**Final Report:** Microporous Magnets for the Room Temp Separation of Oxygen from Air

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**Overview**

The ISEN booster award has enabled my research group to synthesize ligand radical-supported molecular complexes that serve as models for microporous frameworks. We have demonstrated that record magnetic coupling between paramagnetic metal ions and the azophenine radical ligand can be attained. These results are now guiding our efforts to incorporate similar metal-ligand combinations into frameworks, with the goal of employ these compounds in the magnetic extraction of dioxygen from air.

**Introduction**

The separation of oxygen from air represents a major industrial process, with 100 million tons of O\textsubscript{2} extracted from air annually.\textsuperscript{1} Moreover, this number is expected to rapidly grow, owing in large part to the need for pure O\textsubscript{2} to increase energy efficiency in both pre-\textsuperscript{2} and post-combustion\textsuperscript{3} CO\textsubscript{2} capture in coal-burning power plants. Currently, cryogenic distillation is by far the most widely used process for air separation, and it is the only process capable of high-capacity production and generation of high-purity gases.\textsuperscript{4} Despite the high performance of cryogenic distillation, an enormous amount of energy must be expended in order to reach temperatures necessary to refrigerate the air. One possible alternative to distillation is to separate the components air through porous magnetic media. Here, as the air passes through the pores of the magnet, the paramagnetic \( \mathcal{S} = 1 \) O\textsubscript{2} molecules are attracted to the pore walls, while the diamagnetic components, such as N\textsubscript{2} and argon, are repelled through the material. For magnetic air separation to be energy economical, we must first synthesize porous materials that behave as magnets at or near room temperature. Several experimental\textsuperscript{5,6} and theoretical\textsuperscript{7} studies have focused on membranes embedded with powdered neodymium\textsuperscript{5} or superparamagnetic nanoparticles,\textsuperscript{6} however this strategy suffers from a number of inherent problems, such as dilute and inhomogeneous distribution of magnetic particles, in addition to a lack of synthetic control at the atomic level.

An ideal solution would be to simply synthesize a homogenous material that is both permanently porous and magnetic at room temperature. Currently, however, no porous magnet has been shown to exhibit an ordering temperature above 219 K,\textsuperscript{8} with the vast majority ordering well below 100 K.\textsuperscript{9} These low ordering temperatures result from the fact that porous magnetic materials generally feature paramagnetic inorganic nodes connected to one another by many-atom, diamagnetic bridging ligands. As such, the paramagnetic inorganic centers can then only couple with one another through the bridging ligand via weak, indirect superexchange. Since magnetic ordering temperature is directly correlated to the strength of magnetic coupling between spin centers, the resulting compound only behaves as a magnet at low temperature. As an alternative, the use of paramagnetic organic linkers can lead to strong, direct coupling pathways between inorganic and organic units. In particular, metal-organic framework (MOF) materials are ideally suited for this challenge, as they combine the attributes of permanent porosity and facile synthetic tunability. **We are working to synthesize MOFs comprised of paramagnetic inorganic components connected to one another via redox-active organic bridging ligands.** Here, simple redox chemistry can then be carried out on the bridging ligand to give an \( \mathcal{S} = \frac{1}{2} \) radical organic unit (Fig 1). Direct through-bond interactions between inorganic and organic components will lead to extremely strong magnetic coupling and thus ordering temperatures at unprecedented high temperatures. Our initial work has focused on the synthesis and study of molecular complexes that serve as models for these magnetic MOFs.

**Results**

Our preliminary studies have focused on model complexes of bulky 2,5-diamino-1,4-diiminobenzoquinone ligands (NR\textsubscript{2}L\textsubscript{2}), wherein one NR\textsubscript{2} \textsuperscript{2+} ligand bridges two [L\textsubscript{2}M\textsuperscript{n+}] units, to give the dinuclear complex \([\text{L}\textsubscript{2}M\textsubscript{2}^\mathcal{R}_2]^{3+}\) (Scheme 1). Here, L' is a capping ligand that serves to block the formation of an extended chain. This general synthetic strategy is established, having previously been
employed in the formation of dinuclear complexes bridged by dihydroxybenzoquinone\textsuperscript{10–15} derivatives and by \textit{NRL}\textsuperscript{2,16–19} itself. Note, however, that \textit{NRL}\textsuperscript{2} has only been studied as a bridging ligand between diamagnetic metal ions or \(S = \frac{1}{2}\) Cu\textsuperscript{II} centers, with no investigations of coupling between metal and ligand radical.

Using the phenyl-substituted molecule \textit{NPhLH}\textsubscript{2}\textsuperscript{20,21} as a bridging ligand\textsuperscript{2,13,22} and tris(2-pyridylmethyl)amine (TPyA) as a capping ligand, we have synthesized the series of dinuclear complexes \([\textit{TPyA})\textit{L}^{-}\textit{M}^{2+}(\textit{NPhL}^{2-})]^{2+}\) (\(M = \text{Mn} (1), \text{Fe} (2), \text{Co} (3), \text{Ni} (4)\)) according to the synthetic procedure depicted in Scheme 1. The crystal structures of 1-4 have been determined for all complexes using single-crystal X-ray diffraction, and they are isostructural, as exemplified by complex 2 (Fig 2 upper). In the case of \(M = \text{V}, \text{Cr}, \text{Cu}, \text{and} \text{Zn}\), analogous reactions invariably produce insoluble precipitates upon introduction of \textit{NPhL}^{2-} to \([\textit{TPyA})\textit{M}^{2+}]^{2+}\). Solid-state IR studies of these products indicate the absence of TPyA and protonated amines and the presence of \textit{NPhL}^{2-}, suggesting the formation of extended solids. Work is underway both to vary capping ligand and to crystallize these insoluble products. Finally, we have observed that subtle modification of the bridging ligand aryl substituent can lead to important electronic differences in the resulting dinuclear complex. For instance, carrying out the complex forming reaction for \(M = \text{Fe}\), with the 2-methylphenyl (MePh) groups in place of phenyl groups on the bridging ligand, leads to crystallization of the complex \([\textit{TPyA})\textit{Fe}^{III}(\textit{NMePhL}^{2-})]^{5+}\) (5). The one-electron oxidation of each Fe\textsuperscript{II} center to Fe\textsuperscript{III} is unexpected, given the very similar redox potentials of 2 and 5 (Table 1). Likely, the oxidation is occurring upon crystallization and is the result of crystal-packing effects associated with the MePh substituents, which may slightly shift the redox potential and enable a spontaneous, solvent-assisted oxidation.

To assess the presence of magnetic coupling interactions in 1-5, variable-temperature dc magnetic susceptibility data (Fig 5 lower) were collected and used to construct plots of \(\chi_{M}T\) vs. \(T\), where \(\chi_{M}\) is the molar dc magnetic susceptibility and \(\chi_{M}T\) is proportional to effective magnetic moment. As expected, these data reveal only weak antiferromagnetic (1,2-5) or ferromagnetic (3) superexchange coupling in each complex, occurring between paramagnetic metal centers through the diamagnetic bridging ligand, with fits to the data giving exchange coupling constants of \(J = -1.95\) (1), \(-2.84\) (2), \(-2.59\) (4), and \(-1.01\) (5) \text{cm}^{-1} (Table 1). These values are consistent with coupling constants previously obtained for dinuclear complexes supported by substituted benzoquinonoid bridging ligands.\textsuperscript{10–15}

Cyclic voltammograms collected for 1-4 reveal a rich electrochemistry, with the complexes exhibiting up to three fully reversible redox events (Fig 3 upper; Table 1). Of particular interest is the couple found at ca. -1.65 V vs. Fe/Fe\textsuperscript{3+} for all complexes. The invariance of potential as a function of metal ion for this process suggests that it is ligand-centered, corresponding to the \textit{NPhL}^{2-}/\textit{NPhL}^{3-} couple. Accordingly, this result suggests that a \(\textit{M}^{II}(\textit{NPhL}^{3-})\) composition should be chemically accessible for all complexes. Toward this end, the Fe congener 2 was treated with one equivalent of the strong reductant (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Co (−1.91 V vs. Fe/Fe\textsuperscript{3+} in MeCN)\textsuperscript{23} in MeCN to give an intense blue solution. Subsequent diffusion of diethyl ether vapor into this solution at 3–5 °C gave crystals of the one-electron reduced complex \([\textit{TPyA})\textit{M}^{2+}(\textit{NPhL}^{3-})]^{6+}\) (6; Fig 2 lower). Close comparison of the bond lengths in 2 and 6 reveals several key features (Table 2). First, the average benzoquinone C-C distance decreases from 1.431(5) to 1.417(5) Å in moving from 2 to 6. In contrast, the average benzoquinone C-N distance increases from 1.331(4) to 1.362(4) Å. These differences reveal a net increase in C-C bond order and net decrease in C-N bond order, consistent with the additional electron occupying a molecular

![Figure 2. Reduction of 2 with (C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}Co to 6. Orange, blue, and gray ellipsoids represent Fe, N, and C atoms, respectively; H atoms are omitted for clarity. See Table 2 for bond lengths.](image)

![Figure 3. Upper: Cyclic voltammograms for 1-4 (Table 1). CV for 5 is similar to that of 2. Lower: Dc susceptibility data for 1-5. Black lines correspond to fits to the data (Table 1).](image)
In order to assess the presence of magnetic anisotropy in 6, low-temperature magnetization data were collected at selected dc fields (Fig 6, lower right). The splitting of the resulting isofield curves, along with their saturation well below the expected $M = 7 \, \mu_B$ for an $S = \frac{7}{2}$ ground state with $g = 2$, demonstrates qualitatively the presence of significant magnetic anisotropy. To quantify this effect, the data were fit using the program ANISOFIT 2.0\(^{22}\) to give parameters of $D = -8.4 \, \text{cm}^{-1}$, $|E| = 0.6 \, \text{cm}^{-1}$, and $g = 2.11$. To our knowledge, this value of $D$ is the largest yet observed in a multinuclear single-molecule magnet, surpassing a cyano-bridged Cu\(_{2}\)Fe\(_{2}\) cluster with an $S = \frac{5}{2}$ ground state and $D = -5.7 \, \text{cm}^{-1}$\(^{26}\) and likely stems from a combination of high-anisotropy high-spin Fe\(^{III}\) centers and relatively small spin ground state. This value of $D$ implies that 6 could behave as a single-molecule magnet with a maximum relaxation barrier of $U = (S(S+1)/4)|D| = 101 \, \text{cm}^{-1}$.

Following the observation of a large negative $D$, variable-frequency ac susceptibility data under zero applied dc field were collected in order to probe single-molecule magnet behavior. The frequency-dependent out-of-phase component ($\chi''$) of the ac susceptibility (Fig 5, left) demonstrates that 6 is indeed a single-molecule magnet. The corresponding Arrhenius plot of relaxation time (Fig 5, upper right) exhibits a linear region at high temperature, indicative of a thermally activated relaxation process.\(^{27}\) A fit to the data in the temperature range 5.0-6.8 K provides an effective relaxation barrier of $U_{\text{eff}} = 50(1) \, \text{cm}^{-1}$, with $\tau_0 = 2.7(2) \times 10^{-10}$ s.

In further support of this hypothesis, the average Fe-NL distance decreases from 2.110(3) to 2.074(3) Å, consistent with a stronger Fe -N interaction resulting from a more reduced bridging ligand. Moreover, these structural changes are similar to those previously observed for a ligand-centered reduction in a dinuclear dihydroxybenzoquinone complex.\(^{15}\) Finally, the average Fe-NTPyA distance changes only slightly, leading us to propose a configuration for 6 of [(TPyA)\(_2\)Fe(NPhL\(_3\))]\(^{4+}\). Mössbauer spectroscopic measurements will confirm this assignment and are underway.

Having established the ability to generate a paramagnetic bridging ligand for at least one member of the series of dinuclear complexes, we turned our attention to examining the magnetic behavior engendered through interactions between the metal centers and ligand radical in 6. The plot of $\chi_M T$ vs. $T$ (Fig 4) reveals two key pieces of information. First, the near constant value of $\chi_M T$ is close to that expected for an $S = \frac{7}{2}$ ground state ($g = 2.00$), the result of direct antiferromagnetic coupling between two high-spin Fe\(^{III}\) centers ($2 \times S = 2$) and a ligand radical ($S = \frac{1}{2}$). In addition, the lack of temperature dependence of the data above 100 K demonstrates remarkably strong magnetic coupling. Here, with increasing temperature, no decrease is observed in the data up to 300 K, indicating that the $S = \frac{7}{2}$ ground remains isolated from excited spin states to at least 300 K. In other words, the coupling between Fe centers and ligand radical is so strong that it cannot be overcome by thermal energy even at 300 K. Due to the lack of temperature dependence, it is impossible to fit the data to obtain a coupling constant $J$ in order to quantify the interaction. However, we can simulate a curve for this spin system to obtain a lower bound on the magnitude of $J \geq 900 \, \text{cm}^{-1}$ (Fig 4). This magnitude of $J$ is at least 50× larger than that observed in a similar dihydroxybenzoquinone-bridged Fe\(^{III}\)\(_2\) complex\(^{15}\) and by far the largest ever observed for a single-molecule magnet.\(^{24}\)

In order to explore the presence of magnetic anisotropy in 6, low-temperature magnetization data were collected at selected dc fields (Fig 6, lower right). The splitting of the resulting isofield curves, along with their saturation well below the expected $M = 7 \, \mu_B$ for an $S = \frac{7}{2}$ ground state with $g = 2$, demonstrates qualitatively the presence of significant magnetic anisotropy. To quantify this effect, the data were fit using the program ANISOFIT 2.0\(^{22}\) to give parameters of $D = -8.4 \, \text{cm}^{-1}$, $|E| = 0.6 \, \text{cm}^{-1}$, and $g = 2.11$. To our knowledge, this value of $D$ is the largest yet observed in a multinuclear single-molecule magnet, surpassing a cyano-bridged Cu\(_{2}\)Fe\(_{2}\) cluster with an $S = \frac{5}{2}$ ground state and $D = -5.7 \, \text{cm}^{-1}$\(^{26}\) and likely stems from a combination of high-anisotropy high-spin Fe\(^{III}\) centers and relatively small spin ground state. This value of $D$ implies that 6 could behave as a single-molecule magnet with a maximum relaxation barrier of $U = (S(S+1)/4)|D| = 101 \, \text{cm}^{-1}$.

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Considering the value of $D = -8.4$ cm$^{-1}$ obtained from magnetization data, this relaxation barrier is in exact agreement with the energetic separation between ground $M_S = \frac{7}{2}$ levels and first-excited $M_S = \frac{5}{2}$ levels, given as $6|D| = 51$ cm$^{-1}$. This observation suggests that thermally assisted quantum tunneling between $M_S = \pm \frac{5}{2}$ levels acts as the dominant relaxation pathway for 6 in this temperature range. As temperature is further decreased, the data begin to deviate from linearity, denoting the presence of additional fast relaxation processes, such as quantum tunneling and/or spin-spin relaxation, that shortcut the barrier.

External Funding Resulting from this ISEN Funding
Source: National Science Foundation
Title: CAREER: Synthesis and Studies of One-Dimensional Magnets Supported by Bulky, Redox-Active Benzoquinonoid Bridging Ligands (DMR-1351959)
Role: PI
Period: 3/1/14-2/28/19
Amount: $575,000

Publications Resulting from this ISEN Funding

Invited Presentations Resulting from this ISEN Funding
(1) Missouri University of Science and Technology - Rolla, MO, October 2013
(2) ACS “New Trends in Molecular Magnetic Materials” Symposium - Indianapolis, IN, September 2013
(3) National High Magnetic Field Laboratory - Tallahassee, FL, August 2013

Notes and References