Metal–Oxo and Dioxygen Chemistry in Metal–Organic Frameworks: Applications in Catalysis and Gas Separations

By

Dianne Jing Xiao

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Jeffrey R. Long, Chair
Professor T. Don Tilley
Professor Alexander Katz

Summer 2016
Abstract

Metal–Oxo and Dioxygen Chemistry in Metal–Organic Frameworks: Applications in Catalysis and Gas Separations

By

Dianne Jing Xiao

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Jeffrey R. Long, Chair

The work herein describes progress towards using metal–organic frameworks as scaffolds for stabilizing metal–oxo and dioxygen species, and their application in hydrocarbon oxidation catalysis and O₂/N₂ separations. Metal–organic frameworks are a class of highly porous and functionally versatile crystalline solids consisting of inorganic cations or clusters bridged by organic linkers. They are attractive as solid supports for metal–oxo and dioxygen chemistry for many reasons, including the presence of well-defined, site-isolated metal centers with highly tunable local and outer coordination spheres.

Chapter 1 provides an introduction to the electronic structure, reactivity, and biological relevance of metal–oxo and dioxygen species, with a particular emphasis on iron and cobalt. In addition, a brief historical overview of the development of biomimetic iron–oxo, iron–dioxygen, and cobalt–dioxygen chemistry, with selected molecular and heterogenous examples, is provided. The chapter concludes with a summary of the methods currently used to install coordinatively-unsaturated redox-active metal sites into metal–organic frameworks. A perspective on the potential of metal–organic frameworks in metal–oxo and dioxygen chemistry is given.

Chapter 2 describes an initial foray into metal–organic framework-supported iron–oxo chemistry. Specifically, the nitrous oxide activation and hydrocarbon oxidation reactivity of the coordinatively-unsaturated iron(II) sites in the metal-organic frameworks Fe₂(dobdc) and Fe₀.₁Mg₁₉(dobdc) (dobdc⁻ = 2,5-dioxido-1,4-benzenedicarboxylate) is detailed. In the presence of N₂O, the latter framework is able to selectively and catalytically convert ethane to ethanol upon mild heating. Structural and spectroscopic characterization of the initial iron(II)–N₂O adduct and an iron(III)-hydroxide decay product, reactivity studies, and detailed electronic structure calculations strongly suggest that the active oxidant in this system is a high-spin, S = 2 iron(IV)–oxo. This rare electronic structure is a direct result of the weak ligand field imparted by the dobdc⁺ ligand.

In addition to primary coordination sphere properties such as a weak ligand field, longer-range pore-environment effects could also become a powerful parameter in metal–organic framework catalyst design. Chapter 3 explores this idea in the context of solution-phase cyclohexane oxidation in the biphenyl and terphenyl expanded Fe₂(dobdc) derivatives. A three-
fold enhancement of the alcohol:ketone (A:K) ratio and an order of magnitude increase in turnover number is observed by simply altering the framework pore diameter and installing nonpolar, hydrophobic functional groups near the iron center. The increase in A:K selectivity is attributed to an increased affinity of the pore walls for cyclohexane, which may help increase its local concentration near the iron site.

Chapter 4 departs from iron–oxo chemistry and oxidation catalysis, focusing instead on cobalt–dioxygen binding for O₂/N₂ separation applications. Specifically, this chapter details the reversible O₂ binding properties of Co-BTTri (H₃BTTri = 1,3,5-tri(1H-1,2,3-triazol-5-yl)benzene), a sodalite-type framework containing coordinatively-unsaturated cobalt(II). It was found that the O₂ binding affinity could be tuned by altering the local ligand field. Electronic structure calculations reveal the extent of electron transfer from cobalt to O₂ in these systems is highly dependent on the local environment, and can vary between 0.2 to 0.7 electrons.

Chapter 5 combines aspects of both Chapter 1 and 4, focusing on the development of new iron(II)-based frameworks with tunable primary coordination spheres, and the effect of ligand field on reactivity and gas adsorption properties. The synthesis and characterization of two new sodalite-type frameworks, Fe-BTTri and Fe-BTP (H₃BTP = 1,3,5-tri(1H-pyrazol-4-yl)benzene), is reported. Interesting O₂ and CO gas adsorption properties are displayed by bulk Fe-BTTri, and are briefly described in this chapter. In addition, initial N₂O/ethane oxidation studies performed on Fe-BTT suggest defect sites are responsible for the reactivity seen in this material, highlighting the inhomogeneity present even in highly crystalline metal–organic frameworks.
3.2.2. Catalytic cyclohexane oxidation procedure 62
3.2.3. Solution-phase cyclohexane adsorption studies 63
3.2.4. Gas-phase cyclohexane adsorption studies 63
3.2.5. Isotherm fitting 63
3.2.6. Isosteric heat of adsorption calculations 63
3.3. Results and discussion 64
   3.3.1. Synthesis of expanded Fe₃(dobdc) derivatives 64
   3.3.2. Role of pore diameter on cyclohexane oxidation 65
   3.3.3. Synthesis of Fe₃(dotpdc) and substituted derivatives 66
   3.3.4. Role of hydrophobic pore environment on cyclohexane oxidation 68
   3.3.5. Cyclohexane adsorption in Fe₃(dotpdc₈) frameworks 70
3.4. Conclusions and outlook 73
3.5. Acknowledgements 73
3.6. References and supplementary information 73

Chapter 4: Selective, Tunable O₂ Binding in Cobalt(II)–Triazolate/Pyrazolate Metal–Organic Frameworks 103
4.1. Introduction 103
4.2. Experimental 104
   4.2.1. Synthesis of Co-BTTri 104
   4.2.2. Single-crystal synthesis of Co-BTTri 104
   4.2.3. Single-crystal synthesis of Co-BDTr iP 104
   4.2.4. Low-pressure gas adsorption measurements 104
   4.2.5. Isotherm fitting 105
   4.2.6. Isosteric heat of adsorption calculations 105
   4.2.7. Ideal adsorbed solution theory calculations 105
   4.2.8. Single crystal X-ray diffraction 105
   4.2.9. Magnetic susceptibility 106
   4.2.10. Quantum chemical calculations 106
4.3. Results and discussion 107
   4.3.1. Synthesis of Co-BTTri 107
   4.3.2. Adsorption of O₂ and N₂ in Co-BTTri 108
   4.3.3. Structural characterization of Co-BTTri 110
   4.3.4. Spin-state characterization of Co-BTTri 112
   4.3.5. Electronic structure of Co-BTTri and Co-BTTri–O₂ 113
   4.3.6. Synthesis of Co-BDTr iP 115
   4.3.7. Adsorption of O₂ and N₂ in Co-BDTr iP 116
   4.3.8. Effect of ligand field on O₂ adducts of cobalt-azolate frameworks 119
4.4. Conclusions and outlook 120
4.5. Acknowledgements 120
4.6. References and supplementary information 121

Chapter 5: Synthesis, gas adsorption behavior, and reactivity of sodalite-type Fe(II)-based frameworks 135
5.1. Introduction 135
5.2. Experimental 135
### 5.2.1. Fe-BTTri synthesis

5.2.2. Fe-BTTri single crystal synthesis

5.2.3. Fe-BTP single crystal synthesis

5.2.4. Low-pressure gas adsorption experiments

5.2.5. Mössbauer spectroscopy

5.2.6. Reactivity studies in Fe-BTT, Fe-BTTri, and Fe-BTP

5.2.7. Synthesis of Zn-exchanged Fe-BTT (Zn/Fe-BTT)

### 5.3. Results and discussion

5.3.1. Syntheses and structures of Fe-BTT, Fe-BTTri, and Fe-BTP

5.3.2. O₂ adsorption properties of Fe-BTTri

5.3.3. Defect-site N₂O reactivity in Fe-BTT, Fe-BTTri, and Fe-BTP

### 5.4. Conclusions and outlook

### 5.5. Acknowledgements

### 5.6. References and supplementary information

#### Appendices

Appendix A.1. Synthesis of anthracene terphenyl MOF-74 linkers and frameworks

Appendix A.2. Synthesis of fluorinated terphenyl MOF-74 linkers and frameworks
List of Figures

Chapter 1: Structure, bonding, and reactivity of metal–oxo and dioxygen species

Figure 1.1 Qualitative frontier energy level diagrams of terminal metal–oxo compounds in octahedral, trigonal bipyramidal, and tetrahedral geometries 2
Figure 1.2 The active intermediates of cytochrome p450, soluble methane monooxygenase, and tau-D enzymes 2
Figure 1.3 The radical-rebound mechanism of C–H hydroxylation 3
Figure 1.4 Selected ligands utilized in synthetic heme and nonheme iron–oxo complexes 3
Figure 1.5 Two distinct approaches to achieving high-spin $S = 2$ nonheme iron(IV)–oxo species 4
Figure 1.6 Common bimolecular decomposition pathways of a) metal–superoxo and b) metal–oxo species 6
Figure 1.7 Selected examples of frameworks containing exposed, transition-metal nodes 7
Figure 1.8 Metal complexes incorporated on framework organic struts 7

Chapter 2: Oxidation of ethane to ethanol by N$_2$O in a metal–organic framework with coordinatively-unsaturated iron(II) sites

Figure 2.1 Structure of bare and N$_2$O-dosed Fe$_2$(dobdc) 15
Figure 2.2 Preparation, spectroscopic characterization, and structure of Fe$_2$(OH)$_2$(dobdc) 16
Figure 2.3 N$_2$O activation and reactivity of Fe$_2$(dobdc) in the oxidation of ethane and 1,4-cyclohexadiene 18
Figure 2.4 Structure and qualitative molecular orbital diagram of Fe$_2$(O)$_2$(dobdc) 19

Chapter 3: Pore environment effects on catalytic cyclohexane oxidation in expanded Fe$_2$(dobdc) analogues

Figure 3.1 Structures of Fe$_2$(dobdc), Fe$_2$(dopdc), Fe$_2$(dotpdc) and their corresponding ligands 65
Figure 3.2 (a) Hexagonal channels of Fe$_2$(dotpdc$^R$) frameworks, with substituted central rings and (b) Structures of the derivatized terphenyl linkers used in this work 67
Figure 3.3 Le-Bail refinements of powder X-ray diffraction patterns of (a) Fe$_2$(dotpdc), (b) Fe$_2$(dotpdc$^F$), (c) Fe$_2$(dotpdc$^{CH_3}$), and (d) Fe$_2$(dotpdc$^{Bu}$) frameworks collected at 298 K 68
Figure 3.4 Mössbauer spectra of the four Fe$_2$(dotpdc$^R$) frameworks, collected at 100 K 69
Figure 3.5 Cyclohexane adsorption isotherms for (a) Fe$_2$(dotpdc), (b) Fe$_2$(dotpdc$^F$), (c) Fe$_2$(dotpdc$^{CH_3}$), and (d) Fe$_2$(dotpdc$^{Bu}$) 71
Figure 3.6 Cyclohexane isosteric heats of adsorption ($Q_{st}$) for Fe$_2$(dotpdc) (blue) Fe$_2$(dotpdc$^F$) (red), Fe$_2$(dotpdc$^{CH_3}$) (violet), and Fe$_2$(dotpdc$^{Bu}$) (dark purple). 72
Figure 3.7 Local chemical environment around the Fe(II) centers in Fe$_2$(dotpdc) 72
and Fe₂(dotpdc³⁺).

Chapter 4: Selective, Tunable O₂ Binding in Cobalt(II)–Triazolate/Pyrazolate Metal–Organic Frameworks

Figure 4.1  Structure of Co-BTTri
Figure 4.2  Adsorption isotherms for the uptake of O₂ and N₂ in Co-BTTri at 195 K
Figure 4.3  Uptake and release of O₂ in Co-BTTri
Figure 4.4  Structural changes observed in Co-BTTri upon (a) methanol solvation, (b) desolvation, and (c) O₂ binding
Figure 4.5  Variable-temperature magnetic susceptibility data collected under an applied field of 1 T for samples of Co-BTTri solvated in DMF (blue circles) and activated Co-BTTri (red circles)
Figure 4.6  Spin density of (a) the activated [Co₄Cl(Tri)₈]¹⁻ node and (b) the [Co₄(O₂)₄Cl(Tri)₈]¹⁻ node
Figure 4.7  Ligand and local structure of Co-BDTriP before and after O₂ binding
Figure 4.8  Comparison of O₂ adsorption isotherms collected for Co-BTTri (red) and Co-BDTriP (purple) at 195 K
Figure 4.9  Comparison of O₂ and N₂ isosteric heats for Co-BTTri and Co-BDTriP
Figure 4.10  Ideal adsorbed solution theory (IAST) selectivities for Co-BTTri and Co-BDTriP calculated for a mixture of 0.21 bar O₂ and 0.79 bar N₂

Chapter 5: Synthesis, gas adsorption behavior, and reactivity of sodalite-type Fe(II)-based frameworks

Figure 5.1  Structure of sodalite-type iron(II) frameworks and their corresponding ligands
Figure 5.2  Structure and Mössbauer spectrum of Fe-BTTri
Figure 5.3  O₂ and N₂ adsorption isotherms for Fe-BTTri at 195 K
Figure 5.4  Mössbauer spectrum of O₂-dosed Fe-BTTri (100 K)
Figure 5.5  Mössbauer spectra and powder X-ray diffraction pattern of Zn/Fe-BTT before and after N₂O/ethane treatment
List of Tables

Chapter 2: Oxidation of ethane to ethanol by N₂O in a metal–organic framework with coordinatively-unsaturated iron(II) sites
Table 2.1 Calculated relative energies (kJ/mol) of the cluster model of Fe₂(O)₂(dobdc) 20

Chapter 3: Pore environment effects on catalytic cyclohexane oxidation in expanded Fe₂(dobdc) analogues
Table 3.1 Summary of cyclohexane oxidation results in Fe₂(dobdc), Fe₂(dobpdc), and Fe₂(dotpdc) 66
Table 3.2 Surface areas, pore sizes, and unit cells of Fe₂(dotpdc) and substituted derivatives 67
Table 3.3 Summary of cyclohexane oxidation results in Fe₂(dotpdc⁸) 69

Chapter 4: Selective, Tunable O₂ Binding in Cobalt(II)–Triazolate/Pyrazolate Metal–Organic Frameworks
Table 4.1 Key bond distances (in Å), charge transfer (in electrons) and O₂ enthalpies of adsorption (in kJ/mol, M06/def2-TZVP level of theory) for the three cluster models of the Co-BTT, Co-BTTri, and Co-BTP metal-organic frameworks. 120

Chapter 5: Synthesis, gas adsorption behavior, and reactivity of sodalite-type Fe(II)-based frameworks
Table 5.1 Bond metrics of solvated Fe-BTT, Fe-BTTri, and Fe-BTP. 139
Table 5.2 Mössbauer parameters for O₂-dosed Fe-BTTri (100 K). 141
Table 5.3 Mössbauer parameters of Zn/Fe-BTT before and after N₂O/ethane treatment. 142
Acknowledgements

First, I’d like to thank my undergraduate adviser, Prof. Ted Betley, and my postdoctoral mentor at the time, (now Prof.) Alison Fout. Ted’s passion for fundamental science, his sense of humor about the everyday trials of research (“Yield is just a number”), and his patience with and belief in his students are all qualities I admire and am inspired by. On my last day in the group, Alison gave me a farewell package full of school supplies, so that I would be extra prepared for my first day at Berkeley. But pens and Post-Its aren’t the only things Alison and Ted gave me that helped me get to, and through, graduate school, and for that I am really grateful.

Not many people are able to have even one mentor as good as the two I found in undergrad, and so I’m incredibly lucky to have gone straight from one supportive group to another. My graduate advisor, Prof. Jeff Long, was exceptional in a different but equally important way. Jeff truly trusts his students, giving us the time and resources to shape our own research projects. Because of this freedom and Jeff’s patience, in the past five years I have really grown as a scientist. I am also particularly grateful that Jeff, though busy, spends a lot of time cultivating a close lab environment. By celebrating every major achievement in our graduate careers with us—from qualifying exam parties, to post-paper champagne and farewell barbecues—he shows that he truly appreciates the effort his students and postdocs put into their work, and in this respect he is one of the most generous people I know.

Next I’d like to thank my many collaborators through the years, particularly Prof. Laura Gagliardi, Prof. Donald Truhlar, as well as their graduate students and post-docs, including: Konstantinos Vogiatzis, Nora Planas, and Pragya Verma.

There are so many people that I’m thankful for meeting in grad school, I’m not sure I can list them all! But I’ll start with Eric, Joe, and Jarad first, because they had the bad luck of training me in my first year. Without a doubt, Eric was a huge contributor to the inclusive lab atmosphere I found upon joining the Long group. He is a great chemist, but also a great leader and listener. Often the first in lab (in competition with Jarad), he set an example for everyone with his incredible work ethic. At the same time, he also took the lead in organizing fun activities like trips to the beach and Golden Gate Fields, and Thirsty Thursdays. Amazingly, his wife, Lynn, is equally cool, and I am so glad I got to meet and befriend them both.

Joe was in charge of the glovebox when I joined, and his stern demeanor had me thoroughly terrified. However, though he seemed unapproachable at the start (he always mock-escalated acts of aggression, particularly when directed at Eric or Jarad, and no one would ever risk stealing his glassware or messing up the glovebox), Joe is actually one of the most caring and supportive people I know, as well as the most insightful and creative.

Jarad ended up mentoring me a lot in my first and second year, after Eric gradually got fed up with my questions. I think one of the first questions I asked him was about how to move gas cylinders, which marked the start of a great friendship where I probably got (and continue to get) a lot more advice and help than I ever gave in return. In the right mood, Jarad was also a great source of excellent gossip, which was obviously another big component of our friendship. I also
must thank the candy stash he kept at his desk, which, along with Jarad’s support and encouragement, helped me survive grad school.

My year-mates Miguel and Mike have both set examples for me with their hard work and dedication to science. In my first year, it was not unusual for either of them to stay in lab until the early morning hours. While I’ve seen a lot of drunk graduate students in my time at Berkeley, Mike’s drunk personality is hands-down the best (and most entertaining)—I’ll definitely miss both Mike and his alter-ego a lot. Miguel holds extremely high standards for the impact and quality of his chemistry, and I respect his opinion a lot for those reasons. He also appears to have an infinite store of patience (I’m sure it will run out at some point), and was always available to talk to me about research, often providing really helpful insights. After Eric graduated, Miguel took it upon himself to organize monthly group activities. These outings, combined with his infamous Strawberry Danger cocktails and penchant for practical jokes, were crucial to maintaining the mental health of the group.

In addition to Miguel, the other graduate student members of the catalysis subgroup, David Zee and Jordan, have also left a big impact on me. David, like Miguel, is an incredibly rigorous chemist; his careful and logical thinking has helped me as well as many others in the group so much. He was also one of the first people I went to for life advice, mostly because he usually has strong, but very well-thought-out, opinions on everything. Jordan I admire for her tolerance and warmth, dedication to teaching, and determination. I think we all deserve drinks for making it this far.

I’d like to thank all the senior graduate students I’ve worked with through the years, including: Zoey, for being endlessly optimistic and considerate; Brian, for being so creative and interesting; Tom, for his dedication to the environment; Katie for being so passionate about chemistry and life, and her entertaining frankness; Xiaowen for being good-humored about getting teased; and Dana for her poise and friendliness.

Each year brings along new graduate students, who have each contributed positively to the group. In 2012, Doug, Phil, Matt, and Lucy came onto the scene, forming an interesting intra-year dynamic that was pretty fun to witness. Doug was the ironic hipster with strong opinions on movies and music; Phil came in with an impressive knowledge of chemistry and 80’s pop culture, as well as a steady supply of cookies sent from his loving relatives; and Matt, who I initially thought was somewhat loud and abrasive, turned out to be surprisingly calm in serious situations. Lucy, as the second loudest but most responsible, gets a gold medal for trying to keep everyone in line. All of them have helped me a lot through the years with my chemistry.

Next came Julia, Mercedes, Rodi, and Jon. Julia and I have a special bond as fellow glovebox users, O_2/N_2 separators, and (for a brief time) APS roommates. I always appreciate her snark, delivered so earnestly, even when it is directed at me. Mercedes and I became very good friends through Doug and the early lunch club. I admire her dedication to social causes and assertive presentation style. I am always impressed by Rodi’s surprisingly in-depth knowledge of random things. Jon is a crazy efficient, and will no doubt have a very successful career.
In 2014, the Long group recruited Rebecca and Kristen, two extremely competent researchers who coincidentally happened to be female, and all the women in the group cheered and secretly started planning our takeover. Then came the following year, where we took seven guys plus Rebecca K. Joking aside, these eight first years (in alphabetical order: Ari, Colin, Daniel, Henry, Jesse, Job, Mike Z., and Rebecca K.) are great additions to the group. I’d like to specifically call out Colin, who took my mentoring as a summer undergrad with admirable stoicism and is a great friend to talk to; Job, who we always knew was smart and responsible but also turned out to be surprisingly hilarious; Ari, who is always ready to sacrifice himself upon the altar of comic relief; and Mike Z., whose impressive work ethic and dependability make him almost like a mature adult (we don’t get many of these in the Long group).

The Long group has also had some amazing postdocs over the years that I’m very grateful to have met. JVH started in the group around the same time as me, and we were hood- and desk-neighbors, as well as members of the awesome early morning breakfast/coffee crew. I respect a lot of things about him, including: his originality, artistic and design abilities, resilience, and general niceness to other human beings. Michael Nippe, who was probably one of the most talented synthetic inorganic chemists in our lab, scared me a lot initially but now thinks I’m scarier, which I take as a huge compliment. Keith I remember for his singing of Mariah Carey and Gloria Estefan, and his positive, friendly, and completely selfless personality that made life in lab so awesome and will make him a great mentor to his students. Phill is a relatively recent addition to the lab, and took over from JVH as the resident post-doc of Lewis 210. He has already become a great friend, adviser-in-organic-chemistry, and gossip-buddy.

We’ve also had an impressive run of undergraduate students, many of whom have contributed just as much as graduate students. In particular, I overlapped most with Gygi and Raymond, who both worked so hard and had so much enthusiasm, and will do great things for sure.

My sister Daphne is so awesome, and I’m so lucky to have her as my best friend. I still send her paper drafts and text her when I’m particularly grumpy or struggling, and can always rely on her to give me not just her support, but also her honest assessment. I am so proud of her, and she inspires me to be better all the time. My mom, who has a crazy drive and work ethic, has shown me it is possible to have both a successful career and also a family (though she really needs to give herself more vacations). My dad has taught me so many things, from volleyball to cooking to chemistry. They have never lectured me about my performance in anything, as long as I tried my very best, and both of them have given me so much love and support.

Finally, I’d like to thank Doug, without whom grad school would have been a lot darker and grumpier sort of a place. He was not only a great labmate and excellent collaborator, but also a source of advice, constant encouragement, and occasional goofiness. I’m so lucky that after every day in lab—especially when it was frustrating, discouraging, or tiring, so basically always—I have someone to come home to who will hear me vent, help make dinner, and watch Netflix comedies with me. I’m so glad we’ve been able to explore the Bay area together, and create so many great memories in and outside of lab.

To the people mentioned above as well as the many friends that aren’t listed here, thanks so much for making graduate school some of the best and most rewarding years of my life thus far!
Chapter 1: Structure, bonding, and reactivity of metal–oxo and dioxygen species

1.1. Introduction

Metal–oxo and dioxygen compounds, notably of manganese, iron, and copper, have been widely studied for their biological relevance. Molecular iron, cobalt, and copper–O₂ complexes have been synthesized in order to understand the structure, bonding, and spectroscopic properties of biological dioxygen carriers such as hemoglobin, hemerythrin, and hemocyanin. Similarly, model iron and dinuclear copper–oxo complexes have shed light on the mechanisms of cytochrome p450, methane monooxygenase, and other enzymes that facilitate the transfer of oxygen atoms from O₂ to organic substrates.

Manganese–oxo and dioxygen species have also been targeted as models of the Mn₄Ca cluster of photosystem II, the site of water oxidation.

The significance of the fundamental insights gleaned from these and other studies cannot be overstated. For example, a unified electronic structure model of metal–oxo species, initially developed in the context of the vanadyl ion [VO(H₂O)₅]²⁺, has allowed structural, spectroscopic, and reactivity trends displayed by this entire class of compounds to be rationalized and predicted.

Uncovering the nature of the iron–O₂ bond in hemoglobin is posited by some as the beginning of bioinorganic chemistry, and has spurred the development of synthetic dioxygen carriers relevant to biomedical and industrial air separation applications. Mechanistic studies on O–O bond formation in model metal complexes have guided recent developments in water oxidation catalysis for artificial photosynthesis. Finally, illumination of biological mechanisms of dioxygen activation, metal–oxo formation, and C–H functionalization has inspired new concepts for the selective aerobic oxidation of hydrocarbons.

1.2. Electronic structure of mononuclear metal–oxo species

A general description of the electronic structure of octahedral metal–oxo complexes was first outlined in 1962 by Ballhausen and Gray, and later extended to terminal oxo species of trigonal bipyramidal and tetrahedral geometry. As shown in Figure 1.1, the O²⁻ ligand is capable of forming one σ and two π bonds with the metal center, leading to metal-based dₓ² and dₓz/dᵧz orbitals with σ* and π* character, respectively. A maximum M–O bond order of three is thus achievable in octahedral d⁰ to d² compounds, explaining the ubiquity and relative inertness of such complexes. Higher d-electron counts lead to population of π*ₘₒ orbitals, destabilizing the M–O bond and increasing its reactivity. For example, iron(IV)–oxo complexes (d⁴, formal bond order of 2) are typically competent for both olefin epoxidation and C–H functionalization reactions. The phrase “oxo-wall” has been coined to explain the lack of structurally characterized terminal metal–oxo species (in a tetragonal ligand field) beyond group 8, though the existence of cobalt and copper–oxyl species has been proposed and, in some cases, supported by spectroscopic and mechanistic studies.
1.3. Biological and synthetic iron–oxo chemistry

1.3.1. Iron–oxo chemistry in biology. High-valent iron–oxo intermediates are implicated in a variety of enzymes capable of selective oxidation reactions. One such example is cytochrome p450, which features prominently in biosynthetic and metabolic pathways and carries out C–H hydroxylation, olefin epoxidation, and heteroatom oxidation, among other transformations. The common catalytic intermediate in this diverse reaction portfolio is an iron(IV)–oxo porphyrin π-cation radical species (see Figure 1.2). Similarly, mononuclear, nonheme iron(IV)–oxo intermediates such as those found in TauD are also capable of C–H hydroxylation. Particularly intriguing is the active site of soluble methane monooxygenase, which contains a dinuclear iron core and is capable of converting methane to methanol (see Figure 1.2).

1.3.2. C–H activation mechanism. The radical-rebound mechanism of C–H hydroxylation by cytochrome p450 and related model complexes, first outlined in the late 1970s and subsequently supported by kinetic isotope effects, scrambling experiments, and radical clock studies, is now widely accepted (see Figure 1.3). Recently, deviations from this mechanism have been observed in synthetic nonheme iron(IV)–oxo complexes, where radical dissociation has been shown to compete with the radical rebound step, leading to an iron(III)–hydroxide...
product and freely diffusing carbon-based radicals.\textsuperscript{18} In addition, experimental and theoretical calculations on alkane hydroxylation in nonheme systems suggest that the iron spin state can change over the course of the reaction (i.e., spin-state crossing from $S = 1$ to $S = 2$), a phenomenon that has been coined “two-state reactivity.”\textsuperscript{19}

![Figure 1.3](image)

**Figure 1.3.** The radical-rebound mechanism of C–H hydroxylation. Note that for heme species, the initial intermediate is an iron(IV)–oxo porphyrin radical cation; H-atom abstraction leads to an iron(IV)–hydroxide species. Deviations, such as radical dissociation rather than rebound, has been observed in several synthetic nonheme iron(IV)–oxo systems.

### 1.3.3. Molecular iron–oxo species

The field of synthetic iron–oxo chemistry was pioneered by Groves in the 1980s, who was the first to spectroscopically characterize iron(IV)–oxo porphyrin π-cation radical species and investigate their reactivity.\textsuperscript{20} Prior to this work, the face of homogenous, iron-based oxidation catalysis was Fenton chemistry, wherein simple iron(II) salts decompose $\text{H}_2\text{O}_2$ to form reactive (but unselective) hydroxyl radical intermediates. Nonheme ligand scaffolds were subsequently explored in the 1990s and onwards (see Figure 1.4), leading to the first single crystal X-ray structure of a nonheme iron(IV)–oxo complex in 2003.\textsuperscript{21} Iron–oxo complexes in oxidation states other than +4 represent a new frontier in this field. The first iron(III)–oxo (stabilized by extensive hydrogen bonds) was reported in 2000, followed by the isolation of an iron(V)–oxo complex in 2007.\textsuperscript{22,23}

![Figure 1.4](image)

**Figure 1.4.** Selected ligands utilized in synthetic heme and nonheme iron–oxo complexes, specifically (a) functionalized porphyrins, (b) tetra-amido macrocyclic ligands (TAML), and (c) tetramethylcyclam (TMC). Note that in iron-bound complexes, the porphyrin and tetra-amido ligands are fully deprotonated, with 2– and 4– charges, respectively.

While spectroscopic and theoretical studies have long attributed the reactivity of nonheme enzymatic and synthetic iron(IV)-oxo complexes to a quintet spin state,\textsuperscript{24} only a handful of mononuclear high-spin iron(IV)-oxo species have been characterized.\textsuperscript{25,26,27,28,29,30} Two approaches have been successfully used to achieve a high-spin ground state, namely the use of weak field ligands and trigonal bipyramidal geometry,\textsuperscript{31} and these are illustrated in Figure 1.5.
1.3.4. Heterogeneous iron–oxo species. Alongside the development of molecular transition metal–oxo complexes, similar chemistry was being explored in heterogeneous, zeolite-based systems. Zeolites are structurally diverse, three-dimensional aluminosilicates whose exceptional thermal and chemical stability and porosity have led to numerous industrial applications. The Si\(^{4+}\) ions in the framework can be substituted with Al\(^{3+}\), leading to overall anionic frameworks that are charge-balanced by extra-framework cations. These cations can be alkali, alkaline earth, or transition metal ions; charged transition metal complexes can also be incorporated. While transition metal cations can also be substituted directly into framework sites, the amount of substitution and their stability can be limited.

Reactive intermediates formed in certain iron and copper-exchanged zeolites have been shown to oxidize methane to methanol at low temperatures. Specifically, upon thermal pre-treatment with N\(_2\)O, Fe-ZSM-5 stoichiometrically oxidizes methane to surface-bound methoxide. Similar methane reactivity is seen in O\(_2\)-pretreated Cu-ZSM-5 at 100 °C.

A long-standing challenge is the characterization of catalytic sites in zeolites, as multiple and often ill-defined mono- and multi-nuclear transition metal species can be present, only a minority of which are active. In the case of Cu-ZSM-5, the active sites were estimated to be a mere 5% of the total copper content, hindering conclusive structural characterization by EXAFS and other methods. Despite these challenges, the presence of a signature stretch in the UV-VIS spectra, as well as EPR and Raman studies, strongly support a bis(\(\mu\)-oxo)dicopper(III) core as the site of methane oxidation. In the case of Fe-ZSM-5, the identity of the N\(_2\)O-derived iron oxidant, which has been named the “\(\alpha\)-O core,” has yet to be conclusively determined.

1.4. Biological and synthetic iron and cobalt–dioxygen chemistry

1.4.1. Iron–superoxo and peroxo chemistry in biology. Iron–superoxo (O\(_2^–\)) species are reversibly formed in biological dioxygen carriers such as hemoglobin, serve as intermediates preceding iron–oxo formation in cytochrome p450 and nonheme oxygenases, and have even been identified as active oxidants capable of electrophilic C–H activation in nonheme enzymes such as isopenicillin N synthase and myo-inositol oxygenase. In heme systems, antiferromagnetic coupling between a low-spin Fe(III) center and the superoxide radical anion
leads to an overall diamagnetic ground state. On the other hand, computational and spectroscopic studies suggest that the weaker ligand field found in nonheme enzymes results in a high-spin Fe(III) center, with antiferromagnetic coupling leading to an overall $S = 2$ ground state.\textsuperscript{37}

Like iron–superoxo compounds, iron(III)–peroxy ($O_2^2^+$) species have also been identified as active oxidants in their own right.\textsuperscript{38,39} In particular, high-spin, heme Fe(III)–peroxy species behave as nucleophilic oxidants, and are postulated to carry out aldehyde deformylation in a subset of cytochrome p450 enzymes.

1.4.2. Molecular iron–superoxo and peroxy species. Debates on the geometric structure of the $O_2$-bound heme site in hemoglobin and myoglobin were quickly laid to rest when the first single crystal X-ray structure of a synthetic heme dioxygen complex was obtained in 1974.\textsuperscript{40} This was quickly followed by structural and spectroscopic characterization of the heme protein itself, as well as related picket-fence porphyrin complexes.\textsuperscript{40,41} These studies firmly established the existence of a diamagnetic Fe(III)–superoxo species for this class of biological oxygen carriers, with $O_2^2^+$ bound in a bent, end-on fashion.\textsuperscript{42}

In contrast, the first structurally characterized nonheme Fe(III)–superoxo [Fe(TAML)(O$_2$)]$^{2^-}$ (TAML = tetraamido macrocyclic ligand; see Figure 1.4b, $R$ = methyl), reported in 2014, displays a significantly different electronic structure and geometry.\textsuperscript{43} Here the iron is intermediate spin ($S = 1$), with superoxide bound in a side-on, rather than end-on, fashion. Interestingly, [Fe(TAML)(O$_2$)]$^{2^-}$ was found to be competent for both the electrophilic oxidation of phenolic compounds, as well as the nucleophilic deformylation of aldehydes.

The first nonheme iron(III)–peroxy structure, obtained of the complex [Fe(TMC)(O$_2$)]$^{1^+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), was reported in 2011 and displayed a side-on geometry and a high-spin electronic configuration.\textsuperscript{44} While this peroxo compound was found to be poorly reactive, its protonated hydroperoxo form was competent for both electrophilic and nucleophilic oxidation reactions.

1.4.3. Molecular cobalt–superoxo and peroxy species. The discovery of dioxygen-binding cobalt complexes significantly predates that of iron.\textsuperscript{45} Reversible $O_2$-binding in cobalt(II)-salen ($\text{salen} = N,N'\text{-Bis(salicylidene)ethylenediamine}$) was reported in the mid-1940s.\textsuperscript{46} Since then, a vast number of stable cobalt(II)–$O_2$ compounds, bound by porphyrins, Schiff bases, and other ligand scaffolds, have been structurally characterized, and the thermodynamics of $O_2$ binding reported.\textsuperscript{47} All of the Co(III) compounds are low-spin, with superoxide typically bound in bent, end-on geometries and peroxide bound side-on. Due to their prevalence and greater stability, cobalt complexes were some of the first synthetic transition-metal dioxygen carriers to be investigated for air separation applications.\textsuperscript{6} In addition, the properties of cobalt-reconstituted hemoglobin and its direct molecular analogues were compared to probe the effect of protein environment on $O_2$ binding.\textsuperscript{48} Similar studies could not be done with iron, as sterically unhindered iron(II) porphyrin complexes rapidly and irreversibly oxidize into iron(III) in the presence of $O_2$.

1.5. Metal–oxo and dioxygen chemistry in metal–organic frameworks

1.5.1. Importance of site-isolation. Early on in their studies, metal–oxo and dioxygen complexes, particularly of iron, were found to be highly susceptible to bimolecular decomposition pathways. For many dioxygen complexes, irreversible metal oxidation is initiated via the formation of peroxo-bridged dinuclear complexes (see Figure 1.6a). In the case of iron(IV)–oxos, a common side reaction is the formation of bis($\mu$-oxo)diiron(III) compounds that
are unreactive, thermodynamic sinks (see Figure 1.6b). To prevent bimolecular decomposition, sterically bulky ligand scaffolds, such as picket-fence porphyrins, have been historically used to shelter and protect mononuclear metal sites. An alternative means to eliminate such pathways is the immobilization of metal sites on a solid support such as silica or polystyrene. In practice, however, complexes heterogenized in this manner are challenging to characterize by available techniques, and additional problems associated with steric crowding, site inaccessibility, and metal leaching can arise.\textsuperscript{49,50} As mentioned in section 1.3.4, transition metal cations can also be incorporated into zeolites, either as part of the framework or at extraframework sites. However, while zeolites are exceptionally thermally and chemically stable hosts, characterization of transition metal ions in these materials can be nontrivial due to the presence of multiple species.

Metal–organic frameworks are a relatively new class of porous, crystalline materials made up of inorganic cations or clusters (framework “nodes”) linked together by bridging organic linkers (framework “struts”).\textsuperscript{51} These materials have the potential to revolutionize a variety of gas separation and storage processes\textsuperscript{52} and have also recently been explored for catalytic applications.\textsuperscript{53} The use of a metal–organic framework to support isolated terminal metal–oxo and dioxygen moieties is a relatively unexplored but potentially promising area of research. This concept has been illustrated in Fe\textsubscript{2}(dobdc), a metal–organic framework featuring coordinatively unsaturated Fe(II) sites.\textsuperscript{54} This material stabilizes superoxo and peroxo-like reduced O\textsubscript{2} moieties, which have been thoroughly characterized by powder X-ray diffraction, vibrational spectroscopy, and Mössbauer spectroscopy.

1.5.2. Strategies for incorporating coordinatively-unsaturated redox-active sites into metal–organic frameworks. Several strategies exist for incorporating redox-active metals such as Fe(II) and Co(II) into metal–organic frameworks. In the first approach, materials containing coordinatively-unsaturated metal nodes are targeted. For example, in the M\textsubscript{2}(dobdc) (dobdc\textsuperscript{4−} = 2,5-dioxido-1,4-benzenedicarboxylate),\textsuperscript{55} M\textsubscript{3}(btc)\textsubscript{2} (btc\textsuperscript{3−} = 1,3,5-benzenetricarboxylate),\textsuperscript{56} and M-BTT (BTT\textsuperscript{3−} = 1,3,5-benzenetristetrazolate)\textsuperscript{57} materials, metal-bound solvent molecules can be removed via heat and vacuum procedures, revealing square-pyramidal, exposed metal nodes (see Figure 1.7). This approach has several advantages, including the potential for accessing unusual ligand environments, rare coordination geometries (due to framework-enforced structural rigidity), as well as a high density of metal sites. However, it is less broadly applicable.
as only a few frameworks with coordinatively-unsaturated metal nodes are known, and the same phase is not always obtained when different metal cations are used.

Figure 1.7. Selected examples of frameworks containing exposed, transition-metal nodes, specifically (a) Fe$_2$(dobdc), (b) Cr$_3$(btc)$_2$, and (c) Fe-BTT. The overall framework structure is shown in the top row, with the local metal coordination environment and the protonated form of the bridging ligand displayed underneath. Gray, blue, red, light green, dark green, and orange spheres represent C, N, O, Cl, Cr, and Fe atoms, respectively; H atoms are removed for clarity.

A second strategy involves converting analogues of common chelating ligands such as bipyridine, porphyrin, or salen into framework organic struts (see Figure 1.8). These chelating sites can be first metallated and subsequently incorporated into a metal–organic framework (the “metalloligand” approach), or conversely, first incorporated into a framework and then subsequently metallated (“post-synthetic metallation”). Simple hard-soft acid-base theory can be used to selectively form porous framework structures while keeping the chelating sites open; for example, oxophilic Zr(IV) cations will selectively bind carboxylate moieties over nitrogen-based donors.
Figure 1.8. Metal complexes incorporated on framework organic struts. (a) Examples of framework struts containing central chelating functionalities such as porphyrin, salen, and bipyridine. The peripheral carboxylates are bound to framework nodes. (b) Single crystal X-ray structure of a post-synthetically metallated zirconium framework containing bipyridine sites, taken from reference 58d.

1.6. Conclusions and outlook

As illustrated in sections 1.1–1.4, biological and synthetic metal–oxo and dioxygen species possess a diverse range of geometric and electronic structures as well as intriguing reactivity modes. However, stability issues have hampered their isolation and, in certain cases, their use as catalysts or adsorbents for air separation applications. Furthermore, certain properties of enzymatic active sites, such as the $S = 2$ spin state of nonheme iron(IV)–oxos, have been difficult to replicate in molecular systems. Embedding well-defined iron(II), cobalt(II), and other transition metal ions within a metal–organic framework superstructure could increase the stability of oxo and reduced dioxygen species through site-isolation, while still retaining the tunable primary coordination spheres observed in molecular species. In addition, the tunable pore chemistries of metal–organic frameworks could enable the precise positioning of distal second coordination sphere functionalities, to better mimic enzyme active sites. It is our hope that the rich chemistry displayed by molecular metal–oxo and dioxygen compounds can be both replicated and expanded upon in this new class of porous materials. Efforts towards this goal will be the focus of subsequent chapters of this thesis.

1.7. References


Chapter 2: Oxidation of ethane to ethanol by N$_2$O in a metal–organic framework with coordinatively-unsaturated iron(II) sites

2.1 Introduction

The selective and efficient conversion of light alkanes into value-added chemicals remains an outstanding challenge with tremendous economic and environmental impact, especially considering the recent worldwide increase in natural gas reserves. In nature, C–H functionalization is carried out by copper and iron metalloenzymes, which activate dioxygen and, through metal-oxo intermediates, facilitate two- or four-electron oxidations of organic substrates. Duplicating this impressive reactivity in synthetic systems has been the focus of intense research. In particular, iron(IV)-oxo complexes have now been structurally characterized in various geometries (octahedral, trigonal bipyramidal) and spin states ($S = 1, S = 2$), and have proven to be competent catalysts for a variety of oxygenation reactions. However, in the absence of a protective protein superstructure, terminal iron-oxo species are highly susceptible to a variety of decomposition pathways, including dimerization to form oxo-bridged diiron complexes, intramolecular ligand oxidation, and solvent oxidation. Tethering a molecular iron species to a porous solid support such as silica or polystyrene could potentially prevent many of these side-reactions. In practice, however, complexes heterogenized in this manner are challenging to characterize by available techniques, and additional problems associated with steric crowding, site inaccessibility, and metal leaching inevitably arise. Iron cations can also be incorporated into zeolites, either as part of the framework or at extraframework sites, producing reactive iron centers that have no direct molecular analogue. Fe-ZSM-5, for example, has been shown to oxidize methane to methanol stoichiometrically when pretreated with nitrous oxide. However, characterization of these materials is nontrivial due to the presence of multiple iron species, and the nature of the active sites in Fe-ZSM-5 remains largely a matter of speculation.

The use of a metal-organic framework to support isolated terminal iron-oxo moieties is a currently unexplored yet highly promising area of research. The high surface area, permanent porosity, chemical and thermal stability, and synthetic tunability displayed by many of these materials makes them appealing in this regard. Additionally, metal-organic frameworks are typically highly crystalline with well-defined metal centers suited for characterization by single crystal and/or powder diffraction techniques. Furthermore, while molecular iron(IV)-oxo complexes generally utilize nitrogen-based chelating ligands, the metal cations in metal-organic frameworks are often ligated by weaker-field ligands, such as carboxylates and aryloxides, which are constrained in their coordination position by the extended framework structure. Thus, in addition to increased stability, terminal oxos in these materials might also have novel electronic properties and reactivity imparted by their unique coordination environment.

Herein, we show that the high-spin iron(II) centers within Fe$_2$(dobdc) (dobdc$^{4−}$ = 2,5-dioxido-1,4-benzenedicarboxylate) can activate N$_2$O, most likely forming a transient, high-spin iron(IV)-oxo intermediate, which rapidly reacts to afford Fe$_2$(OH)$_2$(dobdc). Significantly, the magnesium-diluted analogue, Fe$_{0.1}$Mg$_{1.9}$(dobdc), is found to selectively oxidize ethane to ethanol in the presence of N$_2$O under mild conditions.

2.2. Experimental
2.2.1. Synthesis of Fe$_2$(OH)$_{0.6}$(dobdc) (2') and Fe$_2$(OH)$_2$(dobdc) (2). An evacuated Schlenk flask containing fully desolvated Fe$_2$(dobdc) (100 mg, 0.33 mmol) was placed under an atmosphere of 30% N$_2$O and 70% N$_2$. The flask was immersed in an oil bath, and the temperature was increased by 10 °C every 12 h, from 25 °C up to 60 °C, to obtain Fe$_2$(OH)$_2$(dobdc) as a dark red-brown solid. When the reaction was stopped after 12 h at 35 °C, the partially oxidized Fe$_2$(OH)$_{0.6}$(dobdc) (as determined by Mössbauer spectroscopy) was obtained. Anal. Calc. for C$_8$H$_4$Fe$_2$O$_8$: C, 28.28; H, 1.19. Found: C, 29.18; H, 1.16. IR (solid-ATR): 3679 (m), 1532 (s), 1450 (s), 1411 (s), 1361 (s), 1261 (s), 1154 (w), 1129 (w), 1077 (w), 909 (m), 889 (s), 818 (s), 807 (s), 667 (s), 630 (m), 594 (s), 507 (s).

2.2.2. Synthesis of Fe$_{0.1}$Mg$_{1.9}$(dobdc) (3). In a 500-mL Schlenk flask, H$_4$(dobdc) (1.8 g, 8.8 mmol), MgCl$_2$ (1.5 g, 15 mmol), and FeCl$_2$ (0.84 g, 6.6 mmol) were dissolved in a mixture of 310 mL of DMF and 40 mL of methanol. The reaction was stirred vigorously at 120 °C for 16 h. The precipitate was filtered and stirred with 250 mL of fresh DMF at 120 °C for 3 h. Two more DMF washes at 120 °C were performed, after which the precipitate was filtered and soaked in methanol at 60 °C. The methanol exchanges were repeated until no DMF stretches were apparent in the infrared spectrum. The framework was fully desolvated under dynamic vacuum (<15 μbar) at 210 °C for 2 days to afford Fe$_{0.1}$Mg$_{1.9}$(dobdc) as a bright yellow-green solid (2.0 g, 8.2 mmol, 93% yield). The iron to magnesium ratio was determined by ICP-OES. Anal. Calc. for C$_8$H$_2$Fe$_{0.1}$Mg$_{1.9}$O$_6$: C, 39.08; H, 0.82. Found: C, 39.37; H, 0.43. IR (solid-ATR): 1577 (s), 1484 (m), 1444 (s), 1429 (s), 1372 (s), 1236 (s), 1210 (s), 1123 (m), 911 (m), 892 (s), 828 (s), 820 (s), 631 (s), 584 (s), 492 (s).

2.2.3. Reactivity of Fe$_2$(dobdc) (1) and Fe$_{0.1}$Mg$_{1.9}$(dobdc) (3) with N$_2$O and C$_2$H$_6$. In a typical flow-through experiment, a mixture of gases (2 mL/min N$_2$O, 10 mL/min C$_2$H$_6$, and 8 mL/min Ar for a total flow 20 mL/min) was flowed over a packed bed of metal-organic framework (50 to 100 mg) contained within a glass column. The column was heated to 75 °C for 24 h, after which the products were extracted with CD$_3$CN (3 × 1 mL) and analyzed by $^1$H NMR using 1,4-dichlorobenzene as an internal standard. While a cold bath maintained at –78 °C was installed downstream of the glass reactor in order to collect condensable organic products, at the temperatures tested all the products appeared to remain bound to the framework.

In a typical batch experiment, a Parr bomb was charged with N$_2$O (1.5 bar) and C$_2$H$_6$ (7.5 bar) and heated to 75 °C in a sand bath. After 24 h, the bomb was cooled and the products extracted with CD$_3$CN.

2.2.4. Electronic structure calculations. The structures of 2 and 4 were optimized using periodic boundary conditions and the PBE+U exchange-correlation functional. From each of these structures, we carved out a model cluster containing three iron centers along a single helical chain and six organic linkers. These clusters are analogous to the 88-atom cluster model of Fe$_2$(dobdc) employed previously.

The cluster models were further simplified by substituting the two peripheral iron(II) centers with zinc(II) centers, while keeping only the central iron(II) in the cluster. Constrained geometry optimizations were performed where only the central iron and the six oxygen atoms (plus the hydroxide hydrogen in compound 2) of its first coordination sphere were allowed to relax. Single-point multiconfigurational complete active space (CASSCF) calculations followed by second-order perturbation theory (CASPT2) were performed at PBE-optimized (PBE/SDD(Fe,Zn),6-31G(d)(C, H, O)) geometries of the cluster models of 2 and 4.

2.3. Results and Discussion
2.3.1. Nitrous oxide coordination and activation. Of the three-dimensional iron(II)-
containing metal-organic frameworks shown to be stable to desolvation,15,16,17,18 few possess
 coordinatively-unsaturated metal centers in a single, well-defined environment. The compound
Fe₂₉(dobdc) (I), also known as Fe-MOF-74 or CPO-27-Fe, is rare in this regard, as the hexagonal
channels of the framework are lined with a single type of square pyramidal iron(II) site (see
Figure 2.1a). The high density and redox-active nature of these open metal sites engender
excellent O₂/N₂ and hydrocarbon separation properties.18,19 However, with respect to the
reactivity of the framework, only the hydroxylation of benzene to phenol and the oxidation of
methanol to formaldehyde have been reported.20,21 Thus, we embarked on a study of its reactivity
towards nitrous oxide, a gaseous two-electron oxidant and O-atom transfer agent that is widely
employed in industry, anticipating the generation of a highly reactive iron(IV)-oxo species
capable of oxidizing strong C–H bonds.

We first investigated the binding of nitrous oxide to I under conditions in which the Fe–N₂O
interaction is reversible. Experimental studies on the coordination chemistry of N₂O are scarce,
as metal–N₂O adducts are challenging to synthesize due to the poor σ-donating and π-accepting
properties of the molecule.22 Indeed, of the several proposed binding modes, only one—end-on,
η¹-N—has been structurally characterized in a molecular complex.23 To establish the
coordination mode of N₂O in I, powder neutron diffraction data, which are very sensitive to the
atomic assignment of O and N, were collected on a sample dosed with various loadings of N₂O.
At low loadings, the best fit was an average of approximately 60% η¹-O and 40% η¹-N
coordination, with Fe–N₂O distances of 2.42(3) and 2.39(3) Å, respectively. In both cases, a bent
Fe–N₂O angle close to 120° is observed (see Figure 2.1b). Density functional theory (DFT)
studies of N₂O-bound I using the M06 functional24 show excellent agreement with experiment
(see Figure 2.S20). Furthermore, these calculations predict the η¹-O coordination mode to be
favored over the η¹-N mode by just 1.1 kJ/mol (see Tables 2.S17 and 2.S22). This is consistent
with the nearly equal population split observed, although the magnitude of the difference is
smaller than the reliability of the calculations.

While η¹-O coordination with a bent Fe–O–N angle has been proposed in a variety of
systems ranging from isolated metal atoms to iron zeolites,22,25,26 η¹-N coordination with a bent
Fe–N–N angle is much more unusual. It suggests little π-back-bonding from the metal d-orbitals
into the π* of N₂O, in contrast to previously reported vanadium and ruthenium–N₂O adducts,
which have linear metal–N–N–O geometries and for which π-interactions have been invoked as
significant contributors to the stability of the complexes.23,27,28,29 The bent geometry, long Fe–N₂O
bond length, and mixed N- and O-coordination indicate N₂O is bound only weakly to the iron(II)
centers in the framework, a hypothesis corroborated by in-situ transmission-mode infrared
spectroscopy. Spectra collected on a thin-film of I dosed at room temperature with N₂O display a
maximum at 2226 cm⁻¹, which is very close to the fundamental ν(N–N) transition for unbound
N₂O (2224 cm⁻¹), suggesting a physically adsorbed phase with little to no perturbation of the N₂O
molecule (see Figure 2.S1). As expected, this interaction is fully reversible, and the band
completely disappears under applied vacuum. Consistent with these experimental results, DFT
studies calculate binding energies of 45.6 and 44.5 kJ/mol for the η¹-O and η¹-N modes,
respectively, with a natural bond order analysis36 showing weak back-bonding in both
configurations (see Table 2.S23).
Figure 2.1. Structure of bare and N\textsubscript{2}O-dosed Fe\textsubscript{2}(dobdc). (a) Structure of Fe\textsubscript{2}(dobdc), showing hexagonal channels lined with 5-coordinate iron(II) sites. The view is down the c axis, along the helical chains of iron(II) ions. (b) Experimental structures for N\textsubscript{2}O binding in Fe\textsubscript{2}(dobdc), solved from powder neutron diffraction data collected at 10 K. The molecule binds with a bent Fe–N\textsubscript{2}O angle, with a mixture of 60% η\textsuperscript{1}–O coordination and 40% η\textsuperscript{1}–N coordination. For comparison of calculated structures with experimental, see Figure 2.S20. Orange, gray, dark blue, and red spheres represent Fe, C, N, and O respectively; H atoms are omitted for clarity.

Upon heating the N\textsubscript{2}O-dosed framework to 60 °C, the material undergoes a drastic color change from bright green to dark red-brown that is suggestive of oxidization. In addition, \textit{in situ} infrared studies using CO as a probe molecule show that the open metal sites, which coordinate
CO strongly, have been almost entirely consumed (see Figure 2.S9). Characterization of the resulting product is consistent with the formulation $\text{Fe}_2(\text{OH})_2(\text{dobdc})$ (2), in which each iron center is in the +3 oxidation state and bound to a terminal hydroxide anion (see Figure 2.2a). Compound 2 is likely formed via a fleeting iron-oxo intermediate, which rapidly undergoes H-atom abstraction, although the source of the H-atom has not been determined. Mössbauer spectroscopy was used to probe the local environment of the iron centers in the oxidized material. The $^{57}$Fe Mössbauer spectrum of 2 consists of a doublet characterized by an isomer shift ($\delta$) of 0.40(2) mm/s and a quadrupole splitting ($|\Delta E_Q|$) of 0.96(1) mm/s (see Figure 2.2c). The isomer shift for the iron centers in 2 is similar to the parameters obtained for the peroxide-coordinated iron(III) centers in $\text{Fe}_2(\text{O}_2)(\text{dobdc})$,$^{18}$ and is consistent with other high-spin heme and nonheme iron(III) species.$^{31,32,33}$ In addition, the infrared spectrum of 2 shows the appearance of two new bands as compared to the unoxidized framework, which we assign as Fe–OH (667 cm$^{-1}$) and O–H (3678 cm$^{-1}$) vibrations. These bands shift to 639 and 3668 cm$^{-1}$, respectively, when N$_2^{18}$O is employed for the oxidation; the observed differences of 28 and 10 cm$^{-1}$ are very close to the theoretical isotopic shifts of 27 and 12 cm$^{-1}$ predicted by a simple harmonic oscillator model (see Figure 2.2b). Partial oxidation of the framework is achieved by heating at 35 °C for 12 h, leading to the formation of $\text{Fe}_2(\text{OH})_{0.6}(\text{dobdc})$ (2'), which has a similar infrared spectrum (though the bands associated with Fe–OH are less intense) and Mössbauer parameters (see Table 2.S9).

Figure 2.2. Preparation, spectroscopic characterization, and structure of $\text{Fe}_2(\text{OH})_2(\text{dobdc})$.
(a) Reaction scheme for the preparation of $\text{Fe}_2(\text{OH})_2(\text{dobdc})$ (2) from $\text{Fe}_2(\text{dobdc})$ (1). (b) Infrared spectrum of a partially oxidized sample, $\text{Fe}_2(\text{OH})_{0.6}(\text{dobdc})$ (black) and $\text{Fe}_2(\text{OH})_{0.6}(\text{dobdc})$ (dotted red). The peaks at 667 and 3678 cm$^{-1}$ shift to 639 and 3668 cm$^{-1}$, respectively, when N$_2^{18}$O is used, confirming that these are indeed new bands derived from N$_2$O and not simply shifted framework bands. It also strongly supports the assignment of these peaks as Fe–OH and O–H vibrations. (c) Mössbauer spectrum of 2, with the fit in black. The red component has parameters consistent with high-spin Fe(III) ($\delta = 0.40(2)$ mm/s, $|\Delta E_Q|$ = 0.96(1) mm/s, area = 80(2)%). A minor component (green) is assigned as unreacted Fe(II) sites, and another minor component (purple) is assigned as an amorphous Fe(III) decomposition product. (d) The structure of 2 obtained by powder X-ray diffraction data (100 K). The Fe–OH bond distance of 1.92(1) Å is consistent with previously reported Fe(III)–OH compounds. The hydrogen atom on the hydroxide is shown for clarity, but was not found from the diffraction data. Selected interatomic distances (Å) for 2: Fe–O1 = 1.92(1); Fe–O2 = 2.01(1); Fe–O3 =
2.08(1); Fe–O4 = 2.04(1); Fe–O5 = 2.04(1); Fe–O6 = 2.20(1); Fe–Fe = 3.16(1). Orange, red, and light blue spheres represent Fe, O, and H respectively.

The framework maintains both crystallinity and porosity after oxidation, with a Brunauer-Emmett-Teller (BET) surface area of 1013 m²/g and a Langmuir surface area of 1171 m²/g. Rietveld analysis of powder X-ray diffraction data collected at 100 K on 2 firmly establishes the presence of a new Fe–O bond, but does not reveal whether a hydrogen atom is present. However, the Fe–OH bond distance of 1.92(1) Å is consistent with the bond lengths of previously reported octahedral iron(III)-hydroxide complexes (1.84-1.93 Å) (see Figure 2.d). In addition, the trans Fe–Oaxial bond is slightly elongated (Fe–Oaxial = 2.20(1) Å; average Fe–Oequatorial = 2.04(1) Å), with the iron center shifted slightly out of the plane of the four equatorial oxygen atoms by 0.23(1) Å. EXAFS analysis of the same sample, as well as periodic DFT calculations, provide bond lengths that are consistent with those obtained from the diffraction data (see Table 2.S8).

Surprisingly, the iron(III)-hydroxide species is capable of activating weak C–H bonds. When the partially oxidized sample 2′ is exposed to 1,4-cyclohexadiene (C–H bond dissociation energy of 305 kJ/mol) at room temperature, benzene is produced as the sole product in quantitative yield. In the process, the framework converts entirely back to iron(II), as determined by Mössbauer spectroscopy. Such reactivity is rare but not unprecedented for iron(III)-hydroxide compounds. For instance, lipoxygenase, an enzyme that converts 1,4-dienes into alkyl hydroperoxides, is believed to proceed through a non-heme ferric hydroxide intermediate, and several molecular lipoxygenase mimics have also been reported to activate the C–H bond of 1,4-cyclohexadiene and other 1,4-dienes. However, the oxidizing power of 2 and 2′ is limited, and no reaction is observed with less activated C–H bonds.

### 2.3.2. Oxidation of ethane to ethanol.

Because the isolation of an iron(III)-hydroxide product from a reaction employing a two-electron oxidant strongly suggests the intermediacy of an iron(IV)-oxo species, we next carried out the oxidation in the presence of a hydrocarbon substrate containing stronger C–H bonds, specifically ethane (C–H bond dissociation energy of 423 kJ/mol), hoping to intercept the oxo species before its decay. Indeed, flowing an N₂:O:ethane:Ar mixture (10:25:65) over the framework at 75 °C led to the formation of various ethane-derived oxygenates, including ethanol, acetaldehyde, diethyl ether, and other ether oligomers, as determined by °H NMR spectroscopy of the extracted products. The formation of ether products is not unprecedented, as N₂O-treated Fe-ZSM-5 forms a small amount of dimethylether in addition to methanol when exposed to methane, via a mechanism proposed to involve methyl radicals as well as multiple iron sites. We hypothesized that the complex mixture of products was related to the close proximity of reactive iron centers, which are 8.13(2) Å and 6.84(1) Å apart across and along a channel, respectively, in 1. To avoid oligomerization and over-oxidation, a mixed-metal metal-organic framework, Fe₂₁Mg₆₁₉(dobdc) (3), in which the iron(II) sites are diluted with redox-inactive magnesium(II) centers, was synthesized. The BET surface area of 1670 m²/g for this material falls between the surface areas of the pure iron and pure magnesium frameworks (1360 and 1800 m²/g, respectively). While determining the exact distribution of metal centers in heterometallic metal-organic frameworks is challenging, the unit cell parameters of 3 are also in between those of Fe₂(dobdc) and Mg₂(dobdc) (see Table 2.S10), suggesting the formation of a solid solution rather than a mixture of two separate phases. Additionally, the Mössbauer spectrum of 3 shows sharp doublets with a significantly different quadrupole splitting than the all-iron analogue (2.25(1) mm/s versus 2.02(1) mm/s in Fe₂(dobdc); see Table 2.S9), indicating that the iron centers in the magnesium-diluted framework are in an
altered, but uniform, environment. Thus, 3 is likely best described as containing either isolated iron centers or short multiiron segments dispersed evenly throughout a magnesium-based framework.

Exposure of 3 to N₂O and ethane under the same flow-through conditions yields the exclusive formation of ethanol and acetaldehyde in a 10:1 ratio, albeit in low yield (60% with respect to iron). Gas chromatography analysis of the headspace reveals no ethanol, acetaldehyde, or CO, suggesting the products remain bound to the framework (either at open iron or open magnesium sites), which likely explains the high ethanol selectivity. While the framework is still highly crystalline after N₂O/ethane treatment, Mössbauer spectroscopy reveals that roughly 90% of the iron centers have decayed into a species with similar spectral parameters as 2 (see Figure 2.S18 and Table 2.S9). We propose that formation of iron(III)-hydroxide or alkoxide decay products prematurely halts the catalytic cycle, which leads to substoichiometric yields of hydroxylated product (see Figure 2.3). Because glass can be a source of H-atoms, the reaction was subsequently repeated in a batch, rather than flow-through mode, in a Teflon-lined stainless-steel bomb, which produced both higher yields with respect to iron (turnover number = 1.6) and selectivities (25:1 ethanol:acetaldehyde), showing that the system can indeed be modestly catalytic if competing substrates are excluded. However, the yield based on ethane (roughly 1%) is still too low for practical purposes.

Figure 2.3. N₂O activation and reactivity of Fe₂(dobdc) in the oxidation of ethane and 1,4-cyclohexadiene. N₂O activation and reactivity of Fe₂(dobdc) in the oxidation of ethane and 1,4-cyclohexadiene. Heating of N₂O-bound Fe₂(dobdc) (1-N₂O) to 60 °C results in the formation of a transient high-spin Fe(IV)-oxo species (4), which can react with the strong C–H bonds of ethane. In the absence of a hydrocarbon substrate, the Fe(IV)-oxo quickly decays via H-atom abstraction into an Fe(III)-hydroxide (2), which is isolable and well-characterized. This hydroxide species can react with weak C–H bonds such as those in 1,4-cyclohexadiene to form benzene and H₂O-bound Fe₂(dobdc) (1–H₂O).

Electronic structure calculations. As the high reactivity of the iron-oxo species precluded isolation in both Fe₂(dobdc) and its magnesium-diluted analog, electronic structure calculations were performed on Fe₂(O)₂(dobdc) (4) to gain insight into the geometric and electronic structure of iron-oxo units supported within the framework. First, periodic PBE+U³⁹,⁴⁰ geometry optimizations were performed on 4 for the singlet, triplet, and quintet spin states. A quintet ground state was predicted, with a short Fe–O bond length of 1.64 Å, consistent with that
of previously reported iron(IV)-oxo complexes (see Figure 2.4 and Table 2.S11). The periodic structure was then truncated to an 89-atom model cluster containing three metal centers, six organic linkers, and an oxo moiety to facilitate calculations using more accurate methods. The cluster calculations were simplified by replacing the two peripheral iron(II) centers with closed-shell zinc(II) centers, which have the same charge and a similar ionic radius to iron(II) and magnesium(II) cations (see Figure 2.S19). The geometry of this cluster was then optimized for the ground state, with all atoms except for the central iron and its first coordination sphere frozen at the coordinates from the periodic PBE+U optimization. As shown in Table 2.1, the M06 calculations also predict a quintet ground state. Further calculations were performed with several other exchange-correlation functionals, and in each case the ground state was found to be a quintet (see Tables 2.S11–S16). Note that similar results were obtained when the Zn(II) centers in the 89-atom cluster were replaced with Mg(II) centers (see Tables 2.S20 and 2.S21).

The electronic structure of the cluster model of 4 was further examined with single-point multiconfigurational complete active space (CASSCF) calculations followed by second-order perturbation theory (CASPT2). Again, the ground state is predicted to be the quintet state (see Table 2.1 and Table 2.S18). Both M06 and CASPT2 yield a spin density of ~3.7 on iron, consistent with four unpaired spins mainly localized on the metal (see Tables 2.S13 and 2.S19). Density functional and CASPT2 calculations were also performed on the cluster model of 2; all calculations led to a high-spin sextet ground state for the iron(III) center (see Tables 2.S11–S16 and Table 2.S18).

Table 2.1. Calculated relative energies (kJ/mol) of the cluster model of Fe₂(O)₂(dobdc). Density functional and CASPT2 calculations were performed on a truncated model of Fe₂(O)₂(dobdc) (4) containing a central iron atom, two peripheral Zn(II) atoms (to replicate the rigid framework structure), and six organic linkers (see Figure 2.S19). The relative energies of
the cluster models in different spin states are shown below. By both methods, the quintet state ($S = 2$) is the calculated ground state.

<table>
<thead>
<tr>
<th></th>
<th>M06</th>
<th>CASPT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>210.6</td>
<td>249.4</td>
<td></td>
</tr>
<tr>
<td>136.4</td>
<td>127.6</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

While spectroscopic and theoretical studies have long attributed the reactivity of non-heme enzymatic and synthetic iron(IV)-oxo complexes to a quintet spin state, only a handful of mononuclear high-spin iron(IV)-oxo species have been characterized, with all but one exhibiting a trigonal bipyramidal coordination geometry. In these systems, the oxo moiety is either extremely unstable—[Fe(O)(H$_2$O)$_3$]$^{2+}$, for example, has a half life of roughly 10 s—or inaccessible to substrates due to bulky ligand scaffolds, leading to sluggish reactivity. On the other hand, the Fe$_2$(dobdc) framework features sterically accessible, site-isolated metal centers entrench in a weak-field ligand environment. Utilizing these two properties, it is possible not only to generate such a species, albeit fleetingly, but also to direct it towards the facile activation of one of the strongest C–H bonds known.

2.4. Conclusions and outlook

The foregoing results demonstrate through reactivity studies, detailed characterization of decay products, and theoretical calculations that the iron-based metal-organic frameworks Fe$_2$(dobdc) and Fe$_{0.1}$Mg$_{1.9}$(dobdc) are very likely capable of supporting fleeting iron(IV)-oxo species possessing an unusual $S = 2$ spin state. With this, Fe$_2$(dobdc) has now been shown to stabilize iron-superoxo, peroxy, hydroxo, as well as oxo intermediates, highlighting the promise of metal-organic frameworks both as catalysts and as scaffolds for interrogating reactive metal species. Future work will focus on: (i) further exploring the reactivity of Fe$_2$(dobdc) and its expanded analogues with ethane and other hydrocarbon substrates, as well as continued efforts to isolate the iron-oxo species, (ii) the use of dioxygen as the terminal oxidant in such systems, and (iii) the design, synthesis, and reactivity of other metal-organic frameworks with coordinatively-unsaturated iron sites.

2.5. Acknowledgements

Synthesis, basic characterization experiments, and all of the theoretical work, were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under award DE-FG02-12ER16362. Reactivity studies were supported by the Laboratory Directed Research and Development Program of Lawrence Berkeley National Laboratory under U.S. Department of Energy Contract No. DE-AC02-05CH11231. Work at the Molecular Foundry, and XAS experiments performed at the Advanced Light Source (BL 10.3.2), Berkeley, were supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. X-ray diffraction experiments were performed at the Advanced Photon Source at Argonne National Laboratory (17-BM-B). S.B., F.B. and V.C. acknowledge financial support to Ateneo Project 2011 ORTO11RRT5. We also thank NSF for providing graduate fellowship support (D.
J. X. and J. A. M.). In addition, we are grateful for the support of E. D. B. through a Gerald K. Branch fellowship in chemistry, P.V. through a Phillips 66 Excellence Fellowship, and M. R. H. through the NIST/NRC Fellowship Program. We thank Sachin Chavan for help with the infrared spectroscopy experiments and fruitful discussion.

2.6. References and supplementary information


Supplementary Information

Table 2.S1 | Rietveld Refinement (10 K) of Fe₂(dobdc). Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of the bare Fe₂(dobdc) framework at 10 K, space group R-3, \(a = 26.1826(6) \text{ Å}\), \(c = 6.8506(2) \text{ Å}\), and \(V = 4067.1(2) \text{ Å}^3\).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occ.</th>
<th>Uiso*100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.3815(2)</td>
<td>0.3518(2)</td>
<td>0.1416(5)</td>
<td>1.0</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>O1</td>
<td>0.3293(3)</td>
<td>0.2963(3)</td>
<td>0.369(1)</td>
<td>1.0</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>O2</td>
<td>0.3001(3)</td>
<td>0.2259(3)</td>
<td>0.600(1)</td>
<td>1.0</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>O3</td>
<td>0.3550(3)</td>
<td>0.2737(3)</td>
<td>0.011(1)</td>
<td>1.0</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>C1</td>
<td>0.3189(3)</td>
<td>0.2453(3)</td>
<td>0.4267(9)</td>
<td>1.0</td>
<td>0.51(6)</td>
</tr>
<tr>
<td>C2</td>
<td>0.3278(3)</td>
<td>0.2063(3)</td>
<td>0.2915(8)</td>
<td>1.0</td>
<td>0.51(6)</td>
</tr>
<tr>
<td>C3</td>
<td>0.3441(3)</td>
<td>0.2221(3)</td>
<td>0.0908(8)</td>
<td>1.0</td>
<td>0.51(6)</td>
</tr>
<tr>
<td>C4</td>
<td>0.3490(3)</td>
<td>0.1809(3)</td>
<td>-0.030(1)</td>
<td>1.0</td>
<td>0.51(6)</td>
</tr>
<tr>
<td>H</td>
<td>0.3621(5)</td>
<td>0.1922(5)</td>
<td>-0.173(2)</td>
<td>1.0</td>
<td>1.8(3)</td>
</tr>
</tbody>
</table>
Table 2.S2 | Rietveld Refinement (10 K) of Fe₂(dobdc)(N₂O)₀.₇. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of the 0.35 N₂O per Fe²⁺ in the Fe₂(dobdc) framework at 10 K, space group R-3, \( a = 26.1660(4) \text{ Å}, \ c = 6.8595(2) \text{ Å} \), and \( V = 4067.2(2) \ \text{Å}^3 \).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occ.</th>
<th>Uiso*100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.3819(1)</td>
<td>0.3520(2)</td>
<td>0.1437(4)</td>
<td>1.0</td>
<td>0.49(5)</td>
</tr>
<tr>
<td>O1</td>
<td>0.3279(2)</td>
<td>0.2957(2)</td>
<td>0.3676(8)</td>
<td>1.0</td>
<td>0.20(4)</td>
</tr>
<tr>
<td>O2</td>
<td>0.3010(2)</td>
<td>0.2272(2)</td>
<td>0.6019(7)</td>
<td>1.0</td>
<td>0.20(4)</td>
</tr>
<tr>
<td>O3</td>
<td>0.3550(2)</td>
<td>0.2738(2)</td>
<td>0.0084(8)</td>
<td>1.0</td>
<td>0.20(4)</td>
</tr>
<tr>
<td>C1</td>
<td>0.3193(2)</td>
<td>0.2463(2)</td>
<td>0.4292(7)</td>
<td>1.0</td>
<td>0.42(2)</td>
</tr>
<tr>
<td>C2</td>
<td>0.3275(2)</td>
<td>0.2063(2)</td>
<td>0.2887(7)</td>
<td>1.0</td>
<td>0.42(2)</td>
</tr>
<tr>
<td>C3</td>
<td>0.3438(2)</td>
<td>0.2213(2)</td>
<td>0.0924(7)</td>
<td>1.0</td>
<td>0.42(2)</td>
</tr>
<tr>
<td>C4</td>
<td>0.35061(2)</td>
<td>0.1817(2)</td>
<td>-0.0272(7)</td>
<td>1.0</td>
<td>0.42(2)</td>
</tr>
<tr>
<td>H</td>
<td>0.3619(4)</td>
<td>0.1930(3)</td>
<td>-0.1712(15)</td>
<td>1.0</td>
<td>1.3(2)</td>
</tr>
<tr>
<td>O11</td>
<td>0.471(1)</td>
<td>0.358(1)</td>
<td>0.272(4)</td>
<td>0.22(1)</td>
<td>1.6(8)</td>
</tr>
<tr>
<td>N12</td>
<td>0.5174(5)</td>
<td>0.3960(4)</td>
<td>0.2071(17)</td>
<td>0.371(7)</td>
<td>2.9(3)</td>
</tr>
<tr>
<td>N13</td>
<td>0.5607(6)</td>
<td>0.4314(6)</td>
<td>0.1533(26)</td>
<td>0.223(6)</td>
<td>1.6(4)</td>
</tr>
<tr>
<td>N11a</td>
<td>0.4718(9)</td>
<td>0.3605(9)</td>
<td>0.2628(32)</td>
<td>0.161(7)</td>
<td>1.1(6)</td>
</tr>
<tr>
<td>O13a</td>
<td>0.562(2)</td>
<td>0.433(2)</td>
<td>0.146(7)</td>
<td>0.16(1)</td>
<td>3(1)</td>
</tr>
</tbody>
</table>
Table 2.S3 | Rietveld Refinement (10 K) of Fe$_2$(dobdc)(N$_2$O)$_{1.2}$. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement of structural model of the 0.60 N$_2$O per Fe$^{2+}$ in the Fe$_2$(dobdc) framework at 10 K, space group R-3, \(a = 26.1577(4)\) Å, \(c = 6.8671(2)\) Å, and \(V = 4069.1(2)\) Å$^3$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occ.</th>
<th>Uiso*100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.3829(1)</td>
<td>0.3523(2)</td>
<td>0.1428(5)</td>
<td>1.0</td>
<td>0.94(5)</td>
</tr>
<tr>
<td>O1</td>
<td>0.3268(2)</td>
<td>0.2945(2)</td>
<td>0.3667(8)</td>
<td>1.0</td>
<td>0.17(4)</td>
</tr>
<tr>
<td>O2</td>
<td>0.3019(2)</td>
<td>0.2274(2)</td>
<td>0.6000(7)</td>
<td>1.0</td>
<td>0.17(4)</td>
</tr>
<tr>
<td>O3</td>
<td>0.3550(2)</td>
<td>0.2733(2)</td>
<td>0.0093(8)</td>
<td>1.0</td>
<td>0.17(4)</td>
</tr>
<tr>
<td>C1</td>
<td>0.3189(2)</td>
<td>0.2452(2)</td>
<td>0.4273(7)</td>
<td>1.0</td>
<td>0.86(2)</td>
</tr>
<tr>
<td>C2</td>
<td>0.3280(2)</td>
<td>0.2059(2)</td>
<td>0.2857(7)</td>
<td>1.0</td>
<td>0.86(2)</td>
</tr>
<tr>
<td>C3</td>
<td>0.3446(2)</td>
<td>0.2211(2)</td>
<td>0.0933(7)</td>
<td>1.0</td>
<td>0.86(2)</td>
</tr>
<tr>
<td>C4</td>
<td>0.3521(2)</td>
<td>0.1833(2)</td>
<td>-0.0262(7)</td>
<td>1.0</td>
<td>0.86(2)</td>
</tr>
<tr>
<td>H</td>
<td>0.3602(3)</td>
<td>0.1927(3)</td>
<td>-0.170(1)</td>
<td>1.0</td>
<td>1.0(2)</td>
</tr>
<tr>
<td>O11</td>
<td>0.468(1)</td>
<td>0.3533(9)</td>
<td>0.272(3)</td>
<td>0.232(5)</td>
<td>1.5(7)</td>
</tr>
<tr>
<td>N12</td>
<td>0.5145(4)</td>
<td>0.3915(4)</td>
<td>0.211(2)</td>
<td>0.532(7)</td>
<td>7.9(4)</td>
</tr>
<tr>
<td>N13</td>
<td>0.5575(8)</td>
<td>0.4275(8)</td>
<td>0.152(4)</td>
<td>0.232(5)</td>
<td>6.8(7)</td>
</tr>
<tr>
<td>N11a</td>
<td>0.4712(6)</td>
<td>0.3560(6)</td>
<td>0.264(2)</td>
<td>0.310(6)</td>
<td>5.5(5)</td>
</tr>
<tr>
<td>O13a</td>
<td>0.5599(8)</td>
<td>0.4296(8)</td>
<td>0.151(3)</td>
<td>0.310(6)</td>
<td>3.3(6)</td>
</tr>
</tbody>
</table>
Table 2.S4 | Rietveld Refinement (10 K) of Fe$_2$(dobdc)(N$_2$O)$_2$.5$. Fractional atomic coordinates, occupancies, and isotropic displacement parameters obtained from Rietveld refinement (10 K) of the Fe$_2$(dobdc) dosed with 1.25 N$_2$O per Fe$^{2+}$, space group R-3, $a = 26.1243(5)$ Å, $c = 6.87522(2)$ Å, and $V = 4063.6(2)$ Å$^3$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occ.</th>
<th>Uiso*100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.3828(2)</td>
<td>0.3518(2)</td>
<td>0.1479(6)</td>
<td>1.0</td>
<td>0.95(9)</td>
</tr>
<tr>
<td>O1</td>
<td>0.3271(3)</td>
<td>0.2952(3)</td>
<td>0.3619(9)</td>
<td>1.0</td>
<td>0.32(7)</td>
</tr>
<tr>
<td>O2</td>
<td>0.3006(3)</td>
<td>0.2252(3)</td>
<td>0.593(1)</td>
<td>1.0</td>
<td>0.32(7)</td>
</tr>
<tr>
<td>O3</td>
<td>0.3554(3)</td>
<td>0.2736(3)</td>
<td>0.006(1)</td>
<td>1.0</td>
<td>0.32(7)</td>
</tr>
<tr>
<td>C1</td>
<td>0.3194(2)</td>
<td>0.2471(3)</td>
<td>0.4234(9)</td>
<td>1.0</td>
<td>0.81(4)</td>
</tr>
<tr>
<td>C2</td>
<td>0.3267(3)</td>
<td>0.2057(3)</td>
<td>0.2872(8)</td>
<td>1.0</td>
<td>0.81(4)</td>
</tr>
<tr>
<td>C3</td>
<td>0.3457(2)</td>
<td>0.2223(3)</td>
<td>0.0956(9)</td>
<td>1.0</td>
<td>0.81(4)</td>
</tr>
<tr>
<td>C4</td>
<td>0.3507(3)</td>
<td>0.1808(3)</td>
<td>-0.0232(9)</td>
<td>1.0</td>
<td>0.81(4)</td>
</tr>
<tr>
<td>H</td>
<td>0.3632(5)</td>
<td>0.1931(4)</td>
<td>-0.169(2)</td>
<td>1.0</td>
<td>1.35(3)</td>
</tr>
<tr>
<td>O11</td>
<td>0.4704(7)</td>
<td>0.3515(9)</td>
<td>0.249(4)</td>
<td>0.320(8)</td>
<td>3.7(9)</td>
</tr>
<tr>
<td>N12</td>
<td>0.5176(3)</td>
<td>0.3919(3)</td>
<td>0.213(1)</td>
<td>0.639(9)</td>
<td>5.4(4)</td>
</tr>
<tr>
<td>N13</td>
<td>0.5610(5)</td>
<td>0.4309(7)</td>
<td>0.164(3)</td>
<td>0.320(8)</td>
<td>4.9(6)</td>
</tr>
<tr>
<td>N11a</td>
<td>0.4711(5)</td>
<td>0.3630(7)</td>
<td>0.268(2)</td>
<td>0.308(8)</td>
<td>1.4(4)</td>
</tr>
<tr>
<td>N13a</td>
<td>0.5657(6)</td>
<td>0.4187(16)</td>
<td>0.142(4)</td>
<td>0.308(8)</td>
<td>10.4(8)</td>
</tr>
<tr>
<td>N21</td>
<td>0.1468(8)</td>
<td>0.1587(8)</td>
<td>0.605(3)</td>
<td>0.383(5)</td>
<td>10.0(8)</td>
</tr>
<tr>
<td>N22</td>
<td>0.1620(7)</td>
<td>0.1862(7)</td>
<td>0.462(3)</td>
<td>0.383(5)</td>
<td>8.0(7)</td>
</tr>
<tr>
<td>O23</td>
<td>0.1744(1)</td>
<td>0.2166(9)</td>
<td>0.331(3)</td>
<td>0.383(5)</td>
<td>3.8(7)</td>
</tr>
<tr>
<td>N11aa</td>
<td>0.5090(6)</td>
<td>0.3732(7)</td>
<td>0.333(2)</td>
<td>0.310(5)</td>
<td>2.4(5)</td>
</tr>
<tr>
<td>O11aa</td>
<td>0.559(1)</td>
<td>0.403(1)</td>
<td>0.402(4)</td>
<td>0.310(5)</td>
<td>0.7(6)</td>
</tr>
<tr>
<td>N11ab</td>
<td>0.4619(8)</td>
<td>0.3481(8)</td>
<td>0.285(3)</td>
<td>0.310(5)</td>
<td>3.7(6)</td>
</tr>
</tbody>
</table>
Table 2.S5 | Rietveld Refinement (100 K) of Fe$_2$(OH)$_2$(dobdc). Space group R-3, $a = 25.6125(2)$ Å, $c = 6.8036(1)$ Å, and $V = 3865.20(8)$ Å$^3$. This data was obtained from 11-BM at the Advanced photon source at Argonne National Laboratory using a wavelength of 0.7291 Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occ.</th>
<th>U iso*100 (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.3893(1)</td>
<td>0.3510(1)</td>
<td>0.1539(3)</td>
<td>1.0</td>
<td>2.95*</td>
</tr>
<tr>
<td>O1</td>
<td>0.3230(3)</td>
<td>0.2972(4)</td>
<td>0.356(1)</td>
<td>1.0</td>
<td>2.3(2)</td>
</tr>
<tr>
<td>O2</td>
<td>0.3009(4)</td>
<td>0.2289(3)</td>
<td>0.594(1)</td>
<td>1.0</td>
<td>2.3(2)</td>
</tr>
<tr>
<td>O3</td>
<td>0.3553(3)</td>
<td>0.2727(4)</td>
<td>0.000(1)</td>
<td>1.0</td>
<td>2.3(2)</td>
</tr>
<tr>
<td>C1</td>
<td>0.3164(8)</td>
<td>0.2467(6)</td>
<td>0.415(2)</td>
<td>1.0</td>
<td>1.1(2)</td>
</tr>
<tr>
<td>C2</td>
<td>0.3260(6)</td>
<td>0.2052(7)</td>
<td>0.288(2)</td>
<td>1.0</td>
<td>1.1(2)</td>
</tr>
<tr>
<td>C3</td>
<td>0.3431(5)</td>
<td>0.2202(7)</td>
<td>0.092(2)</td>
<td>1.0</td>
<td>1.1(2)</td>
</tr>
<tr>
<td>C4</td>
<td>0.3492(6)</td>
<td>0.1795(7)</td>
<td>-0.044(2)</td>
<td>1.0</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>OH</td>
<td>0.4524(4)</td>
<td>0.3473(5)</td>
<td>0.294(1)</td>
<td>1.0</td>
<td>8.66*</td>
</tr>
</tbody>
</table>

*Uaniso Fe = [U$_{11}$,U$_{22}$,U$_{33}$,U$_{12}$,U$_{13}$,U$_{23}$] = [4.0(2),1.9(2),1.7(1),0.5(2),0.4(2),0.4(2)]; Uaniso Ox = [U$_{11}$,U$_{22}$,U$_{33}$,U$_{12}$,U$_{13}$,U$_{23}$] = [7(1),15(1),8(1),10(1),0.00,0.00]

Table 2.S6 | Rietveld Refinement (298 K) of Fe$_2$(OH)$_2$(dobdc). Space group R-3, $a = 25.6191(2)$ Å, $c = 6.8042(1)$ Å, and $V = 3867.55(9)$ Å$^3$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occ.</th>
<th>U iso*100 (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.3897(1)</td>
<td>0.3512(1)</td>
<td>0.1540(4)</td>
<td>1.0</td>
<td>3.14*</td>
</tr>
<tr>
<td>O1</td>
<td>0.3222(4)</td>
<td>0.2967(4)</td>
<td>0.358(1)</td>
<td>1.0</td>
<td>2.6(2)</td>
</tr>
<tr>
<td>O2</td>
<td>0.3005(4)</td>
<td>0.2295(4)</td>
<td>0.596(1)</td>
<td>1.0</td>
<td>2.6(2)</td>
</tr>
<tr>
<td>O3</td>
<td>0.3553(4)</td>
<td>0.2736(4)</td>
<td>-0.004(2)</td>
<td>1.0</td>
<td>2.6(2)</td>
</tr>
<tr>
<td>C1</td>
<td>0.3167(8)</td>
<td>0.2473(7)</td>
<td>0.416(2)</td>
<td>1.0</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>C2</td>
<td>0.3265(6)</td>
<td>0.2051(7)</td>
<td>0.294(2)</td>
<td>1.0</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>C3</td>
<td>0.3431(6)</td>
<td>0.2219(7)</td>
<td>0.101(2)</td>
<td>1.0</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>C4</td>
<td>0.3488(6)</td>
<td>0.1815(7)</td>
<td>-0.039(2)</td>
<td>1.0</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>Ox</td>
<td>0.4528(5)</td>
<td>0.3489(6)</td>
<td>0.297(1)</td>
<td>1.0</td>
<td>12.2*</td>
</tr>
</tbody>
</table>

*Uaniso Fe = [U$_{11}$,U$_{22}$,U$_{33}$,U$_{12}$,U$_{13}$,U$_{23}$] = [4.4(2),1.8(2),1.5(1),0.3(2),0.5(2),-0.3(2)]; Uaniso Ox = [U$_{11}$,U$_{22}$,U$_{33}$,U$_{12}$,U$_{13}$,U$_{23}$] = [8(1),27(2),9(1),14(1),0.00,0.00]
### Table 2.S7 | EXAFS curve fitting parameters for Fe$_2$(dobdc) and comparison with bond lengths obtained by PXRD.

<table>
<thead>
<tr>
<th>Path</th>
<th>R (Å)</th>
<th>N</th>
<th>$\sigma^2 (\text{Å}^2)$</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PXRD</td>
<td>EXAFS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–O</td>
<td>2.10$^a$</td>
<td>2.06(1)</td>
<td>5</td>
<td>0.010(2)</td>
</tr>
<tr>
<td>Fe–C</td>
<td>3.05$^a$</td>
<td>3.07(5)</td>
<td>5</td>
<td>0.003(4)</td>
</tr>
<tr>
<td>Fe–Fe</td>
<td>3.00(2)</td>
<td>2.96(3)</td>
<td>2</td>
<td>0.010(6)</td>
</tr>
<tr>
<td>Fe–OC</td>
<td>3.23$^a$</td>
<td>3.22(8)</td>
<td>10</td>
<td>0.010(11)</td>
</tr>
</tbody>
</table>

Note: Bold numbers are fixed values. Numbers in parentheses show uncertainty. $^a$Averaged values.

### Table 2.S8 | EXAFS curve fitting parameters for 2 and comparison with bond lengths obtained by DFT (periodic PBE+U) and PXRD (100 K data). Note that although the PXRD and EXAFS are in good agreement overall, there are dissimilarities, especially in the Fe–O$_\text{axial}$ bond lengths for 2. This is because while EXAFS can be used to obtain first-shell distances with great accuracy, it is much more limited when resolution of different bond lengths is needed, especially when the scatterers have both a similar distance and atomic number, as is the case in 2.

<table>
<thead>
<tr>
<th>Path</th>
<th>R (Å)</th>
<th>N</th>
<th>$\sigma^2 (\text{Å}^2)$</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>PXRD</td>
<td>EXAFS</td>
<td></td>
</tr>
<tr>
<td>Fe–OH</td>
<td>1.84</td>
<td>1.92(1)</td>
<td>1.85(3)</td>
<td>1</td>
</tr>
<tr>
<td>Fe–O$_\text{eq}$</td>
<td>2.02$^a$</td>
<td>2.04$^a$</td>
<td>2.02(1)</td>
<td>4</td>
</tr>
<tr>
<td>Fe–O$_\text{ax}$</td>
<td>2.27</td>
<td>2.20(1)</td>
<td>2.33(4)</td>
<td>1</td>
</tr>
<tr>
<td>Fe–C</td>
<td>3.01$^a$</td>
<td>3.03$^a$</td>
<td>2.95(7)</td>
<td>5</td>
</tr>
<tr>
<td>Fe–Fe</td>
<td>3.23</td>
<td>3.16(1)</td>
<td>3.15(9)</td>
<td>2</td>
</tr>
<tr>
<td>Fe–O–C</td>
<td>3.19$^a$</td>
<td>3.21$^a$</td>
<td>3.16(14)</td>
<td>10</td>
</tr>
</tbody>
</table>

Bold numbers are fixed values.
Numbers in parentheses show uncertainty.
$^a$Averaged values.
### Table 2.S9 | Mössbauer spectral parameters.

| Sample                             | δ, mm/s       | |ΔE₀|, mm/s | Γ, mm/s   | Area (%) | Assignment          |
|------------------------------------|---------------|---------------|----------|----------|---------------------|------------------|
| Fe₂(OH)₂(dobdc) (1)               | 0.40(2)       | 0.96(1)       | 0.34(1)  | 80(2)    | Fe³⁺–OH             |
|                                    | 0.40(2)       | 1.80(6)       | 0.50(1)  | 13(2)    | Unknown Fe³⁺        |
|                                    | 1.21(6)       | 1.77(9)       | 0.57(15) | 7(2)     | Fe²⁺                |
| Fe₂(OH)₆(dobdc) (1')               | 0.44(2)       | 0.95(4)       | 0.41(4)  | 30(3)    | Fe³⁺–OH             |
|                                    | 1.08(1)       | 1.98(2)       | 0.44(3)  | 70(4)    | Fe²⁺                |
| Fe₀.₁Mg₁.₀(dobdc) (2)              | 1.08(1)       | 2.25(1)       | 0.31(2)  | 100      | Fe²⁺                |
| Fe₀.₁Mg₁.₀(dobdc) (after N₂O/C₂H₆ treatment) | 1.07(7) | 2.24(11)     | 0.34(12) | 11(3)    | Fe³⁺–OH             |

### Table 2.S10 | Unit cell parameters (298 K) of Fe₂(dobdc), FeₓMg₂₋ₓ(dobdc), and Mg₂(dobdc).

The unit cell constants and volumes of Fe₀.₁Mg₁.₀(dobdc) and Fe₀.₄₄Mg₁.₅₆(dobdc) are in between that of Fe₂(dobdc) and Mg₂(dobdc) and show a linear correlation with magnesium content, in agreement with Vegard’s Law for solid solutions.

<table>
<thead>
<tr>
<th></th>
<th>Fe₂(dobdc)</th>
<th>Fe₀.₄₄Mg₁.₅₆(dobdc)</th>
<th>Fe₀.₁Mg₁.₀(dobdc)</th>
<th>Mg₂(dobdc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>26.1603(10)</td>
<td>25.9964(8)</td>
<td>25.9485(9)</td>
<td>25.9111(20)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>6.8657(4)</td>
<td>6.8465(4)</td>
<td>6.8574(4)</td>
<td>6.8687(12)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>4069.1(3)</td>
<td>4007.1(4)</td>
<td>3998.7(3)</td>
<td>3993.7(7)</td>
</tr>
</tbody>
</table>
Table 2.S11 | Relative energies (kJ/mol)$^a$ and Mulliken atomic spin densities on Fe and O1$^b$ for 2 and 4. Full geometry optimizations were performed by periodic PBE+U for three possible spin states of each 2 and 4.

<table>
<thead>
<tr>
<th>Species</th>
<th>2S</th>
<th>Spin density on Fe</th>
<th>Spin density on O1</th>
<th>Fe–O1 Distance (Å)</th>
<th>Relative energy (kJ/(mol Fe))$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>1.09</td>
<td>0.00</td>
<td>1.81</td>
<td>149.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.34</td>
<td>−0.15</td>
<td>1.87</td>
<td>61.7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.31</td>
<td>0.23</td>
<td>1.84</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>1.64</td>
<td>113.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.51</td>
<td>0.46</td>
<td>1.62</td>
<td>76.7</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.42</td>
<td>0.33</td>
<td>1.64</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$ The lowest-energy spin state for each species has been taken as 0 reference.

$^b$ O1 is the terminal oxygen as shown in Figure 2.S19.
Table 2.S12 | Relative energies (kJ/mol)$^a$, $S$, $S^2$, and Mulliken spin densities on Fe and O1 for 2 and 4 cluster models. Single-point calculations were done on the 89- and 90-atom models using PBE/SDD(Fe, Zn), 6-311+G(2df,p)(C, H, O)//PBE/SDD(Fe, Zn),6-31G(d)(C, H, O).

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>Spin density</th>
<th>Relative energy (kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2M_S$</td>
<td>$S$</td>
<td>$S^2$</td>
</tr>
<tr>
<td>2 (cluster model)</td>
<td>1</td>
<td>0.67</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.52</td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.50</td>
<td>8.76</td>
</tr>
<tr>
<td>4 (cluster model)</td>
<td>0 (open shell)</td>
<td>0.79</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.06</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.01</td>
<td>6.06</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.01</td>
<td>12.01</td>
</tr>
</tbody>
</table>

$^a$Relative energy is computed with respect to the most stable spin state.

Table 2.S13 | Relative energies (kJ/mol)$^a$, $S$, $S^2$, and Mulliken spin densities on Fe and O1 for 2 and 4 cluster models. Single-point calculations were done on the 89- and 90-atom models using M06/SDD(Fe, Zn), 6-311+G(2df,p)(C, H, O)//M06-L/SDD(Fe, Zn),6-31G(d)(C, H, O).

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>Spin density</th>
<th>Relative energy (kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2M_S$</td>
<td>$S$</td>
<td>$S^2$</td>
</tr>
<tr>
<td>2 (cluster model)</td>
<td>1</td>
<td>0.85</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.53</td>
<td>3.87</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.50</td>
<td>8.76</td>
</tr>
<tr>
<td>4 (cluster model)</td>
<td>0 (open shell)</td>
<td>0.99</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.24</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.05</td>
<td>6.28</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.00</td>
<td>12.03</td>
</tr>
</tbody>
</table>

$^a$Relative energy is computed with respect to the most stable spin state.
Table 2.S14 | Relative energies (kJ/mol)$^a$, $S$, $S^2$, and Mulliken spin densities on Fe and O1 for 2 and 4 cluster models. Single-point calculations were done on the 89- and 90-atom models using M08-SO/SDD(Fe, Zn),6-311+G(2df,p)(C, H, O)//M06-L/SDD(Fe, Zn),6-31G(d)(C, H, O).

<table>
<thead>
<tr>
<th>Species State</th>
<th>$2M_S$</th>
<th>$S$</th>
<th>$S^2$</th>
<th>$S_{Fe}$</th>
<th>$S_{O1}$</th>
<th>Relative energy (kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (cluster model)</td>
<td>1</td>
<td>1.01</td>
<td>2.02</td>
<td>1.02</td>
<td>0.01</td>
<td>115.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.51</td>
<td>3.79</td>
<td>2.98</td>
<td>-0.07</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.50</td>
<td>8.76</td>
<td>4.37</td>
<td>0.33</td>
<td>0.0</td>
</tr>
<tr>
<td>4 (cluster model)</td>
<td>0 (open shell)</td>
<td>1.03</td>
<td>2.09</td>
<td>-0.99</td>
<td>1.02</td>
<td>124.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.31</td>
<td>3.03</td>
<td>2.78</td>
<td>-0.87</td>
<td>86.8</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.06</td>
<td>6.29</td>
<td>3.73</td>
<td>-0.13</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.00</td>
<td>12.02</td>
<td>4.28</td>
<td>1.34</td>
<td>55.3</td>
</tr>
</tbody>
</table>

$^a$Relative energy is computed with respect to the most stable spin state.

Table 2.S15 | Relative energies (kJ/mol)$^a$, $S$, $S^2$, and Mulliken spin densities on Fe and O1 for 2 and 4 cluster models. Single-point calculations were done on the 89- and 90-atom models using MPW1B95/SDD(Fe, Zn), 6-311+G(2df, p)(C, H, O)//M06-L/SDD(Fe, Zn), 6-31G(d)(C, H, O).

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>$2M_S$</th>
<th>$S$</th>
<th>$S^2$</th>
<th>$S_{Fe}$</th>
<th>$S_{O1}$</th>
<th>Relative energy (kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (cluster model)</td>
<td>1</td>
<td>0.60</td>
<td>0.96</td>
<td>1.04</td>
<td>0.06</td>
<td>143.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.53</td>
<td>3.88</td>
<td>3.07</td>
<td>-0.13</td>
<td>80.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.50</td>
<td>8.76</td>
<td>4.34</td>
<td>0.29</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>4 (cluster model)</td>
<td>0 (open shell)</td>
<td>0.80</td>
<td>1.44</td>
<td>0.72</td>
<td>-0.61</td>
<td>141.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.24</td>
<td>2.79</td>
<td>2.87</td>
<td>-0.58</td>
<td>96.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.06</td>
<td>6.29</td>
<td>3.69</td>
<td>0.14</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.00</td>
<td>12.02</td>
<td>4.21</td>
<td>1.20</td>
<td>45.3</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Relative energy is computed with respect to the most stable spin state.
Table 2.S16 | Relative energies (kJ/mol)$^a$, $S$, $S^2$, and Mulliken spin densities on Fe and O1 for 2 and 4 cluster models. Single-point calculations were done on the 89- and 90-atom models using PW6B95/SDD(Fe, Zn), 6-311+G(2df, p)(C, H, O)//M06-L/SDD(Fe, Zn), 6-31G(d)(C, H, O).

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>Spin density</th>
<th>Relative energy (kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2M_S$</td>
<td>$S$</td>
<td>$S^2$</td>
</tr>
<tr>
<td>2 (cluster model)</td>
<td>1</td>
<td>0.60</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.53</td>
<td>3.87</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.50</td>
<td>8.76</td>
</tr>
<tr>
<td>0 (open shell)</td>
<td>2</td>
<td>1.23</td>
<td>2.74</td>
</tr>
<tr>
<td>4 (cluster model)</td>
<td>4</td>
<td>2.05</td>
<td>6.25</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.00</td>
<td>12.03</td>
</tr>
</tbody>
</table>

$^a$Relative energy is computed with respect to the most stable spin state.
Table 2.S17 | Calculated relative energies (kJ/mol) for N₂O bound to the Fe(II) site of the 88-atom cluster. The relative energies of η¹-N and η¹-O coordination modes are computed using M06-L and M06 density functionals with the def2-TZVP and SDD(Fe, Zn), 6-31G(d)(C, H, O, N) basis sets. The level of optimization is opt6.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Binding mode</th>
<th>SDD(Fe, Zn), 6-31G(d)(C, H, O, N)</th>
<th>def2-TZVP</th>
</tr>
</thead>
<tbody>
<tr>
<td>M06-L</td>
<td>η¹-O</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>η¹-N</td>
<td>-4.6</td>
<td>-9.5</td>
</tr>
<tr>
<td>M06</td>
<td>η¹-O</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>η¹-N</td>
<td>1.1</td>
<td>-4.5</td>
</tr>
</tbody>
</table>

Table 2.S18 | State energy splitting of 2 and 4 cluster models calculated by CASSCF and CASPT2.

<table>
<thead>
<tr>
<th>Species</th>
<th>2Mₛ</th>
<th>Largest CASSCF configuration weight</th>
<th>$M^a$</th>
<th>Relative CASSCF energy (kJ/mol)</th>
<th>Relative CASPT2 energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (cluster model)</td>
<td>1</td>
<td>94%</td>
<td>0.102</td>
<td>328.4</td>
<td>294.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>79%</td>
<td>0.309</td>
<td>216.7</td>
<td>145.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>100%</td>
<td>0.000</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4 (cluster model)</td>
<td>0</td>
<td>77%</td>
<td>0.272</td>
<td>210.5</td>
<td>249.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>74%</td>
<td>0.306</td>
<td>139.3</td>
<td>127.6</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>77%</td>
<td>0.311</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$M is a diagnostic used to quantify the extent of multireference character of the system, and it is defined to be

$$M = \frac{1}{2} \left( 2 - n(MCDONO) + \sum_{j=1}^{n_{SOMO}} |n(j) - 1| + n(MCUNO) \right)$$

where $n(MCDONO)$, $n_{SOMO}$, and $n(MCUNO)$ are the most correlated doubly occupied natural orbital, a singly occupied natural orbital, and the most correlating unoccupied natural orbital, respectively.
Table 2.S19 | Charge and spin densities of the sextet and quintet ground spin states of the cluster models of 2 and 4 from CASSCF calculations.

<table>
<thead>
<tr>
<th></th>
<th>2 (cluster model)</th>
<th>4 (cluster model)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>O1</td>
</tr>
<tr>
<td>CASSCF Mulliken Spin Density</td>
<td>4.79</td>
<td>0.07</td>
</tr>
<tr>
<td>CASSCF Mulliken Charge Density</td>
<td>1.95</td>
<td>–0.77</td>
</tr>
<tr>
<td>CASSCF LoProp Charge Density</td>
<td>2.21</td>
<td>–1.09</td>
</tr>
</tbody>
</table>

Table 2.S20 | Relative energies (kJ/mol), , , and Mulliken spin densities on Fe and O1 for the cluster model of 4 and the cluster model of 4 with Zn(II) replacing Mg(II). All calculations were done using M06-L/SDD(Fe, Zn), 6-31G(d)(C, H, O, Mg)/opt6.

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>Spin density</th>
<th>Fe–O1 (Å)</th>
<th>Relative energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (cluster model</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with Zn(II))</td>
<td>2</td>
<td>0.77</td>
<td>1.36</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>1.15</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (cluster model</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with Mg(II))</td>
<td>2</td>
<td>0</td>
<td>0.78</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>1.17</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*MRelative energy is computed with respect to the most stable spin state.

Table 2.S21 | Relative energies (kJ/mol), , , and Mulliken spin densities on Fe and O1 for the cluster model of 4 and the cluster model of 4 with Zn(II) replacing Mg(II). All calculations were done using M06/SDD(Fe, Zn), 6-31G(d)(C, H, O, Mg)/opt6.

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>Spin density</th>
<th>Fe–O1 (Å)</th>
<th>Relative energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (cluster model</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with Zn(II))</td>
<td>2</td>
<td>0</td>
<td>0.86</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>1.27</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (cluster model</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with Mg(II))</td>
<td>2</td>
<td>0</td>
<td>0.91</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>1.29</td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*MRelative energy is computed with respect to the most stable spin state.
Table 2.S22 | Binding energies$^a$ (kJ/mol) of η$^1$-N and η$^1$-O coordination modes of N$_2$O bound to the iron(II) site of the 88-atom cluster. The calculations were done using M06-L and M06 density functionals with SDD(Fe, Zn), 6-31G(d)(C, H, O, N) basis set. The level of optimization is opt6.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Binding mode</th>
<th>Binding energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M06-L</td>
<td>η$^1$-O</td>
<td>41.4</td>
</tr>
<tr>
<td></td>
<td>η$^1$-N</td>
<td>46.1</td>
</tr>
<tr>
<td>M06</td>
<td>η$^1$-O</td>
<td>45.6</td>
</tr>
<tr>
<td></td>
<td>η$^1$-N</td>
<td>44.5</td>
</tr>
</tbody>
</table>

$^a$Binding Energy = $E$(cluster) + $E$(N$_2$O) – $E$(complex)

Table 2.S23 | Natural bond analysis of η$^1$-N and η$^1$-O coordination modes of N$_2$O bound to the iron(II) site of the 88-atom cluster.

<table>
<thead>
<tr>
<th>Binding mode</th>
<th>% Back-bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>η$^1$-O</td>
<td>42%</td>
</tr>
<tr>
<td>η$^1$-N</td>
<td>43%</td>
</tr>
</tbody>
</table>
4. Supplementary Figures

Figure 2.S1 | *In situ* transmission-mode FTIR spectra of Fe₂(dobdc) demonstrating reversible N₂O binding at room temperature. **a.** FTIR spectra of Fe₂(dobdc) outgassed at room temperature 2 h (black curve) and activated at 433 K for 18 h (red curve) and in contact with 40 mbar of N₂O at room temperature (blue curve). The spectrum of the activated sample clearly shows the disappearance of all features associated with methanol, with all other bands unchanged. **b.** FTIR spectra (background subtracted) in the 2280–2160 cm⁻¹ spectral range of Fe₂(dobdc) in contact with 40 mbar of N₂O (blue curve) and following progressive desorption at room temperature (light grey curves). A clear maximum is seen at 2226 cm⁻¹. The dotted blue line represents the spectrum of 40 mbar of gaseous N₂O in the same spectral range.
Figure 2.S2 | Rietveld refinement (10 K) of bare Fe$_2$(dobdc). Neutron powder diffraction data obtained from bare Fe$_2$(dobdc) at 10 K. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.
Figure 2.S3 | Rietveld refinement (10 K) of Fe$_2$(dobdc)(N$_2$O)$_{0.7}$. Neutron powder diffraction data obtained from Fe$_2$(dobdc) loaded with approximately 0.35 N$_2$O per Fe$^{2+}$. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns. The data were collected at 10 K.
Figure 2.S4 | Rietveld refinement (10 K) of Fe₂(dobdc)(N₂O)₁₂. Neutron powder diffraction data obtained from Fe₂(dobdc) loaded with approximately 0.6 N₂O per Fe²⁺. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.
Figure 2.S5 | Rietveld refinement (10 K) of Fe$_2$(dobdc)(N$_2$O)$_{2.5}$. Neutron powder diffraction data obtained from Fe$_2$(dobdc) loaded with approximately 1.25 N$_2$O per Fe$^{2+}$. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns. The data were collected at 10 K.
Figure 2.S6 | Fourier difference map of Fe₂(dobdc)(N₂O)₀.₆. Fourier Difference Map of data obtained from Fe₂(dobdc) loaded with 0.35 N₂O per Fe²⁺. Yellow globules represent excess scattering density in the channels of the framework that result from N₂O molecules binding at the Fe²⁺ site.
Figure 2.7 | Fourier difference map of Fe\textsubscript{2}(dobdc)(N\textsubscript{2}O)\textsubscript{2.5}. Fourier Difference Map of data obtained from Fe\textsubscript{2}(dobdc) loaded with 1.25 N\textsubscript{2}O per Fe\textsuperscript{2+}. Yellow globules represent excess scattering density in the channels of the framework that result from N\textsubscript{2}O molecules binding at the Fe\textsuperscript{2+} site. There is a slight rearrangement from the site I N\textsubscript{2}O orientation, denoted site Ia, upon population of the secondary adsorption site.
Figure 2.8 | *In situ* transmission-mode FTIR spectra of Fe$_2$(dobdc) (green) and Fe$_2$(OH)$_2$(dobdc) (red). A thin film of Fe$_2$(dobdc) was activated at 433 K for 18 h (red curve), in contact with 180 mbar of N$_2$O at room temperature (blue curve) and heated at 60 °C for 14 hours (green curve). Inset (a): background subtracted spectra illustrating the $\nu$(N–N) region and inset (b) magnification of 730–610 cm$^{-1}$ spectral range, testifying the formation of Fe$_2$(OH)$_2$(dobdc).
Figure 2.S9 | CO titration experiments before and after heating Fe$_2$(dobdc) in the presence of N$_2$O. a. CO dosed on an activated sample of bare Fe$_2$(dobdc). b. CO dosed on a sample that has contacted N$_2$O at room temperature for one day, and then overnight at 60 °C shows that the number of open Fe(II) sites has been reduced dramatically (less than 10% remaining).
Figure 2S10 | ATR-FTIR spectra of Fe$_2$(OH)$_{0.6}$(dobdc) (black) and Fe$_2$(OH)$_{0.6}$(dobdc) (dotted red).
Figure 2.11 | N₂ Adsorption isotherm in Fe₂(OH)₂(dobdc) at 77 K.
Figure 2.S12 | BET plot of the N$_2$ adsorption isotherm in Fe$_2$(OH)$_2$(dobdc) at 77 K. The black line represents a linear best fit of the data points (red circles). Inset: parameters for the linear best fit and resulting constants for calculation of the BET surface area.
Figure 2.S13 | Rietveld refinement (100 K) of Fe$_2$(OH)$_2$(dobdc). X-ray powder diffraction data obtained from a sample of Fe$_2$(OH)$_2$(dobdc). The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns. The data were collected at 100 K.
Figure 2.S14 | Rietveld refinement (298 K) of Fe$_2$(OH)$_2$(dobdc). X-ray powder diffraction data obtained from a sample of Fe$_2$(OH)$_2$(dobdc). The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns. The data were collected at 298 K.
Figure 2.S15 | Unit cell of Fe$_{0.1}$Mg$_{1.9}$(dobdc). X-ray powder diffraction data obtained from a sample of Fe$_{0.1}$Mg$_{1.9}$(dobdc). $a = 25.9485(9)$ Å, $c = 6.8574(4)$ Å, and $V = 3998.7(3)$ Å$^3$. The crosses and red line represent the experimental and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns. The data were collected at 298 K.
Figure 2.S16 | N₂ adsorption isotherm in Fe₀.₁Mg₁.₉(dobdc) at 77 K.
Figure 2.S17 | BET plot of the N$_2$ adsorption isotherm in Fe$_{0.1}$Mg$_{1.9}$(dobdc) at 77 K. The black line represents a linear best fit of the data points (green circles). Inset: parameters for the linear best fit and resulting constants for calculation of the BET surface area.
Figure 2.18 | Powder X-ray diffraction patterns for Fe$_{0.1}$Mg$_{1.9}$(dobdc) before (green) and after (red) N$_2$O/ethane treatment.
Figure 2.819 | Wireframe representation of the cluster model for 4 (89-atom cluster model). Highlighted in ball and stick, the Fe atom and its first coordination sphere and the Zn centers. The 90-atom cluster model for 2 is similar, except O1 is replaced with an OH. Color code: orange, Fe; blue, Zn; red, O; grey, C and white, H.
Figure 2.S20 | Comparison of the experimental and theoretical structures of the N$_2$O adducts of Fe$_2$(dobdc). **a.** $\eta^1$-O coordination of the N$_2$O molecule. **b.** $\eta^1$-N coordination of the N$_2$O molecule. All distances are in Å and all angles are in degrees. Color code: blue, N; red, O; yellow, Fe (experiment) or purple, Fe (theory).
Figure 2S21 | ¹H NMR spectra of products extracted from the reaction of Fe₂(dobdc) with N₂O and ethane. An N₂O:ethane:argon mixture (10:25:65) was flowed over a packed bed of Fe₂(dobdc) heated to 75 °C. The products were extracted with CD₃CN, and contain a mixture of ethanol, acetaldehyde, diethyl ether, water, as well as other unidentified products. Ethanol, acetaldehyde, diethyl ether, and water are labeled in the spectra with red stars, blue stars, green stars, and black squares, respectively.
Figure 2. $^1$H NMR spectra of products extracted from the reaction of Fe$_{0.1}$Mg$_{1.9}$(dobdc) with N$_2$O and ethane. An N$_2$O:ethane:argon mixture (10:25:65) was flowed over a packed bed of Fe$_{0.1}$Mg$_{1.9}$(dobdc) heated to 75 °C. The products were extracted with CD$_3$CN, and contain a mixture of ethanol and acetaldehyde (labeled in the spectra with a red and blue stars, respectively). The spectra also show a small amount of methanol (black circle), which is residual solvent from the framework synthesis. The internal standard, 1,4-dichlorobenzene, is labeled with a black triangle, and H$_2$O is labeled with a black square.
Chapter 3: Pore environment effects on catalytic cyclohexane oxidation in expanded Fe₄(dobdc) analogues

3.1. Introduction

The strategic placement of noncovalent interactions around a catalytic center can lead to marked increases in selectivity, activity, and stability. First discovered in enzymes, this principle has been subsequently explored in a wide range of molecular, supramolecular, and heterogeneous systems. Bio-inspired design elements such as distal hydrogen bond donors, hydrophobic binding cavities, and confined environments have been incorporated into catalysts for natural product synthesis, small molecule activation, and hydrocarbon cracking. While these examples highlight the importance of functional outer coordination spheres in metal-mediated reactions, precise control over the periphery of an active site remains synthetically challenging in non-biological systems. Often, the most readily modifiable peripheral parameter is the reaction medium, which has been shown to play a significant role in determining reaction outcomes. In zeolites, an additional set of tunable parameters includes the physical dimensions and geometries of the pores, leading to size- and shape-selective catalysis. The hydrophobicity of zeolites can also be controlled by varying the Si/Al ratio and number of hydroxyl defects, guiding selectivity in cases where reactants or products possess large polarity differences. However, the small pores of zeolites, typically less than 1 nm in diameter, restrict further functionalization of the interior surface. Ordered mesoporous silicates possess larger pores and hydroxyl moieties that can be post-synthetically modified, but their surfaces are locally inhomogeneous and poorly defined.

Metal–organic frameworks, a class of highly crystalline solids displaying micro- and mesoporosity, are an intriguing platform for systematically evaluating the effects of pore size, shape, and chemical environment on the behavior of a supported catalyst. Tailored pore environments that maximize favorable noncovalent interactions between the framework surface and specific guest molecules can be readily engineered, and are routinely exploited for selective gas separation and storage applications. Highly complex pore interiors containing multiple functional groups in crystallographically or spectroscopically well-defined arrangements have been achieved in certain structure types. In addition to coordinatively unsaturated metal nodes, a variety of organic, organometallic, and nanoparticle moieties can also be installed within metal–organic frameworks, forming structurally well-defined active sites that, in certain cases, can even be characterized by single crystal X-ray diffraction. Taken together, these findings suggest that the nature of a catalytic center and its spatial organization, the identity and placement of surrounding surface functionalities, and the overall pore architecture can all be manipulated with Ångström-level precision in metal–organic frameworks.

A common outer coordination sphere motif in metalloenzymes, particularly in the context of hydrocarbon oxidation and metal–oxo chemistry, is the presence of a hydrophobic binding pocket near the transition-metal active site. In the field of homogeneous supramolecular catalysis, cyclodextrins, cyclophanes, and other container-shaped molecules have all been investigated as model substrate binding pockets. These hydrophobic cavities shelter reactive intermediates from unwanted side-reactions, enhance reaction rates due to favorable substrate binding properties, and guide regio- and stereoselectivity when complex organic substrates such as steroids are introduced. Furthermore, by selectively increasing the local concentration of a substrate, hydrophobic cavities can also minimize undesirable over-oxidation processes.
anticipated that many of these attractive bio-inspired features can be replicated and even expanded upon in metal–organic frameworks featuring exposed redox-active transition metal sites and modifiable pore walls.

Here, the effect of a local hydrophobic environment on product selectivity and catalyst stability is investigated with respect to cyclohexane oxidation in the expanded analogues of \( \text{Fe}_2(\text{dobdc}) \) (\( \text{dobdc}^{4-} = 2,5\text{-dioxido-1,4-benzenedicarboxylate} \)), a metal–organic framework featuring exposed Fe(II) sites. A three-fold enhancement of the alcohol:ketone (A:K) ratio and an order of magnitude increase in turnover number can be achieved by simply altering the framework pore diameter and installing nonpolar, hydrophobic functional groups near the iron center. Detailed Mössbauer, kinetic isotope effect, and gas sorption studies suggest that the selectivity enhancement is due to the ability of the hydrophobic functional groups to increase the local concentration of cyclohexane near the iron–oxo intermediate.

### 3.2. Experimental

#### 3.2.1. Framework syntheses

Inside a \( \text{N}_2 \)-filled glovebox, \( \text{H}_4(\text{dotpdc}) \) (60 mg, 0.17 mmol, 1.0 eq.), \( \text{FeCl}_2 \) (60 mg, 0.47 mmol, 2.8 eq.), DMF (8 mL), and MeOH (1 mL) were combined in a 20 mL scintillation flask. The vial was sealed with a Teflon-lined cap and heated to 140 °C for 2 days. The resulting precipitate was filtered, washed with DMF (3 x 10 mL at 120 °C) and MeOH (3 x 10 mL at 60 °C), and dried under vacuum at 120 °C for two hours. To exchange the bound methanol molecules for \( \text{CD}_3\text{CN} \), the powder was immersed in 0.5 mL of \( \text{CD}_3\text{CN} \) and exposed to vacuum at 120 °C for another two hours, affording \( \text{Fe}_2(\text{dotpdc})\cdot2\text{CD}_3\text{CN} \) as a yellow-green powder (66 mg, 70% yield). \( \text{Fe}_2(\text{dotpdc})\cdot2\text{CD}_3\text{CN} \), \( \text{Fe}_2(\text{dotpdc})\cdot\text{CH}_3\cdot2\text{CD}_3\text{CN} \), and \( \text{Fe}_2(\text{dotpdc})\cdot\text{tBu}\cdot2\text{CD}_3\text{CN} \) were synthesized in a similar manner.

**Anal. Calc. for \( \text{C}_{24}\text{H}_{10}\text{D}_6\text{Fe}_2\text{N}_2\text{O}_6 \):** C, 52.78; H, 2.95; N, 5.13. Found: C, 52.69; H, 2.55; N, 4.60. IR (solid-ATR): 1615(s), 1553(s), 1541(s), 1519(s), 1466(s), 1432(s), 1399(s), 1380(m), 1303(s), 1235(s), 1146(m), 1104(m), 1052(m), 900(m), 821(s), 724(s), 657(s), 612(s), 580(m).

#### 3.2.2. Catalytic cyclohexane oxidation procedure

General catalytic conditions to determine A:K ratios are as follows: cyclohexane (0.3 mL, 2.8 mmol) and \( \text{CD}_3\text{CN} \) (1.0 mL) were added to a 20 mL scintillation vial containing 5.0 mg of framework (acetonitrile-solvated form, \( \text{Fe}_2(\text{dotpdc})\cdot2\text{CD}_3\text{CN} \)). In a separate vial, 25 mg of \( \text{tBuSO}_2\text{PhIO} \) (0.073 mmol) was combined with 1.0 mL of \( \text{CD}_3\text{CN} \) to form a partially dissolved slurry. This slurry was added to the framework and the combined reaction was stirred vigorously at room temperature. After 1.5 h,
the reaction was stopped, the framework was removed by filtration, and the products were analyzed by $^1$H NMR using 1,4-dichlorobenzene as an internal standard. To determine maximum turnover numbers, the same conditions were used but with 2.5 mg of framework and slightly larger quantities of oxidant (25 to 75 mg). Each reaction was run in triplicate to obtain standard deviations. The overall yields ($A + 2K$, where $A$ and $K$ are cyclohexanol and cyclohexanone, respectively) were calculated based on the amount of oxidant consumed.

3.2.3. Solution-phase cyclohexane adsorption studies. In a 20 mL scintillation vial, 25 mg of Fe$_2$(dotpdc$^R$)$_2$CD$_3$CN was immersed in 1 mL of 1M cyclohexane in acetonitrile. The framework and solution were allowed to sit at room temperature for four hours, after which a small aliquot of the supernatant was removed and filtered to remove framework particles. The concentration of cyclohexane and acetonitrile in this aliquot was analyzed by gas chromatography using 1,4-dichlorobenzene as an internal standard. Each experiment was run in triplicate. The cyclohexane adsorption capacity (mol/mol) was determined according to eq 1.

$$q_t = \frac{(C_i - C_f)V}{m}$$ \hspace{1cm} (1)

In this equation, $q_t$ is the amount of cyclohexane adsorbed at time $t$ (mol/mol framework); $C_i$ is the initial concentration of the adsorbate (mol/L); $C_f$ is the final concentration after adsorption (mol/L); and $m$ is the amount of adsorbent added (mol).

3.2.4. Gas-phase cyclohexane adsorption studies. For all gas adsorption measurements 50–100 mg of Fe$_2$(dotpdc$^R$)$_2$DMF were transferred to a preweighed glass sample tube under an atmosphere of nitrogen and capped with a Transeal. Samples were then transferred to a Micrometerics ASAP 2020 gas adsorption analyzer and heated under dynamic vacuum at 140 °C until the outgas rate at the degassing temperature was less than 2 µbar/min, and were subsequently weighed to determine the mass of sample. Cyclohexane (dried over molecular sieves) was attached to the vapor-dosing manifold of the instrument, and freeze-pump-thawed three times. In between each isotherm, the material was re-activated by heating the sample to 140 °C overnight or until the outgas rate at the degassing temperature was less than 2 µbar/min.

3.2.5. Isotherm fitting. Adsorption isotherms for cyclohexane in Fe$_2$(dotpdc$^R$) were fit with a dual-site Langmuir-Freundlich equation (eq 2), where $n$ is the total amount adsorbed in mmol/g, $P$ is the pressure in bar, $n_{sat,i}$ is the saturation capacity in mmol/g, and $b_i$ is the Langmuir parameter in bar$^{-1}$, and $v_i$ is the Freundlich parameter.

$$n = \frac{n_{sat,1}b_1P^{v_1}}{1 + b_1P^{v_1}} + \frac{n_{sat,2}b_2P^{v_2}}{1 + b_2P^{v_2}}$$ \hspace{1cm} (2)

3.2.6. Isosteric heat of adsorption calculations. Using the Langmuir fits, the isosteric heat of adsorption, $Q_{st}$, can be calculated as a function of the total amount of gas adsorbed, $n$, by using the integrated form of the Clausius–Clapeyron equation (eq 3).

$$(\ln P)_n = \left(\frac{Q_{st}}{R}\right)\left(\frac{1}{T}\right) + C$$ \hspace{1cm} (3)

For example, the cyclohexane Langmuir-Freundlich fits for Fe$_2$(dotpdc) were used to obtain the exact pressures that correspond to specific loadings at 25, 35, and 45 °C. This was done at
loading intervals of 0.1 mmol/g. At each loading, the slope of ln($P$) versus $1/T$ was calculated to obtain the isosteric heat.

3.3. Results and Discussion

First studied in the context of $O_2/N_2$ separations, Fe$_2$(dobdc) (also known as Fe-MOF-74) is a functionally versatile metal–organic framework displaying exceptional performance in applications ranging from olefin/paraffin separations to gradual NO release for biomedical purposes.$^{22,23}$ This versatility is due to the high density of coordinatively-unsaturated Fe(II) sites within the framework, which line the hexagonal pores and are both Lewis acidic as well as redox-active (Figure 3.1). Recently, we discovered that Fe$_2$(dobdc) and its magnesium-diluted analogues also show promise as catalysts for hydrocarbon oxidation processes, converting ethane into ethanol and acetaldehyde in the presence of $N_2O$ as the terminal oxidant.$^{24}$ Detailed computational studies support a high-spin, $S = 2$ iron(IV)–oxo intermediate, which hydroxylates ethane via a radical-rebound mechanism.$^{25}$

Our initial report emphasized the unusual primary coordination environment of the iron sites in Fe$_2$(dobdc), and its role in stabilizing the high-spin electronic structure of the iron–oxo unit. However, pore-expanded analogues of this material are also uniquely suited for exploring outer coordination sphere effects on metal site reactivity. First, framework interpenetration in this structure type is impossible, allowing the pore diameter to be increased at will. This concept was originally illustrated in the syntheses of mesoporous Mg$_2$(dobdc) analogues, with pore diameters ranging from 14 to 98 Å (denoted IRMOF-74-II through XI).$^{26}$ Furthermore, once the organic linker is expanded to three phenylene units and larger, a wide variety of organic substituents can be accommodated on the central rings without adversely affecting framework formation. The incorporation of such ligands directly during framework synthesis leads to pores coated with specifically chosen organic functionalities in crystallographically well-defined locations, whose properties (polarity, proticity, basicity) can be vastly different from the bulk reaction medium. The pore surface can also be chemically modified after synthesis, and post-synthetic incorporation of enzyme-like peptide chains has been recently demonstrated in IRMOF-74-III.$^{27}$ Leveraging these unique properties of the MOF-74 structure type, we sought to uncover the effect of pore diameter and chemical environment on the catalytic behavior of exposed iron sites in Fe$_2$(dobdc) and its related analogues.

3.3.1. Synthesis of expanded Fe$_2$(dobdc) derivatives. The two- and three-phenylene ring versions of Fe$_2$(dobdc), abbreviated Fe$_2$(dobpdc) (H$_4$dobpdc = 4,4’-dihydroxy-[1,1’-biphenyl]-3,3’-dicarboxylic acid) and Fe$_2$(dotpdc) (H$_4$dotpdc = 4,4”-dihydroxy-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylic acid), respectively, can be synthesized solvothermally to produce a series of frameworks possessing systematically increasing pore sizes of 8, 19, and 27 Å (see Figure 3.1). Note that these pore size distributions are calculated experimentally from 77 K $N_2$ adsorption isotherms using DFT methods, and are slightly less than the corresponding crystallographic pore diameters. The Brunauer–Emmett–Teller (BET) surface areas for Fe$_2$(dobdc), Fe$_2$(dobpdc), and Fe$_2$(dotpdc) are 1360, 2610, and 1970 m$^2$/g, respectively.$^{22,28}$ Within a single hexagonal channel, the closest distance between iron sites lies down the c-axis and is independent of linker length (roughly 6.8–6.9 Å in all three frameworks). Therefore, this series primarily investigates the effect of an enlarged pore diameter, with other variables such as spatial separation of active sites and pore chemical environment held relatively constant.
Figure 3.1. Structures of Fe$_2$(dobdc), Fe$_2$(dobpdc), Fe$_2$(dotpdc) and their corresponding ligands. Structures of Fe$_2$(dobdc), Fe$_2$(dobpdc), Fe$_2$(dotpdc) and their corresponding ligands. (a) View of the 1-dimensional hexagonal pores of Fe$_2$(dobdc); inset shows the local coordination environment around each coordinatively unsaturated Fe(II) site. The pore sizes shown here are calculated experimentally from 77 K N$_2$ adsorption isotherms using DFT methods.

3.3.2. Role of pore diameter on cyclohexane oxidation. In order to probe the effect of pore diameter on oxidation catalysis, solution-phase cyclohexane oxidation was investigated in Fe$_2$(dobdc), Fe$_2$(dobpdc), and Fe$_2$(dotpdc) as a representative reaction. Note that t-BuSO$_2$PhIO, a soluble iodosylarene reagent commonly used to generate metal–oxo intermediates, serves as the O-atom transfer reagent and terminal oxidant in these reactions. Deuterated acetonitrile and an excess of cyclohexane were used to minimize possible solvent C–H activation side reactions. Several important conclusions can be drawn from the results of cyclohexane oxidation in Fe$_2$(dobdc), Fe$_2$(dobpdc), and Fe$_2$(dotpdc) (summarized in Table 3.1). First, only framework decomposition and leaching of Fe$^{3+}$ cations was observed in the parent framework Fe$_2$(dobdc), with no detectable cyclohexane conversion. As a bulky oxidant with an approximate van der Waals volume of 221 Å$^3$, t-BuSO$_2$PhIO likely cannot fit into the small channels of Fe$_2$(dobdc). This result provides evidence that the surface sites of Fe$_2$(dobdc), and therefore those of the expanded analogues, are not catalytically active. Diffusion limitations of t-BuSO$_2$PhIO and cyclohexane through the pores of Fe$_2$(dobpdc) may also explain why its turnover number (TON) is an order of magnitude lower than that of Fe$_2$(dotpdc) (0.3 versus 4). In contrast to the results obtained for Fe$_2$(dobdc), metal leaching was not observed for catalytic reactions conducted in the terphenyl derivative Fe$_2$(dotpdc) under these conditions. Furthermore, removal of the framework
by filtration and subsequent addition of oxidant revealed no product formation occurs in the absence of Fe₂(dotpdc).

### Table 3.1. Summary of cyclohexane oxidation results in Fe₂(dobdc), Fe₂(dobpdc), and Fe₂(dotpdc).

<table>
<thead>
<tr>
<th>Framework</th>
<th>A:K</th>
<th>Yield (%)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂(dobdc)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fe₂(dobpdc)²⁴</td>
<td>3.5(1)</td>
<td>54(4)</td>
<td>0.3(1)</td>
</tr>
<tr>
<td>Fe₂(dotpdc)</td>
<td>2.8(1)</td>
<td>76(6)</td>
<td>4(1)</td>
</tr>
</tbody>
</table>

General conditions: 5.0 mg of acetonitrile-solvated framework, 25 mg of oxidant (0.073), 0.30 mL of cyclohexane (2.8 mmol), and 2.0 mL of CD₃CN. ²⁴ Ratio of cyclohexanol (A) to cyclohexanone (K). ²⁵ Moles of product formed per mole of oxidant consumed. Note that cyclohexanone requires two oxidizing equivalents to form. ²⁶ Catalytic turnovers, moles of product per mole of iron in catalyst. ²⁷ 25 mg of framework were used to obtain these results; otherwise, significant framework decomposition and Fe leaching was observed.

While gas-phase oxidation of ethane by Fe₂(dobdc) forms a complex mixture of over-oxidation products and ether oligomers, presumably due to side-reactions of an ethyl radical intermediate,⁴¹ Fe₂(dotpdc) produces cyclohexanol and cyclohexanone as the sole cyclohexane-derived oxidation products in high yield. For reasons that have yet to be conclusively determined, but may be related to the presence of an acetonitrile solvent cage,³¹ the solution-phase cyclohexyl radical intermediate (and, in the case of cyclohexanone formation, the 1-cyclohexanolyl radical intermediate) appears much more well-behaved.

Finally, modest alcohol:ketone (A:K) ratios of 3.5:1 and 2.8:1 are observed for Fe₂(dobpdc) and Fe₂(dotpdc), respectively. These ratios reveal that significant oxidation of the product cyclohexanol to cyclohexanone occurs despite the large excess of cyclohexane present under the reaction conditions. Because the formation of cyclohexanone likely proceeds by oxidation of initially formed cyclohexanol, these modest selectivities can be rationalized by considering the preference of the framework interior, which is lined with Lewis acidic metal sites and carboxylate/aryloxide moieties, for polar adsorbates such as cyclohexanol. Thus, we sought to investigate whether this inherent bias could be suppressed through the introduction of nonpolar, hydrophobic groups to the framework walls.

### 3.3.3. Synthesis of Fe₂(dotpdc) and substituted derivatives.

To determine the effect of local hydrophobic groups on catalyst turnover number and selectivity, we synthesized three new derivatives of Fe₂(dotpdc) in which the central ring is replaced with tetrafluoro-, tetramethyl-, or 1,4-di-tert-butylaryl groups (see Figure 3.2 and Table 3.2). These three frameworks are abbreviated Fe₂(dotpdc⁸) (R = F, CH₃, and tBu), respectively, with Fe₂(dotpdc) representing the completely unfunctionalized material. As a result of their location on the central phenylene ring, which is far removed from the Fe(II) centers, these substituents should exert an influence on the overall pore chemical environment without directly interfering with the desired iron–oxo reactivity. Longer chain alkyl substituents were specifically avoided due to the possibility of ligand hydroxylation or other self-oxidation processes. Solvothermal synthesis conditions were used for all three frameworks, producing yellow, microcrystalline powders with diffraction patterns and unit cells consistent with the expanded M₄(dobdc) structure type (see Figures 3.3 and Table 3.2). As the central substituents increase in size, the BET surface areas and pore sizes
correspondingly decrease (see Table 3.2). However, these differences are relatively minor, with only a ~10% reduction in surface area and pore size between Fe_2(dotpdc) and the most sterically crowded derivative, Fe_2(dotpdc^{tBu}). These results suggest that large reagents such as t-BuSO_2PhIO should still be able to diffuse freely through the substituted terphenyl frameworks.

Table 3.2. Surface areas, pore sizes, and unit cells of Fe_2(dotpdc) and substituted derivatives.

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m^2/g)</th>
<th>Langmuir Surface Area (m^2/g)</th>
<th>Pore Size^a (Å)</th>
<th>Unit Cell Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_2(dotpdc)</td>
<td>1970(30)</td>
<td>4020(30)</td>
<td>27</td>
<td>49.685(8) 6.925(5)</td>
</tr>
<tr>
<td>Fe_2(dotpdc^F)</td>
<td>1880(20)</td>
<td>3870(20)</td>
<td>27</td>
<td>49.693(3) 6.887(1)</td>
</tr>
<tr>
<td>Fe_2(dotpdc^{CH_3})</td>
<td>1860(50)</td>
<td>3580(30)</td>
<td>25</td>
<td>48.876(7) 6.836(2)</td>
</tr>
<tr>
<td>Fe_2(dotpdc^{tBu})</td>
<td>1820(60)</td>
<td>3490(40)</td>
<td>24</td>
<td>49.336(8) 7.369(2)</td>
</tr>
</tbody>
</table>

^a DFT pore sizes calculated from 77 K N_2 adsorption isotherms.

Figure 3.2. (a) Hexagonal channels of Fe_2(dotpdc^R) frameworks, with substituted central rings and (b) Structures of the derivatized terphenyl linkers used in this work. The blue spheres represent H, F, CH_3, or t-Bu. Note that the tertbutyl derivative is di-substituted.
3.3.4. Role of hydrophobic pore environment on cyclohexane oxidation. While the surface areas, pore sizes, and unit cell parameters of the four Fe₂(dotpdc<sup>R</sup>) frameworks are relatively similar, their cyclohexane oxidation A:K selectivities and turnover numbers are dramatically different, increasing in the order of H < F < CH<sub>3</sub> < tBu (see Table 3.3). Overall, a three-fold increase in A:K ratio, from 2.8 to 8.4:1, and a five-fold increase in TON, from 4 to 19, is observed. In all cases, catalysis halts once the framework is removed from the reaction mixture, and no loss in framework crystallinity is observed (see Figure 3.S6). While the ligand C–H bonds in Fe₂(dotpdc<sup>CH<sub>3</sub></sup>) and Fe₂(dotpdc<sup>tBu</sup>) could be susceptible to oxidative degradation, post-catalysis digestion and <sup>1</sup>H NMR analysis reveals no evidence of ligand oxidation (see Figure 3.S7 and 3.S8). The cause of catalyst deactivation appears to be the gradual and
irreversible oxidation of framework Fe(II) sites to inactive Fe(III) species, rather than framework collapse or ligand degradation.

Table 3.3. Summary of cyclohexane oxidation results in Fe₂(dotpdc<sup>R</sup>).

<table>
<thead>
<tr>
<th>Framework</th>
<th>A:K&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt; (A + 2K)</th>
<th>TON&lt;sup&gt;c&lt;/sup&gt; (A + 2K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂(dotpdc)</td>
<td>2.8(1)</td>
<td>76(6)</td>
<td>4(1)</td>
</tr>
<tr>
<td>Fe₂(dotpdc&lt;sup&gt;F&lt;/sup&gt;)</td>
<td>4.3(1)</td>
<td>84(7)</td>
<td>11(2)</td>
</tr>
<tr>
<td>Fe₂(dotpdc&lt;sup&gt;CH₃&lt;/sup&gt;)</td>
<td>6.5(1)</td>
<td>80(4)</td>
<td>13(2)</td>
</tr>
<tr>
<td>Fe₂(dotpdc&lt;sup&gt;Bu&lt;/sup&gt;)</td>
<td>8.4(4)</td>
<td>82(2)</td>
<td>19(1)</td>
</tr>
</tbody>
</table>

General conditions: 5.0 mg of acetonitrile-solvated framework, 25 mg of oxidant (0.073), 0.30 mL of cyclohexane (2.8 mmol), and 2.0 mL of CD₃CN. <sup>a</sup> Ratio of cyclohexanol (A) to cyclohexanone (K). <sup>b</sup> Moles of product formed per mole of oxidant consumed. Note that cyclohexanone requires two oxidizing equivalents to form. <sup>c</sup> Catalytic turnovers, moles of product per mole of iron in catalyst.

To determine whether these differing reactivity profiles are due to changes in ligand field strength arising from substituent inductive effects, Mössbauer spectroscopy was employed to probe the primary coordination sphere of the Fe(II) sites in these frameworks. The Mössbauer spectra of the acetonitrile-solvated frameworks (see Figure 3.4) are remarkably similar across the ligand series. In particular, the isomer shift (δ), a parameter that is highly sensitive to bonding properties such as bond length, metal–ligand covalency, and ligand electronegativity,<sup>32</sup> is between 1.26–1.27 mm/s for all four frameworks (see Table 3.S3). These results suggest ligand electronic effects and differences in the metal site primary coordination sphere are not responsible for the observed catalytic improvements.

Figure 3.4. Mössbauer spectra of the four Fe₂(dotpdc<sup>R</sup>) frameworks, collected at 100 K.
Because the observed reactivity patterns could reflect subtle changes in the nature of the active intermediate or reaction mechanism, H/D kinetic isotope effects (KIE) were used as a mechanistic probe of the putative Fe(IV)–oxo intermediate. For heme and nonheme iron–oxo systems, combined theoretical and experimental efforts have shown that the H/D KIE is highly sensitive to variables such as transition state structure, spin state, and reaction barrier height. Notably, large KIE values (>10) indicative of tunneling are typically observed. For example, the nonheme iron enzyme TauD has a KIE of 37, while experimental values for high-spin iron(IV)–oxo model complexes range from 18 to 25.

The cyclohexane oxidation H/D KIE values for the Fe$_2$(dotpdc$^8$) family were measured using in situ competition experiments between an excess of C$_6$H$_{12}$ and C$_6$D$_{12}$. The obtained values are 15.4(5), 14.4(2), 16.1(8), and 15.5(6), for R = H, F, CH$_3$, and tBu, respectively (see Figure 3.S9 and Table 3.S4). All of these are above the semiclassical limit of 7, supporting the involvement of a metal–oxo species. Furthermore, the similarity of these values indicates the observed reactivity differences are not due to changes in the iron–oxo intermediate.

3.3.5. Cyclohexane adsorption in Fe$_2$(dotpdc$^8$) frameworks. The Mössbauer and KIE experiments detailed above demonstrate that, at least within this series of frameworks, substitution of the remote central phenylene ring does not have a significant effect on the nature of either the Fe(II) ground state or the Fe(IV)–oxo intermediate. Therefore, we turned our attention away from primary coordination sphere properties and towards longer-range pore environment effects. Specifically, the adsorption of cyclohexane to the functionalized framework walls was examined. Liquid-phase adsorption experiments were first carried out using the catalytically relevant conditions of 1 M cyclohexane in acetonitrile. Interestingly, while the solution-phase cyclohexane capacity of Fe$_2$(dotpdc) is around 2.0(3) mol/mol framework, the cyclohexane capacities of the substituted frameworks (R = F, CH$_3$, tBu) are 1.7–2.1 times greater. Though these solution-phase studies do not provide detailed insight into specific framework–cyclohexane interactions, they do reveal that the Fe$_2$(dotpdc$^8$) series of frameworks adsorb significant amounts of cyclohexane in the presence of acetonitrile.

To more closely examine the thermodynamic properties of cyclohexane binding to the framework surface, gas-phase cyclohexane isotherms for all four frameworks were collected in the pressure range of 0–100 mbar at three separate temperatures (see Figure 3.5). Note that the open iron(II) sites, which interact strongly with guest molecules, were capped with N,N-dimethylformamide (DMF) prior to data collection so that only physisorption to the framework walls was interrogated by these measurements. The cyclohexane isotherms for the four frameworks are qualitatively similar, with Langmuir behavior observed at low pressures and capillary condensation within the mesoporous channels occurring at higher pressures. The low-pressure region corresponding to monolayer adsorption was modeled with a single-site Langmuir-Freundlich equation (see Figure 3.5 and Table 3.S5), and isosteric heats of adsorption ($Q_a$) were subsequently calculated from these fits using the Clausius-Clapeyron equation (see Figure 3.6).

A cyclohexane isosteric heat of adsorption of −45(1) kJ/mol was obtained for Fe$_2$(dotpdc), which is consistent with values previously reported for several metal–organic frameworks, faujasite-type zeolites, and carbon-based materials (−40–50 kJ/mol). While only a slightly stronger binding enthalpy of −48(1) kJ/mol is seen in the tetrafluoro-substituted Fe$_2$(dotpdc$^5$), a large jump in adsorption enthalpy is observed once alkyl substituents are introduced to the organic linkers, with values of −54(1) and −57(1) kJ/mol obtained for Fe$_2$(dotpdc$^{CH_3}$) and Fe$_2$(dotpdc$^{tBu}$), respectively (see Figure 3.6).

70
heats track precisely with the A:K selectivities observed for the cyclohexane oxidation reaction (Table 3.3). Coating the channel walls with hydrophobic moieties that interact favorably with cyclohexane may help funnel the substrate towards the iron center, increasing its local concentration relative to cyclohexanol and thus improving the A:K selectivity. The cause of the dramatic increase in TON in Fe₂(dotpdc₄Bu) is not yet clear, but may also be related to the more favorable adsorption of cyclohexane, as well as the confinement of radical intermediates close to the iron site by neighboring tert-butyl groups.

Figure 3.5. Cyclohexane adsorption isotherms for (a) Fe₂(dotdpc), (b) Fe₂(dotpdc⁵), (c), Fe₂(dotpdc₁₈), and (d) Fe₂(dotpdc₄Bu). Blue, purple, and red circles represent experimental data collected at 298, 308, and 318 K, respectively; black lines are the corresponding single-site Langmuir-Freundlich fits.
Figure 3.6. Cyclohexane isosteric heats of adsorption ($Q_{st}$) for Fe$_2$(dotdpc) (gray), Fe$_2$(dotpdc$^\text{tBu}$) (turquoise), Fe$_2$(dotpdc$^\text{CH}_3$) (green), and Fe$_2$(dotpdc$^\text{tBu}$) (orange).

Structural models consistent with powder X-ray diffraction data provide further insight into the origin of the different cyclohexane binding behavior observed in these materials. In Fe$_2$(dotdpc), $\pi-\pi$ stacking interactions between adjacent organic linkers generates a relatively flat, aromatic pore surface (see Figure 3.7 and Figure 3.5S–S6). In contrast, the increased steric bulk of the methyl and tert-butyl groups in Fe$_2$(dotpdc$^\text{CH}_3$) and Fe$_2$(dotpdc$^\text{tBu}$) leads to larger dihedral angles between the central phenylene unit and its neighboring rings. In Fe$_2$(dotpdc$^\text{tBu}$), the large tert-butyl substituents extend directly into the channels, lining the pore wall with hydrophobic residues and providing additional van der Waals interactions for cyclohexane binding. Interestingly, these models suggest the local environment around the iron site in Fe$_2$(dotpdc$^\text{tBu}$) is significantly more sterically congested than in Fe$_2$(dotdpc), which may help maintain the cyclohexane molecule and cyclohexyl radical near the iron center as the reaction progresses.

Figure 3.7. Local chemical environment around the Fe(II) centers in Fe$_2$(dotdpc) and Fe$_2$(dotpdc$^\text{tBu}$). The local structure of the Fe(II) centers in Fe$_2$(dotdpc) and Fe$_2$(dotpdc$^\text{tBu}$). (a) Ball-and-stick model of the iron(II) center in Fe$_2$(dotdpc) and (b) its corresponding space-filling model. (c) Space-filling model of the iron(II) center in Fe$_2$(dotpdc$^\text{tBu}$). White, gray, red, and orange spheres represent H, C, O, and Fe, respectively.
3.4. Conclusions and outlook

Specifically engineered host-guest interactions in metal–organic frameworks, which have been previously utilized for gas separation and storage purposes, are a powerful parameter in catalyst design. Functionalization of remote framework sites can lead to large changes in substrate adsorption and binding patterns that strongly alter catalytic outcomes. Here, incorporation of simple nonpolar groups remarkably increases both the selectivity and stability of framework-embedded iron sites for cyclohexane oxidation catalysis without directly affecting the structure or reactivity of the iron centers themselves. Outer coordination sphere and pore environment effects may prove to be significant in the context of many other metal–organic framework-catalyzed reactions, and represents a future area of research.

3.5. Acknowledgements

The synthetic chemistry, crystal structure determinations, and characterization of gas adsorption properties were supported through the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-SC0001015. The reactivity studies were supported by the Nanoporous Materials Genome Center, funded by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences under Award DE-FG02-12ER16362. This research also used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. D.A.R., M.I.G., and D.Z.Z. are thanked for experimental assistance and helpful discussions.

3.6. References and supporting information


(29) We found that N2O, when used in combination with liquid-phase hydrocarbons, leads to no observable reaction due to its poor metal-binding properties and sluggish oxidation kinetics.


Supporting Information

1. General considerations.

Unless otherwise noted, all procedures were performed under an N$_2$ atmosphere using standard glove box or Schlenk techniques. N,N-dimethylformamide (DMF) was dried using a commercial solvent purification system designed by JC Meyer Solvent Systems and then stored over 4 Å molecular sieves. Anhydrous methanol was purchased from commercial vendors, further dried over 3 Å sieves for 24 h, and deoxygenated prior to being transferred to an inert atmosphere glove box, where it was stored over 3 Å molecular sieves. All other reagents were obtained from commercial vendors and used without further purification. Cyclohexane-d$_{12}$ (≥99.6 atom % D) was purchased from Sigma Aldrich. The oxidant tBuSO$_2$PhIO$^{43}$ and the frameworks Fe$_2$(dobdc)$^{44}$ and Fe$_2$(dobpdc)$^{45}$ were synthesized according to previously published procedures.

C, H, and N analyses were obtained from the Microanalytical Laboratory at the University of California, Berkeley. $^1$H-NMR spectra were obtained using a Bruker AVB-400 instrument.
2. Control experiments.

Filtration control experiments: Post-catalysis (see general catalysis conditions in the experimental section), Fe₂(dotpdc⁸) was removed by filtration and additional tBuSO₂PhIO (10 mg) was added to the filtrate. The resulting mixture was stirred for 1.5 h and the solution analyzed by ¹H NMR. No additional cyclohexane oxidation products were observed after framework removal.

Digestion of Fe₂(dotpdc₇Bu): To make sure the framework ligands are not oxidized over the course of the reaction, particularly in the case of Fe₂(dotpdc₇Bu) which contains methyl groups in close proximity to the iron centers, digestion experiments were performed post-catalysis. Specifically, after a cyclohexane oxidation run, Fe₂(dotpdc₇Bu) (5.0 mg) was filtered, washed with acetonitrile, and stirred for 30 min in the presence of 3 M aqueous HCl (2 mL). This treatment dissolves the Fe³⁺ cations but leaves the water-insoluble terphenyl ligand behind as a precipitate. The precipitate was filtered, washed with H₂O, dried, and dissolved in DMSO-d₆. Analysis by ¹H NMR shows that the ligand stays intact with no evidence of oxidation (e.g. methyl group hydroxylation) (see Figure S4).
3. Ligand syntheses.

Scheme 1. General synthetic route to making H₄(dotpdc), H₄(dotpdc₅), H₄(dotpdcCH₃), and H₄(dotpdc₅Bu). Note that while the first three ligands are made following identical procedures (see below for details), a slightly different palladium catalyst and deprotection conditions were used for H₄(dotpdc₅Bu) due to the increased steric bulk of the tert-butyl groups and their sensitivity to harsh acidic conditions.

A 500 mL roundbottom flask equipped with a stir bar was charged with potassium carbonate (62.1 g, 450 mmol, 5.0 eq.) and 5-bromosalicylic acid (19.6 g, 90.0 mmol, 1.00 eq.). DMF (500 mL) was added, and the roundbottom flask was placed in a cold water bath. Iodomethane (16.8 mL, 270 mmol, 3.00 eq.) was added slowly, and the reaction mixture was allowed to stir vigorously at room temperature for 14 h. The reaction mixture was poured into ice water (2.5 L) and vigorously stirred for 10 minutes. The resulting non-homogeneous mixture was filtered to yield methyl 5-bromo-2-methoxybenzoate (16.6 g, 75% yield) as an off-white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 3 Hz, 1H), 7.51 (dd, J = 9, 3 Hz, 1H), 6.82 (d, J = 9 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H) ppm. The ¹H NMR spectrum is consistent with that reported in the literature.⁴⁶

A 250 mL 3-neck roundbottom flask equipped with a stir bar and reflux condenser was charged with methyl 5-bromo-2-methoxybenzoate (10.0 g, 40.8 mmol, 1.00 eq.), bis(pinacolato)diboron (11.4 g, 44.8 mmol, 1.10 eq.), potassium acetate (12.0 g, 122 mmol, 3.00 eq.), and XPhos Pd G2 precatalyst (645 mg, 0.82 mmol, 0.02 eq.). The flask was placed under high vacuum for 5 minutes and then back-filled with nitrogen. This process was repeated a total of three times. Next, degassed 1,4-dioxane (80 mL) was added via syringe, and the reaction mixture was
allowed to stir at reflux for 14 h. The reaction mixture was allowed to cool to room temperature, and the 1,4-dioxane was removed in vacuo. The crude product was partitioned between CH₂Cl₂ (150 mL) and water (150 mL). The phases were separated, and the aqueous layer was further extracted with CH₂Cl₂ (2 x 50 mL). The combined organic extracts were dried over MgSO₄, filtered through celite, eluting with CH₂Cl₂ (300 mL), and concentrated in vacuo. The resulting light brown solid was triturated with cold hexanes (50 mL), filtered, and washed with additional cold hexanes (2 x 25 mL) to yield methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (9.86 g, 83% yield) as a fluffy white solid. ¹H NMR (300 MHz, CDCl₃): δ 8.22 (s, 1H), 7.90 (d, J = 8 Hz, 1H), 6.95 (d, J = 8 Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 1.33 (s, 12H) ppm. The ¹H NMR spectrum is consistent with that reported in the literature.

A 50 mL 3-neck roundbottom flask equipped with a stir bar and reflux condenser was charged with methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (1.29 g, 4.40 mmol, 2.20 eq.), 1,4-dibromobenzene (472 mg, 2.00 mmol, 1.00 eq.), and XPhos Pd G2 (79 mg, 0.10 mmol, 0.05 eq.). The flask was placed under high vacuum for 5 minutes and then backfilled with nitrogen. This process was repeated a total of three times. Next, degassed THF (8 mL) and degassed aqueous K₂CO₃ (0.5M, 16 mL, 8 mmol, 4 eq.) were added via syringe, and the reaction mixture was allowed to stir at reflux for 14 h, during which time a gray solid precipitated from solution. The reaction mixture was allowed to cool to room temperature, and the reaction mixture was poured into cold water (75 mL). The non-homogenous solution was filtered, and the filtrate was washed thoroughly with cold water (3 x 10 mL). The resulting gray solid was triturated with cold methanol (20 mL), filtered, and washed with cold methanol (2 x 5 mL), to yield dimethyl 4,4''-dimethoxy-[1,1':4',1'"-terphenyl]-3,3''-dicarboxylate (769 mg, 95% yield) as an off-white solid. ¹H NMR (300 MHz, CDCl₃): δ 8.09 (d, J = 2 Hz, 2H), 7.74 (dd, J = 9, 2 Hz, 2H), 7.63 (s, 4H), 7.07 (d, J = 9 Hz, 2H), 3.96 (s, 6H), 3.93 (s, 6H) ppm.
A 100 mL roundbottom flask equipped with a stir bar and reflux condenser was charged with dimethyl 4,4''-dimethoxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate (760 mg, 1.87 mmol, 1.00 eq.). HBr (75 mL) and AcOH (75 mL) were added, and the nonhomogenous reaction mixture was allowed to stir at reflux for 48 h. During this time, the starting material dissolved, the reaction mixture turned orange, and a white solid precipitated from solution. The reaction mixture was allowed to cool to room temperature, poured into cold water (200 mL), and filtered. The filtrate was washed with cold water (2 x 50 mL) to yield H₄(dotpdc) (4,4''-dihydroxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylic acid) (608 mg, 93%) as an off-white solid. ¹H NMR (400 MHz, DMSO-d₆): δ 14.0 (bs, 2H), 11.3 (bs, 2H), 8.08 (s, 2H), 7.88 (d, J = 9 Hz, 2H), 7.70 (s, 4H), 7.08 (d, J = 9 Hz, 2H) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ 172.2, 161.1, 138.1, 134.2, 131.1, 128.2, 127.1, 118.3, 113.8 ppm. Anal. Calc. for C₂₀H₁₄O₆: C, 68.57; H, 4.03. Found: C, 68.28; H, 4.26.

A 50 mL 3-neck roundbottom flask equipped with a stir bar and reflux condenser was charged with methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (1.29 g, 4.40 mmol, 2.20 eq.), 1,4-dibromo-2,3,5,6-tetrafluorobenzene (616 mg, 2.00 mmol, 1.00 eq.), and XPhos Pd G2 (79 mg, 0.10 mmol, 0.05 eq.). The flask was placed under high vacuum for 5 minutes and then back-filled with nitrogen. This process was repeated a total of three times. Next, degassed THF (8 mL) and degassed aqueous K₂CO₃ (0.5M, 16 mL, 8 mmol, 4 eq.) were added via syringe, and the reaction mixture was allowed to stir at reflux for 14 h, during which time a gray solid precipitated from solution. The reaction mixture was allowed to cool to room
temperature, and the reaction mixture was poured into cold water (75 mL). The non-homogenous solution was filtered, and the filtrate was washed thoroughly with cold water (3 x 10 mL). The resulting gray solid was dissolved in hot CH$_2$Cl$_2$ (100 mL). The solution was filtered through celite, eluting with CH$_2$Cl$_2$ (300 mL), and concentrated in vacuo to yield a yellow solid. This solid was triturated with cold methanol (20 mL), filtered, and washed with cold methanol (2 x 5 mL), to yield dimethyl 2',3',5',6'-tetrafluoro-4,4''-dimethoxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate (613 mg, 64% yield) as an off-white solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 2$ Hz, 2H), 7.82 (dd, $J = 9$, 2 Hz, 2H), 7.24 (d, $J = 9$ Hz, 2H), 3.59 (s, 6H), 3.81 (s, 6H) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –143.9 ppm.

A 100 mL roundbottom flask equipped with a stir bar and reflux condenser was charged with dimethyl 2',3',5',6'-tetrafluoro-4,4''-dimethoxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate (478 mg, 1.00 mmol, 1.00 eq.). HBr (50 mL) and AcOH (50 mL) were added, and the nonhomogenous reaction mixture was allowed to stir at reflux for 48 h. The reaction mixture was allowed to cool to room temperature, poured into cold water (100 mL), and filtered. The filtrate was washed with cold water (2 x 50 mL) to yield H$_4$(dotpd$^F$) (2',3',5',6'-tetrafluoro-4,4''-dihydroxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylic acid) (287 mg, 68%) as an off-white solid. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 7.98 (s, 2H), 7.81 (d, $J = 9$ Hz, 2H), 7.16 (d, $J = 9$ Hz, 2H) ppm; $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ 171.3, 161.7, 143.7 (dm, $J = 241$ Hz), 136.9, 132.0, 117.8, 117.4, 113.5 ppm (a $^{13}$C resonance for the biphenyl carbon on the central ring could not readily be observed due to the poor solubility of this compound in DMSO-d$_6$ and the weak signal strength of this resonance resulting from C-F coupling); $^{19}$F NMR (376 MHz, DMSO-d$_6$): $\delta$ –144.0 ppm. HRMS (ESI-TOF) m/z: [M – H]$^-$ Calcd for C$_{29}$H$_9$O$_6$F$_4$ 421.0341; Found 421.0330.
A 50 mL 3-neck roundbottom flask equipped with a stir bar and reflux condenser was charged with methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (1.11 g, 3.77 mmol, 2.20 eq.), 1,4-dibromo-2,3,5,6-tetramethylbenzene (500 mg, 1.72 mmol, 1.00 eq.), and XPhos Pd G2 (68 mg, 0.09 mmol, 0.05 eq.). The flask was placed under high vacuum for 5 minutes and then back-filled with nitrogen. This process was repeated a total of three times. Next, degassed THF (8 mL) and degassed aqueous K$_2$CO$_3$ (0.5M, 14 mL, 7 mmol, 4 eq.) were added via syringe, and the reaction mixture was allowed to stir at reflux for 14 h, during which time a gray solid precipitated from solution. The reaction mixture was allowed to cool to room temperature, and the reaction mixture was poured into cold water (75 mL). The non-homogenous solution was filtered, and the filtrate was washed thoroughly with cold water (3 x 10 mL). The resulting gray solid was dissolved in hot CH$_2$Cl$_2$ (100 mL). The solution was filtered through celite, eluting with CH$_2$Cl$_2$ (300 mL), and concentrated in vacuo to yield a brown solid. This solid was triturated with cold methanol (20 mL), filtered, and washed with cold methanol (2 x 5 mL), to yield dimethyl 4,4''-dimethoxy-2',3',5',6'-tetramethyl-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate (610 mg, 76% yield) as an off-white solid. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.62 (dd, 2H), 7.26 (m, 2H, under CDCl$_3$ peak), 7.07 (d, J = 9 Hz, 2H), 3.98 (s, 6H), 3.88 (s, 6H) ppm.

A 100 mL roundbottom flask equipped with a stir bar and reflux condenser was charged with 4,4''-dimethoxy-2',3',5',6'-tetramethyl-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate (420 mg, 0.91 mmol, 1.00 eq.). HBr (40 mL) and AcOH (40 mL) were added, and the nonhomogenous reaction mixture was allowed to stir at reflux for 48 h. During this time, the starting material dissolved,
the reaction mixture turned orange, and a white solid precipitated from solution. The reaction mixture was allowed to cool to room temperature, poured into cold water (200 mL), and filtered. The filtrate was washed with cold water (2 x 50 mL) to yield H₄(dotpdc) (4,4''-dihydroxy-2',3',5',6'-tetramethyl-[1,1':4',1''-terphenyl]-3,3''-dicarboxylic acid) (309 mg, 84%) as an off-white solid. ¹H NMR (400 MHz, DMSO-d₆): δ 7.48 (d, J = 2 Hz, 2H), 7.27 (d, J = 9 Hz, 2H), 7.05 (dd, J = 9, 2 Hz, 2H), 1.89 (s, 12H) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ 171.9, 159.8, 139.6, 136.6, 132.7, 131.6, 130.4, 117.3, 113.0 18.0. Anal. Calc. for C₂₄H₂₂O₆: C, 70.92; H, 5.46. Found: C, 70.65; H, 5.70.

A 50 mL 3-neck roundbottom flask equipped with a stir bar and reflux condenser was charged with methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (0.466 g, 1.56 mmol, 2.20 eq.), 1,4-dibromo-2,5-ditert-butylbenzene (250 mg, 0.72 mmol, 1.00 eq.), and SPhos Pd G2 (26 mg, 0.04 mmol, 0.05 eq.). Note that the ligand SPhos was used rather than XPhos due to its slightly smaller size. The flask was placed under high vacuum for 5 minutes and then back-filled with nitrogen. This process was repeated a total of three times. Next, degassed THF (16 mL) and degassed aqueous K₂CO₃ (0.5M, 6 mL, 3 mmol, 4 eq.) were added via syringe, and the reaction mixture was allowed to stir at room temperature for 24 h, then 60 °C overnight. The reaction mixture was allowed to cool to room temperature, and the reaction mixture was poured into cold water (75 mL). The non-homogenous solution was filtered, and the filtrate was washed thoroughly with cold water (3 x 10 mL), methanol (3 x 10 mL), and hexanes (3 x 10 mL). The resulting gray solid was dissolved in CH₂Cl₂ (100 mL). The solution was filtered through celite, eluting with CH₂Cl₂ (300 mL), and concentrated in vacuo to yield dimethyl 2',5'-di-tert-butyl-4,4''-dimethoxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate (220 mg, 59% yield) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.78 (d, J = 2 Hz, 2H), 7.43 (dd, J = 9, 2 Hz, 2H), 7.08 (s, 2H), 7.00 (d, J = 9 Hz, 2H), 3.97 (s, 6H), 3.89 (s, 6H), 1.14 (s, 18H) ppm.
Because the tert-butyl groups are not stable under refluxing HBr/HOAc, alternative conditions were used to remove the methyl protecting groups. A 100 mL schlenk flask equipped with a stir bar was charged with 2',5'-di-tert-butyl-4,4''-dimethoxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate (220 mg, 0.42 mmol, 1.00 eq.) and 50 mL of DCM. The solution was vigorously stirred and cooled to −78 °C, and BBr₃ was added dropwise (1M solution in DCM, 5.1 mL, 5.1 mmol, 12 eq.) under an argon atmosphere. The reaction was stirred at room temperature for 24 h. The excess BBr₃ was quenched with water, and the resulting white precipitate was washed with H₂O (3 x 50 mL). A small amount of methyl ester (~30%) still present in the material was subsequently hydrolyzed by stirring the material in 10 mL of THF and 10 mL of 1M NaOH at 50 °C overnight. The solution was neutralized using HCl, the THF removed in vacuo, and the white precipitate washed with H₂O (3 x 50 mL) to afford H₄(dotpdcₘₘₘₘ) (2',5'-di-tert-butyl-4,4''-dihydroxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylic acid) (150 mg over two steps, 76%).¹H NMR (400 MHz, DMSO-d₆): δ 7.64 (d, J = 2 Hz, 2H), 7.43 (dd, J = 9, 2 Hz, 2H), 7.02 (s, 2H), 1.10 (s, 18H) ppm; ¹³C NMR (100 MHz, DMSO-d₆): δ 171.8, 159.9, 144.1, 139.2, 136.9, 135.3, 130.7, 126.4, 118.0, 116.2, 35.4, 32.3. Anal. Calc. for C₂₈H₃₀O₆: C, 72.71; H, 6.54. Found: C, 72.39; H, 6.76.
4. Powder X-ray diffraction data collection and analysis.

**Sample preparation and data collection:** For all powder X-ray diffraction measurements, 1.0 mm diameter borosilicate capillaries were packed with sample (to roughly 8–10 mm in height) inside an N₂-filled glovebox. For very air-sensitive samples, the capillaries were then attached to custom designed gas cells, brought out of the glovebox, evacuated, and flame-sealed. For less sensitive samples (e.g. frameworks post-catalysis), the capillaries were temporarily sealed under N₂ with silicone grease and then flame-sealed. High-resolution powder X-ray diffraction patterns of acetonitrile-solvated Fe₂(dotpdc)∙2MeCN, Fe₂(dotpdcF)∙2MeCN, Fe₂(dotpdcCH₃)∙2MeCN, and Fe₂(dotpdc(tBu))∙2MeCN were collected either on Beamline 17-BM-B (λ = wavelength of 0.72768 Å), or at Beamline 11-BM through the mail-in service (λ = 0.414169), at the Advanced Photon Source at Argonne National Laboratory. High-resolution powder X-ray diffraction patterns of activated (desolvated) Fe₂(dotpdc) and Fe₂(dotpdcF) were collected at Beamline 17-BM-B. Diffraction patterns of all frameworks post-catalysis were collected in-house using a Bruker AXS D8 Advance diffractometer equipped with CuKα radiation (λ = 1.5418 Å).

**General data analysis:** The powder data analysis (pattern indexing, profile fitting, Pawley refinement, and crystal structure model) was performed with the program TOPAS-Academic V4.125. Specifically, a standard peak search, followed by indexing via the Single Value Decomposition approach allowed the determination of approximate unit cell dimensions. Precise unit cell dimensions were determined by performing a structureless Pawley refinement in TOPAS-Academic (see Figures 3.S1–S4). Structural models (assuming frameworks adopt the same structural connectivity was the M₂(dobdc) series) were constructed in Materials Studio (Materials Studio v. 8, Accelrys Software Inc.) and optimized using the Forcite module, which were then used to perform Rietveld refinement of activated Fe₂(dotpdc) and Fe₂(dotpdcF) in TOPAS-Academic.

**Structure solution and Rietveld refinement of activated Fe₂(dotpdc) and Fe₂(dotpdcF):** A structural model of Fe₂(dotpdc) was constructed in Materials Studio based on expansion from the reported Fe₂(dobdc) crystal structure, which was then used to perform a Rietveld refinement of the experimental Fe₂(dotpdc) powder pattern in TOPAS-Academic V4.1. In this refinement, the instrumental and sample parameters were freely refined. A single refined isotropic thermal parameter was assigned to the Fe atom. A single refined isotropic thermal parameter was assigned to the majority of atoms of the dotpdc⁴⁻ ligand, with the exception of the atoms of the central phenyl ring, which had a separately refined isotropic thermal parameter. The atomic positions could not be refined, as the X-ray diffraction pattern did not have enough detail to allow for accurate determination of light atoms. While the powder X-ray diffraction pattern was not of high enough quality to allow for ab initio solution of the structure of Fe₂(dotpdc), the resulting calculated diffraction pattern for the constructed structural model is in agreement with the experimental diffraction pattern (Figure 3.S5). This agreement lends us to believe that the structural model is in fact a fair approximation of the structure of Fe₂(dotpdc). The structure solution and Rietveld refinement of Fe₂(dotpdcF) was performed in a similar manner (Figure 3.S5).
5. Mössbauer data collection and analysis.

Iron-57 Mössbauer spectra were obtained at 100 K with a constant acceleration spectrometer and a cobalt-57 rhodium source. Prior to measurements the spectrometer was calibrated at 295 K with α-iron foil. Samples were prepared inside an N₂-filled glove box and contained 20 mg/cm² of sample (~3 to 4 mg/cm² of iron) diluted with boron nitride. All spectra were fit with Lorentzian quadrupole doublets using the WMOSS Mössbauer Spectral Analysis Software (www.wmoss.org).

The kinetic isotope effect was determined via competition experiments between C\textsubscript{6}H\textsubscript{12} and C\textsubscript{6}D\textsubscript{12}. For each framework, three separate reactions were run using different initial ratios of C\textsubscript{6}H\textsubscript{12} and C\textsubscript{6}D\textsubscript{12} (1:1, 1:2, or 1:5 molar ratios of C\textsubscript{6}H\textsubscript{12}:C\textsubscript{6}D\textsubscript{12}). The general catalytic conditions were used, and after the reaction the ratio of cyclohexanol to [D\textsubscript{11}]-cyclohexanol was determined by GC-MS. A small amount of protio cyclohexanone was also produced (no [D\textsubscript{10}]-cyclohexanone was observed), and quantified using GC-MS and \textsuperscript{1}H NMR. The ratio of protio to deuterated products ([P\textsubscript{H}]/[P\textsubscript{D}]) was plotted against the initial C\textsubscript{6}H\textsubscript{12}/C\textsubscript{6}D\textsubscript{12} ratio, and the kinetic isotope effect was taken as the slope of the best-fit line (see Figure 3.S9 and Table 3.S4).
7. Supplementary tables.

Table 3.S1. Unit cell parameters of acetonitrile-solvated Fe₂(dotpdc)-2MeCN, Fe₂(dotpdc<sup>F</sup>)-2MeCN, Fe₂(dotpdc<sup>CH₃</sup>)-2MeCN, and Fe₂(dotpdc<sup>tBu</sup>)-2MeCN, determined via Pawley fitting of powder X-ray diffraction data.

<table>
<thead>
<tr>
<th></th>
<th>Fe₂(dotpdc)·2MeCN</th>
<th>Fe₂(dotpdc&lt;sup&gt;F&lt;/sup&gt;)·2MeCN</th>
<th>Fe₂(dotpdc&lt;sup&gt;CH₃&lt;/sup&gt;)·2MeCN</th>
<th>Fe₂(dotpdc&lt;sup&gt;tBu&lt;/sup&gt;)·2MeCN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space group</strong></td>
<td>R3</td>
<td>R3</td>
<td>R3</td>
<td>R3</td>
</tr>
<tr>
<td><strong>a / Å</strong></td>
<td>49.685(8)</td>
<td>49.693(3)</td>
<td>48.876(7)</td>
<td>49.336(8)</td>
</tr>
<tr>
<td><strong>c / Å</strong></td>
<td>6.925(5)</td>
<td>6.887(1)</td>
<td>6.836(2)</td>
<td>7.369(2)</td>
</tr>
<tr>
<td><strong>V / Å³</strong></td>
<td>14806(11)</td>
<td>14727(3)</td>
<td>14142(6)</td>
<td>15534(6)</td>
</tr>
<tr>
<td><strong>R&lt;sub&gt;exp&lt;/sub&gt;</strong></td>
<td>1.119</td>
<td>1.168</td>
<td>1.173</td>
<td>4.115</td>
</tr>
<tr>
<td><strong>R&lt;sub&gt;wp&lt;/sub&gt;</strong></td>
<td>2.535</td>
<td>1.628</td>
<td>1.711</td>
<td>4.495</td>
</tr>
<tr>
<td><strong>R&lt;sub&gt;p&lt;/sub&gt;</strong></td>
<td>1.328</td>
<td>1.091</td>
<td>1.120</td>
<td>2.999</td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.727680</td>
<td>0.727680</td>
<td>0.727680</td>
<td>0.414169</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>298 K</td>
<td>298 K</td>
<td>298 K</td>
<td>100 K</td>
</tr>
</tbody>
</table>
Table 3.S2. Unit cell parameters of desolvated \( \text{Fe}_2(\text{dotpdc}) \) and \( \text{Fe}_2(\text{dotpdc}^\text{F}) \) (activated under vacuum at 180 °C), determined via Pawley fitting of powder X-ray diffraction data.

<table>
<thead>
<tr>
<th></th>
<th>( \text{Fe}_2(\text{dotpdc}) )</th>
<th>( \text{Fe}_2(\text{dotpdc}^\text{F}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space group</strong></td>
<td>( R\overline{3} )</td>
<td>( R\overline{3} )</td>
</tr>
<tr>
<td><strong>( a / \text{Å} )</strong></td>
<td>49.86(2)</td>
<td>49.88(4)</td>
</tr>
<tr>
<td><strong>( c / \text{Å} )</strong></td>
<td>6.84(1)</td>
<td>6.84(2)</td>
</tr>
<tr>
<td><strong>( V / \text{Å}^3 )</strong></td>
<td>14730(30)</td>
<td>14730(50)</td>
</tr>
<tr>
<td><strong>( R_{\text{exp}} )</strong></td>
<td>0.471</td>
<td>0.323</td>
</tr>
<tr>
<td><strong>( R_{\text{wp}} )</strong></td>
<td>1.343</td>
<td>2.992</td>
</tr>
<tr>
<td><strong>( R_p )</strong></td>
<td>0.939</td>
<td>1.841</td>
</tr>
<tr>
<td><strong>( c_2 )</strong></td>
<td>2.853</td>
<td>9.252</td>
</tr>
<tr>
<td><strong>Wavelength (\text{Å})</strong></td>
<td>0.727680</td>
<td>0.727680</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>298 K</td>
<td>298 K</td>
</tr>
</tbody>
</table>
Table 3.S3. Mössbauer parameters for acetonitrile-solvated frameworks Fe₂(dotpdc)·2CD₃CN, Fe₂(dotpdc\(^F\))·2CD₃CN, Fe₂(dotpdc\(^{CH₃}\))·2CD₃CN, and Fe₂(dotpdc\(^{tBu}\))·2CD₃CN, collected at 100 K.

<table>
<thead>
<tr>
<th></th>
<th>Fe₂(dotpdc)</th>
<th>Fe₂(dotpdc(^F))</th>
<th>Fe₂(dotpdc(^{CH₃}))</th>
<th>Fe₂(dotpdc(^{tBu}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ (mm/s)</td>
<td>1.267(3)</td>
<td>1.271(3)</td>
<td>1.264(2)</td>
<td>1.259(2)</td>
</tr>
<tr>
<td></td>
<td>ΔE</td>
<td>(mm/s)</td>
<td>2.505(5)</td>
<td>2.468(5)</td>
</tr>
<tr>
<td>Γ (mm/s)</td>
<td>0.39(1)</td>
<td>0.39(1)</td>
<td>0.31(1)</td>
<td>0.31(1)</td>
</tr>
</tbody>
</table>
Table 3.54. Results of C\(_6\)H\(_{12}\) and C\(_6\)D\(_{12}\) competition experiments. \([P_{\text{H}}]/[P_{\text{D}}]\) is the molar ratio of protio to deuterated products.

<table>
<thead>
<tr>
<th>[C(<em>6)H(</em>{12})]/[C(<em>6)D(</em>{12})]</th>
<th>Fe(_2)(dotpdc)</th>
<th>Fe(_2)(dotpdc(^F))</th>
<th>Fe(_2)(dotpdc(^{\text{CH3}}))</th>
<th>Fe(_2)(dotpdc(^{\text{Bu}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>3.6</td>
<td>2.7</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>0.5</td>
<td>7.5</td>
<td>6.9</td>
<td>7.1</td>
<td>7.2</td>
</tr>
<tr>
<td>1</td>
<td>15.6</td>
<td>14.3</td>
<td>15.9</td>
<td>15.3</td>
</tr>
</tbody>
</table>
Table 3.55. Single-site Langmuir-Freundlich parameters for cyclohexane gas adsorption on DMF-solvated Fe$_2$(dpd)$_2$·2DMF, Fe$_2$(dpd$^F$)$_2$·2DMF, Fe$_2$(dpd$^{CH_3}$)$_2$·2DMF, and Fe$_2$(dpd$^{tBu}$)$_2$·2DMF.

\[ n = \frac{n_{sat,1} b_1 P v_1}{1 + b_1 P v_2} \]

<table>
<thead>
<tr>
<th>Framework</th>
<th>Temperature (°C)</th>
<th>$n_1$ (mmol/g)</th>
<th>$b_1$ (bar$^{-1}$)</th>
<th>$v_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$(dpd)</td>
<td>25</td>
<td>3.08</td>
<td>1.48 x 10$^4$</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>3.14</td>
<td>6.80 x 10$^3$</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3.30</td>
<td>3.24 x 10$^3$</td>
<td>1.27</td>
</tr>
<tr>
<td>Fe$_2$(dpd$^F$)</td>
<td>25</td>
<td>2.90</td>
<td>6.91 x 10$^5$</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>2.98</td>
<td>2.17 x 10$^5$</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3.02</td>
<td>8.20 x 10$^4$</td>
<td>1.62</td>
</tr>
<tr>
<td>Fe$_2$(dpd$^{CH_3}$)</td>
<td>25</td>
<td>2.77</td>
<td>8.78 x 10$^5$</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>2.72</td>
<td>3.06 x 10$^5$</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>2.71</td>
<td>1.09 x 10$^5$</td>
<td>1.55</td>
</tr>
<tr>
<td>Fe$_2$(dpd$^{tBu}$)</td>
<td>25</td>
<td>2.13</td>
<td>1.36 x 10$^7$</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>2.11</td>
<td>4.44 x 10$^6$</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>2.04</td>
<td>1.40 x 10$^6$</td>
<td>1.59</td>
</tr>
</tbody>
</table>
8. Supplementary figures.

**Figure 3.S1.** Pawley fit of acetonitrile-solvated Fe$_2$(dotpdc)-2CD$_3$CN. Experimental powder pattern of Fe$_2$(dotpdc)-2CD$_3$CN was taken at APS Beamline 17-BM at 298 K with a wavelength of 0.727680 Å. Blue, red, and gray lines represent experimental data, calculated fits, and the difference between the two, respectively; black tick marks represent calculated Bragg peak positions.
Figure 3.S2. Pawley fit of acetonitrile-solvated Fe$_2$(dotpdc$^5$)-2CD$_3$CN. Experimental powder pattern of Fe$_2$(dotpdc$^5$)-2CD$_3$CN was taken at APS Beamline 17-BM at 298 K with a wavelength of 0.727680 Å. Blue, red, and gray lines represent experimental data, calculated fits, and the difference between the two, respectively; black tick marks represent calculated Bragg peak positions.
Figure 3.S3. Pawley fit of acetonitrile-solvated Fe₂(dotpdc\text{CH₃})·2CD₃CN. Experimental powder pattern of Fe₂(dotpdc\text{CH₃})·2CD₃CN was taken at APS Beamline 17-BM at 298 K with a wavelength of 0.727680 Å. Blue, red, and gray lines represent experimental data, calculated fits, and the difference between the two, respectively; black tick marks represent calculated Bragg peak positions.
Figure 3.S4. Pawley fit of acetonitrile-solvated $\text{Fe}_2(\text{dotpdc}^{\text{Bu}})\cdot2\text{CD}_3\text{CN}$. Experimental powder pattern of $\text{Fe}_2(\text{dotpdc}^{\text{Bu}})$ was taken at APS Beamline 11-BM at 100 K with a wavelength of 0.414169 Å. Blue, red, and gray lines represent experimental data, calculated fits, and the difference between the two, respectively; black tick marks represent calculated Bragg peak positions.
Figure 3.S5. *Top:* Rietveld refinement of activated Fe₂(dotpdc) at 298 K. Blue and red lines represent the observed and calculated diffraction patterns, respectively. The gray line represents the difference between observed and calculated patterns, and the black tick marks indicate calculated Bragg peak positions. Goodness-of-fit parameters: $R_{wp} = 3.20\%$, $R_p = 2.22\%$, $R_{bragg} = 0.79\%$, $\chi^2 = 3.12$. The wavelength was 0.727680 Å.

*Bottom:* Rietveld refinement of activated Fe₂(dotpdc$^F$) at 298 K. Blue and red lines represent the observed and calculated diffraction patterns, respectively. The gray line represents the difference between observed and calculated patterns, and the black tick marks indicate calculated Bragg peak positions. Goodness-of-fit parameters: $R_{wp} = 6.34\%$, $R_p = 6.83\%$, $R_{bragg} = 2.59\%$, $\chi^2 = 6.12$. The wavelength was 0.727680 Å.
Figure 3.S6. Powder X-ray diffraction patterns of the biphenyl and terphenyl Fe$_2$(dobdc) analogues after a catalytic cyclohexane oxidation run. While the frameworks change color from yellow/green to red brown, indicative of oxidation of the Fe(II) centers to Fe(III), no loss in crystallinity is observed.
Figure 3.S7. $^1$H NMR of H$_4$(dotpdc$^{CH_3}$) post-catalysis (DMSO-d$_6$). Acid digestion of Fe$_2$(dotpdc$^{CH_3}$) and $^1$H NMR analysis of the ligand after a cyclohexane oxidation run suggests that the ligand is not hydroxylated or otherwise oxidized over the course of the reaction.
Figure 3.S8. $^1$H NMR of H$_4$(dotpdc$^{tBu}$) post-catalysis (DMSO-d$_6$). Acid digestion of Fe$_2$(dotpdc$^{tBu}$) and $^1$H NMR analysis of the ligand after a cyclohexane oxidation run suggests that the ligand is not hydroxylated or otherwise oxidized over the course of the reaction.
Figure 3.89. Kinetic isotope effect determination for Fe₂(dotpdc), Fe₂(dotpdc$^\text{F}$), Fe₂(dotpdc$^{\text{CH}_3}$), and Fe₂(dotpdc$^{\text{tBu}}$). The ratio of protio to deuterated products, $[P_{\text{H}}]/[P_{\text{D}}]$, was plotted versus the initial $[\text{C}_6\text{H}_{12}]/[\text{C}_6\text{D}_{12}]$ ratio. The slope obtained from fitting these points to a line is the KIE, which was determined to be 15.4(5), 14.4(2), 16.1(8), and 15.5(6) for R = H, F, CH3, and tBu, respectively.
7. Supplementary references.


Chapter 4: Selective, Tunable $\text{O}_2$ Binding in Cobalt(II)–Triazolate/Pyrazolate Metal–Organic Frameworks

4.1. Introduction

Decades after their discovery in the mid-19th century,\textsuperscript{1} synthetic transition metal–dioxoxygen compounds continue to command widespread interest due to their relevance as models of biological oxygen carriers and metalloenzymes,\textsuperscript{2} catalysts in oxidation chemistry,\textsuperscript{3} and adsorbents for industrial air separation applications.\textsuperscript{4} Recently, rising atmospheric CO$_2$ levels have generated increasing impetus for research efforts in this last area, as several proposed carbon capture and sequestration technologies require the use of high purity oxygen.\textsuperscript{5} Briefly, precombustion CO$_2$ capture utilizes O$_2$ for the gasification of coal, while oxyfuel combustion systems burn fuel in the presence of pure O$_2$ diluted in CO$_2$. As high-purity oxygen is currently produced on a large scale via energetically demanding cryogenic distillation,\textsuperscript{6} there is a need for alternative, lower-cost air separation technologies.

Metal–organic frameworks, a relatively new class of highly crystalline and porous materials, have the potential to transform a variety of gas separation and storage processes,\textsuperscript{5b,7} including oxygen purification from air. For example, frameworks containing coordinatively unsaturated redox-active metal centers that can reversibly bind and reduce oxygen, such as Cr$_3$(btc)$_2$, Cr-BTT, and Fe$_2$(dobdc), exhibit much higher selectivities and total capacities than the ion-exchanged zeolites currently used in adsorbent-based air separation plants and devices.\textsuperscript{4c,Ad,8,9} Furthermore, most ion-exchanged zeolites are N$_2$-selective, as their extra-framework cations (e.g., Li\textsuperscript{+}) are generally redox-inactive and interact preferentially with the larger quadrupole moment of nitrogen. Because oxygen constitutes a smaller fraction of air than nitrogen (21\% versus 78\%), O$_2$-selective materials such as the aforementioned metal–organic frameworks are inherently more efficient than N$_2$-selective adsorbents. In spite of these advantages, however, many improvements are still necessary with respect to the thermal stability and cyclability of metal–organic frameworks. Indeed, Fe$_2$(dobdc) irreversibly oxidizes at temperatures above 222 K while chromium frameworks can exhibit gradual capacity losses over multiple cycles. Significantly, all of these framework materials decompose over time when exposed to humid air.

While molecular complexes of cobalt(II) comprise some of the earliest,\textsuperscript{10} prototypical examples of synthetic oxygen carriers, cobalt-based metal–organic frameworks with a strong affinity for O$_2$ are noticeably absent from the literature. This discrepancy may be due to the widespread use of weak-field carboxylate-based bridging ligands as framework struts, leading to electron-poor cobalt(II) nodes that exhibit only weak O$_2$ binding. Additionally, cobalt(III)-superoxo and peroxo species, like most cobalt(III) compounds, adopt low-spin electronic configurations with short equatorial metal-ligand bonds ranging from ~1.9 to 2.0 Å.\textsuperscript{11} These geometric requirements may be incompatible with certain framework structures. For example, it has been shown that transition metal ions in the M$_2$(dobdc) (also known as M-MOF-74) series maintain a high-spin configuration even in the presence of strong-field ligands such as CO, as well as in high oxidation states.\textsuperscript{12,13} Due to the combination of weak ligand field and structural rigidity, the metal centers in Co$_2$(dobdc) have been demonstrated to be redox-inactive in the presence of O$_2$.\textsuperscript{14} Thus, while cobalt(II)-based metal–organic frameworks are appealing targets in the pursuit of new adsorbents for air separations, development of such materials requires the design of new frameworks possessing both strong-field ligands and some degree of structural flexibility.
Herein, we present two such metal–organic frameworks, Co-BTTri and Co-BDTriP, which feature coordinatively unsaturated cobalt(II) centers supported by a combination of electron-donating triazolate and pyrazolate linkers. Gas adsorption measurements reveal that both materials exhibit a strong preference for binding $O_2$ over $N_2$. Electronic structure calculations further show that the extent of charge transfer between the cobalt(II) nodes and dioxygen is highly dependent on the primary coordination sphere of the metal center.

4.2. Experimental

4.2.1. Synthesis of Co-BTTri. A 100-mL Schlenk flask was charged with 200 mg of $H_3$BTTri (0.716 mmol, 1.00 equiv) dissolved in 50 mL of $N,N$-dimethylformamide and methanol (10:1 DMF:MeOH). To this mixture was added 319 mg dimethylformamidium trifluoromethanesulfonate (1.43 mmol, 2.00 equiv) followed by 163 mg CoCl$_2$ (1.26 mmol, 1.75 equiv). The Schlenk flask was sealed using a high vacuum grease suitable for high temperatures, degassed by freeze-pump-thawing three times, and stirred at 393 K for 7 days and 413 K for 2 days. The resulting pink solid was filtered, and under an inert atmosphere washed with DMF ($6 \times 50$ mL, each wash 12 h at 393 K) and exchanged with methanol ($6 \times 50$ mL, each wash 12 h at 343 K). The solid was fully activated by heating at 423 K under dynamic vacuum for 24 h to produce 158 mg of a tan solid (49% yield). The reaction can also be scaled up and concentrated to 1.60 g of $H_3$BTTri in 200 mL of the same solvent mixture, 1.75 equiv of CoCl$_2$, and 1.00 equiv of acid (note reduced acid equivalents) to produce 1.70 g of material (66% yield). Anal. Calcd. for $Co_3[(Co_4Cl)_3(BTTri)_8]_2\cdot14DMF$ (C$_{234}$H$_{194}$Cl$_6$Co$_{27}$N$_{158}$O$_{14}$): C, 38.78; H, 2.70; N, 30.54. Found: C, 39.03; H, 2.59; N, 30.53.

4.2.2. Single-crystal synthesis of Co-BTTri. A 20-mL vial was charged with 10 mg of $H_3$BTTri (0.036 mmol, 1.0 equiv) and 8 mL of solvent (4:1 DMF:MeOH). After the ligand had fully dissolved, 2.2 equiv of concentrated HCl (12 M) was added, followed by 3.0 mg of CoCl$_2$ (0.023 mmol, 0.65 equiv) and 150 $\mu$L of water. The solution was separated into several pyrex tubes, freeze-pump-thawed, and flame-sealed. Heating the sealed tubes at 423 K for four days led to the formation of pink, cubic crystals of Co-BTTri.

4.2.3. Single-crystal synthesis of Co-BDTriP. A 20-mL vial was charged with 20 mg of $H_3$BDTriP (0.072 mmol, 1.0 equiv) and 4 mL of solvent (4:1 DMF:MeOH). After the ligand had fully dissolved, 1.1 equiv of concentrated HCl (12 M) was added (0.079 mmol) along with 250 $\mu$L of water, followed by 9.3 mg of CoCl$_2$ (0.072 mmol, 1.0 equiv). The solution was separated into several pyrex tubes, freeze-pump-thawed, and flame-sealed. Heating the sealed tubes at 423 K for 1 week led to the formation of pink, cubic crystals of Co-BDTriP. The crystals were isolated, transferred into a glovebox, and then washed with DMF ($6 \times 50$ mL, each wash 12 h at 393 K), exchanged with methanol ($6 \times 50$ mL, each wash 12 h at 343 K), and activated at 453 K for 24 h to give 20 mg of activated Co-BDTriP (60% yield). Anal. Calcd. for $Co_3[(Co_4Cl)_3(BDTriP)_8]_2\cdot17DMF$ (C$_{259}$H$_{231}$Cl$_{16}$Co$_{27}$N$_{145}$O$_{17}$): C 41.75; H, 3.13; N, 27.26. Found: C, 42.94; H, 3.15; N, 27.35.

4.2.4. Low-pressure gas adsorption measurements. For all gas adsorption measurements 50-100 mg of sample were transferred to a preweighed glass sample tube under an atmosphere of nitrogen and capped with a Transeal. Samples were then transferred to a Micromeritics ASAP 2020 gas adsorption analyzer and heated under dynamic vacuum until the outgas rate at the degassing temperature was less than 2 $\mu$bar/min, and were subsequently weighed to determine the mass of sample. Adsorption isotherms for the uptake of $O_2$ at 195 K were measured using a
4.2.5. Isotherm fitting. Adsorption isotherms for O\textsubscript{2} and N\textsubscript{2} in Co-BTTri and Co-BDTriP were fit with a multi-site Langmuir equation (eq 1), where \( n \) is the total amount adsorbed in mmol/g, \( P \) is the pressure in bar, \( n_{\text{sat},i} \) is the saturation capacity in mmol/g, and \( b_i \) is the Langmuir parameter in bar\textsuperscript{-1}. While all isotherm data for Co-BTTri could be adequately fit by a dual-site Langmuir equation, the O\textsubscript{2} data for Co-BDTriP required at least a quadruple-site equation due to the mixture of coordination environments for the metal centers.

\[
n = \frac{n_{\text{sat},1}b_1P}{1 + b_1P} + \frac{n_{\text{sat},2}b_2P}{1 + b_2P} + \frac{n_{\text{sat},3}b_3P}{1 + b_3P} + \frac{n_{\text{sat},4}b_4P}{1 + b_4P} \tag{1}
\]

\[
b_i = e^{S_i/R}e^{-E_i/1000RT} \tag{2}
\]

The Langmuir parameter can be expressed using eq 2, where \( S_i \) is the site-specific molar entropy of adsorption in J/mol·K, \( E_i \) is the site-specific binding energy in kJ/mol, \( R \) is the gas constant in J/mol·K, and \( T \) is the temperature in K. The variable temperature isotherms for N\textsubscript{2} and O\textsubscript{2} were each fit simultaneously with a single set of parameters.

4.2.6. Isosteric heat of adsorption calculations. Using the Langmuir fits, the isosteric heat of adsorption, \( Q_{st} \), can be calculated as a function of the total amount of gas adsorbed, \( n \), by using the integrated form of the Clausius–Clapeyron equation (eq 3).

\[
(lnP)_n = \left(\frac{Q_{st}}{R}\right)\left(\frac{1}{T}\right) + C \tag{3}
\]

For example, the O\textsubscript{2} Langmuir fits for Co-BTTri were used to obtain the exact pressures that correspond to specific loadings at 195, 213, and 223 K. This was done at loading intervals of 0.1 mmol/g. At each loading, the slope of \( ln(P) \) versus \( 1/T \) was calculated to obtain the isosteric heat.

4.2.7. Ideal adsorbed solution theory calculations. Ideal adsorbed solution theory (IAST)\textsuperscript{15} was used to predict mixed gas behavior (e.g., 0.21 bar O\textsubscript{2}, 0.79 bar N\textsubscript{2}) from single-component adsorption isotherms. Plots showing IAST selectivities as a function of temperature were calculated using the Langmuir fits for O\textsubscript{2} and N\textsubscript{2} in Co-BTTri and Co-BDTriP. The selectivity factor, \( S \), is defined according to equation 4, where \( n_i \) is the amount adsorbed for each component as determined from IAST and \( x_i \) is the mole fraction of each component in the gas phase at equilibrium.

\[
S = \frac{n_{O_2}}{x_{O_2}}/\frac{n_{N_2}}{x_{N_2}} \tag{4}
\]

4.2.8. Single crystal X-ray diffraction. For all solvated structures, X-ray diffraction analyses were performed on single crystals coated with Paratone-N oil and mounted on Kapton or MiTeGen loops. For activated and gas-dosed structures, a single crystal was epoxied onto a thin glass fiber and carefully inserted into a 1.0 mm borosilicate capillary. The capillary was then attached to a Micromeritics ASAP 2020 instrument via a custom designed gas cell, degassed at a specified temperature using a sand bath, and then dosed with 400 mbar of a specific gas (He or O\textsubscript{2}). After dosing, the capillary was flame-sealed. X-ray data for all Co-BTTri samples were collected at Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National
Laboratory using synchrotron radiation ($\lambda = 0.7749$ Å or $0.8856$ Å) and a Bruker PHOTON100 CMOS diffractometer equipped with a Bruker AXS APEX II CCD detector. X-ray data for the Co-BDTriP samples were collected using a Bruker APEX-II QUAZAR diffractometer (Mo-K$\alpha$, $\lambda = 0.71073$ Å) equipped with a Bruker APEX II detector. For more details on treatment of X-ray data, please see the Supporting Information.

4.2.9. Magnetic susceptibility. Magnetic susceptibility measurements were performed on Co-BTTri and DMF-solvated Co-BTTri using a Quantum Design MPMS2 SQUID magnetometer. Dc magnetic susceptibility measurements were collected in the temperature range 2-300 K under applied magnetic fields of 0.1, 0.5, and 1 T. Diamagnetic corrections were applied to the data using Pascal’s constants. For the activated Co-BTTri sample, data in the temperature range of 50-300 K were simulated using the software program PHI using the simplex method. For more details on sample preparation and data treatment, please see the Supporting Information.

4.2.10. Quantum chemical calculations. Two different cluster models were used in this study. The first was crafted from the X-ray crystal structures of the activated and O$_2$-bound Co-BTTri compounds. The [Co$_4$Cl(Tri)$_8$]$^{1-}$ models (HTri = 1,2,3-triazole) were saturated with H atoms to keep the correct total charge. Geometry optimizations were performed where the position of H atoms was relaxed while the key atoms (Co, Cl, N) were kept fixed. The amount of charge transferred from Co to O$_2$ and the magnetic exchange coupling constants were computed. These properties directly depend on the geometry and for that reason the experimental bond distances and angles of Co, Cl, and triazolate were employed. These calculations were performed by means of density functional theory (DFT) and multiconfigurational wave function theory. All cluster DFT calculations were performed with the M06 functional as implemented in the Gaussian09 program package, and the def2-TZVP all-electron basis sets.

Multiconfigurational calculations with the complete active space self-consistent field (CASSCF) method, and its extension through second-order perturbation theory (CASPT2), were performed on both activated and O$_2$-bound complexes. A minimal active space composed of 4 electrons in the four 3$d$ orbitals (abbreviated as CAS(4,4)) was used for the calculation of the exchange coupling constants $J$ and $J'$. A spin ladder of one quintet, three triplets and one singlet states was formed by considering the spin couplings of four $S = \frac{1}{2}$ centers. CASPT2(4,4) energies were used for the calculation of the $J$ and $J'$ constants. For an in-depth understanding of the local properties of one, non-coupled Co center, CASSCF/CASPT2 calculations were performed on a monocobalt model, i.e. three out of four Co$^{II}$ centers were substituted by closed-shell Mg$^{II}$ centers. A CAS(9,11) composed of the five 3$d$ orbitals of Co, the five orbitals of the second $d$-shell of Co, and the bonding component between the 3$d_{x^2-y^2}$ orbital and four 2$p$ orbitals of the Co-coordinated N atoms was used for the activated node. For the Co–O$_2$ node, a CAS(11,13) was employed, which included the same orbitals of CAS(9,11) augmented with the two singly occupied $\pi^*$ orbitals of O$_2$. The triple-zeta quality ANO-RCC-VTZP basis set was used for Co and O atoms, a double-zeta quality ANO-RCC-VDZP basis set for the atoms forming the first coordination sphere of Co, and a minimal ANO-RCC-MB basis set for all other atoms. All multiconfigurational calculations were performed using the MOLCAS 8.0 program package.

The second cluster model was crafted from the Co-BTTri structure optimized with periodic DFT. The effect of the counter-cation was considered for the periodic DFT geometry optimizations of the activated Co-BTTri material. The negative charge of the framework was balanced with protons placed at the non-coordinated N atoms of the triazolate group. This
approach is similar to the work of Poloni et al.\textsuperscript{23} in which the M-BTT family of materials was optimized using periodic DFT with protonated frameworks. The pyrazolate group of the BTP\textsuperscript{3-} ligand possesses no un-coordinated N atoms and therefore periodic DFT geometry optimizations were not performed on the Co-BTP structure. We also considered cluster models of the isostructural Co-BTT and Co-BTP systems to investigate the effect of the different ligands (BTT\textsuperscript{3-}, BTTri\textsuperscript{3-}, BTP\textsuperscript{3-}) on the Co–O\textsubscript{2} binding. Three out of four Co\textsuperscript{II} centers were substituted by closed-shell Mg\textsuperscript{II} centers. The positions of the modified atoms in the three systems, the Co and its first coordination sphere, and the O\textsubscript{2} molecule bound to Co were relaxed at the M06/def2-TZVP level of theory. All periodic DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP) version 5.3.5.\textsuperscript{24,25} The Perdew-Burke-Ernzerhof (PBE) gradient-corrected, exchange-correlation functional,\textsuperscript{26} combined with Grimme’s D3 dispersion correction (PBE-D3),\textsuperscript{27} was used for all periodic calculations. The electronic self-consistency loop was converged within $10^{-5}$ eV and the ionic positions and lattice constants were fully relaxed until forces were converged within 0.05 eV/Å. Finally, a plane wave energy cutoff of 400 eV was used while the Brillouin zone was sampled at the Gamma point only.

4.3. Results and discussion

4.3.1. Synthesis of Co-BTTri. Solvated Co-BTTri, or Co\textsubscript{3}[(Co\textsubscript{4}Cl\textsubscript{3}(BTTri))\textsubscript{4}]\textsubscript{58}DMF, can be readily synthesized under air-free conditions through the reaction of H\textsubscript{3}BTTri, CoCl\textsubscript{2}, and dimethylformamidium trifluoromethanesulfonate in a mixture of N,N-dimethylformamide (DMF) and methanol at 393 K. The powder X-ray diffraction pattern of this product (see Figure 4.S1) is in good agreement with a family of cubic, sodalite-type frameworks whose general structure consists of square [M\textsubscript{4}Cl\textsubscript{4}]\textsuperscript{2+} clusters linked by tritopic bridging ligands to form an overall anionic framework (Figure 4.1). To maintain charge balance, there are three extra-framework Co\textsuperscript{2+} cations for every 24 framework cobalt centers. In solvated Co-BTTri, the framework metal cations are ligated by four equatorial triazolates, one chloride anion, and a solvent molecule. The axial solvent molecule can be removed by heating to 423 K under dynamic vacuum, leading to a porous material with coordinatively unsaturated cobalt(II) centers and a Brunauer-Emmett-Teller (BET) surface area of 1595(4) m\textsuperscript{2}/g (Langmuir surface area of 1853(7) m\textsuperscript{2}/g). Even after activation, elemental and infrared analyses indicate that residual DMF remains within the material, the majority of which is likely ligated to the extra-framework cations (Figure 4.S2). The overall formula of activated Co-BTTri is thus Co\textsubscript{3}[(Co\textsubscript{4}Cl\textsubscript{3}(BTTri))\textsubscript{4}]\textsubscript{14}DMF.

Analogues of Co-BTTri have previously been synthesized with a variety of nitrogen heterocycle-containing linkers and transition metals. These systems include tetrazolates (M-BTT; H\textsubscript{3}BTT = 1,3,5-tri(1H-tetrazol-5-yl)benzene; M = Cr, Mn, Fe, Co, Ni, Cu, Cd),\textsuperscript{8,28} triazolates (M-BTTri; H\textsubscript{2}BTTri = 1,3,5-tri(1H-1,2,3-triazol-5-yl)benzene; M = Fe, Cu),\textsuperscript{29} and pyrazolates (M-BTP; H\textsubscript{2}BTP = 1,3,5-tri(1H-pyrazol-4-yl)benzene; M = Cu, Ni).\textsuperscript{30} The pK\textsubscript{a} of the protonated form of the bridging ligand, which increases in the order of H\textsubscript{3}BTT < H\textsubscript{3}BTTri < H\textsubscript{2}BTP, was found to be positively correlated with the chemical stability of the overall framework and inversely related to the Lewis acidity of the open metal site. Due to the high basicity and donating ability of pyrazolate linkers, the metal ions in Ni-BTP adopt low-spin configurations.\textsuperscript{30} On the other hand, it has been shown that the intermediate basicity of triazolates allows the iron(II) centers in Fe-BTTri to convert between high-spin and low-spin configurations, depending on the identity of the axial guest molecule.\textsuperscript{29b} Intriguingly, these examples suggest that
this structure type should be able to accommodate other low-spin metal ions, such as low-spin cobalt(III).

Figure 4.1. Structure of Co-BTTri. Structure of Co-BTTri, with the truncated octahedral cages highlighted in light purple. Expanded view: Local coordination environment of the framework cobalt(II) centers. Each metal is ligated by four equatorial triazolates and one axial chloride, while the sixth coordination site is occupied by a solvent molecule that can be removed by pulling vacuum at 423 K. Purple, grey, blue, and green spheres represent Co, C, N, and Cl atoms, respectively; H atoms are omitted for clarity.

4.3.2. Adsorption of O₂ and N₂ in Co-BTTri. Initial low temperature gas adsorption measurements indicated that the cobalt(II) centers in Co-BTTri interact much more strongly with O₂ than with N₂. At 195 K, the O₂ loading rapidly rises to 3.3 mmol/g at 0.21 bar and reaches a maximum of 4.8 mmol/g at 1 bar, while the N₂ isotherm is much flatter, achieving only 2.0 mmol/g at 1 bar (Figure 4.2). To further quantify the gas adsorption properties of Co-BTTri, O₂ and N₂ isotherms were collected at three different temperatures between 195 and 223 K (Figure 4.S3). Each set of three isotherms was simultaneously modeled by a dual-site Langmuir equation, and isosteric heats of adsorption, as well as ideal adsorbed solution theory (IAST) selectivities, were then calculated from these fits (Figures S4 and S5). At low loadings, the isosteric heat (Qₛₐ) of O₂ adsorption is −34(1) kJ/mol, which turns over near 2.8 mmol/g and subsequently decreases to −5(1) kJ/mol (Figure 4.S4). The large isosteric heat at low loadings is due to interactions between O₂ and the coordinatively unsaturated cobalt(II) centers, while the lower isosteric heat at higher loadings is a result of weak physisorption to the framework surface. The amount of strongly bound O₂, as determined from the inflection point in the Qₛₐ plot, corresponds to roughly 0.85 per framework cobalt center, suggesting the formation of a 1:1 cobalt-dioxygen adduct. In comparison, the framework interaction with N₂ is significantly weaker, with an isosteric heat that is relatively constant at −12(1) kJ/mol (see Figure 4.S4).
Figure 4.2. Adsorption isotherms for the uptake of $O_2$ and $N_2$ in Co-BTTri at 195 K. The filled circles and solid lines represent experimental data and corresponding dual-site Langmuir fits, respectively.

We subsequently employed IAST to model mixed-gas behavior and predict the purity of $O_2$ gas that can be achieved from air using Co-BTTri. The resulting selectivities, calculated for a mixture of 0.21 bar $O_2$ and 0.79 bar $N_2$, reach 41 at 195 K and gradually drop to 13 by 243 K (see Figure 4.S5). These values correspond to $O_2$ purities of 92% and 77%, respectively. While lower than Cr$_3$(btc)$_2$ and Cr-BTT, these selectivities are significantly higher than Fe$_2$(dobdc), which reaches a maximum selectivity of only 11 at 201 K. Notably, the higher $O_2/N_2$ selectivities displayed by Co-BTTri are not the result of a particularly strong interaction with $O_2$, as previously reported iron and chromium frameworks exhibit much larger $O_2$ isosteric heats. Rather, the selectivities are due to the combination of moderate $O_2$ affinities coupled with exceptionally weak $N_2$ binding. Indeed, the isosteric heat of $N_2$ adsorption in Co-BTTri is nearly three times lower in magnitude than that of Fe$_2$(dobdc) ($Q_a = -12(1)$ versus $-35$ kJ/mol). This distinction is important, because while large $O_2$ isosteric heats often lead to high selectivity, they also result in punitive regeneration energies and highly exothermic adsorption processes that can, quite literally, spark framework decomposition. For example, Fe$_2$(dobdc), Cr$_3$(btc)$_2$, and Cr-BTT have all been shown to lose crystallinity and capacity if the $O_2$ adsorption temperature and/or adsorption rate are not carefully regulated. As a result of this strong interaction and corresponding sensitivity, these materials cannot be easily handled in air without significant reductions in their gas adsorption properties, hindering their utilization in practical processes. On the other hand, materials such as Co-BTTri, which exhibit weaker interactions with $O_2$ and also
significantly more robust framework architectures, can be regenerated under mild conditions and are much more likely to be stable over many adsorption/desorption cycles.

To illustrate this concept, we performed multiple O$_2$ adsorption/desorption cycles at 195 K/323 K and 0.21 bar to investigate the reversibility of O$_2$ binding in Co-BTTri. Gratifyingly, no change in O$_2$ uptake, crystallinity, or surface area was observed after ten cycles (Figure 4.3). In addition, the framework can be exposed to room temperature air at 90% relative humidity for 24 h, reactivated at 423 K, and still exhibit no loss in adsorption properties. This stability greatly exceeds that of iron- and chromium-based metal–organic frameworks. Co-BTTri also surpasses the performance of many cobalt-based molecular complexes, which are susceptible to irreversible ligand and metal oxidation (the latter occurring via predominantly bimolecular pathways).$^{31}$ This remarkable stability, combined with a high O$_2$/N$_2$ selectivity, makes Co-BTTri an excellent candidate adsorbent for air purification applications.

**Figure 4.3. Uptake and release of O$_2$ in Co-BTTri.** Adsorption was carried out at 195 K and 0.21 bar, while desorption was performed by quickly heating the sample to 323 K for five minutes. Note that the before the last cycle, the sample was exposed to humid air (90% relative humidity) for 24 h and then reactivated at 423 K for 6 h.

4.3.3. **Structural characterization of Co-BTTri.** In order to structurally probe the Co–O$_2$ interaction in Co-BTTri, pink crystals of Co-BTTri were grown at 423 K inside sealed tubes. Methanol-solvated Co-BTTri (Co-BTTri–MeOH) adopts the primitive space group $Pm\bar{3}m$, much like previously reported frameworks of this structure type. Analysis of the bond lengths in the solvated structure reveals Co–N bond distances of 2.041(2) Å, which are slightly shorter than bond lengths observed in the tetrazolate congeners of this framework (2.06-2.32 Å) (Figure 4.4a).$^{8,28}$ We note that the extra-framework cobalt centers, which are likely ligated by solvent, could not be located in Co-BTTri–MeOH.
Figure 4.4. Structural changes observed in Co-BTTri upon (a) methanol solvation, (b) desolvation, and (c) O$_2$ binding. Purple, grey, blue, and green spheres represent Co, C, N, and Cl atoms, respectively; H atoms are omitted for clarity. Note that in the structure of Co-BTTri–O$_2$ the bound O$_2$ units are disordered over two positions with slightly differing tilt angles, only one of which is depicted here.

To obtain a desolvated structure, a single crystal was heated to 453 K under dynamic vacuum inside a glass capillary, and then subsequently flame-sealed under 400 mbar of helium. Note that roughly 38(2)% of the cobalt centers remain solvated in the activated single crystal, as determined by X-ray crystallography. Because gas adsorption experiments revealed that at least 85% of the framework sites are accessible to O$_2$, this incomplete activation is likely a reflection of imperfect capillary sealing and the sensitivity of a single crystal to adventitious water.

Surprisingly, upon heat and vacuum treatment, the crystal structure distorts from $Pm\overline{3}m$ to face-centered $Fm\overline{3}c$ symmetry. In this lower symmetry space group, the opposing [Co$_4$Cl]$_7^+$ squares of each truncated octahedral cage are slightly twisted with respect to each other (Figure 4.S7a). In addition, the triazolate rings are ordered, such that the non-coordinating nitrogen atoms of neighboring heterocycles are pointed away from each other (Figure 4.4b). However, there is almost certainly a small amount of disorder in the triazolate orientations, as residual electron density corresponding to the extra-framework Co$_2^+$ cations was located in between adjacent heterocycles (Figure 4.S7c). Presumably, as the crystal is activated, the extra-framework cations lose some of the coordinated solvent, migrate, and bridge adjacent triazolate nitrogen atoms.

In addition to the symmetry reduction, upon activation the Co–N and Co–Cl bond lengths within Co-BTTri each decrease by ~0.1 Å, to 1.953(2) Å and 2.367(1) Å, respectively (Figure 4.4b). While it was not possible to definitively assign a spin state using the Co–N bond distances in Co-BTTri–MeOH, the much shorter bond lengths observed in the activated material strongly suggest the presence of low-spin cobalt(II).

To gain insight into the Co–O$_2$ interaction within the activated material, an activated crystal was dosed with 400 mbar of O$_2$ and cooled to 100 K. The $Fm\overline{3}c$ symmetry is maintained, and O$_2$ was found to coordinate to each metal in an end-on fashion with a Co–O$_2$ bond length of 1.973(6) Å. This distance is somewhat longer than previously reported octahedral cobalt–superoxide complexes, which possess Co–O$_2$ bond lengths between 1.86 and 1.90 Å.$^{11,32}$ In Co-BTTri, the O$_2$ is further disordered over two positions, with bent Co–O–O angles of 122(1)$^\circ$ and 130(2)$^\circ$ and occupancies of 42(3)% and 58(3)%, respectively (Figure 4.4c). Due to this disorder, the O–O bond length could not be accurately determined and was constrained to values near 1.21 Å. The relatively long Co–O separation, combined with the essentially unchanged Co–N bond...
lengths, suggests partial electron transfer to O\textsubscript{2} rather than full reduction to superoxide. This hypothesis is fully consistent with the moderate O\textsubscript{2} binding energies observed in the gas adsorption studies, and indicates only very slight activation of the O–O bond.

4.3.4. Spin-state characterization of Co-BTTril. To further probe the cobalt(II) spin state in these materials, DC magnetic susceptibility measurements were carried out on both activated and DMF-solvated Co-BTTril (Co-BTTril–DMF) samples under an applied magnetic field of 1 T. As some solvent loss was observed during the preparation of methanol-soaked Co-BTTril samples, DMF was used instead to solvate Co-BTTril due to its lower volatility.

The Co–N bond lengths observed in the activated crystal structure suggest that the 24 Co\textsuperscript{II} centers per formula unit are low-spin (\(S = \frac{1}{2}\)), while the three charge-balancing extra-framework Co\textsuperscript{II} centers are likely high-spin (\(S = \frac{3}{2}\)). The expected \(\chi_M T\) value for such a spin system, if all metal centers are magnetically non-interacting with \(g = 2\), is 14.63 emu·K/mol. As shown in Figure 4.5 (red circles), the \(\chi_M T\) value observed at 300 K and \(H_{dc} = 1\) T for Co-BTTril is notably higher at 18.99 emu·K/mol. This value can be rationalized in part by considering that the \(g\) values for high-spin cobalt(II) complexes are typically substantially higher than 2.\textsuperscript{33} Furthermore, the linear shape of the susceptibility curve suggests a temperature independent paramagnetism contribution to the susceptibility, which would also contribute to a larger than predicted room temperature \(\chi_M T\) value.

**Figure 4.5.** Variable-temperature magnetic susceptibility data collected under an applied field of 1 T for samples of Co-BTTril solvated in DMF (blue circles) and activated Co-BTTril (red circles). The black line represents a fit to the data using the Hamiltonian and parameters described in the text.

A fit to the magnetic susceptibility data for activated Co-BTTril was obtained using the Hamiltonian in Equation 5 in order to further understand the magnetic exchange interactions.
within the [Co₄Cl]⁷⁺ clusters. The magnetic data were corrected by subtracting the expected contributions from the extra-framework Co⁺⁺ centers, and should thus reflect the magnetic behavior of a single [Co₄Cl]⁷⁺ square (see Supporting Information for details).

\[ \hat{H} = -2J\left(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_4 + \mathbf{S}_4 \cdot \mathbf{S}_1\right) - 2J'\left(\mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_4\right) \]  

(5)

In Eq 5, \( J \) reflects the magnetic coupling between two low-spin (\( S = \frac{1}{2} \)) Co⁺⁺ centers through a triazolate bridge (i.e., the coupling between nearest-neighbor metals) and \( J' \) reflects the magnetic coupling between two low-spin (\( S = \frac{1}{2} \)) Co⁺⁺ centers across the \( \mu_4 \)-chloride bridge. In addition, an unfixed temperature-independent paramagnetism parameter, \( \chi_{\text{TIP}} \), was included during fitting. This Hamiltonian provided a good fit to the data in the temperature range 50-300 K using the parameters \( J = -10 \text{ cm}^{-1} \), \( J' = -98 \text{ cm}^{-1} \), and \( \chi_{\text{TIP}} = 0.0038 \text{ emu/mol} \). The large negative value of \( J' \) is not unreasonable, as halide-bridged low-spin Co⁺⁺ centers have been previously shown to exhibit large antiferromagnetic coupling.³⁴ It was not possible to fit magnetic data below 50 K, possibly due to the presence of additional magnetic coupling pathways that are favored at lower temperatures. The fitting parameters obtained should be considered as approximate, since neither zero-field splitting nor spin-orbit coupling of the Co⁺⁺ centers were included, and only the primary magnetic coupling pathways have been modeled. Mixture of the \( S = \frac{1}{2} \) state of the Co⁺⁺ centers with a high-spin excited state is also possible, and may be reflected in the large value of \( \chi_{\text{TIP}} \) extracted from fitting.

Compared to the activated sample, in which the framework cations maintain a low-spin configuration over the entire observed temperature range, Co-BTTri–DMF shows markedly different magnetic behavior that is suggestive of a broad spin-crossover transition (Figure 4.5, blue circles). At 300 K the \( \chi_M T \) product is 57.64 emu·K/mol, which is larger than the 50.65 emu·K/mol anticipated for 27 non-interacting \( S = \frac{1}{2} \) centers with \( g = 2 \). Again, this larger value is expected, given that the magnetic moment for octahedral high-spin cobalt(II) centers is generally higher than the spin-only value. The \( \chi_M T \) value smoothly decreases with temperature until it approaches a value consistent with 24 non-interacting \( S = \frac{1}{2} \) centers and three non-interacting \( S = \frac{3}{2} \) centers at about 90 K. Further decreases in the \( \chi_M T \) product below 90 K are attributed to antiferromagnetic coupling between Co⁺⁺ centers. The spin-crossover behavior of the Co⁺⁺ centers within the [Co₄Cl]⁷⁺ squares is likely solvent dependent,³⁵ although solvents aside from DMF were not investigated.

### 4.3.5. Electronic structure of Co-BTTri and Co-BTTri–O₂

The extent of charge transfer in metal–O₂ adducts is typically probed by vibrational spectroscopy via the O–O stretching frequency.³⁶ However, due to the weak binding of O₂ in this system, it was not possible to identify this stretch in the infrared spectra collected for Co-BTTri–O₂ at room temperature. For this reason, quantum chemical calculations were performed to gain insight into the electronic structures of both Co-BTTri and Co-BTTri–O₂. These calculations were carried out on a simplified model of the [Co₄Cl]⁷⁺ building unit, in which each ligand was truncated into a simple triazolate ring (Figure 4.6). Geometry optimizations were performed keeping the Co, Cl, and N atoms fixed at coordinates experimentally observed in the single crystal structures (for more details, see the Experimental Section above).
Figure 4.6. Spin density of (a) the activated $[\text{Co}_4\text{Cl}\text{(Tri)}]^{7+}$ node and (b) the $[\text{Co}_4\text{(O}_2\text{)}_4\text{Cl}\text{(Tri)}]^{7+}$ node. The positions of the Co, N, and Cl atoms are fixed according to the experimental crystal structures. Red density corresponds to alpha electron excess, yellow density to beta electron excess (isosurface: 0.01 a. u.).

For the activated framework, both DFT and CASSCF/CASPT2 methods predict an open-shell singlet for the ground state of the $[\text{Co}_4\text{Cl}]^{7+}$ node, consistent with experimental measurements. The spin density of the broken symmetry singlet (Figure 4.6a) shows antiferromagnetic coupling between the four metal centers. Each cobalt(II) center has an unpaired electron in the $3d_{z^2}$ orbital, and these are antiferromagnetically coupled across the $\mu_4$-chloride bridge. The energy levels obtained from the Hamiltonian shown in Eq 5 are given as:

$$E(S) = -J[S(S + 1) - S_{13}(S_{13} + 1) - S_{24}(S_{24} + 1)]$$
$$-J'[S_{13}(S_{13} + 1) + S_{24}(S_{24} + 1) - 4S_1(S_1 + 1)]$$ (6)

Here, $S_1$ is the spin on each of the metal centers, $S_{13}$ and $S_{24}$ are intermediate spins, and $S$ is the total spin of the Co$_4$ node. Solving Eq 6 using the CASPT2(4,4) energies for $S = 2$, 1, and 0 gives the ratio $J/J' = 0.1$, which is in agreement with the exchange coupling constants obtained from fitting the magnetic susceptibility data.

The character of the Co–O$_2$ bonding interaction was subsequently examined by means of electronic structure theory. As in the case of the activated node, the open-shell singlet state was found to be the ground state of the $[\text{Co}_4(\text{O}_2)_4\text{Cl}]^{7+}$ node (Figure 4.6b). The spin density on each Co$^{II}$ center suggests that little oxidation occurs upon O$_2$ binding. The extent of electron transfer from cobalt to dioxygen is about 0.25 electrons (M06 functional), and the partial occupation numbers of the CASSCF multiconfigurational wave function verified this weak charge transfer (0.20 electrons). Therefore, the Co–O$_2$ adduct in Co-BTTri has more Co(II)–dioxo character than Co(III)–superoxo (O$_2^-$) character. This conclusion is in agreement with previous EPR measurements on molecular 1:1 cobalt–dioxygen complexes, which showed that the extent of electron transfer to O$_2$ can vary between 0 and 1 electrons, and depends heavily upon the ligand.
field. Finally, the DFT-calculated enthalpy of O\(_2\) adsorption is \(-32.8\) kJ/mol (M06), within error of the experimental value of \(-34(1)\) kJ/mol.

### 4.3.6. Synthesis of Co-BDTriP

While Co-BTTri represents the first cobalt-based metal–organic framework to show appreciable O\(_2\) binding at pressures below 1 bar and demonstrates excellent air stability, its isosteric heat of \(-34(1)\) kJ/mol is relatively low. For comparison, enthalpies of oxygenation for cobalt(II) molecular complexes typically range between \(-40\) to \(-75\) kJ/mol. As a result of the low binding energy exhibited by Co-BTTri, low O\(_2\) adsorption and poor selectivity are observed for this material at room temperature. In principle, however, it should be possible to tune the ligand environment around the metal centers in Co-BTTri to facilitate a greater O\(_2\) uptake and greater selectivity at higher temperatures.

Towards this end, we sought to synthesize an analogous framework with H\(_3\)BTP, a tritopic linker containing only pyrazole moieties. However, various synthetic conditions led only to the formation of alternate phases featuring tetrahedral cobalt centers. All attempts to access a mixed-ligand framework, wherein H\(_3\)BTP and H\(_3\)BTTri were added simultaneously in various ratios, led to poorly crystalline material with low surface areas and poor O\(_2\) uptake. We succeeded, however, in synthesizing the new ligand H\(_3\)BDTriP (5,5"-(5-(1H-pyrazol-4-yl)-1,3-phenylene)bis(1H-1,2,3-triazole)), wherein one of the triazole moieties is replaced with a pyrazole (Figure 4.7a). Gratifyingly, single crystals of Co-BDTriP can be grown following similar procedures as Co-BTTri, and desolvation of the material under vacuum at 453 K leads to a porous material with a BET surface area of 1332(4) m\(^2\)/g (Langmuir surface area = 1517(2) m\(^2\)/g). Note that the lower surface area is likely due to a small amount of ligand or solvent remaining in the pores, which could not be removed by high temperature DMF and methanol washes or prolonged evacuation.

Crystals of Co-BDTriP form in the space group \(Pm\bar{3}m\), with all heterocycle moieties randomly distributed. The orientations of the triazolate groups are similarly disordered. The compound is thus expected to contain a statistical distribution of five distinct cobalt centers ligated by a combination of triazolate and pyrazolate rings. Because of this disorder, the metal–ligand bond lengths in this structure are the weighted average of five different coordination environments, and may not necessarily reflect any individual cobalt center. Finally, as with Co-BTTri, the extra-framework cation in Co-BDTriP was found to reside in between the nitrogen atoms of two neighboring triazolate ligands.

Overall, the solvated, activated, and O\(_2\)-dosed structures of Co-BDTriP closely resemble those of Co-BTTri (Figure 4.7b). This similarity is not unexpected, due to the only minor change in the ligand composition. The Co–N and Co–Cl bond lengths in methanol-solvated Co-BDTriP are very slightly shorter than those in Co-BTTri–MeOH (1.983(3) and 2.451(1) Å, respectively). As was the case with Co-BTTri, a completely activated crystal structure could not be obtained for Co-BDTriP due to difficulties in single-crystal sample preparation. However, in the 60% desolvated material the Co–N and Co–Cl distances significantly contract to 1.950(2) and 2.383(1) Å. Finally, the Co–O\(_2\) distance in Co-BDTriP is within error to that found in Co-BTTri (1.967(8) Å), with a similarly bent Co–O–O angle of 128(1)°. Note that the O\(_2\) is disordered over two positions related by a mirror plane.
Figure 4.7. Ligand and local structure of Co-BDTriP before and after O$_2$ binding. (a) Structure of the ligands used in this work, BTTri$^{3-}$ and BDTriP$^{3-}$. In BDTriP$^{3-}$, one of the bridging triazolates is replaced with a more electron-donating pyrazolate. (b) Structural changes observed for Co-BDTriP upon O$_2$ binding. Purple, grey, blue, and green spheres represent Co, C, N, and Cl atoms, respectively; due to ligand disorder, the black spheres represent either C or N atoms; H atoms are omitted for clarity. Note that in the structure of Co-BBDTriP–O$_2$ the bound O$_2$ units are disordered over two positions, which are related by a mirror plane.

4.3.7. Adsorption of O$_2$ and N$_2$ in Co-BDTr iP. While the O$_2$-dosed crystal structures of Co-BDTr iP and Co-BTTri are quite similar, a qualitative comparison of the steepness of their 195 K O$_2$ isotherms indicates that Co-BDTr iP has a much higher affinity for O$_2$ (Figure 4.8). To quantify this difference, O$_2$ and N$_2$ isotherms were measured at three different temperatures and fit to a Langmuir model to obtain isosteric heats of adsorption (Figure 4.8S). Because of the asymmetry of the BDTriP$^{3-}$ linker and the presence of many different metal coordination environments within the framework, at least a quadruple-site Langmuir equation was needed to accurately fit the O$_2$ isotherms for Co-BDTr iP.
Figure 4.8. Comparison of O$_2$ adsorption isotherms collected for Co-BTTri (red) and Co-BDTriP (purple) at 195 K. The filled circles and solid lines represent experimental data and their corresponding Langmuir fits, respectively. Inset: Low-pressure region of the 195 K O$_2$ isotherms. The Co-BDTriP O$_2$ uptake is significantly steeper at these low pressures than Co-BTTri.

From chemical intuition, one would expect a fraction of the binding sites in Co-BDTriP to be significantly stronger than Co-BTTri, with the remainder possessing either moderately higher or similar binding energies. Indeed, roughly 12% of the accessible open metal sites have an extremely high affinity for O$_2$, with an isosteric heat of $-47(1)$ kJ/mol (Figure 4.9). This strong binding at low loadings is attributed to interactions with cobalt centers bound by three or more pyrazolate ligands, which, in a purely statistical mixture, should account for 11% of the total metal sites. The isosteric heat then gradually decreases in magnitude to $-32(1)$ kJ/mol, a value very close to that determined for Co-BTTri, before turning over at 2.1 mmol/g (Figure 4.9). This saturation capacity is lower than observed for Co-BTTri (2.8 mmol/g), and is likely due to incomplete activation of the framework or unreacted ligand in the pores, which is also consistent with the comparatively lower surface area of Co-BDTriP. In addition to an increased O$_2$ affinity at low loadings, Co-BDTriP also exhibits a lower N$_2$ isosteric heat that gradually plateaus to $-9(1)$ kJ/mol (Figure 4.9). This decrease is expected, given the weaker Lewis acidity of pyrazolate-bound metal centers, and should also contribute to a higher O$_2$/N$_2$ selectivity.
Figure 4.9. Comparison of O₂ and N₂ isosteric heats for Co-BTTri (filled red and blue circles, respectively) and Co-BDTriP (open red and blue circles, respectively).

Figure 4.10. Ideal adsorbed solution theory (IAST) selectivities for Co-BTTri and Co-BDTriP calculated for a mixture of 0.21 bar O₂ and 0.79 bar N₂. Co-BDTriP is significantly more selective at all temperatures between 195 K and 240 K.
Although the chemical change between Co-BTTri and Co-BDTriP is modest, the IAST selectivities for Co-BDTriP are dramatically improved due to the combination of higher O\textsubscript{2} and lower N\textsubscript{2} binding energies observed for this framework (Figure 4.10). Indeed, the IAST selectivity more than doubles to 105 (97% purity) at 195 K and drops only to 40 at 243 K (91% purity). Notably, even with these higher O\textsubscript{2} binding affinities, no loss in stability is observed and Co-BDTriP can also be cycled multiple times without any loss in adsorption capacity (Figure 4.S10).

In addition to selectivity and stability, another important metric used to evaluate adsorbents is their working capacity, or the amount of gas that can be recovered during one adsorption and desorption cycle. Regeneration of commercial, zeolite-based air separation units is typically accomplished through vacuum swing adsorption (VSA).\textsuperscript{9} In this scenario, the adsorbent bed is held at a constant temperature and cycled between ambient pressure and a lower desorption pressure, \(P_D\). For a VSA air separation process, the working capacities can be roughly estimated from single component O\textsubscript{2} isotherms as the difference between the quantity of O\textsubscript{2} adsorbed at 0.21 bar and the quantity adsorbed at \(P_D\). Depending on the shape and steepness of the O\textsubscript{2} isotherm, this value can be much less than the total O\textsubscript{2} uptake of a material at 0.21 bar.

For \(P_D = 0.05\) bar, the working capacities of Co-BTTri and Co-BDTriP are both maximized at a bed temperature of ~230 K. At this temperature the calculated O\textsubscript{2} capacities of Co-BTTri and Co-BDTriP are 1.2 mmol/g and 0.6 mmol/g, respectively, while the resulting O\textsubscript{2} purity is 83% and 93%, respectively (see Figure 4.S11). Interestingly, although Fe\textsubscript{2}(dobdc) exhibits a significantly higher total O\textsubscript{2} uptake than Co-BTTri at 211 K (5.8 versus 3.0 mmol/g at 0.21 bar), its working capacity is only slightly higher, at 1.4 mmol/g.\textsuperscript{4d} Because of its higher working capacity, Co-BTTri may be better suited for processes where large volumes of O\textsubscript{2} are needed, while Co-BDTriP may be preferable if high O\textsubscript{2} purities are important. Although significantly higher working capacities can be achieved in both of these materials with lower desorption pressures, at a certain point the cost of achieving deeper vacuum levels will outweigh the benefits of increased capacity. Alternative regeneration conditions, such as temperature swing adsorption, or a combined temperature and pressure swing process, can also be envisioned and might lead to greater O\textsubscript{2} recovery.

\textbf{4.3.8. Effect of ligand field on O\textsubscript{2} adducts of cobalt-azolate frameworks.} While the experimental results above demonstrate that a small change in the organic linker can lead to large increases in the O\textsubscript{2} heat of adsorption, more detailed characterization of the Co–O\textsubscript{2} adducts in Co-BDTriP is hindered by its inherent structural disorder. A deeper understanding of the effect of ligand field on Co–O\textsubscript{2} interactions in metal–organic frameworks is desirable, however, as it may lead to the identification of new synthetic targets for O\textsubscript{2}/N\textsubscript{2} separation applications. Thus, O\textsubscript{2} binding in the isostructural series Co-BTT, Co-BTTri, and Co-BTP was explored systematically by computational methods to probe the relationship between equatorial ligand field, electronic structure, and heat of adsorption.

Because experimental structures of activated Co-BTT and Co-BTP and their oxygen-bound derivatives are not available, the cluster models used for this study were carved from the Co-BTTri structure optimized by periodic DFT (see experimental methods section for more details). While this approach leads to structural parameters that are slightly different from what is experimentally observed in Co-BTTri, particularly with respect to the Co–Cl bond distances (Table 4.1), the trends found in this series should hold nonetheless. Table 4.1 summarizes the results obtained from the geometry optimizations of the three models of the nodes within Co-BTT, Co-BTTri, and Co-BTP upon binding O\textsubscript{2}. The Co–O, Co–N, and Co–Cl bond distances
decrease according to the series Co-BTT > Co-BTTri > Co-BTP, while the extent of charge transfer and the strength of the Co–O₂ interaction follows the opposite trend. In addition, unlike Co-BTTri, the hypothetical Co-BTP dioxygen adduct can be more accurately thought of as a Co(III)–superoxo species. Such a material, if it can be synthesized, may be intriguing for both higher temperature air separation applications as well as aerobic oxidation catalysis. Remarkably, despite the simplicity of the three models, the calculated enthalpies of O₂ adsorption for the triazolate and pyrazolate clusters are in agreement with the measured O₂ heats of adsorption (at low loadings) for Co-BTTri and Co-BDTDriP, respectively.

**Table 4.1.** Key bond distances (in Å), charge transfer (in electrons) and O₂ enthalpies of adsorption (in kJ/mol, M06/def2-TZVP level of theory) for the three cluster models of the Co-BTT, Co-BTTri, and Co-BTP metal-organic frameworks. Note that these cluster models were carved from periodic DFT-optimized structure of Co-BTTri, and not from experimental data.

<table>
<thead>
<tr>
<th></th>
<th>Co-BTT</th>
<th>Co-BTTri</th>
<th>Co-BTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–O</td>
<td>2.182</td>
<td>2.053</td>
<td>1.917</td>
</tr>
<tr>
<td>Co–N&lt;sub&gt;avg&lt;/sub&gt;</td>
<td>1.954</td>
<td>1.924</td>
<td>1.904</td>
</tr>
<tr>
<td>Co–Cl</td>
<td>2.355</td>
<td>2.321</td>
<td>2.273</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>0.14</td>
<td>0.31</td>
<td>0.72</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>−28.6</td>
<td>−33.0</td>
<td>−47.5</td>
</tr>
</tbody>
</table>

**4.4. Conclusions and outlook**

One of the most promising aspects of metal–organic frameworks is their structural diversity and chemical tunability, both of which facilitate the rational design of materials with specifically tailored properties. Indeed, we have shown here how the judicious choice of both framework structure and ligand basicity results in two cobalt-based frameworks that not only exhibit exceptional oxidative stability but also display some of the highest O₂/N₂ selectivities reported to date. Deeper insights into the nature of the Co–O₂ bond gained by electronic structure calculations reveal that tuning the ligand field changes the O₂ heats of adsorption and also drastically alters the extent of electron transfer from cobalt to O₂ (from ~0.3 to 0.7 electrons). Finally, while not the focus of this work, the temperature- and solvent-dependent spin state changes in Co-BTTri are of fundamental interest and could be of potential use in sensing applications. Future work will focus on further development of pyrazolate-containing cobalt frameworks and evaluation of such materials as catalysts for aerobic oxidation processes.

**4.5. Acknowledgements**

The synthetic chemistry, crystal structure determinations, and characterization of the fundamental gas adsorption properties were supported through the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-SC0001015. The measurement and analysis of magnetic susceptibility data and the computational work were supported by the Nanoporous Materials Genome Center, funded by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences,
Geosciences and Biosciences under Award DE-FG02-12ER16362. Stability and adsorption/desorption cycling measurements, as well as assessments of the suitability of these materials for a practical air separation, were funded by IHI Corporation. This research used resources of the Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This research also used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We thank Dr. Antonio DiPasquale and the Chexray Facility for assistance with X-ray crystallographic analysis (NIH shared Instrumentation Grant S10-RR027172). We further thank Dr. Jarad A. Mason, David Gygi, Julia Oktawiec, and Douglas Reed for helpful discussions, and Dr. Zoey Herm and Rebecca Siegelman for experimental assistance. We also thank NSF for providing graduate fellowship support for D.J.X. and L.E.D. Dr. Katie R. Meihaus is acknowledged for editorial assistance.

4.6. References and supplementary information


Synthesis of **2**:
30 mL of anhydrous DMF were sparged with argon and cooled to 0 °C. While stirring, 2.85 mL of POCl₃ (3 equiv) were added dropwise, and the mixture was allowed to warm to room temperature and stirred for 1 h. Then 3 g of **1** (1 equiv.) was added, and the reaction was stirred at 90 °C for 4 h and at room temperature overnight. The flask was then cooled in an ice bath, and 26 g of ice was added and this mixture stirred for 15 min. Then, 3.75 g of NaClO₄ (3 equiv) dissolved in 4 mL of H₂O was added while stirring, resulting in precipitation of the iminium perchlorate salt, which was filtered, washed with cold water, and used directly in the next step without further purification.

To form the pyrazole ring, the isolated perchlorate salt was stirred in 67 mL of EtOH and 21 mL of H₂O. To this mixture was added 0.6 mL of hydrazine monohydrate (1.2 equiv). This mixture was refluxed for 2 h and then stirred at room temperature overnight. The product was precipitated with H₂O, filtered, and washed with H₂O to yield **2** in 81% yield (2.50 g). ¹H NMR (400 MHz, DMSO-d₆): 13.09 (s, 1H), 8.39 (s, 1H), 8.07 (s, 1H), 7.89 (d, J = 2 Hz, 2H), 7.60 (s, 1H).

---

**Scheme 4.51.** Overall synthesis of **H₃BDTriP**.

**H₃BDTriP**, 70%

---
Synthesis of 3:
2.50 g of pyrazole 2 was stirred in 20 mL DCM and 1.73 mL NEt₃ (1.5 equiv). To this mixture was added 2.70 g di-tert-butyl dicarbonate (1.5 equiv), and this mixture was stirred overnight at room temperature. The reaction was quenched with water, extracted with EtOAc, and dried over MgSO₄. Removal of solvent led to isolation of 3 in quantitative yield (3.33 g). ¹H NMR (400 MHz, DMSO-d₆): 8.98 (s, 1H), 8.45 (s, 1H), 8.09 (d, J = 2 Hz, 2H), 7.73 (m, 1H), 1.60 (s, 8H).

Synthesis of 4:
25 mL of THF and 25 mL of NEt₃ were sparged with argon for 1 h. Then, 3.30 g of the Boc-protected pyrazole 3 were added, along with 130 mg of Pd(PPh₃)₂Cl₂ (2.2 mol%) and 53 mg of CuI (3.3 mol%), then the mixture was stirred for 5 min at room temperature. 2.60 mL ethynyltrimethylsilane (2.2 equiv) was subsequently added, and the mixture was heated to 60 °C and stirred for 18 h. When the reaction was complete, the solvent was removed in vacuo and the mixture was redissolved in Et₂O and filtered over celite. A silica plug was used to remove trace palladium, and evacuation of solvent led to 3.01 g of 4 (84% yield). ¹H NMR (400 MHz, DMSO-d₆): 8.97 (s, 1H), 8.45 (s, 1H), 7.92 (d, J = 1.6 Hz, 2H), 7.40 (s, 1H), 1.60 (s, 9H), 0.25 (s, 18H).

Synthesis of 5:
2.03 g of 4 was stirred in 160 mL of THF cooled to 0 °C. To this mixture was added 10.0 mL of tetra-n-butylammonium fluoride (1.0 M in THF, 2.2 equiv), and the reaction was stirred for 30 minutes at 0 °C and allowed to warm to room temperature. The solvent was removed and the solid extracted with EtOAc, washed with NH₄Cl, and dried over MgSO₄. Because some of the pyrazole was deprotected during this procedure, the pyrazole was re-protected using di-tert-butyl dicarbonate in dichloromethane and NEt₃ (see synthesis of 3 for detailed procedures). Yield: 90%. ¹H NMR (400 MHz, DMSO-d₆): 8.94 (s, 1H), 8.43 (s, 1H), 7.97 (s, 2H), 7.45 (s, 1H), 4.41 (s, 2H), 1.60 (s, 9H).

Synthesis of H₃BDTriP:
6.9 mL of formaldehyde solution (37 weight % in H₂O, 20 equiv), 0.79 mL of acetic acid (3 equiv), and 20 mL of THF were stirred at room temperature for 15 min. Then, 0.91 g of NaN₃ (3 equiv) and 1.36 g of alkyne 5 (1 equiv) were added and the reaction was stirred for 10 min. 0.37 g of sodium ascorbate (0.4 equiv) and 74 mg of CuSO₄ (0.1 equiv, dissolved in 0.3 mL of H₂O) were added and the reaction stirred at room temperature for 48 h. The solvent was removed in vacuo, the solid extracted with EtOAc, and the solution concentrated to give 1.69 g of protected H₃BDTriP. To deprotect both the pyrazole and triazole rings, the solid was stirred in 50 mL of 3:1 MeOH:2N NaOH for 24 h. The solution was filtered to remove precipitated Cu(OH)₂, then neutralized with acetic acid, filtered, washed with H₂O, and dried to give 0.75 g H₃BDTriP (58% over two steps). ¹H NMR (400 MHz, DMSO-d₆): 15.30 (s, 2H), 13.05 (s, 1H), 8.44 (s, 2H), 8.21 (s, 2H), 8.18 (s, 1H), 8.05 (s, 2H).
Table 4.51. Langmuir parameters for Co-BTTri N\textsubscript{2} and O\textsubscript{2} isotherms. Variable-temperature N\textsubscript{2} and O\textsubscript{2} isotherms were each fit simultaneously, with a single set of parameters, using the dual-site Langmuir equation, 

\[ n = \frac{n_{\text{sat,1}}b_1P}{1+b_1P} + \frac{n_{\text{sat,2}}b_2P}{1+b_2P}, \]

where 

\[ b_i = e^{S_i/R}e^{-E_i/1000/RT}. \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Co-BTTri, N\textsubscript{2}</th>
<th>Co-BTTri, O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{\text{sat,1}} ) (mmol/g)</td>
<td>0.26</td>
<td>2.78</td>
</tr>
<tr>
<td>( E_1 ) (kJ/mol)</td>
<td>-19.87</td>
<td>-34.59</td>
</tr>
<tr>
<td>( S_1 ) (J/mol⋅K)</td>
<td>-78.56</td>
<td>-132.49</td>
</tr>
<tr>
<td>( n_{\text{sat,2}} ) (mmol/g)</td>
<td>7.21</td>
<td>7.05</td>
</tr>
<tr>
<td>( E_2 ) (kJ/mol)</td>
<td>-11.90</td>
<td>-5.18</td>
</tr>
<tr>
<td>( S_2 ) (J/mol⋅K)</td>
<td>-70.17</td>
<td>-33.96</td>
</tr>
</tbody>
</table>

Table 4.52. Langmuir parameters for Co-BDTr iP N\textsubscript{2} and O\textsubscript{2} isotherms. Variable-temperature N\textsubscript{2} and O\textsubscript{2} isotherms were each fit simultaneously, with a single set of parameters, using the multi-site Langmuir equation, 

\[ n = \frac{n_{\text{sat,1}}b_1P}{1+b_1P} + \frac{n_{\text{sat,2}}b_2P}{1+b_2P} + \frac{n_{\text{sat,3}}b_3P}{1+b_3P} + \frac{n_{\text{sat,4}}b_4P}{1+b_4P}, \]

where 

\[ b_i = e^{S_i/R}e^{-E_i/1000/RT}. \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Co-BDTr iP, N\textsubscript{2}</th>
<th>Co-BDTr iP, O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{\text{sat,1}} ) (mmol/g)</td>
<td>0.57</td>
<td>0.25</td>
</tr>
<tr>
<td>( E_1 ) (kJ/mol)</td>
<td>-19.73</td>
<td>-47.03</td>
</tr>
<tr>
<td>( S_1 ) (J/mol⋅K)</td>
<td>-86.04</td>
<td>-124.62</td>
</tr>
<tr>
<td>( n_{\text{sat,2}} ) (mmol/g)</td>
<td>5.82</td>
<td>0.80</td>
</tr>
<tr>
<td>( E_2 ) (kJ/mol)</td>
<td>-6.78</td>
<td>-36.23</td>
</tr>
<tr>
<td>( S_2 ) (J/mol⋅K)</td>
<td>-45.81</td>
<td>-110.96</td>
</tr>
<tr>
<td>( n_{\text{sat,3}} ) (mmol/g)</td>
<td>-</td>
<td>1.08</td>
</tr>
<tr>
<td>( E_3 ) (kJ/mol)</td>
<td>-</td>
<td>-32.36</td>
</tr>
<tr>
<td>( S_3 ) (J/mol⋅K)</td>
<td>-</td>
<td>-120.60</td>
</tr>
<tr>
<td>( n_{\text{sat,4}} ) (mmol/g)</td>
<td>-</td>
<td>6.75</td>
</tr>
<tr>
<td>( E_4 ) (kJ/mol)</td>
<td>-</td>
<td>-11.34</td>
</tr>
<tr>
<td>( S_4 ) (J/mol⋅K)</td>
<td>-</td>
<td>-61.81</td>
</tr>
<tr>
<td></td>
<td>Co-BTTri–DMF (100 K)</td>
<td>Co-BTTri–DMF (298 K)</td>
</tr>
<tr>
<td>------------------</td>
<td>----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td><strong>Formula</strong></td>
<td>C₂₆₄ H₂₆₄ Cl₆ Co₂₄ N₁₆₈ O₂₄</td>
<td>C₂₆₄ H₂₆₄ Cl₆ Co₂₄ N₁₆₈ O₂₄</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>Fm₃c</td>
<td>Fm₃c</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>37.4139(16)</td>
<td>37.7048(13)</td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, (Å³)</td>
<td>52372(7)</td>
<td>53603(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Radiation, λ (Å)</strong></td>
<td>Synchrotron, 0.7749 Å</td>
<td>Synchrotron, 0.7749 Å</td>
</tr>
<tr>
<td><strong>Data / Restraints / Parameters</strong></td>
<td>2643 / 62 / 108</td>
<td>2322 / 21 / 96</td>
</tr>
<tr>
<td><strong>Goodness of Fit on F²</strong></td>
<td>1.071</td>
<td>1.104</td>
</tr>
<tr>
<td>R₁, wR₂ (I&gt;2σ(I))</td>
<td>0.0671, 0.1996</td>
<td>0.0481, 0.1432</td>
</tr>
<tr>
<td>R₁, wR₂ (all data)</td>
<td>0.0768, 0.2164</td>
<td>0.0535, 0.1506</td>
</tr>
<tr>
<td><strong>Largest Diff. Peak and Hole (e Å⁻³)</strong></td>
<td>1.436 and −0.623</td>
<td>1.338 and −0.499</td>
</tr>
</tbody>
</table>

\[ R₁ = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR₂ = \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2}]^{1/2}. \]
### Table 4.S4. Crystallographic Data.

<table>
<thead>
<tr>
<th>Crystallographic Data</th>
<th>Co-BDTriP–DMF</th>
<th>Co-BDTriP–MeOH</th>
<th>Co-BDTriP</th>
<th>Co-BDTriP–O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C140 H140 Cl14.40 N76 O14.40</td>
<td>C100 H76 Cl13 N80 O12</td>
<td>C109.02 H71.02 Cl13.44 N63.98 O5.04</td>
<td>C87.98 H39.98 Cl13.5 N80.02 O23.62</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>Pm₃m</td>
<td>Pm₃m</td>
<td>Pm₃m</td>
<td>Pm₃m</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>18.8345(7)</td>
<td>18.7059(4)</td>
<td>18.6522(5)</td>
<td>18.6011(7)</td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, (Å³)</td>
<td>6681.3(7)</td>
<td>6545.4(4)</td>
<td>6489.2(5)</td>
<td>6436.0(7)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Radiation, λ (Å)</strong></td>
<td>Synchrotron, 0.7749</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>Data / Restraints / Parameters</strong></td>
<td>1577 / 0 / 57</td>
<td>1108 / 9 / 56</td>
<td>1208 / 0 / 53</td>
<td>1367 / 8 / 59</td>
</tr>
<tr>
<td><strong>Goodness of Fit on F²</strong></td>
<td>1.114</td>
<td>1.078</td>
<td>1.118</td>
<td>1.159</td>
</tr>
<tr>
<td><strong>R₁, wR²</strong> (I&gt;2σ(I))</td>
<td>0.0462, 0.1537</td>
<td>0.0593, 0.1690</td>
<td>0.0463, 0.1099</td>
<td>0.0619, 0.1830</td>
</tr>
<tr>
<td><strong>R₁, wR²</strong> (all data)</td>
<td>0.0503, 0.1590</td>
<td>0.0650, 0.1761</td>
<td>0.0610, 0.1233</td>
<td>0.0701, 0.1918</td>
</tr>
<tr>
<td><strong>Largest Diff. Peak and Hole (e Å⁻³)</strong></td>
<td>0.773 and −0.441</td>
<td>1.405 and −0.682</td>
<td>0.484 and −0.897</td>
<td>1.399 and −0.508</td>
</tr>
</tbody>
</table>

*aR₁ = \frac{\sum|F_o| - |F_c|}{\sum|F_o|} / \sum|F_o|, b wR₂ = \frac{\sum[w(F_o^2 - F_c^2)]^2}{\sum[w(F_o^2)]^2} \right)^{1/2}.*
Figure 4.S1. Powder diffraction pattern of as-synthesized Co-BTTri. $\lambda = 0.7500900$ Å.

Figure 4.S2. Infrared spectra of activated Co-BTTri. Peak at around 1620 cm$^{-1}$ is assigned as residual DMF, bound to the extraframework cations.
Figure 4.S3. Variable temperature O\textsubscript{2} (left) and N\textsubscript{2} (right) isotherms for Co-BTTri. The three temperatures were fit simultaneously to a dual-site Langmuir equation.

Figure 4.S4. Isothermic heats of adsorption for O\textsubscript{2} (red circles) and N\textsubscript{2} (blue circles) in Co-BTTri.
Figure 4.S5. Ideal adsorbed solution theory (IAST) selectivities for Co-BTTri as a function of temperature, calculated using the Langmuir fits (see Supplementary Table 4.S1), for a theoretical mixture of 0.21 bar O$_2$ and 0.79 bar N$_2$.

Figure 4.S6. Cycling experiments for Co-BTTri, with O$_2$ adsorption occurring at 195 K and 0.21 bar. Desorption was performed by quickly heating the sample to 323 K for five minutes. Note that before the last cycle, the sample was exposed to humid air for 24 h and then reactivated at 423 K for 6 h, demonstrating the excellent air-stability of Co-BTTri.
Figure 4.S7. Distortion from $Pm\bar{3}m$ symmetry and structural changes observed after activating methanol-solvated Co-BTTri. a) Two opposing $[\text{Co}_4\text{Cl}]^{7+}$ squares overlayed on top of each other in the activated structure. The squares are not completely aligned, and are tilted with respect to each other. b) The orientations of the triazolate rings are largely ordered, such that the non-bonding nitrogen atoms of neighboring triazolates are pointed away from each other. c) A small amount of disorder is present in the material, as 7% of the non-bonding triazolate nitrogen atoms are pointed at each other with an extra-framework cation bridging between them. Purple, grey, blue, and green sphere represent Co, C, N, and Cl atoms, respectively; H atoms are omitted for clarity.

Figure 4.S8. Variable temperature $\text{O}_2$ (left) and $\text{N}_2$ (right) isotherms for Co-BDTrP. The three temperatures were fit simultaneously to a dual-site Langmuir equation.
Figure 4.S9. Isosteric heats for $\text{O}_2$ (purple circles) and $\text{N}_2$ (cyan circles) in Co-BDTriP.

Figure 4.S10. Cycling experiments for Co-BDTriP, with $\text{O}_2$ adsorption occurring at 195 K and 0.21 bar. Desorption was performed by quickly heating the sample to 323 K for five minutes.
Figure 4.S11. Vacuum swing adsorption (VSA) working capacity (cycling between ambient pressure and 0.05 bar) as a function of temperature for Co-BTTri (red circles) and Co-BDTriP (purple circles).
Chapter 5: Synthesis, gas adsorption behavior, and reactivity of sodalite-type Fe(II)-based frameworks

5.1. Introduction

Chapters 2 and 3 examined the role of weak-field primary coordination spheres and hydrophobic pore environments in hydrocarbon oxidation reactions catalyzed by Fe_2(dobdc) and its expanded analogues. In this chapter, attention is turned to developing new iron(II)-based frameworks with tunable primary coordination spheres, to investigate the effect of ligand field on reactivity and gas adsorption properties. Towards this goal, two new sodalite-type frameworks, Fe-BTTr (H_3BTTr = 1,3,5-tri(1H-1,2,3-triazol-5-yl)benzene) and Fe-BTP (H_3BTP = 1,3,5-tri(1H-pyrazol-4-yl)benzene), were synthesized. While the main focus of this chapter is to report their synthesis and physical characterization, preliminary gas adsorption and reactivity studies were also performed on Fe-BTTr, as well as the previously reported tetrazolate congener Fe-BTT (H_3BTT = 1,3,5-tri(1H-tetrazol-5-yl)benzene). Interesting O_2 and CO gas adsorption properties are displayed by bulk Fe-BTTr, and will be briefly described. On the other hand, initial N_2/O/ethane oxidation studies performed on Fe-BTT suggest defect sites are responsible for the reactivity seen thus far, highlighting the inhomogeneity present even in these highly crystalline frameworks.

5.2. Experimental

5.2.1. Fe-BTTr synthesis. To a 25 mL Schlenk flask charged with a stir bar and a solution of H_3BTTr (50 mg, 1.0 equiv, 0.18 mmol) and dimethylformamidium trifluoromethanesulfonate (180 mg, 4.5 equiv, 0.81 mmol) in DMF (8 mL) was added a solution of FeCl_2 (230 mg, 10 equiv, 1.8 mmol) in 2 mL of methanol. The yellow solution was stirred at 120 °C for 10 days. The resulting yellow powder was collected by filtration, rinsed with DMF, and soaked in 10 mL of DMF at 120 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh DMF was added. This process was repeated nine times so that the total time washing with DMF was 5 days. The yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times so that the total time washing with methanol was 5 days. The resulting yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of DMF at 120 °C for 10 days. The supernatant solution was decanted, and 10 mL of fresh DMF was added. This process was repeated nine times so that the total time washing with DMF was 5 days. The resulting yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times so that the total time washing with methanol was 5 days. The resulting yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times so that the total time washing with methanol was 5 days. The resulting yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times so that the total time washing with methanol was 5 days. The resulting yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times so that the total time washing with methanol was 5 days. The resulting yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times so that the total time washing with methanol was 5 days. The resulting yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times so that the total time washing with methanol was 5 days. The resulting yellow powder was collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times so that

5.2.2. Fe-BTTr single crystal synthesis. To a stainless steel bomb charged with a solution of H_3BTTr (12 mg, 2.2 equiv, 0.043 mmol) and dimethylformamidium trifluoromethanesulfonate (24 mg, 5.4 equiv, 0.11 mmol) in DMF (8 mL) was added a solution of FeCl_2 (2.5 mg, 1.0 equiv, 0.020 mmol) in methanol (2 mL). The solution was heated at 160 °C for 3 days. Small yellow crystals were isolated by decanting the supernatant solution, rinsed with DMF, and soaked in 10 mL of DMF at 120 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh DMF was added. This process was repeated four times so that the total time washing with DMF was 5 days. The yellow crystals were collected by filtration, rinsed with methanol, and soaked in 10 mL of methanol at 60 °C for 12 h. The supernatant solution was decanted, and 10 mL of fresh methanol was added. This process was repeated nine times, so that
the total time washing with methanol was 5 days. The yellow crystals were collected by filtration, and heated at 150 °C under dynamic vacuum (<0.01 mbar) for 2 days, affording ~2 mg of pale red crystals of Fe-BTTri.

5.2.3. Fe-BTP single crystal synthesis. Fe-BTP was synthesized under an N$_2$ atmosphere according to the follow procedure. To a 20 mL scintillation vial was added 25 mg of H$_3$BTP (0.090 mmol, 1.0 equiv) dissolved in 7.5 mL of DMF, along with 150 mg of dimethylformamidium trifluoromethanesulfonate (0.68 mmol, 7.5 equiv). After the ligand and acid were fully dissolved, a solution of 3.0 mg of NH$_4$Cl (0.060 mmol, 0.65 equiv) in 2.5 mL of MeOH was added, followed by 56 mg of Fe(CF$_3$SO$_3$)$_2$ (0.16 mmol, 1.8 equiv). The reaction mixture was heated for 7 days at 120 °C to produce dark brown, cubic crystals of solvated Fe-BTP. These crystals were washed with DMF (6 × 10 mL at 120 °C for 12 h each), methanol (6 × 10 mL at 60 °C for 12 h each), and then activated at 160 °C overnight to produce 24 mg (70%) of activated Fe-BTP. Elemental analyses on the activated framework indicate residual methanol (likely bound to the extra-framework cations) and ligand trapped within the pores, to give a final molecular formula of [Fe(CH$_3$OH)$_6$]$_3$(Fe$_4$Cl$_3$(BTP)$_8$)$_2$[H$_3$BTP]$_6$.5

5.2.4. Low-pressure gas adsorption experiments. For all gas adsorption measurements 50-100 mg of sample were transferred to a preweighed glass sample tube under an atmosphere of nitrogen and capped with a Transeal. Samples were then transferred to a Micromeritics ASAP 2020 gas adsorption analyzer and heated under dynamic vacuum until the outgas rate at the degassing temperature was less than 2 µbar/min, and were subsequently weighed to determine the mass of sample. Adsorption isotherms for the uptake of O$_2$ at 195 K were measured using a dry ice/isopropanol cold bath.

5.2.5. Mössbauer spectroscopy. Iron-57 Mössbauer spectra were obtained at 100 K with a constant acceleration spectrometer and a cobalt-57 rhodium source. Prior to measurements the spectrometer was calibrated at 295 K with α-iron foil. Samples were prepared inside an N$_2$-filled glovebox and contained 20 mg/cm$^2$ of sample diluted with boron nitride. All spectra were fit with symmetric Lorentzian quadrupole doublets using the WMOSS Mössbauer Spectral Analysis Software (www.wmoss.org).5

5.2.6. Reactivity studies on Fe-BTT, Fe-BTTri, and Fe-BTP. For reactivity studies, 30 mg of activated framework was loaded into a stainless steel bomb, which was dosed with 14 bar of N$_2$O and ethane (1:7 ratio), and heated to 120 °C for 14 h. After 14 h, the reaction vessel was cooled, depressurized, and brought into an N$_2$-filled glovebox. There the framework was washed with CD$_3$CN, and the products analyzed by $^1$H NMR spectroscopy using 1,4-dichlorobenzene as an internal standard. For cycling studies, the framework was recovered from the reaction vessel, washed with CH$_3$CN (2 × 60 °C) and then reactivated under vacuum at 135 °C for 24 h.

5.2.7. Synthesis of Zn-exchanged Fe-BTT (Zn/Fe-BTT). Zn-exchanged Fe-BTT was prepared following similar literature preparations as cation-exchanged Mn-BTT. Briefly, the framework was immersed in excess ZnCl$_2$ dissolved in methanol for 24 h at room temperature. The framework was filtered, washed with methanol (3 × 10 mL at room temperature), CH$_3$CN (3 × 10 mL at 60 °C), and activated at 135 °C for 24 h. ICP results show the exchanged material contains 18% Zn.

5.3. Results and discussion
5.3.1. Syntheses and structures of Fe-BTT, Fe-BTTri, and Fe-BTP. The overall structure of Fe-BTT and its derivatives is shown in Figure 5.1. Square \([\text{Fe}_4\text{Cl}]^{7+}\) clusters are connected by tritopic linkers, which can be tetrazolate, triazolate, or pyrazolate-based, to form a cubic framework with sodalite-type cages. The base framework is anionic, with three charge-balancing extra-framework iron(II) centers for every 24 framework iron atoms, leading to an overall formula of \(\text{Fe}_4[(\text{Fe}_4\text{Cl})_3L_8]_2\), where \(L_3^- = \text{BTT}^{3-}, \text{BTTri}^{3-}\), or \(\text{BTP}^{3-}\). These extra-framework cations have been located crystallographically in previously reported M-BTT frameworks,\(^4\) and typically reside bound between two neighboring heterocycles in the tetrazolate and triazolate materials. Thus, despite the deceptively high symmetry of its cubic crystal structure, the iron(II) centers in Fe-BTT are not spectroscopically identical. Indeed, the Mössbauer spectrum of DMF-solvated Fe-BTT is a broad doublet that can be fit with five different iron(II) environments (one extra-framework, and four framework).\(^1\) As the BTT\(^3-\) ligand can be replaced with other tritopic ligands of varying basicities, the ligand field can be systematically tuned in this structure type (see Figure 5.1b).

\[ \text{Fe}_4[\text{Fe}_4\text{Cl}]^{7+} \]

\[ L_3^- = \text{BTT}^{3-}, \text{BTTri}^{3-}, \text{BTP}^{3-}\]

Figure 5.1. Structure of sodalite-type iron(II) frameworks and their corresponding ligands. (a) Structure of Fe-BTT, with sodalite-type cages highlighted in light blue. The zoomed insets show the \([\text{Fe}_4\text{Cl}]^{7+}\) squares, and the local coordination environment of the iron(II) center. (b) Structure of the tritopic ligands that can be used to form this structure type, along with their corresponding pK\(_a\) values. Orange, gray, and blue spheres represent Fe, C, and N, respectively; H atoms are removed for clarity.

The analogous framework to Fe-BTT wherein each tetrazolate is replaced with a triazolate, Fe-BTTri or \(\text{Fe}_3[(\text{Fe}_4\text{Cl})_3(\text{BTTri})_3]_2\cdot18\text{CH}_3\text{OH}\), can be synthesized as a yellow, microcrystalline
powder from the reaction between FeCl$_3$, H$_3$BTTri, and dimethylformamidium trifluoromethanesulfonate in DMF and methanol.$^5$ Exchange of bound DMF molecules with methanol, followed by activation at 180 °C under vacuum, yields the desolvated Fe-BTTri as a tan powder with a Langmuir surface area of 1930 m$^2$/g and a Brunauer–Emmett–Teller (BET) surface area of 1630 m$^2$/g. Note that elemental analyses indicate residual methanol remains within the framework even after activation, likely bound to extra-framework cations.

Cubic single crystals of Fe-BTTri suitable for X-ray diffraction can be grown under similar conditions using more dilute iron and ligand concentrations and higher acid concentration. Interestingly, the DMF solvated form of a Fe-BTTri crystal displays $Fm\overline{3}c$ symmetry, rather than the $Pm\overline{3}m$ symmetry of Fe-BTT. In this space group, opposing squares on each truncated octahedron are offset by approximately 6° (see Figure 5.2a). Furthermore, the triazolate groups are well ordered within Fe-BTTri, with the non-coordinating nitrogen atoms of neighboring heterocycles pointed away from each other (see Figure 5.2b). The location of the charge balancing extra-framework Fe$^{II}$ cations within the pores of the framework could not be determined from the electron difference map obtained from the X-ray diffraction data. However, the Mössbauer spectrum of the activated material, similar to Fe-BTT, shows a broad doublet that can be fit with five different species, suggesting that the extra-framework cations are bound in a way that slightly perturbs the local environment of each framework cation (see Figure 5.2c).

**Figure 5.2. Structure and Mössbauer spectrum of Fe-BTTri.** (a) Structure of a single truncated octahedral cage in methanol-solvated Fe-BTTri. The opposing [Fe$_4$Cl]$_7^{7+}$ squares are slightly tilted from each other, whereas in Fe-BTT they are perfectly aligned. (b) Local coordination environment of each Fe(II) center in DMF-solvated Fe-BTTri. The triazolates are ordered such that the non-coordinating nitrogen of each triazolate is pointed away from each other. (c) Mössbauer spectrum of activated Fe-BTTri (100 K). The broad doublet is fit as the sum of five species with parameters consistent with high-spin Fe(II). Orange, gray, blue, and red spheres represent Fe, C, N, and O, respectively; H atoms are removed for clarity.
Single crystals of Fe-BTP, which adopt the \( Pm\overline{3}m \) space group, can be synthesized and activated in a similar manner as Fe-BTTri, leading to a porous framework with a Langmuir surface area of 1640 m\(^2\)/g. Note that this value is lower than expected compared to Fe-BTT and Fe-BTTri, suggesting some ligand or solvent remains trapped within the pores. Indeed, elemental analyses indicate an overall formula of \([\text{Fe(CH}_3\text{OH)}_6][(\text{Fe}_4\text{Cl}_3)(\text{BTP})_8][\text{H}_3\text{BTP}]_{0.5}\), in which the extra-framework cations are octahedrally ligated by methanol and 6.5 equivalents of \( \text{H}_3\text{BTP} \) reside within the pores. Further optimization of synthetic or activation parameters may be necessary to obtain pristine material.

Table 5.1. Bond metrics of solvated Fe-BTT, Fe-BTTri, and Fe-BTP.

<table>
<thead>
<tr>
<th></th>
<th>Fe-BTT-DMF</th>
<th>Fe-BTTri-DMF</th>
<th>Fe-BTP-DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>( Pm\overline{3}m )</td>
<td>( Fm\overline{3}c )</td>
<td>( Pm\overline{3}m )</td>
</tr>
<tr>
<td>Unit cell dimensions (Å)</td>
<td>18.8235(11)</td>
<td>38.0680(11)</td>
<td>19.3213(15)</td>
</tr>
<tr>
<td>( a = b = c )</td>
<td>2.133(2)</td>
<td>2.143(2)</td>
<td>2.147(2)</td>
</tr>
<tr>
<td>Fe–N (Å)</td>
<td>2.6487(2)</td>
<td>2.6008(8)</td>
<td>2.5758(6)</td>
</tr>
</tbody>
</table>
| Fe–Cl (Å)            | 5.3.2. O\(_2\) adsorption properties of Fe-BTTri. We subsequently evaluated the \( \text{O}_2 \) binding properties of Fe-BTTri, whose triazolate ligand environment is significantly more electron-donating than the aryloxide and carboxylate ligands found in Fe\(_2\)(dobdc). Note that Fe-BTT was not investigated due to its instability; related M-BTT frameworks have been found to be prone to exothermic decomposition when fully activated.\(^4\,^6\) At 195 K, activated Fe-BTTri binds \( \text{O}_2 \) semi-reversibly, as shown in Figure 5.4. In the first cycle, the material adsorbs 3.2 mmol/g of \( \text{O}_2 \) by 0.21 bar, and reaches 5.3 mmol/g at 1 bar. On the other hand, Fe-BTTri shows a lower affinity for \( \text{N}_2 \), gradually reaching a capacity of 3.2 mmol/g at 1 bar. Ideal adsorbed solution theory (IAST) was used to predict the adsorption behavior for a mixture of 0.21 bar \( \text{O}_2 \) and 0.79 bar \( \text{N}_2 \). An IAST selectivity value of 65.8 was obtained, which corresponds to 94.6\% purity. While these high purities could be useful for air separation processes, a decrease in capacity was observed in the second cycle, even after heating to 423 K under vacuum. Together, these results show that \( \text{O}_2 \) binding is substantially, but not fully, reversible (see Figure 5.3).
To probe the electronic structure of the iron centers after O$_2$ binding, a fresh sample of activated Fe-BTTri was exposed to O$_2$ at 195 K and then quickly transferred to a pre-cooled Mössbauer spectroscopy sample chamber. At 100 K, three distinct iron sites are observed, two of which correspond to high-spin Fe(II) (36%) and high-spin Fe(III) (17%) (see Figure 5.5). Surprisingly, the major species (47%) has parameters consistent with low-spin Fe(III) (see Figure 5.4 and Table 5.2). Upon warming to room temperature, the low-spin Fe(III) component completely disappears with a concomitant increase in the high-spin Fe(III) component; no significant changes from this state were observed when the sample was re-cooled to 100 K a second time. These results, in combination with the isotherm data, lead us to tentatively propose that at low temperatures, approximately two out of every four iron centers in the [Fe$_4$Cl]$_7^+$ cluster bind O$_2$ to form low-spin Fe(III)–superoxide moieties, a process that is reversible and reminiscent of hemoglobin and iron(II) porphyrin complexes. At higher temperatures, O$_2$ binds irreversibly in a process that leads to high-spin Fe(III) species; this is observed even at 195 K and is responsible for the reduced O$_2$ capacities observed in isotherm cycling studies. While this high-spin Fe(III) species has not been conclusively identified, electron transfer from neighboring iron sites could lead to Fe(III)–peroxide moieties, much like those observed in Fe$_2$(dobdc). 

At the time of this discovery, spin-state transitions of metal nodes triggered by binding events were highly unusual, as the spin state of open metal sites in metal–organic frameworks such as M$_2$(dobdc) are relatively insensitive to the identity of guest molecules. In the case of Fe-BTTri, the framework flexibility, along with the intermediate ligand field of the triazolate bridges, enables the simultaneous oxidation and spin-state conversion of half of the iron sites upon O$_2$ exposure. While the temperature-sensitive O$_2$ binding properties of Fe-BTTri render it impractical for air separation applications, its similarity to hemoglobin and ability to interconvert between high- and low-spin configurations prompted subsequent studies, by other members of our group, on its CO scavenging abilities. These studies revealed Fe-BTTri to possess some of...
the highest selectivities ever reported for CO binding over other small molecules such as N₂, H₂, CO₂, and ethylene.

Table 5.2. Mössbauer parameters for O₂-dosed Fe-BTTRi (100 K).

<table>
<thead>
<tr>
<th>Site</th>
<th>δ (mm/s)</th>
<th></th>
<th>ΔE_q (mm/s)</th>
<th>Area (%)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.07</td>
<td>2.60</td>
<td>36</td>
<td>HS Fe(II)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.33</td>
<td>2.46</td>
<td>47</td>
<td>LS Fe(III)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.44</td>
<td>0.98</td>
<td>17</td>
<td>HS Fe(III)</td>
<td></td>
</tr>
</tbody>
</table>

5.3.3. Defect-site N₂O reactivity in Fe-BTT, Fe-BTTRi, and Fe-BTP. The N₂O reactivity of Fe-BTT, Fe-BTTRi, and Fe-BTP was briefly investigated, to probe the relationship between ligand field and reactivity. We hypothesized that the weak-field tetrazolate ligand of Fe-BTT could lead to similar behavior as Fe₀.1Mg₁.9(dobdc) (see Chapter 2), and therefore this framework was examined first. In an initial test reaction, Fe-BTT was treated with a 1:7 mixture of N₂O and ethane at 14 bar, and heated to 120 °C for 14 h. Interestingly, Fe-BTT was found to oxidize ethane to ethanol with no observable over-oxidation or side-products, albeit in relatively low yields (0.04 equivalents per framework iron). After this treatment, Fe-BTT retains its high crystallinity, as confirmed by powder X-ray diffraction. However, unlike Fe₀.1Mg₁.9(dobdc), where the iron sites have been shown to decay into inactive Fe(III)-hydroxide or alkoxide species after prolonged N₂O exposure, Mössbauer studies showed that >90% of the iron centers in Fe-BTT remain in the +2 oxidation state after N₂O/ethane treatment. This, combined with the low yields, suggest that only a small fraction of the iron sites are active for N₂O decomposition.

Prompted by these results, subsequent efforts were undertaken to elucidate the active site responsible for ethane oxidation in Fe-BTT. In order to rule out the involvement of extra-framework sites, the extra-framework Fe²⁺ cations were post-synthetically exchanged with Zn²⁺ cations. Treating Fe-BTT with excess ZnCl₂ at room temperature in methanol led to the formation of Zn/Fe-BTT, which contains 18% Zn as determined by ICP analysis. These ICP
results indicate that all the extra-framework and a small percentage of the framework cations (~7 to 8%) have been displaced. Zn/Fe-BTT can be desolvated by heating to 130 °C for 24 h, leading to a porous material with a Brunauer-Emmett-Teller (BET) surface area of 1835(7) m²/g (Langmuir surface area = 1982(11) m²/g). The Mössbauer spectrum of the activated material reveals three slightly different iron(II) sites, which we assign as a) framework Fe(II) centers in tetranuclear building units containing no Zn(II) (81%); b) framework Fe(II) centers directly adjacent to a framework Zn(II) site (13%); and c) framework Fe(II) centers directly across a Zn(II) site, linked by the $\mu_4$-chloride bridge (6%) (see Figure 5.7 and Table 5.3).

**Table 5.3. Mössbauer parameters of Zn/Fe-BTT before and after N₂O/ethane treatment.**

| Sample                  | Assignment | $\delta$ (mm/s) | $|\Delta E_q|$ (mm/s) | $\Gamma$ (mm/s) | Area (%) |
|-------------------------|------------|-----------------|----------------------|-----------------|---------|
| Zn/Fe-BTT, pre-N₂O      | Fe(II), site A | 1.14(1)         | 2.88(1)              | 0.32(1)         | 81(1)   |
|                         | Fe(II), site B | 1.12(1)         | 3.65(2)              | 0.23(3)         | 6(1)    |
|                         | Fe(II), site C | 1.07(3)         | 1.55(9)              | 0.77(9)         | 13(2)   |
| Zn/Fe-BTT, post-N₂O     | Fe(II), site A | 1.13(1)         | 2.81(1)              | 0.36(4)         | 78(3)   |
|                         | Fe(II), site B | 1.10(1)         | 3.69(2)              | 0.24(4)         | 10(2)   |
|                         | Fe(II), site C | 1.06(4)         | 1.47(6)              | 0.57(10)        | 13(3)   |

**Figure 5.5. Mössbauer spectra and powder X-ray diffraction pattern of Zn/Fe-BTT before and after N₂O/ethane treatment.** (a) Mössbauer spectra of Zn/Fe-BTT (100 K) before (top) and after (bottom) N₂O/ethane treatment at 120 °C. Gray crosses represent raw data; green, blue, and
turquoise lines represent components assigned as Fe(II) A, B, and C, respectively; the black line represents the overall fit. (b) Powder X-ray diffraction pattern of Zn/Fe-BTT before and after N$_2$O treatment.

Treatment of activated Zn/Fe-BTT with N$_2$O and ethane, under the same conditions as Fe-BTT, also leads to exclusive ethanol formation (~0.04 equivalents per framework iron site). Because these results are identical to the parent Fe-BTT framework, it is highly unlikely that the extra-framework cations are responsible for the observed reactivity. Like Fe-BTT, Mössbauer studies show that the majority of the iron sites in Zn/Fe-BTT remain in the +2 oxidation following N$_2$O/ethane treatment, with only slight changes in the Mössbauer parameters of the three iron sites (see Figure 5.5 and Table 5.3). In addition, the post-treatment framework maintains both its crystallinity and surface area, suggesting that neither decomposition nor pore collapse are occurring (see Figure 5.5).

Next, we investigated whether the recycled framework is capable of oxidizing ethane. The recovered material was re-activated and re-exposed to N$_2$O/ethane at 120 °C. However, no ethanol formation was observed, even though the bulk of the Fe(II) sites in the recovered framework, as probed by Mössbauer studies, powder X-ray diffraction, and surface area measurements, are essentially identical to the pristine material. Following these results, we conclude that a very small fraction of the iron(II) sites, which have yet to be detected spectroscopically, are responsible for the initial reactivity but decay over the course of the first N$_2$O/ethane treatment. These sites could be the result of missing linkers, structural distortions due to thermal activation, surface sites, or crystal fractures, which have been previously shown to be important in metal–organic framework-based catalysis.\(^{11,12}\) Defect site formation during the thermal activation process may also be more likely in Fe-BTT than other frameworks, such as Fe$_x$(dobdc), due to the thermal sensitivity of the tetrazolate linkers.

While the true active site structure in Fe-BTT is still unknown, the weak-field tetrazolate environment undoubtedly plays an important role. Fe-BTTri (H$_3$BTTri = 1,3,5-tri(1H-1,2,3-triazol-5-yl)benzene) and Fe-BTP (H$_3$BTP = 1,3,5-tri(1H-pyrazol-4-yl)benzene) were also studied, and both show poorer reactivity profiles than Fe-BTT. Fe-BTTri shows similar ethane conversions as Fe-BTT (0.03 equivalents of product per framework iron), but with small amounts of ether side-products, while Fe-BTP, which utilizes a much more basic pyrazolate, shows no reactivity under these conditions.

### 5.4. Conclusions and outlook

This chapter details the synthesis and characterization of Fe-BTTri and Fe-BTP, which, in combination with the previously reported Fe-BTT, represent a family of frameworks with similar overall structures but varying ligand fields. Interesting gas adsorption behavior is observed in Fe-BTTri in particular, in which the flexible framework architecture and intermediate ligand field leads to spin state transitions upon O$_2$ and CO binding. While this series of iron-based frameworks is well-suited to probing the effect of ligand field on the chemistry and reactivity of exposed iron(II) sites, caution must be taken when drawing conclusions due to the presence of multiple iron species, include extra-framework cations and defect sites. These defects, which have yet to be structurally characterized, are proposed to play a role in the N$_2$O-mediated oxidation of ethane to ethanol in Fe-BTT and Fe-BTTri.

### 5.5. Acknowledgements
The synthetic chemistry, crystal structure determinations, and characterization of gas adsorption properties were supported through the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-SC0001015. The reactivity studies were supported by the Nanoporous Materials Genome Center, funded by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences under Award DE-FG02-12ER16362. This research used resources of the Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. D.A.R. and M.I.G. are thanked for experimental assistance and helpful discussions.

5.6. References and supplementary information

Appendix 1: Synthesis of Anthracene Terphenyl MOF-74 Linkers and Frameworks

Scheme A1.1. Synthesis of anthracene-substituted ligand, abbreviated LA.

**Synthesis of LA–Me:**
A 100 mL storage flask was charged with methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (0.70 g, 2.20 eq.), 9,10-Dibromoanthracene (0.65 g, 1.00 eq.), K₂CO₃ (2.70 g, 10 eq.), 16 mL of H₂O, and 64 mL of thf. The flask was sparged with argon for 30 minutes, SPhos Pd G2 catalyst was added (35 mg, 3 mol%), and the reaction mixture was allowed to stir at reflux for 14 h. The reaction mixture was allowed to cool to room temperature, and the reaction mixture was poured into cold water (75 mL). The non-homogenous solution was filtered, and the filtrate was washed thoroughly with cold water and methanol to produce LA–Me as an off-white solid (0.58 g, 60% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.92 (m, 2H), 7.70 (dd, J = 4, 8 Hz, 4H), 7.60 (dd, J = 2, 8 Hz, 2H), 7.37 (dd, J = 4, 8 Hz, 4H), 7.25 (m, 2H), 4.08 (s, 6H), 3.89 (s, 6H) ppm.

**Synthesis of LA:**
A 100 ml schlenk flask equipped with a stir bar was charged with LA–Me (0.50 g, 0.99 mmol, 1.00 eq.) and 60 mL of DCM. The solution was vigorously stirred and cooled to −78 °C, and BBr₃ was added dropwise (1M solution in DCM, 11.9 mL, 11.9 mmol, 12 eq.) under an argon atmosphere. The reaction was stirred at room temperature for 24 h. The excess BBr₃ was quenched with water, and the resulting white precipitate was washed with H₂O (3 x 50 mL). A small amount of methyl ester (~30%) still present in the material was subsequently hydrolyzed by stirring the material in 10 mL of THF and 10 mL of 1M NaOH at 50 °C overnight. The solution was neutralized using HCl, the THF removed in vacuo, and the white precipitate washed with H₂O (3 x 50 mL) to afford LA (0.40 g, 90% over two steps). ¹H NMR (400 MHz, DMSO-d₆): δ 7.80 (m, 2H), 7.64 (m, 6H), 7.47 (m, 4H), 7.25 (m, 2H) ppm.

**Synthesis of Fe₂LA:** Inside an N₂-filled glovebox, LA (60 mg, 1.0 eq.), FeCl₂ (2.5 eq.), DMF (8 mL), and MeOH (1 mL) were combined in a 20 mL scintillation flask. The vial was sealed with a Teflon-lined cap and heated to 140 °C for 2 days. The resulting precipitate was filtered, washed with DMF (3 x 10 mL at 120 °C) and MeOH (3 x 10 mL at 60 °C), and dried under vacuum at 120 °C for two hours to afford Fe₂LA·2MeOH as a yellow-green crystalline powder (see Figure...
A1.2). The powder can be activated by heating at 180 °C overnight under vacuum, to afford activated Fe$_2$L$^\Lambda$, a porous material with a Langmuir surface area of 3100(10) m$^2$/g.

![Figure A1.1. Powder X-ray diffraction of DMF-solvated Fe$_2$L$^\Lambda$.](image)

**Figure A1.1.** Powder X-ray diffraction of DMF-solvated Fe$_2$L$^\Lambda$.

**Synthesis of Zn$_2$L$^\Lambda$:** A solution of 4.0 mg L$^\Lambda$ (1.0 equiv.) dissolved in 0.5 mL of DEF was combined with a solution of 2.7 mg ZnCl$_2$ (2.25 equiv.) dissolved in 0.5 mL EtOH. The mixture was sealed inside a glass tube and heated at 100 °C inside an oven for 2 d. The resulting precipitate was filtered and washed with DMF (3 x 10 mL at 100 °C) to afford Zn$_2$L$^\Lambda$·2DMF. The powder is highly crystalline (see Figure A1.2); it is possible that further optimization of this procedure with this or other ligands may afford single crystal samples.

![Figure A1.2. Powder X-ray diffraction of DMF-solvated Zn$_2$L$^\Lambda$ and indexed unit cell parameters.](image)

**Figure A1.2.** Powder X-ray diffraction of DMF-solvated Zn$_2$L$^\Lambda$ and indexed unit cell parameters.
Appendix 2: Synthesis of Fluorinated Terphenyl MOF-74 Linkers and Frameworks

Note that the terphenyl ligand derivatives shown in this section are synthesized by a) Suzuki coupling with (4-methoxyphenyl)boronic acid, b) methoxy group deprotection, c) formylation via the Duff aldehyde synthesis, and d) subsequent aldehyde oxidation to install the carboxylic acid (see Scheme A2.1). This synthesis was originally developed for the synthesis of the unsubstituted bipheloy ligand \( \text{H}_4(\text{dobpdc}) \) (4,4'-dihydroxy-[1,1'-biphenyl]-3,3'-dicarboxylic acid) directly from biphenol, and was subsequently adapted for the following terphenyl linkers. However, direct coupling with methyl 2-methoxybenzoate boronic acid (as in previous \( \text{L}^A \) synthesis) should be possible, and would reduce the overall number of steps.

Scheme A2.1. Synthesis of fluoroalkyl-substituted frameworks \( \text{L}^{\text{CF}3} \) and \( \text{L}^{\text{C}4\text{F}9} \).

**General conditions for step A (synthesis of \( \text{L}^R-\text{OMe} \))**: General palladium coupling conditions: 2.5 mol% Sphos Pd G2, 10 equiv. \( \text{K}_2\text{CO}_3 \), 4:1 thf:H\(_2\)O with approximately 50 ml total solvent for 1 gram of the aryl bromide. All reagents and solvents (except for the palladium catalyst) were added to a 100 mL storage flask and the reaction was sparged with argon for half an hour. The palladium catalyst was then added, and the reaction was refluxed for 1 to 2 d. The product was isolated by precipitation with cold water, and purified by washing with water and methanol (residual palladium catalyst will be removed by following acid deprotection step).

**General conditions for step B (synthesis of \( \text{L}^R-\text{OH} \))**: A round bottom was charged with \( \text{L}^R-\text{OMe} \), 1:1 HBr:HOAc (~100 ml each for 1 g of material), and a stir bar. The reaction was refluxed at 130 °C. After 2 days, the reaction was cooled and water was added to crash out the deprotected product, which was filtered and thoroughly washed with water.
General conditions for step C (synthesis of L^R–A): A roundbottom flask was charged with L^R–OH, 2.2 equiv. of hexamethylenetetramine, trifluoroacetic acid (~100 mL per gram of L^R–OH), and a stir bar. The reaction was refluxed at 70 °C overnight, cooled, and then stirred in 4 M HCl (~300 mL per gram of L^R–OH) for three hours at room temperature. The precipitated product was filtered and then thoroughly washed with water.

General conditions for step D (synthesis of L^R): A roundbottom flask was charged with L^R–A (1 equiv.), thf, DMSO, and a stir bar. The mixture was cooled to 0 °C with stirring. An aqueous solution of sulfamic acid (14 equiv.) was added, followed by the drop-wise addition of an aqueous solution of NaClO_2 (80% w/w, 10 equiv.). Note that the final L^R–A concentration should be ~0.03 M, with a thf:H_2O:DMSO ratio of 20:10:1. The reaction was stirred at 0 °C for two hours, and then room temperature overnight, after which the product was precipitated by diluting the reaction with water. L^R was purified by filtration and washed with water.

L^CF3–OMe: Note that the starting arylbromide, 1,4-dibromo-2,5-bis(trifluoromethyl)benzene, was synthesized according to previously reported procedures. Yield: 97%. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (s, 2H), 7.31 (d, 9 Hz, 4H), 6.98 (d, 9 Hz, 4H), 3.88 (s, 6H) ppm; ^19F NMR: δ –56.67 ppm.

L^CF3–OH: Yield: quantitative. ^1H NMR (400 MHz, DMSO-d_6): δ 9.74 (s, 2H), 7.70 (s, 2H), 7.21 (d, 4H), 6.85 (d, 4H) ppm; ^19F NMR: δ –55.44 ppm.

L^CF3–A: Yield: quantitative. ^1H NMR (400 MHz, DMSO-d_6): δ 11.05 (s, 2H), 10.33 (s, 2H), 7.83 (s, 2H), 7.68 (d, 2H), 7.59 (m, 2H), 7.12 (m, 2H) ppm.

L^CF3: Yield: 80%. ^1H NMR (400 MHz, DMSO-d_6): δ 7.82 (m, 4H), 7.58 (d, 9Hz, 2H), 7.08 (d, 9Hz, 2H) ppm; ^19F NMR: δ –61.44 ppm.

L^C4F9–OMe: Note that the starting arylbromide, 1,4-dibromo-2,5-bis(perfluorobutyl)benzene, was synthesized according to previously published procedures. Yield: 76%. ^1H NMR (400 MHz, CDCl_3): δ 7.56 (s, 2H), 7.22 (d, J = 9 Hz, 4H), 6.96 (d, 9 Hz, 4H), 3.88 (s, 6 H) ppm; ^19F NMR: δ –80.1, –102.8, –119.7, –125.1 ppm.

L^C4F9–OH: Yield: quantitative. ^1H NMR (400 MHz, DMSO-d_6): δ 9.69 (s, 2H), 7.51 (s, 2H), 7.13 (d, J = 8 Hz, 4H), 6.81 (d, J = 8 Hz, 4H) ppm; ^19F NMR: δ –79.6, –102.1, –119.5, –124.8 ppm.

L^C4F9–A: Yield: 71%. ^1H NMR (400 MHz, CDCl_3): δ 11.14 (s, 2H), 9.94 (s, 2 H), 7.62 (s, 2H), 7.51 (s, 2H), 7.48 (d, J = 8 Hz, 2 H), 7.08 (d, J = 8 Hz, 2 H) ppm; ^19F NMR: δ –80.1, –102.9, –119.7, –125.0 ppm.

L^C4F9: Yield: 74%. ^1H NMR (400 MHz, DMSO-d_6): δ 7.72 (s, 2 H), 7.65 (s, 2H), 7.49 (d, J = 9 Hz, 2H), 7.03 (d, J = 9 Hz, 2H) ppm; ^19F NMR: δ –79.6, –102.3, –119.5, –124.8 ppm.

Synthesis of Fe,L^CF3: Inside an N_2-filled glovebox, L^CF3 (60 mg, 1.0 eq.), FeCl_2 (2.5 eq.), DMF (8 mL), and MeOH (1 mL) were combined in a 20 mL scintillation flask. The vial was sealed
with a Teflon-lined cap and heated to 140 °C for 2 days. The resulting precipitate was filtered, washed with DMF (3 x 10 mL at 120 °C) and MeOH (3 x 10 mL at 60 °C), and dried under vacuum at 120 °C for two hours to afford $\text{Fe}_2\text{L}^{\cdot}2\text{MeOH}$ as a yellow-green crystalline powder (see Figure A2.1). The powder can be activated by heating at 180 °C overnight under vacuum, to afford activated $\text{Fe}_2\text{L}^{\text{CF3}}$, a porous material with a Langmuir surface area of 2780(25) m$^2$/g.

**Figure A2.1.** Powder X-ray diffraction pattern of DMF-solvated $\text{Fe}_2\text{L}^{\text{CF3}}$.

**Synthesis of $\text{Fe}_2\text{L}^{\text{C4F9}}$:** Unfortunately, attempts to synthesize $\text{Fe}_2\text{L}^{\text{C4F9}}$ thus far have generated only poorly crystalline material (see Figure A2.2). The best conditions found thus far used 1 equiv. ligand, 2.5 equiv. FeCl$_2$, and a 1:2 DMF:CF$_3$CH$_2$OH solvent mixture at 120 °C for 2 d. After DMF (3x10 mL, 120 °C) and MeOH (3x10 mL, 60 °C) washes and activation at 180°C overnight, a porous material with a Langmuir surface area of 1200 m$^2$/g was obtained.

**Figure A2.2.** Powder X-ray diffraction pattern of DMF-solvated $\text{Fe}_2\text{L}^{\text{C4F9}}$. 
Scheme A2.2. Synthesis of trifluoroaryl-substituted ligand \( L^{C6F3} \) by Suzuki coupling reactions.

**Synthesis of \( L^{Cl-OMe} \) (Step A1):** To a 100 mL storage flask was added 1.00 g of 1,4-dichloro-2,5-dibromobenzene, 4.53 g of \( K_2CO_3 \) (10 equiv.), 1.25 g of 4-methoxyphenylboronic acid (2.5 equiv.), 60 mL of dioxanes, 15 mL of \( H_2O \), and a stir bar. The mixture was sparged under argon for half an hour, 0.38 g of \( Pd(PPh_3)_4 \) (0.10 equiv.) was added, and the reaction was refluxed at 90 °C for 20 hr. The reaction was then cooled to room temperature, solvent was removed \( \text{in vacuo} \), and the precipitate was filtered and washed with \( H_2O \) and \( MeOH \) to produce \( L^{Cl-OMe} \) as an off-white solid. Yield: 87% (1.03 g). \(^1\)H NMR (400 MHz, \( CDCl_3 \)): \( \delta \) 7.52 (s, 2H), 7.25 (d, \( J = 9 \text{ Hz} \), 4H), 6.83 (d, \( J = 9 \text{ Hz} \), 4H), 3.70 (s, 6H) ppm.

**Synthesis of \( L^{R-OMe} \) (Step A2):** Because polyfluorophenyl boronic acids are unstable and quickly deboronate under basic conditions, mild and fast coupling conditions previously developed by the Buchwald group were used for this Suzuki coupling.\(^4\) Specifically, a 25 mL schlenk flask was charged with 200 mg of \( L^{Cl-OMe} \) (1.00 equiv.), 294 mg of (2,4,6-trifluorophenyl)boronic acid (3.00 equiv.), 28 mg of \( Pd XPhos \) G2 (6 mol %), and a stir bar. The...
flask was placed under an inert atmosphere by pulling vacuum/re-filling with argon three times. Then 10 mL of degassed thf, followed by a degassed solution containing 473 mg of K₃PO₄ and 4 mL of H₂O, were cannula-transferred and the reaction was stirred at room temperature for 1 hr. The solvent was then removed in vacuo and the solid precipitate washed with H₂O to afford L⁶⁳⁻OMe as an off-white solid (218 mg, 71% yield). ¹H NMR (400 MHz, DMSO-d₆): δ 7.48 (s, 2H), 7.215 (m, 4H), 7.09 (d, J = 9 Hz, 4H), 6.86 (d, J = 9 Hz, 4H), 3.72 (s, 6H) ppm.

**Synthesis of L⁶³⁻OH:** General conditions for step B were used. Yield: 77%. ¹H NMR (400 MHz, DMSO-d₆): δ 9.50 (s, 2H), 7.42 (s, 2H), 7.20 (m, 4H), 6.95 (d, J = 9 Hz, 4H), 6.65 (d, J = 9 Hz, 4H) ppm.

**Synthesis of L⁶³⁻A:** General conditions for step C were used. Yield: 95%. ¹H NMR (400 MHz, DMSO-d₆): δ 10.83 (s, 2H), 10.20 (s, 2H), 7.57 (m, 2H), 7.46 (m, 2H), 7.23 (m, 6H), 6.92 (m, 2H) ppm; ¹⁹F NMR: δ –107.2, –108.5 ppm.

**Synthesis of L⁶³:** General conditions for step D were used. Yield: 76%. ¹H NMR (400 MHz, DMSO-d₆): δ 7.58 (m, 4H), 7.31–7.22 (m, 6H), 6.87 (d, J = 9 Hz, 2H) ppm; ¹⁹F NMR: δ –107.3, –108.5 ppm.

**Synthesis of Fe₂L⁶³:** Inside an N₂-filled glovebox, L⁶³ (60 mg, 1.0 eq.), FeCl₂ (2.5 eq.), DMF (8 mL), and MeOH (1 mL) were combined in a 20 mL scintillation flask. The vial was sealed with a Teflon-lined cap and heated to 140 °C for 2 days. The resulting precipitate was filtered, washed with DMF (3 x 10 mL at 120 °C) and MeOH (3 x 10 mL at 60 °C), and dried under vacuum at 120 °C for two hours to afford Fe₂L⁶³·2MeOH as a yellow-green powder with moderate crystallinity (see Figure A2.3).

![Figure A2.3. Powder X-ray diffraction pattern of DMF-solvated Fe₂L⁶³.](image-url)
Scheme A2.3. Synthesis of the tetrafluoroaryl-substituted ligand, \( \text{L}^\text{C}6\text{F}4 \). Note that the tetrafluoroaryl group had to be coupled via a Negishi reaction, as tetrafluoroaryl boronic acids are highly unstable.

**Synthesis of \( \text{L}^\text{C}6\text{F}4\)–Cl (Step A1):** The Negishi coupling was performed following previously reported procedures. Specifically, an oven-dried 25 mL schlenk flask, equipped with a magnetic stir bar and fitted with a rubber septum, was evacuated and back-filled with argon (3x) and then bromopolyfluoroarene (1.0 mL, 2.5 equiv.) and 15 mL of degassed THF was added via syringe and cannula, respectively. The solution was cooled to 0 °C, and isopropylmagnesium chloride (2.0 M in THF, 4.5 mL, 2.75 equiv.) was added dropwise via syringe. The reaction was allowed to stir at 0 °C for 1 h. A solution of \( \text{ZnCl}_2 \) (1.9 M in 2-MeTHF, 5.2 mL, 3.0 equiv.) was added dropwise via syringe, and the reaction was warmed to room temperature and stirred for an additional 1 h. Then 1,4-dichloro-2,5-dibromobenzene (1.0 g, 1 equiv.), 2 mol% XPhos, and 2 mol% XPhos Pd G3 were added. The reaction mixture was stirred for 1 d at room temperature, and 1 d at 70 °C. It was quenched with \( \text{H}_2\text{O} \), filtered and washed with \( \text{H}_2\text{O} \) and \( \text{MeOH} \), and used directly in the next step (note – in the future it may be better to do an extraction). Yield: 26%. \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 10.83 (s, 2H), 7.22 (m, 2H) ppm; \(^{19}\text{F} \) NMR: \( \delta \) 137.3 (m), –138.9 (m) ppm.
Synthesis of \( \text{L}^{\text{C6F4}}-\text{OMe} \) (Step A2): To a 100 mL storage flask was added 300 mg \( \text{L}^{\text{C6F4}}-\text{Cl} \) (1 equiv.), 309 mg 4-methoxyphenylboronic acid (3 equiv.), 718 mg \( \text{K}_3\text{PO}_4 \) (5 equiv.), 24 mL of toluene, 6 mL of \( \text{H}_2\text{O} \), and a stir bar. The reaction mixture was sparged under argon for half an hour, and then 15 mg of \( \text{Pd SPhos G2} \) (3 mol%) was added. The reaction was stirred at room temperature overnight, after which the solvent was removed in vacuo and the precipitate filtered and washed with water. Yield: 86%. \(^1\)H NMR (400 MHz, \( \text{CDCl}_3 \)): \( \delta \) 7.46 (s, 2H), 7.14 (d, 4H, \( J = 9 \text{ Hz} \)), 7.02 (m, 2H), 6.81 (d, 4H, \( J = 9 \text{ Hz} \)), 3.81 (s, 6H) ppm; \(^{19}\)F NMR: \( \delta \) –138.2 (m), –139.7 ppm.

Synthesis of \( \text{L}^{\text{C6F4}}-\text{OH} \): General conditions for step B were used. Yield: 80%. \(^1\)H NMR (400 MHz, \( \text{DMSO-d}_6 \)): \( \delta \) 9.58 (s, 2H), 7.90 (m, 2H), 7.61 (s, 2H), 6.99 (d, \( J = 9 \text{ Hz} \), 4H), 6.69 (d, \( J = 9 \text{ Hz} \), 4H) ppm.

Synthesis of \( \text{L}^{\text{C6F4}}-\text{A} \): General conditions for step C were used. Yield: 82%. \(^1\)H NMR (400 MHz, \( \text{DMSO-d}_6 \)): \( \delta \) 10.90 (s, 2H), 10.22 (s, 2H), 7.93 (m, 2H), 7.77 (s, 2H), 7.51 (d, \( J = 2 \text{ Hz} \), 2H), 7.34 (m, \( J = 2, 9 \text{ Hz} \), 2H), 6.95 (d, \( J = 9 \text{ Hz} \), 2H) ppm.

Synthesis of \( \text{L}^{\text{C6F4}} \): General conditions for step D were used. Yield: 80%. \(^1\)H NMR (400 MHz, \( \text{DMSO-d}_6 \)): \( \delta \) 7.97 (m, 2H), 7.79 (s, 2H), 7.62 (m, 2H), 7.33 (m, \( J = 2, 9 \text{ Hz} \), 2H), 6.92 (m, 2H) ppm.

Synthesis of \( \text{Fe}_2\text{L}^{\text{C6F4}} \): Inside an \( \text{N}_2 \)-filled glovebox, \( \text{L}^{\text{C6F4}} \) (60 mg, 1.0 eq.), \( \text{FeCl}_3 \) (2.5 eq.), DMF (8 mL), and MeOH (1 mL) were combined in a 20 mL scintillation flask. The vial was sealed with a Teflon-lined cap and heated to 140 °C for 2 days. The resulting precipitate was filtered, washed with DMF (3 x 10 mL at 120 °C) and MeOH (3 x 10 mL at 60 °C), and dried under vacuum at 120 °C for two hours to afford \( \text{Fe}_2\text{L}^{\text{C6F4}} \cdot 2 \text{MeOH} \) as a yellow-green powder with moderate crystallinity, similar to \( \text{Fe}_2\text{L}^{\text{C6F3}} \).

Appendix 2.1: References

1. This synthesis was developed by a former undergraduate, David Gygi, to eliminate palladium coupling reactions in the synthesis of \( \text{H}_4\text{ dobpdce} \).