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► **To cite this version:**

Kevin Bernot. Get under the Umbrella: A Comprehensive Gateway for Researchers on Lanthanide-Based Single-Molecule Magnets. European Journal of Inorganic Chemistry, 2023, 10.1002/ejic.202300336 . hal-04258245

**HAL Id: hal-04258245**

**<https://hal.science/hal-04258245v1>**

Submitted on 22 Nov 2023

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# Get under the Umbrella: A Comprehensive Gateway for Researchers on Lanthanide-Based Single-Molecule Magnets

Kevin Bernot<sup>\*,[a, b]</sup>

The number of scientific articles that need to be considered to cover a research topic is ever-increasing and quite difficult for a newcomer to assimilate. This is particularly true in dynamic discipline like Molecular Magnetism. In order to help young researchers in this field, this article proposes a “review of reviews” also known as an “umbrella review” on lanthanide-based single-molecule magnets (4f-SMM). As a preamble,

various bibliographic search techniques and AI-based tools for bibliographic search, indexing, and summarization are proposed and commented. Then, the main milestones in 4f-SMM are identified. In the core of the paper, books, book articles, and reviews dealing with 4f-SMM are contextualized and classified by subtopics. This article is therefore proposed as a gateway to the 4f-SMM field.

## 1. Introduction

Finding one’s way through the literature of a new research field can be difficult and confusing for a newcomer, especially if he/she does not have an historical outline of the main milestones in mind. Indeed, there is no ideal literature to take on a subject, and there are many sources whose interest and effectiveness in understanding the issues of a discipline are very subjective.

On one hand, it is easy to find historical books on the beginnings of a discipline. Being recognized pioneers, authors are easily identifiable. These books are known to all and are lying on a shelf in the lab, annotated by all successive PhDs. Of course, a copy is kept in the Head’s office, but those who dared to ask for it are few and are no longer there to talk about it. Legend says that they were allowed to use it to write their thesis, but many doubt this. However, most disciplines rely on a renowned and active author whose regularly re-edited book is enriched with the latest advances in the field.

On the other hand, when one seeks to cover the whole of a subject in a scientific field, review articles are among the most effective documents. Indeed, authors have done a considerable amount of work in identifying and organizing research articles, and they are therefore often exhaustive at the time of publication. Similarly, multi-authored books are collections of



Figure 1. The concept of an “umbrella review”.

very specific chapters, each written by specialists upon invitation by a recognized author acting as editor. In this sense, they are extremely useful for studying a very specific subject. Handbook’s series works similarly. However, both review articles and multi-authored books rarely allow a beginner in the discipline to have a clear and quick idea of the main issues because they are often too specific.

In this context, “tutorial articles” are excellent entry points for understanding a problem in a disciplinary field without being ashamed or afraid to go back to the mathematical, physical, or chemical basics that enable the concepts to be understood. Similarly, short “editorials” or “comment articles” in leading journals help to highlight the scientific advances made by the discipline and are written in such a way as to be accessible to most scientists. This is often the way that newcomers enter a discipline.

However, as the research field is growing, the considerable number of reviews and books that are almost overlapping can overwhelm the readers. The field of molecular magnetism and in particular Lanthanide-based Single-Molecular Magnets (Ln-SMM or 4f-SMM) is no exception. Indeed, in this perspective

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Part of the “Coordination Chemistry Division of the French Chemical Society Prize Winners” Special Collection.

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article, we propose an umbrella review (i.e. a “review of reviews”, Figure 1) about 4f-SMM to allow newcomers and students in the field to quickly find already organized and streamlined research articles.

## 2. Lost in a new research field ... how to collect information?

### 2.1. From hand-picking to social network

The way to collect relevant sources to become familiar with a new field of research is very personal. This can be done through the websites of your favorite journals (via RSS feed or not), and using referencing and alert systems linked to thematic keywords, authors' names, previously cited references, etc. If one is lucky, some renowned researchers in the field monitor and update the literature on their personal websites.<sup>[1]</sup>

However, all these methods of collecting key information about an unknown discipline seem increasingly obsolete. Thus, by habit or ease, the use of social networks is becoming very common. As more and more authors promote their own papers, following a pool of authors of a discipline via their social networks allows access to the latest publications, often even before their publication in journals and as soon as they are posted on platforms such as ChemRxiv<sup>[2]</sup> etc...

More importantly, social media platforms are now widely used to promote publications either by journal offices or by authors themselves. Indeed, most journals communicate on Twitter and some, such as Springer Nature, provide a day-by-day “social media plan” to the authors once their publication is accepted. Then, threads relative to a publication can be unrolled or saved for future reading using Notion<sup>[3]</sup> (@SaveTo-Notion) or Readwise<sup>[4]</sup> plug-ins as well as several markdown editors (Obsidian,<sup>[5]</sup>...). Additionally, as well illustrated very recently, the use of Twitter<sup>TM</sup><sup>[6]</sup> or Mastodon<sup>©</sup><sup>[7]</sup> bots is becoming more frequent and efficient. For example, F. X. Coudert recently reported his source code that he used to create, among other bots, the very popular Twitter bot “@MOF papers” that has



Kevin Bernot graduated in Inorganic Chemistry at the University Rennes 1 (France) in 2004. In 2007 he received his PhD in Inorganic Chemistry under the supervision of Prof. O. Guillou (INSA Rennes) and Prof. A. Caneschi (University of Florence). After a post-doc stay under the supervision of R. Sessoli he got an assistant professor position at INSA Rennes in 2008 and a full Professor position in 2021. He was awarded the “ADocMolMag prize”, best PhD thesis on Molecular Magnetism (2008); “Junior Award 2020 from the Coordination Chemistry Division” of the SCF; “Distinguished Junior Member” of the SCF; 2020–2024 and Junior membership of the Institut Universitaire de France (IUF) 2017–2022.

almost 12000 followers.<sup>[8]</sup> The bot indexes nearly 400 papers per month, which facilitates, or discourages, depending on the perspective, bibliometric work.

### 2.2. Bibliographic research with AI-based tools

Artificial Intelligence (AI) will obviously play an increasingly important role in the collection, re-use, and interpretation of relevant scientific references on a given subject. The progress and appropriation of this technology by the public are incredibly quick and it is difficult to make a relevant state-of-the-art until robust solutions are consolidated.

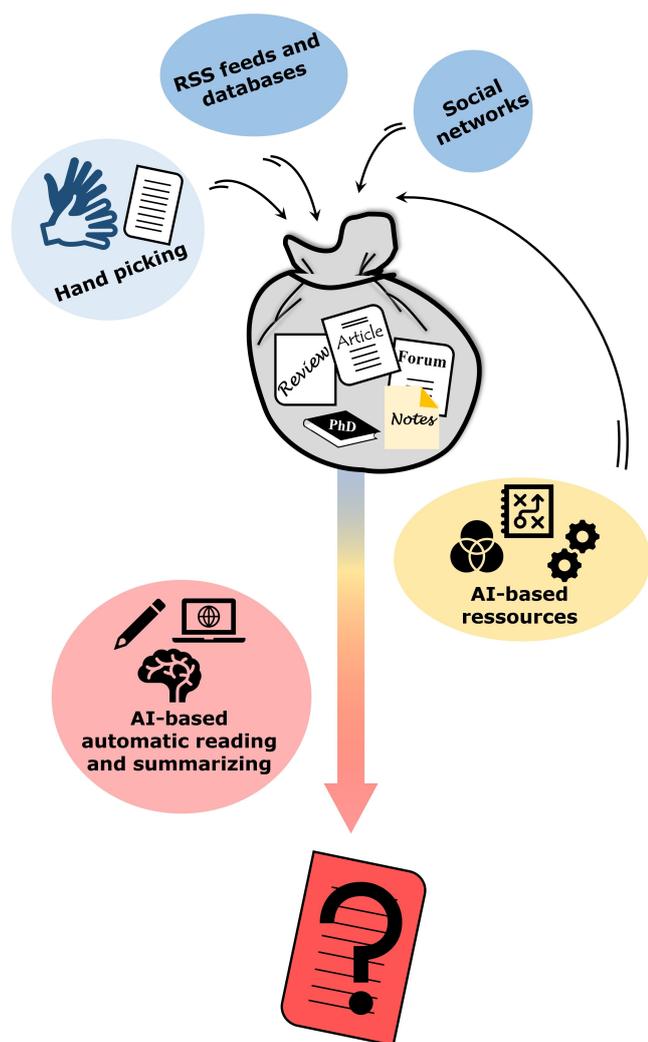
Some solutions are more or less AI-based and the capabilities of search engines are very different and evolve quickly. The most popular platforms are Web of Science,<sup>TM</sup><sup>[9]</sup> Scopus,<sup>©</sup><sup>[10]</sup> ResearchGate,<sup>[11]</sup> Google Scholar<sup>TM</sup>,<sup>[1]</sup>... A study in 2019<sup>[12]</sup> by M. Gusenbauer shows that Google Scholar<sup>TM</sup> was by far the most complete platform at that time, with up to 389 million scientific records archived.

Recently, there was tremendous hype concerning the public release of ChatGPT.<sup>[13]</sup> Although specialists were not surprised by its capabilities, the public had access to this tool and its use exploded. It is worth notice that, as far as bibliographic search is concerned, ChatGPT in its May 14<sup>th</sup> version can give very fancy results depending on the request made. In 2023,<sup>[14]</sup> T. Day tested ChatGPT 3.0 for bibliographic search in geography studies. Results show that the AI “invents” references from scratch, decorrelates authors from paper title, and mixes DOI. The same is found in the field of Molecular Magnetism or 4f-SMM. This is particularly misleading. However, ChatGPT developers highlight that restriction of the search and direct access to some databases (e.g. Google Scholar<sup>TM</sup>) can be performed on the 4.0 version via web browser extensions, but to date, it is somehow similar to browsing the database by hand. Similarly, Google-developed Bard AI<sup>[15]</sup> is expected to provide more accurate results but few is known to date.

There are a lot of recent developments in the field, each of them having a special focus (Figure 2), and many of them have a free option. Semantic Scholar<sup>[16]</sup> works as Google Scholar<sup>TM</sup> but suggests article connections and links with related topics. It can be advantageously completed by Connected Papers<sup>TM</sup>,<sup>[17]</sup> which is a visual tool highlighting connections between papers from the Semantic Scholar database.

Papers are arranged according to their similarity (not a citation tree), with node size as the number of citations and node color as the publishing year. Similar papers have strong connecting lines and clustered together. It identifies all the prior and derivative works, allowing for the export of full citations in a reference indexing software (Zotero, Endnote<sup>TM</sup>,...). Similar features are provided by Inciteful<sup>©</sup><sup>[18]</sup> and Litmaps<sup>©</sup>.<sup>[19]</sup>

Similarly, Research Rabbit<sup>[20]</sup> is a free AI-resource that can source relevant literature via keywords or better via a given article. It then proposes relevant articles by searching either PubMed<sup>©</sup><sup>[21]</sup> or Semantic Scholar<sup>[16]</sup> and allows the exploration of similar, earlier or later work. Tested on 4f-SMM, the results seem correct. One can also cite Elicit<sup>TM</sup>,<sup>[22]</sup> Consensus<sup>TM</sup>,<sup>[23]</sup> or



**Figure 2.** Main developments in scientific bibliographic search from most simple ones (blue) to most recent (red). AI-based resources are indicatives (see text).

Scite<sup>TM</sup>,<sup>[24]</sup> which can answer a given query exploring academic sources and underlining the given paragraph; results are more or less convincing, but one can note that Elicit<sup>TM</sup> seems very good at retrieving PhD dissertations

Then, the use of AI-based article readers is becoming more and more widespread with, for example, solution such as ChatPDF<sup>TM</sup>,<sup>[25]</sup> the best performing PDFgear<sup>TM</sup>,<sup>[26]</sup> or the more academic research-dedicated Scholarcy<sup>®</sup>.<sup>[27]</sup> In short, the AI performs an automatic reading of a given research article and process it to provide various outputs. For example, Scholarcy<sup>®</sup> can write a summary of adjustable length, extract and comment on references. PDFgear<sup>TM</sup> can even “chat” with the user as the AI builds an answer to a query based on the given scientific article. This obviously raises scientific and ethical questions about the robustness and reliability of these results. Tested on a few articles in the field of 4f-SMM, the results are either useful or senseless depending on the article considered.

Moreover, AI-powered “generative search engines” can generate responses to a query aggregating related citations. A recent study by Liu et al. performed in 2023<sup>[28]</sup> on four widely-used generative search engine (Bing Chat<sup>TM</sup>,<sup>[29]</sup> NeevaAI,<sup>[30]</sup> Perplexity.ai,<sup>[31]</sup> and YouChat<sup>®</sup><sup>[32]</sup>) is quite enlightening: “on average, a mere 51.5% of generated sentences are fully supported by citations and only 74.5% of citations support their associated sentence.” These are very low figures of merit and as things stand, these tools must be handled with care.

When it comes to writing a research article, some AI-dedicated tools have also been developed, such as Trinko<sup>©</sup>,<sup>[33]</sup> which is a grammar and writing corrector specially developed for academic writing. It also contains a plagiarism checker.

It is likely that very soon this article will be written using a combination of AI-based bibliographic search, automatic pdf reading and AI-based writing corrector. To date, the technical limitations mentioned above have not been overcome, but it is likely that they will be soon. In some fields of research, the number of articles published each year has become so large that it no longer seems understandable and usable by readers without the technical help of AI-based engines. This raises considerable scientific and ethical questions that currently seem to be relatively unaddressed by the scientific community. Given these concerns, and since the shoemaker’s son always goes barefoot, this article was written the old way.

### 2.3. Various types of reviews

As said above, reviews are the most convenient way to have a pertinent and rapid overview of a discipline. Librarians, consider different reviews types<sup>[34]</sup> that depends both on the scientific discipline and the paper organization.<sup>[35]</sup> They generally agree that they can be of three main types: *narrative*, *scoping* or *systematic reviews*. The *narrative review* ranges from a complete literature review (e.g. “Chem. Rev.” (ACS) or Coord. Chem. Rev. (Elsevier)) to “umbrella review” as this article, that is a review of reviews (Figure 1). The *scoping review* collects selected examples on a given and narrow topic (e.g. in “Chem. Sci.” (RSC) or Chem. Eur. J. (Wiley) for example). They can also be declined following one particular author production, such as in “Acc. Chem. Res.” (ACS). The *systematic review* is quite different as it is a re-performing or re-analysis of a reported experiment with a normative protocol, as done in pharmaceutical, medicine or photovoltaic material studies.

## 3. Selected Milestones of 4f-SMM Developments

In order to better understand the framework of 4f-SMM field, some milestones are proposed below. These can also be found using key books of the discipline, as documented in section 4.2. This allows us to step back and understand the chronological<sup>[36]</sup> and thematic developments in 4f-SMM. Each of the milestones reported hereafter has given rise, or was key, to a new sub-

theme in the field of *4f*-SMM from which “scoping reviews” are reported in section 4.3.3.

The seminal and pioneering work in the field of *4f*-SMM is without a doubt the report of N. Ishikawa et al. in 2003,<sup>[37]</sup> which demonstrated that monometallic complexes of *4f* ions, TbPc<sub>2</sub> (with Pc = phthalocyanine), can behave as SMM with unparalleled performance compared to *3d*-SMM even if no magnetic hysteresis was measured at that time. This molecular platform was successively modified in 2017 to yield the Tb(Pc)[(Pc(N-(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>)<sub>2</sub>)]<sub>8</sub> derivative with an energy barrier of U<sub>eff</sub> = 653 cm<sup>-1</sup> and a hysteresis temperature of T<sub>H</sub> = 30 K for high magnetic field sweep-rate.<sup>[38]</sup>

In 2005, Dy<sup>III</sup> ions were associated with radicals by R. Sessoli et al.<sup>[39]</sup> to form a *4f-2p*-Single Chain Magnet (SCM). This first ever *4f*-based SCM was investigated along the lanthanide series in 2006<sup>[40]</sup> highlighting the effect of single-ion anisotropy on the SCM performances. In these systems the shielding of the *4f* orbitals and their poor ability to give rise to magnetic interactions other than weak dipolar ones was compensated by the inclusion of radical spins on the bridging ligands. This will later inspire the rise of *4f*-radical SMMs. Additionally, angular resolved magnetometry on the monomeric building block of those chains in 2009,<sup>[41]</sup> was one of the first examples of theoretical and experimental investigation of single-ion anisotropy in the framework of *4f*-SMM.

As early as 2008,<sup>[42]</sup> W. Wernsdorfer et al. detailed how SMMs, particularly *4f*-SMM such as TbPc<sub>2</sub>, can be used for molecular spintronic-based devices. The same group showed in 2011<sup>[43]</sup> that graphene-based spintronic devices can be envisioned with *4f*-SMM.

In 2008,<sup>[44]</sup> E. Coronado et al. demonstrated that [ErW<sub>10</sub>O<sub>36</sub>]<sup>9-</sup> polyoxometalate is also an efficient platform to observe SMM behavior, implying also other ions than Tb<sup>III</sup> or Dy<sup>III</sup>. Even if the energy barrier was modest at that time (55 cm<sup>-1</sup>), a large amount of derivative was then reported by various groups (see below).

Also in 2008,<sup>[45]</sup> M. Murugesu et al. reported dinuclear SMM with energy barriers of 40 cm<sup>-1</sup> and 50 cm<sup>-1</sup>. Such dimeric molecules will be then widely investigated because they are the simplest molecules to investigate the nature and the influence of *4f-4f* magnetic interactions in SMM, in particular using magnetic dilution.<sup>[46]</sup>

Other polynuclear systems were also reported in 2008 and in particular triangular *4f*-SMM with spin chirality rationalized on powders (A. Soncini et al.)<sup>[47]</sup> and on single-crystals via angular-resolved magnetometry (R. Sessoli et al.)<sup>[48]</sup> simultaneously. It later gave rise to the field of single-molecule toroids.

In 2010,<sup>[49]</sup> S. Gao et al. reported an open hysteresis at very low temperature (0.5 K) on a diluted mononuclear Dy<sup>III</sup> β-diketonate with an energy barrier of 46 cm<sup>-1</sup>. This opens the way to an incredible number of reports on Dy-SMM that will submerge the literature since.

In 2011, J. R. Long et al. reported the spectacular *4f-4f* magnetic coupling observed on N<sub>2</sub><sup>3-</sup> radical-bridged dimers.<sup>[50]</sup> Molecular magnetic hysteresis at very high temperatures (T<sub>100 s</sub> = 14 K on the Tb<sup>III</sup> derivative) was a long-standing record. This triggered the rebirth of radical-based *4f*-SMM thematics.

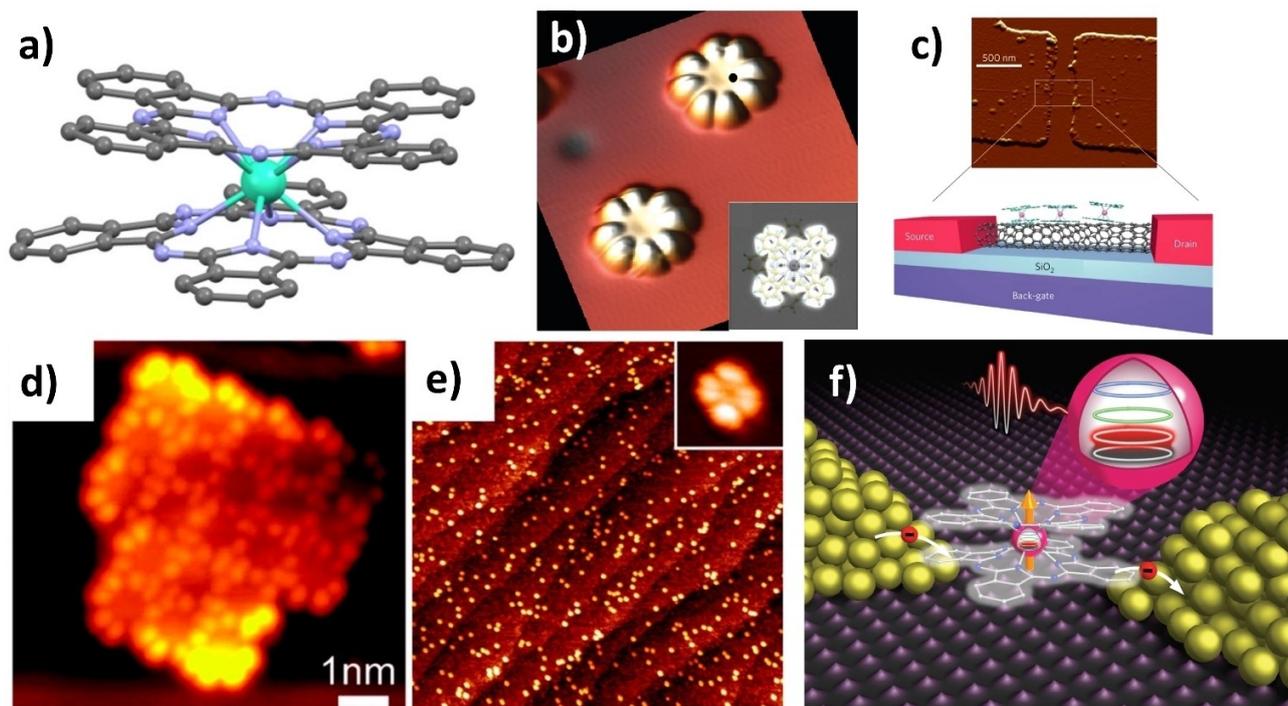
Successive derivatives depict giant coercivity in 2017<sup>[51]</sup> (H<sub>c</sub> = 7.9 T at 10 K) with U<sub>eff</sub> values as high as 564 cm<sup>-1</sup> and T<sub>100 s</sub> up to 20 K.

The TbPc<sub>2</sub> molecules soon came to be the focus of a scientist attention.<sup>[52]</sup> After the first report of the successful and stable deposition of TbPc<sub>2</sub> on Cu (111) in 2008<sup>[52a]</sup> by K. Kern et al., experiments on TbPc<sub>2</sub> grafted on metallic and magnetic surfaces flourished (Figure 3). In 2011,<sup>[53]</sup> M. Yamashita et al. reported that an electric current can manipulate a TbPc<sub>2</sub> grafted on Au(111). The same year P. Gambardella et al.<sup>[54]</sup> coupled the same molecule with ferromagnetic Ni substrate opening the way to SMM-based spin valves as the molecule could be magnetized parallel or antiparallel to the substrate. 2011, also started the tremendous breakthroughs in the applicative use of *4f*-SMM with the saga of devices made of TbPc<sub>2</sub> mainly driven by W. Wernsdorfer and M. Ruben et al. In 2011,<sup>[52b]</sup> a supramolecular spin valve made of TbPc<sub>2</sub> anchored on single-walled carbon nanotubes was reported. This was the first hybrid material made of SMM and here again opened a new era and new application perspective for SMM and anisotropic magnetic molecules in general. TbPc<sub>2</sub> was then an incredibly fruitful playground for this group with the demonstration in 2012,<sup>[55]</sup> but via a different device, that nuclear-spin of individual atoms can be read-out electronically because of the inherent electronic nature of the TbPc<sub>2</sub> SMM. It thus opens the field of molecule-based quantum logic and computing. Several key works followed such as the observation of spin-phonon coupling between TbPc<sub>2</sub> and a carbon nanotube in 2013,<sup>[56]</sup> the demonstration of coherent single nuclear spin manipulation using electric fields in 2014,<sup>[52c]</sup> radical-Tb magnetic interaction in a spin valve in 2015,<sup>[57]</sup> and the observation in 2016<sup>[58]</sup> of total suppression of the molecule's quantum tunnelling of magnetization by Einstein-de Haas experiment at the nanoscale.

In 2011,<sup>[59]</sup> the first organometallic SMM of formula Cp\*ErCOT was reported (Cp\* = pentamethylcyclopentadiene anion, COT = cyclooctatetraene dianion). High energy barriers of 136 cm<sup>-1</sup> and 224 cm<sup>-1</sup> and butterfly-shaped hysteresis up to 5 K were observed, illustrating the huge potential of these derivatives. It opened a new era as organometallic chemists will play an increasingly important role in *4f*-SMM. A Dy<sup>III</sup> derivative was then reported in 2011<sup>[60]</sup> by M. Murugesu et al. that was also well performing, and then further enhanced in 2013<sup>[61]</sup> to produce multidecker polynuclear *4f*-SMM. The best performing SMM of the series was reported in 2016<sup>[62]</sup> by S. Gao et al. with U<sub>eff</sub> = 300 cm<sup>-1</sup>.

In 2011,<sup>[63]</sup> the association of Dy<sup>III</sup> and diamagnetic Zn<sup>II</sup> ions provide a record of U<sub>eff</sub> = 234 cm<sup>-1</sup> that will be soon outperformed on a similar Dy–Zn SMM with U<sub>eff</sub> = 305 cm<sup>-1</sup> in 2013.<sup>[64]</sup>

In 2011, J. Alonso et al.<sup>[65]</sup> demonstrated that magnetocaloric effects (MCE) can be observed on finite Gd-based compounds such as a Gd<sup>III</sup> dimer. In the same year,<sup>[66]</sup> D. Collison et al. identified that for a given finite molecule, either SMM behavior (Dy, anisotropic) or MCE (Gd, isotropic) can be observed depending on the lanthanide ions used. Indeed, in 2012,<sup>[67]</sup> polyoxometalates declined under their Gd<sup>III</sup> version showed remarkable behavior as magnetic refrigerant materials since



**Figure 3.** The TbPC<sub>2</sub> molecule a) molecular structure of the TbPC<sub>2</sub> SMM b) Constant current topograph of two isolated TbPC<sub>2</sub> molecules supported on Cu(111) with surface simulated STM image in inset c) atomic force micrograph of a supramolecular spin valve with scheme of the anchored TbPC<sub>2</sub> molecules d) TbPC<sub>2</sub> deposited on Au (111) e) TbPC<sub>2</sub> deposited on Cu (100) and f) scheme of a nuclear spin qubit transistor based on a single TbPC<sub>2</sub> molecular magnet. Adapted with permission from Ref. [52a], copyright 2008 American Chemical Society; from Ref. [52b], copyright 2011 Springer Nature Limited; from Ref. [52c] copyright 2015 IOP; from Ref. [52d], copyright 2009 American Chemical Society; from Ref. [52e] copyright 2010 American Chemical Society; from Ref. [52f] copyright 2014 AAAS.

their good magnetic insulation enhances their performance under adiabatic demagnetization. In 2013,<sup>[68]</sup> M. Evangelisti et al., demonstrated that Gd-based molecules can still show robust MCE effect when deposited on surfaces, opening new perspectives in the field. Then, the field develop quickly with the observation of quantum signatures in direct MCE measurement in 2014<sup>[69]</sup> or the demonstration of Rotating Magnetocaloric Effect (RMCE) on dimeric Dy-SMM by M. Evangelisti et al. in 2016.<sup>[70]</sup>

In 2012<sup>[71]</sup> and 2013,<sup>[72]</sup> R. Sessoli et al. demonstrated how the luminescent properties of the lanthanides can be used as a fingerprint of the  $M_J$  energy splitting to be compared with ab-initio results and single-crystal magnetic measurements. This allowed magneto-luminescent correlations to be established in SMM that have since been widely used on bifunctional magnetic and luminescent SMM.

In 2013,<sup>[73]</sup> R. E. P. Winpenney et al. reported polynuclear Dy<sub>4</sub> and Dy<sub>5</sub>-SMM with record  $U_{\text{eff}} = 367$  and  $480 \text{ cm}^{-1}$  respectively and a very peculiar symmetry-related arrangement of their anisotropy axes.

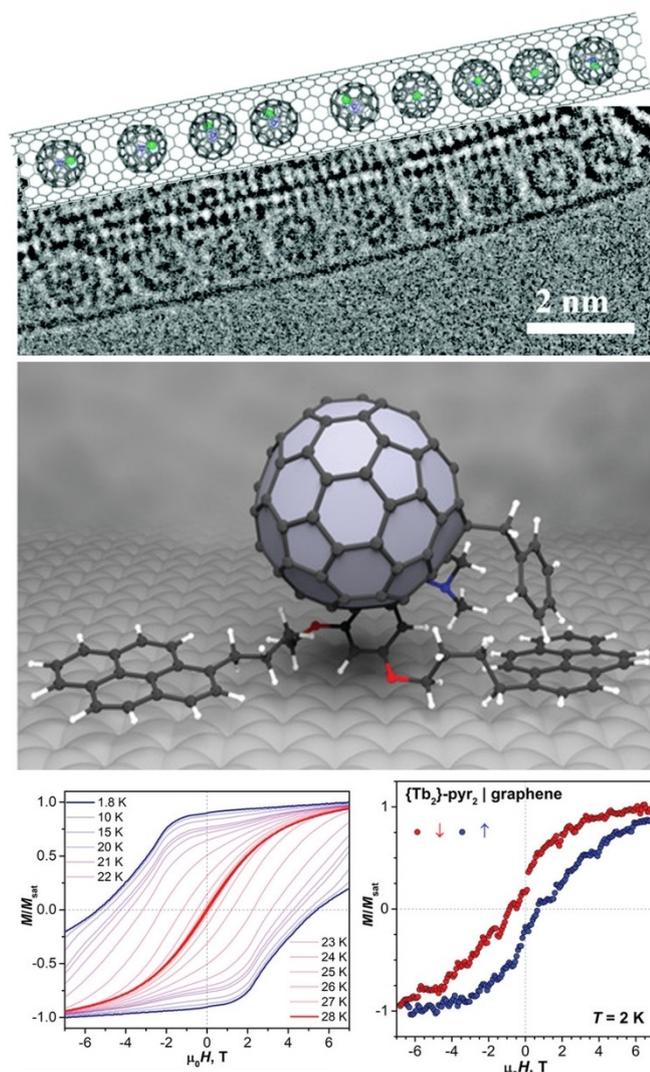
In 2014, the investigation on dinuclear  $4f$ -SMM has taken a big step forward when direct measurement of Dy–Dy has been reported, using among other techniques multi-frequency EPR as reported by R. E. P. Winpenney et al.<sup>[74]</sup> T. Mallah et al. complemented this report on another dimer in 2015.<sup>[75]</sup>

The influence of hyperfine coupling on SMM properties was experimentally demonstrated in 2015<sup>[76]</sup> by F. Pointillart et al. on

mononuclear Dy-SMM diluted in Y<sup>III</sup> isomorphous matrix. The hyperfine coupling was responsible for the hysteresis closing in zero-field, whereas the opening was observed on the nuclear spin-free isotopologue.

In 2016, several  $U_{\text{eff}}$  records for monometallic Dy-SMM were broken using ligands with very localized point charges with for example  $U_{\text{eff}} = 565 \text{ cm}^{-1}$  by S. T. Liddle et al.,<sup>[77]</sup>  $712 \text{ cm}^{-1}$  by M.-L. Tong et al.<sup>[78]</sup> and  $1261 \text{ cm}^{-1}$  by Y.-Z. Zheng et al.<sup>[79]</sup> and  $377 \text{ cm}^{-1}$  along with a record  $T_{\text{H}} = 20 \text{ K}$  by M.-L. Tong et al.<sup>[80]</sup> This approach ultimately leads to a Dy-SMM with quite high performance of  $U_{\text{eff}} = 1130 \text{ cm}^{-1}$  and hysteresis open at 22 K reported by Y.-Z. Zheng et al. in 2020.<sup>[81]</sup> Such geometry also afforded in 2017<sup>[82]</sup> a rare Ho<sup>III</sup>-SMM where isotopically pure Ho<sup>III</sup> allow to observe a hyperfine-interaction-driven suppression of quantum tunneling at zero magnetic field.

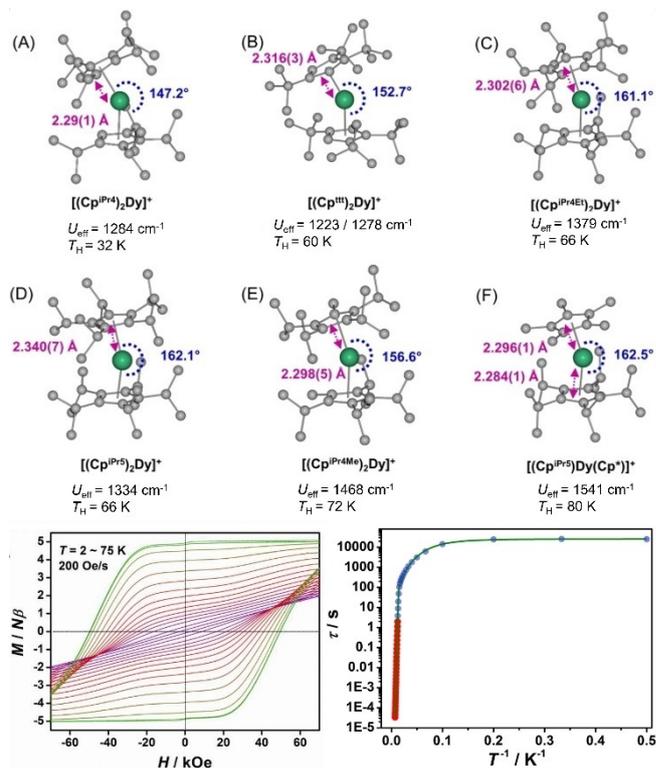
In 2017,<sup>[83]</sup> the encapsulation of  $4f$  ions into fullerenes by A. Popov et al. provided an intriguing and spectacular advance to the field especially when several anisotropic magnetic ions could be trapped and formed metal-metal bonds whose single-electron tailored the Dy<sup>III</sup> magnetic anisotropy. In line with what predicted by G. Rajaraman et al. in 2015,<sup>[84]</sup> a very large magnetic exchange interaction was observed between the two Dy<sup>III</sup> ions together with high energy barrier for spin reversal. This induced magnetic hysteresis up to  $T_{\text{H}} = 21 \text{ K}$  and  $T_{100 \text{ s}} = 18 \text{ K}$ . In 2019<sup>[85]</sup> even better properties were obtained on the Tb derivative with a coercivity of 8.2 T and a  $T_{100 \text{ s}} = 25.2 \text{ K}$  (Figure 4).



**Figure 4.** (Top) TEM image and structural model of the [DySc<sub>2</sub>N@C<sub>80</sub>] fullerene inserted in single-walled carbon nanotubes; (middle) representation of the standing-up configurations of a Tb<sub>2</sub>-fullerene anchored on graphene from molecular dynamics simulations and its magnetic hysteresis as bulk measured by squid magnetometry (bottom left) and monolayer, measured by XMCD at 2 K (bottom right). Adapted from [87] Copyright 2018 American Chemical Society and from [88] with permission from John Wiley and Sons, copyright 2021.

2017 was also the year of the climax of the organometallic revolution in SMM (Figure 5). Indeed, after the work of N. Ishikawa another breakthrough was the simultaneous report of molecular hysteresis at 60 K ( $U_{\text{eff}} = 1223 \text{ cm}^{-1}$ ,  $T_{100\text{s}} = 53 \text{ K}$ ) on dysprosocenium adducts in 2017<sup>[86]</sup> by R. Layfield et al. and N. Chilton et al. This last paper included a very detailed overview of the magnetic relaxation pathways operating in the molecule. Magnetically diluted samples were investigated suggesting that the origin of the hysteresis is linked with the localized metal-ligand vibrational modes.

*ab initio* calculations of spin dynamics further confirmed that magnetic relaxation at high temperature is due to local molecular vibrations. This finding thus identifies new fundamental constraints for chemists eager to design high-perform-



**Figure 5.** (Top) simplified representation of the crystal structures of various Dysprosocenium adducts (ref) with energy barriers ( $U_{\text{eff}}$ ) collected in zero field and highest temperature ( $T_{\text{H}}$ ) at which hysteresis was recorded with openings at  $H = 0 \text{ Oe}$  with sweep rates of (A, C–E)  $31 \text{ Oe s}^{-1}$ , (B)  $22 \text{ Oe s}^{-1}$ , and (F)  $25 \text{ Oe s}^{-1}$ ; (bottom left) magnetic hysteresis loops in the 2 to 75 K temperature range using a field sweep rate of  $200 \text{ Oe s}^{-1}$  and (bottom right) temperature dependence of the relaxation time for the best performing derivative (F). Reproduced from<sup>[92]</sup> with permission from Elsevier, copyright 2019, and from [90], with permission from AAAS, copyright 2018.

ance SMM. This ability to store magnetic information on a molecule at applicative temperature was largely commented<sup>[89]</sup> and has re-opened the perspective of molecular magnetic data storage.

Then, in 2018<sup>[90]</sup> a chemical variation of the previously reported compounds afforded molecular hysteresis at  $T_{\text{H}} = 80 \text{ K}$  and  $T_{100\text{s}} = 65 \text{ K}$  (with  $U_{\text{eff}} = 1541 \text{ cm}^{-1}$ ). This report is still the best performing SMM so far. The dysprosocenium-related library is still growing, and for example, a Tb derivative with  $U_{\text{eff}} = 1205 \text{ cm}^{-1}$  and  $T_{100\text{s}} = 52 \text{ K}$  was reported in 2019<sup>[91]</sup> by J. R. long et al.

Surface deposition of SMM and observation of its magnetic signature was first performed on 3d-SMM in 2009<sup>[93]</sup> and 2010<sup>[94]</sup> by R. Sessoli and D. Gatteschi et al., the iconic TbPc<sub>2</sub> 4f-SMM was adsorbed on a magnetic insulator (MgO/Ag(100)) in 2016.<sup>[95]</sup> Astonishing performances were observed with on-surface magnetic hysteresis visible up to 10 K because of the efficient protection from electron scattering and weak molecule-surface hybridization provided by MgO. Thus, the race to observe stable deposits of SMM with high operating temperatures has been accelerating ever since. Even if not molecules, magnetically anisotropic 4f atoms anchored on surfaces let envision significant development in the field. Hence, magnetic



Then, some key references should be identified, such as highly cited or very recent reviews in the field. At that point, one has to build citation trees starting from one of these key papers, considering the roots (articles cited by the paper) and the leaves (articles citing the paper). Obviously, old key papers will have few roots and many leaves, and vice versa for recent key papers. From about ten key papers, if they are well chosen, and the references are cross-referenced, one has a relatively exhaustive view of a research field (see keywords on Figure 7).

#### 4.2. Iconic books in the field of Molecular Magnetism

Most researchers in the field of Molecular Magnetism will recommend starting by reading first “Magnetochemistry” from R. J. Carlin (1986)<sup>[110]</sup> and then O. Kahn’s eponymous book (1993), recently republished by Dover<sup>[111]</sup> (Figure 8). It details all the experimental and theoretical fundamentals of what was at the time an emerging discipline. As exposed in the introduction of the updated edition, this book already exposed all the seeds of what will later be advanced spin-crossover systems, spin-spin interactions in 1, 2 or 3D topologies, molecules with giant spins, multifunctionality, nanosized magnetic materials, etc. As soon as 1996,<sup>[112]</sup> devices made of magnetic molecules were targeted as in the book “Molecular magnetism, from molecular architectures to the devices” edited by J. S. Miller et al.

It has been followed by the “Magnetism: Molecules to Materials”<sup>[113e]</sup> series in 2005 led by J. S. Miller and M. Drillon, that covers (as performed in a more condensed way in “Magnetic and molecular materials” by D. Gatteschi, 1991)<sup>[113b]</sup> the development of molecular magnetic materials from the experimental and theoretical point of view. This is similar to what was done in “Molecules into materials” by P. Day in 2007.<sup>[113c]</sup> Wider is “Electrons in Molecules; From Basic Principles to Molecular Electronics” from M. Verdaguer and J.-P. Launay (2013)<sup>[113d]</sup> present an interplay of all basic principles involving electrons from magnetism to molecular electronics.



Figure 8. Selection of books dealing with molecular magnetism.<sup>[110–113]</sup>

However, the first book specifically dedicated to single-molecule magnets is “Molecular nanomagnets” (D. Gatteschi, R. Sessoli, J.-P. Villain) published in 2006.<sup>[113f]</sup> This book is a bridge between the communities of physicists and chemists but also between early concepts from Olivier Kahn’s book and the anisotropic and isolated magnetic molecules investigated nowadays. Indeed, the co-existence of classical and quantum properties at the nanomagnet scale is particularly analyzed. Then, C. Benelli and D. Gatteschi published “Introduction to Molecular Magnetism” in 2015,<sup>[114]</sup> which provides an updated overview of the discipline, keeping a strong background in physics but also adapted to a readership involved in the chemistry of the systems.

Consecutively, several collective books have been issued, such as “Molecular Magnets, physics and applications” edited by J. Bartolomé, F. Luis and J. F. Fernandez (2014),<sup>[113h]</sup> “Molecular nanomagnets and related phenomena” edited by S. Gao (2015),<sup>[113j]</sup> “Molecular Magnetic Materials: Concepts and Applications” edited by B. Sieklucka and D. Pinkowicz (2016)<sup>[113j]</sup> and “Single-Molecule Magnets, Molecular Architectures and Building Blocks for Spintronics” (2019)<sup>[115]</sup> edited by M. Hołynska, which can be considered as updates of these genuine books. They can be complemented by the clear and concise book chapter by R. Clérac and R. E. P. Winpenny (2016),<sup>[116]</sup> book chapters by D. P. Mills et al.,<sup>[117]</sup> C. J. Millios<sup>[118]</sup> or Y.-Z. Zheng et al.<sup>[119]</sup> and by recent general reviews such as those of M. Yamashita et al.,<sup>[120]</sup> E. Colacio et al.,<sup>[121]</sup> J. M. Zadrozny et al.<sup>[122]</sup> and A. Ehrmann et al.<sup>[123]</sup> in 2021.

#### 4.3. 4f-SMM bibliography

##### 4.3.1. Starting from chemistry: books on 4f coordination chemistry

For chemists, a good way to enter the field is to gain knowledge on the way the molecules can be synthesized (Figure 9). As most of SMMs are made via coordination chemistry approaches, one can recommend “Introduction to coordination chemistry” (2009)<sup>[124]</sup> of G. A. Lawrance, and the very complete book of J. Ribas “Coordination Chemistry” (2008)<sup>[125]</sup> that also bridges coordination chemistry and Molecular Magnetism. This evolution of coordination chemistry toward molecules designed for their magnetic properties is particularly well illustrated in the article, that could have been a book, retracing the contribution of M. Julve and coworkers to the field (2017).<sup>[126]</sup>

When focusing on lanthanide chemistry, the most iconic book is probably “Lanthanide and Actinide Chemistry” (revised 2006)<sup>[127a]</sup> from S. Cotton, and its heritage, the very complete collective book edited by S. T. Liddle, D. P. Mills and L. Natrajan “The lanthanides and actinides”(2022).<sup>[127b]</sup> As far as only rare-earth ions are concerned C. Huang edited “Rare Earth Coordination Chemistry” in 2010.<sup>[127c]</sup> The very condensed book chapter of J. M. Harrowfield et al. in 2012<sup>[129]</sup> could be a nice way to enter the field and a recent book chapter by R. Layfield in 2021.<sup>[130]</sup>



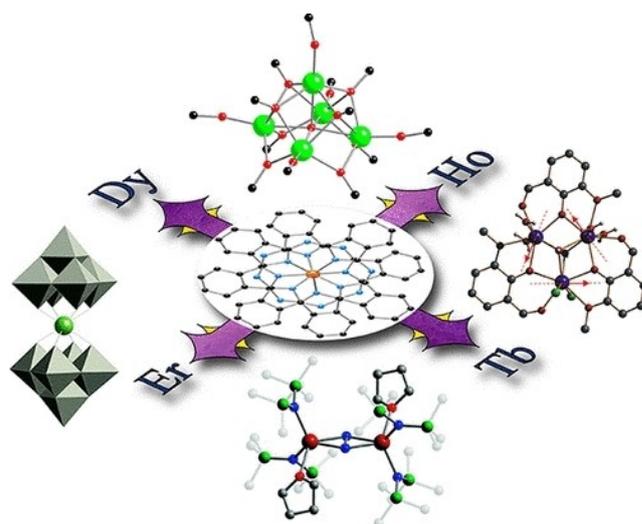
**Figure 9.** (Left) selection of books dealing with coordination chemistry,<sup>[124–125]</sup> (top right) lanthanide coordination chemistry<sup>[127]</sup> and (bottom right) lanthanide molecular magnetism.<sup>[113g,114,128]</sup>

#### 4.3.2. General, narrative books and reviews on 4f-SMM and their properties

Several books specifically dedicated to 4f-SMM have been published. The passage from 3d-based SMM to 4f-based SMM is largely illustrated in the above-mentioned key book of C. Benelli and D. Gatteschi “Introduction to Molecular Magnetism” in 2015.<sup>[113g]</sup> Indeed, the huge potential of lanthanides and their use in SMM, SCM, spintronics, magnetic resonance imaging and magnetocaloric effect is detailed. This book can be advantageously completed by the book of J. Tang and P. Zhang “Lanthanide Single Molecule Magnets” (2015)<sup>[128]</sup> and by the very complete collective book “Lanthanides and Actinides in Molecular Magnetism” in the same year<sup>[114]</sup> edited by R. Layfield and M. Murugesu.

Concerning reviews, in 2011,<sup>[131]</sup> the tutorial review by D. Gatteschi et al. celebrates the fruitful comeback on the lanthanides in Molecular Magnetism, while A. Dei, provided in 2008<sup>[132]</sup> philosophical perspective of the field. However, the first extensive review of 4f-SMM was made by R. E. P. Winpenny and coworkers in 2013<sup>[133]</sup> (Figure 10). It reports 160 molecules gathered by their nuclearity from monometallic (also called Single-Ion Magnets, SIM) to dodecametallic compounds.

This work is key as it rationally organized for the first time this exploding field of research. Its first pages are also particularly interesting as they recontextualize the evolution of SMMs from the iconic Mn<sub>12</sub> to 4f-SMM (updated by E. Colacio et al. in 2019<sup>[121]</sup>), while laying the foundations for future developments in the discipline. It clearly identifies two main challenges: the increasing of SMM working temperature and the need for SMM deposition and magnetic addressing on surfaces. Finally, it also states that the comparison of the SMM performance should be done cautiously and that “Gatteschi, Villain, and Sessoli have proposed  $T_B$  as being the temperature at which the time ( $\tau$ ) taken for the magnetization to relax is 100 s. It would be useful if this definition was universally adopted.” However, the future will tell us that in the race for numbers, this



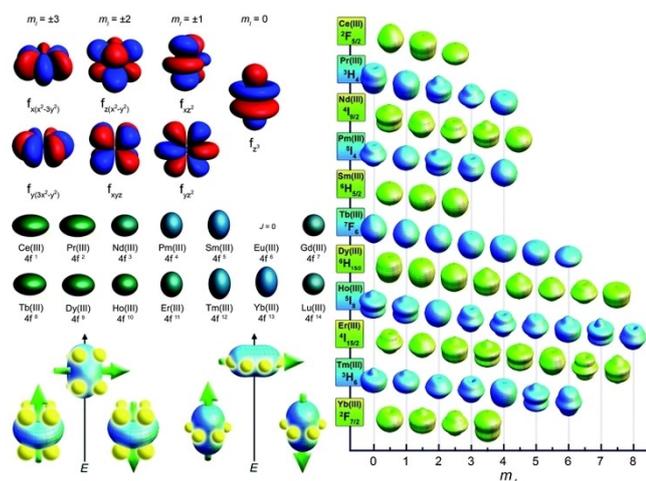
**Figure 10.** Representation of main categories of 4f-SMM as in 2013: the genuine TbPC<sub>2</sub>, Dy<sub>3</sub> triangle with spin chirality, Tb<sub>2</sub> dimer with bridging radical, 4f-polyoxometalates (4f-POM), Dy<sub>5</sub> and complexes of high nuclearity. Reproduced with permission from [133], copyright 2013 American Chemical Society.

definition will never be fully adopted. Only recently one can see papers clearly reporting  $T_{100s}$  and  $T_H$  (temperature at which an open hysteresis is observed, with the field sweep rate indicated). In 2013, the overwhelming majority of reports dealt with Dy-SMM while fewer examples concerned Tb<sup>III</sup> derivatives and very marginally Er<sup>III</sup> and Ho<sup>III</sup>. Later, 4f-SMM built on other Ln<sup>III</sup> ions (Ce<sup>III</sup>, Nd<sup>III</sup>, Tm<sup>III</sup>, Yb<sup>III</sup>) flourished and an update was proposed by F. Pointillart et al. in 2017<sup>[134]</sup> focused on these specific ions as well as heterometallic 4f–4fSMM.

Winpenny's review is based on other key papers such as the reviews of A. K. Powell and S. Sessoli in 2009<sup>[135]</sup> that explores either 4f–2p, 4f–3d and pure 4f systems, and the ones of S. Brooker et al. in 2009,<sup>[136]</sup> R. Sessoli et al. in 2012<sup>[137]</sup> and J. Tang et al. in 2011<sup>[138]</sup> that focused on the magnetic relaxation dynamics in Dy-SMM. Most important is the tutorial review of D. Gatteschi and co-workers in 2011<sup>[131]</sup> on “Lanthanides in molecular magnetism” that updates the one of 2002.<sup>[139]</sup> It recall that the first SIMs were observed in inorganic systems<sup>[140]</sup> and that the iconic TbPC<sub>2</sub> molecule reported by N. Ishikawa et al. in 2003, clearly opened new perspectives in the field.<sup>[37]</sup>

One can also cite two very popular 4f-SMM reviews: the first dealing with dinuclear SMMs by M. Murugesu et al. in 2013<sup>[142]</sup> and the second by J. D. Rinehart and J. R. Long in 2011<sup>[141]</sup> that reintroduced to the community the basic concepts of lanthanide spectroscopic properties and lanthanide magnetic relaxation<sup>[143]</sup> in a didactic way (Figure 11). This review is key in the discipline thanks to the huge didactic effort made by the authors that (re)popularized the oblate/prolate terminology, which will be later widely used. The observation of the asphericity of 4f electron density and its implication in 4f-SMM has been reported by J. Overgaard et al. in 2020<sup>[144]</sup>

In 2014,<sup>[145]</sup> S. Brooker et al., reviewed monometallic 4f and 3d-, 5d–4f SMM and in 2015,<sup>[146]</sup> S. Gao et al. the advances in 4f single-ion magnets (SIM). In 2018,<sup>[147]</sup> F. Tuna et al. proposed a



**Figure 11.** Some of the most popular figures dealing with 4f-SMM with (top left) representations of the 4f orbitals, (middle left) quadrupole approximations of the 4f-shell electron distribution for the tripositive lanthanides, (bottom left) depictions of low- and high-energy configurations of the f-orbital electron density with respect to the crystal field environment for a 4f ion of oblate (left) and prolate (right) electron density; (right) approximations of the angular dependence of the total 4f charge density for  $m_j$  states composing the lowest spin-orbit coupled ( $J$ ) state for each lanthanide. Reproduced from<sup>[141]</sup> with permission from the Royal Society of Chemistry, copyright 2011.

review gathering SIM, SMM and SCM based on 4f ions. More recently in 2020,<sup>[148]</sup> X.-Y. Wang et al. proposed a timeline of the last 40-year developments in the field, including advances in 4f-SMM. J. Tang et al., propose a similar but condensed review in 2022.<sup>[36]</sup> R. E. P. Winpenny et al. reviewed the field in 2021<sup>[119]</sup> focusing on monometallic Dy-SMM, toroics, and radical-bridged 4f-SMM. The last developments on 4f-SMM have been reviewed in 2023<sup>[149]</sup> by X. Zhang et al.

### 4.3.3. Specific, scoping reviews of 4f-SMM

#### 4.3.3.1. Characterization of SMM

Characterization of 4f-SMMs was firstly made using standard magnetic characterization techniques common to every magnetic material. Accordingly in 2016,<sup>[150]</sup> S. Tumanski wrote a very complete book about magnetic measurements which can be completed by a book chapter by J. M. Rawson et al. (2017)<sup>[151]</sup> and the comprehensive collective book edited by B. Dodrill et al. in 2021.<sup>[152]</sup> Parts dedicated to molecular materials can be considered as updates from C. J. O'Connor book chapter about measurements in magnetochemistry in 1982;<sup>[153]</sup> techniques evolved but main concepts remain unchanged. These references are not specific to SMM but will allow the reader to understand the main measurement principles and avoid common pitfalls such as the units used in molecule magnetism, etc....

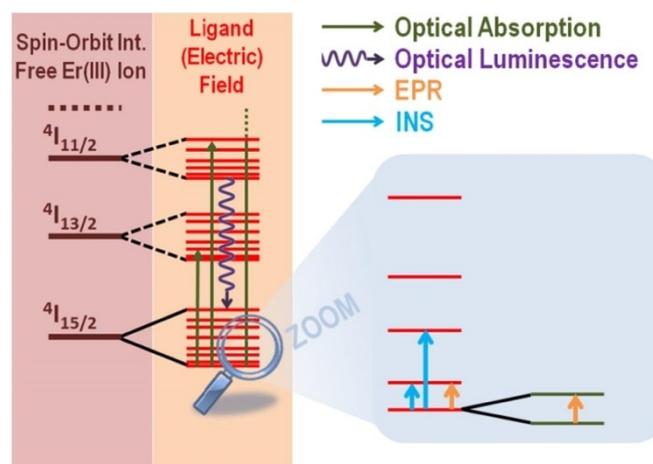
As far as magnetic characterization of 4f-SMM is concerned specific techniques emerged and one may focus on the very complete book chapter written in 2015,<sup>[154]</sup> by R. Clérac et al.

This work extensively reviews the characterization of the SMM behavior itself (static and dynamic magnetic susceptibility, NMR, muons spin rotation ( $\mu$ -SR)) but also of the magnetic anisotropy (single-crystal magnetic measurements), splitting of the ground multiplet (EPR, luminescence, inelastic neutron scattering (INS)) and exchange coupling (X-Ray Magnetic Circular Dichroism (XMCD)). It is definitely an excellent overview of what can be done in the discipline. In some sense it can be considered as an update of the book chapter by E. McInnes in 2006<sup>[155]</sup> that was mainly focused on 3d-SMM at that time.

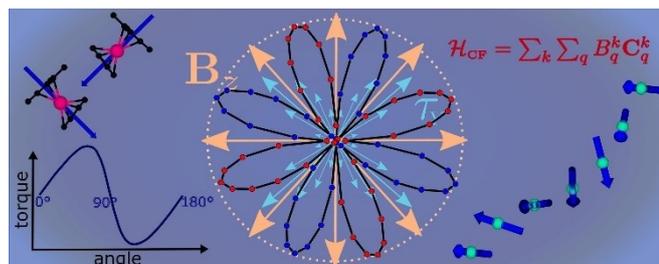
It can be completed by more specific reading. For example, early reports by D. Gatteschi et al. in 1996<sup>[156]</sup> on EPR and NMR techniques, or the special case of magnetic resonance studies of single-molecule magnets in polymer matrices was addressed by M. Dressel et al. in 2008.<sup>[157]</sup> NMR-MRI,  $\mu$ -SR and Mössbauer spectroscopies and their application to molecular magnets were reviewed by A. Lascialfari et al. in 2007.<sup>[158]</sup>

Similarly, S. Hill et al. reviewed the spectroscopic methods used to characterize molecular magnets in 2015,<sup>[159]</sup> focusing on EPR, INS,  $\mu$ -SR and magneto-optical techniques (Figure 12). An update on the special case of NMR for Single Ion Magnets (mainly 4f-SMM) was reported by C. Luchinat et al. in 2021.<sup>[160]</sup> Magneto-optic effects were reviewed for example by C. J. O'Connor, in 1996<sup>[161]</sup> and magnetochiral dichroism by C. Train et al. in 2020<sup>[162]</sup> (see also section 4.3.3.4).

Neutron-based characterization techniques are more and more used for SMM characterization. Their use on magnetic materials was reviewed, for example, in 1996 by J. Schweizer for standard neutron scattering<sup>[163]</sup> and by H. U. Güdel for inelastic neutron scattering.<sup>[164]</sup> In 2017,<sup>[165]</sup> M. Jimenez-Ruiz et al. detailed the main properties and capabilities of neutron scattering-based characterization techniques. This book chapter can be completed by an overview of the application of such techniques on the TbPc<sub>2</sub> molecule by O. Waldmann et al.<sup>[166]</sup> in 2016. The special case of Polarized Neutron Diffraction (PND) and its use to determine magnetic susceptibility tensors on 3d or 4f SMM has been illustrated by B. Gillon et al. in 2021.<sup>[167]</sup>



**Figure 12.** Energy level scheme of Er<sup>III</sup> ion with the energy levels involved in optical, neutron and magnetic resonance spectroscopic techniques. Reproduced with permission from [52c] copyright 2015 IOP.



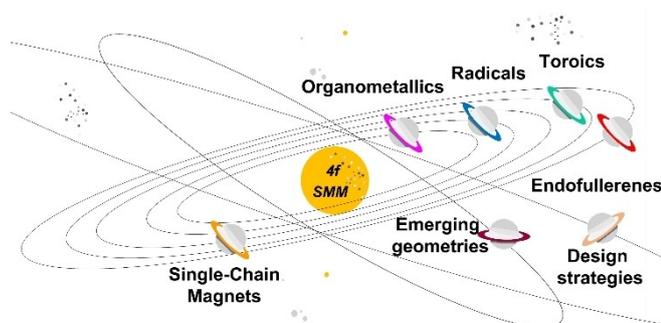
**Figure 13.** Cartoon illustrating the determination of magnetic anisotropy using single-crystal torque measurements. Reproduced from [171], copyright 2017 with permission from Elsevier.

Concerning EPR spectroscopy, which has been widely used on *3d*-SMM, one can consider the contribution of D. Gatteschi et al. in 1990.<sup>[168]</sup> High-Field EPR studies were specifically addressed in 2018<sup>[169]</sup> by J. Telsler et al. Single-crystal magnetic measurements for the determination of magnetic anisotropy, and in particular, torque magnetometry were reviewed by J. van Slageren in 2016<sup>[170]</sup> and M. Perfetti in 2017<sup>[171]</sup> (Figure 13). Low-frequency magnetic dynamic measurements were reviewed by S. J. Blundell et al. in 2018.<sup>[172]</sup>

Measurements of molecular magnets for molecular spintronics (either for devices based on surface deposition, or junctions) were reviewed by L. Bogani in 2015.<sup>[173]</sup> It can be completed by the comprehensive and clearly illustrated review of W. Wernsdorfer et al. on the measurement of molecular magnets for quantum technologies in 2021<sup>[174]</sup> (see also sections 4.3.3.3.7. and 4.3.3.3.8). Surface-dedicated measurement techniques are gathered in section 4.3.3.3.6.

#### 4.3.3.2. Categories of 4f-SMMs

This section gathers review on *4f*-SMM according to their chemical developments or categories (Figure 14).



**Figure 14.** Selected categories of *4f*-SMMs.

#### 4.3.3.2.1. Design strategies and approaches for high performance *4f*-SMM

The themed issue of *Chem. Soc. Rev.* edited by J. S. Miller and D. Gatteschi in 2011<sup>[175]</sup> gather a very large number of contribution of scientists active in the field (see also below). More recently, the specific control of *4f* anisotropy using coordination or organometallic chemistry has been reviewed in detail by many authors. Indeed, many reviews (with more or less overlap) propose “approaches” and “strategies” for the control of magnetic anisotropy and highlight its utmost importance to reach high-performance SMMs.

Dinuclear molecules are the most suited platforms to rationalize the SMM behavior of *4f*-SMM. They have been reviewed in 2013,<sup>[142]</sup> by M. Murugesu et al.. A large amount of dinuclear molecules is considered and the quality of different topological organization and lanthanide bridges (oxygen-, nitrogen-, sulfur-, chloride-, arene- and radical bridges) is discussed to draw perspectives toward high performance SMMs.

In 2014,<sup>[176]</sup> R. Clérac et al. reviewed recent results on *3d*, *4f*, *5d*-SMM focusing on the importance of the topological control of the metal ion building blocks to provide high-nuclearity molecules with controlled and enhanced magnetic properties. It was updated in 2018<sup>[177]</sup> in a book chapter by G. E. Kostakis. It is interesting to note that, in 2015,<sup>[178]</sup> J. Tang et al. illustrated the opposite strategy focusing on *4f*-SMM mainly obtained via serendipity approaches.

As the field was growing, some tutorial articles merged the principal key developments and tendencies, such as the work of S. T. Liddle and J. van Slageren in 2015<sup>[179]</sup> which focused on magnetic relaxation pathways, spectroscopic investigations of SMMs and polynuclear systems. Even if not a review strictly speaking, N. Chilton proposed in 2015<sup>[180]</sup> some design criteria for high-temperature Dy-SMMs. The potential of two-coordinated Dy<sup>III</sup> molecules and their sensitivity to axial ligation by solvent is demonstrated. Similarly, G. Rajamaram et al. reported in 2023<sup>[181]</sup> strategies to quench quantum tunneling of the magnetization in *4f*-SMM, which is the main limiting factor of SMM performances. Local symmetry, super-exchange, direct-exchange, metal-metal bond, toroidal states, and external stimuli are reviewed. These articles can be advantageously completed by the perspective review of E. Coronado et al. previously published in 2017<sup>[182]</sup> focusing on spin states, vibrations and spin relaxation, which are key points in *4f*-SMM.

In 2016,<sup>[183]</sup> A. K. Powell et al. proposed an overview of recent results focusing on the potential of MOF to constrain SMM geometries and enhance their properties. The same year,<sup>[184]</sup> J. Jiang et al. proposed a complete review on the magnetism of *4f* sandwich multiple-decker structures in which the iconic TbPc<sub>2</sub> and related molecules are described.

In 2017,<sup>[185]</sup> F. Tuna et al., reviewed consideration on the design of *4f* and *5f* mononuclear SMM for quantum technologies.

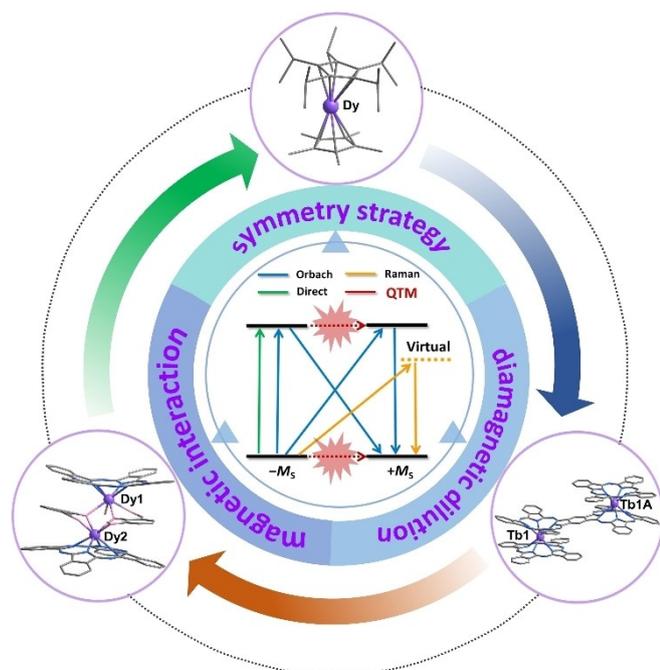
J. Tang et al. reviewed advances in the field of *4f*-SMM every two years, in 2013,<sup>[186]</sup> 2015,<sup>[187]</sup> 2017,<sup>[188]</sup> 2019,<sup>[189]</sup> and 2022.<sup>[190]</sup>

For this last opus, developments focusing on crystal-field, organometallic and radical coupling approaches are reviewed. The same authors focus on the effects of the geometry of the coordination environments on the magnetic behaviors for 4f-SMMs in a book chapter in 2018.<sup>[191]</sup>

In 2018, M. L. Tong et al. proposed two reviews dealing with 4f-SMM. The first,<sup>[193]</sup> survey the progresses in 3d, 4f and 5d-SMM from Single-Ion Magnet perspectives (mononuclear spin carriers). The second,<sup>[194]</sup> proposed strategies for 4f-SMM based on symmetry approaches. It should be noted that a large part of the review dealt with practical aspects of SMM measurement, data treatments and interpretations. The same year,<sup>[195]</sup> R. Murugavel et al. wrote a similar review, with a focus on  $D_{5h}$  symmetry and S. Gao et al.<sup>[196]</sup> on single-ion anisotropy in magnetic molecules.

Design strategies have also been suggested via “in silico” studies reviewing hypothetic molecule families and their potential as 4f-SMMs. M. Murie et al. in 2018<sup>[197]</sup> explored pentagonal bipyramidal Dy-SMM, A. Gaita-Arino et al. in 2019<sup>[198]</sup> targeted dysprosoceniums followed by N. Chilton et al. in 2021.<sup>[199]</sup> This was completed by G. Rajamaran et al. in 2021 that focused on Dy-corannulenes<sup>[200]</sup> and dilanthanofullerenes.<sup>[201]</sup> (See also section 4.3.3.3.9)

The influence of magnetic coupling on SMM performances has been reviewed by M. L. Tong et al. in 2022.<sup>[202]</sup> Authors detailed the influence of the various couplings as a function on their energy range. The special case of metal-metal bond is addressed and has also been extensively reviewed by J. Tang et al. in 2022.<sup>[203]</sup>



**Figure 15.** Design strategies proposed to suppress Quantum Tunneling of the Magnetization (QTM) in SMM. Reproduced from [192] with permission from John Wiley and Sons, copyright 2023.

In 2021,<sup>[204]</sup> F. Pointillart et al. reviewed the templating effect of heteroatoms on the structural and magnetic properties of 4f-POM.

In 2022,<sup>[205]</sup> N. Chilton reviewed the field of Molecular Magnetism and 4f-SMM for a broad audience updating somehow the paper of C. Goodwin in 2020<sup>[206]</sup> but with a special focus on their use as molecular qubits, their modeling and the importance of spin-phonon interaction.<sup>[205]</sup>

In 2023,<sup>[207]</sup> F. Pointillart et al. reviewed the studies on 4f-SMM isotopologues highlighting how design strategies built on the control of hyperfine and super-hyperfine interactions can enhance SMM properties.

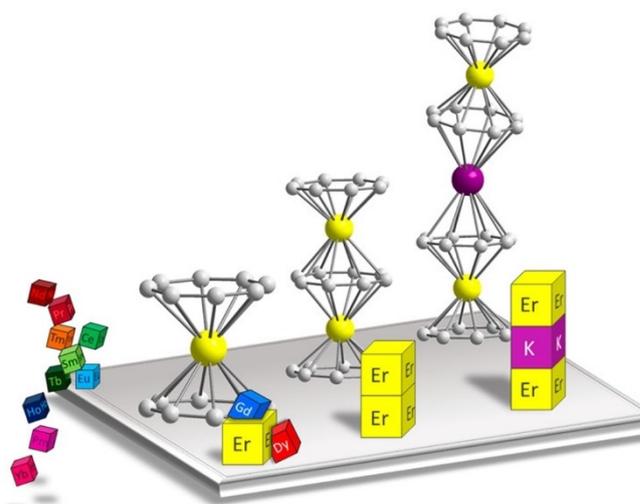
In 2023 also,<sup>[192]</sup> Y. F. Tang et al., provided the last update of 4f-SMM (almost 250 molecules) gathering them by nuclearity (mono- (86), bi-(102), tri- (14), tetra-(27), penta-(7) and hexanuclear (13)) (Figure 15). It is somewhat an update of the large book chapter of Y.-Z. Zheng et al. published in 2016.<sup>[208]</sup>

#### 4.3.3.2.2. Organometallic 4f-SMMs

A good way to grab the main ideas and issues in the field of organometallic lanthanides SMM is the short book chapter of S. T. Liddle published in 2012.<sup>[209]</sup> Then, R. Layfield reviewed the early works in the field in 2014.<sup>[210]</sup> M. Murugesu et al. reviewed their work on 4f-COT derivatives in 2016<sup>[211]</sup> (Figure 16), such as R. Layfield et al. in 2018<sup>[212]</sup> on cyclopentadienyl-based SMM that provides astonishing SMM properties. The same authors updated the review in a wider book chapter in 2019.<sup>[213]</sup>

The annual survey on lanthanide and actinide chemistry reviewed in each of its last editions (2015 to 2019) the yearly progress in the field of organometallic SMM.<sup>[214]</sup>

In 2019,<sup>[113k]</sup> V. Chandrasekhar and F. Pointillart published the collective book “Organometallic magnets” that hosts various



**Figure 16.** Cartoon highlighting the strategies to build SMM from organo-lanthanide building block. Reproduced with permission from [211]. Copyright 2016 American Chemical Society.

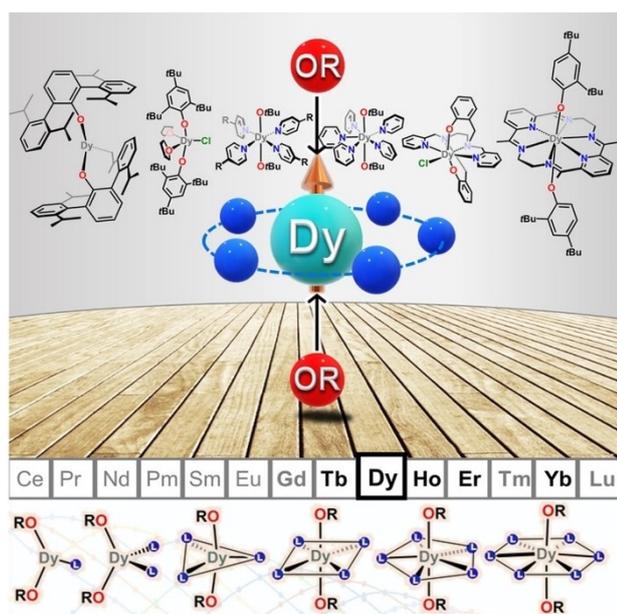
chapters on *4f*-SMM. Also in 2019,<sup>[215]</sup> R. Layfield *et al.*, reported a ligand-centered review where *4f*-SMM were categorized according to *p*-donor ligands. V. Chandrasekhar *et al.*, updated in 2022<sup>[216]</sup> the last finding in this field. It can be complemented by the recent review of R. Layfield *et al.* in 2022<sup>[217]</sup> covering the last decade of organometallic *4f*-SMMs. Last, in 2023<sup>[218]</sup> P. W. Roesky reviewed the properties and reactivity of divalent metallocenes for which little is known from the magnetic point of view.

#### 4.3.3.2.3. Emerging geometries and ligands in *4f*-SMMs

As the field developed, various strategies emerged for the control of magnetic anisotropy. V. Chandrasekar *et al.* reviewed in 2018<sup>[219]</sup> low-coordinate mononuclear complexes that became ever more prominent in the field, many of them being organometallic derivatives. The same authors reviewed the opposite strategies in 2021,<sup>[220]</sup> dealing with high-coordinated *4f*-SMM. In 2020,<sup>[221]</sup> the same leading author reviewed the emerging field of pentagonal bipyramidal *4f*-SMM. It has been updated in 2022,<sup>[222]</sup> by C. Duhayon *et al.* including also *3d*-SMM.

*4f*-SMM based on pyridine alcohol ligands was reviewed in 2016<sup>[223]</sup> by X.-Q. Zhao *et al.* In 2021,<sup>[224]</sup> R. E. P. Winpenny *et al.* focused their review on alkoxide and aryloxide-based SMM since considerable number of high performance SMM has been reported with these ligands (Figure 17). This review clearly illustrates the huge progress of the discipline since the previous one of the same leading author in 2013.<sup>[133]</sup>

Recently, a very complete review by Y. G. Gorbunova *et al.* was reported in 2022<sup>[225]</sup> about rare-earth based tetrapyrrolic sandwiches, including so, all the recent progress on phtalocya-



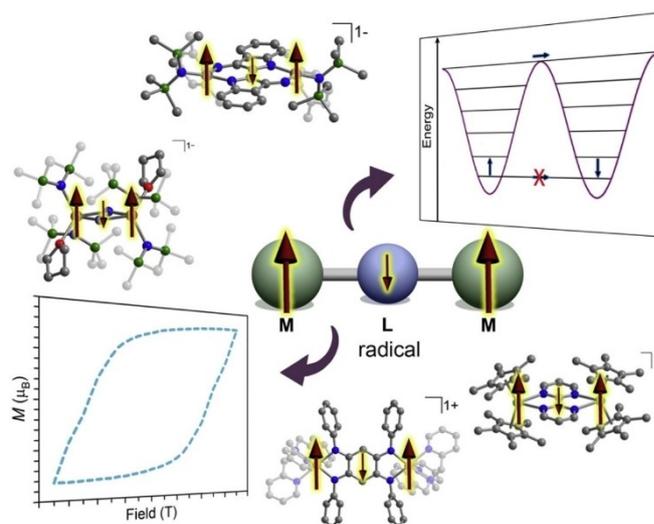
**Figure 17.** Cartoon representing, alkoxide and aryloxide SMMs and the relative geometries. Reproduced from [224] with permission from John Wiley and Sons, copyright 2021.

nine-based *4f*-SMM either at the molecular, material, or device level. This is somewhat an update of the book chapter by M. Ruben *et al.* in 2015.<sup>[226]</sup>

#### 4.3.3.2.4. Radical-based *4f*-SMMs

The review of Harris *et al.*, on radical-based SMM (2015)<sup>[227]</sup> (Figure 18) is in some ways the counterpart of Winpenny's one on *4f*-SMM<sup>[133]</sup> as it exhaustively identifies the radical-SMMs and sets the basis for future challenges for these class of molecules. It is partly based on the seminal review of C. Benelli and D. Gatteschi (2002).<sup>[139]</sup> A large part of this work is dedicated to *4f*-*2p*-SMM and 36 mono or dinuclear examples are reported. Authors reported that such molecules are particularly appealing because the *4f*-radical coupling can shut down fast quantum relaxation pathways and provide enhanced SMM behavior. An update reporting either radical-based *4f*-SMM and *4f*-SCM was published by M. Yamashita *et al.* in 2018.<sup>[228]</sup> The same was done by C. Papatrifiantylopoulou, *et al.* in a book chapter in 2018 too.<sup>[229]</sup> The most recent update was made in 2023<sup>[230]</sup> by M. L. Tong *et al.*

Some more focused reviews on specific radicals have been published, such as the one of P. Rey *et al.* on nitroxide and nitronyl-nitroxide radicals<sup>[231]</sup> (updated by the same leading author in 2005,<sup>[232]</sup> then L. Bogani in 2011<sup>[233]</sup> and D. Luneau in 2020<sup>[234]</sup>). K. E. Preuss reviewed metal-radical coordination complexes of thiazyl and selenazyl ligands in 2015<sup>[235]</sup> some of them being *4f*-*2p*-SMMs. C. Train *et al.*, reviewed nitroxide and verdazyl radicals coordinated with *4f* ions,<sup>[236]</sup> while M. Andruh *et al.* reviewed in 2021<sup>[237]</sup> molecules made of various radicals (nitronyl-nitroxides, imino-nitroxide, TEMPO, verdazyl and TSCQ<sup>-</sup>) but bearing at least two different metallic ions, often *4f* and *3d* ions.



**Figure 18.** Radical-based *4f*-SMMs. Reproduced from [227], copyright 2015 with permission from Elsevier.

#### 4.3.3.2.5. 4f-based Single-Chain Magnets (SCM).

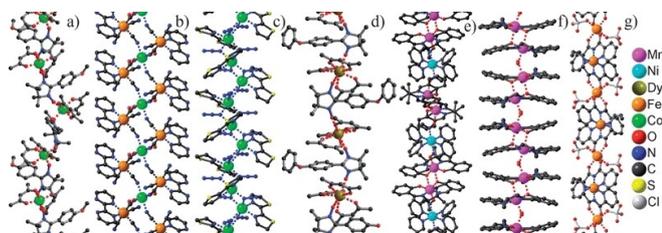
There are quite few examples of 4f-based SCMs, mainly because the required intrachain magnetic interaction is difficult to reach in purely 4f systems because of the strong shielding of 4f orbitals. Indeed, SCMs benefiting from the very large anisotropy of lanthanide ions are also made of bridging 3d ions or radical ligands. SCMs illustrate how the dimensionality of molecular edifices are key to understand their magnetic behavior as reviewed in 1996 by R. Sessoli et al.<sup>[238]</sup> or J. S. Miller et al.<sup>[239]</sup>

A. Vindigni et al. reviewed the theoretical aspects of SCM in 2003<sup>[240]</sup> (further updated by the same authors in 2014<sup>[241]</sup>). Then, R. Clérac et al. reported in 2006<sup>[242]</sup> what can be considered as the first extensive review of SCM. It covers both the theoretical (thermodynamic description, magnetization dynamics, finite-size effects...) and the experimental aspects of SCM (including 4f-based) reviewing the existing compounds at that time. This was somewhat updated by the same leading authors in 2009,<sup>[243]</sup> 2015<sup>[244]</sup> and 2017.<sup>[245]</sup>

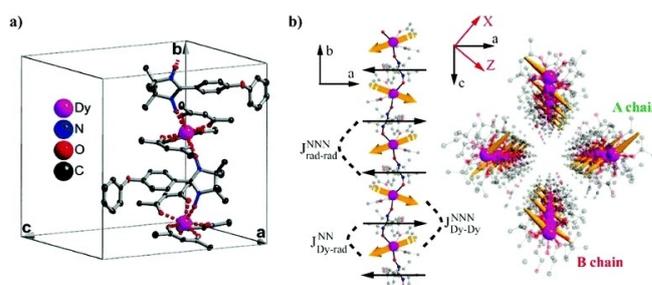
In 2008,<sup>[246]</sup> D. Gatteschi et al. reviewed the emerging field of SCM, gathering advances in the synthesis, characterization, and theoretical understanding of these materials, and highlighting differences and similarities with SMMs (Figure 19). It also proposes future directions in the field such as the organization of SCMs on substrates in order to use of SCMs as nanometric memory units. This was somewhat completed by J. A. Kitchen et al. in 2009.<sup>[136]</sup>

S. Gao et al., reviewed in 2010<sup>[247]</sup> the ferro, ferri and weak ferromagnetic strategies to build SCM, with 4f-radicals SCM that stands in this last category. In 2011,<sup>[248]</sup> J. Vittal et al. reviewed all one-dimensional coordination polymers, and thus recontextualized the research on SCM among other 1D molecular systems. M. Yamashita et al. further reviewed the fast-growing field of SCM in 2013<sup>[249]</sup> with some dedicated parts on single-crystal SCM measurements and multifunctional SCM (Figure 20).

In 2015,<sup>[250]</sup> R. Sessoli et al., reviewed how lanthanides can be used in extended molecular networks including 1D compounds. Special attention is given to the difference between 1D assemblies made of SMM-like relaxing 4f ions and true SCM behavior observable on 4f-3d or 4f-radical based chains. M. Yamashita et al., specifically addressed the concept of organic



**Figure 19.** Representation of SCM molecular structures with: a) Co<sup>II</sup>-radical b) low-spin Fe<sup>III</sup>Co<sup>II</sup> c) Co<sup>II</sup> d) Dy-radical e) Mn<sup>III</sup>-Ni<sup>II</sup> f) Mn<sup>III</sup> h) high-spin Fe<sup>II</sup>/low-spin Fe<sup>III</sup> SCM. Example d) was the first SCM made of 4f ions. Reproduced from<sup>[246]</sup> with permission from the Royal Society of Chemistry, copyright 2008.

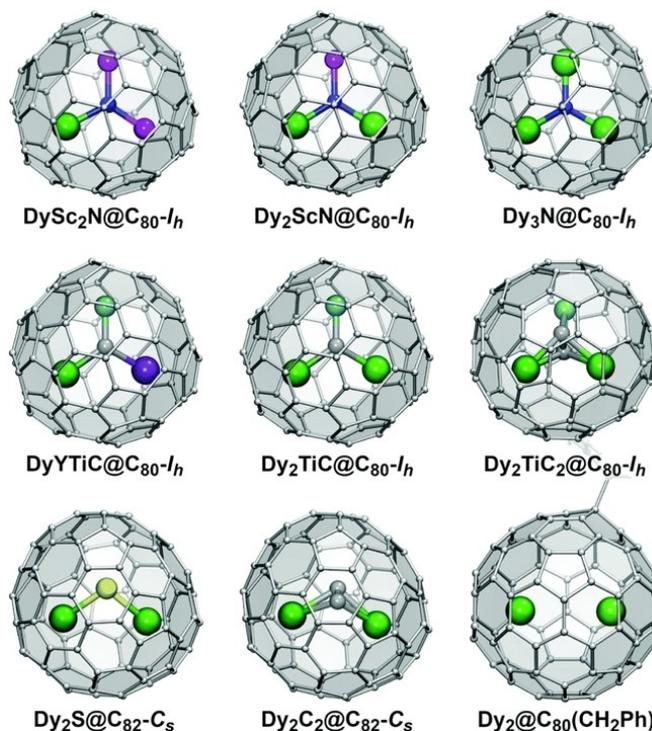


**Figure 20.** Crystal structure of a Dy-radical SCM with representation of the anisotropy axes as determined by single-crystal magnetic measurements. Reproduced from<sup>[249]</sup> with permission from the Royal Society of Chemistry, copyright 2013.

radical-based SMM and SCM in 2018,<sup>[228]</sup> most of 4f-based compounds involving nitronyle or nitronyl-nitroxide-based derivatives. This last specific case was reviewed also by P. Cheng et al. in 2019.<sup>[251]</sup>

#### 4.3.3.2.6. 4f-SMMs in endofullerenes

The main chemical properties of 4f-based endohedral fullerenes have been concisely reviewed by D. A. Atwood et al. in 2012.<sup>[252]</sup> In 2015,<sup>[253]</sup> J. Zhao et al. reviewed the magnetic properties of atomic clusters and endohedral fullerenes, with a part dedicated to 4f-based compounds.



**Figure 21.** Representation of selected Dy metallofullerenes showing single molecule magnetism. Dy is shown in green, Sc – magenta, Ti – cyan, Y – violet, N – blue, C – gray, and S – yellow. Reproduced from<sup>[254]</sup> with permission from the Royal Society of Chemistry, copyright 2019.

The most complete review has been published in 2019<sup>[254]</sup> by A. Popov et al. that reported most of the significant results in this field (Figure 21). The review focuses on Dy-derivatives only, and open perspectives in the organization of the metallofullerenes in 1, 2 or 3D arrays. The same authors completed this paper in the same year,<sup>[255]</sup> reviewing their work with  $4f$  ions in the framework of single-electron lanthanide-lanthanide bonds and the consecutive redox properties.

In 2020,<sup>[256]</sup> T. Akasaka et al. reviewed the chemical functionalization of endohedral metallofullerenes and in 2021<sup>[257]</sup> T. Wang et al., reviewed the most recent progress in the synthesis, electron spin characteristics and magnetic properties of metallofullerenes.

#### 4.3.3.2.7. 4f-SMMs and toroics

Single-molecule toroics were first reviewed in 2014<sup>[258]</sup> by L. Chiboraru et al. with mainly polynuclear Dy-based molecules. They are classified according to their net, mixed, or zero toroidal moment. J. Tang et al. reported more recent developments in 2019,<sup>[259]</sup> including heterometallic  $3d-4f$  metallocycles and Dy-cubane-like molecules. G. Rajamaran et al., reviewed in 2021,<sup>[260]</sup> single-molecule toroics based on triangular  $Dy_3$  motifs.

In 2022, J. Schnack et al., proposed a critical review of toroidal magnetic molecules underlining that, toroidal moments might be considered only if anisotropic exchange is observed. Accordingly, reasonable single-ion anisotropy and anisotropic exchange should coexist in a significant range of temperatures to be exploitable in quantum devices. This was complemented by numerical simulations by the same leading author in 2023.<sup>[261]</sup>

In 2023,<sup>[262]</sup> a collective book edited by K. S. Murray presented the last developments in the field molecular toroics from the experimental and theoretical point of view.

#### 4.3.3.3. Properties and field of applications of 4f-SMM

This section gathers reviews on  $4f$ -SMM according to their main properties (Figure 22).

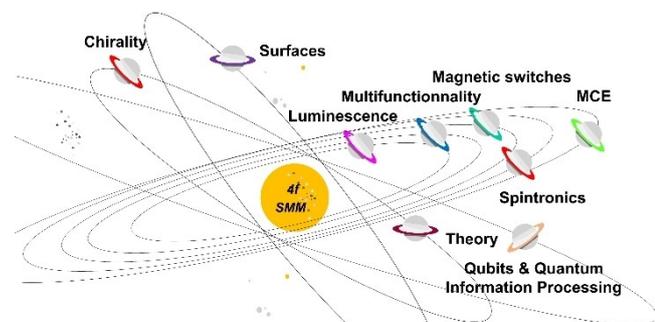


Figure 22. Selected properties of  $4f$  SMMs.

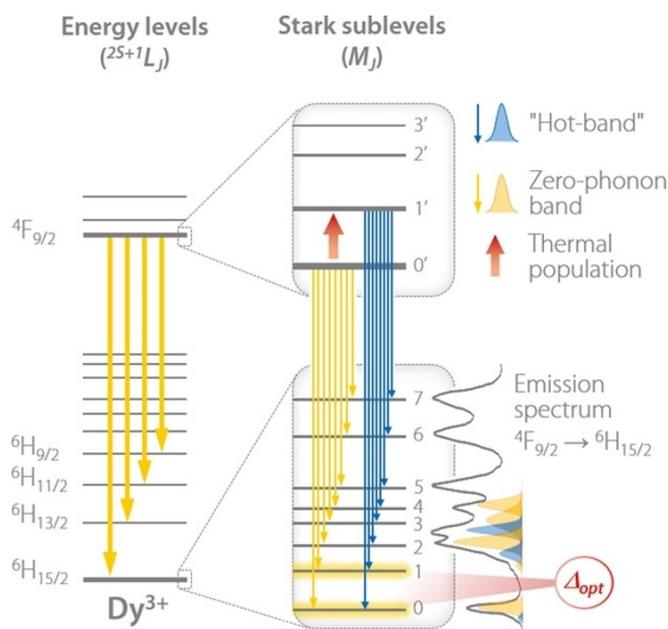


Figure 23. Representation of magneto-luminescent correlations on a Dy-SMM. Reproduced from<sup>[267]</sup> with permission from John Wiley and Sons, copyright 2021.

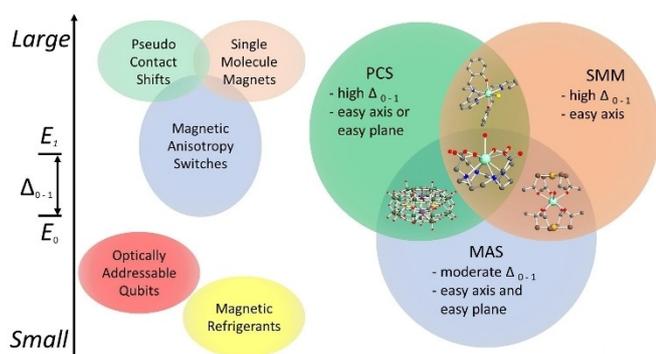
#### 4.3.3.3.1. Luminescent 4f-SMMs

Luminescent and SMM-like molecules have been extensively studied since the demonstration of magneto-optical correlations on such molecules in 2012.<sup>[71]</sup> This finding opened new ways to characterize SMMs and offered easy access to their fine energetic scheme. Indeed, because of the strong emitting power of lanthanide ions, most of the research teams in the field are equipped with fluorimeters and characterization of luminescence of  $4f$ -SMM quickly became routine. It can be noted that the use of optical absorption and luminescence spectra of transition of  $3d$  and  $4f$  ions in the framework of Molecular Magnetism has been reviewed as early as 1996<sup>[263]</sup> by H. Weihe et al.

In 2017,<sup>[264]</sup> L. Ouahab et al. gathered luminescent molecular magnets in a book chapter. Then, results on the thematic have been reviewed almost contemporaneously in 2018 by J. R. Long et al.<sup>[265]</sup> and 2019 by M. L. Tong et al.<sup>[266]</sup> An update was proposed in 2021<sup>[267]</sup> by M. Murugesu et al. with among other a part dealing with luminescent thermometry (Figure 23). The same leading author proposed in 2023,<sup>[268]</sup> a review focused on high nuclearity  $4f$  molecules as tunable luminescent materials for anti-counterfeiting, luminescent thermometry, and molecular upconversion.

#### 4.3.3.3.2. Multifunctional 4f-SMMs

Multifunctionality in Molecular Magnetism was reviewed for example in 2015<sup>[269]</sup> by D. Pinkowicz et al. mainly focused on  $3d$  ions.



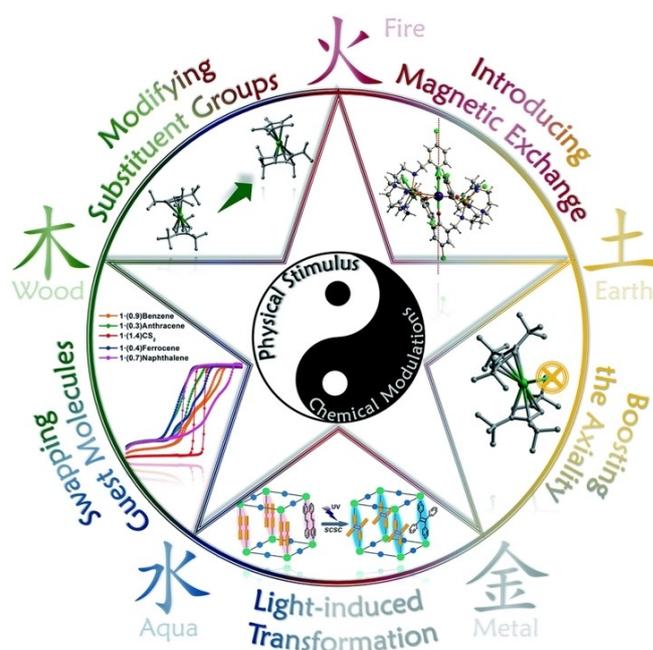
**Figure 24.** (Left) scheme of the classification of molecular magnetic materials based on the separation between their ground and first excited state ( $\Delta_{0-1}$ ); (right) pictographic representation of the compatibility between Magnetic Anisotropy Switches (MAS), Pseudo Contact Shift agent (PCS) and SMM properties. Molecular structure of examples in the intersections. PCS and SMM:  $[\text{Dy}(\text{bbppn})\text{Cl}]$ ,<sup>[275]</sup> PCS and MAS:  $[\text{ErW}_{30}]$ ,<sup>[276]</sup> MAS and SMM:  $[\text{Er}(\text{Pt}(\text{SAc})_2)_2]$ ,<sup>[277]</sup> PCS, MAS and SMM:  $\text{Dy}(\text{DOTA}) \cdot \text{H}_2\text{O}$ .<sup>[278]</sup> Adapted from [279] copyright 2023 with permission from Elsevier.

The interplay between redox, luminescent and magnetic properties of *4f*-SMM has been reviewed by L. Ouahab et al. in 2015<sup>[270]</sup> illustrating their own examples on *4f*-TTF-based SMMs. It was then more largely documented in 2019 in a review<sup>[271]</sup> and a book chapter<sup>[272]</sup> by the same authors on various TTF-lanthanide-based molecules. Also in 2019, the same group reviewed the electro-activity and magnetic switching in *4f*-SMM.<sup>[273]</sup> In 2020,<sup>[274]</sup> N. Chilton et al. reviewed their work on the influence of lanthanide crystal field on their magnetic properties either for SMM or NMR shift purposes.

Multifunctional *4f*-SMM were further reviewed in 2023<sup>[280]</sup> by S. Chorazy et al. focused on multi-functionality of luminescent *4f*-SMM; additionally, molecules with stimuli response, electrical functionalities (proton conductivity or ferroelectricity), and chirality-based optical properties (Circularly Polarized Luminescence (CPL) and magneto-chiral effect (MChD),...) are also reviewed. Similarly in 2023,<sup>[281]</sup> Sun et al., reviewed multifunctional *4f*-SMM with luminescence thermometry, photochromic and ferroelectric properties. Same year,<sup>[279]</sup> M. Perfetti et al. reviewed how the chemical tuning of the energy gap between the ground and first excited state and tailoring the magnetic anisotropy (mainly *4f*) allow the production of multifunctional magnetic materials with potential technological relevance (Figure 24).

#### 4.3.3.3.3. Magnetic switches in *4f*-SMMs

Once bi- or multifunctional molecules are known, the logical development is to combine their different properties and if possible, to correlate them. The remote control of SMM behavior via photoswitching of DTE ligand was documented by M. Yamashita et al. in 2014<sup>[282]</sup> including several *4f* molecules. In 2019,<sup>[273]</sup> the above-mentioned review of F. Pointillart et al., also focuses on magnetic switching of electroactive, redox-, solvato-, photo- or proton-switchable *4f*-SMM. It was somewhat updated



**Figure 25.** Representation of the various approaches to modulate bistable molecular magnetic materials. Reproduced from [284] with permission from the Royal Society of Chemistry, copyright 2020.

in 2020<sup>[283]</sup> by J. Tang et al. that illustrated how external stimuli can modulate the magnetic relaxation of *4f*-SMM, and the same year<sup>[284]</sup> by M. L. Tong et al. that gathered all the examples of physical stimuli and chemical modulations for bistable molecular magnetic materials with a large amount of stimuli-responsive *4f*-SMM (Figure 25).

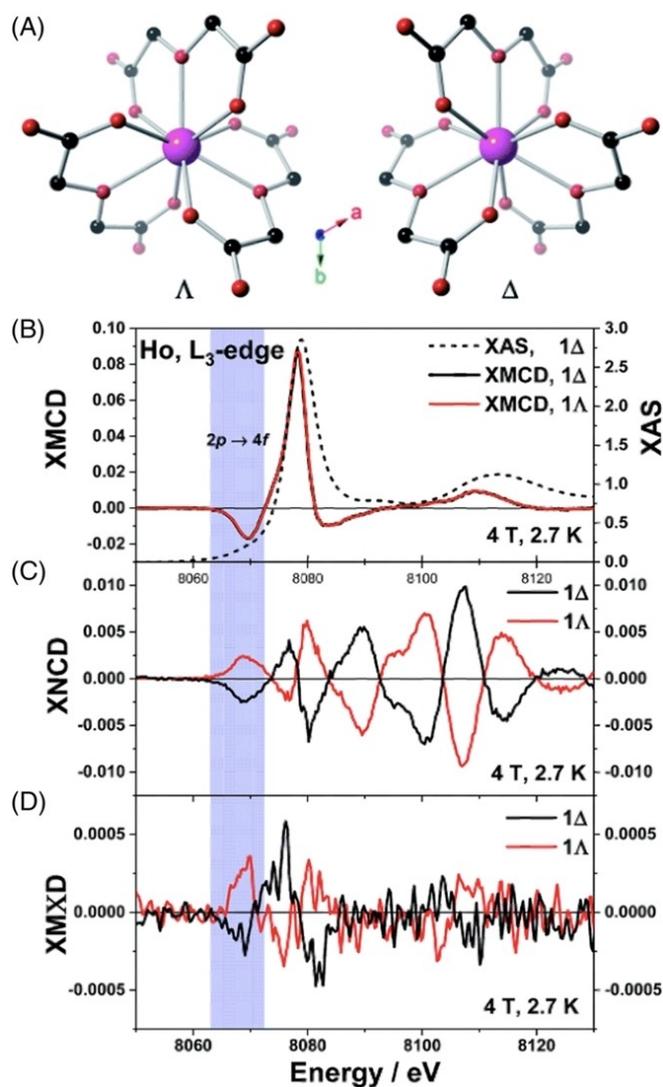
Similarly, C. Boskovic et al. reviewed in 2019<sup>[285]</sup> how ligand and lanthanoid-centered redox-activity in molecular systems can provide new intriguing and switchable magnetic behaviors and ultimately multiconfigurational electronic states and valence tautomerism. A particular focus is pointed toward ligands adapted to divalent and tetravalent lanthanide ions.

#### 4.3.3.3.4. Chirality and magneto-chiral effects in *4f*-SMMs

*4f*-chiral molecules have been reviewed in 2002<sup>[286]</sup> by H. C. Aspinall and the influence of chirality of molecules on their magnetic properties such as the magneto-chiral effect (MChD), was critically reviewed by M. Verdager et al. in 2011.<sup>[287]</sup> This was updated in 2020,<sup>[162]</sup> by C. Train et al. targeting MChD as an optical readout of magnetic data with unpolarized light. Magnetochiral anisotropy was commented on several examples, including *4f* molecules in 2021<sup>[288]</sup> by J. A. Rikken et al. (Figure 26).

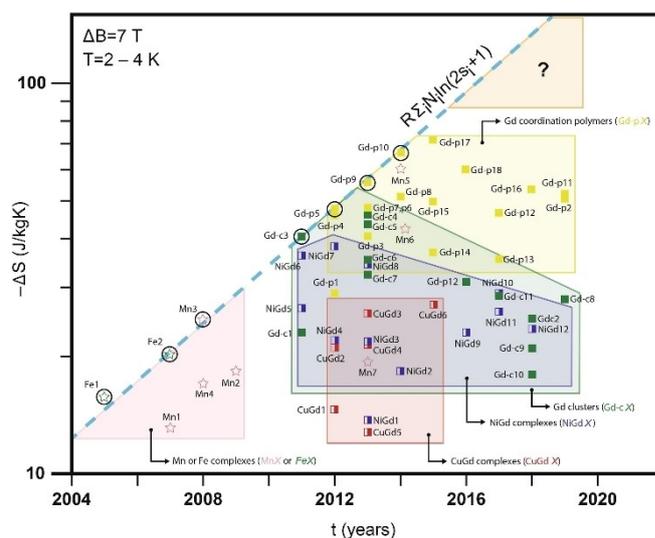
In 2021,<sup>[289]</sup> D. Pinkowicz et al. reviewed recent results on helicene-*4f* complexes in the framework of chiral lanthanide complexes, while in 2023<sup>[280]</sup> the already mentioned review by S. Chorazy et al. complemented the field.

In 2023,<sup>[291]</sup> S. Caretta et al. reviewed how chirality-induced spin selectivity (CISS) can be used in future quantum devices



**Figure 26.** Representation of the various X-ray dichroisms measured on a Ho<sup>III</sup>-complex for holmium. Original data reproduced from [290] with permission from the Royal Society of Chemistry, copyright 2020; and figure panel reported from [288] with permission from John Wiley and Sons, copyright 2021.

including either *3d* or *4f* ions. This interplay between chirality and magnetism on electron transfer processes can allow a spin-to-charge conversion mechanism realized by connecting a molecular spin qubit to an electron donor/acceptor dyad linked by a chiral bridge. Initialization, manipulation, and single-spin readout of molecular qubits and qudits is envisioned (see also section 4.3.3.3.8). A similar approach was reviewed in 2022<sup>[292]</sup> by A. Gaita-Ariño et al. that presented how molecular chirality can be employed to manipulate spin states, also including quantum coherent spin qubit states; several *4f*-based systems were targeted.



**Figure 27.** Representation of results of entropy change at cryogenic temperatures (2–4 K) and 7 Tesla of magnetic field change, over the last fifteen years, for metal complexes. Reproduced from [299] copyright 2020 with permission from Elsevier.

#### 4.3.3.3.5. Magnetic refrigeration with 4f molecules

The thematic of magnetic refrigeration using magnetocaloric effect (MCE) has been reviewed in 2014<sup>[293]</sup> by M. Evangelisti. It details how molecules, initially designed with anisotropic *4f* ions to provide SMM behavior can be efficient for magnetic refrigeration if isotropic Gd<sup>III</sup> derivatives are considered. This can be done either on extended networks, finite molecules or even molecules deposited on surfaces for “on-chip refrigeration”. MCE in molecules has been further reviewed by M.L Tong et al. in 2014<sup>[294]</sup> and completed and focused on *4f*-molecules by the same authors in 2016.<sup>[295]</sup>

In 2015, three consecutive book chapters can be found dealing with MCE: R. Sessoli et al.<sup>[250]</sup> stress the importance of MCE in extended networks, M. Evangelisti et al.<sup>[296]</sup> detailed MCE on Gd-molecules with a special focus on Gd<sup>III</sup>-polyoxometalates and D. Collison et al.<sup>[297]</sup> provided further insights on molecular MCE. These reviews were then updated by H. R. Wen et al. in 2021.<sup>[298]</sup>

In 2020,<sup>[299]</sup> M. Reis gathered results about magneto- but also barocaloric effect considering *3d*, *4f*-*3d* and *4f*-based materials (Figure 27). Last, R. Pelka et al. reviewed in 2022<sup>[300]</sup> the last results in the field with also a special focus on the rotating magnetocaloric effect (RMCE).

#### 4.3.3.3.6. 4f-SMMs on surfaces and hybrid materials

In order to convert *4f*-SMMs into materials and devices, their surface deposition is absolutely key. Thus, as competences in surface science were needed (deposition, imaging, physico-chemical characterization and theoretical modeling), the number of researchers involved in the field increased drastically.

In 2011,<sup>[301]</sup> R. Sessoli et al., reviewed the early results on SMM on surfaces, focusing on  $Mn_{12}$ ,  $Fe_4$ , and  $TbPc_2$  derivatives. The article highlighted the chemical strategies used to assemble SMMs on surfaces and control their orientation. Characterization tools used to examine the intramolecular arrangement of spins, magnetic anisotropy, and the dynamics of their magnetization on surfaces are detailed. Synchrotron-based techniques were also presented. This was completed by some of these authors in 2014.<sup>[302]</sup> Similarly, in 2012,<sup>[303]</sup> D. Ruiz-Molina et al. reviewed the same thematic but with a special focus on the structuring, integration, and magnetic characterization on SMM in devices. In all these examples, the  $4f$ -based SMM was  $TbPc_2$  and its derivatives. Indeed in 2014<sup>[304]</sup> J. Bartolomé et al. reviewed all magnetic properties of metal phthalocyanines, including  $4f$ -based and surface-supported phthalocyanines. The same has been done by M. Ruben et al. in 2015.<sup>[226]</sup> An update has been provided by M. Murugesu et al. in 2017.<sup>[305]</sup>

SMM can be deposited as isolated molecules, thick or thin films on surfaces. These last are particularly targeted to build low-dimensional magnetic materials with molecularly controllable properties. They have been reviewed by M. Affronte et al. in 2017<sup>[306]</sup> or focused on phthalocyanine-based functional molecular materials by J. Jiang et al. in the same year.<sup>[307]</sup>

In 2015,<sup>[52c]</sup> J. Dreiser proposed a very complete overview on mononuclear  $4f$ -SMM, showing that deposition processes and surfaces could affect the properties of molecules, requiring so precise molecule design at the bulk state. Then, the review provides a special focus on on-surface  $4f$ -SMM investigation via X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD, Figure 28) and scanning tunneling microscopy (STM).

E. Carolina Sañudo et al. in 2023<sup>[308]</sup> reviewed and updated the recent findings on SMM on surfaces with many  $4f$ -SMM examples. Special focus is made on comparing the different imaging techniques applied on SMM (Figure 29).

As far as more extended molecular structures made of  $4f$ -SMM are concerned, magnetic material preparation and thin film growth have been reviewed by S. Parkin et al. in 2021.<sup>[309]</sup> The same year,<sup>[310]</sup> O. Guillou et al. reviewed how dimeric  $4f$ -SMM can be converted from bulk SMM to magnetic deposits and luminescent devices. In 2023,<sup>[311]</sup> D. Ecija et al. reviewed  $4f$ -based 2D molecular framework whose constitution  $4f$  ions depict SMM properties.

In 2021,<sup>[312]</sup> A. J. Heinrich et al. reviewed single-atom on surfaces (most of them being  $4f$  ions) and their potential use as atomic-scale magnetic memories. These objects share the same problematic as SMM to be converted as efficient magnetic media: writability, signal-to-noise ratio and thermal stability. This is what the authors called the “magnetic media trilemma” (Figure 30).

Then, other than surfaces, SMMs have been targeted to be deposited in or on various other materials to provide hybrid materials with unique properties. In 2019, M. Murugesu et al., highlighted how SMM with controlled magnetic anisotropy can be embedded into fullerenes and carbon nanotubes to form hybrid materials or deposited on surfaces.<sup>[92]</sup> This was somewhat updated by M. del Carmen Giménez-López, in 2021.<sup>[313]</sup>

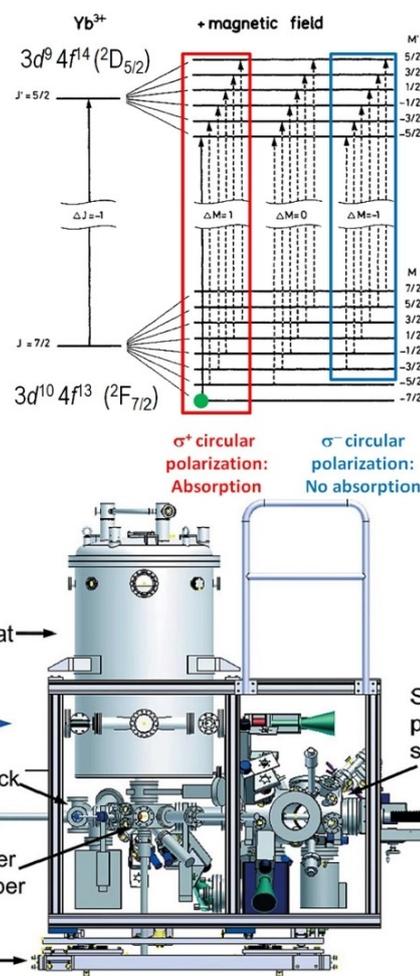


Figure 28. (Top) scheme of the Origin of the XMCD effect in  $Yb^{III}$ -based molecules (bottom). Preparation and measurement chambers (Cryostat) at the X-Treme beam line at the Swiss Light Source. Reproduced from [52c] with permission from IOP, copyright 2015.

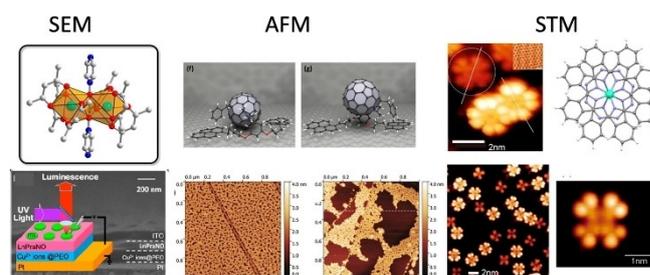
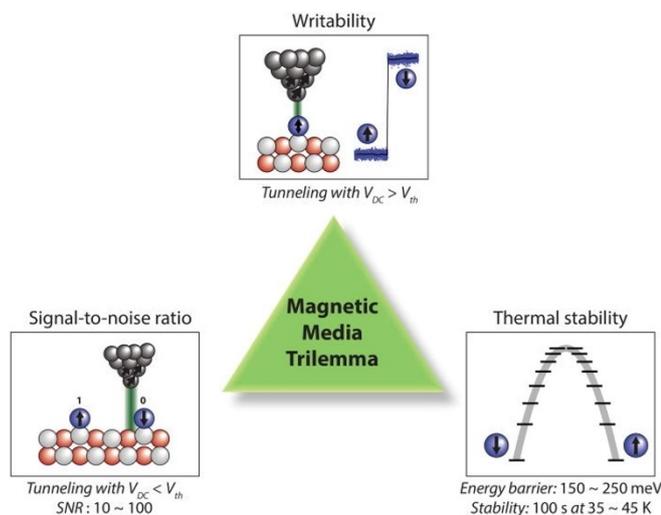


Figure 29. Comparison of images of  $4f$ -SMM obtained by SEM, (Dy dimer), AFM (functionalized  $4f$ -endofullerenes) and STM ( $TbPc_2$ ). Reproduced from Ref. [308], copyright 2023 with permission from Elsevier.

#### 4.3.3.3.7. Molecular Spintronics and $4f$ -SMMs

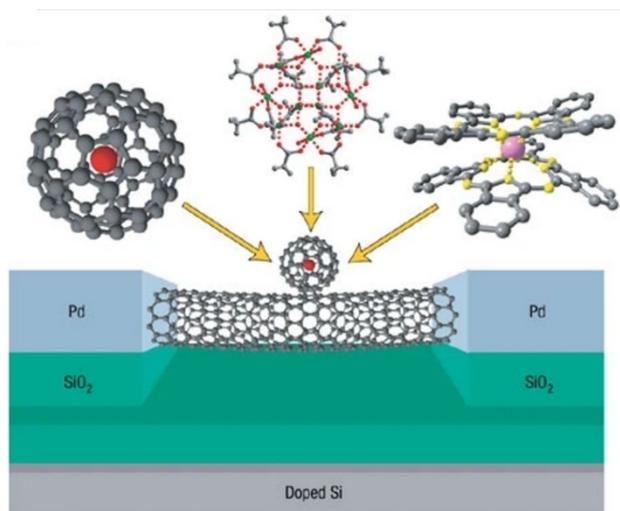
Assembling molecular magnets to build molecular materials and devices has been targeted as early as 1996,<sup>[112]</sup> in the book edited by J. S. Miller et al. (see also above sections).

In 2008,<sup>[42]</sup> molecular spintronics have been reviewed by W. Wernsdorfer et al. targeting state-of-the-art SMM at that time,

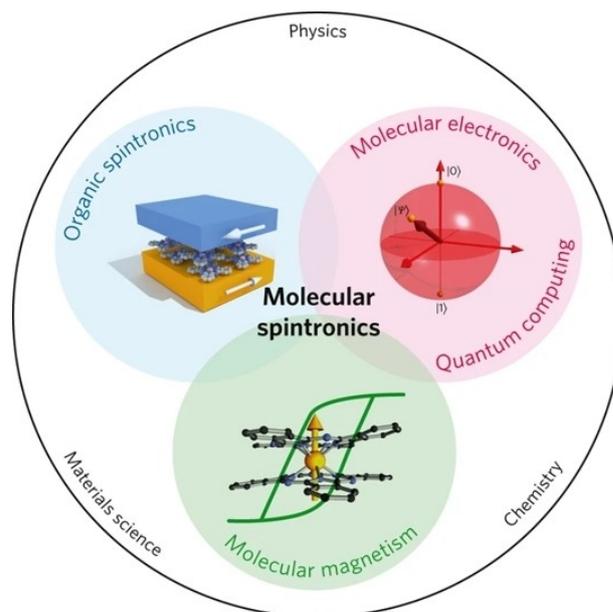


**Figure 30.** The “magnetic media trilemma”, with state-of-the-art values for single-atom magnets. Reproduced from [312] with permission from AIP publishing, copyright 2021.

Mn<sub>12</sub>, 4*f*-endofullerene and TbPc<sub>2</sub> SMM were envisioned as molecules to be used in various devices for applications in information storage and processing (Figure 31). This follows a paper and a review by A. R. Rocha et al. in 2005<sup>[314]</sup> and 2006<sup>[315]</sup> that showed how spin-polarized currents can be carried through molecules affecting their state (no 4*f* ions yet). Thus, the combination of spintronics and molecular electronics could give rise to the new intriguing field of molecular spintronics. It was updated in 2012<sup>[316]</sup> by some of the authors. In 2011,<sup>[317]</sup> S. Sanvito reviewed the field evaluating the ability of various types of molecules to be used in devices where “*the spin is injected, manipulated and detected in the solid state*”. Organic spintronics and single-molecule spintronics are considered.



**Figure 31.** Proof-of-concept scheme of magnetic molecules grafted on carbon nanotubes, a C<sub>60</sub> 4*f*-endofullerene, the Mn<sub>12</sub> SMM and the TbPc<sub>2</sub> SMM. Reproduced from [42] with permission from Springer Nature, copyright 2008.



**Figure 32.** Scheme of the various research fields involved in molecular spintronics. Reproduced from [320] with permission from Springer Nature, copyright 2017.

In 2014, two book chapters reviewed either single-molecule spintronics<sup>[318]</sup> by S. J. van der Zant et al. (no 4*f* ions) and molecular quantum spintronics using single-molecule magnets<sup>[319]</sup> by W. Wernsdorfer et al. For this last, once again, the TbPc<sub>2</sub> molecule is the key target to design SMM-based devices. Indeed, in 2015,<sup>[226]</sup> M. Ruben et al. reviewed the advances in the field using bis(phthalocyaninato) lanthanide(III) complexes to build graphene transistor, supramolecular spin valve, molecular spin resonator and molecular spin transistor.

In 2017,<sup>[320]</sup> A. Cornia and P. Seneor, provide a short but informative overview of the field of molecular spintronics and its potentialities (Figure 32).

In 2019,<sup>[321]</sup> E. Coronado detailed how chemistry allows controlling the spin in molecules, materials, and devices. Molecular spintronics and quantum computation, from which 4*f* examples, are reviewed. Then, a focus is made on MOFs and 2D materials (mainly 3*d* ions).

As key authors in the field, W. Wernsdorfer et al. provided in 2021<sup>[322]</sup> a comprehensive review on SMM and molecular quantum spintronics and highlighted how SMM properties have been transferred into functional devices in the last two decades. Similarly in 2023,<sup>[323]</sup> he proposed recent updates in the field using SMM-based quantum sensing, quantum simulation, quantum computing, and quantum communication.

#### 4.3.3.8. Molecular qubits and quantum information processing with 4*f* molecules

The use of quantum properties of matter such as superposition, tunneling, and entanglement is the basis of most quantum technologies. Indeed, chemist from the SMM communities

propose to use their knowledge gained on the coordination chemistry of metal ions to create objects to be used as qubits or qudits for quantum information processing for example.

One of the first reviews on the thematic was published in 2011<sup>[324]</sup> by R. E. P. Winpenny et al. showing how the incredible library of molecules made of molecular rings can be used for quantum information processing. At that time not  $4f$  ions were considered.

In 2012,<sup>[325]</sup> G. Aromi et al. reviewed how 2-qubit quantum gate can be designed using either molecules containing a pair of well-defined and weakly coupled entities or dinuclear complexes of anisotropic metal ions (mainly  $4f$ – $4f$  molecules) exhibiting dissimilar environments and feeble magnetic coupling. CNOT logic gates are particularly documented.

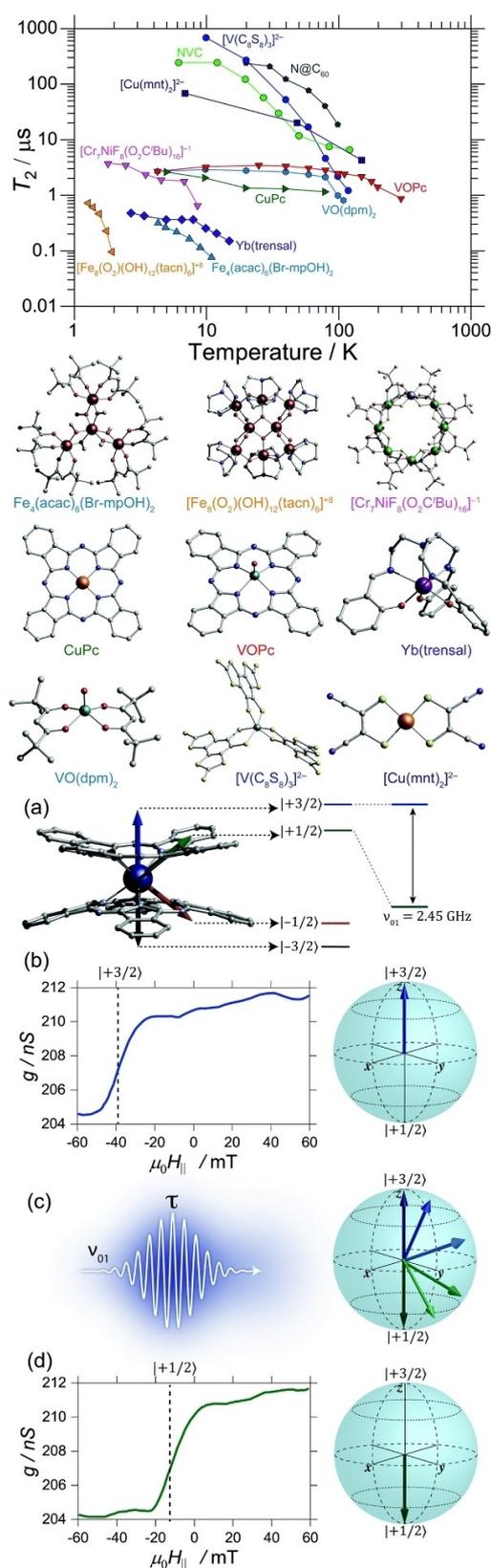
In 2015,<sup>[326]</sup> the same leading author reviewed in a book chapter main advances considering from one side, mononuclear Er-SMM, Gd-POMs,  $4f$ -POM with anisotropic lanthanides as spin qubits and from the other side asymmetric  $4f$  dimers for two-qubit quantum gates. In the same book, A. Gaita-Ariño et al.<sup>[327]</sup> also reviewed their first results obtained on Gd-POMs and their potential use as qubits. An extended update has been made in 2017<sup>[328]</sup> by the same authors with a particular focus on POMs as spin qubits or quantum gates.

Meanwhile, in 2014,<sup>[329]</sup> M. Affronte et al. reviewed the potentialities of molecular nanomagnets for information and communication technologies. A large introduction to the field contextualizes the research and the advantage/disadvantage of using molecules. It was somewhat updated by same authors in 2015.<sup>[330]</sup> In the same book,<sup>[331]</sup> D. Loss et al. demonstrated how molecular magnets can be used for quantum information processing in the framework of the five DiVincenzo criteria.

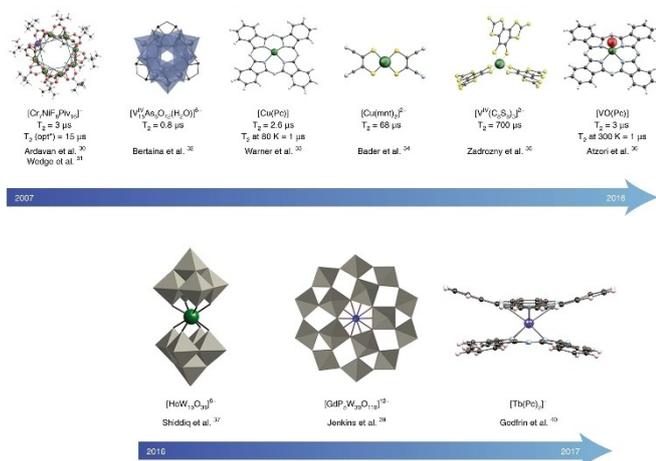
In 2016,<sup>[332]</sup> Y.-Z. Zheng et al. reviewed how mononuclear SMM can be used as qubits, detailing main results based on Gd (in Gd POM), Tb (in TbPc<sub>2</sub>) and Yb ions (in Yb(trensall)) to act as qubits. In 2017,<sup>[333]</sup> Amoretti et al. also reviewed the field, with a special appendix concerning the basics of the field, *i.e.* various key definitions and quantum logic gates. In 2018,<sup>[334]</sup> W. Wernsdorfer et al. published a comprehensive review on the use of molecular qudits in quantum algorithms (Figure 33). The main molecules considered as potential qubits are commented (Figure 34) and special attention is paid on TbPc<sub>2</sub> that can act as a molecular nuclear spin qudit.

In 2019,<sup>[335]</sup> O. Roubeau et al. provided a complete review of  $4f$  molecules for spin-based quantum technologies. The use of  $4f$ -based systems is detailed from spin-relaxation dynamics, quantum coherence, quantum gates, and quantum algorithms with qudits perspectives.

After a comment on last results in the field in 2015,<sup>[336]</sup> R. Sessoli et al. reviewed in 2019,<sup>[337]</sup> the recent findings and proposed the denomination “*second quantum revolution*” to illustrate how quantum effects, understood during the first quantum revolution, are now controlled at the nanoscale in devices targeted for quantum information processing, sensing, optics or cryptography. The same year E. Coronado et al.<sup>[338]</sup> reviewed the last development in molecular spins used for quantum computation with a strong focus on  $4f$ -based qubits and qudits.



**Figure 33.** (Top) representation of electron spin-spin relaxation ( $T_2^*$ ) versus temperature for several qubits; (Bottom) (a) Bloch sphere representation of the nuclear spin of TbPc<sub>2</sub> and the energy separation between the nuclear spin states; (b–d) graphical representation of initialization, manipulation and detection of the  $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$  subspace. Adapted from [334] with permission from the Royal Society of Chemistry, copyright 2018.



**Figure 34.** Selected milestones in magnetic molecules for quantum technologies. Timelines for (top) most relevant spin qubits made  $3d$  ions (bottom) key results obtained for mononuclear  $4f$  molecules. Reproduced from [338] with permission from Springer Nature, copyright 2019.

#### 4.3.3.3.9. Theoretical approaches for the modeling of $4f$ -SMMs magnetic properties

Most of the books cited in this review have a specific chapter dealing with the electronic structure of  $4f$  ions. Their reading is obviously key before entering into the understanding of the theoretical approaches on  $4f$ -SMM.

The theoretical investigation of SMM is one of the disciplinary fields that has evolved most drastically in recent years. This is particularly true for  $4f$ -SMM magnetic analysis that went from simple modeling of magnetic interaction on isotropic derivatives to elaborated quantum chemistry modeling of complete magnetic interaction, magnetic relaxation of anisotropic derivatives and on-surface theoretical investigation. While theoretical modeling played an increasing important role in the discipline, most papers reviewed compounds to test the validity of a new model or to address a specific issue. The opposite is not as common, and the identification of reviews or tutorial articles accessible to non-specialists is not as straightforward as in the other sub-fields of Molecular Magnetism. Moreover, some advances, which are described as decisive and universal, can be quickly questioned in subsequent papers. We will therefore provide here only some recent and subjectively chosen “review-like” references and not developments tested on few or specific molecules.

In 2013, A. Soncini et al.<sup>[339]</sup> and Murray et al.<sup>[340]</sup> reported two consecutive works focusing on a simple electrostatic model for the interpretation of magnetic anisotropy in Dy-SMM. On the opposite in 2015,<sup>[341]</sup> L. F. Chibotaru et al. reviewed the main advances in state-of-the-art computational modeling of  $4f$ -SMM with a focus on Complete Active Space Self-Consistent Field (CASSCF) methods and *ab initio* approach. It was compared with density functional theory (DFT) methods and phenomenological crystal field theory. Among other, the capabilities and outcomes of the now widely used SINGLE ANISO and POLY ANISO programs are described in a didactic way. The same

year,<sup>[342]</sup> a book chapter by A. Kerridge et al. reviewed in a didactic way the application of CASSCF to  $4f$  molecular complexes; while in the same book,<sup>[343]</sup> relativistic all-electron approaches to the study of  $f$  element in surveyed by Visscher et al.<sup>[344]</sup> This was somewhat updated by G. Rajamaran et al. in a book chapter in 2018,<sup>[345]</sup> with a particular focus on  $Er^{III}$  and “uncommon”  $4f$ -SMM. Same authors provided further review on the thematic but focused on organometallic  $4f$ -SMM in 2019.<sup>[346]</sup>

Also in 2015,<sup>[347]</sup> L. F. Chibotaru focused in another book chapter on the key notion needed for theoretical understanding of anisotropy in molecular nanomagnets. He emphasizes on the differences in the manifestation of magnetic anisotropy between complexes with weak and strong spin-orbit coupling as well as differences between single-ion and polynuclear compounds.

In 2015,<sup>[348]</sup> E. Ruiz et al., published an important review about the prediction of magnetic anisotropy on  $3d$  on  $4f$  ions using CASSCF (or CASPT2/NEVPT2) methods. For  $4f$  ions, a direct relationship was established between the electrostatic field generated by the ligands and the magnitude, shape, and orientation of the anisotropic electron density. Accordingly, a histogram was proposed for all possible geometries of  $[Dy(OH)_3(H_2O)_{n-3}]$  with coordination numbers from 2 to 9 and their corresponding  $U_{eff}$ ,  $g_z$ , and main mechanism of the spin relaxation determined via CASSCF + RASSI calculations.

In 2015, F. Totti et al. reviewed the modelization of on-surface SMM properties via DFT<sup>[349]</sup> and *ab-initio* approaches.<sup>[350]</sup>

In 2016,<sup>[351]</sup> S. Gao et al., proposed a review of magneto-structural correlation on mononuclear  $3d$  and  $4f$ -SMM based on their own molecules. Magnetic anisotropy is addressed through the displaced-charge electrostatic model and correlated with angular-resolved magnetometry that experimentally provides its strength and direction. Similarly, magnetic anisotropy in SMM was reviewed in 2019 by J. Bendix et al.<sup>[352]</sup> N. Chilton et al. reviewed in 2020<sup>[274]</sup> their own works about the ligand field in  $4f$  coordination complexes, showing its considerable influence on magnetic susceptibility anisotropy, paramagnetic NMR shift, and relaxation behavior. In particular, the strong limitations of Bleaney's theory on magnetic anisotropy are underlined. magnetic susceptibility anisotropy, paramagnetic NMR shift, and relaxation behavior. In particular, the strong limitations of Bleaney's theory on magnetic anisotropy are underlined.

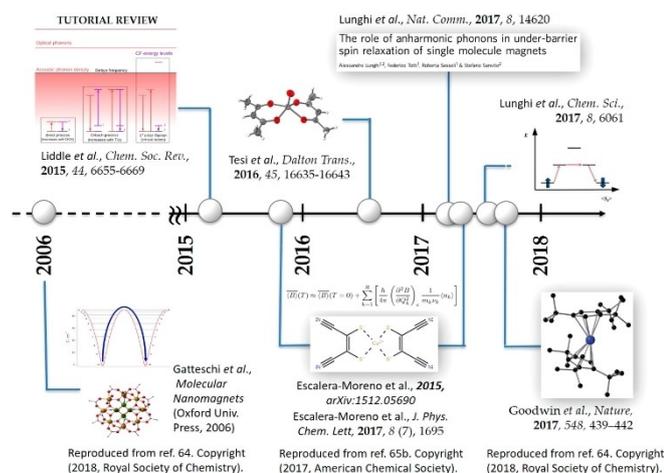
In 2016,<sup>[354]</sup> E. Coronado et al. reported not a review, but a useful demonstration of the predictive capabilities of complete active space *ab initio* methods (CASSCF and CASPT2) and semi-empirical radial effective charge (REC) model and critically discussed the limitations of these theoretical approaches. In 2017,<sup>[355]</sup> F. Bartolomé et al., proposed in a book chapter a complete examination of magnetic slow relaxation on  $4f$ -SMM from a theoretical to an experimental point of view. It is particularly suitable for experimental chemists who want to gain knowledge on theoretical modeling. This very complete review contains a specific and accessible chapter on the computational tools and theoretical models used in the discipline. It thoroughly detailed the evolution of the discipline from the simplest approaches (electrostatic models) to elaborated ones (quantum chemistry methods).

The same didactic line is provided by E. Ruiz et al. in 2020<sup>[357]</sup> in a perspective article on spin dynamics in SMM and molecular qubits. Both experimental and theoretical approaches for the calculation of blocking temperature (for SMM) and relaxation times T1 and T2 (for molecular qubits) are described. This focus on blocking temperature was further reviewed by Y. Bing et al. in 2022.<sup>[358]</sup>

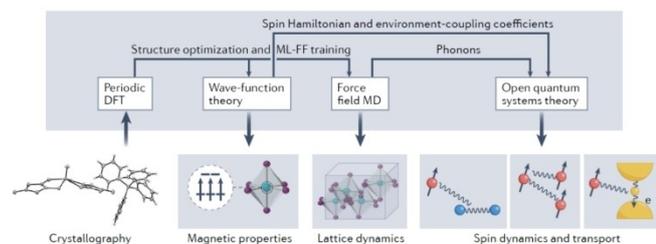
In 2017,<sup>[359]</sup> de C. Graff et al. highlighted in a book chapter the differences between “*ab initio*” approach (wavefunctions of the electronic system) and spin Hamiltonian calculations (description in terms of spin degrees of freedom). These last and their application to SMMs are also described by G. Rajaraman et al. in 2016<sup>[360]</sup> and Y.-Z. Zheng in 2021.<sup>[361]</sup>

In 2018,<sup>[182]</sup> E. Coronado et al. explored in a critical perspective of recent advances in molecular nanomagnetism toward the goal of integrating spin-phonon interactions into the current computational methodologies of spin relaxation.

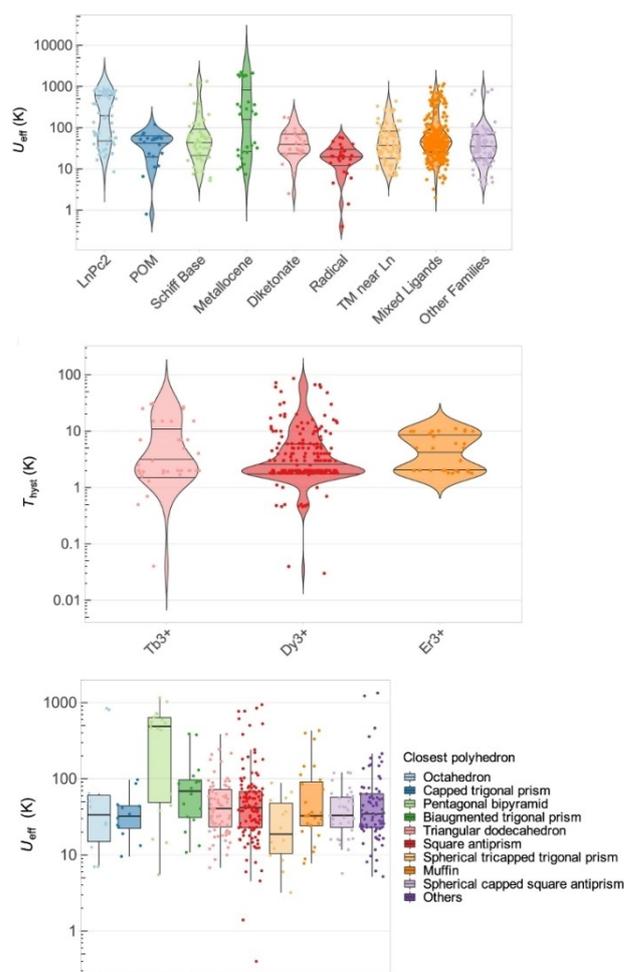
E. Coronado et al. explored in 2019<sup>[353]</sup> the high-temperature frontier in molecular nanomagnets with a particular highlight on the milestones in the theoretical modeling of vibration-mediated spin relaxation in molecular nanomagnets (Figure 35). This feature has been also further reviewed on dysprosocenium derivatives by A. Gaita-Ariño et al. in 2019,<sup>[198]</sup> S. Carretta et al. in 2020<sup>[362]</sup> and N. Chilton et al. in 2021.<sup>[199]</sup>



**Figure 35.** Scheme of the milestones in the theoretical modeling of vibration-mediated spin relaxation in molecular nanomagnets. Reproduced with permission from [353]. Copyright 2019 American Chemical Society.



**Figure 36.** Scheme of the process used to model magnetic molecules. Reproduced from [356] with permission from Springer Nature, copyright 2022.



**Figure 37.** (Top) values of  $U_{\text{eff}}$  (in K) for samples in each chemical family; (middle) values of  $T_{\text{hyst}}$  for samples containing  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$ ; (bottom) dependence between  $U_{\text{eff}}$  and coordination polyhedral. Reproduced from [105] with permission from Springer Nature, copyright 2022.

The key point of spin-phonon interaction has been reviewed in 2022<sup>[205]</sup> by N. Chilton in an already mentioned general review article. A deeper review on spin-phonon coupling and magnetic relaxation is provided by the same leading author in 2023.<sup>[363]</sup>

Spin-lattice relaxation and their effect on molecular dynamics have been reviewed by A. Lungchi et al. in 2022<sup>[364]</sup> using  $Co^{2+}$  and  $Dy^{3+}$ -based SMM. The sensitivity of various relaxation rates to low-energy phonons was detailed.

The same year,<sup>[356]</sup> S. Sanvito et al. reviewed how *ab initio* computational methods, combined with data-driven approaches to materials modeling, can be used to define design rules for magnetic molecules (Figure 36). Similarly, in the same year<sup>[105]</sup> A. Gaita-Ariño et al., constructed a dataset to review 1400 experiments on *4f*-SMM and gathered several figures of merit such as relaxation times,  $U_{\text{eff}}$ , blocking temperature,... This dataset is very informative on its own (Figure 37). Then, it is used as machine-learning input that further allow to propose chemical strategies for *4f*-SMM development and target molecules.

## 5. Conclusions

In conclusion, the appropriation of a scientific field can be a difficult and laborious task. Review articles and book chapters help facilitate this work, but when these become too numerous, the reader can become overwhelmed. Indeed, it seems reasonable to assume that the number of reviews in the field published each year is exaggerated, with thematic and temporal overlaps, and sometimes done more for bibliometric considerations than to make a real scientific contribution to the field. As such, if one wishes to capture the essence of a research field, it seems wise to limit oneself to a few authoritative books (collective or not) and a few major review articles.

Advanced bibliographic tools (referencing software, AI-based searches engine, pdf indexing and reading, etc...) can be as productive as they are stressful for a young PhD student, who can get lost in the number of resources and become unnecessarily bored. In this sense, and provided that ethical and scientific concerns are resolved, AI-based bibliographic searching, reading, and indexing assistant could be useful.

This umbrella review is thus a modest tentative to propose an overview of how the field is organized to date, which will itself quickly become outdated.

Finally, training and learning certainly occur through good bibliographic research, but other obvious tools can be used, such as university courses, learned society training resources, and the many personal resources available on various authors' websites and blogs. However, it is clear that the greatest progress is made through interaction with professors, colleagues, thesis supervisors, and mentors - in short, live interaction! In this respect, summer schools, workshops, and conferences can be considered the most effective way to familiarize oneself with a research field.

## Acknowledgements

The French Chemical Society and the Coordination Chemistry Division of the French Chemical Society (SCF-DCC) are acknowledged for the "SCF-DCC Young Investigator Prize 2020" motivating this special collection. All the collaborators who allowed me to obtain this award are kindly thanked. A special and very warm thank to all the members from the INSA group for their daily support and kindness. INSA Rennes, CNRS, Region Bretagne, Rennes Metropole and IUF are acknowledged for funding.

## Conflict of Interests

The author declare no conflict of interest.

**Keywords:** 4f ions · Lanthanides · Molecular Magnetism · Single-Molecule Magnets · Umbrella review

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Manuscript received: May 31, 2023

Revised manuscript received: July 4, 2023

Accepted manuscript online: July 7, 2023

Version of record online: July 7, 2023



In order to help young researchers in Molecular Magnetism, this article proposes a “review of reviews” also known as an “umbrella review” on lanthanide-based monomolecular magnets (4f-SMM). Bibliographic search techniques are commented

together with AI-based tools for bibliographic search, indexing, and summarization. Milestones in 4f-SMM are identified. Books, book articles, and reviews are contextualized. This article is therefore proposed as a gateway to the 4f-SMM field.

Prof. K. Bernot\*

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