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Molecular single-ion magnets based on lanthanides and actinides: Design considerations and new advances in the context of quantum technologies

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Abstract

Over the past fifteen years or so, the study of *f*-element single-ion magnets (*f*-SIMs) has gone from being a sub-discipline of molecular magnetism to an established field of research in its own right. The major driving force has been their exceptional promise in applications such as ultra-high-density data storage, spintronics, and quantum information processing (QIP). Recent demonstrations that *f*-SIMs preserve their intrinsic magnetic properties even when deposited onto substrates have reinforced the interests in the field.

Here, we review the current state of the field of lanthanide and actinide *f*-SIMs; discuss the principal factors affecting the magnetic and quantum properties of such single-ion magnets; review the latest chemical approaches in designing *f*-SIMs with superior properties; and highlight new trends in single molecule magnetism, including using *f*-SIMs as potential spin qubits for quantum computers.

Keywords: Lanthanides, Actinides, Single-ion Magnets, Quantum Information Processing, Slow Magnetic Relaxation

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1. Introduction

Molecules that exhibit a measurably slow relaxation of their magnetisation are named single-molecule magnets (SMMs) [1-6]. Single-ion magnets (SIMs) are simply a subclass of SMMs wherein the electronic spin term originates from a single magnetic centre [7,8]. In SIMs, the ion bearing the spin is most commonly a transition metal [9-13], lanthanoid [14-22], or actinoid [23-30]. The term SIM is somewhat of a misnomer: all SIMs are molecular in nature since the ligand field is a vital prerequisite for their slow relaxation. In other words, slow magnetic relaxation does not originate from the free ion state, but only when the metal ion is placed in a ligand field that removes orbital degeneracy [31]. Still, it has persisted as a way to distinguish mononuclear complexes from those containing multiple spin centres, where exchange interactions influence the magnetic behaviour.

Over the last fifteen years or so, the field of molecular magnetism has undergone a shift of focus away from polynuclear complexes towards SIMs, and in particular toward those containing f-block elements [32-40]. This change in direction was largely driven by research progress, being realised that the parameters defining the magnetic relaxation barrier of SMMs, the total spin (S) and the axial anisotropy (D), are not easily achievable by simply scaling molecules to contain more spin-bearing atoms. A promising and fundamentally different approach was proposed in 2003 by Ishikawa and co-workers [14], who successfully demonstrated that slow magnetic relaxation could occur in mononuclear lanthanide complexes, such as those in which a lanthanide (Ln) ion is sandwiched between two phthalocyanine (Pc) ligands, $(\text{Bu}_4\text{N})[\text{LnPc}_2]$ (Ln = Tb^{III} (**1**), or Dy^{III} (**2**), Bu_4N = tetrabutylammonium). This rather unexpected result marked the beginning of a new era in single-molecule magnetism, with many research groups investing a great deal of effort in trying to understand this behaviour [41-47]. Real progress has been made in determining which factors affect most significantly the spin dynamics of Ln-SIMs [17, 48]. Ab-initio models have been routinely employed to predict which ligand environments allow for the best optimisation of the spin relaxation times [49-51], in view of fabricating molecular devices that could store and process information above cryogenic temperatures. Recent work has made significant gains in this direction, with reports of slow magnetic relaxation at temperatures as high as 100 K and magnetic blocking at 5–30 K in Dy- [32-36], Er- [52, 53] and Tb- [54, 55] SIMs. Other notable achievements are the observation of Rabi oscillations in f -element single molecules [56-59], and the detection of ‘atomic clock transitions’ in a Ho-SIM system [60].

In this review, we focus on f -element (lanthanoid and actinide) SIMs, and we highlight some of the most impactful results arising from the field over the last decade or so. We then discuss how this work has led to useful design parameters that are enabling chemists to target specific properties in novel SIMs - not only large relaxation barriers, but specific quantum properties that could be

exploited in emerging applications such as quantum information processing.

2. Lanthanide Single-Ion Magnets (Ln-SIMs)

2.1. Slow magnetic relaxation

The phenomenon of slow magnetic relaxation in molecular complexes was first reported in 1991 by Sessoli and co-workers [2], and since then has been extensively studied [6, 31, 61-63]. Very briefly, slow magnetic relaxation occurs when there is an energetic barrier to the reorientation of the molecular magnetic moment. If the low energy electronic states in a system are split by anisotropic interactions in a way that results in a ground state magnetic doublet ($\pm m_J$ or $\pm m_S$) having (i) a large value (ideally the maximum value), and (ii) a large energetic separation between the ground and first excited state, then the system will exhibit a so-called bistability of its magnetic moment, which can potentially result in a measurably slow relaxation of the magnetisation.

For f -element complexes, spin-orbit coupling generally has a much greater influence on the ground electronic state than crystal field effects (this is especially true for 4f elements), and as a result, the total angular momentum, J , is used to classify the states of the low energy manifold. In this picture, the barrier to relaxation is determined by the energetic spacing of the m_J microstates. In the case of $(\text{Bu}_4\text{N})[\text{TbPc}_2]$ a spacing between the ground state $m_J = \pm 6$ and the first excited state $m_J = \pm 5$ of ca. 400 cm^{-1} leads to its SMM behaviour [14, 41]. In some situations, magnetic relaxation via the first excited state is blocked, and this leads to higher excited states providing the relaxation pathway, resulting in even larger magnetisation blocking barriers and implicitly longer relaxation times [32, 36, 64]. The key feature in all cases is a strong axial ligand field that maximises the energy gap between $|m_J|$ states so that mixing between them is inhibited. If the anisotropy axes of the ground and first excited $|m_J|$ states are co-parallel, then thermal relaxation involving these states cannot occur.

Slow magnetic relaxation manifests as a hysteresis in the field-dependent magnetisation of a compound (above a threshold sweeping rate), as the magnetic moment is prevented from relaxing to its equilibrium value in time. The loop width generally increases with a decrease of temperature and with an increase of the field-charging rate [32]. The most used method for detecting and characterising slow magnetic relaxation is through the use of alternating current (ac) magnetic susceptibility measurements [65-70]. Wherein, a small oscillating magnetic field is applied to the sample, and the in-phase and out-of-phase components of magnetic susceptibility are measured over a range of temperatures, oscillation frequencies, and static magnetic fields. From this, relaxation parameters under the various conditions are extracted, with the real (χ') and imaginary (χ'') components of the ac susceptibility being given by Eq. 1:

$$\chi'(\omega) = \frac{\chi_{dc}}{1 + \omega^2\tau^2} \quad \text{and} \quad \chi''(\omega) = \frac{\chi_{dc} \omega \tau}{1 + \omega^2\tau^2} \quad (1)$$

Here, χ_{dc} represents the static magnetic field and $\omega = 2\pi\nu$. In the simplest case, according to the generalised Debye model [71], the relaxation time τ is associated with the inverse of the frequency at which the out-of-phase susceptibility $\chi''(\omega)$ attains its maximum, $\tau = 1/\omega_{\max}$, where $\omega_{\max} = 2\pi\nu_{\max}$. However, this interpretation becomes confusing in situations when more than one $\chi''(\omega)$ peak is observed [32, 52, 64, 72]. For mononuclear SIMs, the multi-peak feature of $\chi''(\omega)$ data has routinely been linked to extrinsic factors, such as the existence of crystallographically inequivalent metal sites, or the occurrence of intermolecular dipolar interactions that occur in the solid state. However, Ho and Chibotaru have recently demonstrated that intrinsic effects can actually give rise to two ac maxima in mononuclear f -SIMs [73].

Relaxation of the magnetization in SIMs occurs via a number of different mechanisms. At the lowest temperatures of a few Kelvin, the dominant relaxation mechanism is usually QTM (quantum tunnelling of the magnetisation), which is governed by environmental factors, such as the presence of nuclear spins and dipolar coupling. QTM between magnetic ground states is naturally temperature-independent [3]; however it is possible for magnetisation to tunnel the energy barrier through excited states. This relaxation process, known as thermally-activated quantum tunnelling (TA-QTM), is temperature dependent [64]. For the design of single molecule magnets, QTM needs to be inefficient. This situation generally occurs in compounds with strictly axial ligand field environments [32, 34].

Fig. 1. Illustration of the three primary mechanisms for spin-lattice relaxation of magnetisation and their temperature dependence.

At slightly higher temperatures, coupling of the magnetic moment to lattice phonons becomes important, and thus other relaxation mechanism become operative. The most relevant ones are presented in Fig. 1, where the symbols (+1) and (-1) denote the Zeeman-split components of the $|m_z\rangle$ ground state involved in relaxation, and (+2) and (2*) symbolise a real and a virtual excited state respectively. In the so-called direct process, the relaxation of the magnetisation from (+1) to (-1) takes place via the emission of a single phonon of energy $h\nu = E_{(+1)} - E_{(-1)}$,

where $E_{(+1)}$ and $E_{(-1)}$ are the energies of states (+1) and (-1) [74]. As there is a low density of phonons that match such a condition, this process is not efficient in single-ion magnets [63]. In contrast, the Orbach and Raman processes depicted in Fig. 1 are expected to be more efficient, as they involve phonons of higher energies, where the density of states is higher than those relevant to the direct process. In both cases, the energy difference between an absorbed and emitted phonon is equal to the ground-state Zeeman splitting ($E_{(+1)} - E_{(-1)}$) [31]. The two processes differ in the energies of the phonons, and thus the nature of the excited state that is involved in relaxation. While in the case of an Orbach process the phonon energies match the energy separation between real electronic states, the Raman process proceeds through absorption and reemission of virtual phonons [74, 75]. These processes can be distinguished by characteristic magnetisation relaxation rates as a function of temperature (Eq. 2) [44]:

$$\tau^{-1} = \underbrace{\frac{B_1}{1+B_2H^2}}_{\text{QTM}} + \underbrace{AH^{n_1}T}_{\text{direct}} + \underbrace{CT^{n_2}}_{\text{Raman}} + \underbrace{\tau_0^{-1}\exp(-\frac{\Delta_{CF}}{k_B T})}_{\text{Orbach}} \quad (2)$$

Here, H represents the applied field, T is temperature, and Δ_{CF} is an intermediate crystal-field parameter that conventionally measures the energy gap to the first or second excited state, with some exceptions cited [32, 49, 64]. The parameters A–C and τ_0 are determined by empirical means, while n_1 and n_2 take the typical values reported in the literature [63].

In practice, the barrier height is determined through the use of the Arrhenius law, $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$, which relates the experimentally-determined relaxation time, τ , to the effective energy, U_{eff} , and the relaxation rate, τ_0 . This energy barrier, usually expressed in wavenumber (cm^{-1}) or kelvin (K) units, acts as a figure of merit for SMM complexes, and is one of the parameters that researchers aim to maximise. The Arrhenius law above implies that magnetic relaxation occurs via excited states and involves an Orbach process. This is especially true at high temperatures, where thermal relaxation dominates the dynamics of the magnetisation. At low temperatures, competing mechanisms are more effective, and can greatly affect the relaxation rate [32]. Indeed, studies suggest that Orbach relaxation cannot *a priori* be considered as the main mechanism determining the spin dynamics of single molecule magnets, as there are examples where other mechanisms, predominantly Raman, have controlled the dynamics [76].

The situation is therefore quite challenging for synthetic chemists aiming to design new systems with desirable SMM properties (e.g. large U_{eff} values, high T_B). In this section, we will present and discuss a select number of studies that have contributed significantly to the field of $4f$ -SIMs by demonstrating the importance (and in some cases, the lack thereof) of various structural and electronic parameters.

2.2. Effect of local geometry

In the case of $4f$ complexes, crystal field (CF) effects are paramount in determining the magnetic relaxation properties. This is because CF is the primary source of anisotropic splitting of the low energy manifolds in $4f$ compounds, with the spin–orbit coupling (SOC) being significantly larger than CF. Based on the presumption that the desired low energy manifold should have the highest m_J value lowest in energy in order to achieve bistability, and that the energy gap to the first excited state should be as high as possible, the question becomes: for a given lanthanoid ion, which local geometry will give the best arrangement of m_J states?

This question was tackled elegantly to a first approximation by Rinehart and Long, who outlined an approach that takes into consideration the interaction that a particular crystal field would have with the electron density of a given Ln^{3+} ion [77]. The radial distribution of the total electron density of the entire $4f$ shell was approximated for all Ln^{3+} ions in the free ion state, and used to illustrate how radial anisotropy varies across the group between extremes where the density elongates along the axial direction (prolate) to where it extends into the equatorial direction (oblate). Using this simple model, it becomes straightforward to predict the ligand environment favouring an energetic distribution of the m_J states in the desired order (that is, where the sub-states with the highest m_J values are lowest in energy). For example, the highly oblate densities exhibited by Tb^{3+} and Dy^{3+} would benefit from strongly axial ligand fields, while strong equatorial ligand fields are better suited to ions with prolate electron clouds.

A more involved theory was outlined shortly thereafter by Ungur and Chibotaru, whose *ab initio* calculations predicted an enormous magnetic anisotropy in cases where a lanthanide ion with oblate density (*e.g.* Dy^{3+}) is closely bound to only one or two negatively charged donor atoms (*i.e.* a linear coordination environment). The extremely short Ln–L bond length expected—much shorter than the bonds observed in more typical Ln^{3+} coordination environments with eight or more ligand atoms—ensures a good overlap between metal and ligand electron clouds, greatly enhancing the axiality of the ligand field felt by the

metal ion. This effect is demonstrated using the hypothetical $[\text{Dy–O}]^+$ moiety; its perfect axial symmetry gives rise to an energy barrier of over 3000 K with greatly suppressed QTM [49].

Thus, both electrostatic models and *ab initio* calculations support the idea that linear complexes providing local environments approaching perfect axiality represent ideal SIM candidates. Unfortunately, such low coordination numbers are extremely uncommon for f -elements, which instead tend to form compounds with large coordination numbers due to their extended orbital radii and large electronic charge. Thus, the majority of the work in the field has settled for more achievable geometries, but with an emphasis on targeting high axiality.

2.2.1. Polynuclear six-coordinate complexes

With work in our own laboratory on oxo-centered, polylanthanide alkoxide cage systems such as $[\text{Dy}_5\text{O}(\text{O}^i\text{Pr})_{13}]$ (**3**) and $[\text{Dy}_4\text{K}_2\text{O}(\text{O}^i\text{Bu})_{12}]$ (**4**), and their Dy-doped yttrium analogues, $\text{Dy}@\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ (**5**) and $\text{Dy}@\text{Y}_4\text{K}_2\text{O}(\text{O}^i\text{Bu})_{12}$ (**6**), we showed that even in systems with Ln sites in a relatively high coordination environment LnO_6 , a short Ln–O bond length was sufficient to influence the anisotropy direction [64, 65]. Indeed, in all of these compounds, the anisotropy axes of the ground and lowest-lying excited states were parallel in each Dy site, being oriented along the oxide–dysprosium–terminal alkoxide axis. The Dy–O bond length to the terminal alkoxide is shorter than that to the central μ_n -oxide ($n = 5$ or 6) by around 0.2–0.3 Å. This disfavors relaxation via the first excited state and suppresses zero-field QTM, yielding energy barriers for relaxation of the magnetisation exceeding 800 K, with slow magnetic relaxation being observed up to 50 K (Table 1) [64].

The isostructural Ho analogue of **3**, $[\text{Ho}_5\text{O}(\text{O}^i\text{Pr})_{13}]$ (**7**), showed slow magnetic relaxation to 30 K [66]. Despite possessing an energy barrier to relaxation of 400 K (an order of magnitude higher than any other holmium single molecule magnet), and a highly axial magnetic structure, the large tunnel splittings associated to the ground doublet

Table 1.

Complex	Local Symmetry	U_{eff} [K] ^a	H_{dc} [kOe] ^b	τ_0 [s] ^c	T_B (Hys)[K] ^d	Ref
$[\text{Pc}_2\text{Tb}^{\text{III}}](\text{Bu}_4\text{N})$ (1)	D_{4d}	330	0	6.2×10^{-8}		[14]
$[\text{Pc}_2\text{Dy}^{\text{III}}](\text{Bu}_4\text{N})$ (2)	D_{4d}	40	0	6.2×10^{-6}		[14]
$[\text{Dy}^{\text{III}}_5\text{O}(\text{O}^i\text{Pr})_{13}]$ (3)	C_{4v}	528	0	4.7×10^{-10}		[65]
$[\text{Dy}^{\text{III}}_4\text{K}_2\text{O}(\text{O}^i\text{Bu})_{12}]$ (4)	C_{4v}	692	0	6.6×10^{-11}	(5)	[64]
		316	0	2.6×10^{-9}		
$\text{Dy}^{\text{III}}@\text{Y}^{\text{III}}_5\text{O}(\text{O}^i\text{Pr})_{13}$ (5)	C_{4v}	804	0		(5)	[64]
$\text{Dy}^{\text{III}}@\text{Y}^{\text{III}}_4\text{K}_2\text{O}(\text{O}^i\text{Bu})_{12}$ (6)	C_{4v}	842	0		(5)	[64]
$[\text{Ho}^{\text{III}}_5\text{O}(\text{O}^i\text{Pr})_{13}]$ (7)	C_{4v}	400	5.5	1.5×10^{-9}		[66]
$[\text{Dy}^{\text{III}}(\text{BIPM})_2]$ (8)	<i>pseudo</i> - D_{5h}	721	0	1.1×10^{-12}	10 (16)	[32]
		813	0	5.6×10^{-13}		
$[\text{Dy}^{\text{III}}(\text{OPCy}_3)_2(\text{H}_2\text{O})_5]^{3+}$ (9)	<i>pseudo</i> - D_{5h}	543	0	2.0×10^{-11}	(20)	[33]
$[\text{Dy}^{\text{III}}(\text{bbpen})\text{Br}]$ (10)	<i>pseudo</i> - D_{5h}	1025	0	4.2×10^{-12}	9.5 (14)	[34]
$[\text{Dy}^{\text{III}}(\text{OP}^i\text{Bu}(\text{NH}^i\text{Pr})_2)_2(\text{H}_2\text{O})_5]^{3+}$ (11)	<i>pseudo</i> - D_{5h}	735	0	5.8×10^{-12}	12 (12)	[35]
$[\text{Dy}^{\text{III}}(\text{O}^i\text{Bu})_2(\text{py})_5]^+$ (12)	<i>near</i> - D_{5h}	1815	0	1.2×10^{-12}	14	[36]
$[\text{Nd}^{\text{III}}(\text{OP}^i\text{Bu}(\text{NH}^i\text{Pr})_2)_2(\text{H}_2\text{O})_5]^{3+}$ (13)	<i>pseudo</i> - D_{5h}	25	0			[37]
		39	2			

^a Effective energy barrier determined from ac susceptibility measurements

^b Value of the dc field used in ac susceptibility measurements

^c Pre-exponential factor of Eq. 2 denoting the thermal relaxation rate

^d Reported blocking temperature and the maximum temperature at which hysteresis was observed

Fig. 2. (a) Molecular structure of $[\text{Dy}^{\text{III}}(\text{BIPM})_2][\text{K}(\text{18C6})(\text{THF})_2]$ (**8**); (b) Calculated magnetic relaxation barrier for **8**, where the x-axis shows the magnetic moment of each state along the C=Dy=C axis; Reprinted with permission from [32]. Published by The Royal Society of Chemistry.

of this non-Kramers ion facilitated a pronounced zero-field QTM [64]

2.2.2. Pseudo-linear O_h and D_{5h} complexes

The isolation of strictly linear two-coordinate L–Ln–L compounds is a daunting synthetic challenge as such species are highly unstable. Because of this, a surrogate approach has been the isolation of dysprosium complexes having either O_h or D_{5h} symmetries with two negatively-charged ligands disposed along the principal axis, and with much weaker ligand donors in the equatorial plane. The resulting complexes can be considered as pseudo-linear, in that they are expected to carry some of the benefits of true linear complexes due to the dominating influence of the axial ligand donors. Representative examples of such compounds are given in Table 1, and will be discussed below.

In $[\text{Dy}^{\text{III}}(\text{BIPM})_2]$ (**8**, $\text{BIPM}^{\text{TMS}} = \{\text{C}(\text{PPh}_2\text{NSiMe}_3)_2\}^{2-}$), the Dy^{3+} ion adopts a pseudo-octahedral geometry, being coordinated by two tridentate carbene ligands that place two dianionic carbon donors along the z -axis and four neutral nitrogen donors in the xy plane of the coordination sphere (Fig. 2a). Here, the C=Dy=C axis is nearly linear, mimicking the desired linear arrangement of negatively charged donors and thus leading to high molecular magnetic anisotropy. This compound has rich magnetic dynamics, as evidenced by detailed magnetic studies reported by our group [32]. It shows frequency- and temperature-dependent single-ion magnet behaviour, with

Fig. 3. Molecular structures of selected Dy pentagonal bipyramidal complexes: (a) $[\text{Dy}^{\text{III}}(\text{OPCy}_3)_2(\text{H}_2\text{O})_5]^{3+}$ (**9**); (b) $[\text{Dy}^{\text{III}}(\text{bbpen})\text{Br}]$ (**10**) [34]. (c) $[\text{Dy}^{\text{III}}(\text{OP}^t\text{Bu}(\text{NH}^t\text{Pr})_2)_2(\text{H}_2\text{O})_5]^{3+}$ (**11**); (d) $[\text{Dy}^{\text{III}}(\text{O}^t\text{Bu})_2(\text{py})_5]^+$ (**12**) along with the out-of-phase component χ'' of the ac magnetic susceptibility data plotted versus temperature for each compound. Reprinted with corresponding permissions from [33] and [34] - Copyright 2016 American Chemical Society [35] - Published by The Royal Society of Chemistry [36] - Reproduced with permission from John Wiley and Sons.

Fig. 4. A structural correlation of axiality and coordination environment of the compounds **8**–**12** in respect to their magnetic behaviour: exact bond lengths, E-Dy-E bond angles of the charged donor atoms along the local *pseudo*- C_4 or C_5 of the molecules (in bold) and mean bond lengths of donor atoms along the equatorial plane or above it in the case of **8** (in italics). Adapted with corresponding permissions from refs. [32] and [35] –published by Royal Society of Chemistry; [33] and [34] – Copyright 2016 American Chemical Society; [36] – John Wiley and Sons.

out-of-phase maxima being observed up to the temperature of 42 K at zero dc field. Relaxation of the magnetisation involves: (i) a thermally-activated Orbach process that dominates at high temperatures and takes place over two relaxation barriers ($U_{\text{eff}} = 721$ K and 813 K); and (ii) a two-phonon Raman process that becomes important as temperature is lowered. Additionally, magnetic hysteresis of a molecular origin has been observed in **8** at temperatures as high as 10 K, which coincides with the blocking temperature of the magnetisation.

Interestingly, *ab initio* calculations independently modelled the magnetic data remarkably well, suggesting that the three lowest-lying Kramers doublets of the ground $^6H_{15/2}$ multiplet of **8** are essentially pure, well-isolated $|\pm 15/2\rangle$, $|\pm 13/2\rangle$, and $|\pm 11/2\rangle$ states quantised along the near-linear C=Dy=C axis. As a result, thermal relaxation of the magnetisation via the second and third excited states is quenched, and the magnetisation is therefore forced to relax via the fourth and fifth excited states (Fig. 2b), which lie 742 K and 810 K above the ground multiplet, respectively.

Compounds **9**–**12** each possess pentagonal bipyramidal D_{5h} symmetry with negatively-charged oxygen donor atoms occupying the axial sites (Fig. 3a-d) [33–36]. In $[\text{Dy}^{\text{III}}(\text{OPCy}_3)_2(\text{H}_2\text{O})_5]^{3+}$ (**9**, OPCy₃ = tricyclohexylphosphine oxide) and $[\text{Dy}^{\text{III}}(\text{OP}^i\text{Bu}(\text{NH}^i\text{Pr})_2)_2(\text{H}_2\text{O})_5]^{3+}$ (**11**), the anionic oxygen donors are provided by sterically bulky phosphine oxide ligands [33; 35], while in $[\text{Dy}^{\text{III}}(\text{bbpen})\text{Br}]$ (**10**, bbpen = N,N'-bis(2-hydroxybenzyl)-N,N'-bis(2-methylpyridyl)ethylenediamine), a polydentate N,O-ligand places anionic phenoxide donors in the axial positions of the pentagonal bipyramid [34]. Compound **12** owes its large magnetic anisotropy to the bis-*trans*-disposed *tert*-butoxide ligands placing five neutral pyridine donors in the equatorial sites [36]. All of these compounds show SIM behaviour with rich magnetisation dynamics. The large effective relaxation barriers (U_{eff}) of **9**: 543 K; **10**: 1025 K (1191 K when diluted); **11**: 735 K; and **12**: 1815 K, place them among the Ln-SIMs with the largest U_{eff} yet observed, with **12** holding the record for the largest energy barrier to magnetic relaxation for any SMM. It should be noted that the U_{eff} values observed are only relevant to magnetic

relaxation at high temperatures, where the Orbach relaxation process dominates. In all cases, a two-phonon Raman process takes over as the temperature is lowered, eventually dominating the spin dynamics.

Magnetic hysteresis was also present in compounds **9**–**12**, with magnetisation blocking temperatures of **9**: 20 K; **10**: 14 K; **11**: 12 K (30 K when diluted); and **12**: 14 K. The larger relaxation barrier in **12** is explained as arising from its nearly perfect pentagonal bipyramidal geometry, where a large axiality of the crystal field at Dy^{III} arises due to the presence of weak pyridine-nitrogens at the equatorial positions [36].

It is obvious that the coordination environment of the lanthanide ion is of crucial importance for the design of high-performance *f*-SIMs, and in the case of Dy^{III} complexes with O_h and D_{5h} symmetry (Fig. 4), the placement of negatively-charged coordinating atoms along the main axes (C_4 or C_5) is advantageous for a number of reasons, including suppression of QTM, stabilisation of the ground $m_j = |\pm 15/2\rangle$ multiplet, and enhancement of the level splitting. Indeed, the computed *g*-tensors of the ground state Kramers doublets in these systems were reported to be purely Ising in nature, with a g_{zz} value approaching 20, and with a negligible transverse term. Such properties are the main reason for the observed zero-field QTM quenching. Furthermore, *ab initio* calculations undertaken on several compounds of O_h and D_{5h} symmetries indicate that one or more excited states are strongly axial in nature, and oriented along the principal axis [32, 34, 36]. This situation disfavors crossing of the barrier though pure, low lying states, further explaining the high energy barriers obtained in these compounds [49].

The benefit of a high-symmetry coordination environment coupled with strong axial and weak equatorial ligation is expected to hold for lighter lanthanides with oblate electronic densities, and indeed has been experimentally demonstrated for a Nd^{III} complex with pseudo- D_{5h} symmetry [37]. Here, the axial ligation of two phosphine oxide ligands in the pentagonal bipyramidal complex $[\text{Nd}(\text{OP}^i\text{Bu}(\text{NH}^i\text{Pr})_2)_2(\text{H}_2\text{O})_5]^{3+}$ (**13**) stabilised the ground $m_j = |\pm 9/2\rangle$ multiplet, giving rise to unprecedented SIM behaviour at zero field for this ion, with an effective

magnetic relaxation barrier of $U_{\text{eff}} = 25$ K, that was enhanced to 39 K by an external dc field of 2000 Oe. The smaller relaxation barrier in **13** is due to a weaker spin-orbit coupling as compared to heavier lanthanide homologues.

2.2.3. High rotational symmetry axial ligands

Another approach toward maximizing the axiality of the ligand field around the $4f$ ion is to employ highly symmetrical ligands possessing no bonding atoms along the symmetry axis. Examples include the single- and double-decker type complexes, including the first and most studied $4f$ -SIM, $(\text{Bu}_4\text{N})[\text{Ln}(\text{Pc})_2]$. Here, the Ln(III) ion is sandwiched between two phthalocyaninate ligands with C_4 symmetry, resulting in a molecular symmetry close to D_{4d} [14].

If the symmetry was exactly D_{4d} , then all of the compounds in this series, irrespective of the lanthanide ion, would be perfectly axial, that is, with completely suppressed QTM in the ground state [49]. However, small deviations from perfect D_{4d} symmetry reduce the ligand field axiality, allowing QTM to occur. Still, both Tb and Dy phthalocyaninato double-decker compounds show magnetization blocking due to a large level splitting of their ground multiplets and stabilisation of the $m_J = |\pm 6\rangle$ and $m_J = |\pm 13/2\rangle$ substates, respectively (Fig. 9a)[41]. The more pronounced oblate electronic density of the Tb^{3+} ion better suits the coordination modes of the Pc ligands, leading to much larger separations between m_J sub-states, and thus a larger energy barrier for $[\text{Tb}^{\text{III}}\text{Pc}_2]^-$ (**1**) ($U_{\text{eff}} = 330$ K), as compared to $[\text{Dy}^{\text{III}}\text{Pc}_2]^-$ (**2**) ($U_{\text{eff}} = 40$ K), and which increases to 938 K [15] by ligand modifications (see section 2.3). Field-dependent magnetisation studies in the subkelvin range revealed magnetic blocking for the Ho derivative, along with resonant QTM that occurs via electronuclear states—a mechanism that differs from that of cluster-SMMs

[78]. Across the lanthanide series, the magnetic anisotropy of $[\text{Pc}_2\text{Ln}]^-$ changes from easy-axis in Tb, Dy and Ho complexes, to easy-plane in Er and Tm, and thus no other member of this family shows SIM behaviour.

In an effort to emulate the favourable SIM properties observed in phthalocyaninates, and encouraged by *ab-initio* predictions [51], various groups have pursued the use of ligands with even higher rotational symmetry, such as the planar cyclooctatetraene (COT) and cyclopentadienyl (Cp^*) anions (Table 2). In one example, Gao and co-workers examined the magnetic properties of the organometallic complex $[(\text{COT})\text{Er}(\text{Cp}^*)]$ (**14**), first reported by Evans and co-workers [79], and proved its SIM behaviour, with an effective barrier of $U_{\text{eff}} = 323$ K and magnetic hysteresis below 5 K [52]. The axial character of the ligand field was found to be responsible for the observed SIM behaviour and stabilisation of an Ising ground state of $m_J = \pm 15/2$, well-separated from the $m_J = \pm 13/2$ excited state. The two relaxation peaks observed were attributed to the presence of two different conformers. The authors noted that in spite of a large spin-reversal barrier, quantum-tunnelling relaxation under zero static field and low temperatures still occurs in this compound, as a result of symmetry distortions caused by the tilting of the two rings.

Further studies into the $[(\text{COT})\text{Ln}(\text{Cp}^*)]$ family of compounds included those with Ln = Tb, Dy, Ho, Er, Tm, and Y, among which Dy and Ho also exhibit SIM behaviour (Fig. 5.) [72]. The quantum tunnelling relaxation rate increased from Er to Ho to Dy, in line with the increase in transverse anisotropy originating from the tilting of the two aromatic rings present in the molecule. From an electrostatic viewpoint, it could be argued that the arrangement of π -bonding molecular orbitals in the COT^{2-} and $[\text{Cp}^*]^-$ ligands furnishes a predominantly equatorial ligand field, benefiting the most prolate $m_J = 15/2$ state of Er(III) [82]. Angular-resolved magnetic measurements provided evidence that $[(\text{COT})\text{Er}(\text{Cp}^*)]$ (**14**) possesses an

Fig. 5. Molecular structure of $(\text{Cp}^*)\text{Er}^{\text{III}}(\text{COT})$ (**14**), along with plots of the out-of-phase component χ'' against frequency over a temperature range from 2 to 30 K (Reprinted with permission from [52]. Copyright 2011 American Chemical Society) and the energy states of the Ln series simulated from the CONDON program (Reprinted with permission from [72]. Copyright 2012 American Chemical Society).

Table 2.

Complex	Local Symmetry	U_{eff} [K] ^a	H_{dc} [kOe] ^b	τ_0 [s] ^c	T_B (Hys)[K] ^d	Ref
(Cp*)Er ^{III} (COT) (14)	$C_{\infty v}$	323	0	8.2×10^{-11}	5 (5)	[52]
[Er ^{III} (COT'') ₂][Li(DME) ₃] (15)	D_{8d}	197	0	3.1×10^{-9}		
[Dy ^{III} (COT'') ₂][Li(DME) ₃] (16)	D_{8d}	187	0	4.0×10^{-8}	8 (8)	[53]
[Er ^{III} (COT) ₂][K(18-c-6)] (17)	low/non C_{8h}	25	0	6.0×10^{-6}		[81]
[Dy ^{III} (COT) ₂][K(18-c-6)] (18)	D_{8d}	286	0	3.7×10^{-8}	6 (12)	[51]
[Er ^{III} (COT) ₂][K(18-c-6)] (19)	D_{8h}	11	0	2.2×10^{-5}		[51]
[Er ^{III} (COT) ₂][K(18-c-6)(THF) ₂] (20)	pseudo- D_{8d}	212	0	8.3×10^{-8}	(10)	[82]
[Er ^{III} (COT) ₂][K(18-c-6)(THF) ₂] (20)	pseudo- D_{8d}	216	0	6.9×10^{-8}	(10)	[82]
[Er ^{III} ₂ (COT'') ₃] (21)		335	0	1.9×10^{-10}	(14)	[83]
[Er ^{III} ₂ (COT) ₄][K ₂ (THF) ₄] (22)		309	0	5.0×10^{-9}	(12)	[83]
[Cp* ₂ Tb ^{III} (BPh ₄)] (23)	C_2	311	2.4	8.0×10^{-10}	(2.5)	[84]
[Cp* ₂ Dy ^{III} (BPh ₄)] (24)	C_2	476	1.6	1.0×10^{-9}	(5.3)	[84]
[Er ^{III} {N(SiMe ₃) ₂] ₃] (25)	C_{3v}	122	0	9.3×10^{-9}	(1.9)	[85]
[Er ^{III} (NHPPh'Pr ₂) ₃ (THF) ₂] (26)	C_{3v}	25	0.4	6.4×10^{-8}		[85]
[Dy ^{III} (NHPPh'Pr ₂) ₃ (THF) ₂] (27)	C_{3v}	34	0	2.1×10^{-5}	(1.9)	[85]
[Er ^{III} {N(SiMe ₃) ₂] ₃ Cl][Li(THF) ₄] (28)	C_{3v}	63	0	1.1×10^{-7}		[86]
[Er ^{III} (W ₅ O ₁₈) ₂] ⁻⁹ (29)	D_{4d}	56	0	1.6×10^{-8}		[17]
[Tb ^{III} (Pc) ₂] ⁶ (30)	D_{4d}	590	0	1.5×10^{-9}		[93]
[Tb ^{III} {Pc(OEt) ₈] ₂ }(Bu ₄ N) (31)	D_{4d}	728	0			[93]
[Tb ^{III} {Pc(OEt) ₈] ₂ }(SbCl ₆) (32)	D_{4d}	791	0	4.2×10^{-11}		[93]
[Tb ^{III} (Pc)(Pc')] (33)	D_{4d}	938	0	1.1×10^{-11}		[15]
[Dy ^{III} {Mo ₅ O ₁₃ (OMe) ₄ NNC ₆ H ₄ -p-NO ₂] ₂] ³⁻ (34)	D_{4d}	38	1	6.6×10^{-8}		[91]
[Yb ^{III} {Mo ₅ O ₁₃ (OMe) ₄ NNC ₆ H ₄ -p-NO ₂] ₂] ³⁻ (35)	D_{4d}	23	1	6.7×10^{-6}		[91]
[Dy ^{III} P ₅ W ₃₀ O ₁₁₀] ¹²⁻ (36)	C_5	24	0		(2)	[18]
[Ho ^{III} P ₅ W ₃₀ O ₁₁₀] ¹²⁻ (37)	C_5	0.8	0	6.0×10^{-3}	(2)	[18]

^a Effective energy barrier determined from ac susceptibility measurements

^b Value of the dc field used in ac susceptibility measurements

^c Pre-exponential factor of Eq. 2 denoting the thermal relaxation rate

^d Reported blocking temperature and the maximum temperature at which hysteresis was observed

Ising axis anisotropy [80], which is probably responsible for the observed magnetic behaviour [52].

Murugesu and co-workers reported an Er^{III} sandwich complex, [Li(DME)₃][Er^{III}(COT'')₂] (15, DME = dimethoxyethane), based on 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (COT''). This compound shows SIM behaviour with a blocking barrier of 187 K, and magnetic hysteresis below 8 K [53]. The better

SIM performance of this compound compared to [(COT)Er(Cp*)] ($T_B = 5$ K) was attributed to a greater equivalence of ligand donation above and below the xy plane, and thus a more pronounced axial orientation of the anisotropy axis. The two COT'' ligands in compound 15 bind to Er in an η^8 fashion, generating a predominantly equatorial ligand field. The isostructural [Li(DME)₃][Dy^{III}(COT'')₂] (16) shows SIM behaviour with a much smaller energy barrier of only 25 K [81]. This result is well supported by *ab initio* calculations proving the ligand field around the Dy^{III} ion is more equatorial than axial [81], favouring the destabilisation of the $m_J = \pm 15/2$ doublet since it corresponds to an oblate charge density distribution [77]. A similar result was obtained from studies on the sandwich complexes [K(18-crown-6)][Ln(COT)₂], with Ln = Er^{III} (17), or Dy^{III} (18), which possess a high symmetry axis due to a parallel arrangement of the eightfold symmetry axes of individual COT ligands. The symmetry of the Er complex is close to D_{8d} , while that of the Dy complex is more eclipsed, being closer to D_{8h} . Despite such structural similarities, the magnetic behaviours of these two compounds are radically different. While compound 18 shows weak SIM behaviour with no magnetic coercivity, compound 17 shows magnetic hysteresis with a large coercive field of 7000 Oe at $T = 1.8$ K, and a large U_{eff} of 286 K (Table 2). The coercivity persists up to about 6 K, while the hysteresis loop persists to 12 K (Fig. 6).[51].

A comparative analysis of the magnetism of two η^8 -cyclooctatetraenide sandwich complexes containing different counterions, [K(18-crown-6)][Er(COT)₂] (19) and [K(18-crown-6)(THF)₂][Er(COT)₂] (20), has shown that, regardless of small difference in symmetry, the dynamics of

Fig. 6. Molecular structure of [K(18-crown-6)][Ln(COT)₂]: (a) Ln = Er^{III} (17) and (b) Dy^{III} (18) along with corresponding plots of the magnetization hysteresis loops [51]. Reprinted with permission from John Wiley and Sons.

the magnetisation are very similar. The compounds exhibit slow magnetic relaxation with high relaxation barriers of *ca.* 216 K, and a waist-restricted magnetic hysteresis [82]. The low-temperature relaxation dynamics were heavily influenced by dipolar interactions that triggered a bulk ‘magnetic avalanche effect’, and fast tunnelling of the magnetisation. These phenomena were substantially quenched by magnetic dilution in a diamagnetic yttrium matrix, resulting in magnetic coercivity being observed up to 10 K.

Using a modular approach to increase spin by dimerization, Murugesu *et al.* successfully synthesized a triple-decker dinuclear compound, $[\text{Er}^{\text{III}}_2(\text{COT}'')_3]$ (**21**) and a K-bridged double-decker dimeric compound, $\text{K}_2(\text{THF})_4[\text{Er}^{\text{III}}_2(\text{COT})_4]$ (**22**), which exhibit remarkably large blocking temperatures (335 K (**21**) and 306 K (**22**)) due to a linear structure and strictly axial anisotropy [83]. These values surpass those of the mononuclear precursors, **15** and **17**.

The compounds also exhibit magnetic hysteresis up to 12 K in the solid state, and up to 14 K in solution. This 4 K increase in blocking temperature of compound **21** over the double-decker analogue, **15**, was attributed to an additional mechanism of magnetisation blocking arising from

exchange coupling between Er^{III} ions. In **22**, the enhancement of SMM properties compared to the $[\text{Er}^{\text{III}}(\text{COT})_2]^-$ precursor (**17**) may arise from a slight increase in the axial crystal field around Er, as no magnetic coupling is expected to occur in this compound [83].

Along with organometallic sandwiched compounds, Long and co-workers have reported low-symmetry lanthanide complexes $[(\text{Cp}^*)_2\text{Ln}(\text{BPh}_4)]$ ($\text{Ln} = \text{Tb}$ (**23**) and Dy (**24**)) with large spin reversal barriers of 311 K and 476 K, respectively [84]. Compound **24** showed hysteretic behaviour up to 5.3 K, with no remnant magnetisation due to pronounced QTM and a dipole-mediated magnetic avalanche. Dilution within a matrix of $[(\text{Cp}^*)_2\text{Y}(\text{BPh}_4)]$ considerably suppressed QTM. These barriers were unexpected, as the complexes lack a clear symmetry axis. The weak ligand fields imposed on the Ln^{III} ions by the BPh_4^- anions contribute to this behaviour, not in the sense of engendering a large overall magnetic anisotropy but rather bestowing a weak transverse anisotropy.

Lastly, Tang and co-workers have reported the magnetic properties of $[\text{Er}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (**25**), the first example of an equatorially coordinated Ln-SIM (Fig. 7). This three-coordinate compound exhibits slow magnetisation dynamics with an energy barrier, $U_{\text{eff}} = 122$ K, and

Fig. 7. (Left) X-ray structure of $[\text{Er}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (**25**); (Right) Out-of-phase component χ'' of the ac magnetic susceptibility data plotted versus frequency over a temperature range of 1.9 to 20 K. Reprinted with permission from [85]. Copyright 2014 American Chemical Society.

Fig. 8. (Left) X-ray structure of $[\text{Er}\{\text{N}(\text{SiMe}_3)_2\}_3\text{Cl}][\text{Li}(\text{THF})_4]$ (**28**) (Right) Out-of-phase component of the ac magnetic susceptibility data plotted versus frequency over a temperature range of 1.8 to 11 K under zero dc field. [86]. Reprinted with permission from John Wiley and Sons.

magnetic hysteresis occurring below 1.9 K [85]. Notably, the isostructural Dy^{III} analogue does not show any SIM behaviour. To some extent, this discrepancy is expected due to the equatorially coordinating crystal field, which is more favourable to the Er^{III} ion (⁴I_{15/2}) with a prolate electronic density, than to the Dy^{III} ion (⁵H_{15/2}) with an oblate electronic density [77]. For the Er complex, this results in the stabilisation of the ground state with the largest quantum numbers ($m_J = \pm 15/2$), as well as effective suppression of QTM. In contrast, the small ground state ($m_J = \pm 1/2$), stabilised in the Dy analogue is unfavourable for single-molecule magnetism [85].

Five-coordinate trigonal bipyramidal compounds containing both Er and Dy ions have been synthesized: [Ln(NHPh^tPr₂)₃(THF)₂] (Ln = Er (**26**) or Dy (**27**)). Both exhibit slow magnetisation dynamics, although much weaker than the three-coordinated Er compound (**25**), since they are dominated by QTM at low temperatures.

More recently, Dunbar *et al.* have reported the first trigonal-pyramidal Er-SIM, [Er{N(SiMe₃)₂}₃Cl][Li(THF)₄] (**28**), notable for having a chloride anion placed in the axial position (Fig. 8). The complex shows slow relaxation of the magnetization under zero dc field with an effective barrier of $U_{\text{eff}} = 63.3$ K, and magnetic hysteresis up to 3 K [86]. The authors have argued that this compound tests the validity of Long's simple electrostatic model, which states that oblate or prolate lanthanides must be stabilized with the appropriate ligand framework in order for SMM behaviour to be favoured [77].

2.2.4. POMs

The coordinative versatility of POMs toward lanthanide ions provides an ideal opportunity to influence magnetic relaxation by tuning the local lanthanide ion symmetry, and thus the crystal field splitting. POMs are not only chemically robust, but also act as a magnetic insulator for metal ions, and, importantly, provide a nuclear spin-free environment to the metal ion due to coordination via oxygen donors. This is particularly important for quantum information processing, as the nuclear spins are a major source of quantum decoherence at low temperatures [87]. In terms of coordination geometries, these ligands are able to stabilise Ln complexes with similar symmetries as the 'double-decker' LnPc₂ single-ion magnets, but also of other symmetries, with both D_{4d} and C_5 resulting in SIM behaviour [88, 89].

The Lindqvist-type [Er(W₅O₁₈)₂]⁹⁻ (**29**) was the first 4f-SIM based on POM ligands to be synthesised [17]. Here the lanthanide ion is encapsulated between the two W₅O₁₈ POM units, which provide square-antiprismatic coordination geometry to the metal ion. While this D_{4d} symmetry is similar to that of the bis(phthalocyaninate) Ln complexes [14], minor geometrical differences in the crystal fields are sufficient to cause significant differences in the magnetic properties. Compound **29** exhibits slow magnetisation dynamics with a U_{eff} barrier of 56 K, while [ErPc₂]⁻ does not show SIM behaviour at all [17]. In turn, the Tb-containing POM derivative, [Tb(W₅O₁₈)₂]⁹⁻, does not show slow relaxation, despite [TbPc₂]ⁿ exhibiting rich

Fig. 9. Crystal structure representation, perspective along the coordination z-axis showing the square-antiprismatic coordination of the central Ln ion and the ϕ twist angle, and energy level diagrams of the state multiplets of a) [LnPc₂]⁻ and b) [Ln(W₅O₁₈)₂]⁹⁻. (a) Reprinted with permission from [41]. Copyright 2004 American Chemical Society. (b) Reprinted with permission from [90]. Copyright 2009 American Chemical Society.

magnetisation dynamics with large magnetic relaxation barriers (**1**: 230 K; **30**: 590 K; **31**: 728 K; **32**: 791 K; **33**: 938 K; Table 3.) [14, 15, 41, 94]. An explanation for this discrepant behaviour could be the difference in ligand fields caused by small deviations from the ideal D_{4d} symmetry and the different coordinating donors. The twist angle between the planes of the coordinating oxygen donors of compound **29** is 44.2° , with axial compression of the coordination environment. This angle is very close to that expected for an ideal D_{4d} symmetry ($\phi = 45^\circ$). In contrast, a twist angle of only 41.4° between Pc planes is present in the double-decker compounds **1** and **2** [14], resulting in a small axial elongation of the square-antiprismatic coordination geometry (Fig. 9a). These distortions, although small, impact the ligand field by stabilizing larger m_J values ($m_J = \pm 13/2$) for Er and the singlet $m_J = 0$ for Tb in $[\text{Ln}(\text{W}_5\text{O}_{18})]^{9-}$ (Fig. 9b) [17, 90]. In contrast, for the bis(phthalocyaninate)lanthanide complexes, the ground states were $m_J = \pm 1/2$ Kramer doublet for the Er derivative, and $m_J = \pm 6$ for the Tb derivative (Fig. 9a) [41]. The faster magnetic relaxation of Ln-POMs compared to $[\text{LnPc}_2]^-$ is attributed to smaller energy gaps between the lower-lying crystal-field sub-states [91].

The effects of even more pronounced distortions from the ideal D_{4d} symmetry were studied in the polyoxomolybdate complexes, $[\text{Ln}(\beta\text{-Mo}_8\text{O}_{26})_2]^{5-}$ and $[\text{Ln}\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4\text{NNC}_6\text{H}_4\text{-}p\text{-NO}_2\}_2]^{3-}$ ($\text{Ln}^{3+} = \text{Tb, Dy, Ho, Er, and Yb}$) [92]. They showed inferior SIM behaviour compared to the analogous polyoxotungstenate complexes due to smaller crystal field splittings, mixing between m_J substates, and pronounced QTM. Thus, no magnetisation blocking would be expected to occur in the absence of an external magnetic field. The Dy (**34**) and Yb (**35**) members of the LnMo_{10} family show SIM behaviour at low temperatures, characterised by anisotropy barriers, U_{eff} , of 38 K and 23 K respectively. The dynamics of the magnetisation involve both a Raman and an Orbach relaxation processes.

The effect of a fivefold axial symmetry C_5 was investigated in $[\text{LnP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ ($\text{Ln}^{3+} = \text{Dy}$ (**36**) and Ho (**37**)) with both compounds showing SIM behaviour [18]. The lower symmetry of this anion gave rise to a larger off-diagonal anisotropy that affects the spin dynamics, particularly at low temperatures, facilitating the occurrence of fast tunnelling processes. The Dy derivative had an activation barrier of $U_{\text{eff}} = 24$ K with an observable hysteresis below 2 K. Between 5 K and 10 K magnetic relaxation proceeds via thermal excitations to the first excited doublet, and between 2 K and 5 K relaxation is dominated by pure quantum tunnelling processes.

2.3. Effect of ligand modification

While molecular symmetry is empirically a fundamental determinant of magnetic anisotropy, ligand modification provides an additional versatile route to controlling SIM behaviour. Examples of ligand modifications include chemical modifications, such as oxidation or protonation; the substitution of coordinated donor atoms as a means to

alter electrostatic potential and/or Ln-donor atom bond lengths; and peripheral ligand functionalization/substitution.

Fig. 10. Magnetic hysteresis curves of (a) $[\text{Pc}_2\text{Tb}]^{0/+}$. Reprinted with permission from [96]. Copyright 2011 American Chemical Society; and (b) $[\text{F}_{64}\text{Pc}_2\text{Tb}]^{1-/2-/3-}$. Reprinted with permission from [97]. Copyright 2013 American Chemical Society.

2.3.1. Ligand oxidation and reduction

$(\text{Bu}_4\text{N})[\text{Tb}^{\text{III}}\text{Pc}_2]$ (**1**) and $(\text{Bu}_4\text{N})[\text{Dy}^{\text{III}}\text{Pc}_2]$ (**2**) complexes were the first lanthanide SIMs to be reported [40]. The measured relaxation barriers of 330 K (~ 230 cm^{-1}) and 40 K (~ 28 cm^{-1}), respectively, are in agreement with the different energy-level structures (Fig. 9a) that show a larger energy separation in **1** between the ground state ($m_J = \pm 6$) and first excited state ($m_J = \pm 5$). This originates from strong ligand field effects that remove the 13-fold $^7\text{F}_6$ ground state degeneracy. As the Orbach relaxation mechanism occurs through excited states, its probability of taking place at low temperatures is low. In contrast, the energy gaps in **2** are much smaller and as such the relaxation becomes much faster [41, 93]. As a means to increase this activation barrier, several ligand modifications have been reported. Firstly, Ishikawa et al. showed that a one electron oxidation of $[\text{Pc}_2\text{Tb}^{\text{III}}]^-$ (**1**) to $[\text{Pc}_2\text{Tb}^{\text{III}}]^0$ (**30**) increased U_{eff} to 590 K, but the mechanism was not elucidated [94]. Subsequently, a two electron oxidation of $[\{\text{Pc}(\text{OEt})_8\}_2\text{Tb}]^-$ (**31**) to $[\{\text{Pc}(\text{OEt})_8\}_2\text{Tb}]^+$ (**32**) resulted in an increase of U_{eff} by 8% to 748 K due to an amplified ligand field splitting through shortening Pc–Pc distances, and hence a reduced Tb^{III} coordination space [94]. A follow-up study used molecular circular dichroism to probe hysteretic behaviour and found the neutral complex $[\text{Pc}_2\text{Tb}]^0$ (**30**) to have a well-defined hysteresis loop marked by coercivity. In contrast, compounds **31** and **32** only showed a butterfly-shaped hysteresis (Fig. 10a) [96]. Although such complexes have low redox potentials, the redox stability could be improved by peripheral functionalisation of the Pc ligands with electron withdrawing groups. For example, replacement of all hydrogens with fluorine to form $[\text{F}_{64}\text{Pc}_2\text{Tb}]^{1-/2-/3-}$ stabilises highly reduced states [97]. While $[\text{F}_{64}\text{Pc}_2\text{Tb}]^{2-}$ showed a clearly defined open-loop hysteresis, $[\text{F}_{64}\text{Pc}_2\text{Tb}]^{2-/3-}$ showed a butterfly-shaped magnetic

Table 3.

Complex	Local Symmetry	U_{eff} [K] ^a	H_{dc} [kOe] ^b	τ_0 [s] ^c	T_B (Hys)[K] ^d	Ref
[Tb ^{III} (TPP) ₂] ⁻ (38)	D_{4d}	387	0	1.6×10^{-11}	(1.8)	[98]
		407	2	6.2×10^{-12}		
[Dy ^{III} (H ₂ dabph) ₂](NO ₃) ₃ (40)	D_4	32	1		(1.3)	[99]
[Dy ^{III} (H ₂ dabph)(Hdabph)](NO ₃) ₂ (41)	D_4	19	1		(1.3)	[99]
[Dy ^{III} (H ₄ daps)(H ₂ O) ₃ (NO ₃)](NO ₃) ₂ (42)	C_5	33	2	1.8×10^{-6}		[100]
[Dy ^{III} (H ₃ daps)(H ₂ O) ₂ (NO ₃)](NO ₃) (43)	C_5	24	2	9.1×10^{-5}		[100]
[Dy ^{III} (Pc)(TBPP)](Bu ₄ N) (44)	D_{4d}	40	0	9.4×10^{-7}		[101]
[Dy ^{III} (Pc)(OTBPP)] (45)	D_{4d}	136	0	8.0×10^{-8}	(3)	[101]
		183	2			
[Dy ^{III} (Pc)(STBPP)] (46)	D_{4d}	194	0	4.7×10^{-8}	(3.5)	[101]
		227	2			
[(dtc) ₃ Dy ^{III} (phen)] (47)	D_{4d}	20	0.4	1.8×10^{-8}		[102]
[(dbm) ₂ Dy ^{III} (dtc)(phen)] (48)	D_{4d}	40	0	4.1×10^{-8}		[102]
[Li(THF) ₄][Dy(NPh ₂) ₄] (49)	D_{2d}	25	1.6	6.4×10^{-8}		[103]
[Dy ^{III} (Ph ₃ CO) ₃ (NPh ₂)] [Li(THF)] (50)	C_{3v}	36	0.7	1.2×10^{-8}		[103]
[Dy ^{III} (hfac) ₃ (bpy)] (52)	D_{4d}	38	0	1.1×10^{-6}	(1)	[104]
[Dy ^{III} (bimdd)] (53)	D_{4d}	50	1	6.8×10^{-7}	(3)	[105]
[Dy ^{III} (bamdd)] (54)	D_{4d}	34	1	2.5×10^{-6}		[105]
[Dy ^{III} (acac) ₃ (H ₂ O) ₂] (dilution) (55)	D_{4d}	66	0	8.0×10^{-7}	(2)	[110]
[Dy ^{III} (acac) ₃ (phen)] (56)	D_{4d}	64	0	5.7×10^{-6}		[111]
[Dy ^{III} (acac) ₃ (dpq)] (57)	D_{4d}	136	0	3.1×10^{-8}	(1.9)	[112]
[Dy ^{III} (acac) ₃ (dppz)] (58)	D_{4d}	187	0	1.3×10^{-8}	(2)	[112]

^a Effective energy barrier determined from ac susceptibility measurements^b Value of the dc field used in ac susceptibility measurements^c Pre-exponential factor of Eq. 2 denoting the thermal relaxation rate^d Reported blocking temperature and the maximum temperature at which hysteresis was observed

hysteresis. Thus, hysteresis loop profile depends on the parity of the redox state of the Pc₂Tb complex, with a butterfly hysteresis occurring with odd charges (+1, -1, and -3) and an open loop hysteresis occurring in even charged redox states (0 and -2) (Fig. 10b). This was attributed to the suppression of QTM in the even charged redox states because of strong coupling between the lanthanide *f*-orbital and the radical ligand π -orbital [97].

2.3.2. Ligand protonation or deprotonation

Fig. 11 Crystal structures of (a) Dy(H₂dabph)₂](NO₃)₃ (**40**); and (b) [Dy(H₂dabph)(Hdabph)](NO₃)₂ (**41**). Red circle denotes the position of deprotonated nitrogen. Reprinted with permission from [99] Published by The Royal Society of Chemistry.

Protonation or deprotonation of the ligands also has profound effects on SIM behaviour. For example, protonation of one nitrogen of a tetraphenylporphyrin (TPP) based Tb^{III} double-decker complex to force heptacoordination to the metal led to the slow magnetic relaxation being switched off. The native square anti-prismatic [Tb^{III}(TPP)₂]⁻ (**38**) complex shows pronounced SIM behaviour, defined by a large relaxation barrier $U_{\text{eff}} = 407$ K. The lack of SIM behaviour in the protonated species [Tb^{III}H(TPP)₂]⁻ (**39**) is explained by a lower symmetry of the Tb^{III} coordination sphere, with the twist angle between ligands being altered to 35° from the standard 45° with protonation. This allows mixing between m_J states, large transverse anisotropy, and reordering of energy substates, which naturally accelerate magnetic relaxation [97].

Similar trends have been observed in Dy^{III} complexes. Compounds [Dy(H₂dabph)₂](NO₃)₃ (**40**) and [Dy(H₂dabph)(Hdabph)](NO₃)₂ (**41**, dabph = 2,6-diacetylpyridinebis(benzoic acid hydrazine)) differ only through the deprotonation of a ligand amino nitrogen (Fig. 11). Both compounds display a ten-coordinate distorted bicapped square antiprismatic geometry with a twist angle of 27° and 29° and an interplane distance of 3.1 Å and 2.3 Å, respectively. The U_{eff} barrier decreased upon deprotonation from 32 K to 19 K, while magnetic hysteresis was observed for both complexes below 1.3 K. The faster relaxation of complex **41** is attributed to two shorter bonds adjacent to the deprotonated amino group, and thus a larger symmetry distortion [99].

[Dy(H₄daps)(H₂O)₃(NO₃)](NO₃)₂ (**42**) and [Dy(H₃daps)(H₂O)₂(NO₃)](NO₃) (**43**, H₄daps = 2,6-bis(1-salicyloylhydrazonoethyl) pyridine) are another pair of compounds in which symmetry distortions through amine nitrogen deprotonation, as well as variations in the binding

Fig. 12. Molecular structures of a) $[\text{Dy}^{\text{III}}(\text{Pc})(\text{XTBPP})]$ ($\text{X} = \text{N}$ (**44**); O (**45**) and S (**46**)); Reprinted with permission from [101]; (b) $[(\text{dtc})_3\text{Dy}(\text{phen})]$ (**47**) and $[(\text{dbm})_2\text{Dy}(\text{dtc})(\text{phen})]$ (**48**) [102]. Adapted by permission of The Royal Society of Chemistry.

modes of the NO_3^- anion, resulted in a decrease of the U_{eff} barrier [100].

2.3.3. Donor atoms

Substitution of the porphyrin pyrrole nitrogen in $(\text{Bu}_4\text{N})[\text{Dy}^{\text{III}}(\text{Pc})(\text{TBPP})]$ (**44**, $\text{TBPP} = 5,10,15,20$ -tetrakis[(4-tert-butyl)phenyl]porphyrin), with either oxygen or sulphur resulted in novel double-decker complexes, $[\text{Dy}^{\text{III}}(\text{Pc})(\text{OTBPP})]$ (**45**) and $[\text{Dy}^{\text{III}}(\text{Pc})(\text{STBPP})]$ (**46**) respectively. While both complexes retain the square antiprismatic coordination geometry with twist angles of 44.2 and 43.3° , respectively, the $\text{Dy}-\text{O}$ ($2.510 \text{ \AA}$) and $\text{Dy}-\text{S}$ ($2.769 \text{ \AA}$) bond lengths are significantly larger than the $\text{Dy}-\text{N}$ (pyrrole) bond lengths in the native complex, **44**. The impact of this is an increased U_{eff} from 40 K in compound **44** to 136 K in **45**, and 194 K in **46** (Fig. 12a.). Compounds **45** and **46** display butterfly hysteresis loops in their field-dependent magnetisation at 3 K and 3.5 K , respectively, in contrast to **44**, which does not show magnetic hysteresis. DFT calculations suggest the improved SIM behaviour is a result of a reduced charge distribution over the oxygen and sulphur atoms, and increased bond lengths that ultimately diminish repulsive electrostatic potential amongst the ligands and f -electron clouds, which in turn stabilises the $|\pm 15/2\rangle$ ground state [101].

Substitution of two sulphur-coordinating dithiocarbamate (dtc^-) ligands in the complex $[(\text{dtc})_3\text{Dy}(\text{phen})]$ (**47**, $\text{phen} = 2,2$ phenanthroline) with two oxygen-coordinating dibenzoylmethanoate (dbm^-) ligands to form $[(\text{dbm})_2\text{Dy}(\text{dtc})(\text{phen})]$ (**48**) (Fig. 12b and c), produced SIM behaviour at zero field, while the original complex only showed weak relaxation dynamics under a dc field. The U_{eff} barrier also doubled in **48** compared to **47**. The improved SIM behaviour is associated with the shortened $\text{Dy}-\text{O}$ bond ($\sim 2.3 \text{ \AA}$), which allows enhanced repulsive electrostatic potential amongst the ligands and f -electrons clouds; this focuses charge unidirectionally, enhancing the magnetic anisotropy in this low-symmetry environment [102]. Comparison between the two four-coordinated Dy^{III} complexes, $[\text{Li}(\text{THF})_4][\text{Dy}(\text{NPh}_2)_4]$ (**49**) and $[\text{Dy}(\text{Ph}_3\text{CO})_3(\text{NPh}_2)][\text{Li}(\text{THF})]$ (**50**), with local symmetries D_{2d} $\{\text{Dy}^{\text{III}}\text{N}_4\}$ and C_{3v} $\{\text{Dy}^{\text{III}}\text{O}_3\text{N}\}$, respectively, has revealed that only the latter shows slow magnetic relaxation under zero dc field ($U_{\text{eff}} = 36 \text{ K}$). This is again attributed to the short $\text{Dy}-\text{O}$ bond ($2.07 \text{ \AA}$) that breaks the high symmetry environment bestowed by the spherically coordinated nitrogens, thus boosting axial magnetic anisotropy at Dy^{III} [103].

In another example, coordination of 2,2'-bipyridine to $[\text{Dy}(\text{hfac})_3]$ (**51**; $\text{hfac} = \text{hexafluoroacetylacetonate}$) evokes SIM behaviour with $U_{\text{eff}} = 38 \text{ K}$, due to a distorted D_{4d} local

Fig. 13. Overlay of X-ray structures of $[\text{Dy}(\text{bimdd})]$ (**53**) (black) and $[\text{Dy}(\text{bamdd})]$ (**54**) (grey) and their relevant χ'' trends. Reprinted with permission from [105]. Copyright 2014 American Chemical Society.

symmetry in $[\text{Dy}(\text{hfac})_3(\text{bpy})]$ (**52**) that lifts the 16-fold degeneracy at Dy^{III} [104]. Lastly, two isostructural Dy^{III} complexes based on a hexadentate ligand that differs in containing either two imine groups, $[\text{Dy}(\text{bimdd})]$ (**53**, $\text{bimdd} = \text{N,N}'\text{-bis(imine-2-yl)methylene-1,8-diamino-3,6-dioxaoctane}$), or two amine groups, $[\text{Dy}(\text{bamdd})]$ (**54**, $\text{bamdd} = \text{N,N}'\text{-bis(amine-2-yl)methylene-1,8-diamino-3,6-dioxaoctane}$), showed field-dependent slow magnetic relaxation with U_{eff} values of 50 K and 34 K respectively (Fig. 13). The differences in magnetic properties were ascribed to a stronger ligand field in **53**, due to increased electron density of the imine group, and small structural changes as a result of alterations in the coordination environment. Interestingly, the lowest-lying sublevels seem to have a large contribution from the $|\pm 15/2\rangle$ state in **53**, and from the $|\pm 13/2\rangle$ state in **54**. [105].

2.3.4. Peripheral ligands

The functionalisation of peripheral ligands is another method used to alter SIM behaviour [106]. However, it is important to note that in some cases this approach can have little to no effect on the magnetic properties. For example, peripheral ligand functionalisation with iodinated groups to form $[\text{Tb}^{\text{III}}(\text{PcI}_4)_2]$ did not significantly alter magnetic behaviour [107]. Equally, the introduction of cyano-groups onto $[\text{Dy}^{\text{III}}\text{Pc}_2]^-$, while altering the electronic structure, did not affect the U_{eff} [108]. In contrast, a systematic study on peripheral ligand functionalisation of homoleptic ($[\text{Tb}(\text{Pc})_2]$) and heteroleptic ($[\text{Tb}(\text{Pc})(\text{Pc}')]$) ($\text{Pc}' = \text{octa(tert-}$

butylphenoxy)-substituted Pc ring) compounds with different peripheral patterns (*i.e.* *tert*-butyl or *tert*-butylphenoxy groups), stabilised in their neutral and anionic forms, revealed the radical forms to exhibit larger energy barriers for spin reversal than the corresponding reduced compounds [15]. In addition, the heteroleptic complexes with an electron donor on one Pc ligand showed higher effective barriers and blocking temperatures than their homoleptic derivatives. In particular, the heteroleptic, *tert*-butylphenoxy-substituted derivative (**33**) displayed SIM behaviour with a U_{eff} energy barrier of 938 K, the highest ever reported for a Tb^{III} system. This result is assigned to the bulky functional groups that not only increase intermolecular separations, but also lengthen the intramolecular N–Tb distances to the substituted Pc ring, bringing the Tb^{3+} ion closer to the unsubstituted Pc ring, and leading to an enhancement of the ligand field effects.

In another study, a small family of structurally similar $[\text{Er}^{\text{III}}(\text{trens})]$ SIMs ($\text{H}_3\text{trens} = 2, 2', 2''\text{-tris(salicylideneimino)triethylamine}$) has been investigated by INS spectroscopy and magnetometry. The compounds differed by peripheral ligand modifications (*i.e.* different peripheral substituents: H, Cl or I, on the trensal ligand backbone), and the presence or lack of three-fold symmetry (C_{3v}) at Er^{III} . The introduction of such substituents, although a large distance from the first coordination sphere, leads to vastly different magnetic properties due to modification of the low-lying energy spectrum [109].

Lastly, $[\text{Dy}(\text{acac})_3(\text{H}_2\text{O})_2]$ (**55**, $\text{acac} = \text{acetylacetonate}$) and $[\text{Dy}(\text{acac})_3(\text{phen})]$ (**56**) both have local D_{4d} symmetry

Table 4.

Complex	Local Symmetry	U_{eff} [K] ^a	H_{dc} [kOe] ^b	τ_0 [s] ^c	T_B (Hys)[K] ^d	Ref
$[\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}]\text{U}^{\text{IV}}(\eta^2\text{-N}_2\text{Ph}_2)]$ (59)		14	1	1.2×10^{-6}	(1.7)	[118]
$[\text{U}^{\text{III}}(\text{Ph}_2\text{BPz}_2)_3]$ (61)	D_{3h}	28.8	1	1×10^{-9}		[24]
$[\text{U}^{\text{III}}(\text{H}_2\text{BPz}_2)_3]$ (62)		11.5				[119]
$[\text{U}^{\text{III}}\text{Tp}_3]$ (63)	D_{3h}	5.5	0.1	7.0×10^{-5}		[24]
$[\text{Nd}^{\text{III}}\text{Tp}_3]$ (64)	D_{3h}	4.1	0	4.2×10^{-5}		[24]
$[\text{U}^{\text{III}}(\text{COT}')_2][\text{Li}(\text{DME})_3]$ (65)	D_{8d}	27	1	4.6×10^{-6}		[120]
$[\text{Nd}^{\text{III}}(\text{COT}')_2][\text{Li}(\text{DME})_3]$ (66)	D_{8d}	21	1	5.5×10^{-5}		[120]
$[\text{U}^{\text{III}}(\text{Bc}^{\text{Me}_2})_3]$ (68)	C_{3h}	47	1.5	1.0×10^{-7}		[28]
$[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_4][\text{K}(\text{18c6})]$ (69)	T_d	26		2.6×10^{-7}		[121]
$[\text{U}(\text{N}(\text{SiMe}_3)_2)_4][\text{K}(\text{18c6})]$ (70)	T_d	23		2.2×10^{-8}		[121]
$[\text{U}^{\text{III}}(\text{TpMe}_2)_2(\text{bipy})]\text{I}$ (71)	C_2	26	0.5	1.4×10^{-7}	(3)	[30]
$[\text{U}^{\text{III}}(\text{Tp}^{\text{Me}_2})_2]\text{I}$ (72)	C_{2v}	30	0.5	1.8×10^{-7}	0.3 (3.5)	[122]
$[\text{U}(\text{TpMe}_2)_2(\text{bipy})]$ (73)	C_2	28		3.3×10^{-7}	(0.8)	[123]
$[\text{U}(\text{THF})_4]$ (74)	C_{2v}	19		6.4×10^{-7}		[27]
$[\text{UN}''_3]$ (75)	C_{3v}	29		1.0×10^{-11}		[27]
$[\text{U}(\text{BIPM}^{\text{TMS}})(\text{I})_2]$ (76)	C_1	23		2.9×10^{-7}		[27]
$[\text{U}^{\text{V}}(\text{O})(\text{Tren}^{\text{TIPS}})]$ (77)	C_{3v}	21.5	1	2.6×10^{-7}	(3)	[25]
$[\text{U}^{\text{V}}(\text{Tren}^{\text{TIPS}})(\text{N})]^{n-}$ (78)	C_{3v}	20–40	1			[26]
$[\text{Np}^{\text{VI}}\text{O}_2\text{Cl}_2][\text{Np}^{\text{V}}\text{O}_2\text{Cl}(\text{THF})_3]$ (80)		139	0			[124]
$[\{[\text{U}^{\text{V}}\text{O}_2(\text{salen})]_2\text{Mn}^{\text{II}}(\text{Py})_3\}_6]$ (81)	C_{2v}	142	0	3.0×10^{-12}	4	[125]
$[\{[\text{Mn}^{\text{II}}(\text{TPA})]\text{I}][\text{U}^{\text{V}}\text{O}_2(\text{Mesaldien})][\text{Mn}^{\text{II}}(\text{TPA})\text{I}]\text{I}]$ (82)	C_{2v}	81	0	5.0×10^{-10}		[126]
$[\text{U}^{\text{V}}\text{Fe}^{\text{II}}_2\text{TPA}]$ (83)	C_{2v}	54	0	3.4×10^{-9}	2.1	[127]
$[\text{U}^{\text{V}}\text{Ni}^{\text{II}}_2\text{BPPA}]$ (84)	C_{2v}	27	0	2.4×10^{-8}		[127]
$[\text{U}^{\text{V}}\text{Co}^{\text{II}}_2\text{BPPA}]$ (85)	C_{2v}	35	1.5	2.9×10^{-9}		[128]
$[\{[\text{U}^{\text{V}}\text{O}_2(\text{salen})(\text{py})][\text{Mn}^{\text{II}}(\text{py})_4(\text{NO}_3)]_n\}]$ (86)	C_{2v}	134	0	3.1×10^{-11}	6	[129]
$[\{[\text{U}^{\text{V}}\text{O}_2(\text{Mesaldien})][\text{Mn}^{\text{II}}(\text{NO}_3)(\text{Py})_2]\}]$ (87)	C_{2v}	122	0	5.0×10^{-10}	3	[130]

^a Effective energy barrier determined from ac susceptibility measurements

^b Value of the dc field used in ac susceptibility measurements

^c Pre-exponential factor of Eq. 2 denoting the thermal relaxation rate

^d Reported blocking temperature and the maximum temperature at which hysteresis was observed

and exhibit SIM behaviour ($U_{\text{eff}} \sim 65 \text{ K}$) [110, 111]. Replacing the 2,2'-phenanthroline ligand with bulkier derivatives increased U_{eff} to 136 K in $[\text{Dy}(\text{acac})_3(\text{dpq})]$ (**57**, $\text{dpq} = \text{dipyrido}[3,2\text{-d}:2',3'\text{-f}]\text{quinoxaline}$), and to 187 K in $[\text{Dy}(\text{acac})_3(\text{dppz})]$ (**58**, $\text{dppz} = \text{dipyridophenazine}$), due to the increased square-antiprismatic ligand field, and hence larger energy gaps between the ground and excited states [112]. Some capping ligands can also cause distortions of the D_{4d} symmetry, which results in larger off-diagonal anisotropy, and implicitly enhanced QTM [113].

Recent experimental and theoretical studies of low coordinate Ln complexes suggest that it is not only the coordinating donor atoms and their ligand field that determine the anisotropy of Ln-SIMs, but also the electrostatic potential of the entire ligand, which ultimately relates to molecular symmetry [114]. It seems the latter plays an even more significant role than the ligand field, which contradicts to some extent the electrostatic model proposed by Long et al [77].

It is of note that a near-linear, two-coordinate bis(amide)Sm complex has been synthesised by Winpenny and co-workers [115]. *Ab initio* calculations have predicted that a Dy^{III} analogue would have unprecedented SMM properties with an estimated energy barrier for reorientation of the magnetisation of 1800 cm^{-1} ($\sim 2590 \text{ K}$), with even higher barriers anticipated if dianionic monodentate ligands could be incorporated in the structure of the compound.

3. Actinide Single-Ion Magnets (An-SIMs)

3.1. Ligand field and symmetry effect

Mononuclear actinide complexes that exhibit slow magnetic relaxation are an emerging class of SIMs, differentiated from Ln-SIMs by a larger radial extension of the 5f orbitals compared with the 4f orbitals of lanthanides, which enables a greater overlap with the ligand-based orbitals, and thus stronger covalency. The enhanced magnetic coupling and larger crystal field splittings possible for actinides is attractive for developing new SIMs. Indeed, the crystal field splitting for U^{3+} is significant, and in U^{5+} is even larger, by an order of magnitude, compared to lanthanides [63]. However, to date the magnetic relaxation properties of lanthanide complexes have eclipsed those of actinides in benchmark properties of magnetisation blocking barrier and hysteresis temperature [116]. This

could be explained to some extent by the concerted effort devoted to lanthanides rather than actinides, but also in the difficulty in crystallising such high-symmetry actinide complexes.

The most feasible 5f element to be employed in SIM research appears to be uranium, which has Russell–Saunders ground states of $^4\text{I}_{9/2}$ (like Nd^{3+}), $^3\text{H}_4$ (like Pr^{3+}), and $^2\text{F}_{5/2}$ (like Ce^{3+}), in its +3, +4, and +5 oxidation states, respectively. Indeed, some examples of 5f-SIM systems based on U^{3+} ($5f^3$, $J = 9/2$) [24, 27, 28, 30, 118–123], and U^{5+} ($5f^1$, $J = 5/2$) [25, 26] ions have been reported in the last few years. Both are Kramers ions ($S = \text{half integer}$) with large values of angular momentum, J , which are guaranteed to possess a doubly-degenerate $\pm m_J$ ground state—an important requirement in SIM research. In contrast, U^{4+} ($5f^2$, $J = 4$) is a non-Kramers ion, and thus no SIM behaviour is expected as it generally exhibits an orbital singlet ground state at low temperatures [117]. However, Coronado and co-workers have recently demonstrated that an appropriate choice of the ligand environment at U^{4+} and the presence of a radical can circumvent this constraint. In fact, coupling of the radical with the paramagnetic 5f metal in a uranium(IV) complex containing an azobenzene radical ligand, $[(\text{SiMe}_2\text{NPh})_3\text{tacn}\{\text{U}^{\text{IV}}(\eta^2\text{-N}_2\text{Ph}_2\bullet)\}]$ (**59**, $\text{tacn} = 1, 4, 7$ triazacyclononane), switched the parity from non-Kramers to Kramers, allowing slow magnetic relaxation to occur [118]. Interestingly, the uranium(III) analogue, $[\text{U}^{\text{III}}\{(\text{SiMe}_2\text{NPh})_3\text{tacn}\}]$ (**60**), showed no SIM behaviour, likely due to repulsive electrostatic potential amongst the ligands and f-electron clouds that destabilised the m_J ground state.

The first monometallic uranium(III) complex to show SIM behaviour was $[\text{U}^{\text{III}}(\text{Ph}_2\text{BPz}_2)_3]$ (**61**, $\text{Ph}_2\text{BPz}_2^- = \text{diphenyl(bispyrazolyl)borate}$). This complex possesses a trigonal prismatic geometry arising from three coordinating bidentate Ph_2BPz_2 ligands (Fig. 14a), which are well-suited to the oblate-type anisotropy of the U^{3+} ion. The resultant axial ligand field removed the m_J substate degeneracy, resulting in slow magnetic relaxation under zero applied field with a $U_{\text{eff}} = 28.8 \text{ K}$ [24].

Subsequent studies explored avenues to influence SIM behaviour through subtle electronic structure adjustments controlled by ligand modifications. For example, replacement of the phenyl groups with hydrogen atoms in **61** gave rise to the compound $[\text{U}^{\text{III}}(\text{H}_2\text{BPz}_2)_3]$ (**62**, $\text{H}_2\text{BPz}_2^- = \text{dihydrobispyrazolylborate}$), with a tricapped trigonal

Fig. 14. Molecular structures of compounds a) $[\text{U}^{\text{III}}(\text{Ph}_2\text{BPz}_2)_3]$ (**61**). Reprinted with permission from [24]. Copyright 2009 American Chemical Society b) $[\text{U}^{\text{III}}(\text{Bp}^{\text{Me}})_3]$ (**67**); and c) $[\text{U}^{\text{III}}(\text{Bc}^{\text{Me}})_3]$ (**68**). Reprinted with permission from [28]. Copyright 2014 American Chemical Society.

Fig. 15. Molecular structures of compounds a) $[\text{U}^{\text{V}}(\text{O})(\text{Tren}^{\text{TIPS}})]$ (**77**) [25] – Reprinted with permission from John Wiley and Sons; b) $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{N})]^-$ (**78**) and c) $[\text{U}(\text{Tren}^{\text{TIPS}})(\mu\text{-N})\{\text{M}(\text{crown})\}]$ (**79**) [26]. Reprinted with permission from [26], Nature Publishing group.

prismatic geometry. Due to the equatorial electronic density, a much smaller energy barrier (11.5 K) was observed, with a dc field being required to trigger SIM behaviour [119]. Intriguingly, computational analyses predicted energy gaps to the first excited state of 190 and 230 cm^{-1} for **61** and **62**, respectively, which are one order of magnitude larger than the experimentally determined U_{eff} values. A similar discrepancy between calculated energy gaps and U_{eff} values were observed in several other uranium single ion magnets. For example, the U_{eff} energy barrier of $[\text{U}^{\text{III}}\text{Tp}_3]$ (**63**; $\text{Tp}^- = \text{trispyrazolylborate}$) is approximately two orders of magnitude smaller than the calculated ground to first excited state gap (267 cm^{-1}) [116]. The authors attributed this to a combined effect of intermolecular dipolar interactions, nuclear coupling, and mixing between low-lying excited states. Nevertheless, this complex showed slower magnetisation dynamics than its isostructural and isoelectronic lanthanide derivative, $[\text{NdTp}_3]$ (**64**), due to the larger orbital $5f$ radial extension compared to the $4f$ orbitals, and due to enhanced ligand field effects [116]. A similar trend has been observed in studies of the structurally similar U^{III} and Nd^{III} sandwich complexes, $[\text{Li}(\text{DME})_3][\text{U}^{\text{III}}(\text{COT}^{\prime\prime})_2]$ (**65**) and $[\text{Li}(\text{DME})_3][\text{Nd}^{\text{III}}(\text{COT}^{\prime\prime})_2]$ (**66**), of D_{8d} symmetry, which showed SIM behaviours under applied field with U_{eff} barriers of 27 K and 21 K, respectively [120].

Long and co-workers investigated the effect of changing donor atoms in compounds with the same molecular symmetry. Through comparing the magnetic properties of two isostructural compounds, $[\text{U}^{\text{III}}(\text{Bp}^{\text{Me}})_3]$ (**67**, $\text{Bp}^{\text{Me}-} = \text{dihydrobis(methylpyrazolyl)borate anion}$), and $[\text{U}^{\text{III}}(\text{Bc}^{\text{Me}})_3]$ (**68**, $\text{Bc}^{\text{Me}-} = \text{dihydrobis(methylimidazolyl)borate anion}$), which coordinate to the metal via N or C respectively (Fig. 14b and c), the more strongly donating N-heterocyclic carbene ligands promoted a greater anisotropy and covalency, leading to the observation of slow magnetic relaxation in **68**, under applied dc field. The thermally activated relaxation barrier $U_{\text{eff}} = 47.5$ K (~ 33 cm^{-1}) is among the highest yet observed for monometallic $5f$ -SIMs [28]. Mazzanti *et al.* compared the effect of substituting oxygen for nitrogen within systems possessing pseudo-tetrahedral coordination environments, such as $[\text{K}(18\text{-crown-}$

6)] $[\text{U}^{\text{III}}(\text{OSi}(\text{O}^t\text{Bu})_3)_4]$ (69**) and $[\text{K}(18\text{-crown-6})][\text{U}^{\text{III}}(\text{N}(\text{SiMe}_3)_2)_4]$ (**70**). The compounds showed SIM behaviour with U_{eff} barriers of 26 K and 23 K respectively, with the small differences attributed to minor variations in ligand field strength between compounds [121].**

The cationic $[\text{U}(\text{Tp}^{\text{Me}_2})_2(\text{bipy})]\text{I}$ (**71**, $\text{Tp}^{\text{Me}_2} = \text{hydrotris(3,5-dimethylpyrazolyl)borate}$) with a distorted dodecahedral geometry (C_2 symmetry), notably without axial coordination environment, also showed slow relaxation under dc field, but with a smaller relaxation barrier of $U_{\text{eff}} = 26$ K (18.2 cm^{-1}). The difference in behaviour is ascribed to the weaker ligand field felt by the U^{III} ion due to a softer electron donating ability of the bipy ligand, and longer U–N distances [30]. The precursor of this complex, $[\text{U}(\text{Tp}^{\text{Me}_2})_2\text{I}]$ (**72**) showed SIM behaviour under a small applied field, with $U_{\text{eff}} = 30$ K (21 cm^{-1}), which is slightly larger than that of **71** [122]. Notably, the calculated energy gaps of 146 and 138 cm^{-1} for **71** and **72**, respectively, again overestimate the U_{eff} values. The need for a dc field to trigger slow magnetic relaxation suggests that QTM is the relaxation pathway at low temperatures. Indeed, the 2,2'-bipyridine radical adduct, $[\text{U}(\text{Tp}^{\text{Me}_2})_2(\text{bipy}^\bullet)]$ (**73**), generated by reduction with sodium amalgam of compound **72**, shows slow magnetic relaxation under zero dc field with $U_{\text{eff}} = 28.5$ K (~ 19.8 cm^{-1}), and magnetic hysteresis at 1.7 K. This suggests coupling between the metal and radical reduces QTM [123].

A systematic study of three different U^{III} complexes with different ligands and symmetries: $[\text{U}^{\text{III}}\text{I}_3(\text{THF})_4]$ (**74**) with three weak-field iodide ligands (C_{2v} symmetry); $[\text{U}^{\text{III}}\text{N}''_3]$ (**75**, $\text{N}'' = \text{N}(\text{SiMe}_3)_2$) with three nitrogen ligands (C_{3v} symmetry); and $[\text{U}(\text{BIPM}^{\text{TMS}})(\text{I})_2(\text{THF})]$ (**76**, $\text{BIPM}^{\text{TMS}} = \text{CH}(\text{PPh}_2\text{NSiMe}_3)_2$) with an assortment of ligands (C_s symmetry), has shown the compounds to possess SIM behaviour with energy barriers ($U_{\text{eff}} = 19\text{--}29$ K) that are all comparable with those of previously reported uranium complexes. Thus, the authors have suggested that the U^{III} SIM behaviour is intrinsic to the ion and less dependent on symmetries and ligands [27].

It is also of note that all U^{III} -SIMs, subject to theoretical or *ab initio* studies, were measured to have U_{eff} values one or two order of magnitude smaller than the respective energy gaps between the ground and first excited states, and

Fig. 16. Energy level diagrams for **77**, **78** and **79**, and model U(V) compounds (ab-initio calculations); (a) $[\text{UN}]^{2+}$, (b) symmetrized $[\text{U}(\text{NH}_3)(\text{NH}_2)_3(\text{N})]^-$, (c) low symmetry $[\text{U}(\text{NH}_3)(\text{NH}_2)_3(\text{N})]^-$, (d) $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{N})]$, (e) average of **78** and **79**, (f) average of **78** and **79** with SOC, (g) **77** with SOC, and (h) **77**. The arrows refer to optical transitions within the j_z electronic manifold from ground to excited states and the colour references the orbital l_z parentage of the given transition. Reprinted with permission from [26], Nature Publishing group.

with slow relaxation behaviours normally occurring over a small temperature range, typically below 7 K. As such, a Raman rather than an Orbach process could dominate the dynamics of the magnetisation, which would make the reported U_{eff} values meaningless. Indeed, Meihaus and Long showed that the temperature-dependent data of many U^{III} -SIMs can be fit well to a power dependence of temperature, *i.e.* $\tau^{-1} = CT^n$, corresponding to a two-phonon Raman process (see eq. (2)) [23]. Although it is still unclear why Orbach relaxation is largely inaccessible in mononuclear actinide complexes, it is necessary to consider all relevant relaxation processes when analysing the dynamics of the magnetisation in such systems.

U^{V} -SIMs are less well explored due to a smaller total angular momentum ($J = 5/2$) of uranium(V) compared to uranium(III), and the possibility of disproportionation to uranium(IV/VI) in aqueous media [115]. However, we have previously shown that a highly anisotropic, strongly axially coordinated ligand environment at uranium(V) increases magnetic anisotropy, and in turn engenders a slow magnetic relaxation, despite a smaller J and $5f^1$ configuration. The first monometallic uranium(V) complex, studied in collaboration with Liddle and co-workers, was $[\text{U}^{\text{V}}(\text{O})(\text{Tren}^{\text{TIPS}})]$ (**77**, $\text{Tren}^{\text{TIPS}} = \{\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^{\text{t}}\text{Pr}_3)_3\}^{3-}$) (Fig. 15a) showed SIM behaviour with an energy barrier U_{eff} of 21.5 K, and a magnetic hysteresis at 3 K, due to a strongly axial ligand field with C_{3v} symmetry imposed by bulky $\text{Tren}^{\text{TIPS}}$ ligands [25].

In a subsequent study, a series of uranium(V) nitrides assembled from the same ligand, $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{N})][\text{M}(\text{crown})_2]$ (**78**) and $[\text{U}(\text{Tren}^{\text{TIPS}})(\mu\text{-N})\{\text{M}(\text{crown})\}]$ (**79**), ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$) (Fig.

15b and c) demonstrated improved SIM behaviour ($U_{\text{eff}} = 20 - 40 \text{ K}$) [26], due to an enhanced ligand field splitting at uranium(V). The study enabled an increased understanding of crystal field effects in U^{V} -SIMs by replacing O^{2-} with N^{3-} in such isostructural and isoelectronic compounds. Moreover, it allowed quantification of the parameters defining the electronic structures of the compounds with combined spectroscopic, magnetic and computational methods. For the O^{2-} complex **77**, the ground state is $j_z = \pm 3/2$. However, for the N^{3-} based complexes **78** and **79**, the ground state is either $j_z = \pm 5/2$, or near-degenerate $\pm 5/2, \pm 3/2$, which is more complex than could have been predicted from computational approaches alone (Fig. 16). This highlighted the importance of using experimental data for elucidating the electronic structure of $5f$ complexes. Akin to $\text{U}(\text{III})$ single ion magnets, the calculated energy gaps between the ground and first excited state (*ca.* 600 cm^{-1}) of these U^{V} -SIMs are significantly larger than experimental U_{eff} values deduced from ac susceptibility data under the assumption of Orbach relaxation. However, we showed that Arrhenius plots could bias this interpretation, as even Raman behaviour can appear to have a linear high-temperature region, given the small temperature range.

3.2. Magnetic exchange with 3d metals

The enhanced covalency of actinides provides greater opportunity for magnetic exchange with other metal ions, in contrast to the greater inclination of the lanthanides to form ionic bonds. A well-established route to superexchange is

Fig. 17. a) Molecular structure of $\{U^V Mn^{II}\}_2$ (**82**); b) View of the linear core with corresponding bond lengths and angles. Atom colours: C (gray), O (red), Mn (violet), N (light blue), I (purple), U (green.); and c) hysteresis loops of (**82**) polycrystalline (left) and pyridine solution (right); Reprinted with permission from [126]. Reprinted with permission from John Wiley and Sons.

through cation–cation interactions that involve oxo-ligands of an actinyl moiety, such as uranyl(V) or neptunyl(VI), binding to another metal centre. The resulting oxo-bridges between metal centres could facilitate strong magnetic exchange. Indeed, two polymetallic complexes, $[Np^V O_2 Cl_2][Np^V O_2 Cl(THF)_3]$ (**80**) and $[\{U^V O_2(salen)\}_2 Mn^{II}(Py)_3\}_6]$ (**81**), both showing strong magnetic exchange and SMM behaviour under zero dc field, were successfully assembled through this approach. Notably, magnetic interactions in compound **80** can only occur between actinides ions [124], whilst in compound **81**, the actinide ion interacts with the $3d$ metal [124]. The magnetic relaxation barriers of the compounds were 139 K and 142 K for **80** and **81** respectively, which are considerably higher than those of the monometallic actinide SIMs, which lack magnetic interaction. Additionally, complex **81** displayed an open magnetic hysteresis loop with a large coercive field of 1.5 T at 2.25 K [125], with coercivity persisting up to 4 K. The improved magnetic behaviour compared to U-SIMs was ascribed to the Ising anisotropy of the uranyl(V) moiety, and strong coupling to the Mn(II) ions. However, the structural complexity of the molecule precluded any magnetic analysis.

In collaboration with Mazzanti and co-workers, we reported the first family of linear $\{M^{II}-U^V-M^{II}\}$ ($M^{II} =$

Mn^{II} , Ni^{II} , Fe^{II} , Co^{II}) trinuclear complexes, and the first $\{U^V-Mn^{II}\}_2$ polymers, all assembled by cation–cation interactions, and presenting slow magnetic relaxation under zero dc field. Coupling of U^V to the $3d$ metals clearly impacted the magnetisation dynamics [126–1230]. One such example is compound $[\{Mn(TPA)I\}[UO_2(Mesaldien)] [Mn(TPA)I]I]$ (**82**, TPA = tris(2-pyridyl-methyl)amine Mesaldien = N,N'-(2-aminomethyl)diethylenebis (salicylidene imine)), which enables strong ferromagnetic exchange between the uranyl(V) ion and the two adjacent Mn^{II} ions, with a coupling constant of $J = +8 \text{ cm}^{-1}$. The compound showed slow magnetic relaxation at zero dc field ($U_{\text{eff}} = 81 \text{ K}$) with a large hysteresis loop (*i.e.* a coercive field of 1.9 T at 1.8 K). The coercivity of the compound persists up to 3 K, and increases with dilution (Fig. 17c) [126].

A follow-up study varied the d -block metal ion of the trinuclear compound to include either Fe^{II} ($s = 2$), Ni^{II} ($s = 1$), or Co^{II} ($s = 3/2$) instead of Mn^{II} ($s = 5/2$). Whilst $[U^V Fe^{II}_2 TPA]$ (**83**) and $[U^V Ni^{II}_2 BPPA]$ (**84**, BPPAH = bis(2-picolyl)(2-hydroxybenzyl)amine) showed magnetic relaxation under zero dc field with an U_{eff} of 54 and 27 K, respectively [127], a magnetic field was needed to trigger SIM behaviour in $[U^V Co^{II}_2 BPPA]$ (**85**) ($U_{\text{eff}} = 30 \text{ K}$) [128]. This suggests the 5d-3d interactions influence the dynamics

Fig. 18. (a) Molecular structure of $\{[UO_2(Mesaldien)][Mn(NO_3)(Py)_2]\}$ (**87**); (b) view of the linear core with associated distances and angles. Atom colours: C (grey), O (red), N (blue), Mn (pink) and U (green); and (c) field dependent magnetisation of (**87**) at different temperatures. Reprinted with permission from [130] - Published by The Royal Society of Chemistry

of the magnetisation.

Magnetic exchange coupling through cation–cation interactions was also present in the 1D coordination polymer $[\{[\text{UO}_2(\text{salen})(\text{py})][\text{Mn}(\text{py})_4(\text{NO}_3)\}_n]$ (**86**), which display single-chain magnet (SCM) behaviour with a U_{eff} of 134 K, and a large coercive field of 3.4 T at 2 K [129]. Compound $\{[\text{UO}_2(\text{Mesaldien})][\text{Mn}(\text{NO}_3)(\text{Py})_2]\}$ (**87**) with a ‘zig-zag’ architecture (Fig. 18a and b), also shows SCM behaviour with a U_{eff} of 122 K, and a large hysteresis with a coercive field of 1.75 T at 2 K (Fig. 18c). In both cases the SCM behaviour was attributed to intra-chain magnetic exchange, in addition to the large anisotropy of the uranyl(V) dioxo group [130].

4. Quantum information processing (QIP) with molecular *f*-SIMs

Single ion magnets hold major potential as molecular quantum bits (qubits) for quantum information processing (QIP)—a field that promises to revolutionise computing by enabling faster implementation of algorithms that would otherwise require calculation times longer than the age of the universe. Although there is still a long way to go until a universal quantum computer is built, significant progress has been made in this direction [131, 132].

The key concept in QIP is that a qubit—the quantum unit of information—is not limited to only the values of 0 or 1, as is the case for classical computer bits, but can be an arbitrary superposition of 0 and 1; that is, any quantum state of the form $|\varphi\rangle = \alpha|0\rangle + \beta|1\rangle$. Thus, quantum computing gains a significantly increased power from encoding the vast Hilbert space of a general quantum state, and by using quantum mechanics to implement calculation algorithms [133].

Areas that could benefit from the computational power of quantum computers include cryptography (safe data protection and secure communication), data management (efficient searching in large databases), material design, and science (*i.e.* simulation of quantum systems). However, before such applications can be realised, a number of

scientific and technological problems must be addressed. One of them regards the physical realization of suitable qubits, and their organization into quantum gates that will ultimately perform the algorithms [134].

Proposed qubit candidates include: superconducting circuits [135], quantum optical cavities [136], ultracold atoms [137] and spin qubits [138, 139]. Each of these possess advantages and disadvantages, and thus it is still unclear which approach will prove successful despite the significant experimental progress in all directions over the last decade or so.

Molecular spin qubits have the advantage of a uniform size and wide tunability, both at the intermolecular and intramolecular level [140], where behaviours are governed purely by quantum mechanics [141]. Many of them possess a ground spin-doublet that can be described in terms of a two-level quantum system [142], the minimum requirement for a qubit.

Another essential requirement in QIP is that the quantum nature of the qubit is tenable. This requires a long quantum decoherence time, which is the length of time that quantum information in a qubit is stored before being lost through interactions with the surroundings. Major sources of such spin decoherence are interactions of the spin qubit with the neighbouring electron spins (dipolar interactions); the nuclear spin bath (hyperfine interactions); and phonons [143]. Thus, approaches to engineer molecular spin qubits with long coherence times (T_2) must address quantum decoherence. Successful strategies resulting in enhanced coherence times include the use of nuclear spin-free ligands [144], ligand deuteration [145], and magnetic dilutions [146, 147]. With a sufficiently long T_2 time, an electron spin qubit can access any arbitrary superposition of the ‘up’ and ‘down’ spin states. The coherent spin dynamics can be experimentally proven using pulsed electron paramagnetic resonance spectroscopy (EPR), through a transient nutation experiment (Rabi oscillations) [148]. Only a limited number of magnetic molecules [144–150], in general, and very few *f*-element single-ion magnets have been reported to possess such a property [39, 56, 60, 143].

Fig. 19. (a) A graphical representation of the single molecule transistor based on $[\text{TbPc}_2]^+$ (**1**). The nuclear spin states of Tb^{III} (coloured circles) are measured and manipulated using an electric field pulse [59] - Reproduced with permission from Science; (b) Splitting of the ground state $m_J = \pm 6$ doublet into four different sub-states by hyperfine coupling to Tb^{III} nuclear spin ($I = 3/2$). Coloured lines correspond to the L_z components: $-3/2$ (purple); $-1/2$ (blue); $1/2$ (green); and $3/2$ (red) [152] - Reproduced with permission from Nature Publishing Group.

Fig. 20. (a) Molecular structure of [Yb^{III}(trensal)] (**88**); (b) Left: Rabi oscillations at selected field positions ($B_0 \perp C_3$), 5 K and microwave attenuation 3 dB; Right: Corresponding Fourier transforms; (c) EDFS spectra of oriented single crystal ($B_0 || C_3$ – blue; $B_0 \perp C_3$ – red) of **88** at 9.6 GHz and 5 K. Reprinted with permission from [56]. Copyright 2016 American Chemical Society.

In this section we review the most up-to-date achievements in the quantum information field, with specific focus on *f*-element single-ion magnets, which are a promising class of compounds to be exploited in this direction.

The bis(phthalocyaninato)terbium(III) complex [Tb^{III}Pc₂][−] (**1**) is one of the most studied magnetic molecules in molecular spintronics, showing great potential as an electronic nano-device [42] and qubit [151]. With many advantages, such as structural robustness, versatile ligand functionalisation, and stable metal ion oxidation state, it is possible to graft the molecule to various surfaces, including to carbon nanotubes [42, 15]. This enables the detection of the spin reversal for a single molecule, as well as the readout and coherent manipulation of electronuclear states, with the aid of magnetic or electric RF fields [59]. Additionally, the conjugated π system of the planar Pc ligands conducts electrons, which prevents the current flow from altering the metal ion oxidation state [153].

With all these characteristics, it is possible to fabricate a spintronic device with the molecule acting as part of an electrode (Fig. 19a). The Tb^{III} nuclear spin ($I = 3/2$) couples to the electron magnetic moment ($J_z = 6$ ground state; $m_J = \pm 6$) via hyperfine interactions, resulting in four electronuclear substates (Fig. 19b), that can be initialized as quantum microstates. While level anti-crossing was observed at low magnetic fields, individual nuclear states were detected by varying the magnetic field. Notably, by using a nuclear spin with a long coherence time (exceeding 60 μ s), and by exploiting the hyperfine electric Stark effect, it was possible to manipulate the nuclear spin of a single molecule. Both nuclear spin trajectories [154], and Ramsey interference fringes were measured [59]. Moreover, the

results are comparable with those reported for p-doped Si [138], showing the great potential of *f*-SIMs in quantum technologies. The T_2 coherence time of **1** was measured with a two-pulse microwave sequence, by varying the interpulse delay, τ . Rabi oscillations were obtained by including a microwave pulse of frequency ν_0 and duration τ between initialization and probe. The resulting oscillating magnetic field enables coherent manipulation at 40 mK of the two lower states of the nuclear spin qubit [59].

The ability to manipulate and read out arbitrary superpositions of states in molecules is clearly a major prerequisite for QIP, and is thus used to select qubit candidates. A relevant figure of merit is the ratio between the manipulation time and the electron spin coherence time (T_2). With typical pulsed EPR set-ups, the time to manipulate an electron spin is about 10 ns. As such, both T_1 (the spin lattice relaxation time) and T_2 must be long enough to allow observation of quantum coherent Rabi oscillations.

Recently, we demonstrated that it is possible to coherently manipulate all electronuclear transitions of an Yb^{III}-SIM using pulsed EPR [56]. The complex, [Yb^{III}(trensal)] (**88**), has a C_{3v} symmetry, and a strongly axial magnetic structure, resulting in the anisotropy axis being parallel to the crystallographic 3-fold rotation axis. Combined ac magnetic susceptibility, and optical data indicated that **88** shows slow magnetisation dynamics ($U_{\text{eff}} = 55$ K) that proceed through Raman and QTM processes rather than an Orbach process [76]. In agreement with this, the temperature dependence of T_1^{-1} , measured on a single crystal of **88** magnetically diluted in the isostructural diamagnetic host [Lu^{III}(trensal)] (**89**), follows a power function (*i.e.* CT^n) describing a two-phonon Raman process (see Eq.(2)). The results suggest that relying on magnetic

Fig. 21. (a) Zeeman diagrams corresponding to the hyperfine splitting $m_I = \pm 4$ ground states calculated for $B_0 \parallel z$ of the molecule. Left is an axial model and right is “axial + B_{44} ”. The blue arrows correspond to the eight high-frequency (50.4 GHz) resonances and the red arrows in denote the predicted X-band resonance positions based on the different parameterizations; The large (~ 9 GHz) tunnelling gap, in the middle of the “axial + B_{44} ” energy diagram shifts the predicted resonance positions (red arrows) such that they agree reasonably well with the spectrum on the left [154] - Published by The Royal Society of Chemistry; (b) Field swept T_2 recorded at 5 K and indicated frequencies and fields for (**90**) ($x=0.001$) [60] - Reproduced with permission from Nature Publishing Group.

anisotropy as the sole parameter in the optimisation of SIM behaviour is inadequate, as interactions with the phonon bath could accelerate the spin dynamics.

Echo-detected field-swept (EDFS) pulsed EPR spectra (9.6 GHz; X-band) of the single crystal of **88**, orientated along ($B_0 \parallel C_3$) and perpendicular ($B_0 \perp C_3$) to the crystallographic 3-fold rotation, enabled all electronuclear transitions of single Yb^{III} centres to be identified (14% ^{171}Yb : $I = 1/2$; 16% ^{173}Yb : $I = 5/2$) (Fig. 20c). Quantum coherence, manifested in the phase memory times, showed T_2 values as long as 0.5 μs below 5 K. Coherent Rabi oscillations were observed for all electronuclear transitions, making **88** a good candidate for coherent manipulations of

the electron spin for more than 70 rotations. The ability to bring the oriented $[\text{Yb}^{\text{III}}(\text{trensal})]$ crystal into an arbitrary coherent superposition of states, and to manipulate any electronuclear Yb isotope state, are essential prerequisites for a SIM quantum computer [56].

The effects of dilution and optimisation of the ligand field around the metal ion were studied in POMs. In the case of $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$ (**90**), the Ho^{III} ion is encapsulated between two POM ligand units, providing an antiprismatic coordination geometry with a symmetry close to D_{4d} . Using X-band and high frequency EPR spectroscopy, hyperfine splittings were observed and calculated, as well as a tunnelling gap of ~ 9 GHz between the $m_j = \pm 4$ states,

Fig. 22. (a) Molecular structures and energy levels of (**91**) and (**92**) [57] - Reproduced with permission from Physical Reviews Letters; (b) Above, X band cw-EPR at room temperature on a single crystal of $\text{Y}_{0.95}\text{Gd}_{0.05}\text{W}_{30}$. Inset of the orientation of the crystal. Below, Zeeman diagram of the GdW_{30} spin energy levels vs H_x with arrows of the seven transitions between these states; (c). Rabi oscillations for $\text{Y}_{0.99}\text{Gd}_{0.01}\text{W}_{30}$ at indicated transitions (adapted with permission from [156])

Fig. 23. Molecular structure of [Th(Cp^{*})₃] (**93**) along with spin lattice relaxation (T_1) and spin-memory times (T_m) of **93** as a function of time. Reprinted with permission from [157]

quantified via the off-diagonal part of the crystal field Hamiltonian (Fig. 21a) [155]. Recently, the spin qubit character of this molecule was studied using pulsed EPR in a series of single crystals dilutions of Na₉[Ho_xY_(1-x)(W₅O₁₈)₂]*n*H₂O (**90**) (x ranging from 0.001 to 0.25) giving long T_2 coherence times up to 8.4 μs at 5 K (for $x = 0.001$ and with a small decrease in T_2 for $x = 0.01$) (Fig. 21b) [60].

The most remarkable finding was that by measuring at certain values of the magnetic field in which there are crossings in the energy levels of Ho, the transitions proved to be independent of the magnetic field up to the first order. These “atomic clock transitions” effectively shield the nanomagnet to the magnetic field at these points, reducing the decoherence effect from magnetic noise and neighbouring spins. This effect can be exploited to increase the concentration of spin qubits for the realization of qubit ensembles for QIP.

Although Gd^{III} as a free ion is magnetically isotropic, certain coordination environments can induce the necessary anisotropy for observing SIM behaviour. For example, compounds [Gd(W₅O₁₈)₂]⁹⁻ (**91**) and [Gd(P₅W₃₀O₁₁₀)]¹²⁻ (**92**), in which the Gd(III) ion is coordinated to different polyoxometalate moieties, showed slow magnetic relaxation at very low temperatures (mK region), which is characteristic of single-ion magnets. The relaxation times of **91** followed typical thermally-activated SIM behaviour for $T > 0.2$ K ($U_{\text{eff}} = 2.2$ K), and became temperature independent below 0.2 K due to quantum tunnelling relaxation. In contrast, the behaviour of **92** was dominated by QTM, although a pure quantum regime was not reached [57]. The contrast in behaviour was ascribed to differences in local Gd^{III} coordination geometry, which determines not only the magnetic anisotropy and resulting crystal field, but also relaxation rates and quantum tunnelling. The coordination environment of Gd^{III} was square anti-prismatic (nearly D_{4d} symmetry; $\phi = 44.2^\circ$) in compound **91**, and close to C_{5v} symmetry for **92**. While **91** has a strongly axial magnetic structure with a well-defined easy-axis magnetic anisotropy, compound **92** exhibits an easy-plane anisotropy [57]. The weaker magnetic anisotropy and favourable level structure of **92**, deduced from EPR, encouraged further studies to probe potential qubit properties with the premise

that a small magnetic field applied along the y -axis will lift the energy-level degeneracy (Fig. 22a). As anticipated, a 2 GHz split of the ground state could be achieved with a magnetic field of 10 mT, resulting in a ground state initialisation of 99.99% at $T = 10$ mK [57]. Pulsed EPR experiments confirmed that all eight M_S transitions enable coherent spin manipulation, making the molecule a promising three-qubit system ($2^N = 8$; $N = 3$). Although the measured coherence times are only in the range 410–600 ns, it is still possible to implement *ca.* 80 quantum operations within the coherence time at 5 K. Notably, the oscillation frequency varied with the static field, B_0 , instead of the microwave magnetic field, B_1 , suggesting coherence transfer between the electron and the nuclear spin, which leads to an increased number of coherent rotations [58].

In a subsequent study, an oriented single crystal of **92**, magnetically diluted in the corresponding yttrium(III) derivative, was studied by EPR as a possible three qubit processor. Seven allowed transitions between the $2S+1$ spin states of Gd^{III} were able to be independently addressed. Coherent Rabi oscillations were observed for all transitions, with the oscillation frequency notably increasing with the microwave power. The authors argued that one of the coherent oscillations observed experimentally is an example

Fig. 24. T_2 comparison of compounds discussed in the text and compounds from [139], [144], [146], [158], [159], [160] [161], [162].

Fig. 25. (Left) U_{eff} comparison of some of the Er, Tb and Dy compounds discussed and 3d metals SIMs ([11], [163] and [164]), (Right) U_{eff} comparison of the Actinide SIMs (right).

of a CCNOT three-qubit gate [156]. Incorporation of multiple qubits in a single metal ion is another way to reduce quantum decoherence, and an example of molecular magnet tunability. In the quest for addressable spin-qubit arrays in complex architectures, the multi-qubit property of lanthanoid SIMs might prove to be a powerful tool [157].

Until recently, actinide SIMs were not considered for QIP applications, as there was no evidence that such complexes would present a detectable electron spin (Hahn) echo, which is necessary to measure quantum coherence via pulsed EPR. However, recently, we reported such data for the first family of isostructural (C_{3v} symmetry) organometallic actinide complexes $[\text{An}(\text{Cp}^{\text{u}})_3]$ ($\text{An}^{\text{III}} = \text{Th}^{\text{III}}$ (**93**), and U^{III} (**94**) ($\text{Cp}^{\text{u}} = [\text{C}_5\text{H}_3\text{Bu}_2\text{-1,3}]^-$) (Fig. 23), displaying quantum coherence measurable by pulsed EPR over a large temperature range [157]. In particular, the Th derivative, **93**, showed spin lattice relaxation (T_1) and spin-memory (T_2) times measurable over the 5–150 K range and reaching $T_1 = 21$ ms at 5 K, and $T_2 = 4$ μs below 20 K. In contrast, the U derivative, **94**, showed faster relaxation, detectable below 10 K ($T_1 = 0.9$ ms; $T_2 = 0.8$ μs at 2.7 K). This discrepancy in behaviour is likely due to different electronic configurations in the two compounds. While **93** behaves as a spin-only d -block ion ($6d^1$), the electronic configuration of **94** is best described as $5f^3$. The larger orbital extension of the $5f$ orbitals in **94** compared to the $6d$ orbitals in **93** facilitates greater covalency, stronger hyperfine interactions with the nuclear bath, and thus faster quantum decoherence, which explains the observed properties. Combined ESEEM and HYSORE experiments enabled the measurement of the hyperfine interactions to the ^1H and ^{13}C nuclei of the Cp ligands, providing information on chemical bonding of the actinide. A larger spin delocalization was found in the uranium compound **94**, which explains the faster decoherence compared to **93** [158].

Conclusions and perspectives

The field of f -SIMs has matured over the last decade or so into a broad discipline driven by the joint effort of theoretical and synthetic chemists. Design principles outlined by theoreticians have been pursued by groups with the required expertise to isolate and characterise the target molecules, and have led to either the validation or subsequent refinement of these principles. We have outlined a number of the criteria that have been determined to be important in the control of the electronic structure of f -SIMs, and have listed a range of chemical approaches that have been undertaken to influence these. This approach has yielded a large database to guide the tailoring of ligand field in future compounds.

Although the goal of the majority of studies was the maximisation of the energy barrier U_{eff} (Fig. 25), as a means to increase the magnetisation blocking temperature, greater control of electronic structure has led to the application of f -SIMs in a broader range of topics within spintronics [165], and in particular within the field of quantum information processing [166] (Fig. 24). Applications such as these are likely to play a leading role in the future development of f -SIMs given their unrivalled potential for tunability and paradigms of robustness.

Actinide f -SIMs have been comparatively less well studied, but are starting to gain momentum among various groups due to their unusual electronic properties and increased tendency to form covalent interactions, which may lead to more exotic behaviours than can be achieved with lanthanides.

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