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**Multiscale Studies and Parameter Developments for Metal-
Organic Framework Fe-MOF-74**

ADHITYA MANGALA PUTRA MOELJADI
SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
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Organic Framework Fe-MOF-74**

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List of Abbreviations

MOFs	Metal–Organic Frameworks
PCPs	Porous Coordination Polymers
PCNs	Porous Coordination Networks
MCPs	Microporous Coordination Polymers
HKUST	Hong Kong University of Science and Technology
IRMOF	Isorecticular Metal–Organic Frameworks
MIL	Materials Institute Lavoisier
ZIF	Zeolitic Imidazolate Framework
CUK	Cambridge University-Korea Research Institute of Chemical Technology
POST	Pohang University of Science and Technology
SBUs	Secondary Building Units
bdc	Benzene-1,4-dicarboxylate
btc	Benzene-1,3,5-tricarboxylate
bdtt	Benzene-1,4-ditetrazolate
btt	Benzene-1,3,5-tritetrazolate
tatb	4,4',4''-s-Triazine-2,4,6-triyl-tribenzoate
bda	2,2'-Dihydroxy-1,1'-binaphthalene-5,5'- dicarboxylate
ndc	2,6-Naphthalenedicarboxylate
dobdc	2,5-dioxido-1,4-benzenedicarboxylate

List of Abbreviations (cont.)

BET	Brunauer-Emmett-Teller theory
HF	Hartree-Fock
LCAO	Linear Combination of Atomic Orbitals
CI	Configuration Interaction method
MP2	The Second-Order Møller-Plesset Perturbation Theory
MP4	The Fourth-Order Møller-Plesset Perturbation Theory
MCSCF	Multiconfigurational Self-Consistent Field method
CASSCF	Complete Active Space Self-Consistent Field method
DFT	Density Functional Theory
KS	Kohn-Sham
LDA	Local Density Approximation
LSDA	Local Spin Density Approximation
GGA	Generalized Gradient Approximation
B3LYP	Becke Three Parameter Hybrid Functional
VWN	Vosko, Wilk and Nusair correlation functional
LYP	Lee, Yang and Parr correlation functional

List of Abbreviations (cont.)

QM	Quantum Mechanics
MM	Molecular Mechanics
QM/MM	Quantum Mechanics and Molecular Mechanics
AMBER	Assisted Model Building with Energy Refinement force field
MM3	Molecular Mechanics 3 force field
ONIOM	Our own N-layered Integrated molecular Orbital and molecular Mechanics
ME	Mechanical Embedding
EE	Electronic Embedding
P450	Cytochrome P450
Cpd I	Compound I
Tau-D	Taurine: α -ketoglutarate dioxygenase
OMS	Open Metal Sites
CPO	Coordination Polymer of Oslo
UB3LYP	unrestricted-B3LYP functional
ZPE	Zero Point Energy
UFF	Universal Force Field
RC	Reactant Complex
TS	Transition State
Pro	Product
HAT	Hydrogen Atom Transfer

List of Abbreviations (cont.)

PCET	Proton-Coupled Electron Transfer
SNOs	Spin Natural Orbitals
BDE	Bond Dissociation Energy
MD	Molecular Dynamics
GCMC	Grand Canonical Monte Carlo simulation
GA	Genetic Algorithm
MOF-FF	Force Field for MOFs
vdW	van der Waals
RMSD	Root-Mean Squared Deviation
PBC	Periodic Boundary Condition
FM	Ferromagnetic

Abstract

Metal–Organic Frameworks (MOFs) is class of materials, constructed from an extensive network of coordination polymers that exhibits distinct properties and architectures, depending on the nature of its elementary building unit. Since the introduction of MOFs nearly two decades ago, they have inspired a growing body of research to accomplish practical applications in various scientific and industrial fields. In particular, the design and application of MOFs for gas absorption and storage, gas separation technology as well as selective catalysts are already established and well documented. From computational perspective, an in-depth understanding of chemical processes at a microscopic level can benefit the pursuit of applicability by providing insight as to how to achieve truly exceptional materials. On the other hand, since MOFs feature an extended system with staggering size, it also motivates the development of new theoretical methods that provides accurate description of real systems based on reasonable models. Through this thesis, computational methods such as density functional theory (DFT), molecular mechanics (MM), hybrid quantum mechanics/molecular mechanics (QM/MM) method as well as periodic calculations are developed and applied to some examples of important chemical processes in MOFs. In this thesis, we present our findings as our contribution to the ongoing efforts to utilize computational methods in the field of MOFs.

Chapter 1 Introduction

1.1 Metal–Organic Frameworks (MOFs)

Ever since their first entry to the field of materials science approximately two decades ago, Metal–organic frameworks, or MOFs, have been the subject of enthusiastic research, and have since rapidly developed into a distinct research area of their own. Today, having experienced an almost unprecedented growth, MOFs still represent an exciting field of science that offers many unexplored opportunities: one only needs to look at the sheer number of related publications, and the ever-growing list of potential applications in important fields to appreciate the importance and diversity of the MOF chemistry.[1-11]

Figure 1.1. Schematic diagrams of the porous frameworks of HKUST-1 and IRMOF-1 (also known as MOF-5), generally regarded as among the earliest MOFs that promoted further development of many other MOFs.[12, 13]

1.1.1 General Background on MOFs

MOFs go by many names: porous coordination polymers (PCPs),[3] porous coordination networks (PCNs),[14] and microporous coordination polymers (MCPs), just to name a few.[15] They are a class of porous, hybrid organic-inorganic materials featuring an infinite, uniform framework built from specific organic ligands—termed “linkers”—and inorganic metal “nodes”, or a metal containing cluster (Figure 1.2).[1-2, 5, 10]

Figure 1.2. Representation of widely used SBUs in MOF synthesis, including (a) metal–cluster based SBUs and (b) common carboxylate-based linkers. Color scheme: metal, green; O, red; C, gray.

These elementary components of MOFs constitute secondary building units (SBUs), which ultimately determine the final topology of the framework.[16-18] Recent studies have shown that the geometry of a SBU is dependent not only on the chemical structure of ligand and type of metal, but also on the ligand to metal ratio, as well as the solvent and counter-anions used during the synthesis of MOFs.[19] Pores are formed as

the empty space between the frameworks of MOFs: a great deal of chemistry in this field has been dedicated to controlling their size, shape and properties (Figure 1.3).

Figure 1.3. Schematic diagram illustrating the pore (represented by purple sphere) formed by the frameworks of PCN-9.[14]

Owing to the hybrid nature of these materials, the crystalline frameworks of MOFs can be rigid or highly flexible when exposed to external stimuli. Rigid frameworks are commonly found in conventional porous inorganic materials such as zeolites, and organic polymers can typically be considered flexible materials. In

comparison to these materials, MOFs are unique in the sense that they maintain both crystalline order and flexibility. The structural flexibility is a distinguishing feature of MOFs, and this offers diverse pore environments in which various chemical processes take place.[20-23]

1.1.2 Structural Design of MOFs

In the most basic sense, a MOF is an extensive network of coordination polymers, exhibiting distinct properties and architectures depending on the nature of its elementary building unit.[24] Consequently, the hallmark of MOFs is their almost limitless possibilities, which is made possible by the vast number of available combination between linkers and metals.[9-11, 16-18, 24] Virtually all important properties of MOFs can be tuned by substituting the building units, demonstrating the highly designable nature of MOFs. More importantly, MOFs also benefit from the highly developed chemistry of their individual components, which enable chemists to formulate post-synthesis modifications of MOFs as a supplementary method for adjusting their properties or introducing further functionalities with relative ease.[25, 26] In addition, the synergy between the physical properties of the inorganic nodes and organic components occasionally generate intriguing, novel properties, which open up the possibility for applications in new areas.[27-31]

The high variability of structure is also enabled by the crystalline nature of MOFs. Since the coordination network in MOFs is highly regular, their structures can be easily determined by single crystal X-ray diffraction, allowing one to find correlations between measured properties and well-defined structures easily. The identification of appropriate structural attributes for a specific set of functionalities, in

turn, may establish design principles for the development of ideal structures for certain applications in the future.

These factors—the diversity of starting materials, the tunability of the resulting framework, the wealth of knowledge available from inorganic and organic chemistry and the steady advance in design principles—allow material chemists to pursue the design of new materials that exhibit outstanding performance for a specific function. Arguably the most important of these adjustable attributes is the topological structure, which, by extension, regulates the pore dimension, surface area and internal surface properties of MOFs.

Figure 1.4. Structural representation of an interpenetrated IRMOF-1 derivative, composed of two identical, independent frameworks differentiated by color. Left: (100) face; Right: (101) face. The resultant MOF exhibits a smaller pore dimension than the individual networks.[32]

MOFs are known for their ultrahigh porosity and exceptionally high internal surface area, far beyond that of traditional porous materials such as zeolites.[6, 33] Taking advantage of the adjustable nature of these intrinsic properties, MOFs can be tuned to accomplish different goals: they can be designed to exhibit large pores, which are advantageous for carrying out many chemical processes with guest molecules. Multiple frameworks can be designed to interpenetrate one another, as shown in Figure 1.4,[34] greatly reducing the size of pores, and also allowing MOFs to achieve an even higher internal surface areas to promote adsorption of guest molecules.[35] The shape and dimension of pores can be adjusted to selectively bind molecules with specific size, functional groups or properties. The frameworks can be covalently modified to prompt guest molecules to adopt a certain geometry inside the cavity. The properties of organic linkers and metal nodes can be designed to induce luminescence upon interaction with guest molecule.[36-40] The topology can be controlled to adopt a specific form such as a channel, which when combined with internal surface modification will exclusively benefit a particular chemical process – the list goes on and on. This flexibility allows for the possibility to produce MOFs in various forms – be they as flexible thin films[41] or nanoparticle forms[42] – which will surely benefit the effort to utilize MOFs as new materials for practical applications.

1.1.3 Potential Applications of MOFs

As briefly outlined in the earlier sections, the properties of MOFs, and the immense opportunities for practical application that they offer have inspired a growing body of research, dedicated to pursuing exceptional materials for use in various scientific and industrial fields. In addition to the already extensive scope of applications, chemists continue to explore new areas of implementation. Among these, the applications of MOFs for gas absorption and storage, gas separation technology as well

as selective catalysts are already established and well documented, and will be discussed in this section. Other potential applications of MOFs include membrane filtration,[43] luminescent materials and sensing,[36-39] and biomedical imaging[44, 45] as well as drug storage and delivery.[45] In addition, there are ongoing efforts to explore the optical[30, 31] and ferromagnetic properties of MOFs,[27-29] as well as their potential applications.

(a) MOFs for gas absorption and storage

Porous adsorbent material provides an extensive surface area capable of binding strongly to volatile gases in a relatively small volume, allowing a gas to be compactly stored at a substantially lower pressure. In doing so, porous adsorbent acts as a safer and more economical alternative to conventional gas storage methods such as high-pressure tanks and multi-stage compressors. Several porous adsorbents such as activated carbon, carbon nanotubes and zeolites have been closely studied in the past as a possible candidate for efficient gas storage.[46]

Due to their extraordinarily high surface area to volume ratio, MOFs have received considerable attention as the state-of-the-art material for similar applications. Moreover, the diversity of available materials as well as the highly adjustable attributes of its structure serve as an exceptional advantage possessed by MOFs over earlier porous materials.

While in principle the great tunability of MOFs means that MOF-based adsorbents may be developed for the storage of any volatile gas, the development of MOF for gas storage has been driven largely by the same incentives for the development of its predecessors, namely, to develop a practical hydrogen storage system as a part of an ongoing effort to promote an alternative energy source and reduce the global reliance

on fossil fuels. Furthermore, there have been systematic studies of similar applications for oxygen and methane storage (Table 1.1). Whether a successful application for these purposes is possible still remains to be seen; nevertheless MOF-based gas storage systems have generally achieved significantly improved performance compared to other adsorbents.

Table 1.1 Surface area, porosity and storage capacity of several metal–organic frameworks.

Compound	Adsorbate	Structural properties ^[a]		Storage capacity ^[c]		
		Surface area (m ² /g)	Pore volume (cm ³ /g)	Pressure ^[b] (bar)	w%	[ref]
MIL-53(Al)	H ₂	1100	0.59	16	3.8	[47]
	CH ₄			35	10.2	[48]
MIL-53(Cr)	H ₂	1100	0.56	16	3.1	[47]
	CH ₄			35	10.2	[48]
MIL-101	H ₂	2693	1.90	80	6.1	[49]
	CH ₄			125	14.2	[50]
Mn-BTT	H ₂	2100	0.80	1.2	2.2	[51]
Cu-BTT	H ₂	1710	—	1.2	2.42	[52]
PCN-9	H ₂	1064	0.51	1	1.53	[14]
IRMOF-1	H ₂	2296	—	1	4.7	[53]
HKUST-1	H ₂	1239	0.62	1	2.18	[54]
	CH ₄			150	15.7	[50]

^[a] Surface area measured according to BET theory, ^[b] Pressure of gas during measurement,

^[c] Gas storage capacity measured at 77 K and 298.15 K for H₂ and CH₄, respectively.

Most MOF-based gas storage systems rely on physisorption, where guest molecules bind to surfaces mainly *via* weak van der Waals interactions. As a result, the system exhibits fast kinetics and high reversibility. However, at a higher temperature range that is required for most practical applications, dispersion force alone is not strong enough to allow for significant gas absorption. On the other hand, in the chemisorption approach, guest molecules are allowed to undergo chemical transformations and form strong chemical bonds with the storage material. This leads to greater storage density at the expense of kinetics and reversibility. As such, it has become increasingly clear that the most important step towards achieving an operational gas storage system, is to increase the interactions between gas molecules and MOF-based gas storage system.

Traditionally, since physisorption is favoured by higher surface area, MOFs developed for gas storage are designed to have larger surface areas and lower densities.[55] For this purpose, framework interpenetration has been suggested as a possibly advantageous feature in MOFs, as it is desirable to increase the ratio of internal surface area to volume.[56] However, framework interpenetration is extremely difficult to control, which limits its usefulness in practical MOF design.[34]

Another way to achieve this goal is to take advantage of wall potentials; maximizing the overlap of wall potentials by adjusting the dimension of pores allows guest molecules to experience an enhanced interactions with the framework of MOFs. The most efficient pore size will naturally be dependent on the identity of guest molecules: for example, a theoretically-backed experimental results suggest that the optimal pore size for hydrogen adsorption should be able to accommodate two layers of hydrogen molecule (approximately 6 Å).[57]

Figure 1.5. Adsorption of methane in HKUST-1, displayed from the (001) face. Color scheme: Cu, orange; O, red; C in HKUST-1 framework, green; H, white; C in methane, blue and purple, representing CH₄ molecule adsorbed between frameworks and on open Cu site respectively.[60]

An additional advantage of MOFs over conventional porous materials is the availability of open metal sites (OMS), which allow gaseous molecules to bind to unsaturated metal nodes instead of organic linkers. Hydrogen gas, for example is known to bind strongly to metals compared to carbon-based molecules.[58, 59] Since different metals exhibit different interaction energies, it is possible to take advantage of this binding process if the framework is designed to possess a high concentration of metal

ions with exposed coordination sites. Just as importantly, the overall properties of MOFs will have to be carefully tuned to preserve absorption reversibility. As an example, HKUST-1 has been developed as a promising material for methane adsorption. Using diffraction techniques, it has been shown that methane is adsorbed both on the surface of frameworks and on the exposed Cu sites (Figure 1.5).[60] The availability of secondary adsorption sites can be advantageous to increase gas storage capacity of MOFs.

(b) MOFs for gas separation technology

Figure 1.6. Schematic figure illustrating the adsorption of acetylene on the exposed Fe(II) sites of $\text{Fe}_2(\text{dobdc})$ frameworks.[61] Color scheme: Fe, yellow; O, red; C in $\text{Fe}_2(\text{dobdc})$ framework, grey; C in C_2H_2 , blue; H, white.

The application of MOFs for the adsorption-based separation of light gases is closely related to their efficiency as porous adsorbent materials. In general, the adsorbent material used for separation of a mixture should exhibit different behaviour towards the different components. Passing a mixture through the adsorbent will then lead to the removal of strongly adsorbed guest molecules from the mixture, effectively separating the components based on their physical or chemical properties. Aside from selectivity, in order for a MOF-based adsorbent to find practical applications, the material must also be designed so that the adsorption step can be reversed.

To achieve a high degree of selective adsorption, MOF designs generally rely on different adsorbate-surface interaction strength or size- and shape-based exclusion. The former takes advantage of the higher binding affinity of a gas molecule with framework surfaces. Consequently, MOFs are designed such that preferential adsorption of a specific gas molecule takes place over the other components. An example is shown in Figure 1.6, where Fe(II) sites in Fe₂(dobdc) bind preferably to acetylene compared to other light gas hydrocarbons, due to the greater attraction between Fe(II) and the unsaturated bond of acetylene.[61] The latter relies on the size and shape of pores, which is adjusted to allow only a specific gas to enter the inner cavities and undergo adsorption process, while other components of the mixture are prevented from entering. This is known as molecular sieving effect, or steric separation, and is commonly found in zeolites. In general, these mechanisms are not mutually exclusive: MOFs can be designed to utilize either mechanism independently or both of them at the same time. Currently, there is a great deal of interest in the application of MOF-based adsorbents for the purification of hydrogen and methane, CO₂ and CO capture, separation of gaseous hydrocarbon mixture as well as the removal of toxic volatiles (Table 1.2).

Table 1.2 Examples of adsorption-based gas separation using rigid metal–organic frameworks.

Compound	Structural properties		Adsorption Selectivity	Ref.
	Pore size (Å)	Pore volume (cm ³ /g)		
Mg ₃ (ndc) ₃	3.46–3.64	0.62	O ₂ and H ₂ over N ₂ and CO	[62]
MIL-96	2.5 – 3.5	0.32	CO ₂ over CH ₄	[63]
MIL-102	4.4	—	CO ₂ over CH ₄ and N ₂	[64]
Cu-BDT	—	0.72	O ₂ over N ₂ and H ₂	[65]
PCN-13	3.5	0.30	H ₂ and O ₂ over N ₂ and CO	[66]
MOF-177	7.1 – 7.6	1.31	O ₂ over N ₂	[67]
ZIF-68	7.5	0.46	CO ₂ over CO	[68]
CUK-1	11.1	0.28	O ₂ and H ₂ over N ₂ and Ar	[69]
Cu(hfipbb)(H ₂ hfipbb) _{0.5}	3.2 and	0.072	C ₂ , C ₃ n-C ₄ olefins and	[70]
	7.3		alkanes over all branched	
			alkanes and all other hydrocarbons over C ₄	
Fe ₂ (dobdc)	11	—	O ₂ over N ₂ , C ₂ H ₂ over C ₂ H ₄	[71]
			and saturated hydrocarbons	[61]

(c) MOFs for selective catalysis

As a novel class of porous crystalline materials, MOFs represent a new opportunity for heterogeneous catalysis. In principle, the shape and dimension of the inner pores can be specifically tailored to achieve an optimized chemical environment

for a specific catalytic reaction. Between the high metal content of the framework, the diverse properties afforded by a wide variety of metal nodes and the crystalline nature of the material, MOFs provide a uniform environment around a large number of reaction centers, offering the possibility to achieve truly efficient catalysis. Additionally, post-synthetic modifications can be used to install various scaffolds on the framework in order to introduce steric effects, which enable chemists to pursue the design of enantioselective MOF-based catalysts.

Table 1.3 Examples of catalysis in rigid metal–organic frameworks.

Compound	Catalyzed reactions
D-POST-1	Transesterification of alcohols [72]
$\text{Mn}_3[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{CH}_3\text{OH})_{10}]_2$	Cyanosilation of aromatic aldehydes and ketones, Mukaiyama aldol reactions [73]
$\text{Cu}_2(5,5'\text{-BDA})_2$	Nucleophilic addition of aniline to cyclohexeneoxide [74]
Zr-BDC	Nucleophilic addition of amines, alcohols and thiophenol to epoxide and olefins [75]
$\text{Fe}_2(\text{dobdc})$	Phenol hydroxylation, oxidation of methanol to formaldehyde, oxidation of 1,4-cyclohexadiene, hydroxylation of ethane [76-78]
$\text{Co}_2(\text{dobdc})$	Ring opening of styrene oxide with CO_2 [79]

Such materials exist, and the application of a particular MOF as a heterogeneous catalyst and its associated mechanism constitute a part of this thesis (Table 1.3).

1.2 Computational Chemistry

The development of quantum mechanics in the early twentieth century served as the foundation to computational chemistry as a discipline and a unique, meaningful way to systematically study the reality of chemical events. Generally speaking, computational chemistry—often interchangeable with theoretical chemistry and molecular modelling—is concerned with the application of concepts derived from both classical and quantum mechanics such as force, atomic structures, molecular orbitals as well as electron density and configuration to describe the many features of contemporary chemical reactions.

1.2.1 Basic Approximations to Quantum Chemistry

Fundamental to the field of quantum and computational quantum chemistry is the eponymous Schrödinger wave equation, which was developed to describe quantum mechanical properties. To say that the entire field of computational chemistry was started and evolved in order to apply and solve the Schrödinger equation for complex chemical systems would not be an exaggeration. The Schrödinger equation exists in a time-dependent and time-independent forms, both useful in their own rights. However, for the systems studied in the present thesis the time-independent Schrödinger equation of the form $H\varphi = E\varphi$ will be sufficient.

While the Schrödinger equation provides the necessary physical laws to describe virtually every chemical systems, rigorous applications of such laws were found to inevitably lead to equations that cannot be solved due to their sheer complexity. Indeed, while the Schrödinger equation can be solved exactly for one-electron problems, the same cannot be said of any systems with more than two particles. Out of this necessity, throughout the development of quantum mechanics endeavoring physicists and

chemists have proposed various approximations, some of which have directed further developments in the field. The simplest of these, the Born-Oppenheimer approximation was formulated to treat electrons and nuclei separately. It is based on the substantial difference between the mass of nucleus and electron, which results in the much slower movement of the nucleus compared to that of the electrons. The approximation stated that the slow motion of nuclei can therefore be neglected; in doing so, for practical purposes the conformation of nuclei is considered fixed and the nuclear repulsion energy will be constant. Using the frozen nuclei conformation, the electronic energy can then be obtained. Calculating the electronic energy for various nuclear arrangements enables the construction of a potential energy surface, which defines the energy of a molecule as a function of its conformation. The concept of potential energy surface is useful to evaluate the stability of a given molecular conformation.

It was not until the Hartree-Fock (HF) method was properly formulated in the 1930s that quantum chemists were able to bypass the insoluble equations arising from the direct application of Schrödinger equation on many-body problems. Perhaps one of the most important approximations in the field of computational chemistry, the HF method associate each electron in the system with a spin orbital, which is a one-electron wave function that contains both spatial and spin information of the electron. The molecular orbitals in a molecule are constructed in accordance with the Linear Combination of Atomic Orbitals (LCAO) approach. To satisfy the Pauli anti-symmetry principle, the HF method assumes that the system is sufficiently approximated by a single Slater determinant and constructs a trial wave function from spin orbital in the form of such determinant. The Schrödinger equation can then be solved numerically, and the expectation value of the energy can be obtained following a minimization process.

The approximate solution for a many-body system is made possible in the HF method by adopting the mean field approximation. The approximation contends that the explicit treatment of electron-electron interactions as interactions between particles is untenable. Instead, it assumes that each electron interacts with an average field arising from the presence of all other electrons, and seeks to describe such interaction as an interaction between a particle and a field. While approximating electron-electron interactions in this way significantly reduces calculation complexity and made computation possible, the mean field approximation also introduces a limit to the accuracy of HF method since it neglects a fraction of electron-electron interaction energy referred to as the correlation energy.

Going beyond the accuracy of the HF method requires a new set of approaches that explicitly account for electron correlation. Such method exists: configuration interaction (CI) methods, Møller-Plesset perturbation methods (such as MP2 and MP4 method) and coupled cluster methods accomplish this goal by describing the wave function with multiple Slater determinants. These methods, as well as multireference methods such as multiconfigurational self-consistent field (MCSCF) and complete active space self-consistent field (CASSCF) methods have generally been developed to obtain highly accurate results at the expense of computational costs.

1.2.2 Density Functional Theory

Since its inception in the early 1960s, Density Functional Theory (DFT) has established itself as a crucial part of modern chemical sciences and many scientific fields such as chemistry, biology, engineering and materials design.[80-84] In contrast to the wave function methods described in the previous section, DFT attempts to describe a system in terms of electron density. While Thomas, Fermi and Dirac have proposed

earlier ideas on how to describe many-electron systems using their electron density, the theoretical foundations for modern DFT were firmly laid by Hohenberg and Kohn in 1964 by showing that the total electron density of an N -electron system completely determines all properties of the system. Furthermore, it also shows that the energy of a system is a unique functional of electron density, and provided that an exact functional is used, DFT will give an exact result.[85, 86]

To numerically evaluate the electronic ground state of a many-electron system, Kohn and Sham prescribed an elegant method in which a fictitious system with non-interacting electrons is used as a starting point.[87] The energy of the system E can then be written as

$$E[\rho] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)] \quad (\text{eq.1})$$

or equivalently

$$E[\rho] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + E_{XC}[\rho(r)] \quad (\text{eq.2})$$

where T_{ni} , V_{ne} , and V_{ee} refers to the kinetic energy of the fictitious non-interacting system, the nuclear-electron interaction, and the classical electron-electron interaction respectively. The last two terms, ΔT and ΔV_{ee} serve as a correction to the kinetic energy due to the interacting nature of the system and correction for the non-classical aspect for the electron-electron interaction. These correction terms are collectively referred to as E_{XC} , or the exchange correlation energy. The energetic terms depend on the total density ρ , which itself is a function of nuclear coordinates r .

The next step is to minimize the total energy of the system. To do this, Kohn and Sham introduced non-interacting one electron orbitals ϕ_{KS} , called Kohn-Sham (KS) orbitals. The total electron density can be expressed as a sum of the squared KS orbitals,

$$\rho(r) = \sum_{i=1}^N |\varphi_{KSi}(r)|^2 \quad (\text{eq. 3})$$

and energy is minimized by solving the equation

$$\hat{h}_i^{KS} \varphi_{KSi} = \varepsilon_i \varphi_{KSi} \quad (\text{eq.4})$$

with the Kohn-Sham one-electron operator $\hat{h}_i^{KS}$ defined as

$$\hat{h}_i^{KS} = -\frac{1}{2} \nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{|r_i - r_k|} + \int \frac{\rho(r')}{|r_i - r'|} dr' + \frac{\delta E_{XC}}{\delta \rho} \quad (\text{eq.5})$$

The first three terms on the right hand side are well-defined and refer to the kinetic energy operator, nuclear-electron interaction energy operator, and classical coulomb energy operator respectively. The exact form of last term, the exchange-correlation energy operator is unknown. The accuracy of DFT method therefore depends on how accurately the functional describes the exchange-correlation energy E_{XC} .

Since 1965 there have been many distinct approaches used to formulate different functionals, be it to satisfy fundamental quantum mechanical (QM) requirements or parametrization to reproduce experimental results. They are generally classified into different classes based on their approximation scheme for E_{XC} . The Local Density Approximation (LDA) and Local Spin Density Approximation (LSDA) functionals are the most simple and assume that the exchange-correlation energy can be obtained exclusively from the value of local electron density. To improve the accuracy of LDA methods in molecular system where the electron density is typically non-uniform, the Generalized Gradient Approximation (GGA) functionals were made to include a correction from the gradient of density. The meta-GGA method takes a step further and include a correction from the second derivative of density. Finally, the hybrid method

combines Hartree-Fock exchange energy with GGA method (hybrid-GGA) or with meta-GGA method (meta-hybrid-GGA).[88-94]

The hybrid methods are widely regarded as the best in terms of balancing a manageable computational cost and high quality result. Of all the modern hybrid functional, B3LYP has been the most popular to this date, capable of reproducing experimental results with remarkable accuracy. The formulation of B3LYP combines the Slater exchange and VWN correlation functional of LSDA, Becke exchange and LYP correlation functional as correction from GGA method, Hartree-Fock exchange and three optimized parameters.[95-97] B3LYP functional has the form

$$E_{XC}^{B3LYP} = (1 - a)E_X^{Slater} + aE_X^{HF} + b\Delta E_X^B + (1 - c)E_C^{VWN} + cE_C^{LYP} \quad (\text{eq.6})$$

where a , b and c are empirically determined parameters, E_X^{Slater} is Slater exchange, E_X^{HF} is Hartree-Fock exchange, ΔE_X^B is Becke exchange, E_C^{VWN} is VWN correlation functional, and E_C^{LYP} is LYP correlation functional. The B3LYP functional has been the functional of choice throughout the studies presented in the current thesis.

1.2.3 Basis Sets

In computational chemistry, basis set is a general term that refers to a set of mathematical functions used to represent the orbitals in both wave function and Kohn-Sham DFT method. Presently, an expansive selection of basis set have been developed and published in the literature by many contributing research groups.[88, 98, 99] As modern theoretical methods and computer technology advanced, many of such basis sets were constructed to achieve greater computational accuracy, or for use in a specific type of chemical systems.

The most commonly used basis sets are expanded as a series of Gaussian functions: some of the widely used basis sets belonging to this class are the Pople basis sets,[100] Dunning's correlation consistent basis sets [101-106] as well as the basis sets developed by Ahlrics and coworkers.[107-110] Another type of basis set, the plane wave-basis sets are occasionally used in the study of periodically infinite (typically solid state) systems.

Throughout the works included in this thesis, the split-valence Pople basis sets were chosen for non-metal elements.[100] These basis sets are known to yield decent results with generally reasonable computational costs, and have been extensively used in the literature. A split-valence basis set describes the non-valence orbitals with a linear expansion of Gaussian-type functions, while the description of valence orbitals are split into arbitrarily many set of functions. Such basis sets are sometimes called "valence-multiple- ζ " or "multiple-zeta" quality basis set: double-zeta if valence orbitals are described with two set of Gaussian sums, triple-zeta for three set of Gaussian sums and so on. From a chemical standpoint, using split-valence basis set introduces an extended flexibility of valence basis functions to describe orbital variations as a result of chemical bonding. Generally, the higher zeta quality a basis set has, the more accurate the results will be, albeit at an increased computational cost due to the inclusion of additional Gaussian functions.

The quality of split-valence basis sets can be improved by including polarization and diffuse functions. Polarization functions are Gaussian functions with a higher angular momentum number which can be included to improve the description of anisotropic electron distribution, for example in the distortion of orbitals in the presence of other atomic centers. As such, *p*-type Gaussian functions are usually added to polarize the *s*-functions in hydrogen and helium atoms, *d*-type functions are added to polarize *p*-

functions in heavier elements and so on. However, it is also possible to use more than one set of polarization functions in a split-valence basis set.

Another set of functions that is commonly used is the diffuse functions, which is important to describe the diffuse electron distribution usually found in anions, excited states, transition states and molecules with one or more lone pair of electrons. In such systems, electrons are weakly bound and as a result, the spatial distribution of electrons tend to be relatively far from atomic centers. Diffuse functions are vital in the theoretical prediction of acidity and electronic affinity. In the Pople basis sets, usually an additional *s*- and *p*-type diffuse functions are added to heavy atoms, while an additional *s*-type diffuse function is added for hydrogen atoms.

The Pople split-valence basis sets have the general notation of $X\text{-}YZ\text{++}G^{**}$, where X represents the number of primitive Gaussian functions representing non-valence orbitals, while subsequent number Y and Z indicate the number of Gaussians in several set of sums describing valence orbitals—if there are two numbers it is a double-zeta basis set, if there are three, a triple-zeta and so on. The ‘*’ (pronounced ‘star’) indicates the presence of polarization functions on heavy atoms, while a second star indicates the addition of polarization functions on hydrogen and helium. When more than one set of polarization functions is used, an explicit enumeration of these functions should be used in place of the star nomenclature. Finally, the ‘+’ indicates that the basis set has been augmented with diffuse functions on heavy atoms, while a second plus indicates the presence of diffuse functions on hydrogen and helium atoms.

The 6-31G* basis set was chosen for baseline calculations in this thesis, with the triple-zeta 6-311+G(df,p) typically used in subsequent calculations for increased accuracy. In addition to the Pople basis sets, the effective core potential basis set SDD

was used for metal atoms.[111] In these basis sets, the functions representing the non-valence, or “core” electrons are replaced with an approximate pseudopotential. Since in most cases it is the valence electrons that determine many useful chemical properties such as bond length, polarizability, electron affinity, ionization potential as well as molecular geometries, these basis sets has the advantage of substantially reducing the computational cost of calculations by eliminating the need to include the many Gaussian functions required to represent core electrons.

1.2.4 Molecular Mechanics and Force Fields

Diametrically opposed to the QM methods is the molecular mechanics (MM) approach, which seeks to describe molecular systems using classical terms instead of *ab initio* (quantum) principles. In the MM model, molecules are treated as classical objects and potential energy is represented as a function of nuclear coordinates, evaluated with classical mechanics; a homodiatomic molecule, for example, is described as two identical balls connected with a spring, and the potential energy can be expressed by a simple harmonic oscillator or the Morse potential.[88]

Generally, MM methods employ force fields, which is a collection of transferrable parameters designed to accurately represent energy as a function of molecular arrangements. These parameters are associated to a specific atom type and chemical environments, and are assigned to a molecule during MM calculation according to standard building blocks specified in the force field.

There are numerous force fields available, each of them follows a distinct logic of construction and uses different set of development criteria. For example, a force field may be designed to replicate high level *ab initio* calculation results or available empirical data, be it heat of formation, spectroscopic results, vibrational frequencies or

structural data of a specific set of molecules. Consequently, a force field may be designed for a specific use, sacrificing transferability for accuracy or *vice versa*. AMBER force field,[112, 113] for instance was primarily designed for the simulation of biomolecular systems, such as protein or DNA, while MM2 and MM3 force fields were parametrized for a broad range of molecules.[114-122] Despite the various developmental differences between force fields, the general mathematical expression of energy is given as

$$E_{\text{MM}} = E_{\text{bonded}} + E_{\text{non-bonded}} \quad (\text{eq.7})$$

or equivalently,

$$E_{\text{MM}} = (E_{\text{stretch}} + E_{\text{bend}} + E_{\text{tors}}) + (E_{\text{coul}} + E_{\text{vdW}}) \quad (\text{eq.8})$$

where E_{MM} is the total potential energy, which comprises contributions from bonded as well as non-bonded electrostatic (E_{coul}) and van der Waals (E_{vdW}) interactions. The bonded interactions are described by bond-stretching (E_{stretch}), angle-bending (E_{bend}), and torsion (E_{tors}) terms. In some force fields, additional terms such as out-of-plane bending (E_{opb}) and cross terms (E_{cross}) are included to obtain more accurate results.

Since MM replace the quantum mechanical electronic interactions with a collection of simple bonded and non-bonded interactions, MM approaches significantly reduce the computational cost compared to QM methods. This is especially true for systems containing very large number of atoms such as proteins or periodic systems, where the number of atoms renders QM calculations impossible. In exchange, chemical processes which involve bond breaking or bond formation processes may not be described adequately by MM.

1.2.5 Hybrid Computational Methods: Our own *N*-layered Integrated molecular Orbital and molecular Mechanics (ONIOM)

As described briefly in the preceding sections, an important consideration in choosing a proper computational method is managing the balance between accuracy and computational costs. Generally, a more accurate method is highly desirable provided that the computational cost remains affordable. However, for many systems of interest in modern chemistry—supramolecules, enzymatic catalysis, solvent structure, and periodic systems to name a few—the trade-off between accuracy and cost is much trickier. For these systems, computational demands of full quantum mechanical calculations based on DFT is likely to be prohibitively expensive, especially if hybrid functionals are used. On the other hand, since MM methods evaluate the system as a collection of simple bonded and non-bonded interactions, the computational costs is reduced significantly. However, chemical reactions cannot be described with MM methods, rendering such methods unusable for a lot of chemical processes. Additionally, even when availability of method is not an issue, in some cases MM methods may inadequately describe chemically important interactions in the system such as solvent polarization, π donor-acceptor interactions and C–H- π interactions, which may lead to significantly less accurate results compared to QM methods. Attempting to perform a computational study on such systems require a theoretical approximation that can provide a meaningful chemical description with reasonably high accuracy and practical computational costs.

For this reason, many multiscale or hybrid approaches have been developed to provide a reasonable compromise between accuracy and computational cost. In a hybrid model, the entire system is partitioned into several subsystems, which will be treated using different levels of theory. While in principle any combination of methods is

possible, and although the levels of theory used is not strictly limited to a quantum mechanics and a molecular mechanics (QM/MM) method, hybrid QM/MM methods have been generally very popular and developed continuously by various research groups ever since Honing and Karplus introduced a method to combine QM and MM calculations in 1970.[123]

Figure 1.7. A fictional system illustrating the construction of a hybrid QM/MM model. In a large system, a relatively small region where chemical processes occur is evaluated with quantum mechanical principles, while a molecular mechanics method is used to represent the rest.

Multiscale QM/MM methods seek to utilize the accuracy of QM and the rapid calculations of MM methods, and was devised to combine the best of both worlds. The reasoning for hybrid QM/MM models is conceptually simple: while a chemical system may contain a substantially large number of atoms, only a relatively small fraction of the system is involved in a chemical process. Therefore, a QM approach may be used to accurately describe a limited region where the chemical process of interest occurs, while

the large majority of the system is treated using an inexpensive MM method, as shown in Figure 1.7.

For a hybrid QM/MM model, the energy of the system can be expressed by either additive or subtractive schemes:

$$E_{\text{add}} = E_{\text{QM}}(\text{QM}) + E_{\text{MM}}(\text{MM}) + E_{\text{QM-MM}} \quad (\text{eq.9})$$

$$E_{\text{sub}} = E_{\text{QM}}(\text{QM}) + E_{\text{MM}}(\text{QM} + \text{MM}) - E_{\text{MM}}(\text{QM}) \quad (\text{eq.10})$$

where the notation in parentheses stands for the respective partitioned region and subscripts stand for the level of theory used.[124-126] In additive schemes, the QM subsystem is embedded in a larger MM subsystem. The potential energy for the whole system is evaluated as the sum of MM energy of MM subsystem $E_{\text{MM}}(\text{MM})$, QM energy of QM subsystem $E_{\text{QM}}(\text{QM})$, and the interaction energy between the two subsystems $E_{\text{QM-MM}}$ which can be treated with a varying degree of sophistication. This explicit treatment of the interaction energy is the hallmark of additive schemes, and have significant implications in how QM/MM models are constructed.

In contrast to the additive schemes, in subtractive schemes the QM/MM energy is evaluated by taking the sum of the QM energy of the isolated QM subsystem $E_{\text{QM}}(\text{QM})$ with the MM energy of the total system $E_{\text{MM}}(\text{QM}+\text{MM})$, and subtracting the MM energy of the QM subsystem $E_{\text{MM}}(\text{QM})$. The last step serves as a correction for computing the interactions within the QM subsystem twice. In discussing subtractive schemes it is common to use the terms “model” and “real” to refer to the partitioning of the system: “model” refer to the QM subsystem and “real” refer to the whole system. For a two-layer hybrid model, the QM/MM energy is then evaluated as

$$E_{\text{QM/MM}} = E_{\text{QM,model}} + E_{\text{MM,real}} - E_{\text{MM,model}} \quad (\text{eq.11})$$

The most widely used subtractive QM/MM scheme is the ONIOM (Our own *N*-layered Integrated molecular Orbital and molecular Mechanics) scheme, developed by Morokuma's group.[127-131] By design, the ONIOM method has several advantages over additive QM/MM schemes. First, by avoiding the explicit treatment of interaction energy between two regions, it avoids unnecessary errors from an otherwise difficult quantity to evaluate accurately. Second, the method can be applied with different levels of QM methods and not strictly limited to QM/MM combination. Third, ONIOM was designed to readily accommodate additional layers to construct *n*-layered systems as necessary, although in the current implementation the number of layer is limited to three.

Additionally, there are two important aspects of calculation that must be considered by hybrid QM/MM schemes. The first main issue to consider is the treatment of electrostatic interaction between the two layers. In the simplest scheme, the interaction is described completely by classical MM terms. This includes the electrostatic interactions: in this scheme, the charges in both subsystems are fixed, and the Coulomb equation is used to evaluate the electrostatic interaction between partial charges in both subsystem. This approach is usually known as the mechanical embedding (ME), and is the default approach used by ONIOM. The second approach, referred to as the electronic embedding (EE), allows for the polarization of QM subsystem by MM charges. In other words, the QM subsystem is allowed to respond to the charge distribution in its surrounding environment. EE scheme generally gives a better description for the electronic interaction between the two regions, at the expense of having a higher computational cost than ME.

The second major issue to address is the treatment of covalent bonds between the two regions. While ideally the partitioning in QM/MM models does not involve a boundary across chemical bonds, in practice more often than not it is necessary to do

so. In such cases, the resulting dangling valence bonds must be saturated in a chemically sensible manner. Various methods have been developed to provide a reliable description of the boundary region; such methods include link atoms, frozen localized orbitals and boundary atoms.[88, 131-136]

Figure 1.8. Link atom method in ONIOM, represented with ethane. A scale factor Q is used to determine the position of link atom LA along the C–C bond according to the equation $d(LA-LAC) = Q \cdot d(LAH-LAC)$ such that it is placed between the two regions.

Among these, the link atom method represents one of the simplest and most general approach to solve the dangling bonds problem.[131] It is implemented in a majority of QM/MM calculation schemes, including ONIOM. By introducing an additional monovalent atom along every bond cut by the QM/MM partition, QM calculations can be performed with a saturated model system without affecting the real system. For this purpose hydrogen atoms are usually used, although in theory any atom can be used to mimic the part of the system that it substitutes. While in principle each

link atom will introduce three additional degrees of freedom to the system, in practice the position of link atom is placed at a fixed position along the bond—usually determined using a scale factor to ensure that it is correctly placed between the two regions—thereby removing the additional degrees of freedom (Figure 1.8).

Hybrid multiscale QM/MM models has been applied to a variety of molecular systems, most notably enzymes, and QM/MM studies of extended framework systems have increasingly been performed in recent years. While such systems can be studied by pure QM methods, it would require a substantial truncation of the real system, at the risk of losing the environmental influence of surrounding structures. ONIOM method provides a more realistic description of the system, offering accurate insights on chemical processes with relatively affordable computational costs, which enables an efficient theoretical studies of contemporary chemical systems.

1.3 The Aim of Current Thesis

The first part of the present thesis is concerned with the reaction mechanism of ethane hydroxylation by Fe-MOF-74, an iron-containing metal–organic framework. While catalysis has been regarded as one of the most promising applications of MOFs, only a handful of reported examples have been studied computationally. By exploring the energetically feasible pathways in C–H bond hydroxylation and comparing the results with those of enzymes which catalyse similar reactions, the trend can be rationalized using similar concepts established from earlier computational studies of enzymatic reactions.

The second part of the thesis is focused on the development of accurate force field parameters for the ferrous and ferric form of Fe-MOF-74. The parameters were obtained from the calculated geometry and energy derivatives of *ab initio* calculations

on the non-periodic cluster model of Fe-MOF-74. The energy expression of these parameters follow the prescription of MOF-FF, a class of parameters which has been shown to closely reproduce the experimental structures, vibrational modes and thermal behaviour of periodic MOFs.

The third part of the thesis attempts to apply the previously developed MOF-FF force field parameters in a periodic multiscale QM/MM calculations to model the binding process of O₂ in Fe-MOF-74. The effect of metal substitution in the framework on oxygen binding energy was then studied with various divalent metal ions (Mg, Ni, Zn, Co, and Mn).

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Chapter 2 High-Spin Rebound Mechanism in the Reaction of the Oxoiron(IV) Species of Fe-MOF-74

2.1 Introduction

The rich, diverse chemistry of high-valent oxoiron(IV) species is well documented.[1, 2] The crucial role that they play in a great number of reactions, and the associated mechanisms have been the subject of intense studies for both theoretical and experimental chemists. In nature, such species are frequently involved in carrying out difficult chemical transformations in mild conditions, often with high selectivity and efficiency. In particular, they display a remarkable potency in the functionalization of the chemically inert C–H bonds, which may occur in heme and non-heme enzymes such as cytochrome P450 enzymes (P450)[3-5] and taurine: α -ketoglutarate dioxygenase (Tau-D)[2] that routinely utilize high-valent oxoiron(IV) species to catalyze alkane hydroxylation, olefin epoxidation, and other types of biologically important oxidation reactions.

Given the tremendous economic and environmental impacts of the selective and efficient conversion of alkanes into commercially valuable chemicals, the remarkable potency of enzymatic high-valent oxoiron(IV) species has fueled considerable efforts of theoretical and experimental chemists to replicate their reactivity with non-enzymatic, synthetic equivalents.[6-17] To this end, chemists seek to utilize the insights from extensive studies performed on these enzymatic systems.

At present, the synthesis of several heme[6-8] and non-heme[8-17] oxoiron(IV) complexes has been reported, and their reactivity profiles have also been characterized. However, while several examples of reactive synthetic oxoiron(IV) species have been found, the majority of these complexes are highly susceptible to decomposition or fail

to exhibit significant catalytic activity. Extensive computational studies have been performed to address the inactivity of synthetic oxoiron(IV) catalysts, which showed that most of these complexes tend to favour low-spin states as opposed to the high-spin states found in metalloenzymes.[18] The previous quantum chemical works of Shaik on the oxoiron(IV) center of P450s, for example, have predicted that although low-spin states are more stable, high-spin states oxoiron(IV) species will have a lower energy barrier compared to the low-spin state counterpart due to an enhanced exchange stabilization in high-spin state processes.[18-21] This computationally derived concept implies that, if a high-spin oxoiron(IV) species can be realized, or that if high-spin electronic configurations can participate in a reaction, the difficulty of a chemical transformation can be reduced substantially.

At the same time, the emergence of metal–organic framework (MOFs) as new porous materials offers a novel, promising approach to catalyst design.[22-27] The properties associated with MOFs—the high surface area, the adjustable and selective inner pores, the thermal and chemical stability of the frameworks as well as tuneable reactivity—provide ample opportunities for catalytic applications.[28] Furthermore, as opposed to most nitrogen-based modular organic ligands used in the synthesis of oxoiron(IV) complexes, weak-field oxygen-based ligands such as carboxylates are commonly used in the construction of MOFs. Such ligands are expected to give rise to a completely different chemical environment around metal centers. Consequently, when redox-active transition metals are embedded as open metal sites (OMS) in MOFs, their unique coordination environments may induce a powerful catalytic behaviour analogous to those found in metalloenzymes.

Indeed, several MOFs have been proposed to act as efficient heterocatalysts for chemical transformations. Among them is the recently synthesized $\text{Fe}_2(\text{dobdc})$ (dobdc^{4-}

= 2,5-dioxido-1,4-benzenedicarboxylate), commonly known as Fe-MOF-74 or CPO-27-Fe.[29-35] This particular MOF is a member of the MOF-74 series, M-MOF-74 (M=Mg, Mn, Fe, Co, Ni, Cu or Zn) that features an extensive honeycomb-like network with hexagonal-shaped pores and accessible metal sites, constructed from M(II) cations interconnected by bridging dobdc^{4-} linkers.[29-33] Fe-MOF-74 has been shown to allow phenol hydroxylation,[35] conversion of methanol to formaldehyde,[36] and oxidation of 1,4-cyclohexadiene to proceed.[37] Most interestingly, Fe-MOF-74 and its magnesium-diluted analogue was shown to catalyze the hydroxylation of ethane by N_2O under mild conditions.[37]

Figure 2.1. Proposed mechanism for the hydroxylation of ethane by N_2O in Fe-MOF-74.

Due to the very strong C–H bonds in ethane, ethane hydroxylation is unlikely to occur with most iron species. For this reason, it was proposed that a high-spin oxoiron(IV) species was generated *in-situ* and acted as the active species that catalyzes the transformation, as shown in Figure 2.1.[37] The reaction profile remains unchanged when the majority of iron(II) sites were substituted with redox-inactive magnesium(II) to form mixed-metal $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$, which supported the idea that an active species containing a single iron center is involved in the reaction. Additionally, the preliminary theoretical studies on the electronic structure of Fe-MOF-74 indeed suggested that the coordination environment in the framework favors the formation of oxoiron(IV) species with high-spin configuration. As a part of a continued efforts to study the catalytic activity of oxoiron(IV) species, here theoretical methods will be used to provide mechanistic insights into the reactivity of oxoiron(IV) in Fe-MOF-74, as well as how they differ from the oxoiron(IV) species in the more extensively studied P450s.

2.2 Methodology

Since MOFs feature an extended framework with a staggeringly high dimensionality, the sheer size of the system in this study necessitates the use of multiscale QM/MM models for adequate theoretical description of the reaction environment. Another approach is to use QM methods on a substantially simplified model to represent the active site involved in the catalytic reaction. While the former is often more desirable, the results obtained from the latter are often useful for preliminary studies and comparison, as well as to form the basis for further calculations with increased complexity.

2.2.1 Initial QM Calculations on Cluster Model

Initial QM calculations were performed on a truncated cluster model obtained from the published crystal structure of Fe-MOF-74, originally in the Fe(III)-OH form.[37] The cluster model was intended as a compromise between accuracy and realistic description of the reaction site: it should be small enough to be studied using accurate DFT calculations, but large enough to include the important moieties that formed the structure surrounding the oxoiron(IV) center. Since the periodic structure is charge neutral, it was also desirable to truncate the periodic structure in a way that would eliminate excess negative charge originating from the carboxylate based ligands. By replicating the physical features of the reaction site, the model was expected to successfully mimic the chemical properties as well as the reactivity of the Fe(IV)O group that was observed in the experimental studies.

Considering that hydroxylation of ethane was experimentally found to occur in the highly diluted $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$ frameworks, it is reasonable to assume that catalytic reaction does not require multiple iron centers. For this reason, magnesium ions were used to replace non-participating Fe(III)-OH groups, which also has the advantage of simplifying the model. The reacting iron site was replaced accordingly with Fe(IV)O group. Finally, hydrogen atoms were added to cap dangling valences appropriately and water molecules were used as ligands to terminate the cluster, as well as keeping the cluster model charge neutral. The final mixed-metal cluster used for calculations contain 72 atoms, including two magnesium ions and one oxoiron(IV) group (Figure 2.2).

It should be noted that due to these considerations, the truncated model described in this section might not be suitable to study chemical or physical processes in which

metal–metal interactions play a significant role. Similarly, the model is unlikely to accurately describe the additional interactions between substrate and framework ligands, which is sometimes important in determining substrate selectivity as well as distinguishing unique binding structures. In such cases, it is important to extend the model appropriately to include the adjacent metal atoms or framework as necessary.

In recent computational studies involving analogous MOFs, several groups have used similar line of reasoning to design various truncated cluster models that preserve the environment in the proximity of the chemical center, while allowing greater flexibility in more distant groups.[38-41] These clusters can be varied in size to suit the intended purpose of the study.

Figure 2.2. The cluster model of $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$ used in DFT calculation. Color scheme: Fe, yellow; Mg, green; O, red; C, gray; H, white.

All geometry optimizations were performed with DFT methods, as implemented in Gaussian09.[42] Unrestricted B3LYP functional was used with the combined basis set of SDD with pseudopotential (for Fe) and 6-31G* (for others).[43-47] Frequency calculations were performed at the same level of theory to characterize the optimized geometry and obtain zero-point energy (ZPE) corrections.

2.2.2 Hybrid QM/MM Calculations on Multiscale Model

Following the same rationale used in building the truncated cluster model for QM calculations, the multiscale QM/MM model was built from the crystal structure of Fe-MOF-74, as shown in Figure 2.3.[37] Three Fe(III)-OH groups were initially included in the QM region. The central Fe(III)-OH was substituted with Fe(IV)O group as the designated site for reaction, while the neighbouring groups were substituted with Mg^{2+} cation. The final QM region contain six organic linkers, a central oxoiron(IV) and two terminal Mg^{2+} cations as shown in Figure 2.4.

Figure 2.3. The entire system used for QM/MM studies, indicating the approximate boundary of optimized layer. Optimized atoms are shown in ball-and-stick representation, while unoptimized atoms are represented as wire. Color scheme: Fe, yellow; O, red; C, gray; H, white.

Figure 2.4. (a) Representation of QM region in QM/MM model. Atoms in the QM region are shown in ball-and-stick representation, while atoms outside the QM region are shown in stick and wire representations for optimized and unoptimized atoms respectively. Color scheme: Fe, yellow; Mg, green; O, red; C, blue; H, white. (b) A schematic diagram of the QM region. Numbered C atoms on benzene ring indicates a connection to either a carboxylate or a phenolate group through QM/MM boundary.

The ONIOM scheme as implemented in Gaussian09 was used to perform calculations on the two-layer QM/MM model.[48-51] The B3LYP functional was used in conjunction with SDD effective core potential (for Fe) and 6-31G* basis sets (for others) for geometry optimization and vibrational frequency analysis. ZPEs obtained from frequency calculation was included in the reported energy as correction. For MM atoms, the universal force field (UFF) was used.[52] The atom type “Fe6+2” (octahedral coordinated) of UFF was used for iron atoms. In addition, the optimized geometries were subjected to single point energy calculation with 6-311+G(df,p) basis set on all atoms. G4 calculations were performed to estimate the homolytic bond dissociation energies (BDEs) of ethane and ethanol.[49]

2.3 Results and Discussion

Figure 2.5. Potential energy profiles (in kcal/mol) for the hydroxylation of ethane by oxoiron(IV) species determined from DFT calculation at B3LYP/B1+ZPE level.

DFT calculations were initially performed on the simplified cluster model to probe the activation of C–H bond in ethane and the subsequent formation of ethanol. The triplet (low-spin) and quintet (high-spin) states were considered. The reaction pathway begins with the formation of reactant complex RC, where ethane approaches the oxo group of MOF-74 cluster. In contrast to the findings in P450 Cpd I and the majority of reported synthetic non-heme oxoiron(IV) complexes, the quintet spin state

is more stable than the triplet spin state during the initial formation of RC.[17] This is consistent with the results of preliminary computational studies, and support the hypothesis that high-spin states of oxoiron(IV) is favored by the weak ligand field of carboxylate-based linkers in both Fe-MOF-74 and the magnesium-diluted variant.[37] Furthermore, as shown in Figure 2.5, the quintet spin state remain exclusively as the ground state throughout the entirety of the reaction pathway, which is distinct from the cases of many reported non-heme oxoiron(IV) complexes. Such complexes frequently feature a low-spin ground state and a spin crossover phenomenon to higher-spin states along the reaction coordinate. The C–H bond cleavage by oxoiron(IV) leads to the formation of an intermediate Int containing a stable ethyl radical and a reduced Fe(III)OH moiety. The ethyl radical then proceeds to form an alcohol product PC *via* a radical rebound step followed by dissociation, generating a vacant Fe(II) metal site in the process.

Based on the results of preliminary QM calculations, the determination of potential energy profile for the hydroxylation of ethane was refined using multiscale QM/MM model. The results from QM/MM calculation reaffirmed earlier DFT findings that suggest only high-spin intermediates participate in the transformation of ethane to ethanol (Figure 2.6). A somewhat higher energy barrier of 15.6 kcal/mol was obtained from QM/MM calculation compared to 10.3 kcal/mol determined with the DFT model. However, the energy barrier is still remarkably low considering the fact that the homolytic C–H BDE of ethane was calculated to be as large as 100.7 kcal/mol, as determined with G4 method (Table 2.1).

Figure 2.6. (a) Potential energy profiles (in kcal/mol) for the hydroxylation of ethane by oxoiron(IV) species in triplet and quintet electronic states, as determined from QMMM calculation at the ONIOM(B3LYP/B2:UFF)//ONIOM(B3LYP/B1:UFF)+ZPE level. (b) The first coordination sphere and key bond distances (in Å) are shown for the intermediate and transition states of the quintet catalytic cycle. Color scheme: Fe, yellow; O, red; C, gray; H, white.

This low energy barrier suggest that in the chemical environment of MOF-74, oxoiron(IV) species can abstract hydrogen from ethane and act as the active species in the hydroxylation process. While in reality the calculated barrier height might differ due to the limited accuracy of B3LYP functional, the reactivity of high-spin states during H-abstraction was also predicted by GGA-type BP86 and hybrid M06 functional (Table 2.2).

Figure 2.7. The QM region obtained from the optimization of TS1 and TS2 for quintet electronic state. Key distances are shown in Å. Color scheme: Fe, yellow; Mg, green; O, red; C, blue; H, white.

Table 2.1 Homolytic bond dissociation energies (BDE) calculated with G4 method.

Bond	BDE ^[a] (kcal/mol)
Ethane (C–H)	100.7
Ethanol (C–H)	94.5
Ethanol (O–H)	104.1

^[a] Calculated using the enthalpy data at 298.15 K and 1 atm

Table 2.2 Functional dependence of the H-abstraction barrier height.

Functional	Relative barrier height ^[a] (kcal/mol)	
	Quintet	Triplet
B3LYP	15.6	32.8
BP86	24.2	37.0
M06L	6.9	33.5

^[a] Determined at the ONIOM(DFT/B2:UFF)//ONIOM(B3LYP/B1:UFF)+ZPE level

In the real reaction environment of MOF-74, the ferrous species resulting from the radical rebound step may be oxidized by N₂O to form Fe(III)OH or regenerate oxoiron(IV) species. Although the calculated rebound barrier is low (9.4 kcal/mol), the result does not necessarily rule out the possibility that the ethyl radical may further react with other available Fe(III)OH or Fe(IV)O groups within the MOF cavity, instead of recombining with the hydroxyl radical from the same reaction site where C–H bond cleavage was initiated, as shown in Figure 2.7. Indeed, the situation is different from enzyme active sites that generally utilize their structural surroundings to confine the movement of substrates during reaction. On the contrary, the movement, position and orientation of substrate molecule in the inner cavity of MOF is not necessarily regulated by electrostatic and dispersion interactions with the surrounding frameworks, especially for small molecules like ethane. In fact, it has been shown that without the ability to strongly anchor the substrate to the reaction center, in the reaction of a synthetic non-heme oxoiron(IV) complex the substrate radical can dissociate without undergoing the radical rebound step.[54] Similarly, due to the relatively unrestricted movement of substrate molecules in MOF cavities, an analogous substrate dissociation during reaction cannot be excluded.

Figure 2.8. Spin population of Fe, C and O in the quintet state reaction pathway, obtained from ONIOM(B3LYP/B1:UFF) results.

The barrier heights for H-abstraction were calculated as 15.6 and 32.8 kcal/mol for quintet and triplet states, respectively. The lower energy barrier of the quintet pathway can be rationalized by the enhanced exchange stabilization at the iron center. Examination of the changes in the atomic spin population values for relevant atoms—Fe, O atom of the oxo group, and the C atom of ethane from which hydrogen is abstracted—at different stages of the reaction allows for the observation of electron redistribution process along the reaction coordinate (Figure 2.8). For quintet pathway, the spin population of Fe increased from 3.3 to 4.1 as TS1 is being formed, while the population of C decreases from 0.0 to -0.5. These changes indicate that as the hydrogen atom is being abstracted, an electron with α -spin is transferred from ethane to the Fe

center. As a result, formal oxidation state of Fe is reduced from 4+ to 3+, and the number of unpaired electron increases from 4 to 5. This particular electronic arrangement produces additional exchange stabilization as H-abstraction progresses, lowering the energy barrier in a fashion typically observed from high-spin oxoiron(IV) reactions in heme and non-heme systems.[18-21]

Further observation on the spin density of C atom of ethane and the O atom of the oxo group reveals that, while some spin population was present in O in the course of the reaction, the negative spin density of C atom was much more significant. As such, it was likely that the spin population on O atom was redistributed from the reduced Fe atom. On the other hand, the negative spin density of C atom in ethane indicates that a radical species with a β -spin is present after the formation of intermediate Int. The radical intermediate was subsequently quenched to form a non-radical product, as shown by the negligible spin population of C in the product complex PC. These observations are in agreement with the formation of ethyl radical species, as well as the subsequent radical rebound proposed in the reaction mechanism.

Despite the fact that computational studies have long predicted the reactivity of synthetic heme and non-heme monoiron complexes bearing high-spin oxoiron(IV) group [18-21], only a few examples have been reported in literature.[6-17, 55] These systems commonly feature an oxo group that is inaccessible for chemical reactions, due to the extremely unstable nature of the moiety: the aqueous Fe(IV)O complex, for example, has a half-life of roughly 10 seconds.[55] Other complexes require ligands with a bulky scaffold to serve as steric protection for the oxo group, which prevent physical access to substrates and resulting in a sluggish catalytic activity. In contrast, the theoretical findings from the reactivity profile as well as the spin population of oxoiron(IV) center in MOF-74 highlighted the capability of metal–organic frameworks

to promote and stabilize transient, accessible high-spin oxoiron(IV) groups by utilizing the weak ligand field of carboxylate-based linkers. As such, when compared with the reported mononuclear oxoiron(IV) complexes, the robust Fe-MOF-74 framework might be regarded as a more advantageous structural template to achieve practical activations of strong C–H bonds.

Experimentally, acetaldehyde was also found in the product mixture, presumably as a result of subsequent reaction between ethanol with oxoiron(IV).[37] To simulate the formation of acetaldehyde from ethanol, two possible reaction pathways involving two consecutive H-abstraction steps were examined. The first pathway involves an initial H-abstraction from C–H bond followed by a second H-abstraction from O–H bond. Alternatively, in the second pathway hydrogen atom was initially abstracted from the O–H bond, followed by a subsequent H-abstraction from C–H bond. Similar to the formation of ethanol, the reaction can be assumed to require only a single oxoiron(IV) site, although participation of multiple iron centers is certainly possible. Since the high-spin state intermediates have already been shown to be much more energetically accessible in the hydroxylation of ethane, only quintet state pathway is considered for the subsequent formation of acetaldehyde (Figure 2.9).

Surprisingly, a low overall energy barrier of 7.2 kcal/mol was found for the initial H-abstraction from O–H bond of ethanol, compared to 9.9 kcal/mol calculated for initial abstraction from C–H bond. This is somewhat counter-intuitive to the results of G4 calculations, which predicted a very strong O–H bond in ethanol. The G4-calculated BDEs for the C–H and O–H bonds in ethanol predicted a higher BDE of 104.1 kcal/mol for O–H bond, compared to the calculated BDE of 94.5 kcal/mol for C–H bond (Table 2.1).

Figure 2.9. (a) Potential energy profiles (in kcal/mol) for the secondary oxidation of ethanol to acetaldehyde by oxoiron(IV) species in quintet electronic states, as determined from QMMM calculation at the ONIOM(B3LYP/B2:UFF)// ONIOM(B3LYP/B1:UFF)+ZPE level. (b) The first coordination sphere and key bond distances (in Å) are shown for the intermediate and transition states of the quintet catalytic cycle. Color scheme: Fe, yellow; O, red; C, gray; H, white.

Figure 2.10. Visualization of SNOs for TS1_{OH} and TS1_{CH}, calculated at B1-level theory. Color scheme: Fe, yellow; Mg, green; O, red; C, gray; H, white.

To rationalize this inconsistency, further analysis of the spin natural orbitals (SNOs) for the transition states formed during initial H-abstraction, TS1_{OH} and TS1_{CH}, was performed. Visualization of these orbitals revealed that the SNO for TS1_{OH} was not localized on the O–H bond, but instead featured an amplitude perpendicular to the bond (Figure 2.10). As such, this orbital has a significant character of the oxygen lone-pair orbital, resulting in the stabilization of the transition state by the proton-coupled electron transfer (PCET) effect.[56] In contrast, the SNO for TS1_{CH} was localized on the C–H bond, indicating that the process can be characterized as hydrogen atom-transfer (HAT). In an analogous manner, a synthetic high-spin, non-heme diiron(IV) complex was experimentally found to selectively cleave the O–H bonds of methanol and *tert*-butyl alcohol rather than the weaker C–H bonds.[57] In both cases, the PCET scenario appear to be a reasonable explanation for the observed selectivity.

The second H-abstraction step in both mechanisms was found to be essentially barrierless. Having assumed that only a single oxoiron(IV) center participated in the reaction, both pathways ultimately result in the formation of acetaldehyde and a water molecule, bound to a regenerated Fe(II) site of MOF-74.

Figure 2.11. (a) Potential energy profiles (in kcal/mol) for the hydroxylation of ethane to ethanol by Fe(III)OH species in sextet electronic state, as determined from QMMM calculation at the ONIOM(B3LYP/B2:UFF)//ONIOM(B3LYP/B1:UFF)+ZPE level. (b) The first coordination sphere and key bond distances (in Å) are shown for the intermediate and transition states of the quintet catalytic cycle. Color scheme: Fe, yellow; O, red; C, gray; H, white.

Finally, the participation of Fe(III)OH as the catalytic species in the ethane hydroxylation was briefly examined. Only the sextet spin state was considered. As shown in Figure 2.11, the energy barrier for H-abstraction by Fe(III)OH was found to be very high (34.9 kcal/mol), much higher than the activation barrier calculated for oxoiron(IV). Therefore, the possibility that Fe(III)OH may have acted as an active species during ethane hydroxylation can be safely ruled out. This finding also provides a reasonable basis to explain why the low energy barrier predicted theoretically for ethane hydroxylation was not translated to a very high yield in experiments. [37] Since Fe(III)OH species is unreactive, the disparity might be explained if oxoiron(IV) species quickly decays to form Fe(III)OH before the majority of ethane in reaction starts to react.

2.4 Conclusion

In conclusion, both DFT and QM/MM calculations indicated that the ethane hydroxylation by N₂O in Fe-MOF-74 proceeds in a two-step mechanism, involving H-abstraction by a reactive oxoiron(IV) species and a subsequent radical rebound step. Unlike most known heme and non-heme oxoiron(IV) complexes, the reaction proceeds exclusively in high-spin pathways. As a result of the high-spin electronic configuration, the increased exchange stabilization at the iron center substantially lowers the energy barrier for H-abstraction, even for strong C–H bonds of ethane, to a reasonable level. The experimentally observed formation of acetaldehyde was also studied. The presence of acetaldehyde was proposed to be the result of ethanol oxidation by oxoiron(IV) species, which was found to occur *via* H-abstraction from the strong O–H bonds rather than C–H bonds, due to the presence of stabilizing PCET effects during O–H bond cleavage step.

The results of computational studies highlighted the capability of Fe-MOF-74 to stabilize transient high-spin oxoiron(IV) species by utilizing the weak ligand field of carboxylate-based linkers. As such, the results demonstrated the potential of Fe-MOF-74 both as a catalyst as well as a scaffold to support reactive metal species.

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Chapter 3 *Ab Initio* Parametrized Force Field for the Metal–Organic Framework Fe-MOF-74

3.1 Introduction

The synthesis and discovery of metal–organic frameworks (MOFs) have attracted considerable efforts to study the extraordinary mechanical and chemical attributes of these materials. The exploration of their attractive properties and potential applications is developing rapidly, motivated by early successes in key industrial areas such as gas storage, purification and separation technologies, selective heterocatalysts as well as sensing materials.[1-11]

In this endeavor, theoretical models have contributed significantly to achieve a fundamental understanding of MOFs. Computational methods have been shown to be useful not only in providing explanations for the exceptional performance of MOFs in various fields, but also in identifying key design principles to assist future rational design of MOFs. In particular, periodic density functional theory (DFT) methods are often used to study the electronic structure of MOF frameworks, while molecular dynamics (MD) and Grand Canonical Monte Carlo (GCMC) simulations are used in the study of adsorption and diffusion of guest molecules.[12-15] However, realistic description of MOFs is often complicated by the extended nature of the frameworks. Computational demands of full quantum mechanical DFT calculations with a periodic setting can often be prohibitively expensive, especially if atomic-orbital basis sets and hybrid functionals are used. In contrast to the complex quantum mechanical electronic interactions in DFT, molecular mechanics (MM) approximates the potential energy of MOFs as a function of nuclear coordinates, using a collection of relatively simple

classical equations to evaluate bonded and non-bonded interactions. Although MM methods cannot simulate chemical reactions, they significantly reduce the computational cost required to perform a broad range of simulations on periodic systems.

In recent years, theoretical chemists have recognized the need to improve existing generic MM parameters or force field (FF), such as the universal force field (UFF),^[16] MM3 ^[17-25] and DREIDING,^[26] to obtain a more accurate description of MOF systems.^[27-30] Several extension schemes for these existing parameters have been proposed. Most notably, Schmid and coworkers developed a systematic parametrization strategy based on higher-level theoretical reference data for a variety of MOFs, to derive a tailored force field called MOF-FF.^[31-34] This scheme was initially developed as a manually-fitted extension of the MM3 force field,^[31] but the more recent version of the parametrization scheme was designed to combine the *ab initio* reference data with a genetic algorithm (GA) based reparametrization approach, delivering a flexible parameter set that accurately reproduces the structures and physical properties of various MOFs.^[32-34] Following this general strategy, several other parameter sets have been developed from first-principles calculations for different series of MOFs.^[35, 36] In particular, they were shown to be especially successful in simulating dynamic structural deformations as a result of heating, as well as interactions between guest molecules and framework in flexible MOFs.

In a previous study, the catalytic mechanism of ethane hydroxylation by the oxoiron(IV) active species formed in Fe-MOF-74 was investigated using multiscale QM/MM models, where UFF parameters were used in combination with QM method to perform ONIOM(QM:MM) calculations.^[37] Here, DFT calculation results were used to refine specific MM parameters for Fe-MOF-74 in the Fe(II) and Fe(III)OH form,^{[38-}

45] in accordance with the MOF-FF scheme.[32-34] In the future, development of a specific parameter set also allows for possible implementations with hybrid computational schemes to accurately describe various chemical systems involving Fe-MOF-74.

3.2 Methodology

3.2.1 Energy Expression of MOF-FF

The general energy expression of the force field used in this work is given by

$$E_{\text{MM}} = E_{\text{stretch}} + E_{\text{bend}} + E_{\text{opb}} + E_{\text{tors}} + E_{\text{coul}} + E_{\text{vdW}} \quad (\text{eq.1})$$

where E_{MM} is the total energy, which comprises contributions from bonded as well as non-bonded electrostatic (E_{coul}) and van der Waals (E_{vdW}) interactions. The bonded terms are described by bond (E_{stretch}), angle (E_{bend}), torsion (E_{tors}) as well as out-of-plane (E_{opb}) effects. The expressions for E_{stretch} , E_{bend} and E_{tors} covalent terms followed the formulations used in the MM3 force field[17-25] and are given as

$$E_{\text{stretch},i} = \frac{1}{2} k_{r,i} (r_i - r_{i,0})^2 \times \left[1 - 2.55(r_i - r_{i,0}) + \frac{7}{12} (2.55(r_i - r_{i,0}))^2 \right] \quad (\text{eq.2})$$

$$E_{\text{bend},i} = \frac{1}{2} k_{\theta,i} (\theta_i - \theta_{i,0})^2 \times \left[1 - 0.14(\theta_i - \theta_{i,0}) + 5.6 \times 10^{-5}(\theta_i - \theta_{i,0})^2 - 7 \times 10^{-7}(\theta_i - \theta_{i,0})^3 + 2.2 \times 10^{-8}(\theta_i - \theta_{i,0})^4 \right] \quad (\text{eq.3})$$

$$E_{\text{tors},i} = \sum_n \frac{V_i^n}{2} [1 + \cos(n\tau_i + \tau_i^n)] \quad (\text{eq.4})$$

where k values are the force constants, r and r_0 represents the bond distance and equilibrium distance, and θ and θ_0 represents the bond angle and equilibrium angle. For the cosine series expansion in the torsion term, V^n and τ^n are the expansion coefficient and phase shift, respectively, for the n -fold term with τ_i being the torsion angle.

The out-of-plane bending energy expression, E_{opb} is calculated with a simple harmonic potential, given as

$$E_{\text{opb},i} = \frac{1}{2} k_{\varphi,i} \varphi_i^2 \quad (\text{eq.5})$$

with the k value being the force constant for a specific trigonal center and φ being the out-of-plane angle.

For non-bonded electrostatic (E_{coul}) and van der Waals (E_{vdW}) interactions, we followed the formulations used by the Schmid group for MOF-FF.[34]

$$E_{\text{coul},ij} = \frac{1}{4\pi\epsilon} q_i q_j \frac{\text{erf}(\frac{d_{ij}}{\sigma_{ij}})}{d_{ij}} \quad (\text{eq.6})$$

Instead of point charges, the formulation employs spherical Gaussian type charge distribution, which effectively dampens electrostatic interactions between highly charged groups at close distances. Such situation commonly occur in MOFs, where alternating charges can be found in the framework, often with large values. This allows for the inclusion of 1–2 and 1–3 interactions, which is usually excluded in MM calculations. For electrostatic interactions, d_{ij} is the interatomic distance between atom i

and j with atomic charges q_i and q_j , respectively. The Gaussian atomic charge distributions σ_i and σ_j were used to calculate σ_{ij} as $(\sigma_i^2 + \sigma_j^2)^{1/2}$. In the present work, fixed atomic charges are employed as parameters.

On the other hand, the van der Waals interactions use the dispersion damped Buckingham potential,[34, 46, 47] which is given as

$$E_{vdW,ij} = \varepsilon_{ij} \left\{ 1.85 \times 10^5 \exp\left(-12 \frac{d_{ij}}{d_{ij}^0}\right) - 2.25 \left(\frac{d_{ij}^0}{d_{ij}}\right)^6 \left[1 + 6 \left(\frac{0.25d_{ij}^0}{d_{ij}}\right)^{14}\right]^{-1} \right\} \quad (\text{eq.7})$$

where d_{ij} is the interatomic distance between atoms i and j , d_{ij}^0 is the sum of vdW radii of atoms i and j , and ε_{ij} is the energy parameter for the interactions between the two atoms calculated as the geometric mean $(\varepsilon_i \varepsilon_j)^{1/2}$. The dispersion damped Buckingham potential is much less repulsive than the commonly used Lennard-Jones potential, and provides a better description of vdW interactions at close distances. The required vdW parameters were taken from the MM3 parameter library and remain constant throughout the reparametrization process.[17-25, 34]

Additionally, for special cases in the coordination environment of Fe(II) and Fe(III) centers with multiple angular minima at 90 and 180°, the Fourier-type bend potential[33, 34, 48, 49] is used as

$$E_{bend,i}^{Fourier} = \frac{k_{\theta,i}}{2} [1 + \cos(\theta)] [1 + \cos(2\theta)] \quad (\text{eq.8})$$

where k_{θ} is the adjustable force constant and θ is the bond angle.

To limit the number of independent parameters in the energy expression, force field parameters are assigned based on atom types. For covalent interactions, unique parameters are exclusively assigned to each distinct pair (for bonds), triplet (for angles) or quadruplet (for torsions and out-of-plane bendings) of force field atom types. Each atom type is also assigned with a set of atomic vdW parameters and an atomic charge.

3.2.2 *Ab Initio* Reference Calculation of the Model System

The force field parameterization in this study followed the general GA-based strategy of MOF-FF developed by Schmid et al.[34]

Figure 3.1. Non-periodic reference models used for the force-field parameterization. Reference models of Fe-MOF-74 in the (a) Fe(III)-OH form and (b) the Fe(II) form. (c) Definition of atom types in the dobdc^{4-} ligand. (d) Local environment of Fe(III)-OH in Fe-MOF-74. Color scheme: Fe, yellow; O, red; C, gray; H, white.

DFT calculations on non-periodic cluster models were performed initially to obtain reference data for the force field parameterization. The cluster models of Fe-MOF-74 was carved from the published crystal structure in Fe(III)OH form and modified accordingly (Figure 3.1a and 3.1b) to afford the native Fe(II) form.[50] Both models were optimized using the hybrid B3LYP functional and the combination of SDD effective core potential basis set used for Fe and the 6-31G* basis set used for C, H and O.[51-55] Furthermore, frequency calculation was performed at the same level of theory to confirm the nature of the optimized structure. The frequency analysis also provides the Hessian matrix, which contains analytical second order derivatives of energy with respect to coordinates required to approximate the initial values of bonded parameters. To derive atomic charges that are used for the calculations of E_{coul} , the Merz-Kollman method was used with a vdW radius of 1.20 Å for Fe.[56] All reference calculations were performed with Gaussian09.[57]

3.2.3 GA Optimization of Parameters

After the initial bonded parameters and atomic charges had been assigned, the GA optimizer was used to optimize bond-stretching and angle-bending parameters within a permitted range of values. Initially, the quality of optimized force-field parameters was internally measured by the objective function, which is related to the fitness of geometry simulated using the optimized parameter set. Once the objective function converges to a value, the optimization cycle is finished. To obtain parameters of higher quality, the resulting parameters from previous optimization were used as initial values for the subsequent fitting. Between two consecutive optimization sequence, the optimized value of parameters were checked for any instances where an intermediary value is very close to the lower or the upper limit of the defined range. Such cases indicate that a more optimal parameter value may be found outside the

currently permissible interval, and the permissible values for parameter optimization was modified accordingly. This process was repeated until the final parameter set was able to reproduce the DFT geometry reasonably well (Appendix B, Table S1, Table S2), as demonstrated by the root-mean squared deviation (RMSD) value obtained from the validation tests.

Table 3.1 Effects of Optimized Out-of-plane and Torsion Terms

<i>Parameter</i>	<i>RMSD of MM Optimization</i>	
	Cluster Model ^[a]	Periodic Model ^[b]
<i>Reference^[c]</i>	0.944	0.247
<i>Fitting #1</i>	0.895	0.261
<i>Fitting #2</i>	0.852	0.261
<i>Fitting #3</i>	0.671	0.278
<i>Fitting #4</i>	0.685	0.292
<i>Fitting #5</i>	0.580	0.322
<i>Fitting #6</i>	0.553	0.320
<i>Fitting #7</i>	0.619	0.322
<i>Fitting #8</i>	0.538	0.319

^[a] RMSD values were measured against the DFT-based reference geometry. ^[b] RMSD values were measured against the available crystal structure. ^[c] Reference parameter sets in which out-of-plane and torsion parameters were not optimized.

In principle, it is possible to include the optimization of out-of-plane and torsion terms for MOF-74 in GA reparametrization process. However, in the present work, the inclusion of both out-of-plane and torsion terms did not improve the quality of the resultant parameter sets significantly (Table 3.1), despite a sizeable increase in computational cost from the inclusion of additional terms in optimization. Therefore the out-of-plane, torsion and cross-terms were not included into consideration during GA optimization, and instead parametrization was focused mainly on the optimization of covalent parameters related to bond and angle terms.

3.2.4 Validation of Parameters

Figure 3.2. Periodic model for periodic MM calculations, applied using periodic boundary conditions (PBC). The unit cell and cell parameters are shown. Color scheme: Fe, yellow; O, red; C, gray.

To validate the optimized force field, several MM geometry optimizations were carried out using the reparametrized parameter sets on the respective reference cluster model as well as the periodic structure. For each structure, RMSD value from the corresponding MM optimization should be no worse than 0.20 Å. The periodic models contain approximately 980 atoms, obtained by extending the published crystal structure of Fe-MOF-74 in the Fe(III)-OH form and modified accordingly (Figure 3.2). All calculations were performed with a modified version of the TINKER program package.[58] Simple distance-based cutoffs were used in the computation of pairwise interactions in periodic systems. With the current approach, the interactions between a pair of sites beyond a certain cutoff distance were set to zero. The standard cutoff distances for periodic systems in TINKER were used, i.e., 9.0 Å for both electrostatic and vdW interactions.

3.3 Results and Discussion

3.3.1 Final MOF-FF Parameter Set

The finalized parameter set for Fe(II) and Fe(III)OH model is listed in Table 3.2, each containing three parts: (1) the GA optimized covalent parameter values for bond lengths, angles as well as their respective force constants, (2) covalent parameter values for the remaining out-of-plane bendings and torsions determined from reference calculation, as well as (3) predetermined non-covalent parameters for electrostatic and vdW interactions. Parameter values for the out-of-plane bendings and torsions are similar for the two forms of Fe-MOF-74. Entries marked as “anglef” indicates that the parameter uses the Fourier-type angle-bending potential to describe an angle with periodic minima.

Table 3.2 Final force-field parameters for Fe(II)-MOF-74 and Fe(III)-MOF-74

<i>Force-Field Parameters</i>				
<i>Atom Types</i>	Bond Stretches			
	Fe(II)-MOF-74		Fe(III)-MOF-74	
	$r_{i,0}$ [Å]	k_r [mdyne/Å]	$r_{i,0}$ [Å]	k_r [mdyne/Å]
<i>Fe – O_{ca}</i>	2.073	1.180	2.090	1.240
<i>Fe – O_{cb}</i>	1.942	1.450	1.935	1.170
<i>Fe – O_{po}</i>	2.036	1.350	2.060	1.500
<i>Fe – O_{OH}</i>	—	—	1.882	3.040
<i>C_{ca} – O_{ca}</i>	1.310	8.655	1.310	8.655
<i>C_{ca} – O_{cb}</i>	1.262	11.666	1.262	11.666
<i>C_{po} – O_{po}</i>	1.291	9.043	1.291	9.043
<i>C_{pc} – C_{ca}</i>	1.464	4.975	1.464	4.975
<i>C_{pc} – C_{ph}</i>	1.386	7.016	1.386	7.016
<i>C_{pc} – C_{po}</i>	1.420	6.038	1.420	6.038
<i>C_{po} – C_{ph}</i>	1.402	6.639	1.402	6.639
<i>C_{ph} – H_{ph}</i>	1.101	5.623	1.101	5.623
<i>O_{OH} – H_{OH}</i>	—	—	1.000	7.030

	Angle Bendings			
	Fe(II)-MOF-74		Fe(III)-MOF-74	
	$\theta_{i,o}$ [deg]	k_θ [mdyne/rad ²]	$\theta_{i,o}$ [deg]	k_θ [mdyne/rad ²]
$Fe - O_{OH} - H_{OH}$	—	—	112.67	0.18
(Anglef)				
$O_{OH} - Fe - O_{ca}$	—	—	—	0.00
$O_{OH} - Fe - O_{po}$	—	—	98.43	0.03
$O_{OH} - Fe - O_{cb}$	—	—	96.55	0.68
$O_{po} - Fe - O_{po}$	157.38	0.35	160.31	0.42
$O_{po} - Fe - O_{cb}$	103.50	0.00	90.82	1.35
$O_{po} - Fe - O_{ca}$	87.93	0.16	82.97	0.00
(Anglef)				
$O_{ca} - Fe - O_{cb}$	—	0.09	—	0.00
$O_{ca} - Fe - O_{ca}$	102.98	1.09	85.44	0.84
$C_{po} - O_{po} - Fe$	128.55	0.45	121.54	0.27
$C_{ca} - O_{cb} - Fe$	125.00	0.00	132.25	0.04
$C_{ca} - O_{ca} - Fe$	131.70	0.26	128.51	0.54
$O_{ca} - C_{ca} - O_{cb}$	123.03	1.41	123.03	1.47
$C_{pc} - C_{ca} - O_{ca}$	118.36	0.67	118.36	0.33
$C_{pc} - C_{ca} - O_{cb}$	118.58	0.93	118.38	1.17
$C_{po} - C_{pc} - C_{ca}$	124.29	0.86	124.29	0.81
$C_{ph} - C_{pc} - C_{ca}$	118.33	1.15	118.33	1.00
$O_{po} - C_{po} - C_{pc}$	123.88	0.53	123.88	0.13
$H_{ph} - C_{ph} - C_{pc}$	117.56	0.34	117.56	0.39
$C_{ph} - C_{po} - C_{pc}$	118.63	0.28	118.63	0.46
$C_{ph} - C_{po} - O_{po}$	117.47	1.35	117.47	1.44
$H_{ph} - C_{ph} - C_{po}$	117.29	0.43	117.29	0.41
$C_{po} - C_{pc} - C_{ph}$	118.58	1.19	118.59	1.33
$Fe - O_{ca} - Fe$	85.85	0.00	95.86	0.00
$Fe - O_{po} - Fe$	87.42	0.03	102.37	0.00
	Out-of-plane Bendings			
	$\varphi_{i,o}$ [deg]		k_φ [mdyne/rad ²]	
$C_{pc} (C_{ca}, C_{ph}, C_{po})$	0.00		0.08	
$C_{po} (O_{po}, C_{ph}, C_{pc})$	0.00		0.12	
$C_{ca} (O_{ca}, O_{cb}, C_{pc})$	0.00		0.12	
$C_{ph} (H_{ph}, C_{pc}, C_{po})$	0.00		0.05	
	Torsion			
	n	V^n_i [kcal/mol]	τ^n_i [deg]	
$O_{ca} - C_{ca} - C_{pc} - C_{po}$	2	0.45	180.0	
$O_{ca} - C_{ca} - C_{pc} - C_{ph}$	2	0.45	180.0	
$O_{cb} - C_{ca} - C_{pc} - C_{po}$	2	0.45	180.0	
$O_{cb} - C_{ca} - C_{pc} - C_{po}$	2	0.45	180.0	

$C_{ca} - C_{pc} - C_{po} - O_{po}$	2	0.19	180.0	
$C_{ca} - C_{ca} - C_{pc} - C_{ph}$	2	0.19	180.0	
$C_{ph} - C_{pc} - C_{po} - O_{po}$	2	0.19	180.0	
$C_{ph} - C_{pc} - C_{po} - C_{ph}$	2	0.19	180.0	
$C_{ca} - C_{pc} - C_{ph} - H_{ph}$	2	0.90	180.0	
$C_{po} - C_{pc} - C_{ph} - H_{ph}$	2	0.90	180.0	
$O_{po} - C_{po} - C_{ph} - H_{ph}$	2	0.19	180.0	
$C_{pc} - C_{po} - C_{ph} - H_{ph}$	2	0.67	180.0	
van der Waals Parameters				
	d_{ij}	ϵ_i [kcal/mol]		
Fe	2.20	0.020		
O	1.82	0.059		
C	1.96	0.056		
H	1.50	0.020		
Atomic Charges				
	Fe(II)-MOF-74		Fe(III)-MOF-74	
	q_i	σ_i	q_i	σ_i
Fe	1.008	2.073	1.198	2.073
O _{OH}	—	—	- 0.762	1.118
O _{ca}	- 0.617	1.118	- 0.575	1.118
O _{cb}	- 0.617	1.118	- 0.575	1.118
O _{po}	- 0.645	1.118	- 0.605	1.118
C _{ca}	0.568	1.163	0.689	1.163
C _{pa}	- 0.179	1.163	- 0.235	1.163
C _{po}	0.354	1.163	0.412	1.163
C _{ph}	- 0.116	1.163	- 0.131	1.163
H _{ph}	0.117	0.724	0.118	0.724
H _{OH}	—	—	0.366	0.724

The development of parameter set, as outlined in the preceding methodology section, sacrifices transferability in favour of increased accuracy: generally, a new parameter set will have to be generated for new MOFs containing different building blocks. At the same time, the consistent parametrization scheme made it possible to expand the parameter list with new parameters for different type of organic linkers and inorganic metal nodes. Due to the unique coordination and framework structure found

in both Fe(II)-MOF-74 and Fe(III)-MOF-74 used in this work, the cluster model used for reference calculation had to be chosen in such a way that is unlikely to benefit from the addition of new building block parameters to the force-field library.

Nonetheless, in such cases where additional parametrization have to be performed on new building blocks, a suitable *ab initio* method may be chosen for reference calculation to obtain an accurate representation of the real system. By keeping the same energy expression used in previous force-field development, new parameters can be added to the library and compatibly used alongside an already existing parameter set.

3.3.2 Force Field Validation

The first validation of the parametrized force fields for Fe(III)-MOF-74 and Fe(II)-MOF-74 involves the correct prediction of geometry of the respective non-periodic reference cluster models (Figure 3.3a and 3.3b). The former contains Fe(III)-OH moieties, whereas the latter has Fe(II) open metal sites. Both models contain one benzoate ligand and three salicylate ligands (which are simplified models of *dobdc*⁴⁻), and the terminal Fe centers are terminated by water ligands.

As expected, most of the structure, including the first coordination sphere of iron is reproduced very well by MM optimization. Comparing key geometric parameters from the DFT-optimized reference model and the MM-optimized structure, the largest discrepancy associated with an optimized parameter can be seen in the prediction of the equatorial Fe–O_{ca} bond in Fe(II)-MOF-74, as well as the Fe–O_{po}–Fe angle in Fe(III)-MOF-74 (0.07 Å and 3.7° respectively). In these cases, relatively large deviations in the first coordination sphere was presumably a result of sharing the same FF parameters with other bonds or angles of the same type. For instance, in Table 3.3, the shorter

equatorial Fe–O_{ca} bond share the same bond type with the much longer axial Fe–O_{ca}' bond in the reference DFT structure. Both reference values were used to approximate the initial parameter value, resulting in parameter that was too soft to replicate the short equatorial Fe–O_{ca} bond, and too rigid to obtain. Similar circumstances can be observed in the case of Fe–O_{po} and Fe–O_{po}' bonds, as well as the Fe–O–Fe angles for both Fe(II) and Fe(III) models. The introduction of cross terms in a future FF development can potentially alleviate this issue, however, at present this issue is unlikely to be resolved with additional parametrization cycles.

Additionally, for both MM optimized models a noticeable distortion in a non-planar carboxylate ligand was observed. In said ligand, the dihedral angle of the carboxylate group showed a significant deviation, up to 36.7° for the salicylate ligand in Fe(III)OH and 30.7° for the benzoate ligand in Fe(II) (Figure 3.3c and 3.3d). Such defects are not uncommon, and usually occur as the consequence of representing the real periodic system with a truncated cluster; in this case, representing the complete *dobdc*⁴⁻ ligand in the Fe(III)OH and Fe(II) cluster model respectively is the salicylate and benzoate group. These ligands lack the coordination to another Fe centers *via* a phenoxy and a carboxylate group. As a result, the absence of coordination with the surrounding environment may cause a significant deviation. Furthermore, the associated torsion parameter was determined from the reference DFT structure containing multiple carboxylate groups with different coordination environments. Since the torsional parameters were not included in GA optimization, it is possible that the derived parameter was too soft to prevent the rotation of this particular carboxylate group during MM optimization. Excluding these non-planar ligands from RMSD evaluation yielded a small value (< 0.05 Å) for both models, indicating that the non-planar ligands were the only significant source of structural deviation from the reference DFT structure. In

a periodic system, the coordination environment of each ligand will be uniform, and such deformation is not expected to occur. Since the RMSD value for both structures demonstrate that the overall deviation is still within a tolerable margin, further reoptimization with additional GA cycles does not seem necessary.

Figure 3.3. Comparison of the geometries of non-periodic Fe-MOF-74 cluster models obtained from reference DFT calculations (Fe, yellow; O, red; C, gray; H, white) and MM calculations. Ligand with non-planar carboxylate group is indicated. (a) Fe(III)-OH form (Fe, orange; C, tan); (b) Fe(II) form (Fe, orange; C, blue); (c) Comparison of distorted carboxylate group in MM calculations with reference structure; (d) Measurement of the dihedral angle in MM result.

Table 3.3 Structural comparison between crystal structure, reference DFT and MM optimization results of non-periodic model

a) Fe center		DFT		MM	
	<i>crystal</i> ^[a]	Fe(II)	Fe(III)	Fe(II)	Fe(III)
bond lengths [Å]					
<i>Fe – O_{OH}</i>	1.92	-	1.85	-	1.84
<i>Fe – O_{Ca}</i>	2.08	2.02	2.12	2.09	2.08
<i>Fe – O_{po}'</i>	2.04	2.10	2.08	2.07	2.06
<i>Fe – O_{cb}</i>	2.01	2.04	2.03	1.99	2.01
<i>Fe – O_{po}</i>	2.04	2.03	2.03	2.05	2.03
<i>Fe – O_{Ca}'</i>	2.20	2.13	2.28	2.09	2.28
<i>Fe(III) – Fe(III)'</i>	3.16	-	3.13	-	3.22
<i>Fe(II) – Fe(II)'</i>	2.99 ^[b]	2.85	-	2.77	-
bending angles [deg]					
<i>Fe–O_{Ca}–Fe</i>	95.2	85.8	94.7	83.7	95.8
<i>Fe–O_{po}–Fe</i>	105.9	87.4	98.5	85.1	102.3

b) dobdc⁴⁻ ligand		DFT		MM	
	<i>crystal</i> ^[a]	Fe(II)	Fe(III)	Fe(II)	Fe(III)
bond lengths [Å]					
<i>C_{Ca} – O_{Ca}</i>	1.29	1.31	1.30	1.31	1.30
<i>C_{Ca} – O_{Cb}</i>	1.27	1.24	1.25	1.26	1.24
<i>C_{Ca} – C_{pc}</i>	1.49	1.49	1.49	1.48	1.49
<i>C_{po} – O_{po}</i>	1.42	1.34	1.33	1.29	1.34
<i>C_{pc} – C_{po}</i>	1.39	1.41	1.42	1.43	1.42
<i>C_{pc} – C_{ph}</i>	1.36	1.41	1.41	1.40	1.40
<i>C_{po} – C_{ph}</i>	1.40	1.41	1.41	1.41	1.41
bending angles [deg]					
<i>O_{Ca}–C_{Ca}–O_{Cb}</i>	121.9	121.9	122.3	123.0	122.1
<i>O_{Ca}–C_{Ca}–C_{pc}</i>	119.3	118.1	118.7	118.4	118.9
<i>O_{Cb}–C_{Ca}–O_{pc}</i>	118.7	119.9	119.0	118.4	118.9
<i>C_{Ca}–C_{pc}–C_{po}</i>	123.9	125.1	124.6	123.6	124.7
<i>C_{Ca}–C_{pc}–C_{ph}</i>	117.6	116.4	116.5	118.3	116.7
<i>C_{pc}–C_{po}–O_{po}</i>	123.4	124.0	123.6	124.3	123.7
<i>C_{pc}–C_{po}–C_{ph}</i>	118.9	118.5	118.2	118.8	118.9
<i>C_{pc}–C_{ph}–C_{po}</i>	122.6	122.3	122.2	122.0	122.1
<i>C_{ph}–C_{po}–O_{po}</i>	117.7	117.4	118.0	117.0	117.3

^[a] For the Fe(III)-OH form. ^[b] Value taken from DFT-optimized geometry in Reference [59].

Further parameter validation was done for two periodic systems: Fe(III)-MOF-74 and Fe(II)-MOF-74, which exhibit iron centers in the Fe(III)-OH and Fe(II) forms, respectively. These models were built from the published crystal structure of Fe-MOF-74 in the Fe(III)-OH form, extended to replicate the desired periodic system (Figure 3.4). With regard to Fe(III)-MOF-74, the periodic MM-optimized geometry agrees very well with the published crystal structure at a level no worse than that corresponding to a RMSD value of 0.15 Å.

Compared with the crystal structure, somewhat large deviations were observed in the periodic MM-optimized geometries of Fe(II)-MOF-74 (Table 3.4), for which both axial Fe–O_{ca}' bond length and Fe–Fe interatomic distance were underestimated in a manner similar to both the results of reference QM and non-periodic MM calculations. This is not completely surprising, because the absence of hydroxide coordination is expected to result in a shortening of the axial Fe–O bond. Since the parameter set was optimized to mimic the reference QM structure, this deviation is to be expected in the periodic MM calculations as well. In addition, the periodic MM calculation largely underestimated Fe–O–Fe angles in Fe(II)-MOF-74, which resulted in a different geometry with a much shorter Fe–Fe distance compared to the geometry obtained by periodic DFT.

Overall, the geometry from periodic MM geometry optimization gives a satisfactory agreement with the published crystal structure, which supports our assumption that the formulated energy expression and parameterized force-field parameters are reliable in reproducing experimental structures.

Figure 3.4. Comparison of the geometries of periodic Fe-MOF-74 models obtained from crystal structure (Fe, yellow; O, red; C, gray) and periodic MM calculations. (a) Fe(III)-OH form (Fe, orange; C, tan); (b) Fe(II) form (Fe, orange; C, blue).

Table 3.4 Structural comparison between crystal structure and periodic MM optimization result of periodic model

a) Fe center		MM (Periodic)	
	<i>crystal</i> ^[a]	Fe(II)	Fe(III)
		bond lengths [Å]	
<i>Fe – O_{OH}</i>	1.92	-	1.90
<i>Fe – O_{Ca}</i>	2.08	2.12	2.08
<i>Fe – O_{po}'</i>	2.04	2.00	2.07
<i>Fe – O_{cb}</i>	2.01	2.08	2.00
<i>Fe – O_{po}</i>	2.04	2.06	2.06
<i>Fe – O_{Ca}'</i>	2.20	1.99	2.12
<i>Fe(III) – Fe(III)'</i>	3.16	-	3.03
<i>Fe(II) – Fe(II)'</i>	2.99 ^[b]	2.69	-
		bending angles [deg]	
<i>Fe–O_{Ca}–Fe</i>	95.2	81.8	91.9
<i>Fe–O_{po}–Fe</i>	105.9	82.9	93.9

b) dobdc⁴⁻ ligand		MM (Periodic)	
	<i>crystal</i> ^[a]	Fe(II)	Fe(III)
		bond lengths [Å]	
<i>C_{Ca} – O_{Ca}</i>	1.29	1.30	1.30
<i>C_{Ca} – O_{Cb}</i>	1.27	1.27	1.26
<i>C_{Ca} – C_{pc}</i>	1.49	1.47	1.48
<i>C_{po} – O_{po}</i>	1.42	1.43	1.44
<i>C_{pc} – C_{po}</i>	1.39	1.40	1.41
<i>C_{pc} – C_{ph}</i>	1.36	1.28	1.29
<i>C_{po} – C_{ph}</i>	1.40	1.38	1.39
		bending angles [deg]	
<i>O_{Ca}–C_{Ca}–O_{Cb}</i>	121.9	123.4	123.0
<i>O_{Ca}–C_{Ca}–C_{pc}</i>	119.3	112.4	116.0
<i>O_{Cb}–C_{Ca}–O_{pc}</i>	118.7	122.3	120.2
<i>C_{Ca}–C_{pc}–C_{po}</i>	123.9	123.2	124.6
<i>C_{Ca}–C_{pc}–C_{ph}</i>	117.6	118.2	117.2
<i>C_{pc}–C_{po}–O_{po}</i>	123.4	129.6	126.2
<i>C_{pc}–C_{po}–C_{ph}</i>	118.9	120.3	118.9
<i>C_{pc}–C_{ph}–C_{po}</i>	122.6	120.4	122.9
<i>C_{ph}–C_{po}–O_{po}</i>	117.7	115.1	115.0

^[a] For the Fe(III)-OH form. ^[b] Value taken from DFT-optimized geometry in Reference [59].

3.4 Conclusion

New force field parameters for Fe-MOF-74 were developed from *ab initio* reference calculations on non-periodic clusters. The force field comprises contributions from electrostatic terms based on fixed atomic charges derived from Merz-Kollman scheme, a vdW term with parameters from MM3 model, as well as covalent terms fitted with GA optimization approach. The energy expression follows the formulation used in MOF-FF developed by Schmid. Subsequently, validation of force field was carried out by performing MM optimization on the truncated cluster model and periodic model constructed from crystal structure. The results showed that the energy expression and optimized parameters were able to reproduce experimental structure very well.

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Chapter 4 Dioxygen Binding to Fe-MOF-74: Microscopic Insights from Periodic QM/MM Calculations

4.1 Introduction

Large scale separation of O₂ from air is an essential process in the industrial field. It is among the largest volume industrial gas, valued for its reactivity and importance for combustion or oxidative processes involved in welding, metal and chemical manufacturing, coal gasification and pharmaceutical industry.[1-4] To meet these industrial demands, an efficient, low-cost separation process of O₂ is of utmost importance. Currently, the most common large-scale production method of high purity oxygen is the cryogenic distillation method, which is energy intensive.[5] Additionally, production of oxygen at lower purity is accomplished with adsorption methods, such as the pressure swing adsorption technology which utilizes specific adsorptive materials. One such class of material, Zeolites, is widely used for O₂/N₂ separation in the industrial field with some degree of success. However, the material was noted for having modest selectivity, resulting in an inherently inefficient process.[6, 7] In order to find practical applications in industrial-scale gas storage and separation, the development of innovative materials with high selectivity and thermal stability remains as a priority.

As a result of their exceptional performance as porous adsorbents, the recently synthesized series of MOF-74 have received considerable attention for applications in this field. In general, the characteristic high surface areas and tuneable pore size of MOFs is favorable for efficient adsorption-based processes.[8-13] Furthermore, the exposed, coordinatively unsaturated metal sites in M-MOF-74 (M = Mg, Mn, Fe, Co, Ni, Cu or Zn) make MOF-74 particularly attractive as novel O₂ separation materials.

Since O_2 is the only major redox-labile component in dry and clean air,[14] a separation strategy can take advantage of the different adsorption behavior of O_2 and other redox-rigid components in air. If redox-active metals are used as exposed metal nodes in MOF-74 frameworks, the inner surface of MOFs can be expected to selectively adsorb O_2 with the aid of partial redox mechanism or similar electron transfer processes.[15-18]

Figure 4.1. Selective binding of O_2 over N_2 in Fe-MOF-74. The exposed Fe(II) metal sites preferentially adsorbs O_2 due to the higher electron affinity of the molecule. Color scheme: Fe, yellow; C, gray; O, red; N, blue; H, white.

For this purpose, Fe(II) is an obvious candidate due to its ubiquity in nature as biological O_2 carrier.[19-22] Fe-MOF-74 have previously been shown to be a promising

material for gas separation, with higher selectivity and capacity in hydrocarbon separation than the zeolite-based solid adsorbents.[16, 23-25] In particular, the material displayed exceptional performance when tested for the separation of a C1-C3 hydrocarbon mixture at relatively high temperature compared to that for cryogenic distillation, with the high selectivity attributed to the presence of uncoordinated Fe(II) sites.[24, 25] Similarly for gas separation in a O₂/N₂ mixture, studies have demonstrated the higher selectivity of Fe-MOF-74 towards O₂ at substantially higher temperature than the currently used cryogenic condition in industrial processes (Figure 4.1).[16] However, at room temperature, the iron centers in MOF-74 undergo the formation of ferric-peroxide species, preventing desorption of oxygen.[16, 18] Although the results confirm the potential of frameworks with redox-active metal centers for selective gas separation, future MOFs designed to achieve a fully reversible process must account for additional factors that could affect the binding strength between metal sites and O₂.

From a computational perspective, periodic multiscale QM/MM computations is a reasonable starting point to obtain fundamental understanding of microscopic processes in MOFs. In recent years, periodic multiscale calculations have been shown to give accurate prediction on experimentally observed structures and properties of extended framework systems, allowing theoretical methods to contribute meaningful insights at molecular level.[26-31] In this study, the oxygen binding process of Fe(II)-MOF-74 and its diluted, mixed-metal analogues where Fe(II) centers were substituted by M(II) ions (M = Mg, Ni, Zn, Co, or Mn) is studied using multiscale QM/MM methodology. Furthermore, the previously developed force field parameters for Fe(II)-MOF-74 will be implemented as the MM parameters in a periodic hybrid calculation scheme.[32]

4.2 Methodology

Periodic QM/MM calculations were carried out with the ONIOM scheme[33-36] with two-layer QM/MM approach (or the ONIOM2(QM:MM)). In the case of ONIOM2(QM:MM), the energy and forces of the system are calculated as

$$E_{\text{ONIOM}} = E_{\text{QM,model}} + E_{\text{MM,real}} - E_{\text{MM,model}} \quad (\text{eq.1})$$

$$\vec{F}_{\text{ONIOM}} = \vec{F}_{\text{QM,model}} + \vec{F}_{\text{MM,real}} - \vec{F}_{\text{MM,model}} \quad (\text{eq.2})$$

In this work, the real system was described by MM calculations in a periodic boundary condition. Therefore, separate codes were required to evaluate the energy and forces for the QM and MM calculations. An interface code was used to handle the data transfer process (Figure 4.2). Gaussian 09 (revision D.01) was used for QM calculations, and its “external” function was used to execute MM calculations outside of Gaussian 09.[37] All MM calculations were performed with a modified version of TINKER.[38] Energy and forces were obtained from these codes independently and collected within Gaussian 09 to apply equations 1 and 2.

The interactions between the QM (model) region and outside the QM region were described with the mechanical embedding (ME) scheme, in which the non-bonded interactions are treated with MM terms. In theory, the use of electronic embedding (EE) scheme will give a more realistic description of the interregional interactions, since QM atoms are allowed to respond to the charge distribution outside of the QM region. However, EE calculations require increased computational costs, and the EE scheme cannot be directly implemented in our current protocol. Therefore, implementation of EE calculations were not pursued in this study.[39, 40]

Figure 4.2. Schematic diagram illustrating the flow in an external QM/MM calculation using G09 and TINKER.

Geometry optimization for the periodic model of Fe-MOF-74, shown in Figure 4.3, was carried out using the ONIOM2(B3LYP/B1:MOF-FF) method; B1 stands for a combination of the SDD effective core potential basis set and the 6-31G* basis set used for C, H and O.[41-45] To reduce the computation time required for geometry optimization, a spherical region centered at the QM region with a radius of 10 Å was defined for the initial unoptimized periodic system built from the published crystal structure. Only those atoms within this region were relaxed, while the rest of the atoms were frozen. In addition to the B1 basis set that was used for geometry optimization, the

combined SDD/6-311+G(df,p) basis set (B2) was also used for ONIOM2(B3LYP/B2:MOF-FF) single-point energy calculations. Note that the 6-31G* basis set was used for Mg in geometry optimization, while SDD was used for the other metals. However, here, the SDD effective core potential basis set was used for all metals in the single-point calculations, for fair energetic comparisons. Unless stated otherwise, the system was assumed to adopt the highest possible multiplicity, where all spin centers are coupled in a ferromagnetic (FM) fashion.

To account for the periodicity of the system, simple distance-based cutoffs were used in the computation of non-covalent interactions. The standard cutoff distances for periodic systems in TINKER were used, meaning that non-covalent interactions are evaluated only for a pair of sites within 9.0 Å radius. The cutoff distance applies for both electrostatic and vdW interactions.

Figure 4.3. Periodic model for periodic QM/MM calculations, applied using periodic boundary conditions (PBC). The unit cell and cell parameters are shown. Dashed lines indicate approximate QM/MM boundary. Color scheme: Fe, yellow; O, red; C, gray.

4.3 Results and Discussion

To verify that the periodic QM/MM scheme has been successfully implemented for periodic systems, periodic ONIOM2(QM:MM) calculations were performed on the periodic models of Fe(II)-MOF-74 and Fe(III)-MOF-74, which contain Fe(II) and Fe(III)-OH centers respectively. The initial structures were constructed from the published crystal structure of Fe-MOF-74 in the Fe(III)-OH form, modified accordingly and subsequently extended to replicate the desired periodic system.[46] The designated QM region contains approximately 85 atoms, including three Fe(II) or Fe(III)-OH sites and six partial dobdc^{4-} ligands. Final geometries obtained from periodic QM/MM optimization of both models were evaluated in comparison with the published crystal structure (Figure 4.4).

For Fe(III)-MOF-74, the QM/MM optimization gives near identical bond lengths and angles in the QM region of Fe(III)-MOF-74. Previously, periodic MM optimization for an identical system using GA-optimized MOF-FF parameters was shown to give a good level of agreement with crystal structure with a root-mean squared deviation value of 0.15 Å. In contrast, a larger deviation was observed for several Fe–O bonds in the QM region of Fe(II)-MOF-74, reflecting a very different coordination environment of the Fe(II) center compared to the Fe(III)-OH in the crystal structure (Table 4.1). Nevertheless, the optimized QM region should be able to accurately describe the coordination in the real system, as shown by the agreeable interatomic Fe(II)–Fe(II) distance between periodic QM/MM and periodic DFT optimization results.[47]

Figure 4.4. Comparison of the geometries of periodic Fe-MOF-74 models obtained from crystal structure (Fe, yellow; O, red; C, gray; H, white) and periodic MM calculations. (a) Fe(III)-OH form (Fe, orange; C, tan); (b) Fe(II) form (Fe, orange; C, blue).

Table 4.1 Structural comparison between crystal structure and periodic QM/MM optimization result of periodic model

a) Fe center		<i>QM/MM (Periodic)</i> ^[a]	
	<i>crystal</i> ^[b]	Fe(II)	Fe(III)
		bond lengths [Å]	
<i>Fe – O_{OH}</i>	1.92	-	1.85
<i>Fe – O_{Ca}</i>	2.08	1.99	2.08
<i>Fe – O_{po}'</i>	2.04	2.13	2.04
<i>Fe – O_{cb}</i>	2.01	2.05	2.05
<i>Fe – O_{po}</i>	2.04	2.14	2.01
<i>Fe – O_{Ca}'</i>	2.20	2.07	2.24
<i>Fe(III) – Fe(III)'</i>	3.16	-	3.25
<i>Fe(II) – Fe(II)'</i>	2.99 ^[c]	3.07	-
		bending angles [deg]	
<i>Fe–O_{Ca}–Fe</i>	95.2	97.0	98.4
<i>Fe–O_{po}–Fe</i>	105.9	93.4	101.8

b) dobdc⁴⁻ ligand		<i>MM (Periodic)</i>	
	<i>crystal</i> ^[a]	Fe(II)	Fe(III)
		bond lengths [Å]	
<i>C_{Ca} – O_{Ca}</i>	1.29	1.29	1.30
<i>C_{Ca} – O_{Cb}</i>	1.27	1.24	1.24
<i>C_{Ca} – C_{pc}</i>	1.49	1.49	1.49
<i>C_{po} – O_{po}</i>	1.42	1.43	1.42
<i>C_{pc} – C_{po}</i>	1.39	1.42	1.41
<i>C_{pc} – C_{ph}</i>	1.36	1.33	1.31
<i>C_{po} – C_{ph}</i>	1.40	1.39	1.40
		bending angles [deg]	
<i>O_{Ca}–C_{Ca}–O_{Cb}</i>	121.9	122.1	117.5
<i>O_{Ca}–C_{Ca}–C_{pc}</i>	119.3	113.9	115.8
<i>O_{Cb}–C_{Ca}–O_{pc}</i>	118.7	124.0	121.6
<i>C_{Ca}–C_{pc}–C_{po}</i>	123.9	127.5	125.0
<i>C_{Ca}–C_{pc}–C_{ph}</i>	117.6	116.3	117.2
<i>C_{pc}–C_{po}–O_{po}</i>	123.4	125.8	125.5
<i>C_{pc}–C_{po}–C_{ph}</i>	118.9	117.6	117.6
<i>C_{pc}–C_{ph}–C_{po}</i>	122.6	123.3	125.1
<i>C_{ph}–C_{po}–O_{po}</i>	117.7	116.6	117.0

^[a] Values in the QM region is reported. ^[b] For the Fe(III)-OH form. ^[c] Value taken from DFT-optimized geometry in Reference [47].

Having shown that the periodic QM/MM calculation scheme has been successfully implemented for structural optimization with MOF-FF parameters, in the next step the procedure was adopted to calculate binding energies between molecular oxygen and Fe-MOF-74 variants. To obtain suitable binding models of Fe-MOF-74, the optimized structure of Fe(II)-MOF-74 was modified by adding a triplet oxygen molecule at an appropriate position in the QM region. Additionally, the diluted, mixed-metal analogue of Fe-MOF-74 was constructed by substituting the terminal Fe(II) centers surrounding the oxygen binding Fe(II) site in the QM region with divalent M(II) cations ($M = \text{Mg, Ni, Zn, Co or Mn}$). Afterwards, the modified model, termed as Fe-MOF-74(M), was reoptimized using the periodic QM/MM procedure described in the previous section (Figure 4.5).

Figure 4.5. QM region of the diluted mixed-metal analogue of Fe-MOF-74 in periodic QM/MM calculations. Terminal Fe(II) centers were replaced with various metal ions.

Prior to the evaluation of the binding energy of oxygen with Fe-MOF-74(M), several aspects related to the additional modifications must be considered. Since MOF-FF is a connectivity based force-field, new atomic connectivities will have to be defined for the newly added modifications. Consequently, to enable calculations at the MM level, supplementary MM parameters must be defined for new atom types and connectivities as necessary, in a consistent manner with the formulation of MOF-FF. Firstly, non-covalent parameters for the oxygen molecule was added to the MOF-FF parameter set (Table 4.2). While covalent parameter for the O–O bond were easily obtained from DFT reference calculation on a free oxygen molecule, the determination of parameter for Fe–O₂ bond is not as obvious, partly due to the absence of an appropriate binding model. Having considered that the Fe–O₂ binding interactions is included in the QM region, as a compromise the atomic connectivity between Fe(II) and dioxygen was left undefined. As a result, the binding interaction will be treated entirely by non-covalent terms in MM calculation.

Table 4.2 Supplementary force-field parameters for adsorbed O₂

<i>Force-Field Parameters</i>		
<i>Atom Types</i>	Bond Stretches	
	$r_{i,o}$ [Å]	k_r [mdyne/Å]
O _{O2} – O _{O2}	1.210	12.890
	van der Waals Parameters	
	d_{ij}	ϵ_i [kcal/mol]
O	1.82	0.059
	Atomic Charges	
	q_i	σ_i
O _{O2}	0.000	1.118

Unlike the Fe–O₂ binding interaction, which is unique for the system and is present only in the QM region, the coordination environment around M(II) centers in the Fe-MOF-74(M) frameworks constitute a majority of bonded interactions outside of the QM region, and similar treatment with only non-bonded terms in MM calculation will likely introduce a high degree of uncertainty. Therefore, in the mixed-metal variants of MOF-74, connectivity of M(II) centers was explicitly defined. Consequently, additional covalent parameters associated with new bond, angle and dihedral connectivities of M(II) must be determined as well.

Ideally, supplementary parameters for Mg, Ni, Zn, Co and Mn must be independently determined from *ab initio* reference calculation and subsequently fitted with GA-optimizer. However, taking this approach would require a large amount of work required to completely reparametrize each Fe-MOF-74(M).[32] Therefore, instead of pursuing a complete parametrization approach, the required parameters for M(II) was taken from the corresponding optimized Fe(II) parameters. Although this approach is neither optimal nor reflect a rigorous application of the underlying theory, given that the oxygen binding energy will be evaluated mainly by QM calculations, and that these parameters are used only for two metal centers (out of the 108 metal centers contained in the periodic system), the error arising from the use of “dummy” parameters is expected to be marginal and will not affect the conclusion in a significant way. In addition, the use of subtractive QM/MM scheme means that the errors from MM parameters are cancelled out as a consequence of subtracting the result from two different types of MM calculations. As a caveat, such simplified approach is possible for the current study due to the local focus on the QM region: for the purpose of evaluating binding energy between oxygen and iron center, the other metal centers outside of the QM region will not interact strongly to the oxygen binding site since these

metal cations are separated by a long distance, and are unlikely to contribute significantly to the binding conformation of oxygen molecule. However, when similar procedure is intended to study a global feature of a periodic system, an analogous simplification may not be justified. For example, if periodic QM/MM were to be used to study diffusion processes of substrates in the pore space of MOFs, most of the metal centers will participate in the process and individually optimized parameters should be used.

For each Fe-MOF-74 analogue, the oxygen binding energy is defined as the difference in potential energy between oxygen bound and unbound states:

$$E_{\text{binding}}^{\text{B2}} = E_{\text{O}_2, \text{bound}}^{\text{QM(B2)/MM}} - (E_{\text{unbound}}^{\text{QM(B2)/MM}} + E_{\text{O}_2}^{\text{QM(B2)}}) \quad (\text{eq.3})$$

For each periodic Fe-MOF-74(M) system, two distinct optimized geometries corresponding to two different oxygen binding modes were found (Figure 4.6). In the first binding conformation, the oxygen molecule binds in a symmetric side-on manner, with the average Fe–O bond distance being 2.17 Å. The calculated O–O bond distance is 1.30 Å, which is between the DFT-calculated internuclear O–O bond distances of a free O₂ molecule and a superoxo ion (1.220 and 1.355 Å, respectively). The elongation of the internuclear O–O distance indicates a partial electron migration from the Fe(II) site to the oxygen, which was also observed experimentally in the oxygen adsorption by bare Fe-MOF-74 at low temperature.[16, 48] In the second binding coordination mode, the oxygen molecule coordinates to the Fe(II) site in an asymmetric end-on fashion. As in the side-on binding geometry, a slightly longer O–O bond was found (1.28 Å), indicating an analogous charge transfer process from the Fe(II) site. Compared to available experimental results, the largest deviation found for all bond lengths in the

first coordination sphere of our QM/MM-optimized geometries is 0.08 Å. The good agreement with experimental data indicates that the periodic QM/MM calculation scheme can reasonably describe the oxygen binding process in MOF-74.

The calculated side-on adsorption energy of oxygen in Fe-MOF-74 is 9.65 kcal/mol, which is in excellent agreement with the recent theoretical and experimental results (9.98 kcal/mol[47] and 9.80 kcal/mol,[16] respectively). A comparison of the calculated binding energies (Table 4.3) indicates that the introduction of M(II) cations generally lowers the oxygen binding strength of Fe-MOF-74(M) variants to varying degrees, by up to 3.06 kcal/mol in the case of Mn(II). Additionally, in all studied MOF-74 analogues, the side-on oxygen coordination mode was found to be energetically more favorable compared to the end-on mode, by 0.45 to 2.06 kcal/mol. This finding is consistent with the experimentally observed oxygen adsorption structure in Fe-MOF-74, which exclusively displayed a symmetric side-on adsorption geometry at low temperature.[16] The same trend was roughly reproduced when GGA-type PBE/PBE and hybrid B3LYP* functionals were used (Appendix C, Table S3, S6).

Despite the good agreement between theoretical and experimental binding energies for Fe-MOF-74, it should be noted that the theoretical values are based on potential energy, unlike enthalpy used in the experiment. In fact, inclusion of the enthalpy correction, as determined from DFT vibrational frequency calculation of the cluster model, tends to decrease the binding energy by several kcal/mol. However, the dispersion effect,[49-51] which is another key factor affecting molecular binding energies, increases the binding energy by a few kcal/mol when factored into calculation. Due to the opposing effect of these two corrections, the simple B3LYP potential energy values can give good approximations to the binding energy including enthalpy and dispersion corrections (Appendix C, Table S4-S6).

Figure 4.6. QM/MM optimized geometries. (a) Side-on and (b) end-on oxygen adsorption. (c) First coordination sphere of the Fe(II) center in the side-on and end-on oxygen adsorption geometries of Fe-MOF-74.

Table 4.3 Calculated binding and deformation energy for O₂ adsorption in Fe-MOF-74(M)

<i>M(II)</i>	<i>Binding Energy (kcal/mol)</i>		<i>Deformation Energy (kcal/mol)</i>	
	Side-On	End-On	Side-On	End-On
<i>Fe (expt)</i>	9.80	-	-	-
<i>Fe</i>	9.65	8.27	5.35	1.66
<i>Mg</i>	7.76	7.31	7.52	2.85
<i>Ni</i>	9.74	7.69	5.81	2.79
<i>Zn</i>	7.20	6.31	7.28	3.19
<i>Co</i>	8.81	7.87	6.43	2.82
<i>Mn</i>	6.59	4.53	7.76	4.23

To explain how the different neighboring metal centers affect the oxygen binding capability of Fe-MOF-74(M) analogues, the deformation of periodic MOF structures as a result of oxygen adsorption at the Fe(II) center was evaluated as deformation energy. For each variant, the deformation energy was calculated by removing the adsorbed oxygen molecule from the optimized binding structure and performing a single-point energy calculation using the ONIOM2(QM:MM) method with the B2 basis set as described above. In this way, the deformation energy can be interpreted as the destabilization of MOFs, arising from the structural distortion in the frameworks required to accommodate an oxygen molecule. The results (Table 4.3) show a reasonable correlation between the deformation and oxygen binding energies: MOF-74 analogues that have higher deformation energies tend to exhibit lower oxygen binding capability. This observation suggests that substitution of Fe(II) centers with M(II) in Fe-MOF-74 could affect the capability of the Fe(II) center to deform, lowering the energy cost of framework distortion and influencing the binding strength between Fe(II) and O₂ as a result.

Ever since the permanent porosity of MOFs were discovered in the 1990s, the structural design and synthetic strategy of frameworks has developed at an incredible pace. As a result of the continuous effort from synthetic and material chemists, presently it is possible for several MOFs to achieve a high level of performance as porous adsorbents for gas storage and separation, compared to other conventional porous materials. Nevertheless, further innovation in design is desirable to achieve an even higher efficiency.

For this purpose, it should be possible to take advantage of the tunability of MOF frameworks to introduce an interplay between multiple functionalities existing in porous structures. The preceding computational results described in this section highlighted a connection between the redox functionality of metal nodes to the structural stability and adsorption capacity of MOFs. By introducing an additional function, the cooperation between physical or chemical properties can be investigated and subsequently designed to achieve novel designs of efficient MOFs. For example: porosity, magnetism, luminescence, dynamic flexibility and optical properties are independent functions found in MOFs that have been extensively studied. Considering the paramagnetic property of oxygen, it is conceivable that the porosity and magnetism of framework material may display a cooperative behavior, resulting in an enhanced adsorption activity. Together with the atomistic scale approach to framework designs, future efforts to design novel materials may need to consider as well the controlled integration of multiple functionalities.

4.4 Conclusion

Periodic multiscale calculation scheme was implemented to perform ONIOM2(QM:MM) calculations on periodic Fe-MOF-74 systems and several other mixed-metal variants. Reparametrized MOF-FF parameters, which has been shown previously to reasonably reproduce the experimental structure of Fe-MOF-74 with periodic MM calculations, was used as MM parameters in all MM calculations. Initial QM/MM calculations on the periodic structure of Fe-MOF-74 in the Fe(II) and Fe(III)-OH form was able to accurately replicate the experimental structures with a good level of agreement, indicating that periodic ONIOM2(QM:MM) scheme has been implemented successfully for geometry optimization.

Subsequently, the protocol was implemented to evaluate O₂ binding process in the periodic system of Fe(II)-MOF-74 as well as Fe-MOF-74(M), where the terminal Fe(II) centers surrounding the oxygen binding Fe(II) was substituted with divalent cations (M = Mg, Ni, Zn, Co or Mn). To enable MM calculations in these systems, supplementary MOF-FF parameters were supplied for O₂ while “dummy” parameters were assigned for M(II) cations. The trend in binding energy was explained in terms of the different deformation energies of MOF analogues during oxygen adsorption.

Earlier computational results described in this thesis, as well as from literature highlighted the connection between a single functionality existing in MOFs and the performance of the material for practical uses. By introducing an additional function, the cooperation between physical or chemical properties can be investigated and subsequently designed to achieve novel designs of efficient MOFs. Considering the paramagnetic property of oxygen, it is conceivable that the porosity and magnetism of framework material may display a cooperative behavior, resulting in an enhanced

adsorption activity. In the future, efforts to design novel porous materials may need to consider the controlled integration of multiple functionalities.

4.5 References

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Appendix A Chapter 2

Table S1. Raw energy data for the hydroxylation of ethane by oxoiron(IV) species in Fe-MOF-74 (DFT, B3LYP/B1)

	ΔE [kcal/mol]	$\Delta(E+ZPE)$ [kcal/mol]	E [Eh]	ZPE [Eh]	E+ZPE [Eh]
3RC	9.3	10.4	-2890.147818	0.586015	-2889.561803
5RC	0.0	0.0	-2890.162721	0.584346	-2889.578375
3TS1	32.2	28.8	-2890.111445	0.579052	-2889.532393
5TS1	14.3	10.3	-2890.139936	0.578032	-2889.561904
3Int	23.7	22.3	-2890.124924	0.582070	-2889.542854
5Int	4.0	1.0	-2890.156380	0.579600	-2889.576780
3TS2	35.2	33.0	-2890.106594	0.580738	-2889.525856
5TS2	8.6	5.8	-2890.149004	0.579847	-2889.569157
3PC	-19.1	-17.5	-2890.193195	0.586976	-2889.606219
5PC	-44.5	-42.6	-2890.233672	0.587334	-2889.646338

Table S2. Bond order for UFF calculation

Atom pair	Fe-O _a	Fe-O _b	Fe-O _c	O _a -C _a	O _b -C _a	O _c -C _c	C _a -C _b	C _b -C _c	C _b -C _d	C _c -C _d
Bond order	0.5	0.5	0.5	1.5	1.5	1.0	1.0	1.5	1.5	1.5

Atom pair	C _d -H
Bond order	1.0

Table S3. Raw energy data for the hydroxylation of ethane by oxoiron(IV) species in Fe-MOF-74

(a) ONIOM(B3LYP/B1:UFF)

	ΔE [kcal/mol]	$\Delta(E+ZPE)$ [kcal/mol]	E [Eh]	ZPE [Eh]	E+ZPE [Eh]
3RC	14.2	14.4	-3386.762407	1.266493	-3385.495914
5RC	0.0	0.0	-3386.785018	1.266173	-3385.518845
3TS1	37.7	33.1	-3386.724990	1.258865	-3385.466125
5TS1	20.6	15.5	-3386.752258	1.258150	-3385.494108
3Int	28.6	25.4	-3386.739466	1.261148	-3385.478318
5Int	11.5	7.8	-3386.766735	1.260372	-3385.506363
3TS2	34.9	33.1	-3386.729403	1.263299	-3385.466104
5TS2	15.0	11.9	-3386.761134	1.261313	-3385.499821
3PC	-29.7	-27.2	-3386.832410	1.270281	-3385.562129
5PC	-55.7	-53.0	-3386.873852	1.270489	-3385.603363

(b) ONIOM(B3LYP/B2:UFF)//ONIOM(B3LYP/B1:UFF)

	ΔE [kcal/mol]	$\Delta(E+ZPE)$ [kcal/mol]	E [Eh]	ZPE [Eh]	E+ZPE [Eh]
3RC	13.5	13.7	-4527.524564	1.266493	-4526.258071
5RC	0.0	0.0	-4527.546095	1.266173	-4526.279922
3TS1	37.4	32.8	-4527.486525	1.258865	-4526.227660
5TS1	20.7	15.6	-4527.513151	1.258150	-4526.255001
3Int	25.7	22.5	-4527.505150	1.261148	-4526.244002
5Int	9.2	5.5	-4527.531481	1.260372	-4526.271109
3TS2	31.2	29.4	-4527.496440	1.263299	-4526.233141
5TS2	12.5	9.4	-4527.526222	1.261313	-4526.264909
3PC	-30.3	-27.8	-4527.594433	1.270281	-4526.324152
5PC	-55.5	-52.8	-4527.634605	1.270489	-4526.364116

Table S4. Determination of homolytic bond dissociation energies (BDE) with G4 method

	H(RH) [Eh]	H(R) [Eh]	H(H) [Eh]	BDE [kcal/mol]
ethane (C–H)	-79.733661	-79.074152	-0.49906	100.7
ethanol (C–H)	-154.928612	-154.279014	-0.49906	94.5
ethanol (O–H)	-154.928612	-154.263721	-0.49906	104.1

Table S5. ONIOM(B3LYP/B1:UFF) Mulliken group spin populations of the stationary points for the hydroxylation of ethane by oxoiron(IV) species in Fe-MOF-74

	Fe	O	C
3RC	1.35	0.78	0.00
5RC	3.33	0.47	0.00
3TS1	2.98	-0.58	-0.61
5TS1	4.13	-0.11	-0.53
3Int	2.93	-0.07	-1.07
5Int	4.19	0.34	-1.07
3TS2	2.55	0.08	-0.81
5TS2	4.12	0.31	-0.91
3PC	2.02	0.00	0.00
5PC	3.79	0.00	0.00

Table S6. Raw energy data for the oxidation of ethanol to acetaldehyde by oxoiron(IV) species in Fe-MOF-74 in quintet state

(a) ONIOM(B3LYP/B1:UFF)

	ΔE [kcal/mol]	$\Delta(E+ZPE)$ [kcal/mol]	E [Eh]	ZPE [Eh]	E+ZPE [Eh]
RC2	0.0	0.0	-3461.998700	1.271330	-3460.727370
TS1_{OH}	12.1	6.9	-3461.979350	1.262999	-3460.716351
TS1_{CH}	11.8	8.6	-3461.979836	1.266155	-3460.713681
Int_{OH}	7.9	4.8	-3461.986183	1.266487	-3460.719696
Int_{CH}	-6.3	-8.4	-3462.008803	1.268030	-3460.740773
TS2_{OH}	10.0	4.7	-3461.982815	1.262907	-3460.719908
PC2	-44.1	-44.7	-3462.068917	1.270376	-3460.798541

(b) ONIOM(B3LYP/B2:UFF)//ONIOM(B3LYP/B1:UFF)

	ΔE [kcal/mol]	$\Delta(E+ZPE)$ [kcal/mol]	E [Eh]	ZPE [Eh]	E+ZPE [Eh]
RC2	0.0	0.0	-4602.792486	1.271330	-4601.521156
TS1_{OH}	12.5	7.2	-4602.772604	1.262999	-4601.509605
TS1_{CH}	13.1	9.9	-4602.771608	1.266155	-4601.505453
Int_{OH}	8.6	5.6	-4602.778708	1.266487	-4601.512221
Int_{CH}	-8.6	-10.7	-4602.806169	1.268030	-4601.538139
TS2_{OH}	10.1	4.8	-4602.776348	1.262907	-4601.513441
PC2	-44.9	-45.5	-4602.864039	1.270376	-4601.593663

Table S7. Raw energy data for the hydroxylation of ethane by Fe(III)-OH species in Fe-MOF-74 in sextet state

(a) ONIOM(B3LYP/B1:UFF)

	ΔE [kcal/mol]	$\Delta(E+ZPE)$ [kcal/mol]	E [Eh]	ZPE [Eh]	E+ZPE [Eh]
RC'	0.0	0.0	-3387.419068	1.275964	-3386.143104
TS1'	38.7	35.6	-3387.357357	1.270999	-3386.086358
Int'	28.0	27.4	-3387.374405	1.275035	-3386.099370

(b) ONIOM(B3LYP/B2:UFF)//ONIOM(B3LYP/B1:UFF)

	ΔE [kcal/mol]	$\Delta(E+ZPE)$ [kcal/mol]	E [Eh]	ZPE [Eh]	E+ZPE [Eh]
RC'	0.0	0.0	-4528.183806	1.275964	-4526.907842
TS1'	38.0	34.9	-4528.123246	1.270999	-4526.852247
Int'	26.7	26.1	-4528.141303	1.275035	-4526.866268

Appendix B Chapter 3

Table S1. Details of GA optimization results for relevant internal coordinates of Fe(II)-MOF-74 cluster

#	Internal Coordinates	Ref. ^[a]	Opt. ^[a]	Deviation ^[a]	Deviation %
1	stretch___Fe1-O2	2.1271	2.0867	0.0403	-1.90%
2	stretch___Fe1-O5	2.0243	2.0940	-0.0697	-3.44%
3	stretch___Fe1-O8	2.0371	1.9862	0.0509	-2.50%
4	stretch___Fe1-O13	2.0278	2.0507	-0.0229	-1.13%
5	stretch___Fe1-O14	2.0963	2.0713	0.0250	-1.19%
6	stretch___O2-C15	1.2835	1.3039	-0.0204	-1.59%
7	stretch___O2-Fe64	2.0679	2.0288	0.0391	-1.89%
8	stretch___O3-C16	1.3121	1.3110	0.0011	-0.08%
9	stretch___O3-Fe65	1.9462	2.0755	-0.1293	-6.65%
10	stretch___O4-C17	1.2711	1.3106	-0.0395	-3.11%
11	stretch___O4-Fe64	2.0775	2.0663	0.0111	-0.54%
12	stretch___O5-C18	1.3098	1.3102	-0.0004	-0.03%
13	stretch___O5-Fe65	2.1502	2.0926	0.0576	-2.68%
14	stretch___O6-C15	1.2708	1.2623	0.0085	-0.67%
15	stretch___O6-Fe65	2.0296	1.9821	0.0475	-2.34%
16	stretch___O7-C16	1.2299	1.2623	-0.0324	-2.63%
17	stretch___O8-C17	1.2662	1.2628	0.0034	-0.27%
18	stretch___O9-C18	1.2412	1.2613	-0.0201	-1.62%
25	stretch___O12-C27	1.3147	1.2908	0.0239	-1.82%
26	stretch___O12-Fe64	1.9717	2.0459	-0.0742	-3.76%
27	stretch___O13-C31	1.3357	1.2874	0.0483	-3.62%
28	stretch___O13-Fe65	2.0887	2.0298	0.0589	-2.82%
29	stretch___O14-C34	1.3368	1.2879	0.0489	-3.66%
30	stretch___O14-Fe64	2.0365	2.0355	0.0009	-0.05%
31	stretch___C15-C19	1.4666	1.4777	-0.0112	-0.76%
32	stretch___C16-C23	1.5050	1.4798	0.0252	-1.67%
33	stretch___C17-C24	1.4912	1.4753	0.0158	-1.06%
34	stretch___C18-C26	1.4867	1.4767	0.0100	-0.67%
35	stretch___C19-C27	1.4336	1.4347	-0.0011	-0.08%
36	stretch___C19-C41	1.4059	1.3955	0.0103	-0.73%
37	stretch___C20-C28	1.3973	1.3994	-0.0021	-0.15%
38	stretch___C20-C39	1.3843	1.3927	-0.0084	-0.61%
39	stretch___C20-H57	1.0918	1.0826	0.0092	-0.85%
40	stretch___C21-C29	1.3938	1.4024	-0.0085	-0.61%
41	stretch___C21-C40	1.3941	1.4025	-0.0083	-0.60%
42	stretch___C21-H55	1.0895	1.0825	0.0070	-0.65%
43	stretch___C22-C30	1.3983	1.3998	-0.0015	-0.11%
44	stretch___C22-C42	1.3837	1.3934	-0.0097	-0.70%
45	stretch___C22-H59	1.0902	1.0829	0.0073	-0.67%
46	stretch___C23-C31	1.4180	1.4307	-0.0128	-0.90%
47	stretch___C23-C36	1.4028	1.3960	0.0068	-0.49%
48	stretch___C24-C32	1.3979	1.3928	0.0051	-0.36%

49	stretch__C24-C37	1.3995	1.3930	0.0065	-0.46%
50	stretch__C25-C33	1.4002	1.3997	0.0005	-0.04%
51	stretch__C25-C35	1.3813	1.3936	-0.0123	-0.89%
52	stretch__C25-H61	1.0909	1.0828	0.0081	-0.74%
53	stretch__C26-C34	1.4209	1.4277	-0.0068	-0.48%
54	stretch__C26-C38	1.4051	1.3956	0.0095	-0.68%
55	stretch__C27-C35	1.4169	1.4078	0.0091	-0.65%
56	stretch__C28-C36	1.3863	1.3951	-0.0088	-0.64%
57	stretch__C28-H56	1.0893	1.0823	0.0070	-0.64%
58	stretch__C29-C37	1.3903	1.3951	-0.0049	-0.35%
59	stretch__C29-H53	1.0892	1.0823	0.0068	-0.63%
60	stretch__C30-C38	1.3839	1.3950	-0.0111	-0.80%
61	stretch__C30-H58	1.0885	1.0827	0.0059	-0.54%
62	stretch__C31-C39	1.4105	1.4074	0.0032	-0.23%
63	stretch__C32-C40	1.3901	1.3953	-0.0052	-0.37%
64	stretch__C32-H54	1.0878	1.0997	-0.0119	-1.09%
65	stretch__C33-C41	1.3818	1.3947	-0.0129	-0.93%
66	stretch__C33-H60	1.0883	1.0827	0.0055	-0.51%
67	stretch__C34-C42	1.4103	1.4081	0.0022	-0.16%
68	stretch__C35-H43	1.0892	1.1004	-0.0112	-1.03%
69	stretch__C36-H44	1.0885	1.1002	-0.0117	-1.07%
70	stretch__C37-H45	1.0880	1.0997	-0.0116	-1.07%
71	stretch__C38-H46	1.0878	1.1005	-0.0127	-1.17%
72	stretch__C39-H47	1.0882	1.1007	-0.0125	-1.15%
73	stretch__C40-H48	1.0892	1.0823	0.0069	-0.63%
74	stretch__C41-H49	1.0880	1.1005	-0.0126	-1.16%
75	stretch__C42-H50	1.0890	1.1004	-0.0114	-1.04%
1	bend__O2-Fe1-O5	90.2030	100.0730	-9.8700	-10.94%
2	bend__O2-Fe1-O8	106.6330	103.8460	2.7863	-2.61%
3	bend__O2-Fe1-O13	89.5410	78.8020	10.7390	-11.99%
4	bend__O2-Fe1-O14	83.9210	88.3000	-4.3789	-5.22%
5	bend__O5-Fe1-O8	161.1260	154.9810	6.1454	-3.81%
6	bend__O5-Fe1-O13	91.0260	93.3200	-2.2939	-2.52%
7	bend__O5-Fe1-O14	84.4140	84.8810	-0.4668	-0.55%
8	bend__O8-Fe1-O13	97.4400	98.3720	-0.9325	-0.96%
9	bend__O8-Fe1-O14	88.8670	88.5730	0.2936	-0.33%
10	bend__O13-Fe1-O14	172.0020	166.4780	5.5244	-3.21%
11	bend__Fe1-O2-C15	133.7750	128.2440	5.5309	-4.13%
12	bend__Fe1-O2-Fe64	84.9680	85.0300	-0.0619	-0.07%
13	bend__C15-O2-Fe64	133.4600	127.5430	5.9169	-4.43%
14	bend__C16-O3-Fe65	136.3760	131.1930	5.1832	-3.80%
15	bend__C17-O4-Fe64	121.2050	120.4810	0.7234	-0.60%
16	bend__Fe1-O5-C18	137.0720	130.8000	6.2729	-4.58%
17	bend__Fe1-O5-Fe65	86.7080	82.2210	4.4873	-5.18%
18	bend__C18-O5-Fe65	128.2870	127.7800	0.5067	-0.40%
19	bend__C15-O6-Fe65	120.8850	119.1550	1.7302	-1.43%
20	bend__Fe1-O8-C17	129.0290	124.8760	4.1538	-3.22%
27	bend__C27-O12-Fe64	131.1670	127.6950	3.4723	-2.65%
28	bend__Fe1-O13-C31	132.8310	129.4900	3.3408	-2.52%

29	bend__Fe1-O13-Fe65	88.2860	84.8460	3.4398	-3.90%
30	bend__C31-O13-Fe65	127.6920	130.4570	-2.7653	-2.17%
31	bend__Fe1-O14-C34	129.7520	128.1290	1.6229	-1.25%
32	bend__Fe1-O14-Fe64	86.5580	85.2610	1.2974	-1.50%
33	bend__C34-O14-Fe64	121.3230	131.2910	-9.9684	-8.22%
34	bend__O2-C15-O6	121.3760	122.7770	-1.4015	-1.15%
35	bend__O2-C15-C19	118.1830	116.3300	1.8536	-1.57%
36	bend__O6-C15-C19	120.4360	119.5690	0.8671	-0.72%
37	bend__O3-C16-O7	122.1020	123.5050	-1.4037	-1.15%
38	bend__O3-C16-C23	118.3830	117.8690	0.5143	-0.43%
39	bend__O7-C16-C23	119.5140	118.5190	0.9949	-0.83%
40	bend__O4-C17-O8	125.2490	122.3700	2.8796	-2.30%
41	bend__O4-C17-C24	117.9950	118.5350	-0.5407	-0.46%
42	bend__O8-C17-C24	116.7520	118.7180	-1.9667	-1.68%
43	bend__O5-C18-O9	121.9300	122.9590	-1.0294	-0.84%
44	bend__O5-C18-C26	118.0890	118.4630	-0.3735	-0.32%
45	bend__O9-C18-C26	119.9800	118.3580	1.6223	-1.35%
46	bend__C15-C19-C27	122.9020	123.5750	-0.6735	-0.55%
47	bend__C15-C19-C41	117.5600	118.2060	-0.6460	-0.55%
48	bend__C27-C19-C41	119.5380	118.2150	1.3235	-1.11%
49	bend__C28-C20-C39	120.0800	119.2350	0.8452	-0.70%
50	bend__C28-C20-H57	120.5450	120.8790	-0.3338	-0.28%
51	bend__C39-C20-H57	119.3740	119.8800	-0.5053	-0.42%
52	bend__C29-C21-C40	119.9650	119.8090	0.1562	-0.13%
53	bend__C29-C21-H55	120.0390	120.0940	-0.0552	-0.05%
54	bend__C40-C21-H55	119.9960	120.0900	-0.0938	-0.08%
55	bend__C30-C22-C42	120.2470	119.2650	0.9822	-0.82%
56	bend__C30-C22-H59	120.2710	120.5990	-0.3280	-0.27%
57	bend__C42-C22-H59	119.4810	120.1360	-0.6543	-0.55%
58	bend__C16-C23-C31	125.6610	123.8390	1.8228	-1.45%
59	bend__C16-C23-C36	116.2230	118.1910	-1.9685	-1.69%
60	bend__C31-C23-C36	118.1080	117.9670	0.1414	-0.12%
61	bend__C17-C24-C32	120.6810	119.8560	0.8257	-0.68%
62	bend__C17-C24-C37	119.8840	119.9910	-0.1069	-0.09%
63	bend__C32-C24-C37	119.4220	119.0290	0.3934	-0.33%
64	bend__C33-C25-C35	120.6720	119.3610	1.3115	-1.09%
65	bend__C33-C25-H61	120.0000	120.5330	-0.5331	-0.44%
66	bend__C35-C25-H61	119.3270	120.1060	-0.7788	-0.65%
67	bend__C18-C26-C34	125.0950	123.6560	1.4392	-1.15%
68	bend__C18-C26-C38	116.3480	118.3290	-1.9804	-1.70%
69	bend__C34-C26-C38	118.5150	118.0140	0.5015	-0.42%
70	bend__O12-C27-C19	125.5830	125.0510	0.5320	-0.42%
71	bend__O12-C27-C35	117.5620	116.3150	1.2473	-1.06%
72	bend__C19-C27-C35	116.8470	118.6300	-1.7834	-1.53%
73	bend__C20-C28-C36	118.8560	119.6920	-0.8368	-0.70%
74	bend__C20-C28-H56	120.6730	120.5510	0.1223	-0.10%
75	bend__C36-C28-H56	120.4710	119.7540	0.7166	-0.59%
76	bend__C21-C29-C37	120.1030	119.5270	0.5756	-0.48%
77	bend__C21-C29-H53	120.1120	120.7010	-0.5892	-0.49%

78	bend__C37-C29-H53	119.7850	119.7650	0.0194	-0.02%
79	bend__C22-C30-C38	118.9480	119.7090	-0.7604	-0.64%
80	bend__C22-C30-H58	120.6570	120.5720	0.0842	-0.07%
81	bend__C38-C30-H58	120.3930	119.7180	0.6757	-0.56%
82	bend__O13-C31-C23	123.3120	124.8960	-1.5836	-1.28%
83	bend__O13-C31-C39	117.8080	116.3120	1.4961	-1.27%
84	bend__C23-C31-C39	118.8790	118.7920	0.0877	-0.07%
85	bend__C24-C32-C40	120.3330	120.8480	-0.5145	-0.43%
86	bend__C24-C32-H54	118.5740	117.8130	0.7609	-0.64%
87	bend__C40-C32-H54	121.0910	121.3380	-0.2470	-0.20%
88	bend__C25-C33-C41	118.6320	119.7490	-1.1177	-0.94%
89	bend__C25-C33-H60	120.7790	120.5630	0.2159	-0.18%
90	bend__C41-C33-H60	120.5900	119.6870	0.9023	-0.75%
91	bend__O14-C34-C26	124.0470	124.3540	-0.3073	-0.25%
92	bend__O14-C34-C42	117.4280	116.8850	0.5437	-0.46%
93	bend__C26-C34-C42	118.5230	118.7610	-0.2377	-0.20%
94	bend__C25-C35-C27	122.1380	121.4870	0.6505	-0.53%
95	bend__C25-C35-H43	120.9520	121.3980	-0.4461	-0.37%
96	bend__C27-C35-H43	116.9090	117.1120	-0.2026	-0.17%
97	bend__C23-C36-C28	122.6470	122.0770	0.5694	-0.46%
98	bend__C23-C36-H44	116.0120	117.2870	-1.2751	-1.10%
99	bend__C28-C36-H44	121.3410	120.6340	0.7069	-0.58%
100	bend__C24-C37-C29	120.1830	120.8540	-0.6710	-0.56%
101	bend__C24-C37-H45	118.5810	117.8340	0.7473	-0.63%
102	bend__C29-C37-H45	121.2330	121.3080	-0.0757	-0.06%
103	bend__C26-C38-C30	122.2970	121.9350	0.3613	-0.30%
104	bend__C26-C38-H46	116.6550	117.5070	-0.8523	-0.73%
105	bend__C30-C38-H46	121.0480	120.5570	0.4909	-0.41%
106	bend__C20-C39-C31	121.4210	121.4710	-0.0501	-0.04%
107	bend__C20-C39-H47	121.1070	121.3920	-0.2841	-0.23%
108	bend__C31-C39-H47	117.4700	117.1190	0.3509	-0.30%
109	bend__C21-C40-C32	119.9930	119.5830	0.4095	-0.34%
110	bend__C21-C40-H48	120.0330	120.6480	-0.6146	-0.51%
111	bend__C32-C40-H48	119.9730	119.7680	0.2058	-0.17%
112	bend__C19-C41-C33	122.1580	121.9530	0.2055	-0.17%
113	bend__C19-C41-H49	116.8920	117.6080	-0.7162	-0.61%
114	bend__C33-C41-H49	120.9490	120.4390	0.5102	-0.42%
115	bend__C22-C42-C34	121.4550	121.1270	0.3285	-0.27%
116	bend__C22-C42-H50	121.2910	121.2190	0.0719	-0.06%
117	bend__C34-C42-H50	117.2530	117.6530	-0.3996	-0.34%
118	bend__O2-Fe64-O4	107.0790	101.2380	5.8413	-5.46%
120	bend__O2-Fe64-O12	84.4630	83.8650	0.5974	-0.71%
121	bend__O2-Fe64-O14	86.9440	90.8930	-3.9484	-4.54%
123	bend__O4-Fe64-O12	119.9830	109.8020	10.1810	-8.49%
124	bend__O4-Fe64-O14	97.1770	93.9780	3.1988	-3.29%
127	bend__O12-Fe64-O14	142.7640	156.2050	-13.4418	-9.42%
128	bend__O3-Fe65-O5	111.6720	101.9570	9.7147	-8.70%
129	bend__O3-Fe65-O6	149.8130	160.8800	-11.0669	-7.39%
131	bend__O3-Fe65-O13	86.8920	84.1880	2.7033	-3.11%

132	bend___O5-Fe65-O6	98.0630	96.7860	1.2775	-1.30%
134	bend___O5-Fe65-O13	85.9830	93.9710	-7.9881	-9.29%
136	bend___O6-Fe65-O13	100.7070	98.3530	2.3536	-2.34%

^[a] Values for stretch and bend internal coordinates are given in Å and degrees, respectively.

Table S2. Details of GA optimization results for relevant internal coordinates of Fe(III)-MOF-74 cluster

#	Internal Coordinates	Ref. ^[a]	Opt. ^[a]	Deviation ^[a]	Deviation %
1	stretch___Fe1-O2	2.2848	2.1185	0.1663	-7.28%
2	stretch___Fe1-O5	2.0764	2.0887	-0.0123	-0.59%
3	stretch___Fe1-O8	2.0148	1.9864	0.0285	-1.41%
4	stretch___Fe1-O13	2.0320	2.0802	-0.0482	-2.37%
5	stretch___Fe1-O14	2.0577	2.0759	-0.0182	-0.88%
6	stretch___Fe1-O53	1.8418	1.9008	-0.0590	-3.20%
7	stretch___O2-C15	1.2905	1.3016	-0.0111	-0.86%
8	stretch___O2-Fe70	2.0503	2.0799	-0.0296	-1.44%
9	stretch___O3-C16	1.3170	1.3089	0.0081	-0.62%
10	stretch___O3-Fe71	1.9546	2.1047	-0.1501	-7.68%
11	stretch___O4-C17	1.2653	1.3099	-0.0446	-3.52%
12	stretch___O4-Fe70	2.1422	2.1064	0.0359	-1.67%
13	stretch___O5-C18	1.2991	1.3069	-0.0078	-0.60%
14	stretch___O5-Fe71	2.2596	2.1416	0.1180	-5.22%
15	stretch___O6-C15	1.2611	1.2592	0.0019	-0.15%
16	stretch___O6-Fe71	2.0983	1.9730	0.1253	-5.97%
17	stretch___O7-C16	1.2274	1.2603	-0.0329	-2.68%
18	stretch___O8-C17	1.2648	1.2601	0.0046	-0.37%
19	stretch___O9-C18	1.2449	1.2598	-0.0150	-1.20%
26	stretch___O12-C27	1.3120	1.2907	0.0212	-1.62%
27	stretch___O12-Fe70	1.9604	2.0929	-0.1326	-6.76%
28	stretch___O13-C31	1.3470	1.2892	0.0578	-4.29%
29	stretch___O13-Fe71	2.0640	2.0908	-0.0268	-1.30%
30	stretch___O14-C34	1.3369	1.2890	0.0480	-3.59%
31	stretch___O14-Fe70	2.1144	2.0664	0.0481	-2.27%
32	stretch___C15-C19	1.4757	1.4710	0.0047	-0.32%
33	stretch___C16-C23	1.5018	1.4796	0.0222	-1.48%
34	stretch___C17-C24	1.4926	1.4719	0.0207	-1.39%
35	stretch___C18-C26	1.4917	1.4800	0.0117	-0.78%
36	stretch___C19-C27	1.4298	1.4321	-0.0023	-0.16%
37	stretch___C19-C41	1.4038	1.3952	0.0086	-0.61%
38	stretch___C20-C28	1.3966	1.3992	-0.0026	-0.19%
39	stretch___C20-C39	1.3852	1.3923	-0.0071	-0.51%
40	stretch___C20-H60	1.0909	1.0820	0.0089	-0.82%
41	stretch___C21-C29	1.3940	1.4027	-0.0088	-0.63%
42	stretch___C21-C40	1.3938	1.4028	-0.0090	-0.65%
43	stretch___C21-H58	1.0894	1.0809	0.0085	-0.78%
44	stretch___C22-C30	1.3969	1.3992	-0.0023	-0.16%
45	stretch___C22-C42	1.3853	1.3927	-0.0075	-0.54%
46	stretch___C22-H62	1.0899	1.0818	0.0081	-0.75%
47	stretch___C23-C31	1.4142	1.4330	-0.0188	-1.33%
48	stretch___C23-C36	1.4004	1.3966	0.0038	-0.27%
49	stretch___C24-C32	1.3974	1.3935	0.0038	-0.27%

50	stretch__C24-C37	1.3993	1.3938	0.0054	-0.39%
51	stretch__C25-C33	1.3994	1.3995	-0.0001	-0.01%
52	stretch__C25-C35	1.3816	1.3934	-0.0119	-0.86%
53	stretch__C25-H64	1.0905	1.0818	0.0087	-0.80%
54	stretch__C26-C34	1.4190	1.4354	-0.0164	-1.15%
55	stretch__C26-C38	1.4027	1.3966	0.0062	-0.44%
56	stretch__C27-C35	1.4155	1.4081	0.0074	-0.52%
57	stretch__C28-C36	1.3870	1.3954	-0.0085	-0.61%
58	stretch__C28-H59	1.0891	1.0814	0.0077	-0.70%
59	stretch__C29-C37	1.3904	1.3960	-0.0057	-0.41%
60	stretch__C29-H56	1.0891	1.0810	0.0081	-0.74%
61	stretch__C30-C38	1.3860	1.3952	-0.0092	-0.67%
62	stretch__C30-H61	1.0884	1.0815	0.0068	-0.63%
63	stretch__C31-C39	1.4052	1.4076	-0.0023	-0.17%
64	stretch__C32-C40	1.3898	1.3960	-0.0062	-0.44%
65	stretch__C32-H57	1.0877	1.0981	-0.0104	-0.95%
66	stretch__C33-C41	1.3838	1.3948	-0.0111	-0.80%
67	stretch__C33-H63	1.0882	1.0817	0.0065	-0.60%
68	stretch__C34-C42	1.4079	1.4079	0.0000	0.00%
69	stretch__C35-H43	1.0888	1.1001	-0.0113	-1.04%
70	stretch__C36-H44	1.0884	1.0993	-0.0110	-1.01%
71	stretch__C37-H45	1.0883	1.0988	-0.0105	-0.97%
72	stretch__C38-H46	1.0876	1.0994	-0.0118	-1.09%
73	stretch__C39-H47	1.0880	1.1010	-0.0130	-1.19%
74	stretch__C40-H48	1.0891	1.0810	0.0080	-0.74%
75	stretch__C41-H49	1.0876	1.0997	-0.0121	-1.11%
76	stretch__C42-H50	1.0890	1.1005	-0.0115	-1.06%
77	stretch__O51-H66	0.9701	0.9867	-0.0165	-1.71%
78	stretch__O51-Fe70	1.8548	1.8956	-0.0408	-2.20%
79	stretch__O52-H68	0.9694	0.9844	-0.0150	-1.55%
80	stretch__O52-Fe71	1.8527	1.8994	-0.0467	-2.52%
81	stretch__O53-H69	0.9721	0.9840	-0.0120	-1.23%
1	bend__O2-Fe1-O5	77.4470	83.3760	-5.9291	-7.66%
2	bend__O2-Fe1-O8	85.0120	87.6780	-2.6656	-3.14%
3	bend__O2-Fe1-O13	80.4460	79.4440	1.0023	-1.25%
4	bend__O2-Fe1-O14	76.1260	80.8650	-4.7392	-6.23%
5	bend__O2-Fe1-O53	172.7880	174.4670	-1.6791	-0.97%
6	bend__O5-Fe1-O8	162.2560	169.7260	-7.4705	-4.60%
7	bend__O5-Fe1-O13	83.8440	90.3160	-6.4722	-7.72%
8	bend__O5-Fe1-O14	83.9540	80.8310	3.1227	-3.72%
9	bend__O5-Fe1-O53	95.3590	91.5600	3.7986	-3.98%
10	bend__O8-Fe1-O13	95.9850	93.0090	2.9753	-3.10%
11	bend__O8-Fe1-O14	89.3080	92.7940	-3.4864	-3.90%
12	bend__O8-Fe1-O53	102.1490	97.1610	4.9882	-4.88%
13	bend__O13-Fe1-O14	155.4310	159.2100	-3.7791	-2.43%
14	bend__O13-Fe1-O53	99.4510	102.8870	-3.4362	-3.46%
15	bend__O14-Fe1-O53	102.8580	96.1660	6.6916	-6.51%
16	bend__Fe1-O2-C15	132.0000	128.8840	3.1154	-2.36%
17	bend__Fe1-O2-Fe70	96.8730	95.8870	0.9861	-1.02%

18	bend__C15-O2-Fe70	122.3090	126.7970	-4.4884	-3.67%
19	bend__C16-O3-Fe71	126.0690	126.7340	-0.6646	-0.53%
20	bend__C17-O4-Fe70	127.9420	125.6300	2.3119	-1.81%
21	bend__Fe1-O5-C18	128.0260	126.9670	1.0594	-0.83%
22	bend__Fe1-O5-Fe71	94.8400	89.5370	5.3024	-5.59%
23	bend__C18-O5-Fe71	134.6900	135.7910	-1.1008	-0.82%
24	bend__C15-O6-Fe71	131.0700	121.1420	9.9286	-7.57%
25	bend__Fe1-O8-C17	133.4380	125.2010	8.2373	-6.17%
32	bend__C27-O12-Fe70	124.6930	128.4400	-3.7464	-3.00%
33	bend__Fe1-O13-C31	120.2750	121.3550	-1.0803	-0.90%
34	bend__Fe1-O13-Fe71	102.5300	91.1740	11.3558	-11.08%
35	bend__C31-O13-Fe71	119.9540	126.0750	-6.1203	-5.10%
36	bend__Fe1-O14-C34	121.1510	123.2590	-2.1076	-1.74%
37	bend__Fe1-O14-Fe70	102.2080	97.6240	4.5836	-4.48%
38	bend__C34-O14-Fe70	121.6130	126.0550	-4.4426	-3.65%
39	bend__O2-C15-O6	122.0670	122.8990	-0.8312	-0.68%
40	bend__O2-C15-C19	119.0180	115.6590	3.3590	-2.82%
41	bend__O6-C15-C19	118.8550	119.6110	-0.7559	-0.64%
42	bend__O3-C16-O7	122.3990	122.9630	-0.5638	-0.46%
43	bend__O3-C16-C23	117.3030	117.5220	-0.2192	-0.19%
44	bend__O7-C16-C23	120.2590	119.5090	0.7499	-0.62%
45	bend__O4-C17-O8	125.5200	122.4760	3.0445	-2.43%
46	bend__O4-C17-C24	118.1930	118.4230	-0.2299	-0.19%
47	bend__O8-C17-C24	116.2870	118.4180	-2.1313	-1.83%
48	bend__O5-C18-O9	122.1250	123.0540	-0.9293	-0.76%
49	bend__O5-C18-C26	118.9300	116.3960	2.5338	-2.13%
50	bend__O9-C18-C26	118.9340	119.5220	-0.5886	-0.49%
51	bend__C15-C19-C27	123.3010	123.1920	0.1091	-0.09%
52	bend__C15-C19-C41	117.4970	118.3200	-0.8230	-0.70%
53	bend__C27-C19-C41	119.1250	118.4790	0.6462	-0.54%
54	bend__C28-C20-C39	120.1010	119.3090	0.7920	-0.66%
55	bend__C28-C20-H60	120.4670	120.7750	-0.3082	-0.26%
56	bend__C39-C20-H60	119.4320	119.9020	-0.4696	-0.39%
57	bend__C29-C21-C40	119.9820	119.7820	0.2002	-0.17%
58	bend__C29-C21-H58	120.0320	120.0870	-0.0547	-0.05%
59	bend__C40-C21-H58	119.9860	120.0760	-0.0900	-0.07%
60	bend__C30-C22-C42	120.1650	119.2970	0.8681	-0.72%
61	bend__C30-C22-H62	120.3050	120.5370	-0.2312	-0.19%
62	bend__C42-C22-H62	119.5290	120.1660	-0.6374	-0.53%
63	bend__C16-C23-C31	124.8720	123.6290	1.2435	-1.00%
64	bend__C16-C23-C36	116.9030	118.3580	-1.4555	-1.25%
65	bend__C31-C23-C36	118.1890	118.0120	0.1773	-0.15%
66	bend__C17-C24-C32	120.5530	119.7990	0.7538	-0.63%
67	bend__C17-C24-C37	119.9420	119.8450	0.0973	-0.08%
68	bend__C32-C24-C37	119.5010	118.9530	0.5487	-0.46%
69	bend__C33-C25-C35	120.5230	119.3750	1.1482	-0.95%
70	bend__C33-C25-H64	120.0350	120.4520	-0.4161	-0.35%
71	bend__C35-C25-H64	119.4410	120.1740	-0.7327	-0.61%
72	bend__C18-C26-C34	124.7010	123.7560	0.9445	-0.76%

73	bend__C18-C26-C38	116.7670	118.2610	-1.4938	-1.28%
74	bend__C34-C26-C38	118.4410	117.9820	0.4591	-0.39%
75	bend__O12-C27-C19	124.4840	125.4620	-0.9778	-0.79%
76	bend__O12-C27-C35	117.9560	116.0610	1.8952	-1.61%
77	bend__C19-C27-C35	117.5600	118.4770	-0.9170	-0.78%
78	bend__C20-C28-C36	119.1270	119.8450	-0.7186	-0.60%
79	bend__C20-C28-H59	120.5450	120.3520	0.1932	-0.16%
80	bend__C36-C28-H59	120.3280	119.8000	0.5279	-0.44%
81	bend__C21-C29-C37	120.1560	119.5570	0.5995	-0.50%
82	bend__C21-C29-H56	120.0630	120.5770	-0.5145	-0.43%
83	bend__C37-C29-H56	119.7810	119.8570	-0.0765	-0.06%
84	bend__C22-C30-C38	119.1150	119.8460	-0.7315	-0.61%
85	bend__C22-C30-H61	120.5850	120.3910	0.1941	-0.16%
86	bend__C38-C30-H61	120.2950	119.7610	0.5338	-0.44%
87	bend__O13-C31-C23	123.4240	124.6470	-1.2229	-0.99%
88	bend__O13-C31-C39	117.1370	116.1690	0.9676	-0.83%
89	bend__C23-C31-C39	119.4390	119.1730	0.2658	-0.22%
90	bend__C24-C32-C40	120.3600	120.9950	-0.6351	-0.53%
91	bend__C24-C32-H57	118.7530	117.9850	0.7685	-0.65%
92	bend__C40-C32-H57	120.8830	121.0200	-0.1367	-0.11%
93	bend__C25-C33-C41	118.8340	119.7160	-0.8818	-0.74%
94	bend__C25-C33-H63	120.7280	120.4560	0.2718	-0.23%
95	bend__C41-C33-H63	120.4380	119.8280	0.6100	-0.51%
96	bend__O14-C34-C26	123.7330	125.0630	-1.3298	-1.07%
97	bend__O14-C34-C42	117.3250	115.9800	1.3452	-1.15%
98	bend__C26-C34-C42	118.8880	118.9550	-0.0662	-0.06%
99	bend__C25-C35-C27	121.7660	121.5880	0.1779	-0.15%
100	bend__C25-C35-H43	121.1640	121.1180	0.0457	-0.04%
101	bend__C27-C35-H43	117.0660	117.2940	-0.2277	-0.19%
102	bend__C23-C36-C28	122.1920	122.1270	0.0647	-0.05%
103	bend__C23-C36-H44	116.3410	117.8330	-1.4918	-1.28%
104	bend__C28-C36-H44	121.4660	120.0400	1.4254	-1.17%
105	bend__C24-C37-C29	120.0620	120.9810	-0.9183	-0.76%
106	bend__C24-C37-H45	118.6730	117.9000	0.7729	-0.65%
107	bend__C29-C37-H45	121.2650	121.1140	0.1506	-0.12%
108	bend__C26-C38-C30	122.1430	122.1040	0.0389	-0.03%
109	bend__C26-C38-H46	116.8790	117.9420	-1.0637	-0.91%
110	bend__C30-C38-H46	120.9730	119.9530	1.0197	-0.84%
111	bend__C20-C39-C31	120.9500	121.5150	-0.5649	-0.47%
112	bend__C20-C39-H47	121.5040	120.9510	0.5524	-0.45%
113	bend__C31-C39-H47	117.5460	117.5240	0.0226	-0.02%
114	bend__C21-C40-C32	119.9370	119.5860	0.3506	-0.29%
115	bend__C21-C40-H48	120.0980	120.5870	-0.4887	-0.41%
116	bend__C32-C40-H48	119.9640	119.8220	0.1428	-0.12%
117	bend__C19-C41-C33	122.1600	121.8320	0.3279	-0.27%
118	bend__C19-C41-H49	117.1510	117.9100	-0.7587	-0.65%
119	bend__C33-C41-H49	120.6880	120.2580	0.4299	-0.36%
120	bend__C22-C42-C34	121.2160	121.5020	-0.2853	-0.24%
121	bend__C22-C42-H50	121.5370	121.1750	0.3619	-0.30%

122	bend__C34-C42-H50	117.2470	117.3220	-0.0752	-0.06%
123	bend__H66-O51-Fe70	116.3500	111.0160	5.3336	-4.58%
124	bend__H68-O52-Fe71	110.0110	110.1900	-0.1787	-0.16%
125	bend__Fe1-O53-H69	111.6470	112.5950	-0.9483	-0.85%
126	bend__O2-Fe70-O4	90.1890	84.9970	5.1919	-5.76%
128	bend__O2-Fe70-O12	85.6680	81.3440	4.3234	-5.05%
129	bend__O2-Fe70-O14	80.2060	82.0100	-1.8040	-2.25%
130	bend__O2-Fe70-O51	105.4170	98.1860	7.2316	-6.86%
132	bend__O4-Fe70-O12	91.3330	88.0260	3.3071	-3.62%
133	bend__O4-Fe70-O14	84.3580	86.4060	-2.0482	-2.43%
134	bend__O4-Fe70-O51	163.6030	176.6230	-13.0202	-7.96%
138	bend__O12-Fe70-O14	165.1990	162.8420	2.3570	-1.43%
139	bend__O12-Fe70-O51	94.7760	93.5540	1.2220	-1.29%
140	bend__O14-Fe70-O51	93.2260	92.9010	0.3249	-0.35%
141	bend__O3-Fe71-O5	88.6960	86.3830	2.3131	-2.61%
142	bend__O3-Fe71-O6	168.5530	168.8640	-0.3117	-0.18%
144	bend__O3-Fe71-O13	85.0560	80.3180	4.7381	-5.57%
145	bend__O3-Fe71-O52	98.8540	93.5170	5.3371	-5.40%
146	bend__O5-Fe71-O6	81.5490	85.9360	-4.3871	-5.38%
148	bend__O5-Fe71-O13	78.6830	88.5920	-9.9096	-12.59%
149	bend__O5-Fe71-O52	172.4500	176.1870	-3.7372	-2.17%
151	bend__O6-Fe71-O13	87.1560	91.4420	-4.2856	-4.92%
152	bend__O6-Fe71-O52	90.9440	93.6120	-2.6683	-2.93%
155	bend__O13-Fe71-O52	101.8610	87.6340	14.2263	-13.97%

^[a] Values for stretch and bend internal coordinates are given in Å and degrees, respectively.

Appendix C Chapter 4

Table S1. Raw extrapolated energy data for Fe-MOF-74(M)

(a) ONIOM(B3LYP/B1:MOF-FF)

M	Geometry	E^[a] [Eh]	ΔE^[b] [kcal/mol]
Fe	Unbound	-3033.411531	0.00
	Side-On	-3183.748720	-12.92
	End-On	-3183.741176	-8.18
Mg	Unbound	-3185.856784	0.00
	Side-On	-3336.194718	-13.38
	End-On	-3336.188256	-9.33
Ni	Unbound	-3127.414472	0.00
	Side-On	-3277.755176	-15.12
	End-On	-3277.747498	-10.30
Zn	Unbound	-3239.771584	0.00
	Side-On	-3390.107605	-12.18
	End-On	-3390.101567	-8.39
Co	Unbound	-3077.230126	0.00
	Side-On	-3227.569010	-13.98
	End-On	-3227.561141	-9.04
Mn	Unbound	-2994.329905	0.00
	Side-On	-3144.664644	-11.38
	End-On	-3144.657863	-7.12
O₂	—	-150.316605	—

^[a] Extrapolated energy from ONIOM(B3LYP/B1:MOF-FF) calculations. ^[b] Binding energies were taken as the difference of energy between oxygen bound and unbound states.

(b) ONIOM(B3LYP/B2:MOF-FF)//ONIOM(B3LYP/B1:MOF-FF)

M	Geometry	E^[a] [Eh]	ΔE^[b] [kcal/mol]
Fe	Unbound	-3034.294151	0.00
	Side-On	-3184.683010	-9.65
	End-On	-3184.680818	-8.27
Mg	Unbound	-3186.744499	0.00
	Side-On	-3337.130351	-7.76
	End-On	-3337.129640	-7.31
Ni	Unbound	-3128.302609	0.00
	Side-On	-3278.691620	-9.74
	End-On	-3278.688355	-7.69
Zn	Unbound	-3240.663056	0.00
	Side-On	-3391.048023	-7.20
	End-On	-3391.046597	-6.31
Co	Unbound	-3078.117232	0.00
	Side-On	-3228.504748	-8.80
	End-On	-3228.503258	-7.87
Mn	Unbound	-2995.214066	0.00
	Side-On	-3145.598048	-6.59
	End-On	-3145.594772	-4.53
O₂	—	-150.373485	—

^[a] Extrapolated energy from ONIOM(B3LYP/B2:MOF-FF)//ONIOM(B3LYP/B1:MOF-FF) calculations. ^[b] Binding energies were taken as the difference of energy between oxygen bound and unbound states.

Table S2. Raw extrapolated energy data for the deformation energy of Fe-MOF-74(M)

ONIOM(B3LYP/B2:MOF-FF)

M	Geometry	E^[a] [Eh]	ΔE^[b] [kcal/mol]
Fe	Unbound	-3034.294151	0.00
	Side-On	-3034.285623	5.35
	End-On	-3034.291500	1.66
Mg	Unbound	-3186.744499	0.00
	Side-On	-3186.732503	7.53
	End-On	-3186.739949	2.85
Ni	Unbound	-3128.302609	0.00
	Side-On	-3128.293344	5.81
	End-On	-3128.298162	2.79
Zn	Unbound	-3240.663056	0.00
	Side-On	-3240.651446	7.29
	End-On	-3240.657964	3.20
Co	Unbound	-3078.117232	0.00
	Side-On	-3078.106987	6.43
	End-On	-3078.112735	2.82
Mn	Unbound	-2995.214066	0.00
	Side-On	-2995.201692	7.76
	End-On	-2995.207329	4.23

^[a] Extrapolated energy from ONIOM(B3LYP/B2:MOF-FF) single-point energy calculations. ^[b] Deformation energies were taken as the difference of energy between modified bound and unbound states.

Table S3. Effect of B3LYP* functional on the binding energy of Fe-MOF-74(M)
 ONIOM(B3LYP*/B2:MOF-FF)// ONIOM(B3LYP/B1:MOF-FF)

M	Geometry	E^[a] [Eh]	ΔE^[b] [kcal/mol]
Fe	Unbound	-3032.643826	0.00
	Side-On	-3182.963327	-11.44
	End-On	-3182.960753	-9.83
Mg	Unbound	-3185.003268	0.00
	Side-On	-3335.322523	-11.29
	End-On	-3335.321420	-10.59
Ni	Unbound	-3126.642632	0.00
	Side-On	-3276.965077	-13.29
	End-On	-3276.961348	-10.95
Zn	Unbound	-3238.990943	0.00
	Side-On	-3389.309184	-10.65
	End-On	-3389.307377	-9.52
Co	Unbound	-3076.460627	0.00
	Side-On	-3226.781613	-12.37
	End-On	-3226.779822	-11.25
Mn	Unbound	-2993.561722	0.00
	Side-On	-3143.878968	-10.03
	End-On	-3143.875312	-7.73
O₂	—	-150.301270	—

^[a] Extrapolated energy from ONIOM(B3LYP*/B2:MOF-FF)// ONIOM(B3LYP/B1:MOF-FF) calculations. ^[b] Binding energies were taken as the difference of energy between oxygen bound and unbound states.

Table S4. Effect of D3BJ correction on O₂ binding energy of Fe-MOF-74(M)

ONIOM(B3LYP/B2:MOF-FF)//ONIOM(B3LYP/B1:MOF-FF)

M	Geometry	E^[a] [Eh]	D3BJ^[b] [Eh]	E+D3BJ [Eh]	ΔE^[c] [kcal/mol]	Δ(E+D3BJ)^[c] [kcal/mol]
Fe	Unbound	-3034.294151	-0.240858	-3034.535009	0.00	0.00
	Side-On	-3184.683010	-0.244424	-3184.927434	-9.65	-11.67
	End-On	-3184.680818	-0.248861	-3184.929679	-8.27	-13.08
Mg	Unbound	-3186.744499	-0.234356	-3186.978854	0.00	0.00
	Side-On	-3337.130351	-0.238389	-3337.368740	-7.76	-10.08
	End-On	-3337.129640	-0.236211	-3337.365851	-7.31	-8.26
Ni	Unbound	-3128.302609	-0.238093	-3128.540702	0.00	0.00
	Side-On	-3278.691620	-0.241859	-3278.933479	-9.74	-11.89
	End-On	-3278.688355	-0.246048	-3278.934403	-7.69	-12.47
Zn	Unbound	-3240.663056	-0.235916	-3240.898972	0.00	0.00
	Side-On	-3391.048023	-0.240175	-3391.288198	-7.20	-9.66
	End-On	-3391.046597	-0.244508	-3391.291105	-6.31	-11.49
Co	Unbound	-3078.117232	-0.235592	-3078.352824	0.00	0.00
	Side-On	-3228.504748	-0.239497	-3228.744245	-8.80	-11.04
	End-On	-3228.503258	-0.243723	-3228.746982	-7.87	-12.76
Mn	Unbound	-2995.214066	-0.242172	-2995.456239	0.00	0.00
	Side-On	-3145.598048	-0.245517	-3145.843565	-6.59	-8.47
	End-On	-3145.594772	-0.249937	-3145.844709	-4.53	-9.19
O₂	—	-150.373485	-0.000344	-150.373830	—	—

^[a] Extrapolated energy from ONIOM(B3LYP/B2:MOF-FF)//ONIOM(B3LYP/B1:MOF-FF) calculations. ^[b] Dispersion energies of ONIOM optimized structures were calculated with D3 corrections and BJ potential at QM layer. ^[c] Binding energies were taken as the difference of energy between oxygen bound and unbound states.

Table S5. Effect of Enthalpy inclusion on O₂ binding energy of Fe-MOF-74(M)
B3LYP/B1

M	Geometry	H^[a] [Eh]	D3BJ^[b] [Eh]	H+D3BJ [Eh]	ΔH^[c] [kcal/mol]	Δ(H+D3BJ)^[c] [kcal/mol]
Fe	Unbound	-3003.395010	-0.240858	-3003.635868	0.00	0.00
	Side-On	-3153.716742	-0.244424	-3153.961166	-7.66	-9.68
	End-On	-3153.714762	-0.248861	-3153.963623	-6.42	-11.23
Mg	Unbound	-3155.821086	-0.234356	-3156.055442	0.00	0.00
	Side-On	-3306.147252	-0.238389	-3306.385641	-10.44	-12.76
	End-On	-3306.144709	-0.236211	-3306.380920	-8.85	-9.80
Ni	Unbound	-3097.388017	-0.238093	-3097.626110	0.00	0.00
	Side-On	-3247.711942	-0.241859	-3247.953801	-9.04	-11.19
	End-On	-3247.707160	-0.246048	-3247.953208	-6.04	-10.81
Zn	Unbound	-3209.769321	-0.235916	-3210.005237	0.00	0.00
	Side-On	-3360.082118	-0.240175	-3360.322293	-2.06	-4.51
	End-On	-3360.079912	-0.244508	-3360.324420	-0.67	-5.85
Co	Unbound	-3047.214513	-0.235592	-3047.450105	0.00	0.00
	Side-On	-3197.539766	-0.239497	-3197.779263	-9.87	-12.11
	End-On	-3197.536411	-0.243723	-3197.780134	-7.77	-12.65
Mn	Unbound	-2964.321939	-0.242172	-2964.564111	0.00	0.00
	Side-On	-3114.644156	-0.245517	-3114.889673	-7.97	-9.85
	End-On	-3114.641262	-0.249937	-3114.891199	-6.15	-10.81
O₂	—	-150.309522	-0.000344	-150.309866	—	—

^[a] Enthalpies were calculated from the full optimization of QM atoms at the B3LYP/B1 level. ^[b] Dispersion energies of DFT structures were calculated with D3 corrections and BJ potential. ^[c] Binding energies were taken as the difference of energy between oxygen bound and unbound states.

Table S6. Effect of PBEPBE functional on the binding energy of O₂ in Fe-MOF-74(M)

(a) Effect of D3BJ correction with PBEPBE functional

M	Geometry	E^[a] [Eh]	D3BJ^[b] [Eh]	E+D3BJ [Eh]	ΔE^[c] [kcal/mol]	Δ(E+D3BJ)^[c] [kcal/mol]
Fe	Unbound	-3031.192015	-0.139899	-3031.331914	0.00	0.00
	Side-On	-3181.443358	-0.142774	-3181.586132	-11.75	-13.39
	End-On	-3181.438458	-0.144943	-3181.583401	-8.68	-11.67
Mg	Unbound	-3183.378239	-0.136427	-3183.514665	0.00	0.00
	Side-On	-3333.623941	-0.139602	-3333.763543	-8.21	-10.04
	End-On	-3333.621925	-0.138355	-3333.760280	-6.95	-7.99
Ni	Unbound	-3125.201208	-0.138735	-3125.339943	0.00	0.00
	Side-On	-3275.450289	-0.141741	-3275.592030	-10.33	-12.05
	End-On	-3275.445291	-0.143780	-3275.589071	-7.20	-10.19
Zn	Unbound	-3237.540057	-0.137663	-3237.677720	0.00	0.00
	Side-On	-3387.784033	-0.140912	-3387.924946	-7.13	-9.00
	End-On	-3387.781401	-0.143039	-3387.924439	-5.48	-8.68
Co	Unbound	-3075.012673	-0.137296	-3075.149969	0.00	0.00
	Side-On	-3225.261767	-0.140349	-3225.402116	-10.34	-12.09
	End-On	-3225.258731	-0.142416	-3225.401148	-8.44	-11.48
Mn	Unbound	-2992.100158	-0.140335	-2992.240493	0.00	0.00
	Side-On	-3142.342628	-0.143078	-3142.485706	-6.18	-7.74
	End-On	-3142.338181	-0.145233	-3142.483414	-3.39	-6.30
O₂	—	-150.232615	-0.000267	-150.232882	—	—

^[a] Extrapolated energy from ONIOM(PBEPBE/B2:MOF-FF)//ONIOM (B3LYP/B1:MOF-FF) calculations. ^[b] Dispersion energies of ONIOM optimized structures were calculated with D3 corrections and BJ potential at QM layer. ^[c] Binding energies were taken as the difference of energy between oxygen bound and unbound states.

(b) Effect of Enthalpy inclusion with PBEPBE functional

M	Geometry	H^[a] [Eh]	D3BJ^[b] [Eh]	H+D3BJ [Eh]	ΔH^[c] [kcal/mol]	Δ(H+D3BJ)^[c] [kcal/mol]
Fe	Unbound	-3000.336679	-0.240858	-3000.476578	0.00	0.00
	Side-On	-3150.533389	-0.244424	-3150.676163	-16.75	-18.38
	End-On	-3150.523576	-0.248861	-3150.668519	-10.59	-13.59
Mg	Unbound	-3152.507382	-0.234356	-3152.643809	0.00	0.00
	Side-On	-3302.689561	-0.238389	-3302.829163	-7.63	-9.46
	End-On	-3302.687122	-0.236211	-3302.825477	-6.10	-7.14
Ni	Unbound	-3094.335053	-0.238093	-3094.473788	0.00	0.00
	Side-On	-3244.519187	-0.241859	-3244.660928	-8.86	-10.58
	End-On	-3244.513753	-0.246048	-3244.657533	-5.45	-8.45
Zn	Unbound	-3206.688676	-0.235916	-3206.826339	0.00	0.00
	Side-On	-3356.865719	-0.240175	-3357.006631	-4.41	-6.28
	End-On	-3356.864317	-0.244508	-3357.007356	-3.53	-6.73
Co	Unbound	-3044.154399	-0.235592	-3044.291695	0.00	0.00
	Side-On	-3194.344623	-0.239497	-3194.484972	-12.68	-14.43
	End-On	-3194.340684	-0.243723	-3194.483100	-10.21	-13.25
Mn	Unbound	-2961.250434	-0.242172	-2961.390769	0.00	0.00
	Side-On	-3111.434223	-0.245517	-3111.577301	-8.64	-10.19
	End-On	-3111.430307	-0.249937	-3111.575540	-6.18	-9.09
O₂	—	-150.170019	-0.000344	-150.170286	—	—

^[a] Enthalpies were calculated from the full optimization of QM atoms at the PBEPBE/B1 level. ^[b] Dispersion energies of DFT structures were calculated with D3 corrections and BJ potential. ^[c] Binding energies were taken as the difference of energy between oxygen bound and unbound states.

List of publications

1. Multiscale Model for a Metal-Organic Framework: High-Spin Rebound Mechanism in the Reaction of the Oxoiron(IV) Species of Fe-MOF-74
Hajime Hirao, Wilson Kwok Hung Ng, Adhitya Mangala Putra Moeljadi, Sareeya Bureekaew. *ACS Catal.*, **2015**, 5, 3287-3291.
2. Dioxygen Binding to Fe-MOF-74: Microscopic Insights from Periodic QM/MM Calculations
Adhitya Mangala Putra Moeljadi, Rochus Schmid, Hajime Hirao. *Can. J. Chem.*, **2016**. DOI: 10.1139/cjc-2016-0284

Other Publications

1. Selective photocatalytic C-C bond cleavage under ambient conditions with earth abundant vanadium complexes
Sarifuddin Gazi, Wilson Kwok Hung Ng, Rakesh Ganguly, Adhitya Mangala Putra Moeljadi, Hajime Hirao, Han Sen Soo. *Chem. Sci.*, **2015**, 6, 7130-7142.
2. Enantioselective Sulfoxidation Catalyzed by a Bisguanidium Diphosphatobisperoxo-tungstate Ion Pair
Xinyi Ye, Adhitya Mangala Putra Moeljadi, Kek Foo Chin, Hajime Hirao, Lili Zong, Choon-Hong Tan. *Angew. Chem. Int. Ed.*, **2016**, 55, 7101-7105.
3. Bisguanidium Dinuclear Oxodiperoxomolybdatesulfate Ion Pair Catalyzed Enantioselective Sulfoxidation
Lili Zong, Chao Wang, Adhitya Mangala Putra Moeljadi, Xinyi Ye, Rakesh Ganguly, Yongxin Li, Hajime Hirao, Choon-Hong Tan. *Nat. Comm.*, **2016**, 7, 13455.

List of Presentations

1. Multiscale Model for a Metal–Organic Framework: High-Spin Rebound Mechanism in the Reaction of the Oxoiron(IV) Species of Fe-MOF-74
Hajime Hirao, Wilson Kwok Hung Ng, Adhitya Mangala Putra Moeljadi, Sareeya Bureekaew. *Southeast Asia Catalysis Conference 2015 (SACC2015), Singapore, 14th–15th May 2015 (Poster).*
2. Ab Initio Parametrization and Application of Force Field for Metal–Organic Framework Fe-MOF-74
Adhitya Mangala Putra Moeljadi, Hajime Hirao. *Asian Network for Natural and Unnatural Materials IV (ANNUMIV), Singapore, 8th–10th June 2016 (Poster).*
3. Computational Insights to the Enantioselective Sulfoxidation Catalyzed by Bisguanidium Dinuclear Oxodiperoxomolbidosulfate Ion Pair
Adhitya Mangala Putra Moeljadi, Lili Zong, Chao Wang, Xinyi Ye, Hajime Hirao, Choon-Hong Tan. *The 14th International Symposium for Chinese Organic Chemists & the 11th International Symposium for Chinese Inorganic Chemists (ISCOC-ISCIC2016), Singapore, 8th–10th December 2016 (Poster).*
4. Dioxygen Binding in Fe-MOF-74: First-principles Parametrization and Application for Multiscale Studies
Adhitya Mangala Putra Moeljadi, Rochus Schmid, Hajime Hirao. *9th Singapore International Chemistry Conference (SICC9), Singapore, 11th–14th December 2016 (Poster).*

5. Dioxygen Binding in Fe-MOF-74: First-principles Parametrization and Application for Multiscale Studies

Adhitya Mangala Putra Moeljadi, Rochus Schmid, Hajime Hirao. *The 2016 International Conference for Leading and Young Materials Scientists (IC-LYMS 2016), Sanya, 27th December 2016 (Poster).*

6. Dioxygen Binding in Fe-MOF-74: First-principles Parametrization and Application for Multiscale Studies

Adhitya Mangala Putra Moeljadi, Hajime Hirao. *Collaborative Conference on Organic Synthesis, Hanoi, 15th March 2017 (Poster).*

7. Dioxygen Binding in Fe-MOF-74: First-principles Parametrization and Application for Multiscale Studies

Adhitya Mangala Putra Moeljadi, Rochus Schmid, Hajime Hirao. *Global Conference on Polymer and Composite Materials (PCM 2017), Guangzhou, 23rd–25th May 2017 (Poster).*