

PROBING NANOMAGNETISM THROUGH A MATERIALS APPROACH:
PARAMAGNETIC IONS WITHIN NANOMATERIALS

by

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Abstract

This thesis will describe the magnetic behavior found in a scaling array of magnetic nanomaterials that have been uniquely designed, synthesized and characterised in order to better understand their properties with regards to potential future applications. Within Chapter 1 will be a detailed, yet accessible, introduction to nanomagnetism and the fundamental principles and practical techniques essential to the study of this unique mélange of physics and chemistry. This chapter will be designed to give the reader the necessary tools to understand key literature concepts found in Chapter 2, as well as the work presented in the following chapters. Chapter 2 will provide an overview of relevant literature in the field of magnetic nanomaterials, including: nanoparticles, single-molecule magnets, single-chain magnets and metal-organic frameworks.

Chapter 3 will describe work performed on nanoparticles doped with lanthanide ions in order to explore their resulting size, shape, crystallinity and magnetic properties. The relevance of the chosen particles (NaYF_4) pertains to their proposed use in a variety of applications due to their known luminescent properties, which we sought to hybridize with interesting magnetic properties, thus creating multimodal imaging capabilities. Doping with a variety of desired ratios of lanthanide ions (Gd^{III} , Tb^{III} , Dy^{III} , Er^{III} and Yb^{III}) was successful, producing crystalline nanoparticles with tunable size and shape. Magnetic measurements displayed a clear absence of superparamagnetic behavior, indicating that these materials have the potential to be well-suited to applications in biomedicine as multimodal imaging probes and MRI contrast agents.

Chapter 4 will build on the previously explored doped nanomaterials through creating a hybrid nanomaterial by tethering lanthanide-based magnetic molecules to the surface of nanoparticles. This is performed through the synthetic design of a SMM with two anisotropic Dy^{III} ions, which was synthesized and designed to bear terminal S-groups in order to promote the binding of the magnetic molecule to capping agent free gold nanoparticles. Upon confirmation of the successful surface attachment of the molecules, magnetic measurements displayed that the magnetic molecules maintained their static properties, however, their dynamic properties were altered. This system was the first example of this type of novel approach to the study of magnetic molecules on surfaces for data storage, spintronics, and quantum computing applications.

Chapter 5 will expand on the previous study of ordering arrays of magnetic molecules on the surface of nanoparticles by tethering them into 1D chain networks. We successfully synthesized chain networks with Y^{III} , Eu^{III} , Gd^{III} , Tb^{III} and Dy^{III} lanthanide ions. Magnetic

characterisation revealed slow relaxation of the magnetization with no significant interactions between magnetic ions, thus these are discrete magnetic molecules in 1D. Rather surprisingly, the isotropic Gd^{III} analogue displayed field induced slow relaxation of the magnetisation, necessitating the use of ab initio calculations in order to shed light on the potential causes of this unexpected behavior. Overall, through the formation and study of these structures, we observed a new potential method of SMM assembly for the study of ordered arrays of molecular magnets.

Chapter 6 will focus on ordering of discrete magnetic systems in 3D. With this in mind, we successfully isolated the first Co_8 cuboctahedron MOF. Magnetic measurements displayed that each SBU was well-isolated, with significant antiferromagnetic coupling between Co^{II} ions, leading to an $S = 0$ ground state. These interactions were then modelled using density functional theory. This type of study promotes the future development of novel high-nuclearity MOF structures with interesting and tuneable magnetic properties, as well as the potential for assembly of discrete molecular magnetic units in 3D using MOFs.

Chapter 7 utilizes the principles of Chapter 3, wherein magnetic ions are doped into a diamagnetic material; in this case, MOF-5. We sought to isolate one Co^{II} ion in each SBU, and build upon this by adding additional magnetic ions and probing their interactions. Through magnetic measurements we observed a scaling magnetic moment with Co^{II} content, and with higher dopant percentages we began to observe magnetic interactions occurring within the SBUs. Interestingly, we also observed a change in coordination environment with higher dopant percentages, likely as a result of the previously suggested capability of one Zn^{II} ion within the MOF-5 SBU to become hexacoordinate, allowing Co^{II} doping up to a maximum of 25%. Consequently, this study points to the cause of the structural instability that plagues MOF-5 in the presence of air and moisture. We probed this system further in Chapter 8 using Fe^{III} as a dopant ion, and were able to obtain the first crystallographic evidence of the coordination change of Zn^{II} in MOF-5. Furthermore, the structure obtained with Fe^{III} was the first example of metal ion addition within a MOF that bound two interpenetrated frameworks together. This new MOF was found to have the potential to be a more practical material for gas storage and separation, and/or for catalysis. Thus, this study was informative in regards to the inherent instability of the parent framework, as well as a new method of metal addition to a known MOF structure.

Chapter 9 will conclude the work with a discussion of what was performed in, and learned from, each thesis section, as well as provide an outlook and perspective on the novel work that may be derived from these projects going forward.

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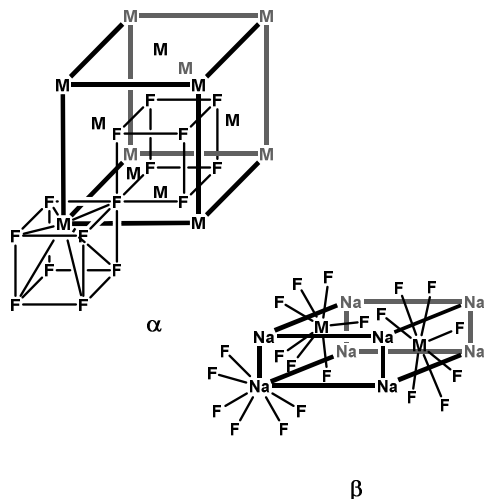
List of Abbreviations

α	Distribution parameter
μ_{eff}	Effective magnetic moment
ν	Frequency
τ	Relaxation time
χ	Magnetic susceptibility
ac	Alternating current
AuNP	Gold nanoparticles
BET	Brunauer-Emmett-Teller
C	Curie constant
CNT	Carbon nanotube
D	Axial magnetic anisotropy parameter
dc	Direct current
DFT	Density Functional Theory
DEF	Diethylformamide
DMF	Dimethylformamide
g	Landé g factor
H	Magnetic field
HOPG	Highly-ordered pyrolytic graphite
HRTEM	High Resolution Transmission Electron Microscopy
ICP-OES	Inductively-Coupled Plasma-Optical Emission Spectroscopy
IR	Infrared Spectroscopy
k	Boltzmann constant
K	Kelvin
M	Magnetisation
M_{sat}	Saturation magnetisation
M_r	Remnant magnetisation
M_s	Magnetic spin states
MCD	Magnetic Circular Dichroism
MOF	Metal-organic framework
MRI	Magnetic Resonance Imaging
NP	Nanoparticle
NMR	Nuclear Magnetic Resonance

Oe	Oersted
O_h	Octahedral
QTM	Quantum Tunneling of the Magnetisation
<i>S</i>	Spin
SAM	Self-assembled monolayer
SCM	Single-chain magnet
SCXRD	Single-Crystal X-ray Diffraction
SEM	Scanning Electron Microscopy
SIM	Single-ion magnet
SMM	Single Molecule Magnet
SSNMR	Solid-State Nuclear Magnetic Resonance
STM	Scanning Tunneling Microscopy
SQUID	Superconducting Quantum Interference Device
T	Tesla
<i>T</i>	Temperature
<i>T_B</i>	Blocking temperature
<i>T_C</i>	Curie temperature
<i>T_d</i>	Tetrahedral
<i>T_N</i>	Néel temperature
TEM	Transmission Electron Microscopy
TM	transition metal
<i>U_{eff}</i>	Anisotropy (energy) barrier, effective
UV-Vis	Ultraviolet-Visible Spectroscopy
XMCD	X-ray Magnetic Circular Dichroism
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XRPD	X-ray Powder Diffraction
ZFC/FC	Zero-field cool/Field cool
ZFS	Zero-field splitting

Materials by Chapter with Chemical Formulas and Abbreviated Names

Chapter 3



NaMF_4 ; where $M = \text{Ln}$ or Na :

NaYF_4 (**3.1**)

$\text{NaY}_{0.70}\text{Er}_{0.04}\text{Yb}_{0.26}\text{F}_4$ (NaYF_4 : 2% Er, 18% Yb, **3.2**)

$\text{NaY}_{0.64}\text{Er}_{0.04}\text{Yb}_{0.19}\text{Gd}_{0.12}\text{F}_4$ (NaYF_4 : 2% Er, 18% Yb, 15% Gd, **3.3**)

$\text{NaY}_{0.47}\text{Er}_{0.04}\text{Yb}_{0.22}\text{Gd}_{0.26}\text{F}_4$ (NaYF_4 : 2% Er, 18% Yb, 30% Gd, **3.4**)

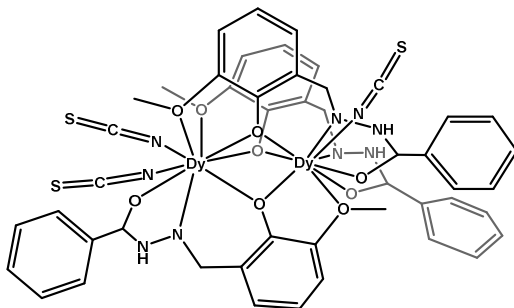
$\text{NaY}_{0.50}\text{Er}_{0.04}\text{Yb}_{0.22}\text{Tb}_{0.23}\text{F}_4$ (NaYF_4 : 2% Er, 18% Yb, 15% Tb, **3.5**)

$\text{NaY}_{0.29}\text{Er}_{0.05}\text{Yb}_{0.31}\text{Tb}_{0.35}\text{F}_4$ (NaYF_4 : 2% Er, 18% Yb, 30% Tb, **3.6**)

$\text{NaY}_{0.59}\text{Er}_{0.04}\text{Yb}_{0.15}\text{Dy}_{0.22}\text{F}_4$ (NaYF_4 : 2% Er, 18% Yb, 15% Dy, **3.7**)

$\text{NaY}_{0.41}\text{Er}_{0.03}\text{Yb}_{0.14}\text{Dy}_{0.42}\text{F}_4$ (NaYF_4 : 2% Er, 18% Yb, 30% Dy, **3.8**)

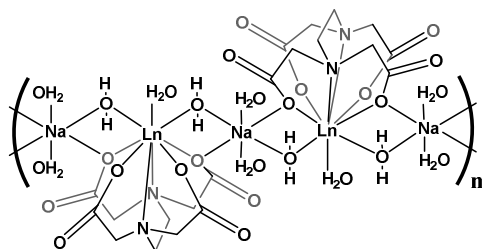
Chapter 4



$[\text{Dy}^{\text{III}}_2(\text{Hhmb})_3(\text{NCS})_3] \cdot 2\text{MeOH} \cdot \text{py}$ (**4.1**)

$[\text{Dy}^{\text{III}}_2(\text{Hhmb})_3(\text{NCS})_3] \cdot 2\text{MeOH} \cdot \text{py}$ on AuNPs (**4.2**)

Chapter 5



$\text{Na}[\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$; where Ln is:

Y^{III} (Y-EDTA, **5.1**)

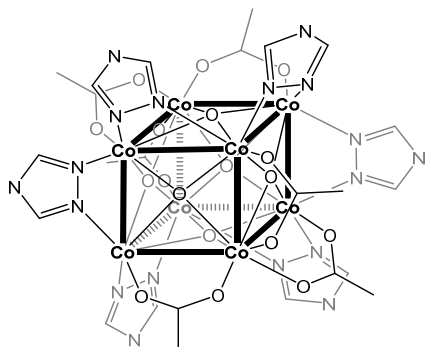
Eu^{III} (Eu-EDTA, **5.2**)

Gd^{III} (Gd-EDTA, **5.3**)

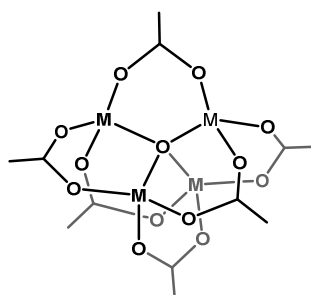
Tb^{III} (Tb-EDTA, **5.4**)

Dy^{III} (Dy-EDTA, **5.5**)

Chapter 6



Chapter 7



$\text{M}_4\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$; where M:

$\text{Zn}_4\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$ (MOF-5)

$\text{Zn}_{3.79}\text{Co}_{0.21}\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$ (5% Co-MOF-5, **7.1**)

$\text{Zn}_{3.59}\text{Co}_{0.41}\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$ (10% Co-MOF-5, **7.2**)

$\text{Zn}_{3.32}\text{Co}_{0.67}\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$ (15% Co-MOF-5, **7.3**)

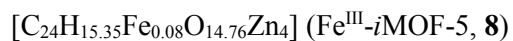
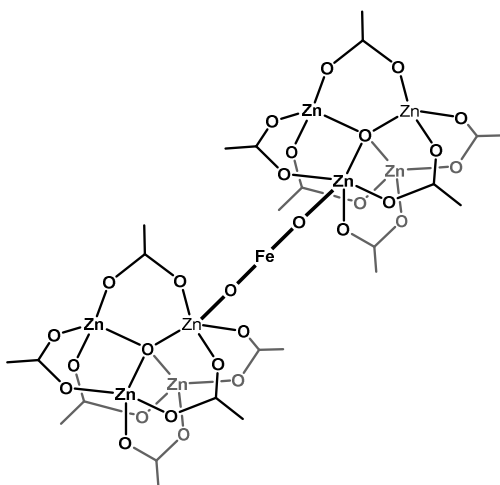
$\text{Zn}_{3.03}\text{Co}_{0.97}\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$ (25% Co-MOF-5, **7.4**)

$\text{Zn}_{2.14}\text{Co}_{1.86}\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$ (50% Co-MOF-5, **7.5**)

$\text{Zn}_{1.22}\text{Co}_{2.78}\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$ (75% Co-MOF-5, **7.6**)

$\text{Zn}_{3.80}\text{Co}_{0.20}\text{O}(\text{C}_8\text{H}_4\text{O}_4)_3$ (100% Co-MOF-5, **7.7**)

Chapter 8



Published Contributions

The contributions which have arisen during the course of this Ph.D. are listed below, with the authorship contribution bolded for clarity.

Peer-Reviewed Contributions:

1. **Holmberg, R. J.**, Kuo, C. -J., Gabidullin, B., Clérac, R., Murugesu, M., Lin, P. -H. (2016) Propeller-shaped u4-carbonate hexanuclear dysprosium cluster with high energetic barrier to magnetic relaxation. Submitted: CC-COM-07-2016-005766.
2. **Holmberg, R. J.**, Korobkov, I., Murugesu, M. (2016) Enchainning EDTA-Chelated Lanthanide Molecular Magnets into Ordered 1D Networks. RSC Adv. 6: 72510-72518.
3. **Holmberg, R. J.**, Burns, T., Greer, S. M., Kobera, L., Stoian, S. A., Korobkov, I., Hill, S., Bryce, D. L., Woo, T. K., Murugesu, M. (2016) Intercalation of Coordinatively Unsaturated Fe^{III} Ion within Interpenetrated MOF-5. Chem. Eur. J. 22: 7711–7715.
4. **Holmberg, R. J.**, Polovkova, M. A., Martynov, A. G., Gorbunova, Y. G., Murugesu, M. Impact of Coordination Environment on Magnetic Properties of Single-Molecule Magnets Based on Homo- and Hetero-Dinuclear Terbium(III) Heteroleptic Tris(Crownphthalocyaninate). Dalton Trans. 45: 9320-9327.
5. Harriman, K. L. M., Le Roy, J. J., Ungur, L., **Holmberg, R. J.**, Korobkov, I., Murugesu, M. (2016) Bridging Ln^{III} ions through seven-membered cycloheptatrienyl trianion to produce new dinuclear SMMs. Chem. Sci. Submitted: SC-EDG-03-2016-001224.
6. Jiang, Y., **Holmberg, R. J.**, Habib, F., Ungur, L., Korobkov, I., Chibotaru, L. F., Murugesu, M. (2016) Lanthanide contraction within a series of centrosymmetric dinuclear complexes. RSC Adv. 6: 56668-56673.
7. Carter, K. P., Thomas, K. E., Pope, S. J. A., **Holmberg, R. J.**, Butcher, R. J., Murugesu, M., Cahill, C. L. (2016) Supramolecular assembly of molecular rare-earth-3,5-dichlorobenzoic acid-2,2':6',2''-terpyridine materials: structural systematics, luminescence properties, and magnetic behavior. Inorg. Chem. 55: 6902-6915.
8. **Holmberg, R. J.**, Ho, L. T. A., Ungur, L., Korobkov, I., Chibotaru, L. F., Murugesu, M. (2015) Observation of unusual slow-relaxation of the magnetisation in a Gd-EDTA chelate. Dalton Trans. 44: 20321-20325.
9. **Holmberg, R. J.**, Murugesu, M. (2015) Adhering magnetic molecules to surfaces. J. Mater. Chem. C, 3: 11986-11998.

10. Kuo, C. -J., **Holmberg, R. J.**, Lin, P. -H. (2015) Slight synthetic changes eliciting different topologies: synthesis, structure and magnetic properties of novel dinuclear and nonanuclear dysprosium complexes. *Dalton Trans.* 44: 19758-19762.
11. Wu, N., Melan, C. F. C., Stevenson, K. A., Fleischel, O., Guo, H., Habib, F., **Holmberg, R. J.**, Murugesu, M., Mosey, N. J., Nierenharten, H., Petitjean, A. (2015) Systematic study of the synthesis and coordination of 2-(1,2,3-triazol-4-yl)-pyridine to Fe(II), Ni(II) and Zn(II); ion-induced folding into helicates, mesocates and larger architectures, and application to magnetism and self-selection. *Dalton Transactions.* 44: 14991-15005.
12. Safin, D. A., **Holmberg, R. J.**, Burgess, K. M. N., Robeyns, K., Bryce, D. L., Murugesu, M. (2014) Hybrid Material Constructed from Hg(NCS)₂ and 2,4,6-Tris(2-pyrimidyl)-1,3,5-triazine (TPymT): Coordination of TPymT in a 2,2-Bipyridine-Like Mode. *Dalton Transactions.* 3: 441-446.
13. Hutchings, A. -J., Habib, F., **Holmberg, R. J.**, Korobkov, I., Murugesu, M. (2014) Structural Rearrangement through Lanthanide Contraction in Dinuclear Complexes. *Inorganic Chemistry.* 53: 2102-2112.
14. **Holmberg, R. J.**, Kay, M., Korobkov, I., Kadantsev, E., Aharen, T., Desgreniers, S., Woo, T. K., Murugesu, M. (2014) An Unprecedented Co^{II} Cuboctahedron as the Secondary Building Unit in a Co-based Metal-Organic Framework. *Chemical Communications.* 50: 5333-5335.
15. **Holmberg, R. J.**, Hutchings, A. -J., Habib, F., Korobkov, I., Scaiano, J. C., Murugesu, M. (2013) Hybrid Nanomaterials: Anchoring Magnetic Molecules on Naked Gold Nanocrystals. *Inorganic Chemistry.* 52: 14411-14418.
16. Wong, J. W. L., Mailman, A., Winter, S. M., Robertson, C. M., **Holmberg, R. J.**, Murugesu, M., Dube, P. A., Oakley, R. T. (2013) Supramolecular architecture, crystal structure and transport properties of the prototypal oxobenzene-bridged bisdithiazolyl radical conductor. *Chemical Communications.* 50: 785-787.
17. **Holmberg, R. J.**, Aharen, T., Murugesu, M. (2012) Paramagnetic Nanocrystals: Remarkable Lanthanide-Doped Nanoparticles with Varied Shape, Size and Composition. *Journal of Physical Chemistry Letters.* 3: 3721-3733.

Forthcoming Contributions:

18. **Holmberg, R. J.**, Murugesu, M. Systematic Study of Co-doped MOF-5 through Magnetic Correlation. (Manuscript in preparation)

19. Lacelle, T., Brunet, G., Pialat, A., **Holmberg, R. J.**, Korobkov, I., Murugesu, M. High thermal relaxation barrier of a tetranuclear Dy^{III} single-molecule magnet formed from a novel Schiff base ligand with a tetrazine ring. (Manuscript in preparation)

Chapter 1

Introduction to Nanomagnetism

1.1 Nanomagnetism

Nanomagnetic materials are a subclass of magnetic materials; a term which can technically define any material (*vide infra*). Specifically they are discrete molecular and/or very small-scale finite entities, which have been shown to orient themselves with the application of a magnetic field. Despite its name, nanomagnetism is a term often used to refer to molecular and particulate systems which may fall outside of the usual 1-100 nm dimensional range. That being said, this thesis will solely discuss a variety of finite magnetic materials which fall within this defined nano range in at least one dimension.

Nanomagnetism is an area of research whose scope includes molecular systems, frameworks, nanoparticles, nanodots, nanowires, thin films, and macroscopic materials which contain nanoscopic regimes.¹ They are characterised by their size, phase, packing, and molecular features; all of which dictate their magnetic properties. These magnetic properties can include: slow relaxation of the magnetisation and hysteretic behaviour, as is commonly found in bulk ferromagnetic materials; quantized spin states; quantum tunnelling; etc. Due to their varied potential magnetic properties nanomagnets have many practical applications. Naturally occurring nanomagnets are employed in geology in order to study the evolution of the Earth's magnetism and anthropic activities through measuring the effect of the geomagnetic field on their magnetic moments,² as well as in biology where magnetotactic bacteria produce nanometric grains of magnetic material in a variety of living organisms.³ Synthetic nanomagnets are employed in (i) medicine as magnetic resonance imaging (MRI) contrast agents, drug delivery systems and as materials for magnetic hyperthermia;⁴ in (ii) acoustics and loudspeakers;⁵ and most significantly in (iii) magnetic recording, where magnetic nanomaterials have been able to exponentially increase the density of magnetic storage within hard disks over several decades.⁶

Nanoscale magnets have also been proposed to be the future of a significant number of rapidly developing and/or expanding technological fields, such as: molecular high-density information storage,⁷ quantum computing,⁸⁻¹¹ molecular spintronics,¹²⁻¹⁵ magnetic refrigeration,^{16,17} etc. Information storage has already been discussed as being one of the fields that has historically reaped the largest benefit from nanomagnetism. Furthermore, with the introduction of molecular magnets, or single-molecule magnets (SMMs), it has also been the

most cited field for their potential future employment. The reasoning behind desiring molecular systems in particular for information storage is that they possess the capability to be synthetically tailored, crystallographically studied, and engineered to form incredibly high-density quantum systems with classical bulk magnet-like properties. The general principle in the past has been to decrease the size of magnetic domains within a hard disk, thus leading to higher density binary (spin up/spin down being equivalent to the 1,0 binary information system) storage, and thus it follows that nanomagnets have been, and still remain, a desirable future alternative to bulk magnetic domains. Therefore, these systems have been proposed for use in the broader field of spintronics; the fundamental principle of spin manipulation using both magnetic and electrical fields. Spintronics encompasses a large number of different applications; including transistors and sensors. Furthermore, due to their clean quantum properties, such nanomagnetic systems are also proposed for use in quantum computing. Quantum computing exploits quantum phenomena, such as superposition, entanglement, and tunnelling in order to perform computational operations. Making use of quantum phenomena in this way allows for the efficiency of computational operations to be vastly improved, and tasks once considered to be impossible with classical computers to be envisioned. Though quantum computing may not be able to replace conventional computing for all potential tasks, it has surpassed conventional transistor-based systems in its ability to perform incredible amounts of simultaneous operations, and thus will lend itself to being an incredible asset within certain niches.¹⁸ Finally, on the greener side of nanomagnetism is magnetic refrigeration, which employs the magnetocaloric effect to eliminate the need for harmful, ozone-depleting coolants. Beyond the environmental concerns, magnetic refrigeration is safer, quieter and more efficient than current refrigeration technology. It works on the principle that the application of a magnetic field affects the heat capacity of the material. Therefore, when spins align with a magnetic field this causes heating and a loss of thermal energy through phonons. When the field is lowered, the nanomagnetic material absorbs thermal energy, resulting in cooling. Thus, it is clear that an array of future technologies have the potential to be further miniaturized, and in some cases merely realized, through the employment of nanomagnetic materials of various shapes, sizes and compositions.

Given that these materials are so widely applicable in current and future technologies, it is important to have a grasp on the fundamental concepts of nanomagnetism; discussed herein in an effort to prepare the reader for the following literature review of relevant fields (Chapter 2), novel work on the design, synthesis and characterisation of novel magnetic nanomaterials of this

thesis (Chapter 3 through Chapter 8), and finally a conclusion, perspective, and proposal for the future directions of this work (Chapter 9).

1.2 Principles of Magnetism

1.2.1 Spin and Magnetic Anisotropy

All materials, nano or otherwise, can be classed into two distinct categories inherent to the arrangement of their spins: diamagnetic or paramagnetic. All materials possess some diamagnetic character, meaning that they contain paired electrons, hereafter referred to as spins. Diamagnetic materials will weakly repel an applied magnetic field (H), eliciting a measured magnetic susceptibility (χ) of $\sim -10^{-6} \text{ cm}^3\text{mol}^{-1}$. Diamagnetic susceptibility can be estimated for molecular systems, since it is additive in nature, using Pascale's constants or known characteristic values for atomic susceptibilities. In order to understand the relationship between magnetic field and susceptibility, the concept of the measured magnetic response of a material, magnetisation (M) can be defined as:

$$M = \chi \cdot H \quad (1)$$

where the applied field and magnetic susceptibility of a material are the defining factors of its magnetisation.

In contrast to diamagnetism, paramagnetism is not present within all materials, as it is defined by the presence of unpaired spins. Paramagnetic materials will attract an applied magnetic field, which causes their spins to align under such a field, and subsequently revert to random orientation when the field is removed. Paramagnetic materials also have the potential to possess different types of magnetic ordering, each of which exhibit clear variations in their magnetic properties. Such ordering will only be observed below a certain temperature, inherent to each material; the Curie temperature (T_C) for ferro- and ferrimagnetic systems and the Néel temperature (T_N) for antiferromagnetic systems, above which spins are randomized due to the presence of adequate thermal energy. These types of magnetic ordering are: ferromagnetism, antiferromagnetism, and ferrimagnetism. Ferromagnetism in materials is a phenomenon where the introduction, and subsequent increase in strength, of a magnetic field causes the spins to align parallel to the applied field, eventually reaching a saturation value (M_{sat}).¹⁹ As the field is removed, the magnetisation remains, and can be observed as a separation or coercivity at $H = 0$, thus displaying the magnetic information retained within the system, or remnant magnetisation (M_r). Conversely, antiferromagnetic materials have spins aligned anti-parallel with one another,

thus resulting in a diamagnetic material at absolute zero, 0 Kelvin (K). Similarly, ferrimagnetic materials have anti-parallel spin alignment, however, the magnetic moments are not equal in strength, and thus the resulting material is non-diamagnetic.

Furthermore, very small paramagnetic materials can also be classified as being superparamagnetic, below a certain blocking temperature (T_B). The blocking temperature is the temperature below which ferromagnet-like behaviour can be observed; in the form of magnetic remanence and coercivity. Besides the blocking temperature, the energy barrier is the other crucial parameter in superparamagnetic materials. An energy barrier is a thermally activated relaxation regime, by which a spin reversal may occur; arising from a combination of non-negligible ground state spin (S) and an appreciable uniaxial magnetic anisotropy (D).¹⁹ The zero field splitting (ZFS) parameter, D , can either be defined as having Ising-type anisotropy (the stable orientation of the magnetic moment being parallel to an easy axis, z), where the parameter is negative; or a preferential alignment of the magnetic moment along the easy plane (xy plane), where the parameter is positive, and the rhombic anisotropy parameter, E , becomes non-negligible. Interestingly, D is referred to as the ZFS parameter due to the origin of magnetic anisotropy. This phenomenon arises from the removal of spin microstate degeneracy in the absence of an applied magnetic field (zero field splitting). Degeneracy is lifted as a consequence of molecular electronic structure and/or spin density distribution. Since spin-orbit coupling can be a significant contributor to the magnitude of ZFS, it follows that metallic systems with the potential for large orbital angular momentum parameters have been employed and studied towards their fundamental contributions to superparamagnetic properties (*vide infra*).

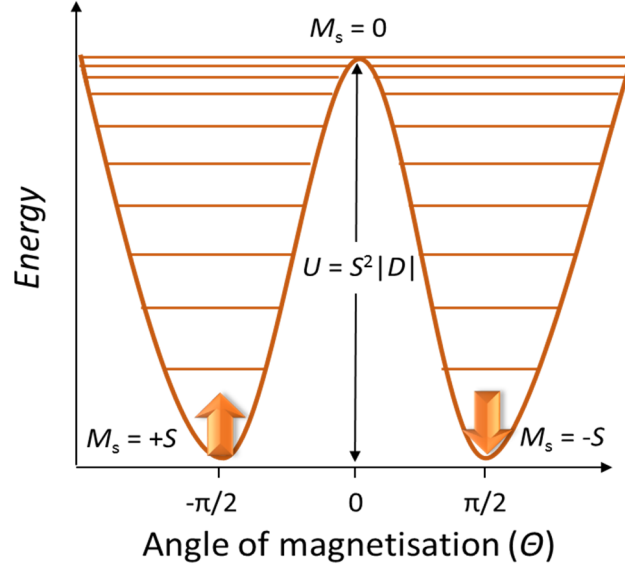


Figure 1. Energy of an Ising-type magnet as a function of the angle of the magnetisation from the easy axis (z).

In returning to the Ising-type system, relaxation must occur along the z axis, thus requiring spins to traverse the electron density-rich xy plane. Due to the energetically unfavourable electron-electron repulsion elicited in crossing this region; a bistable ground state is formed through the stabilisation of the highest $\pm M_s$ level. Thus, the energy of the system can be portrayed as a function of the orientation of the magnetic moment (Figure 1). In order to cross this energetic barrier, spins are typically modeled to follow a thermally activated regime, which gives rise to an experimental dependence of the energy barrier with so-called Arrhenius behavior:

$$\tau = \tau_0 e^{\frac{U_{eff}}{k_B T}} \quad (2)$$

Through modelling of this relationship the value for the effective energy barrier, U_{eff} , can be obtained. Conversely, if non-Ising-like anisotropy were observed, there would be no energetic barrier to spin flip, and thus no SMM behavior under zero applied magnetic field.

1.2.2 Quantum Tunneling of the Magnetisation

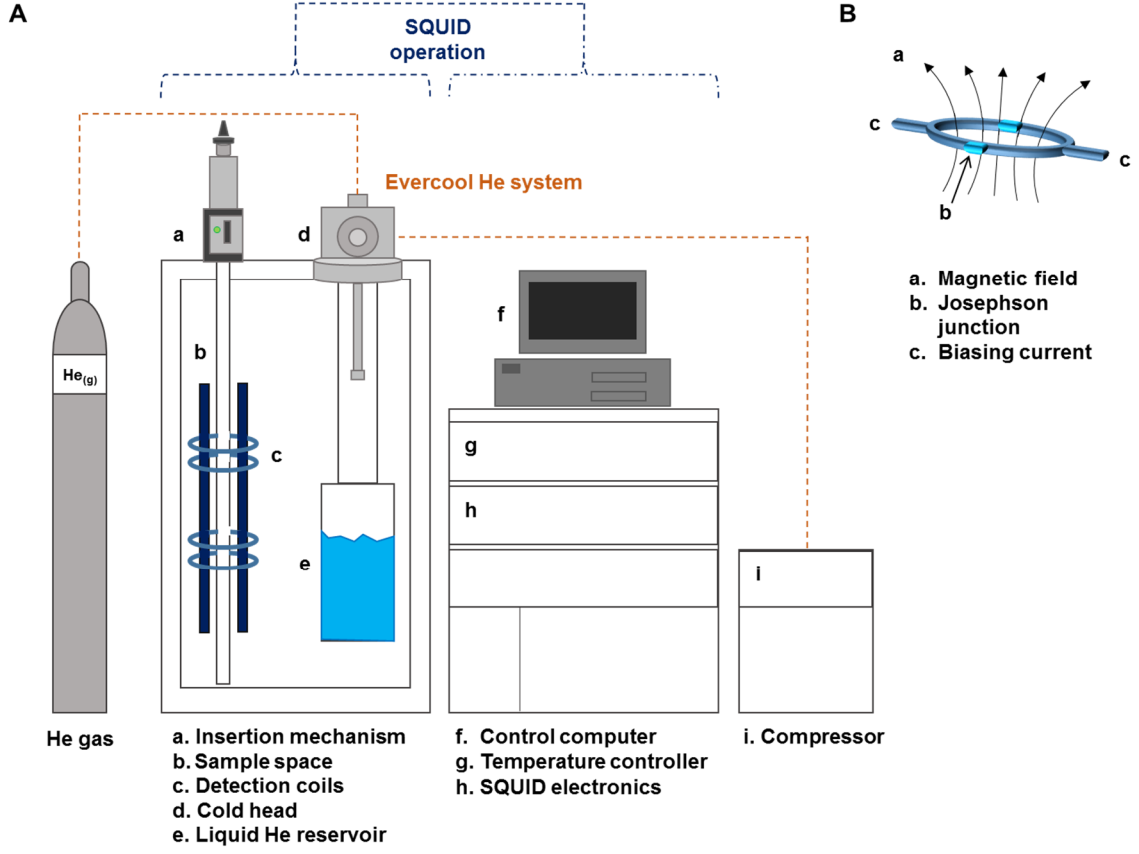
Another important magnetic phenomenon as concerns the energetic barrier to spin reversal is quantum tunneling of the magnetisation (QTM). This well-known phenomenon amongst quantum physicists occurs at low temperatures within small particles/systems. Specifically, instead of relaxation occurring over an energetic barrier (Figure 1), and not being able to return again

without re-crossing the barrier, QTM involves spin relaxation as a superposition of both states between degenerate $\pm M_S$ levels. Thus, QTM may either occur in the ground state, or through thermally accessed excited states, only requiring that M_S levels be degenerate in energy, and that they interact through wave function mixing. Importantly, QTM has been frequently suggested to be forbidden in systems with half-integer spins (Kramer's ions) as the wave functions in this case theoretically cannot interact/mix, even if the degeneracy requirement is fulfilled. Magnetochemists and physicists often look towards anisotropic metals such as Co^{II} and Dy^{III} (Kramer's ions) in order to prevent QTM from completely suppressing the energetic barrier to spin reversal (ground state QTM), or from significantly decreasing the value of U_{eff} (thermally assisted QTM). However, this strategy has been shown to be somewhat inaccurate, as hyperfine coupling frequently plays an important role in opening relaxation channels that would otherwise be forbidden, while simultaneously masking relaxation at zero field.²⁰ Therefore, since QTM is still frequently observed in Kramer's ion systems, magnetochemists have looked towards symmetrical coordination environments, which have been shown to significantly reduce the occurrence of QTM.²¹

Through magnetic measurements QTM can often be observed and studied (*vide infra*). In this case, the application of a static magnetic field is frequently employed in order to lift the degeneracy of the states, thus allowing for improvement in the magnetic properties. The degeneracy is removed as a result of the magnetic field causing stabilisation of one of the M_S wells, while simultaneously destabilizing the other, and thus removing the energetic equivalency between microstates. Magnetic nanomaterials studied under an applied static field in this way are referred to as possessing field-induced magnetic properties.

1.3 Magnetic Measurements

Magnetic properties are most commonly assessed by magnetochemists using a Superconducting Quantum Interference Device (SQUID). This instrument is one of the most sensitive methods of measuring magnetic flux, as it is capable of discerning magnetic fields with a resolution of $\sim 10^{-15}$ T.²² The instrument itself (Figure 2A) is composed of a superconducting loop, separated in two places by thin parallel insulating barriers: Josephson junctions (Figure 2B).



A SQUID is fundamentally composed of a superconducting loop, within which are two Josephson junctions that typically consist of a non-superconducting material sandwiched within a superconductor. The principle of a superconductor is that, due to the attraction between paired electrons within the material below a certain T , an energy gap forms as a result of this lowering in energy where electric current experiences negligible resistance. A Josephson junction allows current to tunnel through the non-superconducting barrier when it is below a critical current value, however, above this critical value a separate voltage will develop across the junction. This voltage is time-dependent (ac voltage), thus causing a lowering of the critical current value within the junction, and further increasing the ac voltage across the junction. The resulting voltage is measured across the terminals of the loop, and since it oscillates with a change in magnetic flux:

$$\Phi = \frac{h}{2e} = 2.0678 \times 10^{-15} \text{ Tm}^2 \quad (3)$$

where flux quantum is defined as Φ . Thus, the movement of a sample through the superconducting loop allows for the finite sample-induced flux to be measured.

The methods by which the magnetic properties of a chemical sample are studied can be divided into two categories of electromagnetism, based on the type of frequency of the applied magnetic field: direct current (dc) and alternating current (ac) SQUID measurements.

1.3.1 Direct Current Magnetometry

Direct current magnetic measurements determine the equilibrium magnetisation within a sample through the application of a constant, static dc field and the subsequent measurement of the magnetic moment response of the sample. The moment response is measured by induction, which is accomplished by moving the sample relative to the superconducting pickup coils, allowing the resulting current generated within the coils to be measured. These measurements are most commonly plotted as the temperature dependence of the magnetic susceptibility (χ) and the field dependence of the magnetisation (M). It is important to note that this is molar susceptibility, which has taken into account the molecular weight of a sample and can also be expressed as χ_m . However, as in the majority of publications, we will use χ in order to refer to molar susceptibility throughout this thesis. From the susceptibility data, information on the dominant magnetic interaction within the sample, and in some cases its strength, can be extracted. The most common magnetic susceptibility plots are of the temperature dependence of the inverse of the magnetic susceptibility, χ^{-1} , and of the χT product; as can be seen in Figure 3.

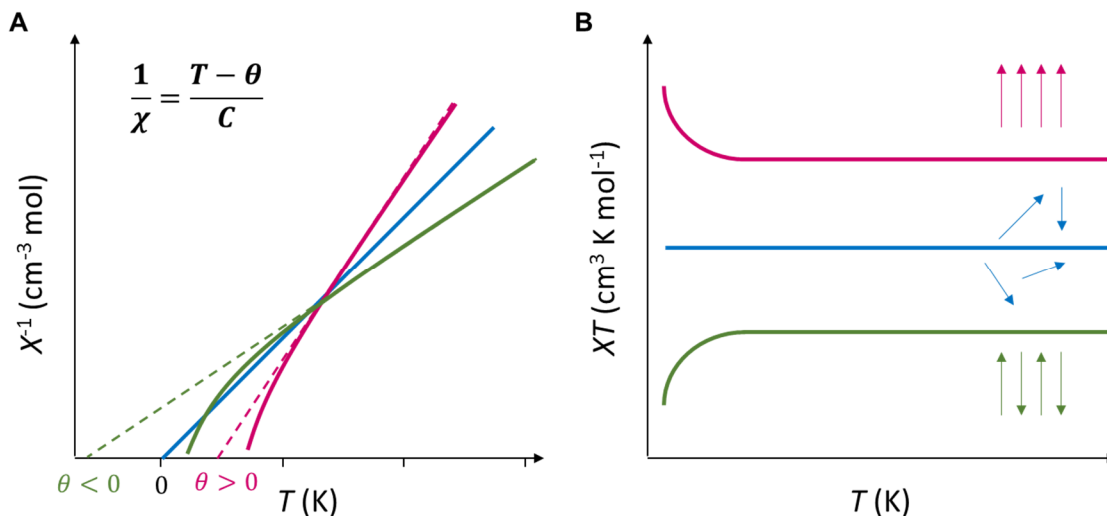


Figure 3. Temperature dependence of the inverse of the magnetic susceptibility, χ^{-1} (A) and of the χT product (B), displaying the curves elicited by ferromagnetic (pink), antiferromagnetic (green) and paramagnetic (blue) spin interactions. Adapted from ref. 23.²³

The plots displayed in Figure 3 exhibit the behavior that is indicative of the dominant magnetic interactions within a sample. If the sample is simply paramagnetic, without any spin coupling, then there will be a linear dependence of the inverse susceptibility with temperature, which corresponds to the Curie Law for non-interacting magnetic ions:

$$\chi = \frac{Ng^2\mu_B^2}{3kT} S(S+1) \quad (4)$$

where N is Avogadro's number, g is the Landé g factor or the spectroscopic splitting factor, μ_B is the Bohr magneton, and k is the Boltzmann constant ($0.685039 \text{ cm}^{-1} \text{ K}^{-1}$). The introduction of a magnetic interaction parameter yields the Curie-Weiss Law:

$$\chi = \frac{Ng^2\mu_B^2 S(S+1)}{3kT} \cdot \frac{1}{T-\theta} = \frac{C}{T-\theta} \quad (5)$$

where θ is the Weiss constant. A linear fit of the χ^{-1} vs. T data yields the Weiss constant, θ , at the intersection of the fit line with the x-axis, which indicates dominant ferromagnetic interactions if its value is positive, and dominant antiferromagnetic interactions if its value is negative. Conversely in the χT vs. T plot, Curie paramagnetic behavior elicits no change in χT value, whereas ferromagnetic interactions cause an increase, and antiferromagnetic interactions a decrease at low temperatures. Thus, through these two plots, the interactions between magnetic ions become apparent by the shapes of the curves. In some cases the χT vs. T plot can also be fit using an equation called the Van Vleck equation in order to obtain an idea of the strength of the magnetic interaction. Finally, the χT vs. T plot is also often employed in order to ascertain the effective magnetic moment of the sample through measuring the magnitude of the value at 300 K. The effective magnetic moment, μ_{eff} is defined as follows:

$$\mu_{\text{eff}} = \left(\frac{3k}{N\mu_B^2} \right)^{\frac{1}{2}} (\chi T)^{\frac{1}{2}} \quad (6)$$

For simplicity, as well as to avoid confusion with some other common parameters, such as μ_e (magnetic moment of an electron), many researchers use $\chi_m T$ or χT instead:

$$\chi T = \frac{Ng^2\mu_B^2}{3k} S(S+1) = \frac{g^2}{8} S(S+1) \quad (7)$$

This formula is equivalent to a theoretical value of χT at 300 K, and thus, unlike in the case of μ_{eff} , elicits units of $\text{cm}^3 \text{Kmol}^{-1}$. For heavier transition metal (TM) ions and lanthanide (Ln) ions, spin-orbit coupling causes the magnetic moment to deviate from the spin-only formula, and thus it must be taken into account using the non-simplified formula above, however, for first-row

transition metal ions the magnitude of the magnetic moment is a simple function of the number of unpaired electrons (spin-only formula). The spin-only formula is thus simplified by $g = 2$ to the following:

$$\chi T = \frac{S(S+1)}{2} \quad (8)$$

Thus, through the use of these formulas, theoretical values of χT are commonly compared to experimental values of the magnetic moment in order to confirm the identity of the material.

The dependence of the magnetisation on the applied field (H) and on the reduced applied field (HT^{-1}) are also commonly measured at low temperatures (1.8 to 7 K). The shape and saturation value at low temperature and high applied field are both commonly analyzed. In the M vs. H plot characteristic behavior of an isotropic system is the presence of magnetic saturation at $T = 1.8$ K and $H = 7$ T, where $M = gS$. In the reduced plot, M vs. HT^{-1} , an isotropic system would display curves which overlap on a single mastercurve. Thus, if these plots deviate from this isotropic behaviour, it can be concluded that the measured system possesses magnetic anisotropy, and that only qualitative information may be obtained. This measurement, when cycled over a range of positive to negative H in order to elicit magnetic saturation in both directions through an applied field, is often referred to as a hysteresis measurement due to the observed hysteretic behavior of coercive loop opening (Figure 4).

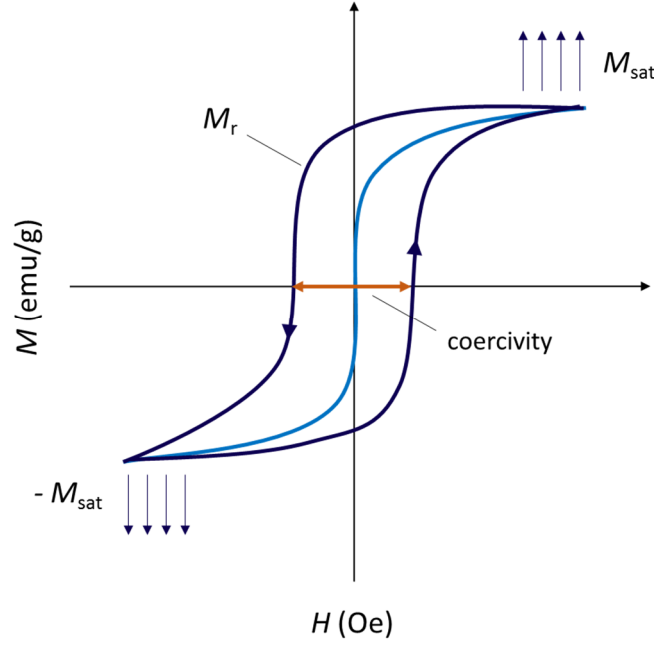


Figure 4. Simulated hysteresis curve (M vs. H) for a ferromagnetic material (dark blue), and a paramagnetic material (light blue). Magnetic saturation (M_{sat}), remnant magnetisation (M_r), and coercivity are clearly labelled, and the field direction is indicated by dark blue arrows.

When magnetisation is retained within a material, there is a loop-opening phenomenon by which the strength or hardness of a magnet may be measured through the value of coercivity at $H = 0$. This type of behavior is observed in ferromagnets and ferrimagnets, as well as in superparamagnetic systems below their T_B . Furthermore, information may be gained on the relaxation dynamics through the shape of the curve, for example QTM can often be observed in step-wise transitions occurring within a hysteresis curve.

Finally, another simple method of estimating the T_B is through a dc measurement called zero-field-cool/field-cool (ZFC/FC). This involves cooling of a sample from room temperature in zero applied dc magnetic field, followed by the application of a small dc field (typically 100 Oe) where the magnetisation is recorded upon warming. After this the sample is cooled under an applied field, and magnetisation is once again recorded upon warming. The idea is that spins will be aligned with the magnetic field at low T in the FC curve, whereas they will remain randomly oriented at low T in the ZFC curve. Thus, in the ZFC curve, as the temperature increases under the small applied field, thermal energy causes magnetic moments to align with the external field up to a maximum, T_B , after which the thermal energy becomes sufficient to randomize the

magnetic moments, lowering the value of magnetisation. The different types of curves for paramagnetic and superparamagnetic systems can be seen in Figure 5.

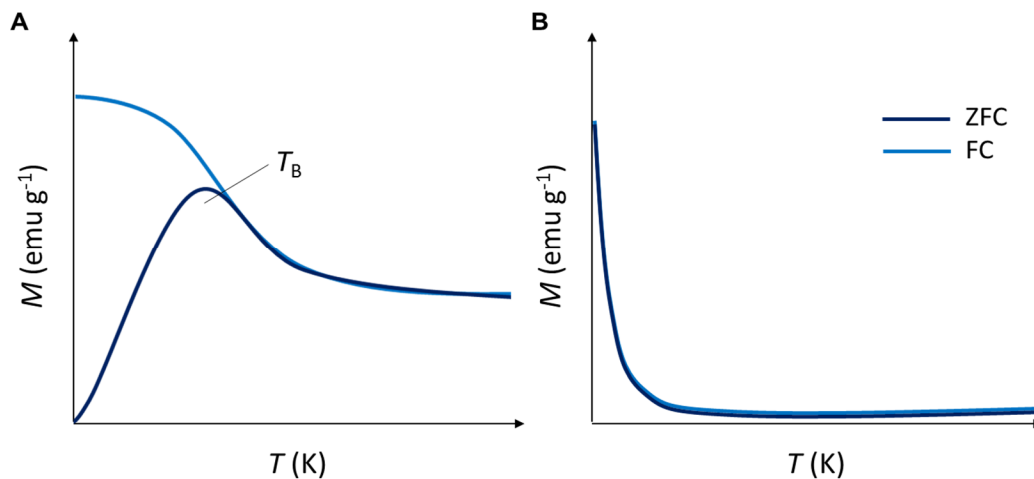


Figure 5. Simulated ZFC/FC curves for superparamagnetic (A) and paramagnetic (B) systems.

Thus, overall dc magnetic measurements can provide information on magnetic interactions between spin carriers, both in type and magnitude, on the number of unpaired spins within a magnetic species, and on the strength of a magnet if it retains magnetisation. Furthermore, the presence of magnetic anisotropy can also be elucidated from these measurements, thus indicating that slow relaxation of the magnetisation could be present within the studied material. In order to probe the dynamics of this type of relaxation process, ac measurements are performed.

1.3.2 Alternating Current Magnetometry

Alternating current magnetic measurements instead apply an alternating magnetic field which is superimposed on the dc field, causing a time-dependent moment within the sample. The field of this moment induces a current within the coils, allowing measurement without sample movement. The primary coils within the system induce the magnetic moment in the sample through a weak alternating field, while the secondary coil detects the time-dependent moment (voltage induced by the oscillating magnetic field in both phase and amplitude) from within the primary coil, resulting in measurement of the dynamic properties discussed herein.

In dc magnetometry, magnetisation varies linearly with H , which is less sensitive to small perturbations in the magnetic field. Conversely, in ac magnetometry measurements can be taken outside of the linear region for M/H , thus, a phase shift relative to the drive signal (φ) is measured; separating χ_{ac} into an in-phase component (χ') and an out-of-phase component (χ''):

$$\chi_{ac} = \sqrt{\chi'^2 + \chi''^2} \quad (9)$$

$$\chi' = \chi \cos \varphi \quad (10)$$

$$\chi'' = \chi \sin \varphi \quad (11)$$

It follows that if the sample follows the drive field completely, or not at all, the out-of-phase signal will be nil. This is due to the fact that this is a measurement of the dissipative processes occurring within the sample. Consequently, this data provides crucial information about magnetic remanence. Plots of the frequency dependence of χ' and χ'' are shown in Figure 6.

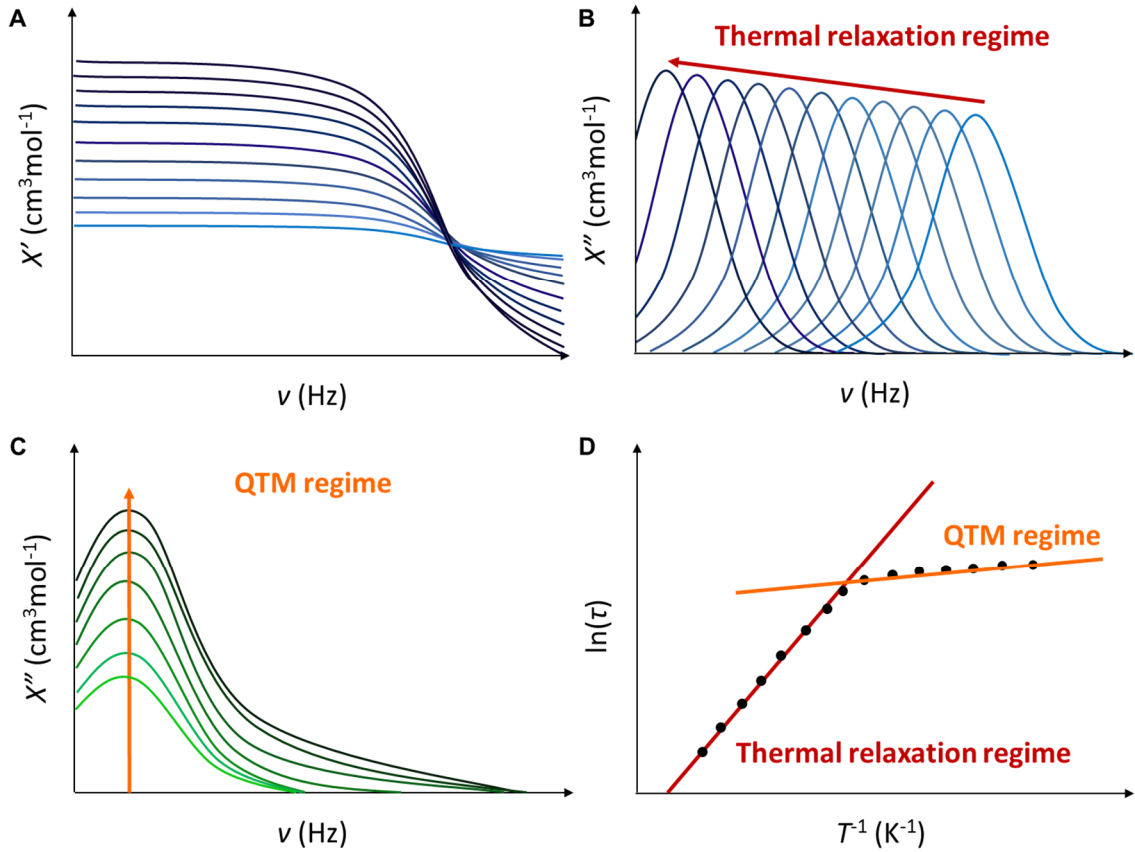


Figure 6. Frequency dependence of the (A) in-phase (χ') and (B), (C) out-of-phase in-phase (χ'') magnetic susceptibilities. Arrows indicate the direction of decreasing temperature. (D) Relaxation

times of the magnetisation $\ln(\tau)$ vs. T^{-1} (Arrhenius plot using χ' and/or χ'' ac data). The solid red line corresponds to the fit of the data.

Since all paramagnets show a χ' signal, the data obtained from χ'' measurements has been a more common focus for magnetochemists. These measurements can be performed with a dependency on frequency, temperature and/or field, depending on the desired information. Frequency dependent data is more commonly studied at this time, as more data is collected and it is more accurate due to the ability of the magnetometer to more precisely control frequency than temperature. When looking at frequency dependent χ'' data, two phenomena become apparent: (i) peak shifting to lower frequency with decreasing temperature, indicative of the presence of slow relaxation of the magnetisation (Figure 6B); and/or peaks overlapping at the same frequency with decreasing temperature, indicative of QTM (Figure 6C). The peaks no longer shift with frequency in this case due to the occurrence of a much faster relaxation process (tunnelling). If peak shifting is observed, the peaks can be fit using either a Gaussian model where each peak corresponds to $\tau = (2\pi\nu)^{-1}$, or a generalised Debye model with a distribution (α) of relaxation times (τ), where the in-phase and out-of-phase ac susceptibility can be expressed as the following:

$$\chi' = \chi'_{\infty} + \frac{(\chi'_0 - \chi'_{\infty}) \left[1 + (2\pi\nu\tau)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) \right]}{1 + 2(2\pi\nu\tau)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) + (2\pi\nu\tau)^{2(1-\alpha)}} \quad (12)$$

$$\chi'' = \frac{(\chi'_0 - \chi'_{\infty}) (2\pi\nu\tau)^{1-\alpha} \cos\left(\frac{\alpha\pi}{2}\right)}{1 + 2(2\pi\nu\tau)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) + (2\pi\nu\tau)^{2(1-\alpha)}} \quad (13)$$

It follows that through modelling frequency dependent χ'' data using the generalised Debye model, relaxation time values can be extracted from both in-phase and out-of-phase data, and compared thereafter. In the case of both Gaussian and Debye models, the resulting relaxation times are then attributed to an Arrhenius law (*vide supra*) in order to extract the value of U_{eff} (Figure 6D). These measurements provide a measure of the experimentally obtained energetic barrier to magnetic relaxation, as well as an indication of any presence of QTM, multiple relaxation processes, etc. This combination of measurements (dc and ac magnetometry) provides a detailed overview of the magnetic behaviour of a nanomagnetic sample.

1.4 Context of Nanomagnetism within this Thesis

What has been described within this chapter will come into context within the following chapter, where a brief review of relevant literature will be detailed in order to provide context for the following chapters on the novel work of this thesis. Specifically, nanomagnetism will be

discussed within a variety of relevant nanoscopic architectures. The following chapters in the thesis will relate back to the literature discussion in Chapter 2, and will rely on the knowledge gained from Chapter 1 on the basics of nanomagnetism and nanomagnetic study through magnetometry techniques. Finally, the closing chapter will provide a perspective and conclusion summary of the work throughout the thesis, taking into account future aspirations for each nanomagnetic project.

Chapter 2

Literature Review of Relevant Crystalline Nanomagnetic Materials

2.1 Doped Magnetic Nanoparticles

2.1.1 Magnetic Nanoparticles

Nanoparticles (NPs) are nanoscale entities that possess large surface-to-volume ratios, large surface area, and unique chemical and physical properties due to their quantum confinement characteristics. The most studied nanoparticulate materials are composed of metallic species, thus providing the necessary magnetic properties for use in some of the varied applications described in the previous chapter. Many metallic nanoparticles are designed towards applications with either a primary or secondary magnetic functionality. An example of primary functionality is within information storage,¹² where the magnetic bistability (*vide supra*) of magnetic NPs is employed in order to store binary information; thus exploiting the magnetic properties for the desired application itself. This is also true within magnetic resonance imaging applications, where the paramagnetic or superparamagnetic nature of a particle is employed in order to alter the relaxation properties of water molecules for improved contrast in medical imaging.^{24,25} Conversely, magnetic nanoparticles have also been frequently employed in catalysis, where the magnetic properties are exploited in a secondary manner in order to separate and/or remove the NP from a mixture through attraction to a magnetic field.²⁶ This is also the principle behind magnetic separation for water purification,²⁷ and many other secondary magnetic functionalities. Thus, depending on the specific magnetic properties of the NP, its potential applicability can vary widely.

Magnetically, nanoparticles have size-dependent properties, meaning that below a specific material-dependent size they act as finite entities, as opposed to bulk magnets. Ferromagnets, antiferromagnets and ferrimagnets commonly possess magnetic moments which point along a preferred (easy) axis upon removal of an applied field. This is also true for superparamagnets, where this type of magnetic anisotropy is fundamental to the magnitude of the energetic barrier to spin reversal, U_{eff} . However, the difference lies in the anisotropy energy, a requirement to preventing randomized spin reversal. In bulk magnets, the anisotropy energy scales linearly with the volume. In the case of superparamagnets, their magnetocrystalline anisotropy energy is often on the order of $k_{\text{B}}T$, thus allowing thermal energy to promote

fluctuation of the magnetic moments. This is frequently observed in small magnetic species, which exhibit superparamagnetic properties below a specific blocking temperature, T_B . Thus, in nanoparticles this type of magnetism is commonly observed, as opposed to bulk magnetic properties, which are inherent to larger systems. This is important, as the magnetism discussed throughout this chapter, as well as within the novel work of this thesis, will be solely on the nanoscale.

As mentioned, the applicability of magnetic nanoparticles varies significantly depending on their magnetic properties, therefore a fundamental understanding of these properties is essential. One important parameter to consider for magnetic nanoparticles is the magnetic saturation value, M_{sat} (Figure 4).²⁸ This is due to the fact that higher saturation magnetisation leads to higher sensitivity and efficiency in biosensing applications,²⁹ MRI contrast,³⁰ drug delivery,^{31,32} etc.³³ Consequently, studies have been performed comparing M_{sat} to size,³⁴ shape and geometry,^{35,36} as well as composition. These findings included evidence that saturation magnetisation increases linearly with size, until reaching the bulk value.³⁴ Unfortunately, this linear relationship does not hold for shape and geometry, as there has not yet been a consistent trend observed between these factors and M_{sat} values, thereby illustrating the importance of continued research on fundamental magnetic properties.^{35,36} Despite the lack of conclusive results on shape and geometry effects, it has been proposed that surface area may be a very influential parameter.³⁷ Furthermore, composition has been shown to play a significant role in the magnetic saturation value. This means that altering the elemental makeup through doping or by changing the crystalline distribution has a significant effect on this important magnetic property. Since the above applications for high M_{sat} materials are biomedical in nature, it is mainly through these studies that such fundamental information has been gleaned. Unfortunately, due to toxicity concerns there have been limitations on compositional studies within biomedical systems; meaning that there is not yet sufficient information on different particle compositions and the resulting effects on magnetic behaviour.³³ This toxicity concern is the motivation behind the extensive research performed on biocompatible coatings for magnetic nanoparticles, as they prevent contact between the metallic NP and a biological host.³⁸ It is important to note that once a biocompatible coating has been found for a material, it has the potential to enhance, or significantly reduce, the magnetic properties of the core. As such, the shell and nanoparticle must be optimised together.^{39,40} For these reasons, this is another impactful area of extensive and ongoing fundamental research.

Other than magnetic saturation, the energetic barrier to magnetic relaxation, blocking temperature, and coercivity all play essential roles in the performance of a magnetic nanoparticle. High energetic barriers to magnetic relaxation in nanoparticles are desirable in order to maintain the magnetic moment directionality. Thus, this is a form of magnetic strength, representing the energy input required for spin reversal to take place.⁴¹ The value of U_{eff} is largely dependent upon the anisotropy of the system (*vide supra*). With increasing anisotropy through changes in particle size,⁴² shape,⁴³ and composition,⁴⁴ the barrier is significantly affected either negatively or positively. This relationship has also been observed through alterations in nanoparticle composition, where compositional changes have increased anisotropy, resulting in an increased blocking temperature,⁴⁴⁻⁴⁷ and coercivity.⁴⁵ The blocking temperature is an important parameter for applications which require remnant magnetisation upon removal of an applied magnetic field, such as in information storage. Since data storage relies on spins retaining a specific directionality in order to hold information, the value of T_B represents the maximum temperature at which a system could function for this type of application. Furthermore, T_B is also important in biosensing, drug delivery and hyperthermia applications.^{31,32,48} Interestingly, the value of T_B has shown linear proportionality to the particle volume/size,^{49,50} as well as a dependence on particle shape.⁴³ Finally, applications requiring magnetic remanence also focus on the value of coercivity, which represents the resistance of a magnetic system to being demagnetised (zero magnetisation). The value of coercivity at zero applied field has also been shown to vary significantly with particle size,⁵¹ shape,⁵² and composition.⁴⁵ Overall, we can conclude from these studies that the physical properties of magnetic nanoparticles have a significant effect on the resulting magnetic properties, and therefore also on the potential applications of the material. Thus, through controlled doping of a nanoparticulate material it is possible to fine-tune the physical, and therefore magnetic, properties of the system.

2.1.2 Transition Metal Doping

The most commonly studied and utilised magnetic nanoparticles are composed of iron oxide; specifically maghemite (Fe_2O_3) and magnetite (Fe_3O_4). The extensive employment of these particular systems is in part due to their tendencies to exhibit high values for magnetic saturation and size-dependent superparamagnetism, as well as the fact that other magnetic transition metal ions, such as Co^{II} and Ni^{II} , are easily oxidized into toxic materials. Accordingly, iron oxide materials have been frequently studied within biomedical applications, and any applications where toxicity would be a concern. Furthermore, doping studies have been performed on such

systems in order to explore the magnetic tunability through addition of various transition metal ions into the lattice.⁵³ This was demonstrated with $M^{II}Fe_2O_4$, where M^{II} represents divalent transition metal ions with different magnetic properties than those of iron, such as Mn^{II} , Ni^{II} and Co^{II} .⁵⁴ The traditional material, Fe_3O_4 , is ferrimagnetic in nature, with the magnetic behavior arising from tetrahedral, T_d , Fe^{III} and octahedral, O_h , Fe^{III} and Fe^{II} ions within the lattice structure. Fundamental magnetic studies have shown that upon application of a magnetic field, the magnetic ions within the O_h sites align parallel to the field, while those within T_d sites align antiparallel to the field. Thus, with their varied *d*-electron count, the magnetic saturation value is altered by the addition of each TM dopant, eliciting tunable MR contrast enhancement effects. This is a strategy of significant importance for clinical application, as the ability to reduce dosage levels of nanoparticle agents with stronger enhancement effects has a significant benefit on patient health and treatment costs.⁵⁵ Furthermore, this is also an integral example of the capability to tune a system through doping, and gain a better fundamental understanding of the resulting properties through magnetic studies.

Despite the aforementioned drawbacks, nickel and cobalt nanoparticles are still frequently studied for use in non-biological magnetic applications, some examples of which being: in micropumps⁵⁶ and bioactuation applications.⁵⁷ Furthermore, Co^{II} and Ni^{II} have also been employed as dopant ions in other iron oxide particles. A recent study performed Co^{II} doping within three different materials: Fe_3O_4 , Fe_3O_4 with an Au shell, and Fe_3O_4 with a FeO shell.⁴⁵ Interestingly, in the Au core/shell system, doping anisotropic Co^{II} into the lattice induced an increase in the T_B from 250 to 310 K, and doubled the coercivity. This type of improvement in the magnetic properties of iron oxide through Co^{II} doping was also shown to increase magnetic saturation and energy barrier values in a separate study.⁵⁸ Similarly, Ni^{II} has been doped in specific amounts into iron oxide nanoparticles in order to facilitate tuning of the magnetic properties.⁵⁹ No change in magnetic saturation was observed in this case, however, the blocking temperature was improved from that of the parent iron oxide nanoparticles. This was rationalized to be due to increased grain size as a result of Ni^{II} doping, as volume and size of nanoparticles are known to increase T_B (*vide supra*). Through merely doping an anisotropic ion into a biocompatible system, the magnetic properties can be improved without necessarily imparting toxicity to the material. It follows that this can also be applied to iron oxide systems which are not intended for biomedical use.⁶⁰

Transition metal nanoparticle semiconductors have also been employed as parent structures in doping studies, in which dopant ions have been incorporated in order to target

diluted magnetic semiconductors for spintronics applications.^{61,62} As a whole, transition metal doping within nanoparticles has provided a strategy for compositional optimisation towards tuning the magnetic properties of magnetic NP systems.

2.1.3 Lanthanide Doping

Lanthanide-containing nanoparticles continue to become increasingly popular due to their shielded 4f orbitals, which yield uniquely desirable luminescent and magnetic properties.^{63,64} The most popularised nanostructured imaging probes have been constructed with the capabilities to be utilised as optical and magnetic resonance imaging modalities (multimodal). This combination of functionalities is especially useful considering that these are non-invasive imaging methods, which, when combined, are capable of achieving high spatial resolution in both *in vitro* and *in vivo* studies.⁶⁵ Multifunctional lanthanide-doped materials have been achieved through the formation of composite materials; commonly synthesized by combining iron oxide nanoparticles with a fluorescent moiety.⁶⁶⁻⁶⁸ Unfortunately, composite materials such as these have significant drawbacks due to the effects that each material has on the other; often in the form of destruction of the desired properties of the composite material.⁶⁹ Therefore, doped materials can be an attractive alternative to composites, allowing for tunability without necessitating the challenge of combining very different materials within one nanoparticle.

Many studies have been performed with the goal of achieving luminescent nanoparticles that can also perform MRI contrast enhancement. One example of such a doping study was performed on GdO₃ NPs,⁶⁹ where the parent nanoparticle was previously known to enhance MR contrast, and was subsequently doped with compositions of Yb^{III}, Er^{III} and Tm^{III} in order to promote strong luminescent characteristics. Optical and magnetic resonance studies were able to confirm the desired multimodal capabilities of these materials, and biocompatibility studies were performed in order to demonstrate their potential as practical imaging probes. These types of probes, as opposed to iron oxide NPs, are positive contrast agents; meaning that they shorten the spin-lattice (longitudinal) relaxation time, T_1 , of water protons within the tissue of interest.^{70,71} Since iron oxide particles act as superparamagnets they have been classed as negative contrast agents; meaning that they change the spin-spin (transverse) relaxation time, T_2 .⁷²⁻⁷⁴ The main difference between the two types of relaxation is that T_1 relaxation involves interaction with the surroundings (lattice) through intra-magnetic exchange, whereas, T_2 relaxation involves

decoherence through interaction with the phases of other spins. It has been shown that T_2 contrast agents have a tendency to experience dark signal drawbacks due to negative contrast and distorted background images from susceptibility artifacts.^{25,75,76} Thus, the focus on positive contrast agents with multimodal capabilities has produced a wide array of examples within the literature. Most commonly these probes are of the type: NaMF_4 , where for MRI contrast $M = \text{isotropic Gd}^{\text{III}}$ due to its isotropic nature and high number of unpaired electrons.⁷⁷ This composition is well-known to be biocompatible, chemically stable, and luminescent depending on the metal ion(s) incorporated.⁶⁵ Thus, these systems are frequently doped with a variety of lanthanide ions in order to fine-tune the luminescent properties.⁷⁸⁻⁸³ However, rather surprisingly, the fundamental magnetic properties of these systems are frequently left unexplored (*vide infra*).

Lanthanide-doped nanoparticles have also been proposed as an alternative for optical magnetic field sensing, owing to their sharp emission characteristics, long lifetimes and photostability.⁸⁴⁻⁸⁶ This is based on the magneto-optical effect, where the photoluminescence behavior of a material changes upon application of a magnetic field. This effect has been proposed as a candidate to probe the intensity of surrounding magnetic fields, especially for remote detection when nanoscale probes are employed. As semiconductor, quantum dot (QD), and organic dye based nanoparticles tend to exhibit broadband luminescence, the precise determination of band shifts is not possible. Furthermore, the toxic characteristics of many different varieties of QDs and poor photostability of organic dyes are known to hinder their lifetime as probes.^{87,88} This niche was recently explored for NaYF_4 particles, which were doped with a small percentage (5%) of Eu^{III} .⁶⁵ These particles displayed a clear trend, where luminescence bands were gradually suppressed and shifted upon increased magnetic field strength, thus promoting their potential employment in sensing. This recent study displays the potential for lanthanide doping within nanoparticles to be applicable for a wide-array of potential roles in both research and industry.

As briefly mentioned above, lanthanide doping has rarely been performed alongside fundamental magnetic studies, such as those discussed in Chapter 1, in order to study the fundamental behavior of the magnetic ions within a nanocrystalline lattice. We will study this in Chapter 3, where we employed luminescent Er^{III} and Yb^{III} , isotropic Gd^{III} and anisotropic Tb^{III} and Dy^{III} as dopants within a known luminescent nanocrystalline material, and studied the resulting fundamental magnetic properties.

2.2 Single Molecule Magnets on Surfaces

2.2.1 Single Molecule Magnets

It has been more than two decades since the first example of a molecule exhibiting magnetic bistability was reported.⁸⁹ These molecules, termed single molecule magnets (SMMs) exhibit slow relaxation of the magnetisation of purely molecular origin, and thus behave as single domain (0D) nanoscale magnetic entities with a barrier (U_{eff}) to the reversal of the magnetisation below a blocking temperature (T_{B}). Since many SMMs are plagued by significant QTM, T_{B} values are often below a measurable range using conventional magnetometers, and thus U_{eff} is more commonly reported and employed for comparative purposes between SMMs.

During recent years, the desire for SMMs with high energy barriers has led to the use of highly anisotropic lanthanide metal ions, such as Dy^{III} and Tb^{III}.⁹⁰⁻⁹⁶ Very recently, two new records have been set; both by Dy^{III} single-ion magnets (SIMs), which exhibited a record blocking temperature of $T_{\text{B}} = 20$ K,⁹⁷ and a record energy barrier of $U_{\text{eff}} = 712$ cm⁻¹, 1025 K.⁹⁸ Until now the highest blocking temperature was held by a radical bridged Tb^{III} dimer ($T_{\text{B}} = 14$ K), which was published in 2011,⁹⁹ and the highest energy barrier was held, since 2013, by a heteroleptic TbPc₂⁻ complex ($U_{\text{eff}} = 653$ cm⁻¹, 939 K).¹⁰⁰ With these systems and others, researchers within the field of molecular magnetism target potential applications in high-density information storage,⁷ quantum computing,^{8-11,101} magnetic refrigeration,^{16,17} molecular spintronics,^{12-15,102,103} etc. More recently, through further understanding of the underlying physics within these nanosystems, the most promising applications for these systems have been proposed to be in quantum computing and molecular spintronics.¹⁰⁴ However, since these applications require the molecular entity to be functionalised on a surface, while controlling and/or retaining its magnetic properties, it is crucial that magnetochemists explore the attachment of these systems on surfaces. Despite the logical path towards coupling surface science and molecular magnetism, the study of SMMs on surfaces is still far from the main focus of the field overall. This can be attributed to a number of factors; including (i) the fact that SMMs have not yet reached the necessary properties for feasible application; (ii) surface attachment is not facile, and often the inherent properties of the molecule are lost upon functionalisation; (iii) the required techniques for study of magnetic properties on surfaces are often not readily available, and can be rather costly to employ; (iv) and finally due to the often organometallic nature of high-performing SMMs their chemical stability does not lend itself well to manipulation and study under ambient conditions. Due to these reasons, among others, only a small number of researchers are exploring

the coupling of SMMs to surfaces, and studying the resulting properties. These studies will be outlined herein, in order to provide context for the work explored in Chapter 4.

2.2.2 Transition Metal SMMs on Surfaces

The molecule mentioned at the beginning of this section, Mn_{12}Ac (Figure 7a), was not only the first example of a SMM, but is also the most studied to date. Many derivatizations of the original structure have been synthesized and studied on a variety of different surfaces (Figure 7). The extensive study of this molecule has been motivated by the fact that it remained the highest-performing Mn-based SMM ($U_{\text{eff}} = 62$ K, $T_{\text{B}} = 4$ K) until 2006, when another Mn_{12} complex exceeded the energy barrier,¹⁰⁵ and 2007 when a Mn_6 complex exceeded the blocking temperature.¹⁰⁶

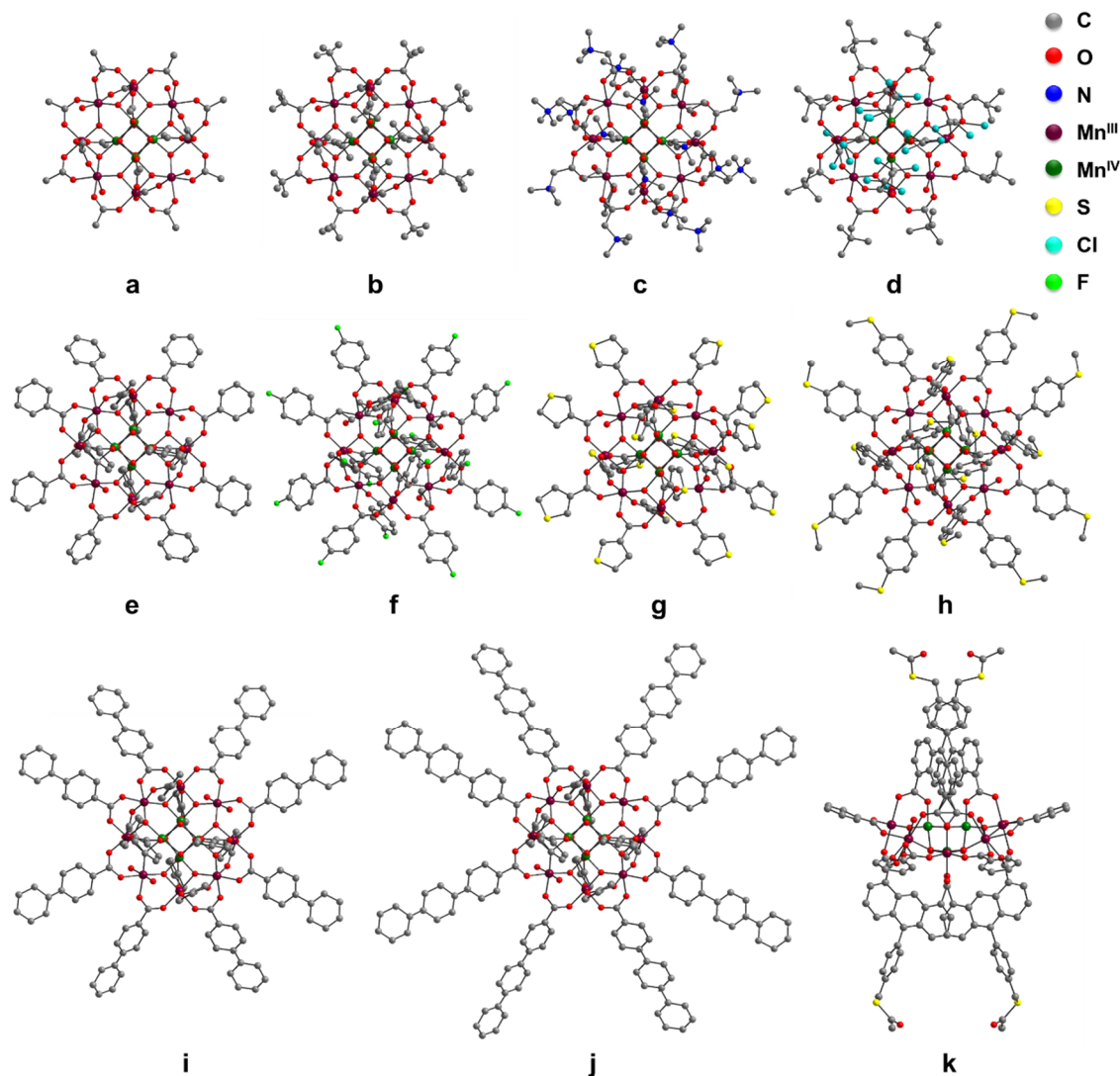


Figure 7. Top-down (**a-j**) and side-on (**k**) molecular structures of Mn_{12} complexes which have been successfully attached to various surfaces through their displayed functionalities. Structures **b**, **i**, and **j** were modelled for visual representation, as crystal structures were not reported. Hydrogen atoms are omitted for clarity.

The first surface study involving Mn_{12}Ac was in 2003, where the SMM was deposited on $\text{Au}(111)$.¹⁰⁷ $\text{Au}(111)$ was chosen due to the accessible atomically flat surface, the conductive properties, which allow for the use of scanning tunneling microscopy (STM) techniques for study and molecular manipulation, as well as the well-established affinity of Au for soft donor atoms, such as sulfur. The reasoning behind mentioning STM is the aforementioned capability for molecular manipulation, which could potentially facilitate the utilisation of the individual nature

of SMMs on a surface for a variety of applications.¹⁰⁸ Another important consideration is that Au has an already well-known surface attachment method; through self-assembled monolayers (SAMs). This approach was employed in the first adhesion study of Mn_{12}Ac to Au(111), and was confirmed to have been successful using a variety of analytical techniques. However, though attempted, SQUID measurements were not conclusive in this study, as the measured signal was too weak. This problem was likely due to the low ratio of paramagnetic to diamagnetic contribution from the sample. The first magnetic study of surface attached SMMs was performed using Mn_{12}Ac and Mn_{12}Bz (Figure 7e).¹⁰⁹ Molecules were attached using two different methods; namely the SAM method as well as a lipid-based monolayer method which provided order for the SMMs within the layer.¹¹⁰ In this case a magnetic signal was discernable, and a blocking temperature of 2 K was demonstrated for materials obtained through both attachment methods. This was an important result, as it became the first example of SMMs retaining any magnetic integrity on surfaces, albeit with some alteration of the properties. In order to further improve the practicality of SMMs, it is necessary to have control over the organisation and position of the molecules on the chosen surface. An important technological advancement towards achieving this control was gained through the employment of electrospray deposition for the deposition of Mn_{12}Ac on Au(111).^{111,112} The motivation behind using this particular technique is the control it offers over the surface coverage, as well as the fact that the molecule of interest does not have to be volatile in order to be deposited. The interaction between molecules on the surface was thereafter modelled using Mn_{12}Ac on Au(111). In particular, it was found that there was a molecular templating effect that causes the surface assembly upon electrospray deposition.¹¹¹ A later study of Mn_{12}Ac and Mn_{12}Bz on Au(111) confirmed that the core Mn ions were reduced upon surface attachment, which was proposed to be due to a surface charge transfer mechanism, thus causing the rearrangement to a more thermodynamically stable Mn^{II} oxide.¹¹² This drastic change in the electronic structure of Mn_{12} clusters upon surface interaction was then employed to rationalize previously observed changes to magnetic properties upon surface adhesion, and led to additional strategies in trying to avoid this reduction, *vide infra*.

Towards the specific employment of SMMs in electronics-based technologies, SAM techniques were also employed to adhere Mn_{12}Ac and cationic Mn_{12}Bet (Figure 7c) to SiO_2 ¹¹³ and Mn_{12}Ac to Si(100).¹¹⁴⁻¹¹⁶ The magnetic properties were either shown to be lost,¹¹⁶ or dramatically different from that of the bulk.¹¹⁴ The loss of magnetic integrity was rationalized by the change in Jahn-Teller elongation properties of the cluster through the use of X-ray Magnetic Circular Dichroism (XMCD) and SQUID magnetometry measurements. This finding was essential to the further development of the field, as it meant that alterations other than the previously observed

reduction of the metal cluster could also lead to change in, and/or loss of, the desired magnetic properties.

More recently, specialised surface structures have been employed as substrates for Mn_{12}Ac attachment, such as: carbon nanotubes (CNTs),¹¹⁷ Rh(111)/boron nitride (BN),¹¹⁸ and Bi(111).¹¹⁹ Thus, studies on conducting and insulating surfaces were performed in order to further the fundamental understanding of the effects of conductivity of a surface on the magnetic properties of the SMM. When placed on the interior surfaces of CNTs, Mn_{12}Ac molecules experienced a reduction of the observed energy barrier ($U_{\text{eff}} = 57$ K) and blocking temperature ($T_{\text{B}} = 2.5$ K, calculated) from the reported bulk values ($U_{\text{eff}} = 72$ K, $T_{\text{B}} = 3$ K, calculated). This was attributed to increased QTM, which was observed in the hysteresis measurements. This result was encouraging in regards to the ability of the molecules to retain some of their magnetic properties, however, these same properties were reduced (lower values of U_{eff} and T_{B}) due to the effects of QTM, thus illustrating another potential factor at play in alleviating SMMs of their magnetisation. Interestingly, overall insulating surfaces were shown to retain more of the bulk magnetic behaviour of SMMs upon surface attachment.

Another archetype of Mn_{12} was developed in 2005;¹²⁰ Mn_{12}Piv , Figure 7b. This complex, being soluble in organic solvents, was designed in order to prevent intermolecular interactions using the peripheral tBu groups. This strategy was employed thereafter in order to functionalize Mn_{12} with a variety of groups for specific purposes. In order to attempt to minimize the redox chemistry within the Mn_{12} core upon surface attachment a cationic SMM, Mn_{12}Bet , Figure 7c,^{121,122} was studied on Au(111), and an axially functionalised SMM, $\text{Mn}_{12}\text{dichloroacetate}$, Figure 7d, was studied on Si(100).^{123,124} However, magnetic studies were either not performed, or were inconclusive, in these cases. A more successful magnetic study was performed on the previously discussed Mn_{12}Bz complex (Figure 7e) and a terphenyl functionalized SMM structure, Mn_{12}tpc ,¹²⁵ (Figure 7j), which were studied in order to determine whether or not the extended terphenyl structure would aid in the insulation of the Mn_{12} core from the surface. It was found that the bulky ligand did indeed insulate the core from the previously observed surface interactions that led to reduction. This bulky ligand approach was also taken by another group, developing a fluorinated SMM, Mn_{12}pfb , Figure 7f, which was then adhered to Au(111).¹²⁶ The electronic structure was also shown to be conserved in this case, however, magnetic properties were not investigated post-attachment.

Thereafter, a series of functionalised Mn_{12} molecules were synthesized in order to further explore the surface attachment capabilities and shielding properties of various ligands. On

Au(111) two different S-terminated clusters were developed and studied; namely Mn_{12}Th (Figure 7g),¹²⁷⁻¹²⁹ and $\text{Mn}_{12}\text{PhSMe}$ (Figure 7h).^{130,131} Unfortunately, neither cluster was studied magnetically post-attachment. A commonly studied derivative remains the biphenyl functionalised cluster, $\text{Mn}_{12}\text{biph}$ (Figure 7i), which was adhered to: Si,¹³² highly-ordered pyrolytic graphite (HOPG),¹³³ and polymeric substrates.¹³⁴⁻¹³⁶ Initially, one of the attractive properties of $\text{Mn}_{12}\text{biph}$ was its hydrophobicity, allowing it to easily be deposited on Si(100) from solution,¹³² and subsequently studied. Due to the chemical and thermal stability of $\text{Mn}_{12}\text{biph}$, this hydrophobicity, and the propensity for $\pi\cdots\pi$ interactions between phenyl groups, it was chosen for assembly on HOPG.¹³³ Despite achieving control over the molecular assembly on the surface, no magnetic studies were performed in this work. $\text{Mn}_{12}\text{biph}$ molecules were subsequently placed on polymeric substrates,^{134,135} where magnetic measurements elicited two energy barriers ($U_{\text{eff}} = 56$ and 36 K) that were consistent with Mn_{12}Ac .¹³⁶ Thus, the polymeric substrate did not induce dampening of the magnetic properties of this SMM. However, the orientation of the molecules remained problematic, as their anisotropy axes would necessitate alignment in order to be practical. In an effort to expand on this type of position control, a rather complicated ligand structure was axially functionalized on the Mn_{12} cluster, forming Mn_{12}adc (Figure 7k).¹³⁷ Though the position of the anisotropy axes were not experimentally or theoretically confirmed to have been successful, magnetic blocking was retained up to 2 K. Overall, these studies showed that functionalisation of Mn_{12} onto a conducting surface was possible, however, whether or not the magnetic properties are retained thereafter remains extremely dependent upon the structure of the molecule and conditions involved.

The extensive surface-based work on various iterations of Mn_{12} can be directly linked to the success achieved with more recent systems, which will be discussed herein. The broad array of work and understanding gained through the study of the most ubiquitous SMM, Mn_{12} , did indeed lead the field in a new and productive direction.¹³⁸ Aside from Mn_{12} , various other Mn-based SMMs have been studied on surfaces.^{139,140} However, the most important result in the field, post Mn_{12} , came from the introduction of Fe_4 systems (Figure 8), which played a significant role in the advancement of this area of research.

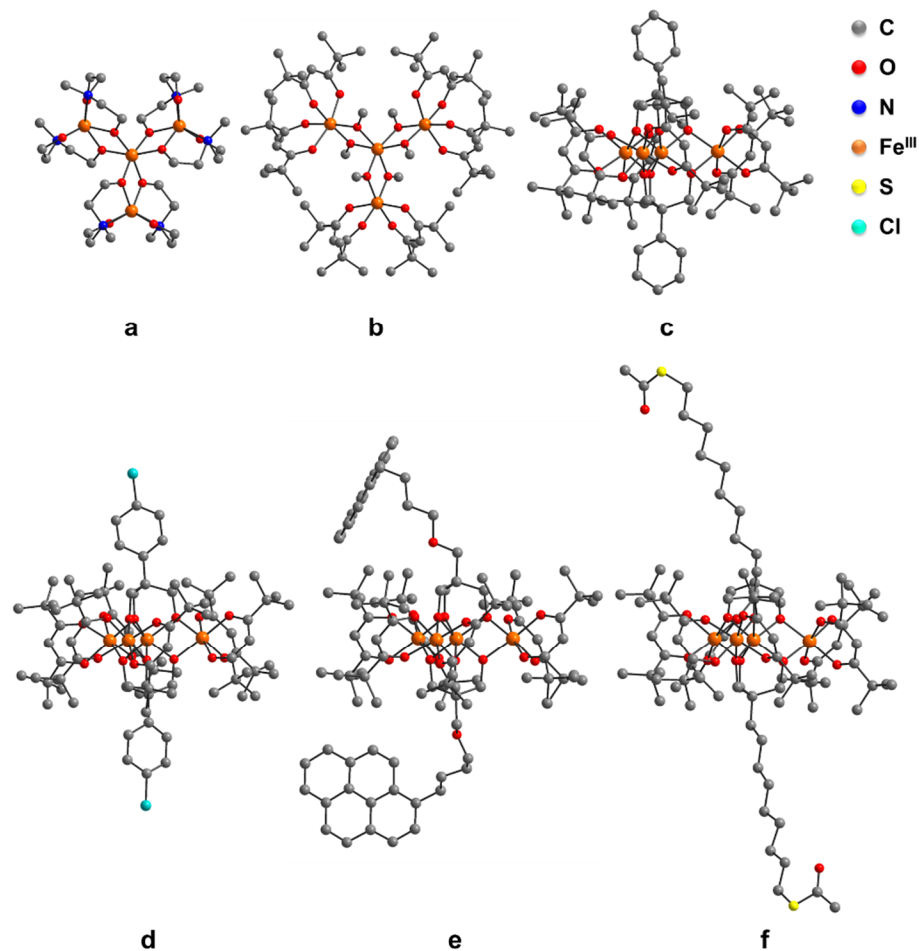


Figure 8. Top-down (**a** and **b**) and side-on (**c-f**) molecular structures of Fe_4 complexes, which have been successfully attached to various surfaces through their displayed functionalities. Hydrogen atoms are omitted for clarity.

The structure of Fe_4 was first presented as a star-shaped molecule (Figure 8a) with moderate SMM behaviour ($U_{\text{eff}} = 14.25$ K, $T_{\text{B}} = 1.2$ K), and was attached to the surface of HOPG.¹⁴¹ This system was then functionalised, taking advantage of the ability of the bridging and non-bridging ligands to be independently varied (Figure 8c, d, e and f). Additionally, studies were performed on Si(100),^{142,143} Al foil,¹⁴⁴ and CNTs.¹⁴⁵ Unfortunately, these studies share similar drawbacks: either no magnetic measurements were performed following adhesion, or significant losses in magnetic behaviour were observed upon attachment. A breakthrough was published shortly after these studies, wherein arguably the most famous example of SMM surface attachment was published; a thiol chain functionalised Fe_4 molecule (Figure 8f).¹⁴⁶ This molecule was designed for attachment to Au(111) through its axially located S-terminated ligands. In order

to measure the magnetic behaviour of the surface-bound SMMs, XMCD was employed, illustrating the first example of fully retained hysteretic behaviour of a SMM on a surface. The same group then synthesized a nearly identical version with slightly shortened alkyl chains, and proceeded to compare and contrast their magnetic behaviour. However, the shorter linkers were shown to promote increased QTM behaviour,¹⁴⁷ and were consequently less desirable candidates for surface adhesion. Additional studies on this system were performed; one study employed different solvents to complete the surface-assembly process, thus studying the effects of solvent on surface adhesion and assembly.¹⁴⁸ Another replaced the central Fe^{III} with a Cr^{III} ion in order to study the magnetic effects of this alteration in the core structure when adhered to a gold surface thereafter.¹⁴⁹ These results stimulated the field, promoting researchers to believe that SMMs could, as long predicted, be utilised in practical applications. Overall, Fe₄ clusters, as well as other Fe systems,¹⁵⁰ were able to bring the field of molecular magnetism forward from Mn₁₂ and into a new era of magnetic materials.

2.2.3 Lanthanide SMMs on Surfaces

In 2003, the first terbium bisphthalocyanine, TbPc₂, complex (Figure 9) was published as a SMM with an energy barrier of 230 cm⁻¹, 331 K.¹⁵¹ Until recently, it was also a TbPc₂ SMM that held the aforementioned record energy barrier.¹⁰⁰ Thus, extensive work has been performed on synthetically varying the Pc ligands, homoleptically or heteroleptically, in order to study and optimize the inherent magnetic properties of the system, as well as to design the SMM to adhere to a variety of surfaces. The unsubstituted TbPc₂ (Figure 9a) has been studied on surfaces for its interesting magnetic, electrochromic, and semiconducting properties.^{152,153}

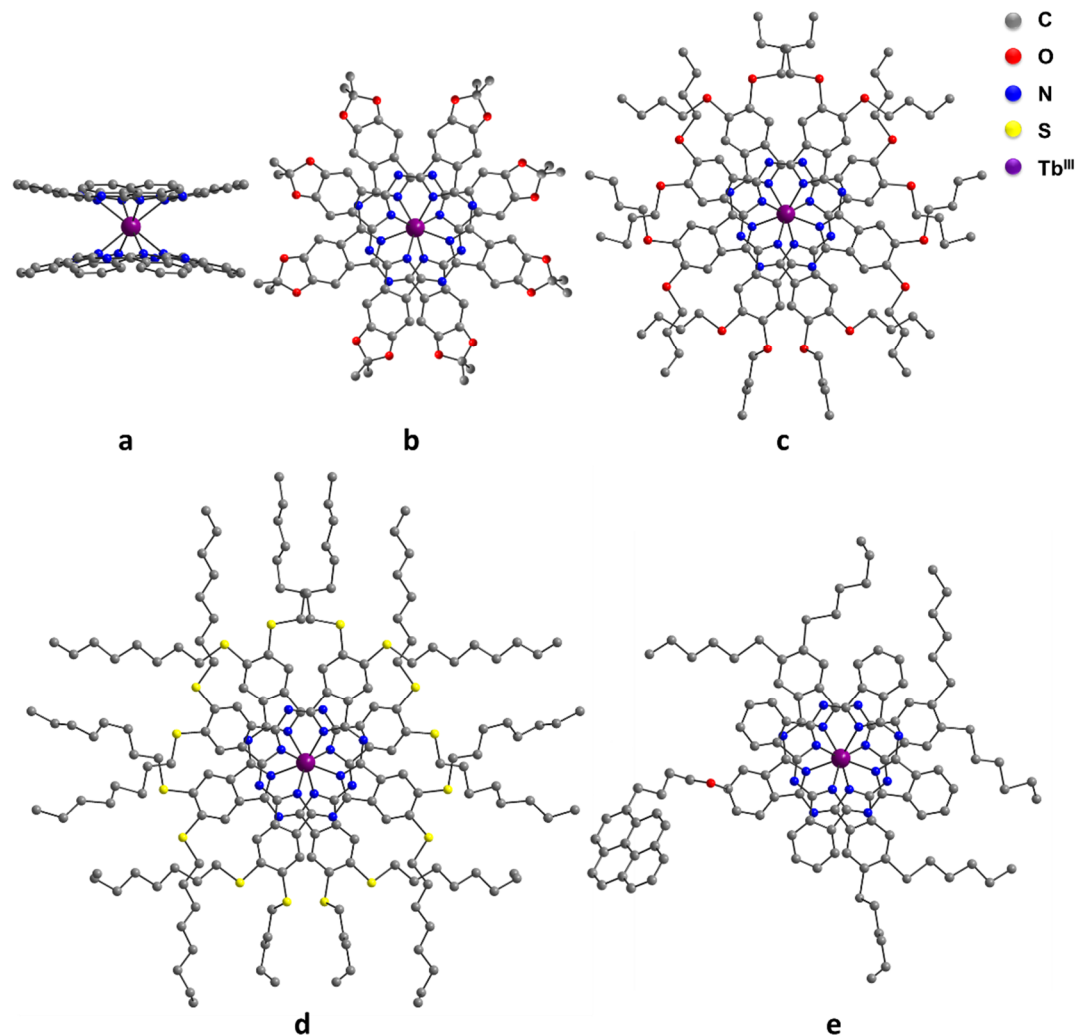


Figure 9. Side-on (a) and top-down (b-d) molecular structures of TbPc₂ complexes which have been successfully attached to various surfaces through their displayed functionalities. Structures b, c, and e were modelled for visual representation, as crystal structures were not reported. Hydrogen atoms are omitted for clarity.

The first report of TbPc₂ on a surface was performed on Cu(111), and subsequently modelled using DFT in order to determine the perturbation effects of the surface adhesion on the 4*f* orbitals.¹⁵⁴ Since no perturbations were found, it was assumed that the magnetic properties would be retained. The first study capable of confirming experimentally that the crystal field and magnetic properties were indeed robust upon surface attachment was performed in 2010, on Cu(100).¹⁵⁵ This study employed XMCD in order to follow the magnetic moment experimentally, thus concluding that although the lower Pc ligand had a significant interaction with the Cu

substrate, the ligand field and magnetic moment remain intact. Thereafter, many magnetic studies have been performed on TbPc₂; including its coupling with ferromagnetic substrates.^{156,157} Theoretical studies were also performed, pertaining to spin dynamics and spin-splitting of the adsorbed SMM in order to gain fundamental understanding of their potential future application; specifically in spintronics.^{158,159} Finally, TbPc₂ was also studied on a wide variety of surfaces in order to understand its: electron transfer properties,¹⁶⁰ Kondo effect properties,¹⁶¹⁻¹⁶⁵ chiral and achiral structural switching,¹⁶⁶ and exchange bias properties.¹⁶⁷ Overall, the studies on TbPc₂ are extensive, and relate to a variety of research areas and potential applications. However, in order to further improve the material for its magnetic properties, as well as its surface adhesion properties, the next step is naturally ligand modification.

The first study involving a substituted TbPc₂ SMM on a surface was reported in 2006, where homoleptic substitution of butoxy groups on the Pc ligands (Figure 9c) allowed for self-organised assembly of the molecules on HOPG.¹⁶⁸ Magnetic measurements were attempted, but ultimately were unsuccessful. This was attributed to the thermal instability of the molecule and/or a lack of adequate response from a monolayer of magnetic molecules on a bulk surface. A similar TbPc₂ molecule, homoleptically substituted with acetal groups (Figure 9b), was also studied on HOPG.^{169,170} XMCD was used in one report to confirm that the magnetic properties were retained, including hysteretic behaviour at 7 K.¹⁷⁰ The final homoleptically substituted TbPc₂ structure studied on a surface was designed with long alkylthio chains (Figure 9d),¹⁷¹ however, once attached to Au(111) the magnetic properties were not explored further. Thus, the magnetic properties of TbPc₂ have been shown to be able to be retained on a surface, however, unfortunately the alignment of anisotropy axes remains a problem.

An interesting and important synthetic advancement in the design and control of TbPc₂ SMMs on surfaces was the ability to heteroleptically substitute only one of the Pc ligands. Initially, the substitution involved a pyrenyl group, in order to promote interactions with CNT and HOPG surfaces. This structure (Figure 9e) was studied initially on CNTs, where the magnetic properties were not only retained, but actually showed some improvement upon surface adhesion ($U_{\text{eff}} = 351 \text{ cm}^{-1}$, 505 K, $T_B = 0.04 \text{ K}$).¹⁷² Thus, this study clearly presented the potential for this system to be employed in future applications. The same system was then adhered to graphene,¹⁷³ and an interaction between the SMM and graphene substrate was observed, providing researchers with hope for potential SMM-based transistor systems. Due to the success achieved with these systems, a CNT-TbPc₂ molecular spin-valve was synthesized and found to exhibit strong spin-phonon coupling, garnering further interest for application in spintronics.^{102,174} The studies of

TbPc₂ systems on and off of surfaces continue to be performed in order to further the progression of the field of molecular magnetism towards practical employment.

Thus far, little exploration has been performed on lanthanide-based SMM systems aside from TbPc₂. More recently, an Er^{III} SMM (Figure 10) was studied on both Au(111) and Ni-coated Cu(100).¹⁷⁵

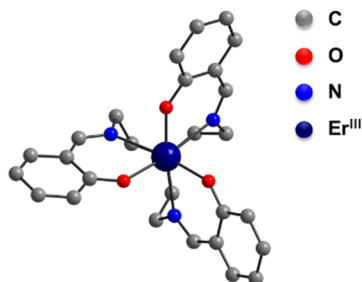


Figure 10. Molecular structure of Er(trensal). Hydrogen atoms are omitted for clarity.

Magnetic measurements were performed using XMCD, and showed that on Au(111) a weak SMM-surface interaction was present, which allowed molecules to randomly orient themselves on the surface, eliciting no significant changes in the magnetic behaviour. On the Ni-coated surface, the SMM had a much stronger (covalent) interaction with the surface, which aligned the molecules and elicited antiferromagnetic coupling. This coupling was posited as the reason behind the suppression of QTM. This is an interesting result, and one which will hopefully encourage researchers to continue studying the coupling of SMMs to various surface materials to gain valuable and fundamental understanding going forward.

2.2.4 SMMs on Metal Nanoparticles

One of the most unique approaches to the study of magnetic molecules on surfaces has been the use of non-conventional substrates; for example, metal nanoparticles. In this case, magnetic properties can be studied using conventional magnetometry techniques in place of specialised techniques, such as XMCD. Furthermore, analyses can be performed on a bulk powder sample as well as a colloidal solution, thus widening the range of potential analytical methods available. Other notable features of nanoparticle substrates are their high surface area and their tunable size,

shape and crystalline properties, thus making them a very customizable material to be utilised as a substrate.

Despite the promise of this method as a facile means for the investigation of molecular magnetic relaxation on various surface templates, thus far only two studies of this type have been performed; one with a 3*d*-based SMM¹⁷⁶ and the other with a 4*f*-based SMM.¹⁷⁷ The 3*d*-based SMM study was performed using a Fe₄ system, similar to the system discussed above, which was wired to a Au(111) surface.¹⁴⁶ The gold nanoparticles (AuNPs) employed had an average diameter of 5 nm, and were capped using hexadecylamine, followed by reaction with the 1,2-dithiolane ligands of the SMM (Figure 11). Thereafter, the Fe₄ complex was studied on the surface of AuNPs using a variety of analytical techniques, including SQUID magnetometry. From the ac susceptibility data a barrier was extracted ($U_{\text{eff}} = 8.0$ K), which was lower than that of the magnet itself ($U_{\text{eff}} = 14.0$ K).¹⁷⁸ Thus, the magnetic relaxation process was faster upon surface attachment, which indicates the increased presence of QTM.¹⁷⁹

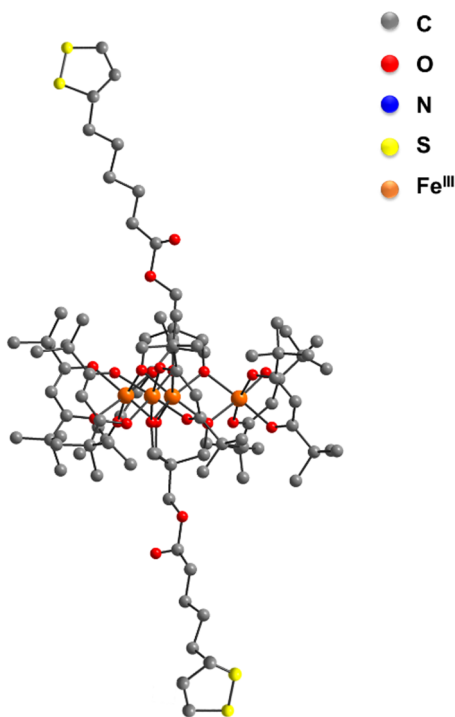


Figure 11. Molecular structure of Fe₄ system later adhered to the surface of AuNPs. Structure was modelled for visual representation, as a crystal structure was not reported. Hydrogen atoms are omitted for clarity.

Through the attachment of SMMs to nanomaterials instead of bulk substrates, the applicability becomes open ended and the techniques for analysis broaden. Thus, these hybrid materials are incredibly promising in the advancement of the still expanding field of molecular magnetism. The 4f-based SMM study will be discussed in detail within Chapter 4.

2.3 Molecular Chain Magnets

Magnetic molecular chains, or single chain magnets (SCMs) are 1D chains of paramagnetic spin carriers which display magnetic properties. Akin to the SMMs discussed above, at low temperatures SCMs are superparamagnetic below a characteristic T_B . Their characteristics, thus, evoke those of better known, and previously discussed, magnetic nanoparticles and SMMs. However, there are numerous significant differences which make the synthesis, characterisation and fundamental understanding of SCMs worthwhile in order to better design magnetic materials for successful future applications. Discrete 0D entities are often the focus of the field of molecular magnetism, whether they be single ion magnets (SIMs), or molecules with multiple magnetic spin carriers (SMMs), such as the aforementioned Mn_{12} cluster. Interestingly, 1D chain networks have been found to be flexible alternatives to SMMs, often allowing for tailoring of the anisotropic barrier through varying bridging moieties, etc.¹⁸⁰ Furthermore, 1D chain networks can provide an opportunity to tether magnetic molecules together in an ordered fashion, similar to their adherence to surfaces discussed above.

2.3.1 Transition Metal SCMs

Interestingly, SCMs were initially developed with the motivation of increasing the blocking temperature of SMMs, through coupling of magnetic ions within the chain network. The first example was reported in 2001, with Co^{II} ions bridged by organic radical ligands, $[Co(hfac)_2(NITPhOMe)]$; hfac = hexafluoroacetylacetonate; NITPhOMe = 4'-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), which is shown in Figure 12a.¹⁸¹ This SCM displayed ferrimagnetic behaviour between spin carriers, which induced slow relaxation of the magnetisation, eliciting a $U_{eff} = 154(2)$ K, and hysteretic behaviour up to $T_B = 4$ K. This behaviour was particularly significant at the time, considering that the energetic barrier of the archetypical Mn_{12} was much lower than this value (*vide supra*). Furthermore, several SCM systems with modest energetic barriers have been synthesized with a variety of different TMs,¹⁸²⁻¹⁸⁷ further illustrating the remarkable properties of this initial structure. Interestingly, a similar

ferrimagnetic radical ligand-bridged system has since been reported with Co^{II} , $[\text{Co}(\text{hfac})_2(\text{PyrNN})]$; where $\text{PyrNN} = 2-(1'\text{-pyrenyl})-4,4,5,5\text{-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl}$ (Figure 12b).¹⁸⁸ This structure displayed a record $T_{\text{B}} = 14$ K, and two relaxation processes with $U_{\text{eff}} = 377 \pm 18$ K, and 396 ± 13 K. This behavior was attributed to the strong coupling between spin carriers and significant anisotropy within the chain, and thus this system remains the highest performing SCM to date. This points to the fact that these radical bridged systems display significant potential for practical advancement of such materials. This is not altogether surprising considering the properties that have been observed for radical bridged SCMs,^{189,190} and SMMs, as a radical bridged Tb^{III} SMM held the record for highest T_{B} in a single-molecule magnet until very recently.⁹⁹

One of the most commonly explored SCM systems has been a $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ structure, coupled through cyanide bridges. These chains have garnered interest as a result of their magneto-optical properties,¹⁹¹ as they have been shown to display photoinduced spin-crossover phenomena.^{192,193} Several cyanide bridged systems have also displayed SCM behaviour in the form of slow relaxation of the magnetisation. Significant ferromagnetic coupling between Co^{II} and Fe^{III} spin carriers has elicited high energetic barriers in these systems, comparable to the first reported SCM. One representative example is $[\{\text{Fe}^{\text{III}}(\text{L})(\text{CN})_4\}_2\text{Co}^{\text{II}}(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$; where $\text{L} = 2,2'\text{-bipyridine (bpy) or } 1,10\text{-phenanthroline (phen)}$, which has a $U_{\text{eff}} = 142$ K (Figure 12c).¹⁹⁴ This type of short cyanide bridging moiety was successful in producing interesting SCM materials, and consequently was also employed to couple Fe^{III} and Cu^{II} in $[(\text{Tp})_2\text{Fe}^{\text{III}}_2(\text{CN})_6\text{Cu}(\text{CH}_3\text{OH}) \cdot 2\text{CH}_3\text{OH}]$, eliciting a $U_{\text{eff}} = 112.3$ K and $T_{\text{B}} = 6$ K.^{195,196} Several cyanide-bridged SCM structures composed of a variety of mixed metals have also been presented with barriers ranging between $U_{\text{eff}} = 16 - 134$ K.¹⁹⁷⁻²⁰⁰

Due to the success of these cyanide bridged systems, a similar strategy of exploiting short linkers between Co^{II} ions was employed using azido bridges, resulting in the formation of $[\text{Co}(2,2\text{-bithiazoline})(\text{N}_3)_2]$ (Figure 12d).²⁰¹ These ferromagnetically coupled chains display clear superparamagnetic behaviour, with $U_{\text{eff}} = 94(2)$ K, and hysteretic behaviour to $T_{\text{B}} = 5$ K. Azide bridges in particular have been proposed to strengthen magnetic coupling in a variety of systems, including $[\text{Mn}_3\text{O}(\text{tBu-sao})_3\text{N}_3(\text{CH}_3\text{OH})_4] \cdot \text{CH}_3\text{OH} \cdot 0.5\text{H}_2\text{O}$.²⁰²⁻²⁰⁴ In this study, analogous structures were synthesized with formate and azide bridging moieties, and the azide-bridged structure displayed a significant improvement in energetic barrier and blocking temperature values, as compared to the formate structure ($U_{\text{eff, formate}} = 47.9$ K, $U_{\text{eff, azide}} = 96.6$ K and $T_{\text{B}} = 3.5$

K). Thus, through tailoring bridging moieties, there is a tunable nature to the magnetic behaviour of these 1D systems.

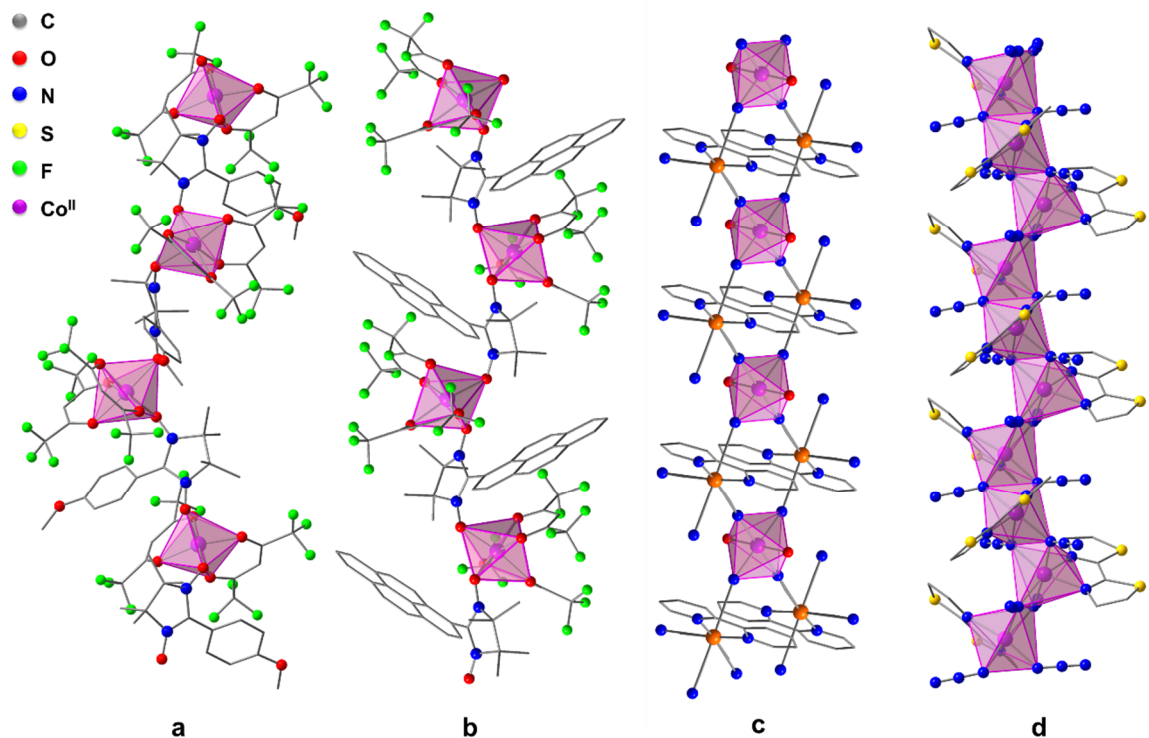


Figure 12. Molecular structures of (a) $[\text{Co}(\text{hfac})_2(\text{NITPhOMe})]$, (b) $[\text{Co}(\text{hfac})_2(\text{PyrNN})]$, (c) $[\{\text{Fe}^{\text{III}}(\text{L})(\text{CN})_4\}_2\text{Co}^{\text{II}}(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, and (d) $[\text{Co}(\text{2,2-bithiazoline})(\text{N}_3)_2]$. Hydrogen atoms are omitted for clarity.

In order to better compare these systems with SMMs, and fundamentally characterize their magnetic units, SCMs have been broken up so that their individual repeating units may be studied.²⁰⁵ The resulting monomeric units frequently displayed slow magnetisation dynamics, thus they were shown to be behaving like SMMs. This methodology was applied to a family of complexes: $[\text{Mn}_2(\text{saltmen})_2\text{Ni}(\text{pao})_2(\text{py})_2](\text{ClO}_4)_2$; $\text{saltmen}^{2-} = \text{N,N}'\text{-(1,1,2,2-tetramethylethylene)-bis(salicylideneimine)}$; $\text{pao} = \text{pyridine-2-aldoximate}$.²⁰⁶⁻²⁰⁸ These $\text{Mn}^{\text{III}}\text{-Ni}^{\text{II}}$ systems displayed modest SCM magnetic properties with $U_{\text{eff}} = 67 - 72 \text{ K}$, and $T_{\text{B}} = 3.5 \text{ K}$.²⁰⁶⁻²⁰⁸ Interestingly, a building block unit was synthesized in order to mimic the chain structure,²⁰⁷ while in another study anions were employed in order to separate chains from one another.²⁰⁸ This type of

isolation study was first demonstrated in a different way for $[(\text{NEt}_4)[\text{Mn}_2(5\text{-MeOsalen})_2\text{Fe}(\text{CN})_6]; 5\text{-MeOsalen}_2 = \text{N,N-ethylethylene bis-salicylideneimine}]$,¹⁹⁷ where cations were employed in order to separate chains within the crystalline packing. The separation of chains from one another using these methods resulted in a better understanding of the magnetisation being derived from single chains, as opposed to through interchain interactions. One unique study was able to correlate relaxation rate to chain length; explaining that the faster relaxation process observed was attributed to shorter chains.²⁰⁹ This is a phenomenon that is worth studying since, as discussed previously, size has a significant effect on the fundamental magnetic properties within nanomaterials.

These pioneering building block isolation studies prompted the development of new SCM materials from known SMM clusters.²¹⁰ The first attempt to utilize SMMs as building blocks towards 1D magnetic materials was attempted by employing Mn_{12} clusters as precursor materials. However, instead of forming a chain network, the clusters were broken apart during synthesis and reassembled into $[\text{Mn}_7\text{O}_8(\text{O}_2\text{SePh})_8(\text{O}_2\text{Me})(\text{H}_2\text{O})]; \text{PhSeO}_2\text{H} = \text{benzeneseleninic acid}$.²¹¹ Despite their efforts, the smaller clusters formed had very modest magnetic properties as compared to the original cluster ($U_{\text{eff}} = 14.2 \text{ K}$). Similar ideas have been explored through the use of weak one-dimensional H-bonds in order to connect SMM units,²¹² and through coupling a Mn^{III} porphyrin complex with a radical-containing ligand.²¹³ These systems all have a commonality, which is that SMMs placed in a chain formation generally experience further slowing of their relaxation dynamics as a result of the dipolar and/or superexchange interactions induced between spin carriers.¹⁸⁰ This indicates that the original purpose of SCMs, to increase the performance of SMMs, has the potential to be realized. However, owing to the unpredictable magnetic nature of these chain networks, understanding the interplay of the relaxation dynamics requires extensive further study.

2.3.2 Lanthanide SCMs

Examples of lanthanide SCMs are rare, and often formed through employing bulky ligands to avoid the formation of 3D networks, as was shown in $[\text{Dy}(\text{hfac})_3\text{NIT}(\text{C}_6\text{H}_4\text{OPh})]$; $\text{hfac} = \text{hexafluoroacetylacetonate}$; $\text{NIT}(\text{R}): 2\text{-(4'-R)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide}$ (Figure 13).²¹⁴ This chain structure was the first lanthanide SCM reported. Similar to the first example of a SCM with Co^{II} , this system employs an anisotropic ion, in this case Dy^{III} , and a radical-containing ligand employed as a bridging mechanism. Magnetic characterisation resulted in the observation of two relaxation processes of $U_{\text{eff}} = 69(1)$ and $42(1) \text{ K}$, and $T_{\text{B}} = 3 \text{ K}$. The rich

relaxation behaviour was shown within hysteresis measurements, where steps in the curve indicated competing inter- and intrachain interactions between Dy^{III} and radical spins.

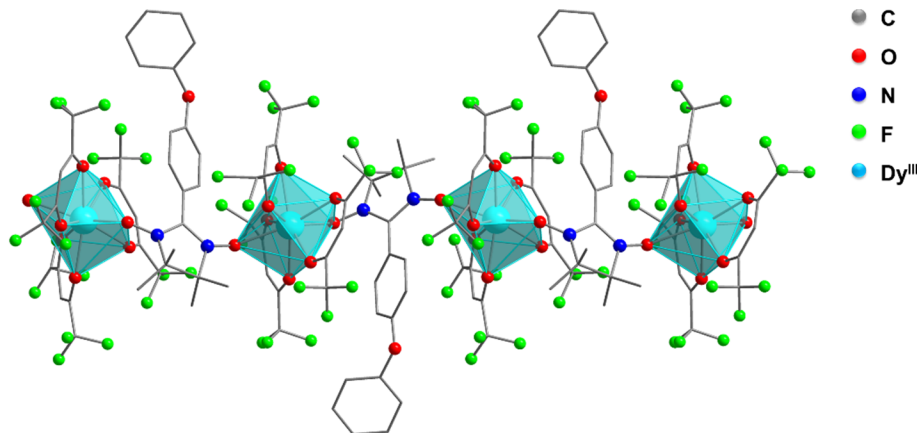


Figure 13. Molecular structure of $[M(hfac)_3]NIT(C_6H_4OPh)$; $M = Dy^{III}$. Hydrogen atoms are omitted for clarity.

The first family of isostructural lanthanide SCMs, which were analogous structures to that discussed above for Dy^{III} (Figure 13), were published shortly after with Eu^{III}, Gd^{III}, Tb^{III}, Ho^{III}, Er^{III} and Yb^{III}.²¹⁵ Slow magnetic relaxation was observed in anisotropic ions: Tb^{III} ($U_{eff} = 45(1)$ K), Ho^{III} ($U_{eff} = 34(2)$ and $18(2)$ K) and Er^{III} (no extractable barrier) systems, as well as in the original Dy^{III} system, thus displaying the varied magnetic properties that can be derived from exploring different ions and their properties, across the lanthanide group. Furthermore, they were able to conclude that single ion contributions to the energy barrier were able to compensate for weak $4f$ - $4f$ interactions, thus suggesting that 1D lanthanide materials may be applicable to orienting SIM-type systems along one dimension, without the occurrence of long-range ordering (*vide infra*).

More recently, a similar radical bridged Dy^{III} SCM, $[Dy_2(hfac)_6(NITThienPh)_2]$; NITThienPh = 2-(5-phenyl-2-thienyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide), was presented with two relaxation processes: $U_{eff} = 98$ and 53 K, and $T_B = 3.7$ K.²¹⁶ This structure represents the first example of a lanthanide SCM synthesized using a building block approach. Furthermore, the building block was shown to possess paramagnetic properties down to 2 K, while the chain structure experienced clear slow relaxation of the magnetisation, indicating superparamagnetic properties. Therefore, we may conclude that in specific systems lanthanide

ions have the potential to experience some of the benefits observed for TMs in 1D chains, if slow magnetic relaxation is desired.

Lanthanide-based SCMs will be further discussed in Chapter 5, where a unique approach to building 1D chains composed of isolated magnetic systems has been employed in order to study fundamental magnetic behaviour in an ordered 1D array. It follows that the concepts introduced in the previous section regarding magnetic molecules will be coupled with those in this section to facilitate better understanding of the work presented.

2.4 Magnetic Metal-Organic Frameworks

2.4.1 Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are 3D crystalline porous materials, which are composed of an organic linker and an inorganic secondary building unit (SBU). The organic linker is often a bidentate, or in some cases multidentate, ligand that is capable of binding to a metal ion/cluster SBU. These hybrid organic/inorganic materials have garnered extensive interest, mainly as a result of their synthetic tenability, ultrahigh porosity, high surface area, and high thermal and chemical stability.²¹⁷ These, combined with other favorable properties, have induced interest in MOF materials for a range of applications; most commonly gas storage and separation, as well as catalysis.

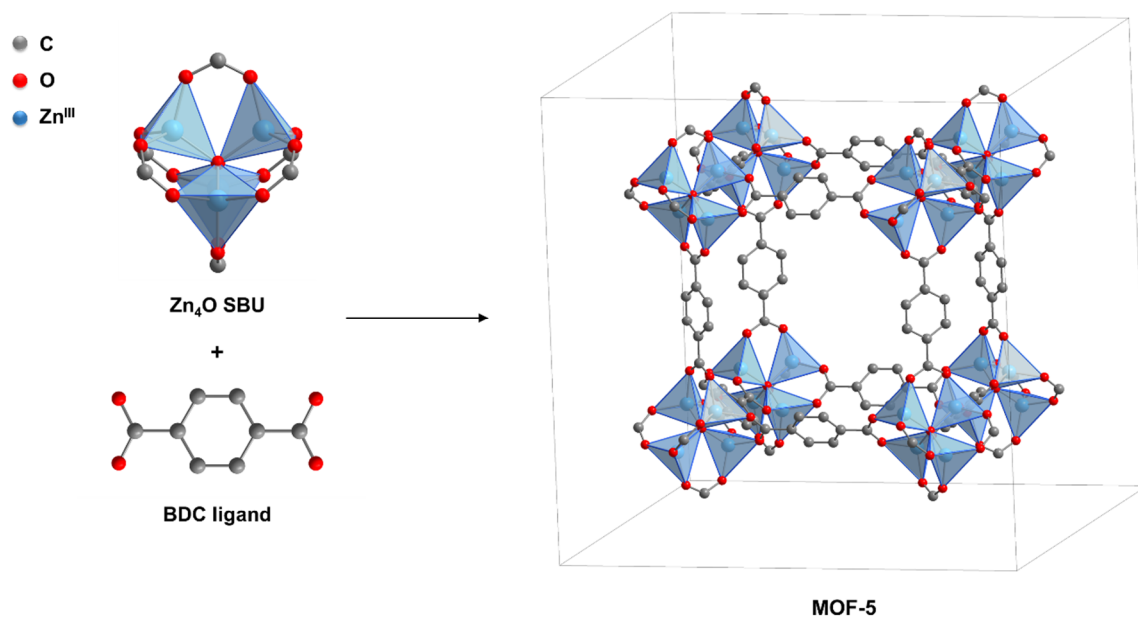


Figure 14. Scheme displaying the composition and molecular structure of MOF-5. Structure displayed with unit cell edges visible (faint lines) and hydrogen atoms omitted for clarity.

Porosity in MOFs, as in zeolites, was one of the first properties that initialised the ever-expanding interest in these materials. In particular, permanent porosity was desired in order to allow sorption of gases into the void spaces without the material losing its structural integrity. This concept was first proven by Yaghi and co-workers with a material that they entitled MOF-2 [Zn(bdc); bdc = 1,4-benzenedicarboxylate],²¹⁸ and shortly thereafter with MOF-5 [Zn₄O(bdc)₃] (Figure 14),^{219,220} which still remains one of the most studied MOFs to date.

MOF-5 continues to be relevant due to its remarkable properties, such as thermal stability up to 470°C and a Brunauer-Emmett-Teller (BET) surface area of 2320 m²/g.²²¹ This surface area value in particular was notable as it outperformed zeolite and activated carbon materials at the time.²²¹ From this point, a race to obtain the highest-performing porous material was underway. In 2004, MOF-177 [Zn₄O(BTB)₂; BTB = 4,4',4''-benzene-1,3,5-triyl-tribenzoate] was reported with a record-breaking BET surface area of 3780 m²/g, and a porosity of 83%.²²² This record held until 2010, when it was outshone by MOF-200 and MOF-210 [Zn₄O(BBC)₂ and (Zn₄O)₃(BTE)₄(BPDC)₃, respectively; BBC = 4,4',4''-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate; BTE = 4,4',4''-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoate; BPDC = biphenyl-4,4'-dicarboxylate]. These materials reported ultrahigh surface area (and porosity) values of 4530 m²/g (90%) and 6240 m²/g (89%), respectively.²²³ The current benchmark is held by NU-110 [Cu₃(BHEHPI); BHEHPI = 5,5',5''-(((benzene-1,3,5-triyltris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))-tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))trisophthalate] with a surface area of 7140 m²/g.²²⁴ This framework contains alkyne-rich (as opposed to phenylene-rich) linkers, which had been previously theoretically predicted to increase the number of available adsorption sites, as well as the surface area.²²⁵ Interestingly, it has been proposed that the measure of surface area per volume is a more relevant comparison for practical application. By this standard, MOF-5 still retains the best reported value (2200 m²/cm³).²²⁰

Another important property to consider in MOFs is their stability under thermal and chemical strain. Due to the strong metal-ligand bonds, MOFs have been shown to be stable to high temperatures; often within the range of 250-500°C.²²⁰ Chemical stability, however, is much rarer due to the propensity for MOFs to undergo post synthetic alteration upon solvent soaking, guest alteration, or even air exposure (*vide infra*). Several MOF examples have now been

published that are capable of withstanding reflux conditions in methanol, water and in some cases even under harsh acidic conditions.²²⁶⁻²³⁰ These materials would, therefore, be best suited to applications which require a porous material to withstand such conditions; such as in water-containing processes like CO₂ capture from humid flue gas.²²⁰

The performance of a MOF in gas adsorption and catalysis can be measured by many of the above discussed parameters, as well as by more specific measures. In reference to catalysis, it is important for a MOF to possess high surface area and tunable pore metrics, while also possessing an open pore structure with a high density of available active sites. MOFs possessing these characteristics have been used for a variety of catalytic applications; including, but not limited to, supporting, stabilizing and encapsulating catalysts, as well as performing molecular size selectivity.²³¹ In reference to gas adsorption, MOFs are frequently reported along with gas adsorption isotherms in order to quantify the amount of a specific gas that a MOF is capable of sorbing by percent weight (wt.%). These quantities are measured at a variety of applied pressures and temperatures. The practice of quantifying gas sorption in this way was introduced by Yaghi with MOF-5 in 2003,²³² and has since become ubiquitous in the MOF community. Currently, the benchmarks for the most common gases are as follows: NU-100 [Cu₃(TTEI); TTEI = 5,5',5''-(((benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))trisophthalate] has a hydrogen uptake of 9.0 wt.% at 77 K, under 56 bar of pressure;²³³ PCN-14 [Cu₂(H₂O)₂(adip), 2dimethylformamide (DMF); adip = 5,5'-(9,10-anthracenediyl)diisophthalate] has a methane uptake of 212 mg/g at 290 K, under 35 bar of pressure;²³⁴ and MOF-200 has a CO₂ uptake of 2347 mg/g at 298 K, under 50 bar of pressure.²²³ Thus, these are some of the most important benchmarks within the porous materials community, as MOFs, zeolites, and other porous materials are striving to be utilised in gas storage more than in any other market.

Aside from the aforementioned niches, MOFs also have potential as proton conductors, molecular sensors, and, if they possess magnetic properties: magnetic refrigerants, high-density electronics materials, and biomedical media for drug storage and/or imaging.²³⁵ Magnetic MOF materials will be briefly discussed herein in order to develop a background for the studies presented in Chapter 6, Chapter 7, and Chapter 8.

2.4.2 Magnetic Metal-Organic Frameworks

The study of magnetic MOFs originally arose from the incorporation of paramagnetic metals and/or open-shell organic ligands into the synthetic scheme for fabrication. Due to the nature of MOF SBUs, the presence of multiple spin carriers within a reasonable range for interaction to occur is frequently observed. Thus, MOFs can either show long range magnetic ordering, as is present within bulk magnets through close contact between spin carriers, or they can display discrete magnetic behavior if spin carriers are adequately separated. This type of discrete magnetic behavior arises from paramagnetic ions within the MOF SBUs, and is akin to the behavior of SMMs. Magnetically, MOFs may thus mimic the behavior of bulk systems or nanomagnetic systems, depending on their structure.²³⁶ It follows that magnetic MOFs provide a fascinating architecture in order to explore the magnetic behavior of ions within a controlled 3D framework.

2.4.2.1 Transition Metal-Based Magnetic MOFs

Initially, magnetically studied porous materials were very rare, and into the early 2000's they merely consisted of a few transition metal systems exhibiting long range ordering and antiferromagnetic interaction below their Néel temperature, T_N .²³⁷⁻²⁴¹ Researchers strived for ferromagnetic ordering in order to promote a net magnetic moment in the ordered state. Interestingly, the first example of magnetic hysteresis within a porous system was from a Prussian blue analogue with ferrimagnetic behavior below $T_N = 38$ K.²⁴² As porous materials were becoming more and more popular in the literature, studies arose on their long range magnetic interactions,²⁴³⁻²⁵⁵ and on rare occasions resulting low temperature hysteretic behavior was observed and presented.²⁵⁶⁻²⁶⁴ Interestingly, a finite number of MOFs have been shown to display superparamagnetic behavior in the form of slow relaxation of the magnetisation due to their discrete, isolated SBUs. It will quickly become apparent within this brief literature review that this type of behavior in MOFs is overwhelmingly dominated by the employment of one particular anisotropic metal ion: Co^{II} .

The initial example of such behavior in a MOF was presented in 2006, where both Co^{II} and Cu^{II} analogues of the same MOF, $[\text{M}_3(\text{bime})_2(\mu_3\text{-OH})_2(\text{HO-bdc})_2]$; $\text{M} = \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}$; $\text{bime} = 1,2\text{-bis}(\text{imidazol-1'-yl})\text{ethane}$, $\text{HO-H}_2\text{bdc} = 5\text{-hydroxyisophthalic acid}$, were synthesized and studied.²⁶⁵ This MOF structure is composed of chain-like arrangements of Co^{II} ions, which can be clearly observed in Figure 15a. This arrangement of Co^{II} ions exhibit ferrimagnetic ordering, which leads to a hysteretic behavior at 2 K. Interestingly, studies were also performed to probe the relaxation dynamics, where it was found that the chain-like networks of Co^{II} within the MOF

act as SCMs, eliciting an energetic barrier to magnetic relaxation, $U_{\text{eff}} = 76(1)$ K. The behavior observed for this MOF was consistent with previously synthesized Co^{II} SCMs, thus, displaying the potential for a wide array of magnetic behavior to be present within 3D systems. Shortly following this study, within the same year, a Co^{II} MOF, $[\text{Co}_2\text{Na}(\text{4-cpa})_2(\mu_3\text{-OH})(\text{H}_2\text{O})]$; 4-cpa = 4-carboxylphenoxyacetate, was presented with similar chain-like formations of the magnetic ions (Figure 15b), once again exhibiting SCM-like behavior.²⁶⁶ The chains in this system are composed of octahedral Co^{II} ions in close contact ($\sim 3.0\text{-}4.2$ Å), arranged in a zig-zag-like conformation. Adjacent chains are connected through Na^+ ions, which bring the $\text{Co}\cdots\text{Co}$ interchain distance to ~ 7.15 Å. Rather unsurprisingly, the chain networks interact primarily through intrachain mechanisms, which are shown to be primarily ferrimagnetic in nature. Hysteresis measurements were performed at 2 K and observed a coercive loop-opening phenomenon, thus confirming a $T_{\text{B}} = 2$ K. Furthermore, ac susceptibility measurements were able to discern an energetic barrier at zero applied dc field of $U_{\text{eff}} = 106$ K.

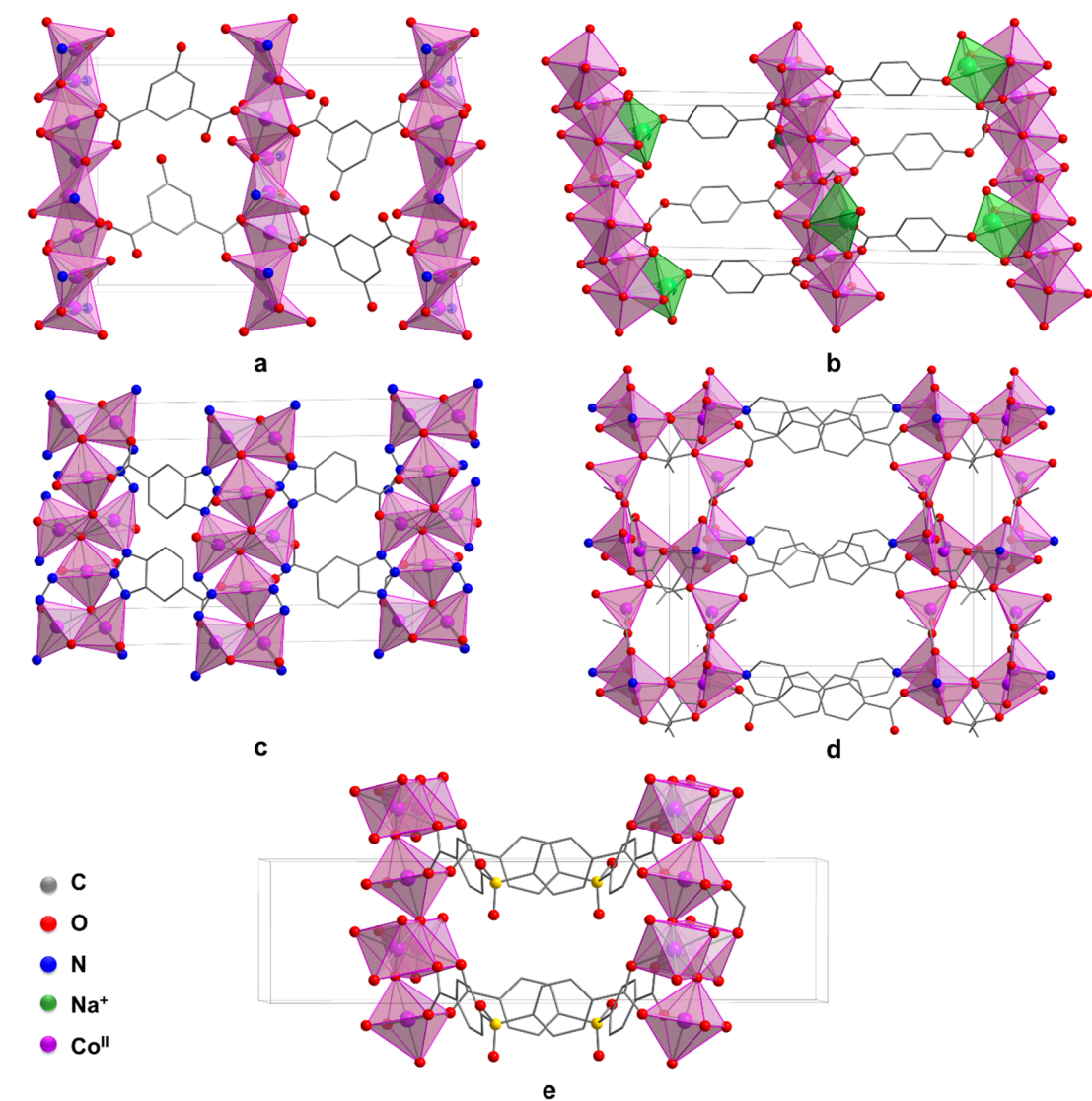


Figure 15. Molecular structures of (a) $[M_3(\text{bime})_2(\mu_3\text{-OH})_2(\text{HO-bdc})_2]$, (b) $[\text{Co}_2\text{Na}(4\text{-cpa})_2(\mu_3\text{-OH})(\text{H}_2\text{O})]$, (c) $[\text{Co}_3(\text{OH})_2(\text{btca})_2]$, (d) $[\text{Co}_3(\text{lac})_2(\text{pybz})_2]$, and (e) $[\text{Co}_3(\text{OH})_2(\text{dbsf})_2(\text{H}_2\text{O})_3(\text{EtOH})]$, highlighting the chain-like formations of Co^{II} ions. Structure displayed with unit cell edges visible and hydrogen atoms omitted for clarity.

Another Co^{II} MOF with SCM-like magnetic properties, $[\text{Co}_3(\text{OH})_2(\text{btca})_2]$; H_2btca = benzotriazole-5-carboxylic acid, was published shortly thereafter in 2007 (Figure 15c).²⁶⁷ In this case, Co^{II} ions form triangle-like arrangements within a chain-like architecture. The magnetic behavior was shown to be very similar to the previous frameworks, with ferrimagnetic ordering, hysteretic magnetic remanence present at 2 K, and $U_{\text{eff}} = 122$ (6) K. Thus, SCM-like behavior has shown itself to commonly arise from ferrimagnetic Co^{II} -based 1D networks within 3D systems.

A slightly different example of SCM-like behavior was recently reported in a dual-pillared magnetic MOF Co^{II} MOF $[\text{Co}_3(\text{lac})_2(\text{pybz})_2]$; pybz = 4-pyridyl benzoate, lac = D- and L-lactate (Figure 15d).²⁶⁸ This MOF exhibited guest dependent magnetism, where the resulting materials with varied guests displayed: antiferromagnetic, ferromagnetic, ferrimagnetic, and SCM behaviour. The variation that exhibited SCM behaviour showed slow relaxation of the magnetisation with $U_{\text{eff}} = 41(8)$ K. The stability of this MOF due to its dual-pillared structure, and its sensitivity to solvents and I_2 uptake, has caused it to be suggested as a viable candidate for chemical sensing. Another example of solvent-dependent SCM-like behavior was observed in a MOF with a Co_3 SBU, $[\text{Co}_3(\text{OH})_2(\text{dbsf})_2(\text{H}_2\text{O})_3(\text{EtOH})]$; dbsf = 4,4'-dicarboxybiphenyl sulfone, as is shown in Figure 15e.²⁶⁹ The SBUs were able to interact as chain-like networks, thus eliciting ferrimagnetic properties which produced a guest solvent dependent barrier of $U_{\text{eff}} = 110$ K for the solvated structure, and 130 K for the desolvated structure. Both the solvated and desolvated structures exhibited hysteretic behavior at 2 K. Thus, despite the small differences in magnetic behavior between the solvated and desolvated structures, this provides another example of the potential for magnetic MOFs in sensing applications, and as SCMs. This is an interesting finding as stability is often a concern within MOFs (*vide supra*).

Magnetism in MOFs is not necessarily categorised as either being long-range or SCM-like in nature; conversely, it can also be a blend of different behaviours. As an example, rare magnetic behavior was exhibited in a Co_4 MOF, which could only be explained as being attributed to thermally activated excitations arising from a 2D network, which were neither long range, nor superparamagnetic in nature.²⁷⁰ This MOF displayed an energetic barrier of $U_{\text{eff}} = 489$ K, with hysteretic behavior to 14 K. However, since these values were not consistent between single crystals and powder samples, it was determined that the behavior was not superparamagnetic in nature. Thus, this system displays a rare and complex combination of inter- and intramolecular interactions, eliciting a strong magnetic signal that arises from a 2D network, as opposed to a molecular unit, 1D chain or 3D network. This type of slow relaxation of the magnetisation arising from both discrete molecular magnetism and long range order in Co^{II} -based MOFs has been observed in other structures as well.²⁷¹ These are not ideal systems, as clean magnetic behavior is necessary for predictability and reliability of a magnetic material. Thus, it is preferred that a magnetic system show either long range ordering or discrete magnetic behavior, depending on the desired application.

In regards to discrete magnetic behavior, a unique example of molecular magnetic behavior in MOF systems was published with a Co_7 SBU, $[\text{KCo}_7(\text{OH})_3(\text{ip})_6(\text{H}_2\text{O})_4] \cdot 12\text{H}_2\text{O}$; H_2ip

= isophthalic acid (Figure 16),²⁷² where the SBUs were isolated (not in chain-like networks), thus elucidating a discrete, SMM-like, magnetic behavior. The discrete SBUs showed antiferromagnetic coupling amongst the Co^{II} ions in the cluster, leading to ferrimagnetic behavior overall, which elicited hysteretic magnetic remanence at 2 K. Furthermore, the SBUs displayed slow relaxation of the magnetisation, producing an energy barrier of $U_{\text{eff}} = 102$ K. Interestingly, this system also showed reversibly modulated behavior in the magnetism upon guest uptake, thus, as was the case for some previously discussed SCM-like magnetic MOFs, it was proposed for potential use in sensing applications.

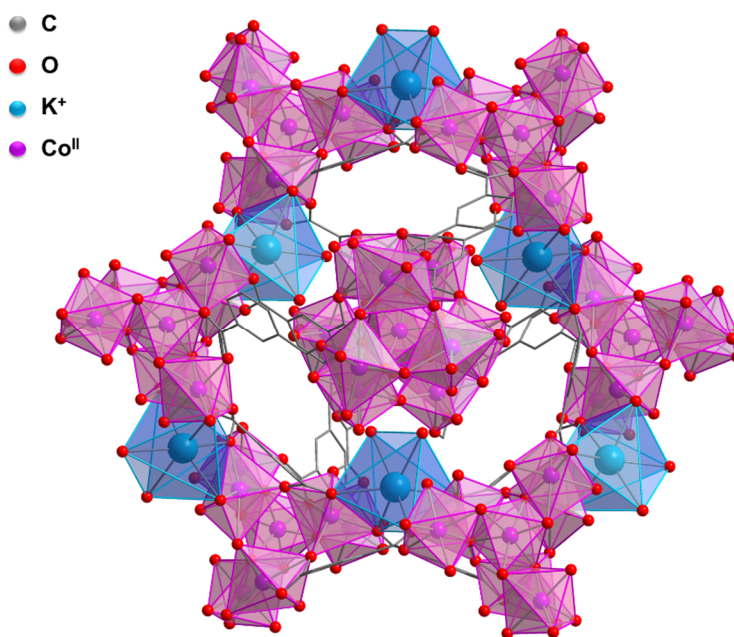


Figure 16. Molecular structure of $[\text{KCo}_7(\text{OH})_3(\text{ip})_6(\text{H}_2\text{O})_4] \cdot 12\text{H}_2\text{O}$, highlighting the individual Co_7 SBUs. Structure displayed with hydrogen atoms omitted for clarity.

The most recent example of a transition metal MOF exhibiting discrete, SMM-like magnetic behavior was in a Co^{II} single-ion SBU framework, $[\text{Co}(\text{bpeb})_2(\text{NCS})_2]$; bpeb = 1,4-bis(pyridine-4-ylethynyl)benzene.²⁷³ This Co^{II} MOF also displayed guest-dependent magnetism, where the framework exhibited field-induced slow relaxation of the magnetisation, eliciting a range of energetic barriers, $U_{\text{eff}} = 11.5 - 31.3 \text{ cm}^{-1}$, for a variety of guest solvents. Through exploring discrete magnetic systems in the SBUs of MOFs, the ability to correlate magnetic

behavior with guest molecule dependence was much simpler than in the cases where SCM or long range ordering are observed. Thus, this becomes a very effective strategy in gaining further fundamental understanding of the potential for these systems in sensing applications.

From the examples discussed thus far, it is apparent that Co^{II} dominates the field of magnetic MOFs due to its magnetic anisotropy and range of available, stable geometries.²⁷⁴ Since anisotropy has proven to have a significant impact on magnetic behavior, particularly in recent fundamental studies on molecular magnetic systems,²⁷⁵ we can conclude that this is likely the most important factor in the magnetism of the above systems.

2.4.2.2 Lanthanide-Based Magnetic MOFs

Despite the prevalence of transition metal-based MOF systems in the literature, lanthanide ions have also been frequently employed in MOF SBUs. Due to the shielded nature of the lanthanide $4f$ orbitals, these types of frameworks are not expected to exhibit the same type of long range order as was frequently found in the transition metal-based systems discussed above. This, along with their inherent large spin ground state and anisotropy, promotes the potential for SMM-like properties in lanthanide-based MOFs. Initially, many examples were reported with mixed lanthanide-transition metal SBUs, attributed to the growing interest in mixed $3d$ - $4f$ systems for catalysis, luminescence, and magnetism.^{276,277} One recent example of a mixed TM-Ln MOF system that displayed magnetic behavior was synthesized with Ni^{II} and Dy^{III} , $[\text{NH}_2(\text{CH}_3)_2]_2[\text{NiDy}_2(\text{HCOO})_2(\text{abtc})_2]$; $\text{H}_4\text{abtc} = 3,3',5,5'$ -azobenzene-tetracarboxylic acid.²⁷⁸ This framework displayed field-induced slow relaxation of the magnetisation, where two relaxation processes became apparent ($U_{\text{eff}} = 40$ K, 42 K under 1000 Oe applied dc field). The multiple relaxation processes were proposed to be attributed to the Dy^{III} ion, as well as the weak coupling between Dy^{III} and Ni^{II} magnetic ions. These types of interactions between TM and Ln ions are not simply understood, and extensive research has been put forth in order to gain more fundamental knowledge in this area.²⁷⁶ Despite these efforts, in regards to MOFs, these types of interactions have not yet produced magnetic systems with competitive energetic barriers and blocking temperatures.²⁷⁶

Lanthanide-based MOFs were first synthesized in 2007, with Tb^{III} , Dy^{III} , Ho^{III} , Er^{III} , Tm^{III} and Yb^{III} .²⁷⁹ However, these particular systems merely showed an antiferromagnetic coupling between ions, and no SMM-like properties. Similar systems have since been published, showing very modest magnetic signals, despite the wide range of Ln ions employed.^{280,281} However, more recently slow relaxation of the magnetisation has been observed in lanthanide MOFs, and similar

to the TM systems explored above, a trend quickly emerges within the literature surrounding one particular anisotropic metal: Dy^{III}.

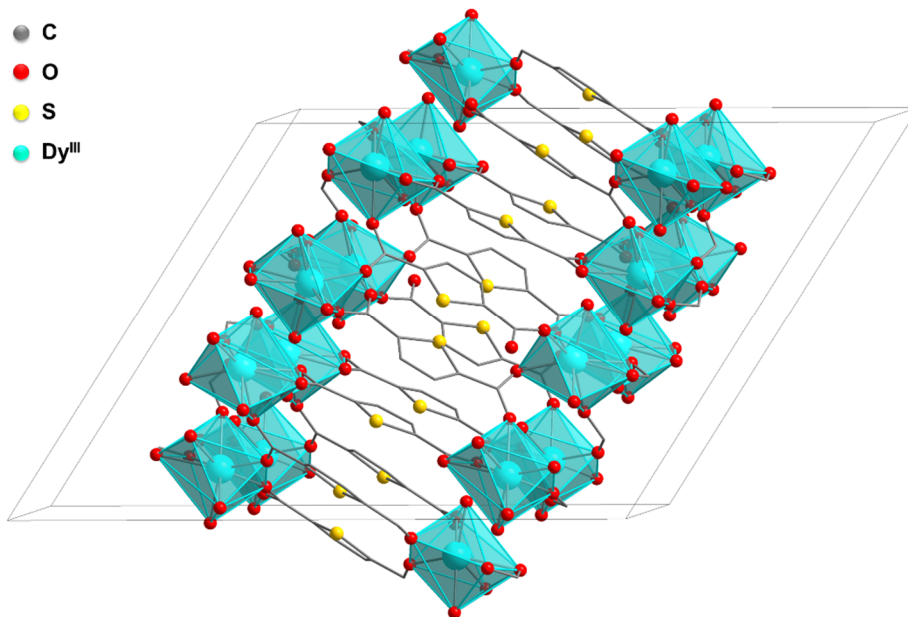


Figure 17. Molecular structure of {Dy(TDA)_{1.5}(H₂O)₂}, highlighting the individual Dy^{III} ions. Structure displayed with unit cell visible and hydrogen atoms omitted for clarity.

Isostructural MOFs composed of Dy^{III} and Gd^{III} ions, {Ln(TDA)_{1.5}(H₂O)₂}; TDA = thiophene-2,5-dicarboxylic acid anion; Ln = Gd, Dy (Figure 17), were reported with SMM-like magnetic behavior in 2009.²⁸² The Dy^{III} system displayed a zero-field barrier of $U_{\text{eff}} = 44.2$ K, which was attributed solely to the single-ion behavior of Dy^{III}, despite the weak ferromagnetic interactions observed at low T in the static magnetic measurements. This is due to the aforementioned shielded 4f orbitals preventing a more significant interaction between spin carriers. Another single-ion Dy^{III} magnetic MOF, [KDy(C₂O₄)₂(H₂O)₄]; C₂O₄²⁻ = oxalate dianion (Figure 18),²⁸³ was shown to display a unique alteration in its fundamental magnetic properties with dehydration and rehydration of the porous structure; eliciting a switching mechanism between antiferromagnetic and ferromagnetic behavior. Furthermore, the slow relaxation of the magnetisation was observed with a significant energetic barrier of $U_{\text{eff}} = 417$ K. These properties display the multifunctional potential for porous materials to show magnetic property switching

behavior upon sensing a guest molecule, as well as the potential for their use as bistable magnetic systems in of themselves.

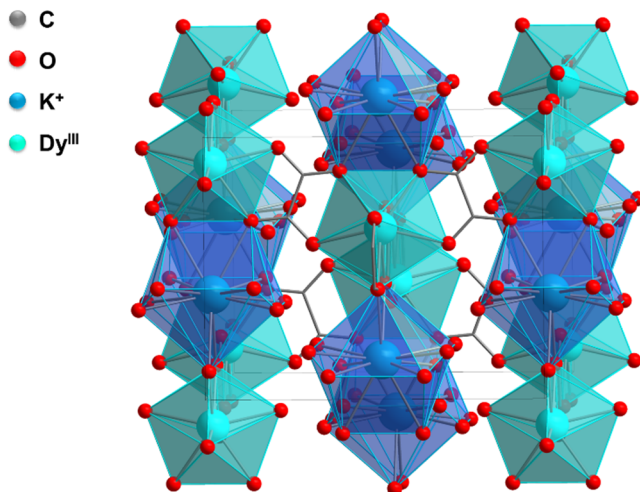


Figure 18. Molecular structure of [KDy(C₂O₄)₂(H₂O)₄], highlighting the individual Dy^{III} and K⁺ ions. Structure displayed with unit cell visible and hydrogen atoms omitted for clarity.

More recently, a single-ion-type lanthanide MOF was synthesized, which also displayed luminescent properties: [Ln(notpH₄)(H₂O)]·ClO₄·3H₂O; notpH₆ = 1,4,7-triazacyclononane-1,4,7-triyl-tris(methylenephosphonic acid; Ln = Dy^{III}, Ho^{III}).²⁸⁴ Interestingly, the Dy^{III} analogue showed two distinct field-induced slow relaxation processes, which were each analysed under optimised fields in order to elicit energetic barriers of $U_{\text{eff}} = 39.9$ K at 500 Oe, and 19.4 K at 1500 Oe. These two relaxations were attributed to single ion anisotropy and weak intermolecular interactions between Dy^{III} ions, as had been previously suggested for systems with similar behaviour under an applied dc field.²⁸⁵ Despite the modest properties of this system, the hybrid functionality further promotes the study of multifunctional materials in more than one dimension.

Non-single-ion-based SBUs have also been synthesized with Dy^{III}, such as [Dy₂(FDA)₃(DMF)₂] with DMF or CH₃OH; H₂FDA = furan-2,5-dicarboxylic acid (Figure 19a).²⁸⁶ The Dy₂ SBU exhibits dominant non-negligible ferromagnetic interactions at low temperature, and field-induced slow relaxation of the magnetisation with $U_{\text{eff}} = 41.8$ K and 67.5 K for DMF- and CH₃OH-containing structures, respectively. It is proposed that the higher energy barrier for the CH₃OH-containing MOF can be attributed to a less distorted D_{4d} coordination sphere, likely

causing further suppression of QTM, as has been shown for more symmetric systems.²¹ A similar study on solvent dependent magnetic properties in Dy₂-based magnetic MOFs was published very recently on [Dy₂(INO)₄-(NO₃)₂]; HINO = isonicotinic acid N-oxide (Figure 19b).²⁸⁷ This complex also exhibits dominant ferromagnetic interaction between the two Dy^{III} ions within the SBU. Furthermore, the structure which contains CH₃CN displayed an energetic barrier of $U_{\text{eff}} = 110$ K, whereas the structure containing DMF was found to display a negligible barrier to magnetic relaxation. Theoretical calculations were performed on the system, and were able to determine that the difference arose from fast relaxation due to significant QTM present in the DMF-containing MOF. These results display the importance of solvent within the framework structure, as small distortions based on a different solvent have significant effects on magnetic behavior.

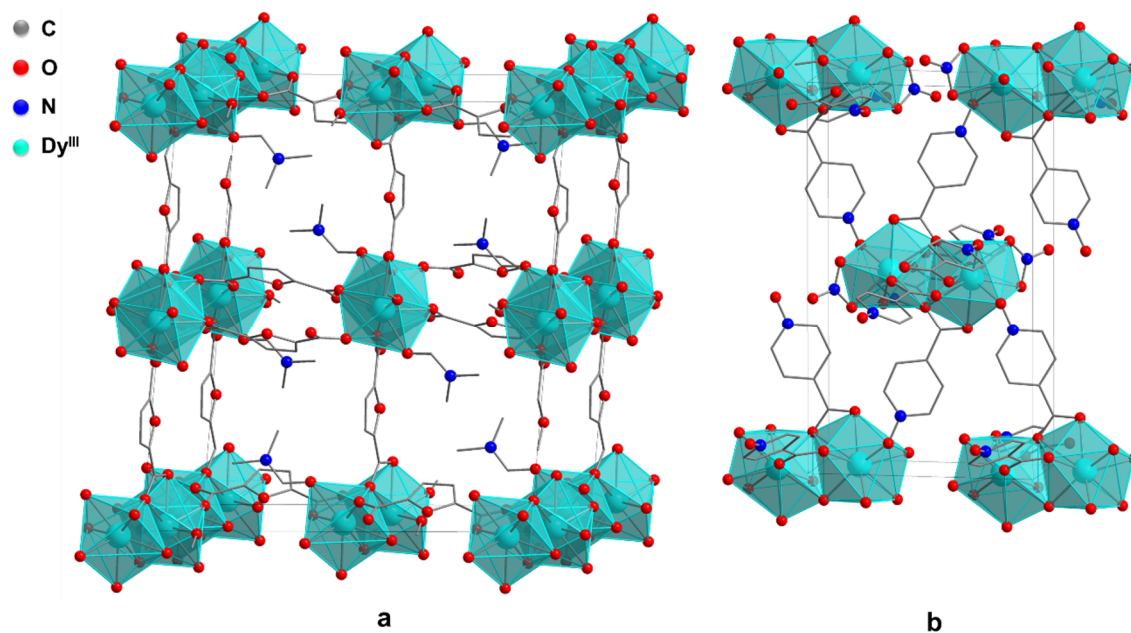


Figure 19. Molecular structures of (a) [Dy₂(FDA)₃(DMF)₂] and (b) [Dy₂(INO)₄-(NO₃)₂], highlighting the Dy₂ SBUs. Structures displayed with unit cells visible and hydrogen atoms omitted for clarity.

Aside from the aforementioned trend of Dy^{III}, like Co^{II}, being a dominant spin carrier in MOFs due to its inherent magnetic anisotropy, we have also observed that due to inherent 4f orbital shielding in Ln MOFs, more discrete magnetic (SMM-like) behavior is observed. Despite these consistent properties, a distinct variation in the overall magnetic behavior of Dy^{III} has been observed, in part due to the presence of significant QTM in certain coordination environments.

Thus, further fundamental studies are continuously needed to better design these types of systems.

2.4.2.3 Composite Magnetic MOFs

Apart from the synthetic strategy of incorporating magnetic ions within the SBU of a MOF, magnetic MOFs are also commonly synthesized as composite materials. These are frequently magnetic nanoparticles, which are coated or otherwise coupled with MOF materials. Interestingly, depending upon the MOF material employed and the design of the composite, there have been a wide variety of applications that have been proposed, and in some cases realized, for these materials; including drug delivery,²⁸⁸ catalysis,^{289,290} sensing,^{291,292} separation,²⁹³⁻²⁹⁶ pollution control,²⁹⁷ fluorescence probes,²⁹⁸ etc.²⁹⁹ Many of the potential applications merely employ the inherent magnetic properties in order to conveniently separate and sequester the material from a matrix for removal and potential future use. Thus, these are hybrid materials, where the MOF and underlying magnetic NP have different purposes within a common goal. This concept was previously discussed for other magnetic nanomaterials, and is an important method of designing advanced materials towards a variety of niches.

The most ubiquitous magnetic NPs within composite materials are Fe₃O₄ (magnetite) particles. In some cases they have been formed within a MOF material, thus creating a superparamagnetic MOF material.³⁰⁰ In other cases the MOF has been a capping agent for the magnetite nanoparticles, eliciting a unique surface structure with porous functionality.³⁰¹ A variation on this technique involves the synthesis of capsules with the NPs and MOF materials formed around hydrogels, as a methodology for the capture of biological molecules.³⁰² Aside from the use of magnetite NPs, Co-based magnetic nanomaterials have also been studied in composite MOF materials towards their potential application in catalysis²⁹³ and sensing.^{292,299}

Despite the prevalence of composite materials composed of magnetic nanoparticles, magnetic MOF composite materials are not limited to this type of NP-MOF coupling; as they could technically be any combination of MOF and magnetic entity. One of the more recent examples, akin to the above discussed method of employing a nanoparticle as a substrate for the study of SMM-surface interactions, is the employment of a MOF towards orienting SMMs within its pores.³⁰³ This study employed a diamagnetic MOF to contain and orient Mn₁₂Ac (Figure 7a), and study the magnetic properties of the arrays of SMMs within the MOF thereafter. Thus, any concern involving intermolecular interaction within crystalline lattices is removed and,

preferably, alignment of anisotropic axes becomes feasible. They were able to show that the structure remained intact upon becoming a guest within the pores of the framework through synchrotron-based X-ray powder diffraction (XRPD). Furthermore, aside from a slight deviation due to an altered chemical environment within the crystalline lattice of the MOF structure, the magnetic properties remained relatively intact ($U_{\text{eff}} = 57 \text{ K}$). Thus, this unique composite material points to an interesting method of sequestering and orienting magnetic molecules, and is now paving the way for further studies on magnetic molecules being incorporated within the structure and/or pores of MOF materials.³⁰⁴

2.4.3 Metal Ion Addition and Exchange in MOFs

There are many methods of altering a MOF in order to fine-tune its properties for a specific purpose; potentially one of the most common methods has been through facile ligand modification, which allows for the ability to retain the structural integrity of the metal node.³⁰⁵ However, isomorphic metal substitution is another recently explored possibility. In catalysis, the technique of incorporating additional active sites through metal substitution or addition has been vital to the development of improved materials.³⁰⁶⁻³⁰⁸ The techniques of metal ion addition into a MOF framework³⁰⁹⁻³¹¹ and full or partial metal exchange³¹²⁻³²¹ are relatively recent in MOF chemistry, but have had a significant impact on the field within this short time span. Together, these methods are referred to as post-synthetic modification (PSM), and can be visualized schematically in Figure 20A and B.

Metal ion addition has been exhibited in rare examples, where in all cases a ligand was designed within a MOF to possess coordinative pockets capable of facilitating further functionalisation. With this pre-designed coordination pocket within a MOF structure, post-synthetic addition of a metal salt allows for complexation. This strategy was performed initially by synthesizing a MOF with pendant alcohol groups in order to facilitate the addition of alkali metal ions to the ligand framework of a Zn-based MOF.³¹⁰ The addition of metal ions in this case was shown to improve the H_2 sorption properties within the MOF, and was thereafter proposed to be a potential route toward improved separation and catalysis in MOFs. This theory turned out to have merit when, merely a year later, gas selectivity was indeed improved within an Al-based MOF through the addition of a transition metal ion complexed within the ligand framework.³⁰⁹ Both Pd^{II} and Cu^{II} were complexed within the ligand architecture post-synthetically, and in studying the gas adsorption properties the Cu-complexed MOF exhibited an increase in selectivity for CO_2 over N_2 by a factor of more than four, as compared with the parent structure.

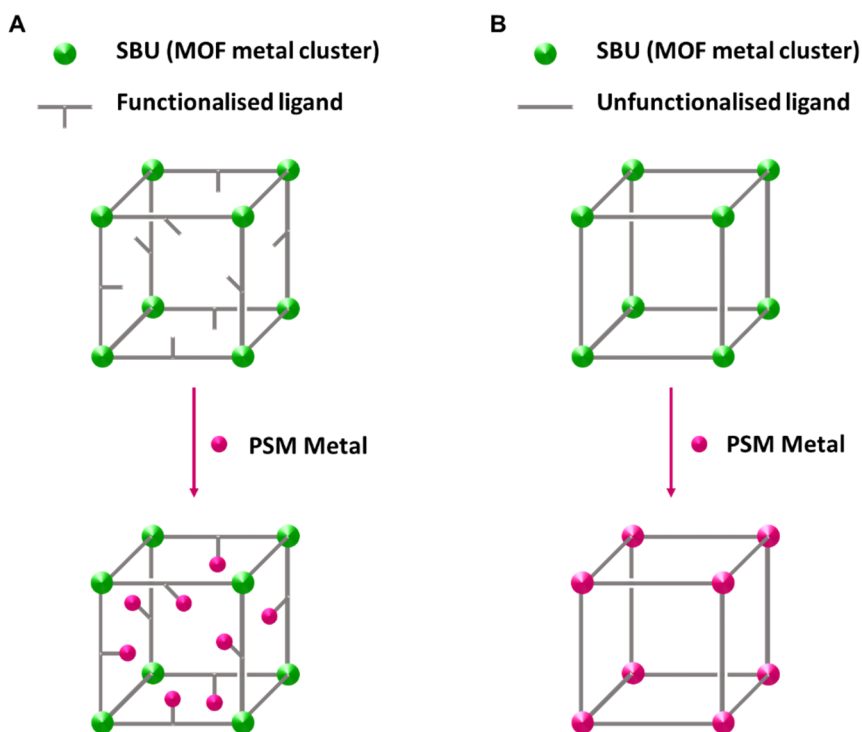


Figure 20. Schematic of post-synthetic metal ion doping in MOFs; (A) metal ion addition into a pre-functionalised ligand architecture, and (B) metal ion exchange/substitution of original metal ions in the MOF SBU.

Further proof of concept was provided in 2011, where a series of transition metals were synthetically complexed within the ligand framework of a Zn-based MOF.³¹¹ This study also displayed the potential for these systems to have the metal ion in the ligand site removed (demetalated) and subsequently to complex the ligand with another metal ion (remetalated). Thus, with the success and practicality imposed by these studies towards potential future applications, this methodology of complexing MOF ligands with additional metal ions has promoted the incorporation of metal species within a variety of organic linkers.³²²⁻³²⁶

Metal substitution or exchange within MOFs has been much more widely studied than metal addition, as it can be performed through merely soaking MOF crystals in a metal salt solution. This procedure allows for the single-crystal to single-crystal transformation of a MOF into an analogue of itself with different metal ions within the SBU. Cation exchange within a MOF was initially performed on a Mn^{II} MOF, where Li^{I} , Cu^{I} , Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} ions were all post-synthetically doped into the MOF in an effort to induce exchange with Mn^{II} ions,

and study the resulting effects on H₂ adsorption.³¹² MOFs which were not accessible through conventional synthetic means were isolated through this method, allowing for improved properties in gas adsorption and separation, fluorescence, catalysis, etc.³¹³⁻³²¹

Interestingly, the majority of metal ion exchange studies in MOFs have involved a Zn-based MOF being substituted with paramagnetic transition metal ions. Despite the plethora of studies on incorporation and addition of transition metal ions within MOF structures, magnetic properties have not been the focus of researchers to this date. Due to the interesting magnetic properties discussed above in a variety of magnetic MOF structures we have explored transition metal MOF systems with discrete magnetic Co₈ SBUs (Chapter 6), and we have employed the unique concept of doping magnetic Co^{II} and Fe^{III} ions within a diamagnetic MOF framework (Chapter 7 and Chapter 8).

Chapter 3

Doping Magnetic Properties into Nanocrystals: Ln^{III}-doped NaYF₄

3.1 Abstract

Coupling the quantum magnetic properties of nanoparticles to other functionalities has the potential to elicit advanced multimodal materials. Through careful synthetic design and optimisation of magnetic ion dopants, we have synthesized particles containing varied percentages of lanthanide dopants. NaYF₄ nanoparticles (**3.1**) were synthesized, and doped with a known up-conversion luminescence optimised lanthanide concentration (**3.2**), followed by varied percentages of magnetically interesting Gd^{III} (**3.3**, **3.4**), Tb^{III} (**3.5**, **3.6**), and Dy^{III} (**3.7**, **3.8**). Particles were studied for their composition using ICP-OES, followed by electron microscopy methods. Through these analyses, we were able to display a strong relationship between dopant type and concentration, as well as particle size, shape and crystallinity. These findings are of interest as they demonstrate the ability to tune a variety of physical properties of nanoparticles via lanthanide doping. Most importantly, the magnetic properties were studied using SQUID magnetometry, finding that these materials were non-superparamagnetic down to 2 K. This study illuminates the potential applications of lanthanide-doped NaYF₄ nanoparticles; as multimodal imaging probes, up-conversion fluorescent markers, and MRI contrast agents. For this reason, the work within this chapter has been published in: Holmberg, R. J.; Aharen, T.; Murugesu, M. *J. Phys. Chem. Lett.* **2012**, 3, 3721-3733.

3.2 Introduction

The synthesis and study of nanoparticles has illuminated the fact that they are a unique conduit that joins bulk and molecular materials, thus explaining the countless potential niches that they have already occupied in industry, technology and medicine. Interestingly, many of the proposed applications for nanoparticle systems stem from their electronic and magnetic properties.³²⁷⁻³³³ As discussed in Chapter 2, various nanoparticle systems have been isolated towards their employment in advanced electronics and biomedical technologies that exploit their inherent magnetic properties.³³⁴⁻³³⁸ Through probing the fundamental properties of magnetic ions within nanoparticles from a molecular magnetism perspective, the necessary tools to design and optimize advanced nanomagnetic systems towards a practical future in biomedical and/or commercial technology can be gathered.

Despite the popularity of transition metal systems in nanoparticle synthesis, lanthanide-containing nanoparticles continue to garner interest due to their unique electronic properties. The shielded $4f$ orbitals of lanthanides yield uniquely desirable magnetic and luminescent properties (*vide supra*).^{63,64} In particular, complexes which contain anisotropic Dy^{III} and Tb^{III} ions have been shown to be magnetically interesting due to their inherent large spin ground state and magnetic anisotropy.^{90,339,340} Furthermore, lanthanide chemistry also lends well to doping, due to the isostructural tendency of lanthanide ions; namely their common oxidation state and similar ionic radii. Due to these inherent properties, lanthanide ions have become desirable dopants in multimodal nanoparticles.

Lanthanide nanoparticles have been previously synthesized with down-conversion and up-conversion luminescence in order to tailor their properties to a wider variety of optical applications; such as biomedical imaging.^{335,336,341-345} Down-conversion is a process involving a normal fluorescence response, wherein the absorption of a photon leads to subsequent emission of a lower energy, longer wavelength photon. This is a less desirable process in biomedicine due to the emission wavelength being readily absorbed by biological tissues.³⁴⁶ Up-conversion, contrastingly, is a process where two or more photons are absorbed, leading to emission of a higher energy, shorter wavelength photon.^{342,347-349} Photon up-conversion requires the long excited state lifetimes and evenly spaced ladder arrangements of lanthanide ion energy levels.³⁴² In particular, the coupling of Er^{III} and Yb^{III} has been found to be the highest efficiency combination for up-conversion, due to their efficient energy transfer caused by the separation between the $^2\text{F}_{7/2}$ ground state of Yb^{III} and the $^2\text{F}_{5/2}$ excited state, matching the transition energies between $^4\text{I}_{11/2}$ and $^4\text{I}_{15/2}/^4\text{F}_{7/2}$ states of Er^{III} .³⁴²

The coupling of magnetism with fluorescence elicits potential applications for lanthanide nanomaterials in MRI contrast, labeled cell and protein separation, fluorescent marking, and drug, gene and radionuclide delivery, among others.^{25,350} In particular, MRI contrast agents have been isolated using magnetic particles with either superparamagnetic or paramagnetic properties.^{25,351-355} Superparamagnetic contrast agents are often used in T_2 MRI contrast, where they have been found to experience some dark signal drawbacks due to negative contrast, and distorted background images due to susceptibility artifacts.^{25,75,76} Conversely, paramagnetic agents are commonly used to promote T_1 enhancement. Most commonly these agents are composed of isotropic Gd^{III} , due to its high spin ground state ($7/2$) and isotropic nature.^{356,357}

Thus, depending on the electronic and magnetic properties of lanthanide-doped nanoparticles, they could have the unique ability to provide multimodal imaging capabilities. We

chose to employ NaYF₄ as the host material in our doping study due to its low toxicity, chemical stability and photostability, and high luminescence efficiency.^{358,359} We then doped this material with the optimised up-conversion composition of 2% Er^{III} and 18% Yb^{III}, followed by magnetically interesting isotropic Gd^{III}, and anisotropic Tb^{III} and Dy^{III}. All materials were extensively studied for their shape, size and crystallinity, as well as their resulting magnetic properties.

3.3 Experimental

3.3.1 Synthetic Information

All reagents were purchased from the following sources: Alfa Aesar, Acros Organics, Strem Chemicals and Sigma Aldrich, and employed without further purification.

3.3.1.1 Preparation of lanthanide-doped NaYF₄ particles

Particles were synthesized based on a previously described method.^{63,75,76} Lanthanide doping was performed by adjusting the molar percentages of LnCl₃·6H₂O; Ln = Y^{III}, Dy^{III}, Tb^{III}, Gd^{III}, Er^{III}, Yb^{III}. according to the desired dopant amounts: NaYF₄ (**3.1**), NaYF₄: 2% Er, 18% Yb (**3.2**), NaYF₄: 2% Er, 18% Yb, 15% Gd (**3.3**), NaYF₄: 2% Er, 18% Yb, 30% Gd (**3.4**), NaYF₄: 2% Er, 18% Yb, 15% Tb (**3.5**), NaYF₄: 2% Er, 18% Yb, 30% Tb (**3.6**), NaYF₄: 2% Er, 18% Yb, 15% Dy (**3.7**), and finally NaYF₄: 2% Er, 18% Yb, 30% Dy (**3.8**). The resulting precursor mixture was solubilised in MeOH (0.2 M), and added to oleic acid (3 mL) and 1-octadecene (7 mL). The mixture was heated to 160°C for 30 minutes, followed by cooling to room temperature and stirring with NH₄F (1.6 mmol) and NaOH (1.0 mmol) in 5 mL of MeOH for 30 minutes. MeOH was then removed from the mixture *in vacuo* and heated under active N₂ to 300°C for 1.5 hours. Upon cooling, particles were precipitated by adding EtOH, followed by centrifugation for 10 mins at 5000 rpm. The resulting solid was washed with EtOH/MeOH and finally redispersed in cyclohexane. Particle suspensions ranged from opaque off-white to light beige in colour.

3.3.2 Characterisation Techniques

3.3.2.1 ICP-OES

Inductively-coupled plasma-optical emission spectroscopy measurements were performed using a Varian Vista Pro CCD-ICP-OES Spectrometer. Samples were separately digested, in duplicates,

prior to analysis. The duplicates were in good agreement, and were averaged in order to obtain the final analyte relationship calculations. Each element was monitored at multiple wavelengths in order to validate the data and rule out interferences. All concentrations were calculated in ppm (w/w basis), and are presented as a percentage composition.

3.3.2.2 SEM/TEM

Scanning electron microscopy images were taken with a JSM-7500F FESEM (JEOL), and transmission electron microscopy images were taken with a JEM-2100F FETEM (JEOL). HR-TEM (JEOL JEM-2100F) was also used to study the intrinsic crystallography of the samples. In order to obtain particle size distribution graphs, 100 particles were sampled for size.

3.3.2.3 XRPD

X-ray powder diffraction experiments employed a RIGAKU Ultima IV, equipped with a Cu-K α radiation source ($\lambda = 1.541836 \text{ \AA}$), and a graphite monochromator. Scanning of the 2θ range was performed from 15 to 48°, depending on the particular sample. In order to assign the peaks corresponding to particular crystalline phases, PDXL software equipped with the RIGAKU apparatus was used with the ICDD database.

3.3.2.4 SQUID

Magnetic measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL7, operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Measurements were performed on nanoparticle samples which were centrifuged and dried: **3.2** (14.2 mg), **3.3** (9.9 mg), **3.4** (6.2 mg), **3.5** (7.3 mg), **3.6** (14.0 mg), **3.7** (17.6 mg), and **3.8** (9.5 mg). All samples were wrapped within a polyethylene membrane. The magnetisation data were initially collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples.

3.4 Results and Discussion

Lanthanide-based crystalline nanoparticles with finely-tuned size, shape and magnetic properties were designed using a strategy that was based on the synthetic method employed by Wang *et al.*³⁶⁰ These sodium yttrium fluoride (NaYF₄) nanomaterials were chosen due to their: (i) well-established synthetic methods; (ii) doping induced up-conversion luminescent properties;^{360,361} (iii) potential for interesting magnetic properties; and (iv) interchangeability between Y^{III} and

lanthanide ions.^{64,360} Oxide-based lanthanide-doped particles were shown to not have the desired synthetic tenability in their size, shape and crystalline properties, which was another reason for our interest in these particular nanoparticles.³⁵⁵

Since the structural characteristics of any crystalline material are greatly influenced by ionic radii, the relation between ionic radii and coordination number can be observed in Table 1. We selected Gd^{III}/Tb^{III}/Dy^{III}/Er^{III}/Yb^{III} ions as lanthanide dopants, based on the stable +3 oxidation state of lanthanide ions, the similarities in their respective coordination environment/numbers, similar ionic radii, and their luminescent and magnetic properties.⁶³ Due to the similar ionic radii between Y^{III} and the trivalent lanthanide ions, as well as their +3 oxidation state, it is likely that the sites occupied by Y^{III} are selectively replaced during doping. Further investigation into the coordination number-dependent radii of the lanthanides reveals that with a coordination number of 9 the ionic radii fall in the range of 1.04-1.11 Å (Table 1).^{63,362,363} Since the radii of Y^{III} and Na⁺ are 1.08 and 1.02 Å,³⁶³ respectively, Na⁺ is also likely to be replaced by lanthanide dopants. However, due to the oxidation state of Na⁺, it is likely that doping will be favoured at the Y^{III} position.³⁶⁰

Table 1. Effective ionic radii according to coordination number for lanthanide ions of interest.^{63,362,363}

Ion	Effective ionic radii (Å) according to coordination number (N)				
	N = 6	N = 7	N = 8	N = 9	N = 10
Y ^{III}	0.90	0.96	1.02	1.08	—
Gd ^{III}	0.94	1.00	1.06	1.11	1.17
Tb ^{III}	0.92	0.98	1.04	1.10	1.15
Dy ^{III}	0.91	0.97	1.03	1.09	1.14
Er ^{III}	0.89	0.95	1.01	1.06	1.12
Yb ^{III}	0.87	0.93	0.99	1.04	1.10

Inductively-coupled plasma-optical emission spectroscopy (ICP-OES) measurements were initially performed in order to study the detailed composition of the particles (Table 2). Each isotope was monitored with respect to percentage composition digested in solution. As such, these results display the quantitative amounts of dopant successfully incorporated within each sample. The dopant amounts closely resemble the desired ratios. Trends immediately emerge

within these results, where; (i) Er^{III} and Yb^{III} are shown to replace the Y^{III} within the lattice due to their similar ionic radii; (ii) Dy^{III} , Tb^{III} , and Gd^{III} further replace Y^{III} ions, and begin to replace Na^+ upon addition of higher dopant percentages; and (iii) overall dopant ions selectively replace similarly sized ions. All samples doped with magnetically interesting Ln ions displayed a dopant profile that was fairly consistent with the desired outcome of 15 and 30%, where: **3.3** and **3.4** contained 9.22 and 21.12% Gd^{III} , respectively; **3.5** and **3.6** were more consistent, containing 16.69 and 24.47% Tb^{III} , respectively; and finally **3.7** and **3.8** were the most consistent with 16.53 and 34.61% Dy^{III} , respectively. The reasoning behind this trend in doping is likely due to the ionic radii, where Dy^{III} has the closest ionic radius to that of both Y^{III} and Na^+ .

Table 2. ICP-OES analyte percentage compositions for **3.1-3.8**.

Distribution (%)	Formula	Analyte Compositions (%)				
		Na^+	Y^{III}	Er^{III}	Yb^{III}	$\text{Dy}^{\text{III}}/\text{Tb}^{\text{III}}/\text{Gd}^{\text{III}}$
NaYF_4	NaYF_4	21.70	77.63			
NaYF_4 : 2% Er, 18% Yb	$\text{NaY}_{0.70}\text{Er}_{0.04}\text{Yb}_{0.26}\text{F}_4$	20.85	54.58	3.09	19.91	
NaYF_4 : 2% Er, 18% Yb, 15% Gd	$\text{NaY}_{0.64}\text{Er}_{0.04}\text{Yb}_{0.19}\text{Gd}_{0.12}\text{F}_4$	23.10	49.55	3.11	14.97	9.22 (Gd)
NaYF_4 : 2% Er, 18% Yb, 30% Gd	$\text{NaY}_{0.47}\text{Er}_{0.04}\text{Yb}_{0.22}\text{Gd}_{0.26}\text{F}_4$	19.62	37.89	3.02	17.97	21.12 (Gd)
NaYF_4 : 2% Er, 18% Yb, 15% Tb	$\text{NaY}_{0.50}\text{Er}_{0.04}\text{Yb}_{0.22}\text{Tb}_{0.23}\text{F}_4$	28.15	36.05	3.17	15.71	16.69 (Tb)
NaYF_4 : 2% Er, 18% Yb, 30% Tb	$\text{NaY}_{0.29}\text{Er}_{0.05}\text{Yb}_{0.31}\text{Tb}_{0.35}\text{F}_4$	29.35	20.42	3.27	21.33	24.47 (Tb)
NaYF_4 : 2% Er, 18% Yb, 15% Dy	$\text{NaY}_{0.59}\text{Er}_{0.04}\text{Yb}_{0.15}\text{Dy}_{0.22}\text{F}_4$	23.72	44.12	2.88	11.27	16.53 (Dy)
NaYF_4 : 2% Er, 18% Yb, 30% Dy	$\text{NaY}_{0.41}\text{Er}_{0.03}\text{Yb}_{0.14}\text{Dy}_{0.42}\text{F}_4$	16.54	34.27	2.42	11.53	34.61 (Dy)

Upon confirmation of the composition of each doped material, electron microscopy was employed in order to study their shape, size and crystallinity. Scanning electron microscopy (SEM) images were initially taken of the parent particles, with composition: NaYF_4 , **3.1**. These particles displayed a distorted hexagonal shape with uneven side lengths (Figure 21A). Particle size distributions were measured by electron microscopy (Figure 21B), showing a mean size of 106.4 nm for NaYF_4 particles, with a standard deviation of 8.4 nm. A small portion of particles grouped together displayed a size that was well outside of the range (10-30 nm roughly), and

were not included due to their infrequent occurrence. It was concluded that the occurrence of smaller particles was indicative of the nucleation process occurring from smaller particles, likely through agglomeration, prior to capping with a surface agent. Using high-resolution transmission electron microscopy (HRTEM) we investigated the crystallinity of the particles (Figure 21C), in particular with Fourier transform analysis of the image (Figure 21D) we were able to calculate the d-spacing values. The average d-spacing values for NaYF₄ particles were found to be 0.19, 0.30, and 0.51 nm, which correspond to (101) and (100) hexagonal crystal orientations. Previously synthesized NaYF₄ particles were reported with different size and shape properties,^{364,365} likely due to different crystalline phases forming during nucleation.

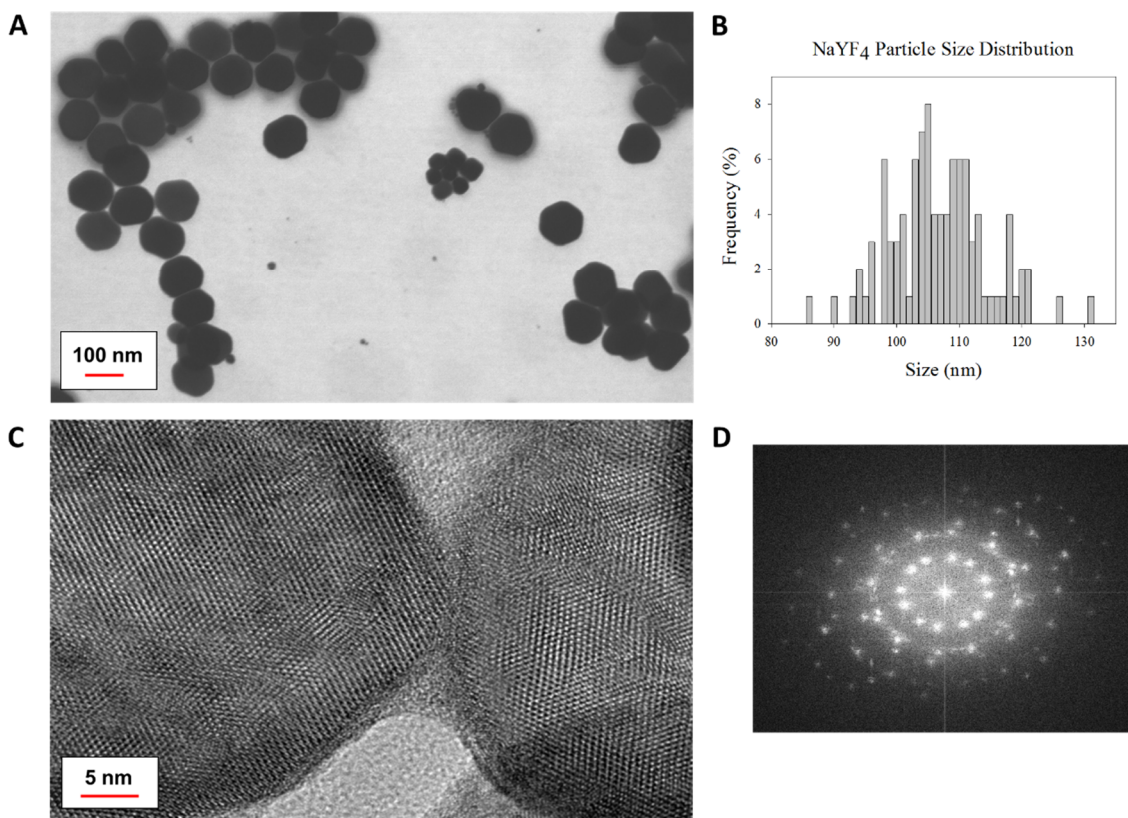


Figure 21. (A) SEM image of NaYF₄ nanoparticles, **3.1**, illustrating their size (roughly 100 nm) and their rounded hexagonal shape, (B) particle size distribution graph, (C) HRTEM image displaying lattice structure, and (D) the corresponding Fourier transform image.

The first dopants added to the parent structure were 2% Er^{III} and 18% Yb^{III}, **3.2**, which were previously optimised for efficient up-conversion luminescence.³⁶⁶ A SEM image of these particles can be seen in Figure 22A, displaying different size and shape properties from those

previously reported,^{337,360,367-369} likely attributed to the presence of different crystalline phases. These particles appear to have a rounded shape, and a much smaller size profile (~20 nm) to that observed for **3.1** (Figure 22B). This shift in size can be attributed to Er^{III} and Yb^{III} dopants, which have smaller atomic radii, replacing Y^{III} in the crystal lattice. The specific mean size was shown to be 23.4 nm, with a standard deviation of 3.1 nm. HRTEM (Figure 22C) studies confirmed the crystallinity of the particles, while providing d-spacing calculations of 0.20 and 0.33 nm (Figure 22D), corresponding to the (111*) cubic crystal orientation. The diffraction pattern was not well-defined as compared to that of **3.1**, indicating a decrease in crystalline stacking and likely an increase in amorphous material within the smaller particles.⁶³

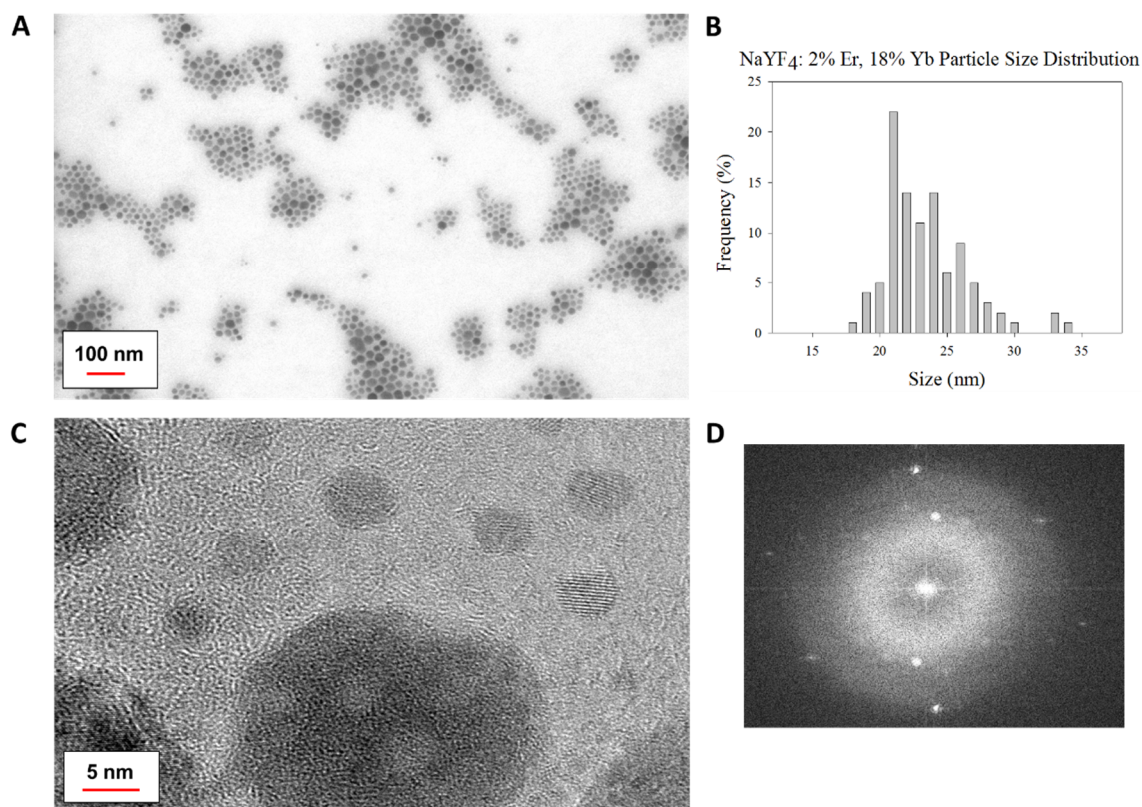


Figure 22. (A) SEM image of NaYF₄ (2% Er, 18% Yb) nanoparticles, **3.2**, imaged using SEM, illustrating their size (roughly 20 nm), and their rounded shape, (B) particle size distribution graph, (C) HRTEM image displaying lattice structure, and (D) the corresponding Fourier transform image.

In addition to the previous lanthanide ions, we chose isotropic Gd^{III} and anisotropic Tb^{III} and Dy^{III} as magnetically interesting dopants. Particles doped with 15% Gd^{III}, **3.3**, were imaged

using SEM, the results of which can be seen in Figure 23A. It is immediately apparent that doping with Gd^{III} produces a different particle size and shape from previously studied samples. These oval shaped particles were calculated to have a mean size of 24.4 nm, with standard deviation 2.5 nm (Figure 23B). The particles are crystalline and the average d-spacing values were found to be 0.17 and 0.31 nm, representing the (111*) cubic orientation (Figure 23C and D). Conversely, particles doped with 30% Gd^{III} were found to have a rounded hexagon shape, similar to that of the parent particles (Figure 24A). The mean size of **3.4** particles was found to be 131.8 nm, with standard deviation of 5.1 nm (Figure 24B). The average d-spacing value was calculated to be 0.32 nm, representing the (111*) cubic crystal orientation (Figure 24C and D).

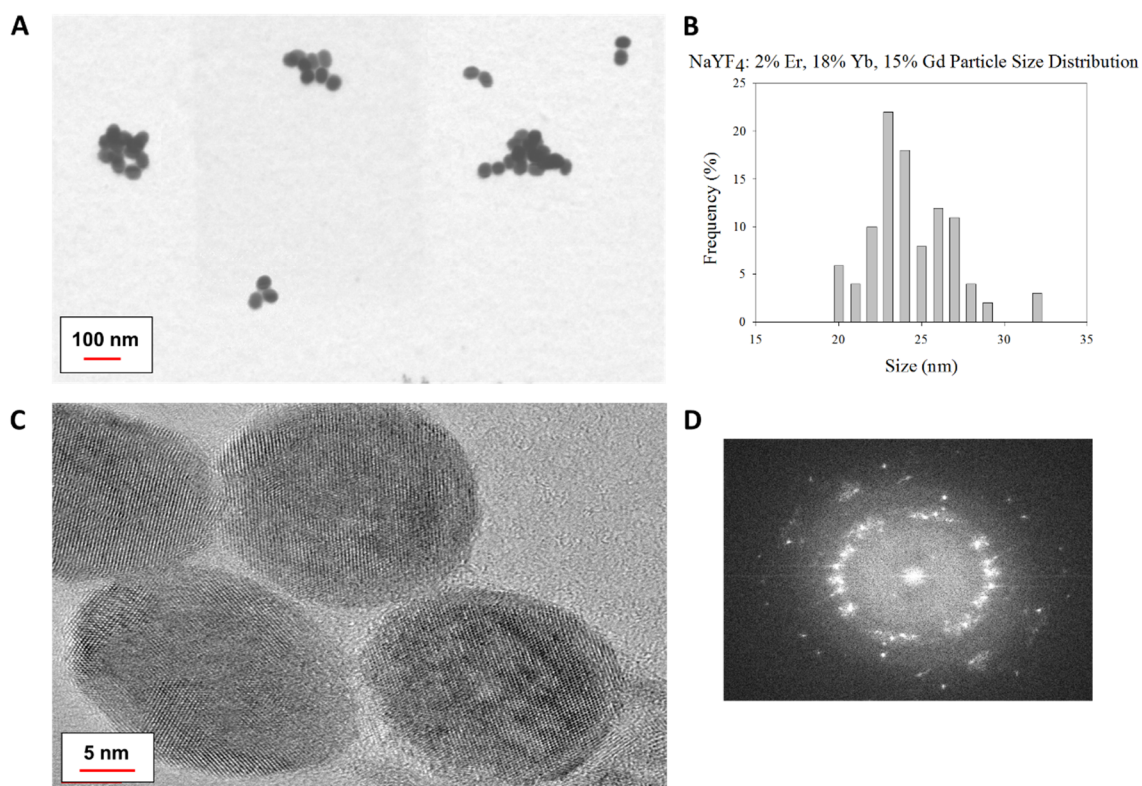


Figure 23. (A) SEM image of NaYF_4 (2% Er, 18% Yb, 15% Gd) nanoparticles, **3.3**, illustrating their size (roughly 24 nm), and their distinct oval shape, (B) particle size distribution graph, (C) HRTEM image displaying lattice structure, and (D) the corresponding Fourier transform image.

Doping was next performed with Tb^{III} , which neighbors Gd^{III} and possesses a comparably smaller atomic radius. The goal of this comparative study was to investigate the subsequent crystalline packing and lattice structure effects induced by altering the lanthanide ion dopant.

SEM images were taken of these particles (NaYF_4 : 2% Er, 18% Yb and 15% Tb, **3.5**), and the representative image can be observed in Figure 25A. Particles doped with 15% Tb, **3.5**, show a mean size of 7.8 nm with a standard deviation of 1.4 nm (Figure 25B). In order to elucidate the crystalline properties of the sample, HRTEM was employed (Figure 25C), and the inset Fourier transform was used to gain an average d-spacing value of 0.32 nm (Figure 25D), representing a (111*) cubic orientation. Akin to with Gd^{III} , we chose to synthesize a sample doped with 30% Tb^{III} next in order to compare the effects of dopant concentration and ionic radii on the physical properties.

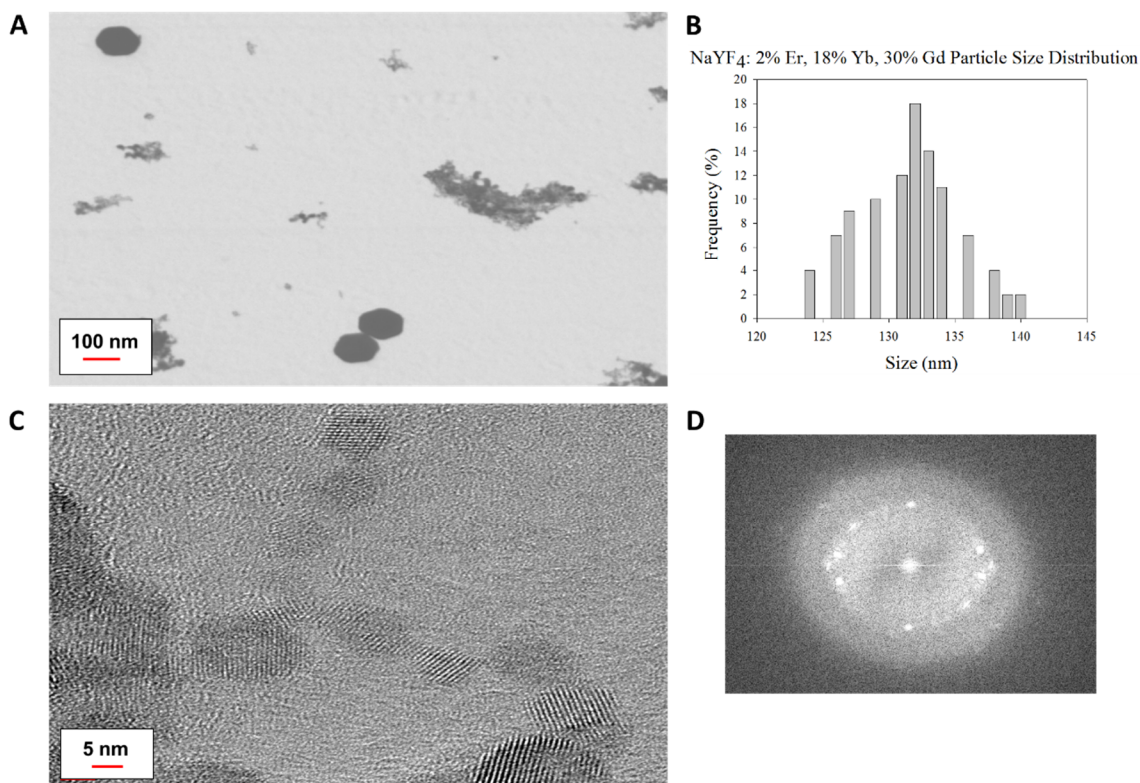


Figure 24. (A) SEM image of NaYF_4 (2% Er, 18% Yb, 30% Gd) nanoparticles, **3.4**, illustrating their size (roughly 130 nm), and their distinct rounded hexagonal shape, (B) particle size distribution graph, (C) HRTEM image displaying lattice structure, and (D) the corresponding Fourier transform image.

Upon increasing the Tb^{III} dopant concentration, as was performed with Gd^{III} , hexagonally shaped nanoparticles were formed, the size and shape of which were investigated using SEM (Figure 26A). Particles doped with 30% Tb^{III} , **3.6**, have a distinct hexagonal shape, and are much

larger in size than those doped with 15% Tb^{III}. The mean size is 122.9 nm, with standard deviation of 9.6 nm (Figure 26B). Crystallinity is retained (Figure 26C and D), and the average d-spacing values calculated from the inset Fourier transform of smaller particles displaying crystallinity were 0.20 and 0.33 nm, corresponding to the (111*) cubic orientation. It is immediately apparent that these particles are well-defined in their hexagonal shape, as compared to the 30% Gd^{III}-doped samples. This is likely a result of further completion of the nucleation process, as well as the ionic radius of the dopant ion being closer to that of the Y^{III} site replaced by Tb^{III}.

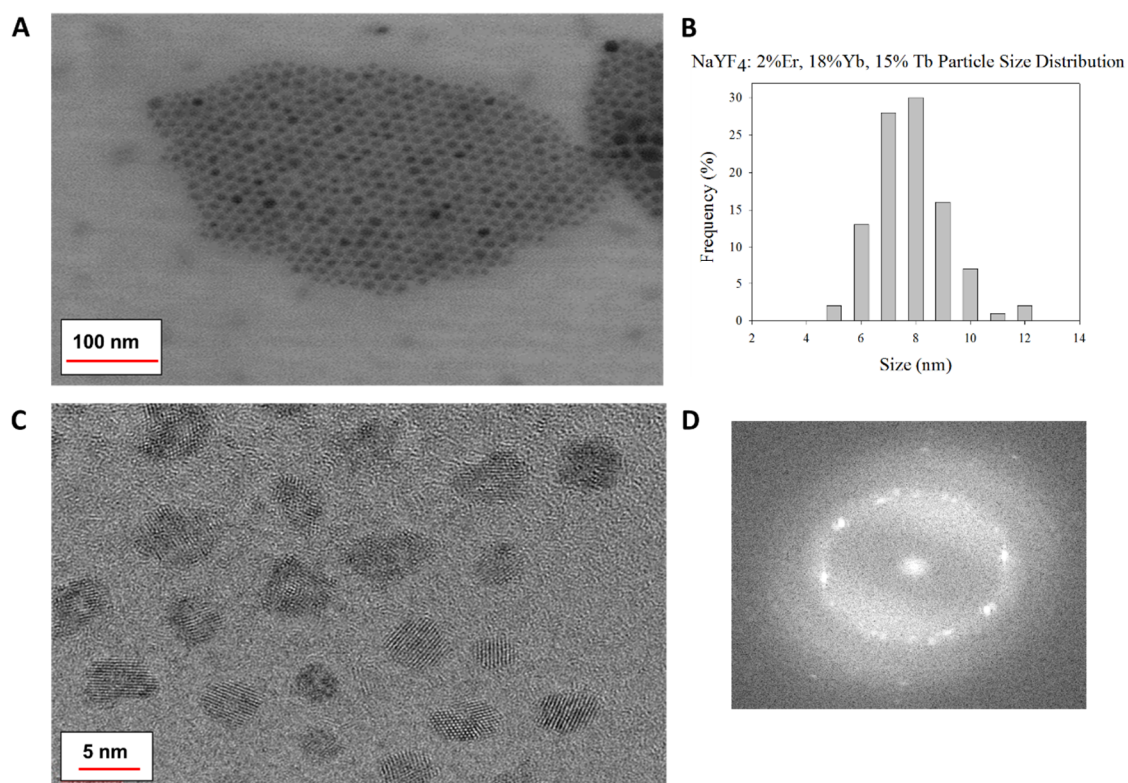


Figure 25. (A) SEM image of NaYF₄ (2% Er, 18% Yb, 15% Tb) nanoparticles, **3.5**, illustrating their size (roughly 8 nm), and their distinct rounded hexagonal shape, (B) particle size distribution graph, (C) HRTEM image displaying lattice structure, and (D) the corresponding Fourier transform image.

Since the compositional percentages obtained through ICP-OES measurements were similar between 15% Dy^{III}- and Tb^{III}-doped samples, their structural properties are expected to share similarities. This is indeed the case, where a similar trend in size and shape distribution is

present between Dy^{III} - and Tb^{III} -doped samples. Particles doped with 15% Dy^{III} , **3.7**, were synthesized and investigated in order to further study the species replacement trends within the lattice structure. Figure 27A shows the electron microscopy images taken of these small rounded hexagonal particles. These particles are quite small, with a mean size of 7.1 nm and standard deviation of 0.9 nm (Figure 27B). HRTEM (Figure 27C) studies displayed the uniformly sized crystalline particles, with calculated d-spacing values of 0.19 and 0.30 (Figure 27D), corresponding to a (101) hexagonal crystal orientation. These d-spacing values are similar to those found for NaYF_4 particles, with fewer values as the smaller particles experience less crystal stacking.

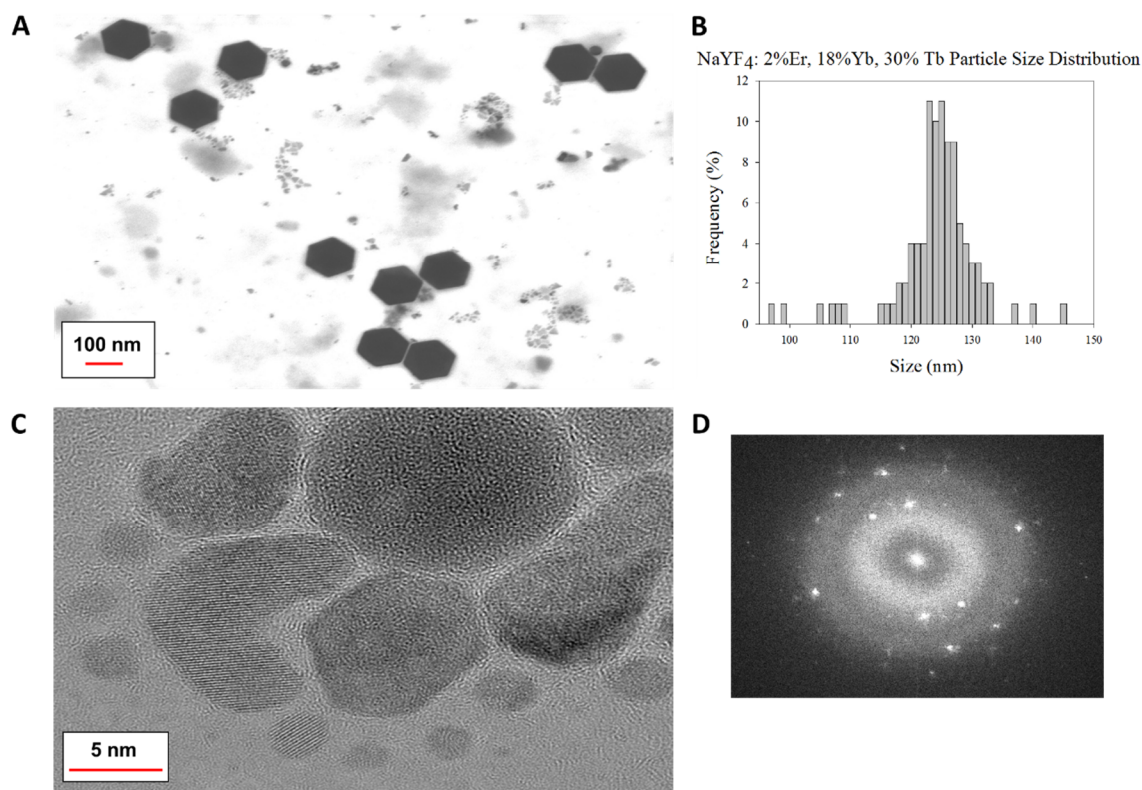


Figure 26. (A) SEM image of NaYF_4 (2% Er, 18% Yb, 30% Tb) nanoparticles, **3.6**, illustrating their size (roughly 120 nm), and their distinct hexagonal shape, (B) particle size distribution graph, (C) HRTEM image displaying lattice structure, and (D) the corresponding Fourier transform image.

Hexagonal particles were produced upon the addition of 30% Dy dopant, **3.8**, as can be observed in Figure 28A. These large well-defined hexagonal nanocrystals have a mean size of 120.0 nm, with standard deviation of 8.9 nm (Figure 28B). As was observed for NaYF₄, smaller particles are also present, however, in this case they are more prevalent, thus we calculated a separate mean size for these particles (22.2 nm with a standard deviation 3.9 nm). As was observed for the previous sample doped with Dy^{III}, these particles clearly demonstrate a crystalline nature, which can be observed through the use of HRTEM in Figure 28C. The Fourier transform image (Figure 28D) allowed for d-spacing calculations of smaller particles displaying crystallinity, which presented a value of 0.27, corresponding to a cubic crystalline orientation of (200*). This is consistent with the results for the 30% Tb^{III}-doped sample, where the nucleation has allowed for larger, well-defined hexagonal crystals with a cubic crystalline lattice structure.

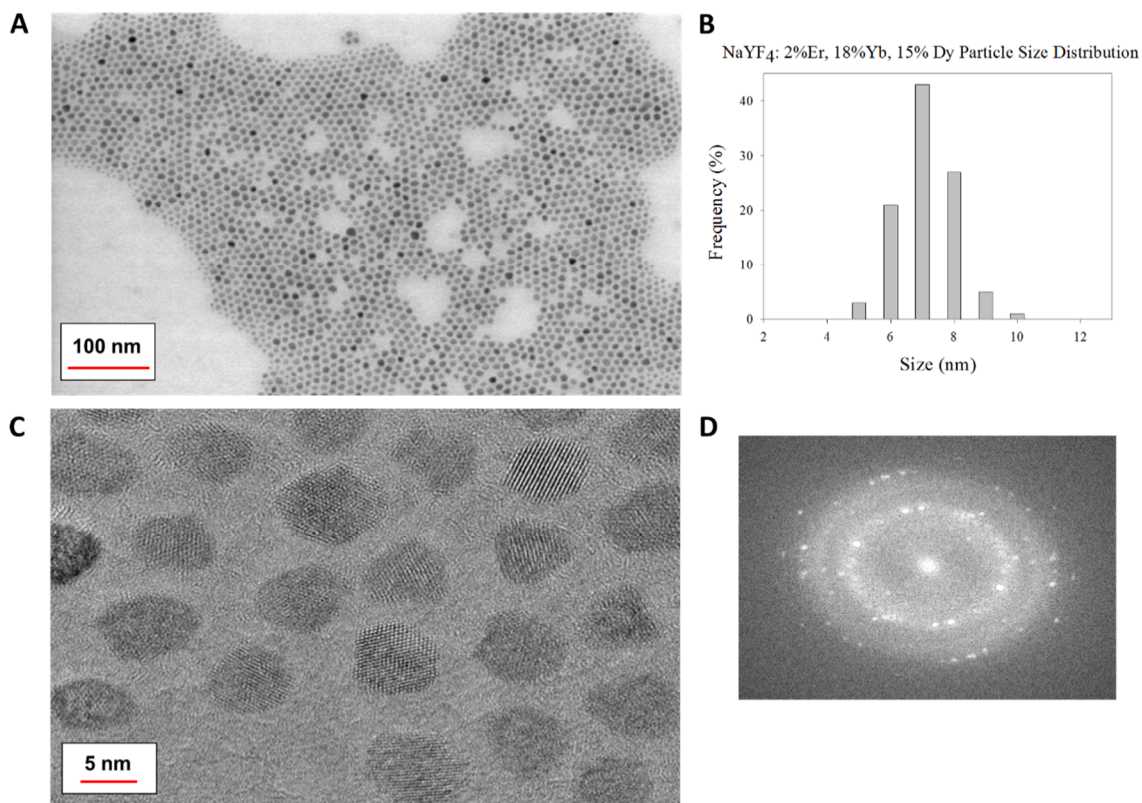


Figure 27. (A) SEM images of NaYF₄ (2% Er, 18% Yb, 15% Dy) nanoparticles, **3.7**, illustrating their size (roughly 7 nm), and their rounded shape, (B) particle size distribution graph, (C) HRTEM image displaying lattice structure, and (D) the corresponding Fourier transform image.

Overall, from electron microscopy and HRTEM diffraction experiments we can conclude that the effects of slight changes in dopant ionic radii are significant on particle shape, size, and crystalline properties. Small amounts of dopant appear to form smaller nanocrystals with less well-defined shapes. Upon doping with larger amounts of lanthanide ions, the cubic crystalline phase becomes dominant, and the particles are larger, with a defined hexagonal shape. Thus far we can posit that Dy^{III} is an optimal dopant for site replacement, owing to the accurate percentage replacement values from ICP-OES, as well as the well-defined shape and crystallinity displayed by electron microscopy for Dy^{III} -doped particles.

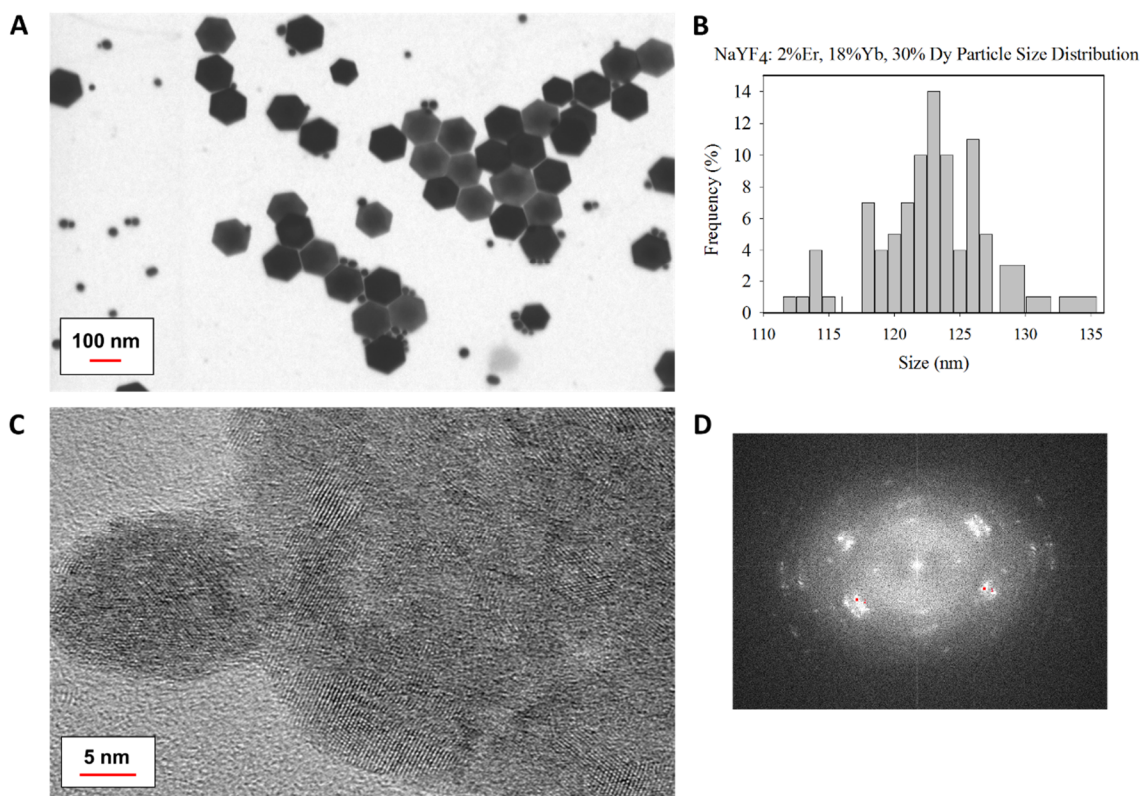


Figure 28. (A) SEM image of NaYF_4 (2% Er, 18% Yb, 30% Dy) nanoparticles, **3.8**, illustrating their size (roughly 120 nm), and their distinct hexagonal shape, (B) particle size distribution graph, (C) HRTEM image displaying lattice structure, and (D) the corresponding Fourier transform image.

It is possible that the crystalline phases will be quite different in the bulk sample, as opposed to within specific nanocrystals, thus, the crystalline properties of the particles were explored further through XRPD measurements. Through measuring the diffraction patterns of the

bulk material we can observe the predominant crystalline phases that are present within each sample. It is notable that substitution of Y^{III} with larger ions would most likely display a systematic peak shifting effect to lower angles within the XRPD pattern due to cell expansion.^{363,370}

It has been previously reported that NaYF_4 particles possess two possible crystalline phases, cubic (α) and hexagonal (β). These phases were mentioned in reference to HRTEM d-spacing values, and will be comparatively discussed in the following section on XRPD measurements. A representation of the structures of these two phases can be observed in Figure 29 for clarity.

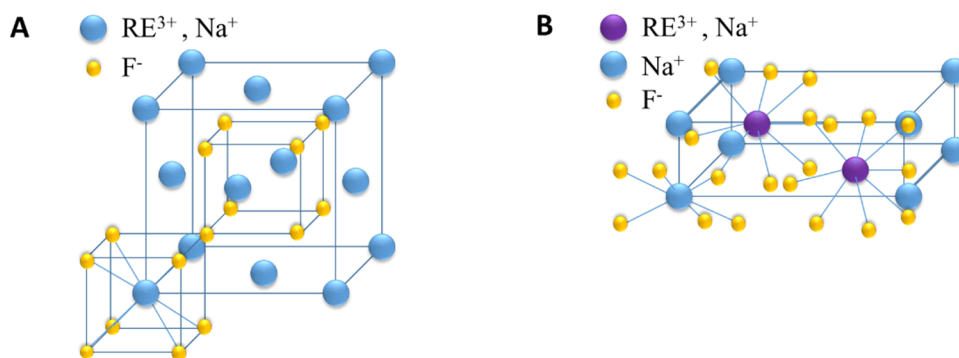


Figure 29. Representation of the (A) cubic and (B) hexagonal crystal forms of NaYF_4 . Adapted by permission from Macmillan Publishers Ltd: Nature, copyright (2010), <http://www.nature.com/nature/journal/v463/n7284/full/nature08777.html>.^{63,360}

Results from XRPD for **3.1-3.8** display the presence of both cubic and hexagonal crystalline phases within the bulk of the majority of samples. The peaks which have been marked with an asterisk within the patterns represent cubic phase lattice planes (JCPDS 006-0342), while non-marked peaks represent hexagonal phase lattice planes (JCPDS 016-0334).⁶³

The pattern for the parent NaYF_4 particles (**3.1**), Figure 30A, shows a strong hexagonal peak (210), as well as two smaller hexagonal peaks (110) and (101), which are consistent with the calculated d-spacing values from HRTEM. There is also a high intensity peak representing the cubic (200*) phase, and a low intensity peak representing (111*), suggesting the presence of both cubic and hexagonal crystalline phases within the bulk material. This likely points to the fact that

nucleation was still occurring, and not all particles are fully formed. Conversely, **3.2** particles display an intense peak representing the cubic (α) phase (200^*), with no lower intensity peaks visible (Figure 30B). Upon closer inspection it becomes apparent that other peaks would easily be dwarfed by the intensity of this peak, thus the particles are predominantly composed of the cubic crystal phase. This is consistent with the previously discussed calculated d-spacing values from HRTEM. This is interesting, as the small particles were shown to have a relatively small particle size distribution, thus it is possible that these particles had reached a later stage of nucleation than what was observed for **3.1**.

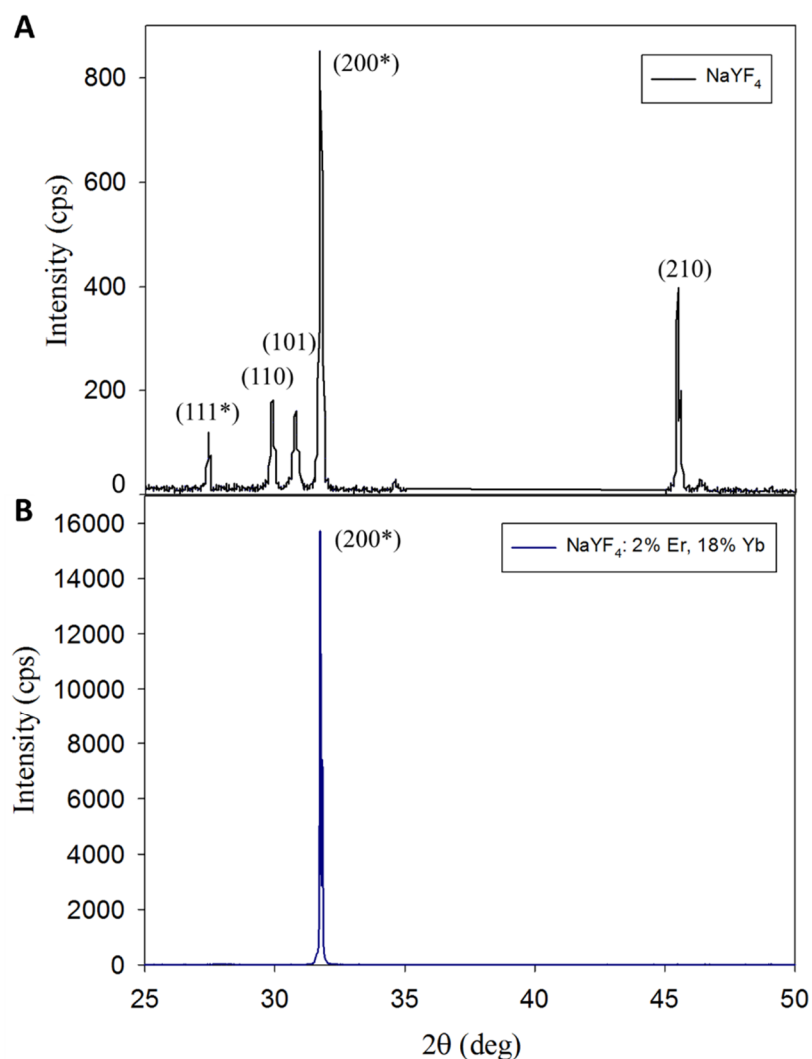


Figure 30. Powder X-ray diffraction pattern for (A) **3.1** and (B) **3.2**. Selected 2θ regions from (A) 25-35 and 45-50 degrees and (B) 25-50 degrees.

Doping with Gd^{III} caused a significant change in the characteristics that were observed for **3.1** and **3.2**. The pattern for **3.3** (Figure 31A) displays very broad peaks of low intensity, indicating poorly defined crystalline character. There are three hexagonal peaks: (110), (101), and (210), as well as two cubic peaks: (210*) and (111*). A preference is apparent towards the hexagonal crystalline phase, which is consistent with previous findings upon increasing Gd^{III} dopant concentration.³⁶⁰ The 30% Gd^{III} doped particles, however, showed extremely low intensity, broad peaks (Figure 31B). This is most likely due to slow nucleation processes, as well as a more amorphous particle overall.

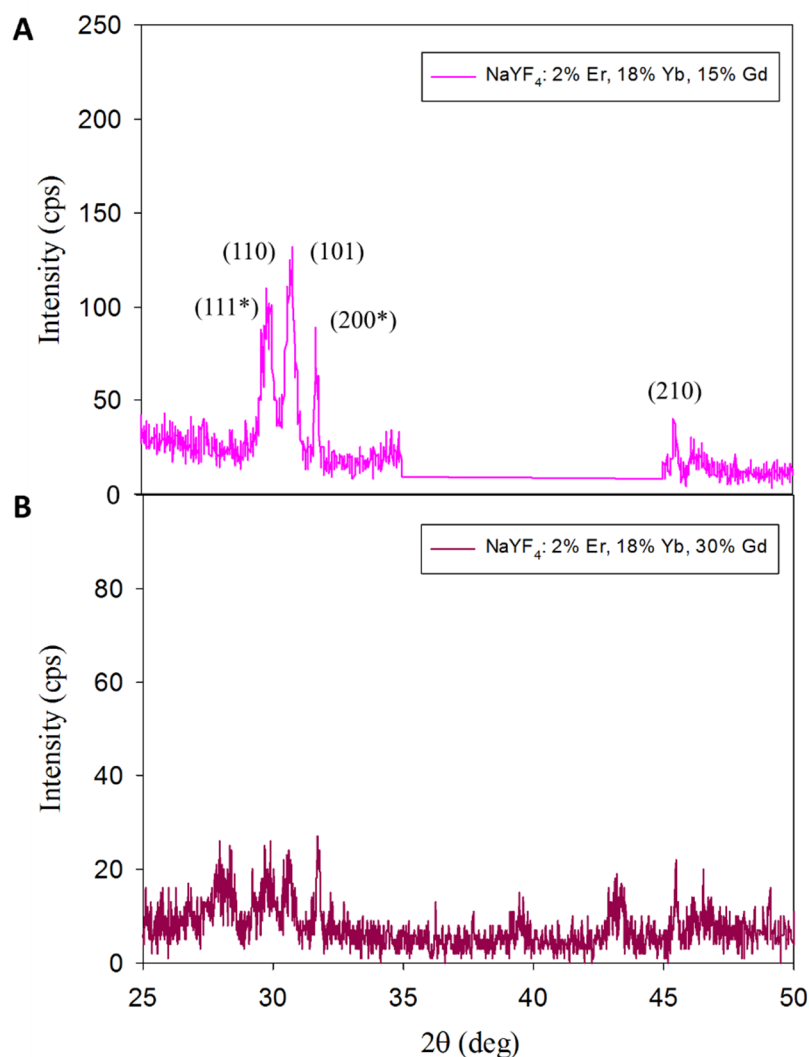


Figure 31. Powder X-ray diffraction pattern for (A) **3.3** and (B) **3.4**. Selected 2θ regions from (A) 25-35 and 44-50 degrees and (B) 25-50 degrees.

The pattern for **3.5** (Figure 32A) displays a strong cubic (200*) peak, and two broad peaks representing (111*) and (220*). There is also a small hexagonal peak which represents (210). The cubic phase was also shown to be favored in the calculated d-spacing value, which represented the (111*) crystal orientation. The diffraction pattern obtained by HRTEM was, however, not well defined, thus these particles may have very few crystalline phases. Not surprisingly, the pattern for **3.6** (Figure 32B) shows a strong α peak (200*), and a weak α peak (111*), as well as a small β peak (210).

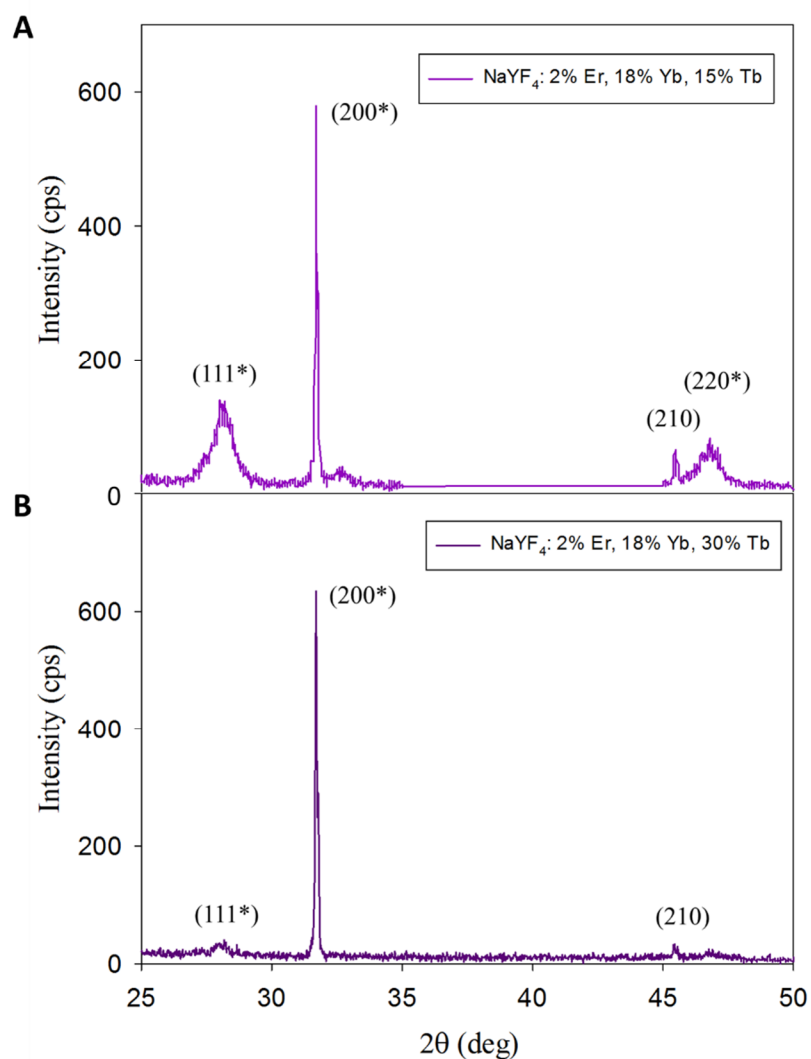


Figure 32. Powder X-ray diffraction pattern for (A) **3.5** and (B) **3.6**. Selected 2θ regions from (A) 25-35 and 44-50 degrees and (B) 25-50 degrees.

The pattern for **3.7** (Figure 33A) shows a cubic (200*) peak, as well as a wide region of intensity which represents (111*). One hexagonal peak is also present (210), however, due to the intensity distribution we can conclude that the cubic phase is more prevalent within these particles. Since d-spacing values were similar to that of the parent particles, **3.1**, we expected to find (210) and (200*) present in the pattern. When doped with 30% Dy^{III} (**3.8**, Figure 33B), the pattern still shows a strong peak representing the cubic (α) phase (200*), as well as four low intensity peaks representative of the β phase (110), (101), (201) and (210). Comparative study between XRPD and HRTEM results regarding crystallinity appear to indicate that there is an agreement between the defined hexagonal structure of 30% doped Dy^{III} particles, and the pattern including more β phase peaks. Thus, we conclude that as nucleation of the particles progresses towards larger more hexagonally-shaped particles; it is representative of an increase in β character.

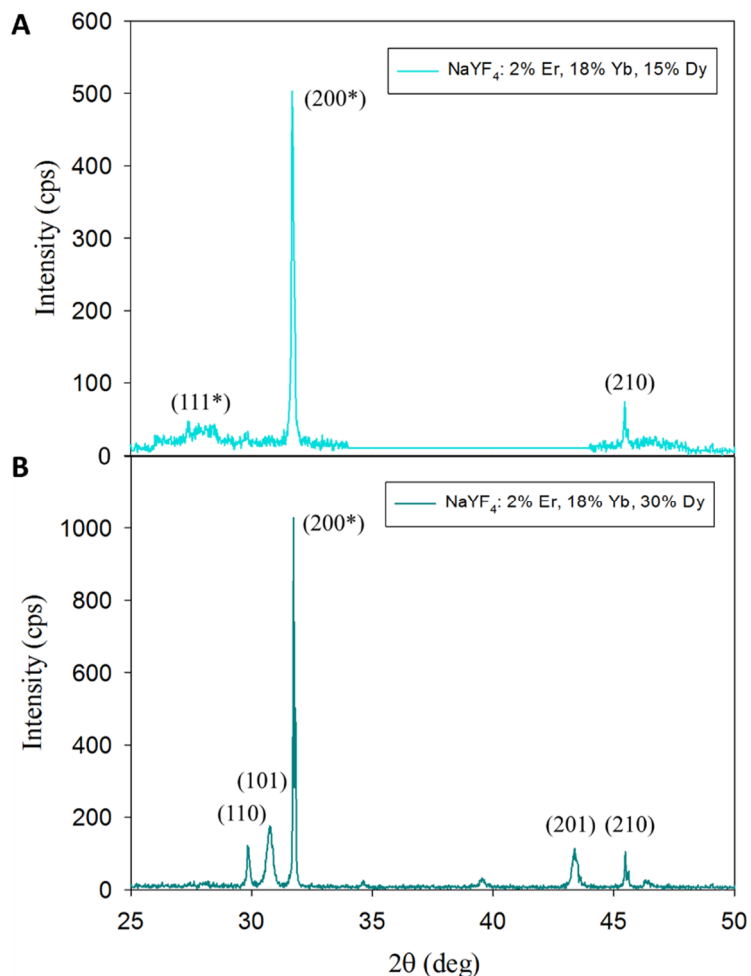


Figure 33. Powder X-ray diffraction pattern for (A) **3.7** and (B) **3.8**. Selected 2θ regions from (A) 25-35 and 44-50 degrees and (B) 25-50 degrees.

Overall, we can comment on the presence of α and β crystalline phases present in the structure of the particles discussed above. While indexing the spectra, a noticeable shift to lower angles was found for most peaks, thus showing that Y^{III} is being replaced by larger ions within the crystal lattice.^{63,360} Furthermore, the two most striking particle types were those doped with 30% Tb^{III} and 30% Dy^{III} , which were similar in size and in their well-defined hexagonal shape. It is possible that these factors can be attributed to a shifting from the cubic to hexagonal crystalline phase during nucleation and growth.⁶³ However, since the cubic character in the bulk crystalline material is dominant, it is difficult to make an absolute conclusion on the hexagonal character of each material. Overall, due to the clear, well-defined peaks of Dy^{III} -doped materials we concluded that Dy^{III} was the optimal dopant, as was previously discussed.

In order to probe the magnetic behavior of samples doped with magnetically interesting lanthanide ions, SQUID magnetometry measurements were performed. Due to the diamagnetic nature of Y^{III} , **3.1** was not magnetically studied. All paramagnetic samples were initially characterised using low temperature hysteresis measurements (Figure 34).

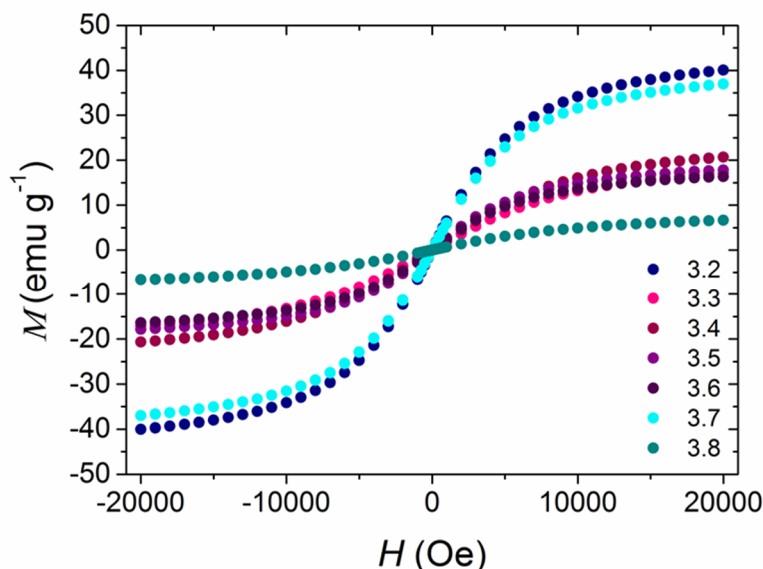


Figure 34. Magnetic hysteresis data at 2 K for: **3.2**, **3.3**, **3.4**, **3.5**, **3.6**, **3.7**, and **3.8**.

Magnetisation vs. field (hysteresis) experiments did not exhibit a loop-opening phenomena (Figure 34), thus there was no slow magnetic relaxation observed at low temperature (2 K). These measurements were performed with an average sweep rate of 35 Oe/s in order to facilitate reasonable comparison with other nanomagnetic materials. The existence of superparamagnetic behavior was further probed by zero-field-cool/field-cool (ZFC/FC) measurements between 300 and 2 K (Figure 35). ZFC/FC lines were found to superimpose, indicating that no magnetic blocking was observed down to 2 K. From these measurements we were able to confirm that these materials are non-superparamagnetic down to 2 K. In order to explore potential interactions between dopant ions within the nanocrystalline framework, dc magnetic susceptibility measurements were performed. Inverse susceptibility plots (Figure 36) showed a linear relationship with temperature, the only exception being **3.8**, which had a slightly non-linear deviation below 100 K, likely due to weak dipolar interactions between close contact Dy^{III} ions. This behavior is commonly observed in molecular magnets.³⁷¹

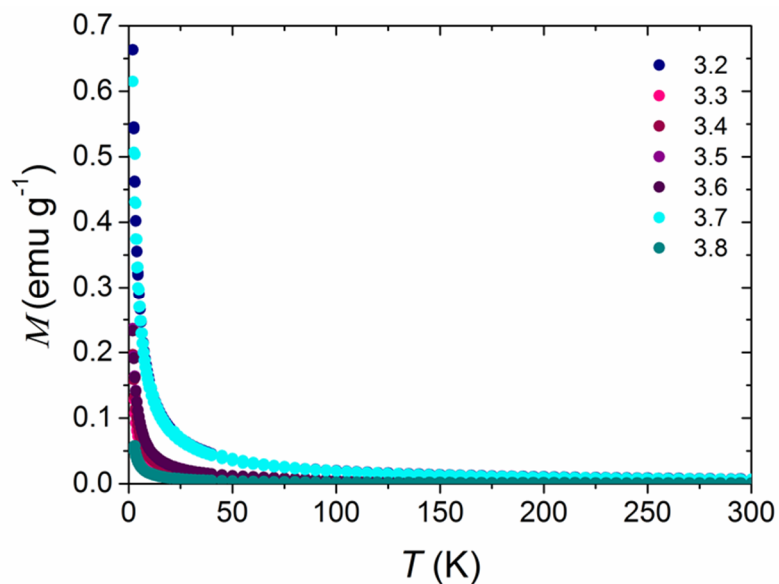


Figure 35. Zero-field-cool/Field cool data for 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, and 3.8, where the applied field was 100 Oe.

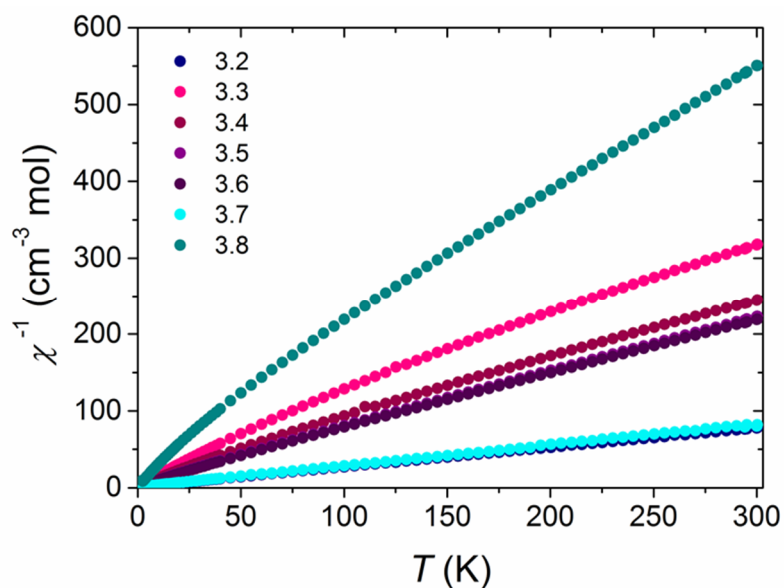


Figure 36. Temperature dependence of χ^{-1} at 100 Oe for 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, and 3.8.

The non-superparamagnetic nature of these particles down to 2 K dictates that they are not well-suited to applications necessitating magnetic translation with the application of a magnetic field. Instead, these materials could potentially be applicable as T_1 MRI contrast agents, with multimodal capabilities as up-conversion fluorescence probes.

3.5 Conclusions

This chapter has presented a successful synthetic strategy of doping NaYF₄ nanomaterials with specific amounts of desired lanthanide ion dopants. Initially, NaYF₄ was doped with an up-conversion optimized dopant profile, followed by two dopant percentages of magnetically interesting lanthanide ions.

Through the use of ICP-OES measurements, confirmation that the desired dopant percentages were achieved in their targeted ratios within each material was obtained. A correlation became apparent between doping accuracy and efficiency of dopant, which clearly showed Dy^{III} to be the optimal candidate for Y^{III} replacement within the lattice, as particles doped with Dy^{III} were found to have the closest composition to that which was intended, due to their close ionic radii. Particles were then studied using SEM, TEM, and HRTEM in order to gain information about their shape, size and crystallinity. Electron microscopy images, as well as resulting particle size distribution graphs, revealed that the size of the particles increased with dopant percentage. Thus, nanoparticle physical properties can be tuned through lanthanide dopant and percentage. Interestingly, with larger dopant percentages, Tb^{III} and Dy^{III}-doped particles also became more defined in shape (hexagonal). All particles displayed similar XRPD patterns and d-spacing values from HRTEM; clearly displaying crystalline character, with the majority exhibiting both cubic and hexagonal phases. Observed size similarities between hexagonal particles doped with 30% of Dy^{III} and Tb^{III} were correlated with a likely shift towards the hexagonal crystal phase. Dy^{III}-doped nanoparticles displayed well-defined shapes and crystalline peaks, further confirming that Dy^{III} was the optimal lanthanide dopant. Finally, magnetic measurements concluded an absence of superparamagnetic behavior down to 2 K, with no blocking temperature between 2 and 300 K. Thus, their magnetic properties disable their employment in any application necessitating magnetic translation, however, they could be applicable in a variety of paramagnetic applications. Though we did not explore the potential multimodal capabilities of these materials, this opens up a wide-array of potential for future studies to be performed, as will be discussed in Chapter 9.

Overall, the alterations in physical properties with each lanthanide dopant and percentage were important due to the known up-conversion fluorescent properties of NaYF₄: 2% Er, 18% Yb particles, as the electronic properties vary greatly according to the composition, and the luminescence is further altered by changes in crystalline phases. Furthermore, the multifunctional

properties of these doped nanoparticles could make them applicable in biomedicine, and in particular, as a result of their magnetic properties, as MRI contrast agents.

Chapter 4

Anchoring Magnetic Molecules on Naked Gold Nanocrystals: Dy^{III}

SMM-capped AuNPs

4.1 Abstract

Nanoparticles have been shown to possess unique and desirable properties; including magnetism, as discussed in previous chapters of this thesis. However, there is a large gap between the finite control over the magneto-structural properties of molecular systems (SMMs) and nanoparticle systems. Thus, many of the strategies used to synthesize and study magnetic nanomaterials focus solely on molecular nanomagnets. Furthermore, as demonstrated in Chapter 2, the efforts made to successfully functionalize these magnetic systems onto surfaces toward their potential future use are greatly lacking. As such, through combination of the synthetic methods employed in creating unique molecular magnets and carefully designed nanoparticle substrates, we have been able to introduce a new method of study for magnetic molecules on surfaces. This chapter details the synthesis and study of a new Dy^{III} SMM (**4.1**) on the surface of uniquely synthesized naked gold nanoparticles to form a novel hybrid material (**4.2**). The SMM, NPs, and the resulting hybrid material have been extensively characterised for their structural and physical properties, followed by a comparison using SQUID magnetometry. We were able to confirm that the static properties of the SMM were retained upon surface attachment, however, the dynamic properties were altered due to a change in the local anisotropy of Dy^{III}. This study provides a new method of: gaining better understanding of the fundamental magnetic properties of multifunctional nanomaterials, as well as studying substrate-bound magnetic molecules. For this reason, this work has been published in: Holmberg, R. J.; Hutchings, A. -J.; Habib, F.; Korobkov, I.; Scaiano, J. C.; Murugesu, M. *Inorg. Chem.* **2013**, 52, 14411-14418.

4.2 Introduction

The combination of nano-atomic scale materials, each with distinctive properties, in a controlled manner has tremendous potential to create materials with groundbreaking, multifunctional characteristics. Recently, several unique approaches have been reported employing top-down methods towards the isolation of nanoparticles with magnetic properties.^{372,373} Similarly, bottom-up approaches are constantly employed in the fundamental study and application of small

molecular magnetic materials.^{339,374,375} These small molecular magnetic materials (SMMs) show clean quantum behavior, and synthetic tunability, which makes them appealing candidates for use in the design of a new generation of molecular electronics.¹⁴⁵ Successful functionalisation with control over the directionality of these molecules on surfaces will be the key ingredient in bridging the gap between top-down and bottom-up approaches to synthesizing magnetic nanomaterials, and in utilizing the full potential of molecular magnets.¹³⁸ However, the goal of achieving successful surface attachment of magnetic molecules has proven to be a challenge for many researchers, especially as the inherent and desirable magnetic properties are often lost upon adhesion (*vide supra*).

As discussed in Chapter 2, it is necessary to answer a fundamental question of what happens to the magnetic behaviour of molecules when introduced to a surface, and whether or not this knowledge can then be exploited in the rational design of advanced materials. Despite the challenges faced, crucial and fundamental understanding of the nature of magnetic molecules on surfaces has been gained through extensive surface study of the Mn_{12} cluster (Figure 7) and its eventual successor Fe_4 (Figure 8), which was the first SMM that was capable of maintaining hysteretic behavior upon surface attachment.¹³⁸ However, both of these systems have been overshadowed by the remarkable magnetic properties of lanthanide-based SMMs; in particular TbPc_2 (Figure 9).¹³⁸ TbPc_2 systems continue to be incredibly promising surface attachment candidates due to their ligand architecture, sandwich-type structure, and potential to exhibit high energy barriers to magnetic relaxation (until recently a TbPc_2 molecule was the record holding system; $U_{\text{eff}} = 653 \text{ cm}^{-1}$, 939 K).¹⁰⁰ However, since these systems significantly underperform in regards to their blocking temperature, it is indeed time to explore a wider variety of lanthanide systems on surfaces. Furthermore, the potential for exploiting the inherent properties of the substrate material as an advantage has been greatly undervalued to this point. Thus, many possibilities await in order for the necessary fundamental understanding of this field to develop into the potential employment of molecular magnetic materials in future technological applications.

To date several studies have brought forth intricate work on surface attachment of molecular magnetic materials. Unfortunately, a vast majority of these studies have not involved magnetic characterisation upon surface adhesion. This can be partially explained in many cases by the necessity to employ expensive and specialised techniques, such as XMCD, in order to achieve a suitable magnetic signal arising from the magnetic molecules on a diluting diamagnetic surface. Alternatively, our idea involved the use of AuNPs as the substrate, and the study of the

magnetic properties of an SMM on the surface using conventional SQUID magnetometry. A similar concept was illustrated for the study of a radical complex grafted to a Au(111) single crystal through beam deposition.³⁷⁶ An important advantage to this approach, other than the use of conventional characterisation techniques, is that more SMMs per mass unit will be available to adhere to the surface due to the high bulk surface area of a nanoparticle, as opposed to that of a flat substrate, thus minimizing the aforementioned magnetic dilution effect of the diamagnetic substrate.

To this end, we chose a nanoparticle substrate which was entirely without a capping agent in order to avoid any obstruction to anchoring our magnetic molecules, and any interactions on the surface induced by separate structures, thus only allowing nanoparticle nucleation to be arrested by full surface adhesion of the magnetic molecules. Although not trivial, we were able to employ a strategy recently published by our collaborators involving the synthesis of “naked” gold nanoparticles.³⁷³ The choice of AuNPs as the substrate was motivated in part by the incredible affinity of gold to bind with sulphur (40-50 kcal mol⁻¹),^{377,378} thus allowing for a simple design strategy to bind molecules to the particle surface. Another advantage of AuNPs is that they possess unique optical and transport properties which have promoted their use in molecular marking, diagnostic imaging and catalysis.^{372,373,379-383} These properties, coupled with the magnetic properties from the capping agent on the particle surface, have the potential to elicit a unique hybrid material.

Presented herein is the capping of laser ablation synthesized water stable “naked” gold nanoparticles with a thiocyanate-functionalised dinuclear Dy^{III} SMM (**4.1**), and the subsequent study of the magnetic properties upon adhesion. This hybrid magnetic nanostructure was able to provide a novel means of studying SMM-based nanomaterials. Furthermore, through the inherent properties of this type of magnetic-plasmonic nanotechnology, new applications can be envisioned in optoelectronics, targeted imaging, magnetic separation, photothermal therapy, etc.^{334,384-386}

4.3 Experimental

4.3.1 Synthetic Information

All manipulations were performed under aerobic/ambient conditions. All reagents were purchased from the following sources: Alfa Aesar, Acros Organics, Strem Chemicals, TCI and Sigma Aldrich, and were employed without further purification.

4.3.1.1 Preparation of *N'*-(2-hydroxy-3-methoxybenzylidene) benzhydrazide (H₂hmb)

N'-(2-hydroxy-3-methoxybenzylidene) benzhydrazide (H₂hmb) was synthesized by following a previously reported procedure.³⁸⁷ A solution of benzhydrazide (0.02 mol, 2.72 g) in 10 mL MeOH was combined with a solution of *o*-vanillin (0.02 mol, 3.04 g) in 10 mL MeOH, and stirred for 24 h at 300 K. A white powder crashed out and was collected through vacuum filtration, then washed with MeOH. Yield = 85%. IR: 2060(w), 1655(s), 1605(m), 1572(m), 1534(w), 1466(s), 1405(m), 1365(s), 1347(s), 1088(s), 1076(s), 965(s), 937(s), 774(s), 719(s), 691(s).

4.3.1.2 Preparation of [Dy^{III}₂(Hhmb)₃(NCS)₃]·2MeOH·py (4.1)

[Dy^{III}₂(Hhmb)₃(NCS)₃]·2MeOH·py (4.1) was synthesized by the addition of DyCl₃·6H₂O (0.25 mmol, 0.094 g) in 5 mL MeOH to a solution of: H₂hmb (0.25 mmol, 0.067 g), NaSCN (1.0 mmol, 0.081 g), and pyridine (1.0 mmol, 0.078 mL) in 5 mL MeOH. The solution was stirred for 5 minutes, filtered, and placed in an ether bath at 300 K. X-ray quality yellow block crystals were collected within 3 days by vacuum filtration. Yield: 32%. Selected IR data: 2360(w), 2078(s), 2059(s), 1606(s), 1549(m), 1458(m), 1372(s), 1299(m), 1221(m), 1077(m), 899(m), 858(w), 789(w), 737(s), 709(s), 687(s), 638(m) cm⁻¹.

4.3.1.3 Preparation of Au Nanoparticles (AuNPs)

Gold nanoparticles were synthesized using a slightly modified photochemical procedure that employed hydrogen peroxide as a mild reducing agent.^{372,373} An aqueous solution of 35 wt.% H₂O₂ and 0.33 mM NaAuCl₄ in Millipore water was irradiated for 10 min using 14 UVA lamps in a LZC-L4V photoreactor (Luzchem Research, Inc.).

Laser ablation was performed in order to prepare uniform, spherical particles using frequency-doubled 532 nm (8 ns) pulses from a Continuum Q-switched Nd/YAG laser. Initially the beam was focused on a drop of the solution prepared above, which was generated by a computer-controlled syringe pump mechanism. This mechanism was automated to create equal drop formations (volume 7-10 μL) through a Teflon tube (1.6 mm diameter). Photographs and videos were taken with a Nikon D90 DSLR camera equipped with a Sigma 105 mm f 2.8 macrolens, controlled by the same software as the laser-drop system. Irradiated drops were collected in a cuvette containing the desired capping agent/stabilizer, where the 4.1-capped AuNPs (4.2) were formed. A schematic diagram of the laser drop system is shown in Figure 37.

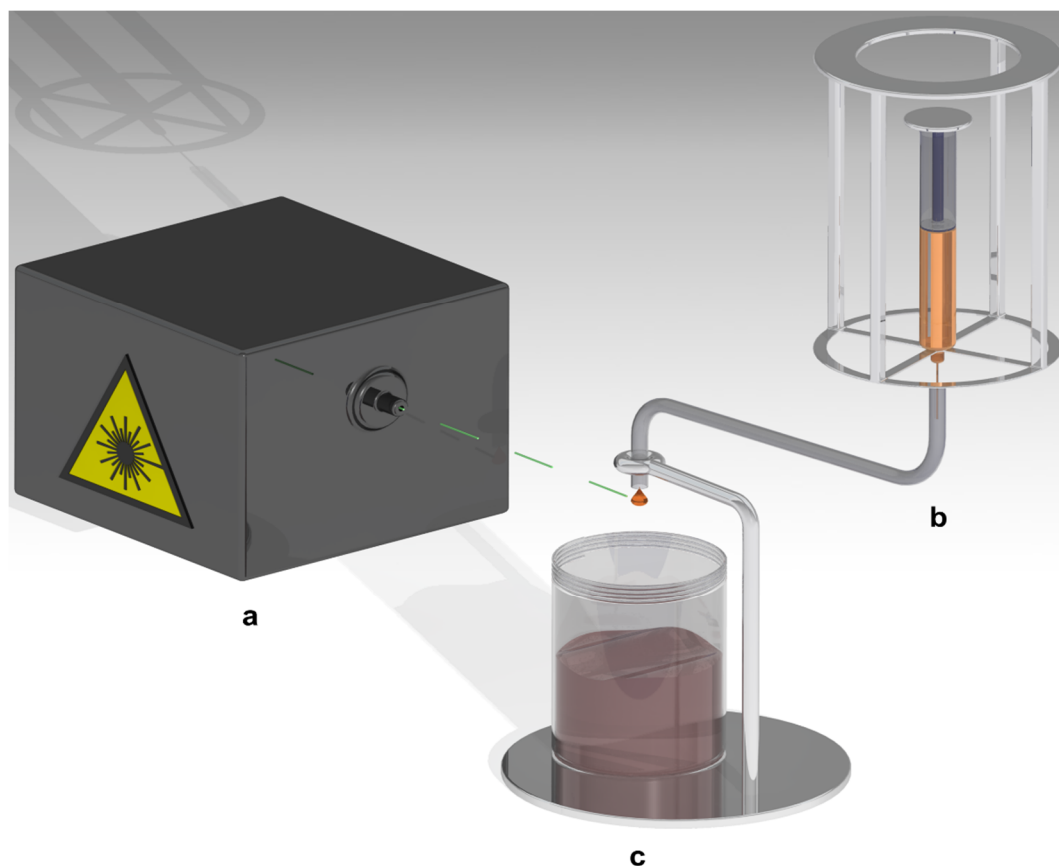


Figure 37. Schematic representation of the laser ablation setup employed, where (a) is the 532 nm Nd/YAG laser, (b) is the syringe pump mechanism filled with AuNPs, and (c) is the SMM capping agent (**4.1**) in MeOH.

4.3.2 Characterisation Techniques

4.3.2.1 Infrared Spectroscopy

Infrared spectra were recorded on all samples in the solid state on a Varian 640 FT-IR spectrometer in the 575-4000 cm^{-1} range.

4.3.2.2 ICP-OES

Inductively-coupled plasma-optical emission spectroscopy measurements were performed using a Varian Vista Pro CCD-ICP-OES Spectrometer. Each sample was digested separately, in triplicates, prior to analysis. The triplicates agreed well, and were averaged to obtain the final analyte relationship calculations. Each element was monitored at more than one wavelength in order to validate the data and rule out interferences. All concentrations were calculated in ppm (w/w basis), and are presented as percentage composition values.

4.3.2.3 SCXRD

Single-crystal X-Ray diffraction data was collected on a Bruker APEX-II CCD device with graphite Mo-K α radiation ($\lambda = 0.71073$ Å). Data reduction included correction for Lorentz and polarisation effects, with an applied multi-scan absorption correction (SADABS). The crystal structure of **4.1** was solved and refined using the SHELXTL program suite (Table 3). Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms.

Table 3. Crystallographic data of the dinuclear Dy^{III} complex **4.1**.

Compound	4.1
Empirical formula	C ₅₄ H ₄₈ Dy ₂ N ₁₀ O ₁₀ S ₃
Formula weight (g/mol)	1445.27
Crystal system	triclinic
Space group	P1
Temperature (K)	200(2)
Crystal size (mm)	0.10 x 0.04 x 0.01
<i>Z</i>	2
<i>a</i> (Å)	11.6516(3)
<i>b</i> (Å)	14.9787(3)
<i>c</i> (Å)	18.9061(6)
α (°)	108.702(2)
β (°)	100.444(2)
γ (°)	104.1450(10)
Volume (Å ³)	2907.01(13)
Calculated density (gcm ⁻³)	1.651
Absorption coefficient (mm ⁻¹)	2.726
<i>F</i> (000)	1440
θ range for data collection (°)	2.26 – 27.27
Limiting indices	$h = \pm 16, k = \pm 20, l = \pm 27$
Reflections collected/unique	27080/17269
<i>R</i> (int)	0.0423
Completeness to $\theta = 30.53$ (%)	0.99
Max. and min. Transmission	0.7722 and 0.9733
Data/restraints/parameters	17269/0/680
Goodness-of-fit on <i>F</i> ²	1.005
Final <i>R</i> indices [<i>I</i> 2 σ (<i>I</i>)]	$R_1 = 0.0423, wR_2 = 0.0787$
<i>R</i> indices (all data)	$R_1 = 0.0792, wR_2 = 0.0914$
Largest diff. Peak/hole, eÅ ⁻³	1.380 and -0.937

4.3.2.4 XRPD

X-ray powder diffraction experiments were performed using a RIGAKU Ultima IV, equipped with a Cu-K α radiation source ($\lambda = 1.541836 \text{ \AA}$), and a graphite monochromator. Scanning of the 2θ range was performed from 5-40° and 35-50/60-80°. In order to assign the peaks corresponding to particular crystalline phases, PDXL software equipped with the RIGAKU apparatus was used with the ICDD database.

4.3.2.5 SEM/TEM

Scanning electron microscopy images were taken using a JSM-7500F FESEM (JEOL), and transmission electron microscopy images were taken with a JEM-2100F FETEM (JEOL). HR-TEM (JEOL JEM-2100F) was also used to study the intrinsic crystallography of the samples.

4.3.2.6 XPS

Surface analysis by X-ray photoelectron spectroscopy was performed using a Kratos Axis Ultra DLD spectrometer employing a monochromated Al K α X-ray source at 140 W of X-ray energy.

4.3.2.7 SQUID

Magnetic measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL7, operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Susceptibility measurements were performed on: a freshly filtered crushed polycrystalline sample of 9.1 mg **4.1** in grease, and a powder sample of 32.7 mg **4.2**, each wrapped within polyethylene membranes. Direct current susceptibility measurements were performed under an applied dc field of 1000 Oe, and alternating current susceptibility measurements were performed under an oscillating ac field of 3.78 Oe, and an optimised applied dc field of 1000 Oe for **4.1** and 3000 Oe for **4.2**, with ac frequencies ranging from 0.1-1500 Hz. The magnetisation data was initially collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples.

4.4 Results and Discussion

Our initial synthetic goal was to design a multinuclear lanthanide-based magnetic molecule which possessed terminal S groups, thus allowing for AuNP surface adhesion. We decided to specifically employ Dy^{III} as our lanthanide metal source due to previously mentioned inherent magnetic properties; such as high spin ground state ($S = 5/2$) and magnetic anisotropy, as well as its propensity to form high coordination number complexes, and thus incorporate S-terminated ligands. The ligand that we synthesized for this complex was *N'*-(2-hydroxy-3-methoxybenzylidene)benzhydrazide (H₂hmb),³⁸⁸ which was chosen for its multidentate

coordinating pockets due to their potential to accommodate multiple lanthanide metal centres. Furthermore, H₂hmb coordinates through phenol oxygen atoms, which, upon deprotonation, possess the potential to provide magnetic superexchange pathways between Dy^{III} ions. Therefore, a dinuclear Dy^{III} complex, [Dy^{III}₂(Hhmb)₃(NCS)₃]·2MeOH·py, **4.1**, (Figure 38) was synthesized with three thiocyanate groups sterically available to bind to the surface of AuNPs.^{177,389} The synthesis was based on previously successful *o*-vanillin-derived lanthanide SMMs.^{387,388,390} The complex is composed of three phenoxide bridging oxygens (O1, O4, O7), bridging the dinuclear Dy^{III} core, which are all encapsulated by three monoanionic Hhmb⁻ ligands. The remainder of the coordination environment around each Dy^{III} centre is composed of one and two SCN⁻ groups on Dy1 and Dy2, respectively. Both Dy^{III} ions have a distorted monocapped square antiprism geometry, and a metal-metal distance of 3.56 Å, with an average Dy-O-Dy angle of 99.3°.

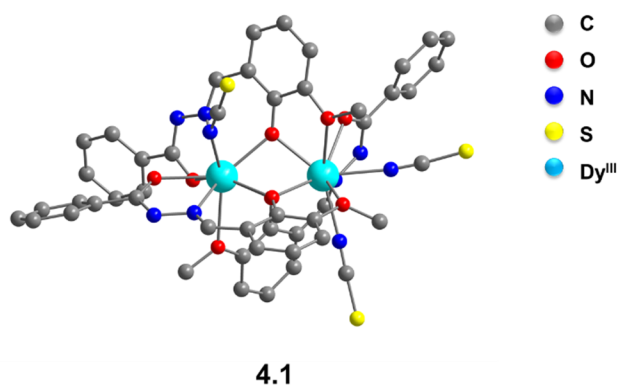


Figure 38. Molecular structure of [Dy^{III}₂(Hhmb)₃(NCS)₃]·2MeOH·py, **4.1**. Hydrogen atoms and solvent molecules removed for clarity.

The aforementioned synthetic methods for AuNPs were derived from previously published methods developed by our collaborators,^{372,373} which were designed to produce capping-agent free nanoparticles. The synthesis involves the use of hydrogen peroxide as a mild reducing agent under UV irradiation, where the clean by-products are O₂ and H₂O. When AuCl₄⁻ is irradiated in the presence of hydrogen peroxide, a hydroperoxyl radical, HOO•, and its conjugate base, O₂^{-•}, are produced, and can then act as one-electron reducing agents.³⁷² After the reduction process is complete the particle clusters are of varied sizes and shapes, and are merely surface coated with Cl⁻ remaining from the tetrachloroaurate starting material. This polydispersed solution of Au particulates is then laser ablated in sequential drops in order to obtain uniform particle shape, size and distribution. Each drop then falls into a solution of a customised capping

agent, which in this case was an optimised concentration of **4.1** in MeOH. Upon addition of particles into the solution of SMMs in MeOH, the Au-S bond can form on their surface, thus halting further particle nucleation and growth. The setup can be clearly observed via a schematic representation in Figure 37.

In order to extract the particles from solution for study, they are carefully collected by centrifugation. This method proposes a challenge for uncapped AuNPs, as they tend to redistribute within solution immediately upon removal from a centrifuge. Conversely, upon introduction to the solution of **4.1** in MeOH, the resulting material (**4.1**-coated AuNPs, **4.2**) experienced a considerable improvement in the ease of precipitation, even with low spinning speeds. This initial observation was promising, and warranted further investigation. It was essential that we not only prove the presence of our SMM capping agent on the surface of AuNPs, but also that we maintain the desired structure (**4.1**) upon attachment. Thus we sought to investigate any potential changes in the physical properties of **4.1** upon complexation to produce **4.2**.

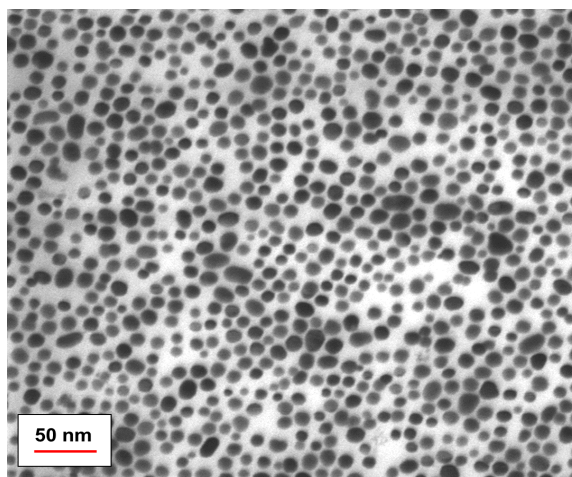


Figure 39. SEM image of naked AuNPs, displaying their size and shape distribution.

Initial evidence of the surface attachment of **4.1** on AuNPs was gathered using electron microscopy techniques. SEM, TEM and HRTEM images were taken in order to study the similarities and differences between AuNPs and SMM-capped AuNPs (**4.2**). Uncapped AuNPs were studied using SEM, which showed evenly distributed particles across the grid, which were in possession of a uniform round shape, with a mean size of 11.0 nm (Figure 39). Interestingly,

once the capping agent was applied to produce **4.2**, we observed a chain formation phenomenon through TEM (Figure 40A).

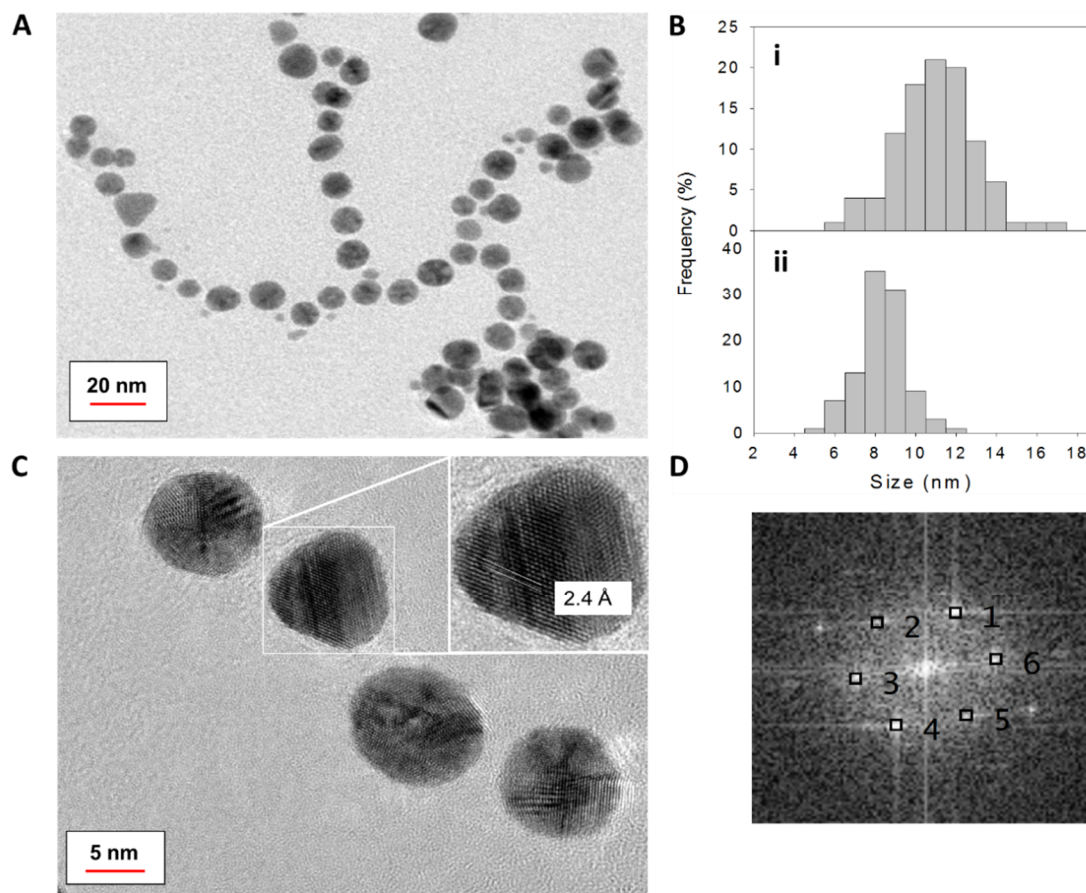


Figure 40. (A) TEM image of **4.2**, (B) particle size distribution plots for (i) AuNPs and (ii) **4.2**, confirming the presence of **4.1** on the surface of the particles, (C) HRTEM image of **4.2**, showing d-spacing value of 2.4 Å, and (D) the corresponding Fourier transform image.

These networks indicate that there is a significant interaction between capping agents on AuNPs, either through magnetic interaction or peripheral ligand moieties. Due to the uncertainty of the cause of this interaction, a control experiment was performed in order to determine that the chain-like formations of particles were not due to solvent effects. Thus, we added an equivalent amount of MeOH to that employed in forming **4.2** to the naked AuNP solution, and monitored the effects using electron microscopy. SEM confirmed that the particles, even with the addition of MeOH, were still evenly distributed across the surface of the grid. Consequently, we were able to confirm that this interaction was not merely due to solvent effects, and **4.2** was then studied with

HRTEM. Through these methods we were able to determine that **4.2** possessed a d-spacing value of 2.4 Å (Figure 40C and D), which is consistent with the Au(111) crystalline phase.

Another important parameter to control within electron microscopy experimentation was the timing between laser ablation and placement on a TEM grid, as the particles will continue to nucleate if left naked, or uncapped. Due to this concern, the particles were placed on a TEM grid within equivalent timeframes for both uncapped and capped AuNPs in order to maintain consistency. The average size of AuNPs was found to be significantly smaller, 8.3 nm (*versus* 11.0 nm) when capped with **4.1** (Figure 40B). The smaller size of AuNPs in **4.2** is due to the capping agent arresting particle nucleation earlier than if the AuNPs were left uncapped, which further confirmed that **4.1** molecules were indeed attached to the particle surfaces.

The next technique employed in the confirmation of the presence of **4.1** on the surface of AuNPs was X-ray photoelectron spectroscopy (XPS), which allowed for surface species identification. These experiments clearly showed a peak for Dy^{III} with a binding energy of 155.0 eV (Figure 41). Despite the low concentration of **4.1**, as compared with AuNPs, the former was still able to provide a discernible signal, and must thus occupy a significant area on the surface. Subsequently, the typical Au⁰ 4f doublet was also present, however, the binding energy was noticeably lower (82.5, 86.1 eV) than the bulk values (~84, 87 eV). This effect is most likely due to surface modifications to the particles, which represent, in this case, the attachment of **4.1**. Finally, a peak was also observed for S on the AuNP surface, with a binding energy of 162.1 eV.

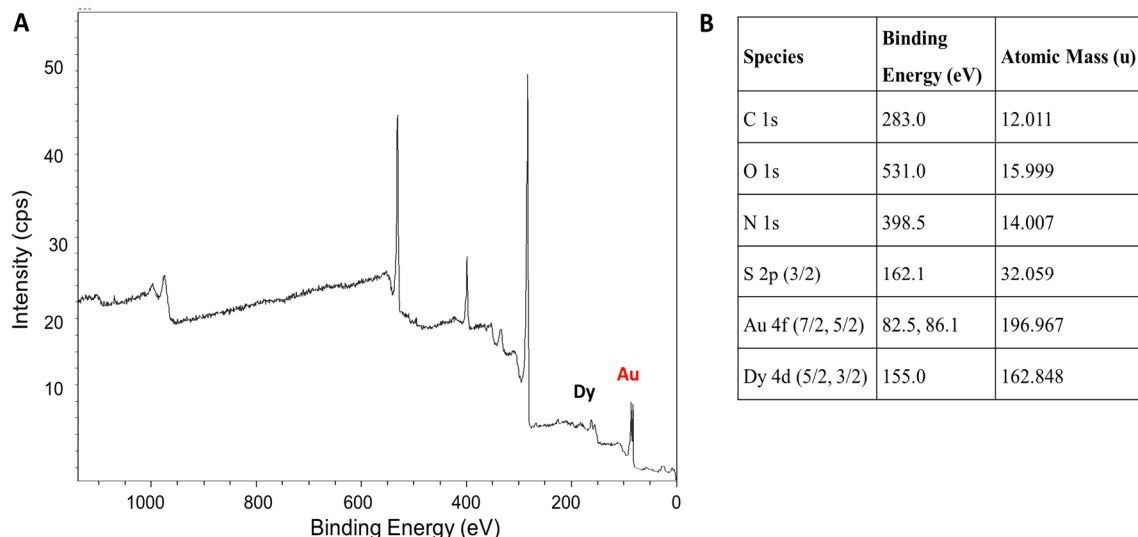


Figure 41. (A) XPS spectrum of **4.2**, and (B) table of XPS data, clearly displaying species present on the surface of AuNPs.

The elements of interest were also monitored using ICP-OES, and the analyte composition results can be seen in Table 4. Measurements were performed using both solid- and solution-based samples, before and after the attachment of **4.1** on the surface of AuNPs to produce **4.2**. The results provide a 2:3 Dy:S ratio for both **4.1**, as expected, and for **4.2**. These consistent ratios demonstrate that not only have we successfully adhered the molecules to the surface of the AuNPs, but also that they have subsequently remained structurally intact even after washing with MeOH/H₂O and air drying.³⁹¹

Table 4. ICP-OES measurements performed for **4.1** and **4.2**. The analytes measured and averaged are shown as follows: (a) Dy, (b) Au, and (c) S.

a. Dysprosium					
		Dy ^{340.780}	Dy ^{353.171}	Dy ^{364.540}	Dy ^{387.211}
Limit of Detection (ppm):		0.00019	0.00062	0.00042	0.00037
Sample Portion	Sample Mass (g)	Dy in the solution (ppm)			
4.1	0.0141	32.17	31.02	32.23	33.45
4.2	0.0056	2.08	2.34	1.99	2.07
		Dy in the solid (%)			
4.1	0.0141	2.35	2.30	2.33	2.40
4.2	0.0056	0.50	0.50	0.51	0.52
b. Gold					

		Au ^{242.794}	Au ^{267.594}	Au ^{242.794}	Au ^{267.594}
Limit of Detection (ppm):		0.031	0.011	0.031	0.011
Sample Portion	Sample Mass (g)	Au in the solution (ppm)		Au in the solid (%)	
4.1	0.0141	0.00	0.00	0.00	0.00
4.2	0.0056	3.67	3.70	1.28	1.34
c. Sulfur					
		S ^{180.669}	S ^{181.972}	S ^{180.669}	S ^{181.972}
Limit of Detection (ppm):		0.069	0.039	0.069	0.039
Sample Portion	Sample Mass (g)	S in the solution (ppm)		S in the solid (%)	
4.1	0.0141	57.78	58.56	6.02	5.67
4.2	0.0056	3.70	3.53	0.78	0.74

In order to further explore the Au-S linkage, while simultaneously gaining insight into the structural features of **4.1** on AuNPs, infrared (IR) spectroscopic analysis was carried out. IR was able to provide additional information regarding the presence of the Au-S bond between thiocyanate linkers of **4.1** and AuNPs in **4.2** (Figure 42). Characteristic stretches for N-bonded thiocyanate were observed in the spectrum of **4.1**; $\nu(\text{CN}) = 2078(\text{s}), 2059(\text{s}) \text{ cm}^{-1}$, and $\nu(\text{CS}) = 858(\text{s}), 789(\text{s}) \text{ cm}^{-1}$.³⁹² The spectrum for **4.2** was investigated closely and found to also display characteristic N-bonded thiocyanate stretches. More interestingly, **4.2** was also found to exhibit S-bonded thiocyanate stretches, including a bridging M-NCS-M' stretch at $\nu(\text{CN}) = 2110(\text{w}) \text{ cm}^{-1}$. This stretch displays a clear connection between Dy^{III} and Au^0 through a thiocyanate linker. Thus, we can confirm that **4.1** is indeed bound to the surface of AuNPs through the designed S-terminated ligands. Further relevant stretches were: $\nu(\text{CS}) = 834(\text{m}), 805(\text{m}), 779(\text{m}) \text{ cm}^{-1}$, and finally a strong sulphur bonded stretch observed at $\nu(\text{CS}) = 700(\text{s}) \text{ cm}^{-1}$.³⁹²

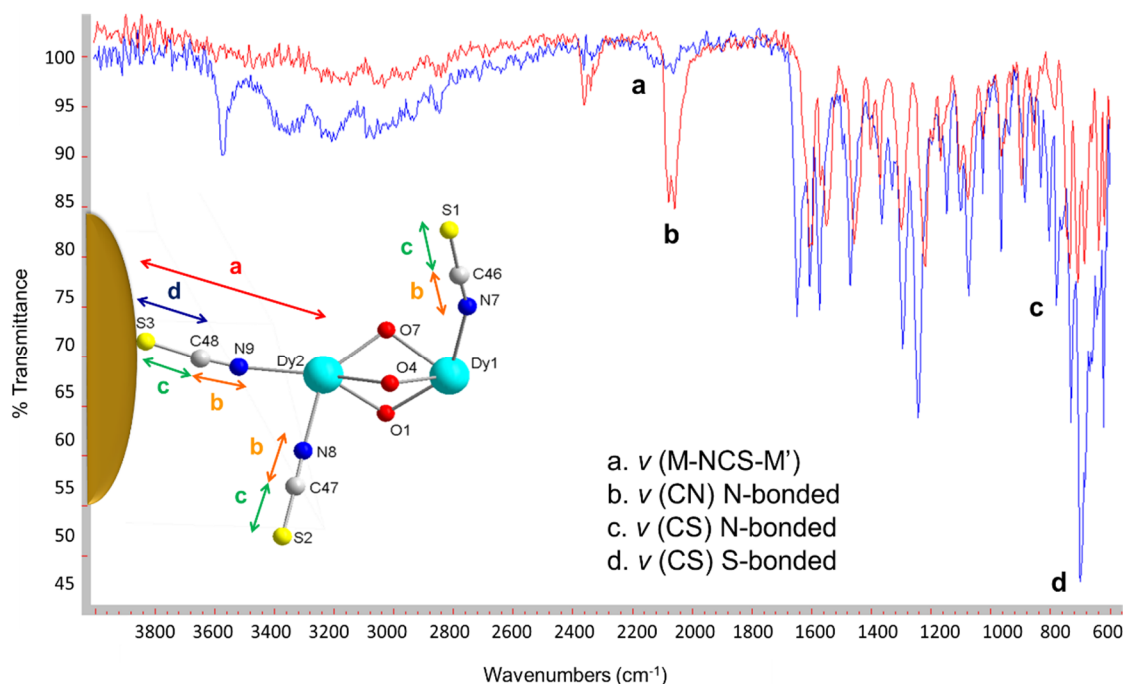


Figure 42. Infrared spectra comparing **4.1** (red) and **4.2** (blue), with labelled thiocyanate-based stretches.

For further confirmation of the structural integrity of **4.1**, once attached to the surface of AuNPs, additional IR studies were also performed. The following vibration bands were recorded: $\nu(\text{OH}) = 3300 \text{ cm}^{-1}$, 3200 cm^{-1} , $\nu(\text{NH}) = 3170 \text{ cm}^{-1}$, 3165 cm^{-1} , $\nu(\text{CH, Ar-H}) = 3065 \text{ cm}^{-1}$, 3062 cm^{-1} , $\nu(\text{CH, O-CH}_3) = 2943 \text{ cm}^{-1}$, 2940 cm^{-1} , $\nu(\text{C}\equiv\text{N}) = 1605 \text{ cm}^{-1}$, 1605 cm^{-1} , $\nu(\text{CO, Ar-O}) = 1296 \text{ cm}^{-1}$, 1299 cm^{-1} , and metal coordination through oxygen to a ligand phenol group; $\nu(\text{M-O-Ar})_{4.1} = 1243 \text{ cm}^{-1}$, 1147 cm^{-1} and $\nu(\text{M-O-Ar})_{4.2} = 1235 \text{ cm}^{-1}$ and 1150 cm^{-1} ; for **4.1** and **4.2**, respectively.³⁹³ Furthermore, XRPD patterns were employed in order to compare the structure of naked AuNPs, and those in **4.2** (Figure 43A). The pattern for **4.2** displayed the same peaks as that for AuNPs, however, they were broader and lower intensity which is indicative of the smaller size distribution, as was discussed above in regards to electron microscopy results. The pattern for naked AuNPs had a high-intensity (111) peak (JCPDS 001-1172), which was previously observed through HRTEM studies, showing a d-spacing value of $2.4 \text{ \AA}$. The significance of the Au(111) surface structure is that this is the most common phase employed in Au-S surface bonding studies.³⁷⁷ Furthermore, peaks from (200), (220), and (311) lattice planes were also present, which were expected within the chosen 2θ range for AuNPs. Finally, the stability of **4.1** in MeOH and H₂O was tested using both IR and XRPD after dissolution. IR spectra were superimposable

with one another,¹⁷⁷ and XRPD patterns displayed that even after dissolution and drying there is a definite matching of crystalline phase peaks with those from single-crystal X-ray diffraction (SCXRD), thus the structural integrity of **4.1** is maintained upon dissolution (Figure 43B).

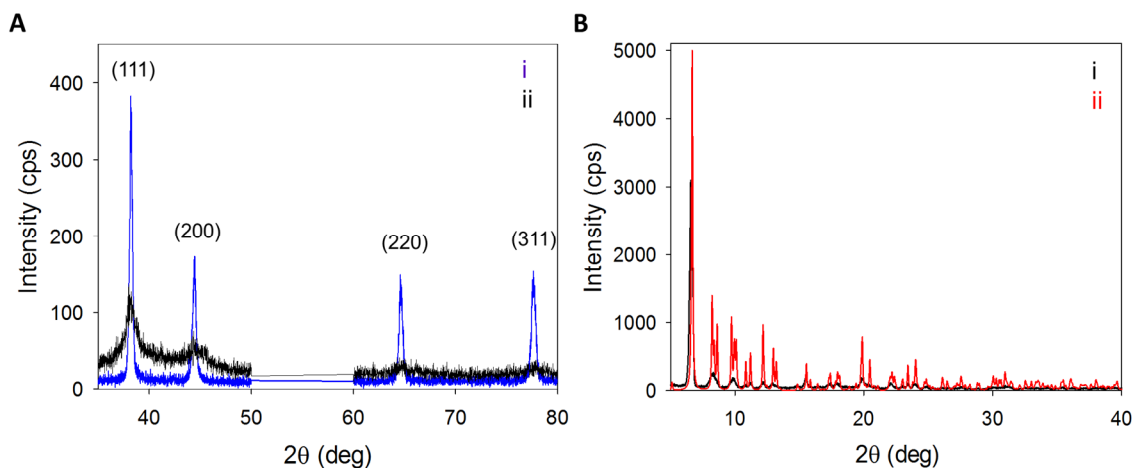


Figure 43. (A) XRPD pattern in the 35-50 and 60-80° 2θ region comparing AuNP (i), and **4.2** (ii), and (B) SCXRD-calculated pattern of **4.1** (i), compared with XRPD pattern in the 5-40° 2θ region of **4.1** after dissolution in MeOH/H₂O (ii).

Upon successful confirmation of the structural integrity of **4.1** on the surface of AuNPs, we desired to explore the effects of the capping agent on the surface modification of AuNPs. Since these are plasmonic materials, it is essential to investigate their absorption characteristics through ultraviolet-visible (UV-Vis) spectroscopy. A comparative study between AuNPs and **4.2** has shown that the capped particles displayed a characteristic shifting and broadening of the plasmon band at 530 nm (Figure 44B).³⁹⁴ This effect is caused by a surface attachment phenomenon, which, in this case, is the addition of a capping agent, **4.1**. There was a distinct change in colouration from a light orange-pink to grey-brown between laser ablated AuNPs and **4.2** (Figure 44A, i and ii), which is further indicative of plasmonic properties changing by surface modification.

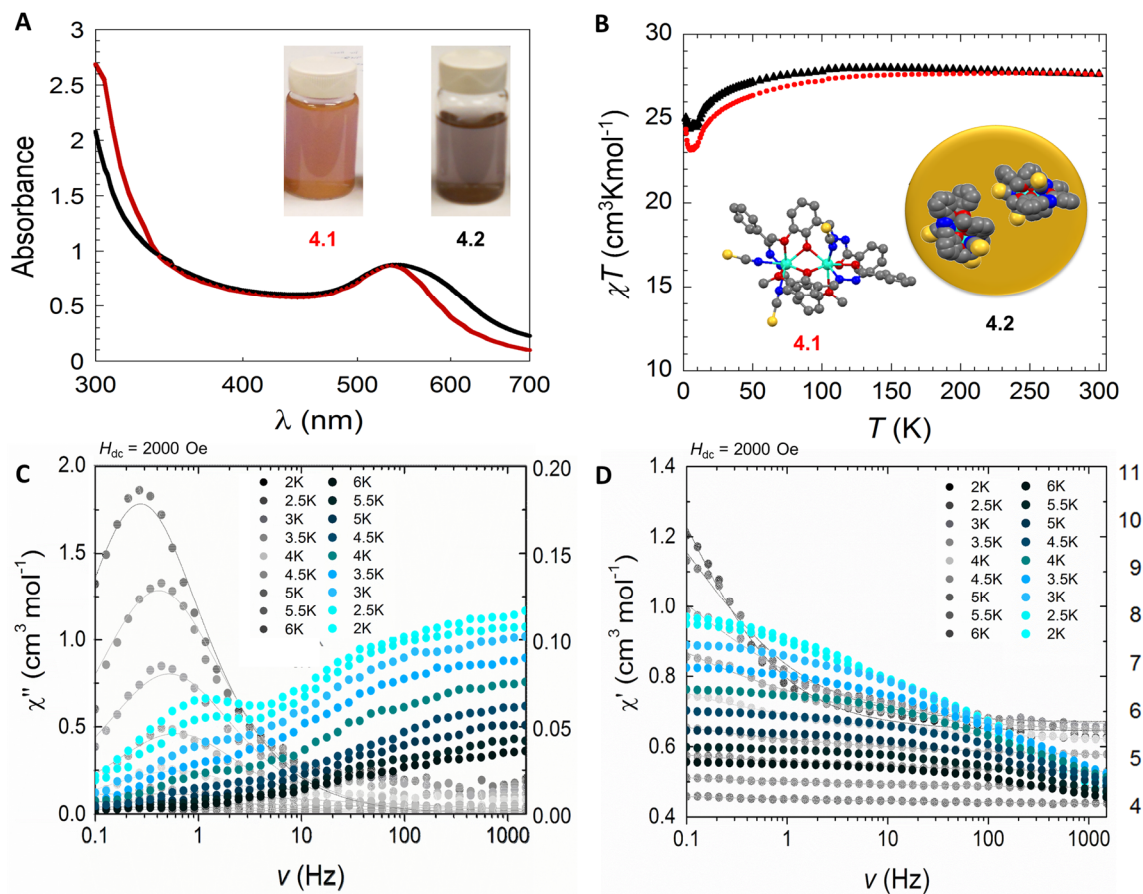


Figure 44. (A) UV-Vis spectra of uncapped AuNP and **4.2**, solution colour shown in inset images, (B) Temperature dependence of the χT product at 1000 Oe for **4.1** and for **4.2**, (C) Frequency dependence of the out-of-phase susceptibility (χ''), and (D) the in-phase (χ') ac susceptibility for **4.1** (greyscale), and **4.2** (coloured), from 2 K to 6 K under 1000 Oe and 3000 Oe static fields, respectively. Solid lines are fits to a generalised Debye model.

Finally, we observe an increase in scattering at lower energy, which is indicative of the particle chain formations observed by TEM in the colloidal solution. Thus, the particles must be forming these networks rapidly in solution, which has been observed previously through the intentional use of a connecting ligand between particles.³⁹⁵ These measurements were subsequently used for the calculation of total Au concentration (based on an absorbance of 0.9) of 0.28 mM,³⁹⁴ corresponding to [AuNP] of 16.0 nanomolar based on 8.3 nm particles, having about 17750 atoms per particle, of which 3322 are on the surface. This concentration is very close to the initially employed Au concentration in the reaction of 0.33 mM. Taking these parameters into account, as well as the longest measured distance across the **4.1** molecule with a potential S-Au

binding site (18.53 Å H13A-H28A), we can estimate that there might be ~20 molecules of SMM on the surface of each AuNP.¹⁷⁷

Despite the limited number of SMMs per AuNP, we were able to obtain a magnetic signal for **4.2** in our conventional SQUID magnetometer, as desired. The magnetic response of both **4.1** and **4.2** was probed with magnetic susceptibility measurements on polycrystalline **4.1** and powder **4.2** samples. Similar static behaviour was observed for the magnetic molecule before and after surface adhesion, as can be observed in Figure 44B. The room temperature χT value for **4.1** was 27.65 cm³ K mol⁻¹, which is slightly lower than the theoretical value of 28.34 cm³ K mol⁻¹ for two non-interacting Dy^{III} ions (⁶H_{15/2}, $S = 5/2$, $L = 5$, $g = 4/3$, $\chi T = 14.17$ cm³ K mol⁻¹). For **4.2**, the χT value at 300 K is very similar to that of **4.1**. Both χT products remain stable upon temperature decrease, until 175 K, where a gradual decrease is observed before a dramatic drop to 21.14 cm³ K mol⁻¹ at 5.4 K (**4.1**) and 24.46 cm³ K mol⁻¹ at 4.5 K (**4.2**). This decrease is due to the presence of significant magnetic anisotropy inherent to Dy^{III} ions. Below these temperatures there is a rapid increase in both χT products, thus indicating non-negligible ferromagnetic interaction between Dy^{III} ions at low temperature. As the smallest intermolecular distance between Dy ions in **4.1** is 8.56 Å, and this behaviour is mimicked by the molecules when spread out on a surface, the interaction is most likely intramolecular in origin. This was an astounding result, as retaining any inherent magnetic behaviour upon surface adhesion has been shown to be very challenging in several previous studies, as discussed in Chapter 2.

We wanted to explore the magnetic properties further, in order to see if we could retain any of the slow relaxation of the magnetisation in **4.2** that was present in **4.1**. Thus, dynamic magnetic behavior was probed using ac susceptibility measurements. Under zero-applied static field, no ac signal was observed in either sample, however, upon application of a dc field the appearance of the ac signal was indicative of a field-induced SMM. This behavior is attributed to significant QTM within the system at zero field. In order to optimize the slow relaxation process through reduction of the effects of QTM, optimal fields were chosen at the minimum corresponding frequency (1000 Oe for **4.1** and 3000 Oe for **4.2**). Frequency dependent out-of-phase (χ'') and in-phase (χ') magnetic susceptibility measurements were performed on both systems at the indicated temperatures in Figure 44C and D, respectively. It should be noted that even with the application of a small dc field, the peak maxima shifting was minimal and therefore the presence of QTM was significant. The effective energy barrier and relaxation time were obtained through fitting using an Arrhenius equation $\tau_0 \exp(U_{\text{eff}}/kT)$, which resulted in a value of $U_{\text{eff}} = 2.4(0)$ K.^{177,389} Upon attachment, the molecule displays significant changes in the ac signal

dynamics, along with further increased QTM, thus an energy barrier could not be determined. This change is proposed to be due to the subtle change in local anisotropy of the Dy^{III} ions upon binding to the AuNP surface through the SCN⁻ moiety.³⁹⁶⁻³⁹⁹ From the literature reviewed in Chapter 2, we know that this type of behaviour upon surface adhesion isprecedented. However, it was interesting to observe the retained static behaviour, while the dynamic behaviour changed significantly, thus displaying the importance of retaining local symmetry, even in the case of shielded 4f systems.

4.5 Conclusions

This chapter has presented a new hybrid material, composed of a naked nanoparticle, capped with molecular magnets. This material was created through an innovative approach to studying these molecules on surfaces, without necessitating non-commercially available techniques for magnetic study. A new magnetic molecule was designed and synthesized for this study, with S-terminated groups in order to facilitate attachment to the surface of AuNPs. The synthesized AuNPs employed a uniquely capping agent-free method, ensuring exclusive capping by the intended molecular magnets.

Upon capping the SMM to the AuNPs, the attachment and SMM structural integrity were extensively characterised using electron microscopy, XPS, IR, XRPD, etc. in order to confirm the identity of the hybrid material. Upon which, SQUID magnetometry was employed in order to compare the magnetic properties of the synthesized SMM with the hybrid material. Magnetic studies displayed retained static magnetic behaviour upon surface attachment, however, the dynamic behaviour was found to have been altered due to a slight change in local anisotropy of the Dy^{III} ions of the SMM upon adhesion to AuNPs. The loss of the dynamic slow magnetic relaxation observed for the SMM was a fault of the short linker employed (SCN⁻). Furthermore, the molecule employed displayed significant QTM, which explains that very small changes on the coordination environment proved to be detrimental to studying its magnetic behaviour on a surface. Thus, as will be discussed in Chapter 9, there are extensive improvements that can be made to this methodology in future studies.

Overall, these findings were pioneer in the development of a new practical method of studying the fundamental effects of surface attachment of molecular magnets. This method eliminated the necessity for costly, impractical analytic methods, and instead employed conventional commercial techniques. Many challenges remain in the field, as was discussed in

Chapter 2, however, through fundamental surface studies these challenges are systematically being conquered. For example, a recent paper reported a new strategy towards molecular spin control on graphene,⁴⁰⁰ illustrating that with continued creative efforts it is indeed possible for magnetic molecules to be realised in future technologies.

Chapter 5

Tethering Molecular Magnets into Ordered 1D Chains: Ln^{III}-EDTA

5.1 Abstract

As discussed in the literature review above (Chapter 2), extending molecular systems into chain networks is a unique method with which to orient SMMs in a well-ordered fashion along one dimension, and study their resulting properties. Complexes of the formula Na[Ln(EDTA)(H₂O)₃]·5H₂O are presented, where Ln = Y^{III} (5.1), Eu^{III} (5.2), Gd^{III} (5.3), Tb^{III} (5.4), Dy^{III} (5.5). EDTA chain-like architectures were obtained in water by adding Na⁺ as a bridging ion. Structures were characterised using SCXRD, and XRPD. Infrared spectroscopy and elemental analysis were performed on all samples in order to confirm bulk purity of products. Direct current and alternating current magnetic susceptibility measurements were carried out on all paramagnetic complexes in order to investigate any potential magnetic interactions between ions, as well as potential dynamic magnetic properties. Surprising magnetic behavior was observed for isotropic Gd^{III} (5.3), where spin-phonon transitions induced slow magnetic relaxation under an applied dc field. This incited interest in performing a magneto-structural comparison of this isotropic Gd^{III} system with anisotropic Tb^{III} (5.4) and Dy^{III} (5.5) compounds. This study represents a new potential method, as well as a generally overlooked dimensionality, for organizing discrete molecular magnetic materials, whereby the effects of their 1D ordered array on the magnetic properties of the molecular unit can be studied accordingly. Due to the breadth of this work, it has been published in: Holmberg, R. J.; Ho, L. T. A.; Ungur, L.; Korobkov, I.; Chibotaru, L. F.; Murugesu, M. *Dalton Trans.* **2015**, 44, 20321-20325; and Holmberg, R. J.; Korobkov, I.; Murugesu, M. *RSC Adv.* **2016**, Accepted: RA-ART-04-2016-009831.

5.2 Introduction

Despite the immense success of lanthanides discussed throughout this thesis within the context of discrete molecular magnetic materials,^{97,99,100} 4f ions have very scarcely been employed in targeting 1D chain networks for magnetic applications. This is unexpected, as lanthanide-based single-ion magnets have shown significant magnetic improvement over their transition metal counterparts; holding records for both blocking temperature ($T_B = 20$ K),⁹⁷ as well as energetic barrier to magnetic relaxation ($U_{\text{eff}} = 1025$ K).⁹⁸ Due to these successes, lanthanide SIMs have been proposed as ideal candidates for potential employment in information storage,⁷ molecular

spintronics,^{12-15,102,103} quantum computing,^{8-11,101} and related areas of technological advancement. Recently, Google and NASA published a breakthrough in quantum computing; producing a material that is capable of performing a complex calculation at a speed approximately two orders of magnitude faster than a conventional computer.¹⁸ This was arguably the first evidence of quantum computing being a feasible technological advancement within our lifetime. Thus, nanomagnetic materials, such as single-molecule magnets (SMMs) and SIMs, have the potential to play a significant role in the future of high-density, high-performance, energy-saving electronics.

It is important to consider that for any of the aforementioned applications, nanomagnets will need to be strategically arranged, such that their magnetic moments may be practically manipulated (*vide supra*). This has been extensively explored on bulk surfaces, and in some cases nanomaterials, however, in many studies the orientation of the molecular unit and/or magnetic behaviour inherent to the molecular unit cannot be controlled upon adhesion to a surface.¹³⁸ Thus, the controlled assembly of discrete lanthanide-based magnetic systems into well-separated ordered networks has the potential to be a beneficial technique towards the isolation of advanced molecular magnetic materials.¹³⁸ Interestingly, it has been shown that coupling transition metal SMMs through the formation of 1D arrangements has the potential to improve magnetic behaviour.^{180,213,216,401} This effect is a result of the dipolar and/or superexchange interactions induced between spin carriers, which further slow the magnetic relaxation.¹⁸⁰

In regards to 1D lanthanide systems, only one family of lanthanide chain magnets have been reported to date.²¹⁵ Recently, a Dy^{III} SCM was reported using a building block approach, where paramagnetic Dy^{III} architectures were assembled into 1D chains through radical ligand coupling, eliciting an improvement in magnetic behaviour.²¹⁶ These systems are impressive, but unfortunately pale in comparison to the previously mentioned SIM (0D) lanthanide systems in regards to U_{eff} and T_B values. This is due to the weak interactions between spin carriers, resulting from shielded 4f electrons, as well as the lack of control over the specific coordination environment of each lanthanide ion in the chain.

In designing 1D systems towards magnetic applications, the employment of chelating ligands has the potential to elicit a more predictable structure, as they provide a bulky and often rigid coordination sphere, thus promoting ordered arrays and structural control. Ethylenediaminetetraacetic acid (EDTA) is a low-cost chelating ligand with biocompatible properties.⁴⁰²⁻⁴⁰⁴ It has been extensively explored as a metal trapping agent in a variety of

industries, such as: chemical separation, cosmetics, textiles, water treatment, pulp and paper, food, dentistry and medicine.⁴⁰⁵ Despite these industrial applications and interesting properties, very few investigations have considered the magnetic properties of EDTA-chelated metal complexes.^{406,407} One of the few examples of a magnetic study being performed on EDTA-chelated complexes was performed on composite materials that are employed in metal ion capture and removal.⁴⁰⁸⁻⁴¹¹ In these studies, magnetic NPs (typically iron oxide) were surface functionalised with EDTA ligands, and employed thereafter as metal ion capture agents, where the metallic NP was merely a means to sequester the captured metal ions from the mixture. This type of composite material was discussed in Chapter 2, where the magnetic NP has a secondary purpose within the overall goal of the nanomagnetic material. Such studies exhibit the practical nature of EDTA as a ligand architecture, as well as the continued interest in magnetic nanomaterials within a variety of applications.

We chose to explore a series of lanthanide EDTA chain structures with varying magnetic properties: $\text{Na}[\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$, hereafter termed **5.1**, **5.2**, **5.3**, **5.4** and **5.5**, for Ln: Y^{III} , Eu^{III} , Gd^{III} , Tb^{III} , and Dy^{III} , respectively. Our aim was to compare the diamagnetic, isotropic and anisotropic analogues through a comparative magnetic study. The solid-state structural features are discussed through SCXRD, XRPD, IR spectroscopy, and elemental analysis (EA), followed by magnetic characterisation using SQUID magnetometry.

5.3 Experimental

5.3.1 Synthetic Information

All manipulations were performed under aerobic/ambient conditions. All reagents were purchased from the following sources: Alfa Aesar, Acros Organics, Strem Chemicals, and Sigma Aldrich, and were employed without further purification.

5.3.1.1 Preparation of $\text{Na}[\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$ (**5.1-5.5**)

Procedures for synthesis of **5.1-5.5** were very similar to those previously reported for lanthanide EDTA complexes.⁴¹² Slight differences can be found in the employment of a strong base, as well as two different ligand salts, in order to explore the potential isolation of a monomeric structure. Colourless crystals were prepared by placing $\text{Na}_2\text{H}_2\text{EDTA}$ (0.186 g, 0.5 mmol) or H_4EDTA (0.146 g, 0.5 mmol) and $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (0.132 g, 0.5 mmol) in water (25 mL). A solution of 1M aq. NaOH was added dropwise until the ligand was solubilised. The suspension was stirred and

heated to reflux until dissolved. Once dissolved, the solution was filtered and allowed to slowly evaporate until crystals formed. In some cases EtOH was layered in order to promote the formation of crystals. Elemental analysis; expected: Y-EDTA, **5.1**; C 22.07%, H 5.19%, N 5.15%; Found: C 22.35%, H 4.89%, N 5.17%, Eu-EDTA, **5.2**; C 19.78%, H 4.65%, N 4.61 %; Found: C 19.79%, H 4.49%, N 4.57%, Gd-EDTA, **5.3**; C 19.61%, H 4.61%, N 4.57%; Found: C 19.79%, H 4.43%, N 4.56%, Tb-EDTA, **5.4**; C 19.55%, H 4.59%, N 4.56%; Found: C 19.81%, H 4.40%, N 4.56%, Dy-EDTA, **5.5**; C 19.44%, H 4.57%, N 4.53%; Found: C 19.54%, H 4.36%, N 4.54%.

5.3.2 Characterisation Methods

5.3.2.1 Elemental Analysis

Elemental analysis was performed at the Laboratoire d'Analyse Élémentaire de l'Université de Montréal.

5.3.2.2 Infrared Spectroscopy

Infrared spectra were recorded in the solid state on a Nicolet 6700 FT-IR spectrometer in the 4000-600 cm^{-1} region.

5.3.2.3 SCXRD

Single-crystal X-Ray diffraction experiments were performed on a Bruker AXS SMART single-crystal diffractometer with a sealed Mo tube APEX II CCD detector, which was used to collect the unit cell and intensity data using graphite Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction included correction for Lorentz and polarisation effects, with an applied multi-scan absorption correction (SADABS). Crystal structures were solved and refined using SHELXTL. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated geometrically, and were riding on their respective atoms.

Further crystallographic information for **5.1**, **5.2**, **5.3**, **5.4**, and **5.5** can be observed in Table 5 and Table 6.

5.3.2.4 XRPD

X-ray powder diffraction experiments were performed using a RIGAKU Ultima IV, equipped with a Cu-K α radiation source ($\lambda = 1.541836 \text{ \AA}$), and a graphite monochromator. Scanning of the 2θ range was performed from 5-45°. XRPD patterns were consistent in 2θ values with the

generated patterns from SCXRD, with slight discrepancies in some intensities of peaks attributed to preferred orientation.

Table 5. Crystallographic data for **5.1**, **5.2**, and **5.3**.

Compound	5.1	5.2	5.3
Empirical formula	C ₁₀ H ₂₈ Y N ₂ Na O ₁₆	C ₁₀ H ₂₈ Eu N ₂ Na O ₁₆	C ₁₀ H ₂₈ Gd N ₂ Na O ₁₆
Formula weight (g/mol)	544.24	607.29	612.58
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Fdd2	C c (no. 9)	C c (no. 9)
Temperature (K)	200(2)	200(2)	200(2)
Crystal size (mm)	0.16 x 0.15 x 0.14	0.26 x 0.23 x 0.20	0.24 x 0.19 x 0.16
Z	16	8	8
a (Å)	19.2891(14)	12.0642(3)	12.0641(4)
b (Å)	35.214(3)	19.4184(4)	19.3270(6)
c (Å)	12.0446(9)	18.7257(4)	18.6758(6)
α (°)	90.00	90.00	90.00
β (°)	90.00	108.7808(8)	108.7327(13)
γ (°)	90.00	90.00	90.00
Volume (Å ³)	8181.2(5)	4153.25(16)	4123.8(2)
Calculated density (gcm ⁻³)	1.767	1.942	1.973
Absorption coefficient (mm ⁻¹)	2.955	3.122	3.319
F(000)	4480	2432	2440
θ range for data collection (°)	2.31 – 28.42	2.30 – 28.32	2.40 – 28.34
Limiting indices	h = ±20, k = ±31, l = ±16	h = ±16, k = ±24, l = ±24	h = ±16, k = ±25, l = ±24
Reflections collected/unique	13330/4461	22962/8861	29817/9608
R(int)	0.0749	0.0195	0.0216
Completeness to θ = 30.53 (%)	0.964	0.994	0.997
Max. and min. Transmission	0.6057 and 0.7457	0.6080 and 0.7457	0.6143 and 0.7457
Data/restraints/parameters	4461/43/275	8861/2/541	9608/2/542
Goodness-of-fit on F ²	1.013	1.022	1.050
Final R indices [I.2σ(I)]	R ₁ 0.0749, wR ₂ = 0.1985	R ₁ = 0.0195, wR ₂ = 0.0518	R ₁ = 0.0216, wR ₂ = 0.0576
R indices (all data)	R ₁ = 0.0776, wR ₂ = 0.2010	R ₁ = 0.0201, wR ₂ = 0.0521	R ₁ = 0.0217, wR ₂ = 0.0577
Largest diff. Peak/hole, eÅ ⁻³	0.894 and -1.086	0.676 and -1.932	0.601 and -0.844

Table 6. Crystallographic data for **5.4** and **5.5**.

Compound	5.4	5.5
Empirical formula	C ₁₀ H ₂₈ TbN ₂ NaO ₁₆	C ₂₀ H ₅₆ Dy ₂ N ₄ Na ₂ O ₃₂
Formula weight (g/mol)	614.25	1235.66
Crystal system	monoclinic	monoclinic
Space group	C c (no. 9)	C c (no. 9)
Temperature (K)	200(2)	200(2)
Crystal size (mm)	0.19 x 0.16 x 0.14	0.24 x 0.18 x 0.14
<i>Z</i>	8	4
<i>a</i> (Å)	12.0542(10)	12.0650(4)
<i>b</i> (Å)	19.2934(15)	19.3114(8)
<i>c</i> (Å)	18.6466(15)	18.6307(7)
α (°)	90.00	90.00
β (°)	108.7877(13)	108.5057(15)
γ (°)	90.00	90.00
Volume (Å ³)	4105.5(6)	4116.4(3)
Calculated density (gcm ⁻³)	1.988	1.994
Absorption coefficient (mm ⁻¹)	3.548	3.733
<i>F</i> (000)	2448	2456
θ range for data collection (°)	2.64 – 28.33	2.63 – 28.31
Limiting indices	<i>h</i> = ±16, <i>k</i> = ±25, <i>l</i> = ±24	<i>h</i> = ±16, <i>k</i> = ±25, <i>l</i> = ±24
Reflections collected/unique	23327/9773	29350/9562
<i>R</i> (int)	0.0236	0.0148
Completeness to θ = 30.53 (%)	0.997	1.002
Max. and min. Transmission	0.6527 and 0.7457	0.5218 and 0.7457
Data/restraints/parameters	9773/2/542	9562/2/542
Goodness-of-fit on <i>F</i> ²	1.071	1.052
Final <i>R</i> indices [<i>I</i> 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0236, w <i>R</i> ₂ = 0.0580	<i>R</i> ₁ = 0.0148, w <i>R</i> ₂ = 0.0374
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0240, w <i>R</i> ₂ = 0.0582	<i>R</i> ₁ = 0.0149, w <i>R</i> ₂ = 0.0375
Largest diff. Peak/hole, eÅ ⁻³	0.401 and -1.898	1.404 and -1.062

5.3.2.5 SQUID

Magnetic measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL7, operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Susceptibility measurements were performed on freshly filtered, crushed crystalline samples of: **5.2** (18.8 mg), **5.3** (22.2 mg), **5.4** (21.4 mg), and **5.5** (24.1 mg), each wrapped within a polyethylene membrane. The magnetisation data were initially collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples. Solution measurements were also performed in order to elicit dilution behavior in **5.3** (3.5 mg), where the sample was dissolved in 0.3 mL H₂O and sealed in a polyethylene casing. After measurements were completed, the solution sample was re-dried and

measured for sample weight accuracy.

5.3.2.6 Computational Studies

All ab initio calculations were performed using the MOLCAS program package,⁴¹³ and were of CASSCF/RASSI/SINGLE_ANISO type.

Table 7. Calculated low-lying spin-orbit energy states for both Gd^{III} sites, arising from the zero-field splitting of the ground $S = 7/2$ (in cm⁻¹). Anisotropy parameters D and E are given for the zero-field splitting Hamiltonian: $H_{ZFS} = DS_z^2 + E(S_x^2 - S_y^2)$.

	Gd1						
	A1	A2	A3	B1	B2	C1	C2
	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.179	0.309	0.269	0.078	0.294	0.062	0.140
	0.341	0.618	0.536	0.212	0.537	0.176	0.321
	0.597	1.113	0.961	0.416	0.916	0.349	0.608
	<i>g</i> tensor for the ground Kramers doublet						
<i>g_x</i>	0.466	0.588	0.572	1.594	0.351	1.736	0.984
<i>g_y</i>	0.774	1.027	0.994	4.201	0.550	4.955	2.010
<i>g_z</i>	13.455	13.317	13.336	11.267	13.583	10.686	12.748
	Anisotropy parameters (<i>D</i> and <i>E</i>)						
<i>D</i>	0.045	0.085	0.073	-0.021	0.067	0.029	0.048
<i>E</i>	0.010	0.016	0.014	-0.016	0.017	0.002	-0.006
	Gd2						
	A1	A2	A3	B1	B2	C1	C2
	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.157	0.284	0.253	0.103	0.358	0.080	0.241
	0.314	0.570	0.494	0.233	0.610	0.190	0.415
	0.564	1.026	0.879	0.439	0.975	0.360	0.665
	<i>g</i> tensor for the ground Kramers doublet						
<i>g_x</i>	0.584	0.588	0.518	0.952	0.182	1.058	0.188
<i>g_y</i>	1.019	1.030	0.880	1.920	0.258	2.224	0.268
<i>g_z</i>	13.316	13.311	13.395	12.800	13.751	12.608	13.741
	Anisotropy parameters (<i>D</i> and <i>E</i>)						
<i>D</i>	0.043	0.079	0.067	-0.025	0.068	-0.009	0.046
<i>E</i>	-0.008	0.000	0.000	-0.015	0.022	0.000	0.015

Three structural models (A, B, and C) were designed to reproduce the environment of each Gd^{III} site in 5.3. Each model has been computationally described within three basis set approximations: 1, 2, and 3. Active space of the CASSCF method included 7 electrons in 7

orbitals, where all available spin states were optimized within state-average calculations. Overall, 7 computational approximations were calculated within the range of our computational resources (Table 7).

Broken-symmetry DFT calculations were employed to explore the exchange coupling between Gd^{III} ions within the chain. The ORCA program package was employed with the B3LYP functional for this scope,⁴¹⁴ with two structural models based on the SCXRD structure. In all cases, the calculated exchange coupling was found to be negligible. Model structures and further computational details can be found in the supporting information of the publication.⁴⁰⁷

5.4 Results and Discussion

Lanthanide EDTA chain structures, Na[Ln(EDTA)(H₂O)₃] · 5H₂O; where Ln = Y^{III} (**5.1**), Eu^{III} (**5.2**), Gd^{III} (**5.3**), Tb^{III} (**5.4**), and Dy^{III} (**5.5**), were prepared through solvothermal synthetic methods, followed by gradual solvent evaporation in order to isolate X-ray quality single crystals. Lanthanide EDTA complexes are well-known within the literature,^{403,412,415-427} however, their magnetic properties have, to the best of our knowledge, never been explored.

Complex **5.1** crystallizes to form a one-dimensional chain structure in the orthorhombic space group, Fdd2, with cell constants *a*, *b*, *c*, of 19.2891(14) Å, 35.214(3) Å, and 12.0446(9) Å, respectively, and *α*, *β*, *γ* parameters of 90°. Conversely, the other chain structures crystallized in the monoclinic space group, *Cc*, with cell parameters *α*, *β*, *γ* of 90°, 108°, 90°, and similar cell constants. Further crystallographic information can be found in Table 5 and Table 6. Each Ln^{III} ion is nonacoordinate; with one EDTA ligand, two Na⁺ ion linkers and one coordinated water molecule within the coordination sphere (Figure 45). EDTA is bound hexadentate through two N atoms (N1, N2 or N3, N4) and four O atoms (O12, O14, O16, O18 or O1, O3, O5, O7) of the unidentate carboxylate groups. Two of the carboxylate groups additionally coordinate to Na. The remaining coordination sites are occupied by two O atoms (O10, O11 or O21, O22) from bridging water molecules, which, along with the O atoms (O5, O7 or O16, O18) from EDTA, provide a bridge between Na and Ln ions. Na ions are additionally coordinated to two water molecules. Intramolecular Ln distances are as follows: 6.0746(3) Å for **5.1**, 6.1013(1) Å for **5.2**, 6.0782(5) Å for **5.3**, 6.0716(3) Å for **5.4**, and 6.0927(2) Å for **5.5**. Closest intermolecular distances, conversely, are: 9.2971(1) Å for **5.1**, 9.3036(6) Å for **5.2**, 9.4729(6) Å for **5.3**, 9.3176(5) Å for **5.4**, and 9.2932(7) Å for **5.5**. Thus, it can be said that any interactions between spin carriers are likely arising from intramolecular influence.

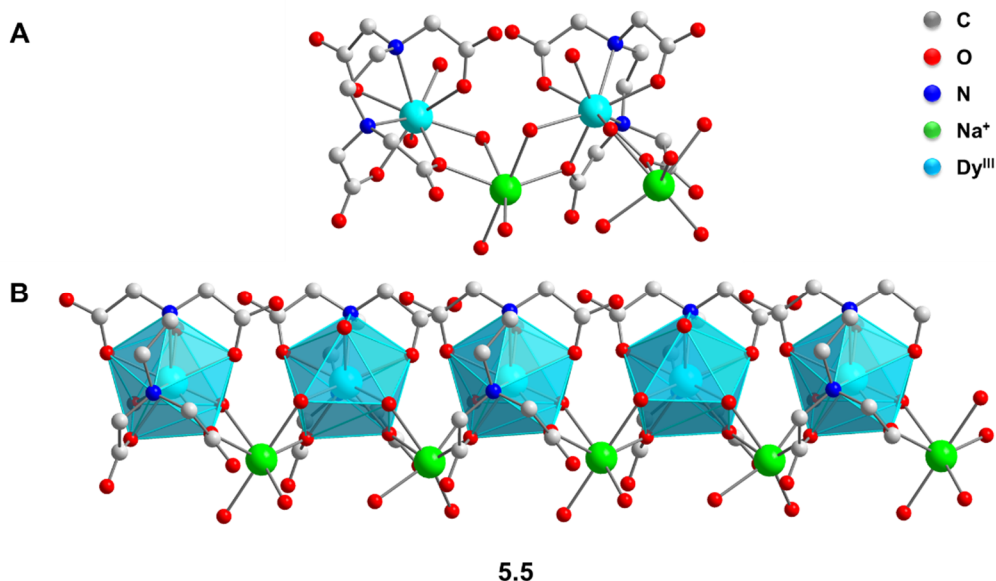


Figure 45. Single-crystal X-ray structure of **5.5**, displaying (A) the molecular unit in the chain, and (B) the chain structure with coordination polyhedra. Hydrogen atoms and water molecules within the lattice omitted for clarity.

The isostructural complexes, **5.2-5.5**, display very similar structural properties, which prompted us to consider the shape measure approach in order to determine the degree of similarity. We followed the method of Raymond and co-workers:⁴²⁸

$$AM = \min \left[\frac{1}{m} \sum_{i=1}^m (\delta_i - \theta_i)^2 \right] \quad (14)$$

Where AM = analogous measurement, δ_i = dihedral angle of polyhedral of complex of interest, θ_i = dihedral angle of polyhedra of reference complex, and m = number of dihedral angles. Employing the isotropic Gd^{III} analogue as reference, we obtained the following values for each structure: AM_{5.2} = 0.546842, AM_{5.4} = 0.484377, AM_{5.5} = 0.55259 (Table 8).

Table 8. Dihedral angles along the edges of coordination polyhedra, used to determine the analogous measurement (AM) of complexes **5.2-5.5**, where **5.3** was employed as reference.

Dihedral Angle	5.3, Ref	5.2	5.4	5.5
	Gd1	Eu1	Tb1	Dy1
N2-N1-O3^O7-N2-O3	22.075(340)	21.445(157)	21.880(397)	20.902(135)
N2-N1-O3^O1-N2-N1	66.272(357)	66.697(125)	66.770(372)	67.411(123)
N2-N1-O3^O3-N1-O9	66.731(283)	67.090(119)	66.617(364)	67.570(108)
N2-O7-O3^O7-O3-O10	53.199(261)	52.878(124)	53.346(312)	53.438(104)
N2-O7-O3^N2-O7-O5	61.510(253)	61.933(114)	62.031(299)	62.402(106)
O1-N2-N1^N1-O1-O9	58.226(302)	58.057(129)	57.454(342)	58.212(120)
O1-N2-N1^O1-N2-O5	40.494(317)	40.215(127)	41.467(362)	41.02(11)
O5-O1-N2^O11-O1-O5	38.221(253)	38.176(119)	36.871(290)	37.160(107)
O5-O1-N2^O7-O5-N2	59.007(261)	58.771(106)	59.322(314)	58.471(91)
O11-O5-O1^O9-O1-O11	54.455(269)	54.383(125)	55.187(323)	55.482(108)
O11-O5-O1^O11-O10-O5	75.165(241)	75.395(111)	75.10(28)	74.644(92)
O10-O9-O3^O7-O3-O10	54.385(249)	55.212(119)	54.349(311)	54.725(103)
O10-O5-O11^O10-O9-O11	69.787(287)	70.588(125)	69.717(329)	69.884(103)
O9-O10-O11^O11-O1-O9	56.485(288)	56.711(113)	56.709(333)	56.484(97)
O9-O10-O11^O9-O3-O10	50.199(271)	50.142(109)	49.625(307)	49.489(98)
O9-O11-O1^O9-N1-O1	36.301(297)	35.759(131)	35.643(375)	35.183(114)
N1-O9-O1^O9-O3-N1	57.130(337)	56.806(144)	57.272(439)	57.298(111)
O9-O3-N1^O9-O3-O10	35.427(257)	34.768(123)	35.352(346)	35.016(115)
O5-O7-O10^O11-O5-O10	8.541(273)	8.031(124)	9.261(300)	9.097(98)
O5-O7-O10^N2-O5-O7	57.659(275)	57.926(129)	57.158(328)	57.364(109)
O5-O7-O10^O7-O10-O3	65.861(250)	66.589(110)	65.759(270)	66.057(82)
	Gd2	Eu2	Tb2	Dy2
O22-O20-O21^O20-O12-O21	49.254(306)	49.949(106)	48.729(338)	48.511(93)
O22-O20-O21^O20-O14-O22	56.674(315)	56.677(116)	56.159(357)	56.446(102)
O22-O20-O21^O22-O18-O21	70.990(321)	70.733(125)	71.158(346)	71.225(99)
O20-O21-O12^O12-O16-O21	55.559(252)	55.291(111)	55.972(326)	55.594(92)
O20-O21-O12^O20-N3-O12	34.333(297)	34.811(131)	34.164(354)	34.434(102)
O16-O12-O21^O18-O21-O16	66.683(229)	66.610(103)	66.580(285)	66.049(80)
O16-O12-O21^O16-N4-O12	53.449(284)	52.860(124)	53.592(346)	53.564(95)
O18-O16-N4^N4-O16-O12	62.705(283)	61.984(113)	62.655(294)	62.736(98)
O18-O16-N4^N4-O14-O18	58.312(291)	58.730(121)	58.463(300)	58.560(98)
O18-O14-N4^O14-O22-O18	37.998(257)	38.156(125)	38.125(319)	37.603(106)
O18-O14-N4^O14-N3-N4	40.582(335)	40.227(136)	40.000(344)	40.936(122)
O14-N3-N4^N4-N3-O12	68.027(345)	66.751(136)	68.477(340)	68.112(130)
O14-N3-N4^N3-O20-O14	57.472(329)	58.172(123)	58.440(305)	57.501(113)
O20-N3-O12^O14-N3-O20	56.858(349)	56.778(140)	56.738(337)	57.005(112)
O20-N3-O12^N3-N4-O12	67.808(296)	67.148(123)	68.629(345)	67.637(104)
O22-O18-O21^O14-O22-O18	74.594(266)	75.273(126)	74.272(275)	74.286(92)
O18-O16-O21^O18-N4-O16	57.968(307)	57.779(127)	57.703(326)	57.358(101)
O12-N4-N3^O16-O12-N4	19.798(414)	21.467(142)	19.463(393)	20.293(137)
O14-O20-N3^O20-O22-O14	35.739(295)	35.607(133)	35.257(333)	35.387(109)
O18-O21-O16^O21-O22-O18	8.578(279)	7.997(116)	8.704(292)	9.146(93)
O20-O22-O14^O18-O14-O22	54.403(299)	54.577(132)	54.706(315)	55.053(109)
AM	0	0.546842	0.484377	0.55259

The slight changes in dihedral angles between complexes are likely the result of one or more of the following: geometrical constraints of the multidentate ligand, ligand field effects and/or lanthanide contraction.³⁸⁹

Table 9. Dihedral angles along the edges of the coordination polyhedra used to determine the analogous measurement (AM) of polyhedra Gd1 vs. Gd2, Tb1 vs. Tb2, and Dy1 vs. Dy2 within complexes **5.3**, **5.4**, and **5.5**.

Dihedral Angle	Gd1	Tb1	Dy1
O5-O7-O10^O11-O5-O10	22.075(340)	9.261(300)	9.097(98)
N2-N1-O3^O7-N2-O3	66.272(357)	21.880(397)	20.902(135)
O9-O3-N1^O9-O3-O10	66.731(283)	35.352(346)	35.016(115)
O9-O11-O1^O9-N1-O1	53.199(261)	35.643(375)	35.183(114)
O5-O1-N2^O11-O1-O5	61.510(253)	36.871(290)	37.160(107)
O1-N2-N1^O1-N2-O5	58.226(302)	41.467(362)	41.02(11)
O9-O10-O11^O9-O3-O10	40.494(317)	49.625(307)	49.489(98)
N2-O7-O3^O7-O3-O10	38.221(253)	53.346(312)	53.438(104)
O10-O9-O3^O7-O3-O10	59.007(261)	54.349(311)	54.725(103)
O11-O5-O1^O9-O1-O11	54.455(269)	55.187(323)	55.482(108)
O9-O10-O11^O11-O1-O9	75.165(241)	56.709(333)	56.484(97)
N1-O9-O1^O9-O3-N1	54.385(249)	57.272(439)	57.298(111)
O5-O7-O10^N2-O5-O7	69.787(287)	57.158(328)	57.364(109)
O1-N2-N1^N1-O1-O9	56.485(288)	57.454(342)	58.212(120)
O5-O1-N2^O7-O5-N2	50.199(271)	59.322(314)	58.471(91)
N2-O7-O3^N2-O7-O5	36.301(297)	62.031(299)	62.402(106)
O5-O7-O10^O7-O10-O3	57.130(337)	65.759(270)	66.057(82)
N2-N1-O3^O1-N2-N1	35.427(257)	66.770(372)	67.411(123)
N2-N1-O3^O3-N1-O9	8.541(273)	66.617(364)	67.570(108)
O10-O5-O11^O10-O9-O11	57.659(275)	69.717(329)	69.884(103)
O11-O5-O1^O11-O10-O5	65.861(250)	75.10(28)	74.644(92)
	Gd2	Tb2	Dy2
O18-O21-O16^O21-O22-O18	49.254(306)	8.704(292)	9.146(93)
O12-N4-N3^O16-O12-N4	56.674(315)	19.463(393)	20.293(137)
O20-O21-O12^O20-N3-O12	70.990(321)	34.164(354)	34.434(102)
O14-O20-N3^O20-O22-O14	55.559(252)	35.257(333)	35.387(109)
O18-O14-N4^O14-O22-O18	34.333(297)	38.125(319)	37.603(106)
O18-O14-N4^O14-N3-N4	66.683(229)	40.000(344)	40.936(122)
O22-O20-O21^O20-O12-O21	53.449(284)	48.729(338)	48.511(93)
O16-O12-O21^O16-N4-O12	62.705(283)	53.592(346)	53.564(95)
O20-O22-O14^O18-O14-O22	58.312(291)	54.706(315)	55.053(109)
O20-O21-O12^O12-O16-O21	37.998(257)	55.972(326)	55.594(92)
O22-O20-O21^O20-O14-O22	40.582(335)	56.159(357)	56.446(102)
O20-N3-O12^O14-N3-O20	68.027(345)	56.738(337)	57.005(112)
O18-O16-O21^O18-N4-O16	57.472(329)	57.703(326)	57.358(101)
O14-N3-N4^N3-O20-O14	56.858(349)	58.440(305)	57.501(113)
O18-O16-N4^N4-O14-O18	67.808(296)	58.463(300)	58.560(98)
O18-O16-N4^N4-O16-O12	74.594(266)	62.655(294)	62.736(98)
O16-O12-O21^O18-O21-O16	57.968(307)	66.580(285)	66.049(80)
O20-N3-O12^N3-N4-O12	19.798(414)	68.629(345)	67.637(104)
O14-N3-N4^N4-N3-O12	35.739(295)	68.477(340)	68.112(130)
O22-O20-O21^O22-O18-O21	8.578(279)	71.158(346)	71.225(99)
O22-O18-O21^O14-O22-O18	54.403(299)	74.272(275)	74.286(92)
AM	0.646245	0.78927	0.346301

We also performed shape analysis on polyhedra of **5.3**, **5.4** and **5.5** in order to compare the shape of the coordination sphere around Ln1 *versus* Ln2 in each complex. The results can be

seen in Table 9, where Gd1/Gd2 and Tb1/Tb2 polyhedra differed significantly from one another in **5.3** (0.646245) and **5.4** (0.78927), as compared to Dy1/Dy2 polyhedra in **5.5**, which showed a much more modest AM value (0.346301).

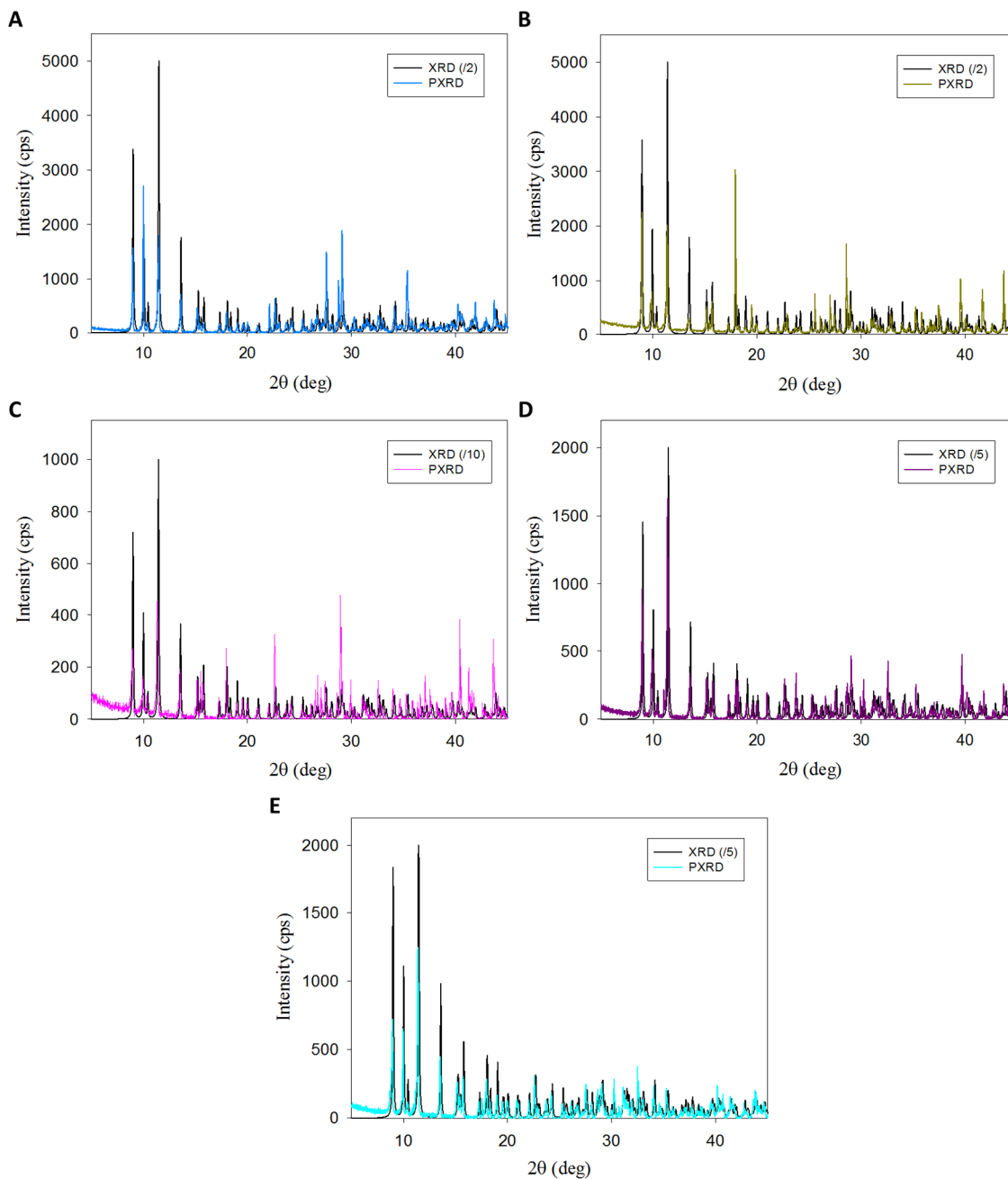


Figure 46. XRPD patterns of (A) **5.1** (blue), (B) **5.2** (gold), (C) **5.3** (pink), (D) **5.4** (purple), and **5.5** (cyan) for air-dried single crystals in the 5–45° 2θ region, as compared with the theoretical pattern generated from SCXRD data of each structure (black).

X-ray powder diffraction experiments were employed in order to obtain the bulk purity and crystalline phase purity of the materials. The diffraction patterns were all in excellent agreement with the calculated patterns obtained from SCXRD experiments (Figure 46). IR spectroscopic analyses were also performed in order to provide an additional structural fingerprint (Figure 47).

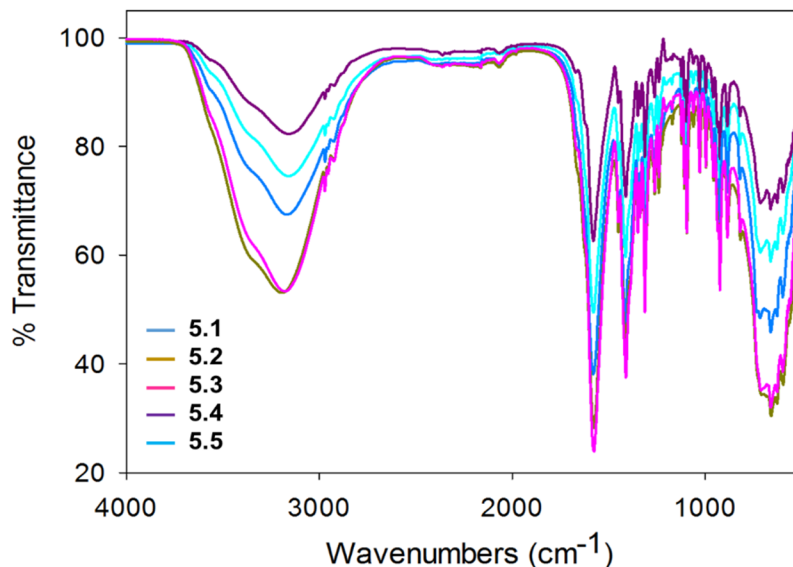


Figure 47. FTIR spectra of **5.1-5.5** for vacuum filtered crystals in the 4000-600 cm^{-1} region.

In order to investigate any potential dipolar or superexchange interactions through bridging moieties in these chain structures, static magnetic measurements were performed. Due to the diamagnetic nature of Y^{III} , **5.1** was not investigated using SQUID magnetometry. However, for the remaining samples the temperature dependence of the direct current (dc) magnetic susceptibility was measured between 1.8 and 300 K, with an applied static dc field of 1000 Oe (Figure 48). The room temperature χT value for **5.2** was found to be $1.28 \text{ cm}^3\text{Kmol}^{-1}$, which is attributed to the presence of thermally populated excited states (Eu^{III} : 7F_0 , $S = 3$, $L = 3$, $g = 5$). The low temperature value, $\chi T_{1.8 \text{ K}} = 0.01 \text{ cm}^3\text{Kmol}^{-1}$, is indicative of the non-magnetic ground state. Conversely, the room temperature χT value for **5.3**, $7.37 \text{ cm}^3\text{Kmol}^{-1}$, was consistent with the theoretical value of $7.88 \text{ cm}^3\text{Kmol}^{-1}$ for an isolated Gd^{III} ion (${}^8S_{7/2}$, $S = 7/2$, $L = 0$, $g = 2$). The χT product remains constant upon decreasing T , as expected for isotropic Gd^{III} , however, at very low T we observe a decrease in the value to $7.12 \text{ cm}^3\text{Kmol}^{-1}$. As mentioned, according to the SCXRD structure, any interactions between ions likely arise from intra-chain interactions.

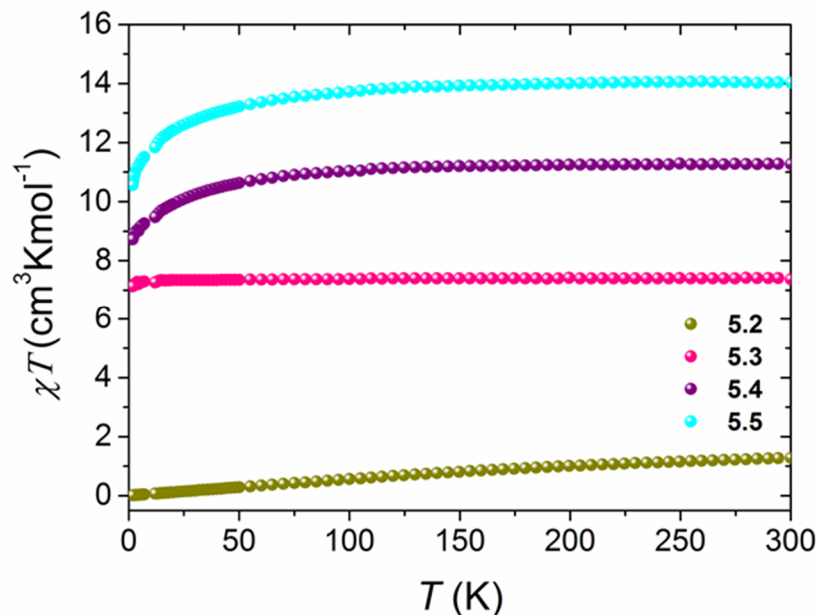


Figure 48. Temperature dependence of the χT product at 1000 Oe for **5.2**, **5.3**, **5.4** and **5.5**.

The room temperature χT value for **5.4** was found to be $11.27 \text{ cm}^3\text{Kmol}^{-1}$, which is consistent with the theoretical value, $11.82 \text{ cm}^3\text{Kmol}^{-1}$, for a single Tb^{III} ion (7F_6 , $S = 5/2$, $L = 3$, $g = 3/2$). The χT value remains consistent until around 50 K, where it begins to decrease to a low temperature value of $\chi T_{1.8 \text{ K}} = 8.72 \text{ cm}^3\text{Kmol}^{-1}$. This decrease is indicative of one of the following possible contributions: (i) antiferromagnetic interactions between the lanthanide centers; (ii) the thermal depopulation of the Stark sub-levels; and/or (iii) the presence of significant magnetic anisotropy. Finally, the room temperature χT value for **5.5** was found to be $14.03 \text{ cm}^3\text{Kmol}^{-1}$, which is consistent with the theoretical value, $14.17 \text{ cm}^3\text{Kmol}^{-1}$, for a single Dy^{III} ion ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$). Similar behaviour to that observed for **5.4** is shown by **5.5** where the χT value decreases, in this case from around 100 K, to a low temperature value of $\chi T_{1.8 \text{ K}} = 10.56 \text{ cm}^3\text{Kmol}^{-1}$, likely due to the inherent magnetic anisotropy of Dy^{III} ions. Due to the anisotropic nature of Tb^{III} and Dy^{III} ions, any minimal interaction between spin carriers is difficult to confirm.

In order to further probe potential magnetic interactions and/or the presence of magnetic anisotropy indicated by the static behaviour of Gd^{III} ions in **5.3**, field dependent magnetisation data was collected between 1.8 and 7 K (Figure 49B). The M vs. H data for the solid crystalline sample below 7 K demonstrates a rapid increase in magnetisation at low fields, up to 1 T. This behaviour is followed by a gradual increase to plateau at $6.77 \mu_{\text{B}}$ at 1.8 K. The M vs. HT^{-1} data displays magnetically saturated curves, overlapping on a single master curve, thus indicating the

isotropic nature of Gd^{III} . We subsequently probed the static behaviour in frozen solution (Figure 49A and C), where the previously observed drop in χT value down to 1.8 K is no longer observed, likely due to the lack of close contact remaining between ions in the diluted sample. Furthermore, the M vs. HT^{-1} plot displays that a saturation point is not reached, and curves no longer overlay on a single master curve, indicating the presence of minimal magnetic anisotropy in the diluted sample and/or low lying excited states.

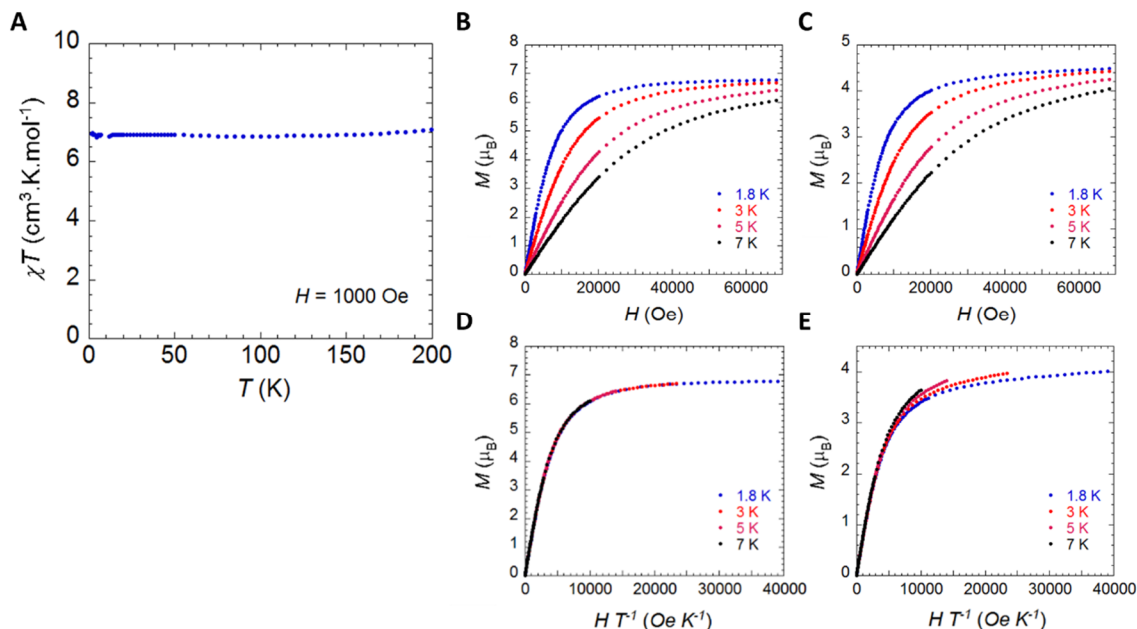


Figure 49. (A) Temperature dependence of the χT product at 1000 Oe for 2 mM **5.3** in frozen aqueous solution. Field dependence of the magnetisation for crystalline solid **5.3** (B), and 2 mM **5.3** in frozen aqueous solution (C). M vs. HT^{-1} plot for crystalline solid **5.3** (D) and for 2 mM **5.3** in frozen aqueous solution (E), at indicated temperatures.

Field dependent magnetisation measurements were also performed for **5.2**, **5.4** and **5.5** (Figure 52). The thermal population of the ground state for **5.2** (Figure 52A) results in a magnetisation close to zero, as expected. The M vs. H curves for **5.3** and **5.4** display a lack of saturation to 7 T, as is commonly observed for lanthanide systems. Plots of the M vs. H/T data for **5.4** and **5.5** do not superimpose on a single master curve, indicating the presence of significant magnetic anisotropy.

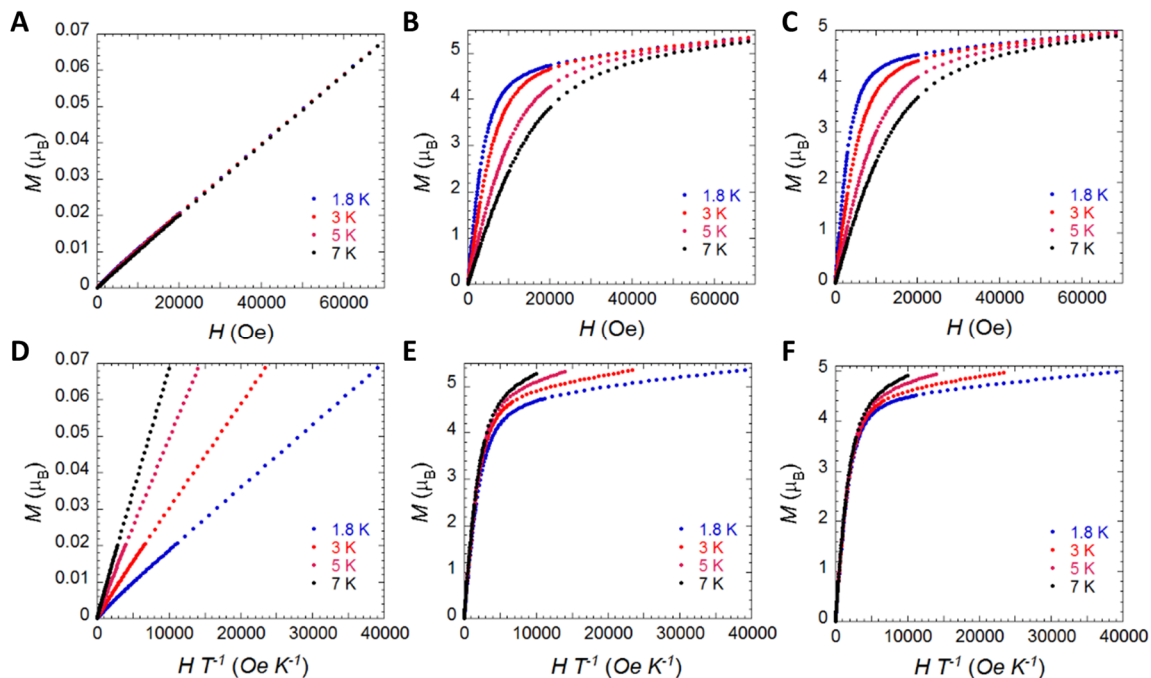


Figure 50. Field dependence of the magnetisation for: **5.2** (A), **5.4** (B) and **5.5** (C), and M vs. HT^{-1} plot for: **5.2** (D), **5.4** (E) and **5.5** (F), at indicated temperatures.

Potential dynamic magnetic properties were investigated using alternating current magnetic measurements on isotropic **5.3** and anisotropic **5.4** and **5.5**. Initially, measurements were performed under zero applied dc field, however, due to the presence of fast relaxation processes, likely attributed to significant QTM, we were not able to fully discern peak maxima in the out-of-phase susceptibility. In particular, due to the isotropic nature of Gd^{III}, no out-of-phase signal is observed under zero field, which is attributed to large transversal magnetic moments eliciting fast QTM.^{407,429} In order to minimize QTM, and promote the appearance of clear peak maxima, an optimised dc field was applied to each sample, which was found to be 4500 Oe for **5.3**, 3000 Oe for **5.4** and 1200 Oe for **5.5**. The dynamic behaviour of these complexes was then investigated under their respective optimised fields. Frequency dependent in-phase (χ') and out-of-phase (χ'') magnetic susceptibility plots can be observed in Figure 51 and Figure 52.

The frequency dependent data, χ' and χ'' , from 17-1.9 K for **5.3** clearly displays two very distinct relaxation processes, which were fit accordingly using a Gaussian model. The effective energy barriers and relaxation times were obtained through fitting data using the Arrhenius equation ($\tau = \tau_0 \exp(U_{\text{eff}}/kT)$), which elicited a value of $U_{\text{eff}} = 6.1(0)$ K ($\tau_0 = 4.1(2) \times 10^{-2}$ s) for the low frequency relaxation process, and $U_{\text{eff}} = 83.8(4)$ K ($\tau_0 = 7.9(7) \times 10^{-7}$ s) for the high frequency

process, as can be seen inset within Figure 51. Furthermore, the ac behavior was also investigated in aqueous solution, where a signal was no longer observed under an applied static field.

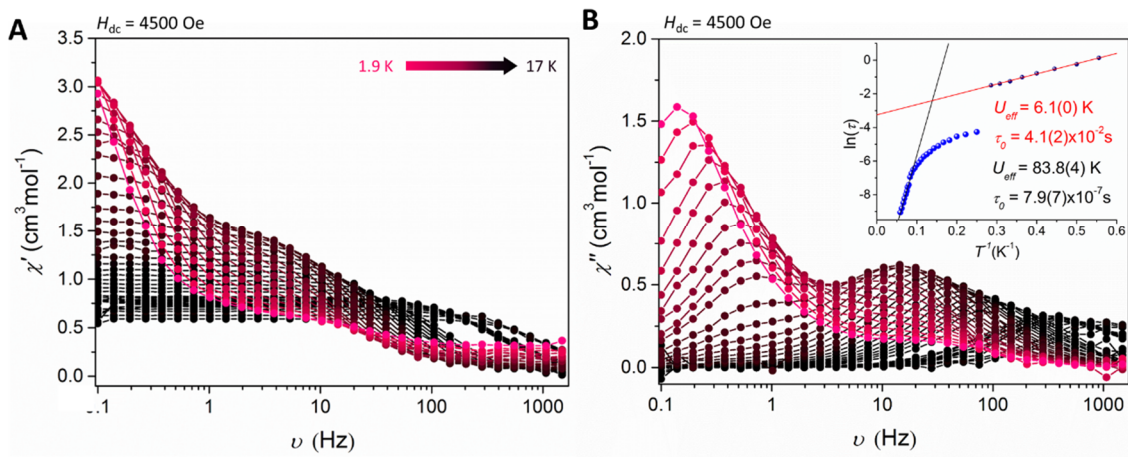


Figure 51. Frequency dependence of the (A) in-phase (χ') and (B) out-of-phase (χ'') susceptibility for **5.3** between 1.8 and 7 K under a 4500 Oe applied dc field. Solid lines are guides for the eye. Inset is the Arrhenius plot using χ'' (blue) ac data, for each relaxation process, under 4500 Oe applied dc field. The solid lines correspond to the fits of the data.

In order to gain insight into the origin of the unusual dynamic magnetic behaviour of **5.3**, *ab initio* calculations were performed on individual Gd^{III} sites.⁴⁰⁷ The performed calculations reveal a weak zero-field splitting of the ground spin $S = 7/2$ (~ 0.6 cm⁻¹) for both Gd^{III} metal sites. The obtained values are in agreement with the anisotropy parameters obtained from DFT calculations. Furthermore, the splitting of isotropic $S = 7/2$ in applied field of 4500 Oe is 2.94 cm⁻¹, while the total splitting including the calculated ZFS on Gd^{III} does not exceed 3.5 cm⁻¹. This shows that the activation barriers extracted above cannot correspond to any excited states on Gd^{III} sites. This was further probed through broken-symmetry DFT calculations performed on binuclear fragment models, which revealed negligible exchange interaction between Gd^{III} sites within the chain. Therefore, intra- and inter-chain magnetic interactions between Gd^{III} sites are mostly of dipolar origin. Calculations show that the dipolar coupling between isotropic spins of nearest neighbour Gd^{III} ions induce a splitting of only ~ 0.38 cm⁻¹. Given the lowest measuring temperature of 1.8 K, this interaction cannot be responsible for the observed slowing down of magnetic relaxation. This is due to the fact that intermolecular magnetic interaction in crystals can contribute to magnetic blocking only at temperatures that are significantly lower than the

interaction between neighbour sites (corresponding exchange/dipolar splitting), and only for quasi one-dimensional structures, SCMs.^{430,431} Thus, if the interaction between chains is not sufficiently weak, magnetic ordering through intermolecular interactions will occur before this interaction can contribute to magnetic blocking. In this case, the dipolar interaction acts in the opposite manner, eliciting faster relaxation on Gd^{III} sites. This is in agreement with the lack of signal observed under zero dc field, which is expected for isotropic systems such as Gd^{III} since they possess large transversal magnetic moments, leading to fast QTM.^{407,429} The applied field of 4500 Oe suppresses QTM (Arrhenius plot inset within Figure 51), thus confirming that the observed slow magnetic relaxation processes are due to interlevel spin-phonon transitions on each different Gd^{III} site. Spin-phonon relaxation rates in Gd^{III} complexes are expected to be orders of magnitude smaller than in strongly anisotropic compounds, thus explaining why slow relaxation was observed even at T up to 17 K (Figure 51). Contrary to other lanthanides, the magnetic relaxation for Gd^{III} does not reduce to a dynamic within the two lowest energy levels, even at low temperatures, but instead involves transitions between many levels. This becomes evident from simulations of temperature dependence of τ in the low- T domain which is found to significantly differ from conventional lanthanide cases.^{285,432,433}

The frequency dependent data, χ' and χ'' , from 7-1.9 K for **5.4** and **5.5** was fit using a generalised Debye model, with a distribution (α) of relaxation times (τ).^{434,435} The results of these fittings confirmed that the distribution parameter has a wide range for **5.4**, and a slightly narrower range for **5.5** at low temperature, which widens as the temperature approaches 7 K. These values confirm the presence of multiple relaxation processes present in the 1.8-7 K range for **5.4**. This can be clearly observed in Figure 52A, where it becomes apparent that **5.4** does not exhibit Arrhenius-type relaxation behaviour ($U_{\text{eff}} = 5.7(0)$ K, $\tau_0 = 3.3(5) \times 10^{-2}$ s), and therefore cannot be fit using this model. The application of high magnetic fields promotes the occurrence of intra- and inter-chain interactions, making it difficult to pinpoint the exact behaviour due to the collective nature of such interactions. Thus, this can serve as a caution when applying static dc fields in order to study such systems.

An effective energy barrier was obtained for **5.5** through modelling relaxation time data using the Arrhenius equation ($\tau = \tau_0 \exp(U_{\text{eff}}/kT)$), giving a value of $U_{\text{eff}} = 55.5(2)$ K ($\tau_0 = 4.0(0) \times 10^{-10}$ s) for **5.5** (Figure 52B, inset). Thus, a significant difference in relaxation rate is observed between Gd^{III}, Tb^{III} and Dy^{III} ions within these 1D chains. This can likely be attributed to a combination of factors, including; (i) the absolute values of D , (ii) the influence of non-integer Kramer systems in low-symmetry environments, as well (iii) as the variation in

directionality of anisotropy axes between spin carriers due to their differing coordination polyhedra, which has shown to have an incredible effect on the resulting relaxation properties.^{436,437}

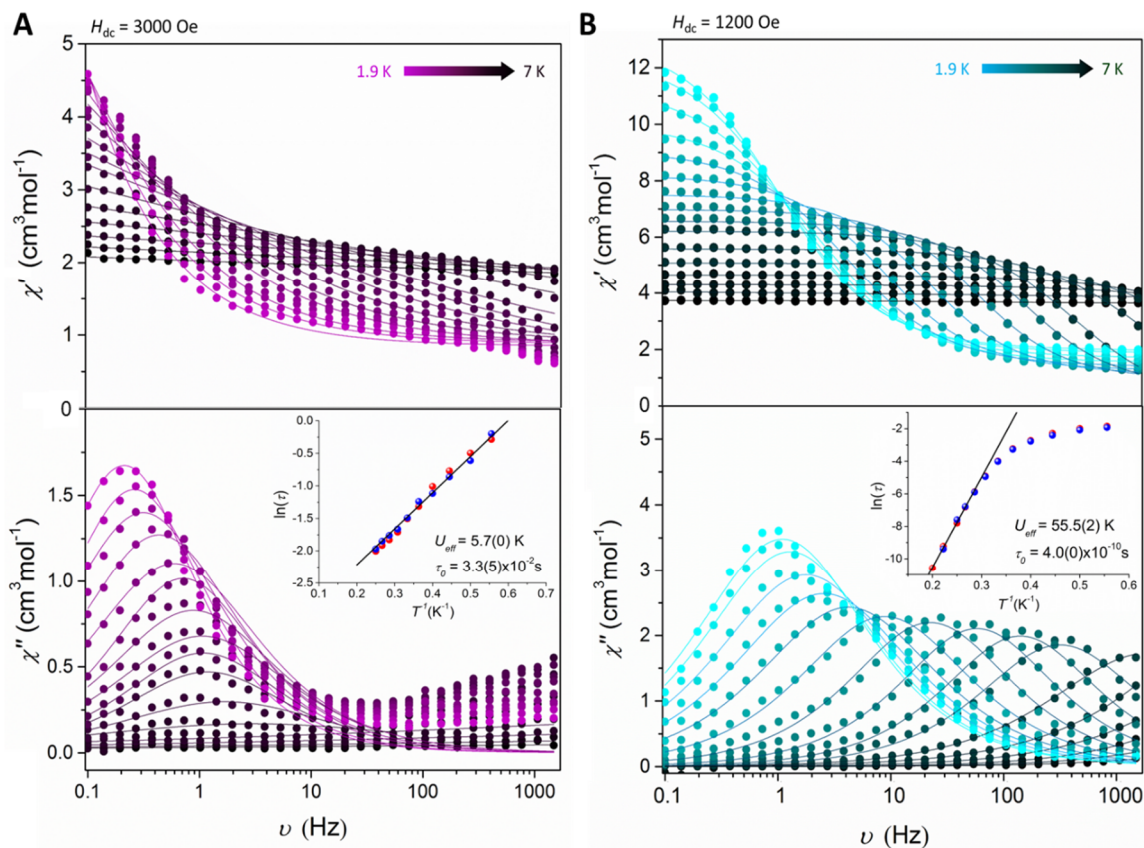


Figure 52. (A) Frequency dependence of the (top) in-phase (χ') and (bottom) out-of-phase (χ'') susceptibility for **5.4** between 1.8 and 7 K under a 3000 Oe applied dc field. (B) Frequency dependence of the (top) in-phase (χ') and (bottom) out-of-phase (χ'') susceptibility for **5.5** between 1.8 and 7 K under a 1200 Oe applied dc field. Solid lines are fits to a generalised Debye model. Inset are the Arrhenius plots using χ' (red) and χ'' (blue) ac data under 3000 Oe (**5.4**) and 1200 Oe (**5.5**) applied dc field. The solid black lines correspond to the fits of the data.

The anisotropy axes were modelled for **5.3** and **5.5** (Figure 53), illustrating the similarity between the g_z vectors for Gd2 and Dy2, respectively. However, the axes for Gd1 and Dy1 are quite different in their orientation. Ideally, anisotropic axes would be aligned along one direction, allowing for the magnetic moments to become additive. In **5.3** the vectors are almost

perpendicular in orientation, however, in **5.5** the vectors are in close alignment with one another. Despite their similar orientation, the magnetic moments of Dy^{III} ions within **5.5** have not displayed significant magnetic interactions, thus we must conclude that the observed magnetic relaxation behaviour is attributed to single-ions. Interestingly, since it was determined that the unexpected slowing of magnetic relaxation in the Gd^{III} system was not attributed to the weak dipolar interactions between single ions, but was instead a result of interlevel spin-phonon transitions on each Gd^{III} site,⁴⁰⁷ this cannot be ruled out as a contributing factor to the relaxation processes discussed above for **5.4** and **5.5**.

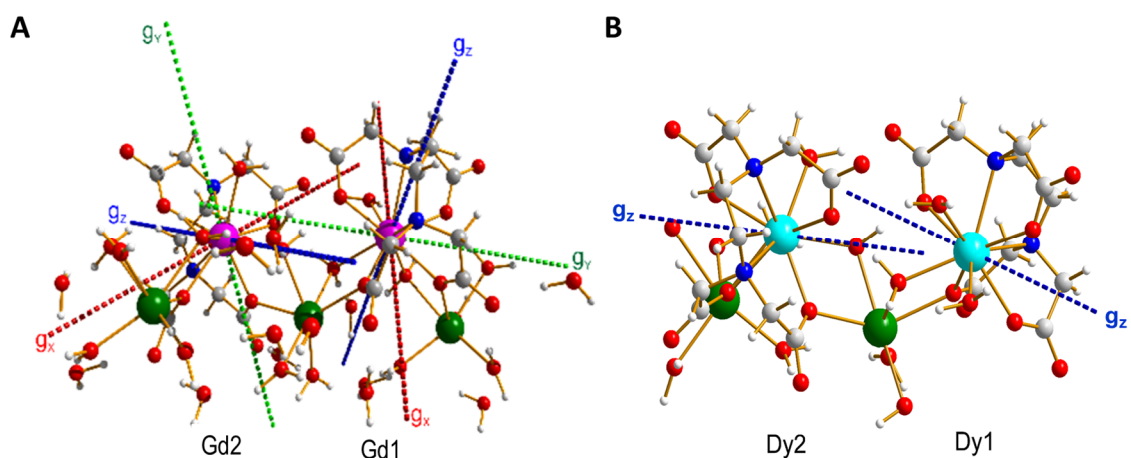


Figure 53. Magnetic anisotropy of the ground Kramers doublets on (A) Gd^{III} sites in **5.3** and (B) Dy^{III} sites in **5.5**, with respect to the molecular frame, arising due to spin-orbit coupling on metal sites. Axes modelled according to the results from (A) ab initio calculations, and (B) Magellan magnetic software.⁴³⁸

Cole-Cole plots were employed in order to further study the multiple relaxation processes observed within **5.3**, **5.4** and **5.5**. A generalised Debye model, akin to those employed in fitting the in-phase and out-of-phase frequency dependent susceptibility data for **5.4** and **5.5** was employed in fitting **5.5** in order to probe the goodness-of-fit of this data to a single relaxation process model. The curves were able to be fit, and the resulting distribution values were in good agreement with the other Debye fitted data. Thus, we can confirm that Dy^{III} ions within **5.5** relax independently, however, due to their comparable coordination environments they exhibit similar relaxation behaviour at low T . As discussed in the structural characterisation section above, there

are two distinct metal sites within each chain structure. We were able to show that Gd^{III} and Tb^{III} ions within **5.3** and **5.4** differ more significantly in their polyhedral shapes. Consequently, this contributes significantly to their distinct relaxation processes. The two Dy^{III} sites in **5.5**, however, differ only slightly in their coordination polyhedra, which explains the much more subtle appearance of a secondary relaxation process. From these results, we believe that we can rule out single-ion-derived multiple relaxation processes, as were observed in a Dy^{III} chelated single-ion complex with chelating DOTA as the ligand.⁴³⁹

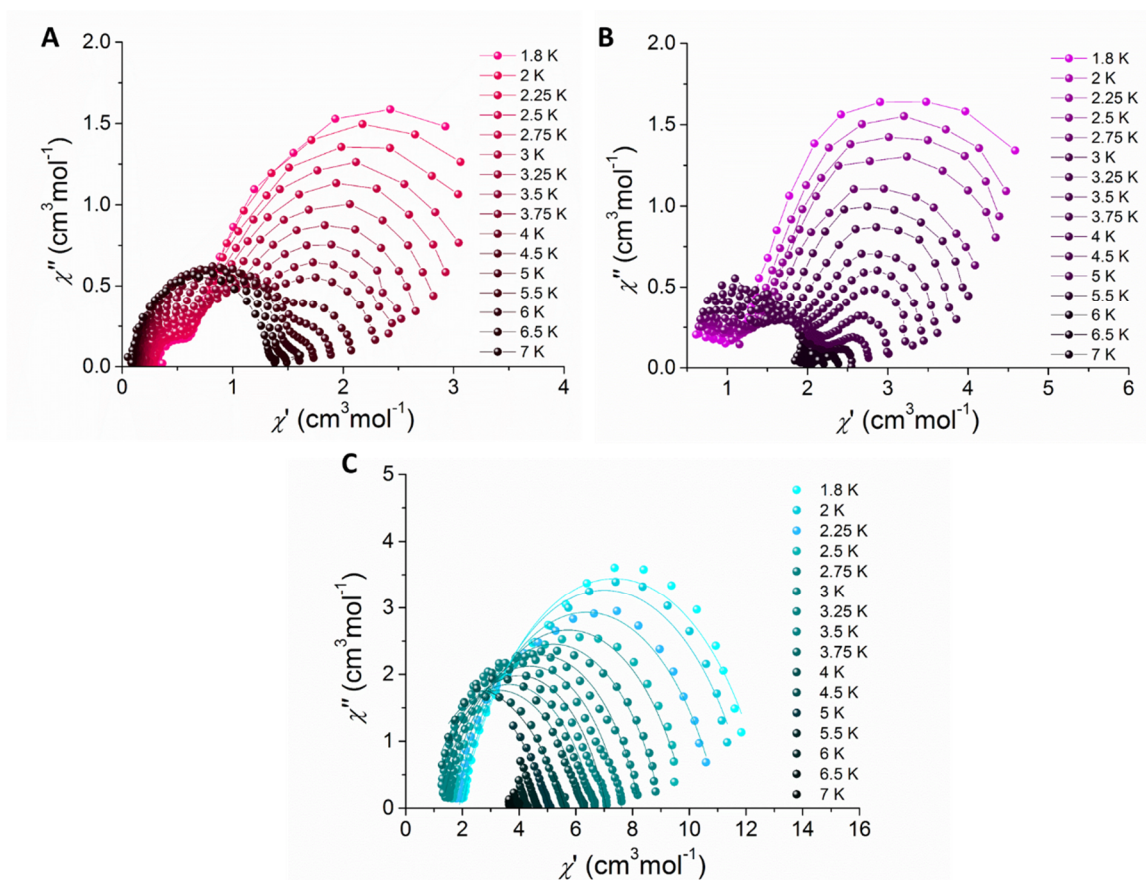


Figure 54. Cole-Cole plot for frequency dependent ac susceptibility data of: (A) **5.3** under 4500 Oe applied dc field, (B) **5.4** under 3000 Oe applied dc field, and (C) **5.5** under 1200 Oe applied dc field. Solid lines are guides for the eye in (A) and (B). Solid lines are the best fit to the generalised Debye model in (C).

5.5 Conclusions

This chapter has presented a family of lanthanide molecular magnets with chelating ligand EDTA and Na^+ ion bridges causing the formation of 1D networks. These structures were characterised through SCXRD and XRPD. Shape analyses were performed in order to compare the similarity in coordination of each analogous structure. Furthermore, shape analyses were performed in order to compare coordination polyhedra of each crystallographically unique lanthanide ion within isotropic Gd^{III} and anisotropic Tb^{III} and Dy^{III} complexes.

The structural characterisations were performed in order to facilitate magneto-structural comparisons using SQUID magnetometry. No interactions between magnetic ions were able to be confirmed, however, we did observe slow relaxation of the magnetisation in Gd^{III} , Tb^{III} and Dy^{III} chain structures. Thus, these structures act as molecular entities as opposed to SCMs. The Gd^{III} chain was the most surprising, as the zero-field behavior observed was typical of a theoretical isotropic paramagnet, however, under an applied static field, peak shifting phenomena characteristic of anisotropic field-induced molecular magnets was observed. This was attributed to spin-phonon transitions between Gd^{III} levels, which are not separated by an energy barrier. This mechanism of slow magnetic relaxation is possible due to small spin-phonon rates, and can be attributed to the chain architecture, as the diluted frozen solution measurements did not show this behavior. Interestingly, the Gd^{III} and Tb^{III} chains displayed multiple relaxation processes as a result of the varied coordination environments shown from shape analysis between the two crystallographically different Ln ions within the molecular unit of the chain. Conversely, the Dy^{III} structure displayed a single relaxation process, however, an additional process began to appear at higher T .

Overall, these structures display the potential to study well-separated 1D networks of magnetic molecules, and the effects of their ordered array on the magnetic properties of the unit. Due to the interest in controlling arrays of magnetic molecules in various dimensionalities, this work has shown that it is possible to form ordered 1D chains of molecular magnets, without necessarily inducing SCMs through significant magnetic interaction. Some unique potential applications of these structures will be further discussed in Chapter 9.

Chapter 6

Studying Magnetic Clusters in 3D: Co^{II} Cuboctahedron as the SBU in a Novel MOF

6.1 Abstract

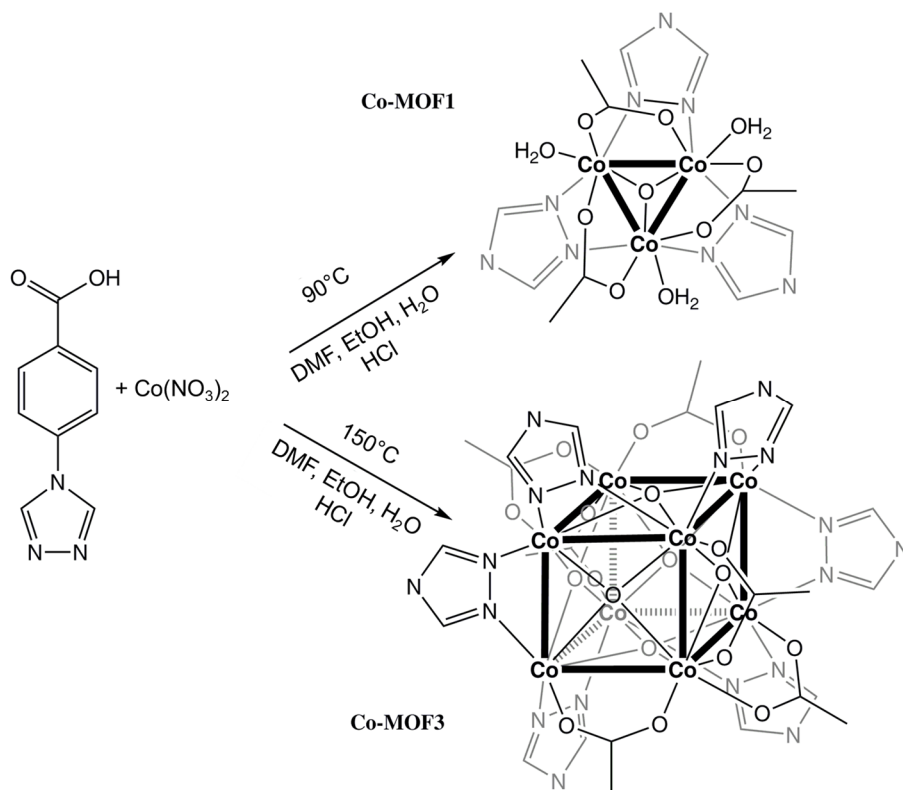
Magnetic metal-organic frameworks with well-separated SBUs present an interesting methodology for studying discrete molecular magnetic systems ordered in three dimensions. As discussed in Chapter 2, interesting magnetic properties have been displayed by Co^{II} MOF systems with discrete SBUs, as well as those with chain-like networks of paramagnetic ions. One challenge that arises in the design of such systems is the gap between the finite control over the properties of molecular systems (SMMs) and 3D magnetic networks. Thus, through the use of specific design strategies we will focus on the development of a new MOF material with high-nuclearity paramagnetic SBUs, which are well-separated from one another as a result of carefully designed ligands. This chapter details the synthesis and study of a new Co^{II} MOF with a unique cuboctahedron SBU (**6**). The MOF is extensively characterised for its structural properties through SCXRD and XRPD, as well as its thermal stability and gas adsorption properties for comparative purposes with other frameworks. Furthermore, its magnetic interactions and their resulting properties were studied using SQUID magnetometry and modelled with DFT in order to gain a better understanding of the fundamental magnetic properties of discrete magnetic clusters ordered in 3D. This work was published in a special Emerging Investigators Issue: Holmberg, R. J.; Kay, M.; Korobkov, I.; Kadantsev, E.; Aharen, T.; Desgreniers, S.; Woo, T. K.; Murugesu, M. *Chem. Commun.* **2014**, 50, 5333-5335.

6.2 Introduction

The synthesis of novel MOF materials facilitates the exploration of a wide variety of properties, leading to potential applications within: magnetism,^{236,440} catalysis,^{231,441,442} gas storage,⁴⁴³⁻⁴⁴⁶ chemical sensing,^{447,448} separation and drug delivery,^{236,449-453} among many others. Thus, novel synthetic methods for MOFs are constantly being diversified through the use of different metal ions and organic linkers, based on their potentially beneficial properties. Often the organic linkers are rigid in order to promote controlled synthetic pathways towards desired topologies and pore architectures, however, despite the extensive research in this area the majority of MOF structures

are inadvertently obtained. The secondary building unit of a MOF is often directly responsible for its inherent properties, and thus is frequently the primary focus of synthetic design. Often, low metal nuclearity SBUs are obtained, as large cluster formation is difficult to control. As such, the nucleation of suitable single crystals often occurs without synthetic control of the composition and/or coordination within the SBU.⁴⁵⁴⁻⁴⁵⁷

Two unique cobalt-containing MOF structures were previously reported by our group; Co-MOF1 and Co-MOF2.⁴⁵⁸ These structures were obtained through the use of an asymmetric ligand, 4-(4'-carboxyphenyl)-1,2,4-triazole (Hcpt), which yielded a 2D structure and a 3D structure with a triangular SBU (Scheme 1). This type of triangular building unit has often been observed in MIL series MOF structures.^{454,459,460} Thus, we sought to isolate a synthetically controlled MOF structure using the rigid Hcpt ligand structure with a high-nuclearity SBU, and study the magnetic, isothermal, and physical properties accordingly.



Scheme 1. Synthetic scheme representing the effects of subtle alterations in conditions which produced drastically different MOF secondary building unit structures. Co-MOF3 being the structure discussed herein: **6**.^{440,458}

Several MOF structures have been synthesized with Co^{II}-based cluster SBUs (Chapter 2). These structures have been shown to possess interesting magnetic properties, and have displayed the potential to synthesize MOF structures with discrete magnetic SBUs, as if assembling molecular magnets in 3D. Herein, we present a novel MOF structure, Co-MOF3 (**6**), which can be observed in Scheme 1. This structure is composed of well-separated Co₈ cuboctahedron SBUs, which are the first of their kind. Using IR, SCXRD, XRPD, SEM, TGA, and magnetic measurements coupled with DFT modeling, we have characterised this novel MOF material for its structure and corresponding magnetic properties.

6.3 Experimental

6.3.1 Synthetic Information

6.3.1.1 Preparation of 4-(4'-carboxyphenyl)-1,2,4-triazole (Hcpt)

The synthesis of the employed ligand system was modeled after a method previously reported by our group.^{440,461} This method initially involved the addition of formylhydrazide (90%, 0.11 g, 1.9 mmol) to ethanol (99%, 5 mL) in a microwave vial. After dissolution was complete, triethylorthoformate (TEOF, 0.47 mL, 1.9 mmol) was added, and the sealed vial was mounted in a Biotage initiator microwave. After 5 min at 150 °C and 10 bars of pressure, a clear solution was obtained. Immediately after the initial reaction (formation of diformylhydrazide), 4-aminobenzoic acid (0.25 g, 1.8 mmol) was added, and the vial was placed back in the microwave. The reaction conditions for the formation of Hcpt were identical to that of the previous step. A beige-white powder was obtained in a slightly pink solution, and the product was purified by recrystallisation in 10 mL of hot DMF. After recrystallisation, the product was washed with diethyl ether in order to obtain a fine, shiny white powder Hcpt ligand (110 mg, 30%), the purity of which was confirmed by ¹H NMR and compared to the reported data (d⁶-DMSO, 400 MHz): δ(ppm) 13.20 (s, 1H), 9.21 (s, 2H), 8.06 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H). Yield: 25%. Selected FTIR (cm⁻¹) ν = 3112, 2455, 1894, 1685, 1608, 1321, 1245.

6.3.1.2 Preparation of [Co^{II}₈(OH)₆(cpt)₁₂][CoCl₄] (Co-MOF3, **6**)

The above described ligand, Hcpt (58.5 mg, 0.31 mmol), and Co(NO₃)₂·6H₂O (220 mg, 0.75 mmol), were placed in an autoclave Teflon bomb (20 mL) along with a solvent mixture composed of DMF (10 mL), EtOH (99 %, 3 mL), water (0.3 mL), and HCl (10 M, 0.1 mL). The vial was then sealed and placed in an oven where a temperature program was initiated, heating the

autoclave to 150 °C within 1 hour, and remaining at this temperature for 24 hours, followed by cooling at a rate of 6.54 min /°C. This optimised thermal treatment yielded spherical dark blue cubic crystals (Figure 55) (126 mg). Selected FTIR (cm^{-1}) ν = 3384(br), 3099(m), 2359(m), 1656, 1601, 1566, 1408, 1315, 1250.

6.3.2 Characterisation Techniques

6.3.2.1 NMR Spectroscopy

Nuclear magnetic resonance spectroscopic analyses were conducted using a Bruker Avance 400 MHz spectrometer, at room temperature.

6.3.2.2 Infrared Spectroscopy

Infrared spectra were recorded on all samples in the solid state on a Nicolet 6700 FT-IR spectrometer in the 4000-600 cm^{-1} region.

6.3.2.3 SCXRD

Single-crystal X-Ray diffraction experiments were performed on a Bruker AXS SMART single-crystal diffractometer with a sealed Mo tube APEX II CCD detector, which was used to collect the unit cell and intensity data using graphite Mo- $K\alpha$ radiation (λ = 0.71073 Å). Data reduction included correction for Lorentz and polarisation effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using SHELXTL (Table 10). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated geometrically, and were riding on their respective atoms. Partially occupied water molecules were localised and modeled during refinement.

6.3.2.4 XRPD

X-ray powder diffraction experiments were performed using a RIGAKU Ultima IV, equipped with a Cu- $K\alpha$ radiation source (λ = 1.541836 Å), and a graphite monochromator. Scanning of the 2θ range was performed from 5-40°.

6.3.2.5 SEM

Scanning electron microscopy images were taken of single crystals using a JSM-7500F FESEM (JEOL). Crystals were adhered to an Al cylinder plate using isopropanol paint.

6.3.2.6 TGA

Thermogravimetric analysis data were recorded using an SDT 2960 Simultaneous DSC-TGA, TGA Q5000 V3.13 Build 261 instrument. The analysis was carried out under air flow (20 mL min⁻¹) with a heating rate of 10°C min⁻¹ from room temperature up to 800°C, with complementary nitrogen flow (100 mL min⁻¹) as a protective gas.

Table 10. SCXRD data for **6**.

Compound	6
Empirical formula	C _{13.5} H _{14.5} C ₁₂ Co _{2.5} N _{4.5} O _{6.5}
Formula weight (g/mol)	562.06
Crystal system	cubic
Space group	F23 (no. 196)
Temperature (K)	200(2)
Crystal size (mm)	0.15 x 0.11 x 0.10
<i>Z</i>	16
<i>a</i> (Å)	23.3565(6)
<i>b</i> (Å)	23.3565(6)
<i>c</i> (Å)	23.3565(6)
α (°)	90.00(6)
β (°)	90.00(6)
γ (°)	90.00(6)
Volume (Å ³)	12741.58(57)
Calculated density (gcm ⁻³)	1.17185
Absorption coefficient (mm ⁻¹)	1.487
<i>F</i> (000)	4488
θ range for data collection (°)	2.47 - 30.49
Limiting indices	<i>h</i> = ±31, <i>k</i> = ±28, <i>l</i> = ±33
Reflections collected/unique	55588/3203
<i>R</i> (int)	0.0294
Completeness to θ = 30.49 (%)	0.99
Max. and min. Transmission	0.8077 and 0.8655
Data/restraints/parameters	3203/6/65
Goodness-of-fit on <i>F</i> ²	1.046
Final <i>R</i> indices [<i>I</i> 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0512, w <i>R</i> ₂ = 0.1138
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0632, w <i>R</i> ₂ = 0.1182
Largest diff. Peak/hole, eÅ ⁻³	0.489 and -0.693

6.3.2.7 SQUID

Magnetic measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL7, operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Susceptibility measurements were performed on the freshly filtered, crushed crystalline **6** (23.6 mg), wrapped

within a polyethylene membrane. The magnetisation data were initially collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples.

6.3.2.8 Computational Studies

Periodic DFT^{462,463} calculations were performed with the VASP code,⁴⁶⁴⁻⁴⁶⁶ using the PBE exchange-correlation functional.⁴⁶⁷ A plane wave basis set with PAW^{468,469} pseudopotentials was utilized with a kinetic energy cut-off of 400 eV. The reciprocal space was sampled with a single Γ -point. All calculations reported were spin polarized. Initial guess of the various magnetic moments on the Co^{II} atoms was obtained using MAGMOM option within VASP.

Two structural configurations were explored due to the inability of SCXRD studies to differentiate the exact arrangement of the asymmetric cpt⁻ ligands (which end, O- or N- binds to each edge of the cluster). The first model (asymmetric model) is shown in Figure 56B, and was constructed allowing for the cpt⁻ ligand coordination to alternate on opposite edges. This conformation allowed construction of a simulation cell containing a single 8 cubane SBU and 150 atoms (including 2 [CoCl₄]²⁻ counter ions). In the asymmetric model half of the Co^{II} atoms coordinate to 5 O (3 μ_4 -O and two carboxylate oxygens) and 1 N, while the other half of the Co^{II} atoms coordinate instead with 4 O (3 μ_4 -O and one carboxylate oxygen) and two N. The second model (symmetric model) is shown in Figure 56A, and is constructed such that the opposing edges coordinate to the same end of a cpt⁻ ligand. This model requires a much larger simulation cell (4x, with 600 atoms). In the symmetric model, each Co^{II} is coordinated with 4 O and 2 N.

The energies discussed were modelled for the asymmetric model, where the geometry was fixed to the SCXRD structure, and the antiferromagnetic solutions are given with respect to the energy of the ferromagnetic solution. Our conclusions hold qualitatively for the symmetric model as well. The most stable antiferromagnetic solution (antiferromagnetic ground state) lies 4.5 kcal/mol below the ferromagnetic solution. The total integrated spin-polarization in this antiferromagnetic ground state is almost zero due to the cancellation of magnetic moments on the Co^{II} atoms (which were found to be $\sim \pm 2.4$ μ_B). This contrasts the total magnetization in the ferromagnetic state, which was calculated to be approximately 20 μ_B . We have also examined spin-density in the antiferromagnetic ground state and several excited antiferromagnetic configurations. We find that the antiferromagnetic ground state corresponds to the parallel arrangement of magnetic moments on the "same facet" of 8 atom Co^{II} SBU (top right corner of Figure 61). Conversely, the most unstable antiferromagnetic configuration which lies, ~ 13.5 kcal/mol above the ferromagnetic solution, corresponds to the arrangement of parallel magnetic

moments located in the opposite corners of 8 atom Co^{II} SBU. This most unstable antiferromagnetic solution is shown in the bottom right corner of Figure 61). The parallel spins in this configuration cannot interact directly via Co-Co bond as in the antiferromagnetic ground state and, as a result, this configuration becomes highly destabilized.

Gas adsorption isotherms, void fraction, and surface area calculations were performed on the asymmetric model. The physical properties relating to the available pore space in **6** were invariant with respect to how the cpt ligands coordinate to the cuboctahedral Co^{II} clusters. The void volume (0.18 cm³/g) and surface area (1201 m²/g) for **6** were also calculated using the Zeo++ code,^{470,471} with probe radii corresponding to N₂ gas molecules. All calculations were performed with the CoCl₄ counter-ions in the pores to provide a neutral framework.

Grand Canonical Monte Carlo calculations were performed in order to evaluate the CO₂ and N₂ adsorption isotherms. During these calculations the framework was held fixed while gas molecules were assumed rigid, such that the guest-host interaction energies were calculated as a sum of non-bonded interactions. The electrostatic component was determined by partial atomic charges assigned to atoms on the framework and gas molecules. The partial atomic charges on the framework atoms were calculated with the REPEAT method⁴⁷² using the electrostatic potential defined from the lowest energy spin polarized configuration. The dispersive and steric repulsive interactions were defined using an isotropic 12-6 Lennard Jones (L-J) potential at each atom-centre. The ϵ and σ parameters defining atom-specific L-J functions were taken from the universal force field (UFF).⁴⁷³ Heteroatomic L-J interactions were computed using the Lorentz-Berthelot mixing rules. The parameters defining the interactions of the gas molecules were taken from the TraPPE force field (N₂)⁴⁷⁴ and the work of García-Sánchez *et al* (CO₂).⁴⁷⁵

Further information on specific experimental parameters of DFT calculations can be found in the supporting information of the publication.⁴⁴⁰

6.4 Results and Discussion

In a synthetic attempt to form a high-nuclearity MOF with well-separated SBUs for magnetic study, a novel octanuclear Co^{II} MOF, [Co^{II}₈(OH)₆(cpt)₆][CoCl₄]₂·2H₂O (Co-MOF3), has been obtained through the above synthetic methods, and will hereafter be referred to as **6**.⁴⁴⁰ With a carefully optimised synthetic procedure based on a previous publication from our group,⁴⁵⁸ including an appropriate gradual cooling rate as well as an optimised ratio of solvents (DMF,

ethanol and water), SCXRD quality crystals were obtained. Supplementary to the previously reported synthetic optimisation, we observed the importance of the low pH of the mother liquor, as concentrated HCl was found to be a necessary component of the synthetic mixture. Due to the addition of chloride ions we observed the presence of counter ions composed of $[\text{CoCl}_4]^{2-}$, that were formed in order to stabilize both the charge and lattice framework. The resulting crystals of **6** were octahedron-shaped purple-blue crystals with distinct triangular faces (Figure 55).

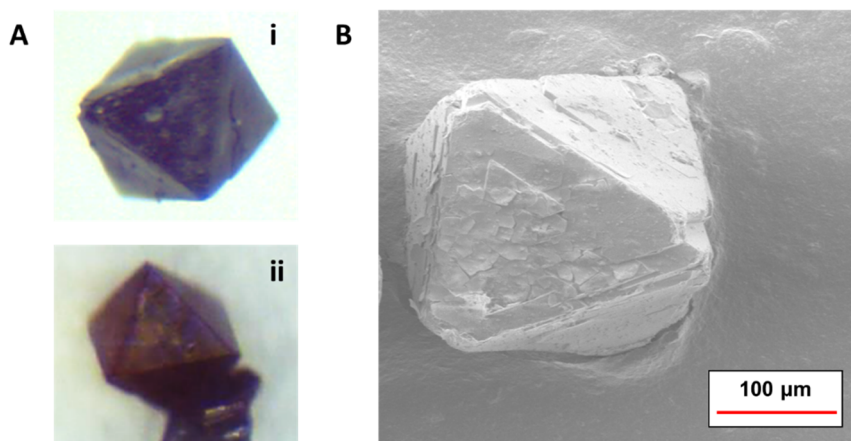


Figure 55. Crystals of **6** observed (A) under an optical microscope, and (B) under a scanning electron microscope.

Further structural analysis showed that **6** crystallizes to form a cubic MOF structure with a highly symmetrical framework. The structure is composed of an octanuclear Co^{II} core (Figure 56), which is the SBU of the MOF. The cubic space group is $F23$ with cell constants $a, b, c = 23.3565(6) \text{ \AA}$, and $\alpha, \beta, \gamma = 90^\circ$. The Co-Co bond lengths are $2.999(1) \text{ \AA}$, and the corner angles are $90.00(6)^\circ$. The faces of the SBU are capped by μ_4 -hydroxide groups possessing Co-OH-Co angles of $86.19(8)^\circ$. Each Co^{II} ion in the SBU is in an octahedral environment, coordinated to: one O atom (O2/O3) from the carboxylate group of a cpt^- ligand, two N atoms (N2/N3) from triazole rings of other cpt^- ligands, and three μ_4 -O (O1) atoms discussed above as forming the faces of the cubane core. There are also two tetrahedral $[\text{CoCl}_4]^{2-}$ guest molecules present, per SBU, which serve as counter ions to stabilize the lattice, as well as prevent solvent disorder in the lattice. There were, however, some solvent molecules (water) present in the structural voids which were localised and modelled during refinement. Additional details regarding crystallographic information can be found in Table 10.

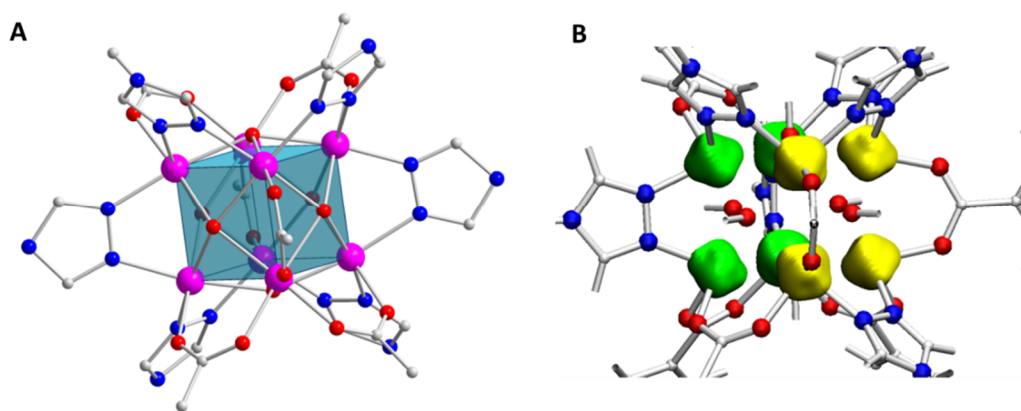


Figure 56. (A) Molecular structure of the SBU of **6**, [Co^{II}₈(OH)₆(cpt)₁₂]²⁻. (B) Isosurface plot showing the difference in spin density of the calculated $S = 0$ spin ground state.

The Co₈ core in **6** constitutes a novel high-nuclearity building block, which, as stated above, is a rarity in MOF chemistry. Each cubic core is connected by disordered cpt ligands, thus linking it to 12 neighbouring SBUs and forming a cuboctahedron (Figure 57). This three-dimensional network has a face-centered cubic (*fcc*) style packing of cuboctahedra, reminiscent of a ubt framework topology.^{456,476,477} The cubic character of this novel MOF is consistent with previously demonstrated high surface area and symmetrical MOFs, such as: MOF-5.⁴⁷⁶

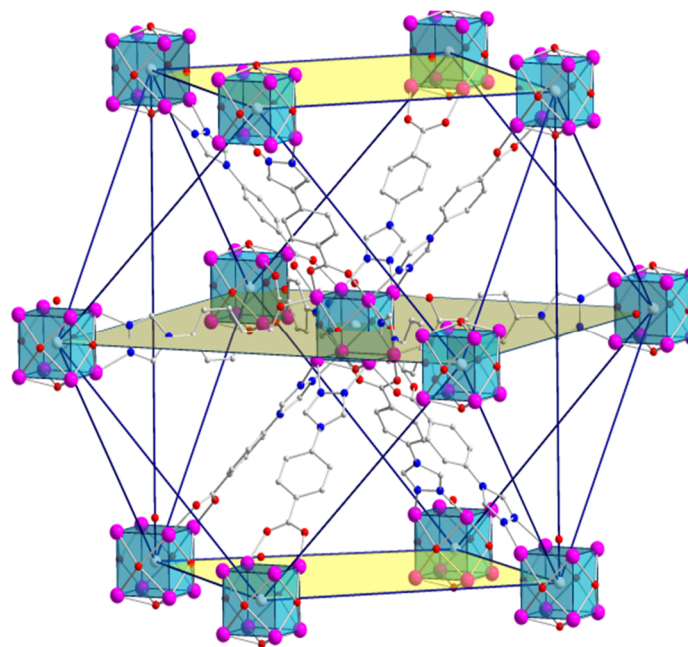


Figure 57. Molecular structure of the arrangement formed by 13 interconnected SBUs within **6**.

The Co^{II} SBUs are well-separated within the lattice framework, with the nearest distances being as follows: Co₈-Co₈ (Co1-Co1) 12.275(1) Å, Co₈-CoCl₄ (Co1-Co3) 7.5169(7) Å, and CoCl₄-CoCl₄ (Co3-Co4) 11.6783(3) Å. These intermolecular distances preclude any potential intercluster interactions (*vide infra*).

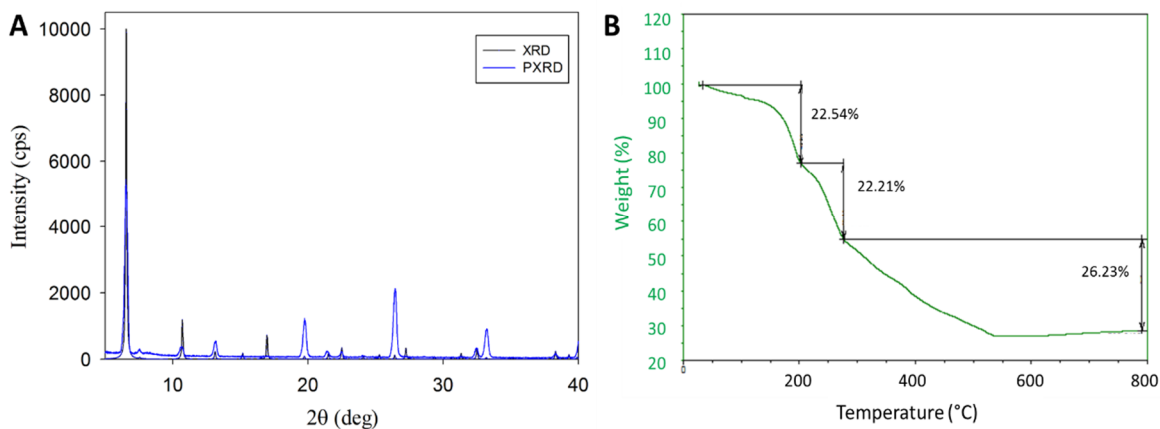


Figure 58. (A) XRPD pattern for air-dried single crystals of **6** in the 5-40° 2θ region, and (B) TGA for vacuum filtered crystals of **6**.

X-ray powder diffraction experiments were performed in order to investigate bulk crystalline purity within the MOF sample, as compared with the calculated pattern from SCXRD (Figure 58A). The patterns are consistent, illustrating that **6** possesses bulk phase purity of the crystalline lattice shown in the structure obtained from SCXRD, however, there are slight discrepancies in peak intensity which can be attributed to preferred crystallite orientations coming from limited sample size. Furthermore, according to thermogravimetric analysis (TGA) measurements (Figure 58B), **6** maintains thermal stability up to 200°C. The ligand undergoes decomposition in two stages found at 200°C and 275°C where significant weight changes can be observed. Prior to 200°C, the weight change is attributed to the loss of two water molecules (6.4% wt.).

Gas adsorption behaviour was also investigated through modelling isotherms for N₂ and CO₂ (Figure 59). Uptake of N₂ at 77 K was shown to be much higher than that of CO₂ at 298 K. However, uptake for N₂ at 298 K is almost negligible, where uptake values at 1.0 bar were ~ 14, 6 and 0.2 mmol/g for N₂ (77 K), CO₂ (298 K) and N₂ (298 K), respectively. These results show that this MOF displays significant selectivity for CO₂ over N₂ at room temperature, however, when compared with other MOF materials it is not a competitive CO₂ uptake candidate overall.^{478,479} For comparative purposes with other MOF materials we performed void volume (0.18 cm³/g) and surface area (1201 m²/g) calculations on **6**. These modest values display that this framework material is not an ideal candidate for gas adsorption and/or storage with its low uptake and surface area values.

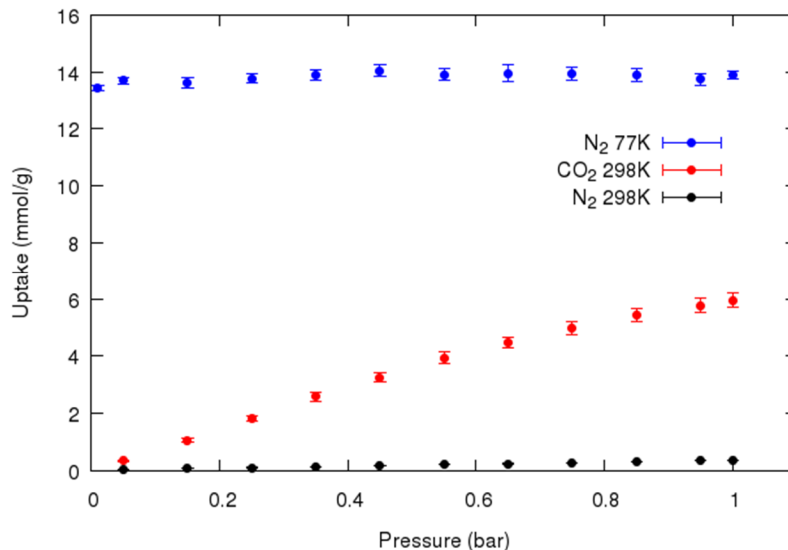


Figure 59. Gas adsorption isotherms for CO₂ and N₂. The y-error bars denote the standard deviation in the uptake values associated with the statistical sampling of the grand canonical ensemble.

The magnetic behaviour of **6**, in particular the Co₈ SBU, was investigated by performing dc magnetic susceptibility measurements. The Co₈ core was previously stated to be well-isolated according to the crystal structure, with the shortest Co-Co distance being (Co1-Co3) 7.5169(7) Å. Thus, we can conclude that any magnetic interactions between Co^{II} ions are derived from within the octanuclear core. The temperature dependence of the dc magnetic susceptibility was investigated between 1.8 and 300 K under an applied dc field of 1000 Oe. The temperature dependence of the χT product can be seen in Figure 60A. The room temperature value of χT decreases from 14.76 cm³Kmol⁻¹ to 2.88 cm³Kmol⁻¹ at 1.8 K, which indicates the presence of significant antiferromagnetic interactions developed at high temperatures, as the plot does not show saturation of χT in the measured range. Further evidence of the high temperature antiferromagnetic interaction is that the theoretical spin-only value for a single non-interacting Co^{II} ion is 1.88 cm³Kmol⁻¹ (⁴F_{9/2}, $S = 3/2$, $L = 3$, $g = 2$), thus per molecular formula the theoretical value would be 18.8 cm³Kmol⁻¹. Furthermore, the decrease to a value of 2.88 cm³Kmol⁻¹ at 1.8 K indicates an $S = 0$ ground state for the Co₈ core, attributed to the significant antiferromagnetic interactions present, as well as the 2 isolated Co^{II} counter ions previously discussed (3.76 cm³Kmol⁻¹). This coupling behaviour involving an $S = 0$ ground state was previously reported in a Ni₈ molecular species,⁴⁸⁰ as well as in some other Co-based frameworks.⁴⁵⁶ In order to further explore the antiferromagnetic interactions within the SBU, the temperature dependence of χ^{-1} was

plotted (Figure 60B), and fit in order to obtain the values of the Weiss constant, $\Theta = -32.07$ K, and the Curie constant, $C = 8.34$ cm³Kmol⁻¹. The Weiss constant has a negative value, thus indicating non-negligible antiferromagnetic interaction between Co^{II} ions within the SBU. This type of strong antiferromagnetic coupling has also been observed in previous Co₇ SBU MOF systems.^{481,482}

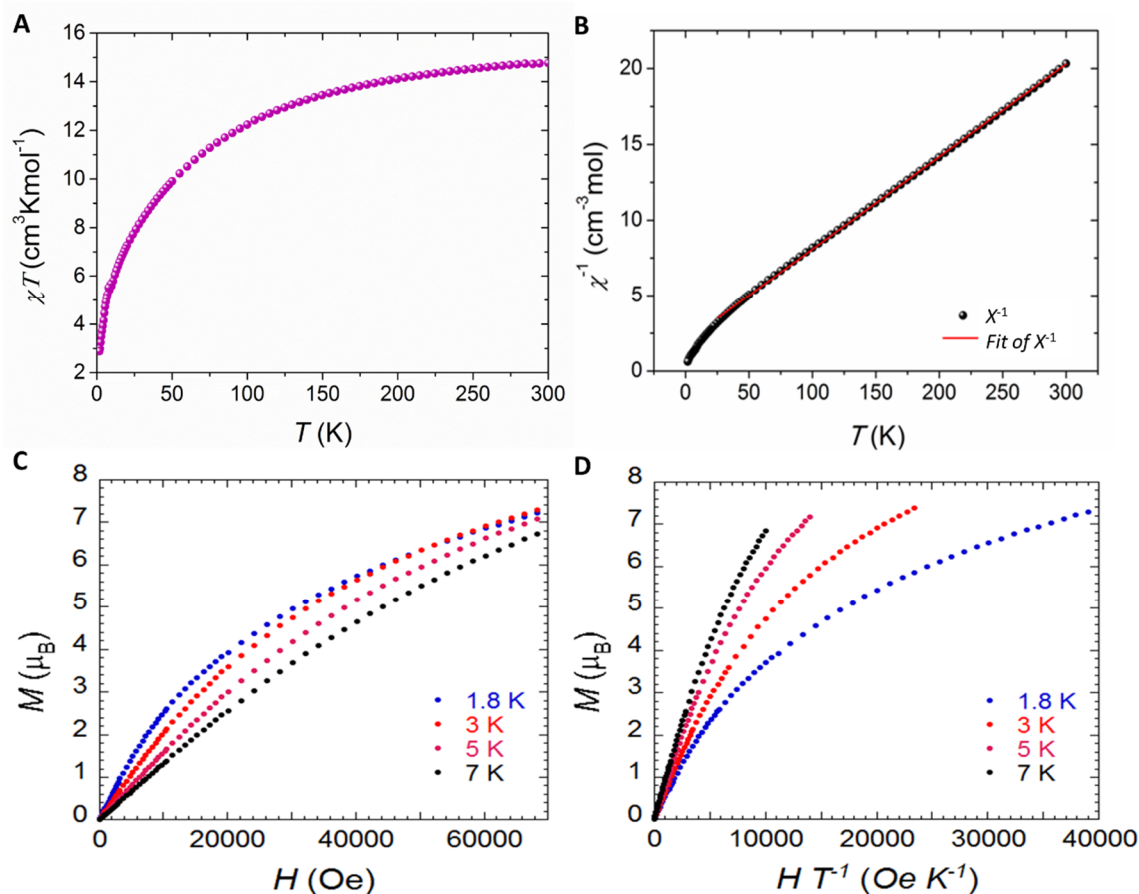


Figure 60. Temperature dependence of the χT product (A) and χ^{-1} (B) at 1000 Oe for **6**. Solid red line represents Curie-Weiss fitting of data. (C) Field dependence of the magnetisation of **6** at indicated temperatures, and (D) M vs. HT^{-1} plot for **6** at indicated temperatures.

Isotherm magnetisation measurements were also performed, and can be seen in Figure 60C. Due to the lack of saturation of the magnetisation up to 7 T at 1.8 K, we can confirm the presence of non-negligible anisotropy within the system, common for Co^{II}, as well as population of excited states present even at 1.8 K. This behaviour can most likely be attributed to the Co^{II} counter ions within the lattice, as the molecular cluster has been shown to possess a singlet

ground state, however, we cannot rule out population of excited states for the Co₈ cluster. Figure 60D shows the reduced magnetisation plot at indicated temperatures, where isothermal lines do not superimpose, thus further indicating the presence of magnetic anisotropy within the system. From these measurements, as well as the results from the previously studied Ni₈ analogue mentioned above,⁴⁸⁰ we may conclude that the low temperature behaviour is primarily due to the isolated [CoCl₄]²⁻ counter ions.

Our interest in the magnetic behavior of the SBU prompted further investigation of the Co-Co interactions using periodic DFT calculations. The details of the computational models can be found in the experimental section above, and in the supporting information of the publication.⁴⁴⁰ The energies discussed herein employed the results obtained for the asymmetric model, where the geometry was fixed to that of the SCXRD structure. All conclusions hold qualitatively for the symmetric model as well. The fully ferromagnetic and various antiferromagnetic arrangements of magnetic moments on the Co^{II} atoms were calculated. The antiferromagnetic configuration (4 spin up, 4 spin down) possesses 35 possible arrangements (8!/4!4!2) of the magnetic moments, some of which are symmetry related. Figure 61 displays the energy spectrum of the antiferromagnetic states relative to the ferromagnetic state. In agreement with the measured magnetic susceptibility data this plot shows an antiferromagnetic ground state which is 4.5 kcal/mol lower in energy than the ferromagnetic solution. Interestingly, the lowest energy antiferromagnetic $S = 0$ state corresponds to a parallel arrangement of magnetic moments, meaning that the spins on opposing faces of the octanuclear cluster would be 4 up and 4 down. This is shown by the calculated spin density of the ground state (Figure 56B). The most unstable antiferromagnetic configuration lies approximately 13.5 kcal/mol above the ferromagnetic solution, and corresponds to parallel magnetic moments on opposite corners of the 8 atom SBU (Figure 61C). The parallel spins in this configuration cannot interact through Co-Co bonds as in the antiferromagnetic ground state, and thus this configuration is highly destabilized.

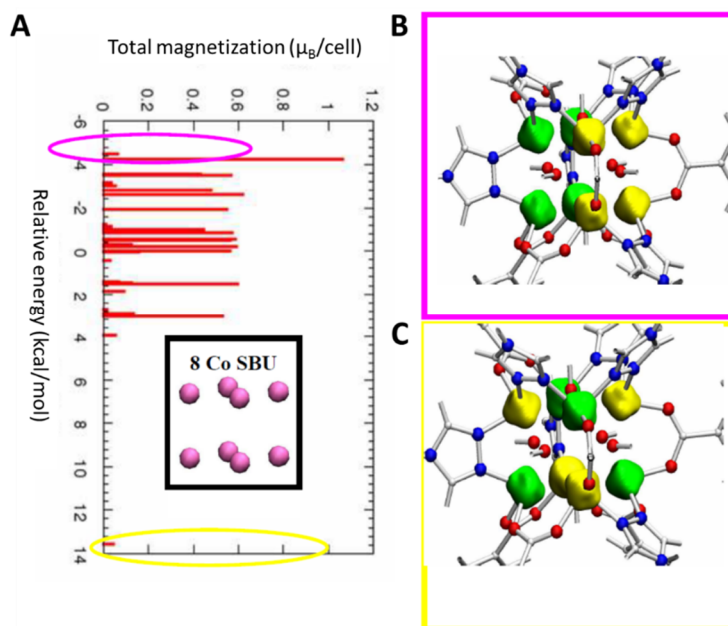


Figure 61. (A) The energy spectrum of the antiferromagnetic solutions relative to the ferromagnetic ground state in a primitive unit cell containing one 8 atom Co^{II} SBU, (B) Isosurface of the spin density difference in the antiferromagnetic ground state, and (C) most excited antiferromagnetic state. The magnetisation is localised on Co^{II} atoms. The green (yellow) isosurfaces correspond to the regions with dominant spin-up (or down) component.

In order to further validate the results, the same calculations were performed using a symmetric model discussed in the experimental section above. This larger supercell is in excellent agreement to the results obtained with the asymmetric model. The lowest energy antiferromagnetic state is determined to be 4.6 kcal/mol lower in energy than the ferromagnetic state, whereas with the asymmetric model the ground state was found to be 4.5 kcal/mol lower in energy than the ferromagnetic state. The calculations were also repeated on the smaller asymmetric model, whereby the geometry was optimised in the ferromagnetic state and the lowest energy antiferromagnetic state. We found, once again, that the antiferromagnetic configuration was energetically preferable, with an energy difference of 5.5 kcal/mol.

6.5 Conclusions

This chapter has presented the design and synthesis of a novel cubic MOF structure with a high nuclearity Co^{II} SBU. This structure represents the first Co_8 cuboctahedron MOF, which possessed

well-separated SBUs, thus allowing for magnetic characterisation of individual clusters ordered in 3D.

The MOF structure was structurally characterised using SCXRD, and its bulk purity was confirmed with XRPD. Gas adsorption was modelled, illustrating modest properties in CO₂/N₂ separation and CO₂ uptake, and modest values for void volume (0.18 cm³/g) and surface area (1201 m²/g). Furthermore, this unique framework was also found to be stable up to 200°C. Thus, the gas adsorption and thermal properties are not competitive when compared with the benchmark MOFs discussed in Chapter 2. This is unsurprising, considering we were attempting to achieve a high-nuclearity SBU, without a focus on design for physical properties that are non-magnetic. However, in future endeavours it would be interesting to take this into account within SBU and ligand design in order to facilitate hybrid functionality in a magnetic MOF.

The cuboctahedral arrangement of 8 Co^{II} ions in the SBU elicited a ubt framework topology which was shown to interact antiferromagnetically with opposing faces of the cube aligning spins (4 up and 4 down). These core interactions lead to an $S = 0$ ground state, which is supported through the use of magnetic and DFT investigations. These significant magnetic interactions within a high-nuclearity SBU display the potential for interesting magnetic studies to be performed on magnetic clusters assembled in 3D.

This highly symmetrical MOF is an important building block toward the development of additional high nuclearity SBUs in MOF structures, especially through structural modifications using different rigid ligand architectures and various metal ions to elicit new applicable frameworks. Furthermore, since SBUs were well-separated, this structure displays the potential for studying ordered arrays of molecular magnets in 3D using MOF chemistry.

Chapter 7

Doping Magnetic Properties into 3D Networks: Co^{II}-doped MOF-5

7.1 Abstract

Herein, we demonstrate that substitution of Zn^{II} ions within the SBU of MOF-5 is possible with varying amounts of Co^{II}, exceeding a single Co^{II} ion, doped into the lattice framework. Syntheses of Co^{II}-doped MOF-5 materials were performed without necessitating lengthy post-synthetic ion metathesis methods, and instead employed direct synthetic methods in order to incorporate molar dopant percentages of 0% (MOF-5), 5% (7.1), 10% (7.2), 15% (7.3), 25% (7.4), 50% (7.5), 75% (7.6) and 100% (7.7). The suspected phenomenon of one Zn^{II} ion within the SBU becoming O_h through DMF coordination is evidenced through site replacement with Co^{II} in this location. Upon site replacement with more than 1 Co^{II} per SBU (above 25% doping), Co^{II} ions adopted T_d coordination within the framework, causing structural distortions. Study of the structural identities of Co-MOF-5 materials was performed through the use of IR, XRPD, SEM/EDX, diffuse reflectance spectroscopy, TGA, and SQUID magnetometry. Interestingly, Co-MOF-5 doped with 2 Co^{II} ions in 7.5 (50% doping) exhibited clear interaction between Co^{II} ions at low temperature, as well as SMM-like behavior, with a magnetic relaxation barrier at zero-field of $U_{\text{eff}} = 46.0(7)$ K. This study sheds light on the inherent structural properties of a well-known high-performing 3D framework, and how they are affected by the introduction of magnetic ions through synthetic site replacement. The publication of this work is forthcoming: Holmberg, R. J.; Murugesu, M. Systematic Study of Co-doped MOF-5 through Magnetic Correlation. (Manuscript in preparation).

7.2 Introduction

Following its unveiling in 1999, ²¹⁹ MOF-5 has been a benchmark for gas adsorption and separation due to its significant Langmuir surface area (3995 m²g⁻¹), void space (60%), pore volume and diameter (10Å) as well as its thermal stability (~470°C).^{223,483-488} Despite these characteristics, considerable effort has been put forth in order to further improve the properties of MOF-5 for these green energy applications, as well as others, through various synthetic and post-synthetic alterations. Though there are many methods of altering a MOF in order to fine-tune its properties for a specific purpose, one method which has been recently explored with MOF-5 is isomorphic substitution. In catalysis this technique of adding additional active sites through metal

substitution has been vital to the development of better materials.^{306,307} This technique of full or partial metal exchange has rarely been reported for MOFs.^{312,489-494} However, the Dincă group have recently reported their findings using post-synthetic doping of MOF-5 with Ni^{II},⁴⁹⁵ followed by several other transition metals.⁴⁹⁶ These studies displayed the potential for isomorphic metal substitution in this MOF structure through post-synthetic doping in small percentage amounts. Interestingly, these studies motivated the Dincă group to suggest that one of the Zn^{II} sites in the MOF-5 SBU is capable of becoming hexacoordinate (O_h), through coordination to DMF solvent molecules.⁴⁹⁷ Interestingly, this has also been suggested to be the site of choice for any potential TM site replacement, thus explaining the 25% maximum site replacement previously achieved within the MOF-5 SBU (1 TM ion per Zn₄O SBU).⁴⁹⁶

It has been theoretically shown that replacement of one or more of the Zn^{II} ions in MOF-5 by a transition metal ion, such as Co^{II}, would increase H₂ affinity, promote catalytic behavior, and elicit desirable properties for semiconductor applications.^{306,307,498-501} The reasoning for specifically mentioning Co^{II} is that it has been previously shown to induce an increase in the affinity for H₂ adsorption when substituted into MOF frameworks.^{312,493,494,501} One study was performed on Co^{II} doping within the MOF-5 SBU, where two doping concentrations (8 and 21%) were achieved using a previously reported synthetic procedure, and studied using reflectance spectroscopy, TGA and XRPD.⁵⁰¹ The study was able to conclude that MOF-5 materials doped with a single Co^{II} atom in the SBU indeed possessed a higher adsorption capacity for gases such as H₂, CO₂ and CH₄ than the standard Zn^{II} homologue.⁵⁰¹

With a desire to further explore the effects of Co^{II} doping on the structure and properties of MOF-5 we synthetically doped the structure with Co^{II} of the following molar compositions: 0% (MOF-5), 5% (**7.1**), 10% (**7.2**), 15% (**7.3**), 25% (**7.4**), 50% (**7.5**), 75% (**7.6**) and 100% (**7.7**). Thus, with a gradient of Co-dopant concentrations we are able to provide insight into the properties elicited by this isomorphic substitution of Co^{II} for Zn^{II} beyond merely the previously explored site of interest (O_h Zn^{II} within the SBU). Using IR, XRPD, SEM, Electron Dispersive X-ray Spectroscopy (EDX), diffuse reflectance spectroscopy, TGA, and SQUID magnetometry, we have probed the inherent changes in the structure of MOF-5 with increasing Co^{II} site replacement within the SBU, thus gaining information on the parent structure itself, as well as the potential for fine-tuning the properties of these novel site-replaced materials.

7.3 Experimental

7.3.1 Synthetic Information

All chemicals were purchased from Thermofisher Scientific or Alfa Aesar, and were used without further purification. DMF (HPLC grade) was dried, deaerated and stored in a N₂ environment over 3 Å molecular sieves.

7.3.1.1 Preparation of MOF-5 [Zn₄O(bdc)₃]

MOF-5 was prepared using a modified solvothermal approach to those previously published.⁴⁸⁷ In an autoclave Teflon bomb (20 mL), under flow of N₂, Zn(NO₃)₂·6H₂O (0.357 g, 1.2 mmol) and 1,4-benzenedicarboxylic acid (0.066 g, 0.4 mmol) were added, followed by 10 mL anhydrous DMF. The bomb was then sealed under N₂ and placed in a programmable oven with the following settings: heating 1.5 °C/min to 120 °C, held under autogenous pressure at 120 °C for 48 h, followed by slow cooling for 12 h to 40 °C. Small crystals were produced, and soaked in fresh anhydrous DMF prior to analysis.

7.3.1.2 Preparation of Co-MOF-5 [Co_xZn_yO(bdc)₃], 7.1-7.7.

Synthetically doped Co-MOF-5 was prepared using the above method, substituting molar degrees of Zn(NO₃)₂·6H₂O by Co(NO₃)₂·6H₂O (5% = **7.1**, 10% = **7.2**, 15% = **7.3**, 25% = **7.4**, 50% = **7.5**, 75% = **7.6** and 100% = **7.7**). Small crystals not suitable for SCXRD were produced, and soaked in fresh anhydrous DMF prior to analysis.

7.3.2 Characterisation Techniques

7.3.2.1 ICP-OES

Inductively-coupled plasma-optical emission spectroscopy measurements were performed using a Varian Vista Pro CCD-ICP-OES Spectrometer. Samples were separately digested, in duplicates, prior to analysis. The duplicates were in good agreement, and were averaged in order to obtain the final analyte relationship calculations. Each element was monitored at multiple wavelengths in order to validate the data and rule out interferences. All concentrations were calculated in ppm (w/w basis), and are presented as a percentage composition.

7.3.2.2 Infrared Spectroscopy

Infrared spectra were recorded on all samples in the solid state on a Nicolet 6700 FT-IR spectrometer in the 4000-600 cm⁻¹ region.

7.3.2.3 XRPD

X-ray Powder diffraction experiments were performed using a RIGAKU Ultima IV, equipped with a Cu-K α radiation source ($\lambda = 1.541836 \text{ \AA}$), and a graphite monochromator. Scanning of the 2θ range was performed from 5–40°. XRPD patterns were consistent in 2θ values with the generated pattern for MOF-5 from SCXRD,⁴⁸³ barring those with structural distortions (*vide infra*). Slight discrepancies in some intensities of peaks are attributed to preferred orientation due to limited sample size.

7.3.2.4 SEM/EDX

Scanning electron microscopy images were taken of MOF-5 and crystals of **7.1–7.7** using a JSM-7500F FESEM (JEOL). Crystals were adhered to an Al cylinder plate using isopropanol paint. Elemental compositions were determined by an energy dispersive X-ray spectrometer connected to the FESEM, and were processed using INCA software. EDX samples were probed in 5 different areas and averaged, while illustrating consistency in composition between a variety of crystalline and amorphous particle types.

7.3.2.5 Diffuse Reflectance Spectroscopy

Diffuse reflectance spectra were obtained with a Varian Cary 100 spectrometer using polytetrafluoroethylene (PTFE) as a reference. Kubelka-Munk spectra were normalized to allow meaningful comparisons.

7.3.2.6 TGA

Thermogravimetric analysis data were recorded using an SDT 2960 Simultaneous DSC-TGA, TGA Q5000 V3.13 Build 261 instrument. The analysis was carried out under air flow (20 mL min⁻¹) with a heating rate of 5°C min⁻¹ from room temperature up to 700°C, with complementary nitrogen flow (100 mL min⁻¹) as a protective gas.

7.3.2.7 SQUID

Magnetic measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL7, operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Susceptibility measurements were performed on freshly filtered, crushed crystalline Co-MOF complexes (employed sample weights: **7.1** = 18.2 mg, **7.2** = 17.1 mg, **7.3** = 13.4 mg, **7.4** = 29.4 mg, **7.5** = 25.7 mg, **7.6** = 31.5 mg) wrapped within a polyethylene membrane. The magnetisation data were initially collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples.

7.4 Results and Discussion

Direct solvothermal synthesis of Co-MOF-5 samples was achieved through employing anhydrous, deaerated DMF as solvent and utilizing an autoclave Teflon bomb with a specific temperature program in order to favor the formation of crystalline Co-doped MOF-5 of varying molar compositions. We were able to employ a synthetic procedure in order to promote site replacement within the crystalline framework. Therefore, we chose to employ molar percentages of Co^{II} doped into the MOF-5 framework: 5% (7.1), 10% (7.2), 15% (7.3), 25% (7.4), 50% (7.5), 75% (7.6) and 100% (7.7). This allowed for comprehensive study of the effects of varying dopant percentages on the structure and its inherent properties.

The desired percentages were initially corroborated by ICP-OES, where the results can be seen in Table 11. Each isotope was monitored with respect to percentage composition in acid-digested solution. These results display the quantitative amounts of Co^{II} dopant successfully incorporated within each sample, illustrating their consistency with the desired ratios.

Table 11. ICP-OES analyte percentages for 7.1-7.7.

Sample	Formula	Analyte Composition (%)	
		Co ^{II}	Zn ^{II}
MOF-5	Zn ₄ O(C ₈ H ₄ O ₄) ₃	0.00	100.00
7.1	Zn _{3.79} Co _{0.21} O(C ₈ H ₄ O ₄) ₃	5.31	94.69
7.2	Zn _{3.59} Co _{0.41} O(C ₈ H ₄ O ₄) ₃	10.34	89.66
7.3	Zn _{3.32} Co _{0.67} O(C ₈ H ₄ O ₄) ₃	16.85	83.15
7.4	Zn _{3.03} Co _{0.97} O(C ₈ H ₄ O ₄) ₃	24.27	75.73
7.5	Zn _{2.14} Co _{1.86} O(C ₈ H ₄ O ₄) ₃	46.52	53.48
7.6	Zn _{1.22} Co _{2.78} O(C ₈ H ₄ O ₄) ₃	69.61	30.39
7.7	Zn _{0.24} Co _{3.76} O(C ₈ H ₄ O ₄) ₃	100.00	0.00

Infrared spectroscopic analysis of Co-doped MOF-5 samples confirmed that the structural fingerprint of MOF-5 was present in Co-doped MOF-5 samples (Figure 62), however, some shifted/additional bands were observed for the 50, 75 and 100% doped Co-MOF-5 samples. It was predicted that substitution of more than one Co^{II} ion per SBU of the MOF-5 lattice would elicit a slightly altered structural motif. Specifically, the Dincă group proposed that one Zn^{II} ion within the MOF-5 SBU was capable of being O_h, instead of T_d,⁴⁹⁷ thereby introducing a

selectivity of site-replacement with different TM ions. As such, these findings were not entirely surprising, and warranted further investigation.

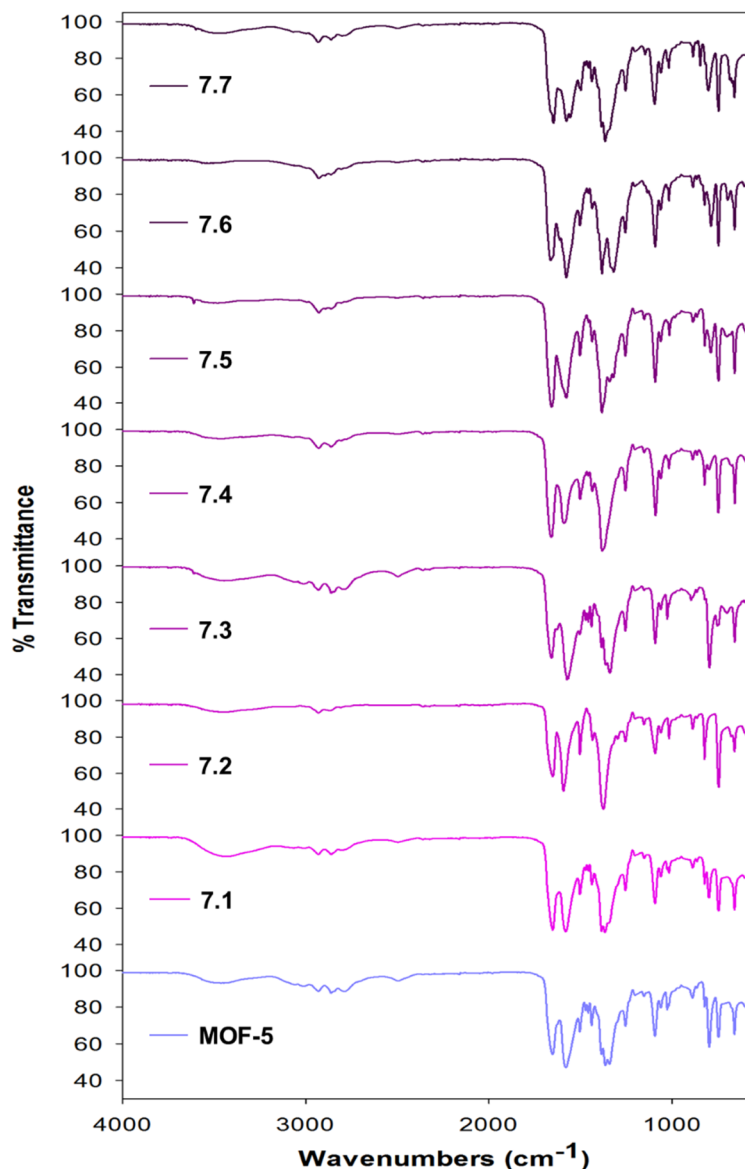


Figure 62. Infrared spectra comparing as-prepared Co-doped samples, 7.1-7.7, and MOF-5.

X-ray powder diffraction patterns on fine crystalline samples confirmed the presence of the MOF-5 morphology as the primary crystalline component of as-prepared MOF-5 and Co-doped samples up to a doping percentage of 25% (Figure 63). The discrepancies in peak intensities are attributed to grinding samples and various equivalencies of solvent released from MOF pores, as well as preferential alignment of crystallites. Above a doping percentage of 25% (50, 75 and 100%) we observe structural changes, most likely due to Co^{II} ions adopting different

coordination environments. It is likely that more than one Co^{II} ion within the SBU causes significant structural distortions, as previous studies on TM doping of MOF-5 were not capable of acquiring TM site-replaced MOF-5 materials with a dopant percentage above 25%.

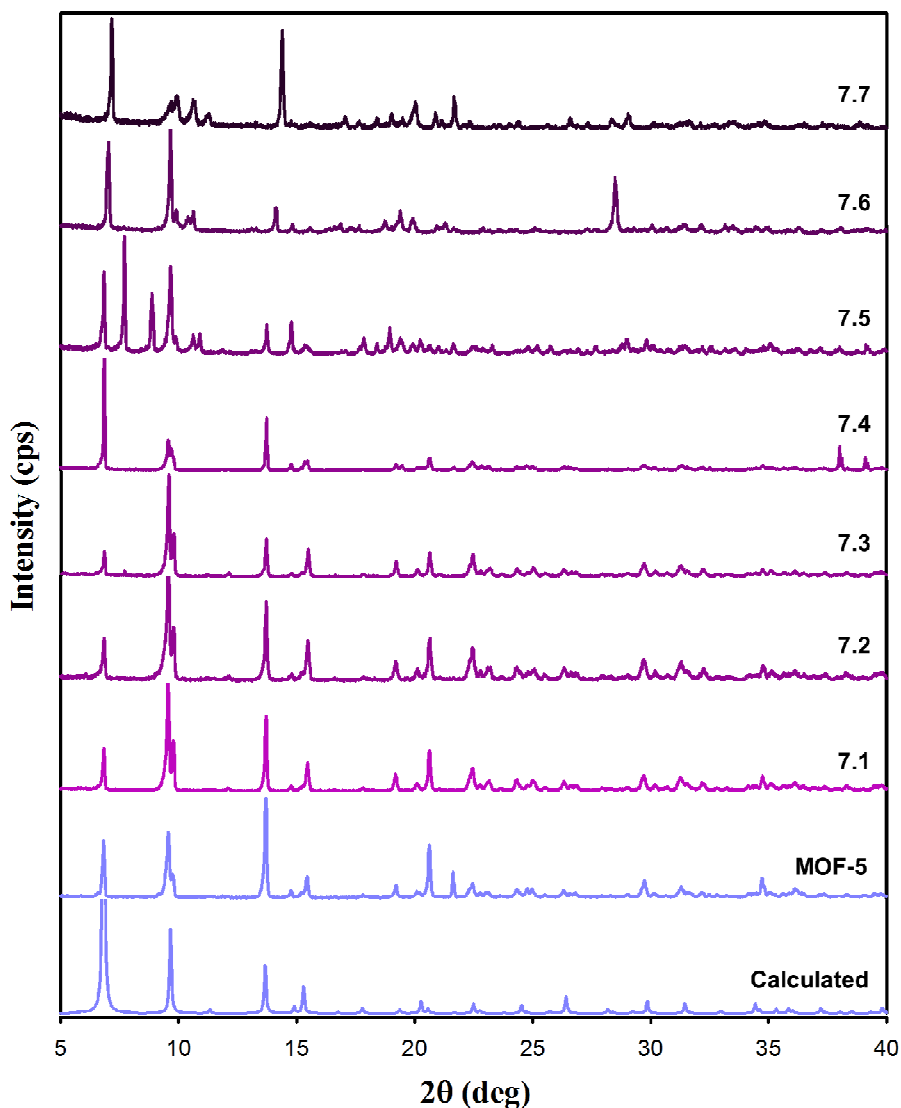


Figure 63. XRPD patterns in the 5-40° 2θ region comparing as-prepared Co-doped samples, 7.1-7.7, and MOF-5, with the calculated pattern from SCXRD for MOF-5.

SEM images were taken of both single crystals and area maps of crystals for: MOF-5 (Figure 64A, B), as well as 7.1 (Figure 65A, B), 7.2 (Figure 66A, B), 7.3 (Figure 67A, B), 7.4 (Figure 68A, B), 7.5 (Figure 69A, B), 7.6 (Figure 70A, B), and 7.7 (Figure 71A).

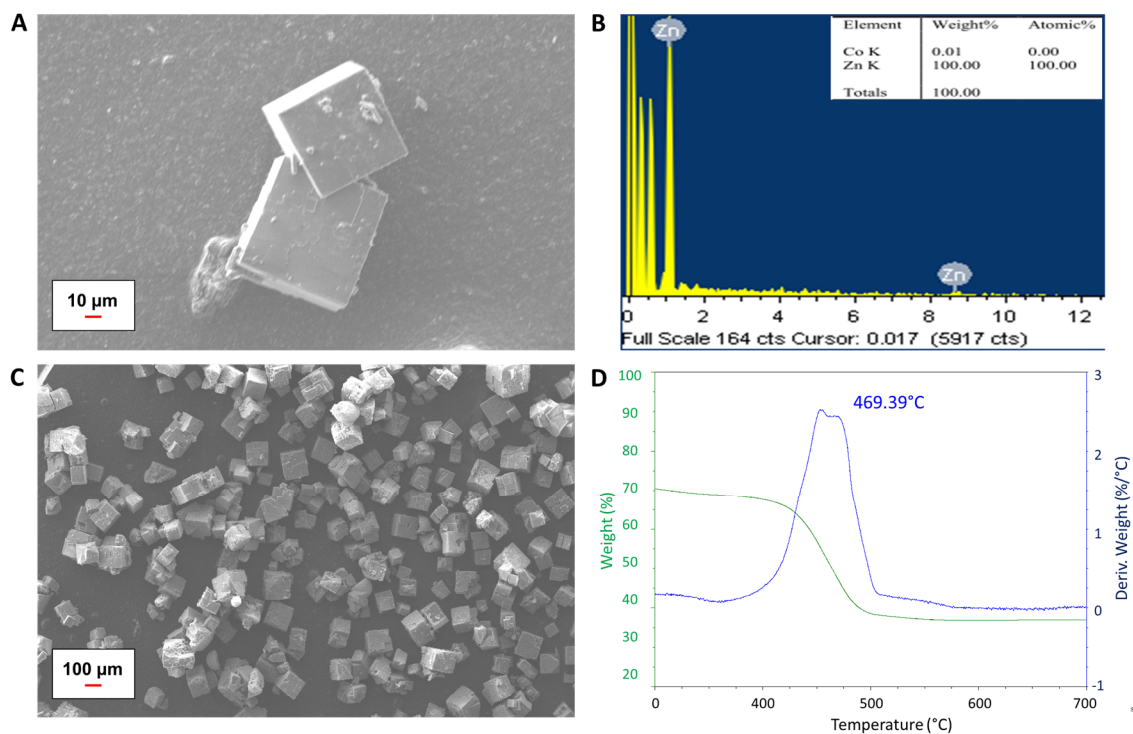


Figure 64. (A, C) Cubic crystals of MOF-5 observed under a scanning electron microscope. (B) EDX spectrum for crystals of MOF-5, and percentage comparison between Zn^{II} and Co^{II} from EDX. (D) Thermogravimetric analysis for crystals of MOF-5.

Images of MOF-5 and Co-doped MOF-5 crystals with dopant percentages up to 25% display a clear cubic crystal morphology, which is consistent with that previously reported for MOF-5,²²³ as well as post-synthetic metal substituted MOF-5.^{495,496} Area maps illustrate that this cubic crystalline shape is consistent throughout the material for these samples. However, for the 50% and 75% doped samples we begin to observe a change in the cubic crystalline morphology. We still observe an overall cubic shape, however, this shape is no longer well-defined or consistent throughout the material. Thus, these samples evidently possess some MOF-5 character, but are not structurally consistent with those of lower dopant percentages. Finally, the 100% Co-MOF-5 sample displays a different structure entirely, forming more plate-like crystals which display no discernable cubic character. Thus, this sample most likely does not possess significant structural similarities to the original MOF-5, as expected for a complete synthetic alteration of metal precursors. Due to this result, **7.7** will not be considered in the comparative magnetic study.

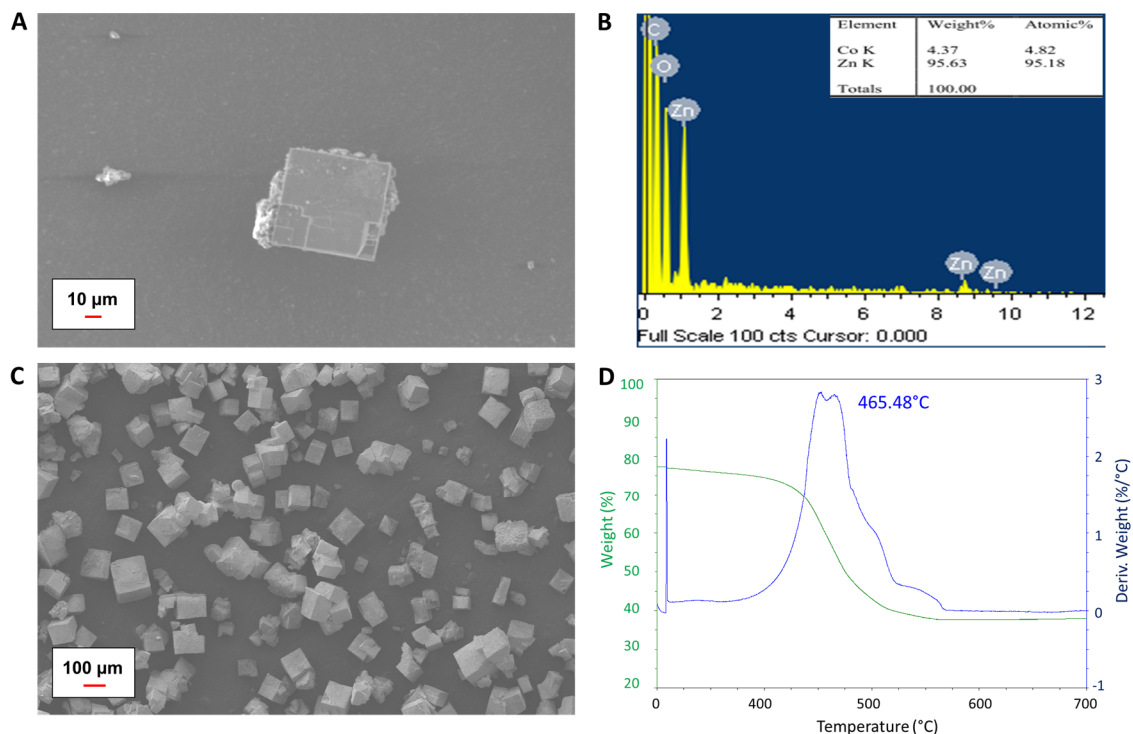


Figure 65. (A, C) Cubic crystals of **7.1** observed under a scanning electron microscope. (B) EDX spectrum for crystals of **7.1**, and percentage comparison between Zn^{II} and Co^{II} from EDX. (D) Thermogravimetric analysis for crystals of **7.1**.

EDX spectra and the resulting elemental analyses are also displayed for: MOF-5 (Figure 64C), as well as **7.1** (Figure 65C), **7.2** (Figure 66C), **7.3** (Figure 67C), **7.4** (Figure 68C), **7.5** (Figure 69C), **7.6** (Figure 70C), and **7.7** (Figure 71C). EDX was performed over an average area of crystalline material for each sample and a minimum of 5 sample maps were compared for consistency of data. This data depicts the presence of each metal ion (Zn^{II} and Co^{II}), as well as their atomic percentages within the averaged area map. Thus, we may confirm that the Co^{II} ions are homogeneously substituted throughout the crystals, not solely in one area, or merely on the surface. The atomic percentages provided by EDX analysis are also consistent with ICP-OES data, and the intended dopant percentages.

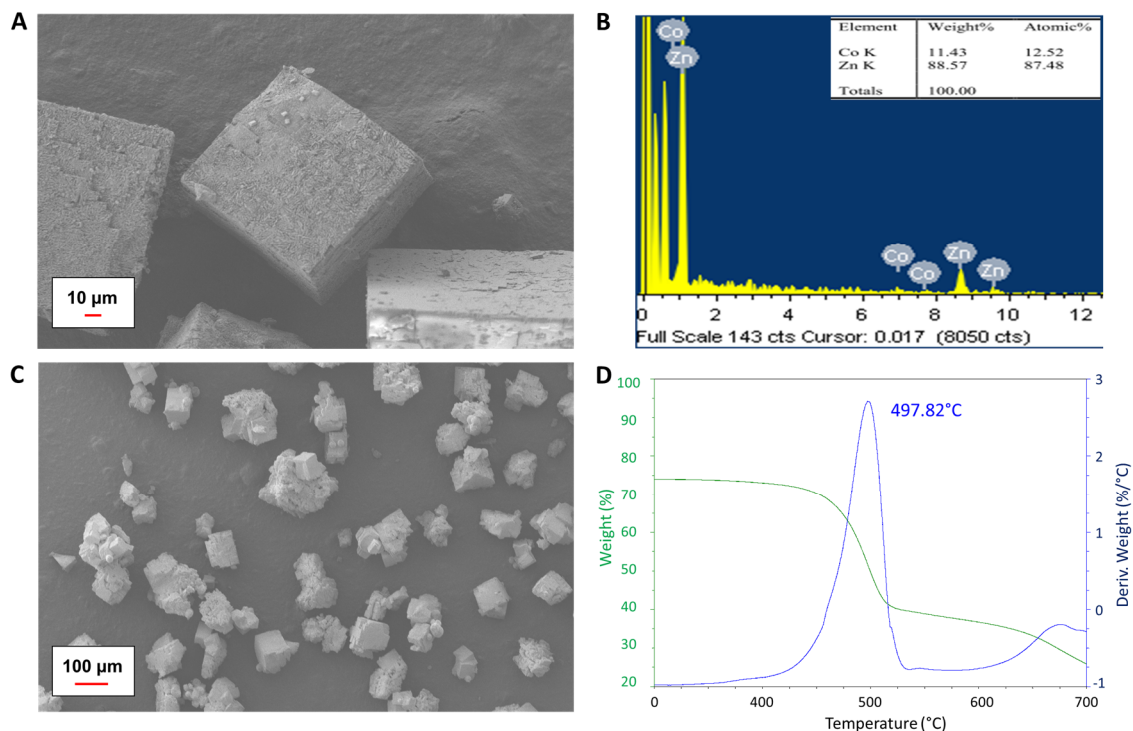


Figure 66. (A, C) Cubic crystals of **7.2** observed under a scanning electron microscope. (B) EDX spectrum for crystals of **7.2**, and percentage comparison between Zn^{II} and Co^{II} from EDX. (D) Thermogravimetric analysis for crystals of **7.2**.

Thermogravimetric analysis was carried out in order to investigate the thermal stability of: MOF-5 (Figure 64D), as well as **7.1** (Figure 65D), **7.2** (Figure 66D), **7.3** (Figure 67D), **7.4** (Figure 68D), **7.5** (Figure 69D), **7.6** (Figure 70D), and **7.7** (Figure 71D). Samples were employed as-prepared and, as such, significant initial weight loss due to the presence of DMF in MOF pores was observed. Initially, the thermal stability of the as-synthesized MOF-5 was investigated, and found to be 469°C, which is consistent with previously reported MOF-5 TGA results.^{223,501} The values for doped Co-MOF-5 samples decreased slightly with increasing Co^{II} content, most likely due to the tendency of Co^{II} to be oxidized at low temperature.⁵⁰¹ Overall, the values were similar to that of MOF-5, except in the case of **7.2** (498°C). This higher thermal stability value was also observed for Ni-MOF-5 with a similar dopant percentage (~9%).⁴⁹⁵ Thus, for applications requiring higher thermal stability, we can conclude that 10% doping of Co^{II} into MOF-5 would likely be optimal. This also further proves that Co^{II} is within the framework, as the presence of Co^{II} in extra-framework positions would not have such an effect on linker decomposition temperature.⁵⁰¹

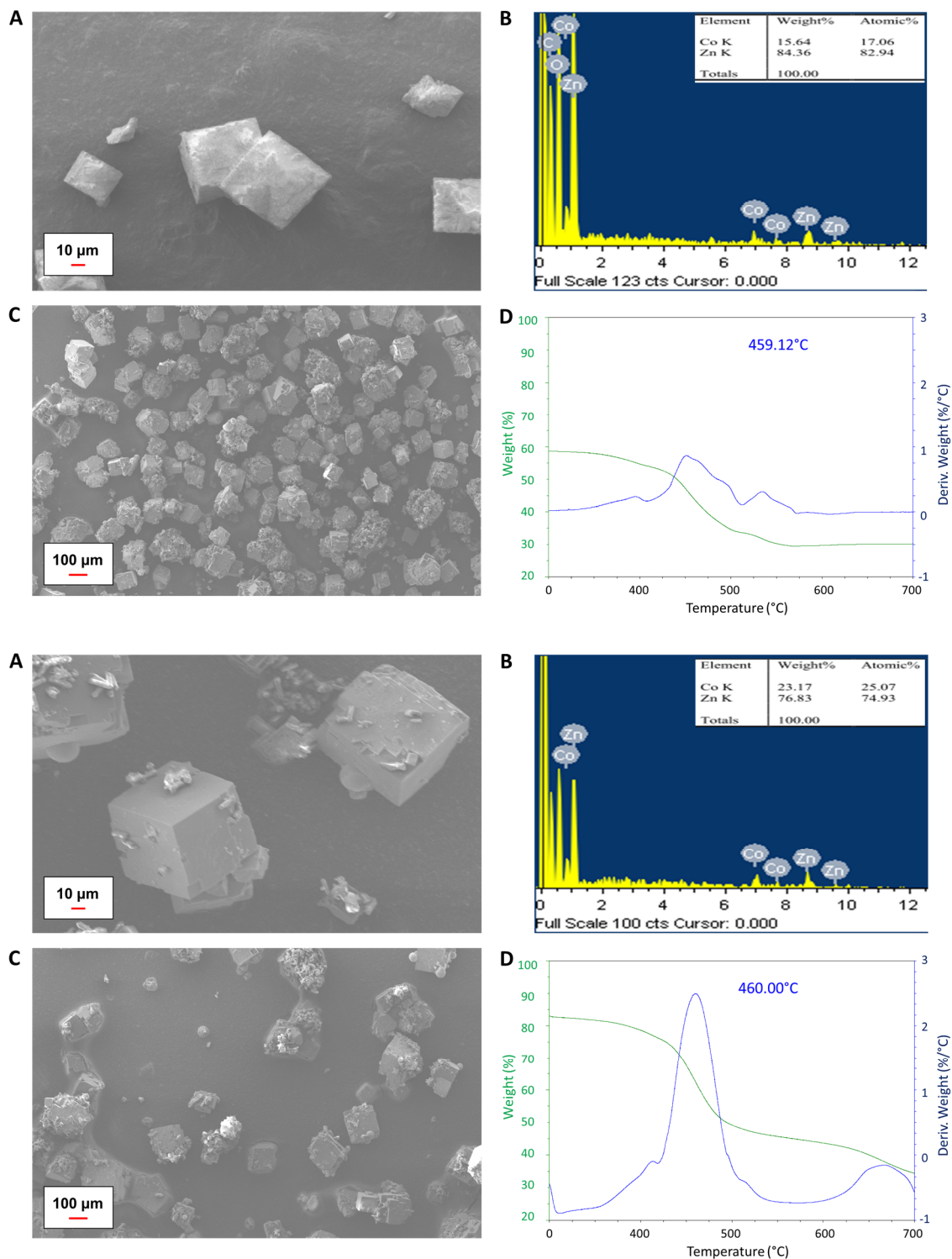


Figure 67 (above) and Figure 68 (below). (A, C) Cubic crystals of **7.3** (top) and **7.4** (bottom) observed under a scanning electron microscope. (B) EDX spectrum for crystals of **7.3** (top) and **7.4** (bottom), and percentage comparison between Zn^{II} and Co^{II} from EDX. (D) TGA for crystals of **7.3** (top) and **7.4** (bottom).

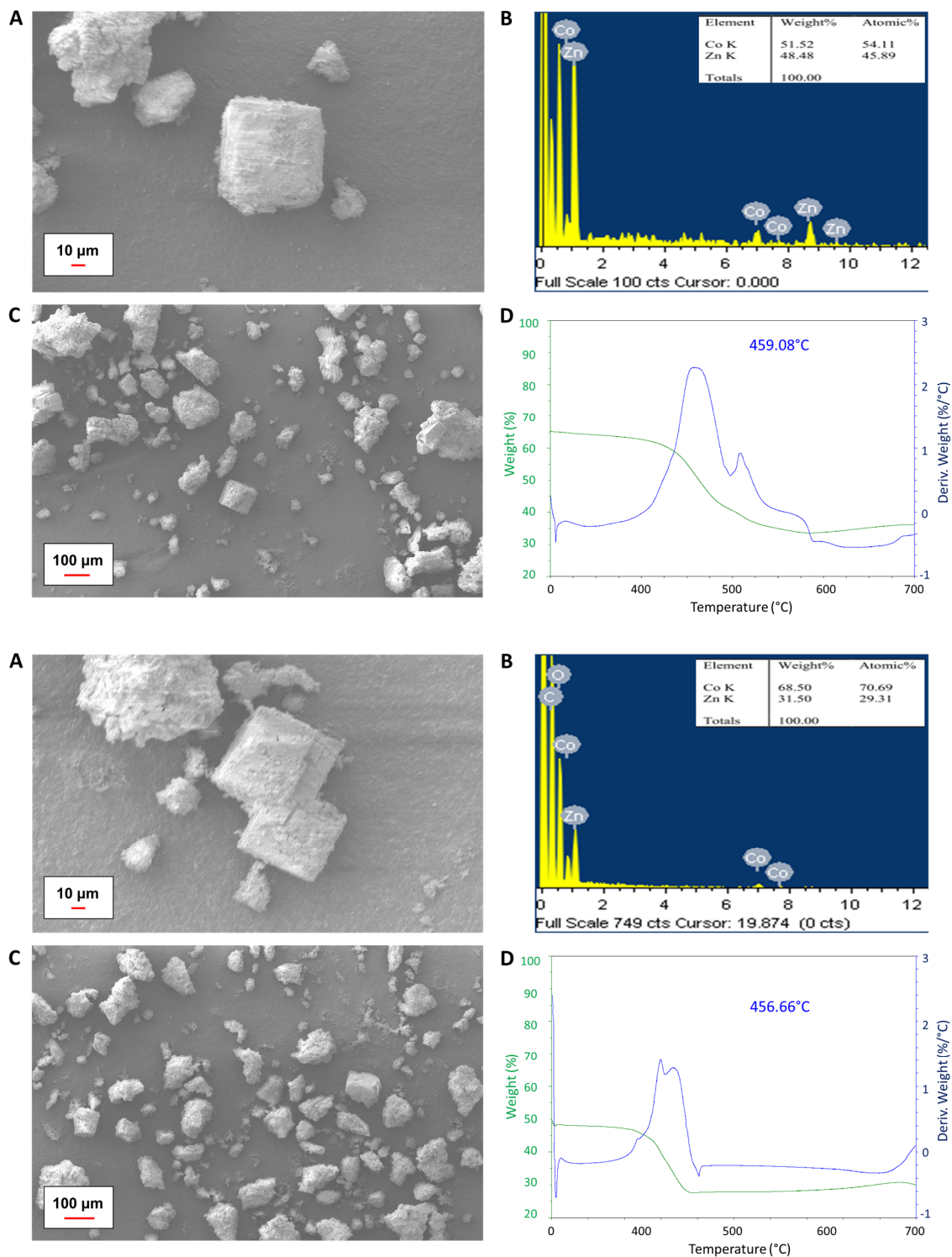


Figure 69 (above) and Figure 70 (below). (A, C) Crystals of **7.5** (top) and **7.6** (bottom) observed under a scanning electron microscope. (B) EDX spectrum for crystals of **7.5** (top) and **7.6** (bottom), and percentage comparison between Zn^{II} and Co^{II} from EDX. (D) Thermogravimetric analysis for crystals of **7.5** (top) and **7.6** (bottom).

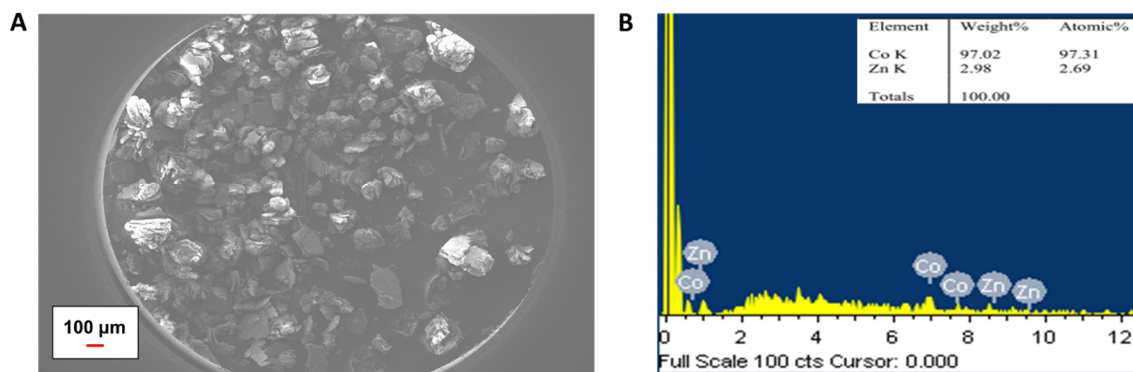


Figure 71. (A) Crystals of **7.7** observed under a scanning electron microscope. (B) EDX spectrum for crystals of **7.7**, and percentage comparison between Zn^{II} and Co^{II} from EDX.

Diffuse reflectance spectroscopy was performed in order to probe the coordination environment around site-replaced Co^{II} ions (Figure 72). The spectrum for MOF-5 displays a band exclusively in the UV region, as expected for a d^{10} Zn^{II} complex, which can be attributed to intraligand $n-\pi^*$ and $\pi-\pi^*$ transitions. These ligand-based transitions are, as expected, also present within the spectra for Co-doped MOF-5 samples. Shoulders present below 400 nm can most likely be attributed to metal-to-ligand and ligand-to-metal charge transfer processes. However, in the visible region, $d-d$ transitions are observed for Co^{II} ions. These bands can provide useful insight into the potential coordination environment of the metal. Samples with a lower molar percentage of Co^{II} in the lattice (5, 10, 15, 25%) display three overlapping peaks between 425 and 550 nm which represent transitions characteristic of an O_h coordination environment around the Co^{II} metal.⁵⁰¹⁻⁵⁰³ The peak structure is attributed to spin orbit interaction, causing splitting with transitions in doublet states of similar intensity.^{502,503} With increasing dopant percentages (50, 75 and 100 %), this fine structure shifts slightly to lower energy, as has been previously observed for T_d Co^{II} systems.^{501,504} Furthermore, a high energy band at ~ 470 nm and a lower energy band at ~ 760 nm also begin to appear, which can likely be attributed to the structural distortions induced by Co^{II} site-replacing tetrahedral Zn^{II} within MOF-5. One potential explanation for the appearance of these bands could be that upon site replacement of more than one Zn^{II} ion within the SBU, one of the T_d sites becomes pentacoordinate, as $d-d$ transitions for trigonal bipyramidal Co^{II} have been observed at similar energies.⁵⁰⁵ Thus, through examination of diffuse reflectance data, we can conclude that with lower dopant percentages only one Co^{II} ion replaces Zn^{II} in the SBU at the O_h coordination site. Conversely, additional Co^{II} replacements (2-3 ions) will most likely coordinate in a T_d site, distorting the MOF-5 framework, and causing multiple absorption bands to be present in **7.5**, **7.6** and **7.7**.

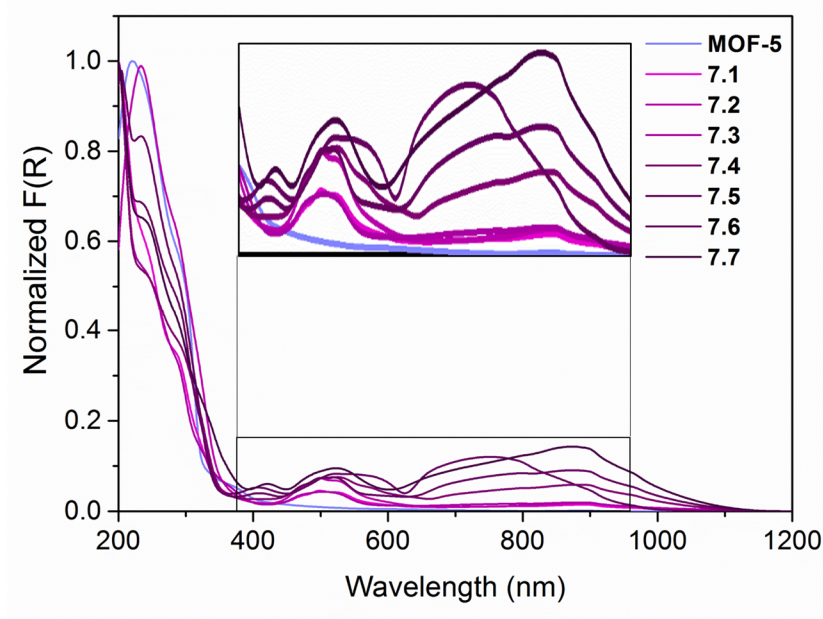


Figure 72. Normalized Kubelka-Munk diffuse reflectance spectra of **7.1-7.7**, compared with MOF-5. Inset zoomed in image of visible region displayed for clarity.

In order to elucidate the magnetic properties induced by the addition of various percentages of paramagnetic Co^{II} to the SBU of diamagnetic MOF-5, SQUID magnetometry experiments were performed. The direct current susceptibility of **7.1-7.6** was measured between 300-1.8 K, with an applied dc field of 1000 Oe (Figure 73). Due to the observed structural differences of **7.7** from the original MOF we chose not to magnetically compare this structure. Since there are four Zn^{II} ions present within the SBU, we will first discuss the sample doped with 25% Co^{II} (one Co^{II} ion per SBU) for clarity. The room temperature χT product for **7.4** is $1.88 \text{ cm}^3\text{Kmol}^{-1}$, which is in excellent agreement with the theoretical spin-only value for a single non-interacting Co^{II} ion ($\chi T = 1.88 \text{ cm}^3\text{Kmol}^{-1}$, $^4\text{F}_{9/2}$, $S = 3/2$, $L = 3$, $g = 2$). The room temperature χT value decreases gradually and monotonically to $0.45 \text{ cm}^3\text{Kmol}^{-1}$ at 1.8 K. This behaviour indicates the presence of significant magnetic anisotropy, which is expected for Co^{II} (*vide supra*). Further evidence that Co^{II} within **7.4** is O_h also arises from this behaviour. It is known that $\text{O}_h \text{Co}^{\text{II}}$ exhibits a spin of $S = 1/2$ at low temperature due to the spin orbit coupling behaviour, which would mean the χT product at 1.8 K would be near a value of $0.38 \text{ cm}^3\text{Kmol}^{-1}$ if the Co^{II} ion were in an O_h coordination environment.^{19,506-509}

Similar dc susceptibility behaviour is exhibited by **7.1**, **7.2** and **7.3**, with room temperature χT products of: 0.35, 0.73 and $1.01 \text{ cm}^3\text{Kmol}^{-1}$, respectively. These values match

well with the expected theoretical values for each percentage of Co^{II} within the framework ($\chi T_{5\%} = 0.38 \text{ cm}^3\text{Kmol}^{-1}$, $\chi T_{10\%} = 0.75 \text{ cm}^3\text{Kmol}^{-1}$, $\chi T_{15\%} = 1.13 \text{ cm}^3\text{Kmol}^{-1}$). The dc magnetic behaviour of **7.5** and **7.6** was, conversely, quite different from the lower percentages. The room temperature χT value for **7.5** decreases from $3.47 \text{ cm}^3\text{Kmol}^{-1}$ at 300 K ($\chi T_{50\%} = 3.76 \text{ cm}^3\text{Kmol}^{-1}$), to $2.30 \text{ cm}^3\text{Kmol}^{-1}$ at 26 K, followed by a sharp increase to $3.10 \text{ cm}^3\text{Kmol}^{-1}$ at 5 K, and finally a decrease to $2.42 \text{ cm}^3\text{Kmol}^{-1}$ at 1.8 K. This behaviour is indicative of the presence of non-negligible ferromagnetic interactions developing between Co^{II} ions at low temperature, where below 5 K antiferromagnetic interactions become predominant. This behaviour is mimicked by **7.6**, where the room temperature χT value decreases from $5.20 \text{ cm}^3\text{Kmol}^{-1}$ at 300 K ($\chi T_{75\%} = 5.64 \text{ cm}^3\text{Kmol}^{-1}$), to $3.17 \text{ cm}^3\text{Kmol}^{-1}$ at 16 K, followed by a sharp increase to $3.45 \text{ cm}^3\text{Kmol}^{-1}$ at 9 K, and finally a decrease to $2.71 \text{ cm}^3\text{Kmol}^{-1}$ at 1.8 K. Overall the dc magnetic data indicates the presence of only one Co^{II} ion within the SBU of MOF-5 up to a doping percentage of 25%, whereas with a higher percentage of dopant we observe multiple Co^{II} ions interacting within the SBU. We can verify that any Co-Co interactions observed must be occurring within the SBU as the Co-Co intramolecular distance is $3.180 \text{ \AA}$, whereas the shortest Co-Co intermolecular distance is $10.698 \text{ \AA}$. Thus, the magnetic interactions observed for **7.5** and **7.6** confirm that multiple Co^{II} ions were indeed incorporated into the MOF-5 SBU.

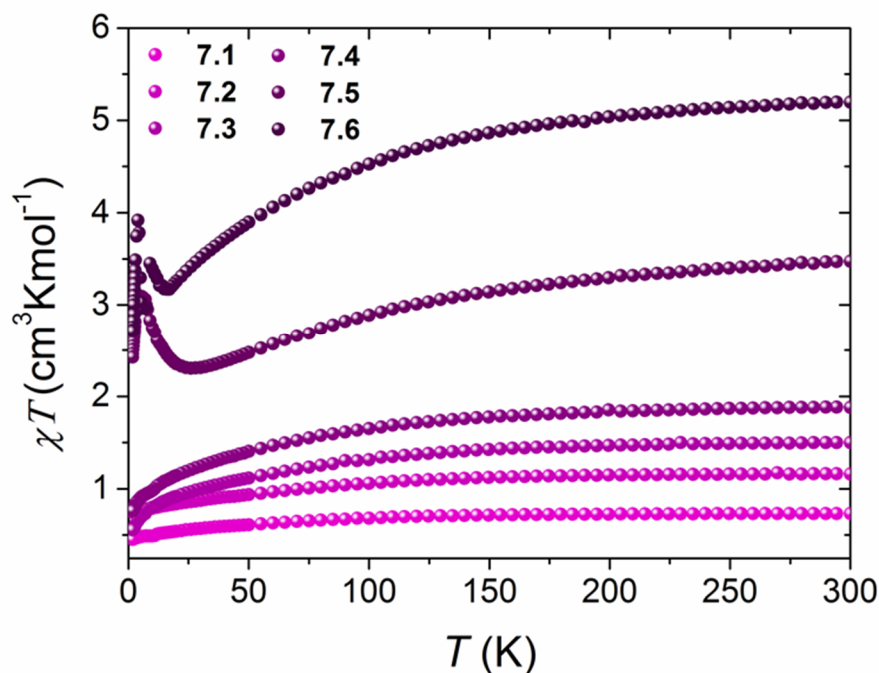


Figure 73. Temperature dependence of the χT product at 1000 Oe for Co-doped samples: **7.1-7.6**.

In order to investigate magnetic anisotropy within each doped sample, field dependent and reduced magnetisation studies were performed (Figure 74 and Figure 75). Field dependent curves display a rapid increase in magnetisation without reaching saturation up to 7 T. This behaviour is followed by a gradual increase to non-saturated values at 7 T of: $0.22 \mu_B$ (7.1), $0.57 \mu_B$ (7.2), $0.76 \mu_B$ (7.3), $1.17 \mu_B$ (7.4), $1.94 \mu_B$ (7.5), and $3.45 \mu_B$ (7.6) at 1.8 K.

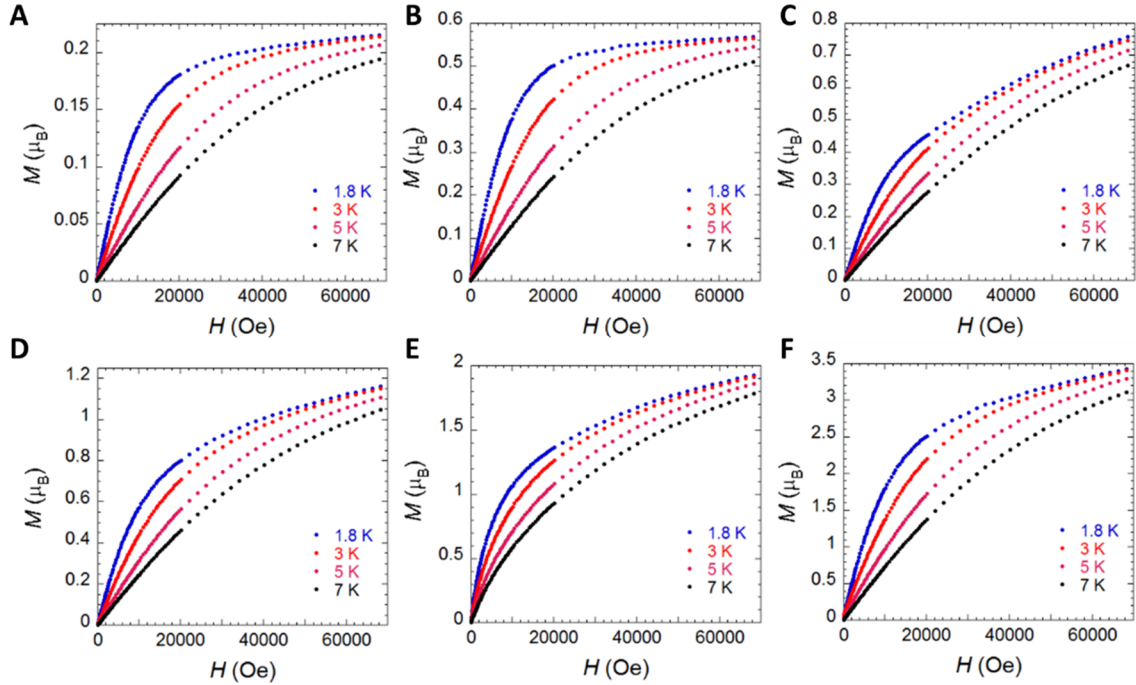


Figure 74. Field dependence of the magnetisation for: 7.1 (A), 7.2 (B), 7.3 (C), 7.4 (D), 7.5 (E) and 7.6 (F), at indicated temperatures.

Reduced magnetisation plots clearly display a separation of iso-temperature lines at indicated temperatures (Figure 75). Due to the lack of both saturation and superimposition of the curves in these plots we can confirm the presence of magnetic anisotropy in all Co-doped samples measured.

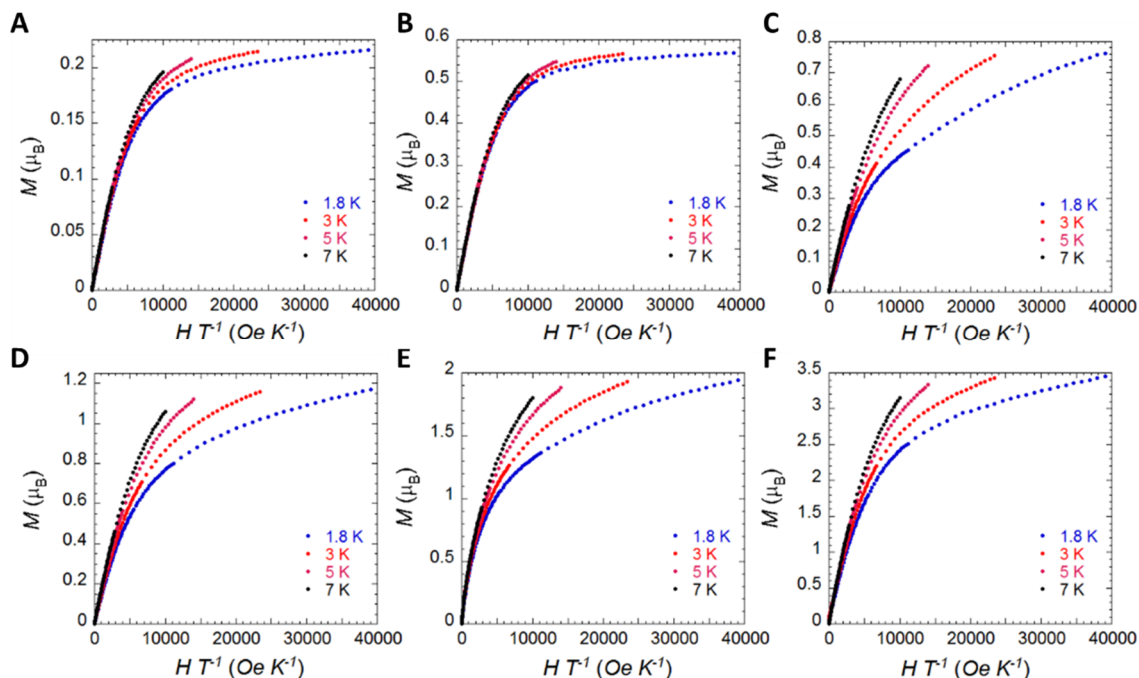


Figure 75. M vs. HT^{-1} plots for: **7.1** (A), **7.2** (B), **7.3** (C), **7.4** (D), **7.5** (E) and **7.6** (F), at indicated temperatures.

Alternating current susceptibility measurements were also performed in order to investigate potential slow relaxation of the magnetisation in Co-MOF-5 complexes. In particular, frequency dependent in-phase (χ') and out-of-phase (χ'') magnetic susceptibility signals were observed for **7.5**, under 0 Oe applied dc field (Figure 76). Shifting peak maxima observed in the χ'' plot indicate that this doped MOF-5 framework exhibits SMM-like behaviour. This magnetic relaxation data was fit using a generalised Debye model down to 2.25 K, where multiple relaxation processes become evident. A Gaussian model was also employed due to this low T behaviour, and the data was compared between the two models accordingly. The resulting relaxation times were fit using an Arrhenius equation in order to yield an effective energy barrier of $U_{\text{eff}} = 46.0(7)$ K, with a pre-exponential factor of $\tau_0 = 2.9(2) \times 10^{-10}$ s (inset within Figure 76). Remaining doped samples were probed for ac magnetic behaviour, however, only tails of peaks were observable within instrument range under small applied dc fields.

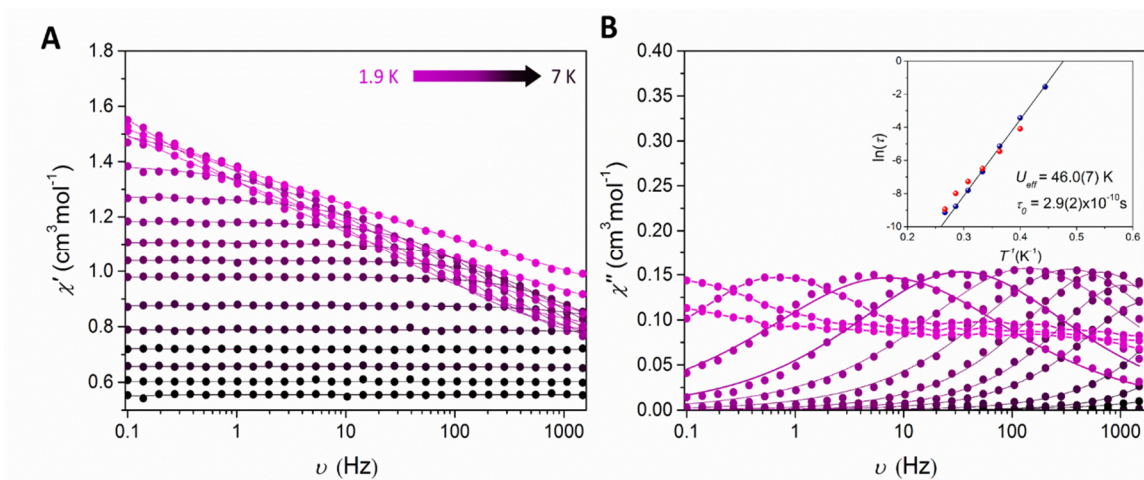


Figure 76. Frequency dependence of the in-phase susceptibility, χ' , (A); and the out-of-phase, χ'' , (B) ac susceptibility for **7.5** from 1.9 to 7 K under 0 Oe applied dc field. Solid lines are fits to a generalised Debye model down to 2.5 K, below which they serve as guides for the eye. Inset is the Arrhenius plot using χ' (red) and χ'' (blue) ac data under 0 Oe applied dc field. The solid lines correspond to the fits of the data.

7.5 Conclusions

This chapter has presented the successful site replacement of diamagnetic Zn^{II} ions with magnetically interesting Co^{II} , in the well-known, high-performing MOF-5 framework. Co-doped MOF-5 samples of varying molar percentages (5%, 10%, 15%, 25%, 50%, 75%, 100%) were synthesized without necessitating post-synthetic site replacement methods.

These structures were explored using IR, XRPD, SEM, EDX, diffuse reflectance spectroscopy, TGA, and magnetic measurements. We were thus able to probe the previously suggested O_h Zn^{II} site within the MOF-5 SBU, where TM site replacement appears to take place up to a 1:4 TM: Zn^{II} ratio. Thus, the O_h Zn^{II} site is first site replaced up to 25% molar substitution (1 Co^{II} ion per SBU). Upon doping with a higher percentage molar substitution (2-3 Co^{II} ions per SBU), a significant change in the Co^{II} coordination environment is observed. This is believed to be due to the site replacement of T_d Zn^{II} , which results in clear structural distortions. The next step will be to isolate each SCXRD structure in order to further comprehend the process occurring in synthetic site-replacement. With these structures we could gain valuable information on the MOF-5 structure, its stability, and the magneto-structural correlations needed to fully understand the behaviour observed in these materials.

Thermal stability measurements displayed a discrepancy, where 10% doped Co-MOF-5 was the most resistant to thermal decomposition. This was not entirely unprecedented, and suggests that it would potentially be a useful dopant percentage for applications requiring higher temperature conditions. Finally, through exploration of the magnetic properties we were able to lend further evidence to the Co^{II} dopant percentages. However, interestingly we were also able to visualize Co-Co interactions within the SBUs of 50% and 75% doped frameworks, where more than one Co^{II} ion is site replaced into the SBU. Due to the large distance between SBUs in the lattice, this interaction was concluded to arise from Co^{II} ions that were site-replaced within the SBU. Furthermore, the 50% doped sample exhibited SMM-like slow relaxation behaviour, with a zero-field energy barrier of $U_{\text{eff}} = \sim 46$ K.

Overall, we have performed a systematic study on the doping profile of MOF-5, whereby confirming the previously theorized O_h Zn^{II} site in the MOF-5 SBU, thus explaining the previously observed 25% maximum for TM site replacement. This may also aid in explaining the inherent instability of MOF-5 to air and moisture. This particular issue will be further explored in Chapter 8. Finally, we have synthesized a new magnetic MOF material with zero field SMM-like behaviour.

Chapter 8

Paramagnetic Metal Site Addition into 3D Networks: Fe^{III}-doped MOF-5

8.1 Abstract

Paramagnetic Fe^{III} metal sites were successfully incorporated into the iconic MOF-5 framework. This new structure, Fe^{III}-iMOF-5, is the first example of an interpenetrated MOF linked through subsumated metal ions. Structural characterisation was performed with SCXRD and XRPD, followed by extensive analysis by spectroscopic methods and solid-state NMR, which reveals the paramagnetic ion through its interaction with the framework. EPR and Mössbauer spectroscopy confirmed that the iron ions were indeed Fe^{III}, while DFT calculations were employed to ascertain the unique pentacoordinate architecture around the Fe^{III} ion. Interestingly, this is also the first crystallographic evidence of pentacoordinate Zn^{II} within the MOF-5 SBU, thus serving to help explain the inherent instability of MOF-5. This new structure displays the potential for metal site addition into a known high-performing MOF as a framework connector, thus creating further opportunity for the innovative development of new MOF materials. This work was recently published in: Holmberg, R. J.; Burns, T.; Greer, S. M.; Kobera, L.; Stoian, S. A.; Korobkov, I.; Hill, S.; Bryce, D. L.; Woo, T. K.; Murugesu, M. *Chem. Eur. J.* **2016**, 22, 7711–7715.

8.2 Introduction

Metal-organic frameworks are a unique class of materials with countless potential niches, ranging from green energy applications through gas storage and separation to catalysis, and even to biomedical applications such as drug delivery.^{217,235} Among the thousands of MOFs reported to date, MOF-5 continues to captivate researchers due to its cubic porous network, high surface area, and significant adsorption capacity.^{219,223,483-488} As discussed in Chapter 2, a significant testament to the importance of MOF-5 as a material is that it has become one of the first and only MOF structures to be targeted for commercialisation. To that end, BASF has invested greatly in the large-scale production and application of MOF-5.⁵¹⁰⁻⁵¹² One of the challenges associated with this type of practical application of MOFs is the ability to ensure their stability, since MOFs are known to frequently collapse upon heating and removal of the guest solvent molecules from their lattice. Despite the fact that MOF-5 shows remarkable thermal stability, up to ~470°C,^{219,223,483-488} its major drawback is its inherent instability to air and water exposure. To date, the reasons for the

decomposition of MOF-5 upon exposure to moisture are not well understood. In order to overcome such issues, further studies are required at the molecular level to elucidate its crystallinity loss upon decomposition.

Upon looking at the structure of MOF-5 (Figure 14), it becomes clear that terephthalic acid acts as a pillar, while Zn_4O cluster units act as self-assembled metal SBUs. As such, various derivatives of terephthalic acid have been successfully employed in fine-tuning the MOF towards a variety of desired applications.^{484,511,513-516} In all of these systems, it was reported that the Zn_4O unit retained its structural integrity, and acted as a reliable and robust SBU. Recently, MOF-5 has been post-synthetically doped, where the Zn_4O unit has been site-replaced with various first-row transition metal ions.^{495-497,517-519} In these studies, divalent and trivalent transition metal ions efficiently replaced Zn^{II} ions within the SBU, while retaining the parent MOF-5 structure. Nevertheless, the same authors postulated that tetrahedral coordination in the SBU might not be as stable as was previously assumed, and that the Zn^{II} ions could potentially adopt different geometries. Despite this assertion, no single crystal X-ray structure has been reported as evidence in support of this hypothesis. It is critical to scrutinize the coordination environment of the Zn^{II} ions in the SBU in order to attempt to gain control over the instability that plagues this framework. With this in mind we have focused our attention towards incorporating metal ions within the pores of MOF-5 in order to investigate their interaction with the host network and, more specifically, with the Zn_4O SBU.

Despite the potential that has clearly been displayed by metal substitution within MOF-5, there have not yet been any reports of metals successfully added to the structure aside from within the Zn_4O SBU. There is considerable motivation to perform metal substitution experiments within MOF-5 due to the already remarkable improvements to various properties observed as a result of these substitutions. Furthermore, the incorporation of a coordinatively unsaturated metal could lead to a wide variety of outstanding properties, such as a drastic improvements to catalytic performance.⁵²⁰⁻⁵²² We therefore set out to explore the incorporation of paramagnetic Fe^{III} ions into MOF-5. Herein, we present the successful isolation of $\text{Fe}^{\text{III}}\text{-iMOF-5}$, **8**, which is the first crystallographically isolated example of five-coordinate Zn^{II} ions within the MOF-5 SBU. This is an important initial step toward the understanding of how water molecules coordinate to Zn^{II} ions in the SBU, and thereafter affect the stability of the MOF structure. Moreover, these results also represent the first example of an interpenetrated MOF linked through a metal ion. Remarkably, the linking Fe^{III} centers are low coordinate, and can likely (*vide infra*) be forced to become a coordinatively unsaturated system with significant catalytic potential.

8.3 Experimental

8.3.1 Synthetic Information

All chemicals were purchased from Thermofisher Scientific or Alfa Aesar, and were used without further purification. DMF (HPLC grade) was dried, deaerated and stored in a N₂ environment over 3 Å molecular sieves.

8.3.1.1 Preparation of [C₂₄H_{15.35}Fe_{0.08}O_{14.76}Zn₄] (Fe^{III}-iMOF-5, **8**)

Preparation of **8** employed a modified solvothermal approach to those previously published.⁴⁸⁷ In an autoclave Teflon bomb (50 mL), under flow of N₂, Zn(NO₃)₂·6H₂O (0.535 g, 1.8 mmol), Fe(NO₃)₃·9H₂O (0.242 g, 0.6 mmol) and 1,4-benzenedicarboxylic acid (0.132 g, 0.8 mmol) were added, followed by 20 mL anhydrous DMF. The bomb was then sealed under N₂ and placed in a programmable oven with the following settings: heating 1.5°C/min to 120°C, held under autogenous pressure at 120°C for 48 h, followed by slow cooling for 12 h to 40°C. Large cubic crystals suitable for SCXRD were produced, and soaked in fresh anhydrous DMF prior to analysis. Yield: 250 mg. ICP-OES elemental analysis; comparative ratio: Zn 97.51%, Fe 2.48%.

8.3.2 Characterisation Techniques

8.3.2.1 ICP-OES

Inductively-coupled plasma-optical emission spectroscopy was performed by POS Bio-Sciences in Saskatoon, SK, Canada.

8.3.2.2 Infrared Spectroscopy

Infrared spectra were recorded on all samples in the solid state on a Nicolet 6700 FT-IR spectrometer in the 4000-600 cm⁻¹ region.

8.3.2.3 SCXRD

Single-crystal X-ray diffraction data collection results for compound **8** represent the best data set obtained in several trials. The crystal was mounted on thin glass fiber using paraffin oil. Prior to data collection crystals were cooled to 200.15 K. Data was collected on a Bruker AXS KAPPA single-crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS.⁵²³ All hydrogen atom positions were calculated based on

the geometry of related non-hydrogen atoms. All hydrogen atoms were treated as idealised contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.⁵²⁴

More detailed crystallographic information can be found in Table 12, while more detailed experimental information can be found in the supporting information of the publication.⁵²⁵

Table 12. Crystallographic data for **8**.

Compound	8
Empirical formula	C ₂₄ H _{15.35} Fe _{0.08} O _{14.76} Zn ₄
Formula weight (g/mol)	805.76
Crystal system	trigonal
Space group	R -3 m (no. 166)
Temperature (K)	200(2)
Crystal size (mm)	0.12 x 0.09 x 0.06
<i>Z</i>	12
<i>a</i> (Å)	18.3904(4)
<i>b</i> (Å)	18.3904(4)
<i>c</i> (Å)	43.7829(9)
α (°)	90
β (°)	90
γ (°)	120
Volume (Å ³)	12823.8(6)
Calculated density (gcm ⁻³)	1.252
Absorption coefficient (mm ⁻¹)	2.291
<i>F</i> (000)	4794
θ range for data collection (°)	2.26 - 30.50
Limiting indices	<i>h</i> = ±26, <i>k</i> = ±26, <i>l</i> = ±62
Reflections collected/unique	63553/4707
<i>R</i> (int)	0.0404
Completeness to θ = 30.50 (%)	0.987
Max. and min. Transmission	0.7461 and 0.6867
Data/restraints/parameters	4707/8/198
Goodness-of-fit on <i>F</i> ²	1.045
Final <i>R</i> indices [<i>I</i> 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0719, w <i>R</i> ₂ = 0.2036
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0949, w <i>R</i> ₂ = 0.2233
Largest diff. Peak/hole, eÅ ⁻³	1.666 and -1.529

8.3.2.4 XRPD

X-ray Powder Diffraction experiments were performed using a RIGAKU Ultima IV, equipped with a Cu-K α radiation source ($\lambda = 1.541836 \text{ \AA}$), and a graphite monochromator. Scanning of the 2θ range was performed from 5-40°. XRPD pattern was consistent in 2θ values with the generated pattern from SCXRD, with slight discrepancies in some intensities of peaks attributed to preferred crystallite orientation.

8.3.2.5 SEM/EDX

Scanning electron microscopy images were taken of MOF-5 and crystals of **8** using a JSM-7500F FESEM (JEOL). Crystals were adhered to an Al cylinder plate using isopropanol paint. Elemental compositions were determined by an energy dispersive X-ray spectrometer connected to the FESEM, and were processed using INCA software.

8.3.2.6 TGA

Thermogravimetric analysis data were recorded using an SDT 2960 Simultaneous DSC-TGA, TGA Q5000 V3.13 Build 261 instrument. The analysis was carried out under air flow (20 mL min⁻¹) with a heating rate of 10°C min⁻¹ from room temperature up to 1000°C, with complementary nitrogen flow (100 mL min⁻¹) as a protective gas.

8.3.2.7 Solid-state NMR Spectroscopy

Solid-state NMR spectra were recorded for **8** at 9.4 T and 11.7 T using Bruker AVANCE III and AVANCE spectrometers at Larmor frequencies $\nu(^1\text{H}) = 400.130$ and 500.13 MHz , $\nu(^{13}\text{C}) = 100.613$ and 125.758 MHz . Measurements were performed using 4 mm and 2.5 mm cross-polarisation (CP)/magic angle spinning (MAS) probes at spinning speeds of 12.5 kHz and 30 kHz, respectively. The ^1H DUMBO/MAS NMR experiment was collected at 10 kHz spinning speed. The ^1H MAS NMR and ^{13}C MAS NMR isotropic chemical shift was calibrated with adamantane (^1H : 1.85 ppm; central signal) and glycine (^{13}C : 176.03 ppm; carbonyl signal), respectively, as external standards. A 2000 μs contact time period was used for transfer of magnetisation for the ^{13}C CP/MAS NMR spectra. During the signal acquisition of ^{13}C CP/MAS NMR spectrum, high-power proton decoupling (SPINAL64) was used to eliminate strong heteronuclear dipolar couplings. Very high spinning speed spectra (VF/MAS) were carried out with a spin-echo approach (1 loop) in order to remove background distortion. The recycle delays for homo-/hetero- decoupled and VF/MAS NMR measurements were 5 s and 2 s, respectively. The dried samples were placed into the ZrO₂ rotors and all NMR experiments were performed at 300 K.⁵²⁶ The assignments of ^1H and ^{13}C MAS NMR spectra were based on literature data.⁵²⁷

8.3.2.8 EPR Spectroscopy

The high-frequency electron paramagnetic resonance spectrum of **8** was recorded at 204.8 GHz and 10 K, using a transmission-type spectrometer that is equipped with a 17 T superconducting magnet.⁵²⁸ Tunable microwave radiation was generated by a phase-locked Virginia Diodes solid-state source operating at 13 ± 1 GHz, followed by a chain of solid-state multipliers and amplifiers. Field modulation was employed in conjunction with a phase-sensitive homodyne detection scheme using a cold bolometer, yielding derivative mode spectra. Temperature control was achieved in both experiments using He gas flow cryostats. This instrument is available at the EMR division of the National High Magnetic Field Laboratory (NHMFL). The sample used for these measurements consisted of ground powder of **8** and was contained in an appropriate polyethylene sample holder.

8.3.2.9 Mössbauer Spectroscopy

The experiment was performed in zero applied field at 80 K using the same sample and container employed for the EPR experiment. The isomer shift is reported relative to that of α -Fe at room temperature. The spectrum was collected with a constant acceleration spectrometer and a $^{57}\text{Co}/\text{Rh}$ source. Spectral simulations were generated using the WMOSS software package (SEE Co. formerly WEB Research Co., Edina, MN). The apparent signal intensity is low due to the high non-resonant absorption coefficient of the large Zn^{II} excess contained in the sample.

8.3.2.10 Computational Studies

To further understand the coordination environment surrounding the Fe^{III} center, DFT calculations were performed using a cluster model (Figure 84) composed of the metal center and the nearest inorganic and organic SBUs. The coordinates of the atoms in inorganic and organic SBUs were frozen to the experimental SCXRD values, while the coordinates of the Fe^{III} center and coordinated hydroxyl and water molecules were fully geometry optimized. All calculations were performed with the Gaussian 09 program⁵²⁹ using the M06-L⁵³⁰ exchange-correlation functional. Structures built were initially optimized with the def2-SVP^{531,532} basis set for all atoms. These optimized structures were then used as starting points for further geometry optimization where the def2TZVP basis set^{531,532} was used for Fe^{III} and the atoms in the first coordination sphere, including the 5-coordinate Zn^{II} atoms, while the def2SVP basis set^{531,532} was used for the remainder of the atoms (these atoms are frozen to their SCXRD positions). Reported Mayer bond orders were calculated using the NBO 6.0 program.⁵³³⁻⁵³⁹

The SCXRD structure shows two bridging O atoms, and a number of equatorial O atoms about the Fe^{III} center. We can assign three of the O atoms to hydroxyl ions in order to maintain charge neutrality, while we can assume the remaining oxygen atoms are coordinated water molecules. We constructed and geometry optimized various structures with 3 hydroxyls and between 0 to 3 coordinated water molecules placed in different combinations of bridging and equatorial positions. To be consistent with the SCXRD results, all initial structures contained two bridging oxygen moieties that linked the Fe^{III} center to each of the two Zn^{II} centers. Although 3- and 4-coordinate Fe^{III} centers are very unlikely we examined the possibility. When no coordinated water molecules were included (3-coordinate), geometry optimization resulted in the displacement of Fe^{III} from the SCXRD position. Structures with no coordinated water molecules were not further considered since geometry optimization resulted in both the loss of an O atom that bridges the Zn^{II} and Fe^{III} centers, as well as significant displacement of the Fe^{III} center. Four initial structures with 1 coordinated water molecule (4-coordinate) were considered, however, geometry optimization of these structures resulted in loss of at least one Fe-Zn bridging oxygen atom and a large displacement of the Fe^{III} center (minimum of 1.1 Å) from the SCXRD Fe^{III} position. Thus, 4 coordinate structures were not considered further.

Given that Fe^{III} strongly prefers an octahedral coordination environment, structures with 3 coordinated water molecules giving a coordination number of 6 were initially thought to be the most likely for **8**. Various initial structures with 3 coordinated waters were considered. However, geometry optimization of these initial structures (and various perturbations of these structures) resulted in ejection of one water molecule out of the coordination sphere of the Fe^{III} center, in all but one case. Surprisingly, only one 6-coordinate structure could be located, **m2** (Figure 84). Structure **m2**, is found to be highly asymmetric, in that the Fe^{III} center is 1.21 Å closer to one Zn^{II} atom than the other Zn^{II} atom. This is in stark contrast to the SCXRD structure where it is centered between the two Zn^{II} atoms.

Optimized structures with 2 coordinated water molecules gave the best agreement with the SCXRD structure. Interestingly, all attempts to place both hydroxyl groups in the two Fe-Zn bridging positions resulted in the ejection of one of the hydroxyl groups out of the bridging position. The only structure which preserved the two bridging water molecules, **m1** (Figure 84), was also the lowest energy 5-coordinate structure. Structure **m1** has both coordinated water molecules in the bridging position and the three hydroxyl groups in the equatorial positions. To determine whether the 5-coordinate structure, **m1**, or the 6-coordinate structure, **m2**, is more energetically favoured, we added an additional water molecule to **m1** and optimized the

geometry. The **m1**+H₂O structure preserved the coordination around the Fe^{III} center, with the additional water hydrogen bonding to the OH and bridging H₂O moieties. The additional water molecule was added to **m1** in a number of different configurations; the lowest energy of which (5-coordinate structure) was determined to be 3.21 kcal/mol more stable than the 6-coordinate structure.

Finally, in order to determine the energy required to remove one of the bridging water molecules from **m1**, the initial modelled geometries were geometry optimized. The lowest energy structure was that of structure **m4** (Figure 84).

Further details on models employed and DFT calculations can be found in the supporting information of the publication.⁵²⁵

8.4 Results and Discussion

In order to explore the properties of a different paramagnetic ion within the framework of MOF-5, we chose to dope the framework with Fe^{III}. Through careful pre-synthetic fine tuning, bright orange crystals of Fe^{III}-iMOF-5, **8**, were isolated (Figure 77).

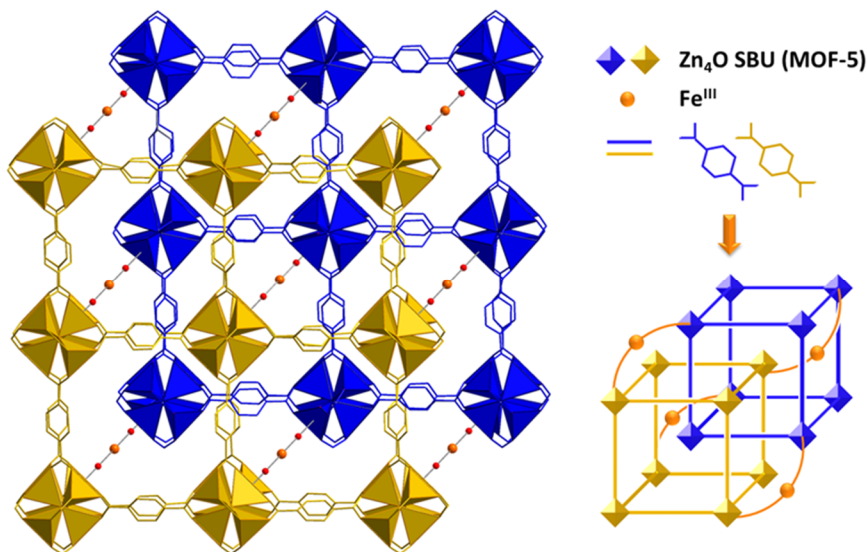


Figure 77. Single-crystal X-ray structure of C₂₄H_{15.35}Fe_{0.08}O_{14.76}Zn₄ (Fe^{III}-iMOF-5, **8**), displaying the Fe^{III} coordination within interpenetrated MOF-5 frameworks. Color code: blue and yellow (interpenetrated MOF-5). Hydrogen atoms omitted for clarity.

The direct solvothermal synthesis of **8** was achieved through the employment of anhydrous, deaerated DMF as solvent and the utilisation of a Teflon autoclave bomb with a specific temperature program in order to favor the formation of SCXRD quality crystals. This method provides a different approach than the previously reported procedure of soaking MOF-5 crystals in concentrated metal solutions over time in order to promote site replacement within the crystalline framework.^{495-497,517-519} Though post-synthetic modification was evidently effective in replacing Zn^{II} within the SBU with carefully chosen transition metal ions, it was not successful in adding an additional metal site. Conversely, when synthetically incorporated through this method, as opposed to post-synthetic site replacement, Fe^{III} ions are found to be integrated within the pores of interpenetrated MOF-5 (Figure 77).

Single-crystal X-ray diffraction studies revealed this structure to be the first example of an interpenetrated MOF structure with a metal site linker between the two frameworks. Interpenetrated networks are typically not connected together by any means, however, even without this type of stable connection interpenetrated frameworks have been found to be exceptionally useful in modifying and improving MOFs for stability, and subsequently for gas adsorption, separation, and selectivity.^{444,540,541} In fact, studies on interpenetrated MOF-5 have been performed, where it was found that interpenetration of the framework results in higher H₂ adsorption.⁵⁴²⁻⁵⁴⁴ This result is encouraging with regards to the future of H₂ storage, as well as in other potential applications of an interpenetrated MOF-5 framework with a metal site linker.

The MOF structure, **8**, crystallizes in the trigonal space group, $R\bar{3}m$, with cell constants a , b , c : 18.3904(4) Å, 18.3904(4) Å, and 43.7829(9) Å (Table 12), respectively. Unlike the original cubic MOF-5 structure, this structure crystallizes in a hexagonal arrangement, which is due to the interpenetrated network.^{542,543} More importantly, the two interpenetrated frameworks are linked *via* an Fe^{III} center through coordination of O atoms (O9) to two Zn^{II} ions in the Zn₄O SBU. It is noteworthy that Zn^{II} ions coordinated to the bridging Fe^{III} units are no longer tetrahedral, but adopt a distorted trigonal bipyramidal coordination environment (Figure 78). This remarkable change in the Zn^{II} coordination environment of the MOF-5 structure was recently suggested by Dincă and co-workers; however, this is the first time that this has been evidenced through SCXRD.⁴⁹⁷ This observation evidences a potential explanation for the previously reported moisture vulnerability of MOF-5, as this hindrance could be attributed to a change in the coordination environment around the Zn^{II} ions in the Zn₄O SBUs, causing loss of crystallinity and stability. Despite dry synthetic conditions, there is a finite amount of water within the structure

due to hydrated metal precursors. Furthermore, residual DMF is present within the pores, as the MOF was not evacuated prior to analysis (Figure 82). However, unlike in the case of MOF-5, these factors did not reduce the quality of the X-ray crystals of **8**.

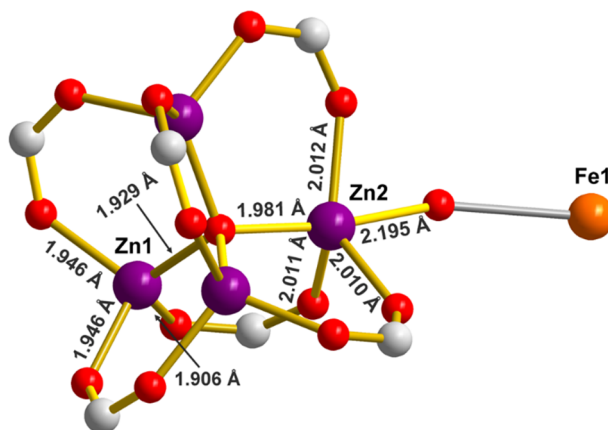


Figure 78. Molecular structure of **8**, displaying the pentacoordinate Zn^{II} coordination within the Fe^{III} -bound SBUs. Hydrogen atoms omitted for clarity.

The framework retains high symmetry due to the rhombohedral orientation of Fe^{III} sites throughout the MOF-5 lattice. The closest Fe^{III} --- Fe^{III} distance of 18.0480(3) Å within the MOF framework suggests that interactions between Fe^{III} centers can be neglected. The bridging Fe^{III} ions fit in between Zn_4O SBUs forming an intermetal Zn^{II} --- Zn^{II} distance of 9.2507(13) Å. This distance/pocket size is ideal for selectively trapping the Fe^{III} metal center (Figure 79).

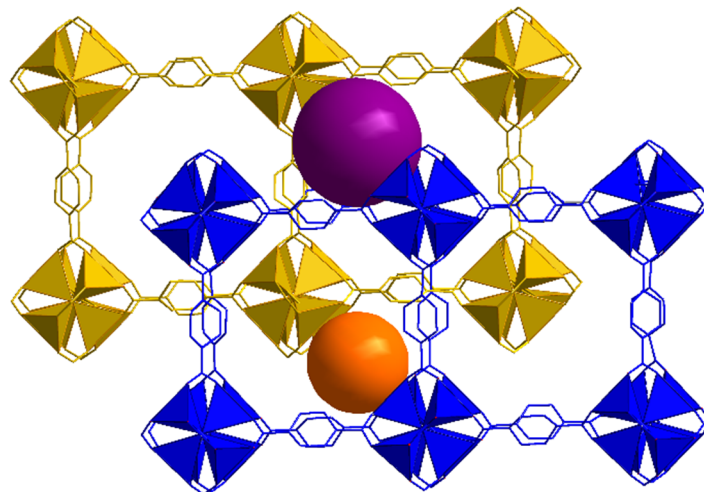


Figure 79. X-ray crystal structure of **8** displaying two pore sizes with internal diameters = 6.0 (orange) and 7.6 Å (purple).

In order to complement SCXRD measurements, a wide variety of spectroscopic and imaging techniques were employed. XRPD patterns were compared with the calculated pattern from SCXRD in order to confirm the bulk phase purity of **8**. The patterns were in excellent agreement with one another (Figure 80A), thus confirming the crystalline phase purity of the sample. In addition, IR spectroscopic analysis was performed in order to serve as a structural fingerprint, which was in good agreement with MOF-5 (Figure 80B).

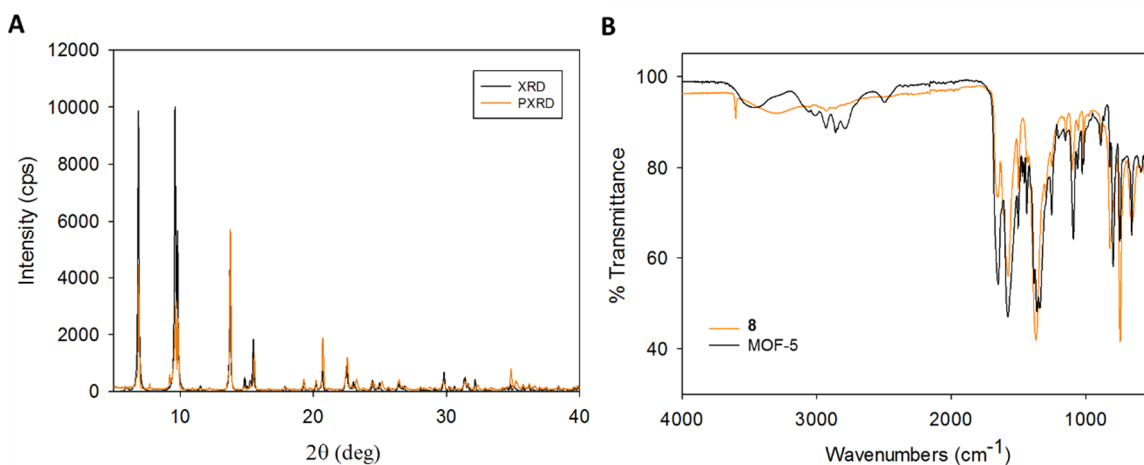


Figure 80. (A) XRPD pattern of **8** (orange) for single crystals in the 5-40° 2θ region, compared with the calculated pattern from SCXRD data (black). (B) FTIR spectra of **8** (orange) for vacuum filtered crystals in the 4000-600 cm^{-1} region, compared with MOF-5 (black).

Furthermore, SEM images were taken of single crystals of **8** in order to further explore the cubic crystalline shape and its consistency throughout the bulk of the crystals. These images, as well as the EDX spectroscopic analysis of the material can be observed in Figure 81. EDX was performed over an average area of crystalline material, with a minimum of five analyses compared for consistency of data. This data depicts the presence of Zn^{II} and Fe^{III} within the crystalline material, as well as their atomic percentages. This value was very close to that which was expected from X-ray analysis (2.48% Fe to 97.52% Zn). This was further confirmed through ICP-OES measurements, which elicited a precise percentage comparison between the amount of Zn^{II} and Fe^{III} within the structure of 2.54% Fe to 97.45% Zn.

Thermal stability measurements were performed on as-prepared **8** using TGA, and found the decomposition temperature to be 533°C (Figure 81D). This value is consistent with results for interpenetrated MOF-5.^{542,543} In comparison to MOF-5 this material is very stable, as the decomposition temperature for the original MOF is ~470°C.⁴⁸³

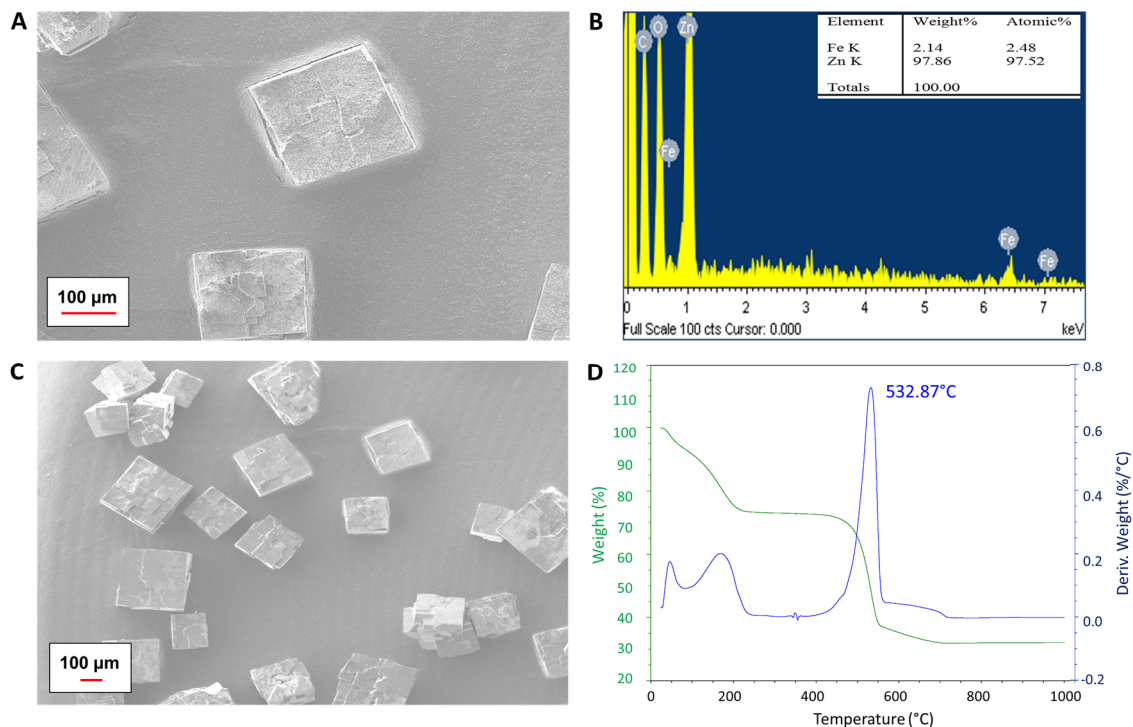


Figure 81. (A, C) Cubic crystals of **8** observed under a scanning electron microscope. (B) EDX spectrum for crystals of **8**, and percentage comparison between Zn^{II} and Fe^{III} from EDX. (D) Thermogravimetric analysis for crystals of **8**.

The presence of paramagnetic metal centres has an influence on solid-state nuclear magnetic resonance (SSNMR) spectra due to interactions with unpaired electrons.⁵⁴⁵⁻⁵⁴⁷ This interaction is similar to J-coupling in principle, and can manifest itself through an isotropic shift, as well as through anisotropic broadening. The magnitude of the interaction depends on the type of paramagnetic nuclei, and its coordination within the structure. A through-bond (Fermi contact) or through-space (pseudo-contact) transfer will result in larger or smaller changes of chemical shift, respectively. In addition, the presence of paramagnetic metal centres often causes extremely rapid longitudinal and transverse relaxation of the nearby nuclei due to electron spin couplings. As a result, a non-traditional SSNMR approach is required for detailed characterisation of samples containing paramagnetic centres. Traditional techniques at relatively low spinning speeds, combined with RF dipolar decoupling, inhibit sensitivity and resolution enhancement.^{548,549} This inconvenience can be solved by using a very fast magic angle spinning (VF/MAS > 20 kHz) technique, which removes large parts of ^1H - ^{13}C and ^1H - ^1H dipolar couplings and improves the sensitivity by suppression of spinning sidebands.^{548,549} Since the investigated

sample contains a relatively small number of paramagnetic metal centres (2.5% Fe^{III}, as compared with Zn^{II} content), both the traditional RF-decoupled and VF/MAS experiments were necessary to observe and discriminate between resonances affected by a paramagnetic interaction with Fe^{III}, and those that are not affected.

The acquired ¹H MAS NMR spectra (Figure 82A) are comprised of seven resonances; where the signal at $\delta = -0.4$ ppm can be attributed to Zn-OH-Zn bridging hydroxides, the lines at $\delta = 2.43$ ppm and 7.52 ppm can be assigned to the methyl and aldehyde functional groups of DMF, and the two relatively broad signals at $\delta = 6.8$ and 8.37 ppm are attributed to bdc.^{527,550} Additionally, no acidic protons (COOH) from bdc were observed, which confirms that all linkers are fully reacted into a three-dimensional network. Two new signals systematically shifted to lower position, at $\delta = 1.31$ ppm and 5.11 ppm, were detected in the ¹H VF/MAS NMR spectrum, and attributed to methyl groups of DMF and the protons of the aromatic rings. These new signals are attributed to parts of the structure which are in close contact with Fe^{III} ions. These signals do not survive the DUMBO MAS NMR sequence due to their rapid relaxation.

The ¹³C VF/MAS and ¹³C CP/MAS NMR spectra (Figure 82B) display: signals at $\delta = 31.2$, 36.1 and 163.8 ppm that are respectively attributed to the methyl (-CH₃) and aldehyde (-CHO) groups of DMF molecules, and signals at 130.4 and 136.2 ppm that can be assigned to the tertiary (=CH-) and quaternary (=C<) carbons of the aromatic rings, respectively, while the signal at 173.8 ppm corresponds to carboxylic functional groups of bdc linkers.⁵²⁷ In addition, as in the case of ¹H VF/MAS NMR spectra, new signals were observed using ¹³C VF/MAS NMR (indicated by red asterisks). In comparison to ¹³C CP/MAS NMR spectra, there is an evident systematic shift to higher values. These changes in chemical shift values (~2 ppm) indirectly confirm the presence of paramagnetic ions in the MOF-5 structure. The new signals are attributed to parts of the structure which are in close contact with Fe^{III} ions. These signals do not survive the CP/MAS NMR sequence due to their rapid relaxation. For the same reason, these new peaks appear with high intensity in the VF/MAS spectrum; the resonances due to the diamagnetic regions of the compound are not fully relaxed, and thus the ¹³C spectrum is not quantitative.

Solid-state ¹H and ¹³C nuclear magnetic resonance analysis of **8**, thus, confirmed the presence of two component structures: the known diamagnetic structure of bdc-linked MOF-5,⁵²⁷ and that of Fe^{III} paramagnetic ion linkers within the interpenetrated structure. The presence of paramagnetic centres was confirmed using VF/MAS, as evidenced by the existence of new, slightly shifted signals in both ¹H and ¹³C spectra, relative to those obtained using multipulse

sequences which do not show resonances associated with sites influenced by rapid relaxation due to coupling with Fe^{III} (see red asterisks). The new peaks observed under VF/MAS conditions thereby confirm the presence of through-space interactions among nuclei from bdc linkers, as well as DMF, with the paramagnetic Fe^{III} atoms. Overall SSNMR findings are consistent with the structural model determined via X-ray diffraction as well as with the computationally optimised position of the Fe^{III} ions (*vide infra*).

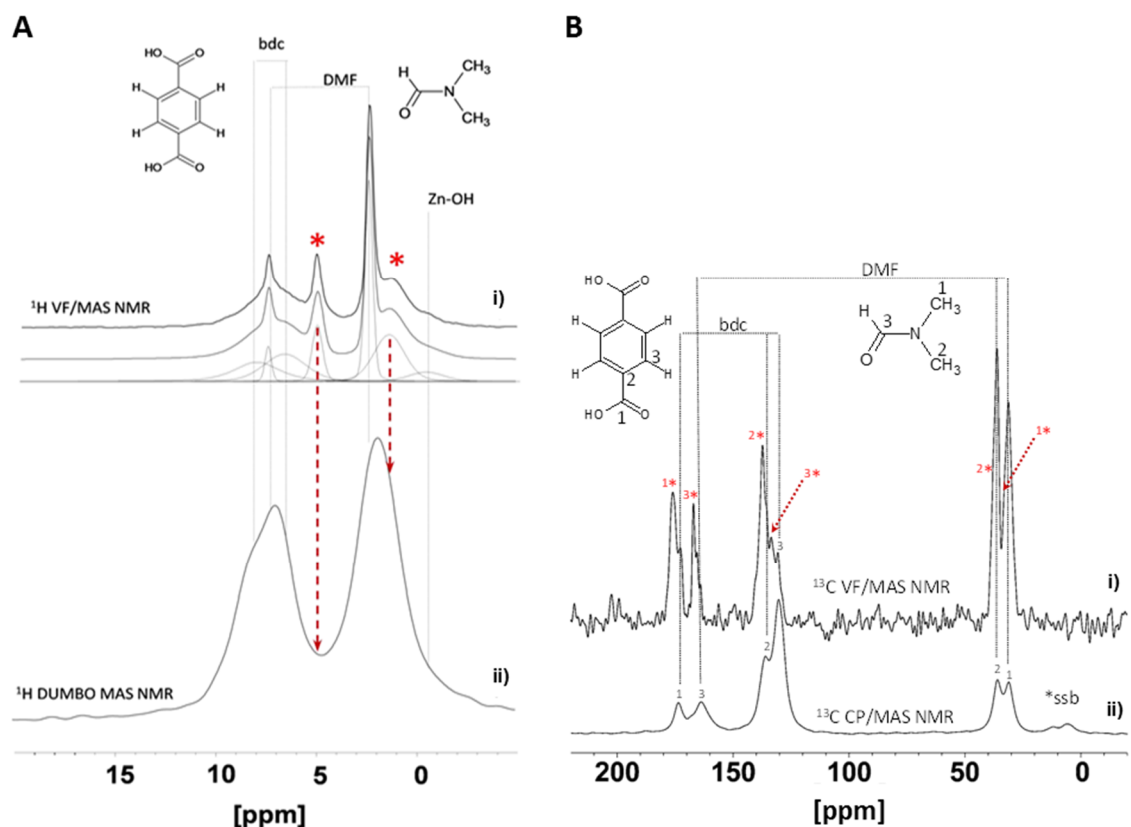


Figure 82. (A) Experimental (i) ^1H VF/MAS NMR (30 kHz; 11.75 T) and (ii) ^1H DUMBO/MAS NMR (10 kHz; 9.4 T) spectra (simulated and fitted spectrum below) of **8**. (B) Experimental (i) ^{13}C VF/MAS NMR (30 kHz; 11.75 T) and (ii) ^{13}C CP/MAS NMR (12.5 kHz; 9.4 T) spectra of **8**.

From charge considerations, coloration, and precursor composition it was posited that the Fe ion within the framework was Fe^{III} . This was confirmed through EPR and Mössbauer studies (Figure 83). The high-frequency EPR spectrum of **8**, recorded at 204.8 GHz and 10 K, exhibits a single broad feature that is centered at $g = 2.01$. The observed g -value, which is close to that of a free electron ($g_e = 2.0023$), suggests that the spectrum of **8** originates from a species with low

magnetic anisotropy. Consequently, this spectrum indicates that each of the linkers enclose a high-spin ferric site. In order to further corroborate the presence of high-spin Fe^{III} sites derived from the analysis of the EPR spectra we have measured a zero-field ⁵⁷Fe Mössbauer spectrum of **8** at 80 K. The observed spectrum exhibits two relatively broad resonances (quadrupole doublet) and is characterised by an isomer shift, $\delta = 0.45(7)$ mm/s and a quadrupole splitting, $\Delta E_Q = 0.7(1)$ mm/s. These parameters are typical of a high-spin Fe^{III} site and confirm that the Fe bridging units are indeed ferric.

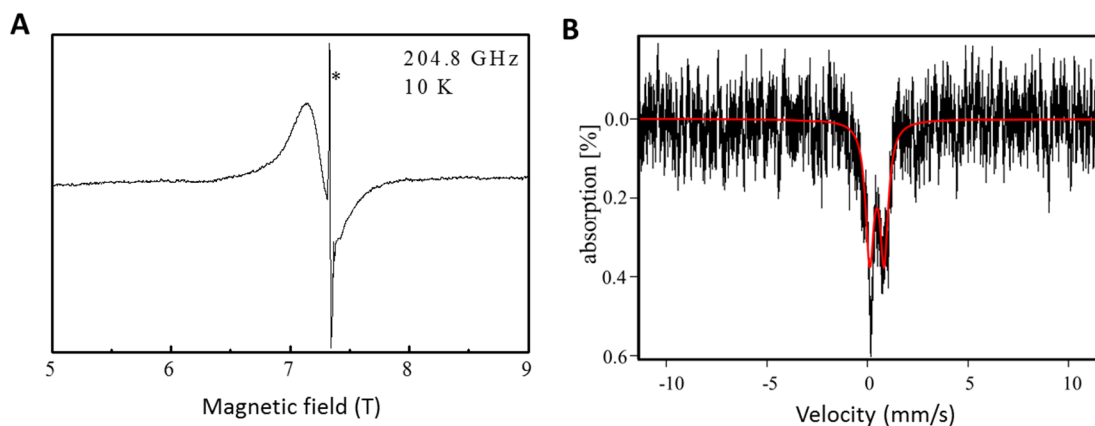


Figure 83. (A) EPR spectrum of **8** recorded at 204.8 GHz and 10 K. The narrow feature marked with an asterisk likely originates from a free radical-type impurity. The single broad feature at $g = 2.01$ is indicative of a ferric site. (B) ⁵⁷Fe Mössbauer spectrum of **8** recorded at 80 K, and fit (red line) characterised by an isomer shift, $\delta = 0.45(7)$ mm/s, and a quadrupole splitting, $\Delta E_Q = 0.7(1)$ mm/s.

In order to explore the coordination around the Fe^{III} center that was not fully discernable through SCXRD, a DFT study was performed. A cluster model composed of the Fe^{III} and the nearest inorganic and organic SBUs, as depicted in Figure 84A, was utilised where the SBU atoms were frozen. The M06-L functional⁵³⁰ was used with the def2TZVP basis set⁵³¹ for the Fe^{III} center and atoms in its first coordination shell (including Zn^{II}), while the def2SVP basis set was used for all other (frozen) atoms. We constructed and optimised over 20 structures with 3 hydroxyls (to maintain charge balance) and between 0 to 3 coordinated waters placed in different combinations of bridging and equatorial positions. Examples of the structures (**m1-3**) are shown in Figure 84B. Geometries with 0 to 1 coordinated waters all optimised to structures which lost a

bridging oxygen moiety and displaced the Fe^{III} center at least 1.1 Å from the SCXRD position. These structures were not considered further. Optimisation of structures with 2 coordinated waters resulted in two stable structures, where the lowest energy structure, **m1**, is shown in Figure 84A. Geometry optimisation of structures with 3 coordinated waters generally resulted in the ejection of one water out of the coordination sphere of the Fe^{III} center. After significant effort, one stable hexacoordinate structure was located, **m2**, as sketched in Figure 84B. However, the hexacoordinate structure was found to be 3.2 kcal/mol less stable than the pentacoordinate structure with a water molecule added. Moreover, the geometry of the pentacoordinate structure, **m1**, was in much better agreement with the SCXRD geometry than the hexacoordinate structure, **m2**. For example, the Fe^{III} center in the **m1** is equidistant to each Zn^{II} atom (4.63 Å) just as it is in the SCXRD structure, whereas in the 6 coordinate structure, **m2**, the Fe^{III} center is 1.21 Å closer to one Zn^{II} atom than to the other.

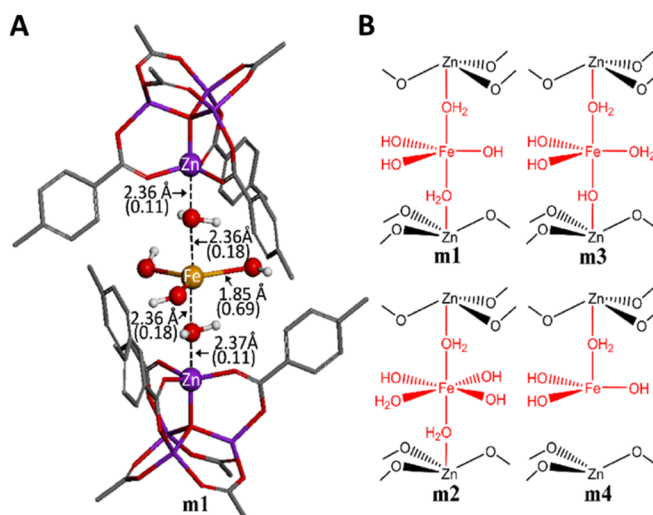


Figure 84. (A) Cluster model used for DFT calculations of the coordination environment around the Fe^{III} center in **8**. The geometry shown is that of the lowest energy pentacoordinate structure identified, **m1**. Relevant bond distances are given with Mayer bond orders in parentheses. H atoms on the organic SBUs are removed for clarity. (B) Coordination environment of Fe^{III} center in selected starting and optimised structures of the model system.

Overall, from the DFT study, we propose that the Fe^{III} center in **8** is a pentacoordinated trigonal bipyramidal structure with two coordinated water units occupying the axial positions that bridge the Fe^{III} and Zn^{II} centers, and three hydroxyl groups occupying the equatorial positions.

Pentacoordinate Fe^{III} is relatively rare, but has been previously observed in porphyrin and diimine complexes.⁵⁵¹⁻⁵⁵³ The optimised model structure is shown in Figure 84A with relevant bond distances depicted and Mayer bond orders given in parenthesis. Using these parameters, bond valence sum calculations were performed and yielded a value consistent with Fe^{III} of 3.23.⁵⁵⁴ The bridging water molecules form dative bonds with the metal centers, which exhibit weak but significant covalent interactions. This is evidenced by the calculated Fe-O_w bond order of 0.18, and the Zn-O_w bond order of 0.11. For comparison, the coordinated hydroxyl groups, which occupy the equatorial sites, have a Fe-O_{OH} bond order of 0.65. Removal of one of the bridging water molecules in **m1** resulted in the formation of structure **m4**, and a calculated water binding energy of 20.5 kcal/mol. The modest thermodynamic barrier to removing one water molecule from **m1** suggests that a MOF containing an even lower coordination number with active open metal sites could be accessible through **8**. This could subsequently lead to high catalytic performance, as has been previously exhibited.⁵²⁰⁻⁵²²

8.5 Conclusions

This chapter has presented the synthesis and structural characterisation of a novel paramagnetic MOF material. This material, based on well-known MOF-5, is the first example of metal site addition within a MOF that is bridging two interpenetrated frameworks. It is notable that previous reports of metal site addition in MOFs had only been accomplished through site-replacement or coordination within a pre-designed ligand pocket.

Single crystals were thoroughly studied through SCXRD, which was corroborated through extensive methods of study. In particular, EPR and Mössbauer measurements were able to confirm that the Fe ion linker was indeed in the 3+ oxidation state, as was suspected from charge considerations and crystalline colour. DFT calculations suggest that the Fe^{III} site is in a 5-coordinate trigonal bipyramidal environment with bridging waters that link the Fe^{III} to the inorganic SBUs. Furthermore, this MOF has also provided the first crystallographic evidence for pentacoordinate Zn^{II} in MOF-5, thus providing confirmation of the proposed mechanism for moisture instability within this ubiquitous framework.

The value of these findings lies in the ability to synthetically add a potentially coordinatively unsaturated metal site within a well-known performing MOF framework. Through this approach, MOFs which are known to possess certain desirable properties may be

straightforwardly modified to have additional properties inherent to the inserted metal site. Thus, proposed future studies based on this system will be discussed in Chapter 9.

Chapter 9

Perspective and Proposal for Future Work

The most significant challenge facing the advancement of magnetic nanotechnology remains the ability to control the spins of magnetic ions within practical materials in order to harness their properties on the nanoscale and beyond. This entails a great deal of fundamental exploration into the behavior of paramagnetic ions within various architectures in order to better understand how we might be able to go about controlling their properties. As discussed throughout, the most important properties of nanomagnets for many applications are the energetic barrier to magnetic relaxation, U_{eff} , and the temperature under which magnetic blocking occurs, T_B . By improving these parameters, we take steps towards the production of magnetic nanomaterials that are capable of operating over extended time periods and at practical temperatures. The work within this thesis has served to exploit the properties of paramagnetic ions within various nanoarchitectures, thus affording crucial insight into some of the possible synthetic approaches to the feasible development of tunable, ordered magnetic nanomaterials.

Upon the initial design of projects surrounding the study of the fundamental magnetism of nanoarchitectures, we saw potential within NaYF_4 nanoparticles, as they had already been doped with Er^{III} and Yb^{III} lanthanide ions in order to elicit luminescent properties. For our purposes, we were interested in exploring the magnetic potential of other lanthanide ions in similar systems. Thus, in Chapter 3, we demonstrated that isotropic Gd^{III} and highly anisotropic Dy^{III} and Tb^{III} ions can also replace Y^{III} , producing highly crystalline nanoparticles, while consequently tuning their physical properties. A trend in the size, shape and crystalline properties of nanoparticles dependent upon the type and concentration of each dopant within the lattice was discovered, thus providing the desired potential for nanomaterial tunability. Through studying the difference between the desired compositions of each nanomaterial, as well as the actual elemental makeup, we discerned an ionic radii dependence, where Dy^{III} was seemingly the most successful replacement for Y^{III} . Each lanthanide-doped material was magnetically studied, and found to be non-superparamagnetic down to 2 K (no magnetic blocking from 2-300 K). This resolved the question of whether or not up-converting lanthanide-doped nanoparticles could be applicable candidates in electronics, or whether they were better suited to biomedicine. Due to the lack of bulk magnet-like properties down to 2 K, we concluded that these materials had potential as multimodal MRI contrast agents. Comparative luminescence studies with each doped material were not performed, but this is something that should indeed be explored alongside the

magnetism in order to truly fine-tune the materials towards a desired functionality. Interestingly, since the publication of this work, we have discussed a potential collaboration with a new researcher at the University of Ottawa whose expertise lies in MRI contrast and biomedical imaging. This study would allow for fine tuning through lanthanide doping to be studied with a variety of different types of expertise, which were unavailable to us at the time. However, in order for these materials to be truly applicable in biomedicine they will require an outer shell structure that is capable of providing biocompatibility, while not simultaneously quenching the luminescence of the particle. Since these up-conversion particles have already made an incredible impact within the literature, it is a worthwhile endeavor to explore their potential as multimodal probes through detailed lanthanide doping studies.

Following working with nanoparticles, we wished to delve into the field of molecular magnetism, while still retaining a nanomaterials approach. This was motivated by the finite control available to magnetochemists in synthesizing molecular magnets. Despite the incredible work performed within the field of molecular magnetism, the control over these systems once they have been attached to a surface has been incredibly lacking. Thus, the materials side of this field is still under development and trying to catch up to the well-developed and long-studied fundamental chemistry. Our initial approach was to develop a new SMM with the capability to be attached to a nanoparticle surface. At this time, dinuclear lanthanide systems showed promising magnetic properties due to the inherent high spin ground state and highly anisotropic nature of these ions, as well as their shielded $4f$ orbitals. In particular, several studies had been performed illustrating the incredible magnetic properties of Dy^{III} within a variety of different ligand environments. We successfully isolated a dinuclear Dy^{III} complex, which was specifically designed with S-terminated groups in order to facilitate a strong S-Au bond with our intended nanoparticle host. We chose a nanoparticle surface because we envisioned the capability of performing analytical studies in both solution and in the solid state, thus opening the doors to a wealth of potential available techniques for studying such a material. Furthermore, isolation of the material as a powder through centrifugation was available, thus, magnetic measurements could be performed using a conventional SQUID magnetometer. This was important, as the majority of previous studies on magnetic molecules attached to a bulk surface necessitated the use of specialized techniques, such as XMCD. With this in mind, we wanted to have our SMM be the only component on the surface of the particles, which led to a collaboration with another group at the University of Ottawa to synthesize unique “naked” AuNPs. These nanoparticles were capping agent-free thanks to an innovative synthetic method that involved laser ablation of the particles.

Characterisation of this hybrid material confirmed surface attachment of the molecules in question, which was a challenging goal. Upon confirmation that the structure was retained upon surface attachment, magnetic studies were performed, which displayed that the static magnetic behaviour was retained upon surface attachment. This was promising, as magnetic molecules have been known to experience significant chemical and structural changes upon surface attachment, which have completely changed or destroyed their magnetic properties. However, the dynamic behaviour was indeed altered, which we attributed to a slight change in local anisotropy of the Dy^{III} ions. This was likely a result of the short thiocyanate linker employed in attaching the magnetic molecule to the surface of AuNPs. This method could possibly be improved upon through the employment of longer linkers, as to not perturb the coordination environment, and anisotropy axes, of the magnetic ions. Going forward, it would be interesting to synthesize a mononuclear magnetic system with zero-field slow magnetic relaxation to enable a more facile comparative study when placed on the surface of NPs. Furthermore, the linker employed could be synthesized with varying lengths, allowing a study to be performed on the effect of plasmonic radiation on the magnetic behaviour of a SIM. Since magneto-optical studies are becoming more and more prevalent within the literature, this could be probed through excitation at the plasmon band wavelength of the employed AuNPs. This type of study has been performed in relation to luminescent properties, however, it has never been linked with magnetic behaviour.

These findings were pioneer in the development of a new practical method of studying the fundamental effects of surface attachment of molecular magnets. There has been extensive study of molecular magnets on flat bulk surfaces since SMMs have been proposed as the future of information storage. However, as discussed in Chapter 2, this was one of the first and only examples using nanoparticles as a substrate. Despite the incredible work being done, many challenges persist in the field of molecular magnetism, including, but not limited to: surface design and optimisation, coverage and assembly, ordering and control over spins and anisotropic axes, electronic coupling, chemical stability, and ideally a design-based improvement in the overall magnetic performance of the material. Thus, it will be fascinating to see this field develop as the physics and materials science catch up to the chemistry, which is constantly being reinvented.

After successfully adhering molecular magnets on surfaces, we wished to explore a slightly different type of ordered assembly; namely 1D chains. Molecular magnetism has delved into 1D with SCMs, however, the assembly of well-separated, discrete molecular magnets is frequently performed solely in 2D, on surfaces. We synthesized a family of lanthanide molecular

magnets with chelating ligand EDTA and introduced Na^+ ion bridges, causing the formation of 1D networks. These chelated chain architectures displayed magnetic properties without long range ordering, thus, despite their dimensionality, they did not exhibit SCM behavior. Surprisingly, however, we observed slow relaxation of the magnetisation in the Gd^{III} -EDTA chain structure. The behavior of the Gd^{III} chain was unexpected, as the zero-field response was typical of a theoretical isotropic paramagnet, however, under an applied static field, we observed field-induced peak shifting phenomena. In order to better understand this behavior, we collaborated with theoretical chemists and were able to attribute the slow relaxation to spin-phonon transitions between Gd^{III} levels, which are not separated by an energy barrier. This mechanism of slow magnetic relaxation was found to be possible due to small spin-phonon rates caused by the chain architecture. We then magnetically studied the anisotropic Tb^{III} and Dy^{III} EDTA chains, which also displayed field-induced slow magnetic relaxation.

We realized the potential to study controlled 1D networks of magnetic molecules, and the effects of their ordered array on the magnetic properties of the unit. These networks are currently being investigated for their MRI contrast behavior with the aforementioned internal biomedical collaboration. They are particularly applicable to this area due to their coordinated water molecules, and high water solubility. These systems could also be of interest in the development of 1D networks for study in monolayer spintronics applications. Currently this field is mainly investigating 2D arrays of molecular systems, and graphene-based sheets, however, there has been a recent shift towards the study of 1D structures.^{555,556} These low-dimensional lanthanide assemblies crystallize easily and are very water soluble, thus making them excellent potential candidates for study in molecular electronics.

Upon studying magnetic molecules within 1D chains, we chose to study the effects of cluster chemistry within 3D frameworks; namely MOFs. MOFs provide an interesting method of exploring molecular magnetic units in ordered arrays, as their SBUs can be well-separated as a result of the chosen ligand architecture. We synthesized a unique cubic MOF structure with a high nuclearity Co^{II} SBU. Co^{II} was chosen due to its inherent magnetic anisotropy, and the high nuclearity SBU was desired for the purpose of studying complex magnetic interactions in isolated 3D architectures. This was the first Co_8 cuboctahedron MOF, which was highly-symmetrical and could be structurally characterised using SCXRD. The thermal stability and gas adsorption properties were studied and found to be incredibly modest in relation to other MOF materials. However, our interest was mainly in the magnetic properties of the Co_8 SBU. The cuboctahedral arrangement of 8 Co ions in the SBU induced non-negligible antiferromagnetic interactions,

which were modelled in collaboration with another group at the University of Ottawa. It was found that the faces of the cube were ferromagnetically coupled, however, opposing faces were antiferromagnetically coupled (4 up and 4 down), leading to an $S = 0$ ground state.

Overall, this highly-symmetrical MOF was a building block toward the development of other high nuclearity SBUs in MOF structures, especially through structural modifications employing different rigid ligand architectures and various metal ions to elicit new magnetic frameworks. Furthermore, the isolation of well-separated magnetic clusters as SBUs of MOF networks is an interesting method for potentially aligning and separating ordered arrays of nanomagnets.

After exploring the nature of more complex magnetic interactions in high-nuclearity multinuclear 3D networks, we chose to explore a more systematic approach through doping. Consequently, we chose to gradually dope anisotropic Co^{II} into a well-known MOF (MOF-5). MOF-5 was chosen due to its known high-performance and previously demonstrated propensity for Zn^{II} site replacement with other TM ions. We were interested in exploring the coordination of Co^{II} ions within the SBU and probing their magnetic properties. It was previously suggested that MOF-5 possessed Zn^{II} ion within each SBU that was capable of being in an O_h coordination environment, thus potentially facilitating the instability to moisture that is known to be detrimental to the framework. We found that when Co^{II} was incorporated into the MOF-5 lattice through substitution with Zn^{II} , the suspected O_h site is first site replaced up to 25% molar substitution (1 Co ion per SBU). Upon doping with a higher percentage molar substitution (2-3 Co^{II} ions per SBU), a significant change in the coordination environment is observed. It is likely that one of the T_d Zn^{II} ions is being site replaced in these structures with higher percentages of dopant, leading to structural distortions. Interestingly, magnetic studies displayed non-negligible interactions between Co^{II} ions occurring within the SBUs upon doping with 50 and 75% Co^{II} . Due to the well-separated nature of SBUs, these interactions were confirmed to take place within the same SBU. The dynamic magnetic properties were also probed, showing that 50% doped Co-MOF-5 exhibits SMM-like behaviour, with a zero-field energy barrier of $U_{\text{eff}} = \sim 46$ K.

These systems require further study in order to attempt to obtain further information on their structural properties. We have performed post-synthetic doping in molar amounts, eliciting colour changes in the crystals, however, we have not yet been able to obtain a SCXRD structure. Through further structural characterisation, these systems can be explored in more detail in order to explain the slow relaxation of the magnetisation occurring within the 50% Co-doped sample. It would also be beneficial to perform gas adsorption studies on these systems, as low percentages

of Co^{II} doped into the SBU of MOF-5 have been shown to have improved adsorption properties to those of the original MOF.

Despite the interesting magnetic properties within the Co^{II} -doped MOF-5 materials, we wished to explore a slightly different magnetic ion as dopant, hoping to obtain valuable structural information using a different dopant ion. We chose to synthesize MOF-5 with Fe^{III} , and were able to synthesize and fully characterise the first example of metal site addition within a MOF that is bridging two interpenetrated frameworks. Instead of site-replacement occurring in the non- T_d Zn^{II} site, a new MOF-5 structure was obtained, wherein two Zn^{II} ions within the SBUs of different interpenetrated frameworks were coordinatively linked to one Fe^{III} ion in a rhombohedral arrangement. This structure was also the first crystallographic evidence for 5-coordinate Zn^{II} in MOF-5, thus confirming the previously proposed site of instability within MOF-5. Likely as a result of this coordinated interpenetrated framework structure, it was not only found to be more stable to atmospheric conditions than MOF-5, but was also more thermally stable. Upon extensive structural characterisation, we found ourselves wondering what the exact coordination environment around the linking Fe^{III} would be, as it could not be discerned crystallographically. Thus, through a collaboration within the University of Ottawa, DFT was employed in order to probe the Fe^{III} site. It was confirmed that the Fe^{III} was in a 5-coordinate trigonal bipyramidal environment with bridging waters that linked the Fe^{III} to the inorganic SBUs. It is notable that metal site addition in the past had only been accomplished through site-replacement or coordination within a pre-designed ligand pocket. We also employed DFT in order to calculate the binding energy of terminal ligands on the Fe^{III} , and were able to determine that the energy to further unsaturate the metal site was by no means unsurmountable.

The value of these findings lies in the displayed ability to synthetically add a metal site with the potential to become coordinatively saturated to a well-known MOF framework. It would be a valuable experiment to attempt to remove one of the terminal ligands on Fe^{III} , followed by gas adsorption and catalytic studies. Along these lines, it would also be interesting to coordinate different ligands to the Fe^{III} site in order to employ UV-Vis spectroscopy to study charge transfer bands. A proof of concept would be to attempt this method using other trivalent transition metals as potential bridging architectures and study their thermal and chemical stabilities, as well as their gas adsorption properties. Finally, since Co^{II} has been shown to be available for site replacement in the non- T_d Zn^{II} site in MOF-5, and the Fe^{III} linker coordinates to this site in order to bridge the two interpenetrated networks, there is potential for combining these two systems in order to probe a potential spin-crossover behaviour within this MOF system.

The design strategies developed and illustrated within this thesis towards the synthesis of novel magnetic nanomaterials of varied dimensionalities can provide new ideas for researchers in this field, as well as in materials, engineering and physics. The focus on developing molecular systems with rigid control and record-breaking properties is indeed a worthy and high-impact effort, however, if they are ever to be practically employed it is necessary that magnetic nanomaterials be explored by collaborative efforts of researchers in the wide-variety of fields just mentioned, as it is not a feasible unilateral effort. On a more modest level, there are still a wide variety of directions that can be taken with the projects discussed within this thesis. The perspectives and future directions summarized in this chapter have the potential to be continued for some time by future members of the group, as there is still much to learn from each nanomagnetic system.

Chapter 10

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