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# Magnetic molecular materials with paramagnetic lanthanide ions

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**The diverse magnetic properties of lanthanide-based magnetic molecular materials are introduced in the following organization. First, the general aspects of magnetic molecular materials and electronic states of lanthanide ions are introduced. Then the structures and magnetic properties are described and analyzed for molecules with one lanthanide ion, 4f-4f, 4f-3d and 4f-p magnetic coupling interactions. In each section, magnetic coupling, magnetic ordering and magnetic relaxation phenomenon are briefly reviewed using some examples. Finally, some possibilities of developing magnetic molecular materials containing lanthanide ions are discussed in the outlook part.**

lanthanide, coordination compound, magnetic coupling, magnetic ordering, magnetic relaxation, single-molecule magnet, single-chain magnet, single-ion magnet

## 1 Introduction

Lanthanides have been widely used in traditional magnet technology for many years. For example,  $\text{SmCo}_5$  and  $\text{Nd}_2\text{Fe}_{14}\text{B}$  have been both good permanent magnets for producing large static magnetic field over the past decades. However, the magnetic molecular materials are different species from the perspectives of compositions, structures, and magnetic characteristics. First, the structures of the materials are more complex and more diverse than those of the conventional inorganic/ionic materials. The number of molecular materials will be very large, even unlimited theoretically, for example, many kinds of molecular magnetic ordering systems include transition metal ions, radicals, lanthanide ions and so on. Second, they can be constructed using bottom up method in the framework of coordination chemistry. Therefore, identical structures and iso-orientated magnetic objects are assembled in the form of molecular crystals. They serve as ideal models for studying the origin of magnetism theoretically, for example, it is easier to understand the magnetic coupling mechanism from a dinuclear molecule than a bulk material. At last, molecular

systems often permit the incorporation of other useful functionality to produce multifunctional materials. They could be hybrids of different functional parts with no interaction using an inert linker, or they may be more definite couplings of different physical properties, such as luminescence, ferroelectricity, catalysis, and gas sorption. For example, a light-induced magnetic ordering appears in spin crossover Prussian blue phases. These types of materials can not only offer model systems for testing theories on many body problems to scientists, but also provide new materials and find highly specific and novel applications. They can also expand human beings' understanding of different macroscopic quantum phase behaviors.

Although there exist many differences between conventional and non-conventional magnetic materials, they found the common ground in magnetism. As the important source of magnetism, lanthanide ions are well

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known for the magnetic properties which are dominated by the internal nature of the f orbitals. Different from the 3d orbitals of transition metal ions and the p orbitals of radicals, the f orbitals of lanthanide ions have strong unquenched orbital angular momentum which can induce effective spin-orbit coupling. The trivalent ions are characterized by  $f^n$  configurations, which give rise to  $2S+1L$  multiplets, further split by spin-orbit coupling to give  $J$  states

$$E(2S+1L_J) = (\lambda/2)[J(J+1) - L(L+1) - S(S+1)] \quad (1)$$

where  $J$  is defined by the angular momentum summation rules  $|L-S| \leq J \leq |L+S|$ , and  $\lambda = \pm \xi/2S$ .  $\xi$  is the spin-orbit coupling constant which ranges from 600 to 3000  $\text{cm}^{-1}$  throughout the lanthanide series, the highest values corresponding to the heaviest lanthanide ions. The + sign applies for  $n < 7$  and the - sign for  $n > 7$ . The sign of the spin-orbit coupling constant  $\lambda$  implies that in the ground-state  $J=L-S$  for  $n < 7$  and  $J=L+S$  for  $n > 7$ . For  $f^7$  ions such as Gd (III),  $L=0$  and  $S=7/2$ , the orbital momentum is completely quenched in the ground state.

The  $g$  factor of the Zeeman Hamiltonian of a given  $J$  multiplet is given by

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (2)$$

The ground state terms,  $g$  values, calculated and experimental  $\chi T$  values at room temperature for the dif-

ferent lanthanide ions are listed in Table 1.

From Table 1, the Ln(III) ions have both the large spin-angular-momentum part and the large unquenched orbital-angular-momentum part associated with the internal nature of the valence f orbitals. Compared with the d electrons of transition-metal ions, the orbital component of the magnetic moment is much more important for the rare-earth ions because the crystal-field effects are smaller and spin-orbit coupling larger for f electrons. The magnetic properties of rare-earth ions are strongly influenced by this feature, specially for the large magneto-crystalline anisotropy. As far as the magnetic properties are concerned, the large anisotropic moments coming from the large spin-orbital coupling make lanthanide ions appealing building blocks in the synthesis of magnetic molecular materials. As early as 1976, Landolt et al.<sup>[1]</sup> used Ln(III) ions for the preparation of a series of Prussian blue analogs which exhibited magnetic ordering with large hysteresis loops. Since then, numerous compounds containing lanthanide ions associated with paramagnetic centers such as transition metal ions or organic radicals have been produced. They show abundant geometry structures and rich magnetic phenomena, such as ferromagnetic ordering, ferrimagnetic ordering, single-molecular magnet behavior, single-chain magnet behavior, especially single-ion magnet behavior, which has not been found in transition metal complexes and organic radical systems yet<sup>[2,3]</sup>.

**Table 1** Ground state,  $g$  values, calculated and experimental room temperature  $\chi T$  values for Ln(III) ions

Ln(III)	Configuration	Ground state	$g_J$	$\chi T_{\text{cal}}^{\text{a)}$ ( $\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$ )	$\chi T_{\text{exp}}$ ( $\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$ )
Ce	$f^1$	$^2F_{5/2}$	6/7	0.80	0.66–0.78
Pr	$f^2$	$^3H_4$	4/5	1.60	1.45–1.62
Nd	$f^3$	$^4I_{9/2}$	8/11	1.64	1.45–1.53
Pm	$f^4$	$^5I_4$	3/5	0.90	1.05
Sm	$f^5$	$^6H_{5/2}$	2/7	0.09	0.32
Eu	$f^6$	$^7F_0$	0	0	1.53
Gd	$f^7$	$^8S_{7/2}$	2	7.88	7.61–7.80
Tb	$f^8$	$^7F_6$	3/2	11.82	11.76–12.01
Dy	$f^9$	$^6H_{15/2}$	4/3	14.17	13.01–14.05
Ho	$f^{10}$	$^5I_8$	5/4	14.07	13.26–13.78
Er	$f^{11}$	$^4I_{15/2}$	6/5	11.48	11.05–11.28
Tm	$f^{12}$	$^3H_6$	7/6	7.15	7.03
Yb	$f^{13}$	$^2F_{7/2}$	8/7	2.57	2.53

a)  $\chi T_{\text{cal}} = (1/8) g_J^2 [J(J+1)]$ .

From the general rule of chemistry, composition, structure and property, we tell the story of lanthanide-based magnetic molecular materials in the following sequences. We start the review with the structure and properties of single-ion magnet, in which the magnetic properties come from only isolated magnetic lanthanide ion. Then the magnetic molecular systems composed of lanthanide-lanthanide ions (4f-4f), lanthanide and transition metal ions (4f-3d), lanthanide ions and radicals (4f-radical) are described separately, in which the magnetic properties come from the magnetic coupling interaction between lanthanide ions and other paramagnetic centers and exhibit the magnetic relaxation and magnetic ordering phenomenon. Finally, a simple outlook gives some clue of the development of lanthanide-based magnetic molecular materials in the future.

## 2 Magnetic relaxation of single lanthanide ion systems

Relaxation is a process, which involves a system at an equilibrium state going to a new equilibrium state after perturbation. The time between the two equilibrium states is called relaxation time. As to magnetic relaxation, the perturbation is the change of the magnetic field. Magnetic relaxation time  $\tau$  is used to describe the magnetic relaxation process. The AC susceptibility is usually measured for understanding the magnetic relaxation phenomenon, which can be expressed as:

$$\chi_{AC}(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (3)$$

$\chi'$  is the in phase response with the driven field  $H(t)$ , which is called magnetic dispersion, and  $\chi''$  is the out of phase one which describes the energy absorption from the field, and is always referred to as magnetic absorption. AC susceptibility is a function of frequency, which means, at a certain temperature, a series of in phase and out of phase susceptibility can be obtained by scanning the frequency. The plot of the series of  $\chi''$  versus  $\chi'$  is Argand diagram<sup>[4]</sup>, which is a semicircle if only one relaxation process happens.

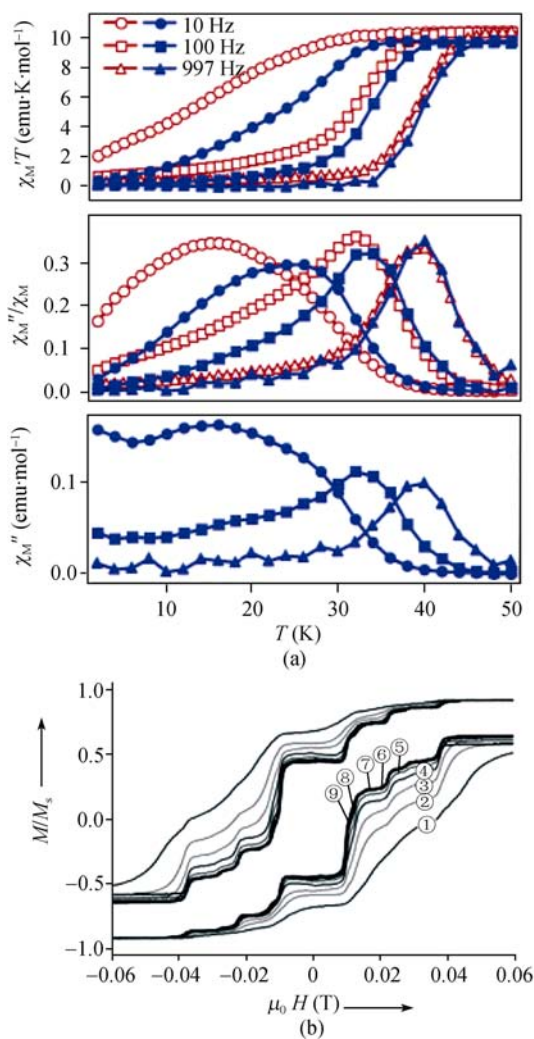
Two kinds of interesting magnetic relaxation phenomena are found in magnetic molecular materials containing only one magnetic lanthanide ion, single-ion magnet and field dependent relaxation phenomenon. They are both briefly reviewed in the following section.

### 2.1 Single-ion magnet

In 2003, Ishikawa discovered that some of lanthanide

phthalocyanine complexes exhibit an extremely slow relaxation rate so that the electronic magnetic moment of the system is fixed to a certain direction. There is no magnetic ordering observed due to the negligible inter-molecular interaction<sup>[5]</sup>. This kind of molecules is defined as single-ion magnet (SIM).

The first SIM found by Ishikawa is bis (phthalocyaninato) terbium or dysprosium anion complex which has a double-decker structure. AC susceptibilities as a function of temperature were measured on polycrystalline powder sample of  $[\text{Pc}_2\text{Tb}]^-\cdot\text{TBA}^+$  where  $\text{TBA}^+ = (\text{C}_4\text{H}_9)_4\text{N}^+$ . The  $\chi_M''/\chi_M'$  reaches the maximum at 15, 32 and 40 K with the frequency of 10, 100 and 997 Hz, respectively (the red plots in Figure 1(a)). The measurement for a diluted sample of diamagnetic iso-structural yttrium complex  $[\text{Pc}_2\text{Y}]^-\cdot\text{TBA}^+$  shows that the  $\chi_M''/\chi_M'$  peaks remained (the solid plots in Figure 1(a)).



**Figure 1** Frequency dependence of  $[\text{Pc}_2\text{Tb}]^-\cdot\text{TBA}^+$  (a) (Reprinted with permission from ref. [6], copyright 2003, American Chemical Society).

This clearly proves that the slow magnetization relaxation is the single molecular property of  $[\text{Pc}_2\text{Tb}]^-$ , rather than resulting from intermolecular interactions and magnetic ordering. By magnetic measuring of micro-SQUID, quantum tunneling effect was observed in the  $[\text{Pc}_2\text{Tb}]^-\cdot\text{TBA}^+$  complex<sup>[6]</sup> (Figure 1 (b)). These measurements all indicate the coordination compound containing single lanthanide ion shows the magnet-like slow magnetization relaxation behavior.

In order to find the source of slow magnetization relaxation, further investigation on the electronic structure of the compound<sup>[7,8]</sup> is performed. It reveals that the electron sub-structures splitting induced by the ligand field effect makes Orbach relaxation process possible. In the Tb complex<sup>[9]</sup>, the lowest substates formally correspond to  $J_z = \pm 6$ , which are the maximum and minimum values and correspond to the “spin-up” and “spin-down” states in the  $J = 6$  ground multiplet (Figure 2, left). It means that the complex has strong uniaxial magnetic anisotropy, which is also necessary for a single-molecule magnet. Arrhenius analysis shows the two-phonon Orbach process is dominant in the temperature range 25–40 K. The energy barrier through which the Orbach process occurs is estimated to be  $2.6 \times 10^2 \text{ cm}^{-1}$  (Figure 2 right). This energy separation is close to the energy difference between the lowest and the second lowest sublevels, supporting the dominance of the Orbach process.

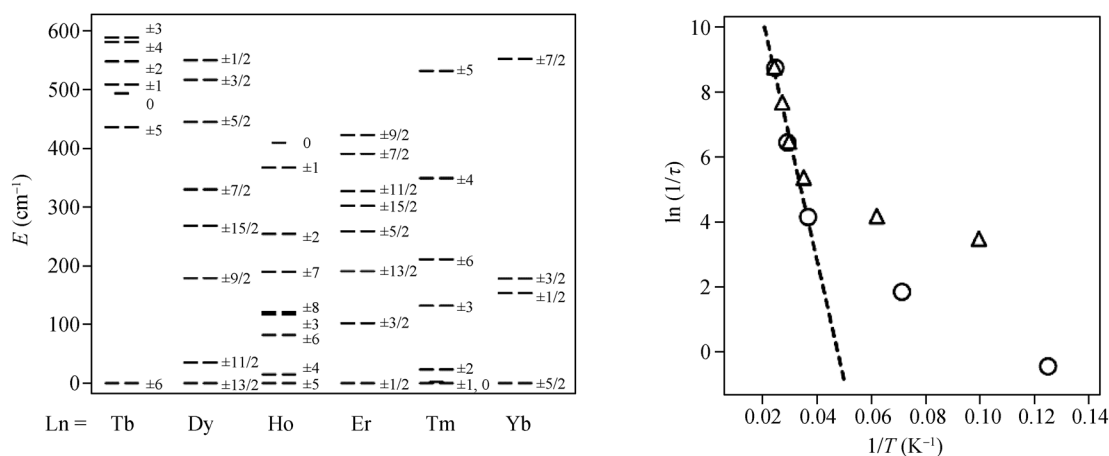
Generally speaking, stronger ligand field leads to larger splitting of electron energy spectrum, which will produce higher temperature  $\chi_M''/\chi_M'$  peak. This has been verified by oxidation of  $[\text{Pc}_2\text{Tb}]^-$  to  $[\text{Pc}_2\text{Tb}]$ , the peak of  $\chi_M''/\chi_M'$  against temperature of new compound shift

from 40 K to 52 K<sup>[10–12]</sup>. The quantum tunneling effect could be explained by the coupling of electron spin moments, orbit angular moments, nuclei spin moments by the disturbance of hyperfine interaction term  $A_{\text{hf}}J \cdot I$  and the nuclear quadrupole interaction term  $P\{I_z^2 - 1/3I(I+1)\}$ <sup>[13,14]</sup>.

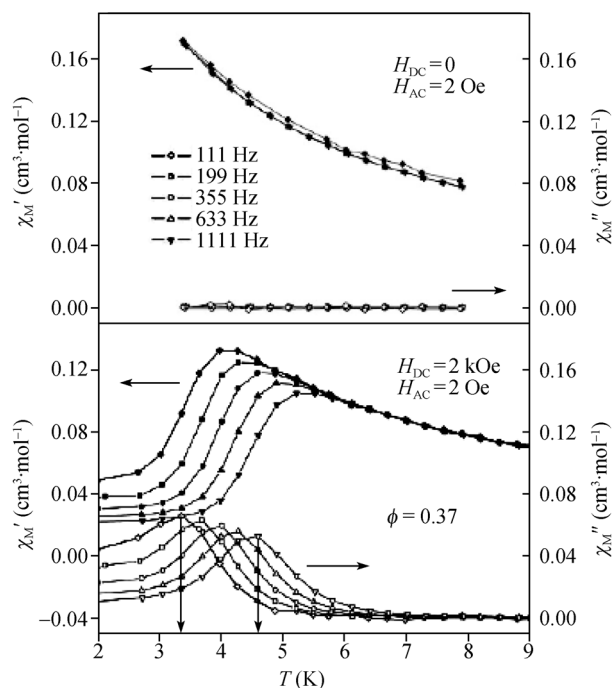
The anisotropy of the double-decker lanthanide compound comes from the shape of ligand field which is different from regular SMMs and SCMs. It should be noted that the coordination polyhedron is mostly anti-square, and relaxation phenomena in single lanthanide ion is also discovered in some other systems<sup>[15,16]</sup>.

## 2.2 Field dependent relaxation phenomenon in isolated lanthanide systems

In 2001, Gao and coworkers discovered a dc field dependent relaxation phenomenon in isolated lanthanide systems which is quite different from the one in normal spin glass or superparamagnets<sup>[17]</sup>. The dc magnetic susceptibility down to 2 K of compound  $[\text{NdCo}(\text{bpym})(\text{H}_2\text{O})_4(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , where bpym = 2,2'-bipyrimidine and Co is diamagnetic ion, shows no long range magnetic ordering existing in this isolated lanthanide molecule. However, unexpected ac susceptibility behavior was found in the presence of an applied field of 2000 Oe (Figure 3). In fact, measurements at a zero field showed normal paramagnetic behavior without slow relaxation, but it emerged on the contrary in the presence of a dc field. This behavior was tentatively regarded as the attribution of the spin frustration which is incrementally unveiled by the external magnetic field<sup>[18]</sup>. However, because the coupling between  $\text{Nd}^{3+}$  ions (1 nm separation) should be very weak, it is essentially an “isolated



**Figure 2** The structure configurations of  $[\text{Pc}_2\text{Ln}] \cdot \text{TBA}^+$ , where  $\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ ; and Arrhenius analysis for  $[\text{Pc}_2\text{Tb}] \cdot \text{TBA}^+$  (Reprinted with permission from ref. [9], copyright 2004, American Chemical Society).



**Figure 3** Frequency dependence of ac susceptibility at 0 and 2 kOe dc bias field for compound  $[\text{NdCo}(\text{bpy})(\text{H}_2\text{O})_4(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ . The filled symbols are for the in-phase component  $\chi_M'$ ; the open symbols are for the out-of-phase component  $\chi_M''$ . (Reprinted with permission from ref. [17], copyright 2001, Wiley).

ion” or “isolated ion like” system. In this respect, an explanation for the origin of dc-field-induced relaxation might be the lifting of the Kramer’s degeneracy by the magnetic field. Anyway, this seems to be a rather general phenomenon in many weak-coupled or isolated magnetic molecular systems<sup>[19,20]</sup>, and the question is still open and more efforts are expected.

Ishikawa discovered similar field induced magnetic relaxation in isolated lanthanide ions<sup>[21]</sup>. By serial measurement of ac susceptibility of  $[\text{N}(\text{C}_2\text{H}_5)_4]^{3+}[\text{Ln}(\text{dipic})_3]^{3-}$ , where dipic = pyridine-2,6-dicarboxylate, Ln = Tb, Dy, Ho, Er, Tm and Yb, none of the six complexes showed magnetization relaxation ranged  $10-10^3$  Hz above 1.8 K at a zero dc field. However, when a dc field of 1000 Oe is applied, the Dy, Er and Yb compounds show slow relaxation behavior. This phenomenon is explained to be caused by the elimination of a fast relaxation path, which is only effective for the Kramers doublet ground states in nearly zero field. At higher static fields, the remaining paths such as Orbach and/or direct processes govern the dynamics of the two-level systems composed of spin-up and spin-down states. The non-Kramers complexes were found to have a nondegenerate ground state

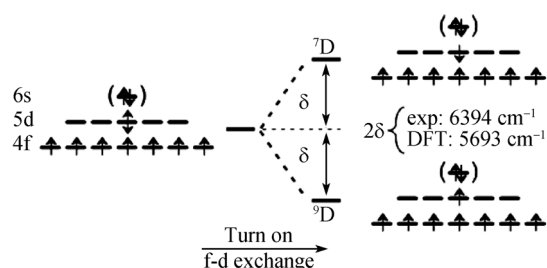
with large energy gaps from higher states, so fast magnetization relaxation happened and no slow magnetic relaxation existed.

### 3 Magnetic molecular systems with 4f-4f magnetic coupling interactions

From the viewpoint of magnetic carriers, lanthanide ions have not only possible large spin moments associated with spin unpaired electrons, but also large orbital moments coming from unquenched orbital angular momentum, which both originate from the internal nature of the valence f orbitals. Compared with the transition metal ions, the spin carriers used in many magnetic molecular materials, all paramagnetic lanthanide ions except for Gd(III) and Eu(II) with  $f^7$  electron configuration have orbitally degenerate ground states, which are further split by spin-orbit coupling and ligand field effects. Therefore, the magnetic properties of lanthanide containing materials are much influenced by the large spin-orbit coupling and orbital magnetic moment contribution, so few studies have been carried out on 4f-4f systems except for  $4f^7$ - $4f^7$  complex for theoretical difficulties.

#### 3.1 Magnetic coupling in Gd(III)-Gd(III) systems

Different from the unpaired d electrons of transition metal ions and s, p electrons of organic radicals, the unpaired f electrons of lanthanide ions are highly contracted and energetically shielded deeply by outer 5d, 6s shells. Therefore, the direct magnetic interaction between  $4f^7$ - $4f^7$  electrons is very weak, the value of coupling constant  $J$  is normally smaller than  $1\text{ cm}^{-1}$ <sup>[22]</sup>. Different from the indirect pathway involving the 4f localized electrons and conduction electrons responsible for the magnetic ordering of rare-earth intermetallic compounds, the magnetic interaction is mediated by the spin



**Figure 4** Electronic splitting of the Gd atom as a function of 4f-5d exchange perturbation (Reprinted with permission from ref. [23], copyright 2006, American Chemical Society).

polarized 5d, 6s valence electrons. To a good approximation, the  $4f^7$  exchange field can be regarded as a kind of contact effect<sup>[23]</sup>, which only exerts its influence on the orbitals centered on Gd atom. This local character of  $4f^7$  exchange field can be treated by a simple perturbative molecular orbital (PMO) model<sup>[23]</sup> and accounts for the perturbation of the  $4f^7$  cores exerting on electrons that reside in molecular orbitals with 5d and 6s characters.

Figure 4 illustrates how the potential from the  $4f^7$  core affects electrons with 5d and 6s characters of the Gd atom. At the left side of this figure, an “unperturbed” system is depicted wherein the valence d electron experiences an average exchange potential from the half-filled 4f shell, so the d electron has no preferred spin orientation. Upon application of the exchange field, the spin aligned with (or against) the 4f spins is stabilized (or destabilized) by the energy  $\delta$ . For a Gd atom,  $2\delta$  is just the difference between the  $^9D$  ground state and the first excited state  $^7D$ . These exchange interactions are intrinsically “ferromagnetic”, favoring parallel alignment of the 4f and 5d spins<sup>[23]</sup>.

Since the magnetic interactions are commonly weak, Gd(III)-Gd(III) systems are less studied in the synthetic chemistry. Some oxygen (from carboxylate, phenoxide ligand, and so on) bridged dinuclear Gd(III) complexes are reported and exhibit weak antiferromagnetic<sup>[24,25]</sup> and ferromagnetic<sup>[26,27]</sup> interactions. The exchange coupling constants range from  $-0.198\text{ cm}^{-1}$  to  $0.21\text{ cm}^{-1}$  and are all much smaller than the values from Gd(III)-TM compounds. It turns to nearly zero  $0.006\text{ cm}^{-1}$  in some compounds<sup>[28]</sup>. Therefore, no magnetic ordering has been found.

### 3.2 Magnetic relaxation in pure 4f systems

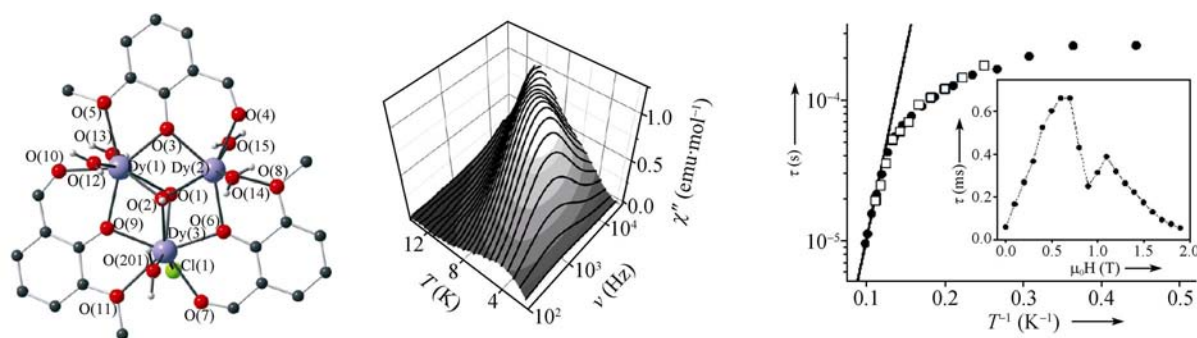
The magnetic relaxation phenomenon in lanthanide containing complexes covers a wide range, and single-molecule magnets (SMMs) are one of the most important families. Single-molecule magnet<sup>[29]</sup> is an object composed of molecules each of which behaves as a superparamagnet. Different from traditional magnets, SMMs cannot behave long range ordering, which means in SMMs, the unpaired spins cannot align parallel to each other in domains spontaneously. The interaction between clusters in SMMs can be negligible. We consider SMMs as a kind of magnet because they possess the capability of holding the spin state under blocking temperature ( $T_B$ ) just as traditional magnets do under

Curie ( $T_C$ , for ferromagnet) or Neel ( $T_N$ , for antiferromagnet) temperature. SMM clusters possess a high spin ground state ( $S_T$ ) and a high negative zero field splitting value ( $D$ ) due to high uniaxial magnetic anisotropy. Thanks to the two properties above, a large energy barrier ( $\Delta E$ ) between the two possible ground spin states exists ( $\Delta E = |D|S_T^2$  for integer  $S_T$ , and  $\Delta E = |D|(S_T^2 - 1/4)$  for half integer  $S_T$ ), which gives rise to SMMs holding the spin state under  $T_B$ .

There are few pure 4f clusters behaving as single-molecule magnets<sup>[30,31]</sup>. Powell reported two pure lanthanide SMMs in 2006<sup>[31]</sup>, both of which are  $Dy_3$  clusters. The two compounds are  $[Dy_3(\mu_3-OH)_2L_3Cl_2(H_2O)_4][Dy_3(\mu_3-OH)_2L_3Cl(H_2O)_5]Cl_5 \cdot 19H_2O$  and  $[Dy_3(\mu_3-OH)_2L_3Cl(H_2O)_5]Cl_3 \cdot 4H_2O \cdot 2CH_3OH \cdot 0.7CH_3CN$ , where  $HL = o$ -vanillin. Both structures consist of triangles of  $Dy^{3+}$  centers capped by to  $\mu_3$ -hydroxy bridges and they are almost in a plane (Figure 5, left). The dc susceptibilities of the two compounds show antiferromagnetic coupling between intratrimer spin centers as well as the gadolinium analogs. Dynamics of the magnetization studies are undertaken for both compounds. The ac susceptibilities of the complexes show strong frequency dependence below 20 K. The  $\chi_M''$  reaches peaks under 8 K, the positions of frequency dependence as typically observed for SMMs. However, the peaks are quite distorted with a shoulder structure (Figure 5, middle). Plotting of the relaxation time versus the inverse temperature reveals that the behavior is only linear at very high temperature, and the energy barrier is 61.7 K and the relaxation time constant is  $2.2 \times 10^{-8}\text{ s}$  (Figure 5, right). Although the ground state is almost non-magnetic, typical features of SMM behavior are observed for the thermally populated excited state. This observation indicates the presence of a large spin ground state appears not to be a necessary condition for observing slow relaxation of the magnetization.

## 4 Magnetic molecular systems with 4f-3d magnetic coupling interactions

The basic model for understanding the magnetic coupling properties was developed by Anderson about 50 years ago. He reduced the complex theory to only take account of simplified magnetic orbitals containing one unpaired electron. The magnetic interaction is antiferromagnetic when the two magnetic orbitals on different



**Figure 5** The structures of  $\text{Dy}_3$  and its relaxation behavior (Reprinted with permission from ref. [31], copyright 2006, Wiley).

centers have nonzero overlap. For example, Kahn applied the concept of nature magnetic orbital to analyze a dinuclear system and deduced the approximate magnetic coupling constant

$$J = 2k + 4\beta S \quad (4)$$

where  $k$  is two-electron exchange integral. It is always positive and favors the ferromagnetic interaction.  $S$  is the two-electron overlap integral ( $S$  is spin multiplet in other parts of this chapter, and means overlap integral only in this paragraph). For a molecular magnetic system,  $S$  and  $\beta$  are of opposite sign, so  $4\beta S$  is negative and favors antiferromagnetic interaction. Hu<sup>[32]</sup> made some further approximations and proposed the linear relationship of  $J$  and  $S^2$ , which is the square of overlap integral among HOMOS with  $\alpha$  and  $\beta$  spins. If the magnetic orbitals are orthogonal to each other, the overlap integral  $S$  tends to zero and the magnetic interaction should be ferromagnetic with unpaired electron possessing parallel configuration. There are also some other theoretical models to explain the magnetic properties of different materials, but almost all the simplified models of magnetic interaction regard the exchange or superexchange interaction as a form of weak bonding between two paramagnetic centers. This general model could understand the mechanism of magnetic coupling interaction between different kinds of paramagnetic centers, such as 3d transition metal ions, radicals and lanthanide ions.

#### 4.1 Magnetic coupling mechanism of $4f^7$ -3d systems

Mixed 3d-4f compounds are probably the most studied magnetic complexes containing lanthanide ions for their attracting properties in the field of molecular magnetism and coordination chemistry, such as single-molecule magnet and magnetic ordering materials.  $\text{Gd(III)}$ -3d systems are widely studied by experimentalists and theoreticians due to the presence of the largest possible

magnetic moment  $S=7/2$  and the lack of orbital contribution that facilitates the analysis of the magnetic properties. Among this kind of clusters, various binuclear and polynuclear complexes containing  $\text{Gd(III)}$ - $\text{Cu(II)}$  unit have pronounced magneto-structure correlations and exhibit the widespread ferromagnetic coupling between  $\text{Gd(III)}$  and  $\text{Cu(II)}$  ion with only several exceptions.

Through reacting tetradentate copper(II) Schiff's bases with  $\text{Gd(ClO}_4)_3$ , Gatteschi et al. obtained the first full characterized magnetic molecule composed of  $\text{Gd(III)}$ - $\text{Cu(II)}$  core<sup>[33]</sup>. Following this example, many  $\text{Gd(III)}$ - $\text{Cu(II)}$  systems were synthesized and characterized. For it is easier to deduce the magnetic coupling information between  $\text{Gd(III)}$  and 3d or p spin carriers than other rare earth ions with unquenched orbital moment, dinuclear  $\text{Gd(III)}$ - $\text{Cu(II)}$  complexes grow a big branch of the family of 3d-4f compounds. Costes et al. synthesized some  $\text{Gd(III)}$ - $\text{Cu(II)}$  compounds with varied coordination of  $\text{Cu(II)}$  ions. Magnetic measurements indicate almost all the couplings between  $\text{Gd(III)}$  and  $\text{Cu(II)}$  are ferromagnetic in Costes's series. The maximum value of the coupling constant is  $12.6 \text{ cm}^{-1}$  evaluated on the basis of the HDVV approach<sup>[34]</sup>. Only one example of weak antiferromagnetic interaction was observed with small negative  $J$  value  $-0.49 \text{ cm}^{-1}$ <sup>[36]</sup>. After analyzing the whole series of compounds, Costes et al. proposed a correlation between the magnitude of the magnetic interaction and the exponential of the dihedral angle between two halves ( $\text{Gd-O-Gd}$  and  $\text{O-Cu-O}$ ) of the bridging core (listed in Table 2). This is verified by the theoretical calculations performed by Ruiz<sup>[35]</sup>.

The abundant geometry structures and magnetic measurements stimulate the structure-magneto correlation studies on the  $\text{Gd(III)}$ - $\text{Cu(II)}$  complexes. Ruiz<sup>[35]</sup> found that the exchange coupling constant seemed to be



**Table 2** Structural data of the Gd(III)-Cu(II) complexes, Cu-O-Gd-O torsion angle and experimental  $J$  exchange coupling constants

	Cu-O-Gd-O (°)	$J_{\text{exp}}$ (cm <sup>-1</sup> )	Ref.
CuLiGd(NO <sub>3</sub> ) <sub>3</sub>	38.3	-0.49	[36]
Gd(hfa) <sub>3</sub> Cu(salen)	32.99	0.4	[37]
Cu(salabza)Gd(hfac) <sub>3</sub>	34.28	0.8	[38]
Cu(salen)Gd(pta) <sub>3</sub>	23.72	1.21	[39]
LCuGd(NO <sub>3</sub> ) <sub>3</sub> ·Me <sub>2</sub> CO	4.05	1.3	[40]
Cu(ehphi)Gd(hfac) <sub>3</sub>	30.78	1.91	[41]
CuGd(hmp) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	15.32	3.36	[42]
[CuGd(ems)(NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O] Cu(ems)	17.77	3.76	[43]
LCuGd(NO <sub>3</sub> ) <sub>3</sub> ·CH <sub>3</sub> OH	23.31	4.33	[44]
LCu(C <sub>3</sub> H <sub>6</sub> O)Gd(NO <sub>3</sub> ) <sub>3</sub>	13.52	4.8	[45]
LCuGd(NO <sub>3</sub> ) <sub>3</sub>	14.12	4.98	[46]
LCu(H <sub>2</sub> O)Gd(NCS) <sub>3</sub> ·Me <sub>2</sub> CO	15.44	5.5	[47]
LCuGd(NO <sub>3</sub> ) <sub>3</sub> ·Me <sub>2</sub> CO	9.6	5.6	[48]
LCuGd(NO <sub>3</sub> ) <sub>3</sub> ·Me <sub>2</sub> CO	10.15	7.0	[49]
LCuGd(NO <sub>3</sub> ) <sub>3</sub> ·Me <sub>2</sub> CO	10.05	7.3	[50]
LCuGd(NO <sub>3</sub> ) <sub>3</sub> ·Me <sub>2</sub> CO	9.29	7.4	[51]
LCuGd(NO <sub>3</sub> ) <sub>3</sub>	7.45	7.6	[52]
LCuGd(NO <sub>3</sub> ) <sub>3</sub>	3.36	8.08	[53]
LCuGd(NO <sub>3</sub> ) <sub>3</sub> ·Me <sub>2</sub> CO	8.96	8.63	[54]
[LCuCl <sub>2</sub> Gd(H <sub>2</sub> O) <sub>4</sub> ]Cl·2H <sub>2</sub> O	1.38	10.1	[55]
LCuGd(NO <sub>3</sub> ) <sub>3</sub>	5.5	10.8	[34]
LCuGd(NO <sub>3</sub> ) <sub>3</sub>	1.61	12.6	[34]

directly related with the Cu-O-Gd-O torsion angle based on DFT+BS calculations. Therefore, the ferromagnetic coupling becomes stronger for planar CuGdO<sub>2</sub> frameworks. The analysis of the overlap integrals for the 3d-4f interactions confirms such magnetostructural correlation due to an increase of the overlap for the non-planar structures, and consequently a larger antiferromagnetic contribution.

Gatteschi<sup>[56,57]</sup> proposed spin polarization mechanism, which owes to the orbital interaction between the 6s orbital of Gd and delocalization tails of the 3d orbital of Cu on the ligand. In this scheme, it is considered that the most important contribution comes from the overlap of the magnetic orbital of copper(II) with the empty d or s orbitals of gadolinium(III). Therefore, a fraction of unpaired electron is transferred into the empty orbitals and electrons parallel to each other according to the Hund's rule. Kahn<sup>[58]</sup> gave an alternate explanation that attributes the ferromagnetic coupling to the interaction between the Gd(III)-Cu(II) ground state configuration and

excited state configuration arising from the occupied 3d(Cu) → vacant 5d (Gd) electron transfer. Chen<sup>[59]</sup> reported the spin density maps and Mulliken-type population analysis also on the basis of the DFT+BS calculation, and interpreted the magnetic coupling as a spin delocalization from the copper center and a spin polarization from the gadolinium center, but gave no discussion about the role of 6s vs. 5d polarization mechanisms.

These magnetic coupling mechanisms of Gd(III)-Cu(II) system are further discussed by Hirao based on their state-of-art CASSCF and CASPT2 calculations<sup>[60]</sup>. They concluded that the ferromagnetic gap is intrinsic to the Cu(II)-Gd(III) pair but appears with a low magnitude for the naked dimer. The pure ligand field (electrostatic and polarization effects, without covalence) slightly increases the ferromagnetic gap. The spin polarization picture is supported by the computation experiments based on CASSCF method, involving the ligand and the 5d orbitals of Gd(III). From the view of state-of-art calculation, the polarization mechanisms of Kahn and Gatteschi are not mutually contradictory, but interconvertible by appropriate transformations of the magnetic orbitals, thereby adjusting the portion of pure Cu(3d) and ligand tails, in the active orbital that interacts with Gd(6s) or Gd(5d). The magnetic orbital analysis shows the orbital orthogonal exchange pathway transmits the ferromagnetic interaction in this kind of complexes.

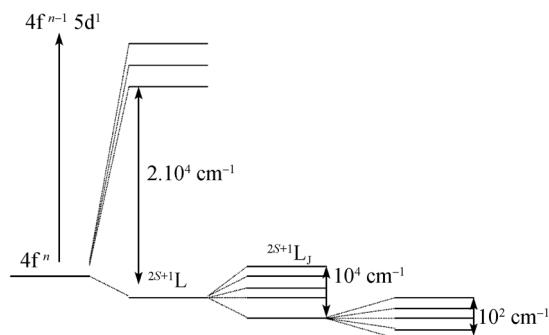
Similar compounds with Cu(II) ions replaced by other transition metal ions are less documented and characterized. The magnetic couplings have no strong tendency to be ferromagnetic and no obvious magneto-structure correlation as Gd(III)-Cu(II) systems. It seems that the magnetic coupling properties are mainly governed by the nature of the chemical linker between the spin carriers, but not always right either. For example, ferromagnetic couplings happened for Mn(III)<sup>[61]</sup>, Fe(II)<sup>[62]</sup>, Co(II)<sup>[63]</sup> and Ni(II)<sup>[64–66]</sup> when the bridges between Gd(III) and TM ions were oxygen atoms of a series of Schiff base derivatives. However, both ferro- and antiferromagnetic interactions were found for paramagnetic V(IV) ions<sup>[67,68]</sup>. If a CN ligand was selected as the bridge, antiferromagnetic interactions were found for Gd(III)-Cr(III) and Gd(III)-Fe(III) compounds<sup>[69–71]</sup>.

## 4.2 Magnetic coupling in 4f-3d systems with orbital moment contribution

Besides the spin magnetic moment, orbital contribution

and the ligand field can also affect the magnetic properties of Ln(III) containing compounds. For a lanthanide ion with  $4f^n$  configuration, the ground state energy is split by inter-electronic repulsion in spectroscopic terms, the one with the highest spin multiplicity ( $2S+1$ ) is the lowest in energy according to Hund's rule of maximum spin multiplicity (Figure 6). Each of these terms is further split by the spin-orbit interaction into  $^{2S+1}L_J$  spectroscopic levels, with  $|L-S| \leq J \leq L+S$ . For a  $4f^n$  configuration with  $n < 7$  the ground level has the lowest  $J$  value, but for  $n > 7$  the ground state has the highest  $J$ -value. Now  $J$  replaced  $S$  becomes the good quantum number and should be taken into account when the magnetic properties of Ln(III) containing compounds are described. Each of these levels can be further split into Stark sublevels by the ligand field effect. Because of the shielding of the  $4f$  orbitals, the ligand field splitting is usually only a few hundreds of  $\text{cm}^{-1}$  and much smaller than that for the  $3d$  orbitals of transition metal ions. This energy scale is comparable with the  $k_B T$  and changes the population of sublevels from room to low temperature. Therefore, the orbital moment has unnegligible contribution to  $\chi_{\text{Ln}} T$  values. Obviously, the temperature dependence of  $\chi_{\text{Ln}}$  deviates from the Curie law at this time.

The magnetic properties originate from the intrinsic electron properties of lanthanide ions, and can be modulated by the surrounding ligand field and geometry symmetry of the compound. There is no general analytical model to simulate the orbital magnetic contribution of this kind of compounds. At the same time, the effect of orbital contribution to magnetic susceptibility is overlapped with the spin moment donation. Thus, it is difficult to analyze the overall magnetic behavior of

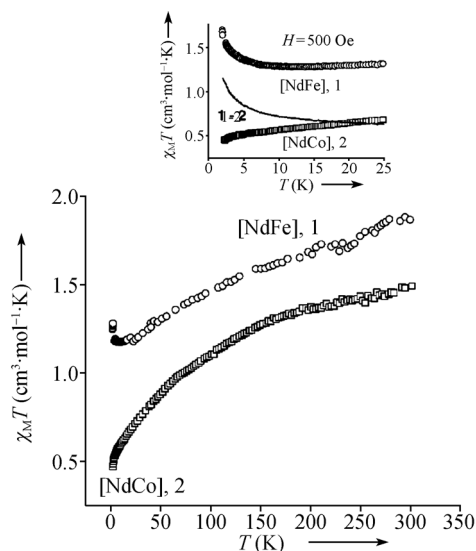


**Figure 6** Schematic energy diagram showing the relative magnitude of the interelectronic repulsion, the spin-orbit coupling, and ligand-field effects. (Reprinted with permission from ref. [2], copyright 2005, Wiley).

$4f^n$ - $3d$  containing compounds by a simple theoretical model. However, the knowledge of periodic table of elements provides a rather simple experimental approach to overcome the problem and give some qualitative insight into the interactions occurring between Ln(III) ions and other spin carriers. On the basis of the above discussion, this approach requires two compounds: one is an exchange coupling system including Ln(III) and another spin carrier; the other molecule is an isostructural compound in which the coordination sphere of the Ln center is identical, but the other spin carrier is replaced by diamagnetic ion. Then the nature of the magnetic interaction taking place in the exchange coupled system can be extracted by the comparison of the magnetic behaviors of the two compounds.

For instance, the magnetic studies on  $[\text{NdM}(\text{bpym})-(\text{H}_2\text{O})_4-(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  ( $\text{M}=\text{Fe}, \text{Co}$ ) coordination polymers synthesized by Gao's group<sup>[17]</sup> show the strength of this method. The temperature dependences of the  $\chi_M T$  for crystalline samples Nd-Fe(III) and Nd-Co(III) measured at 10 kOe and 500 Oe fields are shown in Figure 7. To exclude the contribution of spin-orbital coupling of the Nd(III) ion, the  $\chi_M T$  of Nd-Co(III) is subtracted from that of Nd-Fe(III). It is found that the difference (solid line in the inset of Figure 7) increases steadily with cooling, which indicates ferromagnetic interactions between the Nd(III) and Fe(III) ions happened.

Other examples have been reported for Ln(III)- $3d$  and



**Figure 7** Temperature dependence of  $\chi_M T$  for  $[\text{NdFe}]$  1 (○) and  $[\text{NdCo}]$  2 (□) at 10 kOe. The inset is the curve of  $\chi_M T$  versus  $T$  at 500 Oe. (Reprinted with permission from ref. [17], copyright 2001, Wiley)

Ln(III)-radical systems<sup>[72–74]</sup>. There is no general magneto-structure correlation relationship deduced from the reported compounds for limited number of studies. It is also restricted by the difficulties of theoretical modeling and calculation for the spin-orbit coupling.

### 4.3 Magnetic ordering of 4f-3d heterometallic systems

The magnetic systems mentioned above are mainly zero dimension clusters if only lanthanide ions are considered. By increasing the dimensionality of the geometry structures and magnetic coupling interactions, molecular materials can also exhibit the magnetic ordering properties as conventional magnets. Among these materials, the 4f-3d heterometallic complexes have attracted much attention as the tremendous development of molecular magnetism<sup>[2,3]</sup>.

A large family of heterometallic 4f-3d coordination polymers is constructed by using anionic polycyano complexes as building blocks<sup>[75]</sup>. Among them, paramagnetic  $[\text{M}(\text{CN})_6]^{3-}$  ( $\text{M} = \text{Fe}, \text{Cr}$ )<sup>[76]</sup> anions are the simple and direct building blocks to construct cyano-bridged heterometallic complexes, for the N end of cyanide is strong donor atom to link two metal ions. A rational strategy for the synthesis of the network is suitable combination of cyanide-contained precursors and other co-ligands as well as adjusting their stoichiometries.

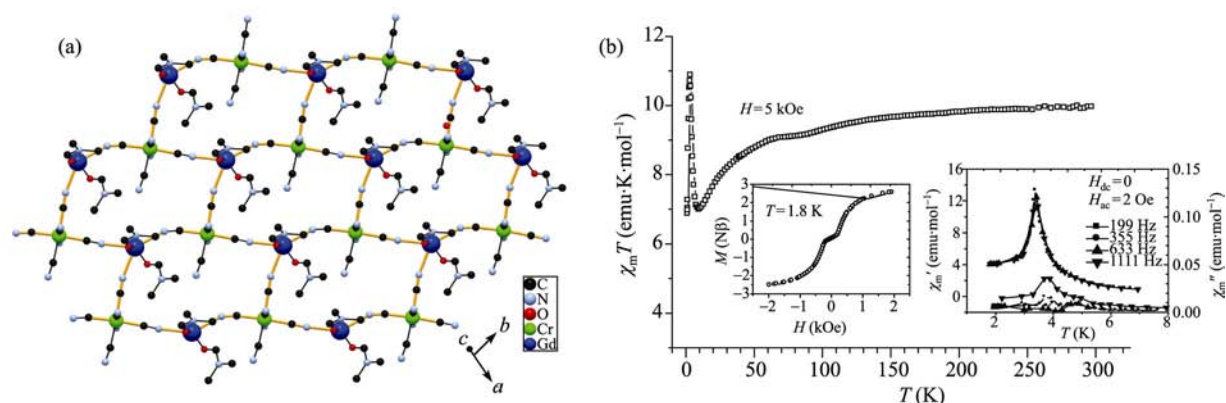
For example, adding DMF to the reaction system of  $\text{Ln}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  and  $\text{K}_3[\text{Cr}(\text{CN})_6]$  produced two 2D isostructural bimetallic complexes  $[\text{Ln}(\text{DMF})_2(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$  ( $\text{M} = \text{Gd}, \text{Sm}$ )<sup>[69,70]</sup>, which consist of brick-wall-like neutral layers with slightly distorted  $\text{Cr}_3\text{Ln}_3$  rectangles (Figure 8 (a)). For these two compounds, the magnetic interactions between the adjacent Ln(III) and

Cr(III) ions are antiferromagnetic couplings in two dimensions. The magnetic property measurements indicate the compounds behave as metamagnets (Figure 8(b)), which is also the first observation for two-dimensional cyano-bridged 3d-4f complexes. Due to the AF interaction between the ferrimagnetic layers, they reach a long-range antiferromagnetic ordering at 3.5 K and 4.2 K, respectively.

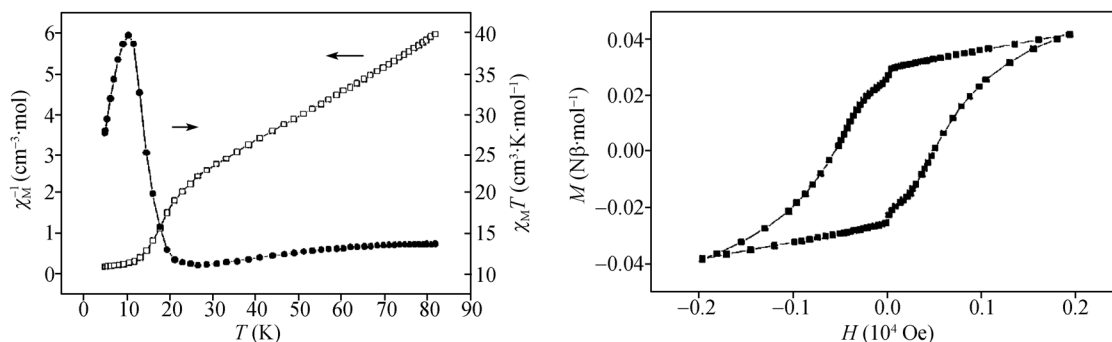
Inserting  $[\text{M}(\text{CN})_6]^{3-}$  ions to the 3d-4f compounds can form a few 3d-3d'-4f coordination polymers, which used the oligonuclear 3d-4f complexes as nodes<sup>[77–79]</sup>. Among this kind of compounds,  $[\text{Co}^{\text{II}}_2\text{Gd}^{\text{III}}\text{L}_2(\text{H}_2\text{O})_4]\{\text{Cr}^{\text{III}}(\text{CN})_6\} \cdot 2\text{H}_2\text{O}$  [ $\text{H}_2\text{L} = 2,6\text{-di}(\text{acetoacetyl})\text{pyridine}$ ] is a 3D network exhibiting 3D ferromagnetic ordering with  $T_c = 15.4$  K. It is the highest critical temperature among PB analogues incorporating lanthanide ions.

The reaction of  $\text{K}_3\text{Mn}(\text{CN})_6$ , DMF and  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Tb}, \text{Dy}$  or  $\text{Er}$ ) affords cyano-bridged 1D coordination polymers,  $\text{Ln}(\text{DMF})_4(\text{H}_2\text{O})_2\text{Mn}(\text{CN})_6 \cdot \text{H}_2\text{O}$  ( $\text{TbMn}, \text{DyMn}$  and  $\text{ErMn}$ , respectively)<sup>[80]</sup>. In particular,  $\text{Er}(\text{DMF})_4(\text{H}_2\text{O})_2\text{Mn}(\text{CN})_6 \cdot \text{H}_2\text{O}$  is the only one among these compounds which exhibits long-range magnetic ordering. The DC temperature dependent magnetic behaviors (Figure 9) of compound  $\text{ErMn}$  are similar to those of compound  $[\text{SmFe}]_n$ . The critical temperature is determined to be 17.5 K by the  $\chi'(T)$  peak maximum. Figure 9 right provides the field-dependent magnetization hysteresis curve for  $\text{ErMn}$  complex under the applied magnetic field from  $-2000$  to  $+2000$  Oe at 5.7 K, which reveals a stronger coercive field  $H_c$  of 980 Oe and a remnant magnetization  $M_R$  of  $0.03 \text{ N}\beta \text{ mol}^{-1}$ .

So far, not plenty of 3D magnetic ordered lanthanide-



**Figure 8** (a) Brick-wall-like structure of  $[\text{Gd}(\text{DMF})_2(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$ . (b) Temperature dependence of  $\chi_M T$  for  $[\text{Gd}(\text{DMF})_2(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$ . Inset: left, isothermal magnetization at 1.8 K; right, real and imaginary AC susceptibilities in zero applied DC field and an AC field of 2 Oe at different frequencies. (Reprinted with permission from ref. [69], copyright 2001, American Chemical Society).



**Figure 9** Variable temperature (4–82 K) susceptibility (left) and hysteresis loop (right) for ErMn at 5.7 K. (Reprinted with permission from ref. [80], copyright 2001, Springer).

based molecular materials are obtained. However, the existing examples provide much experimental or theoretical knowledge and experience. The research of 3D magnetic ordered lanthanide-based molecular materials is still open for chemists and physicists.

#### 4.4 Magnetic relaxation in 4f-3d heterometallic systems

Below blocking temperature  $T_B$ , SMMs can relax to another ground spin state under thermal perturbation, and the relaxation time ( $\tau$ ) obeys the thermally activated Arrhenius law:

$$\tau(T) = \tau_0 \exp(\Delta E/k_B T) \quad (5)$$

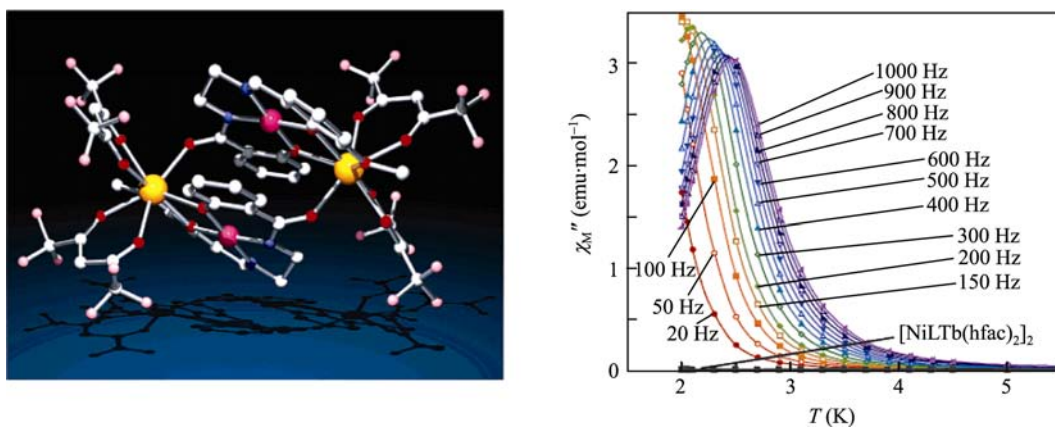
It can be easily found that, with larger energy barrier  $\Delta E$ , the relaxation time  $\tau$  becomes longer and the blocking temperature will be higher. Therefore, it is very important to increase the ground state spin value and uniaxial magnetic anisotropy. Because the relativistic effect is important for lanthanide ions, the strong spin-orbit coupling makes magnetic anisotropy a common property

for most of lanthanide ions. It is believed that introducing lanthanide ions into the molecules would exert a positive effect on the magnetic properties of the SMMs.

#### Single-molecule magnet including lanthanide ions

To design SMMs, the most frequently used lanthanide ions are heavy rare earth ions: terbium ( $\text{Tb}^{3+}$ ,  $f^8$ , ground state  $^7F_6$ ), dysprosium ( $\text{Dy}^{3+}$ ,  $f^9$ , ground state  $^6H_{15/2}$ ) and holmium ( $\text{Ho}^{3+}$ ,  $f^{10}$ , ground state  $^5I_8$ ), because of their large uniaxial anisotropy and large ground spin state.

The first example of 4f-3d containing SMMs is  $[\text{Cu-L-Tb}(\text{hfac})_2]_2$  cluster<sup>[81]</sup>, where  $\text{H}_3\text{L} = 1-(2\text{-hydroxybenz-amido})-2-(2\text{-hydroxy-3-methoxy-benzylideneamino})\text{-ethane}$ ,  $\text{Hhfac} = \text{hexafluoroacetylacetone}$ , and  $\text{Ln} = \text{Tb}^{3+}$  and  $\text{Dy}^{3+}$ . For  $[\text{Cu-L-Tb}(\text{hfac})_2]_2$  cluster, at 3 Oe oscillating field in the frequency range of 20–1000 Hz at a zero static field, the out of phase susceptibility shows frequency-dependent peaks (Figure 10), which indicates the slow relaxation of the magnetization happened. Through Arrhenius analysis, the energy barrier is 21 K and relaxation time constant is  $2.7 \times 10^{-8}$  s.



**Figure 10** The structure of the  $[\text{Cu-L-Tb}(\text{hfac})_2]_2$  cluster and its relaxation behavior (Reprinted with permission from ref. [82], copyright 2004, American Chemical Society).

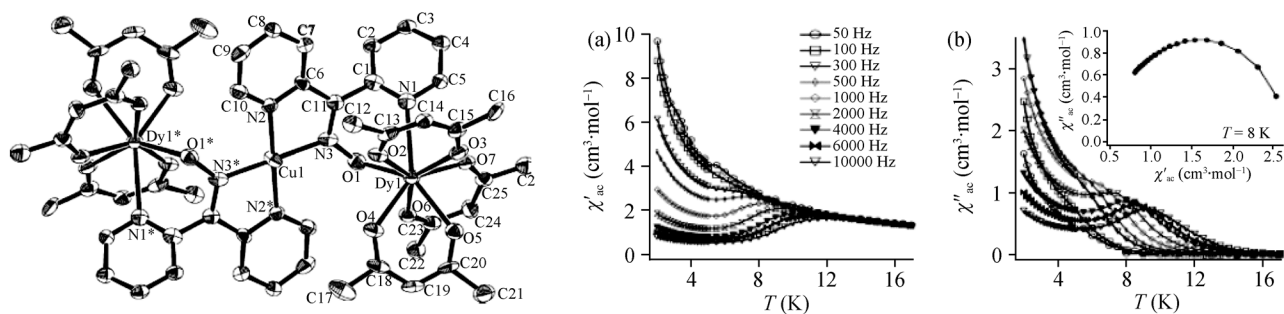
Another example of 4f-3d SMM is  $[\text{Dy}(\text{hfac})_3]_2\text{Cu}(\text{dpk})_2$ <sup>[82]</sup>, where dpk = di-2-pyridyl ketoximate. On taking the alternative current susceptibility measurement from 2 to 17 K at 50–10000 Hz, both the in phase and out of phase susceptibilities are found frequency dependent (Figure 11). The energy barrier is found to be 47 K and  $\tau_0$  is  $1.1 \times 10^{-7}$  s. Additionally, the authors plotted  $\chi_M''$  against  $\chi_M'$  as depicted in Figure 11 at 8 K from 50 to 10000 Hz, and the result is a semicircle which means a single relaxation process happened. Another increment of  $\chi_M''$  and  $\chi_M'$  is found below 6 K, and this kind of increment is also found in other systems<sup>[83–85]</sup>. It is supposed that intermolecular interaction in such low temperature region may give rise to the phenomenon.

Gadolinium ion possesses an  $f^7$  configuration and an  $^8S_{7/2}$  ground state. Principally, it is an isotropic ion and has no spin-orbit coupling effect. However, its big spin ground state  $S=7/2$  can produce overall big spin ground state of the 3d-4f clusters, and it is also an appealing paramagnetic center to construct SMMs<sup>[86]</sup>. The high-nuclearity Gd-Mn complex with the formula of  $[\text{Mn}^{\text{II}}_9\text{Mn}^{\text{II}}_2\text{Gd}^{\text{III}}_2\text{O}_8(\text{OH})_2(\text{piv})_{10.6}(\text{fca})_{6.4}(\text{NO}_3)_2(\text{H}_2\text{O})] \cdot 13\text{CH}_3\text{-}$

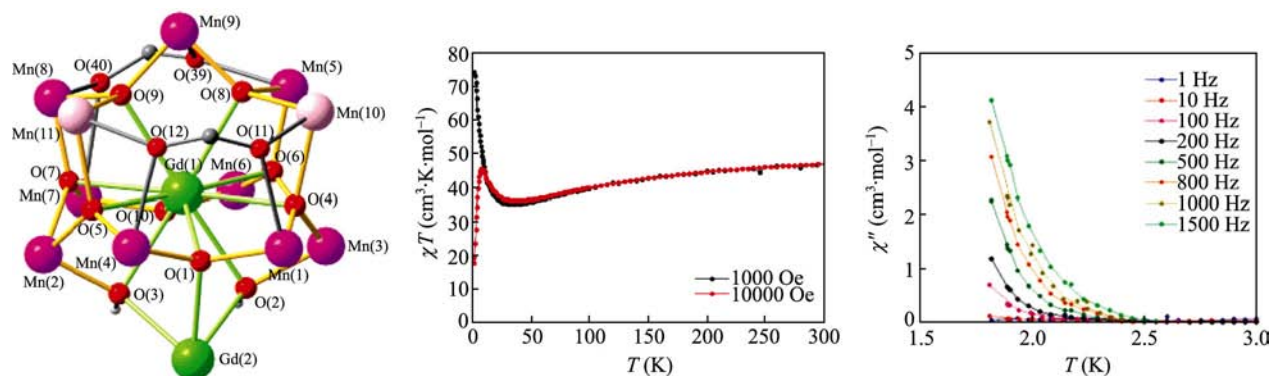
$\text{CN} \cdot \text{H}_2\text{O}$ , where pivH = *t*-BuCOOH, fcaH = 2-furan-carboxylic acid, can be described as a bell and the two Gd ions are the bell's clappers (Figure 12 left). The dc magnetic susceptibility of the complex measured at 1000 Oe reveals that it possesses a well-defined high-spin ground state at low temperature (Figure 12 middle). By taking ac susceptibility of the complex over 1–1500 Hz from 1.8 to 3 K, the out of phase susceptibility is frequency dependent (Figure 12 right), however, none of the curves reaches a peak at 1.8 K. The dc magnetization decay method<sup>[87,88]</sup> determined effective barrier 18.4 K and the relaxation time constant  $2 \times 10^{-12}$  s. As mentioned above,  $\text{Gd}^{3+}$  is a magnetic isotropic ion, the major anisotropy contribution comes from the  $\text{Mn}^{3+}$  ion, which is the one of the most important anisotropy source in the designation of SMMs. The anisotropy source can also come from the  $\text{Co}^{2+}$  ion in the  $\text{Gd}^{3+}$ -3d SMMs as in the compound  $[\text{L}_2\text{Co}_2\text{Gd}][\text{NO}_3] \cdot 2\text{CHCl}_3$ , where  $\text{LH}_3 = (\text{S})\text{P}[\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-2\text{-OH-3-OCH}_3]_3$ <sup>[89]</sup>.

#### Single chain magnet including lanthanide ions

Roy J. Glauber, the 2005 Nobel Prize winner in physics, predicted that slow relaxation can be observed in



**Figure 11** The structure of  $[\text{Dy}(\text{hfac})_3]_2\text{Cu}(\text{dpk})_2$  and the frequency dependence of AC susceptibility (Reprinted with permission from ref. [83], copyright 2006, American Chemical Society).



**Figure 12** The structure of  $\text{Mn}_{11}\text{Gd}_2$  cluster (left),  $\chi_M T$  versus  $T$  in 1000 and 10000 Oe field (middle) and the relaxation behavior (Reprinted with permission from ref. [87], copyright 2007, American Chemical Society).



one dimensional ferromagnetic Ising chain at low temperature 40 years ago<sup>[90]</sup>. This prediction became true when the first SCM was found in 2001<sup>[91]</sup>. In principle, one dimensional Ising chain is in paramagnetic state in all finite temperature ranges, and the long-range ordering can only be reached at zero Kelvin. However, if the magnetic coupling interactions between spin centers within the chain are strong enough but negligible between chains and the uniaxial anisotropy is big enough, the magnetic behavior of the chain will be similar to SMMs. Usually, the  $T_B$  of SCMs could be higher than that of SMMs because of its larger ground spin state value, and larger uniaxial anisotropy came from both the exchange and single ion anisotropy. It should be noticed that to design SCMs, inter-chain interaction should be avoided<sup>[92,93]</sup>. Although the 3d-4f or 4f-4f magnetic interaction is weaker than that of 3d-3d, lanthanide ions are still considered because of their large uniaxial magnetic anisotropy.

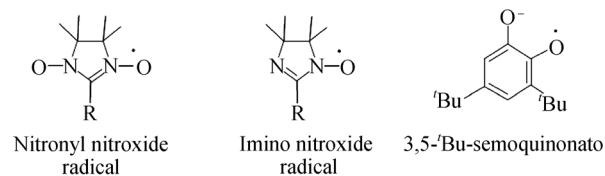
The first SCM reported by using rare earth ions as the anisotropic source is  $(LCu)_2Tb(NO_3)^{[94]}$ , where  $H_3L=2$ -hydroxy-*N*-2-[(2-hydroxyethyl) amino] ethyl benzamide). The frequency dependency of the  $\chi_M''$  is observed below 5 K for frequency ranging from 1 to 1000 Hz. Through Arrhenius analysis, the energy barrier is 28.5 K and relaxation time constant is  $3.8 \times 10^{-8}$  s. It should be noticed that the author failed to get the crystal structure of the compound and the formula is determined on the basis of elemental analysis.

## 5 Magnetic molecular systems with 4f-p magnetic coupling interactions

For the direct bonding between lanthanide ions and radicals, shorter interacting distance is reached than the spin carriers bridged by diamagnetic ligands, which is a favorable situation in transmitting exchange coupling interactions, and improves somewhat the strength of the exchange interaction in Ln ions containing compounds. Therefore, the 4f-radical (4f-p) system is another appealing area in the research of lanthanide containing magnetic molecular materials.

### 5.1 Magnetic coupling in 4f-p systems

Several Gd(III)-radical compounds were reported in which the organic parts are mainly nitronyl nitroxide radicals<sup>[95–97]</sup>, imino nitroxide radicals<sup>[98,99]</sup> and semiquinone<sup>[100,101]</sup> derivatives. The structures of radicals concerned are depicted in Figure 13.



**Figure 13** The radical structures of nitronyl nitroxide radical (NITR), imino nitroxide radical and semiquinone.

Interestingly, the magnetic coupling properties appear to be greatly influenced by the chemical nature of the organic radicals. For nitronyl nitroxide radicals and derivatives, the exchange interactions are mainly ferromagnetic and can be as large as  $6.1 \text{ cm}^{-1}$ <sup>[102]</sup> between lanthanide ions and radicals. This coupling intensity is comparable with the magnetic coupling between Gd(III) and transition metal ions. Attended by the strong magnetic coupling between radicals themselves, Gd(III)-radical complexes can reach magnetic ordering at low temperature. For compound  $Gd(Tp)_2(SQ)$ , where Tp is hydro-trispyrazolyl borate and SQ is 3,5-di-tert-butylsemiquinonato, the coupling constant  $J = -11.4 \text{ cm}^{-1}$  of Gd-semiquinone interaction is the maximum value among the magnetic coupling intensities between Gd(III) and other paramagnetic centers including lanthanide ions, transition metal ions and organic radicals. This unusually strong interaction has been proposed to reflect a rather strong chemical link between the two paramagnetic centers. Tetracyanoethylene (TCNE) and tetracyanodimethane (TCNQ) radicals are also effective spin carriers to couple with Gd(III) ions. It is worth mentioning that TCNQ can link the Gd(III) to form extended structure and behave as a ferrimagnet at low temperatures<sup>[103,104]</sup>.

### 5.2 Magnetic ordering of 4f-p molecular materials

Although molecular magnetic materials based on 3d metals and organic radicals are quite common, analogous 4f element compounds are relatively rare.

The organic radicals NITR have one unpaired electron which is equally shared by the two NO groups. As far as the magnetic exchange is concerned, they behave as a single atom with  $S = 1/2$ . They are usually employed as organic spin carriers, which can link the neighboring metal ions through their two NO groups, forming one-dimensional chains.

Among these compounds,  $Dy(hfac)_3NITet$  exhibits an overall antiferromagnetic coupling between  $Dy^{3+}$  and NITet radical, but undergoes magnetic phase transition

at ca. 4 K, ordering as a weak ferromagnet due to spin canting<sup>[105,106]</sup>. For comparison, Mn(hfac)<sub>2</sub>NITR has a similar chain structure and a strong intrachain anti-ferromagnetic coupling of ca. 400 K, reaching long range magnetic ordering at ca. 8 K. Er(hfac)<sub>3</sub>NITet shows magnetic phase transitions at temperatures ranging from 1.2 to 3.2 K. The relatively high critical temperatures for Ln(hfac)<sub>3</sub>NITet compounds may be essentially attributed to the strong antiferromagnetic exchange between the lanthanide ions mediated through the radicals.

Both TCNE and TCNQ are widely employed organic radicals to construct lanthanide-based molecular magnetic materials. Slow diffusion of deoxygenated water solutions of GdCl<sub>3</sub>·6H<sub>2</sub>O and Li[TCNQ] (1:1 ratio) yields crystals of {[Gd<sub>2</sub>(TCNQ)<sub>5</sub>(H<sub>2</sub>O)<sub>9</sub>][Gd(TCNQ)<sub>4</sub>·(H<sub>2</sub>O)<sub>3</sub>]}·4H<sub>2</sub>O<sup>[104]</sup>, which consist of alternating anionic and cationic layers perpendicular to the *c* axis, exhibiting different ratios of Gd(III) and TCNQ<sup>•−</sup> radicals, both of which are based on a 2D network of Gd(III) ions coordinated by TCNQ radical anions (Figure 14 left). The different ratios of Gd(III) and TCNQ<sup>•−</sup> in the two independent layers lead to the unusual existence of both cationic and anionic networks.

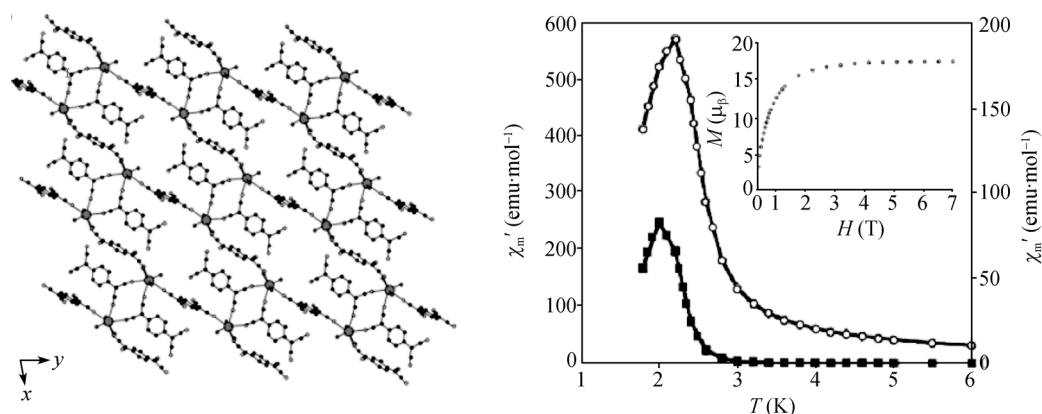
For this compound, susceptibility data fitting to Curie-Weiss law at high-temperature give Curie constant of 27.1 emu·K·mol<sup>−1</sup>, which is consistent with the expected value for three isolated Gd(III) ions (*S* = 7/2) and nine TCNQ<sup>•−</sup> radical anions (*S* = 1/2) (27 emu·K·mol<sup>−1</sup> for *g* = 2). The Weiss constant (*θ* = −5.07 K) is small and negative, indicative of antiferromagnetic coupling interactions between Gd<sup>3+</sup> and radicals. It is actually magneti-

cally three-dimensional with multiple interactions. In addition to the intra-layer interactions, including direct exchange (Gd-TCNQ) and superexchange (between TCNQ groups through the Gd bridges, and vice versa), there are also strong magnetic interactions between layers through the short p-p contacts between TCNQ units in adjacent layers. It can be clearly seen from AC magnetic susceptibility measurements (Figure 14 right) that the material exhibits an out-of-phase signal at *T*<sub>c</sub> = 3.5 K. This material is a ferrimagnet and behaves as a soft magnet without obvious hysteresis at 1.8 K. It is the first lanthanide-TCNQ magnet.

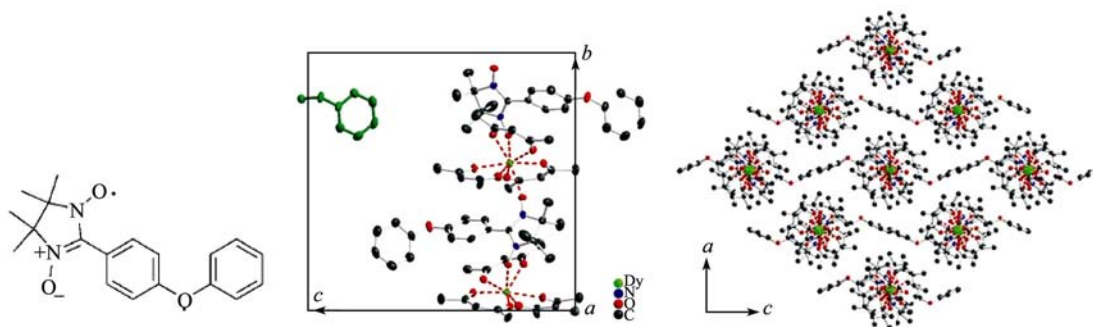
### 5.3 Magnetic relaxation in 4f-p systems

[Dy(hfac)<sub>3</sub>NIT(C<sub>6</sub>H<sub>4</sub> *p*-OPh)] is a 4f-p based SCM, where NIT(C<sub>6</sub>H<sub>4</sub> *p*-OPh) is a radical as shown in Figure 15<sup>[107]</sup>. The shortest Dy-Dy inter-chain distance is 10.76 Å, and only weak dipolar inter-chain interaction takes effect. By changing the ethyl into biphenyl substituent, the free volume between the chains is alternatively occupied by the biphenyl substituent, which is surrounded by the fluorine atoms to minimize any weak magnetic interactions between the radicals. In this way, the average volume according to per metal center increases from 881 to 1001 Å<sup>3</sup>, and more importantly, all different chains are separated as well. The shortest distance between two Dy centers grows from 10.76 to 11.35 Å (Figure 15).

The dc magnetic susceptibility measurement for a powder sample shows that *χ*<sub>M</sub>*T* reaches a minimum at 8.6 K and a rounded peak of 68.5 emu·K·mol<sup>−1</sup> at 3.6 K, which is a typical 1D behavior (Figure 16). The ac magnetic susceptibility measurement shows that *χ*<sub>M</sub>''



**Figure 14** Top view of the 2D anionic network (terminal TCNQ have been omitted for clarity) in {[Gd<sub>2</sub>(TCNQ)<sub>5</sub>(H<sub>2</sub>O)<sub>9</sub>][Gd(TCNQ)<sub>4</sub>·(H<sub>2</sub>O)<sub>3</sub>]}·4H<sub>2</sub>O (left); AC susceptibility data for {[Gd<sub>2</sub>(TCNQ)<sub>5</sub>(H<sub>2</sub>O)<sub>9</sub>][Gd(TCNQ)<sub>4</sub>·(H<sub>2</sub>O)<sub>3</sub>]}·4H<sub>2</sub>O, in-phase (empty circle), out-of-phase (solid square). Inset: plot of *M*-*H* performed at 1.8 K (right). (Reprinted with permission from ref. [104], copyright 2003, Wiley).



**Figure 15** Structures of the compound and ligand (Reprinted with permission from ref. [108], copyright 2005, Wiley).

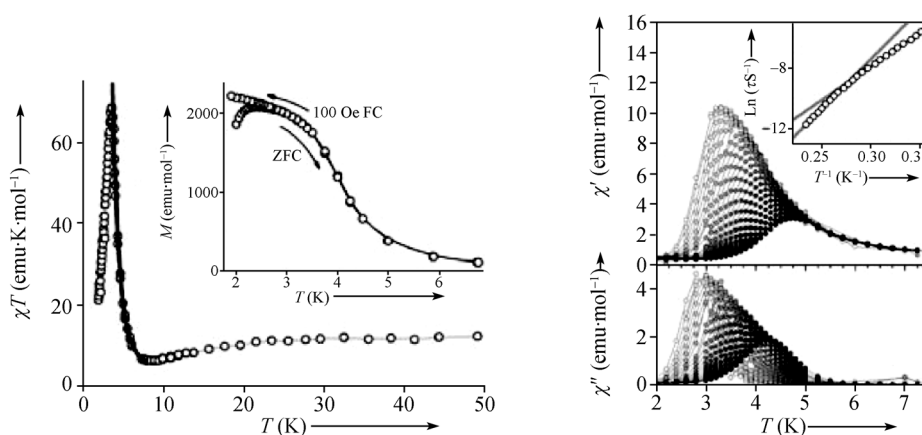
reaches peaks under 4.2 K ranging from 2.5 to 20000 Hz. The Arrhenius plot extracted from ac measurement shows the presence of a crossover between two different activated regimes, both of which give best-fits with physical  $\tau_0$  values ( $5.6 \times 10^{-10}$  and  $1.9 \times 10^{-12}$  s for the low- and high-temperature regimes, respectively) and two different barriers (42 and 69 K, respectively) (Figure 16). The two different activated regimes of SCMs may be due to finite-size effects.

## 6 Outlook

For the complicated electronic structures of ground and low excited states, lanthanide ions are good spin carriers to construct magnetic molecular materials. Various magnetic compounds with 4f-3d, 4f-p, 4f-4f exchange coupling interactions are synthesized and exhibit diverse magnetic phenomena, such as magnetic ordering, single-molecule magnet behavior, and single-chain magnet behavior. In addition, different from the magnetic materials composed of transition metal ions, there exist single-ion magnet and field dependent relaxation phenomenon, which are originated from the intrinsic property of lan-

thanide ions. These two special kinds of magnetic materials show the strength of lanthanide ions in constructing magnetic molecular materials. However, studies on magnetic molecular materials containing lanthanide ions are far from developed and plenty of questions and opportunities still exist.

First, besides the spin magnetic moment, the orbital moment contribution is also important in the determination of the magnetic properties of lanthanide ions. The large spin-orbit interaction complicates the properties of ground and low excited state of lanthanide ions, and puts the essence of magnetism of lanthanide ions in the mist. Although the compensation method can give some information on the magnetic coupling of 4f system indirectly, it is still not enough for understanding the mechanism of the interactions between 4f electrons and other spin carriers. Therefore, comprehension of the spin-orbit effect and orbital moment contribution to the magnetic properties, especially control the resulted magnetic anisotropy of lanthanide ions, is a great challenge theoretically and experimentally in the designation of magnetic molecular materials, for example, questions



**Figure 16** The dc and ac magnetic susceptibility of  $[\text{Dy}(\text{hfac})_3]\text{NIT}(\text{C}_6\text{H}_4\text{ } p\text{-OPh})$  (Reprinted with permission from ref. [108], copyright 2005, Wiley).



such as why Dy(III) ion appears so frequently in SMMs, SCMs and single-ion magnets, and whether it is possible to control the magnetic anisotropy through tuning up the symmetry and strength of the ligand field.

Second, the critical temperatures of magnetic ordering reported so far are all in low temperature range, although magnetic ordering does exist in some lanthanide ions containing systems, such as 4f-3d, 4f-4d, and 4f-p complexes. This tendency is attributed to the weak exchange coupling between lanthanide ions and transition metal ions or organic radicals. Therefore, how to enhance the strength of magnetic coupling interactions is another appealing question in the molecular-magnetism research of lanthanide containing systems, for example, searching for new bridge ligand which can transmit stronger magnetic coupling, increasing the efficiency of linker in constructing magnetic compounds from low dimension to high dimension, and utilizing the character of spin frustration are all effective methods to get higher critical

temperature of magnetic ordering or to find new magnetic phenomenon. Especially, it is worthwhile to focus on the power of the strong delocalized, even conducting electrons in transmitting magnetic exchange coupling when designing magnetic materials with high ordering temperature, such as the situation in mixed valence systems.

Finally, for the aim of industrial application, assembling the magnetic molecules onto different substrates is another important task but less studied. Understanding the interactions between materials and substrates when manipulating the spin and electronic state of the target system is highly concerned with the application of magnetic molecular materials in the manufacture of molecule based memory devices, quantum computing, and spintronics devices<sup>[108]</sup>.

*The authors acknowledge coworkers and collaborators whose names appear in the references.*

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