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Review

Recent advances in luminescent lanthanide based Single-Molecule Magnets

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ABSTRACT

Luminescent lanthanide-based Single-Molecule Magnets (SMM) are multifunctional molecule-based materials that combine luminescence and magnetic properties in the same crystalline structure, which can exist separately or act in synergy. Here we present a short overview focalizing on recent advances in this family of SMM and give the outlook on the future researches in this domain.

Contents

1. Introduction

Multifunctional molecular materials belong to a class of multifunctional compounds of various dimensionality composed by metal ions and organic or inorganic ligands, which combine several physical or chemical properties into a single crystalline structure and are capable to exhibit diverse physical responses when subjected to external stimuli. In comparison with metallic or metal-oxide materials, they have received less attention, despite numerous advantages associated with their molecular nature, namely light density, optical transparency or tuneable physical properties (magnetism, optics, electrochemical behaviour and others) [1,2]. Such systems have attracted a great deal of attention in the molecular chemistry community in the last few years due to their fundamental interest and potential applications in various technological fields, such as quantum computing and/or spintronics [3], gas separation, sensors, catalysis, or biomedicine [4]. Among different multifunctional systems [1], a particular emphasis has been made to design magnetic molecular materials with additional functionalities. Thus, recent advances have been performed by combining magnetic properties with optical or

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non-linear activity [5–7], porosity [8], conductivity [9], luminescence [10] or ferroelectricity [11,12]. While the simple superposition of the constitutive properties can be considered as the starting point, the mutual interaction and *in fine* the synergy implying the control of one property by another have recently been envisaged. However, this implies the chemical design of optimized systems, as well as the experimental evidences of such synergistic effects, that still constitutes a real challenge in the field of multifunctional molecular materials.

Surprisingly, bi-functional molecular-based materials combining luminescence with magnetic properties have been far less investigated despite the fact that these systems can open new horizons in various applications, such as information storage, sensing (optical detection of magnetic compounds) and bio-imaging (combining for instance Magnetic Relaxation Imaging (MRI) and fluorescence labelling). The main reason explaining such scarcity relies on the fact that the usual spin carriers, such as, for instance paramagnetic transition metals ions Mn^{III}, Co^{II}, Ni^{II}, not only do not exhibit emission properties, but usually quench the luminescence of organic dyes, which may be used as ligands in molecular structures. Moreover, most transition metal ions employed to build luminescent architectures, such as Cu^{I}, Co^{III}, Zn^{II}, Ru^{III}, Pt^{II}, Pd^{II} or Ir^{III} are indeed diamagnetic, at the exception of the Cr^{III} ion ($S = 3/2$). In this connection, considerable advances in magneto-luminescent molecular materials have been made since the "rebirth" of trivalent lanthanide ions (Ln^{3+}) in molecular magnetism after the demonstration of the occurrence of a slow relaxation of the magnetization in mononuclear bis-phtalocyanine $[Ln(Pc)_2]^-$ complexes by Ishikawa [13]. Indeed, these ions constitute the most evident choice for designing multifunctional materials and to take advantage of both properties. On the one hand, paramagnetic lanthanides present a large unquenched orbital moment associated with "core" *f* magnetic orbitals, which leads to the occurrence of a high magnetic anisotropy. In this sense, Single-Molecule Magnets (SMM) have emerged as nanomagnets with fascinating molecular architectures and great potentialities in future technological applications, such as data storage and quantum computing [14,15]. On the other hand, Ln^{3+}-based materials exhibit exceptional luminescence features, with a narrow bandwidth, long-lived emission, ligand-induced large Stokes shifts, ligand-dependent luminescence sensitization, and generally high luminescence quantum yields [16]. Though a relatively rapid development of Ln^{3+}-based SMM, a relatively weak number of these reported molecular architectures have exhibited a combination of a slow relaxation of the magnetization with luminescence.

While numerous reviews have been published on either Ln^{3+}-based SMM [14,15,17–20] or Ln^{3+} luminescence [16,21–23], to the best of our knowledge, the scope of multifunctional magneto-luminescent SMM has been far less highlighted [24,25]. Thus, though paramagnetic Ln^{3+} complexes have been known for decades, the first report of a coexistence of a slow relaxation of the magnetization and a Ln^{3+}-based luminescence has been published only less than ten years ago [26]. Moreover, the correlation between the relaxation dynamics and emission has only been performed in 2012 [27], while an inductive effect between the magnetic field and luminescence has only been demonstrated in 2016 [28].

In the present review, after a brief overview on the optical and magnetic properties of Ln^{3+}-based architectures, we focus on examples exhibiting both SMM properties and luminescence (systems showing only ligands based luminescence are not described here), and we try to shed light on the mutual benefits of such bi-functional systems. Lastly, upcoming challenges and perspectives will be considered.

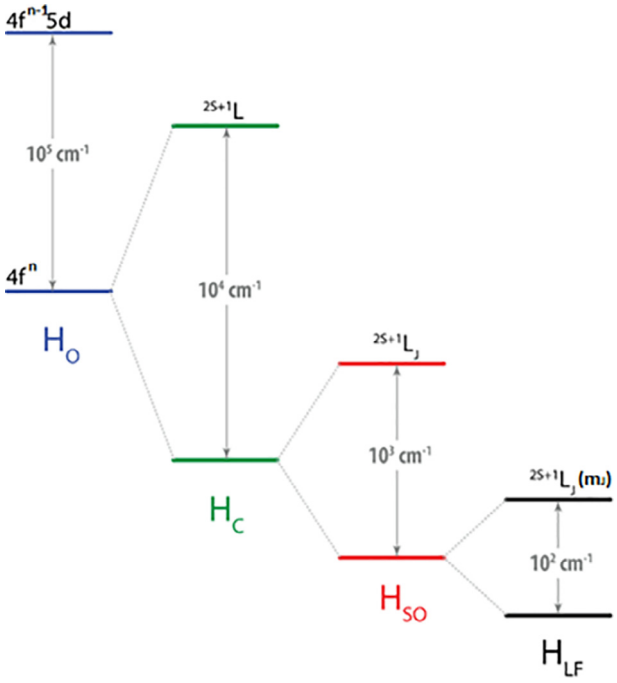

Fig. 1. Schematic representation and order of magnitude of the effects of the intra-atomic interactions acting on a $4f^n$ configuration. Adapted from Ref. [29].

2. Exploiting the optical and magnetic properties of the 4*f* ions

2.1. Luminescence in lanthanide complexes

The electronic configuration of Ln^{3+} ions corresponds to [Xe] $4f^n$, *n* varying from 1 (Ce^{3+}) to 14 (Lu^{3+}). The 4*f* electrons are inner-core electrons and the 4*f* orbitals are shielded from the interaction with the surroundings (called *Crystal-Field* or *Ligand-Field* interaction) by the filled $5s^2$ and $5p^6$ orbitals [29,30]. Although weak ($\sim 10^2$ cm^{-1}) when compared to the order of magnitude of the effects of the interelectronic repulsion ($\sim 10^4$ cm^{-1}) and spin–orbit ($\sim 10^3$ cm^{-1}) intra-atomic interactions [29], ligand field interaction is essential to explain the Ln^{3+}-based materials fascinating optical properties in disparate areas, such as phosphors, sensors, solar energy conversion, local probes, security tags, bio-imaging, photodynamic and photothermal therapies, and protein target and tracking [31–36].

The energy levels of the 4*f* electrons can be determined with good accuracy from a sum of the free ion interaction with the ligand-field Hamiltonian (H_{LF}). The free ion part is composed by the central field Hamiltonian (H_0) with several other interactions, which are generally treated as perturbations. Among these interactions, the interelectronic Coulomb repulsion (represented by the Hamiltonian H_c) and the spin–orbit interaction (Hamiltonian H_{SO}) are the most relevant. The ligand field distorts the 4*f* shell and removes, to a certain degree depending on the local symmetry around the metal ion, the m_J degeneracy of the free ion 4*f* levels (the well-known *Stark effect*), where $m_J = -J, -J+1, \ldots, +J$, with *J* the total angular momentum satisfying the condition $|L - S| \leq J \leq L + S$, *L* being the total orbital angular momentum and *S* the spin momentum. A schematic representation of the intra-atomic and ligand-field interactions (including their typical order of magnitude) is presented in Fig. 1.

The characteristic absorption and emission spectra of Ln^{3+}-based complexes are formed by parity (and sometimes also spin) forbidden 4*f*–4*f* transitions, with typically molar absorption coefficients <10 M^{-1} cm^{-1} (absorption cross-sections < 10^{-20} cm^2)