Review

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

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A B S T R A C T

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.

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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 sub-class 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 toward 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, (Bu$_4$N)[LnPc$_2$] (Ln = Tb^{III} (**1**), or Dy^{III} (**2**), Bu$_4$N = 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 (Bu$_4$N)[TbPc$_2$] a spacing between the ground state $m_J = \pm6$ and the first excited state $m_J = \pm5$ 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):

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

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].