields a charge that is 3.4 times larger than the expected charge for a 1-electron redox process of the surface exposed iron centers in the Fe-N-C material. The potential of the wave is comparable to the value for (Pc)Fe and (phen2N2)Fe and this is inconsistent with the expectation that the extended π framework in Fe-N-C should raise the Fe(III/II) potentials. Fourth, Fe-N-C catalyzes ORR at potentials ~0.2 V positive of the observed redox wave. Thus, if the observed 0.6 V redox wave were assigned to the Fe(III/II) couple, the equilibrium fraction of catalytically active Fe(II)-N4 sites at catalytic onset would be very small. Finally, other reports have observed waves for Fe-N-C materials at ~0.8 V in line with the onset of ORR catalysis at Fe-N-C materials (see below). We postulate that the actual Fe(III)-OH/Fe(II)-OH2 redox process for this Fe-N-C material is obscured by the large double-layer charging background and the likely distribution of iron redox potentials. We also note that some iron redox centers may not engage in PCET reactivity and would not be expected to display a redox wave.

The redox potentials extracted from the model compounds provide valuable information about the factors that may contribute to the redox potentials of the iron centers in Fe-N-C materials. Despite the fact that both (Pc)Fe and (OEP)Fe have pyrrolic ligating atoms, the redox potential for (Pc)Fe is ~0.3 V positive of the redox potential of (OEP)FeCl. The principle structural differences between (Pc)Fe and (OEP)Fe are the presence of N vs C atoms in the meso positions and the presence of a more extended π system in (Pc)Fe. One study has found that iron octaethyltetraazaporphyrin possesses a similar Fe(III/II) redox potential to (Pc)Fe, suggesting that the presence of electronnegativity meso-N atoms is the principal contributor to the dramatic positive shift observed. Notably, whereas (phen2N2)FeCl possesses two non-ligating nitrogen atoms in the local environment, (Pc)FeCl has four, yet their Fe(III/II) potentials are comparable. This highlights that the less electron-donating pyridinic coordination environment in (phen2N2)FeCl is an ideal structural motif for pushing the Fe(III/II) positive. Together, the data suggest that for the iron centers in the Fe-N-C material, the effective redox potential is due, not only to the ligating heterocycles, but also the nitrogen population near the Fe center. Thus, even Fe-N4 sites with identical primary coordination spheres may display a distribution of redox properties depending on the population and position of non-ligating proximal nitrogen atoms.

The observed Fe(III/II) redox waves result from only a fraction of the catalyst loaded into the dropcast film. The integrated charge in the Fe(III/II) redox waves of (phen2N2)FeCl, (OEP)FeCl, and (Pc)FeCl catalyst film corresponds to 7%, 43%, and 2% of the total catalyst loading for each compound, respectively (Fig. 6, inset). We attribute the higher electroactive percentage of (OEP)FeCl film to the improved solubility of the porphyrin catalyst, which leads to superior catalyst dispersion within the film. Nonetheless, these PCET redox potentials provide a good indication that the iron centers in (phen2N2)Fe and (Pc)Fe are more electropositive than those in (OEP)Fe.

(Pc)PeCl catalyzes ORR with similar activity to (Pc)FeCl. (Pc)FeCl is a potent catalyst for the ORR. In O2-saturated 0.1 M HClO4, the reversible surface redox wave at 0.59 V (Fig. 6, black) is replaced by a large catalytic wave that displays an onset potential of 0.75 V (all onset potentials correspond to a current density of ~0.1 mA cm\(^{-2}\) and all electrochemical performance parameters are collected in Supplementary Table 11) and reaches a current plateau at ~0.5 V (Fig. 6, red). This catalytic wave spans the same potential range as the reversible redox feature in the absence of O2 suggesting that ORR catalysis is mediated by the Fe(III/II) redox process (Fig. 6, inset). We also find that the Fe center is critical for activity. The unmetallated (phen2N2)H2 ligand has activity comparable to the carbon background (Fig. 7, green) in acidic media with an onset potential of 0.34 V (Fig. 7, magenta) and activity slightly higher than background in alkaline media with an onset potential of 0.75 V, 140 mV negative of (phen2N2)FeCl (Supplementary Figs. 24 and 25). Catalytic onset for (phen2N2)FeCl (Fig. 7, blue) is 320 and 30 mV positive of the onset observed for (OEP)FeCl and (Pc)FeCl, respectively. Catalytic activity is improved in basic media with an onset of 0.89 V in 0.1 M KOH (Supplementary Fig. 24, blue) for (phen2N2)FeCl, similar to the onset observed for (Pc)FeCl and 150 mV positive of the onset for (OEP)FeCl.

The above qualitative activity trends are also reflected in the per site TOF values for the three model complexes. TOF values, in electrons passed per site per second, were extracted as a function of potential by dividing the current density by the integrated charge passed in the Fe(III/II) redox feature. In accordance with...
beyond the scope of this work, the observed correlation among overpotentials. While a detailed mechanistic analysis of the ORR activity among adsorbed porphyrins and phthalocyanines, and showed that catalytic activity is positively correlated with the Fe(III/II) potential. These results are in line with prior work that identified scaling relationships in ORR activity among adsorbed porphyrins and pyrrolic complexes such as (Pc)FeCl and (Pc)FeCl display TOF values that are 280- and 1100-fold higher than (OEP)FeCl at 0.80 V (Supplementary Fig. 26b and Supplementary Table 12).

This positive shift in onset potential and the corresponding increase in TOF for (phen2N2)FeCl and (Pc)FeCl relative to (OEP)FeCl is consistent with the positive shift of the corresponding Fe(III/II) redox potentials for the former compounds. These results are in line with prior work that identified scaling relationships in ORR activity among adsorbed porphyrins and pyrrolic complexes such as (Pc)FeCl and (Pc)FeCl display TOF values that are 280- and 1100-fold higher than (OEP)FeCl at 0.80 V (Supplementary Fig. 26b and Supplementary Table 12).

In this sequence, at any given E, the rate of the reaction will be given by the product, \( k_1 \times k_2 \), of the equilibrium constant, \( K_1 \), for the Fe(III)-OH to Fe(II)-OH, conversion, Eq. (1), and the rate constant, \( k_2 \), for rate-limiting O2 binding, Eq. (2). If \( k_2 \) is roughly insensitive to the local structure of the Fe center, then the reaction rate will be predominantly gated by the Fe(III/II) redox process and the higher redox potentials will correlate with more available Fe(II) at a given E, resulting in faster catalysis. We acknowledge that the above mechanistic picture is speculative and will require more studies to validate, but it nonetheless provides a simple framework for rationalizing the observed reactivity trend. Furthermore, our data provide the first experimental evidence that changing from pyrrolic to pyridinic coordination does not dramatically alter the scaling relationship between ORR activity and Fe(III/II) potential. This provides further support for the notion that Fe-N-C materials contain pyridinic Fe-N4 sites with sufficiently high redox potentials to mediate ORR at relatively low overpotentials.

The electrocatalytic data establish that (phen2N2)FeCl and (Pc)FeCl have superior activity relative to (OEP)FeCl, whereas both remain at a deficit to Fe-N-C. While the Fe(III/II) redox potential is difficult to discern for Fe-N-C, the positive shift of the Fe(III) peak in the XPS suggests that the iron centers in Fe-N-C are even more electropositive than those in (phen2N2)FeCl and (Pc)FeCl. This change may contribute to the higher onset potentials of 0.85 and 0.90 V observed for the Fe-N-C catalyst in acidic and alkaline media, respectively. We stress that although (Pc)FeCl and (phen2N2)FeCl display comparable activity for ORR, (Pc)FeCl is an inferior structural model on the basis of the spectroscopic results presented above. In aggregate, the spectroscopic as well as electrochemical results strongly suggest that (phen2N2)FeCl is the more effective model complex for mimicking iron-containing active sites in Fe-N-C relative to pyrrolic complexes such as (Pc)FeCl. Furthermore, it follows that observing high catalytic ORR performance is insufficient evidence to establish a molecular complex as an accurate and comprehensive molecular model for the active sites in Fe-N-C materials.

Fe-N-C materials are relatively stable, we observe limited stability of the (phen2N2)FeCl catalyst with activity decaying in acidic media over the course of several slow-scan cyclic voltammograms (15–20 min). Analogous deactivations are also observed for the pyrrolic complexes and are documented in the literature. These observations highlight the important role of the carbon framework in increasing the relative stability of Fe-N4 sites in Fe-N-C materials against oxidative and protolytic decomposition induced by the acidic conditions and the presence of parasitic amounts of H2O2. Indeed, we posit that extending the aromatic periphery around the (phen2N2)FeCl active site could enhance stability and allow for the bottom-up synthesis of robust Fe-based ORR catalysts. The results reported herein provide a molecular perspective on the structure and oxygen reduction reactivity of Fe-N4 active sites.
in Fe–N–C materials. We have synthesized a new (phen2N2)Fe fragment and demonstrated that it is a superior molecular model for the putative Fe–N2 active sites in Fe–N–C materials compared to existentially studied iron porphyrin and phthalocyanine complexes. Electrochemical studies establish that ORR activity is positively correlated to the Fe(III/II) potential and that, while (OEP)Fe has too low of a potential to mediate efficient catalysis, both phthalocyanine- and pyridine-based ligand environments in (Ph)Fe and (phen2N2)Fe can generate a positive shift of the Fe (III/II) potential and a corresponding increase in ORR activity. Among the model complexes, the (phen2N2)Fe platform is unique in displaying both high activity and near 100% selectivity for four-electron oxygen reduction in acidic media, the very characteristics found in Fe–N–C materials. Since high electrochemical performance does not necessarily imply structural similarity, our spectroscopic results provide additional discrimination. In particular, the pyridinic ligation environment in (phen2N2)Fe leads to XPS and XAS signatures that are remarkably similar to those of Fe–N–C materials and notably distinct from those of either (OEP)Fe or (Ph)Fe. Taking in aggregate, the spectroscopic similarity and the electrochemical activity and selectivity trends indicate that, relative to (OEP)Fe or (Ph)Fe, (phen2N2)Fe is a significantly improved structural and functional model of Fe–N–C materials. Since the (phen2N2)Fe core can be readily derivatized100,101 and used as the building block for catalytic functional materials, the molecular model complex developed here provides a powerful platform with which to advance the synthesis and understanding of single-site heterogeneous electrocatalysts for critical energy conversion reactions.

Methods
General synthetic considerations. Where indicated, synthetic procedures were carried out under an inert atmosphere in a nitrogen-filled glovebox. All other synthetic transformations were carried out on the benchtop without effort to exclude dioxygen or moisture. Anhydrous 1,10-phenanthroline (99%), 1,3-dibromopropane (98%), tert-butanol (99%), phosphorus pentachloride (98%), and phosphalnitrile (98%) were obtained from Alfa Aesar and used as received. Potassium tert-butoxide (97%) and phosphoryl chloride (99%) were obtained from TCI and Sigma Aldrich, respectively and used as received.

In the present study, we report on the synthesis of (phen2N2)H2 and (phen2N2)FeCl2 by a straightforward procedure to obtain Fe-N active sites in Fe–N–C materials. A detailed synthetic route to (phen2N2)FeCl2 is outlined in the literature102. We have used the synthetic route published previously19,48 for the preparation of (phen2N2)FeCl2, which we report herein. The perspectives published previously19,48 arefollowed closely. 0.019 g (0.11 mmol), Fe(OAc)2, 0.206 g (1.14 mmol, 4.59 equiv.) NCl3, and 0.280 g (0.506 mmol, 66% combined yield) of 3bH,10bH-1,14:7,8-diethenote- tion, precipitation, and washing sequence as before to yield a second crop. In total, 1.528 g of (phen2N2)FeCl2 was synthesized via alkylation of 1,10-phenanthroline using an excess of 1,3-dibromopropane in refluxing toluene, 10.787 g (59.86 mmol) 1,10-phenanthroline was suspended in 105 mL toluene. The mixture was stirred and heated to 70 °C and, subsequently, 28 mL (55.47 g, 275 mmol, 4.59 equiv.) 1,3-dibromopropane was added. The temperature was increased to 120 °C and the mixture was refluxed for 4 h. After allowing the reaction vessel to cool, the mixture was filtered and washed with hexane to yield 18.688 g (82%) of compound 2 as a yellow powder. The observed NMR peaks in D2O matched the reported literature102.

Synthesis of 6,7-dihydro-5H-1,4-diazepino[1,2,3,4-Imn][1,10]phenanthroline-4,8-dium bromide (2). Compound 2 was synthesized via alkylation of 1,10-phenanthroline using an excess of 1,3-dibromopropane in refluxing toluene. 10.787 g (59.86 mmol) 1,10-phenanthroline was suspended in 105 mL toluene. The mixture was stirred and heated to 70 °C and, subsequently, 28 mL (55.47 g, 275 mmol, 4.59 equiv.) 1,3-dibromopropane was added. The temperature was increased to 120 °C and the mixture was refluxed for 4 h. After allowing the reaction vessel to cool, the mixture was filtered and washed with hexane to yield 18.688 g (82%) of compound 2 as a yellow powder. The observed NMR peaks in D2O matched the reported literature102.

Synthesis of 2,9-dichloro-1,10-phenanthroline (4). Under inert atmosphere, a mixture of 2.29 g (9.06 mmol) 3 and 3.77 g (18.1 mL, 2.00 equiv.) PCl3 was suspended in 35 mL POCl3. The mixture was refluxed under inert atmosphere for 4 h. After cooling to room temperature, the solution was poured onto 600 mL of ice and the resulting mixture was neutralized with aq ammonia at 114 psi. The pink solution was warmed and basified with 4 M NaOH and stirred for an additional 12 h. The precipitate was filtered and sequentially washed with ethanol and chloroform until the washings were colorless. The combined washings were concentrated to dryness by rotary evaporation to yield 1748 g (52%) of compound 3 as a brown solid. The observed NMR peaks in CDCl3 matched those reported in the literature102.

Synthesis of (phen2N2)H2. Preparation of (phen2N2)H2 has been previously described in the literature103,104, however an alternate method is presented here. 0.547 g (2.19 mmol) 2,9-dichlorophenanthroline was added to a cylindrical glass insert and enclosed in room temperature at a 100 mL Parr bomb equipped with a rupture disk. The bomb was pressurized with anhydrous ammonia at 114 psi. The bomb was then immersed in a bed of aluminum beads and heated to 280–300 °C with a heating mantle for 24 h. Following additional heating for 12 h at 300 °C, the bomb was allowed to return to room temperature. The residual ammonia was vented and the crude product was dissolved in a mixture of trifluoroacetic acid, acetic acid and methanol and stirred for 30 min. The mixture was neutralized and basified with 4 M NaOH and stirred for an additional 12 h. The precipitate was filtered and sequentially washed with ethanol and chloroform until the washings were colorless. The isolated material was then dried at 60 °C for 12 h. The filtrate was concentrated in vacuo and heated to 300 °C under inert atmosphere for a period of 24 h in a 500 mL round bottom flask affixed to a microdistillation setup. After cooling to room temperature, the solid derived from the filtrate was treated with an identical dissolu- tion, precipitation, and washing sequence as before to yield a second crop. In total, 0.280 g (0.506 mmol, 66% combined yield) of 3H4,f10H,11E,7,8-dioxethenote- trapyrido[2,1,d:2′,1′,6,f2″′,1″′,5″″,6″″]-octa[1,3,5,8,10,12]hexaazacyclotetradecine (pyrrole-b) was isolated as an brown solid. 3H4,f10H (C8D6, n/a, A): δ 9.41 (4, 4H, 10H), 8.76 (s, 4H, 8,4H, 8,4H, 10H). MALDI– MS (POPPOP) matrix: m/z 386.03 ([M]+ calc. for C32H29N10, 386.13). UV–Vis (DMSO): λmax = 287 nm (ε = 23,419 L mol−1 cm−1), 322 (81,152, 339 (0,504), 360 (4,828), 376 (4,069), 439 (550), 467 (202). Anal. Calc. for (phen2N2)2H2O (C8H18N3O2). C: 71.28; H, 3.99; N, 20.78. Found: C, 70.93; H, 3.47; N, 21.12.
Sample was frozen with liquid nitrogen before handling outside the glovebox. All MgSO\textsubscript{4} and 10\% by volume of 2 M NaOH. The mixture was then cooled overnight at -38 °C and the resulting precipitate was filtered and washed with copious amounts of ether and CH\textsubscript{2}Cl\textsubscript{2} to yield 54 mg (73%) of [1,3,5,8,10,12]hexa-azacyclotetradecine)iron(III), [(phen\textsubscript{2}N\textsubscript{2})Fe\textsuperscript{III}].

To a solution of 5.5 mg (0.002 mmol) FeCl\textsubscript{3} as a solution in DMF is synthesized by exposing FeCl\textsubscript{3} to a resistivity of 18.2 MΩ. The 400 MHz Fourier transform of the isotropic 1H NMR spectrum was collected as a function of the DMF temperature. High-resolution scans were collected with a pass energy of 200 eV and a step size of 1 eV. High-resolution scans were collected with a pass energy of 50 eV and a step size of 0.1 eV. All data were analyzed with the Thermov Advantage software. The amount of CO\textsubscript{2} peak area 

Moossauer (90 K): \(\delta = 0.39\) mm s\(^{-1}\), \(\mu\) = 2.95 mm s\(^{-1}\) (vs. NaFeO\textsubscript{2}), \(\lambda\) = 0.36 mm s\(^{-1}\) (vs. NaFeO\textsubscript{2}), \(\lambda\) = 0.41 mm s\(^{-1}\) (vs. NaFeO\textsubscript{2}).

The XPS N:Fe ratio: 6.3:1. \(\Delta\)Mössbauer spectrum (see Supplementary Fig. 5, middle) which was attributed to variation caused by the insoluble nature of (phen\textsubscript{2}N\textsubscript{2})Fe complexes which allows small amounts of chloride salts to be carried through the metatation and Soxhlet procedures. A possible assignment in this case is a small amount of triethylammonium chloride, [(Et\textsubscript{3}N)\textsubscript{3}Fe]. For the O 1s XP spectrum, the background results from gaps in the microcrystalline molecular film that exposes the background carbon support.

X-ray absorption spectroscopy. XAS experiments were performed at the 10-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory. All measurements were performed at the Fe K edge (7.12 eV) in transmission mode in fast scan from 250 eV below the edge to 530 eV above the edge. Samples were pressed into a stainless-steel sample holder. For catalysts containing 1 wt% Fe, -12 mg was loaded. For catalysts containing 8-10 wt% Fe, -1 mg diluted in boron nitride to reach a total of -10 mg was loaded. The sample holder was placed in a leak-proof sample cell with gas flow capabilities and purged with He at room temperature. The cell was sealed and transferred to the beamline to be scanned.

The data were interpreted using WinXAS 3.1 software to find the coordination number (CN) and bond distance (R) using standard procedures. The phase and amplitude functions for Fe-N and Fe-O were extracted from theoretical FEXAFS calculations. Theoretical phase and amplitude files were created for the Fe-CN (CN = 1.9 Å) and Fe-O (CN = 1.3 Å) scattering pairs obtained from known reference compounds. Least squares fits of the first shell of r-space and isolated q-space were performed on the k\textsuperscript{2}-weighted Fourier transform data over the range 2.71-10\(^{-1}\) in each spectrum to fit all other EXAFS data. WinXAS software provides error calculations for each parameter, generated from a correlation matrix during the least square fit. These values are on the order of +/−10% for the CN, +/−5% for R, and +/−0.0001 for the Debye-Waller factor (S\textsuperscript{2}).

The data were processed using the software package VESTA\textsuperscript{115} to model solvation, the implicit solvation model IEF-PCM with a dielectric constant of 78.4 was used\textsuperscript{115}. All molecular images were generated using the software package VESTA\textsuperscript{115}. The geometries of (phen\textsubscript{2}N\textsubscript{2})Fe(III) and [(phen\textsubscript{2}N\textsubscript{2})Fe(III)]\textsuperscript{+} were optimized with spin states \(S = 1/2, 3/2, 5/2\). The most stable spin state was found to be \(S = 3/2\) in both cases.

General electrochemical methods. Sodium hydroxide (99.99%, semiconductor grade), potassium ferricyanide (ACS grade) and potassium sulfate (99.99%, semiconductor grade) were obtained from Sigma Aldrich and used as received. 5 wt% perfluorinated Naion\textsuperscript{®} resin solution was obtained from Ion Power Inc. and used as received. Aqueous electrolyte solutions were prepared with deionized water and adjusted to pH 7 with 0.1 M H\textsubscript{2}SO\textsubscript{4} or 0.1 M NaOH using a Millicell-120 pH meter (Millipore Corporation). Votronics VXC72R carbon powders were obtained from Cabot Corporation and used as received. Glassy carbon disk electrodes were obtained from Pine Research Instrumentation, Inc. Hg/HgO and Hg/HgSO\textsubscript{4} reference electrodes were obtained from CH Instruments, Inc. A titanium mesh was used as the counter electrode for all electrochemical experiments. The titanium counter was constituted of titanium wire (99.9%) and titanium gauze (40 mesh) obtained from Alfa Aesar and was treated with aqua regia prior to use.

The data were interpreted using the software package VESTA\textsuperscript{115}. The phase and amplitude functions for Fe-N and Fe-O were extracted from theoretical FEXAFS calculations. Theoretical phase and amplitude files were created for the Fe-CN (CN = 1.9 Å) and Fe-O (CN = 1.3 Å) scattering pairs obtained from known reference compounds. Least squares fits of the first shell of r-space and isolated q-space were performed on the k\textsuperscript{2}-weighted Fourier transform data over the range 2.71-10\(^{-1}\) in each spectrum to fit all other EXAFS data. WinXAS software provides error calculations for each parameter, generated from a correlation matrix during the least square fit. These values are on the order of +/−10% for the CN, +/−5% for R, and +/−0.0001 for the Debye-Waller factor (S\textsuperscript{2}).

The s\textsuperscript{2} stands for the mean square variation in the bond distances.

Computational details. All DFT calculations were performed using the ab-initio software package Q-Chem\textsuperscript{109} the multi-hybrid functional TPSb-95\textsuperscript{110} and the basis set 6-31+G(\*\*\*)-\textsuperscript{111}. To model solution, the implicit solvation model IEF-PCM with a dielectric constant of 78.4 was used\textsuperscript{115}. All molecular images were generated using the software package VESTA\textsuperscript{115}. The geometries of (phen\textsubscript{2}N\textsubscript{2})Fe(III) and [(phen\textsubscript{2}N\textsubscript{2})Fe(III)]\textsuperscript{+} were optimized with spin states \(S = 1/2, 3/2, 5/2\). The most stable spin state was found to be \(S = 3/2\) in both cases.

General electrochemical methods. Sodium hydroxide (99.99%, semiconductor grade), potassium ferricyanide (ACS grade) and potassium sulfate (99.99%, semiconductor grade) were obtained from Sigma Aldrich and used as received. 5 wt% perfluorinated Naion\textsuperscript{®} resin solution was obtained from Ion Power Inc. and used as received. Aqueous electrolyte solutions were prepared with deionized water and adjusted to pH 7 with 0.1 M H\textsubscript{2}SO\textsubscript{4} or 0.1 M NaOH using a Millicell-120 pH meter (Millipore Corporation). Votronics VXC72R carbon powders were obtained from Cabot Corporation and used as received. Glassy carbon disk electrodes were obtained from Pine Research Instrumentation, Inc. Hg/HgO and Hg/HgSO\textsubscript{4} reference electrodes were obtained from CH Instruments, Inc. A titanium mesh was used as the counter electrode for all electrochemical experiments. The titanium counter was constituted of titanium wire (99.9%) and titanium gauze (40 mesh) obtained from Alfa Aesar and was treated with aqua regia prior to use.

The data were interpreted using the software package VESTA\textsuperscript{115}. The phase and amplitude functions for Fe-N and Fe-O were extracted from theoretical FEXAFS calculations. Theoretical phase and amplitude files were created for the Fe-CN (CN = 1.9 Å) and Fe-O (CN = 1.3 Å) scattering pairs obtained from known reference compounds. Least squares fits of the first shell of r-space and isolated q-space were performed on the k\textsuperscript{2}-weighted Fourier transform data over the range 2.71-10\(^{-1}\) in each spectrum to fit all other EXAFS data. WinXAS software provides error calculations for each parameter, generated from a correlation matrix during the least square fit. These values are on the order of +/−10% for the CN, +/−5% for R, and +/−0.0001 for the Debye-Waller factor (S\textsuperscript{2}).

The s\textsuperscript{2} stands for the mean square variation in the bond distances.
All electrochemical experiments were conducted at ambient temperature using a Biologic VSP 16-channel potentiostat and a three-electrode electrochemical cell. In all cases, the Ti counter electrode was isolated from the working compartment by a porous glass frit. Hg/HgO and Hg/HgSO4 reference electrodes were used for all experiments conducted in alkaline and acidic aqueous electrolytes, respectively. The Hg/HgO reference was stored in 3 M NaOH solution between measurements. Electrode potentials measured in aqueous alkaline media were converted to the RHE scale using the following relationship: \[ E_{\text{RHE}} = E_{\text{Hg/HgSO}_4} + 0.0997 \text{V} + 0.0591 \text{V} \times \text{pH} \] The Hg/HgSO4 electrode was stored in saturated K2SO4 solution between measurements. Electrode potentials measured in aqueous acidic media were converted to the RHE scale using the relationship: \[ E_{\text{RHE}} = E_{\text{Hg/HgSO}_4} + 0.0591 \text{V} \times \text{pH} \] Reference electrodes were periodically checked against a pristine reference to ensure against potential drift.

Routine electrochemical measurements were performed with a 5 mm diameter glassy carbon disk working electrode rotated at 2000 rpm. All scan rates were 5 mV s\(^{-1}\) to allow for equilibration and to approximate steady state catalytic operation. Cyclic and linear sweep voltammograms were initiated at the open circuit potential. In all cases, the potential was swept in the negative direction. Solution resistance values were < 10\(\Omega\) and were ignored. All voltammograms were recorded without \(iR\) compensation. Solutions were sparged for 10 min before each experiment with either N2 or O2 and for another 10 min upon changing between gases. During an experiment, the headspace of the cell was continually flushed with the working gas to minimize solution contamination by atmospheric gases. All experiments were conducted using 10 \(\mu\)L of catalyst ink dropcast onto a polished glassy carbon RDE. Catalytic onset potentials were taken to be the potential at which the observed current density reached ~0.1 mA cm\(^{-2}\). Buffers used for the pH-dependence study of the (phen\(_2\)N\(_2\)Fe)Cl, (Pc)FeCl and (OEP)FeCl inks were performed with a platinum ring while experiments conducted in aqueous alkaline media were performed with a blank glassy carbon disk. Fe2(SO4)3 and K3Fe(CN)6 were used as the redox agents for the collection efficiency measurements in acid and base, respectively. The collection efficiency was calculated using Eq. (5) and found to be 10–11% at the Pt ring and 22–23% at the Au ring: \[ N = \frac{i_{\text{ring}} - i_{\text{disk}}}{i_{\text{disk}}} \] Since calculated \(\%\)H2O values are unreliable when disk currents are small (near the ORR onset region), each \%H2O trace is shown starting where dependable data are available and noise in the measurement has been minimized. Although each catalyst is distinct, this point was located between 50–100 mV past the ORR onset potential in all cases.

Data availability
Data generated or analysed during this study are included in this article and its supplementary information files. Raw data are available from the authors on request.

Received: 29 July 2020; Accepted: 22 September 2020; Published online: 19 October 2020

References
1. Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: insights into materials design. Science 355, eaad4998 (2017).
2. Shao, M., Chang, Q., Dodelet, J.-P. & Chenitz, R. Recent advances in electrocatalysts for oxygen reduction reaction. Chem. Rev. 116, 3594–3657 (2016).
3. Sealy, C. The problem with platinum. Mater. Today 11, 65–68 (2008).
4. Steele, B. C. H. & Heinzel, A. Materials for fuel-cell technologies. Nature 414, 345–352 (2001).
5. Gasteiger, H. A., Kocha, S. S., Sompalli, B. & Wagner, F. T. Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs. Appl. Catal. B Environ. 56, 9–35 (2005).
6. Kinumoto, T. et al. Stability of Pt-catalyzed highly oriented pyrolytic graphite against hydrogen peroxide in acid solution. J. Electrochem. Soc. 153, A58–A63 (2006).
7. Ramaswamy, N., Hakim, N. & Mukerjeje, S. Degradation mechanism study of perfluorinated proton exchange membrane under fuel cell operating conditions. Electrochim. Acta 53, 3279–3295 (2008).
8. Seiburhan, V. A., Weidner, J. W., Haug, A. T., Motupally, S. & Pretsailo, L. V. Hydrogen peroxide formation rates in a PEMFC anode and cathode. J. Electrochem. Soc. 155, B50–B57 (2008).
9. Wu, G. et al. Performance durability of polyaniline-derived non-precious cathode catalysts. ECS Trans. 25, 1299–1311 (2009).
10. Jasinski, R. A new fuel cell cathode catalyst. Nature 201, 1212–1213 (1964).
11. Jasinski, R. Cobalt phthalocyanine as a fuel cell cathode. J. Electrochem. Soc. 112, 526 (1965).
12. Jauern, F. et al. Toward platinum group metal-free catalysts for hydrogen/oxygen exchange membrane fuel cells. Johns. Matthey Technol. Rev. 62, 231–255 (2018).
13. Leclère, M., Proietti, E., Jauern, F. & Dodelet, J.-P. Iron-based catalysts with improved oxygen reduction activity in polymer electrolyte fuel cells. Science 324, 71–74 (2009).
14. Bezerra, C. W. B. et al. A review of Fe/N/C and Co/N/C catalysts for the oxygen reduction reaction. Electrochim. Acta 53, 4937–4951 (2008).
15. Liu, W. et al. Discriminating catalytically active FeN\(_x\) species of atmosically dispersed Fe–N–C catalyst for selective oxidation of the C–H bond. J. Am. Chem. Soc. 139, 10790–10790 (2017).
16. Kramm, U. I. et al. Structure of the catalytic sites in Fe/N/C catalysts for O\(_2\)-reduction in PEM fuel cells. Phys. Chem. Chem. Phys. 14, 11673–11688 (2012).
17. Bouwkamp-Wijnoltz, A. L. et al. On active-site heterogeneity in pyrolyzed carbon-supported iron porphyrin catalysts for the electrochemical reduction of oxygen: an in situ Mössbauer study. J. Phys. Chem. B 106, 12993–13001 (2002).
18. Bron, M., Radnik, J., Fieber-Erdmann, M., Bogdanoff, P. & Fiechter, S. EXAFS, XPS and electrochemical studies on oxygen reduction catalysts obtained by heat treatment of iron phenanthroline complexes supported on high surface area carbon black. J. Electroanal. Chem. 535, 113–119 (2002).
19. Zitolo, A. et al. Identification of catalytic sites for oxygen reduction in iron and nitrogen-doped graphene materials. Nat. Mater. 14, 937–942 (2015).
20. Jauern, F., Marcotte, S., Dodelet, J.-P. & Lindbergh, G. Oxygen reduction catalysts for polymer electrolyte fuel cells from the pyrolysis of iron acetate adsorbed on various carbon supports. J. Phys. Chem. B 107, 1376–1386 (2003).
21. Dodelet, J.-P. In Electrocatalysts in Fuel Cells (ed. Shao, M.) vol. 9, 271–338 (Springer London, 2013).
70. Jia, Q. et al. Experimental observation of redox-induced Fe–N switching behavior as a determinant role for oxygen reduction activity. ACS Nano 9, 12425–12435 (2015).
71. Sa, Y. J. et al. A general approach to preferential formation of active Fe–N sites in Fe–N/C electrocatalysts for efficient oxygen reduction reaction. J. Am. Chem. Soc. 138, 15046–15056 (2016).
72. Colomban, C. et al. Synthesis and characterization of µ-nitrido, µ-carbido and µ-oxy complexes of iron and ruthenium for oxygen reduction reaction. Inorg. Chem. 24, 2215–2233 (2015).
73. Lee, H. M., Olimstead, M. M., Gross, G. G. & Balch, A. L. Cocystallization of binuclear iron(III) porphyrins with CoO: bending of μ-(Fe-O) (octaethylporphyrin) and the first structure of the iron(III) octaethylporphyrin dimer. Cryst. Growth Des. 3, 691–697 (2003).
74. Westre, T. E. et al. A multiple analysis of Fe-k-edge is → 3d pre-edge features of iron oxides. J. Am. Chem. Soc. 119, 6297–6314 (1997).
75. Palmer, S. M. et al. Preparation, structures, and physical properties of two products from the iodination of (phthalocyaninato)iron(II). Inorg. Chem. 287, 101–104 (1999).
76. Janczak, J., Kubiak, R. & Hahn, F. A neutral molecule of I2 as a bridge for the dimerization of iodine iron(III) phthalocyanine. J. Photochem. 12, 699–701 (2001).
77. Alsudairi, A. et al. Resolving the Iron Phthalocyanine Redox Transitions for ORR Catalysis in Aqueous Media. Nature Commun. 11:5283, https://doi.org/10.1038/s41467-020-18969-6 (2020).
78. He, Q. et al. Molecular catalysis of the oxygen reduction reaction by iron phthalocyanine dimer. Tetrahedron Lett. 54, 7099–7101 (2013).
79. van Veen, J. A. R. & Colijn, H. A. Oxygen reduction on transition-metal porphyrins in acid electrolyte I. Activity. Ber. Bunsenges. F. Phys. Chem. 85, 693–700 (1981).
80. van Veen, J. A. R. & Colijn, H. A. Oxygen reduction on transition-metal porphyrins in acid electrolyte II. Stability. Ber. Bunsenges. F. Phys. Chem. 85, 700–704 (1981).
81. Baranton, S., Coutanceau, C., Roux, C., Hahn, F. & Leger, J.-M. Oxygen reduction catalysis at iron phthalocyanine dispersed on high surface area carbon substrate: tolerance to methanol, stability and kinetics. J. Electroanal. Chem. 577, 223–234 (2005).
82. Luo, F. et al. Accurate evaluation of active-site density (SD) and turnover behavior as a determinant role for oxygen reduction activity. Energy Environ. Sci. 11, 3176–3182 (2018).
83. Wang, W.-J., Sengul, A., Luo, C.-F., Kao, H.-C. & Cheng, Y.-H. Facile one-step synthesis of a sulfur-bridged bis-1,10-phenanthroline macrocycle. Tetrahedron Lett. 50, 3195–3197 (2009).
84. Gao, H.-C., Zheng, R.-H. & Jiang, H. Improved synthesis of 2-dichloro-1,10-phenanthroline. J. Org. Chem. 66, 4927–4929 (2001).
85. Annibale, V. T., Batcup, R., Bai, T., Hughes, S. J. & Song, D. RuCp* complexes of ambidentate 4,5-diazafuran-4-ones: from linkage isomers to coordination-driven self-assembly. Organometallics 32, 6511–6521 (2013).
86. Zhang, J., Yang, L., Wang, Y., Li, D. & Wilkinson, D. P. Temperature and pH dependence of oxygen reduction catalyzed by iron fluorophosphoryl adenosine on a graphite electrode. J. Electrochem. Soc. 152, A2421–A2426 (2005).
87. Jackson, M. N., Pegis, M. L. & Surendranath, Y. Graphite-conjugated acids reveal a molecular framework for proton-coupled electron transfer at electrode surfaces. ACS Cent. Sci. 5, 831–841 (2019).
88. Luo, F. et al. Accurate evaluation of active-site density (SD) and turnover frequency (TOF) of PGM-free metal-nitrogen-doped carbon (MNC) electrocatalysts using CO cryo adsorption. ACS Catal. 9, 4841–4852 (2019).
89. Asset, T. & Atanassov, P. Iron-Nitrogen-Carbon Catalysts for Proton Exchange Membrane. Fuel Cells Joulle 4, 33–44 (2020).
90. Tylus, U. et al. Elucidating oxygen reduction reaction sites in pyrrolyzed metal-nitrogen coordinated non-precious-metal electrocatalyst systems. J. Phys. Chem. C 118, 8999–9008 (2014).
91. Li, J. et al. Structural and mechanistic basis for the high activity of Fe–N/C catalysts toward oxygen reduction. Energy Environ. Sci. 9, 2418–2432 (2016).
92. Zúñiga, C. et al. Elucidating the mechanism of the oxygen reduction reaction for exfoliated Fe–N/C catalysts in basic media. Electrochem. Commun. 102, 78–82 (2019).
93. Jackson, M. N. et al. Strong electronic coupling of molecular sites to graphite electrodes via pyrazine conjugation. J. Am. Chem. Soc. 140, 1004–1010 (2018).
94. Fitzgerald, J. P., Hagerty, B. S., Reginold, A. L., May, L. & Brewer, G. A. Iron octaethyltetraazaporphyrins: synthesis, characterization, coordination chemistry, and comparisons to related iron porphyrins and phthalocyanines. Inorg. Chem. 31, 2066–2073 (1992).
95. Kramm, U. L., Lefèvre, M., Larouche, N., Schmeiser, D. & Dodelet, J.-P. Correlations between mass activity and physicochemical properties of Fe/N/C catalysts for the ORR in PEM fuel cell via 2FeMossbauer spectroscopy and other techniques. J. Am. Chem. Soc. 136, 978–985 (2014).
96. Chen, Y., Matanovic, I., Weiler, E., Atanassov, P. & Artysyukova, K. Mechanism of oxygen reduction reaction on transition metal-nitrogen–carbon catalysis: establishing the role of nitrogen-containing active sites. ACS Appl. Energy Mater. 1, 5948–5953 (2018).
97. Zagal, J. H. & Koper, M. T. M. Reactivity descriptors for the activity of molecular MN4 catalysts for the oxygen reduction reaction. Angew. Chem. Int. Ed. 55, 14510–14512 (2016).
98. Zagal, J. H. et al. A Possible Interpretation for the high catalytic activity of heat-treated non-precious metal Ni/C catalysts for O2 reduction in terms of their formal potentials. Electrochem. Solid-State Lett. 15, 890 (2012).
99. Bonakdarpour, A. et al. Impact of Loading in RRDE Experiments on Fe–N–C Catalysts: Two Experiments to Sour-Electron Oxygen Reduction? Electrochem. Solid-State Lett. 11, B105 (2008).
100. Muthukrishnan, A., Nabae, Y., Okajima, T. & Ohsaka, T. Kinetic approach to investigate the mechanistic pathways of oxygen reduction reaction on Fe-containing N-doped carbon catalysts. ACS Catal. 5, 5194–5202 (2015).
101. Ragby, M., Karp, S., Pegis, M., Deloisy, D. J. M. Medium effects are as important as catalyst design for selectivity in electrocatalytic oxygen reduction by iron–porphyrin complexes. J. Am. Chem. Soc. 137, 4296–4299 (2015).

Acknowledgements
This research was primarily supported as part of the Center for Molecular Electrocataysis, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES). The computational work was supported by a seed grant from the MIT Energy Initiative. T. M.-R. acknowledges the Defense of Defense (DoD) for a National Defense Science & Engineering Graduate Fellowship (NDSEG). Use of the Advanced Photon Source is supported by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. MRCAT operations are supported by the Department of Energy and the MRCAT member institutions. XPS investigations were performed at the Center for
Nanoscale Systems (CNS), a member of the National Nanotechnology Coordinated Infrastructure Network (NNCI), which is supported by the National Science Foundation under NSF award no. 1541959. CNS is a part of Harvard University. Y.S. acknowledges the Sloan Foundation, Research Corporation for Science Advancement (Cottrell Scholar), and the Canadian Institute for Advanced Research (CIFAR Azrieli Global Scholar).

Author contributions
Y.S. and T.M.-R. conceived of the research. T.M.-R. synthesized all compounds and catalysts, collected XPS and electrochemical data and analysed spectroscopic and electrochemical results. N.J.L. and J.T.M. collected and analysed the XAS data. A.T.W. and K.J.A. collected and analysed the $^{57}$Fe Mössbauer spectra. M.L.P. collected electrochemical data. N.D.R. and T.V.V. performed computations. Y.S. assisted with experimental design and data analysis. T.M.-R. and Y.S. wrote the manuscript with input from all authors.

Competing interests
The authors declare the following competing financial interest(s): T.M.-R. and Y.S. are inventors on patent application 62/818,284, submitted by the Massachusetts Institute of Technology, that covers the hexaazaamacrocycle iron complex and related catalyst ink described in this work.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-18969-6.

Correspondence and requests for materials should be addressed to Y.S.

Peer review information Nature Communications thanks the anonymous reviewers for their contribution to the peer review of this work.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2020