

# Gaining Insights into the Interplay between Optical and Magnetic Properties in Photoexcited Coordination Compounds

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We describe early and recent advances in the fascinating field of combined magnetic and optical properties of inorganic coordination compounds and in particular of 3d–4f single molecule magnets. We cover various applied techniques which allow for the correlation of results obtained in the frequency and time domain in order to highlight the specific properties of these compounds and the future challenges towards multi-

dimensional spectroscopic tools. An important point is to understand the details of the interplay of magnetic and optical properties through performing time-resolved studies in the presence of external fields especially magnetic ones. This will enable further exploration of this fundamental interactions *i.e.* the two components of electromagnetic radiation influencing optical properties.

## Introduction

Ultrafast magnetisation dynamics after photoexcitation in molecules are still poorly understood, largely due to limitations in the experimental set-ups which generally do not, for example, include the application of external fields with the exception of some pioneering efforts made by the Johansson group, as will be described later. With the ultimate goal of being able to predict and control the response of a system to photoexcitation via ultrashort laser pulses in mind, the intricate details of the coupling to the electronic, vibrational and magnetic properties must be investigated. To achieve this goal comprehensive knowledge regarding the excited state energy landscape and the associated possible relaxation pathways after excitation is required. For this experimental data are needed

which can be evaluated in order to illuminate the interplay of electronic excitation and magnetisation dynamics.

This article aims to give a perspective view on how to obtain such experimental data. It also highlights some of the challenges that lie ahead in the development of ultrafast photoactive magnetic materials. Given that such materials could revolutionise the world of data storage and molecular electronics in general, this represents an exciting challenge for photo-chemists and physicists.<sup>[1–6]</sup>

## Background Information

### Photoactive Magnetic Coordination Compound Systems

There are many well-known examples of photoactive magnetic materials which have been studied as multifunctional units for use in molecular electronics with a view towards possible applications.<sup>[7–8]</sup> Prussian Blue  $\{\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3\}$ , which was discovered in the early 18<sup>th</sup> century,<sup>[9]</sup> provides a starting point for such applications using the compound itself and also the so-called PBAs (Prussian Blue Analogues) which are derived using building blocks of Prussian Blue in combination with other transition metal species to form infinite or 0D analogues of the parent system. Prussian Blue owes its dark blue colour to its optically-induced intervalence charge transfer (IVCT) resulting in the transformation of an  $\text{Fe}^{\text{III}}$  high-spin (HS) centre into an  $\text{Fe}^{\text{II}}$  HS centre whilst essentially simultaneously transforming a neighbouring  $\text{Fe}^{\text{II}}$  low-spin (LS) centre to an  $\text{Fe}^{\text{III}}$  LS centre. This makes Prussian Blue one of the prime examples for a Class II compound in the Robin and Day classification.<sup>[10]</sup> The ultrafast dynamics associated with the IVCT of Prussian Blue has been investigated in 1995 by Arnett *et al.* who observed the emergence of a sub-picosecond component for a charge-transferred state which then persisted for tens of picoseconds (see Figure 1). Moreover, Fourier power spectra obtained from transient anisotropy revealed the importance of a  $270\text{ cm}^{-1}$

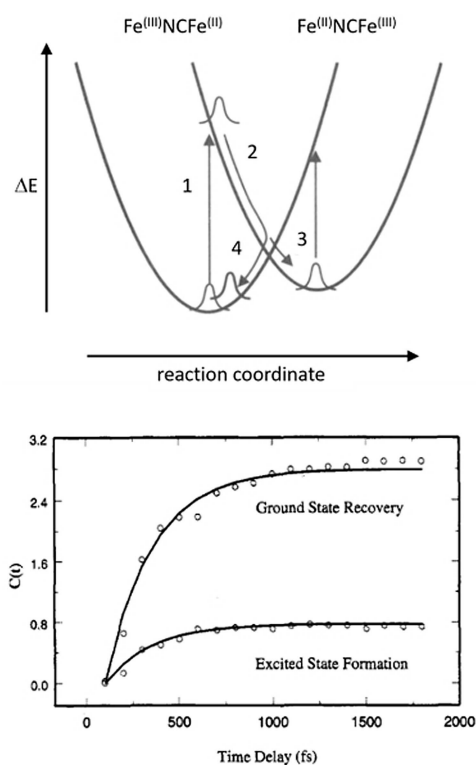
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**Figure 1.** Marcus<sup>[13–15]</sup> type potential energy diagram with excitation of wavepacket (1) and relaxation processes (2–4) (top) and ultrafast correlation function  $C(t)$  demonstrating the ultrafast recovery (bottom). Adapted with permission from reference<sup>[11]</sup> [American Chemical Society] copyright [1995].

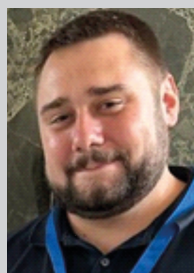
coherent oscillation associated with Fe–CN–Fe motion in the excited electronic state.<sup>[11]</sup> It should be noted that the first time-resolved study highlighting photo-induced electron transfer was performed at the University of Minnesota by Paul Barbara

and co-workers in a mixed-valence system consisting of a  $\text{Ru}^{\text{III}}\text{CNFe}^{\text{II}}$  moiety.<sup>[12]</sup>

Since then many analogues of Prussian Blue (PBAs) have been discovered using a range of transition metal ions (TM). Some of these are room temperature magnets such as  $\{\text{KV}^{\text{II}}[(\text{Cr}^{\text{III}}(\text{CN})_6)]_x\}$  which has a Curie temperature of 376 K.<sup>[16]</sup> Others such as the mixed-valent Co–Fe PBAs show a photomagnetic effect. These diamagnetic PBAs consisting of  $\text{Co}^{\text{III}}$  (LS) and  $\text{Fe}^{\text{II}}$  (LS) exhibit paramagnetism after photoexcitation through the formation of  $\text{Co}^{\text{II}}$  (HS) and  $\text{Fe}^{\text{III}}$  (LS).<sup>[17–18]</sup>

The advantages of using PBAs over metal oxides, and thus employing a molecular approach towards magnets and photomagnets, have been described by Ohkoshi and Hashimoto: The possibility to tune the magnetic exchange interaction by using different transition metals facilitates the design of materials with the desired properties. Furthermore, next nearest neighbour interactions can be neglected in PBAs since they are much weaker than the nearest neighbour interactions when compared with the corresponding interactions in metal oxides.<sup>[18]</sup>

This approach can be further improved by, instead of using extended solid state structures, designing discrete molecules with the desired magnetic interactions. One example for this, linking the extended solid state structures of PBAs to magnetic molecules, is the tetranuclear cyano-bridged compound  $[\text{Co}_2\text{Fe}_2(\text{CN})_6(\text{tp}^*)_2(4,4'\text{-dtbbpy})_4](\text{PF}_6)_2$ . Here it was possible to show intervalence charge transfer after 800 nm excitation in the low-spin  $\text{Co}^{\text{II}}_{\text{LS}}$  species that results within 400 fs in a spin-crossover stabilized  $[\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}}]$  component with a relatively long lifetime exceeding 1 ns. On the other hand, in the high-spin  $\text{Co}^{\text{II}}_{\text{HS}}$  species an ultrafast ground state recovery dominates that is completed within 8 ps. This study is one out of many in recent years that demonstrates the necessity of combining different experimental techniques where ultrafast UV/vis/IR spectroscopy is one where the results need to be correlated with other results, e.g. from  $^{57}\text{Fe}$  Mössbauer, temperature-



Jonas Braun obtained his PhD in 2023 for work conducted on lanthanide and transition metal-based magnetic molecules focussing on systematic variation of intra- and intermolecular influences under the supervision of Prof. Annie Powell at the Karlsruhe Institute of Technology (KIT). He currently is working towards his habilitation on a joint project between the groups of Prof. Annie Powell and Prof. Andreas-Neil Unterreiner on the magnetic and electronic properties of metal complexes after photoexcitation.



Annie Powell gained her PhD degree from the University of Manchester in 1985 and subsequently undertook post-doctoral research at the University of Freiburg, Germany. In 1999 she took up the chair of Supramolecular Chemistry at the University of Karlsruhe, Germany. The main focus of her current research is on the magnetic behaviour of molecular systems with an emphasis on Single Molecule Magnets (SMMs) and novel spin



architectures as well as using coordination chemistry principles in exploring exotic quantum effects.

Andreas-Neil Unterreiner earned his Dr. rer. nat. from the University of Karlsruhe (TH) in 1998, focusing on femtosecond laser systems and ammoniated and hydrated electrons. His postdoc at the University of Chicago integrated laser spectroscopy with confocal microscopy. He completed several research visits at the Vienna University of Technology, the Max Planck Institute in Göttingen, and the Louis Pasteur University in Strasbourg. After his habilitation in 2006, he was appointed as a professor at KIT in 2021, studying ultrafast elementary steps in molecular systems after photoexcitation.

dependent magnetic susceptibility measurements, stationary UV/vis and FTIR spectroscopy – to name only a few – in combination with theoretical calculations, which are typically DFT calculations due to the relatively large size of the molecules.<sup>[19–20]</sup>

After photoexcitation, trap states can play a pivotal role in molecular systems depending on the various domains available. For example, electron transfer can occur on surfaces,<sup>[21]</sup> in nanocrystals<sup>[22]</sup> or in organic solar cells.<sup>[23]</sup> In solution with alkaline metals, they have been observed after photoexcitation of Na<sup>0</sup>/THF solutions, i.e. in the form of transient ion-contact pairs with lifetimes of tens of ps.<sup>[24–25]</sup> This picture has been recently transferred to metalloid cluster complexes where the photo detachment of Zintl-type Ge<sub>9</sub><sup>−</sup> systems resulted in a ligand- and solvent-dependent solvated or trapped excess charge.<sup>[26–27]</sup> Usually, the trapping occurs on the surface of the inorganic cluster as shown, for example, for Au<sub>20</sub> clusters<sup>[28]</sup> and in another structurally related Au<sub>20</sub> cluster with oxidation state 0<sup>[29]</sup> where photoexcitation leads to charge transfer resulting in transiently ambiguous oxidation states. Overall and to the best of our knowledge, the interaction between trap states and magnetic properties of photoexcited systems is still in its infancy.<sup>[30]</sup>

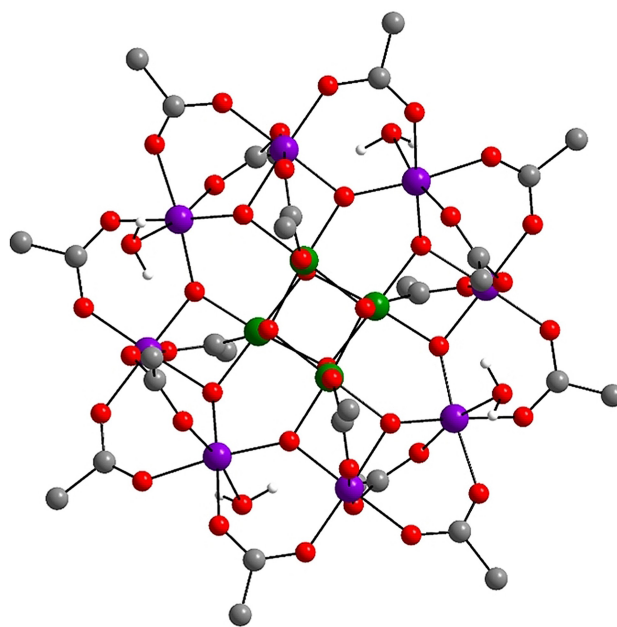
Furthermore, this approach of using molecules as photo-magnetic materials provides vast opportunities in terms of ligand modification to fine-tune the intra- and intermolecular magnetic interactions. Such magnets on a molecular level are known as single molecule magnets (SMMs).

### What Defines an SMM?

The field of SMMs was born with the discovery of magnetic bistability in a Mn<sub>12</sub> cluster (see Figure 2) in 1993.<sup>[31]</sup> Once magnetised by an external magnetic field this cluster retains its magnetisation long after the external magnetic field has been switched off. This is a result of an energy barrier which prevents an immediate return to the non-magnetised equilibrium state creating magnetic hysteresis on a molecular level. This promises possible application in high-density data storage,<sup>[5,32–33]</sup> molecular spintronics<sup>[34–36]</sup> and potential application as qubits in quantum computing.<sup>[37–40]</sup>

The energy barrier for magnetisation reversal in SMMs is defined as  $U = S^2 |D|$  for integer spin systems where  $S$  is the spin ground state and  $D$  the axial zero field splitting parameter. Since it was found that the absolute value of  $D$  is proportional to  $S^{-2}$ ,<sup>[41]</sup> the focus shifted from aiming for the highest possible spin states to that of creating the largest possible uniaxial anisotropy. Thus, highly anisotropic often low nuclearity clusters soon gathered much attention.<sup>[42–45]</sup>

Employing this strategy of using highly anisotropic ions, the focus of large parts of the SMM community has shifted towards lanthanide-based clusters over the last decade(s).<sup>[46–48]</sup> However, the use of lanthanide ions (Ln) not only introduces strong anisotropy but also gives rise to through-barrier processes that need to be quenched in order to retain magnetisation.



**Figure 2.** Molecular structure of the first identified SMM Mn<sub>12</sub>ac with the eight Mn<sup>III</sup> ions in purple and the four Mn<sup>IV</sup> ion shown in green.

In the search for suitable coordination clusters it was found that, although generally 4f ions are considered to be less perturbed by the local ligand field than the spin-orbit coupling, the coordination environment around Ln ions plays a vital role in determining the SMM properties. It was furthermore found that the effectiveness of different relaxation pathways strongly depends on the availability of phonon modes which are a consequence of molecular and lattice vibrations.<sup>[49–54]</sup>

Quenching quantum tunnelling of magnetisation processes, especially at zero field (ZFQTM), is the first step towards a high-performant SMM.<sup>[55]</sup> One of the approaches identified to quench ZFQTM is using strong magnetic exchange interactions such as in 2p–4f systems through employing bridging organic radicals<sup>[56–60]</sup> or 3d–4f systems.<sup>[55,61–64]</sup> Another is to use symmetry considerations on the basis of the anisotropy ellipsoids to avoid transverse fields.<sup>[56]</sup> The latter was found to be extremely successful as shown by the identification of two dysprosium-based SMMs with blocking temperatures above the boiling point of nitrogen.<sup>[65–66]</sup> Although the family of dysprosium SMMs shows high-temperature SMM behaviour, the application of these organometallic compounds remains challenging due to their extreme air sensitivity.<sup>[65–68]</sup>

While in fact there are also many air-stable 4f ion containing SMMs,<sup>[69–70]</sup> studying 3d–4f coordination clusters (CCs), many of which are formed by self-assembly in air, has the advantage of greater tunability. The opportunity to vary both the 3d and 4f ion leads to a plethora of combinations and corresponding properties. In addition, ZFQTM can be quenched by the exchange coupling interactions often observed in such mixed-metal 3d–4f compounds. Unlike in 3d–4f systems, for mononuclear 4f SMMs in particular, the coordination geometry around the Ln<sup>III</sup> ion is critical since even minor deviations from perfect axiality in the case of Dy<sup>III</sup> for example gives rise to

transverse fields opening quantum tunnelling pathways.<sup>[55]</sup> Therefore, in this Concept article members of this class of molecules are proposed as testbed systems to explore the interplay of electronic and magnetic properties.<sup>[64,71–78]</sup> Special attention is paid to 3d–4f cyclic coordination clusters (CCCs) which can be described as 0-dimensional systems where a chain of 3d and 4f ions is cyclised, thereby creating an infinite electronic structure around the cycle which in turn can delocalise charges in a photo-excited state across the whole CCC creating quantum effects which change the magnetic and optical properties.

Efforts in combining the magnetism of SMMs with optical properties have largely been focussed on the characteristic luminescence of Ln<sup>III</sup> ions.<sup>[79–81]</sup> Furthermore, the magnetic field-dependence of luminescent SMMs was investigated in a study on Dy(acac)<sub>3</sub> in which the Dy<sup>III</sup>-based luminescence was probed at variable temperatures between 4 and 180 K as well as with magnetic fields in the range 0 to 45.4 T. Long *et al.*<sup>[82]</sup> were able to show the effect of the Zeeman splitting on the <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> transition. Furthermore, they were able to identify the energy difference between the ground state of the <sup>6</sup>H<sub>15/2</sub> state and the first excited Kramers doublet which corresponds very well to the experimentally obtained energy barrier to magnetisation reversal.<sup>[82]</sup> This was similarly shown by Gao *et al.* who proposed luminescence under applied fields as a means to gain information on the anisotropy barrier in SMMs.<sup>[83]</sup> Moreover, there are examples where light was used to enable SMM behaviour such as observed in an Fe<sup>II</sup> complex exhibiting spin crossover (SCO) from the diamagnetic LS state to the paramagnetic HS state in which slow relaxation of magnetisation was observed.<sup>[84]</sup> Another example for this is the photochromic material [Ln<sub>3</sub>(H-HEDP)<sub>3</sub>(H<sub>2</sub>-HEDP)<sub>3</sub>] in which photo-generated radicals enable magnetic interactions between previously uncoupled Dy<sup>III</sup> ions leading to SMM behaviour.<sup>[85]</sup>

However, although these selected examples highlight the possibility of altering optical properties by applying magnetic fields as well as the possibility to alter magnetic properties through light irradiation, this is all done with continuous rather than pulsed radiation. This leads to a macroscopic understanding of the final result of light irradiation, but the intricate details of the dynamic processes after photoexcitation and their implication on the magnetic properties remain barely explored.

The ultrafast dynamics of Mn<sup>III</sup>-based SMMs have recently been studied by Johansson and co-workers investigating vibrational coherences obtained from ultrafast spectroscopic techniques. Specifically, wavepacket motions in Mn(acac)<sub>3</sub> have been identified to demonstrate the importance of magnetic anisotropy as a function of Jahn-Teller (JT) distortion. Photoexcitation of the lowest optical transition of a Mn(cyclam) complex led to a switch of the elongated JT distortion in the electronic ground state to a compressed one in the excited state. Furthermore, a decrease of the excited state lifetime was observed compared to Mn(acac)<sub>3</sub>.<sup>[86–88]</sup> Vibrational coherences have additionally been identified as a means to drive the design of ligands and complexes to control the properties of photoexcited molecules.<sup>[89–91]</sup>

## Molecular Spectroscopic Methods

Techniques relying on resonance are abundant in our daily life – such as making stable suspension bridges<sup>[92]</sup> which are not liable to collapse – and are applied in spectroscopic techniques such as EPR, NMR, optical excitation and Mössbauer. Detailed studies usually rely on resonant excitation that depends on the electromagnetic frequency, thereby populating the respective Franck-Condon region – *i.e.* a vertical optical excitation (see process (1) in Figure 1). These are generally rare and completely lacking for SMMs. Such investigations give valuable information since they scan the multidimensional energy landscape requiring wavelength-dependent experiments. The advantage of fs excitation lies in the intrinsic properties as a result of the Heisenberg uncertainty principle which leads to a spectral broadening depending on the pulse properties. For example, a Gaussian shaped pulse envelope with a duration of 30 fs allows observation of coherent vibrations below 500 cm<sup>-1</sup>.<sup>[93]</sup> If performed in the time domain, the recovery of the frequencies requires, for example, a Fast Fourier Transform (FFT).<sup>[94–95]</sup> This approach is consistent with the common principles in spectroscopy as excellently summarized in a textbook by S. Mukamel that, “in principle, time-domain and frequency-domain observables are related by multiple Fourier transforms and carry the same information.”<sup>[96]</sup> However, it is evident that the methods must be carefully selected. Often, a combination of frequency and time domain results provides a more comprehensive overview. For example, we will highlight subtle variations in charge localization and recombination times in Fe–Ln nanotubes by altering the lanthanides as a first example or the fine-tuning of excited state lifetimes through ligand variation in the second coordination sphere.<sup>[97–98]</sup>

## Some Basic Concepts of Photoexcitation

Generally, two categories of processes following photoexcitation should be considered: photophysical and photochemical processes. In this Concept Article, we will mainly concentrate on non-reactive channels. For reactive systems, the readers may refer to the many examples using photoreactive ligand systems. One of such ligand systems is that of the are dithienylethene-based ligands which perform ring-closure reactions upon light irradiation leading to altered magnetic and optical properties.<sup>[99–101]</sup> Another example would be the ligand 1,2-bis(4-pyridyl)ethene which engages in photo-driven [2+2] cycloaddition also resulting in changed magnetic behaviour of the newly formed dinuclear clusters.<sup>[102]</sup> Furthermore, a recent perspective by Vöhringer highlights the importance of time-resolved IR spectroscopy to investigate dissociation and fragmentation Fe-containing intermediates in this context,<sup>[103]</sup> whereas, in this Concept Article we explore charge transfer and electron localisation phenomena limited to the inorganic complex moiety without the presence of a chemical reaction or fragmentation. We also present insights into the influence of photoexcitation and the resulting excited state dynamics on the magnetic properties of molecular systems.

In particular in SMMs, the magnetic properties of which are strongly susceptible to changes in the coordination environment regarding geometry and charge distribution, the corresponding states may have completely altered magnetic properties compared with the usually observed behaviour. To this end, it would be important to use an appropriate pump pulse to excite the molecule and propose to follow the relaxation of both electronic states as well as the corresponding magnetic properties on different timescales from seconds to femto-seconds using different experimental techniques. This article provides a perspective on how to understand the entanglement of electronic and spin degrees of freedom with the ultimate goal in mind of harnessing these interactions in order to produce novel light-controlled spintronic devices.

### The Relevance of Using Time vs Frequency Domains to Interpret Data

A good way to illustrate the importance of exploring timescales of molecular processes is to highlight an innovative work<sup>[104]</sup> which at first glance might not be relevant to spintronics. However, it gives the reader an idea why it is important to consider both time and frequency domains. In this example fluorescence quantum yield measurements of 2-aminopurine embedded in DNA assemblies in the frequency domain can show significant changes upon solvent variation or different chemical environments, e.g. in nucleotides. The origin of this variation may be manifold and include processes like energy, proton or charge transfer as well as very efficient internal conversion processes such as conical intersections.<sup>[105–109]</sup> In the frequency domain this leads to different line widths, whereas in the time domain different time constants are observable. As mentioned above the two are intimately related by an inverse relationship via Fourier transformation but so far, no study exists on disentangling the different processes in the frequency domain for this specific system. However, time-resolved studies such as fluorescence upconversion can reveal the major contributions to the decrease in fluorescence quantum yield – in this case via charge transfer on a tens of ps timescale.<sup>[104]</sup> There is also evidence that local binding sites critically determine relaxation pathways including reactive ones such as bond breaking and charge transfer leading for example to ionisation or valence tautomerism.<sup>[110–111]</sup> A further breakthrough for elucidation of such interactions was the development of 2- and multi-dimensional time- and spatially-resolved spectroscopy<sup>[112–116]</sup> because fs laser pulses with pulse duration well below 100 fs are typically spectrally broad due to Heisenberg's uncertainty principle. Such sophisticated experiments have not yet been tested on complicated systems with many degrees of freedom including the ones presented here.

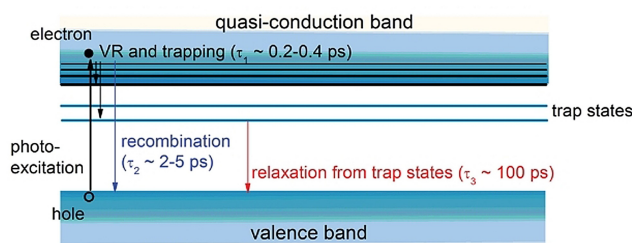
### Intramolecular Interactions Leading to Line-Shape Broadening

The abovementioned case is one example for a system to help understand the material's property-function relations. The most promising approach for this is to test a combination of different techniques that span the different time/frequency domains. Any change in a system will lead to subtle differences in the observable line-shapes.<sup>[117–118]</sup>

A common challenge is to discriminate line broadening mechanisms in a system with many degrees of freedom. In the frequency domain broadening of lineshapes may be homogeneous or inhomogeneous.<sup>[96,119]</sup> To disentangle homogeneous and inhomogeneous line broadening nonlinear processes such as hole-burning techniques can be applied.<sup>[120–123]</sup> A one pulse version called the Lamb-dip approach was initially realised in experiments by Bennett.<sup>[124]</sup> A more recent two-pulse hole-burning study on the magnetisation of Cr<sub>7</sub>Ni CCC at mK temperatures enabled the determination of spin-spin interactions emphasising a broadening mechanism by hyperfine interactions between 1 and 10 GHz.<sup>[125]</sup>

### The Fundamental Steps after Photoexcitation

Following photoexcitation probes electronically excited states of SMMs on an ultrafast time scale. Femtosecond transient broadband absorption spectroscopy revealed the occurrence of three fundamental relaxation steps (see Figure 3 for illustration). In a first step, charge separation and localisation follow photoexcitation. For the Fe-nano-toruses with up to ten moieties including alternating Fe–O and Ln–O units forming an Fe<sub>10</sub>Ln<sub>10</sub> cyclic coordination cluster [Fe<sup>III</sup><sub>10</sub>Ln<sup>III</sup><sub>10</sub>(Me-tea)<sub>10</sub>(Me-teaH)<sub>10</sub>(NO<sub>3</sub>)<sub>10</sub>]<sup>[97]</sup> this process usually happens on a timescale between 200 and 400 fs. This property can, perhaps unexpectedly, be tuned by varying the Ln ion and a correlation to Kramers (relating energy eigenstates with half integer spins) and non-Kramers ions.<sup>[126]</sup> is something worth further investigation. In a second step, some of these localised states will rapidly relax via, a possibly geminate, recombination which is completed within a few ps.<sup>[126,97, 127]</sup> As for the first time constant this second process is also related to whether the ion is Kramers



**Figure 3.** Simplified sketch describing the three relevant photo-induced processes (vibrational relaxation (VR)/trapping, recombination and relaxation of trap states) in Fe<sub>10</sub>Ln<sub>10</sub> nano-toruses and related non-lanthanide containing systems such as an Fe<sub>n</sub> cluster. Reprinted with permission from reference [97] [John Wiley and Sons] copyright [2014].

or non-Kramers. The final and third process is related to trapped states that describe the survival probability of non-recombined states and exceeds the corresponding lifetime typically by a factor of 20 leading to lifetime in the order of 100 ps. The original assignment was done for the interpretation of the ultrafast relaxation dynamics of Fe<sub>2</sub>O<sub>3</sub> nanoparticles and thin films.<sup>[128–129]</sup> Replacing Fe<sup>III</sup> with Ln<sup>III</sup> ions in the structure led to small but notable changes in excited state lifetimes, but does not add additional transitions. This means that the three steps described above remain the key to the underlying dynamics in the 3d–4f nano-torus systems.<sup>[97]</sup>

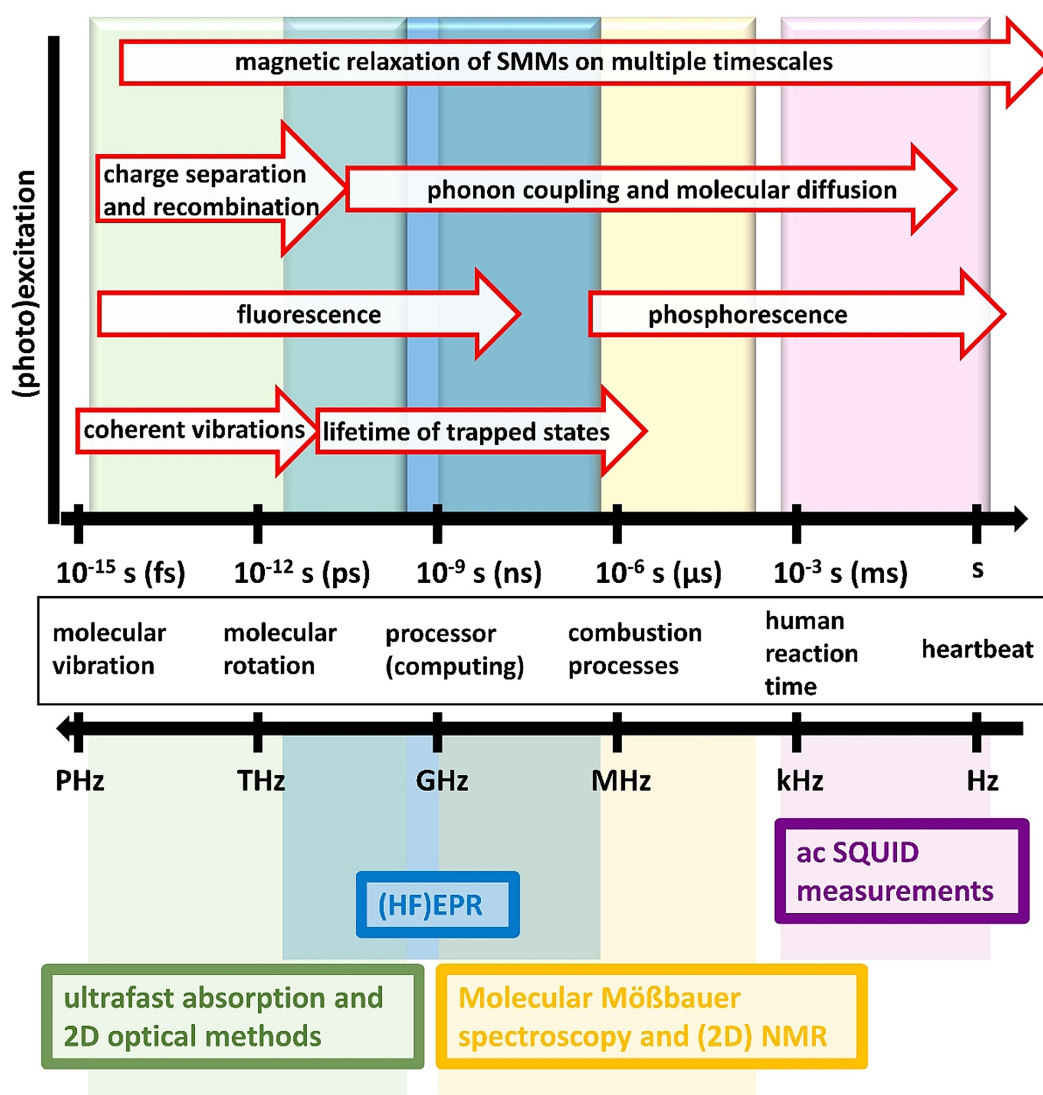
For a comprehensive picture of SMMs, various timescales/frequencies are essential as illustrated in scheme 1. While fundamental processes of magnetic relaxation can start to occur from the earliest timescales of 10 to 100 fs,<sup>[130]</sup> the coupling of many degrees of freedom can lead to magnetisation of molecules being observable for multiple seconds. This culminates in a recent study on a Dy<sub>2</sub> compound with a metal-metal

bond with a bond order of 0.5 shows a relaxation time of 1000 s at 67 K.<sup>[66]</sup>

## Testbed Systems

To be able to use all the tuning handles described above it is necessary to select a system as a testbed which allows for variations in order to study the influence of small structural changes on the ultrafast dynamics as well as the magnetic and electronic properties.

Taking these requirements into account, two types of 3d–4f clusters have been selected as testbed systems with nuclearities of two and four. Some of these systems have been previously characterised regarding their magnetic properties giving reference knowledge on how these compounds behave without photoexcitation. In order to study these subtle differences, it makes sense to start with investigations on dinuclear com-



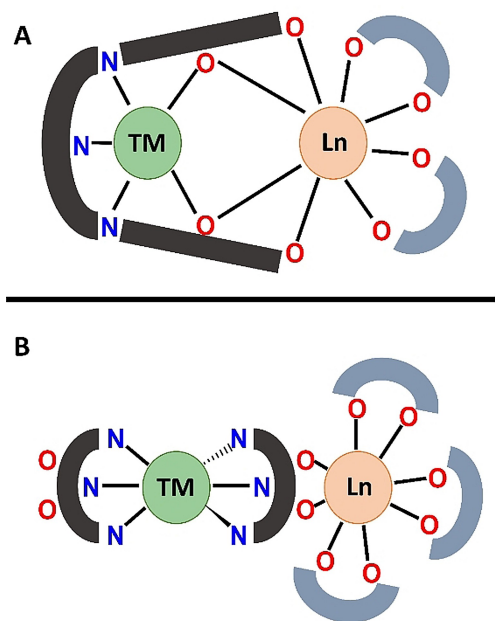
**Scheme 1.** Schematic visualisation of processes on different timescales (red arrows) and different characterisation techniques and the timescale/frequency they are operating at.

pounds with one transition metal and one lanthanide ion. This not only reduces the complexity of the data but also the properties of clusters of this size can be calculated using *ab initio* methods without exceeding the manageable limits in terms of Hilbert space.

### 1) Dinuclear 3d-4f Systems

Using dinuclear mixed-metal 3d-4f systems to explore the cooperativity between the two types of ions has been pursued for many years using two major ideas in terms of ligand design. The first is using compartmental ligands with pockets of two sizes. These ligands can either successively or simultaneously react with a 3d ion to go into the smaller pocket and a 4f ion to be coordinated by the larger pocket. This can be combined with taking advantage of the oxophilic nature of Ln<sup>III</sup> ions by using ligands with well-defined N- or O-based pockets (see Scheme 2 A). The Ln<sup>III</sup> ions will tend to react with the O-based sites while the TM ions will benefit more from N-based donor sites especially when favourable coordination geometries can be achieved. Often oxygen-based solvent molecules such as water or methanol or counter anions such as nitrate can help to complete the coordination sphere of the lanthanide ions. This was successfully employed producing a number of compounds with SMM properties.<sup>[131–136]</sup>

The second approach uses a bifunctional ligand (see scheme 2 B) with well-separated pockets designed to appeal to 4f ions involving oxygen donors as well as pockets suited for 3d ions. This approach was also shown to result in 3d-4f SMMs for example using the Hbpca = bis(2-pyridylcarbonyl)amine ligand. Furthermore, it was shown that this kind of ligand is



**Scheme 2.** A) Compartmental ligand with pockets designed for either 3d or 4f ions. B) schematic visualization of the bifunctional ligand approach to achieve dinuclear 3d-4f SMMs.

able to accommodate a wide range of 3d ions in their 2<sup>+</sup> and 3<sup>+</sup> oxidation state. Interestingly, the compounds using the divalent transition metal ions tend to form 1-dimensional chains.<sup>[137–141]</sup> These could serve to as a comparison to the CCCs helping to gauge the effect the infinite electronic structure of the cyclic compounds has on the excited state dynamics of such compounds compared to finite 1-dimensional chains.

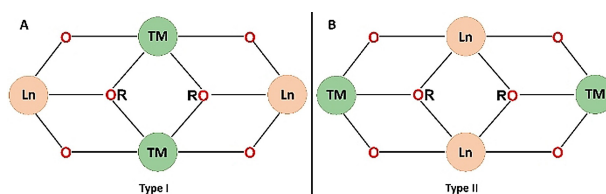
### 2) 3d-4f Butterflies

The second chosen cluster type is the well explored tetranuclear butterfly system consisting of two TM and Ln ions each that alternate in the cluster. Butterfly coordination clusters have two positions for the metal ions described as the “body” (the two positions in the middle) and the “wingtip” position (the outside left and right positions) and can therefore be classified into two types. Type I has the transition metals in the “body” position and the lanthanide ions in the “wingtip” position, for type II this is reversed (see Scheme 3 A and B, respectively).

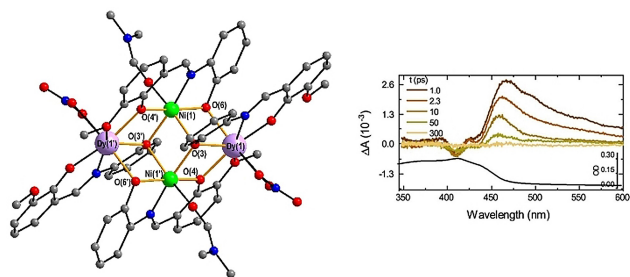
This system has previously been described as a testbed for its many possibilities for modification.<sup>[142–143]</sup> The type I and II butterflies are not only known for many combinations of 3d and 4f ions with the 3d ions in various oxidation states,<sup>[61–63,143–155]</sup> but it was also shown that ligand and co-ligand modifications can influence the magnetic response of the system.<sup>[154,156–157]</sup>

Furthermore, members of the butterfly family were investigated using quantum chemical calculations which provides the opportunity to compare and explain the experimentally observed behaviour.<sup>[62,147,151,155,158]</sup>

It is important to highlight that a study on the ultrafast dynamics after photoexcitation was performed on a Ni<sub>2</sub>Dy<sub>2</sub> butterfly complex by some of us, resulting in the identification of a trapped state with a lifetime of *ca.* 70 ps (see Figure 4). In this study the compound has also been subject to extensive theoretical calculations using coupled-cluster methods with WARC-ZORA. The chromophoric unit {Dy–O–Ni} was stabilised in the first ligand sphere (a methoxybenzylideneaminophenol) with dimethylformamide as solvent. In the calculations this interaction is described using a system-bath coupling constant. However, owing to a large number of possible electronic states, a specific assignment of the ultrafast dynamics to a particular electronic state is challenging even for such a small system with



**Scheme 3.** Schematic visualisation of the two types of butterfly complexes that can be obtained with a wide range of transition metal and lanthanide ions as well as a plethora of ligands and co-ligands making this a perfect system to systematically study the influence of structural changes on the interplay of magnetic and electronic properties after photoexcitation.



**Figure 4.** Molecular structure of the Ni<sub>2</sub>Dy<sub>2</sub> type I butterfly (left) and transient absorption spectra of Ni<sub>2</sub>Dy<sub>2</sub> after excitation at 300 nm with the absorption shown in black for comparison (right, reprinted with permission from reference [127] [John Wiley and Sons] copyright [2021]).

only three elements forming the chromophoric unit. Nevertheless, this appears to be one way to proceed in order to optimise properties of molecular magnets through the information gained from optical observables.<sup>[127]</sup>

Building on these studies on relatively small systems it will be possible to proceed to investigating the detailed properties of the many larger 3d–4f systems that have been described in the literature by our group.<sup>[76,78,159–162]</sup>

## Techniques and their Limitations

In the following we discuss available techniques with respect to the information they can deliver. These have been ordered in terms of increasing frequency.

### SQUID Magnetometry

SQUID magnetometry is an extremely sensitive technique (often better than 10<sup>-7</sup> emu) to investigate the magnetic moment of a sample. Dynamic properties of SMMs are most commonly investigated using alternating current (ac) measurements using frequencies between 0.01 and 10000 Hz.<sup>[163]</sup> The upper limit in terms of frequency range is given here by the ac current source which requires high enough compliance voltages in order to diminish the effect of inductance of the ac drive coil.<sup>[163]</sup> This means that ac SQUID magnetometry utilises the lowest frequencies of the presented methods and is mainly used to directly resolve processes on a ms to s timescale, i.e. relatively long timescales. Through fitting procedures it is however possible to gain rates of magnetic relaxation processes in SMMs which can be much faster.<sup>[164]</sup>

There are, usually lab-built experimental set-ups, that are able to reach frequencies beyond the limits of commercially available instruments. Lower frequencies can be reached by a set-up presented by Hibbs *et al.*, working for Quantum Magnetism Inc. and Quantum Design Inc., which can reach frequencies as low as 0.001 Hz albeit with reduced sensitivity.<sup>[165]</sup> Efforts to overcome the limitations by the electronics mentioned above to improve the accessible bandwidth and therefore time resolution of SQUID magnetometers

has resulted in the report of a novel SQUID sampler able to read out a 240 MHz ac signal.<sup>[166]</sup>

With the emergence of high-performance SMMs, the importance of studying magnetic relaxation on longer timescales outside the frequency range of traditional ac measurements is increasing rapidly. An approach to gain information on such slow relaxation was developed by Hilgar *et al.* who introduced a long timescale ac waveform method to extend the range of ac susceptometry.<sup>[167]</sup>

It is furthermore possible to overcome the limitations of commercial SQUID magnetometers in terms of the accessible frequency range in ac experiments to be able to study magnetic relaxation on longer timescales such as found in high-performance SMMs by measuring the magnetisation decay. For this, the magnetisation of a sample is saturated using a large magnetic dc field which is subsequently switched off and the development of the magnetisation followed over time giving information complementary to that from ac studies.<sup>[31,62,71,168]</sup> Recently Blackmore *et al.* presented a methodology to study slow magnetic relaxation in high-performance SMMs using magnetisation decay measurements on a VSM magnetometer and discussed the fitting procedures of such experiments.<sup>[169]</sup> A further example where the limitations of commercial SQUID magnetometers in terms of accessible frequency range has been overcome by additional complimentary measurements, here operating on a faster timescale is the study performed on an Fe<sub>2</sub>Dy<sub>2</sub> butterfly complex. Here the authors were able to show that by using <sup>57</sup>Fe Mössbauer spectroscopy the relaxation dynamics of the Dy<sup>III</sup> ions could be investigated by exploring their influence on the neighbouring Fe<sup>III</sup> nuclei.<sup>[149]</sup>

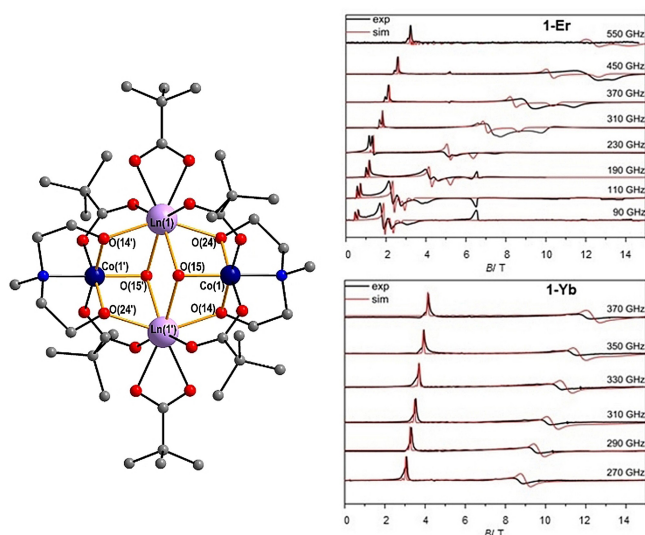
### Further Advanced Resonant Techniques

High-field/high-frequency EPR is a powerful tool to probe the anisotropy and the magnetic interactions in complexes as well as exploring their electronic structure. This method can operate at frequencies up to THz and can therefore resolve processes on a ns-ps timescale.<sup>[170]</sup>

HF-EPR as well as X- and Q-band EPR have previously also been used to characterise 3d–4f SMMs and were able to help gauge the magnetic interactions between the different ions.<sup>[161,171–173]</sup> Such was the case in a series of Co<sup>III</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub> compounds the Er<sup>III</sup> and Yb<sup>III</sup> analogues of which show SMM behaviour (see Figure 5).<sup>[174]</sup>

To reveal couplings between different components in a molecule requires even higher frequencies and here, 2D spectroscopy can be applied.<sup>[175–177]</sup> For example, the study of vibrational transitions in peptides necessitates multiple THz resolution (fs to ps time domain) and can be examined through 2D vibrational spectroscopy. Since this method employs the same principles as 2D-COSY spectra in NMR (μs to ms timescale), the underlying transitions are displayed as cross-peaks. Mukamel and coworkers have demonstrated that these techniques are based on nonlinear susceptibility properties (instead of linear for NMR chemical shift measurements or absorption spectroscopy), specifically  $\chi^{(3)}$  for 2D-IR<sup>[178]</sup> and  $\chi^{(5)}$  for 2D-Raman





**Figure 5.** Molecular structure of the  $\text{Co}_2\text{Ln}_2$  cluster family<sup>[174]</sup> (middle) and the HFEPN of the  $\text{Er}^{\text{III}}$  and  $\text{Yb}^{\text{III}}$  analogues which both show SMM behaviour (top and bottom, respectively). Reproduced with permission from reference [174] [John Wiley and Sons] copyright [2021].

spectroscopy.<sup>[175]</sup> The required high intensity for initiating nonlinear processes are provided by chirped pulse amplified fs laser systems.<sup>[179]</sup> This has been observed in investigations on small isotopically doped peptides which have been studied with 2D IR techniques to understand parts of the energy transfer processes in biological systems. Ideally, combining linear and nonlinear techniques is key to a better understanding.<sup>[180–181]</sup>

Nevertheless, an analysis can be challenging due to the many degrees of freedom in complex molecular systems such as SMMs. On the other hand, suitable small molecule systems may be found in the future that mimic some of the properties of SMMs.

### Femtosecond Transient Absorption Spectroscopy

Valuable information on the initial processes that occur after photoexcitation can be made accessible using transient absorption spectroscopy with femtosecond time resolution. This is a relatively simple technique which can be home-built, and enables the identification of up to three fundamental processes. It allows detailed assignment of charge separation/localisation and recombination after electronic excitation, observable with time constants up to 5 ps. Also, the third, longer time constant that can be extracted from femtosecond transient spectra of TM–Ln complexes, may be relevant for future experiments involving the manipulating of excited trapped states, which could significantly impact magnetic relaxation dynamics. To probe this, it is necessary to apply a magnetic field during the femtosecond spectroscopy measurements. For example, the investigated material itself can act as an internal magnetic field. The first pioneering results by Bigot and coworkers were published in metallic nickel films showing fs optical pulse induced ultrafast sub-ps demagnetisation.<sup>[130]</sup>

The experimental arrangement is still a simple pump-probe fs setup, but with sophisticated polarization dependent detection schemes making use of the fact that the initially linear-polarised excitation beam turns into an elliptical beam after reflection from a magnetic sample. This is part of the so-called magneto-optical Kerr effect (MOKE) which is based on the nonlinear optical Kerr effect and is a  $\chi^{(3)}$  experiment inducing birefringence through transiently changing the refractive index.<sup>[182]</sup> Ultrafast magnetisation can also be observed in lower dimensional states such as nano-fabricated structures and in molecular magnets.<sup>[183]</sup> Two famous examples are the 2D Van-der-Waals ferromagnets  $\text{Cr}_2\text{Ge}_2\text{Te}_6$  and  $\text{CrI}_3$ . The latter showed that magnetic coupling within one sheet is ferromagnetic whereas the inter-sheet interaction was found to be antiferromagnetic.<sup>[184–187]</sup>

The results of time-resolved measurements demonstrate the importance of spin-dependent charge transfer at the interface between the  $\text{WSe}_2$  and  $\text{CrI}_3$ .<sup>[188]</sup> Another study on the  $\text{Cr}_2\text{Ge}_2\text{Te}_6$  emphasises the importance of full experimental protocols to give a true picture of the dynamics of the system.<sup>[189]</sup>

### Mössbauer Spectroscopy

Mössbauer spectroscopy can be visualised as being similar to NMR in the sense that it investigates the environment around the nucleus, using gamma-rays instead of radio waves. While NMR is investigating nuclear ground state transitions, Mössbauer spectroscopy reveals information on nuclear excited states which in turn lead to information regarding the magnetic spin states such as for iron nuclei.<sup>[190]</sup>

The most commonly used form of Mössbauer spectroscopy is  $^{57}\text{Fe}$  Mössbauer spectroscopy. This uses the decay of the radioactive  $^{57}\text{Co}$  isotope to an excited  $^{57}\text{Fe}$  atom which then relaxes to its ground state emitting gamma radiation that can be used to investigate the oxidation, spin state and magnetic relaxation of Fe ions in coordination clusters.<sup>[191–196]</sup> This technique is able to resolve magnetic relaxation on a nano-second timescale which makes it a useful tool to explore magnetic properties on faster time-scales, inaccessible to commonly employed SQUID magnetometry set-ups. The technique is however restricted to the spectroscopy on certain isotopes of certain elements. As mentioned  $^{57}\text{Fe}$  Mössbauer is the most commonly available form of this technique which was originally applied to  $^{191}\text{Ir}$  isotopes as part of Rudolf Mössbauer's PhD thesis, ultimately gaining him the Nobel prize in 1961,<sup>[197]</sup> giving another reason why such a study on time-resolved interactions between electronic and spin degrees of freedom will benefit from the use of 3d–4f (or more precisely Fe–4f) clusters as test subjects.<sup>[71,137,149,198–203]</sup>

Although iron is the most studied element using Mössbauer spectroscopy, it is also possible to use other isotopes such as  $^{161}\text{Dy}$  to elucidate the relaxation processes in  $\text{Dy}^{\text{III}}$ -containing SMMs. This requires work at large-scale facilities since the corresponding Mössbauer source needs to be activated by neutron irradiation.<sup>[204–205]</sup> This activation leads to the decay of the  $^{161}\text{Tb}$ : $^{161}\text{GdF}_3$  source to the first excited state of  $^{161}\text{Dy}$  which

has a lifetime of 42 ns.<sup>[205–206]</sup> Using  $^{161}\text{Dy}$  Mössbauer it was possible to follow the slow magnetic relaxation of a mononuclear  $[\text{Dy}(\text{Cy}_3\text{PO})_2(\text{H}_2\text{O})_5]\text{Br}_3$  complex at various temperatures between 4.2 and 55 K<sup>[69,205]</sup> (see Figure 6) as well as to show that magnetic relaxation in a  $\text{Dy}_6$  toroidal ring is faster than the observable ns time scale. This was attributed to the partial population of low-lying magnetic states at 4.2 K.<sup>[207–208]</sup>

A combination of  $^{57}\text{Fe}$  and  $^{161}\text{Dy}$  as a 2-dimensional experiment enables the individual magnetic contributions of either the Fe or the Dy ions in Fe/Dy SMMs to be disentangled as well as giving insights on the effect either ion has on the other.

### Multitechnique Approach

A combination of some of these techniques using a multitechnique approach (SQUID magnetometry,  $^{57}\text{Fe}$  Mössbauer spectroscopy and high field/high frequency EPR) was previously used on an  $\text{Fe}_4\text{Dy}_2$  CCC and it was possible to determine the magnetic relaxation and gain insight into the magnetic interactions in this compound.<sup>[161]</sup> This combination revealed a dependence of the strength of the ferromagnetic exchange interaction upon Ln ion variation. Mössbauer relaxation measurements showed the onset of slow magnetic relaxation in the Y and Gd analogues. Such relaxation could not be observed in the frequency window of a commercial SQUID magnetometer. Another system thoroughly studied using different techniques is a series of  $\text{Mo}^{\text{III}}$  complexes. In their investigation the authors characterised the ground state using SQUID magnetometry as well as HFEP and X-band EPR. This was accompanied by theoretical calculations which were able to validate the experimental findings.<sup>[209]</sup>

In this article we aim to propose similar systematic studies but add another dimension by studying the effect of photoexcitation on these properties. Ideally further techniques such as far-infrared spectroscopy under applied magnetic fields (FIRMS)<sup>[210]</sup> and torque magnetometry<sup>[211–212]</sup> would allow for the elucidation of the full microscopic electronic structure leading to a deeper understanding of the dynamics after light

irradiation with their implications on the macroscopic properties. This was also pointed out in a recent review by Penfold, Johansson and Eng.<sup>[5]</sup> The main challenges lie in the experimental parameters which include temperature of the measurement, the comparability of solution and solid state data as well as the need to have the possibility to apply magnetic fields during ultrafast measurements only realised in few lab-built setups.<sup>[213–214]</sup>

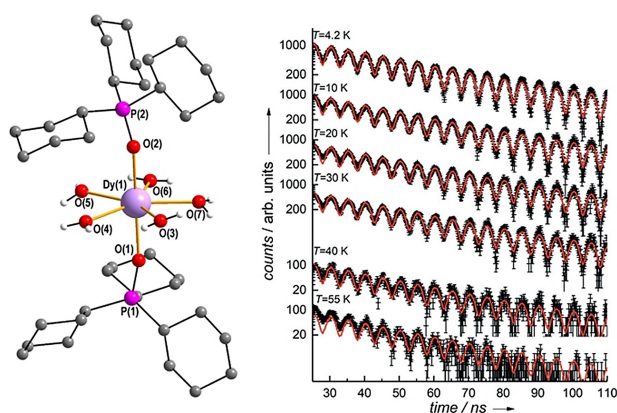
## How to Control Relaxation Dynamics after Photoexcitation

There are multiple opportunities to tune the relaxation dynamics of photoexcited molecules. In particular, investigating 3d–4f CCCs gives plentiful options which are described in the following. The effect of each of these tuning handles on magnetic and optical properties has been separately shown in previous works as outlined below. However, what is missing in order to assert some control over the energy level landscape of photoexcited molecules and the resulting magnetic properties is the understanding how these effects interact with each other. In order to disentangle this, careful and systematic variation of systems is necessary.

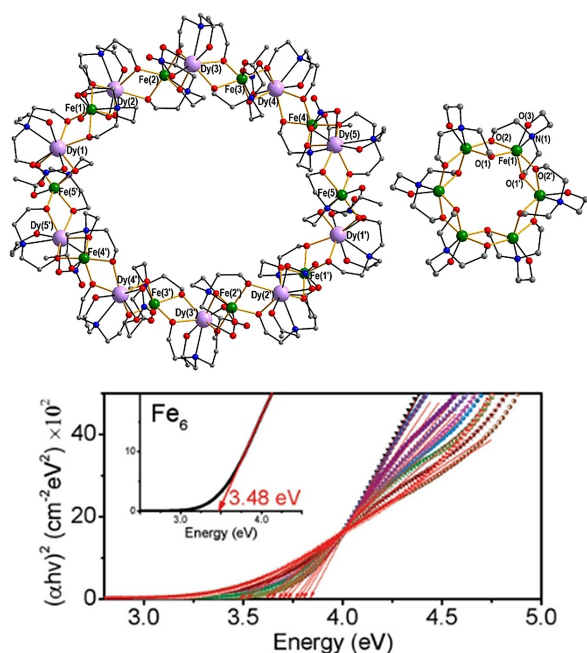
### Changing Ln/TM Ions

The magnetic properties of a 3d–4f cluster will naturally be influenced by a change in metal ion. For example, by changing the  $\text{Ln}^{\text{III}}$  ion, the influence of Kramers and non-Kramers ions on the ultrafast dynamics upon optical excitation was briefly discussed in an earlier section. This allows correlation of amplitudes and time constants with half-integer spins in trivalent lanthanides, but also stationary properties from Tauc plots (see Figure 7).<sup>[215–218]</sup> By applying this method it is possible to precisely determine the energy band gap independent of the metal ion and correlate this to ultrafast absorption studies (see Figure 3). In the scenario of the  $\text{Fe}_{10}\text{Dy}_{10}$  cluster, we can interpret the photodynamics in terms of an exciton species arising from ligand-to-metal transitions (LMCT) with  $\text{O}^{2-}$  as the dominant partner in this system.<sup>[97]</sup>

For the lanthanide ions in terms of magnetism, the biggest difference results from the differently shaped anisotropy ellipsoids of the trivalent ions determining the overall anisotropy in a given ligand environment.<sup>[56]</sup> This has been shown in various studies on isostructural series of lanthanide clusters,<sup>[219–220]</sup> as well as the influence of Kramers vs non-Kramers ions. While Kramers ions such as  $\text{Dy}^{\text{III}}$  come with a doubly degenerate ground state (Kramers doublet) predestined to show magnetic bistability, there are certain symmetry requirements for non-Kramers ions such as  $\text{Tb}^{\text{III}}$  to show a double degenerate ground state.<sup>[46,221]</sup> A degenerate ground state doublet in a non-Kramers ion is then known as an Ising doublet.<sup>[222]</sup>



**Figure 6.** Temperature-dependent  $^{161}\text{Dy}$  Mössbauer (bottom, reproduced from reference<sup>[205]</sup>) used to probe the magnetic relaxation of a mononuclear  $\text{Dy}^{\text{III}}$  SMM (top).<sup>[69,205]</sup>



**Figure 7.** Molecular structures of the Dy analogue of  $[\text{Fe}^{\text{III}}_{10}\text{Ln}^{\text{III}}_{10}(\text{Me-tea})_{10}(\text{Me-teaH})_{10}(\text{NO}_3)_{10}]$  and the  $[\text{Fe}^{\text{III}}_6(\text{tea})_6]$  reference system used in reference<sup>[97]</sup> (top). Tauc plot of the different Ln analogues showing the difference in optical band gaps as a result of changing the Ln<sup>III</sup> ion, with the tauc plot of the  $\text{Fe}_6$  reference system in the inset (bottom, reproduced with permission from reference [97] [John Wiley and Sons] copyright [2014]).

The magnetism of transition metal ions is not only dependent on the changing number of unpaired electrons across the series but is also much more dependent on the ligand field effects as a result of the coordination environment. This effect is much stronger in TM than in Ln ions since most exhibit largely quenched spin-orbit coupling. This makes exchanging the 3d TM ions much more challenging than for their Ln analogues. While the latter behave chemically similar to each other and the most restricting factor is the change in ionic radius across the series consequence of the lanthanide contraction, the former behave chemically totally different from each other. This often means that for TM variations of a given system a new synthetic protocol has to be developed in order to obtain isomorphous compounds. Although difficult this has been demonstrated to be achievable in a number of polynuclear 3d–4f compounds such as the “square-square”  $\text{TM}_4\text{Ln}_4$  compounds with  $\text{TM} = \text{Cr}^{\text{III}}$  and  $\text{Mn}^{\text{III}}$ <sup>[223–224]</sup> as well as  $\text{TM}_5\text{Ln}_8$  compounds with trivalent Mn and Fe as TM ion.<sup>[225–226]</sup> Furthermore, the synthesis of the famous  $\text{TM}_2\text{Ln}_2$  butterfly system which will be presented in more detail in a subsequent section, has been shown to be robust to accommodate for variation of the TM ion.<sup>[143]</sup>

In addition to changing the inherent magnetic properties of either ion it is also possible to probe the cooperativity effects between 3d and 4f ions by using diamagnetic substitution. This means that the paramagnetic contribution of either sort of ion is removed by using a diamagnetic alternative such as  $\text{Co}^{\text{III}}$  low-spin or  $\text{Zn}^{\text{II}}$  instead of a paramagnetic TM ion and  $\text{Y}^{\text{III}}$ ,  $\text{La}^{\text{III}}$  or  $\text{Lu}^{\text{III}}$  instead of paramagnetic Ln ions. This allows the investigation of the magnetic properties of either the 3d or 4f ions on their

own without having to take coupling between 3d and 4f ions into account.

### Fine-Tuning by Ligand Variation

The influence of changes in the first ligand sphere on the magnetic and macroscopic optical properties *e.g.* luminescence of SMMs is well explored and documented in the literature.<sup>[79,221,227–232]</sup> As demonstrated in Figure 7 below the way in which this modifies the ultrafast dynamics, requires systematic investigations in terms of the influence of ligand field in general.

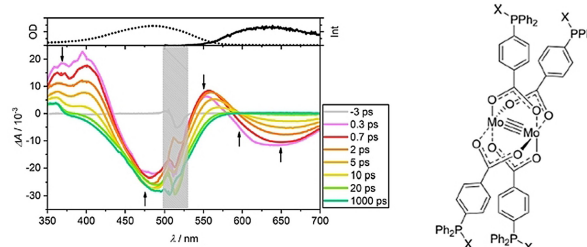
Changes to the second ligand sphere by substituting residues on the ligands can cause subtle changes to the properties of a complex giving the opportunity to fine-tune these properties. This has been shown in terms of the ultrafast dynamics which were studied in some detail on a dimolybdenum metallo-ligand system. In this system, the chromophoric unit is a  $\text{Mo}^{\text{II}}\text{-O}$  moiety, similar to the Fe/Ln nano-toruses described previously. In the  $\text{Mo}_2$ -paddlewheel clusters, triplet dynamics are the dominating overall process, but it could be shown that the lifetime of the first excited state can be varied by a remarkable 40% using different variations of ligands with  $\text{X} = \text{AuCl}_6\text{F}_5$ ,  $\text{RhCl}(\text{cod})$ ,  $\text{IrCl}(\text{cod})$ ,  $\text{BH}_3$  or  $\text{AuCl}$  (see Figure 8).<sup>[98]</sup>

Fine-tuning, using changes in the second ligand sphere was also shown in a  $\text{Fe}_2\text{Dy}_2$  butterfly system where the para-substituent on the benzoic acid ligand was varied and in a second study in which the influence of para- and meta-substituted benzoic acids on the magnetic properties were compared to each other.<sup>[198,202]</sup>

It was furthermore shown that coordinated solvent molecules can influence the SMM behaviour in a  $\text{Co}_2\text{Dy}_2$  system where the coordinated solvents vary from THF, MeOH and DMF.<sup>[150]</sup>

### Conclusion and Outlook

This Concept Article summarises recent advances in the field of SMMs and outlines important experimental tools to observe magnetic and optical properties of electronic ground and excited states with a heavy emphasis on photoexcitation. We



**Figure 8.** Structure of the  $\text{Mo}_2$ -paddlewheel cluster (right) investigated using transient absorption femtosecond spectroscopy revealing dominating triplet dynamics (left). Reproduce with permission from reference [98] [American Chemical Society] copyright [2018].

concentrate here on the potential of magnetic fields but recognise this should not exclude the application of electric fields which would give valuable complementary information. In addition, coupling possibilities for various experimental methods are presented. These make it possible to decipher the correlation between electronic and magnetic properties on various timescales. The effect of Kramers vs. non-Kramers Ln-ions shows a promising approach towards a better understanding of magneto-optical coupling, whereas butterfly complexes offer a valuable class of molecules with manifold possibilities for tailor-made design. In parallel, understanding these coupling effects demands more sophisticated and specific methods for investigations and further tools need to be developed. We believe that this will eventually lead to a plethora of various techniques that simultaneously combine both frequency and time-domain methods. Some further experimental approaches have not been discussed in this article and in particular, the reader is referred to a very recent perspective article by Xue and coworkers<sup>[233]</sup> on spin-phonon coupling and magnetic anisotropy in molecular magnet materials listing some further suitable experimental tools such as Raman techniques with applied magnetic fields (RaMS) and inelastic neutron scattering (INS).

Future systems will ultimately go to more complicated systems using, for example, SMMs with antenna groups e.g. attaching dyes to ligands in order to sensitise metals with chiral moieties.<sup>[234]</sup> It will be interesting to see whether polarisation of pulses can be used to control properties and to explore potential applications of electron transfer between the metal centres analogously to excitonic dynamics in photosynthesis (PSII). Future work should also concentrate on the combination of different techniques from the synthetic perspective including fine tuning of excited state properties to obtain new insights. In particular, chiral molecules have been subject to successfully control a transfer of enantiomer-specific states (ESST for enantiomer-specific state transfer) using microwave-driven coherent population transfer.<sup>[235–236]</sup> This approach typically implies circularly polarized light and it will be interesting to observe further advances towards a quantitative ESST.<sup>[237–238]</sup>

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

This is a concept on data and their interpretation for future research that have already been published in more than 230 articles.

**Keywords:** 3d–4f Single Molecule Magnets · Ultrafast Processes · Time and Frequency Domain Spectroscopy · Applied Magnetic Fields · Photoexcitation

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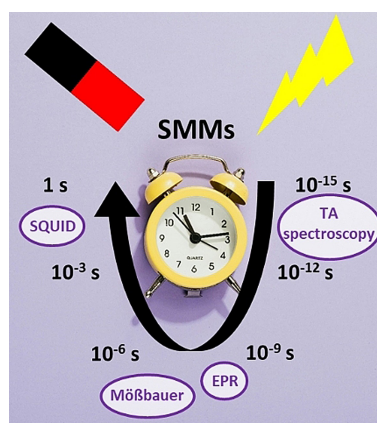
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## CONCEPT

This concept article explores the understanding of the interplay of electronic and magnetic properties on the optical signatures of 3d–4f single molecule magnets (SMMs). It presents a combination of multiple time and frequency domain techniques including transient absorption (TA) spectroscopy, electron paramagnetic resonance (EPR), Mössbauer spectroscopy and superconducting quantum interference device (SQUID) magnetometer measurements.



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**Gaining Insights into the Interplay  
between Optical and Magnetic Prop-  
erties in Photoexcited Coordination  
Compounds**