



Isotopologue Engineering: Nuclear Spin Effects on the Magnetic Properties of Lanthanide Complexes

Zur Erlangung des akademischen Grades eines

DOKTORS DER NATURWISSENSCHAFTEN
(Dr. rer. nat.)

von der KIT-Fakultät für Chemie und Biowissenschaften
des Karlsruher Instituts für Technologie (KIT)

genehmigte
DISSERTATION

von

M. Eng., Yaorong Chen

1. Referent: Prof. Dr. Mario Ruben

2. Referentin: Prof. Dr. Annie K. Powell

Tage der mündlichen Prüfung: 16.07.2026

Eidesstattliche Erklärung

Die eidesstattliche Versicherung ist in der Regel schriftlich abzugeben. Die Möglichkeit einer Aufnahme der eidesstattlichen Versicherung zur Niederschrift bleibt unberührt. Die schriftliche Erklärung hat folgenden Wortlaut:

Eidesstattliche Versicherung gemäß § 13 Absatz 2 Ziffer 3 der Promotionsordnung des Karlsruher Instituts für Technologie für die KIT-Fakultät für Chemie und Biowissenschaften:

1. Bei der eingereichten Dissertation zu dem Thema

Isotopologue Engineering: Nuclear Spin Effects on the Magnetic Properties of Lanthanide Complexes

handelt es sich um meine eigenständig erbrachte Leistung.

2. Ich habe nur die angegebenen Quellen und Hilfsmittel benutzt und mich keiner unzulässigen Hilfe Dritter bedient. Insbesondere habe ich wörtlich oder sinngemäß aus anderen Werken übernommene Inhalte als solche kenntlich gemacht.

3. Die Arbeit oder Teile davon habe ich bislang nicht an einer Hochschule des In- oder Auslands als Bestandteil einer Prüfungs- oder Qualifikationsleistung vorgelegt.

4. Die Richtigkeit der vorstehenden Erklärungen bestätige ich.

5. Die Bedeutung der eidesstattlichen Versicherung und die strafrechtlichen Folgen einer unrichtigen oder unvollständigen eidesstattlichen Versicherung sind mir bekannt.

Ich versichere an Eides statt, dass ich nach bestem Wissen die reine Wahrheit erklärt und nichts verschwiegen habe.

Ort und Datum

Unterschrift

Eidesstattliche Versicherung Belehrung

Die Universitäten in Baden-Württemberg verlangen eine Eidesstattliche Versicherung über die Eigenständigkeit der erbrachten wissenschaftlichen Leistungen, um sich glaubhaft zu versichern, dass der Promovend die wissenschaftlichen Leistungen eigenständig erbracht hat.

Weil der Gesetzgeber der Eidesstattlichen Versicherung eine besondere Bedeutung beimisst und sie erhebliche Folgen haben kann, hat der Gesetzgeber die Abgabe einer falschen eidesstattlichen Versicherung unter Strafe gestellt. Bei vorsätzlicher (also wissentlicher) Abgabe einer falschen Erklärung droht eine Freiheitsstrafe bis zu drei Jahren oder eine Geldstrafe.

Eine fahrlässige Abgabe (also Abgabe, obwohl Sie hätten erkennen müssen, dass die Erklärung nicht den Tatsachen entspricht) kann eine Freiheitsstrafe bis zu einem Jahr oder eine Geldstrafe nach sich ziehen.

Die entsprechenden Strafvorschriften sind § 156 StGB (falsche Versicherung an Eides Statt) und § 161 StGB (fahrlässiger Falscheid, fahrlässige falsche Versicherung an Eides Statt).

§ 156 StGB: Falsche Versicherung an Eides Statt Wer vor einer zur Abnahme einer Versicherung an Eides Statt zuständigen Behörde eine solche Versicherung falsch abgibt oder unter Berufung auf eine solche Versicherung falsch aussagt, wird mit Freiheitsstrafe bis zu drei Jahren oder mit Geldstrafe bestraft.

§ 161 StGB: Fahrlässiger Falscheid, fahrlässige falsche Versicherung an Eides Statt Absatz 1: Wenn eine der in den § 154 bis 156 bezeichneten Handlungen aus Fahrlässigkeit begangen worden ist, so tritt Freiheitsstrafe bis zu einem Jahr oder Geldstrafe ein. Absatz 2: Straflosigkeit tritt ein, wenn der Täter die falsche Angabe rechtzeitig berichtigt. Die Vorschriften des § 158 Absatz 2 und 3 gelten entsprechend.

Ort und Datum

Unterschrift

Versicherung gemäß § 13 Absatz 2 Satz 2 Ziffer 5 der Promotionsordnung des Karlsruher Instituts für Technologie (KIT) für die KIT-Fakultät für Chemie und Biowissenschaften

1. Einen erheblichen Verstoß gegen die Grundsätze guter wissenschaftlicher Praxis habe ich bislang nicht begangen.
2. Es gab bisher keine Promotionseignungsprüfung oder gleichwertige Prüfung an einer Universität oder dieser gleichgestellten Hochschule, an der ich erfolglos teilgenommen habe.
3. Diesem Promotionsverfahren gingen keine anderen Promotionsverfahren voran und ich bin in keinen weiteren Promotionsverfahren Kandidat.
4. Ein entgeltliches Vertragsverhältnis, das eine gewerbliche Promotionsberatung zum Gegenstand hat und zur Unselbstständigkeit zumindest einer Promotionsleistung führen kann, besteht bzw. bestand nicht.
5. Die „Regeln zur Sicherung guter wissenschaftlicher Praxis am Karlsruher Institut für Technologie (KIT)“ habe ich beachtet.
6. In die Dissertation wurden Vorveröffentlichungen einbezogen, bei denen ich im Rahmen einer Mitautorenschaft jeweils einen signifikanten Teil selbstständig erbracht habe. Eine Aufstellung mit den Angaben:
Autoren/Autorinnen:
Titel der Vorveröffentlichung:
Veröffentlicht in:
Ausführliche Darlegung des selbstständig erbrachten, signifikanten Beitrages der Vorveröffentlichung oder der zur Veröffentlichung eingereichten Arbeit:
ist dieser Erklärung beigelegt. Die Aufstellung ist Bestandteil dieser Erklärung.
7. Die Dissertation oder Teile davon wurden nicht bei einer anderen Fakultät als Dissertation eingereicht.
8. Die Richtigkeit der vorstehenden Erklärungen bestätige ich.

Ort und Datum

Unterschrift

Declaration

I hereby declare that:

1. I have authored the present work independently.
2. This thesis has not been submitted to any other university.
3. I have not used sources other than those specified and cited in the bibliography.
4. Where I have consulted the published work of others, this is always clearly attributed.
5. The electronic version of the work is consistent with the written version.
6. I have acknowledged all main sources of help.

The presented work was carried out at Karlsruhe Institute of Technology under the supervision of Prof. Dr. Mario Ruben.

Table of Contents

Acknowledgements	1
Abbreviations used	3
Abstract	4
Zusammenfassung	6
Chapter 1. Introduction	8
1.1 Lanthanide elements	9
1.2 Single-molecule magnets.....	14
1.2.1 Lanthanide single-molecule magnets.....	14
1.2.2 Relaxation mechanism of single-molecule magnets.....	16
1.3 Lanthanide-based single-molecule magnets	21
1.3.1 Mononuclear lanthanide-based single-molecule magnets	21
1.3.2 Multinuclear lanthanide-based single-molecule magnets	22
1.3.3 3d-4f hybrid lanthanide-based single-molecule magnets.....	25
1.3.4 Radical-contained lanthanide-based single-molecule magnets.....	26
1.4 Strategies for designing lanthanide-based single-molecule magnets	28
1.4.1 Molecular structure symmetry	28
1.4.2 Hyperfine interactions.....	34
1.4.3 The strength of the ligand field	40
1.4.4 Intermolecular interactions and dipole-dipole interactions.....	43
1.4.5 Molecular vibrations	47
1.5 Qubit.....	51
1.5.1 Mechanism of spin qubits	52
1.5.2 Progress on lanthanide-based qubits	53
Chapter 2. Isotopologue Ligands: Magnetic Properties of D-, ¹⁴ N- and ¹⁵ N-enriched TbPc ₂ Double-decker Complexes	55
2.1 Introduction	55
2.2 Synthesis details	57
2.3 Molecular structures	62
2.3.1 Respective structures of [TbPc ₂] ⁰ , [TbPc ₂ - ¹⁵ N] ⁰ , and [TbPc ₂ -D] ⁰	62
2.3.2 Respective structures of 5% diluted [TbPc ₂][TEA] ⁺ , [TbPc ₂ - ¹⁵ N][TEA] ⁺ , and [TbPc ₂ -D][TEA] ⁺	66
2.4 Magnetic properties of [TbPc ₂] ⁰ , [TbPc ₂ - ¹⁵ N] ⁰ , and [TbPc ₂ -D] ⁰	71

2.4.1 SQUID measurement	71
2.4.2 μ -SQUID measurement	80
2.5 Magnetic properties of diluted $[\text{TbPc}_2][\text{TEA}]^+$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$	82
2.5.1 SQUID measurement	82
2.5.2 μ -SQUID measurements	86
2.6 Conclusion	95
Chapter 3. Isotopologue Complexes: Magnetic Properties of [2x2] Grid Dysprosium Complexes	96
3.1 Introduction	96
3.2 Synthesis details	98
3.3 Molecular structures	100
3.3.1 Structures of Ln_4L_4 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Y}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$)	100
3.3.2 Structures of Dy_4L_4 and the isotopologues ($^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$)	105
3.4 Optical properties of Gd_4L_4 , Eu_4L_4 , and Yb_4L_4	109
3.5 Magnetic properties of Dy_4L_4	112
3.5.1 SQUID measurement	112
3.5.2 CASSCF calculations	115
3.5.3 μ -SQUID measurement	117
3.6 Magnetic properties of isotopologue $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$	120
3.6.1 SQUID measurement	120
3.6.2 CASSCF calculations	123
3.6.3 μ -SQUID measurement	125
3.7 Conclusion	133
4. Concluding remarks	134
5. Experimental details	137
5.1 Materials	137
5.2 Equipment	137
5.3 Computational details	138
5.4 Dipolar Matrix	139
6. Appendix	141
7. List of publications	156
8. References	157

Acknowledgements

From 2021 to 2026, from China to Germany, from growing “impossible” crystal to refining PhD thesis, this 5-year journey finally comes to an end. From Master to Doctor, my sincere thanks go to everyone who supported me during this brief yet profound chapter of my life.

First, I would like to express my deepest gratitude to my supervisor Prof. Dr. Mario Ruben for offering me the opportunity to join his research group. His profound knowledge, keen insight into scientific frontiers, and pioneering mindset have set a benchmark for me. His extensive collaborative network has vastly broadened my horizons. Throughout this journey, he provided me a great degree of freedom in my research and unwavering support, inspiring me at every stage. It is my great honor to grow into a Doctor under his mentorship.

I would like to extend my most heartfelt gratitude to Dr. Svetlana Klyatskaya, who guided me from being a complete newbie to a confident researcher in synthesis. She offered me immense support whenever I encountered obstacles; even during her challenging times, she was still concerned about whether I need help. Throughout this journey, she has been my Polaris to keep me moving forward, I am profoundly grateful.

Sincere thanks to Dr. Eufemio Moreno-Pineda, for being both a great collaborator and an outstanding mentor. From the latter stage of this journey, working with him has been a rewarding experience. His assistance was the cornerstone of this work. This journey could not have reached its destination without him.

A big thank you to Dr. Senthil Kumar Kuppusamy, not only for the knowledge and guidance he shared with me, but also for his unwavering support. He was and is always there, whenever help was needed, consistently willing and ready to give a hand no matter how difficult the challenge.

I would like to thank Prof. Dr. Dieter Fenske and Dr. Olaf Fuhr for measuring my tiny crystal. I truly appreciate their tireless efforts and patience to make the determination of these crystals from impossible to possible.

I would also like to thank Dr. Zhaoyang Jing, Dr. Sören Schlittenhardt and Dr. Sagar Paul for sharing their constructive suggestions with me. The discussions we had were incredibly fruitful, offering fresh perspectives when I felt stuck.

I am deeply grateful to my collaborators for their invaluable assistance. Prof. Dr. Wolfgang Wernsdorfer group, especially Dr. Sagar Paul, and Appu Sunil for performing the μ -SQUID measurement; Prof. Dr. Stefanie Dehnen group, especially Dr. Yaofeng Wang, Dr. Shangxin Wei, Dr. Zhou Wu, Jie Wang, and Franziska Ganslmaier for their valuable help with the analysis of crystal structures, composition, and mass spectrum.

And of course, many thanks to my labmates, Dr. Ting-ting Ruan, Dr. Sai Prasanna Kumar, Dr. Conchi Molina Jiron de Moreno, Dr. Shirin Shakouri, Dr. Nithin Suryadevara, Dr. Barbora Brachnakova, Dr. Jordan Appleton, Dr. Michal Valasek, Dr. Camila Gouveia Barbosa, Dr. Sujit

Kamilya, Dr. Kaushik Krishna, Dr. Ingrid Popovici, Dr. Masoumeh Zakerighadi, Dr. Joe Komeda, Nikoleta Malinova, Moritz Rodert, Jason Hofmann, Christian Mina, Rihab Sayid. It is my pleasure to work with these outstanding colleagues.

Also, special thanks to Andrei Poddelskii, Hagen Sparrenberger, and Nicolai Bartnick for supplying the lab supplies and kindly assistance.

Thank the China Scholarship Council (CSC) for offering me this opportunity and funding me to study in Germany.

Last but not least, my sincere thanks to all my beloved families and friends for their unconditional love and endless support throughout this journey. Their constant encouragement and generous support in both emotional and material freed me from all worries and allowed me to focus entirely on my studies. Thank you for being my safe harbor through every storm.

Moving forward to the next chapter, I will remember the lesson of this journey: Science is still correct and Nature gives us the last word.

Abbreviations used

AC	Alternating current
CASSCF	Complete active space self consistent field
Cp	Cyclopentadienyl
CShM	Continuous shape measure
DC	Direct current
EPR	Electron paramagnetic resonance
IR	Infrared
KD	Kramer's doublet
Ln	Lanthanide
NMR	Nuclear magnetic resonance
Pc	Phthalocyanine
PXRD	Powder X-ray diffraction
QTM	Quantum tunnelling of magnetization
RASSCF	Restricted active space self consistent field
REE	Rare earth element
SC-XRD	Single-crystal X-ray diffraction
SMM	Single molecule magnet
SOC	Spin orbit coupling
SQUID	Superconducting quantum interference device
TA-QTM	Thermally assisted quantum tunnelling of magnetization
UV	Ultraviolet
XRD	X-ray diffraction

Abstract

Magnetic complexes, owing to the unique quantum properties at the molecular scale, are regarded as pivotal materials for realizing next-generation quantum information processing and ultra-high-density information storage, possessing immense strategic significance. Single-molecule magnets with slow magnetic relaxation behavior offer a platform for enhancing computational speed and exponentially increasing storage density. By leveraging electron/nuclear spin as quantum resource, these systems enable precise control through the energy level splitting and the construction of quantum superposition states, demonstrating immense potential in quantum processing procedures. With more than three decades of in-depth development, several breakthroughs have been achieved in this field, such as raising the blocking temperature above that of liquid nitrogen, observing quantum coherence phenomena at room temperature, and operating quantum algorithms in single magnetic molecules. However, significant challenges remain regarding how to effectively suppress quantum tunneling of magnetization and control quantum decoherence. Over years of development, scientists have figured out that beyond molecular structure symmetry, ligand field strength, intermolecular interactions, and molecular vibrations, nuclear spins play a pivotal role in the magnetic relaxation process through hyperfine or super-hyperfine interactions. Compared to traditional chemical modification methods, the isotopologue engineering strategy allows the precise isolation and manipulation of nuclear spins without changing the molecular geometric structure and electronic structure. This strategy not only provides an ideal approach to explore the magnetic relaxation dynamics, but also effectively elucidates the intrinsic relationship between nuclear spins and magnetic properties, laying a solid foundation for the rational design of high performance molecular-based quantum materials. In this thesis, two experiments designed to separately investigate the influence of ligand isotopes and metal isotopes on the magnetic relaxation process are presented as follows:

(1) Magnetic properties of ligand-isotope-enriched bis(phthalocyaninato)terbium.

Based on classic single-molecule magnet, bis(phthalocyaninato)terbium, fully D and ^{15}N isotope enriched complexes were synthesized and the isotope effects of H/D and $^{14}\text{N}/^{15}\text{N}$ were characterized by SQUID and μ -SQUID measurements. The results demonstrate that H/D substitution significantly changes the phonon density of states, thereby attenuating the spin-phonon coupling. While the influence of $^{14}\text{N}/^{15}\text{N}$ is manifested in the characteristics of the equilibrium state: the smaller nuclear spin (^{15}N , $I = 1/2$) promotes the relaxation toward thermodynamic equilibrium due to the reduced tunneling splitting, whereas the intricate super-hyperfine manifold of ^{14}N ($I = 1$) traps the system in a non-thermodynamic equilibrium state.

(2) Magnetic properties of metal-isotope-enriched [2x2] dysprosium grid complex.

A series of tetranuclear [2x2] grid complexes, $[\text{Ln}_4\text{L}_4(\mu_2\text{-OH})_4]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}, \text{Y}$; $\text{L} = 3,6\text{-bis}(2\text{-}1\text{-(pyridin-2-yl)ethylidene)hydrazineyl-1,2,4,5-tetrazine}$), were designed and synthesized. To explore the isotopologue effect of metal, ^{163}Dy ($I = 5/2$) and ^{164}Dy ($I = 0$) isotopologues were synthesized, and their magnetic properties were characterized using SQUID and μ -SQUID measurements. The experimental results combined with CASSCF

calculation reveal that both isotopologues exhibit a toroidal ground state stabilized by non-collinear magnetic anisotropy axes and competing interactions. An unconventional phenomenon was observed: the nuclear spin of ^{163}Dy does not accelerate relaxation but facilitate the transition between ferromagnetic states and the antiferromagnetic states through hyperfine-mediated ground state trapping. Such nuclear-spin-driven population trapping significantly suppresses the zero-field quantum tunneling of magnetization, resulting in slower magnetization and larger opening in hysteresis. To the best of our knowledge, these findings demonstrate for the first time that nuclear spins exert a constructive influence on the relaxation behavior of single-molecule magnets.

Zusammenfassung

Aufgrund ihrer einzigartigen Quanteneigenschaften auf molekularer Ebene gelten magnetische Komplexe als Schlüsselmaterialien für die Realisierung der Quanteninformationsverarbeitung der nächsten Generation sowie der Informationsspeicherung mit extrem hoher Datendichte und sind daher von großer wissenschaftlicher und technologischer Bedeutung. „Single-molecule magnets“ (SMMs) mit langsamer magnetischer Relaxation bieten eine mögliche Plattform zur Steigerung der Rechengeschwindigkeit und zu einer exponentiell erhöhten Speicherdichte. Durch die Nutzung von Elektronen- oder Kernspins als Quantenressource ermöglichen diese Systeme eine präzise Steuerung mittels Energieniveaufspaltung und der Erzeugung von Quantensuperpositionszuständen, was ein enormes Potenzial für die Quanteninformationsverarbeitung aufzeigt. In den vergangenen mehr als drei Jahrzehnten intensiver Forschung wurden auf diesem Gebiet bedeutende Durchbrüche erzielt, wie etwa das Anheben der „blocking temperature“ über den Siedepunkt von flüssigem Stickstoff hinaus, die Beobachtung von Quantenkohärenzphänomenen bei Raumtemperatur und die Ausführung von Quantenalgorithmen in einzelnen magnetischen Molekülen. Dennoch bestehen bis zur Anwendung weiterhin erhebliche Herausforderungen hinsichtlich des effektiven Verhinderns von Quantentunnelphänomenen oder der Kontrolle der Quantendekohärenz. Nach jahrelanger Forschung haben Wissenschaftler herausgefunden, dass neben der molekularen Symmetrie, der Ligandenfeldstärke, intermolekularen Wechselwirkungen und Molekülschwingungen, auch der Kernspin durch Hyperfein- oder Superhyperfeinwechselwirkungen eine entscheidende Rolle im magnetischen Relaxationsprozess spielt. Im Vergleich zu herkömmlichen chemischen Modifizierungsmethoden ermöglicht das Austauschen von Isotopen eine präzise und isolierte Kontrolle des Kernspins, ohne die Molekülgeometrie und die elektronische Struktur zu verändern. Diese Strategie bietet nicht nur einen idealen Ansatz zur Erforschung der magnetischen Relaxationsdynamik, sondern verdeutlicht auch den intrinsischen Zusammenhang zwischen Kernspin und magnetischen Eigenschaften und legt damit eine solide Grundlage für das rationale Design leistungstarker molekularbasierter Quantenmaterialien. Diese Dissertation stellt zwei Experimente vor, die die Auswirkungen von Liganden- bzw. Metallisotopen auf den magnetischen Relaxationsprozess untersuchen:

(1) Magnetische Eigenschaften von Bis(phthalocyaninato)terbium Komplexen mit Ligandenisotopen.

Am Beispiel von Bis(phthalocyaninato)terbium, einem klassischen Einzelmolekülmagneten, wurden Komplexe synthetisiert, die vollständig mit den Isotopen D und ^{15}N angereichert waren. Die H/D- und $^{14}\text{N}/^{15}\text{N}$ -Isotopeneffekte wurden mittels SQUID- und μ -SQUID-Messungen charakterisiert. Die Ergebnisse zeigen, dass die H/D-Substitution die Phononenzustandsdichte signifikant verändert und dadurch die Spin-Phonon-Kopplung schwächt. Der Effekt von $^{14}\text{N}/^{15}\text{N}$ spiegelt sich in den Eigenschaften des Gleichgewichtszustands wider: Der kleinere Kernspin (^{15}N , $I = 1/2$) fördert die Relaxation zum thermodynamischen Gleichgewicht durch Verringerung der Tunnelaufspaltung; im Gegensatz dazu fixiert die komplexe

Hyperfeinstruktur von ^{14}N ($I = 1$) das System in einem kinetisch ausgeglichenen, aber thermodynamisch nicht im Gleichgewicht befindlichen Zustand.

(2) Magnetische Eigenschaften von angereicherten [2x2] Dysprosium-Gitter Komplexen mit Metallisotopen.

Eine Reihe tetranuklearer [2x2] Gitterkomplexe $[\text{Ln}_4\text{L}_4(\mu_2\text{-OH})_4]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}, \text{Y}$; $\text{L} = 3,6\text{-Bis}(2\text{-(1-(pyridin-2-yl)ethylen)hydrazino})\text{-1,2,4,5-tetraazin}$) wurde entworfen und synthetisiert. Zur Untersuchung des Metallisotopeneffekts wurden die Isotopenisomere ^{163}Dy ($I = 5/2$) und ^{164}Dy ($I = 0$) synthetisiert und ihre magnetischen Eigenschaften mittels SQUID- und $\mu\text{-SQUID}$ -Messungen charakterisiert. Experimentelle Ergebnisse in Kombination mit CASSCF-Rechnungen zeigten, dass beide Isotopenisomere einen toroidalen Grundzustand aufweisen, der durch nicht-kollineare magnetische Anisotropieachsen und konkurrierende Wechselwirkungen stabilisiert wird. In dieser Studie wurde ein ungewöhnliches Phänomen beobachtet: Der Kernspin von ^{163}Dy beschleunigte nicht die Relaxation, sondern erleichterte den Übergang zwischen ferromagnetischen und antiferromagnetischen Zuständen indem das System, durch den Einfluss der Hyperfeinwechselwirkung, im Grundzustand gefangen wird. Dieser spin-induzierte Populationseinfang unterdrückte signifikant den Quantentunnelprozess der Magnetisierung im Nullfeld, was zu einem langsameren Magnetisierungsprozess und einer vergrößerten Hystereseschleife führte. Unserer Erkenntnis nach sind dies die ersten Ergebnisse, die zeigen, dass der Kernspin das Relaxationsverhalten von Einzelmolekülmagneten fördert.

Chapter 1. Introduction

Information storage has always been a crucial component of human societal activities. From the advent of writing to the birth of information carriers such as paper, hard drives, and optical discs, the knowledge and information humanity has gained through exploring the world have been continuously accumulated and preserved. With the rapid development of big data and artificial intelligence, the long-term effective processing of information has become a key issue affecting the development of information technology. In the post-Moore's Law era, as the size of electronic devices continues to shrink to its limit, the quantum effects that dominate at this scale, while making further miniaturization difficult, have triggered a revolution based on the quantum nature of matter for information processing.

By harnessing the power of quantum superposition and entanglement, qubits serve as the primary catalysts for the upcoming digital revolution. Unlike classical bits, which are limited by the binary constraints of 0 and 1, qubits enable an exponential leap in computing power by utilizing quantum superposition of states. Furthermore, through entanglement, qubits establish coherent correlations over the long physical distance. More importantly, qubits offer a new perspective for solving quantum mechanical problems that are unsolvable using traditional methods.^{1, 2} These unique characteristics make qubits play a crucial role in achieving rapid computation, breaking complex encryption, simulating quantum phenomena, etc. From the first realization of quantum gate operation with two qubits in 1998,³ to the current largest quantum computer array with 6100 qubits,⁴ qubits has become one of the current research priorities.

To implement this, a huge number of qubits with specific characteristic frameworks are needed. Basically, qubits require two or more stable states of quantum resource for operating, for example, orientation of spin states.⁵ In this context, the development of novel materials as building blocks has attracted extensive research, giving rise to a series of material platforms hosting qubits, such as, defects in solids,^{6, 7} photons,⁸ trapped ions,⁹ quantum dots,¹⁰ superconducting systems,¹¹ and molecules.^{12, 13} Among them, molecular materials are considered as potentially ideal platforms due to the advantages of flexible chemical tunability and monodispersity, especially the “bottom-up” construction methods enable the scalability of quantum systems.^{14, 15} Lanthanide complexes have emerged as promising qubit candidate owing to their distinctive $4f$ electronic configuration of rare-earth ions. The distinctive optical and magnetic properties of lanthanide complexes pave the way for the functional application of molecular-based materials, offering promising prospects in high-density data storage, quantum information processing, and quantum computing.^{13, 16, 17}

Based on the research content of this thesis, the objective is first to introduce the background and fundamental concepts relevant to the research topic, together with a review of recent developments and emerging trends in the field. In addition, the core experimental techniques and analytical protocols employed in this study are described here, providing a perspective for understanding the experiment results and interpreting the research conclusions.

1.1 Lanthanide elements

The lanthanide elements (Ln), so called as the lanthanides or *4f* elements, consist of 15 elements with atomic numbers from lanthanum (La, $Z = 57$) to lutetium (Lu, $Z = 71$) in the periodic table. The term 'rare earth elements' (REEs) was historically established due to the scarcity of concentrated lanthanide-bearing minerals and the significant technical challenges associated with their high-purity extraction from the earth's crust. Although Scandium (Sc, $Z=21$) and Yttrium (Y, $Z=39$) are transition metals, they are grouped with the lanthanide series together as REEs (Figure 1.1.1) due to their analogous chemical behaviors and their frequent co-existence with lanthanides in natural deposits.

1 H Hydrogen																	2 He Helium						
3 Li Lithium	4 Be Beryllium																	5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium																	13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton						
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon						
55 Cs Cesium	56 Ba Barium	57-71 Lanthanides	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon						
87 Fr Francium	88 Ra Radium	89-103 Actinides	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson						

57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Figure 1.1.1 Elements of the lanthanide and rare earth series in the periodic table are highlighted in black.

The history of lanthanide chemistry can be traced back to 1794, when Gadolin first isolated yttrium from a mineral found in Ytterby, Sweden. However, the separation and purification of individual rare earth elements remained a formidable challenge for over a century. This is due to the lanthanide contraction effect, where the differences in radii between adjacent rare earth ions is extremely small, resulting in a high degree of similarity in their physical and chemical properties. Furthermore, in aqueous solution, these elements predominantly exist in a stable trivalent state, where the high affinity for water molecules masks the subtle elemental differences. With the development of separation techniques and characterization methods, until the early 20th century, the series of rare earth elements could be fully isolated and characterized. With the advancements in geochemical detection techniques, the lanthanide elements have been revealed to be relatively abundant in the earth's crust, in some cases even superior to common industrial metals. The distribution of lanthanide elements (Table 1.1.1) follows the Odd-Harkins rule, which states that elements with even atomic numbers are more abundant than odd

atomic numbers due to the increased nuclear stability. Among them, cerium is the most plentiful, with an abundance comparable to that of copper, while thulium is the rarest stable lanthanide at approximately 0.52 ppm in the earth's crust. Promethium is radioactive with a short half-life, and is therefore virtually non-existent in nature.

Table 1.1.1 Estimated abundance of lanthanide elements (ppm) in the earth's crust.

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
39	66.5	9.2	41.5	Trace	7.05	2	6.2	1.2	5.2	1.3	3.5	0.52	3.2	0.8

The general electron configuration of a lanthanide atom is represented as $[\text{Xe}]4f^n5d^m6s^2$, where $n = 0-14$ and $m = 0$ or 1 (Table 1.1.2). The electrons, after [Xe] core, are primarily filled into the inner $4f$ orbitals, resulting in highly similar electronic structures in the outer and penultimate shells across the series. As the number of protons increases, the atomic radius of lanthanides gradually decreases from La (188 pm) to Lu (173 pm). This phenomenon, so-called the lanthanide contraction, is essentially caused by the weak shielding effect of the inner $4f$ electrons on the nuclear charge, insufficient to effectively counteract the strong attraction of the growing nuclear charge to the outer electrons (especially the $5d$ and $6s$ electrons), resulting in both the atomic and ionic radius being smaller than the conventionally expected values. Due to the varying degrees of $4f$ electron involvement, lanthanides exhibit differences in physical properties (such as melting point and magnetism) and chemical properties (for instance, the relatively weak metallic bond strength of Eu and Yb).

Table 1.1.2 Electron configurations and radius of lanthanide atoms and their oxidation states.

Element	Electronic configuration				Radius (pm)	
	Ln	Ln ²⁺	Ln ³⁺	Ln ⁴⁺	Ln	Ln ³⁺
La	$[\text{Xe}]5d^16s^2$	$[\text{Xe}]5d^1$	$[\text{Xe}]$		187.9	116.0
Ce	$[\text{Xe}]4f^15d^16s^2$	$[\text{Xe}]4f^2$	$[\text{Xe}]4f^1$	$[\text{Xe}]$	182.5	114.3
Pr	$[\text{Xe}]4f^36s^2$	$[\text{Xe}]4f^3$	$[\text{Xe}]4f^2$	$[\text{Xe}]4f^1$	182.8	112.6
Nd	$[\text{Xe}]4f^46s^2$	$[\text{Xe}]4f^4$	$[\text{Xe}]4f^3$		182.1	110.9
Pm	$[\text{Xe}]4f^56s^2$	$[\text{Xe}]4f^5$	$[\text{Xe}]4f^4$		181.0	109.5
Sm	$[\text{Xe}]4f^66s^2$	$[\text{Xe}]4f^6$	$[\text{Xe}]4f^5$		180.4	107.9
Eu	$[\text{Xe}]4f^76s^2$	$[\text{Xe}]4f^7$	$[\text{Xe}]4f^6$		204.2	106.6
Gd	$[\text{Xe}]4f^75d^16s^2$	$[\text{Xe}]4f^75d^1$	$[\text{Xe}]4f^7$		180.1	105.3
Tb	$[\text{Xe}]4f^96s^2$	$[\text{Xe}]4f^9$	$[\text{Xe}]4f^8$	$[\text{Xe}]4f^7$	178.3	104.0
Dy	$[\text{Xe}]4f^{10}6s^2$	$[\text{Xe}]4f^{10}$	$[\text{Xe}]4f^9$	$[\text{Xe}]4f^8$	177.4	102.7
Ho	$[\text{Xe}]4f^{11}6s^2$	$[\text{Xe}]4f^{11}$	$[\text{Xe}]4f^{10}$		176.6	101.5
Er	$[\text{Xe}]4f^{12}6s^2$	$[\text{Xe}]4f^{12}$	$[\text{Xe}]4f^{11}$		175.7	100.4
Tm	$[\text{Xe}]4f^{13}6s^2$	$[\text{Xe}]4f^{13}$	$[\text{Xe}]4f^{12}$		174.6	99.4
Yb	$[\text{Xe}]4f^{14}6s^2$	$[\text{Xe}]4f^{14}$	$[\text{Xe}]4f^{13}$		193.9	98.5
Lu	$[\text{Xe}]4f^{14}5d^16s^2$	$[\text{Xe}]4f^{14}5d^1$	$[\text{Xe}]4f^{14}$		173.5	97.7

Lanthanides can form oxidation states of +2, +3, and +4. In general, due to the ionization energies required for losing two $6s$ and one $5d$ (or $4f$) electrons are relatively low, thus the

trivalent oxidation state (Ln^{3+} , with a $[\text{Xe}]4f^n$ configuration) emerges as the most stable and common form in the solid or solution states. Owing to their high charge density and relatively small ionic radius, especially for the heavy lanthanides, trivalent lanthanide ions are categorized as hard Lewis acids. Notably, scandium and yttrium only form trivalent ions with relative stability of empty or filled subshells. They are chemically similar to lanthanide metals, for example their atomic radii, and are therefore often used in research for diamagnetic dilution to reduce the dipolar interaction.¹⁸⁻²⁰ Compared to trivalent lanthanides, Ln^{2+} and Ln^{4+} have extremely strong reduction or oxidation properties, respectively. Therefore, these ions are quite unstable especially in solution state. For Ln^{4+} , as a strong oxidation agent, only Ce^{4+} can exist in solution. For Ln^{2+} , Eu^{2+} has the highest stability, followed by Yb^{2+} and Sm^{2+} .

As mentioned before, Ln^{3+} ions are hard Lewis acids and hence predominantly coordinate with ligands via electrostatic interactions rather than covalent interactions. Compared to transition metal complexes, which exhibit specific coordination configurations due to strong ligand field effects, lanthanide complexes show a weaker geometry preference due to the significant shielding of the $4f$ orbitals by the outer electrons. Typically, the coordination numbers for light lanthanides ions (from La to Eu) range from 8 to 10, whereas those for heavy lanthanides ions (from Gd to Lu) are 7 to 9.

In open shell systems where $L > 0$ (L is the total orbital angular momentum quantum number), spin-orbital coupling (SOC) is a prevalent relativistic effect. For lanthanides, the $4f$ orbital exhibits a significant inward contraction and is effectively shielded by the outer $5s$ and $5p$ orbitals, making it difficult for the ligand crystal field environment to completely quench its orbital angular momentum. Together with the partial occupancy of the $4f$ shell, and the fact that the SOC strength is proportional to the fourth power of the atomic number, lanthanides exhibit extremely strong spin-orbit coupling, thereby inducing significant magnetic anisotropy in their ground state energy levels.

Table 1.1.3 $^{2S+1}L_J$ ground state for each trivalent lanthanide ion.

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
$^2F_{5/2}$	$^3H_4$	$^4I_{9/2}$	$^5I_4$	$^6H_{5/2}$	$^7F_0$	$^8S_{7/2}$	$^7F_6$	$^6H_{15/2}$	$^5I_8$	$^4I_{15/2}$	$^3H_6$	$^2F_{7/2}$

Consequent to the formidable spin-orbit coupling, the electronic structure of lanthanide ions follows the Russell-Saunders coupling scheme, where the total angular momentum quantum number (J) defined by the total orbital angular momentum (L) and total spin angular momentum (S) are introduced to describe the primary quantum number of lanthanide ions. The value of J ranges from $|L-S|$ to $|L+S|$, where both are integer number and S is the sum of unpaired electrons and L is equal to 0, 1, 2, 3, 4, 5, 6 corresponding to S, P, D, F, G, H, I respectively. The ground states of lanthanide ion are governed by Hund's rules, namely: (1) Under the premise of satisfying the Pauli exclusion principle, S should be maximized in order to minimize the coulomb repulsion between electrons. (2) L should be taken as the maximum allowable value. (3) For less than half-filled $4f$ shells, $J = |L-S|$; while for more than half-filled shell, $J = L+S$. Under the Russell-Saunders coupling scheme, the spectroscopic term symbol $^{2S+1}L_J$ defines the energy levels of lanthanide, where the energy of $^{2S+1}L_J$ is determined as below:

$$E(^{2s+1}L_J) = \left(\frac{\lambda}{2}\right) [J(J+1) - L(L+1) - S(S+1)] \quad \text{Equation 1.1.1}$$

Where λ is the spin-orbit coupling constant, taking a positive sign for the early lanthanides ($4f^n$ with $n < 7$) and a negative sign for the late lanthanides ($4f^n$ with $n > 7$). Among trivalent lanthanides, Gd^{3+} is a special case where the orbital angular momentum is completely suppressed ($L = 0$) due to its $4f^7$ electron configuration, resulting in a pure spin magnetic moment and high magnetic isotropy. In contrast, La^{3+} ($4f^0$) and Lu^{3+} ($4f^{14}$) are diamagnetic ions with both zero total orbital angular momentum and zero spin angular momentum. The remaining trivalent lanthanide ions exhibit paramagnetic behavior due to the presence of unpaired $4f$ electrons.

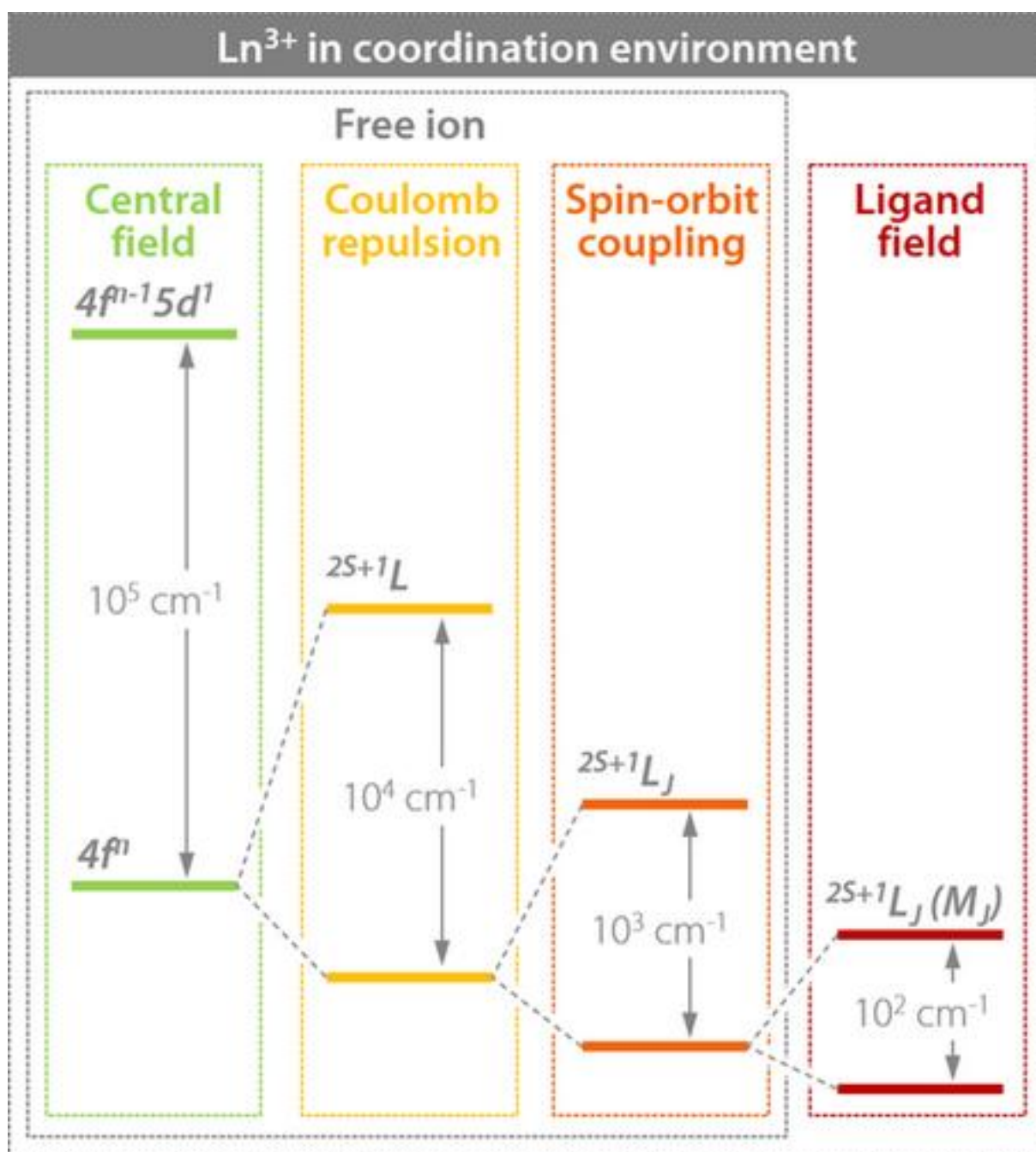


Figure 1.1.2 The contribution of different factors on the energy levels of trivalent lanthanide ions in a specific coordination environment.²¹

Notably, in lanthanide ions, the ligand field (or crystal field) effect acts as a weaker interaction compared to the dominant spin-orbit coupling. As illustrated in the Figure 1.1.2,²¹ spin-orbital coupling induces electronic state splitting on the order of 10^3 cm^{-1} , while the ligand field effect results in much finer splitting, typically around 10^2 cm^{-1} . Thus, the ligand field effect is generally regarded as a perturbation to the $^{2S+1}L_J$ multiplicity established by spin-orbit coupling. Such perturbation disrupts the spatial degeneracy of the $^{2S+1}L_J$ state, splitting into multiple M_J sublevels, namely Stark sublevels. The M_J sublevels represent the azimuthal projections of the total angular momentum, ranging in integer steps from $-J$ to J . Since the splitting gap between M_J sublevels is generally comparable to thermal energy, their electron populations are highly temperature-dependent, which plays a crucial role in controlling the magnetic behavior of materials and the fine structure of their photophysical transitions. The specific effects of the crystal field on magnetic and optical properties will be discussed in the following chapters.

1.2 Single-molecule magnets

Single-molecule magnets (SMMs) are a special class of metal-organic complexes. Unlike traditional magnetic materials, where magnetism originates from long-range magnetic ordering driven by cooperative effects, the magnetic behavior of SMMs arises entirely from the paramagnetic ground state and/or magnetic anisotropy of individual molecules. Consequently, each molecule can function as an independent nanoscale magnetic storage unit. More importantly, classical and non-classical magnetic phenomena (such as quantum tunneling of magnetization, QTM) can be observed at the molecular level.

1.2.1 Lanthanide single-molecule magnets

In open-shell systems, the spin of unpaired electrons produces a measurable magnetic moment. Such materials exhibiting a non-zero magnetic moment are known as paramagnetic, and their magnetic moments align with the direction of the external magnetic field. While closed-shell systems are diamagnetic due to the lack of magnetic moment, meaning the induced field is opposite to the direction of the external field. Although most electrons are paired in any system, resulting in the objective existence of the diamagnetic effect, the paramagnetic effect is about 1000 times stronger. Consequently, paramagnetic effect remains the dominate feature even in a system with just only one unpaired electron. The magnetic moment of such a system can be characterized by the following formula:

$$\mu = g_s \sqrt{S(S+1)} \mu_B \quad \text{Equation 1.2.1}$$

Where μ is the magnetic moment, g_s is the Landé factor, S is the spin quantum number, which is the sum of the electron spin, and μ_B is the Bohr magneton.

To describe how the molecular materials react with the external magnetic field, molar magnetic susceptibility (χ_{mol}) is employed and derived from the volume magnetic susceptibility (χ_V , which equals the ratio of volume magnetization over the external magnetic field) as shown below:

$$\chi_{mol} = \chi_V \cdot V \cdot \frac{M}{m} \quad \text{Equation 1.2.2}$$

Where V is the volume, M is the molar mass of the sample and m is the mass of the sample.

In molecular magnetism, the measurements of molar magnetic susceptibility are limited to small external magnetic field, where this above definition remains valid. If the applied field is too high, the magnetization will reach saturation state where all magnetic moments within the sample are fully aligned. Both magnetization and magnetic susceptibility are temperature dependent. At high temperature, the alignment in an external magnetic field is disturbed by the thermal motion of particles, resulting in an inverse relationship between susceptibility and temperature, which is defined by Curie's law:

$$\chi_{mol} = \frac{C}{T} \quad \text{Equation 1.2.3}$$

Where C is the Curie constant and T is the temperature. This expression is strictly applicable only to the molecular systems without first-order spin-orbit coupling. For systems where spontaneous interaction between adjacent spins induces magnetic ordering at low temperature, a correction is required via Curie-Weiss law:

$$\chi_{mol} = \frac{C}{T-\theta} \quad \text{Equation 1.2.4}$$

Where θ is the Weiss constant, describing the magnetic behavior of materials at different temperatures, C is the Curie constant, and T is the temperature. The equation 1.2.3 could be rewritten based on the total angular momentum (J) as below:

$$\chi_{mol}T = \frac{N_A \cdot g_J^2 \cdot \mu_B^2}{3 \cdot k_B} \cdot J(J+1) \quad \text{Equation 1.2.5}$$

$$g_J = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \text{Equation 1.2.6}$$

Where T is the temperature, N_A is Avogadro constant, μ_B is the Bohr magneton, g_J is the Landé g-factor, k_B is Boltzmann constant, S is the total spin angular momentum, and L is the total orbital angular momentum.

Consequently, the product of susceptibility and temperature ($\chi_{mol}T$) serves as a more ideal description, as it remains temperature-independent under these assumptions. By applying Equation 1.2.5, the expected $\chi_{mol}T$ value for any given lanthanide element can be readily derived, as shown in table 1.2.1.

Table 1.2.1 g_J and $\chi_{mol}T$ value of trivalent lanthanide ion.

Element	g_J	$\chi_{mol}T$ ($cm^{-3} \cdot K \cdot mol^{-1}$)
La	-	0.00
Ce	6/7	0.80
Pr	4/5	1.60
Nd	8/11	1.64
Pm	3/5	0.90
Sm	2/7	0.09
Eu	5	0.00
Gd	2	7.88
Tb	3/2	11.82
Dy	4/3	14.17
Ho	5/4	14.07
Er	6/5	11.48
Tm	7/6	7.15
Yb	8/7	2.57
Lu	-	0.00

1.2.2 Relaxation mechanism of single-molecule magnets

Relaxation refers to the dynamic process by which a physical system gradually returns from a non-equilibrium state to its thermodynamic equilibrium state after being subjected to external disturbances. In the field of single-molecule magnets, the magnetism primarily originates from the intrinsic spin of individual molecules. Without external magnetic field, the molecules are in thermal equilibrium with their molecular magnetic moments randomly and equally distributed in two degenerated $\pm M_S$ states, resulting in total zero net magnetization. Once an external magnetic field is applied, the energy level of ground state undergoes Zeeman splitting, lowering the energy ($-M_S$) level that parallel to the direction of the field, following the increase in the population in this state. When the external field is removed, the bistable states become degenerate and the system returns to equilibrium again. Due to the significant intrinsic magnetic anisotropy of molecules, the reversal of the magnetization direction requires overcoming an effective energy barrier (U_{eff}) and follows the quantum selection law ($\Delta M_S = \pm 1$). When the energy levels of two states are equal and in resonance, quantum tunneling of magnetization (QTM) may occur due to the overlap of the wave functions. When the thermal perturbation ($k_B T$) of the system is higher than the energy barrier, the molecular magnetic moment flips rapidly; however, as the temperature decreases, the thermal excitation is limited and the flipping rate drops drastically, giving rise to slow relaxation. This process can be described by the following equation:

$$\frac{dM}{dt} = (M_0 - M)/t \quad \text{Equation 1.2.7}$$

Where M_0 is the equilibrium magnetization and M is the magnetization at time t .

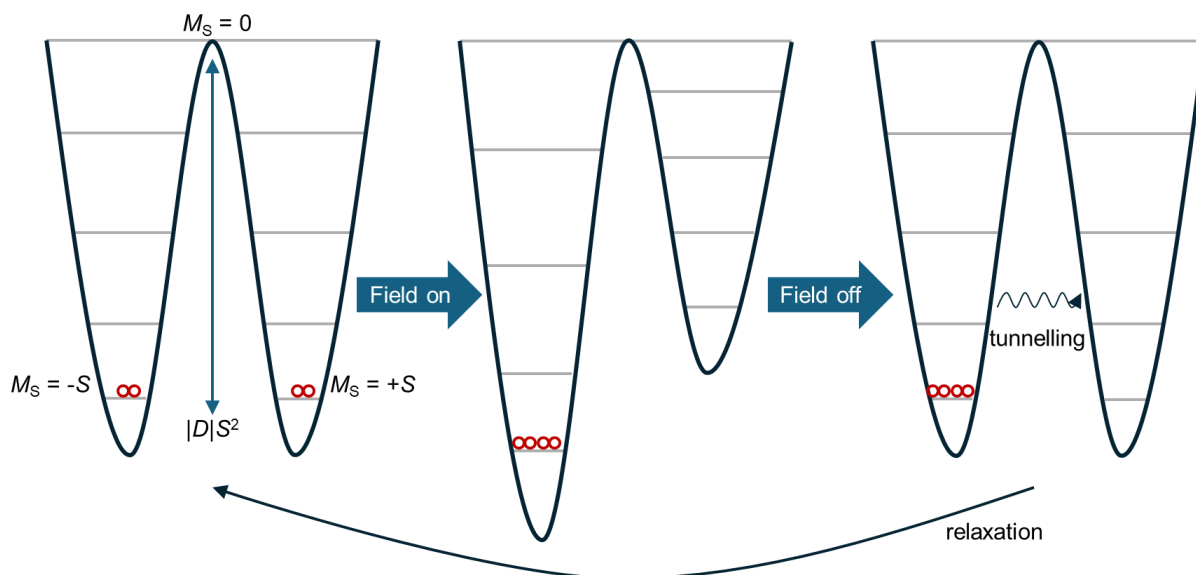


Figure 1.2.1 Schematic diagram of the SMMs double-well potential and the corresponding magnetic relaxation process.

The preceding content primarily focused on the interaction between molecular magnets and static direct current (DC) magnetic field, which is a 'static snapshot' of the system in

thermodynamic equilibrium state. However, this is inherently insufficient for describing the slow relaxation behavior of SMMs. Under an alternating current (AC) magnetic field, the magnetic moment reversal of the sample depends on the interplay between its intrinsic relaxation time (τ) and the oscillation frequency of the magnetic field (ω). A system with rapid relaxation will follow the field in-phase, while a phase lag is induced when relaxation time is comparable to the AC period, which is the out-of-phase susceptibility, helping for probing energy barrier, quantum tunneling, and spin-bath interactions. Therefore, the AC magnetic susceptibility is more meaningful for analyzing the properties of SMMs. According to the generalized Debye model, the relationship among alternating magnetic susceptibility (including real and imaginary parts), relaxation time (τ), and angular frequency of the alternating magnetic field (ω) is described as below:

$$\chi'(\omega) = \chi_S + \frac{(\chi_T - \chi_S)[1 + (\omega\tau)^{1-\alpha} \sin(\pi\alpha/2)]}{1 + 2(\omega\tau)^{1-\alpha} \sin(\pi\alpha/2) + (\omega\tau)^{2-2\alpha}} \quad \text{Equation 1.2.8}$$

$$\chi''(\omega) = \frac{(\chi_T - \chi_S)(\omega\tau)^{1-\alpha} \cos(\pi\alpha/2)}{1 + 2(\omega\tau)^{1-\alpha} \sin(\pi\alpha/2) + (\omega\tau)^{2-2\alpha}} \quad \text{Equation 1.2.9}$$

Where χ' is the in-phase of the AC susceptibility and χ'' is the out-phase of the AC susceptibility. χ_S refers to the adiabatic susceptibility and χ_T is the isothermal susceptibility. α is the dispersion parameter ranging from 0 to 1, describing the distribution of the relaxation time. A larger value of α indicates a broader distribution, signifying that the system deviates from ideal behavior due to multiple relaxation processes or local structural inhomogeneities. When $\alpha = 0$, the relaxation dynamic of the system is described as single process.

The slow relaxation of magnetization in SMMs is characterized by a complex interplay of multiple processes. Generally, the mechanisms of relaxation are categorized into phonon-independent quantum tunneling of magnetization and phonon-dependent spin-lattice relaxation.^{22, 23} In spin-lattice relaxation process, the spin system dissipates excess absorbed energy into the surrounding lattice environment through spin-phonon coupling, thereby returning from a non-equilibrium state to a thermal equilibrium state. Considering the differences in the exchange between spin and phonon, this process is further subdivided into the direct relaxation process, the Raman relaxation process and the Orbach relaxation process, as shown below:

$$\tau^{-1} = \tau_{QTM}^{-1} + AH^m T + CT^n + \tau_0^{-1} \exp\left(-\frac{U_{eff}}{k_B T}\right) \quad \text{Equation 1.2.10}$$

Where τ is the experimental relaxation time. The first term is the temperature-independent quantum tunneling, τ_{QTM} is the QTM relaxation time. The second term is the direct process, A and m are the direct relaxation parameters, H is the applied magnetic field, and T is the temperature. The third term is the Raman process, C and n are Raman constants. And the last term is the Orbach process, τ_0 is the Orbach relaxation time, k_B is Boltzmann constant, and U_{eff} is the effective energy barrier.

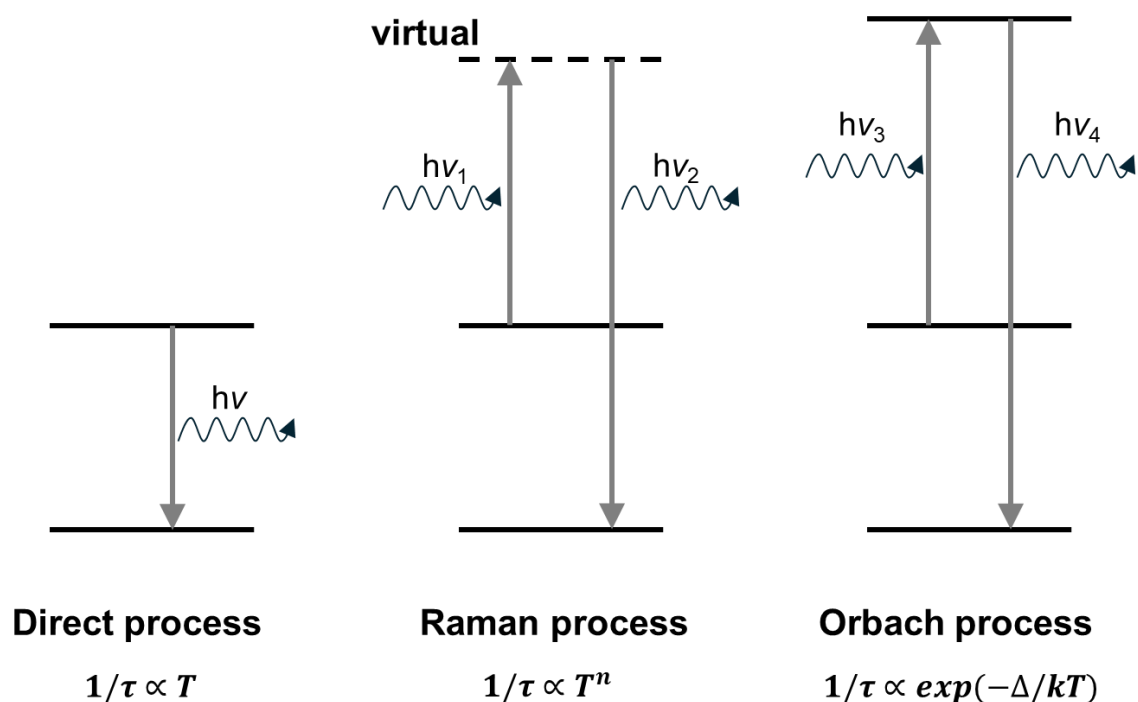


Figure 1.2.2 Schematic diagram of phonon-dependent relaxation process in the slow relaxation behavior of a single-molecule magnet.

QTM is a purely quantum mechanical behavior in single-molecule magnet. Without an external magnetic field, the ground-states of spin doublets are energetically degenerate. Due to the overlap of wavefunctions, the magnetic moment is allowed to directly flip its orientation by tunneling through the energy barrier without thermal activation,²⁴ this favors the reduction in the effective energy barrier and quenches the slow relaxation behavior. The factors driving this non-thermal activation process mainly include: the transverse magnetic anisotropy originating from the ligand field, the dipole-dipole interactions between adjacent spin centers, and the hyperfine interactions with nuclear spins. On applying an external magnetic field, Zeeman effect induces energy level splitting and breaks the original degeneracy. As the overlap of the wavefunction is decoupled, quantum tunneling is typically suppressed. However, in multi-level systems, a specific external magnetic field can fine tune different spin states into proximity, resulting the overlap wavefunction of spin states with different quantum numbers, thereby creating new quantum tunnelling at a specific field.

The direct process involves single-phonon transitions between non-degenerate ground state energy levels with a small energy gap. The energy transition between states is facilitated by the absorption or emission phonons with a specific frequency. Since direct relaxation occurs between non-degenerate ground-state doublets, for Kramers ions, like Dy^{3+} , the ground state doublets remain degenerate under zero magnetic field due to the symmetry. Consequently, the direct relaxation process is strictly forbidden through the Van Vleck cancellation. However, once an external magnetic field is applied, the ground state doublets split due to Zeeman effect, lifting this degeneracy enabling the direct relaxation process. Since the direct process requires matching phonons of a corresponding frequency and the phonon density of states varies

significantly with the magnetic field, direct process exhibits a strong magnetic field dependence. Typically, in the Kramers ions system, the energy level difference originated from the Zeeman splitting is proportional to the magnetic field (normally H^4 or H^2).

Both the Raman and Orbach relaxation processes are two-phonon process. In the Raman process, a particle absorbs a phonon to reach a virtual intermediate state, followed by emitting another phonon to decay to another real stable state, thus facilitating the reversal of the magnetization. In contrast, the Orbach process only involves actual excited states, where the system is lifted to a discrete higher energy level of excited state by absorbing a phonon before decaying back to the ground state by the emission of another phonon. In the Raman relaxation process, the decay rate of the relaxation time typically follows a power law relationship with the temperature. Theoretically, the values of Raman n parameter for Kramers ions and non-Kramers ions are 9 and 7, respectively. However, the experimental observations often yield lower values (generally in the range between 1 and 6), which is originated by the participation of both the optical and acoustic phonons. As for Orbach relaxation process, the mechanism involves magnetization reversal via a real excited state, making its dynamics inherently sensitive to the coordination environment and magnetic exchange coupling of the molecule. Typically, the splitting energy levels of total angular momentum under ligand field are obtained through theoretical calculations (such as *ab initio* calculations, e.g. CAASSCF) or spectroscopic analysis. In magnetic experimental analysis, the effective energy barrier is obtained by fitting the linear portion of the high temperature relaxation data via Arrhenius equation. Ideally, the energy barrier derived from Arrhenius equation corresponds to the gap between the ground state and the excited state, which is consist with the Orbach process. However, comparing the experimental analysis with theoretical calculations (or spectroscopic analysis) reveals that the obtained energy barriers for most SMMs are much lower than intrinsic energy gap between their ground state and first excited state. This significant difference suggests that the slow relaxation of these systems does not entirely follow the Orbach process. Instead, these magnetization reversals are likely achieved via alternative pathways, such as phonon-assisted quantum tunneling.

It is noteworthy that a special type of slow relaxation behavior originates from the phonon bottleneck effect rather than the inherent energy barrier of a SMM.²⁵ In such system, which is not belonging to SMMs, the density of lattice phonons matching the energy gap is significantly lower than the number of magnetic particles, meaning the energy released by the particles in excited state cannot be dissipated into the surrounding environment in time. Such lag behavior in the energy transition prolongs the time for the system to reach thermal equilibrium, resulting in slow relaxation behavior. This phenomenon is often accompanied by a phonon trapping effect, where the released phonons are absorbed by neighboring ground state particles before escaping the crystal lattice, and then forming a cyclic process. These compounds generally exhibit following notable characteristics: (1) The slow relaxation behavior is typically observable only in the presence of an external magnetic field. (2) Under adiabatic conditions, such as in pulsed magnetic field, the magnetic hysteresis is observable at temperature higher

than blocking temperature. (3) The relaxation time is closely related to the size of crystal. Smaller crystals facilitate faster energy dissipation, resulting in a faster relaxation rate.

For single-molecule magnets to achieve practical applications, the blocking temperature must be raised to the level of liquid nitrogen, implying that a sufficiently high energy barrier for magnetization reversal is required. However, the ‘under barrier’ relaxation process which refers to QTM, direct processes, and Raman processes significantly reduces the effective energy barrier of molecules.²⁶ Therefore, suppressing these non-Orbach relaxation is of paramount importance in the pursuit of high blocking temperature and energy barrier. Currently, the Raman process, due to its complexity, lacks effective control method, while constructing degenerate ground state doublets is sufficient to suppress the direct process. In this context, how to suppress the zero-field quantum tunneling effect is a crucial issue. Over the past decade, it has been established that QTM is modulated by molecular symmetry, magnetic exchange coupling, the strength of ligand-field, hyperfine splitting, the isotope effect, intramolecular vibrations, and dipole-dipole interactions. Based on this, a brief overview of the strategies and latest progress for constructing high-performance SMMs is given in following sections.

1.3 Lanthanide-based single-molecule magnets

In 1993, Sessoli *et al.* reported the first single-molecule magnets (Mn_{12}Ac).²⁷ As illustrated in Figure 1.3.1, a central Mn^{IV} tetrahedron is surrounded by an outer layer of eight Mn^{III} ions, featuring a $[\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4(\mu_3\text{-O})^{12}]^{16+}$ core with D_{2d} symmetry. In this system, all the metal ions are antiferromagnetically coupled, forming a complex spin-frustration. The combination of the large ground state spin ($S = 10$) and significant negative magnetic anisotropy (D) allows Mn_{12}Ac to exhibit hysteresis behavior.

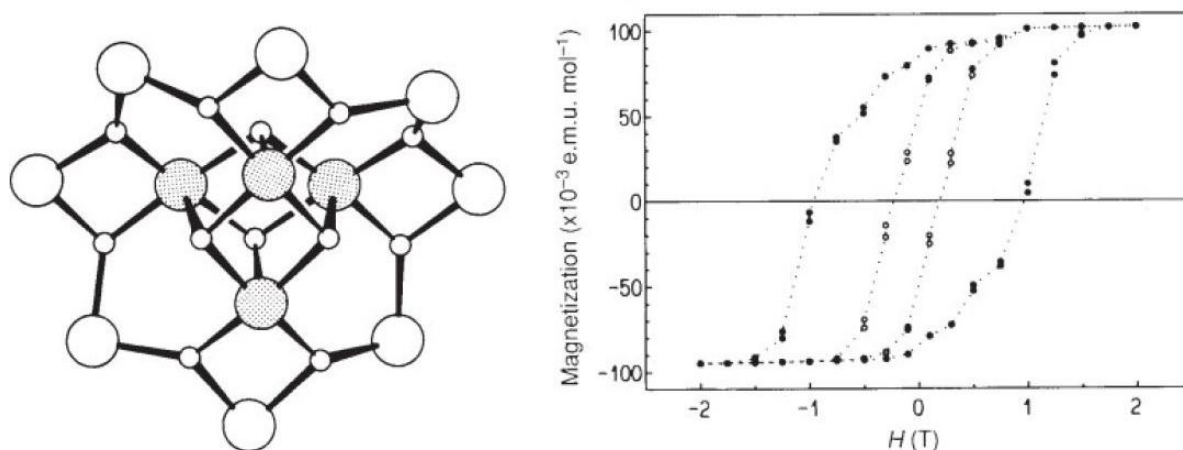


Figure 1.3.1 The core molecular structure of Mn_{12}Ac (left), and its hysteresis loops at low temperature (right).²⁷

However, due to the strong crystal field effects, the advancement of transition metal based SMMs is often limited by the quenching of orbital angular momentum in typical coordination environments, hindering breakthroughs in their energy barrier and blocking temperature. In contrast, for lanthanide ions, their $4f$ electrons are effectively shielded by the outer shells, preserving significant orbital angular momentum and exhibiting strong spin-orbital coupling. This intrinsic anisotropy within single ion allows lanthanide complexes as a superior alternative to construct SMMs with high energy barrier and blocking temperature. Therefore, the following sections will focus on the types of lanthanide-based SMMs and the progress in the strategies in constructing high performance SMMs.

1.3.1 Mononuclear lanthanide-based single-molecule magnets

Mononuclear lanthanide-based SMMs, which contain only one lanthanide ion in the molecule, are the most widely studied system. The prototype molecule is the first lanthanide-based SMM, $[\text{NBu}_4]^+[\text{TbPc}_2]^-$, reported by Ishikawa *et al.* in 2003,²⁸ which is also the first single-ion magnet. This complex exhibits a classic sandwich-type structure as shown in Figure 1.3.2, where a Tb^{III} ion is encapsulated by two phthalocyanine (Pc) ring, forming a square antiprismatic coordination geometry (D_{4d}) where eight N atoms of two Pc rings coordinate to the central Tb^{III} ion. The AC magnetic susceptibility measurements reveal a significant SMM behavior with energy barrier of 230 cm^{-1} and a butterfly-shaped hysteresis loop observed at 1.7 K. Subsequently, such SMM behavior was also identified in isostructural Dy^{III} and Ho^{III} analogues. Following this, extensive investigation, prominently led by the groups of Mario Ruben,^{19, 29-31}

Masahiro Yamashita,³²⁻³⁵ and Jianzhuang Jiang,^{36, 37} has expanded this family through chemical modification. By introducing different functional group into phthalocyanine or porphyrin ligands, a series of double-decker and multi-decker sandwich like complexes were synthesized, and the energy barrier has been successfully pushed toward 1000 K. Furthermore, due to their excellent chemical and physical stability, and tunable structures, these complexes are regarded as ideal candidate materials for constructing molecular spintronic device and quantum bit prototypes.^{31, 38-42}

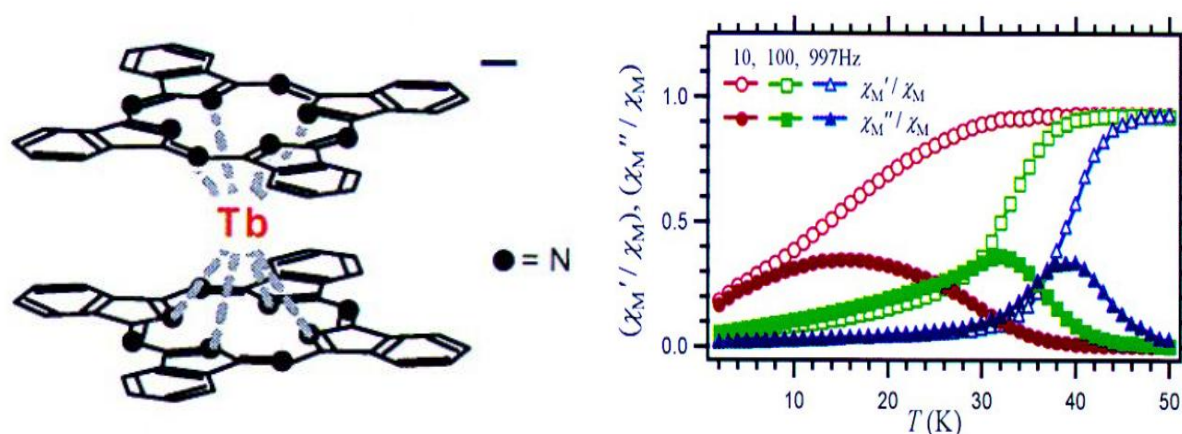


Figure 1.3.2 The molecular structure of [TbPc₂]⁻ (left) and the temperature-dependent ac susceptibility of [NBu₄]⁺[TbPc₂]⁻ at variable frequencies (right).²⁸

1.3.2 Multinuclear lanthanide-based single-molecule magnets

As the name suggests, multinuclear lanthanide-based SMMs contain multiple lanthanide ion centers and are classified into homonuclear and heteronuclear complexes. Through chemical modification and synthetic methods, the number of nuclei has expanded from binuclear complexes to clusters containing as many as 140 lanthanide centers.⁴³

Due to the highly contracted nature of 4*f* orbitals, the magnetic exchange interactions between lanthanide ions are significantly weaker than that of 3*d* SMM and 3*d*-4*f* SMM (*vide infra*). The magnetic coupling strength is intrinsically governed by the topology of the metal skeleton, remaining fundamental to elucidating the correlation between magnetic property and structure. However, the contribution of the significant orbital angular momentum and the complexity of crystal field splitting make it difficult to apply the isotropic spin Hamiltonians, often requiring specific case-by-case analysis.⁴⁴ Furthermore, as the number of lanthanide ions increases, the complexity of these factors scales dramatically, posing severe challenges for the analysis and understanding of high-nuclear-number systems. Consequently, current research primarily focused on low-nuclear-number systems. As illustrated in Figure 1.3.3, the diverse metal skeletal types for up to hexanuclear lanthanide-based SMMs include: linear,^{33, 45-47} triangular,⁴⁸⁻⁵⁰ rhombus,^{51, 52} pyramid,^{53, 54} rectangular or square,⁵⁵⁻⁵⁹ pentagon,^{60, 61} tetragonal pyramid,^{62, 63} super triangle,⁶⁴ butterfly-like pattern,⁶⁵ hexagon,^{66, 67} triangular prism,⁶⁸ hexagon disc,⁶⁹ and square anti-prism.^{70, 71}

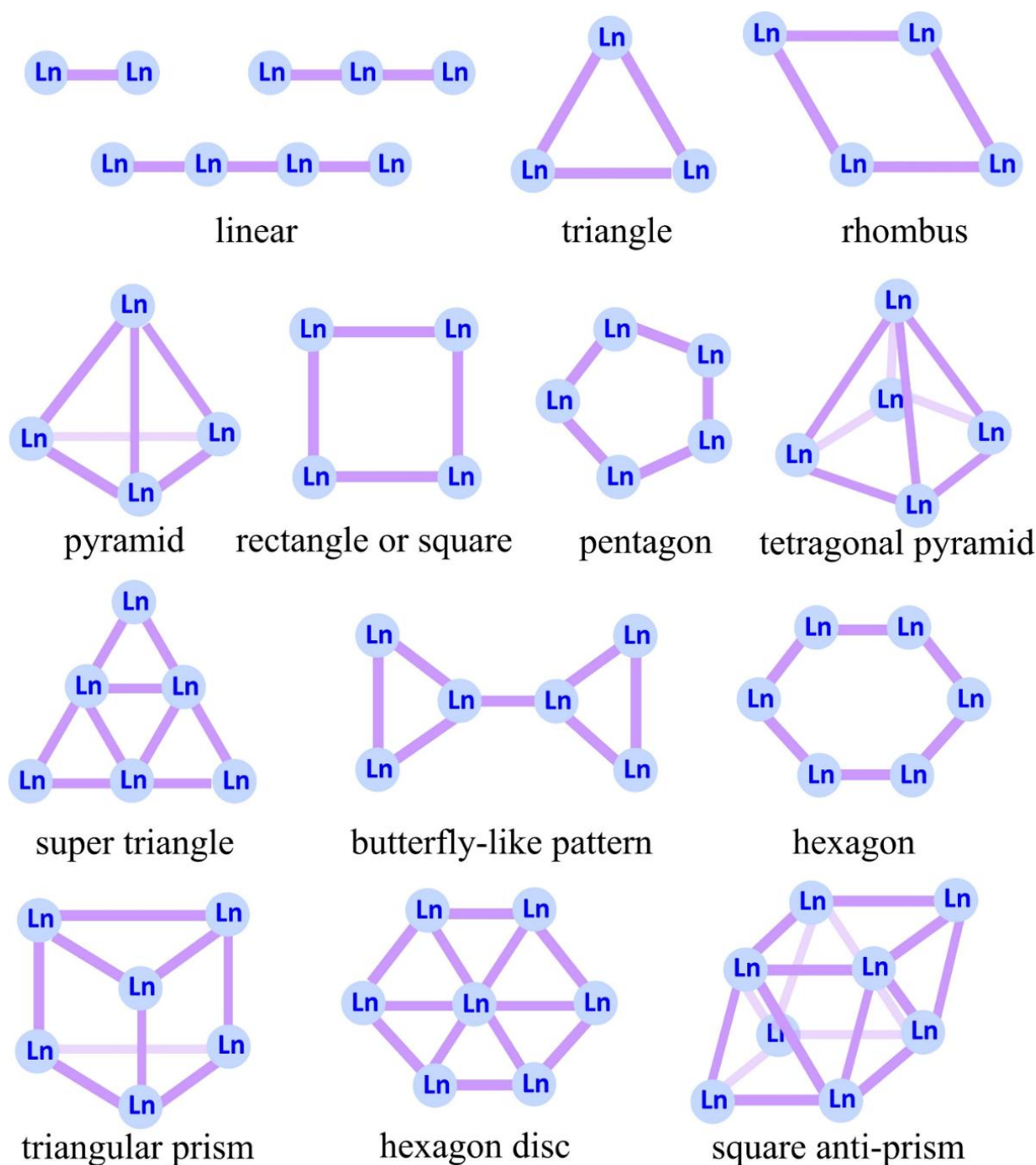


Figure 1.3.3 Diverse metal skeletal types of lanthanide-based SMMs.⁴⁴

Among the aforementioned metal skeletal types, single-molecule toroids (SMTs), as a novel class of materials possessing unique topological and magnetic properties, have gradually attracted attention. Typically, SMTs exhibit wheel-like or local wheel-like topologies. The local magnetic moments within the molecule are vortex arranged through the specific magnetic anisotropy and the exchange interactions between metal centers.^{72, 73} Consequently, the toroidal moments are not only dependent on the symmetry of the molecule and the orientation of the local magnetic moments, but also affected by the magnetic interactions such as dipole-dipole interactions and exchange interactions between lanthanide ions, rendering the whole system

insensitive to the magnetic fields.⁷⁴ Moreover, the rapid decay of the magnetic field generated by the net toroidal moment facilitates high-density integration of qubits.⁷²

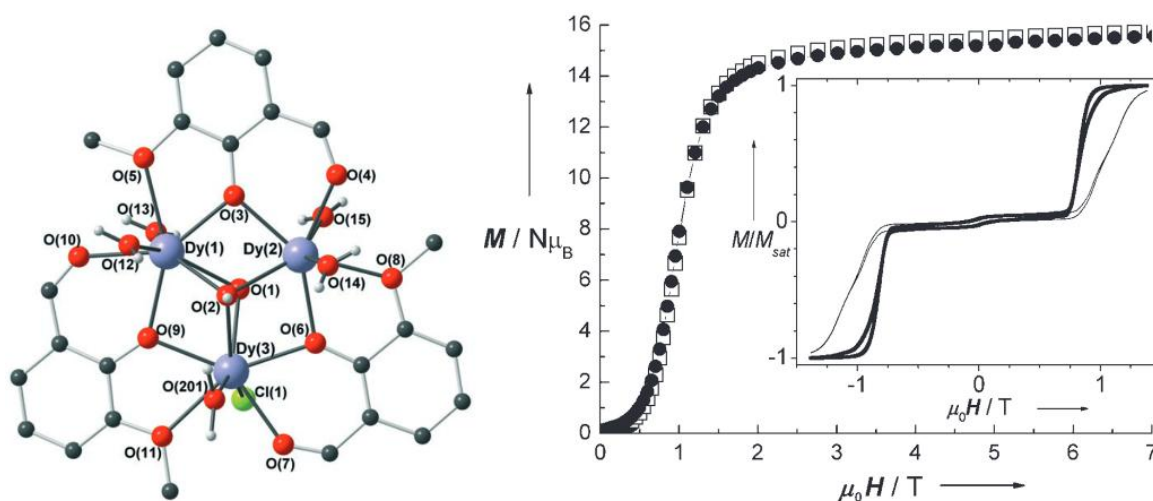


Figure 1.3.4 The crystal structure of Dy₃ complex (left) and the field-dependence of magnetization (right). The inset in the right panel is the magnetic hysteresis loop at 0.1 K.⁵⁰

In 2006, Tang *et al.* reported the first Dy₃ complex exhibiting SMT behavior.⁵⁰ The core structure, as shown in Figure 1.3.4, consists of three Dy^{III} ions and three o-vanillin ligands, where the Dy^{III} centers are bridged by two μ₃-O to form a triangular topological structure. Due to the weak antiferromagnetic coupling between the Dy^{III} ions, the complex exhibits a ground with $S = 0$. Therefore, the slow magnetic relaxation behavior originates from the excited state rather than ground state. More interestingly, this complex exhibits SMM behavior even under zero field.

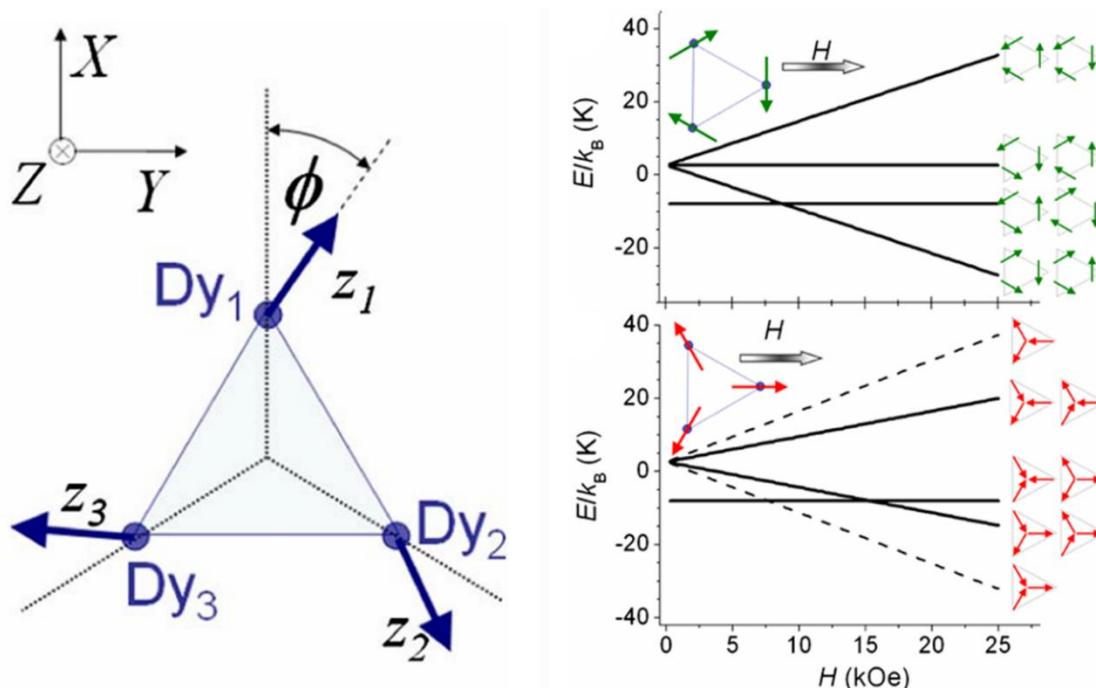


Figure 1.3.5 Schematic of the possible spin arrangement in Dy₃ complex (left) and the Zeeman splitting diagrams of the Dy₃ complex and the corresponding orientations of the magnetic easy axes.⁷⁵

Although the initial investigation did not recognize the correlation with toroidal behavior, subsequent theoretical calculations and further experiments by Luzon *et al.* revealed that the magnetic easy axes of three Dy^{III} ions are arranged in a triangular plane with head-to-tail orientation (Figure 1.3.5).⁷⁵ Such unique spin chirality alignment allows the local magnetic moments to generate a significant toroidal magnetic moment, thus initiating investigation on SMT.

1.3.3 3d-4f hybrid lanthanide-based single-molecule magnets

Recognizing the inherently weak magnetic exchange between lanthanide ions, Osa *et al.* innovatively incorporated 3d metal ions into 4f systems.⁷⁶ With such strategy, the quantum tunneling of magnetization is effectively suppressed by the strong magnetic interaction between 3d and 4f ions, thereby significantly improving the energy barrier. Furthermore, the significant differences in coordination preferences between 3d ions (low coordination numbers and specific geometries) and 4f ions (high coordination numbers) facilitate the customized design complexes with specific geometries.

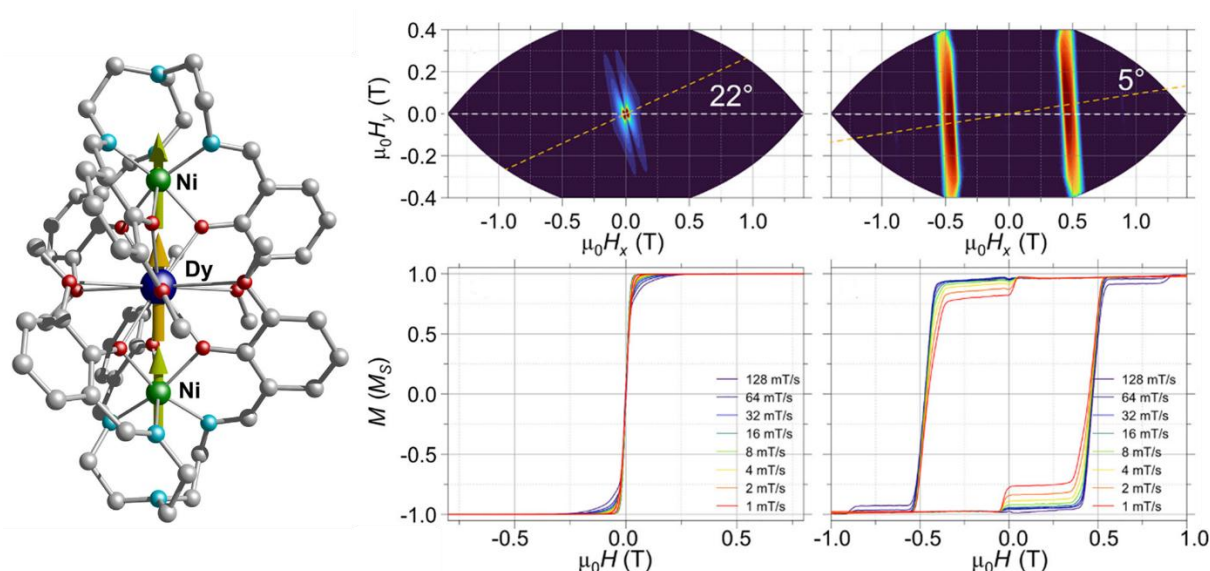


Figure 1.3.6 The crystal structure of Ni₂Dy complex (left). At 30 mK, the angle dependence of the $M(H)$ loops with a fixed sweep rate of 64 mT/s and the sweep-rate dependent $M(H)$ loops for Zn₂Dy (middle) and Ni₂Dy (right).⁷⁷

Liu *et al.* designed and synthesized a Fe^{II}-Dy^{III} complex with high energy barrier and significant slow relaxation behavior at high temperature.⁷⁸ However, no hysteresis loop was observed at a low temperature of 1.8 K, which is primarily attributed to the non-collinear easy axes of the Fe^{II} and Dy^{III} ions. Recently, Jing *et al.* successfully synthesized a series of 3d-4f-3d trinuclear complexes with linear arrangements of metal centers and collinear anisotropic axes.⁷⁷ μ -SQUID measurements revealed that the antiferromagnetically coupled Zn₂Dy complex exhibits a rapid magnetic relaxation and closed hysteresis loops 30 mK. In contrast, a significant slow magnetic relaxation behavior and broad open hysteresis loops are observed in the ferromagnetically coupled Ni₂Dy complex (Figure 1.3.6). By coupling Ni^{II} ions (with moderate anisotropy and zero-field QTM) with Dy^{III} ion and minimizing transverse interactions

through the structural alignment, the magnetic performance was significantly enhanced. Such design not only yields exchange spring magnets in molecular scale but also provides a unique perspective for designing SMMs with tunable relaxation behavior and magnetic bistable states by optimizing $3d$ - $4f$ interactions.

1.3.4 Radical-contained lanthanide-based single-molecule magnets

In addition to the aforementioned strategy of introducing strong intramolecular coupling through $3d$ metal ions, paramagnetic radicals are considered as another ideal candidates. Its core advantage lies in the fact that the diffuse orbitals of radicals penetrate the outer shell electrons of lanthanide ions, facilitating strong exchange coupling and inducing a significant giant spin effect.^{79, 80} To date, various ligands containing radicals have been reported for constructing single-molecule magnets, such as dinitrogenyl,^{79, 81, 82} triazinyl,⁸³ phthalocyanine,^{84, 85} tetrazine,^{59, 86} nitronly nitroxide⁸⁷ for example.

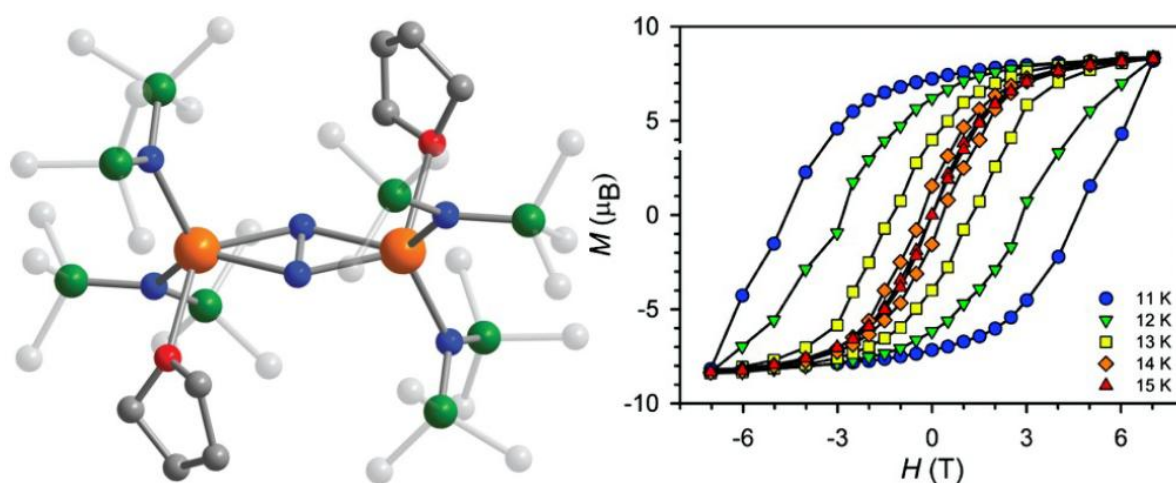


Figure 1.3.7 The crystal structure of $[\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Ln}\}_2(\mu\text{-}\eta_2\text{:}\eta_2\text{-N}_2)]^-$ anion (left) and the hysteresis loops of Tb analogue at low temperature (right).^{79, 81}

In 2011, Rinehart *et al.* reported a series of dinitrogen radical-bridged dinuclear lanthanide complexes, $[\text{K}(18\text{-crown-6})(\text{THF})_2][\{[(\text{Me}_3\text{Si})_2\text{N}]_2(\text{THF})\text{Ln}\}_2(\mu\text{-}\eta_2\text{:}\eta_2\text{-N}_2)]$ ($\text{Ln} = \text{Gd}^{\text{III}}, \text{Tb}^{\text{III}}, \text{Dy}^{\text{III}}, \text{Ho}^{\text{III}}, \text{Er}^{\text{III}}$) (Figure 1.3.7).⁷⁹ Each Ln^{III} center is coordinated with two $(\text{Me}_3\text{Si})_2\text{N}^-$ ions, one THF molecule and a bridging N_2^{3-} ligand, forming a distorted tetragonal pyramidal geometry (Figure 1.3.7). From a magnetic coupling perspective, the antiferromagnetic coupling exists in both $\text{Ln}^{\text{III}}\text{-Ln}^{\text{III}}$ and $\text{Ln}^{\text{III}}\text{-radical}$ interactions, forming an in-plane linear spin-frustrated arrangement. However, due to the extremely strong antiferromagnetic coupling between lanthanide ion and radical, the $\chi_m T$ - T curves overall exhibit ferromagnetic coupling behavior. Except for Gd analogue, all these lanthanide analogues function as single-molecule magnets with energy barrier of 277.0 cm^{-1} for Tb analogue, 123 cm^{-1} for Dy analogue, 73 cm^{-1} for Ho analogue and 36 cm^{-1} for Er analogue, respectively. Notably, the Tb analogue exhibits a coercivity of up to 5 T at 11 K with a blocking temperature of 14 K, while for the Dy analogue, a coercivity of 1.5 T at 2 K and a blocking temperature of 8.3 K as observed. For comparison and analysis, a series of analogous complex but with closed-shell N_2^{2-} bridged ligand were synthesized, of which only Dy derivate possess SMM behavior and the energy barrier drops

dramatically to 18 cm^{-1} . This significant difference indicates that the strong exchange coupling introduced by the radical disrupts the magnetic anisotropy of Dy^{III} ion itself. Consequently, the molecule follows the giant spin model, where the SMM behavior originates from the strong coupling rather than the contribution of a single lanthanide ion, reflecting that strong magnetic exchange coupling can effectively suppress quantum tunneling of the magnetization.

1.4 Strategies for designing lanthanide-based single-molecule magnets

As mentioned above, lanthanide-based SMMs have been extensively investigated due to their strong magnetic anisotropy and chemical tunability. These unique advantages position lanthanide-based SMMs as a potential candidate for quantum computing and high-density storage, although they are currently limited by relatively low energy barriers and blocking temperatures. Motivated by this, through long-term research efforts, the key factors affecting the performance of lanthanide-based SMMs have been gradually clarified, and the corresponding optimization strategies have been proposed accordingly. These factors mainly include molecular structure symmetry, hyperfine interactions, the strength of the ligand field, intermolecular interactions and dipole-dipole interactions, and intramolecular vibrations. The following section will describe their roles in lanthanide-based SMMs in detail.

1.4.1 Molecular structure symmetry

The spin Hamiltonian corresponding to a metal center ion within specific ligand field can be express as:

$$\hat{H}_{CF} = \sum B_q^k \hat{O}_q^k \quad \text{Equation 1.4.1}$$

Where B_q^k represents the crystal field parameters and $\hat{O}_q^k$ denotes the Stevens operators.^{88, 89} For transition metal ions, $q = 2, 4$, while for lanthanide ion, $q = 2, 4, 6$ and $|k| \leq q$. When $k = 0$, the B_q^k terms correspond to the axial crystal field parameter; in contrast, the B_q^k terms represent the transverse crystal field parameter as $k \neq 0$. The latter induces the transverse magnetic anisotropy, which is a crucial factor driving the zero-field quantum tunneling of magnetization. Therefore, minimizing the magnitude of B_q^k is crucial for obtaining high-performance SMMs. Theoretical studies indicate that for highly symmetric coordination environments, such as $C_{\infty v}$, $D_{\infty h}$, D_{4d} , D_{5h} , D_{6d} and I_4 , the B_q^k parameter is theoretically equal to zero. Although only few actual complexes strictly satisfy these ideal symmetries, tailoring the coordination geometry via synthetic method to form an approximate point group can significantly reduce the magnitude of transverse parameters, thereby effectively suppressing zero-field QTM processes.

As mentioned before, due to the shielding effect, the ligand field interaction is relatively weak, preserving the specific electronic characteristics of lanthanide ions. Therefore, aligning the symmetry of the ligand field with the specific electron distribution of the lanthanide ion is a paramount approach for enhancing the magnetic properties. Rinehart and Long systematically classifies the electron cloud shapes of trivalent lanthanide ions into three types⁹⁰ based on their quadrupolar moments: (1) Oblate for Ce^{III} , Pr^{III} , Nd^{III} , Tb^{III} , Dy^{III} , and Ho^{III} . (2) Prolate for Pm^{III} , Sm^{III} , Er^{III} , Tm^{III} , and Yb^{III} . (3) Spherical for Gd^{III} and Lu^{III} due to the half-filled or fully filled electron configurations. While Eu^{III} has no magnetism due to $J = 0$ as shown in Figure 1.4.1.

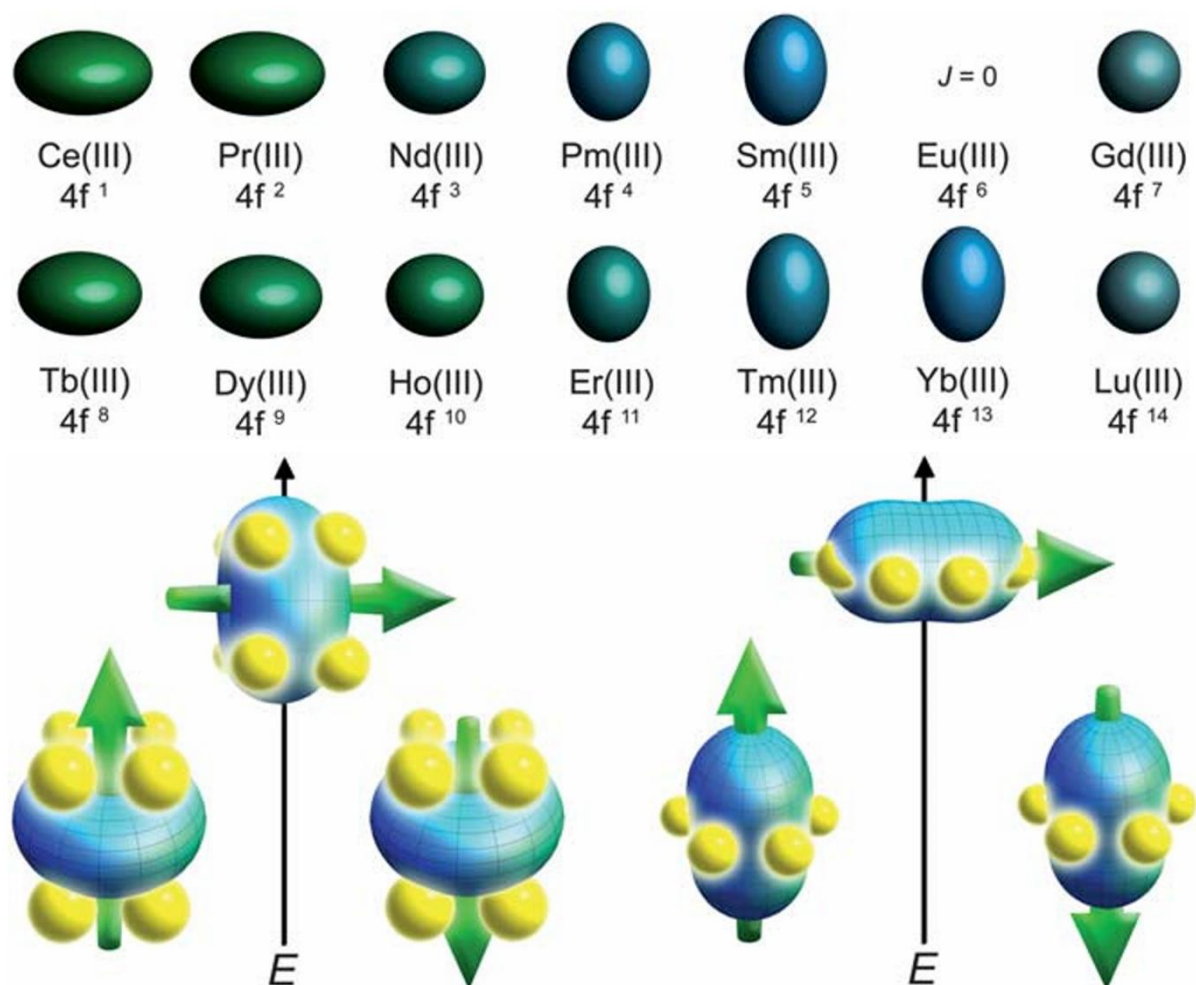


Figure 1.4.1 Schematic of the electron distribution of trivalent lanthanide ions in the ground state (top). And the influence of ligand Field charge distribution on the direction of magnetic axis under oblate or prolate electron cloud shapes (bottom).⁹⁰

To maximize the axial magnetic anisotropy of the ground state and suppress the QTM effect, the contributions of the ligand field are required to be positioned in a suitable location. For example, Tb^{III} and Dy^{III} are typical oblate to distribute negative charges in the axial direction of the ligand field, thereby lowering the energy of ground state, while prolate ions (Er^{III} and Yb^{III}) requiring equatorial distribution. This explains why different lanthanide ions exhibit drastically different magnetic properties under the same molecular configuration. For example, the complexes Ln[N(SiMe₃)₂]₃ system reported by Zhang *et al.* are isostructural with C_{3v} symmetry; the Er analogue exhibits SMM behavior while Dy analogue is not a SMM.⁹¹ Similarly, in (COT)₂Ln system, Dy analogue fails to be SMM while Er analogue is a SMM.⁹² Thus, the key to fabricating high-performance SMMs lies in designing suitable ligand fields that match the electron cloud shape of the ground state from the chosen lanthanide ions.

In 2011, Jiang *et al.* reported a sandwich-type organometallic complex, CpEr(COT),⁹³ in which the central Er^{III} ion is approximately D_{∞h} (Figure 1.4.2). Below 25 K, the AC magnetic susceptibility exhibits temperature-frequency dependence with two relaxation processes, and the values of their energy barriers are 197 and 323 K, respectively. These two relaxations are

attributed to the coexistence of two stable conformations of the COT ligand at low temperature. Similarly, in 2013, Long and co-workers reported a sandwich-type complex, $[\text{K}(18\text{-crown-6})][\text{Er}(\text{COT})_2]$,⁹⁴ featuring a central Er^{III} in D_{8h} coordination geometry (Figure 1.4.3). This compound exhibits slow magnetic relaxation behavior below 27 K with an effective energy barrier of 150 cm^{-1} . Notably, the hysteresis loops are observable at temperatures up to 10 K and the coercive field reached 1.3 T at 1.8 K, which is a remarkably rare achievement in the field of SMM.

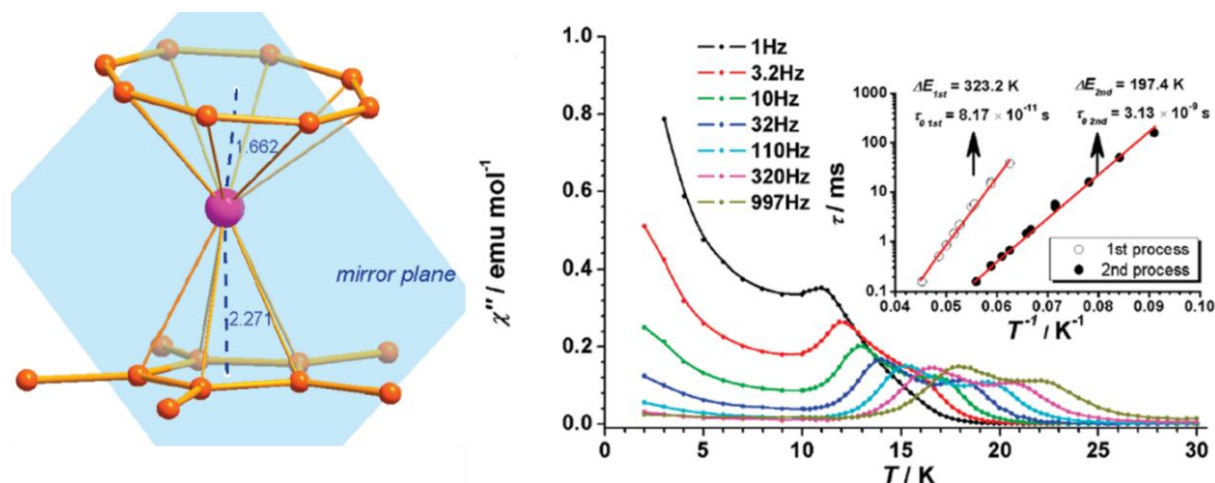


Figure 1.4.2 The core structure of $\text{CpEr}(\text{COT})$ (left) and the frequency-dependence of measurement at various temperature under zero field (right).⁹³

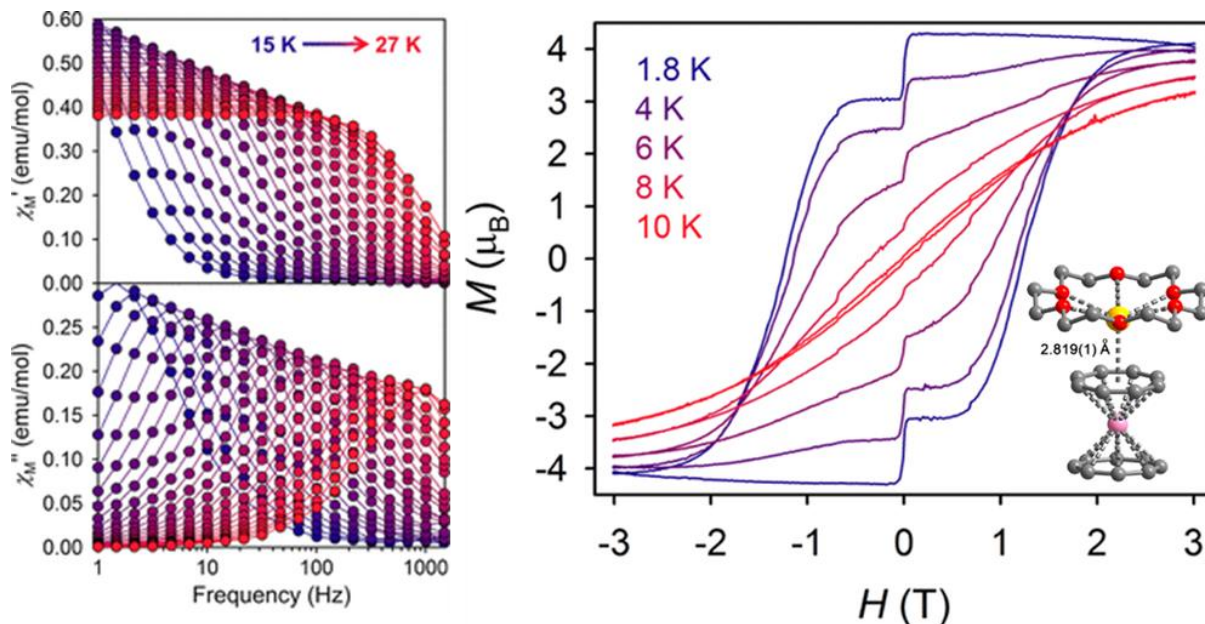


Figure 1.4.3 The temperature-dependent ac measurement under zero field for $[\text{K}(18\text{-c-6})][\text{Er}(\text{COT})_2]$ (left) and its hysteresis loops at different temperatures (right). Its crystal structure is inserted.⁹⁴

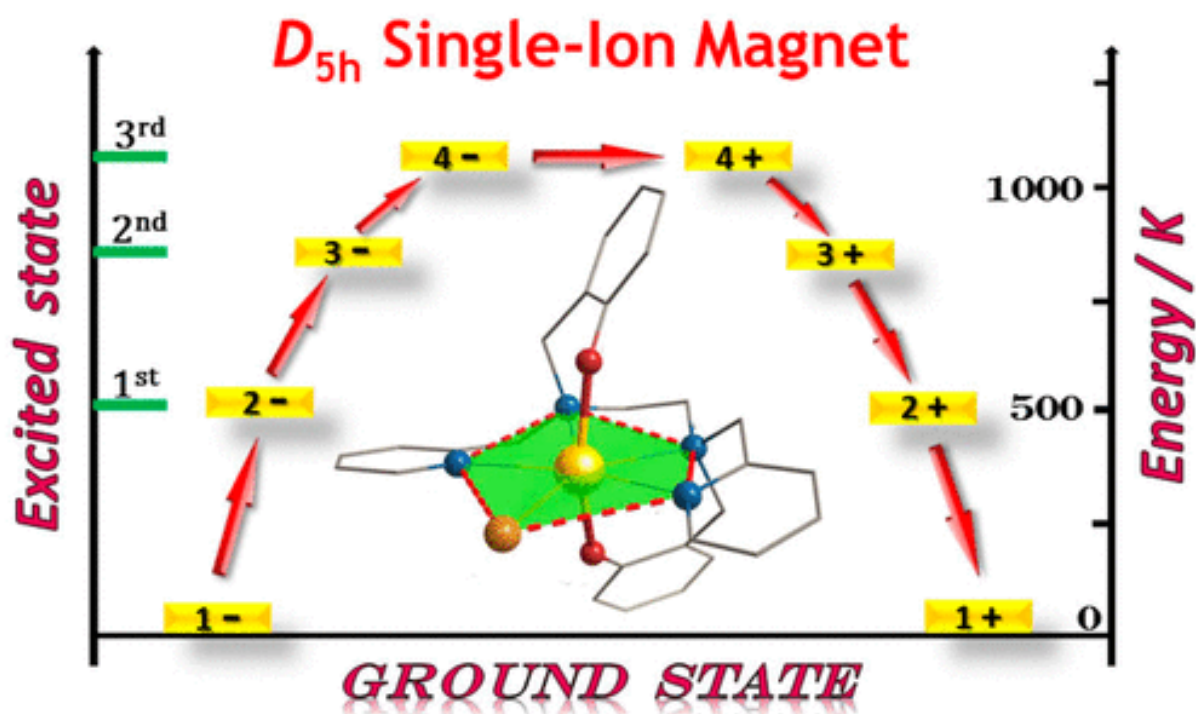


Figure 1.4.4 The molecular structure of $[\text{Dy}(\text{bbpen})\text{Br}]$ and its relaxation pathway.⁹⁵

In 2016, Liu *et al.* reported two complexes, $[\text{Dy}(\text{bbpen})\text{Cl}]$ and $[\text{Dy}(\text{bbpen})\text{Br}]$, in which a pentagonal plane (four N atoms from the ligand and one halide anion coordinate with Dy) together with the axially positioned O atoms from the ligand forms a pentagonal bipyramidal local geometry (Figure 1.4.4).⁹⁵ For both complexes, the structure analysis reveal that the axial Dy-O bond lengths are both around 2.16 Å, which are shorter than the bond lengths of Dy-N (around 2.58 Å) or Dy-X (X represent halide atoms, 2.68 Å for Cl and 2.85 Å for Br, respectively). Combining with the O-Dy-O angles of 154.3(2)° for $[\text{Dy}(\text{bbpen})\text{Cl}]$ and 155.8(2)° for $[\text{Dy}(\text{bbpen})\text{Br}]$, the significant axial compression generates an extremely strong axial crystal field and orients the easy axis perpendicular to the equatorial plane. According to the ac measurements, at a frequency of 1488 Hz, the temperature peaks of $[\text{Dy}(\text{bbpen})\text{Cl}]$ and $[\text{Dy}(\text{bbpen})\text{Br}]$ reach 50 K and 60 K, respectively. Combining this with further theoretical calculations revealed that the magnetic moment reversal of $[\text{Dy}(\text{bbpen})\text{Cl}]$ is achieved via a second excited state, while $[\text{Dy}(\text{bbpen})\text{Br}]$ is relaxed via a third excited state, resulting energy barriers of 708 K and 1025 K for $[\text{Dy}(\text{bbpen})\text{Cl}]$ and $[\text{Dy}(\text{bbpen})\text{Br}]$, respectively, $[\text{Dy}(\text{bbpen})\text{Br}]$ was the highest recorded energy barrier of SMMs at that time.

Later, Ding *et al.* synthesized a new complex as shown in Figure 1.4.5, $[\text{Dy}(\text{OtBu})_2(\text{py})_5][\text{BPh}_4]$, under anhydrous and inert conditions.⁹⁶ Five pyridine molecules coordinated in the equatorial plane and two OtBu bonded along the axial direction form a pentagonal bipyramidal configuration, where the bond lengths of Dy-N vary from 2.534(3)–2.580(3) Å and the bond lengths of Dy-O are 2.110(2) and 2.114(2) Å with a near linear O-Dy-O angle of 178.91(9)°, creating a strong axial crystal field. Theoretical calculations revealed its Stark sublevel configuration to be $m_J = \pm 15/2, \pm 13/2, \pm 11/2, \pm 9/2$, corresponding to energy levels of 0, 564, 940, and 1141 cm^{-1} , respectively. This complex exhibits superior zero-field

SMMs behavior with a peak temperature of 100 K at a frequency of 1488 Hz according to the ac analysis. The experimentally fitted effective energy barrier, 1261 cm^{-1} , is in accordance with the calculated energy of the fourth excited state, confirming that the relaxation process is dominated by the fourth state. This achievement represents a further advancement in the energy barrier of single-molecule magnets.

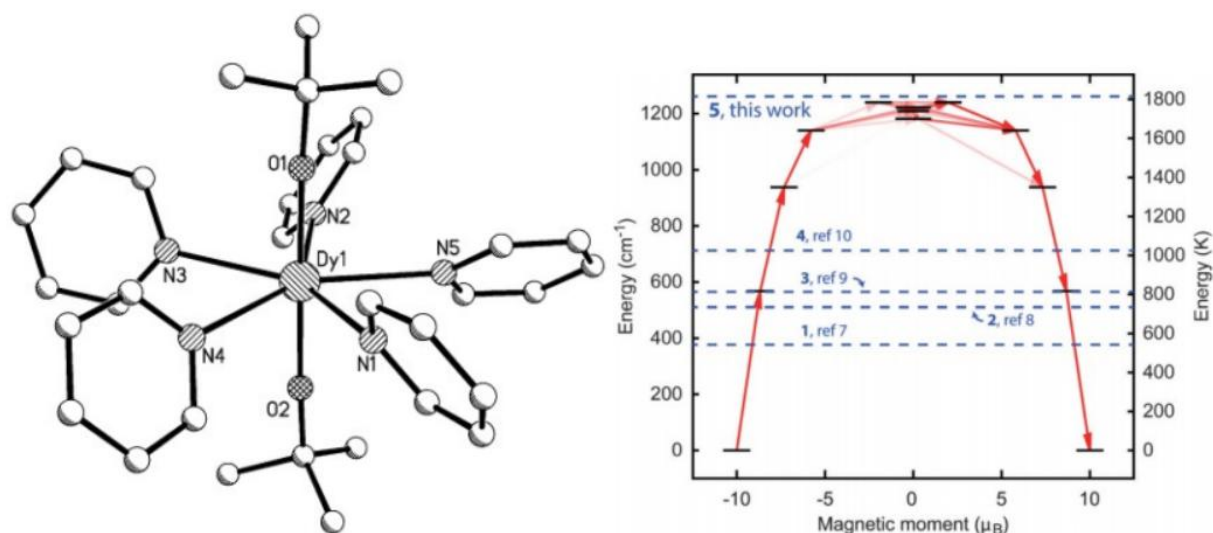


Figure 1.4.5 The crystal structure of $[\text{Dy}(\text{OtBu})_2(\text{py})_5][\text{BPh}_4]$ (left) and the energy level splitting diagram of the ground state (right). The red arrows indicate the path of magnetic susceptibility reversal.⁹⁶

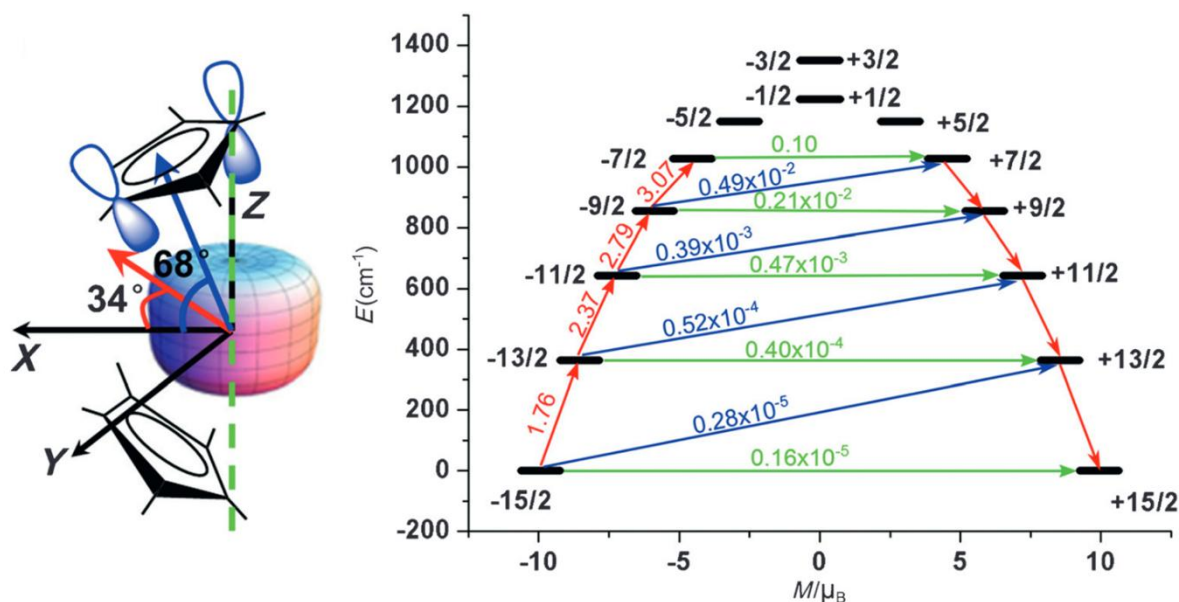


Figure 1.4.6 The structure of $[\text{Cp}_2\text{Dy}]^+$ as model for calculation (left) and the energy level splitting diagram of the $J = 15/2$ ground state (right). The red arrows represent the relaxation pathways.⁹⁷

In 2016, based on detailed theoretical calculations in the classical $[\text{Cp}_2\text{DyX}]$ system, Meng *et al.* discovered that the presence of the counterions actually weakens the purity of the axial crystal field, and predicted that the magnetic relaxation barrier could theoretically break through

the 1000 cm^{-1} barrier by removing the counterion to construct a $[\text{Cp}_2\text{Dy}]^+$ (Figure 1.4.6).⁹⁷ This insightful hypothesis initiated a huge sensation in the field of SMMs because it suggested that single-molecule magnets could potentially retain magnetization information at liquid nitrogen temperatures and even higher. Subsequently, numerous top research groups worldwide engaged in a fierce synthetic race, aiming to overcome the chemical challenge of the highly reactive and hard isolate $[\text{Cp}_2\text{Dy}]^+$ cation.

In 2017, the Layfield⁹⁸ and Mills⁹⁹ groups reported a $[\text{Dy}(\text{Cp}^{\text{III}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ complex with remarkable SMM properties. The design cleverly introduced three electron-donated isopropyl groups into the cyclopentadiene rings to increase the steric hindrance, where the two Cp ring planes are tilted at a certain angle and encapsulate the Dy^{III} center to form a distorted sandwich structure. Such low-coordinate, strong-axis design generates extremely strong crystal field splitting, effectively suppressing the QTM effect in the ground state. As magnetic measurements reveal, this complex exhibits a clearly open hysteresis loop even at a high temperature of 60 K, a coercivity of up to 2 T at 2 K and the out-of-phase peak locates at 111 K at a frequency of 1488 Hz. Moreover, the experimental fitted energy barrier reaches 1256 cm^{-1} , proving the effectiveness of this strategy.

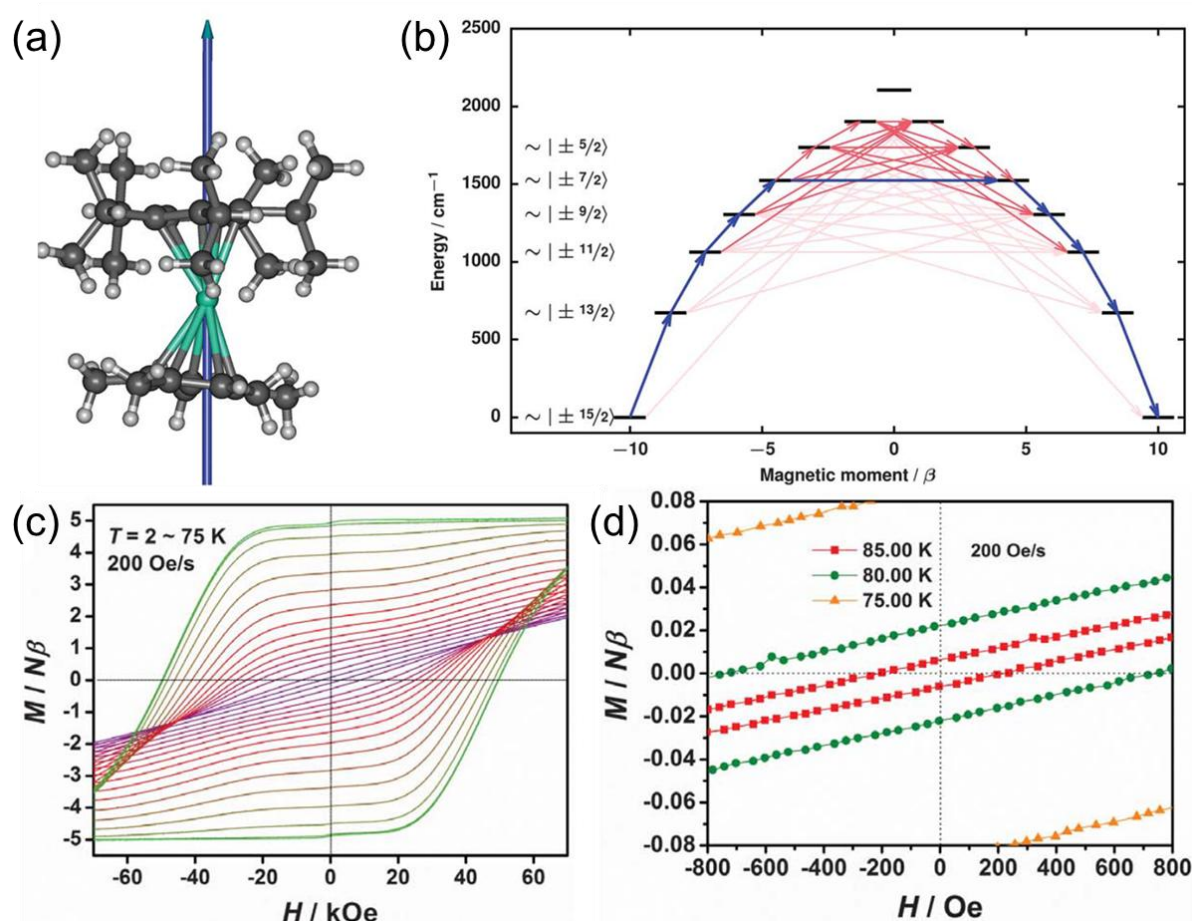


Figure 1.4.7 (a) The molecular structure of $[(\text{Cp}^{\text{iPr}_5})\text{Dy}(\text{Cp}^*)][\text{B}(\text{C}_6\text{F}_5)_4]$. (b) The energy level splitting diagram of the $J = 15/2$ ground state. The red arrows show the relaxation pathways. The magnetic hysteresis loops across temperature intervals of 2-75 K (c) and 75-85 K.¹⁰⁰

In 2018, Layfield and Tong groups collaborated to report a milestone dysprosium cation complex, $[(\text{Cp}^{\text{iPr5}})\text{Dy}(\text{Cp}^*)][\text{B}(\text{C}_6\text{F}_5)_4]$ (Figure 1.4.7).¹⁰⁰ Compared with the earlier complexes of this type, the two Cp rings of this complex adopt a nearly parallel orientation, where the highly symmetric sandwich-type configuration produces an exceptionally magnetic anisotropy. Theoretical calculations reveal that the magnetic axes of its ground state and high-energy excited states are highly aligned, both crossing through the geometric centers of the two Cp rings, of which the perfect collinearity of the magnetic axes greatly suppresses the QTM between low-energy states. Under an AC frequency of 1488 Hz, the out-of-phase peak locates at 138 K, and an astonishing effective energy barrier of 1524 cm^{-1} . More importantly, this complex achieved a blocking temperature of 80 K, successfully surpassing the temperature of liquid nitrogen, with a coercive field of 5 T at 2 K. Currently, it still holds the record for both the highest energy barrier and blocking temperature in SMMs. Beyond the role of symmetry, based on theoretical analysis, they also pointed out that the spin-phonon coupling, specifically the vibrational modes within the Cp rings, plays a dominant role in the thermally activated relaxation process.

1.4.2 Hyperfine interactions

After discussing the influence of ligand field symmetry on electronic level structure, it is also worth mentioning that the slow relaxation behavior of SMMs is also constrained by the more subtle microscopic interactions. In nature, all elements with atomic numbers below 94 possess at least one isotope and different isotopes of the same element generally contain different nuclear spins. Table 1.4.1 lists the natural isotope lanthanide.

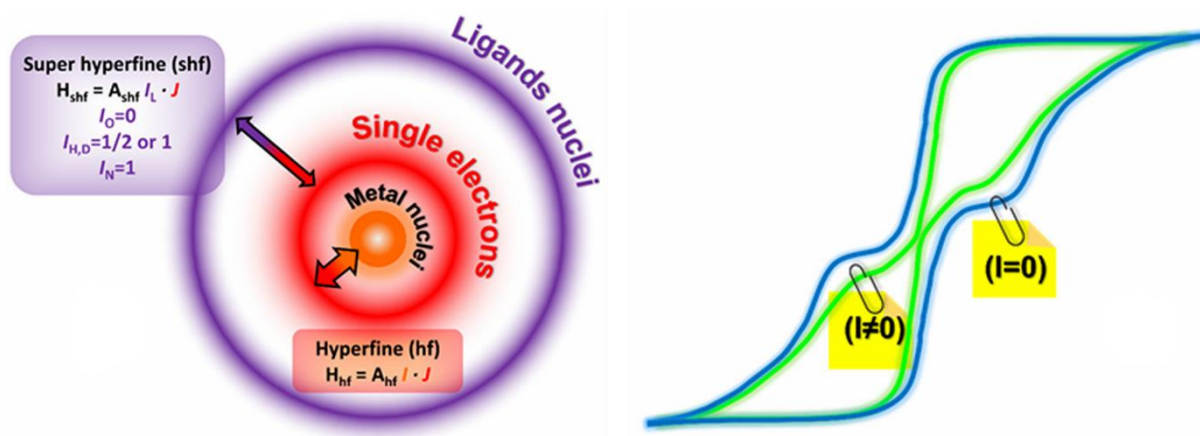


Figure 1.4.8 Scheme of the hyperfine interaction between the electron and the metal nuclei, and the super-hyperfine interaction between the electron and the ligand nuclei (left). Scheme of hysteresis loops for isotopologues (right).¹⁰¹

These nuclear spins interact with electron spins through hyperfine coupling, resulting in further splitting of the Stark levels (For $I = 0$, there is no interaction). Due to the small splitting energy level via hyperfine coupling, in zero or low magnetic field, the hyperfine interactions cause frequent intersections and overlaps between different states, which are reflected in the Zeeman diagram with so-called level anti-crossing. These different states with degenerate or quasi-degenerate energy can trigger many quantum effects. Likewise, the spin couples to the

ligand nuclei through super-hyperfine interaction, though a typically weaker effect compared to hyperfine coupling (Figure 1.4.8).¹⁰¹ Therefore, an in-depth understanding of how nuclear spins influence the properties of SMMs is crucial for providing design insights. Building upon established theories, several examples are introduced for illustration.

Table 1.4.1 The natural abundance of stable lanthanide elements and their nuclear spin.¹⁰²

Element	Isotope, natural abundance and nuclear spin
La	¹³⁹ La (100%, <i>I</i> = 7/2)
Ce	¹⁴⁰ Ce (89%, <i>I</i> = 0), ¹⁴² Ce (11%, <i>I</i> = 0)
Pr	¹⁴¹ Pr (100%, <i>I</i> = 5/2)
Nd	¹⁴² Nd (27%, <i>I</i> = 0), ¹⁴³ Nd (12%, <i>I</i> = 7/2), ¹⁴⁴ Nd (24%, <i>I</i> = 0), ¹⁴⁵ Nd (8%, <i>I</i> = 7/2), ¹⁴⁶ Nd (17%, <i>I</i> = 0), ¹⁴⁸ Nd (6%, <i>I</i> = 0), ¹⁵⁰ Nd (6%, <i>I</i> = 0)
Sm	¹⁴⁴ Sm (3%, <i>I</i> = 0), ¹⁴⁷ Sm (15%, <i>I</i> = 7/2), ¹⁴⁸ Sm (11%, <i>I</i> = 0), ¹⁴⁹ Sm (14%, <i>I</i> = 7/2), ¹⁵⁰ Sm (7%, <i>I</i> = 0), ¹⁵² Sm (27%, <i>I</i> = 0), ¹⁵⁴ Sm (23%, <i>I</i> = 0)
Eu	¹⁵¹ Eu (48%, <i>I</i> = 5/2), ¹⁵³ Eu (52%, <i>I</i> = 5/2)
Gd	¹⁵⁴ Gd (2%, <i>I</i> = 0), ¹⁵⁵ Gd (15%, <i>I</i> = 3/2), ¹⁵⁶ Gd (21%, <i>I</i> = 0), ¹⁵⁷ Gd (16%, <i>I</i> = 3/2), ¹⁵⁸ Gd (25%, <i>I</i> = 0), ¹⁶⁰ Gd (22%, <i>I</i> = 0)
Tb	¹⁵⁹ Tb (100%, <i>I</i> = 3/2)
Dy	¹⁶⁰ Dy (2%, <i>I</i> = 0), ¹⁶¹ Dy (19%, <i>I</i> = 5/2), ¹⁶² Dy (25%, <i>I</i> = 0), ¹⁶³ Dy (25%, <i>I</i> = 5/2), ¹⁶⁴ Dy (28%, <i>I</i> = 0)
Ho	¹⁶⁵ Ho (100%, <i>I</i> = 7/2)
Er	¹⁶⁴ Er (2%, <i>I</i> = 0), ¹⁶⁶ Er (33%, <i>I</i> = 0), ¹⁶⁷ Er (23%, <i>I</i> = 7/2), ¹⁶⁸ Er (27%, <i>I</i> = 0), ¹⁷⁰ Er (15%, <i>I</i> = 0)
Tm	¹⁶⁹ Tm (100%, <i>I</i> = 1/2)
Yb	¹⁷⁰ Yb (3%, <i>I</i> = 0), ¹⁷¹ Yb (14%, <i>I</i> = 1/2), ¹⁷² Yb (22%, <i>I</i> = 0), ¹⁷³ Yb (16%, <i>I</i> = 5/2), ¹⁷⁴ Yb (32%, <i>I</i> = 0), ¹⁷⁶ Yb (13%, <i>I</i> = 0)
Lu	¹⁷⁵ Lu (97%, <i>I</i> = 7/2), ¹⁷⁶ Lu (3%, <i>I</i> = 7)

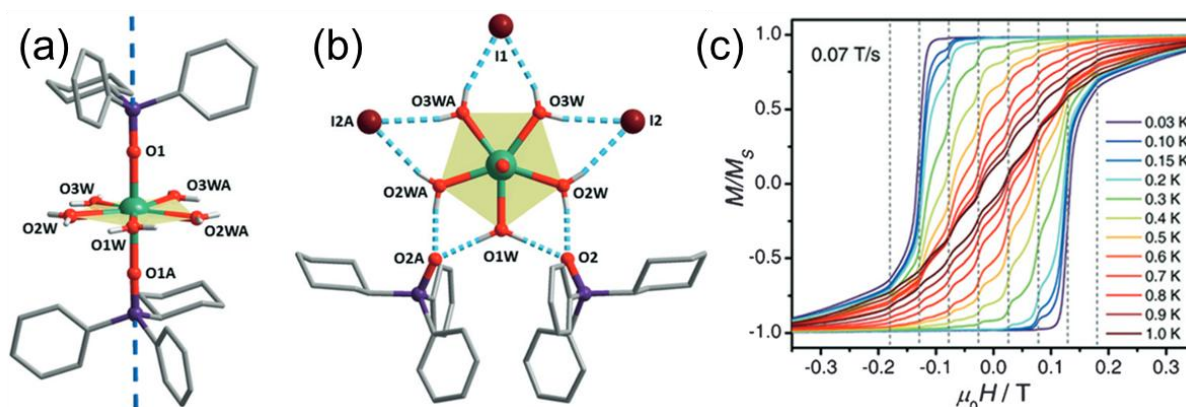


Figure 1.4.9 The molecular structure (a) and the coordination environment (b) of $[\text{Ho}(\text{CyPh}_2\text{PO})_2(\text{H}_2\text{O})_5]\text{I}_3 \cdot 2(\text{CyPh}_2\text{PO}) \cdot \text{H}_2\text{O} \cdot \text{EtOH}$. (c) The hysteresis loops under low temperature.¹⁰³

Chen *et al.* reported a mononuclear holmium complex, $[\text{Ho}(\text{CyPh}_2\text{PO})_2(\text{H}_2\text{O})_5]\text{I}_3 \cdot 2(\text{CyPh}_2\text{PO}) \cdot \text{H}_2\text{O} \cdot \text{EtOH}$, featuring a pentagonal bipyramidal coordination geometry (Figure 1.4.9).¹⁰³ This complex contains five water molecules in the equatorial plane and two CyPh_2PO ligands along the axial direction, and exhibits significant SMM with an energy barrier of 237 cm^{-1} within the temperature range of 2–24 K. Notably, a distinct parallelogram-shaped hysteresis loops with equidistant steps can be observed at low temperature, where the magnetic fields corresponding to the steps align precisely with the calculated hyperfine coupling between the electron spin and nuclear spin of ^{165}Ho . As a non-Kramers ion, ^{165}Ho with $J = 8$ ground state typically exhibits strong quantum tunneling under zero field conditions. However, the authors point out that due to the hyperfine interaction with nuclear spin ($I = 7/2$), the system forms a ‘Kramers-like’ ground state, which effectively suppresses the quantum tunneling under zero field and thereby improves magnetic properties.

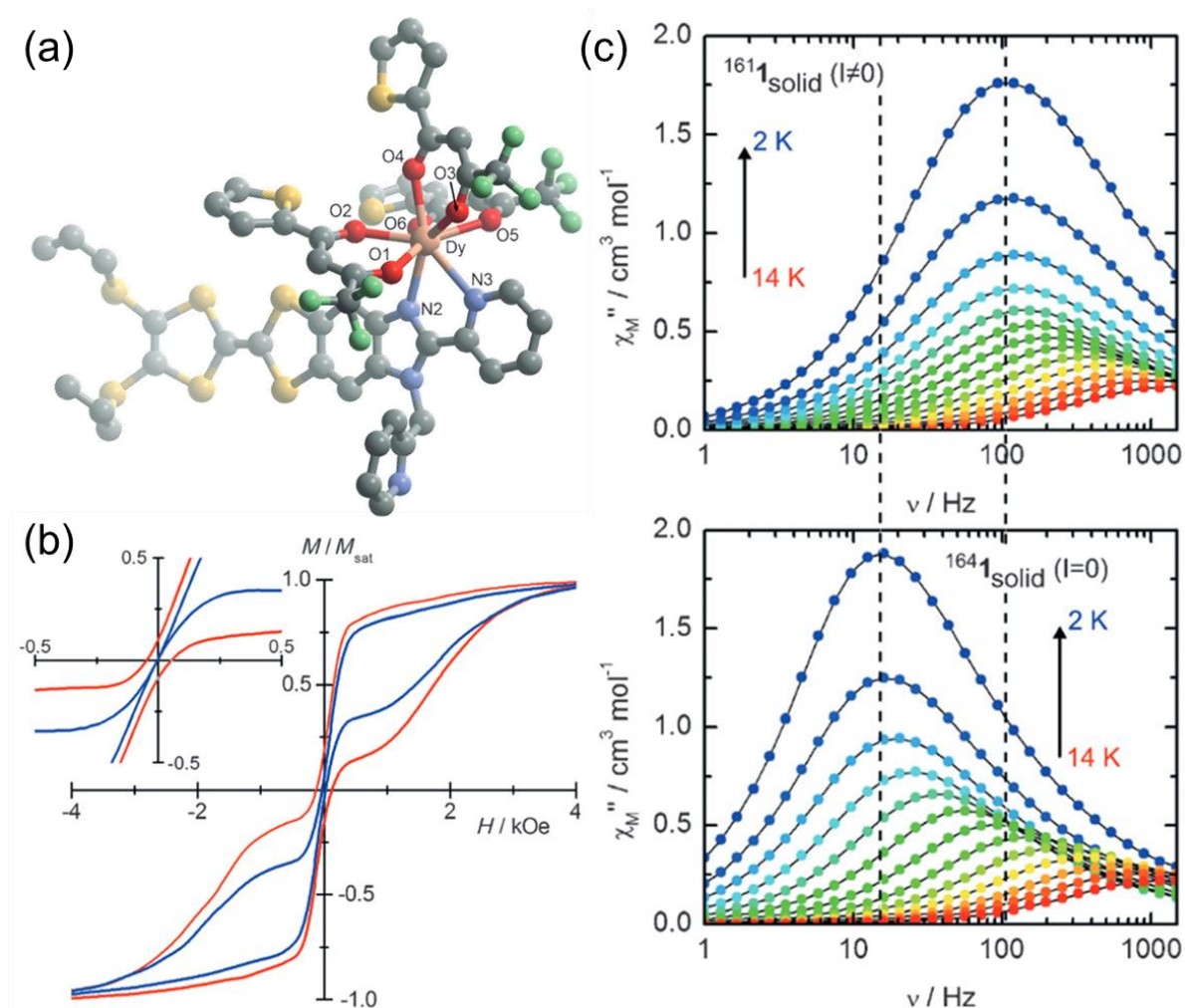


Figure 1.4.10 (a) The molecular structure of $[\text{Dy}(\text{tta})_3(\text{L})] \cdot \text{C}_6\text{H}_{14}$. (b) Hysteresis loops of ^{161}Dy (blue) and ^{164}Dy (red) isotopologues at 0.46 K. (c) Frequency dependence magnetic susceptibility of ^{161}Dy and ^{164}Dy isotopologues under zero field at 2–14 K.¹⁰⁴

Pointillart *et al.* investigated the SMM behavior of isostructural dysprosium complexes, $[\text{Dy}(\text{tta})_3(\text{L})] \cdot \text{C}_6\text{H}_{14}$ (tta = 2-thenoyltrifluoroacetate, and L = 4,5-bis(propylthio)tetrathiafulvalene-2-(2-pyridyl)-benzimidazolemethyl-2-pyridine) (Figure

1.4.10a), by utilizing two abundant isotopes, ^{161}Dy and ^{164}Dy .¹⁰⁴ A comparison of the frequency-dependent magnetic susceptibility for ^{161}Dy and ^{164}Dy isotopologues under zero field within the temperature range of 2-14 K reveals a distinct difference: at low temperature, the relaxation time of the ^{164}Dy analogue ($I = 0$) is about an order of magnitude longer than that of ^{161}Dy analogue ($I = 5/2$); while in high temperature regime, the relaxation times of both isotopologues gradually converged. This phenomenon indicates that the hyperfine coupling primarily accelerates the relaxation at low temperature by providing quantum tunneling channels, whereas its effect becomes negligible at high temperature where thermal activation dominates. Furthermore, as shown in the hysteresis loops at 0.46 K, though both isotopologues exhibit hysteresis, only ^{164}Dy analogue has a coercive field while ^{161}Dy is a closed curve at zero field, which demonstrates that the hyperfine coupling originated from the nuclear spin significantly enhances the quantum tunneling.

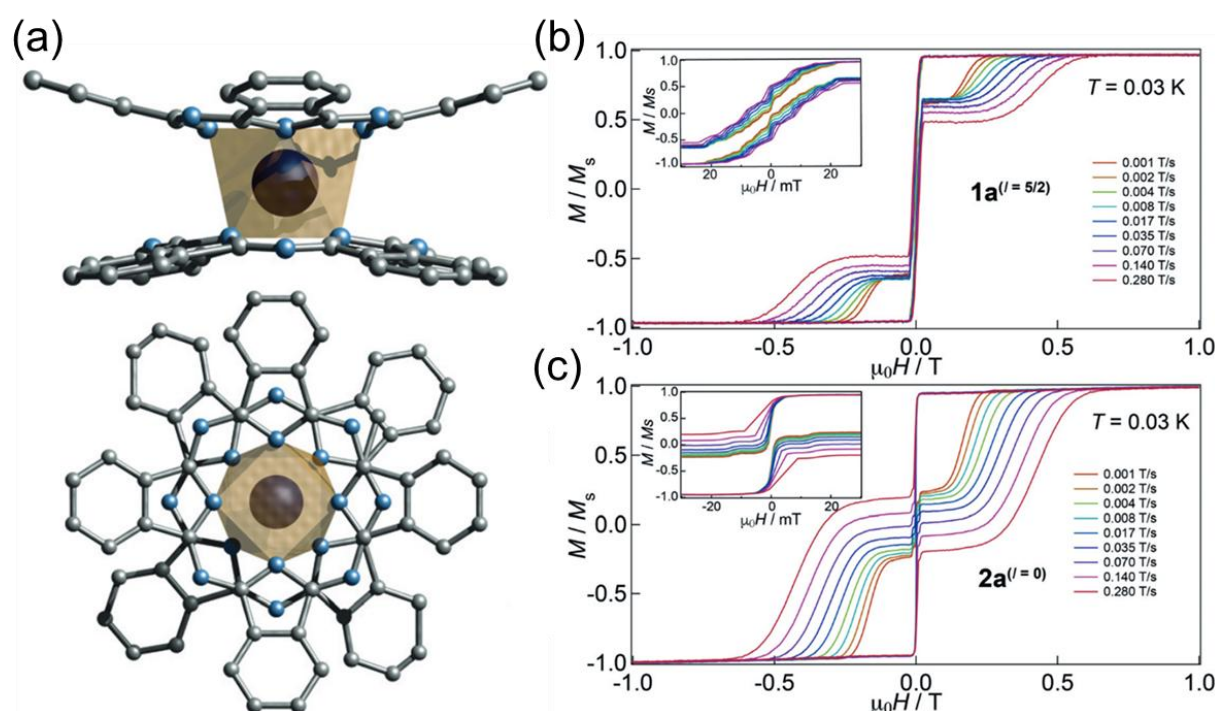


Figure 1.4.11 (a) The molecular structure of $\text{Et}_4\text{N}[\text{DyPc}_2]$. The hysteresis loops with different sweep rate at 0.03 K for ^{163}Dy (b) and ^{164}Dy (c).¹⁹

In 2017, Moreno-Pineda *et al.* systematically compared the magnetic properties of the ^{163}Dy and ^{164}Dy isotopes with classical isostructural $\text{Et}_4\text{N}[\text{DyPc}_2]$ as shown in Figure 1.4.11.¹⁹ Both isotopologues exhibit typical SMM slow relaxation behavior under zero field, where the peak frequencies for ^{163}Dy and ^{164}Dy are located at 0.22 Hz and 0.1 Hz, respectively. The fitted shorter relaxation time of ^{163}Dy compared to ^{164}Dy indicates that the hyperfine coupling promote the QTM process. The fitted effective energy barriers were determined to be 34.5 K for ^{163}Dy and 34.7 K for ^{164}Dy , revealing similar magnetic properties. However, a significant difference was observed when measuring the relaxation behavior under different external fields at 3 K, as ^{164}Dy only exhibited a single peak whereas ^{163}Dy exhibited multiple. This indicates that ^{163}Dy undergoes quantum tunneling at various magnetic fields. To further demonstrate this,

μ SQUID was employed to compare the isotopologues, where ^{163}Dy displays numerous steps while ^{164}Dy shows considerably fewer. These steps originate from the hyperfine splitting of the ground state and correspond to the energy level crossings in the Zeeman diagram, introducing the quantum tunneling.

Ruan *et al.* extended the investigation into binuclear system by synthesizing and characterizing two Dy-based isotope complexes, $[\text{Dy}_2(\text{tmhd})_6(\text{tape})]$ (tmhd = 2,2,6,6-tetramethylheptandionate and tape = 1,6,7,12-tetraazaperylene.), to explore the influence of isotope effects through Dy-Dy interactions on the magnetic properties (Figure 1.4.12).⁴⁷ Both isotopologues exhibit zero-field SMM behavior below 20 K. Consistent with the trend in previously discussed examples; ^{163}Dy analogue shows a shorter relaxation time than that of ^{164}Dy , with derived effective energy barrier of 70 K and 80 K, respectively. Sweep-rate and temperature dependency μ SQUID measurements revealed that due to the lack of nuclear spin, ^{164}Dy analogue exhibits broader and less sweep-rate sensitive hysteresis loops compared with ^{163}Dy analogue, confirming the nuclear spin enhances the magnetic relaxation by facilitating the phonon bath coupling. Combining with the CASSCF calculations indicates that the coupling in this system is dominated by the intramolecular interactions, where the shortest intermolecular Dy-Dy distance is approximately 0.5 Å longer than the intramolecular Dy-Dy distance according to the molecular structure. However, although in this system the coupling is still relatively weak, enhancing intramolecular interactions, such as shorter and robust Dy-Dy distance, is crucial for expanding the Hilbert space for multilevel qudits.

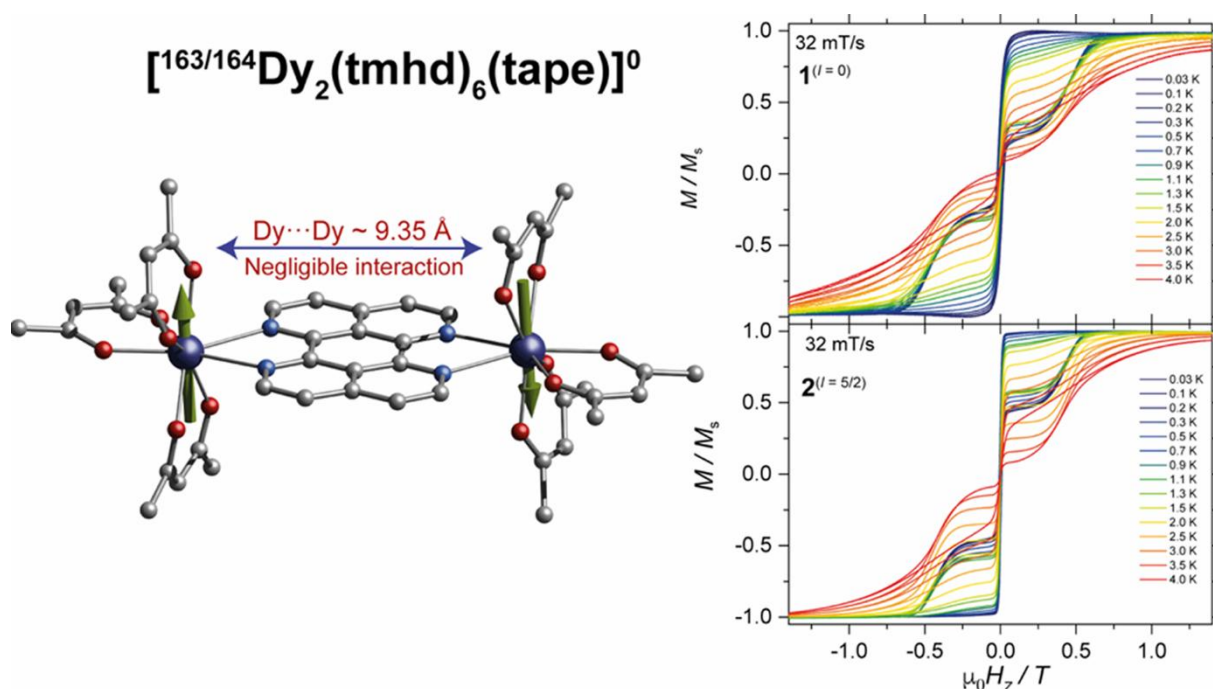


Figure 1.4.12 The molecular structure of $[\text{Dy}_2(\text{tmhd})_6(\text{tape})]$ (left), and the temperature-dependent hysteresis loops at low temperature with a fixed 32 mT/s sweep rate (right).⁴⁷

After examining the isotope effect from the lanthanide on the SMM behavior, a natural extension question is: Considering the isotopic compositions of the ligand is a key component of the chemical environment surrounding the spin center, how does it influence the magnetic

behavior? Yet, ligands are generally composed of light elements with low atomic numbers (such as H, C, and N), resulting in a relatively weak super-hyperfine coupling compared with hyperfine coupling. Thereby, the contribution of the isotope effect on the ligand is often limited and requires much stricter experimental conditions. Furthermore, considering the cost of synthesis, where constructing fully isotopically labeled complex organic ligands usually involves lengthy synthetic routes, a careful evaluation of the cost-effectiveness is required. Nevertheless, optimizing SMM properties through isotopic modification on the ligand still remains valuable. For example, deuteration can significantly decrease the contribution of low vibrational energy, thereby mitigating magnetic relaxation by modulating the spin-phonon coupling pathway^{26, 105} (this will be discussed in detail in Section 1.4.5). However, the investigations about isotope effects via ligand enrichment on the coupling interactions are scarcely reported.

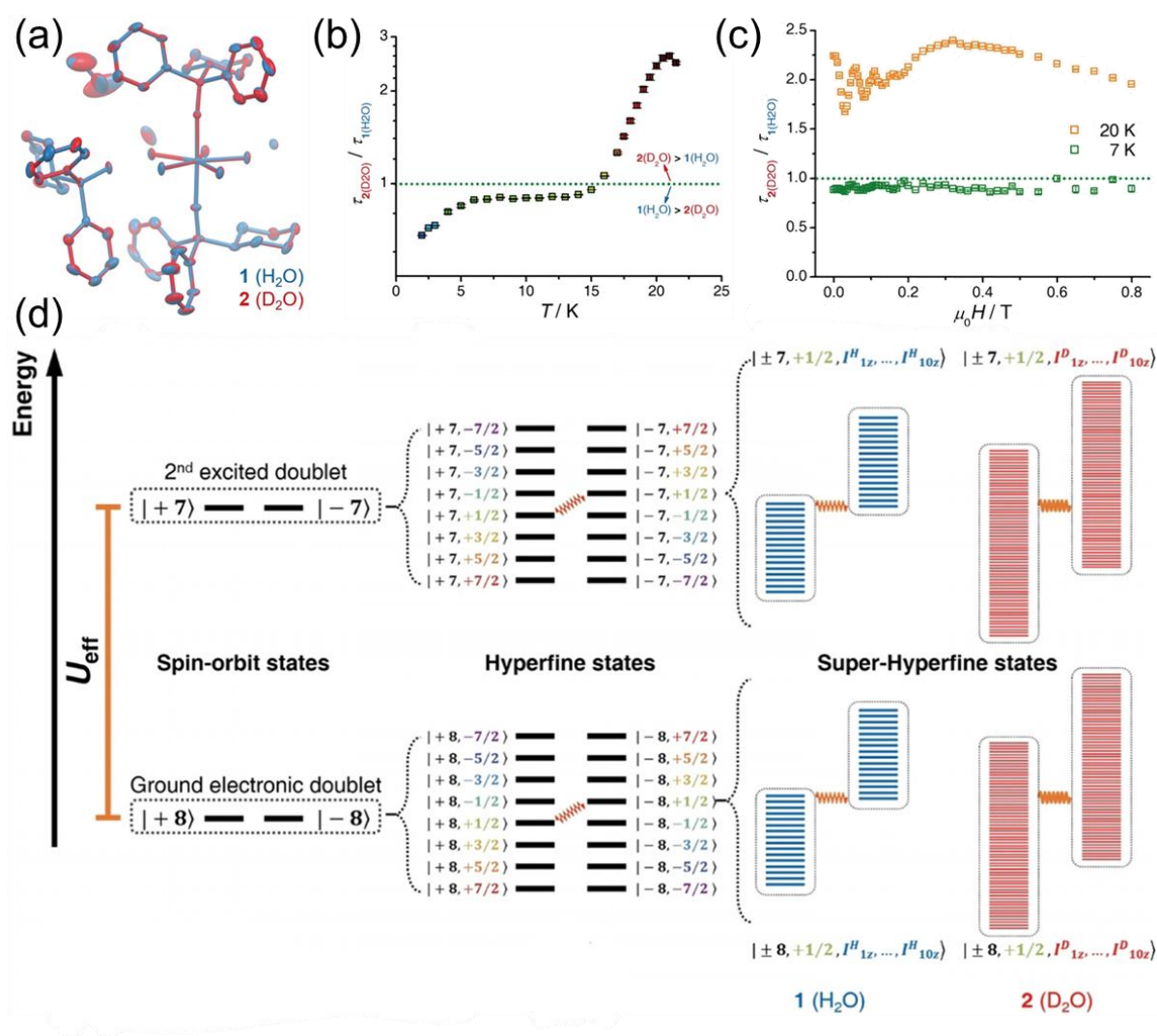


Figure 1.4.13 (a) The molecular structure of $\text{Ho}(\text{CyPh}_2\text{PO})_2(\text{H}_2\text{O})_5]\text{I}_3 \cdot 2(\text{CyPh}_2\text{PO}) \cdot 2\text{EtOH}$. (b) The temperature dependence of $\tau_{\text{D}_2\text{O}}/\tau_{\text{H}_2\text{O}}$ under zero magnetic field. (c) The field dependence of $\tau_{\text{D}_2\text{O}}/\tau_{\text{H}_2\text{O}}$ at 7 K (green) and 20 K (yellow). (d) Energy spectrum for both isotopologues.¹⁰⁶

Liu *et al.* based on the complex $\text{Ho}(\text{CyPh}_2\text{PO})_2(\text{H}_2\text{O})_5\text{I}_3 \cdot 2(\text{CyPh}_2\text{PO}) \cdot 2\text{EtOH}$ reported the only case for investigating the isotope effect of ligand on the lanthanide-based SMM via deuteration strategy.¹⁰⁶ In this structure, five water (or deuterated water) molecules occupy the equatorial plane, and two CyPh_2PO ligands are located along the axis with a nearly linear O-Ho-O coordination, forming a pentagonal bipyramidal geometry. This design maximizes the introduction of isotopic water molecules while maintaining high symmetry, providing an ideal platform for investigating magnetic dynamics influenced by H/D substitution (Figure 1.4.13). Notably, the ratio of the relaxation time between these isotopologues ($\tau_{\text{D}_2\text{O}}/\tau_{\text{H}_2\text{O}}$) increases as the temperature increases, exhibiting a significant temperature dependence of the isotope effect. To elucidate the mechanism, 20 K, where the isotope effect is most prominent, and 7 K, where the H-isotopologue exhibits relatively slower relaxation, were selected to perform the field-dependent measurements. At 20 K, the D-isotopologue exhibits a longer relaxation time and a periodic oscillation in the low-field region with a period of approximately 0.06 T. In contrast, no oscillations were observed at 7 K. CASSCF calculations revealed that, due to the larger nuclear spin of D ($I = 1$), a much higher density of energy splitting states in ground state is generated through super-hyperfine interaction, effectively widening the window for quantum tunneling of magnetization. Therefore, the relaxation of the H-isotopologue is slower than that of the D-isotopologue at low temperature. While the field-dependent oscillations observed at high temperature are attributed to the competition between the hyperfine-electronic energy levels avoid crossings corresponding to the positive peaks and the energy levels avoid crossings corresponding to the negative peaks, thus affecting the relaxation behaviors.

1.4.3 The strength of the ligand field

When looking into the progress in SMMs, some mononuclear complexes exhibit extraordinary magnetic properties despite lacking high symmetric structure. For example, for Dy^{III} derivatives, the introduction of one or two ligands with strong field into the coordination environment often yields high-performance SMMs. The core of this phenomenon lies in the fact that the presence of strongly electron-withdrawing or electron-donating ligands allows the electronic structure of the complex to be approximated as a mono-coordinated or di-coordinate configuration, generating an extremely strong axial ligand field and thereby significantly enhancing the magnetic anisotropy of metal ions. Such strong-field ligands mainly include particular short bond lengths or typical organometallic bonds.

Gregson *et al.* reported a six-coordinated dysprosium complex, $[\text{Dy}(\text{BIPM}^{\text{TMS}})][\text{K}(\text{18C6})(\text{THF})] \cdot 2\text{THF}$, with a core character of $\text{C}=\text{Dy}=\text{C}$ bonding (Figure 1.4.14).¹⁰⁷ The structure of this compound exhibits a nearly linear $\text{C}=\text{Dy}=\text{C}$ angle of 176.6° with $\text{C}=\text{Dy}$ bond lengths of around 2.434 Å, which is shorter than the average bond length of Dy-N bond (around 2.461 Å). Although the bond length difference is marginal, as the ligand field strength of C^{2-} is significantly stronger than the neutral N atom, the complex is approximately regarded as a quasi-two coordinated linear dysprosium system, which is expected to have high energy. AC susceptibility measurements revealed two distinct maximum peaks below 41 K, indicating two kinds of relaxation processes with fitted effective energy barrier of 721 K and 813 K, respectively. These results are well aligned with the theoretical

calculations that the magnetic moment reversal of the former occurs via third excited state while the latter relaxes through the fourth excited state.

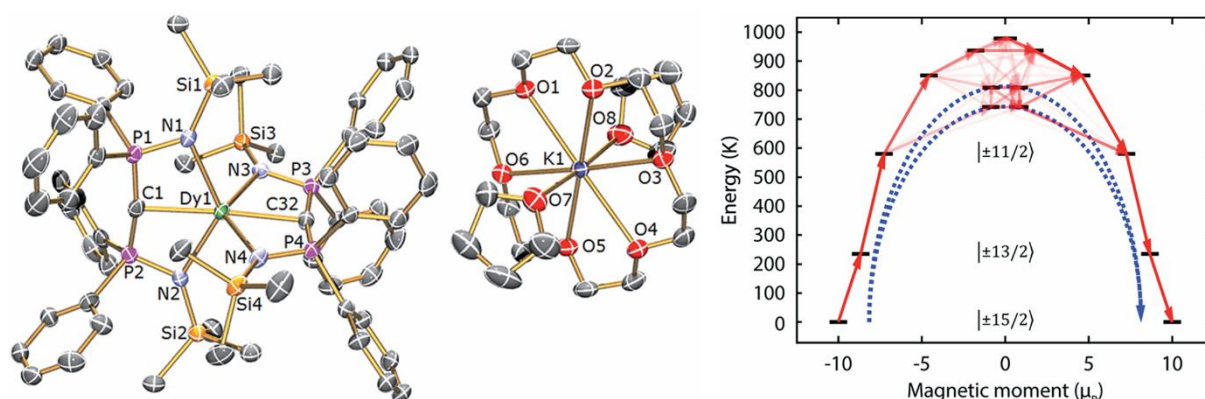


Figure 1.4.14 The molecular structure of $[\text{Dy}(\text{BIPM}^{\text{TMS}})][\text{K}(\text{18C6})(\text{THF})] \cdot 2\text{THF}$ (left), and the diagram of the calculated ground state Stark sublevel energy level and its relaxation pathway (right).¹⁰⁷

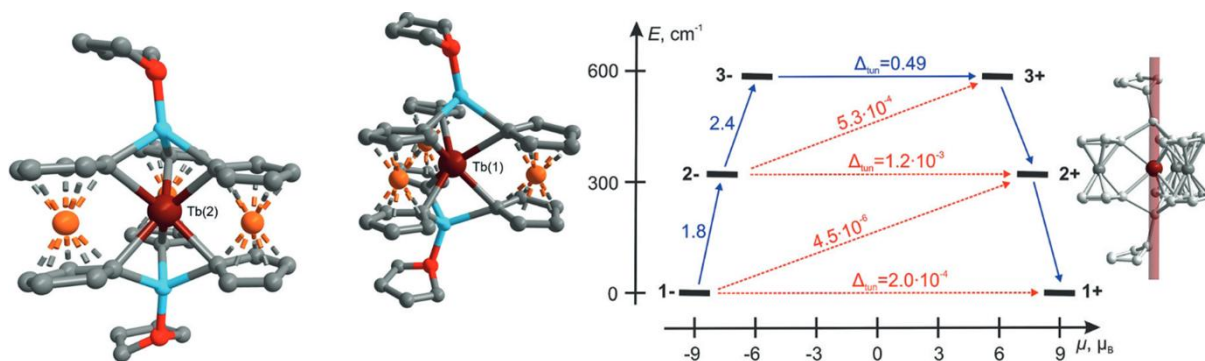


Figure 1.4.15 The molecular structure of $[\text{Li}(\text{THF})_4][\text{TbFc}_3(\text{THF})_2\text{Li}_2]$ (left), and the diagram of splitting energy levels of ground state and its relaxation pathways (right).¹⁰⁸

In 2018, Latendresse *et al.* reported a terbium SMM with a six-coordinate distorted trigonal prismatic geometry, $[\text{Li}(\text{THF})_4][\text{TbFc}_3(\text{THF})_2\text{Li}_2]$ (Figure 1.4.15).¹⁰⁸ Since Tb^{III} is a non-Kramers ion, it is inherently prone to quantum tunneling under zero field condition. Considering the D_{3h} coordination geometry, the crystal field parameters representing transverse magnetic anisotropy in the spin Hamiltonian operator (B_4^3, B_6^3, B_6^6) are non-zero, which theoretically significantly increases the probability of QTM at ground state. However, according to the ac magnetic susceptibility measurement, the complex exhibits excellent SMM behavior. The 100% concentrated sample exhibits a slow relaxation behavior in the temperature range of 2–30 K, though it is severely affected by QTM at low temperature. Upon diamagnetic dilution with Y-analogue to 8%, the QTM at low temperature is effectively suppressed, extending the observation range of relaxation to 40 K with a fitted effective energy barrier of 247 cm^{-1} . This indicates that dipole-dipole interactions are the key factor dominating spin relaxation. Furthermore, by applying external dc field of 4800 Oe, the relaxation temperature and the energy barrier were further increased to 50 K and 401 cm^{-1} , respectively. Such field-dependent behavior reflects that although the strong ligand field partially suppresses the QTM, the tunneling effect caused by the symmetry deviation of the molecular structure still remains.

In the same year, Norel *et al.* reported an F-coordinated mononuclear dysprosium SMM, $[\text{Dy}(\text{Tppy})\text{F}(\text{dioxane})_2](\text{PF}_6)$ (Figure 1.4.16).¹⁰⁹ In this structure, the Dy-F bond length is only 2.094 Å, which is much shorter than that of Dy-N and Dy-O bond. Therefore, it could be approximated as a single-coordinated Dy^{III} system. Consequently, the easy axis points towards the direction of Dy-F bond confirmed by theoretical calculations gives effective energy barriers of 432 cm⁻¹ and 528 cm⁻¹ corresponding to the two relaxation processes. More interestingly, such high axial anisotropy is maintained up to the third excited state.

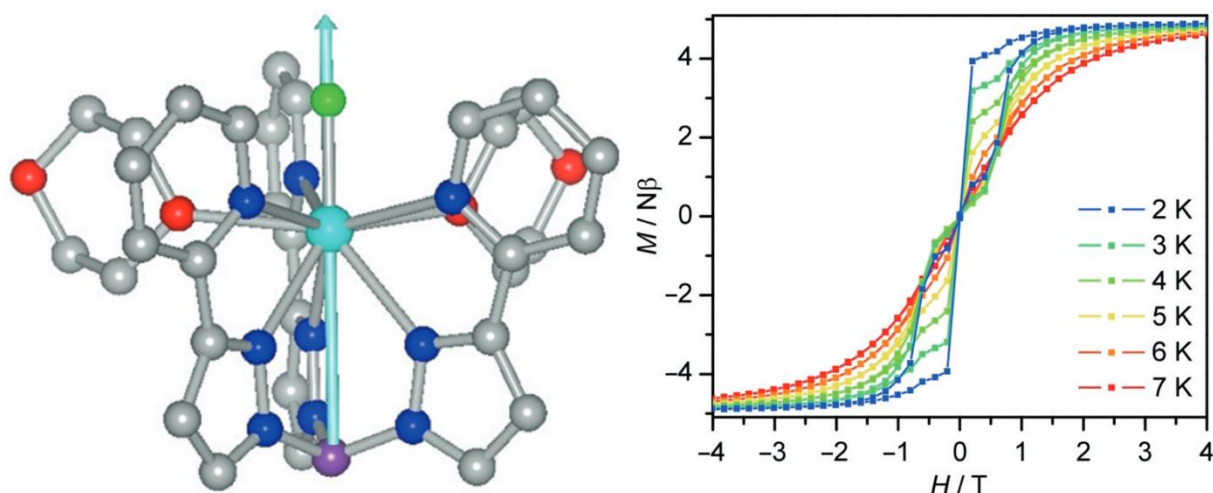


Figure 1.4.16 The molecular structure of $[\text{Dy}(\text{Tppy})\text{F}(\text{dioxane})_2](\text{PF}_6)$ (left), and the hysteresis loops at low temperature (right).¹⁰⁹

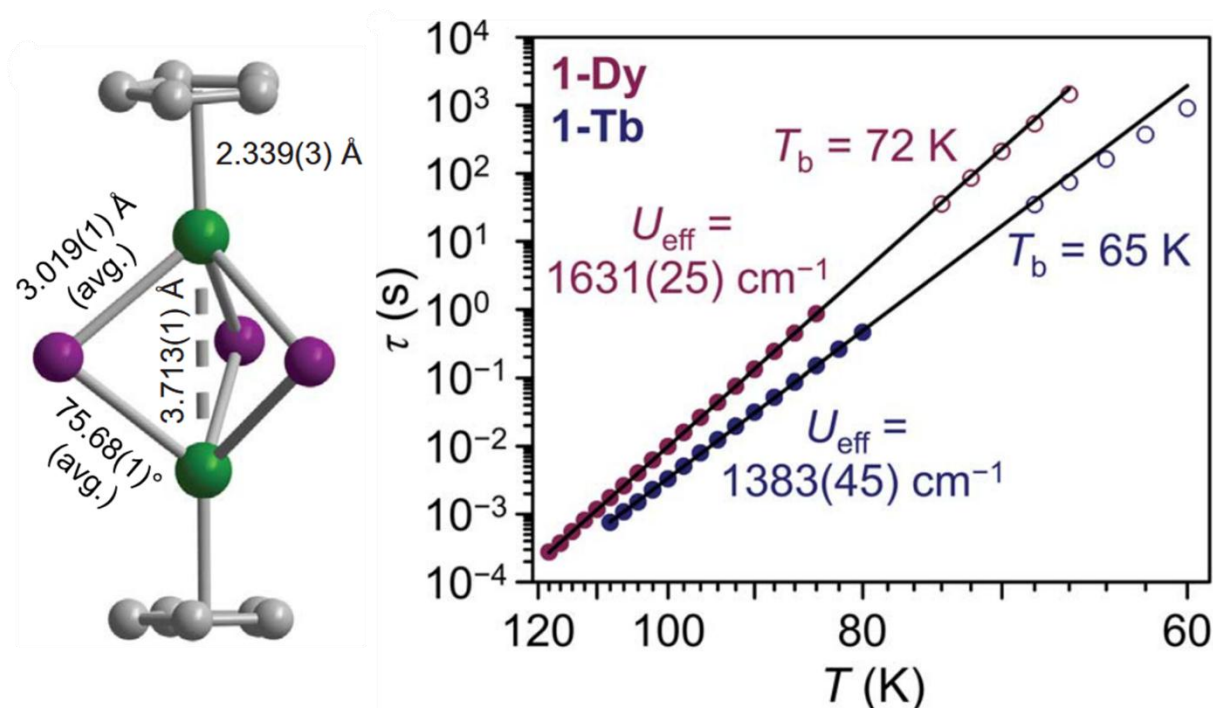


Figure 1.4.17 The molecular structure of $(\text{Cp}^{\text{iPr5}})_2\text{Ln}_2\text{I}_3$ (left), and the fitted relaxation time vs temperature for Tb (blue) and Dy (purple) analogues (right).¹¹⁰

Subsequently, Gould *et al.* successfully synthesized the binuclear complexes, $(\text{Cp}^{\text{iPr5}})_2\text{Ln}_2\text{I}_3$ (where Cp^{iPr5} = pentaisopropylcyclopentadienyl, Figure 1.4.17),¹¹⁰ by the reduction of

(Cp^{iPr5})₂Ln₂I₄ with KC₈ in n-hexane. In these structures, a single electron occupied the d_{z^2} σ -bonding orbitals, thereby exhibiting significant valence delocalization rather than discrete Ln^{II} and Ln^{III} ions. This Robin-Day Class III formalism bonding interaction allows the two lanthanide centers to equally share the d electron. In accordance with Hund's rule, the σ -bonding electron and the f electrons are highly aligned, generating a well isolated high-spin ground state that remains thermally robust even at room temperature. In the cases of Tb and Dy analogues, the combination of the well isolated high-spin ground state and the pronounced axial magnetic anisotropy leads to the largest coercive magnetic field to date. Specifically, the Dy analogue exhibits an effective energy barrier of 1631 cm⁻¹, breaking the record held by Tong.

1.4.4 Intermolecular interactions and dipole-dipole interactions

In any crystalline system, intermolecular interactions and long-range dipolar-dipolar interactions are inherently present. Typically, the intermolecular magnetic interactions are governed by the dipole-dipole coupling unless alternative efficient methods are available to enable strong magnetic exchange.¹¹¹ These interactions play an important role in regulating the SMM behavior often induce complex phenomena, multiple relaxation processes, a significant enhancement of the QTM at low temperatures, and the modulation of the coercive field in the hysteresis loop. A deep understanding and manipulation of these two types of interactions is crucial for optimizing the quantum coherence of SMMs and increasing their blocking temperature. Currently, the mainstream research strategy is to disperse effective magnetic centers, such as through diamagnetic dilution. Although it has been briefly touched upon in the previous discussion, this section will employ several examples to further discuss.

Taking the classic double-decker lanthanide phthalocyanine complexes as illustrative examples, researchers have designed and successfully synthesized a series of derivatives based on LnPc₂, aiming to optimize the SMM properties by modulating the dipole interactions between magnetic centers. By introducing a bridge group between two building blocks, Horii *et al.* obtained a dimer with a more broadened hysteresis loop under zero field compared to the mononuclear complex, indicating that the magnetic dipolar interaction between Tb^{III} centers can be tuned and thereby optimizing the SMM behavior.¹¹² Similarly, they further prepared a dinuclear complex using a fused-phthalocyanine. Magnetic measurements revealed that the weak intermolecular interactions more effectively suppress the QTM, where the off-diagonal terms and the collinearity of dipole-dipole interactions involve.³³ Wang *et al.* through a systematic comparison of the magnetic properties of a series of isostructural quadruple-decker complexes revealed that the long-range intramolecular Tb-Tb interactions suppress the QTM,¹¹³ which is also observed in higher dimension systems.¹¹⁴ Horii *et al.* functionalized phthalocyanine rings with crown ether moieties to form a dimer bridged by four K⁺ ions. Although the effective energy barrier of the dimer remained almost the same as before dimerization, the relaxation time the dimer expanded by approximately 1000 times, strongly demonstrating that the QTM was significantly suppressed.¹¹⁵ Similarly, Chen *et al.* observed a more than 10-fold increase in blocking temperature by bridging two building blocks with two Na⁺ ions.¹¹⁶

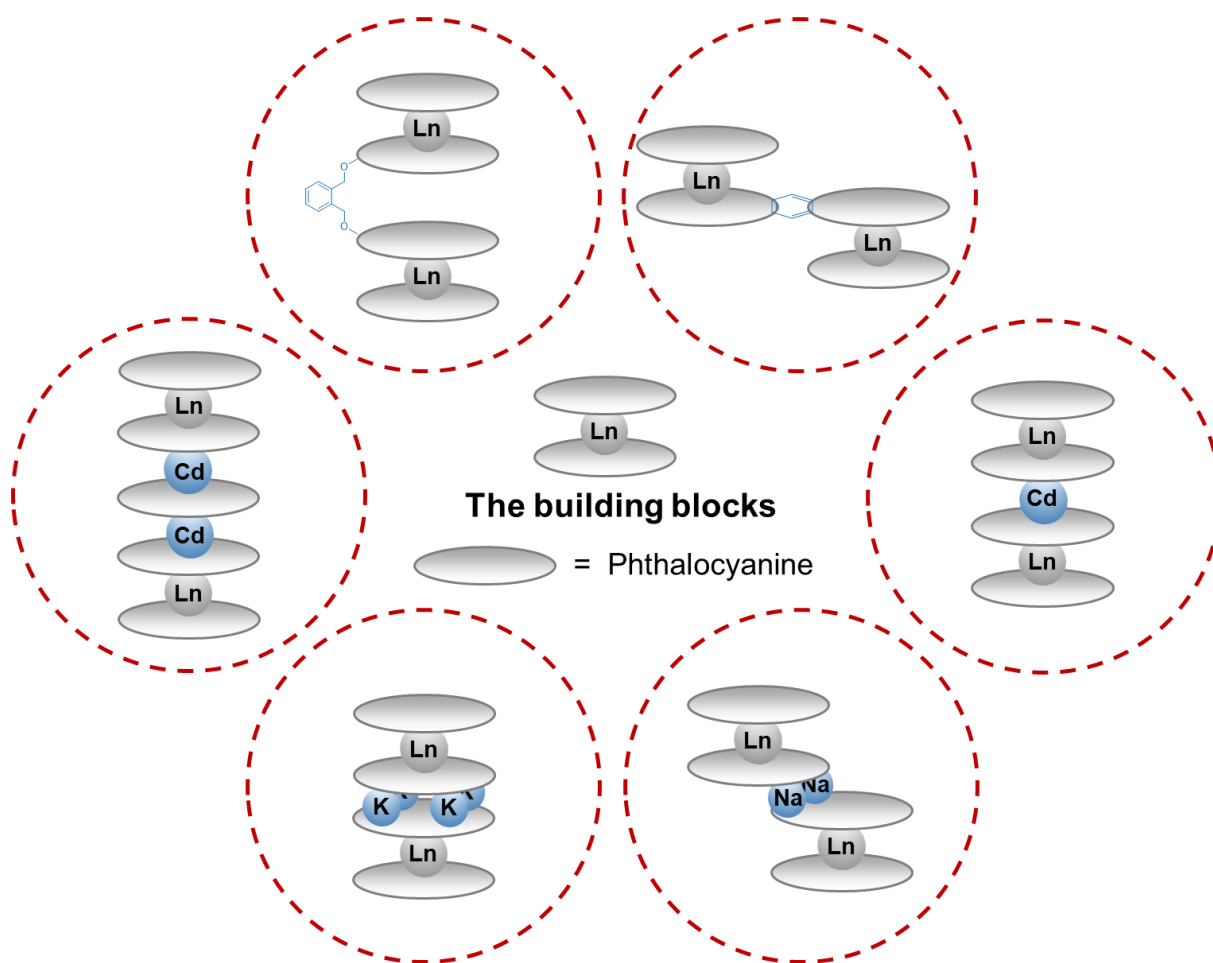


Figure 1.4.18 Multiple-decker SMMs based on LnPc_2 building blocks.

However, chemical modification demands significant synthetic efforts and inevitable involve fine-tuning the electronic structure of the molecule, increasing the complexity of analysis. In contrast, dilution offers an alternative strategy for suppressing intermolecular interactions while the electronic properties of the molecule remain.

Ishikawa *et al.* in their pioneering report on single-molecule magnetic behavior of $[\text{Pc}_2\text{Ln}]\cdot\text{TBA}$ ($\text{Ln} = \text{Tb}, \text{Dy}$), astutely observed the significant different SMM behavior induced by the dilution effect.²⁸ In the $[\text{Pc}_2\text{Tb}]\cdot\text{TBA}$ complex, the peaks of the χ''_M locate at 15, 32, and 40 K with frequencies of 10, 100, and 997 Hz, respectively. In contrast, as the sample diluted with $[\text{Pc}_2\text{Y}]\cdot\text{TBA}$ to 25%, these peaks shift to approximately 26, 34, and 40 K, respectively. Such shift indicates that the dilution effectively suppresses the magnetic dipole reversal, also experimentally confirms that the slow relaxation behavior originates from the intrinsic properties of molecule itself rather than long-range magnetic order. This was also observed in $[\text{Pc}_2\text{Dy}]\cdot\text{TBA}$. Ruan *et al.* conducted a more detailed comparison of the magnetic behavior at different dilution ratios.²⁰ When the sample of TbPc_2 was diluted to below 30%, distinct butterfly-shaped hysteresis loops were observed, providing robust evidence that the introduction of diamagnetic YPc_2 can effectively compensate for the insufficient shielding of the interaction between Tb ions by the phthalocyanine rings, thereby enhancing the SMM properties. Quantitative analysis of the opening area of the hysteresis loop revealed that 30% is

the optimal dilution ratio for this system. Similarly, besides dilution with isostructural diamagnetic analogues, regulating the distribution of non-magnetic solvent molecules or counter-ions is another approach. This research group further compared the magnetic characteristics of TbPc_2 before and after absorbing a DCM molecule,¹¹⁷ finding that the effective energy barrier of $\text{TbPc}_2\cdot\text{DCM}$ reaches to 790 K while without DCM molecule is around 600-740 K according to the previous results. However, it should be noted that in this system, the introduction of DCM molecule actually shortens the distance between Tb-Tb molecules and, to some extent, fine-tunes the molecular structure and the packing. Therefore, this phenomenon is a complex outcome influenced by multiple factors. Nevertheless, this approach remains an effective strategy, but more careful and comprehensive consideration is required when selecting the solvent or counter-ion, while dilution with diamagnetic isomers is undoubtedly most simple, direct, and efficient strategy for regulating SMM properties.

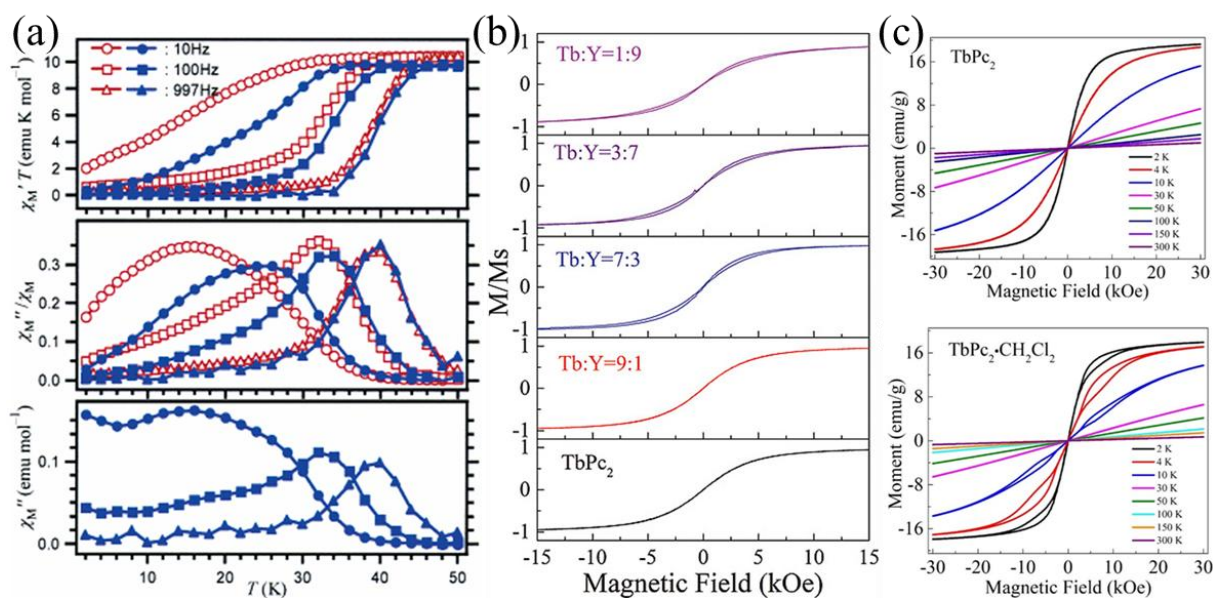


Figure 1.4.19 (a) The temperature-dependent dc and ac susceptibility for $[\text{Pc}_2\text{Tb}]\cdot\text{TBA}$ (open) and diluted $[\text{Pc}_2\text{Tb}]\cdot\text{TBA}$ (filled).²⁸ (b) The hysteresis loops for different diluted TbPc_2 with different ratio of Tb/Y at 2K, field-sweep rate, 30 Oe/s.²⁰ (c) The hysteresis loops for $\text{TbPc}_2\cdot\text{DCM}$ (bottom) and TbPc_2 (top) with variable temperature.¹¹⁷

Habib *et al.* further explored the effect of dilution on the regulation of magnetic properties in a binuclear system by a series of diluted samples synthesized with different Y/Dy ratio (0/100, 50/50, 90/10, 95/5).¹¹⁸ ICP analysis confirmed that the Dy contents (5.31%, 10.24%, and 50.56%) were highly consistent with the target ratios. Under zero field conditions, all the diluted and non-diluted samples exhibited significant frequency dependence below 20 K, indicating their SMM characteristics. Notably, the diluted samples exhibited two kinds of frequency dependencies, and the additional frequency dependency increases as the dilution ratio increases. From a statistical perspective, this system is a mixture of Y_2 , YDy , and Dy_2 that the hetero-dinuclear YDy gradually dominant the magnetic behavior rather than homo-dinuclear Dy_2 as the dilution ratio increases. Hysteresis loops at low temperature reveal that the tunneling steps near zero field become more pronounced with the increase of dilution ratio, corresponding to

the zero-field QTM of the YDy centers. Therefore, in this diluted system, the slow magnetic relaxation mainly originates from the contribution of the single Dy ion, while the dilution effect on the intermolecular interactions is masked. However, combining with the previous example, it is still reasonable and of high potential to explore the intrinsic magnetic properties of molecule itself by using pure homonuclear diamagnetic complex to dilute.

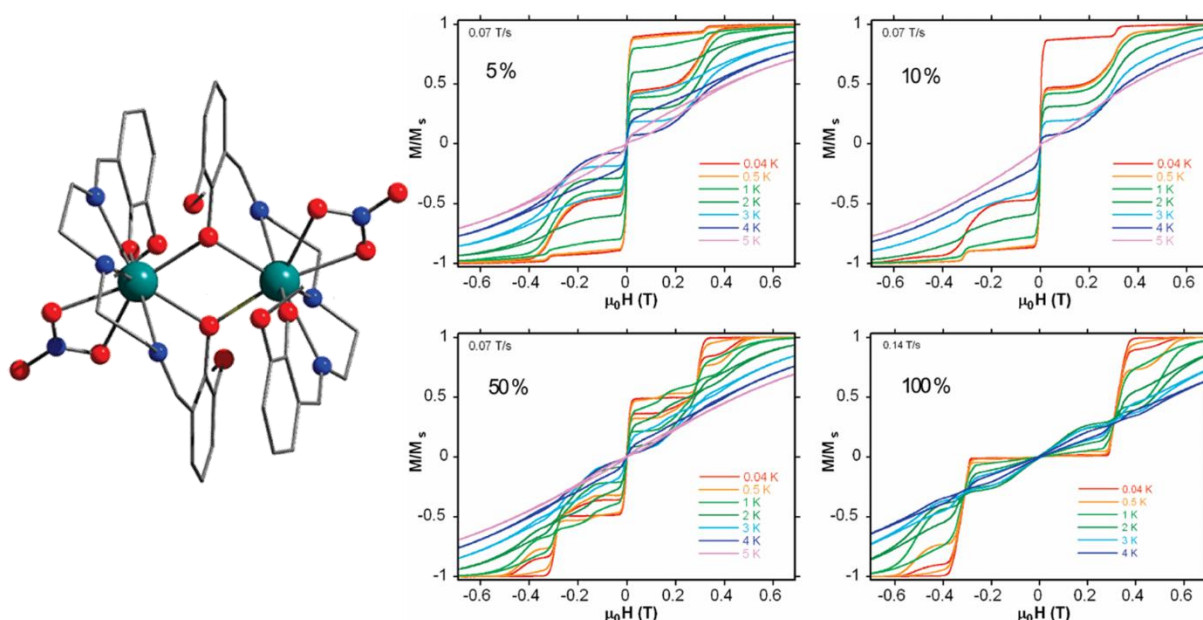


Figure 1.4.20 The molecular structure of $[\text{Dy}_2(\text{valdien})_2(\text{NO}_3)_2]$ (left), and the hysteresis loops at variable temperatures for the diluted samples with a fixed indicated magnetic field-sweep rate (right).¹¹⁸

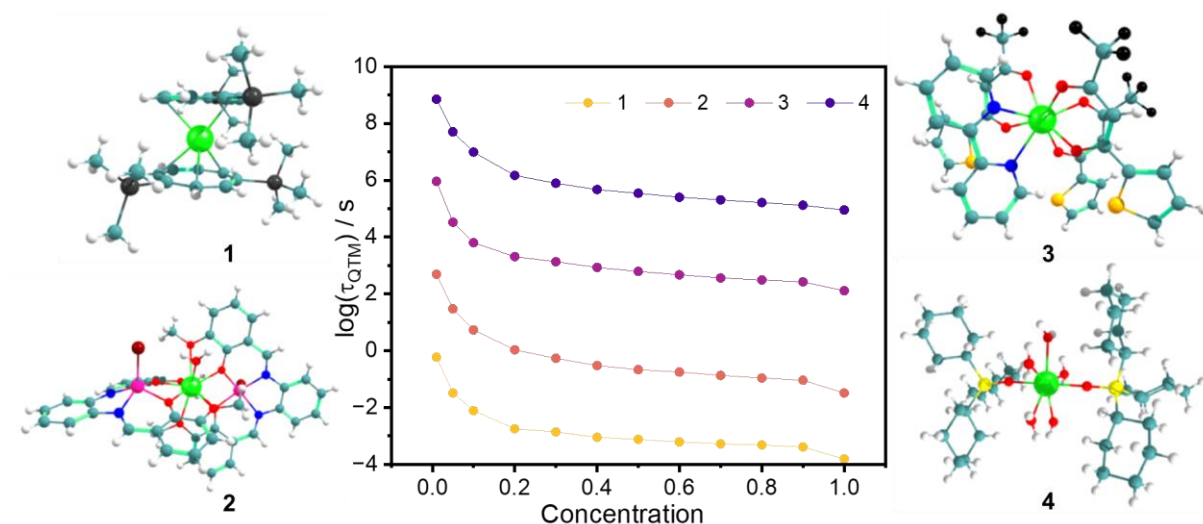


Figure 1.4.21 Recreated scheme diagram of the relationship between the calculated quantum tunneling relaxation time and the concentration of effective magnetic center for different complexes.¹¹⁹ 1 is $[\text{Dy}(\text{COT})_2\text{Li}(\text{THF})(\text{DME})]$;¹²⁰ 2 is $[\text{DyZn}_2(\text{L})_2(\text{H}_2\text{O})\text{Br}_2] \cdot [\text{ZnBr}_4]_{0.5}$, $\text{L} = N,N'$ -bis(3-methoxysalicylidene)phenylene-1,2-diamine;¹²¹ 3 is $[\text{Dy}(\text{BPY})(\text{TTA})_3(\text{H}_2\text{O})_2]$;¹²² 4 is $[\text{Dy}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5]\text{Br}_3 \cdot 2(\text{Cy}_3\text{PO}) \cdot 2\text{H}_2\text{O} \cdot 2\text{EtOH}$.¹²³

Llanos and Aravena employed *ab initio* computation methods to systematically investigate the relationship between quantum tunneling relaxation time and the diamagnetic dilution ratio based on 18 typical mononuclear dysprosium or erbium SMM.¹¹⁹ The computation results exhibit high fidelity when cross-referenced with available experimental results. The predictive models reveal a general trend that the relaxation time significantly elongates as the concentration of effective magnetic ion decreases due to the suppression of intermolecular interaction, exhibiting a quadratic relationship (Figure 1.4.21). Under extreme dilution conditions (the concentration of effective magnetic ion is 1%), the relaxation time is enhanced by up to four orders of magnitude. These findings provide a theoretical quantification of the efficacy of dilution strategies and underscore the important role of the dipolar decoupling in extending the quantum tunneling relaxation time of SMM.

1.4.5 Molecular vibrations

As discussed in Section 1.2.2, the magnetic relaxation of SMMs essentially originates from the coupling between the electronic spins and lattice vibration (phonon), where the direct, Raman, and Orbach processes are fundamentally phonon-dependent. Taking a simple model (CO₂) as an example, the three different vibrational modes (translations, rotations, vibrations) correspond to different energies as shown in Figure 1.4.22,¹²⁴ which transfer and dissipate in the lattice to participate the relaxation. When these come to more complicate complex systems, the interaction exhibits higher dimensionality and complexity. For example, theoretical simulations of [(tpaPh)Fe] by Lunghi *et al.* revealed that the spin reversal in low temperature region is mainly driven by the doublet transitions induced by the low energy phonon modes.²⁶ In addition, phonons generated by intrinsic intramolecular vibrations significantly interfere with the slow relaxation processes, which may be the main reason why the ideal Orbach process is difficult to observe experimentally. Subsequently, they demonstrated through experiments that the slow relaxation behavior is caused by vibrations within the molecule.¹²⁵ Escalera-Moreno *et al.* pointed out that low-energy vibrations significantly enhance the coupling constant.¹²⁶ To address this issue, suppressing harmful vibrations through heavy atom effect (e.g. deuteration¹⁰⁶) or introducing rigid ligands has proven to be an effective strategy for improving thermal stability.¹²⁷ However, in some specific case, the “harmful” low-energy vibration modes can facilitate the modulations for large anisotropic tensor, thereby favoring the magnetic relaxation.¹¹¹ Currently, the precise mechanism of vibrational modulation relaxation remains to be fully elucidated. Although current investigations on electronic spin and molecular vibrational modes mainly address on transition metal complexes, its nature, how vibrations modulate electronic states, remains consistent across lanthanide systems. A thorough analysis of spin-phonon coupling induced by the molecular vibration is important for understanding and optimizing the magnetic behavior in single-molecule magnets.

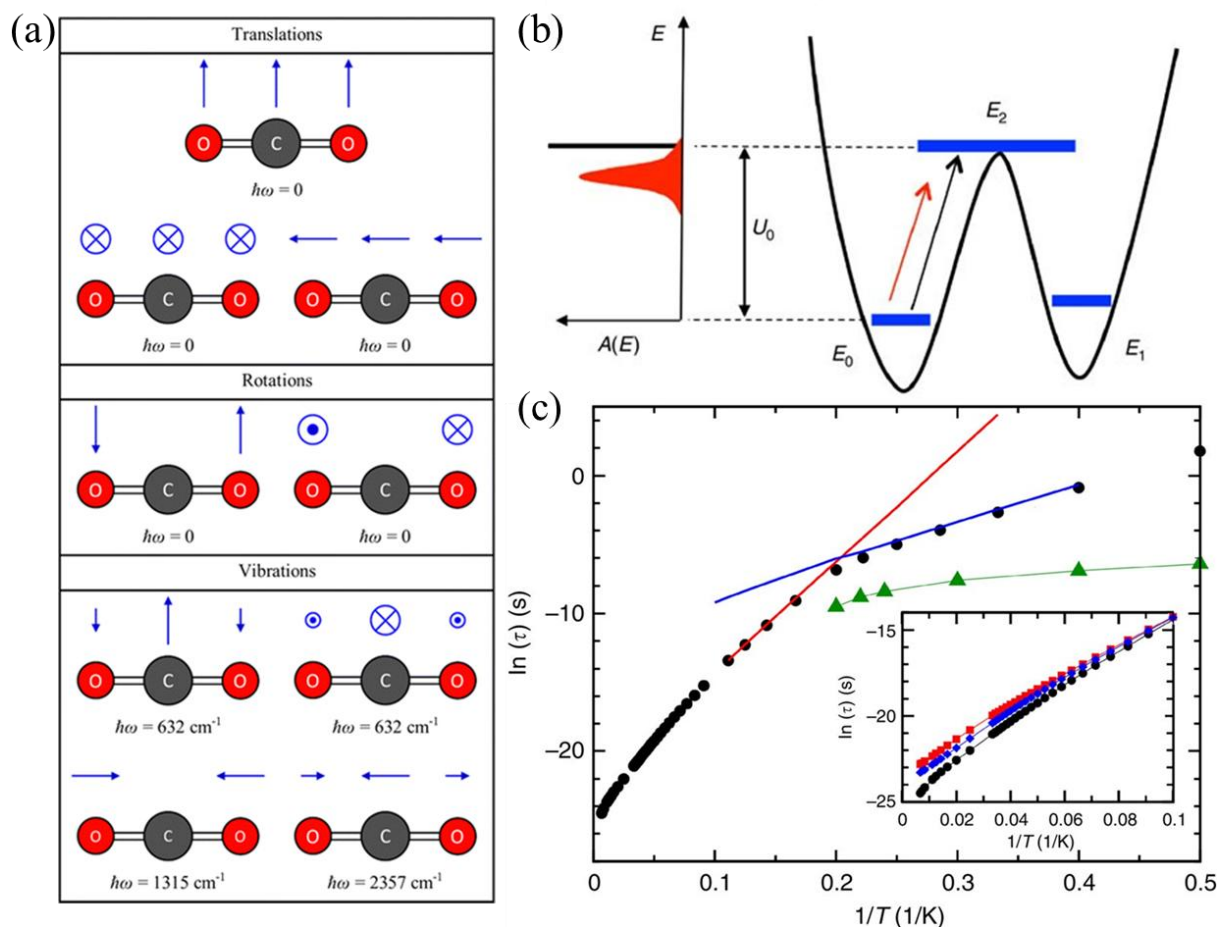


Figure 1.4.22 (a) Three vibration modes of CO₂ and their corresponding energy.¹²⁴ (b) The Lorentzian/Dirac-like phonon density of states and bistable energy level diagrams for phonon-induced spin relaxation in a system with $S = 1$. (c) Calculated relaxation process for [(tpaPh)Fe].²⁶

Ortu *et al.* analyzed the vibrational modes of three high energy barrier molecules: [Dy(^tBuO)Cl(THF)₅][BPh₄] (665 cm⁻¹), [K(18-crown-6-ether)(THF)₂][Dy(BIPM)₂] (BIPM = C{PPh₂NSiMe₃}₂, 565 cm⁻¹), and [Dy(Cp^{III})₂][B(C₆F₅)₄] (1223 cm⁻¹).¹²⁸ Experimental results revealed that the hysteresis loops significantly broaden as the rigidity of molecular structural increases. DFT calculations on the displacements between the coordinated atoms and the dysprosium ion were performed to examine the impact of various vibrational modes. They found that the ordering of the average vibrational energy of molecules is in high agreement with their coercive field strength, where [Dy(Cp^{III})₂][B(C₆F₅)₄] possesses the highest average vibrational energy while [Dy(^tBuO)Cl(THF)₅][BPh₄] with the lowest, which is also observed in another dysprosium systems. However, QTM is not directly mediated by the excitation or relaxation of the vibrational modes due to the absence of sufficient exchange via QTM above 100 cm⁻¹. Nevertheless, the rigidity of molecular structure suppresses the perturbation of spin-phonon coupling on electronic states, enhancing the magnetic hysteresis behaviors. Subsequent theoretical investigations further point out that effective resonance decoupling between the molecular vibrational modes and the electronic excitations helps to improve the SMM

properties.¹²⁹ Furthermore, it is noteworthy that the vibrational modes of non-coordinated atoms participate in spin relaxation via electrostatic polarization effect.¹³⁰

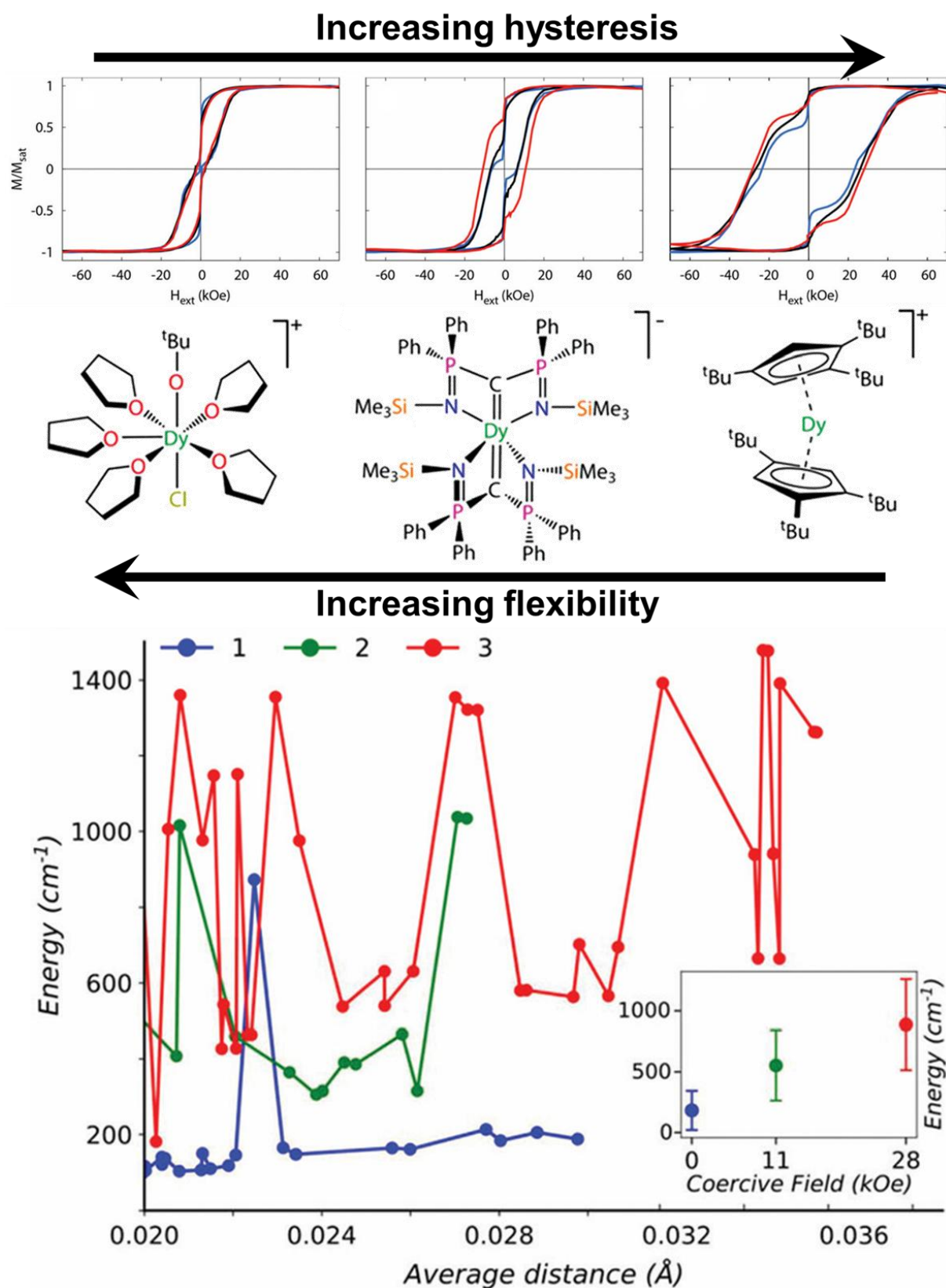


Figure 1.4.23 The molecular structure of selected molecules and their hysteresis loops (top), and their corresponding average distance vs. energy diagram (bottom).¹²⁸

Yu *et al.* designed and synthesized two highly similar seven-coordinated dysprosium complexes, $[\text{Dy}(\text{L})_2(\text{py})_5][\text{BPh}_4]$ ($\text{HL} = (\text{S})\text{-}(-)\text{-}1\text{-phenylethanol}$) and $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{py})_5][\text{BPh}_4]$ as shown in Figure 1.4.24.¹³¹ Both structures possess a pentagonal bipyramidal geometry with five pyridine molecules occupy the equatorial plane and the two oxygen-containing ligands coordinate at axial positions. The introduction of a rigid benzene ring resulted in significant influence on different relaxation processes: for Orbach process, the relaxation rate of $[\text{Dy}(\text{L})_2(\text{py})_5][\text{BPh}_4]$ is ca. ten times faster, while in the Raman process dominated region, $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{py})_5][\text{BPh}_4]$ is approximately three times faster. Although both complexes exhibit similar effective energy barriers and significant hysteresis behavior at 2 K under zero field, the step of hysteresis loop for $[\text{Dy}(\text{L})_2(\text{py})_5][\text{BPh}_4]$ is much smaller, indicating the introduction of benzene ring effectively suppresses the QTM, thus extending the hysteresis behavior to higher temperature range. Combining with CASSCF-SO calculations revealed that although how the benzene ring involve in the Raman process through low-energy vibrational modes remains to be clarified, in Orbach process, this rigid strategy alters the energy of the vibrational modes and the energy of the electronic states involved in relaxation, thereby promoting hysteresis.

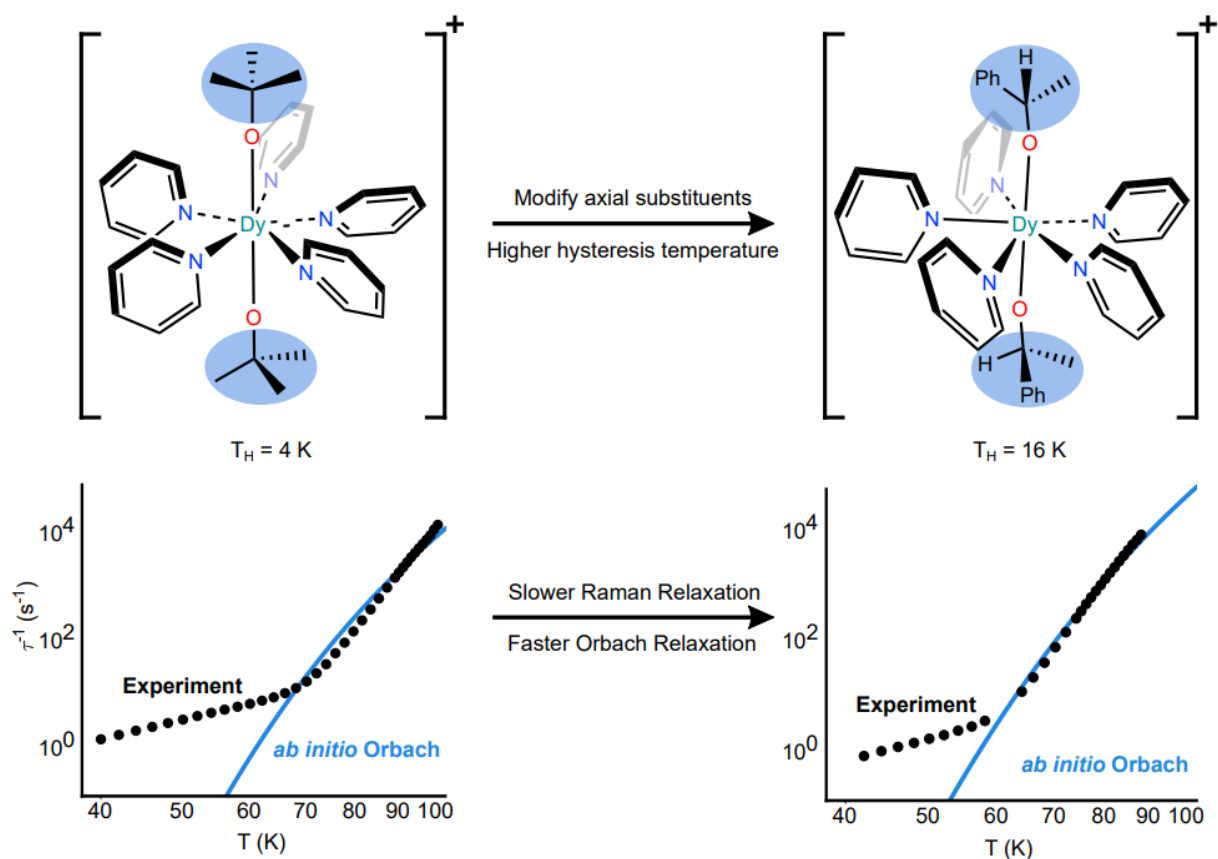


Figure 1.4.24 The molecular structure of $[\text{Dy}(\text{L})_2(\text{py})_5][\text{BPh}_4]$ and $[\text{Dy}(\text{O}^t\text{Bu})_2(\text{py})_5][\text{BPh}_4]$ (top), and their corresponding relaxation vs. temperature diagrams (bottom).¹³¹

1.5 Qubit

In 1981, at the first conference on physics and computation technology held at MIT in Boston, Dr. Richard Feynman delivered his famous lecture entitled "Simulating Physics with Computers."¹ In this presentation, he posed a series of thought-provoking arguments: he first demonstrated the limitations of classical Turing machines in simulating quantum phenomena, and profoundly pointed out that, given the quantum nature of the intrinsic properties of the microscopic world, to truly simulate the laws of nature, it is necessary to construct an operating mechanism consistent with the logic of nature, that is, the quantum computing paradigm. This landmark speech is the first deep convergence of physics and computer science, prompting computer scientists to re-examine the research progress in quantum mechanics. Consequently, extensive researches were spurred into qubits, quantum algorithms, and breakthroughs in quantum information, communication, and teleportation, marking the beginning of a new era in quantum computing.

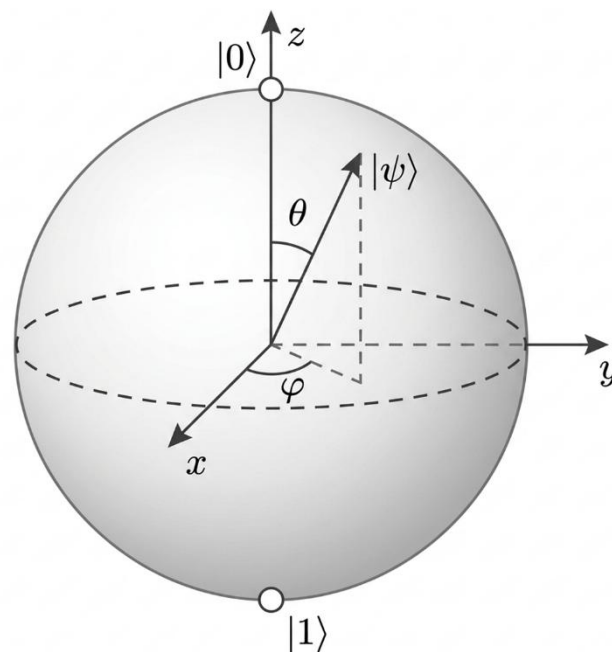


Figure 1.5.1 The Bloch sphere representing a qubit.

Similar to the classical bit as the smallest information unit of classical computing, the qubit represents the basic storage unit in quantum computing. Classical bits based on deterministic logic represent mutually exclusive 0 or 1 states through high or low voltage. In contrast, qubits rooted in the superposition principle of quantum mechanics represent a superposition of two states, $\psi = \alpha|0\rangle + \beta|1\rangle$ ($|\alpha|^2 + |\beta|^2 = 1$), corresponding to any point on the Bloch sphere (Figure 1.5.1). This fundamental difference leads to a leap in information capacity. For example, n -bits classical system can only store one of 2^n states at a given time, while n -qubits system can encompass all 2^n states at any given time. This inherent quantum parallelism allows quantum computers to increase their computational speed exponentially when processing specific algorithms.

Quantum computers must meet DiVincenzo criteria: (1) specific qubits. (2) stable initialization. (3) sufficiently long decoherence time. (4) the ability to form quantum gates. and (5) the ability to perform quantum information measurement.^{5, 132} In this thesis, either nuclear or electron spin is the platform, therefore, the spin-lattice relaxation time (T_1) is the initialization time, and the spin-spin relaxation time (T_2) is the decoherence time.

1.5.1 Mechanism of spin qubits

Under a specific magnetic field, electrons absorb radiation with resonant frequencies to achieve energy level transitions. As illustrated in the Bloch sphere, when the system is excited by a $\pi/2$ microwave pulse, the magnetization vector, which was originally in equilibrium along the longitudinal (z-axis), is flipped to the transverse plane (xy). Subsequently, due to energy exchange with the lattice, the magnetization vector gradually returns to its initial state. The time required for the longitudinal magnetization component M_z to recover to $(1-1/e)$ times of its thermal equilibrium value is defined as the spin-lattice relaxation time (T_1), which can be derived using Equation 1.5.1:

$$M_z(t) = M_{z,eq} - [M_{z,eq} - M_z(0)]e^{-t/T_1} \quad \text{Equation 1.5.1}$$

If $M_z(0) = -M_{z,eq}$, the equation is rewritten as:

$$M_z(t) = M_{z,eq}(1 - 2e^{-t/T_1}) \quad \text{Equation 1.5.2}$$

Similarly, in this process, the time required for the component M_{xy} in the xy plane to reach $1/e$ of its initial value is defined as the spin-spin relaxation time (T_2), which can be obtained from the following equation:

$$M_{xy}(t) = M_{xy}(0)e^{-t/T_2} \quad \text{Equation 1.5.3}$$

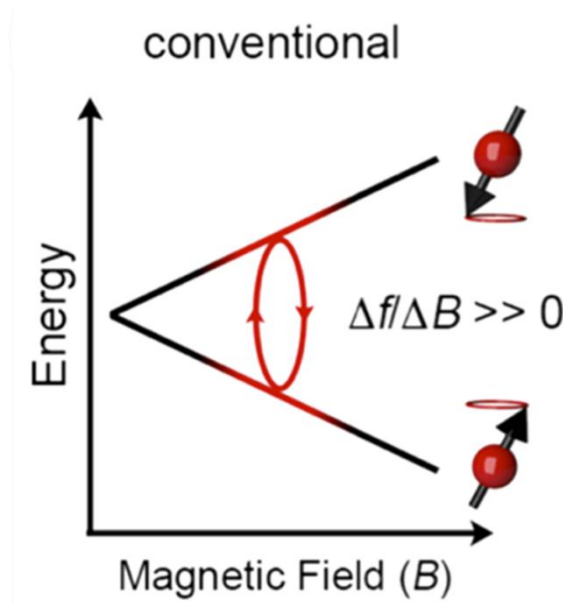


Figure 1.5.2 The diagrams of electron paramagnetic resonance for conventional electron transition.¹³³

In 1950, Erwin Hahn discovered the spin echo in NMR, laying the foundation for the precise measurement of spin-lattice relaxation and spin-spin relaxation times. In pulsed microwave experiments, a spin echo is generated by sequentially applying pulses of $\pi/2$ and π , manifesting the coherent superposition state of the ground and the excited states. By monitoring the attenuation of the echo signal intensity (manifested as microwave radiation or electrical signal) with the pulse interval, the time required for the signal to decay to its initial intensity, which is the decoherence time (T_2), can be determined. These characteristics demonstrate that electron spins fully satisfy the fundamental requirements for implementation as qubits.

1.5.2 Progress on lanthanide-based qubits

Since Leuenberger and Loss proposed the use of single-molecule magnets for quantum computing in 2001,¹³⁴ SMMs have gained significant attention as potential qubits. In particular, recent investigations have revealed a high degree of similarity between the multi-level states derived from hyperfine splitting and multi-level states in single-molecule magnets due to the zero-field splitting, suggesting their potential application in more simple systems, such as systems with $S = 1/2$ and mononuclear system. According to the DiVincenzo criterion, qubits must be correlated to form quantum logic gates for quantum computing. Quantum logic gates encompass various types, such as C-NOT gates, SWAP gates, and Hadamard gates.

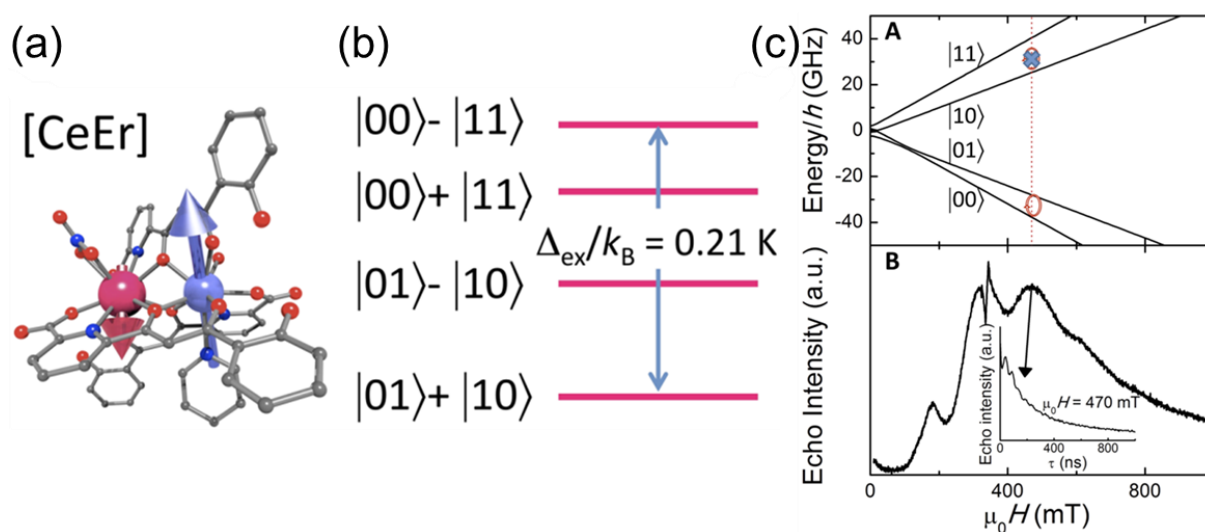


Figure 1.5.3 (a) The molecular structure of [CeEr(HL)₂(H₂L)(NO₃)(py)(H₂O)]. (b) The arrangement of the four lowest magnetic energy levels. (c) C-NOT gate operation.¹³⁵

Aguilà *et al.* successfully realized C-NOT gate operations by using the heterodinuclear complex, [CeEr(HL)₂(H₂L)(NO₃)(py)(H₂O)] (H₃L = 6-(3-oxo-3-(2-hydroxyphenyl)propionyl)pyridine-2-carboxylic acid), as shown in Figure 1.5.3.¹³⁵ The distinct sizes of the two coordination pockets within the complex facilitate the selective formation of the Ce-Er heterometallic structure. The weak coupling between Ce and Er centers induces four low-lying energy levels with a total splitting of less than 0.21 K, ensuring resonant transitions under X-band microwave radiation. The intensity of field-swept spin echo experiments exhibited a clear quantum transition from $|00\rangle$ to $|01\rangle$ at 4 K with a lifetime of 410 ns for the coherent superposition state. The properties align with the logical definition of the C-NOT gate,

providing an important physical model for constructing quantum logic gates based on coordination compounds.

Currently, the construction of quantum computing prototype devices based on coordination complex qubits is still in its early stages. Generally, from an application perspective, converting the spin state of qubits into electrical signal output is the most feasible solution, as electrical detection offers significant advantages in sensitivity, accuracy, and detection limit. In particular, since electronic technology has a deep foundation, achieving the conversion of spin-echo signals into electrical signals would be a major step forward in advancing coordination compounds in the field of quantum computing. Wernsdorfer and Ruben groups have made extensive progress in this field by successfully constructed a single-molecule three-terminal device with TbPc₂, where the benzene rings of phthalocyanine were weakly coupled to the gold electrode.^{41, 42} By utilizing gate voltage to tune the hyperfine coupling between electron and nuclear spins, and employing external magnetic fields to control the reversal of nuclear spin, four states corresponding to the flips of each nuclear spin were electrically readout. Building upon this, Hadamard logic gates were further introduced to achieve coherent manipulation of molecular spin states through pulsed electric fields, and successfully realize the Grover quantum algorithm at the molecular level.³⁸

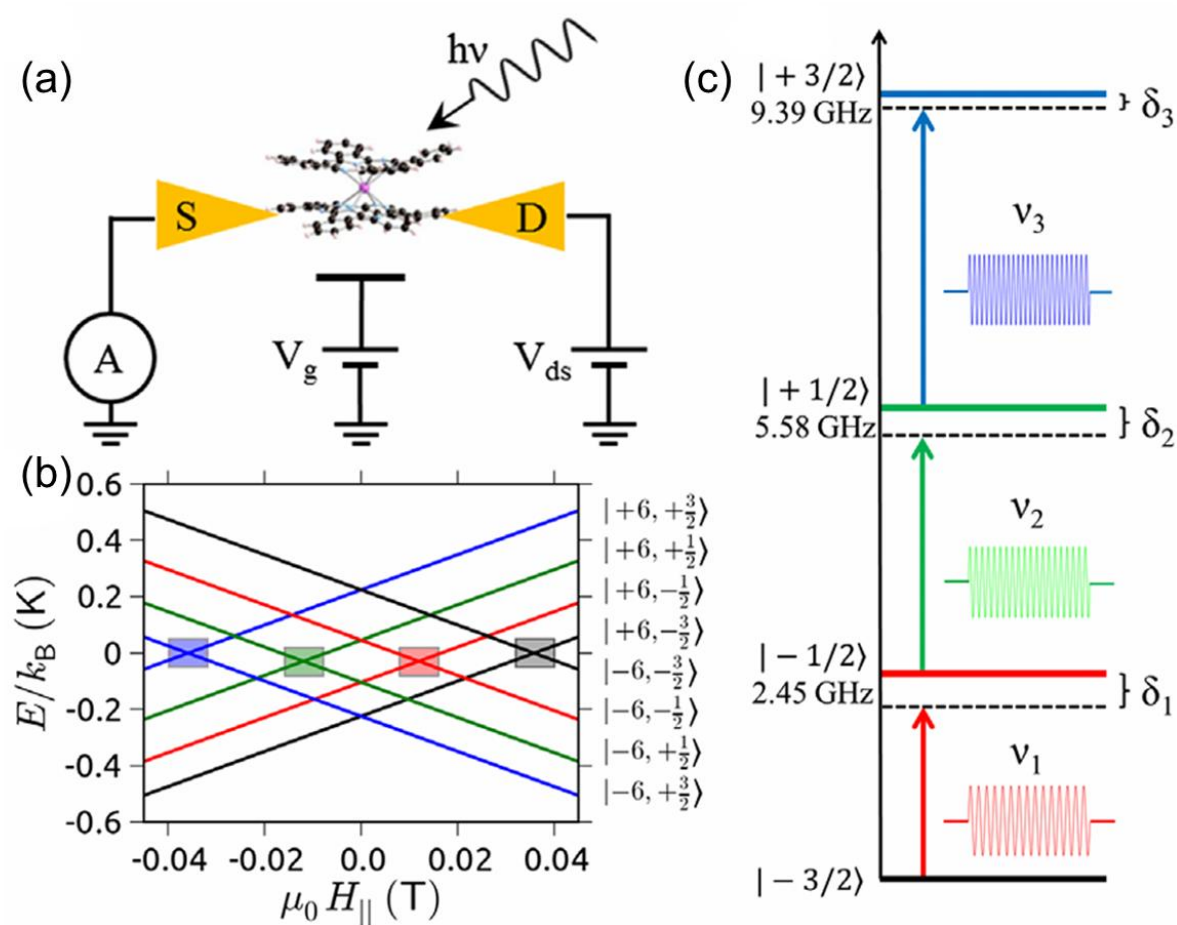


Figure 1.5.4 (a) Schematic of single-molecule device. (b) Zeeman diagram of the TbPc₂. (c) Under a specific magnetic field, the energy corresponding to each energy level transition.³⁸

Chapter 2. Isotopologue Ligands: Magnetic Properties of D-, ^{14}N - and ^{15}N -enriched TbPc_2 Double-decker Complexes

2.1 Introduction

In the cutting-edge intersection of quantum physics and condensed matter physics, single-molecule magnets (SMMs) are attracting attention due to their immense potential in quantum computing, high-density information storage, and molecular electronics.^{14, 136, 137} SMM investigations mainly focus on the manipulation of electron spins through strong ligand fields and appropriate molecular symmetry to adjust the anisotropy barrier.¹³⁸ However, although electronic spins possess large magnetic moments, making them easily manipulated by the external magnetic field, their high sensitivity to the environment leads to decoherence.¹³⁹ In contrast, nuclear spins, despite the smaller magnetic moments, exhibit remarkably long coherence time due to the weak coupling with the environment.^{12, 111, 140} Therefore, the successful manipulations currently achieved in single-molecule devices based on lanthanide SMMs qubits fundamentally relies on the exploitation of nuclear spin.^{38, 41, 42} Nevertheless, though the electronic spin and the nuclear spin play different roles in quantum coherence and relaxation mechanisms, they complement each other in the pursuit of the final goal to make accessible quantum operations like computing, sensing, communication, and simulation.^{14, 136} Moreover, nuclear spin not only serves as robust storage qubits for quantum information, but also modulates the SMM properties via hyperfine or super-hyperfine interactions.^{101, 111} Therefore, a comprehensive investigation into the isotope effect is of significance for revealing the fundamental regulation of SMM behavior by nuclear spin and constructing high-performance quantum materials.^{101, 137}

As previously introduced in Chapter 1.4.2, the isotope effect modulates SMM properties through two dimensions: from the dynamic dimension, by changing the mass of specific atoms, the vibrational modes of the molecule are significantly affected, thereby modulating the spin-phonon coupling, which is crucial in thermally activated relaxation processes.^{26, 124} From quantum dimension, by introducing isotopes with different nuclear spins, the quantum tunneling of magnetization is suppressed via hyperfine interactions or super-hyperfine interactions, thereby extending the coherent time.^{19, 47, 103, 105, 106, 141} This unique property makes the isotope strategy an ideal surgical tool for exploring the relaxation nature of single-molecule magnets.

To date, significant progress has been made in exploring the SMM behavior via isotope strategies. Related investigations are mainly limited to isotope substitution of the metal center, where the quantum tunneling of magnetization is suppressed by utilizing the nuclear-spin-free isotope metal center.^{19, 47, 101} However, the magnetic behavior of single-molecule magnets is essentially the result of the interaction between the central metal ion and the surrounding ligand field.^{111, 124, 142} Given the complex electronic coupling and energy exchange between ligand orbitals and metallic $4f$ orbitals, in-depth exploration of ligand isotope effects is important for a comprehensive understanding of spin relaxation mechanisms.¹⁵

Although the influence of ligand isotope effects on the molecular vibrations has been widely established in physics and chemistry,¹⁴³⁻¹⁵⁰ its applications in SMMs are still at an early stage, with current works mostly confined to the transition complexes,^{105, 141, 142, 147, 151} with only one example of a lanthanide complex by Tong.¹⁰⁶ These studies mainly focus on the deuteration effect, where the vibrational modes are significantly changed, thereby mitigating the phonon-dependent relaxation process and suppressing thermal activation.^{26, 124} Although Tong's work pointed out that the increase in nuclear spin upon deuteration widens the window for quantum tunneling through super-hyperfine coupling,¹⁰⁶ this modulation is still an indirect effect since the H or D atoms are not directly coordinated to the metal ions, which may be the reason why the effect is relatively weak.

Considering the aforementioned gaps, our studies shifted the focus from the peripheral atoms to the donor atoms directly involved in coordination, aiming to further elucidate how the isotope effects of coordinating atoms affect the SMM properties. To address this, bis(phthalocyaninato) terbium (TbPc_2) is selected as an ideal SMM for investigation. The reasons are: First, the TbPc_2 possesses a highly symmetrical molecular structure, which facilitates the enrichment of high-purity isotopologues and simplifies the interpretation of subtle physical changes. Second, its excellent chemical and thermal stability provides a broad experimental window for investigation. More importantly, as one of the most well-established SMM frameworks, the detailed background of TbPc_2 allows us to unearth elusive phenomena driven by ligand isotope effects that are difficult to detect through a less established or more complex system.^{32, 127, 152-154}

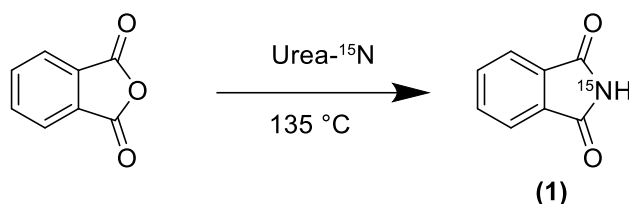
Herein, to ensure the isotopic enrichment and chemical purity of the target products, the building block approach is employed to synthesize the natural $[\text{TbPc}_2]^0$ and fully isotope-enriched $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ and $[\text{TbPc}_2\text{-D}]^0$ complexes. Through temperature-dependent and magnetic-field-dependent SQUID measurements, the influence of isotope effects on the relaxation, in terms of spin-phonon coupling and super-hyperfine interactions, is investigated. To address the specific contributions of the isotope effect, these isotopologues are reduced to remove the radical, leading to negatively charged complex moieties with a counterbalancing tetraethylammonium (TEA). Through high-sensitivity μ -SQUID measurements, we systematically compared the $[\text{TbPc}_2]\text{-[TEA]}^+$ and $[\text{TbPc}_2\text{-}^{15}\text{N}]\text{-[TEA]}^+$ systems by analyzing the population of nuclear spin states and the fraction of transitions between different states after different waiting time, revealing the role of isotope effects in reshaping the effective tunneling splitting. Our findings demonstrate the potential of isotope engineering in controlling the quantum coherence of single-molecule magnets and provide a guidance for designing high-performance molecular qubits.

2.2 Synthesis details

General procedures

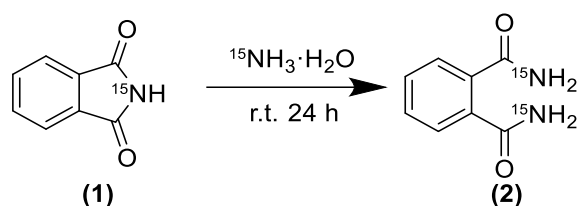
All chemicals and reagents purchased from commercial sources (Sigma-Aldrich, TCI chemicals, BLD) were of reagent grade and used without further purification. [TbPc₂]⁰ and [YPc₂]⁰ were synthesized according to the previously reported procedure with some modifications.

Synthesis of ¹⁵N-enriched Phthalimide-¹⁵N (1)



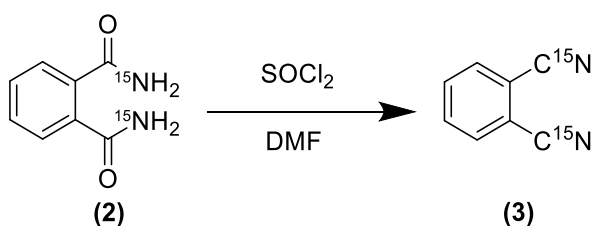
A mixture of phthalic anhydride (2342.7 mg, ~15.83 mmol) and ¹⁵N-enriched urea (478.8 mg, 7.72 mmol, 98 atom % ¹⁵N) in a 50 mL flask was stirred and heated to 135 °C. After all samples melted, the solution gradually turned into solid over approximately 12 minutes. After complete curing, the reaction was cooled to room temperature. The formed solid was collected by filtration, washed with saturated NaHCO₃ solution and water three times, and dried at ambient conditions overnight to afford pale yellow phthalimide-¹⁵N (C₈H₅O₂¹⁵N, FW = 148.12, 1925.9 mg, 13.00 mmol, 84.18% yield based on ¹⁵N-enriched urea). ESI-MS m/z: [M+H]⁺ 149.04 (calcd: 149.03). ¹H-NMR (500 MHz, DMSO-d₆): δ [ppm] = 11.34 (d, J_{NH} = 94 Hz, 1H, NH), 7.84 (s, 4H, ArH). ¹³C-NMR (500 MHz, DMSO-d₆) δ 169.71, 134.81, 133.07, 123.42 (see appendix Figure S1).

Synthesis of ¹⁵N-enriched Phthalamide-¹⁵N (2)



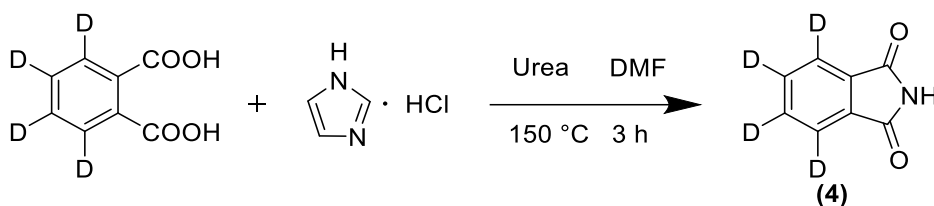
To a slurry of phthalimide-¹⁵N (1, 6062.1 mg, ~40.93 mmol) in 2 mL water was added 8 mL of ¹⁵N-enriched ammonium hydroxide (6 mol/L, 48 mmol, 98 atom % ¹⁵N). The slurry quickly turned white. After stirring at room temperature for 24 h, the precipitate was filtered and dried at ambient conditions to afford white phthalamide-¹⁵N (C₈H₈O₂¹⁵N₂, FW = 166.16, 5838.9 mg, 35.14 mmol, 85.86% yield based on phthalimide-¹⁵N). ESI-MS m/z: [M+H]⁺ 167.10 (calcd: 167.06). ¹H-NMR (500 MHz, DMSO-d₆): δ [ppm] = 7.72 (d, J_{NH} = 90 Hz, 2H, NH), 7.84 (s, 4H, ArH), 7.33 (d, J_{NH} = 87 Hz, 2H, NH). ¹³C-NMR (500 MHz, DMSO-d₆) δ 170.66, 136.73, 129.63, 128.04 (see appendix Figure S2).

Synthesis of ¹⁵N-enriched Phthalonitrile-¹⁵N (3)



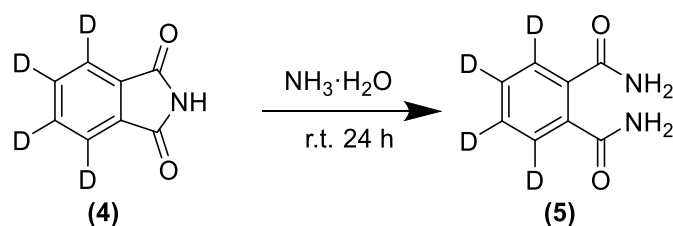
Phthalamide-¹⁵N (**2**, 4114.2 mg, ~24.76 mmol) was dissolved in 100 mL DMF, and stirred for 10 minutes in the bath of dry ice and MeCN. Thionyl chloride (50 mL) was added dropwise (if gas is generated, immediately stop adding, wait until the gas disappears). After adding, the white solution gradually turned transparent. After 2 h of stirring in an ice bath, slowly warm to room temperature overnight. After stirring at room temperature overnight, the mixture was poured into ice water. The white precipitate was filtered, washed with water, and then dried at ambient conditions to afford white phthalonitrile-¹⁵N (C₈H₄¹⁵N₂, FW = 130.13, 2625.0 mg, 20.17 mmol, 81.46% yield based on phthalamide-¹⁵N). ESI-MS m/z: [M+H]⁺ 131.17 (calcd: 131.13). ¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 7.87 (m, 2H, ArH), 7.80 (m, 2H, ArH), 7.33 (d, *J*_{NH} = 87 Hz, 2H, NH) ¹³C-NMR (500 MHz, CDCl₃) δ 133.60, 133.22, 116.10, 115.25 (see appendix Figure S3).

Synthesis of D-enriched Phthalimide-D (**4**)



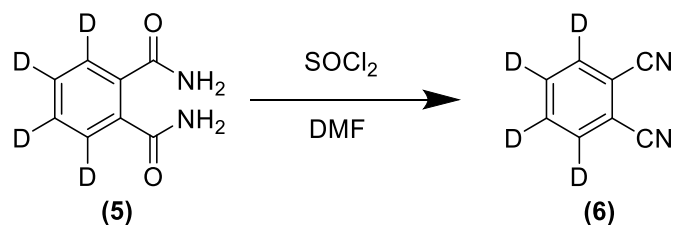
Phthalic acid-D₄ (2912.2 mg, ~17.11 mmol, 98 atom % D), urea (2118.4 mg, ~35.31 mmol), and imidazole hydrochloride (3649.9 mg, ~34.93 mmol) were mixed, ground into a fine powder, and then transferred into a 100 mL flask. 1 mL of DMF was added, stirred, and heated to 150 °C for 3 h. As the temperature increased, the solid melted together with the gas generated. After around 10 min stirring at 150 °C, a yellow solid formed. After cooling to room temperature, the crude solid was ground, added 100 mL 2 mol/L HCl, and stirred at room temperature for 10 min. The formed precipitate was collected by filtration, washed with ethanol, and dried at ambient conditions to afford pale yellow phthalimide-D (C₈D₄HO₂N, FW = 151.13, 2374.0 mg, 15.71 mmol, 91.78% yield based on phthalic acid-d₄). ESI-MS m/z: [M+H]⁺ 151.98 (calcd: 152.03). ¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 11.34 (s, 1H, NH) ¹³C-NMR (500 MHz, CDCl₃) δ 169.82, 134.35, 133.22, 123.27 (see Appendix Figure S4).

Synthesis of D-enriched Phthalamide-D (**5**)



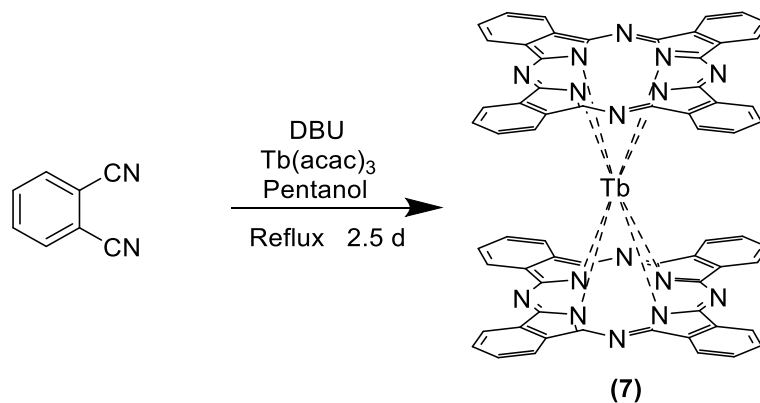
Following the procedure described for compound **2**, the target compound was synthesized by utilizing the following reagents: phthalimide-D (**4**, 3165.8 mg, ~20.95 mmol) and ammonium hydroxide (13.3 mol/L, 12.5 mL, 166.25 mmol), affording white phthalamide-D ($\text{C}_8\text{D}_4\text{H}_4\text{O}_2\text{N}_2$, FW = 168.16, 3170.0 mg, 18.85 mmol, 89.99% yield based on phthalimide-D). Only solvent peaks were observed in the ^1H -NMR spectrum (500 MHz, CDCl_3). ESI-MS m/z : $[\text{M}+\text{H}]^+$ 169.04 (calcd: 169.06). ^{13}C -NMR (500 MHz, CDCl_3) δ 170.62, 136.75, 129.21, 127.76 (see appendix Figure S5).

Synthesis of D-enriched Phthalonitrile-D (**6**)



Following the procedure described for compound **3**, the target compound was synthesized by utilizing the following reagents: phthalamide-D (**5**, 3354.0 mg, ~19.95 mmol), 80 mL DMF, and 40 mL thionyl chloride, affording white phthalonitrile-D ($\text{C}_8\text{D}_4\text{N}_2$, FW = 132.13, 2105.7 mg, 15.94 mmol, 79.90% yield based on phthalamide-D₄). ESI-MS m/z : $[\text{M}+\text{H}]^+$ 133.11 (calcd: 133.13). ^1H -NMR (500 MHz, CDCl_3): δ [ppm] = 7.87 (m, 2H, ArH), 7.80 (m, 2H, ArH), 7.33 (d, $J_{\text{NH}} = 87$ Hz, 2H, NH). ^{13}C -NMR (500 MHz, CDCl_3) δ 133.46-132.44, 115.93, 115.30 (see appendix Figure S6).

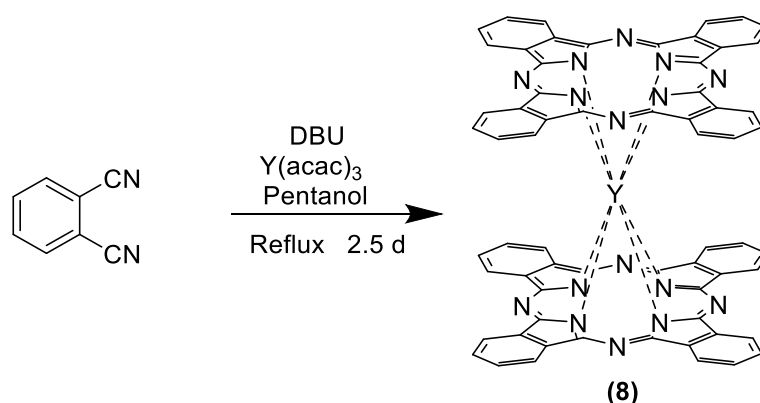
Synthesis of Terbium(III) bis(phthalocyaninato) complex (**7**, $[\text{TbPc}_2]^0$)



To a mixture of phthalonitrile (21 mmol, 2688.0 mg) and terbium acetylacetonate hydrate (2.5 mmol, 1140.6 mg) in 25 mL of 1-pentanol was added 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 10.5 mmol, 1598.52 mg). Then the reaction mixture was refluxed at 145 °C for 60 h.

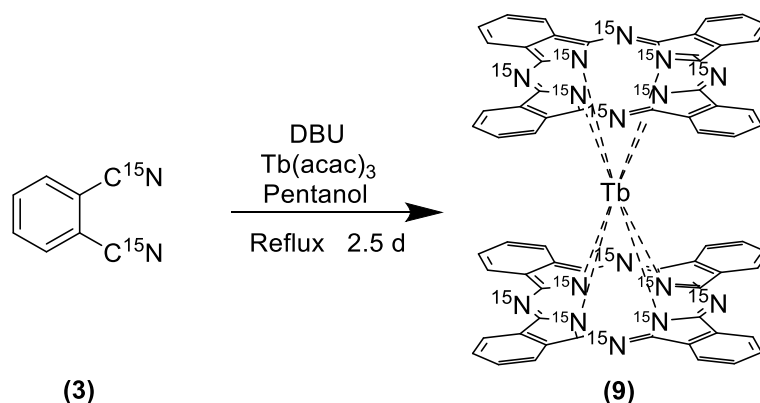
After cooling to room temperature, acetic anhydride (20 mL) was added, and the mixture was heated to 100 °C for 30 minutes. After heating, the formed precipitate was collected by filtration and thoroughly washed with n-hexane (20 mL), acetone (20 mL), and diethyl ether (20 mL) three times. The crude product was dissolved in CHCl₃, and insoluble species were then filtered off, leaving a dark green filtrate. The filtrate was concentrated under reduced pressure and purified via column chromatography on basic alumina oxide (deactivated with 4.6% water, level IV) using CHCl₃ as eluent. The green fraction was collected and recrystallized by layering n-hexane on the solution, affording black crystalline solid of **[TbPc₂]⁰** (C₆₄H₃₂N₁₆Tb, FW = 1183.22, 825.6 mg, 0.70 mmol, 27.9% yield based on terbium acetylacetonate hydrate). MALDI MS m/z, calcd. (found): 1183.2250 (1183.5752) (positive mode).

Synthesis of Yttrium(III) bis(phthalocyaninato) complex (**8**, **[YPc₂]⁰**)



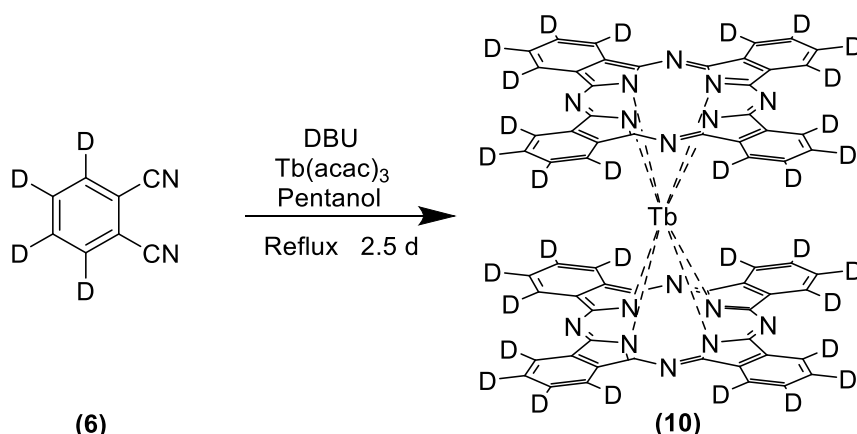
Following the procedure described for compound **[TbPc₂]⁰**, the target compound was synthesized by utilizing the following reagents: phthalonitrile (6721 mg, ~52.5 mmol), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 4007 mg, ~26.25 mmol), yttrium acetylacetonate hydrate (2414 mg, ~6.25 mmol), and 80 mL 1-pentanol, affording black crystalline solid **[YPc₂]⁰** (C₆₄H₃₂N₁₆Y, FW = 1112.9, 1718.2 mg, 1.54 mmol, 24.7% yield based on yttrium acetylacetonate hydrate). MALDI MS m/z, calcd. (found): 1199.1775 (1198.9536) (positive mode).

Synthesis of ¹⁵N-enriched Terbium(III) bis(phthalocyaninato)-¹⁵N complex (**9**, **[TbPc₂-¹⁵N]⁰**)



Following the procedure described for compound **[TbPc₂]⁰**, the target compound was synthesized by utilizing the following reagents: phthalonitrile-¹⁵N **3** (1366.1 mg, ~10.5 mmol), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 808.9 mg, ~5.25 mmol), terbium acetylacetonate hydrate (560.0 mg, ~1.25 mmol), and 12.5 mL 1-pentanol, affording black crystalline solid **[TbPc₂-¹⁵N]⁰** (C₆₄H₃₂¹⁵N₁₆Tb, FW = 1199.22, 427.3 mg, 0.36 mmol, 3.4% yield based on phthalonitrile-¹⁵N). MALDI MS m/z, calcd. (found): 1199.1775 (1198.9536) (positive mode).

Synthesis of D-enriched Terbium(III) bis(phthalocyaninato)-D complex (**10**, **[TbPc₂-D]⁰**)



Following the procedure described for compound **[TbPc₂]⁰**, the target compound was synthesized by utilizing the following reagents: phthalonitrile-D **6** (1355.9 mg, ~10.5 mmol), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 806.9 mg, ~5.25 mmol), terbium acetylacetonate hydrate (560.6 mg, ~1.25 mmol), and 12.5 mL 1-pentanol, giving black crystalline solid **[TbPc₂-D]⁰** (C₆₄D₃₂N₁₆Tb, FW = 1216.48, 416.5 mg, 0.34 mmol, 3.3% yield based on phthalonitrile-¹⁵N). MALDI MS m/z, calcd. (found): 1216.4832 (1216.4492) (positive mode).

Syntheses of diluted **[TbPc₂]⁻[TEA]⁺** (**11**), **[TbPc₂-¹⁵N]⁻[TEA]⁺** (**12**) and **[TbPc₂-D]⁻[TEA]⁺** (**13**) samples

For 5% diluted sample: To a suspension of **[TbPc₂]⁰** (~0.00169 mmol) and **[YPc₂]⁰** (~0.0320 mmol) in 10 mL methanol was added tetraethylammonium iodide ([TEA]⁺I⁻, 8.9 mg, ~0.0346 mmol). After stirring at room temperature for 5 min, hydrazine hydrate (0.2 mL, 64%) was added into the mixture, and the solution immediately turned into blue. A deep blue solution containing purple crystalline powder was obtained after stirring at room temperature overnight. The purple precipitate was collected by filtration and re-dissolved in acetone to give a clear blue solution. A vial containing the solution was subjected to an 80 °C bath with mechanical shaking to promote evaporation and prevent bumping. Once the solution changes into deep blue, quickly close the vial and stand at room temperature to crystallize. In a few minutes, the purple-red crystal was formed. The samples used for SC-XRD, SQUID, and μ -SQUID measurements were collected after 3 days.

1% and 2% diluted samples were prepared following the same procedures but with different molar ratios of **[TbPc₂]⁰** and **[YPc₂]⁰** (1/99 and 1/49, respectively).

Diluted samples (1%, 2%, 5%) of $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$ (or $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$) were prepared using the above method with $[\text{TbPc}_2\text{-}^{15}\text{N}]$ (or $[\text{TbPc}_2\text{-D}]$) instead of $[\text{TbPc}_2]^0$.

2.3 Molecular structures

2.3.1 Respective structures of $[\text{TbPc}_2]^0$, $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and $[\text{TbPc}_2\text{-D}]^0$

All crystals were obtained by dissolving the respective complexes in CHCl_3 and followed by layering n-hexane above the solution. The obtained unit cell parameters of the crystals are in close agreement with the previously reported values.^{155, 156} Single crystal X-ray diffraction analysis revealed that all these three complexes crystallize in the orthorhombic space group ($P2_12_12_1$) with $Z = 4$ (Table 2.3.1).

In these crystal structures, all the asymmetric units contain one Tb^{III} ion coordinated by two deprotonated phthalocyanine ligands. As shown in Figures 2.3.1-2.3.3, the central terbium ion possesses an N_8 coordination environment, which can be described as a square antiprism (D_{4d}) geometry based on continuous shape measure (CShM) analysis.¹⁵⁷ The corresponding CShM values are 0.749, 0.791, and 0.759 for $[\text{TbPc}_2]^0$, $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ and $[\text{TbPc}_2\text{-D}]^0$, respectively (Table 2.3.2).

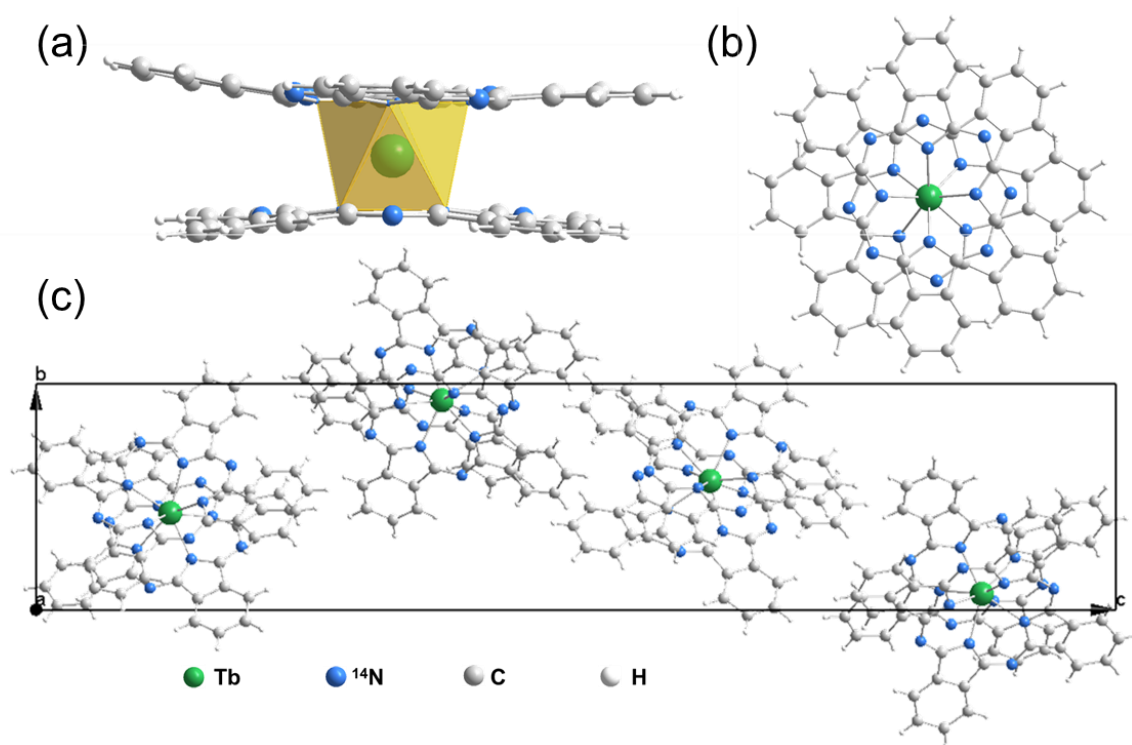


Figure 2.3.1 The molecular structure of $[\text{TbPc}_2]^0$. (a) Side view with polyhedral representation of the Tb^{III} ions. (b) Top view. (c) Unit cell of $[\text{TbPc}_2]^0$. Color code: Tb, green; ^{15}N , light blue; C, grey; H, white.

At first glance, the three crystal structures can be regarded as isostructural, as they share the same overall packing motif and coordination geometry. However, a more detailed comparison reveals subtle differences in their coordination environments, which may arise from isotopic substitution.

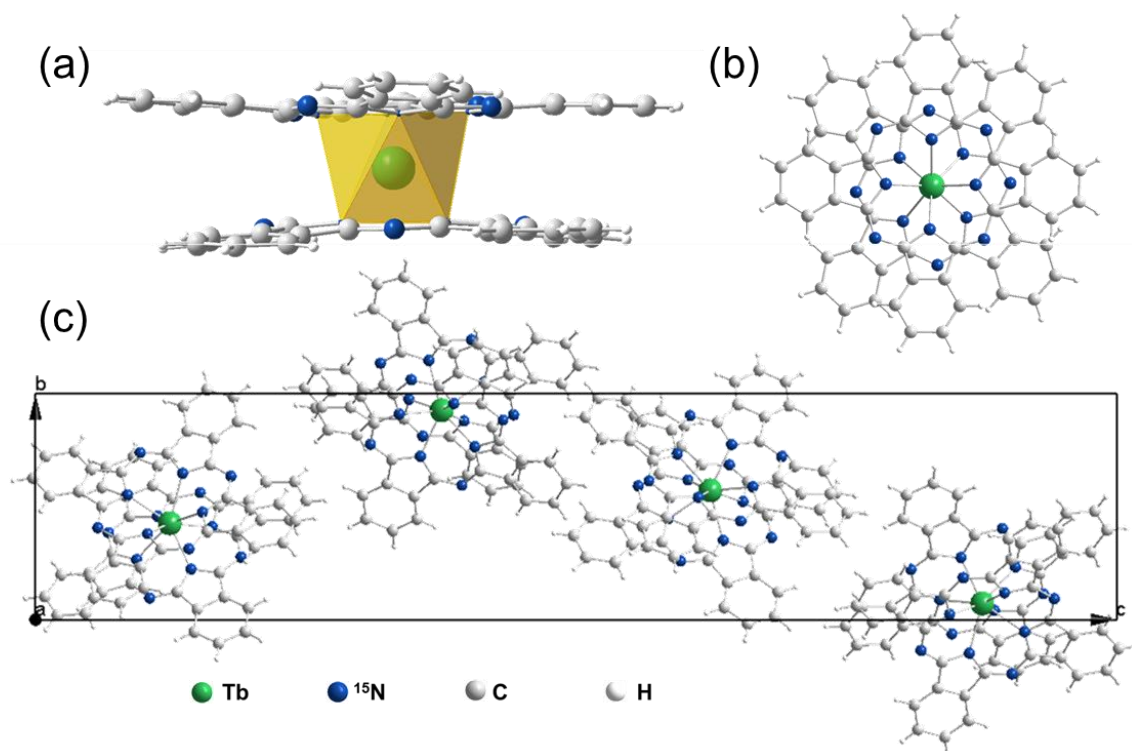


Figure 2.3.2 The molecular structure of $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$. (a) Side view with polyhedral representation of the Tb^{III} ions. (b) Top view. (c) Unit cell of $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$. Color code: Tb, green; ^{15}N , dark blue; C, grey; H, white.

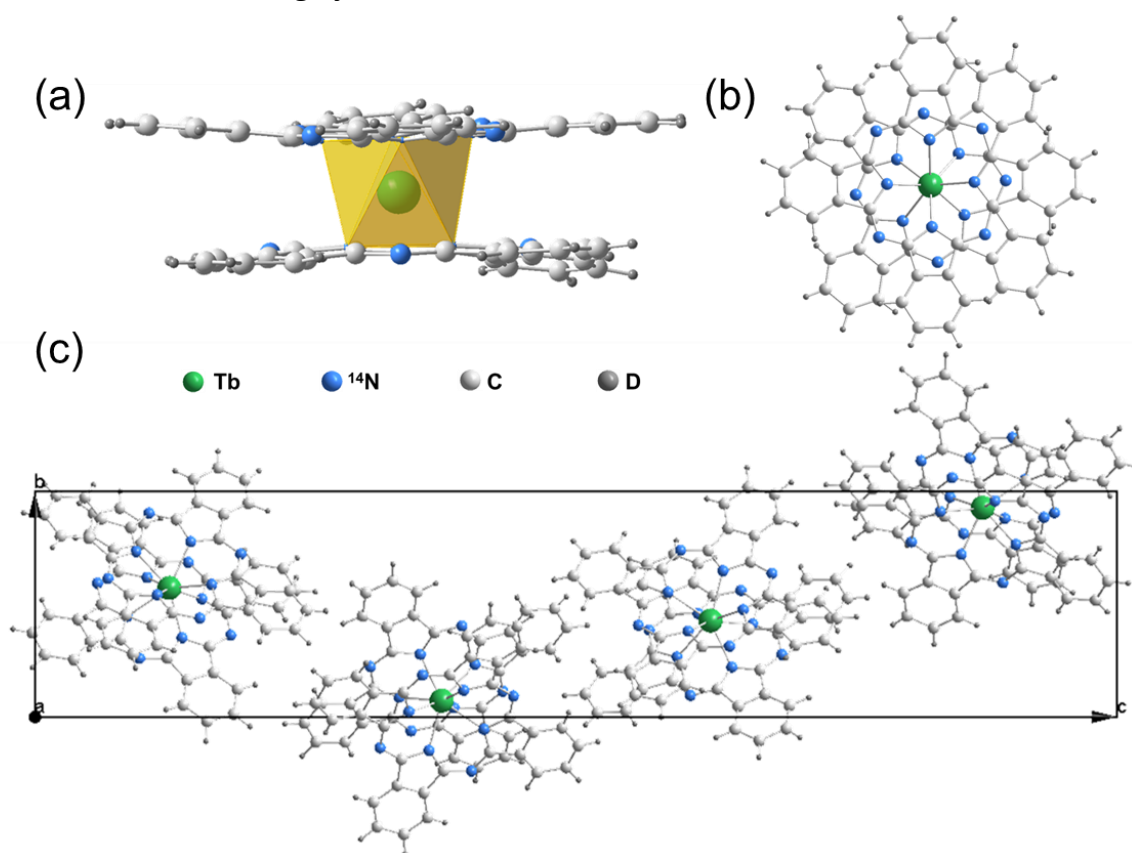


Figure 2.3.3 The molecular structure of **[TbPc₂-D]⁰**. (a) Side view with polyhedral representation of the Tb^{III} ions. (b) Top view. (c) Unit cell of **[TbPc₂-D]⁰**. Color code: Tb, green; ¹⁴N, light blue; C, grey; D, dark grey.

Table 2.3.1 Crystallographic information for **[TbPc₂]⁰**, **[TbPc₂-¹⁵N]⁰**, and **[TbPc₂-D]⁰**

No.	[TbPc₂]⁰ ¹⁵⁵	[TbPc₂-¹⁵N]⁰	[TbPc₂-D]⁰
Formula	C ₆₄ H ₃₂ N ₁₆ Tb	C ₆₄ H ₃₂ ¹⁵ N ₁₆ Tb	C ₆₄ D ₃₂ N ₁₆ Tb
Fw	1183.97	1199.97	1216.17
Temperature/K	101(2)	180	180
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	8.8136(6)	8.8518(1)	8.8537(1)
<i>b</i> /Å	10.5756(7)	10.5947(2)	10.5911(1)
<i>c</i> /Å	50.713(3)	50.8430(7)	50.8004(7)
α /°	90	90	90
β /°	90	90	90
γ /°	90	90	90
Volume/Å ³	4726.9(5)	4768.17(12)	4763.58(10)
<i>Z</i>	4	4	4
ρ_{calc} /cm ³	1.664	1.649	1.696
μ /mm ⁻¹	1.563	8.196	8.204
<i>R</i> _{int}	0.0952	0.0432	0.0384
Goodness-of-fit on <i>F</i> ²	1.184	1.140	1.074
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^a	<i>R</i> ₁ = 0.0501 <i>wR</i> ₂ = 0.0815	<i>R</i> ₁ = 0.0536 <i>wR</i> ₂ = 0.1686	<i>R</i> ₁ = 0.0412 <i>wR</i> ₂ = 0.1067
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	<i>R</i> ₁ = 0.0567 <i>wR</i> ₂ = 0.0832	<i>R</i> ₁ = 0.0585 <i>wR</i> ₂ = 0.1719	<i>R</i> ₁ = 0.0451 <i>wR</i> ₂ = 0.1082

$$^a R_1 = \|F_o\| - \|F_c\| / \sum \|F_o\|, wR_2 = \{w[(F_o)^2 - (F_c)^2]^2 / w[(F_o)^2]^2\}^{1/2}$$

As summarized in Table 2.3.3, the Tb···N bond lengths for **[TbPc₂]⁰**, **[TbPc₂-¹⁵N]⁰**, and **[TbPc₂-D]⁰** fall within the ranges of 2.397(5)–2.427(5) Å, 2.393(7)–2.431(7) Å, and 2.398(5)–2.421(5) Å, respectively. Overall, these values are highly comparable and lie within typical crystallographic standard deviations, confirming that the primary coordination sphere of the Tb(III) center is largely unaffected by isotopic substitution. Nevertheless, a closer inspection reveals minor trends: **[TbPc₂-D]⁰** exhibits the narrowest distribution of Tb···N bond lengths, indicating a slightly more uniform coordination environment, whereas **[TbPc₂-¹⁵N]⁰** shows a somewhat broader distribution. This subtle variation may be attributed to isotope effects influencing vibrational dynamics and, consequently, the refined structural parameters.

To further quantify structural differences between the isotopologues, a centroid at the centers of the four coordinating nitrogen atoms in both the upper and lower phthalocyanine ligands was introduced. This approach allows for a consistent definition of the ligand planes and facilitates the analysis of interplanar distances and relative orientations. The distances of the Tb^{III} ion from

these mean planes show only minor variations: 1.395/1.398 Å for **[TbPc₂]⁰**, 1.399/1.4055 Å for **[TbPc₂-¹⁵N]⁰**, and 1.399/1.400 Å for **[TbPc₂-D]⁰**. These values indicate that the Tb^{III} ion remains nearly symmetrically positioned between the two ligands in all three structures, with only very slight deviations.

Table 2.3.2 The CShM values calculated by using SHAPE analysis for **[TbPc₂]⁰**, **[TbPc₂-¹⁵N]⁰**, and **[TbPc₂-D]⁰**

	[TbPc₂]⁰	[TbPc₂-¹⁵N]⁰	[TbPc₂-D]⁰
OP-8 (<i>D</i> _{8h}) Octagon	33.668	33.849	33.702
HPY-8 (<i>C</i> _{7v}) Heptagonal pyramid	23.375	23.322	23.391
HBPY-8 (<i>D</i> _{6h}) Hexagonal bipyramid	15.945	15.838	15.924
CU-8 (<i>O</i> _h) Cube	8.357	8.227	8.280
SAPR-8 (<i>D</i>_{4d}) Square antiprism	0.749	0.791	0.759
TDD-8 (<i>D</i> _{2d}) Triangular dodecahedron	2.391	2.370	2.336
JGBF-8 (<i>D</i> _{2d}) Johnson gyrobifastigium J26	17.108	17.206	17.177
JETBPY-8 (<i>D</i> _{3h}) Johnson elongated triangular bipyramid J14	30.485	30.650	30.652
JBTPR-8 (<i>C</i> _{2v}) Biaugmented trigonal prism J50	3.524	3.593	3.533
BTPR-8 (<i>C</i> _{2v}) Biaugmented trigonal prism	2.904	2.966	2.914
JSD-8 (<i>D</i> _{2d}) Snub diphennoid J84	5.921	5.947	5.896
TT-8 (<i>T</i> _d) Triakis tetrahedron	9.207	9.070	9.116
ETBPY-8 (<i>D</i> _{3h}) Elongated trigonal bipyramid	25.689	25.800	25.764

In line with this observation, the interplanar distance between the two phthalocyanine ligands exhibits small but systematic differences. The largest separation is observed for **[TbPc₂-¹⁵N]⁰** (2.8045 Å), followed by **[TbPc₂-D]⁰** (2.799 Å) and **[TbPc₂]⁰** (2.793 Å). Although these differences are small, they suggest a slight expansion of the coordination environment in the isotopically substituted systems, particularly for the ¹⁵N-labeled complex.

The relative orientation of the two phthalocyanine ligands can be described by the twist angle between their coordinating nitrogen planes. All three complexes adopt the characteristic square

antiprismatic coordination geometry, with average twist angles of 41.2° for **[TbPc₂]⁰**, 41.0° for **[TbPc₂-¹⁵N]⁰**, and 41.1° for **[TbPc₂-D]⁰**. These values are lower than the ideal *D*_{4d} symmetry value of 45°, which is typical for lanthanide bis(phthalocyanine) complexes and reflects a small distortion from the ideal geometry. Importantly, the twist angles are nearly identical across the series, indicating that isotopic substitution has a negligible effect on the overall ligand orientation.

Table 2.3.3 The distances between atom-atom or atom-plane, and the twist angles of **[TbPc₂]⁰**, **[TbPc₂-¹⁵N]⁰**, and **[TbPc₂-D]⁰**

	[TbPc₂]⁰	[TbPc₂-¹⁵N]⁰	[TbPc₂-D]⁰
Tb···N/Å	2.397(5)-2.427(5)	2.393(7)-2.431(7)	2.398(5)-2.421(5)
Shortest Tb···Tb/Å	8.8136(6)	8.8518(1)	8.8537(1)
Tb···plane/Å	1.395(3), 1.398(3)	1.399(3), 1.406(3)	1.399(3), 1.400(2)
plane···plane/Å	2.793(4)	2.80449(3)	2.799(4)
Twist angle/°	40.9(2), 41.3(2), 41.0(2), 41.8(2)	40.6(3), 41.2(3), 40.7(3), 41.3(3)	41.4(2), 41.0(2), 41.2(2), 40.7(2)
Average twist angle/°	41.2(2)	41.0(3)	41.1(2)

Finally, differences in intermolecular packing can be assessed by considering the shortest Tb···Tb distances. These follow the trend **[TbPc₂]⁰** (8.8136 Å) < **[TbPc₂-¹⁵N]⁰** (8.8518 Å) < **[TbPc₂-D]⁰** (8.8537 Å). This gradual increase suggests a slight expansion of the unit cell and minor perturbations in lattice packing upon isotopic substitution. Although the effect is subtle, it is consistent with the small structural variations observed within the coordination sphere.

Overall, while the three complexes are structurally very similar, a detailed analysis reveals small but systematic differences that can be correlated with isotopic substitution, particularly in terms of bond-length distribution, interplanar separation, and crystal packing.

Although the three complexes exhibit only minor structural differences, such subtle variations can still have an impact on their magnetic and electronic properties. In lanthanide phthalocyanine systems, properties such as magnetic anisotropy and relaxation dynamics are highly sensitive to the local coordination environment, including metal–ligand distances, ligand plane separation, and slight distortions from ideal symmetry. Therefore, even the small changes observed in Tb···N bond distribution, interplanar distances, and crystal packing may contribute to measurable differences in magnetic behavior or intermolecular interactions. In particular, variations in intermolecular Tb···Tb distances could influence dipolar interactions in the solid state, potentially affecting collective magnetic phenomena.

2.3.2 Respective structures of 5% diluted **[TbPc₂][TEA]⁺**, **[TbPc₂-¹⁵N][TEA]⁺**, and **[TbPc₂-D][TEA]⁺**

All the crystals were obtained as described in Section 2.2 and were found to crystallize in the tetragonal space group *P*4₂1₂ with *Z* = 2, as determined by single crystal X-ray diffraction. However, significant disorder of both the solvent molecules and the counterion [TEA]⁺ molecule was observed. Although PLATON software^{158, 159} suggested a higher symmetry space

group ($P4/nmm$), and the overall packing arrangement is consistent with previously reported analogous $\text{Et}_4\text{N}[\text{DyPc}_2]$ structures¹⁹ (as shown in Figures 2.3.4-2.3.6c), the lower symmetry group was retained. This choice was made to better account for the observed electron density and to ensure a more reliable structural model. The full crystallographic details are summarized in Table 2.3.4.

Similar to the crystal structures of the neutral double-decker complexes, the asymmetric unit in all three ionic species consistently contains one Tb^{III} ion coordinated by two deprotonated phthalocyanine ligands. As shown in Figures 2.3.4–2.3.6, the terbium centers adopt an N_8 coordination environment characteristic of lanthanide bis(phthalocyanine) systems.

Continuous Shape Measure (CShM) analysis (Table 2.3.5) confirms that all coordination polyhedra closely approximate a square antiprismatic (D_{4d}) geometry,¹⁵⁷ with values of 0.712 for $[\text{TbPc}_2][\text{TEA}]^+$, 0.651 for $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and 0.570 for $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$. These values indicate only moderate distortions from the idealized geometry, with $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$ exhibiting the smallest deviation among the three complexes.

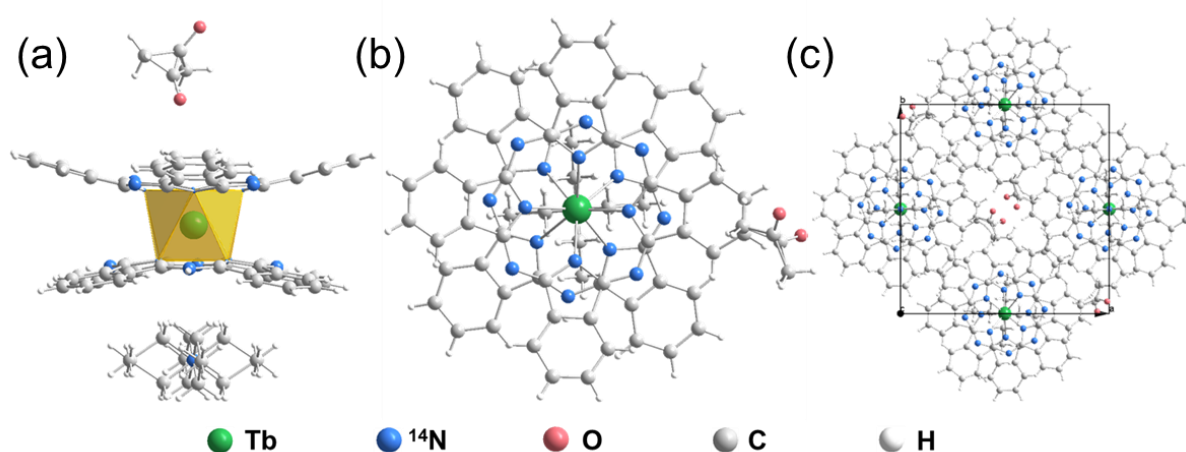


Figure 2.3.4 The molecular structure of $[\text{TbPc}_2][\text{TEA}]^+$. (a) Side view with polyhedral representation of the Tb^{III} ion. (b) Top view. (c) Unit cell of $[\text{TbPc}_2][\text{TEA}]^+$. Color code: Tb, green; ¹⁴N, light blue; O, red; C, grey; H, white.

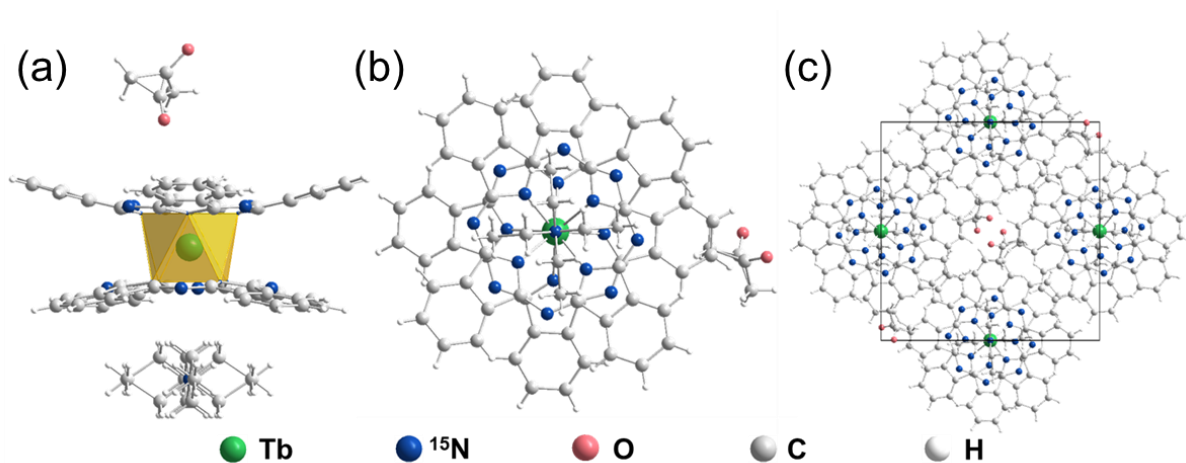


Figure 2.3.5 The molecular structure of $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$. (a) Side view with polyhedral representation of the Tb^{III} ion. (b) Top view. (c) Unit cell of $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$. Color code: Tb, green; ^{15}N , dark blue; O, red; C, grey; H, white.

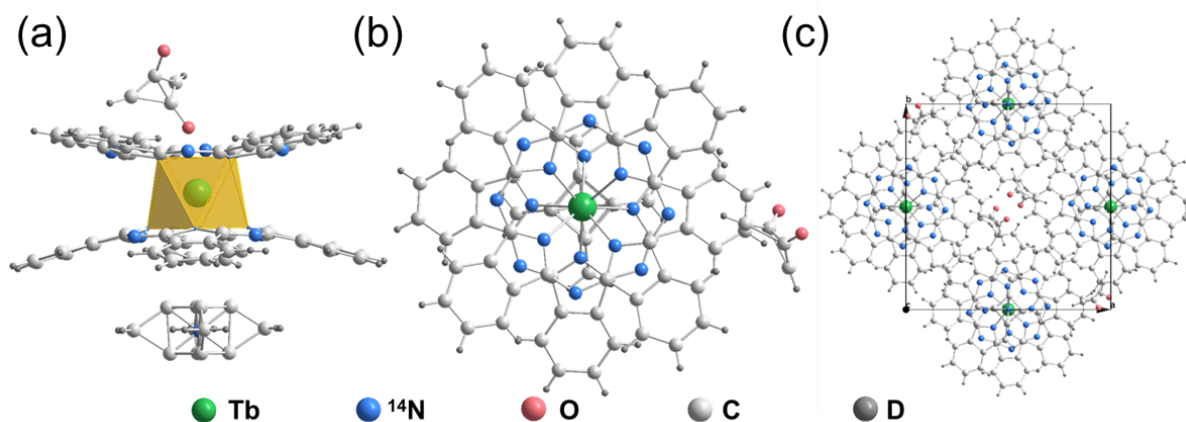


Figure 2.3.6 The molecular structure of $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$. (a) Side view with polyhedral representation of the Tb^{III} ion. (b) Top view. (c) Unit cell of $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$. Color code: Tb, green; ^{14}N , light blue; O, red; C, grey; D, dark grey.

Table 2.3.4 Crystallographic information for $[\text{TbPc}_2][\text{TEA}]^+$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$

No.	$[\text{TbPc}_2][\text{TEA}]^+$	$[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$	$[\text{TbPc}_2\text{-D}][\text{TEA}]^+$
Formula	$\text{C}_{78}\text{H}_{64}\text{N}_{17}\text{O}_2\text{Tb}$	$\text{C}_{78}\text{H}_{64}\text{}^{15}\text{N}_{17}\text{O}_2\text{Tb}$	$\text{C}_{78}\text{D}_{32}\text{H}_{32}\text{N}_{17}\text{O}_2\text{Tb}$
Fw	1430.38	1446.38	1462.38
Temperature/K	180	180	180
Crystal system	tetragonal	tetragonal	tetragonal
Space group	$P4_212$	$P4_212$	$P4_212$
$a/\text{\AA}$	17.471(3)	17.4422(3)	17.4771(2)
$b/\text{\AA}$	17.471(3)	17.4422(3)	17.4771(2)
$c/\text{\AA}$	10.776(2)	10.7600(2)	10.7362(2)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	90	90	90
$\gamma/^\circ$	90	90	90
Volume/ $\text{\AA}^3$	3289.1(14)	3273.52(13)	3279.36(10)
Z	2	2	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.448	1.451	1.534
μ/mm^{-1}	5.902	5.930	5.963
R_{int}	0.1068	0.0377	0.0153
Goodness-of-fit on F^2	0.880	1.062	1.212
R_1, wR_2 ($I > 2\sigma(I)$) ^a	$R_1 = 0.0450$ $wR_2 = 0.0794$	$R_1 = 0.0299$ $wR_2 = 0.0830$	$R_1 = 0.0860$ $wR_2 = 0.2341$

$R_1, wR_2(\text{all data})$	$R_1 = 0.0806$ $wR_2 = 0.0867$	$R_1 = 0.0340$ $wR_2 = 0.0848$	$R_1 = 0.0871$ $wR_2 = 0.2386$
------------------------------	-----------------------------------	-----------------------------------	-----------------------------------

$$^a R_1 = \|F_o\| - \|F_c\| / \sum \|F_o\|, wR_2 = \{w[(F_o)^2 - (F_c)^2]^2 / w[(F_o)^2]^2\}^{1/2}$$

Table 2.3.5 The CShM values calculated by using SHAPE analysis for $[\text{TbPc}_2][\text{TEA}]^+$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$

	$[\text{TbPc}_2][\text{TEA}]^+$	$[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$	$[\text{TbPc}_2\text{-D}][\text{TEA}]^+$
OP-8 (D_{8h}) Octagon	33.502	33.202	32.824
HPY-8 (C_{7v}) Heptagonal pyramid	23.499	23.510	23.530
HBPY-8 (D_{6h}) Hexagonal bipyramid	16.077	16.230	16.536
CU-8 (O_h) Cube	8.389	8.555	8.889
SAPR-8 (D_{4d}) Square antiprism	0.712	0.651	0.570
TDD-8 (D_{2d}) Triangular dodecahedron	2.414	2.422	2.463
JGBF-8 (D_{2d}) Johnson gyrobifastigium J26	17.366	17.374	17.435
JETBPY-8 (D_{3h}) Johnson elongated triangular bipyramid J14	30.747	30.643	30.513
JBTPR-8 (C_{2v}) Biaugmented trigonal prism J50	3.518	3.455	3.377
BTPR-8 (C_{2v}) Biaugmented trigonal prism	2.928	2.854	2.780
JSD-8 (D_{2d}) Snub diphenoid J84	5.896	5.851	5.803
TT-8 (T_d) Triakis tetrahedron	9.262	9.427	9.757
ETBPY-8 (D_{3h}) Elongated trigonal bipyramid	25.968	25.891	25.822

When compared quantitatively to the neutral analogues discussed previously, the ionic species systematically display lower CShM values, suggesting a more regular coordination environment upon charge compensation by the $[\text{TEA}]^+$ counterion. This trend implies that electrostatic stabilization in the ionic systems reduces structural distortions within the N_8 coordination sphere.

Despite this improvement in local symmetry, none of the complexes reaches an ideal D_{4d} configuration (CShM = 0), indicating that residual distortions remain intrinsic to the phthalocyanine ligand framework and stacking constraints. The observed differences between the three isotopologues are small but systematic, supporting the conclusion that isotopic substitution has a measurable but secondary influence compared to crystal packing and charge effects.

Importantly, even such subtle variations in coordination symmetry and ligand field regularity can have a direct impact on the magnetic anisotropy and slow magnetic relaxation behavior characteristic of Terbium-based single-molecule magnets (SMMs), where deviations from ideal D_{4d} symmetry are known to modulate the crystal-field splitting and, consequently, the effective energy barrier for magnetization reversal.

Table 2.3.6 The distances between atom-atom or atom-plane, and the twist angles of $[\text{TbPc}_2][\text{TEA}]^+$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$

	$[\text{TbPc}_2][\text{TEA}]^+$	$[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$	$[\text{TbPc}_2\text{-D}][\text{TEA}]^+$
Tb $\cdots$ N/Å	2.429(4)-2.435(5)	2.431(3)-2.434(3)	2.415(4)- 2.420(4)
Shortest Tb $\cdots$ Tb/Å	10.776(1)	10.760(2)	10.736(2)
Tb $\cdots$ plane/Å	1.400(2)/1.413(2)	1.393(2)/1.407(2)	1.375(8)/1.391(9)
plane $\cdots$ plane/Å	2.813(2)	2.800(5)	2.767(7)
Twist angle/ $^\circ$	41.3(4), 41.3(4), 41.3(4), 41.3(4)	41.7(1), 41.7(1), 41.7(1), 41.7(1)	42.5(2), 42.5(2), 42.5(2), 42.5(2)
Average twist angle/ $^\circ$	41.3(4)	41.7(1)	42.5(2)

The Tb $\cdots$ N bond lengths of these structure are in the range of 2.429(4)-2.435(5) Å, 2.431(3)-2.434(3) Å, and 2.415(4)- 2.420(4) Å for $[\text{TbPc}_2][\text{TEA}]^+$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$, respectively. Using the same analysis approach, the distances between terbium ion and phthalocyanine are 1.400(2)/1.413(2) Å for $[\text{TbPc}_2][\text{TEA}]^+$, 1.393(2)/1.407(2) Å for $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and 1.375(8)/1.391(9) Å for $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$. The corresponding average twist angles are determined to be 41.3(4) $^\circ$, 41.7(1) $^\circ$, and 42.5(2) $^\circ$ for $[\text{TbPc}_2][\text{TEA}]^+$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$, respectively, indicating only minor structural variations across the series.

However, it should be noted that the counterion (TEA), the solvent (acetone), and the diamagnetic diluted matrix (YPC₂) are not isotopically substituted. Especially under these highly diluted conditions, the obtained crystallographic parameters primarily reflect the structural features of the $[\text{YPC}_2][\text{TEA}]^+$. Therefore, the observed variations between the isotopologues cannot be unambiguously attributed to isotope effects alone, as lattice and matrix contributions are likely dominant.

Nevertheless, for these three complexes, the shortest distances of Tb $\cdots$ Tb atoms are all larger than 10.7 Å, which is approximately 1.2 times larger than those of the neutral complexes,

indicating significantly reduced intermolecular magnetic interactions and providing a suitable platform for probing subtle isotope-dependent effects, including hyperfine contributions.

2.4 Magnetic properties of $[\text{TbPc}_2]^0$, $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and $[\text{TbPc}_2\text{-D}]^0$

2.4.1 SQUID measurement

The temperature-dependent direct current (dc) magnetic susceptibility measurements are carried out using a Quantum Design MPMS-XL SQUID magnetometer in the temperature range of 2–300 K under an applied field of 1000 Oe. Polycrystalline samples are used to probe the intrinsic magnetic properties, and the raw data are corrected for diamagnetic contributions using Pascal's constants. A consistent protocol for samples preparation and data correction is applied throughout this study.

As shown in Figure 2.4.1, the temperature dependence of $\chi_M T$ for all the samples exhibits a similar trend, where the room-temperature $\chi_M T$ values for $[\text{TbPc}_2]^0$, $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and $[\text{TbPc}_2\text{-D}]^0$ are 12.14, 12.17, and 12.15 $\text{cm}^3 \text{ K mol}^{-1}$, respectively. These values are in good agreement with the theoretical value ($\chi_M T = 12.195 \text{ cm}^3 \text{ K mol}^{-1}$, Equation 1.2.5) expected for a free Tb^{3+} ion ($J = 6$, $g_J = 3/2$, $\chi_M T = 11.82 \text{ cm}^3 \text{ K mol}^{-1}$) coupled to an organic radical ($S = 1/2$, $g = 2$, $\chi_M T = 0.375 \text{ cm}^3 \text{ K mol}^{-1}$), confirming that isotopic substitution does not alter the electronic ground state at room temperature.

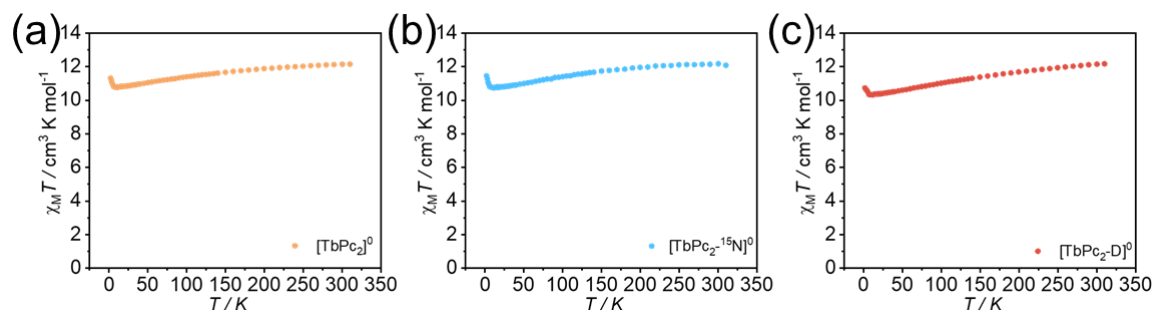


Figure 2.4.1 The $\chi_M T$ versus T plots for $[\text{TbPc}_2]^0$ (a, yellow), $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ (b, blue), and $[\text{TbPc}_2\text{-D}]^0$ (c, red) with an applied field of 1000 Oe.

Upon cooling, all three complexes exhibit a similar qualitative behavior: an initial gradual decrease in $\chi_M T$ followed by an upturn at low temperatures. The decrease is attributed to thermal depopulation of the Stark sublevels of the Tb^{3+} ion, possibly combined with weak antiferromagnetic interactions, whereas the low-temperature upturn suggests ferromagnetic exchange coupling between the Tb^{3+} center and the phthalocyanine radical.

A closer comparison reveals that the $\chi_M T$ curves for $[\text{TbPc}_2]^0$ and $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ are nearly identical, reaching minima of 10.77 and 10.76 $\text{cm}^3 \text{ K mol}^{-1}$ at 9 K, respectively. In contrast, $[\text{TbPc}_2\text{-D}]^0$ exhibits a more pronounced decrease, reaching a lower minimum value of 10.32 $\text{cm}^3 \text{ K mol}^{-1}$. However, structural analysis does not support a straightforward correlation between this behavior and static geometric parameters: the shortest $\text{Tb}\cdots\text{Tb}$ distances, as well

as interplanar separations and twist angles, are comparable across the series. Therefore, changes in coordination symmetry or lattice contraction can be reasonably excluded as the primary origin of the observed differences.

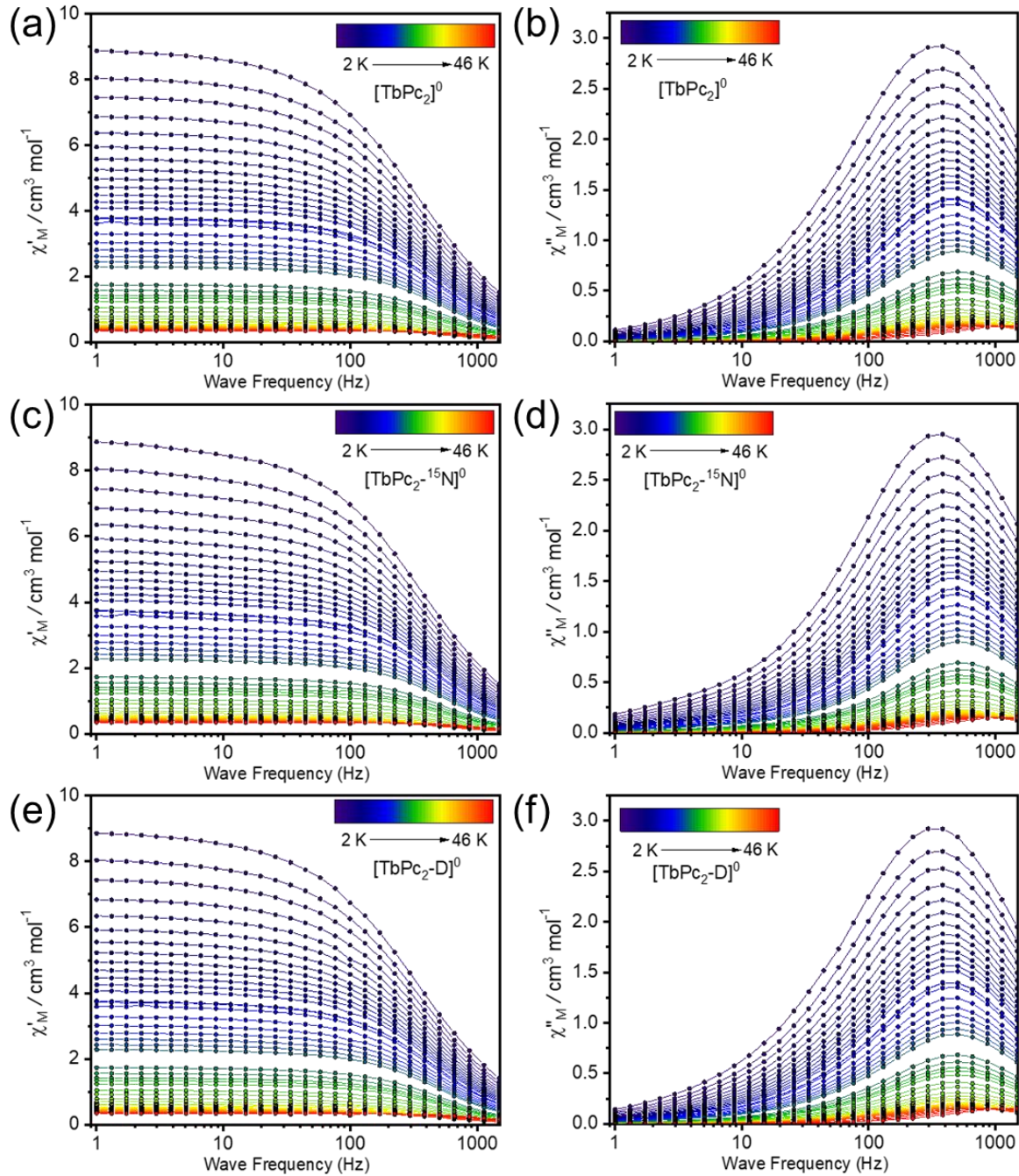


Figure 2.4.2 The experimental frequency-dependent ac magnetic susceptibility data of the in-phase (left) and out-of-phase (right) for $[\text{TbPc}_2]^0$ (a, b), $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ (c, d), and $[\text{TbPc}_2\text{-D}]^0$ (e, f) at a zero DC field from 2 K to 46 K. The solid lines are guided for eyes.

A more plausible explanation involves isotope-induced modifications of vibrational dynamics. The substitution of hydrogen with deuterium lowers vibrational frequencies, which can alter spin-phonon coupling and potentially enhance relaxation pathways or effective

magnetic interactions, thereby promoting more efficient thermal depopulation of magnetic states.¹⁶⁰ Furthermore, alternative explanations, such as subtle differences in sample microstructure, packing disorder, or residual intermolecular interactions, cannot be entirely ruled out. The absence of a comparable effect in $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ supports the notion that not all isotopic substitutions have a significant dynamical impact, particularly when the substituted atoms are structurally constrained within the ligand framework.

Therefore, while the observed trend for $[\text{TbPc}_2\text{-D}]^0$ is consistent with an isotope effect mediated through vibrational dynamics, this conclusion should be treated with caution and ideally supported by complementary techniques, such as AC susceptibility, EPR spectroscopy, or phonon analysis, which are more sensitive to dynamic processes and spin–lattice interactions.

Alternating current (AC) magnetic susceptibility measurements are performed to probe the single-molecule magnet (SMM) behavior of the three complexes. Figure 2.4.2 shows the frequency dependence of the in-phase (χ_M') and out-of-phase (χ_M'') components for $[\text{TbPc}_2]^0$, $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and $[\text{TbPc}_2\text{-D}]^0$. In the absence of an external dc field, all three compounds exhibit pronounced frequency-dependent χ_M'' peaks in the temperature range of 2–46 K, accompanied by a corresponding decrease in χ_M' , confirming slow relaxation of magnetization characteristic of intrinsic SMM behavior.

Specifically, at 2 K, the χ_M'' peak maxima are observed at approximately 360 Hz for $[\text{TbPc}_2]^0$, ~ 350 Hz for $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and ~ 340 Hz for $[\text{TbPc}_2\text{-D}]^0$. While these small shifts may suggest minor variations in relaxation dynamics, they remain within experimental uncertainty and are insufficient to conclusively demonstrate an isotope effect. Overall, the three isotopologues display highly comparable SMM behavior.

With increasing temperature, the χ_M'' peaks systematically shift to higher frequencies, reaching the upper limit of the measurement window (1488 Hz) at 46 K. This trend is consistent with thermally activated relaxation processes dominating in this temperature regime. However, it should be noted that the limited frequency window of the SQUID instrument constrains the accessible relaxation times, particularly at higher temperatures, and may obscure faster relaxation processes.

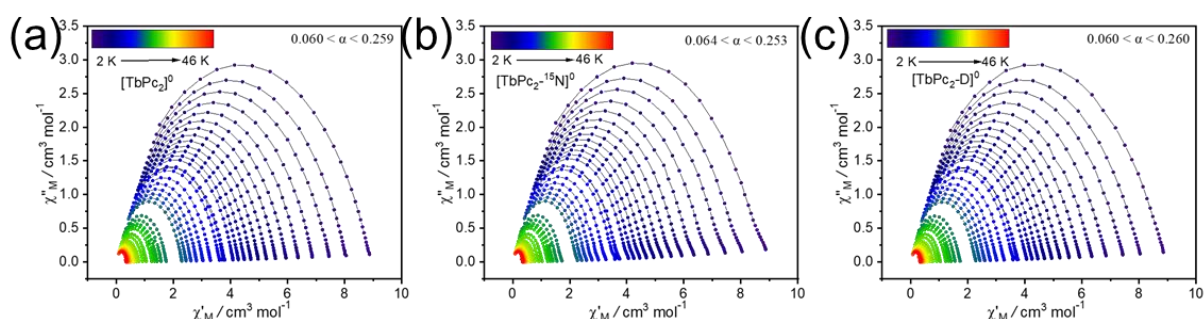


Figure 2.4.3 The Cole-Cole plots under zero field for $[\text{TbPc}_2]^0$ (a), $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ (b), and $[\text{TbPc}_2\text{-D}]^0$ (c). The solid lines are guided for eyes.

The AC data were further analyzed using the generalized Debye model to construct Cole–Cole plots (Figure 2.4.3). The resulting semicircular profiles yield α parameters in the ranges of 0.060-0.259 for $[\text{TbPc}_2]^0$, 0.064-0.253 for $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and 0.060-0.260 for $[\text{TbPc}_2\text{-D}]^0$, indicating a relatively narrow distribution of relaxation times across all three systems. While this supports the presence of a well-defined dominant relaxation process, it does not exclude the coexistence of multiple relaxation pathways with similar timescales.

To further elucidate the relaxation dynamics, the measurements were extended up to 51 K. Although the χ_M'' maxima shift beyond the accessible frequency window at higher temperatures, the data could still be reasonably fitted using the generalized Debye model, providing estimates of relaxation times. It should be noted, however, that these values become increasingly model-dependent in this regime, as the absence of well-defined peak maxima reduces the robustness of the fitting procedure.

The resulting relaxation times were used to construct $\ln(\tau)$ vs. T^{-1} plots (Figure 2.4.4). The non-linear behavior observed across the full temperature range clearly indicates the presence of multiple relaxation pathways. Notably, the relaxation rates remain temperature-dependent even at low temperatures, suggesting that quantum tunneling of magnetization (QTM) is not the dominant relaxation mechanism under the present conditions. Instead, the relaxation dynamics are more appropriately described by a combination of thermally activated processes. In the high-temperature regime, the data were fitted using an Arrhenius-type expression to approximate an Orbach contribution.

$$\ln(\tau) = \frac{U_{eff}}{k_B} \frac{1}{T} + \ln(\tau_0) \quad \text{Equation 2.4.1}$$

The fitting curves are presented as the green dot lines in Figure 2.4.4, where the energy barriers of $[\text{TbPc}_2]^0$, $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and $[\text{TbPc}_2\text{-D}]^0$ are 586(20) K, 558(26) K, and 594(22) K, respectively. For all three isotopologues, the U_{eff} values are comparable to previously reported, and the values of pre-exponential factor (τ_0) are in a reasonable range (10^{-6} - 10^{-12} s).¹⁵³ To fit the entire temperature range and minimize parameter over-parameterization, these Orbach-related parameters were fixed. Given that the absence of QTM plateau at low temperature, a combined Orbach and Raman mechanism was employed to describe the relaxation dynamics.

$$\tau^{-1} = \tau_0^{-1} \exp(-U_{eff}/k_B T) + CT^n \quad \text{Equation 2.4.2}$$

Where the first term donates for the Orbach process and the second term represents the Raman process. However, although the fitting combined with the Orbach process and the Raman process yields visually satisfying curves (represented by the purple solid line), the Raman term severely violates physical intuition. Specifically, the obtained coefficients (C , all larger than 2300) and the power-law exponents (n , all less than 0.07) are deviated significantly from the theoretically anticipated range for Raman relaxation, which implies the Raman terms function as a temperature-independent constant. This not only contradicts the physical essence of the Raman mechanism but also fails to reasonably explain the slow relaxation dynamics that still exist in the low temperature range, indicating the Raman model is insufficient to describe the

complex dynamics of these systems. Overall, the analysis supports a multi-mechanistic relaxation scenario dominated by thermally assisted and phonon-mediated processes, while the precise weighting of individual contributions remains uncertain due to experimental and fitting constraints.

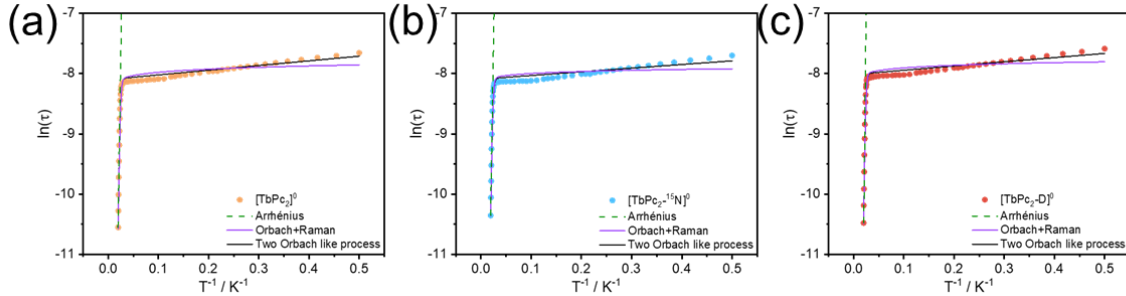


Figure 2.4.4 The $\ln(\tau)$ vs. T^{-1} plots under zero field for $[\text{TbPc}_2]^0$ (a), $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ (b), and $[\text{TbPc}_2\text{-D}]^0$ (c). The green dashed lines denote the Arrhenius fitting in the high temperature range, the purple lines represent the fitting by Orbach and Raman processes, and the black lines are the best fitting from two Orbach-like processes.

Following the theoretical framework proposed by Gu *et al.*, the Raman process is regarded as an Orbach-like mechanism characterized by a vibronic barrier model.¹⁶¹ In this approach, the relaxation rate is expressed as a summation of discrete vibrational contributions, and the Equation 2.4.2 can be rewritten as:

$$\tau^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/k_B T) + \sum_n \tau_n^{-1} e^{-U_n/k_B T} \quad \text{Equation 2.4.3}$$

Where τ_n and U_n represent the pre-exponential factors and energy level of the n -th vibrational modes, respectively. This fitting model was employed based on two consideration: (1) the quantum tunneling of magnetization is significantly suppressed in the relevant temperature range, forcing the spin system to tend towards thermally activated relaxation along low-energy vibrational or other pathways; and (2) molecules with highly rigid phthalocyanine ring structures exhibit significant discontinuity in their phonon spectrum, namely, the magnetic relaxation is confined to specific discrete vibrational modes rather than a continuous distribution.

Table 2.4.1 The effective energy barriers and the pre-exponential factors of $[\text{TbPc}_2]^0$, $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and $[\text{TbPc}_2\text{-D}]^0$.

	U_{eff}/k_B (K)	τ_0 (s)	C ($\text{s}^{-1} \text{K}^{-n}$)	n	U_n/k_B (K)	τ_n (s)
$[\text{TbPc}_2]^0$	586(20)	2.844×10^{-10}	2451	0.076	0.774(0.149)	3.036×10^{-4}
$[\text{TbPc}_2\text{-}^{15}\text{N}]^0$	558(26)	6.219×10^{-10}	2664	0.048	0.608(0.168)	3.054×10^{-4}
$[\text{TbPc}_2\text{-D}]^0$	594(22)	2.650×10^{-10}	2349	0.063	0.694(0.153)	3.307×10^{-4}

By employing a two-Orbach-like model, an improved fit of the relaxation data is obtained (see black lines in Figure 2.4.4). However, it should be emphasized that such fitting remains largely empirical, and the physical meaning of the extracted parameters must be treated with caution. In particular, the resulting vibronic barriers ($U_n \approx 0.6\text{--}0.8$ K) are orders of magnitude

lower than the typical intramolecular vibrational mode energies of TbPc_2 ($\sim 10^2$ K), which immediately raises questions regarding their assignment to genuine molecular vibrational excitations.

This significant discrepancy suggests that the fitted “Orbach-like” processes are unlikely to correspond to well-defined rigid-framework vibrations of the isotopologues. Instead, the extracted parameters more plausibly reflect effective low-energy relaxation channels, which may arise from a convolution of low-frequency lattice phonons, disorder-induced modes, or weak intermolecular dipolar interactions. Consequently, the model should be regarded as an effective description of the relaxation dynamics rather than a direct representation of discrete physical vibrational states.

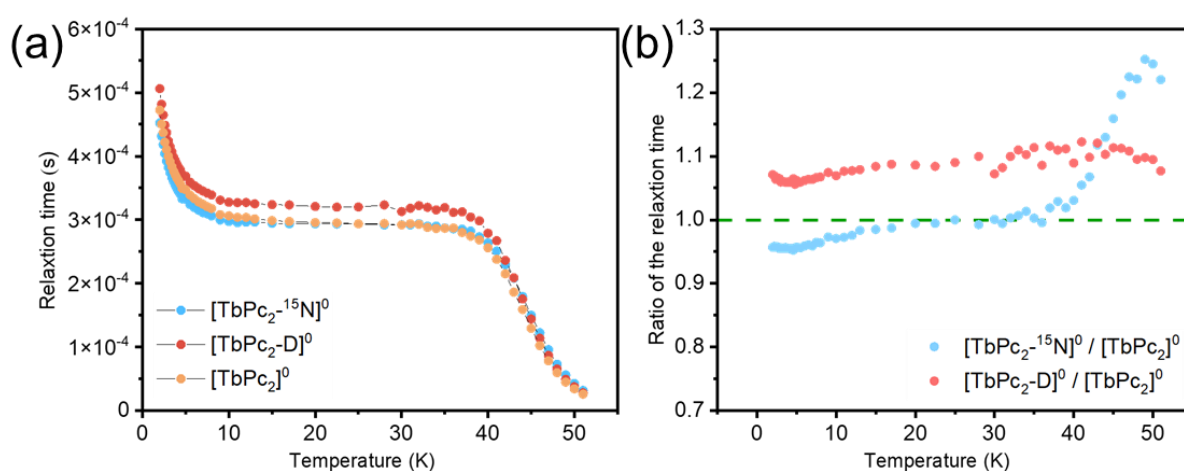


Figure 2.4.5 (a) The temperature dependence of relaxation time under zero dc magnetic field for $[\text{TbPc}_2]^0$ (yellow), $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ (blue), and $[\text{TbPc}_2\text{-D}]^0$ (red). The solid lines are guides for eyes. (b) The temperature dependence of the relaxation time ratios under zero dc magnetic field for $[\text{TbPc}_2\text{-}^{15}\text{N}]^0/[\text{TbPc}_2]^0$ (light blue) and $[\text{TbPc}_2\text{-D}]^0/[\text{TbPc}_2]^0$ (light red).

Despite the complexity of the relaxation mechanisms, which are not fully resolved and likely require further experimental and theoretical investigation, isotope-dependent differences in relaxation times are still discernible (Figure 2.4.5a). To better visualize these subtle variations, the ratios of relaxation times for $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and $[\text{TbPc}_2\text{-D}]^0$ relative to $[\text{TbPc}_2]^0$ are analyzed (Figure 2.4.5b).

Although the absolute deviations are relatively small, $[\text{TbPc}_2\text{-D}]^0$ consistently exhibits slower relaxation behavior than the sample without isotope substitution across the entire temperature range, with a ratio of $[\text{TbPc}_2\text{-D}]^0/[\text{TbPc}_2]^0$ varying between 1.05 and 1.12. Notably, this ratio shows no clear temperature dependence, suggesting a systematic but weak isotope effect. In contrast, the ratio of relaxation time for $[\text{TbPc}_2\text{-}^{15}\text{N}]^0/[\text{TbPc}_2]^0$ increases as the temperature increases, indicating a strong temperature dependency in the variation of their magnetic dynamics. Due to the presence of a delocalized radical, strong exchange coupling between the Tb^{3+} ion and the radical spin lifts degeneracy of the low-lying energy states, effectively suppressing quantum tunneling of magnetization at zero field. As a result, magnetic

relaxation is predominantly governed by thermally activated processes. Consequently, as mentioned before, the magnetic relaxation highly relies on the thermal activation process. However, the fitting energy barriers (0.774 K for $[\text{TbPc}_2]^0$, 0.608 K for $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$, and 0.694 K for $[\text{TbPc}_2\text{-D}]^0$) are remarkably lower than any internal rigid vibrational mode of the phthalocyanine (generally > 50 K), suggesting that the relaxations in the temperature regime of 2–51 K are not mediated by high-frequency vibrations. A reasonable explanation is that the presence of the delocalized radical introduces multiple magnetic relaxation channels for the Tb^{3+} ion, which is facilitated through exchange coupling between the Tb^{3+} ion and the radical.¹⁶²

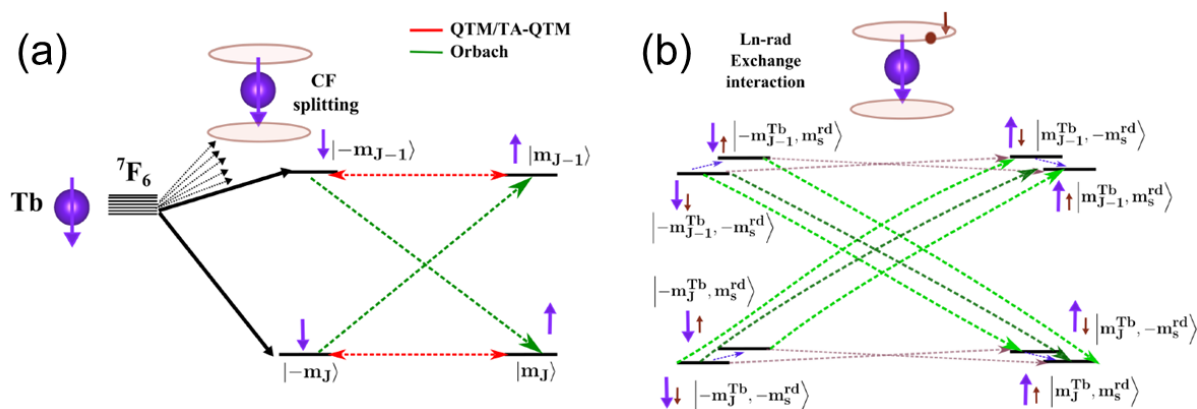


Figure 2.4.6 Schematic representation of magnetic reversal pathways in bis(phthalocyaninato) terbium system (a) without radical and (b) with radical.¹⁶²

The $[\text{TbPc}_2\text{-D}]^0/[\text{TbPc}_2]^0$ system is considered first, as the H/D substitution occurs at positions spatially distant from the Tb^{3+} center, rendering direct super-hyperfine coupling effects negligible. In this case, any isotopic influence is expected to arise predominantly from modifications of the vibrational (phonon) spectrum rather than from direct electronic interactions.

Although the delocalized radical provides low-energy electronic states that can facilitate relaxation pathways, spin transitions between these states still require coupling to lattice phonons to satisfy energy conservation. Therefore, the relaxation dynamics in this system are governed by spin–phonon interactions, and any isotope effect is most plausibly mediated through changes in vibrational frequencies and lattice dynamics induced by deuteration.

According to the ideal vibrational frequency function $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ (where k is the force constant and μ is the reduced mass defined as $\mu = \frac{m_1 m_2}{m_1 + m_2}$), as mass is increased ($m_D > m_H$), the heavier deuterium atom leads to an increased reduced mass ($\mu_D > \mu_H$). Consequently, the vibrational energies of the C–D bonds and the coordinated Tb–N bonds are shifted downward.^{105, 126} Generally, such a redshift in vibrational energy levels directly attenuates the strength of spin–phonon coupling, resulting in smaller dynamic displacement amplitudes in $[\text{TbPc}_2\text{-D}]^0$ system under thermal excitation. Thus, regardless of the low-energy barrier, deuteration systematically reduces the spin–phonon coupling, decreasing the probability of energy dissipation from the spin system to the lattice. The consistent isotopic divergence observed across the entire

temperature range suggests that magnetic relaxation remains limited by phonon-mediated dissipation, though owing to rigid structure, such a difference is relatively weaker than previous works.^{105, 106, 163}

In contrast, the $[\text{TbPc}_2\text{-}^{15}\text{N}]^0/[\text{TbPc}_2]^0$ system exhibits a more complex behavior, suggesting the presence of competing effects. At high temperature, although the coordination environment of $^{15}\text{N}/^{14}\text{N}$ atoms is more rigid than that of H/D atoms, the ratios of the relaxation time between $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ and $[\text{TbPc}_2]^0$ are larger than 1, which may be attributed to the slight effect of mass shift on the spin-phonon coupling. Despite the same trend as previous work about H/D, $^{106} \text{ }^{15}\text{N}$ with $I = 1/2$ exhibits faster relaxation at low temperatures compared to ^{14}N with $I = 1$, which cannot be explained by the influence of the isotope effect on the quantum tunneling windows. It should be mentioned that, although QTM is effectively suppressed due to the presence of the radical, different nuclear spins of nitrogen atoms still determine the fine structure and the energy level width of the low-lying energy states. Especially in this system, the nitrogen atoms directly coordinated to the Tb^{3+} ion introduce a strong contact effect, which explains why the value of the ratio at high temperature is larger than that of $[\text{TbPc}_2\text{-D}]^0/[\text{TbPc}_2]^0$, thereby influencing the exchange coupling between the Tb^{3+} ion and the delocalized radical within the phthalocyanine ring. Although the isotope effect theoretically contributes negligibly to the ground state energy level splitting of Tb^{3+} ions, which is the main contributor, it may, as an intermediary between radicals within the phthalocyanine and Tb^{3+} ion, cause a slight perturbation to the exchange interaction.

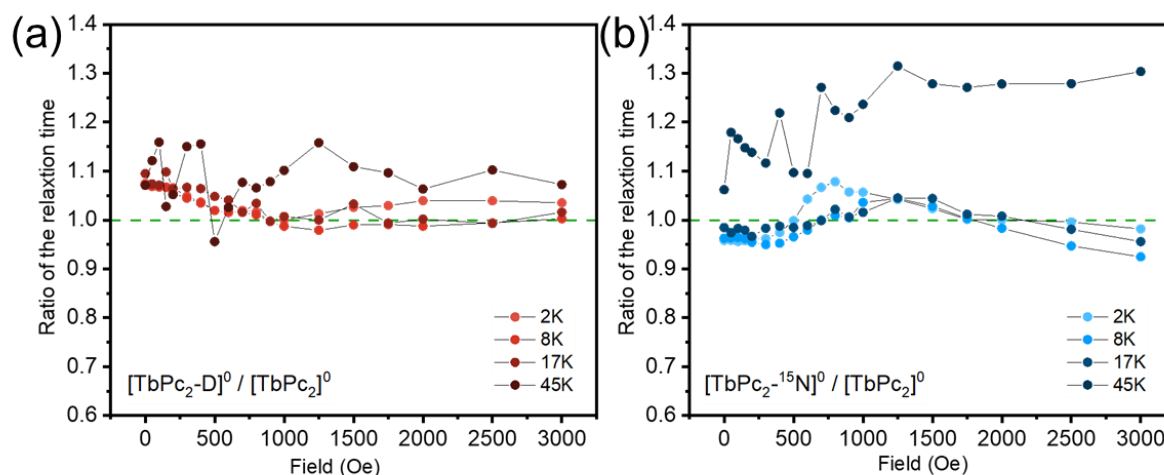


Figure 2.4.7 The field dependence of the relaxation time ratios in the range of 0-3000 Oe at different temperatures for (a) $[\text{TbPc}_2\text{-D}]^0/[\text{TbPc}_2]^0$ and (b) $[\text{TbPc}_2\text{-}^{15}\text{N}]^0/[\text{TbPc}_2]^0$.

To further investigate the isotope effect on the relaxation, field-dependent AC measurements were carried out. For D/H isotopologues, at temperatures of 2, 8, and 17 K, the ratio of relaxation time decreases with the increase of the external magnetic field, and then fluctuates around 1. This trend indicates that the Zeeman splitting effect dominates the electronic energy levels as the applied magnetic field increases. Consequently, the difference in relaxation disappears at the high field regime. In contrast, $[\text{TbPc}_2\text{-D}]^0$ exhibits slower relaxation behavior

than $[\text{TbPc}_2]^0$ at high temperature. Considering that this temperature range is mainly dominated by the Orbach process, the relaxation depends on the efficiency of spin transitions between the ground states and excited states. Compared with the energy barrier of > 580 K, the energy fluctuations induced by the external magnetic field are insufficient. While, as intrinsic properties, deuteration decreases the phonon density of states, attenuating the spin-phonon coupling, and featuring field-independent behavior.

Similarly, comparing the relaxation times of $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ and $[\text{TbPc}_2]^0$ at 45 K reveals a consistent phenomenon, yet its ratio outperforms that of the $[\text{TbPc}_2\text{-D}]^0/[\text{TbPc}_2]^0$ system. Combined with the fact that the pre-exponential factor of $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ obtained by fitting at high temperatures is more than twice that of $[\text{TbPc}_2]^0$, while no such pronounced difference exists between $[\text{TbPc}_2]^0$ and $[\text{TbPc}_2\text{-D}]^0$, this phenomenon indicates that it is the result of the synergistic effect of mass and contact effects, where the directly coordinated nitrogen atoms more effectively causes a redshift in the local phonon density of states.

However, in the low-temperature regime, the ratio curves exhibit non-monotonic evolution with the magnetic field, starting from below 1, first increasing and then decreasing. The transition points shift slightly with increasing temperature, located at 500 Oe and 1750 Oe for 2 K, 700 Oe and 1750 Oe for 8 K, and 700 Oe and 2000 Oe for 17 K, respectively. Considering the opposite gyromagnetic ratio values of ^{15}N and ^{14}N , a reasonable hypothesis is that, under zero field, ^{15}N (with a negative gyromagnetic ratio) vectorially and partially cancels out the local exchange field from the radical ligand, slightly perturbing the ground-state symmetry of the central Tb^{3+} ion, thus increasing the probability of transitions and exhibiting fast relaxation behavior. As the external field increases, the Zeeman effect gradually dominates the structure of electronic levels, while the influence of the gyromagnetic ratio is overwhelmed. Concurrently, the influence of nuclear spin is also revealed. Compared to ^{14}N ($I = 1$) with three nuclear spin levels (+1, 0, -1), ^{15}N ($I = 1/2$, with levels of -1/2 and 1/2) features a more concise super-hyperfine energy level distribution. Eight directly coordinated ^{15}N atoms produce total super-hyperfine states of 2^8 (256), which is only 4% of those for ^{14}N ($3^8 = 6561$). Although QTM is not directly observed, these dense super-hyperfine windows in the $[\text{TbPc}_2]^0$ significantly increase the probability of phonon-assisted tunneling. Consequently, once the gyromagnetic ratio effect is compensated by the Zeeman effect, the purer quantum state of ^{15}N ensures a longer relaxation time. As for the high-field region, the declining ratio suggests that isotope effects may also play a different role in the direct process.

Overall, although isotope effects in these systems remain subtle, they provide valuable insight into the interplay between spin–phonon coupling, hyperfine interactions, and exchange effects. The results highlight that H/D substitution primarily influences vibrational dynamics, whereas ^{15}N substitution introduces additional complexity through direct involvement in the coordination sphere and hyperfine coupling, leading to competing effects on magnetic relaxation.

2.4.2 μ -SQUID measurement

To further investigate the influence of super-hyperfine interactions arising from ligand nuclear spins, μ -SQUID measurements were performed at lower temperatures in collaboration with the group of Prof. Wolfgang Wernsdorfer. In the experiments, the crystals were placed near the μ -SQUID loops on a chip and cooled down to 30 mK in a dilution refrigerator. A 3d vector magnet was used to adjust the orientation of the external magnetic field to align with the easy axis of the molecules. The magnetization of the crystal was measured using the μ -SQUID with a standard measurement protocol that the magnetic field starts at 0 T, sweep sequentially to -1 T, 1 T, -1 T, and finally returned to 0 T.

[TbPc₂-D]⁰ was randomly selected as the first sample to evaluate the magnetic relaxation dynamics. To maximally suppress the thermal activated relaxation process and reflect the intrinsic quantum behavior of the molecule, the magnetic sweep-rate-dependent hysteresis loops at 30 mK were measured. All the hysteresis loops exhibit a characteristic S-shape and open butterfly-like hysteresis loops within a broad sweep rate window ranging from 1 mT/s to 128 mT/s (Figure 2.4.8a), indicating a typical single-molecule magnet behavior. As the magnetic sweep rate increases, the opening of hysteresis loops widens, suggesting that the magnetic sweep rate is faster than the timescale of the quantum tunneling. Consequently, the reversal of the magnetization via QTM process increasingly lags behind the variation of the external magnetic field.

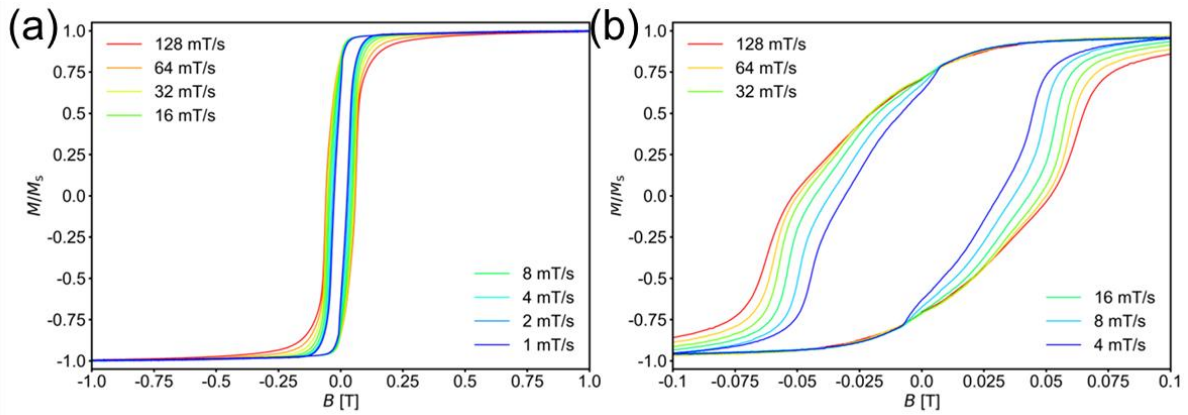


Figure 2.4.8 (a) The magnetic sweep-rate-dependent hysteresis loops for **[TbPc₂-D]⁰** at 30 mK, and (b) the zoom view of the opening of the hysteresis loops.

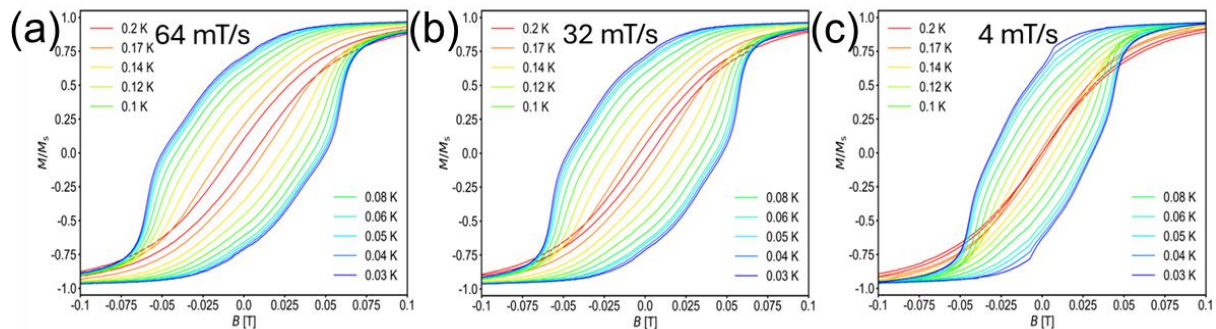


Figure 2.4.9 The temperature-dependent hysteresis loops for $[\text{TbPc}_2\text{-D}]^0$ with a fixed magnetic sweep rate of (a) 64 mT/s, (b) 32 mT/s, and (c) 4 mT/s.

To further clarify and differentiate the isotope effects of the QTM process and the thermal-activated relaxation process, the temperature dependence of the hysteresis behavior was subsequently investigated (Figure 2.4.9). Under different scan rates, a decrease in opening of hysteresis loop and much smoother curves were observed with increasing temperature from 0.03 K to 0.2 K, indicating that the contribution of the thermal-activated process to the magnetization reversal gradually increased. Especially, with a fixed rate of 4 mT/s, the hysteresis loop completely closes at a temperature of 0.2 K. Such evolution clearly reveals the transition of the system from quantum tunneling dominated relaxation to thermal activated process dominated relaxation.

It is noteworthy that while a closer examination of the magnetization details near zero field reveals step-like features which is originating from the quantum tunneling of magnetization, these steps are extremely inconspicuous, significantly different from the clear tunneling steps reported in previous work.¹⁸ This phenomenon is primarily attributed to the presence of unpaired radical in the ligand, which inevitably introduces strong interaction to the Tb^{3+} ion, thereby significantly broadening the steps corresponding to the nuclear spin. Such distinct broadening completely obscures the fine structure generated by the super-hyperfine coupling between the atoms of ligand and the Tb^{3+} ion, making it difficult to further quantitatively analyze the super-hyperfine interactions through these steps. Given the severe broadening signal induced by the radical observed in $[\text{TbPc}_2\text{-D}]^0$, we inferred that the isotopologues would face the same problem, and therefore the μ -SQUID measurements for $[\text{TbPc}_2\text{-}^{15}\text{N}]^0$ and $[\text{TbPc}_2]^0$ are not performed. In principle, isolating the contributions of radicals from those of ligand isotopes through theoretical calculations is an alternative method. However, due to the complicated interactions within the system (radical-radical interaction, terbium-terbium interaction, and radical-terbium interaction), a suitable model to describe these systems remains challenging. So far, a satisfied conclusion or explanation for how isotope of ligand affects the SMM behavior remains elusive, requiring further investigation.

2.5 Magnetic properties of diluted $[\text{TbPc}_2][\text{TEA}]^+$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$

To address the aforementioned broadening problem generated by radical, another promising alternative strategy is removing the delocalized radical within the phthalocyanine through chemical reduction method. Though this strategy cannot directly verify the hypothesis about how the ligand isotopes mediate the exchange interaction between the radical and Tb^{3+} ion, it provides a pure environment that may allow us to determine the isotope effect on the super-hyperfine interactions. To accentuate the subtle signatures of super-hyperfine coupling, a diamagnetic dilution method that introducing the diamagnetic matrix $[\text{YPc}_2][\text{TEA}]^+$ as described in Section 2.2 was employed, which significantly weakens the long-range dipole-dipole interaction, thus creating an optimal window for the analysis.

2.5.1 SQUID measurement

As detailed in the synthesis, to ensure a strictly homogeneous and molecular level dispersion, the diamagnetic dilution was performed synchronously with the reduction, followed by co-crystallization. However, due to the difference in the crystallization kinetics, the actual dilution ratio in the crystals for the magnetic measurements deviates slightly from the expected molecular stoichiometry. As shown in the EDX measurement (Figure S7), for expected 5% diluted $[\text{TbPc}_2][\text{TEA}]^+$ crystal, the proportion of Tb fluctuates within the range of 5.0% to 5.4% in different selected regions. This uncertainty in the exact molar fraction introduces a non-negligible systematic error into the dc magnetic susceptibility measurement, which highly relies on precise mass. Therefore, we skipped the dc measurements and focused on the ac magnetic susceptibility measurements.

Figure 2.5.1 details the frequency dependence of the in-phase and out-of-phase components of the ac magnetic susceptibility components of the $[\text{TbPc}_2][\text{TEA}]^+$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$. In these three isotopologues, clear, distinct, and strong frequency-dependent out-of-phase peaks are observable within a temperature range of 5.6 K to 32 K under zero dc magnetic field, indicating all these isotopologues possess excellent SMM properties. Specifically, due to the slow relaxation behavior, below 5.6 K, the SMM peaks shifted beyond the lower frequency limitation as the relaxation time are longer than the timescale of the ac measurement. While as the temperature increases, the out-of-phase peaks for isotopologues exhibit a consistent trend of shifting towards the high frequency region and reach the upper limitation at 32 K. This classic temperature-dependent characteristic strongly demonstrates that in this temperature range, the slow relaxation behaviors of the isotopologues are mainly dominated by the thermal activated processes.

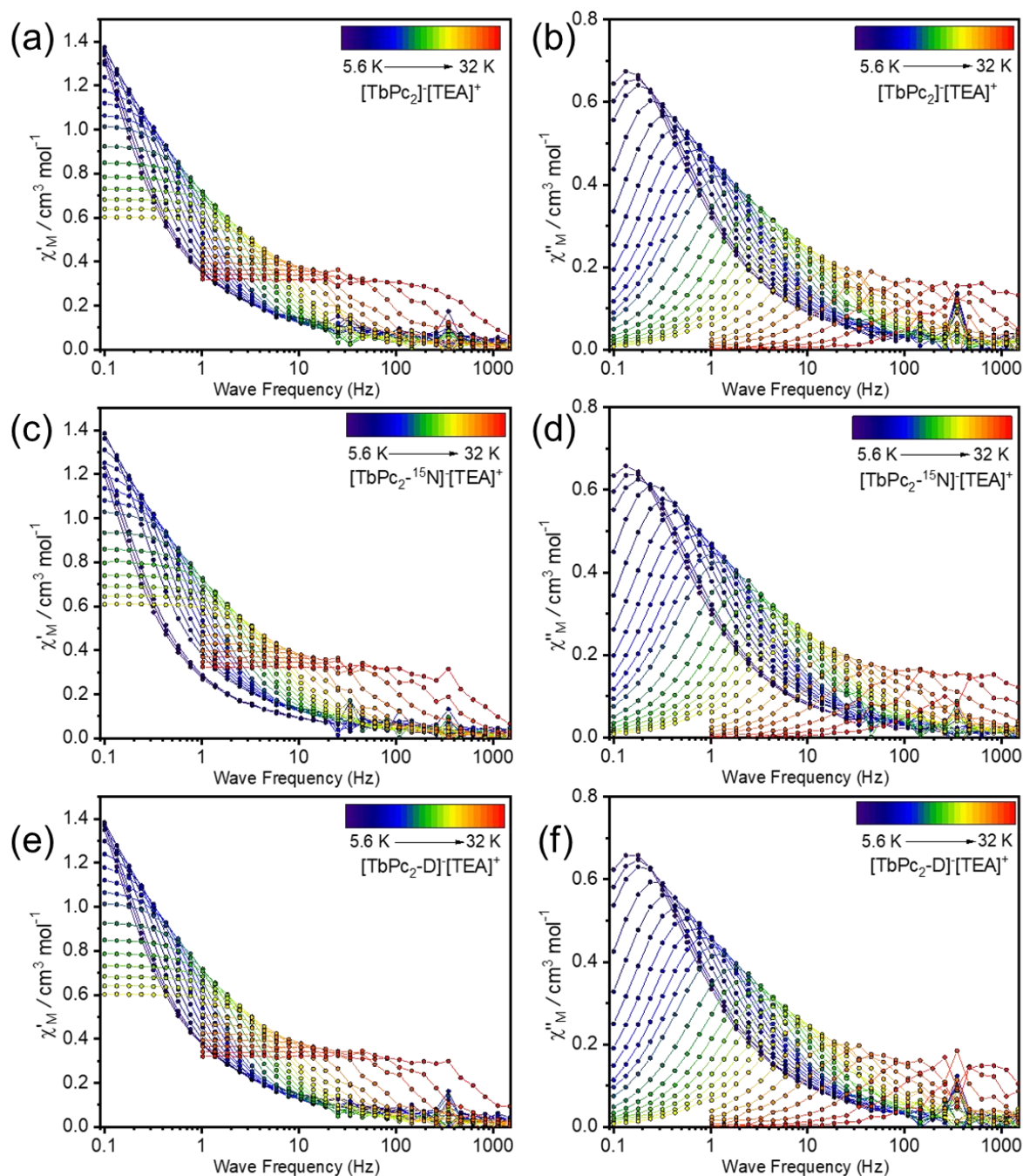


Figure 2.5.1 The experimental frequency dependent ac magnetic susceptibility data of the in-phase (left) and out-of-phase (right) for 5% diluted $[\text{TbPc}_2][\text{TEA}]^+$ (a, b), $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$ (c, d), and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$ (e, f) at a zero DC field from 5.6 K to 32 K. The solid lines are guided for eyes.

To further evaluate the slow relaxation behavior, the ac magnetic susceptibility data were fitted using the generalized Debye model. The corresponding Cole-Cole plots reveal a temperature dependence in the relaxation time distribution parameters. The values of α span from 0.04 to 0.45 for $[\text{TbPc}_2][\text{TEA}]^+$, 0.03 to 0.40 for $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and 0 to 0.43 for $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$. The value approached zero at high temperature indicates a single relaxation

channel. Conversely, as the temperature is decreased to 5.6 K, the value around 0.4 implies the presence of multiple relaxation mechanisms.

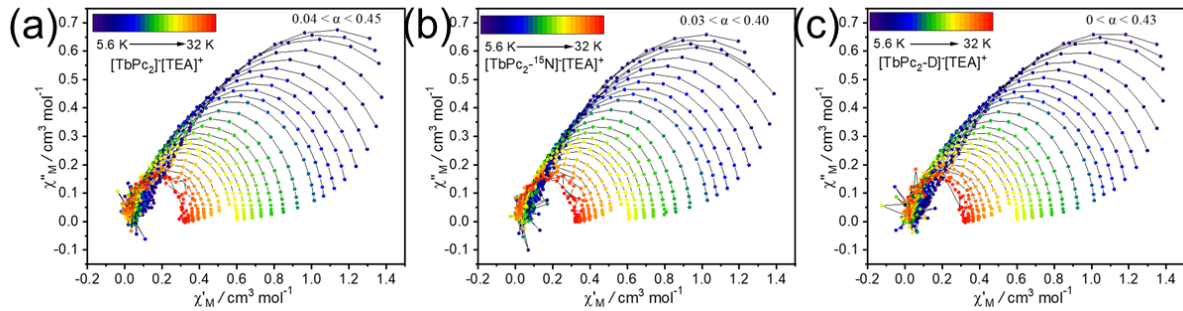


Figure 2.5.2 The Cole-Cole plots under zero field for 5% diluted $[\text{TbPc}_2][\text{TEA}]^+$ (a), $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$ (b), and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$ (c). The solid lines are guided for eyes.

Furthermore, the relationships between the relaxation time and temperature for each isotopologue are plotted to reveal the relaxation dynamics (Figure 2.5.3). It is noteworthy that the curves of relaxation time do not exhibit a typical temperature-independent plateau within the entire temperature range, indicating that QTM process is not yet dominate in this regime. Therefore, the slow relaxation behaviors of isotopologues are mainly governed by the Raman and the Orbach processes. To avoid over-parameterization, Arrhenius equation was employed to fit the data in high temperature regime:

$$\ln(\tau) = \frac{U_{\text{eff}}}{k_B} \frac{1}{T} + \ln(\tau_0) \quad \text{Equation 2.5.1}$$

The green dot lines present the fitting curves, which give an energy barriers of 361(26) K for $[\text{TbPc}_2][\text{TEA}]^+$, 359(24) K for $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and 345(25) K for $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$, respectively. While the pre-exponential factors are located at around $3.2(3.0) \times 10^{-9}$ s for $[\text{TbPc}_2][\text{TEA}]^+$, $3.2(2.8) \times 10^{-9}$ s for $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$, and $5.2(4.5) \times 10^{-9}$ s for $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$, respectively. Subsequently, these parameters are fixed and used for fitting across the entire temperature range with the Raman and Orbach processes:

$$\tau^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/k_B T) + CT^n \quad \text{Equation 2.5.2}$$

The fitted Raman parameters are found that $[\text{TbPc}_2][\text{TEA}]^+$ with $C = 2.5(0.6) \times 10^{-3} \text{ s}^{-1} \text{ K}^{-n}$ and $n = 3.48(0.10)$, $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$ with $C = 2.3(0.6) \times 10^{-3} \text{ s}^{-1} \text{ K}^{-n}$ and $n = 3.51(0.10)$, and $[\text{TbPc}_2\text{-D}][\text{TEA}]^+$ with $C = 2.7(0.6) \times 10^{-3} \text{ s}^{-1} \text{ K}^{-n}$ and $n = 3.46(0.10)$, respectively. Considering the fitting error and the system error during the measurement, these fitted parameters are statistically indistinguishable though close to the previous reported values.^{30, 153} It should be noted that, in these diluted crystal systems, the diamagnetic diluted molecules (YPc_2), the counter-ions (TEA), and the co-crystallized solvent molecule (acetone) are all standard samples with natural isotopic abundances. Consequently, these overwhelmingly dominant non-isotopic matrices determine the phonon density of states, corresponding to the consistency of the relaxation dynamics. Especially within this temperature range dominated by phonon-dependent

relaxation mechanisms, isotope-enriched TbPc₂, though as the only magnetic center, cannot significantly affect the spin-phonon bath of the system. Based on the results of ac measurement under zero field, the phonon effect in thermal activated process, which is generated by the mass difference, is completely masked in the diluted lattice, especially in the comparison of [TbPc₂]⁺[TEA]⁺ and [TbPc₂-D]⁺[TEA]⁺. However, these diluted molecules are all diamagnetic, and the magnetic properties are mainly originated from the TbPc₂. Therefore, the influence of isotope effects on hyperfine interactions may be preserved. Similar to the above discussion, H/D atoms, located relatively far from the magnetic center Tb³⁺ ion, theoretically influence the spin-lattice relaxation primarily by altering the phonon density of states in the crystal lattice, although it is covered by the dilution. Conversely, the N atoms, which are directly coordinated to the central Tb³⁺ ion, allow the nuclear spin of nitrogen to directly couple to the magnetic center via super-hyperfine interactions. Although this effect is relatively weak, the Tb-Tb dipole interaction is severely weakened under highly diluted conditions, thus providing a pure expression window. Therefore, in subsequent magnetic measurements, the focus will be on the comparison between [TbPc₂]⁺[TEA]⁺ and [TbPc₂-¹⁵N]⁺[TEA]⁺.

Table 2.5.1 The fitted parameters of diluted [TbPc₂]⁺[TEA]⁺, [TbPc₂-¹⁵N]⁺[TEA]⁺, and [TbPc₂-D]⁺[TEA]⁺.

	U_{eff}/k_B (K)	τ_0 (s)	C (s ⁻¹ K ⁻ⁿ)	n
[TbPc ₂] ⁺ [TEA] ⁺	361(26)	3.2(3.0)×10 ⁻⁹	2.5(0.6)×10 ⁻³	3.48(0.10)
[TbPc ₂ - ¹⁵ N] ⁺ [TEA] ⁺	359(24)	3.2(2.8)×10 ⁻⁹	2.3(0.6)×10 ⁻³	3.51(0.10)
[TbPc ₂ -D] ⁺ [TEA] ⁺	345(25)	5.2(4.5)×10 ⁻⁹	2.7(0.6)×10 ⁻³	3.46(0.10)

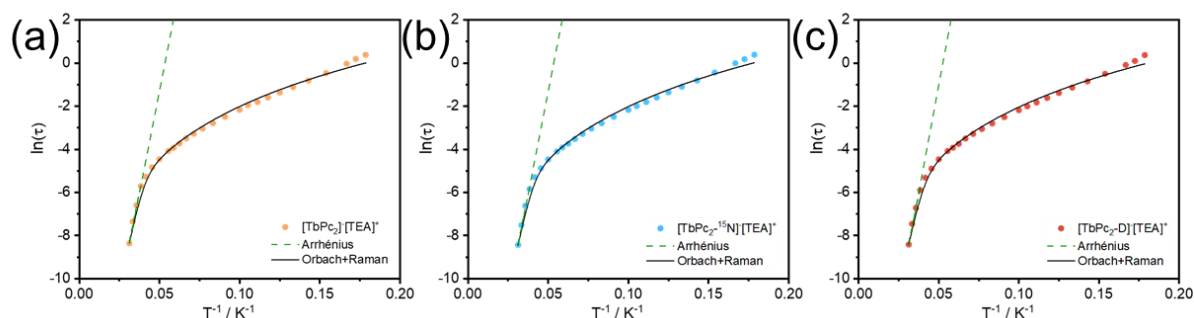


Figure 2.5.3 The $\ln(\tau)$ vs. T^{-1} plots under zero field for [TbPc₂]⁺[TEA]⁺ (a), [TbPc₂-¹⁵N]⁺[TEA]⁺ (b), and [TbPc₂-D]⁺[TEA]⁺ (c). The green dashed lines denote the Arrhenius fitting in the high temperature range, and the black lines are the best fitting obtained from the combination of Orbach and Raman processes.

In the following, the relaxation times of [TbPc₂]⁺[TEA]⁺ and [TbPc₂-¹⁵N]⁺[TEA]⁺ under different magnetic field at 8 K are compared. As illustrated in Figure 2.5.4, the relaxation times of both isotopologues exhibit complicated field-dependent behavior. Within the low-field regime, the relaxation time of [TbPc₂-¹⁵N]⁺[TEA]⁺ is always longer than that of [TbPc₂]⁺[TEA]⁺, though the difference is relatively small due to the relaxation is dominated by Raman and Orbach processes at this temperature. This is because the smaller nuclear spin of ¹⁵N ($I = 1/2$) compared to ¹⁴N ($I = 1$) reduces the window for quantum tunneling, thereby suppressing

the QTM and prolonging the relaxation time. The complicated changes with increasing magnetic field may be attributed to field-induced resonant quantum tunneling. For both complexes, the relaxation times reach the maximum at around 1400 Oe. Notably, as the magnetic field increases, the difference between $[\text{TbPc}_2][\text{TEA}]^+$ and $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$ gradually decreases. When the applied field is higher than 700 Oe, the ratio of relaxation times ($[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+ / [\text{TbPc}_2][\text{TEA}]^+$) begins to fluctuate at around 1. This phenomenon indicates that the external magnetic field breaks the degeneracy of the ground state levels via Zeeman splitting, thereby quenching the QTM. Consequently, the relaxation behavior is completely dominated by phonon-dependent processes. Moreover, under high diamagnetic diluted condition, the highly similar environments of the two isotopologues determine their highly consistent phonon density of states and dynamical behavior, corresponding to the indistinguishable relaxation times at high fields. As for the gyromagnetic ratio, its effect is extremely weak due to the lack of the radical. While the significant reduction in relaxation time in the high-field region is attributed to the dominance of the direct process, thereby leading to a significant acceleration of the relaxation. Although the field-dependent measurements at 8 K reveal the slight influence of ligand isotopes on quantum tunneling, the relaxation process is not dominated by QTM process. To better compare the difference of $^{14}\text{N}/^{15}\text{N}$ in super-hyperfine interaction, it is important to place the comparison within the QTM dominated temperature range while minimizing the thermal fluctuations.

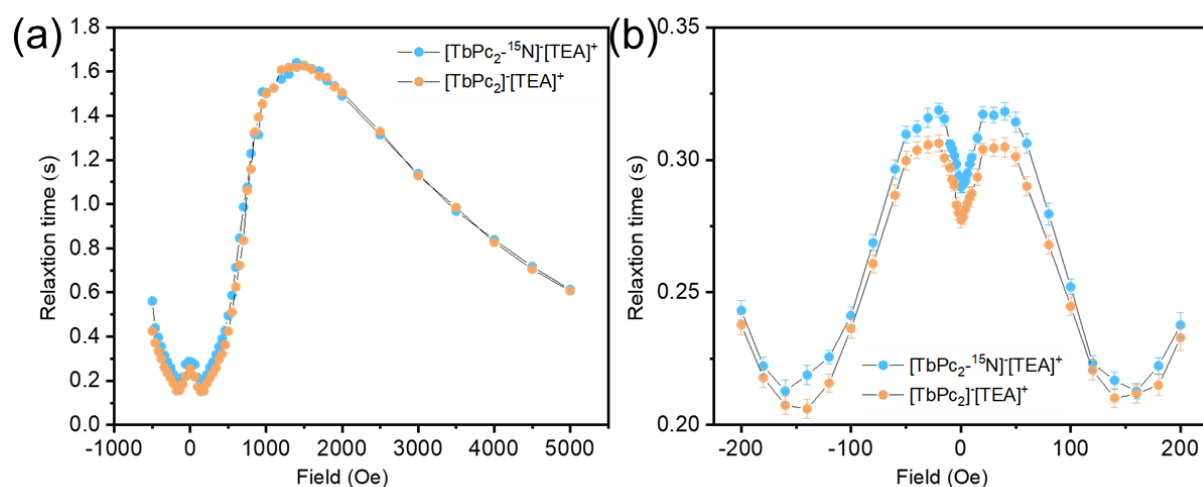


Figure 2.5.4 External magnetic field dependence of the relaxation time for $[\text{TbPc}_2][\text{TEA}]^+$ (orange) and $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$ (blue) at 8 K.

2.5.2 μ -SQUID measurements

To more intuitively address the intrinsic effects of ligand isotopes through hyperfine interactions in the pure quantum states, μ -SQUID measurements are employed, which provides an effective method to reveal the nuclear spin effect in sub-kelvin through QTM resonances.¹⁶⁴⁻¹⁶⁶ The crystals are placed in μ -SQUID arrays into a dilution refrigerator. The magnetic easy axes of molecules are determined by combining the transverse-field mapping with derivative angular plots (Figure 2.5.5). By using a 3d vector magnet, the applied magnetic field precisely

aligns with the easy magnetic axis of molecule and sweeps in a range between -1.4 T to 1.4 T. Subsequently, by systematically adjusting the temperature and magnetic field sweep rate, we conducted an in-depth investigation into the magnetic behavior of $[\text{TbPc}_2][\text{TEA}]^+$ and $[\text{TbPc}_2\text{-}^{15}\text{N}][\text{TEA}]^+$ (hereinafter referred to as **N14** and **N15**, respectively) at different diamagnetic dilution concentrations (1%, 2%, and 5%). Given that both systems exhibit consistent phenomena across different dilution conditions, and high dilution provides pristine window for observing the intrinsic isotope effect, thus the following discussion only focuses on the 1% diluted results. The experimental results for 2% and 5% dilution conditions are provided in the Appendix.

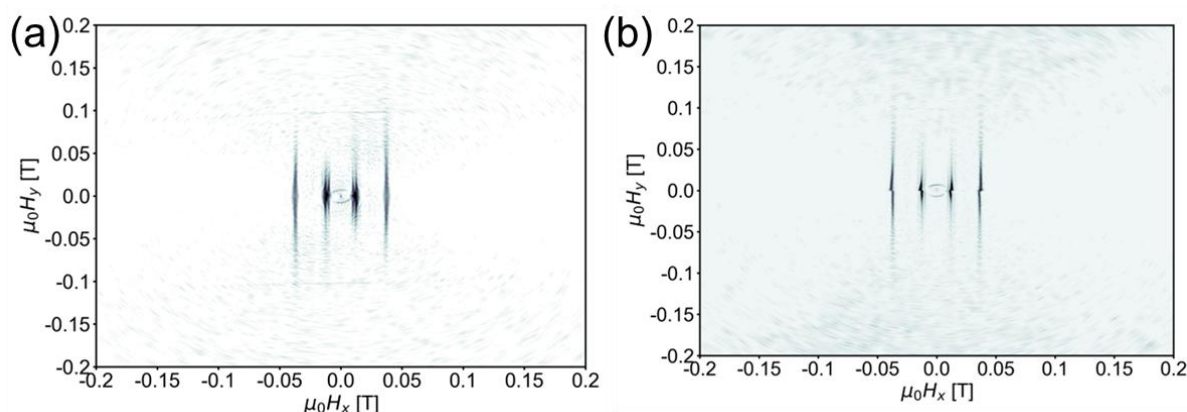


Figure 2.5.5 The field-angle maps for 1% diluted **N14** (a) and **N15** (b). The black dashed lines represent the easy axis of the crystal samples.

The temperature dependence for both isotope-enriched samples (**N14** and **N15**) are investigated. As shown in Figure 2.5.6, both results reveal that, in the range from 30 mK to 3.5 K with a fixed sweep rate of 16 mT/s, the thermal contribution of the magnetization reversal increases with increasing temperature, thereby broadening the sharp hysteresis loop and overall exhibiting a smoother curve. However, even at the highest temperature (3.5 K), the characteristic step structures corresponding to the quantum tunneling of magnetization events remain clearly visible, indicating both isotopologues possess a high magnetic blocking temperature.

Based on this, the magnetic field sweep rate dependence is further investigated. The experimental results at 30 mK show that the hysteresis loop profile significantly changes with increasing sweep rate (Figure 2.5.7). The core feature is that, as the magnetic field sweep rate decreases, the fraction of spins undergoing magnetization reversal via QTM exhibits a significant increase, indicating the sweep rates are faster than the timescale of the quantum tunneling. This phenomenon is highly consistent with the classical Landau-Zener tunneling mode, where the slower the sweep rate, the longer the spins remain at the resonant energy level crossing, thus increasing the tunneling probability. Overall, ligand isotope substitution does not directly change the transition of different nuclear spin states. Both 1% diluted **N14** and **N15** samples exhibit highly consistent positions of resonance magnetic field for different nuclear spin states transitions, indicating hyperfine interactions are stronger than super-hyperfine interactions. Regarding the phenomenon of drastic changes in the tunneling profile at the fastest

sweep rate which settles down to a common pattern in the later measurements, this non-equilibrium state is attributed to the thermal effects induced by rapid sweeping.

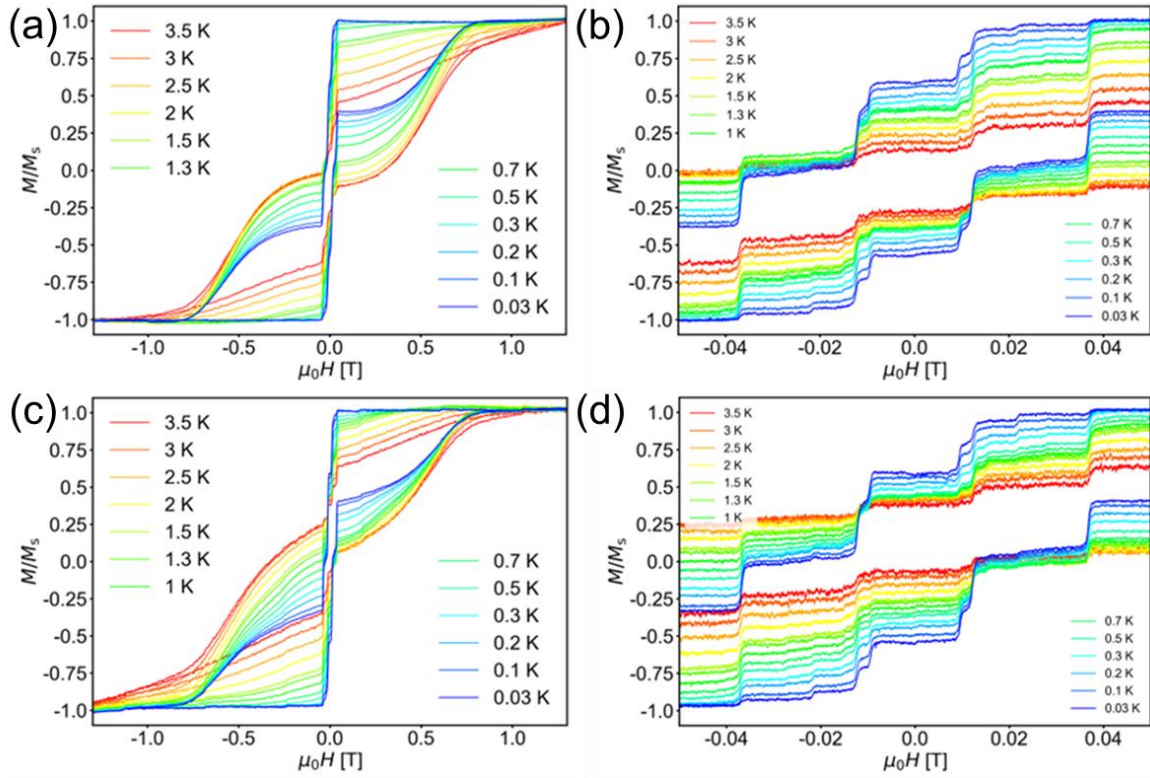


Figure 2.5.6 The temperature-dependent hysteresis loops with 16 mT/s sweep rate and their zoom view for 1% diluted N14 (a, b) and N15 (c, d).

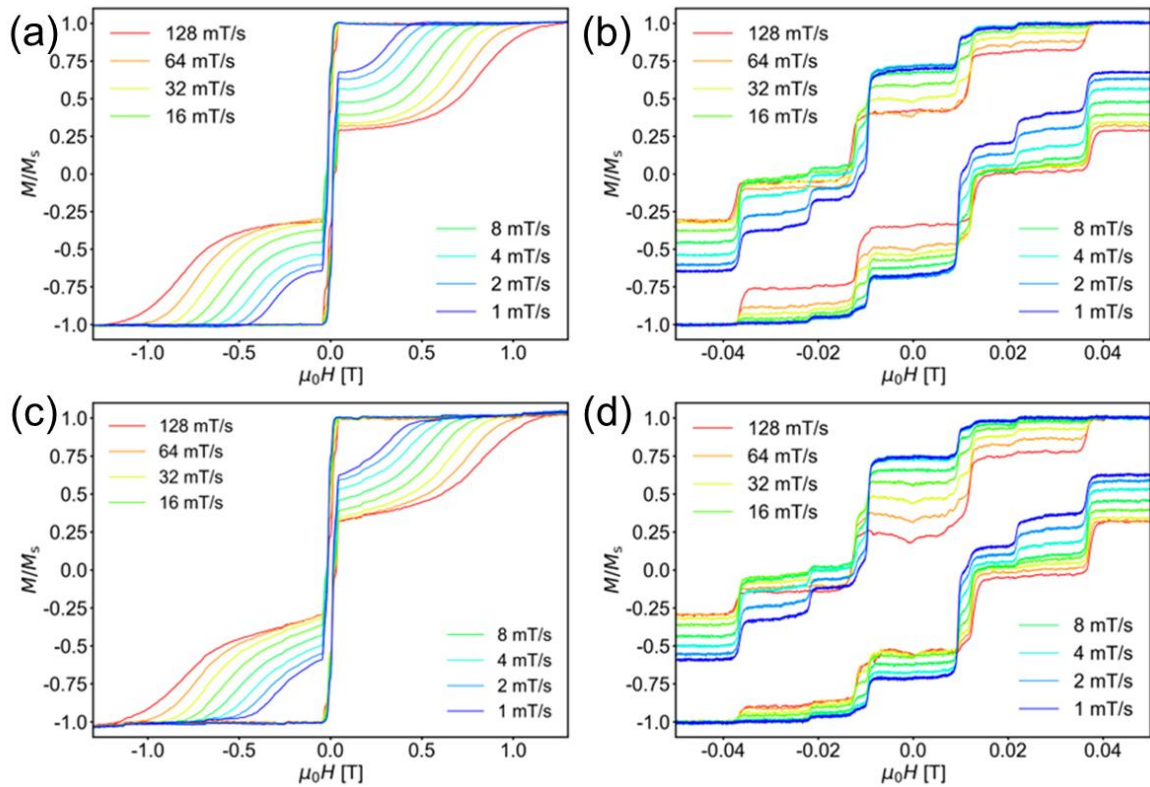


Figure 2.5.7 The magnetic field sweep-rate-dependent hysteresis loops at 30 mK and their zoom view for 1% diluted N14 (a, b) and N15 (c, d).

Although the contribution of super-hyperfine interactions generated by the ligand nitrogen atoms is exceedingly small, the additional energy level crossings for QTM introduced by the super-hyperfine interactions modulate the probabilities of quantum tunneling.¹⁰⁶ Such modulation may in turn dictates the transition between different nuclear spin states, thus affecting the relaxation dynamics.

To further investigate this phenomenon, we implemented an experimental protocol, consisting of a state-preparation followed by a state-readout. The crystal samples were first placed at 30 mK under -1.4 T for different waiting time to achieve specific equilibrium nuclear spin states distributions. Subsequently, the magnetic field was increased to 1.4 T. To address the population of each nuclear spin states, a moderate sweep rate of 64 mT/s was employed to avoid the heating events.¹⁶⁴

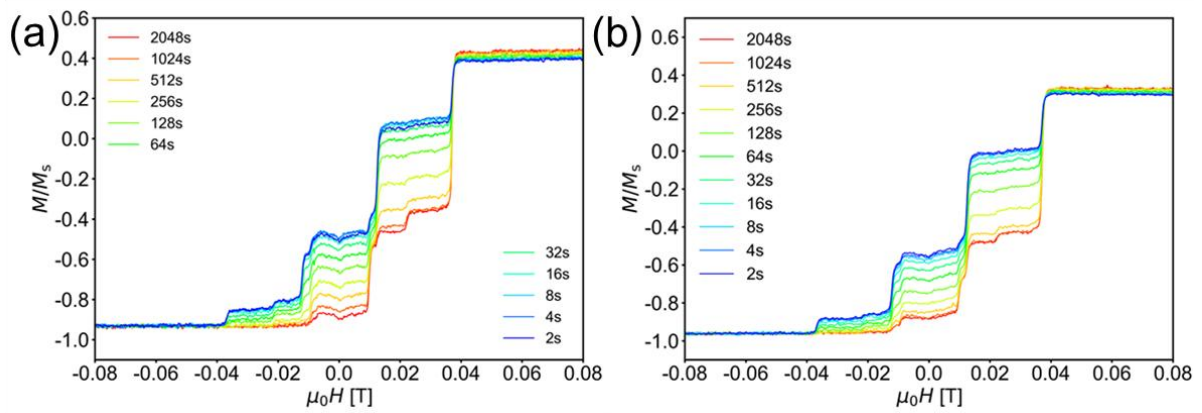


Figure 2.5.8 The hysteresis loops at 30 mK with a fixed 64 mT/s sweep rate after different waiting time for 1% diluted **N14** (a) and **N15** (b).

The waiting time dependent magnetic hysteresis loops for 1% diluted **N14** and **N15** were recorded from 2 s to 2048 s, as illustrated in Figure 2.5.8. A comparative analysis of μ -SQUID data reveals two significant features: First, regardless of the initial state, the positions of resonant magnetic fields for the nuclear spin transitions in both samples remain highly consistent, demonstrating the isotopic substitution is insufficient to significantly change the energy level structure. Second, as the waiting time changes, the heights of the steps corresponding to the transitions between different nuclear spin significantly change, indicating different nuclear spin states distributions in the initial states after different waiting time. More importantly, the discernible discrepancy in the heights of steps between the **N14** and **N15** samples provides unequivocal evidence that the ligand isotope plays a role in the population of the nuclear states.

Zeeman energy diagram provides a platform to quantitatively translate the magnetization data to the population of nuclear spin states by calculating the height of the steps in the hysteresis loops at the positions of energy level crossing corresponding to the specific transitions between nuclear spin states.¹⁶⁴ To achieve this, we isolate one of the four nuclear spin states branching from the $m_J = -6$ electronic ground state within the Zeeman diagram. By tracing this line, four distinct resonance points where it crosses with other energy levels are indentified, and their

magnetic field coordinates are precisely aligned with the experimentally obtained hysteresis loops to determine if quantum tunneling happens. The extracted heights of quantum tunneling steps at each specific magnetic field are divided with the total height to get the total proportion of spins tunnelled from that state. Subsequently, a fraction of the total tunnelling population after different waiting time plot is obtained as Figure 2.5.9, where P1, P2, P3, and P4 represent the nuclear spin state of $-3/2$, $-1/2$, $1/2$, and $3/2$, respectively.

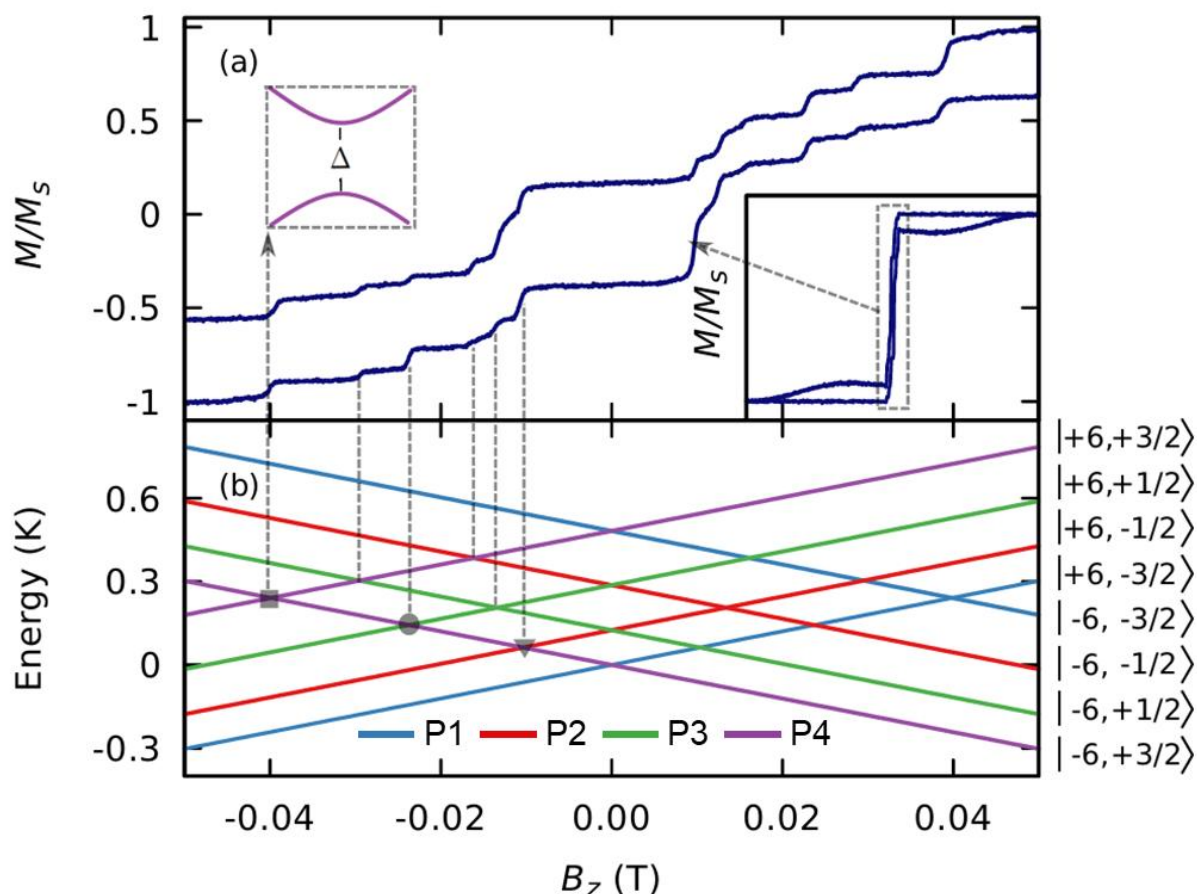


Figure 2.5.9 The hysteresis loops (upper) and the Zeeman diagram (lower) for 1% diluted $[\text{TbPc}_2][\text{TBA}]^+$ sample.¹⁶⁴

According to Figure 2.5.10, after long waiting time at -1.4 T for relaxation, the populations of each nuclear spin states have almost reached equilibrium. Both samples exhibit a similar trend that as the waiting time increases, the tunneling population of P1 gradually rises, while the populations of P2, P3, and P4 decrease, and eventually these variations in all four states become stable. As for the unusual data points of 1 s waiting time, they are attributed to extremely non-equilibrium caused by thermal effect. The distributions after waiting 4096 s reveals that the **N15** exhibits a higher population in ground state while less population in the excited state compared with the **N14**, suggesting a more relaxed final state. As detailed in Table 2.5.2, **N15** shows a drastic increase in its population of ground state to 59.6%, while **N14** only accounts for 50.3%. The vast majority of this increase is accounted for the reduction in the tunneling population of the excited states (6.4%). This distinct distribution characteristic indicates a clear lowering of the effective spin temperature of the nuclear spins in **N15** compared to **N14**, where

N15 undergoes a more profound relaxation under same conditions. However, even considering the redistribution, there is a significant fraction (2.5%) still remains unaccounted for. Consequently, this discrepancy elevates the total fraction of spins undergoing QTM to 65.8% for **N15**, which is higher than the 63.3% observed for **N14** and consistent across three diluted conditions.

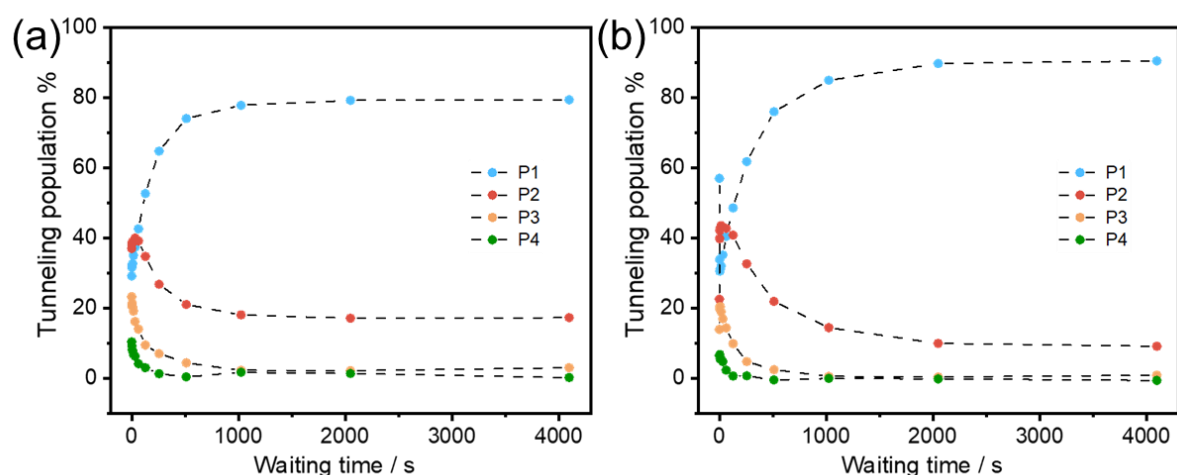


Figure 2.5.10 The tunneling population after different waiting time (1 s to 4096 s) of each nuclear spin states for **N14** (a) and **N15** (b).

Table 2.5.2 The population of different nuclear spin states after waiting 4096 s for **N14** and **N15**, and their difference.

	P1	P2	P3	P4	Total
N14	50.3%	10.9%	1.9%	0.2%	63.3%
N15	59.6%	6%	0.6%	0%	65.8%
N15-N14	+9.3%	-4.9%	-1.3%	-0.2%	+2.5%

From thermodynamic view, one possibility is that the lower spin temperature of the sample may be making the tunneling more efficient. Assuming the system reaches thermodynamic equilibrium after long waiting time, the populations of the higher and lower energy levels must follow the Boltzmann distribution:

$$\frac{P_{n+1}}{P_n} = \exp\left(-\frac{\Delta E}{k_B T_{spin}}\right) = C \quad \text{Equation 2.5.3}$$

Where $\Delta E/k_B$ is the energy differences between the nuclear spin states, C is a constant representing the decay rate. Generally, within an individual sample, as the waiting time increases and the population cools down, an increase in the fraction of spins that undergo tunneling is observed. By employing the Equation 2.5.3, the spin temperature of **N15** is determined as ~ 52.3 mK, while **N14** gives different values of spin temperature that using P2/P1 for 78.5 mK and using P3/P2 for 68.6 mK, respectively.⁴¹ However, considering the thermal contribution, from the extremely non-equilibrium population (extremely heated, corresponding

to 1s waiting time) to the almost equilibrium population (cold enough, corresponding to 4096 s waiting time), the total tunneling fractions for **N14** and **N15** only increase by 2.4% (from 60.9% to 63.3%) and 1.1% (from 64.7% to 65.8%), respectively. Since such drastic thermodynamic relaxation only brings a limited increase in tunneling, especially with the 1 s waiting time even giving us negative temperatures, the difference in the tunneling cannot be explained by their difference in spin temperature, which is merely ~ 20 mK scale. Moreover, after waiting 4096 s, the **N15** exhibits consistency in the decay rate, where $P2/P1 \approx P3/P2 = 0.100$, suggesting a fully relaxation to thermodynamic equilibrium state. While for **N14**, a pronounced divergence ($P2/P1 = 0.217$ vs $P3/P2 = 0.174$) remains, indicating that although the system appears to have reached equilibrium (the tunneling population percentage curve reached plateau), it still lags behind the thermodynamic equilibrium state. Thus, a purely thermodynamic explanation is invalid in this system.

Within the framework of quantum dynamics, the tunneling fraction is governed by three factors: the magnetic field sweep rate, the temperature, and the effective tunneling splitting. With the magnetic field sweep rate being fixed, and the temperature being insufficient to explain the large change in tunneling fraction, we further investigate the effective tunnel splitting by analyzing the fraction of tunneling between different nuclear spin states. By analyzing the specific resonant magnetic field where nuclear spin transition happens and the height of corresponding QTM step, the fractions of different transitions are determined. However, some of the signals associated with specific transitions are too weak to be quantified, here we only focus on the major contributing terms.

Table 2.5.3 The fraction of tunneling transitions from P1 to other states after waiting 4096 s for **N14** and **N15**.

	$\Delta m = 0$	$\Delta m = 1$	$\Delta m = 2$	Total
N14	37.4%	3%	9.9%	50.3%
N15	38.5%	5.4%	15.7%	59.6%
N15-N14	+1.1% (2.9%)	+2.4% (80%)	+5.8% (58.6%)	+9.3% (18.5%)

Table 2.5.3 depicts the fractions of tunneling transitions from P1 to other states after 4096 s. Both isotopologues exhibit a highly consistent phenomena in the transitions: the $\Delta m = 0$ transition is dominate, followed by the $\Delta m = 2$ transition, while the $\Delta m = 1$ transition is the lowest. Interestingly, the total tunneling fraction of **N15** dramatically increases by 9.3% compared to **N14** (absolute population increment). More importantly, this increment is not homogeneously distributed and the main contribution stems from the transition with relatively low fraction (where $\Delta m = 2$ contributes 62.4% of the total increment), which is more pronounced in the percentage increase in each of the transitions. Contrary to the expectations of temperature-driven thermodynamic models, the experimentally observed relative increases in tunneling transitions showed a high degree of inconsistency with the total increasement of 18.5%: the $\Delta m = 0$ transition only slightly increased by 2.9%, while the increases in the $\Delta m = 1$ and $\Delta m = 2$ transitions soared by 80% and 58.6%, respectively. One point to note here is the order in which the main transitions take place: The first main transition is the $\Delta m = 2$ transition

of P1, followed by the $\Delta m = 0$ transition of P2, the $\Delta m = 1$ transition of P1, and finally the $\Delta m = 0$ transition of P1. These four events together account for almost all the tunneling (92.75% for **N14**, 96.07% for **N15**). Considering that the overall transition distribution does not exhibit a gradually decreasing or increasing trend, and the intermediate ($\Delta m = 1$ in P1) exhibits the highest relative change, this further illustrates that the heat generated by the previous tunneling events is insufficient to alter the equilibrium population of the energy levels. Notably, all these transitions happen in less than half a second, which is extremely short compared to the relaxation timescale of the nuclear spins. Therefore, the change in the effective tunneling splitting caused by ligand isotopes should be the main reason for the above differences.

Table 2.5.4 The fraction of tunneling transitions from P2 to other states after waiting 4096 s for **N14** and **N15**.

	$\Delta m = 0$	$\Delta m = 2$	Total
N14	9.03%	1.92%	10.95%
N15	3.95%	2.08%	6.03%
N15-N14	-5.08% (56.3%)	+0.16% (8.3%)	-4.92% (44.9%)

To investigate the ligand isotope effects, the effective Hamiltonian for the splitting of an electronic doublet in the electronic localized basis¹⁰⁶ can be approximately modelled as:

$$\mathcal{H}_0 \approx \begin{pmatrix} 0 & \Delta/2 \\ \Delta/2 & 0 \end{pmatrix} + A_{hf} \tilde{S}_z I_z + \sum_{i=1}^8 A_{shf} \tilde{S}_z I_{z,i} + g_z \mu_B \tilde{S}_z H_z \quad \text{Equation 2.5.4}$$

where Δ is the tunnelling splitting gap of the investigating electronic doublet, $\tilde{S}_z$ is the pseudospin 1/2 corresponding to the electronic doublet, A_{hf} and A_{shf} are respectively the hyperfine and super-hyperfine coupling constants, I_z is the nuclear spin operator of Tb^{3+} ion along the easy axis of the electronic doublet, $I_{z,i}$ is the nuclear spin operator of $^{14}\text{N}/^{15}\text{N}$ nuclear spin with $I = 1/2$ (^{15}N) or 1 (^{14}N) along the easy axis, and the last term is responsible for the Zeeman interaction.

As illustrated in the Equation 2.5.4, the difference in the relaxation of both isotopologues depends on the tunneling splitting and the splitting of the electronic doublet under super-hyperfine interactions, especially the bandwidth broadening induced by the super-hyperfine interactions, which can be found by estimating the magnitude order of each interaction without complex diagonalization. Assuming the N-Tb contact bonding are the same, the maximum broadening contribution of nitrogen atoms for **N15** is $4A_{shf}$ while for **N14** is $8A_{shf}$. In other words, the bandwidth broadening originated from super-hyperfine interactions in **N14** is twice that of **N15**. Furthermore, the difference in the nuclear spin quantum number results in a much denser density of states for **N14** (3^8 , 6561 states), while for **N15** only 2^8 (256) states.

Combining with experimental results, due to the different nuclear spin of ^{14}N ($I = 1$) and ^{15}N ($I = 1/2$), the super-hyperfine interaction in **N15** is relatively weaker than that of **N14**, resulting in a much narrow and sparse window for quantum tunneling. Therefore, in its dynamic features, the quantum tunneling events are limited in finite resonance conditions, facilitating the efficient

unidirectional relaxation in the system and thus rapidly reaching the thermodynamic equilibrium state dominated by the Boltzmann distribution. Conversely, the nuclear spin of ^{14}N ($I = 1$) gives more sublevels (-1, 0, 1), significantly increasing the channel for tunneling. Together with the broadening, this characteristic facilitates quantum tunneling in **N14**, making the system much faster to reach equilibrium (as shown in Figure 2.5.10), but it also increases the probabilities of bidirectional transitions between different nuclear spin states. Compared to **N15**, these frequent bidirectional tunneling events within the widened tunneling splitting hinder the relaxation toward the ground state and continuously “heat” the system through the energy absorption or release, resulting in a higher spin temperature. Consequently, **N14** is trapped in a non-thermodynamic equilibrium state, which manifests as an ineffective accumulation for the population of low energy level (P1), while the population redistributed itself to higher energy levels. More importantly, the inherent non-zero nuclear electric quadrupole moment of ^{14}N introduces additional quadrupole interactions, leading to a more complex tunneling splitting distribution. This complex coupling, in turn, results in the irregular variations in the fractions of transitions between different states when comparing **N14** and **N15**.

It should be noted that, during the preparation, absolute control of the precise dilution ratio and the quality of crystal is challenging. Nevertheless, highly consistent phenomena are observed in multiple repeated experiments with different dilution ratios, confirming the intrinsic nature of the ligand isotope effect. Therefore, the discussion here is primarily upon qualitative analysis rather than rigorous quantitative fitting.

2.6 Conclusion

In conclusion, isotope-enriched terbium bis(phthalocyaninato) complexes have been successfully synthesized, and their magnetic properties systematically investigated to elucidate the role of ligand isotope substitution on relaxation dynamics.

In the first part, focusing on the neutral radical-containing systems, it was found that isotope-dependent mass increase induces a redshift of low-frequency vibrational modes, effectively weakening spin-phonon coupling, thereby favoring the slow relaxation. In contrast, the comparison between ^{14}N and ^{15}N substitution reveals a more complicated scenario, where competing effects arising from differences in gyromagnetic ratio, super-hyperfine interactions, and spin-phonon coupling collectively govern the relaxation behavior. However, the presence of the delocalized radical introduces additional relaxation pathways via exchange coupling, which complicates the direct analysis of super-hyperfine interactions, particularly in μ -SQUID measurements and theoretical modeling.

In the second part, the removal of the radical and the use of magnetically diluted samples allowed us to elucidate the role of isotopes on modulating the quantum tunneling through μ -SQUID measurements. Experimental results demonstrate that ^{15}N ($I = 1/2$) leads to a narrower tunneling splitting and a more well-defined energy landscape, facilitating efficient unidirectional relaxation toward thermodynamic equilibrium. In contrast, ^{14}N ($I = 1$) with its additional nuclear spin states and quadrupole moment, generates a denser and more heterogeneous super-hyperfine manifold, which promotes the trapping in a non-thermodynamic equilibrium state.

Overall, this work provides experimental insight into the interplay between electronic spin and ligand nuclear spins, highlighting the critical role of super-hyperfine interactions in determining magnetic relaxation pathways. These findings demonstrate that isotope substitution can serve as a powerful and controlled strategy to tune spin dynamics in single-molecule magnets. Looking forward, this approach can be extended to other molecular systems, where ligand nuclear spins, solvent environments, or matrix effects influence central spin dynamics. By exploiting isotopic substitution as a tool to modulate spin-phonon coupling and hyperfine interactions, future studies may advance the understanding of decoherence mechanisms and support the rational design of molecular qubits and quantum materials with tailored spin environments.

Chapter 3. Isotopologue Complexes: Magnetic Properties of [2x2] Grid Dysprosium Complexes

3.1 Introduction

Against the backdrop of the exponential growth of artificial intelligence and big data technologies, the post-Moore's Law era faces a severe challenge, where traditional semiconductor fabrication scaling is not enough to support the leap in computing power by simply shrinking chip size.^{137, 167, 168} Compared to traditional materials, SMMs offer unique advantages owing to their molecular-scale magnetic hysteresis behavior, enabling a single molecule to exhibit a magnetic memory effect analogous to that of a bulk magnet.¹⁶⁹⁻¹⁷¹ The slow relaxation of magnetization of SMMs arises from magnetic moment reversal with anisotropic effective energy barrier under low temperature, while exhibiting superparamagnetic blocking below the blocking temperature.^{90, 172, 173} The magnitude and symmetry of this barrier are governed by the coordination environment and electronic structure, offering a direct route to tuning magnetic bistability and relaxation pathways.^{138, 174} Despite milestone achievements such as the implementation of Grover's quantum logic operations, highlighting its potential,³⁸ current qubits manipulation based on nuclear spin in lanthanide complexes is mostly confined to mononuclear systems, thereby posing challenges in meeting the requirements of quantum supremacy and high-density integration.^{14, 136, 137}

A fundamental limitation of conventional SMMs, where magnetic moments align along the easy axis, is their susceptibility to quantum tunneling of magnetization (QTM) under external fields or high-density aggregation, which may lead to the loss of stored magnetic information due to decoherence.^{24, 111, 139, 175} Furthermore, when dealing with multinuclear systems, constructing a collinear alignment of magnetic anisotropies of different magnetic centers presents significant challenges in chemical synthesis.^{15, 138, 176} In contrast, single-molecule toroids (SMTs), which originated from more intricate topologies, provide a novel solution. In SMTs system, each metal ion possesses a large axial magnetic anisotropy, and the magnetic moments of each metal ion are toroidally distributed on the plane, resulting in a non-collinear multipolar magnetic ground state.¹⁷⁷⁻¹⁸⁰ Consequently, through such a vortex-like arrangement, the ground state exhibits zero net dipole moment while retaining a nonzero toroidal vector. Due to the near-zero overall magnetic moment and faster magnetic field decay generated by the net toroidal moment compared with the decay of the dipolar induced magnetic field, these toroidal states facilitate the manipulation by electric fields, rendering them as promising candidates for ultra-high-density quantum information storage, molecular spintronics, and topologically protected qubit architectures.^{179, 181}

Constructing stable SMTs presents a significant challenge in molecular design,¹⁸² requiring a full consideration of well-arranged magnetic anisotropic axes, high molecular symmetry, and strong intra-dipolar and exchange interactions. Lanthanides, especially dysprosium, are widely employed to investigate SMTs properties due to the strong uniaxial magnetic anisotropy, typically Dy₃ triangles,^{50, 183} Dy₄ coplanar,¹⁸⁴⁻¹⁸⁶ Dy₄ cubane,¹⁸⁷ Dy₆ hexagons,^{73, 188} and larger

cyclic architectures.^{177, 189, 190} In typical ferrotoroidic configurations, local magnetic moments align along the same rotation (clockwise or counterclockwise), reinforcing the toroidal vector while canceling the net magnetization. Dy₄ clusters are considered as ideal building blocks due to the medium symmetry, which allow the magnetic anisotropy direction of each Dy³⁺ ion to be fine-tuned by the ligand environment and arranged in a toroidal way, providing an effective framework for understanding and manipulating the SMTs behaviors.¹⁷⁹

In this context, the integration of the isotope effects of lanthanide and SMTs is an intriguing and rarely explored dimension.^{101, 104, 137} Isotope substitution can significantly affect hyperfine interactions and spin-lattice relaxation by varying nuclear spin and mass without altering the molecular coordination environment and electronic structure.^{19, 47, 191, 192} Isotopologues with non-zero nuclear spin can reshape the low-energy spectrum through hyperfine coupling, thereby modulating quantum tunneling of magnetization behavior and relaxation dynamics at low temperatures. Conversely, for zero nuclear spin isotopologues, such interactions are suppressed by eliminating noise within the electronic environment, potentially enhancing the coherence.^{19, 47, 106, 191-193} Therefore, leveraging lanthanide isotope effects to modulate nuclear spin interactions within single-molecule toroids provide an ideal model for analyzing quantum decoherence mechanisms, facilitating the construction of high-dimensional Hilbert spaces and the optimization of qubit performance.¹³⁷

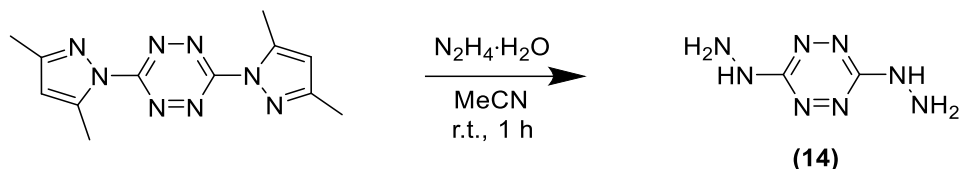
Herein, a series of self-assemble square [2×2] lanthanide grid complexes, [Ln₄L₄(μ₂-OH)₄] (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y), are constructed using a new multidentate Schiff-base ligand, 3,6-bis(2-1-(pyridin-2-yl)ethylidene)hydrazineyl-1,2,4,5-tetrazine (H₂L). Comprehensive magnetic characterizations employing both SQUID and μ-SQUID techniques reveal that the dysprosium analogue exhibits distinct SMM behavior. To further explore the relaxation mechanism, an isotopologue chemistry strategy is adopted, comparatively investigating the influence of different dysprosium isotopes, specifically, ¹⁶³Dy (*I* = 5/2) and ¹⁶⁴Dy (*I* = 0), on the SMM properties. A combined analysis of theoretical CASSCF calculations and experimental data confirms the emergence of toroidal-like magnetic states. Notably, an unconventional phenomenon is observed that the isotopologues containing nuclear spin exhibit longer QTM times, consistent with an enhanced tunneling probability into the toroidal ground state. Contrary to the conventional cases where nuclear spins typically accelerate quantum relaxation, we observe hyperfine-mediated population trapping in the toroidal state, that is, the presence of nuclear spin significantly enhances the stability of the toroidal magnetic moment. These findings not only provide new insights into the molecular design of SMMs but also first elucidate the active role of the nuclear spin in shaping the quantum magnetic properties of magnetic molecules, thereby opening new avenues for the development of high-density information storage and quantum materials.

3.2 Synthesis details

General procedures

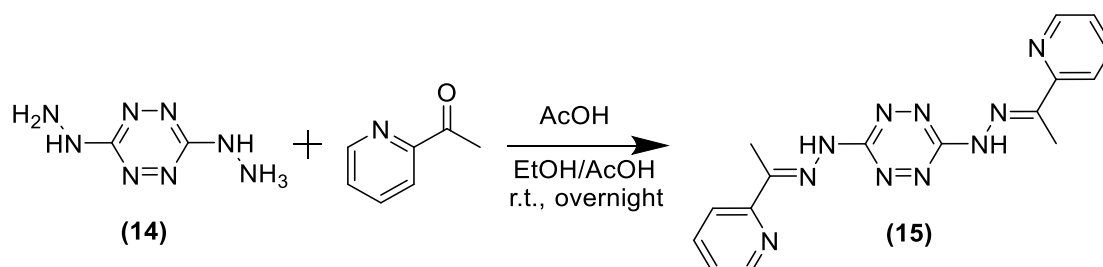
All commercially purchased (Sigma-Aldrich, TCI chemicals, abcr, BLD) chemicals and reagents were of reagent grade and used without further purification.

Synthesis of 3,6-dihydrazino-1,2,4,5-tetrazine (**14**)



To a suspension of 3,6-Bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine (2976.0 mg, ~11.01 mmol) in 30 mL CH₃CN was drop wise added hydrazine monohydrate (1.4 mL, ~28.86 mmol) at ambient conditions. During the addition, dark red precipitate was formed immediately. After the addition, the slurry was stirred for 2 h, then filtered, washed with toluene and dried to afford brown-red 3,6-dihydrazino-1,2,4,5-tetrazine. (C₂H₆N₈, FW = 142.12, 1375.3 mg, 9.68 mmol, 87.89% yield based on 3,6-Bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine). ¹H-NMR (400 MHz, DMSO-d₆): δ [ppm] = 8.39 (s, 2H, NH), 4.25 (s, 4H, NH). ¹³C-NMR (400 MHz, DMSO-d₆) δ 163.82 (see appendix Figure S11).

Synthesis of 3,6-bis(2-1-(pyridin-2-yl)ethylidene)hydrazineyl-1,2,4,5-tetrazine (**15**, **H₂L**)



To a stirred suspension of 3,6-dihydrazino-1,2,4,5-tetrazine (**7**, 284.3 mg, ~2 mmol) in 20 mL EtOH and 20 mL acetic acid was added 2-Acetylpyridine (0.5 mL, ~4.37 mmol). After stirring at room-temperature overnight, the mixture was filtered, washed with EtOH and water, and dried under vacuum to afford pink 3,6-bis(2-1-(pyridin-2-yl)ethylidene)hydrazineyl-1,2,4,5-tetrazine powder. (C₁₄H₁₆N₁₀, FW = 324.34, 348.4 mg, 1.07 mmol, 53.69% yield based on 3,6-dihydrazino-1,2,4,5-tetrazine). Due to poor solubility, only its ¹H-NMR spectra were obtained. ¹H-NMR (400 MHz, DMSO-d₆): δ [ppm] = 11.09 (s, 2H, NH), 8.61 (dd, 2H, ArH), 8.14 (dt, 2H, ArH), 7.85 (td, 2H, ArH), 7.39 (m, 2H, ArH). ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 8.68 (s, 2H, ArH), 8.60 (d, 2H, ArH), 8.30 (d, 2H, ArH), 7.73 (td, 2H, ArH), 2.55 (s, 6H, CH) (see appendix Figure S12).

Syntheses of $[\text{Ln}_4\text{L}_4(\mu_2\text{-OH})_4]\cdot\text{H}_2\text{O}\cdot 4\text{CH}_2\text{Cl}_2$ (**Ln₄L₄**)

H_2L (26.1 mg, 0.075 mmol), $\text{LnCl}_3\cdot 6\text{H}_2\text{O}$ (0.075 mmol, $\text{Ln} = \text{Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$) and 2,2,6,6-Tetramethyl-3,5-heptanedione (31 mg, 0.17 mmol) were suspended in a mixture of 6 mL methanol and 6 mL acetonitrile. After adding triethylamine (40 μL , 0.285 mmol), the solution was quickly turned dark and the insoluble solid gradually dissolved. After half an hour, brown solid and green crystalline gradually precipitated. After overnight stirring at room temperature, the precipitate was filtered and dried in the air to give brown powder contains green crystalline. The powder was redissolved in DCM and slowly evaporated to give green crystals (Yield: 15.6%-21.9%).

Note that: These reaction conditions are generally more favorable for crystal growth, which may be attributed to the competitive coordination between 2,2,6,6-tetramethyl-3,5-heptanedione (tmhd) and **H₂L** ligand for the metal centers. This competition effectively slows the self-assembly process and suppresses rapid nucleation, thereby creating an ideal environment for the growth of larger single crystals. However, with this synthetic route, the reaction involving yttrium salt uniquely yielded a binuclear, $\text{Y}_2\text{L}(\text{tmhd})_4(\text{MeOH})_2$ (for information on the crystallographic details, see Appendix).

Syntheses of **Dy₄L₄** and isotopologues (**¹⁶³Dy₄L₄** and **¹⁶⁴Dy₄L₄**)

A mixture of dysprosium chloride hexahydrate (28.5 mg, 0.075 mmol, the isotope dysprosium chloride salts are obtained by reacting the oxides with HCl) and ligand H_2L (26.1 mg, 0.075 mmol) in 12 mL MeOH and 12 mL DCM was stirred at room temperature for 0.5 h. During the dropwise addition of triethylamine (40 mL, 0.285 mmol), the insoluble solid began to dissolve gradually and turned into a dark brown solution. After stirring overnight, the solution was filtered and allowed to slowly evaporate under ambient conditions. Dark green crystals suitable for X-ray analysis were obtained after 3 days. Yield: 11.4 mg (18.3%-28.7%).

Maldi-Tof MS: (M)⁺: For **¹⁶³Dy₄L₄** ($\text{C}_{68}\text{H}_{70}\text{Cl}_8^{163}\text{Dy}_4\text{N}_{40}\text{O}_5$) calcd. (found): 2105.2935 (2105.8110), for **¹⁶⁴Dy₄L₄** ($\text{C}_{68}\text{H}_{70}\text{Cl}_8^{164}\text{Dy}_4\text{N}_{40}\text{O}_5$) calcd. (found): 2109.2935 (2108.8564), see Figure S14. Elemental analysis, for **¹⁶³Dy₄L₄·4CH₂Cl₂·4.5H₂O**, calcd. (found): C = 32.32 % (32.31 %), N = 22.18% (22.20 %), H = 3.07% (3.22%). For **¹⁶⁴Dy₄L₄·4CH₂Cl₂·4.5H₂O**, calcd. (found): C = 32.28 % (32.25%), N = 22.14 % (22.16%), H = 3.07 % (3.21%).

3.3 Molecular structures

3.3.1 Structures of Ln_4L_4 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Y}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$)

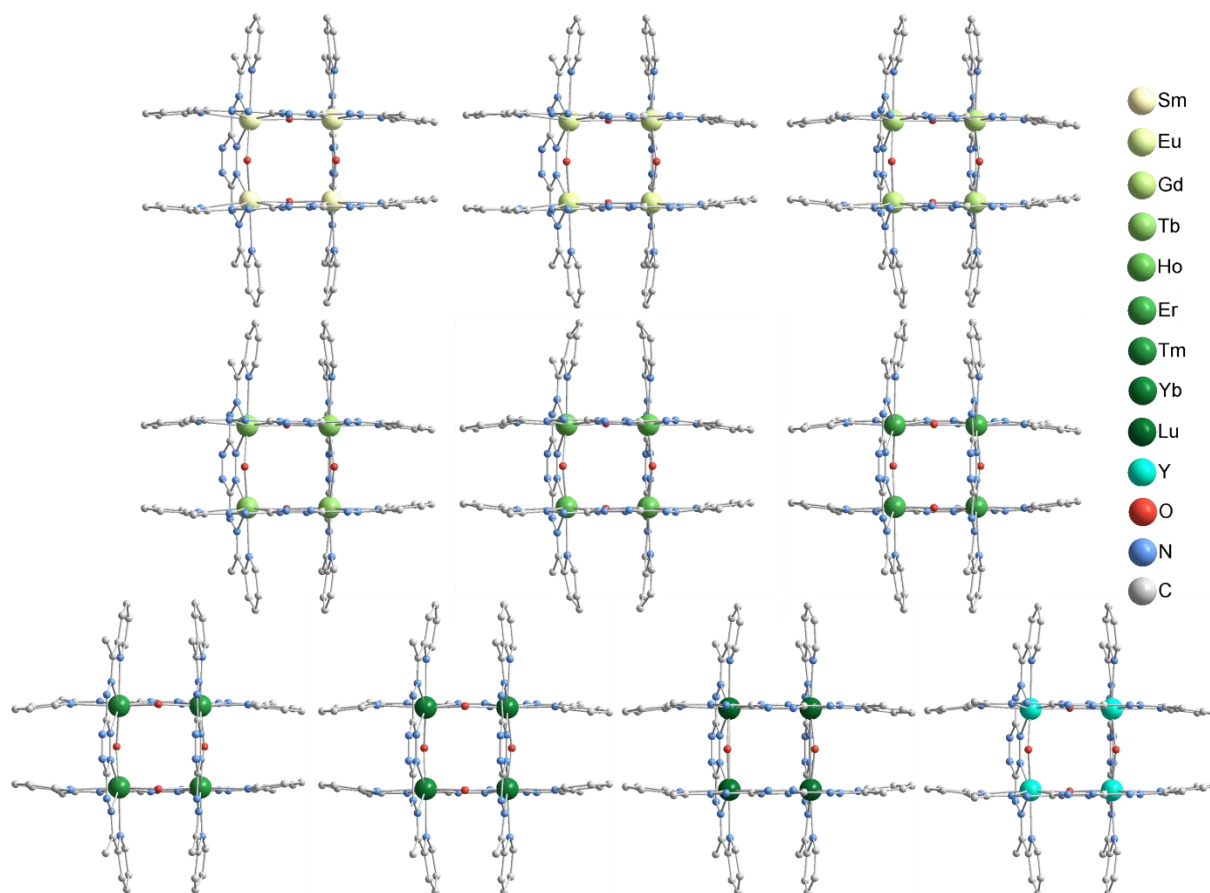


Figure 3.3.1 The molecular structure of Ln_4L_4 (Top: $\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$; Middle: $\text{Ln} = \text{Tb}, \text{Ho}, \text{Er}$; Bottom: $\text{Ln} = \text{Tm}, \text{Yb}, \text{Lu}, \text{Y}$). H atoms are omitted for clarity. Color code: Lanthanide elements from Sm to Lu are represented in a green-toned gradient; Y, cyan; O, red; N, blue; C, grey.

Single-crystal X-ray diffraction (SC-XRD) analysis reveal that the structures of a series of lanthanides from Sm to Lu including Y are isostructural, contains four Ln ions, four ligands and four bridging OH groups. Crystallographic data demonstrate that all these complexes crystallize in the orthorhombic Pnma space group, exhibiting a high degree of structural consistency. Continuous Shape Measure (CShM) analysis further indicates that, in this structural series, the local coordination geometries around each lanthanide metal center are best described as a triangular dodecahedron (D_{2d}).¹⁵⁷

By comparing the unit cell parameters, it can be observed that as the atomic number of the central rare earth metal increases, the unit cell volume of the complex generally exhibits a shrinking trend, decreasing from $9243.0 \text{ \AA}^3$ for Sm_4L_4 to $8690.8 \text{ \AA}^3$ for Lu_4L_4 , which is in excellent agreement with the classic lanthanide contraction effect. As for Y_4L_4 , the unit cell volume ($9038.6 \text{ \AA}^3$) falls exactly between those of Dy_4L_4 and Ho_4L_4 , perfectly aligning with the objective trend of the effective ionic radius of Y^{3+} within the lanthanide series.

Table 3.3.1 Crystallographic information for **Ln₄L₄** (Ln = Sm, Eu, Gd, Tb, Y).

No.	Sm₄L₄	Eu₄L₄	Gd₄L₄	Tb₄L₄	Y₄L₄
Formula	C ₆₈ H ₇₀ Cl ₈ Sm ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ Eu ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ Gd ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ Tb ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ Y ₄ N ₄₀ O ₅
Fw	2412.61	2419.03	2440.17	2446.87	2166.79
Temp/K	180	180	180	180	180
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	Pnma	Pnma	Pnma	Pnma	Pnma
a/Å	16.8937(4)	17.0017(7)	17.0025(14)	17.1682(5)	17.1012(8)
b/Å	24.7465(6)	24.5206(7)	24.1080(3)	24.3515(6)	24.2889(11)
c/Å	22.1092(6)	22.0715(6)	21.6662(18)	21.9103(5)	21.7603(7)
α/°	90	90	90	90	90
β/°	90	90	90	90	90
γ/°	90	90	90	90	90
Volume/Å ³	9243.0(4)	9201.4(5)	8880.9(14)	9160.1(4)	9038.6(7)
Z	4	4	4	4	4
ρ _{calc} /cm ³		1.570	1.697	1.795	1.489
μ/mm ⁻¹		14.833	16.132	3.355	2.763
R _{int}		0.0855	0.0957	0.0828	0.1724
Goodness-of-fit on F ²		0.823	0.701	0.844	0.905
R ₁ , wR ₂ (I > 2σ(I)) ^a		R ₁ = 0.0513, wR ₂ = 0.1140	R ₁ = 0.0358, wR ₂ = 0.0634	R ₁ = 0.0357, wR ₂ = 0.0759	R ₁ = 0.0666, wR ₂ = 0.1427
R ₁ , wR ₂ (all data)		R ₁ = 0.0955, wR ₂ = 0.1264	R ₁ = 0.1091, wR ₂ = 0.0701	R ₁ = 0.0700, wR ₂ = 0.0794	R ₁ = 0.1622, wR ₂ = 0.1756

$$^a R_1 = \|F_o\| - \|F_c\| / \sum \|F_o\|, wR_2 = \{w[(F_o)^2 - (F_c)^2]^2 / w[(F_o)^2]^2\}^{1/2}$$

Table 3.3.2 Crystallographic information for **Ln₄L₄** (Ln = Ho, Er, Tm, Yb, Lu).

No.	Ho₄L₄	Er₄L₄	Tm₄L₄	Yb₄L₄	Lu₄L₄
Formula	C ₆₈ H ₇₀ Cl ₈ Ho ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ Er ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ Tm ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ Yb ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ Lu ₄ N ₄₀ O ₅
Fw	2470.89	2480.21	2486.91	2503.33	2511.04
Temp/K	180	180	180	180	180
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	Pnma	Pnma	Pnma	Pnma	Pnma
a/Å	17.0380(18)	17.1085(17)	17.0208(4)	17.0456(3)	17.0305(6)
b/Å	24.2010(3)	23.933(3)	23.9902(5)	23.7118(3)	23.6901(9)
c/Å	21.6110(3)	21.455(3)	21.4486(4)	21.4890(3)	21.5411(9)
$\alpha/^\circ$	90	90	90	90	90
$\beta/^\circ$	90	90	90	90	90
$\gamma/^\circ$	90	90	90	90	90
Volume/Å ³	8911.3(19)	8785.1(16)	8758.2(3)	8685.5(2)	8690.8(6)
Z	4	4	4	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.667	1.859	1.763	1.916	1.761
μ/mm^{-1}	16.799	14.136	14.358	15.938	6.657
R _{int}	0.1125	0.1206	0.0442	0.0535	0.0655
Goodness-of-fit on F ²	1.222	0.696	1.063	1.023	0.863
R ₁ , wR ₂ (I > 2 σ (I)) ^a	R ₁ = 0.1470, wR ₂ = 0.3727	R ₁ = 0.0352, wR ₂ = 0.0545	R ₁ = 0.0450, wR ₂ = 0.1318	R ₁ = 0.0417, wR ₂ = 0.1156	R ₁ = 0.0539, wR ₂ = 0.1273
R ₁ , wR ₂ (all data)	R ₁ = 0.2047, wR ₂ = 0.4063	R ₁ = 0.0979, wR ₂ = 0.0587	R ₁ = 0.0725, wR ₂ = 0.1434	R ₁ = 0.0547, wR ₂ = 0.1236	R ₁ = 0.1022, wR ₂ = 0.1417

$$^a R_1 = \|F_o\| - \|F_c\| / \sum \|F_o\|, wR_2 = \{w[(F_o)^2 - (F_c)^2]^2 / w[(F_o)^2]^2\}^{1/2}$$

Table 3.3.3 The CShM values calculated by using SHAPE analysis for **Ln₄L₄** (Ln = Sm, Eu, Gd, Tb, Y, Ho, Er, Tm, Yb, Lu).

	Sm₄L₄	Eu₄L₄	Gd₄L₄	Tb₄L₄	Y₄L₄	Ho₄L₄	Er₄L₄	Tm₄L₄	Yb₄L₄	Lu₄L₄
OP-8 (<i>D</i> _{8h})	31.479	31.478	31.196	30.971	31.364	30.866	31.458	31.229	31.305	31.539
Octagon	31.633	31.273	31.138	31.198	30.983	30.594	30.959	30.595	31.032	30.952
HPY-8 (<i>C</i> _{7v})	25.557	25.099	24.922	25.266	25.336	25.489	25.164	25.187	25.097	25.253
Heptagonal pyramid	25.156	25.276	25.209	25.141	25.532	24.977	25.413	25.465	25.451	25.731
HBPY-8 (<i>D</i> _{6h})	13.615	13.929	13.627	13.932	14.104	14.265	14.202	14.069	14.311	14.428
Hexagonal bipyramid	13.815	13.572	13.842	14.078	13.846	13.944	14.148	14.205	14.400	14.300
CU-8 (<i>O</i> _h)	12.083	12.204	11.966	12.027	12.192	12.596	12.306	12.264	12.435	12.515
Cube	11.947	12.096	12.289	12.377	12.252	12.326	12.499	12.276	12.599	12.532
SAPR-8 (<i>D</i> _{4d})	4.620	4.441	4.449	4.095	4.268	4.098	4.203	4.207	4.148	4.116
Square antiprism	4.495	4.455	4.360	4.253	4.147	3.841	4.119	3.852	3.995	3.922
TDD-8 (<i>D</i>_{2d})	2.358	1.957	1.991	2.030	1.750	1.745	1.700	1.754	1.660	1.594
Triangular dodecahedro	2.091	2.249	2.033	1.881	1.969	1.910	1.814	1.834	1.735	1.682
JGBF-8 (<i>D</i> _{2d})	9.709	10.438	10.342	9.939	10.474	9.982	10.447	10.496	10.448	10.571
Johnson gyrobiafastigium J26	10.238	9.564	10.118	10.473	9.910	9.769	10.266	10.217	10.338	10.318
JETBPY-8 (<i>D</i> _{3h})	25.536	25.569	25.279	25.734	25.869	25.947	25.884	25.861	25.835	26.156
Johnson elongated triangular bipyramid J14	25.368	25.134	25.269	25.586	25.951	25.356	25.657	25.759	25.882	26.200
JBTPR-8 (<i>C</i> _{2v})	3.569	3.490	3.527	3.232	3.384	3.208	3.343	3.404	3.277	3.298
Biaugmented trigonal prism J50	3.673	3.316	3.428	3.351	3.358	2.949	3.267	3.125	3.180	3.184
BTPR-8 (<i>C</i> _{2v})	2.817	2.773	2.956	2.543	2.789	2.574	2.768	2.747	2.689	2.701
Biaugmented trigonal prism	3.008	2.706	2.859	2.656	2.704	2.424	2.673	2.532	2.583	2.589
JSD-8 (<i>D</i> _{2d})	2.653	2.568	2.515	2.498	2.368	2.189	2.322	2.411	2.285	2.288
Snub diphenoid J84	2.532	2.541	2.428	2.488	2.422	2.272	2.326	2.375	2.263	2.284
TT-8 (<i>T</i> _d)	12.505	12.967	12.755	12.444	12.994	13.201	13.106	13.035	13.232	13.319
Triakis tetrahedron	12.766	12.573	12.906	13.001	12.631	12.733	13.013	12.649	12.943	12.900
ETBPY-8 (<i>D</i> _{3h})	20.972	21.394	21.385	21.468	22.037	21.993	22.042	22.033	22.115	22.403
Elongated trigonal bipyramid	21.205	20.910	21.313	21.496	21.822	21.451	21.776	21.859	22.033	22.390

It should be noted that, the self-assembly process of such tetranuclear [2×2] grid architectures involve complex thermodynamic and kinetic equilibrium, making it difficult to obtain high-quality single crystals for SC-XRD measurement (generally too small to measure). Another problem is the significant symmetry conflict in crystallographic analysis: while the main structure of the complex exhibits high symmetry (*Pnma* space group), the free solvent molecules (CH_2Cl_2 and H_2O) within the lattice display extremely high disorder. Although it is difficult to handle these highly disordered solvent molecules in most cases, the SC-XRD results are sufficient to describe the coordination environment of the metal center and the connectivity of the main structure.

Table 3.3.4 The selected atom-atom distances and bond angles for **Ln₄L₄** (Ln = Sm, Eu, Gd, Tb, Y, Ho, Er, Tm, Yb, Lu).

	Ln···N / Å	Ln···O / Å	Ln···Ln / Å	Ln–O–Ln / °
Sm₄L₄	2.528(9)-2.578(9)	2.272(8)-2.296(1)	4.208(9)-4.275(7)	135.0(1)-137.2(2)
Eu₄L₄	2.512(5)-2.577(6)	2.266(3)-2.304(5)	4.212(1)-4.261(3)	134.7(5)-137.2(5)
Gd₄L₄	2.498(5)-2.551(6)	2.250(2)-2.255(4)	4.188(1)-4.226(6)	136.8(2)-139.4(1)
Tb₄L₄	2.490(3)-2.546(3)	2.252(1)-2.263(2)	4.196(7)-4.237(6)	136.8(2)-139.0(1)
Y₄L₄	2.463(5)-2.537(4)	2.219(2)-2.237(4)	4.164(1)-4.204(4)	138.8(3)-140.1(2)
Ho₄L₄	2.414(2)-2.563(2)	2.223(1)-2.250(6)	4.193(2)-4.197(2)	137.7(4)-139.7(6)
Er₄L₄	2.457(4)-2.498(4)	2.213(2)-2.224(3)	4.155(1)-4.186(1)	138.2(2)-140.7(2)
Tm₄L₄	2.432(9)-2.501(1)	2.187(4)-2.213(7)	4.138(3)-4.160(1)	140.0(2)-142.4(3)
Yb₄L₄	2.437(4)-2.481(4)	2.186(2)-2.200(3)	4.115(1)-4.157(6)	140.0(2)-142.0(2)
Lu₄L₄	2.415(5)-2.488(6)	2.177(2)-2.194(4)	4.106(4)-4.142(6)	140.0(1)-141.9(2)

To further investigate the evolution of geometric parameters within this series of lanthanide isostructural grid complexes, the bond lengths ($\text{Ln}\cdots\text{N}$ and $\text{Ln}\cdots\text{O}$), the distances between adjacent lanthanide atoms, and the bond angles ($\text{Ln}-\text{O}-\text{Ln}$) of the main [2×2] crystal structure are extracted and systematically compared. The analysis results reveal that this lanthanide complexes series exhibit a trend with the increase of the central metal atomic number (from Sm to Lu). Specifically, both the coordination bond lengths and the intramolecular $\text{Ln}\cdots\text{Ln}$ distances show a monotonically decreasing trend. Specifically, the $\text{Ln}\cdots\text{N}$ and $\text{Ln}\cdots\text{O}$ bond lengths gradually shorten from 2.528(9)-2.578(9) Å in **Sm₄L₄** to 2.415(5)-2.488(6) Å in **Lu₄L₄**, and from 2.272(8)-2.296(1) Å in **Sm₄L₄** to 2.177(2)-2.194(4) Å in **Lu₄L₄**, respectively. Simultaneously, the distances between adjacent metal ions within the molecule ($\text{Ln}\cdots\text{Ln}$) also significantly contracted from 4.208(9)-4.275(7) Å in **Sm₄L₄** to 4.106(4)-4.142(6) Å in **Lu₄L₄**. Such regular shortening of coordinate bonds and $\text{Ln}\cdots\text{Ln}$ distances serves as a direct manifestation of the classic lanthanide contraction effect in coordination geometry that as the effective nuclear charge increases, the radius of the lanthanide ion decreases, increasing its attraction to the ligand electron cloud and resulting in a more compact coordination environment.

Notably, contrary to the contraction trends of bond lengths or $\text{Ln}\cdots\text{Ln}$ distance, the $\text{Ln}-\text{O}-\text{Ln}$ bond angles, constructed by bridging oxygen atoms, exhibits a gradually increasing trend

with the increase in atomic number. This bridging bond angles gradually increase from 135.0(1)-137.2(2) ° in **Sm₄L₄** to 140.0(1)-141.9(2) ° in **Lu₄L₄**. This increase in angle can be rationalized as a geometric compensation effect. Due to the lanthanide contraction effect, the structures become more compact. To minimize the steric hindrance and the repulsive forces induced by the shortened distances, the complexes undergo configurational relaxation by increasing the Ln–O–Ln bridging angle.

Furthermore, the parameters of the pseudo-lanthanide yttrium complex lie between the **Dy₄L₄** and **Er₄L₄**, validating the objective position of the Y³⁺ ionic radius. However, it should be objectively pointed out that although the overall trend is clear, the parameters of **Ho₄L₄** slightly deviate from the strictly monotonic trend. This is attributed to the relatively high R-factors of this specific single-crystal diffraction dataset, increasing the uncertainty of the coordinate positions of light atoms (O and N atoms) and thereby resulting in fluctuations in the calculated specific bond parameters. Nevertheless, considering the unit cell parameters, the unit volume of **Ho₄L₄** strictly follows the volume shrinkage trend. Since the determination of unit cell parameters depends on the spatial position of diffraction peaks rather than the diffraction intensity, the results have extremely high accuracy and robustness compared with the distance or angle parameters. Consequently, even though the local parameters are limited by the poor quality of crystal, the lanthanide contraction is still theoretically valid and actually occurs in this series of complexes.

3.3.2 Structures of **Dy₄L₄** and the isotopologues (¹⁶³**Dy₄L₄** and ¹⁶⁴**Dy₄L₄**)

The Single-crystal X-ray diffraction analysis revealed that **Dy₄L₄** and its isotopologues (¹⁶³**Dy₄L₄** and ¹⁶⁴**Dy₄L₄**) are isostructural and crystallized in the orthorhombic crystal system with *Pnma* space group (*Z* = 4), which is the same as the aforementioned lanthanide series. As for the slight difference in the cell volume, this is attributed to the different testing temperature (180 K vs 150 K), reflecting the thermal expansion and contraction of the crystal lattice, and does not change the overall isostructural nature. The asymmetric unit consists of a single independent molecule, and the other three are generated by crystallographic symmetry operations involving inversion centers, mirror planes, and glide planes. Based on these symmetry elements, only two crystallographically distinct molecular orientations are presented within the unit cell with each orientation occurring twice.

Structurally, the molecular backbones of the natural **Dy₄L₄** and isotopologues (¹⁶³**Dy₄L₄** and ¹⁶⁴**Dy₄L₄**) are consist of four Dy³⁺ ions, four doubly deprotonated ligands (L²⁻), and four bridging μ₂-OH⁻ groups, which self-assemble to form a highly compact [2×2] grid topological structure. Within the cores of these tetranuclear systems, each Dy³⁺ center is eight-coordinated and situated within an N₆O₂ coordination environment constructed by the six nitrogen atoms from two tridentate L²⁻ ligands and two oxygen atoms from two μ₂-OH⁻ bridges. Continuous shape measure (CShM) analysis confirms that the local coordination geometry around each Dy³⁺ ion across all three complexes is best described as a triangular dodecahedron (1.780 and 1.945 for **Dy₄L₄**, 1.914 and 1.913 for ¹⁶³**Dy₄L₄**, and 1.862 and 1.863 for ¹⁶⁴**Dy₄L₄**, respectively).¹⁵⁷

Table 3.3.5 Crystallographic information for **Dy₄L₄** and isotopologue ¹⁶³**Dy₄L₄** and ¹⁶⁴**Dy₄L₄**.

No.	Dy₄L₄	¹⁶³ Dy₄L₄	¹⁶⁴ Dy₄L₄
Formula	C ₆₈ H ₇₀ Cl ₈ Dy ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ ¹⁶³ Dy ₄ N ₄₀ O ₅	C ₆₈ H ₇₀ Cl ₈ ¹⁶⁴ Dy ₄ N ₄₀ O ₅
Fw	2461.17	2463.17	2467.17
Temp/K	180	150	150
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	Pnma	Pnma	Pnma
a/Å	17.0576(3)	17.0066(5)	17.035(4)
b/Å	24.3309(4)	24.0538(6)	24.122(6)
c/Å	21.8377(4)	21.5916(6)	21.636(5)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å ³	9063.2(3)	8832.5(4)	8890(3)
Z	4	4	4
ρ _{calc} /cm ³	1.706	1.849	1.837
μ/mm ⁻¹	18.041	19.182	19.078
R _{int}	0.0392	0.1661	0.1760
Goodness-of-fit on F ²	1.054	0.972	0.906
R ₁ , wR ₂ (I > 2σ(I)) ^a	R ₁ = 0.0466, wR ₂ = 0.1330	R ₁ = 0.0586, wR ₂ = 0.1576	R ₁ = 0.0634, wR ₂ = 0.1577
R ₁ , wR ₂ (all data)	R ₁ = 0.0692, wR ₂ = 0.1445	R ₁ = 0.0889, wR ₂ = 0.1695	R ₁ = 0.1201, wR ₂ = 0.1707

$$^a R_1 = \|F_o\| - \|F_c\| / \|F_o\|, wR_2 = \{w[(F_o)^2 - (F_c)^2]^2 / w[(F_o)^2]^2\}^{1/2}$$

Table 3.3.6 The selected atom-atom distances and bond angles for **Dy₄L₄** and isotopologues ¹⁶³**Dy₄L₄** and ¹⁶⁴**Dy₄L₄**.

	Dy···N / Å	Dy···O / Å	Dy···Dy / Å	Dy–O–Dy / °
Dy₄L₄	2.474(5)-2.525(7)	2.228(2)-2.249(4)	4.177(1)-4.213(1)	137.4(2)-139.2(2)
¹⁶³ Dy₄L₄	2.475(7)-2.543(9)	2.225(6)-2.258(6)	4.174(1)-4.208(1)	137.8(4)-139.7(3)
¹⁶⁴ Dy₄L₄	2.468(8)-2.533(8)	2.232(3)-2.244(6)	4.184(2)-4.220(1)	137.9(4)-140.4(3)

To comprehensively investigate the isotope effect, a comparative analysis was performed on the critical crystallographic parameters. As illustrated in Table 3.3.6, the isotopic substitution in dysprosium exerts a negligible effect on the geometric parameters across the three complexes. The Dy···N bonds length for **Dy₄L₄** span a range of 2.474(5)-2.525(7) Å, which highly overlaps with those of ¹⁶³**Dy₄L₄** (2.475(7)-2.543(9) Å) and ¹⁶⁴**Dy₄L₄** (2.468(8)-2.533(8) Å). Similarly, the relatively short Dy···O bond lengths ranges from 2.228(2) to 2.249(4) Å for **Dy₄L₄**, 2.225(6) to 2.258(6) Å for ¹⁶³**Dy₄L₄**, and 2.232(3) to 2.244(6) Å for ¹⁶⁴**Dy₄L₄**, respectively, reflecting the strong affinity of the Dy³⁺ for oxygen donors. These small differences in bond lengths all fall within the experimental standard deviations, which is attributed to the minuscule mass

differences among the dysprosium isotopes, resulting a negligible bond length distortion. A closer examination of the intramolecular Dy···Dy distances and bridging angles reveals slight differences. Specifically, the [2×2] grid topological structure is maintained by four Dy³⁺ centers with bridging μ_2 -OH groups, where the Dy-O-Dy bridging angles are distributed in a narrow and highly consistent range [137.4(2)-139.2(2) ° for **Dy₄L₄**, 137.8(4)-139.7(3) ° for **¹⁶³Dy₄L₄**, and 137.9(4)-140.4(3) ° for **¹⁶⁴Dy₄L₄**]. Such specific geometry may originate from the low rigidity of the coordinated μ_2 -OH groups, and results in short intramolecular Dy···Dy distances of approximately 4.17 to 4.22 Å, suggesting the presence of intramolecular magnetic dipole-dipole interactions. Overall, these parameters confirm **Dy₄L₄** and the isotopologues (**¹⁶³Dy₄L₄** and **¹⁶⁴Dy₄L₄**) are isostructural, rendering this system an ideal platform for investigating isotope effects.

Table 3.3.7 The CShM values calculated by using SHAPE analysis for **Dy₄L₄** and isotopologue **¹⁶³Dy₄L₄** and **¹⁶⁴Dy₄L₄**.

	Dy₄L₄	¹⁶³Dy₄L₄	¹⁶⁴Dy₄L₄
OP-8 (<i>D</i> _{8h})	31.131	30.804	31.353
Octagon	31.080	30.804	31.340
HPY-8 (<i>C</i> _{7v})	25.372	25.299	24.844
Heptagonal pyramid	25.481	25.300	24.850
HBPY-8 (<i>D</i> _{6h})	14.128	13.908	14.161
Hexagonal bipyramid	13.946	13.909	14.161
CU-8 (<i>O</i> _h)	12.317	12.447	12.320
Cube	12.250	12.447	12.318
SAPR-8 (<i>D</i> _{4d})	4.222	4.127	4.270
Square antiprism	4.134	4.127	4.270
TDD-8 (<i>D</i>_{2d})	1.780	1.914	1.862
Triangular dodecahedron	1.945	1.913	1.863
JGBF-8 (<i>D</i> _{2d})	10.398	10.202	10.382
Johnson gyrobifastigium J26	9.986	10.203	10.383
JETBPY-8 (<i>D</i> _{3h})	25.845	25.554	25.375
Johnson elongated triangular bipyramid J14	25.766	25.555	25.372
JBTPR-8 (<i>C</i> _{2v})	3.387	3.319	3.363
Biaugmented trigonal prism J50	3.259	3.318	3.364
BTPR-8 (<i>C</i> _{2v})	2.741	2.666	2.760
Biaugmented trigonal prism	2.597	2.665	2.759
JSD-8 (<i>D</i> _{2d})	2.374	2.475	2.444
Snub diphonoid J84	2.438	2.476	2.443
TT-8 (<i>T</i> _d)	13.102	12.862	13.111
Triakis tetrahedron	12.659	12.863	13.109
ETBPY-8 (<i>D</i> _{3h})	21.914	21.550	21.488
Elongated trigonal bipyramid	21.612	21.549	21.483

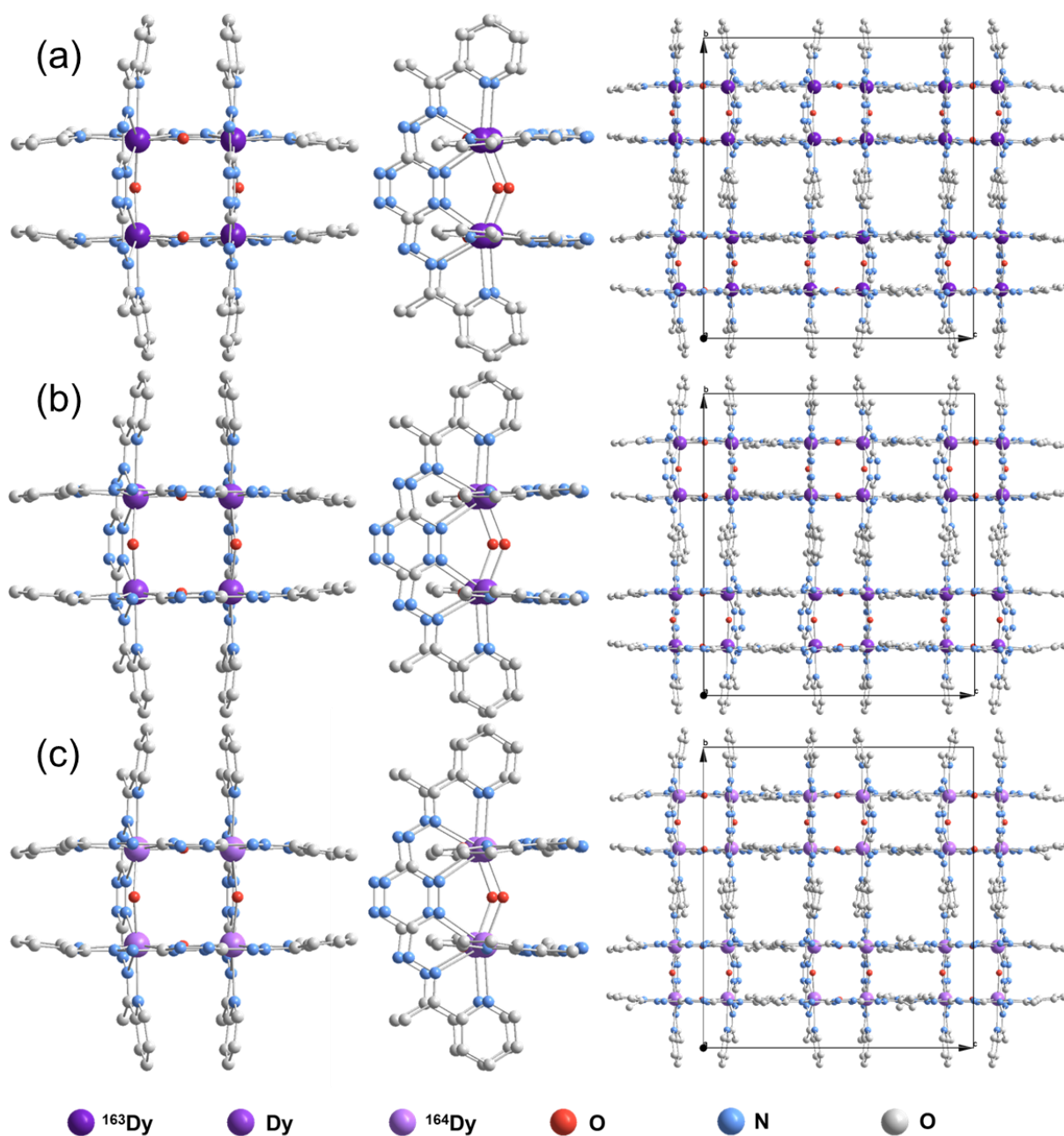


Figure 3.3.2 The top view (left), side view (middle), and the packing diagram within the unit cell (right) of the molecular structure for $^{163}\text{Dy}_4\text{L}_4$ (a), Dy_4L_4 (b), and $^{164}\text{Dy}_4\text{L}_4$ (c). H atoms and solvent molecules are omitted for the sake of clarity. Color code: ^{163}Dy , dark purple; Dy, purple; ^{164}Dy , light purple; O, red; N, blue; C, grey.

3.4 Optical properties of **Gd₄L₄**, **Eu₄L₄**, and **Yb₄L₄**

Before conducting solid-state photoluminescence measurements, the photophysical properties of the free ligand in chloroform solution were evaluated using UV-Vis absorption spectroscopy. As illustrated in Figure 3.4.1a, the free ligand (**H₂L**) in chloroform at room temperature exhibits a distinct absorption peak with maxima centered at 338 nm. This absorption peak is typically attributed to the π - π^* transitions occurring within the conjugated system of the ligand, reflecting the inherent light-harvesting ability of the ligand and providing a reliable reference for selecting the optimal excitation wavelength in subsequent temperature-dependent solid-state photoluminescence experiments.

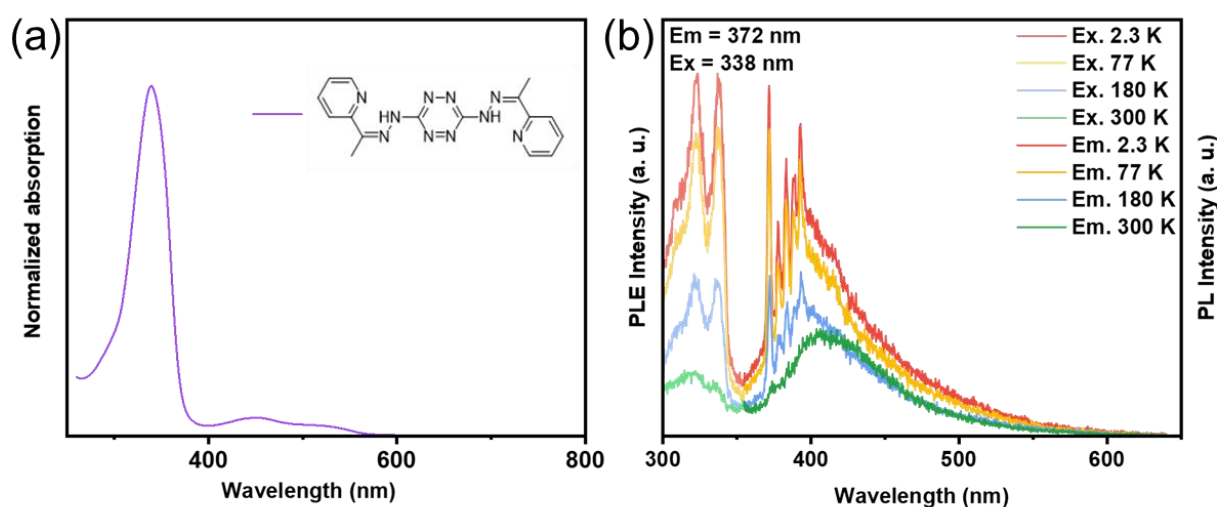


Figure 3.4.1 (a) The UV-Vis spectrum of the **H₂L** ligand in CHCl_3 at room temperature. (b) Steady-state photoluminescence characteristics of **Gd₄L₄** in the solid state recorded at different temperatures using an excitation wavelength of 338 nm and an emission wavelength of 372 nm.

To investigate the photoluminescence properties of this complex systems, the representative lanthanide ions ($\text{Ln} = \text{Gd}, \text{Eu}, \text{Yb}$) in the luminescence field are initially employed as the subjects of study. Typically, Eu^{3+} and Yb^{3+} complexes are widely investigated for their excellent visible and near-infrared luminescent performances, respectively. While Gd^{3+} complexes, due to the large energy gap between the ground state ($^8\text{S}_{7/2}$) and the first excited state ($^6\text{P}_{7/2}$), approximately 32000 cm^{-1} , are regarded as ideal models to determine the triplet energy level of ligands and to reveal the intrinsic luminescent behaviors of the ligands.

Based on this, Figure 3.4.1b shows the excitation and emission spectra of **Gd₄L₄** recorded on solid state at different temperatures. In the excitation spectrum at 2.3 K, the maximum excitation wavelengths observed are found at 320 nm and 380 nm, which match the absorption spectrum of the ligand, confirming that the luminescence of the complex mainly originates from the effective light absorption by the ligand. At 2.3 K, upon excitation at 338 nm, due to the significant suppression of molecular thermal vibrations, the emission spectrum exhibits an extremely clear fine structure with a series of narrow emission peaks (located at 372 nm, 378

nm, 384 nm, 388 nm, and 393 nm), representing the ligand-centered $T_1 \rightarrow S_0$ phosphorescence. As for the shoulder around 400 nm, it may be attributed to the weak π - π stacking interactions of the intramolecular pyridine rings. As the temperature gradually increased from 2.3 K to 300 K, due to the thermal broadening effect, these narrow emission peaks gradually lose their fine structures and undergo thermal quenching, existing only a broadened peak (420 nm) at room temperature. Since the energy of the first excited state of the Gd^{3+} ion is relatively high, the energy transfer is prohibited. Consequently, no f - f transition occurred, further confirming that the luminescence of **Gd₄L₄** originates purely from the ligand.

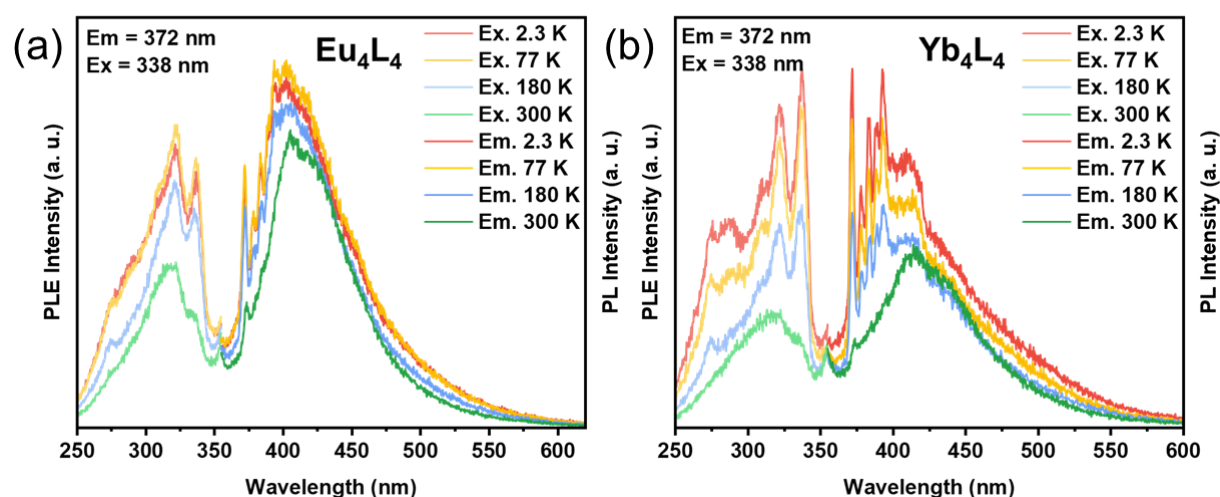


Figure 3.4.2 Steady-state photoluminescence characteristics of **Eu₄L₄** (a) and **Yb₄L₄** (b) in solid state recorded at different temperatures using an excitation wavelength of 338 nm and an emission wavelength of 372 nm.

After clarifying and identifying the characteristic emission peaks of the ligand, the steady-state photoluminescence measurements for **Eu₄L₄** and **Yb₄L₄** are further performed and characterized as illustrated in Figure 3.4.2. Remarkably, **Eu₄L₄** and **Yb₄L₄** exhibit spectral characteristics of the excitation and emission spectrums that are almost identical to those of the **Gd₄L₄**. Upon excitation wavelength of 338 nm at 2.3 K, both complexes exhibit the same vibrational fine structures as **Gd₄L₄**, though the peaks of **Eu₄L₄** located at 388 nm and 393 nm are barely visible. This may be attributed to the fact that the relatively larger unit cell volume of **Eu₄L₄** allows more freedom of the molecular vibration. Similarly, as the temperature is elevated to 300 K, the narrow peaks were thermally quenched, and the spectra became overwhelmingly dominated by the broad emission peak red-shifted to approximately 420 nm. More importantly, although Eu^{3+} and Yb^{3+} are typically excellent energy acceptor, the emission of f - f transition is absent in the spectrum.

These experimental results demonstrate that the antenna effect is ineffective in these lanthanide systems, as the absorbed energy fails to transfer to the central lanthanide ion. The main reason for this energy transfer failure may be due to the existing low-energy charge-transfer bands, which quench both energy transfer to lanthanides and the emission from

lanthanides. In summary, within this series of grid lanthanide complexes, the lanthanide ions serve merely as structural nodes to construct the [2×2] framework, rather than acting as luminescent centers. However, this interpretation needs to be ascertained with further experimental studies. Given that this thesis focuses on the magnetic properties of lanthanides, as presented in the following section, rather than the emission, thus, this part of the discussion, which is beyond the scope of this thesis, will not be further explored in later discussions.

3.5 Magnetic properties of **Dy₄L₄**

In the systematic magnetic investigations of this [2×2] grid lanthanide complexes series, the field-dependent ac magnetic susceptibility measurements reveal that only **Dy₄L₄** exhibits field-induced SMM behavior. While for the other lanthanide analogues, no observable SMM features are detected within the window of magnetic measurement. Therefore, the subsequent discussions on magnetic properties will focus on the **Dy₄L₄** to explore the magnetic relaxation mechanism.

3.5.1 SQUID measurement

To investigate the static magnetic properties of **Dy₄L₄**, the temperature-dependent dc magnetic susceptibility measurement is performed on powdered polycrystalline samples in the temperature range of 2–300 K under an applied external magnetic field of 1000 Oe (Figure 3.5.1a). The $\chi_M T$ value for **Dy₄L₄** at room temperature is 54.7 cm³ K mol^{−1}, which is consistent with the theoretically expected value of 54.8 cm³ K mol^{−1} for four isolated Dy³⁺ ions ($J = 15/2$, $g = 4/3$). The slight difference is attributed to the strong crystal field effect, resulting in a reduced magnetic moment compared to the ideal free ions. As the temperature gradually decreases from 300 K to around 50 K, the $\chi_M T$ exhibits a slow and continuous decrease, which is attributed to the thermal depopulation of the excited Stark sublevels. Upon further cooling to 2 K, the $\chi_M T$ drops rapidly to 21.2 cm³ K mol^{−1}, indicating the emergence of antiferromagnetic interactions.

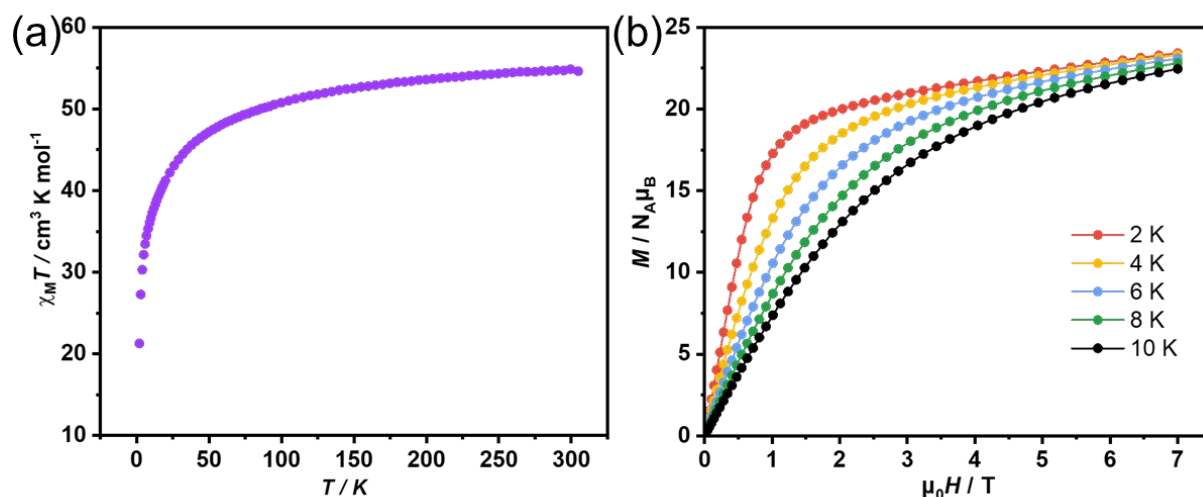


Figure 3.5.1 (a) The $\chi_M T$ versus T plots and (b) variable temperature magnetization data for **Dy₄L₄**. Solid lines are guided for eyes.

To further elucidate the magnetic anisotropy, the field-dependent magnetization is recorded at temperatures of 2, 4, 6, 8, and 10 K (Figure 3.5.1b). None of the M - H curves exhibit a clear saturation plateau under high fields, but rather a non-coincident increase trend as the magnetic field increases. Specifically, in the low magnetic field region, the magnetization increases rapidly with the applied magnetic field. While in the high magnetic field region, the increment

slows down and reaches a maximum value of $23.4 N_{\text{A}}\mu_{\text{B}}$ at 2 K and 7 T, indicating the strong magnetic anisotropy of the ground states.

To further investigate the magnetization relaxation dynamics of **Dy₄L₄**, ac magnetic susceptibility measurements are conducted. However, under a zero-dc field, no characteristic peak associated with slow relaxation of magnetization is observed (Figure 3.5.2), which is frequently encountered in lanthanide systems and primarily attributed to the fast QTM process. Generally, the QTM process could be suppressed by an external magnetic field. Thus, to address the optimal dc field, magnetic field-dependent ac susceptibility measurements at 2 K are employed, revealing an optimal field of 1400 Oe.

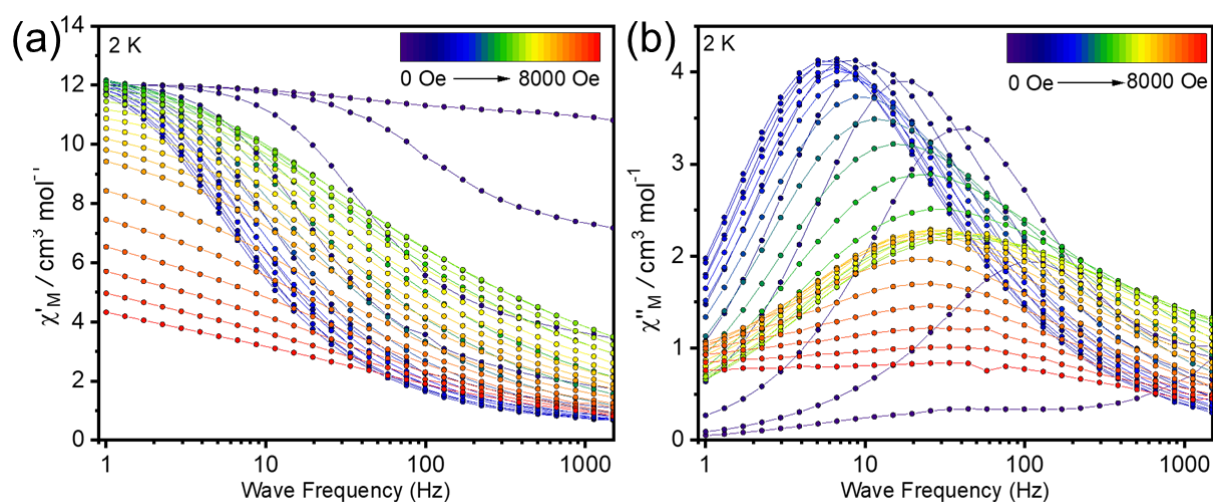


Figure 3.5.2 The experimental frequency-dependent ac magnetic susceptibility data at 2 K and varied magnetic fields of the in-phase (a) and out-of-phase (b) for **Dy₄L₄**. Solid lines are guided for eyes.

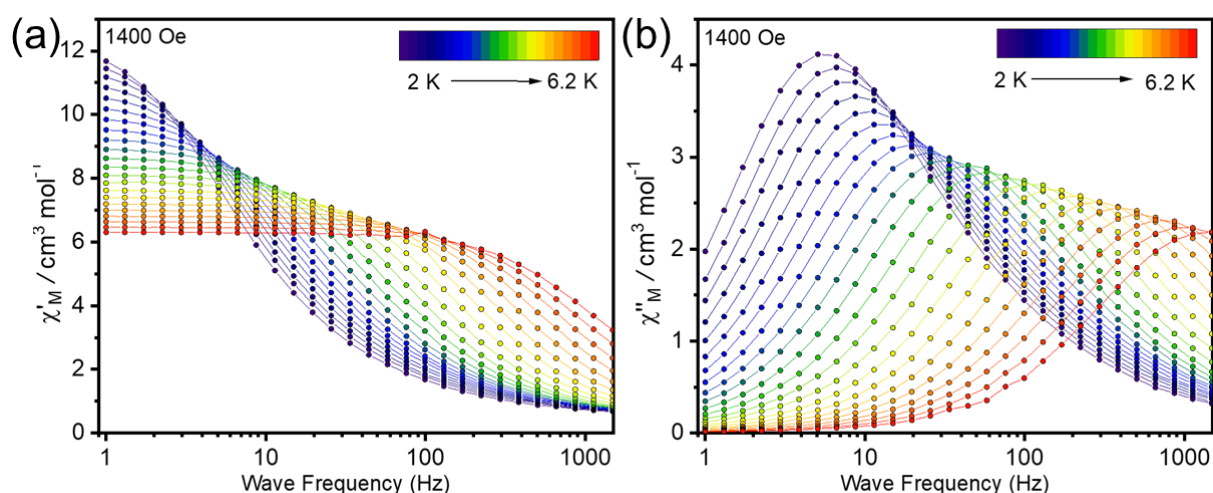


Figure 3.5.3 The experimental frequency-dependent ac magnetic susceptibility data at 1400 Oe optimal field and varied temperatures of the in-phase (a) and out-of-phase (b) for **Dy₄L₄**. Solid lines are guided for eyes.

As illustrated in Figure 3.5.3, under an applied dc field of 1400 Oe, the out-of-phase component of **Dy₄L₄** exhibits significant and frequency-dependent maxima in the temperature range of 2 K to 6.2 K. As expected for slow magnetic relaxation, the emergence of maxima in the out-of-phase component is accompanied by a concomitant decrease of the in-phase signal. At the lowest temperature of 2 K, the maximum is found at approximately 5.5 Hz. As the temperature increases, the characteristic SMM peak continuously shifts toward higher frequencies, indicating that the absence of QTM process and the relaxation of **Dy₄L₄** is primarily dominated by temperature-dependent relaxation processes. Specifically, the maximum is slowly shifted to higher frequencies up to approximately 4 K; while a more significant shift is observed as the temperature is further increased, reaching the highest frequency of 1488 Hz at 6.2 K. This phenomenon is typically attributed to the gradual transitions from Raman-dominated to Orbach-dominated relaxation. This feature is further confirmed by the Cole-Cole plot with fitted α parameters using the generalized Debye model (Figure 3.5.4a), where the value of α decreases from 0.22 at 2 K to 0.15 at 6.2 K, indicating the relaxation is approaching a single relaxation process.

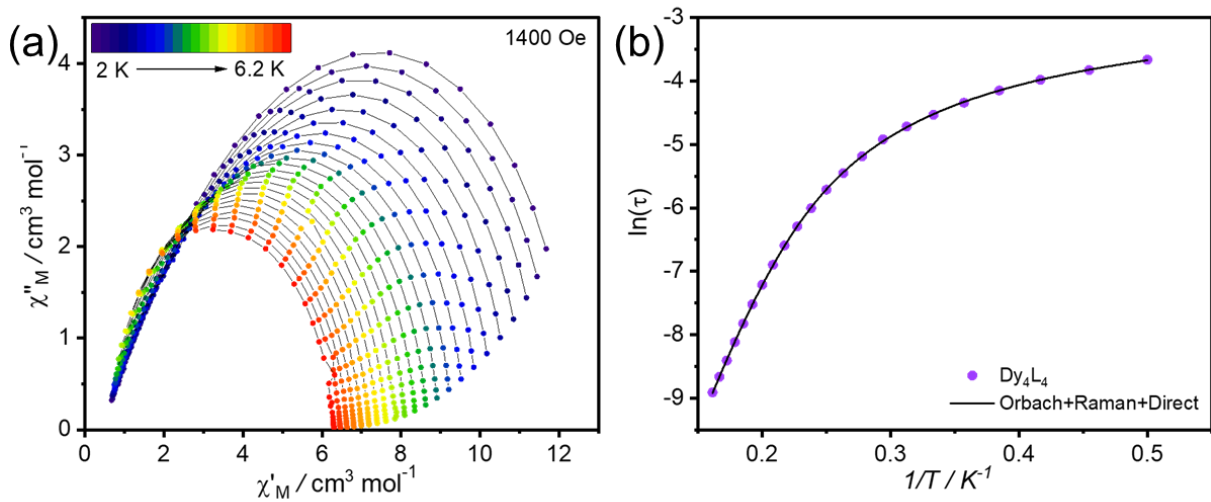


Figure 3.5.4 (a) The Cole-Cole plots under a 1400 Oe field for **Dy₄L₄**. The solid lines represent the best fits to a generalized Debye model. Solid lines are guided for eyes. (b) The $\ln(\tau)$ vs. T^{-1} plot under a 1400 Oe magnetic field for **Dy₄L₄**. The black lines are the best fitting from the Orbach process, Raman process, and Direct process.

To further investigate the slow relaxation mechanism of **Dy₄L₄**, the relaxation time extracted from the frequency-dependent ac susceptibility data across the entire temperature range are fitted using a combination model of the Orbach process, the Raman process, and the Direct process:

$$\tau^{-1} = \tau_0^{-1} \exp(-U_{eff}/k_B T) + CT^n + AT \quad \text{Equation 3.5.1}$$

As illustrated in the Figure 3.5.4b, for **Dy₄L₄**, the energy barrier is 55(1) K with pre-exponential factor of $2.7(0.4) \times 10^{-8}$ s; the fitted Raman parameters are found $C = 8.6(2.1) \times 10^{-2}$

$\text{s}^{-1} \text{K}^{-n}$ with $n = 5.56(0.19)$, and the fitted Direct parameter is $A = 17.61(0.3) \text{ s}^{-1} \text{K}^{-1}$. The pre-exponential factor falls within the characteristic range expected for typical single-molecule magnets (10^{-6} - 10^{-12} s), confirming that the observed slow relaxation behavior originates from the intrinsic paramagnetic property of the molecule. For the Dy^{3+} ion, as a Kramers ion, the Raman n parameter is theoretically expected to be 9. However, the experimentally obtained $n = 5.56$ is relatively lower, which is attributed to the under-barrier processes originating from the phonons in the spin-lattice.^{26, 194}

3.5.2 CASSCF calculations

To further elucidate the mechanism of magnetic relaxation dynamics in **Dy₄L₄**, complete active space self-consistent field (CASSCF) calculations based on the crystal structure (solvent molecules are excluded) are performed with OPENMOLCAS program package.¹⁹⁵⁻¹⁹⁷ Due to the symmetry of the structure, only two inequivalent sets of Dy^{3+} ions (Dy1 and Dy2) are present in the system and are calculated individually. To reliably evaluate the single-ion anisotropy, during the calculation of a given Dy^{3+} ion, the remaining three Dy^{3+} ions are replaced by Y^{3+} ions. The basis sets employed for all atoms are atomic natural orbitals taken from the MOLCAS ANO-RCC library: ANO-RCC-VTZP was assigned to the Dy^{3+} ion; ANO-RCC-VDZP to the coordinated N and O atoms; and ANO-RCC-VDZ to all other distant atoms. The calculations utilized the second-order Douglas-Kroll-Hess Hamiltonian to account for scalar relativistic contractions within the basis sets, while the spin-orbit coupling was handled via the restricted active space state interaction (RASSI-SO) procedure. For each Dy^{3+} fragment, active electrons in 7 active spaces include all f electrons (CAS (9 in 7)) in the CASSCF calculation. All the roots in the active space are calculated, and the maximum number of spin-free state which was possible with our hardware (all from 21 sextets, 128 from 224 quadruplets, 130 from 490 doublets) are mixed. The SINGLE_ANISO module was utilized to extract the energy levels, m_J values, magnetic axes g -tensors, etc., based on the CASSCF/RASSI-SO calculations.

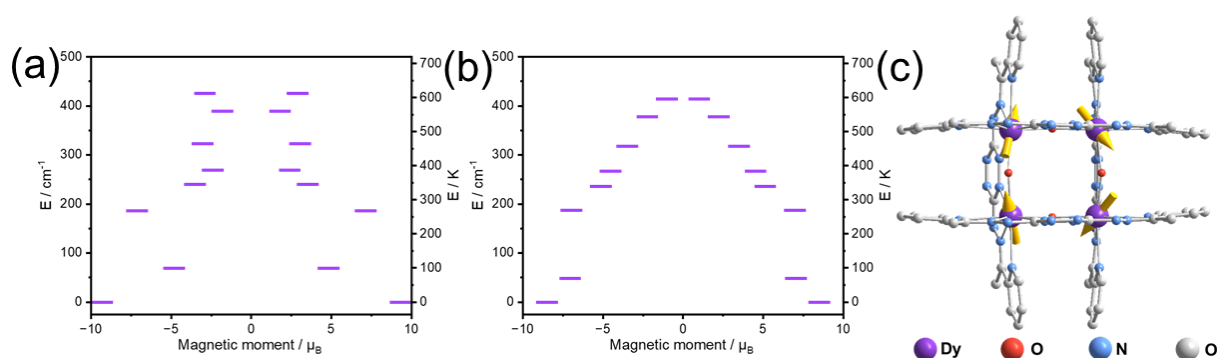


Figure 3.5.5 (a, b) The calculated energy diagram for the two Dy^{3+} fragments in **Dy₄L₄**. (c) The easy axes of magnetization on Dy^{3+} ions in **Dy₄L₄** (yellow arrows). Color code: Dy, purple; O, red; N, blue; C, grey.

Comparing the calculated Kramers doublet (KDs) energy levels of the two inequivalent Dy^{3+} ions and their corresponding magnetic moment arrangements reveals distinctly different energy distribution. The ground state of Dy1 displays a larger magnetic moment projection and a

relatively steeper anisotropic barrier compared with those of Dy2, indicating Dy1 possesses a relatively robust local SMM characteristic. However, Dy2 exhibits a denser arrangement of excited state energy levels, which typically anticipates severe state mixing and more accessible quantum tunneling of magnetization relaxations. More interestingly, the easy axes of the four Dy³⁺ ions are vortex-like arranged within the [2×2] grid plane, with two nearly colinear axes, generating a pseudo-triangular geometry (Figure 3.5.5b).

Table 3.5.1 Calculated $\mathbf{g}$ (g_x, g_y, g_z) tensors and wave functions with definite projection of the total moment $|m_J\rangle$ for the lowest two KDs of individual Dy³⁺ fragments for **Dy₄L₄**.

Dy1	$\mathbf{g}$ (g_x, g_y, g_z)	Wave functions*
1	0.015, 0.109, 18.646	85.4% ±15/2>+5.1% ±11/2>
2	0.066, 0.135, 17.005	19.8% ±13/2>+18.7% ±7/2>+16.5% ±5/2>+14% ±3/2> +11.6% ±9/2>+10.4% ±1/2>
3	0.960, 1.086, 14.790	67.6% ±13/2>+6.6% ±5/2>+6.5% ±1/2>+6.3% ±15/2> +5.8% ±3/2>
4	10.599, 8.205, 2.814	41.7% ±11/2>+14.9% ±9/2>+12.5% ±3/2>+11.9% ±1/2> +7.8% ±5/2>+7.6% ±7/2>
5	3.711, 5.614, 8.320	25.3% ±11/2>+18.2% ±9/2>+17.9% ±1/2>+15.4% ±7/2> +14% ±3/2>+7.7% ±5/2>
6	3.276, 3.897, 7.464	24.1% ±1/2>+23.7% ±9/2>+15.2% ±5/2>+11.8% ±7/2> +10.3% ±11/2>+7.9% ±3/2>+6.5% ±13/2>
7	0.633, 3.533, 7.478	31.5% ±3/2>+18.8% ±1/2>+16.5% ±9/2>+16.3% ±7/2> +9% ±5/2>+7.2% ±11/2>
8	1.451, 6.813, 13.374	35.3% ±5/2>+28.3% ±7/2>+13.4% ±3/2>+10.6% ±9/2> +9.8% ±1/2>
Dy2	$\mathbf{g}$ (g_x, g_y, g_z)	Wave functions*
1	0.007, 0.201, 17.002	54.3% ±15/2>+34.7% ±11/2>+6.9% ±7/2>
2	0.059, 0.255, 14.691	49.2% ±13/2>+36.7% ±9/2>+5.5% ±5/2>
3	1.475, 1.608, 14.051	34.9% ±15/2>+25.1% ±7/2>+19% ±11/2>+8.2% ±13/2> +5% ±3/2>
4	0.912, 3.761, 14.270	28.8% ±9/2>+20.5% ±13/2>+18.1% ±11/2>+13.1% ±7/2> +7.3% ±5/2>+7.1% ±1/2>
5	2.292, 3.824, 9.187	23.4% ±5/2>+21.5% ±7/2>+17.5% ±9/2>+11.9% ±13/2> +11.7% ±11/2>+10.5% ±3/2>
6	3.301, 4.409, 8.142	28.3% ±5/2>+20.8% ±7/2>+14.5% ±3/2>+9.8% ±1/2> +9.6% ±11/2>+8.3% ±9/2>
7	0.784, 4.007, 8.600	39.7% ±3/2>+26.7% ±5/2>+20.5% ±1/2>
8	1.220, 5.615, 14.541	59.4% ±1/2>+25.6% ±3/2>

*Only components with contribution over 5% are listed.

To quantitatively verify the aforementioned phenomena, the specific parameters extracted from the CASSCF calculations were further analyzed (Table 3.5.1). For the Dy1 center, the

KDs ground states are dominated by $M_J = \pm|15/2\rangle$ substates with 85.4% contribution. The g-tensor exhibits a strong axial characteristic ($g_z = 18.646$), close to the pure Ising-type Dy^{3+} ion. The first excited state (KD2) is located at 68.6 cm^{-1} , maintaining a reasonable gap with the ground state. However, the Dy2 center in a different coordination environment exhibits significant degradation of magnetic anisotropy. Its ground state undergoes severe wave function mixing, composed primarily of 54.3% $M_J = \pm|15/2\rangle$ substates and a substantial 34.7% $M_J = \pm|11/2\rangle$ substates. Such mixed states directly weaken its axial magnetism (g_z decreases to 17.002). More importantly, the energy level of the first excited state is significantly reduced to 47.8 cm^{-1} . These results suggest a fact that the absence of SMM behavior under a zero dc field is primarily due to the strong wave function mixing and the large transverse g component of the Dy2 central ground state, which significantly promotes QTM at zero field. As for the relatively high energy barrier values compared with the experimentally obtained energy barrier, this may be attributed to the under-barrier relaxation.²⁶

3.5.3 μ -SQUID measurement

To further investigate the magnetization relaxation dynamics of **Dy₄L₄** in the pure quantum region, where the thermal activation process is completely frozen, μ -SQUID measurements at extremely low temperatures are employed. Initially, the angular dependence map of **Dy₄L₄** is recorded to determine the easy axis of **Dy₄L₄**. Notably, the angular-resolved loops exhibit a spindle-shaped pattern corresponding to the magnetic switching, implying the toroidal arrangement.

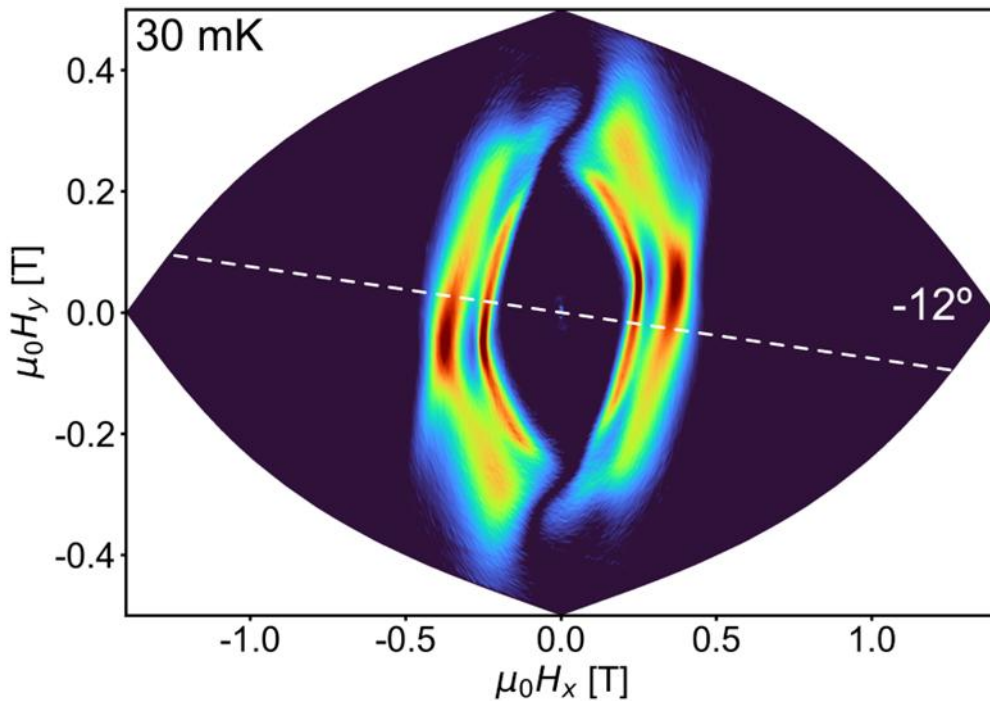


Figure 3.5.6 The angular dependence of the $M(H)$ loops, derived from mapping the corresponding dM/dH curves of **Dy₄L₄**. The dashed line highlights the direction of the easy axis of the crystal.

With the external field precisely aligned with the easy axis, the temperature-dependent and magnetic field sweep-rate-dependent hysteresis loop measurements at extremely low temperatures are conducted. Under a fixed magnetic field sweep rate of 16 mT/s, the temperature-dependent hysteresis loops (Figure 3.5.7a) illustrate a distinct dynamic evolution: As the temperature decreases, the hysteresis gradually opens. Furthermore, distinct steps arising from quantum tunneling are observable at 30 mK, indicating the relaxation mechanism is gradually transited from thermal-activated dominated relaxation to QTM-dominated relaxation. The magnetic field sweep-rate-dependent hysteresis loop at 30 mK (Figure 3.5.7b) reveals that as the rate increases, the step at around 0.25 T becomes steeper and more pronounced. Moreover, near the zero dc magnetic field (0 T), the magnetization of **Dy₄L₄** remains nearly unchanged, indicating that zero-field quantum tunneling is strongly suppressed. Conversely, the majority of magnetization reversals are severely delayed, occurring when the external magnetic field reaches the high field of approximately ± 0.25 T and ± 0.38 T. For better visualization, derivative analysis was performed on the hysteresis loops recorded at 30 mK under different magnetic field sweep rates. As illustrated, Figure 3.5.8a deviates from the symmetric distribution observed in TbPc₂, suggesting that these peaks are not simply associated with transitions between different nuclear spins. Particularly noteworthy is the pronounced sweep-rate dependence of the peak intensity at 0.25 T. Although 30 mK is insufficient to drive the thermal-activated process, the fast sweep rate introduces heating effect. According to the Landau-Zener model, a faster sweep rate results in less spin-flip, which is confirmed by the slight increase in quantum tunneling under zero field. However, the intensity of the dM/dH peak dramatically increases with the increasing sweep rate, strongly suggesting a thermally assisted quantum tunneling (TA-QTM) mechanism.

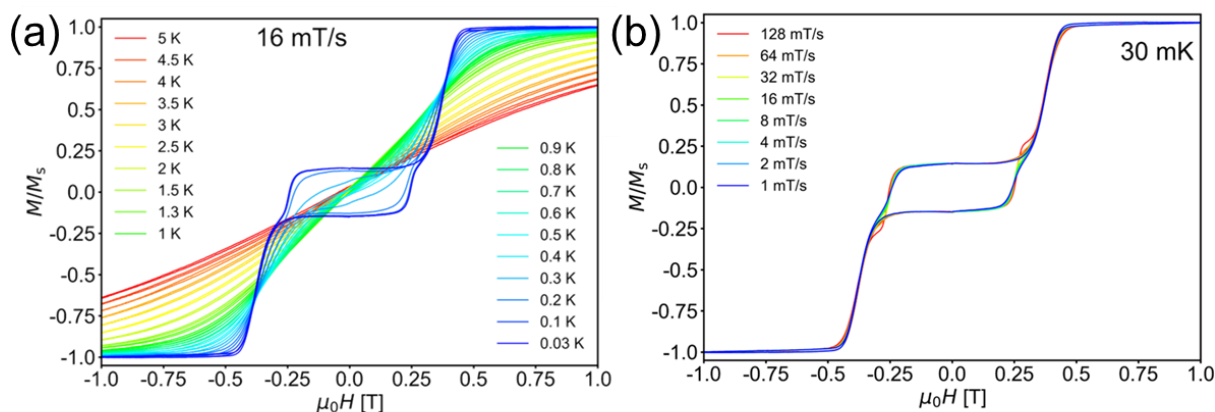


Figure 3.5.7 (a) The magnetic field sweep-rate-dependent hysteresis loops at 30 mK. (b) The temperature-dependent hysteresis loops with a fixed sweep rate of 16 mT/s.

Combined with the characteristics of the ideal single-molecule toroids and the observable symmetric peak at ± 0.38 T, it can be inferred that pseudo-triangular geometry of **Dy₄L₄** endows the system with antiferromagnetic toroidal ground states. When the applied magnetic field reaches ± 0.38 T, the introduced Zeeman energy is sufficient to overcome the strong magnetic dipole-dipole interactions within the molecule, resulting in energy level crossing, where

undergoes the QTM transition between antiferromagnetically coupled ground states and ferromagnetic excited states. To intuitively illustrate this complex magnetization relaxation dynamics, Zeeman diagram is required. However, it should be noted that, since the Dy in the measured **Dy₄L₄** consists of seven naturally abundant isotopes, it is difficult to accurately calculate its specific Zeeman energy level diagram. Therefore, the relaxation of **Dy₄L₄** is interpreted here based on the experimental results together with the Zeeman diagram of ideal single-molecule toroids complex.

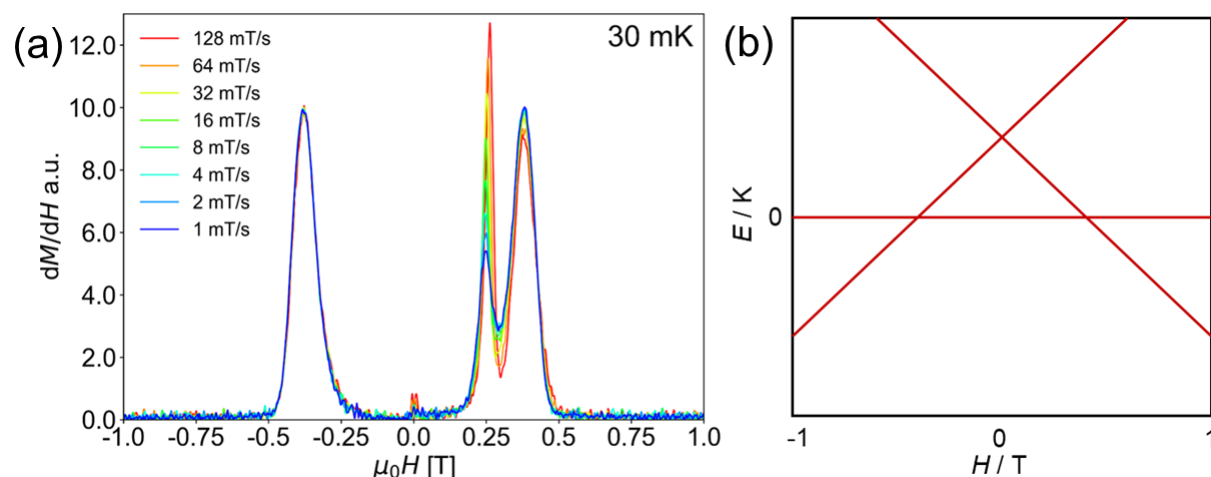


Figure 3.5.8 (a) The dM/dH plot corresponding to Figure 3.5.7b. (b) Simplified Zeeman diagram for ideal single-molecule toroids complex.

As illustrated in Figure 3.5.8, during the continuous magnetic field sweep at 30 mK from -1 T to 1 T, the avoided level crossings located at ± 0.38 T represent the quantum tunneling windows for the spins to tunnel into or out of the toroidal ground states, therefore exhibiting very weak dependence on the magnetic field sweep rate. When the magnetic field sweep rate increases, spin reversal lags behind the variation of the field, allowing more spin populations to remain in the ferromagnetic states and undergo zero-field quantum tunneling at near zero field, which corresponds to the steps at 0 T under high sweep rates. More importantly, the heating effect generated by the fast sweep rate enhances thermally assisted quantum tunneling of magnetization (TA-QTM),⁵³ thus exhibiting more pronounced peak at 0.25 T.

However, as mentioned before, although a reasonable explanation can be given, the role of nuclear spin remains unclear due to the mixed compositions of dysprosium. Especially the observed phenomena at low temperatures are all related to the quantum tunneling of magnetization. Thus, to fundamentally probe the role of the nuclear spin on the magnetic relaxation, isotope enrichment is necessary and of highly interest.

3.6 Magnetic properties of isotopologue $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$.

To address the isotope effect, specifically how the nuclear spin affects the magnetic behavior of toroidal-like SMM, ^{163}Dy and ^{164}Dy are selected for comparative investigation due to the slight mass difference and the different nuclear spin (^{164}Dy with $I = 0$ and ^{163}Dy with $I = 5/2$, hereafter denoted $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$, respectively). This part of the thesis is based on the published paper “Unconventional Nuclear-Spin-Dependent Toroidal Ground States in Isotopologue $^A\text{Dy}_4 [2 \times 2]$ Complexes”.¹⁹⁸

3.6.1 SQUID measurement

Before exploring the magnetic behavior dominated by quantum tunneling of magnetization, the magnetic properties of these two isotopologues in the temperature range of 300 K to 2 K are first compared. The dc magnetic susceptibility measurements of powder samples $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$ exhibit a similar temperature-dependent trend consistent with that of Dy_4L_4 (Figure 3.6.1a). The $\chi_M T$ values at room temperature are $56.4 \text{ cm}^3 \text{ K mol}^{-1}$ and $56.8 \text{ cm}^3 \text{ K mol}^{-1}$ for $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$, respectively, which are highly consistent with the theoretical values for four independent Dy^{3+} free ions ($56.68 \text{ cm}^3 \text{ K mol}^{-1}$). As the temperature drops below 50 K, the dramatically decrease in both $\chi_M T$ values is attributed to thermal depopulation of the excited Stark sublevels and the antiferromagnetic interactions. As the applied magnetic field increases, the magnetization of the system gradually increases and the experimental maximum are obtained at 2 K and 7 T ($23.1 N_A \mu_B$ for $^{164}\text{Dy}_4\text{L}_4$ and $23.0 N_A \mu_B$ for $^{163}\text{Dy}_4\text{L}_4$), indicating the ground states are of highly magnetic anisotropy.

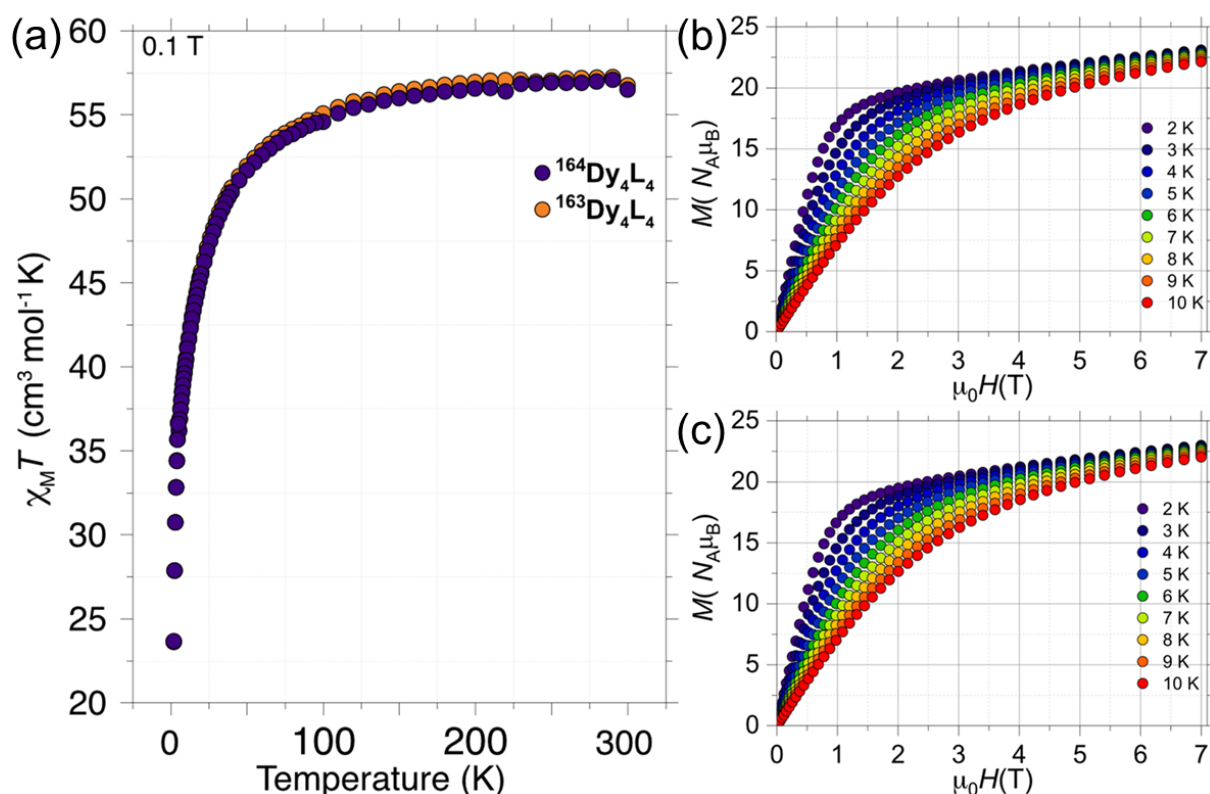


Figure 3.6.1 (a) The $\chi_M T$ versus T plots for $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$. And the variable temperature $M(H)$ data for (b) $^{164}\text{Dy}_4\text{L}_4$ and (c) $^{163}\text{Dy}_4\text{L}_4$.

The dynamic magnetic properties were further characterized by ac magnetic susceptibility measurements via SQUID. Again, although neither $^{164}\text{Dy}_4\text{L}_4$ nor $^{163}\text{Dy}_4\text{L}_4$ exhibits SMM behavior under zero magnetic field, the applied dc field induces slow magnetic relaxation, corresponding to the field-induced SMMs. Similarly, under an optimal dc field of 1400 Oe, clear and distinct signals of χ_M'' are observed in both isotopologues within the temperature range of 2-6.2 K. For $^{164}\text{Dy}_4\text{L}_4$, the maxima of out-of-phase component is located at approximately 8 Hz at 2 K, whereas that of $^{163}\text{Dy}_4\text{L}_4$ appears at a slightly higher frequency. As the temperature increases, the peaks in both cases rapidly shift toward the higher frequency region and reaches the upper frequency limit of SQUID at 6.2 K (Figure 3.6.2).

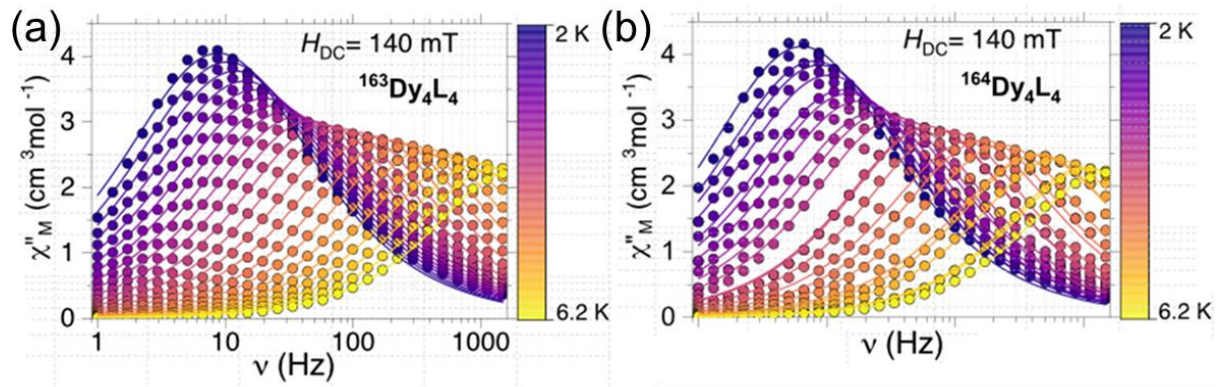


Figure 3.6.2 The experimental frequency-dependent ac magnetic susceptibility data at 1400 Oe optimal field and varied temperatures of out-of-phase for (a) $^{163}\text{Dy}_4\text{L}_4$ and (b) $^{164}\text{Dy}_4\text{L}_4$. The solid lines are the best fit using a generalized Debye model.

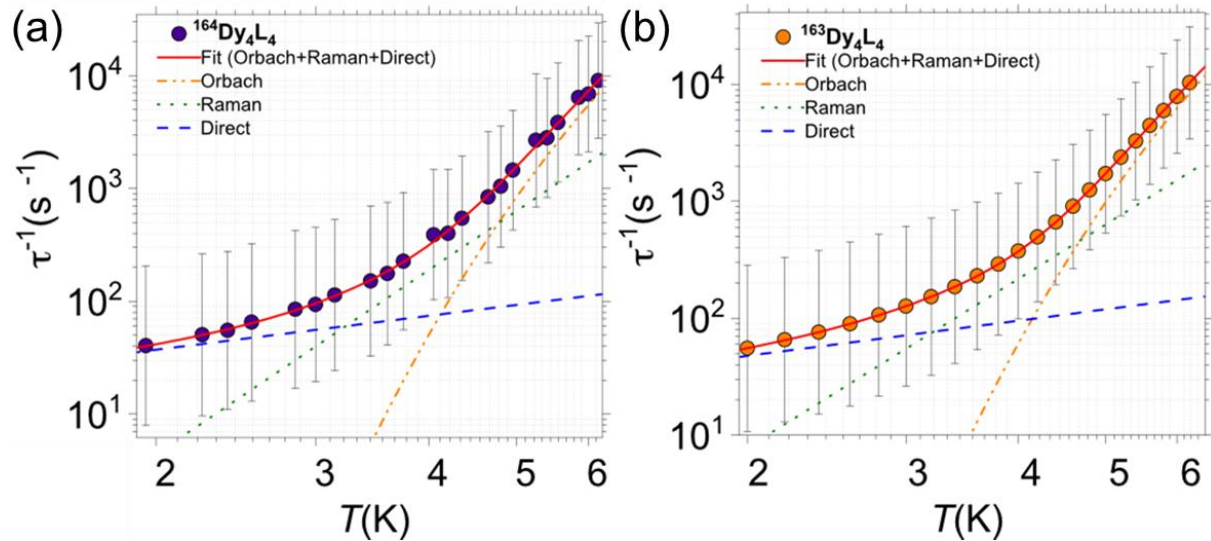


Figure 3.6.3 The temperature dependence of the relaxation time ($\tau(T)$) obtained from ac data for $^{164}\text{Dy}_4\text{L}_4$ (a) and (d) $^{163}\text{Dy}_4\text{L}_4$. The solid lines are the best fit to Equation 3.6.1.

Due to the relaxation is highly temperature-dependent, the QTM process is not considered in this temperature. Thus, to extract the temperature-dependent relaxation times, the χ_M' and χ_M''

are simultaneously fitted by a generalized Debye model containing the Orbach process, the Raman process, and the Direct process, using the following Equation:

$$\tau^{-1} = \tau_0^{-1} \exp(-U_{eff}/k_B T) + CT^n + AHT^2 \quad \text{Equation 3.6.1}$$

As illustrated in Figure 3.6.3, the best-fit parameters are $U_{eff} = 56(2)$ K, $\tau_0 = 1.5(6) \times 10^{-8}$ s, $C = 1(1) \times 10^{-1} \text{ s}^{-1} \text{ K}^{-n}$, $n = 5.4(5)$, and $A = 9.5(8) \times 10^2 \text{ s}^{-1} \text{ K}^{-2} \text{ T}^{-1}$, for $^{164}\text{Dy}_4\text{L}_4$. While $U_{eff} = 55(2)$ K, $\tau_0 = 1.5(6) \times 10^{-8}$ s, $C = 2.8(2) \times 10^{-1} \text{ s}^{-1} \text{ K}^{-n}$, $n = 4.8(1)$, and $A = 1.21(2) \times 10^3 \text{ s}^{-1} \text{ K}^{-2} \text{ T}^{-1}$ are obtained for $^{163}\text{Dy}_4\text{L}_4$. Overall, for isotopologue $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$, the differences in these fitted parameters are negligible, indicating that the isotope enrichment in dysprosium does not affect the magnetic relaxation dynamics of such system within this temperature range. As for the lower Raman n parameter compared with the theoretical value, this is due to the contribution of under-barrier processes.²⁶

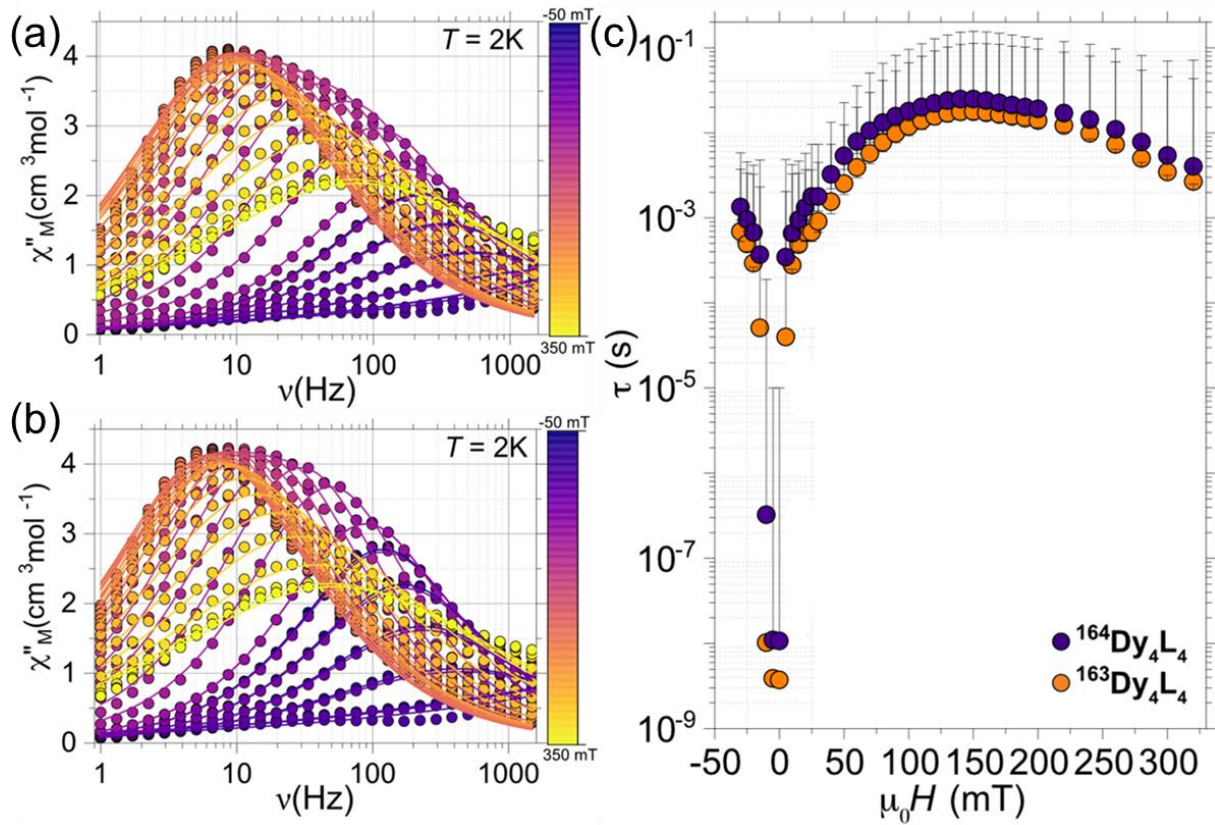


Figure 3.6.4 The experimental frequency-dependent ac magnetic susceptibility data at 2 K and varied magnetic field of out-of-phase for (a) $^{163}\text{Dy}_4\text{L}_4$ and (b) $^{164}\text{Dy}_4\text{L}_4$. The solid lines are the best fit using a generalized Debye model. (c) The field dependence of the relaxation time obtained from ac data.

Compared with other isotopologue systems, $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$ exhibit no significant differences in magnetic properties.^{19, 47} As shown in Figure 3.6.4, although $^{163}\text{Dy}_4\text{L}_4$ exhibits a slightly shorter relaxation time than that of $^{164}\text{Dy}_4\text{L}_4$ due to the fact that non-zero nuclear spin promotes quantum tunneling of magnetization, this difference is very small. Considering the relatively high temperature and the fact that the electronic energy levels defined by the local

crystal field environment is almost the same in both cases and dominate the magnetism, the effect induced by nuclear spin is nearly masked.

3.6.2 CASSCF calculations

Complete-active-space self-consistent field (CASSCF) calculations on the basis of single-crystal X-ray determined geometry, which are nearly identical (Figure 3.6.5a), have been carried out with the OpenMolcas program package.¹⁹⁵⁻¹⁹⁷ The CASSCF/SO-RASSI/SINGLE_ANISO studies were performed employing the experimentally determined structure of the corresponding compounds, with the ion of interest being Dy^{3+} , while the remaining three Dy^{3+} ions were replaced with Y^{3+} . The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Dy^{3+} ; VDZP for close N and O; VDZ for distant atoms. The calculations employed the second-order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were considered in the basis set, and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. Optimization of the molecular orbitals (MOs) was achieved by state-averaged CASSCF calculations. The active space of Dy^{3+} was defined by the nine 4f electrons in the seven 4f orbitals. Three calculations were carried out (RASSCF routine) with 21, 224, and 490 states for $S = 5/2$, $S = 3/2$, and $S = 1/2$, respectively. The CASSCF wavefunctions were subsequently mixed by spin-orbit coupling, employing the RASSI routine with all 21 states for $S = 5/2$ being included, while 128 and 130 states were included for $S = 3/2$ and $S = 1/2$. Lastly, the crystal field decomposition of the ground $J = 15/2$ multiplet of the $^6\text{H}_{15/2}$ term was executed with the SINGLE_ANISO module.

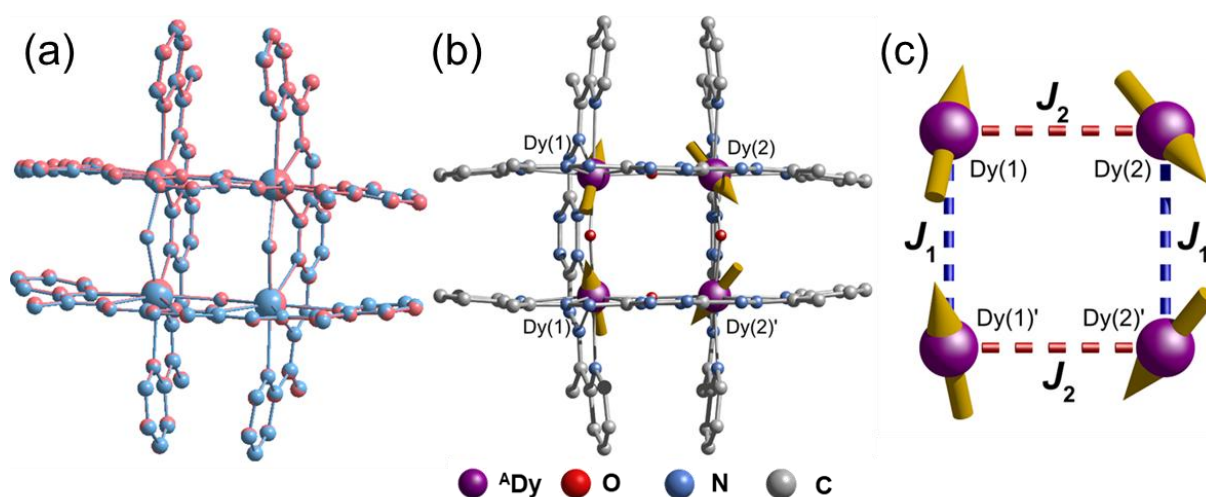


Figure 3.6.5 (a) The overlap molecular structures of $^{163}\text{Dy}_4\text{L}_4$ (pink) and $^{164}\text{Dy}_4\text{L}_4$ (blue). (b) CASSCF calculated anisotropy axes for the $^{163}\text{Dy}^{3+}$ ions in $^{163}\text{Dy}_4\text{L}_4$ (yellow arrows), viewed along the pseudo C_4 axis. (c) The model contains anisotropy axes and Dy...Dy interactions for the low-lying electronic structure simulation. Color code: $^{\text{A}}\text{Dy}$, purple; O, red; N, blue; C, grey.

Table 3.6.1 Calculated energy, g (g_x, g_y, g_z) tensors, and wave functions with definite projection of the total moment m_J ($>10\%$) for the lowest two KDs of individual Dy^{3+} fragments for $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$

$^{164}\text{Dy}(1)$ Energy(cm^{-1})	g_x, g_y, g_z	Wavefunction
0.0	0.0247, 0.2665, 16.9060	51.4% $ \pm 15/2\rangle$ +39.5% $ \pm 11/2\rangle$
45.6	0.0359, 0.3000, 14.6331	53.5% $ \pm 13/2\rangle$ +40.8% $ \pm 9/2\rangle$
179.3	1.1067, 1.3268, 14.7635	40.5% $ \pm 15/2\rangle$ +27.8% $ \pm 7/2\rangle$ +23.6% $ \pm 11/2\rangle$
222.5	10.3530, 8.1526, 2.4402	34.7% $ \pm 9/2\rangle$ +29.8% $ \pm 13/2\rangle$ +10.7% $ \pm 3/2\rangle$
251.2	3.8155, 4.0748, 9.6898	44.0% $ \pm 7/2\rangle$ +13.9% $ \pm 5/2\rangle$ +13.8% $ \pm 11/2\rangle$ +12.0% $ \pm 9/2\rangle$
308.7	2.0684, 4.3238, 7.6885	67.3% $ \pm 5/2\rangle$ +11.7% $ \pm 11/2\rangle$
374.4	2.7707, 3.6317, 9.4111	68.1% $ \pm 3/2\rangle$ +10.2% $ \pm 1/2\rangle$
$^{164}\text{Dy}(2)$ Energy(cm^{-1})	g_x, g_y, g_z	Wavefunction
0	0.0198, 0.1953, 17.3649	61.9% $ \pm 15/2\rangle$ +25.8% $ \pm 11/2\rangle$
52.0	0.0431, 0.2213, 15.0514	42.3% $ \pm 13/2\rangle$ +28.9% $ \pm 9/2\rangle$ +12.0% $ \pm 7/2\rangle$
182.9	1.4496, 1.6357, 13.9418	25.2% $ \pm 15/2\rangle$ +24.7% $ \pm 13/2\rangle$ +18.1% $ \pm 7/2\rangle$ +14.4% $ \pm 11/2\rangle$
224.5	0.8654, 3.0263, 15.5718	30.1% $ \pm 11/2\rangle$ +20.4% $ \pm 5/2\rangle$ +18.3% $ \pm 9/2\rangle$
258.5	1.8335, 3.6353, 10.2433	28.5% $ \pm 9/2\rangle$ +22.2% $ \pm 3/2\rangle$ +17.0% $ \pm 11/2\rangle$ +11.9% $ \pm 13/2\rangle$
306.1	3.3101, 4.7404, 8.5955	33.0% $ \pm 7/2\rangle$ +18.1% $ \pm 1/2\rangle$ +14.8% $ \pm 9/2\rangle$ +14.4% $ \pm 3/2\rangle$
366.5	0.8899, 3.3407, 9.9543	42.1% $ \pm 1/2\rangle$ +29.0% $ \pm 5/2\rangle$ +10.3% $ \pm 7/2\rangle$
$^{163}\text{Dy}(1)$ Energy(cm^{-1})	g_x, g_y, g_z	Wavefunction
0.0	0.0246, 0.2814, 16.7814	50.3% $ \pm 15/2\rangle$ +39.9% $ \pm 11/2\rangle$
44.3	0.0341, 0.3134, 14.3939	50.8% $ \pm 13/2\rangle$ +43.4% $ \pm 9/2\rangle$
175.1	1.7796, 2.2779, 13.5167	37.0% $ \pm 15/2\rangle$ +30.2% $ \pm 7/2\rangle$ +19.2% $ \pm 11/2\rangle$
205.2	0.0270, 2.1646, 16.1502	29.8% $ \pm 7/2\rangle$ +26.8% $ \pm 9/2\rangle$ +15.2% $ \pm 13/2\rangle$
243.9	0.8886, 3.0669, 11.3543	29.9% $ \pm 5/2\rangle$ +24.3% $ \pm 13/2\rangle$ +18.0% $ \pm 7/2\rangle$ +12.1% $ \pm 9/2\rangle$
289.1	3.2810, 5.5553, 8.7577	49.5% $ \pm 5/2\rangle$ +17.1% $ \pm 11/2\rangle$
347.0	0.1760, 3.2144, 10.5426	68.0% $ \pm 3/2\rangle$
$^{163}\text{Dy}(2)$ Energy(cm^{-1})	g_x, g_y, g_z	Wavefunction
0.0	0.0216, 0.1549, 17.7594	68.4% $ \pm 15/2\rangle$ +21.0% $ \pm 11/2\rangle$
59.9	0.0165, 0.1554, 15.4499	41.3% $ \pm 13/2\rangle$ +25.8% $ \pm 9/2\rangle$ +13.3% $ \pm 7/2\rangle$
188.8	0.8684, 1.0760, 14.5103	33.6% $ \pm 13/2\rangle$ +21.7% $ \pm 15/2\rangle$ +17.3% $ \pm 11/2\rangle$ +10.8% $ \pm 7/2\rangle$
235.8	1.7218, 4.1301, 14.3493	36.1% $ \pm 11/2\rangle$ +16.9% $ \pm 9/2\rangle$ +13.6% $ \pm 5/2\rangle$ +13.0% $ \pm 7/2\rangle$
270.3	1.5916, 4.8073, 9.3753	35.9% $ \pm 9/2\rangle$ +16.8% $ \pm 11/2\rangle$ +15.2% $ \pm 3/2\rangle$ +13.5% $ \pm 5/2\rangle$
328.4	7.5032, 5.5247, 2.4945	34.2% $ \pm 7/2\rangle$ +24.8% $ \pm 3/2\rangle$ +14.0% $ \pm 9/2\rangle$ +13.9% $ \pm 1/2\rangle$
395.1	1.5223, 3.2584, 10.2206	42.5% $ \pm 1/2\rangle$ +32.9% $ \pm 5/2\rangle$ +13.6% $ \pm 7/2\rangle$

CASSCF calculations reveal that the electronic structures of Dy^{3+} ions are quite similar in $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$. The ground doublets in both isotopologues are primarily dominated by $m_J = \pm|15/2\rangle$ and $m_J = \pm|11/2\rangle$ substates ($51.4\% \pm|15/2\rangle + 39.5\% \pm|11/2\rangle$ and $61.9\% \pm|15/2\rangle + 25.8\% \pm|11/2\rangle$ for $^{164}\text{Dy}_4\text{L}_4$, and $50.3\% \pm|15/2\rangle + 39.9\% \pm|11/2\rangle$ and $68.4\% \pm|15/2\rangle + 21.0\% \pm|11/2\rangle$ for $^{163}\text{Dy}_4\text{L}_4$, respectively), aligns with the pronounced magnetic anisotropy and the magnetization values observed in magnetic measurement for both isotopologues.

For both complexes, the first excited states are situated at above 45 cm^{-1} . Moreover, the calculated g -tensors exhibit pronounced axiality that $g_z \geq 16$ and relatively small transverse components ($g_x < g_y < 0.29$).

Structurally, for both isotopologue $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$, the local magnetic anisotropy axes of each Dy^{3+} ions are arranged in a noncollinear and toroidal-like configuration within the $[2 \times 2]$ grid. Specifically, the axes associated with Dy(2) and Dy(2') exhibit the most significant tilting angles, whereas the axes of Dy(1) and Dy(1') are nearly collinear and aligned with the crystallographic a -axis (Figure 3.6.5b,c). This specific spatial orientation of the anisotropy axes is pivotal in defining the overall symmetry and addressing the nuclear spin effect on the magnetic relaxation of $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$ (*vide infra*).

3.6.3 μ -SQUID measurement

Although the nuclear spin of lanthanide elements is expected to significantly influence the relaxation dynamics of SMMs, its experimental manifestation strongly depends on the accessible temperature range relative to the blocking temperature. Therefore, only very subtle differences were observed in conventional SQUID measurements. To explore the nuclear spin effect on QTM, μ -SQUID measurements on microcrystals at sub-kelvin temperatures are employed.^{164, 165} Considering the sensitivity of single-molecule toroids to the direction of magnetic field, the magnetic easy axes of $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$ are determined by transverse magnetic field mapping combined with derivative angle diagrams and make sure the μ SQUID measurements are performed along the crystallographic b and c planes, which is confirmed by the analysis of the angular maps (Figure 3.6.6).¹⁹⁹

Intriguingly, the angular dependence maps exhibit a pronounced hexagonal pattern in both isotopologues, reminiscent of toroidal triangular arrangements, originating from the magnetic switching between spin-flip states and toroidal states at the quantum tunneling of magnetization crossings. The magnetic sweep-rate-dependent μ -SQUID measurements exhibit robustly open hysteresis loops for both $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$ at 30 mK (Figure 3.6.7a,b). The observation that increasing the magnetic sweep rate from 128 mT s^{-1} to 0.5 mT s^{-1} induces only slight change in the opening of hysteresis loops underscores the slow relaxation and long relaxation time in this temperature, which is nearly temperature-independent. Furthermore, as shown in Figure 3.6.7c,d, with a fixed magnetic sweep rate of 16 mT s^{-1} , the hysteresis loops remain open up to $\sim 400\text{ mK}$, while completely close at higher temperature, indicating the transition from QTM-dominated relaxation to thermal-activated dominated relaxation.

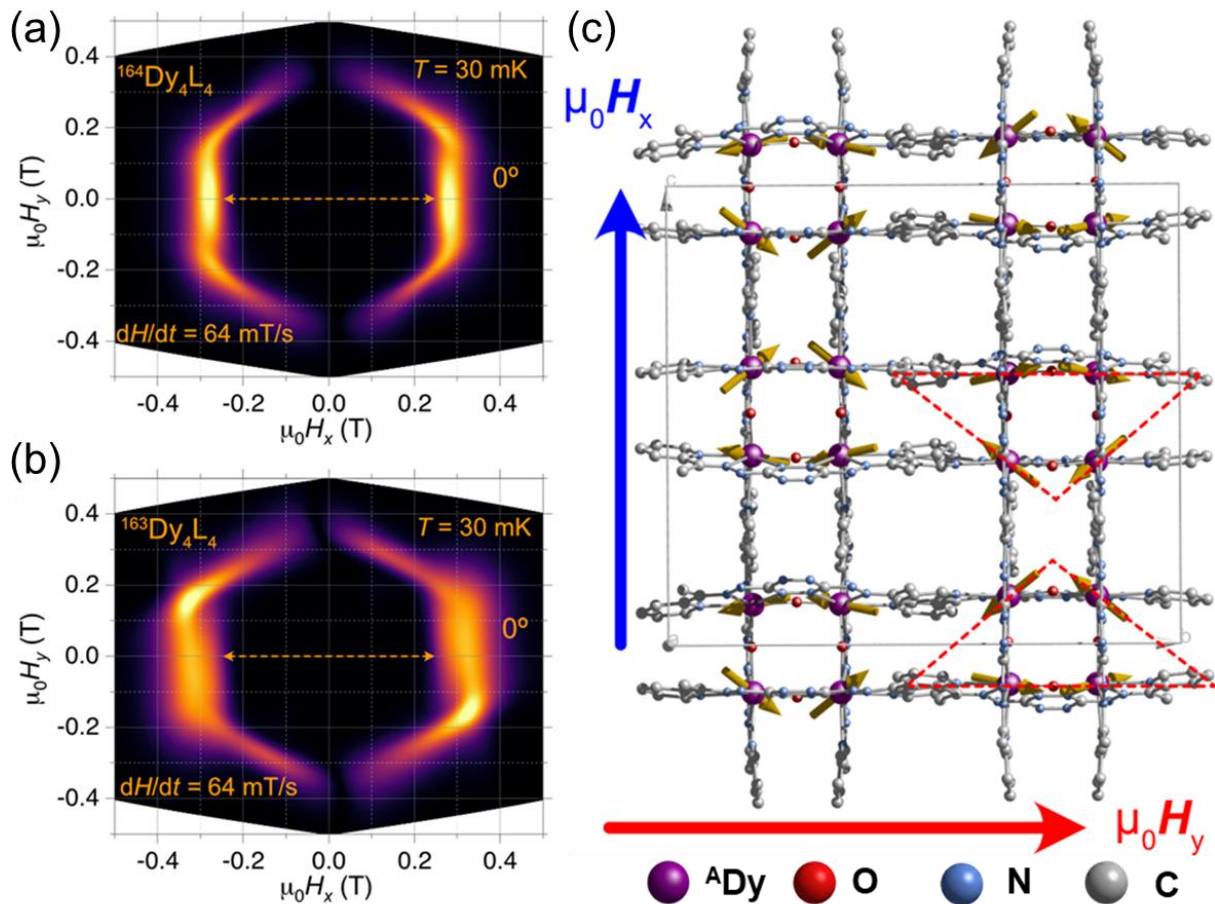


Figure 3.6.6 The angle dependence of the hysteresis loops obtained by mapping the corresponding derivatives dM/dH for (a) $^{164}\text{Dy}_4\text{L}_4$ and (b) $^{163}\text{Dy}_4\text{L}_4$. (c) The molecular packing within the unit cell. The red and blue arrows represent the direction of magnetic field for μ -SQUID measurements. The dashed arrows represent the nearly triangular arrangement of the Dy^{3+} vectors. Color code: ^{164}Dy , purple; N, blue; O, red; C, grey. Hydrogens are omitted for clarity.

Such open, S-shaped butterfly hysteresis loops for both isotopologues indicates the toroidal ground states and the antiferromagnetic coupling between Dy^{3+} ions. The inflection points extracted from the hysteresis loops are determined to be ± 0.28 T for $^{164}\text{Dy}_4\text{L}_4$ and ± 0.32 T for $^{163}\text{Dy}_4\text{L}_4$, allowing the quantitative estimation of the internal exchange field by utilizing the equation:

$$H_{ex} = -J_{ex}m_J/g_J\mu_B \quad \text{Equation 3.6.2}$$

Where, for Dy^{3+} ion, $m_J = 15/2$ and $g_J = 4/3$. The derived exchange parameters (J_{ex}) are 0.012 cm^{-1} (-17 mK) and -0.013 cm^{-1} (-19 mK) for $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$, respectively. These two close values exceed the theoretical predicted value for the purely dipolar model with pure $m_J = 15/2$ states, suggesting a significant exchange contribution (see Appendix).

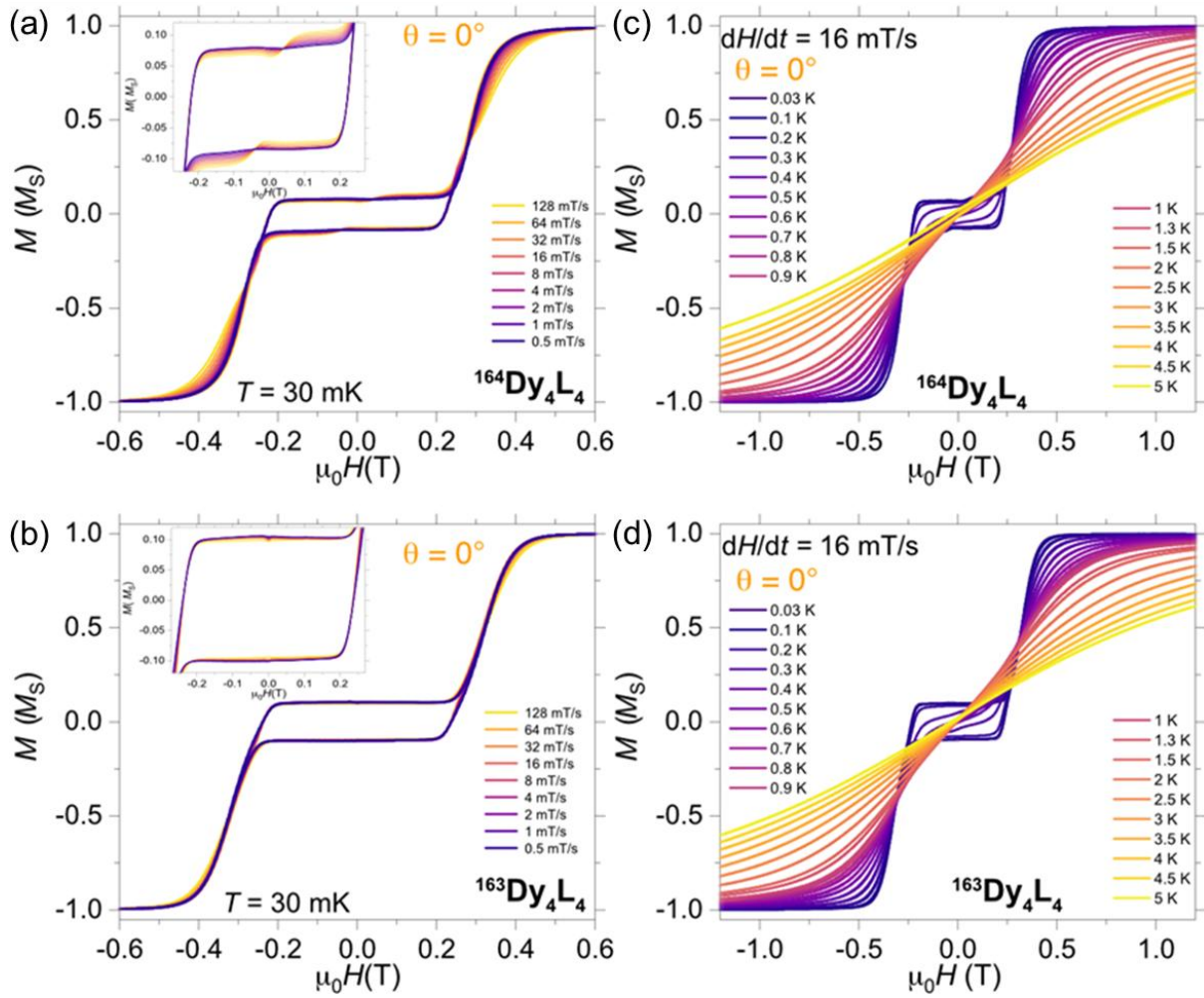


Figure 3.6.7 The magnetic sweep-rate-dependent hysteresis loops at 30 mK for $^{164}\text{Dy}_4\text{L}_4$ (a) and $^{163}\text{Dy}_4\text{L}_4$ (b). The insets display the zoom view of the opening of the hysteresis loops. And the temperature-dependent hysteresis loops with a fixed sweep rate of 16 mT/s for $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$.

Despite the overall similarities, the differences in the magnetic relaxation behavior induced by isotopes are still observable. Compared with $^{163}\text{Dy}_4\text{L}_4$, the angular dependence maps for $^{164}\text{Dy}_4\text{L}_4$ exhibit much sharper transitions. This contrast is attributed to the absence of hyperfine interactions (for $^{164}\text{Dy}^{3+}$, $I = 0$), resulting in a narrow window for quantum tunneling. Another difference is observed in the hysteresis loop opening: $^{163}\text{Dy}_4\text{L}_4$ possesses much larger opening ($0.10 M_S$ for $^{163}\text{Dy}_4\text{L}_4$ versus $0.08 M_S$ for $^{164}\text{Dy}_4\text{L}_4$), which is unconventional trend that deviating from previous work on lanthanide isotope-enriched complexes. Furthermore, $^{164}\text{Dy}_4\text{L}_4$ exhibit more pronounced sweep-rate dependent, and deviating from the expectations in previous natural Dy_4L_4 system, the subtle step around zero field only appears in $^{164}\text{Dy}_4\text{L}_4$. These difference, though seemingly subtle, indicates crucial role of nuclear spin in QTM.

The magnetization decay curves are investigated in the temperature range of 30-400 mK by sweeping from the saturation field to the zero field. Figure 3.6.8 presents the normalized decay profiles for $^{164}\text{Dy}_4\text{L}_4$ and $^{163}\text{Dy}_4\text{L}_4$, where τ_{01} is the zero-field QTM time (τ_{QTM}) and τ denotes the relaxation time. By analyzing the intersection of these curves, striking and counterintuitive

isotopic differences are clearly observed: the nuclear-spin-free $^{164}\text{Dy}_4\text{L}_4$ relaxes much faster than $^{163}\text{Dy}_4\text{L}_4$ ($I = 5/2$). Notably, the blue curve of $^{163}\text{Dy}_4\text{L}_4$ exhibits almost no change in magnetization during the 2 hours waiting time. The magnetic data are extracted, and fitted by Orbach-like, Raman, and QTM processes using following equation:

$$\tau^{-1} = \tau_0^{-1} \exp(-\Delta_A/k_B T) + CT^n + \tau_{QTM}^{-1} \quad \text{Equation 3.6.3}$$

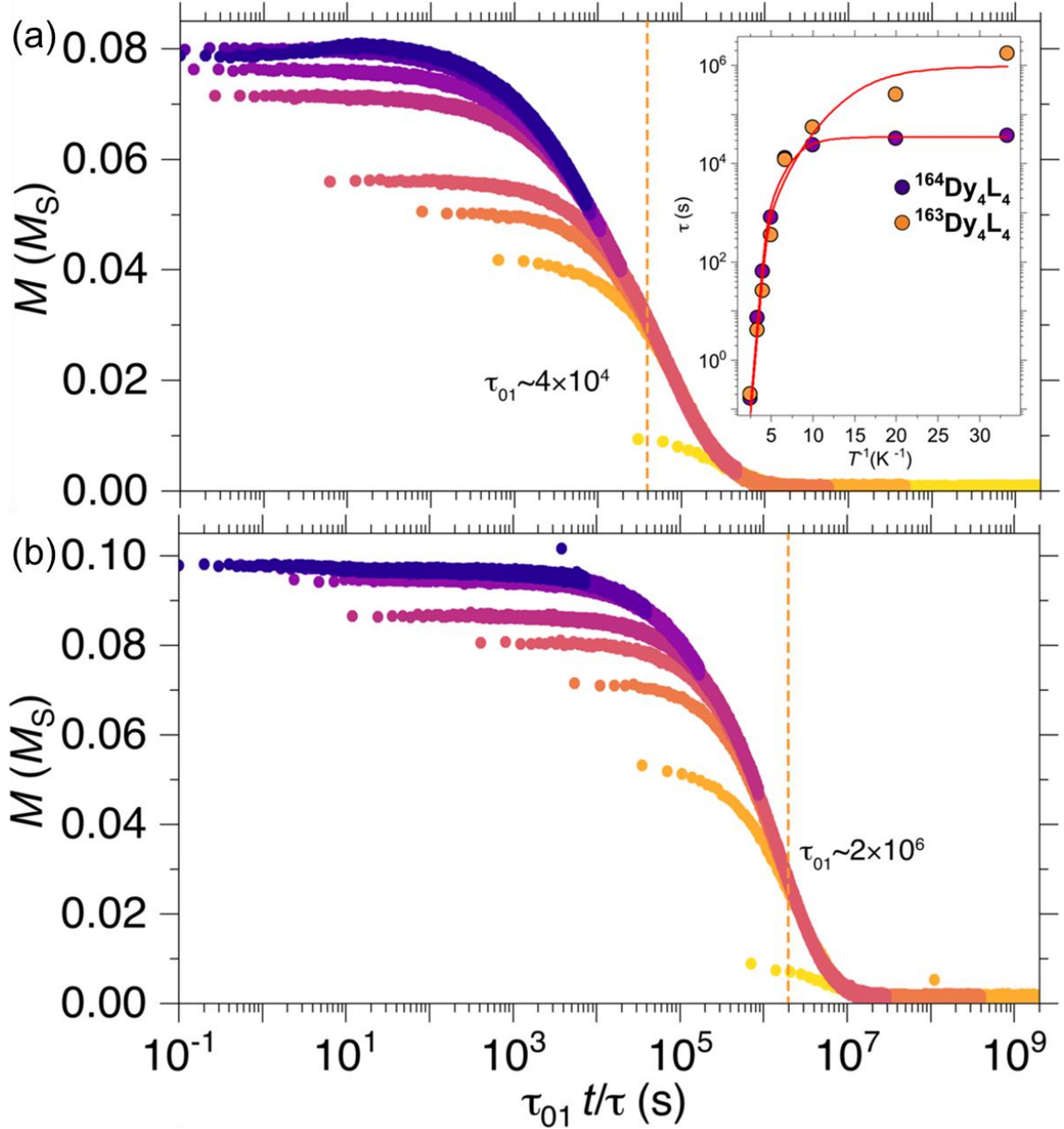


Figure 3.6.8 The magnetization decay curves obtained by sweeping the magnetic field from the saturation field to the zero field in the temperature range from 30 mK to 400 mK for (a) $^{164}\text{Dy}_4\text{L}_4$ and (b) $^{163}\text{Dy}_4\text{L}_4$. The inset: temperature-dependent relaxation time for both isotopologues.

The fitted parameters are $\Delta_A = 4.7(3)$ K, $\tau_0 = 9(3) \times 10^{-7}$ s, $C = 5(1)$ s⁻¹ K⁻ⁿ, $n = 5.6(1)$, and $\tau_{\text{QTM}} = 4(4) \times 10^4$ s for ¹⁶⁴Dy₄L₄; while $\Delta_A = 4.6(4)$ K, $\tau_0 = 9(3) \times 10^{-7}$ s⁻¹, $C = 4(2)$ s⁻¹ K⁻ⁿ, $n = 5.1(3)$, and $\tau_{\text{QTM}} = 2(2) \times 10^6$ s for ¹⁶³Dy₄L₄. It is noteworthy that, in ¹⁶³Dy₄L₄, there is a slight deviation between the fitting curve and the experimental data, which may be attributed to the thermal-activated QTM, especially the relaxation time of QTM is large. In contrast, such difference is nearly absent in ¹⁶⁴Dy₄L₄, where the intrinsically more efficient zero field QTM strongly suppresses the thermal contribution.

Previous works suggest that the rates of quantum tunneling of magnetization of individual electronic states should be insensitive to nuclear spin due to the fact that hyperfine interactions do not introduce the transverse components for mixing the electronic manifold. On the other hand, hyperfine splitting induces multiple channels for tunneling, thereby widening the QTM windows and enhancing relaxation. However, opposite phenomenon is observed here. As mentioned before, due to the purely isotope enrichment, a quantitative comparison of $I = 0$ and $I = 5/2$ via Zeeman diagrams is feasible to reveal this unconventional difference. Since the dominant QTM events do not occur at zero field but are located at approximately ± 0.28 T, thus, the hyperfine interactions promote the population of spin to transit into the toroidal state near the avoided crossings.

To elucidate the magnetic behavior at low temperature for ¹⁶³Dy₄L₄ and ¹⁶⁴Dy₄L₄, the low-lying electronic states are modeled by using effective spin formalism, which is justified by the thermal population of only the lowest states within the temperature range and the strong axuality of the Dy³⁺ ions. However, the model with effective $S_{\text{eff}} = 1/2$ is highly sensitive to the transverse magnetic field components, resulting in an unreliable tunnel splittings. Moreover, a full Hamiltonian diagonalization, containing crystal-field parameters derived by CASSCF, nuclear spins, four Dy³⁺ ions, and Euler rotations, demands immense Hilbert spaces. The dimensions reach approximately 6×10^4 and 8×10^6 for ¹⁶⁴Dy₄L₄ and ¹⁶³Dy₄L₄, respectively, presenting a formidable computational challenge.

To circumvent these computational constraints, a simplified model is adopted, where the employed fictitious spin of $S = 3/2$ together with the large axial zero-field splitting of $D = -100$ cm⁻¹ yield a well-isolated ground doublet and minimize the transverse mixing. Within this model, the g-tensors is assumed isotropic, namely $g_{xx} = g_{yy} = 0$, $g_{zz} = 20/3$; while the local anisotropy axes are determined by the Euler angles and the electrostatic analysis. Under these assumptions, considering the absence of nuclear spin effects due to $I = 0$, the Hamiltonian for ¹⁶⁴Dy₄L₄ can be expressed as:

$$\begin{aligned} {}^{164}\text{Dy}_4\hat{H} = & \sum_{i=1}^4 \mu_B \mathbf{H}^T \mathbf{g}_i \hat{\mathbf{S}}_{i\text{Dy}} + h D_i (\hat{S}_{zi,\text{Dy}}^2 - S_i(S_i + 1)/3) - h_2 \sum_{\langle i,j \rangle_{\text{short}}} J_1 S_i \cdot S_j \\ & - h_2 \sum_{\langle i,j \rangle_{\text{long}}} J_2 S_i \cdot S_j \end{aligned}$$

Equation 3.6.4

In the Equation 3.6.4, the first term donates the Zeeman interaction; the second term represents axial zero-field splitting; the third term accounts for the exchange interactions along the short edges, which are Dy(1)···Dy(1') and Dy(2)···Dy(2') with 4.1733(7) Å for $^{163}\text{Dy}_4\text{L}_4$ and 4.1860(1) Å for $^{164}\text{Dy}_4\text{L}_4$; and the fourth term is the long-edged exchange interactions, which are Dy(1)···Dy(2') and Dy(1')···Dy(2) with 4.2078(6) Å for $^{163}\text{Dy}_4\text{L}_4$ and 4.2196(6) Å for $^{164}\text{Dy}_4\text{L}_4$.

By incorporating two distinct exchange couplings, an optimal fit to the experimental data is achieved, where ferromagnetic interactions ($J_1 = +0.55 \text{ cm}^{-1}$) along the short edges and antiferromagnetic interactions ($J_2 = -0.33 \text{ cm}^{-1}$) along the long edges (Figure 3.6.9). These parameters effectively reproduce the energy level crossing at $\pm 0.28 \text{ T}$ along both the $\mu_0 H_x$ and $\mu_0 H_y$ directions, corresponding to the transition of QTM between the antiferromagnetically coupled ground states and the ferromagnetic excited states.

As for $^{163}\text{Dy}_4\text{L}_4$, the nonzero nuclear spin ($I = 5/2$) introduces hyperfine interactions between the nuclear spins and the electronic spins. To address the nuclear spin effect, the Hamiltonian should include the nuclear quadrupolar term and the hyperfine interaction, thus, expressed as:

$$^{163}_{\text{Dy}}\hat{H} = ^{164}_{\text{Dy}}\hat{H} + \sum_{i=1}^4 A_{\text{hyp}} \mathbf{I}^i \cdot \boldsymbol{\sigma}_i + P_{\text{quad}} I_z^i I_z^i \quad \text{Equation 3.6.5}$$

Where A_{hyp} is the hyperfine interaction and P_{quad} represents the nuclear quadrupolar term.

However, the introduction of nuclear spin dramatically increases the Hamiltonian, where the Hilbert spaces are enlarged to $(2S+1)^4 \cdot (2I+1)^4 \approx 8 \times 10^6$ states, making it difficult to complete full diagonalization. A reasonable approach is to assign each Dy^{3+} ion to a pseudo-nuclear spin of $I = 1/2$, and then qualitatively evaluate the nuclear spin effects by diagonalizing the simplified model. Based on the hyperfine coupling constant and the exchange parameters J_1 and J_2 derived from $^{164}\text{Dy}_4\text{L}_4$, the Zeeman diagram for $^{163}\text{Dy}_4\text{L}_4$ is plotted as Figure 3.6.9b.

By combining the experimental and theoretical results, the unconventional magnetic behaviors of $^A\text{Dy}_4\text{L}_4$ can be rationalized.

For both isotopologues, the angular-dependent maps reveal pronounced hexagonal pattern, which is characteristic of toroidal arrangement and generates diamagnetic-like hysteresis loops. CASSCF calculations indicate the local anisotropy axes for four $^A\text{Dy}^{3+}$ ions are inequivalent. Specifically, the easy axes of $^A\text{Dy}(1)$ and $^A\text{Dy}(1')$ are nearly colinear, overall generating a pseudo-triangular geometry (Figure 3.6.6c). In conjunction with $^A\text{Dy}-^A\text{Dy}$ exchange coupling, pseudo-toroidal ground states are stabilized. Based on this, for both isotopologues, the initial -1.4 T magnetic field populates a ferromagnetic-like excited state, which is spin-flip states. As the applied field reaches approximately -0.28 T, the spins flip through QTM, resulting in population trapping in the toroidal ground states until +0.28 T, where the spins transit back to the spin-flip states.

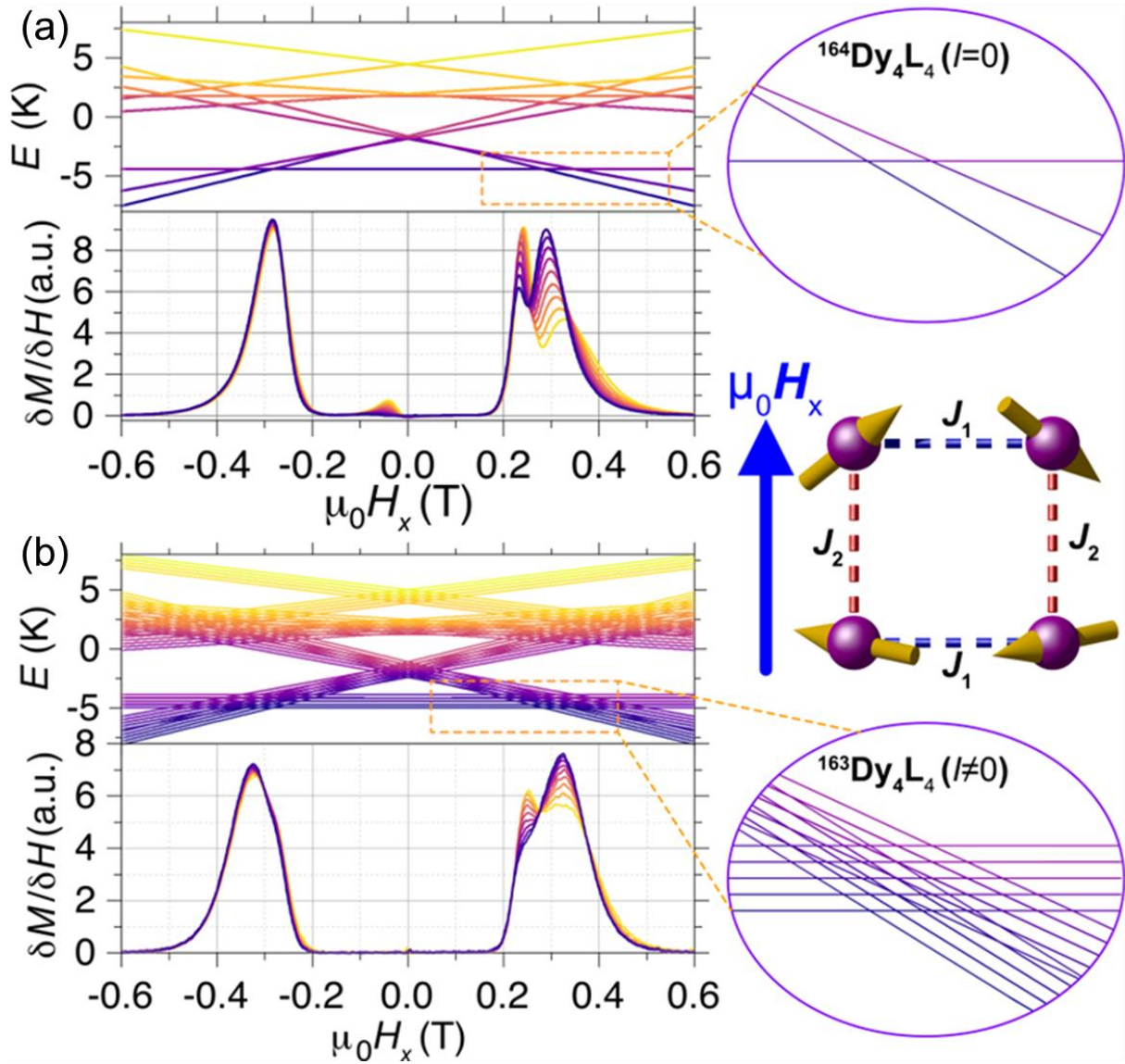


Figure 3.6.9 The Zeeman diagram and the dM/dH plots corresponding the magnetic sweep-rate- dependent at 30 mK for (a) $^{164}\text{Dy}_4\text{L}_4$ and (b) $^{163}\text{Dy}_4\text{L}_4$. The zoom views highlight the electronic crossing for $^{164}\text{Dy}_4\text{L}_4$ and the hypothetical $^{163}\text{Dy}_4\text{L}_4$ case, respectively.

The predominant single-ion anisotropy, exhibiting Ising-like behavior, constrains the Dy^{3+} spins to only flip exclusively along their local easy axes. Within the pseudo-triangular geometry, these easy axes align along three distinct orientations, thus constructing the hexagonal pattern in the angular dependence maps. The line width of the hexagon indicates the magnetic field range where the resonant QTM occurs. As shown in Figure 3.6.6b, the broadened linewidth signifies the more active QTM events, which may be attributed to multiple QTM pathways generated by the hyperfine interactions. The hyperfine interactions split the single avoided crossing into $(2I+1)^4$ manifold spread over ± 0.2 T around ± 0.28 T. Such dense window makes it more efficiently to tunnel into the toroidal ground state.

While nonzero nuclear spin splits the crossing for zero-field QTM into multiple non-zero-field positions, when spin reversal is only allowed at conserved nuclear spin crossings, the total probability of tunneling remains equivalent to that of a $I = 0$ system. Another explanation is,

the quadrupole terms facilitate the mixing of transverse fields, thereby enabling non-conserved nuclear spin crossings, where these additional channels serve to enhance the overall relaxation. The dM/dH plots of sweep-rate-dependent hysteresis loops confirms this argument: in $^{164}\text{Dy}_4\text{L}_4$, as the magnetic field-sweep rate slows, thermal processes assist the QTM at ± 0.28 T, while the same phenomena is not observed in $^{163}\text{Dy}_4\text{L}_4$.

Crucially, the energy scales associated with hyperfine splitting are exceedingly small, facilitating coupling only with low-energy phonons. However, at 30 mK, these phonons are effectively frozen. Considering the slower relaxation of $^{163}\text{Dy}_4\text{L}_4$ and the fact that isotope effects occur in a temperature range where relaxation is almost independent of temperature, the relaxation behavior is not governed by phonon-mediated processes.

In an ideal single-molecule toroids system, due to the perfect cancellation of in-plane magnetic moments, the system is magnetically silent. However, the subtle out-of-plane tilting in $^A\text{Dy}_4\text{L}_4$ system generates a weak but detectable moment, which is crucial for detecting the toroidal moments.

The tunneling efficiency of the population transition between the ferromagnetic excited states and the toroidal ground states depends on the density of tunneling channels. In $^{164}\text{Dy}_4\text{L}_4$, due to the zero nuclear spin, the single sharp crossing offers limited opportunities for population transfer. Consequently, a significant fraction of spins remains in spin-flip states. These remaining population undergo faster relaxation due to the enhanced under-barrier processes, which is confirmed by the small step near zero field and shorter relaxation time. Conversely, in $^{163}\text{Dy}_4\text{L}_4$, the hyperfine splitting generates a much dense window for tunneling, promoting the transition into the toroidal ground state as shown in Figure 3.6.9b, thus, resulting in the larger hysteresis opening and slower zero-field dynamics. In this case, the stabilized pure toroidal ground states result in a two-order-of-magnitude increase in the zero-field tunneling time at 30 mK, which is attributed to the profound suppression of many-body tunneling.²⁰⁰

The temperature-dependent relaxation times at low temperature further reinforce the difference between isotopologues. In $^{163}\text{Dy}_4\text{L}_4$, the predominant population of the toroidal ground state exerts a profound suppression on zero-field QTM, leading to a longer τ_{QTM} and revealing the contributions of thermal-assisted tunneling. Conversely, in $^{164}\text{Dy}_4\text{L}_4$, the zero-field QTM originating from spin-flip pathways reduces the τ_{QTM} , therefore lowering the demand for thermal-assisted mechanism. Collectively, these results underscore the crucial role of hyperfine interactions: the population trapping in the toroidal ground state is enhanced by opening additional relaxation channels, ultimately promoting slow zero-field magnetic relaxation in the toroidal systems.

3.7 Conclusion

In conclusion, we have successfully synthesized a series of lanthanide grid complexes and dysprosium isotope-enriched **Dy₄L₄**.

The combined magnetic experiments and theoretical calculations reveal how the nuclear spin profoundly and unconventionally influence magnetic dynamics of **Dy₄L₄** grid single-molecule magnets at the low-temperature.

Contrary to expectations, nuclear spins do not always accelerate the zero-field relaxation but instead may facilitate hyperfine-induced population trapping into the toroidal ground states, eventually exhibiting slower zero-field dynamics and larger openings for ¹⁶³**Dy₄L₄**. This behavior originates from the dense manifold of hyperfine-split tunneling channels, which promotes population transfer into the toroidal ground state and stabilizes it over an extended magnetic field range. The temperature- and sweep-rate dependent measurements further underline the distinct relaxation mechanisms, pointing to a nuclear spin-driven onset of thermally assisted QTM.

Overall, these results first demonstrate that nuclear spins can exert a constructive influence on the toroidal single-molecule magnets. By enhancing hyperfine-mediated population trapping, they offer an additional lever for controlling magnetic relaxation in low-temperature and the quantum dynamics of magnetic molecules. This work situates isotopically enriched toroidal lanthanide assemblies as promising platforms for probing quantum tunneling, spin-phonon coupling, and molecular-scale information storage/processing—key ingredients for future quantum technologies.

4. Concluding remarks

The objective of this thesis is to investigate the influence of isotope effects on magnetic properties of the lanthanide complexes while preserving their electronic structures. To achieve this, isotopic substitution strategies involving both the ligand atoms and the central lanthanide ion were employed to elucidate the role of nuclear spin in the magnetic relaxation of single-molecule magnets via spin-phonon coupling, hyperfine interactions, and super-hyperfine interactions.

The study in Chapter 2 focuses on the isotope effects of the ligand atoms on the magnetic relaxation dynamic of terbium(III) phthalocyanine (TbPc_2). To precisely isolate the influence of ligand atoms on magnetic relaxation behavior, a series of isotopically enriched derivatives with high isotopic purity, including ^{15}N -enriched and deuterated $[\text{TbPc}_2]^0$ complexes, were successfully synthesized and characterized. To minimize the dipolar interaction, their reduced analogues and diamagnetic diluted systems with different diluted ratio (1%, 2%, and 5%) were further prepared and investigated.

With the present of the organic, ligand-based electronic radical of $S = 1/2$, the H/D isotopic substitution primarily modulates the vibrational mode through mass effects. The heavier deuterium atoms result in a redshift of low-frequency vibrational modes, leading to a reduction in the phonon density of states and consequently weaker spin-phonon coupling. As a result, $[\text{TbPc}_2\text{-D}]^0$ consistently exhibits slower magnetic relaxation across the entire temperature range, indicating that its origin fundamentally lies in phonon-mediated processes. In contrast, the $^{14}\text{N}/^{15}\text{N}$ system exhibits more complex features. In addition to the variation in vibrational modes via mass effect, the isotope effect on the exchange coupling between Tb^{3+} ion and radical through contact effect, the differences in the gyromagnetic ratio of $^{14}\text{N}/^{15}\text{N}$, and distinct hyperfine energy level structures due to the quadrupole interactions and nuclear spin via super-hyperfine interactions, are all potential explanations for this complicated phenomenon. However, due to the presence of radical, a complete understanding and quantitative interpretation remain challenging, requiring further investigations.

To further elucidate the isotope effect of the ^{14}N and ^{15}N , the $^{14}\text{N}/^{15}\text{N}$ system was subsequently reduced and diluted with diamagnetic matrix. μ -SQUID measurements at ultra-low temperatures demonstrated that even though the coupling between the central Tb^{3+} ion and the coordinated nitrogen atoms is relatively weak, isotopic substitution of the ligands induces measurable changes in the nuclear spin dynamics of the central Tb^{3+} ion. The ^{15}N -enriched system ($I = 1/2$) exhibits narrower tunneling splittings and a sparser hyperfine energy level structure, allowing the nuclear spin population to gradually relax toward thermodynamic equilibrium over time. Conversely, the ^{14}N -enriched system ($I = 1$), together with an additional quadrupole effect, generates an extremely dense super-hyperfine splitting of each hyperfine electronic state, facilitating the transition between different spin states. More importantly, although the enhanced tunneling probability accelerates the equilibration of the nuclear-spin population compared with the ^{15}N system, the bidirectional tunneling events hinder the relaxation toward thermodynamic equilibrium. These findings demonstrate that isotope

engineering can reshape the coherence of single-molecule magnets without structural perturbations. This strategy offers a platform for understanding the contributions of ligand-nuclear-spins to quantum tunneling, thermalization, and decoherence, providing deeper insight into the design of molecular qubits with tailored spin environments.

Chapter 3 focuses on the isotope effects of the central lanthanide ion. To explore the role of nuclear spin in higher dimensional systems, the scope of the study was expanded from mononuclear system to tetranuclear system. A series of novel $[2 \times 2]$ grid complexes, $[\text{Ln}_4\text{L}_4(\mu_2\text{-OH})_4]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}, \text{Y}$; $\text{L} = 3,6\text{-bis}(2\text{-}1\text{-(pyridin-2-yl)ethylidene)hydrazineyl-1,2,4,5-tetrazine}$), were successfully synthesized and characterized. Targeted isotope enrichment (^{163}Dy with $I = 5/2$, and ^{164}Dy with $I = 0$) was performed on the dysprosium derivatives to elucidate how the nuclear spin of central metal ion affects the magnetic relaxation behavior.

Under conventional SQUID measurement, both $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$ exhibit field-induced SMM behavior with only subtle difference, which is consistent with previous reports that nuclear-spin-free system possesses a relatively longer relaxation time. However, $\mu\text{-SQUID}$ measurements at ultralow temperatures observed a contrasting and unconventional phenomenon. At 30 mK, both isotopologues exhibit open hysteresis loops. Surprisingly, $^{163}\text{Dy}_4\text{L}_4$ displays a larger opening, corresponding to slower magnetic relaxation dynamics, which contradicts the expectation that nuclear spins accelerate relaxation.

A combination of angle-dependent measurements, *ab initio* calculations, and spin-Hamiltonian modeling reveals that both isotopologues possess a pseudo-toroidal ground state, stabilized by the non-collinear anisotropy axes of each $^{\text{A}}\text{Dy}^{3+}$ ion and the competing interactions, endowing the systems with hexagonal feature in angular maps and S-shaped magnetic hysteresis loops. $^{164}\text{Dy}_4\text{L}_4$ with $I = 0$, where the magnetization reversal is constrained by limited tunneling channels, exhibit sharp quantum tunneling of magnetization. In contrast, the hyperfine interactions introduced by the nuclear spins in $^{163}\text{Dy}_4\text{L}_4$ further split the low-lying energy levels and generate dense avoided level crossing for tunneling, thereby profoundly reshaping the relaxation dynamics. Unexpectedly, these hyperfine-induced energy level crossings do not simply accelerate relaxation by the enhanced tunneling probabilities; instead, they facilitate hyperfine-mediated population transfer into the toroidal ground state, leading to slower relaxation dynamics and larger opening in hysteresis loops. In this context, nuclear spins play a constructive role through hyperfine interactions to stabilize the spin in the toroidal ground state, thereby suppressing the fast zero-field quantum tunneling of magnetization ($\sim 2 \times 10^6$ s for $^{163}\text{Dy}_4\text{L}_4$ versus $\sim 4 \times 10^4$ s for $^{164}\text{Dy}_4\text{L}_4$). Further investigations of temperature and magnetic-field sweep-rate dependences reveal two different relaxation mechanisms. In $^{164}\text{Dy}_4\text{L}_4$, the relaxation is dominated by pure quantum tunneling, whereas thermally assisted processes significantly contribute in $^{163}\text{Dy}_4\text{L}_4$.

Overall, these findings demonstrate for the first time that nuclear spins can exert a constructive influence on the relaxation of toroidal-like single-molecule magnets, providing new insights to control magnetic behavior at low-temperature. Moreover, this study again demonstrates that

isotopologue engineering holds promise as a crucial strategy for investigating quantum tunneling, quantum coherence, and information storage and quantum processing at the molecular scale.

5. Experimental details

5.1 Materials

Chemicals: All the chemicals used in the synthesis were commercially obtained and directly used without further purification.

Chromatography: Thin-layer chromatography (TLC) was performed on aluminum plates precoated with Merck 5735 silica gel 60 F254. Column chromatography was performed with Merck silica gel 60 (230–400 mesh) or water-activated basic alumina (particle size ranging from 0.063 to 0.2 mm).

5.2 Equipment

Nuclear Magnetic Resonance (NMR) spectroscopy: ¹H-NMR, ¹³C-NMR, and ¹⁵N-NMR spectra were recorded on Bruker Ultrashield plus 500 MHz (or 400 MHz) spectrometer employing deuterated solvent. The data analysis was performed using TopSpin 4.0.6 software.

ATR-IR: The IR spectra were recorded in the range of 400–4000 cm⁻¹ on Nicolet's iS50 FTIR spectrometer. The data analysis was performed using OPUS 7.0 software.

UV-VIS: The UV-Vis spectra were performed on Cary 500 Scan instrument (Varian), and recorded on Specord 205 (Analytic Jena) spectrometer and a lambda 950 UV/VIS/NIR absorption spectrometer (Perkin Elmer).

ESI-MS: The mass spectra were recorded either on a Thermo Fischer Scientific Finnigan LTQ-FT spectrometer or a Bruker TIMS-TOF instrument.

Part of the mass spectra was performed by Franziska Ganslmaier.

Maldi-MS: The mass spectra were recorded on Waters Synapt MALDI-TOF and IMMS Instrument.

Powder X-ray Diffraction (PXRD): The PXRD data were measured at room temperature on polycrystalline samples using a Stoe StadiMP diffractometer with Cu-K α radiation in transmission mode. The data analysis was performed using WinXPOW.

Single-Crystal X-ray Diffraction (SC-XRD): Single crystal X-ray data of the complexes were collected at either 150 K or 180 K on a STOE StadiVadi diffractometer with monochromated GaK α -radiation ($\lambda_{\text{GaK}\alpha} = 1.34143 \text{ \AA}$). The structure was solved by intrinsic phasing methods and refined with full-matrix least squares procedures on *F*² using SHELXL 2018/3²⁰¹⁻²⁰³ implemented in Olex2 1.5.²⁰⁴ The locations of the non-hydrogen atoms were determined from the difference Fourier maps. The non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

The SC-XRD measurements were performed by Prof. Dr. Dieter Fenske and Dr. Olaf Fuhr.

Energy Dispersive X-ray Spectroscopy (EDS): The analyses of single crystals were carried out using an Oxford Instruments X-MaxN 50 mm² Silicon Drift Detector within a Leo Gemini SEM.

The EDS measurements were performed by Dr. Svetlana Klyatskaya.

SQUID measurement: Magnetic susceptibility was measured on polycrystalline samples using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 1 T magnet. The samples were ground and fixed in gelatine capsules using small amounts of eicosane to avoid any movement of the samples. The data obtained were corrected for diamagnetic contributions of the eicosane, the gelatine capsule and the sample holder. Diamagnetic corrections for the sample were estimated using Pascal's constants.

μ -SQUID measurement: Low temperature (0.03 – 5 K) magnetization measurements were performed on single crystals using a μ -SQUID apparatus. In all cases, the field was aligned along the easy axis of the crystal, employing the transverse field method. The studies were carried out on single crystals with the field applied along the principal anisotropic axis. Hysteresis loops were obtained at different sweep rates and temperatures, ranging from 5 K to 30 mK and from 1 to 128 mT/s.

The μ -SQUID measurements were performed by Dr. Eufemio Moreno-Pineda, Dr. Sagar Paul and Appu Sunil.

5.3 Computational details

Complete-active-space self-consistent field (CASSCF) calculations on the basis of single-crystal X-ray determined geometry have been carried out with the OpenMolcas program package.^{196, 205-208} The CASSCF/SO-RASSI/SINGLE_ANISO studies were performed employing the experimentally determined structure of the corresponding compounds, with the ion of interest being Dy³⁺, while the remaining three Dy³⁺ ions were replaced with Y³⁺. The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library²⁰⁹: ANO-RCC-VTZP for Dy³⁺; VDZP for close N and O; VDZ for distant atoms. The calculations employed the second-order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were considered in the basis set, and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. Optimization of the molecular orbitals (MOs) was achieved by state-averaged CASSCF calculations. The active space of Dy³⁺ was defined by the nine 4f electrons in the seven 4f orbitals. Three calculations were carried out (RASSCF routine) with 21, 224, and 490 states for $S = 5/2$, $S = 3/2$, and $S = 1/2$, respectively. The CASSCF wavefunctions were subsequently mixed by spin-orbit coupling, employing the RASSI routine with all 21 states for $S = 5/2$ being included, while 128 and 130 states were included for $S = 3/2$ and $S = 1/2$. Lastly, the crystal field decomposition of the ground $J = 15/2$ multiplet of the ⁶H_{15/2} term was executed with the SINGLE_ANISO module.¹⁹⁷

Part of the calculations was performed by Dr. Eufemio Moreno-Pineda.

5.4 Dipolar Matrix

Dipolar magnetic interactions between Dy(III) ions were computed using a custom Python script that evaluates the full anisotropic dipole–dipole coupling tensor based on spin orientation from the *ab initio* SINGLE_ANISO outputs. For each metal center, the principal magnetic axes (g_x , g_y , g_z) were taken fully anisotropic, i.e., $g_x = g_y = 0$ and $g_z = 20$, together with the corresponding unit vectors that define the local magnetic frame. An orthonormal right-handed rotation matrix was constructed from these vectors and used to transform the principal axis g -tensor into the laboratory frame.

Pairwise dipolar couplings between ions i and j were calculated from the standard Hamiltonian:

$$H_{dip} = -2\mathbf{S}_i^T \mathbf{D}_{ij} \mathbf{S}_j,$$

where the full dipolar tensor $\mathbf{D}_{ij}$ is given by

$$\mathbf{D}_{ij} = \frac{\mu_0 \mu_B^2}{4\pi r_{ij}^3} - \left[\mathbf{g}_i^T \cdot \mathbf{g}_j - 3(\mathbf{g}_i^T \cdot \hat{\mathbf{r}}_{ij}) \cdot (\mathbf{g}_j^T \cdot \hat{\mathbf{r}}_{ij})^T \right]$$

Here r_{ij} is the Dy–Dy separation, and $\hat{\mathbf{r}}_{ij}$ is the corresponding unit vector.

The obtained dipolar matrix for Dy(1)⋯Dy(1'), Dy(2)⋯Dy(2'), and Dy(1)⋯Dy(2'), in $^{164}\text{Dy}_4\text{L}_4$ has the form (for an $-2J$ Hamiltonian):

$$\mathbf{D}_{1-1'} = \begin{pmatrix} -0.552 & -0.576 & 0.508 \\ 0.576 & 0.602 & -0.530 \\ 0.508 & 0.530 & -0.467 \end{pmatrix} \text{cm}^{-1}$$

$$\mathbf{D}_{2-2'} = \begin{pmatrix} -0.429 & -0.665 & -0.405 \\ 0.665 & 1.029 & 0.627 \\ -0.405 & -0.627 & -0.382 \end{pmatrix} \text{cm}^{-1}$$

$$\mathbf{D}_{1-2} = \begin{pmatrix} -0.394 & 0.610 & -0.372 \\ 0.411 & -0.637 & 0.388 \\ 0.363 & -0.561 & 0.342 \end{pmatrix} \text{cm}^{-1}$$

For $^{163}\text{Dy}_4\text{L}_4$, the dipolar matrix for Dy(1)⋯Dy(1'), Dy(2)⋯Dy(2'), and Dy(1)⋯Dy(2') are:

$$\mathbf{D}_{1-1'} = \begin{pmatrix} -0.502 & 0.291 & 0.580 \\ -0.291 & 0.169 & 0.336 \\ 0.580 & -0.336 & -0.670 \end{pmatrix} \text{cm}^{-1}$$

$$\mathbf{D}_{2-2'} = \begin{pmatrix} -0.484 & -0.597 & -0.634 \\ -0.280 & -0.346 & -0.367 \\ 0.559 & 0.689 & 0.732 \end{pmatrix} \text{cm}^{-1}$$

$$\mathbf{D}_{1-2} = \begin{pmatrix} -0.380 & 0.470 & -0.498 \\ -0.470 & 0.580 & -0.616 \\ -0.499 & 0.616 & -0.654 \end{pmatrix} \text{cm}^{-1}$$

Note that the dipolar interactions were calculated employing fully anisotropic g-values ($g_x = g_y = 0$ and $g_z = 20$), which leads to a larger dipolar coupling than when employing the SINGLE_ANISO g-values outputs. These dipolar interaction values can be projected into an $m_J = 15/2$ state by multiplication by a 1/225 factor. Even with an overestimation of the dipolar values, due to the employed g-values, the strongest component of the calculated dipolar coupling is $4.6 \times 10^{-3} \text{ cm}^{-1}$ (6.6 mK), which is smaller than the experimentally obtained values from the exchange field.

The dipolar calculations were performed by Dr. Eufemio Moreno-Pineda.

6. Appendix

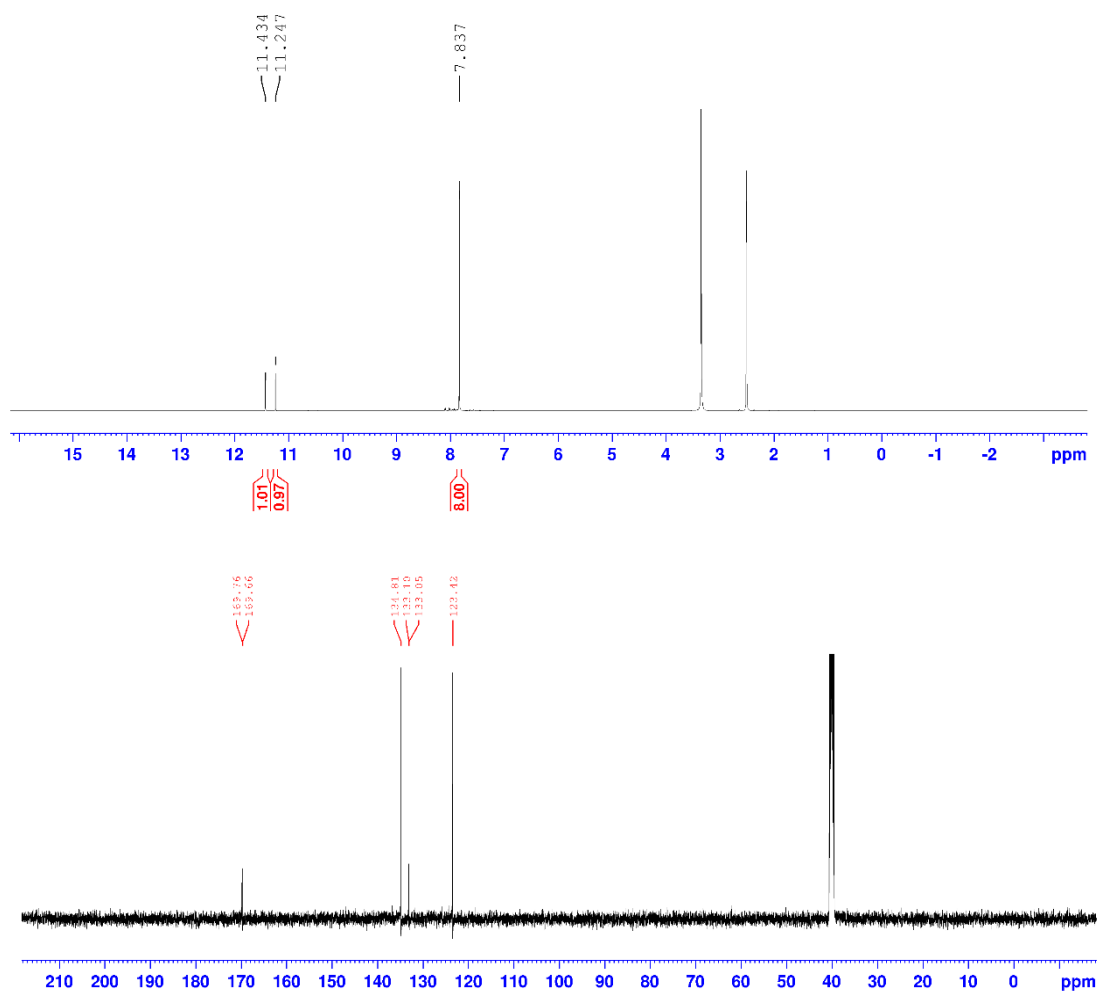
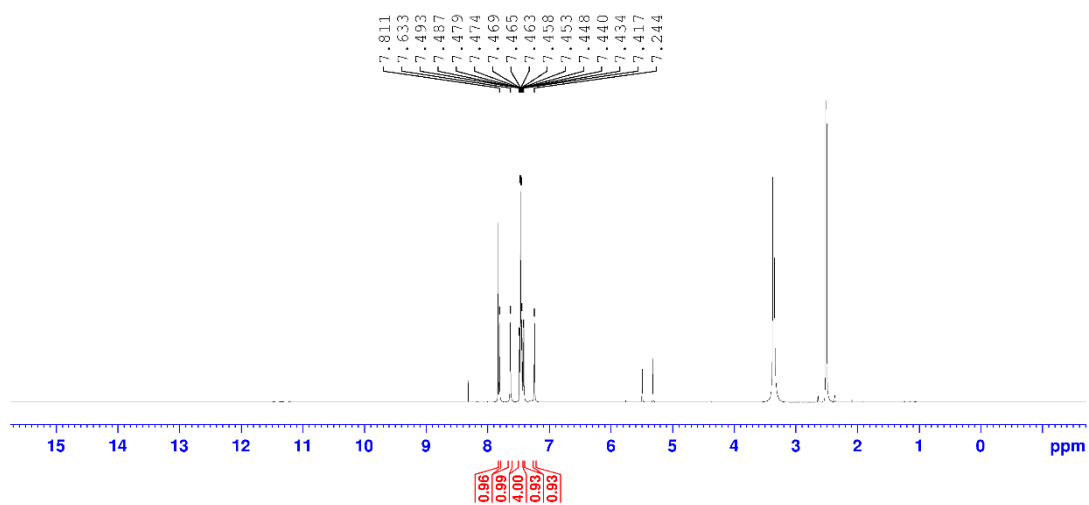


Figure S1. The ¹H and ¹³C NMR spectra in DMSO-d₆ for Phthalimide-¹⁵N (1).



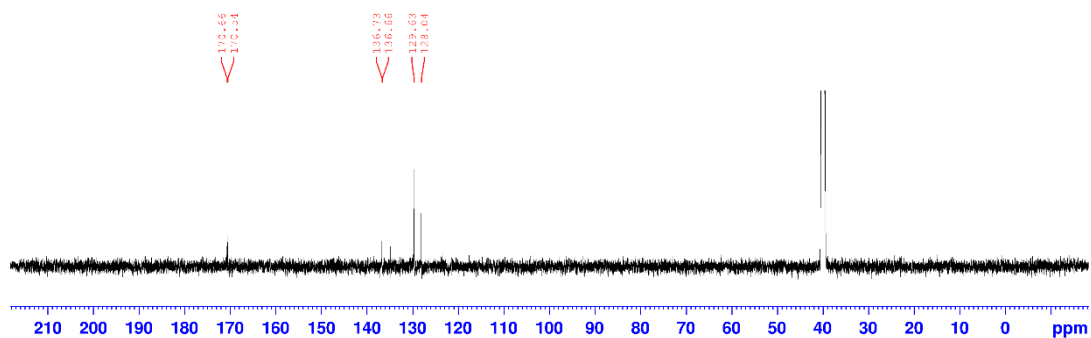


Figure S2. The ¹H and ¹³C NMR spectra in DMSO-d₆ for Phthalamide-¹⁵N (2).

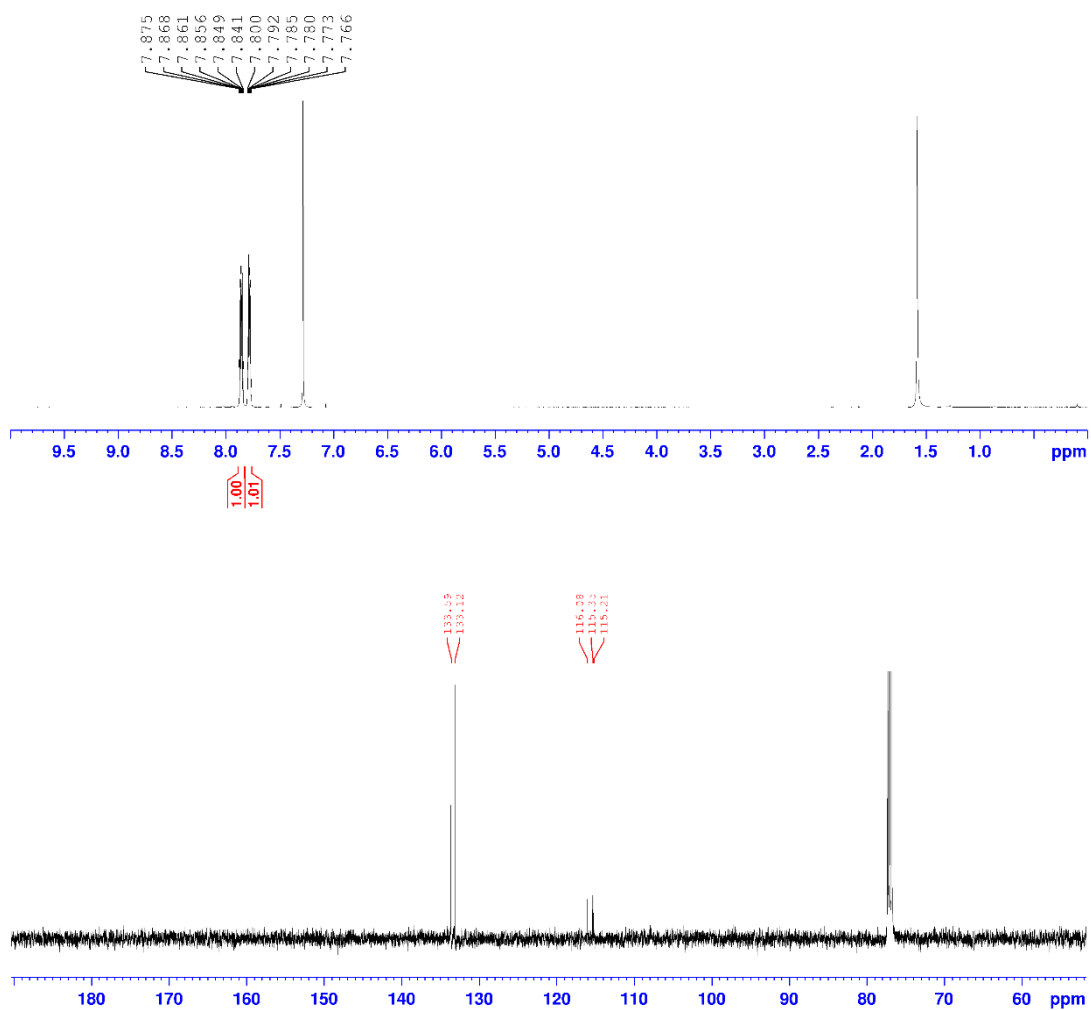


Figure S3. The ¹H and ¹³C NMR spectra in CDCl₃ for Phthalonitrile-¹⁵N (3).

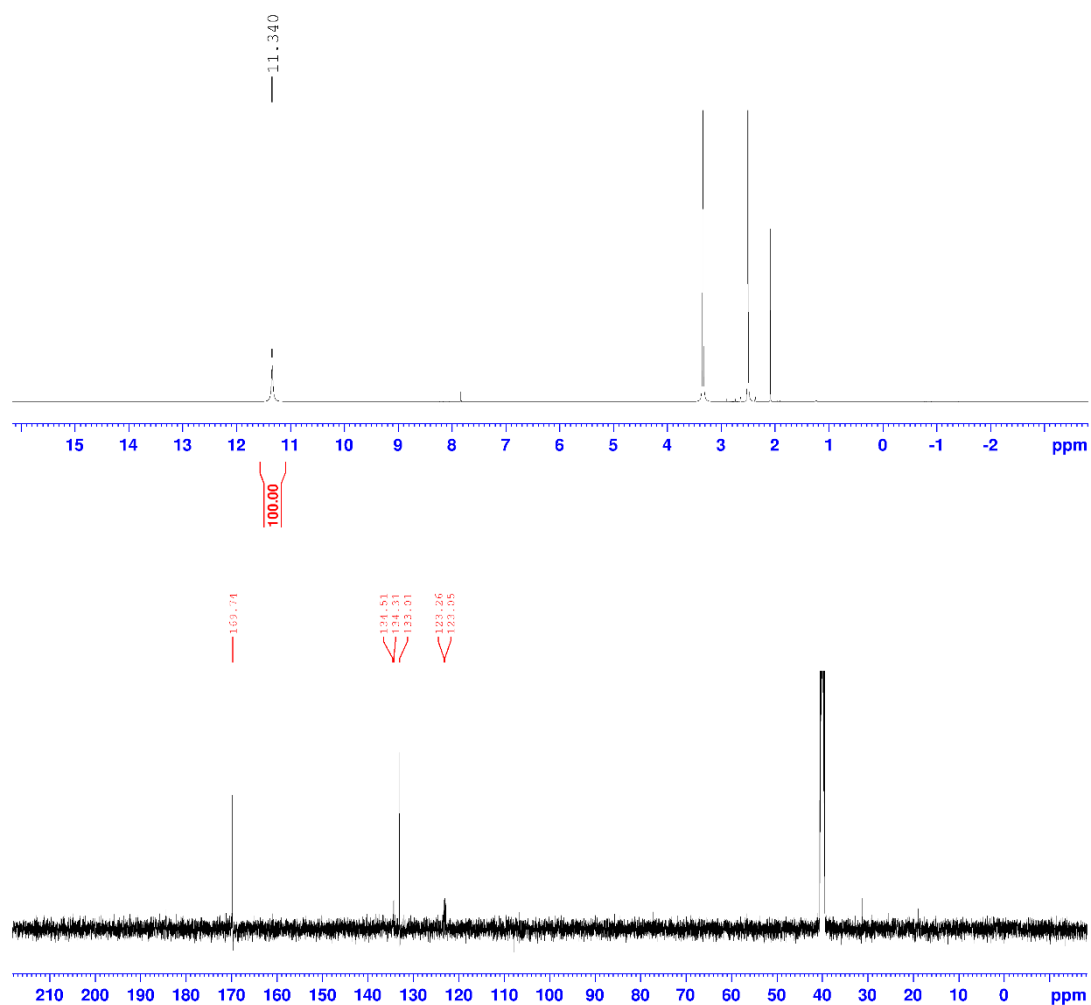
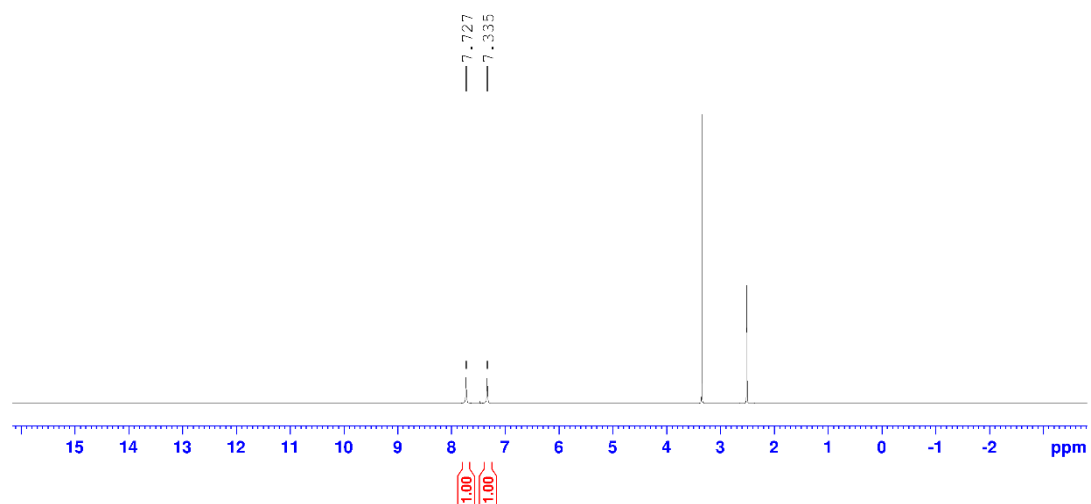


Figure S4. The ¹H and ¹³C NMR spectra in DMSO-d₆ for Phthalimide-D₄ (4).



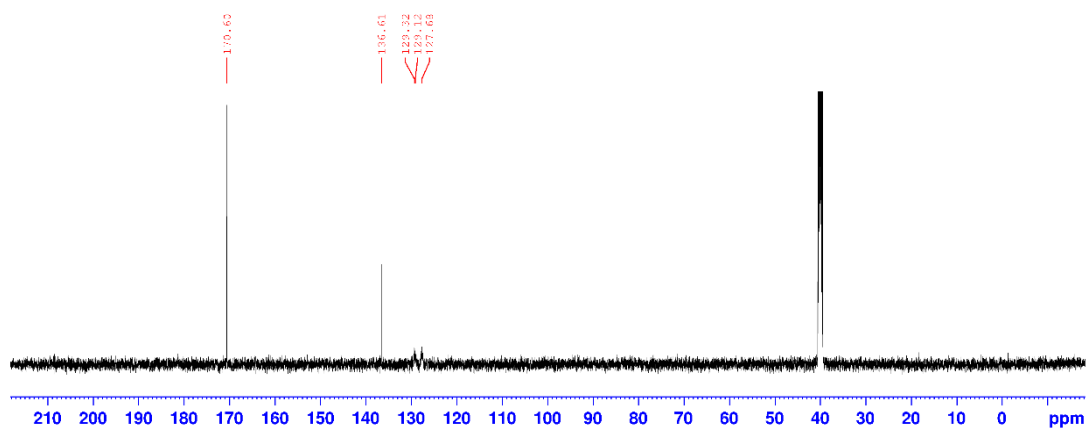


Figure S5. The ¹H and ¹³C NMR spectra in DMSO-d₆ for Phthalamide-D₄ (5).

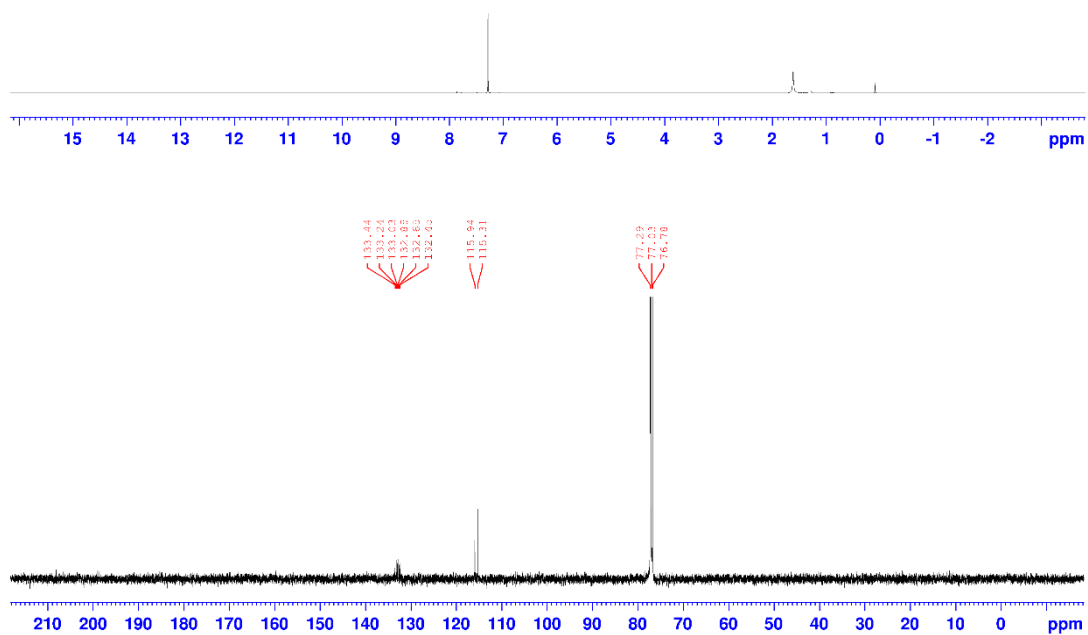


Figure S6. The ¹H and ¹³C NMR spectra in CDCl₃ for Phthalonitrile-D (6).

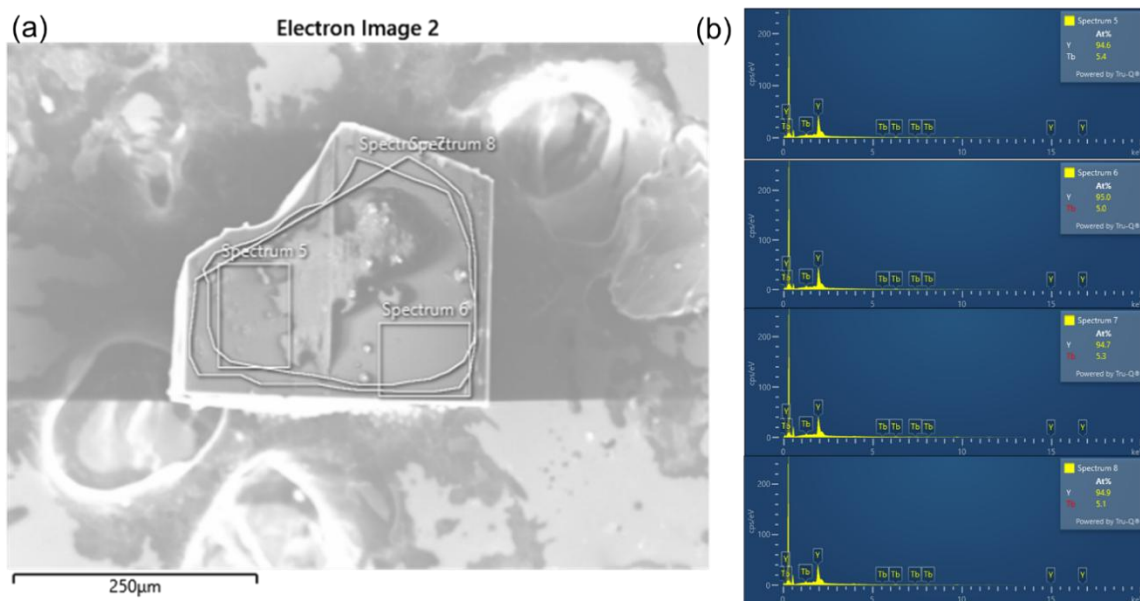


Figure S7. (a) The scanning electron microscopy image of the 5% diluted single crystal of $[\text{TbPc}_2][\text{TEA}]^+$, and (b) the corresponding energy-dispersive X-ray spectra for Spectrums 5–8 corresponding to the regions in (a).

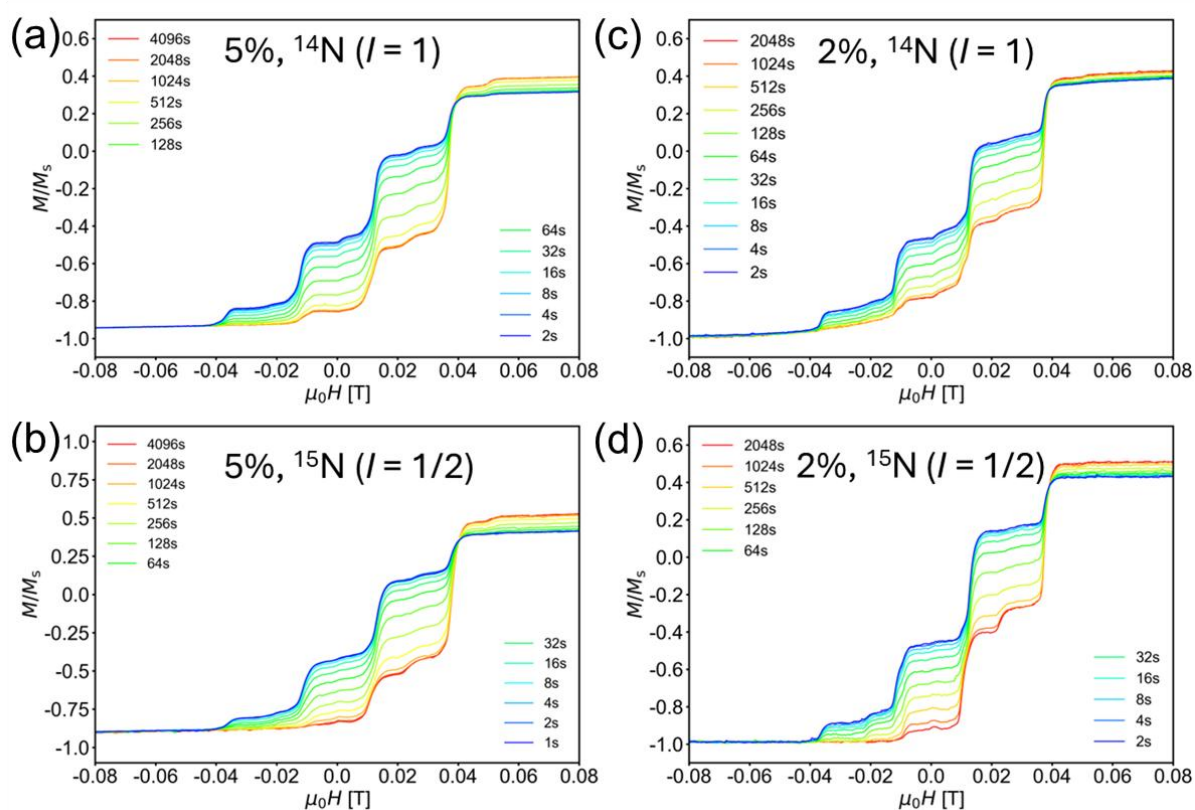


Figure S8. The hysteresis loops at 30 mK with a fixed 64 mT/s sweep rate after different waiting time for 5% diluted **N14** (a) and **N15** (b); and 2% diluted **N14** (c) and **N15** (d).

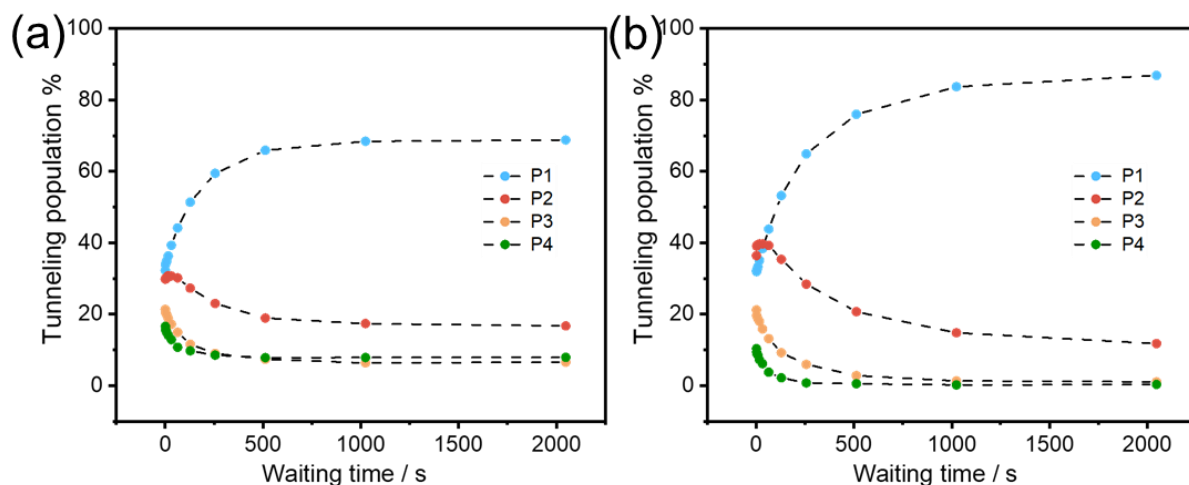


Figure S9. The tunneling population after different waiting time (1 s to 2048 s) of each nuclear spin states for 2% diluted N14 (a) and N15 (b).

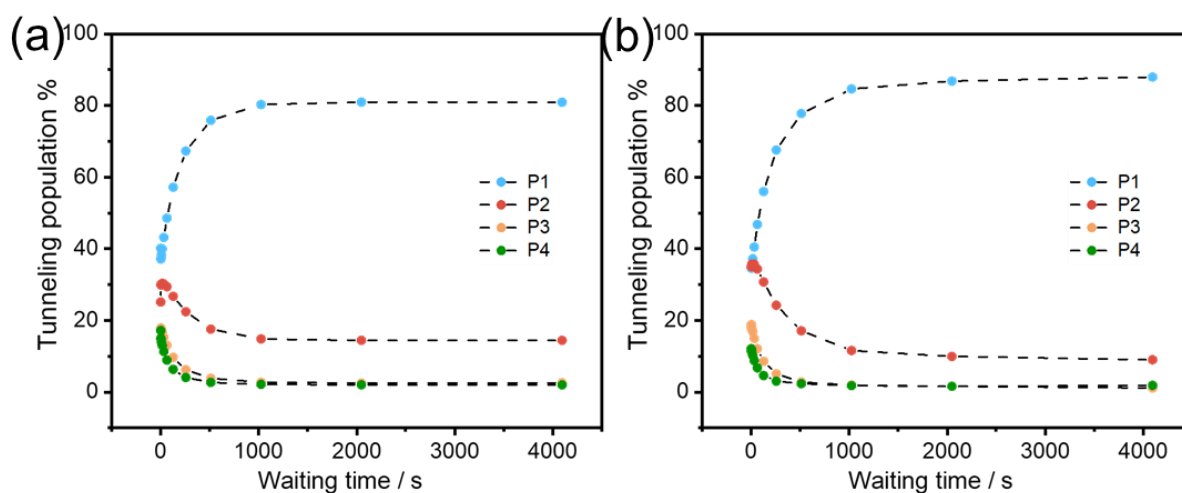


Figure S10. The tunneling population after different waiting time (1 s to 4096 s) of each nuclear spin states for 5% diluted N14 (a) and N15 (b).

Table S1. The fraction of step height for 1% diluted **N14** and **N15**.

N14 / time	4 to -4	3 to -4	4 to -2	3 to -3	2 to -4	0	1 to -3	2 to -2	1 to -2	1 to -1
1	0.0448	0.0166	0.0188	0.1253	0.0184	0.0135	0.036	0.2074	0.0066	0.1354
2	0.0403	0.0129	0.0171	0.1142	0.0219	0.0114	0.0402	0.2145	0.0109	0.1439
4	0.0371	0.015	0.013	0.1164	0.0196	0.0157	0.0416	0.2147	0.0079	0.1472
8	0.0367	0.0141	0.0126	0.1111	0.0214	0.0164	0.0387	0.2191	0.0087	0.1543
16	0.0276	0.0161	0.0153	0.1029	0.0229	0.011	0.0453	0.2182	0.0116	0.1605
32	0.0242	0.0121	0.015	0.0884	0.0293	0.0142	0.0462	0.2187	0.0128	0.1728
64	0.0166	0.0127	0.0094	0.0743	0.0304	0.0128	0.0535	0.2127	0.0115	0.1994
128	0.0077	0.0126	0.0113	0.0468	0.0303	0.0081	0.0667	0.1873	0.0144	0.2489
256	0.0049	0.0046	0.0034	0.0396	0.0245	0.013	0.077	0.1433	0.0205	0.3076
512	0.0021	0.0074	0.0005	0.0204	0.0231	0.0109	0.0879	0.1089	0.0195	0.3564
1024	0.0064	0.0004	0.0046	0.0143	0.0213	0.0095	0.0959	0.0943	0.0265	0.3746
2048	0.003	-0.0003	0.006	0.0143	0.0199	0.0058	0.1027	0.0897	0.0281	0.3758
4096	-0.0002	0.0025	0.0017	0.0167	0.0192	0.0064	0.099	0.0903	0.0301	0.3738
N15 / time	4 to -4	3 to -4	4 to -2	3 to -3	2 to -4	0	1 to -3	2 to -2	1 to -2	1 to -1
1	0.0393	0.0158	0.0026	0.0747	0.0402	0.0011	0.0749	0.1059	0.0264	0.2679
2	0.0348	0.0253	0.0069	0.1035	0.0481	-0.0016	0.0497	0.2102	0.0125	0.1577
4	0.0366	0.0255	0.0074	0.1066	0.0501	0.0031	0.0433	0.2218	0.0108	0.1432
8	0.0313	0.0243	0.0042	0.108	0.0541	-0.0011	0.045	0.2241	0.0101	0.1469
16	0.0279	0.0239	0.0074	0.0984	0.0544	0.0028	0.043	0.2263	0.011	0.1523
32	0.0234	0.023	0.0077	0.0874	0.0533	0.0046	0.0488	0.2253	0.0095	0.1696
64	0.0115	0.0248	0.0037	0.0683	0.0556	0.0068	0.0605	0.2205	0.0097	0.1915
128	0.0029	0.022	0.0015	0.0428	0.0676	0.0029	0.0687	0.2001	0.0128	0.2371
256	0.0022	0.0102	0.0026	0.0214	0.0668	0.0022	0.0923	0.1484	0.0172	0.2977
512	-0.0042	0.0099	0.0012	0.0066	0.0581	0.002	0.1169	0.0869	0.0345	0.3512
1024	-0.0015	0.002	0.0015	0.0017	0.0419	0.0008	0.1412	0.0552	0.0393	0.3891
2048	-0.0012	0.0016	0.0004	0.001	0.0269	-0.0021	0.1608	0.0397	0.0548	0.3835
4096	-0.0038	0.0034	0.0001	0.0026	0.0208	0.0028	0.1571	0.0395	0.0538	0.3849

Table S2. The fraction of step height for 2% diluted **N14** and **N15**.

N14 / time	4 to -4	3 to -4	4 to -2	3 to -3	2 to -4	0	1 to -3	2 to -2	1 to -2	1 to -1
1	0.0775	0.0241	0.0246	0.1073	0.0227	0.0273	0.0369	0.1612	0.0253	0.1368
2	0.0743	0.0242	0.0221	0.1025	0.0234	0.0257	0.0381	0.1617	0.0245	0.1468
4	0.0717	0.0239	0.0235	0.1005	0.0228	0.0268	0.0382	0.1605	0.0255	0.1473
8	0.069	0.0238	0.0222	0.0976	0.0233	0.0271	0.0387	0.1631	0.0242	0.1513
16	0.0648	0.0245	0.0221	0.0917	0.0249	0.0264	0.0399	0.1651	0.0262	0.158
32	0.0583	0.0228	0.0209	0.0831	0.0255	0.0269	0.0421	0.1637	0.0276	0.1725
64	0.0489	0.0236	0.0176	0.0691	0.0254	0.0254	0.0474	0.1616	0.0285	0.1981
128	0.0447	0.0212	0.0164	0.0514	0.0256	0.0239	0.0545	0.1455	0.0294	0.2379
256	0.0394	0.0205	0.0142	0.036	0.0238	0.0249	0.0579	0.1206	0.0314	0.2838
512	0.0383	0.0184	0.0113	0.0284	0.0212	0.0246	0.0626	0.0987	0.0334	0.3223
1024	0.0377	0.0172	0.0123	0.0232	0.0205	0.0234	0.0669	0.0898	0.0349	0.333
2048	0.038	0.0173	0.0121	0.0244	0.0177	0.0257	0.0673	0.0883	0.0358	0.3332
N15 / time	4 to -4	3 to -4	4 to -2	3 to -3	2 to -4	0	1 to -3	2 to -2	1 to -2	1 to -1
1	0.0556	0.0266	0.0148	0.1181	0.0534	0.0118	0.0748	0.1948	0.02	0.1241
2	0.0496	0.0268	0.0146	0.107	0.0564	0.0116	0.0747	0.211	0.0164	0.1273
4	0.0453	0.0283	0.0148	0.1033	0.0555	0.013	0.0731	0.2121	0.0175	0.1299
8	0.0442	0.0278	0.0145	0.1005	0.0568	0.0123	0.076	0.2124	0.0188	0.1329
16	0.0365	0.0303	0.013	0.0926	0.0572	0.0105	0.0798	0.2139	0.0179	0.142
32	0.031	0.0272	0.0111	0.0818	0.0607	0.0094	0.0872	0.2121	0.0184	0.158
64	0.0176	0.0303	0.0083	0.0609	0.0666	0.0087	0.0941	0.2052	0.0191	0.1902
128	0.0098	0.0237	0.0055	0.041	0.0706	0.0074	0.1072	0.1779	0.0239	0.2428
256	0.0017	0.0168	0.0035	0.0252	0.0702	0.0063	0.1261	0.1309	0.0275	0.3058
512	0.0008	0.0074	0.003	0.0128	0.0591	0.0062	0.1499	0.0897	0.0409	0.3558
1024	0.0001	0.0013	0.0012	0.0081	0.0367	0.007	0.1712	0.0699	0.0554	0.3769
2048	0.0015	0	0.0007	0.0076	0.0209	0.0078	0.1835	0.0639	0.0659	0.3776

Table S3. The fraction of step height for 5% diluted **N14** and **N15**.

N14 / time	4 to -4	3 to -4	4 to -2	3 to -3	2 to -4	0	1 to -3	2 to -2	1 to -2	1 to -1
1	0.0635	0.0153	0.0395	0.09	0.0226	0.0199	0.0515	0.1282	0.0248	0.1645
2	0.0497	0.0139	0.0406	0.0932	0.0258	0.0205	0.0568	0.1532	0.0251	0.1405
4	0.0476	0.0133	0.0404	0.0929	0.0252	0.0214	0.0567	0.1546	0.0249	0.142
8	0.0439	0.0133	0.0397	0.0913	0.0257	0.0207	0.0576	0.1548	0.0258	0.1456
16	0.0392	0.0118	0.0387	0.0881	0.0259	0.0208	0.0598	0.156	0.0255	0.1542
32	0.0317	0.0114	0.0362	0.0805	0.0257	0.0198	0.0622	0.1554	0.0273	0.1696
64	0.0224	0.01	0.0318	0.0694	0.0251	0.0181	0.066	0.1536	0.0295	0.1994
128	0.0157	0.008	0.0233	0.0516	0.0233	0.0161	0.0708	0.141	0.0322	0.2482
256	0.0102	0.0056	0.0152	0.0334	0.0198	0.013	0.073	0.1204	0.0343	0.3132
512	0.0072	0.0037	0.0101	0.0209	0.0154	0.0109	0.0729	0.097	0.0372	0.3747
1024	0.0063	0.0019	0.0075	0.0158	0.0116	0.0109	0.073	0.0843	0.0397	0.4058
2048	0.0066	0.0015	0.0067	0.0149	0.011	0.0104	0.0739	0.0824	0.0404	0.409
4096	0.0066	0.0018	0.0064	0.0151	0.0112	0.0111	0.0739	0.0822	0.0399	0.4092
N15 / time	4 to -4	3 to -4	4 to -2	3 to -3	2 to -4	0	1 to -3	2 to -2	1 to -2	1 to -1
1	0.0471	0.0196	0.033	0.1002	0.0401	0.022	0.0556	0.1915	0.0298	0.1451
2	0.0465	0.0231	0.0291	0.1015	0.0404	0.0241	0.0572	0.192	0.0308	0.1408
4	0.0505	0.0207	0.0286	0.0996	0.0415	0.0199	0.0594	0.192	0.0267	0.1452
8	0.0454	0.0203	0.0286	0.0968	0.0414	0.0231	0.0579	0.1954	0.0297	0.1478
16	0.0386	0.0197	0.0291	0.0919	0.0387	0.0232	0.06	0.197	0.0304	0.1557
32	0.033	0.0195	0.0256	0.0803	0.0406	0.0212	0.0632	0.1966	0.0318	0.1743
64	0.0227	0.0171	0.0224	0.0637	0.04	0.0176	0.0692	0.1895	0.0324	0.2111
128	0.0172	0.0158	0.0142	0.0424	0.0377	0.017	0.0744	0.1703	0.0361	0.2685
256	0.0119	0.0107	0.0092	0.0249	0.0343	0.0131	0.0801	0.1344	0.0397	0.3504
512	0.0111	0.0063	0.0057	0.0136	0.0261	0.0135	0.0827	0.0958	0.0428	0.428
1024	0.0101	0.0043	0.003	0.0099	0.0151	0.0116	0.0889	0.069	0.0514	0.4728
2048	0.0074	0.0064	0.0044	0.0054	0.0098	0.0091	0.0933	0.0628	0.0566	0.484
4096	0.0115	0.0028	0.0022	0.0058	0.0048	0.0108	0.0956	0.0609	0.0604	0.4839

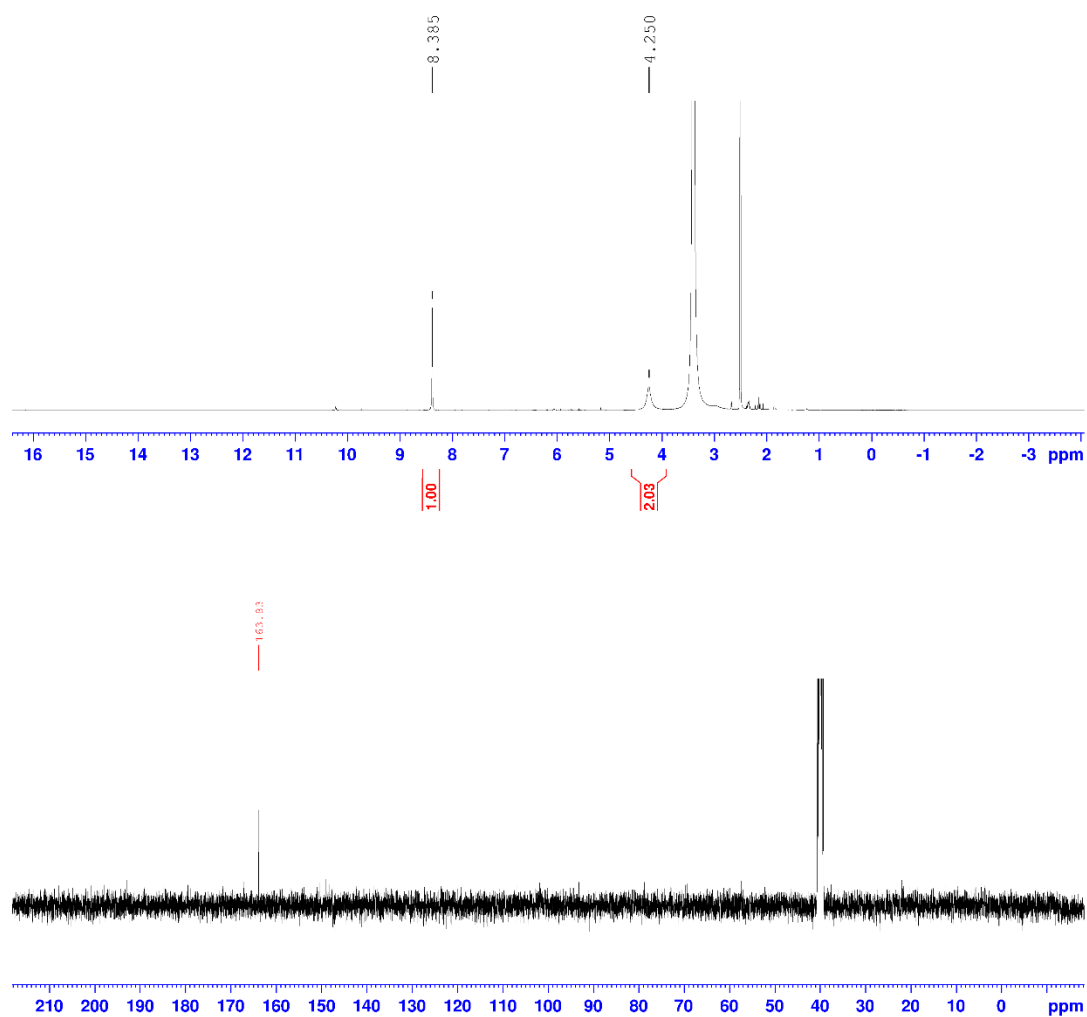
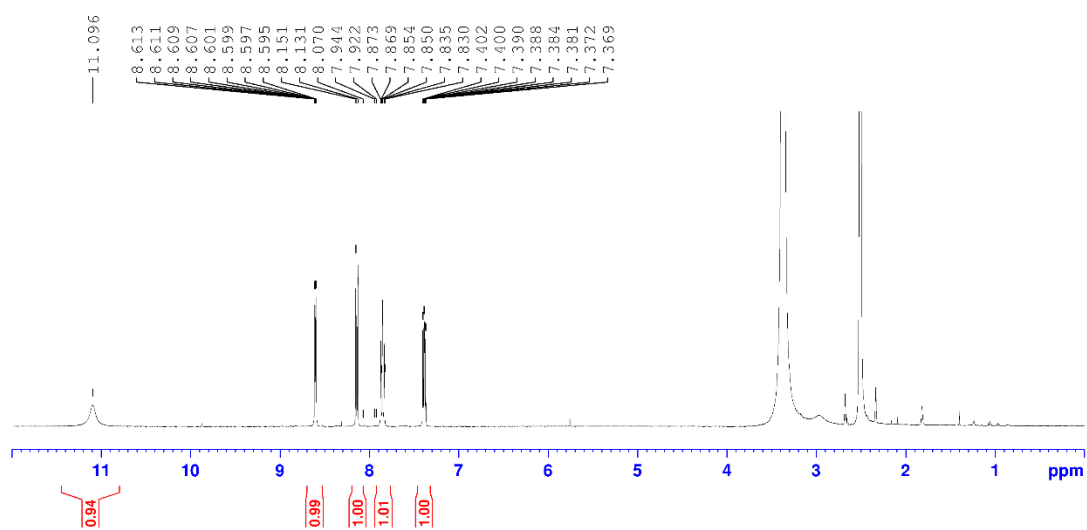


Figure S11. The ^1H and ^{13}C NMR spectra in DMSO- d_6 for 3,6-dihydrazino-1,2,4,5-tetrazine (14).



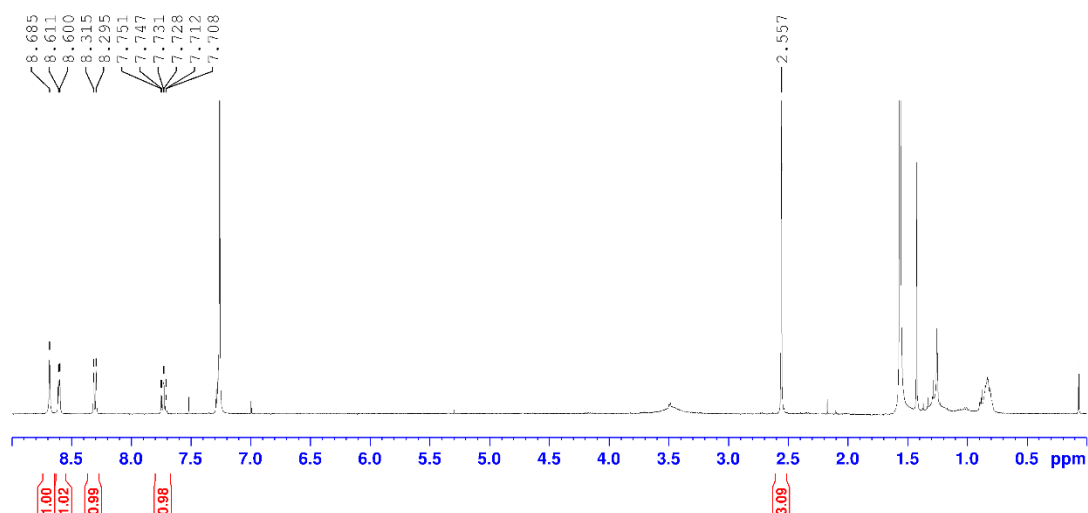


Figure S12. The ^1H NMR spectra in DMSO-d_6 (top) and CDCl_3 (bottom) for 3,6-bis(2-1-(pyridin-2-yl)ethylidene)hydrazineyl-1,2,4,5-tetrazine (**15**).

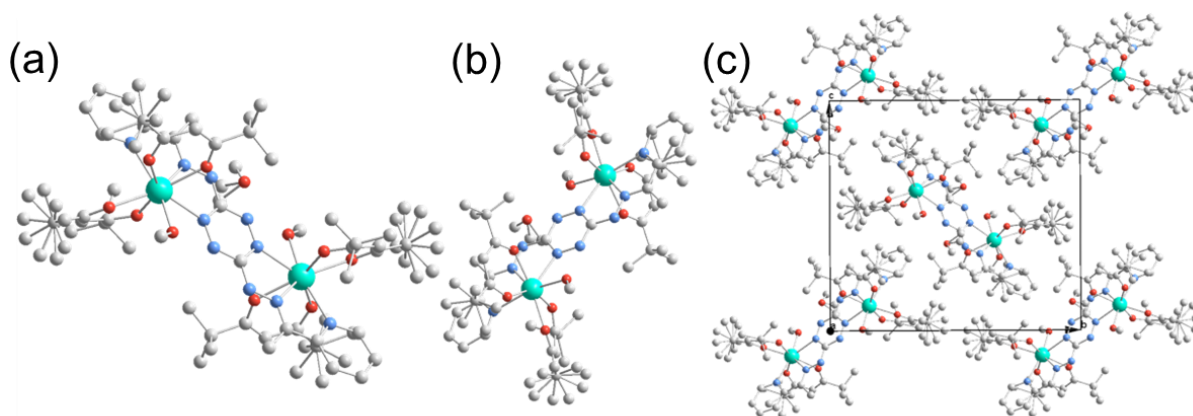
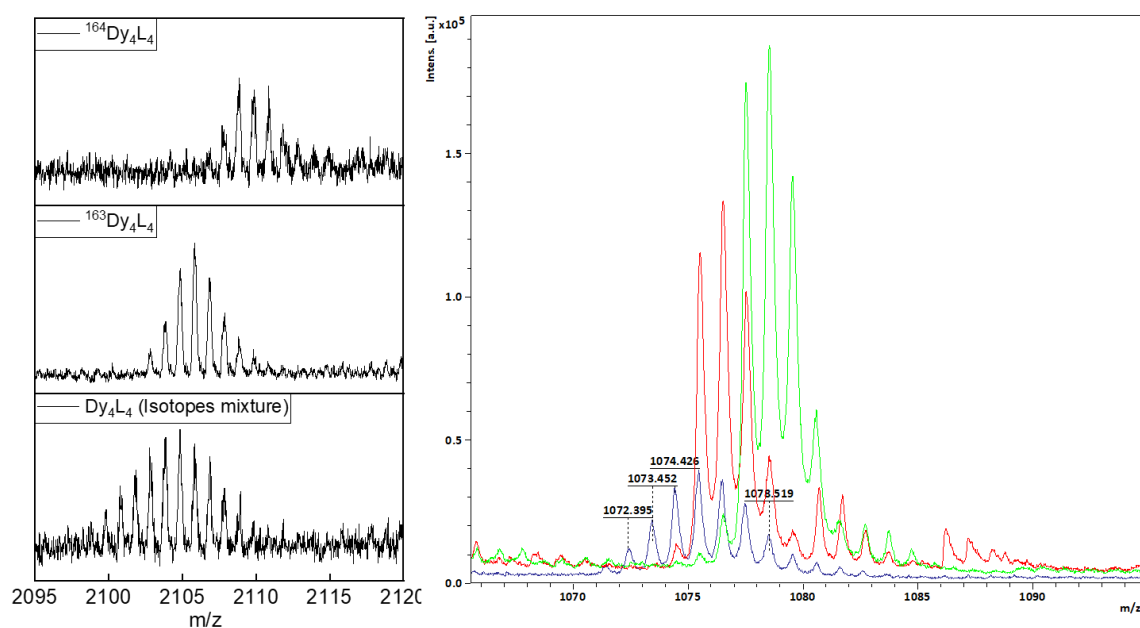


Figure S13. The top view (a), side view (b), and the packing diagram within the unit cell (c) of the molecular structure for $\text{Y}_2\text{L}(\text{tmhd})_4(\text{MeOH})_2 \cdot \text{MeOH}$, tmhd = 2,2,6,6-Tetramethyl-3,5-heptanedione. H atoms are omitted for clarity. Color code: Y, cyan; O, red; N, blue; C, grey.

Table S4. Crystallographic information for Y₂L(tmhd)₄(MeOH)₂·MeOH.

No.	Y ₂ L(tmhd) ₄ (MeOH) ₂ ·MeOH
Formula	C ₆₄ H ₁₀₆ N ₁₀ O ₁₂ Y ₂
Fw	1385.40
Temp/K	150
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	11.6139(5)
b/Å	18.8016(5)
c/Å	17.3942(7)
α/°	90
β/°	97.366(3)
γ/°	90
Volume/Å ³	3766.9(2)
Z	2
ρ _{calc} /cm ³	1.221
μ/mm ⁻¹	1.690
R _{int}	0.1382
Goodness-of-fit on F ²	0.838
R ₁ , wR ₂ (I > 2σ(I)) ^a	R ₁ = 0.0387, wR ₂ = 0.0716
R ₁ , wR ₂ (all data)	R ₁ = 0.1078, wR ₂ = 0.0833

$$^a R_1 = \|F_o\| - \|F_c\| / \|F_o\|, wR_2 = \{w[(F_o)^2 - (F_c)^2]^2 / w[(F_o)^2]^2\}^{1/2}$$

**Figure S14.** MALDI mass spectra for ¹⁶³Dy₄L₄ (red) and ¹⁶⁴Dy₄L₄ (green), and their decomposed fragments (compared with Dy₄L₄ (blue)).

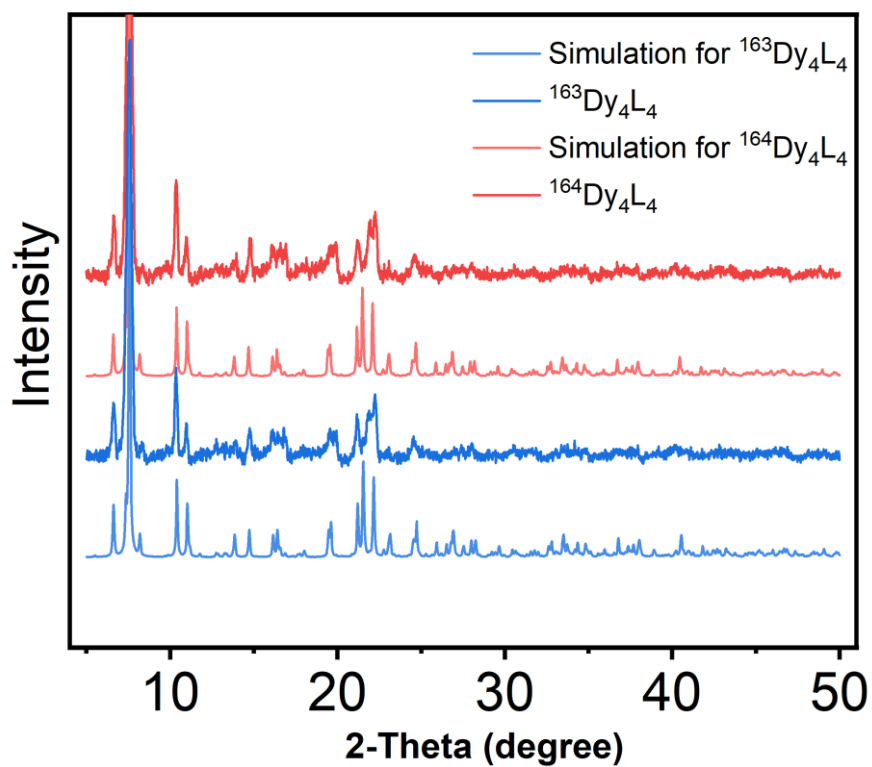


Figure S15. Powder-XRD for $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$.

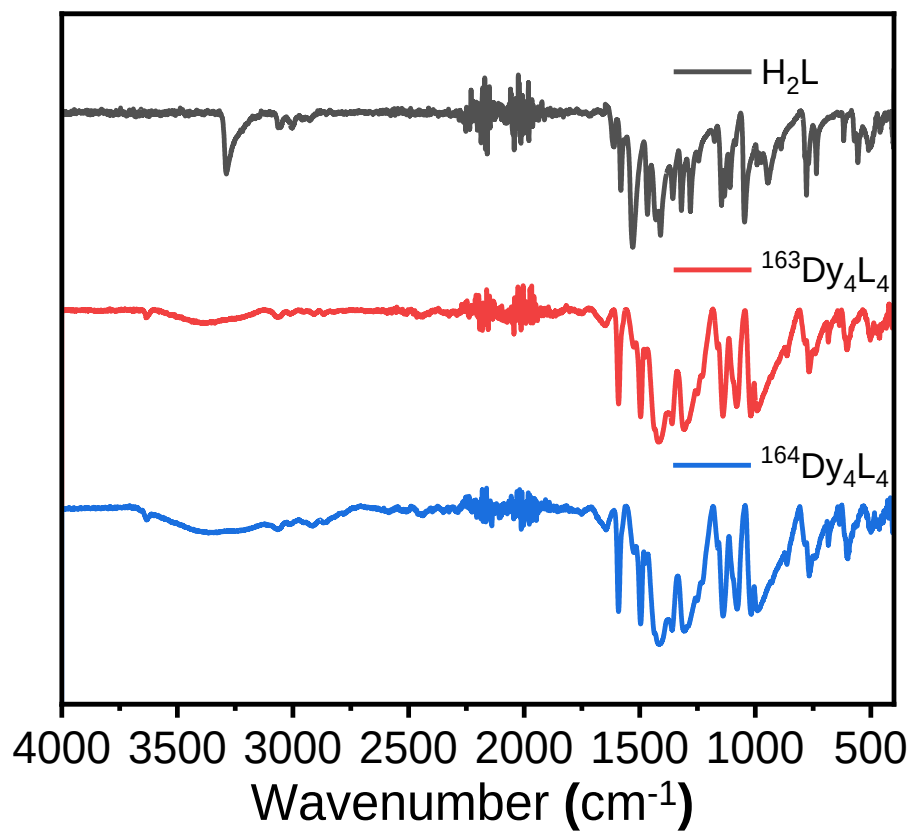


Figure S16. ATR Infrared for H_2L , $^{163}\text{Dy}_4\text{L}_4$ and $^{164}\text{Dy}_4\text{L}_4$.

Table S5. Crystal field Hamiltonian is given as $\hat{H}_{CF} = \sum_{k,q} B_k^q O_k^q$ and the extended Stevens operator coefficients B_k^q are extracted from CASSCF calculations for the $^{164}\text{Dy}_4\text{L}_4$ systems.

		B_k^q			
		$^{164}\text{Dy}_4\text{L}_4$		$^{163}\text{Dy}_4\text{L}_4$	
k	q	Dy(1)	Dy(2)	Dy(1)	Dy(2)
2	-2	-0.2596	-0.10379	0.14425	-0.01556
2	-1	0.30742	-1.47254	-1.71682	0.24867
2	0	-1.64007	-1.47653	-1.70109	-1.41089
2	1	-0.30131	-0.18385	-0.43756	-0.52791
2	2	1.01273	1.15576	1.09911	0.94977
4	-4	-0.00267	-0.00554	-0.00446	3.70309E-4
4	-3	0.00281	0.02922	0.0531	0.01164
4	-2	0.00323	-4.01719E-5	-0.00518	-0.00442
4	-1	-0.00722	0.03424	0.03575	-0.00345
4	0	0.00362	0.00103	7.58414E-4	0.00335
4	1	-4.83421E-4	-0.00246	0.00391	-7.26194E-4
4	2	0.03115	0.02226	0.01888	0.03036
4	3	0.03675	-0.03929	-0.02865	-0.03573
4	4	-0.00383	-0.00453	-0.0087	-0.0032
6	-6	-3.70193E-5	-1.10671E-4	-1.59284E-4	7.29968E-6
6	-5	4.78767E-4	-8.32416E-4	-3.18849E-4	5.35888E-4
6	-4	-6.41497E-5	-1.49162E-4	-9.60142E-5	6.78417E-5
6	-3	-2.59847E-5	1.5342E-5	-8.42517E-5	-1.72005E-5
6	-2	9.10541E-6	7.27377E-6	-1.48926E-5	-9.25791E-6
6	-1	2.89375E-5	-1.19726E-4	-1.13306E-4	3.99893E-5
6	0	-2.05176E-5	-1.33381E-5	-1.39913E-5	-2.20829E-5
6	1	9.56039E-5	-4.79255E-5	-6.7335E-5	-7.02966E-5
6	2	6.47378E-5	1.33358E-4	1.38859E-4	7.91339E-5
6	3	-1.22255E-4	1.39057E-4	1.29659E-4	2.1852E-5
6	4	-1.42056E-4	-6.40164E-5	-1.29921E-4	-1.51247E-4
6	5	0.00115	-5.52752E-4	-9.32021E-4	-0.00101
6	6	-1.90612E-5	7.40379E-5	-2.17645E-5	-2.93764E-5

Table S6. Average value of the matrix element of the transition magnetic moment ($|\mu_x| + |\mu_y| + |\mu_z|$)/3 for $^{163}\text{DyL4}$ and $^{164}\text{DyL4}$.

Multiplet	$^{163}\text{Dy}(1)$	$^{163}\text{Dy}(2)$	$^{164}\text{Dy}(1)$	$^{164}\text{Dy}(2)$
Matrix Element	Average magnetic moment μ_B			
$\langle +1.1 -1.1 \rangle$	2.94E-02	5.10E-02	4.85E-02	3.58E-02
$\langle +2.1 -2.1 \rangle$	3.59E-02	6.58E-02	5.96E-02	5.34E-02
$\langle +3.1 -3.1 \rangle$	3.28E-01	6.79E-01	4.09E-01	5.20E-01
$\langle +4.1 -4.1 \rangle$	1.27E+00	7.71E-01	2.11E+00	9.70E-01
$\langle +5.1 -5.1 \rangle$	1.32E+00	8.06E-01	1.90E+00	9.89E-01
$\langle +6.1 -6.1 \rangle$	1.48E+00	1.69E+00	1.18E+00	1.54E+00
$\langle +7.1 -7.1 \rangle$	1.67E+00	1.37E+00	2.02E+00	1.61E+00
$\langle +8.1 -8.1 \rangle$	1.40E+00	3.13E+00	2.45E+00	1.50E+00

7. List of publications

- [1] **Yaorong Chen**, Eufemio Moreno-Pineda, Sagar Paul, Olaf Fuhr, Dieter Fenske, Wolfgang Wernsdorfer, and Mario Ruben. Unconventional Nuclear-Spin-Dependent Toroidal Ground States in Isotopologue $^{\text{A}}\text{Dy}_4$ $[2 \times 2]$ Complexes. *Journal of the American Chemical Society*, 2026, 148(16), 17324-17332.
- [2] Zhaoyang Jing, Eufemio Moreno-Pineda, Sagar Paul, Appu Sunil, Olaf Fuhr, **Yaorong Chen**, Wolfgang Wernsdorfer, and Mario Ruben. Leveraging 3d-4f Coordination: Molecular Quantum Spring-Magnet Behavior in Axial Ni_2Ln Complexes. *Angewandte Chemie International Edition*, 2026, 65(5), e22076.
- [3] Joe Komeda, Sören Schlittenhardt, Asato Mizuno, Eufemio Moreno-Pineda, **Yaorong Chen**, Olaf Fuhr, Jordan L. Appleton, Athanassios K. Boudalis, Svetlana Klyatskaya, and Mario Ruben. A Stable Radical in Cationic Dinuclear Rare-Earth Triple-Decker Complexes Featuring Switchable Magnetic Properties. *Journal of the American Chemical Society*, 2025, 147(43), 39367-39378.
- [4] William J. A. Blackmore, **Yaorong Chen**, Svetlana Klyatskaya, Andrea Mattioni, Olaf Fuhr, Mario Ruben, and Nicholas F. Chilton. Re-Examination of the Relaxation Dynamics of $[\text{TbPc}_2][\text{NBu}_4]$. *Inorganic Chemistry*, 2025, 64(35), 17745-17753.
- [5] Arijit Jana, Yaofeng Wang, Lukas Guggolz, **Yaorong Chen**, Franziska Ganslmaier, Bastian Weinert, Mario Ruben, and Stefanie Dehnen. Bonding Features and Magnetic Ordering in Thiolate-Bridged Copper-Nickel Clusters Synthesized at Elevated Temperature. *Small*, 2025, 21(38), e06920.

8. References

- (1) Feynman, R. P. Simulating Physics with Computers. *International Journal of Theoretical Physics* **1982**, 21 (6-7), 467-488.
- (2) Deutsch, D. Quantum-Theory, the Church-Turing Principle and the Universal Quantum Computer. *Proceedings of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **1985**, 400 (1818), 97-117.
- (3) DiVincenzo, D. P. Real and realistic quantum computers. *Nature* **1998**, 393 (6681), 113-114.
- (4) Manetsch, H. J.; Nomura, G.; Bataille, E.; Lv, X.; Leung, K. H.; Endres, M. A tweezer array with 6,100 highly coherent atomic qubits. *Nature* **2025**, 647 (8088), 60-67.
- (5) DiVincenzo, D. P. The physical implementation of quantum computation. *Fortschritte Der Physik-Progress of Physics* **2000**, 48 (9-11), 771-783.
- (6) Childress, L.; Dutt, M. V. G.; Taylor, J. M.; Zibrov, A. S.; Jelezko, F.; Wrachtrup, J.; Hemmer, P. R.; Lukin, M. D. Coherent dynamics of coupled electron and nuclear spin qubits in diamond. *Science* **2006**, 314 (5797), 281-285.
- (7) Jelezko, F.; Gaebel, T.; Popa, I.; Domhan, M.; Gruber, A.; Wrachtrup, J. Observation of coherent oscillation of a single nuclear spin and realization of a two-qubit conditional quantum gate. *Physical Review Letters* **2004**, 93 (13), 130501.
- (8) Milburn, G. J. Photons as qubits. *Physica Scripta* **2009**, T137, 014003.
- (9) Blatt, R.; Wineland, D. Entangled states of trapped atomic ions. *Nature* **2008**, 453 (7198), 1008-1015.
- (10) Nowack, K. C.; Koppens, F. H. L.; Nazarov, Y. V.; Vandersypen, L. M. K. Coherent control of a single electron spin with electric fields. *Science* **2007**, 318 (5855), 1430-1433.
- (11) Clarke, J.; Wilhelm, F. K. Superconducting quantum bits. *Nature* **2008**, 453 (7198), 1031-1042.
- (12) Bogani, L.; Wernsdorfer, W. Molecular spintronics using single-molecule magnets. *Nature Materials* **2008**, 7 (3), 179-186.
- (13) Serrano, D.; Kuppusamy, S. K.; Heinrich, B.; Fuhr, O.; Hunger, D.; Ruben, M.; Goldner, P. Ultra-narrow optical linewidths in rare-earth molecular crystals. *Nature* **2022**, 603 (7900), 241-246.
- (14) Moreno-Pineda, E.; Godfrin, C.; Balestro, F.; Wernsdorfer, W.; Ruben, M. Molecular spin qubits for quantum algorithms. *Chemical Society Reviews* **2018**, 47 (2), 501-513.
- (15) Atzori, M.; Sessoli, R. The Second Quantum Revolution: Role and Challenges of Molecular Chemistry. *Journal of the American Chemical Society* **2019**, 141 (29), 11339-11352.
- (16) Layfield, R. A.; Layfield, R. A.; Murugesu, M.; Ebook Central Academic, C. *Lanthanides and actinides in molecular magnetism*; Wiley-VCH, 2015.
- (17) Yang, Y. L.; Hu, X. M.; Yang, Z.; Huang, W. Insights into Molecular Lanthanide Complexes: Construction, Properties and Bioimaging and Biosensing Applications. *Advanced Functional Materials* **2025**, 35 (2), 2412970.
- (18) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. Quantum tunneling of magnetization in lanthanide single-molecule magnets: Bis(phthalocyaninato)terbium and bis(phthalocyaninato)dysprosium anions. *Angewandte Chemie-International Edition* **2005**, 44 (19), 2931-2935.
- (19) Moreno-Pineda, E.; Damjanovic, M.; Fuhr, O.; Wernsdorfer, W.; Ruben, M. Nuclear Spin Isomers: Engineering a EtN[DyPc] Spin Qudit. *Angewandte Chemie-International Edition* **2017**, 56 (33), 9915-9919.
- (20) Ruan, L. X.; Tong, J. W.; Qin, G. W.; Zhou, L. Q.; Jiao, X. C.; Zhang, X. M. Magnetic Modification and the Mechanism of Tb-Phthalocyanine Single Molecule Magnets Prepared by a High Yield Method. *European Journal of Inorganic Chemistry* **2020**, 2020 (21), 2112-2117.
- (21) Marin, R.; Brunet, G.; Murugesu, M. Shining New Light on Multifunctional Lanthanide Single-Molecule Magnets. *Angewandte Chemie-International Edition* **2021**, 60 (4), 1728-1746.
- (22) Shrivastava, K. N. Theory of Spin-Lattice Relaxation. *Physica Status Solidi B-Basic Research* **1983**, 117 (2), 437-458.

- (23) Buchbinder, I. L.; Paszkiewicz, T. Influence of Phonons on Low-Temperature Paramagnetic Relaxation. *Journal of Physics C-Solid State Physics* **1974**, 7 (2), 279-288.
- (24) Gatteschi, D.; Sessoli, R. Quantum tunneling of magnetization and related phenomena in molecular materials. *Angewandte Chemie-International Edition* **2003**, 42 (3), 268-297.
- (25) Stoneham, A. M. The Phonon Bottleneck in Paramagnetic Crystals. *Proceedings of the Physical Society* **1965**, 86 (6), 1163-1177.
- (26) Lunghi, A.; Totti, F.; Sessoli, R.; Sanvito, S. The role of anharmonic phonons in under-barrier spin relaxation of single molecule magnets. *Nature Communications* **2017**, 8 (1), 14620.
- (27) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. Magnetic Bistability in a Metal-Ion Cluster. *Nature* **1993**, 365 (6442), 141-143.
- (28) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. Lanthanide double-decker complexes functioning as magnets at the single-molecular level. *Journal of the American Chemical Society* **2003**, 125 (29), 8694-8695.
- (29) Moreno-Pineda, E.; Klyatskaya, S.; Du, P.; Damjanovic, M.; Taran, G.; Wernsdorfer, W.; Ruben, M. Observation of Cooperative Electronic Quantum Tunneling: Increasing Accessible Nuclear States in a Molecular Qudit. *Inorganic Chemistry* **2018**, 57 (16), 9873-9879.
- (30) Blackmore, W. J. A.; Chen, Y. R.; Klyatskaya, S.; Mattioni, A.; Fuhr, O.; Ruben, M.; Chilton, N. F. Re-Examination of the Relaxation Dynamics of [TbPc][NBu]. *Inorganic Chemistry* **2025**, 64 (35), 17745-17753.
- (31) Urdampilleta, M.; Klyatskaya, S.; Cleuziou, J. P.; Ruben, M.; Wernsdorfer, W. Supramolecular spin valves. *Nature Materials* **2011**, 10 (7), 502-506.
- (32) Katoh, K.; Komeda, T.; Yamashita, M. Surface morphologies, electronic structures, and Kondo effect of lanthanide(III)-phthalocyanine molecules on Au(111) by using STM, STS and FET properties for next generation devices. *Dalton Transactions* **2010**, 39 (20), 4708-4723.
- (33) Morita, T.; Damjanovic, M.; Katoh, K.; Kitagawa, Y.; Yasuda, N.; Lan, Y. H.; Wernsdorfer, W.; Breedlove, B. K.; Enders, M.; Yamashita, M. Comparison of the Magnetic Anisotropy and Spin Relaxation Phenomenon of Dinuclear Terbium(III) Phthalocyaninato Single-Molecule Magnets Using the Geometric Spin Arrangement. *Journal of the American Chemical Society* **2018**, 140 (8), 2995-3007.
- (34) Katoh, K.; Yamashita, S.; Yasuda, N.; Kitagawa, Y.; Breedlove, B. K.; Nakazawa, Y.; Yamashita, M. Control of the Spin Dynamics of Single-Molecule Magnets by using a Quasi One-Dimensional Arrangement. *Angewandte Chemie-International Edition* **2018**, 57 (30), 9262-9267.
- (35) Morita, T.; Katoh, K.; Breedlove, B. K.; Yamashita, M. Controlling the Dipole-Dipole Interactions between Terbium(III) Phthalocyaninato Triple-Decker Moieties through Spatial Control Using a Fused Phthalocyaninato Ligand. *Inorganic Chemistry* **2013**, 52 (23), 13555-13561.
- (36) Chen, Y. X.; Ma, F.; Zhang, Y. H.; Zhao, L. Y.; Wang, K.; Qi, D. D.; Sun, H. L.; Jiang, J. Z. Heteroleptic chiral bis(phthalocyaninato) terbium double-decker single-ion magnets. *Inorganic Chemistry Frontiers* **2018**, 5 (8), 2006-2012.
- (37) Liu, W. B.; Zeng, S. Y.; Chen, X.; Pan, H. H.; Qi, D. D.; Wang, K.; Dou, J. M.; Jiang, J. Z. Hemiporphyrizine-Involved Sandwich Dysprosium Double-Decker Single-Ion Magnets. *Inorganic Chemistry* **2018**, 57 (19), 12347-12353.
- (38) Godfrin, C.; Ferhat, A.; Ballou, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F. Operating Quantum States in Single Magnetic Molecules: Implementation of Grover's Quantum Algorithm. *Physical Review Letters* **2017**, 119 (18), 187702.
- (39) Amokrane, A.; Klyatskaya, S.; Boero, M.; Ruben, M.; Bucher, J. P. Role of π -Radicals in the Spin Connectivity of Clusters and Networks of Tb Double-Decker Single Molecule Magnets. *Acs Nano* **2017**, 11 (11), 10750-10760.
- (40) Godfrin, C.; Thiele, S.; Ferhat, A.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F. Electrical Read-Out of a Single Spin Using an Exchange-Coupled Quantum Dot. *Acs Nano* **2017**, 11 (4), 3984-3989.
- (41) Vincent, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F. Electronic read-out of a single nuclear spin using a molecular spin transistor. *Nature* **2012**, 488 (7411), 357-360.

- (42) Thiele, S.; Balestro, F.; Ballou, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W. Electrically driven nuclear spin resonance in single-molecule magnets. *Science* **2014**, *344* (6188), 1135-1138.
- (43) Gállico, D. A.; Calado, C. M. S.; Murugesu, M. Lanthanide molecular cluster-aggregates as the next generation of optical materials. *Chemical Science* **2023**, *14* (22), 5827-5841.
- (44) Wang, J.; Sun, C. Y.; Zheng, Q.; Wang, D. Q.; Chen, Y. T.; Ju, J. F.; Sun, T. M.; Cui, Y.; Ding, Y.; Tang, Y. F. Lanthanide Single-molecule Magnets: Synthetic Strategy, Structures, Properties and Recent Advances. *Chemistry-an Asian Journal* **2023**, *18* (7), e202201297.
- (45) Bernbeck, M. G.; Orlova, A. P.; Hilgar, J. D.; Gembicky, M.; Ozerov, M.; Rinehart, J. D. Dipolar Coupling as a Mechanism for Fine Control of Magnetic States in ErCOT-Alkyl Molecular Magnets. *Journal of the American Chemical Society* **2024**, *146* (11), 7243-7256.
- (46) Shome, S.; Maurya, N. C.; Adarsh, K. V.; Konar, S. Dy-SMM for Standalone Magneto Thermometry and Opto-Magnetic Temperature Sensing via Multiple Linear Regression. *Inorganic Chemistry* **2025**, *64* (49), 23990-23998.
- (47) Ruan, T. T.; Moreno-Pineda, E.; Schulze, M.; Schlittenhardt, S.; Brietzke, T.; Holdt, H. J.; Kuppusamy, S. K.; Wernsdorfer, W.; Ruben, M. Hilbert Space in Isotopologue Dy(III) SMM Dimers: Dipole Interaction Limit in $^{163/164}\text{Dy}_2(\text{tmhd})_6(\text{tape})^0$ Complexes. *Inorganic Chemistry* **2023**, *62* (37), 15148-15156.
- (48) Lu, G.; Liu, Y.; Deng, W.; Huang, G. Z.; Chen, Y. C.; Liu, J. L.; Ni, Z. P.; Giansiracusa, M.; Chilton, N. F.; Tong, M. L. A perfect triangular dysprosium single-molecule magnet with virtually antiparallel Ising-like anisotropy. *Inorganic Chemistry Frontiers* **2020**, *7* (16), 2941-2948.
- (49) Gould, C. A.; Darago, L. E.; Gonzalez, M. I.; Demir, S.; Long, J. R. A Trinuclear Radical-Bridged Lanthanide Single-Molecule Magnet. *Angewandte Chemie-International Edition* **2017**, *56* (34), 10103-10107.
- (50) Tang, J. K.; Hewitt, I.; Madhu, N. T.; Chastanet, G.; Wernsdorfer, W.; Anson, C. E.; Benelli, C.; Sessoli, R.; Powell, A. K. Dysprosium triangles showing single-molecule magnet behavior of thermally excited spin states. *Angewandte Chemie-International Edition* **2006**, *45* (11), 1729-1733.
- (51) Chandrasekhar, V.; Hossain, S.; Das, S.; Biswas, S.; Sutter, J. P. Rhombus-Shaped Tetranuclear $[\text{Ln}_4]$ Complexes $[\text{Ln} = \text{Dy(III)} \text{ and } \text{Ho(III)}]$: Synthesis, Structure, and SMM Behavior. *Inorganic Chemistry* **2013**, *52* (11), 6346-6353.
- (52) Wang, Q. L.; Wu, R. F.; Cai, C. Z.; Yue, R. X.; Gao, Y.; Shi, P. F.; Wang, W. M. A series of rhombus-shaped Ln_4 clusters: Syntheses, structures, luminescence properties and the SMM behavior of the Dy_4 analogue. *Polyhedron* **2018**, *150*, 92-96.
- (53) 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. *Nature Chemistry* **2013**, *5* (8), 673-678.
- (54) Lin, P. H.; Korobkov, I.; Wernsdorfer, W.; Ungur, L.; Chibotaru, L. F.; Murugesu, M. A Rare μ_4 -O Centred Dy_4 Tetrahedron with Coordination-Induced Local Chirality and Single-Molecule Magnet Behaviour. *European Journal of Inorganic Chemistry* **2011**, (10), 1535-1539.
- (55) Guo, P. H.; Liu, J.; Wu, Z. H.; Yan, H.; Chen, Y. C.; Jia, J. H.; Tong, M. L. Single-Molecule-Magnet Behavior in a $[2 \times 2]$ Grid $\text{Dy}^{\text{III}4}$ Cluster and a Dysprosium-Doped $\text{Y}^{\text{III}4}$ Cluster. *Inorganic Chemistry* **2015**, *54* (16), 8087-8092.
- (56) Anwar, M. U.; Thompson, L. K.; Dawe, L. N.; Habib, F.; Murugesu, M. Predictable self-assembled $[2 \times 2]$ Ln(III) square grids ($\text{Ln} = \text{Dy, Tb}$)-SMM behaviour in a new lanthanide cluster motif. *Chemical Communications* **2012**, *48* (38), 4576-4578.
- (57) Thompson, L. K.; Dawe, L. N. Magnetic properties of transition metal (Mn(II) , Mn(III) , Ni(II) , Cu(II)) and lanthanide (Gd(III) , Dy(III) , Tb(III) , Eu(III) , Ho(III) , Yb(III)) clusters and $[\text{nxn}]$ grids: Isotropic exchange and SMM behaviour. *Coordination Chemistry Reviews* **2015**, *289*, 13-31.
- (58) Kumar, P.; Swain, A.; Acharya, J.; Li, Y. L.; Kumar, V.; Rajaraman, G.; Colacio, E.; Chandrasekhar, V. Synthesis, Structure, and Zero-Field SMM Behavior of Homometallic Dy_2 , Dy_4 , and Dy_6 Complexes. *Inorganic Chemistry* **2022**, *61* (30), 11600-11621.

- (59) Bajaj, N.; Mavragani, N.; Kitos, A. A.; Chartrand, D.; Maris, T.; Mansikkamäki, A.; Murugesu, M. Hard single-molecule magnet behavior and strong magnetic coupling in pyrazinyl radical-bridged lanthanide metallocenes. *Chem* **2024**, *10* (8), 2484-2499.
- (60) Tian, H. Q.; Su, J. B.; Bao, S. S.; Kurmoo, M.; Huang, X. D.; Zhang, Y. Q.; Zheng, L. M. Reversible ON-OFF switching of single-molecule-magnetism associated with single-crystal-to-single-crystal structural transformation of a decanuclear dysprosium phosphonate. *Chemical Science* **2018**, *9* (30), 6424-6433.
- (61) Tian, H. Q.; Zhao, L.; Lin, H. F.; Tang, J. K.; Li, G. S. Butterfly-Shaped Pentanuclear Dysprosium Single-Molecule Magnets. *Chemistry-a European Journal* **2013**, *19* (39), 13235-13241.
- (62) Kariaka, N. S.; Kolotilov, S. V.; Gawryszewska, P.; Kasprzycka, E.; Weselski, M.; Dyakonenco, V. V.; Shishkina, S. V.; Trush, V. A.; Amirkhanov, V. M. Structures and Spectral and Magnetic Properties of a Series of Carbacylamidophosphate Pentanuclear Lanthanide(III) Hydroxo Complexes. *Inorganic Chemistry* **2019**, *58* (21), 14682-14692.
- (63) Blagg, R. J.; Murn, C. A.; McInnes, E. J. L.; Tuna, F.; Winpenny, R. E. P. Single Pyramid Magnets: Dy Pyramids with Slow Magnetic Relaxation to 40 K. *Angewandte Chemie-International Edition* **2011**, *50* (29), 6530-6533.
- (64) Wang, Y. F.; Wang, W. M.; Sun, H. F.; Wang, W. T.; Wang, M. Y.; Tang, Y. T.; Wu, Z. L. A New Planar Hexanuclear Dysprosium Cluster Exhibiting Slow Magnetic Relaxation Features. *Zeitschrift Fur Anorganische Und Allgemeine Chemie* **2019**, *645* (22), 1291-1295.
- (65) Hewitt, I. J.; Tang, J.; Madhu, N. T.; Anson, C. E.; Lan, Y.; Luzon, J.; Etienne, M.; Sessoli, R.; Powell, A. K. Coupling Dy Triangles Enhances Their Slow Magnetic Relaxation. *Angewandte Chemie-International Edition* **2010**, *49* (36), 6352-6356.
- (66) Yu, S.; Hu, Z. B.; Chen, Z. L.; Li, B.; Zhang, Y. Q.; Liang, Y. N.; Liu, D. C.; Yao, D.; Liang, F. P. Two Dy(III) Single-Molecule Magnets with Their Performance Tuned by Schiff Base Ligands. *Inorganic Chemistry* **2019**, *58* (2), 1191-1200.
- (67) Das, S.; Hossain, S.; Dey, A.; Biswas, S.; Sutter, J. P.; Chandrasekhar, V. Molecular Magnets Based on Homometallic Hexanuclear Lanthanide(III) Complexes. *Inorganic Chemistry* **2014**, *53* (10), 5020-5028.
- (68) Guo, Y. N.; Chen, X. H.; Xue, S. F.; Tang, J. K. Molecular Assembly and Magnetic Dynamics of Two Novel Dy and Dy Aggregates. *Inorganic Chemistry* **2012**, *51* (7), 4035-4042.
- (69) Sharples, J. W.; Zheng, Y. Z.; Tuna, F.; McInnes, E. J. L.; Collison, D. Lanthanide discs chill well and relax slowly. *Chemical Communications* **2011**, *47* (27), 7650-7652.
- (70) Tian, H. Q.; Zhao, L.; Tang, J. K. Exploiting Miraculous Atmospheric CO Fixation in the Design of Dysprosium Single-Molecule Magnets. *Crystal Growth & Design* **2018**, *18* (2), 1173-1181.
- (71) Wang, Y. H.; Qin, Y.; Tang, S.; Teng, Q. H.; Zhu, M. M.; Peng, S.; Wang, K.; Liang, F. P. Asymmetric {Dy₄} metallogrid and double-layered {Dy₈} cage clusters from carboxylic decorated -vanillin Schiff bases: syntheses, topological variation, and single molecule magnet behaviors. *New Journal of Chemistry* **2023**, *47* (4), 2052-2059.
- (72) Soncini, A.; Chibotaru, L. F. Toroidal magnetic states in molecular wheels: Interplay between isotropic exchange interactions and local magnetic anisotropy. *Physical Review B* **2008**, *77* (22), 220406.
- (73) Ungur, L.; Langley, S. K.; Hooper, T. N.; Moubaraki, B.; Brechin, E. K.; Murray, K. S.; Chibotaru, L. F. Net Toroidal Magnetic Moment in the Ground State of a {Dy₆}-Triethanolamine Ring. *Journal of the American Chemical Society* **2012**, *134* (45), 18554-18557.
- (74) Spaldin, N. A.; Fiebig, M.; Mostovoy, M. The toroidal moment in condensed-matter physics and its relation to the magnetoelectric effect. *Journal of Physics-Condensed Matter* **2008**, *20* (43), 434203.
- (75) Luzon, J.; Bernot, K.; Hewitt, I. J.; Anson, C. E.; Powell, A. K.; Sessoli, R. Spin chirality in a molecular dysprosium triangle: The archetype of the noncollinear ising model. *Physical Review Letters* **2008**, *100* (24), 247205.

- (76) Osa, S.; Kido, T.; Matsumoto, N.; Re, N.; Pochaba, A.; Mrozinski, J. A tetranuclear 3d-4f single molecule magnet: $[\text{Cu}^{\text{II}}\text{LTb}^{\text{III}}(\text{hfac})_2]_2$. *Journal of the American Chemical Society* **2004**, 126 (2), 420-421.
- (77) Jing, Z. Y.; Moreno-Pineda, E.; Paul, S.; Sunil, A.; Fuhr, O.; Chen, Y. R.; Wernsdorfer, W.; Ruben, M. Leveraging 3d-4f Coordination: Molecular Quantum Spring-Magnet Behavior in Axial Ni_2Ln Complexes. *Angewandte Chemie-International Edition* **2025**, 65 (5), e22076.
- (78) Liu, J. L.; Wu, J. Y.; Chen, Y. C.; Mereacre, V.; Powell, A. K.; Ungur, L.; Chibotaru, L. F.; Chen, X. M.; Tong, M. L. A Heterometallic $\text{Fe}^{\text{II}}\text{-Dy}^{\text{III}}$ Single-Molecule Magnet with a Record Anisotropy Barrier. *Angewandte Chemie-International Edition* **2014**, 53 (47), 12966-12970.
- (79) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. Strong exchange and magnetic blocking in N_2^{3-} -radical-bridged lanthanide complexes. *Nature Chemistry* **2011**, 3 (7), 538-542.
- (80) Liu, F. P.; Spree, L.; Krylov, D. S.; Velkos, G.; Avdoshenko, S. M.; Popov, A. A. Single-Electron Lanthanide-Lanthanide Bonds Inside Fullerenes toward Robust Redox-Active Molecular Magnets. *Accounts of Chemical Research* **2019**, 52 (10), 2981-2993.
- (81) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. A N_2^{3-} Radical-Bridged Terbium Complex Exhibiting Magnetic Hysteresis at 14 K. *Journal of the American Chemical Society* **2011**, 133 (36), 14236-14239.
- (82) Demir, S.; Gonzalez, M. I.; Darago, L. E.; Evans, W. J.; Long, J. R. Giant coercivity and high magnetic blocking temperatures for N_2^{3-} radical-bridged dilanthanide complexes upon ligand dissociation. *Nature Communications* **2017**, 8 (1), 2144.
- (83) Morgan, I. S.; Mansikkamäki, A.; Rouzières, M.; Clérac, R.; Tuononen, H. M. Coexistence of long-range antiferromagnetic order and slow relaxation of the magnetization in the first lanthanide complex of a 1,2,4-benzotriazinyl radical. *Dalton Transactions* **2017**, 46 (38), 12790-12793.
- (84) Wang, H. L.; Wang, B. W.; Bian, Y. Z.; Gao, S.; Jiang, J. Z. Single-molecule magnetism of tetrapyrrole lanthanide compounds with sandwich multiple-decker structures. *Coordination Chemistry Reviews* **2016**, 306, 195-216.
- (85) Komeda, J.; Schlittenhardt, S.; Mizuno, A.; Moreno-Pineda, E.; Chen, Y. R.; Fuhr, O.; Appleton, J. L.; Boudalis, A. K.; Klyatskaya, S.; Ruben, M. A Stable Radical in Cationic Dinuclear Rare-Earth Triple-Decker Complexes Featuring Switchable Magnetic Properties. *Journal of the American Chemical Society* **2025**, 147 (43), 39367-39378.
- (86) Mavragani, N.; Kitos, A. A.; Brusso, J. L.; Murugesu, M. Enhancing Magnetic Communication between Metal Centres: The Role of Tetrazine Based Radicals as Ligands. *Chemistry-a European Journal* **2021**, 27 (16), 5091-5106.
- (87) Demir, S.; Jeon, I. R.; Long, J. R.; Harris, T. D. Radical ligand-containing single-molecule magnets. *Coordination Chemistry Reviews* **2015**, 289, 149-176.
- (88) Stevens, K. W. H. Matrix Elements and Operator Equivalents Connected with the Magnetic Properties of Rare Earth Ions. *Proceedings of the Physical Society of London Section A* **1952**, 65 (387), 209-215.
- (89) Bleaney, B.; Stevens, K. W. H. Paramagnetic Resonance. *Reports on Progress in Physics* **1953**, 16, 108-159.
- (90) Rinehart, J. D.; Long, J. R. Exploiting single-ion anisotropy in the design of f-element single-molecule magnets. *Chemical Science* **2011**, 2 (11), 2078-2085.
- (91) Zhang, P.; Zhang, L.; Wang, C.; Xue, S. F.; Lin, S. Y.; Tang, J. K. Equatorially Coordinated Lanthanide Single Ion Magnets. *Journal of the American Chemical Society* **2014**, 136 (12), 4484-4487.
- (92) Ungur, L.; Le Roy, J. J.; Korobkov, I.; Murugesu, M.; Chibotaru, L. F. Fine-tuning the Local Symmetry to Attain Record Blocking Temperature and Magnetic Remanence in a Single-Ion Magnet. *Angewandte Chemie-International Edition* **2014**, 53 (17), 4413-4417.
- (93) Jiang, S. D.; Wang, B. W.; Sun, H. L.; Wang, Z. M.; Gao, S. An Organometallic Single-Ion Magnet. *Journal of the American Chemical Society* **2011**, 133 (13), 4730-4733.

- (94) Meihäus, K. R.; Long, J. R. Magnetic Blocking at 10 K and a Dipolar-Mediated Avalanche in Salts of the Bis(η^8 -cyclooctatetraenide) Complex $[\text{Er}(\text{COT})_2]^-$. *Journal of the American Chemical Society* **2013**, *135* (47), 17952-17957.
- (95) Liu, J.; Chen, Y. C.; Liu, J. L.; Vieru, V.; Ungur, L.; Jia, J. H.; Chibotaru, L. F.; Lan, Y. H.; Wernsdorfer, W.; Gao, S.; et al. A Stable Pentagonal Bipyramidal Dy(III) Single-Ion Magnet with a Record Magnetization Reversal Barrier over 1000 K. *Journal of the American Chemical Society* **2016**, *138* (16), 5441-5450.
- (96) Ding, Y. S.; Chilton, N. F.; Winpenny, R. E. P.; Zheng, Y. Z. On Approaching the Limit of Molecular Magnetic Anisotropy: A Near-Perfect Pentagonal Bipyramidal Dysprosium(III) Single-Molecule Magnet. *Angewandte Chemie-International Edition* **2016**, *55* (52), 16071-16074.
- (97) Meng, Y. S.; Zhang, Y. Q.; Wang, Z. M.; Wang, B. W.; Gao, S. Weak Ligand-Field Effect from Ancillary Ligands on Enhancing Single-Ion Magnet Performance. *Chemistry-a European Journal* **2016**, *22* (36), 12724-12731.
- (98) Guo, F. S.; Day, B. M.; Chen, Y. C.; Tong, M. L.; Mansikkamäki, A.; Layfield, R. A. A Dysprosium Metallocene Single-Molecule Magnet Functioning at the Axial Limit. *Angewandte Chemie-International Edition* **2017**, *56* (38), 11445-11449.
- (99) Goodwin, C. A. P.; Ortu, F.; Reta, D.; Chilton, N. F.; Mills, D. P. Molecular magnetic hysteresis at 60 kelvin in dysprosocenium. *Nature* **2017**, *548* (7668), 439-442.
- (100) Guo, F. S.; Day, B. M.; Chen, Y. C.; Tong, M. L.; Mansikkamäki, A.; Layfield, R. A. Magnetic hysteresis up to 80 kelvin in a dysprosium metallocene single-molecule magnet. *Science* **2018**, *362* (6421), 1400-1403.
- (101) Pointillart, F.; Bernot, K.; Le Guennic, B.; Cador, O. Isotopic enrichment in lanthanide coordination complexes: contribution to single-molecule magnets and spin qubit insights. *Chemical Communications* **2023**, *59* (55), 8520-8531.
- (102) Meija, J.; Coplen, T. B.; Berglund, M.; Brand, W. A.; De Bièvre, P.; Gröning, M.; Holden, N. E.; Irrgeher, J.; Loss, R. D.; Walczyk, T.; et al. Isotopic compositions of the elements 2013 (IUPAC Technical Report). *Pure and Applied Chemistry* **2016**, *88* (3), 293-306.
- (103) Chen, Y. C.; Liu, J. L.; Wernsdorfer, W.; Liu, D.; Chibotaru, L. F.; Chen, X. M.; Tong, M. L. Hyperfine-Interaction-Driven Suppression of Quantum Tunneling at Zero Field in a Holmium(III) Single-Ion Magnet. *Angewandte Chemie-International Edition* **2017**, *56* (18), 4996-5000.
- (104) Pointillart, F.; Bernot, K.; Golhen, S.; Le Guennic, B.; Guizouarn, T.; Ouahab, L.; Cador, O. Magnetic Memory in an Isotopically Enriched and Magnetically Isolated Mononuclear Dysprosium Complex. *Angewandte Chemie-International Edition* **2015**, *54* (5), 1504-1507.
- (105) Li, J.; Xiong, S. J.; Li, C.; Jin, B.; Zhang, Y. Q.; Jiang, S. D.; Ouyang, Z. W.; Wang, Z.; Wu, X. L.; van Tol, J.; et al. Manipulation of Molecular Qubits by Isotope Effect on Spin Dynamics. *CCS Chemistry* **2020**, *3* (9), 2548-2556.
- (106) Liu, Y.; Ho, L. T. A.; Huang, G. Z.; Chen, Y. C.; Ungur, L.; Liu, J. L.; Tong, M. L. Magnetization Dynamics on Isotope-Isomorphic Holmium Single-Molecule Magnets. *Angewandte Chemie-International Edition* **2021**, *60* (52), 27282-27287.
- (107) Gregson, M.; Chilton, N. F.; Ariciu, A. M.; Tuna, F.; Crowe, I. F.; Lewis, W.; Blake, A. J.; Collison, D.; McInnes, E. J. L.; Winpenny, R. E. P.; et al. A monometallic lanthanide bis(methanediide) single molecule magnet with a large energy barrier and complex spin relaxation behaviour. *Chemical Science* **2016**, *7* (1), 155-165.
- (108) Latendresse, T. P.; Vieru, V.; Wilkins, B. O.; Bhuvanesh, N. S.; Chibotaru, L. F.; Nippe, M. Magnetic Properties of a Terbium-[1]Ferrocenophane Complex: Analogies between Lanthanide-Ferrocenophane and Lanthanide-Bis-phthalocyanine Complexes. *Angewandte Chemie-International Edition* **2018**, *57* (27), 8164-8169.
- (109) Norel, L.; Darago, L. E.; Le Guennic, B.; Chakarawet, K.; Gonzalez, M. I.; Olshansky, J. H.; Rigaut, S.; Long, J. R. A Terminal Fluoride Ligand Generates Axial Magnetic Anisotropy in Dysprosium Complexes. *Angewandte Chemie-International Edition* **2018**, *57* (7), 1933-1938.

- (110) Gould, C. A.; McClain, K. R.; Reta, D.; Kragoskow, J. G. C.; Marchiori, D. A.; Lachman, E.; Choi, E. S.; Analytis, J. G.; Britt, R. D.; Chilton, N. F.; et al. Ultrahard magnetism from mixed-valence dilanthanide complexes with metal-metal bonding. *Science* **2022**, 375 (6577), 198-202.
- (111) Chen, Y. C.; Tong, M. L. Single-molecule magnets beyond a single lanthanide ion: the art of coupling. *Chemical Science* **2022**, 13 (30), 8716-8726.
- (112) Horii, Y.; Katoh, K.; Breedlove, B. K.; Yamashita, M. Elongation of magnetic relaxation times in a single-molecule magnet through intermetallic interactions: a clamshell-type dinuclear terbium(III)-phthalocyaninato quadruple-decker complex. *Chemical Communications* **2017**, 53 (61), 8561-8564.
- (113) Wang, H. L.; Liu, T.; Wang, K.; Duan, C. Y.; Jiang, J. Z. Tetrakis(phthalocyaninato) Rare-Earth-Cadmium-Rare-Earth Quadruple-Decker Sandwich SMMs: Suppression of QTM by Long-Distance f-f Interactions. *Chemistry-a European Journal* **2012**, 18 (25), 7691-7694.
- (114) Horii, Y.; Katoh, K.; Cosquer, G.; Breedlove, B. K.; Yamashita, M. Weak Dy-Dy Interactions in Dy-Phthalocyaninato Multiple-Decker Single-Molecule Magnets Effectively Suppress Magnetic Relaxation. *Inorganic Chemistry* **2016**, 55 (22), 11782-11790.
- (115) Horii, Y.; Kishiue, S.; Damjanovic, M.; Katoh, K.; Breedlove, B. K.; Enders, M.; Yamashita, M. Supramolecular Approach for Enhancing Single-Molecule Magnet Properties of Terbium(III)-Phthalocyaninato Double-Decker Complexes with Crown Moieties. *Chemistry-a European Journal* **2018**, 24 (17), 4320-4327.
- (116) Chen, Y. X.; Liu, C.; Ma, F.; Qi, D. D.; Liu, Q. Y.; Sun, H. L.; Jiang, J. Z. Fabricating Bis(phthalocyaninato) Terbium SIM into Tetrakis(phthalocyaninato) Terbium SMM with Enhanced Performance through Sodium Coordination. *Chemistry-a European Journal* **2018**, 24 (32), 8066-8070.
- (117) Ruan, L. X.; Tong, J. W.; Luo, F. F.; Qin, G. W.; Tian, F. B.; Jiao, X. C.; Zhang, X. M. Magnetic Improvement and Relaxation Mechanism of the Tb-Phthalocyanine Single-Molecule Magnet by Absorbing CH₂Cl₂ Molecules. *Journal of Physical Chemistry C* **2021**, 125 (18), 10165-10172.
- (118) Habib, F.; Lin, P. H.; Long, J.; Korobkov, I.; Wernsdorfer, W.; Murugesu, M. The Use of Magnetic Dilution To Elucidate the Slow Magnetic Relaxation Effects of a Dy₂ Single-Molecule Magnet. *Journal of the American Chemical Society* **2011**, 133 (23), 8830-8833.
- (119) Llanos, L.; Aravena, D. Relaxation time enhancement by magnetic dilution in single-molecule magnets: An ab initio study. *Journal of Magnetism and Magnetic Materials* **2019**, 489, 165456.
- (120) Jeletic, M.; Lin, P. H.; Le Roy, J. J.; Korobkov, I.; Gorelsky, S. I.; Murugesu, M. An Organometallic Sandwich Lanthanide Single-Ion Magnet with an Unusual Multiple Relaxation Mechanism. *Journal of the American Chemical Society* **2011**, 133 (48), 19286-19289.
- (121) Sun, W. B.; Yan, P. F.; Jiang, S. D.; Wang, B. W.; Zhang, Y. Q.; Li, H. F.; Chen, P.; Wang, Z. M.; Gao, S. High symmetry or low symmetry, that is the question - high performance Dy(III) single-ion magnets by electrostatic potential design. *Chemical Science* **2016**, 7 (1), 684-691.
- (122) Bi, Y.; Guo, Y. N.; Zhao, L.; Guo, Y.; Lin, S. Y.; Jiang, S. D.; Tang, J. K.; Wang, B. W.; Gao, S. Capping Ligand Perturbed Slow Magnetic Relaxation in Dysprosium Single-Ion Magnets. *Chemistry-a European Journal* **2011**, 17 (44), 12476-12481.
- (123) Chen, Y. C.; Liu, J. L.; Ungur, L.; Liu, J.; Li, Q. W.; Wang, L. F.; Ni, Z. P.; Chibotaru, L. F.; Chen, X. M.; Tong, M. L. Symmetry-Supported Magnetic Blocking at 20 K in Pentagonal Bipyramidal Dy(III) Single-Ion Magnets. *Journal of the American Chemical Society* **2016**, 138 (8), 2829-2837.
- (124) Kragoskow, J. G. C.; Mattioni, A.; Staab, J. K.; Reta, D.; Skelton, J. M.; Chilton, N. F. Spin-phonon coupling and magnetic relaxation in single-molecule magnets. *Chemical Society Reviews* **2023**, 52 (14), 4567-4585.
- (125) Atzori, M.; Tesi, L.; Benci, S.; Lunghi, A.; Righini, R.; Taschin, A.; Torre, R.; Sorace, L.; Sessoli, R. Spin Dynamics and Low Energy Vibrations: Insights from Vanadyl-Based Potential Molecular Qubits. *Journal of the American Chemical Society* **2017**, 139 (12), 4338-4341.

- (126) Escalera-Moreno, L.; Suaud, N.; Gaita-Ariño, A.; Coronado, E. Determining Key Local Vibrations in the Relaxation of Molecular Spin Qubits and Single-Molecule Magnets. *Journal of Physical Chemistry Letters* **2017**, 8 (7), 1695-1700.
- (127) Jin, P. B.; Luo, Q. C.; Zheng, Y. Z. Regulating Lanthanide Single-Molecule Magnets with Coordination Geometry and Organometallic Chemistry. *Accounts of Chemical Research* **2026**, 59 (2), 221-233.
- (128) Ortu, F.; Reta, D.; Ding, Y. S.; Goodwin, C. A. P.; Gregson, M. P.; McInnes, E. J. L.; Winpenny, R. E. P.; Zheng, Y. Z.; Liddle, S. T.; Mills, D. P.; et al. Studies of hysteresis and quantum tunnelling of the magnetisation in dysprosium(III) single molecule magnets. *Dalton Transactions* **2019**, 48 (24), 8541-8545.
- (129) Reta, D.; Kragoskow, J. G. C.; Chilton, N. F. Ab Initio Prediction of High-Temperature Magnetic Relaxation Rates in Single-Molecule Magnets. *Journal of the American Chemical Society* **2021**, 143 (15), 5943-5950.
- (130) Briganti, M.; Santanni, F.; Tesi, L.; Totti, F.; Sessoli, R.; Lunghi, A. A Complete View of Orbach and Raman Spin-Lattice Relaxation in a Dysprosium Coordination Compound. *Journal of the American Chemical Society* **2021**, 143 (34), 13633-13645.
- (131) Yu, K. X.; Kragoskow, J. G. C.; Ding, Y. S.; Zhai, Y. Q.; Reta, D.; Chilton, N. F.; Zheng, Y. Z. Enhancing Magnetic Hysteresis in Single-Molecule Magnets by Ligand Functionalization. *Chem* **2020**, 6 (7), 1777-1793.
- (132) Ladd, T. D.; Jelezko, F.; Laflamme, R.; Nakamura, Y.; Monroe, C.; O'Brien, J. L. Quantum computers. *Nature* **2010**, 464 (7285), 45-53.
- (133) Zadrozny, J. M.; Gallagher, A. T.; Harris, T. D.; Freedman, D. E. A Porous Array of Clock Qubits. *Journal of the American Chemical Society* **2017**, 139 (20), 7089-7094.
- (134) Leuenberger, M. N.; Loss, D. Quantum computing in molecular magnets. *Nature* **2001**, 410 (6830), 789-793.
- (135) Aguilà, D.; Barrios, L. A.; Velasco, V.; Roubeau, O.; Repollés, A.; Alonso, P. J.; Sesé, J.; Teat, S. J.; Luis, F.; Aromí, G. Heterodimetallic [LnLn'] Lanthanide Complexes: Toward a Chemical Design of Two-Qubit Molecular Spin Quantum Gates. *Journal of the American Chemical Society* **2014**, 136 (40), 14215-14222.
- (136) Moreno-Pineda, E.; Wernsdorfer, W. Magnetic Molecules as Building Blocks for Quantum Technologies. *Advanced Quantum Technologies* **2025**, 8 (2).
- (137) Wernsdorfer, W.; Ruben, M. Synthetic Hilbert Space Engineering of Molecular Qudits: Isotopologue Chemistry. *Advanced Materials* **2019**, 31 (26), 1806687.
- (138) Liu, J. L.; Chen, Y. C.; Tong, M. L. Symmetry strategies for high performance lanthanide-based single-molecule magnets. *Chemical Society Reviews* **2018**, 47 (7), 2431-2453.
- (139) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. Exchange-biased quantum tunnelling in a supramolecular dimer of single-molecule magnets. *Nature* **2002**, 416 (6879), 406-409.
- (140) Moreno-Pineda, E.; Wernsdorfer, W. Measuring molecular magnets for quantum technologies. *Nature Reviews Physics* **2021**, 3 (9), 645-659.
- (141) Wernsdorfer, W.; Caneschi, A.; Sessoli, R.; Gatteschi, D.; Cornia, A.; Villar, V.; Paulsen, C. Effects of nuclear spins on the quantum relaxation of the magnetization for the molecular nanomagnet Fe₈. *Physical Review Letters* **2000**, 84 (13), 2965-2968.
- (142) Atzori, M.; Morra, E.; Tesi, L.; Albino, A.; Chiesa, M.; Sorace, L.; Sessoli, R. Quantum Coherence Times Enhancement in Vanadium(IV)-based Potential Molecular Qubits: the Key Role of the Vanadyl Moiety. *Journal of the American Chemical Society* **2016**, 138 (35), 11234-11244.
- (143) Durig, J. R.; Craven, S. M.; Lau, K. K.; Bragin, J. Low-Frequency Vibrations of Molecular Solids. X. CH₃CCl₃, CD₃CCl₃, CH₃CCl₂H, and CH₃CF₃. *Journal of Chemical Physics* **1971**, 54 (2), 479-487.
- (144) Harris, A. B. Properties of solid hydrogen. II. Theory of nuclear magnetic resonance and relaxation. *Physical Review B-Solid State* **1970**, 2 (9), 3495-3525.
- (145) Taddei, G.; Bonadeo, H.; Marzocchi, M. P.; Califano, S. Calculation of Crystal Vibrations of Benzene. *Journal of Chemical Physics* **1973**, 58 (3), 966-978.

- (146) Kearley, G. J.; Johnson, M. R.; Tomkinson, J. Intermolecular interactions in solid benzene. *Journal of Chemical Physics* **2006**, *124* (4), 044514.
- (147) Moseley, D. H.; Stavretis, S. E.; Thirunavukkuarasu, K.; Ozerov, M.; Cheng, Y. Q.; Daemen, L. L.; Ludwig, J.; Lu, Z. G.; Smirnov, D.; Brown, C. M.; et al. Spin-phonon couplings in transition metal complexes with slow magnetic relaxation. *Nature Communications* **2018**, *9*, 2572.
- (148) Shi, C.; Zhang, X.; Yu, C. H.; Yao, Y. F.; Zhang, W. Geometric isotope effect of deuteration in a hydrogen-bonded host-guest crystal. *Nature Communications* **2018**, *9*, 481.
- (149) Kainosho, M.; Torizawa, T.; Iwashita, Y.; Terauchi, T.; Ono, A. M.; Güntert, P. Optimal isotope labelling for NMR protein structure determinations. *Nature* **2006**, *440* (7080), 52-57.
- (150) Perrin, C. L.; Shrinidhi, A.; Burke, K. D. Isotopic-Perturbation NMR Study of Hydrogen-Bond Symmetry in Solution: Temperature Dependence and Comparison of OHO and ODO Hydrogen Bonds. *Journal of the American Chemical Society* **2019**, *141* (43), 17278-17286.
- (151) Zadrozny, J. M.; Niklas, J.; Poluektov, O. G.; Freedman, D. E. Millisecond Coherence Time in a Tunable Molecular Electronic Spin Qubit. *Acs Central Science* **2015**, *1* (9), 488-492.
- (152) Katoh, K.; Isshiki, H.; Komeda, T.; Yamashita, M. Molecular Spintronics Based on Single-Molecule Magnets Composed of Multiple-Decker Phthalocyaninato Terbium(III) Complex. *Chemistry-an Asian Journal* **2012**, *7* (6), 1154-1169.
- (153) Ishikawa, N.; Sugita, M.; Tanaka, N.; Ishikawa, T.; Koshihara, S. Y.; Kaizu, Y. Upward temperature shift of the intrinsic phase lag of the magnetization of bis(phthalocyaninato)terbium by ligand oxidation creating an $S = 1/2$ spin. *Inorganic Chemistry* **2004**, *43* (18), 5498-5500.
- (154) Pineda, E. M.; Komeda, T.; Katoh, K.; Yamashita, M.; Ruben, M. Surface confinement of TbPc-SMMs: structural, electronic and magnetic properties. *Dalton Transactions* **2016**, *45* (46), 18417-18433.
- (155) Dailey, M.; Besson, C. Selective crystallization of four bis(phthalocyaninato)lanthanoid(III) polymorphs. *Crystengcomm* **2021**, *23* (40), 7151-7161.
- (156) Katoh, K.; Yoshida, Y.; Yamashita, M.; Miyasaka, H.; Breedlove, B. K.; Kajiwar, T.; Takaishi, S.; Ishikawa, N.; Isshiki, H.; Zhang, Y. F.; et al. Direct Observation of Lanthanide(III)-Phthalocyanine Molecules on Au(111) by Using Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy and Thin-Film Field-Effect Transistor Properties of Tb(III)- and Dy(III)-Phthalocyanine Molecules. *Journal of the American Chemical Society* **2009**, *131* (29), 9967-9976.
- (157) Alvarez, S.; Alemany, P.; Casanova, D.; Cirera, J.; Llunell, M.; Avnir, D. Shape maps and polyhedral interconversion paths in transition metal chemistry. *Coordination Chemistry Reviews* **2005**, *249* (17-18), 1693-1708.
- (158) Spek, A. L. Single-crystal structure validation with the program. *Journal of Applied Crystallography* **2003**, *36*, 7-13.
- (159) Spek, A. L. SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallographica Section C-Structural Chemistry* **2015**, *71*, 9-18.
- (160) Le, N. T. A.; Son, Y.; Kim, I.; Tokunaga, R.; Hayami, S.; Min, K. S. Deuterium-Enhanced Photoluminescence and Magnetic Properties in Octanuclear Terbium(III) Complexes Containing a Hexadentate $N_2O_4^-$ -Type Ligand. *Crystal Growth & Design* **2025**, *25* (7), 2193-2205.
- (161) Gu, L.; Wu, R. Q. Origins of Slow Magnetic Relaxation in Single-Molecule Magnets. *Physical Review Letters* **2020**, *125* (11), 117203.
- (162) Gupta, S.; Ali, M. E. Exchange Interactions Induce Multiple Magnetic Relaxation Channels in Single Molecule Magnets. *chemRxiv* **2024**.
- (163) Pointillart, F.; Bernot, K.; Poneti, G.; Sessoli, R. Crystal Packing Effects on the Magnetic Slow Relaxation of Tb(III)-Nitronyl Nitroxide Radical Cyclic Dinuclear Clusters. *Inorganic Chemistry* **2012**, *51* (22), 12218-12229.
- (164) Taran, G.; Bonet, E.; Wernsdorfer, W. Decoherence measurements in crystals of molecular magnets. *Physical Review B* **2019**, *99* (18), 180408.
- (165) Taran, G.; Bonet, E.; Moreno-Pineda, E.; Ruben, M.; Wernsdorfer, W. Thermalization of Nuclear Spins in Lanthanide Molecular Magnets. *Inorganic Chemistry* **2023**, *62* (22), 8598-8604.

- (166) Taran, G.; Bonet, E.; Wernsdorfer, W. The role of the quadrupolar interaction in the tunneling dynamics of lanthanide molecular magnets. *Journal of Applied Physics* **2019**, 125 (14), 142903.
- (167) Guldi, D. M.; Nishihara, H.; Venkataraman, L. Molecular wires. *Chemical Society Reviews* **2015**, 44 (4), 842-844.
- (168) Leiserson, C. E.; Thompson, N. C.; Emer, J. S.; Kuszmaul, B. C.; Lampson, B. W.; Sanchez, D.; Schardl, T. B. There's plenty of room at the Top: What will drive computer performance after Moore's law? *Science* **2020**, 368 (6495), eaam9744.
- (169) Chiesa, A.; Santini, P.; Garlatti, E.; Luis, F.; Carretta, S. Molecular nanomagnets: a viable path toward quantum information processing? *Reports on Progress in Physics* **2024**, 87 (3).
- (170) Gaita-Ariño, A.; Luis, F.; Hill, S.; Coronado, E. Molecular spins for quantum computation. *Nature Chemistry* **2019**, 11 (4), 301-309.
- (171) Wasielewski, M. R.; Forbes, M. D. E.; Frank, N. L.; Kowalski, K.; Scholes, G. D.; Yuen-Zhou, J.; Baldo, M. A.; Freedman, D. E.; Goldsmith, R. H.; Goodson, T.; et al. Exploiting chemistry and molecular systems for quantum information science. *Nature Reviews Chemistry* **2020**, 4 (9), 490-504.
- (172) Meng, Y. S.; Jiang, S. D.; Wang, B. W.; Gao, S. Understanding the Magnetic Anisotropy toward Single-Ion Magnets. *Accounts of Chemical Research* **2016**, 49 (11), 2381-2389.
- (173) Woodruff, D. N.; Winpenny, R. E. P.; Layfield, R. A. Lanthanide Single-Molecule Magnets. *Chemical Reviews* **2013**, 113 (7), 5110-5148.
- (174) Chilton, N. F. Design Criteria for High-Temperature Single-Molecule Magnets. *Inorganic Chemistry* **2015**, 54 (5), 2097-2099.
- (175) Thomas, L.; Lioni, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. Macroscopic quantum tunnelling of magnetization in a single crystal of nanomagnets. *Nature* **1996**, 383 (6596), 145-147.
- (176) Sessoli, R. Toward the Quantum Computer: Magnetic Molecules Back in the Race. *Acs Central Science* **2015**, 1 (9), 473-474.
- (177) Chauhan, D.; Paul, S.; Borah, D.; Sunil, A.; Wernsdorfer, W.; Shanmugam, M.; Rajaraman, G. Ultraslow Relaxation of Toroidal State in Ferrotoroidal Dysprosium Complex. *Journal of the American Chemical Society* **2025**, 147 (43), 39572-39581.
- (178) Hymas, K.; Soncini, A.; Vignesh, K. R.; Chauhan, D.; Swain, A.; Benjamin, S. L.; Borah, D.; Shanmugam, M.; Wernsdorfer, W.; Rajaraman, G.; et al. Discriminating ferrotoroidic from antiferrotoroidic ground states using a 3d quantum spin sensor. *Npj Quantum Materials* **2024**, 9 (1).
- (179) Ungur, L.; Lin, S. Y.; Tang, J. K.; Chibotaru, L. F. Single-molecule toroids in Ising-type lanthanide molecular clusters. *Chemical Society Reviews* **2014**, 43 (20), 6894-6905.
- (180) Li, X. L.; Wu, J. F.; Tang, J. K.; Le Guennic, B.; Shi, W.; Cheng, P. A planar triangular $Dy_3 + Dy_3$ single-molecule magnet with a toroidal magnetic moment. *Chemical Communications* **2016**, 52 (61), 9570-9573.
- (181) Rao, S. V.; Ashtree, J. M.; Soncini, A. Toroidal moment in a family of spin -frustrated heterometallic triangular nanomagnets without spin -orbit coupling: Applications in a molecular spintronics device. *Physica B-Condensed Matter* **2020**, 592.
- (182) Vignesh, K. R.; Rajaraman, G. Strategies to Design Single-Molecule Toroids Using Triangular $\{Ln_3\}_n$ Motifs. *Acs Omega* **2021**, 6 (48), 32349-32364.
- (183) Chibotaru, L. F.; Ungur, L.; Soncini, A. The origin of nonmagnetic Kramers doublets in the ground state of dysprosium triangles: Evidence for a toroidal magnetic moment. *Angewandte Chemie-International Edition* **2008**, 47 (22), 4126-4129.
- (184) Yang, Q. Q.; Ungur, L.; Wernsdorfer, W.; Tang, J. K. Toroidal magnetic moments in Tb_4 squares. *Inorganic Chemistry Frontiers* **2022**, 9 (4), 784-791.
- (185) Mondal, S.; Chauhan, D.; Guizouarn, T.; Pointillart, F.; Rajaraman, G.; Steiner, A.; Baskar, V. Self-Assembled Lanthanide Phosphinate Square Grids ($Ln = Er, Dy, \text{ and } Tb$): Dy_4 Shows SMM/SMT and Tb_4 SMT Behavior. *Inorganic Chemistry* **2024**, 63 (47), 22338-22348.

- (186) Gusev, A.; Herchel, R.; Nemec, I.; Shul'gin, V.; Eremenko, I. L.; Lyssenko, K.; Linert, W.; Trávníček, Z. Tetranuclear Lanthanide Complexes Containing a Hydrazone-type Ligand. Dysprosium [2 x 2] Gridlike Single-Molecule Magnet and Toroid. *Inorganic Chemistry* **2016**, *55* (23), 12470-12476.
- (187) Garcia, G. F.; Guettas, D.; Montigaud, V.; Larini, P.; Sessoli, R.; Totti, F.; Cador, O.; Pilet, G.; Le Guennic, B. A Dy₄ Cubane: A New Member in the Single-Molecule Toroids Family. *Angewandte Chemie-International Edition* **2018**, *57* (52), 17089-17093.
- (188) Langley, S. K.; Vignesh, K. R.; Gupta, T.; Gartshore, C. J.; Rajaraman, G.; Forsyth, C. M.; Murray, K. S. New examples of triangular terbium(iii) and holmium(iii) and hexagonal dysprosium(iii) single molecule toroids. *Dalton Transactions* **2019**, *48* (41), 15657-15667.
- (189) Zhang, H. L.; Zhai, Y. Q.; Qin, L.; Ungur, L.; Nojiri, H.; Zheng, Y. Z. Single-Molecule Toroid Design through Magnetic Exchange Coupling. *Matter* **2020**, *2* (6), 1481-1493.
- (190) Zhang, Q.; Baker, M. L.; Li, S. Q.; Sarachik, M. P.; Baldoví, J. J.; Gaita-Ariño, A.; Coronado, E.; Alexandropoulos, D. I.; Stamatatos, T. C. Experimental determination of single molecule toroid behaviour in a Dy₈ single molecule magnet. *Nanoscale* **2019**, *11* (32), 15131-15138.
- (191) Gonzalez, J. F.; Pointillart, F.; Cador, O. Hyperfine coupling and slow magnetic relaxation in isotopically enriched Dy^{III} mononuclear single-molecule magnets. *Inorganic Chemistry Frontiers* **2019**, *6* (4), 1081-1086.
- (192) Moreno-Pineda, E.; Taran, G.; Wernsdorfer, W.; Ruben, M. Quantum tunnelling of the magnetisation in single-molecule magnet isotopologue dimers. *Chemical Science* **2019**, *10* (19), 5138-5145.
- (193) Gonzalez, J. F.; Douib, H.; Le Guennic, B.; Pointillart, F.; Cador, O. Ytterbium-Centered Isotopic Enrichment Leading to a Zero-Field Single-Molecule Magnet. *Inorganic Chemistry* **2021**, *60* (2), 541-545.
- (194) Garlatti, E.; Albino, A.; Chicco, S.; Nguyen, V. H. A.; Santanni, F.; Paolasini, L.; Mazzoli, C.; Caciuffo, R.; Totti, F.; Santini, P.; et al. The critical role of ultra-low-energy vibrations in the relaxation dynamics of molecular qubits. *Nature Communications* **2023**, *14* (1), 1653.
- (195) Galván, I. F.; Vacher, M.; Alavi, A.; Angeli, C.; Aquilante, F.; Autschbach, J.; Bao, J. J.; Bokarev, S. I.; Bogdanov, N. A.; Carlson, R. K.; et al. OpenMolcas: From Source Code to Insight. *Journal of Chemical Theory and Computation* **2019**, *15* (11), 5925-5964.
- (196) Aquilante, F.; Autschbach, J.; Baiardi, A.; Battaglia, S.; Borin, V. A.; Chibotaru, L. F.; Conti, I.; De Vico, L.; Delcey, M.; Galvan, I. F.; et al. Modern quantum chemistry with [Open]Molcas. *Journal of Chemical Physics* **2020**, *152* (21), 214117.
- (197) Ungur, L.; Chibotaru, L. F. Ab Initio Crystal Field for Lanthanides. *Chemistry-a European Journal* **2017**, *23* (15), 3708-3718.
- (198) Chen, Y. R.; Moreno-Pineda, E.; Paul, S.; Fuhr, O.; Fenske, D.; Wernsdorfer, W.; Ruben, M. Unconventional Nuclear-Spin-Dependent Toroidal Ground States in Isotopologue ^ADy₄ [2 × 2] Complexes. *Journal of the American Chemical Society* **2026**, *148* (16), 17324-17332.
- (199) Wernsdorfer, W.; Chakov, N. E.; Christou, G. Determination of the magnetic anisotropy axes of single-molecule magnets. *Physical Review B* **2004**, *70* (13).
- (200) Vignesh, K. R.; Soncini, A.; Langley, S. K.; Wernsdorfer, W.; Murray, K. S.; Rajaraman, G. Ferrotoroidic ground state in a heterometallic {Cr^{III}Dy^{III}6} complex displaying slow magnetic relaxation. *Nature Communications* **2017**, *8*.
- (201) Sheldrick, G. M. Crystal structure refinement with. *Acta Crystallographica Section C-Structural Chemistry* **2015**, *71*, 3-8.
- (202) Sheldrick, G. M. A short history of SHELX. *Acta Crystallographica a-Foundation and Advances* **2008**, *64*, 112-122.
- (203) Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallographica a-Foundation and Advances* **2015**, *71*, 3-8.
- (204) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* **2009**, *42*, 339-341.

- (205) Manni, G. L.; Galván, I. F.; Alavi, A.; Aleotti, F.; Aquilante, F.; Autschbach, J.; Avagliano, D.; Baiardi, A.; Bao, J. J.; Battaglia, S.; et al. The OpenMolcas: A Community-Driven Approach to Advancing Computational Chemistry. *Journal of Chemical Theory and Computation* **2023**, *19* (20), 6933-6991.
- (206) Aquilante, F.; Autschbach, J.; Carlson, R. K.; Chibotaru, L. F.; Delcey, M. G.; De Vico, L.; Galván, I. F.; Ferré, N.; Frutos, L. M.; Gagliardi, L.; et al. Molcas 8: New capabilities for multiconfigurational quantum chemical calculations across the periodic table. *Journal of Computational Chemistry* **2016**, *37* (5), 506-541.
- (207) Olsen, J.; Roos, B. O.; Jorgensen, P.; Jensen, H. J. A. Determinant Based Configuration-Interaction Algorithms for Complete and Restricted Configuration-Interaction Spaces. *Journal of Chemical Physics* **1988**, *89* (4), 2185-2192.
- (208) Siegbahn, P. E. M.; Almlöf, J.; Heiberg, A.; Roos, B. O. The Complete Active Space Scf (Casscf) Method in a Newton-Raphson Formulation with Application to the H₂O Molecule. *Journal of Chemical Physics* **1981**, *74* (4), 2384-2396.
- (209) Zobel, J. P.; Widmark, P. O.; Veryazov, V. The ANO-R Basis Set. *Journal of Chemical Theory and Computation* **2020**, *16* (1), 278-294.