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Design and Synthesis of High-Performance Lanthanide-Based
Single-Molecule Magnets

By

Colin A. Gould

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Jeffrey R. Long, Chair
Professor Robert G. Bergman
Professor Michael F. Crommie

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Abstract

Design and Synthesis of High-Performance Lanthanide-Based Single-Molecule Magnets

By

Colin A. Gould

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Jeffrey R. Long, Chair

This dissertation describes the synthesis and characterization of various lanthanide-based single-molecule magnets. Analysis of these compounds reveals design strategies to increase the operating temperature of molecular magnets. In particular, methods to minimize deleterious through-barrier magnetic relaxation pathways in metallocenes and radical-bridged complexes are outlined. This dissertation also investigates rare electronic structures that arise in lanthanide-based single-molecule magnets through the lens of fundamental chemistry principles, such as aromaticity and Hund's rules.

Chapter 1 provides a general introduction to single-molecule magnet research and the electronic structure of lanthanide complexes. Key figures of merit are defined, and factors that control the magnetic properties of a single-molecule magnet are outlined. In particular, the importance of mitigating deleterious through-barrier relaxation pathways to enable higher operating temperatures is discussed, and progress towards this goal in metallocenes and radical-bridged complexes is highlighted.

Chapter 2 describes the synthesis of the first trinuclear lanthanide single-molecule magnet. Magnetic characterization of this species and comparison with analogous dinuclear compounds demonstrates that increased nuclearity does not result in enhanced single-molecule magnet performance. Instead, the strength of magnetic exchange coupling is shown to control the operating temperature.

Chapter 3 describes the synthesis of a series of radical-bridged dilanthanide complexes. Variation of the substituent on the organic radical bridging ligand tunes the strength of magnetic exchange coupling interactions in these compounds, which in turn impacts the rate of magnetic relaxation. An empirical correlation is derived from the magnetic properties of this series which can be used to guide the synthesis of radical-bridged dysprosium complexes with higher operating temperatures.

Chapter 4 describes the synthesis of a novel binucleating ligand which binds one lanthanide ion on each face of a central benzene dianion diradical. Magnetic susceptibility measurements reveal the strongest magnetic exchange coupling yet observed between a lanthanide ion and a bridging ligand. In addition, structural and computational analysis reveal Baird aromaticity, a reversal of Hückel's rule that has been predicted for molecules with $4n$ π -electrons in the triplet state.

Chapter 5 describes the synthesis of a series of dysprosium metallocenium cation salts. Variation of the substituents on the cyclopentadienyl ligands results in substantial changes to

molecular structure, which in turn impact magnetic relaxation. Magneto-structural correlations are derived to guide the synthesis of dysprosium metallocenium cation salts with higher operating temperatures.

Chapter 6 describes the synthesis of divalent lanthanide metallocenes. Magnetic characterization of these compounds demonstrates that lanthanide reduction enhances the operating temperature for terbium and diminishes it for dysprosium. Electronic structure analysis reveals $j-j$ coupling, a deviation from Hund's rules that has only yet been reported for lanthanide ions in the gas phase.

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Chapter 1: Lanthanide-Based Single-Molecule Magnets

1.1 Applications of Single-Molecule Magnet Research

Magnetism is integral to modern society, facilitating diverse technologies that range from entertainment to healthcare. Indeed, loudspeakers, credit cards, electric motors, wind turbines, compasses, solid-state hard drives in computers, and a variety of medical devices, including magnetic resonance imaging (MRI) scanners, all rely on magnetic interactions.¹ The invention of these devices was enabled by a fundamental understanding of magnetism, developed through scientific research that began as early as 585 B.C. and which continues to thrive today.^{1a}

One important thrust of contemporary magnetism research focuses on molecules that possess a bistable magnetic ground state, termed single-molecule magnets.² Such molecules show potential as nanoscale information storage or spintronics devices, and they could revolutionize computers, if sufficient operating temperatures are achieved.³ For example, the single-molecule magnet TbPc₂ (Pc = phthalocyanine) can be utilized as an electrically-controlled nuclear spin qubit, the basic unit of information in a quantum computer.^{3a}

Research on single-molecule magnets can also reveal design principles to guide the synthesis of novel bulk magnetic materials.⁴ For instance, studies on the single-molecule magnet $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]^-$ demonstrate that a linear coordination geometry can engender high single-ion magnetic anisotropy in an iron(I) atom.⁵ Incorporation of numerous linear iron (I) sites in the bulk material $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$ results in the largest coercive field yet reported for magnetic hysteresis measurements at 2 K (Figure 1.1).⁶ Analogous materials that display magnetic ordering at ambient temperatures could provide an inexpensive replacement for rare earth-based magnets in electric motors or generators.

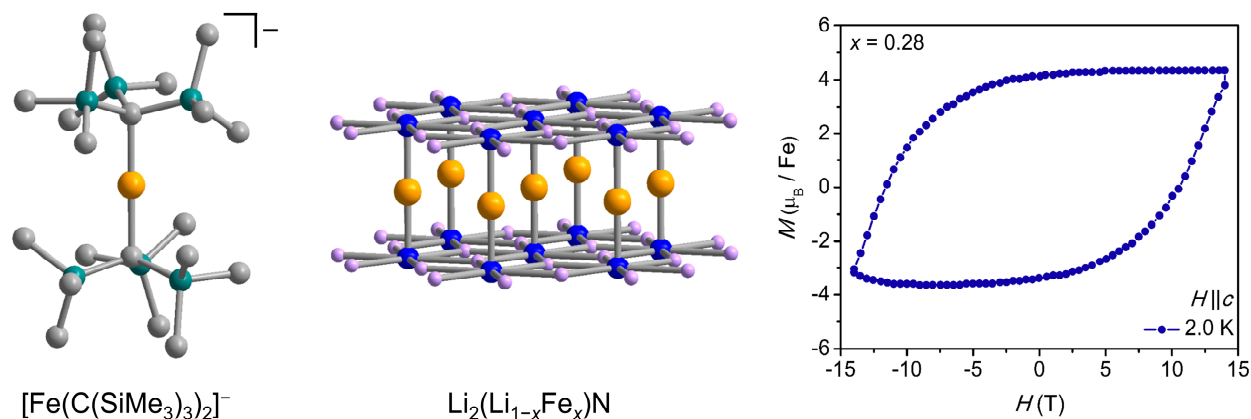


Figure 1.1. Single crystal X-ray diffraction structure of the single-molecule magnet $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]^-$ and the bulk material $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$,^{5,6} and magnetic hysteresis measurements for $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$ ($x = 0.28$) collected at 2 K.⁶ Orange, gray, green, blue, and purple spheres represent iron, carbon, silicon, nitrogen, and lithium atoms, respectively.

Single-molecule magnet research also pushes the boundaries of synthetic chemistry, resulting in molecules with exotic coordination geometries and electronic structures.⁷ As an example, the linear two-coordinate complex $\text{Co}(\text{C}(\text{SiMe}_2(\text{ONaph}))_3)_2$ (naph = naphthyl) was recently isolated.⁸ This molecule possesses a weak ligand field and strong spin-orbit coupling, giving rise to an

electronic ground state that violates the Aufbau principle.⁸ Such studies contribute to a deeper understanding of the electronic structure of metal complexes.

In sum, research on single-molecule magnets can enable nanoscale spin-based devices, provide design criteria for high-performance magnetic materials, and offer unique insight into basic chemistry principles, contributions that enhance our fundamental understanding of magnetism and lay the groundwork for next-generation technologies.

1.2 Key Objectives and Figures of Merit

Single-molecule magnets possess a bistable magnetic ground state and a thermal barrier to re-orientation of the magnetic moment (U_{eff}).^{2a} As a result, these molecules can retain the orientation of their magnetic moment after removal of an external field, a property that could be utilized in information storage or spintronics applications.³ A key research objective is therefore to maximize the length of time that magnetic polarization is maintained—termed the magnetic relaxation time, τ —and to increase the temperature at which large τ values are observed.

One important figure of merit for a single-molecule magnet is the magnitude of the thermal barrier to re-orientation of the magnetic moment. The value of U_{eff} dictates the rate of thermally-activated magnetic relaxation—termed Orbach relaxation—according to the equation $\tau^{-1} = \tau_0^{-1} e^{-U_{\text{eff}}/kT}$, where τ_0 is a pre-exponential factor, k is the Boltzmann constant, and T is the temperature.⁹ Increasing the value of U_{eff} for a single-molecule magnet can lead to larger τ values and a higher operating temperature, although this correlation is not always linear due to the presence of competing magnetic relaxation pathways (see Section 1.4).¹⁰

The operating temperature of a single-molecule magnet is another important figure of merit. This is commonly defined by the blocking temperature (T_b), which is the temperature at which $\tau = 100$ s.^{2a} An alternative definition of the operating temperature is the temperature at which a plot of magnetization (M) versus applied magnetic field (H) remains open at zero field. These data are obtained through magnetic hysteresis measurements; however, the M versus H plots for a molecule depend on the rate at which the external magnetic field is swept during data collection.² As a result, magnetic hysteresis data for two molecules obtained at different sweep rates cannot be compared accurately. The 100-s blocking temperature is therefore the preferred figure of merit for single-molecule magnets in this dissertation, although the maximum temperature at which magnetic hysteresis is observed will also be reported.

1.3 Maximizing the Thermal Barrier to Magnetic Relaxation in Lanthanide Complexes

Lanthanide-based systems have been responsible for most breakthroughs in achieving large U_{eff} and high T_b values over the past decade.¹¹ This is the result of the unparalleled single-ion magnetic anisotropy of the lanthanide ions, which arises from their unique electronic structure.¹² Lanthanide ions in molecular complexes typically exist in the trivalent oxidation state, which is characterized by contracted valence 4f orbitals.¹³ The 4f orbitals interact weakly with the ligand field, maintaining near degeneracy and imparting unquenched orbital angular momentum.¹³ Indeed, spin-orbit coupling in lanthanide ions is substantially stronger than ligand field interactions, and therefore the electronic states can be derived through an L - S coupling scheme.¹² For instance, $L = 5$ and $S = 5/2$ for Dy^{3+} , which leads to a $^6\text{H}_{15/2}$ spin-orbit coupled ground state (Figure 1.2).

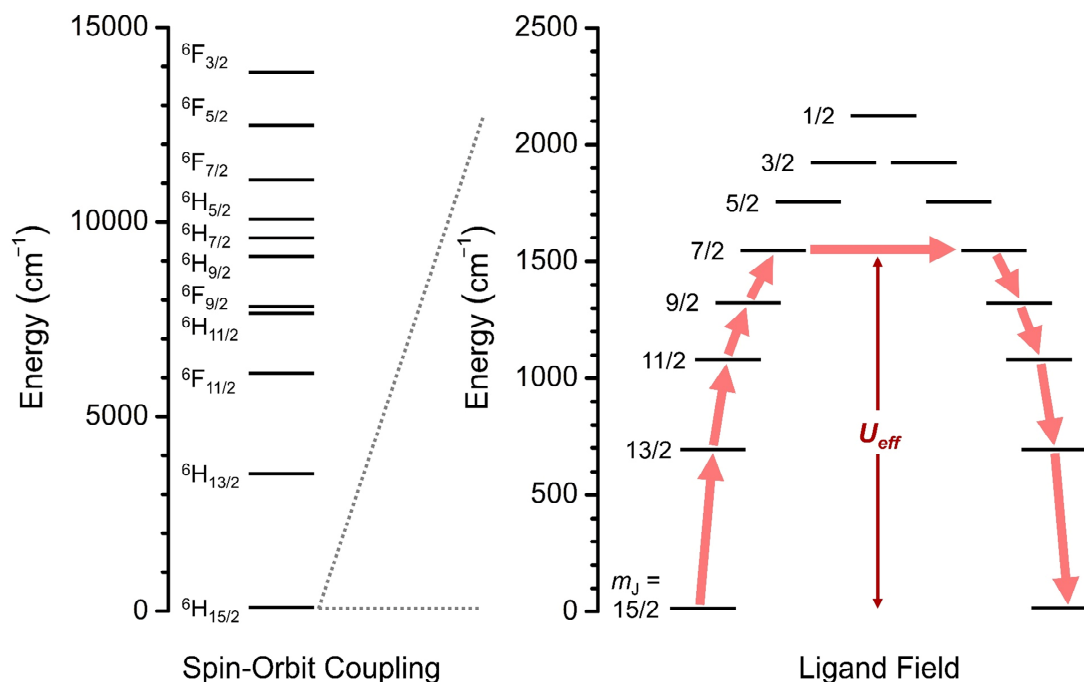


Figure 1.2. Low-energy electronic structure of $[\text{DyCp}^*\text{Cp}^{\text{iPr5}}][\text{B}(\text{C}_6\text{F}_5)_4]$ showing the effects of spin-orbit coupling and the ligand field. The thermal barrier to magnetic relaxation (U_{eff}) is highlighted with red arrows. Adapted from Refs. 14a and 16.

The magnitude of the thermal barrier to magnetic relaxation (U_{eff}) in a lanthanide single-molecule magnet is determined by the energetic splitting of the spin-orbit coupled ground state.¹¹ For example, in Dy^{3+} complexes the relative energy of the m_J microstates in the $M_J = 15/2$ ground state dictates the value of U_{eff} (Figure 1.2). This energetic splitting is induced by weak interactions with the ligand field, which can be predicted through empirical and computational models.¹⁴ Such models provide clear design criteria for maximizing U_{eff} in lanthanide-based complexes: the energetic splitting of m_J microstates in oblate Ln^{3+} ions (e.g., Dy^{3+} or Tb^{3+}) is maximized by an axial ligand field, while microstate splitting for prolate Ln^{3+} ions (e.g., Ho^{3+} or Er^{3+}) is maximized by an equatorial ligand field.^{14a} Numerous experimental studies have confirmed the validity of these design criteria,¹⁵ and U_{eff} values as large as 1541 cm^{-1} in $[\text{DyCp}^*\text{Cp}^{\text{iPr5}}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Cp}^* = \text{pentamethylcyclopentadienyl}$; $\text{Cp}^{\text{iPr5}} = \text{penta}(\text{iso-propyl})\text{cyclopentadienyl}$) have been achieved.¹⁶

1.4 Through-Barrier Magnetic Relaxation Processes

Although large U_{eff} values can be achieved in lanthanide complexes through rational design principles, increasing U_{eff} does not always result in higher operating temperatures (Figure 1.3).¹⁰ For instance, $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{py})_5][\text{BPh}_4]$ ($\text{py} = \text{pyridine}$) shows $U_{\text{eff}} = 1261 \text{ cm}^{-1}$, which should correspond to a 100-s blocking temperature of 55 K, but magnetic hysteresis loops are closed at zero field for this complex even at 2 K.¹⁷ This disparity arises due to fast through-barrier magnetic relaxation processes, which compete with Orbach relaxation and lead to low values of T_b .¹⁰

The two most significant through-barrier relaxation processes in single-molecule magnets are quantum tunneling of the magnetization and Raman relaxation. Quantum tunneling of the magnetization is a direct transition between the $+m_J$ and $-m_J$ microstates of the bistable magnetic

ground state, while Raman relaxation is a thermally-activated transition via a virtual intermediate state of the lattice.¹⁰ Both relaxation pathways are influenced by the local vibrational modes of the molecule and those of the extended lattice in the solid-state, termed phonons.^{10a} The rate of quantum tunneling of the magnetization is also strongly affected by the spin of the molecule, with larger spin values leading to slower tunneling rates.¹⁰

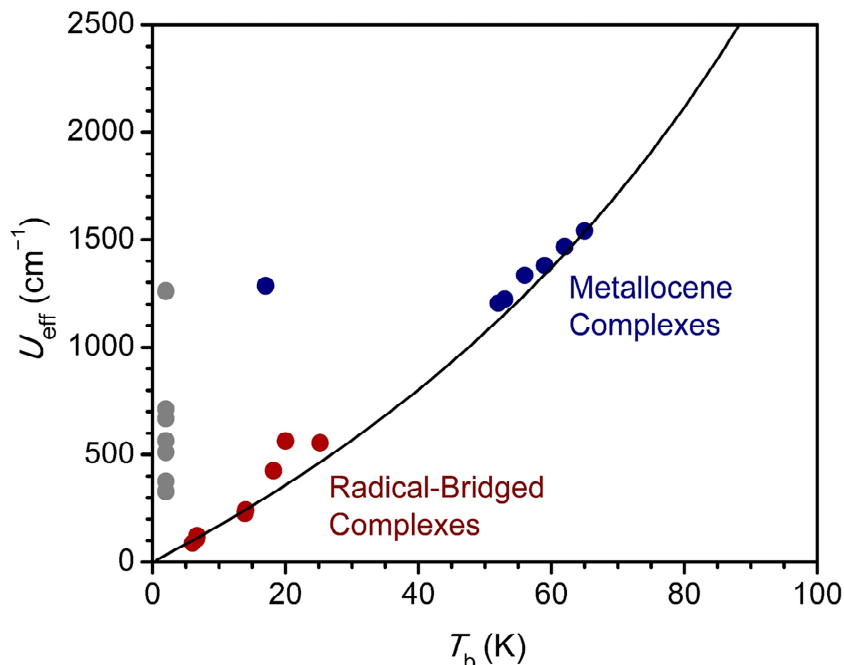


Figure 1.3. A plot of the thermal barrier to magnetic relaxation (U_{eff}) versus the 100-s magnetic blocking temperature (T_b) for lanthanide-based single-molecule magnets. The black line represents the theoretical value of T_b for a given value of U_{eff} ; the value of τ_0 used to calculate this line is a function of U_{eff} , as determined by a fit to literature data.¹⁶⁻²⁰ Data for selected complexes are shown as circles with radical-bridged and metallocene complexes highlighted in red and blue, respectively.¹⁶⁻²⁰

Although the majority of single-molecule magnets display fast through-barrier magnetic relaxation and low T_b values, these deleterious relaxation pathways can be mitigated. Indeed, multinuclear lanthanide complexes bridged by open-shell ligands and lanthanide metallocene complexes of the type $[\text{Dy}(\text{Cp}^R)_2]^+$ (Cp^R = substituted cyclopentadienyl) display large T_b values that correspond to thermally-activated magnetic relaxation via an Orbach mechanism (Figure 1.3).^{19,20} This dissertation seeks to rationalize the magnetic behavior of both classes of molecules and to develop design principles to guide the further optimization of their properties.

1.5 Radical-Bridged Lanthanide Complexes

Increasing the spin (S) of a molecule can reduce the rate of through-barrier magnetic relaxation.^{2a} This design principle is illustrated by research on transition metal single-molecule magnets: multinuclear clusters with large spin (e.g., $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4$, $S = 10$) are characterized by thermally-activated Orbach relaxation, while mononuclear complexes (e.g., $[(\text{tpa}^{\text{Mes}})\text{Fe}]^+$, $S = 2$) typically display fast quantum tunneling of the magnetization at low temperatures.^{2a,21,22} Synthesizing high-spin multinuclear lanthanide complexes presents a

significant challenge due to the contracted nature of the 4f orbitals, which limit magnetic interactions between metal centers.^{12,13} These interactions can be quantified in terms of an exchange coupling constant, J , which is determined by fitting the dc magnetic susceptibility data to a spin-only Hamiltonian. Typically, J values for lanthanide complexes are reported for the isotropic Gd^{3+} derivative, as dc susceptibility data for anisotropic lanthanide ions cannot be easily modelled.^{23,24} The majority of multinuclear lanthanide complexes possess $|J| < 1 \text{ cm}^{-1}$, several orders of magnitude smaller than values typically observed for transition metal complexes, due to the more limited radial extension of the valence orbitals in 4f-elements.²³ As a result, the magnetic properties of most multinuclear lanthanide complexes are dominated by single-ion behavior and fast through-barrier magnetic relaxation.²⁵

One promising method to achieve high-spin multinuclear lanthanide complexes is to link metal ions via open-shell bridging ligands, which can mediate strong direct exchange interactions.²³ The efficacy of this strategy is demonstrated by the complexes $(\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})\text{Gd})_2(\mu\text{-N}_2)$ and $[(\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})\text{Gd})_2(\mu\text{-N}_2)]^+$: the former complex possesses a diamagnetic N_2^{2-} bridging ligand and $J_{\text{Gd-Gd}} = -0.5 \text{ cm}^{-1}$, while the latter complex possesses an open-shell N_2^{3-} -bridge and $J_{\text{Gd-rad}} = -27 \text{ cm}^{-1}$.^{19a} Other radical ligands and open-shell metalloligands can also engage in strong magnetic coupling with lanthanide ions, although the J value determined for the aforementioned N_2^{3-} -bridged complex is the largest yet reported for a gadolinium-ligand interaction (Figure 1.4).²³ In addition, strong magnetic exchange can be achieved in fullerene molecules that contain two lanthanide ions and an unpaired electron. For instance, $\text{Gd}_2@\text{C}_{80}(\text{CH}_2\text{Ph})$ possesses $J = 160 \text{ cm}^{-1}$.^{19e} While the electronic structure of endohedral lanthanide fullerenes (i.e. a one-electron Ln-Ln bond) cannot be easily replicated in non-encapsulated molecular complexes, these results demonstrate that lanthanide ions can engage in exchange interactions of comparable magnitude to transition metal ions.

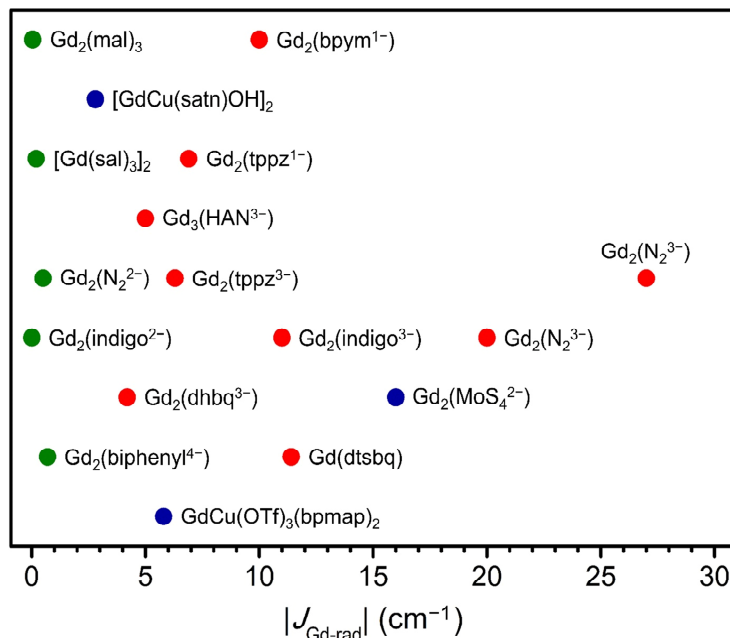


Figure 1.4. Values of $J_{\text{Gd-rad}}$ ($2J$ formalism; arbitrary y-axis) for various lanthanide complexes bridged by diamagnetic ligands (green), radical ligands (red), and open-shell metalloligands (blue). Ancillary ligands on the Gd^{3+} ions are not reported for brevity. The two values reported for $\text{Gd}_2(\text{N}_2^{3-})$ were extracted from complexes with different ancillary ligands.^{23,27,19a-d}

Radical-bridged lanthanide complexes display some of the highest operating temperatures reported to date for single-molecule magnets due to the mitigation of deleterious through-barrier relaxation processes.¹⁹ Indeed, $[(\text{Tb}(\text{Cp}^{\text{Me4H}})_2)_2(\mu\text{-N}_2)]^-$ possesses $T_b = 20$ K and $\text{Tb}_2@\text{C}_{80}(\text{CH}_2\text{Ph})$ possesses $T_b = 25.2$ K.^{19d,e} Research on this class of molecules has revealed several key design principles to increase values of U_{eff} and T_b . First, the single-ion anisotropy of the individual lanthanide ions in the molecule must be maximized. This can be accomplished through tuning the ligand field according to the aforementioned empirical and computational models for increasing U_{eff} values in mononuclear lanthanide complexes (for example, the axiality of the ligand field should be maximized for Tb^{3+}).¹⁴ As an example of this design criterion, removal of an equatorial tetrahydrofuran ligand from $[(\text{Tb}(\text{thf})(\text{Cp}^{\text{Me4H}})_2)_2(\mu\text{-N}_2)]^-$ to form $[(\text{Tb}(\text{Cp}^{\text{Me4H}})_2)_2(\mu\text{-N}_2)]^-$ results in an increase in T_b from 14 to 20 K.^{19d} The strength of the magnetic exchange interaction must also be maximized in radical-bridged lanthanide complexes. For complexes with high single-ion anisotropy, the magnitude of $J_{\text{Ln-rad}}$ is linearly correlated to the value of U_{eff} , and increasing the coupling strength also facilitates higher T_b values.²⁸ Developing novel bridging ligands that can mediate strong exchange coupling is thus essential to the design of single-molecule magnets with high operating temperatures.

1.6 Lanthanide Metallocene Complexes

Increasing the rigidity of a molecule can decrease the rate of through-barrier relaxation processes by eliminating low-energy phonons (see Section 1.4).¹⁰ This strategy is exemplified by $[\text{Dy}(\text{Cp}^{\text{tut}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Cp}^{\text{tut}} = 1,2,4\text{-tri}(\text{tert-butyl})\text{cyclopentadienyl}$), which possesses rigid $\eta^5\text{-cyclopentadienyl}$ ligands that constrain metal-ligand vibrational modes and displays a remarkable operating temperature of $T_b = 53$ K.^{20a,b} The discovery of $[\text{Dy}(\text{Cp}^{\text{tut}})_2]^+$ sparked a surge of interest in lanthanide metallocenes, including studies on the optimization of $[\text{Dy}(\text{Cp}^{\text{R}})_2]^+$ molecules.^{20c,29} Currently, $[\text{DyCp}^*\text{Cp}^{\text{iPr5}}][\text{B}(\text{C}_6\text{F}_5)_4]$ displays the highest operating temperature for a single-molecule magnet, with $T_b = 65$ K and open magnetic hysteresis loops up to 80 K.¹⁶

Despite the success of $[\text{Dy}(\text{Cp}^{\text{R}})_2]^+$ molecules, molecular rigidity has yet to be broadly applied as a design criterion for single-molecule magnets. This is likely due to the challenge of engineering molecules that display rigidity and of quantifying this property. Indeed, computational analysis of the relationship between molecular vibrations and magnetic relaxation remains time-intensive, and methods have not yet been developed to address through-barrier relaxation processes.^{20a} Recently, characterization of $[\text{Dy}(\text{L})_2(\text{py})_5]^+$ ($\text{L} = \text{tert-butoxide}$, $S(-)-1\text{-phenylethoxide}$) demonstrated that incorporation of intramolecular $\text{C-H}\cdots\pi$ interactions results in open magnetic hysteresis loops to 22 K; for comparison, hysteresis loops are closed at zero field at 2 K in $[\text{Dy}(\text{O}^i\text{Bu})_2(\text{py})_5]^+$, which displays no $\text{C-H}\cdots\pi$ interactions.³⁰ This study offers an important demonstration of how molecular rigidity can be rationally implemented to mitigate through-barrier relaxation processes. Further investigation of the relationship between molecular rigidity and magnetic relaxation is clearly essential to the widespread application of this design criteria.

1.7 Conclusions and Outlook

This dissertation seeks to develop design principles for the synthesis of lanthanide-based single-molecule magnets with high operating temperatures. The mitigation of through-barrier magnetic relaxation pathways is essential to this goal, and thus both radical-bridged and metallocene complexes are analyzed in detail.

Chapters 2-4 focus on radical-bridged lanthanide single-molecule magnets. The synthesis of the first trinuclear radical-bridged lanthanide complex is described (Chapter 2) and the effect of ligand substitution on a series of radical-bridged dilanthanide complexes is investigated (Chapter 3). The latter study establishes a rational method to increase the strength of magnetic exchange coupling interactions in this class of molecules and outlines an empirical model that can be used to interpret the electronic structure of radical-bridged dysprosium complexes. The isolation of a ground-state benzene diradical in a lanthanide inverse sandwich complex is also described (Chapter 4). Characterization of this species reveals the strongest magnetic exchange coupling yet observed for a lanthanide-ligand interaction, demonstrating the potential of biradical bridging ligands in the design of single-molecule magnets.

Chapters 5 and 6 focus on lanthanide metallocene single-molecule magnets. Magneto-structural correlations are elucidated for a series of $[\text{Dy}(\text{Cp}^{\text{R}})_2]^+$ complexes (Chapter 5), illustrating methods to increase the operating temperature of this class of molecules. The magnetic properties of divalent lanthanide metallocenes are also investigated (Chapter 6). The $4f^75d^1$ electronic structure of the lanthanide ions in these molecules is shown to facilitate both high magnetic anisotropy and a linear coordination geometry, diminishing the rate of through-barrier magnetic relaxation processes.

In addition to identifying methods to improve the operating temperature of single-molecule magnets, this dissertation investigates rare electronic structures that arise in lanthanide single-molecule magnets. Baird aromaticity—a reversal of Hückel’s rule predicted for molecules with $4n$ π -electrons in the triplet ($S = 1$) state—is characterized in the central benzene dianion of a lanthanide inverse sandwich complex (Chapter 4). Analysis of divalent lanthanide metallocene complexes reveals a j - j coupled electronic structure (Chapter 6), a deviation from Hund’s rules that has previously only been observed in gas-phase lanthanide ions.

In sum, this dissertation aims to advance the synthesis of high-performance lanthanide single-molecule magnets and to identify fundamental insights into chemistry principles that can be gleaned through single-molecule magnet research.

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Chapter 2: A Trinuclear Radical-Bridged Lanthanide Single-Molecule Magnet

C. A. Gould, L. E. Darago, M. I. Gonzalez, S. Demir, J. R. Long, *Angew. Chem. Int. Ed.* **2017**, *56*, 10103–10107.^a

2.1 Introduction

Single-molecule magnets possess a bistable magnetic ground state with a thermal barrier (U_{eff}) to re-orientation of the magnetic moment. While this bistability could potentially be exploited in information storage or spin-based computing, low operating temperatures currently render such applications impractical.¹ A particularly promising approach to increasing the magnetic blocking temperatures for such molecules is through the coupling of multiple high-anisotropy lanthanide ions via radical bridging species. In these complexes, the diffuse spin of the bridging radical can directly engage the lanthanide centers in strong magnetic exchange coupling, leading to classical “giant spin” behavior, in which the molecule behaves as a single magnetic unit with a high angular momentum ground state.² Thus, while the magnetic relaxation in most multinuclear lanthanide complexes is dominated by single-ion effects³—such as quantum tunneling of the magnetization, promoted by mixing of electronic states by rhombic anisotropy—radical-bridged lanthanide complexes can display mainly thermally-activated relaxation, leading to magnetic hysteresis at high temperatures. Indeed, this approach has already produced a dinuclear Tb^{III} complex bridged by N₂³⁻ which exhibits a 100-s blocking temperature of $T_b = 14$ K, the highest yet reported for any molecule.⁴ A variety of dinuclear lanthanide complexes bridged by organic radicals have also since been reported, but higher nuclearity systems have not yet been achieved.⁵ Such systems offer the potential for larger spin-orbit coupled ground state moments, which may in turn lead to complete suppression of tunneling effects and larger thermal relaxation barriers.

The directed synthesis of a radical-bridged trilanthanide complex presents a clear step toward these goals. While triangular single-molecule magnets with three lanthanide centers have been investigated for their unusual magnetic properties, which include spin frustration⁶ and toroidal magnetic moments,⁷ the incorporation of a central radical bridge as a means of aligning the metal-based spins in complexes of this type has not yet been accomplished. A promising candidate for the bridging ligand in such a molecule is hexaazatrinaphthylene (HAN), a symmetrical, tritopic, redox-active ligand.⁸

Indeed, HAN[•] was recently employed as a central bridging ligand in the assembly of $[(\text{Me}_3\text{Si})_2\text{N})_6\text{Co}_3(\mu_3\text{-HAN})]^-$, a complex that exhibits strong antiferromagnetic exchange coupling as characterized by SQUID magnetometry.⁹ While this complex did not show single-molecule magnet behavior, the utilization of HAN as a radical bridging ligand for aligning the moments of three highly anisotropic lanthanide centers remained to be tested.

2.2 Results and Discussion

The complexes Cp*₆Ln₃(μ₃-HAN) (Cp* = pentamethylcyclopentadienyl; Ln = Gd (**1**), Tb (**2**), and Dy (**3**)) were readily synthesized by combining Cp*₂Ln(BPh₄) with the HAN ligand in THF, followed by reduction with KC₈ to generate the trianionic state of the bridging ligand.¹⁰

^a C.A.G. synthesized the compounds, collected the crystal structure data, and collected and interpreted the magnetic data. L.E.D. and S.D. assisted in the interpretation of the magnetic data. M.I.G. solved and refined the crystal structure data. C.A.G. and J.R.L. wrote the manuscript and all authors contributed to editing it.

Recrystallization from concentrated THF solutions afforded sufficient product for magnetic measurements of **1-3** and single crystals suitable for x-ray structure determinations for **2** and **3**. While only microcrystalline material could be isolated for **1**, its identity was confirmed through mass spectrometry, elemental analysis, and magnetic susceptibility measurements.

Compounds **2** and **3** are isostructural, crystallizing in space group *Pnma* (Figure 2.1). The $\text{Cp}^*\text{Ln}_3(\mu_3\text{-HAN})$ complexes reside on a crystallographic mirror plane that bisects each molecule and is oriented perpendicular to the plane of the HAN^{3-} bridging ligand. The three Ln^{III} centers form an essentially ideal equilateral triangle, in which each metal is coordinated by two Cp^* ligands and two N atoms of the HAN^{3-} bridge. The C–C distances within the central HAN^{3-} ligand lie in the range 1.36(2)–1.42(2) Å for **2** and 1.375(7)–1.421(7) Å for **3**, while the C–N distances lie in the range 1.35(2)–1.39(2) Å for **2** and 1.352(6)–1.391(7) Å for **3**. These metrics are consistent with those reported for the only other known complex containing HAN^{3-} , $(\text{HAN})[\text{Mg}(\text{nacnac})]_3$ (nacnac = N,N'-(2,6-diisopropylphenyl)-3,5-dimethyldiketimate).^{8a}

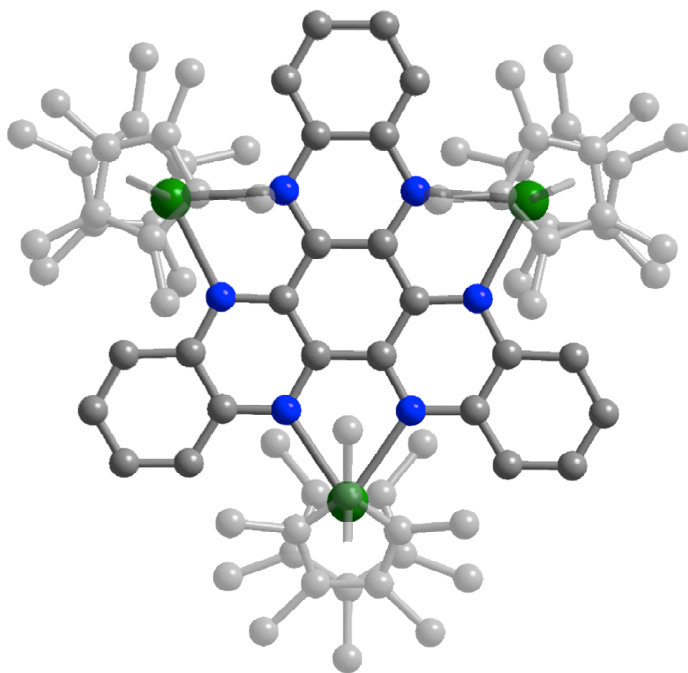


Figure 2.1. Crystal structure of the triangular complex $\text{Cp}^*_6\text{Dy}_3(\mu_3\text{-HAN})$ (**3**). Green, blue, and gray spheres represent Dy, N, and C atoms, respectively; H atoms are omitted for clarity. Compound **2** is isostructural (Figure S2.1). Selected mean interatomic distances (Å) for **2** and **3**, respectively: Ln–N 2.41(1), 2.389(4); Ln···Ln 7.67(1), 7.664(1).

Variable-temperature dc magnetic susceptibility data were collected for **1-3** from 2 to 300 K in order to analyze the magnetic exchange coupling (Figure 2.2). Under a 1-kOe applied magnetic field, the χ_{MT} values at room temperature for **1** and **2** are larger than expected in the absence of magnetic exchange coupling, due to the presence of temperature-independent paramagnetism (TIP). At 10-kOe, where TIP is greatly reduced by the stronger applied magnetic field, the room temperature χ_{MT} values of 39.8, 31.3 and 23.6 $\text{emu}\cdot\text{K}/\text{mol}$ obtained for **1-3**, respectively, are slightly lower than the respective values of 42.8, 35.8, and 24.0 $\text{emu}\cdot\text{K}/\text{mol}$ expected for three non-interacting Ln^{III} centers and an $S = 1/2$ organic radical spin (Figure S2.2). With decreasing temperature, shallow minima in χ_{MT} are reached at 185, 130, and 95 K for **1-3**, respectively. This

decrease at high temperatures is partly due to thermal depopulation of the M_J manifolds of the individual ions. It also suggests the presence of antiferromagnetic exchange coupling. The minima are followed by a rise in $\chi_M T$ at lower temperatures, due to the formation of a high angular momentum, “giant spin” ground state via the antiferromagnetic $\text{Ln}^{\text{III}}\text{--HAN}^{3\cdot-}$ exchange coupling. The maximum $\chi_M T$ values of 70.4, 46.2, and 33.9 emu·K/mol for **1-3**, respectively, under a 1-kOe applied field are substantially higher than those observed for dinuclear, organic radical-bridged complexes containing the same Ln^{III} centers,^{5a,b} suggesting that all three metals are effectively coupled through the $\text{HAN}^{3\cdot-}$ bridge in **1-3**. This rise is followed by a steep drop at lower temperatures, which is likely attributable to the Zeeman effect associated with thermal depopulation of the M_J manifold of the exchange-coupled magnetic ground state, possibly combined with weak intermolecular magnetic coupling.

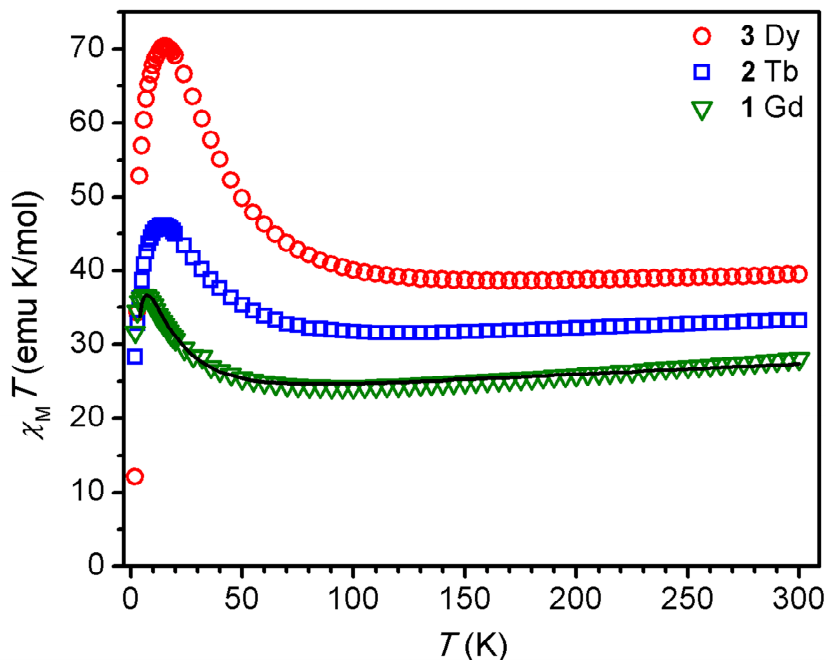


Figure 2.2. Dc magnetic susceptibility data for compounds **1-3** under an applied field of 1-kOe. The black line represents a fit to the data for **1**, yielding $J_{\text{Gd-rad}} = -5.0 \text{ cm}^{-1}$.

The isotropic nature of the $4f^7$ electron configuration of the Gd^{III} centers in **1** allowed the strength of the magnetic exchange coupling giving rise to its $S = 10$ ground state to be quantified. Dc magnetic susceptibility data were fit using the spin-only Hamiltonian: $\hat{H} = -2J_{\text{Gd-rad}}\hat{S}_{\text{rad}} \cdot (\hat{S}_{\text{Gd}(1)} + \hat{S}_{\text{Gd}(2)} + \hat{S}_{\text{Gd}(3)})$, where $J_{\text{Gd-rad}}$ represents the intramolecular Gd^{III} –radical exchange coupling constant, $\hat{S}_{\text{rad}}$ represents the spin operator for the organic radical bridging ligand, and $\hat{S}_{\text{Gd}(n)}$ represents the spin operator for each paramagnetic metal center. A fit to the 1-kOe susceptibility data afforded $J_{\text{Gd-rad}} = -5.0 \text{ cm}^{-1}$, with a TIP contribution of $1.3 \times 10^{-2} \text{ emu/mol}$ and a small intermolecular coupling contribution of $J' = -0.01 \text{ cm}^{-1}$. Significantly, this is one of the largest exchange constants yet reported for Gd^{III} , and is only surpassed in dinuclear complexes bridged by the radical species 2,3,5,6-tetra(2-pyridyl)pyrazine^{1-/3-} ($-6.9/-6.3 \text{ cm}^{-1}$),^{5b} bipyrimidine¹⁻ (-10 cm^{-1}),^{5a} and N_2^{3-} (-27 cm^{-1}).^{2a} The temperatures at which the aforementioned shallow minima in $\chi_M T$ occur suggest that $|J_{\text{Dy-rad}}| > |J_{\text{Tb-rad}}| > |J_{\text{Gd-rad}}|$, such that -5.0 cm^{-1} represents a lower limit to

the strength of the antiferromagnetic exchange coupling in the triangular complexes **2** and **3**. This assessment is potentially complicated by differences in single-ion terms between the complexes.

The magnetization relaxation dynamics of **2** and **3** were probed by ac magnetic susceptibility measurements from which in-phase (χ_M') and out-of-phase (χ_M'') components of the susceptibility were extracted (Figures 2.3 and S2.3). A simultaneous fit to a generalized Debye model for the χ_M' and χ_M'' data was used to extract magnetic relaxation times, τ (Figures S2.4 and S2.5). Arrhenius plots of inverse temperature versus $\log(\tau)$ were then employed to examine the temperature dependence of the magnetic relaxation in the two compounds.

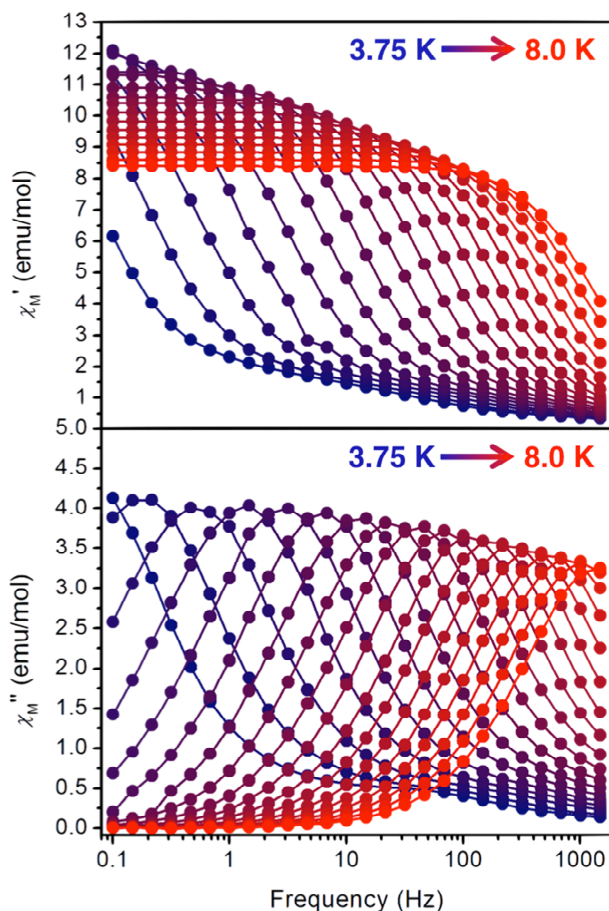


Figure 2.3. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **3** under zero applied dc field at frequencies from 0.1–1500 Hz and temperatures from 3.75–8.00 K. The colored lines are guides for the eye.

For $\text{Cp}^*\text{Tb}_3(\mu_3\text{-HAN})$ (**2**), the exponential shape of the Arrhenius plot from 2 to 3 K suggests that the relaxation in this temperature regime is dominated by a Raman process (Figure 2.4), wherein reversal of the moment proceeds via a phonon-promoted excitation to a virtual excited state created by coupling of an excited magnetic state to a vibrational mode of the molecule.¹¹ The temperature independence of τ below 2 K indicates that quantum tunneling of the magnetization becomes dominant at very low temperature. A fit to the data (Figure S2.6) was therefore calculated using the following equation to account for these two relaxation mechanisms:¹²

$$\tau^{-1} = \tau_{\text{tunnel}}^{-1} + CT^n \quad (2.1)$$

Here, τ is the magnetic relaxation time, τ_{tunnel} is the relaxation time for quantum tunneling, T is the temperature, and C and n are free variables that describe Raman relaxation. A term accounting for thermally-activated Orbach relaxation was also included in the calculation, though it trended towards zero in the best fit, and was therefore removed. The best fit yielded $\tau_{\text{tunnel}} = 7.9 \times 10^{-4}$ s, $C = 0.23 \text{ s}^{-1}\text{K}^{-n}$, and $n = 9.6$.

In distinct contrast, the ac susceptibility data for $\text{Cp}^*\text{Dy}_3(\mu_3\text{-HAN})$ (**3**) reveal much longer relaxation times, with an essentially linear Arrhenius plot for the accessible frequency range (red circles, Figure 2.4). In order to probe magnetic relaxation at lower temperatures, dc magnetic relaxation measurements were undertaken. Magnetization versus time plots were used to extract relaxation times by fitting the data with a stretched exponential function of the form $M_t = Ae^{-(t/\tau)^n}$, where M_t is the magnetization at a given measurement time, t is the measurement time, τ is the magnetic relaxation time, and A and n are free variables (Figure S2.7).¹³ A plot of $\log(\tau)$ versus inverse temperature, including values extracted from both ac and dc susceptibility relaxation measurements, is linear between 8 and 3.5 K, and then flattens at lower temperatures. The linear region indicates relaxation via a thermally-activated Orbach process.¹⁴ Quantum tunneling of the magnetization provides the dominant relaxation mechanism at lower temperatures. Accordingly, a fit to the data (Figure S2.8) was calculated using the equation:¹²

$$\tau^{-1} = \tau_{\text{tunnel}}^{-1} + \tau_0^{-1}e^{-U_{\text{eff}}/kT} \quad (2.2)$$

where τ_0 is the attempt time and U_{eff} is the thermal barrier to magnetization reversal. This fit affords $\tau_{\text{tunnel}} = 120$ s, $\tau_0 = 1.2 \times 10^{-8}$ s, and $U_{\text{eff}} = 51 \text{ cm}^{-1}$, and indicates a 100-second magnetic blocking temperature of $T_b = 3.0$ K. Incorporating a term to account for Raman relaxation failed to yield a better fit.

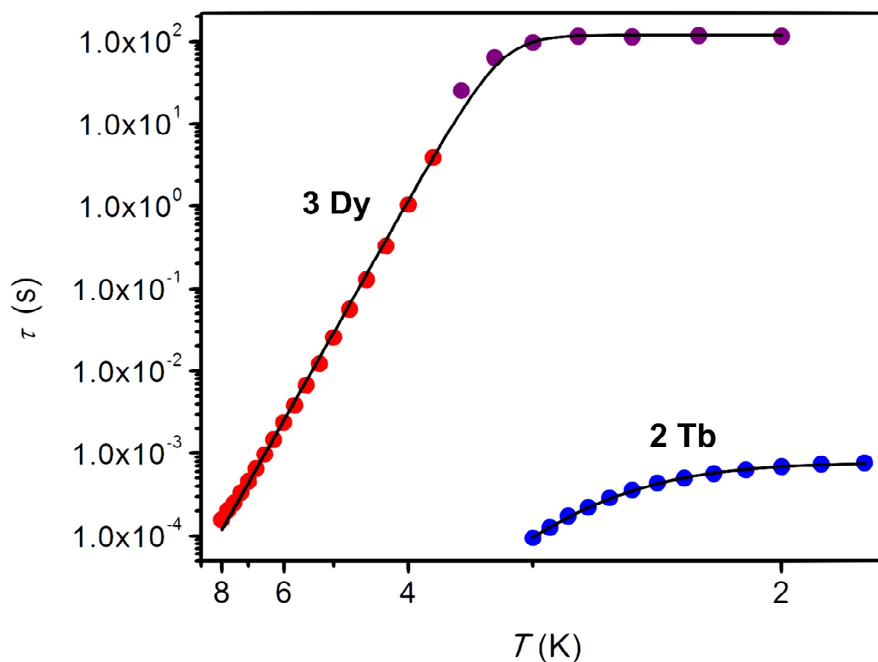


Figure 2.4. Arrhenius plots of magnetic relaxation times for **2** (ac susceptibility, blue circles) and **3** (ac susceptibility, red circles; dc relaxation, purple circles). Black lines represent fits to the data, as described in the main text, yielding $U_{\text{eff}} = 51 \text{ cm}^{-1}$ for **3**.

The thermal barrier of **3** is modest in comparison to many reported Dy^{III} complexes with cyclopentadienyl ligands. The triangular cluster [(Cp'2Dy){μ-As(H)Mes)}₃ (Cp' = methylcyclopentadienyl; Mes = mesityl) exhibits a thermal relaxation barrier of $U_{\text{eff}} = 301 \text{ cm}^{-1}$, while an isostructural cluster with antimony-based ligands—[(Cp'2Dy){μ-Sb(H)Mes)}₃—possesses $U_{\text{eff}} = 345 \text{ cm}^{-1}$.¹⁵ Large thermal barriers have also been reported for mononuclear and dinuclear Dy^{III} cyclopentadienyl complexes.¹⁶ These large barriers are generated by crystal field splitting of M_J states, which is dominated by the axial cyclopentadienyl ligands.¹⁷ The lower barrier in **3** is likely due to the strongly binding, equatorial HAN³⁻ bridging ligand, which competes with the axial ligand field. The magnitude of the exchange coupling constant, $J_{\text{Ln-rad}}$, may also impact U_{eff} . The axial cyclopentadienyl ligands in **3** also likely define the orientation of the easy axes of the Dy^{III} centers. Calculation of the exact orientation of these axes through an electrostatic model is complicated by charge delocalization in HAN³⁻, however.

The differences in magnetic relaxation dynamics for **2** and **3** are notable. These differences, including suppression of Raman relaxation in **3**, are likely due to changes in both anisotropy and magnetic coupling strength generated by switching from Tb^{III} to Dy^{III}. Large changes in the magnetic relaxation of a series of isostructural complexes have also been reported for other radical-bridged lanthanide compounds.^{4,5a} Further investigation of such systems is clearly warranted, as it may provide insight into factors controlling magnetic relaxation, particularly the poorly understood Raman relaxation process.

Magnetic hysteresis measurements performed on a conventional SQUID magnetometer confirm the observed trends in relaxation times for **2** and **3**. For a sweep rate of 4 mT/s, no magnetic hysteresis was observed for **2** at 1.8 K (Figure S2.9), while **3** displayed open hysteresis loops, including a remnant magnetization, at temperatures of up to 3.5 K (Figure 2.5).

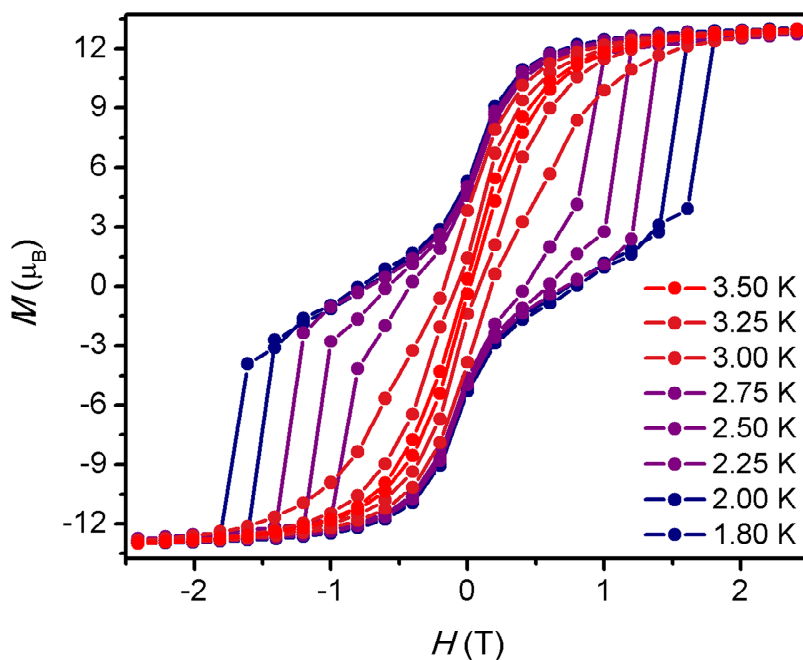


Figure 2.5. Magnetic hysteresis measurements of **3** from 1.8 to 3.5 K at a sweep rate of 4 mT/s.

Interestingly, between 1.80 and 2.75 K, the magnetic hysteresis data for **3** display sharp steps, which shift to higher fields as the temperature is lowered. While similar steps were observed for the triangular cluster $[\text{Dy}_3(\mu_3\text{-OH})_2(\text{L})_3\text{Cl}_2(\text{H}_2\text{O})_4]^{2+}$ (HL = *ortho*-vanillin), these were invariant to temperature and could be attributed to an M_J level crossing between the non-magnetic ground state and the first excited state.^{7a} The temperature dependence of the magnetization steps for **3** (Figure S2.10) suggests instead that thermally assisted quantum tunneling of the magnetization occurs, in which excited states with opposite magnetic polarity are brought into energetic resonance at a particular magnetic field strength, promoting fast tunneling.¹⁸ Quantum tunneling steps at non-zero fields have not been observed for other organic radical-bridged lanthanide complexes.⁵ Such steps were observed in the N_2^{3-} radical-bridged complex $[\{((\text{SiMe}_3)_2\text{N})_2(\text{THF})\text{Tb}\}_2(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-N}_2)\text{K}]$, however, attributed to close energetic spacing of excited M_J states.¹⁹ Close energetic spacing of M_J states is likely also present in **3**, as implied by the low thermal barrier to magnetization reversal.

The magnetic properties of **1-3** show for the first time that it is possible to couple more than just two lanthanide centers through a radical bridge. Significantly, this magnetic coupling helps to suppress rapid quantum tunneling of the magnetization, facilitating the observation of open hysteresis loops for $\text{Cp}^*\text{Dy}_3(\mu_3\text{-HAN})$ (**3**). To the best of our knowledge, this marks only the second example of a triangular, trilanthanide complex with hysteresis loops that show a significant remnant magnetization above 1.8 K.^{3b} While the non-radical triangular complex $\text{Dy}_3(\text{HL})(\text{H}_2\text{L})(\text{NO}_3)_4$ ($\text{H}_4\text{L}=\text{N,N,N',N'}$ -tetrakis-(2-hydroxyethyl)-ethylenediamine) also displays a remnant magnetization at temperatures up to 3.5 K, the hysteresis data were collected at a much faster sweep rate of 280 mT/s.²⁰ Even at the faster sweep rate, this complex displayed drastically reduced hysteresis compared to **3**, which has a remnant magnetization of $M_r = 5.2 \mu_B$ and a coercive field of $H_c = 0.8 \text{ T}$ at 2 K.

2.3 Conclusions and Outlook

Although the relaxation barrier and blocking temperature of **3** are modest compared to those of the record-holding single-molecule magnets,^{4,21} this complex still demonstrates the utility of radical-bridging ligands. The strong magnetic exchange coupling induced by the radical bridging ligand in **3** facilitates enhanced magnetic hysteresis and longer magnetic relaxation times than those observed in comparable trinuclear lanthanide compounds, even those that possess significantly larger thermal barriers.^{6c,15} Inducing even stronger magnetic exchange coupling within such a species can be expected to lead to dramatically enhanced magnetic behavior.²² Toward this end, the important advantage of organic radical species, which lies in the possibility of attenuating the strength of magnetic coupling by introducing electron-donating or -withdrawing substituents in appropriate positions, is clearly worth exploring.

2.4 Acknowledgements

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2.5 References and Footnotes

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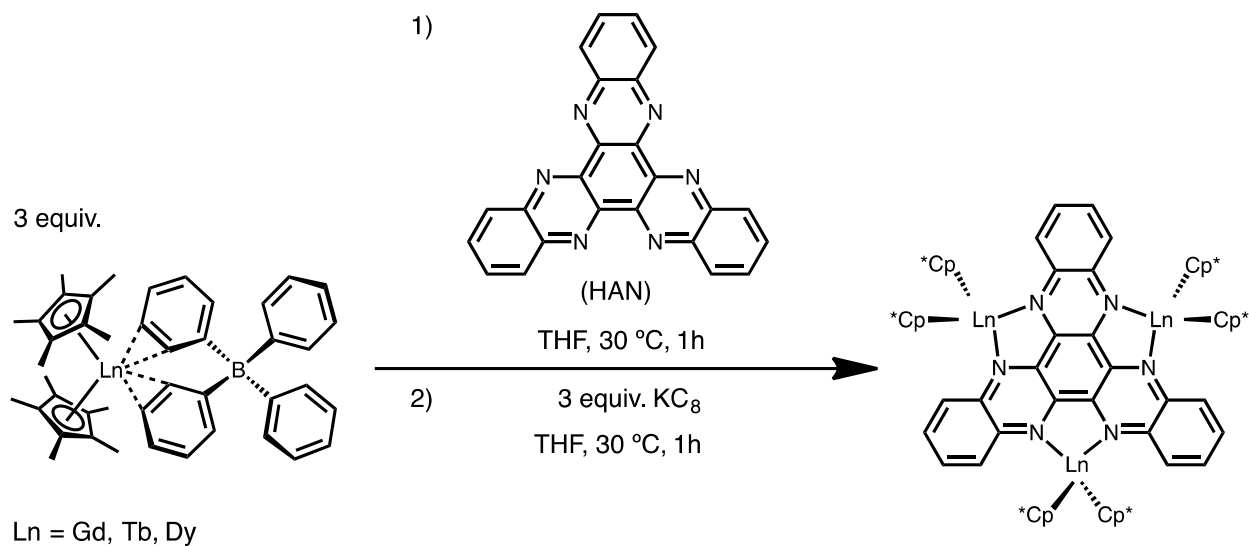
2.6 Supplementary Information

2.6.1 General Information

Unless explicitly noted, all of the following reactions and subsequent manipulations were performed in a nitrogen atmosphere glove box or on a Schlenk line under argon, with rigorous exclusion of air and water. Toluene was dried using a commercial solvent purification system from JC Meyer Solvent Systems.¹ Tetrahydrofuran (THF) was purchased from Fisher Chemical, distilled over sodium benzophenone and subsequently stored over 3 Å activated molecular sieves in a nitrogen atmosphere glovebox. Anhydrous TbCl_3 , hexaketocyclohexane octahydrate, 1,2-phenylenediamine, and KCp^* were purchased from Sigma Aldrich and used as received. Anhydrous LnCl_3 ($\text{Ln} = \text{Gd}, \text{Dy}$) was purchased from Strem and used as received. $(\text{Cp}^*_2\text{Ln})(\text{BPh}_4)$ ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$), hexaazatrinaphthylene (HAN), and KC_8 were prepared according to previous literature reports.²⁻⁴ All other reagents were purchased from commercial suppliers and used as received.

FT-IR spectra were recorded on a Perkin Elmer Avatar Spectrum 400 FTIR Spectrometer equipped with attenuated total reflectance (ATR). Elemental analyses were performed by the Microanalytical Facility at the University of California, Berkeley using a Perkin-Elmer 2400 Series II combustion analyzer.

Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on an Applied Biosystems Voyager-DE PRO Workstation in positive ion mode. Samples were co-crystallized in an anthracene matrix on an AB SCIEX MALDI-TOF stainless steel sample plate. Spectra were averaged over 50 laser pulses at intensities ranging from 2460-2710 with a low mass gate of 300 Dalton and a high mass gate of 2000 Dalton.



Scheme 2.1. Synthetic scheme for the preparation of $\text{Cp}^*_6\text{Ln}_3(\mu_3\text{-HAN})$ ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$).

Cp*₆Gd₃(μ₃-HAN) (1). Hexaazatrinaphthylene (HAN) (0.100 g, 0.26 mmol) was added to a slurry of Cp*₂Gd(BPh₄) (0.583 g, 0.78 mmol, 3 eq) in THF (8 mL). The reaction mixture was stirred for 1 h, changing color from yellow to dark green. To this mixture was added freshly prepared KC₈ (0.106 g, 0.78 mmol, 3 eq). The reaction mixture immediately turned dark, blackish-red and was subsequently stirred for 1 h before the solvent was removed under reduced pressure. The resulting black solid was dissolved in toluene (15 mL) and filtered to remove black and white insolubles. The filtrate was then concentrated to yield crude **1** as a blackish-red solid (0.153 g, 35% yield). The crude product was dissolved in minimal THF (~4 mL) and stored at –30 °C for 5 d, yielding black, block-shaped crystals of **1**. The supernatant was removed, concentrated and stored at –30 °C for another 5 d to yield a second crop of black crystals, which was combined with the first to yield pure **1** (0.012 g, 4% overall yield). The low recovery of pure, crystalline **1** was due to its high solubility across a range of common laboratory solvents. More purified product could likely be recovered by further concentration of the supernatant and collection of additional crops of crystals. MALDI ToF MS *m/z* (rel intensity): 1669.6 ([M]⁺, 100), 1238.4 ([M – GdCp*₂]⁺, 75), 812.3 ([M – 2GdCp*₂]⁺, 23). Isotope patterns were complex and centered around these peaks. IR (neat, cm^{–1}): 3065w, 2966w, 2892w, 2853w, 1557m, 1465m, 1430m, 1400m, 1377m, 1306s, 1239s, 1190s, 1147s, 1134s, 1076s, 1045m, 1027m, 999m, 931m, 895s, 783s, 728s, 622s. Anal. Calcd. For C₈₄H₁₀₂N₆Gd₃: C, 60.50; H, 6.17; N, 5.04. Found: C, 60.09; H, 6.06; N, 4.91.

Cp*₆Tb₃(μ₃-HAN) (2). Analogous to the synthesis of **1**, HAN (0.100 g, 0.26 mmol) was added to Cp*₂Tb(BPh₄) (0.584 g, 0.78 mmol, 3 eq) in THF (8 mL) and subsequently reduced with KC₈ (0.106 g, 0.78 mmol, 3 eq). Solvent removal was followed by dissolution in toluene (15 mL), filtration, and concentration of the filtrate to yield crude **2** as a blackish-red solid (0.178 g, 41% yield). Black, block-shaped crystals of **2** were grown from a concentrated THF solution stored at –30 °C over 5 d. A second crop of crystals was grown from the supernatant over a subsequent 5 d at –30 °C and was combined with the first to yield pure **2** (0.015 g, 4% overall yield). As for **1**, more purified product could likely be recovered by further concentration of the supernatant and collection of additional crops of crystals. MALDI ToF MS *m/z* (rel intensity): 1671.6 ([M]⁺, 100), 1242.4 ([M – TbCp*₂]⁺, 62), 813.3 ([M – 2TbCp*₂]⁺, 20). Isotope patterns were complex and centered around these peaks. IR (neat, cm^{–1}): 3065w, 2965w, 2888w, 2849m, 1557m, 1467m, 1448m, 1426m, 1355m, 1310s, 1250m, 1196m, 1149s, 1134s, 1069m, 1024m, 895m, 785s, 734s, 622s. Anal. Calcd. For C₈₄H₁₀₂N₆Tb₃: C, 60.32; H, 6.15; N, 5.02. Found: C, 60.51; H, 6.33; N, 4.96.

Cp*₆Dy₃(μ₃-HAN) (3). Analogous to the synthesis of **1**, HAN (0.100 g, 0.26 mmol) was added to Cp*₂Dy(BPh₄) (0.587 g, 0.78 mmol, 3 eq) in THF (8 mL) and subsequently reduced with KC₈ (0.106 g, 0.78 mmol, 3 eq). Solvent removal was followed by dissolution in toluene (15 mL), filtration, and concentration of the filtrate to yield crude **3** as a blackish-red solid (0.193 g, 44% crude yield). Black, block-shaped crystals of **3** were grown from a concentrated THF solution stored at –30 °C over 5 d. A second crop of crystals was grown from the supernatant over a subsequent 5 d at –30 °C and was combined with the first to yield pure **3** (0.025 g, 6% overall yield). As for **1**, more purified product could likely be recovered by further concentration of the supernatant and collection of additional crops of crystals. MALDI ToF MS *m/z* (rel intensity): 1683.6 ([M]⁺, 22), 1250.4 ([M – DyCp*₂]⁺, 100), 818.3 ([M – 2DyCp*₂]⁺, 22). Isotope patterns were complex and centered around these peaks. IR (neat, cm^{–1}): 3065w, 2970w, 2901w, 2853m,

1557m, 1467m, 1437w, 1439m, 1305m, 1243m, 1192m, 1149s, 1134s, 1076s, 1050m, 1028m, 895m, 785m, 742s, 729s, 626s, 613s. Anal. Calcd. For $C_{84}H_{102}N_6Dy_3$: C, 59.94; H, 6.11; N, 4.99. Found: C, 60.28; H, 5.97; N, 5.12.

2.6.2 Crystallographic Data

Data collection for **2** was performed on a single crystal coated with Paratone-N oil and mounted on a Kapton loop. The crystal was frozen at 100 K under a stream of N_2 by an Oxford Cryosystems Cryostream during measurements. Data was collected using a Bruker APEX II QUAZAR diffractometer equipped with a Microfocus Sealed Source (Incoatec $I\mu S$; Mo- $K\alpha$, $\lambda = 0.71073$ Å) and APEX-II detector. Raw data were integrated and Lorentz and polarization corrections were calculated and applied in Bruker APEX3.⁵ Absorption correction was calculated and applied using SADABS.⁶

Data for **3** was collected on a single crystal coated in Paratone-N oil and mounted on a MiTeGen loop at Beamline 11.3.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory using synchrotron radiation ($\lambda = 0.7749$ Å) with a Bruker PHOTON100 CMOS detector on a Bruker AXS D8 diffractometer through a combination of shutterless 4° phi and 1° omega scans. Data was collected on a single crystal coated with Paratone-N oil and mounted on a MiTeGen loop. The crystal was frozen at 100 K under a stream of N_2 by an Oxford Cryosystems Cryostream during measurements. Raw data was integrated and Lorentz and polarization corrections were calculated and applied in Bruker APEX3.⁷ Absorption correction was calculated and applied using SADABS.⁶

Space group assignments for all structures were determined by examination of systematic absences, E-statistics and successive refinement of structures. Structures were solved using ShelXT, a direct methods program, and refined by least-squares refinement on F^2 , followed by difference Fourier synthesis using ShelXL as implemented within the software package OLEX2.⁸⁻¹⁰ All hydrogen atoms were included in the final structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Thermal parameters were refined anisotropically for all non-hydrogen atoms. Disorder of the pentamethylcyclopentadienyl ligands in both **2** and **3** and of residual solvent in **3** required distance and displacement parameter restraints. Residual solvent was also found to be disordered within the crystal of **2**, but could not be modeled due to the low resolution of the data set (0.99 Å). Consequently, the unassigned electron density was accounted for using SQUEEZE as implemented in the PLATON interface.^{11,12} In addition, the low resolution of the data set of **2** and the ligand disorder in **3** gave rise to a checkCIF B alert. Responses addressing these alerts have been included in the CIFs and can be read in reports generated by checkCIF.

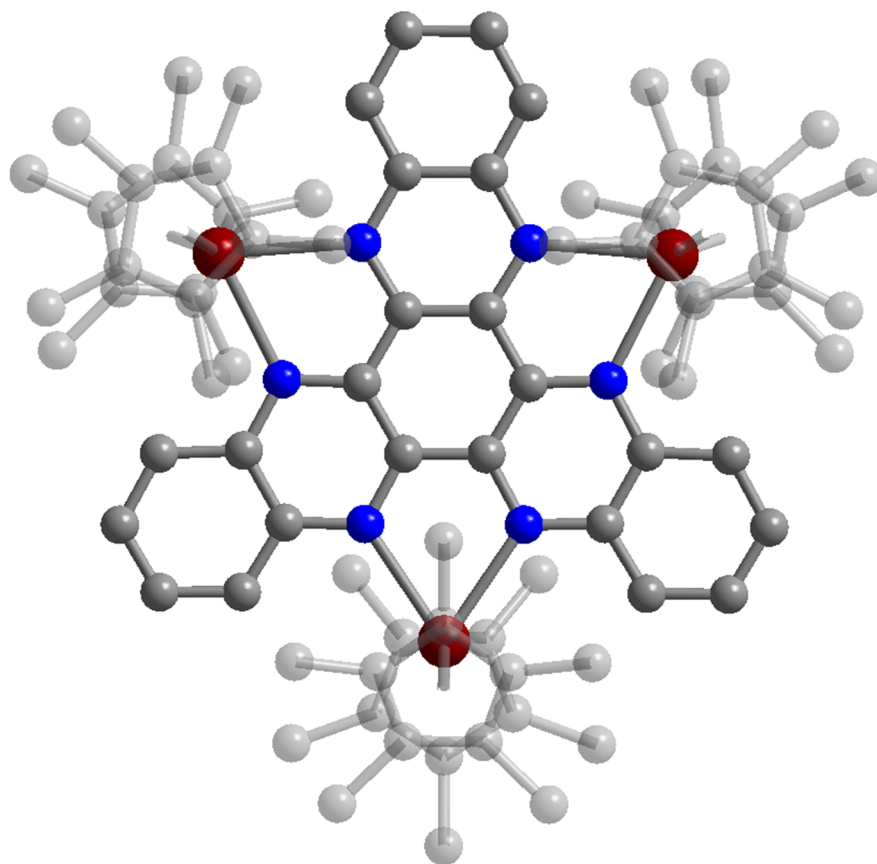


Figure S2.1. Crystal structure of **2**. Red, blue, and gray spheres represent Tb, N and C atoms respectively. H atoms are omitted for clarity.

Common Name	Cp*₆Tb₃(μ₃-HAN)	
Empirical Formula	C ₈₄ H ₁₀₂ N ₆ Tb ₃	
Formula Weight	1672.47	
Temperature	100 (2) K	
Wavelength	MoKα (λ = 0.71073)	
Crystal System	Orthorhombic	
Space Group	<i>Pnma</i>	
Unit Cell Dimensions	<i>a</i> = 17.8564(5) Å <i>b</i> = 23.6812(7) Å <i>c</i> = 18.0010(6) Å	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
Volume	7611.9(4) Å ³	
Z	4	
Density (calculated)	1.459 g/cm ³	
Absorption Coefficient	2.782 mm ⁻¹	
F(000)	3372	
Crystal Size	0.16 x 0.06 x 0.02 mm ³	
Theta range for data collection	1.421 to 21.148°	
Index Ranges	-18 ≤ <i>h</i> ≤ 18, -23 ≤ <i>k</i> ≤ 23, -18 ≤ <i>l</i> ≤ 17	
Reflections Collected	70672	
Independent Reflections	4268 [R _{int} = 0.0814]	
Completeness to theta = 25.00°	99.2%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.946 and 0.767	
Refinement method	Full-matrix least-squares on F ²	
Data/ restraints / parameters	4268/711/578	
Goodness-of-fit on F²	1.058	
Final R indices [I>2σ(I)]	R ₁ = 0.0622, wR ₂ = 0.1390	
R indices (all data)	R ₁ = 0.0921, wR ₂ = 0.1665	
Largest diff. peak and hole	1.951/-2.045 electrons/ Å ³	
Resolution	0.99 Å	

Table S2.1. Crystal data and structure refinement of **2**.

Common Name	Cp*₆Dy₃(μ₃-HAN)	
Empirical Formula	C _{89.27} H ₁₁₀ Dy ₃ N ₆ O _{0.29}	
Formula Weight	1759.20	
Temperature	100(2) K	
Wavelength	Synchrotron ($\lambda = 0.7749$)	
Crystal System	Orthorhombic	
Space Group	<i>Pnma</i>	
Unit Cell Dimensions	$a = 17.7260(6) \text{ \AA}$ $b = 23.7699(8) \text{ \AA}$ $c = 17.9016(6) \text{ \AA}$	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
Volume	7542.8(4) $\text{\AA}^3$	
Z	4	
Density (calculated)	1.549 g/cm ³	
Absorption Coefficient	3.737 mm ⁻¹	
F(000)	3552	
Crystal Size	0.0536 x 0.0536 x 0.0179 mm ³	
Theta range for data collection	2.481 to 30.690	
Index Ranges	$-23 \leq h \leq 23, -31 \leq k \leq 31, -23 \leq l \leq 23$	
Reflections Collected	108638	
Independent Reflections	9222 [$R_{\text{int}} = 0.0635$]	
Completeness to theta = 25.00°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.936 and 0.863	
Refinement method	Full-matrix least-squares on F^2	
Data/ restraints / parameters	9222/265/569	
Goodness-of-fit on F^2	1.074	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0403, wR_2 = 0.0723$	
R indices (all data)	$R_1 = 0.0685, wR_2 = 0.0853$	
Largest diff. peak and hole	2.829/−1.701 electrons/ $\text{\AA}^3$	
Resolution	0.76 $\text{\AA}$	

Table S2.2. Crystal data and structure refinement of **3**.

2.6.3 Magnetic Measurements

Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. Dc magnetic susceptibility measurements were performed at temperatures ranging from 2 to 300 K under applied fields of 1, 5, and 10-kOe (0.1, 0.5, and 1 T). Ac magnetic susceptibility measurements were performed using a 4 Oe ac switching field and zero applied dc field. All data were corrected for diamagnetic contributions from the core diamagnetism and for the diamagnetism of the eicosane used to suspend the sample, estimated using Pascal's constants to give corrections of $\chi_{\text{dia}} = -0.000891$ emu/mol, -0.000887 emu/mol, and -0.000887 emu/mol for **1**, **2**, and **3**, respectively.

Fits to the dc susceptibility data for **1** were performed using PHI,¹³ using the spin-only Hamiltonian $\hat{H} = -2J_{\text{Gd-rad}}\hat{S}_{\text{rad}}(\hat{S}_{\text{Gd}(1)} + \hat{S}_{\text{Gd}(2)} + \hat{S}_{\text{Gd}(3)})$, where $J_{\text{Gd-rad}}$ represents the magnetic exchange coupling between each Gd(III) ion and the organic radical spin. Contributions for temperature-independent paramagnetism and intermolecular coupling were included, as described in the main text. Simultaneous fits to the ac susceptibility data for **2** and **3** were obtained using a generalized Debye model, which relates χ_M' and χ_M'' to isothermal susceptibility (χ_T), adiabatic susceptibility (χ_S), relaxation time (τ), and a parameter representing the distribution of relaxation times (α).¹⁴ All data fit to α values in the range of $0.23 \leq \alpha \leq 0.42$ for **2** and $0.078 \leq \alpha \leq 0.31$ for **3**.

Magnetic samples were prepared by adding crystalline powder (4.4 mg of **1**, 7.1 mg of **2**, and 11.8 mg of **3**) to a 7 mm quartz tube. A layer of eicosane was added to the samples (4.6 mg for **1**, 11.7 mg for **2**, and 19.0 mg for **3**) to provide good thermal contact between the sample and the bath and to prevent crystallite torquing. The tubes were fitted with Teflon sealable adapters, evacuated using a glovebox vacuum pump, and then flame sealed under vacuum. After flame-sealing, the eicosane was melted in a 40 °C water bath.

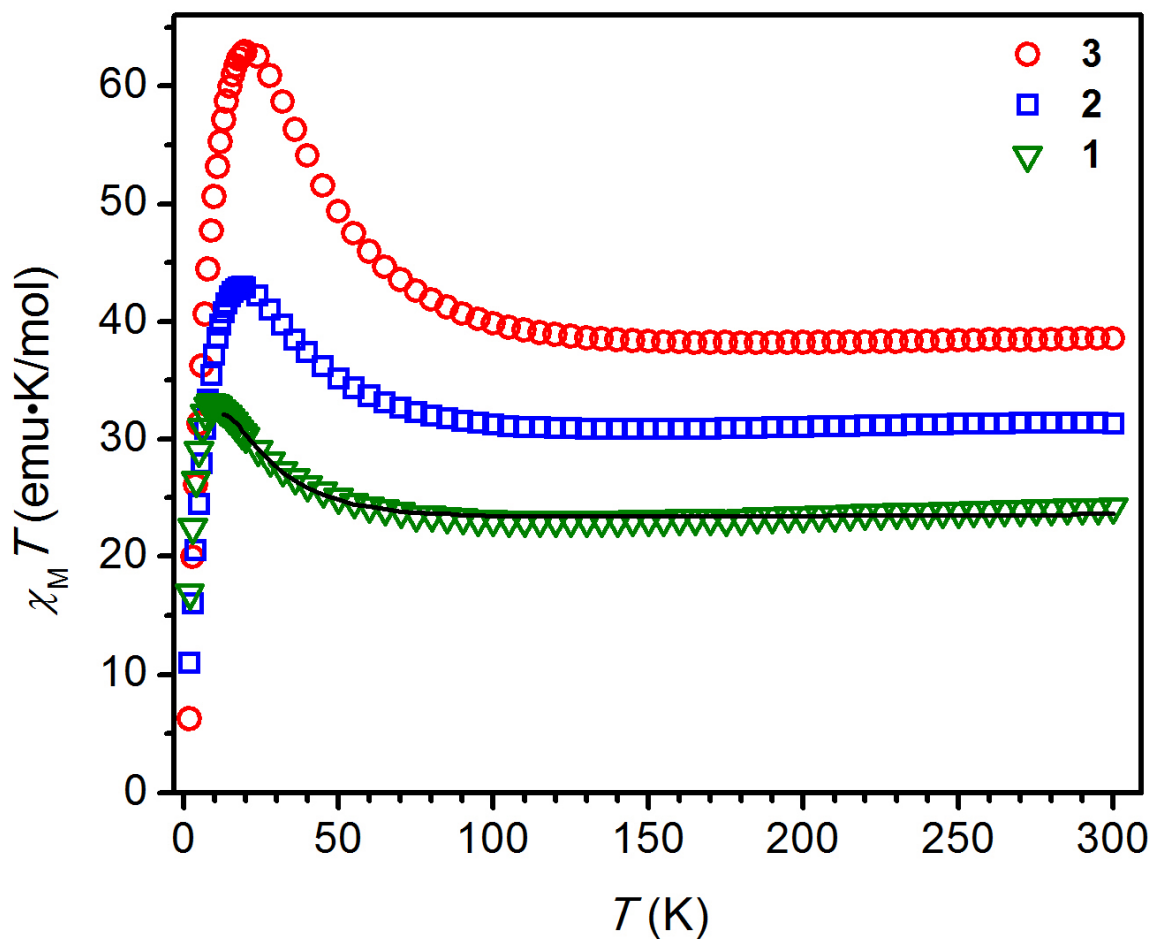


Figure S2.2. Dc magnetic susceptibility measurements for **1–3** under an applied dc magnetic field of 10-kOe. The black line represents a fit to the data, as described in the magnetic measurements section of the SI. Only data above 13 K was fit, due to contributions from the Zeeman effect below this temperature, yielding $J_{\text{Gad-rad}} = -4.8 \text{ cm}^{-1}$ and a weak intermolecular coupling constant of $J' = -0.004 \text{ cm}^{-1}$.

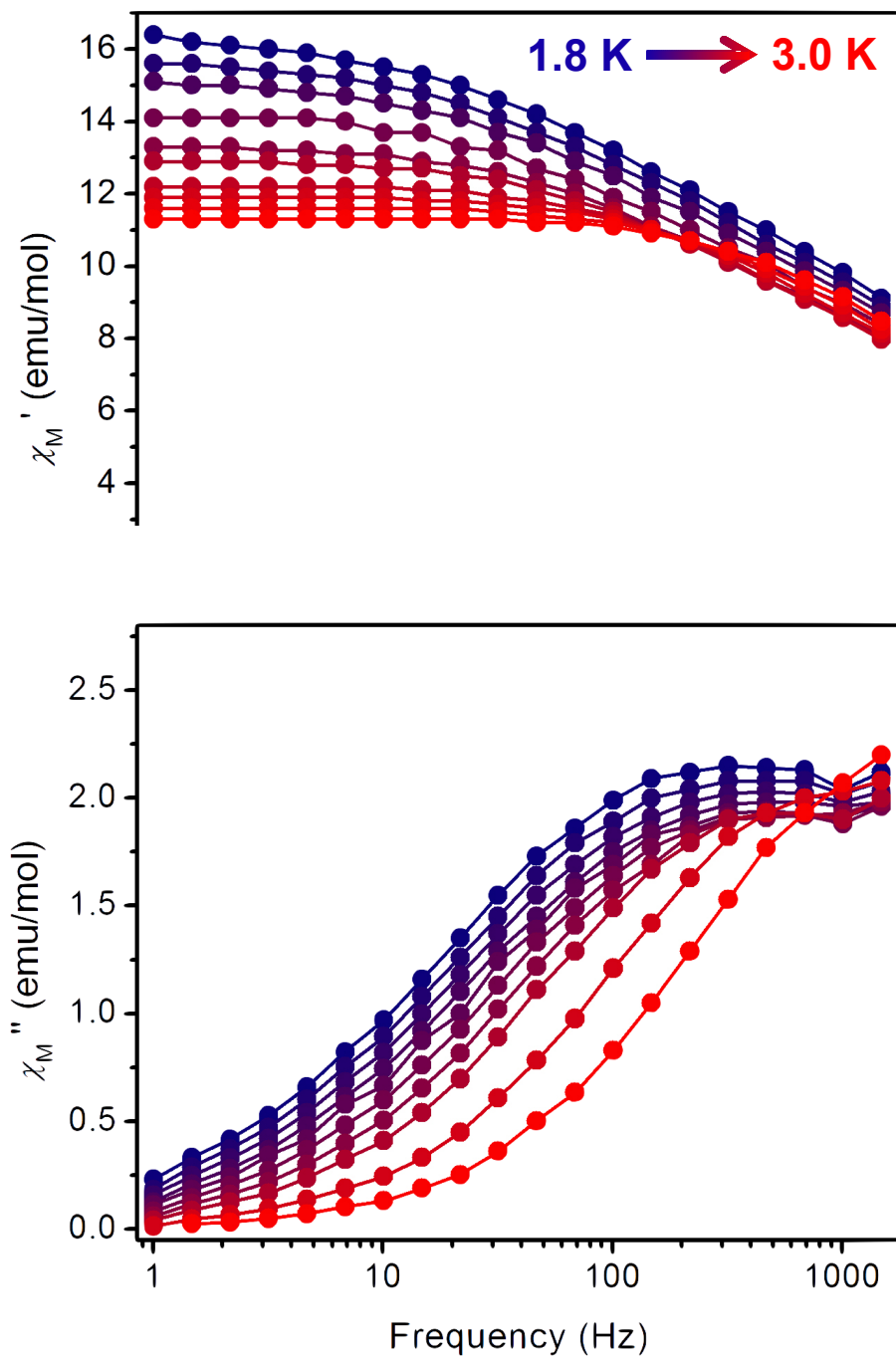


Figure S2.3. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **2** under zero applied dc field at frequencies from 1–1500 Hz and temperatures from 1.8–3.0 K. The colored lines are guides for the eye.

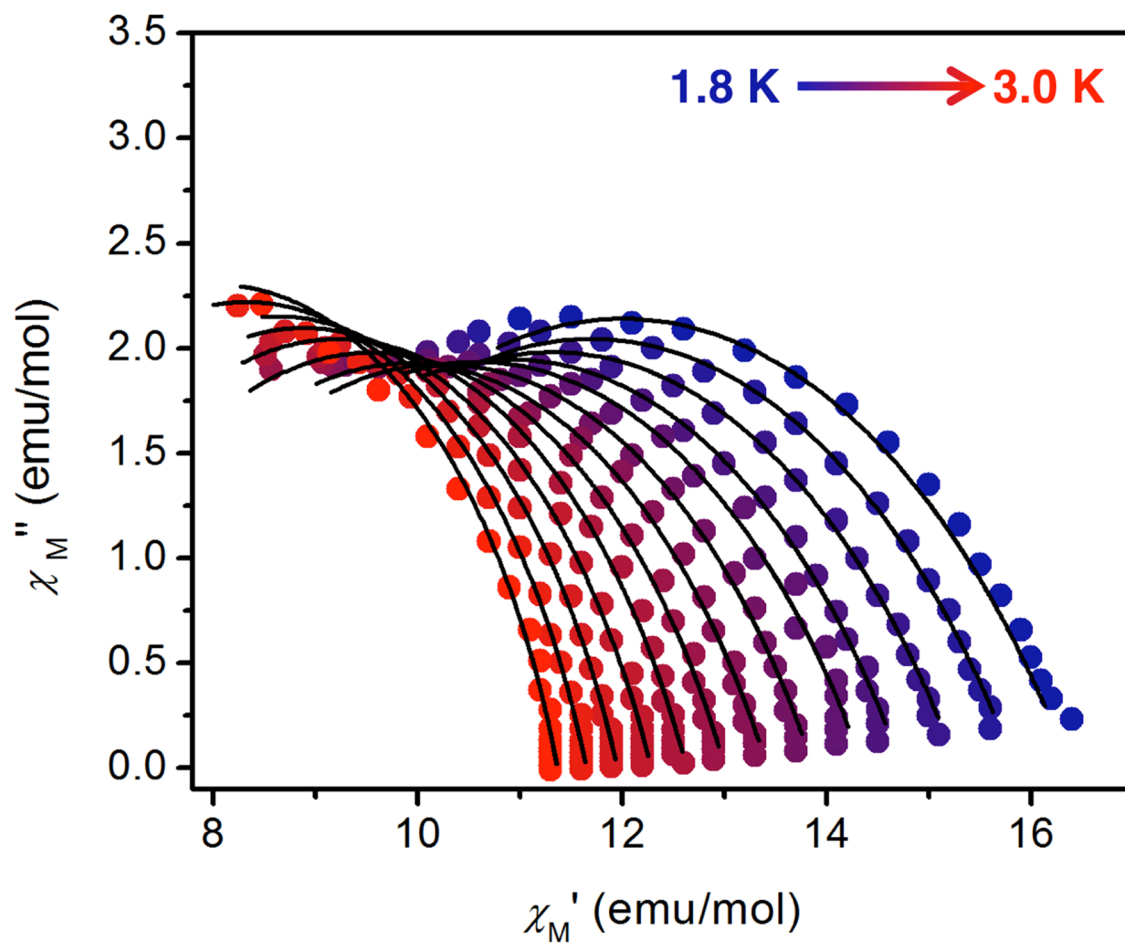


Figure S2.4. Cole-Cole plot for **2**. The black lines represent fits to the data using a generalized Debye model, from which a value for τ at each temperature was extracted.

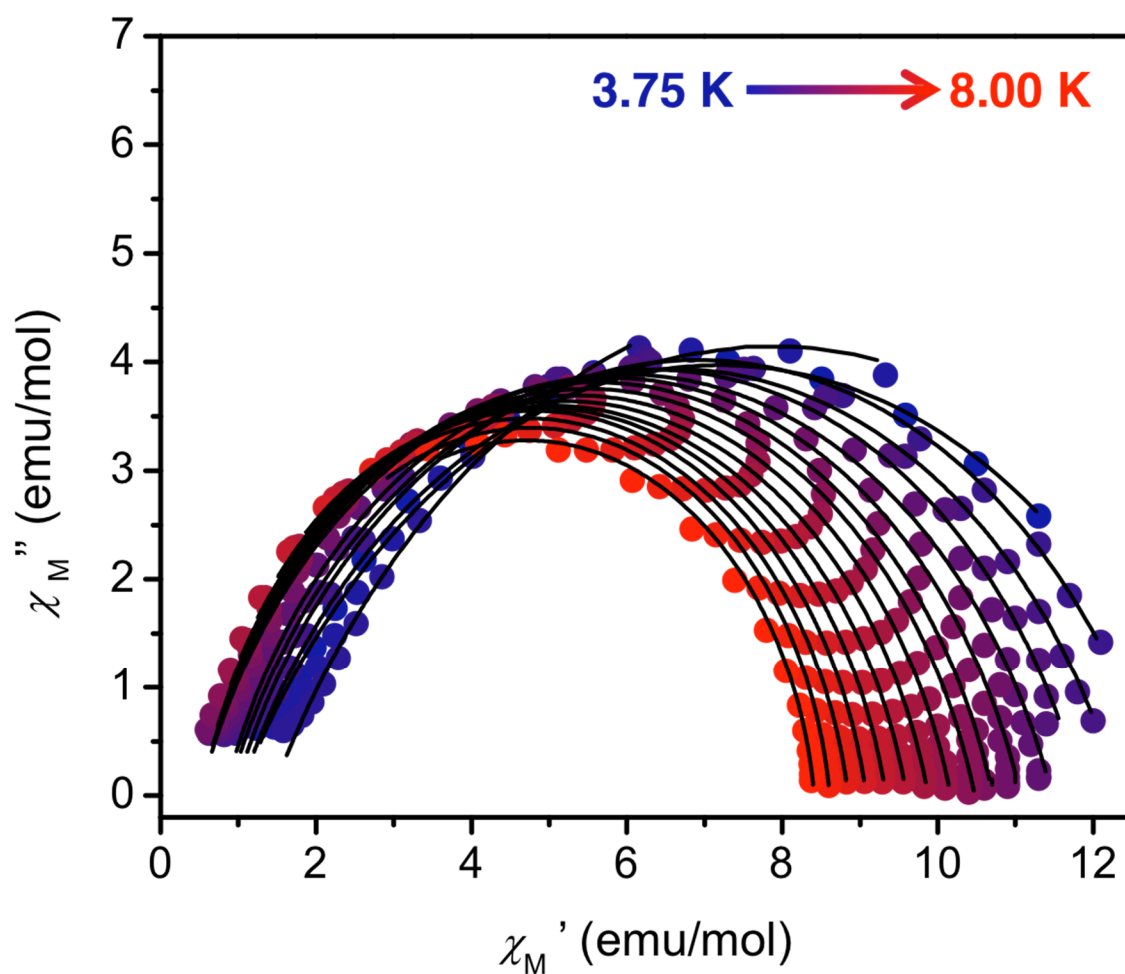


Figure S2.5. Cole-Cole plot for **3**. The black lines represent fits to the data using a generalized Debye model, from which a value for τ at each temperature was extracted.

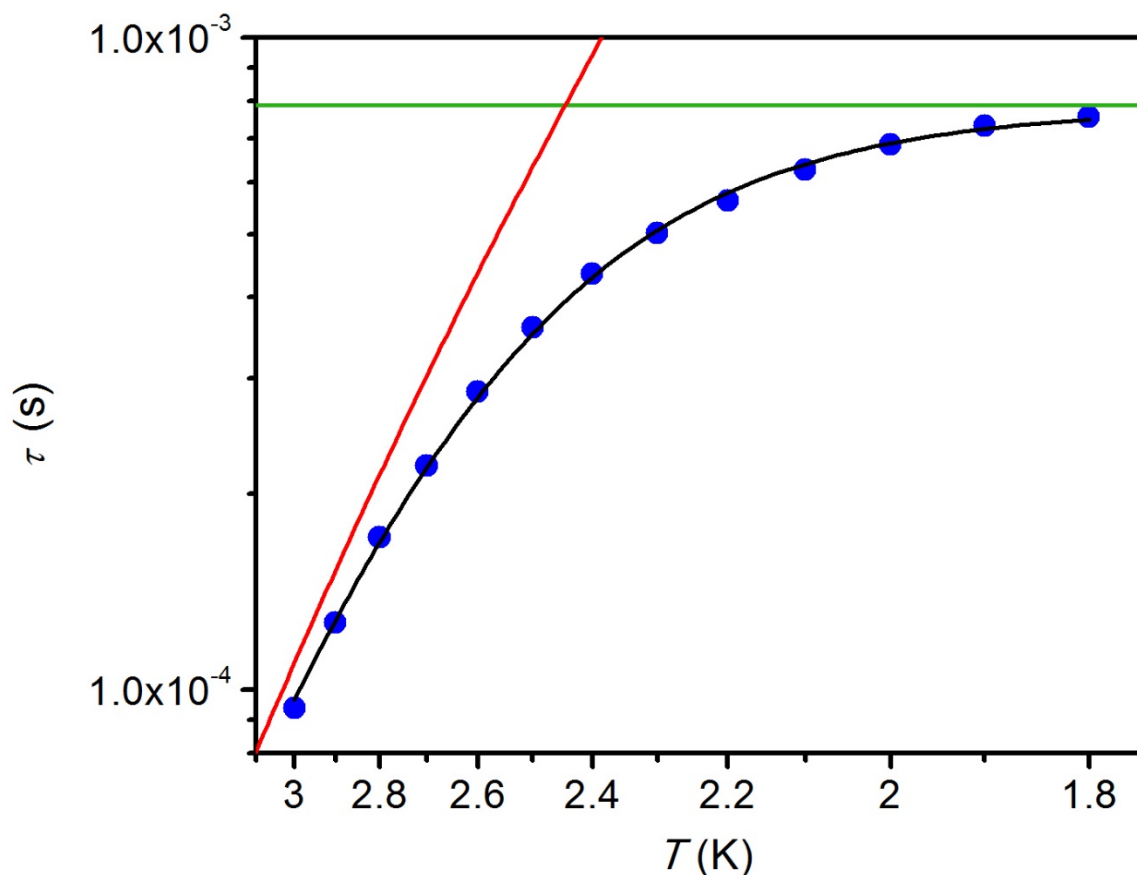


Figure S2.6. Arrhenius plot of the magnetic relaxation time (τ) on a log scale versus temperature on an inverse scale for **2**. Relaxation times extracted from ac magnetic susceptibility measurements are plotted in blue. The black line represents a fit to the data that combines quantum tunneling and Raman relaxation processes, which are individually plotted as green and red lines, respectively. In this fit, $\tau_{\text{tunnel}} = 7.89 \times 10^{-4}$ s, $C = 0.23 \text{ s}^{-1}\text{K}^{-n}$, and $n = 9.6$.

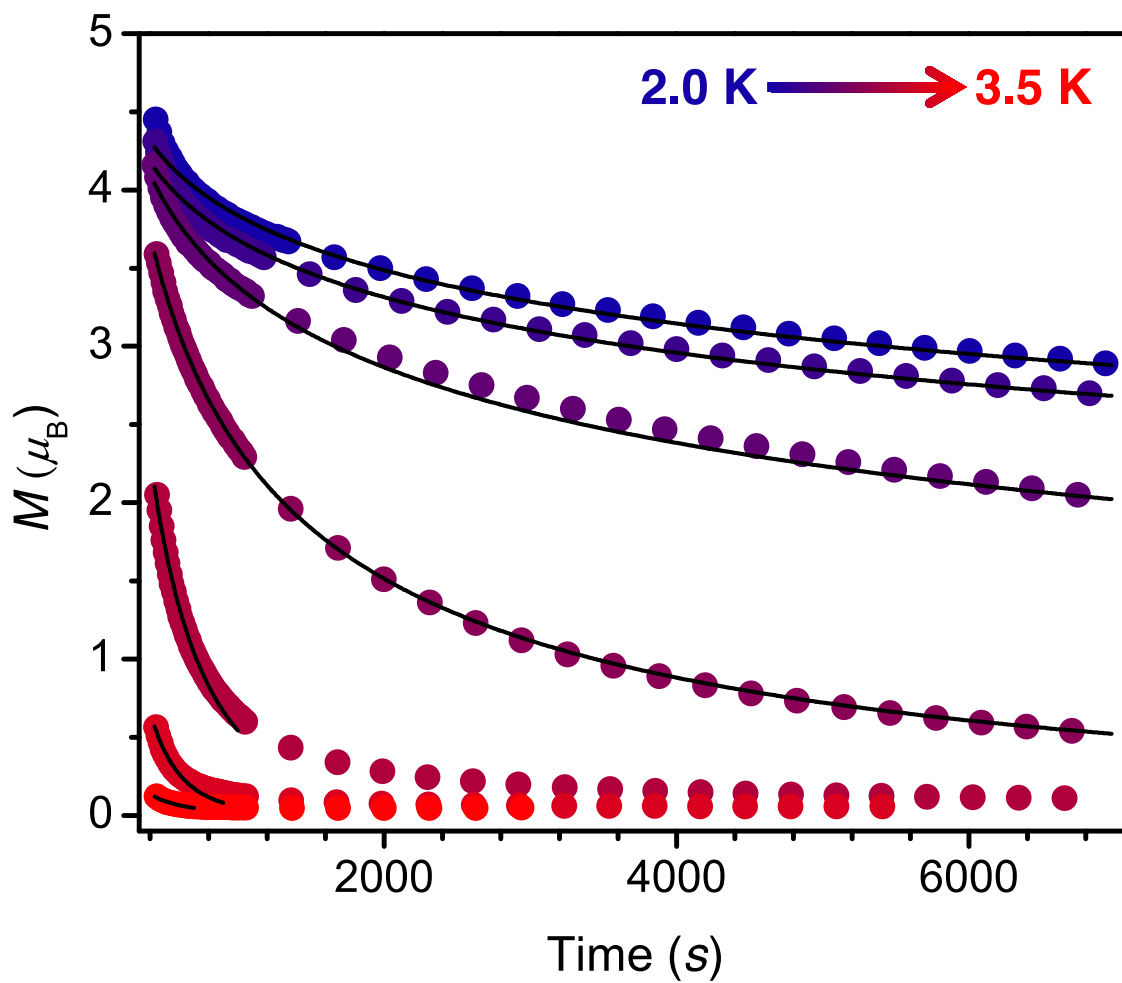


Figure S2.7. Dc magnetic relaxation measurements for **3** from 2.0 to 3.5 K. Black lines represent the fits to the data using stretched exponential functions which were used to extract τ , as discussed in the main text.

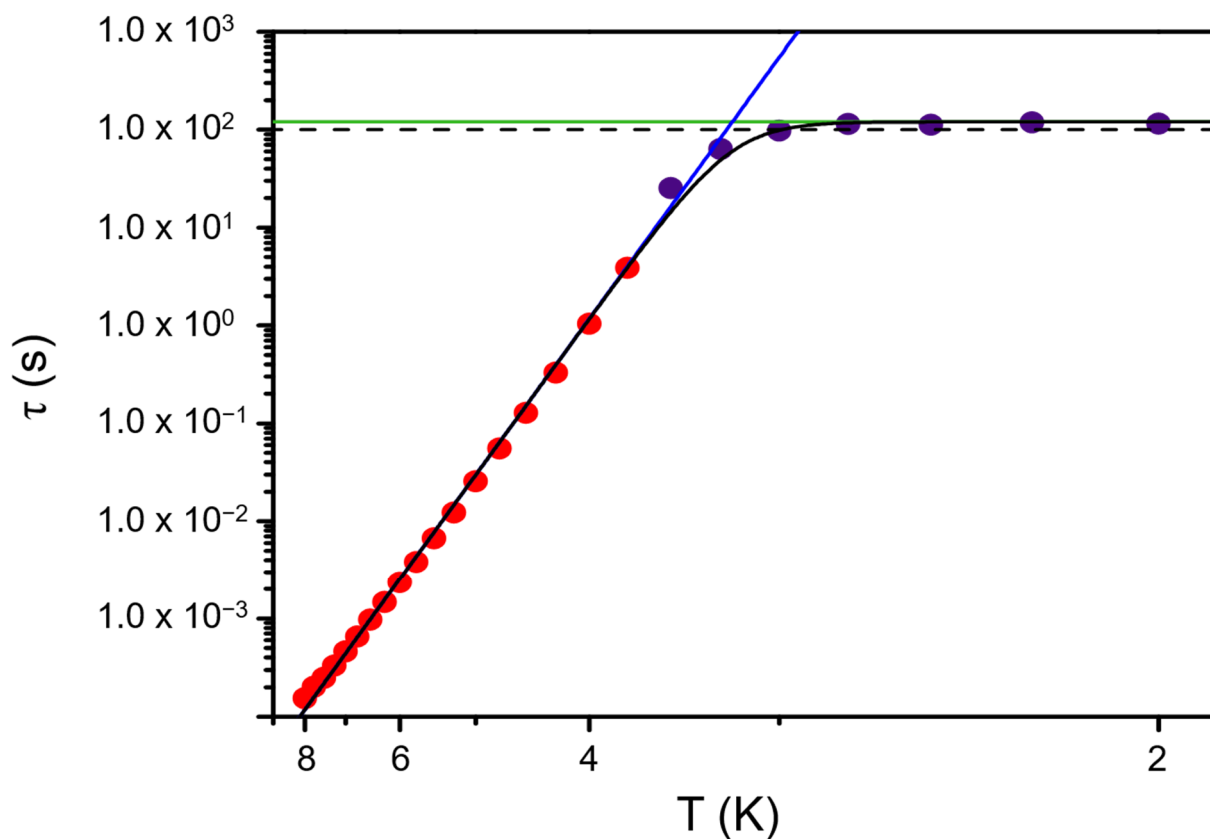


Figure S2.8. Arrhenius plot of the magnetic relaxation time (τ) on a log scale versus temperature on an inverse scale for **3**. Relaxation times extracted from ac magnetic susceptibility measurements are plotted in red; relaxation times extracted from dc magnetic relaxation measurements are plotted in purple. The black line represents a fit to the data that combines quantum tunneling and Orbach relaxation processes, which are individually plotted as green and blue lines, respectively. In this fit, $\tau_{\text{tunnel}} = 1.20 \times 10^2$ s, $\tau_0 = 1.18 \times 10^{-8}$, and $U_{\text{eff}} = 51.2$ cm $^{-1}$. The intersection of the black fit line and the dashed line denotes the hundred-second blocking temperature.

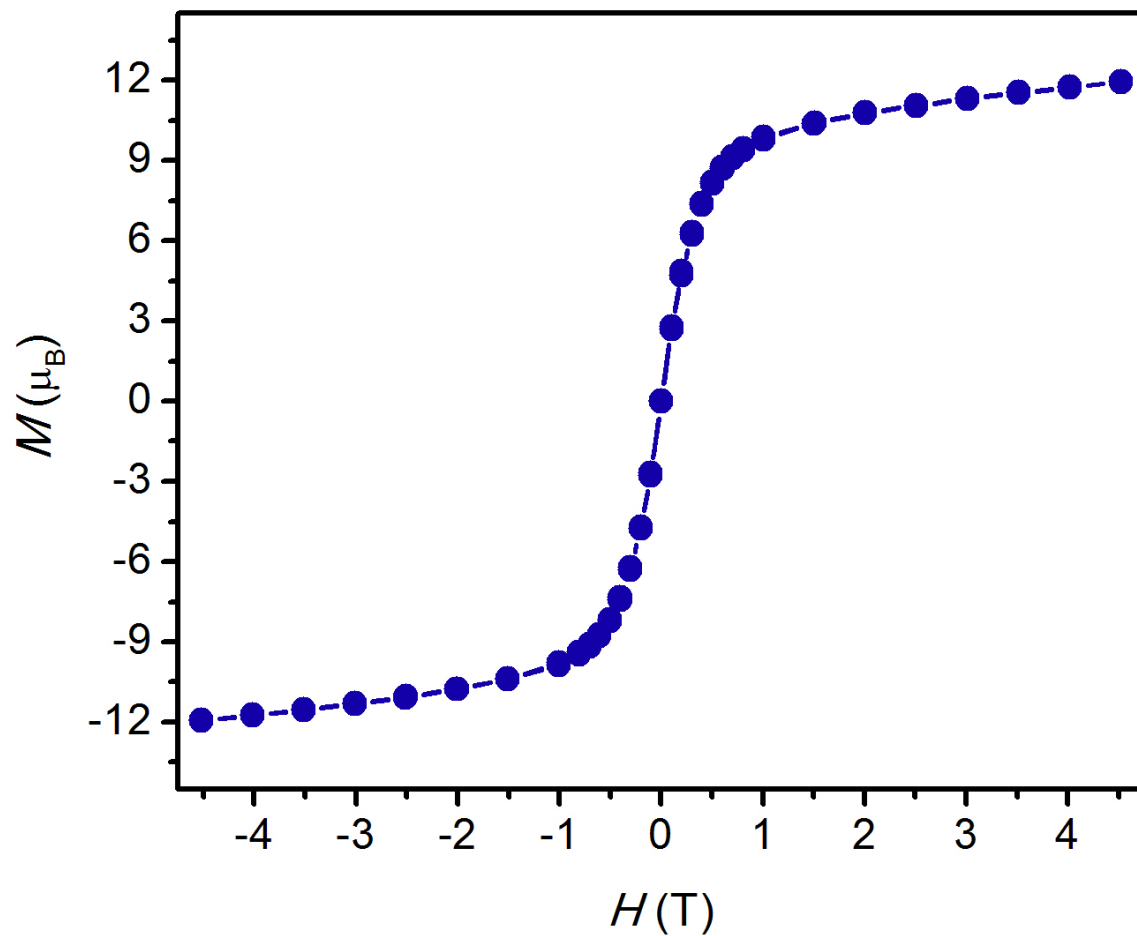


Figure S2.9. Hysteresis measurement of **2** at 1.8 K at an average scan rate of 2 mT/s from -1 to 1 T and a scan rate of 10 mT/s from 1 to 5 T and -1 to -5 T.

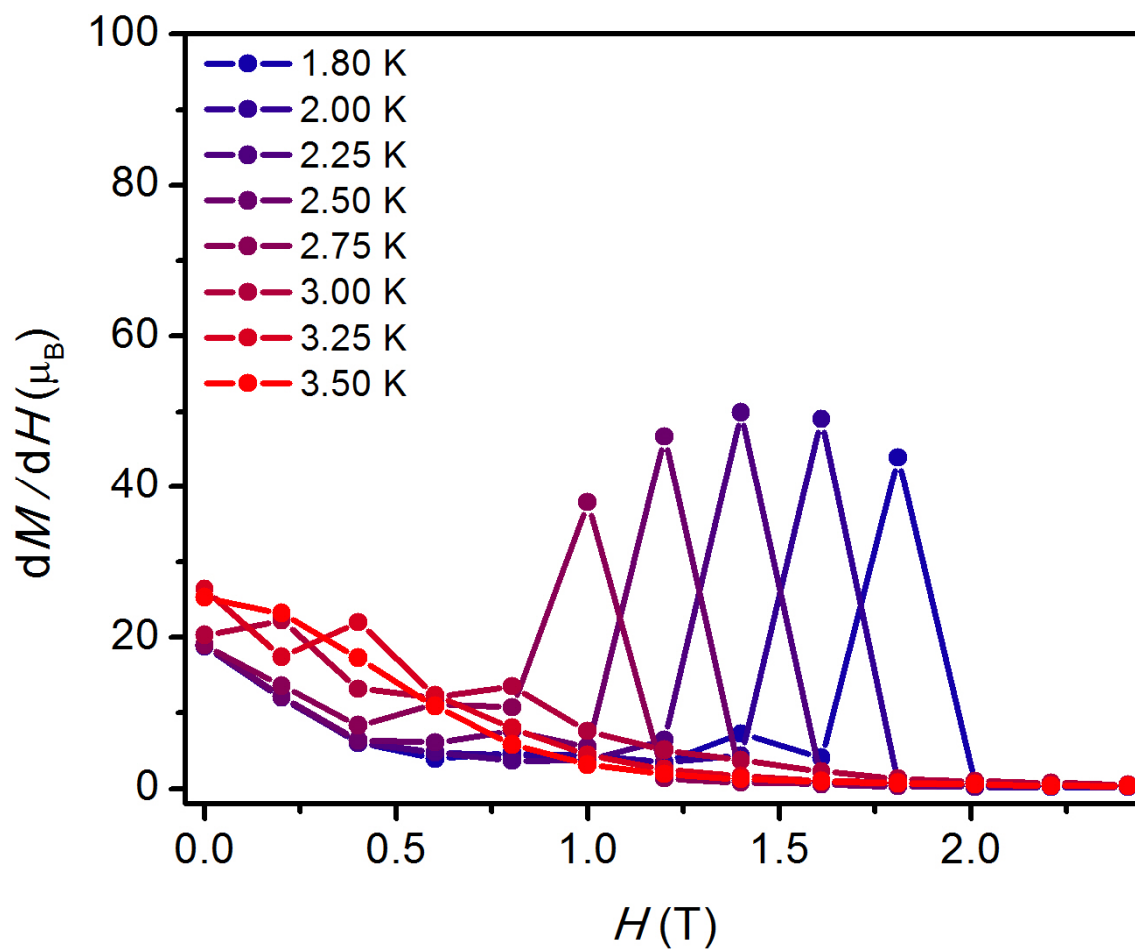


Figure S2.10. Plot of dM/dH versus H for the magnetic hysteresis data for **3** collected from 1.8 to 3.5 K. Peaks from 2.75 to 1.8 K represent the tunneling step observed in each of the respective hysteresis measurements. The temperature variance of these peaks, which shift to higher field at lower temperatures, is indicative of thermally assisted quantum tunneling of the magnetization.

2.6.4 Supplementary Information References

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Chapter 3: Tuning Exchange Coupling and Magnetic Relaxation via Ligand Substitution in a Series of Radical-Bridged Lanthanide Complexes

C. A. Gould, E. Mu, V. Vieru, L. E. Darago, K. Chakarawet, M. I. Gonzalez, S. Demir, L. F. Chibotaru, J. R. Long.^a

3.1 Introduction

Single-molecule magnets display properties typically associated with bulk magnetic materials, such as magnetic hysteresis.¹ This behavior is molecular in origin, and it arises from a bistable magnetic ground state with a thermal barrier to inversion of the magnetic moment (U_{eff}).^{1a} These molecules have garnered substantial interest for applications in information storage or spin-based computing, but their practical implementation is currently precluded by low operating temperatures.²

Over the past decade, most major advances in the field toward increasing the operating temperature of single-molecule magnets have been achieved with lanthanide-based systems.³ Indeed, magnetic hysteresis at temperatures up to 80 K was recently demonstrated in the metallocene complex $[\text{DyCp}^*\text{Cp}^{\text{iPr5}}]^+$ (Cp^* = pentamethylcyclopentadienyl; Cp^{iPr5} = penta-(*iso*-propyl)cyclopentadienyl).^{3g} This and other breakthroughs have been facilitated by the use of empirical or theoretical models that describe the relationship between the molecular or electronic structure of a lanthanide complex and its magnetic properties. For instance, models have been developed for mononuclear lanthanide complexes that describe how coordination geometry can be leveraged to maximize U_{eff} and how molecular symmetry or rigidity can mitigate deleterious through-barrier relaxation processes.⁴ Studies conducted on systematic series of complexes have been crucial in constructing these models and in verifying their predictions.⁵ For example, analysis of $[\text{LnPc}_2]^-$ (Ln = Tb, Dy, Ho, Er, Tm, Yb) demonstrates that an axial ligand field leads to large U_{eff} values for oblate ions (e.g., Tb^{3+} , Dy^{3+}) and small U_{eff} values for prolate ions (e.g., Er^{3+} , Tm^{3+}).^{5a} Additionally, comparison of $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{py})_5]^+$ and $[\text{Dy}(\text{L})_2(\text{py})_5]^+$ (L = *S*-(*-*)-1-phenylethoxide) illustrates that increasing molecular rigidity through facilitating intramolecular C–H $\cdots\pi$ interactions can reduce the rate of quantum tunneling of the magnetization.^{5b}

Extensive research has also focused on developing models to describe the magnetic behavior of strongly coupled multinuclear lanthanide complexes, which display some of the highest operating temperatures yet reported for single-molecule magnets, surpassed only by $[\text{Dy}(\text{Cp}^{\text{R}})_2]^+$ molecules.^{3c,3d,6} Analyses of systematic series of complexes have again proven instrumental in developing models and have produced clear design criteria for maximizing desirable magnetic properties.^{6a,7} For instance, studies have demonstrated that both the single-ion anisotropy of the individual metal centers in a complex and the magnetic exchange interactions between them must be increased in order to achieve higher operating temperatures.^{6a,7} One promising method to achieve strong exchange coupling in lanthanide complexes is to bridge metal ions via open-shell ligands, which can facilitate direct exchange pathways. Indeed, organic radicals (e.g., 2,2'-bipyrimidine⁻), inorganic radicals (e.g., N_2^{3-}), and open-shell metalloligands (e.g., $\text{Cu}(\text{satn})\text{OH}$; satn = *N*-(3-aminopropyl)salicylaldiminato) have all been shown to engage in strong exchange

^a C.A.G. synthesized the compounds and collected and interpreted the magnetic data. E.M. assisted in synthesis and interpretation of the magnetic data. L.E.D. and S.D. assisted in the interpretation of the magnetic data. K.C. and M.I.G. solved and refined the crystal structure data. V.V. and L.F.C. performed *ab initio* calculations. C.A.G. and J.R.L. wrote the manuscript and all authors contributed to editing it.

coupling interactions with lanthanide ions.⁸ Organic radicals represent a particularly appealing class of bridging ligand due to their high degree of tunability; however, few studies have yet investigated the effect of ligand substituents on the strength of exchange coupling interactions in radical-containing lanthanide complexes.⁹ We identified $[(\text{Cp}^*\text{Ln})_2(\mu\text{-bpym})][\text{BPh}_4]$ ($\text{Ln} = \text{Gd}, \text{Dy}$; $\text{bpym} = 2,2'$ -bipyrimidine) as a promising candidate for such a study, as it possesses the highest operating temperature yet reported for a single-molecule magnet bridged by an organic radical.^{8a} We hypothesized that functionalizing the bpym ligand at the 5 and 5' carbons could modulate the spin density in the ligand SOMO, which shows large coefficients at those positions,¹⁰ allowing the strength of magnetic exchange interactions to be tuned and potentially increased. Examining the magnetic properties of the resulting series of molecules would also provide a valuable opportunity to systematically investigate the relationship between the strength of magnetic coupling interactions and the rate of magnetic relaxation processes.

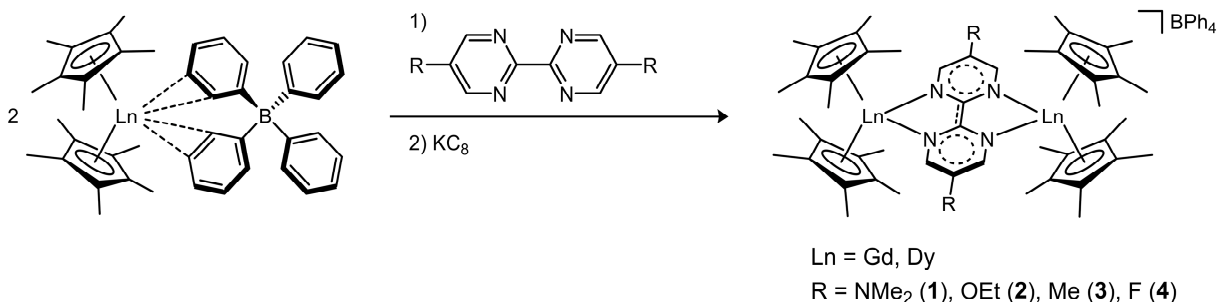
Herein, we report the synthesis and detailed magnetic characterization of the series $[(\text{Cp}^*\text{Ln})_2(\mu\text{-}5,5'\text{-R}_2\text{bpym})][\text{BPh}_4]$ ($\text{R} = \text{NMe}_2$ (**1**), OEt (**2**), Me (**3**), F (**4**); $\text{Ln} = \text{Gd}, \text{Dy}$). Modification of the substituent on the radical anion 5,5'- R_2bpym ligand induces dramatic changes in intramolecular exchange coupling interactions, with electron-donating and -withdrawing substituents decreasing and increasing the magnitude of the exchange coupling constant ($J_{\text{Ln-rad}}$), respectively. The strength of the exchange coupling interaction impacts single-molecule magnet behavior in the dysprosium derivatives, with stronger exchange coupling promoting larger thermal barriers to magnetic relaxation, open magnetic hysteresis loops at higher temperatures, and lower rates of through-barrier relaxation. Notably, an empirical correlation can be derived from the experimental U_{eff} values for **1-Dy** through **4-Dy** and $|J_{\text{Gd-rad}}|$ of the corresponding gadolinium derivative. This correlation can be extended to other radical-bridged dysprosium complexes in the literature and offers clear design principles to increase U_{eff} and the operating temperature for molecules in this class.

3.2 Results and Discussion

The ligand 2,2'-bipyrimidine (bpym) is ubiquitous in coordination chemistry; however, few symmetric 5,5'- R_2bpym derivatives have been synthesized to date. Indeed, 5,5'- R_2bpym molecules have only yet been reported for alkyl, aryl, ether, and bromine substituents.¹¹ Bpym derivatives are typically synthesized via Cu- or Ni-mediated coupling reactions, and thus we first targeted 5,5'- R_2bpym by Ni-catalyzed homocoupling of the corresponding 5-R-2-chloropyrimidine.¹² This approach furnished 5,5'- R_2bpym derivatives with electron donating substituents ($\text{R} = \text{Me}, \text{OEt}, \text{NMe}_2$) in isolated yields of 33-37%, while electron-deficient derivatives ($\text{R} = \text{F}, \text{CF}_3$) could not be isolated. Attempts to synthesize electron-deficient 5,5'- R_2bpym derivatives via Cu-mediated homocoupling reactions were also unsuccessful. These results are consistent with reports on the synthesis of 5,5'- R_2bpy ($\text{bpy} = 2,2'$ -bipyridine), which found lower yields for the Ni-catalyzed homocoupling of 5-R-2-chloropyridine substrates bearing electron-withdrawing substituents.¹³ We next turned to a Stille coupling approach,¹⁴ and we were pleased to observe that the Pd-mediated coupling of 5-fluoro-2-tributylstannylpyrimidine and 5-fluoro-2-chloropyrimidine produced 5,5'- F_2bpym in 57% isolated yield. Although we were unable to isolate 5,5'-(CF_3) $_2\text{bpym}$ by an analogous route, the Pd-catalyzed coupling of 5-trifluoromethyl-2-chloropyrimidine with 5-fluoro-2-tributylstannylpyrimidine furnished 5,5'- $\text{F}(\text{CF}_3)\text{bpym}$ in 46% isolated yield.

Analogous to the synthesis of the radical-bridged lanthanide complexes $[(\text{Cp}^*\text{Ln})_2(\mu\text{-bpym})][\text{BPh}_4]$,^{8a} reaction of $[\text{Cp}^*\text{Ln}][\text{BPh}_4]$ with 5,5'- R_2bpym and subsequent reduction with

potassium graphite yielded the complexes $[(\text{Cp}^*_2\text{Ln})_2(\mu\text{-}5,5'\text{-R}_2\text{bpym})][\text{BPh}_4]$ ($\text{R} = \text{NMe}_2$ (**1**), OEt (**2**), Me (**3**), F (**4**); $\text{Ln} = \text{Gd}$, Dy) in 27–69% isolated yield (Scheme 3.1). A mixture of tetrahydrofuran (THF) and toluene was utilized as the reaction solvent for the synthesis of **1–3**, however, these conditions did not furnish the desired complexes with 5,5'- F_2bpym or 5,5'- $\text{F}(\text{CF}_3)\text{bpym}$. This is likely due to the electron-deficient nature of the fluoro- and trifluoromethyl-substituted ligands, which may result in weaker interactions with lanthanide ions. Exclusion of coordinating solvent from the reaction and crystallization conditions successfully afforded complex **4**, but attempts to isolate radical-bridged lanthanide complexes with 5,5'- $\text{F}(\text{CF}_3)\text{bpym}$, the most electron-deficient ligand in the series, were not successful.



Scheme 3.1. Synthesis of the radical-bridged dilanthanide complexes **1–4**.

The solid-state structures of complexes **1–4** were determined by single-crystal X-ray diffraction (Figure 3. 1) with the exception of **1-Gd**, for which sufficient quality single crystals could not be obtained. The $\text{C}(2)\text{--}\text{C}(2')$ bond distance in a bpym ligand is indicative of its charge state,¹⁵ and the values for **1–4** are within the range 1.403(14)–1.432(18) Å, consistent with previously reported bpym^- complexes in the literature.¹⁶ The average Dy--N and Gd--N bond distances range from 2.424(6) to 2.440(6) and 2.458(2) to 2.469(5) Å, respectively, consistent with the average Ln--N bond distances in $[(\text{Cp}^*_2\text{Ln})_2(\mu\text{-bpym})][\text{BPh}_4]$.^{8a} The plane of the 5,5'- R_2bpym ligand is nearly parallel with the $\text{Ln}\cdots\text{Ln}$ axis, deviating by only 0.6(1)–3.5(1)° in **1–4**. Overall, the bond distances and angles in **1–4** are quite similar across the series and follow no recognizable trend, suggesting that any difference in magnetic properties can be attributed to the electronic influence of the substituent on the 5,5'- R_2bpym ligand, rather than structural differences between the complexes.

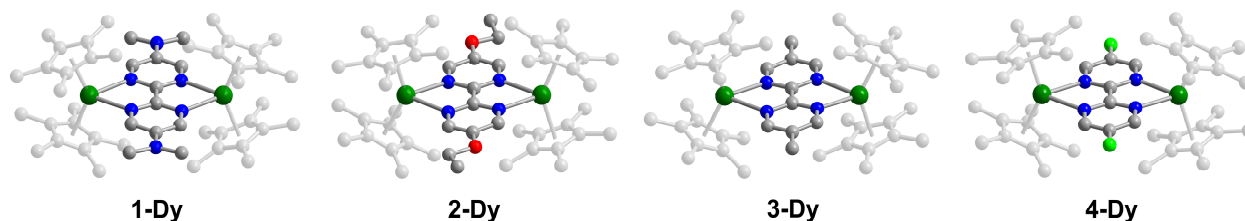


Figure 3.1. Single-crystal X-ray diffraction structures of $[(\text{Cp}^*_2\text{Dy})_2(\mu\text{-}5,5'\text{-R}_2\text{bpym})][\text{BPh}_4]$ ($\text{R} = \text{NMe}_2$ (**1**), OEt (**2**), Me (**3**), F (**4**)). Dark green, gray, blue, red, and lime green spheres represent Dy, C, N, O, and F atoms, respectively. Hydrogen atoms and BPh_4^- counteranions are omitted for clarity.

Dc magnetic susceptibility data were initially collected for **1–4** from 2 to 300 K under a 1 kOe field. The room temperature $\chi_{\text{M}}T$ values for **1-Dy** through **4-Dy** are 27.1, 28.6, 26.8, and 26.3 emu K/mol, respectively, slightly lower than the expected value of 28.7 emu K/mol for two non-

interacting Dy^{3+} centers and an $S = 1/2$ organic radical spin. In contrast, at 1 kOe the room temperature $\chi_{\text{M}}T$ values for the Gd^{3+} congeners are greater than the expected value of 16.1 emu K/mol due to contributions from temperature-independent paramagnetism (Figures S3.38, S3.40, S3.42, and S3.44). This effect is suppressed under a 10 kOe field, resulting in room temperature $\chi_{\text{M}}T$ values of 16.1–16.2 emu K/mol for **1-Gd** through **4-Gd**.

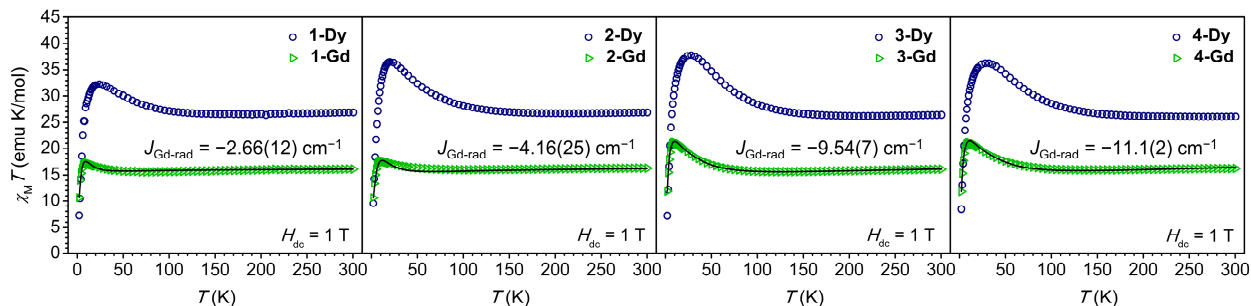


Figure 3.2. Dc magnetic susceptibility data for **1–4** under an applied magnetic field of 10 kOe. The black lines represent fits to the data for **1-Gd** through **4-Gd**, as described in the main text.

A rise in $\chi_{\text{M}}T$ is observed for both series of **1–4** at low temperatures under a 10 kOe field (Figure 3.2), indicative of the formation of a high angular momentum ground state through magnetic exchange coupling interactions. The magnitude of the exchange coupling interaction can be quantified for isotropic Gd^{3+} ($4f^7$) by fitting the dc susceptibility data to the spin-only Hamiltonian: $\hat{H} = -2J_{\text{Gd-rad}}\hat{S}_{\text{rad}} \cdot (\hat{S}_{\text{Gd}(1)} + \hat{S}_{\text{Gd}(2)})$, where $J_{\text{Gd-rad}}$ represents the intramolecular Gd^{3+} –radical exchange coupling constant, $\hat{S}_{\text{rad}}$ represents the spin operator for the organic radical bridging ligand, and $\hat{S}_{\text{Gd}(n)}$ represents the spin operator for each paramagnetic Gd^{3+} ion (Table S3.7–S3.10). Terms that account for temperature-independent paramagnetism and weak intermolecular exchange interactions were also included in the Hamiltonian. The full range of data for **3-Gd** and **4-Gd** could be fit to this equation, yielding $J_{\text{Gd-rad}} = -9.54(7)$ and $-11.1(2) \text{ cm}^{-1}$, respectively, under a 10 kOe field (Figure 3.2, black lines). The value of $J_{\text{Gd-rad}}$ for **4-Gd** is among the largest yet measured for a radical-bridged lanthanide complex and surpasses the value obtained for $[(\text{Cp}^*\text{}_2\text{Gd})_2(\mu\text{-bpym})][\text{BPh}_4]$, $J_{\text{Gd-rad}} = -10 \text{ cm}^{-1}$.^{8a} For **1-Gd** and **2-Gd**, this fit slightly underestimated the rise in $\chi_{\text{M}}T$ at low temperatures. Incorporation of a term that accounts for intramolecular Gd^{3+} – Gd^{3+} exchange coupling ($J_{\text{Gd-Gd}}$) into the Hamiltonian provided a satisfactory fit to the $\chi_{\text{M}}T$ data for **1-Gd** and **2-Gd** at 10 kOe, yielding $J_{\text{Gd-rad}} = -2.66(12)$ and $-4.16(25) \text{ cm}^{-1}$, respectively, and $J_{\text{Gd-Gd}} = 0.125(8)$ and $0.145(5) \text{ cm}^{-1}$, respectively (Figure 3.2, black lines). Weak ferromagnetic Ln^{3+} – Ln^{3+} exchange coupling has been observed previously in dilanthanide complexes bridged by 2,2'-bipyrimidine.¹⁷

The relative strength of the magnetic exchange coupling interaction in **1-Gd** through **4-Gd** and $[(\text{Cp}^*\text{}_2\text{Gd})_2(\mu\text{-bpym})][\text{BPh}_4]$ follows the trend $\text{NMe}_2 < \text{OEt} < \text{Me} < \text{H} < \text{F}$, which can be rationalized by considering the effect of the substituent on radical spin density in the 5,5'-R₂bpym[−] ligand. The singly-occupied molecular orbital (SOMO) for bpym[−] has coefficients on C(2), C(2'), C(5), C(5'), and the nitrogen atoms,¹⁰ and the magnitude of $J_{\text{Gd-rad}}$ is influenced primarily by the spin density on nitrogen. Introducing substituents that are electron-withdrawing by induction (e.g. F) at the 5 and 5' carbons decreases the radical coefficient at that position, thereby increasing the radical spin density at C(2), C(2'), and the nitrogen atoms and the strength of the magnetic exchange interaction. By contrast, introducing electron donating substituents at the 5 and 5' carbons decreases spin density at C(2), C(2'), and the nitrogen atoms, thereby decreasing the

magnitude of $J_{\text{Gd-rad}}$. For the strongly electron donating NMe₂ and OEt substituents, the radical spin density at nitrogen may be reduced so substantially that ferromagnetic superexchange between the lanthanide ions becomes competitive with antiferromagnetic coupling to the radical. Electron paramagnetic resonance (EPR) spectroscopy studies of other radical anion species report similar substituent effects to those observed in **1-Gd** through **4-Gd**.¹⁸ Although the magnitude of the exchange coupling interaction in **1-Dy** through **4-Dy** cannot be quantified using the experimental magnetic susceptibility data due to the anisotropic nature of the Dy³⁺ ion, the relative magnitude of the peak in the $\chi_{\text{M}}T$ versus T plot and the temperature at which this peak is reached follow a similar trend to the Gd derivatives, suggesting a similar ordering of the exchange coupling strength.

The substituent effects observed in this series offer a rational route towards increasing the strength of magnetic exchange coupling interactions in radical-bridged lanthanide complexes. Significantly, these results demonstrate that the magnitude of the exchange coupling constant can be tuned by over a factor of four through ligand modification, from $-2.66(12)$ to $-11.1(2)$ cm⁻¹. This large modulation is notable, given that magnetic exchange coupling interactions are typically weak ($|J| < 1$ cm⁻¹) for lanthanide ions due to the contracted nature of the 4f orbitals and that the maximum value of $J_{\text{Gd-rad}}$ yet reported is only -27 cm⁻¹.^{3c} It is important to emphasize that this effect is achieved by installing substituents on ligand atoms that possess radical spin density in the bpym⁻ SOMO. In contrast, a recent study on tetraoxolene radical-bridged diiron complexes showed that substituent modifications at positions lacking radical spin density in the ligand SOMO had no effect on the magnitude of metal–radical exchange.¹⁹

Magnetic relaxation dynamics were probed in **1-Dy** through **4-Dy** by ac magnetic susceptibility measurements in the frequency range of 0.1–1500 Hz. Two peaks were present in the out-of-phase magnetic susceptibility (χ'') data for **1-Dy** between 4.5 and 11 K, indicative of two independent magnetic relaxation processes occurring at these temperatures (Figure S3.46). For **2-Dy**, there is also evidence of two relaxation processes, although one process is clearly dominant within the measurement window (5 to 13 K, Figure S3.48). In contrast, **3-Dy** and **4-Dy** both exhibit only a single χ'' peak in the same frequency range and temperatures ranging from 9 to 17 K (Figures S3.50 and S3.52). Magnetic relaxation times, τ , were extracted from simultaneous fits of the χ' (in-phase susceptibility) and χ'' data for **1-Dy** through **4-Dy** to a generalized Debye model (Figures S3.47, S3.49, S3.51, S3.53). Arrhenius plots of inverse temperature versus the natural log of τ for **3-Dy** and **4-Dy** and for the dominant relaxation processes in **1-Dy** and **2-Dy** are linear, characteristic of magnetic relaxation via a thermally-activated Orbach mechanism (Figure S3.70–S3.73).²⁰ Accordingly, all data were fit to the equation $\tau^{-1} = \tau_0^{-1} \exp(U_{\text{eff}}/k_{\text{B}}T)$, yielding thermal barriers to magnetic relaxation (U_{eff}) of 31, 40, 82, and 93 cm⁻¹ for **1-Dy** through **4-Dy** respectively. For comparison, [(Cp*₂Dy)₂(μ-bpym)][BPh₄] displays $U_{\text{eff}} = 88$ cm⁻¹.^{8a} Interestingly, the trend observed in the magnitude of these U_{eff} values matches the trend in $|J_{\text{Gd-rad}}|$, namely NMe₂ < OEt < Me < H < F. The minor relaxation process in **1-Dy** and **2-Dy** also displays a linear temperature dependence in plots of $\ln(\tau)$ versus inverse T (Figures S3.70–S3.71), and the data could be fit to an Orbach mechanism, yielding $U_{\text{eff}} = 46$ and 94 cm⁻¹, respectively.

The value of U_{eff} for a radical-bridged lanthanide complex depends on both single-ion anisotropy and exchange coupling interactions. A complex with high anisotropy can be described by the Ising model,²¹ and the splitting of electronic states can be approximated with the Hamiltonian: $\hat{H} = -2J_{\text{Ln-rad}}\hat{S}_{\text{rad}} \cdot (\hat{J}_{\text{Ln}(1)} + \hat{J}_{\text{Ln}(2)}) + \sum B^0_2O^0_2(i)$, where $J_{\text{Ln-rad}}$ represents the intramolecular Ln³⁺–radical exchange coupling constant, $\hat{S}_{\text{rad}}$ represents the spin operator for the organic radical bridging ligand, $\hat{J}_{\text{Gd}(n)}$ represents the angular momentum operator for each Ln³⁺

ion, and B^0_2 and O^0_2 are parameters that describe crystal field interactions.^{6a} Excited state energies correspond to multiples of J_{Ln-rad} and thus the value of U_{eff} —typically the energy difference between the ground and first excited state—is proportional to $|J_{Ln-rad}|$. For instance, $U_{eff} = 15|J_{Dy-rad}|$ for a high anisotropy dysprosium complex.^{6a} By contrast, a complex with low anisotropy will possess low-lying crystal field states that are mixed by the exchange interaction, resulting in a reduction of U_{eff} . This theoretical analysis offers insight into the magnitude of U_{eff} values in radical-bridged lanthanide complexes, however, it can be challenging to implement due to the difficulty of experimentally determining J_{Ln-rad} for non-isotropic lanthanide ions and of quantifying single-ion anisotropy. Indeed, these values are typically obtained through *ab initio* calculations,²² which can be time-intensive to execute and may possess a wide margin of error.

We accordingly sought to develop an empirical model to rationalize the U_{eff} values in **1-Dy** through **4-Dy**. To this end, we plotted $|J_{Gd-rad}|$ for **1-Gd** through **4-Gd** versus the U_{eff} value of the dominant relaxation process in the corresponding Dy complex (Figure 3.3, Table S3.21). The resulting plot is linear, which implies that these molecules can be described by an Ising model (i.e. U_{eff} is directly proportional to $|J_{Ln-rad}|$ for this series). This observation is consistent with the high single-ion anisotropy reported for other dysprosium complexes with axial Cp* ligands.²³ A linear dependence of U_{eff} on $|J_{Dy-rad}|$ was reported previously for $[Cr_2Dy_2(OMe)_2(RN\{(CH_2)_2OH\}_2)(acac)_4(NO_3)_2]$ (R = Me, Et, *n*Bu) (acac = acetylacetonate) using computationally-determined values for the exchange coupling constant.⁷

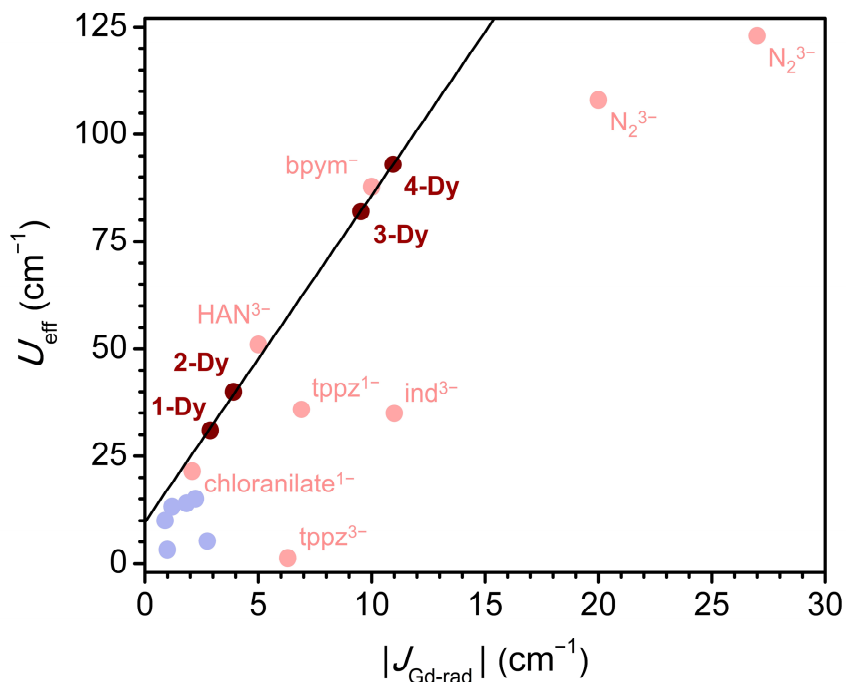


Figure 3.3. Plot of U_{eff} for **1-Dy** through **4-Dy** versus $|J_{Gd-rad}|$ of the corresponding gadolinium complexes (red circles). A linear fit to these data provides an empirical model (black line) to analyze the electronic structure of multinuclear radical-bridged (pink circles) and radical-containing (blue circles) dysprosium complexes.^{3c,8a,22–24} Multinuclear lanthanide complexes bridged by organic radicals that fall along the line display high single-ion anisotropy and can be described by an Ising model, while those that fall below the line display low single-ion anisotropy.

Notably, the empirical model derived for **1-Dy** through **4-Dy** can be used to analyze the electronic structure of multinuclear radical-bridged dysprosium complexes in the literature.²² For instance, $[(\text{Cp}^*\text{Dy})_2(\mu\text{-bpym})][\text{BPh}_4]$, $(\text{Cp}^*\text{Dy})_3(\mu\text{-HAN})$ (HAN = hexaazatrinaphthylene), and $[(\text{HBpz}_3)_2\text{Dy}(\mu\text{-CA})][\text{CoCp}_2]$ (HBpz₃ = hydrotris(pyrazol-1-yl)borate, CA = chloranilate) all fall along the best-fit line calculated for **1-Dy** through **4-Dy**, which implies that these complexes can be described by the Ising model.^{8a,23} By contrast, $[(\text{Cp}^*\text{Dy})_2(\mu\text{-tppz})]^{+/-}$ (tppz = 2,3,5,6-tetra(2-pyridyl)pyrazine) and $[(\text{Cp}^*\text{Dy})_2(\mu\text{-ind})]^-$ (ind = indigo) fall below the line, which suggests that these complexes possess a value of U_{eff} below the Ising limit (i.e. $U_{\text{eff}} < |15J_{\text{Dy-rad}}|$) due to low single-ion anisotropy.²⁴ This analysis is consistent with the stronger equatorial interactions observed for the Dy^{3+} centers in these complexes. Complete active space self-consistent field (CASSCF) calculations performed on $[(\text{Cp}^*\text{Dy})_2(\mu\text{-ind})]^-$ predict that the ground Kramers doublet for each Dy^{3+} ion is relatively close in energy to the first excited state ($\Delta E = 71 \text{ cm}^{-1}$), further confirming the low single-ion anisotropy in this complex (Table S3.23). For comparison, $\Delta E = \sim 200 \text{ cm}^{-1}$ for **1-Dy** through **4-Dy** based on CASSCF calculations (Table S3.23). The empirical model derived for **1-Dy** through **4-Dy** can also be used to analyze complexes in which a single dysprosium ion interacts with an organic radical (see supplementary information for additional details).

The correspondence between the best-fit line for **1-Dy** through **4-Dy** and literature data suggests that this empirical model can be used as a predictive tool for the design of future radical-bridged dysprosium complexes. Indeed, the maximal value of the energetic splitting between the ground and first excited state (i.e., U_{eff}) can be estimated using only $J_{\text{Gd-rad}}$ for the corresponding Gd complex. This model can also predict clear routes to increasing the magnitude of the thermal relaxation barrier. For instance, $U_{\text{eff}} = 35 \text{ cm}^{-1}$ for $[(\text{Cp}^*\text{Dy})_2(\mu\text{-ind})]^-$, but the model presented here predicts that U_{eff} values as large as 93 cm^{-1} could be achieved if the ancillary cyclopentadienyl ligands were modified to maximize the single-ion anisotropy of the Dy^{3+} ions in this system. By contrast, the empirical model predicts that larger values of U_{eff} in the aforementioned HAN-bridged complex cannot be achieved by increasing single-ion anisotropy, and that the magnitude of $J_{\text{Dy-rad}}$ must be increased instead. Notably, this empirical model is facile to implement and relies on parameters that can be easily extracted from experimental data, and it could therefore be used to benchmark future computational studies or provide rapid insight into the electronic structure of new radical-bridged complexes.

It is important to note that several key assumptions are implicit to this analysis, namely that $J_{\text{Gd-rad}}$ is proportional to $J_{\text{Dy-rad}}$ and that the proportionality constant that relates these two values is the same for all complexes. These assumptions appear to be reasonable for complexes in which Dy^{3+} ions interact with organic radicals, however, complexes bridged by N_2^{3-} deviate from the empirical model. For example, while *ab initio* calculations predict that $[(\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})\text{Dy})_2(\mu\text{-N}_2)]^-$ can be described by the Ising model, the data for this complex do not fall along the best-fit line obtained for **1-Dy** through **4-Dy** (Figure 3.3).^{22a} This is likely due to a difference in the magnetic exchange coupling mechanism for complexes bridged by N_2^{3-} , which has been predicted computationally.²² In addition, this empirical model is unlikely to apply to complexes with low values of $|J_{\text{Gd-rad}}|$ ($< 1 \text{ cm}^{-1}$) in which single-ion effects begin to dominate. Clearly, additional studies on series of radical-bridged lanthanide complexes with disparate bridging ligands are necessary in order to elucidate the generality of the empirical model derived for **1-Dy** through **4-Dy**.

Ab initio calculations were performed on **1-Dy** through **4-Dy** in order to provide additional insight into the electronic structure of this series. CASSCF calculations were used to determine

the energy of the crystal field states of the individual Dy^{3+} ions in the complexes (Table S3.23), and broken-symmetry density functional theory (DFT) calculations were used to estimate the strength of the exchange interaction (Figure S3.85–S3.87, Table S3.24; DFT calculations to determine the exchange spectra for **1-Dy** are ongoing). These calculations predict that the ground Kramers doublet of the Dy^{3+} ions in **1-Dy** through **4-Dy** is well-separated from the first excited doublet ($\Delta E = \sim 200 \text{ cm}^{-1}$), consistent with our empirical prediction that these complexes display large single-ion anisotropy and can be described by an Ising model.

The calculated exchange spectra for **2-Dy**, **3-Dy**, and **4-Dy** (Figure 3.4, Table S3.25) yield U_{eff} values of 59, 73, and 83 cm^{-1} , respectively, comparable to the experimental U_{eff} values of 40, 82, and 93 cm^{-1} . The energetic splittings between the ground state and second excited state in **2-Dy** is 116 cm^{-1} , which corresponds to the U_{eff} value of the minor relaxation processes observed for this complex, 94 cm^{-1} . Orbach relaxation via the second excited state has been observed previously in radical-bridged lanthanide complexes.^{6a} This relaxation mechanism is likely not observed for **3-Dy** and **4-Dy** due to the higher energy of the second excited state in these complexes, which renders an Orbach process thermally inaccessible in the temperature regime in which ac susceptibility data were collected. Altogether, these calculations confirm that **1-Dy** through **4-Dy** can be described by the Ising model and that the magnitude of the U_{eff} values in these complexes are dictated by the strength of exchange coupling.

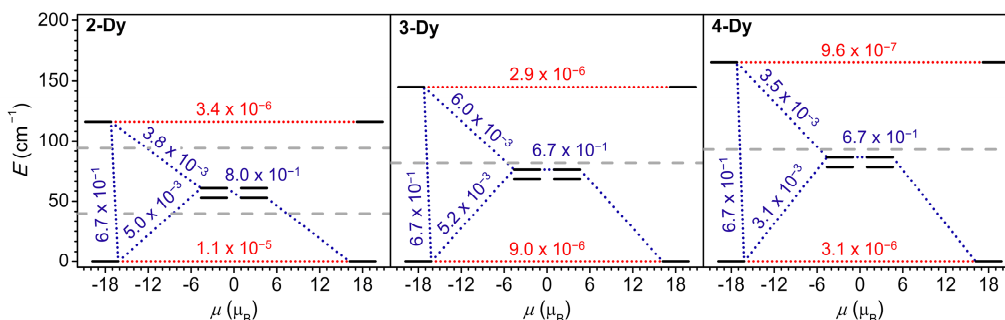


Figure 3.4. Low-lying exchange spectra calculated for **2-Dy**, **3-Dy**, and **4-Dy** showing thermally-activated magnetic relaxation (dotted blue line) and quantum tunneling of the magnetization (dotted red line) pathways with transmission probabilities and the experimentally determined values of U_{eff} (dashed gray line).

Dc relaxation measurements were performed on **1-Dy** through **4-Dy** to probe magnetic relaxation dynamics at lower temperatures. For **3-Dy** and **4-Dy**, magnetic relaxation times, τ , were extracted from magnetization versus time plots by fitting the data to a stretched exponential function. Data for **1-Dy** and **2-Dy** could not be fit accurately by a single stretched exponential function, likely due to the presence of two independent relaxation processes for each complex, as observed in the ac susceptibility measurements. Utilizing a stretched exponential function that accounted for two relaxation processes led to over-parameterization, however, and unique fits to the data for **1-Dy** and **2-Dy** could not be identified.

Plots of $\ln(\tau)$ versus inverse T derived from the dc relaxation data for **3-Dy** and **4-Dy** are non-linear, indicative of Raman relaxation and quantum tunneling of the magnetization. Accordingly, the data were fit to the equation $\tau^{-1} = \tau_{\text{tunnel}}^{-1} + CT^n$, yielding $\tau_{\text{tunnel}} = 660 \text{ s}$, $C = 3.7 \times 10^{-6}$, and $n = 3.7$ for **3-Dy**, and $\tau_{\text{tunnel}} = 350 \text{ s}$, $C = 2.9 \times 10^{-5}$, and $n = 3.0$ for **4-Dy**. As τ_{tunnel} values can be influenced by intermolecular dipolar interactions in the solid state, we also performed dc relaxation measurements on dilute solutions of **3-Dy** (7.8 mM) and **4-Dy** (8.0 mM) in 1,2-difluorobenzene

under applied magnetic fields of zero and 500 Oe. Fits to the zero-field data yielded $\tau_{\text{tunnel}} = 94$ and 93 s for **3-Dy** and **4-Dy**, respectively, and fits to the 500 Oe data yielded $\tau_{\text{tunnel}} = 34,000$ and 35,000 s, respectively. Raman relaxation parameters extracted from fits to these data are also quite similar for **3-Dy** and **4-Dy**. Overall, these results demonstrate that through-barrier relaxation processes in **3-Dy** and **4-Dy** display similar rates at low temperatures, despite the stronger magnetic exchange coupling observed in **4-Dy**.

Magnetic hysteresis data were collected for **1-Dy** through **4-Dy** at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe (Figure 3.5). Hysteresis loops for **1-Dy** through **4-Dy** are open at zero field to temperatures as high as 4.0, 5.0, 6.5, and 7.0 K, respectively. For comparison, hysteresis loops are open at zero field up to 6.5 K in $[(\text{Cp}^*\text{2Dy})_2(\mu\text{-bpym})][\text{BPh}_4]$ for measurements collected with a comparable sweep rate.^{8a} The trend in the maximum hysteresis temperature for **1-Dy** through **4-Dy** is consistent with that observed for U_{eff} and $|J_{\text{Gd-rad}}|$, namely $\text{NMe}_2 < \text{OEt} < \text{Me} = \text{H} < \text{F}$. This result can be explained by examining the Arrhenius plots for **1-Dy** through **4-Dy**, which show that magnetic relaxation at the maximum hysteresis temperature for each complex is dominated by an Orbach mechanism. Thus, the value of $J_{\text{Gd-rad}}$ dictates the magnitude of U_{eff} in this series, which dictates the rate of Orbach relaxation and whether the hysteresis loop is open or closed at high temperatures.

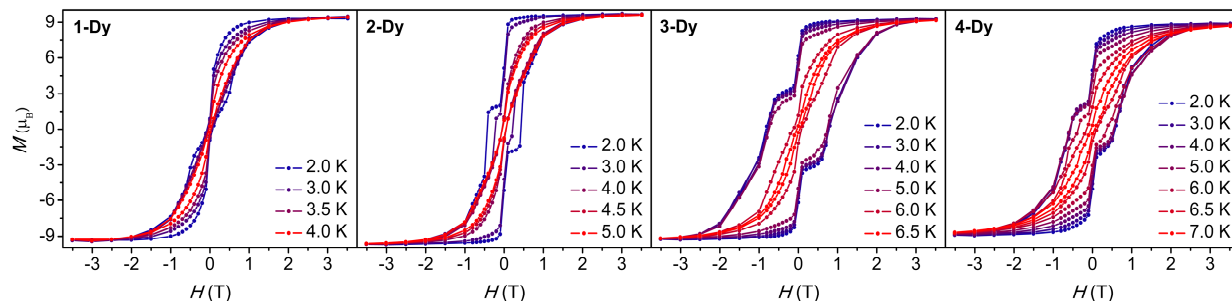


Figure 3.5. Magnetic hysteresis measurements for **1-Dy** through **4-Dy** at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H_{\text{dc}}| < 10$ kOe.

The coercive field (H_c) can be used to compare the rate of magnetic relaxation in a series of complexes if data are collected at comparable sweep rates. As such, the value of H_c can be used to estimate the rate of through-barrier relaxation processes in **1-Dy** through **4-Dy** at low temperatures, where Raman relaxation and quantum tunneling of the magnetization dominate. Values of $H_c = 40$ Oe, 430 Oe, 760 Oe, and 580 Oe were determined for **1-Dy** through **4-Dy**, respectively, at 2 K. For comparison, $H_c = 600$ Oe for $[(\text{Cp}^*\text{2Dy})_2(\mu\text{-bpym})][\text{BPh}_4]$ at 2 K.^{8a} Generally, these results demonstrate that complexes with stronger exchange coupling display slower through-barrier relaxation (e.g., H_c for **3-Dy** and **4-Dy** $\gg H_c$ for **1-Dy**), however, this correlation is not strictly linear. For instance, $|J_{\text{Gd-rad}}|$ follows the trend $\text{Me} (\textbf{3-Dy}) < \text{H} < \text{F} (\textbf{4-Dy})$, while H_c at 2 K follows the trend $\text{F} < \text{H} < \text{Me}$ for both solid-state and solution samples of **3-Dy** and **4-Dy** (Figure S3.80 and S3.83). This result is intriguing, given that CASSCF calculations predict higher single-ion anisotropy for **4-Dy** than **3-Dy**, and both complexes are centrosymmetric in the single-crystal structure, which results in a parallel arrangement of the anisotropy axes of the Dy^{3+} ions.^{8b} This result may indicate that an additional factor influences the rate of through-barrier magnetic relaxation in these complexes, and additional investigation into this behavior is ongoing.

3.3 Conclusions and Outlook

Modifying the ligand substituents in $[(\text{Cp}^*_2\text{Ln})_2(\mu\text{-}5,5'\text{-R}_2\text{bpym})][\text{BPh}_4]$ ($\text{R} = \text{NMe}_2$ (**1**), OEt (**2**), Me (**3**), F (**4**); $\text{Ln} = \text{Gd}$, Dy) induces drastic changes in both intramolecular magnetic exchange coupling interactions and single-molecule magnet behavior. A systematic influence of the substituent on the magnitude of the exchange coupling constant, $|J_{\text{Gd-rad}}|$, is observed: in particular, electron-donating and -withdrawing substituents decrease and increase $|J_{\text{Gd-rad}}|$, respectively. The strength of magnetic exchange coupling impacts magnetic relaxation dynamics in **1-Dy** through **4-Dy**, with larger $|J_{\text{Ln-rad}}|$ being associated with larger thermal barriers to magnetic relaxation (U_{eff}) and maximum hysteresis temperatures, and smaller values of τ for through-barrier relaxation processes. This behavior is supported by *ab initio* calculations conducted on the series. Notably, an empirical correlation could be derived for **1-Dy** through **4-Dy** that relates the experimental value of U_{eff} to $|J_{\text{Gd-rad}}|$ of the corresponding Gd complex. This correlation extends to other radical-bridged dysprosium complexes in the literature and offers clear strategies to increase U_{eff} for these molecules. Altogether, these results demonstrate the utility of studying systematic series of complexes and offer crucial design criteria for the synthesis of future radical-bridged lanthanide single-molecule magnets.

3.4 Acknowledgements

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3.5 References and Footnotes

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3.6 Supplementary Information

3.6.1 General Information and Synthesis

Unless otherwise mentioned, commercial reagents were purchased from Sigma Aldrich, Fischer, Acros, Oakwood, Strem or Alfa Aesar and used without further purification. THF, hexanes, 1,2-difluorobenzene, toluene, and DMF were sparged with argon and then dried by passing through alumina columns in a Glass Contour solvent purification system from JC Meyer. *i*Pr₂NH was dried over activated 4 Å molecular sieves. 5,5'-dimethylbipyrimidine,¹ [Cp*₂Gd][BPh₄],² and [Cp*₂Dy][BPh₄]³ were prepared according to literature reports. 5-Ethoxy-2-chloropyrimidine⁴ and 5-(*N,N*-dimethyl)amino-2-chloropyrimidine⁵ were previously reported in the literature but were prepared via alternative routes. All reactions were carried out in flame-dried glassware under an argon atmosphere using standard Schlenck techniques or in a nitrogen atmosphere glovebox.

Elemental analyses were performed by the Microanalytical Facility at the University of California, Berkeley using a Perkin-Elmer 2400 Series II combustion analyzer. High-res mass spectrometry data were obtained from the Mass Spectrometry Facility at the University of California, Berkeley, on a Finnigan/Thermo LTQ-FT instrument (ESI); data acquisition and processing were performed using the XcaliburTM software.

5-(*N,N*-dimethyl)amino-2-chloropyrimidine. 5-Amino-2-chloropyrimidine (4.5 g, 35 mmol) was dissolved in 90% formic acid (7.3 mL, 30 equiv) and to this solution was added an aqueous solution of formaldehyde (36% formaldehyde in water, 7.8 mL, 18 equiv). The reaction was heated to reflux (~105 °C) for 12 h at which time the solution was cooled to 50 °C and the solvent was removed en vacuo (~200 millitorr). The remaining waxy black solid was triturated with a saturated aqueous solution of sodium bicarbonate (200 mL) and the resulting brown solids were collected via vacuum filtration and purified by sublimation (~80 °C, 200 millitorr). The product was obtained as a colorless solid in 30% yield (1.6 g, 10 mmol).

5-Ethoxy-2-chloropyrimidine. 5-Hydroxy-2-chloropyrimidine (1.0 g, 7.7 mmol) was dissolved in 15 mL DMF and to this solution was added potassium carbonate (1.6 g, 12 mmol, 1.5 equiv) and, dropwise, iodoethane (0.92 mL, 1.8 g, 12 mmol, 1.5 equiv). The reaction was stirred at room temperature for 1 h, at which time water (50 mL) was added. The resulting mixture was extracted with EtOAc (3 x 30 mL) and the organic layers were combined, dried over Na₂SO₄ and concentrated to yield a light brown solid. This solid was dissolved in 25% EtOAc in hexanes and purified via filtration over silica gel. The product was obtained as a colorless solid in 86% yield (1.0 g, 6.6 mmol).

5,5'-Di-(*N,N*-dimethylamino)-2,2'-bipyrimidine ((NMe₂)₂bpym). Analogous to a literature synthesis of 2,2'-bipyrimidine,⁶ nickel(II) chloride hexahydrate (360 mg, 1.5 mmol, 0.25 equiv) and triphenylphosphine (1.6 g, 6.0 mmol, 1 equiv) were placed in a Schlenk flask and dried en vacuo (~200 millitorr) for 20 min. The solids were subsequently dissolved in dry, degassed DMF (30 mL) under argon with vigorous stirring and to this solution was added zinc powder (190 mg, 3.0 mmol, 0.5 equiv). The resulting green solution became deep red in color and was stirred for 1 h at 25 °C, at which point 5-(*N,N*-dimethyl)amino-2-chloropyrimidine (950 mg, 6.0 mmol) was added. The solution became black in color and was stirred for 1 h at 25 °C, followed by 48 h at

50 °C. The black solution was cooled to room temperature, filtered over Celite, and the filter cake washed with DMF (30 mL). The filtrate was concentrated en vacuo (~50 °C, 200 millitorr) to yield a brown oil to which was added a solution of ethylenediaminetetraacetic acid (2.6 g, 9.0 mmol, 1.5 equiv) in aqueous ammonia (7% NH₃ in water; 20 mL). This solution was stirred for 3 h, becoming blue in color and precipitating colorless solids that were collected via vacuum filtration. The solids were triturated in Et₂O (3 x 20 mL) to remove triphenylphosphine and then purified via recrystallization (1:10 CHCl₃:hexanes or MeOH). The product was obtained as a pale yellow solid in 33% yield (480 mg, 2.0 mmol).

¹H-NMR (600 MHz, CDCl₃) δ = 8.40 (s, 4H), 3.10 (s, 12H) ppm. ¹³C-NMR (150 MHz, CDCl₃) δ = 150.0, 142.5, 140.4, 39.7 ppm. HRMS (ESI+) *m/z* calcd. for C₁₂H₁₇N₆ [M+H⁺]: 245.1509; found: 245.1511.

5,5'-Diethoxy-2,2'-bipyrimidine ((OEt)₂bpym). Analogous to the synthesis (NMe₂)₂bpym nickel(II) chloride hexahydrate (380 mg, 1.6 mmol, 0.25 equiv) and triphenylphosphine (1.7 g, 6.4 mmol, 1 equiv) were placed in a Schlenck flask and dried en vacuo (~200 millitorr) for 20 min. The solids were subsequently dissolved in dry, degassed DMF (40 mL) under argon with vigorous stirring and to this solution was added zinc powder (210 mg, 3.2 mmol, 0.5 equiv). The resulting green solution became deep red in color and was stirred for 1 h at 25 °C, at which point 5-ethoxy-2-chloropyrimidine (1.0 g, 6.4 mmol) was added. The solution became black in color and was stirred for 1 h at 25 °C, followed by 48 h at 50 °C. The black solution was cooled to room temperature, filtered over Celite, and the filter cake washed with DMF (40 mL). The filtrate was concentrated en vacuo (~50 °C, 200 millitorr) to yield a brown oil to which was added a solution of ethylenediaminetetraacetic acid (2.7 g, 9.6 mmol, 1.5 equiv) in aqueous ammonia (7% NH₃ in water; 30 mL). This solution was stirred for 3 h, becoming green in color and it was subsequently extracted with CHCl₃ (3 x 30 mL). The organic layers were combined, dried over Na₂SO₄, and concentrated. The resulting solids were triturated in Et₂O (3 x 30 mL) to remove excess triphenylphosphine and then purified via recrystallization (1:10 CHCl₃:hexanes or MeOH). The product was obtained as a colorless solid in 37% yield (580 mg, 2.4 mmol).

¹H-NMR (500 MHz, CDCl₃) δ = 8.55 (s, 4H), 4.20 (q, *J* = 7.0 Hz, 4H), 1.46 (t, *J* = 7.0 Hz, 6H) ppm. ¹³C-NMR (125 MHz, CDCl₃) δ = 154.8, 152.7, 144.3, 64.8, 14.7 ppm. HRMS (ESI+) *m/z* calcd. for C₁₂H₁₅O₂N₄ [M+H⁺]: 247.1190; found: 247.1191.

5-Fluoro-2-tributylstannylpyrimidine. A solution of *i*Pr₂NH (0.78 mL, 5.5 mmol, 1.25 equiv) in dry THF (10 mL) was stirred at 0 °C in a Schlenck flask under argon. To this solution was added *n*-BuLi (2.5 M in hexanes, 2.0 mL, 5.0 mmol, 1.15 equiv) dropwise and the resulting pale yellow solution was stirred for 30 min at 0 °C. HSnBu₃ (1.3 mL, 4.8 mmol, 1.1 equiv) was then added dropwise and the light green solution was stirred for 10 min at 0 °C, cooled to -78 °C for 5 min, and then cannula transferred to a solution of 5-fluoro-2-chloropyrimidine (580 mg, 0.40 mL, 4.4 mmol) in dry THF (20 mL) that had been pre-cooled to -78 °C. The resulting deep orange-red solution was stirred at -78 °C for 2 h and then 0 °C for 2 h, at which point it was quenched by addition of H₂O (30 mL). The reaction mixture was extracted with EtOAc (3 x 30 mL) and the organic layers were dried over Na₂SO₄ and concentrated to yield a brown oil, which was purified via column chromatography on silica gel (*R*_f = 0.70, 10% EtOAc in hexanes). The product was obtained as a colorless oil in 35% yield (590 mg, 1.5 mmol).

¹H-NMR (400 MHz, C₆D₆) δ = 8.14 (s, 2H), 1.72 (m, 6H), 1.40 (m, 6H), 1.29 (t, *J* = 7.3 Hz, 6H), 0.92 (t, *J* = 7.3 Hz, 9H) ppm. ¹³C-NMR (150 MHz, C₆D₆) δ = 184.2 (d, *J* = 10.7 Hz), 157.7 (d, *J* = 266.7 Hz), 142.6 (d, *J* = 15.3 Hz), 29.4, 27.7, 14.0, 10.9 ppm. ¹⁹F-NMR (376 MHz, C₆D₆) −136.7 ppm. HRMS (ESI+) *m/z* calcd. for C₁₆H₃₀N₂FSn [M+H⁺]: 389.1410; found: 389.1410.

5-Trifluoromethyl-2-tributylstannylpyrimidine. Analogous to the synthesis of 5-fluoro-2-tributylstannylpyrimidine, a solution of *i*Pr₂NH (0.58 mL, 4.1 mmol, 1.25 equiv) in dry THF (10 mL) was stirred at 0 °C in a Schlenk flask under argon. To this solution was added *n*-BuLi (2.5 M in hexanes, 1.5 mL, 3.8 mmol, 1.15 equiv) dropwise and the resulting solution was stirred for 30 min at 0 °C. HSnBu₃ (1.0 mL, 3.7 mmol, 1.1 equiv) was then added dropwise and the solution was stirred for 10 min at 0 °C, cooled to −78 °C for 5 min, and then cannula transferred to a solution of 5-trifluoromethyl-2-chloropyrimidine (600 mg, 3.3 mmol) in dry THF (20 mL) that had been pre-cooled to −78 °C. The resulting solution was stirred at −78 °C for 2 h and then 0 °C for 2 h, at which point it was quenched by addition of H₂O (30 mL). The reaction mixture was extracted with EtOAc (3 x 30 mL) and the organic layers were dried over Na₂SO₄ and concentrated to yield a brown oil, which was purified via column chromatography on silica gel (*R*_f = 0.60, 10% EtOAc in hexanes). The product was obtained as a colorless oil in 50% yield (720 mg, 1.6 mmol).

¹H-NMR (600 MHz, C₆D₆) δ = 8.38 (s, 2H), 1.33 (m, 6H), 1.14 (m, 6H), 0.82 (m, 15H) ppm. ¹³C-NMR (150 MHz, C₆D₆) δ = 162.4, 155.4 (t, *J* = 7.6 Hz), 134.2 (q, *J* = 14.3 Hz), 133.2 (q, *J* = 289.7 Hz), 28.9, 27.5, 13.8, 10.4 ppm. ¹⁹F-NMR (376 MHz, C₆D₆) −98.4 ppm. HRMS (ESI+) *m/z* calcd. for C₁₇H₃₀N₂F₃Sn [M+H⁺]: 439.1378; found: 439.1384.

5,5'-Difluoro-2,2'-bipyrimidine (F₂bpym). 5-Fluoro-2-chloropyrimidine (130 mg, 1.0 mmol), 5-fluoro-2-tributylstannylpyrimidine (370 mg, 1.0 mmol, 1 equiv), copper(I) chloride (87 mg, 1.1 mmol, 1.1 equiv), and Pd(dppf)Cl₂ (70 mg, 0.96 mmol, 10 mol%) were dissolved in dry THF (10 mL) in a Schlenk flask under argon. The resulting solution was heated to 70 °C for 18 h, first turning yellow and then brown. The reaction was then cooled to room temperature, concentrated en vacuo, and a solution of ethylenediaminetetraacetic acid (0.43 g, 1.5 mmol, 1.5 equiv) in aqueous ammonia (7% NH₃ in water; 20 mL) was added. This solution was stirred for 3 h, becoming green in color, and then was extracted first with Et₂O (3 x 20 mL) and subsequently with CH₂Cl₂ (3 x 20 mL). The CH₂Cl₂ layers were combined, dried over Na₂SO₄, and concentrated to yield a brown solid that was purified via sublimation (~120 °C, 200 millitorr). The product was obtained as a colorless solid in 57% yield (110 mg, 0.57 mmol).

¹H-NMR (500 MHz, CDCl₃) δ = 8.86 (s, 4H) ppm. ¹³C-NMR (125 MHz, CDCl₃) δ = ppm. ¹⁹F-NMR (376 MHz, CDCl₃) −134.1 ppm. HRMS (ESI+) *m/z* calcd. for C₈H₅N₄F₂ [M+H⁺]: 195.0477; found: 195.0479.

5-fluoro-5'-trifluoromethyl-2,2'-bipyrimidine (F-CF₃-bpym). Analogous to the synthesis of F₂bpym 5-trifluoromethyl-2-chloropyrimidine (280 mg, 1.6 mmol, 1.5 equiv), 5-fluoro-2-tributylstannylpyrimidine (400 mg, 1.1 mmol), copper(I) chloride (110 mg, 1.2 mmol, 1.1 equiv), and Pd(dppf)Cl₂ (76 mg, 0.10 mmol, 10 mol%) were dissolved in dry THF (10 mL) in a Schlenk flask under argon. The resulting solution was heated to 70 °C for 18 h, first turning yellow and then brown. The reaction was then cooled to room temperature, concentrated en vacuo, and a

solution of ethylenediaminetetraacetic acid (0.47 g, 1.6 mmol, 1.5 equiv) in aqueous ammonia (7% NH₃ in water; 20 mL) was added. This solution was stirred for 3 h, becoming green in color, and then was extracted first with hexanes (3 x 20 mL) and subsequently with CH₂Cl₂ (3 x 20 mL). The CH₂Cl₂ layers were combined, dried over Na₂SO₄, and concentrated to yield a brown solid that was purified first via sublimation (~120 °C, 200 millitorr) and then subsequently by reverse-phase chromatography to remove a small amount of homocoupled byproduct. The product was obtained as a colorless solid in 46 % yield (100 mg, 0.41 mmol).

¹H-NMR (500 MHz, CDCl₃) δ = 9.22 (s, 2H), 8.88 (s, 2H) ppm. ¹³C-NMR (125 MHz, CDCl₃) δ = 163.8, 158.2 (d, *J* = 270.0 Hz), 157.4, 155.6 (q, *J* = 3.3 Hz), 146.3 (d, *J* = 20.7 Hz), 125.0 (q, *J* = 34.0 Hz), 122.6 (q, *J* = 271.0 Hz) ppm. ¹⁹F-NMR (376 MHz, CDCl₃) –61.5, –132.3 ppm. HRMS (ESI+) *m/z* calcd. for C₉H₅N₄F₄ [M+H⁺]: 245.0445; found: 245.0446.

[(GdCp*₂)₂(μ-(NMe₂)₂bpym)][BPh₄] (1-Gd). Cp*₂Gd(BPh₄) (42 mg, 0.057 mmol) was suspended in toluene (4 mL) and to this slurry was added (NMe₂)₂bpym (6.9 mg, 0.028 mmol, 0.5 equiv). The resulting solution was stirred for 30 min, during which time it changed color from pale yellow to bright orange. At this point, KC₈ (3.8 mg, 0.028 mmol, 0.5 equiv.) was added in THF (0.5 mL) and the reaction became dark brown in color. After stirring 30 min, solvent was removed under reduced pressure and THF (2 mL) was added to form a dark reddish-black solution. Black and white insolubles were removed by filtration over celite, after which the solution was layered with toluene (2 mL) and cooled to –30 °C, affording red, block-shaped crystals of **1-Gd** after 48 h (22 mg, 55% yield). Anal. Calcd. For C₇₆H₉₆BN₆Gd₂: C, 64.33; H, 6.82; N, 5.92. Found: C, 64.54; H, 6.78; N, 5.92.

[(DyCp*₂)₂(μ-(NMe₂)₂bpym)][BPh₄] (1-Dy). Analogous to the synthesis of **1-Gd**, Cp*₂Dy(BPh₄) (53 mg, 0.071 mmol) was stirred in toluene (4 mL) with (NMe₂)₂bpym (8.7 mg, 0.035 mmol, 0.5 equiv) and then subsequently reduced with KC₈ (4.7 mg, 0.035 mmol, 0.5 equiv). Insolubles were removed by centrifugation and then red, block-shaped crystals of **1-Dy** were grown from a layered THF-toluene solution (2mL THF, 2 mL toluene) cooled to –30 °C for 48 h (27 mg, 54% yield). Anal. Calcd. For C₇₆H₉₆BN₆Dy₂: C, 63.86; H, 6.77; N, 5.88. Found: C, 63.80; H, 6.76; N, 5.76.

[(GdCp*₂)₂(μ-(OEt)₂bpym)][BPh₄] (2-Gd). Analogous to the synthesis of **1-Gd**, Cp*₂Gd(BPh₄) (43 mg, 0.057 mmol) was stirred in toluene (4 mL) with (OEt)₂bpym (7.0 mg, 0.028 mmol, 0.5 equiv) and then subsequently reduced with KC₈ (3.8 mg, 0.028 mmol, 0.5 equiv). Insolubles were removed by centrifugation and then red, block-shaped crystals of **2-Gd** were grown from a layered THF-toluene solution (2mL THF, 2 mL toluene) cooled to –30 °C for 48 h (16 mg, 39% yield). Anal. Calcd. For C₇₆H₉₄BN₄O₂Gd₂: C, 64.24; H, 6.67; N, 3.94. Found: C, 64.55; H, 6.43; N, 4.32.

[(DyCp*₂)₂(μ-(OEt)₂bpym)][BPh₄] (2-Dy) Analogous to the synthesis of **1-Gd**, Cp*₂Dy(BPh₄) (36 mg, 0.047 mmol) was stirred in toluene (4 mL) with (OEt)₂bpym (5.8 mg, 0.024 mmol, 0.5 equiv) and then subsequently reduced with KC₈ (3.2 mg, 0.024 mmol, 0.5 equiv). Insolubles were removed by centrifugation and then red, block-shaped crystals of **2-Dy** were grown from a layered THF-toluene solution (2mL THF, 2 mL toluene) cooled to –30 °C for 48 h (18 mg, 27% yield). Anal. Calcd. For C_{86.5}H₁₀₆BN₄O₂Dy₂ (**2-Dy** · 1.5 toluene, observed in crystal structure): C, 66.19; H, 6.81; N, 3.57. Found: C, 66.30; H, 6.44; N, 3.52.

[(GdCp*₂)₂(μ-Me₂bpym)][BPh₄] (3-Gd). Analogous to the synthesis of **1-Gd**, Cp*₂Gd(BPh₄) (42 mg, 0.057 mmol) was stirred in toluene (4 mL) with **Me₂bpym** (5.3 mg, 0.028 mmol, 0.5 equiv) and then subsequently reduced with KC₈ (3.8 mg, 0.028 mmol, 0.5 equiv). Insolubles were removed by centrifugation and then red, block-shaped crystals of **3-Gd** were grown from a layered THF-toluene solution (2mL THF, 2 mL toluene) cooled to −30 °C for 48 h (14 mg, 36% yield). Anal. Calcd. for C₇₄H₉₀BN₄Gd₂: C, 65.31; H, 6.67; N, 4.12. Found: C, 65.21; H, 6.68; N, 3.86.

[(DyCp*₂)₂(μ-Me₂bpym)][BPh₄] (3-Dy). Analogous to the synthesis of **1-Gd**, Cp*₂Dy(BPh₄) (53 mg, 0.071 mmol) was stirred in toluene (4 mL) with **Me₂bpym** (6.6 mg, 0.035 mmol, 0.5 equiv) and then subsequently reduced with KC₈ (4.7 mg, 0.035 mmol, 0.5 equiv). Insolubles were removed by centrifugation and then red, block-shaped crystals of **3-Dy** were grown from a layered THF-toluene solution (2mL THF, 2 mL toluene) cooled to −30 °C for 48 h (33 mg, 69% yield). Anal. Calcd. for C₇₄H₉₀BN₄Dy₂: C, 64.81; H, 6.62; N, 4.09. Found: C, 64.46; H, 6.34; N, 3.78.

[(GdCp*₂)₂(μ-F₂bpym)][BPh₄] (4-Gd). Cp*₂Gd(BPh₄) (77 mg, 0.10 mmol) was suspended in toluene (4 mL) and to this slurry was added **F₂bpym** (10 mg, 0.052 mmol, 0.5 equiv). This reddish-orange solution was stirred for 30 min and then KC₈ (6.9 mg, 0.052 mmol, 0.5 equiv) was added in toluene (0.5 mL). The resulting reddish-black solution was stirred for 24 h and then concentrated en vacuo, dissolved in 1,2-difluorobenzene (DFB, 2 mL), and filtered over celite. Red, block-shaped crystals of **4-Gd** were grown from a layered DFB-hexanes solution (2mL DFB, 2 mL hexanes) stored at 25 °C for 48 h (31 mg, 43% yield). Anal. Calcd. For C₇₆H₉₆BN₆Dy₂: C, 63.18; H, 6.19; N, 4.00. Found: C, 63.08; H, 6.18; N, 3.79.

[(DyCp*₂)₂(μ-F₂bpym)][BPh₄] (4-Dy). Analogous to the synthesis of **4-Gd**, Cp*₂Dy(BPh₄) (78 mg, 0.10 mmol) was stirred in toluene (4 mL) with **F₂bpym** (10 mg, 0.052 mmol, 0.5 equiv) and then subsequently reduced with KC₈ (6.9 mg, 0.052 mmol, 0.5 equiv) for 24 h. The reaction was concentrated en vacuo, dissolved in DFB, and filtered over celite. Red, block-shaped crystals of **4-Dy** were grown from a layered DFB-hexanes solution (2mL DFB, 2 mL hexanes) stored at 25 °C for 48 h (36 mg, 51% yield). Anal. Calcd. For C₇₆H₉₆BN₆Dy₂: C, 62.70; H, 6.14; N, 4.06. Found: C, 62.90; H, 6.47; N, 3.68.

3.6.2 NMR Spectroscopy

NMR spectroscopy data were obtained on solutions in deuterated solvents (CDCl₃ or C₆D₆) obtained from Cambridge Isotope Laboratories, Inc. ¹H-NMR, ¹³C-NMR, and ¹⁹F-NMR data were recorded on Bruker AVQ-400, DRX-500, AV-500, and AV-600 spectrometers. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak (δ 7.26 for CDCl₃ and δ 7.16 for C₆D₆ for ¹H-NMR; δ 77.16 for CDCl₃ and δ 128.06 for C₆D₆ for ¹³C-NMR). Data for ¹H-NMR are reported in the following format: chemical shift (ppm) (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration). Data for ¹³C-NMR and ¹⁹F-NMR are reported in terms of chemical shift (ppm) with coupling constants for ¹⁹F-¹³C coupling where applicable.

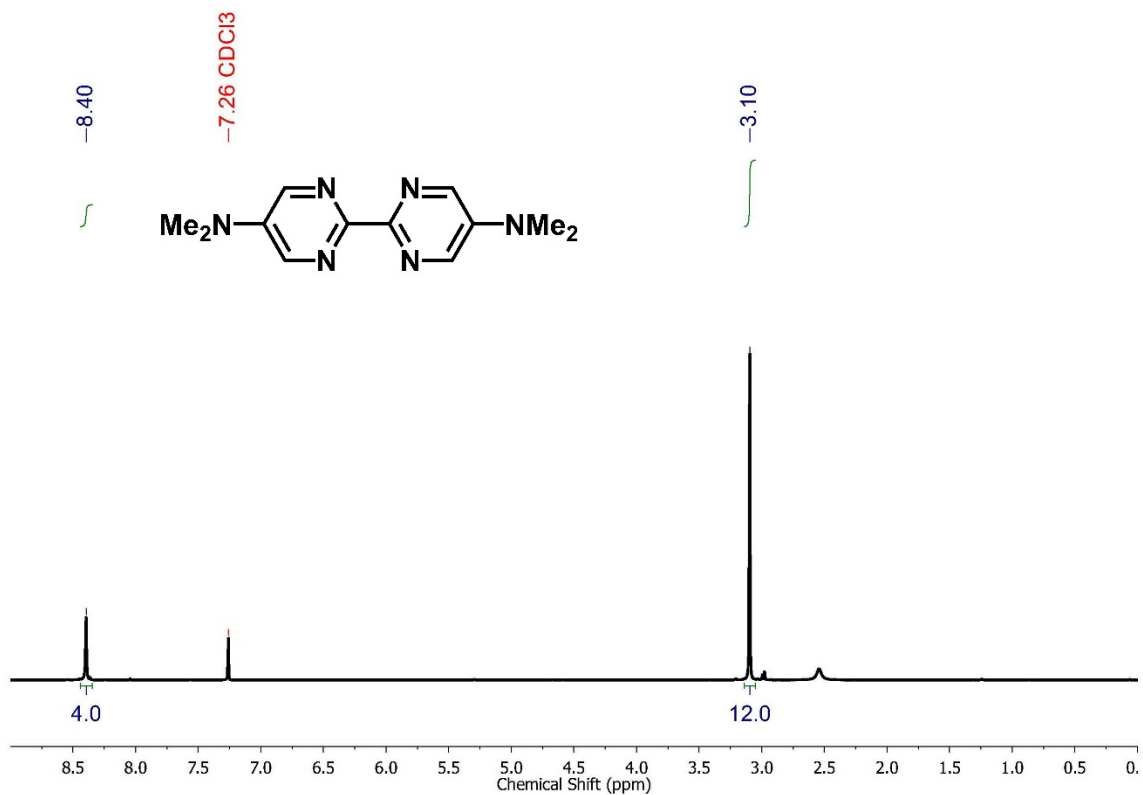


Figure S3.1. ^1H -NMR spectrum of $(\text{NMe}_2)_2\text{bpym}$ in CDCl_3 .

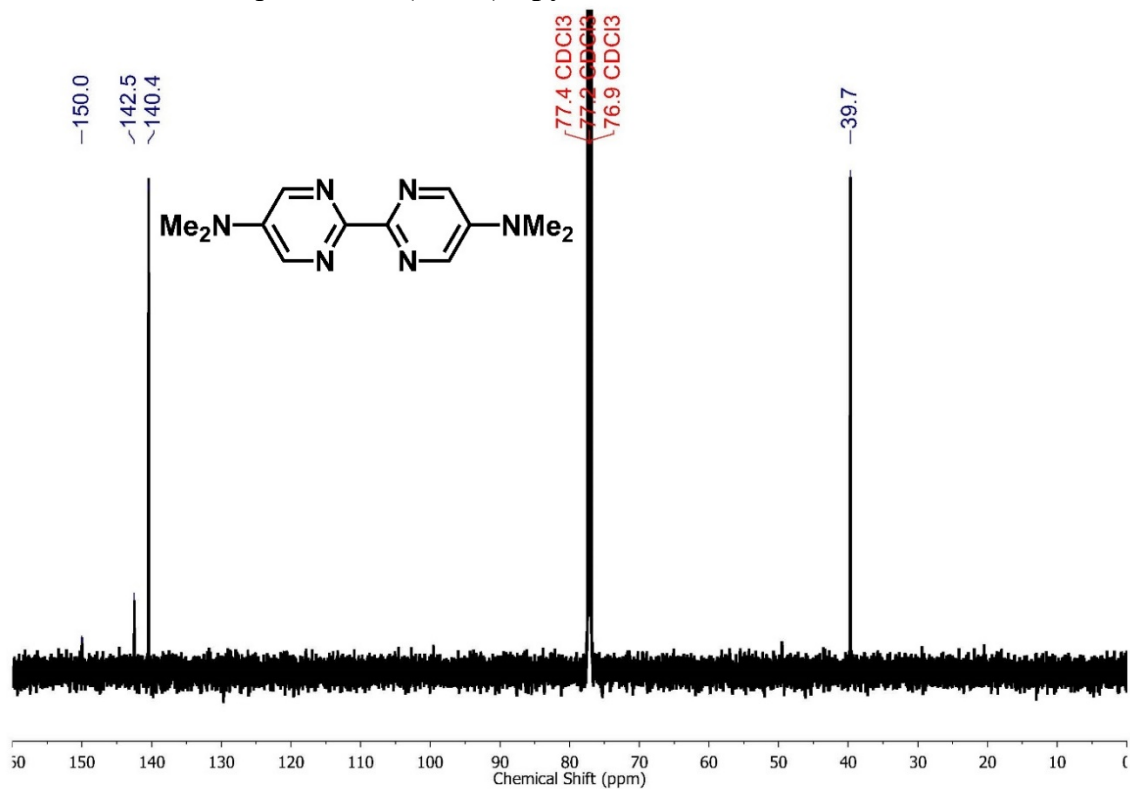


Figure S3.2. ^{13}C -NMR spectrum of $(\text{NMe}_2)_2\text{bpym}$ in CDCl_3 .

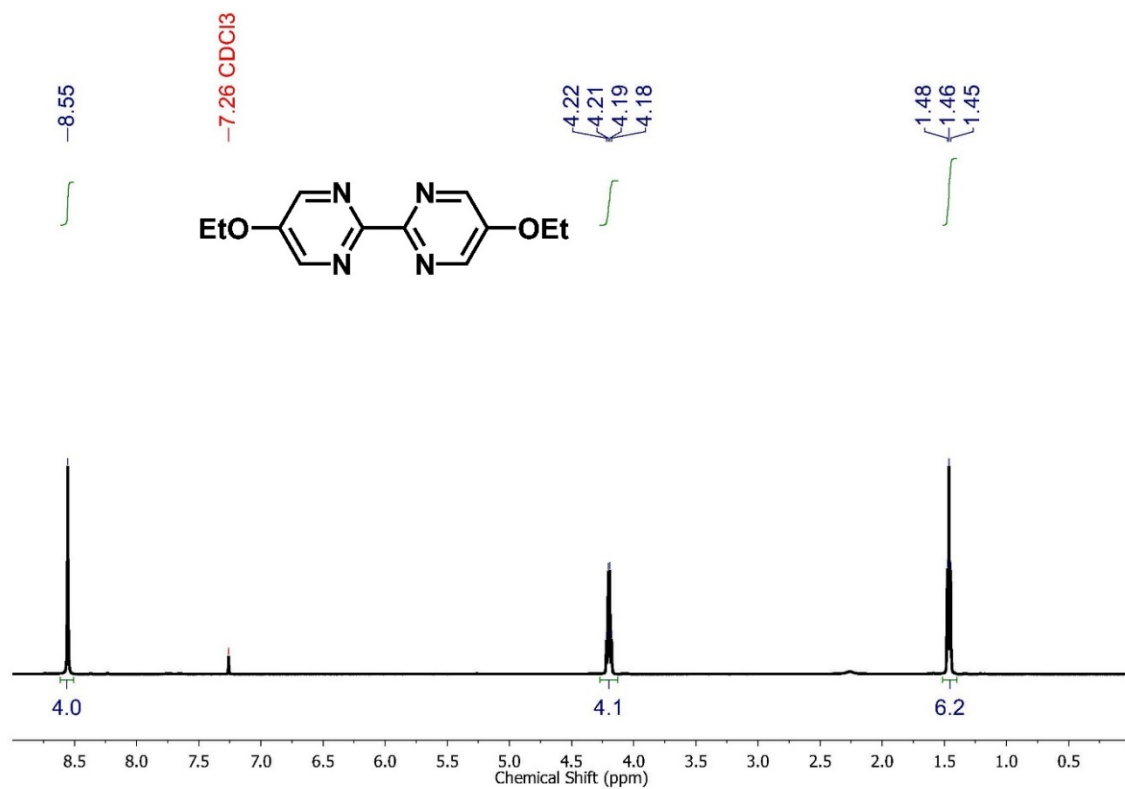


Figure S3.3. ¹H-NMR spectrum of (OEt)₂bpym in CDCl₃.

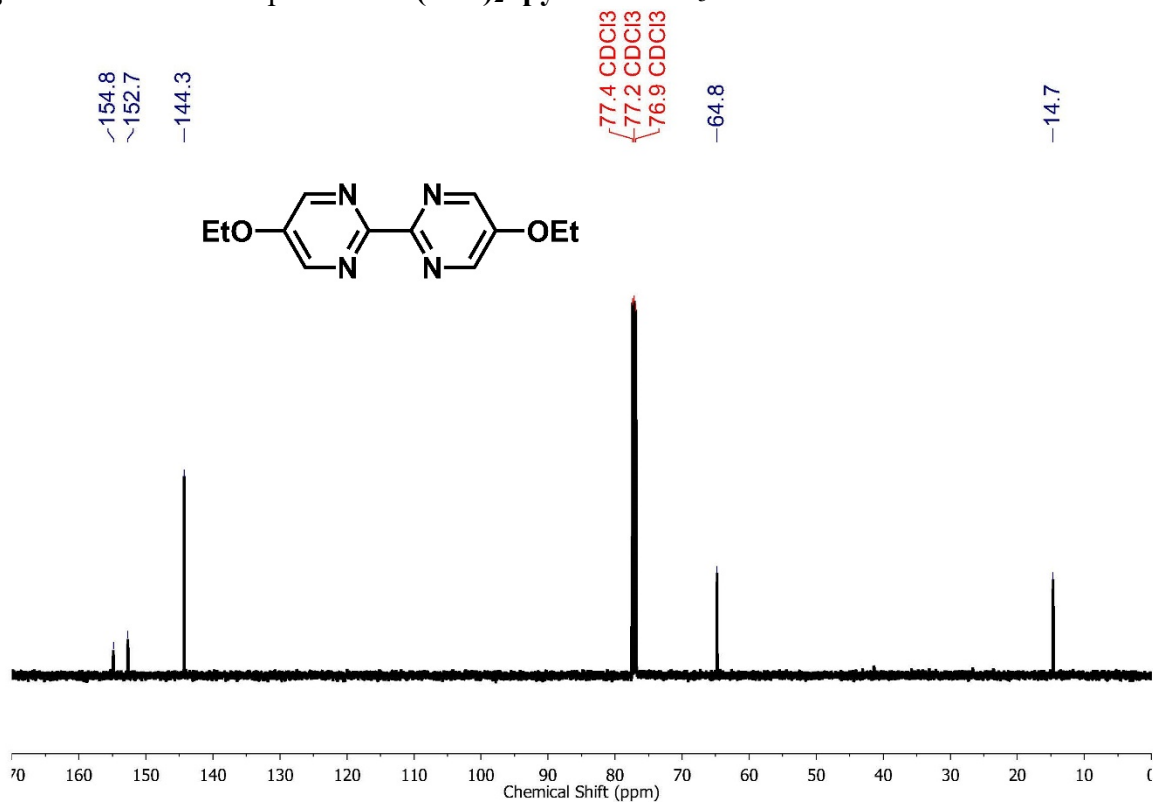


Figure S3.4. ¹³C-NMR spectrum of (OEt)₂bpym in CDCl₃.

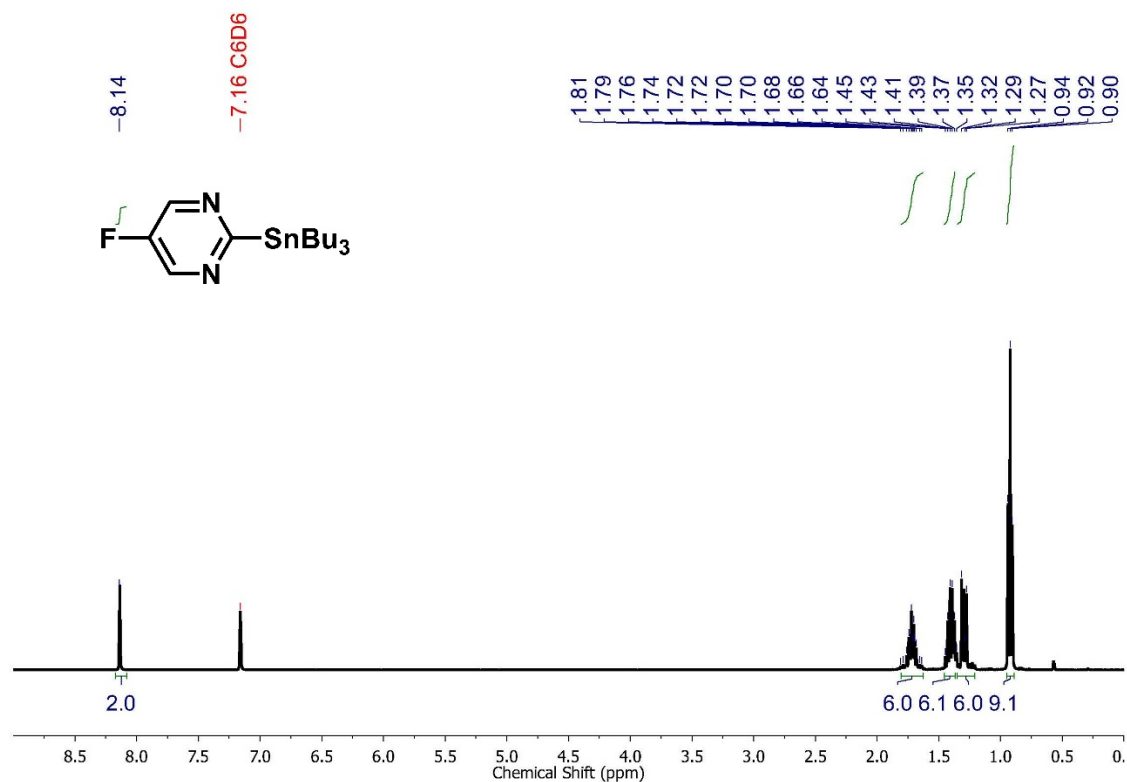


Figure S3.5. ¹H-NMR spectrum of 5-fluoro-2-tributylstannylpyrimidine in C₆D₆.

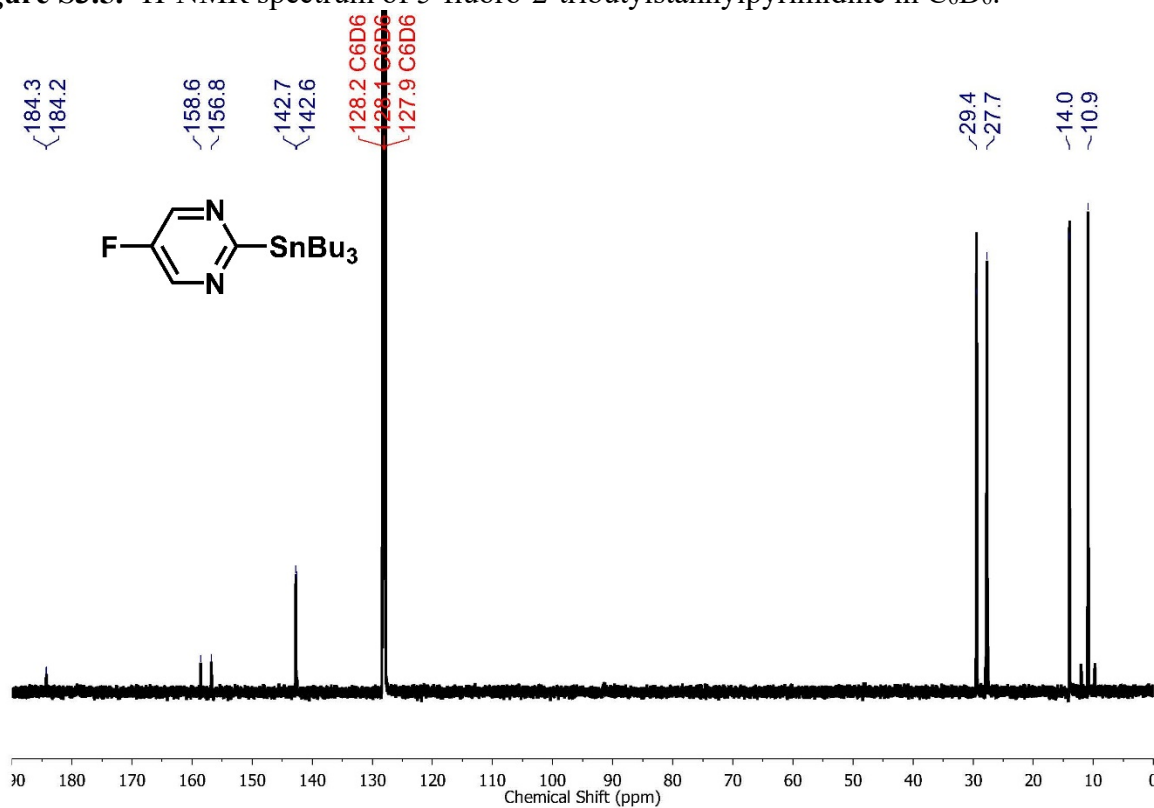


Figure S3.6. ¹³C-NMR spectrum of 5-fluoro-2-tributylstannylpyrimidine in C₆D₆.

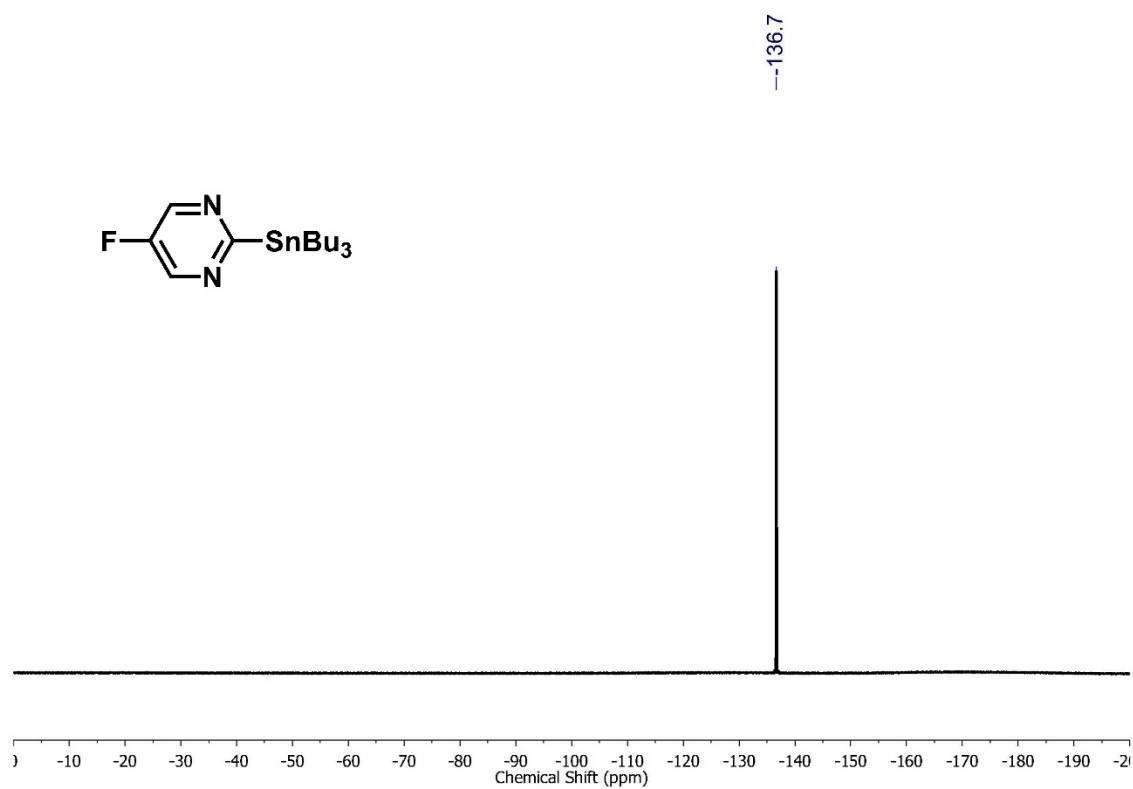


Figure S3.7. ^{19}F -NMR spectrum of 5-fluoro-2-tributylstannylpyrimidine in C_6D_6 .

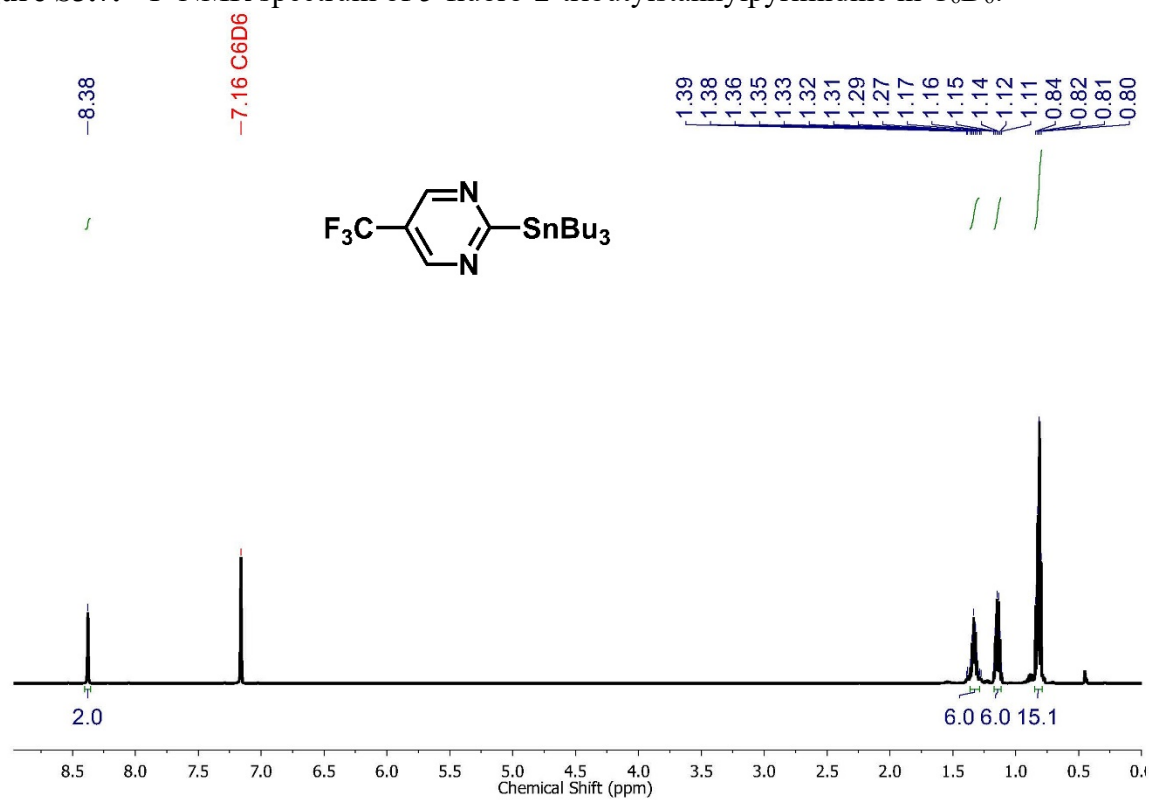


Figure S3.8. ^1H -NMR spectrum of 5-trifluoromethyl-2-tributylstannylpyrimidine in C_6D_6 .

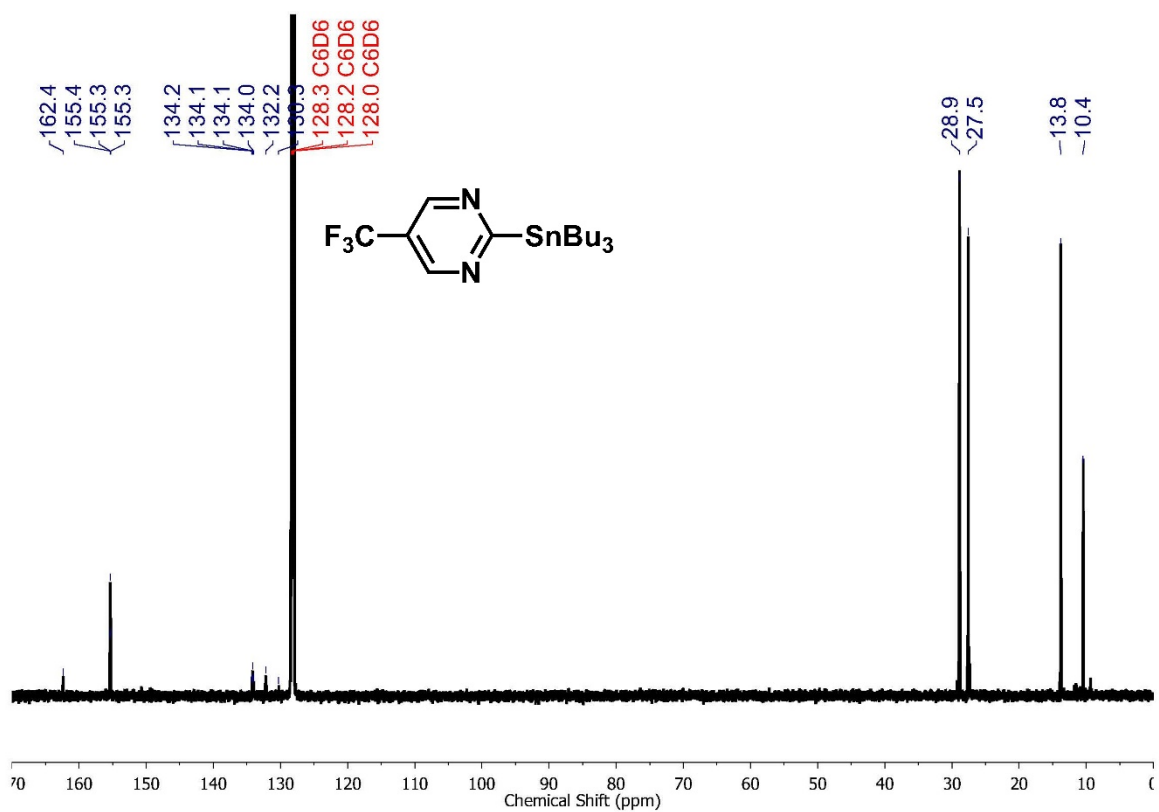


Figure S3.9. ^{13}C -NMR spectrum of 5-trifluoromethyl-2-tributylstannylpyrimidine in C_6D_6 .

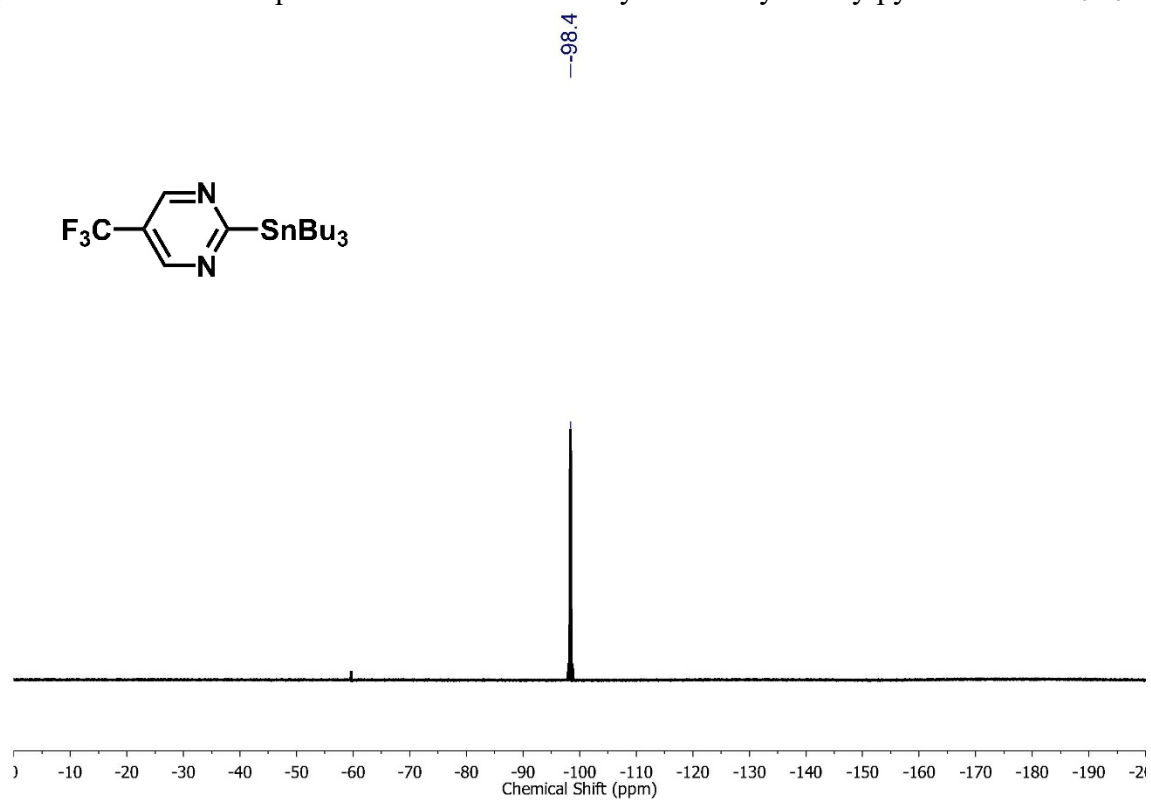


Figure S3.10. ^{19}F -NMR spectrum of 5-trifluoromethyl-2-tributylstannylpyrimidine in C_6D_6 .

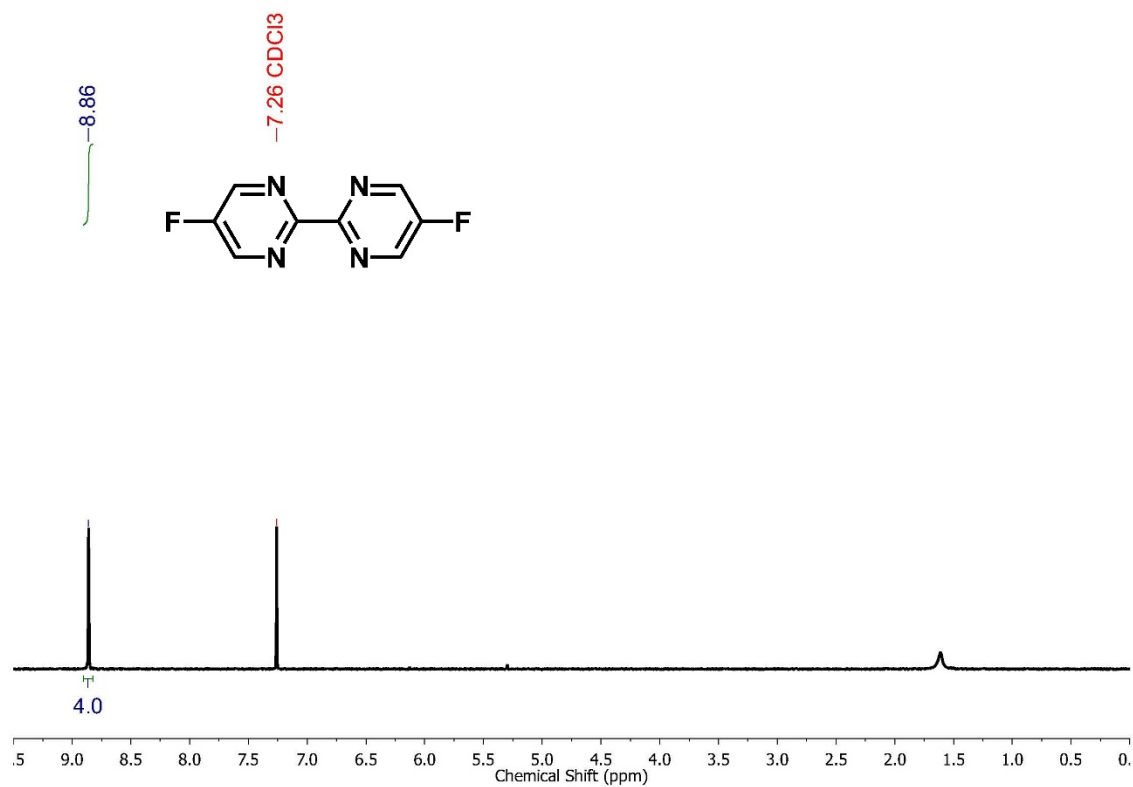


Figure S3.11. ¹H-NMR spectrum of **F₂bpym** in CDCl₃.

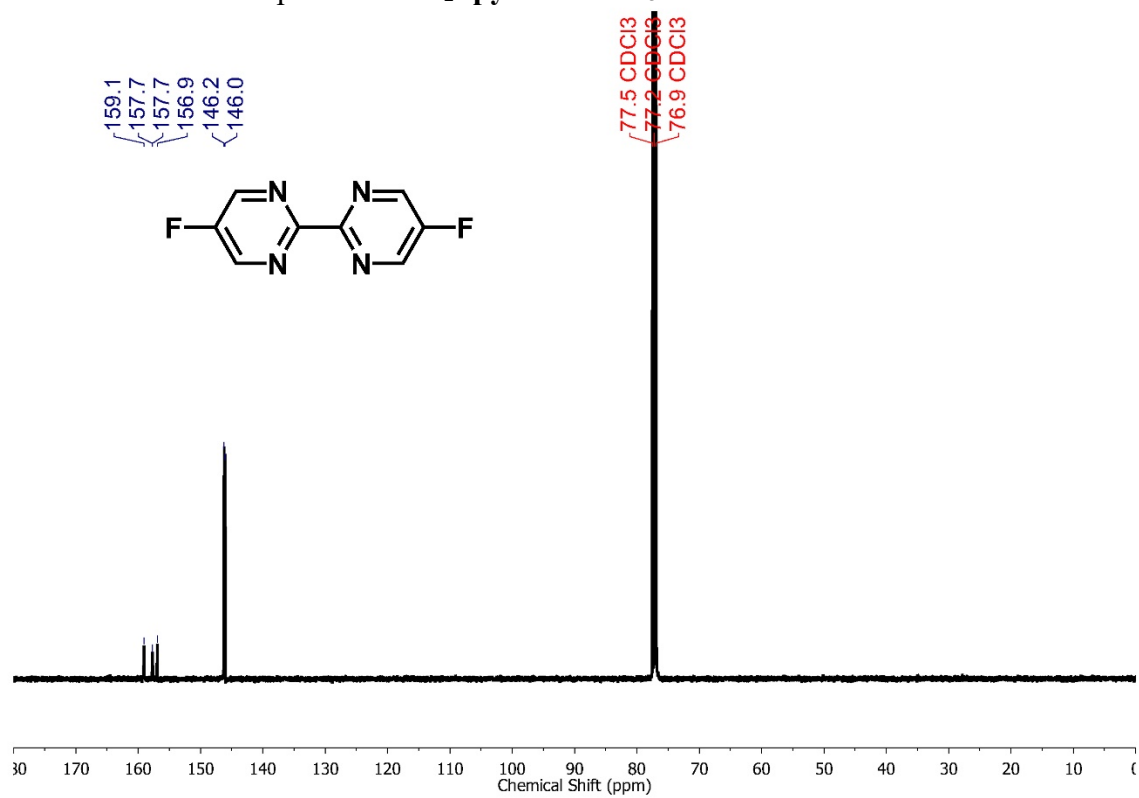


Figure S3.12. ¹³C-NMR spectrum of **F₂bpym** in CDCl₃.

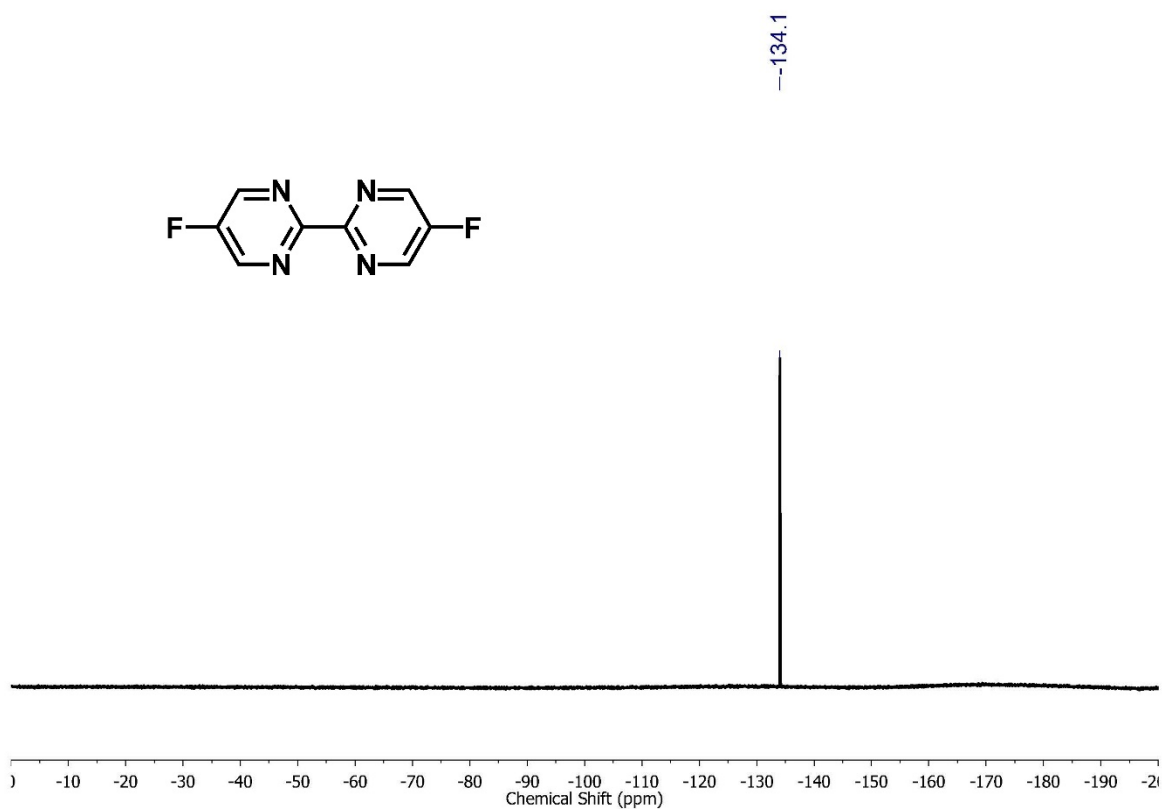


Figure S3.13. ^{19}F -NMR spectrum of F_2bpym in CDCl_3 .

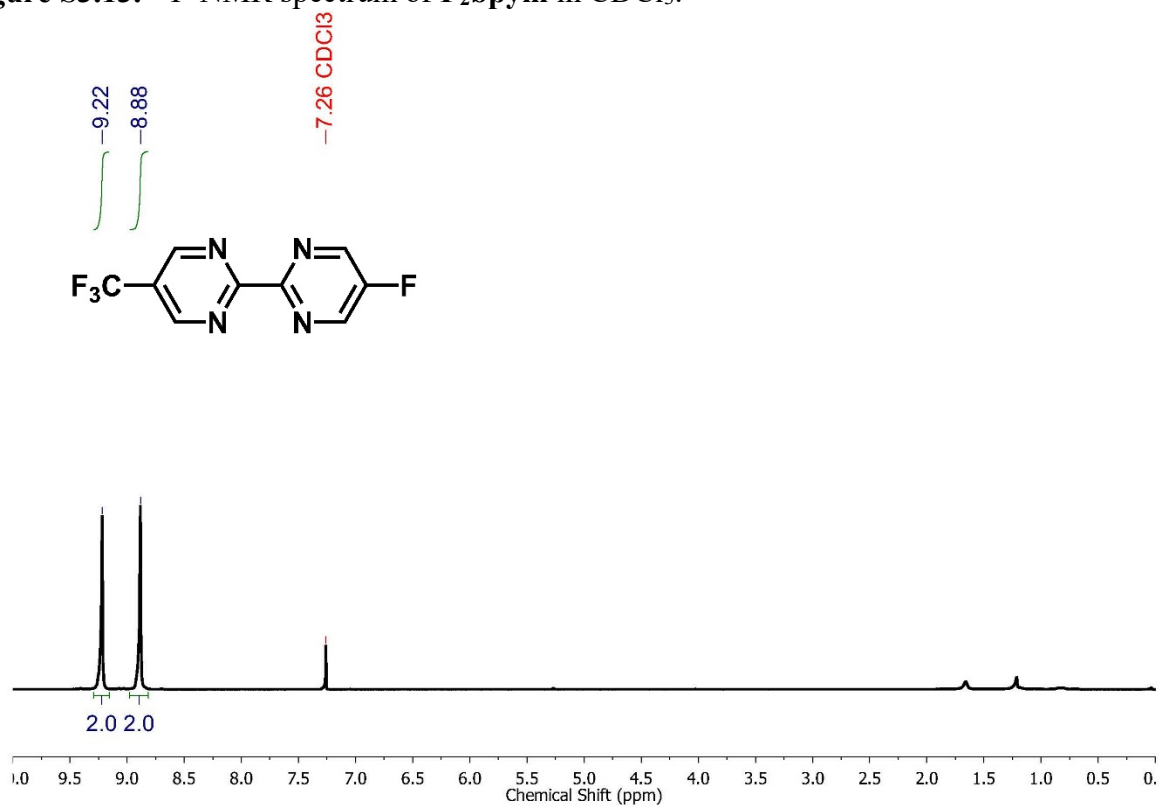


Figure S3.14. ^1H -NMR spectrum of $\text{F}(\text{CF}_3)\text{bpym}$ in CDCl_3 .

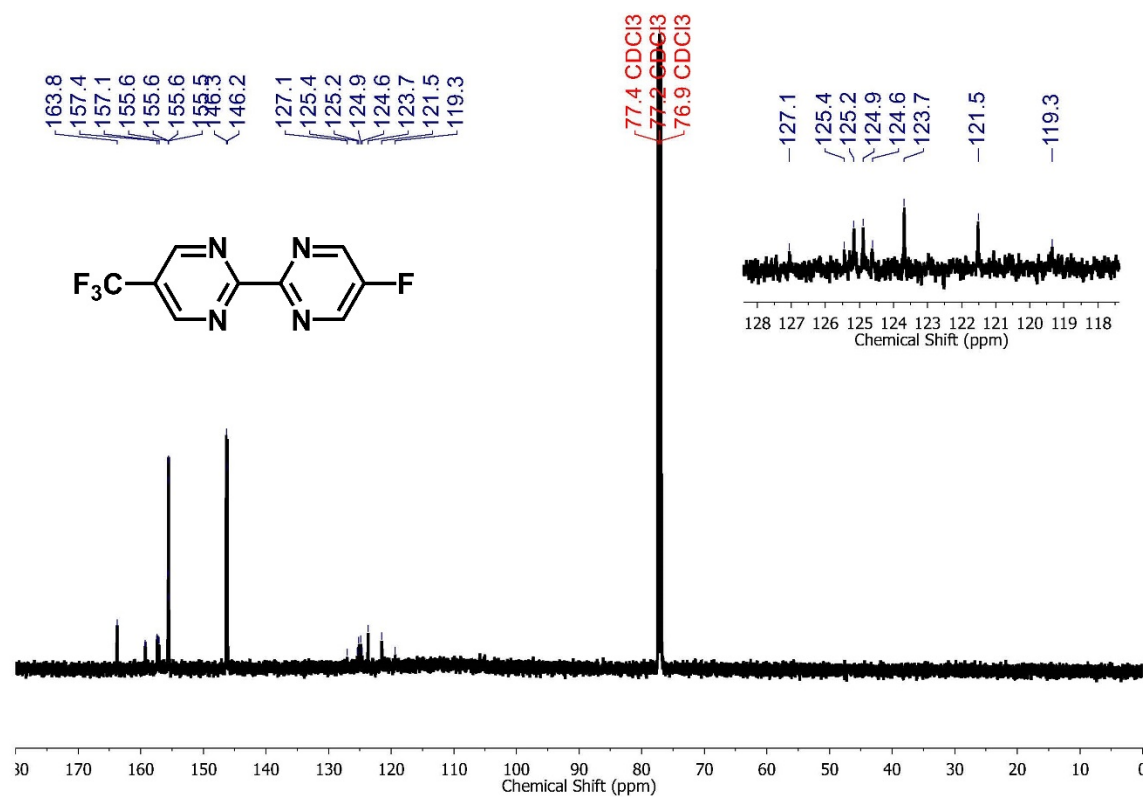


Figure S3.15. ¹³C-NMR spectrum of 5-F(CF₃)bpym in CDCl₃.

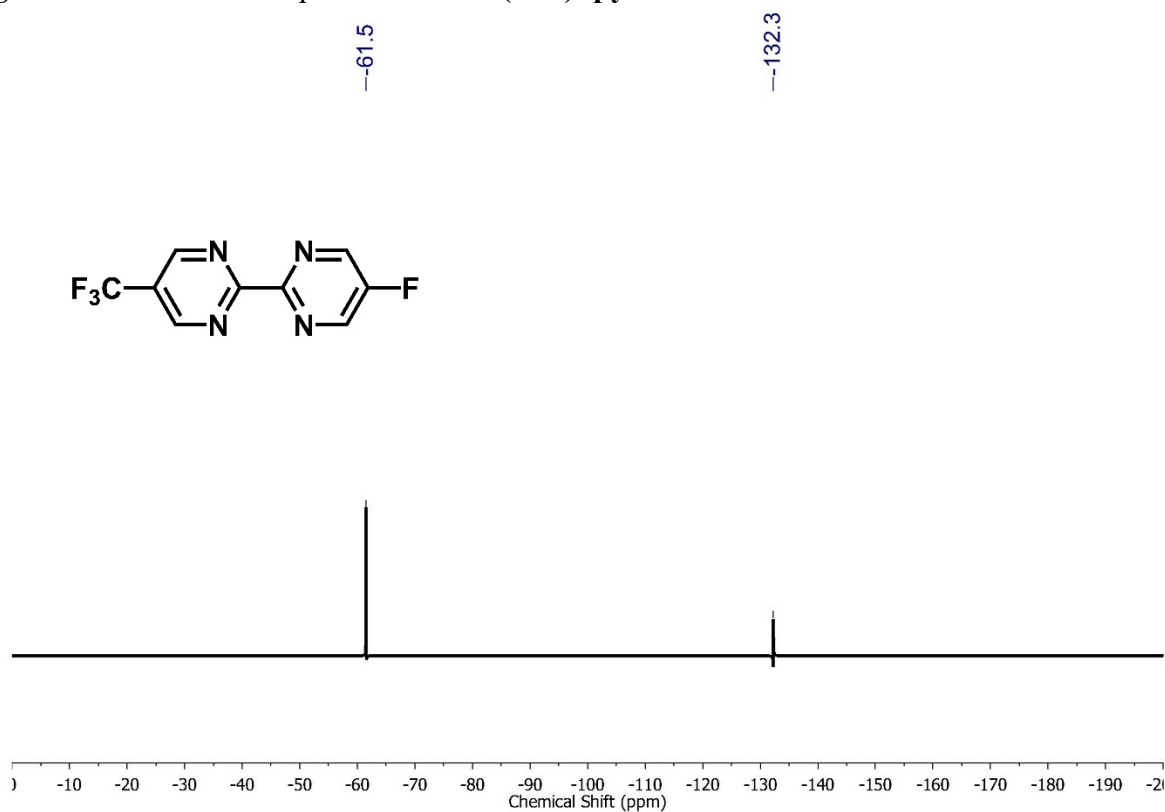


Figure S3.16. ¹⁹F-NMR spectrum of F(CF₃)bpym in CDCl₃.

3.6.3 IR Spectroscopy

FT-IR spectra were recorded on a Perkin Elmer Avatar Spectrum 400 FTIR Spectrometer equipped with attenuated total reflectance (ATR).

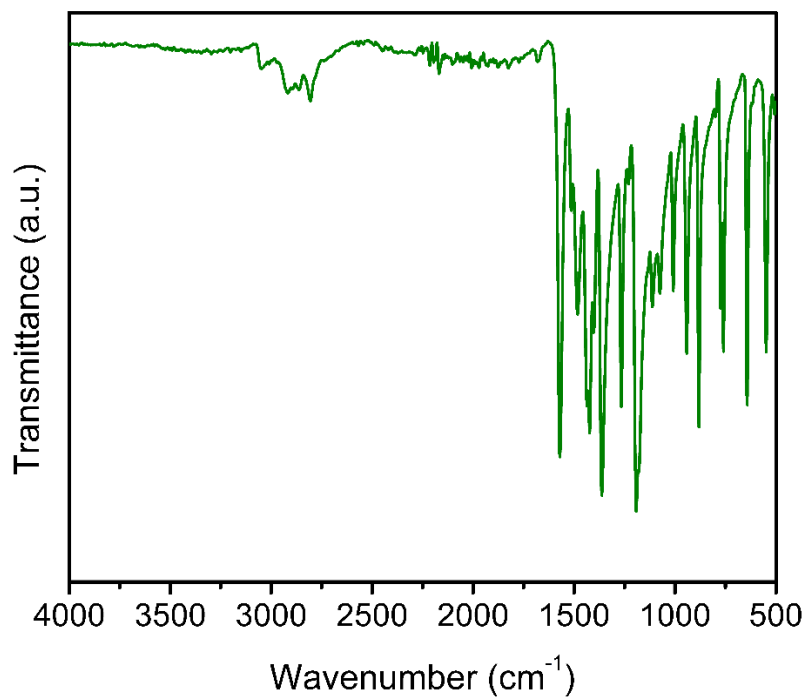


Figure S3.17. IR spectrum of (NMe₂)₂bpym.

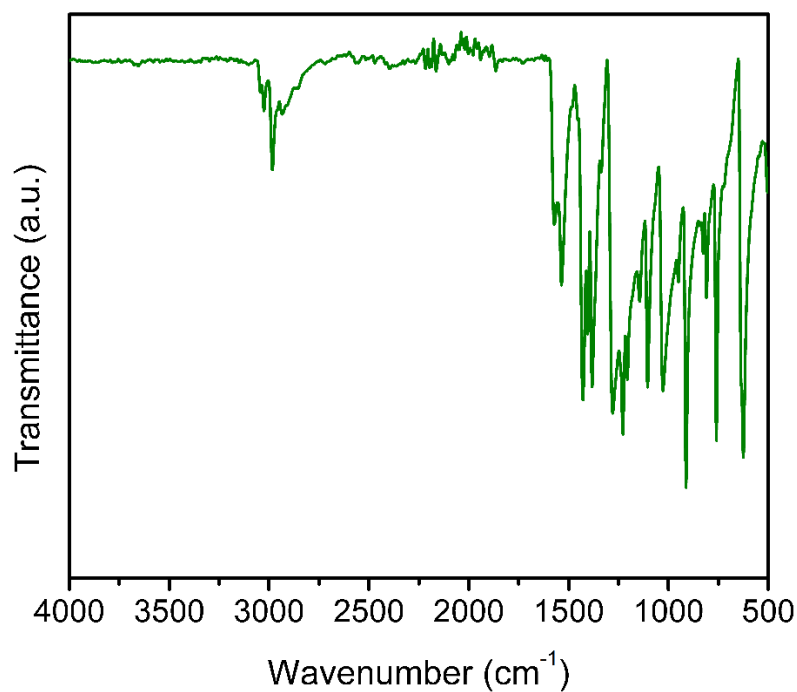


Figure S3.18. IR spectrum of (OEt)₂bpym.

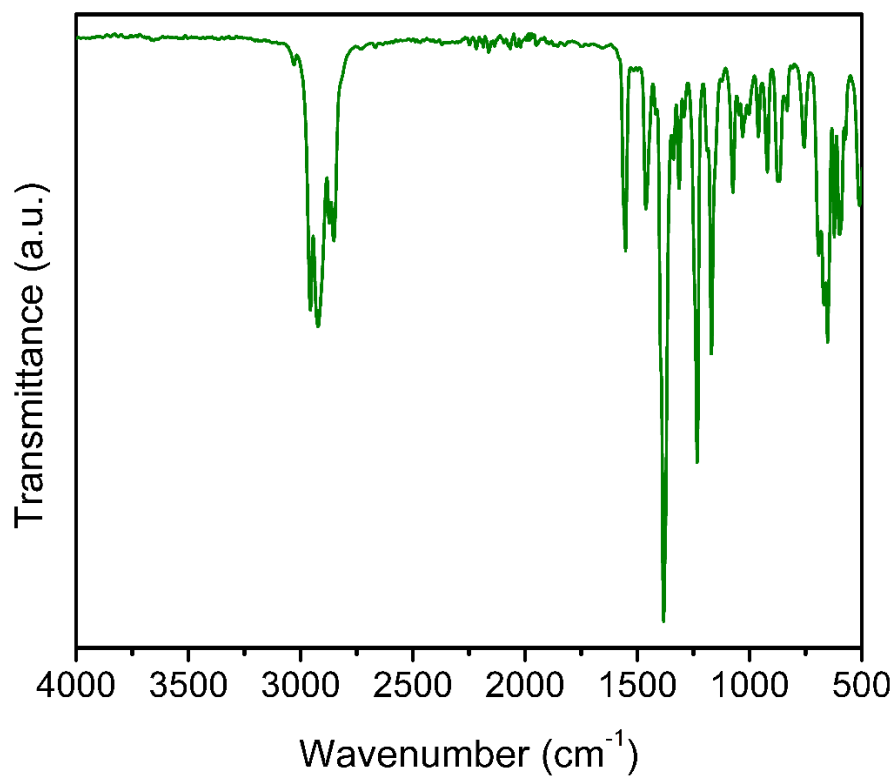


Figure S3.19. IR spectrum of 5-fluoro-2-tributylstannylpyrimidine.

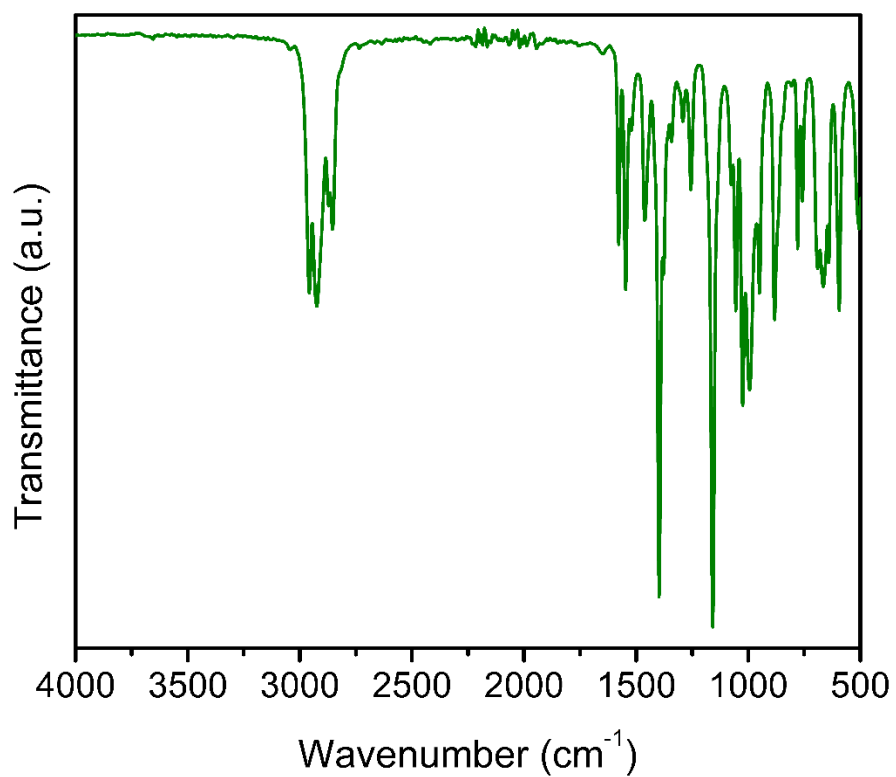


Figure S3.20. IR spectrum of 5-trifluoromethyl-2-tributylstannylpyrimidine.

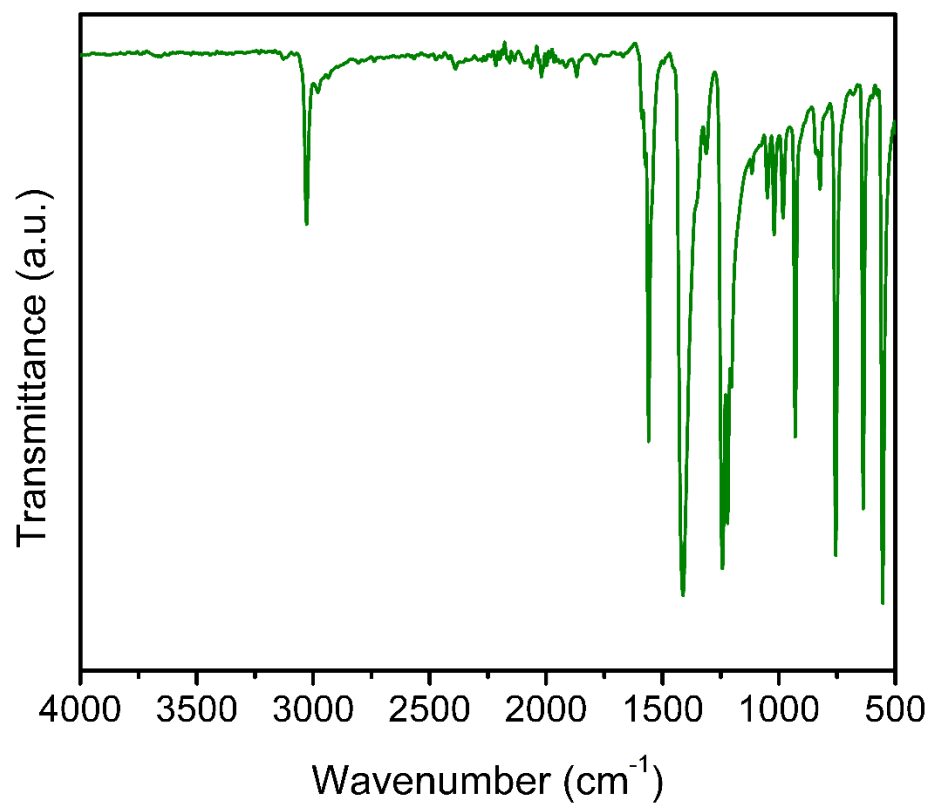


Figure S3.21. IR spectrum of **F₂bpym**.

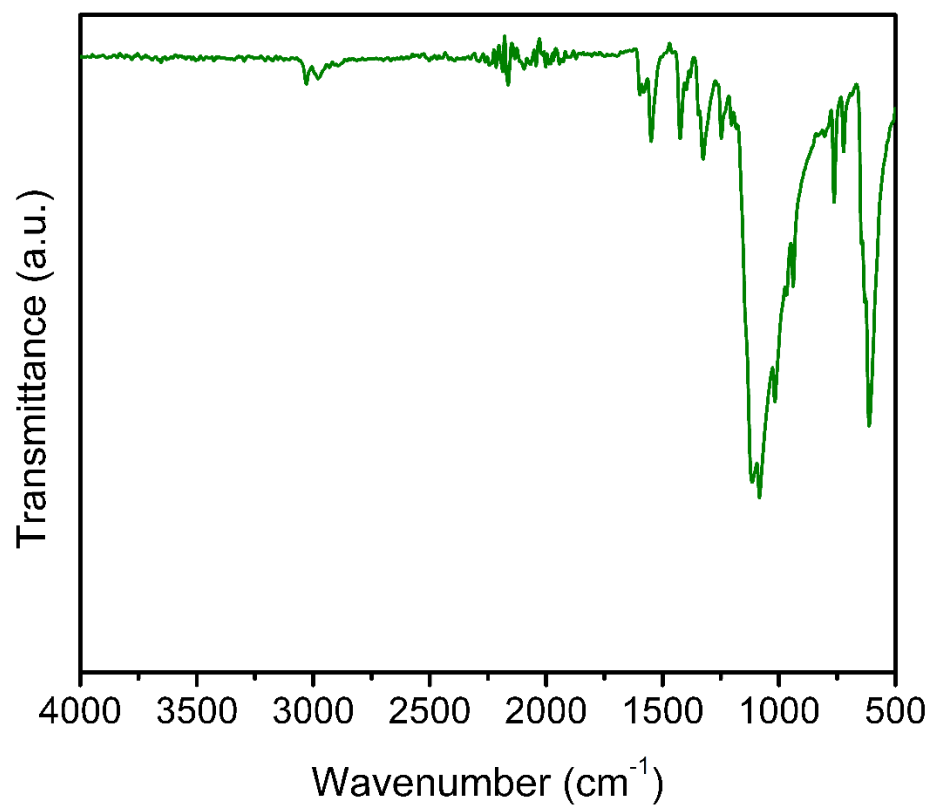


Figure S3.22. IR spectrum of **F(CF₃)bpym**.

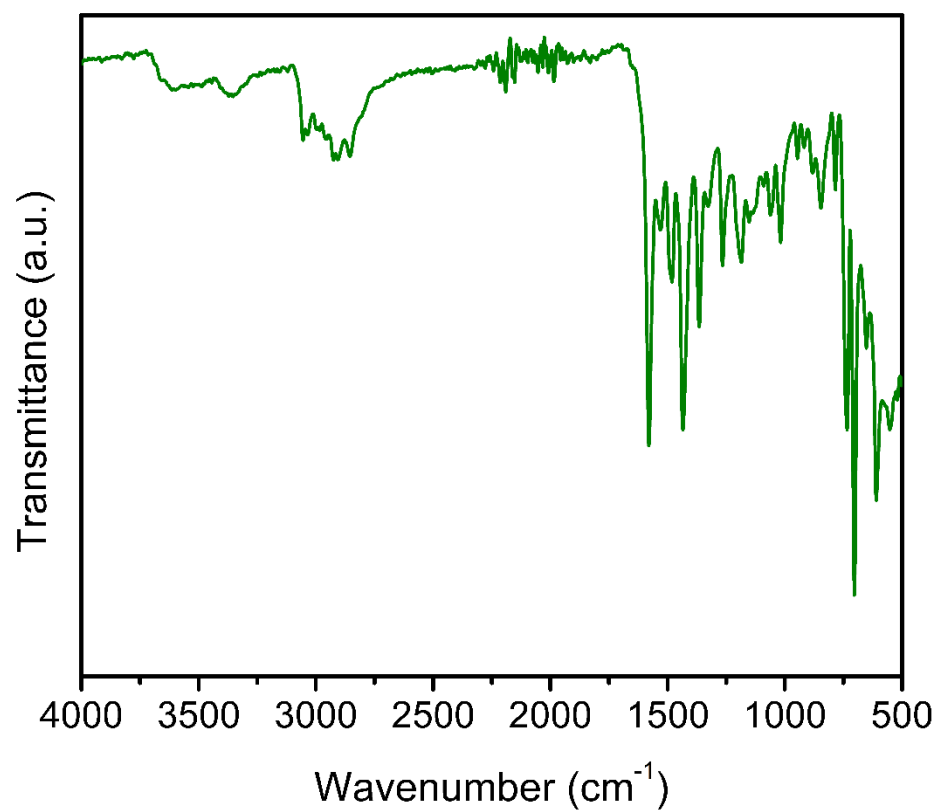


Figure S3.23. IR spectrum of **1-Gd**.

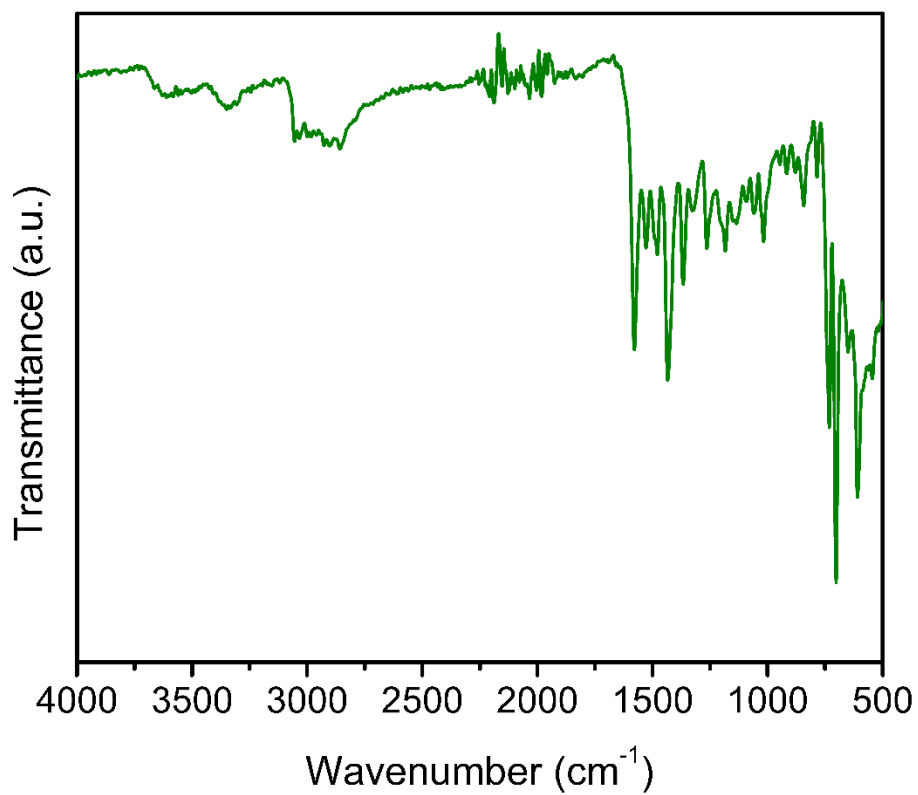


Figure S3.24. IR spectrum of **1-Dy**.

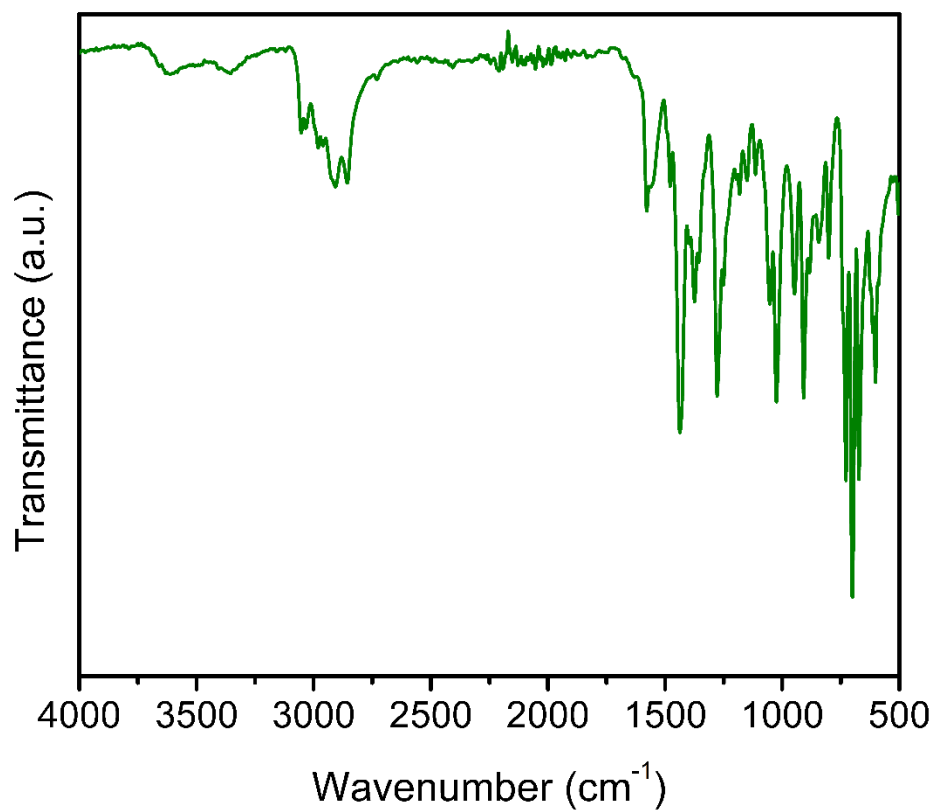


Figure S3.25. IR spectrum of **2-Gd**.

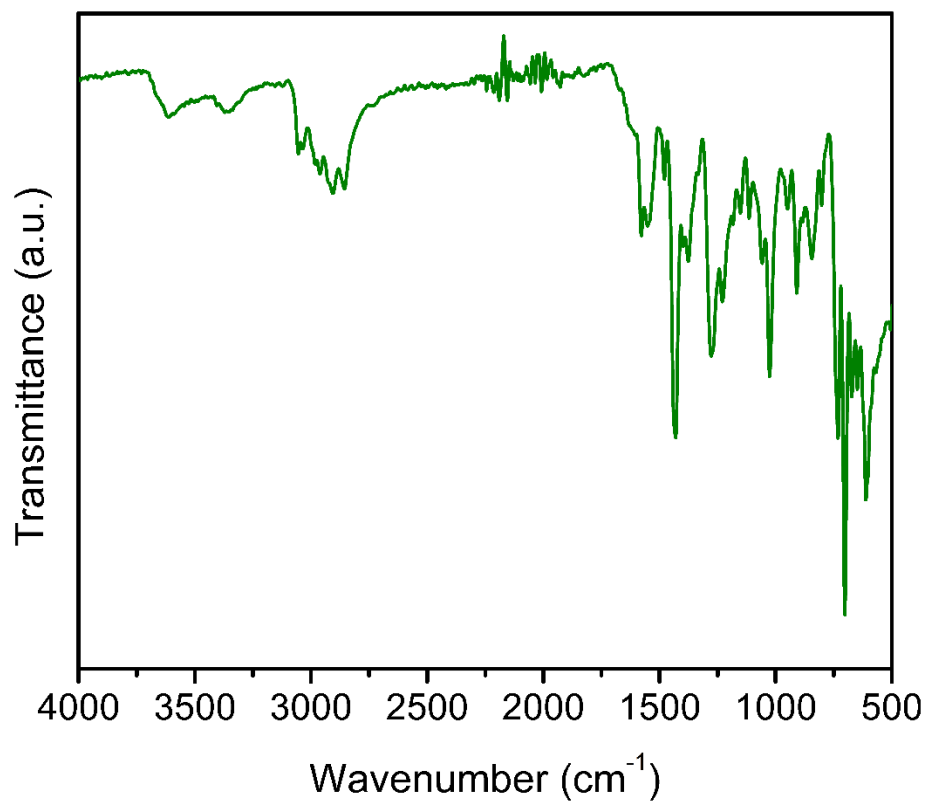


Figure S3.26. IR spectrum of **2-Dy**.

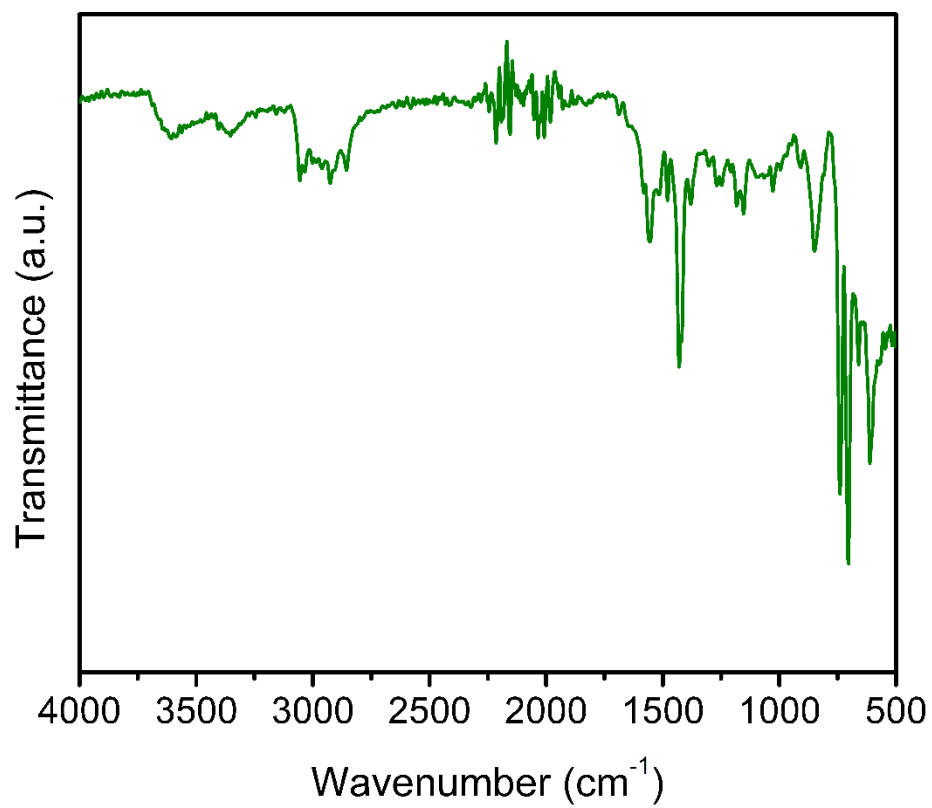


Figure S3.27. IR spectrum of **3-Gd**.

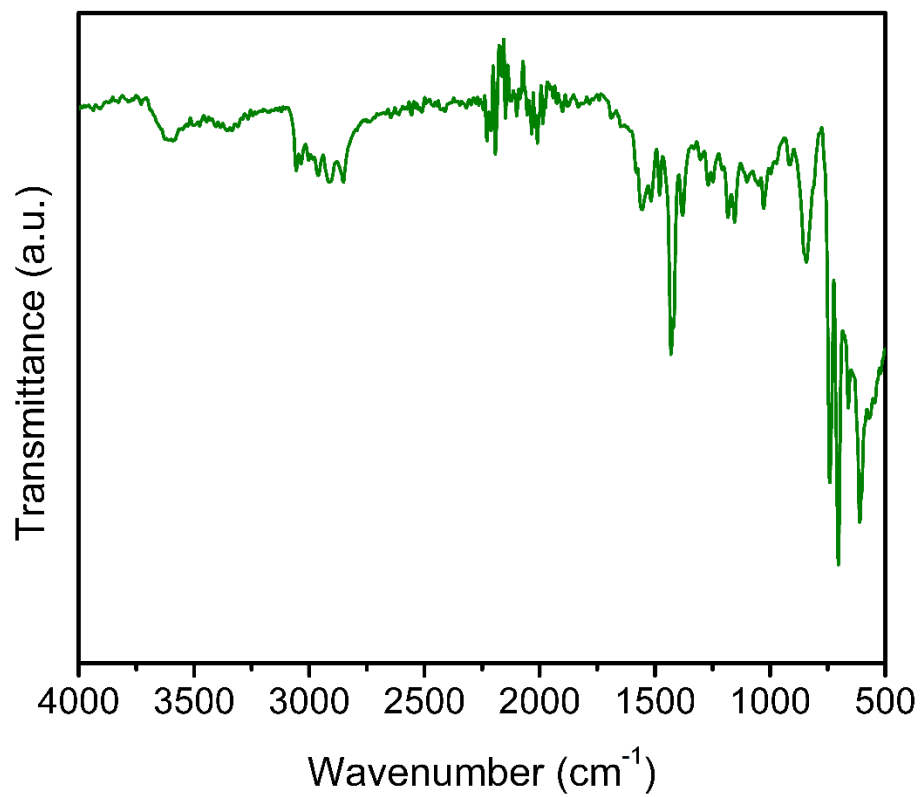


Figure S3.28. IR spectrum of **3-Dy**.

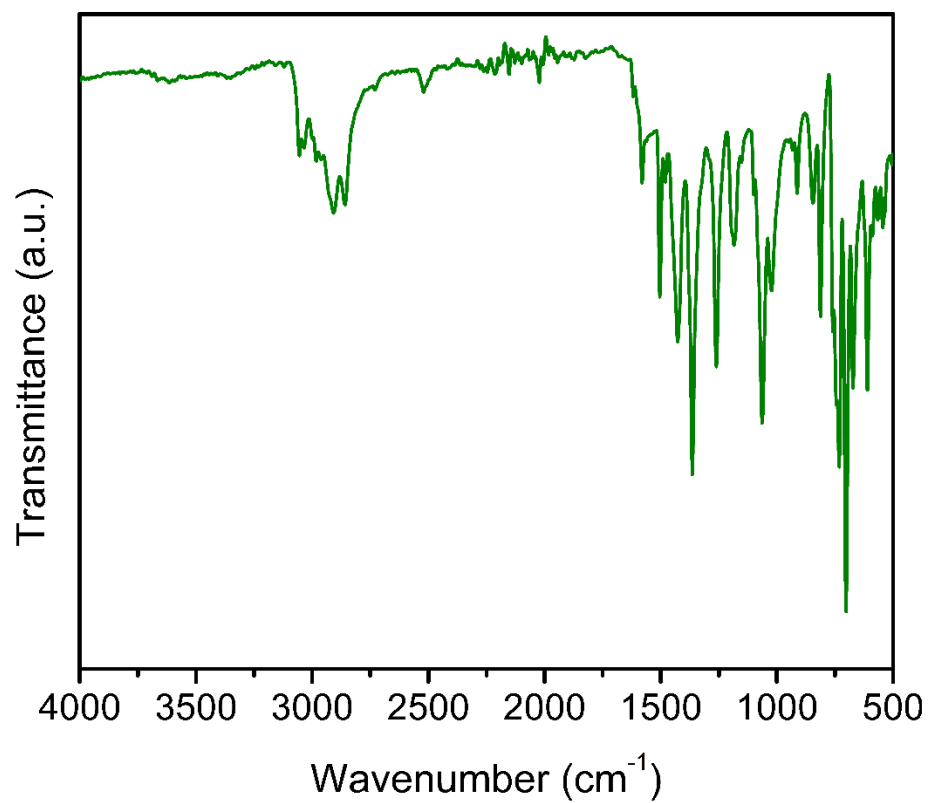


Figure S3.29. IR spectrum of 4-Gd.

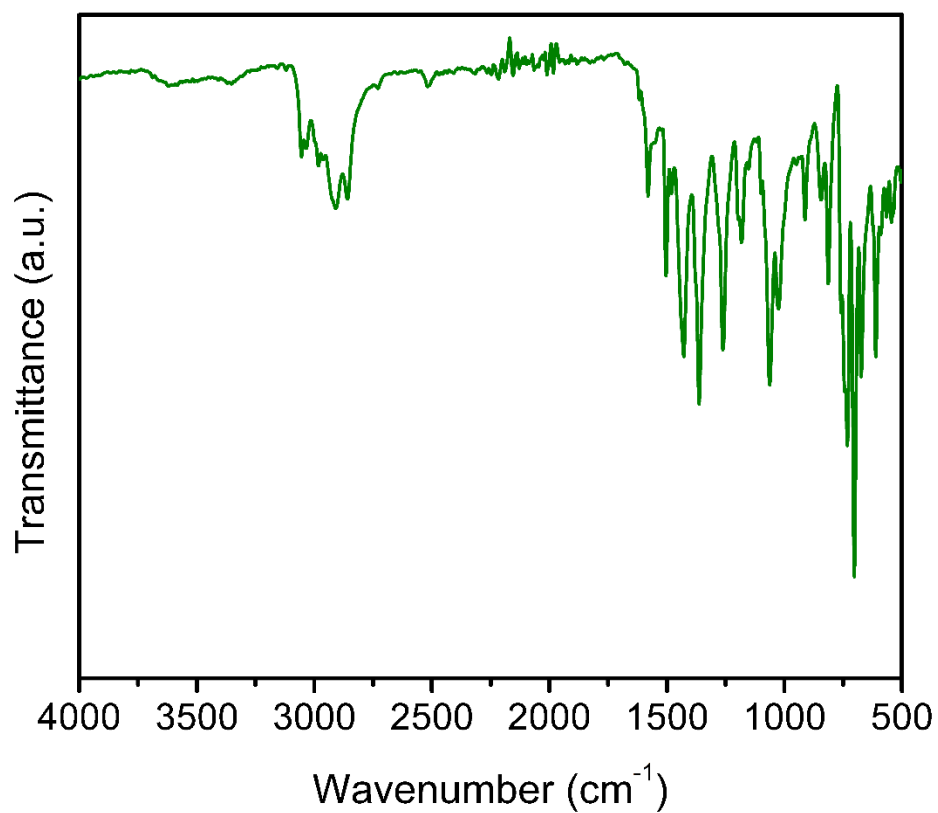


Figure S3.30. IR spectrum of 4-Dy.

3.6.4 X-ray Crystallography Data Collection and Refinement Details

Single-crystal X-ray diffraction data were collected at the small-molecule crystallography beamline (beamline 11.3.1 for **2-Gd**, **3-Gd**, and **3-Dy**; and beamline 12.2.1 for **2-Dy**, **4-Gd**, and **4-Dy**) at the Advanced Light Source, Lawrence Berkeley National Laboratory using synchrotron radiation. Single crystals were coated with Paratone-N oil, mounted on a MiTeGen loop, and frozen at 100 K under a N₂ stream of an Oxford Cryostems Cryostream 700 Plus on a Bruker AXS D8 diffractometer. Data were collected through a combination of 4° and 1° ϕ and ω scans. Data reduction was performed through SAINT and absorption correction through SADABS (or TWINABS for **3-Dy**).⁷⁻⁹

Single-crystal X-ray diffraction data for **1-Dy** were collected at the University of California, Berkeley using a Rigaku XtaLAB p200 equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200K hybrid pixel array detector at 100 K under a N₂ stream of an Oxford Cryostems Cryostream with MoK α radiation (graphite monochromator). The frames were integrated with CrysAlis^{Pro} software, including a multi-scan absorption correction that was applied using the SCALE3 ABSPACK scaling algorithm within CrysAlis^{Pro}.¹⁰

Structure solutions were performed by SHELXT¹¹ using the direct method and were refined by least-square refinement against F^2 by SHELXL¹² following standard procedures via OLEX2 crystallographic software.¹³ For all structures, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed on geometrically calculated positions using the riding model and refined isotropically.

[(DyCp*₂)₂(μ -(NMe₂)₂bpym)][BPh₄] (1-Dy**)**

The compound crystallized in $P\bar{1}$ space group with two half-molecules and a corresponding [BPh₄][−] counteranion in the asymmetric unit. Each Dy ion bears two Cp* rings, one of which is disordered over two positions. The disordered cyclopentadienyl rings were constrained to the geometrically calculated positions of ideal pentagons (AFIX 56). Anisotropic refinement of these disordered Cp* rings were stabilized by the enhanced rigid bond restraints (RIGU). Two toluene molecules co-crystallized in the structure, both of which are disordered over two position. The first toluene molecule was disordered over a crystallographic inversion center, and anisotropic displacement parameters for all seven C atoms were restrained to be the same (EADP). The second toluene molecule was disordered over a general position and was modeled with 2 positions. The phenyl ring of the disordered toluene molecule was constrained to the ideal geometrically calculated position (AFIX 66). Anisotropic refinement of the first disordered component was achieved by using the similar anisotropic displacement parameters (SIMU), while those of the second disordered component needs to be restrained with EADP. All C(sp²)–CH₃ distances, and C–C–CH₃ angles were restrained to be similar (SADI). Additionally, two 1,2-difluorobenzene (DFB) molecules were found in the structure, one of which was disordered over two positions. The phenyl ring of the disordered DFB was constrained to the ideal geometrically calculated position (AFIX 66). Anisotropic refinement of the disordered DFB molecule was restrained by EADP. All C–F distances and C–C–F angles were restrained to be similar (SADI).

[(GdCp*₂)₂(μ-(OEt)₂bpym)][BPh₄] (2-Gd)

The compound crystallized in $P2_1/c$ space group with the whole molecule in the asymmetric unit, together with one and a half molecule of toluene. A toluene molecule was found to be disordered over a crystallographic inversion center. Refinement of this toluene molecule was stabilized by constraining the phenyl ring to be at the geometrically calculated positions (AFIX 66), and anisotropic refinement was stabilized by the enhanced rigid bond restraint.

[(DyCp*₂)₂(μ-(OEt)₂bpym)][BPh₄] (2-Dy)

The compound crystallized in $P\bar{1}$ space group with the whole molecule in the asymmetric unit. One Cp* ring was modeled as a two-component disorder. This disordered Cp* ring was constrained to assume the ideal geometric position using AFIX 56 command. One phenyl ring of the [BPh₄][−] counteranion was found to be disordered over two positions, and the second component was constrained to the ideal geometric position (AFIX 66). Anisotropic refinement of these disordered components were stabilized by the enhanced rigid bond restraints (RIGU). Moreover, one of the ethoxy group appeared to be disordered, as suggested by the unusually large thermal ellipsoids. Disorder modeling of this EtO- group led to an unreasonable model, and thus the disorder was not modeled. Nonetheless, an enhanced rigid bond restraint was placed on this ethoxy group during anisotropic refinement. One molecule of toluene was found in the structure, and there exists a solvent-accessible void with a cloud of electron density. This space was modeled as a toluene molecule disordered over two position, and over the crystallographic inversion center. This disordered toluene molecule was constrained to the ideal geometric position using AFIX 66 commands, and the equal anisotropic displacement restraint (EADP) was employed during the anisotropic refinement.

[(GdCp*₂)₂(μ-Me₂bpym)][BPh₄] (3-Gd)

The compound crystallized in $P2_1/c$ space group with the whole molecule in the asymmetric unit. Three of the four Cp* rings were found to be disordered, and were modeled over two positions. Anisotropic refinement of the disordered Cp* rings was stabilized by application of the enhanced rigid bond restraint (RIGU). Three tetrahydrofuran solvent molecules were found in the structure, and two molecules require the enhanced rigid bond restraint in order to stabilize the anisotropic refinement.

[(DyCp*₂)₂(μ-Me₂bpym)][BPh₄] (3-Dy)

The crystal was found to be a non-merohedral twin, and the structure was refined against both twinned domains. The compound crystallized in $P\bar{1}$ space group with two half-molecules in the asymmetric unit and one [BPh₄][−] counteranion. Three of the four Cp* rings were found to be disordered, and were modeled over two positions. Anisotropic refinement of the disordered Cp* rings was stabilized by application of the enhanced rigid bond restraint (RIGU). Anisotropic refinement of one disordered Cp* ring (C40 to C47 and C40A to C47A) cannot be stabilized by the enhanced rigid bond restraint, and thus equal anisotropic displacement restraint (EADP) were employed on four C atoms (C40, C41, C45, C46, and their second disordered components). A toluene molecule was found in the asymmetric unit.

$[(\text{GdCp}^*)_2(\mu\text{-F}_2\text{bpym})][\text{BPh}_4]$ (4-Gd)

The compound crystallized in $P\bar{1}$ space group with two independent half-molecules in the asymmetric unit. Three of the four independent Cp^* rings were found to be disordered over two positions. Anisotropic refinement of the disordered Cp^* rings were stabilized by the enhanced rigid bond restraints (RIGU), while constraining the sum of the occupancy to unity. One disordered Cp^* ring (C18B–C22B, and its disordered counterpart C18C–C22C) was constrained to the ideal planar pentagon geometry (AFIX 56) to achieve stable refinement. A 1,2-difluorobenzene solvent molecule was found to co-crystallize in the structure. It was found disordered over two positions, and anisotropic refinement was stabilized by rigid bond restraint (SIMU).

 $[(\text{DyCp}^*)_2(\mu\text{-F}_2\text{bpym})][\text{BPh}_4]$ (4-Dy)

The compound crystallized in $P\bar{1}$ space group with two independent half-molecules in the asymmetric unit. All four independent Cp^* rings were found to be disordered. Three Cp^* rings were disordered over two positions, and the other was disordered over three positions. Refinement of the disordered Cp^* rings were stabilized by the application of the enhanced rigid bond restraints (RIGU). The sum of the occupancy of each Cp^* ring was constrained to be unity. A 1,2-difluorobenzene solvent molecule was found to co-crystallize in the structure. It was found disordered over two positions, and anisotropic refinement was stabilized by rigid bond restraint (SIMU).

Table S3.1. Crystal data and structure refinement for [(DyCp*₂)₂(μ-(NMe₂)₂bpym)][BPh₄] (**1-Dy**).

	1-Dy
Empirical formula	Dy ₂ F ₄ N ₆ C _{98.5} BH ₁₁₆
Formula weight (g/mol)	1795.78
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å), α (°)	11.4042(4), 69.062(3)
<i>b</i> (Å), β (°)	20.0634(7), 75.923(3)
<i>c</i> (Å), γ (°)	21.0569(7), 74.924(3)
Volume (Å ³)	4284.2(3)
<i>Z</i>	2
Density (calculated, g/cm ³)	1.392
Absorption coefficient (mm ⁻¹)	1.790
<i>F</i> (000)	1844
Crystal size (mm ³)	n/a
θ range for data collection (°)	2.994 to 25.350
Index ranges	$-13 \leq h \leq 13$ $-24 \leq k \leq 24$ $-25 \leq l \leq 25$
Reflections collected	77485
Independent reflections, <i>R</i> _{int}	15675, 0.0923
Completeness to $\theta = 25.242^\circ$	99.8 %
Absorption correction	Semi-empirical
Max. and min. transmission	1.000 and 0.61089
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	15675 / 564 / 1140
Goodness-of-fit on <i>F</i> ²	1.143
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0830, <i>wR</i> ₂ = 0.2047
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1029, <i>wR</i> ₂ = 0.2146
Extinction coefficient	n/a
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	5.059 and -1.946

Table S3.2. Crystal data and structure refinement for [(GdCp*₂)₂(μ-(OEt)₂bpym)][BPh₄] (**2-Gd**) and [(DyCp*₂)₂(μ-(OEt)₂bpym)][BPh₄] (**2-Dy**).

	2-Gd	2-Dy
Empirical formula	Gd ₂ O ₂ N ₄ C _{86.5} BH ₁₀₆	Dy ₂ O ₂ N ₄ C _{86.5} BH ₁₀₆
Formula weight (g/mol)	1559.06	1569.56
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.8856	0.7288
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å), α (°)	12.192(2), 90	10.9649(17), 89.336(2)
<i>b</i> (Å), β (°)	24.487(5), 101.198(4)	16.592(3), 85.526(2)
<i>c</i> (Å), γ (°)	25.717(5), 90	21.571(4), 85.424(3)
Volume (Å ³)	7531(2)	3900.0(11)
<i>Z</i>	4	2
Density (calculated, g/cm ³)	1.375	1.337
Absorption coefficient (mm ⁻¹)	3.187	2.072
<i>F</i> (000)	3208	1612
Crystal size (mm ³)	0.071 × 0.036 × 0.028	0.11 × 0.086 × 0.05
θ range for data collection (°)	2.122 to 38.566	2.080 to 28.245
Index ranges	-16 ≤ <i>h</i> ≤ 17 -34 ≤ <i>k</i> ≤ 34 -36 ≤ <i>l</i> ≤ 35	-14 ≤ <i>h</i> ≤ 14 -21 ≤ <i>k</i> ≤ 21 -28 ≤ <i>l</i> ≤ 28
Reflections collected	107187	70841
Independent reflections, <i>R</i> _{int}	21908, 0.0502	17878, 0.0608
Completeness to θ	100.0 % (θ = 32.097°)	100.0 % (θ = 25.930°)
Absorption correction	Semi-empirical	Semi-empirical
Max. and min. transmission	0.916 and 0.757	0.903 and 0.742
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	21908 / 45 / 902	17878 / 247 / 983
Goodness-of-fit on <i>F</i> ²	1.083	1.051
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0398, <i>wR</i> ₂ = 0.0911	<i>R</i> ₁ = 0.0490, <i>wR</i> ₂ = 0.1240
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0648, <i>wR</i> ₂ = 0.0997	<i>R</i> ₁ = 0.0686, <i>wR</i> ₂ = 0.1366
Extinction coefficient	n/a	n/a
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	1.702 and -1.496	4.067 and -2.005

Table S3.3. Crystal data and structure refinement for [(GdCp*₂)₂(μ -F₂bpym)][BPh₄] (**3-Gd**) and [(DyCp*₂)₂(μ -F₂bpym)][BPh₄] (**3-Dy**).

	3-Gd	3-Dy
Empirical formula	Gd ₂ O ₃ N ₄ C ₈₆ BH ₁₁₄	Dy ₂ N ₄ C ₈₁ BH ₉₈
Formula weight (g/mol)	1577.12	1463.44
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.7749	0.7749
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å), α (°)	12.549(3), 90	12.2665(7), 84.427(3)
<i>b</i> (Å), β (°)	27.027(6), 91.819(5)	12.8149(8), 83.779(4)
<i>c</i> (Å), γ (°)	22.460(6), 90	22.0900(13), 85.473(4)
Volume (Å ³)	7614(3)	3427.4(4)
<i>Z</i>	4	2
Density (calculated, g/cm ³)	1.376	1.418
Absorption coefficient (mm ⁻¹)	2.210	2.748
<i>F</i> (000)	3260	1498
Crystal size (mm ³)		0.071 × 0.054 × 0.036
θ range for data collection (°)	2.142 to 33.073	2.096 to 27.827
Index ranges	-17 ≤ <i>h</i> ≤ 17 -38 ≤ <i>k</i> ≤ 38 -31 ≤ <i>l</i> ≤ 31	-14 ≤ <i>h</i> ≤ 14 -15 ≤ <i>k</i> ≤ 15 0 ≤ <i>l</i> ≤ 26
Reflections collected	128659	14858
Independent reflections, <i>R</i> _{int}	22278, 0.0564	12511, 0.1733
Completeness to $\theta = 27.706^\circ$	99.9 %	99.6 %
Absorption correction	Semi-empirical	Semi-empirical
Max. and min. transmission	0.9705 and 0.8958	0.908 and 0.783
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	22278 / 522 / 1153	12511 / 450 / 1032
Goodness-of-fit on <i>F</i> ²	1.034	1.099
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0536, <i>wR</i> ₂ = 0.1340	<i>R</i> ₁ = 0.0621, <i>wR</i> ₂ = 0.1368
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0801, <i>wR</i> ₂ = 0.1466	<i>R</i> ₁ = 0.0978, <i>wR</i> ₂ = 0.1497
Extinction coefficient	n/a	n/a
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	4.961 and -2.170	2.762 and -1.500

Table S3.4. Crystal data and structure refinement for [(GdCp*₂)₂(μ-F₂bpym)][BPh₄] (**4-Gd**) and [(DyCp*₂)₂(μ-F₂bpym)][BPh₄] (**4-Dy**).

	4-Gd	4-Dy
Empirical formula	Gd ₂ F ₄ N ₄ C ₇₈ BH ₈₈	Dy ₂ F ₄ N ₄ C ₇₈ BH ₈₈
Formula weight (g/mol)	1482.83	1493.33
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.7288	0.7288
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å), α (°)	11.604(4), 80.776(5)	11.615(2), 80.648(2)
<i>b</i> (Å), β (°)	13.026(4), 85.537(5)	12.991(2), 85.621(2)
<i>c</i> (Å), γ (°)	22.654(8), 87.739(6)	22.607(4), 87.720(3)
Volume (Å ³)	3368.3(19)	3354.7(10)
<i>Z</i>	2	2
Density (calculated, g/cm ³)	1.462	1.478
Absorption coefficient (mm ⁻¹)	2.138	2.411
<i>F</i> (000)	1506	1514
Crystal size (mm ³)	0.13 × 0.07 × 0.064	0.10 × 0.086 × 0.020
θ range for data collection (°)	2.094 to 25.708	1.630 to 28.244
Index ranges	-13 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 15 -26 ≤ <i>l</i> ≤ 26	-15 ≤ <i>h</i> ≤ 15 -16 ≤ <i>k</i> ≤ 16 -29 ≤ <i>l</i> ≤ 29
Reflections collected	50086	59794
Independent reflections, <i>R</i> _{int}	11889, 0.0718	15374, 0.0581
Completeness to θ	99.9 % (θ = 25.708°)	100.0 % (θ = 25.930°)
Absorption correction	Semi-empirical	Semi-empirical
Max. and min. transmission	0.875 and 0.757	0.953 and 0.837
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	11889 / 702 / 1106	15374 / 997 / 1376
Goodness-of-fit on <i>F</i> ²	1.076	1.188
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0545, <i>wR</i> ₂ = 0.1042	<i>R</i> ₁ = 0.0657, <i>wR</i> ₂ = 0.1389
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0751, <i>wR</i> ₂ = 0.1151	<i>R</i> ₁ = 0.0817, <i>wR</i> ₂ = 0.1456
Extinction coefficient	n/a	n/a
Largest diff. peak and hole (e·Å ⁻³)	1.789 and -2.336	2.922 and -3.356

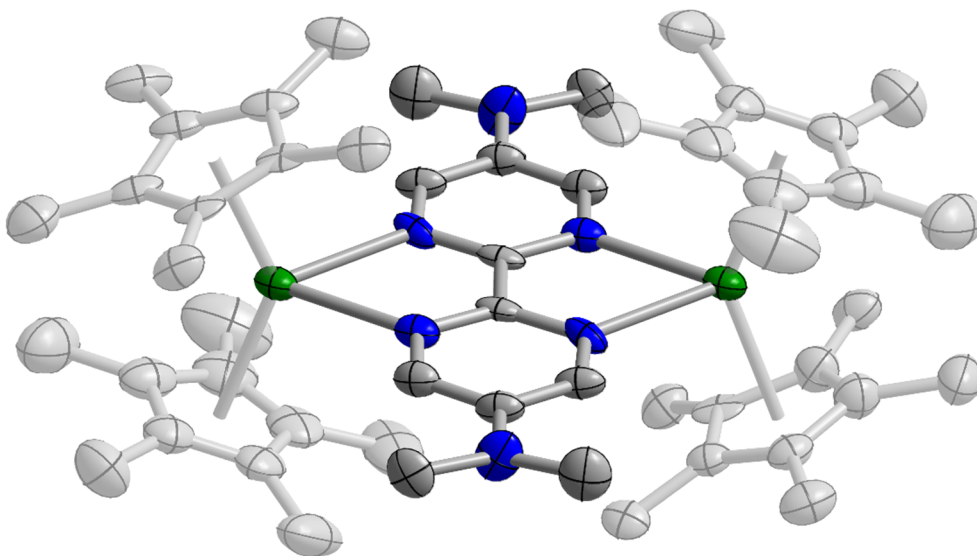


Figure S3.31. Solid-state structure of one of the $[(\text{DyCp}^*)_2(\mu\text{-(NMe}_2)_2\text{bpym})]^+$ cations in **1-Dy** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the BPh_4^- counteranion, solvent molecules, and the second $[(\text{DyCp}^*)_2(\mu\text{-(NMe}_2)_2\text{bpym})]^+$ cation are omitted for clarity. Green, blue, and grey ellipsoids represent Dy, N, and C atoms, respectively.

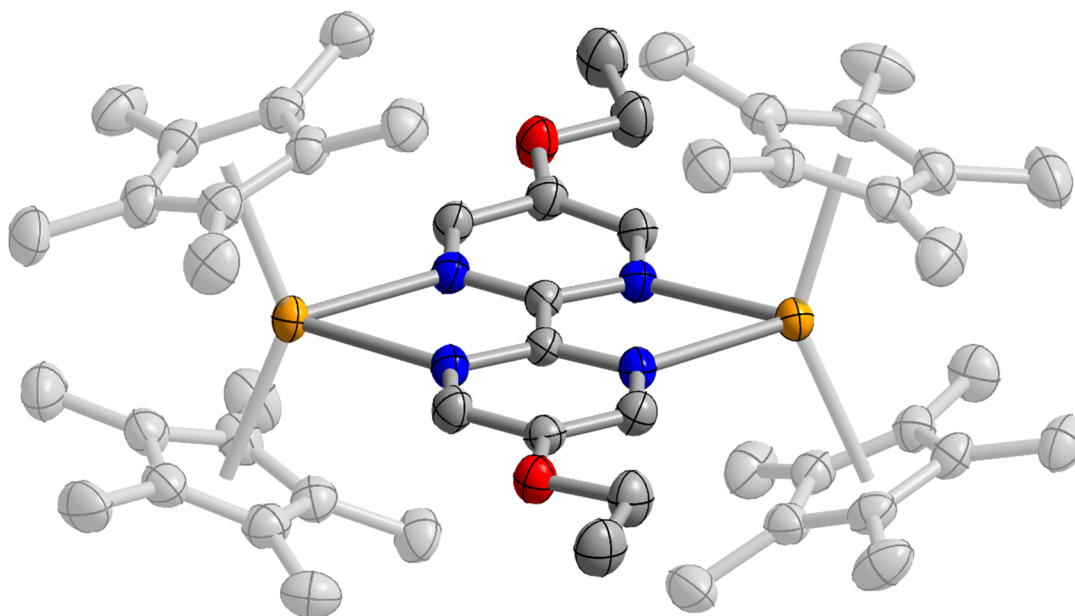


Figure S3.32. Solid-state structure of the $[(\text{GdCp}^*)_2(\mu\text{-(OEt)}_2\text{bpym})]^+$ cation in **2-Gd** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the BPh_4^- counteranion, and solvent molecules are omitted for clarity. Orange, blue, red, and grey ellipsoids represent Gd, N, O, and C atoms, respectively.

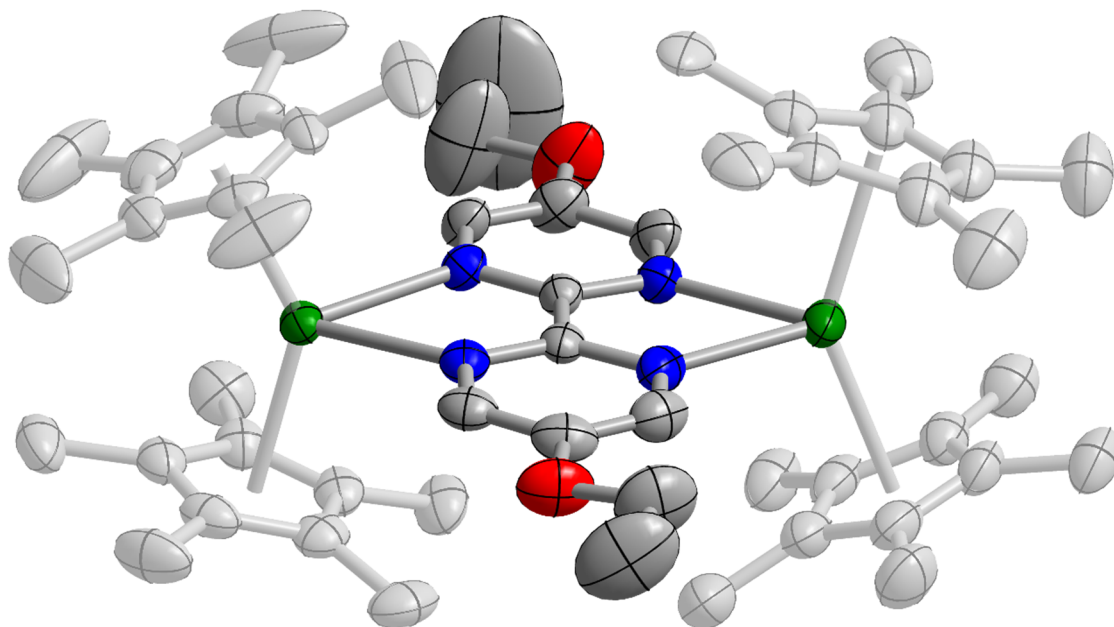


Figure S3.33. Solid-state structure of the $[(\text{DyCp}^*)_2(\mu\text{-(OEt)}_2\text{bpym})]^+$ cation in **2-Dy** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the BPh_4^- counteranion, and solvent molecules are omitted for clarity. The terminal carbon atom in the ethoxy group shows a large thermal ellipsoid due to rotational disorder that could not be modelled. Green, blue, red, and grey ellipsoids represent Dy, N, O, and C atoms, respectively.

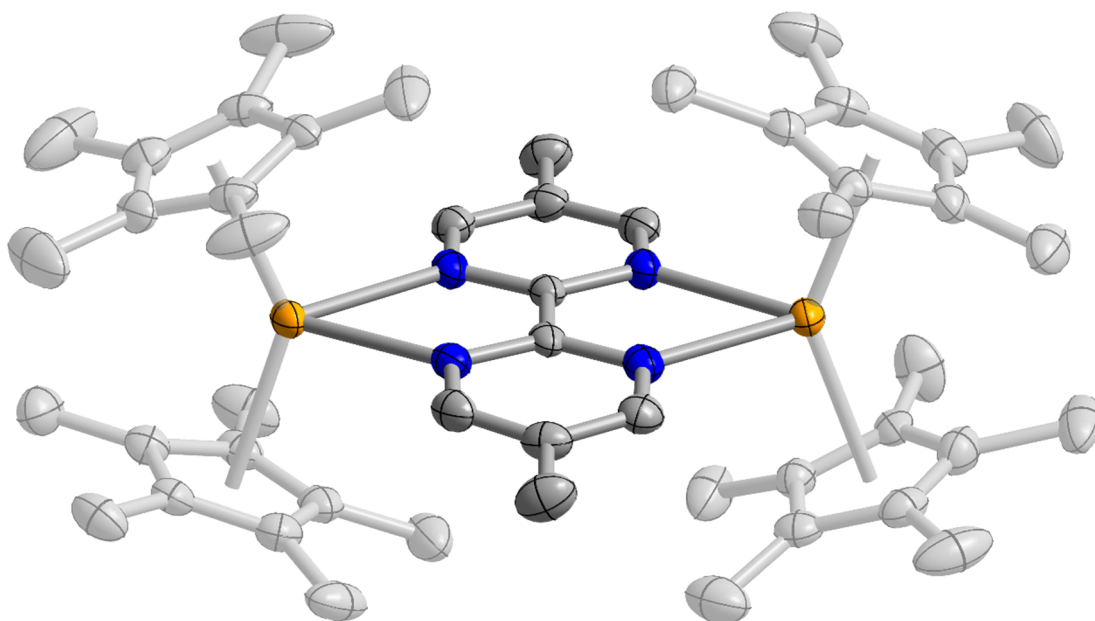


Figure S3.34. Solid-state structure of the $[(\text{GdCp}^*)_2(\mu\text{-Me}_2\text{bpym})]^+$ cation in **3-Gd** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the BPh_4^- counteranion, and solvent molecules are omitted for clarity. Orange, blue, and grey ellipsoids represent Gd, N, and C atoms, respectively.

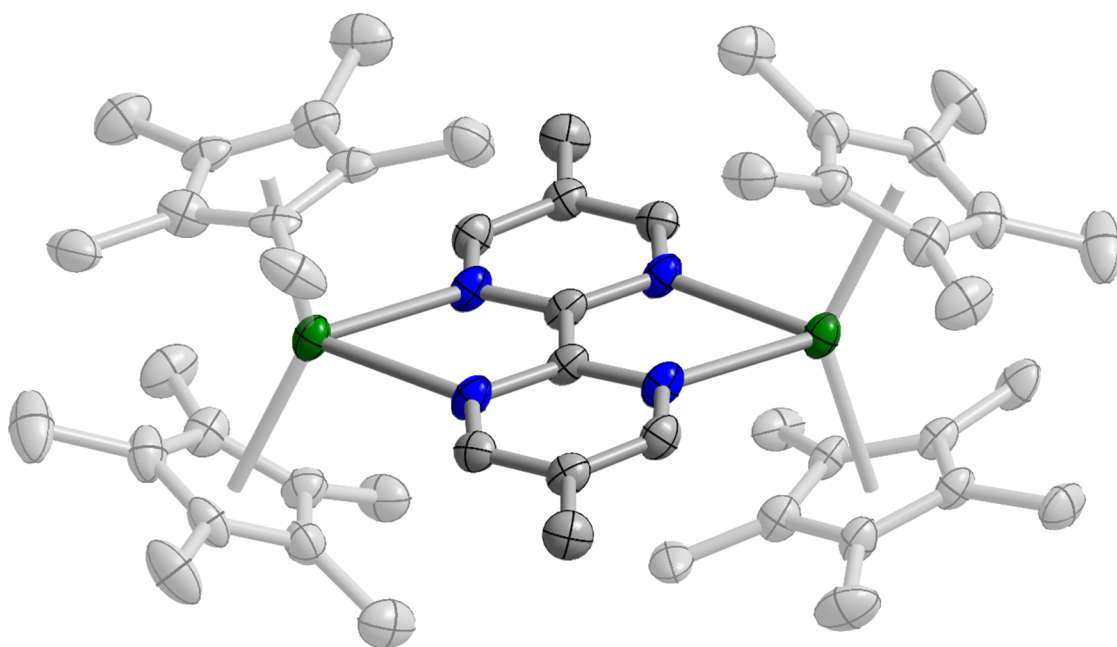


Figure S3.35. Solid-state structure of one of the $[(\text{DyCp}^*_2)(\mu\text{-Me}_2\text{bpym})]^+$ cations in **3-Dy** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the BPh_4^- counteranion, solvent molecules, and the second $[(\text{DyCp}^*_2)(\mu\text{-Me}_2\text{bpym})]^+$ cation are omitted for clarity. Green, blue, and grey ellipsoids represent Dy, N, and C atoms, respectively.

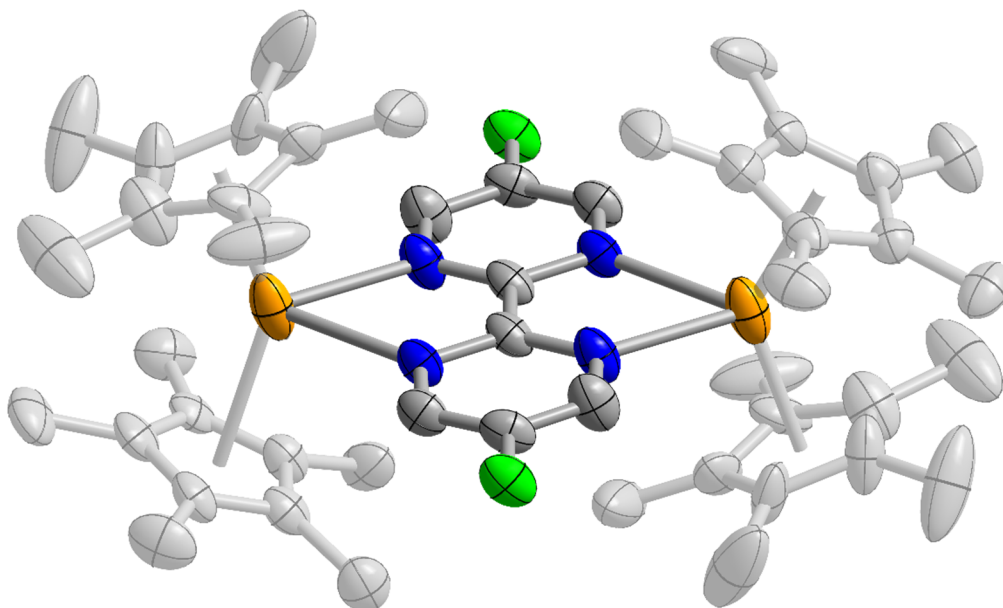


Figure S3.36. Solid-state structure of one of the $[(\text{GdCp}^*_2)(\mu\text{-F}_2\text{bpym})]^+$ cations in **4-Gd** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the BPh_4^- counteranion, solvent molecules, and the second $[(\text{GdCp}^*_2)(\mu\text{-F}_2\text{bpym})]^+$ cation are omitted for clarity. Orange, blue, lime green, and grey ellipsoids represent Gd, N, F, and C atoms, respectively.

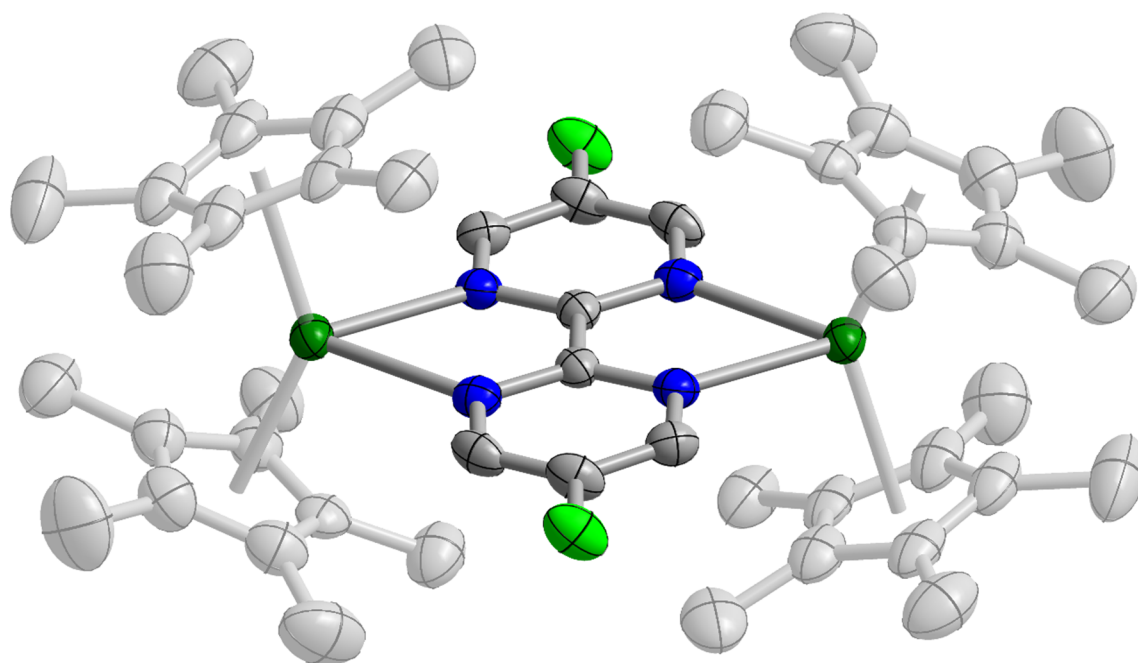


Figure S3.37. Solid-state structure of one of the $[(\text{DyCp}^*_2)(\mu\text{-F}_2\text{bpym})]^+$ cations in **4-Dy** with thermal ellipsoids at the 50% probability level. Hydrogen atoms, the BPh_4^- counteranion, solvent molecules, and the second $[(\text{DyCp}^*_2)(\mu\text{-F}_2\text{bpym})]^+$ cation are omitted for clarity. Green, blue, lime green, and grey ellipsoids represent Dy, N, F, and C atoms, respectively.

Table S3.5. Selected bond distances (Å) and angles (°) for **2-Gd**, **3-Gd**, and **4-Gd**.

	2-Gd	3-Gd	4-Gd ^a
Gd1–N1	2.471(2)	2.462(4)	2.468(5)
Gd1–N1'	2.481(2)	2.476(4)	-
Gd2–N3	2.446(2)	2.450(4)	2.488(5)
Gd2–N3'	2.432(2)	2.457(4)	-
Gd1B–N1B	-	-	2.474(5)
Gd1B–N3B	-	-	2.446(5)
Gd–N(avg)	2.458(2) ^b	2.461(4) ^b	2.469(5)
C2–C2'	1.416(4)	1.409(7)	-
C2–C2	-	-	1.396(13)
C2B–C2B	-	-	1.418(13)
Gd1···Gd2	6.477(1)	6.514(1)	-
Gd1···Gd1	-	-	6.567(1)
Gd1B···Gd1B	-	-	6.504(1)
Gd–bpym torsion ^c	1.8(3)	0.6(1)	1.4(1)
Gd(B)–bpym(B) torsion ^c	-	-	1.8(1)

^a The asymmetric unit of X, Y, and Z contains two discrete halves of the [(Cp*₂Gd)₂(R₂bpym)]⁺ complex, each of which sits on an inversion center.

^b The standard deviation of the average value was estimated from $\sigma = \sqrt{\sum \sigma_i^2 / N}$, where σ_i is the standard deviation of each bond distance i and N is the number of distances averaged.

^c The torsion angle between the plane of the bpym ligand and the Dy···Dy axis

Table S3.6. Selected bond distances (Å) and angles (°) for **1-Dy**, **2-Dy**, **3-Dy**, and **4-Dy**.

	1-Dy ^a	2-Dy	3-Dy ^a	4-Dy ^a
Dy1–N1	2.430(8)	2.418(4)	2.433(6)	2.436(6)
Dy1–N1'	-	2.447(4)	-	-
Dy2–N3	2.429(8)	2.448(4)	2.428(6)	2.456(6)
Dy2–N3'	-	2.421(5)	-	-
Dy1B–N1B	2.430(7)	-	2.423(6)	2.418(6)
Dy1B–N3B	2.433(9)	-	2.411(6)	2.450(6)
Dy–N(ave)	2.430(8) ^b	2.434(4) ^b	2.424(6) ^b	2.440(6) ^b
C2–C2'	-	1.415(7)	-	-
C2–C2	1.426(17)	-	1.406(13)	1.416(13)
C2B–C2B	1.432(18)	-	1.403(14)	1.414(13)
Dy1···Dy2	-	6.431(1)	-	-
Dy1···Dy1	6.409(1)	-	6.415(1)	6.493(1)
Dy1B···Dy1B	6.407(1)	-	6.388(1)	6.439(1)
Dy–bpym torsion ^c	2.6(1)	3.3(8)	4.5(1)	3.2(1)
Dy(B)–bpym(B) torsion ^c	1.4(1)	-	3.2(1)	3.5(1)

^a The asymmetric unit of X, Y, and Z contains two discrete halves of the [(Cp*₂Dy)₂(R₂bpym)]⁺ complex, each of which sits on an inversion center.

^b The standard deviation of the average value was estimated from $\sigma = \sqrt{\sum \sigma_i^2 / N}$, where σ_i is the standard deviation of each bond distance i and N is the number of distances averaged.

^c The torsion angle between the plane of the bpym ligand and the Dy···Dy axis

3.6.5 Magnetic Measurements

General. Samples for magnetic measurements were prepared by adding polycrystalline powder (20.9 mg of **1-Gd**, 13.6 mg of **1-Dy**, 7.0 mg of **2-Gd**, 17.4 mg of **2-Dy**, 6.8 mg of **3-Gd**, 16.2 mg of **3-Dy**, 4.6 mg of **4-Gd**, and 10.6 mg of **4-Dy**) to a 5 mm i.d./7 mm o.d. quartz tube with a raised quartz platform. A layer of eicosane was added on top of the sample (14.5 mg for **1-Gd**, 16.7 mg for **1-Dy**, 15.0 mg for **1-Tb**, 15.7 mg for **2-Gd**, 17.7 mg for **2-Dy**, 18.1 mg for **3-Gd**, 28.8 mg for **3-Dy**, 16.6 mg for **4-Gd**, and 18.7 mg for **4-Dy**) to provide good thermal contact between the sample and the bath and to prevent crystallite torquing. The tubes were fitted with Teflon sealable adapters, evacuated using a glovebox vacuum pump, and then flame sealed with an O₂/H₂ flame under vacuum. After flame-sealing, the eicosane was melted in a 45 °C water bath. Magnetic measurements were also conducted on a 7.8 mM solution of **3-Dy** and an 8.0 mM solution of **4-Dy** in 1,2-difluorobenzene.

Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. All data were corrected for diamagnetic contributions from the core diamagnetism of the sample and for the diamagnetism of the eicosane used to suspend the sample, estimated using Pascal's constants to give corrections of $\chi_{\text{dia}} = -0.000814$ for **1-Gd**, -0.000812 for **1-Dy**, -0.000806 for **2-Gd**, -0.000869 for **2-Dy**, -0.000773 for **3-Gd**, -0.000771 for **3-Dy**, -0.000756 for **4-Gd**, and -0.000754 for **4-Dy**.

Dc Magnetic Susceptibility Measurements. Dc magnetic susceptibility measurements were performed at temperatures ranging from 2 to 300 K under applied fields of 1, 5, and 10 kOe (0.1, 0.5, and 1 T) for **1-4**.

Fits to the dc susceptibility data for **1-Gd** through **4-Gd** were performed using PHI.¹⁴ The spin-only Hamiltonian $\hat{H} = -2J_{\text{Gd-rad}}\hat{S}_{\text{rad}} \cdot (\hat{S}_{\text{Gd}(1)} + \hat{S}_{\text{Gd}(2)})$ was used for **3-Gd** and **4-Gd**, where $J_{\text{Gd-rad}}$ represents the magnetic exchange coupling between each Gd(III) ion and the organic radical spin. This equation underestimated the rise in $\chi_{\text{M}}T$ at low temperatures for **1-Gd** and **2-Gd**, and improved fits to the data could be obtained using the Hamiltonian $\hat{H} = -2J_{\text{Gd-rad}}\hat{S}_{\text{rad}} \cdot (\hat{S}_{\text{Gd}(1)} + \hat{S}_{\text{Gd}(2)}) - 2J_{\text{Gd-Gd}}\hat{S}_{\text{Gd}(1)} \cdot \hat{S}_{\text{Gd}(2)}$, where $J_{\text{Gd-Gd}}$ represents the magnetic exchange coupling between Gd(III) ions. Contributions for temperature-independent paramagnetism (TIP) and intermolecular coupling (zJ) were included when fitting susceptibility measurements for **1-Gd** through **4-Gd**.

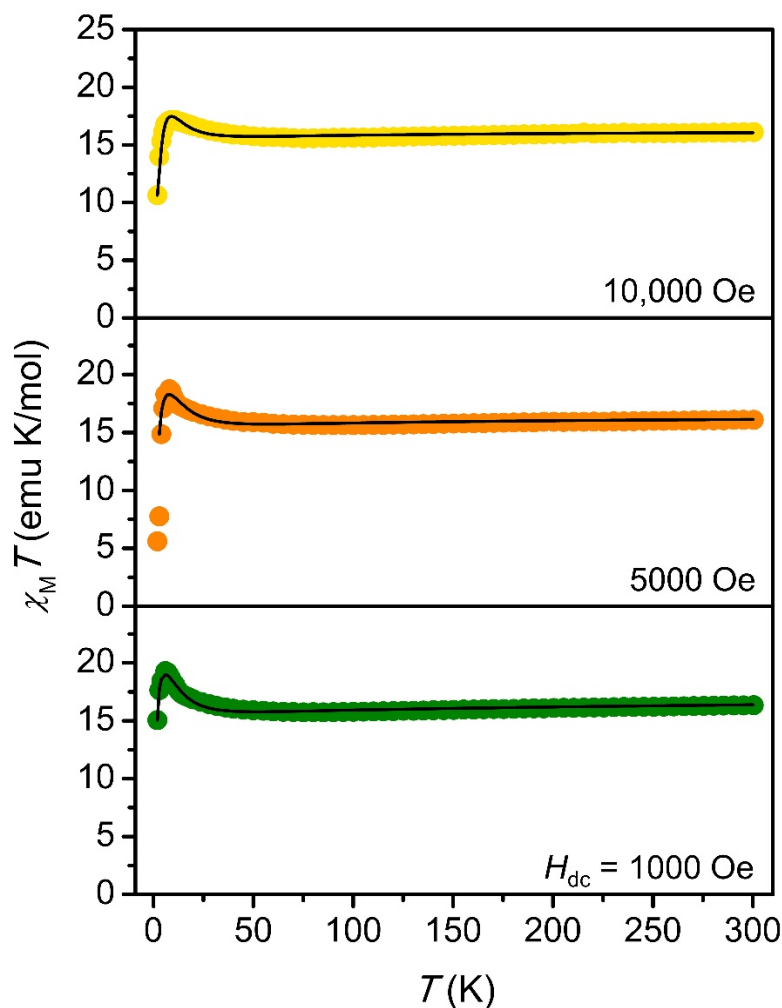


Figure S3.38. Zero-field cooled dc magnetic susceptibility measurements of **1-Gd** under applied fields of 1, 5, and 10 kOe. Black lines represent fits to the data used to extract the magnetic coupling constant (J).

Table S3.7. Parameters used to fit dc magnetic susceptibility data for **1-Gd** and magnetic exchange coupling constants (J) extracted from those fits.

Field (Oe)	$J_{\text{Gd-rad}} (\text{cm}^{-1})$	$J_{\text{Gd-Gd}} (\text{cm}^{-1})$	$zJ (\text{cm}^{-1})$	TIP ($\text{cm}^3\text{mol}^{-1}$)
1000	-2.88(6)	0.122(5)	-0.0108(2)	0.00131(8)
5000	-3.10(11)	0.137(8)	-0.0138(4)	0.000517(2)
10,000	-2.66(12)	0.125(8)	-0.0118(2)	0.000203(3)

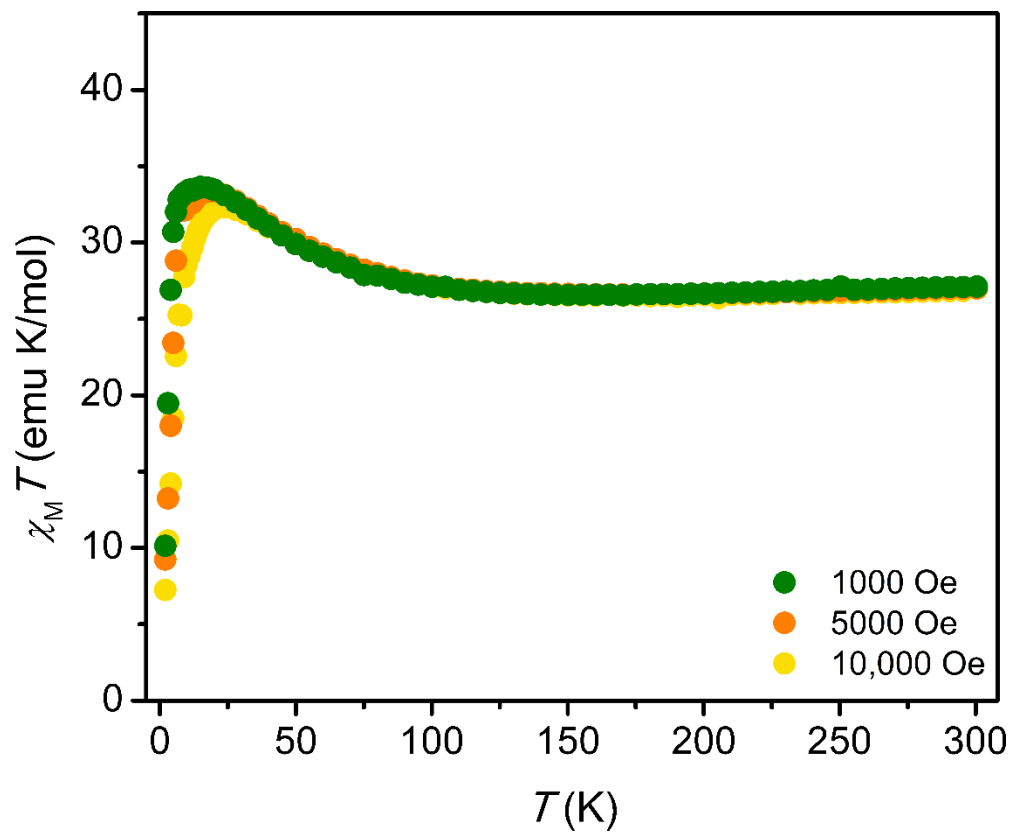


Figure S3.39. Zero-field cooled dc magnetic susceptibility measurements of **1-Dy** under applied fields of 1, 5, and 10 kOe.

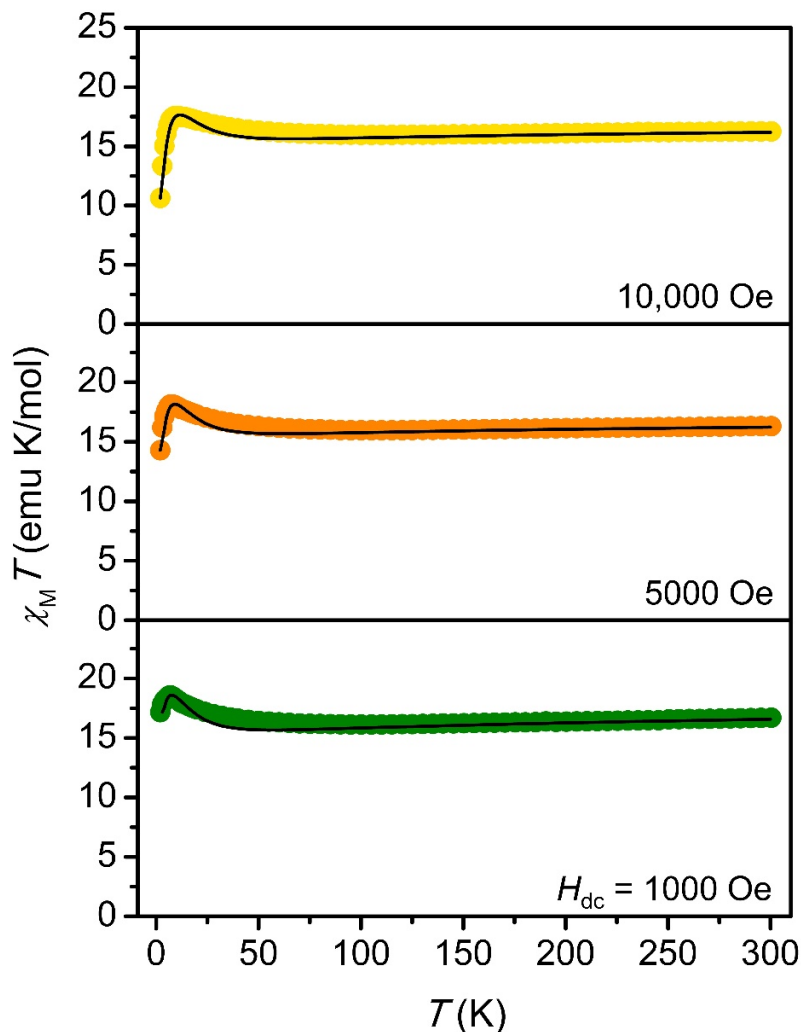


Figure S3.40. Zero-field cooled dc magnetic susceptibility measurements of **2-Gd** under applied fields of 1, 5, and 10 kOe. Black lines represent fits to the data used to extract the magnetic coupling constant (J).

Table S3.8. Parameters used to fit dc magnetic susceptibility data for **2-Gd** and magnetic exchange coupling constants (J) extracted from those fits.

Field (Oe)	$J_{\text{Gd-rad}} (\text{cm}^{-1})$	$J_{\text{Gd-Gd}} (\text{cm}^{-1})$	$zJ (\text{cm}^{-1})$	TIP ($\text{cm}^3\text{mol}^{-1}$)
1000	-3.81(16)	0.108(4)	-0.0149(9)	0.00227(2)
5000	-3.76(15)	0.141(4)	-0.0171(7)	0.00103(1)
10,000	-4.16(25)	0.145(5)	-0.0193(14)	0.000956(2)

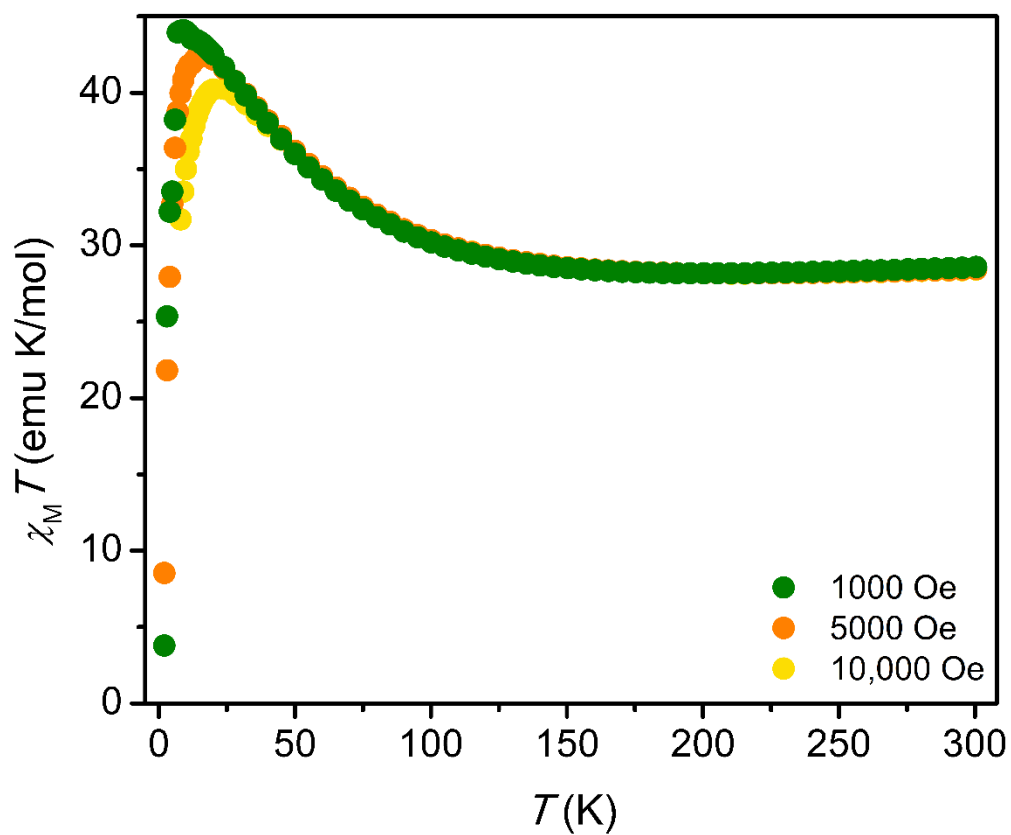


Figure S3.41. Zero-field cooled dc magnetic susceptibility measurements of **2-Dy** under applied fields of 1, 5, and 10 kOe.

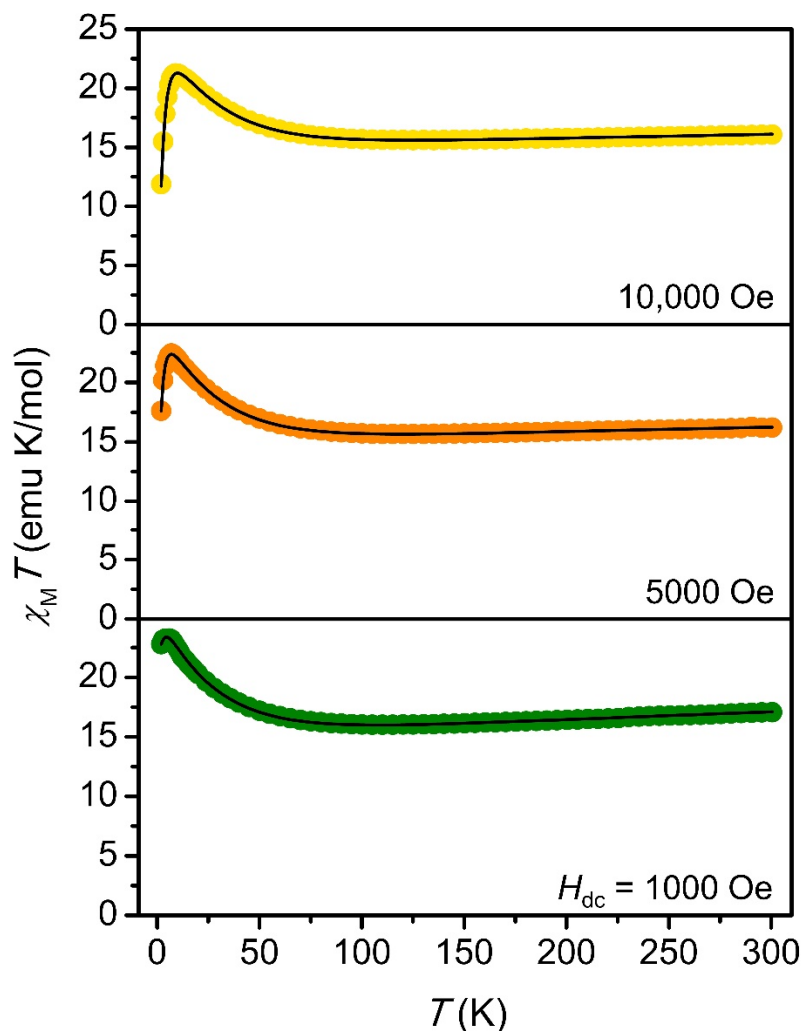


Figure S3.42. Zero-field cooled dc magnetic susceptibility measurements of **3-Gd** under applied fields of 1, 5, and 10 kOe. Black lines represent fits to the data used to extract the magnetic coupling constant (J).

Table S3.9. Parameters used to fit dc magnetic susceptibility data for **3-Gd** and magnetic exchange coupling constants (J) extracted from those fits.

Field (Oe)	J (cm ⁻¹)	zJ (cm ⁻¹)	TIP (cm ³ mol ⁻¹)
1000	-9.63(8)	-0.00142(1)	0.00512(10)
5000	-9.42(8)	-0.00170(1)	0.00220(9)
10,000	-9.54(7)	-0.00168(1)	0.00175(8)

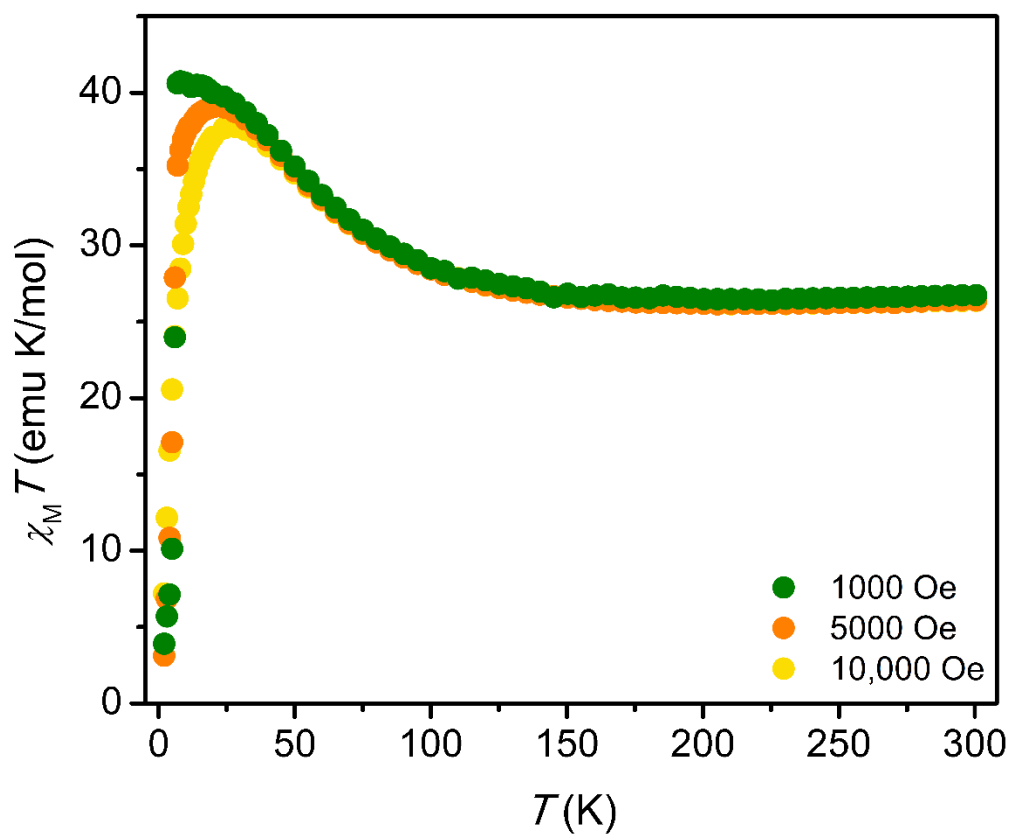


Figure S3.43. Zero-field cooled dc magnetic susceptibility measurements of **3-Dy** under applied fields of 1, 5, and 10 kOe.

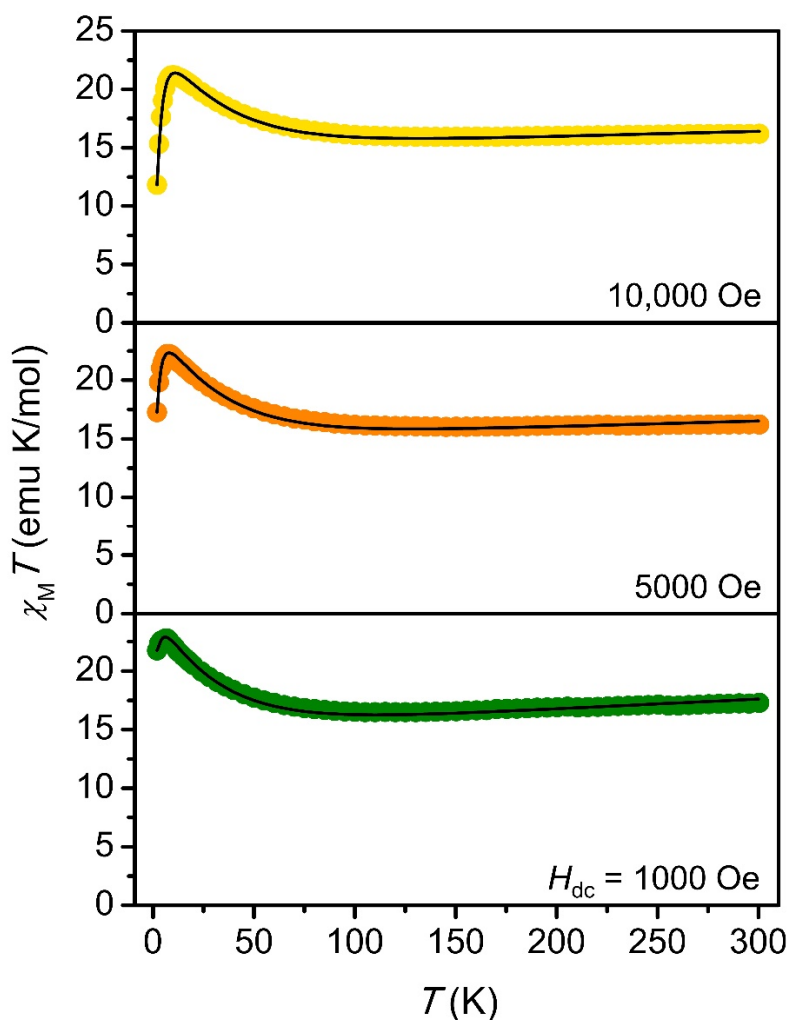


Figure S3.44. Zero-field cooled dc magnetic susceptibility measurements of **4-Gd** under applied fields of 1, 5, and 10 kOe. Black lines represent fits to the data used to extract the magnetic coupling constant (J).

Table S3.10. Parameters used to fit dc magnetic susceptibility data for **4-Gd** and magnetic exchange coupling constants (J) extracted from those fits.

Field (Oe)	J (cm ⁻¹)	zJ (cm ⁻¹)	TIP (cm ³ mol ⁻¹)
1000	-10.8(3)	-0.00297(3)	0.00694(3)
5000	-11.0(3)	-0.00294(3)	0.00335(2)
10,000	-11.1(2)	-0.00310(4)	0.00299(2)

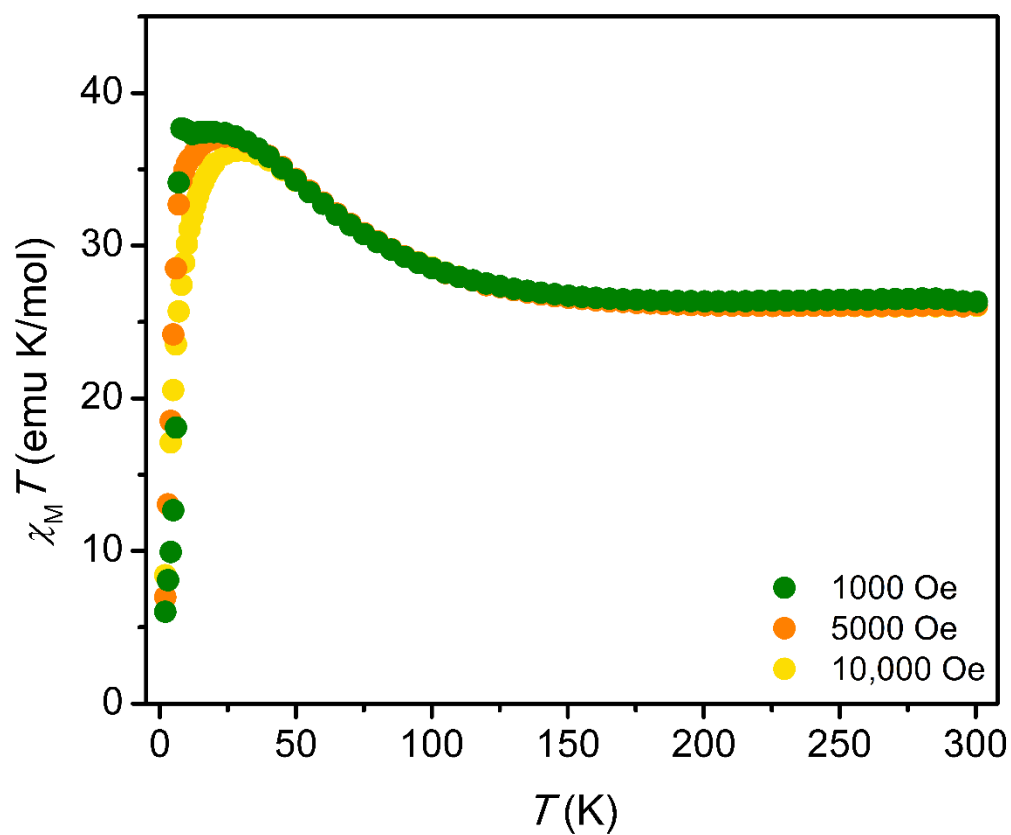


Figure S3.45. Zero-field cooled dc magnetic susceptibility measurements of **4-Dy** under applied fields of 1, 5, and 10 kOe.

Ac Magnetic Susceptibility Measurements. Ac magnetic susceptibility measurements were performed with a probe field of 4 Oe at frequencies ranging from 0.1 to 1500 Hz for **1-Dy**, **1-Tb**, **2-Dy**, **3-Dy**, **4-Dy**, and **4-Tb**. Magnetic relaxation times, τ , were extracted from a simultaneous fit of in-phase (χ_M') and out-of-phase (χ_M'') components of the magnetic susceptibility to a generalized Debye model.

For **1-Dy** and **2-Dy**, two relaxation processes could be distinguished in the ac susceptibility measurements, observed as two separate peaks in the out-of-phase susceptibility plot. For **1-Dy**, one process (the fast process) could be distinguished at low temperatures (4.5 to 5.5 K) and one process (the slow process) remained at higher temperatures (9 to 11 K). χ_M' and χ_M'' data corresponding to each peak were fit separately to a generalized Debye model in these temperature regimes to extract relaxation times for each process. The two relaxation processes overlapped significantly at intermediate temperatures (6 to 8.5 K), but the χ_M' and χ_M'' data at these temperatures could be fit using a generalized Debye model that accounted for both processes. This model was restrained using the relaxation times extracted from fits to the high and low temperature data. It was challenging to obtain a unique fit to the data without restraining the model due to the large number of parameters.

For **2-Dy**, the two relaxation processes could be distinguished across a large temperature range. The fast process was observed from 5 to 10 K and the slow process was observed from 8 to 13 K. χ_M' and χ_M'' data corresponding to each peak were fit separately to a generalized Debye model to extract relaxation times for each process.

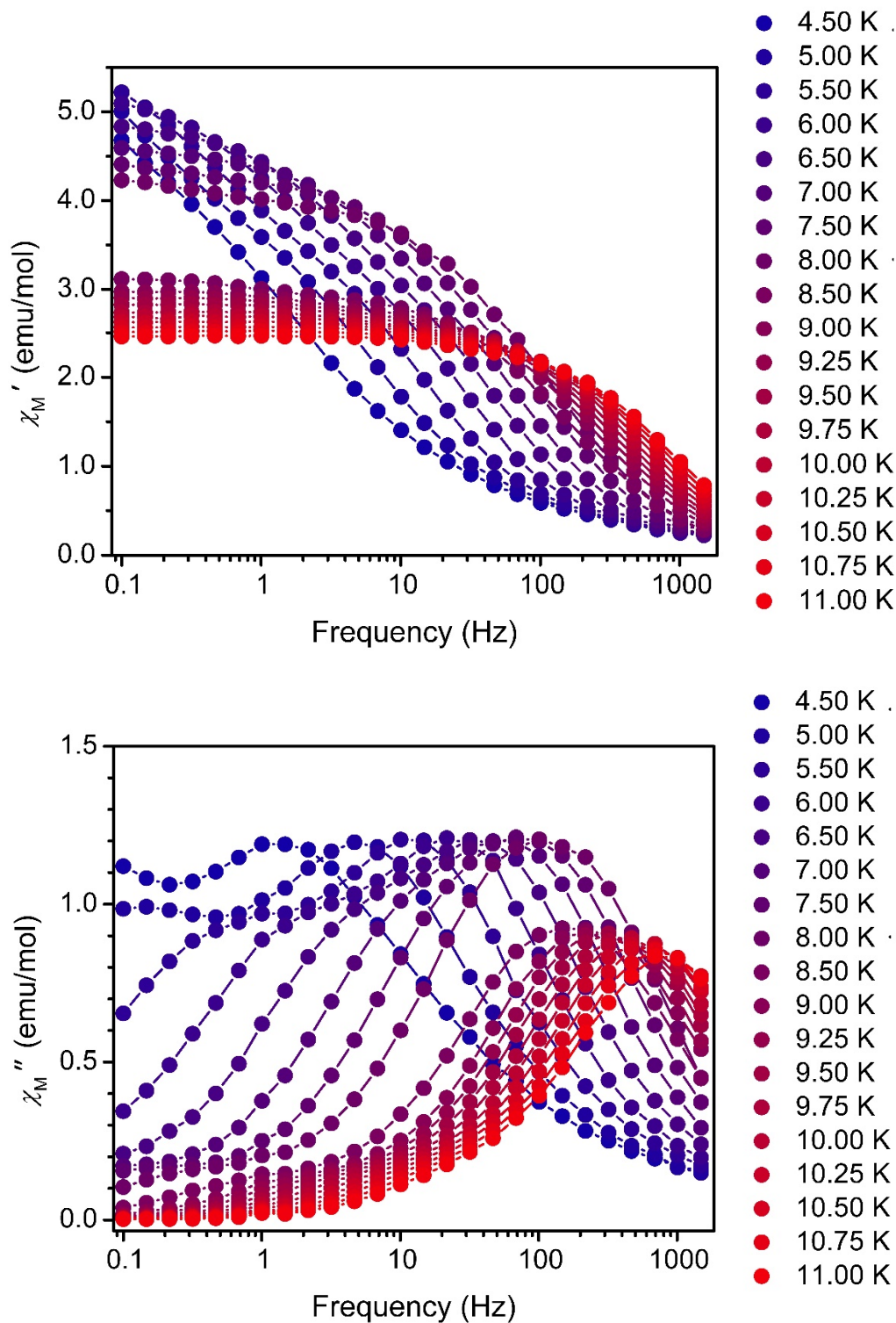


Figure S3.46. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **1-Dy** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 4.5–9 K (0.5 K steps) and 9–11 K (0.25 K steps). The colored lines are guides for the eye.

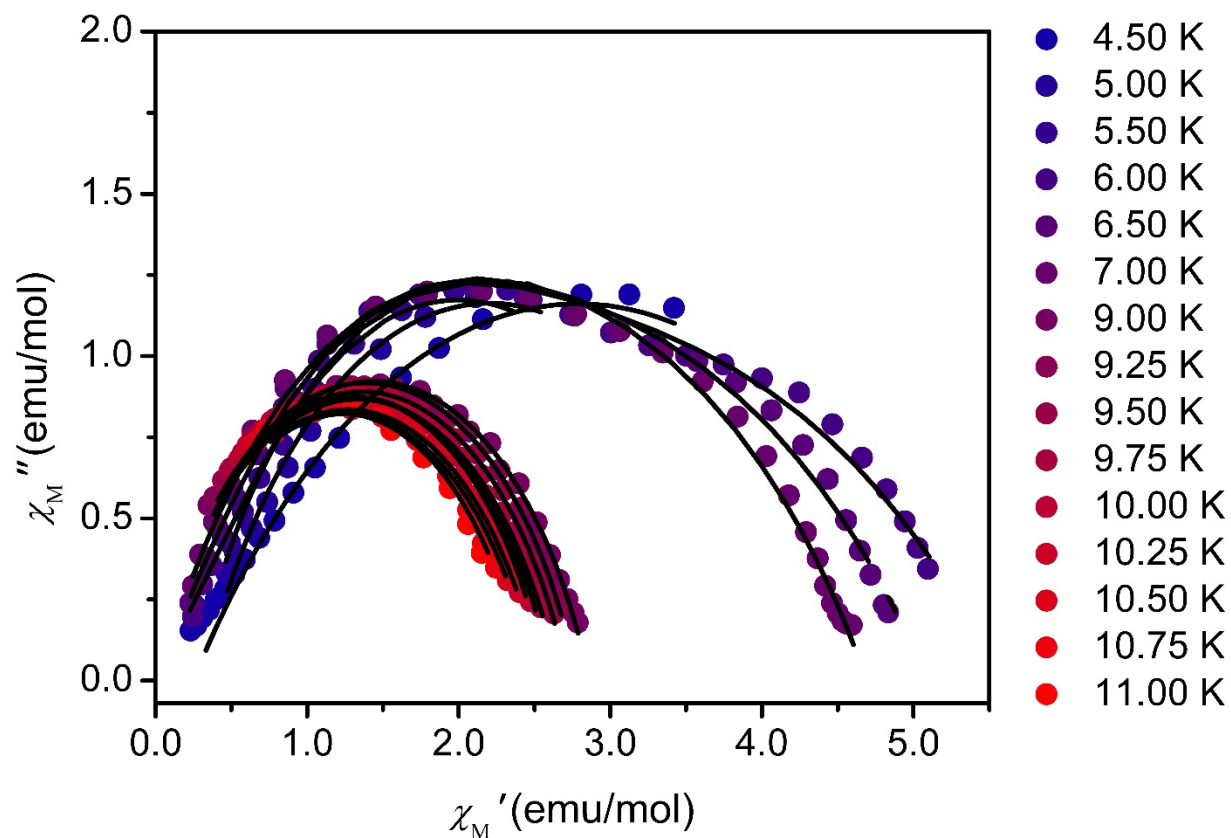


Figure S3.47. Cole-Cole plots for **1-Dy** from 4.5–7 K (0.5 K steps) and 9–11 K (0.25 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

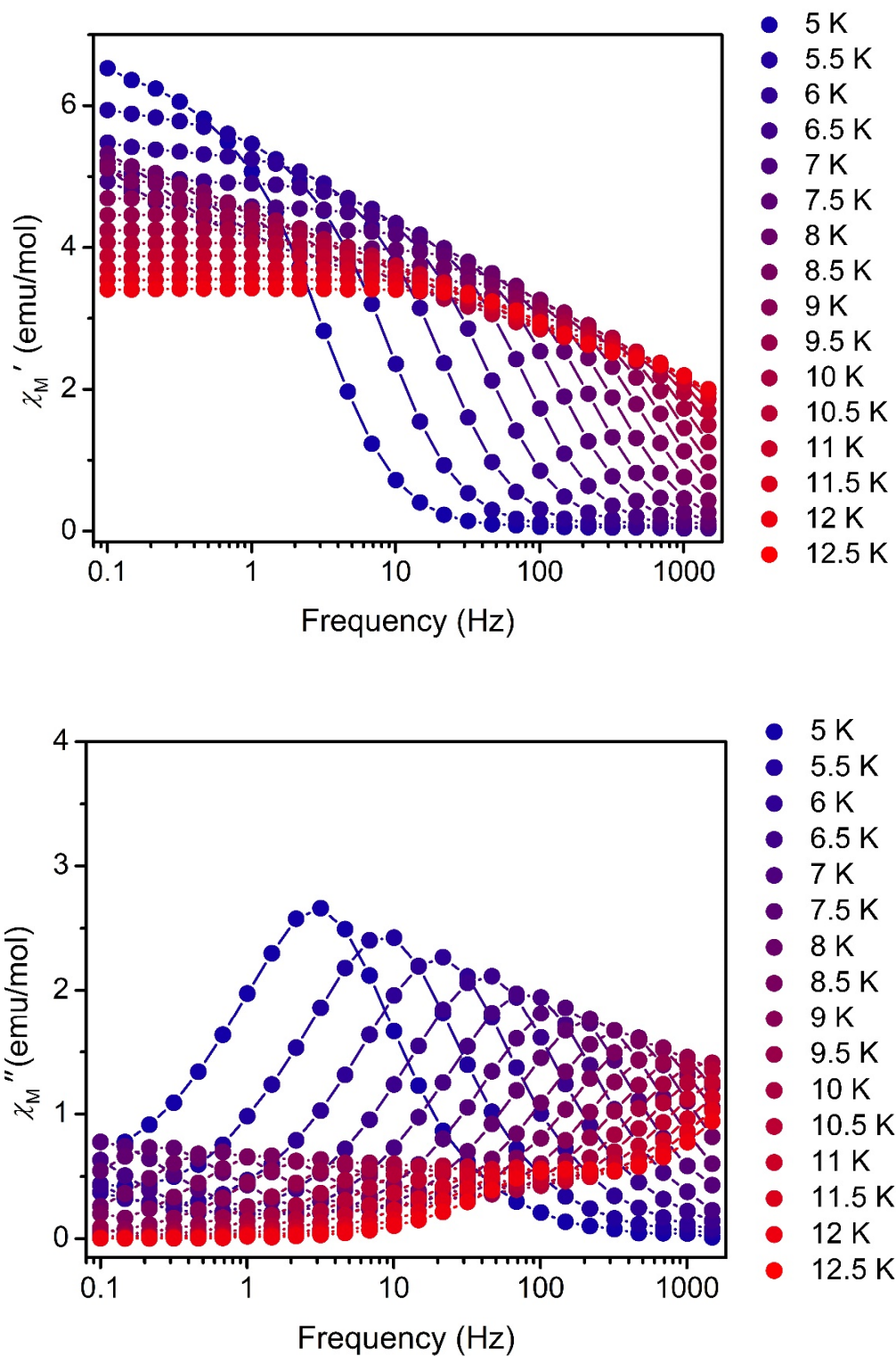


Figure S3.48. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **2-Dy** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 5–13 K (0.5 K steps). The colored lines are guides for the eye.

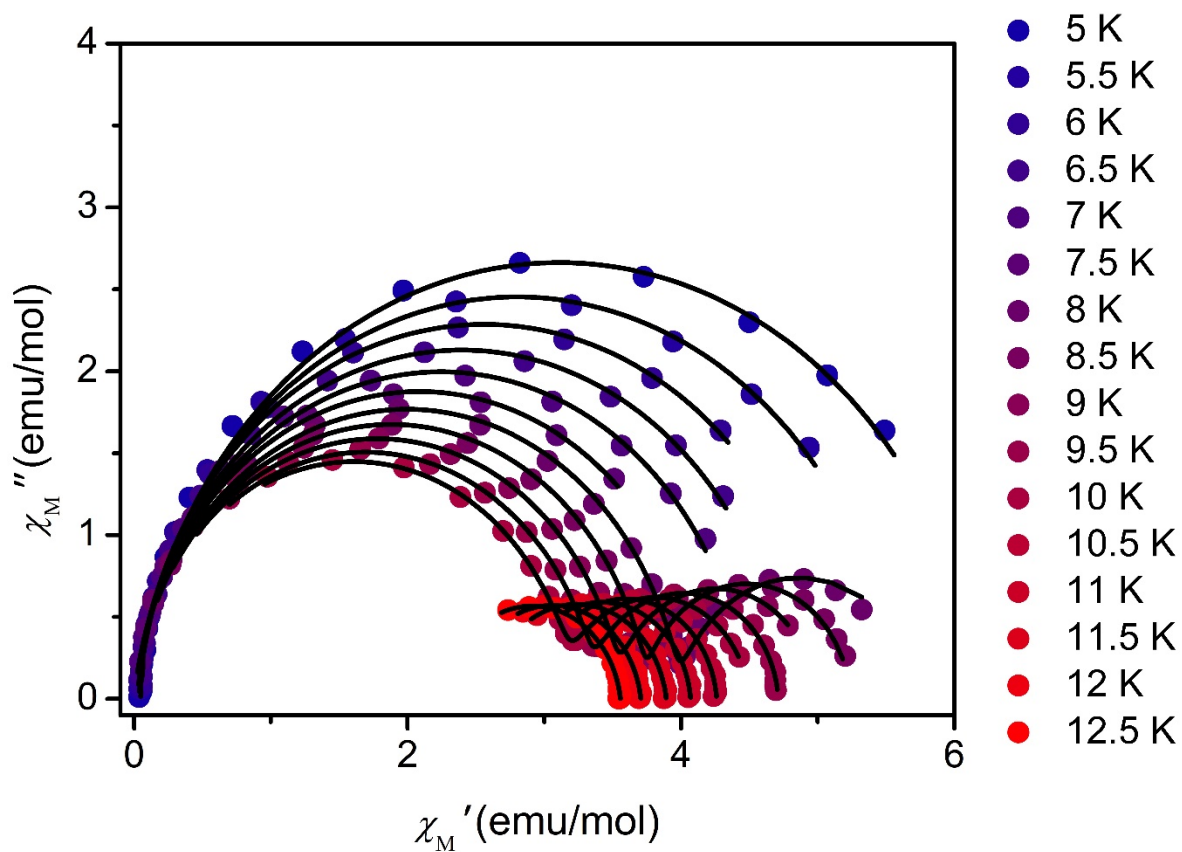


Figure S3.49. Cole-Cole plots for **2-Dy** from 5–13 K (0.5 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

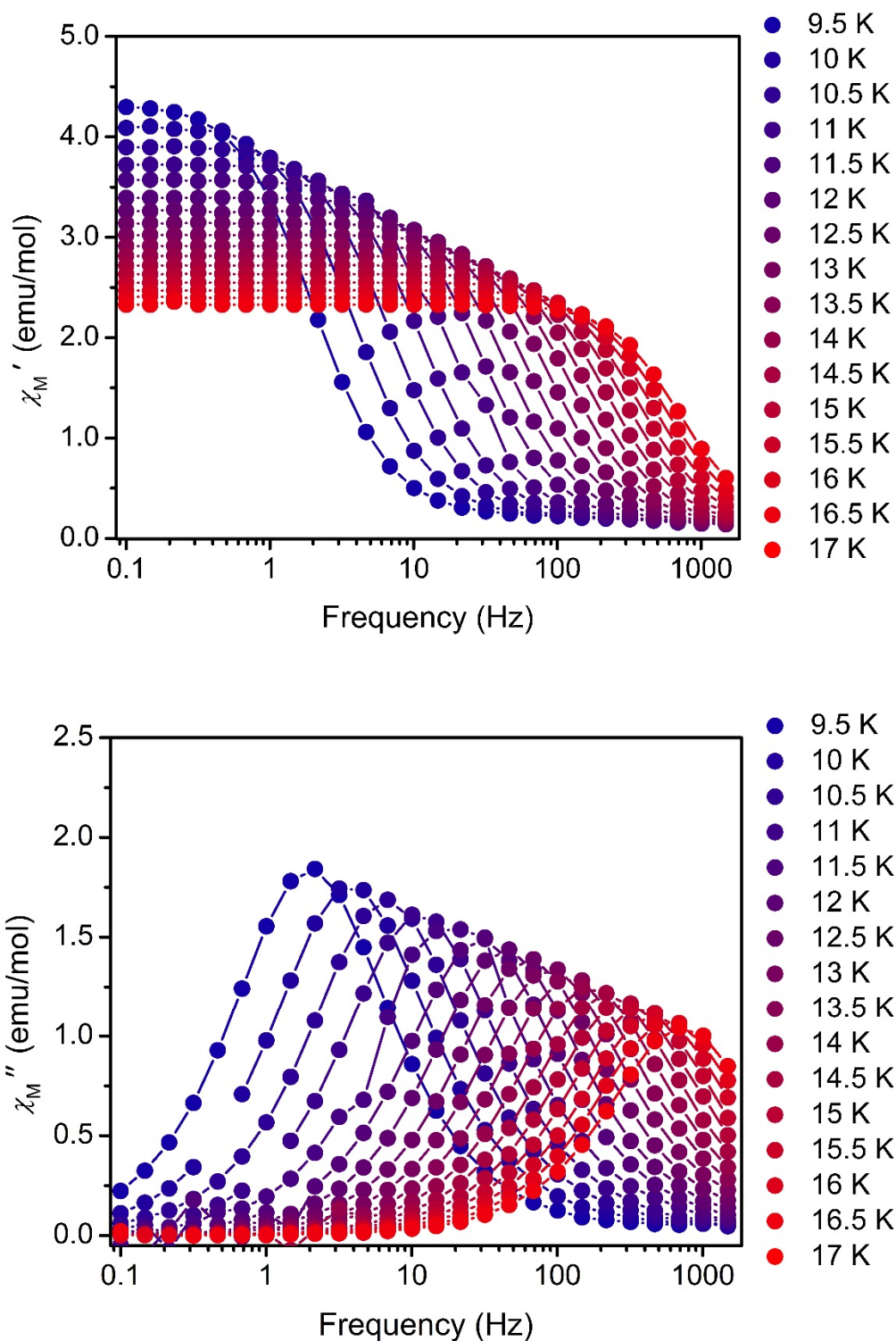


Figure S3.50. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **3-Dy** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 9.5–17 K (0.5 K steps). The colored lines are guides for the eye.

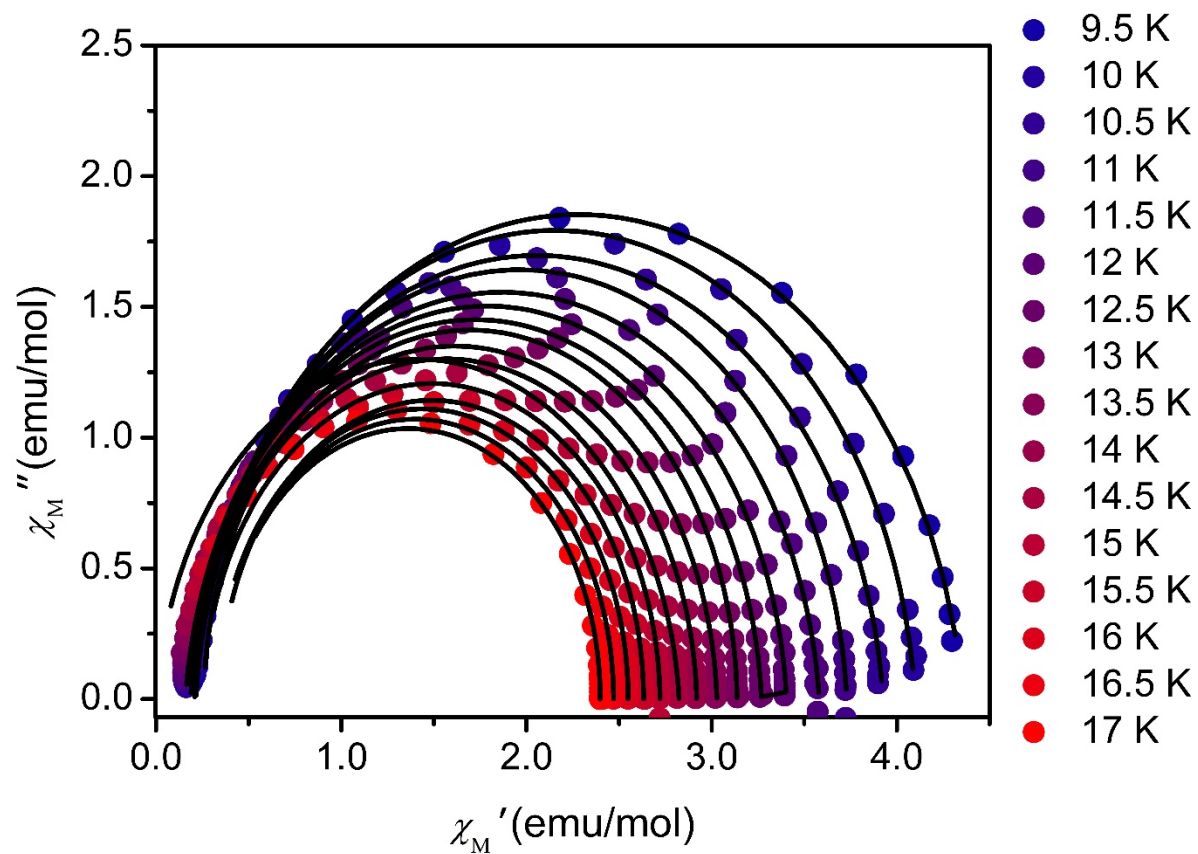


Figure S3.51. Cole-Cole plots for **3-Dy** from 9.5–17 K (0.5 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

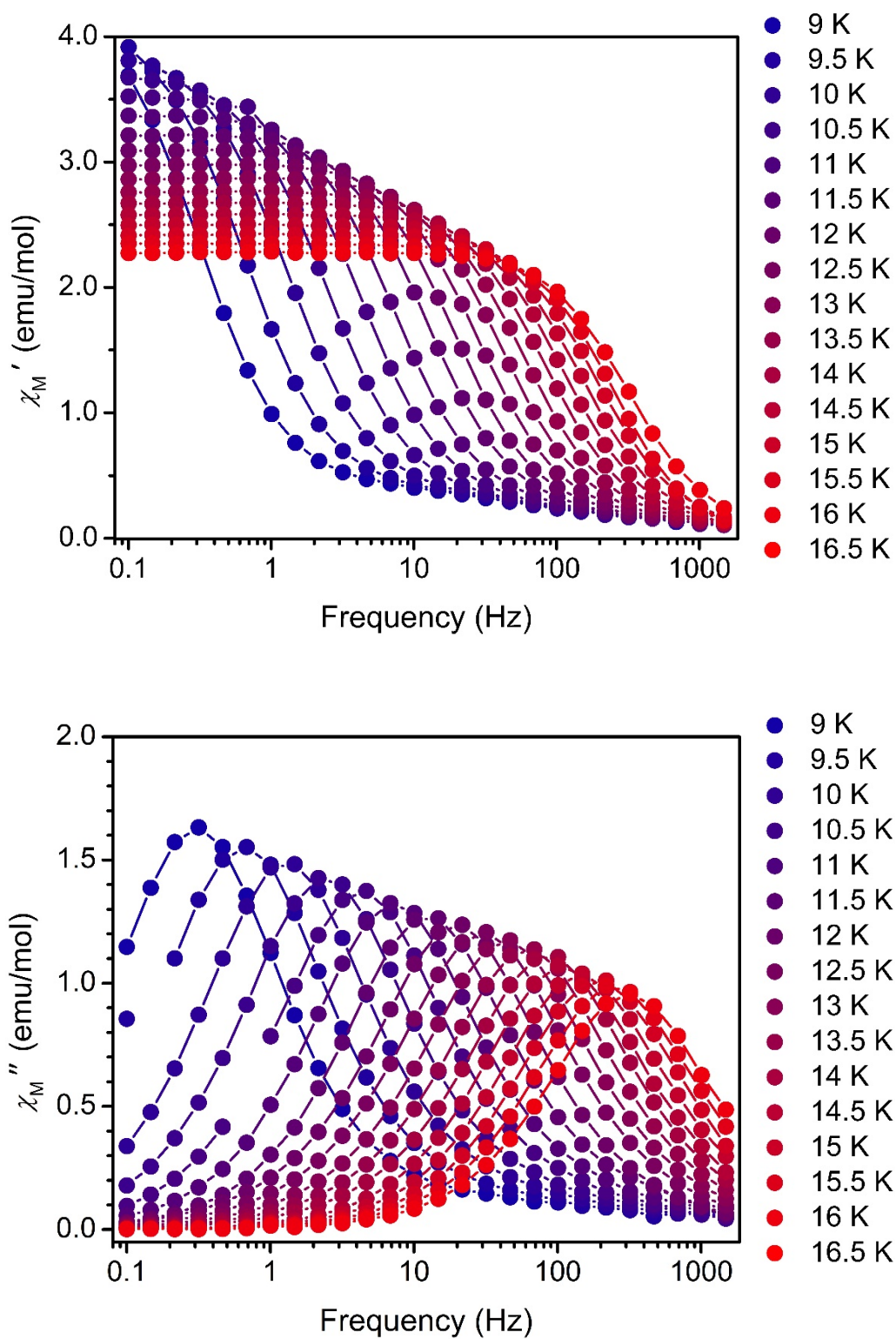


Figure S3.52. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **4-Dy** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 9–16.5 K (0.5 K steps). The colored lines are guides for the eye.

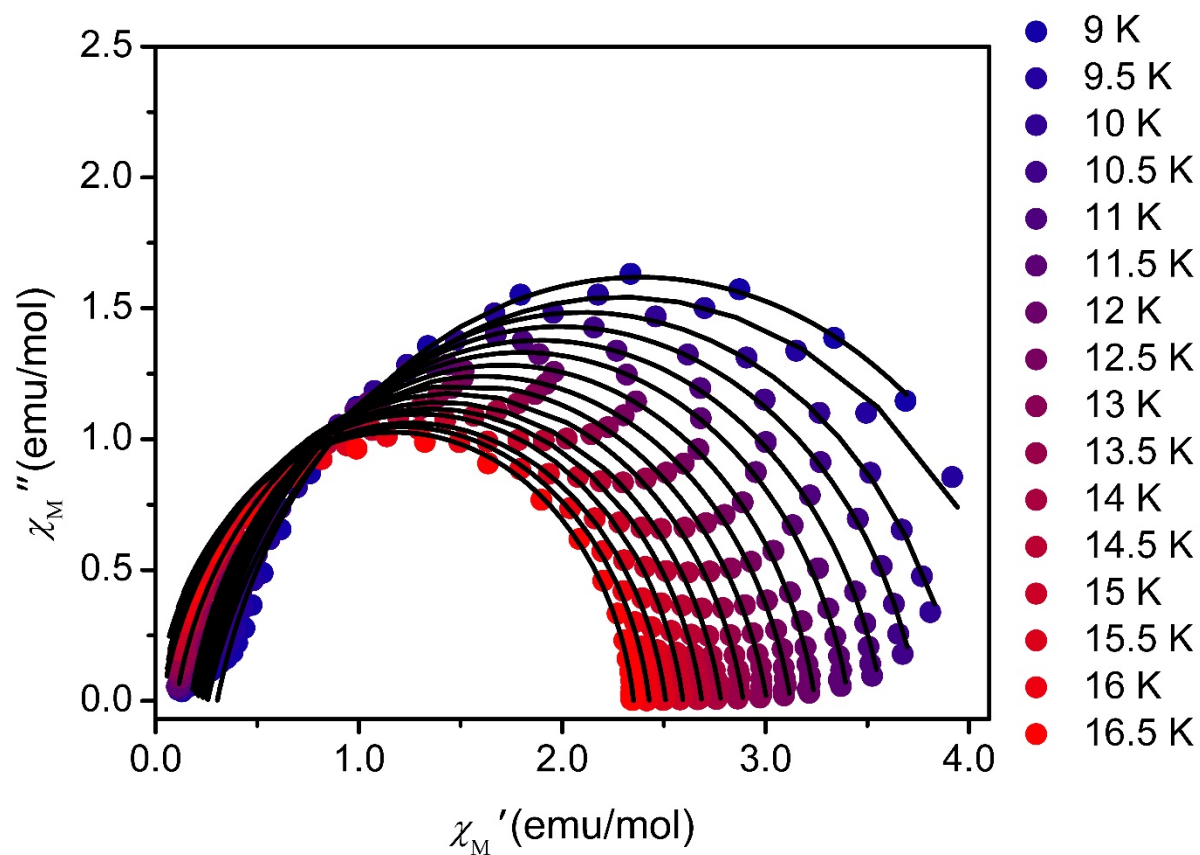


Figure S3.53. Cole-Cole plots for **4-Dy** from 9–16.5 K (0.5 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

Dc Magnetic Relaxation Measurements. Dc magnetic relaxation measurements were collected for **3-Dy** and **4-Dy** by magnetizing a sample at 5 T for 5 minutes and then subsequently returning the field to 0 T (no overshoot, hi-res disabled). The magnetization was then measured at periodic time intervals. Dc magnetic relaxation data were fit to a stretched exponential function:

$$M(t) = M_1 + (M_0 - M_1)(t/\tau)^n$$

where $M(t)$ is the magnetization at time t , M_0 is the initial magnetization measured after the field has been removed, M_1 is the final value of the magnetization at $t = \infty$, τ is the magnetic relaxation time, and n is a free variable. For measurements collected under an applied magnetic field of 500 Oe, M_1 was independently determined by dc susceptibility measurements. For measurements collected at zero applied field, M_1 should equal zero, however, non-zero values were obtained for all dc magnetic relaxation measurements. This likely arises due to a small remnant field. We therefore set M_1 equal to the value of the magnetization measured at the last time point of each experiment. At high temperatures, it was possible to measure the full decay of the magnetization within 5000 s. At lower temperatures, however, magnetic relaxation was significantly slower and thus this length of time was not sufficient to observe the full decay. For these measurements, setting M_1 equal to the last value of the magnetization measured for these experiments represents an overestimate. Better fits to the data for these experiments were obtained by treating M_1 as a free variable (M_1 values marked with an * in the tables below).

In order to test the validity of this strategy, fits to higher temperature experiments with M_1 as a free variable were obtained and compared to fits where M_1 was fixed equal to the last value of the magnetization measured. This resulted in values of τ within 5% error for the two fits. Furthermore, the values obtained for τ with M_1 as a free variable were consistently lower than those obtained with M_1 equal to the last value of the magnetization, demonstrating that this alternative fitting strategy did not overestimate the value of τ at low temperatures.

Data collected for **1-Dy** and **2-Dy** could not be fit to a single stretched exponential function. It is likely that two competing relaxation pathways exist for these complexes in the low-temperature regime, as was observed in ac susceptibility measurements. Unique fits to the data could not be obtained using a stretched exponential function that accounts for two relaxation processes, however, due to over-parameterization.

Table S3.11. Parameters used to fit dc magnetic relaxation data for a solid sample of **3-Dy** collected under zero applied magnetic field and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	4.84269	0.35440*	0.558	662.481
2.5	4.53015	0.28013*	0.579	596.692
3	4.35195	0.20986*	0.585	554.546
3.5	4.21606	0.15901*	0.592	521.259
4	4.10886	0.11277*	0.603	485.203
4.5	3.96565	0.04817	0.623	448.889
5	3.65953	0.01694	0.720	309.010
5.5	2.55888	0.00656	0.804	142.559
6	0.60338	0.00429	0.835	68.025

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

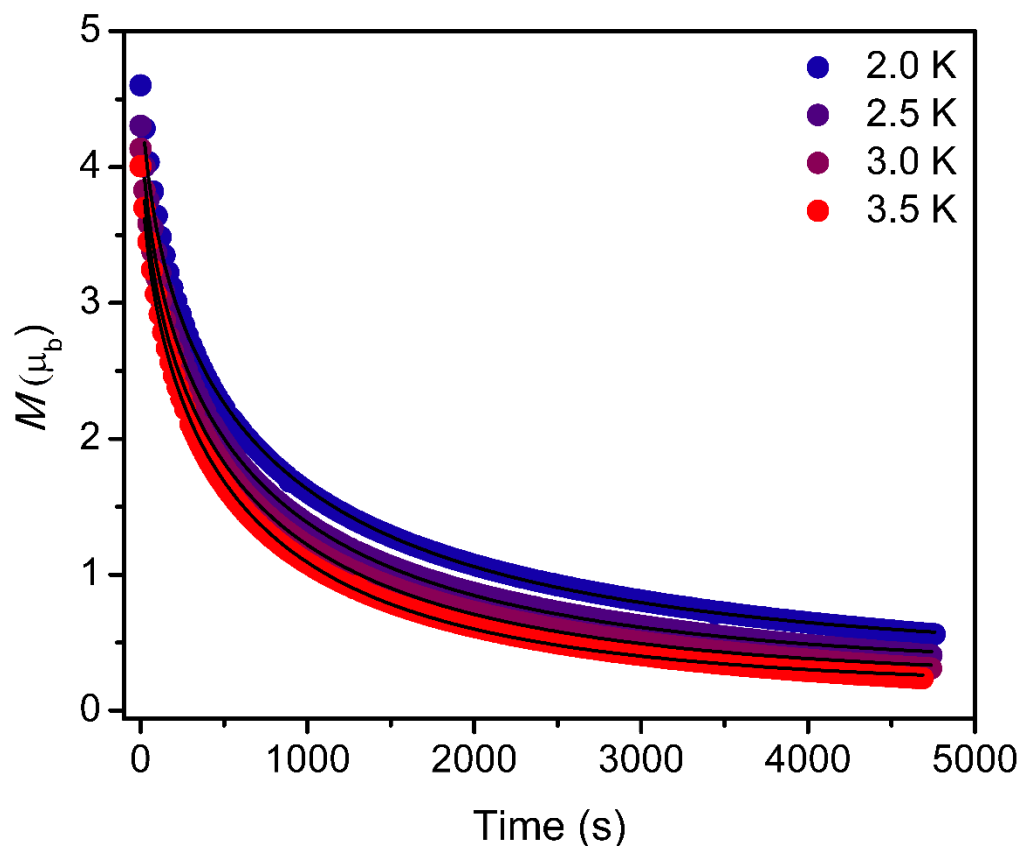


Figure S3.54. Dc magnetic relaxation data for a solid sample of **3-Dy** collected at 2.0, 2.5, 3.0, and 3.5 K under zero applied magnetic field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

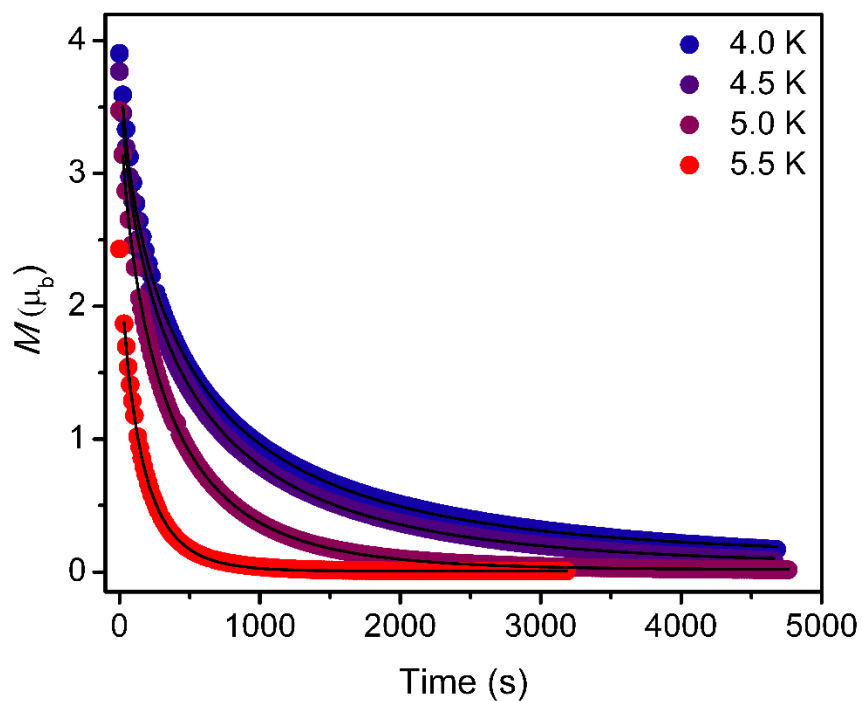


Figure S3.55. Dc magnetic relaxation data for a solid sample of **3-Dy** collected at 4.0, 4.5, 5.0, and 5.5 K under zero applied magnetic field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

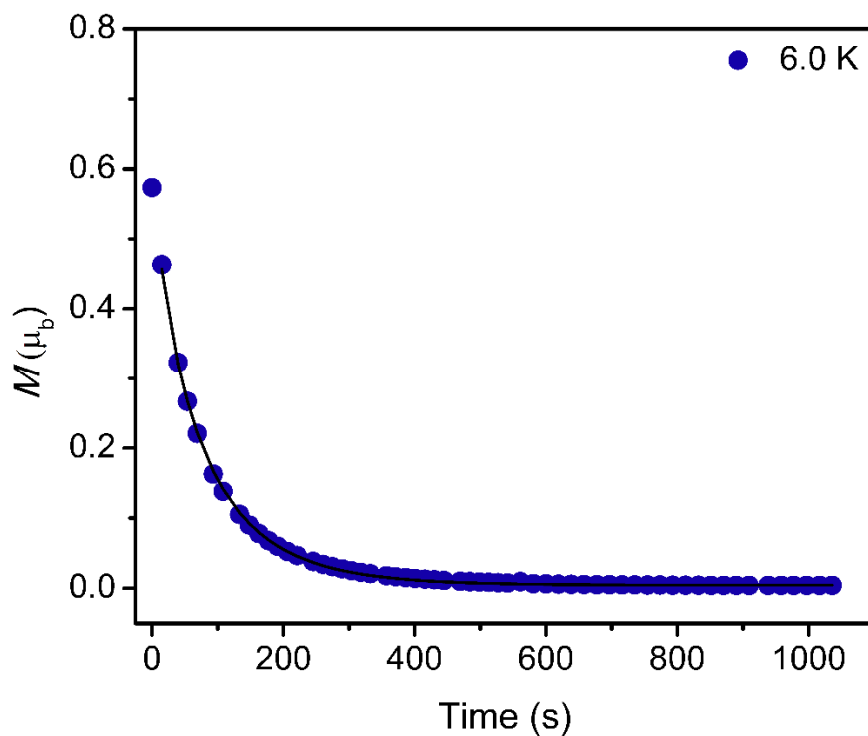


Figure S3.56. Dc magnetic relaxation data for a solid sample of **3-Dy** collected at 6 K under zero applied magnetic field. Black line represents the fit to the data using stretched exponential functions, which was used to extract τ .

Table S3.12. Parameters used to fit dc magnetic relaxation data for a 7.8 mM solution of **3-Dy** collected under zero applied field and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	1.10268	0.04406	0.782	96.274
2.5	1.01419	0.03249	0.784	92.038
3	0.86536	0.01996	0.782	92.343
3.5	0.82655	0.01970	0.796	91.620
4.5	0.72785	0.01698	0.798	86.801
5	0.59102	0.00924	0.798	79.567
5.5	0.29494	0.00606	0.810	64.266

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

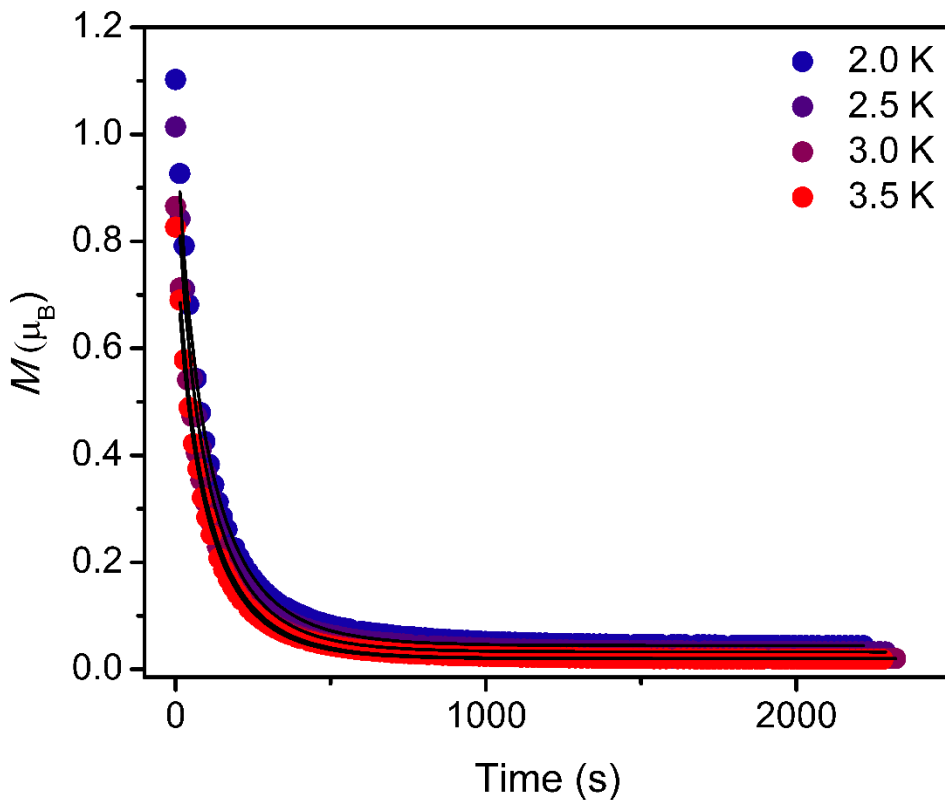


Figure S3.57. Dc magnetic relaxation data for a 7.8 mM of **3-Dy** collected at 2.0, 2.5, 3.0, and 3.5 K under zero applied magnetic field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

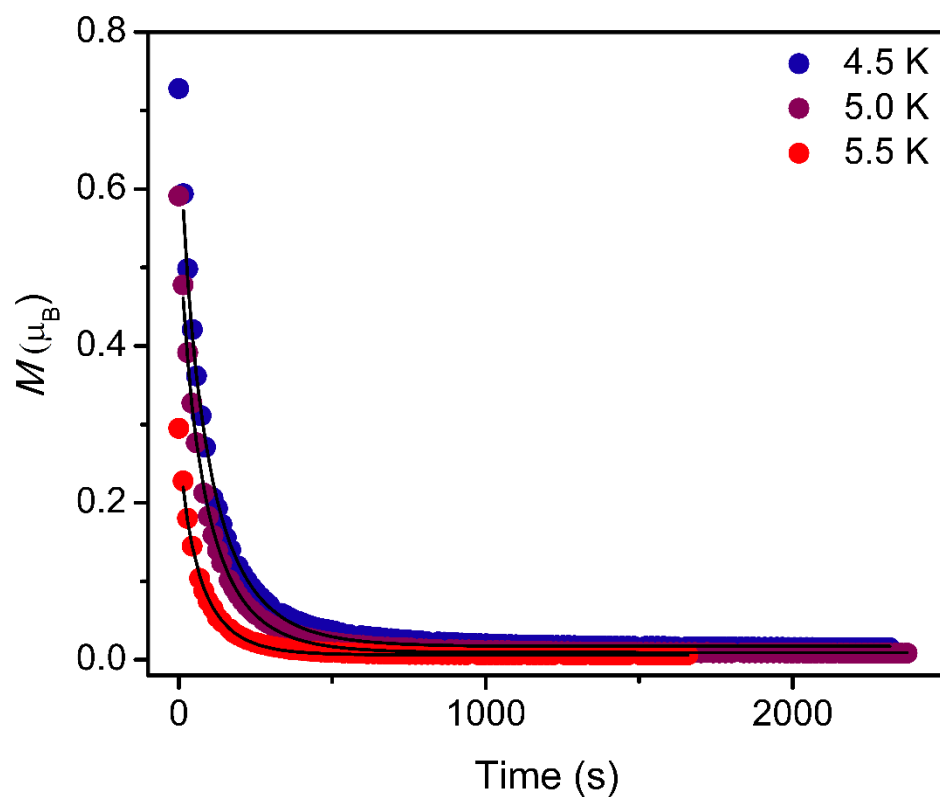


Figure S3.58. Dc magnetic relaxation data for a 7.8 mM of **3-Dy** collected at 4.5, 5.0, and 5.5 K under zero applied magnetic field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S3.13. Parameters used to fit dc magnetic relaxation data for a 7.8 mM solution of **3-Dy** collected under an applied magnetic field of 500 Oe and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	5.67369	1.01498	0.440	38386.401
2.5	5.54410	0.88025	0.441	30165.846
3	5.40343	0.77994	0.452	25713.768
3.5	5.29255	0.72273	0.471	18975.266
4	5.16208	0.68211	0.511	12573.178
4.5	4.91838	0.63007	0.608	4508.859
5	4.10393	0.59884	0.657	1252.540
5.5	2.33356	0.61981	0.745	335.735
6	0.92102	0.55783	0.827	130.599

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

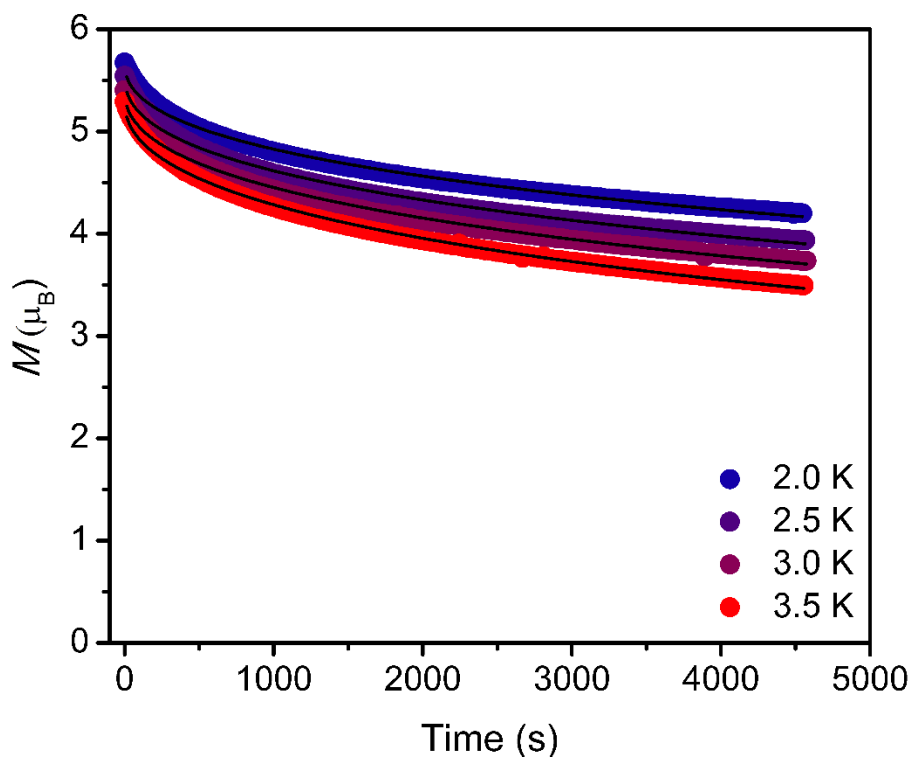


Figure S3.59. Dc magnetic relaxation data for a 7.8 mM of **3-Dy** collected at 2.0, 2.5, 3.0, and 3.5 K under an applied magnetic field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

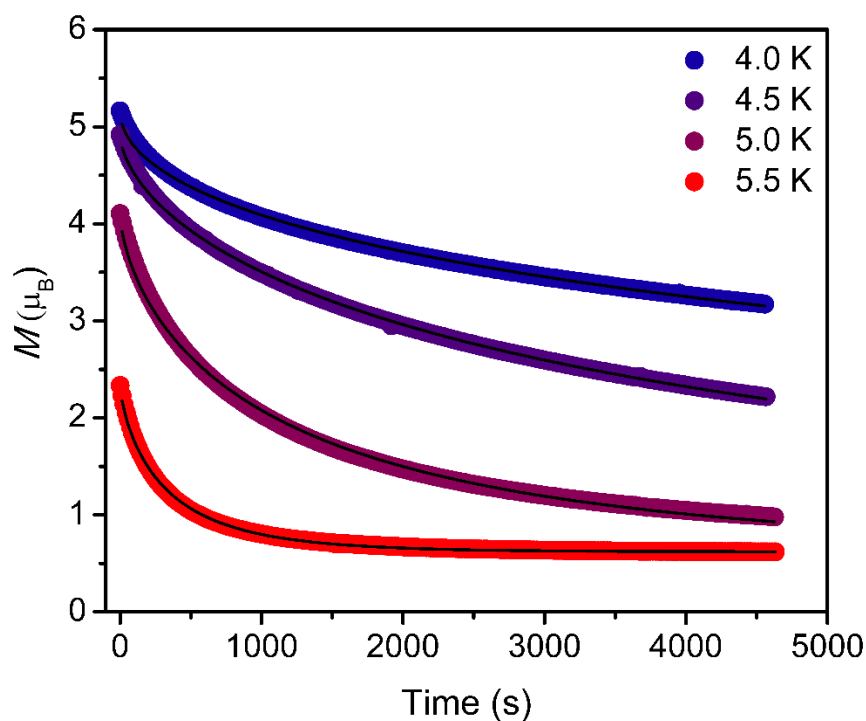


Figure S3.60. Dc magnetic relaxation data for a 7.8 mM of **3-Dy** collected at 4.0, 4.5, 5.0, and 5.5 K under an applied magnetic field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

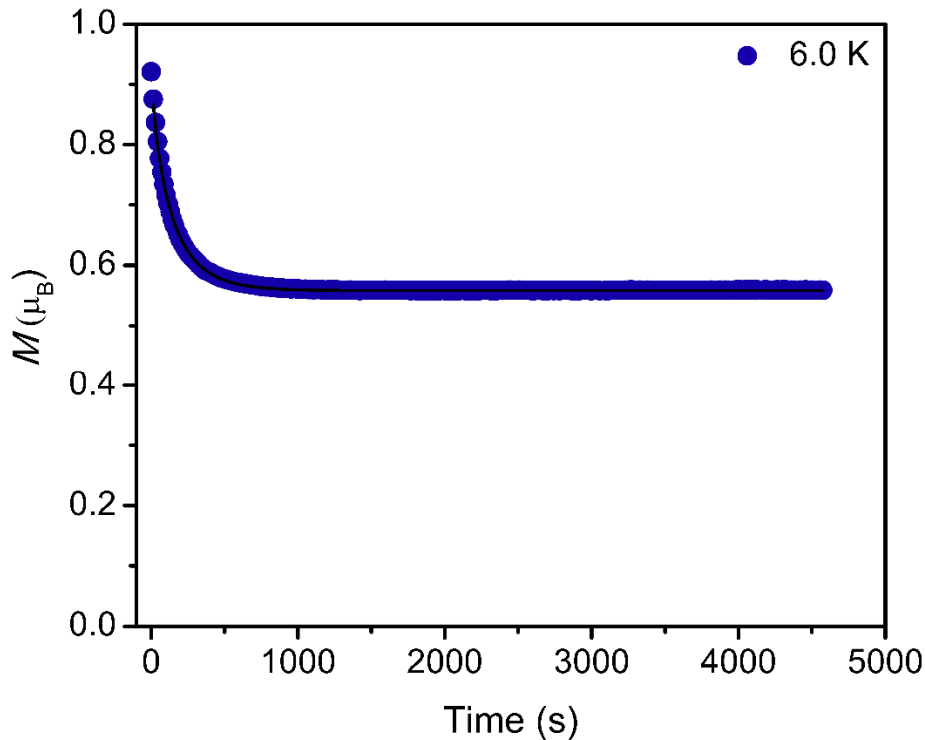


Figure S3.61. Dc magnetic relaxation data for a 7.8 mM of **3-Dy** collected at 6.0 K under an applied magnetic field of 500 Oe. The black line represent the fit to the data using a stretched exponential function, which was used to extract τ .

Table S3.14. Parameters used to fit dc magnetic relaxation data for a solid sample of **4-Dy** collected under zero applied magnetic field and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	3.05575	0.04728	0.720	353.920
2.5	2.87448	0.02656	0.746	304.031
3	2.97010	0.02242	0.751	255.975
3.5	2.47644	0.01347	0.793	240.800
4	2.31350	0.01144	0.816	218.358
4.5	2.15091	0.00969	0.839	196.540
5	1.96927	0.00883	0.873	171.347
5.5	1.62353	0.00394	0.936	129.078
6	0.92276	0.00363	0.960	79.613
6.5	0.27924	0.00199	0.933	56.767

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

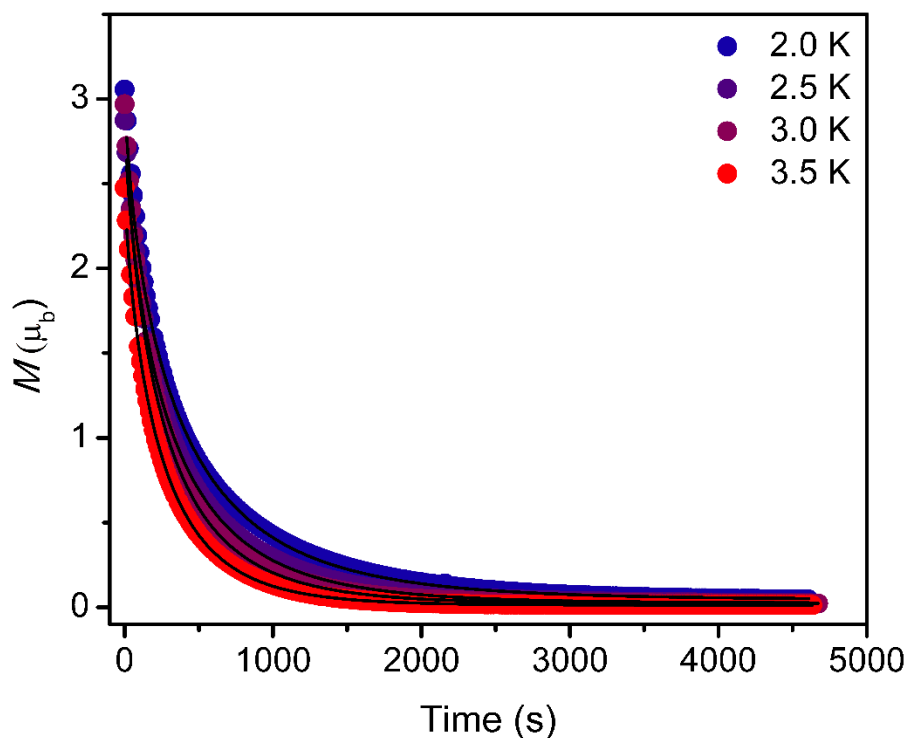


Figure S3.62. Dc magnetic relaxation data for a solid sample of **4-Dy** collected at 2, 2.5, 3 and 3.5 K under zero applied magnetic field. Black line represents the fit to the data using stretched exponential functions, which was used to extract τ .

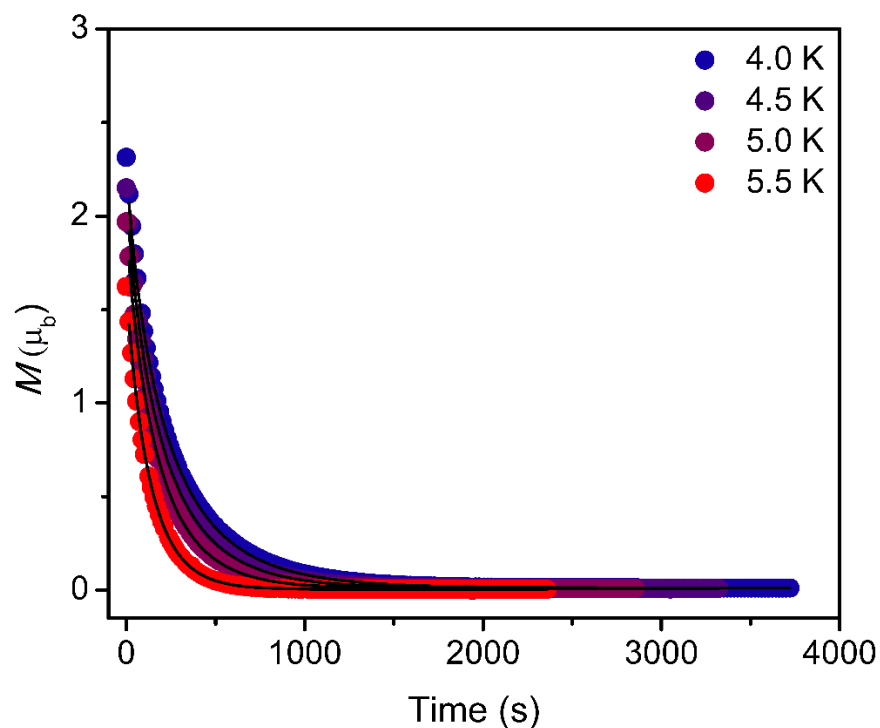


Figure S3.63. Dc magnetic relaxation data for a solid sample of **4-Dy** collected at 4, 4.5, 5 and 5.5 K under zero applied magnetic field. Black line represents the fit to the data using stretched exponential functions, which was used to extract τ .

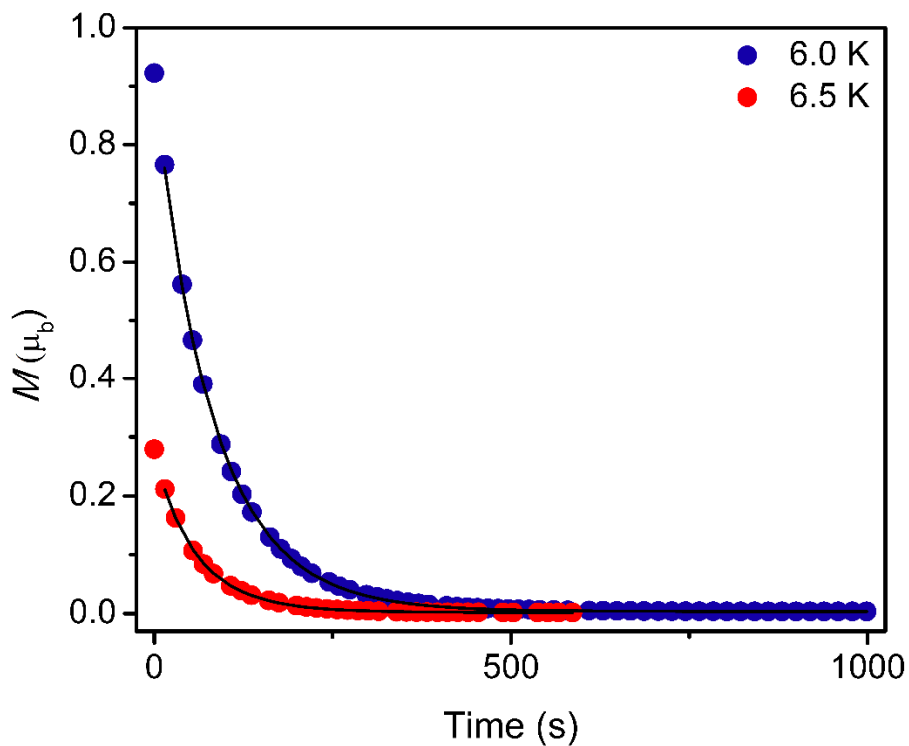


Figure S3.64. Dc magnetic relaxation data for a solid sample of **4-Dy** collected at 6 and 6.5 K under zero applied magnetic field. Black line represents the fit to the data using stretched exponential functions, which was used to extract τ .

Table S3.15. Parameters used to fit dc magnetic relaxation data for an 8.0 mM solution of **4-Dy** collected under zero applied field and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	0.46512	0.03118	0.783	97.035
2.5	0.48708	0.02152	0.786	92.936
3	0.41782	0.01605	0.786	95.310
3.5	0.40869	0.01375	0.780	94.482
4	0.39878	0.01184	0.789	94.369
4.5	0.42105	0.01211	0.848	93.179
5	0.40982	0.01019	0.801	88.046
5.5	0.33137	0.00536	0.818	86.703

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

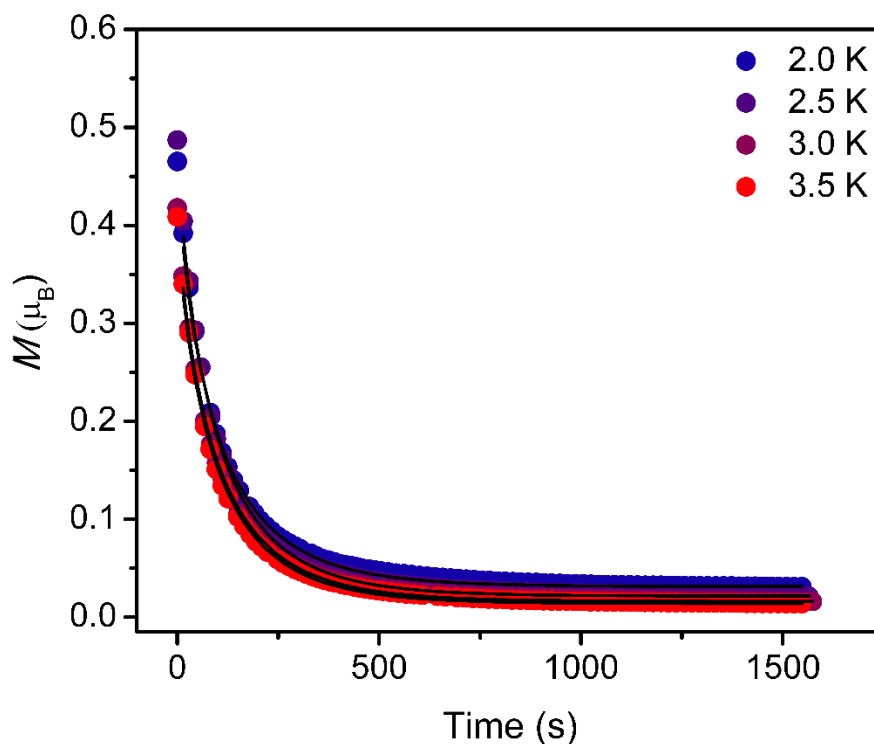


Figure S3.65. Dc magnetic relaxation data for an 8.0 mM of **4-Dy** collected at 2.0, 2.5, 3.0, and 3.5 K under zero applied magnetic field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

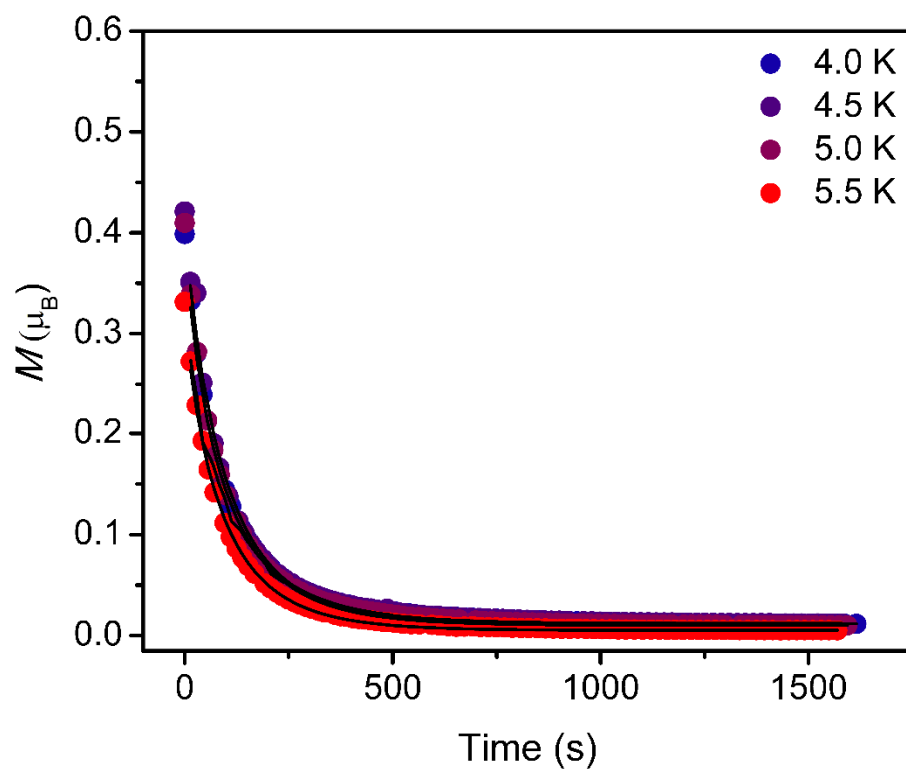


Figure S3.66. Dc magnetic relaxation data for an 8.0 mM of **4-Dy** collected at 4.0, 4.5, 5.0, and 5.5 K under zero applied magnetic field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S3.16. Parameters used to fit dc magnetic relaxation data for an 8.0 mM solution of **4-Dy** collected under an applied magnetic field of 500 Oe and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	2.62304	0.85290	0.401	38450.579
2.5	2.48317	0.71844	0.414	29472.631
3	2.37864	0.62224	0.417	25918.041
3.5	2.29998	0.56128	0.426	21589.703
4	2.23117	0.51234	0.443	17179.222
4.5	2.16330	0.46698	0.472	12442.685
5	2.06905	0.42769	0.555	5434.814
5.5	1.84109	0.39963	0.642	1663.431
6	1.31069	0.40640	0.761	458.109

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

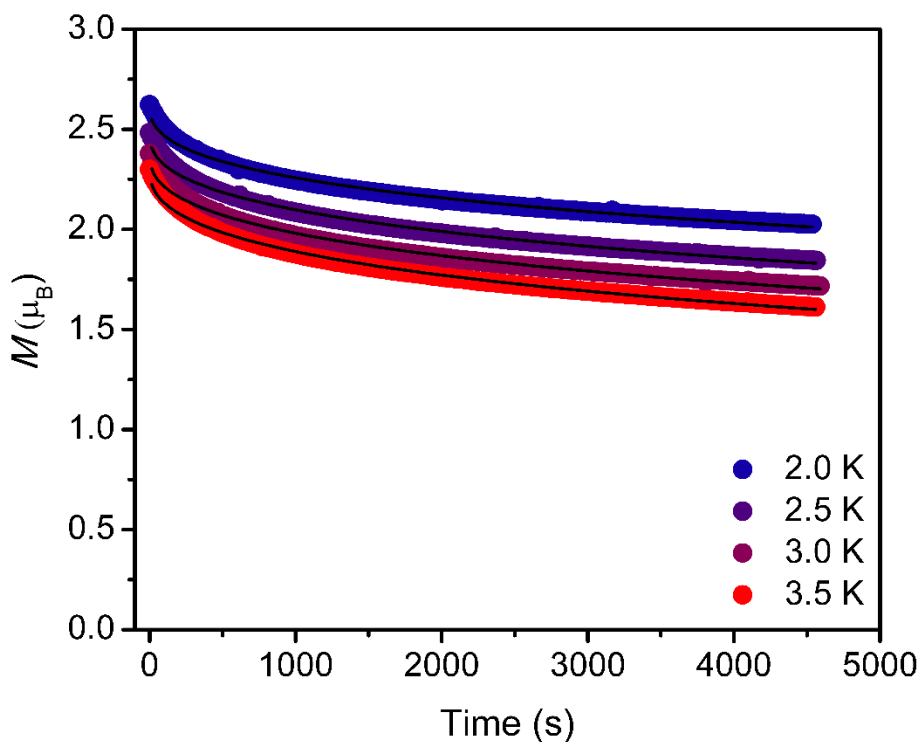


Figure S3.67. Dc magnetic relaxation data for an 8.0 mM of **4-Dy** collected at 2.0, 2.5, 3.0, and 3.5 K under an applied magnetic field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

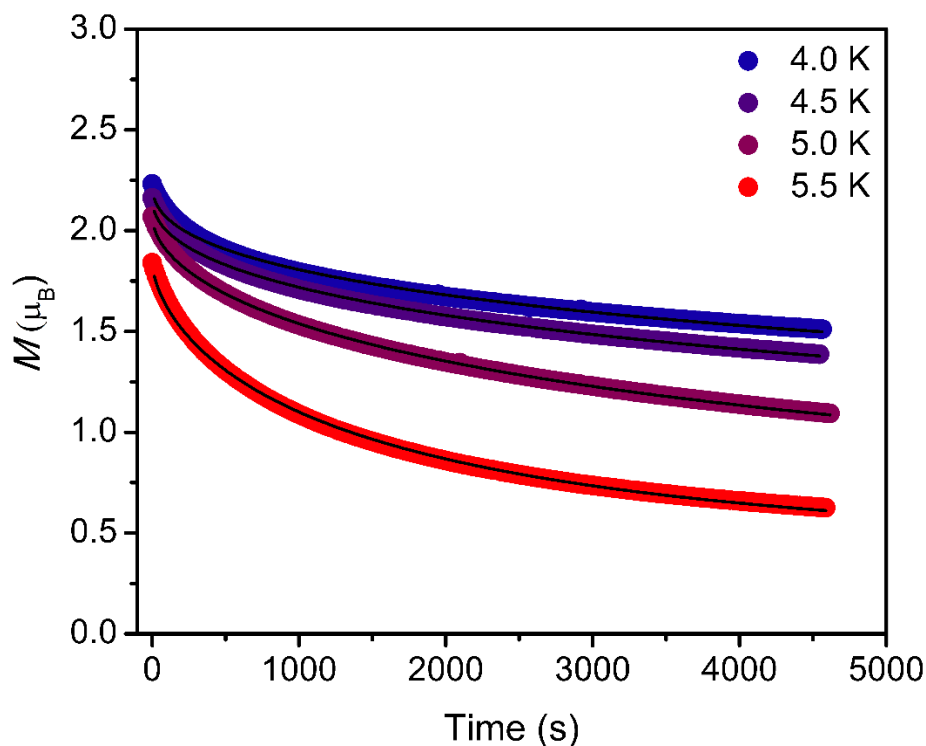


Figure S3.68. Dc magnetic relaxation data for an 8.0 mM of **4-Dy** collected at 4.0, 4.5, 5.0, and 5.5 K under an applied magnetic field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

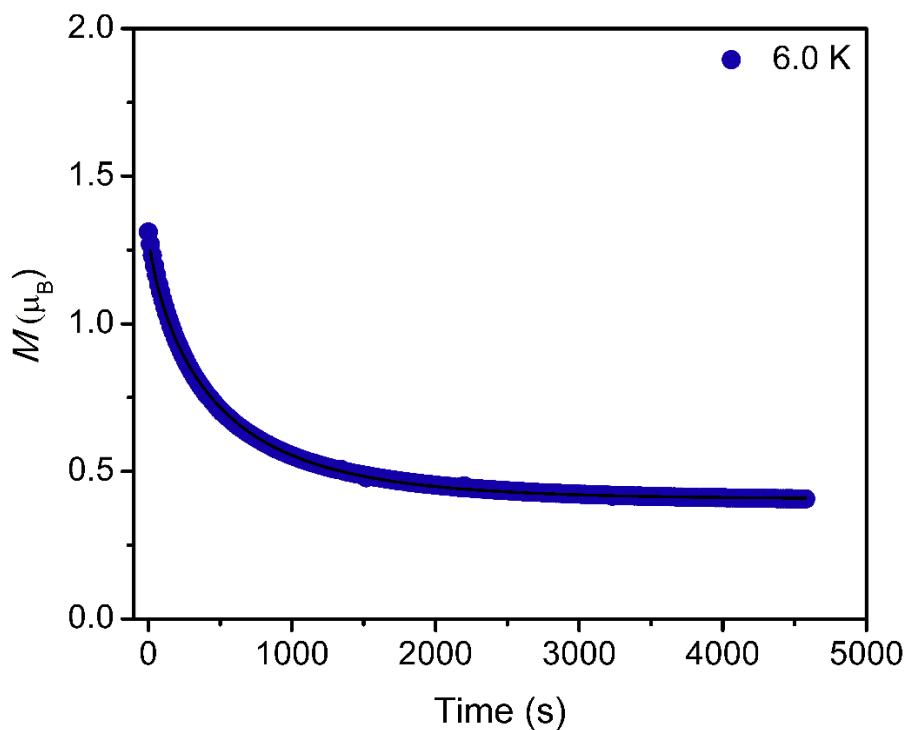


Figure S3.69. Dc magnetic relaxation data for an 8.0 mM of **4-Dy** collected at 6.0 K under an applied magnetic field of 500 Oe. The black line represent the fit to the data using a stretched exponential function, which was used to extract τ .

Analysis of Magnetic Relaxation Dynamics. Plots of $\ln(\tau)$ versus $1/T$ for values extracted from ac susceptibility measurements of **1-Dy** through **4-Dy** were linear, indicative of an Orbach relaxation mechanism. Data were thus fit to the equation:

$$\tau^{-1} = \tau_0^{-1} e^{-U_{eff}/k_b T}$$

where τ is the magnetic relaxation time, τ_0 is the attempt time, U_{eff} is the thermal barrier to magnetization reversal, $k_b = 0.695 \text{ cm}^{-1}\text{K}^{-1}$, and T is temperature.

The full range of magnetic relaxation times extracted from ac susceptibility and dc magnetic relaxation experiments for **3-Dy** and **4-Dy** showed a more complex temperature dependence, indicative of multiple magnetic relaxation pathways. Plots of the log of magnetic relaxation time versus $1/T$ showed an exponential dependence at intermediate temperatures and flattened at low T , suggesting the presence of Raman relaxation and/or quantum tunneling of the magnetization. Accordingly, the data were fit to the equation:

$$\tau^{-1} = \tau_0^{-1} e^{-U_{eff}/k_b T} + \tau_{tunnel}^{-1} + CT^n$$

where τ_{tunnel} is the relaxation time for quantum tunneling of the magnetization and C and n are free variables that describe Raman relaxation. To avoid over-parameterization, τ_0 and U_{eff} were fixed to the values extracted from fits to only the ac magnetic susceptibility measurements. All three relaxation processes were necessary to obtain fits that satisfactorily reproduced the data for **3-Dy** and **4-Dy**.

Table S3.17. Parameters used to fit the Arrhenius plots for **1-Dy**.

	Solid Sample (Dominant Process)	Solid Sample (Minor Process)
$U_{\text{eff}} \text{ (cm}^{-1}\text{)}$	31	46
$\tau_0 \text{ (s)}$	3.3×10^{-6}	4.3×10^{-7}

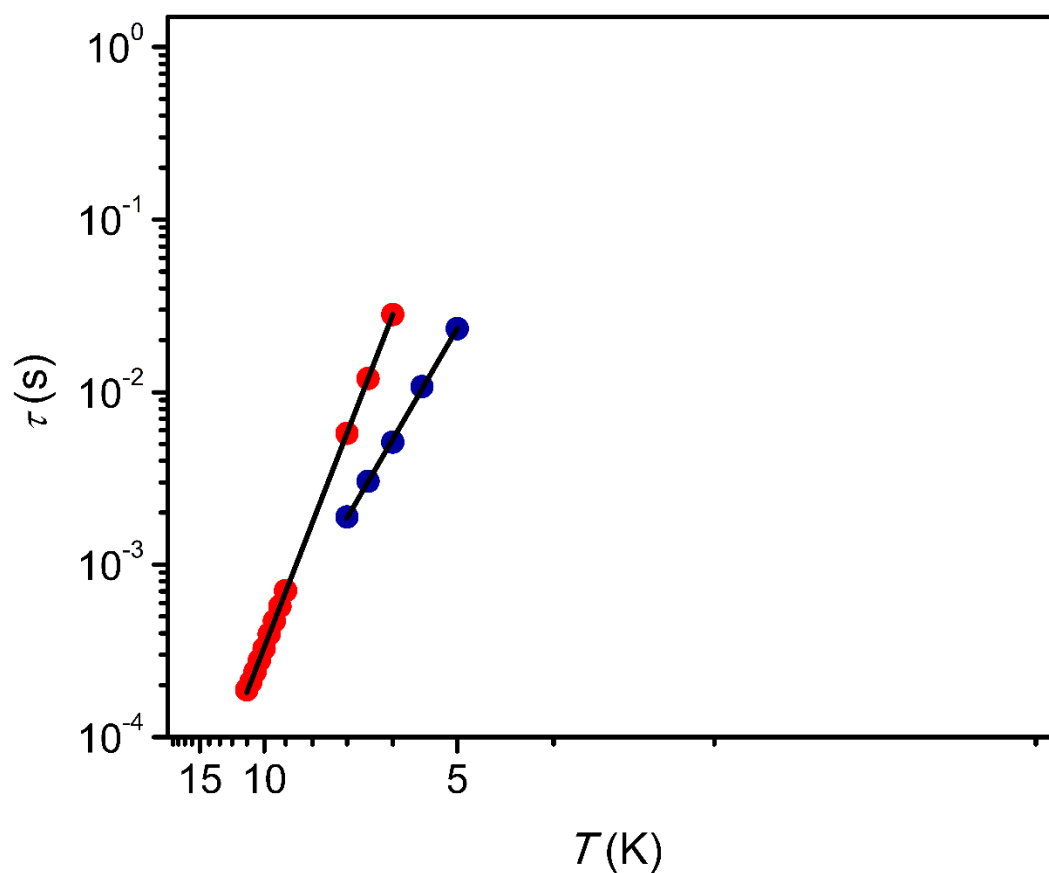


Figure S3.70. Plot of magnetic relaxation time versus temperature for **1-Dy** (dominant process, blue circles; minor process, red circles). Black lines represent fits of the data to Orbach relaxation processes.

Table S3.18. Parameters used to fit the Arrhenius plots for **2-Dy**.

	Solid Sample (Dominant Process)	Solid Sample (Minor Process)
$U_{\text{eff}} \text{ (cm}^{-1}\text{)}$	40	94
$\tau_0 \text{ (s)}$	5.6×10^{-7}	3.4×10^{-8}

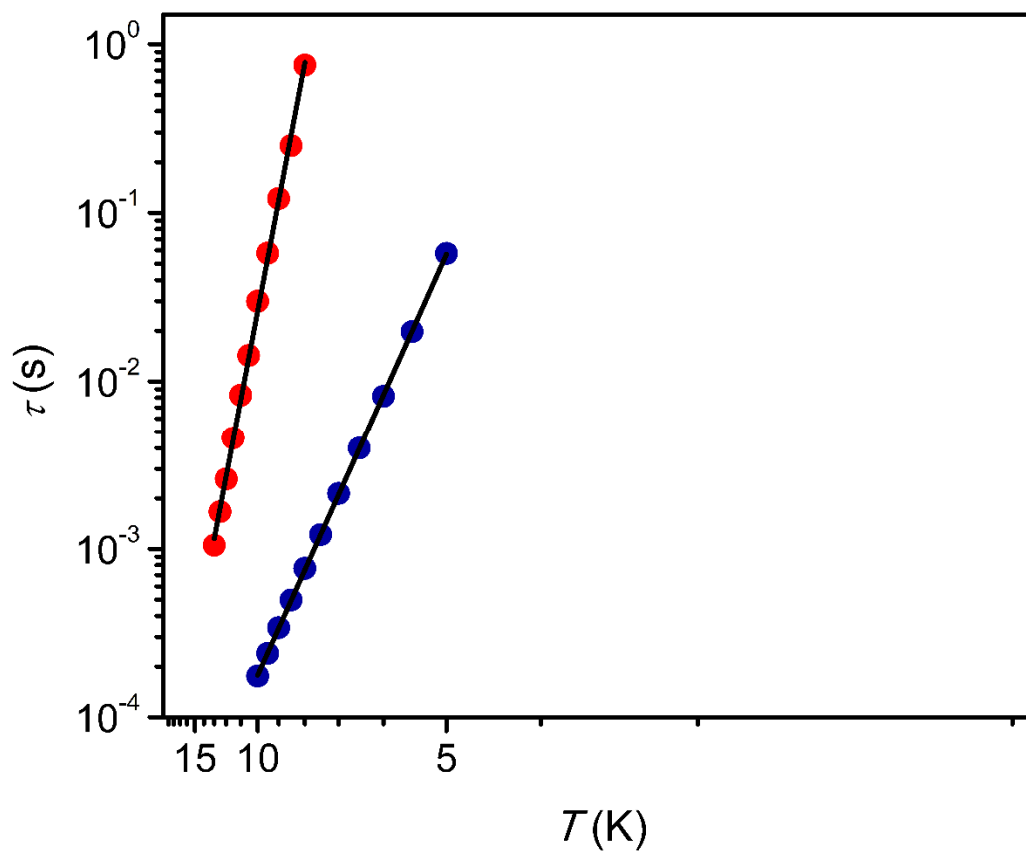


Figure S3.71. Plot of magnetic relaxation time versus temperature for **2-Dy** (dominant process, blue circles; minor process, red circles). Black lines represent fits of the data to Orbach relaxation processes.

Table S3.19. Parameters used to fit the Arrhenius plots for **3-Dy**.

	Solid Sample ($H_{dc} = 0$ Oe)	7.8 mM Solution ($H_{dc} = 0$ Oe)	7.9 mM Solution ($H_{dc} = 500$ Oe)
U_{eff} (cm ⁻¹)	82	-	-
τ_0 (s)	2.9×10^{-7}	-	-
τ_{tunnel} (s)	660	94	34,000
C	3.7×10^{-6}	4.8×10^{-8}	6.8×10^{-10}
n	3.7	6.5	8.3

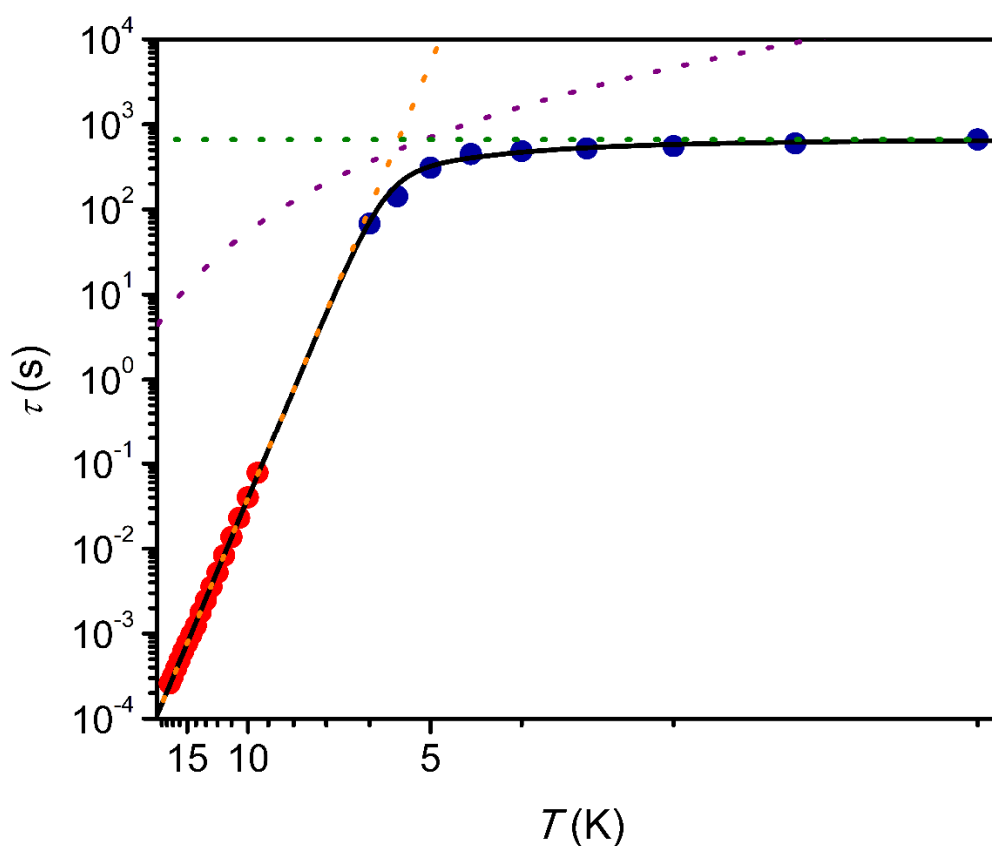


Figure S3.72. Plot of magnetic relaxation time versus temperature for a solid sample of **3-Dy** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data.

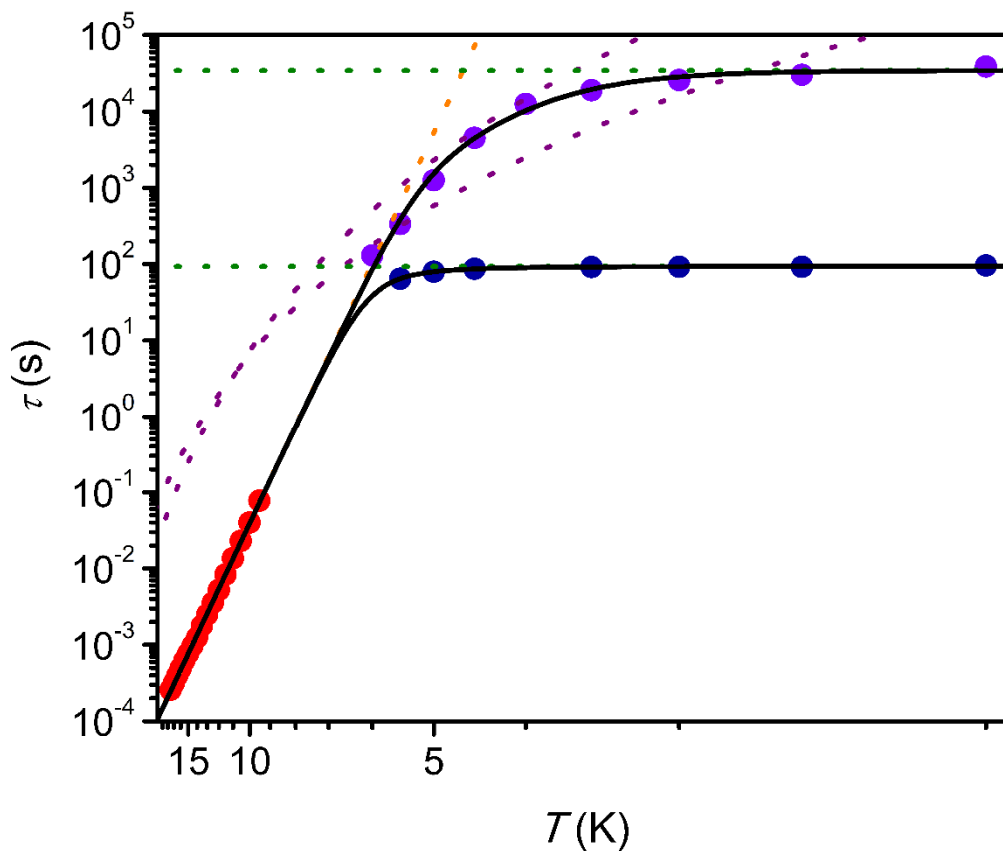


Figure S3.73. Plot of magnetic relaxation time versus temperature for a 7.8 mM solution of **3-Dy** (ac susceptibility for solid sample under zero applied field, red circles; dc relaxation for a 7.8 mM solution under zero applied field, blue circles; dc relaxation for a 7.8 mM solution under an applied field of 500 Oe, violet circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data.

Table S3.20. Parameters used to fit the Arrhenius plots for **4-Dy**.

	Solid Sample ($H_{dc} = 0$ Oe)	8.0 mM Solution ($H_{dc} = 0$ Oe)	8.0 mM Solution ($H_{dc} = 500$ Oe)
U_{eff} (cm ⁻¹)	93	-	-
τ_0 (s)	2.0×10^{-7}	-	-
τ_{tunnel} (s)	350	93	35,000
C	2.9×10^{-5}	-	2.8×10^{-10}
n	3.0	-	8.2

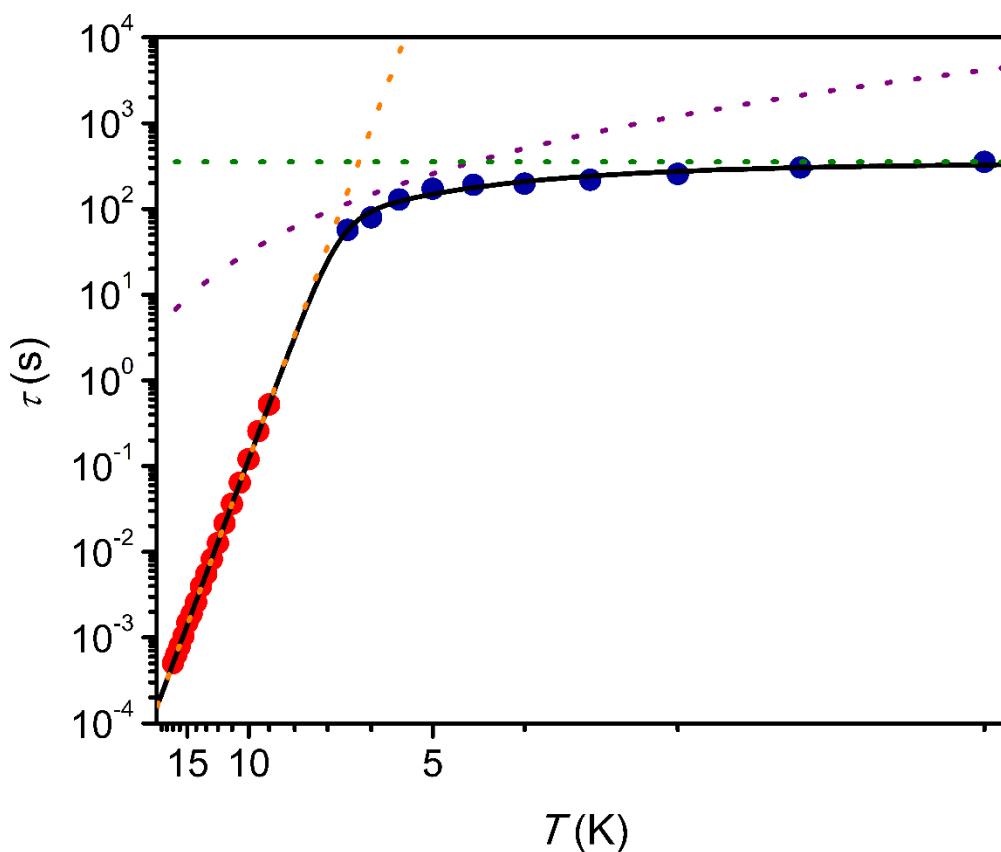


Figure S3.74. Plot of magnetic relaxation time versus temperature for **4-Dy** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data.

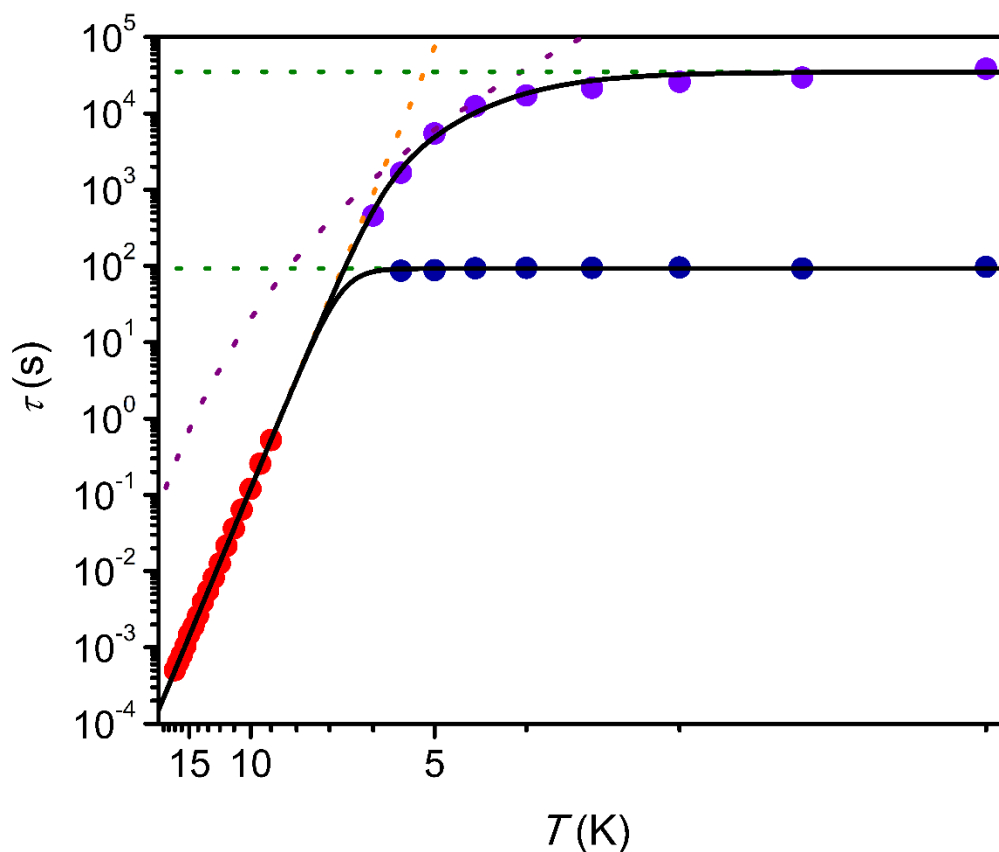


Figure S3.75. Plot of magnetic relaxation time versus temperature for an 8.0 mM solution of **4-Dy** (ac susceptibility for solid sample under zero applied field, red circles; dc relaxation for an 8.0 mM solution under zero applied field, blue circles; dc relaxation for an 8.0 mM solution under an applied field of 500 Oe, violet circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data.

Empirical Correlation Between U_{eff} and $J_{\text{Gd-rad}}$. The energy of electronic excited states in a high-anisotropy, strongly-coupled lanthanide complex can be predicted according to the Ising model, which relates energy differences to $J_{\text{Ln-rad}}$ and the magnitude of ΔJ resulting from a spin flip. For instance, the energy difference between the ground and first excited state for a dysprosium complex is equal to $15|J_{\text{Dy-rad}}|$ (Figure S3.76, left). The energy difference between the ground and first excited state typically corresponds to U_{eff} in radical-bridged lanthanide complexes. If we assume that the coupling constant in a Dy complex ($J_{\text{Dy-rad}}$) is proportional to the coupling constant in a Gd analogue ($J_{\text{Gd-rad}}$) and that the proportionality constant is the same for all complexes, we can derive the relationship: $U_{\text{eff}} = C|J_{\text{Gd-rad}}|$. This implies that a plot of U_{eff} versus $J_{\text{Gd-rad}}$ should be linear, if the aforementioned assumptions hold true.

If a radical-bridged lanthanide complex displays low single-ion anisotropy, it will deviate from the Ising model. Mixing of excited Kramers doublets with the ground doublet will lead to a lower value of U_{eff} (Figure S3.76, right). In this scenario, each complex will show a different relationship between the value of U_{eff} and the value of $J_{\text{Dy-rad}}$, depending on the relative splitting of crystal field states on the Dy^{3+} ions. As such, a plot of U_{eff} versus $J_{\text{Gd-rad}}$ should not be linear.

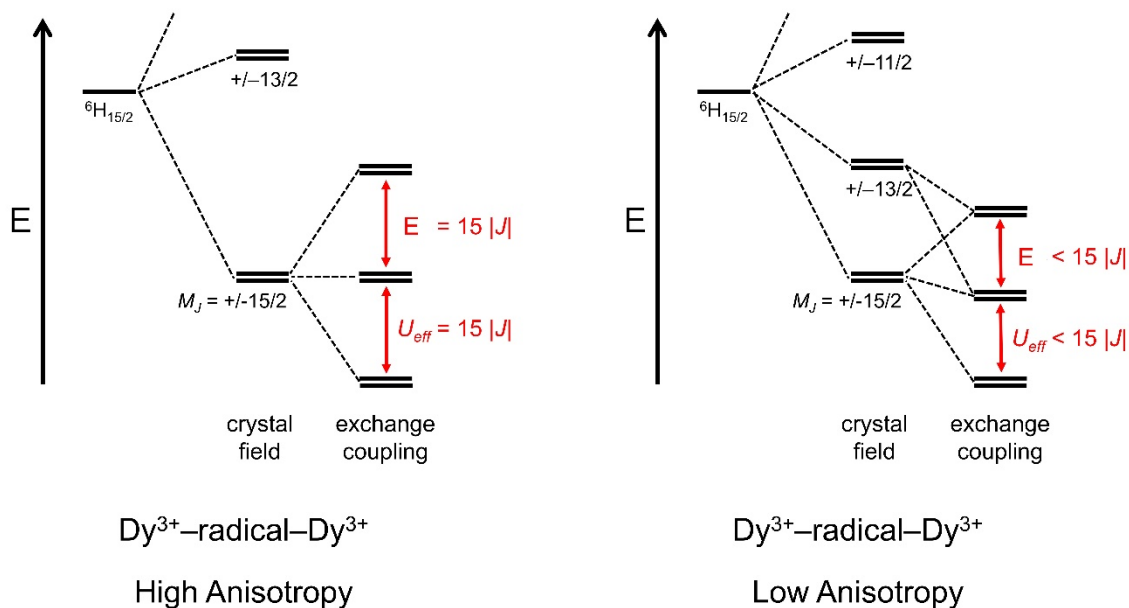


Figure S3.76. Qualitative energy diagrams for dinuclear radical-bridged dysprosium complexes. The complex on the left displays high single-ion anisotropy and can be described by an Ising model. The complex on the right shows lower single-ion anisotropy and thus the exchange interaction mixes the ground Kramers doublet with the excited doublets, leading to a reduction in the value of U_{eff} .

Figure 3 is a plot of the experimental U_{eff} value for the dominant magnetic relaxation process in **1-Dy** through **4-Dy** versus $|J_{\text{Gd-rad}}|$ of the corresponding Gd derivative. $|J_{\text{Gd-rad}}|$ is an average of the values extracted from fits to dc susceptibility data collected at 1 kOe, 5 kOe, and 10 kOe for **1-Gd** through **4-Gd**, as described above. This plot demonstrates that U_{eff} is linearly correlated to $|J_{\text{Gd-rad}}|$ for **1-Dy** through **4-Dy**, with a best-fit line of $U_{\text{eff}} = 7.617|J_{\text{Gd-rad}}| + 9.582$ ($R^2 = 0.9997$). The non-zero value of the y-intercept is likely meaningless, as this relationship does not apply to small

values of $J_{\text{Ln-rad}}$, where single-ion effects begin to dominate. The linear correlation observed for this data suggests that **1-Dy** through **4-Dy** can be accurately described by the Ising model.

In order to test the validity of this empirical model, we plotted the data for all dysprosium complexes that contain an open-shell organic ligand for which both U_{eff} of the complex and $J_{\text{Gd-rad}}$ of the gadolinium analogue have been determined (see Table S3.21 below).¹⁵ Gratifyingly, the best-fit line for **1-Dy** through **4-Dy** accurately models all multinuclear radical-bridged complexes for which we could obtain data (see main text for discussion).

In addition, reasonable predictions are obtained for the U_{eff} values of complexes in which a single Dy^{3+} ion interacts with an organic radical. Experimental U_{eff} values for these complexes are likely lower than the predicted values due to low single-ion anisotropy. Indeed, all of these complexes feature Dy^{3+} ions with high coordination numbers (≥ 7), which limits anisotropy. The empirical model derived for **1-Dy** through **4-Dy** likely breaks down for low values of $|J_{\text{Gd-rad}}|$, as single-ion effects begin to dominate. This may contribute to the discrepancy between experimental and predicted U_{eff} values.

The empirical correlation derived for **1-Dy** through **4-Dy** offers insight into how the U_{eff} value of a radical-bridged dysprosium complex can be increased. If a complex falls along the best-fit line, it displays the maximal value of U_{eff} that is possible given its value of $J_{\text{Gd-rad}}$. In this scenario, U_{eff} can only be increased by further increasing $J_{\text{Ln-rad}}$. Increasing the coupling strength should result in diagonal movement along the best-fit line towards the top right corner of the graph. Increasing single-ion anisotropy will not lead to larger U_{eff} values for these molecules.

If a complex falls below the best-fit line, the value of U_{eff} can be increased by maximizing single-ion anisotropy. This will correspond to vertical movement along the graph towards the best-fit line, which represents the maximal value of U_{eff} for that complex given the strength of magnetic exchange coupling. Increasing the value of $J_{\text{Ln-rad}}$ may increase the value of U_{eff} somewhat, but the relationship between the two variables is hard to predict, as such complexes do not adhere to an Ising model.

Table S3.21. Experimental U_{eff} values (cm^{-1}) for radical-containing dysprosium complexes and $J_{\text{Gd-rad}}$ (cm^{-1}) for the corresponding gadolinium derivative, which were used to construct Figure 3.3. The predicted value of U_{eff} according to the empirical model derived for **1-Dy** through **4-Dy** is also included.

Complex	$J_{\text{Gd-rad}}$ (cm^{-1})	Experimental U_{eff} (cm^{-1})	Predicted U_{eff} (cm^{-1})	Reference
1-Dy	-2.88^a	31	32	This work
2-Dy	-3.91^a	40	39	This work
3-Dy	-9.53^a	82	82	This work
4-Dy	-10.9^a	93	93	This work
$[(\text{Cp}^*_2\text{Dy})_2(\mu\text{-bpym})]^-$	-10	88	86	3
$(\text{Cp}^*_2\text{Dy})_3(\mu\text{-HAN})$	-5.0	51	48	16
$[(\text{HBpz}_3)_2\text{Dy}_2(\mu\text{-CA})]^-$	-2.09	22	25	17
$[(\text{Cp}^*_2\text{Dy})_2(\mu\text{-tppz})]^+$	-6.9	36	62	18
$[(\text{Cp}^*_2\text{Dy})_2(\mu\text{-tppz})]^-$	-6.3	n/a	58	18
$[(\text{Cp}^*_2\text{Dy})_2(\mu\text{-ind})]^-$	-11	35	93	19
$[(\text{Cp}^*_2\text{Dy})_2(\mu\text{-N}_2)]^-$	-20	123	162	20
$[(\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})_2\text{Dy})_2(\mu\text{-N}_2)]^-$	-27	108	215	21
$[\text{Dy}(\text{hfac})_3(\text{NIT4Py})]_2$	0.89	10	16	22, 23
$[\text{Dy}(\text{acac})_3(\text{NIT2Py})] \cdot 0.5\text{NIT}^o\text{Py}$	2.23	15	26	24
$[\text{Dy}(\text{Phtfac})_3(\text{NIT4Py})]_2$	1.84	14	24	25
$[\text{Dy}(\text{hfac})_3(\text{NITPhO})]_2$	2.75	5.2	30.5	26, 27
$\text{Dy}(\text{tfa})_3(\text{NITBzImH})$	0.99	3.2	17	28

^aAverage of values obtained for fits to 0.1, 0.5, and 1 T data.

Magnetic Hysteresis Measurements. Magnetic hysteresis measurements were collected on **1-Dy** through **4-Dy**, **1-Tb**, and **4-Tb** at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe. Hysteresis measurements were also conducted on a 7.8 mM solution of **3-Dy** and an 8.0 mM solution of **4-Dy** in order to eliminate the influence of molecular dipolar interactions.

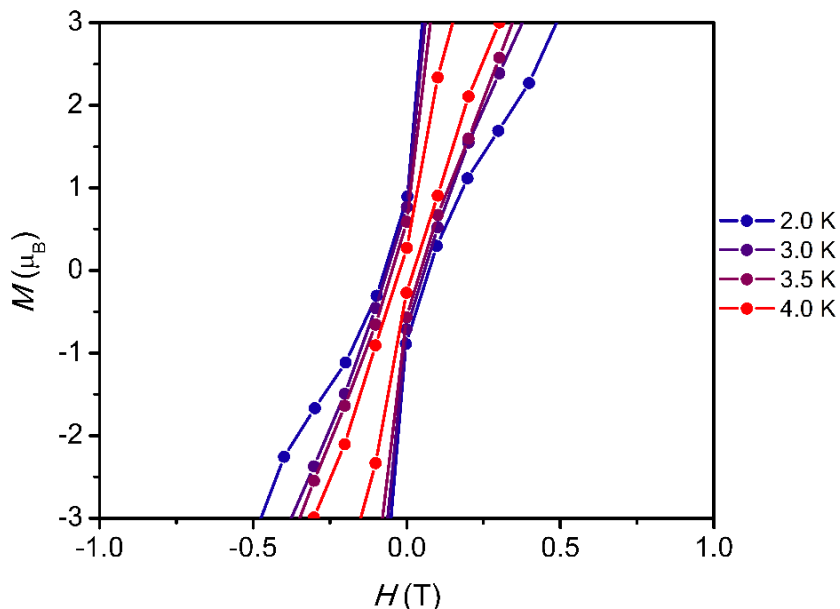


Figure S3.77. Magnetic hysteresis measurements of polycrystalline **1-Dy** from 2.0 to 4.0 K at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe. Only data from -10 kOe to 10 kOe are shown in order to allow H_c to be visualized more clearly (see main text for full data).

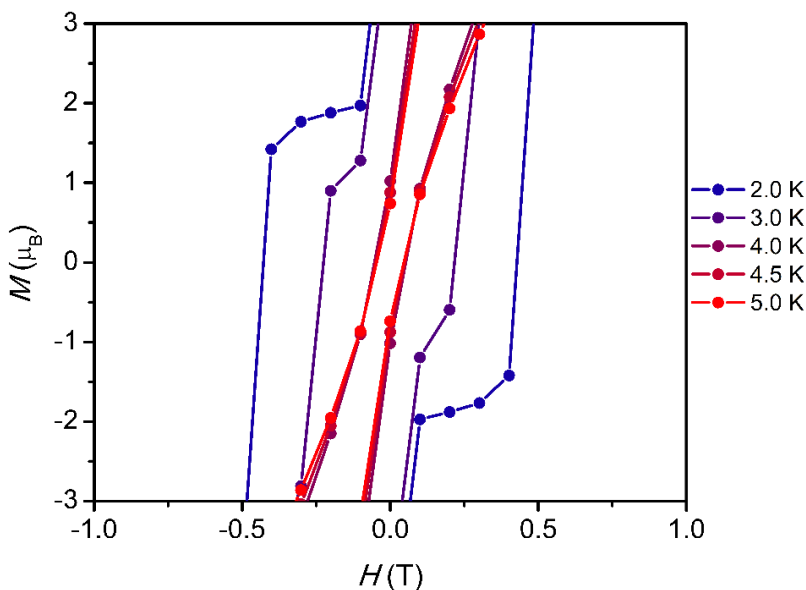


Figure S3.78. Magnetic hysteresis measurements of polycrystalline **2-Dy** from 2.0 to 5.0 K at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe. Only data from -10 kOe to 10 kOe are shown in order to allow H_c to be visualized more clearly (see main text for full data).

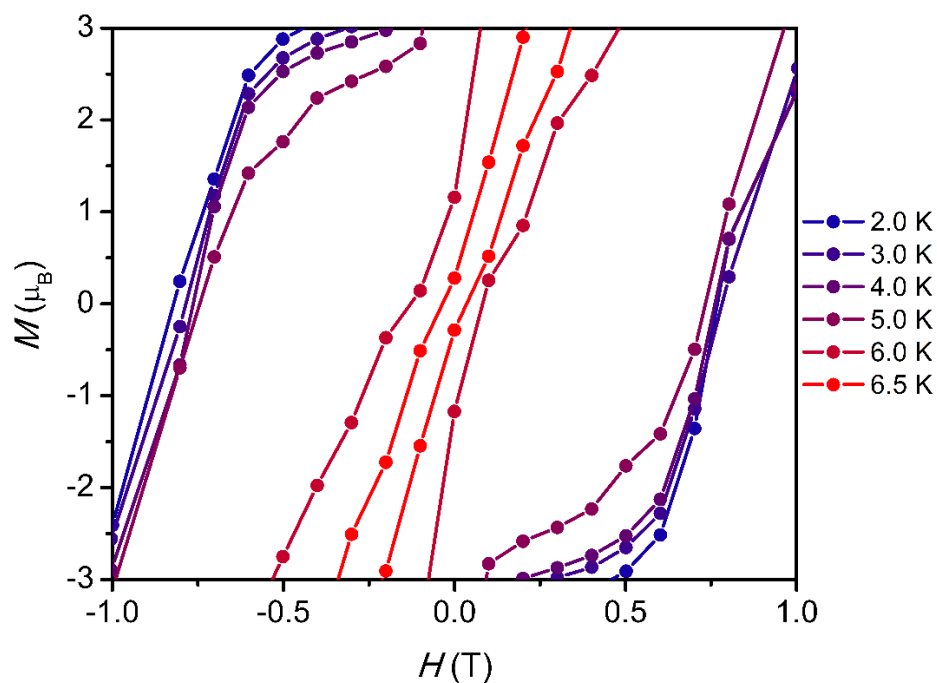


Figure S3.79. Magnetic hysteresis measurements of polycrystalline **3-Dy** from 2.0 to 6.5 K at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe. Only data from -10 kOe to 10 kOe are shown in order to allow H_c to be visualized more clearly (see main text for full data).

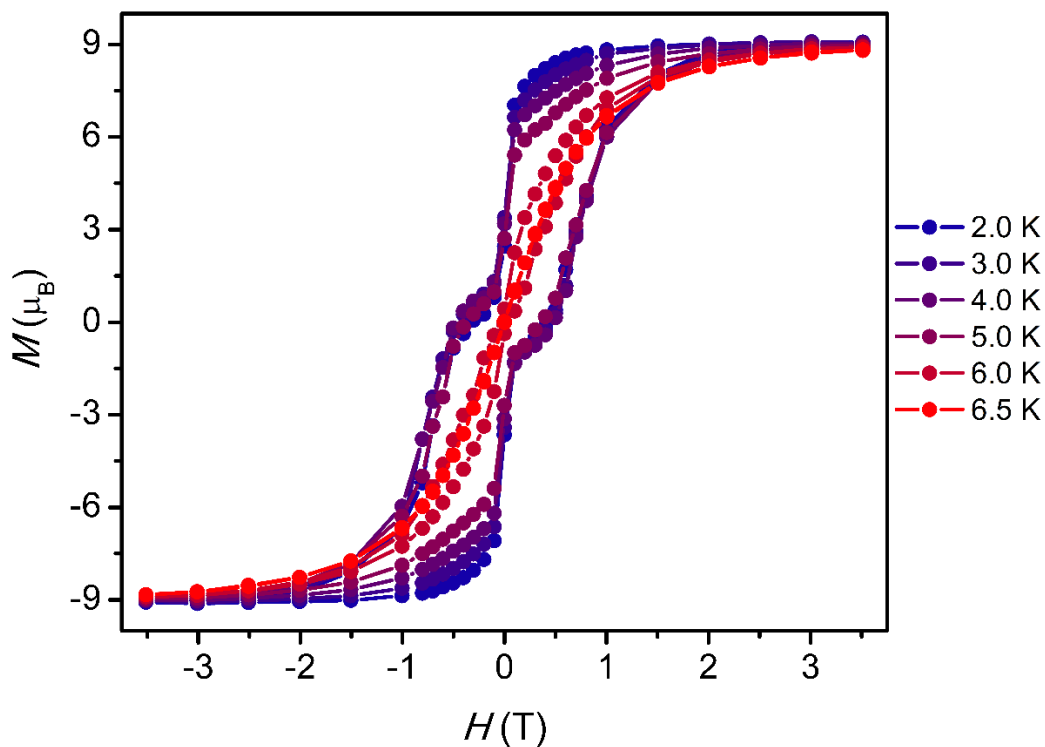


Figure S3.80. Magnetic hysteresis measurements of a 7.8 mM solution of **3-Dy** from 2.0 to 6.5 K at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe.

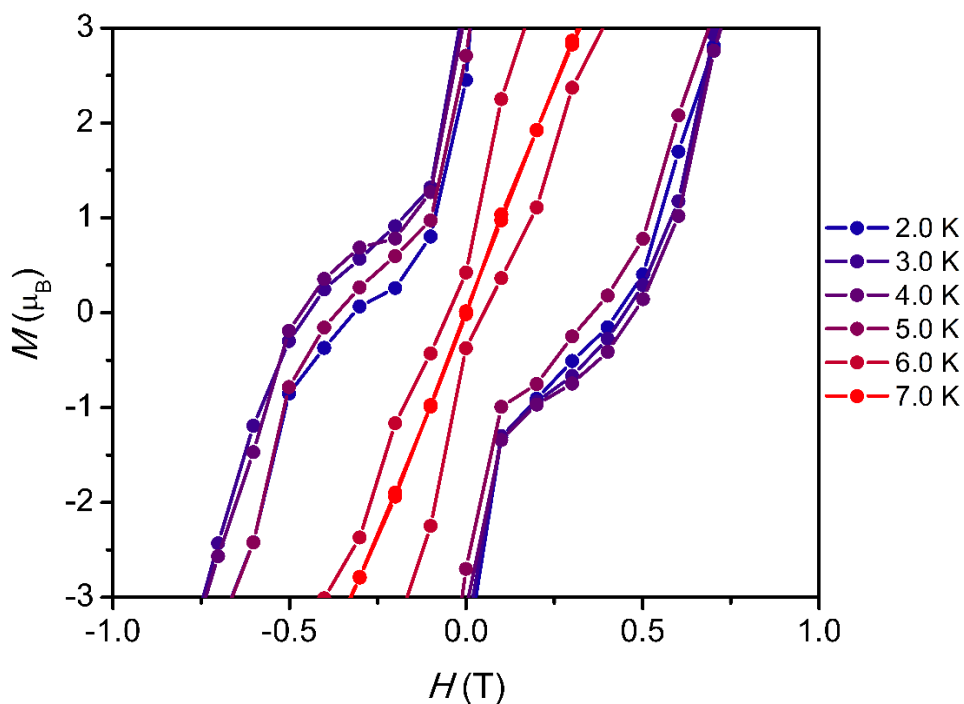


Figure S3.81. Magnetic hysteresis measurements of a 7.8 mM solution of **3-Dy** from 2.0 to 7.0 K at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe. Only data from -10 kOe to 10 kOe are shown in order to allow H_c to be visualized more clearly (see above for full data).

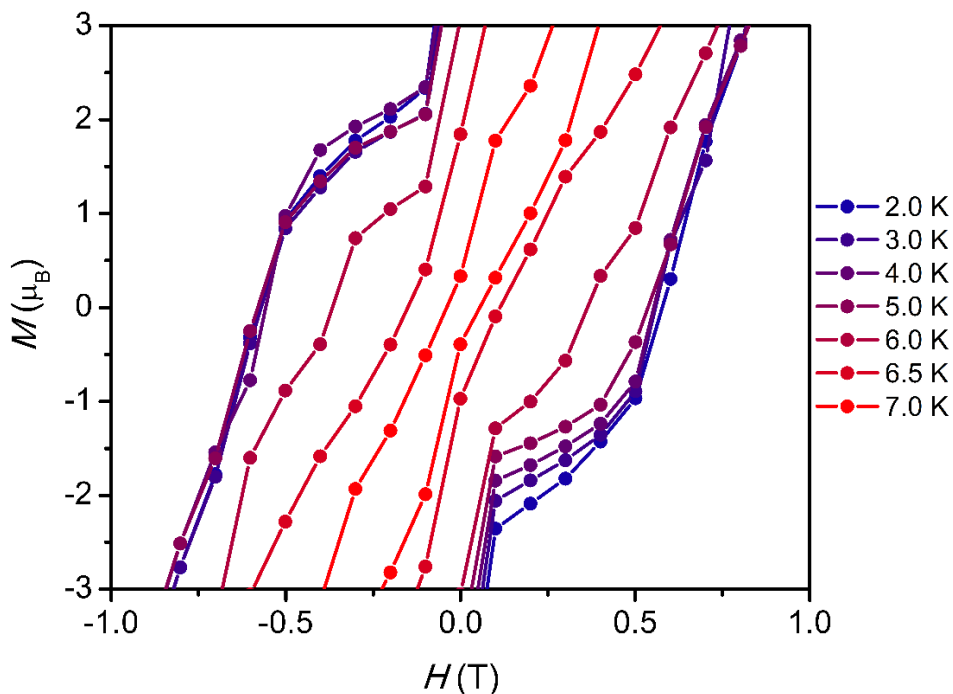


Figure S3.82. Magnetic hysteresis measurements of polycrystalline **4-Dy** from 2.0 to 7.0 K at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe. Only data from -10 kOe to 10 kOe are shown in order to allow H_c to be visualized more clearly (see main text for full data).

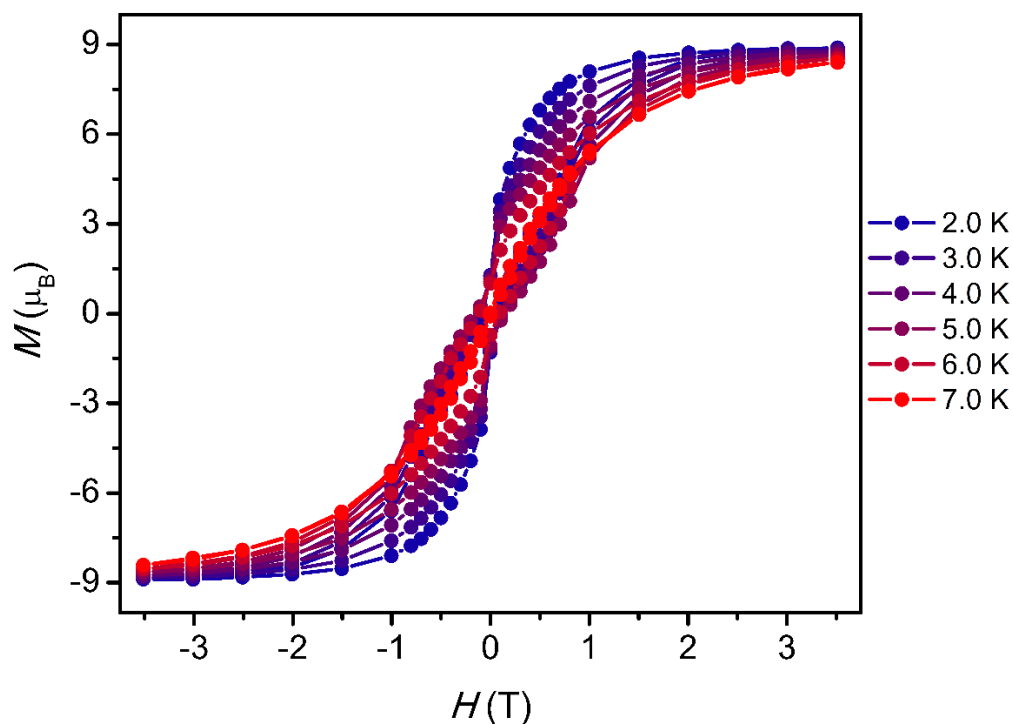


Figure S3.83. Magnetic hysteresis measurements of an 8.0 mM solution of **4-Dy** from 2.0 to 7.0 K at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe.

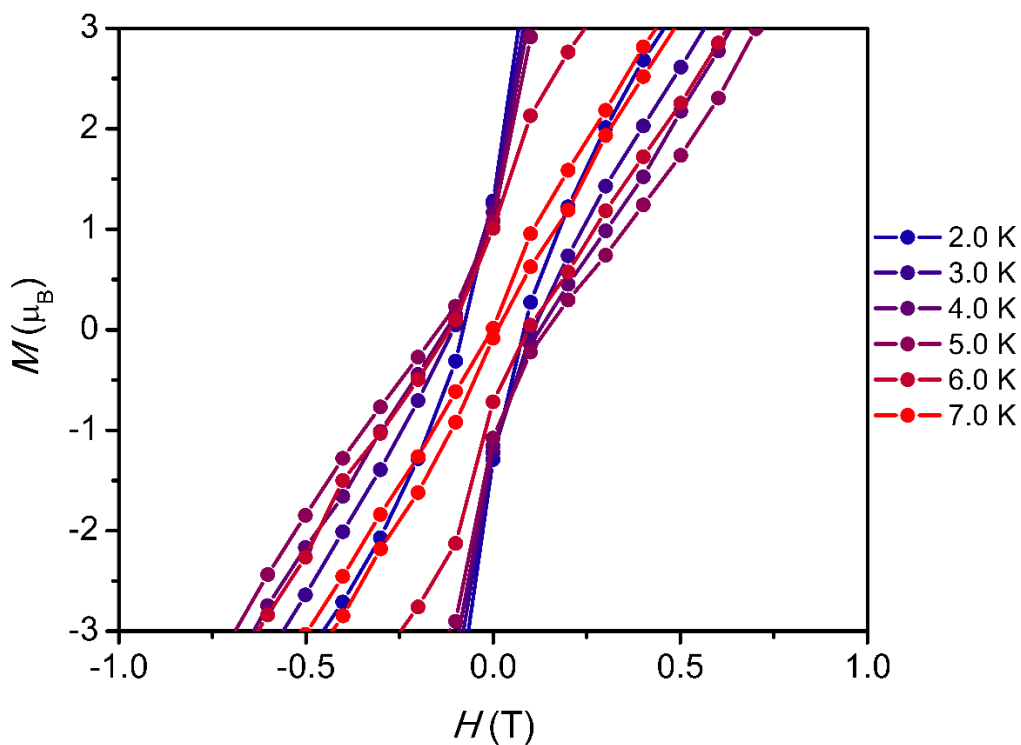


Figure S3.84. Magnetic hysteresis measurements of an 8.0 mM solution of **4-Dy** from 2.0 to 7.0 K at a sweep rate of 82(2) Oe/s for $|H| > 10$ kOe and 24(1) Oe/s for $|H| < 10$ kOe. Only data from -10 kOe to 10 kOe are shown in order to allow H_c to be visualized more clearly (see above for full data).

3.6.6 *Ab initio* Calculations

Local electronic and magnetic properties of the Dy^{3+} ions in **1-Dy** through **4-Dy** and $[(\text{Cp}^*\text{Dy})_2(\mu\text{-ind})]^-$ were calculated with MOLCAS 8.2 program.²⁹ Fragment calculations were performed on the single crystal X-ray diffraction structures with the nearby Dy^{3+} ions replaced with Lu^{3+} . The methyl groups of the cyclopentadienyl ligand around each Lu^{3+} ion were replaced by hydrogen atoms. The Cholesky decomposition threshold was set to $5 \cdot 10^{-8}$ Hartree to save disk space. The ANO-RCC basis set was used for all atoms, as shown in Table S3.22. Four point charges on the bridging carbon and nitrogen atoms, each $-0.25 e$, were included to consider the electrostatic potential from the unpaired electron of bpym-radical bridge. CASSCF calculations comprised seven $4f$ -type orbitals. 21 sextet, 128 quartet and 130 doublet states were admixed by spin-orbit coupling within the RASSI program. Based on the obtained spin-orbital states, local magnetic properties were calculated within the SINGLE_ANISO program.³⁰ Finally, the exchange interaction was included within the POLY_ANISO module.^{31,32}

To estimate the exchange coupling parameters between the Dy^{3+} ions and the bpym-radical ligand, broken-symmetry DFT calculations³³ were employed by using ORCA 3.0.0³⁴ with SVP basis set, B3LYP functional, Grid6 and TightSCF settings. Because Dy^{3+} ions are multiconfigurational in their nature, they cannot be treated adequately by DFT methods. Therefore, the Dy^{3+} ions were replaced with Gd^{3+} , while preserving the position of all atoms intact. In this way one can extract the exchange interaction between the Gd^{3+} ions and the radical and then rescale it to the spin of Dy^{3+} to calculate $J_{\text{Dy-rad}}$. This is achieved by multiplying the former value by $49/25$.³⁵

Table S3.22. Employed basis set.

Dy.ANO-RCC-VTZP
Lu.ANO-RCC-VDZ
C & N (closest): C.ANO-RCC-VDZP
O, F, H, N & C (distant): N.ANO-RCC-VDZ

Calculated local crystal field levels of the Dy^{3+} ions in **1-Dy** through **4-Dy** are shown in Table S3.23. For comparison reasons, crystal field levels of Dy^{3+} ion from $\text{Dy}_2\text{N}_2^{3-}$ complex^{21,36} are shown as well. Calculated local crystal field levels of the Dy^{3+} ions in $[(\text{Cp}^*\text{Dy})_2(\mu\text{-ind})]^-$ are also shown in Table S3.23. These calculations show that the ground Kramers doublet (KD) in **1-Dy** through **4-Dy** is well separated from the excited states and that the first excited states in these complexes are higher in energy than in the N_2^{3-} -bridged complex. By contrast, the ground Kramers doublet in $[(\text{Cp}^*\text{Dy})_2(\mu\text{-ind})]^-$ is much less well separated from the first excited state.

Table S3.23. Energy (cm⁻¹) of low-lying Kramers doublets of individual Dy centers in **1-Dy** through **4-Dy**, [(Cp*₂Dy)₂(μ-ind)]⁻, and [{N(SiMe₃)₂}₂(THF)Dy)₂(μ-N₂)]⁻, and the g-tensor of the corresponding ground doublets as determined by *ab initio* calculations.

1-Dy^a		2-Dy		3-Dy^a	4-Dy^a	[Dy₂(μ-ind)]^{- a}	[Dy₂(μ-N₂)]^{- 36,a}
		Dy(1)	Dy(2)				
0		0	0	0	0	0	0
216		225	238	221	238	71	179
327		347	374	332	374	107	321
377		400	416	385	416	179	407
443		472	481	454	481	209	471
492		530	532	505	532	262	532
596		641	620	611	620	345	623
911		964	923	927	923	576	750
g _x	0.00666	0.00754	0.00960	0.00757	0.00437	0.0282	0.0026
g _y	0.0141	0.01481	0.01857	0.01519	0.00886	0.0882	0.0040
g _z	19.598	19.60265	19.60576	19.60441	19.69793	18.8953	19.6459

^aThis molecule possesses inversion symmetry such that Dy(1) = Dy(2)

The BS-DFT calculated values for $J_{\text{Gd-rad}}$ using the X-ray structure of **2-Dy** through **4-Dy** are -9.8, -10.6, and -10.8 cm⁻¹ respectively. By rescaling these data to the spin 5/2 of Dy³⁺ ions, one obtains estimated $J_{\text{Lines}}(\text{Dy-R})$ constants of -19.1, -20.7 and -21.1 cm⁻¹ for **2-Dy** through **4-Dy**, respectively. Due to the high axiality of the ground Kramers doublet of the Dy ions (Table S3.23, g_x, g_y << g_z) in **2-Dy** through **4-Dy**, the low-lying exchange states can be described within the Ising model. This is further justified given the weaker exchange interaction and higher CF levels on the Dy³⁺ sites of **2-Dy** through **4-Dy** as compared to the N₂³⁻-bridged complex. According to the Ising model:

$$\hat{H}_{\text{exch}} = -J_{\text{Dy-R}}(\tilde{s}_{\text{Dy1}} \cdot \hat{S}_R + \tilde{s}_{\text{Dy2}} \cdot \hat{S}_R)$$

where $\tilde{s}_{\text{Dy}}$ is the pseudospin 1/2 corresponding to the ground Kramers doublet of the Dy³⁺ ion. The BS-DFT extracted values were used as the starting point for the fitting of experimental magnetic susceptibility data and the best fit (Figures S3.85-S3.87) is given by the exchange parameters from Table S3.24. Calculation of the exchange spectrum for **1-Dy** is ongoing.

Table S3.24. Fitted Lines and Ising* exchange parameters for **2-Dy** through **4-Dy** (cm⁻¹).

Complex	$J_{\text{Lines}}(\text{Dy-R})$	$J_{\text{Ising}}(\text{Dy-R})$	zJ' (intermolecular interaction)
2-Dy	-24.0	-120.0	-0.08
3-Dy	-30.0	-150.0	-0.03
4-Dy	-34.0	-170.0	-0.12

*In current case Ising exchange parameters can be obtained by a simple rescaling of the Lines parameters, $J_{\text{Ising}}=5 J_{\text{Lines}}$.

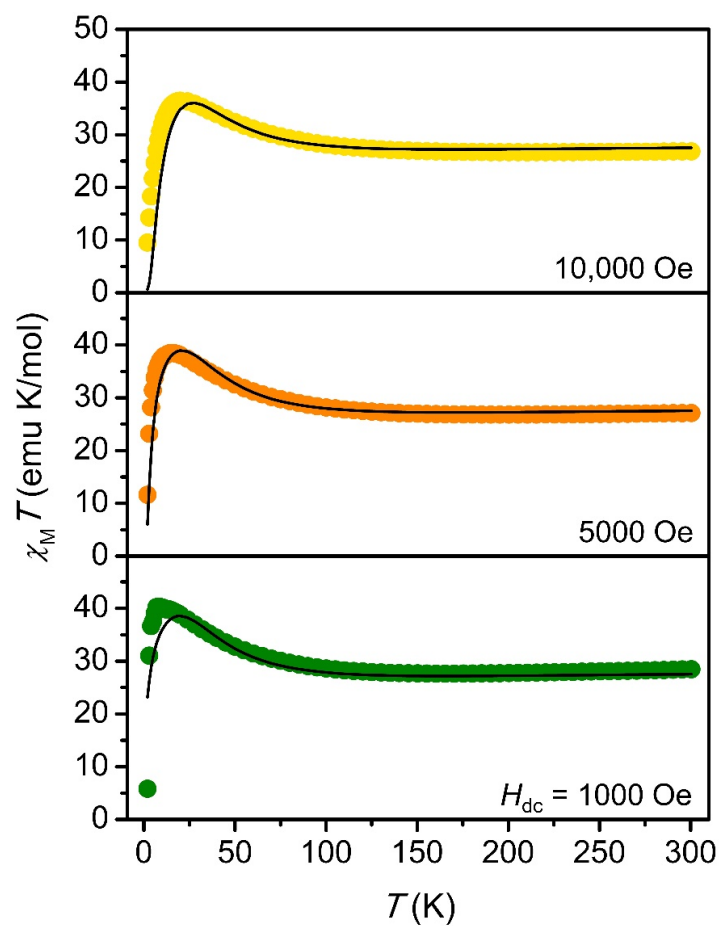


Figure S3.85. Zero-field cooled dc magnetic susceptibility measurements of **2-Dy** under applied fields of 1, 5, and 10 kOe. Black lines represent calculated fits to the data used to extract J_{Lines} .

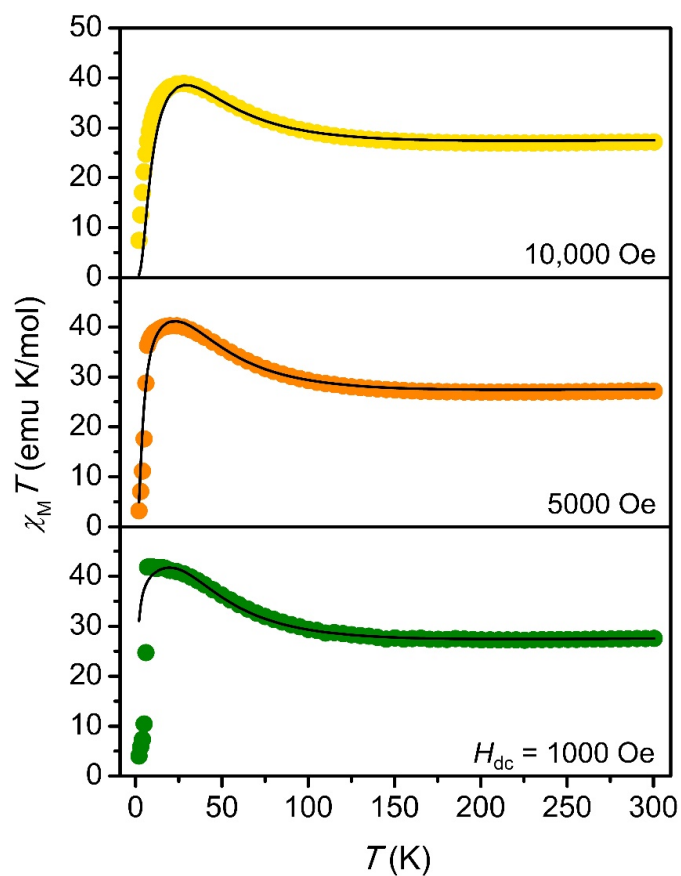


Figure S3.86. Zero-field cooled dc magnetic susceptibility measurements of **3-Dy** under applied fields of 1, 5, and 10 kOe. Black lines represent calculated fits to the data used to extract J_{Lines} . The experimental curves were upscaled by 3%.

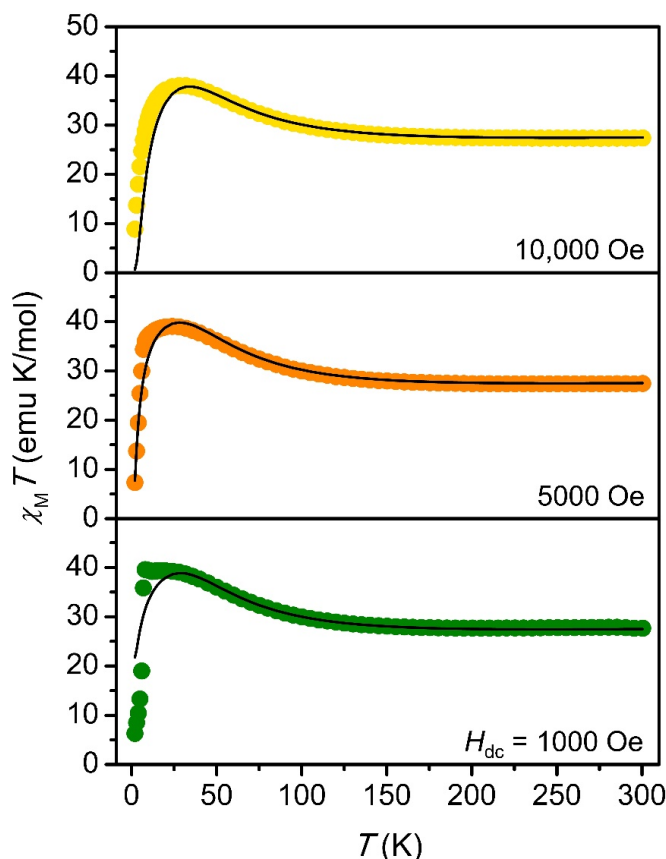


Figure S3.87. Zero-field cooled dc magnetic susceptibility measurements of **4-Dy** under applied fields of 1, 5, and 10 kOe. Black lines represent calculated fits to the data used to extract J_{Lines} . The experimental curves were upscaled by 5%.

The calculated exchange spectra for **2-Dy** through **4-Dy** are shown in Table S3.25 and Figure 3.4 in the main text.³⁷ One can see that the quantum tunneling of magnetization in the ground exchange doublet is small and the relaxation of magnetization would occur via first/second excited doublet in the domain of low temperature, whereas at higher T the relaxation will mainly go via third excited state, which is twice higher in energy. See the main text for further explanation.

Table S3.25. Calculated exchange energy spectrum (cm^{-1}) for **2-Dy** through **4-Dy** calculated with the parameters from Table S3.24.

2-Dy	3-Dy	4-Dy
0.00000	0.00000	0.00000
0.00000	0.00000	0.00000
56.75684	72.50960	82.52796
56.75684	72.50960	82.52796
59.22877	72.50966	82.52798
59.22877	72.50966	82.52798
115.98551	145.01916	165.05590
115.98551	145.01916	165.05590

3.6.7 Supplementary Information References

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Chapter 4: Isolation of a Triplet Benzene Dianion in a Dinuclear Lanthanide Complex

C. A. Gould, J. Marbey, V. Vieru, D. A. Marchiori, R. D. Britt, L. F. Chibotaru, S. Hill, J. R. Long.^a

4.1 Introduction

Aromaticity is a fundamental chemistry principle with broad utility, offering insights into molecular geometry, electronic structure, and chemical reactivity.^{1,2} Applications of aromaticity are diverse and range from the prediction of pericyclic reactions to the design of singlet-fission materials;^{3,4} as such, a significant body of research has focused on developing a deeper understanding of this property.^{1,2,5} Hückel's rule was the first formalism developed for aromaticity, predicting that cyclic, planar π -systems in the ground singlet ($S = 0$) state are stabilized (aromatic) when they possess $4n + 2$ electrons and destabilized (antiaromatic) when they possess $4n$ electrons.^{6,7} Subsequently, theories have been developed to describe more exotic cases: π -systems with a half-twist can display Möbius aromaticity and molecules in the first excited triplet ($S = 1$) state can exhibit Baird aromaticity, both reversals of Hückel's rule in which $4n$ π -electrons give rise to aromaticity.⁸⁻¹⁰

Baird aromaticity is an excited-state property for most annulenes and is therefore quite challenging to study experimentally.¹¹ As a result, current understanding of this property is primarily based on analyses of photochemical reactivity and computational studies, rather than direct experimental observation.^{12,13} While ground-state Baird aromaticity was recently reported for polycyclic and three-dimensionally conjugated macrocycles,^{14,15} this property has remained elusive in monocyclic hydrocarbons,¹¹ the canonical molecules for which the concept of aromaticity was first developed.^{1,2} This is due to large energetic separation between the ground singlet and triplet excited states in monocyclic π -systems with $4n$ electrons, caused by molecular distortion (fig. S4.1). For instance, cyclobutadiene derivatives adopt a rectangular structure and benzene dianions adopt a quinoidal or non-planar conformation, geometries that break conjugation to alleviate Hückel antiaromaticity, producing a non-aromatic, singlet ground state and a high-energy, triplet excited state.^{1,2,16} Indeed, the only known annulenes that possess a triplet ground state are certain cyclopentadienyl cations or benzene dications, however these transient species were only characterized via electron paramagnetic resonance (EPR) spectroscopy after being trapped at low temperature.^{17,18} Thus, the synthesis, isolation, and characterization of a kinetically persistent, monocyclic π -system with a well-separated, Baird-aromatic ground state represents an important and unsolved chemical challenge.

Herein, we report the synthesis and characterization of trigonally-symmetric inverse sandwich complexes $[M_2(\text{BzN}_6\text{-Mes})]^{2-}$ ($M = \text{Y, Gd}$; $\text{BzN}_6\text{-Mes} = 1,3,5\text{-tris}(2',6'\text{-(}N\text{-mesityl)-dimethanamino-4'-tert-butylphenyl)-benzene$), featuring two rare earth metal(III) ions bridged by a benzene dianion (Fig. 4.1). The rigid, trigonal scaffold preferentially stabilizes the D_{6h} -symmetric triplet state of the dianion relative to the C_{2v} - or D_{2h} -symmetric singlet state, leading to a singlet-triplet gap for the diamagnetic Y^{3+} congener that is orders of magnitude smaller than values typically observed for an annulene with $4n$ π -electrons.^{1,2,16} Significantly, incorporation of

^a Synthesis, crystallography, and magnetic characterization were performed by C.A.G. and J.R.L. High-frequency CW-EPR experiments were performed by J.M. and S.H. and D-Band EPR experiments were performed by D.A.M. and R.D.B. DFT calculations were performed by V.V. and L.F.C. The manuscript was written by C.A.G. and J.R.L. and edited by all authors.

paramagnetic Gd^{3+} facilitates strong magnetic exchange coupling, affording even greater stabilization to the triplet state such that it becomes the molecular ground state, enabling complete characterization of its aromaticity.

4.2 Results and Discussion

The synthesis of the new binucleating ligand $\text{BzN}_6\text{-R}$ is highly modular and its steric bulk can be tuned by varying the R group of the aniline in the penultimate step (fig. S4.2). In our hands, metalation and subsequent reduction reactions with $\text{BzN}_6\text{-4-tert-butylphenyl}$ did not yield isolable dianion complexes (fig. S4.13), but use of $\text{BzN}_6\text{-Mes}$ ($\text{Mes} = 2,4,6\text{-trimethylphenyl}$) enabled isolation of the benzene monoanion- and benzene dianion-bridged compounds $[\text{K}(18\text{-crown-6})(\text{THF})_2]_n[\text{M}_2(\text{BzN}_6\text{-Mes})]$ ($\text{M} = \text{Y}, \text{Gd}$; $n = 1$ (**1**), 2 (**2**)) as polycrystalline solids. Significantly, all compounds are indefinitely stable in the solid-state at $-30\text{ }^\circ\text{C}$ under a nitrogen atmosphere. When dissolved in tetrahydrofuran, the half-lives of **2-Y** and **2-Gd** are 10.1 and 26.5 h at $25\text{ }^\circ\text{C}$, respectively (figs. S4.20–S4.23). This kinetic stabilization can be attributed to steric bulk of the ligand and favorable electrostatic interactions between the benzene dianion and the metal cations.

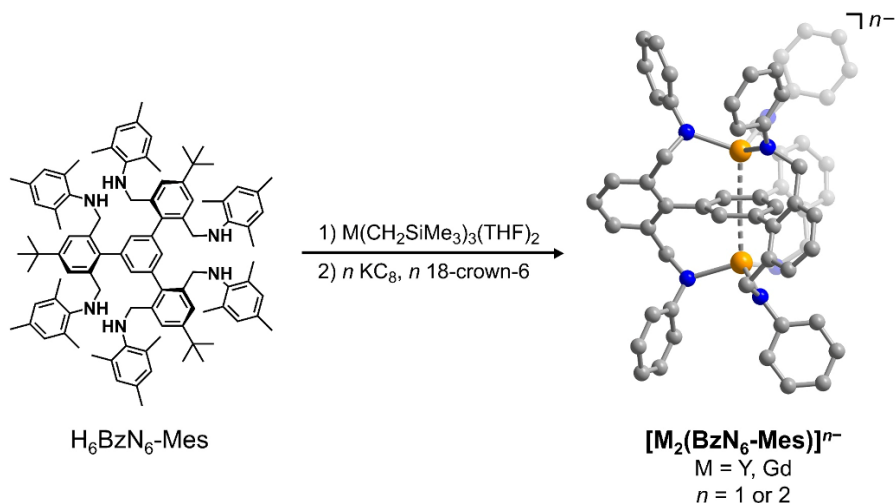


Fig. 4.1. Synthesis and structure of $[\text{M}_2(\text{BzN}_6\text{-Mes})]^{n-}$ complexes. Synthesis of the dinuclear compounds $[\text{K}(18\text{-crown-6})(\text{THF})_2]_n[\text{M}_2(\text{BzN}_6\text{-Mes})]$ ($\text{M} = \text{Y}, \text{Gd}$; $n = 1$ (**1**), 2 (**2**)). (right) Crystal structure of the $[\text{Gd}_2(\text{BzN}_6\text{-Mes})]^{2-}$ anion in **2-Gd**. Blue, gray, and orange spheres represent N, C, and Gd atoms, respectively; mesityl methyl groups, *tert*-butyl groups, and H atoms are omitted for clarity.

The UV-Vis spectra of **1-Y** and **1-Gd** are nearly identical from 400 to 800 nm, as are the spectra of **2-Y** and **2-Gd** (figs. S4.24 and S4.25). These results support ligand-based reduction, as UV-Vis spectra for isostructural Y^{2+} or Gd^{2+} complexes typically feature large differences in the positions of their absorption maxima.¹⁹ Structures of **1-Gd**, **2-Y**, and **2-Gd** determined by single-crystal X-ray diffraction provide further evidence of ligand-based reduction (Fig. 4.1 and figs. S4.35–S4.38; data for **1-Y** were consistently of low resolution, precluding meaningful analysis). The average M–N distances for **2-Y** and **2-Gd** are 2.281(2) and 2.309(2) Å, respectively, within the range typically observed for Y^{3+} and Gd^{3+} ions.²⁰ In **2-Y** and **2-Gd**, the average C–C distance of the central benzene ring is 1.454(6) and 1.442(3) Å, respectively, longer than the corresponding distance of 1.423(11) Å in **1-Gd** and the average of 1.40 Å in neutral benzene. This central ring is also planar in **1** and **2**, as evidenced by small $\text{C}_4\text{--C}_5\text{--C}_1\text{--C}_2$ torsion angles of $|\theta| \leq 1.4^\circ$ (table S4.2).

Comparing the structure of the BzN₆-Mes ligand in **1-Gd** and **2-Gd**, the only bond distance changes occur in the central benzene ring, suggesting that spin density is localized there. This result was confirmed by a density functional theory (DFT) analysis of **2-Y** (fig. S4.50).

High-frequency EPR spectra were collected at 371 GHz from 5 to 200 K on a polycrystalline sample of **2-Y**. The spectra display a nearly isotropic g-tensor centered at 2.00; however, a half-field transition—characteristic of an $S = 1$ state—was not observed. To confirm that the EPR signal in **2-Y** results from an $S = 1$ state, we carried out electron-spin nutation experiments on solutions of **1-Y** and **2-Y** at D-band frequencies (Fig. 4.2A). The nutation frequency in this experiment is determined by the spin-transition matrix element, and thus the difference in oscillation period for two molecules can be used to determine their relative spin quantum numbers.²¹ The oscillation periods for **1-Y** and **2-Y** differ by a factor of $\sqrt{2}$, as expected for total spins of $S = 1/2$ and $S = 1$, respectively.

A modified Bleaney-Bowers equation (see the supplementary information) was used to fit the temperature dependence of the EPR signal intensity (Fig. 4.2B).²² The analysis revealed a singlet ground state with a singlet-triplet gap of $\Delta E_{ST} = 0.025(4)$ kcal/mol ($8.7(1.4)$ cm⁻¹) for **2-Y**, which is corroborated by DFT calculations (table S4.7). This value is substantially smaller than typically observed for annulenes with $4n$ π -electrons and can be attributed to the trigonal symmetry and rigidity of **2-Y**, which energetically disfavors quinoidal distortion. The powerful impact of these effects is apparent from comparisons with ΔE_{ST} values reported for other benzene dianions: D_{2h} -symmetric 1,2,4,5-C₆H₂(SiMe₃)₄²⁻ shows a strong quinoidal distortion and a singlet-triplet gap that is too large to measure, while trigonal C₆(SiMe₂CH₂SiMe₂)₃²⁻ shows a less severe distortion and a ΔE_{ST} of 1.0 kcal/mol.^{23,24}

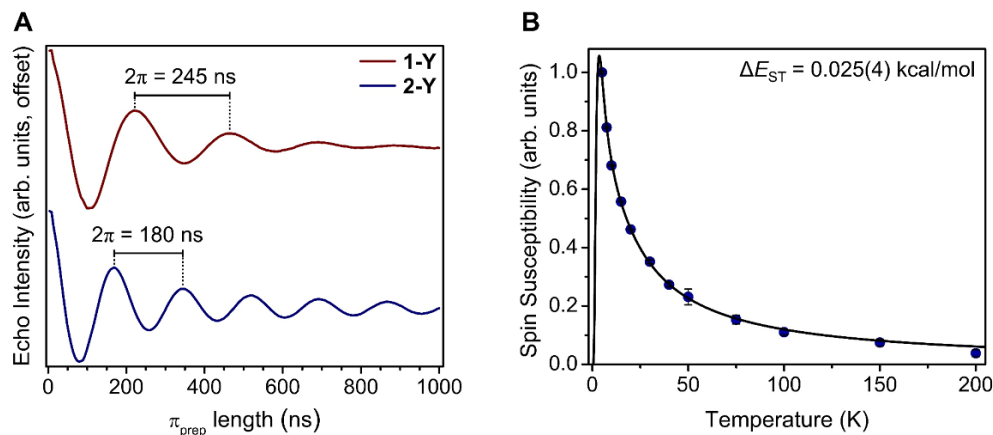


Fig. 4.2. Electron paramagnetic resonance spectroscopy data. (A) Electron-spin nutation data for solutions of **1-Y** and **2-Y**. The difference in oscillation period is consistent with an $S = 1$ state in **2-Y**. (B) Temperature dependence of the EPR spin susceptibility for a polycrystalline sample of **2-Y** (blue circles) fit to a modified Bleaney-Bowers equation (black line).

We hypothesized that the triplet state could be further stabilized through magnetic exchange with Gd³⁺, given that coupling with spin-bearing metal ions is significantly stronger for open-shell triplets than closed-shell singlets.²⁵ Significantly, dc magnetic susceptibility data for **2-Gd** between 2 and 300 K are indicative of an $S = 6$ ground state, arising from antiferromagnetic coupling between the $S = 1$ bridging benzene dianion and two $S = 7/2$ Gd³⁺ ions (Fig. 4.3A and figs. S4.48 and S4.49). The susceptibility data were fit with a spin-only Hamiltonian, which yielded an average exchange coupling constant of $J_{Gd-rad} = -43$ cm⁻¹, representing the strongest coupling

observed to date for any Ln^{3+} -ligand interaction.²⁵ We note that it is important to differentiate **2-Gd** from transition metal or actinide annulene complexes, in which the ligand π -electrons form strong covalent bonds with the metal ion(s) and oxidation state is often ambiguous.^{26,27} In contrast, the valence electrons in **2-Gd** are well-isolated due to the contracted nature of the 4f orbitals and do not engage in covalent bonding, instead favoring metal–ligand magnetic coupling and preservation of the dianion π -system.²⁵ Thus, lanthanide ions are particularly well-suited to stabilize the triplet benzene dianion via exchange coupling, without perturbing its aromaticity.

The relative energy of the benzene dianion singlet and triplet states in **2-Gd** can be estimated using the ΔE_{ST} value established for **2-Y**, while the interactions of the dianion with the Gd^{3+} ions can be evaluated from the magnetic data for **2-Gd** (Fig. 4.3; see also the supplementary information). This analysis revealed that the $S = 6$ ground state of **2-Gd** is stabilized by as much as -1.7 kcal/mol (-580 cm^{-1}) relative to the first excited state (Fig. 4.3B). Significantly, this stabilization is much larger than that observed for other $4n$ π -electron annulenes with a triplet ground state ($|\Delta E_{\text{ST}}| \leq 0.008$ kcal/mol) and enables direct observation and characterization of elusive ground-state Baird aromaticity.^{17,18}

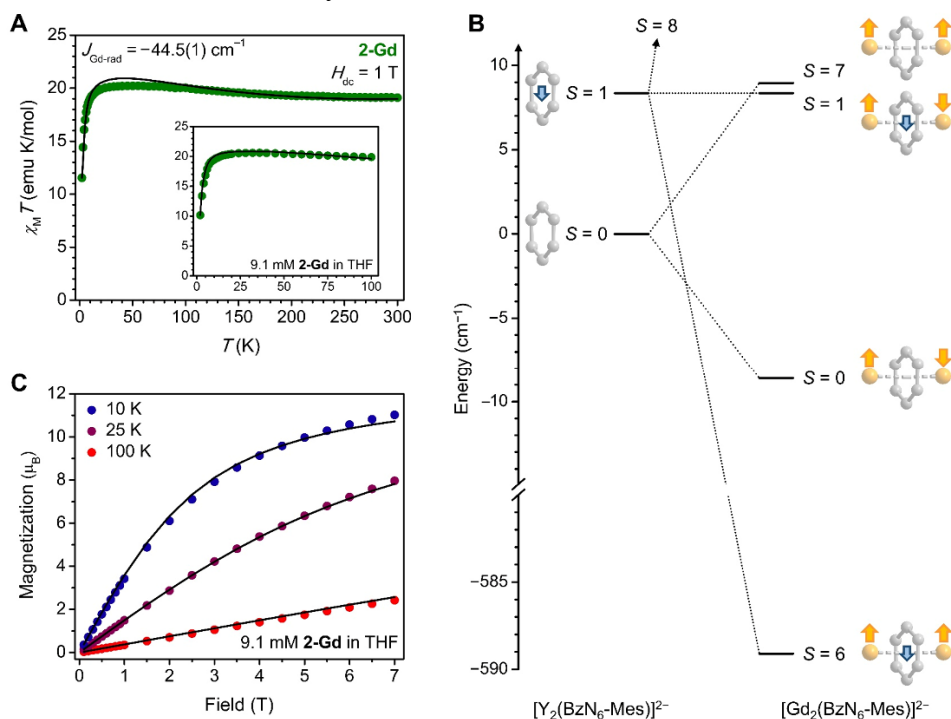


Fig. 4.3. Electronic structure analysis. (A) Dc magnetic susceptibility data for **2-Gd** (green circles) fit to a spin-only Hamiltonian (black line). Fits to data collected at 0.1, 0.5, and 1 T for a polycrystalline sample of **2-Gd** gave an average exchange coupling constant of $J_{\text{Gd-rad}} = -43$ cm^{-1} , while a fit to data collected for a frozen solution, wherein intermolecular interactions are negligible, gave $J_{\text{Gd-rad}} = -50(4)$ cm^{-1} . (B) Electronic states of $[\text{Y}_2(\text{BzN}_6\text{-Mes})]^{2-}$ in **2-Y** (left), with ΔE_{ST} determined by EPR spectroscopy, and of $[\text{Gd}_2(\text{BzN}_6\text{-Mes})]^{2-}$ in **2-Gd** (right), determined from experimental magnetic susceptibility data. The $S = 1$ state of the benzene dianion is preferentially stabilized relative to the $S = 0$ state through antiferromagnetic coupling to the $S = 7/2$ Gd^{3+} ions, resulting in an overall $S = 6$ ground state. (C) Magnetization data for **2-Gd** (colored circles) fit to an $S = 6$ Brillouin function (black line). The $S = 6$ ground state is populated up to at least 100 K, consistent with the electronic structure diagram.

Aromaticity in the singlet and triplet states of the benzene dianion can be analyzed by comparing the crystal structures of **2-Y** and **2-Gd**. The benzene dianion in **2-Y** ($S = 0$) is distorted, with C–C distances ranging from 1.405(5) to 1.486(5) Å and a standard deviation of 0.031 Å, indicative of a non-aromatic state. In contrast, the C–C bond distances of the benzene dianion in **2-Gd** ($S = 1$) exhibit a much smaller standard deviation of only 0.011 Å, revealing bond length equalization characteristic of an aromatic ring (Fig. 4.4A and fig. S4.39). The standard deviation in **2-Gd** is also significantly smaller than that observed for singlet benzene dianions reported in the literature.^{23,24}

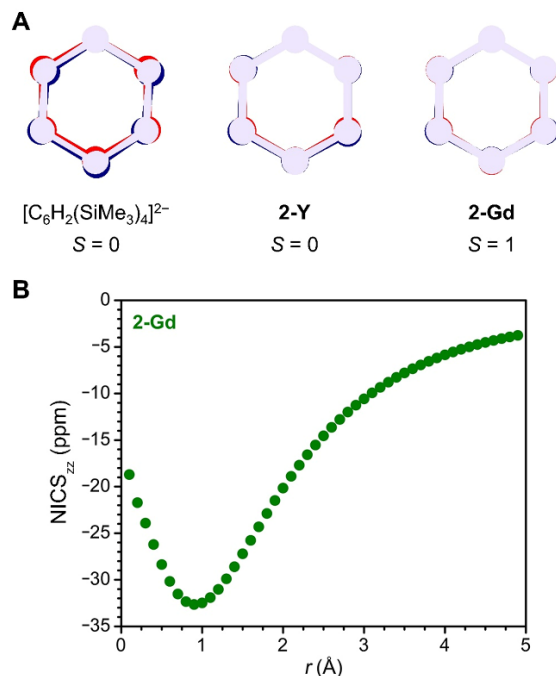


Fig. 4.4 Baird aromaticity in $[Gd_2(BzN_6-Mes)]^{2-}$. (A) Comparison of an idealized D_{6h} -symmetric benzene ring (red) and the dianionic benzene ring from the crystal structures (blue) of $[Li(dimethoxyethane)]_2[C_6H_2(SiMe_3)_4]$, **2-Y**, and **2-Gd** highlighting overlap (light purple).²⁴ For **2-Gd** the bond length equalizations are characteristic of an aromatic ring. (B) Calculated out-of-plane components of the chemical shift ($NICS_{zz}$) along the z -axis for the central benzene dianion in **2-Gd**. The negative values obtained for **2-Gd** and their radial dependence, reaching a minimum at 0.9 Å, are indicative of aromaticity.²⁹

Nuclear magnetic resonance (NMR) spectroscopy can also be used as an experimental probe of aromaticity, but it was not possible to identify resonances associated with the hydrogen atoms of the benzene dianion in **2-Y** and **2-Gd** due to the paramagnetism of the triplet state. Instead, nucleus-independent chemical shift (NICS) calculations were carried out to probe the aromaticity in **2-Gd** and **2-Y**, using the experimentally-determined structure of the central benzene dianion in each complex.²⁸ In this technique, the magnetic shielding is calculated for a virtual nucleus located at position x relative to a ring (e.g., in the center or directly above), and the magnitude and sign of this value is used to determine aromaticity. Positive and negative chemical shift values indicate antiaromaticity and aromaticity, respectively, while values close to zero are indicative of non-aromatic character. Isotropic $NICS(0)$ values of 0.5 and -9.1 ppm obtained for **2-Y** and **2-Gd**,

respectively, are consistent with our analysis of the structural data. The out-of-plane component of the chemical shift was also calculated at distances along the z -axis from 0 to 5 Å for **2-Gd**. The magnitude of the calculated values and their radial dependence are consistent with aromatic character (Fig. 4.4B).²⁹ Isotropic NICS calculations carried out on the entire $[\text{Gd}_2(\text{BzN}_6\text{-Mes})]^{2-}$ complex in **2-Gd** corroborate these results (table S4.8).

Calculations employing a Harmonic oscillator model of aromaticity (30) were also performed with the experimentally-determined structures of **2-Y** and **2-Gd**. This method compares the normalized sum of squared deviations of bond lengths in an annulene to a calculated optimal value, with a value of 1 indicating aromaticity and a value of 0 indicating non-aromatic character. Values of -0.07 and 0.46 were obtained for **2-Y** and **2-Gd**, respectively, further supporting our assignment of the singlet state as non-aromatic and the triplet state as aromatic.

4.3 Conclusions and Outlook

The foregoing analysis demonstrates how molecular symmetry, rigidity, and even magnetic exchange coupling can be leveraged to preferentially stabilize and study a desired electronic state in an organic molecule. Significantly, this approach enables the isolation of a benzene dianion in which the triplet state—typically a high-energy excited state in monocyclic π -systems—instead exists as the well-isolated molecular ground state, enabling direct observation of its aromaticity.

4.4 Acknowledgements

We thank Prof. Louise A. Berben for the use of her gloveboxes and Prof. Robert G. Bergman for insightful discussions. We also thank Dr. Katie R. Meihaus for editorial assistance, Dr. Nicholas S. Settineri for assistance with crystallography, and Ari B. Turkiewicz for keen observations. This work was funded by NSF grant CHE-1800252 (C.A.G.,J.R.L.), NSF grant DMR-1610226 (J.M.,S.H.), and NIH grant 1R35GM126961 (D.A.M.,R.D.B.). High-field EPR was collected at the National High Magnetic Field Laboratory, which is supported by the NSF (DMR-1644779) and the State of Florida.

4.5 References and Footnotes

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4.6 Supplementary Information

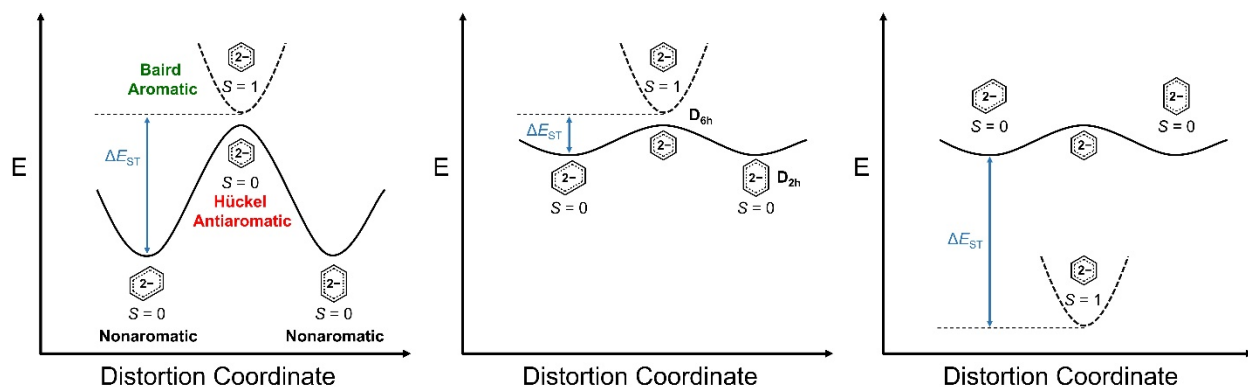


Fig. S4.1. Qualitative electronic structure diagrams showing the estimated energy of electronic states in a benzene dianion (y-axis) as a function of the distortion coordinate (x-axis). The singlet ($S = 0$) and triplet ($S = 1$) energy surfaces are represented by solid and dashed lines, respectively. The singlet-triplet gap (ΔE_{ST}) is shown in blue. (Left) This diagram illustrates the electronic structure of a free benzene dianion. It is typical of a monocyclic π -system with $4n$ electrons and analogous diagrams can be drawn for cyclobutadiene, cyclooctatetraene, and other such annulenes. Two D_{6h} -symmetric states are present in the molecule: a Hückel antiaromatic singlet state and a Baird aromatic triplet state. The Hückel antiaromatic singlet state is typically lower in energy than the triplet state due to mixing with excited singlet states. As a result of the energetic penalty of Hückel antiaromaticity, the benzene dianion will undergo a spontaneous molecular distortion to a non-aromatic ground state that results in overall electronic stabilization. On the diagram, this is illustrated as a quinoidal distortion to D_{2h} symmetry. This distortion can also be understood as a pseudo Jahn-Teller distortion. A large energetic gap exists between the distorted, non-aromatic singlet ground state and the symmetric, Baird aromatic triplet excited state. To reach the Baird aromatic triplet state, the molecule must pass through the Hückel antiaromatic singlet state. A large singlet-triplet gap is observed for the majority of monocyclic π -systems with $4n$ electrons. (Middle) This diagram illustrates the electronic structure of **2-Y**. The trigonal symmetry and rigidity of the $[M_2(BzN_6-Mes)]^{2-}$ complex energetically favors D_{6h} -symmetric states and disfavors distorted D_{2h} -symmetric states. As a result, the energetic favorability of the quinoidal distortion is decreased and the singlet-triplet gap becomes smaller. (Right) This diagram illustrates the electronic structure of **2-Gd**. Magnetic coupling interactions with the two paramagnetic Gd^{3+} ions stabilize the open-shell triplet state relative to the closed-shell singlet state. This results in a well-isolated triplet ground state for the benzene dianion.

4.6.1 General Information

Unless otherwise mentioned, commercial reagents were purchased from Sigma Aldrich, Fischer, Acros, Oakwood, Strem or Alfa Aesar and used without further purification. *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), toluene, and hexanes were sparged with argon and then dried by passing through alumina columns in a Glass Contour solvent purification system from J.C. Meyer. 2-Bromo-5-*tert*-butylbenzene-1,3-dicarbaldehyde and $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ were prepared according to literature reports.^{31,32} Unless otherwise mentioned, all reactions were carried out in flame-dried glassware under an argon atmosphere using standard Schlenk techniques or in an argon- or nitrogen-atmosphere glovebox.

NMR spectroscopy data were obtained on solutions in deuterated solvents (CDCl_3 , C_6D_6 , or $\text{C}_4\text{D}_8\text{O}$) obtained from Cambridge Isotope Laboratories, Inc. ^1H -NMR and ^{13}C -NMR data were recorded on Bruker DRX-500 and AV-500 spectrometers. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak (δ 7.26 for CDCl_3 and δ 7.16 for C_6D_6 for ^1H -NMR; δ 77.16 for CDCl_3 and δ 128.06 for C_6D_6 for ^{13}C -NMR). Data for ^1H -NMR are reported in the following format: chemical shift (ppm) (multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant (Hz), integration). Data for ^{13}C -NMR are reported in terms of chemical shift (ppm).

UV-vis-NIR absorption spectra were collected with a CARY 5000 spectrophotometer interfaced with Varian WinUV software. FT-IR spectra were recorded on a Perkin Elmer Avatar Spectrum 400 FTIR Spectrometer equipped with an attenuated total reflectance (ATR) attachment. Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on an Applied Biosystems Voyager-DE PRO Workstation in positive ion mode. Samples were co-crystallized in an anthracene matrix on an AB SCIEX MALDI-TOF stainless steel sample plate. Spectra were averaged over 200 laser pulses with a low mass gate of 300 Dalton and a high mass gate of 2000 Dalton. Elemental analyses (C, H, N) were performed by the Microanalytical Facility at the University of California, Berkeley using a Perkin-Elmer 2400 Series II combustion analyzer. Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer.

Continuous-wave high-field/frequency electron paramagnetic resonance (CW-EPR) data were collected on a home-built homodyne spectrometer outfitted with a 15/17 T Oxford magnet. Measurements were carried out in the frequency range from 28 to 370 GHz; microwaves were generated via harmonic multiplication using a Virginia Diodes Inc. multiplier chain, then propagated to and from the sample via oversized cylindrical light pipes. The field modulated transmission signal was detected using a wide-band InSb bolometer.³³ D-band (130 GHz) EPR experiments were performed at the CalEPR facility in the Britt lab at the University of California, Davis on a home-built 130 GHz EPR spectrometer, as described previously.³⁴

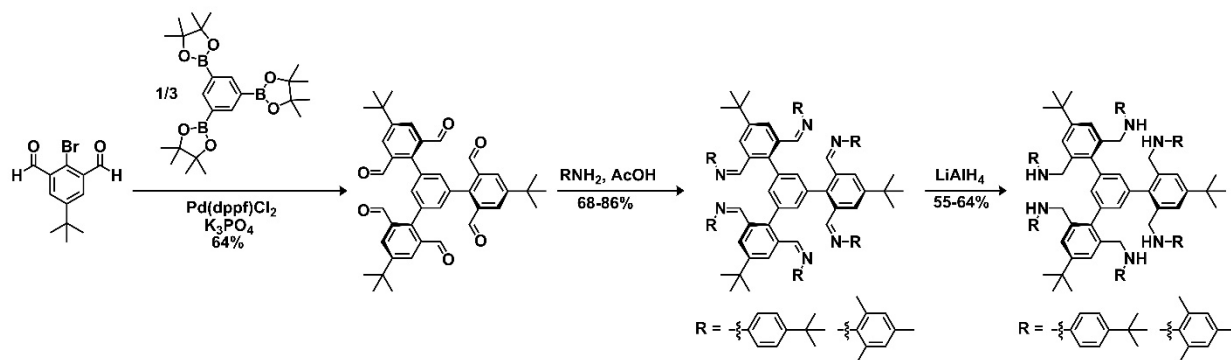


Fig. S4.2. Synthesis of BzN₆-R type ligands.

1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. Prepared according to a modified literature procedure.³⁵ 1,3,5-Tribromobenzene (10.00 g, 31.80 mmol), bis(pinacolato)diboron (25.40 g, 100.0 mmol, 3.1 equiv), potassium acetate (18.70 g, 190.5 mmol, 6 equiv), and Pd(dppf)Cl₂ (870 mg, 1.2 mmol, 4 mol%) were dissolved in 100 mL dry DMF in a Schlenk flask under argon. The resulting solution was heated to 90 °C for 24 h during which time the reaction mixture became black in color. The solution was then cooled to room temperature and added to 1200 mL H₂O in air. Grayish-black precipitate was collected via vacuum filtration, dissolved in ethyl acetate (EtOAc), and passed over a silica gel plug to yield a brown solution. The silica gel was then washed with additional EtOAc (ca. 1000 mL) and the combined filtrates were concentrated to yield a light brown powder. This solid was triturated in MeOH (200 mL), filtered, and washed with additional MeOH (3 × 50 mL) to yield the product as a colorless solid in 75% yield (10.85 g, 23.80 mmol).

1,3,5-Tris(2',6'-dicarbaldehyde-4'-tert-butylphenyl)-benzene. A 200 mL Schlenk flask was charged with a 1:1 dioxane/H₂O solution (150 mL) and the solvent was sparged for 15 min with argon. To this solution was added 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2.50 g, 5.48 mmol), 2-bromo-5-tert-butylbenzene-1,3-dicarbaldehyde (5.08 g, 18.9 mmol, 3.4 equiv), K₃PO₄ (10.7 g, 50.6 mmol, 9.2 equiv), and Pd(dppf)Cl₂ (300 mg, 0.410 mmol, 7.5 mol%). The resulting red solution was heated to 90 °C with stirring for 5 h; an abrupt color change to yellow was observed roughly 15 min after the start of the reaction, followed by a gradual color change to brown. The reaction mixture was then cooled to room temperature and the reaction was quenched in air with a saturated aqueous solution of NH₄Cl (200 mL). The resulting solution was extracted with CH₂Cl₂ (3 × 75 mL) and the organic layers were combined and dried over Na₂SO₄. The combined organic layers were concentrated to yield a dark brown solid that was purified via column chromatography on silica (R_f = 0.21, 15% EtOAc in hexanes) to give the product as a colorless solid in 64% yield (2.25 g, 3.50 mmol).

¹H-NMR (500 MHz, CDCl₃) δ = 10.05 (s, 6H), 8.26 (s, 6H), 7.44 (s, 3H), 1.42 (s, 27H) ppm. ¹³C-NMR (125 MHz, CDCl₃) δ = 190.8, 153.1, 142.3, 134.9, 134.6, 132.3, 131.4, 35.3, 31.2 ppm. IR (ATR, neat) ν 2973, 2871, 2837, 2754, 1735, 1687, 1554, 1461, 1388, 1364, 1235, 1210, 1112, 1044, 975, 955, 906, 870, 829, 805, 733, 702, 632, 528, 493, 473 cm⁻¹. MALDI ToF MS *m/z*: 642.3 [M]⁺, 613.3 [M - HC=O]⁺, 584.3 [M - 2 HC=O]⁺, 555.3 [M - 3 HC=O]⁺, 526.3 [M - 4 HC=O]⁺, 497.3 [M - 5 HC=O]⁺, 468.3 [M - 6 HC=O]⁺.

1,3,5-Tris(2',6'-(4''-tert-butyl-N-aniliny)-diminyl-4'-tert-butylphenyl)-benzene. A 10 mL Schlenk flask was charged with 4 Å molecular sieves (5 g) and heated to 165 °C for 1 h. The flask was then evacuated on a Schlenk line and gently heated with a Bunsen burner until a constant vacuum was achieved (ca. 100 mTorr). The flask was then backfilled with argon and charged with 1,3,5-tris(2',6'-dicarbaldehyde-4'-tert-butylphenyl)-benzene (100 mg, 0.156 mmol), 4-tert-butylaniline (0.50 mL, 2.8 mmol, 18 equiv = 3 equiv per aldehyde), acetic acid (0.1 mL), and toluene (5 mL). The resulting yellow solution was heated to 100 °C for 12 h with stirring. The reaction mixture was then cooled to room temperature, filtered in air over Celite, and the filter pad washed with EtOAc (30 mL). The eluent was concentrated to give a yellow oil and addition of MeOH (5 mL) to this oil resulted in precipitation of the product as a colorless solid in 68% yield (151 mg, 0.106 mmol). The product was collected via filtration and washed with additional MeOH (5 mL) and dried.

¹H-NMR (500 MHz, C₆D₆) δ = 9.02 (s, 12H), 7.35 (d, *J* = 8.1 Hz, 12 H), 7.08 (s, 3H), 7.00 (d, *J* = 8.1 Hz, 12 H), 1.28 (s, 27H), 1.01 (s, 54H) ppm. ¹³C-NMR (125 MHz, C₆D₆) δ = 156.3, 152.2, 150.0, 149.0, 141.2, 137.2, 135.1, 133.6, 127.1, 126.9, 121.4, 35.2, 34.5, 31.4, 31.3 ppm. IR (ATR, neat) ν 2956, 2898, 2868, 1618, 1590, 1501, 1478, 1461, 1394, 1364, 1268, 1246, 1221, 1204, 1175, 1107, 1011, 995, 966, 923, 900, 870, 836, 759, 737, 641, 618, 529, 564, 518, 497 cm⁻¹. MALDI ToF MS *m/z*: 1429.0 [M]⁺, 1281.9 [M – NC₁₀H₁₃]⁺, 1134.8 [M – 2 NC₁₀H₁₃]⁺.

1,3,5-Tris(2',6'-(4''-tert-butyl-N-aniliny)-dimethanamino-4'-tert-butylphenyl)-benzene (BzN₆-4-*t*Bu). A 10 mL Schlenk flask was charged with 1,3,5-tris(2',6'-(4''-tert-butyl-N-aniliny)-diminyl-4'-tert-butylphenyl)-benzene (150 mg, 0.105 mmol) and THF (20 mL). The resulting yellow solution was cooled to 0 °C with stirring and a solution of LiAlH₄ (1.0 M in THF, 1.3 mL, 1.3 mmol, 12 equiv = 2 equiv per imine) was added dropwise via syringe. The reaction mixture was then stirred for 1 h at 0 °C and allowed to warm to 25 °C over 1 h, during which time the solution became deep orange-red. The reaction mixture was next heated to 50 °C for 12 h. The solution was then cooled to 0 °C and quenched via dropwise addition of MeOH (10 mL), filtered over Celite in air, and the filter pad washed with EtOAc (30 mL). The combined organics were concentrated to give light yellow solids. The solids were triturated in hexanes (10 mL) and the mixture was filtered through Celite. The filter pad retained some yellow solids and the eluent was pale yellow. The celite was washed with additional hexanes (10 mL), and the resulting combined eluent was concentrated to give the crude product as a light yellow oil. This oil was purified via column chromatography on deactivated silica (the column was first washed with 4:1:95 Et₃N:EtOAc:hexanes, then the crude product loaded and eluted in 5% EtOAc in hexanes; R_f = 0.25) to give the product as a colorless solid in 55% yield (83 mg, 0.058 mmol). The product is highly soluble in a range of solvents and solidifies as a foam; to obtain a free-flowing powder it is necessary to subject it to high vacuum for 1–2 h, preferably after it has been dissolved in hexanes.

¹H-NMR (500 MHz, C₆D₆) δ = 7.55 (s, 6H), 7.22 (s, 3H), 7.18 (d, *J* = 8.2 Hz, 12 H), 6.41 (d, *J* = 8.2 Hz, 12 H), 4.02 (s, 12H), 3.35 (s, 6H), 1.30 (s, 54H), 1.22 (s, 27H) ppm. ¹³C-NMR (125 MHz, C₆D₆) δ = 151.1, 146.7, 140.1, 139.5, 138.3, 137.9, 129.5, 126.2, 124.9, 113.2, 48.2, 34.8, 34.1, 31.9, 31.5 ppm. IR (ATR, neat) ν 3431, 3410, 3298, 3058, 3024, 2952, 2902, 2866, 1615, 1516, 1461, 1403, 1394, 1361, 1319, 1304, 1253, 1194, 1139, 1126, 1084, 1055, 1026, 1012, 984, 928, 884, 816, 751, 728, 639, 548 cm⁻¹. MALDI ToF MS *m/z*: 1441.1 [M]⁺, 1292.0 [M – HNC₁₀H₁₃]⁺, 1142.8 [M – 2 HNC₁₀H₁₃]⁺, 993.7 [M – 3 HNC₁₀H₁₃]⁺, 844.6 [M – 4 HNC₁₀H₁₃]⁺, 695.5 [M – 5 HNC₁₀H₁₃]⁺.

1,3,5-Tris(2',6'-(*N*-mesityl)-diminyl-4'-*tert*-butylphenyl)-benzene. A 100 mL Schlenk flask was charged with 4 Å molecular sieves (15 g) and heated to 165 °C for 1 h. The flask was then evacuated on a Schlenk line and gently heated with a Bunsen burner until a constant vacuum was achieved (100 mTorr). The flask was then backfilled with argon and charged with 1,3,5-tris(2',6'-dicarbaldehyde-4'-*tert*-butylphenyl)-benzene (450 mg, 0.70 mmol), 2,4,6-trimethylaniline (1.80 mL, 12.8 mmol, 18 equiv = 3 equiv per aldehyde), acetic acid (0.5 mL), and toluene (15 mL). The resulting yellow solution was heated to 100 °C for 12 h with stirring. The reaction mixture was then cooled to room temperature, the mixture filtered over Celite in air, and the filter pad washed with EtOAc (30 mL). The eluent was concentrated to give a yellow oil and addition of MeOH (10 mL) to this oil resulted in precipitation of the product as a yellow solid in 86 % yield (802 mg, 0.596 mmol). The product was collected via filtration and washed with additional MeOH (10 mL) and dried.

¹H-NMR (500 MHz, C₆D₆) δ = 8.90 (s, 6H), 8.24 (s, 6H), 7.49 (s, 3H), 6.64 (s, 12H), 2.10 (s, 18H), 1.87 (s, 36H), 1.38 (s, 27H) ppm. ¹³C-NMR (125 MHz, C₆D₆) δ = 160.0, 152.2, 148.6, 139.8, 136.4, 135.4, 134.0, 133.2, 129.3, 127.2, 127.1, 35.2, 31.2, 20.8, 18.3 ppm. IR (ATR, neat) ν 2964, 2912, 2858, 2729, 1697, 1624, 1478, 1458, 1439, 1397, 1375, 1363, 1297, 1251, 1236, 1203, 1146, 1033, 1012, 991, 965, 933, 899, 855, 827, 773, 738, 666, 641, 631, 609, 600, 581, 550, 523, 507 cm⁻¹. MALDI ToF MS *m/z*: 1344.9 [M]⁺, 1211.8 [M – NC₉H₁₁]⁺.

1,3,5-Tris(2',6'-(*N*-mesityl)-dimethanamino-4'-*tert*-butylphenyl)-benzene (BzN₆-Mes). A 100 mL Schlenk flask was charged with 1,3,5-tris(2',6'-(*N*-mesityl)-diminyl-4'-*tert*-butylphenyl)-benzene (800 mg, 0.594 mmol) and THF (40 mL). The resulting yellow solution was cooled to 0 °C with stirring and a solution of LiAlH₄ (1.0 M in THF, 7.1 mL, 7.1 mmol, 12 equiv = 2 equiv per imine) was added dropwise. The reaction mixture was then stirred for 1 h at 0 °C and allowed to warm to 25 °C over 1 h during which time the solution became deep orange-red. The reaction mixture was next heated to 50 °C for 12 h. The solution was then cooled to 0 °C and quenched via dropwise addition of MeOH (10 mL), filtered over Celite in air, and the filter pad was washed with EtOAc (30 mL). The combined organics were concentrated to give light yellow solids which were triturated in hexanes (10 mL). The mixture was filtered over Celite, the filter pad was washed with additional hexanes (10 mL), and the combined eluents concentrated to give the crude product as a light yellow oil. This oil was purified via column chromatography on deactivated silica (the column was first washed with 4:1:95 Et₃N:EtOAc:hexanes, then the crude product loaded and eluted in 5% EtOAc in hexanes; R_f = 0.25) to give the product as a colorless solid in 64% yield (513 mg, 0.378 mmol). The product is highly soluble in a range of solvents and solidifies as a foam; to obtain a free-flowing powder it is necessary to subject it to high vacuum for 1–2 h, preferably after it has been dissolved in hexanes.

¹H-NMR (500 MHz, C₆D₆) δ = 7.52 (s, 6H), 7.33 (s, 3H), 6.70 (s, 12H), 4.12 (s, 12H), 2.18 (s, 18H), 1.99 (s, 36H), 1.24 (s, 27H) ppm. ¹³C-NMR (125 MHz, C₆D₆) δ = 150.7, 144.0, 140.1, 139.2, 137.3, 131.1, 130.3, 130.1, 129.9, 124.9, 51.8, 34.7, 31.3, 20.9, 18.6 ppm. IR (ATR, neat) ν 3363, 2952, 2912, 2863, 2725, 1726, 1604, 1588, 1482, 1444, 1407, 1362, 1344, 1302, 1228, 1201, 1154, 1071, 1028, 1010, 929, 883, 851, 763, 733, 696, 653, 561, 500, 466 cm⁻¹. MALDI ToF MS *m/z*: 1357.0 [M]⁺, 1221.9 [M – HNC₉H₁₁]⁺, 1096.8 [M – 2 HNC₉H₁₁]⁺, 951.7 [M – 3 HNC₉H₁₁]⁺, 816.6 [M – 4 HNC₉H₁₁]⁺, 681.5 [M – 5 HNC₉H₁₁]⁺, 546.4 [M – 6 HNC₉H₁₁]⁺.

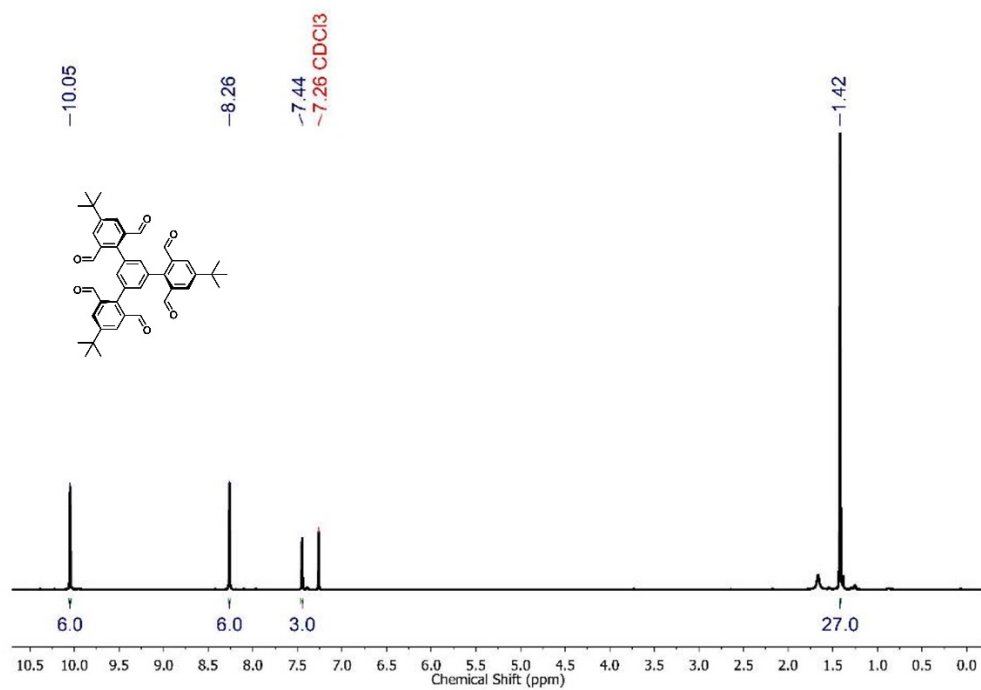


Fig. S4.3. ¹H-NMR spectrum of 1,3,5-Tris(2',6'-dicarbaldehyde-4'-*tert*-butylphenyl)-benzene.

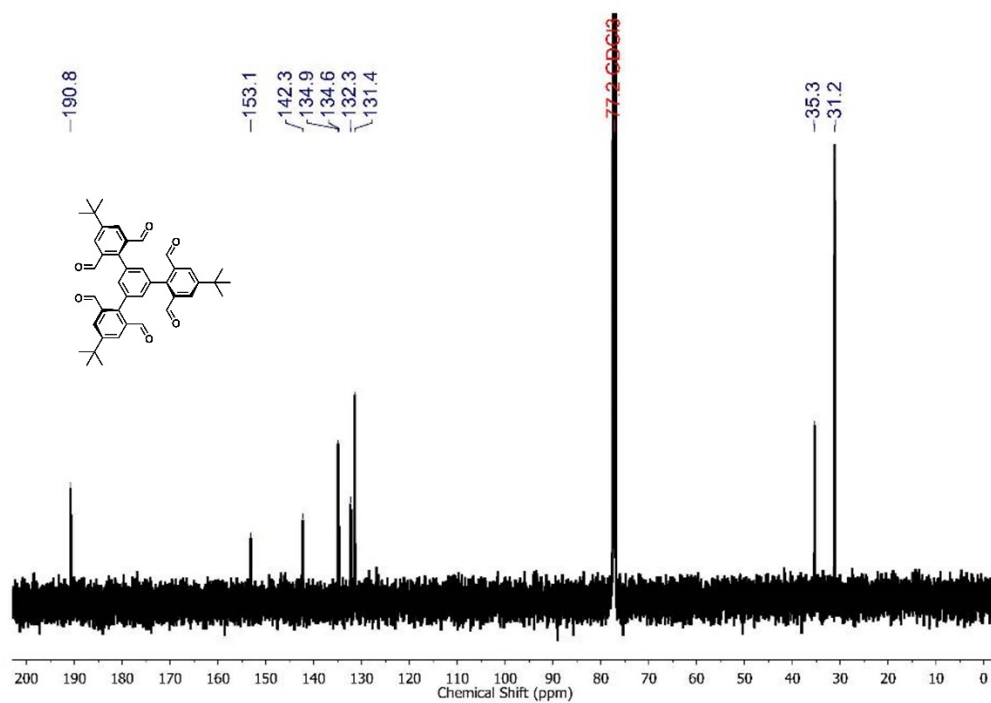


Fig. S4.4. ¹³C-NMR spectrum of 1,3,5-Tris(2',6'-dicarbaldehyde-4'-*tert*-butylphenyl)-benzene.

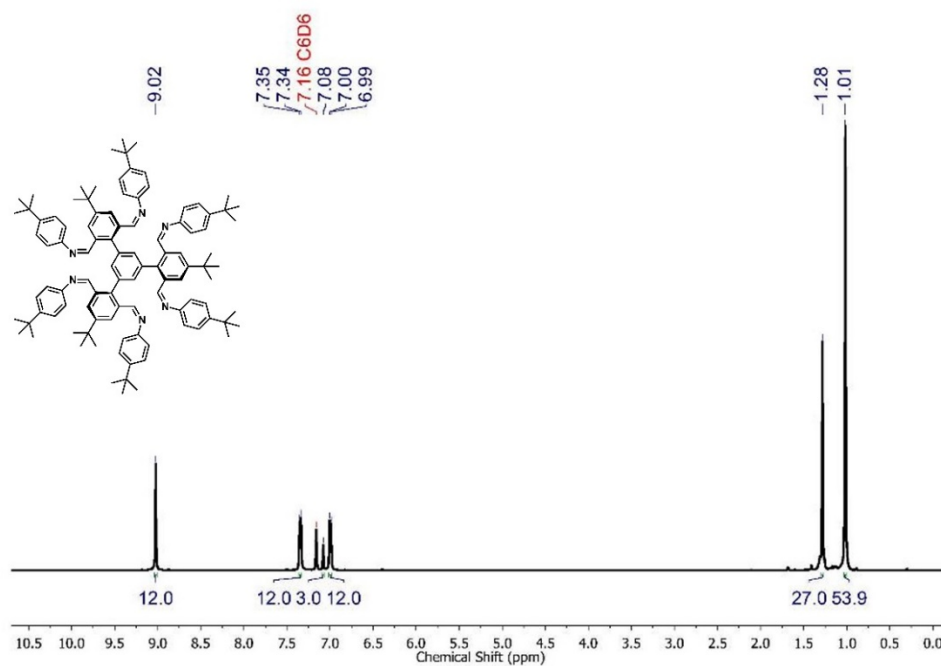


Fig. S4.5. ^1H -NMR spectrum of 1,3,5-Tris(2',6'-(4''-tert-butyl-N-aniliny)-diminy)-4'-tert-butylphenyl)-benzene.

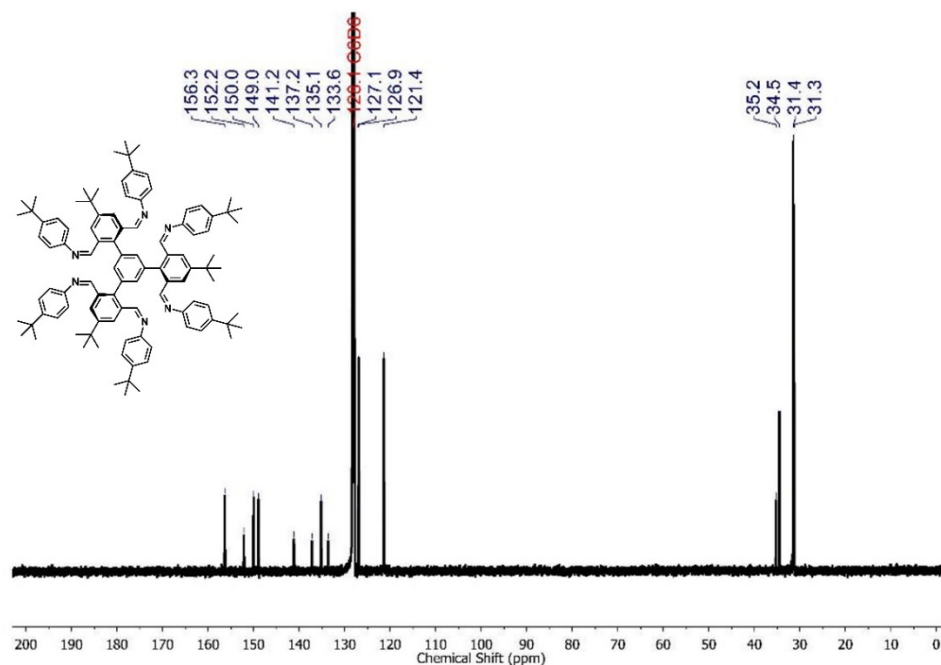


Fig. S4.6. ^{13}C -NMR spectrum of 1,3,5-Tris(2',6'-(4''-tert-butyl-N-aniliny)-diminy)-4'-tert-butylphenyl)-benzene.

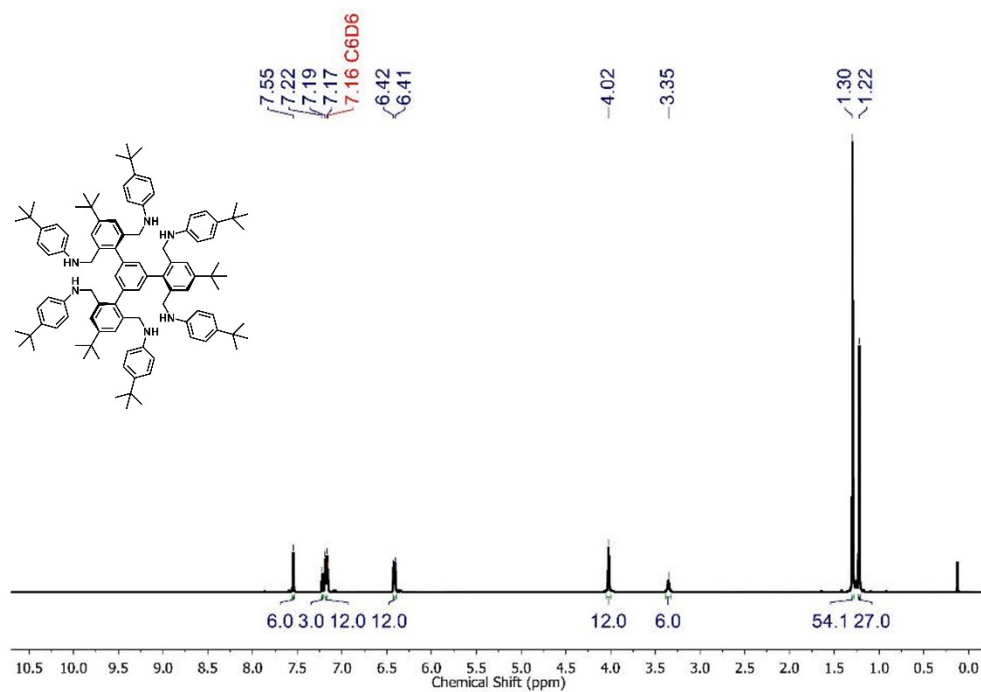


Fig. S4.7. ¹H-NMR spectrum of **BzN₆-4-*t*Bu**.

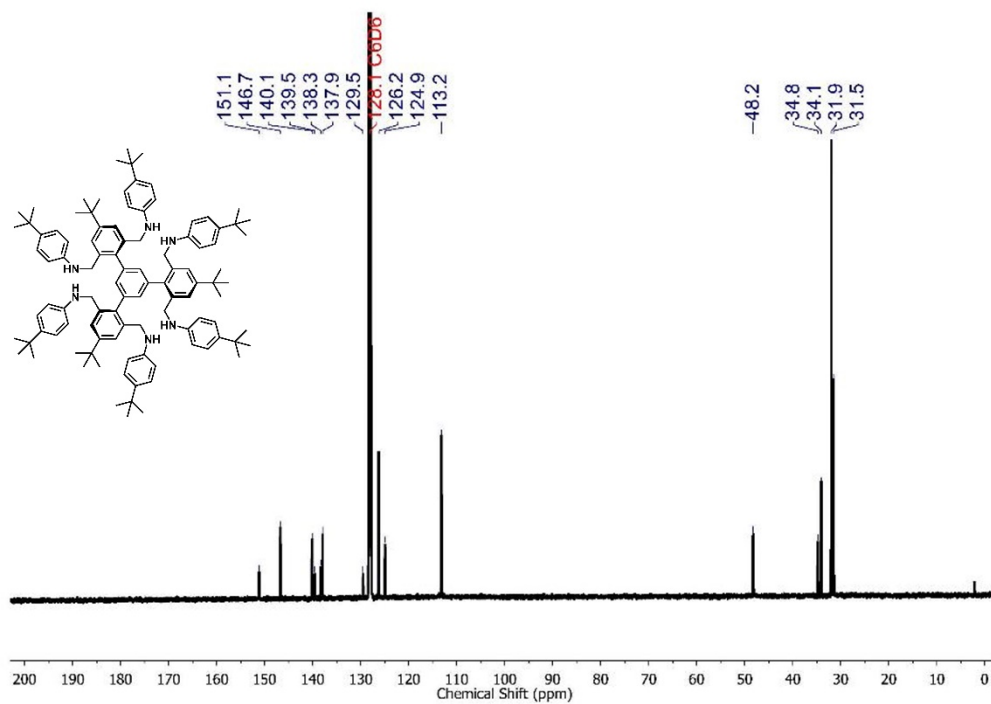


Fig. S4.8. ¹³C-NMR spectrum of **BzN₆-4-*t*Bu**.

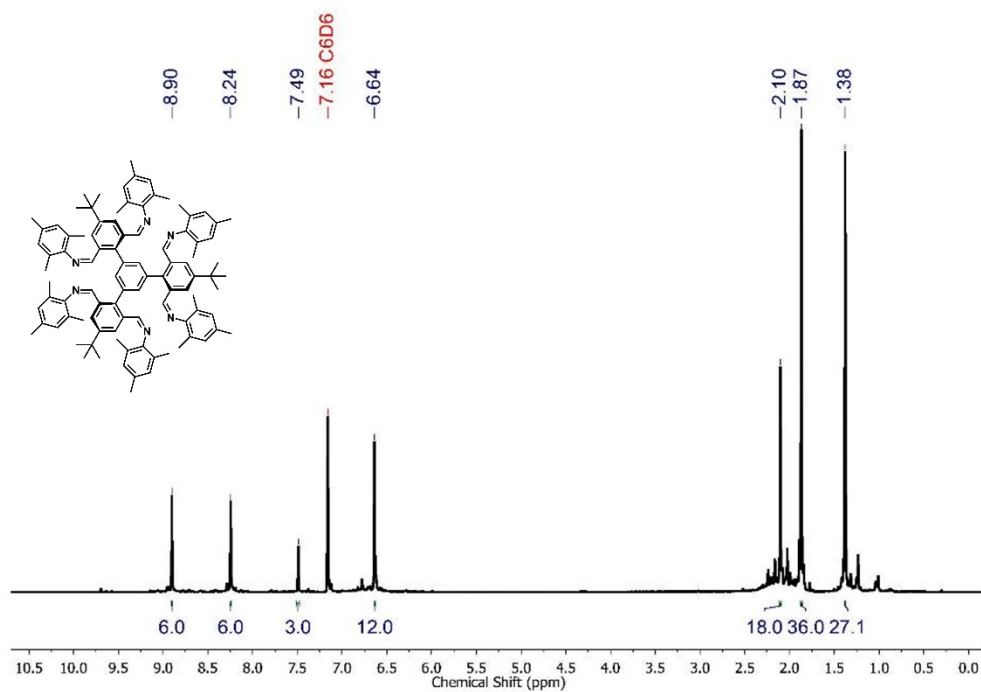


Fig. S4.9. ^1H -NMR spectrum of 1,3,5-Tris(2',6'-(*N*-mesityl)-diminyl-4'-*tert*-butylphenyl)-benzene.

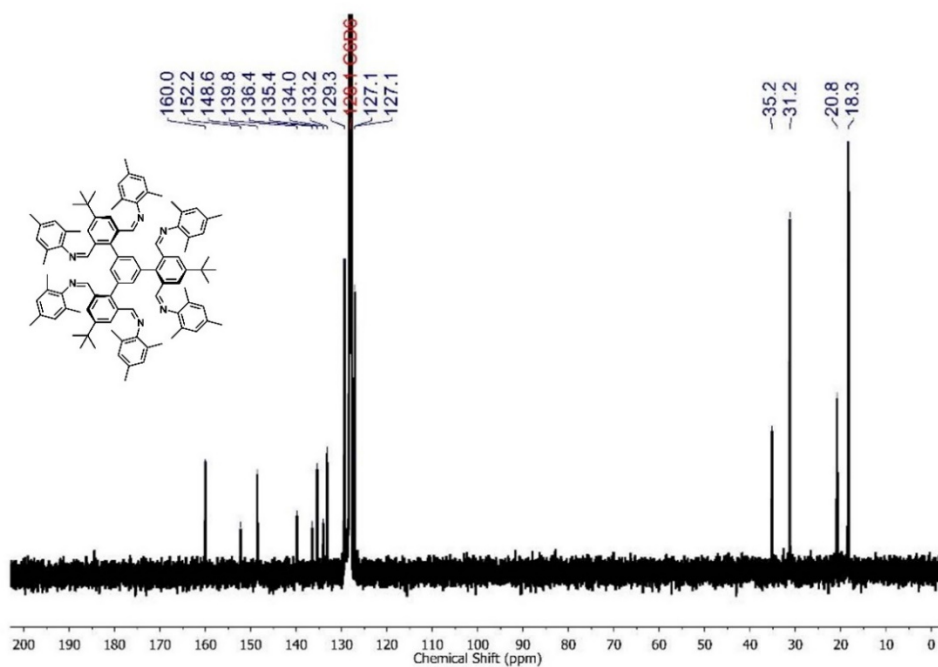


Fig. S4.10. ^{13}C -NMR spectrum of 1,3,5-Tris(2',6'-(*N*-mesityl)-diminyl-4'-*tert*-butylphenyl)-benzene.

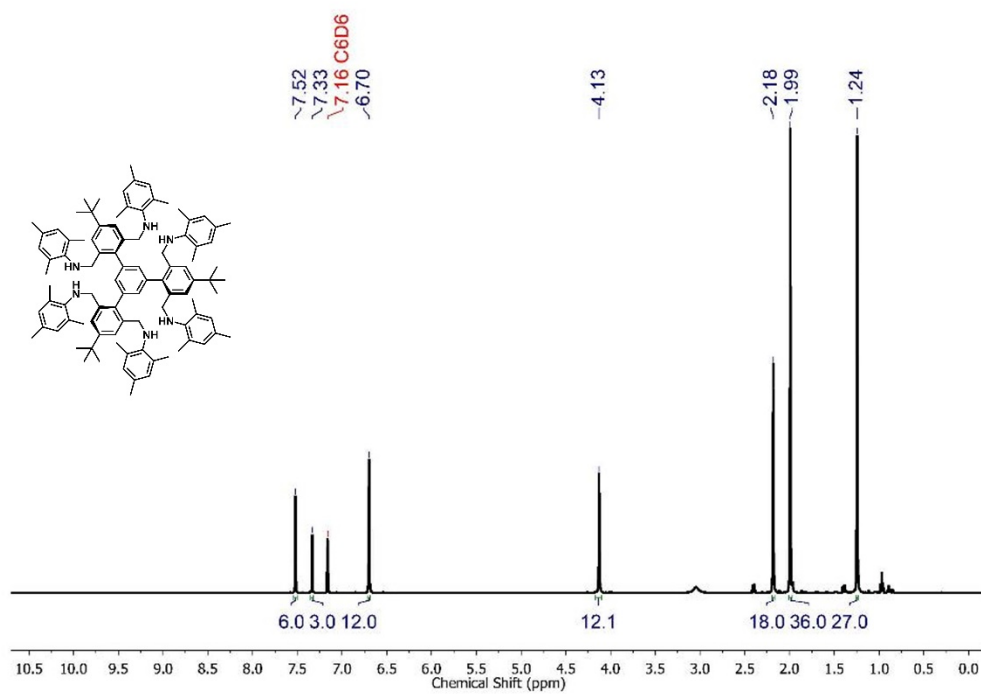


Fig. S4.11. ¹H-NMR spectrum of **BzN₆-Mes**.

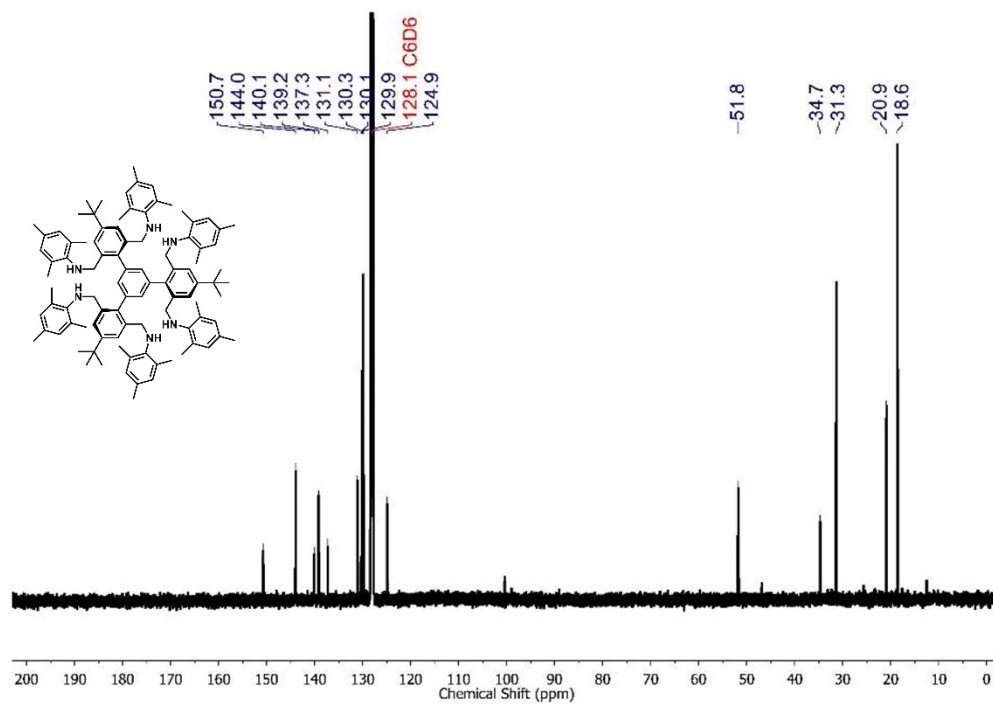


Fig. S4.12. ¹³C-NMR spectrum of **BzN₆-Mes**.

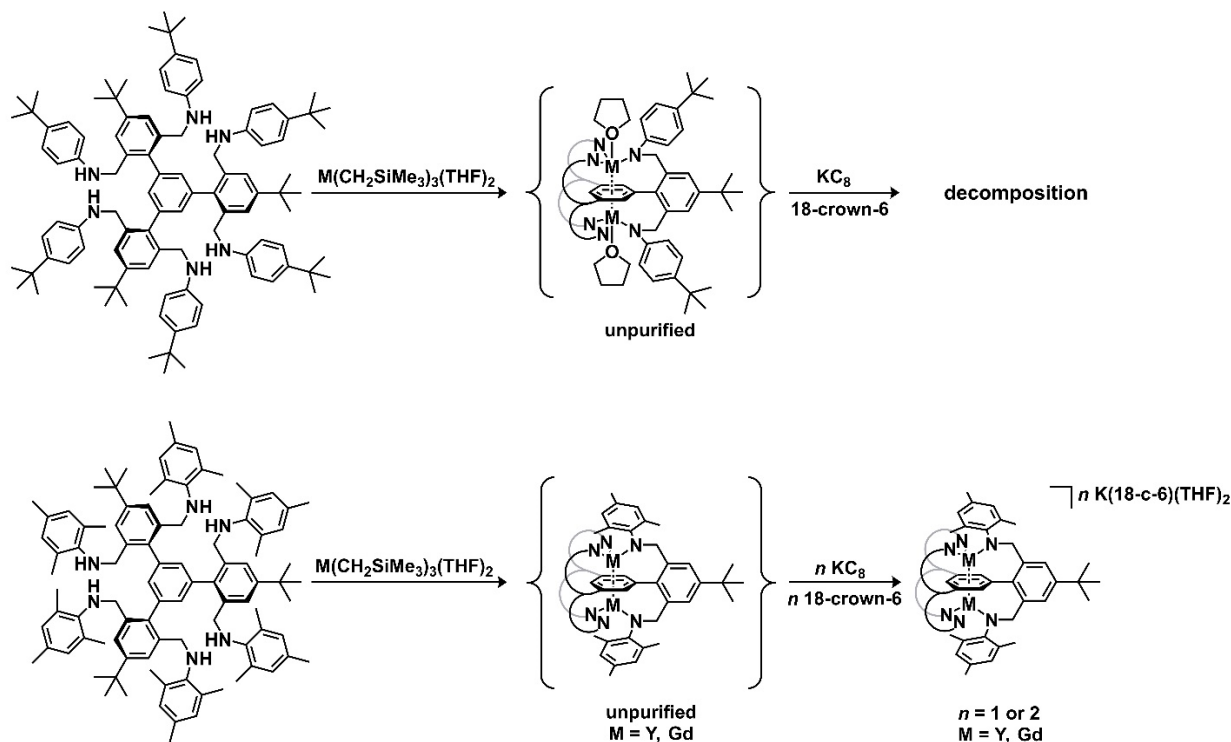


Fig. S4.13. Synthesis of lanthanide inverse sandwich complexes.

$\text{Y}_2(\text{BzN}_6\text{-4-}t\text{Bu})(\text{THF})_2$. In an argon-atmosphere glovebox, ligand **BzN₆-4-*t*Bu** (6.9 mg, 0.0048 mmol) and $\text{Y}(\text{CH}_2\text{TMS})_3(\text{THF})_2$ (5.0 mg, 0.010 mmol, 2.1 equiv) were dissolved in C_6D_6 (0.7 mL) in a 4 mL scintillation vial. The solution immediately became bright yellow and was transferred to a J. Young NMR tube. The reaction was monitored by ^1H -NMR. The reaction was observed to be complete by the time a ^1H -NMR spectrum could be obtained (ca. 5 min). ^1H -NMR spectra obtained after drying the product on high vacuum overnight at 25 °C or at 80 °C for 2 h showed the formation of ligand **BzN₆-4-*t*Bu**, suggesting decomposition. Reduction with KC_8 also resulted in decomposition.

^1H -NMR (500 MHz, C_6D_6) δ = 7.69 (s, 6H), 7.42 (d, J = 8.7 Hz, 12 H), 6.99 (d, J = 8.7 Hz, 12 H), 6.24 (s, 3H), 4.82 (d, J = 14.7 Hz, 6 H), 4.48 (d, J = 14.7 Hz, 6 H), 3.53 (br s, 8H), 1.47 (s, 27H), 1.32 (s, 54H), 0.71 (br s, 8H) ppm. MALDI ToF MS m/z : 1684.9 $[\text{M} - \text{THF}]^+$, 1612.8 $[\text{M} - 2 \text{THF}]^+$, 1435.1 $[\text{M} - 2 \text{THF} - 2 \text{Y}]^+$.

$\text{Y}_2(\text{BzN}_6\text{-Mes})$. In an argon-atmosphere glovebox, ligand **BzN₆-Mes** (20.6 mg, 0.0143 mmol) and $\text{Y}(\text{CH}_2\text{TMS})_3(\text{THF})_2$ (15 mg, 0.030 mmol, 2.1 equiv) were dissolved in C_6D_6 (0.7 mL) in a 4 mL scintillation vial. The solution immediately became yellow and was transferred to a J. Young NMR tube. The reaction was monitored by ^1H -NMR and the solution became darker yellow as the reaction progressed. Although the ^1H -NMR of **$\text{Y}_2\text{BzN}_6\text{-Mes}$** is quite complex, the reaction progress could be monitored by the disappearance of the $\text{CH}_2\text{-TMS}$ peak at -0.68 ppm and the growth of the $\text{H}_3\text{C-TMS}$ peak at 0.00 ppm. The reaction was determined to be complete after 1 h at which point it was concentrated to yield a yellow solid, which was dried via high vacuum for 15 min and dissolved in C_6D_6 (0.7 mL). The ^1H -NMR spectrum of the resulting yellow solution

showed many of the same peaks as the reaction spectrum, but without the peaks corresponding to THF. No sign of decomposition was observed after evacuation. This compound is highly soluble in a variety of common laboratory solvents and thus we were unable to grow crystals suitable for X-ray diffraction or purify it further. We therefore carried this complex on to the next step of the synthesis without isolation.

MALDI ToF MS m/z : 1528.7 $[M]^+$, 1439.8 $[M - Y]^+$, 1351.0 $[M - 2 Y]^+$.

[Y₂BzN₆-Mes][K(18-crown-6)(THF)₂] (1-Y). In an argon-atmosphere glovebox, ligand **BzN₆-Mes** (100.0 mg, 0.07363 mmol) was placed in a 4 mL scintillation vial and dissolved in benzene (3 mL) to give a colorless solution. The solution was added dropwise to a stirred solution of Y(CH₂TMS)₃(THF)₂ (72.9 mg, 0.147 mmol, 2.1 equiv) in benzene (4 mL) in a 20 mL scintillation vial. The mixture turned yellow gradually over the course of ligand addition and the solution was stirred for 3 h, at which point it was concentrated to yield yellow solids. A solution of 18-crown-6 (19.0 mg, 0.0719 mmol, 1 equiv) in THF (4 mL) was added to these solids. To this yellow solution at 25 °C was added KC₈ (9.8 mg, 0.072 mmol, 1 equiv), which resulted in an immediate color change to deep red. The deep red solution was stirred for 30 min. The reaction mixture was then filtered over Celite and the resulting deep red solution was concentrated to 1.5 mL, layered with hexanes (1.5 mL) and stored at -30 °C overnight. The product precipitated as dark red-black polycrystals (93.2 mg, 64% yield). Block-shaped crystals suitable for X-ray diffraction were grown from a THF/hexane solution stored for 48 h at room temperature (25 °C).

(ATR, neat) ν 2950, 2903, 2860, 1603, 1480, 1469, 1394, 1362, 1352, 1328, 1297, 1286, 1246, 1231, 1198, 1151, 1106, 1028, 1007, 962, 884, 868, 851, 786 733, 672, 600, 587, 561, 531, 500 cm⁻¹. MALDI ToF MS m/z : 1528.7 $[M]^+$, 1439.8 $[M - Y]^+$, 1351.0 $[M - 2 Y]^+$. Anal. Calcd. for C₁₁₆H₁₅₄KN₆O₈Y₂: C, 70.46; H, 7.85; N, 4.25; Found: C, 70.41; H, 7.76; N, 4.23.

[Y₂BzN₆-Mes][K(18-crown-6)(THF)₂]₂ (2-Y). Analogous to the synthesis of **1-Y**, ligand **BzN₆-Mes** (100.0 mg, 0.07363 mmol) was dissolved in benzene (3 mL) and added dropwise to a stirred solution of Y(CH₂TMS)₃(THF)₂ (72.9 mg, 0.147 mmol, 2.1 equiv) in benzene (4 mL). The mixture turned yellow gradually over the course of ligand addition. The resulting solution was stirred for 3 h and then concentrated to yield yellow solids. At 25 °C, a solution of 18-crown-6 (38.1 mg, 0.144 mmol, 1 equiv) in THF (4 mL) was added to these solids followed immediately by addition of KC₈ (19.5 mg, 0.144 mmol, 1 equiv), which resulted in a solution color change to deep blue black. The resulting solution was stirred for 10 min. The reaction mixture was then filtered over Celite and concentrated to 1.5 mL, layered with hexanes (1.5 mL) and stored at room temperature (25 °C) for 3 h. The product precipitated as dark blue-black polycrystals (88.8 mg, 50% yield). This complex decomposes in solution at 25 °C, but is indefinitely stable when stored as a solid. It was stored as a solid under inert atmosphere at -30 °C. Block-shaped crystals suitable for X-ray diffraction were grown from a THF/hexane solution stored for 12 h at room temperature (25 °C).

(ATR, neat) ν 2950, 2903, 2859, 1604, 1481, 1394, 1330, 1298, 1285, 1246, 1232, 1198, 1152, 1105, 1029, 1009, 961, 883, 868, 851, 785, 734, 672, 582, 561, 530, 511, 502 cm⁻¹. MALDI ToF MS m/z : 1528.7 $[M]^+$, 1439.8 $[M - Y]^+$, 1351.0 $[M - 2 Y]^+$. Anal. Calcd. for C₁₁₆H₁₅₄KN₆O₈Y₂: C, 67.36; H, 8.06; N, 3.47; Found: C, 67.23; H, 8.10; N, 3.74.

[Gd₂BzN₆-Mes][K(18-crown-6)(THF)₂] (1-Gd). In an argon-atmosphere glovebox, GdCl₃·2.5THF (54.9 mg, 0.124 mmol, 2 equiv) and Li(CH₂SiMe₃) (35.0 mg, 0.372 mmol, 6 equiv)

were placed in a 20 mL scintillation vial with a Teflon-coated stir bar. The solids were suspended in pre-cooled hexanes (6 mL, $-30\text{ }^{\circ}\text{C}$) and the vial was placed in a cold well cooled with an ice/brine bath (ca. $-20\text{ }^{\circ}\text{C}$). The resulting slurry was stirred for 3 h at which point a solution of **BzN₆-Mes** (84.0 mg, 0.0619 mmol, 1 equiv) in benzene (2 mL) was added dropwise. The slurry immediately became a bright yellow solution with colorless solids. After the addition was complete, the reaction mixture was stirred for 3 h at $25\text{ }^{\circ}\text{C}$. The solvent was then removed under reduced pressure and the resulting solids were extracted with hexanes (6 mL). The hexanes extract was filtered over Celite and concentrated to yield a yellow solid. Due to the high solubility of this compound in a variety of common laboratory solvents, it could not be crystallized and was therefore carried on to the next step without further purification. The yellow solids were dissolved in THF (3 mL) in a 20 mL scintillation vial equipped with a Teflon-coated stir bar. A solution of 18-crown-6 (16.0 mg, 0.0605 mmol, 1 equiv) in THF (2 mL) was added to the solution. To the resulting yellow solution was added K₂C₈ (8.2 mg, 0.061 mmol, 1 equiv) and the resulting deep red solution was stirred for 30 min. The reaction mixture was then filtered over Celite and concentrated to 1.5 mL, layered with hexanes (1.5 mL) and stored at $-30\text{ }^{\circ}\text{C}$ overnight. The product precipitated as dark red-black polycrystals (65.1 mg, 50% yield). Block-shaped crystals suitable for X-ray diffraction were grown from a THF/hexane solution stored for 48 h at room temperature ($25\text{ }^{\circ}\text{C}$).

(ATR, neat) ν 2951, 2904, 2862, 1601, 1480, 1393, 1356, 1352, 1311, 1299, 1229, 1197, 1151, 1107, 1018, 1007, 961, 883, 868, 851, 787, 732, 692, 673, 582, 561, 530 cm^{-1} . MALDI ToF MS m/z : 1666.8 [M]⁺, 1508.8 [M – Gd]⁺, 1350.9 [M – 2 Gd]⁺. Anal. Calcd. for C₁₁₆H₁₅₄KN₆O₈Gd₂: C, 65.90; H, 7.34; N, 3.98; Found: C, 66.22; H, 7.31; N, 4.02.

[Gd₂BzN₆-Mes][K(18-crown-6)(THF)₂]₂ (2-Gd). Analogous to the synthesis of **1-Gd**, GdCl₃·2.5THF (54.9 mg, 0.124 mmol, 2 equiv) and Li(CH₂SiMe₃) (35.0 mg, 0.372 mmol, 6 equiv) were placed in a 20 mL scintillation vial with a Teflon-coated stir bar and suspended in pre-cooled hexanes (6 mL, $-30\text{ }^{\circ}\text{C}$). The vial was placed in a cold well (ca. $-20\text{ }^{\circ}\text{C}$) and the resulting slurry was stirred for 3 h, at which point a solution of **BzN₆-Mes** (84.0 mg, 0.0619 mmol, 1 equiv) in benzene (2 mL) was added. The reaction mixture was stirred for 3 h at $25\text{ }^{\circ}\text{C}$. The solvent was then removed under reduced pressure and the resulting solids were extracted with hexanes (6 mL). The hexanes extract was filtered and concentrated to yield a yellow solid. The yellow solids were dissolved in THF (3 mL) in a 20 mL scintillation vial equipped with a Teflon-coated stir bar. A solution of 18-crown-6 (32.0 mg, 0.121 mmol, 2 equiv) in THF (2 mL) was added to the resulting yellow solution. To this yellow solution was added K₂C₈ (16.4 mg, 0.121 mmol, 2 equiv) and the resulting deep blue/black solution was stirred for 10 min. The reaction mixture was then filtered and concentrated to 1.5 mL, layered with hexanes (1.5 mL) and stored at $25\text{ }^{\circ}\text{C}$ for 3 h. The product precipitated as dark blue-black polycrystals (67.2 mg, 42% yield). This complex decomposes in solution at $25\text{ }^{\circ}\text{C}$ although it is indefinitely stable when stored as a solid. It was stored as a solid under inert atmosphere at $-30\text{ }^{\circ}\text{C}$. Block-shaped crystals suitable for X-ray diffraction were grown from a THF/hexane solution stored for 12 h at room temperature ($25\text{ }^{\circ}\text{C}$).

(ATR, neat) ν 2951, 2902, 2860, 1602, 1480, 1469, 1394, 1360, 1352, 1297, 1231, 1200, 1152, 1104, 1018, 961, 883, 867, 852, 786, 734, 671, 589, 587, 560, 529, 503, 493 cm^{-1} . MS m/z : 1666.8 [M]⁺, 1508.8 [M – Gd]⁺, 1350.9 [M – 2 Gd]⁺. Anal. Calcd. for C₁₃₆H₁₉₄K₂N₆O₁₆Gd₂: C, 63.76; H, 7.63; N, 3.28; Found: C, 63.56; H, 7.57; N, 3.64.

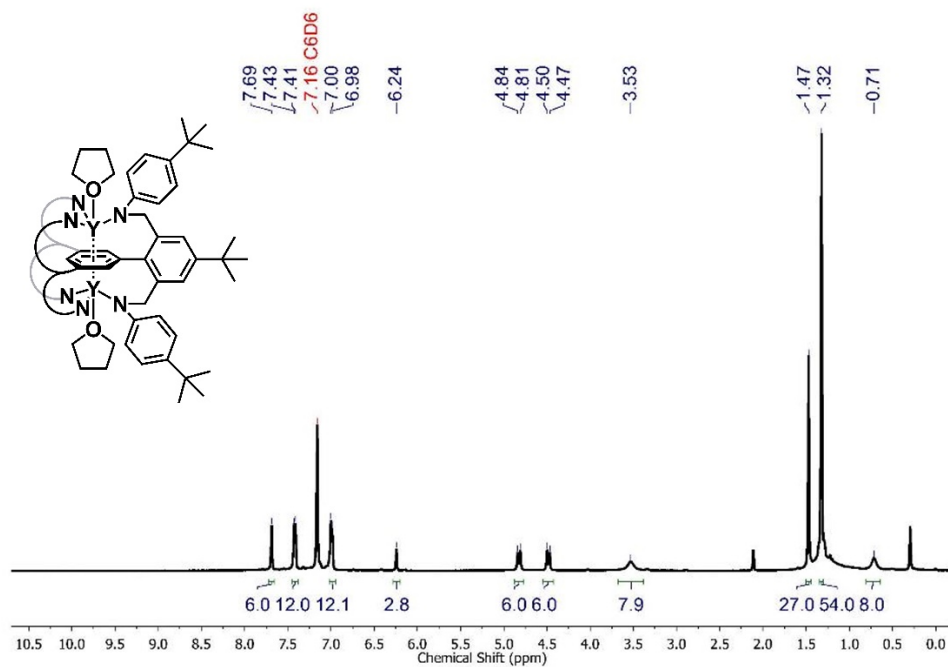


Fig. S4.14. ^1H -NMR spectrum of $\text{Y}_2(\text{BzN}_6\text{-4-}t\text{Bu})(\text{THF})_2$.

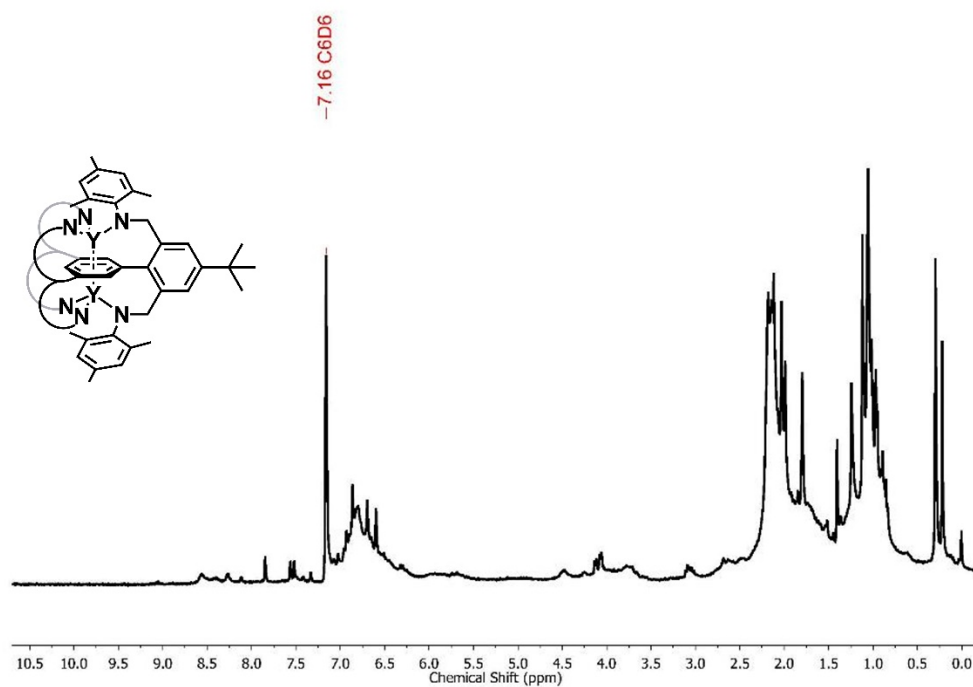


Fig. S4.15. ^1H -NMR spectrum of $\text{Y}_2(\text{BzN}_6\text{-Mes})$.

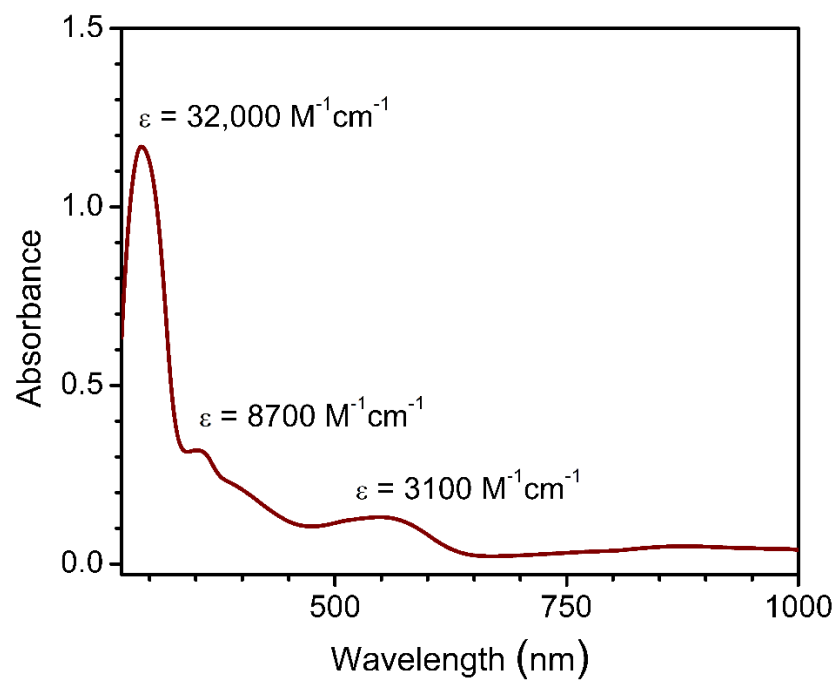


Fig. S4.16. UV-Vis-NIR spectrum of **1-Y**.

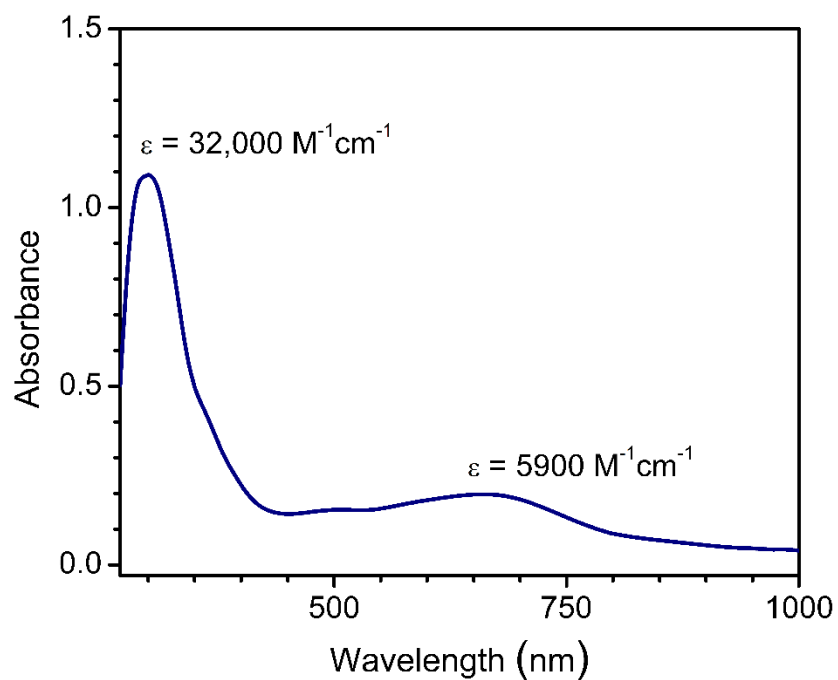


Fig. S4.17. UV-Vis-NIR spectrum of **2-Y**.

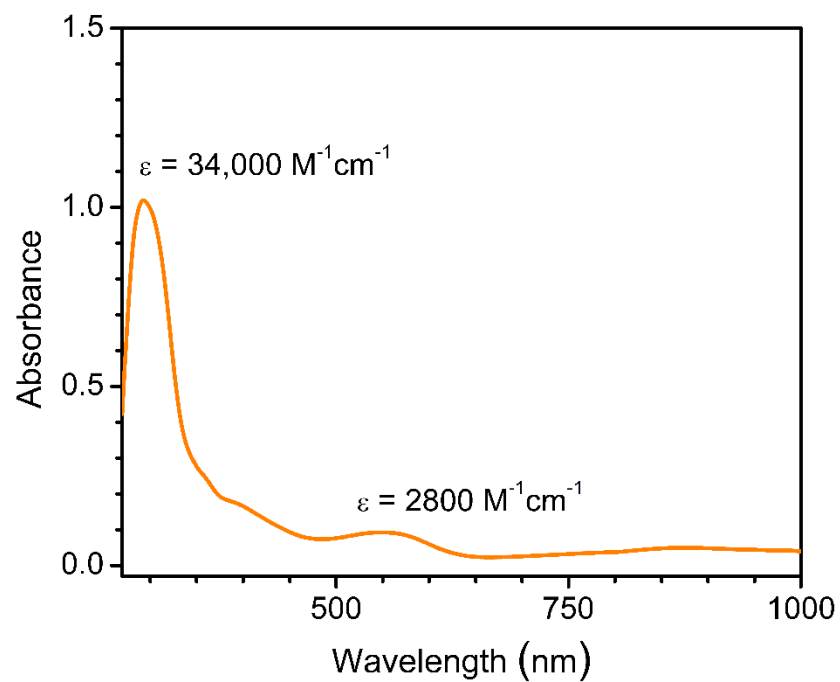


Fig. S4.18. UV-Vis-NIR spectrum of **1-Gd**.

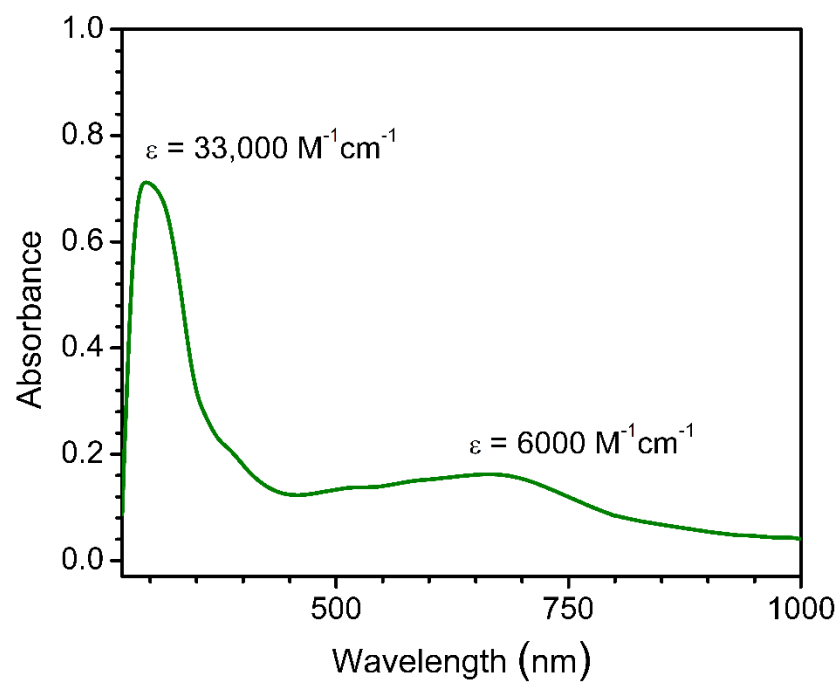


Fig. S4.19. UV-Vis-NIR spectrum of **2-Gd**.

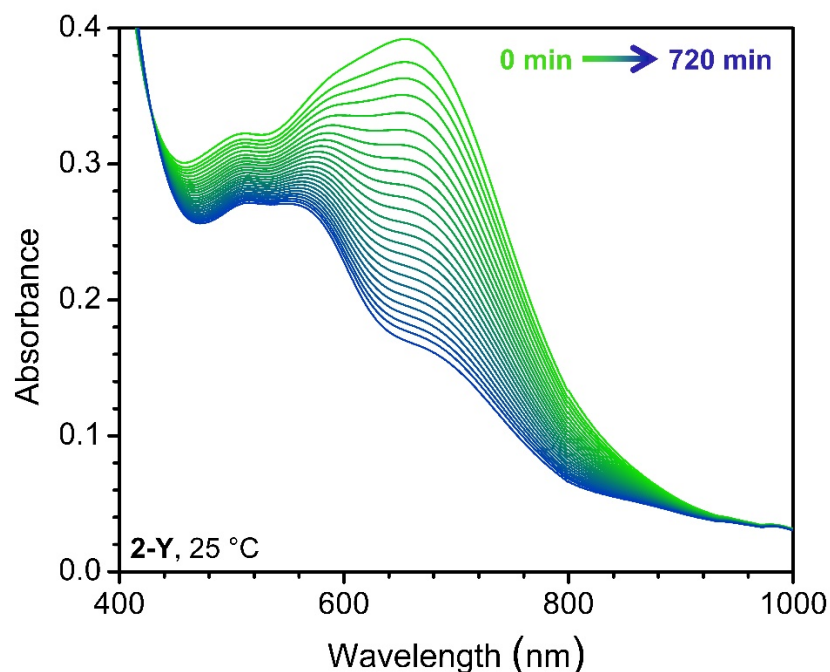


Fig. S4.20. UV-Vis spectra collected over 720 minutes on a solution of **2-Y** dissolved in tetrahydrofuran at 25 °C. Beer's Law was used to determine the change in concentration of **2-Y** over time in order to analyze the rate of decomposition.

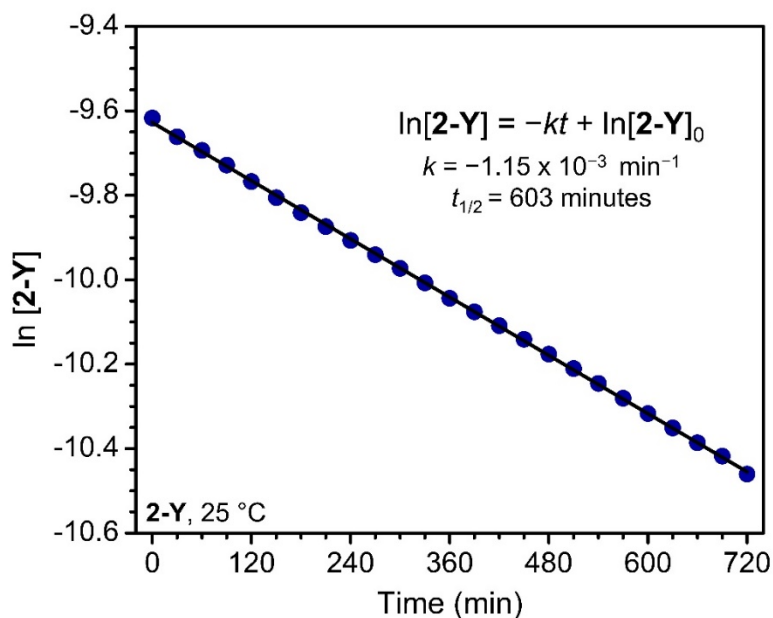


Fig. S4.21. Plot of $\ln[2-Y]$ versus time, where $[2-Y]$ = concentration of **2-Y** as determined by UV-Vis spectroscopy. Data are represented by blue points. A fit to this data with the equation $\ln[2-Y] = -kt + \ln[2-Y]_0$ is represented by the black line. From this fit, a half-life of 580 minutes was extracted.

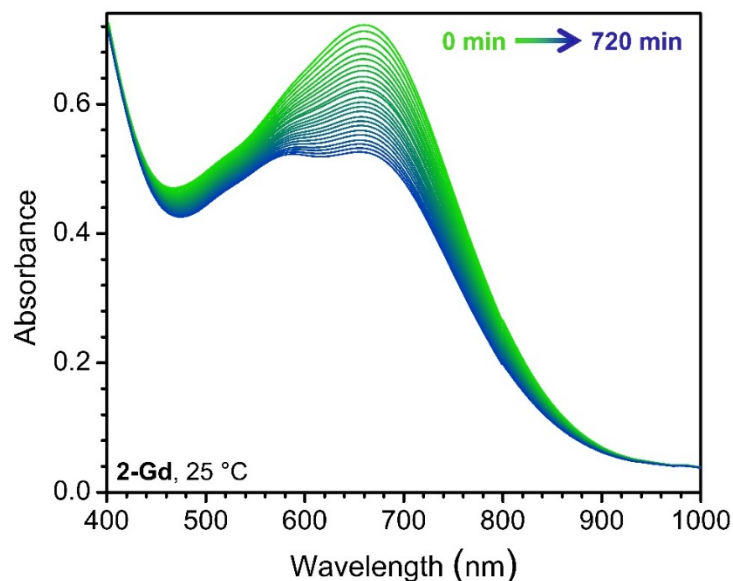


Fig. S4.22. UV-Vis spectra collected over 720 minutes of a solution of **2-Gd** in tetrahydrofuran at 25 °C. Beer's Law was used to determine the change in concentration of **2-Gd** over time in order to analyze the rate of decomposition.

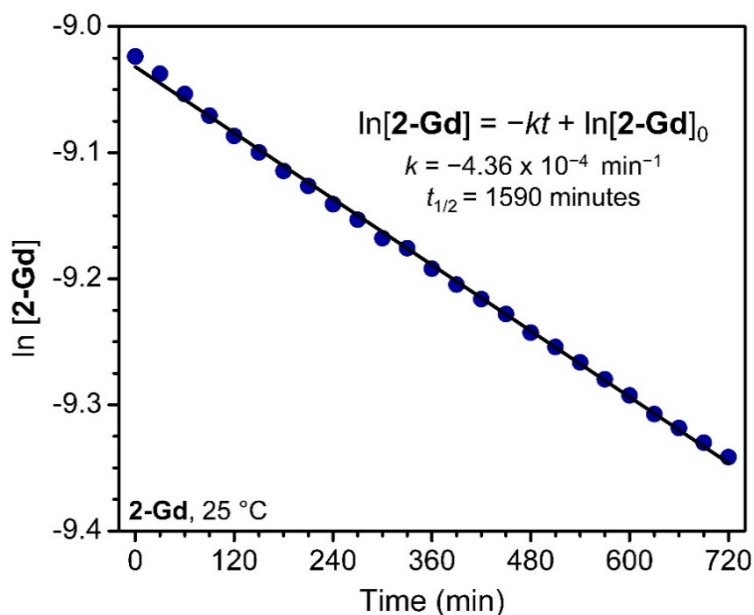


Fig. S4.23. Plot of $\ln[2-Gd]$ versus time, where $[2-Gd]$ = concentration of **2-Gd** as determined by UV-Vis spectroscopy. Data are represented by blue points. A fit to this data with the equation $\ln[2-Gd] = -kt + \ln[2-Gd]_0$ is represented by the black line. From this fit, a half-life of 1590 minutes was extracted.

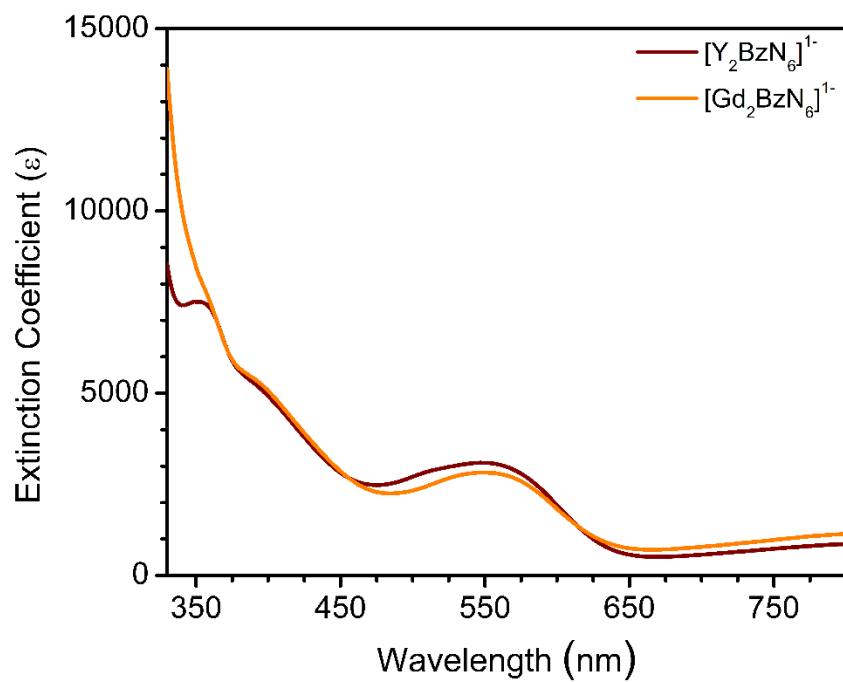


Fig. S4.24. UV-Vis-NIR spectra of **1-Y** (maroon) and **1-Gd** (orange).

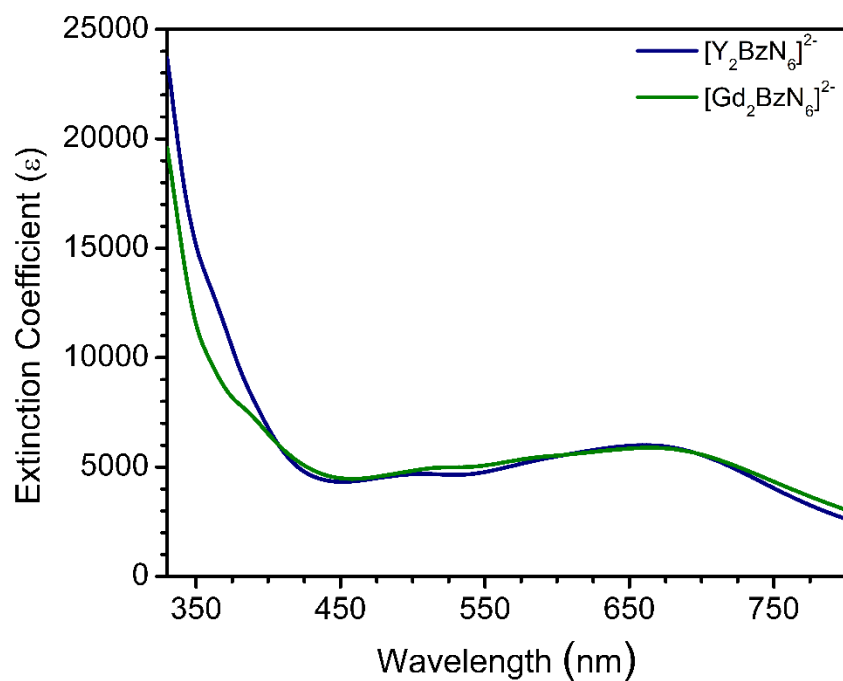


Fig. S4.25. UV-Vis-NIR spectra of **2-Y** (blue) and **2-Gd** (green).

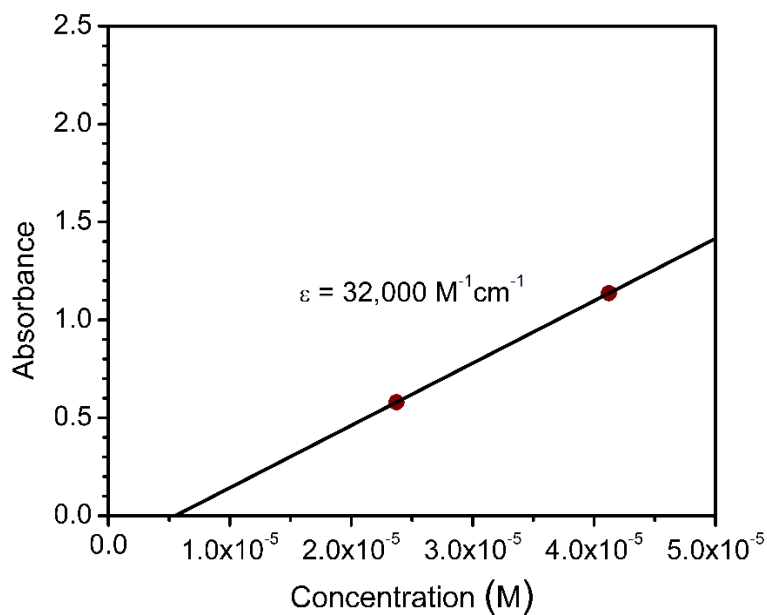


Fig. S4.26. Plot of absorbance versus concentration for the feature at 299 nm in the UV-Vis-NIR spectrum of **1-Y**. Maroon points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

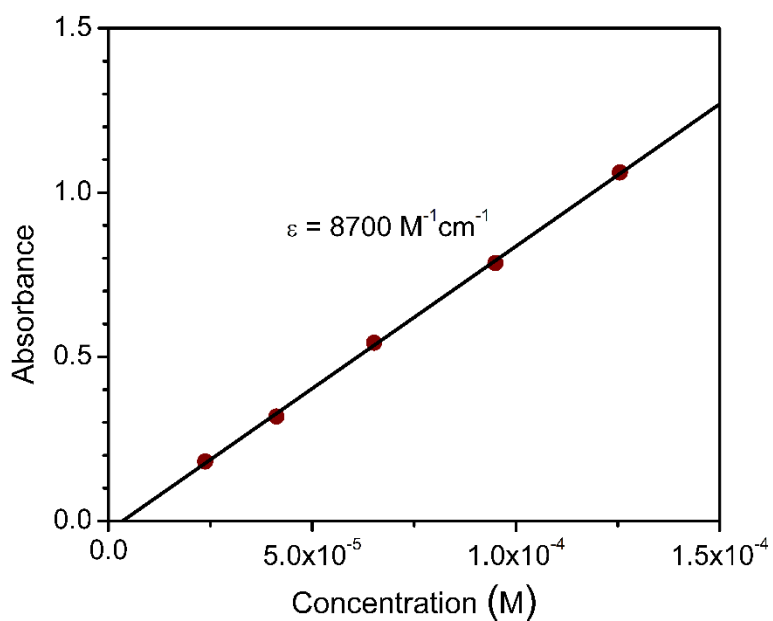


Fig. S4.27. Plot of absorbance versus concentration for the feature at 350 nm in the UV-Vis-NIR spectrum of **1-Y**. Maroon points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

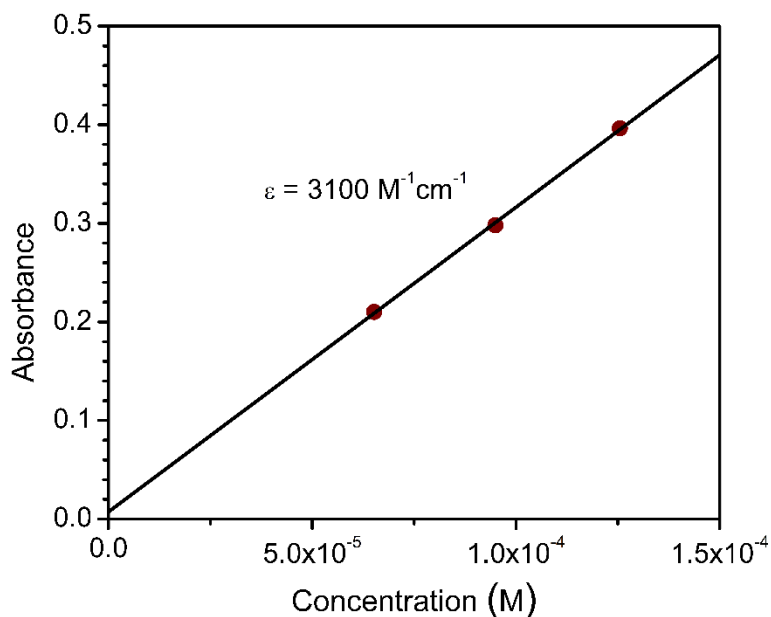


Fig. S4.28. Plot of absorbance versus concentration for the feature at 545 nm in the UV-Vis-NIR spectrum of **1-Y**. Maroon points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

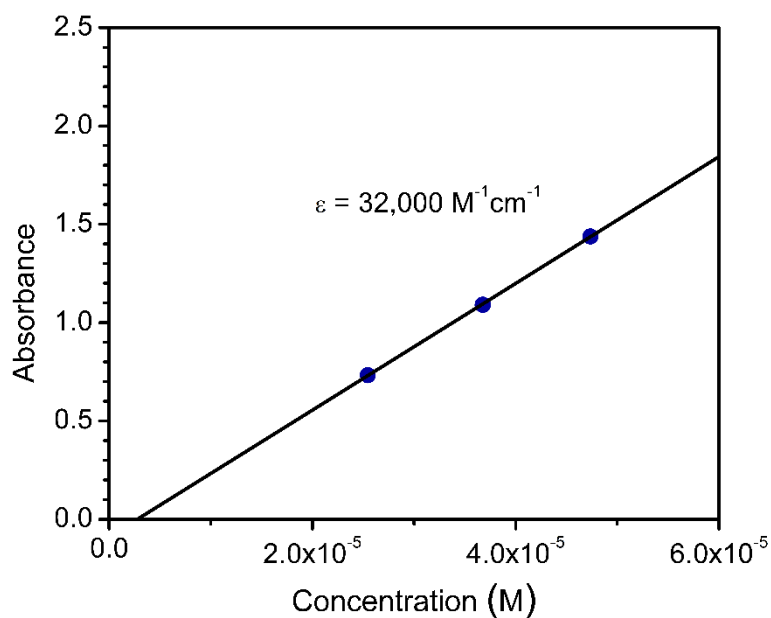


Fig. S4.29. Plot of absorbance versus concentration for the feature at 301 nm in the UV-Vis-NIR spectrum of **2-Y**. Blue points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

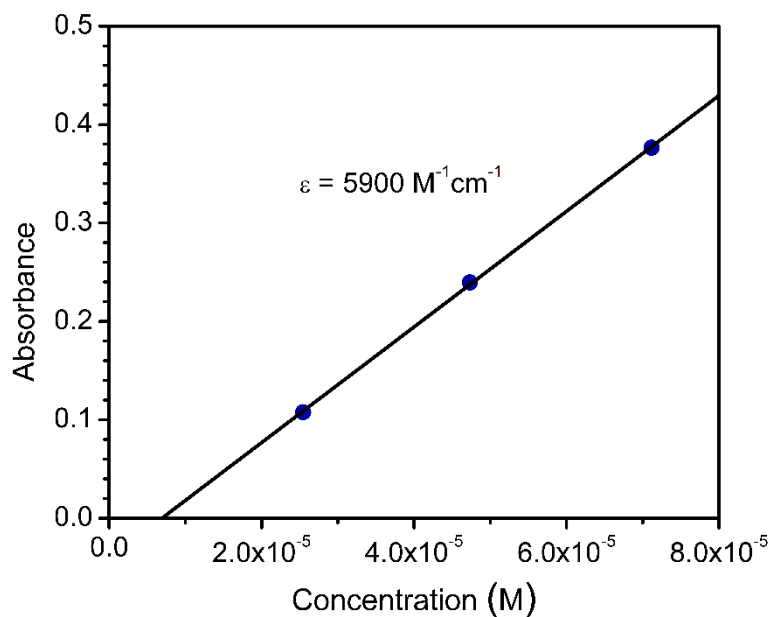


Fig. S4.30. Plot of absorbance versus concentration for the feature at 660 nm in the UV-Vis-NIR spectrum of **2-Y**. Blue points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

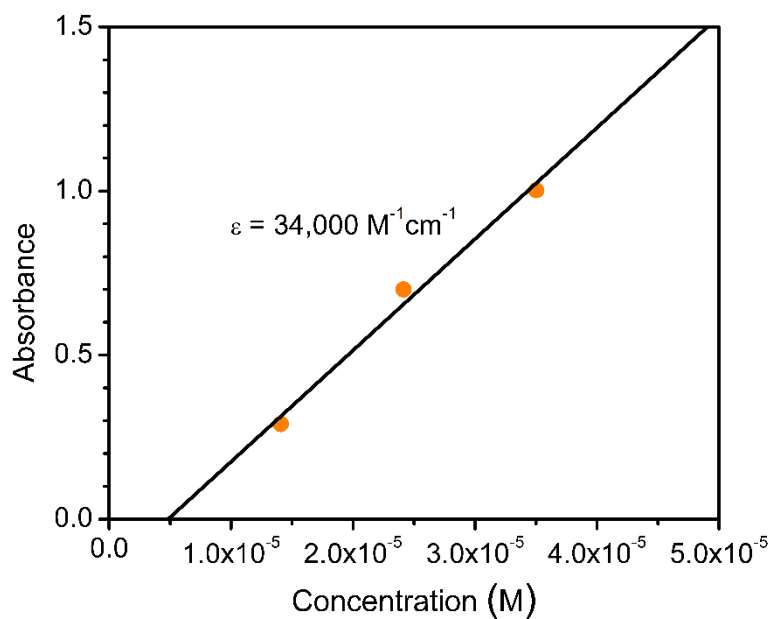


Fig. S4.31. Plot of absorbance versus concentration for the feature at 299 nm in the UV-Vis-NIR spectrum of **1-Gd**. Orange points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

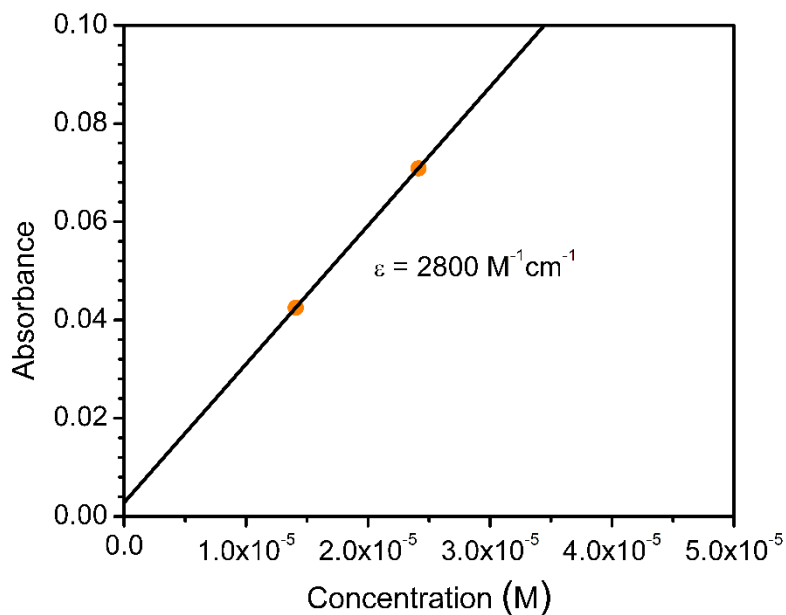


Fig. S4.32. Plot of absorbance versus concentration for the feature at 544 nm in the UV-Vis-NIR spectrum of **1-Gd**. Orange points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

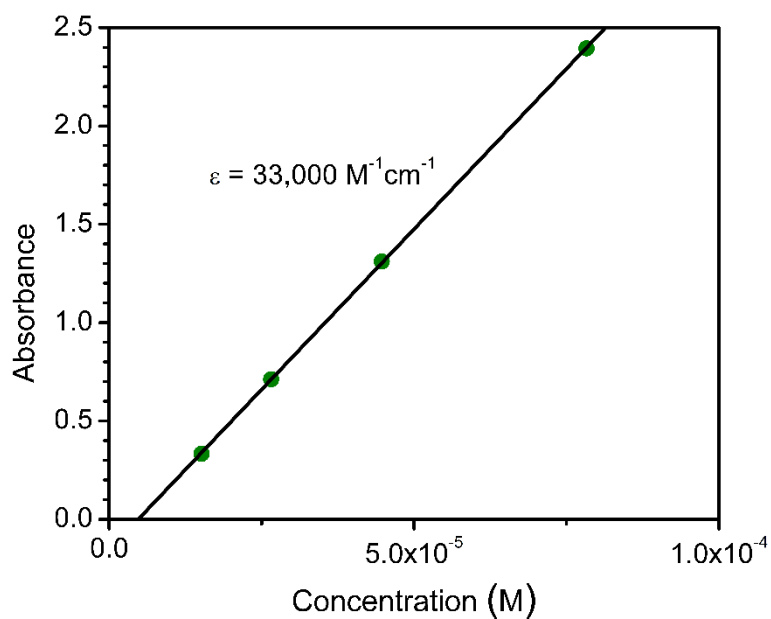


Fig. S4.33. Plot of absorbance versus concentration for the feature at 296 nm in the UV-Vis-NIR spectrum of **2-Gd**. Green points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

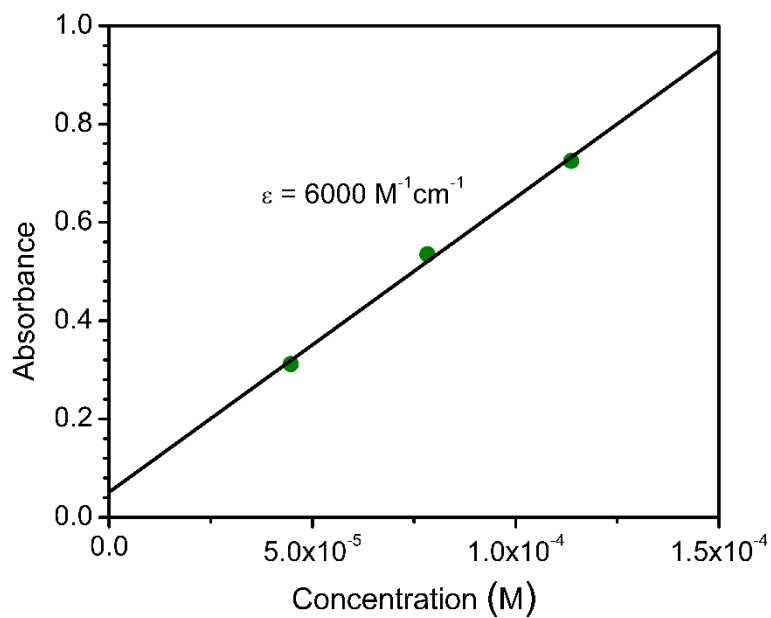


Fig. S4.34. Plot of absorbance versus concentration for the feature at 661 nm in the UV-Vis-NIR spectrum of **2-Gd**. Green points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

4.6.2 Crystallography

Single crystals of **1–2** were coated in Paratone-N-oil and mounted on Kapton loops. X-ray diffraction data were collected at UC Berkeley using a Rigaku XtaLAB p200 equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200K hybrid pixel array detector for **1-Y**, **2-Gd**, and **2-Y** and a Bruker QUAZAR diffractometer equipped with a Bruker AXS Apex II detector for **1-Gd**. Data was collected at 100 K under a N₂ stream from an Oxford Cryostems Cryostream with MoK α radiation (graphite monochromator). The frames were integrated with CrysAlis^{Pro} software, including a multi-scan absorption correction that was applied using the SCALE3 ABSPACK scaling algorithm within CrysAlis^{Pro} for **1-Y**, **2-Gd**, and **2-Y**.³⁶ For **1-Gd**, raw data was integrated and Lorentz and polarization corrections were calculated and applied using Bruker AXS SAINT software.³⁷ Absorption correction was calculated and applied using SADABS.³⁸ Initial structure solutions for **1–2** were determined using direct methods (SHELXT) and refinements were carried out using SHELXL-2014.³⁹

[Y₂BzN₆-Mes][K(18-crown-6)(THF)₂] (1-Y). *Due to poor crystal quality, the resolution of this data set is quite low (1.00 Å). Significant restraints were required for refinement to converge. As a result, bond distances and angles should not be trusted. This data is only included to corroborate the general structure and atomic connectivity in 1-Y, which matches the expected chemical formula determined by elemental analysis and mass spectrometry. The overall structure of 1-Y is analogous to the crystal structures obtained for 1-Gd, 2-Y, and 2-Gd.* The compound crystallized in the space group *P*2₁ with two molecules in the asymmetric unit. A range of crystals were grown in a variety of conditions, however, all measured samples diffracted poorly and displayed signs of twinning. The reported data set was refined as a two-component inversion twin. Significant restraints were required for refinement to converge. 18-crown-6 and THF molecules were stabilized through the application of C–C and C–O bond distance restraints, as well as enhanced rigid bond restraints. The C–C–O bond angles in tetrahydrofuran molecules were also restrained, as necessary. Several of the carbon and oxygen atoms in these disordered components could not be stabilized in the refinement unless identical anisotropic displacement parameters were used, which were determined by analogous atoms in the 18-crown-6 or tetrahydrofuran molecule. In order to stabilize the position of yttrium atoms, Y–C, Y–N, and Y–Y bond distance restraints were applied. All non-H atoms were refined anisotropically. A number of FCF reflections below $\theta_{\min}$ were likely obscured by the beamstop mask and, as a result, are missing. These missing reflections could also be ascribed to the large unit cell in **1-Y**.

[Y₂BzN₆-Mes][K(18-crown-6)(THF)₂]₂ (2-Y). The compound crystallized in the space group *P*2₁/*c* with one molecule in the asymmetric unit. Significant positional disorder was observed for the 18-crown-6 and tetrahydrofuran molecules in the two [K(18-crown-6)(THF)₂]⁺ counteranions. Disordered 18-crown-6 and tetrahydrofuran molecules were modeled over two positions and the refinement was stabilized through application of C–C and C–O bond distance restraints, as well as enhanced rigid bond restraints. The C–C–O bond angles in tetrahydrofuran molecules were also restrained, as necessary. Several of the carbon and oxygen atoms in these disordered components could not be stabilized in the refinement unless identical anisotropic displacement parameters were used, which were determined by analogous atoms in the 18-crown-6 or tetrahydrofuran molecule. Positional disorder was also observed for the *tert*-butyl groups in the BzN₆-Mes ligand. This disorder was modeled over two positions and the refinement was stabilized through application of

C–CH₃ and CH₃...CH₃ distance restraints, as well as enhanced rigid bond restraints. All non-H atoms were refined anisotropically. One reflection (2 2 1) was omitted, as it was affected by the beamstop. In addition, a number of FCF reflections below $\theta_{\min}$ were likely obscured by the beamstop mask and, as a result, are missing. These missing reflections could also be due to the large unit cell in **2-Y**.

[Gd₂BzN₆-Mes][K(18-crown-6)(THF)₂] (1-Gd). The compound crystallized in the space group *P2₁/c* with one molecule in the asymmetric unit. Significant positional disorder was observed for the 18-crown-6 and tetrahydrofuran molecules in the [K(18-crown-6)(THF)₂]⁺ countercation. This countercation was modeled over two positions and each of the 18-crown-6 and tetrahydrofuran molecules that composed each countercation site were also modeled over two positions. The potassium cation in one of the sites was also modeled over two positions. The sum of the [K(18-crown-6)(THF)₂]⁺ positions was constrained to equal an occupancy of one using the SUMP command. The refinement was stabilized through application of C–C and C–O bond distance restraints, as well as enhanced rigid bond restraints. The C–C–O bond angles in tetrahydrofuran molecules were also restrained, as necessary. Several of the carbon and oxygen atoms in these disordered components could not be stabilized in the refinement unless identical anisotropic displacement parameters were used, which were determined by analogous atoms in the 18-crown-6 or tetrahydrofuran molecule. Positional disorder was also observed for the *tert*-butyl groups in the BzN₆-Mes ligand. This disorder was modeled over two positions and the refinement was stabilized through application of C–CH₃ and CH₃...CH₃ distance restraints, as well as enhanced rigid bond restraints. After refinement, a small residual density peak was calculated on Gd1, however this peak could not be modelled as any chemically reasonable species. It likely arises due to the strongly absorbing lanthanide atom or due to problems in the absorption correction. All non-H atoms were refined anisotropically.

[Gd₂BzN₆-Mes][K(18-crown-6)(THF)₂]₂ (2-Gd). The compound crystallized in the space group *P2₁/c* with one molecule in the asymmetric unit. Significant positional disorder was observed for the 18-crown-6 and tetrahydrofuran molecules in the two [K(18-crown-6)(THF)₂]⁺ countercations, as was observed for **2-Y**. Disordered 18-crown-6 and tetrahydrofuran molecules were modeled over two positions and the refinement was stabilized through application of C–C and C–O bond distance restraints, as well as enhanced rigid bond restraints. The C–C–O bond angles in tetrahydrofuran molecules were also restrained, as necessary. Several of the carbon and oxygen atoms in these disordered components could not be stabilized in the refinement unless identical anisotropic displacement parameters were used, which were determined by analogous atoms in the 18-crown-6 or tetrahydrofuran molecule. Positional disorder was also observed for the *tert*-butyl groups in the BzN₆-Mes ligand. This disorder was modeled over two positions and the refinement was stabilized through application of C–CH₃ and CH₃...CH₃ distance restraints, as well as enhanced rigid bond restraints. Residual electron density near the gadolinium atom (ca. 1 Å) could be modeled as positional disorder, however the second position only showed an occupancy of 0.02. We therefore believe that this residual density likely arises from poor crystal quality or is the result of scattering from the heavy Gd atom. All non-H atoms were refined anisotropically. A number of FCF reflections below $\theta_{\min}$ were likely obscured by the beamstop mask and, as a result, are missing. These missing reflections could also be due to the large unit cell in **2-Gd**.

Table S4.1. Structure details for **1-2**.

Parameter	1-Y	2-Y	1-Gd	2-Gd
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å), α (°)	19.0249(7), 90	18.7690(7), 90	16.5727(13), 90	18.7807(3), 90
b (Å), β (°)	33.8338(10), 105.673(4)	28.9313(11), 97.056(3)	20.0693(16), 99.343(4)	29.1167(6), 97.236(2)
c (Å), γ (°)	20.2341(7), 90	24.4716(8), 90	38.531(3), 90	24.4939(5), 90
V (Å ³)	12540.2(8)	13187.7(8)	12645.4(17)	13287.4(4)
Z	2	4	4	4
ρ_{calc} (g/cm ³)	1.123	1.221	1.102	1.281
Crystal size (mm ³)	$0.52 \times 0.11 \times 0.08$	$0.57 \times 0.20 \times 0.14$	$0.30 \times 0.18 \times 0.10$	$0.54 \times 0.32 \times 0.18$
2 θ range for data collection (°)	5.746 to 41.63	5.632 to 50.7	2.49 to 49.426	5.638 to 50.7
Index range	$-18 \leq h \leq 18$ $-33 \leq k \leq 33$ $-20 \leq l \leq 20$	$-20 \leq h \leq 22$ $-34 \leq k \leq 34$ $-29 \leq l \leq 29$	$-17 \leq h \leq 19$ $-23 \leq k \leq 23$ $-45 \leq l \leq 45$	$-22 \leq h \leq 22$ $-35 \leq k \leq 34$ $-29 \leq l \leq 29$
Reflections collected	81388	142181	136727	176029
Independent	25797 (0.1184)	24118 (0.0990)	21569 (0.0632)	24253 (0.0812)
Completeness (%)	98.0	100.0	100.0	100.0
Data / restraints / parameters	25797 / 2403 / 2646	24118 / 1175 / 1871	21569 / 1064 / 1459	24253 / 1127 / 18
Goodness-of-fit on F ²	1.035	1.023	1.047	1.026
R1, wR2 [$I > 2\sigma(I)$]	0.0808, 0.1959	0.0571, 0.1409	0.0779, 0.2084	0.0485, 0.1255
R1, wR2 (all data)	0.1109, 0.2142	0.0908, 0.1598	0.1170, 0.2415	0.0581, 0.1324

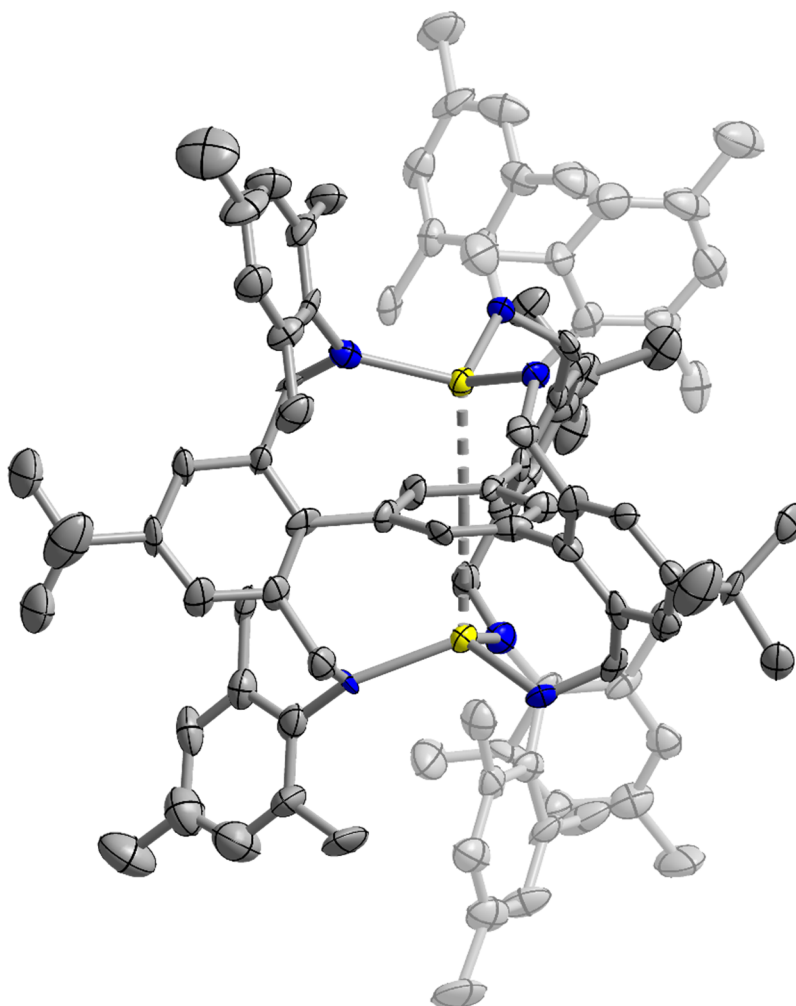


Fig. S4.35. Solid-state structure of **1-Y** with thermal ellipsoids at the 50% probability level. Yellow, gray, and blue ellipsoids represent Y, C, and N atoms, respectively. Hydrogen atoms, counteranion and the disordered component are omitted for clarity. While the asymmetric unit contains two molecules, only one is shown.

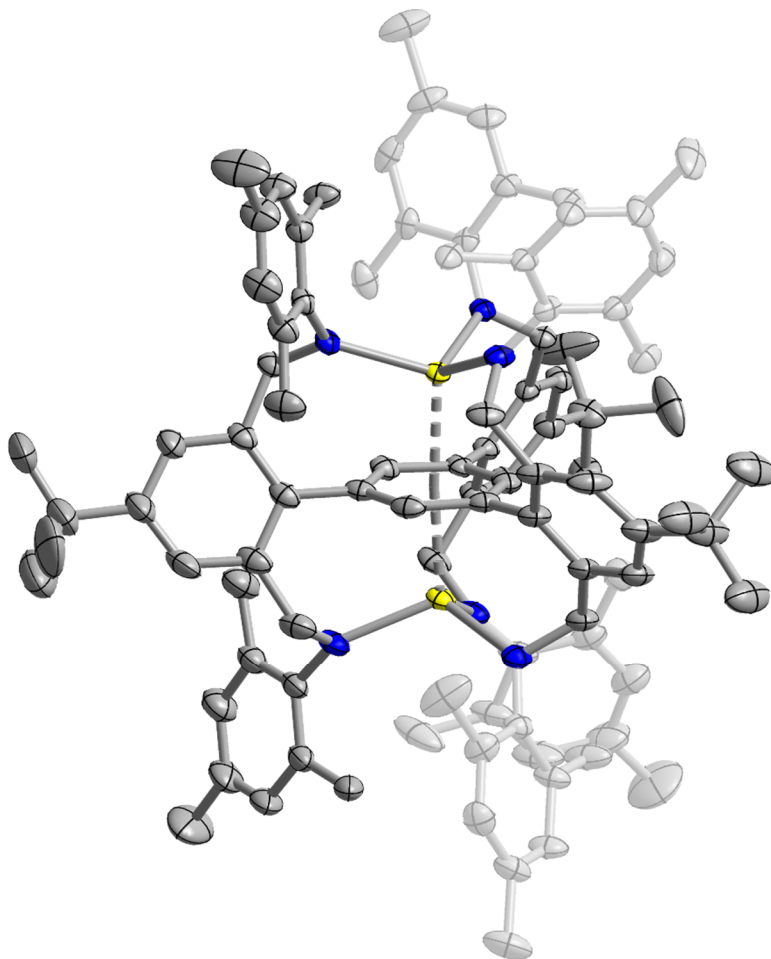


Fig. S4.36. Solid-state structure of **2-Y** with thermal ellipsoids at the 50% probability level. Yellow, gray, and blue ellipsoids represent Y, C, and N atoms, respectively. Hydrogen atoms, counterions and the disordered component are omitted for clarity.

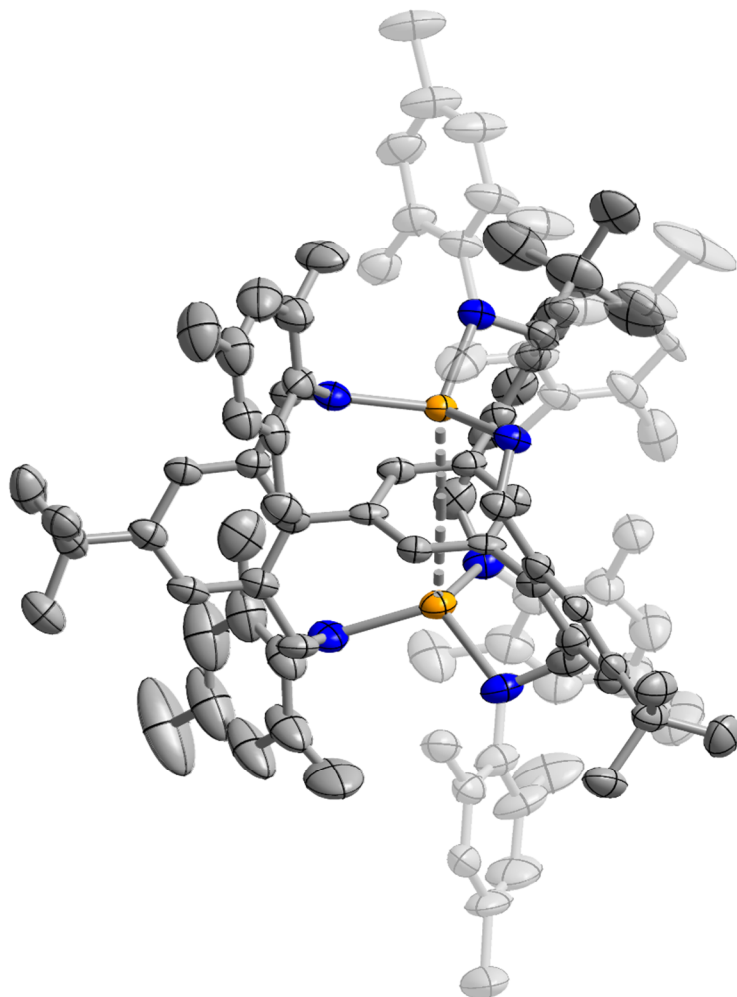


Fig. S4.37. Solid-state structure of **1-Gd** with thermal ellipsoids at the 50% probability level. Orange, gray, and blue ellipsoids represent Gd, C, and N atoms, respectively. Hydrogen atoms, counterion and the disordered component are omitted for clarity.

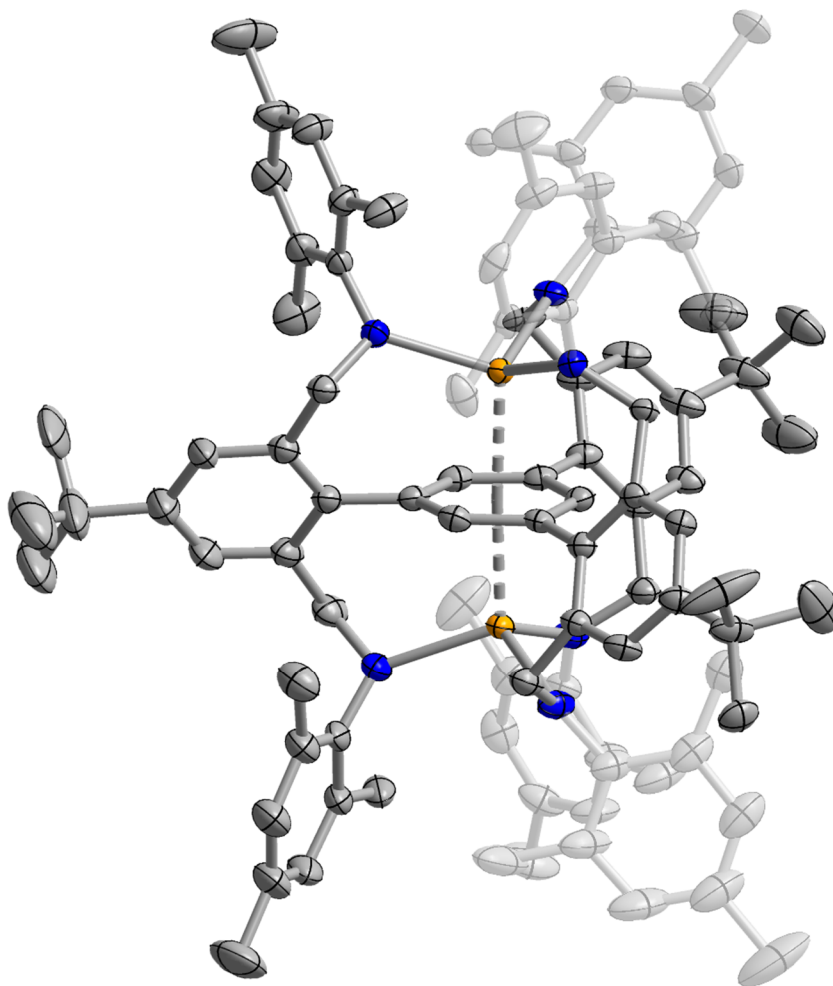


Fig. S4.38. Solid-state structure of **2-Gd** with thermal ellipsoids at the 50% probability level. Orange, gray, and blue ellipsoids represent Gd, C, and N atoms, respectively. Hydrogen atoms, counterions and the disordered component are omitted for clarity.

Table S4.2. Selected bond distances (Å) and angles (°) for **1–2**.

	[Gd ₂ BzN ₆ -Mes] ¹⁻ (1-Gd)	[Y ₂ BzN ₆ -Mes] ²⁻ (2-Y)	[Gd ₂ BzN ₆ -Mes] ²⁻ (2-Gd)
M1–N1	2.234(7)	2.250(3)	2.298(3)
M1–N2	2.246(7)	2.260(3)	2.291(3)
M1–N3	2.230(8)	2.252(3)	2.282(3)
M2–N4	2.247(7)	2.251(3)	2.272(4)
M2–N5	2.232(6)	2.239(3)	2.289(4)
M2–N6	2.244(7)	2.242(3)	2.273(3)
Ln–N(avg) ^a	2.239(8)	2.249(3)	2.284(3)
C1–C2	1.432(11)	1.447(5)	1.440(5)
C2–C3	1.432(11)	1.407(5)	1.443(6)
C3–C4	1.414(11)	1.486(5)	1.455(6)
C4–C5	1.430(11)	1.432(5)	1.424(6)
C5–C6	1.437(11)	1.405(5)	1.435(6)
C6–C1	1.398(11)	1.475(5)	1.457(6)
C–C(avg) ^a	1.424(11)	1.442(5)	1.442(6)
M1–benzene ^b	2.416(3)	2.278(1)	2.309(2)
M2–benzene ^b	2.433(3)	2.282(1)	2.308(2)
C1–C2, C4–C5 torsion	0.3(6)	–1.4(3)	1.1(3)

^aThe standard deviation of the average value was estimated from $\sigma = \sqrt{\sum \sigma_i^2 / N}$, where σ_i is the standard deviation of each bond distance i and N is the number of distances averaged.

^bM–benzene distances were measured from the metal atom to the centroid of the benzene ring.

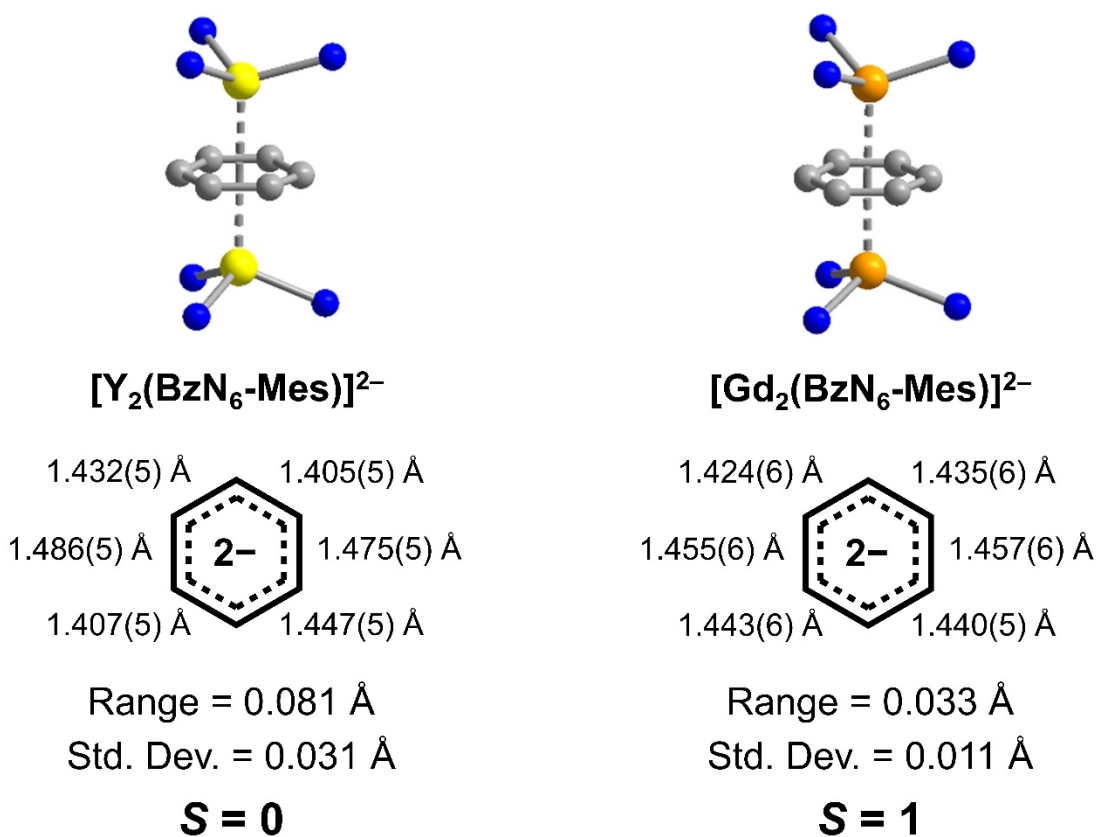


Fig. S4.39. Structure of the bridging benzene dianion in **2-Y** and **2-Gd**. The range in the C–C bond distances decreases from **2-Y** to **2-Gd**, as does the standard deviation in the C–C bond lengths. These structural changes are consistent with a Baird aromatic $S = 1$ ground state for the benzene dianion in **2-Gd** and a non-aromatic $S = 0$ ground state in **2-Y**, as bond-length equalization is predicted for aromatic molecules.

4.6.3 Electron Paramagnetic Resonance (EPR) Spectroscopy

Continuous-wave (CW) EPR measurements were performed on finely ground polycrystalline powder samples of **1-Y** and **2-Y** (ca. 30 mg each). Samples were constrained in polyethylene EPR cups and kept frozen in liquid nitrogen while being loaded into the probe to prevent sample degradation. All CW EPR measurements shown below were collected using field-modulation and phase-sensitive detection, yielding derivative-mode spectra (dI/dB , where I is the absorption intensity and B the magnetic induction).

Representative results for **1-Y** and **2-Y** at 370 GHz and 5 K are compared below in Fig. S4.40. Although the spectra appear at first glance to be quite similar, a small but noticeable kink is present in the spectrum of **2-Y** just as the dI/dB signal passes through zero at $g = 2.002$; the shoulder at $g = 2.005$ is also less pronounced. In other words, there are clear differences in the spectra for the two complexes. It is impossible to reproduce the kink via simulations that assume a spin $S = 1/2$ species with an anisotropic g -tensor. This hints at the presence of a weak zero-field-splitting (ZFS) of the spectrum of **2-Y**, possible only for $S > 1/2$. Frequency-dependent measurements in Fig. S4.41 show that the kink is resolved only at the highest frequencies, presumably due to an increased contribution to the linewidth from intermolecular interactions.

In order to estimate the singlet-triplet gap (ΔE_{ST}) in **2-Y**, temperature dependent CW-EPR measurements (Fig. S4.42) were performed from 5 to 200 K. Data were collected at the highest available frequency (371 GHz) in order to minimize any contributions from intermolecular interactions in the solid state that could potentially influence the spin susceptibility. The spectra in Fig. S4.42 were then doubly integrated, the first integration to obtain the spectral density (absorption intensity, I) and the second to extract a quantity proportional to the spin susceptibility, χ , as shown in Fig. S4.3. The $\chi(T)$ versus T data were then fit to the following expression (Eq. S4.1) that considers a singlet-triplet system in the presence of a magnetic field:

$$\chi = \left(\frac{2Ng^2\mu_B^2}{k_B T} \right) \frac{\left[2 + \left(1 + e^{\Delta E_{ST}/k_B T} \right) \cosh \left(\frac{g\mu_B B}{k_B T} \right) \right]}{\left[1 + e^{\Delta E_{ST}/k_B T} + 2 \cosh \left(\frac{g\mu_B B}{k_B T} \right) \right]^2}. \quad (\text{Eq. S4.1})$$

This expression reduces to the well-known Bleaney-Bowers equation in zero applied magnetic field.²² Anisotropic spin-orbit interactions (either g -anisotropy or ZFS) within the $S = 1$ manifold are completely neglected, thereby greatly streamlining the analysis. This assumption falls well within the error of the data, as any anisotropy is barely discernible in the spectra. The best fit to Eq. S4.1 is presented in Fig. 4.2B of the main text, yielding a singlet-triplet gap, $\Delta E_{ST} = 0.025(4)$ kcal/mol, with an R^2 value of 0.9971. Here, the vertical error bars were estimated from the uncertainty in the baseline given by the double integration in Fig. S4.43. These errors arise from the linear baseline correction made to the raw EPR spectra; meanwhile, the accuracy of the measured temperature falls well within the width of the data points in Fig. 4.2B.

The best fit curve shown in Fig. 4.2B reveals a maximum in the spin susceptibility at a temperature just below the minimum of the employed instrument. This is due to depopulation of the triplet at low temperatures due to the singlet ground state. Experimental observation of this maximum

would obviously have provided greater confidence in the employed model. However, the absence of such a maximum in the experiments also provides compelling evidence for the low-lying triplet, i.e., a larger ΔE_{ST} would surely produce a curve with a maximum at higher/attainable temperatures.

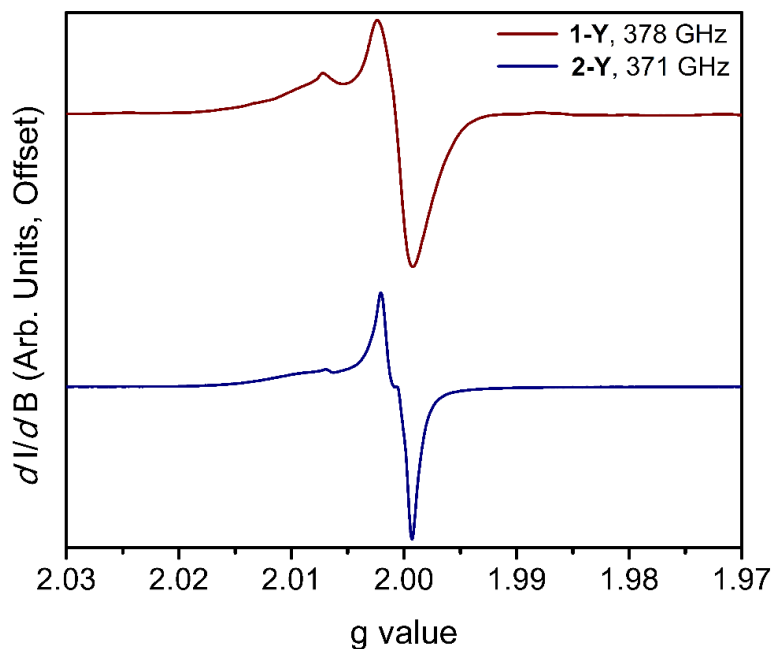


Fig. S4.40. CW-EPR spectra of **1-Y** (maroon) and **2-Y** (blue).

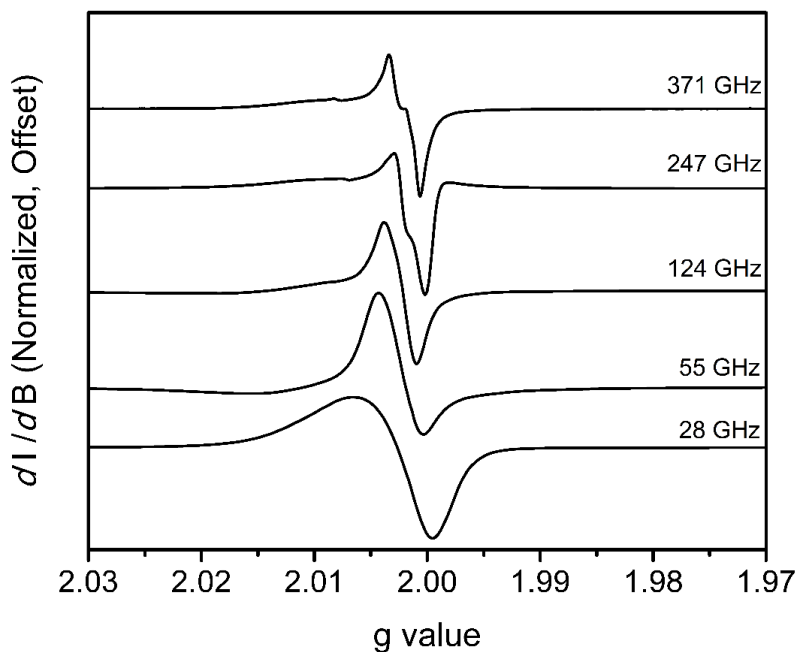


Fig. S4.41. Normalized frequency-dependent CW-EPR spectra of **2-Y** collected at 5 K from 28 to 371 GHz. The abscissa has been re-scaled to give the g-value.

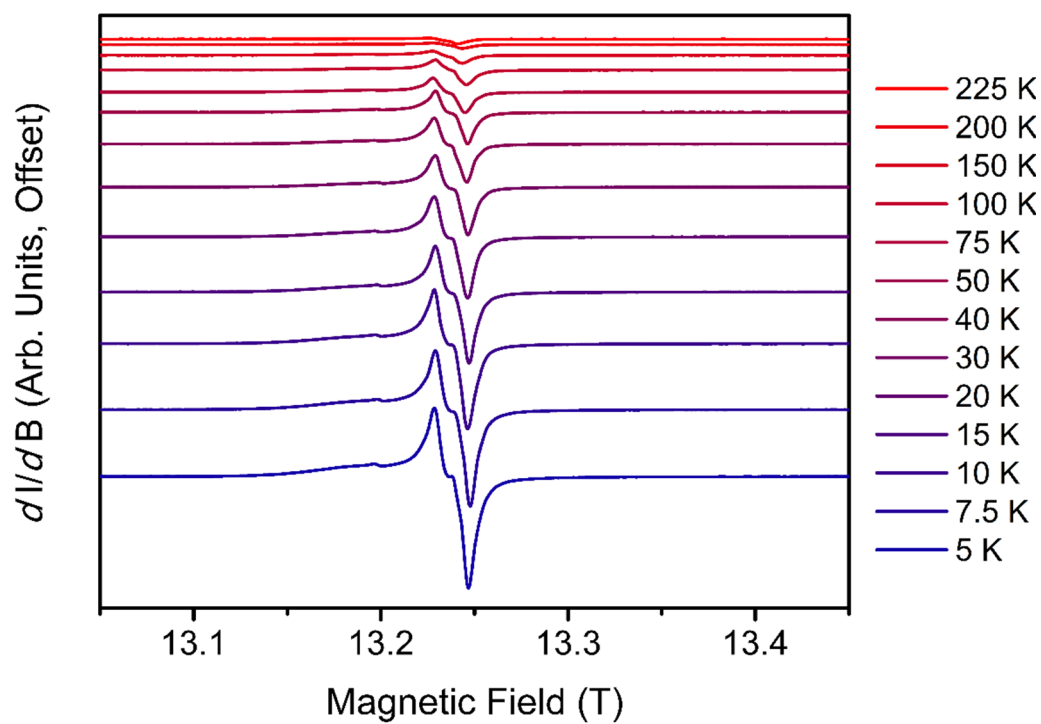


Fig. S4.42. CW-EPR spectra of **2-Y** from 5 to 225 K at 371 GHz.

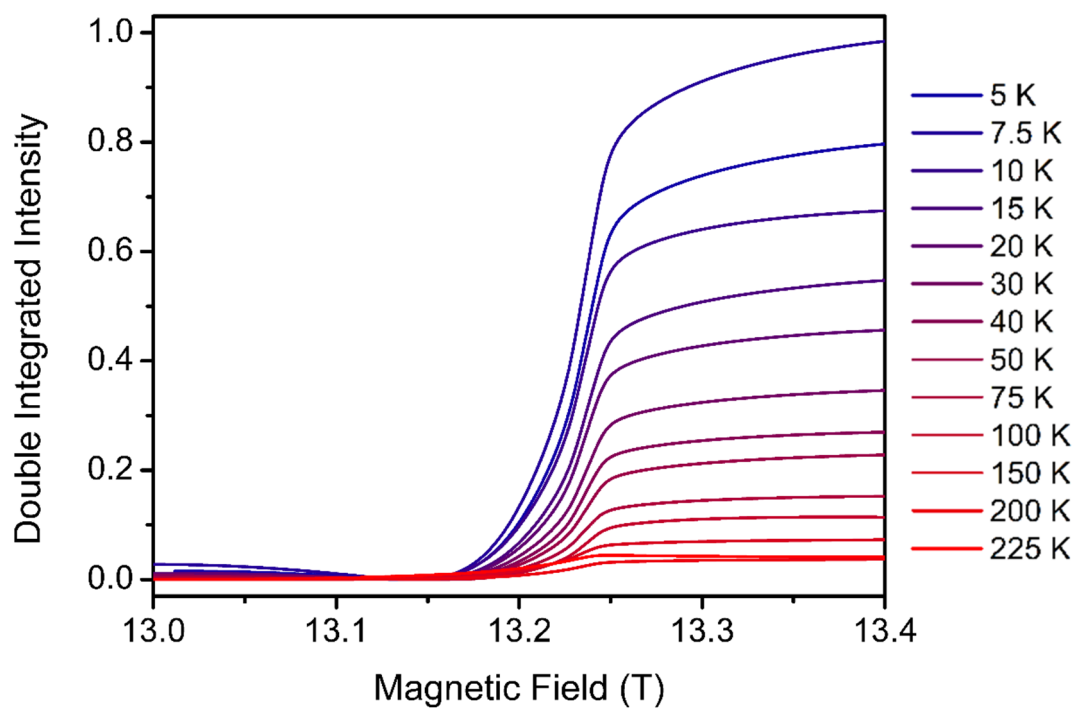


Fig. S4.43. Double integrated absorption of the EPR spectrum of **2-Y** from 5 to 225 K at 371 GHz.

All D-band EPR experiments were performed on solutions of **1-Y** and **2-Y** in tetrahydrofuran (ca. 5 mM) at 5.2 K. Field-swept spectra were collected using a Hahn echo sequence: $\pi/2-\tau-\pi-\tau$ -echo. The length of the microwave pulse π was set to 60 ns and the interpulse delay τ was set to 300 ns. Field-swept spectra represent 20 averages (20 shots per point, 1 scan).

Electron spin nutation experiments were used to assign the ground spin state of **2-Y**. A microwave preparation pulse is varied and followed by a Hahn echo sequence: $\pi_{\text{prep}}-T-\pi/2-\tau-\pi-\tau$ -echo. Electron spin nutation experiments were performed at 4.633 T (**1-Y**) and 4.634 T (**2-Y**). The preparation pulse π_{prep} was swept from 4–1000 ns in 5 ns steps. The length of the microwave pulse π was set to 60 ns and interpulse delays T and τ were set to 3 μ s and 500 ns respectively.

The prefactors that govern the transition probability of a high-spin system can be calculated via the ladder operators S^+ and S^-

$$\begin{aligned} S^+|S \ m_S\rangle &= \hbar\sqrt{S(S+1) - m_S(m_S+1)}|S \ m_S+1\rangle \\ S^-|S \ m_S\rangle &= \hbar\sqrt{S(S+1) - m_S(m_S-1)}|S \ m_S-1\rangle \end{aligned}$$

The prefactors for an $S = 1$ spin system are:

$$\begin{aligned} m_S = |-1\rangle &\rightarrow |0\rangle & \sqrt{2} \\ m_S = |0\rangle &\rightarrow |1\rangle & \sqrt{2} \end{aligned}$$

Comparison of the oscillation periods observed in the electron spin nutation experiments on **1-Y** and **2-Y** show that they differ by a factor of $\sqrt{2}$, as expected for the comparison of an $S = 1/2$ system to an $S = 1$ system.

Table S4.3. Oscillation periods observed in the electron spin nutation experiment on complexes **1-Y** and **2-Y**.

	1-Y	2-Y
Period 1 (ns)	245.25	180.18
Period 2 (ns)	240.24	170.17
Period 3 (ns)	n/a	170.17
Period 4 (ns)	n/a	175.18
Average (ns)	242.74	173.92

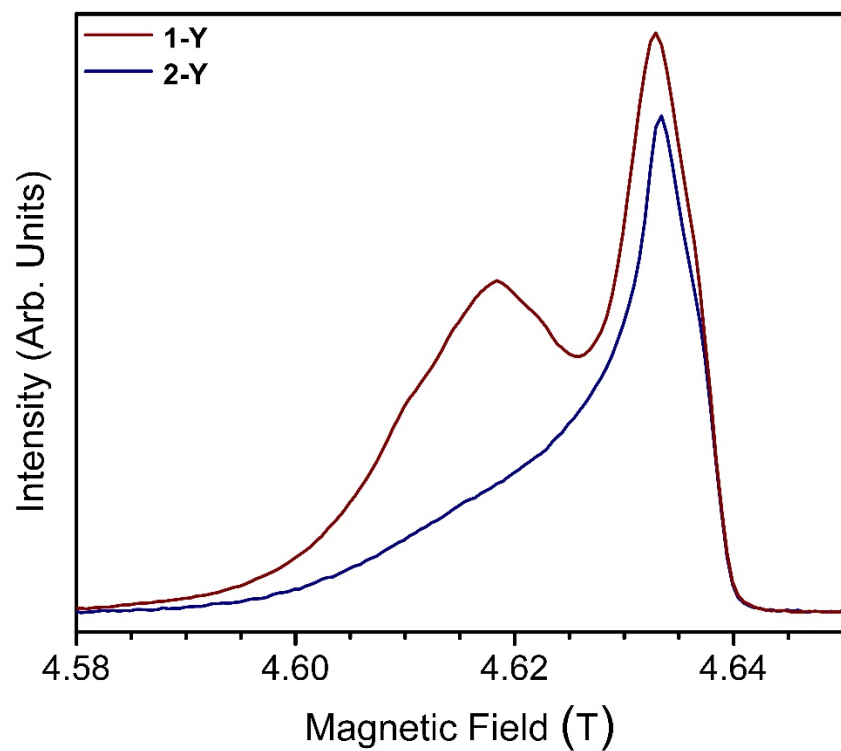


Fig. S4.44. D-Band electron-spin echo (ESE) detected field-swept spectra of **1-Y** (maroon trace) and **2-Y** (blue trace) recorded at 5.2 K.

4.6.4 Magnetic Measurements

Samples were prepared by first adding crystalline powder (11.2 mg of **1-Gd**, 20.4 mg of **2-Gd**) to a 5 mm i.d./7 mm o.d. quartz tube with a raised quartz platform. A layer of eicosane was then added to the samples (18.1 mg for **1-Gd** and 21.4 mg for **2-Gd**) to provide good thermal contact between the sample and the bath and to prevent crystallite torquing. The tubes were fitted with Teflon sealable adapters, evacuated using a glovebox vacuum pump, and then flame sealed with an O₂/H₂ flame under vacuum. After flame-sealing, the eicosane was melted in a 40 °C water bath. Magnetic measurements were also conducted on a 9.1 mM frozen solution of **2-Gd** in 1:1 THF:2MeTHF to ensure that the observed magnetic properties were molecular in origin and not due to long-range interactions in the solid-state.

Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. All data were corrected for diamagnetic contributions from the core diamagnetism and for the diamagnetism of the eicosane used to suspend the sample, estimated using Pascal's constants to give corrections of $\chi_{\text{dia}} = -0.00124$ emu/mol and -0.00152 emu/mol for **1-Gd** and **2-Gd**, respectively.

Dc magnetic susceptibility measurements were performed at temperatures ranging from 2 to 300 K under applied fields of 1, 5, and 10 kOe (0.1, 0.5, and 1 T). Data could only be collected from 2 to 100 K for the 9.1 mM solution of **2-Gd**, as the diamagnetism of the solvent was larger than the paramagnetism of the complex at higher temperatures.

Fits to the dc susceptibility data were performed using PHI,⁴⁰ using the spin-only Hamiltonian $\hat{H} = -2J_{\text{Gd-rad}}\hat{S}_{\text{rad}} \cdot (\hat{S}_{\text{Gd}(1)} + \hat{S}_{\text{Gd}(2)})$, where $J_{\text{Gd-rad}}$ represents the magnetic exchange coupling between each Gd(III) ion and the organic radical spin. $\hat{S}_{\text{rad}}$ values of 1/2 and 1 were used for fits to **1-Gd** and **2-Gd**, respectively. Contributions for temperature-independent paramagnetism and intermolecular coupling were included when fitting susceptibility measurements for solid samples.

Data for **1-Gd** were fit from 40 to 300 K. Strong antiferromagnetic coupling between two $S = 7/2$ Gd(III) ions and an $S = 1/2$ bridging ligand should result in $S_{\text{tot}} = 13/2$ at low temperatures. This corresponds to a theoretical value of 24.38 emu K/mol. The low-temperature peak in $\chi_{\text{M}}T$ for **1-Gd** is less than this predicted value, perhaps due to antiferromagnetic coupling between adjacent molecules in the crystal lattice. This has been observed previously for radical-bridged lanthanide complexes.²⁵

Table S4.4. Parameters used to fit the dc susceptibility data for **1-Gd**.

	Field (T)	$J_{\text{Gd-rad}}$ (cm ⁻¹)	J_{inter} (cm ⁻¹)	TIP (cm ⁻¹)	Residual
Solid Sample	0.1	-28.2(2)	$-5.6(1) \times 10^{-2}$	$5.6(1) \times 10^{-3}$	0.4
Solid Sample	0.5	-27.8(2)	$-5.7(1) \times 10^{-2}$	$4.1(1) \times 10^{-2}$	0.4
Solid Sample	1	-28.0(1)	$-5.6(1) \times 10^{-2}$	$3.8(1) \times 10^{-2}$	0.3

Data for **2-Gd** were fit from 2 to 300 K. Antiferromagnetic coupling between two $S = 7/2$ Gd(III) ions and an $S = 1$ bridging ligand should result in $S_{\text{tot}} = 6$ at low temperatures, corresponding to a theoretical $\chi_{\text{M}}T$ value of 21.00 emu K/mol. The low-temperature peak in the dc susceptibility plots for **2-Gd** fall slightly short of this value, similar to what is observed for **1-Gd**. This is likely the result of intermolecular antiferromagnetic coupling.²⁵ To rule out the effects of intermolecular interactions, a 9.1 mM solution of **2-Gd** in THF was analyzed. Dc susceptibility data could be fit from 2 to 100 K and the low-temperature $\chi_{\text{M}}T$ value matches the value predicted for $S = 6$. The

coupling constant extracted from the fit to the solution data is close to that obtained for solid samples of **2-Gd**.

Table S4.5. Parameters used to fit the dc susceptibility data for **2-Gd**.

	Field (T)	$J_{\text{Gd-rad}} (\text{cm}^{-1})$	$J_{\text{inter}} (\text{cm}^{-1})$	TIP (cm^{-1})	Residual
Solid Sample	0.1	-43.0(1)	$-6.9(8) \times 10^{-3}$	$1.3(5) \times 10^{-2}$	11.3
Solid Sample	0.5	-40.5(1)	$-6.8(9) \times 10^{-3}$	$1.1(6) \times 10^{-2}$	13.5
Solid Sample	1	-44.5(1)	$-5.4(1) \times 10^{-3}$	$1.1(6) \times 10^{-2}$	15.5
9.1 mM Solution	1	-50(4)	-	-	6.7

To confirm the $S = 6$ ground-state in **2-Gd**, magnetization measurements were performed on a 9.1 mM solution of **2-Gd** at temperatures of 10, 25 and 100 K and applied fields ranging from 1 to 70 kOe (0.1 to 7 T). The resulting data could be fit to a Brillouin function for $S = 6$ at all measured temperatures and fields. This suggests that the $S = 6$ ground state in **2-Gd** is exclusively populated up to at least 100 K, consistent with the electronic structure diagram estimated from the magnetic susceptibility data (see Electronic Structure Analysis for **2-Gd**). Measurements could not be performed at higher temperatures, as the diamagnetic contribution of the solvent overwhelmed the paramagnetism of the complex at temperatures above 100 K.

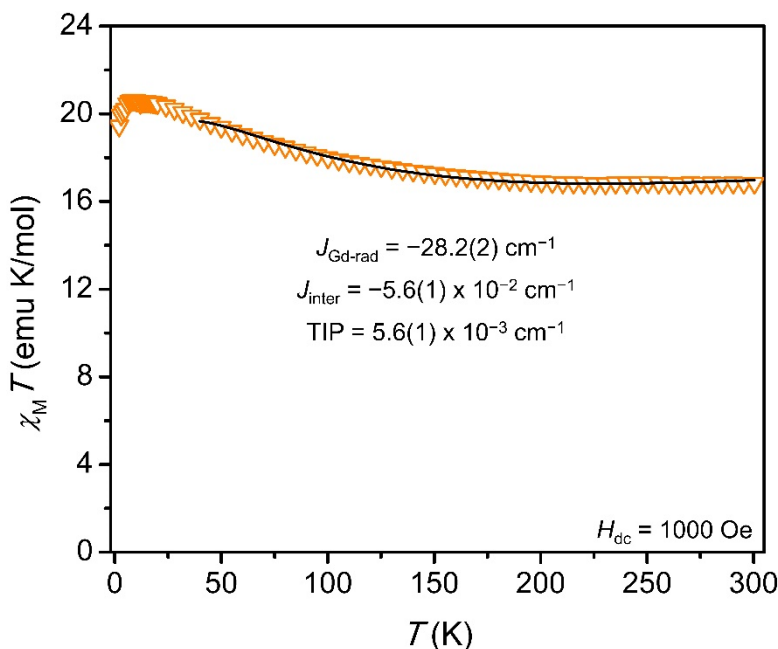


Fig. S4.45. Dc magnetic susceptibility measurement for **1-Gd** under an applied dc magnetic field of 1000 Oe. The black line represents a fit to the data.

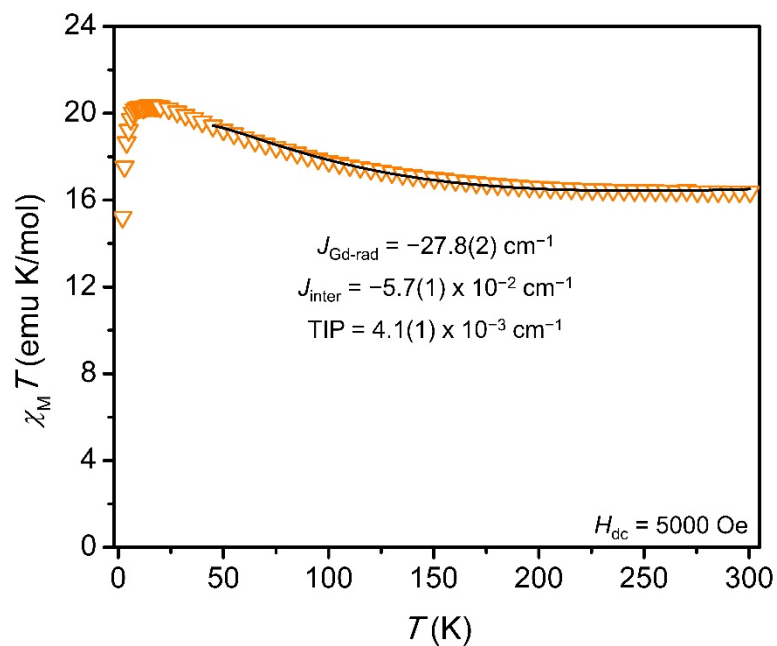


Fig. S4.46. Dc magnetic susceptibility measurement for **1-Gd** under an applied dc magnetic field of 5000 Oe. The black line represents a fit to the data.

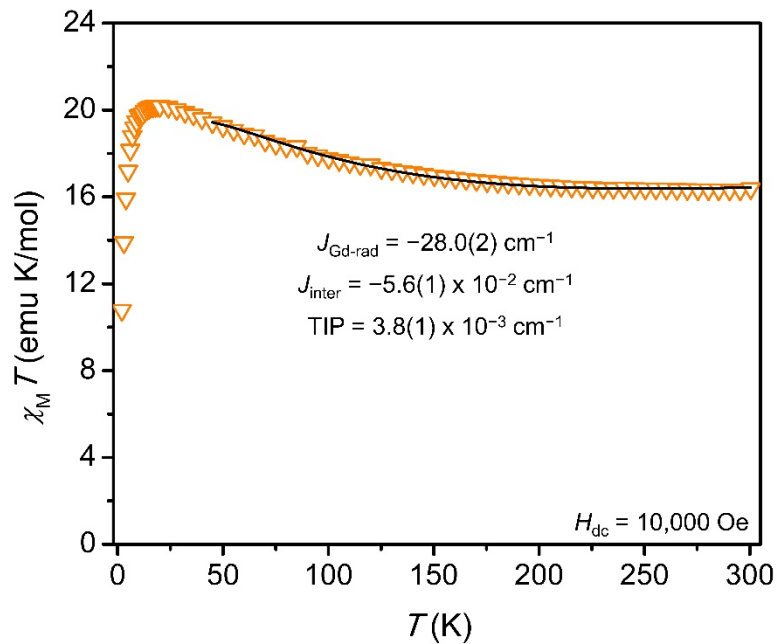


Fig. S4.47. Dc magnetic susceptibility measurement for **1-Gd** under an applied dc magnetic field of 10,000 Oe. The black line represents a fit to the data.

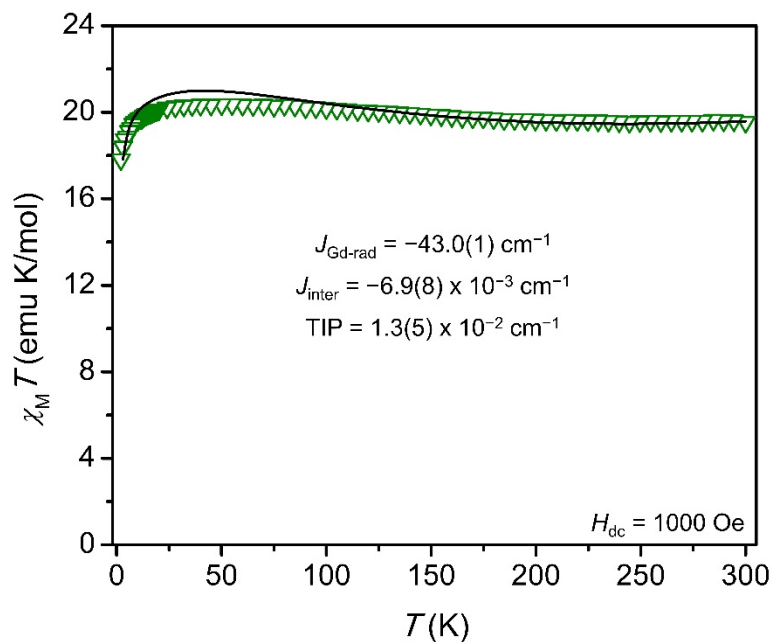


Fig. S4.48. Dc magnetic susceptibility measurement for **2-Gd** under an applied dc magnetic field of 1000 Oe. The black line represents a fit to the data.

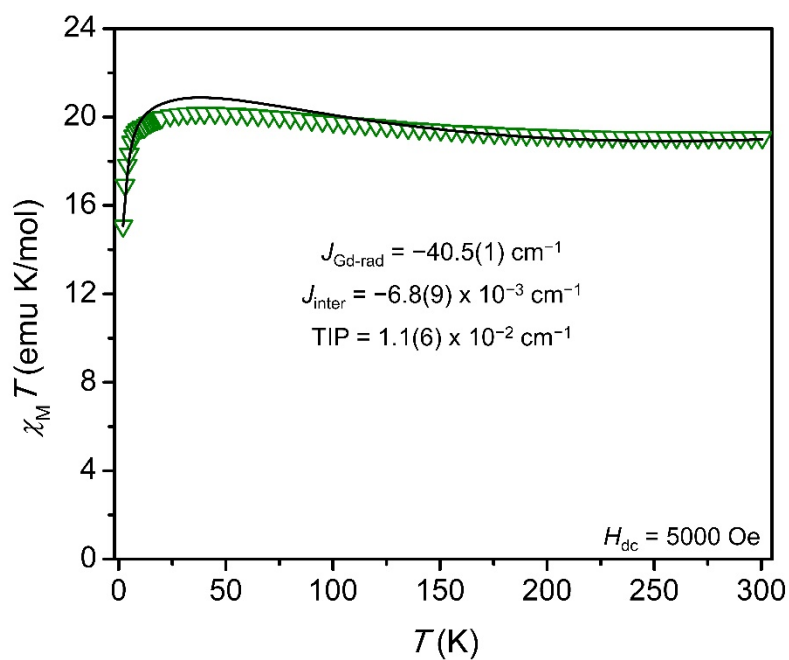


Fig. S4.49. Dc magnetic susceptibility measurement for **2-Gd** under an applied dc magnetic field of 5000 Oe. The black line represents a fit to the data.

4.6.5 Electronic Structure Analysis for 2-Gd

The electronic structure in **2-Gd** can be approximated using experimental data. The benzene dianion in the BzN₆-Mes ligand has two states: $S = 1$ and $S = 0$. The relative energy of these states can be estimated with ΔE_{ST} for **2-Y** (8.7 cm⁻¹), which was determined experimentally via variable temperature CW-EPR. The $S = 0$ state is arbitrarily set to 0 and the $S = 1$ state is therefore placed at 8.7 cm⁻¹. We believe this to be a reasonable approximation, as previous studies have shown that changing the cation coordinated to the benzene dianion has a minimal impact on ΔE_{ST} , resulting in differences of only ~0.1 kcal/mol (35 cm⁻¹).⁴¹ Furthermore, Y³⁺ and Gd³⁺ have similar ionic radii of 104.0 and 107.8 pm, respectively, that should limit structural changes in the [M₂(BzN₆-Mes)]²⁻ complex that could alter ΔE_{ST} .

The two states of the benzene dianion interact with the spin of two $S = 7/2$ Gd³⁺ ions to give rise to the electronic states in **2-Gd**. These interactions can be approximated using exchange coupling constants (J_{Gd-rad} and J_{Gd-Gd}) extracted from fits to experimental magnetic susceptibility data.

The $S = 1$ state of the benzene dianion interacts strongly with the two Gd³⁺ ions to generate $S = 6$, $S = 1$, and $S = 8$ states. This interaction is described by the following spin Hamiltonian:

$$\hat{H} = -2J_{Gd-rad}\hat{S}_{rad}\cdot(\hat{S}_{Gd(1)} + \hat{S}_{Gd(2)})$$

A value of $J_{Gd-rad} = -43.0(1)$ cm⁻¹ can be extracted from fitting the experimental magnetic susceptibility data obtained at 1000 Oe for **2-Gd** to the above Hamiltonian. We believe that this value is reasonable, as a similar value was extracted from the magnetic susceptibility data for **1-Gd** (-28.2(2) cm⁻¹ using data obtained at 1000 Oe). The smaller value of J_{Gd-rad} in **1-Gd** can be explained by the longer Gd-benzene_{cent} distance in **1-Gd** as compared to **2-Gd**. Using J_{Gd-rad} for **2-Gd**, the spin Hamiltonian predicts that the $S = 6$ state is stabilized by 597.8 cm⁻¹ relative to the $S = 1$ state, which is stabilized by an additional 597.8 cm⁻¹ relative to the $S = 8$ state. The $S = 6$, $S = 1$, and $S = 8$ states are thus placed at -592.2, 8.7, and 606.5 cm⁻¹, respectively, on the energy diagram for **2-Gd**.

The $S = 0$ state of the benzene dianion interacts with the two Gd³⁺ ions via a weak superexchange mechanism to generate $S = 7$ and $S = 0$ states. This interaction is described by the following spin Hamiltonian:

$$\hat{H} = -2J_{Gd-Gd}\hat{S}_{Gd(1)}\cdot\hat{S}_{Gd(2)}$$

J_{Gd-Gd} cannot be determined from the magnetic susceptibility data collected for **2-Gd**, as only the $S = 6$ ground state of the complex is observed experimentally. J_{Gd-Gd} can be estimated from literature values, however. For instance, an analogous complex in which two Gd³⁺ ions are bridged by an $S = 0$ tetraanionic biphenyl ligand shows $J_{Gd-Gd} = -0.7$ cm⁻¹.⁴² This is typical for exchange coupling in Gd³⁺ mediated by closed-shell bridging ligands. Indeed, the vast majority of complexes with closed-shell bridging ligands reported in the literature show $|J_{Gd-Gd}| < 1$ cm⁻¹. Using $J_{Gd-Gd} = -0.7$ cm⁻¹, the spin Hamiltonian predicts that the $S = 0$ state is stabilized by 17.2 cm⁻¹ relative to the $S = 7$ state. The $S = 0$ and $S = 7$ states are thus placed at -8.6 and 8.6 cm⁻¹, respectively, on the energy diagram for **2-Gd**.

According to this diagram, the ground electronic state in **2-Gd** arises from an antiferromagnetic interaction between the $S = 1$ state of the benzene dianion and the two Gd^{3+} ions. It is important to note that this is not a covalent interaction. The valence 4f orbitals of the lanthanides are contracted and core-like, thus these elements engage in predominantly electrostatic interactions. This is fundamentally different from the highly covalent interactions observed for transition metal and actinide ions with annulene ligands.^{26,27}

The first excited state in **2-Gd** arises from a weak, antiferromagnetic superexchange interaction between the $S = 0$ state of the benzene dianion and the two Gd^{3+} ions. The energetic separation between the first excited state and the ground state is $\sim 580 \text{ cm}^{-1}$. Although this value is an approximation, it is consistent with experimental observations. The magnetic susceptibility and magnetization data for **2-Gd** is best fit assuming an $S = 6$ ground state. The magnetization data suggest that this ground state is exclusively populated up to at least 100 K. Furthermore, the room temperature $\chi_M T$ value is larger than that expected for a free $S = 1$ ligand and two $S = 7/2$ Gd^{3+} ions, implying that the $S = 6$ ground state is still predominantly occupied at 300 K. Significant occupation of the $S = 0$ excited state would cause this value to decrease substantially.

Table S6. Estimated relative energies for the electronic states in **2-Gd**.

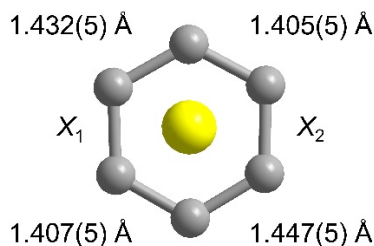
State	Energy (cm^{-1})
$S = 8$	606.5
$S = 7$	8.6
$S = 1$	8.7
$S = 0$	-8.6
$S = 6$	-589.1

4.6.6 Density Functional Theory (DFT) Calculations

All DFT calculations were carried out with the ORCA 4.2.1 program.⁴³ Broken-symmetry DFT calculations were run on **1-Gd** to determine the exchange coupling constants between the Gd(III) ions and the benzene radical.⁴⁴ The DFT calculated values of $J_{\text{Gd1-rad}} = -30.29 \text{ cm}^{-1}$ and $J_{\text{Gd2-rad}} = -29.78 \text{ cm}^{-1}$ are quite close to the fitted values, supporting the strong antiferromagnetic exchange interactions observed in the magnetic data collected for this complex.

The relative energy of the singlet and triplet states in **2-Y** were calculated using the B3LYP functional and def2-TZVP basis set on all atoms together with the RIJCOSX approximation and TightSCF, Grid6 GridX6. The relative energy of the singlet and triplet states were also calculated for complexes in which two parallel C–C bonds in the central benzene ring of **2-Y** were stretched or compressed to simulate a quinoidal distortion, a molecular distortion that is characteristic of dianionic benzene rings. This computational study reveals that the singlet state is preferentially stabilized as the quinoidal distortion lengthens, accompanied by an increase in the singlet-triplet gap (Table S4.7).

Table S4.7. Single-point energy (Ha) of the $S = 1$ and $S = 0$ states for **2-Y** and three distorted structures. Calculations were performed using the experimentally-determined X-ray structure of **2-Y**. Two parallel C–C bonds within the central benzene ring, X_1 and X_2 , were either stretched or compressed to simulate a quinoidal distortion.



	$X_1 = 1.466$ $X_2 = 1.455$	$X_1 = 1.486^a$ $X_2 = 1.475^a$	$X_1 = 1.506$ $X_2 = 1.495$	$X_1 = 1.526$ $X_2 = 1.515$
$S = 1$ state (Ha)	-4129.682008966	-4129.679977731	-4129.67387185	-4129.66677092
$S = 0$ state (Ha)	-4129.681847009	-4129.681289490	-4129.67713529	-4129.67136409
ΔE_{ST} (kcal/mol)	-0.10	0.82	2.05	2.88

^aDistances obtained from the X-ray structure of **2-Y**

These DFT calculations also showed that the highest two singly-occupied molecular orbitals (SOMOs) are localized on the central benzene ring in the BzN₆-Mes ligand (**Fig. S4.50**).

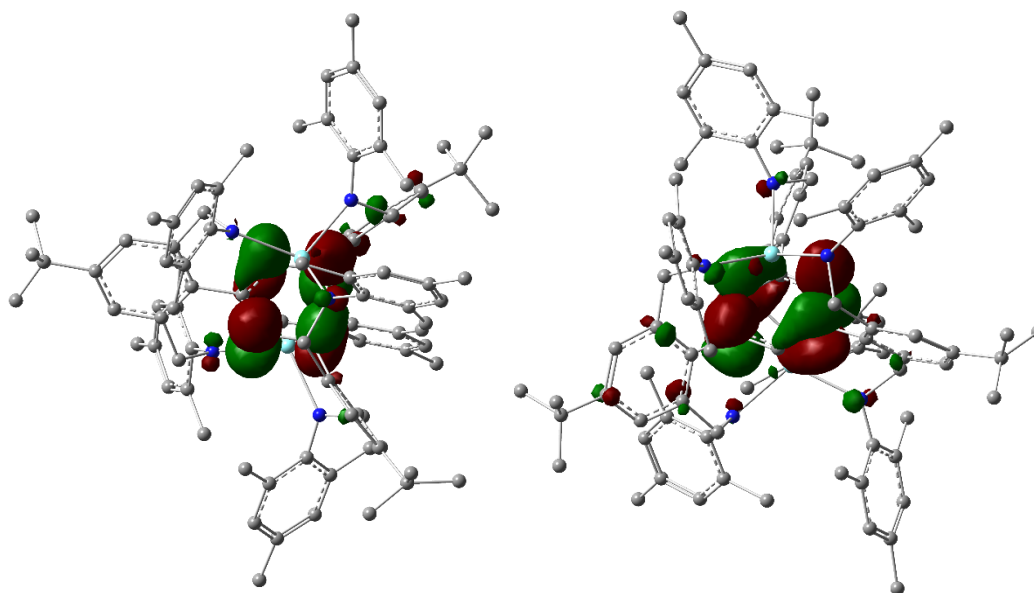


Fig. S4.50. SOMO orbitals in **2-Y** complex obtained from DFT.

Nucleus independent chemical shift (NICS) calculations were performed as described elsewhere, using a PBE0 or B3LYP functional with def2-SVP basis set within the ORCA program (Table S4.8).²⁸⁻²⁹ A dummy atom was employed in the center of the central benzene ring, and two more positions perpendicular to the ring, 0.5 Å and 1.0 Å, were also calculated. The X-ray determined structure was used in the calculation without optimization. Calculations were performed on only the six atoms of the central benzene ring in **2-Y** and **2-Gd** using the B3LYP functional, as the [M₂BzN₆-Mes]²⁻ complex contains 104 non-hydrogen atoms and is therefore quite time-intensive and challenging to investigate. NICS calculations were also performed on the entire [Gd₂BzN₆-Mes]²⁻ complex in the structure of **2-Gd** to corroborate these results. The PBE0 functional was used for this calculation.

Table S4.8. Nucleus independent chemical shift (NICS) values.

	NICS(0)	NICS(0.5)	NICS(1.0)
Central benzene ring, 2-Y ^a	-9.1	-10.9	-11.2
Central benzene ring, 2-Gd ^a	0.5	-1.2	-1.2
[Gd ₂ BzN ₆ -Mes] ²⁻ complex, 2-Gd ^b	-6.9	-7.9	-7.6

^aCalculated using B3LYP functional

^bCalculated using PBE0 functional

The harmonic oscillator model of aromaticity (HOMA) index was calculated for **2-Y** and **2-Gd** by using the following formula:

$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_i - R_{opt})^2$$

where n is the number of C–C bonds in the benzene ring, R_i and R_{opt} correspond to the i th bond length in the analyzed ring and the reference optimized benzene ring and $\alpha = 257.7 \text{ \AA}^{-2}$ is a normalization factor.³⁰ The DFT optimized structures for **2-Y** and **2-Gd** at the BP-RI/def2-SVP level of theory were used for the calculations of HOMA indexes, as were the experimentally determined crystal structures.

4.6.7 Supplementary Information References

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Chapter 5: High-Temperature Magnetic Blocking and Magneto-Structural Correlations in a Series of Dysprosium(III) Metallocenium Single-Molecule Magnets

K. R. McClain,[†] C. A. Gould,[†] K. Chakarawet, S. J. Teat, T. J. Groshens, J. R. Long, B. G. Harvey
Chem. Sci. **2018**, 9, 8492–8503.^a

5.1 Introduction

Single-molecule magnets show potential in spin-based computing and information storage, but such applications are currently precluded by low operating temperatures.¹ The operating temperature is typically defined by the magnetic blocking temperature (T_b)—the temperature at which the magnetic relaxation time, τ , is equal to 100 seconds—or, less quantitatively, by the maximum temperature at which magnetic hysteresis is observed.² Many of the most significant advances in increasing T_b for single-molecule magnets have been made with lanthanide-based systems, as the large anisotropies of the 4f elements can be exploited to achieve unparalleled thermal barriers to magnetic relaxation.³ In particular, strongly-coupled, multinuclear lanthanide complexes have dominated efforts to maximize operating temperature, as the giant-spin ground states of these molecules can suppress rapid through-barrier magnetic relaxation processes that often preclude magnetic hysteresis.⁴

Recently, the Dy^{III} metallocenium salt $[\text{Dy}(\text{Cp}^{\text{t}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Cp}^{\text{t}} = 1,2,4\text{-tri(tert-butyl)cyclopentadienyl}$) was reported to show magnetic hysteresis at temperatures up to 60 K, as observed using a sweep rate of 2.2 mT/s,⁵ a substantial increase over the previous record of 28 K.^{4c} Significantly, this molecule represents an outlier in its class: while the majority of mononuclear single-molecule magnets show only waist-constricted magnetic hysteresis and little or no remanent magnetization due to quantum tunneling of the magnetization,⁶ $[\text{Dy}(\text{Cp}^{\text{t}})_2]^+$ retains polarization at zero field and high temperatures.[§] Magnetic and computational studies suggest that the impressive magnetic properties of $[\text{Dy}(\text{Cp}^{\text{t}})_2]^+$ arise from its unique coordination environment—in particular, the rigid η^5 -cyclopentadienyl ligands constrain metal-ligand vibrational modes, thereby reducing pathways for through-barrier relaxation.^{5b} This represents a new approach to limiting through-barrier magnetic relaxation and enabling higher operating temperatures. It is thus essential to develop a deeper understanding of how structure influences the magnetic properties of $[\text{Dy}(\text{Cp}^{\text{x}})_2]^+$ complexes in order to determine how coordination environment can be tuned to further increase operating temperatures.^{§§}

The design of mononuclear 4f-element single-molecule magnets can be guided by a simple electrostatic model that compares the shape of lanthanide M_J electron distributions to the crystal field.⁷ A number of studies of mononuclear, D_{5h} -symmetric complexes with strongly-donating axial ligands have demonstrated the validity of this qualitative approach, with molecules in this class possessing thermal barriers to magnetic relaxation as large as 1260 cm⁻¹.^{3b-f} Importantly, the electrostatic model provides a rationale for the high anisotropy engendered by the axial cyclopentadienyl ligands in $[\text{Dy}(\text{Cp}^{\text{t}})_2]^+$ and outlines a clear route for improvement. Increasing the Cp–Dy–Cp angle of this bent metallocene from 152.56(7)° toward 180° and shortening the

[†]These authors contributed equally to this work.

^a C.A.G. collected and interpreted the magnetic data. K.R.M. synthesized the compounds. C.A.G., K.C., S.J.T., and T.G. collected the crystal structure data and K. C. solved and refined the structures. The manuscript was written by C.A.G., K.R.M., B.G.H., and J.R.L. and all authors contributed to editing it.

Dy–Cp bond distances should increase the axiality of the crystal field, leading to larger thermal barriers to magnetic relaxation and higher potential operating temperatures.

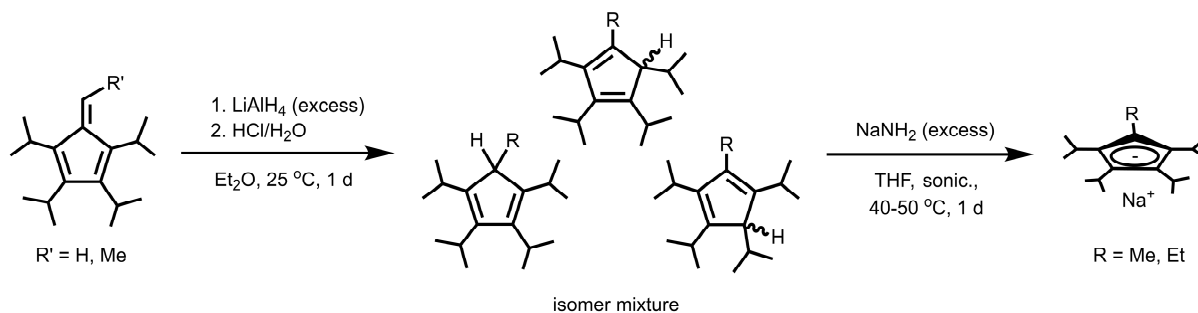
Equally important in the design of new $[\text{Dy}(\text{Cp}^{\text{X}})_2]^+$ molecules are the metal-ligand vibrational modes. Phonons—vibrational modes of the lattice that couple to the electronic states of a molecule—provide the necessary energy for magnetic relaxation⁸ and determine viable relaxation processes at a given temperature. Computational studies indicate that high-temperature magnetic relaxation in $[\text{Dy}(\text{Cp}^{\text{III}})_2]^+$ is induced by Cp–H bending modes,^{5b} leading to the suggestion that substituting the hydrogen positions in this molecule with rigid functional groups could result in more constrained vibrations, further slowing magnetic relaxation and resulting in magnetic hysteresis at higher temperatures.

Herein, we report a series of Dy^{III} metallocenium cation salts, $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (R = H (1), Me (2), Et (3), *i*Pr (4)), in which subtle variation of the substituents on the cyclopentadienyl rings produces molecules with a large range of Dy–C distances and Cp–Dy–Cp angles. This series includes Dy^{III} metallocenium salts of two new cyclopentadienyl ligands, $\text{Cp}^{i\text{Pr}4\text{R}}$ (R = Me, Et). By varying the substituents, it is also possible to tune the metal-ligand vibrational modes in these complexes. Modifications result in a record high thermal barrier to magnetic relaxation (U_{eff}) of 1468 cm^{−1} and a record high 100-s magnetic blocking temperature of 62 K for the methyl-substituted complex, 2. A careful comparison of the structural and magnetic properties in this series elucidates important design principles for the synthesis of further new Dy^{III} metallocenium single-molecule magnets.

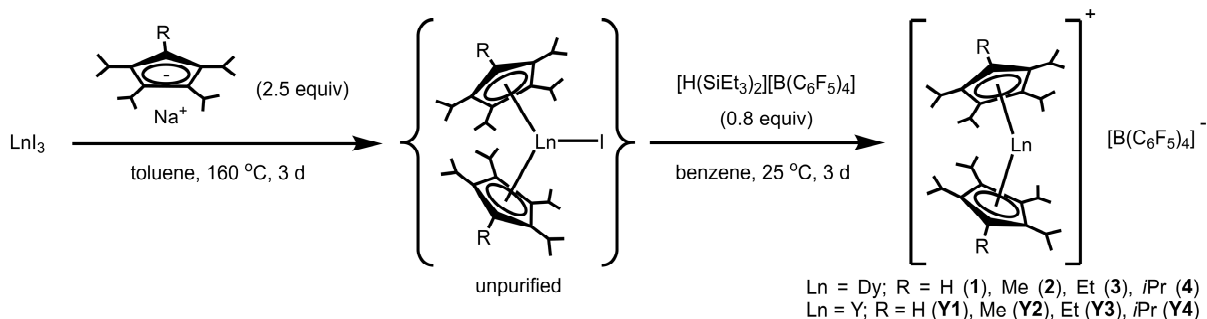
5.2 Results and Discussion

In designing this series of complexes, we sought tetra- and penta-substituted cyclopentadienyl ligands with sufficient steric bulk to preclude coordination of equatorial ligands, such as coordinating solvent. We thus targeted the known tetra- and penta-isopropyl substituted Cp ligands, as well as two new tetraisopropyl substituted Cp variants, all of which were obtained as the sodium salts, $\text{NaCp}^{i\text{Pr}4\text{R}}$ (R = H, Me, Et, *i*Pr). The tetraisopropyl substituted ligand, $\text{NaCp}^{i\text{Pr}4}$ was synthesized as previously described by step-wise deprotonation and alkylation of cyclopentadiene in three steps.⁹ Although it is possible to obtain $\text{NaCp}^{i\text{Pr}5}$ by further direct alkylation of $\text{NaCp}^{i\text{Pr}4}$, the yield for the final alkylation step is very low, producing mainly geminally-substituted isomers. Rather, $\text{NaCp}^{i\text{Pr}5}$ was obtained from $\text{NaCp}^{i\text{Pr}4}$ in four steps using the high-yielding fulvene route.¹⁰ The lithium salt acquired initially was hydrolyzed and then deprotonated with NaNH_2 , activated by sonication, to give the desired sodium salt.¹¹

In order to complete a stepwise series of metallocenium salts in which the R group in $\text{Cp}^{i\text{Pr}4\text{R}}$ varies by only one methyl or methylene group in adjacent members of the series, it was necessary to synthesize the heretofore unknown tetraisopropyl substituted Cp ligand salts $\text{NaCp}^{i\text{Pr}4\text{R}}$ (R = Me, Et). This was achieved by exploitation of the fulvene route used to prepare $\text{NaCp}^{i\text{Pr}5}$. Here, tetraisopropylfulvene and methyl-substituted tetraisopropylfulvene¹⁰ reacted with excess LiAlH_4 and were then hydrolyzed to produce the corresponding cyclopentadiene isomer mixtures. These were then converted to the sodium salts $\text{NaCp}^{i\text{Pr}4\text{Me}}$ and $\text{NaCp}^{i\text{Pr}4\text{Et}}$ with sonication in the presence of excess NaNH_2 (Scheme 5.1). In all cases, the sodium salts were preferred for their moderate solubility and ready accessibility as ether-free compounds, allowing facile workup in subsequent steps. For example, the lithium salt of $\text{Cp}^{i\text{Pr}5}$ is obtained as the diethyl etherate and is soluble in pentane,¹⁰ whereas the sodium salt can be freed of coordinated THF by heating under vacuum and is soluble in arenes but insoluble in alkanes.



Scheme 5.1. Synthesis of $\text{NaCp}^{i\text{Pr}4\text{Me}}$ and $\text{NaCp}^{i\text{Pr}4\text{Et}}$.



Scheme 5.2. Synthesis of metallocene salts **1-4** and **Y1-Y4**.

With the Cp transfer reagents in hand, we turned to the synthesis of the neutral dysprosium compounds, $\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2\text{X}$ ($\text{R} = \text{H, Me, Et, } i\text{Pr}$) ($\text{X} = \text{Cl, Br, I}$). The most common strategy for transfer of Cp ligands to Ln^{III} centers involves the reaction of MCp^x (commonly $\text{M} = \text{Li, Na, K}$) with a lanthanide halide. For Sm, Eu, and Yb, which have relatively stable divalent oxidation states, the initial reaction can occur between MCp^x and LnI_2 , followed by oxidation to obtain the Ln^{III} complex; an example of this approach is the well-known synthesis of SmCp^*_3 .¹²

In many cases, the lanthanide iodide is preferred over the other halides, especially in the case of very bulky ligand environments.¹³ For instance, the reaction of $\text{YCp}''_2\text{X}$ ($\text{Cp}'' = 1,3\text{-bis}(\text{trimethylsilyl})\text{cyclopentadienyl}$, $\text{X} = \text{Cl, I}$) with KCp'' in refluxing toluene to produce YCp''_3 was most successful when $\text{X} = \text{I}$.¹⁴ Our own exploratory reactions with YCl_3 and excess $\text{NaCp}^{i\text{Pr}5}$ (2.2 equiv) in toluene at 130 °C indicated $\text{YCp}^{i\text{Pr}5}\text{Cl}_2$ as the dominant product, and thus we opted for DyI_3 or $\text{DyI}_3(\text{THF})_3$ as the most promising Dy^{III} sources. In some cases, the THF adduct allows for substitutions that are not possible with the unsolvated precursor, such as in the reaction of $\text{YbCp}''_2\text{I}(\text{THF})$ with KCp'' to form YbCp''_3 .¹⁴ Conversely, the presence of THF can result in unproductive side reactions.¹⁵ In our hands, reaction of $\text{DyI}_3(\text{THF})_3$ with $\text{NaCp}^{i\text{Pr}5}$ in toluene at 130 °C resulted in isolation of THF ring-opened products, as has been observed previously during attempts to synthesize SmCp^*_3 from the di-substituted Sm^{III} salt.¹² Therefore, DyI_3 was used in all subsequent reactions.

In general, DyI_3 and a Cp transfer reagent $\text{NaCp}^{i\text{Pr}4\text{R}}$ ($\text{R} = \text{H, Me, Et, } i\text{Pr}$) (2.5 equiv) were heated together at 160 °C in toluene for three days to generate the putative intermediate complexes $\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2\text{I}$ ($\text{R} = \text{H, Me, Et, } i\text{Pr}$), which were isolated from excess ligand and NaI by extraction with pentane (Scheme 5.2). A pressure flask was used to obtain the high temperature necessary for complete di-substitution.

Crystallization of $\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2\text{I}$ from pentane at low temperature (−35 °C) was largely fruitless owing to the high solubility of the compounds. Instead, the crude products were used directly in the subsequent halide abstraction step. The addition of a sub-stoichiometric quantity (0.8 equiv)

of $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ —freshly prepared before use¹⁶—to pale yellow benzene solutions of $\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2\text{I}$ ($\text{R} = \text{H, Me, Et, } i\text{Pr}$) resulted in a rapid color change to a more vibrant color ranging from yellow to orange. In most cases, yellow-orange powdery to oily precipitate was also observed, which changed over the course of several days, typically becoming more solid and increasing in volume. It is known that reactions involving $[\text{SiEt}_3]^+$ in benzene are complex, forming biphasic mixtures.¹⁶ This may be the source of the oily precipitates observed initially in some cases. It was assumed that the initial challenging reaction of DyI_3 with $\text{NaCp}^{i\text{Pr}4\text{R}}$ was not quantitative, therefore a sub-stoichiometric (versus DyI_3) quantity of $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ was employed in the reactions. Here, we wanted to avoid the presence of excess $[\text{SiEt}_3]^+$ in the reaction mixtures, which can render purification more difficult. After stirring for several days at room temperature, the desired Dy^{III} metallocene salts $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{H}$ (**1**), **Me** (**2**), **Et** (**3**), $i\text{Pr}$ (**4**)) were obtained as crude powders (Scheme 5.2) and subsequently recrystallized 2-3 times by layering dichloromethane solutions of the salts with pentane. In this way, analytically pure material and crystals suitable for X-ray diffraction analysis were obtained. After drying under reduced pressure, compounds **1-4** were obtained as yellow (**1**), orange-yellow (**2-3**) or orange crystals (**4**) and found to be indefinitely stable at room temperature under argon; however at ambient temperatures in air they decay rapidly with an accompanying color change to green/blue.

To obtain solid-state dilutions of **1-4**, it was necessary to synthesize the diamagnetic Y^{III} analogues, $[\text{Y}(\text{Cp}^{i\text{Pr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{H}$ (**Y1**), **Me** (**Y2**), **Et** (**Y3**), $i\text{Pr}$ (**Y4**)) (see Supplementary Information 5.6 for experimental procedures). Utilizing an analogous route to that employed for **1-4**, YI_3 was converted to the putative $\text{Y}(\text{Cp}^{i\text{Pr}4\text{R}})_2\text{I}$ ($\text{R} = \text{H, Me, Et, } i\text{Pr}$) complex by reaction with the appropriate $\text{NaCp}^{i\text{Pr}4\text{R}}$ ($\text{R} = \text{H, Me, Et, } i\text{Pr}$) (2.5 equiv) at high temperature, followed by iodide abstraction with $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (Scheme 5.2). The Y^{III} metallocenium complexes were obtained as colorless (**Y1**) to yellow crystals (**Y2-Y4**) after multiple recrystallizations followed by prolonged drying under vacuum. Like the Dy^{III} metallocenes salts, **Y1-Y4** are stable under argon at ambient temperature, but decay rapidly in air as indicated by the appearance of a green/blue color.

NMR spectra were obtained for the diamagnetic Y^{III} analogues **Y1-Y4** to assess their structural dynamics in solution (Figure S5.15-S5.26). **Y1** exhibited sharp, fully resolved signals at 25 °C in the ^1H -NMR spectra. Two methine ($-\text{CH}(\text{CH}_3)_2$) septets and four methyl ($-\text{CH}(\text{CH}_3)_2$) doublets were observed, consistent with restricted Cp- $i\text{Pr}$ bond rotation giving rise to separate methyl group (inner and outer CH_3) environments.¹⁷ At 25 °C, **Y4** displayed somewhat broadened peaks, which sharpened at -10 °C to three methyl ($-\text{CH}(\text{CH}_3)_2$) doublets ($\delta = 1.07, 1.66, 1.69$) and one methine ($-\text{CH}(\text{CH}_3)_2$) septet. The two closely spaced downfield doublets probably correspond to the inner methyl group of the *rac* and *meso* isomers, while the upfield doublet likely corresponds to the outer methyl group of both isomers. Similar features have been associated with *rac* and *meso* isomers for $[(\text{Cp}^{i\text{Pr}5})_2\text{M}]$ ($\text{M} = \text{Ca, Sr, Ba}$).¹⁸ The ^{13}C spectrum of **Y4** also indicates *rac* and *meso* isomers, with four methyl ($-\text{CH}(\text{CH}_3)_2$) and two methine ($-\text{CH}(\text{CH}_3)_2$) peaks. The ^1H spectra of **Y2** and **Y3** vary substantially with temperature. For **Y2**, one methyl singlet (Cp- CH_3), two overlapping methine ($-\text{CH}(\text{CH}_3)_2$) septets and broadened peaks representing the four methyl ($-\text{CH}(\text{CH}_3)_2$) environments are observed at 25 °C, however, when heated to 75 °C, the four methyl ($-\text{CH}(\text{CH}_3)_2$) doublets are sharp and fully resolved. In the case of **Y3** at 25 °C, sharp peaks are observed for the ethyl (Cp- CH_2CH_3) group and one of the methine ($-\text{CH}(\text{CH}_3)_2$) signals, while one methine ($-\text{CH}(\text{CH}_3)_2$) group is broadened and the methyl ($-\text{CH}(\text{CH}_3)_2$) peaks are observed as a single broad resonance. Heating to 85 °C results in sharp peaks for all groups, although three of the four methyl ($-\text{CH}(\text{CH}_3)_2$) doublets are overlapping.

The solid-state structures of the metallocene salts **1-4** were elucidated by single-crystal X-ray diffraction analysis (Figure 5.1). Compounds **1** and **2** crystallize with two $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ molecules in the asymmetric unit, while compounds **3** and **4** crystallize with only one molecule in the asymmetric unit. The structural analyses were complicated by pseudomerohedral twinning for **1** and **2** and positional disorder in **2** and **4**. Two of the cyclopentadienyl ligands in the structure of **2** are disordered, each over two positions, and the Dy^{III} center in the structure of **4** displays positional disorder over four sites (see Supplementary Information 5.6 for refinement details). Twinning and disorder were found to be consistent over several tested crystal samples.

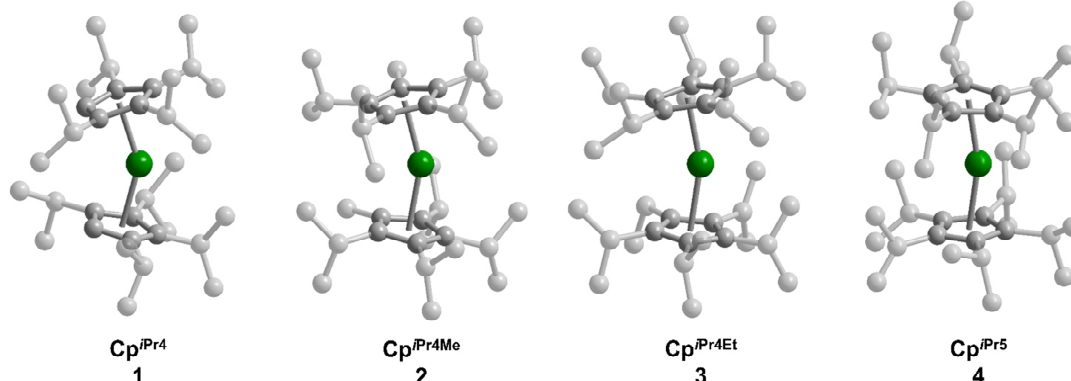


Figure 5.1. Crystal structure of $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{H}, \text{Me}, \text{Et}, i\text{Pr}$). Green and gray spheres represent Dy and C atoms, respectively; hydrogen atoms, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ counteranions, and positional disorder are omitted for clarity.

The Dy–Cp separations, as assessed by the distances from the Dy atom to the centroid of each cyclopentadienyl ligand, lie in the ranges 2.27(1)–2.30(1) Å for **1**, 2.273(3)–2.382(3) Å for **2**, 2.297(4)–2.306(4) Å for **3**, and 2.245(15)–2.392(16) Å for **4**. Because of the disorder present in each structure and the similarity in the resulting bond distances (within statistical error), it was not possible to derive a meaningful structural trend from these distances alone. Nonetheless, a trend can be drawn from the major component in each of the crystal structures: the average Dy–Cp(centroid) distances for the major component are 2.29(1), 2.298(5), 2.302(6), and 2.340(7) Å for **1-4**, respectively (Table 5.1). Although the average Dy–Cp(centroid) distance does not vary by more than the statistical error in some adjacent members of the series (e.g., **1** and **2**), the change is statistically significant across the series as a whole. Similarly, the average Dy–C distances for the major component are 2.587(5), 2.600(3), 2.596(2), and 2.625(3) Å for **1-4**, respectively. The increase of both the average Dy–Cp(centroid) and Dy–C distances suggests elongation of the interaction between the Dy atom and the cyclopentadienyl rings as the series progresses from **1** to **4**. In addition, the Cp–Dy–Cp angle increases across the series, lying in the ranges 146.5(8)–148.0(8), 155.9(3)–157.3(4), 161.1(2), and 157.8(2)–167.9(15)° in **1-4**, respectively (Table 5.1). The angle between the planes formed by the cyclopentadienyl rings follows a similar trend with values in the range of 148.1–150.5, 162.3–162.8, 165.0, and 172.5° for **1-4**, respectively. While the cyclopentadienyl rings in **4** are nearly parallel, the Dy atom moves off-center, leading to a reduced Cp–Dy–Cp angle. These structural trends are consistent with the expected steric environment imposed by the cyclopentadienyl ligands; that is, more sterically-encumbered substituents prompt the two cyclopentadienyl ligands in $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2]^+$ to be positioned further away from each other, increasing linearity and lengthening the average Cp–Dy bond distance.

The solid-state structures of the yttrium metallocene salts **Y1-Y4** were also investigated by single-crystal X-ray diffraction (Figure S5.31–S5.34). As in **1-4**, positional disorder complicated

the structural analyses. Compounds **Y1** and **Y2** crystallize with two molecules in the asymmetric unit; both the Y^{III} center and one cyclopentadienyl ligand display positional disorder over two sites.

Similar structural trends to those seen in **1-4** are observed for the series of Y^{III} congeners. Namely the average Cp–Y bond distance and Cp–Y–Cp angle generally increase across the series from **Y1** to **Y4**. The average Y–Cp(centroid) distances for the major component are 2.273(10), 2.305(6), 2.294(3), and 2.331(2) Å for **Y1-Y4**, respectively, and the average Cp–Y–Cp angles are 145.7(5), 157.1(4), 161.3(1) and 180°. While the Dy atom in **4** moves off-center of the cyclopentadienyl rings, the Y atom in **Y4** sits on an inversion center in the asymmetric unit, leading to a 180° Cp–Y–Cp angle. While both *rac* and *meso* isomers of **Y4** are observed in the ¹H- and ¹³C-NMR spectra, only the *meso* isomer is observed in the crystal structure.

In order to investigate the effect of the structural changes on the magnetic properties of each complex, dc magnetic susceptibility data were collected for **1-4** from 2 to 300 K under an applied magnetic field of 1 kOe (Figures S5.35, S5.37, S5.39, and S5.41). The room temperature χ_{MT} values for **2** and **3** are 14.17 and 14.28 emu K/mol, respectively, agreeing well with the expected value of 14.17 emu K/mol for a free Dy^{III} ion. The room temperature χ_{MT} values for **1** and **4** are slightly higher at 14.62 and 14.57 emu K/mol, respectively, likely due to the presence of weak temperature-independent paramagnetism (TIP). In the presence of a stronger applied field, TIP should be diminished, and accordingly χ_{MT} decreases to 14.18 and 14.25 emu K/mol for **1** and **4**, respectively, under a 10-kOe dc field (Figures S5.36 and S5.42). For all compounds, χ_{MT} gradually decreases as the temperature is lowered followed by a precipitous drop at low temperatures. This sudden decrease in χ_{MT} is indicative of magnetic blocking, wherein the magnetic moments of individual crystallites in the sample become pinned along a preferred axis and no longer respond to an external magnetic field.

Field-cooled and zero-field cooled measurements collected under an applied magnetic field of 1 kOe were compared for **1-4** (Figure 5.2), as the temperature at which these measurements diverge (T_{irrev}) can provide an estimate of the magnetic blocking temperature.² Divergence in these curves occurs at 28, 65, 60, and 60 K for **1** through **4**, respectively. Such a large range in T_{irrev} provided an initial indication that the structural changes across this series induce major changes in the magnetic behavior. This result also suggested that compound **2** might exhibit a higher operating temperature than [Dy(Cp^{III})₂]⁺, which shows a divergence in field-cooled and zero-field cooled data at 61 K.⁵ However, T_{irrev} varies with both the applied magnetic field used to conduct the experiment and the sweep rate,^{2,19} and thus we turned to measurements of the magnetic relaxation time to more accurately determine the operating temperature.

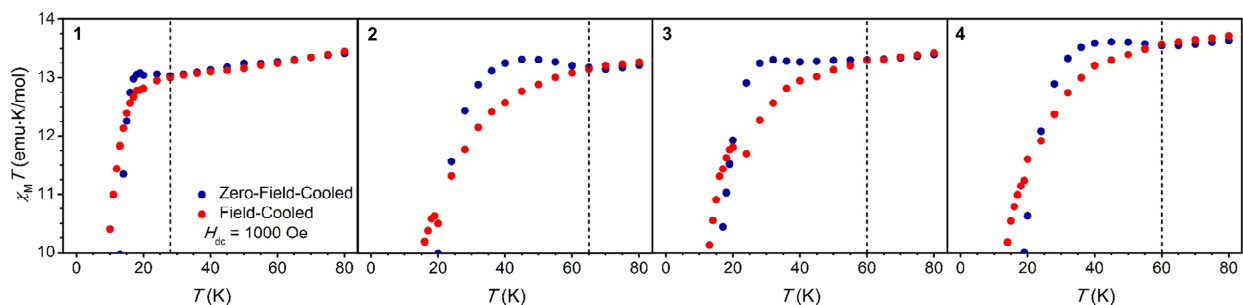


Figure 5.2. Field-cooled (red) and zero-field cooled (blue) magnetic susceptibility measurements collected at $H_{\text{dc}} = 1000$ Oe for **1-4** (left to right). Dashed lines mark T_{irrev} , the temperature at which the two plots diverge.

High-temperature magnetic relaxation in **1-4** was probed by ac magnetic susceptibility measurements from 70 to 114 K (Figure 5.3; Figure S5.43, S5.46, and S5.48). Magnetic relaxation times, τ , were extracted from a simultaneous fit of in-phase (χ') and out-of-phase (χ'') components of the magnetic susceptibility to a generalized Debye model (Figure S5.44, S5.45, S5.47, and S5.49). Despite the two molecules observed in the crystal structures of **1** and **2**, and the positional disorder in **2** and **4**, only one peak was observed in the ac susceptibility data for each compound. In this high temperature regime, Arrhenius plots of inverse temperature versus the natural log of τ are linear, indicative of a thermally-activated Orbach relaxation process (Figure 5.4, red circles).²⁰ All data could be fit to the equation $\tau^{-1} = \tau_0^{-1} e^{-U_{\text{eff}}/kT}$, yielding thermal barriers to magnetic relaxation (U_{eff}) of 1285, 1468, 1380, and 1334 cm^{-1} for **1** through **4**, respectively. These U_{eff} values surpass those reported for $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$, 1277 or 1223 cm^{-1} ,^{5a,5b} and the previous record of $U_{\text{eff}} = 1260 \text{ cm}^{-1}$ for $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{C}_5\text{H}_5\text{N})_5]^+$.^{3f}

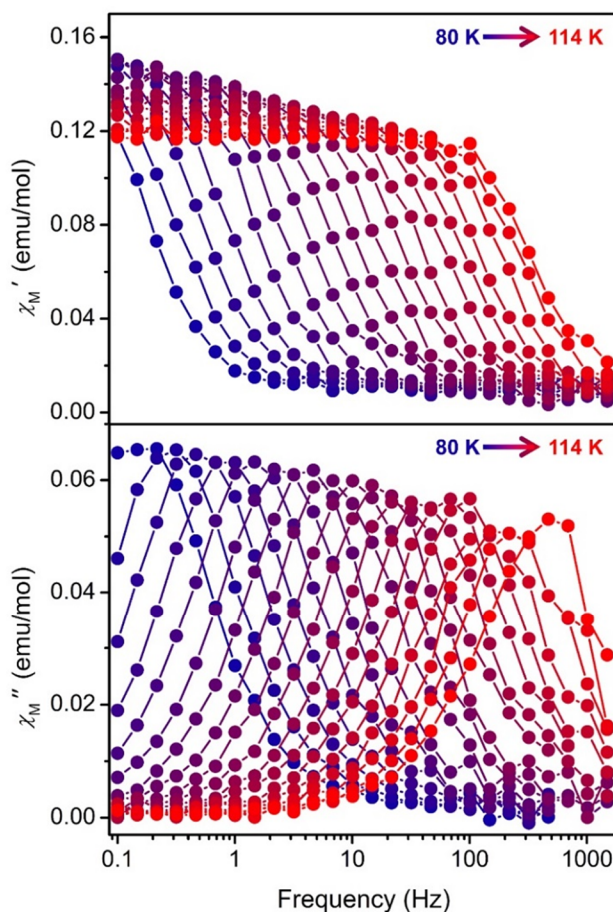


Figure 5.3. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **2** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 80–114 K (2 K steps). The colored lines are guides for the eye.

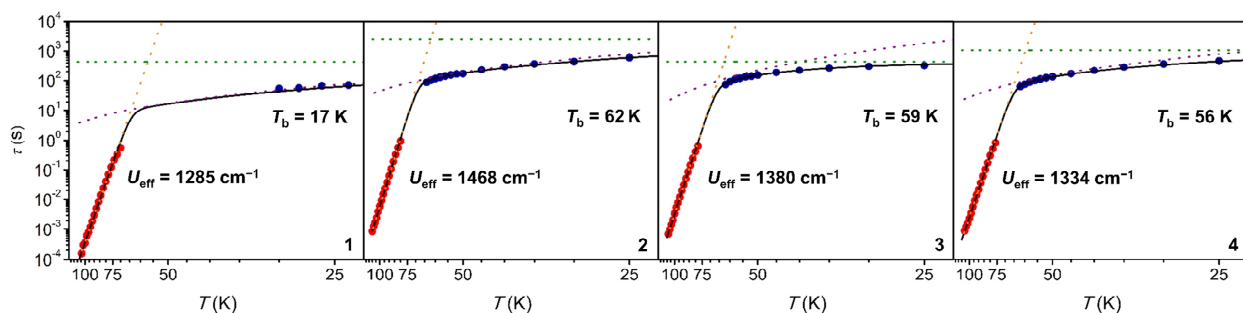


Figure 5.4. Plots of magnetic relaxation time (τ) on a log scale versus temperature (T) on an inverse scale for **1-4** (left to right) extracted from ac susceptibility (red circles) and dc relaxation (blue circles) data. Black lines represent fits to the data as described in the main text and are each a sum of Orbach (dashed orange line), Raman (dashed purple line), and quantum tunneling (dashed green line) relaxation processes.

The values of U_{eff} for **1-4** can be rationalized through structural trends. The magnitude of U_{eff} should depend on both the metal–ligand bond distances and the geometry of the ligand field (i.e., axial or equatorial). Such correlations have been quantified via *ab initio* calculations for a hypothetical two-coordinate Dy^{III} complex with alkyl ligands.²¹ In that study, it was found that U increased linearly with the L–M–L angle at low angles (90 to 150°), tapering its growth at high angles, and flattening above 170°. In contrast, U increased linearly as the M–L bond distance decreased across all bond lengths calculated.

In the series **1-4**, the most bent metallocene is **1**, with a Cp–Dy–Cp angle of 147.2(8)°. Complex **1** also shows the smallest thermal barrier to magnetic relaxation. Linearity increases by nearly 10° in **2** (156.6(3)°) and even further in **3** (161.1(2)°) and **4** (162.1(7)°), resulting in larger U_{eff} values for the high-angle set **2-4**. Within these three compounds, U_{eff} should vary less substantially with bond angle, and instead bond distance should have the largest impact on the relaxation barrier. Indeed, U_{eff} increases upon going from **4** to **2**, as the average Dy–C distance for the major disordered component in the crystal structure decreases.

This magneto-structural correlation is significant for the design of future Dy^{III} metallocene cations. While steric bulk in the cyclopentadienyl ligand increases the linearity of the complex in **1-4**, it also tends to promote longer Dy–C distances. These factors have opposing effects on the magnitude of U_{eff} , with the angle having a larger impact at low angles and the bond distance having a larger impact at high angles. Clearly, cyclopentadienyl ligands that can achieve a balance between promoting a large Cp–Dy–Cp angle and short Dy–C bond distances are worth pursuing.

Increasing the Cp–Dy–Cp angle and decreasing the Dy–C bond distances increases the axiality of the ligand field surrounding the Dy^{III} ion in these metallocenium salts, resulting in larger thermal barriers to magnetic relaxation. This is consistent with electrostatic models that have been used to guide the synthesis of lanthanide-based single-molecule magnets.⁷ Studies on molecules of the type $\text{Cp}^*_2\text{DyE}_n$ (E = equatorial ligand) have also found that increasing the axiality of the ligand field at Dy^{III} results in larger thermal barriers, with weaker equatorial ligands leading to larger U_{eff} .²²

To probe magnetic relaxation behavior at lower temperatures, dc magnetic relaxation measurements were conducted for **1-4** from 2 to 64 K (Figure 5.4, blue circles). Relaxation times were extracted from magnetization versus time plots by fitting the data with a stretched exponential function (for full details see the Supporting Information, Figures S5.50-S5.68, and Tables S5.3-6).

The temperature dependence of τ at intermediate temperatures (20 to 64 K) is indicative of Raman relaxation, while at low temperatures the relaxation time tends toward a constant value, indicative of quantum tunneling of the magnetization. The full range of ac magnetic susceptibility and dc magnetic relaxation data could be fit to the equation $\tau^{-1} = \tau_0^{-1}e^{-U_{\text{eff}}/kT} + CT^n + \tau_{\text{tunnel}}^{-1}$ (Figure 5.4 and Table 5.1).

Table 5.1. Comparison of selected structural parameters and magnetic data for $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (R = H (**1**), Me (**2**), Et (**3**), *i*Pr (**4**)).

	1	2	3	4	$^e[(\text{Cp}^{\text{ttt}})_2\text{Dy}]^+$
$^a\text{Cp-Dy-Cp}$ ($^\circ$)	147.2(8)	156.6(3)	161.1(2)	162.1(7)	152.70(7)
$^b\text{Dy-Cp}$ ($\text{\AA}$)	2.29(1)	2.298(5)	2.302(6)	2.340(7)	2.316(3)
U_{eff} (cm^{-1})	1285	1468	1380	1334	1223 or 1277
cT_b (K)	17	62	59	56	53
τ_{tunnel} (s)	439	2452	447	1187	n/a
$^dT_{\text{max}}$ (K)	32	72	66	66	60
2K M_r (μ_B)	2.6	4.4	3.9	4.2	4.2
2K H_c (T)	1.4	2.4	1.4	1.8	2.4

^aAverage value for all positions in the crystal structure.

^bAverage value for the highest occupancy component in the crystal structure.

^c T_b is defined as the 100-s magnetic blocking temperature.

^d T_{max} is the maximum hysteresis temperature.

^eValues are an average of those reported in Ref. 5.

Hundred-second magnetic blocking temperatures for **1-4** were extracted from the dc magnetic relaxation data, yielding $T_b = 17, 62, 59,$ and 56 K for **1** through **4**, respectively. The values for complexes **2-4** all surpass the 100-s blocking temperature of 53 K measured for $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+.$ ⁵ Indeed, the value for **2** represents the highest magnetic blocking temperature yet measured for a single-molecule magnet. While $\tau = 100$ s has been chosen as the benchmark relaxation time for comparing blocking temperatures, **2** shows longer magnetic relaxation times than $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$ across the entire temperature range measured ($2\text{--}114$ K).

Ab initio spin dynamics calculations performed on $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$ suggest that magnetic relaxation is predominantly moderated by local molecular vibrations.^{5b} In particular, four C–H bending modes of the Cp^{ttt} ligand were identified as giving rise to the initial $M_J = 15/2$ to $13/2$ transition that leads to Orbach relaxation. These calculations led to the proposal that changing ring hydrogens in Cp^{ttt} to a different substituent could lead to changes in magnetic relaxation time, a hypothesis that has yet to be experimentally verified.^{5b} Substituting the ring hydrogen in **1** with alkyl substituents in **2-4** results in up to a 45 K increase in the blocking temperature. This result clearly illustrates that substitution of the cyclopentadienyl ligands in dysprosium metallocene cations is a powerful tool for tuning magnetic relaxation and T_b .

While changes in ligand substitution modify molecular vibrations, molecular structure and anisotropy are also affected. It is therefore likely that a variety of factors influence changes in T_b . Clearly, spin dynamics calculations are worth pursuing to determine if the contributions of molecular vibrations to magnetic relaxation in this series can be generalized to other molecules in this class. It is worth noting that the 100-s blocking temperature for **1-4** occurs in the regime in which Raman relaxation dominates. While spin dynamics calculations can provide insight into the contribution of molecular vibrations to high-temperature, Orbach relaxation, models have not yet been developed for through-barrier relaxation processes such as Raman relaxation or quantum tunneling of the magnetization.^{5b} As such, developing a more quantitative magneto-structural correlation for the operating temperature in this series will require further development of theories on the impact of molecular vibrations on through-barrier magnetic relaxation. A well-characterized series like **1-4** that varies only slightly in substitution, but substantially in molecular structure and magnetic relaxation could lay the experimental groundwork for such theoretical studies. Insights from these calculations could be significant to the design of new cyclopentadienyl ligands to maximize operating temperatures in Dy^{III} metallocene cations.

The rates of quantum tunneling of the magnetization, τ_{tunnel} , extracted from dc relaxation measurements are among the slowest reported for mononuclear single-molecule magnets. This result is consistent with the drastically reduced quantum tunneling of the magnetization for $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$.⁵ While the reduction of quantum tunneling in $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$ has been ascribed to the high axiality of the ligand field (which gives rise to nearly pure M_J states in the lowest eight Kramers doublets^{5a}), this axiality cannot fully account for the observed behavior. Other highly anisotropic mononuclear single-molecule magnets, such as $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{C}_5\text{H}_5\text{N})_5]^+$, possess nearly pure M_J ground doublets and show fast quantum tunneling of the magnetization.^{3f}

Another possible explanation for the reduced quantum tunneling in $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$ is the constrained metal-ligand vibrational modes.^{5b,23} A lack of low-energy, first-coordination sphere metal-ligand vibrations in $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$ —such as those created by the weakly bound, equatorial pyridine ligands in $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{C}_5\text{H}_5\text{N})_5]^+$ —may limit the phonons available for magnetic relaxation at low temperatures. Limiting low-energy phonons has been shown to slow magnetic relaxation at low fields for Ho atoms on an MgO surface,²⁴ as well as for TbPc₂ (Pc²⁻ = phthalocyanine dianion) molecules on carbon nanotubes.²⁵ The hypothesis that local molecular coordination is responsible for limiting quantum tunneling in $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$ is supported by an increase in the zero-field step in magnetic hysteresis measurements performed on solution samples, which differ from bulk samples in accessible metal-ligand vibrational modes.^{5b}

The trend in τ_{tunnel} for **1-4** deviates from that observed for T_b ; namely, compounds **1** and **3** show the fastest quantum tunneling of the magnetization, while **2** and **4** show much larger τ_{tunnel} values (Table 5.1). As the rate of quantum tunneling can be influenced by intramolecular dipole interactions, largely dictated by crystal packing,²⁶ magnetically dilute samples of **1-4** were synthesized in order to enable a more accurate comparison of τ_{tunnel} .

Dilute samples **1-4@Y** were prepared by co-crystallization of **1-4** in a 1:9 ratio with the analogous Y^{III} compound **Y1-Y4**. Dc magnetic susceptibility measurements of the dilute samples matched those of **1-4** at temperatures above 50 K. Relaxation times extracted from dc magnetic relaxation measurements of **1-4@Y** also matched those determined for **1-4** at the highest temperatures measured for each compound. This consistency suggests that the local molecular structure of **1-4**—responsible for the high-temperature magnetic relaxation dynamics—is unchanged upon dilution, despite differences in the structures of **Y1-Y4**. The value of τ_{tunnel} , extracted from dc magnetic relaxation measurements of **1-4@Y** at 2 K, differs from the undiluted

samples, increasing to 1783, 11,200, 1125, and 1956 s, respectively. While the values of τ_{tunnel} for **1-4@Y** are substantially larger than those determined for the undiluted samples, the same overall trend is observed for the series.

The trend in τ_{tunnel} breaks from that observed for the 100-s blocking temperature. While **2@Y** shows the slowest quantum tunneling, **1@Y** shows a value of τ_{tunnel} close to that of **4@Y** and larger than that observed for **3@Y**. Substitution of the ring hydrogen in **1** with alkyl substituents in **2-4** does not have a consistent influence on the rate of quantum tunneling, as it did on the rate of Raman relaxation, which dictates T_b . This underscores the need to develop a deeper understanding of the role of molecular vibrations in through-barrier magnetic relaxation. Though molecular symmetry has been shown to influence magnetic relaxation in single-molecule magnets,²⁷ there is no apparent magneto-structural correlation between molecular symmetry and quantum tunneling of the magnetization or blocking temperature in the series **1-4**, which all possess C_1 symmetry.

Magnetic hysteresis data were collected for **1-4** at several temperatures in the range 2–72 K by sweeping the field between 7 and –7 T. For fields below 2 T, a magnetic field sweep rate of 3.1(4) mT/s was employed, similar to that used in hysteresis measurements of $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$.⁵ A step is observed at zero field at 2 K, resulting in remanant magnetization values (M_r) of 2.6, 4.4, 3.9, and 4.2 μ_B for complexes **1** through **4**. The magnitude of the remanant magnetization and the coercive field (H_c) for each complex mirrors the trend in τ_{tunnel} (Figure 5.5a, Table 5.1).

The hysteresis loops remain open at temperatures as high as 32, 72, 66 and 66 K for **1** through **4**, respectively (Figure 5.5b). The maximum temperatures in the case of complexes **2-4** are higher than the 60 K maximum determined for $[\text{Dy}(\text{Cp}^{\text{ttt}})_2]^+$,⁵ and this observation is consistent with the trend observed in T_b . Notably, the maximum hysteresis temperature for compound **2** is the highest that has yet been reported for a single-molecule magnet, approaching the temperature of liquid nitrogen (77 K).

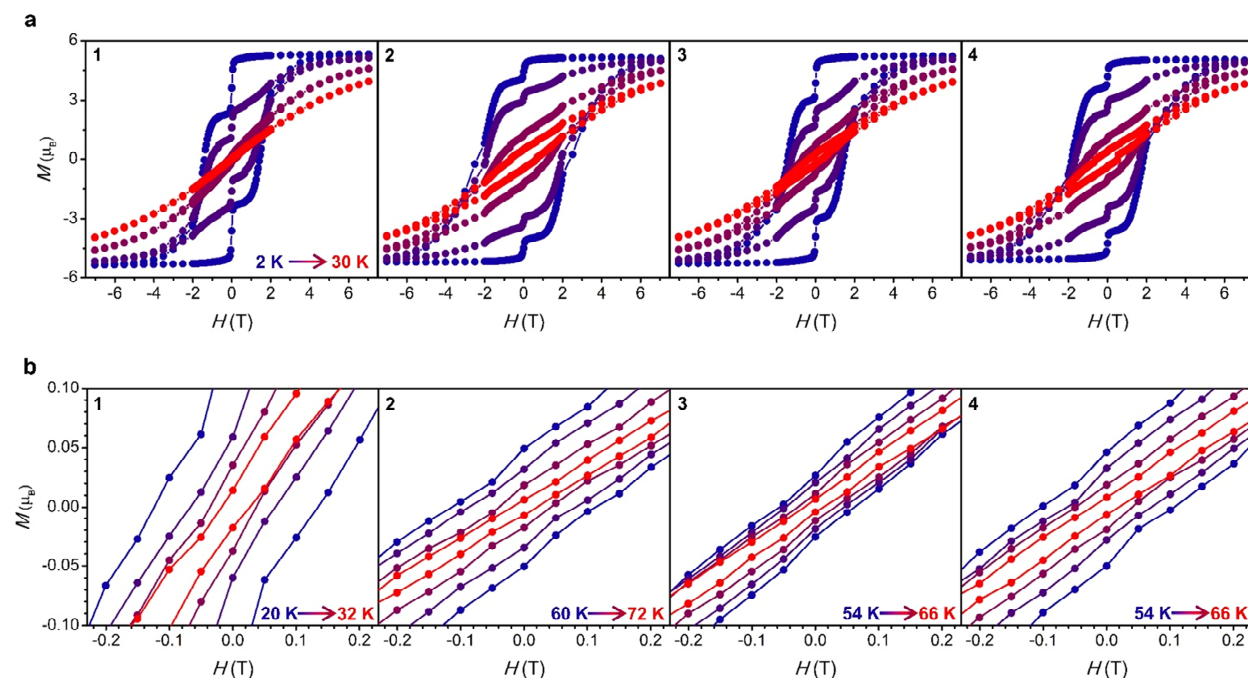


Figure 5.5. (a) Magnetic hysteresis data for **1-4** collected at 2, 10, 20 and 30 K with a sweep rate of 3.1(4) mT/s for $H < 2$ T and 13.2(2) mT/s for $H > 2$ T. (b) Expanded view of the region near zero field at high-temperatures.

5.3 Conclusions and Outlook

The metallocene cation salts $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{H}$ (**1**), Me (**2**), Et (**3**), $i\text{Pr}$ (**4**)) were synthesized by metathesis of DyI_3 and the corresponding $\text{NaCp}^{i\text{Pr}4\text{R}}$ salt, followed by iodide abstraction with $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$. Thorough characterization of this series provides insight into the impact of molecular structure on magnetic properties in Dy^{III} metallocenium complexes. Single-crystal X-ray diffraction studies reveal that more sterically encumbered cyclopentadienyl ligands promote longer average Dy–C distances and larger Cp–Dy–Cp angles. As demonstrated by the record thermal barrier to magnetic inversion of 1468 cm^{-1} determined for compound **2**, a balance must be struck between achieving a large Cp–Dy–Cp angle and short Dy–C distances in order to maximize anisotropy.

Compounds **1–4** provide experimental support for the hypothesis that modifying cyclopentadienyl ring substituents can tune metal-ligand vibrational modes, impacting magnetic relaxation.^{5b} In the series investigated here, substituent modification notably results in a 45 K increase in the magnetic blocking temperature across the series, with complex **2** exhibiting the highest 100-s blocking temperature and hysteresis temperature yet measured for a single molecule magnet. Expanding the magneto-structural correlations presented in this study with *ab initio* calculations is a clear next step towards developing generalizable design principles for the synthesis of $[\text{Dy}(\text{Cp}^{\text{X}})_2]^+$ single-molecule magnets that function above 77 K.

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5.5 References and Footnotes

- § Another notable exception is $[\text{Er}(\text{COT})_2]^-$, which shows open magnetic hysteresis loops to 10 K: K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.* **2013**, *135*, 17952.
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5.6 Supplementary Information

5.6.1 General Information

All manipulations were performed using Schlenk or glovebox techniques under an atmosphere of purified argon with rigorous exclusion of water and oxygen. All solvents were purchased from Sigma-Aldrich as anhydrous grade in Sure/Seal™ bottles, purged for several hours with purified argon and stored over activated 3 Å molecular sieves in an argon filled glovebox. A solution of LiAlH₄ (1.0 M in Et₂O) was purchased from Sigma-Aldrich and used as received. Anhydrous LnX₃ (Ln = Dy, Y; X = Cl, I) were purchased from Alfa Aesar as Ultra Dry™ grade reagents and used as received. The halide abstraction reagent, [H(SiEt₃)₂][B(C₆F₅)₄], was prepared freshly before use via a reported method.¹⁶ The salt NaCp^{iPr4} was synthesized via a literature route⁹ and dried under vacuum to remove traces of THF. Tetraisopropylfulvene and methyl-substituted tetraisopropylfulvene were prepared according to the literature¹⁰ and recrystallized several times from anhydrous ethanol at -70 °C. The obtained fulvenes were assayed via GC-MS, and purities of 86% and 85% were found for tetraisopropylfulvene and methyl-substituted tetraisopropylfulvene, respectively. The main impurity in both cases was a mixture of tetraisopropylcyclopentadiene isomers. The salt NaCp^{iPr5} was obtained from methyl-substituted tetraisopropylfulvene in two steps via a combination of literature methods^{10,11} with modifications detailed below. Methyl-substituted tetraisopropylfulvene was initially converted to the Li⁺ salt of pentaisopropylcyclopentadiene by the method of Dezember et al.¹⁰ and hydrolyzed in situ by careful addition of H₂O to give free pentaisopropylcyclopentadiene after extraction into Et₂O and solvent removal. The resulting compound was deprotonated using excess NaNH₂ (1.2 equiv) in refluxing THF with the aid of sonication via a known method.¹¹ The salt NaCp^{iPr5} was extracted from the crude material (mostly a mixture of NaCp^{iPr4} and NaCp^{iPr5}) with benzene and the solvent removed under vacuum. The off-white solid was dried under vacuum at 100 °C for 2 h to remove coordinated THF, washed with pentane, and dried under vacuum at room temperature to give pure NaCp^{iPr5} as a white powder. GC-MS experiments were performed using a Thermo Scientific Exactive GC-MS (Orbitrap) with a Thermo Scientific Trace 1310 GC using a TG-5SILMS column. NMR spectra were recorded on a Bruker Avance 300 MHz or 500 MHz spectrometer and internally referenced to the residual solvent signals. FT-IR spectra were recorded on a Perkin Elmer Avatar Spectrum 400 FTIR Spectrometer equipped with an attenuated total reflectance (ATR) attachment. Elemental analyses (C, H, N) were performed by the Microanalytical Facility at the University of California, Berkeley using a Perkin-Elmer 2400 Series II combustion analyzer. Metals analyses (Dy, Y) were performed on a Thermo Fisher Scientific iCAP 6300 Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES). Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer.

5.6.2 Synthesis of Compounds and Spectroscopic Characterization

Synthesis of $\text{NaCp}^{i\text{Pr}4\text{Me}}$. Tetraisopropylfulvene (1.00 g, 4.05 mmol) (86% pure by GC-MS) and Et_2O (40 mL) were combined in a 100 mL Schlenk flask to produce a bright orange solution. The solution was cooled to 0 °C and 1.0 M LiAlH_4 in Et_2O (12.1 mL, 12.1 mmol) was added all at once via syringe. The reaction flask was allowed to warm to room temperature and stirred for 20 h. At this point, the initial orange solution had been replaced with a grayish suspension and solvent was removed under vacuum to leave a grayish residue. This residue was slurried in 30 mL pentane for 30 min., filtered and washed with 2×15 mL pentane to leave a white/gray powder. The powder was taken up in 50 mL of Et_2O , cooled to 0 °C, and 20 mL of H_2O was added (H_2O should be added very slowly at first to prevent excessive frothing), followed by 20 mL of 1.0 M HCl . This mixture was stirred vigorously for 30 min and then the layers separated. The aqueous layer was extracted with 2×50 mL of Et_2O and the combined organic fractions were washed with 25 mL of brine, dried with MgSO_4 , and the solvent was removed under vacuum to leave a light yellow oil (0.70 g / 2.8 mmol of $\text{HCp}^{i\text{Pr}4\text{Me}}$ tautomers). This oil was combined with NaNH_2 (0.22 g, 5.60 mmol) and 20 mL of THF in a 50 mL Schlenk flask equipped with a reflux condenser. The reaction flask was immersed in a sonication bath filled with H_2O at a temperature ranging from 40–50 °C and sonicated overnight under argon. The flask was subsequently cooled to room temperature and the solvent was removed under vacuum to leave a beige residue. This residue was transferred to an Ar-filled glovebox, re-suspended in 25 mL of THF, filtered through Celite, and the filter cake was then washed with additional THF to give an amber filtrate. Solvent was removed from the filtrate under vacuum and the resulting off-white solid heated under vacuum at 100 °C for 2 h to remove coordinated THF. This solid was then slurried in 25 mL pentane, filtered, washed with additional pentane, and dried under vacuum at room temperature to give pure $\text{NaCp}^{i\text{Pr}4\text{Me}}$ as a white powder (0.59 g, 54% yield based on tetraisopropylfulvene). ^1H NMR (THF-d_8 , 500 MHz, 338 K): δ = 1.24 (d, 12H, $\text{Cp-CH}(\text{CH}_3)_2$), 1.25 (d, 12H, $\text{Cp-CH}(\text{CH}_3)_2$), 2.19 (s, 3H, Cp-CH_3), 3.19 (m, 4H, $\text{Cp-CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-d_8 , 125 MHz, 338 K): δ = 15.00 (Cp-CH_3), 25.37 ($\text{Cp-CH}(\text{CH}_3)_2$), 26.19 ($\text{Cp-CH}(\text{CH}_3)_2$), 28.21 ($\text{Cp-CH}(\text{CH}_3)_2$), 28.32 ($\text{Cp-CH}(\text{CH}_3)_2$), 104.78 ($-\text{C}(i\text{Pr})-\text{C}(\text{Me})-\text{C}(i\text{Pr})-$), 116.60 ($-\text{C}(i\text{Pr})-\text{C}(i\text{Pr})-\text{C}(i\text{Pr})-$), 118.53 ($-\text{C}(\text{Me})-\text{C}(i\text{Pr})-\text{C}(i\text{Pr})-$). Calcd. $\text{C}_{18}\text{H}_{31}\text{Na}$ (270.44) (%): C 79.94, H 11.55; found (%): C 77.94, H 10.32 (low percent carbon values were obtained across multiple measured samples).

Synthesis of $\text{NaCp}^{i\text{Pr}4\text{Et}}$. Following the general procedure outlined above for the synthesis of $\text{NaCp}^{i\text{Pr}4\text{Me}}$ (the quantity of all solvents was doubled), $\text{NaCp}^{i\text{Pr}4\text{Et}}$ was synthesized from methyl-substituted tetraisopropylfulvene (3.00 g, 11.5 mmol) (85% pure by GC-MS) and 1.0 M LiAlH_4 in Et_2O (34.4 mL, 34.4 mmol) to initially give a light yellow oil after quenching with H_2O (40 mL) and 1.0M HCl (40 mL) (2.1 g / 8.0 mmol of $\text{HCp}^{i\text{Pr}4\text{Et}}$ tautomers). This was deprotonated in the same fashion as $\text{NaCp}^{i\text{Pr}4\text{Me}}$ using NaNH_2 (0.62 g, 16 mmol). Pure $\text{NaCp}^{i\text{Pr}4\text{Et}}$ was isolated as a white powder (2.05 g, 63% yield based on methyl-substituted tetraisopropylfulvene). ^1H NMR (THF-d_8 , 500 MHz, 338 K): δ = 1.02 (t, 3H, $\text{Cp-CH}_2\text{CH}_3$), 1.25 (d, 12H, $\text{Cp-CH}(\text{CH}_3)_2$), 1.26 (d, 12H, $\text{Cp-CH}(\text{CH}_3)_2$), 2.56 (q, 2H, $\text{Cp-CH}_2\text{CH}_3$), 3.14 (br, 2H, $\text{Cp-CH}(\text{CH}_3)_2$), 3.26 (sept, 2H, $\text{Cp-CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-d_8 , 125 MHz, 338 K): δ = 19.79 ($\text{Cp-CH}_2\text{CH}_3$), 21.78 ($\text{Cp-CH}_2\text{CH}_3$), 25.78 ($\text{Cp-CH}(\text{CH}_3)_2$), 26.12 ($\text{Cp-CH}(\text{CH}_3)_2$), 28.14 (br, $\text{Cp-CH}(\text{CH}_3)_2$), 28.51 ($\text{Cp-CH}(\text{CH}_3)_2$), 112.76 ($-\text{C}(i\text{Pr})-\text{C}(\text{Et})-\text{C}(i\text{Pr})-$), 116.89 ($-\text{C}(i\text{Pr})-\text{C}(i\text{Pr})-\text{C}(i\text{Pr})-$), 117.79 ($-\text{C}(\text{Et})-\text{C}(i\text{Pr})-\text{C}(i\text{Pr})-$). Calcd. $\text{C}_{19}\text{H}_{33}\text{Na}$ (284.46) (%): C 80.22, H 11.69; found (%): C 79.91, H 11.66.

Synthesis of $[\text{Dy}(\text{Cp}^{i\text{Pr}5})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (4**).** DyI_3 (0.24 g, 0.44 mmol) and $\text{NaCp}^{i\text{Pr}5}$ (0.33 g, 1.10 mmol) were combined in a 35 mL pressure flask containing a glass-coated magnetic stirring bar. Toluene (15 mL) was then added, and the reaction flask was covered in Al foil and heated gradually to 160 °C with vigorous stirring. After 72 h at 160 °C, the flask was allowed to cool to room temperature, the reaction mixture was filtered through Celite, and the pad was washed with additional toluene (3×5 mL). Solvent was removed from the filtrate under vacuum and the residue was then gently heated (50 °C) under vacuum for 1 h. The residue was taken up in pentane (25 mL), stirred for 0.5 h, filtered through Celite, and the pad washed with additional pentane (3×5 mL). Solvent was removed from the filtrate under vacuum and the residue was then gently heated (50 °C) under vacuum for 0.5 h to give crude $\text{Dy}(\text{Cp}^{i\text{Pr}5})_2\text{I}$. This was dissolved with benzene (10 mL) in a 25 mL Schlenk flask equipped with a Teflon-coated magnetic stirring bar. Under vigorous stirring at room temperature, a solution of $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.36 g, 0.39 mmol) in benzene (5 mL) was added dropwise to the $\text{Dy}(\text{Cp}^{i\text{Pr}5})_2\text{I}$ solution over 5 min. After stirring for 72 h at room temperature, solvent was removed from the reaction mixture under vacuum. The residue was then slurried with pentane (20 mL) for 0.5 h to yield a powder which was collected on a medium-porosity fritted filter and washed with pentane (3×10 mL). This solid was dried under vacuum, dissolved in dichloromethane (4 mL), filtered with the aid of Celite through a 0.2 μm porosity PTFE syringe filter, and layered with pentane (15 mL) in a 20 mL vial. After 48 h at room temperature, well-formed crystals were obtained, isolated on a medium-porosity fritted filter, and washed consecutively with pentane (5 mL), benzene (2×5 mL) and pentane (5 mL). The crystallization was repeated and the twice recrystallized solid was dried under vacuum to yield **4** as orange needles (0.35 g, 57% yield based on DyI_3). Calcd. for $\text{C}_{64}\text{H}_{70}\text{BF}_{20}\text{Dy}$ (1392.54) (%): C 55.20, H 5.07, Dy 11.7; found (%): C 55.21, H 4.80, Dy 11.3 (For **4**, a 3rd recrystallization was needed to obtain acceptable values).

Synthesis of $[\text{Dy}(\text{Cp}^{i\text{Pr}4})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (1**).** Following the general procedure used for the synthesis of **4**, $[\text{Dy}(\text{Cp}^{i\text{Pr}4})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) was synthesized from DyI_3 (0.21 g, 0.39 mmol), $\text{NaCp}^{i\text{Pr}4}$ (0.25 g, 0.98 mmol) and $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.28 g, 0.31 mmol). Subsequent crystallizations were carried out over 24 h at room temperature and 24 h at -35 °C. Compound **1** was obtained as yellow prisms (0.21 g, 41% yield based on DyI_3). Calcd. for $\text{C}_{58}\text{H}_{58}\text{BF}_{20}\text{Dy}$ (1308.38) (%): C 53.24, H 4.47, Dy 12.4; found (%): C 52.88, H 4.45, Dy 12.8.

Synthesis of $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{Me}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (2**).** Following the general procedure used for the synthesis of **4**, $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{Me}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**) was synthesized from DyI_3 (0.20 g, 0.37 mmol), $\text{NaCp}^{i\text{Pr}4\text{Me}}$ (0.25 g, 0.92 mmol) and $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.27 g, 0.30 mmol). The first crystallization was conducted at -35 °C and the second at room temperature. Compound **2** was obtained as orange-yellow prisms (0.25 g, 50% yield based on DyI_3). Calcd: $\text{C}_{60}\text{H}_{62}\text{BF}_{20}\text{Dy}$ (1336.43) (%): C 53.92, H 4.68, Dy 12.2; found (%): C 53.36, H 4.48, Dy 12.6.

Synthesis of $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{Et}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (3**).** Following the general procedure used for the synthesis of **4**, $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{Et}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3**) was synthesized from DyI_3 (0.23 g, 0.42 mmol), $\text{NaCp}^{i\text{Pr}4\text{Et}}$ (0.30 g, 1.05 mmol) and $[\text{H}(\text{SiEt}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.31 g, 0.34 mmol). Crystallizations were carried out in the same manner as **4**. Compound **3** was obtained as orange-yellow needles (0.31 g, 54% yield based on DyI_3). Calc. $\text{C}_{62}\text{H}_{66}\text{BF}_{20}\text{Dy}$ (1364.49) (%): C 54.58, H 4.88, Dy 11.9; found (%): C 54.05, H 4.68, Dy 12.1.

Synthesis of $[Y(Cp^{iPr4Et})_2][B(C_6F_5)_4]$ (Y3**).** Under argon, YI_3 (0.19 g / 0.40 mmol) and $NaCp^{iPr4Et}$ (0.29 g / 1.0 mmol) were combined in a 35 mL pressure flask containing a glass-coated magnetic stirring bar and toluene (15 mL) was added. The reaction flask was covered in Al foil, and heated gradually to 160 °C with vigorous stirring. After 72 h at 160 °C, the flask was allowed to cool to room temperature, the reaction mixture was filtered through Celite and the pad washed with additional toluene (3 X 5 mL). Solvent was removed from the filtrate under vacuum and the residue was gently heated (50 °C) under vacuum for 1 h. The residue was taken up in pentane (25 mL), stirred for 0.5 h, filtered through Celite and the pad washed with additional pentane (3 X 5 mL). Solvent was removed from the filtrate under vacuum and the residue was gently heated (50 °C) under vacuum for 0.5 h to give crude $Y(Cp^{iPr4Et})_2I$. This was dissolved with benzene (10 mL) in a 25 mL Schlenk flask equipped with a Teflon magnetic stirring bar. Under vigorous stirring at room temperature, a solution of $[H(SiEt_3)_2][B(C_6F_5)_4]$ (0.29 g / 0.32 mmol) in benzene (5 mL) was added dropwise to the $Y(Cp^{iPr4Et})_2I$ solution over 5 min. After stirring for 72 h at room temperature, solvent was removed from the reaction mixture under vacuum, the residue was slurried with pentane (20 mL) for 0.5 h and isolated as a powder on a medium-porosity fritted filter after washing with pentane (3 X 10 mL). This was dried under vacuum, dissolved in dichloromethane (4 mL), filtered with aid of Celite through a 0.2 μ m porosity PTFE syringe filter and layered with pentane (16 mL) in a 20 mL vial. After 24 h at 25 °C and 24 h at -35 °C yellow needle crystals were obtained. These were isolated on a medium-porosity fritted filter, washed with pentane (5 mL), benzene (5 mL) and pentane (5 mL). The crystallization was repeated and the crystals dried under vacuum to yield **Y3** as yellow needles (0.21 g / 41% based on YI_3). 1H NMR (TCE- d_2 , 500 MHz, 358 K): δ = 1.14 (t, 6H, Cp- CH_2CH_3), 1.41 (m, 36H, Cp- $CH(CH_3)_2$), 1.50 (d, 12H, Cp- $CH(CH_3)_2$), 2.90 (q, 4H, Cp- CH_2CH_3), 3.30 (sept, 4H, Cp- $CH(CH_3)_2$), 3.39 (sept, 4H, Cp- $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (TCE- d_2 , 125 MHz, 348 K): δ = 15.88 (Cp- CH_2CH_3), 20.63 (Cp- CH_2CH_3), 22.56 (Cp- $CH(CH_3)_2$), 22.95 (Cp- $CH(CH_3)_2$), 23.33 (Cp- $CH(CH_3)_2$), 24.41 (Cp- $CH(CH_3)_2$), 26.59 (Cp- $CH(CH_3)_2$), 27.25 (Cp- $CH(CH_3)_2$), 132.89 (-C(*i*Pr)-C(Et)-C(*i*Pr)-), 137.24 (-C(*i*Pr)-C(*i*Pr)-C(*i*Pr)-), 138.20 (-C(Et)-C(*i*Pr)-C(*i*Pr)-). $C_{62}H_{66}BF_{20}Y$ (1290.89): calcd (%) C 57.69, H 5.15, Y 6.89; found (%) C 57.45, H 5.06, Y 7.01.

Synthesis of $[Y(Cp^{iPr4})_2][B(C_6F_5)_4]$ (Y1**).** Following the general procedure used for synthesis of **Y3**, **Y1** was synthesized from YI_3 (0.22 g / 0.47 mmol), $NaCp^{iPr4}$ (0.30 g / 1.17 mmol) and $[H(SiEt_3)_2][B(C_6F_5)_4]$ (0.34 g / 0.37 mmol). The product was recrystallized twice using the same method outlined for **Y3** to yield colorless prisms of **Y1** (0.30 g / 52% based on YI_3). 1H NMR (CD_2Cl_2 , 500 MHz, 298 K): δ = 1.01 (d, 12H, Cp- $CH(CH_3)_2$), 1.32 (d, 12H, Cp- $CH(CH_3)_2$), 1.36 (d, 12H, Cp- $CH(CH_3)_2$), 1.52 (d, 12H, Cp- $CH(CH_3)_2$), 3.04 (sept, 4H, Cp- $CH(CH_3)_2$), 3.25 (sept, 4H, Cp- $CH(CH_3)_2$), 6.57 (s, 2H, Cp-*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 125 MHz, 298 K): δ = 22.49, 22.90, 23.13, 26.90, 27.15, 28.38, 110.57, 135.90, 137.84, 140.87, 147.79, 149.68. $C_{58}H_{58}BF_{20}Y$ (1234.79): calcd (%) C 56.42, H 4.73, Y 7.20; found (%) C 55.95, H 4.72, Y 7.21.

Synthesis of $[Y(Cp^{iPr4Me})_2][B(C_6F_5)_4]$ (Y2**).** Following the general procedure used for synthesis of **Y3**, **Y2** was synthesized from YI_3 (0.17 g / 0.36 mmol), $NaCp^{iPr4Me}$ (0.25 g / 0.92 mmol) and $[H(SiEt_3)_2][B(C_6F_5)_4]$ (0.27 g / 0.30 mmol). The product was recrystallized twice using the same method outlined for **Y3** to yield yellow prisms of **Y2** (0.24 g / 51% based on YI_3). 1H NMR (TCE- d_2 , 300 MHz, 348 K): δ = 1.26 (d, 12H, Cp- $CH(CH_3)_2$), 1.40 (d, 12H, Cp- $CH(CH_3)_2$), 1.41 (d, 12H, Cp- $CH(CH_3)_2$), 1.52 (d, 12H, Cp- $CH(CH_3)_2$), 3.30 (sept, 4H, Cp- $CH(CH_3)_2$), 3.37 (sept, 4H, Cp- $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (TCE- d_2 , 125 MHz, 348 K): δ = 14.00 (Cp- CH_3), 22.60 (Cp-

CH(CH₃)₂), 22.67 (Cp-CH(CH₃)₂), 22.87 (Cp-CH(CH₃)₂), 23.01 (Cp-CH(CH₃)₂), 26.42 (Cp-CH(CH₃)₂), 27.39 (Cp-CH(CH₃)₂), 127.37 (-C(*i*Pr)-C(Me)-C(*i*Pr)-), 136.55 (-C(*i*Pr)-C(*i*Pr)-C(*i*Pr)-), 139.01 (-C(Me)-C(*i*Pr)-C(*i*Pr)-). C₆₀H₆₂BF₂₀Y (1262.84): calcd (%) C 57.07, H 4.95, Y 7.04; found (%) C 56.80, H 4.81, Y 7.16.

Synthesis of [Y(Cp^{*i*Pr}₅)₂][B(C₆F₅)₄] (Y4). Following the general procedure used for synthesis of **Y3**, **Y4** was synthesized from YI₃ (0.19 g / 0.40 mmol), NaCp^{*i*Pr}₅ (0.30 g / 1.00 mmol) and [H(SiEt₃)₂][B(C₆F₅)₄] (0.29 g / 0.32 mmol). The product was recrystallized three times using the same method outlined for **Y3** to yield yellow needles of **Y4** (0.16 g / 30% based on YI₃). ¹H NMR (CD₂Cl₂, 500 MHz, 263 K): δ = {1.07 outer CH₃ of both isomers} (d, 30H, Cp-CH(CH₃)₂), {1.66 inner CH₃ of isomer A, 1.69 inner CH₃ of isomer B} (d, 30H, Cp-CH(CH₃)₂), 3.35 (sept, 10H, Cp-CH(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz, 263 K): δ = 23.62 (Cp-CH(CH₃)₂), 23.70 (Cp-CH(CH₃)₂), 24.95 (Cp-CH(CH₃)₂), 25.62 (Cp-CH(CH₃)₂), 27.42 (Cp-CH(CH₃)₂), 27.48 (Cp-CH(CH₃)₂), 140.17 (-C(*i*Pr)-C(*i*Pr)-C(*i*Pr)-). C₆₄H₇₀BF₂₀Y (1318.95): calcd (%) C 58.28, H 5.35, Y 6.74; found (%) C 57.73, H 5.05, Y 6.35.

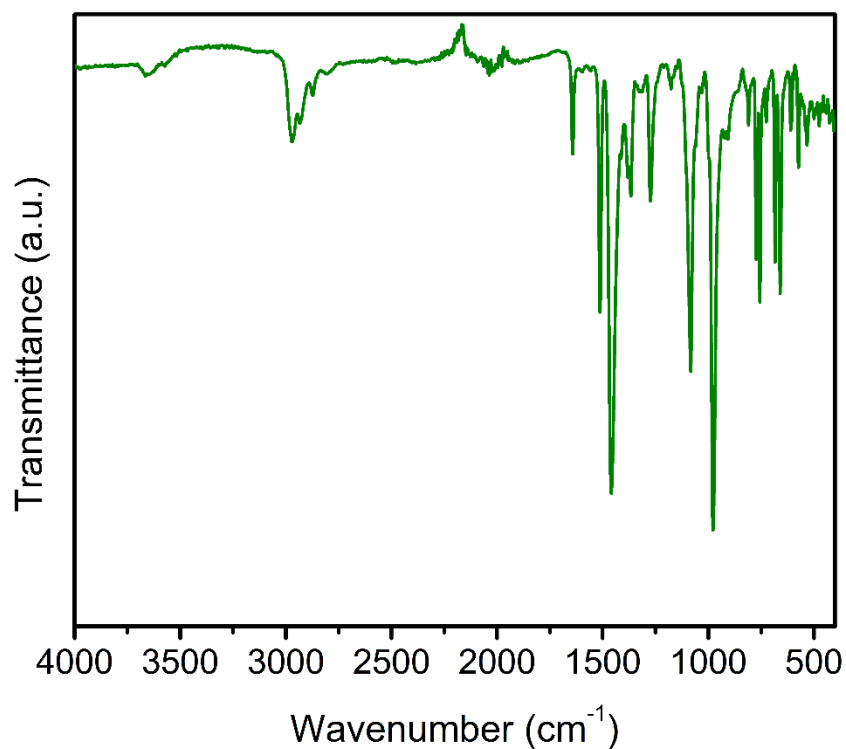


Figure S5.1. Infrared spectrum of **1**.

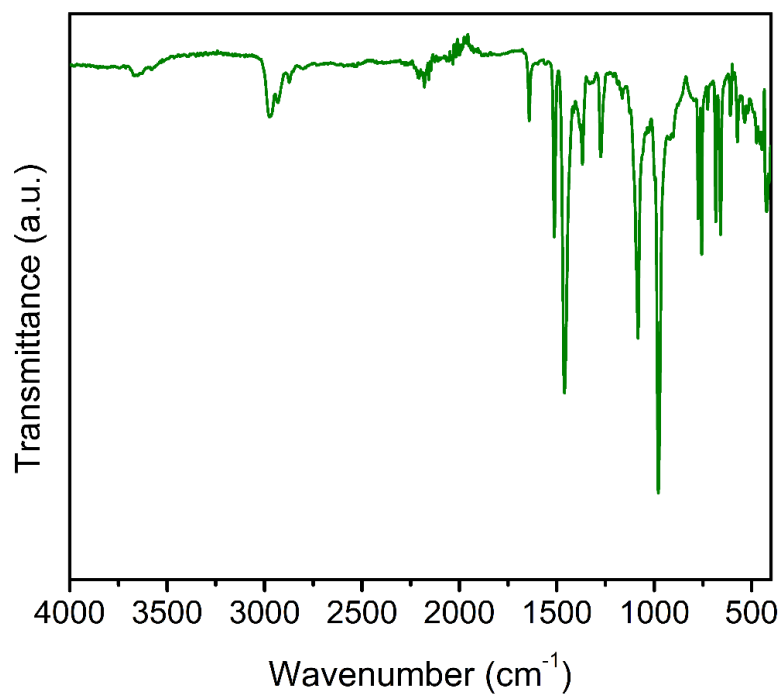


Figure S5.2. Infrared spectrum of **2**.

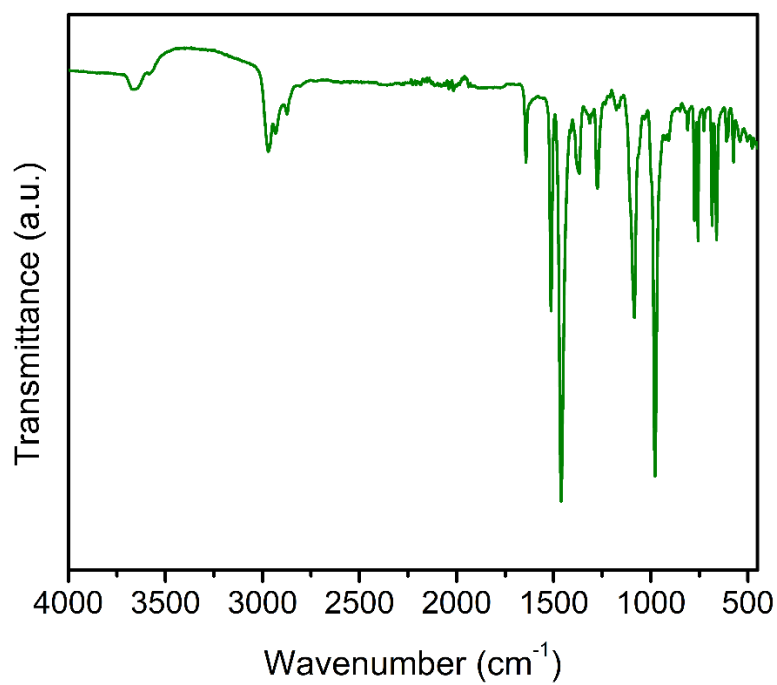


Figure S5.3. Infrared spectrum of **3**.

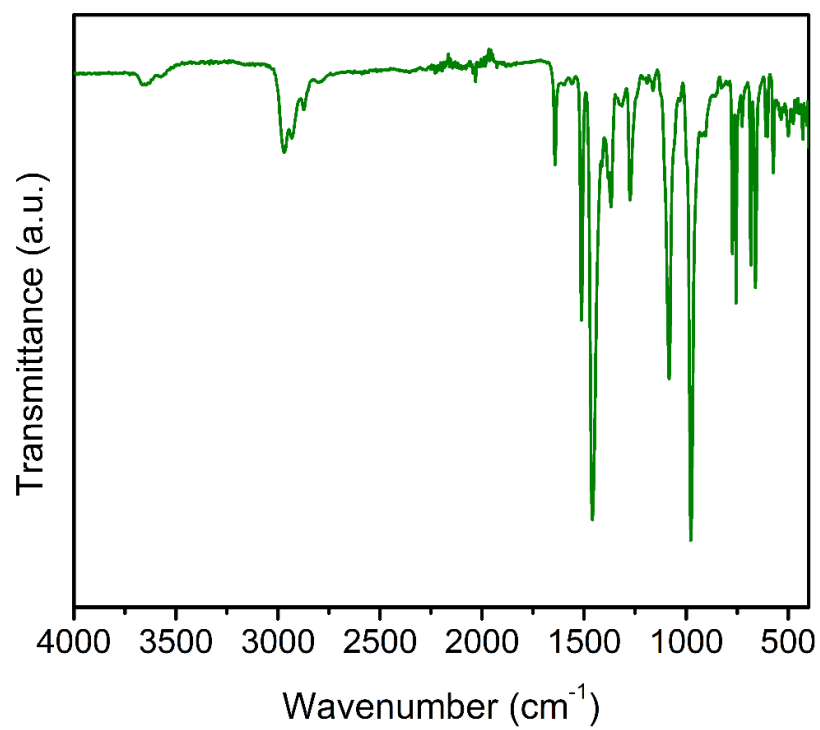


Figure S5.4. Infrared spectrum of **4**.

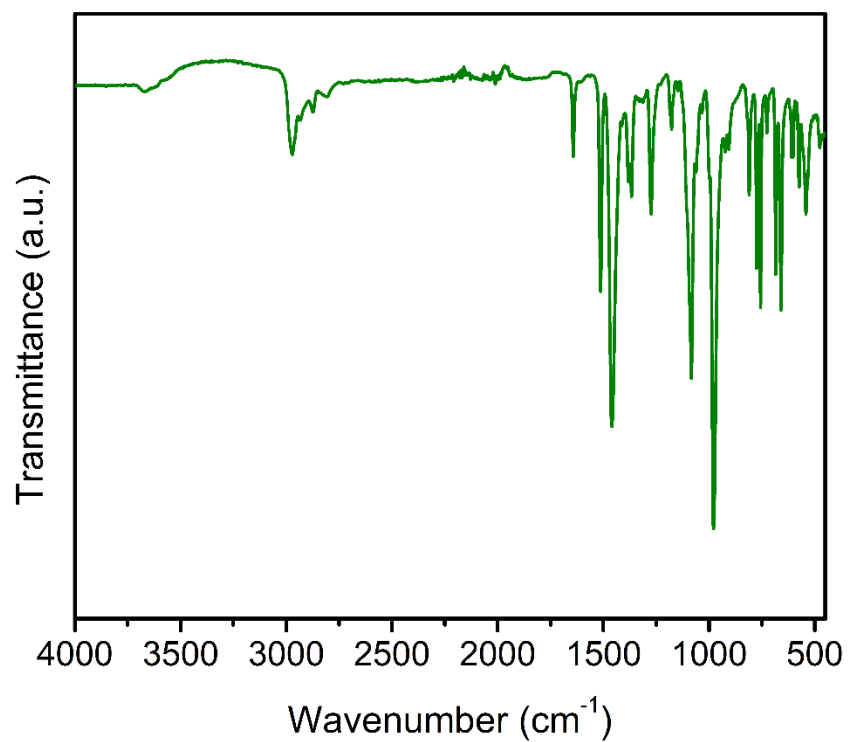


Figure S5.5. Infrared spectrum of **Y1**.

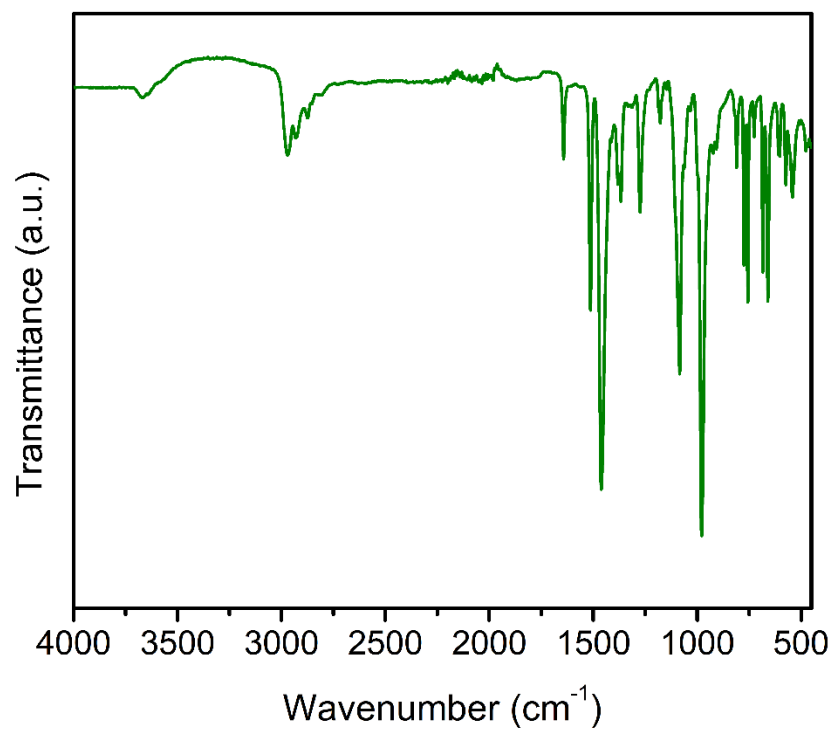


Figure S5.6. Infrared spectrum of Y2.

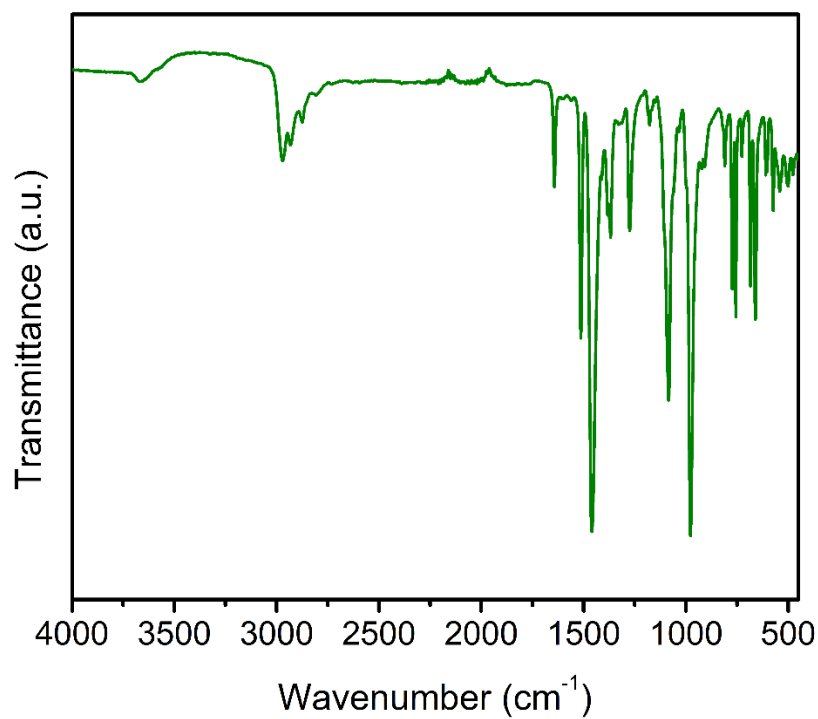


Figure S5.7. Infrared spectrum of Y3.

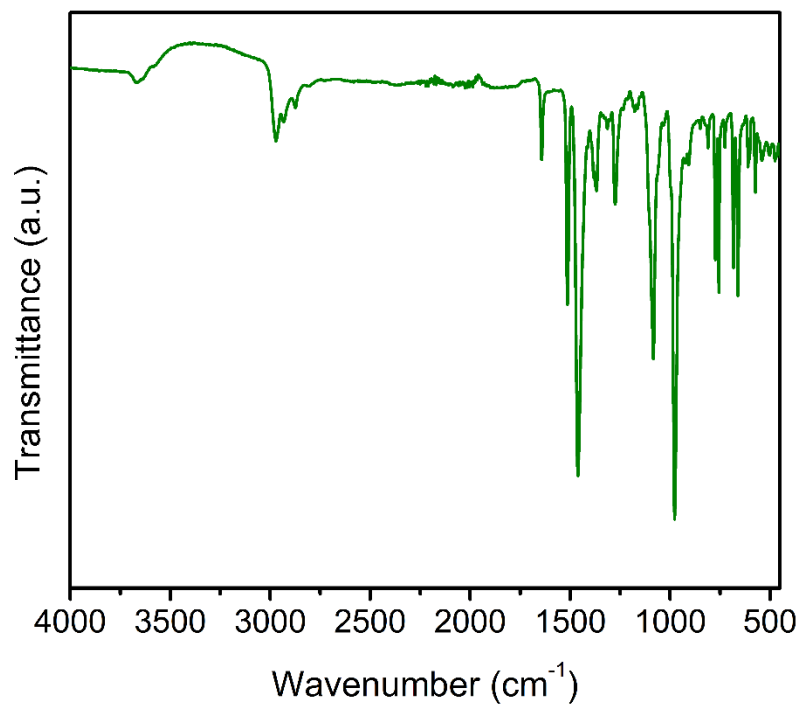


Figure S5.8. Infrared spectrum of Y4.

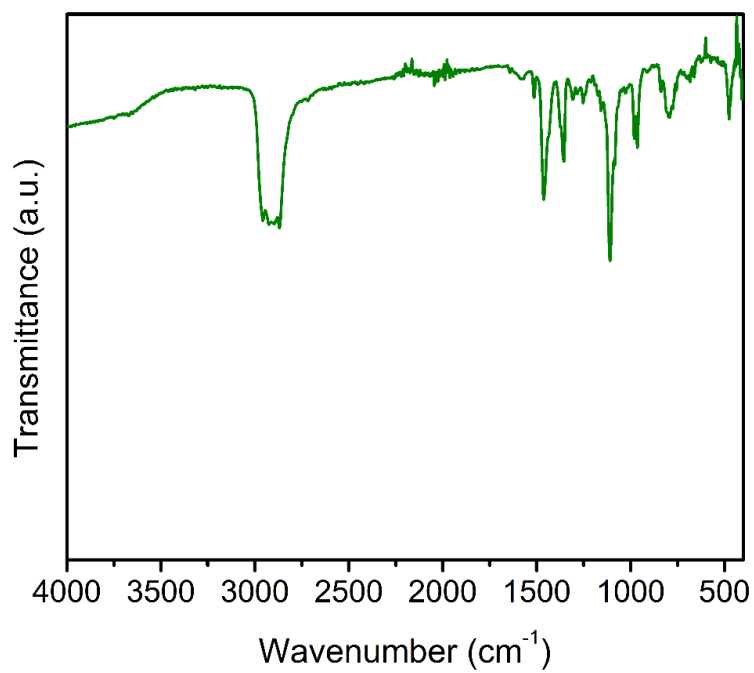


Figure S5.9. Infrared spectrum of NaCp^{*iPr*4Me}.

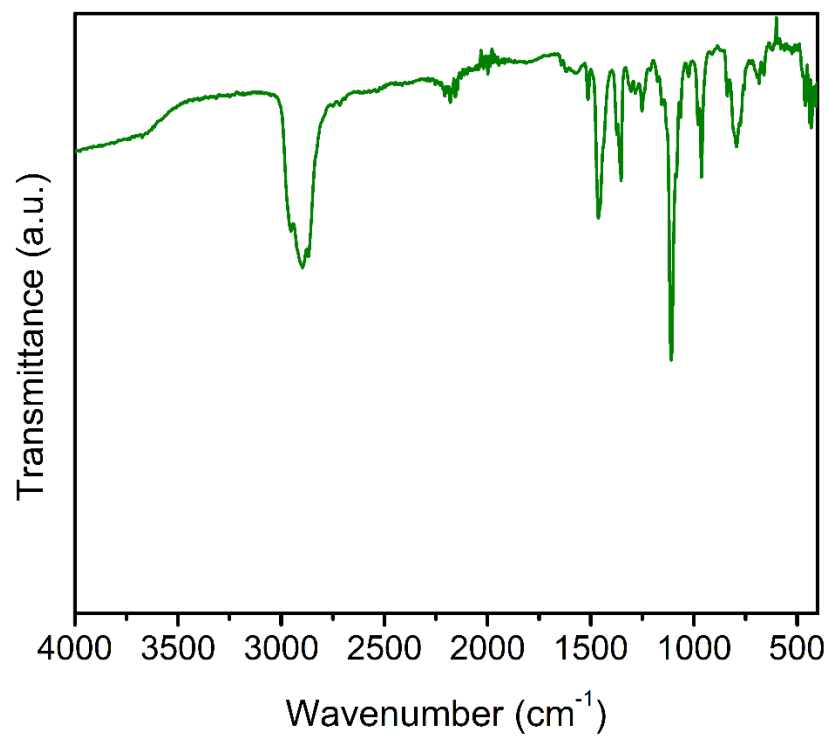


Figure S5.10. Infrared spectrum of NaCp^{*i*Pr₄Et}.

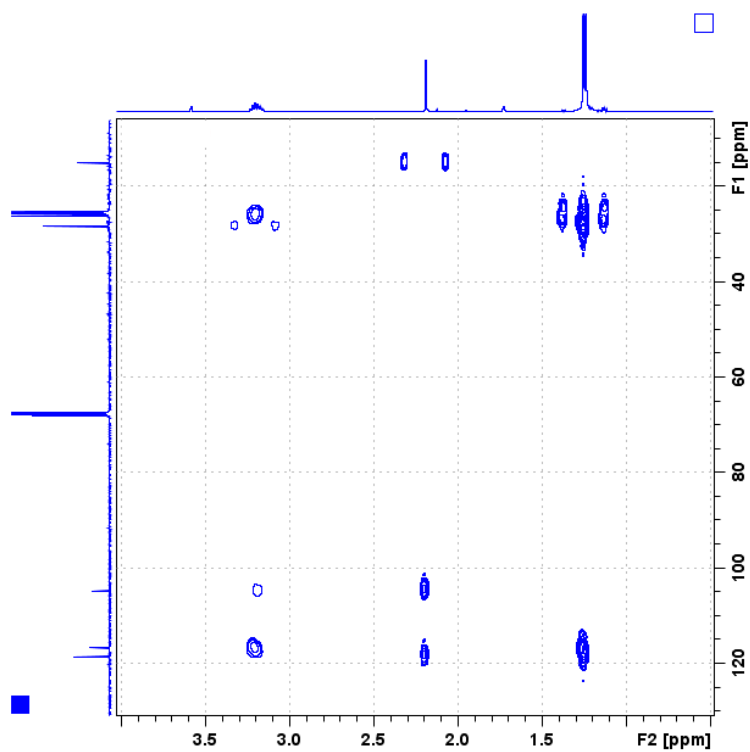


Figure S5.11. ¹³C-¹H HMBC spectrum of NaCp^{*i*Pr₄Me} in THF-d₈ at 65 °C.

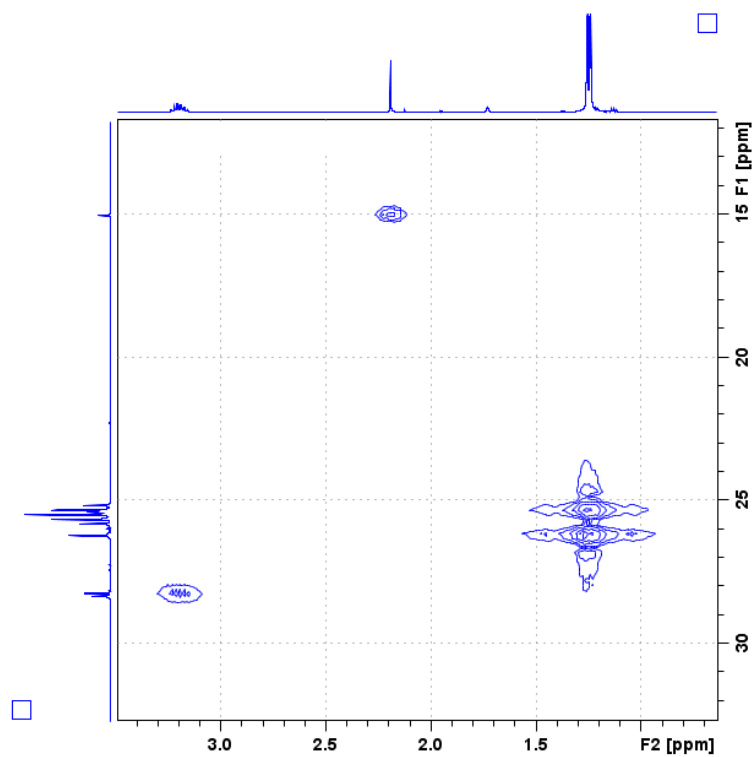


Figure S5.12. ^{13}C - ^1H HMQC spectrum of $\text{NaCp}^{i\text{Pr}4\text{Me}}$ in THF-d_8 at 65°C .

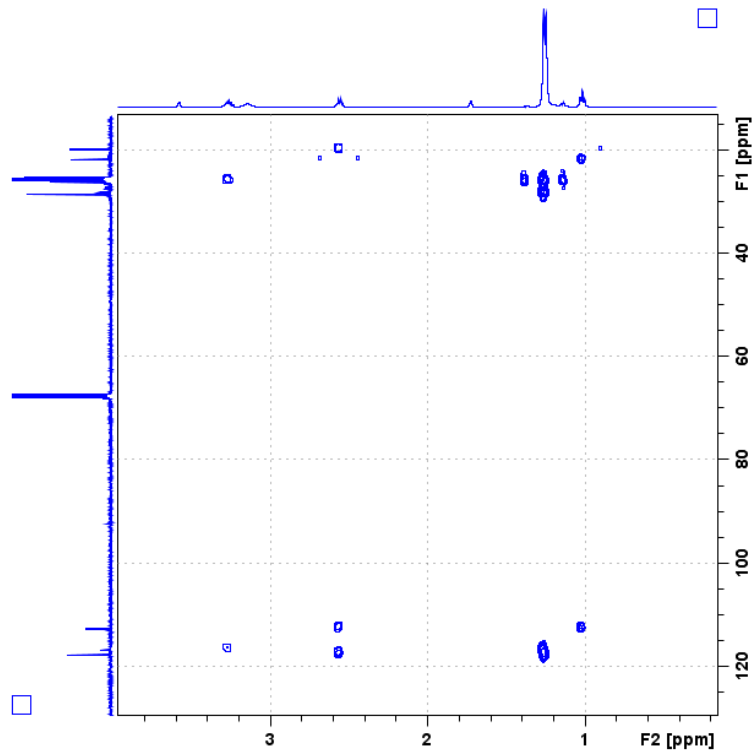


Figure S5.13. ^{13}C - ^1H HMBC spectrum of $\text{NaCp}^{i\text{Pr}4\text{Et}}$ in THF-d_8 at 65°C .

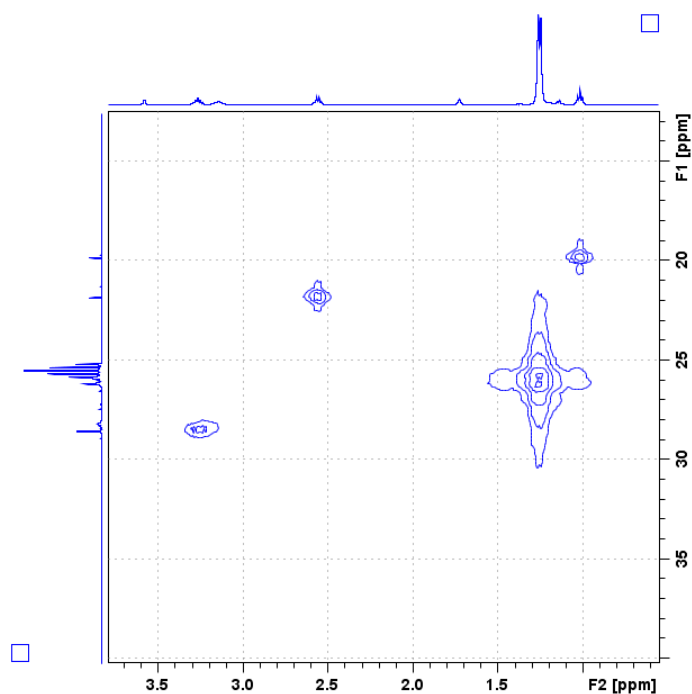


Figure S5.14. ^{13}C - ^1H HMQC spectrum of $\text{NaCp}^{i\text{Pr}4\text{Et}}$ in THF-d_8 at $65\text{ }^\circ\text{C}$.

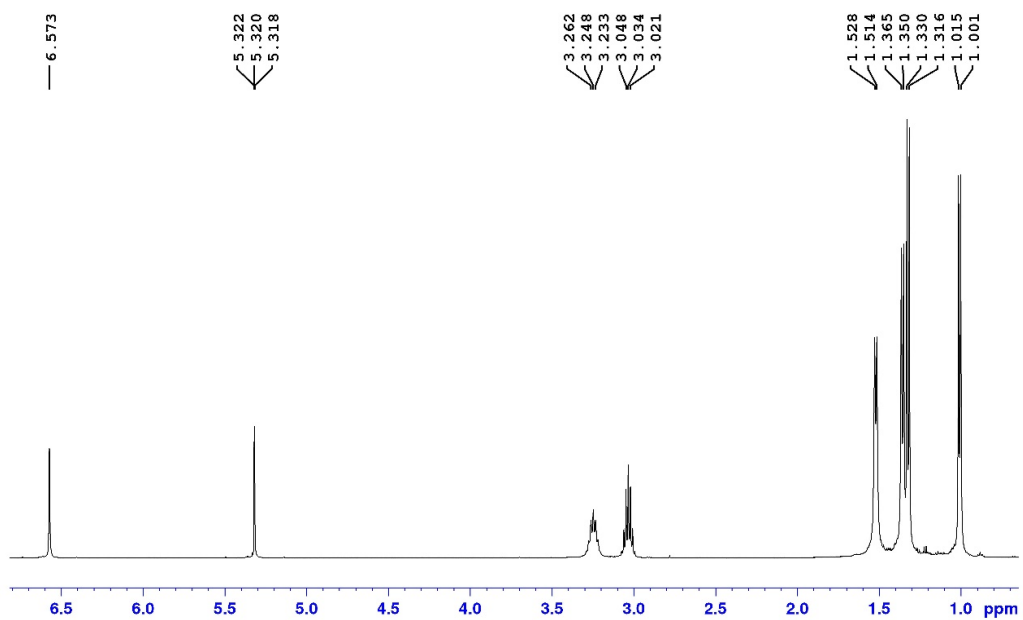


Figure S5.15. ^1H NMR spectrum of **Y1** in CD_2Cl_2 at $25\text{ }^\circ\text{C}$.

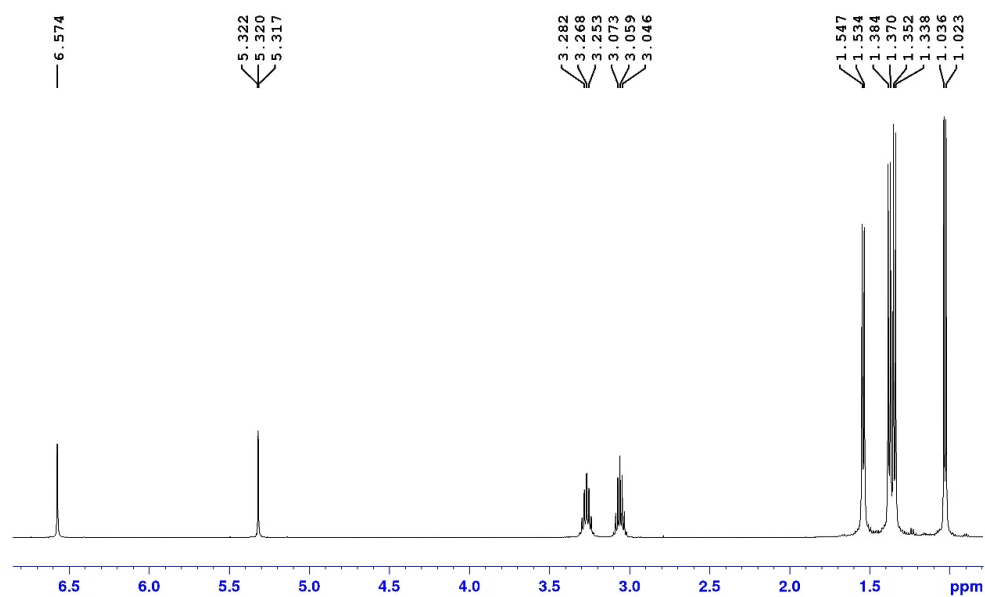


Figure S5.16. ^1H NMR spectrum of **Y1** in CD_2Cl_2 at 45 °C.

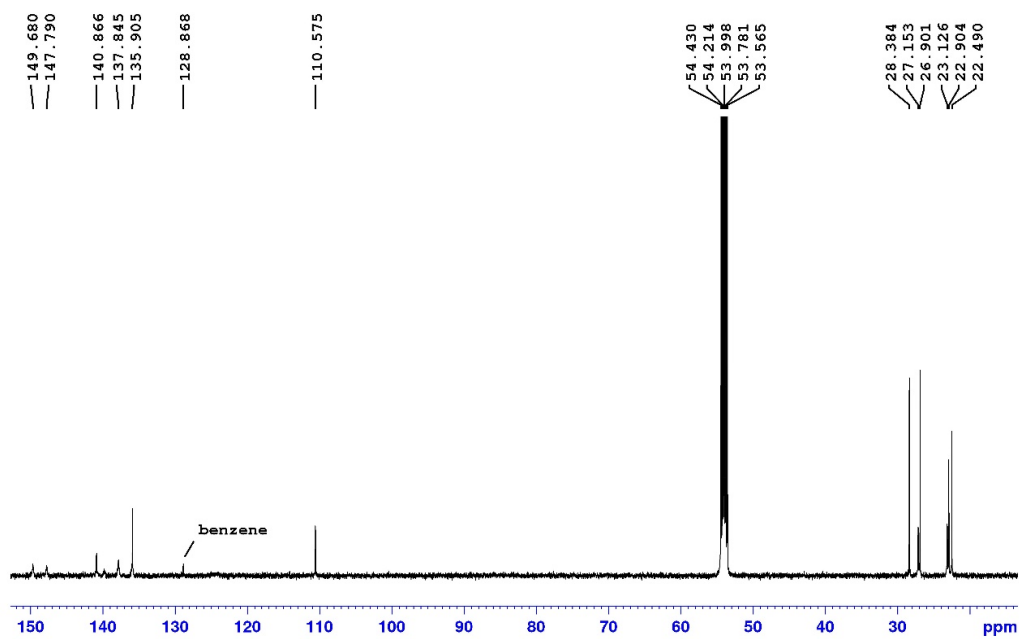


Figure S5.17. ^{13}C NMR spectrum of **Y1** in CD_2Cl_2 at 25 °C.

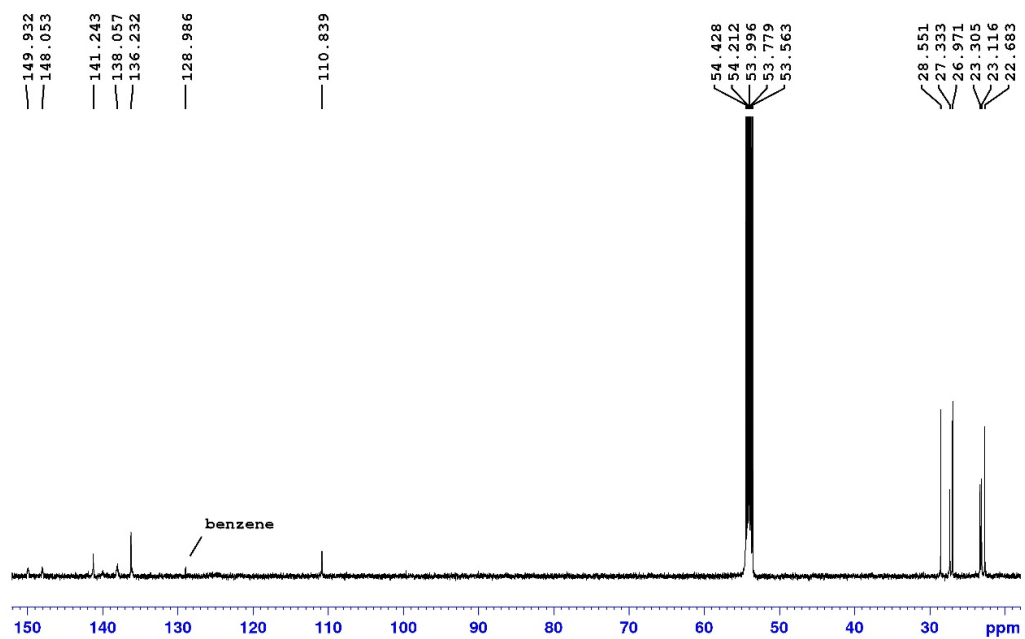


Figure S5.18. ¹³C NMR spectrum of Y1 in CD₂Cl₂ at 45 °C.

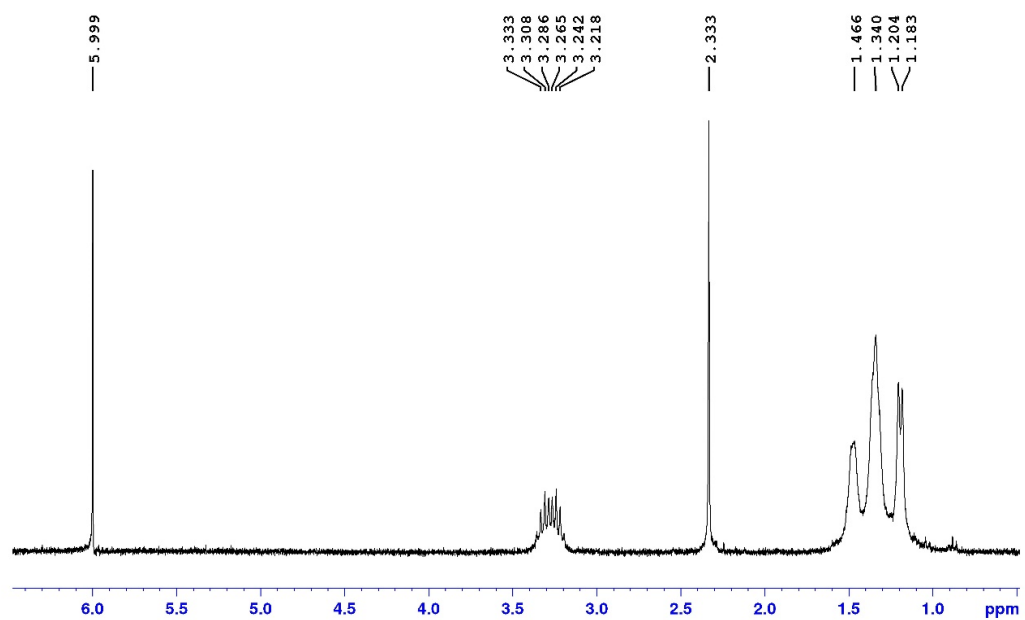


Figure S5.19. ¹H NMR spectrum of Y2 in TCE-d₂ at 25 °C.

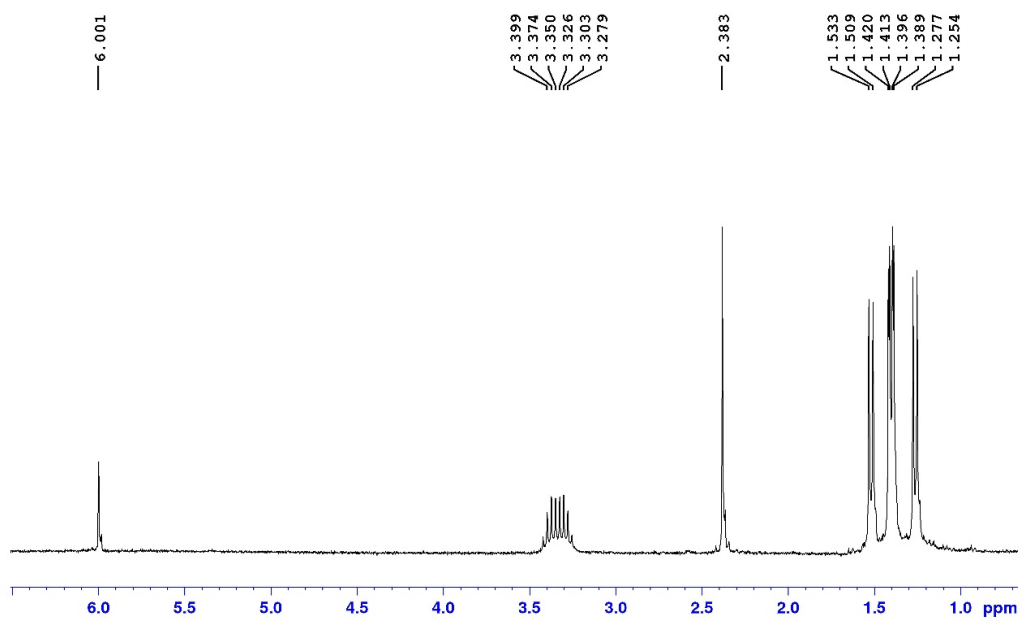


Figure S5.20. ^1H NMR spectrum of **Y2** in TCE- d_2 at 75 °C.

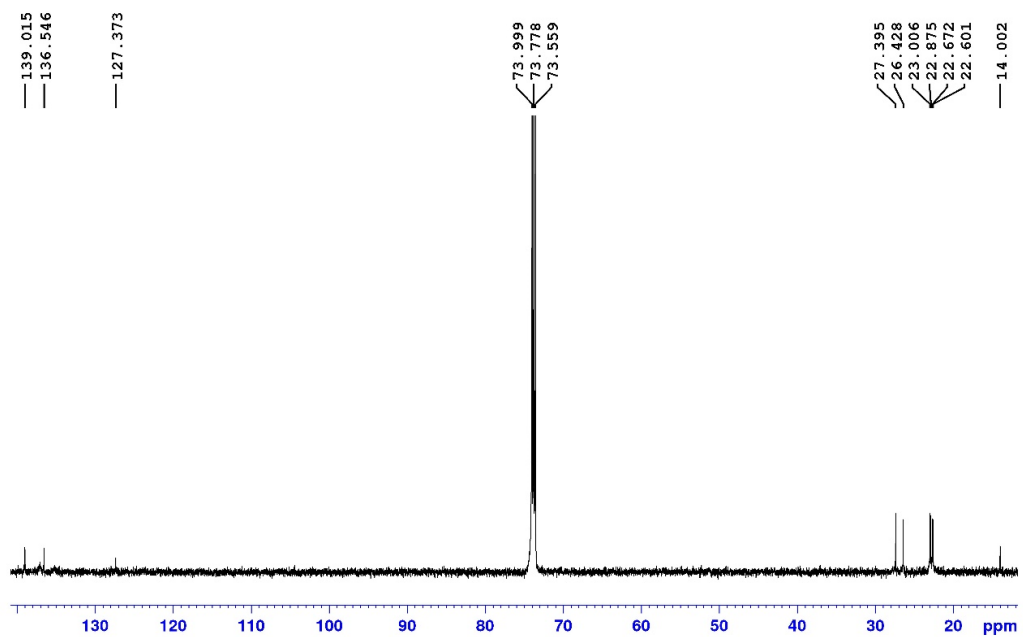


Figure S5.21. ^{13}C NMR spectrum of **Y2** in TCE- d_2 at 75 °C.

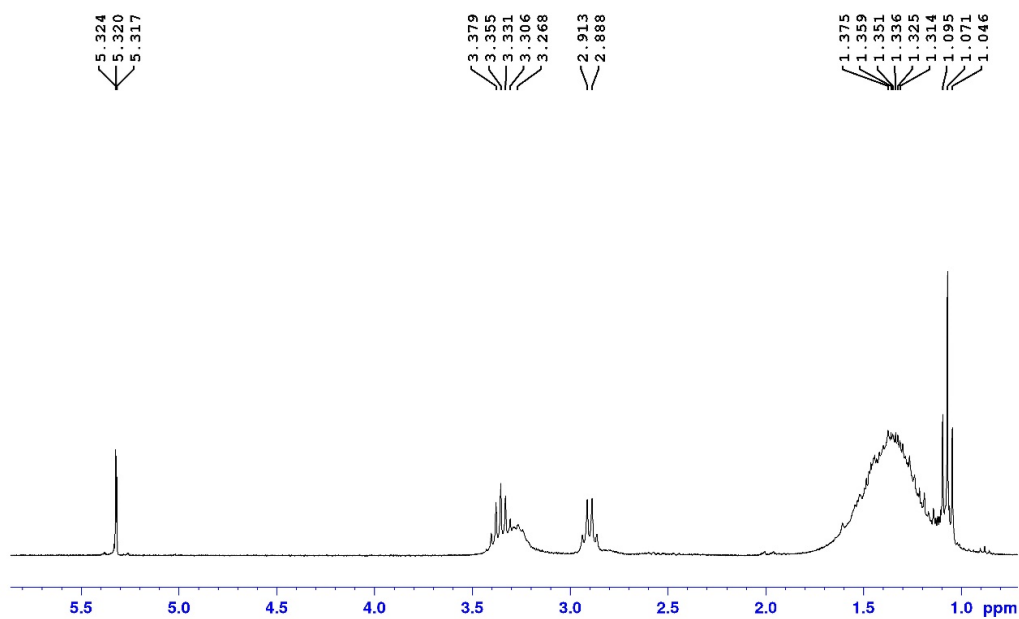


Figure S5.22. ^1H NMR spectrum of **Y3** in CD_2Cl_2 at 25 °C.

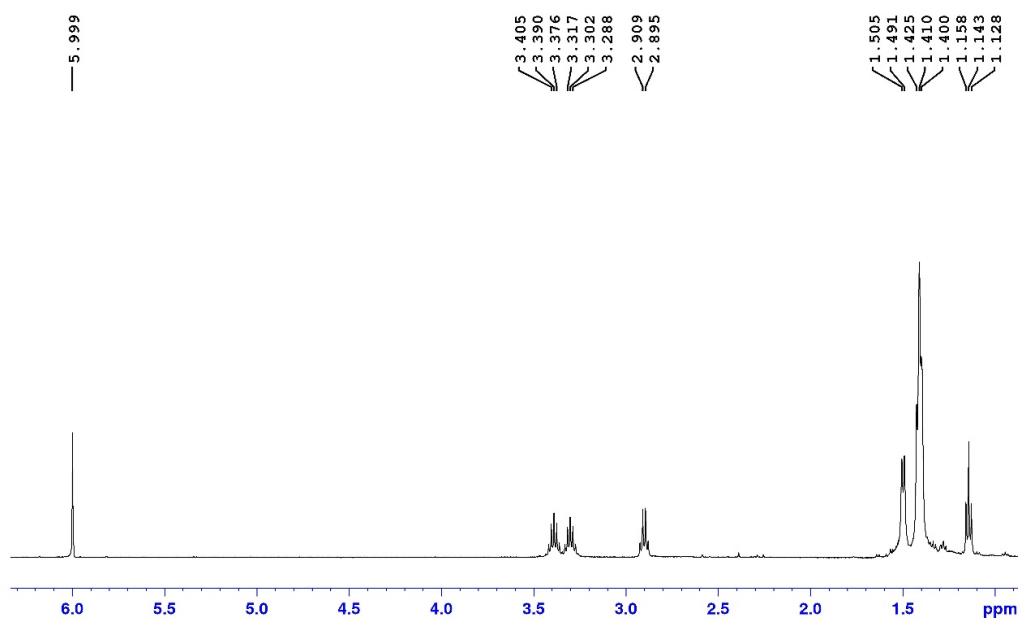


Figure S5.23. ^1H NMR spectrum of **Y3** in TCE-d_2 at 85 °C.

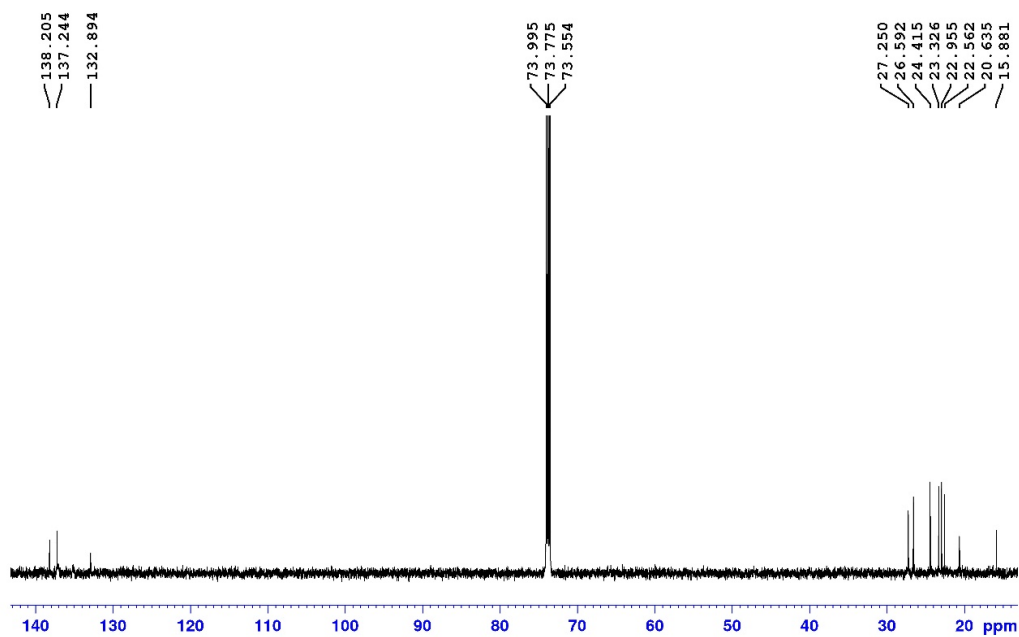


Figure S5.24. ¹³C NMR spectrum of **Y3** in TCE-d₂ at 75 °C.

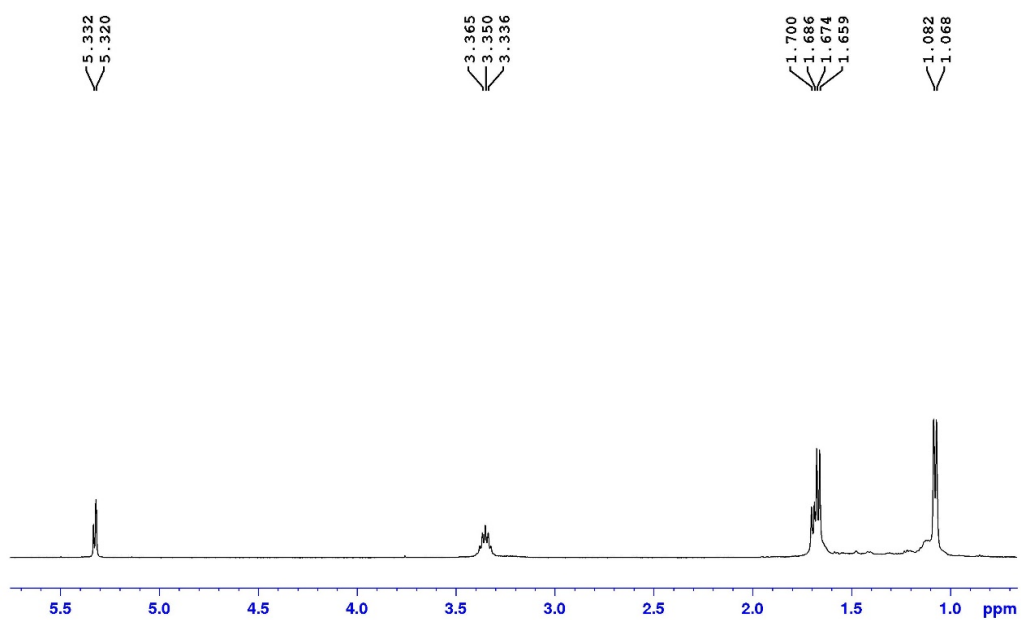


Figure S5.25. ¹H NMR spectrum of **Y4** in CD₂Cl₂ at -10 °C.

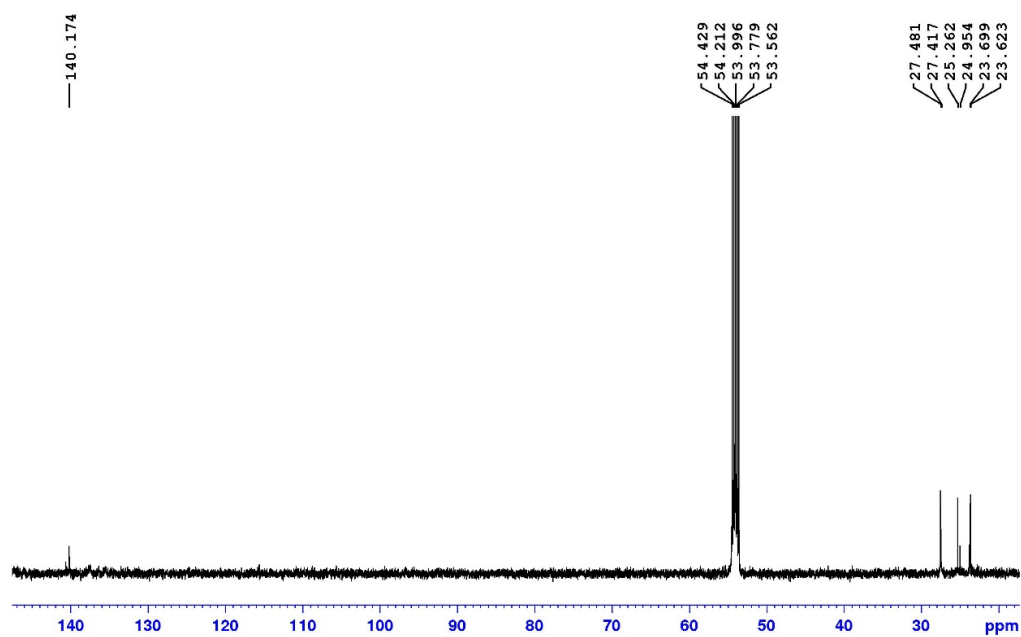


Figure S5.26. ^{13}C NMR spectrum of Y4 in CD_2Cl_2 at -10°C

5.6.3 X-ray Crystallography Data Collection and Refinement Details

Single crystal X-ray diffraction data of **1** and **Y1-Y4** were collected as follows. The sample was coated with Parabar oil and mounted on a MiTeGen polyimide loop in a nitrogen filled glovebox. The X-ray intensity data were measured using a Bruker SMART Apex II diffractometer at 100 K under a N₂ stream of an Oxford Cryostems Cryostream with MoK α radiation (graphite monochromator). Data was collected from four 180° ω scans with 0.5° steps at 90° rotation intervals about ϕ and a CCD detector distance of 5cm. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm.¹ Single crystal X-ray diffraction data of **2-4** were collected at Beamline 12.2.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory using synchrotron radiation ($\lambda = 0.7288$ Å). Single crystals were coated with Paratone-N oil, mounted on a MiTeGen loop, and frozen at 100 K under a N₂ stream of an Oxford Cryostems Cryostream 700 Plus on a Bruker AXS D8 diffractometer. Data were collected through a combination of 4° and 1° ϕ and ω scans with a Bruker PHOTON 100 CMOS detector. Data reduction was performed through SAINT and absorption correction through SADABS,² via Bruker AXS APEX III software.³ Structure solutions were performed by SHELXT using the direct method and were refined by least-square refinement against F^2 by SHELXL following standard procedures through the integrated structure analysis program OLEX2.^{4,6}

[Dy(Cp^{iPr4H})₂][B(C₆F₅)₄] (1). The compound crystallized in the space group $P2_1$ with two molecules in the asymmetric unit. Initial space group determination suggested significant symmetry fulfillment of an orthorhombic $P2_12_12_1$ cell, which pointed to the sign of pseudomeroheredral twinning about a two-fold rotational axis along the a axis. The structure was best modeled in $P2_1$ with a two-fold rotational axis along a as a twin law. In addition, Flack parameter refinement indicated that the crystal was also twinned by inversion. Refinement with four-component twin yielded the twin ratio of 0.29:0.289:0.212:0.209. As a result of significant twinning of the crystal, structure refinement was accomplished only through extensive application of restraints, as discussed below. It should be noted that restrained GooF of 1.059 differs only slightly from GooF of 1.063, indicating that the restraints were appropriately applied. All non-H atoms were refined anisotropically; H atoms were placed on the geometrically calculated positions using the riding model.

Anisotropic refinement of the Cp rings was stabilized by the application of equal anisotropic displacement parameters within the groups of five C atoms of the Cp rings (C1 to C5, C18 to C22, and C52 to C56), the four tertiary C atoms of the isopropyl groups (C6, C9, C12, C15; C23, C26, C29, C32; C40, C43, C46, C49; and C57, C60, C63, C66), the eight terminal –CH₃ arms of the isopropyl groups (C7, C8, C10, C11, C13, C14, C16, C17; C24, C25, C27, C28, C30, C31, C33, C34; C41, C42, C44, C45, C47, C48, C50, C51; and C58, C59, C61, C62, C64, C65, C67, C68). These sets of equal anisotropic displacement parameters were chosen such that the anisotropic displacement parameters would scale with the degree of freedom of the Cp rings (i.e., terminal –CH₃ groups fluctuate more than planar C₅ ring, etc.). The two [B(C₆F₅)₄][–] anions in the asymmetric unit were also subjected to equal anisotropic displacement parameters restraints: five F atoms on the same phenyl group were restrained to have the same anisotropic parameters. Five out of eight phenyl rings of the two [B(C₆F₅)₄][–] anions were subjected to equal anisotropic displacement parameters restraints. The phenyl rings were constrained to assume the ideal planar six-membered ring geometry via AFIX 66 commands. The remaining phenyl rings and the two B atoms were

stabilized by the enhanced rigid bond restraints. A rigid bond restraint was applied to one Cp ring (C35 to C51), for which equal anisotropic displacement parameters restraint was not necessary. Anomalous electron density was found near C42, which was found to interfere with modeling the isopropyl group. Therefore, C40–C41 and C40–C42 distances were restrained to a fixed value of 1.54 Å.

[Dy(Cp^{iPr4Me})₂][B(C₆F₅)₄] (2). The compound crystallized in the *P*2₁/*c* space group with two molecules in the asymmetric unit. The crystal was found to be twinned by pseudo-merohedry, and a two-fold rotational axis along the *a* axis was used as a twin law. Twin refinement results in a two-component twin with a ratio of 0.82:0.18. For each dysprosium cation in the structure, one Cp ring was found to be disordered over two positions. The occupancies of the two components were refined while constraining the sum to unity and yielded ratios of 0.589:0.411 and 0.636:0.364 for the first and second dysprosium ions, respectively. In refining the Cp disorder, the distance between C65A and C66A was restrained. Anisotropic displacement parameters of each disordered Cp ring were restrained to be the same in order to stabilize the refinement. These restraints were necessary as enhanced rigid bond restraints were found to be insufficient in modeling the disorder. Hydrogen atoms were placed on the geometrically calculated positions using the riding model. Anti-bumping restraint was applied to prevent short H···H contacts found in the disordered Cp moieties.

[Dy(Cp^{iPr4Et})₂][B(C₆F₅)₄] (3). The compound crystallized in the *P*2₁/*n* space group with one molecule in the asymmetric unit. All non-H atoms were refined anisotropically. For each Cp ring, one of the isopropyl groups adjacent to the ethyl substituent exhibited signs of disorder. For the first Cp ring, the isopropyl group was modeled such that one –CH₃ group (C38) was disordered over two positions. Refinement yielded an occupancy ratio of 0.63:0.37. For the second Cp ring, modeling the disorder did not yield reasonable model. Thus, the isopropyl group was modeled with only one configuration, even though the anisotropic displacement parameter of C10 is clearly elongated. These two isopropyl groups were subjected to rigid bond restraint in order to stabilize the structure refinement. Hydrogen atoms were placed on the geometrically calculated positions using the riding model.

[Dy(Cp^{iPr5})₂][B(C₆F₅)₄] (4). The compound crystallized in the *P*2₁/*n* space group with one molecule in the asymmetric unit. Anisotropic refinement of the Dy atom resulted in unusually large thermal displacement parameters, suggesting a disorder of the Dy atom. Reasonable thermal displacement parameters were achieved when the Dy atom was modeled over four positions. The occupancy sum of the four Dy positions was constrained to unity, and the occupancy refined to the ratio of 0.408:0.275:0.119:0.197.. It is interesting to note that the four Dy positions approximately lie in the same plane (RMS deviation = 0.0374), which might indicate that the Dy atom moves freely in between the two Cp rings, which have an angle of only 7.03(62)° between each other. The ten isopropyl groups on the two Cp rings were found to be disordered and were modeled over two positions. Refinement of the disordered isopropyl groups were stabilized through application of 1,2 (CH–CH₃) and 1,3 (CH₃···CH₃) distance restraints. The C_{Cp}–C_{Cp}–C(H) angles were restrained to be the same. All non-H atoms were refined anisotropically. Refinement of the disordered isopropyl groups were stabilized through application of 1,2 (CH–CH₃) and 1,3 (CH₃···CH₃) distance restraints. The C_{Cp}–C_{Cp}–C(H) angles were restrained to be the same.

Table S5.1. Structure details for [DyCp^{iPr4R}₂][B(C₆F₅)₄] (R = H (1), Me (2), Et (3), iPr (4)).

[DyCp ^{iPr4R} ₂][B(C ₆ F ₅) ₄], R =	H (1)	Me (2)	Et (3)	iPr (4)
Wavelength (Å)	0.71073	0.7288	0.7288	0.7288
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å), α (°)	16.5863(17), 90	14.50(2), 90	14.9801(4), 90	15.2173(4), 90
<i>b</i> (Å), β (°)	14.4989(15),	16.63(3),	23.0586(7),	22.8792(6),
<i>c</i> (Å), γ (°)	90.0586(16)	90.027(12)	90.789(2)	90.605(1)
<i>V</i> (Å ³)	5461.0(9)	11236(33)	5770.4(3)	5876.9(3)
<i>Z</i>	4	8	4	4
ρ_{calc} (g/cm ³)	1.591	1.580	1.571	1.574
Crystal size (mm ³)	$0.338 \times 0.187 \times 0.044$	$0.107 \times 0.057 \times$	$0.130 \times 0.060 \times$	$0.110 \times 0.071 \times$
θ range for data collection (°)	1.228 to 25.349	0.896 to 26.042	1.544 to 23.880	0.913 to 21.594
Index ranges	$-19 \leq h \leq 19$ $-17 \leq k \leq 17$ $-27 \leq l \leq 27$	$-17 \leq h \leq 17$ $-20 \leq k \leq 20$ $-56 \leq l \leq 56$	$-16 \leq h \leq 16$ $25 \leq k \leq 25$ $-18 \leq l \leq 18$	$-15 \leq h \leq 15$ $-23 \leq k \leq 23$ $-17 \leq l \leq 17$
Reflections collected	61686	163480	71765	47155
Independent reflections (<i>R</i> _{int})	19909 (0.0382)	20570 (0.1408)	8291 (0.0868)	6341 (0.0986)
Completeness (%)	99.8	100.0	100.0	100.0
Data / restraints / parameters	19909 / 93 / 634	20570 / 28 / 1414	8291 / 8 / 767	6341 / 693 / 1085
Goodness-of-fit on <i>F</i> ²	1.069	1.035	1.056	1.060
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0721, 0.1810	0.0570, 0.1354	0.0682, 0.1589	0.0650, 0.1700
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0756, 0.1851	0.0761, 0.1497	0.0854, 0.1711	0.0732, 0.1759

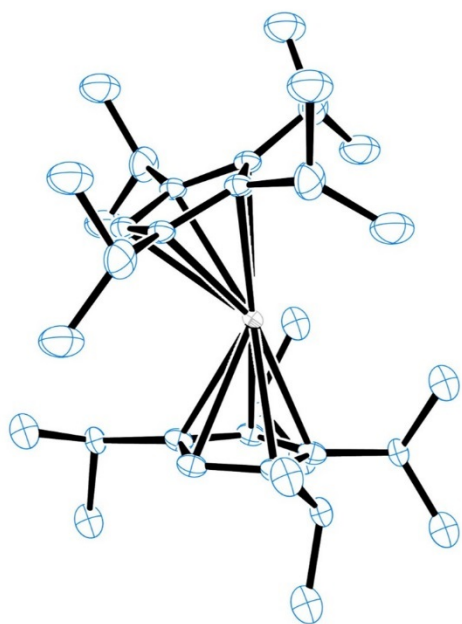


Figure S5.27. Solid-state structure of one of the $[\text{Dy}(\text{Cp}^{\text{iPr4H}})_2]^+$ cations in **1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity

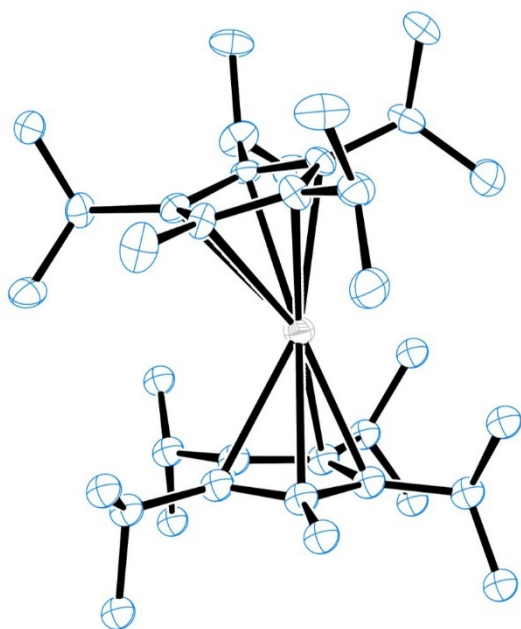


Figure S5.28. Solid-state structure of one of the $[\text{Dy}(\text{Cp}^{\text{iPr4Me}})_2]^+$ cations in **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the second disordered component Cp ring are omitted for clarity.

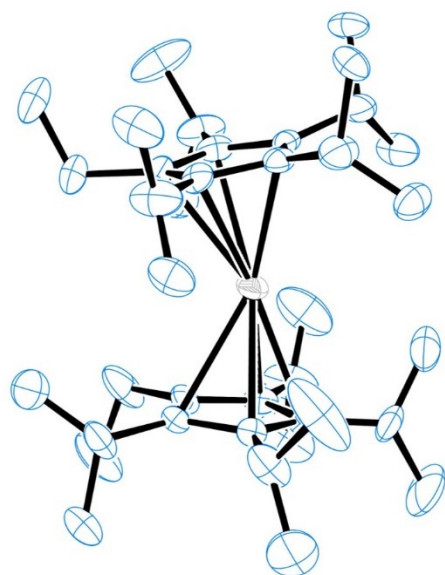


Figure S5.29. Solid-state structure of the $[\text{Dy}(\text{Cp}^{i\text{Pr}4\text{Et}})_2]^+$ cation in **3** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

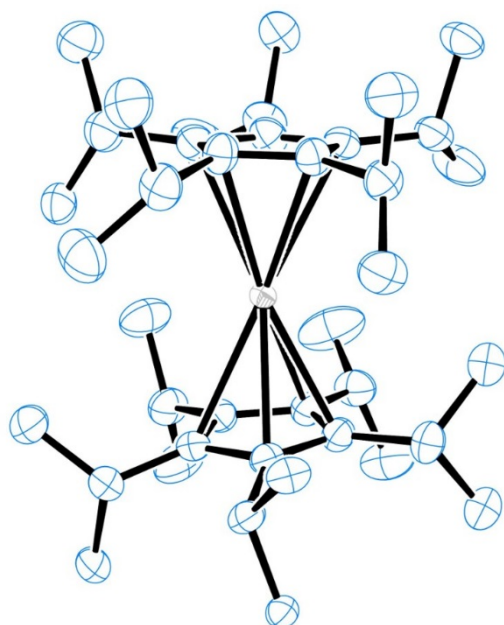


Figure S5.30. Solid-state structure of the $[\text{Dy}(\text{Cp}^{i\text{Pr}5})_2]^+$ cation in **4** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and the disordered component are omitted for clarity.

Table S5.2. Selected bond distances (Å) and angles (°) for **1–4**.

R =	H (1)	Me (2)	Et (3)	iPr (4)
Dy1–C1	2.60(2)	2.623(8)	2.608(8)	2.508(9)
Dy1–C2	2.58(2)	2.672(7)	2.677(7)	2.551(10)
Dy1–C3	2.57(2)	2.648(7)	2.615(7)	2.726(10)
Dy1–C4	2.63(2)	2.567(7)	2.527(7)	2.772(10)
Dy1–C5	2.58(2)	2.544(8)	2.533(7)	2.651(9)
Dy1–C1' ^a	2.59(2)	2.619(17)	2.597(8)	2.448(10)
Dy1–C2' ^a	2.59(2)	2.617(19)	2.607(8)	2.479(10)
Dy1–C3' ^a	2.58(3)	2.542(15)	2.608(7)	2.704(9)
Dy1–C4' ^a	2.54(2)	2.521(15)	2.594(7)	2.775(10)
Dy1–C5' ^a	2.54(2)	2.580(15)	2.597(7)	2.637(10)
Dy2–C35(37) ^b	2.62(3)	2.627(8)	–	–
Dy2–C36(38) ^b	2.64(3)	2.651(7)	–	–
Dy2–C37(39) ^b	2.53(3)	2.646(7)	–	–
Dy2–C38(40) ^b	2.56(3)	2.599(7)	–	–
Dy2–C39(41) ^b	2.59(3)	2.575(8)	–	–
Dy2–C52(55) ^b	2.56(3)	2.627(19)	–	–
Dy2–C53(56) ^b	2.66(2)	2.571(15)	–	–
Dy2–C54(57) ^b	2.63(2)	2.527(17)	–	–
Dy2–C55(58) ^b	2.54(3)	2.587(16)	–	–
Dy2–C56(59) ^b	2.59(3)	2.659(18)	–	–
Dy–C(avg)	2.587(5) ^d	2.600(3) ^d	2.596(2) ^d	2.625(3) ^d
Dy1–Cp(A) ^c	2.29(2) ^e	2.311(8) ^e	2.297(8) ^e	2.358(10) ^{e,f}
Dy1–Cp(B) ^c	2.27(3) ^e	2.273(19) ^{e,f}	2.306(8) ^e	2.321(10) ^{e,f}
Dy2–Cp(C) ^c	2.30(3) ^e	2.319(3) ^e	–	–
Dy2–Cp(D) ^c	2.29(3) ^e	2.288(3) ^{e,f}	–	–
Dy–Cp(avg)	2.29(1) ^d	2.298(5) ^d	2.302(6) ^d	2.340(7) ^d
Cp(A)–Dy1–Cp(B)	148.2(8)	157.35(40) ^f	161.09(20)	157.82(18)
Cp(C)–Dy2–Cp(D)	146.4(8)	155.93(30) ^f	–	–
Cp(A)–Dy2–Cp(B)	–	–	–	158.85(40)
Cp(A)–Dy3–Cp(B)	–	–	–	167.94(152)
Cp(A)–Dy4–Cp(B)	–	–	–	163.91(90)

^a C1' to C5' denote the five C atoms of the second Cp ring in the structure. These correspond to C18–C22 for **1**, C19–C23 for **2**, C20–C24 for **3**, and C21–C25 for **4**.

^b C35(37) to C39(41) and C52(55) to C56(59) are the five C atoms of the first and second Cp rings on Dy2 in the structure of **1(2)**.

^c Cp(A), Cp(B), Cp(C), and Cp(D) refer to the first (C1–C5), second (C1' to C5') Cp rings on Dy1 and first, second Cp rings on Dy2, respectively.

^d The standard deviation of the average value was estimated from $\sigma = \sqrt{\sum \sigma_i^2 / N}$, where σ_i is the standard deviation of each bond distance i and N is the number of distances averaged.

^e Dy–Cp distances were measured from the Dy atom to the centroid of the Cp ring. The standard deviations are estimated as the largest esd of Dy–C distances in the respective Cp ring.

^f The minor disordered component was not taken into account, as it shows significant deviation from typical Dy–Cp distances, likely due to artefact in disorder

[Y(Cp^{iPr4H})₂][B(C₆F₅)₄] (Y1). The compound crystallized in the space group *P2*₁ with two molecules in the asymmetric unit. Initial space group determination suggested significant symmetry fulfillment of an orthorhombic *P2*₁*2*₁*2*₁ cell, which pointed to the sign of pseudo-merohedral twinning about a two-fold rotational axis along the *a* axis. The structure was best modeled in *P2*₁ with a two-fold rotational axis along *a* as a twin law. In addition, Flack parameter refinement indicated that the crystal was also twinned by inversion. Refinement with four-component twin yielded the twin ratio of 0.263(19):0.265(11):0.237(11):0.235(11). As a result of significant twinning of the crystal, structure refinement was accomplished only through extensive application of restraints, as discussed below. It should be noted that restrained GooF of 1.128 differs only slightly from GooF of 1.123, indicating that the restraints were appropriately applied. All non-H atoms were refined anisotropically; H atoms were placed on the geometrically calculated positions using the riding model.

One Cp^{iPr4H} ring on Y1 (C1 to C14) and its disordered ⁱPr group (C13A and C14A) were stabilized by the enhanced rigid bond restraints. The second [Y(Cp^{iPr4})₂]⁺ cation has the Y atom and one Cp^{iPr4H} ligand disordered over two positions. Anisotropic refinement of the disordered Cp^{iPr4H} ring was stabilized by application of equal anisotropic displacement parameters to the 5C ring (C52 to C56 and C52C to C56C), and the four isopropyl groups (C57 to C68 and C57C to C68C). The ordered Cp ring on Y2 was stabilized by the enhanced rigid bond restraints. The Cp rings were constrained to assume ideal planar geometry through AFIX 56 commands. Some disordered isopropyl groups required restraining the C–C bond distances to stabilize the refinement. Anti-bumping restraint was applied to prevent short H···H contacts found in the disordered Cp moieties.

The two [B(C₆F₅)₄][−] anions in the asymmetric unit were disordered over two positions and all B and C atoms, and F atoms were subjected to equal anisotropic displacement parameters restraints. The phenyl rings were constrained to assume the ideal planar six-membered ring geometry via AFIX 66 commands. All C–F and B–C bond distances were restrained to the appropriate values.

[Y(Cp^{iPr4Me})₂][B(C₆F₅)₄] (Y2). The compound crystallized in the *P2*₁/*c* space group with two molecules in the asymmetric unit. The crystal was found to be twinned by pseudo-merohedry, and a two-fold rotational axis along the *a* axis was used as a twin law. Twin refinement results in a two-component twin with a ratio of 0.5378(15):0.4622(15). For each cation in the structure, one Cp ring was found to be disordered over two positions. The occupancies of the two components were refined while constraining the sum to unity and yielded ratios of 0.58:0.42 and 0.59:0.41 for the first and second metallocenium cations, respectively. The disordered Cp rings were constrained to assume the idealized pentagon geometry using AFIX 56 commands. Anisotropic refinement of the Y atom resulted in unusually large thermal displacement parameters, suggesting a disorder of the Y atom. Reasonable thermal displacement parameters were achieved when the Y atom was modeled over two positions. The occupancy sum of the two positions was constrained to unity, and the occupancy refined to the ratio of 0.74:0.26 and 0.75:0.25 for the two molecules, respectively. Anisotropic refinement was stabilized by the enhanced rigid bond restraints. Hydrogen atoms were placed on the geometrically calculated positions using the riding model. Anti-bumping restraint was applied to prevent short H···H contacts found in the disordered Cp moieties.

[Y(Cp^{iPr4Et})₂][B(C₆F₅)₄] (Y3). The compound crystallized in the $P2_1/n$ space group with one molecule in the asymmetric unit. All non-H atoms were refined anisotropically. For each Cp ring, one of the isopropyl groups adjacent to the ethyl substituent exhibited signs of disorder. For the first Cp ring, the isopropyl group was modeled such that one –CH₃ group (C29) was disordered over two positions. Refinement yielded an occupancy ratio of 0.655:0.345. For the second Cp ring, modeling the disorder did not yield reasonable model. Thus, the isopropyl group was modeled with only one configuration, even though the anisotropic displacement parameter of C10 is clearly elongated. These two isopropyl groups were subjected to rigid bond restraint in order to stabilize the structure refinement. Hydrogen atoms were placed on the geometrically calculated positions using the riding model. Refining one pentafluorophenyl group of the [B(C₆F₅)₄][–] anion requires the application of a rigid bond restraint. Anti-bumping restraint was applied to prevent short H···H contacts.

[Y(Cp^{iPr5})₂][B(C₆F₅)₄] (Y4). The compound crystallized in the $C2/c$ space group with half a molecule in the asymmetric unit. The [B(C₆F₅)₄][–] anion was found to be disordered over two positions. Refinement of the disordered [B(C₆F₅)₄][–] was stabilized by the enhanced rigid bond restraints. Hydrogen atoms were placed on the geometrically calculated positions using the riding model. Only the *meso* isomer was observed in the structure.

[YCp ^{iPr4R₂}][B(C ₆ F ₅) ₄], R =				H (Y1)	Me (Y2)	Et (Y3)	iPr (Y4)
Wavelength (Å)				0.71073	0.71073	0.71073	0.71073
Crystal system				Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group				<i>P2₁</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>C2/c</i>
<i>a</i> (Å), <i>α</i> (°)				16.538(2), 90	14.599(10), 90	15.0163(5), 90	27.336(2), 90
<i>b</i> (Å), <i>β</i> (°)				14.4952(18),	16.737(11),	23.1163(8),	11.5772(10),
<i>c</i> (Å), <i>γ</i> (°)				90.053(2)	90.253(11)	90.9020(10)	106.0490(10)
<i>V</i> (Å ³)				5454.3(12)	11514(13)	5824.4(3)	5910.4(9)
<i>Z</i>				4	8	4	4
<i>ρ</i> _{calc} (g/cm ³)				1.504	1.457	1.472	1.482
Crystal size (mm ³)				0.274 × 0.221 ×		0.492 × 0.224 × 0.138	0.327 × 0.268 × 0.140
<i>θ</i> range for data collection				1.405 to 27.103	1.395 to 23.629	1.500 to 21.036	1.550 to 25.349
Index ranges				−21 ≤ <i>h</i> ≤ 21 −18 ≤ <i>k</i> ≤ 18 −29 ≤ <i>l</i> ≤ 29	−16 ≤ <i>h</i> ≤ 16 −18 ≤ <i>k</i> ≤ 18 −52 ≤ <i>l</i> ≤ 52	−15 ≤ <i>h</i> ≤ 15 −23 ≤ <i>k</i> ≤ 23 −16 ≤ <i>l</i> ≤ 16	−32 ≤ <i>h</i> ≤ 32 −13 ≤ <i>k</i> ≤ 13 −23 ≤ <i>l</i> ≤ 23
Reflections collected				70917	84123	43460	33243
Independent reflections				24026 (0.0696)	17198 (0.0538)	6283 (0.0425)	5416 (0.0464)
Completeness (%)				99.8	99.7	100.0	100.0
Data / restraints /				24026 / 600 / 970	17198 / 1156 / 1810	6283 / 67 / 770	5416 / 324 / 599
Goodness-of-fit on <i>F</i> ²				1.123	1.046	1.053	1.032
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]				0.0821, 0.2161	0.0769, 0.1922	0.0638, 0.1591	0.0470, 0.1119
<i>R</i> ₁ , <i>wR</i> ₂ (all data)				0.1146, 0.2386	0.0909, 0.2027	0.0795, 0.1719	0.0685, 0.1255

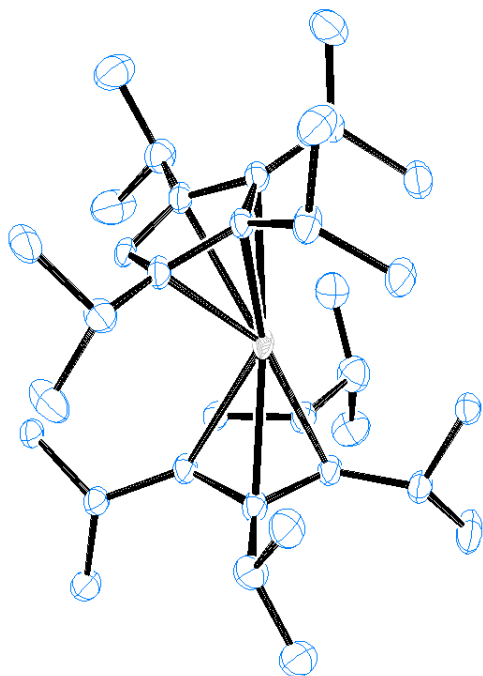


Figure S5.31. Solid-state structure of one of the $[\text{Y}(\text{Cp}^{\text{iPr4H}})_2]^+$ cations in **Y1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the disordered component are omitted for clarity.

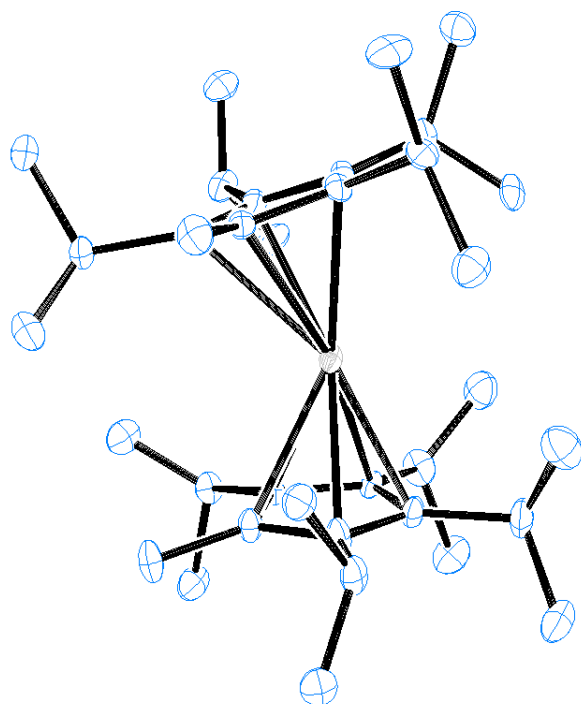


Figure S5.32. Solid-state structure of one of the $[\text{Y}(\text{Cp}^{\text{iPr4Me}})_2]^+$ cations in **Y2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the disordered component are omitted for clarity.

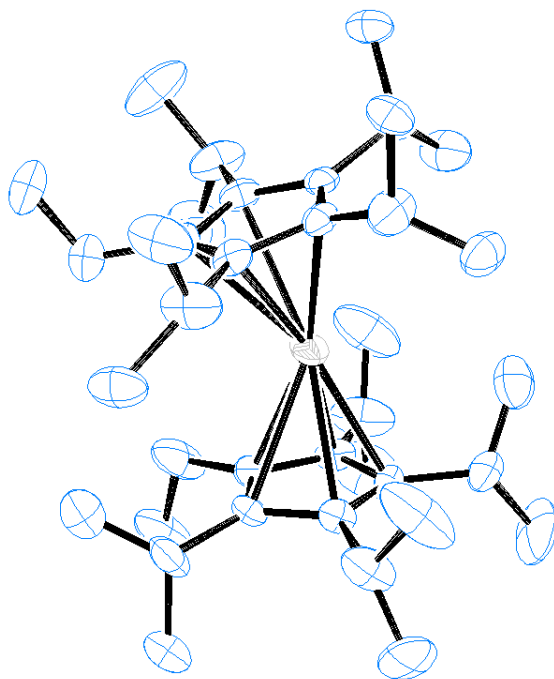


Figure S5.33. Solid-state structure of the $[\text{Y}(\text{Cp}^{\text{iPr4Et}})_2]^+$ cation in **Y3** with thermal ellipsoids at the 30% probability level.

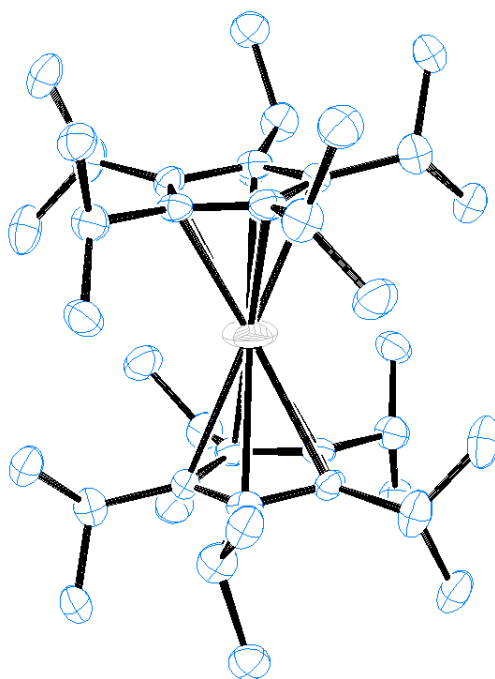


Figure S5.34. Solid-state structure of the $[\text{Y}(\text{Cp}^{\text{iPr5}})_2]^+$ cation in **Y4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

5.6.4 Magnetic Measurements

General. Magnetic samples were prepared by adding crystalline powder (18.2 mg of **1**, 19.4 mg of **2**, 15.8 mg of **3**, and 17.7 mg of **4**) to a 5 mm i.d./7 mm o.d. quartz tube with a raised quartz platform. A layer of eicosane was added to the samples (21.1 mg for **1**, 21.7 mg for **2**, 15.9 mg for **3**, and 20.4 mg for **4**) to provide good thermal contact between the sample and the bath and to prevent crystallite torqueing. The tubes were fitted with Teflon sealable adapters, evacuated using a glovebox vacuum pump, and then flame sealed with an O₂/H₂ flame under vacuum. After flame-sealing, the eicosane was melted in a 40 °C water bath.

Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. All data were corrected for diamagnetic contributions from the core diamagnetism and for the diamagnetism of the eicosane used to suspend the sample, estimated using Pascal's constants to give corrections of $\chi_{\text{dia}} = -0.000670$ emu/mol, -0.000694 emu/mol, -0.000717 emu/mol, and -0.000741 emu/mol for **1**, **2**, **3**, and **4**, respectively.

Dc Magnetic Susceptibility Measurements. Dc magnetic susceptibility measurements were performed at temperatures ranging from 2 to 300 K under applied fields of 1, 5, and 10 kOe (0.1, 0.5, and 1 T) for **1-4**.

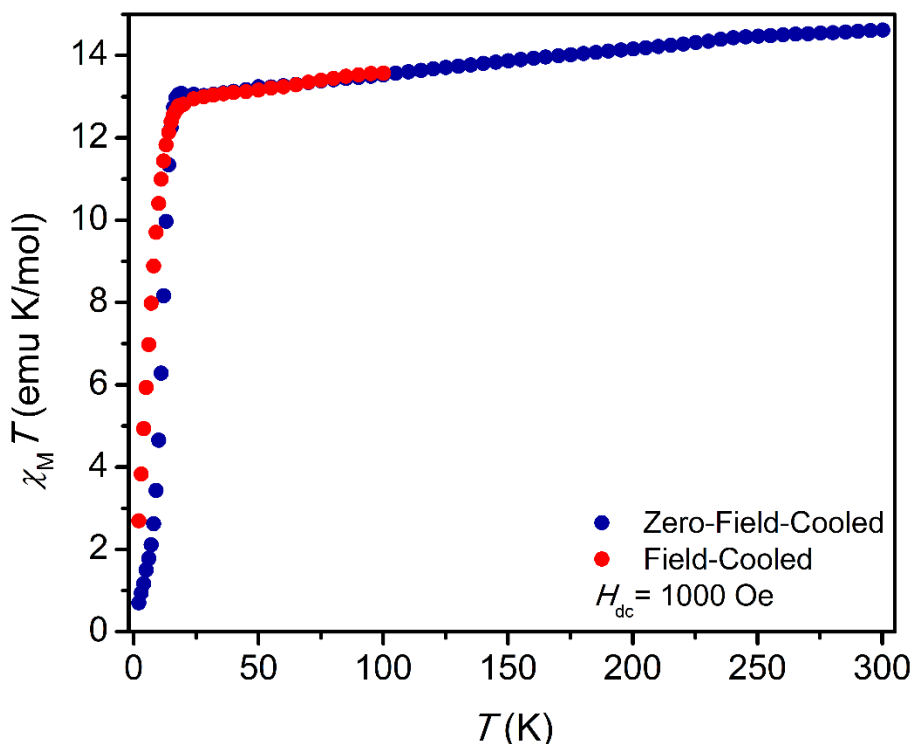


Figure S5.35. Field-cooled (red) and zero-field cooled (blue) measurements of **1** under an applied field of 1 kOe.

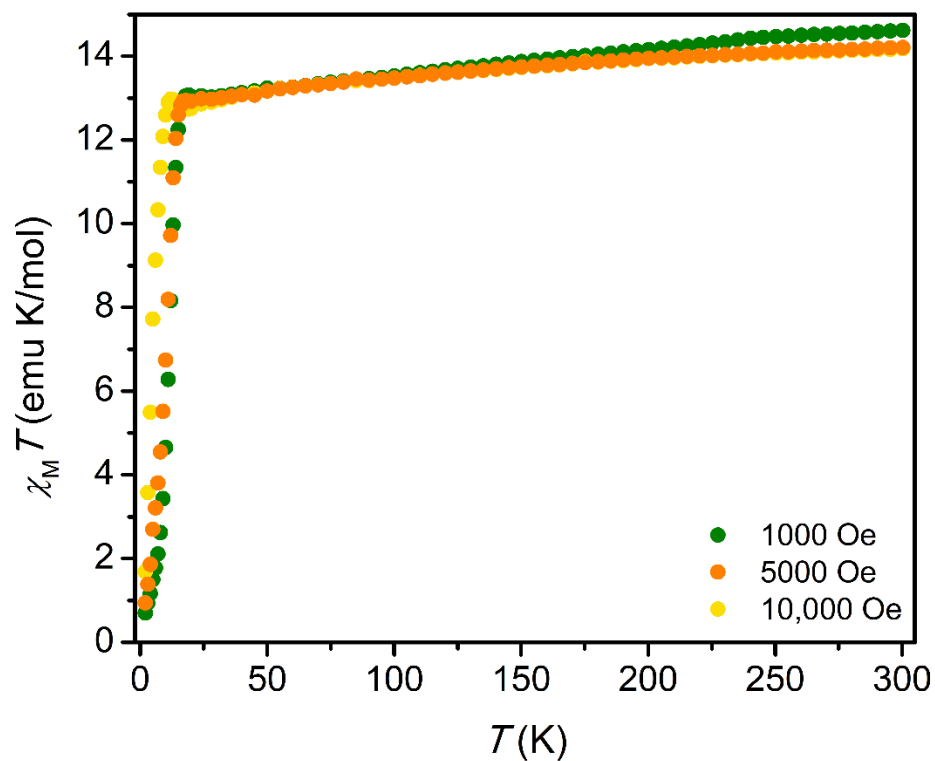


Figure S5.36. Zero-field cooled dc magnetic susceptibility measurements of **1** under applied fields of 1, 5, and 10 kOe.

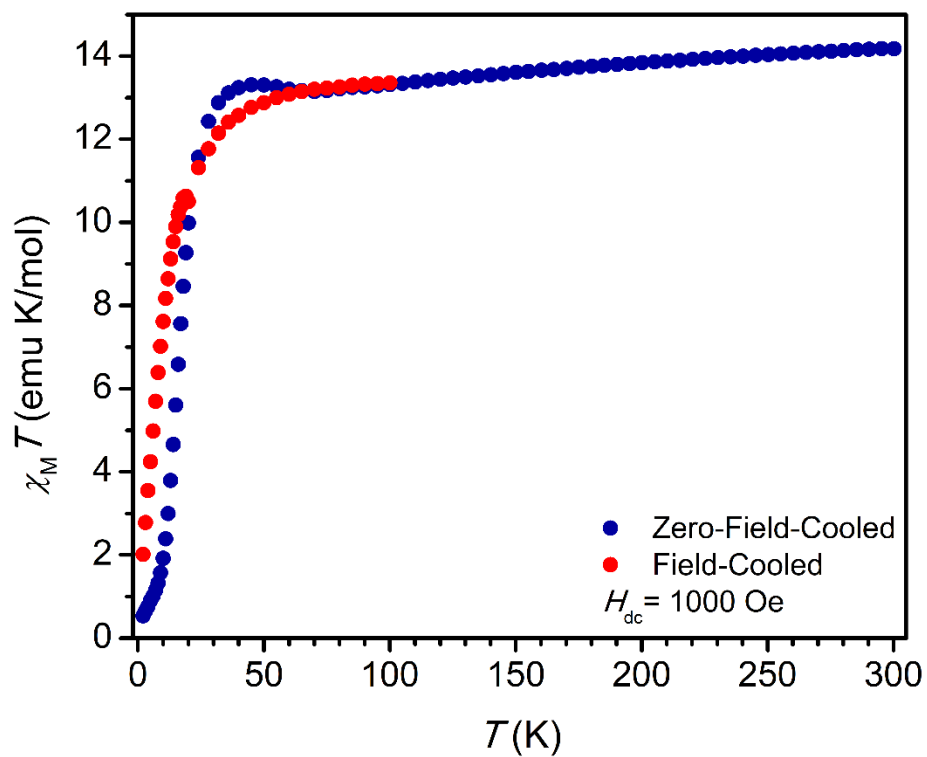


Figure S5.37. Field-cooled (red) and zero-field cooled (blue) measurements of **2** under an applied field of 1 kOe.

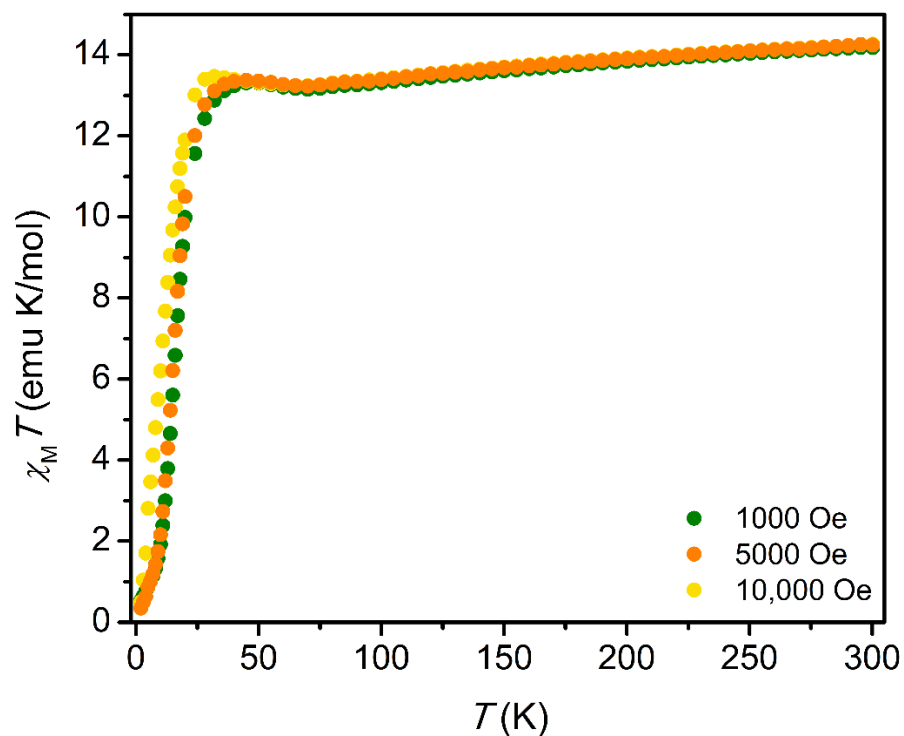


Figure S5.38. Zero-field cooled dc magnetic susceptibility measurements of **2** under applied fields of 1, 5, and 10 kOe.

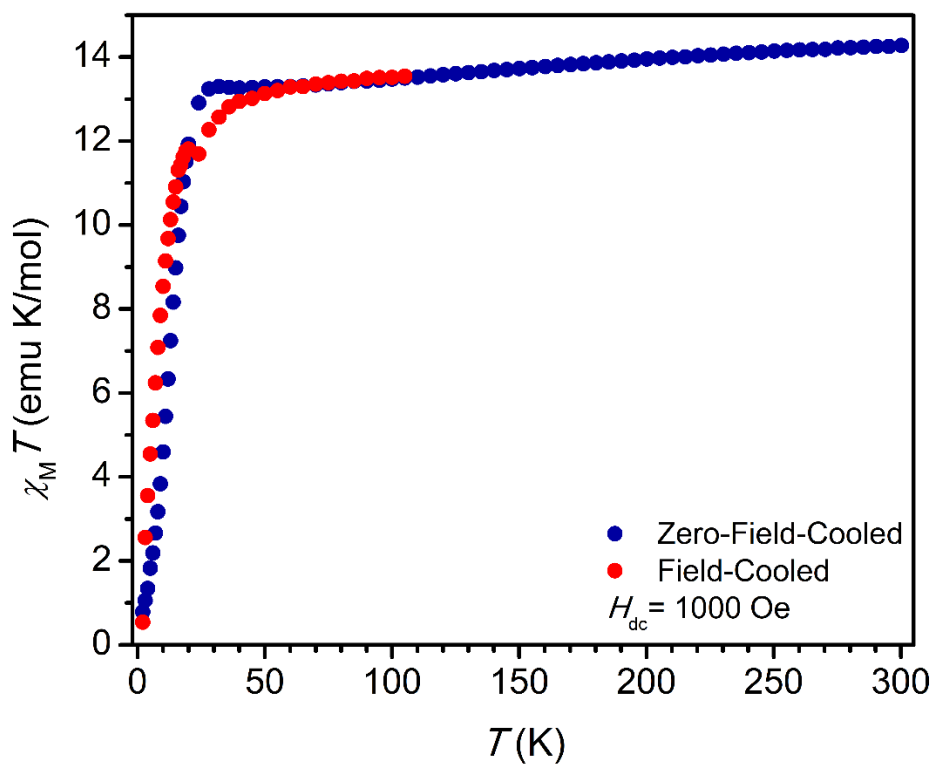


Figure S5.39. Field-cooled (red) and zero-field cooled (blue) measurements of **3** under an applied field of 1 kOe.

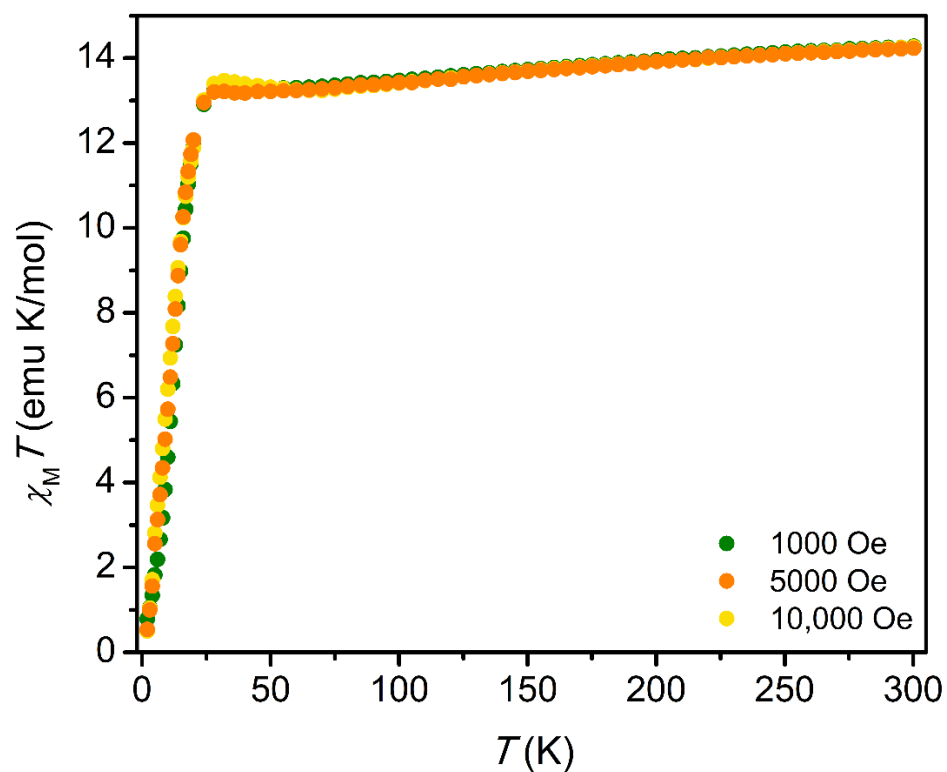


Figure S5.40. Zero-field cooled dc magnetic susceptibility measurements of **3** under applied fields of 1, 5, and 10 kOe.

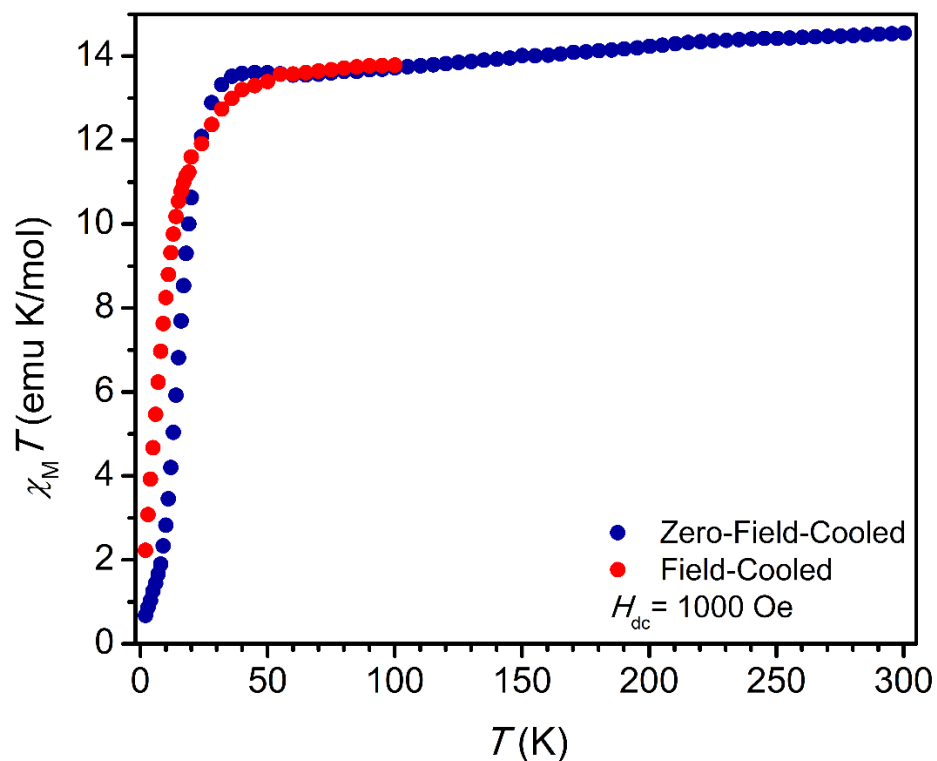


Figure S5.41. Field-cooled (red) and zero-field cooled (blue) measurements of **4** under an applied field of 1 kOe.

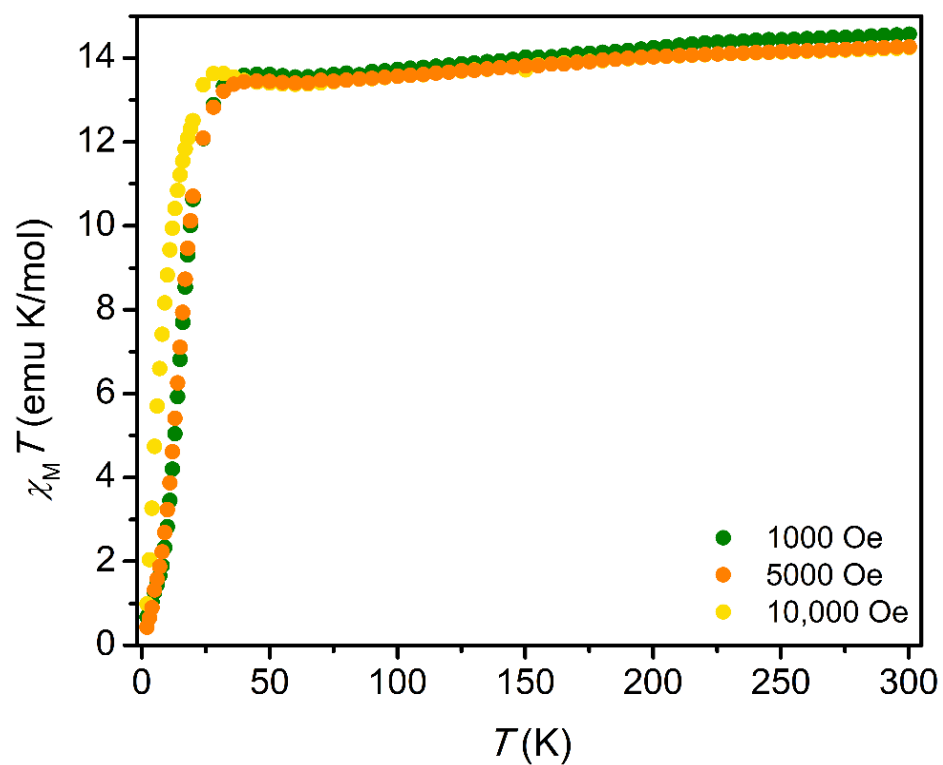


Figure S5.42. Zero-field cooled dc magnetic susceptibility measurements of **4** under applied fields of 1, 5, and 10 kOe.

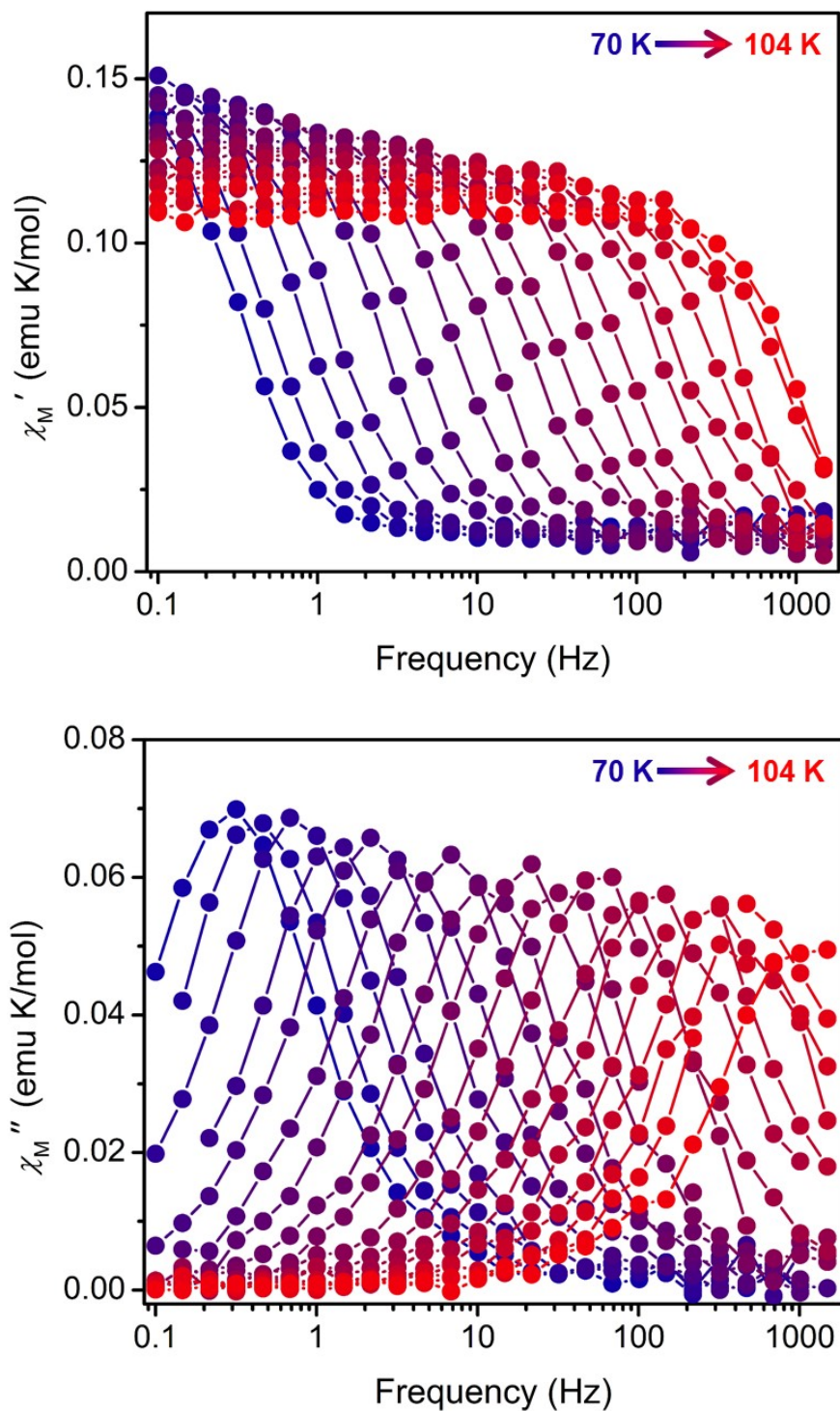


Figure S5.43. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **1** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 70–104 K (2 K steps). The colored lines are guides for the eye.

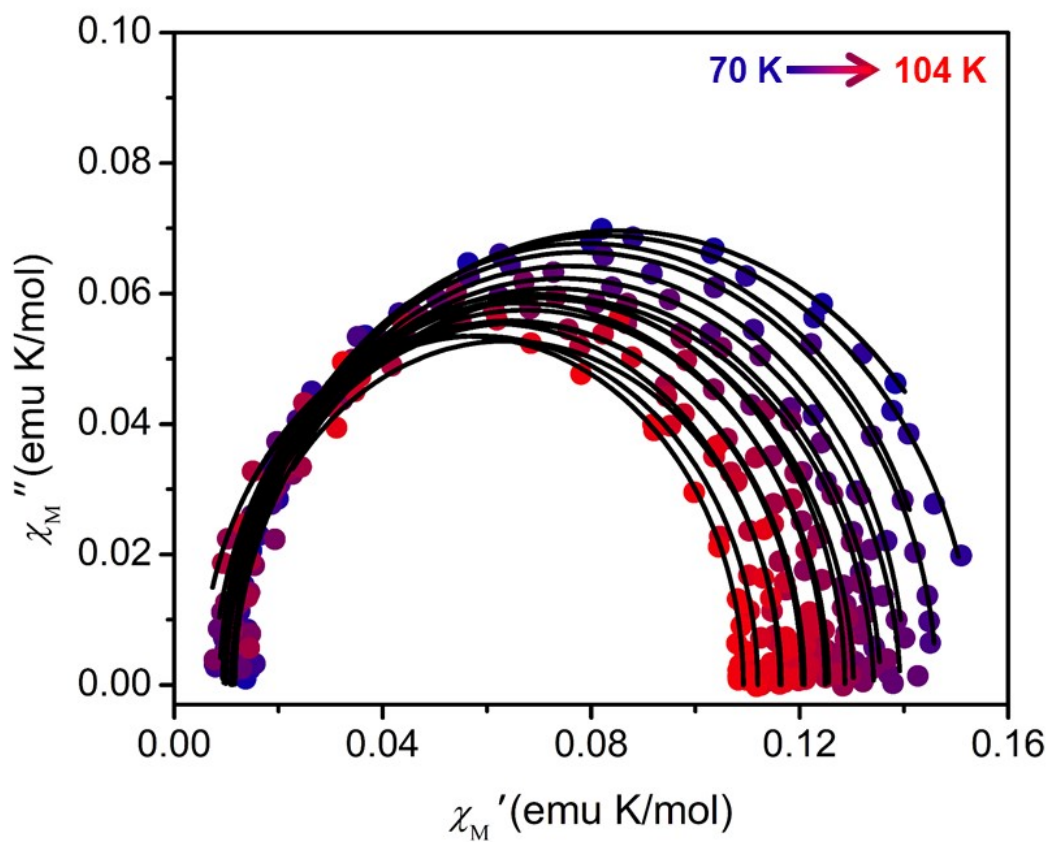


Figure S5.44. Cole-Cole plots for **1** from 70–104 K (2 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

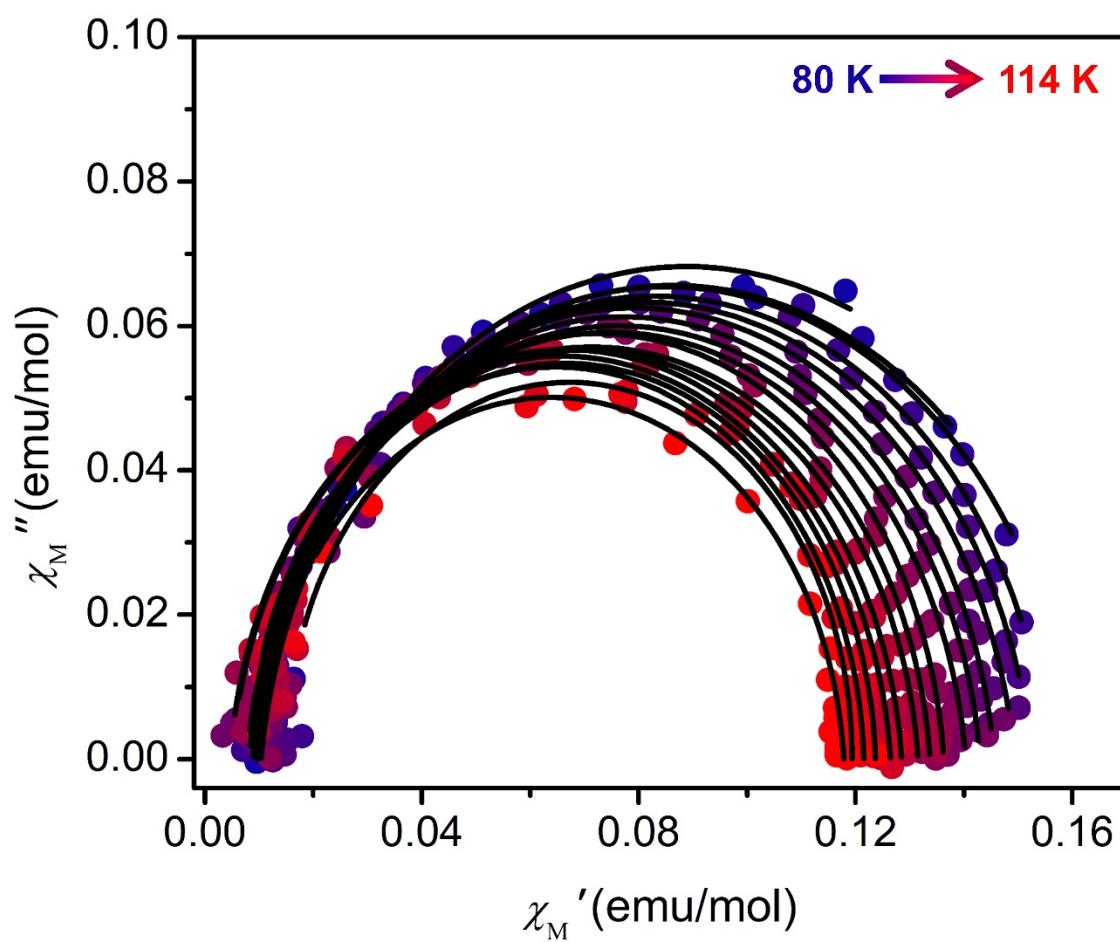


Figure S5.45. Cole-Cole plots for **2** from 80 to 114 K (2 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

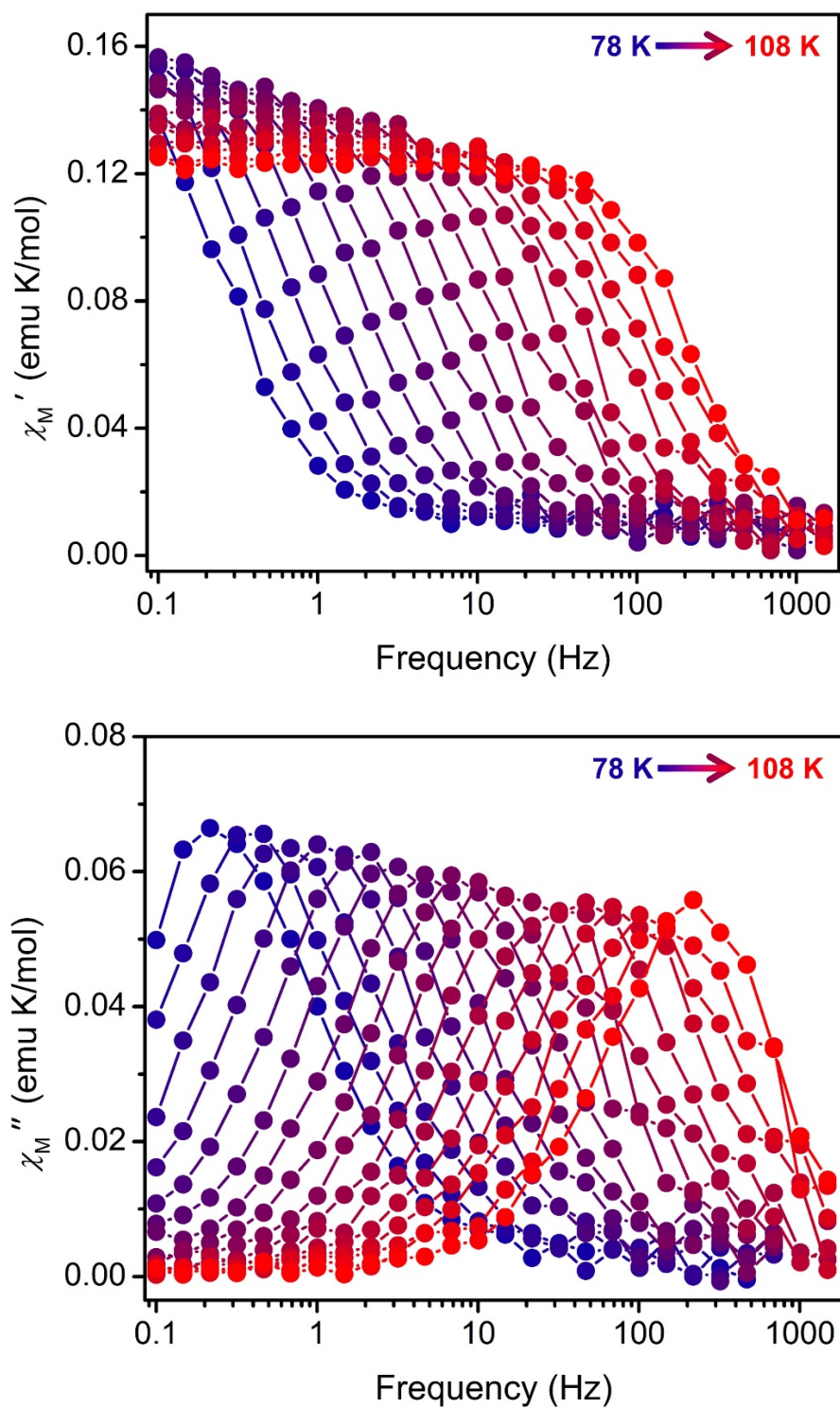


Figure S5.46. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **3** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 78–108 K (2 K steps). The colored lines are guides for the eye.

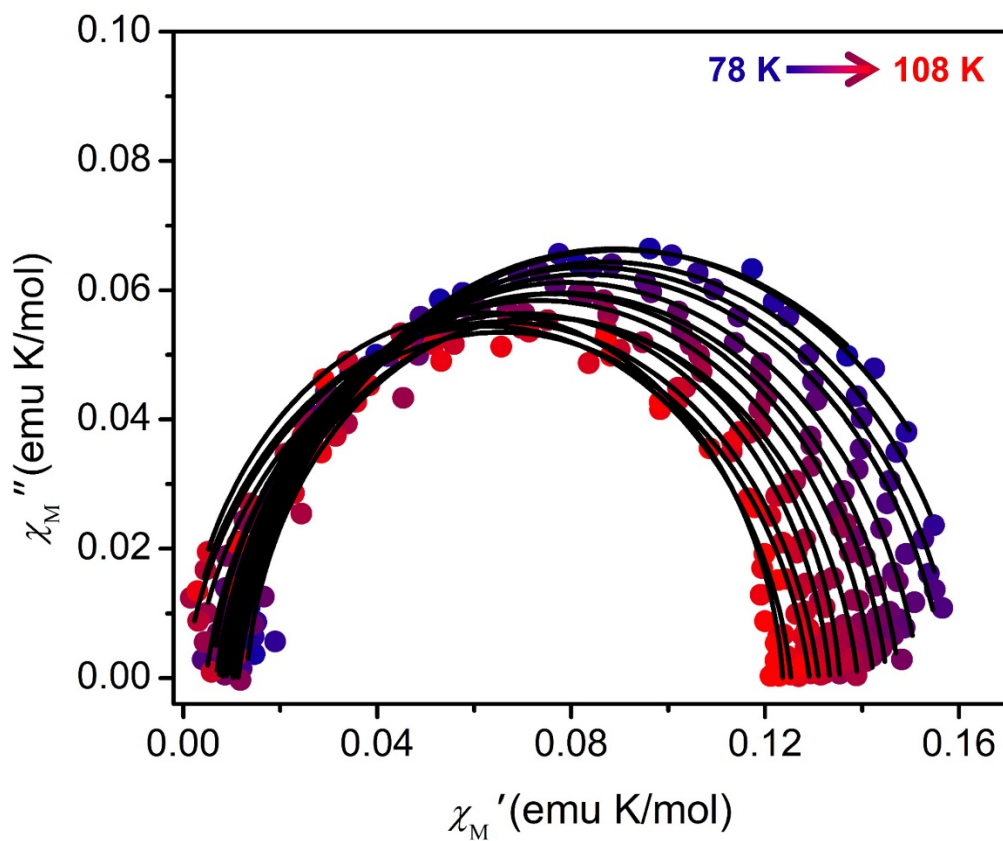


Figure S5.47. Cole-Cole plots for **3** from 78 to 108 K (2 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values for at each temperature.

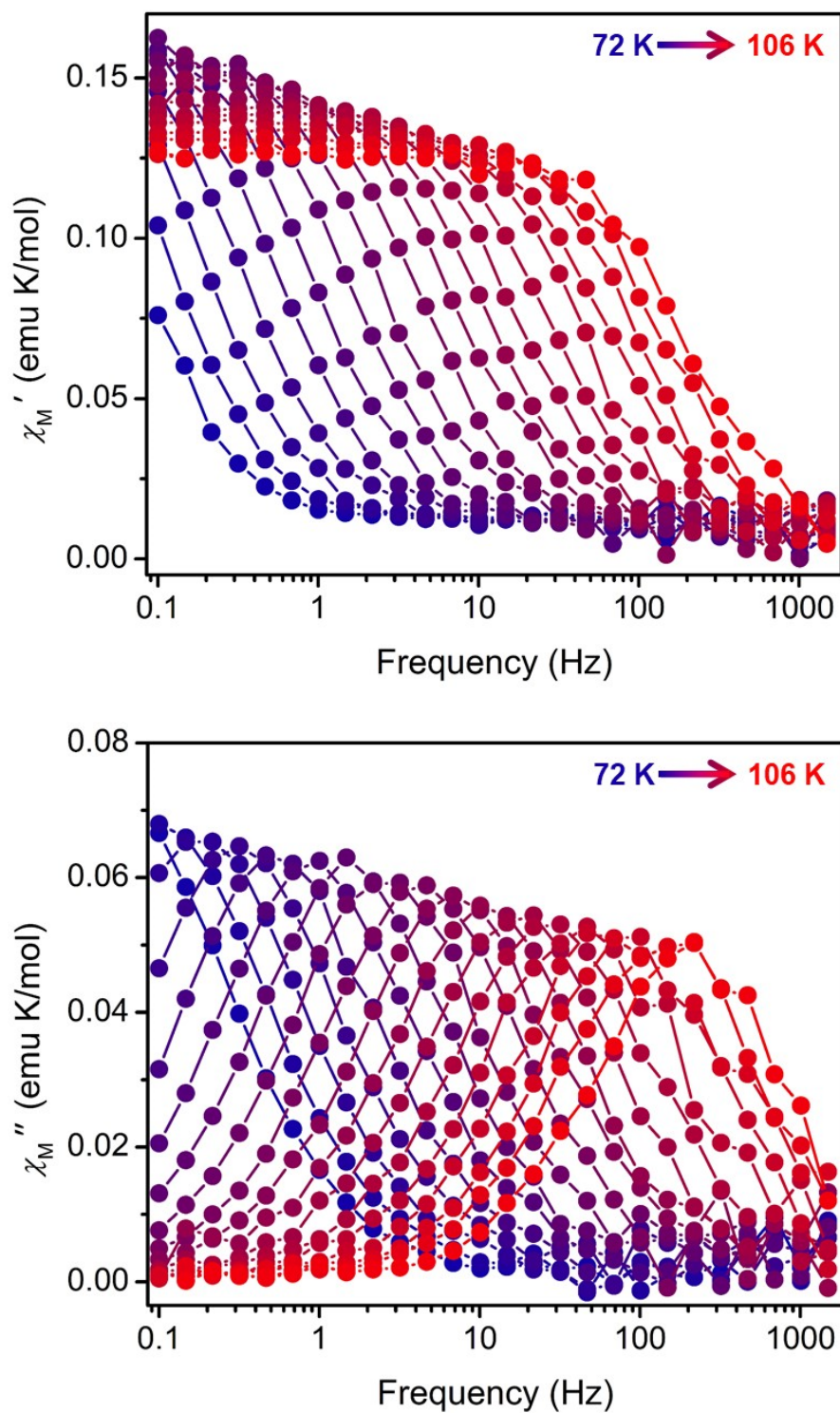


Figure S5.48. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **4** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 72–106 K (2 K steps). The colored lines are guides for the eye.

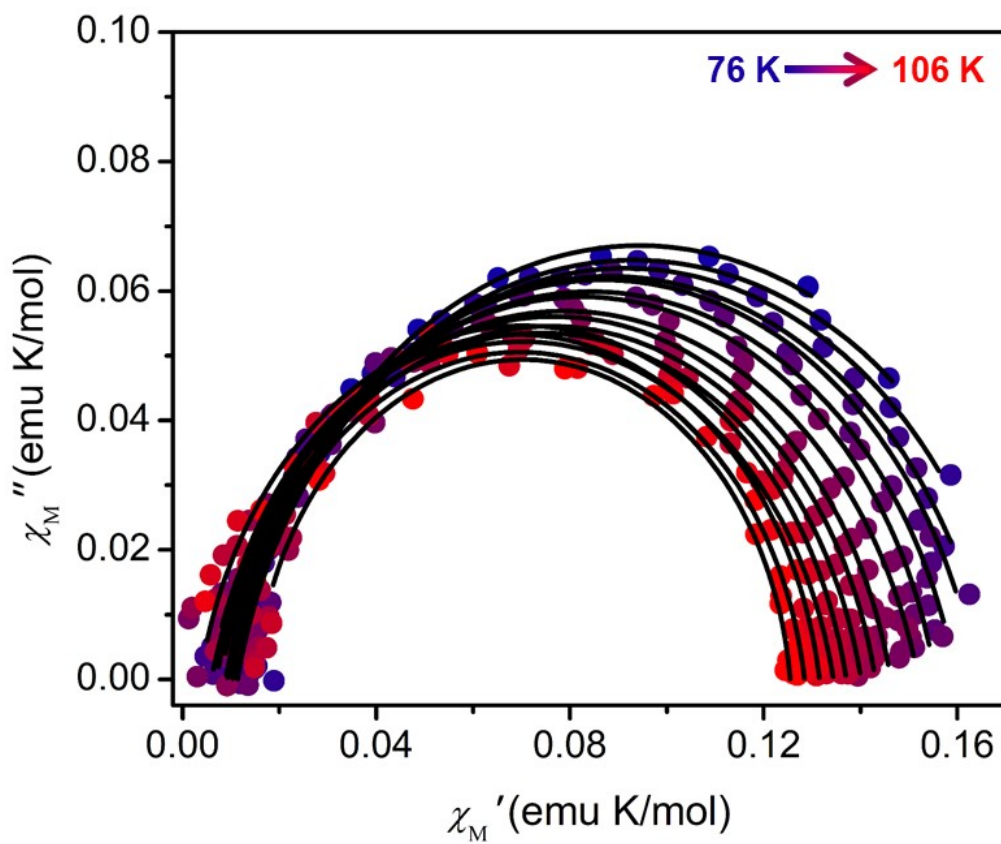


Figure S5.49. Cole-Cole plots for **4** from 76 to 106 K (2 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

Dc Magnetic Relaxation Measurements. Dc magnetic relaxation measurements were collected by magnetizing a sample under an applied field of 5 T, allowing 5 minutes for equilibration, and then subsequently returning the field to 0 Oe (no overshoot, hi-res disabled) and measuring the magnetization at periodic time intervals. Dc magnetic relaxation data were fit to a stretched exponential function according to the equation:

$$M(t) = M_1 + (M_0 - M_1)^{(t/\tau)^n}$$

where $M(t)$ is the magnetization at time t , M_0 is the initial magnetization measured after the field has been removed, M_1 is the final value of the magnetization at $t = \infty$, τ is the magnetic relaxation time, and n is a free variable. Though M_1 should equal zero at zero field, we found non-zero values for all dc magnetic relaxation measurements, likely due to a small remnant field in the superconducting magnet. We therefore set M_1 equal to the value of the magnetization measured at the last time point of each experiment. At high temperatures, it was possible to measure the full decay of the magnetization within 1000 s. At lower temperatures where magnetic relaxation slowed, experiments were conducted for 5000 s. Even this length of time was not sufficient to observe the full decay of the magnetization for measurements of **2-4** at the lowest temperatures measured (2 to 20 K), however, and therefore setting M_1 equal to the last value of the magnetization measured for these experiments represented an overestimate. Better fits to the data for these experiments were obtained by treating M_1 as a free variable (M_1 values marked with an * in the tables below).

In order to test the validity of this strategy, fits to higher temperature experiments with M_1 as a free variable were obtained and compared to previous fits. This resulted in values of τ within 5% of those obtained for fits with M_1 equal to the last value of the magnetization measured in the experiment. Furthermore, the values obtained for τ with M_1 as a free variable were consistently lower than those obtained with M_1 equal to the last value of the magnetization, demonstrating that this alternative fitting strategy did not overestimate the value of τ at low temperatures.

Table S5.3. Parameters used to fit dc magnetic relaxation data for **1** and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_b)	M_1 (μ_b)	n	τ (s) ^a
2	2.45604	0.02609	0.752	438.568
6	1.39036	0.00443	0.829	223.137
10	0.80538	0.00254	0.837	169.852
16	0.23694	0.00226	0.849	104.229
18	0.10969	0.00105	0.849	96.437
20	0.07967	0.00089	0.849	83.856
22	0.03968	0.00047	0.863	74.993
24	0.01524	0.00048	0.853	71.354
26	0.00680	0.00035	0.911	67.146
28	0.00404	0.00033	0.876	56.561
30	0.00215	0.00019	0.856	53.881

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

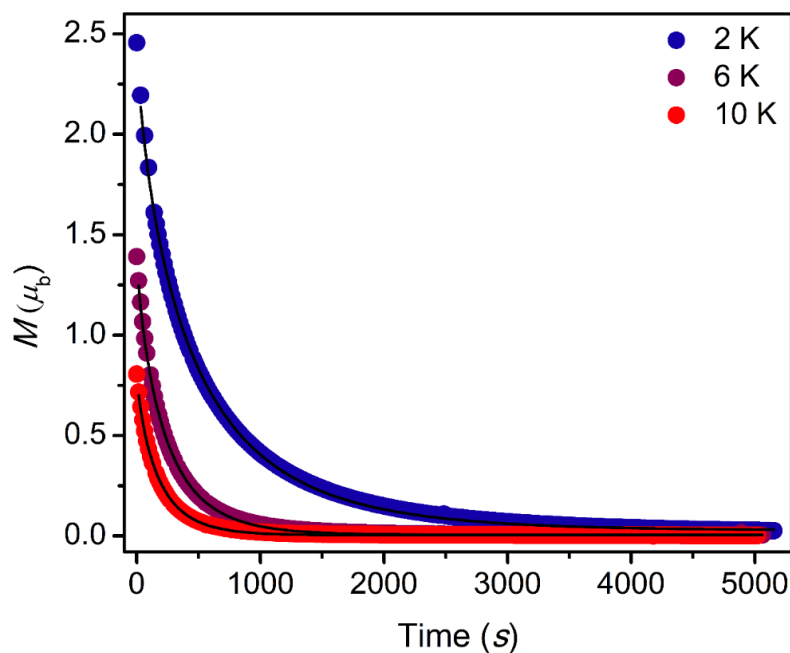


Figure S5.50. Dc magnetic relaxation data for **1** collected at 2, 6, and 10 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

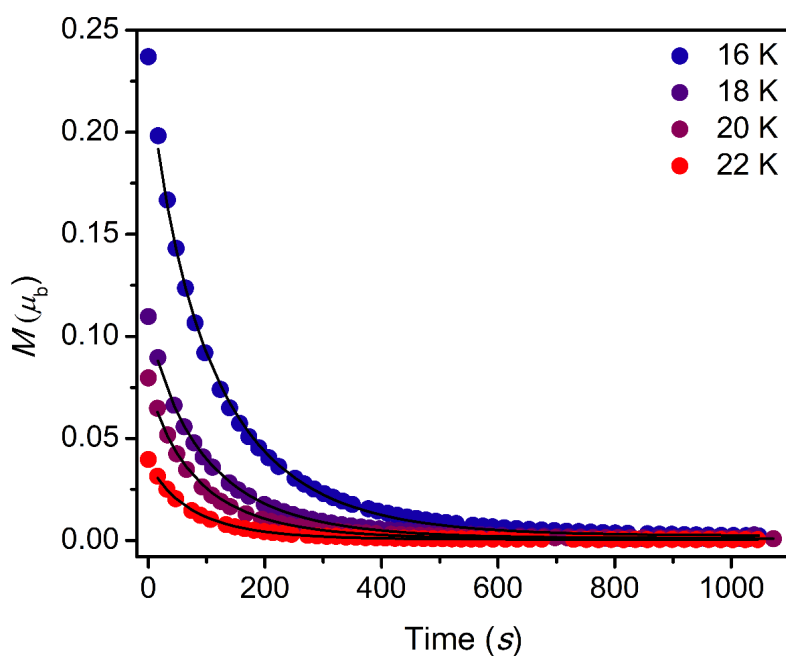


Figure S5.51. Dc magnetic relaxation data for **1** collected from 16 to 22 K in 2 K increments. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

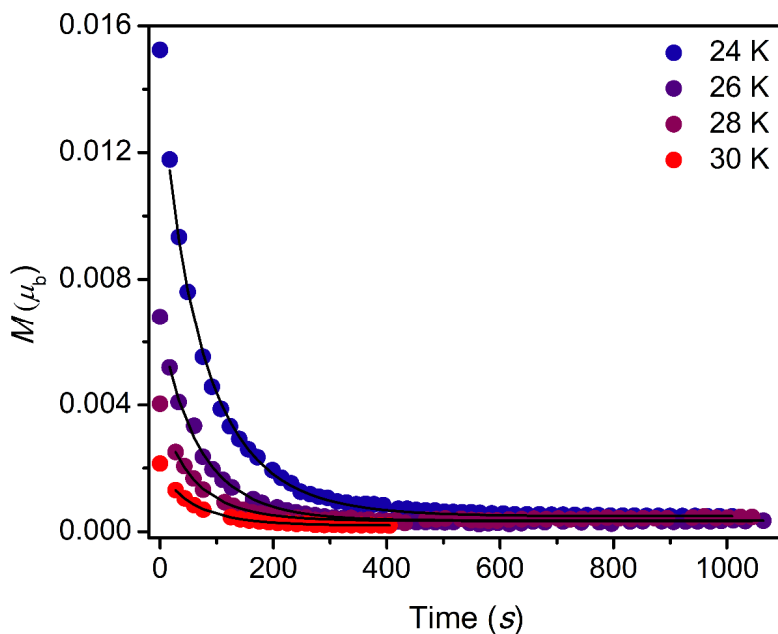


Figure S5.52. Dc magnetic relaxation data for **1** collected from 24 to 30 K in 2 K increments. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S5.4. Parameters used to fit dc magnetic relaxation data for **2** and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	3.75127	0.22840*	0.671	2452.358
5	3.61807	0.21921*	0.676	2306.767
10	3.10026	0.19942*	0.728	1704.762
15	2.38810	0.11536*	0.725	1068.648
20	1.60054	0.04329*	0.742	797.784
25	1.07252	0.01302	0.760	607.850
30	0.77699	0.00275	0.771	451.321
35	0.48148	0.00071	0.824	374.604
40	0.32082	0.00051	0.866	299.806
45	0.23461	0.00028	0.886	232.751
50	0.16549	0.00041	0.906	185.239
52	0.13876	0.00122	0.929	167.607
54	0.11272	0.00067	0.930	154.968
56	0.09686	0.00052	0.948	141.881
58	0.07988	0.00033	0.940	129.358
60	0.05953	0.00017	0.939	116.581
62	0.04424	0.00020	0.951	102.367
64	0.02985	0.00011	0.958	87.195

* M_1 values obtained by treating M_1 as a free variable

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

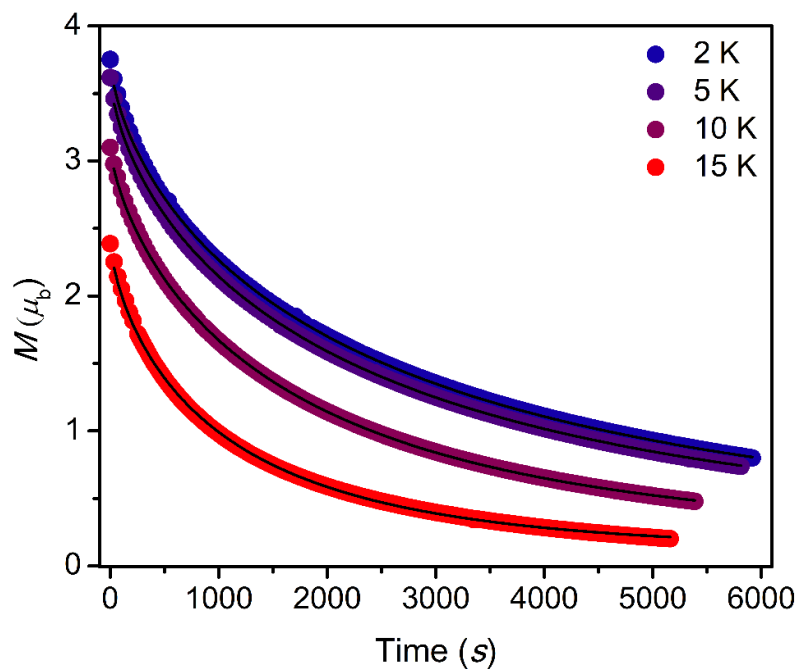


Figure S5.53. Dc magnetic relaxation data for **2** collected at 2, 5, 10, and 15 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

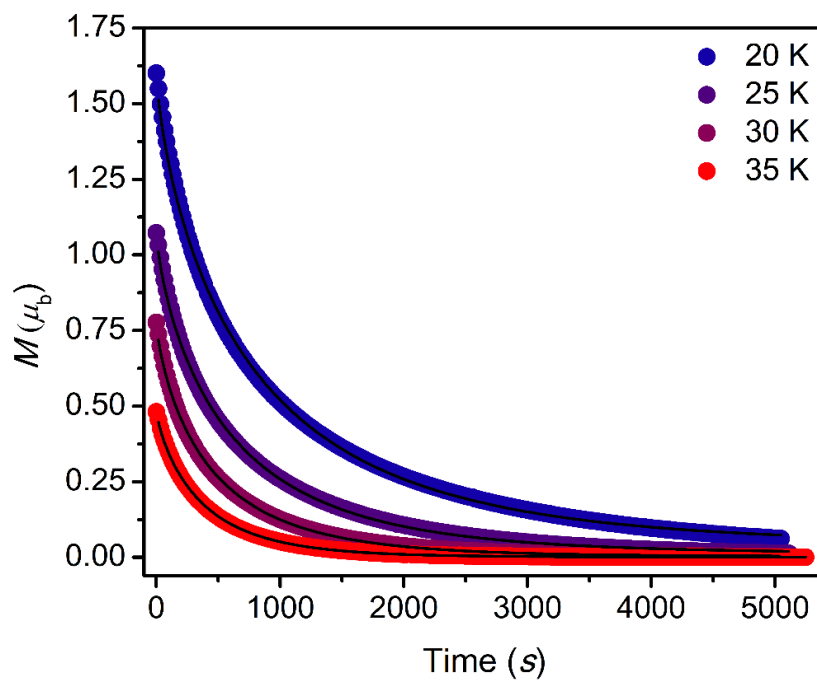


Figure S5.54. Dc magnetic relaxation data for **2** collected at 20, 25, 30, and 35 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

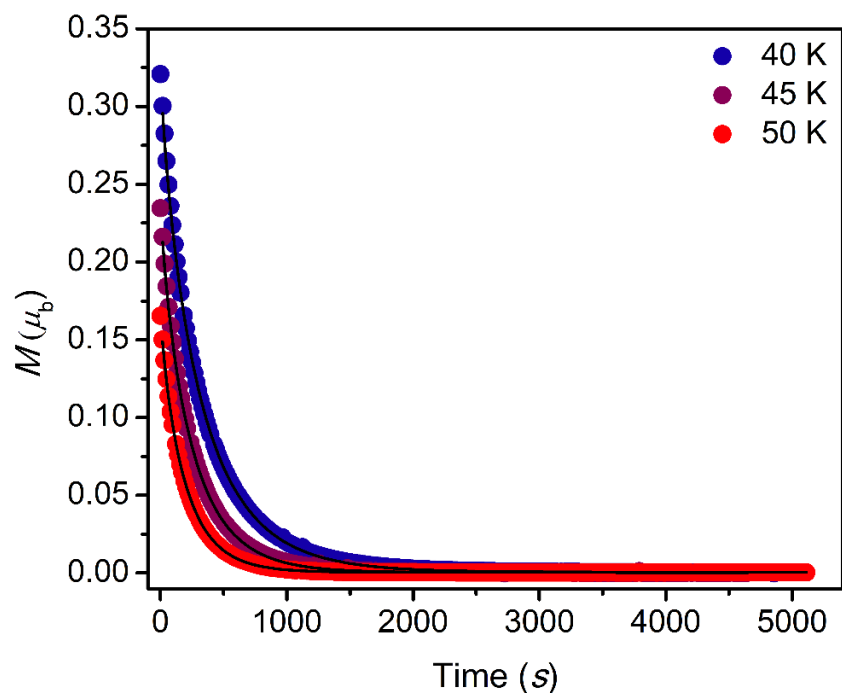


Figure S5.55. Dc magnetic relaxation data for **2** collected at 40, 45, and 50 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

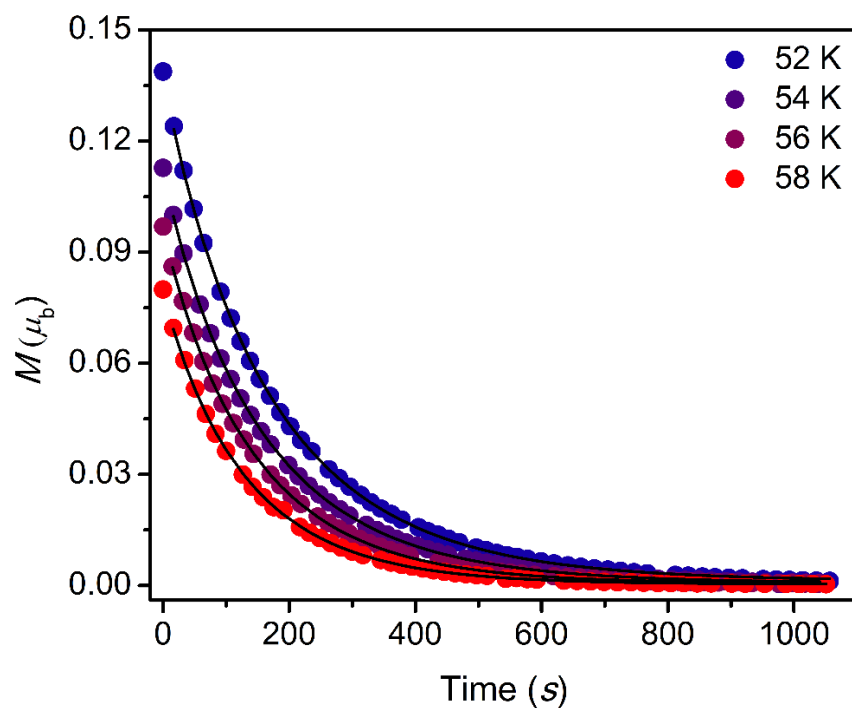


Figure S5.56. Dc magnetic relaxation data for **2** collected in 2 K intervals from 52 to 58 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

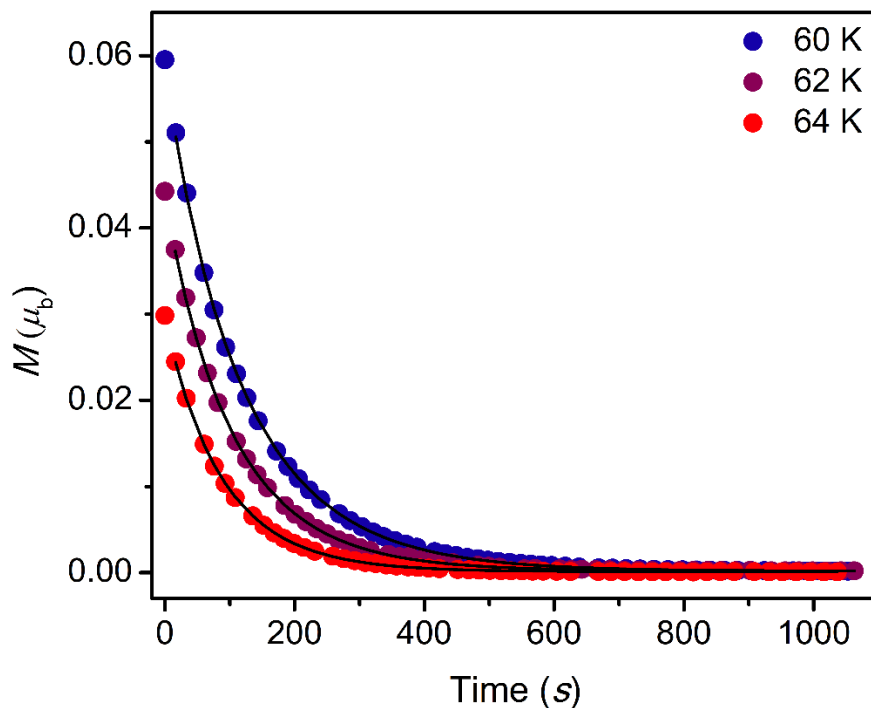


Figure S5.57. Dc magnetic relaxation data for **2** collected at 60, 62, and 64 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S5.5. Parameters used to fit dc magnetic relaxation data for **3** and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	2.59342	0.14798*	0.664	447.490
5	2.34614	0.14711*	0.676	423.118
10	N/A	N/A	N/A	N/A
15	N/A	N/A	N/A	N/A
20	N/A	N/A	N/A	N/A
25	0.43968	0.00908	0.587	328.903
30	0.27154	0.00302	0.632	308.801
35	0.17141	0.00162	0.669	266.721
40	0.11374	0.00138	0.718	223.622
45	0.06901	0.00127	0.752	189.312
50	0.04321	0.00083	0.817	152.663
52	0.03637	0.00052	0.818	140.186
54	0.02747	0.00044	0.838	132.555
56	0.02122	0.00032	0.849	119.390
58	0.01664	0.00028	0.869	108.162
60	0.01138	0.00027	0.897	91.467
62	0.00683	0.00021	0.898	74.450

* M_1 values obtained by treating M_1 as a free variable

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

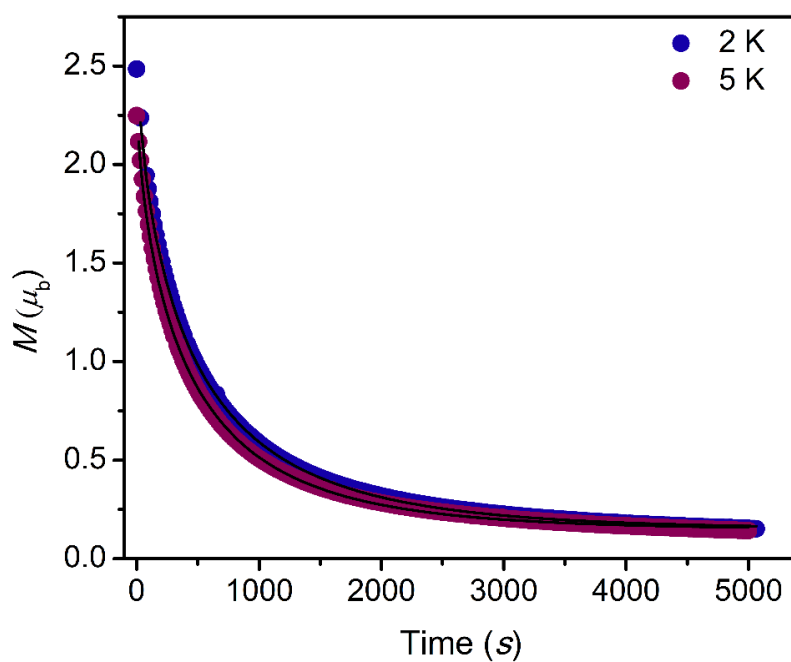


Figure S5.58. Dc magnetic relaxation data for **3** collected at 2 and 5 K. Black lines represent fits to the data using stretched exponential functions, which were used to extract τ .

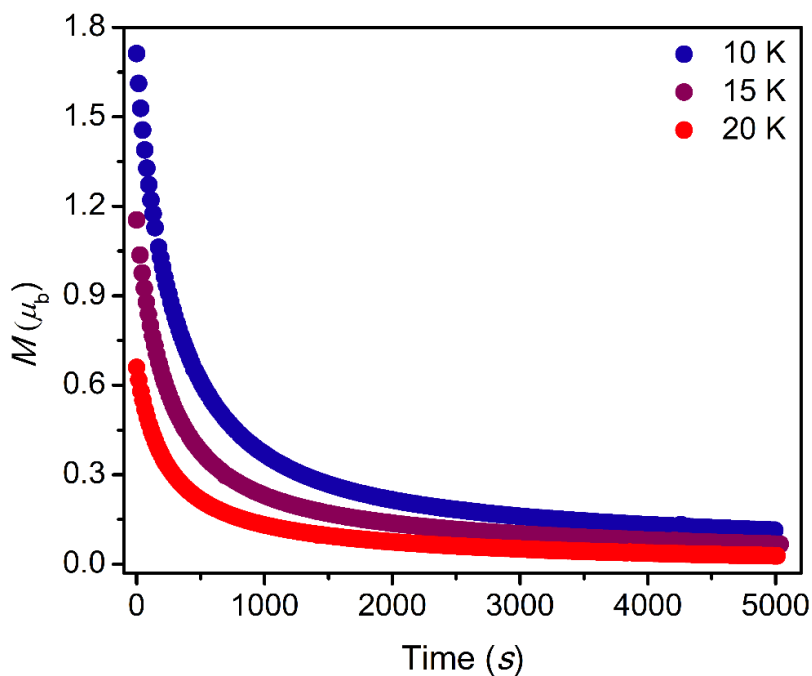


Figure S5.59. Dc magnetic relaxation data for **3** collected at 10, 15, and 20 K. These data could not be fit with a single stretched exponential function, indicating more complex relaxation dynamics.

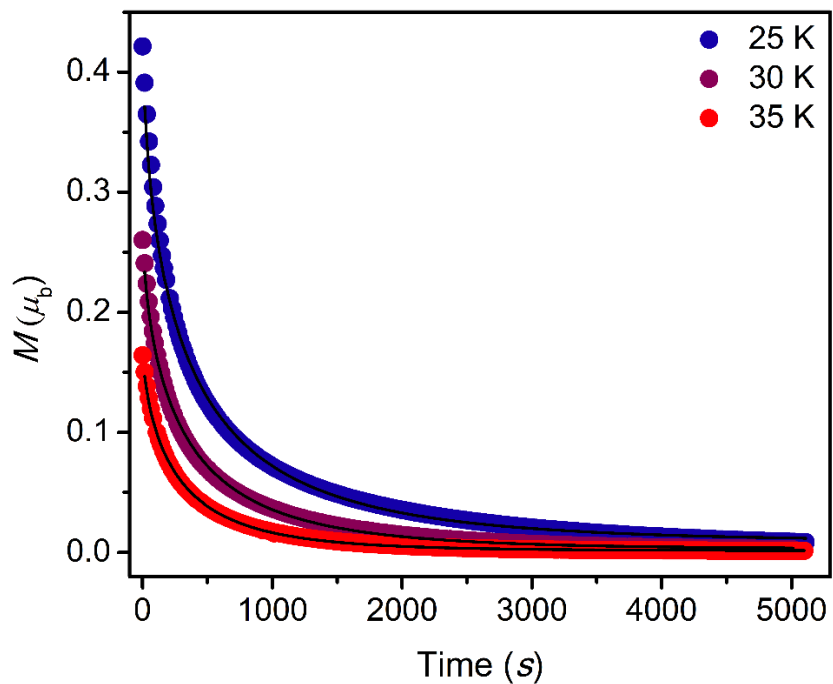


Figure S5.60. Dc magnetic relaxation data for **3** collected at 25, 30, and 35 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

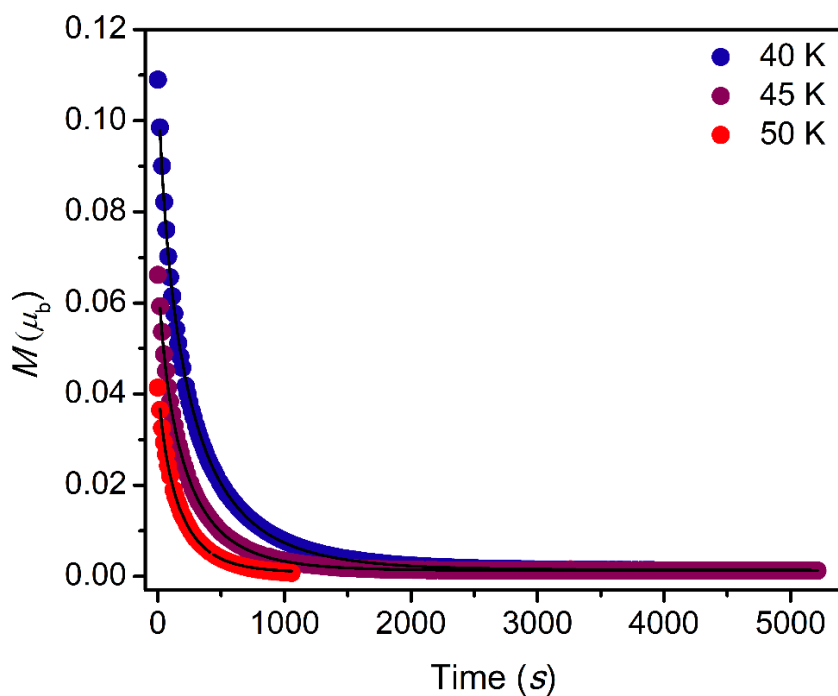


Figure S5.61. Dc magnetic relaxation data for **3** collected at 40, 45, and 50 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

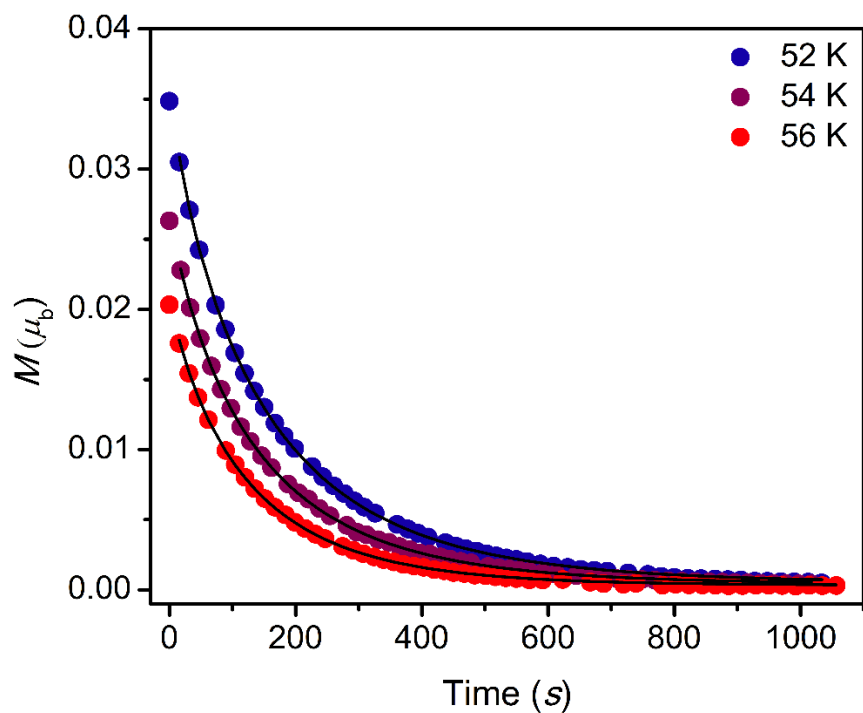


Figure S5.62. Dc magnetic relaxation data for **3** collected at 52, 54, and 56 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

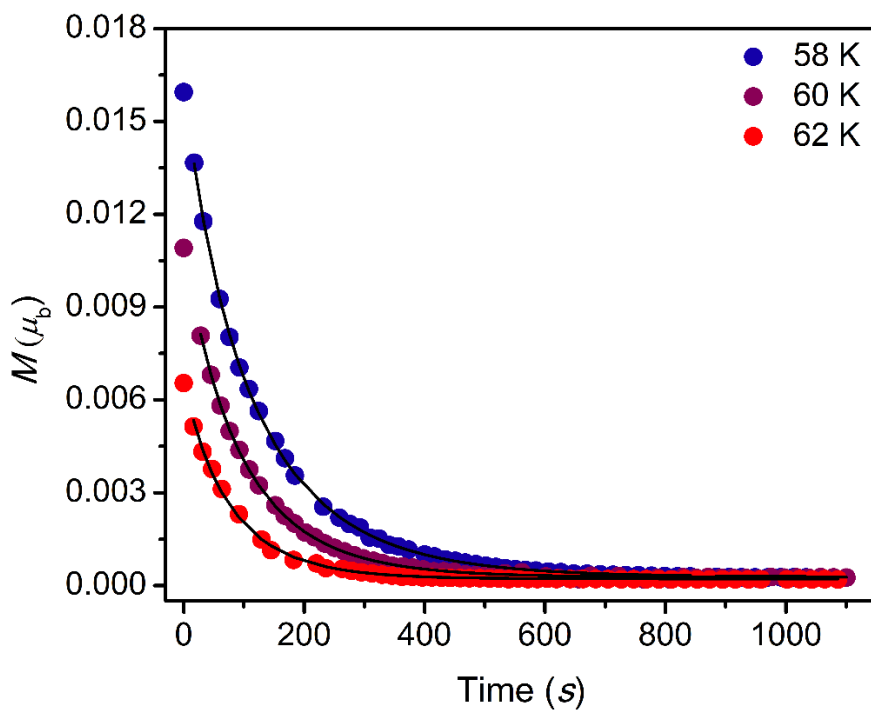


Figure S5.63. Dc magnetic relaxation data for **3** collected at 58, 60, and 62 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S5.6. Parameters used to fit dc magnetic relaxation data for **4** and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_b)	M_1 (μ_b)	n	τ (s) ^a
2	3.17947	0.24655*	0.762	1187.059
5	3.09335	0.18415*	0.696	1025.284
10	2.59245	0.15460*	0.708	878.518
15	1.83666	0.09682*	0.744	727.914
20	1.35344	0.03597	0.723	555.310
25	0.82875	0.00864	0.741	473.395
30	0.53401	0.00236	0.768	370.804
35	0.34532	0.00091	0.798	287.871
40	0.23441	0.00046	0.827	219.949
45	0.14824	0.00052	0.848	171.412
50	0.08026	0.00074	0.885	135.280
52	0.06197	0.00047	0.889	124.468
54	0.04687	0.00035	0.890	112.300
56	0.03473	0.00030	0.890	100.088
58	0.02284	0.00019	0.882	88.474
60	0.01388	0.00016	0.872	75.756
62	0.00792	0.00014	0.878	63.884

* M_1 values obtained by treating M_1 as a free variable

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

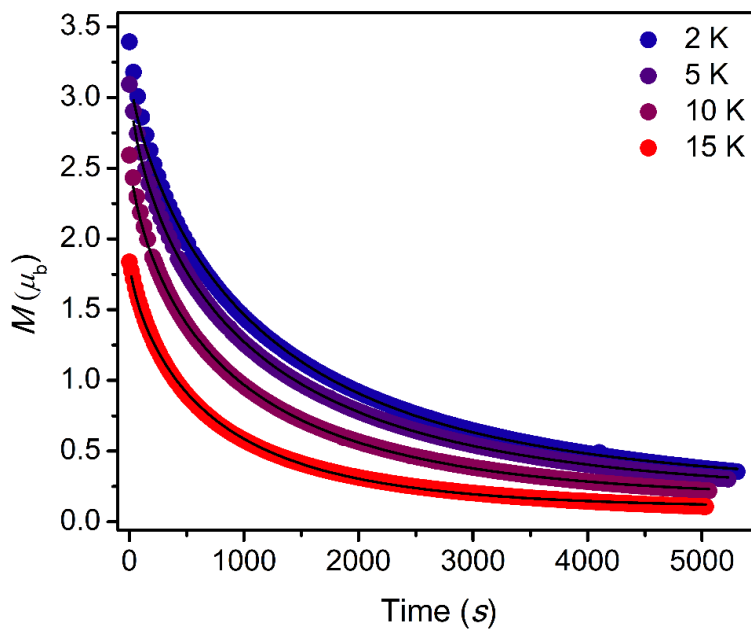


Figure S5.64. Dc magnetic relaxation data for **4** collected at 2, 5, 10, and 15 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

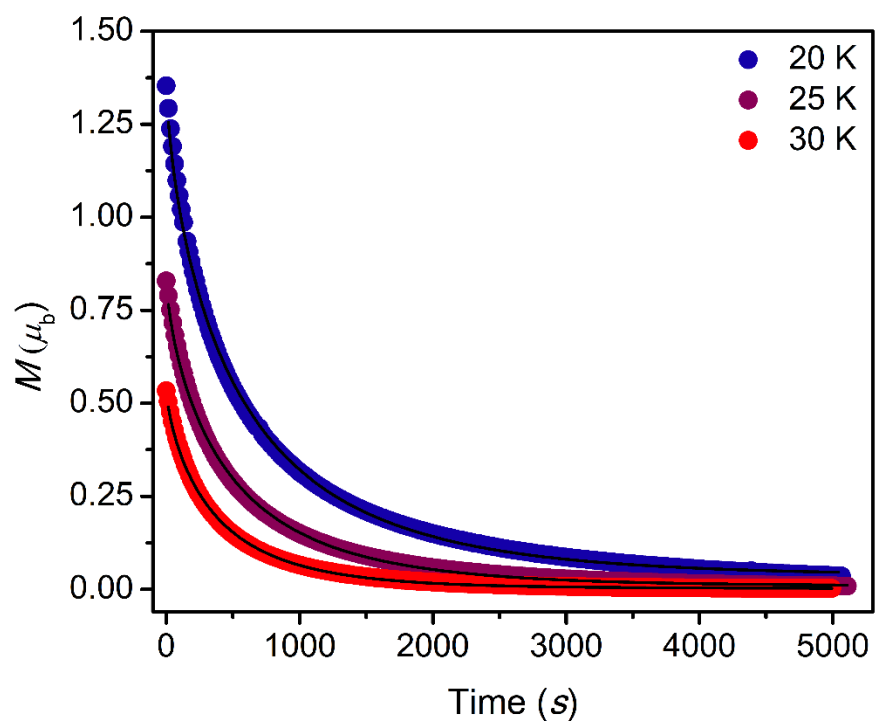


Figure S5.65. Dc magnetic relaxation data for **4** collected at 20, 25, and 30 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

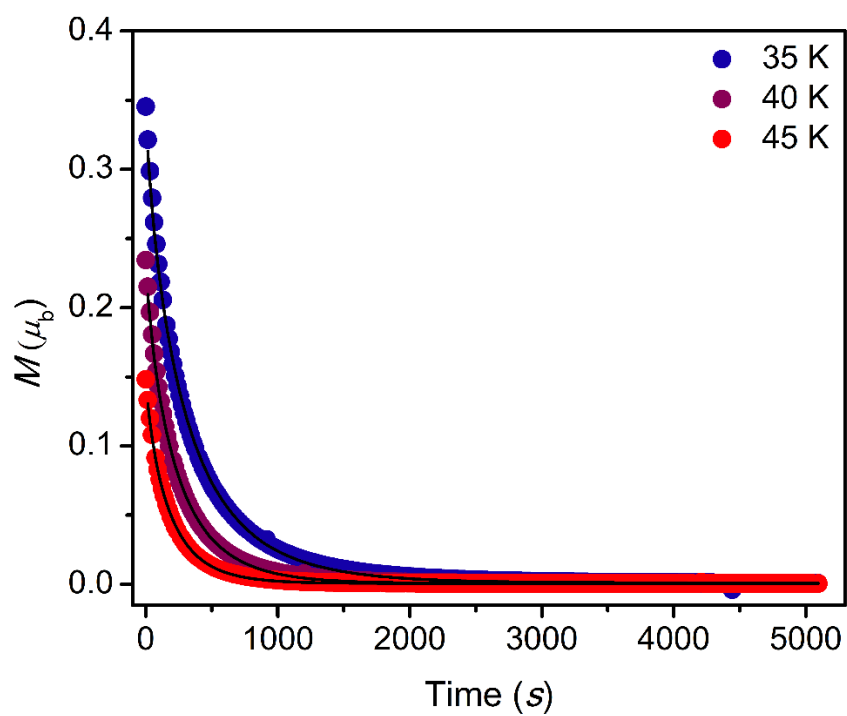


Figure S5.66. Dc magnetic relaxation data for **4** collected at 35, 40, and 45 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

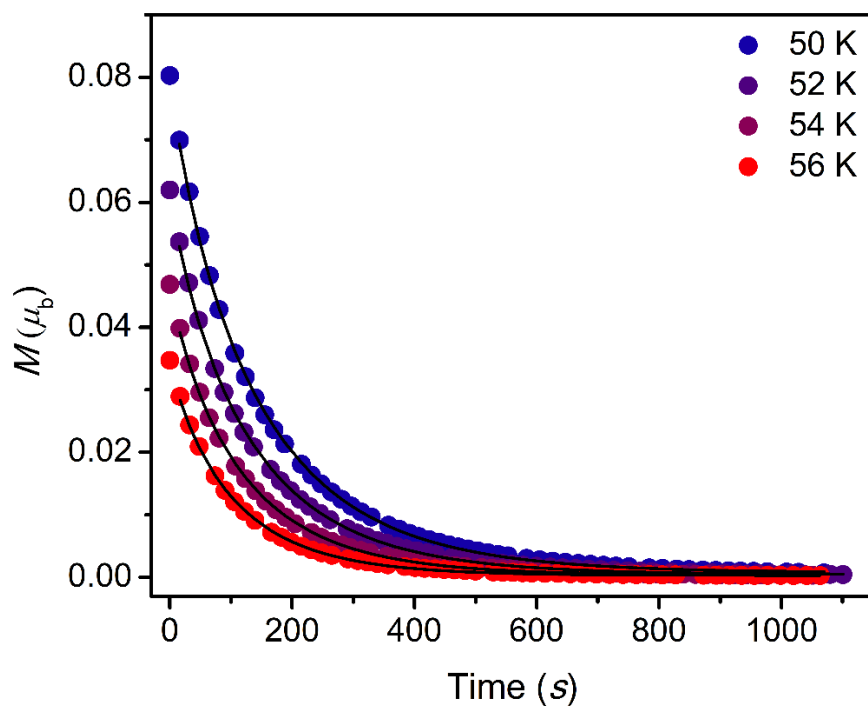


Figure S5.67. Dc magnetic relaxation data for **4** collected in 2 K intervals from 50 to 56 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

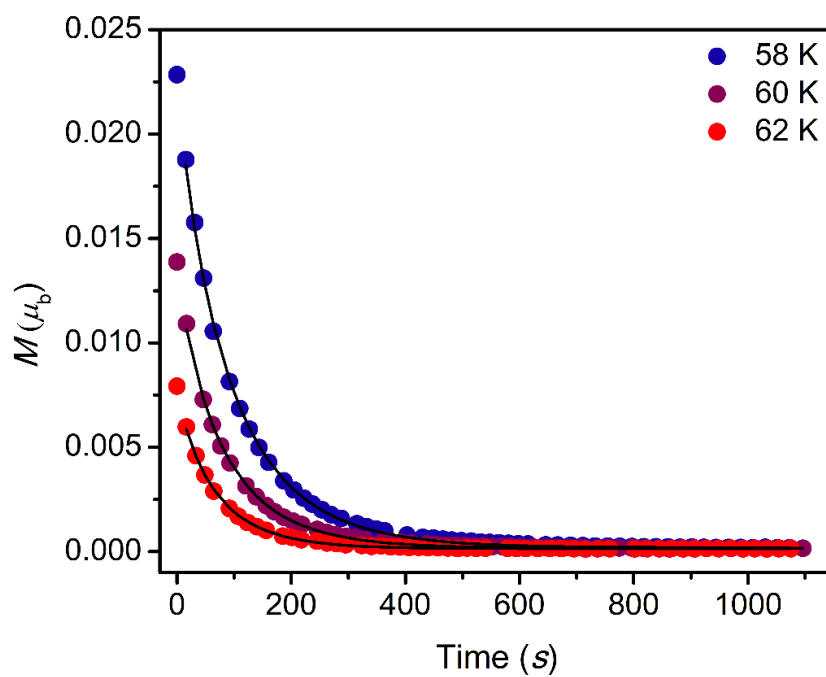


Figure S5.68. Dc magnetic relaxation data for **4** collected at 58, 60, and 62 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Analysis of Magnetic Relaxation Dynamics. Magnetic relaxation times extracted from ac susceptibility measurements of **1-4** showed an exponential dependence on temperature, indicative of an Orbach relaxation mechanism. Data were fit to the equation:

$$\tau^{-1} = \tau_0^{-1} e^{-U_{eff}/k_b T}$$

where τ is the magnetic relaxation time, τ_0 is the attempt time, U_{eff} is the thermal barrier to magnetization reversal, $k_b = 0.695 \text{ cm}^{-1}\text{K}^{-1}$, and T is temperature.

The full range of magnetic relaxation times extracted from ac susceptibility and dc magnetic relaxation experiments showed a more complex temperature dependence, indicative of multiple magnetic relaxation pathways. Plots of the log of magnetic relaxation time versus $1/T$ showed an exponential dependence at intermediate temperatures and flattened at low T , suggesting the presence of Raman relaxation and/or quantum tunneling of the magnetization. Accordingly, the data for **1-4** were fit to the equation:

$$\tau^{-1} = \tau_0^{-1} e^{-U_{eff}/k_b T} + \tau_{tunnel}^{-1} + CT^n$$

where τ_{tunnel} is the relaxation time for quantum tunneling of the magnetization and C and n are free variables that describe Raman relaxation. To avoid over-parameterization, τ_0 and U_{eff} were fixed to the values extracted from fits to only the ac magnetic susceptibility measurements, while τ_{tunnel} was set equal to the 2 K magnetic relaxation time. All three relaxation processes were necessary to obtain fits that satisfactorily reproduced the data.

Table S5.7. Parameters used to fit the Arrhenius plots of **1-4**.

	1	2	3	4
$U_{eff} (\text{cm}^{-1})$	1285	1468	1380	1334
$\tau_0 (\text{s})$	3.39×10^{-12}	4.01×10^{-12}	7.79×10^{-12}	1.18×10^{-11}
$\tau_{tunnel} (\text{s})$	439	2452	447	1187
C	2.27×10^{-5}	1.57×10^{-6}	3.36×10^{-8}	8.04×10^{-7}
n	2.00	2.07	3.02	2.31

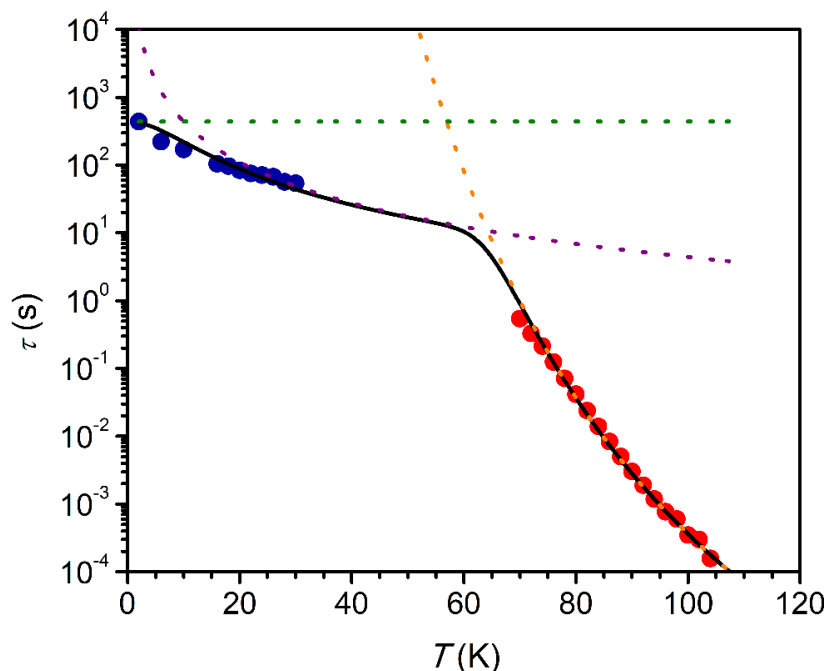


Figure S5.69. Plot of magnetic relaxation time versus temperature for **1** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data.

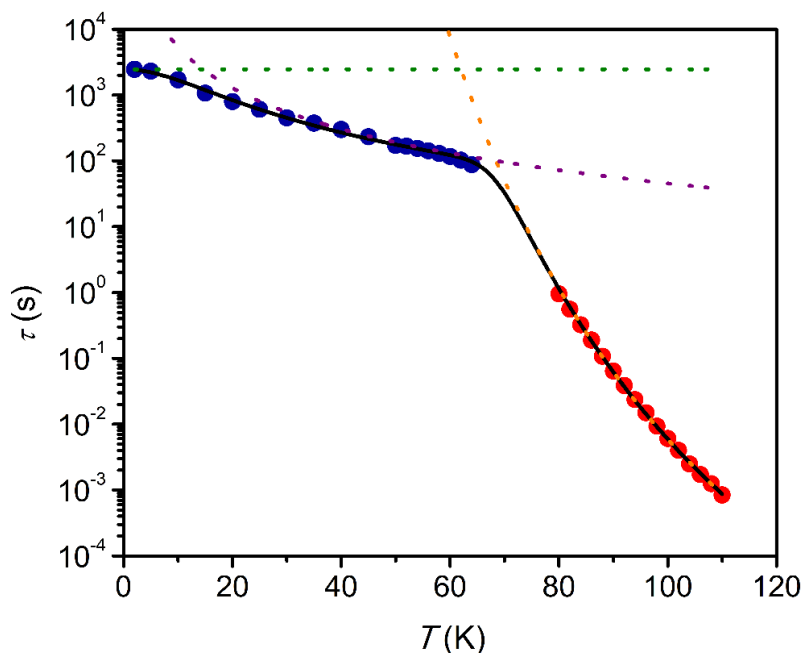


Figure S5.70. Plot of magnetic relaxation time versus temperature for **2** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data.

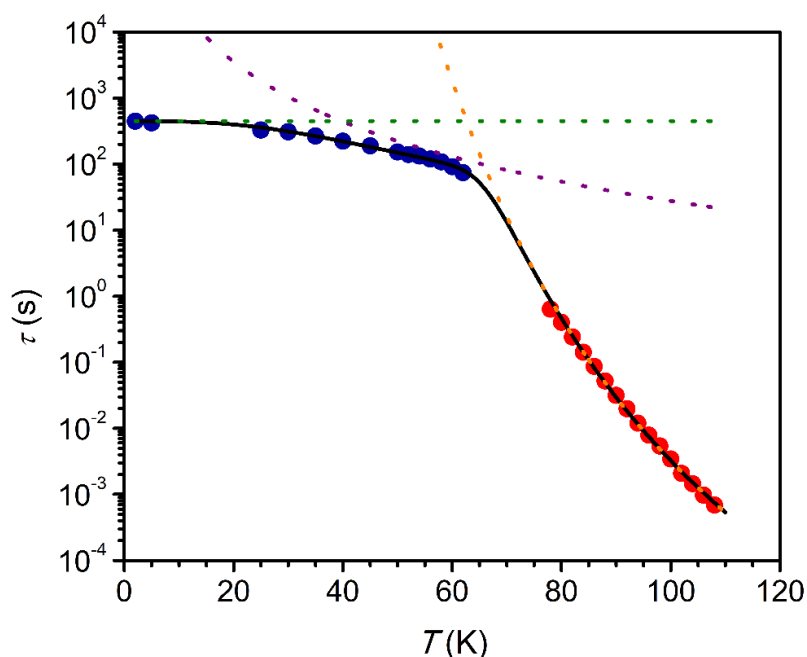


Figure S5.71. Plot of magnetic relaxation time versus temperature for **3** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data.

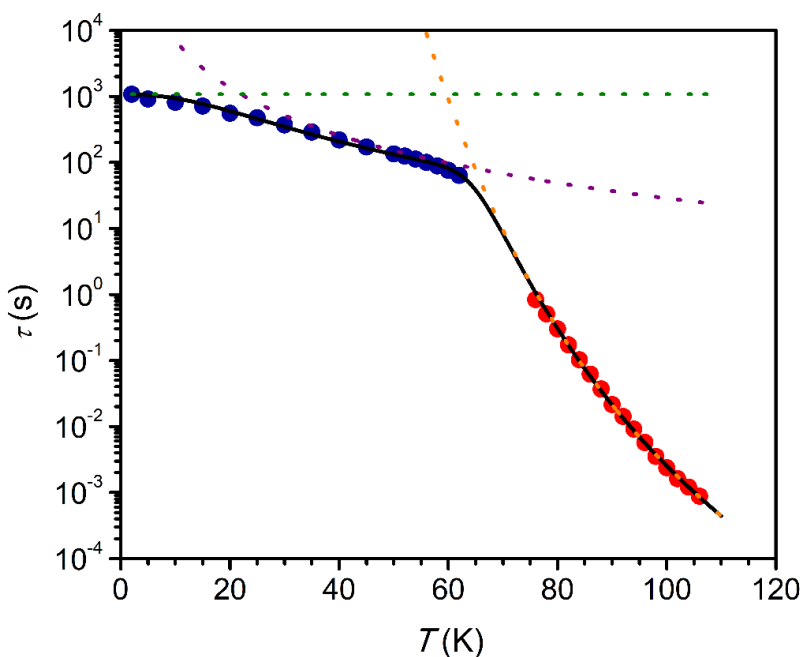


Figure S5.72. Plot of magnetic relaxation time versus temperature for **4** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data.

Magnetic Dilution Measurements. Magnetically dilute sample of **1-4** were prepared by co-crystallization of the compound with the Y^{3+} congener $[Y(Cp^{iPr4R})_2][B(C_6F_5)_4]$ ($R = H$ (**Y1**), Me (**Y2**), Et (**Y3**), *i*Pr (**Y4**)) in roughly a 9:1 Y:Dy molar ratio. The % Dy in this sample was determined by fitting the dc susceptibility curve of the dilution above 60 K to that measured for the undiluted sample. Using this method, the diluted samples **1-4@Y** were determined to contain, 10.9, 8.8, 11.5, and 8.7% Dy, respectively. Dc susceptibility, dc magnetic relaxation, and magnetic hysteresis measurements were conducted as described in the manuscript or earlier in the Supplementary Information.

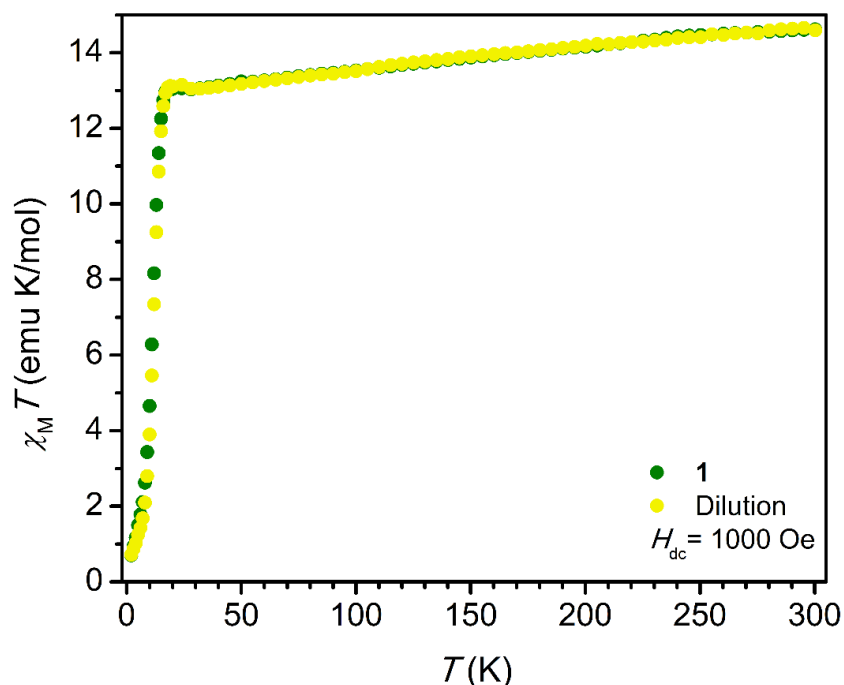


Figure S5.73. Zero-field cooled dc magnetic susceptibility measurements of **1** and the dilution **1@Y** under an applied field of 1000 Oe. Fitting the high temperature region (above 60 K) of these two plots yielded 10.9% Dy as the composition of the dilution.

Table S5.8. Parameters used to fit dc magnetic relaxation data for the dilution **1@Y** and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_b)	M_1 (μ_b)	n	τ (s) ^a
2	3.26016	0.84486*	0.755	1782.653
22	0.08344	0.00103	0.864	89.616
24	0.04897	0.00066	0.867	75.471
26	0.02306	0.00062	0.886	67.707
28	0.01203	0.00051	0.827	62.363
30	0.00634	0.00040	0.934	58.116

* M_1 values obtained by treating M_1 as a free variable

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

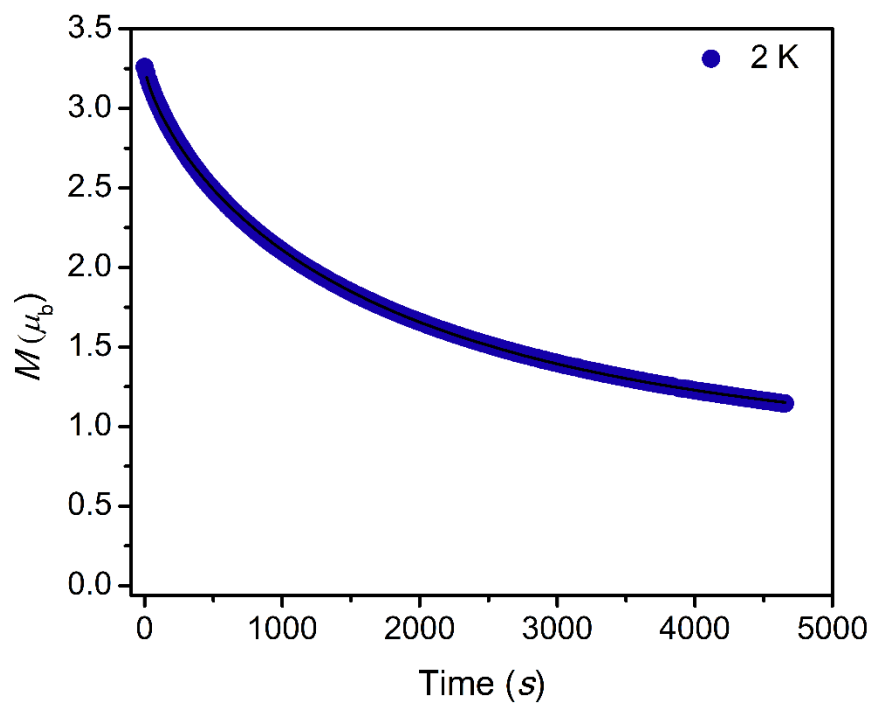


Figure S5.74. Dc magnetic relaxation data for the dilution **1@Y** collected at 2 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

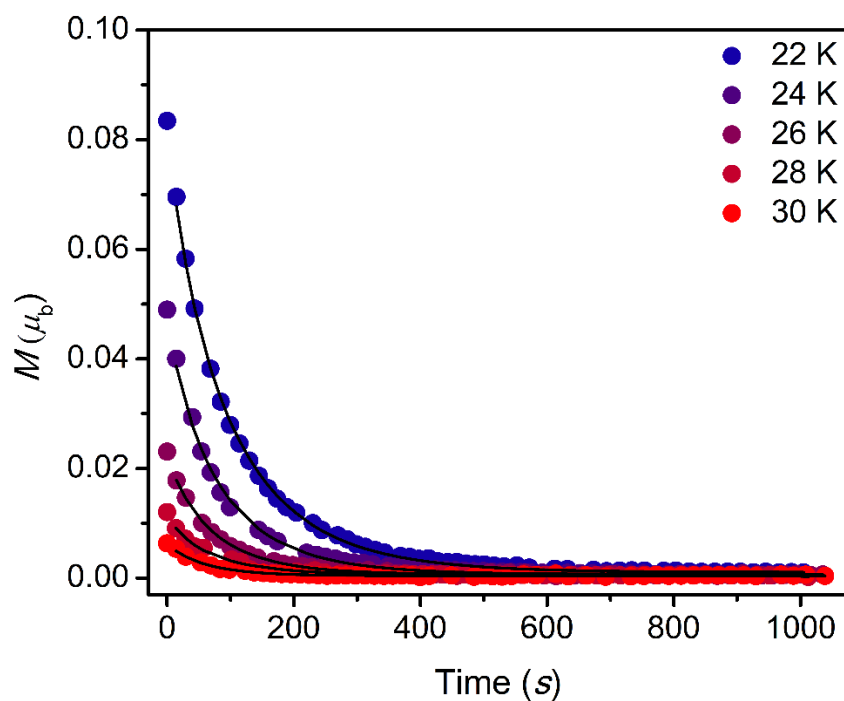


Figure S5.75. Dc magnetic relaxation data for the dilution **1@Y** collected at 22, 24, 26, 28 and 30 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

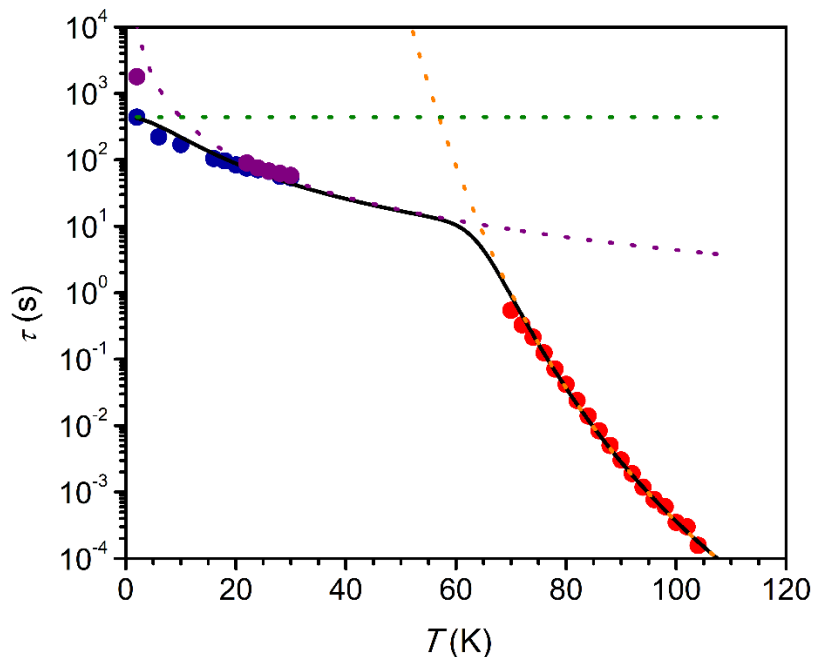


Figure S5.76. Plot of magnetic relaxation time versus temperature for **1** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data. Purple circles represent relaxation times for the dilution **1@Y** extracted from dc relaxation measurements.

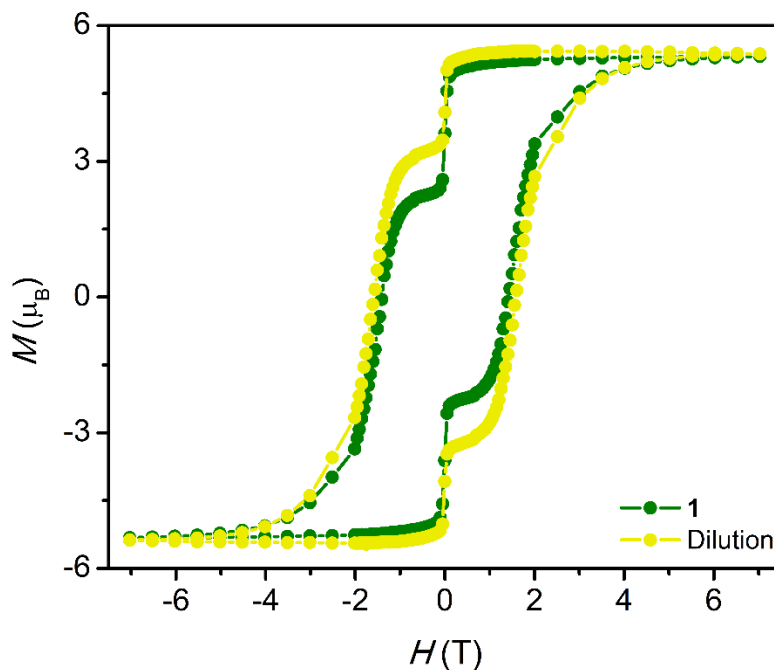


Figure S5.77. Magnetic hysteresis measurements of **1** and the dilution **1@Y** at 2 K at a sweep rate of 3.1(4) mT/s for $H < 2$ T and 13.2(2) mT/s $H > 2$ T.

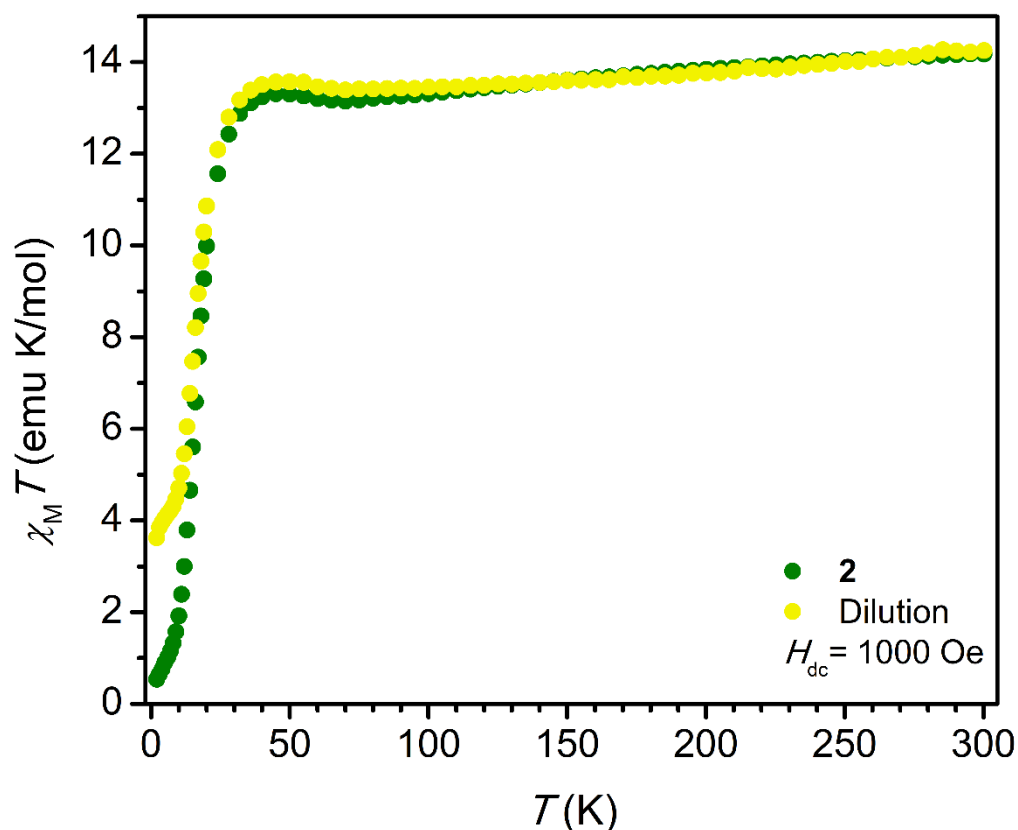


Figure S5.78. Zero-field cooled dc magnetic susceptibility measurements of **2** and the dilution **2@Y** under an applied field of 1000 Oe. Fitting the high temperature region (above 60 K) of these two plots yielded 8.8% Dy as the composition of the dilution.

Table S5.9. Parameters used to fit dc magnetic relaxation data for the dilution **2@Y** and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_b)	M_1 (μ_b)	n	τ (s) ^a
2	3.16566	0.15983*	0.583	11200.173
56	0.07237	0.00134	0.943	146.308
58	0.05892	0.00112	0.958	126.621
60	0.04713	0.00030	0.906	115.470
62	0.03457	0.00044	0.953	105.074
64	0.02213	0.00037	1.000	93.667

* M_1 values obtained by treating M_1 as a free variable

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

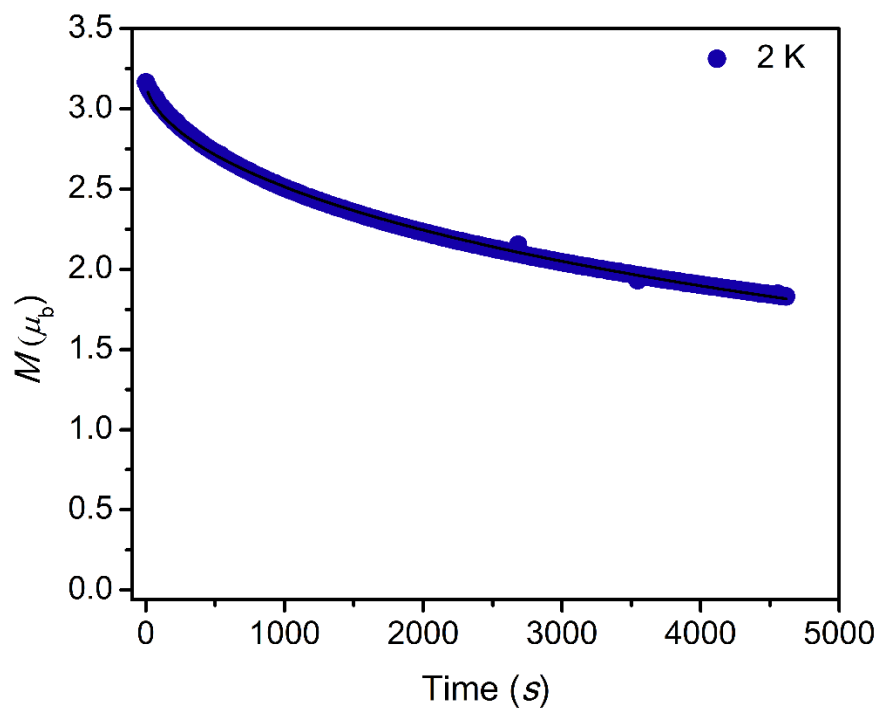


Figure S5.79. Dc magnetic relaxation data for the dilution **2@Y** collected at 2 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

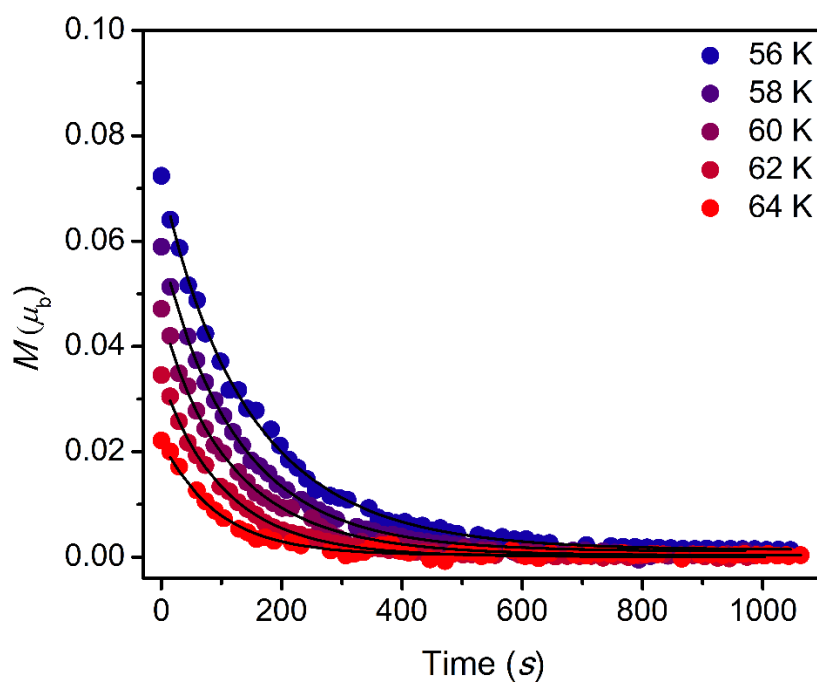


Figure S5.80. Dc magnetic relaxation data for the dilution **2@Y** collected at 56, 58, 60, 62 and 64 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

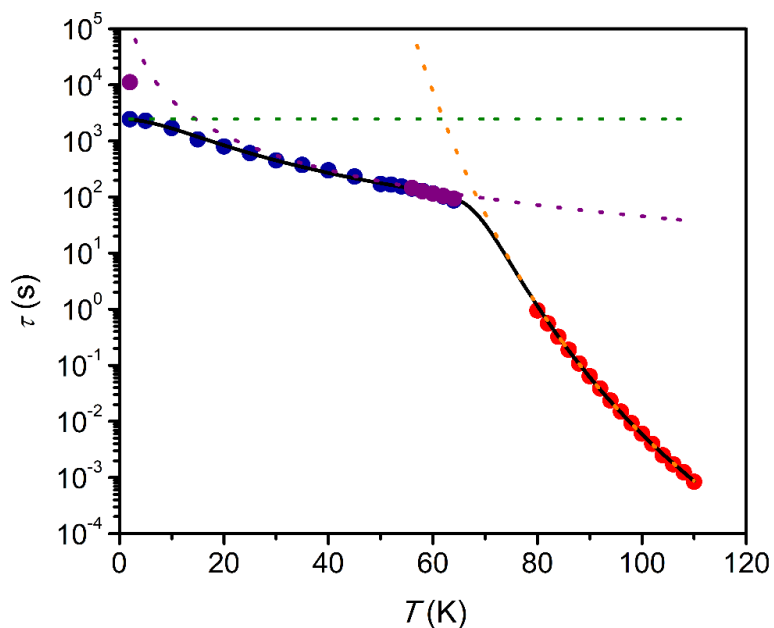


Figure S5.81. Plot of magnetic relaxation time versus temperature for **2** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data. Purple circles represent relaxation times for the dilution **2@Y** extracted from dc relaxation measurements.

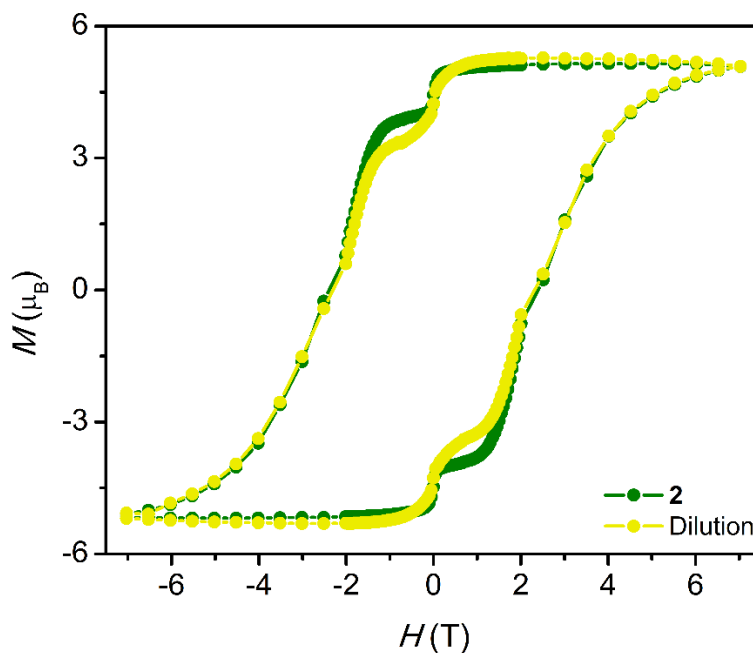


Figure S5.82. Magnetic hysteresis measurements of **2** and the dilution **2@Y** at 2 K at a sweep rate of 3.1(4) mT/s for $H < 2$ T and 13.2(2) mT/s $H > 2$ T.

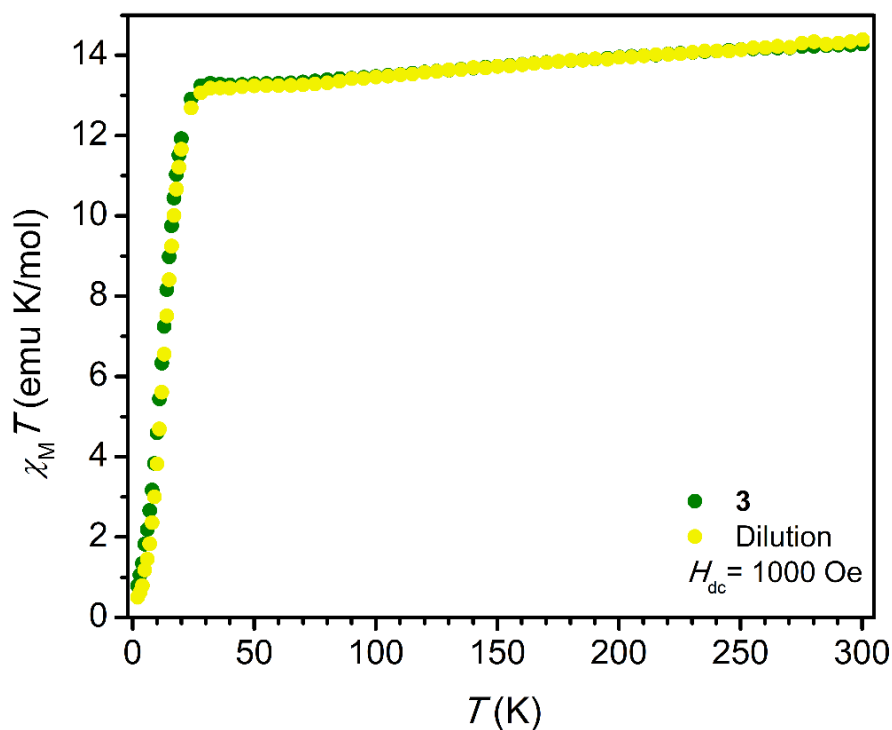


Figure S5.83. Zero-field cooled dc magnetic susceptibility measurements of **3** and the dilution **3@Y** under an applied field of 1000 Oe. Fitting the high temperature region (above 60 K) of these two plots yielded 11.5% Dy as the composition of the dilution.

Table S5.10. Parameters used to fit dc magnetic relaxation data for the dilution **3@Y** and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_b)	M_1 (μ_b)	n	τ (s) ^a
2	3.213927	1.06550*	0.726	1125.215
56	0.02068	0.00038	0.926	135.265
58	0.01548	0.00027	0.928	117.742
60	0.00927	0.00028	1.000	107.402
62	0.00496	0.00021	0.910	75.897
64	0.00265	0.00020	0.998	62.907

* M_1 values obtained by treating M_1 as a free variable

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

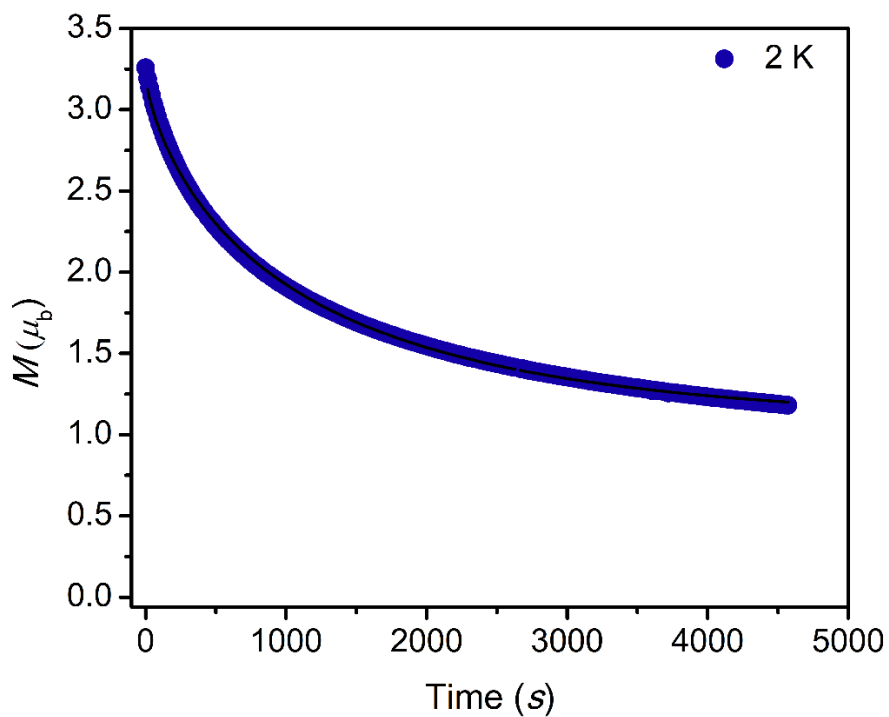


Figure S5.84. Dc magnetic relaxation data for the dilution **3@Y** collected at 2 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

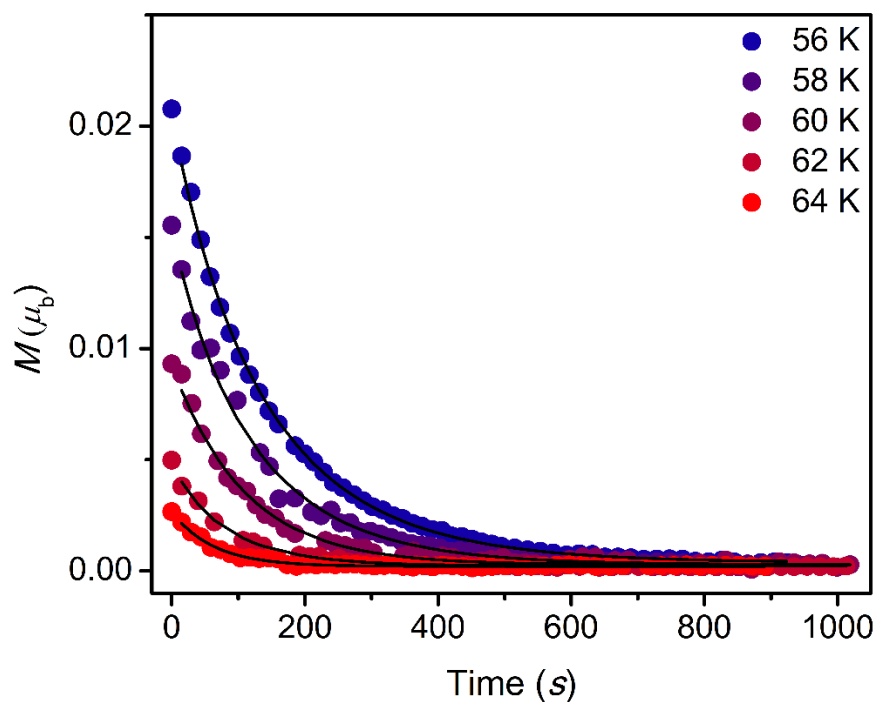


Figure S5.85. Dc magnetic relaxation data for the dilution **3@Y** collected at 56, 58, 60, 62 and 64 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

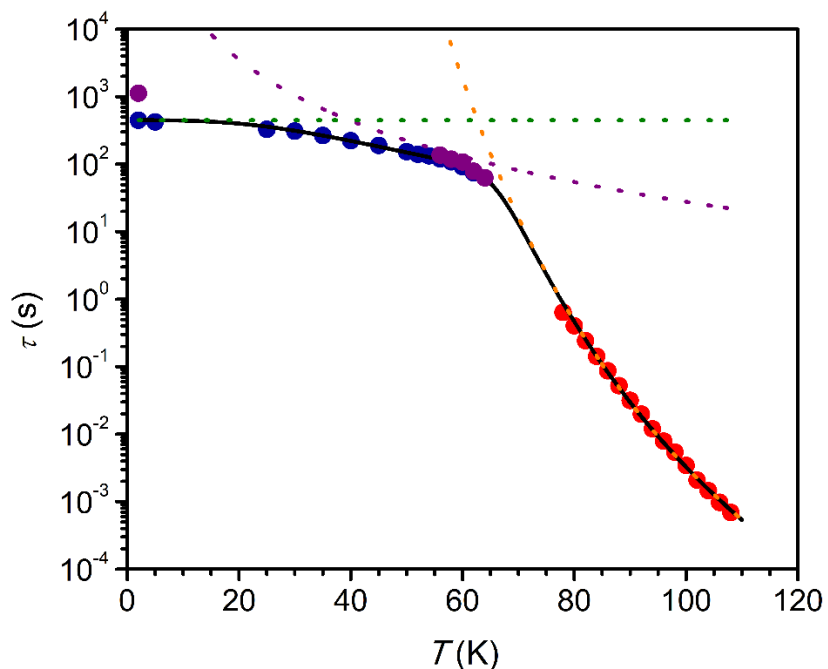


Figure S5.86. Plot of magnetic relaxation time versus temperature for **3** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data. Purple circles represent relaxation times for the dilution **3@Y** extracted from dc relaxation measurements.

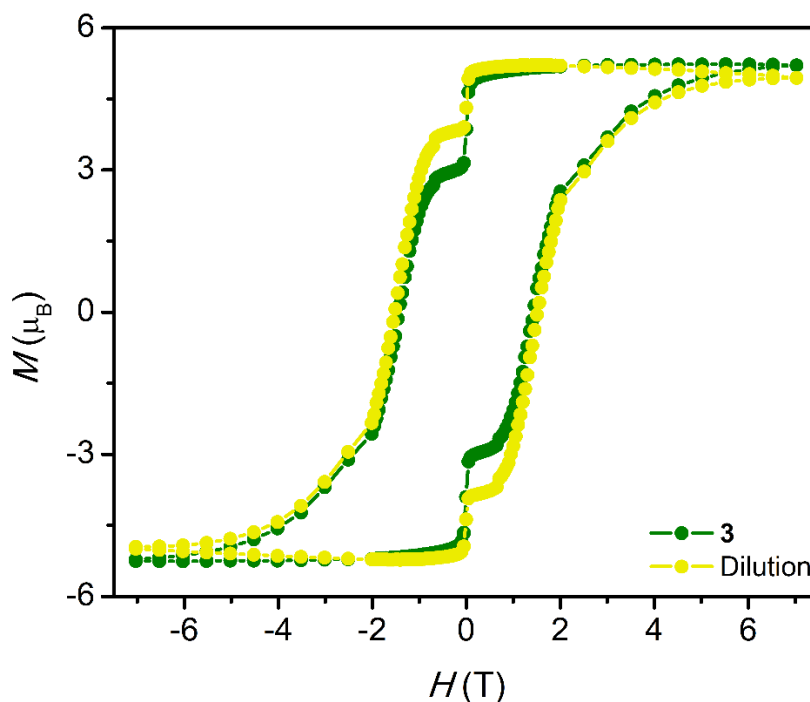


Figure S5.87. Magnetic hysteresis measurements of **3** and the dilution **3@Y** at 2 K at a sweep rate of 3.1(4) mT/s for $H < 2$ T and 13.2(2) mT/s $H > 2$ T.

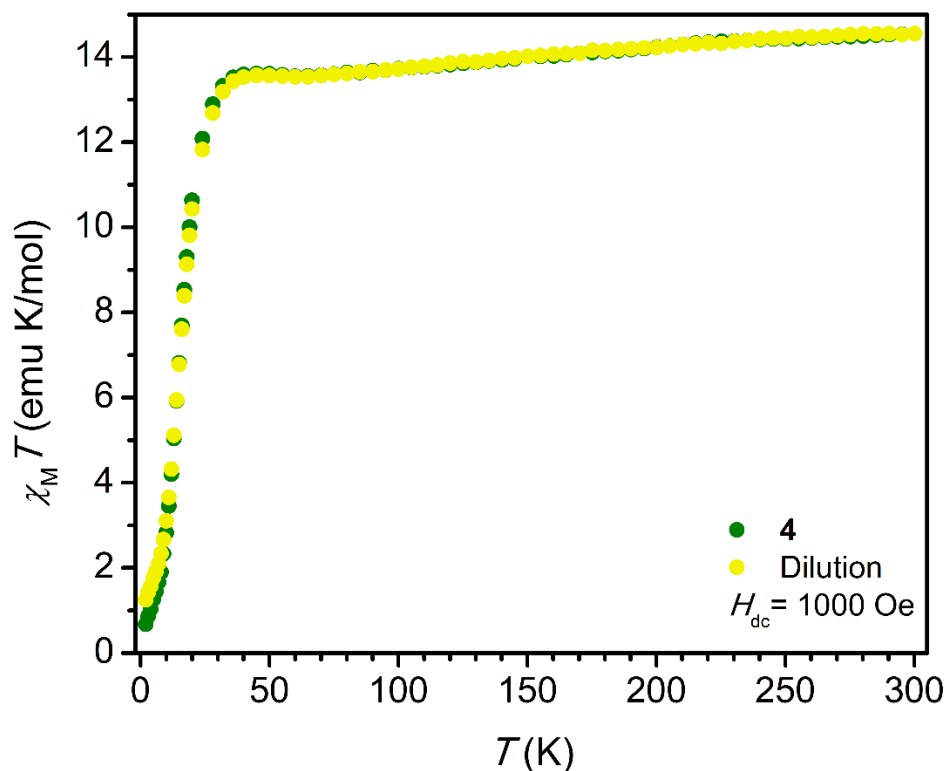


Figure S5.88. Zero-field cooled dc magnetic susceptibility measurements of **4** and the dilution **4@Y** under an applied field of 1000 Oe. Fitting the high temperature region (above 60 K) of these two plots yielded 8.7% Dy as the composition of the dilution.

Table S5.11. Parameters used to fit dc magnetic relaxation data for the dilution **4@Y** and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_b)	M_1 (μ_b)	n	τ (s) ^a
2	3.70041	1.27894*	0.720	1956.098
54	0.04907	0.00084	0.913	112.065
56	0.03621	0.00053	0.894	100.429
58	0.02640	0.00056	0.921	89.353
60	0.01566	0.00050	0.879	72.127
62	0.00865	0.00041	0.737	60.019

* M_1 values obtained by treating M_1 as a free variable

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

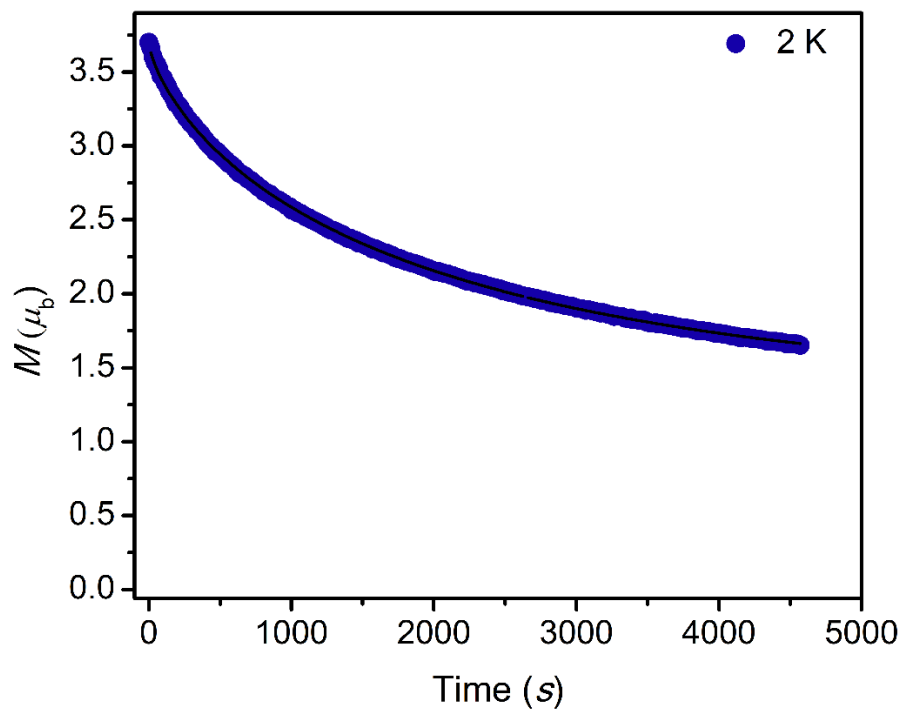


Figure S5.89. Dc magnetic relaxation data for the dilution 4@Y collected at 2 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

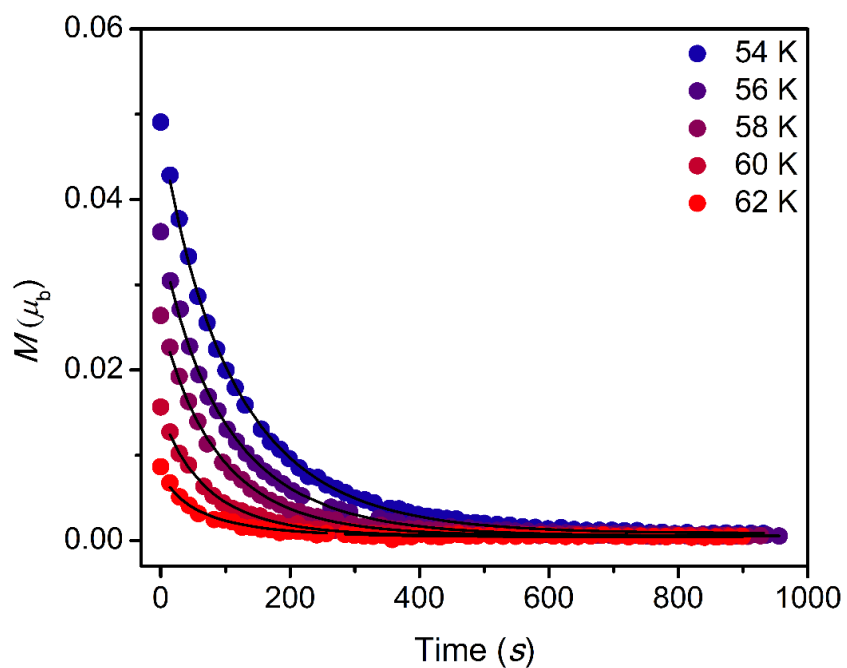


Figure S5.90. Dc magnetic relaxation data for the dilution 4@Y collected at 54, 56, 58, 60 and 62 K. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

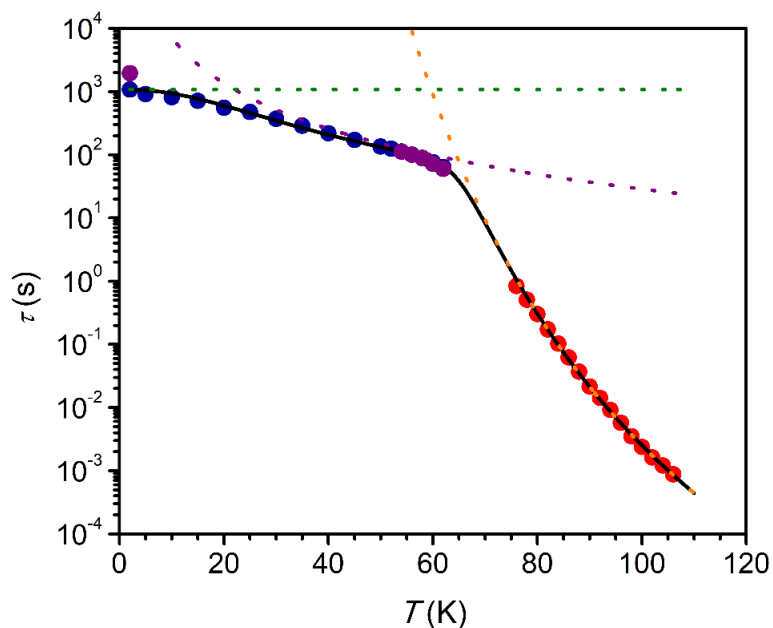


Figure S5.91. Plot of magnetic relaxation time versus temperature for **4** (dc relaxation, blue circles; ac susceptibility, red circles). Green, purple, and orange lines represent fits to quantum tunneling, Raman, and Orbach relaxation processes, respectively. Black line represents the total fit to the data. Purple circles represent relaxation times for the dilution **4@Y** extracted from dc relaxation measurements.

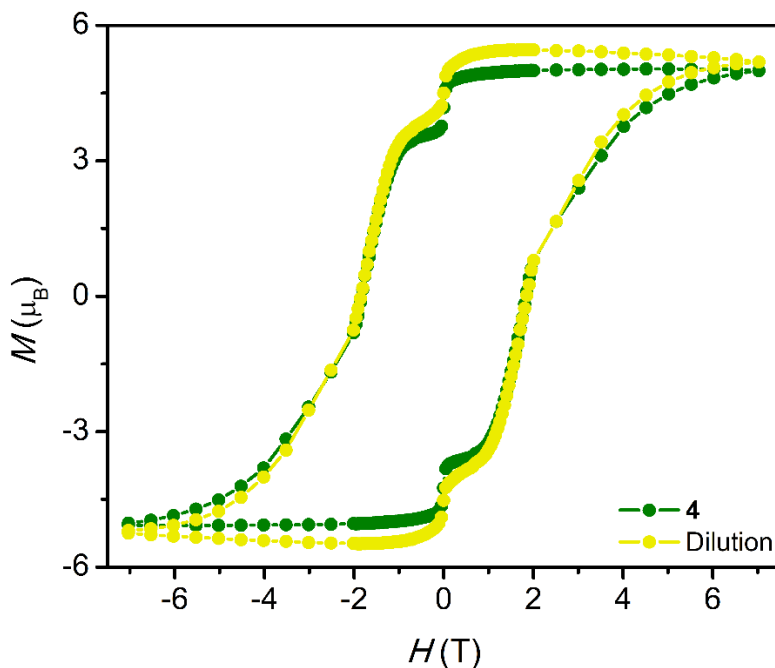


Figure S5.92. Magnetic hysteresis measurements of **4** and the dilution **4@Y** at 2 K at a sweep rate of 3.1(4) mT/s for $H < 2$ T and 13.2(2) mT/s $H > 2$ T.

5.6.6 Supplementary Information References

- (1) SAINT and APEX 2 Software for CCD Diffractometers, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2014.
- (2) Sheldrick, G. M. SADABS, Version 2.03; Bruker Analytical X-ray Systems, Inc: Madison, WI, 2000.
- (3) APEX3, v. 2009; Bruker Analytical X-Ray Systems, Inc: Madison, WI, 2009.
- (4) Sheldrick, G. M. SHELXT, University of Göttingen, Germany, 2015
- (5) Sheldrick, G. M. SHELXL, University of Göttingen, Germany, 2015
- (6) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.

Chapter 6: Synthesis and Magnetism of Neutral, Linear Metallocene Complexes of Terbium(II) and Dysprosium(II)

C. A. Gould,[†] K. R. McClain,[†] J. M. Yu, T. J. Groshens, F. Furche, B. G. Harvey, and J. R. Long, *J. Am. Chem. Soc.* **2019**, *141*, 12967–12973.^a

6.1 Introduction

Lanthanide elements possess contracted valence 4f orbitals, a characteristic that impacts both molecular structure and magnetism.¹ These core-like orbitals engage in weak, predominantly electrostatic interactions with ligands and are therefore nearly degenerate in energy, giving rise to unparalleled single-ion magnetic anisotropies in lanthanide complexes.^{2,3} Due to the electrostatic nature of the 4f-ligand interactions, steric constraints tend to dictate molecular structure and coordination geometry can be challenging to predict.⁴ This situation is in contrast to transition metal complexes, where covalent interactions between ligands and diffuse valence d orbitals typically quench orbital angular momentum, but lead to predictable geometries.⁵

Fine control over coordination geometry is essential to the design of single-molecule magnets. For instance, increasing the axiality of the ligand field can maximize the thermal barrier to magnetization reversal (U_{eff}) for oblate Dy^{III} and Tb^{III} ions and reduce transverse anisotropy, which can, in turn, decrease the rate of through-barrier relaxation.^{6,7} Enforcing a high symmetry is also important, particularly for complexes containing lanthanide ions with integer spin (non-Kramers ions)—such as Tb^{III} —for which $\pm M_J$ degeneracy is not guaranteed.⁸

Recent studies have demonstrated that molecular complexes containing Ln^{II} centers can be isolated across the entire lanthanide series and that these ions can in some instances possess $4f^n 5d^1$ electron configurations.^{9,10} We reasoned that such an electronic structure might enable the synthesis of complexes with predictable, high-symmetry geometries—arising from covalent interactions between ligands and the valence 5d electron—that also maintain the high anisotropy imparted by the $4f^n$ electrons. As complexes of the type $[\text{Dy}(\text{Cp}^{\text{R}})_2]^+$ possess the highest operating temperatures reported to date for single-molecule magnets, we chose to study the effect of metal reduction on bis(cyclopentadienyl) lanthanide complexes.¹¹ Increasing the axial symmetry in such molecules could enhance magnetic properties and this approach could also provide a valuable opportunity to study the impact of reducing Ln^{III} to Ln^{II} on single-molecule magnet behavior.

6.2 Results and Discussion

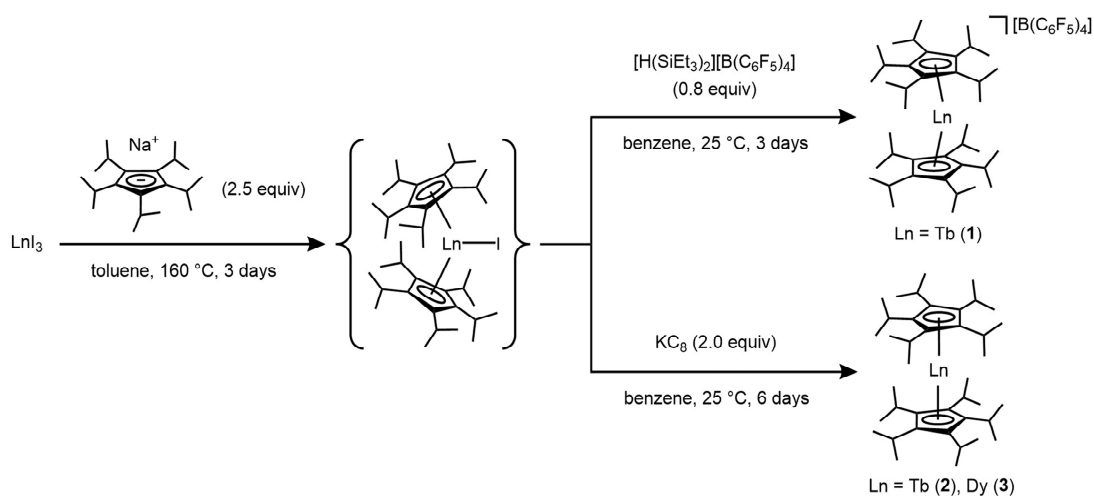
Molecules containing non-traditional Ln^{II} centers are still quite rare and are mostly limited to trigonal, anionic $[\text{Ln}(\text{L})_3]^-$ complexes with $\text{L} = \text{C}_5\text{H}_4\text{SiMe}_3$, $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$, or $\text{N}(\text{SiMe}_3)_2$.⁹ In designing a synthetic route to neutral, divalent lanthanide metallocenes, we identified reports of the reduction of $\text{Ln}(\text{Cp}^{\text{tnt}})_2\text{I}$ ($\text{Ln} = \text{Tm}, \text{Dy}$; $\text{Cp}^{\text{tnt}} = 1,2,4\text{-tri}(\text{tert-butyl})\text{cyclopentadienyl}$).¹² Reduction of $\text{Tm}(\text{Cp}^{\text{tnt}})_2\text{I}$ with KC_8 in a non-polar solvent enabled isolation of the bent THF adduct $\text{Tm}(\text{Cp}^{\text{tnt}})_2(\text{THF})$, while reduction of $\text{Dy}(\text{Cp}^{\text{tnt}})_2\text{I}$ was only successful in the presence of 18-crown-

[†]These authors contributed equally to this work.

^a C.A.G. collected and interpreted the magnetic data. K.R.M. synthesized the compounds. C.A.G. and T.G. collected the crystal structure data and C.A.G. solved and refined the structures. J.M.Y. performed the DFT calculations under the supervision of F.F. The manuscript was written by C.A.G., K.R.M., B.G.H., and J.R.L. and all authors contributed to editing it.

6, leading to an iodide-bridged ‘ate’ complex $(\text{Cp}^{\text{tnt}})_2\text{Dy}(\mu\text{-I}) \text{K}(\text{18-crown-6})$.¹² We reasoned that a $\text{Ln}(\text{Cp}^{\text{R}})_2\text{I}$ intermediate containing the more strongly donating, bulkier, and more symmetric pentaisopropylcyclopentadienyl (Cp^{iPr5}) ligand could facilitate clean reduction to $\text{Ln}(\text{Cp}^{\text{R}})_2$ species.

In order to make direct comparisons between neutral and cationic complexes, we synthesized the terbium(III) complex salt $[\text{Tb}(\text{Cp}^{\text{iPr5}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) via iodide abstraction from $\text{Tb}(\text{Cp}^{\text{iPr5}})_2\text{I}$, in a procedure analogous to the synthesis of $[\text{Dy}(\text{Cp}^{\text{iPr5}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (Scheme 6.1).^{11d} Crucially, reduction of $\text{Ln}(\text{Cp}^{\text{iPr5}})_2\text{I}$ ($\text{Ln} = \text{Tb}, \text{Dy}$) in benzene with KC_8 and subsequent crystallization from hexane afforded orange-amber crystals of $\text{Ln}(\text{Cp}^{\text{iPr5}})_2$ ($\text{Ln} = \text{Tb}$ (**2**), Dy (**3**)), the first neutral, linear metallocenes for any divalent lanthanide more reducing than samarium(II) (Scheme 6.1).¹³ Both **2** and **3** are indefinitely stable under argon in the solid state and hexane solution at 25 °C, in contrast to the aforementioned $[\text{Ln}(\text{L})_3]^-$ complexes, which are prone to decomposition at ambient temperatures.^{9b}



Scheme 6.1. Synthetic routes to the terbium(III) metallocenium salt **1** and lanthanide(II) metallocene complexes **2** and **3**.

The solid-state structures of **1-3** were determined by single-crystal X-ray diffraction analyses (Figure 6.1). Although the cyclopentadienyl rings in **1** are nearly parallel, the Tb^{III} site is situated slightly off-center, with an average Cp-Tb-Cp angle of $159.8(4)^\circ$. The metal center is disordered over four positions, analogous to the disorder observed in $[\text{Dy}(\text{Cp}^{\text{iPr5}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$.^{11d} In contrast, the metal ions in **2** and **3** are located on an inversion center, resulting in a Cp-Ln-Cp angle of 180° and Cp-Ln-Cp core symmetry (excluding isopropyl groups) of D_{5d} . The high-symmetry structures of **2** and **3** are significant, as most $4f^n$ lanthanide metallocenes are bent.¹⁴⁻¹⁶

The solid-state structures of **1-3** can also provide insight into electronic configuration. In $[\text{LnCp}^{\text{R}}_3]^-$ complexes featuring Ln^{II} centers with $4f^{n+1}$ configurations, the $\text{Ln-Cp}^{\text{R}}(\text{centroid})$ distances are larger than those of the trivalent analogues by 0.1–0.2 Å. In contrast, for Ln^{II} centers with $4f^n5d^1$ configurations, the increase in the Ln-Cp^{R} distance is much smaller, 0.02–0.05 Å.⁹ The average Tb-Cp distance in **1** is 2.356(6) Å, lengthening to 2.416(1) Å in **2**, while the average Dy-Cp distance in $[\text{Dy}(\text{Cp}^{\text{iPr5}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ is 2.336(4) Å, lengthening to 2.385(1) Å in **3**. A similar trend is observed for the average Ln-C distance. The average Tb-C distances in **1** and **2** are 2.635(8) and 2.704(2) Å, respectively, and the average Dy-C distances in $[\text{Dy}(\text{Cp}^{\text{iPr5}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and **3** are 2.621(2) and 2.673(4) Å, respectively. These differences support a $4f^n5d^1$ configuration for **2** and **3**.^{9c,f,g,17,18}

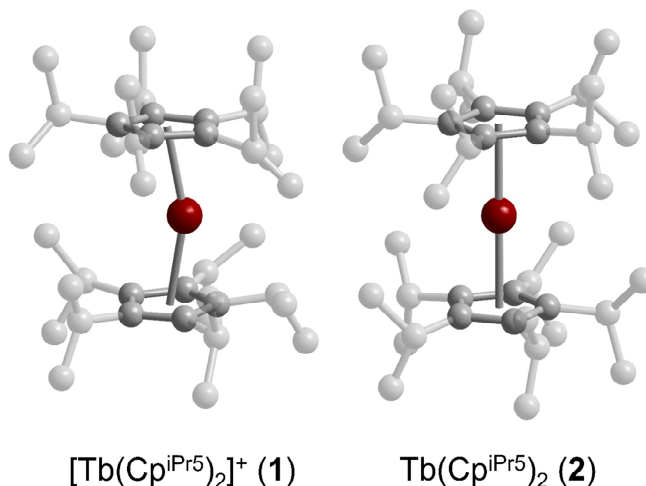


Figure 6.1. Solid-state molecular structures of **1** and **2**. Maroon and grey spheres represent Tb and C atoms, respectively; hydrogen atoms, the [B(C₆F₅)₄][−] counteranion in **1**, and positional disorder are omitted for clarity. Compound **3** is isostructural to **2**.

Density functional theory (DFT) calculations performed on optimized structures of Tb(Cp^{iPr5})₂ and Dy(Cp^{iPr5})₂ afforded ⁸A (in *C*₁ symmetry) and ⁷A₁ (in *D*₅ symmetry) ground terms, respectively, corresponding to a 4f⁷5d¹ configuration (see Supporting Information for details). These calculations support a nondegenerate highest occupied molecular orbital (HOMO) with significant 5d_{z²} character (Figure 6.2). Natural population analysis revealed that the HOMO also has considerable 6s character due to 5d_{z²}-6s orbital mixing.¹⁹ Covalent σ-bonding interactions between these metal-based orbitals and the cyclopentadienyl ligands likely support the linear coordination geometry observed for these divalent metallocenes. The lowest unoccupied molecular orbital (LUMO) is doubly degenerate and has significant d_{xy}/d_{x²-y²} character, consistent with the orbital ordering found in ferrocene.²⁰

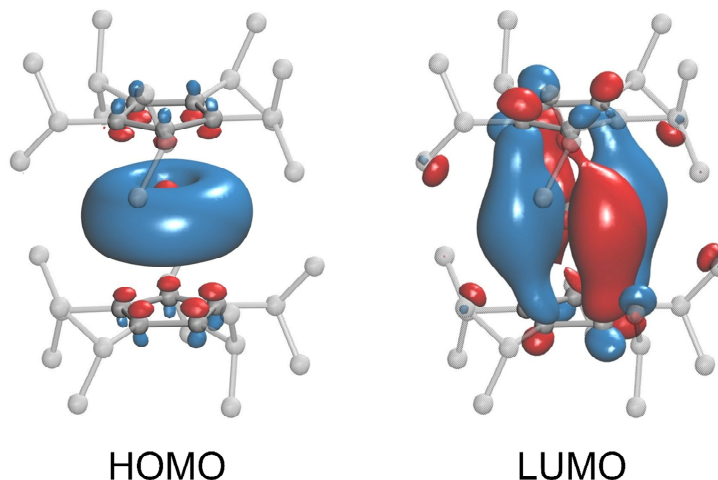


Figure 6.2. HOMO (left, 170Aα contour value 0.03) and LUMO (right, 172Aα contour value 0.03) for **2** with hydrogen atoms excluded for clarity. The HOMO and LUMO for **3** are isolobal.

Dc magnetic susceptibility data were collected for **1-3** from 2 to 300 K under an applied magnetic field of 1000 Oe (Figures S6.13-S6.18). The room temperature χ_{MT} value for **1** is 11.96

emu K/mol, which agrees well with the expected value of 11.82 emu K/mol for a free Tb^{III} ion (4f⁸). Slightly larger values were found for the divalent complexes: 12.72 emu K/mol for **2** and 15.15 emu K/mol for **3**. These values are distinct from the values of 14.13 and 14.07 emu K/mol predicted for a 4f⁹ Tb^{II} ion and a 4f¹⁰ Dy^{II} ion, respectively. Previously reported Ln^{II} complexes with 4fⁿ5d¹ configurations follow an *L–S* coupling scheme, resulting in room temperature $\chi_{\text{M}}T$ values close to the predicted values of 14.42 and 17.01 emu K/mol for Tb^{II} and Dy^{II}, respectively.^{9f}

^h The values for **2** and **3** are substantially lower, suggesting a deviation from *L–S* coupling that can be explained by the strong 5d_{z²}-6s mixing. Indeed, gas-phase spectra of Ln²⁺ ions with 4fⁿ6s¹ configurations reveals that these ions follow a *j–j* coupling scheme due to weak spin-spin coupling between the 4f and 6s orbitals.^{21,22} Evaluating the nature of such complex electronic structures is challenging and we are currently pursuing further insights through a variety of spectroscopic measurements.

Magnetic relaxation in **1–3** was probed by ac magnetic susceptibility and dc magnetic relaxation experiments (Figures S6.19–S6.58). Under zero dc field, a polycrystalline sample of compound **1** exhibited peaks in the out-of-phase susceptibility (χ_{M}'') between 2 and 40 K, indicative of slow magnetic relaxation. Pronounced curvature in a corresponding plot of magnetic relaxation time (τ , log scale) versus T (inverse scale) is indicative of Raman relaxation (Figure 6.3, yellow symbols).²³ Magnetic relaxation is ~ 5 orders of magnitude faster in **1** than in [Dy(Cp^{iPr5})₂][B(C₆F₅)₄], consistent with previous reports on [Ln(Cp^{III})₂][B(C₆F₅)₄] (Ln = Tb, Dy).^{11d,24} This result can be attributed to the non-integer spin of Tb^{III}, which enables mixing of the ground $\pm M_J$ pseudo-doublet that can promote rapid through-barrier relaxation.²⁴

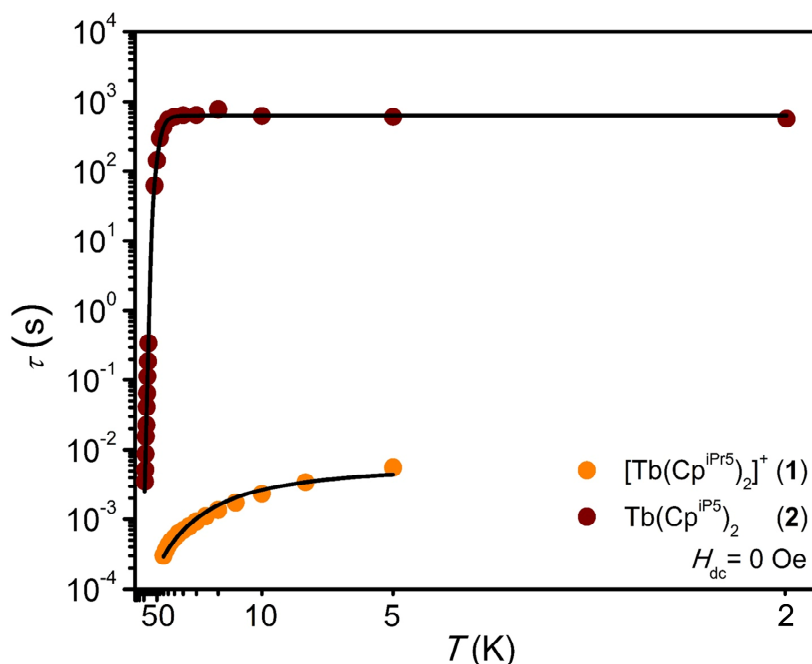


Figure 6.3. Plot of magnetic relaxation time (τ , log scale) versus temperature (T , inverse scale) for polycrystalline samples of **1** (yellow) and **2** (maroon). Black lines represent fits to the data.

A polycrystalline sample of compound **2** exhibited frequency-dependent χ_{M}'' signals under zero dc field from 74 to 92 K. The data could be fit to an Orbach mechanism with a large effective barrier to magnetic relaxation of $U_{\text{eff}} = 1205 \text{ cm}^{-1}$ (Figure S6.61). Additionally, a 100-s magnetic blocking temperature (T_b) of 52 K was extracted from dc relaxation experiments (Figure 6.3,

maroon symbols). The values of U_{eff} and T_b for **2** are the highest yet reported for any single-molecule magnet that is not a dysprosium(III) complex and are only surpassed by the complex $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{py})_5][\text{BPh}_4]$ and molecules of the type $[\text{Dy}(\text{Cp}^R)_2]^+$.^{8f,11,25,26} The substantial increase of over five orders of magnitude in the magnetic relaxation times of **2** as compared to **1** can be attributed to at least two factors. Reduction from terbium(III), a non-Kramers ion, to terbium(II), a Kramers ion, enforces degeneracy of the ground $\pm M_J$ doublet in **2**.²⁷ In addition, increasing the axial symmetry of the coordination environment should reduce transverse anisotropy, suppressing tunneling of the magnetization.

Lanthanide reduction has the opposite effect on magnetic relaxation in the dysprosium metallocene complexes. A polycrystalline sample of **3** does not display slow magnetic relaxation on the timescale of dc magnetic relaxation experiments ($\tau > 50$ s), although a 100-s magnetic blocking temperature of 5 K could be extracted from data obtained for a dilute (28 mM) toluene solution of **3**. This blocking temperature is substantially lower than the value of $T_b = 56$ K observed for $[\text{Dy}(\text{Cp}^{\text{iPr}_5})_2][\text{B}(\text{C}_6\text{F}_5)_4]$, likely due to conversion from dysprosium(III), a Kramers ion, to dysprosium(II), a non-Kramers ion.^{11d} While fast compared to $[\text{Dy}(\text{Cp}^{\text{iPr}_5})_2][\text{B}(\text{C}_6\text{F}_5)_4]$, the rate of magnetic relaxation in **3** is nearly 10^4 times slower than observed for **1**, underscoring the importance of axial symmetry in complexes containing non-Kramers ions.^{8a}

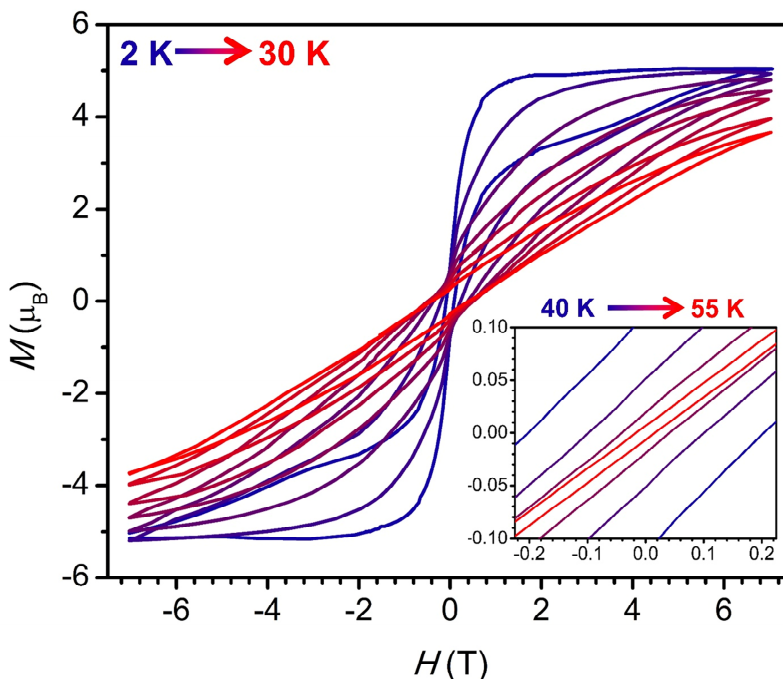


Figure 6.4. Magnetic hysteresis data for **2** collected at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

Magnetic hysteresis measurements further confirmed the trends in magnetic relaxation behavior observed for **1-3**. While hysteresis is largely absent for **1**, even at 2 K (Figure S6.71), **2** exhibits open magnetic hysteresis loops at zero field up to 55 K (Figure 6.4). Surprisingly, the coercive field for **2** increases from 2 to 30 K (Figure S6.73), implying that the rate of magnetic relaxation decreases with increasing temperature. Indeed, dc relaxation measurements performed on polycrystalline **2** and a dilute (19 mM) toluene solution of **2** revealed that the relaxation time increases slightly from 2 to 15 K (Tables S6.3 and S6.5).²⁸ Polycrystalline **3** exhibits butterfly

magnetic hysteresis from 2–75 K (Figures S6.78-S6.80), while measurements performed on a dilute (28 mM) toluene solution of **3** revealed hysteresis loops that are open at zero field as high as 10 K (Figures S6.81-S6.82). Significantly, compounds $\text{Tb}(\text{Cp}^{\text{iPr5}})_2$ and $\text{Dy}(\text{Cp}^{\text{iPr5}})_2$ represent the first single-molecule magnets based on a divalent lanthanide ion to show magnetic hysteresis.²⁹ Importantly, unlike $[\text{Dy}(\text{Cp}^{\text{R}})_2]^+$ salts, these charge-neutral molecules may also be stable to sublimation, offering a ready means of depositing them onto surfaces and within devices.

In order to investigate the unusual low-temperature hysteresis behavior, magnetic relaxation in **2** and **3** was probed by ac susceptibility measurements from 2 to 20 K. The resulting data reveal complicated relaxation dynamics featuring multiple relaxation processes (Figures S6.60-S6.70), which persist in data collected on dilute solution samples of each compound. This behavior likely arises from the complex electronic structure of the divalent metallocenes, and clearly warrants further investigation.³⁰

6.3 Conclusions and Outlook

The foregoing results demonstrate that lanthanide reduction in bis(pentaisopropyl)cyclopentadienyl metallocenes has a substantial impact on both the coordination geometry and magnetic properties. In particular, the $4f^75d^1$ electronic configuration of $\text{Ln}(\text{Cp}^{\text{iPr5}})_2$ supports axial, high-symmetry structures, likely a result of enhanced covalency in metal-ligand interactions. Notably, the more axial symmetry of $\text{Dy}(\text{Cp}^{\text{iPr5}})_2$ results in higher hysteresis temperatures relative to $[\text{Tb}(\text{Cp}^{\text{iPr5}})_2]^+$, although both complexes feature non-Kramers ions. Reduction of terbium(III) to terbium(II) also results in a drastic enhancement of the magnetic relaxation time for $\text{Tb}(\text{Cp}^{\text{iPr5}})_2$ and gives rise to the highest thermal barrier to magnetic inversion and highest magnetic blocking temperature yet observed for a non-dysprosium single-molecule magnet. In total, these results highlight the utility of lanthanide redox chemistry in modulating magnetic relaxation. We are currently pursuing a more detailed understanding of the complex electronic structure and magnetism of these new divalent metallocenes via a variety of spectroscopic methods.

6.4 Acknowledgements

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6.5 References and Footnotes

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- (16) Complexes **2** and **3** form as a mixture of *rac* and *meso* isomers, defined by different orientations of the methyl carbons of the isopropyl groups. The position of the metal atom, the carbon atoms in the cyclopentadienyl rings, and the methine carbon atoms in the isopropyl groups are identical for the two isomers in the crystal structure of **2** and **3**.

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- (26) For reference, the current record values are $U_{\text{eff}} = 1541 \text{ cm}^{-1}$ and $T_b = 65 \text{ K}$, as observed for [Dy(Cp^{iPr5})(Cp*)][B(C₆F₅)₄] (Cp* = pentamethylcyclopentadienyl) (Ref. 11c).
- (27) Kramers' theorem states that a time-reversal symmetric system with half-integer total spin will have eigenstates that are at least doubly degenerate. For lanthanide ions with half-integer values of S , this means that the ground $\pm M_J$ doublet will be degenerate and resistant to direct mixing between the two projections, mitigating through-barrier magnetic relaxation processes. The ground states obtained by DFT calculations for **2** and **3** are ⁸A and ⁷A₁ (or ⁷A_g), respectively, and on this basis we assign **2** as a Kramers ion ($S = 7/2$, non-integer spin) and **3** as a non-Kramers ion ($S = 3$, integer spin). Kramers, H. A. *Proc. Amsterdam Acad.*, **1930**, *33*, 959.
- (28) A decrease in the rate of magnetic relaxation with increasing temperature was also observed for U(H₂BPz₂)₃, although the magnetic relaxation process in this case was found to arise from intermolecular dipolar interactions, rather than the behavior of individual molecules. The relaxation process in **2** that decreases in rate with increasing temperature appears to be molecular in origin, as it is replicated in measurements on a dilute (19 mM) toluene solution of **2** with an average Tb⋯Tb separation of 44 Å. (a) Rinehart, J. D.; Meihaus, K. R.; Long, J. R. Observation of a Secondary Slow Relaxation Process for the Field-Induced Single-Molecule Magnet U(H₂BPz₂)₃. *J. Am. Chem. Soc.* **2010**, *132*, 7572–7573. (b) Meihaus, K. R.; Rinehart, J. D.; Long, J. R. Dilution-Induced Slow Magnetic Relaxation and Anomalous Hysteresis in Trigonal Prismatic Dysprosium(III) and Uranium(III) Complexes. *Inorg. Chem.* **2011**, *50*, 8484–8489.
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- (30) Multiple relaxation processes are often ascribed to the presence of two or more distinct metal sites in a molecule (Refs. 30a-c). While **1-3** are synthesized as a mixture of *rac* and *mer* isomers, it seems unlikely that subtle changes in the orientation of remote methyl groups would cause such large changes in the rate of magnetic relaxation. Multiple relaxation processes have also been observed for a mononuclear single-molecule magnet featuring a single metal environment (Ref. 30d). DFT calculations conducted on **2** and **3** reveal an excited state (⁶A for **2** and ⁵A_g or ⁵A₁ for **3**) ~4 kcal/mol higher in energy than the ground state. The $\pm M_J$ manifold of this excited state may be close enough to mix with the $\pm M_J$ manifold of the ground state, leading to a complex electronic structure that could perhaps complicate the relaxation dynamics of the divalent metallocenes. (a) Blagg, R. J.; Ungur, L.; Tuna, F.; Speak, J.; Comar, P.; Collison, D.; Wernsdorfer, W.; McInnes, E. J. L.; Chibotaru, L. F.; Winpenny, R. E. P. Magnetic relaxation pathways in lanthanide single-molecule magnets. *Nat. Chem.* **2013**, *5*, 673–678. (b) Liu, C. M.; Xiong, J.; Zhang, D.-Q.; Wang, B.-W.; Zho, D.-B. Multiple thermal magnetic relaxation in a two-dimensional ferromagnetic dysprosium(III) metal-organic framework. *RSC Adv.* **2015**, *5*, 104854–104861. (c) Mang, W.-M.; Kang, X.-M.; Shen, H.-Y.; Wu, Z.-L.; Gao, H.-L.; Cui, J.-Z.

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6.6 Supplementary Information

6.6.1 General Procedures.

All manipulations were performed using Schlenk or glovebox techniques under an atmosphere of purified argon with rigorous exclusion of water and oxygen. All solvents were purchased from Sigma-Aldrich as anhydrous grade in Sure/Seal™ bottles, purged for several hours with purified argon and stored over activated 3 Å molecular sieves in an argon filled glovebox. Celite (AW Standard Super-Cel® NF) was purchased from Sigma-Aldrich and dried under vacuum at 150-200 °C overnight before being transferred to the glovebox. KC₈ was purchased from Strem and used as received. Anhydrous LnI₃ (Ln = Dy, Tb) were purchased from Alfa Aesar as Ultra Dry™ grade reagents and used as received. The halide abstraction reagent, [H(SiEt₃)₂][B(C₆F₅)₄], was prepared freshly before use via a reported method.¹ The salt NaCp^{*i*Pr₅} was prepared via a previously published method.² NMR spectra were recorded on a Bruker Avance 300 MHz or 500 MHz spectrometer and internally referenced to the residual solvent signals. FT-IR spectra were recorded on a Perkin Elmer Avatar Spectrum 400 FTIR Spectrometer equipped with an attenuated total reflectance (ATR) attachment. UV-vis-NIR absorption spectra were collected with a CARY 5000 spectrophotometer interfaced with Varian WinUV software. Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on an Applied Biosystems Voyager-DE PRO Workstation in positive ion mode. Samples were co-crystallized in an anthracene matrix on an AB SCIEX MALDI-TOF stainless steel sample plate. Spectra were averaged over 200 laser pulses with a low mass gate of 300 Dalton and a high mass gate of 2000 Dalton. Elemental analyses (C, H, N) were performed by the Microanalytical Facility at the University of California, Berkeley using a Perkin-Elmer 2400 Series II combustion analyzer. Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer.

Synthesis of [Tb(Cp^{*i*Pr₅})₂][B(C₆F₅)₄] (1). Under argon, TbI₃ (0.250 g / 0.463 mmol) and NaCp^{*i*Pr₅} (0.350 g / 1.17 mmol) were combined in a 35 mL pressure flask containing a glass-coated magnetic stirring bar and toluene (15 mL) was added. The reaction flask was covered in Al foil, and heated gradually to 160 °C with vigorous stirring. After 72 h at 160 °C, the flask was allowed to cool to room temperature, the reaction mixture was filtered through Celite and the pad washed with additional toluene (3 X 5 mL). Solvent was removed from the filtrate under vacuum and the residue was gently heated (50 °C) under vacuum for 1 h. The residue was taken up in pentane (25 mL), stirred for 0.5 h, filtered through Celite and the pad washed with additional pentane (3 X 5 mL). Solvent was removed from the filtrate under vacuum and the residue was gently heated (50 °C) under vacuum for 0.5 h to give crude Tb(Cp^{*i*Pr₅})₂I as a yellow powder. This was dissolved with benzene (10 mL) in a 25 mL Schlenk flask equipped with a Teflon magnetic stirring bar to give a yellow solution. Under vigorous stirring at room temperature, a solution of [H(SiEt₃)₂][B(C₆F₅)₄] (0.342 g / 0.375 mmol) in benzene (5 mL) was added dropwise to the Tb(Cp^{*i*Pr₅})₂I solution over 5 min. After stirring for 72 h at room temperature, solvent was removed from the reaction mixture under vacuum, the residue was slurried with pentane (20 mL) for 0.5 h and isolated as an orange powder on a medium-porosity fritted filter after washing with pentane (3 X 10 mL). This was dried under vacuum, dissolved in dichloromethane (4 mL), filtered with aid of Celite through a 0.2 µm porosity PTFE syringe filter and layered with pentane (15 mL) in a 20 mL vial. After 48 h at 25 °C bright orange needle crystals were obtained. These were isolated on a medium-porosity fritted

filter, washed with pentane (5 mL), benzene (5 mL) and pentane (5 mL). The crystallization was repeated and the crystals dried under vacuum to yield **1** as orange needles (0.330 g / 0.238 mmol / 51% based on TbI₃). C₆₄H₇₀BtF₂₀ (1388.97): calcd (%) C 55.34, H 5.08; found (%) C 55.18, H 5.00.

Synthesis of [Tb(Cp^{iPr5})₂] (2**).** Under argon, TbI₃ (0.361 g / 0.670 mmol) and NaCp^{iPr5} (0.50 g / 1.67 mmol) were combined in a 35 mL pressure flask containing a glass-coated magnetic stirring bar and toluene (20 mL) was added. The reaction flask was covered in Al foil, and heated gradually to 160 °C with vigorous stirring. After 72 h at 160 °C, the flask was allowed to cool to room temperature, the reaction mixture was filtered through Celite and the pad washed with additional toluene (3 X 5 mL). Solvent was removed from the filtrate under vacuum and the residue was gently heated (50 °C) under vacuum for 1 h. The residue was taken up in pentane (25 mL), stirred for 0.5 h, filtered through Celite and the pad washed with additional pentane (3 X 5 mL). Solvent was removed from the filtrate under vacuum and the residue was gently heated (50 °C) under vacuum for 0.5 h to give crude Tb(Cp^{iPr5})₂I as a yellow powder. Under argon, the crude Tb(Cp^{iPr5})₂I was placed in a 50 mL Schlenk flask and dissolved with benzene (15 mL) to give a yellow solution, KC₈ (0.180 g / 1.34 mmol) was added and the flask was covered in Al foil and allowed to stir at 25 °C for 6 days (reaction solution gradually changed from yellow to vibrant orange and bronze KC₈ slowly converted to black graphite). Solvent was removed under vacuum, the residue was extracted by stirring with hexane (25 mL) for 30 min., filtered through Celite and the pad washed with additional hexane (3 X 5 mL) to give a vibrant orange filtrate. The solution was concentrated in a 40 mL vial under vacuum until copious precipitation of orange/amber solid (~ 10 mL); this was re-dissolved by heating the solution to boiling. The vial was then wrapped in Al foil and allowed to cool slowly to 25 °C, after several days, orange amber crystals appeared and the vial was then left at -35 °C to complete the crystallization. Orange/amber prisms of **2** were isolated in two crops, washed with cold pentane (2 X 2 mL) and dried under vacuum (0.194 g / 0.273 mmol / 41% based on TbI₃). MALDI ToF MS *m/z*: 709.2 ([M]⁺). C₄₀H₇₀Tb (709.93): calcd (%) C 67.67, H 9.94; found (%) C 67.53, H 9.68.

Synthesis of [Dy(Cp^{iPr5})₂] (3**).** Following the general procedure used for synthesis of **2**, **3** was synthesized from DyI₃ (0.364 g / 0.670 mmol), NaCp^{iPr5} (0.50 g / 1.67 mmol) and KC₈ (0.180 g / 1.34 mmol). The crude product was recrystallized from hexane using the same method outlined for **2**, yielding orange/amber prisms in two crops (0.231 g / 0.324 mmol / 48% based on DyI₃). MALDI ToF MS *m/z*: 713.4 ([M]⁺). C₄₀H₇₀Dy (713.50): calcd (%) C 67.34, H 9.89; found (%) C 67.20, H 9.47.

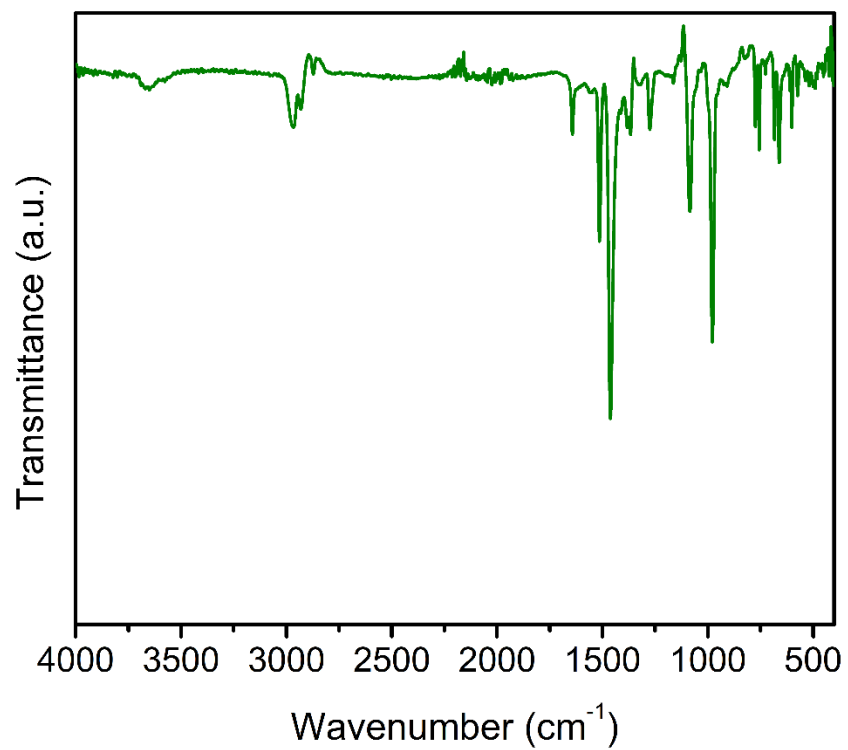


Figure S6.1. Infrared spectrum of **1**.

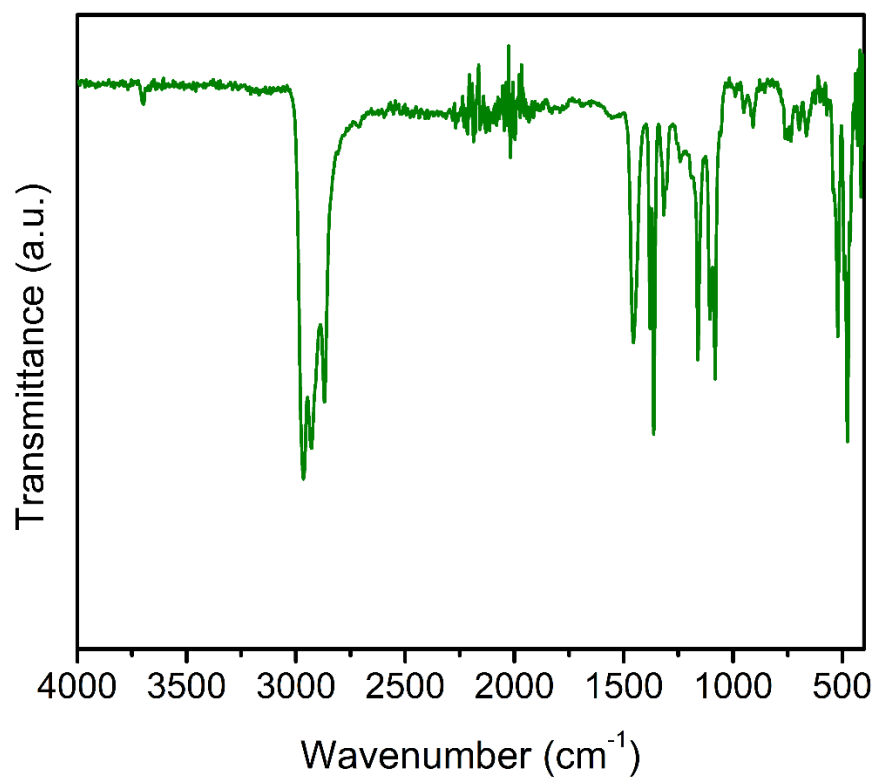


Figure S6.2. Infrared spectrum of **2**.

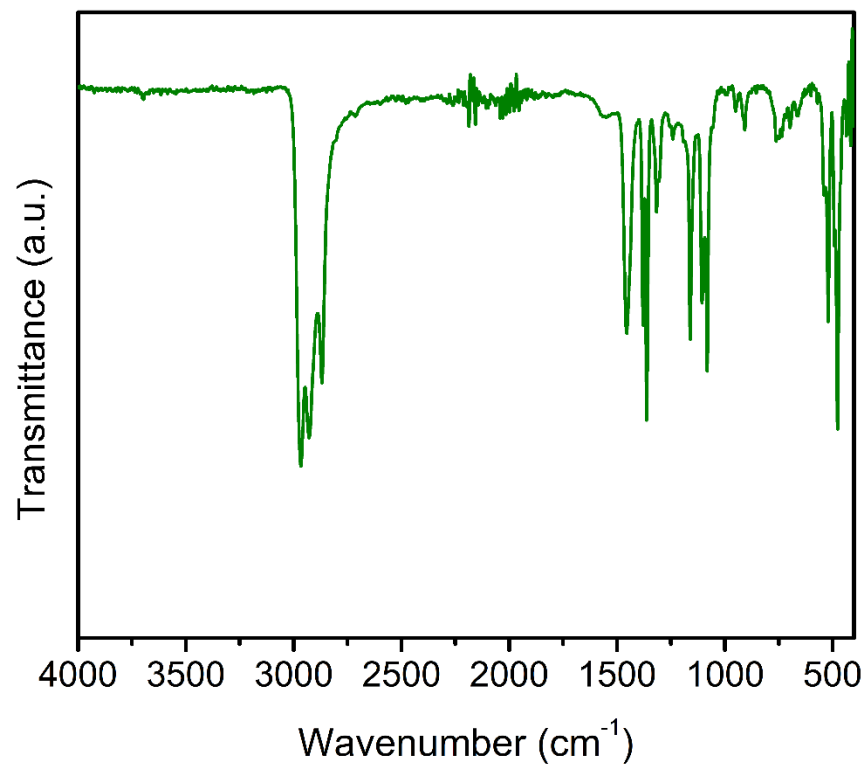


Figure S6.3. Infrared spectrum of **3**.

6.6.2 UV-vis-NIR Spectroscopy.

UV-Vis-NIR spectroscopy was performed on solutions of **2** and **3** in hexanes. Two stock solutions were made for each sample (to avoid mass error), 0.46 mM and 0.53 mM for **2** and 0.48 and 0.58 mM for **3**. A total of seven measurements were made for each sample, four with serial dilutions of the first stock solution and three with serial dilutions of the second stock solution. Plots of concentration versus absorbance were used to extract extinction coefficients for each of the features observed in the spectrum.

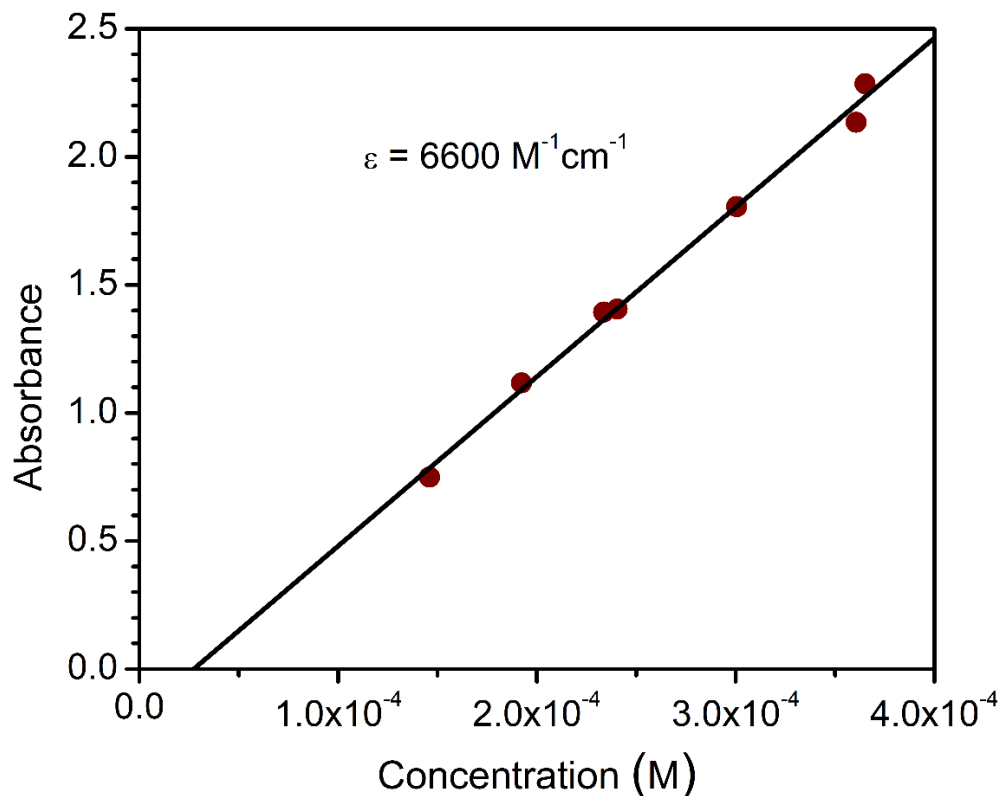


Figure S6.4. Plot of absorbance versus concentration for the feature at 303 nm in the UV-Vis-NIR spectrum of **2**. Maroon points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

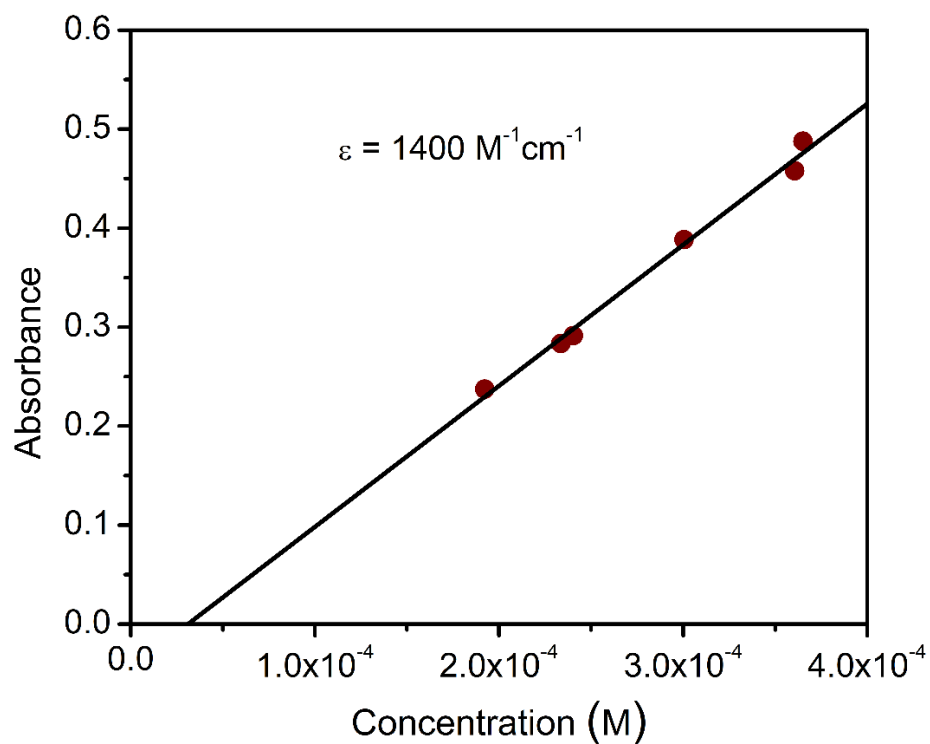


Figure S6.5. Plot of absorbance versus concentration for the feature at 429 nm in the UV-Vis-NIR spectrum of **2**. Maroon points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

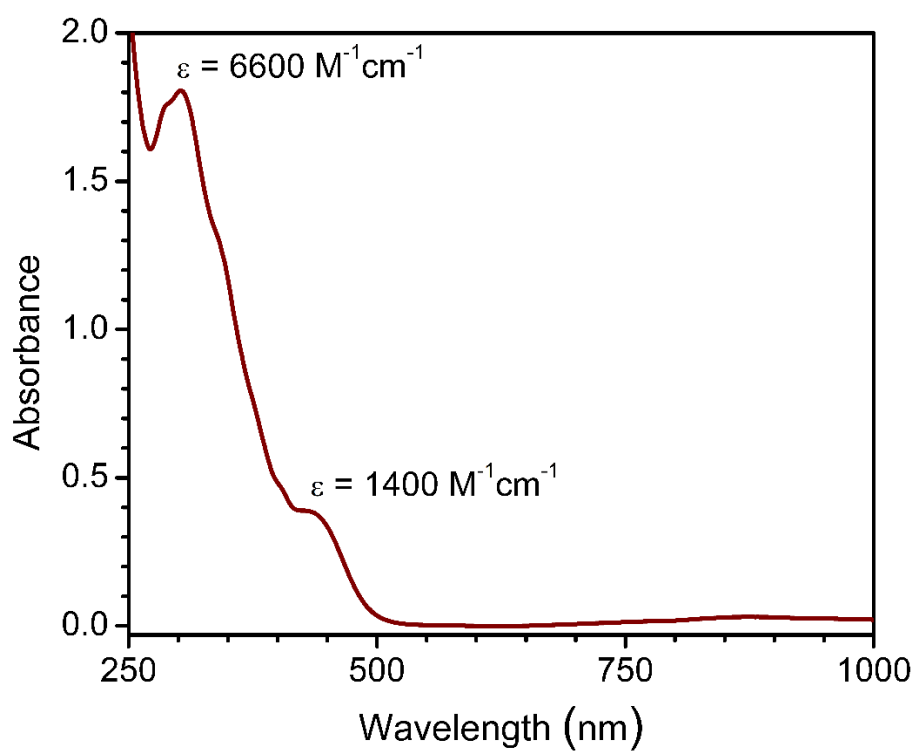


Figure S6.6. UV-Vis-NIR spectrum of **2**.

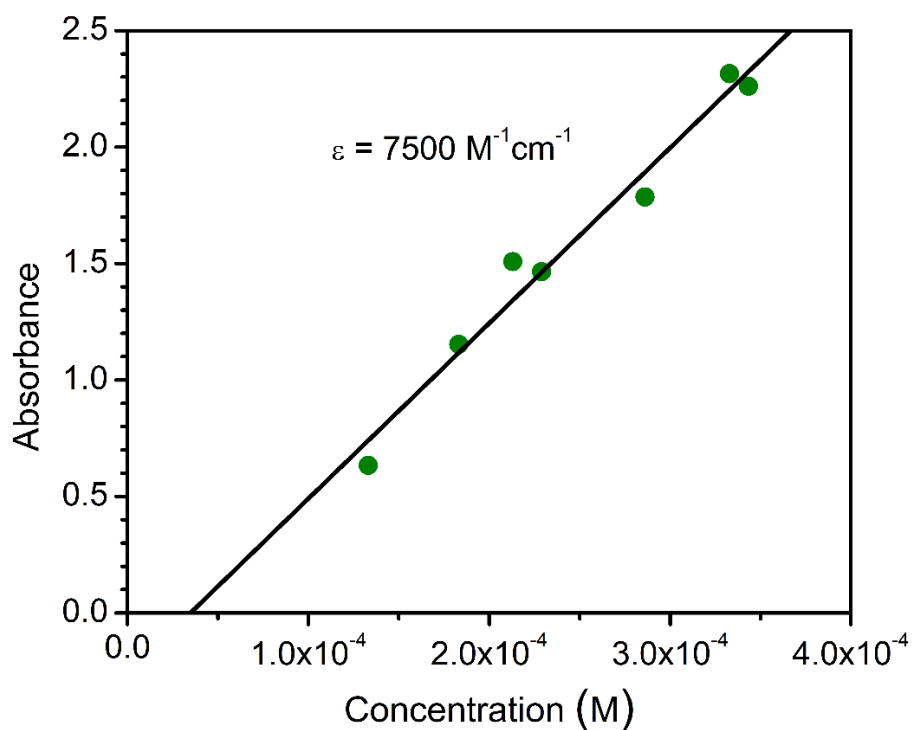


Figure S6.7. Plot of absorbance versus concentration for the feature at 298 nm in the UV-Vis-NIR spectrum of **3**. Green points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

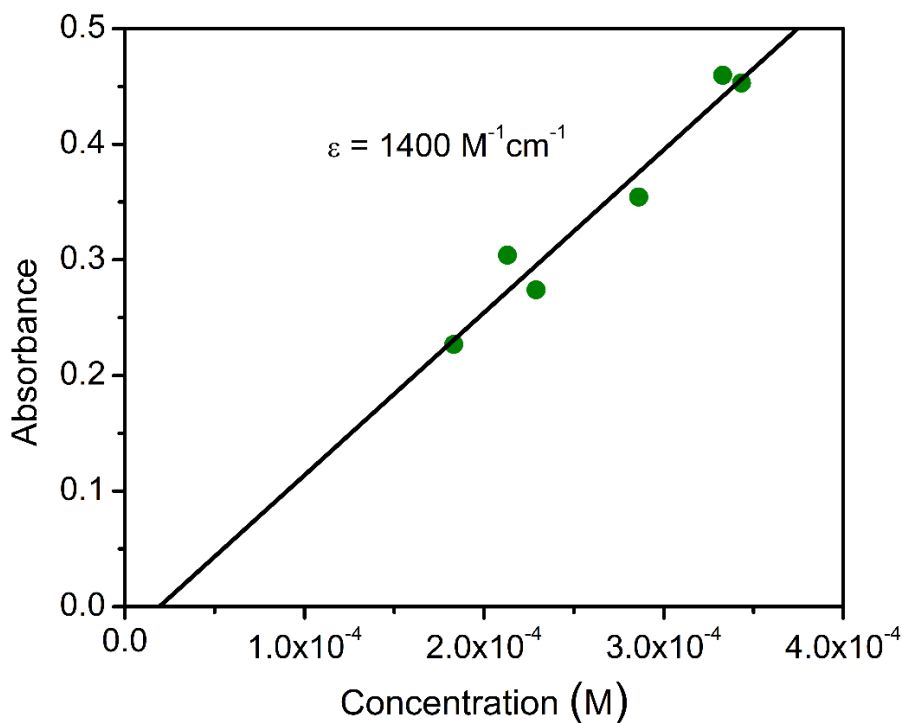


Figure S6.8. Plot of absorbance versus concentration for the feature at 428 nm in the UV-Vis-NIR spectrum of **3**. Green points represent experimental data and the black line represents the fit to the data used to extract the extinction coefficient.

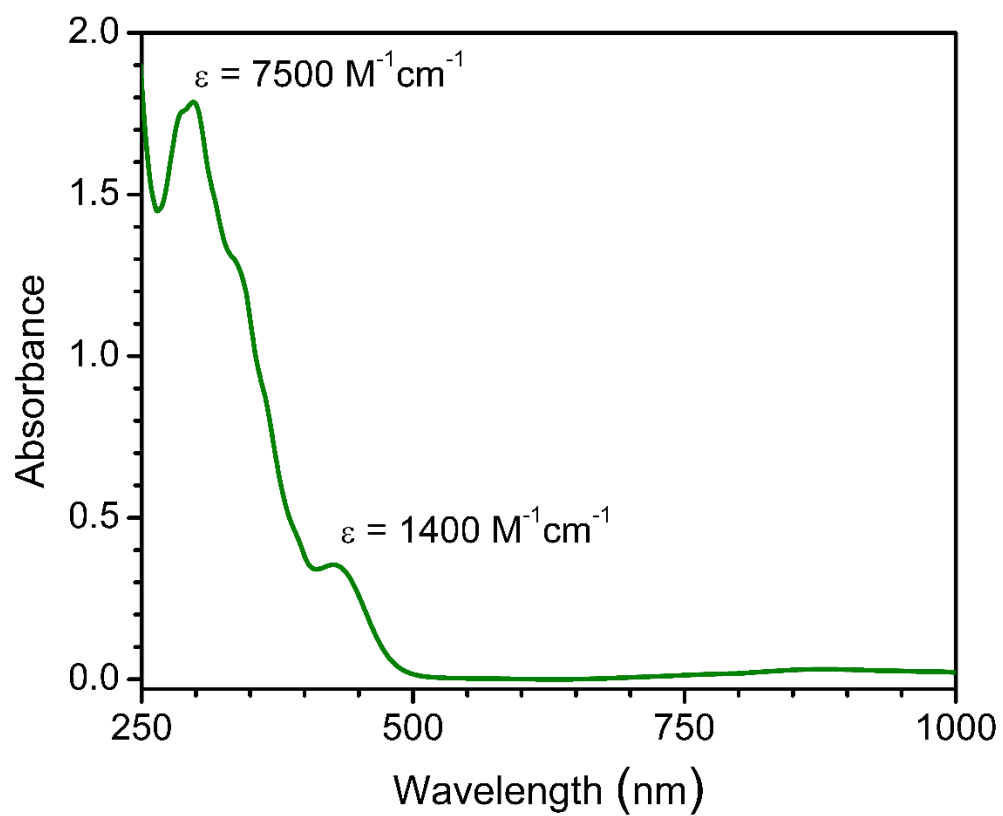


Figure S6.9. UV-Vis-NIR spectrum of **3**.

6.6.3 X-ray Crystallography Data Collection and Refinement Details

Single crystal X-ray diffraction data of **1** and **2** were collected as follows. The sample was coated with Parabar oil and mounted on a MiTeGen polyimide loop in a nitrogen filled glovebox. The X-ray intensity data were measured using a Bruker SMART Apex II diffractometer at 100 K under a N₂ stream of an Oxford Cryostems Cryostream with MoK α radiation (graphite monochromator).³ Data was collected from four 180° ω scans for **1** and seven scans for **2** with 0.5° steps at 90° rotation intervals about ϕ and a CCD detector distance of 5 cm. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm.⁴

Single crystals of **3** were coated in Paratone-N-oil and mounted on a Kaptan loop. X-ray diffraction data were collected at UC, Berkeley using a Rigaku XtaLAB p200 equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200K hybrid pixel array detector at 100 K under a N₂ stream of an Oxford Cryostems Cryostream with MoK α radiation (graphite monochromator). The frames were integrated with CrysAlis^{Pro} software, including a multi-scan absorption correction that was applied using the SCALE3 ABSPACK scaling algorithm within CrysAlis^{Pro}.⁵ Initial structure solutions were determined using direct methods (SHELXT) and refinements were carried out using SHELXL-2014.⁶⁻⁷

[Tb(Cp^{iPr5})₂][B(C₆F₅)₄] (1). The compound crystallized in the space group *P*2₁/*n* with one molecule in the asymmetric unit. As in the structure of [Dy(Cp^{iPr5})₂][B(C₆F₅)₄], anisotropic refinement of the Tb atom resulted in large thermal displacement parameters, suggesting positional disorder. Reasonable thermal displacement parameters were achieved by modeling the Tb atom over four positions. The sum of the four Tb positions was constrained to equal an occupancy of one using the SUMP command, however competitive refinement did not converge satisfactorily to an integer value. Instead, occupancies were fixed to values close to those obtained by competitive refinement (rounded to two significant figures), resulting in a ratio of 0.36:0.10:0.21:0.33. This disorder may indicate that the Tb atom can move freely between the two Cp^{iPr5} rings. The ten isopropyl groups of the Cp^{iPr5} rings also showed positional disorder and were each modeled over two positions. The refinement was stabilized through application of 1,2 (CH–CH₃) and 1,3 (CH₃...CH₃) distance restraints, as well as enhanced rigid bond restraints. In addition, C_{Cp}–C_{Cp}–C(H) angles were restrained to be the same. Two of the isopropyl methyl groups could not be stabilized in the refinement unless identical anisotropic displacement parameters were used for them, which were determined by the other methyl carbon in each isopropyl group. All non-H atoms were refined anisotropically.

[Tb(Cp^{iPr5})₂] (2). The compound crystallized in the space group *P*2₁/*n* with half a molecule in the asymmetric unit. All non-H atoms were refined anisotropically.

[Dy(Cp^{iPr5})₂] (3). The compound crystallized in the space group *P*2₁/*n* with half a molecule in the asymmetric unit. All non-H atoms were refined anisotropically.

Table S6.1. Structure details for 1-3.

Wavelength (Å)	[Tb(Cp ^{iPr5}) ₂][B(C ₆ F ₅) ₄] (1)	Tb(Cp ^{iPr5}) ₂ (2)	Dy(Cp ^{iPr5}) ₂ (3)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å), <i>α</i> (°)	15.2155(6), 90	10.9617(3), 90	11.0200(5), 90
<i>b</i> (Å), <i>β</i> (°)	23.1973(9), 90.9430(10)	13.0994(4), 91.7570(10)	13.0196(6),
<i>c</i> (Å), <i>γ</i> (°)	16.8829(7), 90	12.8416(4), 90	91.917(5)
<i>V</i> (Å ³)	5955.6(4)	1843.1(1)	1842.2(2)
<i>Z</i>	4	2	2
<i>ρ</i> _{calc} (g/cm ³)	1.544	1.279	1.286
Crystal size (mm ³)	0.504 x 0.364 x 0.316	0.423 x 0.287 x 0.184	0.38 x 0.34 x 0.25
<i>θ</i> range for data collection (°)	1.492 to 25.688	2.220 x 30.000	2.862 x 25.347
Index ranges	−18 ≤ <i>h</i> ≤ 18 −28 ≤ <i>k</i> ≤ 28 −20 ≤ <i>l</i> ≤ 20	−15 ≤ <i>h</i> ≤ 15 −18 ≤ <i>k</i> ≤ 18 −18 ≤ <i>l</i> ≤ 18	−13 ≤ <i>h</i> ≤ 13 −15 ≤ <i>k</i> ≤ 15 −15 ≤ <i>l</i> ≤ 15
Reflections collected	69655	45234	36352
Independent reflections (<i>R</i> _{int})	11317 (0.0319)	5372 (0.0232)	3365 (0.0774)
Completeness (%)	100.0	100.0	100.0
Data / restraints / parameters	11317 / 1555 / 1107	5372 / 0 / 197	3365 / 0 / 197
Goodness-of-fit on <i>F</i> ²	1.019	1.077	1.077
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0562, 0.1500	0.0299, 0.0740	0.0522, 0.1164
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0716, 0.1625	0.0349, 0.796	0.0610, 0.1216

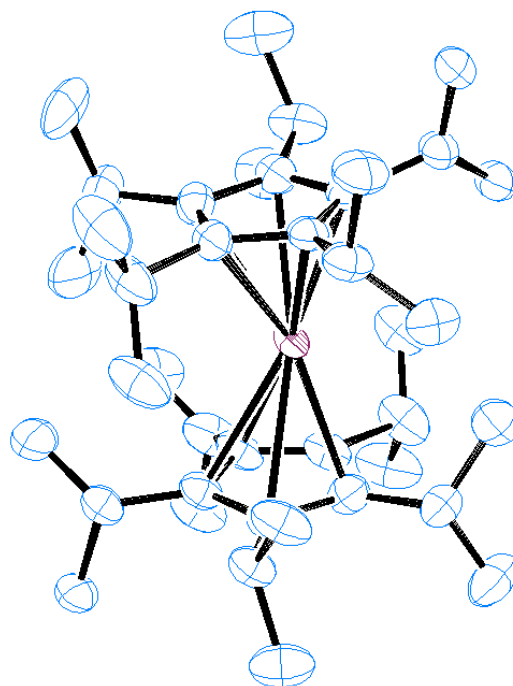


Figure S6.10. Solid-state structure of the $[\text{Tb}(\text{Cp}^{i\text{Pr}5})_2]^+$ cation in **1** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and the disordered component are omitted for clarity.

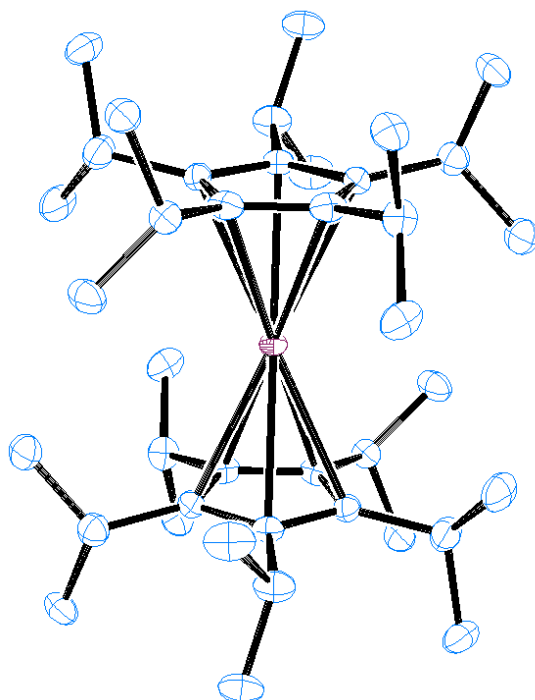


Figure S6.11. Solid-state structure of the $\text{Tb}(\text{Cp}^{i\text{Pr}5})_2$ metallocene **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

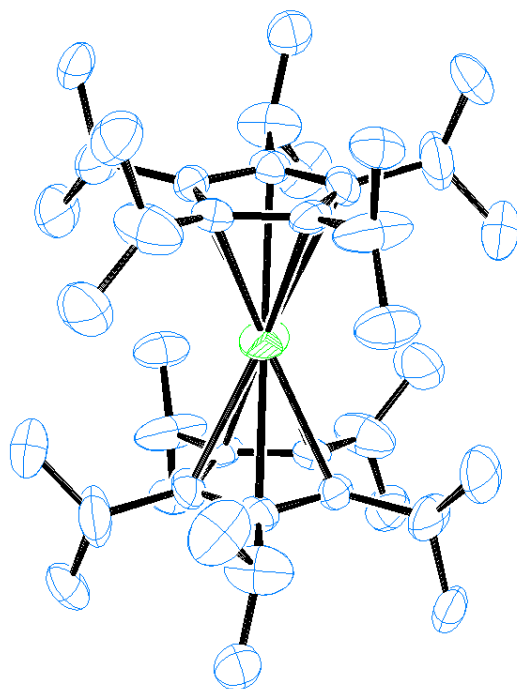


Figure S6.12. Solid-state structure of the $\text{Dy}(\text{Cp}^{i\text{Pr}5})_2$ metallocene **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S6.2. Selected bond distances (Å) and angles (°) for **1–3**.

	[Tb(Cp ^{iPr5}) ₂][B(C ₆ F ₅) ₄] (1) ^a	[Tb(Cp ^{iPr5}) ₂] (2)	[Dy(Cp ^{iPr5}) ₂] (3)
Ln–C1	2.660(7)	2.703(2)	2.662(5)
Ln–C2	2.625(7)	2.704(2)	2.682(5)
Ln–C3	2.616(8)	2.711(2)	2.680(4)
Ln–C4	2.600(7)	2.703(2)	2.680(4)
Ln–C5	2.662(8)	2.702(2)	2.660(4)
Ln–C21	2.587(8)	–	–
Ln–C22	2.702(7)	–	–
Ln–C23	2.725(7)	–	–
Ln–C24	2.634(9)	–	–
Ln–C25	2.536(9)	–	–
Ln–C(ave) ^b	2.635(8)	2.705(2)	2.673(4)
Ln–Cp(A) ^c	2.360(5)	2.417(1)	2.385(1)
Ln–Cp(B) ^c	2.353(6)	–	–
Ln–Cp(ave) ^{b,c}	2.356(6)	2.417(1)	2.385(1)
Cp(A)–Ln–Cp(B) ^c	159.8(4)	180.0	180.0

^bValues for **1** are averages over the four positions of the metal atom.

^bThe standard deviation of the average value was estimated from $\sigma = \sqrt{\sum \sigma_i^2 / N}$, where σ_i is the standard deviation of each bond distance i and N is the number of distances averaged.

^cLn–Cp distances and angles were measured from the Ln atom to the centroid of the Cp ring(s).

6.6.4 Magnetic Measurements

General. Magnetic samples were prepared by adding crystalline powder (18.2 mg of **1**, 18.2 mg of **2**, 22.0 mg of **3**) to a 5 mm i.d./7 mm o.d. quartz tube with a raised quartz platform. A layer of eicosane was added to the samples (20.4 mg for **1**, 29.9 mg for **2**, 30.5 mg for **3**) to provide good thermal contact between the sample and the bath and to prevent crystallite torqueing. The tubes were fitted with Teflon sealable adapters, evacuated using a glovebox vacuum pump, and then flame sealed with an O₂/H₂ flame under vacuum. After flame-sealing, the eicosane was melted in a 40 °C water bath.

Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. All data were corrected for diamagnetic contributions from the core diamagnetism and for the diamagnetism of the eicosane used to suspend the sample, estimated using Pascal's constants to give corrections of $\chi_{\text{dia}} = -0.000741$ emu/mol, -0.000464 emu/mol, and -0.000464 emu/mol for **1**, **2**, and **3**, respectively.

Magnetic measurements were also conducted on frozen toluene solutions of **2** and **3** (19 mM and 28 mM, respectively) to ensure that the observed magnetic properties were molecular in origin and not due to long-range interactions in the solid-state. These frozen solutions correspond to an average Tb...Tb separation of 44 Å in 19 mM **2** and an average Dy...Dy separation of 39 Å in 28 mM **3**.

Dc Magnetic Susceptibility Measurements. Dc magnetic susceptibility measurements were performed at temperatures ranging from 2 to 300 K under applied fields of 1, 5, and 10 kOe (0.1, 0.5, and 1 T) for **1-3**.

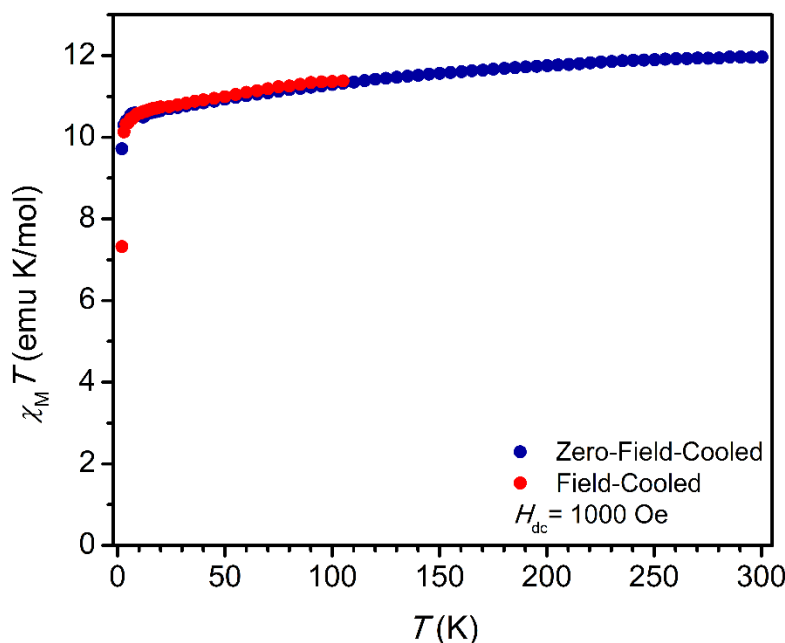


Figure S6.13. Field-cooled (red) and zero-field cooled (blue) measurements of **1** under an applied field of 1 kOe.

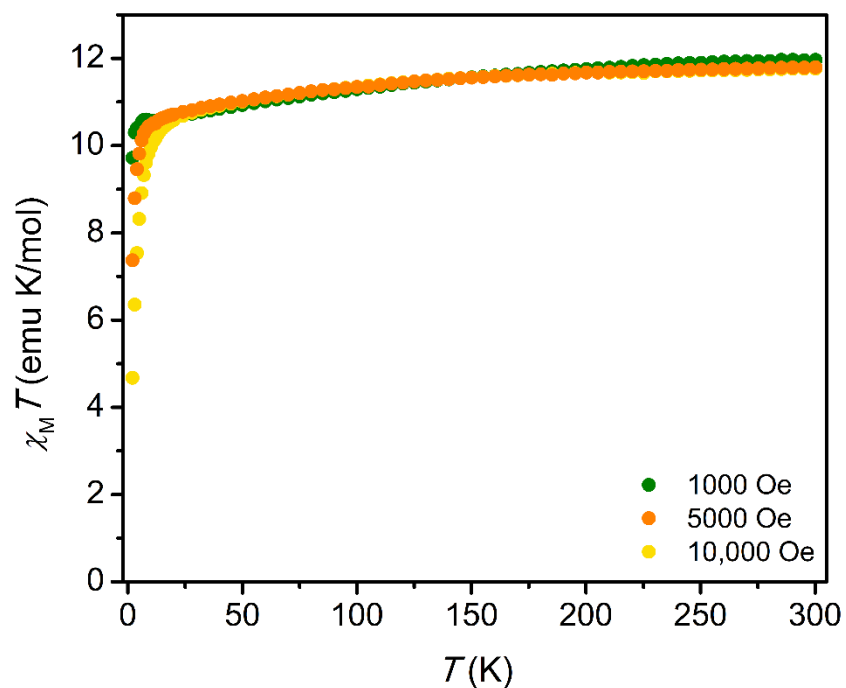


Figure S6.14. Zero-field cooled dc magnetic susceptibility measurements of **1** under applied fields of 1 (green), 5 (orange), and 10 kOe (yellow).

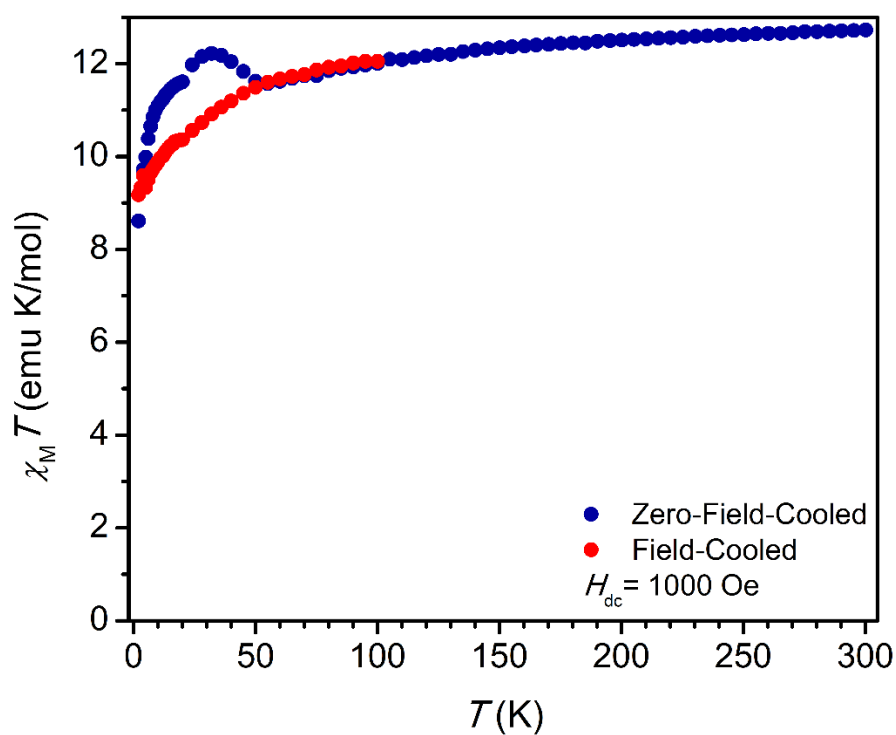


Figure S6.15. Field-cooled (red) and zero-field cooled (blue) measurements of **2** under an applied field of 1 kOe.

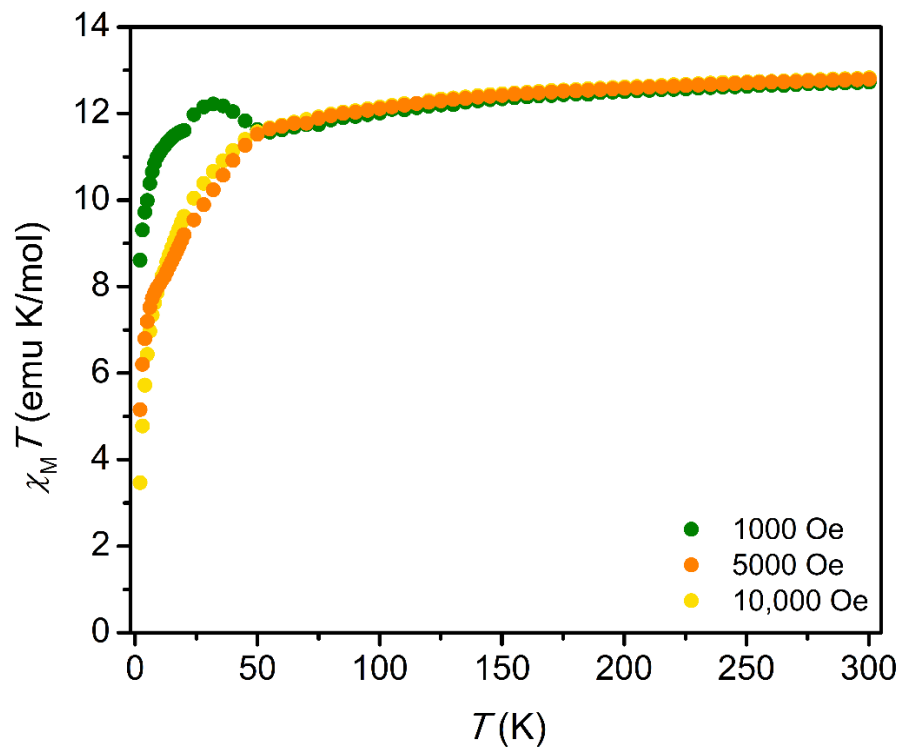


Figure S6.16. Zero-field cooled dc magnetic susceptibility measurements of **2** under applied fields of 1 (green), 5 (orange), and 10 kOe (yellow).

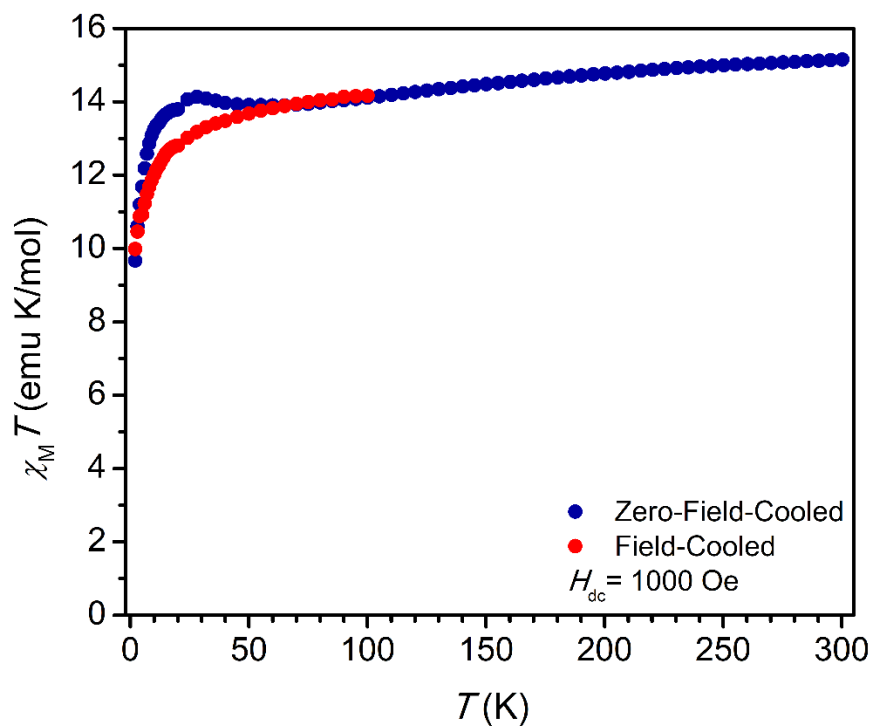


Figure S6.17. Field-cooled (red) and zero-field cooled (blue) measurements of **3** under an applied field of 1 kOe.

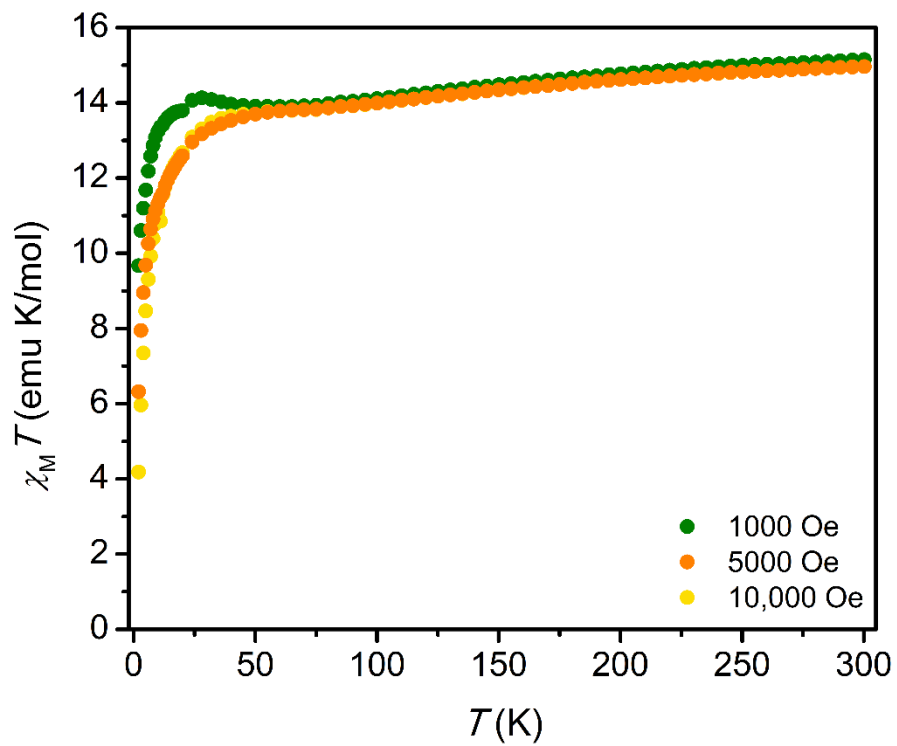


Figure S6.18. Zero-field cooled dc magnetic susceptibility measurements of **3** under applied fields of 1 (green), 5 (orange), and 10 kOe (yellow).

Ac Magnetic Susceptibility Measurements. Ac magnetic susceptibility measurements were performed with a probe field of 4 Oe at frequencies ranging from 0.1 to 1500 Hz under external applied fields of 0 and 500 Oe (0, 0.05 T) for **1-3**. Magnetic relaxation times, τ , were extracted from a simultaneous fit of in-phase (χ_M') and out-of-phase (χ_M'') components of the magnetic susceptibility to a generalized Debye model.

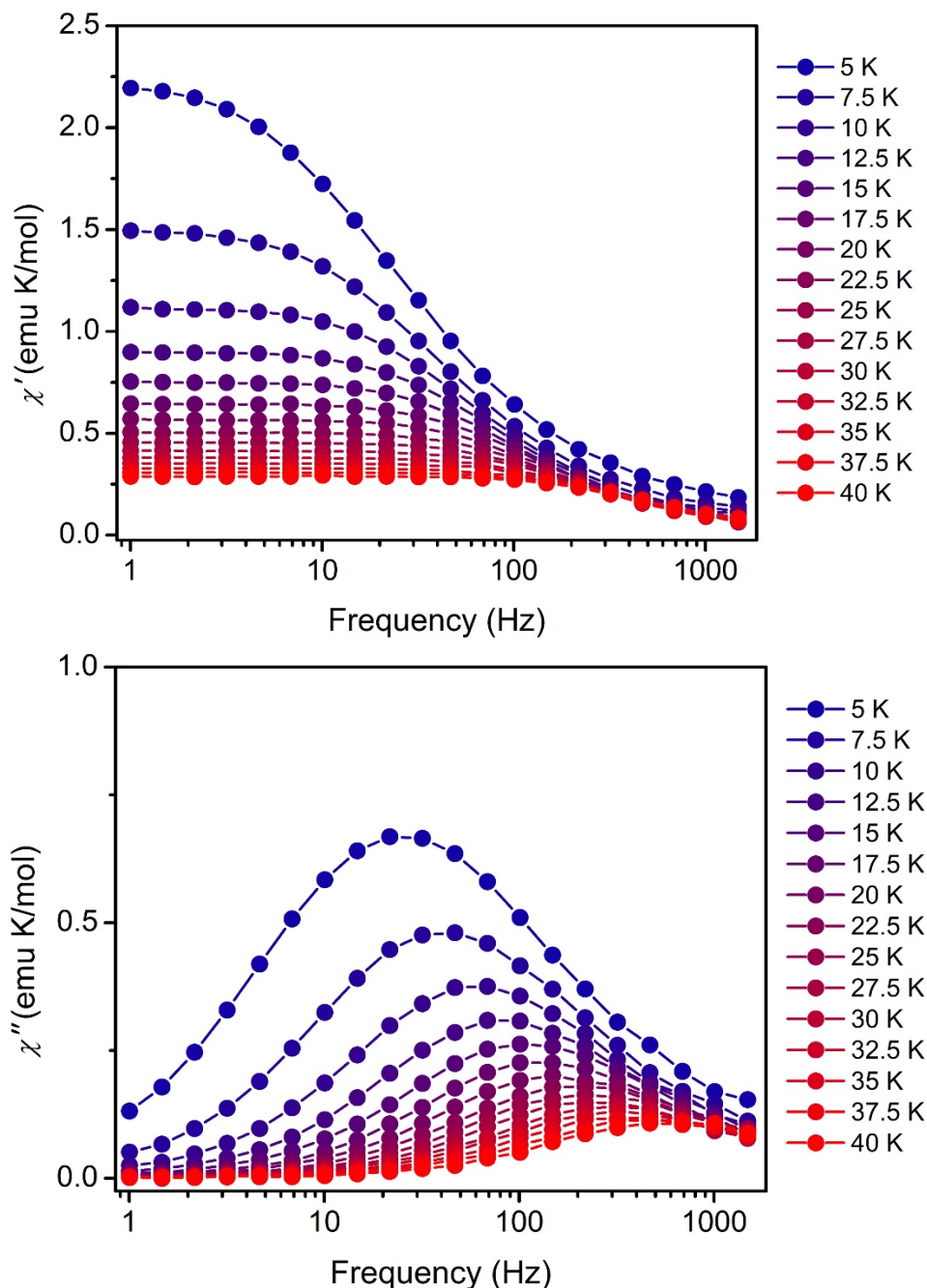


Figure S6.19. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **1** under zero applied dc field at frequencies ranging from 1–1500 Hz and temperatures from 5–40 K (2.5 K steps). The colored lines are guides for the eye.

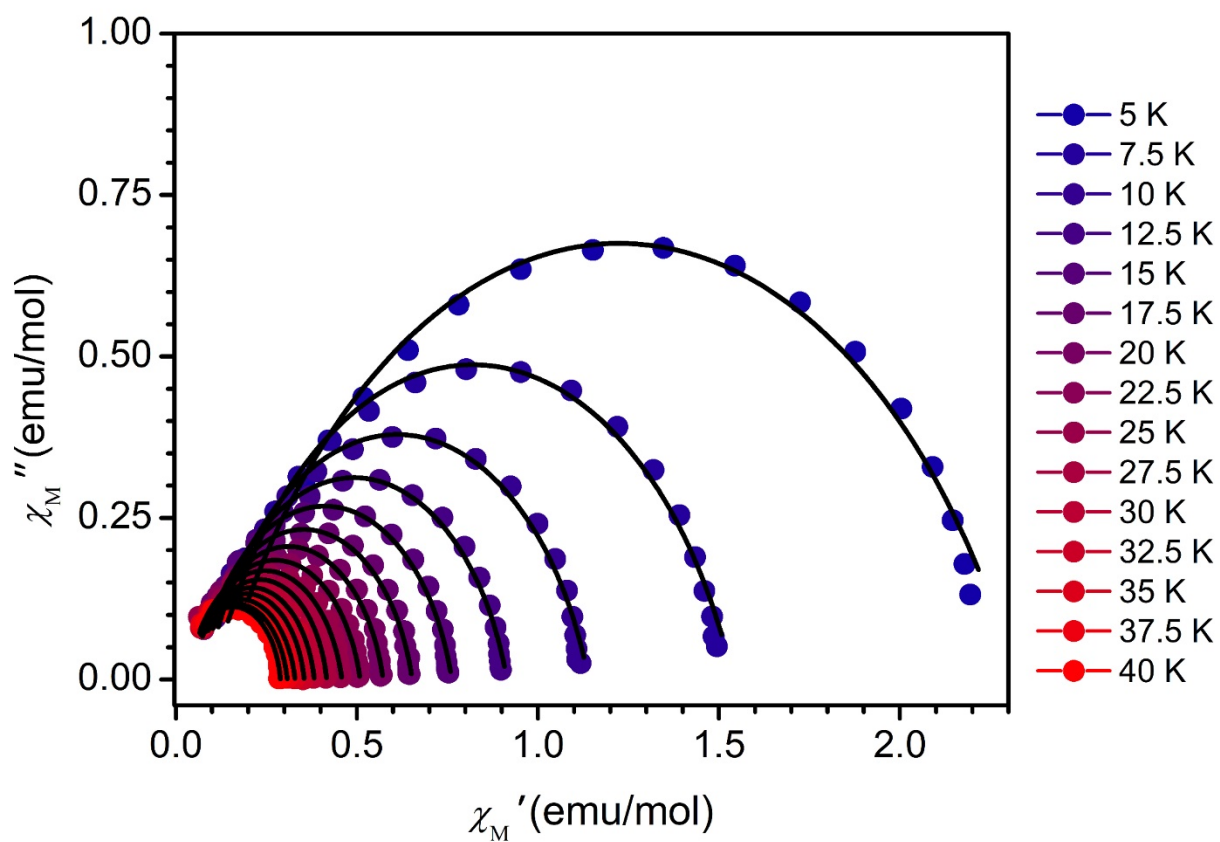


Figure S6.20. Cole-Cole plots for **1** from 5–40 K under zero applied dc field (2.5 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

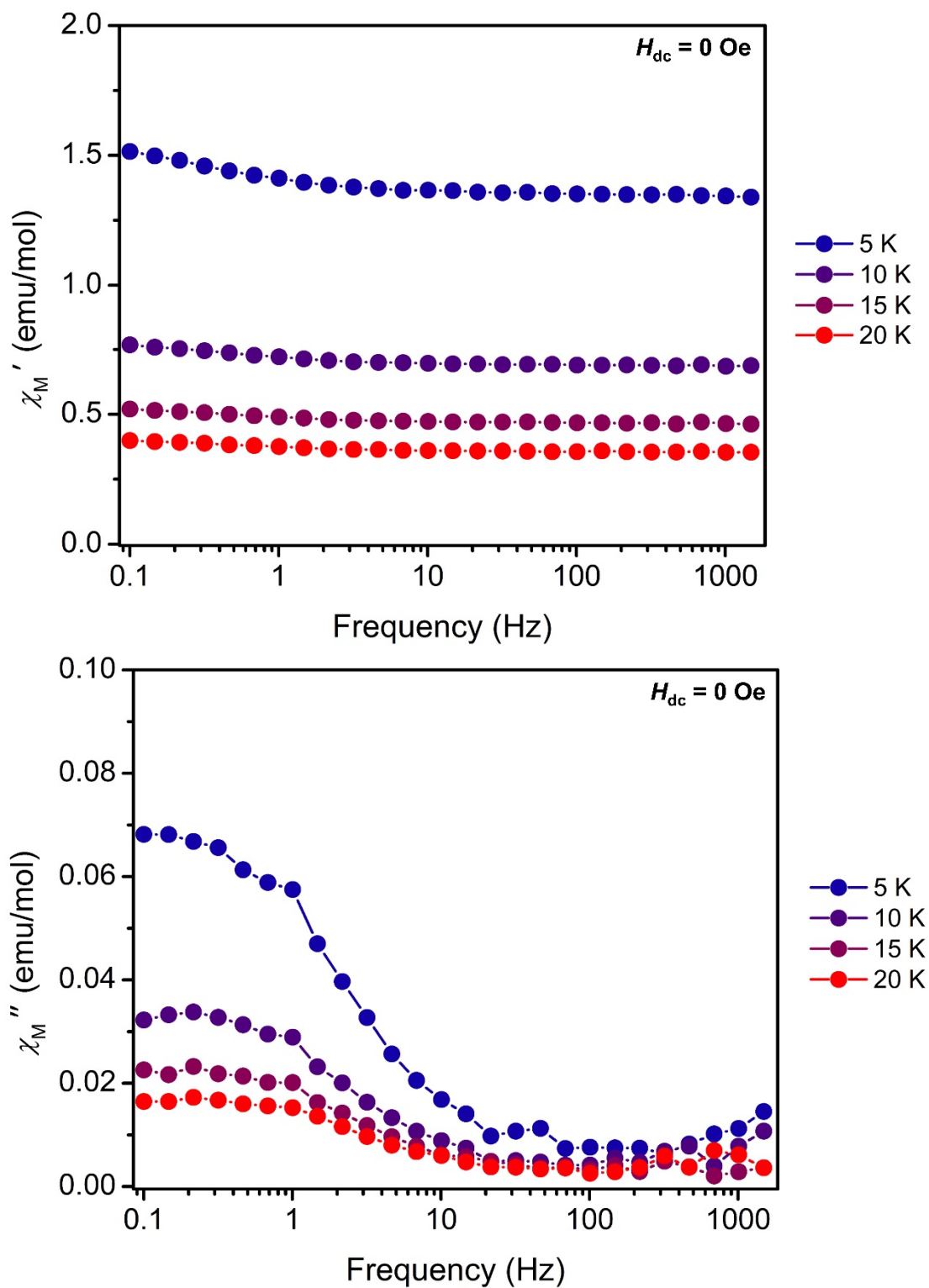


Figure S6.21. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **2** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 5–20 K (5 K steps). The colored lines are guides for the eye.

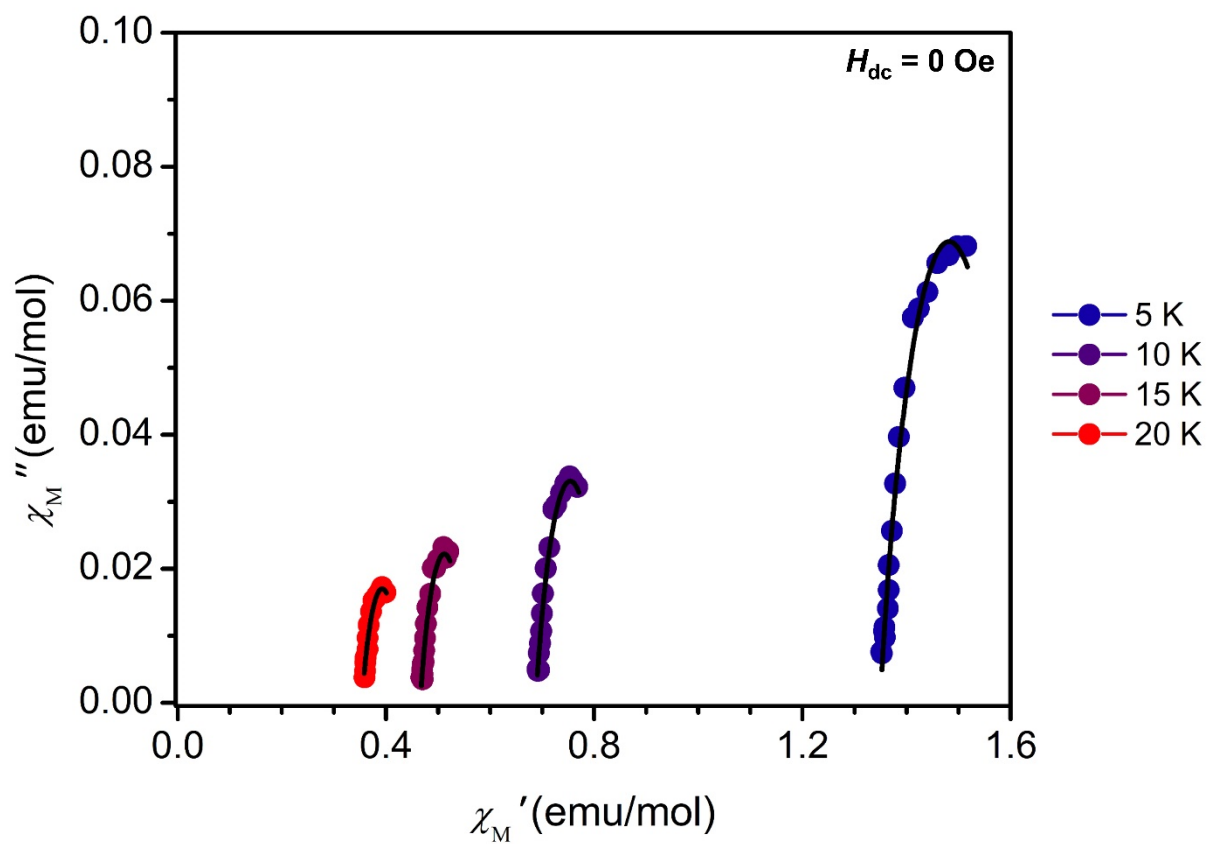


Figure S6.22. Cole-Cole plots for **2** from 5–20 K under zero applied dc field (5 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

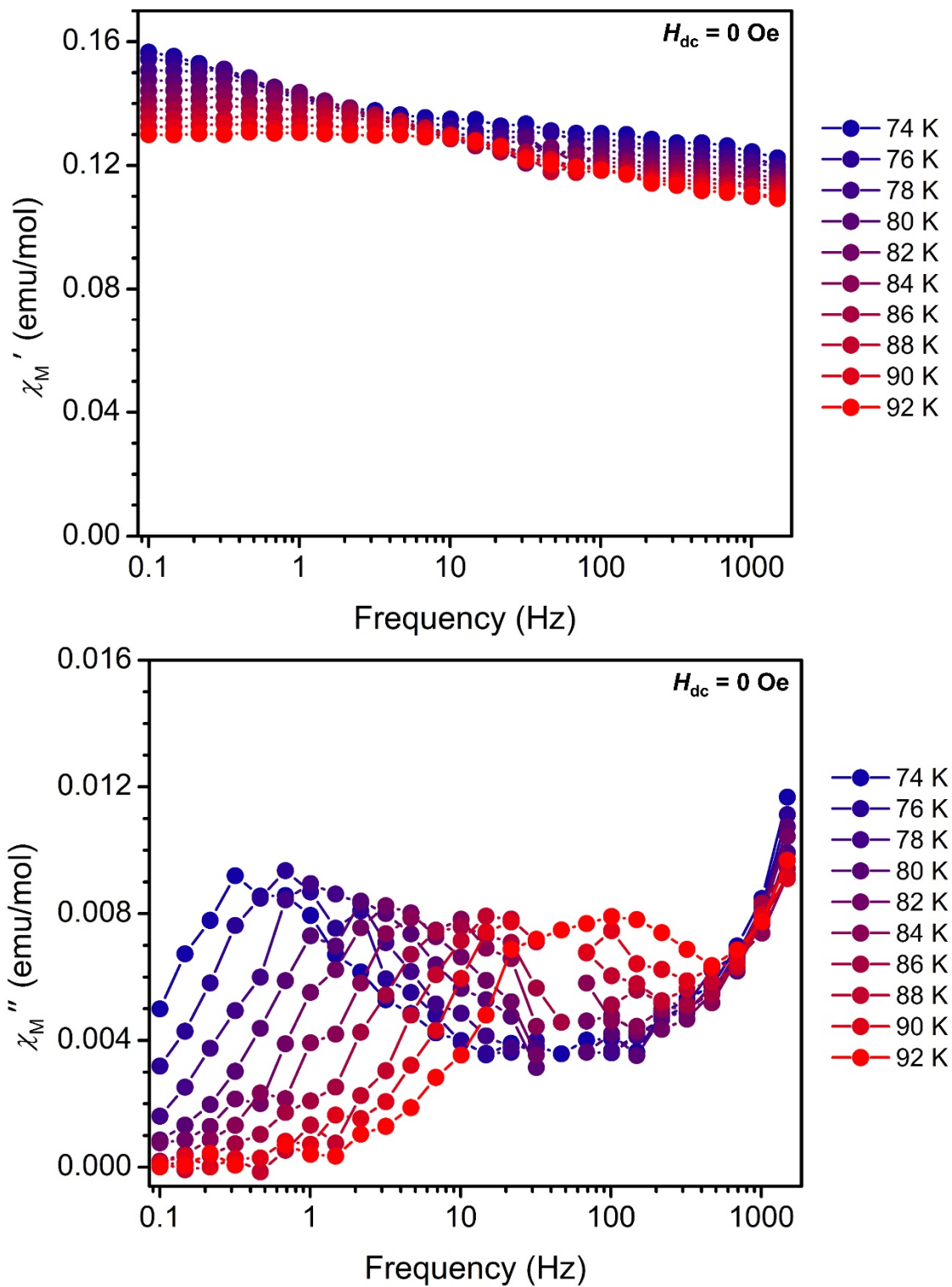


Figure S6.23. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **2** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 74–92 K (2 K steps). The colored lines are guides for the eye.

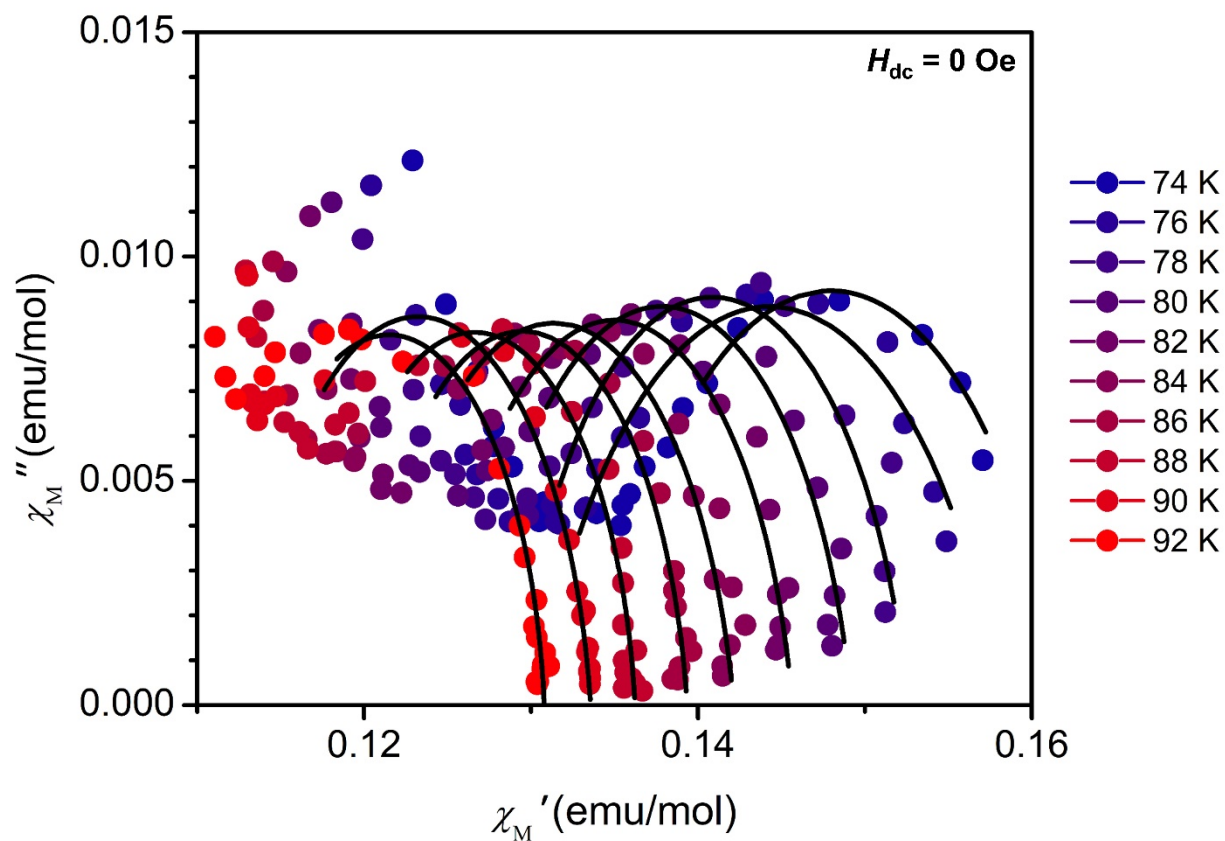


Figure S6.24. Cole-Cole plots for **2** from 74–92 K under zero applied dc field (2 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

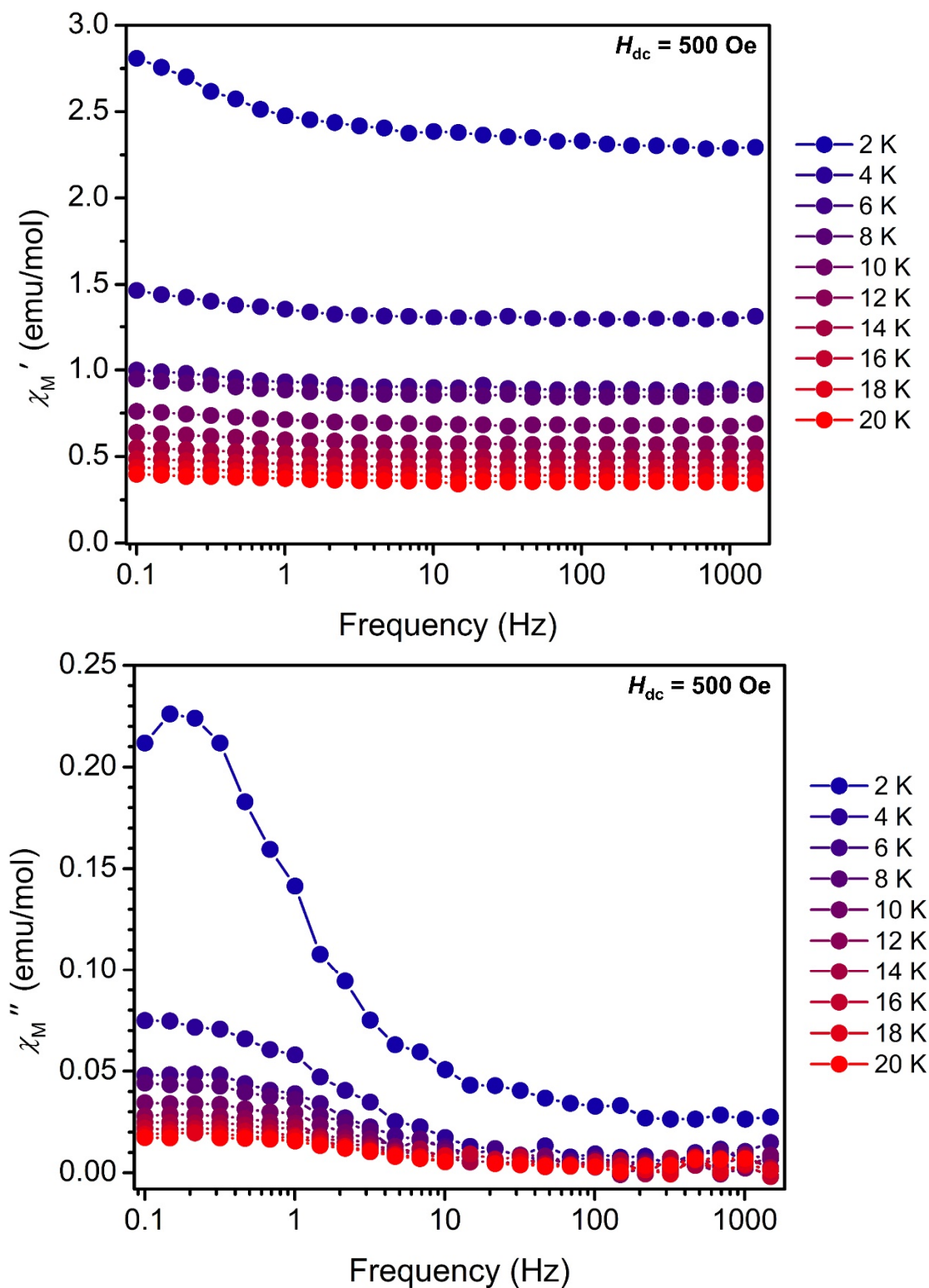


Figure S6.25. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **2** under a 500 Oe applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 2–20 K (2 K steps). The colored lines are guides for the eye.

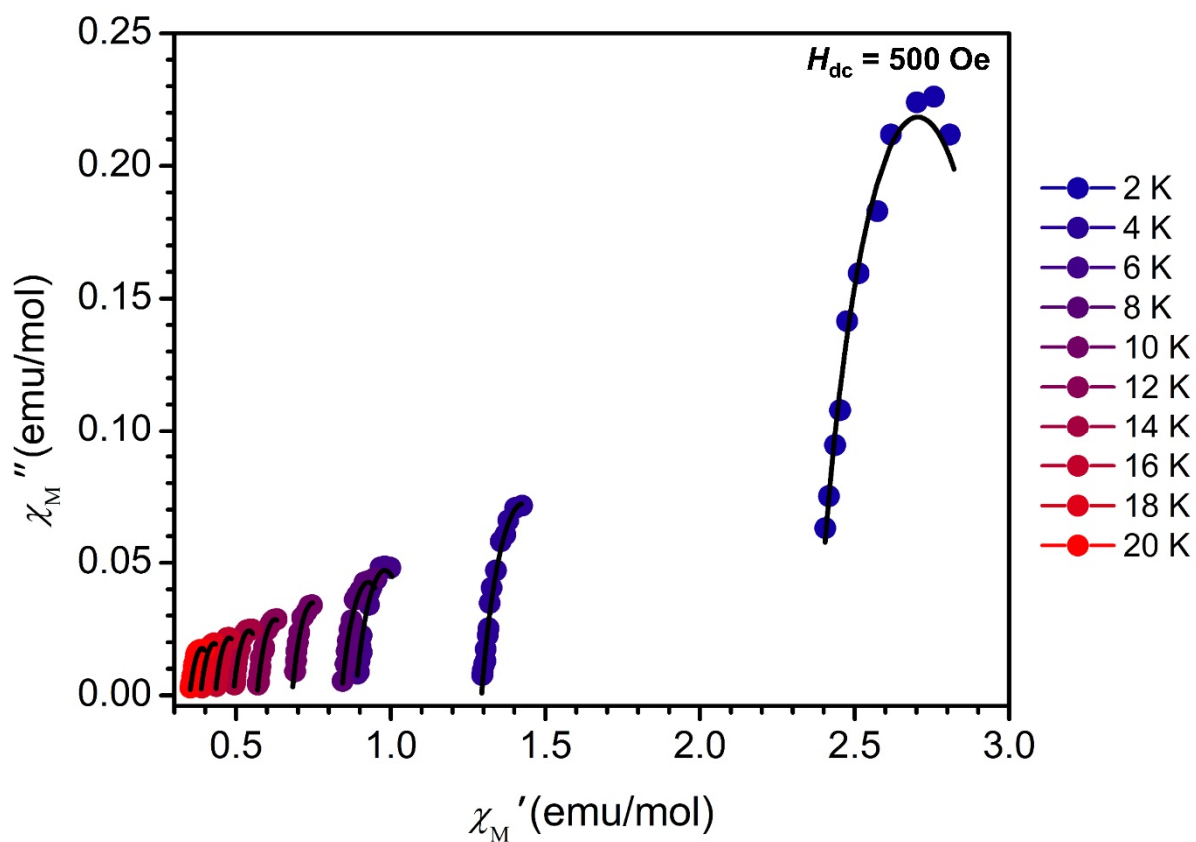


Figure S6.26. Cole-Cole plots for **2** from 2–20 K under a 500 Oe applied dc field (2 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

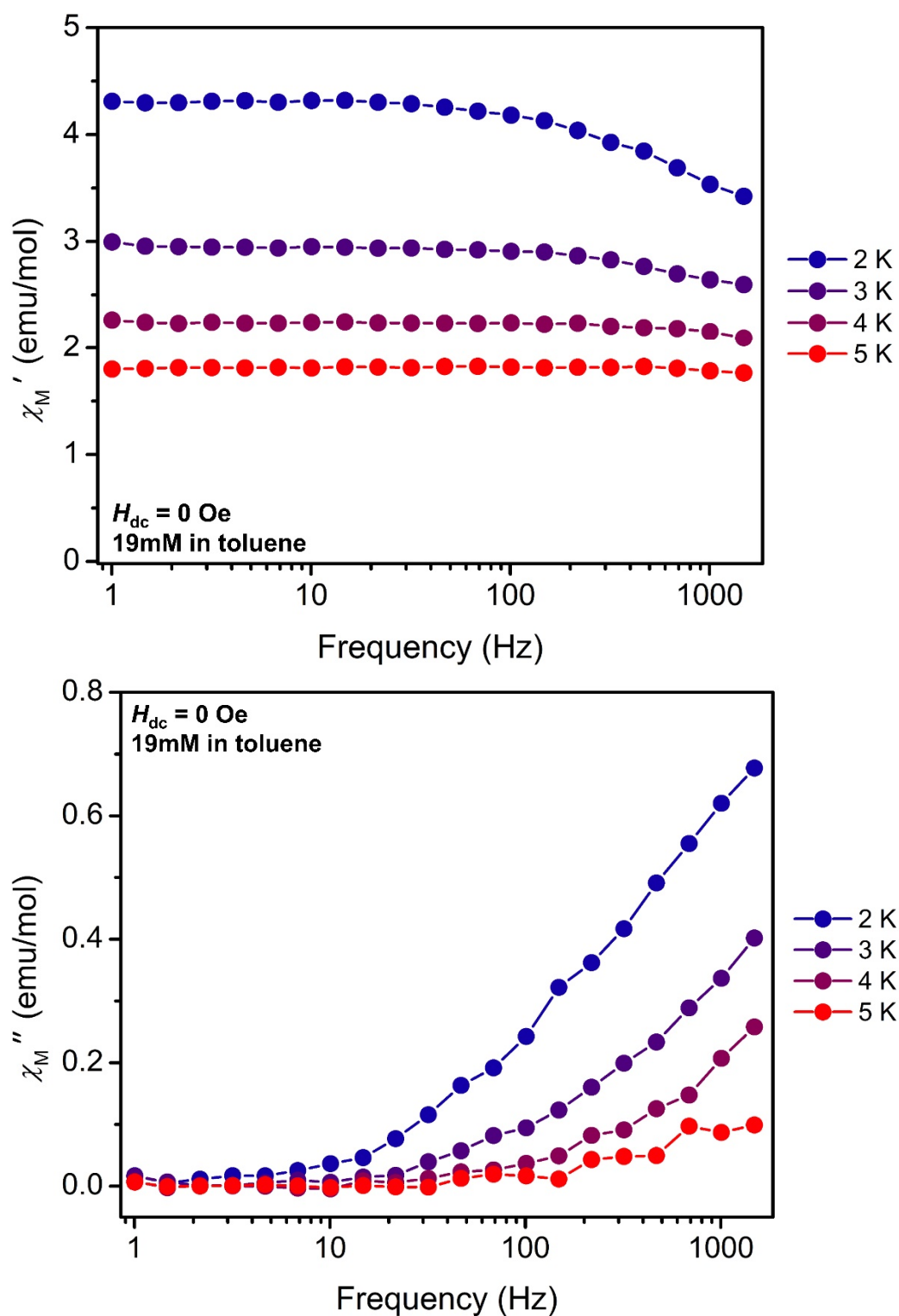


Figure S6.27. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for a 19 mM solution of **2** in toluene under zero applied dc field at frequencies ranging from 1–1500 Hz and temperatures from 2–5 K (1 K steps). The colored lines are guides for the eye.

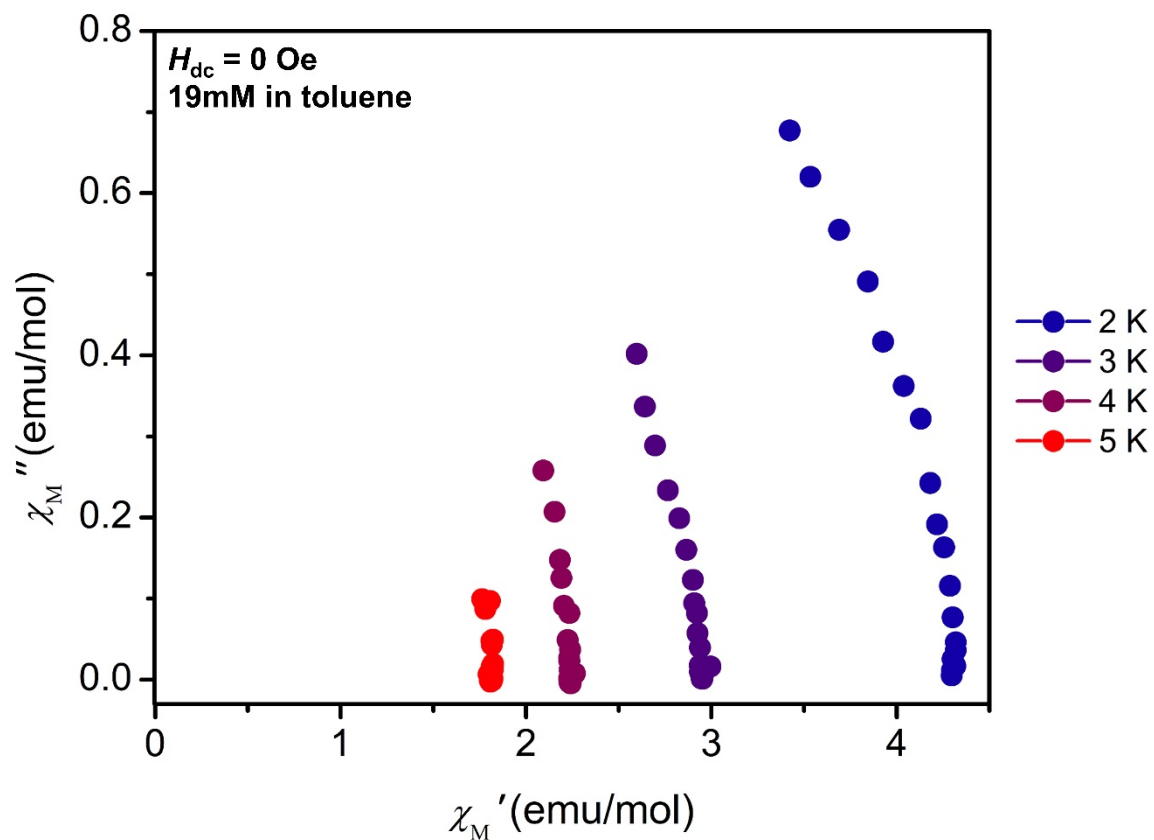


Figure S6.28. Cole-Cole plots for a 19 mM solution of **2** in toluene from 2–5 K under zero applied dc field (1 K steps).

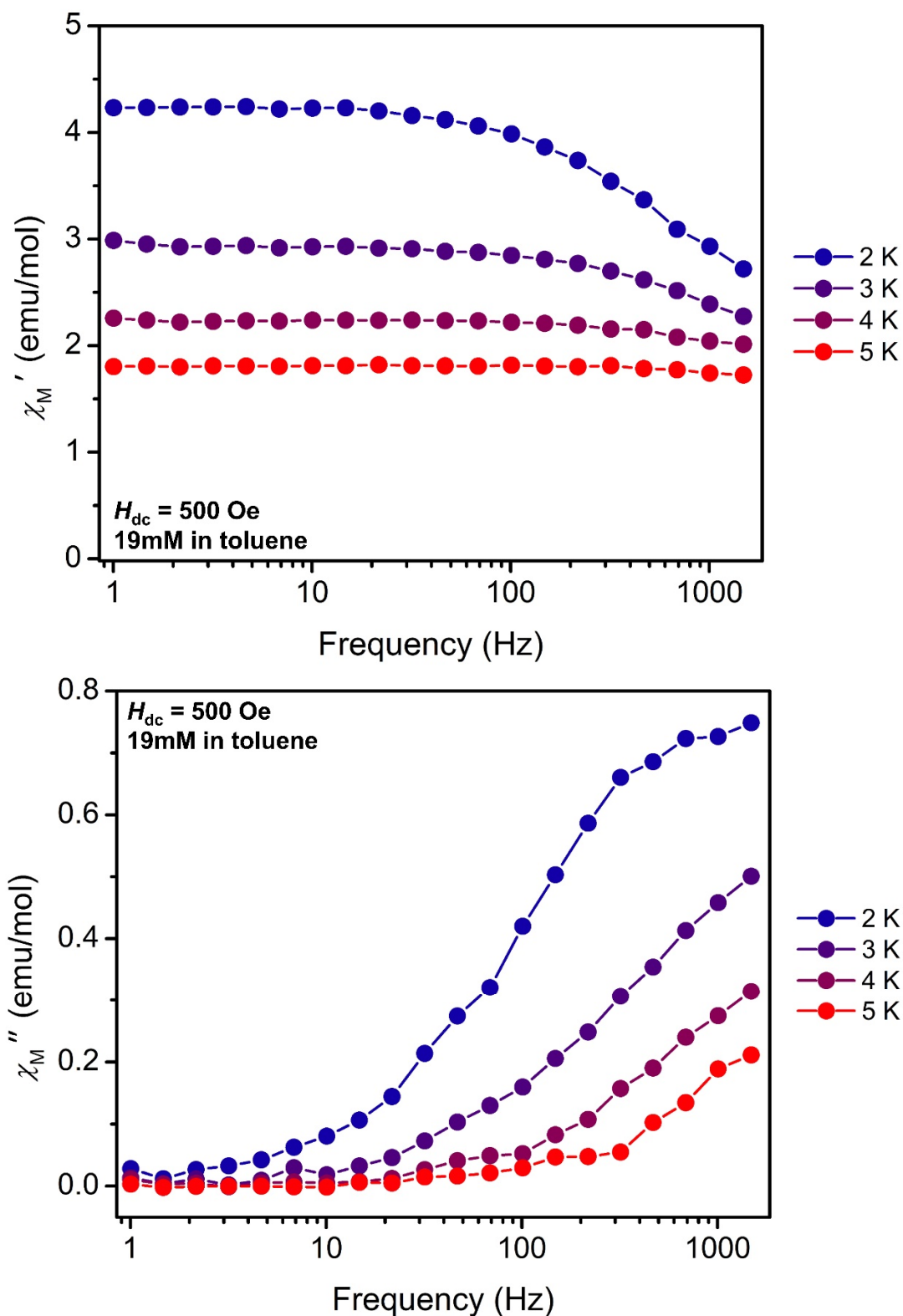


Figure S6.29. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for a 19 mM solution of **2** in toluene under a 500 Oe applied dc field at frequencies ranging from 1–1500 Hz and temperatures from 2–5 K (1 K steps). The colored lines are guides for the eye.

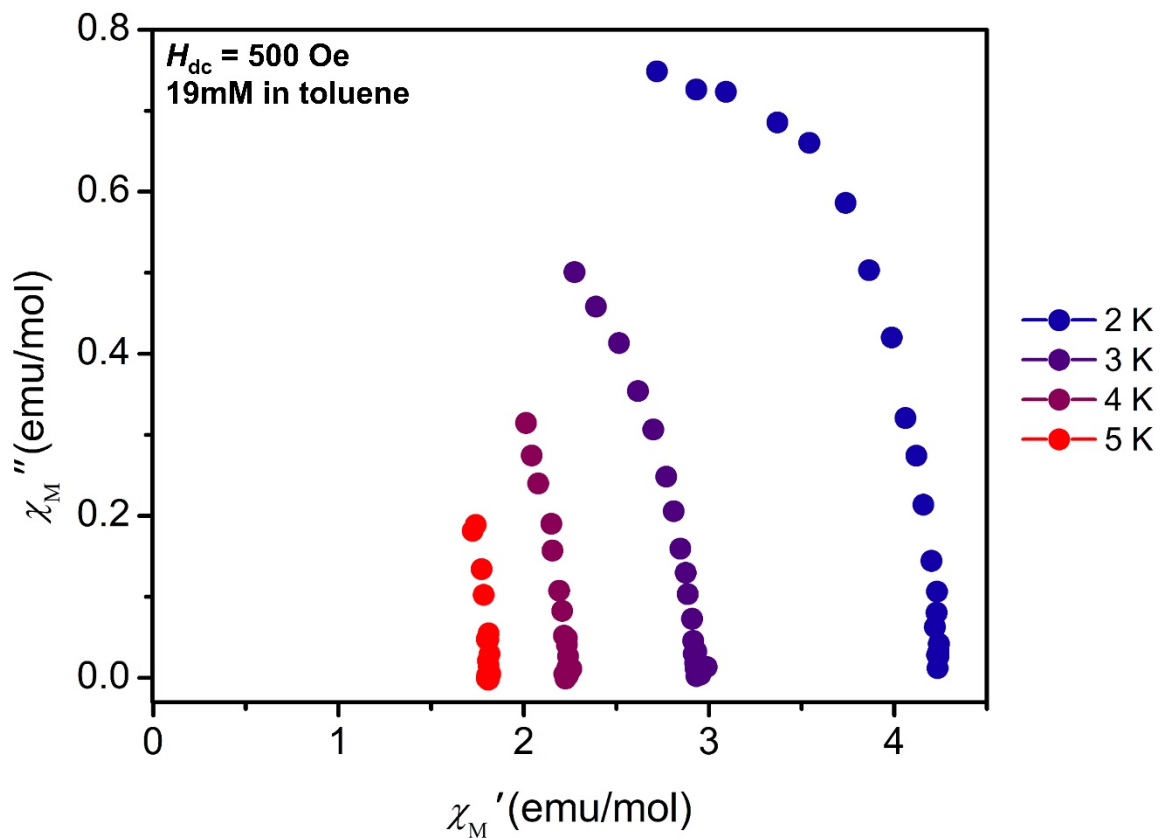


Figure S6.30. Cole-Cole plots for a 19 mM solution of **2** in toluene from 2–5 K under a 500 Oe applied dc field (1 K steps).

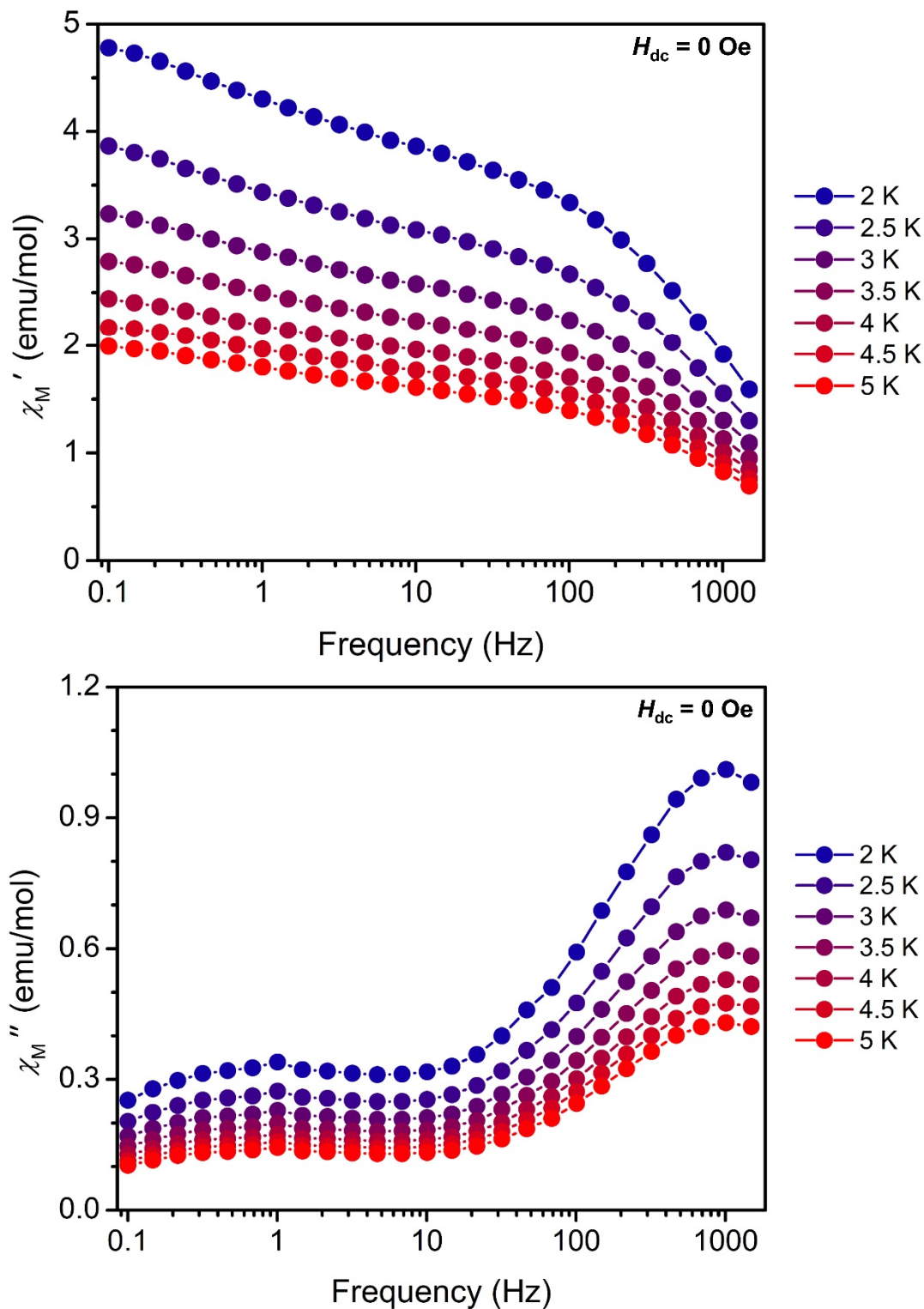


Figure S6.31. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **3** under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 2–5 K (0.5 K steps). The colored lines are guides for the eye.

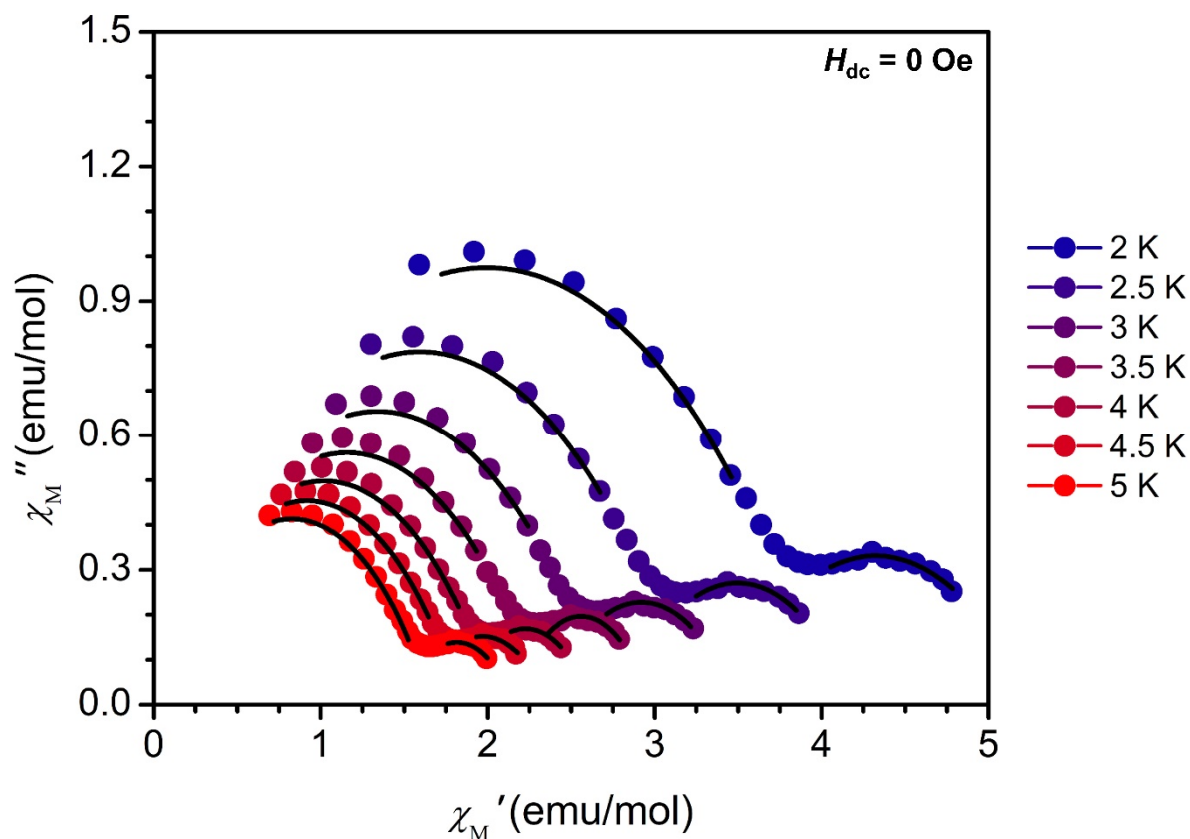


Figure S6.32. Cole-Cole plots for **3** from 2–5 K under zero applied dc field (0.5 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature. Data was fit using two processes.

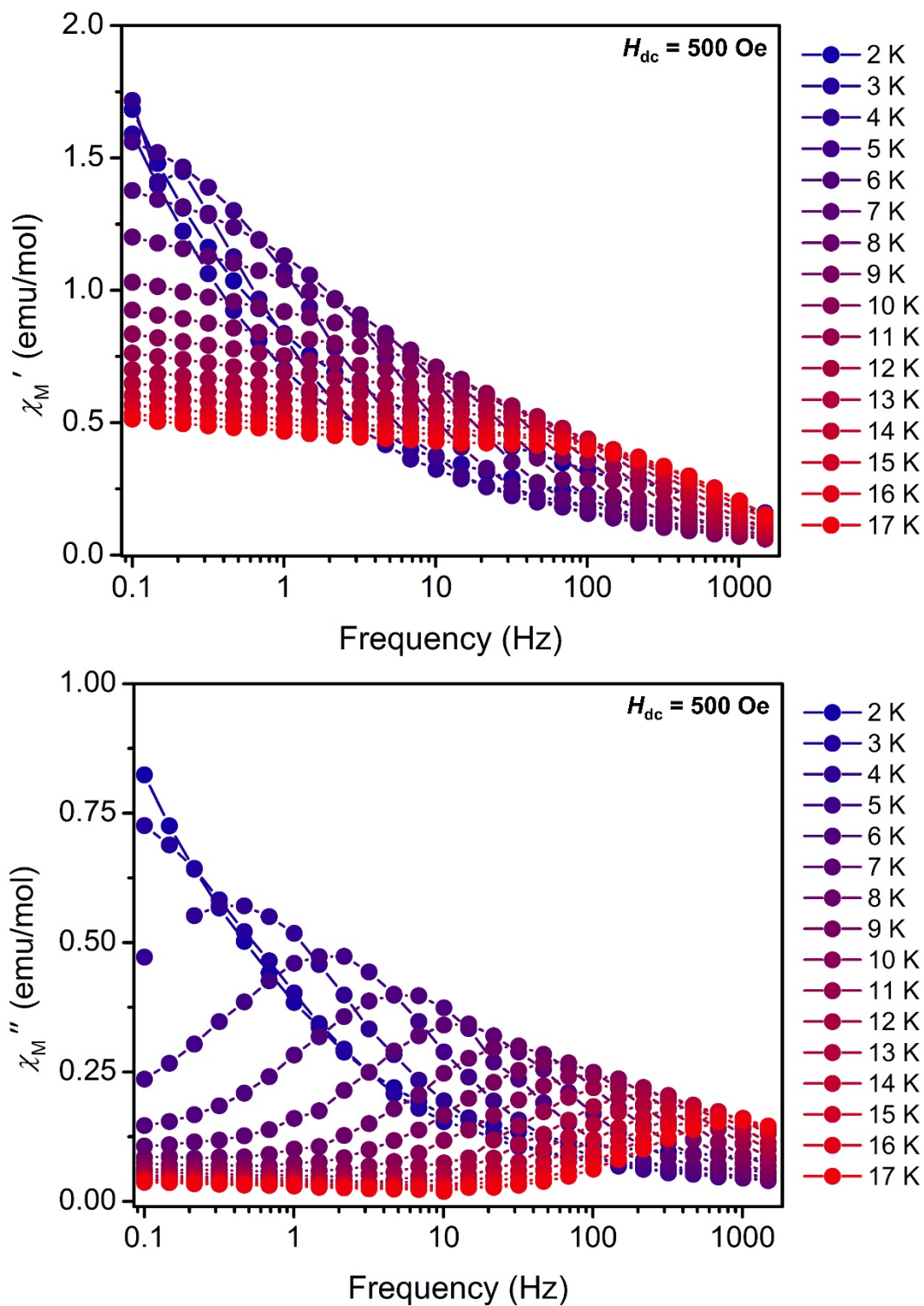


Figure S6.33. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for **3** under a 500 Oe applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 2–17 K (1 K steps). The colored lines are guides for the eye.

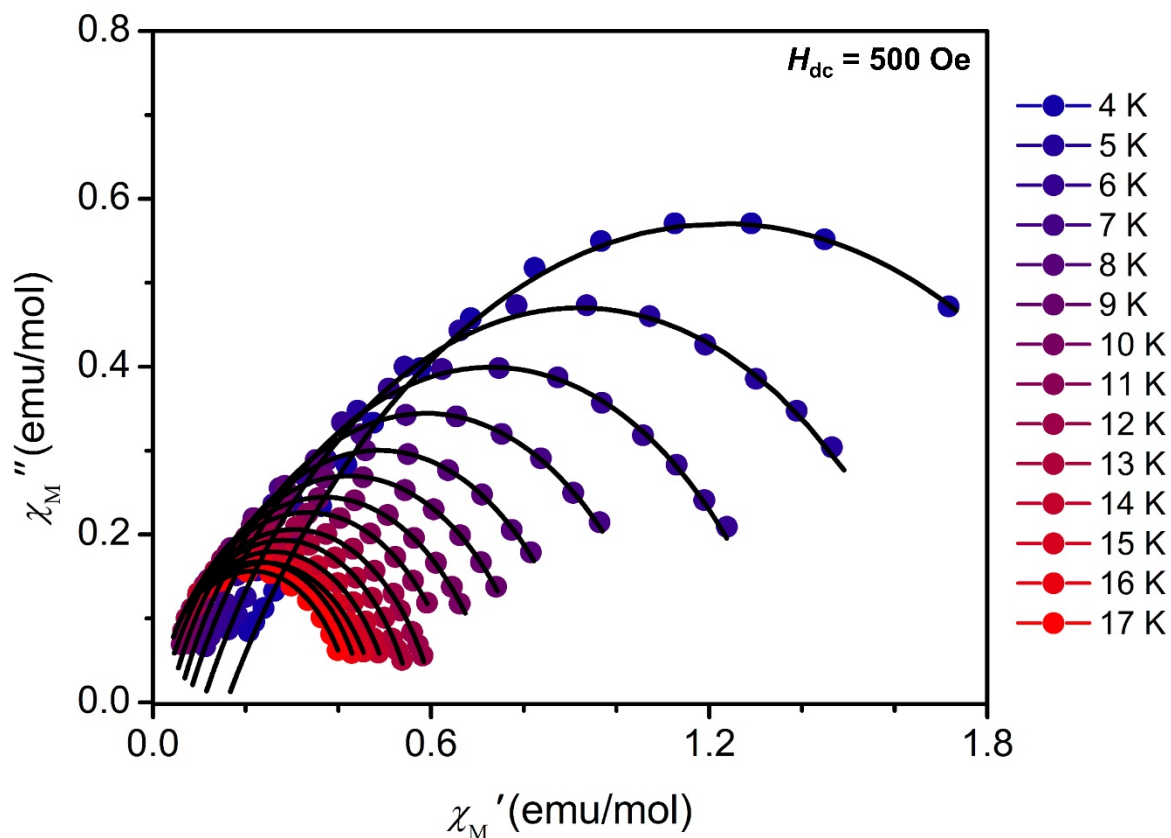


Figure S6.34. Cole-Cole plots for **3** from 4–17 K under a 500 Oe applied dc field (1 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

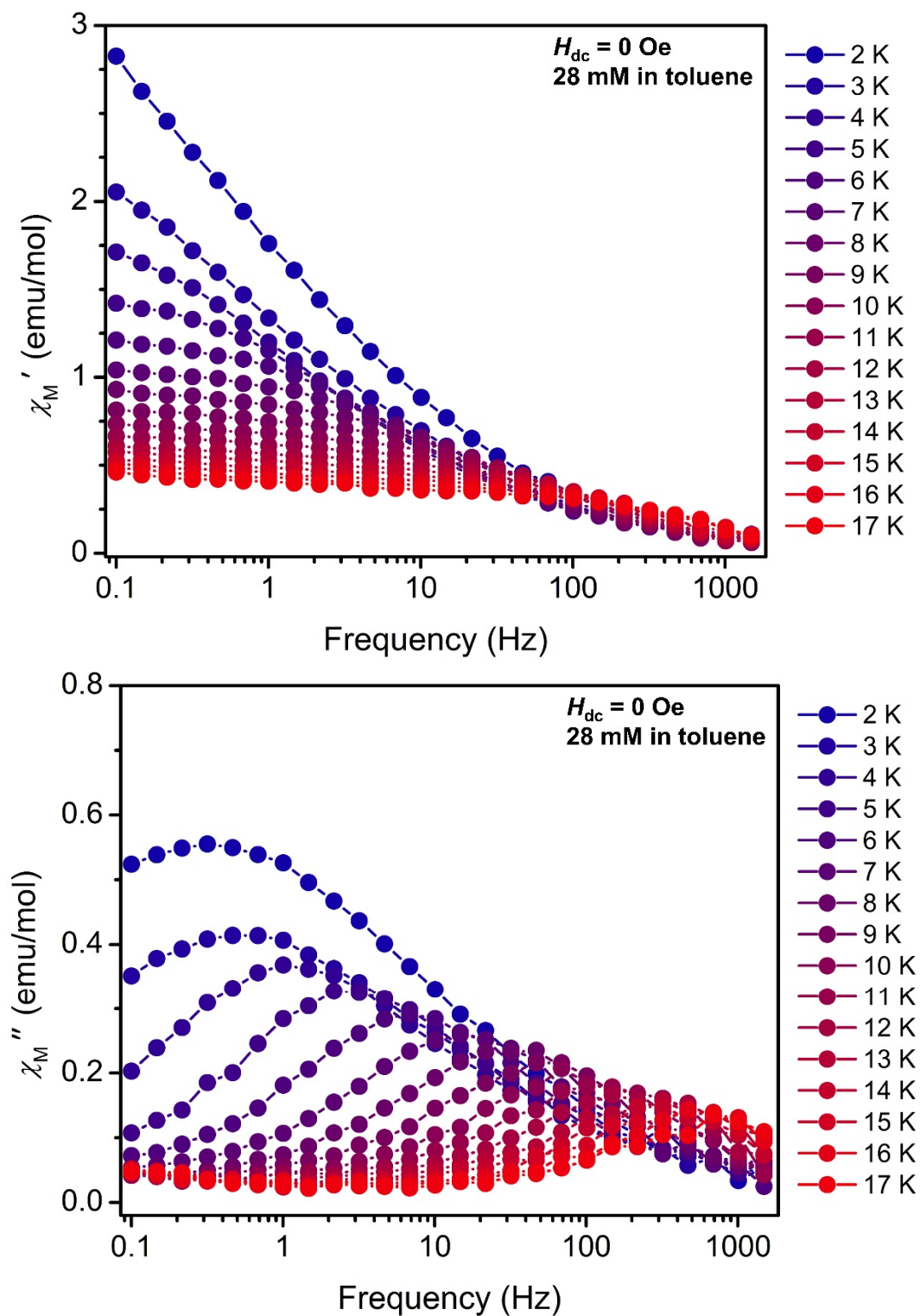


Figure S6.35. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for a 28 mM solution of **3** in toluene under zero applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 2–17 K (1 K steps). The colored lines are guides for the eye.

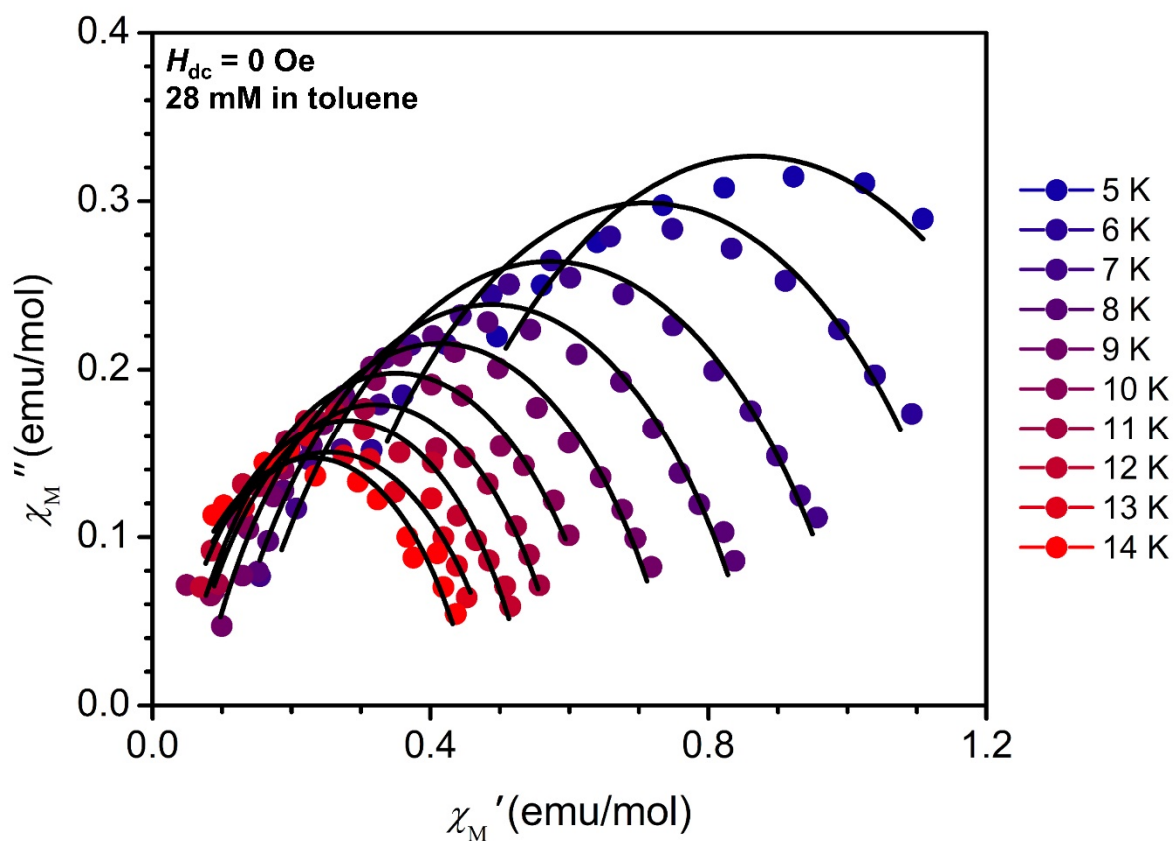


Figure S6.36. Cole-Cole plots for a 28 mM solution of **3** in toluene from 5–14 K under zero applied dc field (1 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

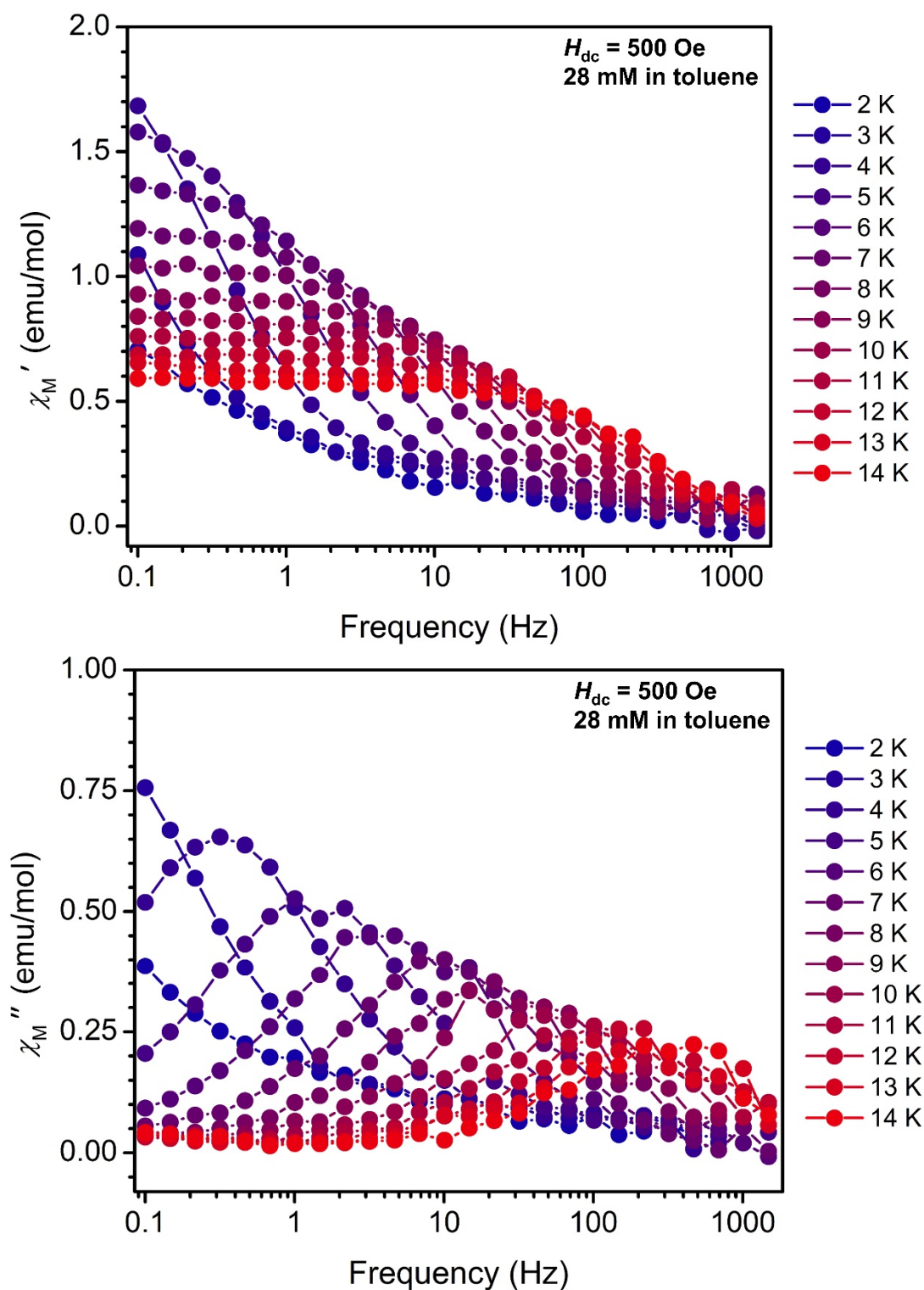


Figure S6.37. In-phase (χ_M' , top) and out-of-phase (χ_M'' , bottom) components of the ac magnetic susceptibility for a 28 mM solution of **3** in toluene under a 500 Oe applied dc field at frequencies ranging from 0.1–1500 Hz and temperatures from 2–14 K (1 K steps). The colored lines are guides for the eye.

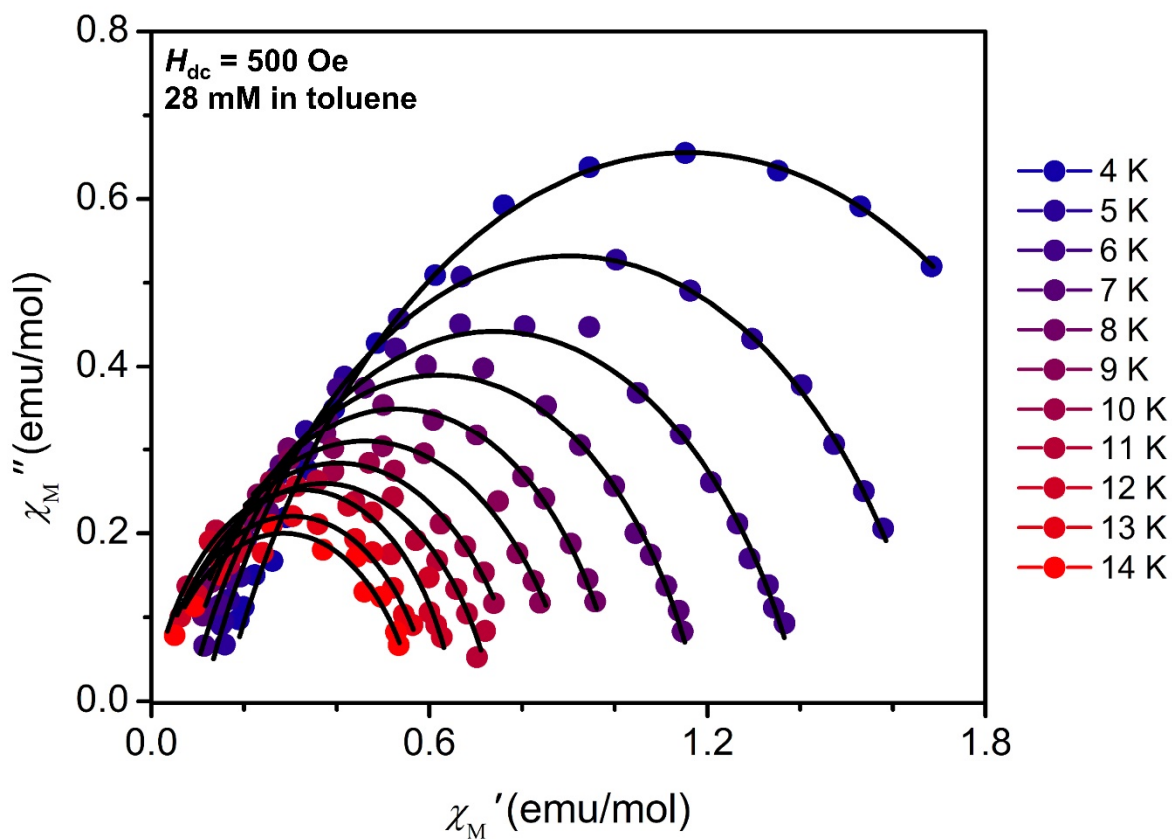


Figure S6.38. Cole-Cole plots for a 28 mM solution of **3** in toluene from 4–14 K under a 500 Oe applied dc field (1 K steps). The black lines represent fits to the data using a generalized Debye model, which were used to extract τ values at each temperature.

Dc Magnetic Relaxation Measurements. Dc magnetic relaxation measurements were collected by magnetizing a sample under an applied field of 5 T, allowing 5 minutes for equilibration, and then subsequently returning the field to 0 Oe (no overshoot, hi-res disabled) or 500 Oe and measuring the magnetization at periodic time intervals. Dc magnetic relaxation data were fit to a stretched exponential function according to the equation:

$$M(t) = M_1 + (M_0 - M_1)^{(t/\tau)^n}$$

where $M(t)$ is the magnetization at time t , M_0 is the initial magnetization measured after the field has been removed, M_1 is the final value of the magnetization at $t = \infty$, τ is the magnetic relaxation time, and n is a free variable. Though M_1 should equal zero at zero field, we found non-zero values for all dc magnetic relaxation measurements T zero field, likely due to a small remnant field in the superconducting magnet. We therefore set M_1 equal to the value of the magnetization measured at the last time point of each experiment. At high temperatures, it was possible to measure the full decay of the magnetization within 1000 s. At lower temperatures where magnetic relaxation slowed, experiments were conducted for 5000 s. Even this length of time was not sufficient to observe the full decay of the magnetization for measurements of **2-3** at the lowest temperatures measured (2 to 20 K), however, and therefore setting M_1 equal to the last value of the magnetization measured for these experiments represented an overestimate. Better fits to the data for these experiments were obtained by treating M_1 as a free variable (M_1 values marked with an * in the tables below).

In order to test the validity of the strategy, fits to higher temperature experiments with M_1 as a free variable were obtained and compared to previous fits. This resulted in values of τ within 5% of those obtained for fits with M_1 equal to the last value of the magnetization measured in the experiment. Furthermore, the values obtained for τ with M_1 as a free variable were consistently lower than those obtained with M_1 equal to the last value of the magnetization, demonstrating that this alternative fitting strategy did not overestimate the value of τ at low temperatures.

For dc relaxation measurements at 500 Oe, field-cooled susceptibility measurements were collected at 500 Oe and these values were used for M_1 .

Table S6.3. Parameters used to fit dc magnetic relaxation data for **2** at zero applied field and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	0.42546	0.04007*	0.644	569.527
5	0.42881	0.04074*	0.661	611.137
10	0.43225	0.03625*	0.635	630.158
15	0.33748	0.02633*	0.696	781.132
20	0.32891	0.03096*	0.711	645.590
25	0.28351	0.02015*	0.725	642.143
30	0.23763	0.01244*	0.749	609.369
35	0.19042	0.00541*	0.775	559.920
40	0.14173	0.00131	0.804	432.189
45	0.08062	0.00680	0.881	297.966
50	0.02577	0.00021	0.934	142.592
55	0.00348	0.00017	0.910	62.242

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

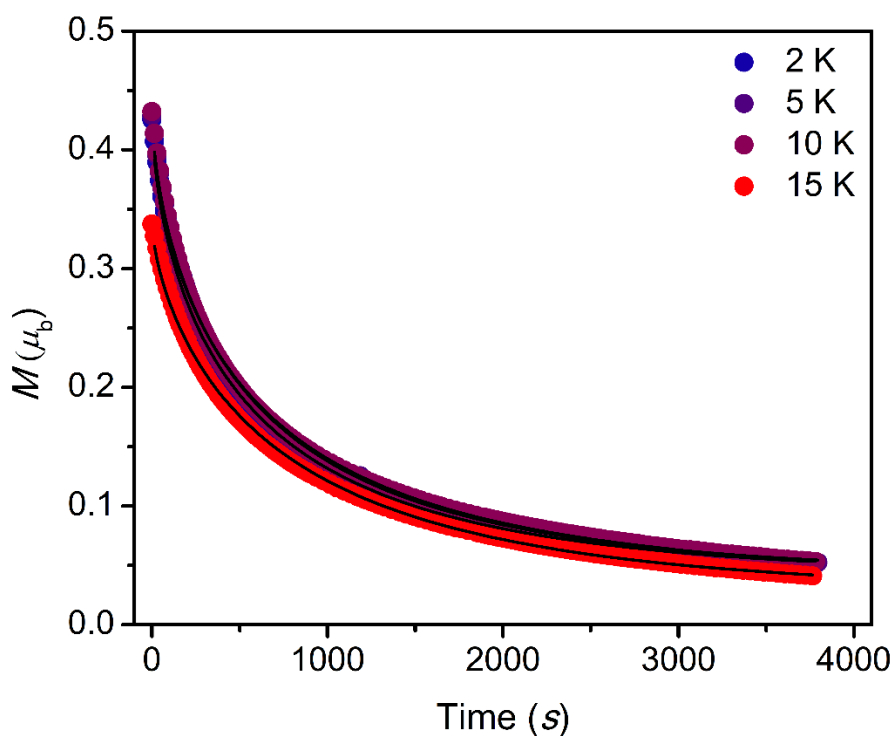


Figure S6.39. Dc magnetic relaxation data for **2** collected at 2, 5, 10, and 15 K and under zero applied dc field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

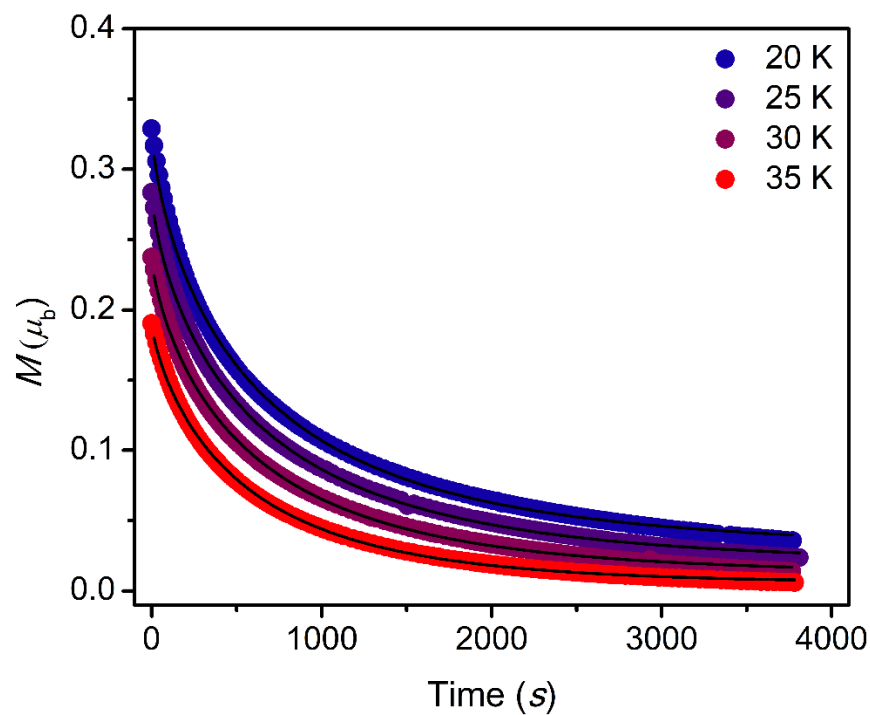


Figure S6.40. Dc magnetic relaxation data for **2** collected at 20, 25, 30, and 35 K and under zero applied dc field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

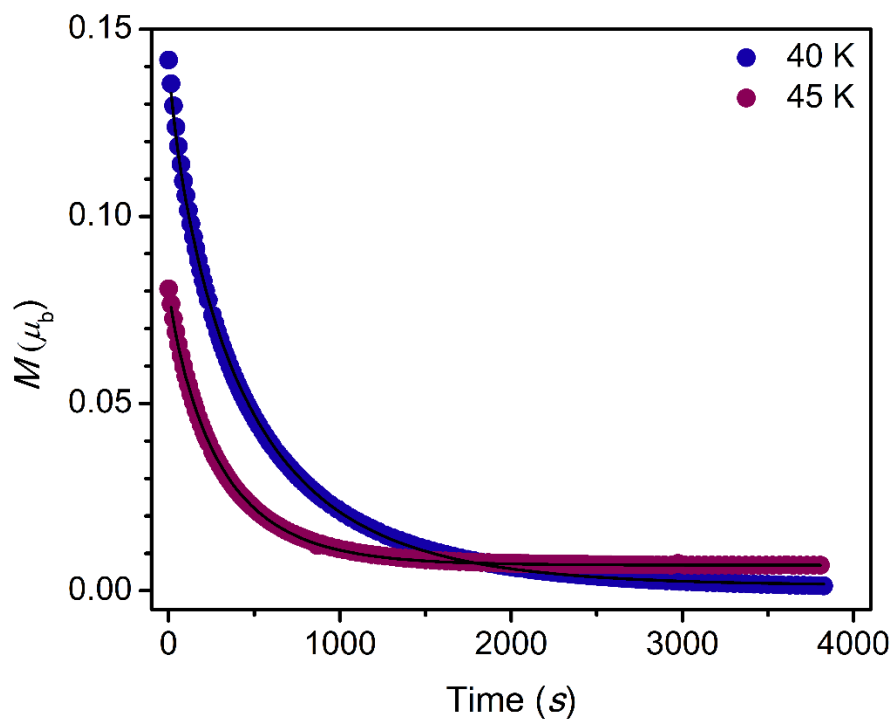


Figure S6.41. Dc magnetic relaxation data for **2** collected at 40 and 45 K and under zero applied dc field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

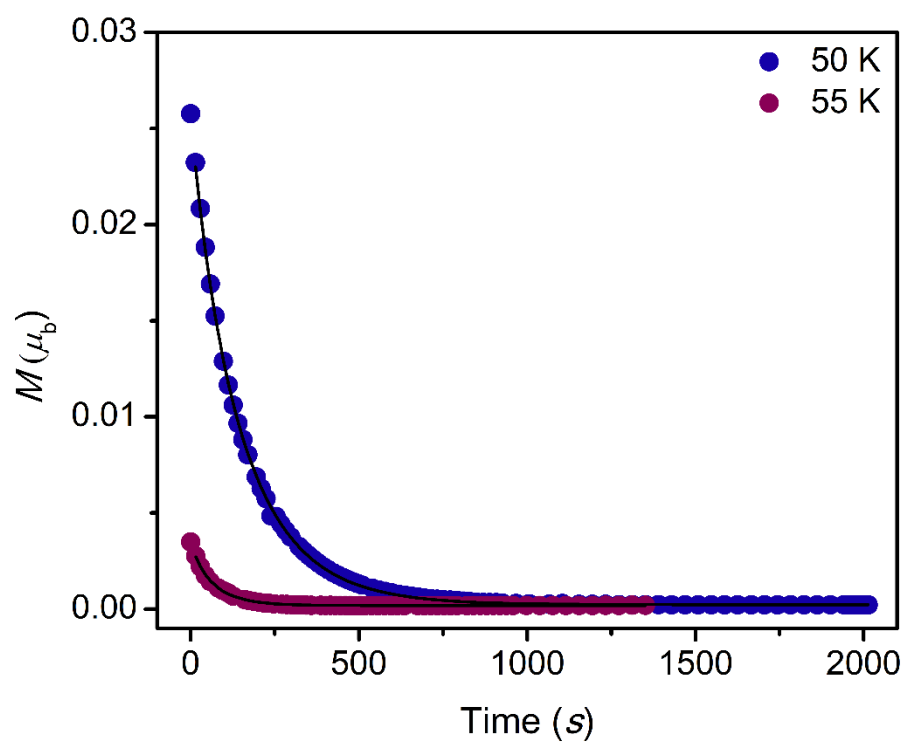


Figure S6.42. Dc magnetic relaxation data for **2** collected at 50 and 55 K and under zero applied dc field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S6.4. Parameters used to fit dc magnetic relaxation data for **2** at 500 Oe and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	0.91201	0.46652*	0.565	794.888
5	0.68669	0.20796	0.597	794.888
10	0.60115	0.11227	0.586	794.888
15	0.52809	0.08374	0.660	794.888
20	0.45144	0.06563	0.642	795.371
25	0.38208	0.05390	0.670	719.045
30	0.31331	0.04526	0.717	653.577
35	0.24366	0.03830	0.780	568.018
40	0.17834	0.03239	0.858	419.568
45	0.10482	0.02407	0.879	280.659
50	0.04586	0.02159	0.879	138.179

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

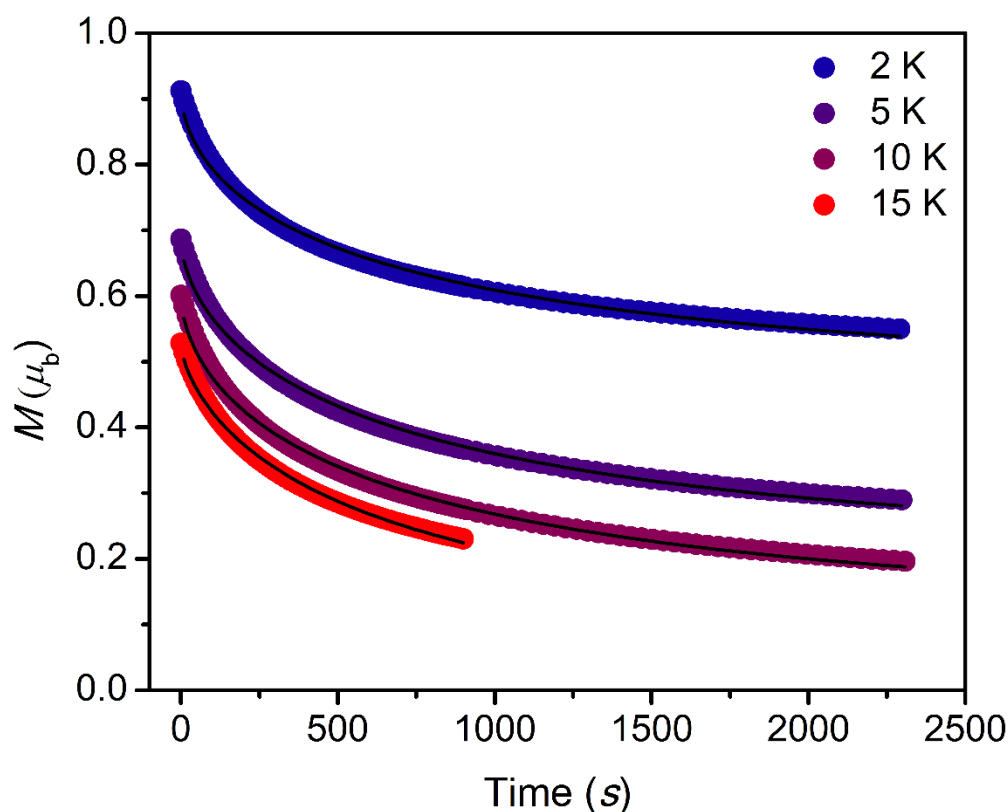


Figure S6.43. Dc magnetic relaxation data for **2** collected at 2, 5, 10, and 15 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

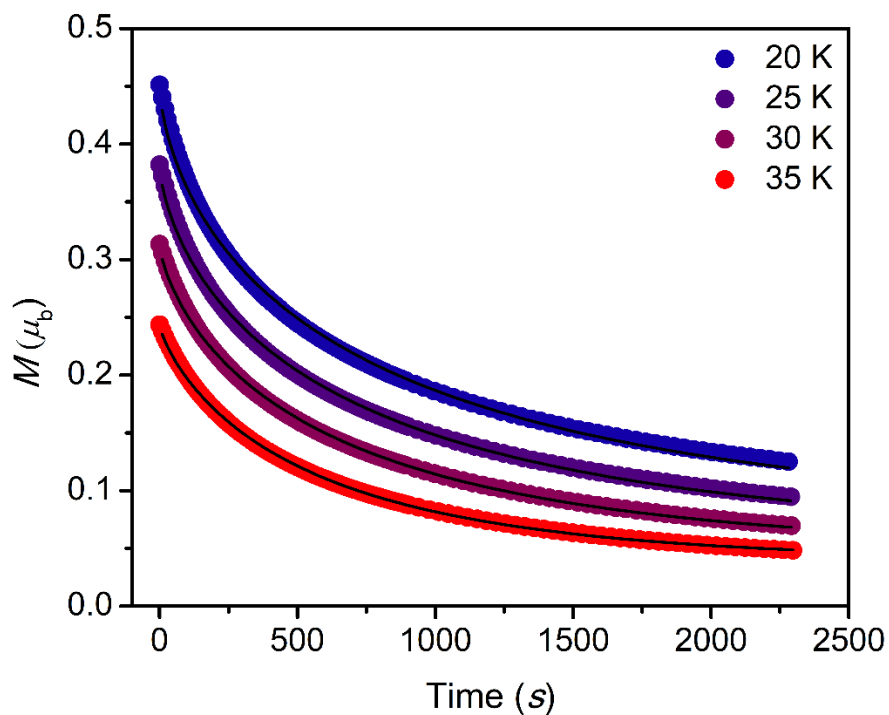


Figure S6.44. Dc magnetic relaxation data for **2** collected at 20, 25, 30, and 35 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

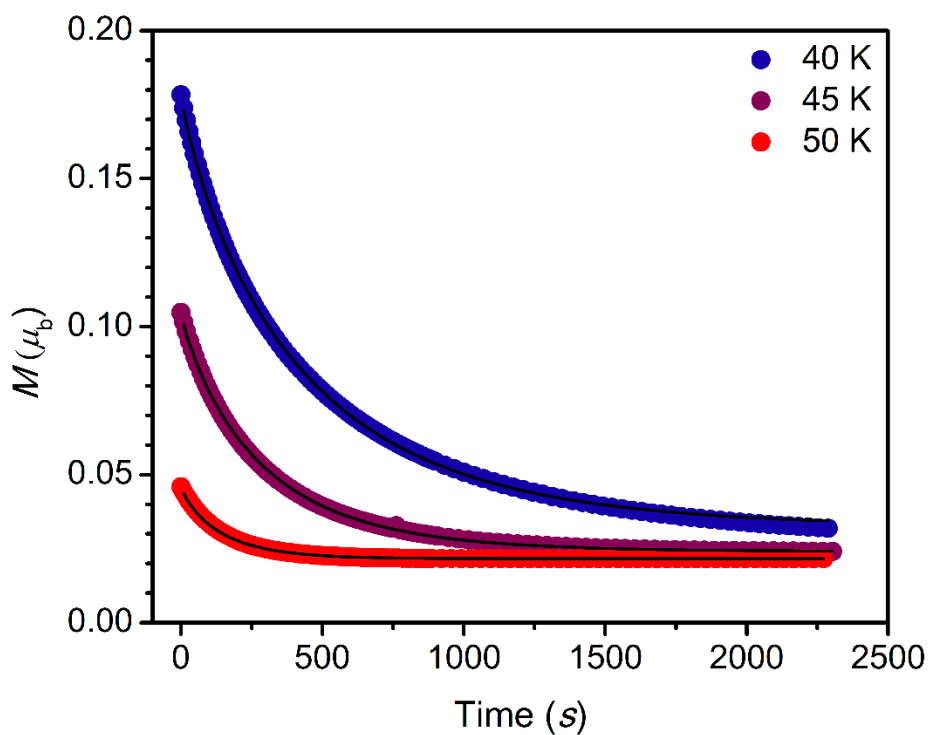


Figure S6.45. Dc magnetic relaxation data for **2** collected at 40, 45, and 50 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S6.5. Parameters used to fit dc magnetic relaxation data for a 19 mM solution of **2** in toluene at zero applied field and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	0.13301	0.10975*	0.510	695.989
5	0.04169	0.00920*	0.571	238.122
10	0.03652	0.00801*	0.558	269.979
15	0.03775	0.00675*	0.506	228.571
20	0.03281	0.00520*	0.542	280.109
25	0.02911	0.00320*	0.548	297.812
30	0.02288	0.00181*	0.637	357.986
35	0.02502	0.00069*	0.526	242.411
40	0.01705	0.00036	0.695	239.050
45	0.01270	0.00027	0.734	142.756
50	0.00500	0.00023	1.000	99.098

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

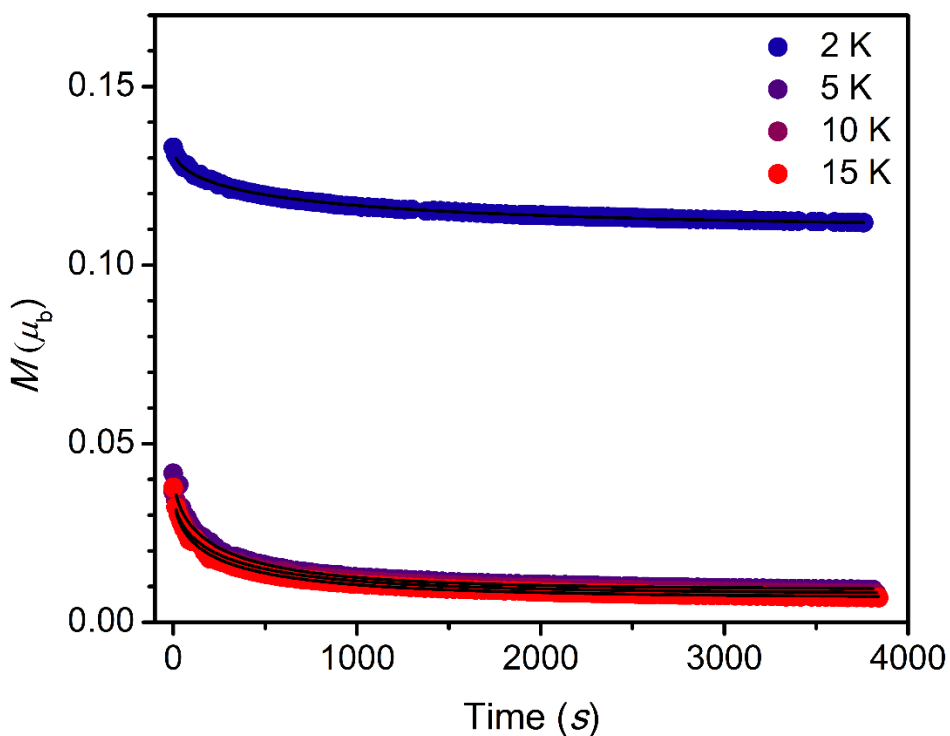


Figure S6.46. Dc magnetic relaxation data for a 19 mM solution of **2** in toluene collected at 2, 5, 10, and 15 K and under zero applied dc field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

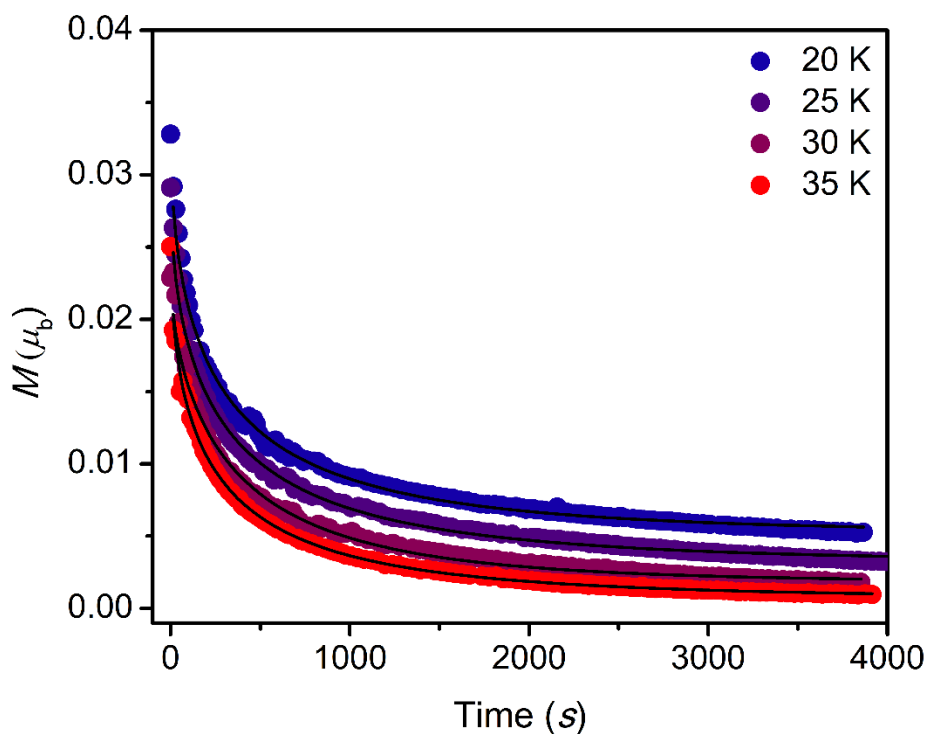


Figure S6.47. Dc magnetic relaxation data for a 19 mM solution of **2** in toluene collected at 20, 25, 30, and 35 K and under zero applied dc field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

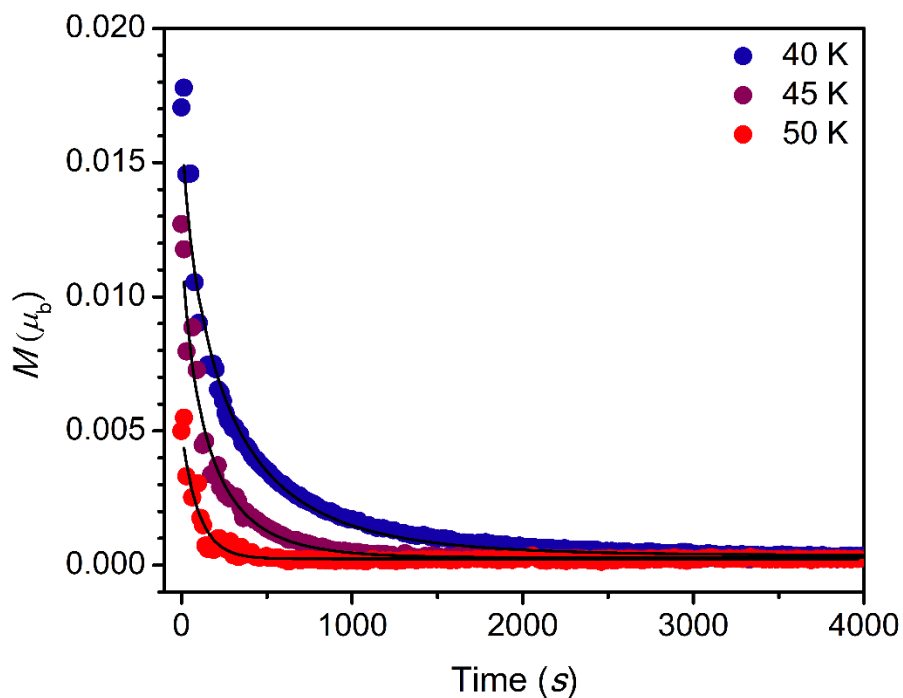


Figure S6.48. Dc magnetic relaxation data for a 19 mM solution of **2** in toluene collected at 40, 45, and 50 K and under zero applied dc field. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S6. Parameters used to fit dc magnetic relaxation data for a 19 mM solution of **2** in toluene at 500 Oe and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	0.53515	0.40510	0.360	3542479.980
5	0.33221	0.17403	0.366	1508689.837
10	0.25195	0.09128	0.479	202520.071
15	0.21301	0.06075	0.586	47303.034
20	0.18323	0.04602	0.647	19883.087
25	0.15536	0.03706	0.724	7910.162
30	0.13101	0.03091	0.758	3844.352
35	0.10878	0.02646	0.832	1902.502
40	0.08491	0.02305	0.870	904.773
45	0.05737	0.02029	0.910	402.213
50	0.03051	0.01784	0.958	182.543

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

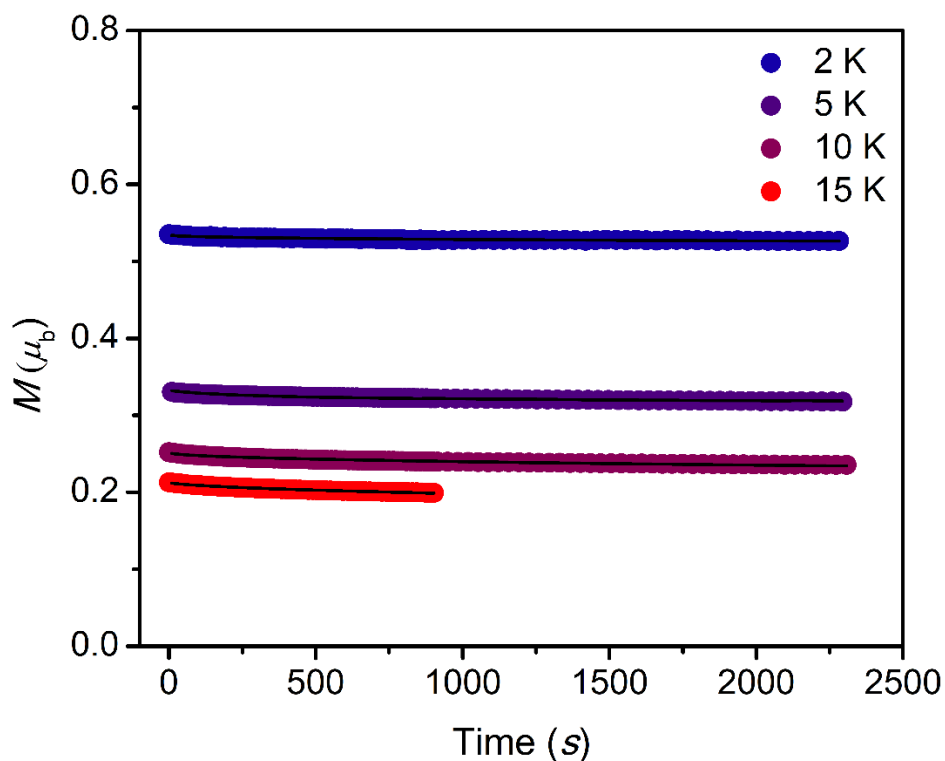


Figure S6.49. Dc magnetic relaxation data for a 19 mM solution of **2** in toluene collected at 2, 5, 10, and 15 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

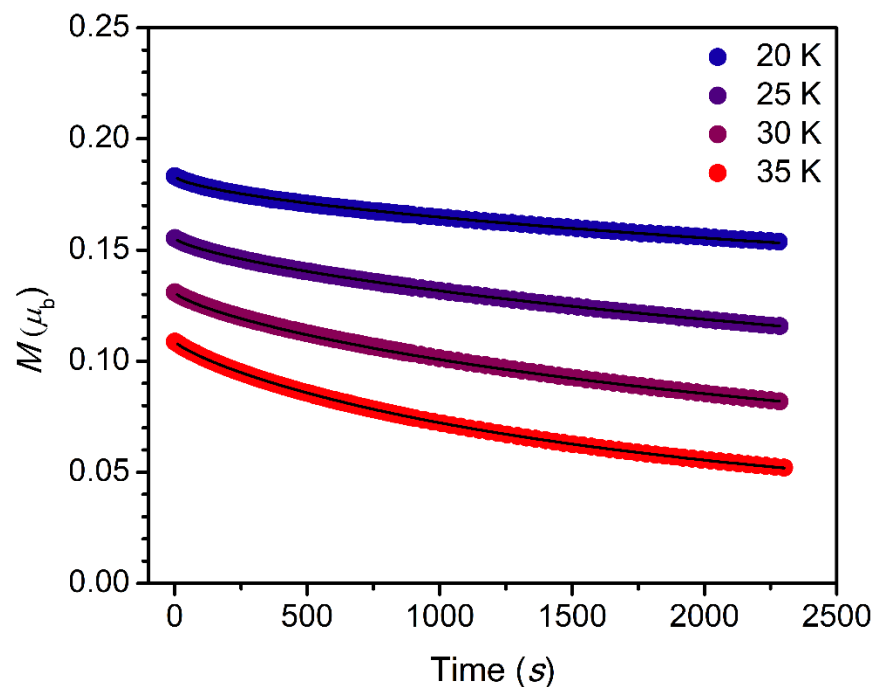


Figure S6.50. Dc magnetic relaxation data for a 19 mM solution of **2** in toluene collected at 20, 25, 30, and 35 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

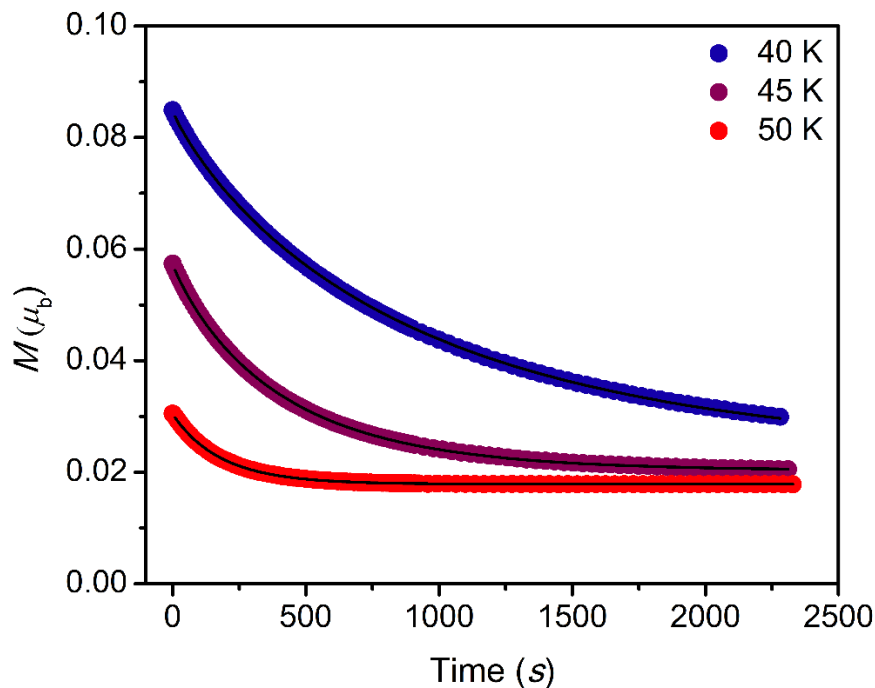


Figure S6.51. Dc magnetic relaxation data for a 19 mM solution of **2** in toluene collected at 40, 45, and 50 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S6.7. Parameters used to fit dc magnetic relaxation data for **3** at 500 Oe and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	0.75484	0.60027	0.531	223.793
5	0.33039	0.24931	0.669	223.882
10	0.19735	0.12884	0.656	223.864
15	0.15168	0.08660	0.678	224.727
20	0.12399	0.06539	0.664	229.226
25	0.10147	0.05163	0.687	213.936
30	0.08415	0.04264	0.700	194.638
35	0.06979	0.03632	0.717	184.311
40	0.05878	0.03160	0.732	171.191
45	0.04967	0.02808	0.730	161.758
50	0.04237	0.02529	0.764	148.359

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

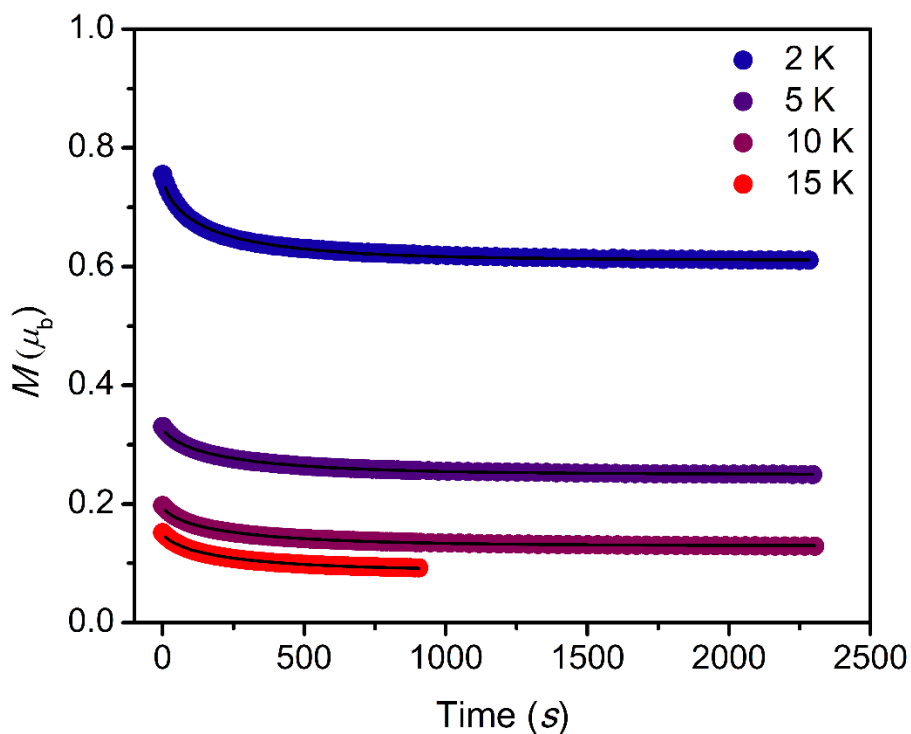


Figure S6.52. Dc magnetic relaxation data for **3** collected at 2, 5, 10, and 15 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

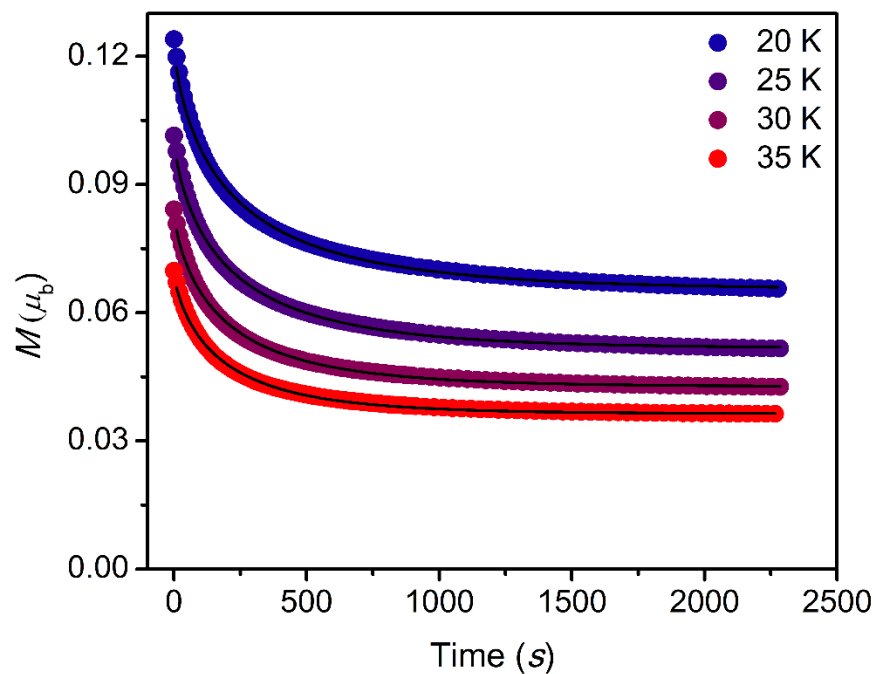


Figure S6.53. Dc magnetic relaxation data for **3** collected at 20, 25, 30, and 35 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

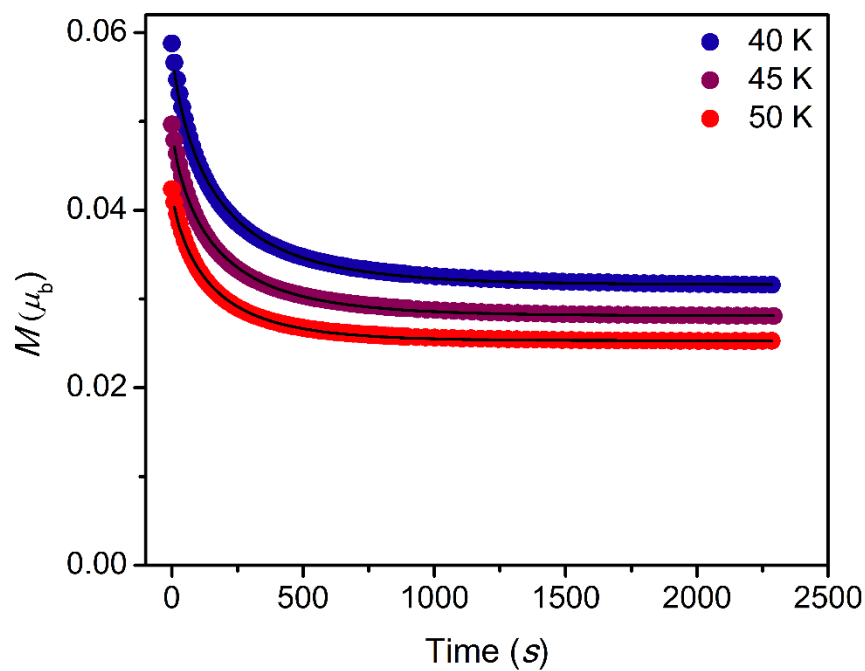


Figure S6.54. Dc magnetic relaxation data for **3** collected at 40, 45, and 50 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S6.8. Parameters used to fit dc magnetic relaxation data for a 28 mM solution of **3** in toluene at zero applied magnetic field and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
2	0.71576	0.13849*	0.752	1652.206
3	0.45533	0.06401*	0.806	967.568
4	0.32806	0.04384	0.833	597.723
5	0.27658	0.03951	0.793	405.136

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

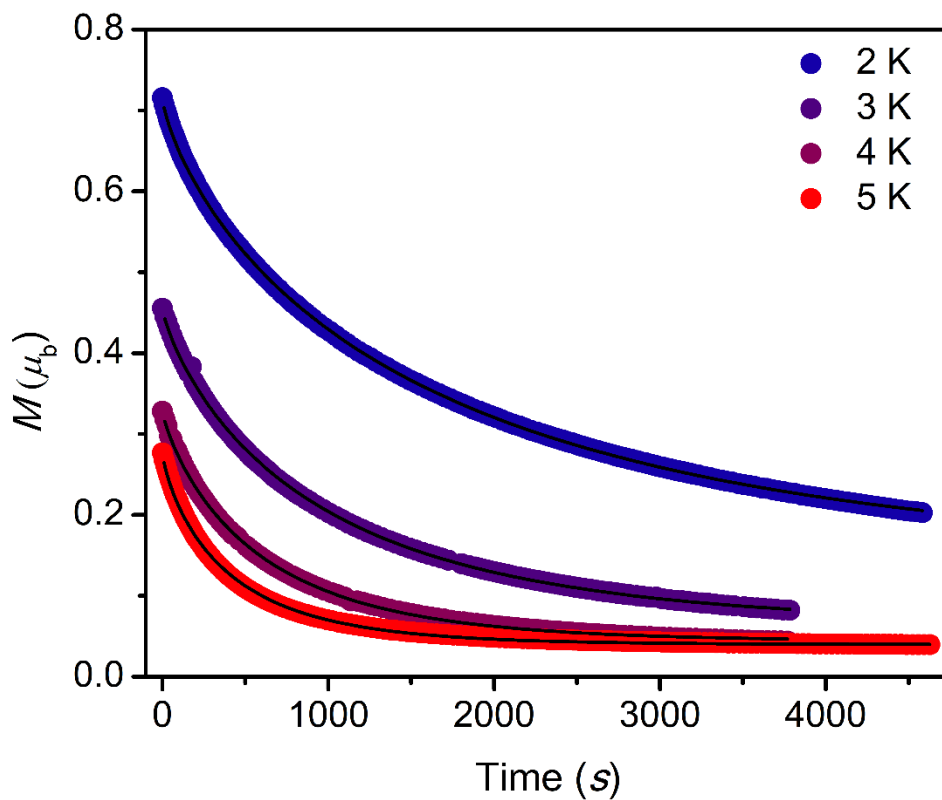


Figure S6.55. Dc magnetic relaxation data for a 28 mM solution of **3** in toluene collected at 2, 3, 4, and 5 K and under an applied dc field of 0 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Table S6.9. Parameters used to fit dc magnetic relaxation data for a 28 mM solution of **3** in toluene at 500 Oe and magnetic relaxation times extracted from these fits.

T (K)	M_0 (μ_B)	M_1 (μ_B)	n	τ (s) ^a
10	0.91364	0.16895	0.729	7499.979
15	0.62748	0.07644	0.694	3311.353
20	0.50794	0.05997	0.716	1872.765
25	0.43559	0.04977	0.720	1333.256
30	0.30633	0.04267	0.725	694.438
35	0.26036	0.03719	0.745	681.890
40	0.20410	0.03273	0.764	536.999
45	0.15955	0.02902	0.790	433.028
50	0.13100	0.02591	0.810	376.474

^aValues for τ are likely only accurate to three significant figures. The full value extracted from the fit is reported for reproducibility.

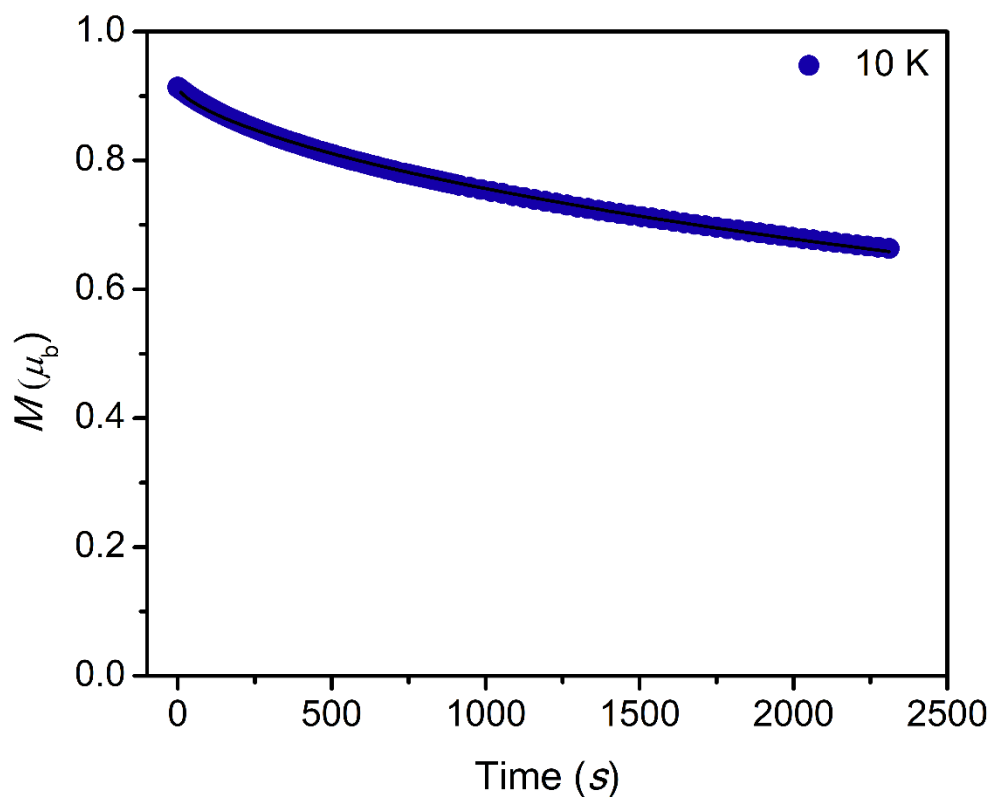


Figure S6.56. Dc magnetic relaxation data for a 28 mM solution of **3** in toluene collected at 10 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

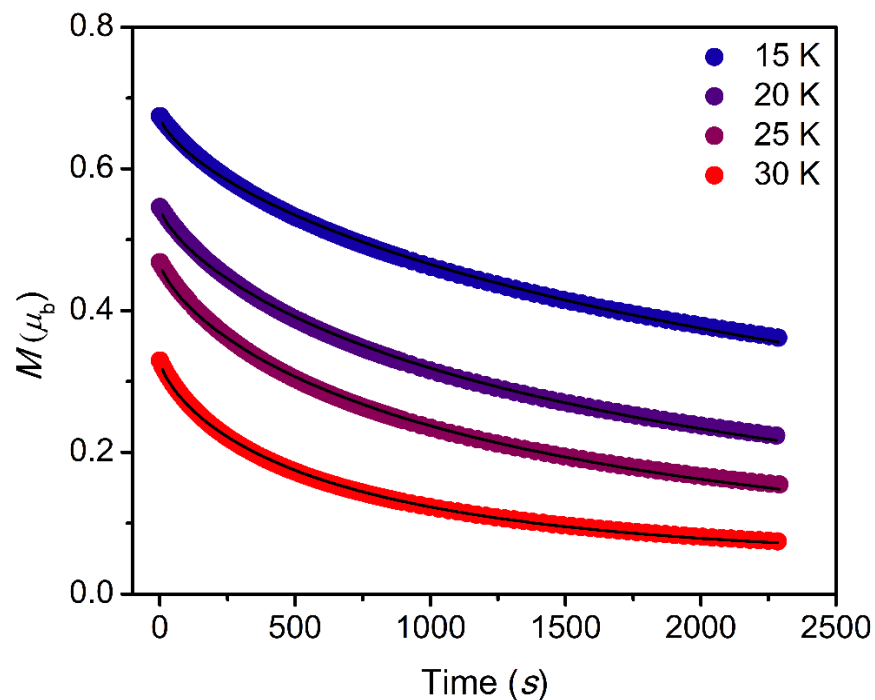


Figure S6.57. Dc magnetic relaxation data for a 28 mM solution of **3** in toluene collected at 15, 20, 25, and 30 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

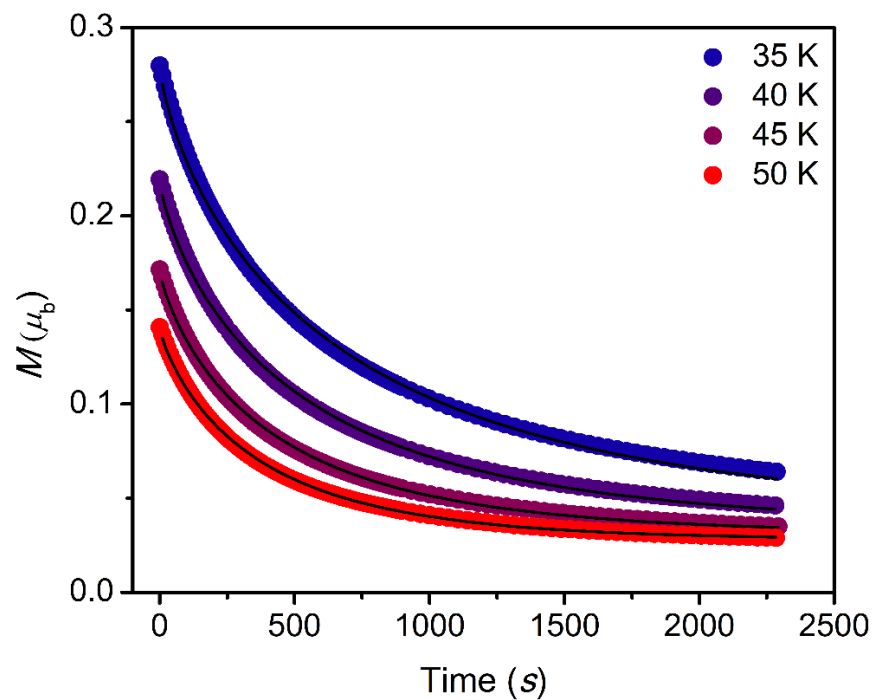


Figure S6.58. Dc magnetic relaxation data for a 28 mM solution of **3** in toluene collected at 35, 40, 45, and 50 K and under an applied dc field of 500 Oe. Black lines represent the fits to the data using stretched exponential functions, which were used to extract τ .

Analysis of Magnetic Relaxation Dynamics. The full range of magnetic relaxation times extracted from ac susceptibility and dc magnetic relaxation experiments of **1-3** showed a complex temperature dependence, indicative of multiple magnetic relaxation pathways. Plots of the log of magnetic relaxation time versus $1/T$ showed an exponential dependence at intermediate temperatures and flattened at low T , suggesting the presence of Raman relaxation and/or quantum tunneling of the magnetization. Accordingly, the data for **1-4** were fit to the equation:

$$\tau^{-1} = \tau_0^{-1} e^{-U_{eff}/k_b T} + \tau_{tunnel}^{-1} + CT^n$$

where τ_{tunnel} is the relaxation time for quantum tunneling of the magnetization and C and n are free variables that describe Raman relaxation. In the following tables, “n/a” represents data for which magnetic relaxation times could not be extracted (signals in the out-of-phase susceptibility were observed but the peak was beyond the detection limit of our magnetometer), while “not observed” corresponds to a lack of signals in ac magnetic susceptibility or dc magnetic relaxation measurements.

Table S6.10. Parameters used to fit the Arrhenius plots of **1**.

	Polycrystalline 1 $H_{dc} = 0$ Oe
U_{eff} (cm ⁻¹)	-
τ_0 (s)	-
τ_{tunnel} (s)	5.72×10^{-3}
C	2.04
n	2.00

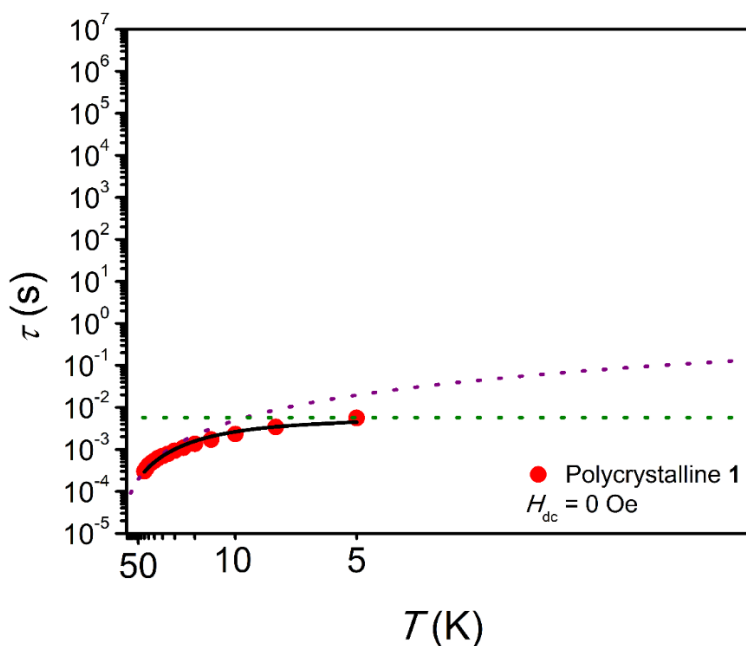


Figure S6.59. Plot of magnetic relaxation time versus temperature for **1**. Green and purple lines represent fits to quantum tunneling and Raman relaxation processes, respectively. Black line represents the total fit to the data.

Table S6.11. Parameters used to fit the Arrhenius plots of **2**.

Fast Process	Polycrystalline 2 $H_{dc} = 0$ Oe	Polycrystalline 2 $H_{dc} = 500$ Oe	19 mM Solution 2 $H_{dc} = 0$ Oe	19 mM Solution 2 $H_{dc} = 500$ Oe
U_{eff} (cm ⁻¹)	-	-	n/a	n/a
τ_0 (s)	-	-	n/a	n/a
τ_{tunnel} (s)	7.92×10^{-1}	7.92×10^{-1}	n/a	n/a
C	-	-	n/a	n/a
n	-	-	n/a	n/a

Slow Process	Polycrystalline 2 $H_{dc} = 0$ Oe	Polycrystalline 2 $H_{dc} = 500$ Oe	19 mM Solution 2 $H_{dc} = 0$ Oe	19 mM Solution 2 $H_{dc} = 500$ Oe
U_{eff} (cm ⁻¹)	1205	-	-	-
τ_0 (s)	2.46×10^{-11}	-	-	-
τ_{tunnel} (s)	6.42×10^2	7.95×10^{-2}	2.54×10^2	2.99×10^6
C	9.69×10^{-18}	1.00×10^{-13}	9.69×10^{-18}	2.07×10^{-10}
n	8.69	6.31	8.69	4.22

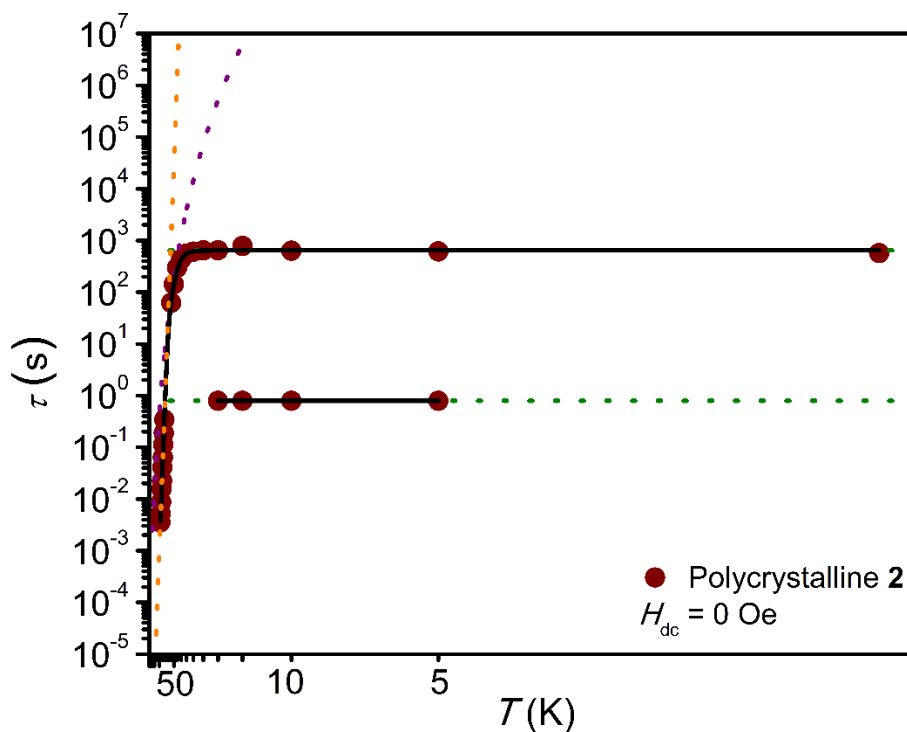


Figure S6.60. Plot of magnetic relaxation time versus temperature for a polycrystalline sample of **2** under zero applied dc field. Green, purple, and orange lines represent fits to quantum tunneling, Raman relaxation, and Orbach processes, respectively. Black line represents the total fit to the data.

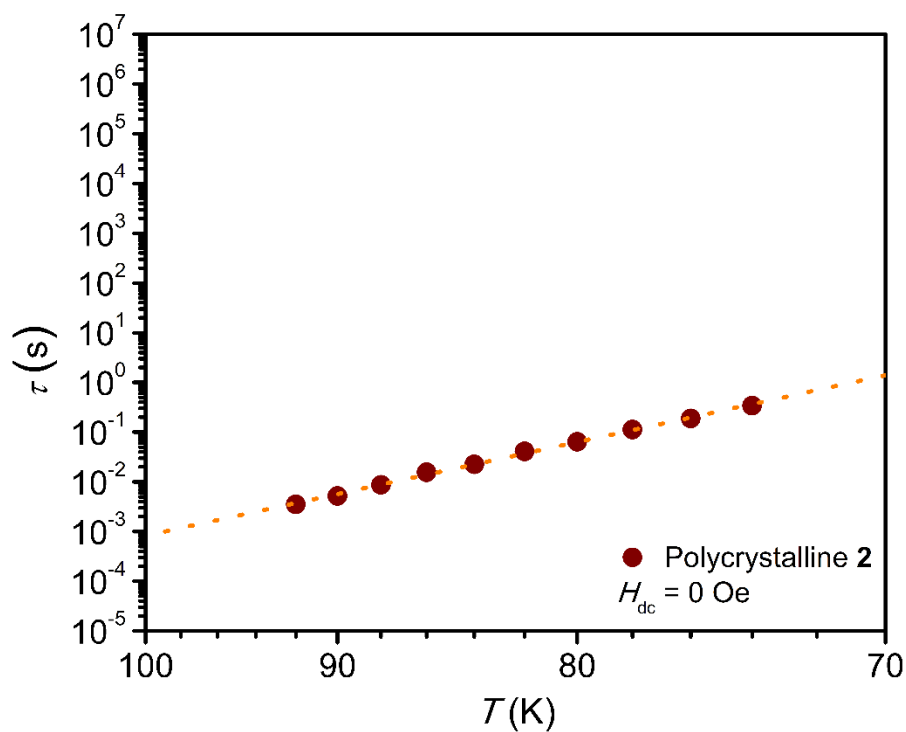


Figure S6.61. Plot of magnetic relaxation time versus temperature for a polycrystalline sample of **2** under zero applied dc field from 70 to 100 K. Orange line represent fits to an Orbach processes.

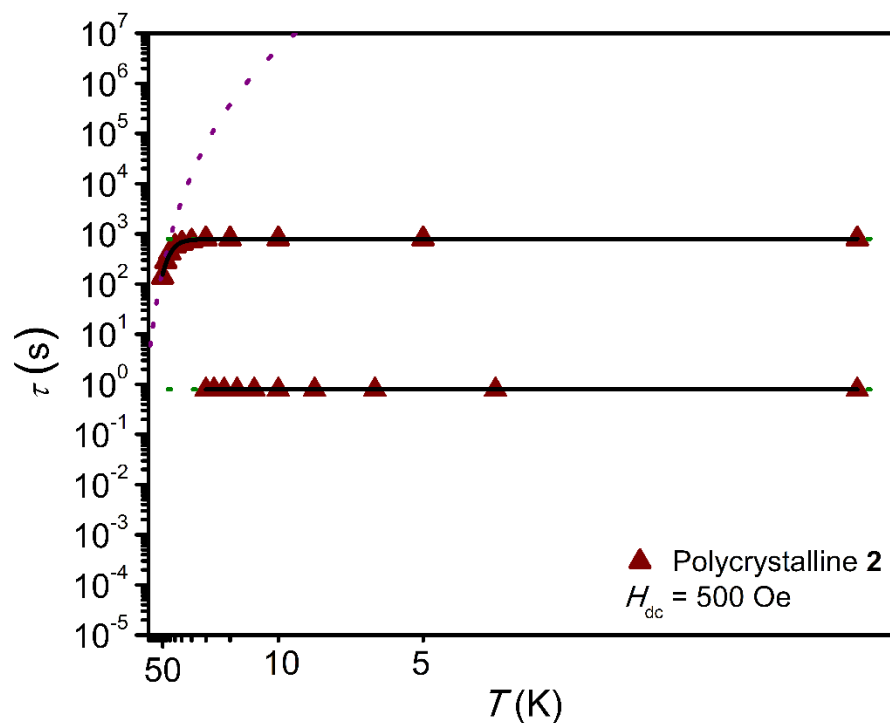


Figure S6.62. Plot of magnetic relaxation time versus temperature for a polycrystalline sample of **2** under an applied dc field of 500 Oe. Green and purple lines represent fits to quantum tunneling and Raman relaxation processes, respectively. Black line represents the total fit to the data

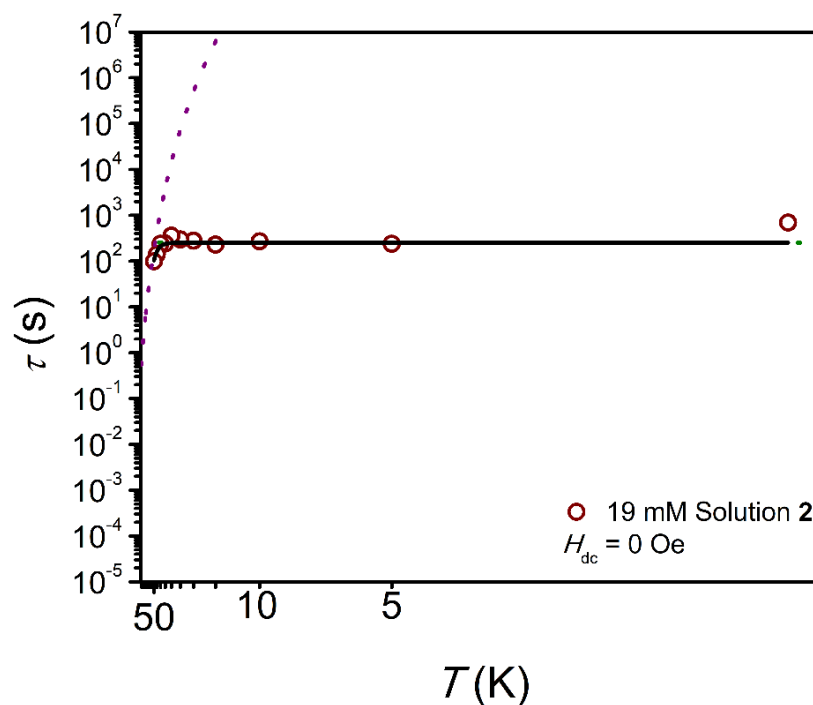


Figure S6.63. Plot of magnetic relaxation time versus temperature for a 19 mM solution of **2** in toluene under zero applied dc field. Green and purple lines represent fits to quantum tunneling and Raman relaxation processes, respectively. Black line represents the total fit to the data.

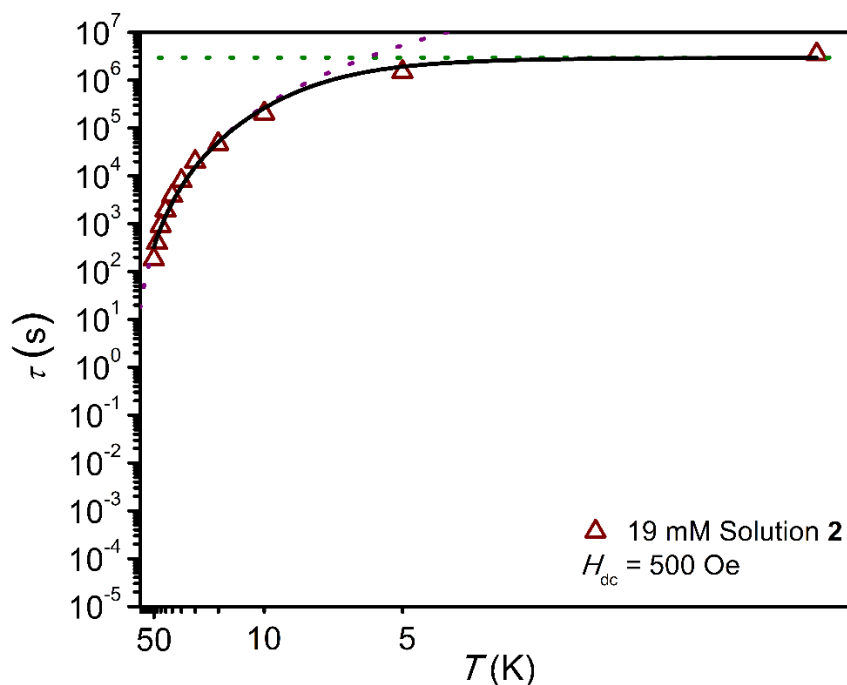


Figure S6.64. Plot of magnetic relaxation time versus temperature for a 19 mM solution of **2** in toluene under an applied dc field of 500 Oe. Green and purple lines represent fits to quantum tunneling and Raman relaxation processes, respectively. Black line represents the total fit to the data.

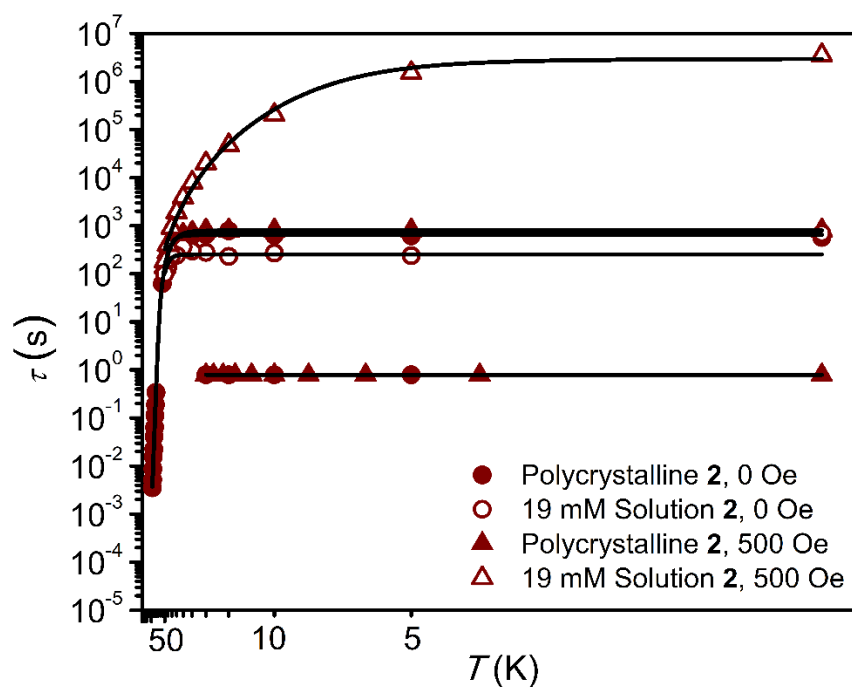


Figure S6.65. Plot of magnetic relaxation time versus temperature for a polycrystalline sample and a 19 mM solution of **2** under zero applied dc field and an applied dc field of 500 Oe. Black lines represent overall fits to the data. The fast tunneling process disappears upon dilution, suggesting that it may be due to dipolar interactions. The slow process overlays at high temperatures for both zero and applied fields, as well as in polycrystalline and solution samples, suggesting that it is molecular in origin. The rate of tunneling in this slow process decreases upon application on an external field, as expected.

Table S6.12. Parameters used to fit the Arrhenius plots of **3**.

Fast Process	Polycrystalline 3 $H_{dc} = 0$ Oe	Polycrystalline 3 $H_{dc} = 500$ Oe	28 mM Solution 3 $H_{dc} = 0$ Oe	28 mM Solution 3 $H_{dc} = 500$ Oe
U_{eff} (cm ⁻¹)	-	37.4	37.4	37.4
τ_0 (s)	-	9.57×10^{-6}	9.57×10^{-6}	1.30×10^{-5}
τ_{tunnel} (s)	1.54×10^{-4} 2.00×10^{-1}	-	-	-
C	-	5.63×10^{-3}	9.33×10^{-1}	1.43×10^{-2}
n	-	4.34	2.00	3.65

Slow Process	Polycrystalline 3 $H_{dc} = 0$ Oe	Polycrystalline 3 $H_{dc} = 500$ Oe	28 mM Solution 3 $H_{dc} = 0$ Oe	28 mM Solution 3 $H_{dc} = 500$ Oe
U_{eff} (cm ⁻¹)	Not observed	-	-	-
τ_0 (s)	Not observed	-	-	-
τ_{tunnel} (s)	Not observed	2.24×10^2	1.65×10^3	1.49×10^4
C	Not observed	2.87×10^{-8}	1.29×10^{-5}	4.94×10^{-7}
n	Not observed	2.89	3.11	2.22

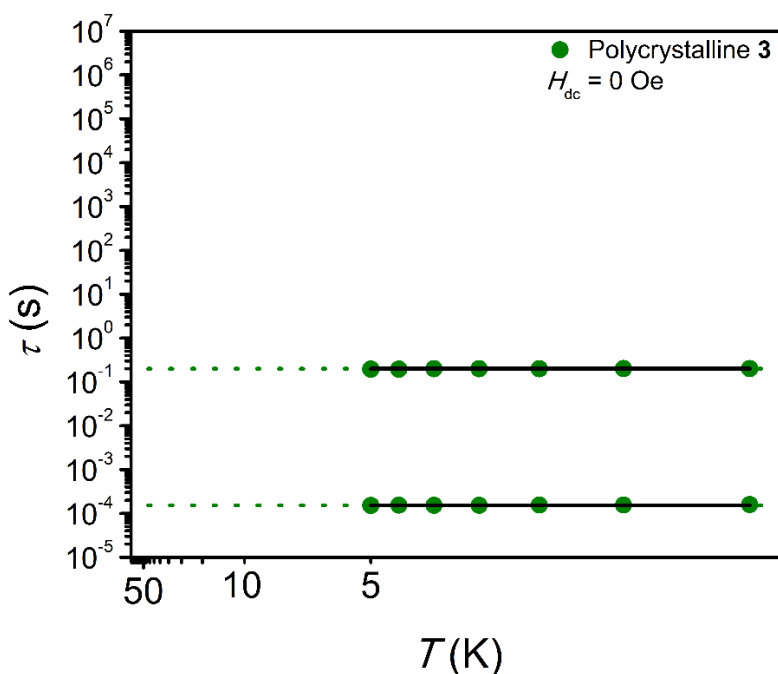


Figure S6.66. Plot of magnetic relaxation time versus temperature for a polycrystalline sample of **3** under zero applied dc field. Green lines represent fits to quantum tunneling processes. Black line represents the total fit to the data. Two relaxation processes were observed in the ac susceptibility measurements.

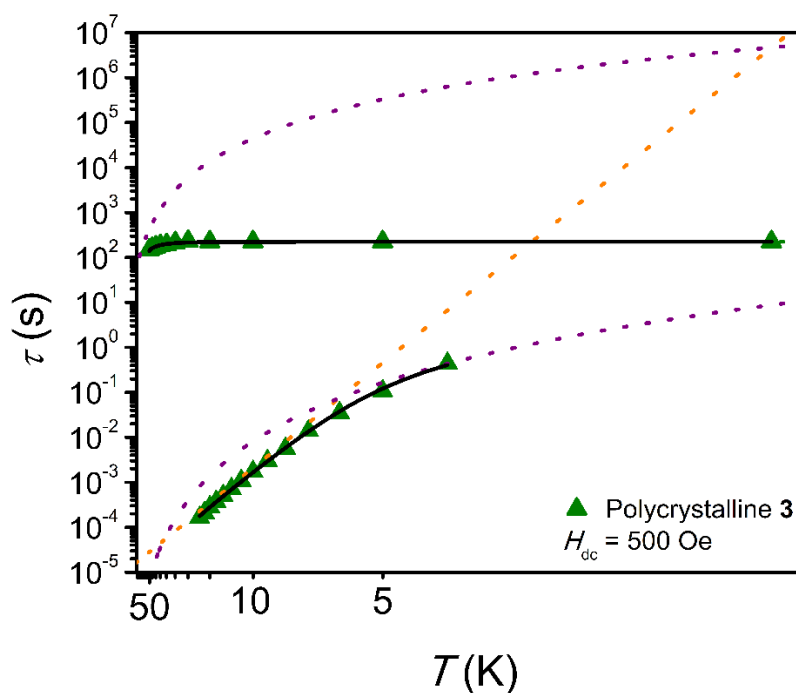


Figure S6.67. Plot of magnetic relaxation time versus temperature for a polycrystalline sample of **3** under an applied dc field of 500 Oe. Green, purple, and orange lines represent fits to quantum tunneling, Raman relaxation, and Orbach processes, respectively. Black line represents the total fit to the data.

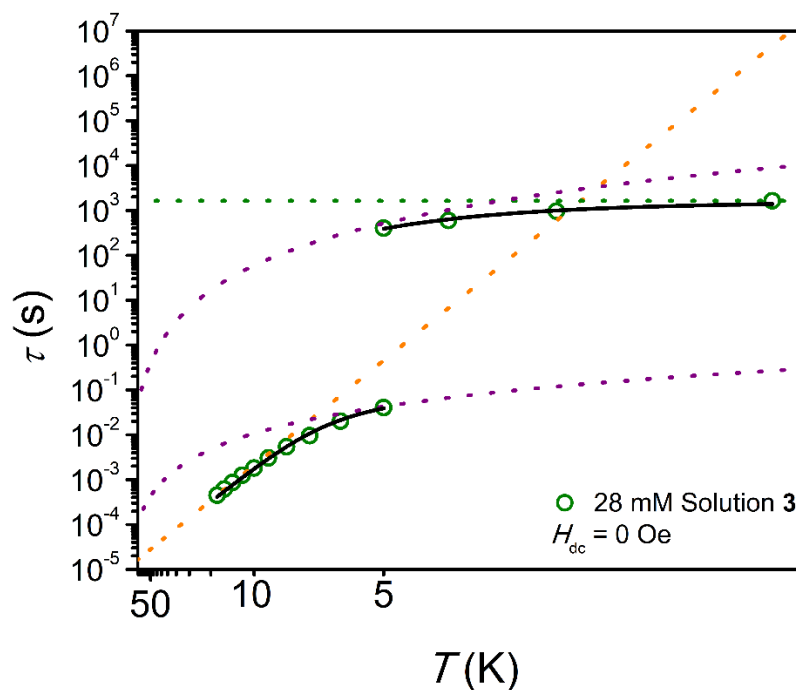


Figure S6.68. Plot of magnetic relaxation time versus temperature for a 28 mM solution of **3** in toluene under zero applied dc field. Green, purple, and orange lines represent fits to quantum tunneling, Raman relaxation, and Orbach processes, respectively. Black line represents the total fit to the data.

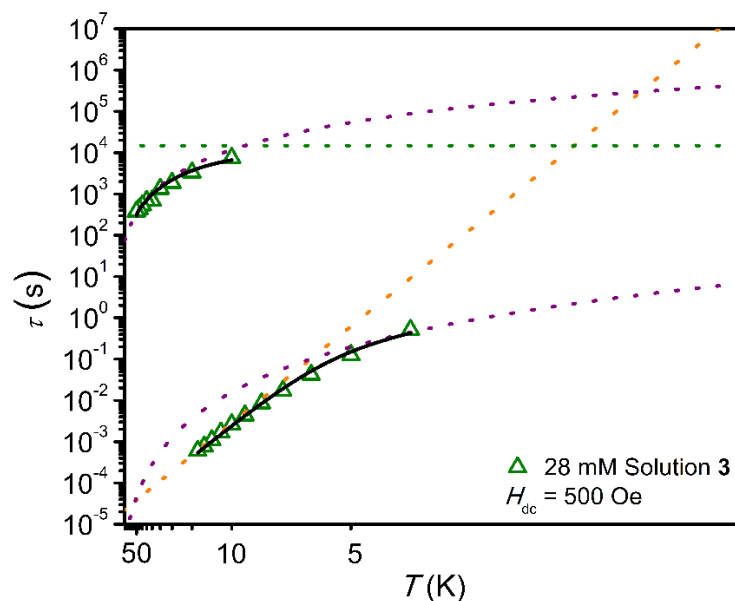


Figure S6.69. Plot of magnetic relaxation time versus temperature for a 28 mM solution of **3** in toluene under an applied dc field of 500 Oe. Green, purple, and orange lines represent fits to quantum tunneling, Raman relaxation, and Orbach processes, respectively. Black line represents the total fit to the data.

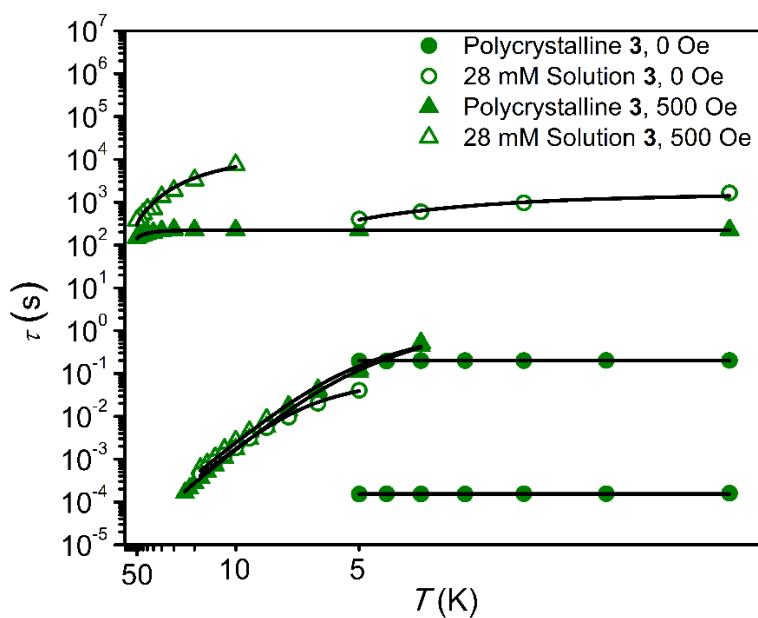


Figure S6.70. Plot of magnetic relaxation time versus temperature for a polycrystalline sample and a 28 mM solution of **3** under zero applied field and an applied dc field of 500 Oe. Black lines represent overall fits to the data. The slow process overlays at high temperatures for polycrystalline and solution samples, suggesting that it is molecular in origin. The fast process with a linear dependence on temperature overlays for both zero and applied fields, as well as in polycrystalline and solution samples, suggesting that it is molecular in origin. The fast tunneling processes observed for polycrystalline **3** under zero applied field disappear in solution, suggesting that these relaxation processes may be dipolar in origin.

Magnetic Hysteresis Measurements. Magnetic hysteresis measurements were collected on **1-3** at a sweep rate of 10.3(7) mT/s for **1** and at sweep rates of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T for **2** and **3**. Magnetic hysteresis measurements were also conducted on a 19 mM solution of **2** in toluene and on a 28 mM solution of **3** in toluene in order to confirm that the magnetic behavior was molecular in origin. Coercivity decreased slightly in **2** which may be due to a change in molecular symmetry or metal-ligand vibrational modes upon dissolution. A decrease in coercivity was also reported for frozen solution measurements of $[\text{Dy}(\text{Cp}^{\text{ttt}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (Cp^{ttt} =1,2,4-tri(*tert*-butyl)cyclopentadienyl). While hysteresis loops are closed at zero field for polycrystalline samples of **3**, they open up to 10 K for frozen solution measurements. This is likely due to a decrease in dipolar interactions upon dilution. Such dipolar interactions often facilitate fast magnetic relaxation and thus removing them allows the molecular slow magnetic relaxation to be observed.

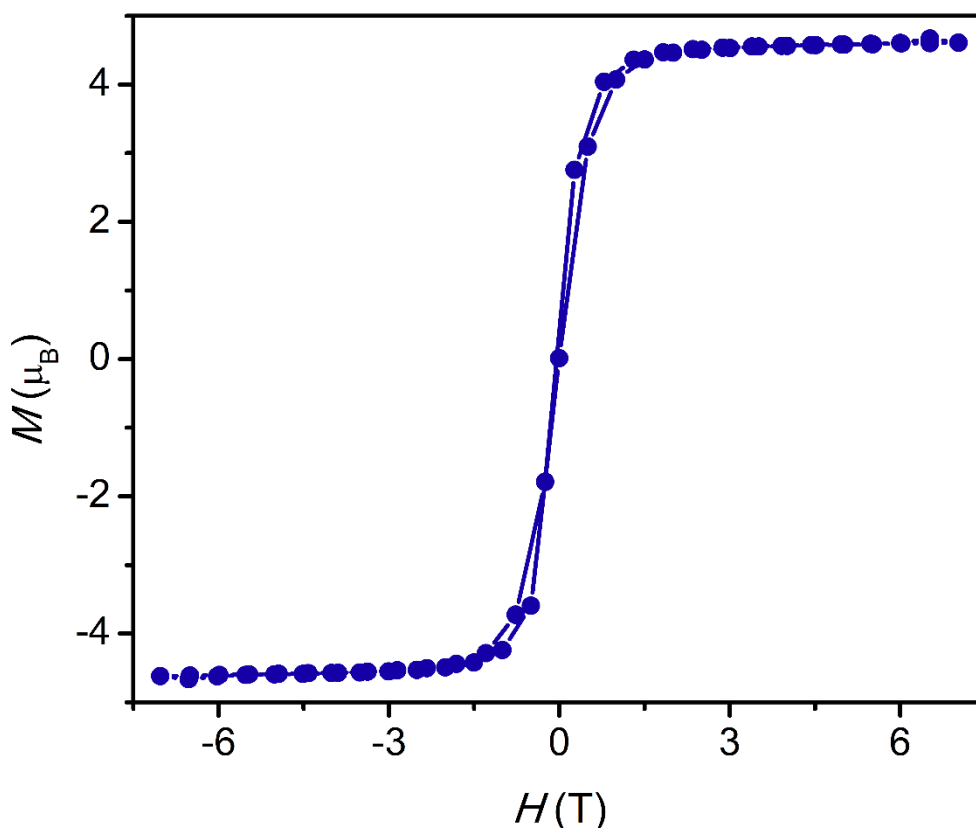


Figure S6.71. Magnetic hysteresis measurements of **1** at 2 K at a sweep rate of 10.3(7) mT/s.

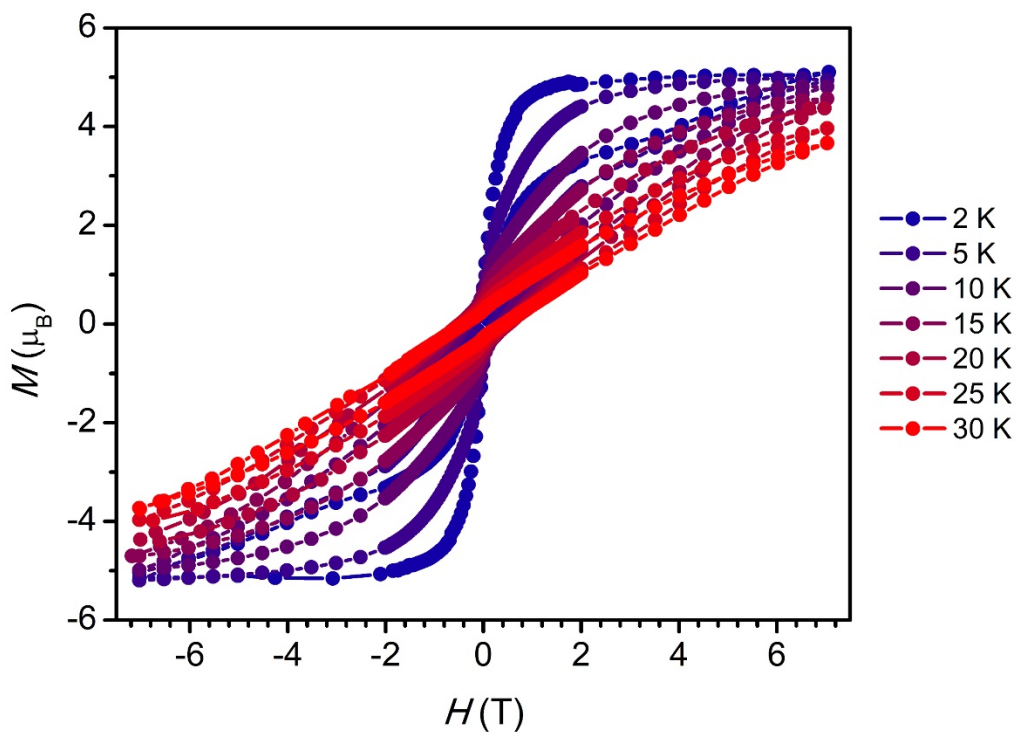


Figure S6.72. Magnetic hysteresis measurements of polycrystalline **2** from 2 to 30 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

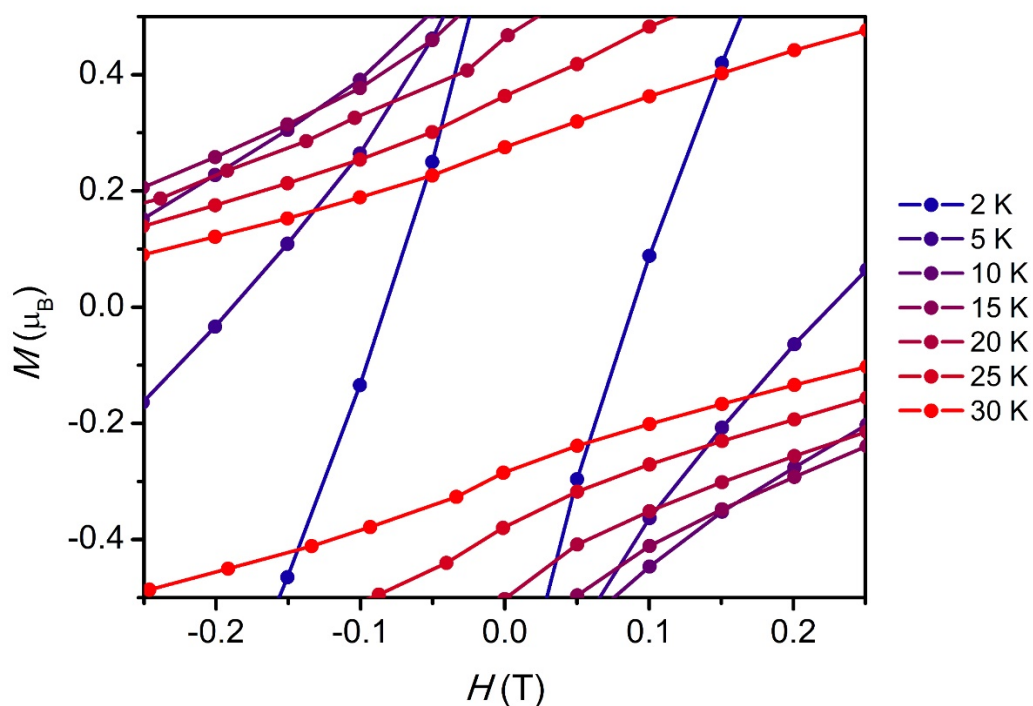


Figure S6.73. Magnetic hysteresis measurements of polycrystalline **2** from 2 to 30 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

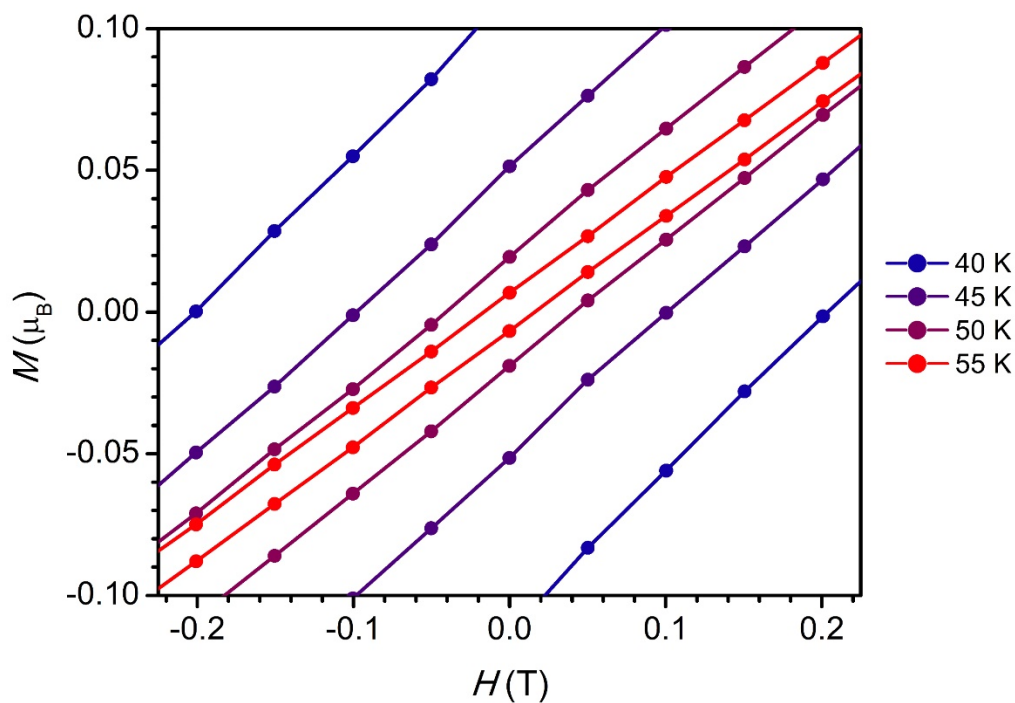


Figure S6.74. Magnetic hysteresis measurements of polycrystalline **2** from 40 to 55 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

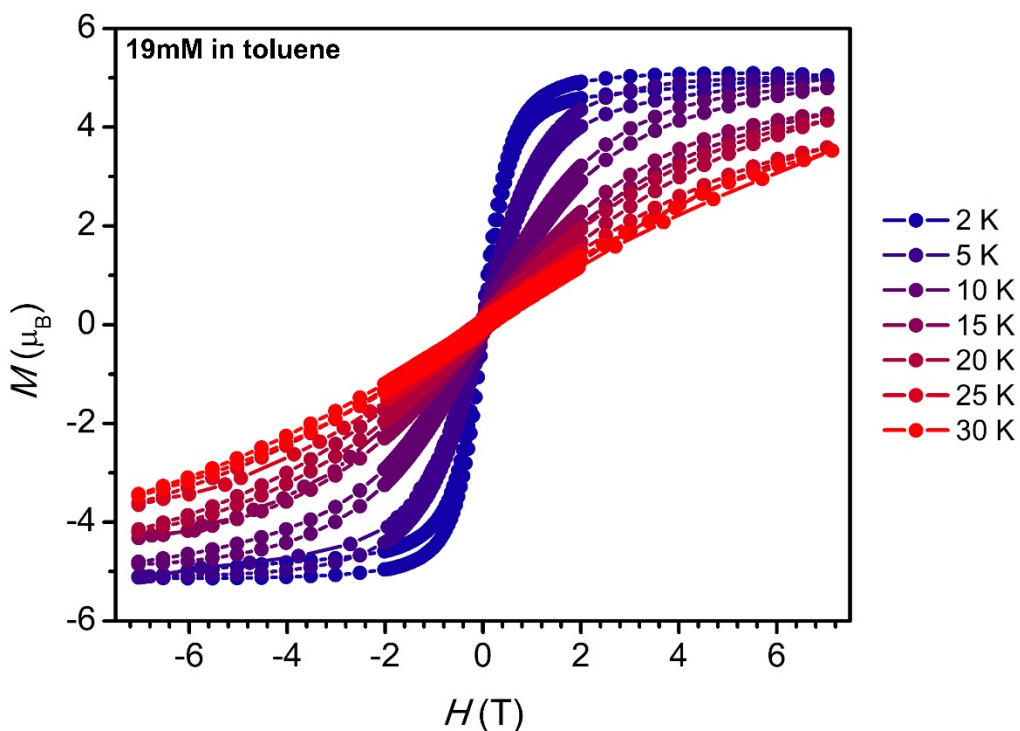


Figure S6.75. Magnetic hysteresis measurements of a 19 mM solution of **2** in toluene from 2 to 30 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

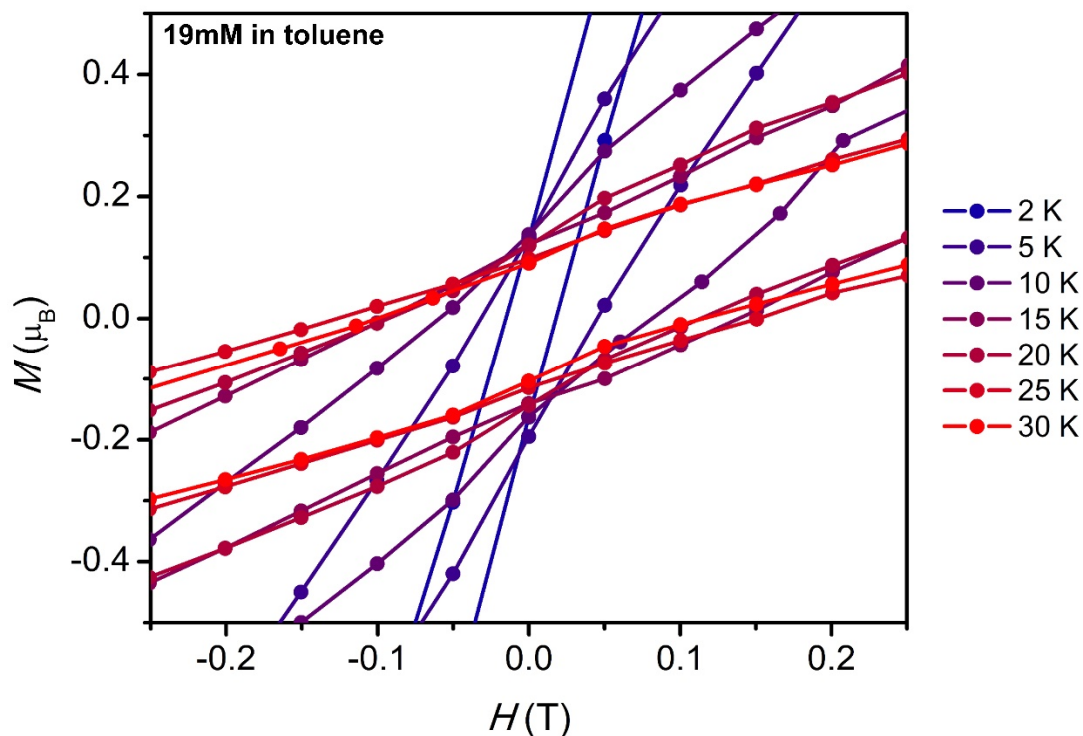


Figure S6.76. Magnetic hysteresis measurements of a 19 mM solution of **2** in toluene from 2 to 30 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

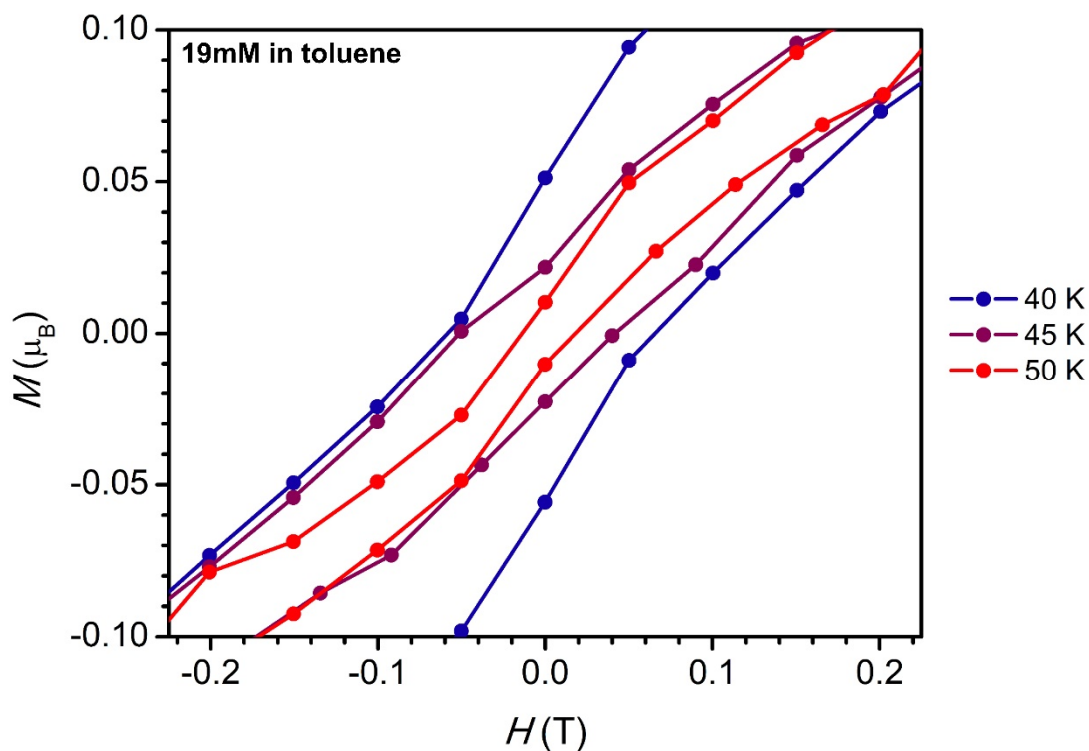


Figure S6.77. Magnetic hysteresis measurements of a 19 mM solution of **2** in toluene from 40 to 50 K (5 K steps) at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

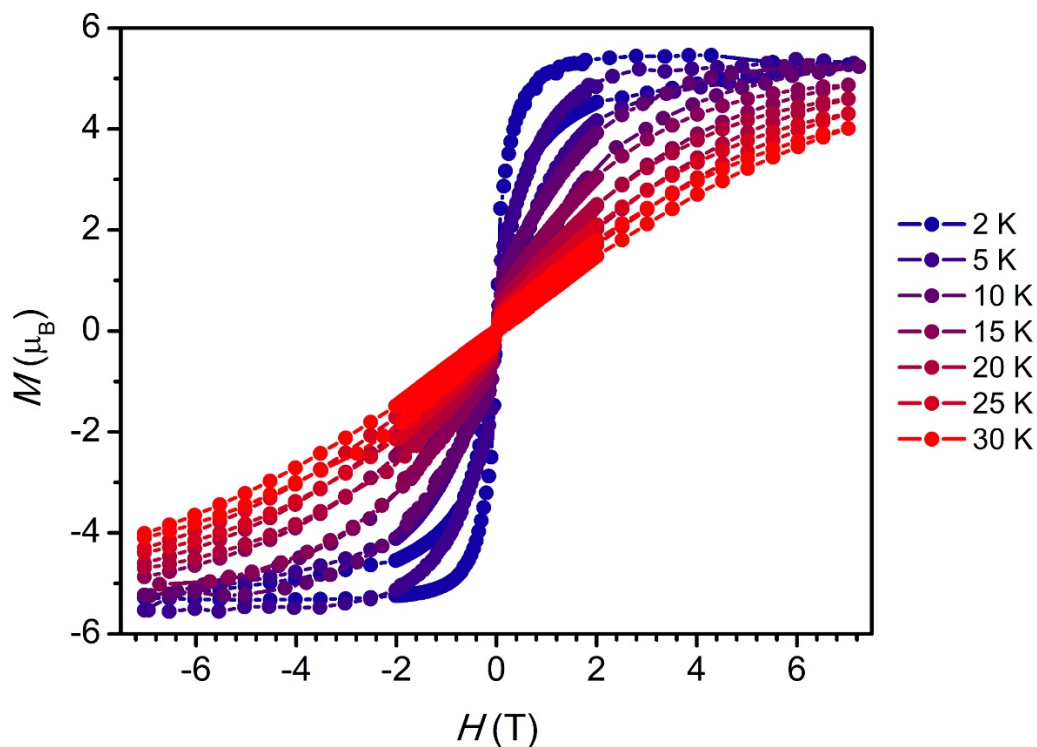


Figure S6.78. Magnetic hysteresis measurements of polycrystalline **3** from 2 to 30 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

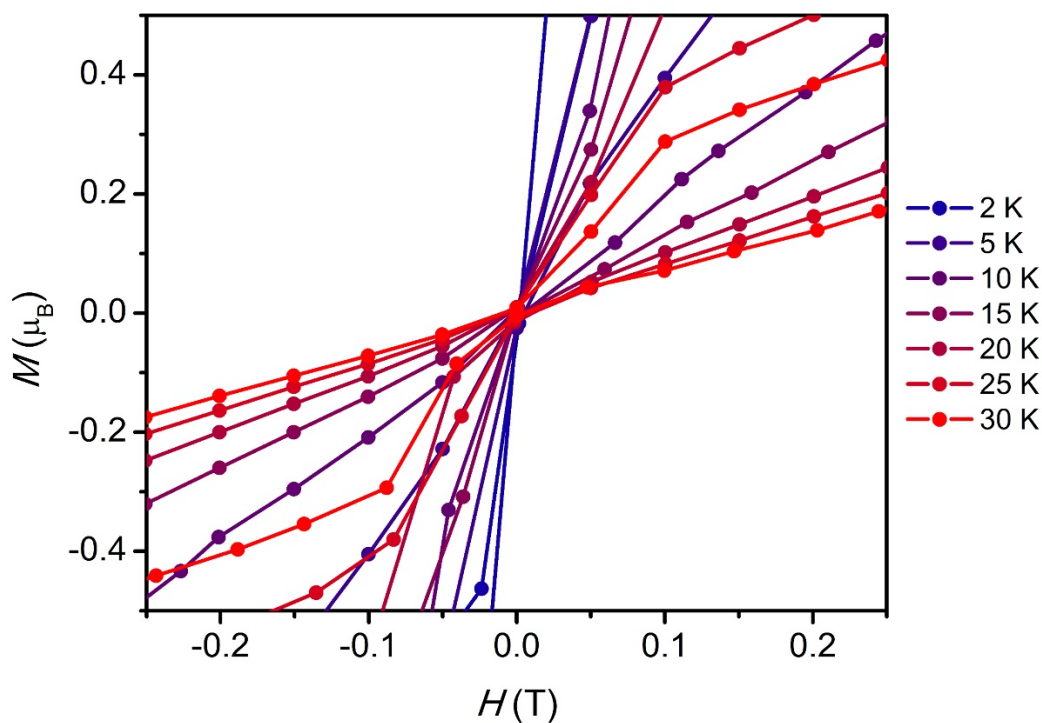


Figure S6.79. Magnetic hysteresis measurements of polycrystalline **3** from 2 to 30 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

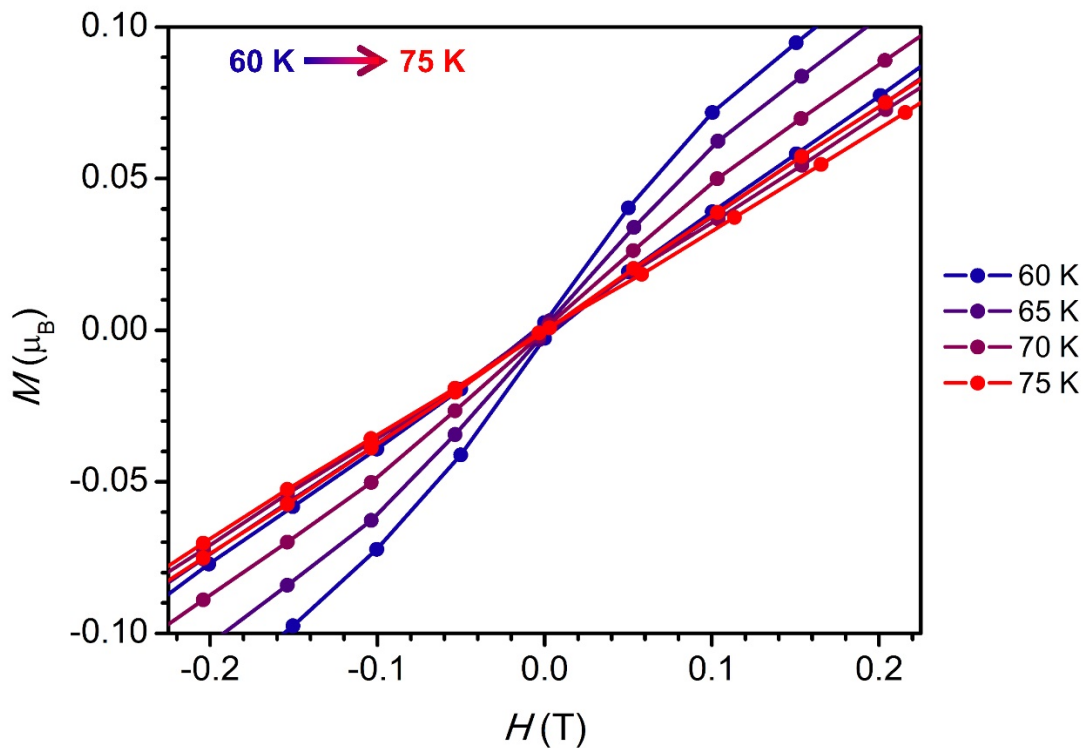


Figure S6.80. Magnetic hysteresis measurements of polycrystalline **3** from 60 to 75 K (5 K steps) at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

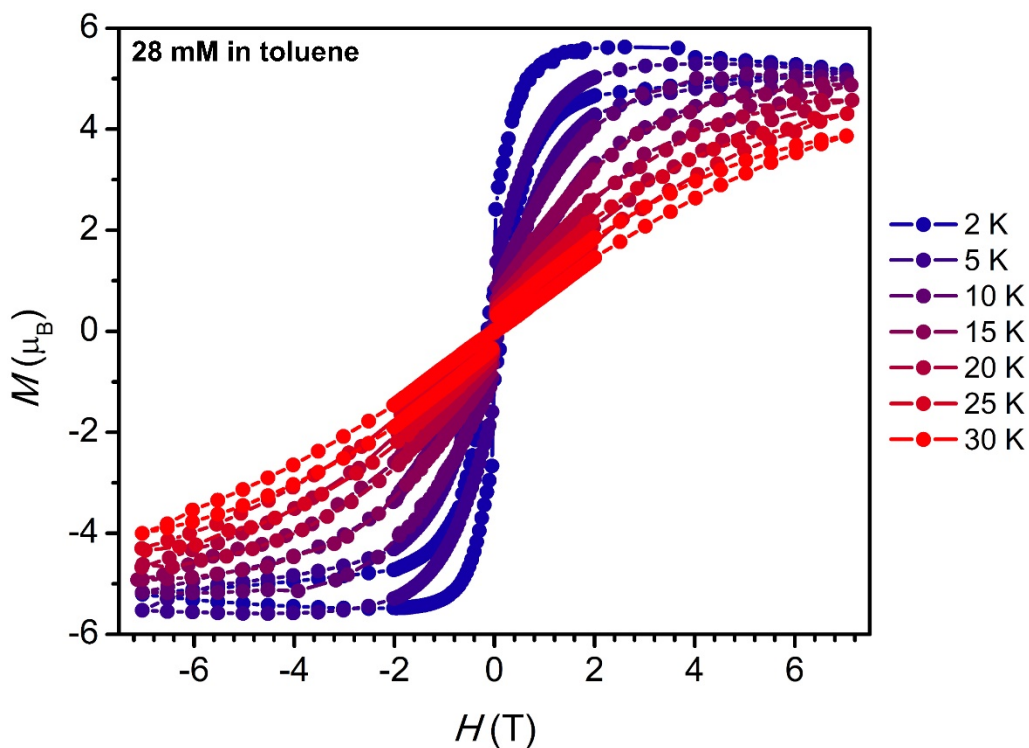


Figure S6.81. Magnetic hysteresis measurements of a 28 mM solution of **3** in toluene from 2 to 30 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

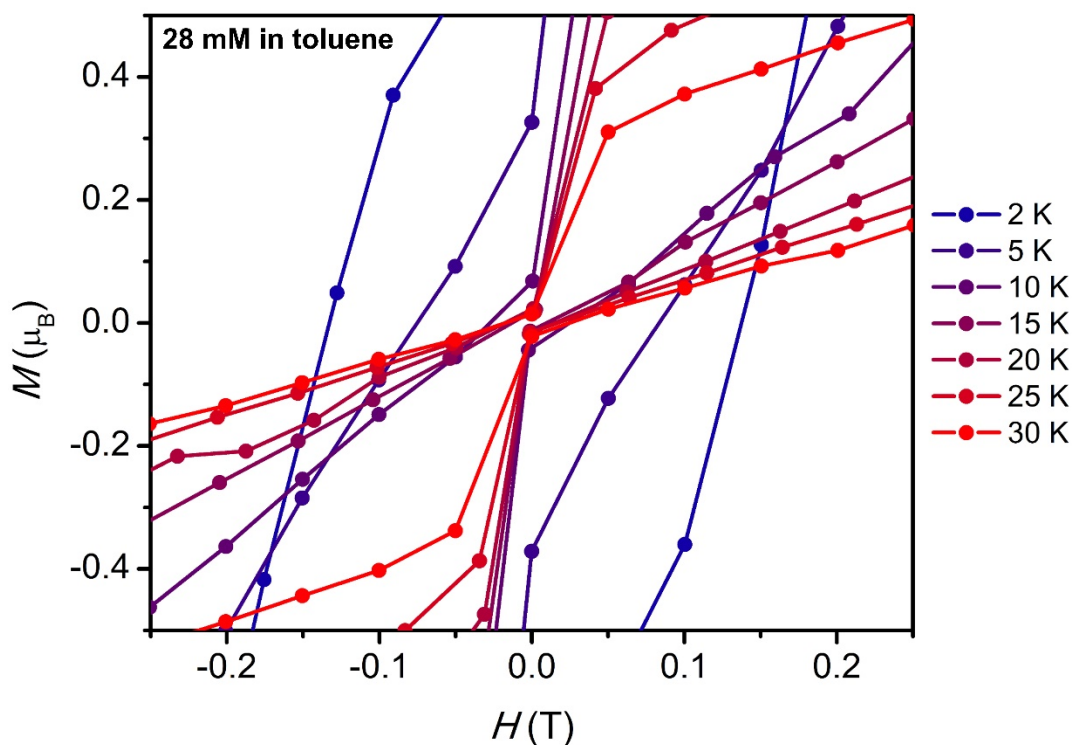


Figure S6.82. Magnetic hysteresis measurements of a 28 mM solution of **3** in toluene from 2 to 30 K at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

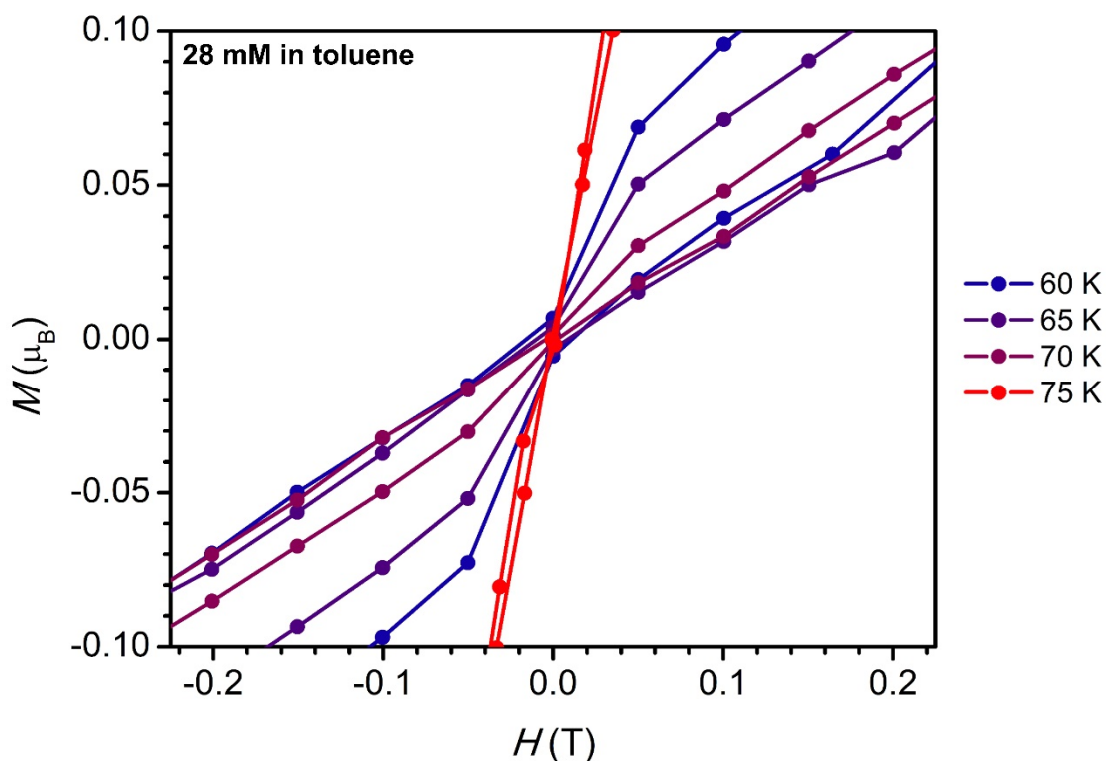


Figure S6.83. Magnetic hysteresis measurements of a 28 mM solution of **3** in toluene from 60 to 75 K (5 K steps) at a sweep rate of 14.7(1) mT/s for $H > 2$ T and 3.9(2) mT/s for $H < 2$ T.

6.6.5 Density Functional Theory Study

Structures were taken from x-ray crystallographic data of $\text{Tb}(\text{Cp}^{\text{iPr5}})_2$ as a starting point for the computational studies of $\text{Ln}(\text{Cp}^{\text{iPr5}})_2$ ($\text{Ln} = \text{Dy}, \text{Tb}$). These structures were optimized via Density Functional Theory (DFT) calculations to a geometry convergence tolerance of 10^{-4} a.u. and an electron density convergence tolerance of 10^{-7} . Quadrature grids of size 4 were used for integral evaluation. The TPSS meta-generalized gradient approximation (meta-GGA) density functional was used for structural optimizations.⁸ Grimme's D3 dispersion correction and the resolution of the identity (RI-J) approximation were also used for computations.^{9,10} In all cases, structural convergence was verified via vibrational analysis.¹¹

For $\text{Ln}(\text{Cp}^{\text{iPr5}})_2$ ($\text{Ln} = \text{Dy}, \text{Tb}$) with $4f^n 5d^1$ valence configurations, both the double- ζ quality split valence basis set with polarization functions (def2-SV(P)) and triple- ζ quality basis set (def2-TZVP) was used.^{12,13} In conjunction, an out-of-core quasi-relativistic def2 effective core potential (ECP) for the Ln atoms was also used.¹⁴

To obtain the relative energy differences between $4f^n 5d^1$ valence configurations where the d electron is aligned or not aligned with unpaired f electrons, Fermi smearing was performed with a starting temperature between 2000-3000 K and ending temperature of 100-200 K with an annealing factor of 0.85 to obtain ground state occupations. The occupation numbers were constrained during Fermi smearing to ensure the desired spin multiplicity.

For study of the $4f^{n+1}$ valence configurations, an f-in-core quasi-relativistic ECP was used with the corresponding basis set (SCecp-mwb) on metal to ensure that the $\text{Ln} = \text{Dy}, \text{Tb}$ atom housed all valence electrons in the 4f orbital.^{15,16} This ECP and basis was available from the Stuttgart-Cologne basis set and pseudopotential library.

Files with optimized atomic coordinates for each configuration of $\text{Ln}(\text{Cp}^{\text{iPr5}})_2$ ($\text{Ln} = \text{Dy}, \text{Tb}$) are attached to this SI, as well as the corresponding list of occupation numbers. Relative energies and metal-ligand distance are reported below.

Time-dependent DFT (TDDFT) calculations were performed for each electronic configuration to obtain excitation energies for $\text{Ln}(\text{Cp}^{\text{iPr5}})_2$ ($\text{Ln} = \text{Dy}, \text{Tb}$).^{17,18,19} These were done using the TPSS hybrid meta-GGA functional and the same choice of basis mentioned above. A convergence tolerance of 10^{-5} was used for the self-consistent procedure. Generation of visible absorption spectra was conducted with the lowest 10 excitations for each IR-active vibrational mode, or the lowest 55 if C_1 symmetry was adopted. Visualizing UV-Vis spectra was performed with a root mean square (RMS) width of 0.15 eV, a blue shift of 0.15 eV, and a vertical scaling of 0.5 eV. The blue-shift value is based on empirical observation of the performance of the TPSS functional.

Orbital visualization was performed with the VMD program with a contour value of 0.03.²⁰ All calculations in this study were performed with the TURBOMOLE 7.3 quantum chemistry package.²¹

Effective Core Potential information

Table S6.13. Number of electrons treated by f-out-of-core and f-in-core ECPs used with basis set.

<i>Ln</i>	<i>f-out-of-core</i> <i>def2-SV(P)/TZVP</i>	<i>f-in-core</i> <i>SCecp-mwb</i>
Dy	28	55
Tb	28	56

Computed properties of Dy(Cp^{iPr5})₂

Optimized structures for Dy(Cp^{iPr5})₂ were found to adopt both D₅ and S₁₀ point group symmetry. Comparison between the structures with both symmetries are included below. For 4fⁿ 5d¹ configurations, further comparison was made between septet and quintet spin multiplicities which were obtained by flipping the spin of the 5d¹ electron. Term symbols denoting the symmetry of the ground state configuration state function were determined by subduction of the direct product representation of the molecular point groups (S₁₀ and C₁) spanned by all occupied molecular orbitals.

Table S6.14. Structural and electronic properties of Dy(Cp^{iPr5})₂ calculated with def2-SV(P) basis set for 4fⁿ 5d¹ configurations. The SCecp-mwb basis set on Dy is used for 4fⁿ⁺¹ configurations.

<i>Point Group</i>	<i>Term Symbol</i>	<i>Main Config.</i>	<i>Relative Energy (eV)</i>	<i>Dy-Cp distance (Å)</i>
S ₁₀	⁷ A _g	4f ⁹ 5d ¹	0	2.482
S ₁₀	⁵ A _g	4f ⁹ 5d ¹	0.15	2.482
S ₁₀	⁵ A _u	[4f ¹⁰]*	-**	2.574
D ₅	⁷ A ₁	4f ⁹ 5d ¹	0.01	2.481
D ₅	⁵ A ₁	4f ⁹ 5d ¹	0.22	2.493
D ₅	⁵ A ₂	[4f ¹⁰]	-	2.547

*Brackets around the electron configuration indicate that the electrons corresponding to the orbital are located inside the core of the ECP.

**Relative energy is not compared for the 4fⁿ⁺¹ case as the number of explicitly included electrons, and thus the computed energy systematically differs.

Table S6.15. Structural and electronic properties of Dy(Cp^{iPr5})₂ with def2-TZVP basis set for 4fⁿ 5d¹ configurations. The SCecp-mwb basis set on Dy is used for 4fⁿ⁺¹ configurations.

<i>Point Group</i>	<i>Term Symbol</i>	<i>Main Config.</i>	<i>Relative Energy (eV)</i>	<i>Dy-Cp distance (Å)</i>
S ₁₀	⁷ A _g	4f ⁹ 5d ¹	0	2.487
S ₁₀	⁵ A _g	4f ⁹ 5d ¹	0.13	2.488
S ₁₀	⁵ A _u	[4f ¹⁰]	-	2.561
D ₅	⁷ A ₁	4f ⁹ 5d ¹	0.01	2.489
D ₅	⁵ A ₁	4f ⁹ 5d ¹	0.15	2.484
D ₅	⁵ A ₂	[4f ¹⁰]	-	2.560

Comparison of Dy-Cp distances from DFT optimized Dy(Cp^{iPr5})₂ structures between the 4fⁿ 5d¹ and 4fⁿ⁺¹ electronic configuration support the experimentally observed lengthening on the order of 5.0x10⁻² Å. These results are in line with previous studies and reinforces the observed 4fⁿ 5d¹ configuration (see full text).²²

Energy differences between the septet and quintet spin multiplicities of the 4fⁿ 5d¹ electron configurations were found to be roughly 0.15 eV, which may indicate a preference towards the high-spin state in the scalar-relativistic picture. Energy differences between Dy(Cp^{iPr5})₂ in the D₅ and S₁₀ point group fall within 0.01 eV, and thus are considered roughly isoenergetic.

Table S6.16. Natural population analysis conducted for the ⁷A₁ term symbol for Dy(Cp^{iPr5})₂.²³

<i>Atom</i>	<i>n(s)</i>	<i>n(p)</i>	<i>n(dz²)</i>	<i>n(d rest)[*]</i>
Dy	0.6947	0	0.1816	0
C ^{**}	0.0068	0.0528	0	0

* Includes natural occupancies from all other d orbitals besides z²

** Represents summed contribution from the 10 Carbon atoms located on the two Cp rings.

Calculation of natural orbital populations for the HOMO revealed significant 6s mixing and small contributions originating from ligand p orbitals. Although the ratio of s to d character seems high, population analysis schemes often largely overestimate the relative s contribution. Mixing from ligand orbitals lead to stabilization of the 5dz² orbital as the HOMO, and the ordering of 5d energies thus differs from the traditional textbook picture. The present results are however supported both from photoionization profiles and more recent computational studies of ferrocene.^{24,25}

Table S6.17. Comparison of significant electronic excitations (> 0.0015 osc str.) for S10 term symbols computed with TDDFT and the TPSS functional. Blue shifted results are also included in parentheses. For these calculations, a triple-ζ quality basis set (def2-TZVP) was used for the metal and a double-ζ quality basis set (def2-SV(P)) for the ligand atoms.

<i>Term Symbol</i>	<i>Wavelength (nm)</i>	<i>Oscillator Str.</i>	<i>Occ-virt orbital transition</i>	<i>Occupied (virtual) energy (eV)</i>	<i>Type of excitation</i>
⁷ A _g	739.0 (678.4)	0.00641	32e _{2u} →34e _{1g}	-2.43 (-0.65)	4f→5d
	403.8 (385.0)	0.01505	38e _{1u} →34e _{1g}	-4.41 (-1.32)	LMCT*
	370.6 (354.7)	0.00539	34e _{2u} →34e _{1g}	-4.80 (-1.32)	4f→5d
	366.9 (351.3)	0.00387	36e _{1u} →20a _g	-4.47 (-1.03)	LMCT
	327.5 (315.0)	0.00256	38e _{1u} →21a _g	-4.77 (-0.08)	LMCT
	325.1 (312.8)	0.00855	34e _{2g} →38e _{1u}	-4.85 (-1.01)	LMCT
	318.5 (306.7)	0.04980	36e _{1u} →34e _{1g} (46%)	-4.47 (-0.65)	LMCT

			38e _{1u} →21a _g (50%)	-4.41 (-0.54)	
	294.0 (283.9)	0.01806	20a _g →40e _{1u}	-3.94 (0.31)	MLCT**
	292.2 (282.2)	0.00480	32e _{2u} →38e _{1g}	-2.43 (1.85)	LMCT
⁵ A _g	937.9 (842.3)	0.00575	32e _{2u} →34e _{1g}	-3.48 (-0.72)	4f→5d
	419.3 (399.1)	0.00285	38e _{1u} →20a _g (44%)	-4.39 (-1.39)	LMCT
			34e _{2g} →19a _u (45%)	-4.88 (-1.92)	
	345.8 (331.9)	0.05037	38e _{1u} →34e _{1g} (42%)	-4.39 (-0.94)	LMCT
			36e _{1u} →34e _{1g} (41%)	-4.49 (-1.07)	
	334.0 (321.0)	0.01010	34e _{2g} →38e _{1u}	-4.88 (-1.13)	LMCT
	312.7 (301.3)	0.02200	20a _g →40e _{1u}	-3.66 (0.32)	MLCT
	294.1 (284.0)	0.09671	20a _g →20a _u	-3.66 (0.55)	MLCT
⁵ A _u	383.5 (368.3)	0.00829	34e _{1u} →18a _g	-4.28 (-1.02)	LMCT
	313.7 (302.2)	0.06953	34e _{1u} →32e _{1g}	-4.28 (-0.49)	LMCT

*Ligand to metal charge transition

**Metal to ligand charge transition

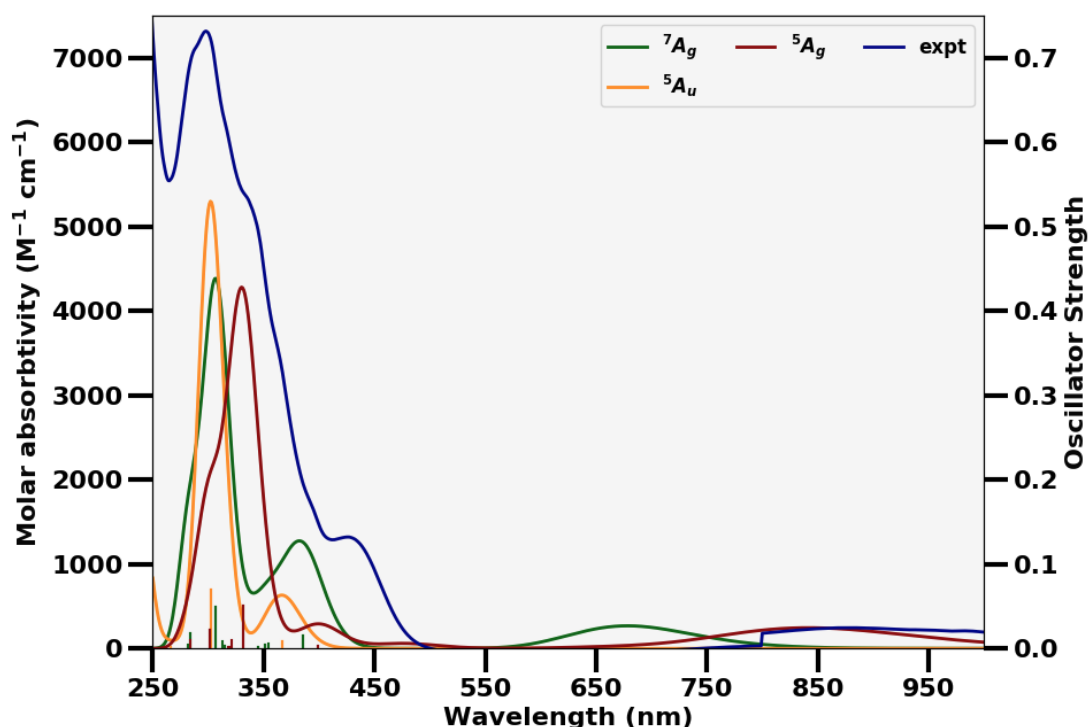
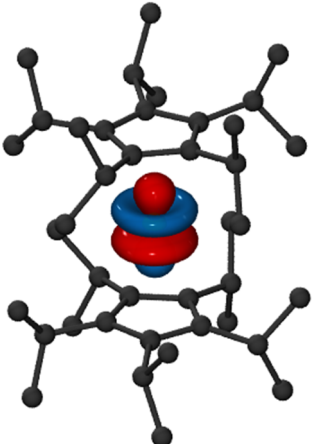
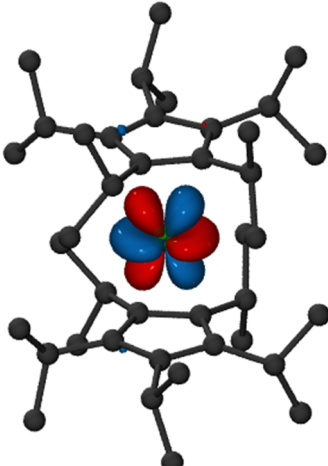
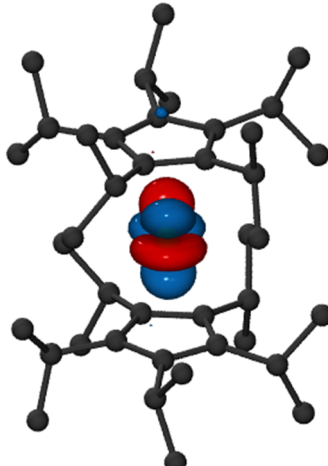


Figure S6.84. Computed UV-Vis spectra for $\text{Dy}(\text{Cp}^{\text{iPr}5})_2$ with corresponding term symbols in the S_{10} point group. A RMS width of 0.15 eV, a blue shift of 0.15 eV, and a vertical scaling of 0.5 eV was used. Information regarding individual excitations can be found in **Table S6.17**.

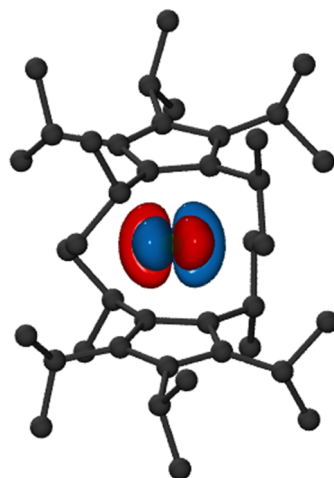
Intense peaks found at around 430 nm and 296 nm in the experimental spectra were predicted as blue-shifted ligand-metal charge transfer excitations through DFT. Between predicted spectra for the 7A_g , 5A_g , and 5A_u term symbols, the two aforementioned peaks occurred in roughly the same locations (although the 5A_g spectra was blue-shifted away from the other two). Broad peaks near the red end of the visible spectrum were found around 680 nm and 840 nm for the 7A_g and 5A_g terms, which were predicted to be due to a 4f to 5d excitation. This peak is notably absent in the 5A_u term, possibly due to the $5d_{z^2}$ orbital sitting further above the 4f orbitals in energy for the $4f^{n+1}$ configuration. These peaks may correspond to that located around 850 nm from the experimentally obtained spectra, and could thus lend further credibility to identifying the suspected $4f^n 5d^1$ configuration.

Table S6.18. Computed metal-centered 4f and 5d molecular orbitals and energies (in eV) for term symbol 7A_1 with def2-TZVP basis. The other 4fⁿ 5d¹ terms in both S10 and D5 yield nearly identical MOs.

<i>Orbital</i>	<i>Energy (eV)</i>	
19 a ₂	-6.70	
34 e ₁	-6.55	
34 e ₁	-6.55	

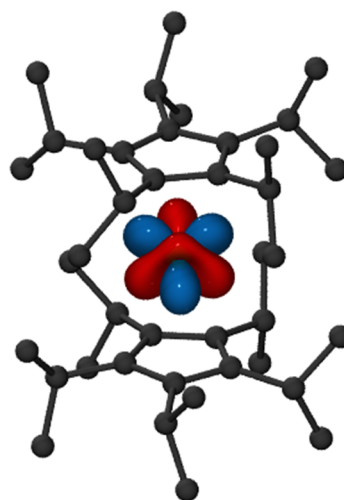
32 e₂

-5.81



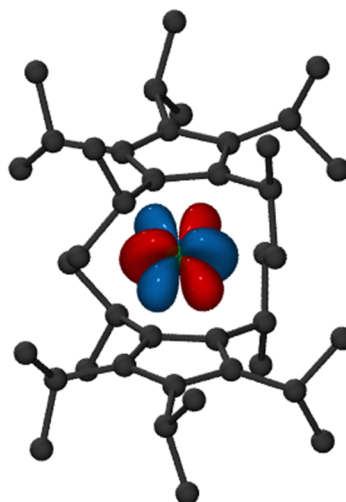
32 e₂

-5.81



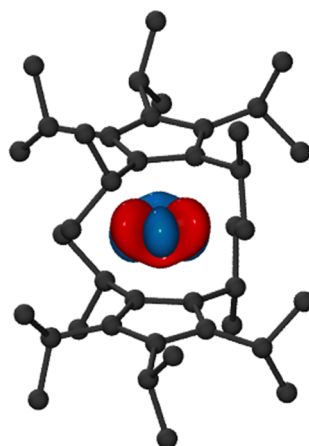
33 e₂

-4.77



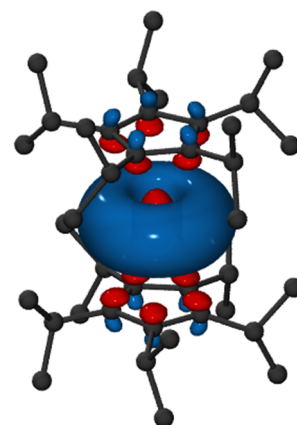
33 e₂

-4.77



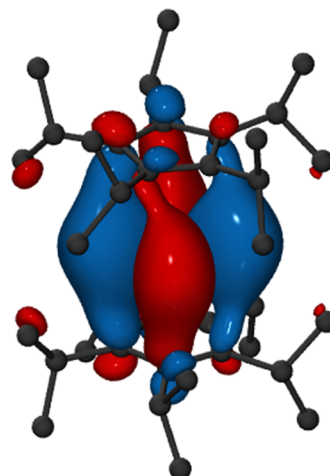
20 a₁

-3.94



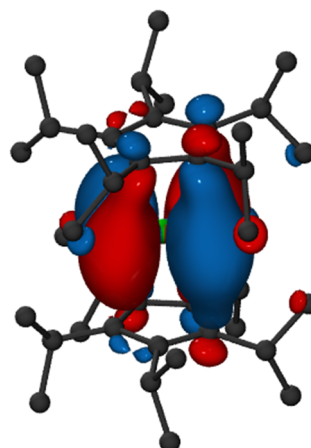
34 e₂

-1.31



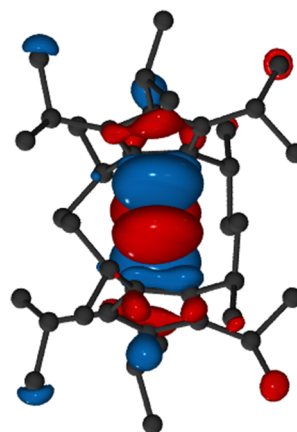
34 e₂

-1.31



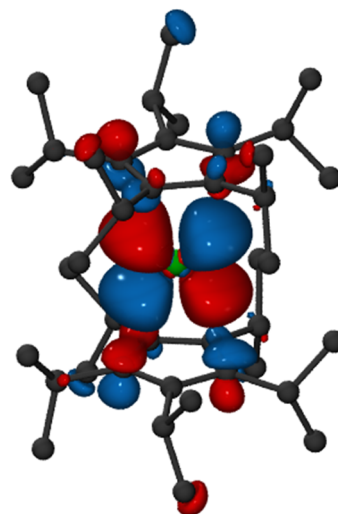
40 e₁

1.60



40 e₁

1.60



Computed properties of Tb(Cp^{iPr5})₂

Optimized geometries for Tb(Cp^{iPr5})₂ were found to have C₁ symmetry, which differs from the Dy(Cp^{iPr5})₂ complex above. This is possibly due to the observance of Jahn-Teller effects from partial occupation of degenerate e orbitals in the S10 and D5 symmetries.

Table S6.19. Structural and electronic properties of Tb(Cp^{iPr5})₂ with def2-SV(P) basis set for 4fⁿ 5d¹ configurations and SCecp-mwb basis set for 4fⁿ⁺¹ configurations.

<i>Point Group</i>	<i>Term Symbol</i>	<i>Main Config.</i>	<i>Relative Energy (eV)</i>	<i>Tb-Cp distance(Å)</i>
C ₁	⁸ A	4f ⁸ 5d ¹	0	2.492
C ₁	⁶ A	4f ⁸ 5d ¹	0.15	2.476
C ₁	⁶ A	[4f ⁹] [*]	-	2.600

^{*}As before, brackets around the electron configuration indicate that the electrons corresponding to the orbital are located inside the core of the ECP.

Table S6.20. Structural and electronic properties of Tb(Cp^{iPr5})₂ with def2-TZVP basis set for 4fⁿ 5d¹ configurations and SCecp-mwb basis set for 4fⁿ⁺¹ configurations.

<i>Point Group</i>	<i>Term Symbol</i>	<i>Main Config.</i>	<i>Relative Energy (eV)</i>	<i>Tb-Cp distance (Å)</i>
C ₁	⁸ A	4f ⁸ 5d ¹	0	2.520
C ₁	⁶ A	4f ⁸ 5d ¹	0.11	2.493
C ₁	⁶ A	[4f ⁹]	-	2.588

Relative energy differences between ⁸A and ⁶A term symbols show similar preference for spin multiplicities in the 4f⁸ 5d¹ configuration. However, the difference is again small (on the order of 2 kcal/mol), and within the accuracy range that DFT typically performs. Comparison of Tb-Cp distances between the 4f⁸ 5d¹ and 4f⁹ electronic configurations again support experimentally observed lengthening, although the computed change is closer to 0.1 Å. These results suggest adoption of the 4f⁹ 5d¹ configuration.

Table S6.21. Natural population analysis conducted for the ⁸A term symbol of Tb(Cp^{iPr5})₂.

<i>Atom</i>	<i>n(s)</i>	<i>n(p)</i>	<i>n(dz²)</i>	<i>n(d rest)[*]</i>
Tb	0.7261	0	0.1555	0
C ^{**}	0.0073	0.0394	0	0

^{*} Includes natural occupancies from all other d orbitals

^{**} Represents summed contribution from the 10 Carbon atoms located on the two Cp rings.

Similar results are observed as from the population analysis as that for Dy(Cp^{iPr5})₂, with the HOMO s orbital stabilization of the 5d z² HOMO. P orbital contributions from the ligand serve to further stabilize the orbital relative to the other 5d orbitals. While the ratio of s to d character is again uncharacteristically high, we attribute this to overestimation of s contributions in the natural population analysis method.

Table S6.22. Comparison of significant electronic excitations (> 0.0015) from the first 55 for C_1 , term symbols computed with TDDFT using the TPSS functional. Blue shifted results are also included in parentheses. A double- ζ quality basis set (def2-SV(P)) was used for these response calculations due to reference instabilities with the triple- ζ quality basis.

<i>Term Symbol</i>	<i>Wavelength (nm)</i>	<i>Oscillator Str.</i>	<i>Occ-virt orbital transition</i>	<i>Occupied (virtual) energy (eV)</i>	<i>Type of excitation</i>
8A	450.2 (426.9)	0.00297	176 a $\rightarrow$ 178 a	-4.29 (-1.48)	LMCT
	447.6 (424.6)	0.00243	175 a $\rightarrow$ 178 a	-4.31 (-1.48)	LMCT
	430.5 (409.2)	0.01223	176 a $\rightarrow$ 179 a	-4.29 (-1.38)	LMCT
	429.6 (408.4)	0.00886	175 a $\rightarrow$ 179 a	-4.31 (-1.38)	LMCT
	420.8 (400.4)	0.00744	170 a $\rightarrow$ 189 a	-1.27 (1.70)	MLCT
	418.5 (398.3)	0.00175	170 a $\rightarrow$ 190 a	-1.27 (1.70)	MLCT
	416.7 (396.7)	0.00192	174 a $\rightarrow$ 178 a	-4.56 (-1.48)	4f $\rightarrow$ 5d
	401.6 (383.0)	0.00314	174 a $\rightarrow$ 179 a	-4.56 (-1.38)	4f $\rightarrow$ 5d
	371.0 (355.1)	0.00430	170 a $\rightarrow$ 196 a	-1.27 (2.10)	4f $\rightarrow$ 5d
	349.6 (335.4)	0.00467	169 a $\rightarrow$ 171 a	-4.42 (-0.82)	LMCT
	349.5 (335.3)	0.00442	168 a $\rightarrow$ 171 a	-4.42 (-0.82)	LMCT
	329.3 (316.6)	0.00622	169 a $\rightarrow$ 173 a (46%)	-4.42 (-0.61)	LMCT
			176 a $\rightarrow$ 180 a (30%)	-4.29 (-0.44)	LMCT
	329.2 (316.6)	0.00768	168 a $\rightarrow$ 173 a	-4.42 (-0.61)	LMCT
	320.7 (308.7)	0.03444	176 a $\rightarrow$ 180 a	-4.29 (-0.44)	LMCT
	319.4 (307.5)	0.03442	175 a $\rightarrow$ 180 a	-4.31 (-0.44)	LMCT
$^6A\ 4f^n\ 5d^1$	415.8 (395.9)	0.00290	175 a $\rightarrow$ 177 a	-4.29 (-1.25)	LMCT
	416.6 (396.6)	0.00291	176 a $\rightarrow$ 177 a	-4.29 (-1.25)	LMCT
	370.1 (354.2)	0.00176	169 a $\rightarrow$ 172 a (28%)	-4.44 (-1.08)	LMCT

			168 a $\rightarrow$ 172 a (19%)	-4.44 (-1.08)	LMCT
			168 a $\rightarrow$ 173 a (18%)	-4.44 (-1.00)	LMCT
370.0 (354.1)	0.00174		168 a $\rightarrow$ 172 a (29%)	-4.44 (-1.08)	LMCT
			169 a $\rightarrow$ 172 a (19%)	-4.44 (-1.08)	LMCT
			169 a $\rightarrow$ 173 a (18%)	-4.44 (-1.00)	LMCT
360.0 (345.0)	0.00774		167 a $\rightarrow$ 171 a	-4.85 (-1.37)	LMCT
360.0 (345.0)	0.00854		166 a $\rightarrow$ 171 a	-4.85 (-1.36)	LMCT
354.7 (340.1)	0.02083		173 a $\rightarrow$ 177 a	-4.86 (-1.25)	LMCT
354.5 (340.0)	0.01968		172 a $\rightarrow$ 177 a	-4.86 (-1.25)	LMCT
354.3 (339.7)	0.01770		173 a $\rightarrow$ 177 a	-4.86 (-1.25)	LMCT
354.1 (339.6)	0.00679		172 a $\rightarrow$ 177 a	-4.86 (-1.25)	LMCT
353.6 (339.1)	0.00524		174 a $\rightarrow$ 179 a	-4.62 (-1.04)	4f $\rightarrow$ 5d
340.1 (326.7)	0.00407		170 a $\rightarrow$ 178 a	-3.56 (0.17)	5d $\rightarrow$ 4f
320.9 (308.9)	0.01209		170 a $\rightarrow$ 179 a	-3.56 (0.40)	5d $\rightarrow$ 4f
317.7 (305.9)	0.00976		170 a $\rightarrow$ 180 a	-3.56 (0.44)	5d $\rightarrow$ 4f
291.3 (281.4)	0.01350			-3.56 (0.73)	MLCT
291.0 (281.1)	0.01358		170 a $\rightarrow$ 181 a	-3.56 (0.74)	MLCT
286.6 (277.0)	0.00885		170 a $\rightarrow$ 182 a	-4.44 (-0.09)	LMCT
286.5 (276.4)	0.00891		169 a $\rightarrow$ 177 a	-4.44 (-0.09)	LMCT
282.9 (273.5)	0.00301		168 a $\rightarrow$ 177 a	-5.71 (-1.25)	4f $\rightarrow$ 5d
			170 a $\rightarrow$ 177 a		
⁶ A 4f ⁿ⁺¹	386.6 (369.3)	0.0070	160 a $\rightarrow$ 161 a	-4.25 (-1.03)	LMCT
	320.3 (308.4)	0.0602	160 a $\rightarrow$ 163 a	-4.25 (-0.52)	LMCT

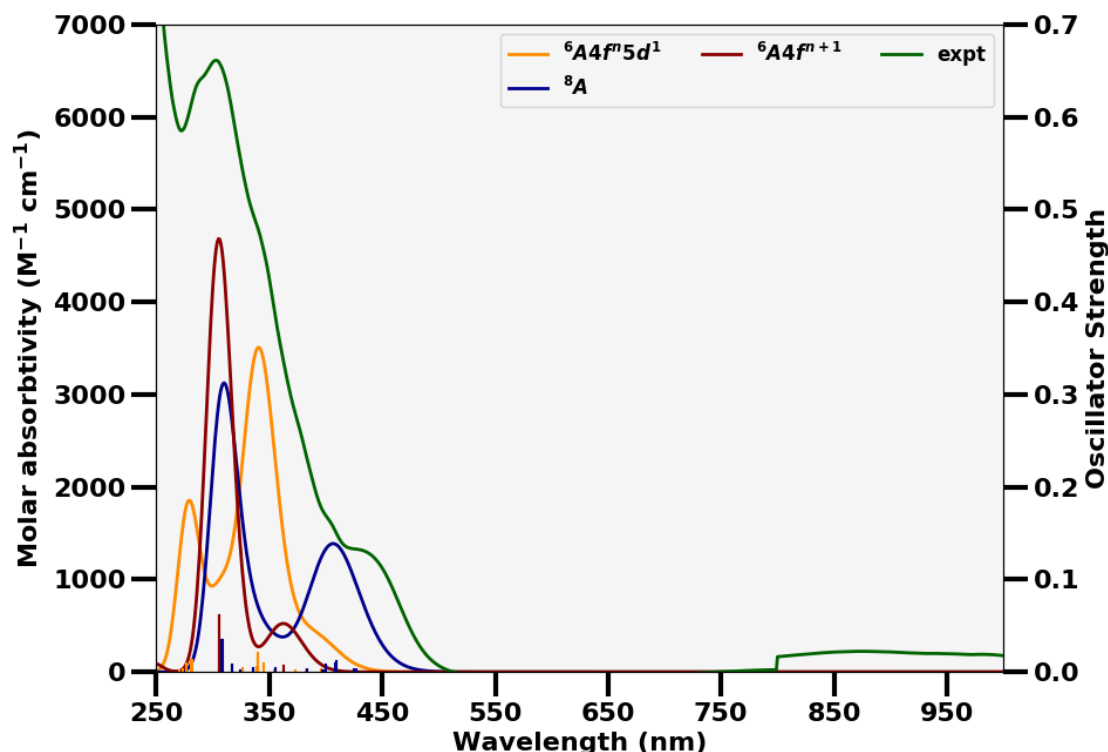
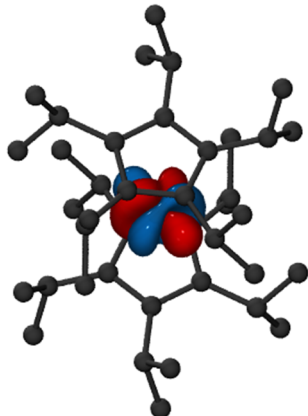
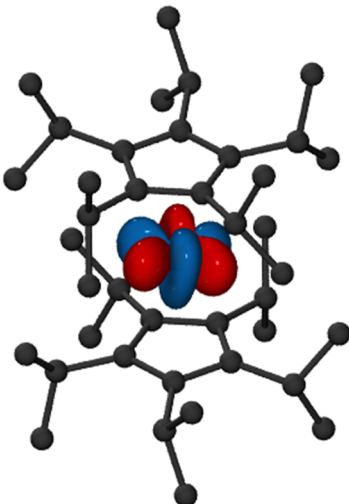
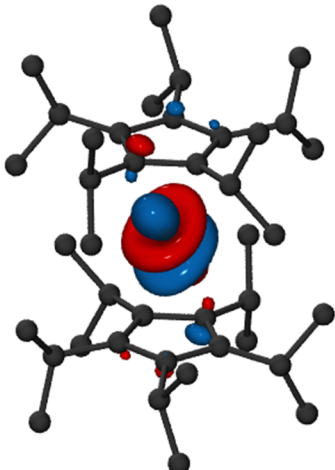


Figure S6.85. Computed UV-Vis spectra for $\text{Tb}(\text{Cp}^{\text{iPr}_5})_2$ with corresponding term symbols in the C_1 point group. A RMS width of 0.15 eV, a blue shift of 0.15 eV, and a vertical scaling of 0.5 eV was used. Details for each individual excitation can be found in **Table S6.22**.

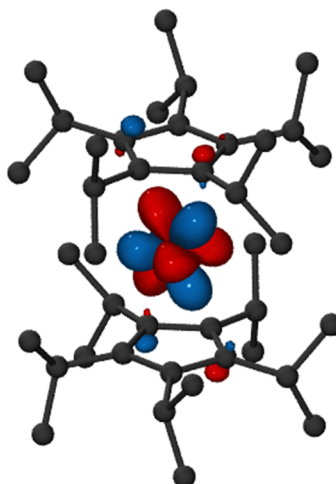
Due to instabilities in the TD-DFT routine, electronic excitations were unable to be computed with a triple- ζ quality basis set on the metal atom, so the def2-SV(P) basis was used. The obtained experimental UV-Vis spectrum is similar to that of $\text{Dy}(\text{Cp}^{\text{iPr}_5})_2$, with two primary peaks predicted to correspond to ligand-metal charge transfer excitations. The spectra predicted with DFT for the ^8A and ^6A terms also correspond well with the Dy case despite being limited to a smaller basis. The $^6\text{A } 4f^n5d^1$ spectrum is again red-shifted from the other two predicted spectra. The ligand-metal excitation is however much weaker than that of the others. There is also an absence of metal-metal excitations with longer wavelengths, as seen in the $\text{Dy}(\text{Cp}^{\text{iPr}_5})_2$ case. This is likely due to the smaller basis set used for the lanthanide atom. The $^8\text{A } 4f^n5d^1$ again qualitatively matches the experimental spectrum better than that of the $4f^{n+1}$ configuration.

Table S6.23. Computed metal-centered 4f and 5d molecular orbitals and energies (in eV) for term symbol 8A with def2-TZVP basis. The other $4f^n 5d^1$ term yields nearly identical MOs. Note that orbital numbering does not necessarily correspond to other term symbols.

<i>Orbital</i>	<i>Energy (eV)</i>	
166 a	-5.80	
167 a	-5.79	
168 a	-5.74	

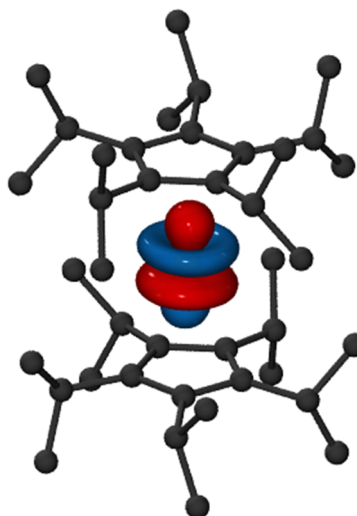
169 a

-5.69



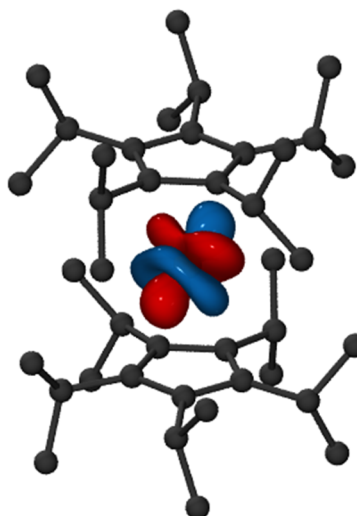
170 a

-5.68



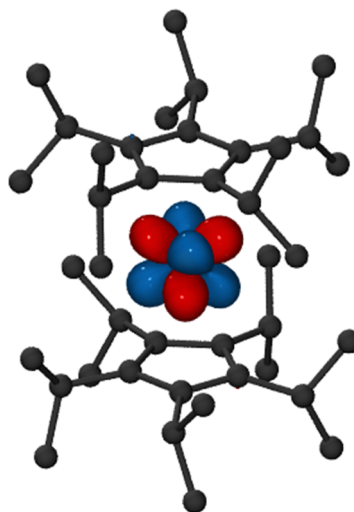
171 a

-5.60



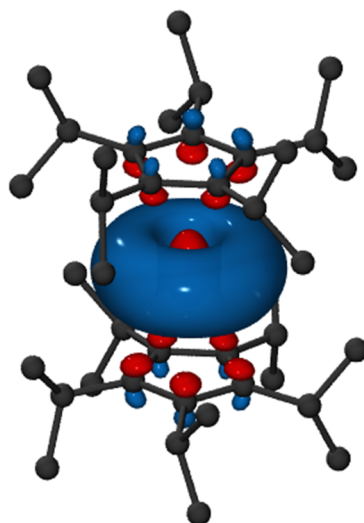
174 a

-4.58



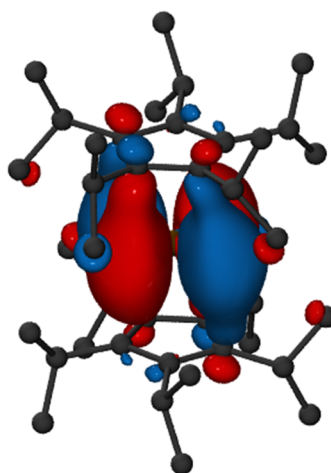
177 a

-3.90



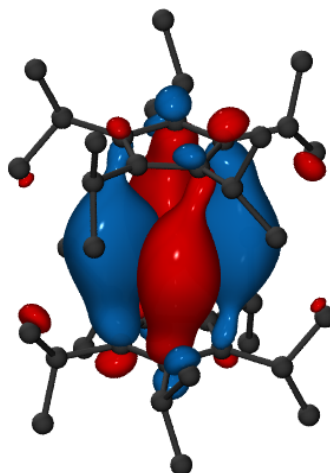
178 a

-1.47



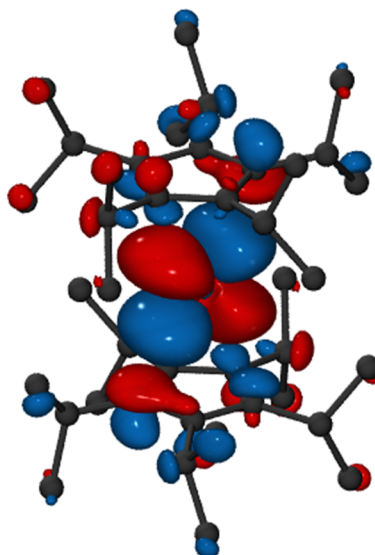
194 b

1.72



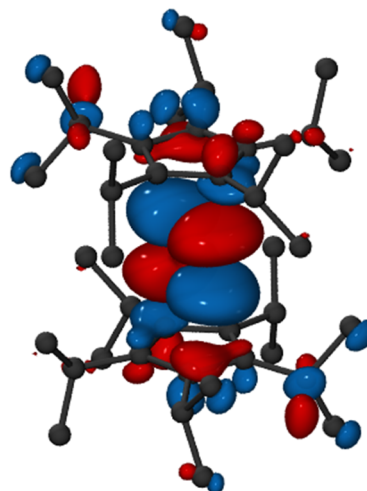
195 b

1.72



196 a

1.93



6.6.6 Supplementary Information References

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