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Introduction

Nitrite (NO_2^-) is a source for physiological production of nitric oxide (NO), which is an important bioregulatory signalling molecule.¹ NO has multiple functions as a vasodilator, neurotransmitter, and has important roles in mammalian immune responses.^{1,2} In these biological contexts, an array of Fe- and Cu-based metalloenzymes (e.g. cytochrome *cd1*- or cytochrome *c* nitrite reductases, *cd1-NiR/cc-NiR*, and *Cu-NiR*) catalyze the reduction of NO_2^- to NO or to NH_3 (*ccNiR*).³ Mutagenesis and computational studies implicate a critical role of specific hydrogen-bonding (H-bonding) amino acids close to the active sites of these enzymes (*i.e.*, in the secondary sphere) for enzymatic function.⁴ Removal of these H-bonding residues in *cd1*- or *cc-NiR* inhibits catalytic activity, affording up to a 99% decrease in catalytic rates, highlighting their roles to both enable and accelerate enzymatic NO_2^- reduction.⁵ Although the dependence on H-bonds for overall function is established, the molecular-level details of these interactions are challenging to clarify because removal induces larger structural changes, obfuscating their role(s) on individual reaction steps.^{4a}

Inorganic model complexes can provide insight into the effects of secondary sphere H-bonds,⁶ and by extension, the mechanisms of enzymatic NO_2^- reduction. Complexes that do not contain H-bond donors often require the addition of an exogenous Brønsted acid and/or (electro)chemical reducing

Rapid nitrite reduction enabled by secondary sphere hydrogen bonds within non-heme iron complexes

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A non-heme iron(II) complex bearing a ligand with secondary sphere hydrogen bond (H-bond) donors, (tris(6-phenylaminopyridylmethyl)amine, TPA^{NHPh}, rapidly reduces nitrite (NO_2^-) to nitric oxide (NO) in the absence of exogenous additives, affording a $\text{Fe}(\text{III})_2(\mu\text{-O})_2$ diamond core. An electronically analogous complex containing a ligand without H-bonds (tris(6-methylpyridylmethylamine), TPA^{Me}, also reduces NO_2^- to NO and forms an $\text{Fe}(\text{III})_2(\mu\text{-O})_2$ core, but is four orders of magnitude slower, highlighting the impact of H-bonds to promote NO_2^- reduction. We compare the structural and spectroscopic differences of the two $\text{Fe}(\text{III})_2(\mu\text{-O})_2$ complexes and show that H-bonding interactions weaken the Fe–O bonds, perturb the electronic structure of the Fe_2O_2 cores, and thereby engender distinct reductive stability profiles.

equivalents to promote NO release.⁷ In contrast, systems containing secondary sphere H-bond donors can induce spontaneous NO_2^- reduction without exogenous acids.⁸ Seminal work by the Fout group reported facile NO_2^- reduction mediated by Fe in a tripodal azafulvine-imine ligand scaffold, producing NO and a monomeric $\text{Fe}(\text{III})-\text{O}(\text{H})$, a result that was attributed to the

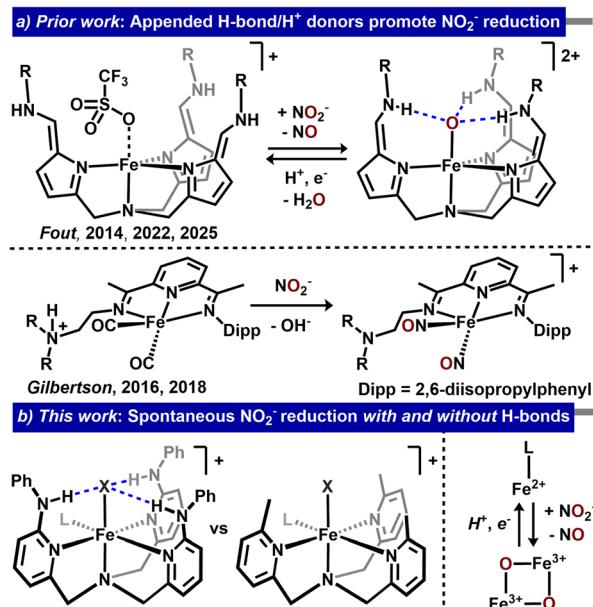


Fig. 1 (a) Previously reported Fe-based systems with secondary sphere H⁺/H-bond donors that spontaneously reduce NO_2^- ,^{8b-d,9,10} (b) this work.

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pendent-imino groups acting as H-bond donors (Fig. 1a).^{8b-d,9} Related reports from the Gilbertson group highlighted Fe-pyridinediimine complexes with tethered amines that reduced NO_2^- to afford an $\{\text{Fe}(\text{NO})_2\}$ ^{9,10} and the Hung group reported an N-confused porphyrin that similarly reduced NO_2^- to form an $\{\text{Fe}(\text{NO})\}$ ^{6/7,11}

While these prior studies demonstrated synthetic examples of H-bond promoted NO_2^- reduction, direct comparisons between ligands that either contain or omit H-bonds are notably absent. Modification of the secondary sphere of a complex can impact its primary coordination sphere *via* perturbations to ligand field environments, redox potentials, or spin states.^{5a,12} These competing effects present challenges when assessing the role(s) of H-bonds during NO_2^- reduction. Our group has attempted to decouple these parameters by comparing reaction outcomes with electronically similar ligands that differ in their secondary sphere,¹³ and we previously showed that a scaffold containing aniline groups as H-bond donors, (tris(6-phenylaminopyridylmethyl)amine, TPA^{NHPh}), promoted capture/activation of O_2 (with Fe, Cu, and Zn)^{13b,f,g} in addition to tandem ClO_4^- reduction/C–H oxygenation (with Fe).^{13a,c} We also reported a Cu(i) complex with a related ligand containing appended OH groups, tris(6-hydroxypyridylmethyl)amine $\text{TPA}^{\text{OH}}\text{Cu}(\text{i})$, which reduced NO_2^- to NO, an example of ligand-promoted H^+/e^- transfer.¹⁴ In this report, we expand these efforts to Fe-mediated NO_2^- reduction.

Results and discussion

Introduction of excess (*ca.* 10 equiv.) $[\text{Bu}_4\text{N}][\text{NO}_2]$ to an MeCN solution of $\text{TPA}^{\text{NHPh}}\text{Fe}(\text{II})$ bis(bis-trifluoromethylsulfonylazanide), ($\text{TPA}^{\text{NHPh}}\text{Fe}(\text{NTf}_2)_2$, **I-NTf₂**, Fig. 2a), under ambient conditions afforded a two-step reaction sequence: a rapid color change from colorless to yellow (seconds), followed by a gradual transition to reddish-brown (hours). Removal of MeCN *in vacuo* followed by precipitation from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ provided a single product, as assessed by ^1H -NMR spectroscopy. A solution-phase IR spectrum of the product contained no Fe–NO stretches between 1600–1850 cm^{-1} , but did exhibit broadened and bathochromically shifted N–H stretches ($\nu_{\text{NH}} = 3232$ and 3188 cm^{-1}) relative to **I-NTf₂** ($\nu_{\text{NH}} = 3361$ and 3278 cm^{-1}), consistent with strengthened H-bond interactions.¹⁵ To examine whether NO was released during this reaction, we allowed **I-NTf₂** to react with excess $[\text{Bu}_4\text{N}][\text{NO}_2]$ in the presence of COTPP (TPP = tetraphenyl porphyrin), which provided quantitative yield of CoTPP(NO) after 5 h.¹⁶ These data are consistent with spontaneous NO_2^- reduction to NO by **I-NTf₂**, potentially with concomitant formation of an Fe–O unit, as we did not observe Fe–NO bond formation.

To determine the molecular composition of the product, we performed a single-crystal X-ray diffraction (XRD) experiment on crystals grown from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Rather than a monomeric Fe–O, the refined structure revealed a $[\text{Fe}(\text{III})_2(\mu\text{-O})_2]^{2+}$ diamond core (**II**, Fig. 2c) enveloped by moderate strength H-bonding interactions (average $\text{O}_1\text{-N}_3$ distance of $2.9 \pm 0.2 \text{ \AA}$).¹⁷ This Fe_2O_2 structural motif is reminiscent of higher valent intermediates within non-heme di-iron enzymes (*e.g.* soluble

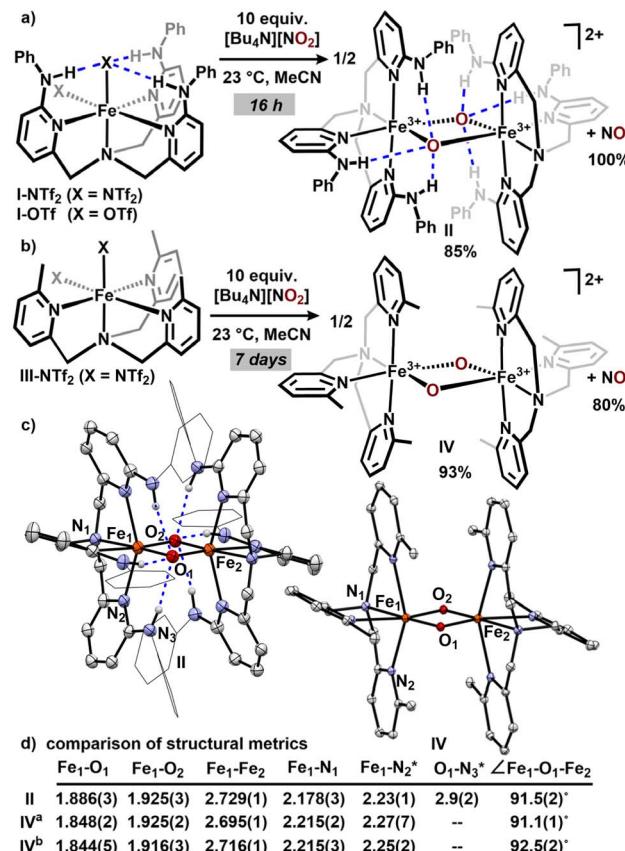


Fig. 2 (a) Reaction of $\text{TPA}^{\text{NHPh}}\text{Fe}(\text{x})_2$ ($\text{x} = \text{OTf}^-$ or NTf_2^- ; **I-OTf** or **I-NTf₂**) with NO_2^- to form $\text{NO}(\text{g})$ and $\text{TPA}^{\text{NHPh}}_2\text{Fe}(\text{III})_2(\mu\text{-O})_2^{2+}$ (**II**). (b) Reaction of $\text{TPA}^{\text{Me}}\text{Fe}(\text{NTf}_2)_2$ (**III-NTf₁**) with NO_2^- to form $\text{TPA}^{\text{Me}}_2\text{Fe}(\text{III})_2(\mu\text{-O})_2^{2+}$ (**IV**) and $\text{NO}(\text{g})$, (c) molecular structures of **II** and **IV** (NO_2^- -derived); 50% probability ellipsoids, short H-bond contacts highlighted in blue, phenyl groups are wireframed, H-atoms not involved in H-bonds, and outer sphere anions omitted for clarity (d). Bond metrics of **II**, **IV^a** and **IV^b** (a: this work, b: ref. 19g, *denotes an average of 3 bond distances).

methane monooxygenase (*sMMO-Q*) in the $\text{Fe}(\text{IV})_2$ state and ribonucleotide reductase (*RNR-X*) in the $\text{Fe}(\text{III})\text{Fe}(\text{IV})$ state)¹⁸ but is comparatively rare in synthetic systems.¹⁹ Que and coworkers reported the first isolated $\text{Fe}(\text{III})_2(\mu\text{-O}_2)$ core, supported by two tris(6-methylpyridylmethyl)amine ligands, ($\text{TPA}^{\text{Me}}_2\text{Fe}(\text{III})_2(\mu\text{-O})_2^{2+}$ **IV**), which was prepared *via* more standard oxygenation reagents (tBuOOH and NEt_3).^{19g} Another related example, reported by Masuda, is a TPA^{NH_2} analogue that formed an H-bonded $\text{Fe}(\text{III})_2(\mu\text{-O})_2$ species from O_2 .^{19c} We found that **IV** could also be prepared directly from $[\text{Bu}_4\text{N}][\text{NO}_2]$, albeit over a longer time frame (1 week, Fig. 2b). Importantly, TPA^{Me} provides an analogous primary sphere environment as TPA^{NHPh} , but does not contain pendent H-bond donors.^{13b} Thus, we propose that differences in the chemical properties of **II** and **IV** can be attributed to the effects of secondary sphere H-bonds.

The structural metrics in **II** are similar to those in **IV**, with a few notable exceptions (Fig. 2d).²⁰ The Fe_2O_2 diamond core in **II** displays two distinct Fe–O bonds ($\text{Fe}_1\text{-O}_1: 1.886(3) \text{ \AA}$, and $\text{Fe}_1\text{-O}_2: 1.925(3) \text{ \AA}$)



O_2 : 1.925(3) Å, an Fe_1 – Fe_2 separation of 2.729(1) Å, and an Fe_1 – O_1 – Fe_2 angle of 91.5(2)°. In comparison, **IV** has a 0.038(4) Å shorter Fe_1 – O_1 bond (1.848(2) Å) and a 0.034(2) Å shorter Fe – Fe distance (2.695(1) Å), but the other Fe_2O_2 core metrical parameters are similar (Fe_1 – O_2 : 1.925(2) Å, and $\angle Fe_1$ – O_1 – Fe_2 : 91.1(1)°). The elongated Fe_1 – O_1 bond likely exhibits a weaker *trans*-influence, which is manifest by the contracted Fe_1 – N_1 distance of **II** (2.178(3) Å) compared to **IV** (2.215(2) Å). We attribute these structural differences to the trifurcated H-bonds surrounding each μ - O^{2-} ligand in **II**, which are proposed to reduce the basicity of oxo ligands, thereby weakening the Fe – O bonds.^{19c,21,22}

To clarify the electronic differences that are imparted by H-bonding interactions, we examined the electronic absorption spectra of **II** and **IV**. Their respective spectra are distinct: **II** exhibits a prominent shoulder band at 433 nm ($\epsilon = 2.6$ mM⁻¹ cm⁻¹) while **IV** displays a similarly intense shoulder band at 375 nm ($\epsilon = 2.0$ mM⁻¹ cm⁻¹), both assigned to LMCT transitions.^{19b} These spectral shifts suggest that H-bonding interactions alter the electronic structure of the $Fe_2(\mu\text{-O})_2$ cores, which we interrogated further by Mössbauer spectroscopy. The zero-field Mössbauer spectrum (Fig. 3, top) of **II** as a solid (at 298 K) displays a symmetric doublet with an isomer shift (δ) of 0.33 mm s⁻¹ and quadrupole splitting (ΔE_q) of 1.422 mm s⁻¹, consistent with two identical high spin $Fe(\text{III})$ centers.^{19a,23} These data are distinct from the reported Mössbauer parameters of **IV**: (symmetric, $\delta = 0.50$ mm s⁻¹; $\Delta E_q = 1.93$ mm s⁻¹). We attribute the differences in δ (lower δ for **II**) to more oxidized/Lewis acidic $Fe(\text{III})$ centers,²² and the differences in ΔE_q values to H-bond induced charge redistribution and/or

orbital rehybridization of the μ - O ligands.²⁴ These effects may also be partially responsible for the decrease in antiferromagnetic coupling in **II** ($J = -28$ cm⁻¹) relative to **IV** ($J = -54$ cm⁻¹).^{19g,25}

The differences in electronic structures of the $Fe(\text{III})_2(\mu\text{-O})_2$ cores within **II** and **IV** allude to distinct redox behaviors, which we investigated by cyclic voltammetry (CV, Fig. 3, bottom). The CV of **II** exhibited three principal features: a reversible $1e^-$ reduction at -0.78 V (vs. $Fe^{0+/+}$, assigned as a $Fe(\text{III})_2/Fe(\text{III})Fe(\text{II})$ couple), and two irreversible events at -1.2 V and $+0.92$ V, see SI. The well-behaved reduction event of **II** is in stark contrast to **IV**, where the CV was not well-defined, and instead, displayed broad features with an $E_{\text{onset}} = -0.80$ V (Fig. 3, see SI).^{28,29}

To probe differences in reductive stability, we evaluated chemical reductions of **II** and **IV**. The reaction of **II** with 1 equiv. Na^0 (as 5% Na/NaCl) in frozen THF afforded a mixture of products (as assessed by ¹H-NMR spectroscopy) but did not induce demetalation. An analogous reduction of **IV** underwent immediate demetalation, generating free ligand as the sole TPA^{Me} containing product. In contrast, introduction of milder reagents capable of delivering H^+/e^- equivalents (*i.e.* H-atom donors) provided tractable reactivity with both **II** and **IV**. Addition of 1.5 equiv. 1,2-diphenylhydrazine (DPH, $N\text{-H}_{\text{BDFF}} = 68$ kcal mol⁻¹)³⁰ to **II** (23 °C, MeCN) provided quantitative formation of $TPA^{N\text{HPh}}Fe(\text{II})(\text{OH})^+$ (**I-OH**, Fig. 4) and azobenzene after 24 h, a net $2H^+/2e^-$ reduction of **II**.³¹ In comparison, addition of 1.5 equiv. DPH to **IV** immediately (*ca.* 15 min, 23 °C) produced a new species (assigned as $TPA^{Me}Fe(\text{II})(H_2O)_x(-MeCN)_y^{2+}$, **III-H₂O**),³² with a low conversion to azobenzene (~20%). The slower reduction of **II** by DPH relative to **IV** is consistent with distinct reductive stability profiles of these $Fe(\text{III})_2(\mu\text{-O})_2$ cores as a result of secondary sphere H-bonding interactions.

The H-bond dependent differences in reaction times for reduction of **II** and **IV** noted above are opposite from

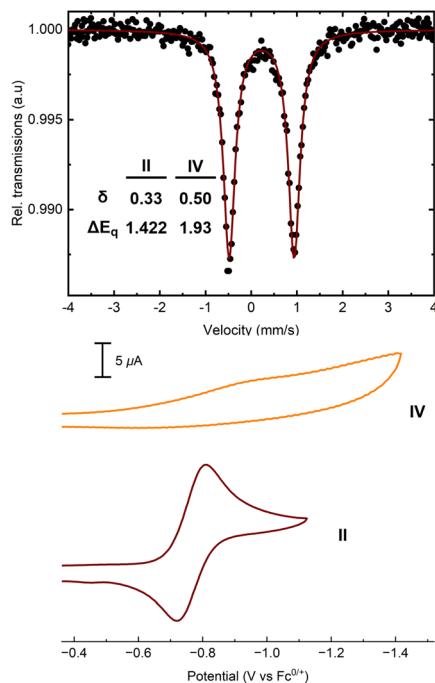


Fig. 3 Top: 298 K Mössbauer spectrum of **II** and associated spectral data for both **II** and **IV**.^{26,27} Bottom: cyclic voltammograms of **II** and **IV** (6 mM $[Fe_2(\mu\text{-O})_2]$, 0.1 M $[Bu_4N][NTf_2]$ in MeCN, 100 mV s⁻¹).

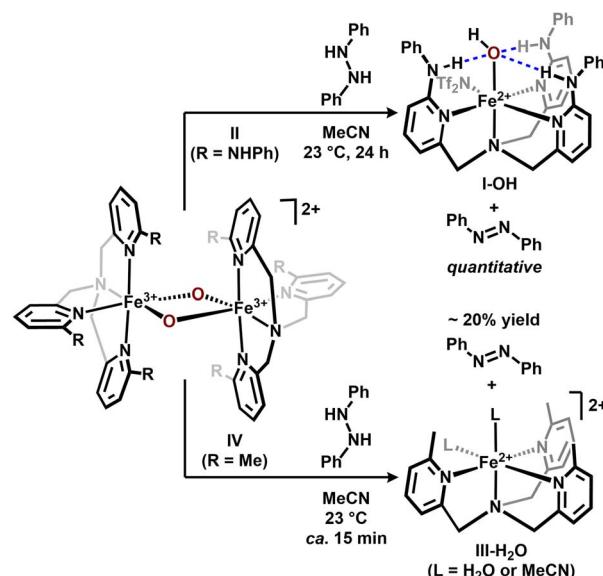


Fig. 4 Reductions of **II** and **IV** with 1,2-diphenylhydrazine (DPH).



observations in Fig. 2 (NO_2^- reactivity). To investigate the role of H-bonds during the initial NO_2^- reduction step, we examined reactions between NO_2^- and the control compound $\text{TPA}^{\text{Me}}\text{Fe}(\text{NTf}_2)_2$ (**III-NTf**₂), which maintains a similar primary sphere environment to **I-NTf**₂ but does not contain secondary sphere H-bonds (Fig. 1b).^{13b} Introduction of excess (*ca.* 10 equiv.) $[\text{Bu}_4\text{N}][\text{NO}_2]$ to a colorless solution of **III-NTf**₂ in MeCN immediately produced a yellow solution that exhibited five broad ¹H-NMR resonances (assigned as NO_2^- binding). After 7 days, the solution turned orange and developed a characteristic UV-vis shoulder feature at 470 nm, corresponding to **IV** in 93% yield (see SI), and a separate NO trapping experiment provided CoTPP(NO) in 80% yield.

Formation of NO from NO_2^- can occur through multiple distinct pathways (inner- or outer-sphere $2\text{H}^+/\text{e}^-$ reduction or through H^+ -mediated disproportionation);³³ thus, we executed additional control experiments to provide further clarity into the mechanism for NO_2^- reduction in this system. To probe a disproportionation process, we introduced an exogenous acid, 1-methyl-2-(phenylamino)pyridinium³⁴ ([HA], Fig. 5), which has a similar structure and charge, and therefore acidity/H-bond donor strength as the appended NHPH groups in **I-NTf**₂, to excess $[\text{Bu}_4\text{N}][\text{NO}_2]$ in MeCN. NO did not form in appreciable amounts after 5 h (3% yield of NO (*via* CoTPP(NO))). To examine outer-sphere reduction, we introduced ferrocene³⁵ to a mixture of 10 equiv. $[\text{Bu}_4\text{N}][\text{NO}_2]$, TPA^{NHPH} , and $\text{Zn}(\text{OTf})_2$, and again did not observe NO formation after 5 h. Collectively, these control experiments suggest that neither disproportionation nor outer-sphere reduction pathways proceed at rates comparable to those occurring during NO_2^- reduction with **I-NTf**₂ or **III-NTf**₂. Because the O-atoms from NO_2^- reduction are incorporated into the terminal Fe-containing products (**II** and **IV**), we propose that an inner-sphere reduction pathway is most likely.

Since both **I-NTf**₂ and **III-NTf**₂ enabled spontaneous reduction of NO_2^- to NO, we quantified the effects of H-bonds on their kinetic profiles (Fig. 6). Evolution of NO (monitored *via* CoTPP trapping) from a reaction between **I-NTf**₂ and 10 equiv. $[\text{Bu}_4\text{N}][\text{NO}_2]$ fit well to a first-order exponential model with $k_{\text{obs}} = (2.3 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$. In contrast, with **III-NTf**₂, we observed a slow reaction (linear fit) with $k_{\text{obs}} \approx (3) \times 10^{-8} \text{ s}^{-1}$, four orders of magnitude slower than **I-NTf**₂. To clarify the extent to which the N-O bond cleavage step is promoted by weak Brønsted acids (including the appended NHPH H-bond donors), we performed a control experiment with [HA] and **III-NTf**₂. Introduction of 3 equiv. [HA] to a mixture of **III-NTf**₂ and 10 equiv. $[\text{Bu}_4\text{N}][\text{NO}_2]$ marginally enhanced NO_2^- reduction, affording $k_{\text{obs}} = (7.0 \pm 0.9) \times 10^{-8} \text{ s}^{-1}$ and a concomitant increase in NO yield to 21%.

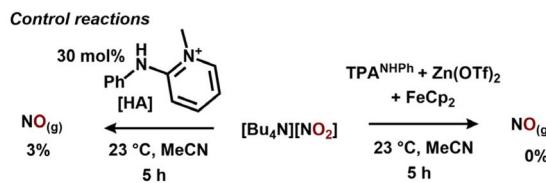


Fig. 5 Assessment of alternative pathways for NO production from NO_2^- .

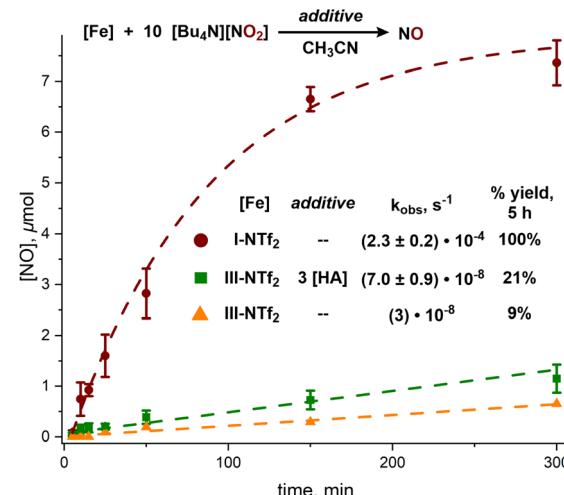


Fig. 6 Kinetic profiles of NO evolution and lines of best fit for NO_2^- reduction with **I-NTf**₂ (red circles, 1st order exponential fit), **III-NTf**₂ (orange triangles, linear fit) or **III-NTf**₂ + 3 equiv. [HA] and 10 equiv. $[\text{NO}_2^-]$ (green squares, linear fit). Error bars represent the range of yields from reactions executed in triplicate.

(5 h). These results contrast with the rapid reaction rate and quantitative NO yield (5 h) afforded by **I-NTf**₂, suggesting a proximity requirement for the weakly acidic-HNPh groups to provide large rate accelerations for NO_2^- reduction activity as an H-bond donor.

Conclusions

In conclusion, we have reported the first examples of spontaneous NO_2^- reduction to afford $\text{Fe}(\text{III})_2(\mu\text{-O})_2^{2+}$ cores, both in the presence and absence of appended H-bonds (**II** and **IV** respectively). The appended H-bonds within **I-NTf**₂ provide a four-order of magnitude rate acceleration for NO_2^- reduction, relative to **III-NTf**₂, which does not contain H-bonds. Control reactions using exogenous reagents of similar H^+/e^- strengths as **I-NTf**₂ illustrate the requirement of preorganization of H-bonding units to facilitate rapid nitrite reduction.

The H-bond interactions surrounding the resulting $\text{Fe}_2(\mu\text{-O})_2$ core of **II** imparts distinct electronic and chemical properties relative to **IV**, and as a consequence, **II** is more challenging to reduce with H-atom donors. These observations illustrate the interplay between Fe–O stabilization and subsequent H^+/e^- transfer necessary to promote a net reductive transformation, of particular relevance to nitrite reductases and reaction intermediates containing $\text{Fe}_2(\mu\text{-O})_2$ cores of dioxygenases, as those found in *sMMO-Q* or *RNR-X*. Ongoing work in our lab is focusing on the effects of H-bonds on the electronic structure and reactivity of $\text{Fe}(\text{III})_2(\mu\text{-O})_2$ cores, as well as their application toward catalytic nitrogen-oxyanion reduction.

Author contributions

The manuscript was written through the contributions of all authors. Project conceptualization: J. D. G. and N. K. S.



collection of experimental data: A. R. L., J. E. G., W. S., and J. D. G. Research supervision: N. K. S.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

CCDC 2448814 and 2448815 contain the supplementary crystallographic data for this paper.^{36a,b}

The data supporting this article have been included as part of the SI. Supplementary information: Experimental procedures and characterization of all species and reaction products. See DOI: <https://doi.org/10.1039/d5sc04153h>.

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