Overview

The ISEN booster award has enabled my research group to carry out a proof-of-concept study that metal-organic frameworks (MOFs) can be used to isolate and study highly-reactive metal-gas complexes. More specifically, we have employed a MOF to isolate a five-coordinate heme dioxygen adduct, a species that could only be observed transiently in molecular form. These results are now guiding our efforts to carry out similar studies involving metal carbon dioxide adducts.

Introduction

The current use of fossil fuels as energy sources is unsustainable, both because they are non-renewable resources, and more importantly, due to the associated rising levels of CO₂ in the atmosphere. Many different sources of alternate energy are currently under investigation, but a central challenge for all of these new technologies is the storage of energy. While battery technology is advancing rapidly, the most attractive option for the storage of intermittent energy sources, such as solar energy, would be to store the energy in the chemical bonds of a fuel. Towards this end, H₂ has been targeted as the simplest possible chemical fuel. Currently the demand for commodity H₂ primarily arises from the manufacturing of NH₃, refined oil, and CH₃OH. This demand is largely filled by steam reforming and, subsequently, the water gas shift reaction (WGSR). Steam reforming requires the heating of alkane fuel and water, resulting in the formation of H₂ and CO. Through the WGSR, these products further react with water to yield H₂ and CO₂ (Fig 1). Despite its efficient production of H₂, these processes effectively amount to a combustion of fossil fuels and still result in terminal formation of a greenhouse gas in CO₂. Among several possible carbon neutral H₂ production schemes, one that seems particularly attractive is to develop a method to catalytically reduce CO₂ back to CO. The combination of such a catalytic system with the well-established chemistry of the WGSR would provide a clean cycle for the production of H₂. Despite substantial progress toward this end, an efficient and scalable system for such catalysis has not yet been discovered. Encouragingly, it has recently been demonstrated that porphyrin iron complexes (Fig 2) act as electrocatalysts for the reduction of CO₂ to CO. The mechanism by which this reduction occurs has been proposed via electrochemical studies, but specific intermediates along the reaction pathway have not yet been isolated or thoroughly characterized. For instance, despite the proposed mechanism which involves CO₂ coordination to a metalloporphyrin center, there are currently no isolated examples of metalloporphyrin CO₂ adducts that have been structurally characterized.

Metal-organic frameworks (MOFs) are highly crystalline materials with porous channels that allow for heterogeneous catalysis, and they pose an interesting solution for the isolation and characterization of intermediates proposed for the metalloporphyrin-mediated reduction of CO₂ to CO. Indeed, we hypothesize that porphyrin iron complexes structured in a MOF will allow for stabilization of highly reactive reduced Fe species. The porosity of the MOF framework will then allow CO₂ to diffuse into the framework and bind to the Fe center, and also allow for reactivity in the gas phase, precluding potentially unwanted side-reactions that may occur in solution phase. Finally, the crystalline nature of the MOF will allow for single-crystal structural analysis of reaction products. Due to these factors, MOFs provide the ideal system for the isolation and study of reactive intermediates formed during CO₂ reduction catalysis.

![Figure 1. The steam reforming and WGSR processes, with the proposed CO₂ reduction path shown in blue.](image1)

![Figure 2. Fe porphyrin catalysts used for the electrocatalytic reduction of CO₂. Ar = C₆H₅, 2,6-(HO)₂C₆H₃, 2,6-(MeO)₂C₆H₃.](image2)
Results

Prior to pursuing metal-CO$_2$ adducts, our initial work has focused on studying the chemistry of O$_2$ with metallated forms of the recently reported Zr$^{IV}$-based MOF PCN-224$^8$ (Fig 3), owing to several key attributes. First, PCN-224 features tetracarboxyphenylporphyrin linkers between Zr$_6$O$_8$ clusters and is highly stable in aqueous conditions over a wide pH and temperature range. Additionally, we have developed a modified synthesis to give PCN-224 as large single crystals, enabling facile structural characterization by single-crystal X-ray diffraction. Furthermore, the structure of PCN-224 features large tetragonal channels with a diameter of 19 Å, which support the facile introduction of both gaseous and solution-phase substrates. Finally, metallation of PCN-224 with Fe$^{III}$, Co$^{II}$, and Ni$^{II}$ ions has already been reported,$^8$ providing an important precedent for the insertion of metal ions into the porphyrin binding pocket.

We carried out metalation of PCN-224 with Fe$^{II}$ following a procedure derived from that previously reported for molecular heme species,$^9$ employing lutidine to deprotonate the free-base porphyrin, to give PCN-224Fe$^{II}$. The crystal structure of this compound, obtained by carrying out the metallation reaction on single crystals of PCN-224, reveals the presence of a square planar Fe$^{II}$ center that resides within the N$_4$ plane of the porphyrin cavity and does not feature axial ligands (Fig 3). In addition to structural characterization, complete metallation was confirmed by a combination of Mössbauer spectroscopy and trace metals analysis.

With PCN-224Fe$^{II}$ in hand, our next steps were to study its chemistry with O$_2$.$^{10}$ Indeed, the chemistry of O$_2$ and molecular metalloporphyrin species has been of interest to scientists for decades, owing primarily to its relevance to oxygen-transporting heme metalloproteins such as hemoglobin and myoglobin.$^{11}$ However, in the absence of a protein superstructure, this chemistry has been greatly limited due to the tendency for molecular species to undergo unwanted side reactions.$^{12}$ We hypothesized that the solid-state scaffold of a MOF would enable the isolation of metal-dioxygen adducts that are not isolable in molecular species. Interestingly, PCN-224Fe$^{II}$ does not react with O$_2$ at room temperature, in stark contrast to the molecular heme models. Nevertheless, exposure of single crystals of PCN-224Fe$^{II}$ to an atmosphere of O$_2$ at −95 °C resulted in a color change from brown to dark red. Low-temperature single-crystal X-ray diffraction analysis of this product revealed a compound containing a five-coordinate porphyrin iron-dioxygen adduct, PCN-224FeO$_2$ (Fig 3). Remarkably, this is the first structurally characterized example of any five-coordinate iron-dioxygen species. Indeed, while low-temperature spectroscopic studies have suggested such a species may exist, its identity has thus far not been confirmed.$^{13,14}$ This result provides an important demonstration of the ability of MOFs to act as solid-state scaffolds for the stabilization of reactive chemical species.

Inspection of the crystal structure of PCN-224FeO$_2$ in Fig 3 reveals several important observations. First, the structure features an Fe-O distance of 1.81(1) Å and Fe-O-O angle of 126(2)$^°$. In Figure 3. Reaction of PCN-224Fe with O$_2$ at −78 °C to form PCN-224FeO$_2$. Green octahedra represent Zr atoms; orange, blue, red, and gray spheres represent Fe, N, O, and C atoms, respectively; hydrogen atoms are omitted for clarity.
addition, the O-O distance is 1.29(4) Å. This distance is in exact agreement with that of the free superoxide ion (O$_2^-$) and suggests that this species can be described as an iron(III) superoxide unit results from one-electron transfer from iron to O$_2$ upon binding. This formulation is consistent with what has been previously observed in six-coordinate porphyrin iron-oxygen species. Interestingly, PCN-224FeO$_2$ features an iron displacement from the porphyrin N$_4$ plane of 0.52(1) Å, in stark contrast to the six-coordinate species that contain iron atoms within the plane. This displacement almost certainly arises due to the absence of an axial ligand in PCN-224FeO$_2$, such that the iron center can distort out of the plane to maximize π overlap between its d$_{xz,xy}$ orbitals and O π* orbitals.

The surprising lack of reactivity of PCN-224Fe$^{II}$ with O$_2$ at room temperature prompted us to examine the thermodynamics of O$_2$ binding using gas adsorption measurements. Consistent with the reactivity described above, the O$_2$ isotherm obtained for PCN-224Fe$^{II}$ exhibits an initial sharp uptake at temperatures below 195 K (Fig 4). The slope of this uptake decreases upon warming to 226 K, and the isotherm becomes nearly linear with pressure upon warming further to 298 K. To quantify the O$_2$ binding, isotherm data at temperatures of 141, 156, 195, 226, 273, and 298 K were independently fit using a dual-site Langmuir model. These fits revealed binding enthalpies of –29(2) and –10.0(2) kJ/mol, which we assign to O$_2$ binding at the Fe centers and physisorption on the remainder of the MOF surface, respectively. Consistent with this assignment, treatment of the 141, 156, and 195 K isotherm data with the Clausius-Clapeyron equation provided an initial isosteric heat of adsorption of –34(4) kJ/mol at low coverage, which ultimately drops to a plateau of –10(2) kJ/mol at loadings greater than 0.7 mmol/g, the value expected for a 1:1 Fe:O$_2$ stoichiometry (Fig 4, inset). Note that, to our knowledge, this represents only the second measurement of O$_2$ adsorption at a coordinatively unsaturated Fe center within a MOF.

The observed O$_2$ binding enthalpy at low coverage of –34(4) kJ/mol in PCN-224Fe$^{II}$ is substantially lower than those of 63-65 kJ/mol previously reported for Fe centers in myoglobin and molecular heme complexes with axial imidazole ligands. We initially hypothesized that this difference may stem from a high-spin electronic configuration for Fe$^{III}$ in PCN-224FeO$_2$, in contrast to the low-spin configuration invariably observed in six-coordinate species. To further probe this possibility, Mössbauer spectra were collected for a pulverized crystalline sample of PCN-224Fe$^{II}$, both in the absence and presence of O$_2$. At 100 K, the spectrum of PCN-224Fe$^{II}$ in the absence of O$_2$ exhibits a quadrupole doublet with an isomer shift of $\delta = 0.580(2)$ mm/s and a quadrupole splitting of $\Delta E_Q = 1.417(6)$ mm/s, both consistent with previously reported values for four-coordinate D$_{4h}$ ferrous heme centers (Fig 5). Upon addition of 1 atm of dry O$_2$ to this sample at –78 °C, the subsequent Mössbauer spectrum at 100 K showed complete consumption of PCN-224Fe$^{II}$ and concomitant formation of primarily PCN-224FeO$_2$ with a small amount of high-spin Fe$^{III}$ impurity. PCN-224FeO$_2$ exhibits a quadrupole doublet with an isomer shift of $\delta = 0.378(2)$ mm/s and a quadrupole splitting of $\Delta E_Q = 2.24(1)$ mm/s, which can be unambiguously assigned to a low-spin ferric heme center.

Figure 4. O$_2$ adsorption data for PCN-224Fe$^{II}$ at 141, 156, 195, 226, 273, and 298 K (blue to red gradient). Circles represent data, and solid lines correspond to fits using a dual-site Langmuir model. Inset: O$_2$ isosteric heat of adsorption curve for PCN-224Fe$^{II}$ as a function of amount adsorbed.

Figure 5. Mössbauer spectra of PCN-224Fe$^{II}$ (top) and PCN-224FeO$_2$ (bottom), collected for pulverized crystalline samples at 100 K. Black crosses represent experimental data, and solid lines correspond to fits to the data.
Indeed, these parameters are very similar to those previously reported for six-coordinate heme-O$_2$ adducts, all of which are also low-spin.\textsuperscript{12} Moreover, the low-spin configuration is consistent with that suggested by a low-temperature NMR study of a five-coordinate heme-O$_2$ adduct.\textsuperscript{14} In stark contrast to previously reported six-coordinate heme-O$_2$ adducts, the spectrum of PCN-224FeO$_2$ undergoes a gradual release of O$_2$ upon warming, converting cleanly back to PCN-224Fe$^{II}$ at 250 K. This observation is consistent with the relatively weak O$_2$ binding enthalpy determined from gas adsorption analysis.

**External Funding Resulting from this Booster Award**

| Source: U. S. Army Research Office |
|----------------|----------------------------------|
| Title: DURIP: UV-Visible-Near IR Spectrophotometer for the Study of Reactive Chemical Species and Small-Molecule Reactivity in Metal-Organic Frameworks |
| Period: N/A |
| Amount: $109,279 |

| Source: U. S. Army Research Office |
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| Title: STIR: Heme-Based Metal-Organic Frameworks for the Oxidative Degradation of Chemical Warfare Agents |
| Period: 4/15/15-1/14/16 |
| Amount: $50,000 |

**Publications Resulting from this ISEN Funding**


**Invited Presentations Resulting from this ISEN Funding**

1. *ACS National Meeting* - Boston, MA, August 2015
2. *University College London* - London, United Kingdom, July 2015
3. *Telluride Science Research Center* - Telluride, CO, June 2015
5. *Loyola University Chicago* - Chicago, IL, November 2014
6. *University of California, Riverside* - Riverside, CA, October 2014
7. *Los Alamos National Laboratory* - Los Alamos, NM, September 2014

**References**