

Gradual Release of Strongly-Bound Nitric Oxide from $\text{Fe}_2(\text{NO})_2(\text{dobdc})$

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Supporting Information Placeholder

ABSTRACT: An iron-based metal-organic framework featuring coordinatively-unsaturated redox-active metal cation sites, $\text{Fe}_2(\text{dobdc})$ ($\text{dobdc}^{4-} = 1,4\text{-dioxido-2,5-benzenedicarboxylate}$), is shown to strongly bind nitric oxide at 298 K. Adsorption isotherms indicate an adsorption capacity greater than 16 wt %, corresponding to the adsorption of one NO molecule per iron center. Infrared, UV-vis, and Mössbauer spectroscopies, together with magnetic susceptibility data, confirm the strong binding is a result of electron transfer from the Fe^{II} sites to form $\text{Fe}^{\text{III}}\text{-NO}^-$ adducts. Consistent with these results, powder neutron diffraction experiments indicate that NO is bound to the iron centers of the framework with an Fe–NO separation of 1.77(1) Å and an Fe–N–O angle of 150.9(5)°. The nitric oxide-containing material, $\text{Fe}_2(\text{NO})_2(\text{dobdc})$, steadily releases bound NO under humid conditions over the course of more than 10 days, making it a much better candidate than other porous materials for certain biomedical applications.

Metal-organic frameworks, which have received a great deal of attention for gas storage and molecular separations,¹ have also recently shown promise for applications in the biomedicine, typically for drug storage and delivery.² Although a number of structures have been synthesized from biologically active ligands,³ bioactive molecules can also be incorporated into a metal-organic framework post-synthetically.⁴ An important example of this is the adsorption and release of nitric oxide by frameworks featuring coordinatively-unsaturated metal centers. The first investigation involved the widely studied metal-organic framework $\text{Cu}_3(\text{btc})_2$ ($\text{btc}^{3-} =$

1,3,5-benzenetricarboxylate, HKUST-1).^{5,6} This compound adsorbs nearly 4.0 mmol/g of NO, a significant improvement over zeolites, which can adsorb NO with maximum capacities of 1 mmol/g under similar conditions.⁷ Upon exposing HKUST-1 to humid air, a slow release of a fraction of the coordinated NO occurs over the course of an hour. Although the amount released is limited to just $\sim 2 \mu\text{mol/g}$, it proved sufficient to inhibit platelet aggregation in biological experiments. In addition to antithrombotic applications, porous materials that can store and deliver the critical biological signaling molecule NO may be useful for antibacterial and wound healing applications.⁸

In order to improve upon the NO release properties of HKUST-1, storage and release by $\text{Ni}_2(\text{dobdc})$ and $\text{Co}_2(\text{dobdc})$ were subsequently studied.^{9,10} These materials feature exceptionally high densities of coordinatively-unsaturated metal cations and are unable to form the $\text{M}^{\text{I}}\text{-NO}^+$ adducts likely responsible for the poor NO release displayed by HKUST-1. Indeed, the frameworks adsorbed close to 7 mmol/g NO at room temperature and released the entire quantity within 15 h of exposure to humid air. These frameworks, however, suffer from biocompatibility issues, as they are based on cobalt or nickel. The NO storage and release properties of a family of biocompatible MIL-88(Fe) based metal-organic frameworks were recently reported.¹¹ However, these materials adsorb and release < 0.35 mmol of NO per gram, significantly less than the $\text{M}_2(\text{dobdc})$ frameworks.

One of the more recently discovered members of the $\text{M}_2(\text{dobdc})$ series, $\text{Fe}_2(\text{dobdc})$,¹² combines the advantages of both systems, exhibiting the high density of accessible sites found in all $\text{M}_2(\text{dobdc})$ compounds and

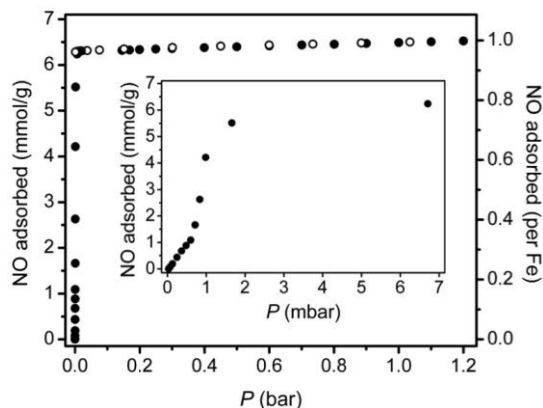


Figure 1. Adsorption of NO in $\text{Fe}_2(\text{dobdc})$ at 25 °C; closed and open symbols represent adsorption and desorption, respectively. Saturation is nearly achieved by 7 mbar (inset).

the biocompatibility of MIL-88(Fe). Moreover, it has been demonstrated that, unlike other members of the $\text{M}_2(\text{dobdc})$ family, $\text{Fe}_2(\text{dobdc})$ displays strong, selective interactions with O_2 based on the accessible redox nature of the Fe^{II} centers in the material. Given these promising attributes, we sought to investigate NO storage and release in $\text{Fe}_2(\text{dobdc})$.

The NO adsorption isotherm at 298 K, shown in Figure 1, offers an initial indication that $\text{Fe}_2(\text{dobdc})$ may be of utility for NO storage and release. Under these conditions the isotherm is extraordinarily steep, approaching saturation near 0.007 bar. At this very low pressure, the adsorption corresponds to 0.95 NO molecules per iron site and reaches 1.00 at 1.2 bar. In contrast, the adsorption of NO in $\text{Co}_2(\text{dobdc})$ and $\text{Ni}_2(\text{dobdc})$ reaches one molecule per accessible metal site at pressures greater than 0.2 bar.⁹ All three frameworks show significant hysteresis in their adsorption isotherms. While the cobalt and nickel analogues desorb approximately 1-2 mmol/g at low pressure, $\text{Fe}_2(\text{dobdc})$ retains 0.95 NO/Fe upon desorption to 0.007 mbar. Similar to the adsorption of O_2 in this framework, the bright green sample turns dark brown upon adsorption of NO, indicating oxidation of the Fe^{II} sites.¹²

Infrared spectroscopy offers a convenient means of investigating the nature of NO binding and has been widely employed to probe the interaction of NO with iron(II) centers.¹³ The N–O stretching frequency of free nitric oxide occurs at 1880 cm^{-1} , and can range from 1500 to 1900 cm^{-1} upon coordination to a transition metal. The specific energy depends on the mode of coordination, with lower frequencies usually corresponding to a significantly bent M–N–O angle. In the case of $\{\text{Fe}-\text{NO}\}^7$, these values typically fall in the range of 1700-1860 cm^{-1} .^{13b,d} Accordingly, $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ displays a single peak at low NO coverage of 1782 cm^{-1} , the small peak around 1810 cm^{-1} is an effect of background subtraction (see Figure 2). The observed red shift is significantly larger than that measured on the isostructural $\text{Ni}_2(\text{dobdc})$ (1845 cm^{-1}) system,¹⁰ and is even larger than that observed upon dosing NO on very active

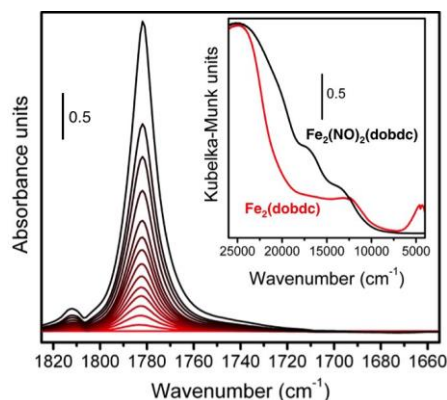


Figure 2. Infrared spectra of $\text{Fe}_2(\text{dobdc})$ in the presence of increasing NO pressure at room temperature (0-0.04 mbar interval), the IR spectrum of activated $\text{Fe}_2(\text{dobdc})$ has been subtracted. Inset: Diffuse reflectance UV–Vis–NIR spectra of $\text{Fe}_2(\text{dobdc})$ (red) and $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ (black).

surface sites such as Cr^{II} (1810 cm^{-1})^{14a} or Fe^{II} (1845-1860 cm^{-1})^{13a} on silica or Cu^{I} (1790-1810 cm^{-1})^{13b-e} in zeolites. This indicates a substantial charge transfer from the Fe^{II} centers in $\text{Fe}_2(\text{dobdc})$ to NO.

The highest coverage spectrum displayed in Figure 2 corresponds to an NO equilibrium pressure (P_{NO}) of 0.04 mbar. Further increases in P_{NO} reveal that the band at 1782 cm^{-1} is already saturated, as it does not move in frequency, reflecting the isolated nature of the Fe^{II} –NO oscillator inside the framework.^{13d} The steep increase of the Fe^{II} –NO band in the low P_{NO} region, fully supports the adsorption data reported in Figure 1. No additional bands ascribable to nitrosylic species were observed at any pressure, indicating that the mono-nitrosyl complex does not evolve into iron poly-nitrosyls, as observed in zeolites.^{13a} This confirms the 1:1 stoichiometry measured in the volumetric adsorption experiment. After NO adsorption, O_2 was introduced to the framework to probe whether any accessible iron(II) sites remain. As shown in Figure S1 of the Supporting Information, the spectrum is nearly unchanged with a minimal amount of hydroxyl formation observed. This additional experiment demonstrates that the NO coordinated to Fe prevents oxidation by O_2 and the decomposition otherwise observed upon exposing $\text{Fe}_2(\text{dobdc})$ to air.¹² Evacuation of $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ at 80 °C does not result in any appreciable NO desorption, while the N–O band disappears almost completely upon evacuation at 160 °C (orange and red spectra in Figure S1).

The formation of a stable Fe^{III} –NO complex with a bent Fe–N–O geometry is also suggested by the UV-vis absorption spectra, as shown in the inset of Figure 2. These spectra reveal the disappearance of the d-d bands around 5,000 and 12,000 cm^{-1} , which is accompanied by the appearance of three new electronic transitions at 14,000, 17,000, and 20,000 cm^{-1} that are likely related to d-d transitions with mixed p character. Extensive mixing of the metal and ligand wave functions in the molecular orbitals of the complex does not allow a distinction be-

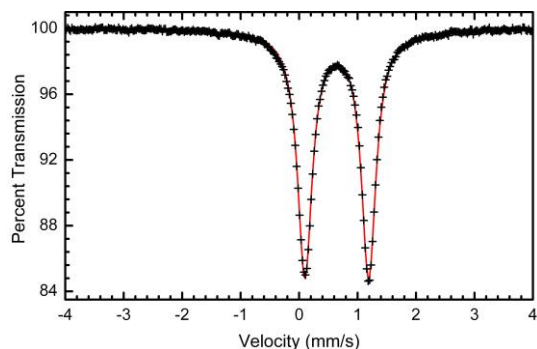


Figure 3. Mössbauer spectrum of $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ recorded at 50 K. The red doublet, attributed to high-spin Fe^{III} , exhibits an isomer shift and quadrupole splitting of 0.645(8) and 1.092(1) mm/s, respectively.

tween ligand field and charge transfer for these transitions.

Both Mössbauer spectroscopy and dc magnetic susceptibility measurements confirm the charge transfer from iron(II) to NO. At room temperature the Mössbauer spectrum of $\text{Fe}_2(\text{dobdc})$ features a simple doublet. This doublet exhibits an isomer shift and quadrupole splitting of 1.094(3) and 2.02(1) mm/s, respectively, both consistent with high-spin iron(II). The Mössbauer spectra of $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ indicates oxidized iron cations with substantially reduced isomer shift and quadrupole splitting (see Figure 3). At 250 K these values, 0.563(4) and 1.057(7) mm/s, respectively, are consistent with high-spin iron(III) in an octahedral coordination environment. Although Mössbauer studies on octahedral $\{\text{Fe}-\text{NO}\}^7$ systems are relatively rare,¹⁵ the parameters for $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ are in good agreement, for example, with the reported values of $\delta = 0.68$ mm/s and $\Delta_E = 1.03$ mm/s for deoxy hemerythrin.¹⁶ The room temperature χ_{MT} value of $3.40 \text{ cm}^3\text{K/mol}$ indicates an $S = 3/2$ system, consistent with an $S = 5/2$ Fe^{III} center antiferromagnetically coupled to an $S = 1$ NO^- moiety.

We turned to powder neutron diffraction to further investigate the binding of NO within $\text{Fe}_2(\text{dobdc})$. A Rietveld refinement was performed against data collected for a sample of $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ at 4 K. From this model a single adsorption site is apparent with coordinated nitric oxide exhibiting a refined occupancy of 0.970(5) NO molecules per Fe site. As expected, NO is N-bound with a bent geometry, featuring an Fe–N distance of 1.785(7) Å and an Fe–N–O angle of 151.4(6)° (see Figure 4). Both of these values are consistent with previously reported $\text{Fe}^{\text{III}}-\text{NO}^-$ species.¹⁷ Accordingly, the equatorial Fe–O bond distances decrease from 2.086 ± 0.076 to 2.045 ± 0.061 Å upon oxidation. As observed previously in $\text{Fe}_2(\text{OH})_2(\text{dobdc})$,¹⁸ the Fe–O bond *trans* to the open coordination site elongates substantially upon NO coordination, shifting from 2.13(2) to 2.31(1) Å. The N–O distance of 1.17(1) Å is slightly elongated from that of free NO (1.154),¹⁹ consistent with the formation of NO^- .

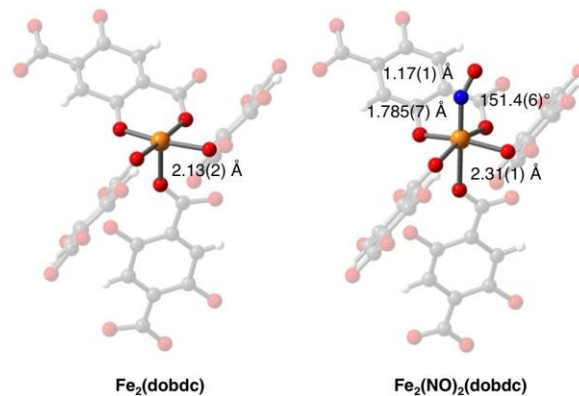


Figure 4. Structures of $\text{Fe}_2(\text{dobdc})$ and $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ as determined from Rietveld analysis of neutron powder diffraction data. Orange, blue, red, gray, and white spheres represent Fe, N, O, C, and H atoms, respectively. Values in parentheses give the estimated standard deviation in the final digit of the number.

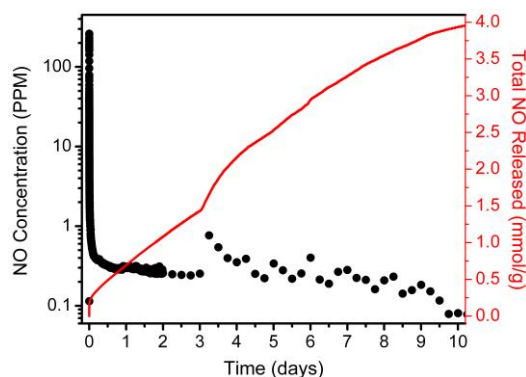


Figure 5. Release of NO by $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ upon contact with humidified N_2 at 310 K. The red curve quantifies the total NO released in mmol/g, while the black data indicates that NO is still evolving after 10 days.

To monitor NO release, a sample of $\text{Fe}_2(\text{NO})_2(\text{dobdc})$ (see the Supporting Information for full experimental procedures) was exposed to N_2 at 11% relative humidity, and the amount of NO released was quantified by chemiluminescence. As shown in Figure 5, the material initially releases a short burst of NO, which is likely attributable to a small amount of physisorbed gas. Over the duration of the experiment, the compound slowly released approximately two-thirds of the strongly bound NO. Although the total quantity of 4.0 mmol/g released was less than released by both $\text{Ni}_2(\text{dobdc})$ and $\text{Co}_2(\text{dobdc})$ (7.0 and 6.7 mmol/g, respectively),⁹ it was delivered in a much more controlled manner, still releasing biologically relevant concentrations after 10 days. As there is approximately 2.0–2.5 mmol/g of NO remaining, this material has the possibility of releasing NO for an even longer period of time. A similar release behavior was observed at room temperature (see Figure S4).

The foregoing results demonstrate that $\text{Fe}_2(\text{dobdc})$ can serve as a biocompatible platform for the slow, moisture-triggered release of NO. The strong binding of nitric oxide to the coordinatively-unsaturated, redox-active Fe^{II} sites within $\text{Fe}_2(\text{dobdc})$ is attributed to the formation of $\text{Fe}^{\text{III}}-\text{NO}^-$ adducts, as characterized spectroscopically

by various methods and structurally by powder neutron diffraction. Most significantly, as a result of the strong binding, Fe₂(NO)₂(dobdc) continues to steadily release biologically-relevant concentrations of NO over the course of at least 10 days.

ASSOCIATED CONTENT

Supporting Information. Experimental details, additional IR and Mössbauer spectra, magnetic susceptibility, powder diffraction pattern, and room temperature triggered release. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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