
Volume 1 | Number 1 | Jan 2013 | Pages 1–100
Dalton Transactions
An international journal of inorganic chemistry
www.rsc.org/dalton
ROYAL SOCIETY OF CHEMISTRY

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Lanthanide single molecule magnets: Progress and perspective

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The last few years have seen a huge renaissance in the study of single molecule magnets (SMM) thanks to the extensive applications of lanthanide ions with large inherent anisotropy in molecular magnetism. Especially, the recent theoretical developments and the experimental expansion into organometallic avenue lead to an eye-catching boost in this field. Here we highlight the recent progresses in this fascinating and challenging field, with an emphasis on several combined experimental and theoretical studies.

Introduction

In recent years, lanthanide complexes have cornered the market in single molecule magnets (SMMs)[1] capable of retaining magnetization at the molecular level below a certain temperature, mainly as a result of their extraordinary performance in the pursuit of new SMMs with high effective barriers (U_{eff}) and blocking temperature (T_B) far surpassing that of transition metal SMMs.[2-4] In fact, the early research on lanthanide SMMs can be dated back to 2003, when Ishikawa et al demonstrated that slow relaxation of the magnetization can occur in mononuclear lanthanide species, that is, the double-decker phthalocyanine lanthanide system $[\mathrm{LnPc_2}]^-$ (Ln = Tb, Dy).[5] Nevertheless, until 2006 the discovery of fascinating $\mathrm{Dy_3}$ triangle showing the coexistence of nonmagnetic ground states and SMM behaviour really stimulated the wide interests in the exploration of pure lanthanide SMM systems with strong local Ising-type anisotropy at metal sites.[6] Therefore, hundreds of such SMMs including mononuclear, dinuclear and larger lanthanide compounds have now been discovered to exhibit high anisotropic barrier for reversing the magnetization,[2, 3] and naturally some remarkable advances follow the experimental and theoretical developments in this field. At first, the anisotropic barrier records have toppled like dominoes for lanthanide SMMs in recent studies.[2, 3] However, it is worth noting that in some recently reported SMMs, the temperature dependence of τ shows obvious deviation from the Arrhenius law, and thus other processes such as Raman, direct and QTM processes may be added to the fitting of τ vs T^{-1} plots.[7, 8]. Remarkably, the highest effective barrier in multinuclear lanthanide SMMs has been as high as 692 K,[9] which is almost comparable to the barrier record of 939 K kept by heteroleptic bis(phthalocyaninate) lanthanide SMM.[10] More importantly, the successful employment of advanced *ab initio* calculations and new experimental technique in several organometallic SMMs enhances the understanding of the relaxation mechanism of SMM, leading to recent discovery of new relaxation pathway via the second excited states.[9, 11, 12] In addition, the simple but amenable electrostatic model developed recently provides crucial input for the theoretical modelling of the important single ion anisotropy requisite for blocking magnetic moments of lanthanide centres.[13-16] Such model can directs the chemical optimizations for better lanthanide SMMs operating at higher temperatures. Since the topic of lanthanide SMMs with the emphasis on ligand design and magnetic properties has been recently reviewed by us and others,[2, 3, 17] this frontier article will focus on the most up-to-date progresses in new electronic model, relaxation mechanism and some special magnetic phenomena, aiming at a better understanding of the characteristics of lanthanide SMMs and one step further, their rational design from synthetic point of view.

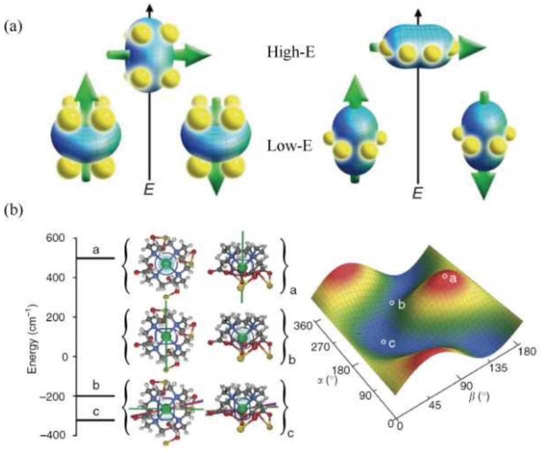


Fig. 1 The electrostatic model: (a) Depictions of low- and high-energy configurations of the *f*-orbital electron density with respect to the crystal field environment for a 4*f* ion of oblate (left) and prolate (right) electron density. Reproduced from Ref. 13 by permission of The Royal Society of Chemistry. (b) The quantitative electrostatic potential map around metal center constructed in $[\mathrm{Dy(DOTA)(H_2O)Na_3}]^{2+}$. Reprinted by permission from Macmillan Publishers Ltd: ref. 14, copyright 2013.

Electrostatic model for determining anisotropy axes

In 2011, the qualitative electrostatic model given by J. R. Long[13] on the basis of the interaction between the single-ion electron density and the crystal field environment serves the clear design principles for maximizing the unaxial magnetic anisotropy of different lanthanide ions with distinct electron density distributions. As shown in Fig. 1a, the model appears to resemble the point-charge model used to create and optimize permanent magnets in the past years,[18] where a given crystal field is able to orient the electronic charge cloud into an energetically favourable direction, and decides the sign of the anisotropy (easy-axis or easy-plane) based on the oblate or prolate shape of electron density distributions. Typically, for Dy or Tb ion with oblate electron density, a crystal field where the ligand charge density is concentrated above and below the *xy* plane is greatly favourable to the ground states with largest m_J quantum number and the corresponding strongly unaxial anisotropy due to the minimizing repulsive interactions between *f*-electron charge clouds and ligand charges, as seen in sandwich-type geometry in bis(phthalocyaninate) complexes [5]. In contrast, an equatorially coordinated geometry is predicted to be preferable for Er ion with prolate electron density. Importantly, recently N. F. Chilton and co-workers have given a quantitative description for the above model via a simple electrostatic energy integral,[14] which provides an important electrostatic potential map around metal centre and thus the orientation of the anisotropy axis is able to be extracted based on a straightforward electrostatic energy minimization (Fig. 1b). Remarkably, such a quantitative method can be easily extended into some low-symmetry systems,[19] yielding consistent anisotropic orientation to that obtained from *ab initio* calculations in monometallic as well as polymetallic systems.

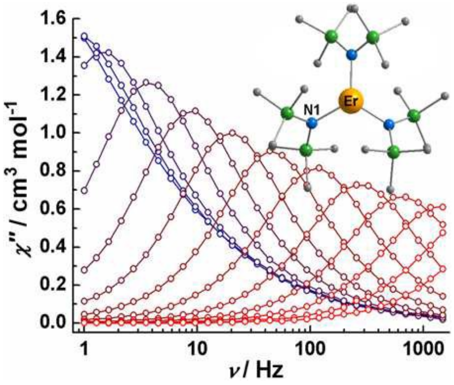


Fig. 2 Three-coordinate Er SMM with equatorial triangle geometry and its relaxation dynamics. Reprinted with permission from ref. 20. Copyright 2014 American Chemical Society.

More importantly, such a simple model based only on an X-ray crystal structure without complex calculations indeed has guided the chemical optimization of lanthanide SMM systems for synthetic chemists, thus leading to the discovery of new SMM systems. As a representative example, the three-coordinate Er-based SMM reported recently by our group represents the first equatorially coordinated mononuclear SMM showing the strongly magnetic blocking behaviour,[20] as seen in Fig. 2, which is well associated to the prediction from the above model.

Experimental determination of magnetic anisotropy and electronic structure

In transition metal SMMs, an easy-axis anisotropy of magnetization leads to a double well-potential landscape for the spin levels, which is directly associated with the height of anisotropic barrier for spin reversal.[1] In contrast, although a different relaxation mechanism is observed in lanthanide SMMs, the similar effects still occur and even magnetic anisotropy seems to be more important in determining the effective barrier especially in mononuclear lanthanide SMMs.[13, 17] Therefore, the accurate measurement on magnetic anisotropy is of fundamental importance for elucidating the relaxation mechanism such as the height of effective barrier and the occurrence of QTM in lanthanide SMMs.

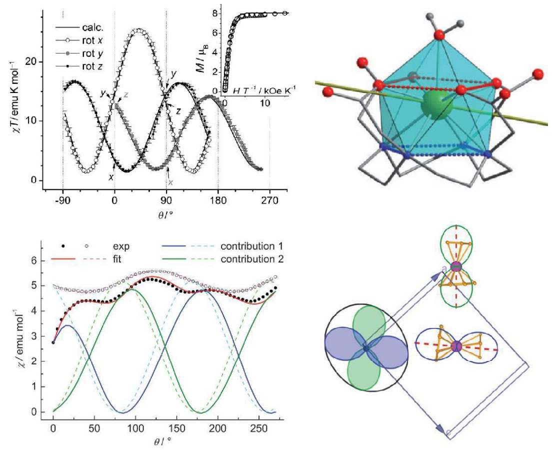


Fig. 3 (Top) Angular-dependent magnetic susceptibility of Dy^{III}-DOTA and the orientation of the experimental easy axis of the magnetization. Reprinted with permission from ref. 22. Copyright 2012 Wiley-VCH. Reprinted by permission from Macmillan Publishers Ltd: ref. 24, copyright 2012. (Below) The fitting of out-of-equilibrium angular-resolved magnetization data of Cp*ErCOT SMM and polar plot of two contributions from two families of molecules. Reprinted with permission from ref. 26. Copyright 2013 Wiley-VCH.

Currently, the anisotropic parameters (g_x, g_y, g_z and the direction of easy axis) evidencing the features of magnetic anisotropy were usually given in most lanthanide SMMs by *ab initio* calculations. However, recently the experimental determination of magnetic anisotropy, mainly through angular-resolved magnetometry developed by R. Sessoli et al, is attracting much attention of researchers. In lanthanide SMMs, the technique was firstly applied in 2009 to Dy^{III}-radical complex $[Dy(hfac)_3(NIT\text{-}R)_2]$, where the obtained angle-dependent magnetic susceptibility gave direct experimental confirmation for uniaxial anisotropy.[21] Remarkably, in 2012 the comparison between experimental and theoretical results exactly revealed the nature of magnetic anisotropy in Ln^{III}-DOTA family (Fig. 3 top), and further suggested that simple analysis based on the idealized symmetry of the lanthanide complex can be misleading.[22-24] In addition, its application in polynuclear Dy_6 SMM in 2010 is directly indicative of the easy-plane magnetic anisotropy of ground state arising from the effective linking of two Dy_3 triangles.[25] However, such a technique was almost limited in triclinic space group before 2013, which greatly prevents its application in SMM field. Recently, some important breakthroughs have been achieved in this respect by R. Sessoli and co-workers through the introduction of new measuring approaches.[26, 27] Although the Cp*ErCOT SMM reported by S. Gao et al crystallizes in the orthorhombic space group *Pnma* with two families of almost perpendicular molecules,[28, 29] the presence of magnetic hysteresis at a relatively high temperature allow the collection of out-of-equilibrium angular-resolved magnetization data (Fig. 3 below), which can be reasonably explained through separating the contributions that come from the two families of molecules.[26] Furthermore, the application of torque magnetometry, not requiring the presence of magnetic hysteresis, proves to be more powerful for determining its magnetic anisotropy, and simultaneously provides additional information on the crystal-field splitting.[27]

In addition, the electronic structure of lanthanide ion under crystal field environment affords important information for better understanding magneto-structural correlation in lanthanide SMM. In most examples, the information was usually given through crystal field or *ab initio* calculations, while the experimental evidence was rarely provided as a result of the great complexity of electronic structure for lanthanide ion.[13] Recently, some sophisticated experimental techniques is being used to gain insight into the electronic structure of lanthanide SMM, such as high-resolution luminescence,[22, 30] far infrared (FIR),[31] and inelastic neutron scattering (INS)[32] spectroscopies. Therefore, the effective combination of theoretical calculations and experimental detections paves the way for deeper magneto-structural correlation, and further directs the rational design of lanthanide SMMs with better magnetic performance.

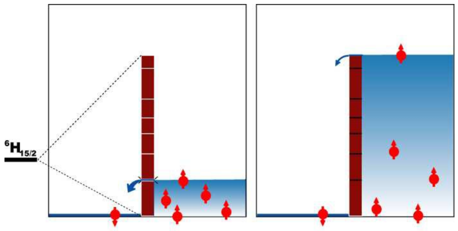


Fig. 4 Barrier levee model for designing Ln-SMMs. Reprinted by permission from Macmillan Publishers Ltd: ref. 11, copyright 2014.

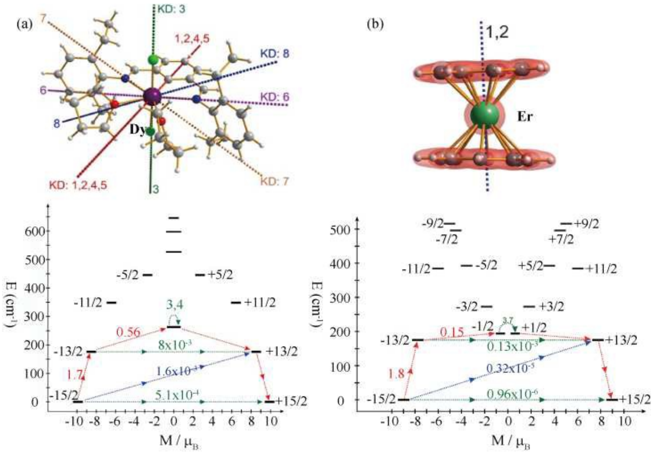


Fig. 5 Low-lying electronic structure for DyNCN and $[Er(COT)_2]^-$ SIMs. (Top) The molecular structure and calculated orientation of the main magnetic axis on Ln ions; (Below) The magnetization blocking barriers in two complexes, the red dashed lines representing the most efficient relaxation pathways. (Left) Reprinted by permission from Macmillan Publishers Ltd: ref. 11, copyright 2013. (Right) Reprinted with permission from ref. 12. Copyright 2012 Wiley-VCH.

Magnetic relaxation via the high excited state

Generally, a double-well model provides a good description for the relaxation mechanism in strongly exchanged transition metal SMMs, such as Mn_{12}[33] and Fe_8,[34] where the reorientation of magnetic moments corresponds to surmounting the anisotropic barrier via consecutive transitions between $|S,m_s\rangle$ states for neighbouring m_s values.[35] Now such a climbing process is still only at a proof-of-principle stage for lanthanide SMMs, most of which give the most efficient relaxation pathway via the first excited states due to the matrix elements of transversal magnetic moment induced by non-coinciding anisotropy axes between the ground and the excited doublets and the fast QTM within the exited doublets.[36] Nevertheless, the total multiplet width of crystal field splitting of the order of 100-1000 cm^{-1} far surpassing the barrier record of multinuclear transition metal SMMs opens huge perspectives for means to obtaining high-performance SMMs through blocking the magnetic moments of excited doublets as efficient as possible, as seen in the barrier *levee* model put forward by our group and coworkers in Fig. 4.[11] Consequently, attempts are currently under way towards achieving this goal and they have already given extremely fascinating results.

The theoretical and experimental investigations have revealed that the blockages of excited doublets of multiplets arise mainly as a result of the strong axial magnetic anisotropy in not only the ground but also excited doublets concomitant with the coinciding anisotropy axes between the ground and the excited doublets, which thus require a higher degree of axiality of the ligand field around lanthanide center, as revealed in the idealized diatomic $[DyO]^+$ complex.[36] Accordingly, L. F. Chibotaru et al pointed out that two critical synthetic strategies should be employed to get such a high unaxial anisotropy of lanthanide ions.[12] One way is to achieve only one very short chemical bond with the lanthanide ion dominating over all other bonds, which can efficiently enhance the intrinsically axial nature of the total ligand field, while the other is to employ highly symmetrical ligands with no bonding atoms on the symmetry axis, which leads to the local coordination geometry with extremely high symmetry around metal center. Very recently, our group and M. Murugesu et al have reported two representative organometallic Dy[11] and Er[12] SMM examples, respectively, as shown in Fig. 5, where their effective barriers have exceeded the energy gap between the ground and first excited states and therefore *ab initio* calculations reveal the most efficient relaxation pathway occurring via the second excited states mainly due to the collinearity of anisotropy axes of the ground and first excited Kramers doublets. In addition, E. J. L. McInnes and co-workers also discovered the occurrence of the same relaxation mechanism in the diluted samples of Dy_4K_2 and Dy_5 SMMs.[9] Such a striking progress further enhances our understanding of the correlation of relaxation processes with the crystal field environment, and opens up a broader space for developing the high-barrier SMM through employing lanthanide ions.

Radical-bridged lanthanide SMMs

In lanthanide SMMs, the large barriers are often attributable to single-ion behaviour due to the weak coupling of lanthanide centres, thus limiting the further increase of ground quantum numbers, which seems to be a crucial roadblock to improve their anisotropy barriers and blocking temperature.[37] Therefore, enhancing the exchange interactions between lanthanide centres has always been one of the most challenging tasks. Remarkably, the radical-bridged lanthanide systems hold great promise in this respect.[38] The first radical-bridged dinuclear lanthanide SMM was investigated by R. Sessoli and co-workers in 2007, where the nitronyl-nitroxide radicals containing pyridine groups bridge two lanthanide ions and thus lead to obvious ferromagnetic interactions in the system.[39] Subsequently, some other dinuclear systems were also studied by their and other groups.[40-42] Strikingly, the recent work by J. R Long group represents the newest developments, i.e. the delocalized N-based radical bridged lanthanide SMMs demonstrate unprecedented strong coupling interactions.[37, 43-45] Fig. 6 exhibits three typical radical bridged systems, all of which behave as strongly blocked SMMs mainly benefiting from the strong magnetic interactions between lanthanide ions and radical ligand. Here the reason for such strong interactions is due to the diffuse spin orbitals present in radical ligands that can penetrate the core electron density of the lanthanide ions.[37] In particular, the N_2^{3-}-radical-bridged lanthanide SMM still represents the hardest SMM magnet known to date, which exhibits the highest blocking temperature, T_B = 14 K, and large coercive fields as a result of the extremely strong magnetic coupling.[37, 43] The fascinating results present in those systems suggest the great ability of delocalized radical bridging ligands to propagate strong magnetic exchange coupling between lanthanide centres, and thus bring the goals of molecule-based information storage and processing closer to reality.

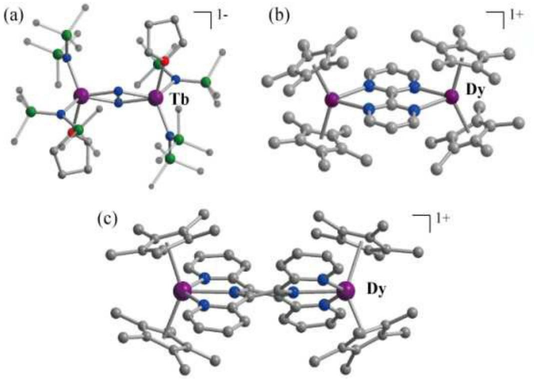
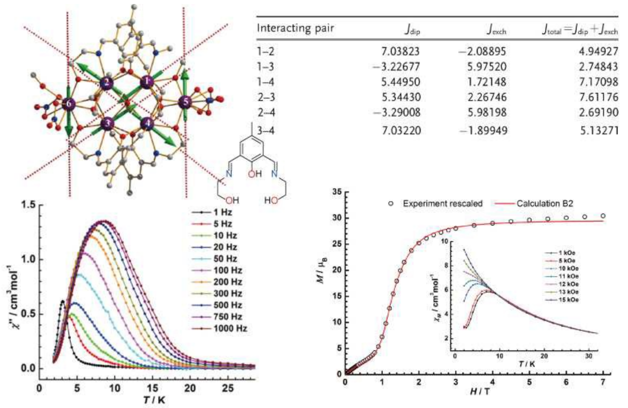


Fig. 6 The molecular structures of three typical radical bridged systems. (a), (c) Figures generated from data first reported in refs. 43 and 45. (b) Reprinted with permission from ref. 44. Copyright 2014 American Chemical Society.

Enhancing the toroidal moment

Our recent tutorial review has systematically examined the magnetic clusters behaving as single-molecule toroics (SMTs),[46, 47] which were defined by analogy with single-molecule magnets (SMMs) due to the toroidal moments of single molecular origin, with a typical example being the Dy_3 triangle. Notably, such an isolated toroidal moment can be viewed as the elementary units constituting ferrotoroidicity i.e. the fourth form of ferroic order showing interesting magneto-optical and magnetoelectric properties.[48] Recently, we have presented a great progress in the coupling of Dy_3 SMTs leading to an enhanced toroidal moment.[49] As shown in Fig. 7, the Dy_6 molecule can be considered as the linkage of two Dy_3 triangular units in a robust edge-to-edge arrangement, which is fixed by one μ_4-O^{2-} ion in the centre and consolidated by four deprotonated phenol oxygen atoms from ligands in the periphery. Therefore, *ab initio* calculations in Fig. 7 reveal that the coupling interactions between two Dy_3 units were obviously enhanced in contrast to the vertex-to-vertex Dy_6 molecule discovered by Powell,[25] leading to a relatively high magnetic excited state above the ground state of the Dy_6 complex.[47] As a result, the strong couplings via a μ_4-O^{2-} ion stabilize two similar anticlockwise toroidal moments, making the toroidal moment of the present Dy_6 cluster maximal, which furthers their prospects in multiferroic systems and magnetic data storage technology.



Interacting pair	J_{dip}	J_{exch}	$J_{total} = J_{dip} + J_{exch}$
1–2	7.03823	−2.08895	4.94927
1–3	−3.22677	5.97520	2.74843
1–4	5.44950	1.72148	7.17098
2–3	5.34430	2.26746	7.61176
2–4	−3.29008	5.98198	2.69190
3–4	7.03220	−1.89949	5.13271

Fig. 7 The molecular structure, magnetic anisotropic axes, magnetic interactions among central Dy ions, relaxation dynamics and static magnetic data of the Dy_6 molecule. Reprinted with permission from ref. 49. Copyright 2012 Wiley-VCH.

Conclusion and perspective

The above five parts represent some of the most recent developments in the field of lanthanide SMMs, highlighting the rational design of crystal field environments for obtaining strongly blocked SMMs and the important exploration into the coupling effects of toroidal moments. Such critical progresses offer a surprising amount of information for future research on how to choose ligand sets for the desired axial magnetic anisotropy requisite for target SMM properties.[50] The following points may summarize some future endeavors in the design of lanthanide SMMs:

(a) Designing a ligand field with desirable charge distribution will be an effective approach to enhancing the axial anisotropy of lanthanide centre, given the potential of electrostatic model in predicting the nature of single ion anisotropy for lanthanide ions which has been demonstrated by combined theoretical and experimental studies.

(b) Elaborating a strongly unaxial ligand field to force the magnetization reversal via higher excited energy levels seems to be a very promising route towards SMM with high anisotropy barrier.

(c) The delocalized radical bridging ligands can provide an efficient magnetic exchange pathway between lanthanide ions, and thus the extension of such system to other radical bridging ligands or larger lanthanide systems might hold great promise in achieving SMM with higher blocking temperature.

(d) The exploration of magnetic coupling effects between SMT molecules is of critical importance for the fundamental understanding of ferrotoroidicity, and further coupling those SMT molecules into a 2D/3D ordering materials seems to be a more challenging task.

Of course, the ultimate goal of this research is to develop the future devices for possible applications in information storage and quantum computing.[50] Therefore, developing new type of SMM family[51-54] is still necessary to obtain feasible SMMs with structural and magnetic stability when anchoring them on surfaces. One representative example is the endohedral fullerene family,[51-53] $Dy_nSc_{3-n}N@C_{80}$ (n = 1, 2, 3), where the SMM properties can be controlled through changing the number of magnetic moments and their interactions, as shown in Fig. 8. Importantly, intensive studies of surface layers of such fullerene molecules on different substrates have been carried out previously,[55] which affords the advantage for developing the envisaged technological applications such as information storage and quantum computing devices.[56]

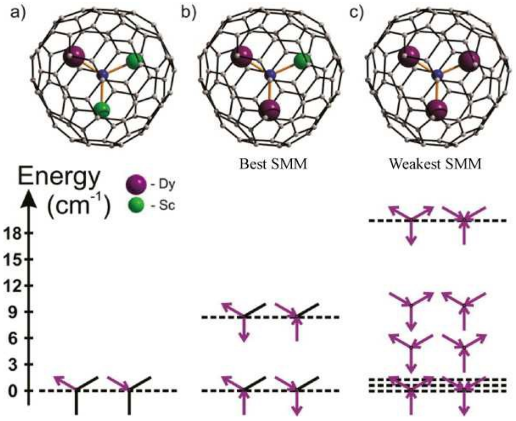


Fig. 8 Atomic structures and low-lying energy levels of $Dy_nSc_{3-n}N@C_{80}$ for n = 1, 2, 3, respectively. Reprinted with permission from ref. 53. Copyright (2014) by The American Physical Society.

Acknowledgement

We thank the National Natural Science Foundation of China (Grants 21371166, 21331003 and 21221061) for financial support.

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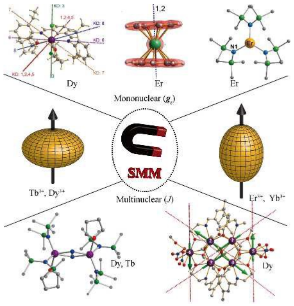
Graphical Abstract



The recent developments in lanthanide SMMs highlighted here indicate the directions to which further synthetic efforts should be focused.