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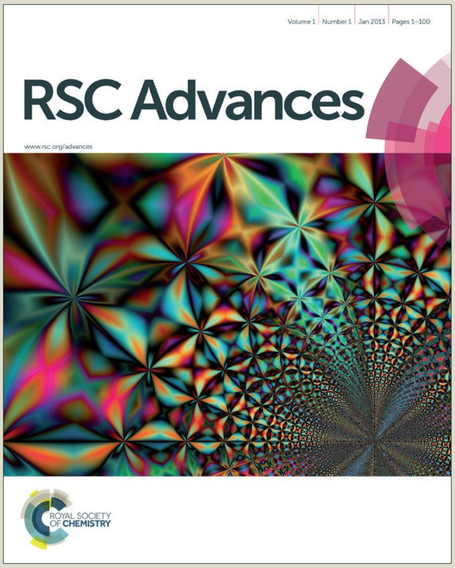

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A family of rare earth complexes with chelating furan biradicals: syntheses, structures and magnetic properties

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Abstract

The combination of anisotropic Ln^{III} ions and furan biradical results in six complexes, namely, $[Ln(hfac)_3(NITFu\textit{m}bis)]_2$ (Ln = La(**1**), Ce(**2**), Pr(**3**), Gd(**4**), Tb(**5**), Dy(**6**); hfac = hexafluoroacetylacetone; NITFu*m*bis = (2,5-bis-(1′-oxyl-3′-oxido-4′,4′,5′,5′-tetramethyl-4,5-hydro-1H-imidazol-2-yl) furan). Compounds **1-3** are isostructural and crystalize in *P*-1 space group, while compounds **4-6** crystalize in $P2_1/c$ space group. For all the six complexes, the coordination number around the lanthanide ion is eight, and the polyhedron is in distorted 4,4-bicappped trigonal prism or triangular dodecahedron coordination geometry (D_{2d} or C_{2v} symmetry) finished by three bischelate $hfac^-$ ligands and one bidentate radical ligand. DC magnetic studies show that the Ln(III) ions interact antiferromagnetically with the directly bonding nitronyl nitroxide radicals in all the six complexes. Especially, for complex **4**, intramolecular antiferromagnetic interaction between the two radicals is observed with the largest j ($j_{\text{Rad–Rad}}$ = -24.89 cm^{-1}) ever reported in Ln(III)-radical systems, and at low temperature, intermolecular ferromagnetic interaction also plays an important role. In addition, complex **6** exhibits field-induced single-molecule magnet (SMM) behavior.

Keywords: Furan nitronyl nitroxide radical**,** Lanthanide complexes**,** Magnetic property**,** Single-molecule magnet

Introduction

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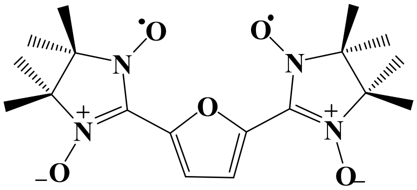
In the last decades, molecular magnetism has attracted continuous interest because it provides genuine opportunities for both the synthesis of new compounds with unconventional properties (especially if following a rational design),[1–3] and for exploring the fundamental aspects of magnetic interactions and magneto-structural correlations in molecular systems, which will further aid the design of new molecular magnets.[4,5] One goal in this field is the synthesis of whole family of systems, which provides a clear indication of the patterns of magnetic interaction and allowed for the rationalization of the magnetic coupling mechanism.[6] Recently, lanthanide-based systems is becoming increasingly interested, due to their large number of unpaired *f*-electrons and large intrinsic magnetic anisotropy.[7–9] Consequently, lanthanides ions, especially heavy lanthanide ions, have become good candidates for the construction of SCMs and SMMs.[10-12] However, because the effective shielding by the outer-shell electrons and the rather large and anisotropic magnetic moments of the rare-earth metal ions, which makes the nature of the magnetic interactions between Ln(III) ions and other spin carries difficult to be treated, and has become an area of research interest.[13] Therefore, synthesizing more lanthanide complexes and systematically studying their magnetic nature is becoming more and more significant.

In recent years, lanthanide compounds involving organic radicals (2*p*-4*f*) have attracted much attention, because several of these lanthanide compounds have been found to exhibit single-molecule[11d,14] and single-chain magnets behavior[12b,15] due to the Ising anisotropy of their 4*f* centers, and the big strength of magnetic interaction promoted organic radicals. Furthermore, the researchers showed that the properties and structures of the lanthanide-radical complexes are affected greatly by modifying the radical ligand.

In order to explore how the electron cloud density of the aromatic ring in the nitronyl nitroxide radical ligand affects the structure and magnetic character of lanthanide-radical complexes, we decided to use a new bis-nitronyl nitroxide radical based on furan ring, named NITFu*m*bis = (1,3-bis-(1′-oxyl-3′-oxido-4′,4′,5′,5′-tetramethyl-4,5-hydro-1H-imidazol-2-yl) furan), its structure is shown in Scheme **1**. Compared with pyridyl or phenyl substituted bis-nitronyl nitroxide radical,[11d,16] furyl ring is rich in electron cloud density, which will affect the strength of magnetic interaction promoted by organic radicals. Up till now, no metal complexes with such radical has been reported. Herein we synthesized a series of isomorphic mononuclear tri-spin lanthanide complexes based on radical NITFu*m*bis with the formula of $[Ln(hfac)_3(NITFu\textit{m}bis)_2]_2$ (Ln = La(**1**), Ce(**2**), Pr(**3**), Gd(**4**), Tb(**5**), Dy(**6**), hfac = hexafluoroacetyl acetonate, NITFu*m*bis = 1,3-bis-(1′-oxyl-3′-oxido-4′,4′,5′,5′-tetramethyl-4,5-hydro-1H-imidazol-2-yl) furan). The static magnetic results suggested that there are antiferromagnetic interactions between Ln and the radicals in all of the six complexes. In addition, dynamic magnetic studies showed that complex **6** exhibit frequency-dependent ac susceptibility at low temperature, which suggest SMMs behavior.



NITFu*m*bis

Scheme 1

Experimental details

Materials and physical measurements

All of the reagents used in the syntheses were of analytical grade, except that the solvents used were distilled prior to use. $Ln(hfac)_3 \cdot 2H_2O$ was synthesized according to the method of the literature.[17] 2,5-Furanedicarboxaldehyde used to synthesize the nitronyl nitroxide radicals was prepared by activated manganese dioxide (Across) and 2,5-bis(hydroxymethyl)furane (Aldrich) according to the literature procedures.[18] The ligand NITFu*m*bis was prepared by condensation of 2,3-bis(hydroxylamino)-2,3-dimethylbutane with 2,5-furanedicarboxaldehyde, followed by oxidation with $NaIO_4$ according to the literature method.[19] Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Perkin–Elmer 240 elemental analyzer. Infrared spectra were recorded from KBr pellets in the 4000–400 cm^{-1} region on a Bruker TENOR 27 spectrometer. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu-Kα radiation. Direct-current (dc) magnetic susceptibilities of crystalline samples were measured on an MPMS-7

SQUID magnetometer in the temperature range of 2–300 K with 1000 Oe applied magnetic field. Alternating-current (ac) susceptibilities were performed on the same magnetometer under 0 or 3000 Oe DC field with an oscillating of 3 Oe. The data were corrected for the diamagnetism of the samples using Pascal constants.

X-Ray crystallography

All crystallographic data were carried out with an Oxford Diffractometer SuperNova TM, which were equipped with graphite monochromatic Mo-Ka radiation (λ = 0.71073 Å). Lorentz polarization and absorption corrections were applied. Structures were solved by direct methods with the SHELXS-97 program and refined by full-matrix least-squares techniques against F^2 with the SHELXTL-97 program package.[20] The disordered fluorine atoms in all the six complexes were refined isotropically. Some restraints are applied, such as ISOR (anisotropic parameter), DFIX (restricting the distance between two atoms). Besides fluorine atoms, all other non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and refined isotropically. Crystallographic data for all of the six compounds are listed in Table 1. CCDC-1410302 (for **1**), CCDC-1410303 (for **2**), CCDC-1410315 (for **3**), CCDC-1410316 (for **4**), CCDC-1410317 (for **5**) and CCDC-1410319 (for **6**), contain the supplementary crystallographic data for this paper.

Preparation of complexes of 1–6

All of the six complexes were obtained by dissolving Ln(hfac)$_3$·2H$_2$O (0.05 mmol) (Ln = La(**1**), Ce(**2**), Pr(**3**), Gd(**4**), Tb(**5**), Dy(**6**)) in boiling *n*-heptane (20 mL). After stirring for 2 h, the solution was cooled to 60 °C, to which NITFu*m*bis (19 mg, 0.05 mmol) in CH$_2$Cl$_2$ (5 mL) was added. The resulting solution was stirred with refluxing for 30 min and then cooled to room temperature. Slowly evaporation of the final solution for about one week yield dark-blue block crystals suitable for single-crystal X-ray analysis.

[La(hfac)$_3$(NITFu*m*bis)]$_2$ (1): Yield 0.026 g, 45%. $C_{66}H_{58}F_{36}La_2N_8O_{22}$(2277.02 g/mol): calcd. for C 34.81, H 2.57, N 4.92; found: C 35.22, H 2.84, N 5.08%. IR (KBr pellet): 2362(w), 1651(s), 1613(w), 1400(vs), 1262(m), 1192(s), 1142(s), 801(w), 617(m) cm^{-1}.

Table 1. Crystallographic Data and Structure Refinement Details for **1-6**

	1	**2**	**3**
formula	$C_{66}H_{58}F_{36}La_2N_8O_{22}$	$C_{66}H_{58}Ce_2F_{36}N_8O_{22}$	$C_{66}H_{58}F_{36}N_8O_{22}Pr_2$
Mr	2277.02	2279.44	2281.02
crystal system	triclinic	triclinic	triclinic
space group	*P*-1	*P*-1	*P*-1
a (Å)	13.895(3)	14.1078(4)	13.9203(4)
b (Å)	17.084(3)	17.1982(6)	17.1400(5)
c (Å)	21.297(4)	21.4263(5)	21.2848(7)
α(°)	108.753(3)	108.562(3)	68.426(3)
β(°)	92.788(3)	93.305(2)	87.010(3)
γ(°)	113.849(3)	113.769(3)	66.321(3)
V (Å^3)	4284.3(13)	4405.4(2)	4297.8(3)
Z	2	2	2
ρcalc (Mg/m^3)	1.765	1.718	1.763
μ (mm^{-1})	1.135	9.233	9.976
F(000)	2248	2252	2256
θ range(°)	1.40~25.01	3.46~68.07	3.49~67.08
GOF on F^2	1.031	1.041	1.042
$R_1/wR_2[I > 2\sigma(I)]$	0.0379, 0.0959	0.0741, 0.1870	0.0411, 0.1025
R_1/wR_2 (all data)	0.0451, 0.1026	0.1051, 0.2063	0.0458, 0.1074
	4	**5**	**6**
formula	$C_{66}H_{58}F_{36}Gd_2N_8O_{22}$	$C_{66}H_{58}F_{36}N_8O_{22}Tb_2$	$C_{66}H_{58}Dy_2F_{36}N_8O_{22}$
Mr	2313.70	2317.04	2324.20
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	29.7235(10)	29.7640(16)	29.6112(12)
b (Å)	12.6890(3)	12.6516(6)	12.6818(5)
c (Å)	23.8780(7)	23.9061(12)	23.9558(10)
α(°)	90	90	90
β(°)	108.287(3)	108.037(1)	107.2800(10)
γ(°)	90	90	90
V (Å^3)	8551.1(4)	8559.7(7)	8589.9(6)
Z	4	4	4
ρcalc (Mg/m^3)	1.797	1.798	1.797
μ (mm^{-1})	11.319	1.791	1.878
F(000)	4552.0	4560	4568
θ range(°)	3.72~67.08	0.72 ~25.01	1.44~25.01
GOF on F^2	1.023	1.105	1.028
$R_1/wR_2[I > 2\sigma(I)]$	0.0732, 0.1785	0.0436, 0.0909	0.0448, 0.0953
R_1/wR_2 (all data)	0.1185, 0.2168	0.0560, 0.0979	0.0599, 0.1036

[Ce(hfac)$_3$(NITFu*m*bis)]$_2$ (2): Yield 0.024 g, 42%. $C_{66}H_{58}Ce_2F_{36}N_8O_{22}$(2279.44

g/mol): calcd. C 34.77, H 2.56, N 4.92; found: C 35.08, H 2.66, N 5.18%. IR (KBr pellet,): 2357(w), 1649(s), 1398(w), 1256(s), 1197(s), 1143(vs), 776(m), 618(m) cm^{-1}.

$[Pr(hfac)_3$(NITFu*m*bis)$]_2$ (3): Yield 0.028 g, 48%. $C_{66}H_{58}F_{36}N_8O_{22}Pr_2$ (2281.02 g/mol): calcd. for C 34.75, H 2.56, N 4.91; found: C 34.88, H 2.92, N 5.13%. IR (KBr pellet) 2361(w), 1651(s), 1562(w), 1502(m), 1399(vs), 1338(s), 1275(vs), 1205(vs), 1154(s), 983(s), 814(m), 660(w), 622(m), 565(m) cm^{-1}.

$[Gd(hfac)_3$(NITFu*m*bis)$]_2$ (4): Yield 0.025 g, 43%. $C_{66}H_{58}F_{36}Gd_2N_8O_{22}$(2313.70 g/mol): calcd. C 34.26, H 2.53, N 4.84; found: C 34.18, H 2.65, N 4.72%. IR (KBr pellet,): 2362(w), 1653(s), 1524(s), 1399(vs), 1326(w), 1262(s), 1192(vs), 1146(vs), 795(w), 649(w), 579(m) cm^{-1}.

$[Tb(hfac)_3$(NITFu*m*bis)$]_2$ (5): Yield 0.024 g, 42%. $C_{66}H_{58}F_{36}N_8O_{22}Tb_2$(2317.04 g/mol): calcd. for C 34.21, H 2.52, N 4.84; found: C 34.14, H 2.68, N 4.96%. IR (KBr pellet): 2362(w), 1650(vs), 1524(s), 1401(vs), 1268(vs), 1192(vs), 1135(vs), 987(w), 789(w), 609(m) cm^{-1}.

$[Dy(hfac)_3$(NITPy*m*bis)$]_2$ (6): Yield 0.026 g, 44%. $C_{66}H_{58}Dy_2F_{36}N_8O_{22}$(2324.20 g/mol): calcd. C 34.10, H 2.51, N 4.82; found: C 34.35, H 2.42, N 4.66%. IR (KBr pellet,): 2361(w), 1653(vs), 1512(s), 1403(vs), 1269(vs), 1190(vs), 1157(vs), 992(vs), 795(s), 606 (m) cm^{-1}.

Results and discussion

Crystal structure

Structures of 1. Single-crystal X-ray diffraction analyses reveal that the molecular structures of **1**–**3** belong to triclinic *P*-1 space group. The asymmetric units in all the three complexes are composed of two crystallographically independent $[Ln(hfac)_3$(NITFu*m*bis)] moieties, and every $[Ln(hfac)_3$(NITFu*m*bis)] exhibits mononuclear tri-spin structure. The molecular structure of complex **1** as an example is shown in Fig. 1, the central La^{III} ion is eight coordinated by three bischelate $hfac^-$ anions and two non-bridged NO groups from two separate organic radicals. The La–O(rad) (nitroxide) distances are in the range of 2.449(2)~2.503(2) Å, and the La–O(hfac) bond lengths are in the range of 2.441(3)~2.556(2) Å. The coordinated N–O bond lengths of the nitronyl nitroxide radicals are in the range of 1.294(2)~1.301(2) Å, which is a little larger than the uncoordinated N-O bonds (1.262(3)~1.268(2) Å). However, both are within the range of N-O bond length of the nitronyl radical. The O_{rad}-La-O_{rad} bond angles are 92.23(8) and 94.53(8)°, respectively. Here the two five membered heterocyclic rings and the furan ring show twist angles range from 22.7(2)º to 32.9(3)°. By employing the classic Continuous Symmetry Measures (CSM) method, the coordination sphere of La1 and La2 is estimated as nearly ideal D_{2d} triangular dodecahedron with the deviation parameter S = 1.862 or C_{2v}-bicapped trigonal prism with the derivation parameter S = 1.102, respectively (Table 2).[21]

The shortest distance between the uncoordinated N–O group is in the 10.924 Å, and the shortest La···La distance is 10.121 Å, hence the two sub-units are incompact, mononuclear moiety is considered for the magnetic analysis. The packing diagram for **1** is given in Fig. 2. There is no π–π stacking interaction in the system, and weak hydrogen bond interactions C–H···F or C–H···O to generate three dimensional networks with H···F distances of 2.460 Å or H···O distances in the range of 2.448–2.484 Å, which are comparable to the literature[11d,14f, 22] of the Ln(hfac)$_3$ complexes.

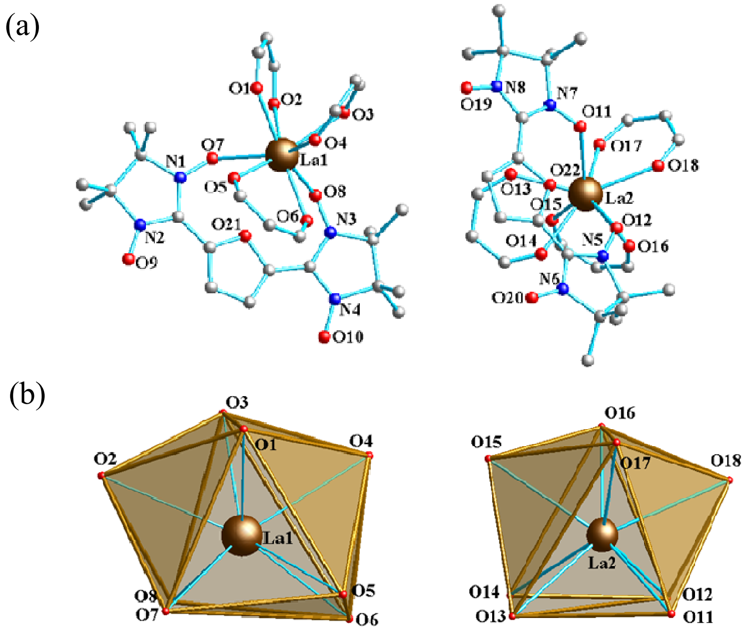


Fig. 1 Simplified view of the crystal structure of **1**. Fluorine, hydrogen, and some carbon atoms are omitted for clarity. (b) Polyhedral of lanthanum atoms.

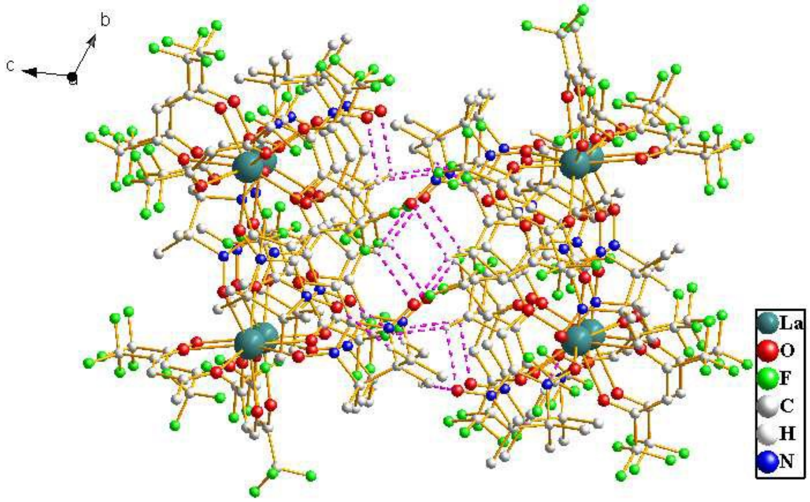


Fig. 2 Packing diagram of LaNITFumbis. (Pink dot line, C17–H17···O9, C50–H50···O20, C17–H17···F33).

Structure of 4. Compound **4–6** crystallizes in space group $P2_1/c$ with Z = 4. The asymmetric unit also contains two crystallographically independent [Ln(hfac)$_3$(NITFu*m*bis)] moieties, and every [Ln(hfac)$_3$(NITFu*m*bis)] exhibits mononuclear tri-spin structure with central metal ion in an LnO$_8$ coordination sphere. The molecular structure of complex **4** as an example is shown in Fig. 3. The Gd–O(hfac) distances range from 2.354(10) to 2.404(7) Å. In contrast to **1**, the Ln-O (radical) bond lengths of compounds **4–6** are in the range of 2.345(8)–2.374(7) Å for **4**, 2.324(14)–2.364(13) Å for **5**, and 2.321(9)–2.349(9) Å for **6**, which exhibits the phenomenon of shrinking the bond distances for heavier lanthanide ions. When applying the C_{2v} symmetry to the GdO8 site, CSM method gives the Gd1 and Gd2 the minimal value of S = 0.825 or S = 1.107, respectively. Similar to **1**, hydrogen bonds C11-H11B···F28, C38-H38···F23, C28-H28B···F7, C50-H50A···O3, C50-H50C···O9 (H···F distances ranging from 2.451(3) to 2.616(5) Å and H···O distances ranging from 2.451(3) to 2.616(5) Å) attach isolated molecules into 3D supermolecular structure (Fig. 4).

Static magnetic properties

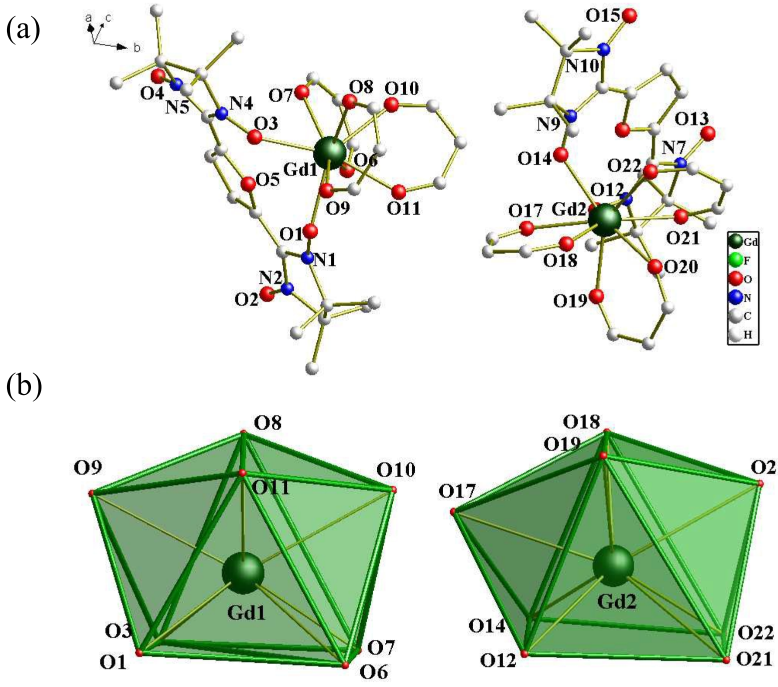


Fig. 3 Simplified view of the crystal structure of **4**. Fluorine, hydrogen, and some carbon atoms are omitted for clarity. (b) Polyhedral of gadolinium atoms.

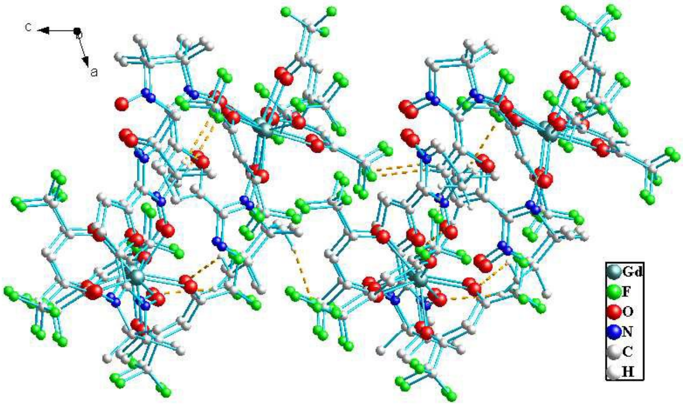


Fig. 4 Packing diagramof GdNITFumbis. (Pink dot line, C11-H11B···F28, C38-H38···F23, C28-H28B···F7, C50-H50A···O3, C50-H50C···O9).

Magnetic measurements were performed on polycrystalline samples of **1-6**. The phase purity of the bulk samples was confirmed by XRD analyses as shown in Fig. S7-8 (ESI).

Direct current (*dc*) magnetic susceptibilities for the six complexes were measured under 1 *k*Oe in the 2–300 K range and the magnetic behaviors are shown in Fig. 5–8.

Table 2 Lanthanide geometry analysis by *SHAPE* software

Ln(III)	D_{2d}-DD	C_{2v}-TP	D_{4d}-AP	Ln(III)	D_{2d}-DD	C_{2v}-TP	D_{4d}-AP
La1	1.862	2.046	4.289	La2	1.964	1.102	2.104
Ce1	1.994	1.839	4.056	Ce2	1.994	1.058	1.770
Pr1	1.804	2.018	4.130	Pr2	2.014	0.990	2.051
Gd1	2.157	0.825	1.912	Gd2	2.963	1.107	3.249
Tb1	2.017	0.709	1.743	Tb2	2.955	1.104	3.244
Dy1	2.250	0.777	1.802	Dy2	2.802	1.056	3.051

Table 3 Selected bond distances (Å) and angles (°) for complexes **1-6**

	1 La	**2** Ce	**3** Pr
Ln–O(hfac)	2.424(7)–2.480(6)	2.377(13)–2.465(4)	2.384(6)–2.433(7)
O(rad)–Ln–O(rad)	86.7(2), 90.5(2)	86.4(2), 90.6(2)	86.1(2), 90.3(2)
Ln–O(rad)	2.404(6)–2.460(6)	2.394(4)–2.426(4)	2.360(5)–2.386(5)
Ln–O(rad)–N	134.2(5)–139.1(5)	134.1(3)–137.7(3)	133.8(4)–137.7(4)
O(rad)–N	1.264(9)–1.305(9)	1.291(6)–1.297(7)	1.277(7)–1.300(7)
	4 Gd	**5** Tb	**6** Dy
Ln–O(hfac)	2.354(10)–2.404(7)	2.350(11)–2.382(12)	2.321(9)–2.380(9)
O(rad)–Ln–O(rad)	86.6(3), 90.7(3)	86.1(5), 90.2(5)	85.8(3), 88.8(3)
Ln–O(rad)	2.345(8)–2.374(7)	2.324(14)–2.364(13)	2.321(9)–2.349(9)
Ln–O(rad)–N	133.9(6)–138.7(7)	134.2(10)–137.7(9)	134.1(7)–137.3(7)
O(rad)–N	1.277(12)–1.307(11)	1.279(19)–1.299(16)	1.288 (13)–1.309(14)

Static magnetic properties for complex 1(La), 2(Ce), and 3(Pr). At room temperature, the value of $\chi_M T$ for complex **1** is 0.76 $cm^3 \cdot K \cdot mol^{-1}$ (Fig. 5), in good agreement with the expected value (0.75 $cm^3 \cdot K \cdot mol^{-1}$) for two organic radicals (S = 1/2, 0.375 $cm^3 \cdot K \cdot mol^{-1}$). Upon cooling, $\chi_M T$ value gradually decreases and reaches a minimum of 0.03 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K. This behavior evidences that weak antiferromagnetic radical-radical interactions operate in the lanthanum complex. The experimental data between 2−300 K are well fitted using a dinuclear model $H = -2J_{Rad\text{-}Rad}\hat{S}_{Rad1} \cdot \hat{S}_{Rad2}$, the magnetic data were analyzed by the equation 1. The least-squares fit to the data of **1** leads to $g = 2.01$, $J_{\text{rad-rad}} = -5.3\ cm^{-1}$.

$$\chi_M = \frac{2Ng^2\beta^2}{kT} \times \frac{1}{3 + e^{-2J/kT}} \qquad (1)$$

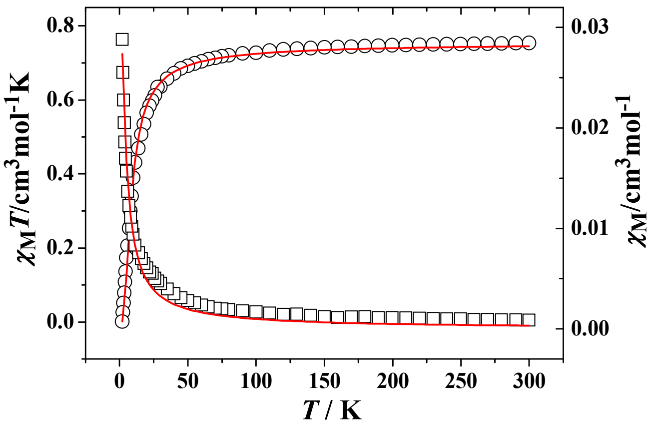


Fig. 5 $\chi_M T$ vs. T (○) and χ_M vs. T (□) plots for complex **1**.

Variable-temperature magnetic susceptibilities for complexes of **2** and **3** are studied and shown in Fig. 6. The observed room-temperature $\chi_M T$ values are 1.53 and 2.37 cm^3·K·mol^{-1} for Ce(III) and Pr(III) mononuclear complexes, respectively. Both the values

are very close to the expected values of 1.55 and 2.35 cm^3·K·mol^{-1} for an uncoupled system of one Ln(III) ion (Ce (III) or Pr(III)) plus two radicals. Upon cooling, the $\chi_M T$ value of **2** continuously decreases and reaches a minimum of 0.14 cm^3·K·mol^{-1} at 2 K. While on decreasing the temperature, the $\chi_M T$ value of **3** decreases gradually and reaches a minimum of 0.07 cm^3·K·mol^{-1} at 2.0 K, which may be ascribed to the progressive depopulation of excited Stark sublevels of Pr^{III} and the weak interactions between Pr(III) ion and radicals.

To obtain a rough quantitative estimate of the magnetic interaction parameters between paramagnetic species (Ce(III) [or Pr(III) ion] and the radicals) in the mononuclear tri-spin system, we assumed that the total magnetic susceptibility χ_{total} is given by the sum of the isolated Ln(III) ion and two radicals (eqn (1)). The Ce(III) [or Pr(III)] ion may be assumed to exhibit a splitting of the m_j energy levels ($\hat{H}= \Delta\hat{J}_z^2$) in an axial crystal field. Thus χ_{Ce} and χ_{Pr} can be described by eqn (3) and (4), respectively.[3e,15a,23] In the expression, Δ is the zero-field-splitting parameter, g is the Lande factor**.** The zJ' parameter based on the molecular field approximation in eqn (5) is introduced to simulate the magnetic interactions between all the paramagnetic species in the system. Thus, the magnetic data can be analyzed by the following approximate treatment of eqn (1)–(5).

$$\chi_{\mathrm{total}} = \chi_{\mathrm{Ln}} + 2\chi_{\mathrm{rad}} \tag{1}$$

$$\chi_{rad} = \frac{N{g_{rad}}^2\beta^2}{3kT}\frac{1}{2}\left(\frac{1}{2}+1\right)(g_{rad}=2) \tag{2}$$

$$\chi_{Ce} = \frac{Ng^2\beta^2}{kT}\times\frac{\frac{50}{4}\exp(-25\Delta/4kT)+\frac{18}{4}\exp(-9\Delta/4kT)+\frac{1}{2}\exp(-\Delta/4kT)}{2\exp(-25\Delta/4kT)+2\exp(-9\Delta/4kT)+2\exp(-\Delta/4kT)} \tag{3}$$

$$\chi_{\mathrm{Pr}} = \frac{Ng^2\beta^2}{kT}\times\frac{2\exp(-\Delta/4kT)+8\exp(-4\Delta/kT)+18\exp(-9\Delta/kT)+32\exp(-16\Delta/kT)}{1+2\exp(-\Delta/4kT)+2\exp(-4\Delta/kT)+2\exp(-9\Delta/kT)+2\exp(-16\Delta/kT)} \tag{4}$$

$$\chi_M = \frac{\chi_{total}}{1-(2zj'/Ng^2\beta^2)\chi_{total}} \tag{5}$$

The observed $\chi_M T$ data were well reproduced (Fig. 6) by using the above approximate eqn (1)–(5), giving the best fitting parameters of $g = 0.89$, $\Delta = 5.76\ \mathrm{cm}^{-1}$, $zj' = -0.52\ \mathrm{cm}^{-1}$ for complex **2** and $g = 0.83$, $\Delta = -18.92\ \mathrm{cm}^{-1}$, $zj' = -1.07\ \mathrm{cm}^{-1}$ for complex **3**. The negative zj' value is indicative of the antiferromagnetic interaction between the paramagnetic ions (Pr(III) and radicals) in the mononuclear tri-spin systems.

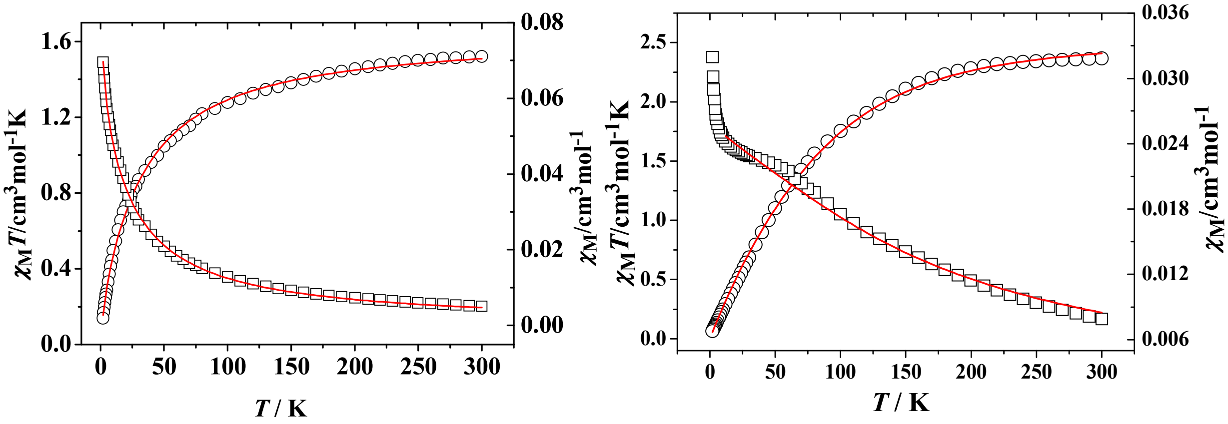


Fig. 6 $\chi_M T$ vs. T (○) and χ_M vs. T (□) plots for complex **2** (left) and **3** (right).

Static Magnetic properties of complex 4. The temperature dependence of magnetic susceptibilities for **4** is studied and shown in Fig. 7. The observed room-temperature $\chi_{\mathrm{M}}T$ value is 8.72 $\mathrm{cm^3{\cdot}K{\cdot}mol^{-1}}$, in agreement with the expected value 8.63 $\mathrm{cm^3{\cdot}K{\cdot}mol^{-1}}$ for one uncoupled $\mathrm{Gd^{III}}$ ion ($^8\mathrm{S}_{7/2}$, $g = 2$) and two organic radicals (S = 1/2). On decreasing the temperature, the $\chi_{\mathrm{M}}T$ value keeps almost constant down to 100 K, then decreases slightly to reach a minimum of 8.04 $\mathrm{cm^3{\cdot}K{\cdot}mol^{-1}}$ at 22 K. Upon further cooling, $\chi_{\mathrm{M}}T$ increases to 8.22 $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K}$ at 2 K. Such a magnetic behavior is consistent with dominant antiferromagnetic interactions. Accordingly, the system was modeled as a mononuclear tri-spin unit, and the magnetic analysis was carried out by using the spin Hamiltonian $H = -2J_{Rad\text{-}Gd}\,(\hat{S}_{Rad1}{\cdot}\hat{S}_{Gd} + \hat{S}_{Rad2}{\cdot}\hat{S}_{Gd}) - 2j_{Rad\text{-}Rad}\hat{S}_{Rad1}{\cdot}\hat{S}_{Rad2}$, where $J_{Rad\text{-}Gd}$ and $j_{Rad\text{-}Rad}$ characterized the exchange interactions for radical-Gd(III) and radical-radical, respectively. At low temperature, the increase of $\chi_{\mathrm{M}}T$ may be assigned to weak intermolecular ferromagnetic interaction, so the mean-field approximation (zj') was introduced. Assuming that radicals and Gd(III) have the same g value,[23] the magnetic data were analyzed by the following approximate treatment equations. [24]

$$\chi = \frac{Ng^2\beta^2}{4kT}\left(\frac{A}{B}\right) \tag{6}$$

$$A = 165 + 84\exp\left(-\frac{9J_{Rad\text{-}Gd}}{kT}\right) + 84\exp\left(-\frac{7J_{Rad\text{-}Gd} + 2j_{Rad\text{-}Rad}}{kT}\right) + 35\exp\left(-\frac{16J_{Rad\text{-}Gd}}{kT}\right)$$

$$B = 5 + 4\exp\left(-\frac{9J_{Rad\text{-}Gd}}{kT}\right) + 4\exp\left(-\frac{7J_{Rad\text{-}Gd} + 2j_{Rad\text{-}Rad}}{kT}\right) + 3\exp\left(-\frac{16J_{Rad\text{-}Gd}}{kT}\right)$$

$$\chi_M = \frac{\chi}{1-(2zj'/Ng^2\beta^2)\chi} \tag{7}$$

The observed $\chi_{\mathrm{M}}T$ data at 2–300 K were well reproduced, giving the best fitting parameters of $g = 2.00$, $J_{\mathrm{Rad\text{-}Gd}} = -1.00\ \mathrm{cm^{-1}}$, $j_{\mathrm{Rad\text{-}Rad}} = -24.89\ \mathrm{cm^{-1}}$ and $zj' = 0.004\ \mathrm{cm^{-1}}$. The negative values of $J_{\mathrm{Rad\text{-}Gd}}$ and $j_{\mathrm{Rad\text{-}Rad}}$ indicate the antiferromagnetic interactions between Gd(III) and the radicals, and also between the two intramolecular radicals.

The fitting results of $J_{\mathrm{Rad\text{-}Gd}}$ is in the range of ever reported $\mathrm{Gd^{III}}$-radicals compounds, the $j_{\mathrm{Rad\text{-}Rad}}$ is larger than the reported highest value ($j_{\mathrm{Rad\text{-}Rad}} = -11.89\ \mathrm{cm^{-1}}$) for Ln-radical systems,[3f] although much larger value for $j_{\mathrm{Rad\text{-}Rad}}$ is found in transition-metal-radical systems.[25] Because a spin delocalization exists from the magnetic orbital π* of NITFu*m*bis to the empty 6s and 5d orbitals on the $\mathrm{Ln^{III}}$ ion, the antiferromagnetic interaction between the intramolecular radicals could be interpreted based on the superexchange of the two radicals through the empty 6s and 5d orbitals of the Ln(III) ion.[7c,26] The shorter bond distances of Gd(III)-O_{rad} (**4**) than La(III)-O_{rad} (**1**) may result in good overlapping of the π* electronic cloud through the empty 6s and 5d orbitals, which is the reason of the more pronounced antiferromagnetic interaction in compound **4** than in **1**. The fact that Gd^{III} mediates the magnetic interaction more efficiently than Y^{III} has already been observed in the literature.[27] The much larger $j_{Rad–Rad}$ for compound **4** than other Gd-radical complexes[3f,16c,16d,27,28] may be not only due to the good conjugation among the furyl ring and the two imidazol rings on which the radicals locate, but also due to the high electronic density of the furyl ring.

The field dependences of magnetization for complexes **4** have been determined at 2 K in the range of 0–70 kOe (Fig. 7(right)). The experimental magnetization is compared to the theoretical magnetization given by the Brillouin function for S = 9/2 of the ferromagnetic and the S = 7/2 for antiferromagnetic state. The experimental magnetization is close to the Brillouin function for S = 7/2, which further confirms the antiferromagnetic interactions between the paramagnetic centers.

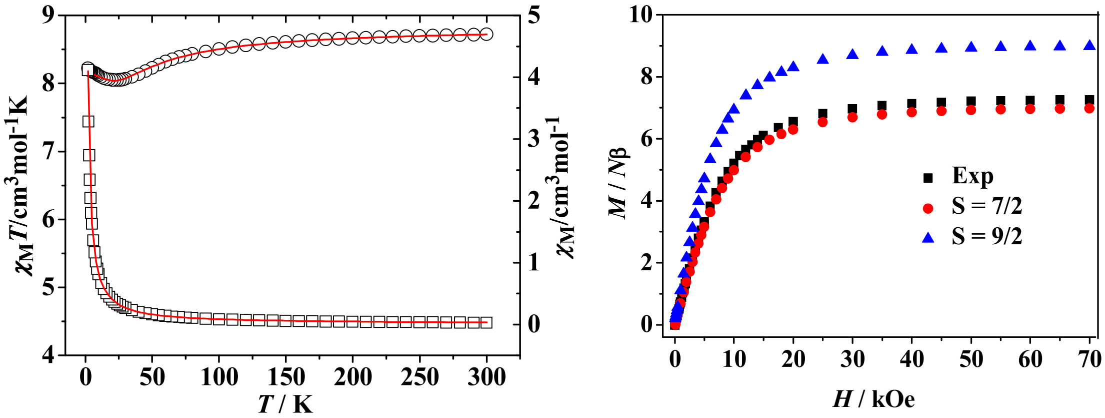


Fig. 7 $\chi_M T$ vs. T (□) and χ_M vs. T (○) plots for complex **4**, and the solid lines represent the theoretical values based on the corresponding equations (left). Field dependence of the magnetization for complex **4** at 2 K (right).

Static Magnetic properties of complex 5 and 6. The direct current (DC) magnetic susceptibility data of **5** and **6** are shown in Fig. 8. For **5**, the value of $\chi_M T$ at 300 K is 12.91 cm^3·K·mol^{-1}, which is a little higher than the expected value 12.50 cm^3·K·mol^{-1} for one uncoupled Tb^{III} ion ($^7F_6$ and g = 3/2) and two organic radicals (S = 1/2). Upon cooling, the value of $\chi_M T$ decreases smoothly till 60 K, and then shows an abrupt decrease to 10.26 cm^3·K·mol^{-1} at 2 K. For **6**, the value of $\chi_M T$ at room temperature is 14.18 cm^3·K·mol^{-1}, which is slightly lower than the expected value of 14.92 cm^3·K·mol^{-1} for one uncoupled Dy^{III} ion ($^6H_{15/2}$) and two organic radicals (S = 1/2). As the temperature is lowered, the $\chi_M T$ value decreases slightly until 100 K and then decays sharply to a minimum of 11.30 cm^3·K·mol^{-1} at 2 K. The decrease of $\chi_M T$ at high temperature regime can be ascribed to the depopulation of the Ln^{III} M_J states and/or antiferromagnetic coupling between spin carriers.

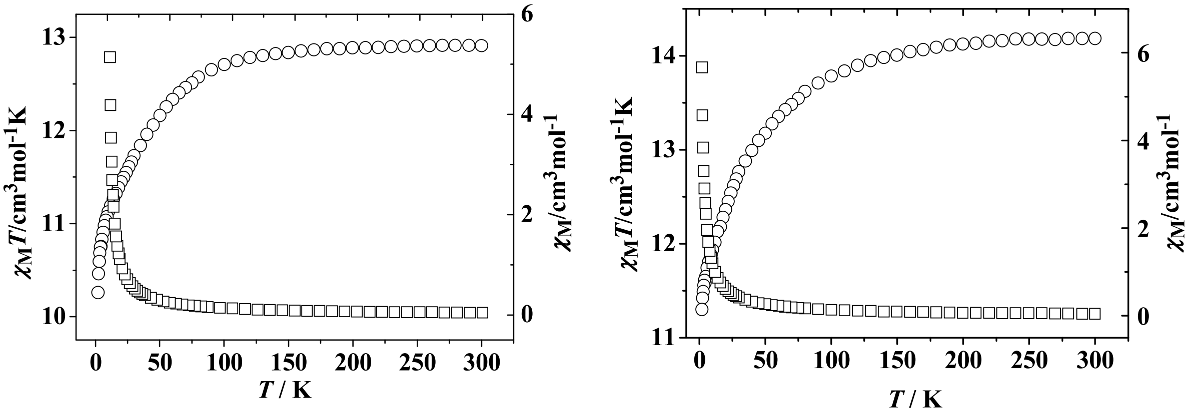


Fig. 8 $\chi_M T$ vs. T (○) and χ_M vs. T (□) plots for **5**(left) and **6**(right).

The field dependences of magnetization (M) for complex **5** and **6** have been determined at 2 K in the range of 0–70 kOe (Fig. 9). For **5**, the field-dependent magnetization value at 2 K shows a rapid increase in the magnetization at low magnetic fields. At higher fields, M increases up to 5.81 $N\beta$ at 2 K and 70 kOe, which is much lower than the saturation values of 11 $N\beta$ (9 $N\beta$ for each Tb^{III} ion for J = 6 and g = 3/2, plus 1 $N\beta$ for each organic radical). For **6**, M increases up to 6.57 $N\beta$ at 2 K and 70 kOe with the increase of the applied field, which also does not reach the expected saturation values of 12 $N\beta$ (10 $N\beta$ for each Dy^{III} ion for J = 15/2 and g = 4/3, plus 1 $N\beta$ for each organic radical). Considering the strong spin-orbit coupling in Ln^{III} ions, the large gaps between experimental data and theoretical saturation values for compounds **5** and **6** can be ascribed to the presence of magnetic anisotropy and/or low-lying excited states in the systems.[11c,12a,14,29]

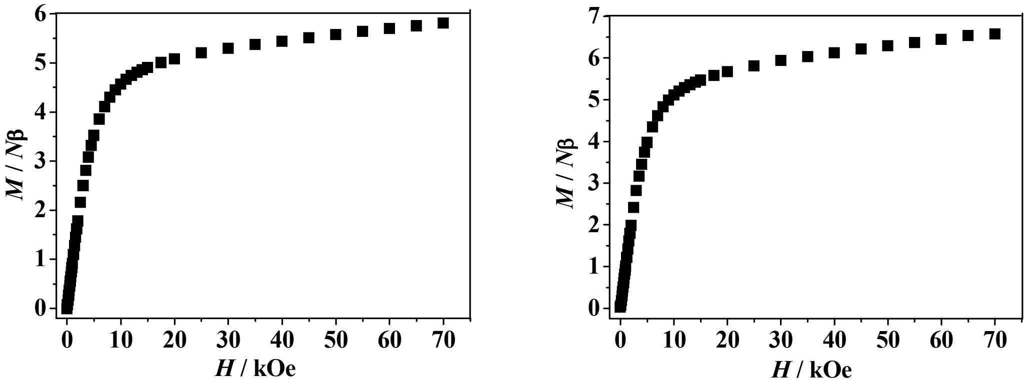


Fig. 9 Field dependence of the magnetization at 2 K for complex **5**(left) and **6**(right).

Dynamic Magnetic Properties for 5 and 6. To examine the spin dynamics of complex **5** and **6**, alternating current (AC) measurements were carried out under a zero DC field or 3000 Oe with an oscillation of 3 Oe. The imaginary component χ'' of the complex **5** does not show any frequency-dependent phenomenon (Fig. S5, see ESI†). As for Dy^{III} compound, the imaginary component of ac magnetic susceptibility data displays temperature dependence with no peaks observed while the real component exhibits a steady increase down to 2 K under zero dc field (Fig. S6, see ESI†). As is well known, magnetization can reverse via quantum mechanical tunneling process in lanthanide SMMs within the lowest energy doublet, which can be suppressed by applying a static magnetic field. Here a DC field of 3000 Oe is applied to probe the dynamic behavior of AC magnetic susceptibility (Fig. 10). Consequently, well-resolved peaks emerge which suggest that the relaxation process is slowed by the external fields. The maximums of the imaginary component of the ac susceptibility are extracted for relaxation time τ. Plots of lnτ versus T^{-1} display linear dependence indicating spin reversed by thermal activated Orbach mechanism process (Fig. 11). Arrhenius fit ($\tau = \tau_0\exp(\Delta_{\mathrm{eff}}/k_B\mathrm{T})$) gives the effect energy gap of 15 K with the pre-exponential τ_0 of 1.25×10^{-6} s, which fall in the range well for SMMs.[14,30]

Conclusions

In conclusion, a nitronyl nitroxide radical NITFu*m*bis and six new compounds [Ln(hfac)$_3$(NITFu*m*bis)]$_2$ have been synthesized. The results show that all of the Ln^{III}-complexes have analogous structures, and each of them features as monometallic tri-spin complex, and the asymmetric unit is composed of two crystallographically independent [Ln(hfac)$_3$(NITPy*m*bis)] moieties. The temperature dependencies of magnetic susceptibilities for the Ln^{III}-complexes are studied, and the results show that there are antiferromagnetic interactions between the paramagnetic ions (Ln(III) and radicals) in all the six complexes. For Gd(III) complex **4**, the fitting results of the magnetic susceptibility reveal that there are two different magnetic interactions between the Gd(III) ion and the NITPy*m*bis ligand (antiferromagnetic interaction between the Gd(III) and the radicals, and also antiferromagnetic interaction between the two intramolecular radicals). The Dy^{III} compound exhibits field-induced SMM behavior with U_{eff} of 15 K and τ_0 of 1.25×10^{-6} s under 3000 Oe external field, while the Tb^{III} compound shows no out-of-phase *ac* signal. The results reported here demonstrated that the local symmetry of lanthanide ions is significant for magnetic anisotropy and for rationally design of new lanthanide SMMs.

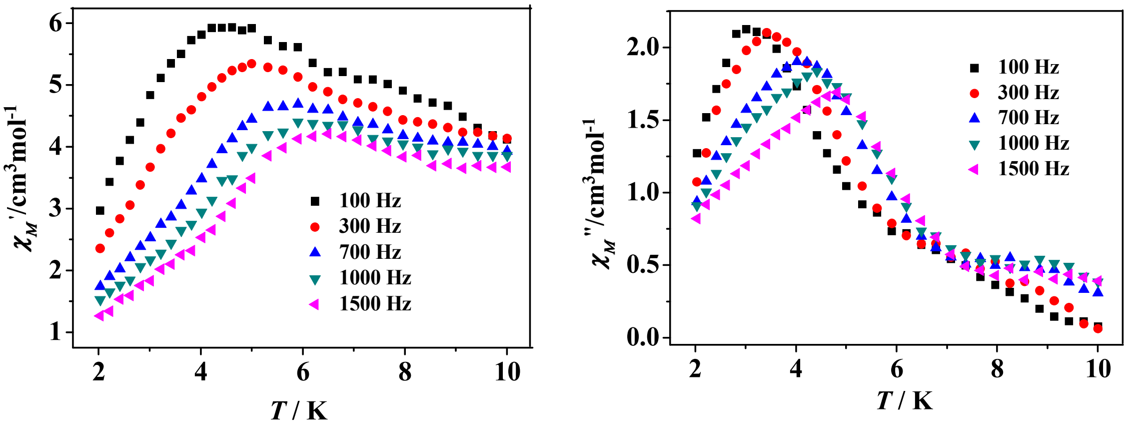


Fig. 10 Temperature dependence of the in-phase(top) and out-of-phase(bottom) components of the AC magnetic susceptibility for complex **6** (right) in a 3000 Oe DC field with an oscillation of 3 Oe.

Acknowledgements

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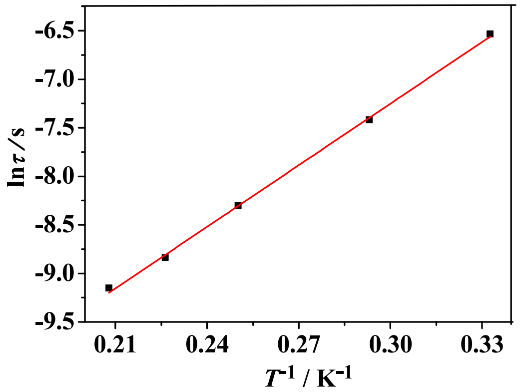

Fig. 11 (a) Magnetization relaxation time, lnτ vs T^{1} plot for **6** under 3000 Oe dc field. The solid line is fitted with the Arrhenius law.

References

1 (*a*) C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, P. Rey, D. P. Shum and R. L. Carlin, *Inorg. Chem.*, 1989, **28**, 272; (*b*) O. Kahn, *Molecular Magnetism*, VCH Publishers: New York, 1993; (*c*) C. Benelli, A. Caneschi, D. Gatteschi and R. Sessoli, *J. Appl. Phys.*, 1993, **73**, 5333; (*d*) M. L. Kahn, J. P. Sutter, S. Golhen, P. Guionneau, L. Ouahab, O. Kahn and D. Chasseau, *J. Am. Chem. Soc.*, 2000, **122**, 3413; (*e*) O. Evans and W. Lin, *Chem. Mater.*, 2001, **13**, 3009; (*f*) M. T. Lemaire, *Pure Appl. Chem.*, 2004, **76**, 277;

2 (*a*) G. St-Pierre, A. Chagnes, N. A. Bouchard, P. D. Harvey, L. Brossard and H. Menard, *Langmuir*, 2004, **20**, 6365; (*b*) A. B. Descalzo, K. Rurack, H. Weisshoff, R. Martinez-Manez, M. D. Marcos, P. Amoros, K. Hoffmann and J. Soto, *J. Am. Chem. Soc.*, 2005, **127**, 184; (*c*) D. Luneau and P. Rey, *Coord. Chem. Rev.*, 2005, **249**, 2591. (*d*) M. A. Aldamen, J. M. Clemente-Juan, E. Coronado, C. Marti-Gastaldo and A. Gaita-Arino, *J. Am. Chem. Soc.*, 2008, **130**, 8874.

3 (*a*) T. C. Stamatatos, S. J. Teat, W. Wernsdorfer and G. Christou, *Angew. Chem., Int. Ed.*, 2009, **48**, 521; (*b*) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2328; (*c*) M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A. M. Talarico, M. A. Arrio, A. Cornia, D. Gatteschi and R. Sessoli, *Nature Mater.*, 2009, **8**, 194; (*d*) P. Dawid, C. Szymon and S. Olaf, *Nature*, 2010, **468**, 417; (*e*) L. Sorace, C. Benelli and D. Gatteschi, *Chem. Soc. Rev.*, 2011, **40**, 3092; (*f*) Y. L. Wang,

Y. Y. Gao, Y. Ma, Q. L. Wang, L. C. Li and D. Z. Liao, *CrystEngComm*, 2012, **14**, 4706.

4 (*a*) A. Caneschi and D. Gatteschi, *Prog. Inorg. Chem.*, 1991, **39**, 331; (*b*) N. Koga and S. Karasawa, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1384; (*c*) G. Christou, *Polyhedron*, 2005, **24**, 2065.

5 (*a*) G. Poneti, K. Bernot, L. Bogani, A. Caneschi, R. Sessoli, W. Wernsdorfer and D. Gatteschi, *Chem. Commun.*, 2007, **43**, 1807; (*b*) P. H. Lin, T. J. Burchell, L. Ungur, L. F. Chibotaru, W. Wernsdorfer and M. Murugesu, *Angew. Chem.*, *Int. Ed.*, 2009, **48**, 9489; (*c*) D. Visinescu, O. Fabelo, C. Ruiz-Perez, F. Lloret and M. Julve, *CrystEngComm*, 2010, **12**, 2454.

6. R. D. Willet, D. Gatteschi and O. Kahn, *Magneto-Structural Correlations in Exchange Coupled Systems*, Reidel Publishing: Dordrecht, The Netherlands, 1983.

7 (*a*) A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1985, **107**, 8128; (*b*) A. Bencini, C. Benelli, A. Caneschi, A. Dei and D. Gatteschi, *Inorg. Chem.*, 1986, **25**, 572; (*c*) C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi and P. Rey, *Inorg. Chem.*, 1990, **29**, 4223; (d) C. Benelli, A. Caneschi, O. Guillou and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1750; (*e*) C. Benelli, A. Caneschi, D. Gatteschi and R. Sessoli, *Inorg.* Chem., 1993, **32**, 4797; (*f*) O. Kahn, *Adv. Inorg. Chem.*, 1995, **43**, 179; (*g*) J. L. Sanz, R. Ruiz, A. Gleizes, F. Lloet, J. Fans, M. Julve, J. J. Borras-Alvenar and Y. Journeaux, *Inorg. Chem*. 1996, **35**, 7384.

8 (*a*) C. Lescop, E. Belorizky, D. Luneau and P. Rey, *Inorg. Chem.*, 2002, **41**, 3375; (*b*) N. Ishikawa, M. Sugita, T. Ishikawa, S. Y. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.*, 2003, **125**, 8694; (*c*) N. Ishikawa, M. Sugita and W. G. Wernsdorfer, *J. Am. Chem. Soc.*, 2005, **127**, 3650; (*d*) Y. N. Guo, G. F. Xu, P. Gamez, L. Zhao, S. Y. Lin, R. P. Deng, J. K. Tang and H. J. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 8538.

9 (*a*) N. Ishikawa, *J. Phys. Chem. A*, 2003, **107**, 5831; (*b*) S. Takamatsu, T. Ishikawa, S. Koshihara and N. Ishikawa, *Inorg. Chem*. 2007, **46**, 7250; (*c*) J. D. Rinehart, M. Evans, W. J. Evans, J. R. Long, *J. Am. Chem. Soc*. 2011, **133**, 14236.

10 (*a*) P. D. W. Boyd, Q. Li, J. B. Vincent, K. Folting, H. R. Chang, W. E. Streib, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1988, **110**, 8537; (*b*) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem.*, 2001, **113**, 1810; (*c*) D. Gatteschi and R. Sessoli, *Angew. Chem. Int. Ed.*, 2003, **42**, 268; (*d*) Mishra, W. Wernsdorfer, K. A. Abboud and G. Christou, *J. Am. Chem. Soc.*, 2004, **126**, 15648; (*e*) N. Ishikawa, M. Sugita and W. Wernsdorfer, *Angew. Chem., Int. Ed.*, 2005, **44**, 2931; (*f*) X. Y. Wang, Z. M. Wang and S. Gao, *Chem. Commun.*, 2008, **44**, 281; (*g*) H. L. Sun, Z. M. Wang and S. Gao, *Coord. Chem. Rev.*, 2010, **254**, 1081; (*h*) J. S. Miller and D. Gatteschi, *Chem. Soc. Rev.*, 2011, **40**, 3065.

11 (*a*) N. Ishikawa, M. Sugita and W. Wernsdorfer, *Angew. Chem*. 2005, **117**, 2991; (*b*) J. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli and A. K. Powell, *Angew. Chem., Int. Ed.*, 2006, **45**, 1729; (*c*) K. Bernot, J. Luzon, L. Bogani, M. Etienne, C. Sangregorio, M. Shanmugam, A. Caneschi, R. Sessoli and D. Gatteschi, *J. Am. Chem. Soc.*, 2009, **131**, 5573; (*d*) K. Bernot, F. Pointillart, P. Rosa, M. Etienne, R. Sessoli and D. Gatteschia, *Chem. Commun.*, 2010, **46**, 6458; (*e*) H. S. Ke, G. F. Xu, Y. N. Guo, P. Gamez, C. M. Beavers, S. J. Teat and J. K. Tang, *Chem. Commun.*, 2010, **46**, 6057; (*f*) S. D. Jiang, B. W. Wang, G. Su, Z. M.

Wang and S. Gao, *Angew. Chem., Int. Ed.*, 2010, **49**, 7448.

12 (*a*) P. H. Lin, T. J. Burchell, R. Clérac and M. Murugesu, *Angew. Chem., Int. Ed.*, 2008, **47**, 8848; (*b*) R. N. Liu, L. C. Li, X. L. Wang, P. P. Yang, C. Wang, D. Z. Liao and J. P. Sutter, *Chem. Commun.*, 2010, **46**, 2566.

13 M. Estrader, J. Ribas, V. Tangoulis, X. Solans, M. Font-Bardia, M. Maestro and C. Diaz, *Inorg. Chem.*, 2006, **45**, 8239.

14 (*a*) J. X. Xu, Y. Ma, D. Z. Liao, G. F. Xu, J. K. Tang, C. Wang, N. Zhou, S. P. Yan, P. Cheng and L. C. Li, *Inorg. Chem.*, 2009, **48**, 8890; (*b*) N. Zhou, Y. Ma, C. Wang, G. F. Xu, J. K. Tang, J. X. Xu, S. P. Yan, P. Cheng, L. C. Li and D. Z. Liao, *Dalton Trans.*, 2009, **38**, 8489; (*c*) X. L. Wang, L. C. Li and D. Z. Liao, *Inorg. Chem.*, 2010, **49**, 4735; (*d*) T. Han, W. Shi, X. P. Zhang, L. L. Li and P. Cheng, *Inorg. Chem.*, 2012, **51**, 13009; (*e*) X. L. Mei, Y. Ma, L. C. Li and D. Z. Liao, *Dalton Trans.*, 2012, **41**, 505; (*f*) X. L. Mei, R. N. Liu, C. Wang, P. P. Yang, L. C. Li and D. Z. Liao, *Dalton Trans.*, 2012, **41**, 2904; (*g*) P. Hu, X. F. Wang, Y. Ma, Q. L. Wang, L. C. Li and D. Z. Liao, *Dalton Trans.*, 2014, **43**, 2234; (*f*) L. L. Li, S. Liu, Y. Zhang, W. Shi and P. Cheng, *Dalton Trans.*2015, **44**, 6118.

15 (*a*) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem., Int. Ed.*, 2001, **40**, 1760; (*b*) L. Bogani, C. Sangregorio, R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed.*, 2005, **44**, 5817; (*c*) K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi and R. Sessoli, *J. Am. Chem. Soc.*, 2006, **128**, 7947; (*d*) T. Han, W. Shi, Z. Niu, B. Na and P. Cheng, *Chem. Eur. J.*, 2013, **19**, 994; (*e*) X. L. Wang, X. Bao, P. P. Xu and L. Li, *Eur. J. Inorg. Chem.*, **2011**, 3586; (*f*) L. L. Li, S. Liu, H. Li, W. Shi and P. Cheng, *Chem. Commun*. 2015, **51**, 10933.

16 (*a*) G. Francese, F. M. Romero, A. Neels, H. Stoeckli-Evans and S. Decurtins, *Inorg. Chem.*, 2000, **39**, 2087; (*b*) H. Oshio, M. Yamamoto, T. Ito, H. Kawauchi, N. Koga, T. Ikoma and S. Tero-Kubota, *Inorg. Chem.*, 2001, **40**, 5518; (*c*) L. Tian, Y. Q. Sun, B. Na and P. Cheng, *Eur. J. Inorg. Chem*. **2013**, 4329; (*d*) S. Y. Zhou, X. Li, T. Li, Li Tian, Z. Y. Liu and X. G. Wang, *RSC Adv*., 2015, **5**, 17131.

17 (*a*) Y. Z. Zheng, Y. Lan, C. E. Anson and A. K. Powell, *Inorg. Chem.*, 2008, **47**, 10813; (*b*) S. Kanegawa, M. Maeyama, M. Nakano and N. Koga, *J. Am. Chem. Soc.*, 2008, **130**, 3079; (*c*) X. L. Wang, L. C. Li and D. Z. Liao, *Inorg. Chem.*, 2010, **49**, 4735.

18 (*a*) N. M. Shavaleev, F. Gumy, R. Scopelliti and J. C. G. Bünzli, *Inorg. Chem.*, 2009, **48**, 5611; (*b*) B. Drahoš, J. Kotek, P. Hermann, I. Lukeš and É. Tóth, *Inorg. Chem.*, 2010, **49**, 3224.

19 (*a*) E. F. Ullmann, L. Call and J. H. Osiecki, *J. Org. Chem.*, 1970, **35**, 3623; (*b*) M. S. Davis, K. Morokum and R. N. Kreilick, *J. Am. Chem. Soc.*, 1972, **94**, 5588.

20 (*a*) G. M. Sheldrick, *SHELXS*-97, *Program for solution of crystal structures*, University of Göttingen, Germany, **1997**; (*b*) G. M. Sheldrick, *SHELXL*-97, *Program for refinement of crystal structures*, University of Göttingen, Germany, **1997**; (*c*) G. M. Sheldrick, *SADABS*, *Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, **1996**.

21 (*a*) H. Zabrodsky, S. Peleg and D. Avnir, *J. Am. Chem. Soc.*, 1992, **114**, 7843; (*b*) M. Pinsky and D. Avnir, *Inorg. Chem.*, 1998, **37**, 5575.

22 Y. L. Wang, B. Gu, Y. Ma, C. Xing, Q. L. Wang, L. C. Li, P. Cheng and D. Z. Liao,

CrystEngComm., 2014, **16**, 2283.

23 M. F. Richardson, W. F. Wagner and D. E. Sands, *J. Inorg. Nucl. Chem*., 1968, **30**, 1275.

24 (*a*) C. Benelli, A. Caneschi, D. Gatteschi, J. Laugier and P. Rey, *Angew. Chem., Int. Ed*., 1987, **26**, 913; (*b*) S. Akine, T. Matsumoto, T. Taniguchi and T. Nabeshima, *Inorg. Chem*., 2005, **44**, 3270; (*c*) Q. H. Zhao, Y. P. Ma, L. Du and R. B. Fang, *Trans. Met. Chem*., 2006, **31**, 593.

25 (*a*) G. Francese, F. M. Romero, A. Neels, H. Stoeckli-Evans and S. Decurtins, *Inorg. Chem*., 2000, **39**, 2087; (*b*) I. A. Gass, C. J. Gartshore, D. W. Lupton, B. Moubaraki, A. Nafady, A. M. Bond, J. F. Boas, J. D. Cashion, C. Milsmann,§ Karl Wieghardt and K. S. Murray, *Inorg. Chem*., 2011, **50**, 3052; (c) I. A. Gass, S. Tewary, A. Nafady, N. F. Chilton, C. J. Gartshore, M. Asadi, D. W. Lupton, B. Moubaraki, A. M. Bond, J. F. Boas, S. X. Guo, G. Rajaraman and K. S. Murray, *Inorg. Chem*., 2013, **52**, 7557.

26 (a) Y. Pei, A. Lang, P. Bergerat, O. Kahn, M. Fettouhi and L. Ouahab, *Inorg. Chem*., 1996, **35**, 193; (b) K. Fegy, A. Lang, P. Bergerat, O. Kahn, M. Fettouhi and L. Ouahab, *Inorg. Chem*., 1998, **37**, 4518.

27 J. P. Sutter, M. L. Kahn, S. Golhen, L. Ouahab, O. Kahn, *Chem. Eur. J.* 1998, **4**, 571;

28 (*a*) C. Lescop, D. Luneau, P. Rey, G. Bussiere and C. Reber, *Inorg. Chem*. 2002, **41**, 5566; (*b*) C. Lescop, D. Luneau, E. Beloeizky, P. Fries, M. Guillot, P. Rey, *Inorg. Chem*.1999, **38**, 5472.

29 (*a*) K. Bernot, L. Bogani, R. Sessoli and D. Gatteschi, *Inorg. Chim. Acta*, 2007, **360**, 3807; (*b*)Y. Ma, G. F. Xu, X. Yang, L. C. Li, J. K. Tang, S. P, Yan, P. Cheng and D. Z. Liao, *Chem. Commun*., 2010, **46**, 8264; (*c*) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba and J. Mrozinski, *J. Am. Chem. Soc*., 2004, **126**, 420; (*d*) Y. M. Bing, N. Xu, W. Shi, K. Liu and P. Cheng, *Chem. Asian J*., 2013, **8**, 1412.

30 (*a*) C. Benelli, A. Caneschi, D. Gatteschi and L. Pardi, *Inorg. Chem*., 1992, **31**,741; (*b*) M. L. Kahn, J. P. Sutter, S. Golhen, P. Guionneau, L. Ouahab, O. Kahn and D. Chasseau, *J. Am. Chem. Soc.*, 2000, **122**, 3413; (*c*) J. X. Xu, Y. Ma, G. F. Xu, C. Wang, D. Z. Liao, Z. H. Jiang, S. P. Yan and L. C. Li, *Inorg. Chem. Commun.*, 2008, **11**, 1356; (*d*) H. X. Tian, R. N. Liu, X. L. Wang, P. P. Yang, Z. X. Li, L. C. Li and D. Z. Liao, *Eur. J. Inorg. Chem.*, **2009**, 4498; (*e*) Y. L. Miao, J. L. Liu, J. Y. Li, J. D. Leng, Y. C. Ou and M. L. Tong, *Dalton Trans*., 2011, **40**, 10229; (*f*) R. N. Liu, C. M. Zhang, L. C. Li, D. Z. Liao and J. P. Sutter, *Dalton Trans*., 2012, **41**, 12139.

Title: A family of rare earth complexes with chelating furan biradicals: syntheses, structures and magnetic properties

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Contents graphic and synopsis

Six Ln^{III}-furan-biradical tri-spin complexes have been synthesized, they exhibit interesting magnetic properties. Dy^{III} complex shows frequency-dependent ac magnetic susceptibilities, which suggests the presence of slow magnetic relaxation.