

An Azophenine Radical-Bridged Fe₂ Single-Molecule Magnet with Record Magnetic Exchange Coupling

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S Supporting Information

ABSTRACT: One-electron reduction of the complex [(TPyA)₂Fe^{II}₂(^{NPh}L²⁻)]²⁺ (TPyA = tris(2-pyridylmethyl)-amine, ^{NPh}LH₂ = azophenine = N,N',N'',N'''-tetraphenyl-2,5-diamino-1,4-diminobenzoquinone) affords the complex [(TPyA)₂Fe^{II}₂(^{NPh}L^{3-•})]⁺. X-ray diffraction and Mössbauer spectroscopy confirm that the reduction occurs on ^{NPh}L²⁻ to give an *S* = 1/2 radical bridging ligand. Dc magnetic susceptibility measurements demonstrate the presence of extremely strong direct antiferromagnetic exchange between *S* = 2 Fe^{II} centers and ^{NPh}L^{3-•} in the reduced complex, giving an *S* = 7/2 ground state with an estimated coupling constant magnitude of $|J| \geq 900 \text{ cm}^{-1}$. Mössbauer spectroscopy and ac magnetic susceptibility reveal that this complex behaves as a single-molecule magnet with a spin relaxation barrier of $U_{\text{eff}} = 50(1) \text{ cm}^{-1}$. To our knowledge, this complex exhibits by far the strongest magnetic exchange coupling ever to be observed in a single-molecule magnet.

Over the past two decades, a number of molecules, known as single-molecule magnets, have been shown to retain a net magnetization upon removal of an applied magnetic field, similar to the behavior exhibited by classical permanent magnets.¹ This slow magnetic relaxation arises due to a uniaxial magnetic anisotropy, quantified by the axial zero-field splitting parameter (*D*), which breaks the degeneracy of the *M_S* levels comprising the spin ground state (*S*) of the molecule. The discovery of single-molecule magnets has generated much interest and excitement, as these species could find use in applications such as high-density spin-based information storage and processing,² quantum computing,³ and spintronics.⁴

With the goal of maximizing the relaxation barrier (U_{eff}) in single-molecule magnets, a tremendous research effort has focused on synthesizing molecules with large values of both *S* and *D*. However, as values of U_{eff} continue to climb, a third critical parameter must also be considered: the strength of magnetic exchange between paramagnetic centers, which is quantified by the exchange coupling constant *J*. Indeed, the separation between spin ground state and excited states is directly correlated to the magnitude of *J*. When *J* is insufficiently large, low-lying spin excited states enable fast relaxation pathways that can shortcut the overall thermal barrier. As such, the development of single-molecule magnets with large values of *J* represents an important challenge. Nevertheless, the vast majority of single-molecule magnets feature multiple paramagnetic metal centers coupled to

one another only weakly through diamagnetic bridging ligands via a superexchange mechanism. As an alternative, incorporation of a paramagnetic bridging ligand between metal centers enables strong direct metal-radical exchange and thus much larger values of *J*. Despite this potential, very few single-molecule magnets have incorporated radical bridging ligands.^{1h,5,6}

Benzoquinonoid bridging ligands offer an ideal platform for the construction of radical-bridged single-molecule magnets with strong magnetic coupling, as these ligands readily undergo redox chemistry to form both diamagnetic and paramagnetic electron-transfer isomers (see Figure 1). Indeed, a number of dinuclear complexes featuring a radical form of 1,2,4,5-tetraoxolene (^OLH₂) and its derivatives have been shown to exhibit strong metal-radical interactions,⁷ in some cases so strong that the spin ground state remains isolated from excited states even at 300 K.⁸ As an extension, a radical form of the related azophenine (^{NR}LH₂) should afford even stronger coupling, owing to the more diffuse orbitals of nitrogen compared to oxygen. In support of this hypothesis, *J* has been shown to increase by 32-fold in moving from a tetraoxolene to an azophenine bridge in Cu₂ complexes.⁹ Moreover, a value of $J = -946 \text{ cm}^{-1}$ ($\hat{H} = -2J(\hat{S}_A \cdot \hat{S}_B)$) has been calculated using DFT for a mononuclear nickel(II) bis(*o*-phenylenediamine radical) complex.¹⁰ Providing an additional advantage over tetraoxolene analogues, derivatives of ^{NR}LH₂ with bulky aryl substituents (*R*) bound to the nitrogen donors can be readily synthesized through palladium-catalyzed cross-coupling reactions, thereby enabling fine control over intermolecular metal-metal separation in complexes.¹¹ Herein, we report the synthesis and magnetic analysis of an azophenine radical-bridged Fe₂ complex that, to the best of our knowledge, exhibits by far the strongest magnetic exchange coupling yet observed in a single-molecule magnet.

Reaction of anhydrous Fe(SO₃CF₃)₂ with TPyA in MeCN, followed by treatment with a mixture of ^{NPh}LH₂ and Li[N(SiMe₃)₂], afforded a dark-brown solution.¹² Subsequent diffusion of diethyl ether vapor into this solution yielded dark-yellow, needle-shaped crystals of [(TPyA)₂Fe^{II}₂(^{NPh}L²⁻)](SO₃CF₃)₂ · 2 MeCN (**1**). The structure of [(TPyA)₂Fe^{II}₂(^{NPh}L²⁻)]²⁺ (see Figure 2, upper) consists of two crystallographically equivalent [(TPyA)Fe^{II}]²⁺ units connected by a deprotonated ^{NPh}L²⁻ bridging ligand. Each Fe^{II} center resides in a distorted octahedral coordination environment, with two cis-disposed sites occupied by neighboring nitrogen donor atoms from ^{NPh}L²⁻ and the other four bound by nitrogen atoms

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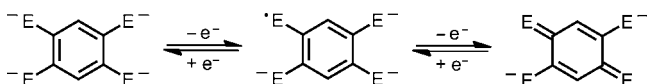


Figure 1. Redox series of deprotonated benzoquinonoid ligands. Left to right: ${}^{\ominus}L^{4-}$, ${}^{\ominus}L^{3-\bullet}$, ${}^{\oplus}L^{2-}$ ($E = O$ and NR).

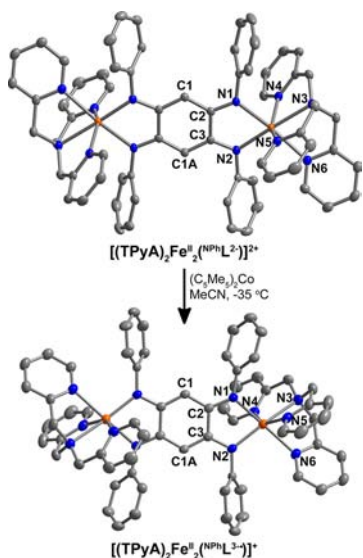


Figure 2. Reduction of $[(TPyA)_2Fe^{II}_2(N^{Ph}L^{2-})]^{2+}$ (upper) to give $[(TPyA)_2Fe^{II}_2(N^{Ph}L^{3-\bullet})]^+$ (lower). Orange, blue, and gray ellipsoids, shown at the 50% probability level, represent Fe, N, and C atoms, respectively; H atoms are omitted for clarity.

from the TPyA capping ligand. The average Fe–N distance of 2.110(3) Å is consistent with a high-spin $S = 2$ electronic configuration. The complex features an intramolecular Fe...Fe distance of 8.154(1) Å and a closest intermolecular Fe...Fe distance of 9.999(1) Å.

The cyclic voltammogram of an acetonitrile solution containing **1**, shown in Figure 3, reveals the presence of three reversible redox processes, centered at +0.32, –0.19, and –1.65 V vs $[Cp_2Fe]^{0/1+}$. Considering precedent in tetraoxolene-bridged Fe_2 complexes, we tentatively assign the first two processes to metal-centered events and the third process to a ligand-based event.^{7,8,13} Indeed, the process at –1.65 V suggests that a $[(TPyA)_2Fe_2(N^{Ph}L)]^+$ complex should be chemically accessible. Toward that end, a solution of **1** in DMF was treated at –35 °C with the strong reductant $Na(C_{10}H_8)$ ¹⁴ to give an intense blue solution.¹² Subsequent addition of diethyl ether into

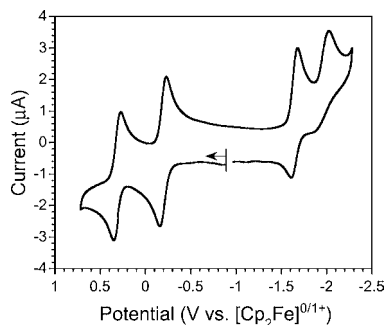


Figure 3. Cyclic voltammogram obtained for an acetonitrile solution of **1** using a platinum electrode, 50 mV/s scan rate, and 0.1 M $(Bu_4N)PF_6$ supporting electrolyte.

this solution at –35 °C afforded the one-electron-reduced compound $[(TPyA)_2Fe_2(N^{Ph}L)](SO_3CF_3) \cdot 3DMF \cdot 0.3Na(SO_3CF_3)$ (**2**) as a dark-blue microcrystalline powder in 79% yield. Alternatively, carrying out the above reaction in MeCN using the reductant $(C_5Me_5)_2Co$,¹⁵ followed by diffusion of diethyl ether vapor into the resulting solution at –35 °C, yielded a product mixture containing crystals of **1** and dark-blue, plate-shaped crystals of $[(TPyA)_2Fe_2(N^{Ph}L)](SO_3CF_3) \cdot 6MeCN$ (**2'**; see Figure 2, lower).

While the cationic complex in **2'** exhibits an overall structure similar to that in **1**, close comparison of the bond lengths in the two complexes reveals several key features (see Table 1). First, the average benzoquinone C–C distance decreases slightly by 0.9%, from 1.431(5) to 1.418(5) Å in moving from **1** to **2'**, while the average benzoquinone C–N distance increases by 2.3%, from 1.331(4) to 1.361(4) Å. These differences highlight a net increase in C–C bond order and net decrease in C–N bond order, consistent with the additional electron occupying a molecular orbital of primarily ligand character. In further support of this inference, the average Fe– N_L distance decreases by 1.8%, from 2.110(3) to 2.073(3) Å, consistent with a stronger Fe–N interaction resulting from a trianionic bridging ligand. These structural changes are similar to those previously observed for a ligand-centered reduction in a chloranilate radical-bridged Co_2 complex.^{7bc} Finally, the average Fe– N_{TPyA} distance changes only slightly, increasing from 2.233(3) to 2.249(3) Å (0.7%), supporting a ligand-centered redox event. Taken together, these observations suggest a configuration for the complex in **2** and **2'** of $[(TPyA)_2Fe^{II}_2(N^{Ph}L^{3-\bullet})]^+$. To our knowledge, **2'** represents the first structurally characterized example of a molecule incorporating a radical bridging ligand derived from azophenine.

In order to confirm the assignment of a primarily ligand-based reduction, Mössbauer spectra were collected for **1** and **2**. The Mössbauer spectrum collected on a solid sample of **1** at 77 K (see Figure 4, left) exhibits a major symmetric quadrupole doublet and a second minor doublet assigned to a small amount of Fe^{III} -containing impurity. A fit to the data provides an isomer shift of $\delta = 1.027(3)$ mm/s and a quadrupole splitting of $\Delta E_Q = 2.775(5)$ mm/s for the major doublet, consistent with two equivalent high-spin Fe^{II} ions. The spectrum of **2** exhibits a similar quadrupole doublet, with an identical isomer shift of $\delta = 1.024(4)$ mm/s and a considerably larger quadrupole splitting of $\Delta E_Q = 3.119(7)$ mm/s. The identical isomer shifts in **1** and **2** provide strong evidence that the reduction is indeed ligand centered, and the larger quadrupole splitting in **2** may stem from the change in ligand field at the Fe^{II} center associated with ligand reduction and the greater distortion from an octahedral coordination environment at iron in **2** compared to **1**. Finally, as temperature is

Table 1. Selected Bond Distances (Å) in **1** and **2'**^a

	1	2'		1	2'
C1–C2	1.410(5)	1.411(5)	Fe–N1	2.142(3)	2.103(3)
C2–C3	1.498(5)	1.461(6)	Fe–N2	2.078(2)	2.042(3)
C3–C1A	1.385(4)	1.381(4)	Fe–N_L	2.110(3)	2.073(3)
C–C	1.431(5)	1.418(5)	Fe–N3	2.297(2)	2.278(3)
N1–C2	1.318(4)	1.350(4)	Fe–N4	2.172(3)	2.314(3)
N2–C3	1.344(4)	1.372(4)	Fe–N5	2.159(3)	2.177(4)
N–C	1.331(4)	1.361(4)	Fe–N6	2.305(3)	2.226(3)
			Fe–N_{TPyA}	2.233(3)	2.249(3)

^aAverage distances are shown in bold.

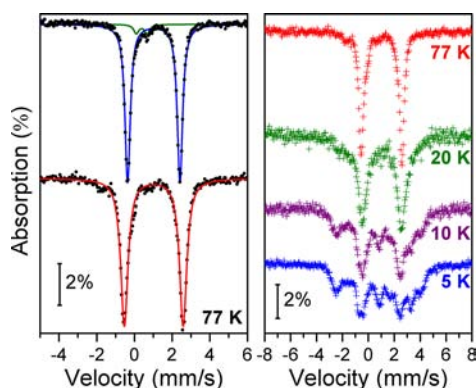


Figure 4. Left: Zero-field ^{57}Fe Mössbauer spectra for **1** (upper) and **2** (lower), collected at 77 K. Black circles correspond to experimental data, and solid lines correspond to fits of the data. Right: Variable-temperature spectra for **2**, revealing the onset of slow magnetic relaxation with lowering temperature.

decreased, the doublet in **2** undergoes spectral broadening, ultimately reaching an unresolved multiplet at 5 K (see Figure 4, right). This phenomenon indicates the onset of slow magnetic relaxation with decreasing temperature, suggesting that **2** exhibits single-molecule magnet behavior at low temperature on the Mössbauer time scale.^{16,17}

To probe and compare magnetic interactions in **1** and **2**, variable-temperature dc magnetic susceptibility data were collected for solid samples under an applied field of 1000 Oe. The resulting plot of $\chi_M T$ vs T for **1** is shown in Figure 5. At 300 K, $\chi_M T = 6.38 \text{ cm}^3 \text{ K/mol}$, corresponding to two magnetically isolated high-spin Fe^{II} centers with $g = 2.06$. As temperature is decreased, the data undergo a gradual then rapid decline, reaching a minimum value of $0.14 \text{ cm}^3 \text{ K/mol}$ at 2 K that corresponds to an $S = 0$ ground state. The decrease in $\chi_M T$ with decreasing temperature is indicative of weak antiferromagnetic superexchange coupling between high-spin Fe^{II} centers through the diamagnetic $^{\text{NPh}}\text{L}^{2-}$ ligand. To quantify this interaction, the data were fit to the Van Vleck equation according to the spin Hamiltonian $\hat{H} = -2J(\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Fe2}})$ to give an exchange constant of $J = -2.90(2) \text{ cm}^{-1}$.¹⁸

The plot of $\chi_M T$ vs T obtained for **2** (see Figure 5) shows a dramatically different profile than that for **1**. At 300 K, $\chi_M T = 8.84 \text{ cm}^3 \text{ K/mol}$, much higher than the value expected for two

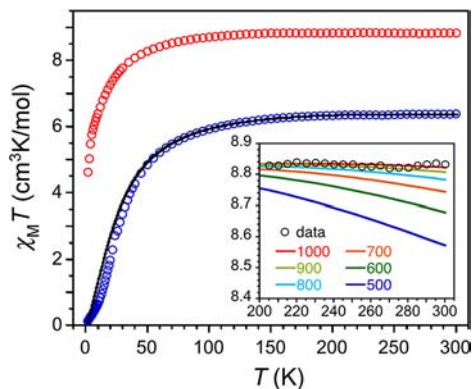


Figure 5. Variable-temperature dc magnetic susceptibility data for **1** (blue) and **2** (red), collected under an applied field of 1000 Oe. The black line corresponds to a fit of the data. Inset: Expanded view of data for **2**; lines correspond to simulations with selected values of $-J$ (cm^{-1}).

magnetically isolated $S = 2 \text{ Fe}^{\text{II}}$ centers and one $S = 1/2 \text{ }^{\text{NPh}}\text{L}^{3-\bullet}$. Instead, this value is in agreement with an $S = 7/2$ ground state ($g = 2.12$) resulting from exceptionally strong antiferromagnetic exchange between Fe^{II} centers and $^{\text{NPh}}\text{L}^{3-\bullet}$ radical. Indeed, the invariance of $\chi_M T$ in the temperature range 130–300 K indicates that the $S = 7/2$ ground state remains well isolated from excited states even up to 300 K. While the temperature independence of $\chi_M T$ precludes a definitive quantitation of J , a lower bound of the magnitude can be estimated. The inset of Figure 5 shows an expanded view of the high-temperature data, along with simulations of the data for selected values of J according to the spin Hamiltonian $\hat{H} = -2J[\hat{S}_{\text{rad}} \cdot (\hat{S}_{\text{Fe1}} + \hat{S}_{\text{Fe2}})]$.¹⁹ These simulations provide a value of $J \leq -900 \text{ cm}^{-1}$ for **2**. This value should be regarded as an estimate, as subtle changes to the diamagnetic correction of the data and/or introduction of additional parameters to the simulation, such as zero-field splitting or intra/intermolecular $\text{Fe} \cdots \text{Fe}$ interactions, can lead to significant variation of J . Nevertheless, this estimated magnitude of J is nearly 50 \times larger than the $J = +19 \text{ cm}^{-1}$ observed in a chloranilate radical-bridged Fe^{II}_2 complex with ferromagnetic metal-ligand radical exchange.^{7c} Most importantly, to the best of our knowledge, this value is by far the largest ever observed in a single-molecule magnet, eclipsing the previous record of $J = -133 \text{ cm}^{-1}$, held by a recently reported nindigo radical-bridged Co^{II}_2 complex.^{6b} Finally, we note that a similar energy separation from excited states has been observed for the $S = 9/2$ ground state of a mixed-valence $[\text{Fe}_2]^{\text{V}}$ complex, however this behavior arises through a double-exchange mechanism due to electron delocalization.¹⁷

In order to assess the presence of magnetic anisotropy in **2**, low-temperature magnetization data were collected at selected dc fields (see Figure 6, lower right). The splitting of the resulting isofield curves, along with their saturation well below the expected $M = 7 \mu_B$ for an $S = 7/2$ 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^{20,21} 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 $\text{Cu}^{\text{II}}_3\text{Fe}^{\text{III}}_2$ cluster with an $S = 5/2$ ground state and $D = -5.7 \text{ cm}^{-1}$,²² and likely stems from a combination of high-anisotropy high-spin Fe^{II} centers and relatively small spin ground state. This value of D

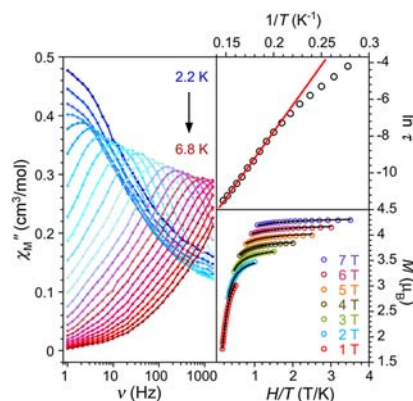


Figure 6. Left: Variable-frequency ac susceptibility data for **2**. Upper right: Arrhenius plot of relaxation time, with $U_{\text{eff}} = 50(1) \text{ cm}^{-1}$. Lower right: Low-temperature magnetization data for **2** at selected fields.

implies that **2** could behave as a single-molecule magnet with a maximum relaxation barrier of $U = (S^2 - 1/4)|D| = 101 \text{ cm}^{-1}$.

Following the observation of slow magnetic relaxation from variable-temperature Mössbauer spectroscopy and presence of a large negative D , variable-frequency ac susceptibility data under zero applied dc field were collected in order to further probe single-molecule magnet behavior. The frequency-dependent out-of-phase component (χ_M'') of the ac susceptibility (see Figure 6, left) demonstrates that **2** is indeed a single-molecule magnet. The corresponding Arrhenius plot of relaxation time (see Figure 6, upper right) exhibits a linear region at high temperature, indicative of a thermally activated relaxation process (see SI). A fit to the data in the temperature range 5.0–6.8 K provides a relaxation barrier of $U_{\text{eff}} = 50(1) \text{ cm}^{-1}$, with $\tau_0 = 2.7(2) \times 10^{-10} \text{ s}$. Considering the value of $D = -8.4 \text{ cm}^{-1}$ obtained from magnetization data, this relaxation barrier is in exact agreement with the energetic separation between ground $M_S = 7/2$ levels and first-excited $M_S = 5/2$ levels, given as $6|D| = 51 \text{ cm}^{-1}$. This observation suggests that thermally assisted quantum tunneling between $M_S = \pm 5/2$ levels acts as the dominant relaxation pathway for **2** 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.

The foregoing results demonstrate that a radical form of azophenine can be employed as a bridging ligand to synthesize single-molecule magnets with magnetic exchange coupling of unprecedented strength. Indeed, the one-electron reduction of a $[\text{Fe}^{\text{II}}_2(\text{N}^{\text{Ph}}\text{L}^{2-})]^{2+}$ complex gives a $[\text{Fe}^{\text{II}}_2(\text{N}^{\text{Ph}}\text{L}^{3-\bullet})]^+$ complex that behaves as a single-molecule magnet with a spin ground state of $S = 7/2$ and a relaxation barrier of $U_{\text{eff}} = 50(1) \text{ cm}^{-1}$. The metal-ligand radical exchange coupling in this complex, with an estimated magnitude of $|J| \geq 900 \text{ cm}^{-1}$, is to our knowledge by far the strongest magnetic exchange yet observed in a single-molecule magnet. Work is underway to incorporate metal centers with stronger magnetic anisotropy and more radially diffuse d-orbitals to this system, append substituents onto $\text{N}^{\text{Ph}}\text{LH}_2$ in order to modulate ligand-centered redox processes, and synthesize related bridging ligands with even more diffuse donor atom orbitals.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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