具有磁弛豫和荧光性能的氮氧自由基-稀土离子环形双核

李弘道* 张胜健 董红梅

(太原工业学院化学与化工系,太原 030008)

摘要:选用手性氮氧自由基与稀土离子反应,成功组装了2例2*p*-4*f*异自旋内消旋配合物[Ln(hfac)₃((*R*)-MePP-Ph-NIT)]₂,其中Ln=Eu (1)、Dy (2), hfac=六氟乙酰丙酮, (*R*)-MePP-Ph-NIT=2-(4-((*R*)-tert-butyl-2-methylpiperazine-1-carboxylate)phenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide。在配合物中,氮氧自由基配体连接2个稀土离子形成环形双核结构。配合物1展现出销离子的特征荧光。在配合物2中,磁弛豫相关的频率依赖的虚部信号说明了其单分子磁体的特性。

关键词: 氮氧自由基; 单分子磁体; 稀土离子; 2*p*-4*f*异自旋 中图分类号: 0614.33⁺8; 0614.342 文献标识码: A 文章编号: 1001-4861(2024)05-0972-07 DOI: 10.11862/CJIC.20230411

Magnetic relaxation and luminescent behavior in nitronyl nitroxide-based annuluses of rare-earth ions

LI Hongdao* ZHANG Shengjian DONG Hongmei

(Taiyuan Institute of Technology, Department of Chemistry and Chemical Engineering, Taiyuan 030008, China)

Abstract: Employing the reaction of chiral nitronyl nitroxide radical and rare-earth ions, two 2p-4f hetero-spin meso complexes [Ln(hfac)₃((*R*)-MePP-Ph-NIT)]₂, where Ln=Eu (1) and Dy (2), hfac=hexafluoroacetylacetone; (*R*)-MePP-Ph-NIT=2-(4-((*R*)-tert-butyl-2-methylpiperazine-1-carboxylate)phenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, have been assembled. In both complexes, two chiral radicals ligate to two Ln(III) ions to produce a cyclic dinuclear structure. Complex 1 shows the characteristic fluorescence emission of the Eu (III) ion. In complex 2, the frequency-dependent out-of-phase susceptibility signals connected with magnetic relaxation confirm single-molecule magnet (SMM) behavior. CCDC: 2304262, 1; 2304263, 2.

Keywords: nitronyl nitroxide; single-molecule magnet; rare-earth ion; 2p-4f hetero-spin

Manufacturing electronic devices at the nanoscale is still an infusive challenge. The generation of such devices is stimulated by ever-increasing demand for higher-density data storage and low-energy electronics. In this regard, single - molecule magnet (SMM) is a promising field^[1-3]. Furthermore, lanthanide compounds have been demonstrated to be an ideal candidate for construction SMMs. Among them, based on the theory of Long et al., the Dy^{III}-compound with a pseudolinear environment could achieve the highest blocking temperature $(T_{\rm B})^{[4]}$. In 2018, the current record $T_{\rm B}$ of 80 K was made by a pseudo-linear Dy^{III} SMM^[5]. Lately, a dinuclear Dy^{III} SMM has matched the record^[6]. Besides, Ln-radical SMMs are of great interest and have been intensely researched on account of Ln-radical direct magnetic couplings effectively inhibiting the quantum tunneling of magnetization (QTM) of Ln^{III} ions. Some infusive achievements have been achieved by virtue of

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^{*}通信联系人。E-mail:lihong.dao@163.com

the Ln-rad strategy^[7-9], for instance, a binuclear Tb-N₂³⁻ radical SMM retains a magnetic memory effect until 20 K^[10]. In 2021, our group reported a dipyridyl-decorated nitronyl nitroxide - Dy^{III} SMM with an effective energy barrier of 146 K^[11]. Nevertheless, it is worth noting that these Ln-radical SMMs primarily rely on achiral radicals and the research of chiral radical-based Ln-SMMs is still rare. On the other hand, investigation of lanthanide-based optical properties has become pervasive involving the superiority of Ln luminescence, such as long lifetimes, the characteristic narrow line - like emissions, and high quantum yields^[12].

Based on the above considerations, we designed and adopted a functionalized chiral nitronyl nitroxide radical 2 - (4 - ((R) - tert - butyl - 2 - methylpiperazine - 1 carboxylate)phenyl)-4,4,5,5-tetramethylimidazoline-1oxyl-3-oxide ((R)-MePP-Ph-NIT, Scheme 1) to construct two mesomerides [Ln(hfac)₃((R)-MePP-Ph-NIT)]₂,where Ln=Eu (1) and Dy (2), and hfac=hexafluoroacetylacetone. Structure, optical activity, and magnetic properties were analyzed. Complex 1 exhibits the characteristic fluorescence emission of the Eu(III) ion, while theDy complex displays SMM behaviour.



Scheme 1 Structure of chiral radical ligand (R)-MePP-Ph-NIT

1 Experimental

1.1 Materials and instruments

Starting reagents such as trichloromethane and heptane were commercially purchased. The nitronyl nitroxide (R)-MePP-Ph-NIT was synthesized by referring to the reported literature^[13]. Elemental analysis was performed by a Perkin-Elmer 240 elemental analyzer. Magnetic property measurement of complex **2** was performed on a Quantum Design MPMS magnetometer. In the light of Pascal constants^[14], DC magnetic susceptibility was corrected involving diamagnetism contribution. The fluorescent spectrum of complex **1** was measured by an F-7000 fluorescence spectrophotometer. At room temperature, the circular dichroism (CD) spectrum of the MePP-Ph-NIT radical ligand was gathered on a JASCO J-815 spectropolarimeter.

1.2 Syntheses of complexes 1 and 2

[Ln(hfac)₃·2H₂O] (0.01 mmol) was suspended in boiling *n*-heptane (98 °C) and kept in reflux condition for 6 h. After cooling down to 80 °C, a CHCl₃ solution (5 mL) of (*R*)-MePP-Ph-NIT (0.01 mmol) was slowly added. After stirring for 30 min, the above-mixed solution was filtered. The filtrate was left to stand at room temperature, and navy-blue bar crystals were separated after 7 d. FTIR (KBr, cm⁻¹): 1 776(s), 1 350(m), 1 180(s), 1 161(s), 1 062(s), 948(s), 859(m), 549(s) for **1**; 1 775(s), 1 350(m), 1 182(s), 1 160(s), 1 062(s), 950(s), 859(m), 551(s) for **2**. Elemental Anal. Calcd. for C₇₆H₇₆Eu₂F₃₆ N₈O₂₀(%): C, 37.88; H, 3.17; N, 4.65. Found(%): C, 37.86; H, 3.18; N, 4.67. Elemental Anal. Calcd. for C₇₆H₇₆Dy₂F₃₆N₈O₂₀(%): C, 37.55; H, 3.15; N, 4.61. Found(%): C, 37.57; H, 3.14; N, 4.62.

1.3 Crystal structure determination

Single crystal X - ray data of complexes 1 and 2 were collected at 150 K on a Bruker APEX II diffractometer with a CCD area detector (Cu $K\alpha$ radiation, $\lambda = 0.154$ 178 nm) and were processed for reduction through the SAINT software^[15]. SADABS was used to correct absorption effects^[16]. Structures of both complexes were solved using direct methods involving SHELXS - 2014^[17] and refined via full - matrix least squares minimization involving the SHELXL - 2014^[18]. Anisotropic displacement parameters were devoted to refining non-H atoms. Meanwhile, H atoms bonded to the carbon and oxygen atoms were placed at ideal positions. Additional crystallographic data and parameters for the two binuclear 2p - 4f complexes are given in Table 1, S1, and S2 (Supporting information).

CCDC: 2304262, 1; 2304263, 2.

2 Results and discussion

2.1 Description of crystal structure

Crystallographic studies show that complexes 1

Parameter	1	2
Empirical formula	$\rm C_{38}H_{38}EuF_{18}N_4O_{10}$	$\rm C_{38}H_{38}DyF_{18}N_4O_{10}$
Formula weight	1 204.68	1 215.22
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
<i>a /</i> nm	3.841 85(5)	1.971 30(10)
<i>b</i> / nm	1.463 76(2)	1.460 68(7)
<i>c</i> / nm	1.987 06(3)	3.500 61(18)
β / (°)	114.631 0(10)	95.723(3)
V / nm^3	10.157 6(3)	10.029 6(9)
Ζ	8	8
$D_{\rm c} / ({\rm g} \cdot {\rm cm}^{-3})$	1.576	1.610
μ / mm $^{-1}$	9.934	9.080
2θ range / (°)	5.06-150.476	5.074-149.148
Reflection collected	54 508	54 749
Unique reflection (R_{int})	10 378 (0.080 5)	10 186 (0.055 0)
GOF (F^2)	0.905	0.902
$R_1, wR_2 [I > 2\sigma(I)]$	0.080 1, 0.204 8	0.091 9, 0.219 9
R_1, wR_2 (all data)	0.088 4, 0.210 9	0.094 2, 0.221 2

 Table 1
 Crystallographic data and structure refinement for complexes 1 and 2

and **2** are isostructural. Here, complex **2** is chosen as representative to describe in detail (Fig. 1). Complex **2** crystallizes in a monoclinic C2/c space group. **2** is centrosymmetric with one asymmetric entity $[Dy(hfac)_3$ ((R)-MePP-Ph-NIT)], and the existence of a symmetry center cancels the chirality contribution of the radical ligand to yield meso form, in which two chiral radicals ligate to both Dy(III) ions via oxygen atoms of NO groups and carboxylates to produce a cyclic dinuclear structure. The direct coordination between two radicals and Dy(III) ions will contribute to charge transfer from the radical π^* orbital to the empty orbitals of the Dy(III) ion, which will lead to the ferromagnetic Dy-rad (radical) coupling^[19]. Besides, the chelate coordination of



Ellipsoids are set at the 30% probability levels; H and F atoms are omitted for clarity; Symmetry code: a: -x, -y, -z.
Fig.1 (a) Molecular structure of meso complex 2; (b) Coordination polyhedra of the Dy(III) ion

hfac⁻ ligand and introduction of radicals are beneficial to sensitize the fluorescence of Ln^{II} ion^[20-21].

The Dy(III) ion is encircled by one O atom (Dy— O_{rad} 0.233 9(5) nm) from the nitroxide group, one O atom (Dy—O_{carb} 0.237 0(6) nm) from one carboxylate and six O donors (Dy—O_{hfac} 0.231 9(6)-0.239 4(6) nm) from three hfac⁻ anions. The Dy(III) ion forms a triangular dodecahedron coordination sphere (D_{2d}) with a CShM (continuous-shape measurement) value of 0.112, verified via SHAPE software^[22-23] (Table 2, Fig. 1). The Dy(III)…Dy(III) distance is 1.058 6 nm in the dimer unit. The packing arrangement shows that the intermolecular minimum distances are 2.055 3 nm for Dy…Dy and 1.253 nm for NO…ON (Fig. 2), hinting that well separates between molecules.

Table 2 SHAPE analysis for complexes 1 and 2*

Complex	SAPR-8	TDD-8	BTPR-8
1	2.574	0.114	2.610
2	2.948	0.112	2.435

*SAPR - 8: square antiprism; TDD - 8: triangular dodecahedron; BTPR-8: biaugmented trigonal prism.



H, F atoms are omitted for clarity.

Fig.2 Packing diagram of complex 2

2.2 Magnetic properties

DC magnetic measurement of annular complex **2** showed that the room temperature $\chi_{\rm M}T$ product was 28.62 cm³·mol⁻¹·K (Fig. 3a), which well matched with the expected value for two isolated Dy(III) ions (S=5/2, L =5, ${}^{6}H_{15/2}$, g=4/3, C=14.17 cm³·mol⁻¹·K) and two chiral radicals (S=1/2, g=2.0, C=0.375 cm³·mol⁻¹·K). Upon cooling, $\chi_{\rm M}T$ product of 2 decreased smoothly before a steep drop at 78 K and attained the minimum of 22.95 cm³·mol⁻¹·K at 2 K indicating the depopulation of $M_{\rm j}$ levels of the Dy(III) ion. M - H plot exhibited a rapid increase of the magnetization on the ramping magnetic field without saturation (Fig.3b).

AC measurements were conducted in 0 Oe and external 1 500 Oe DC field to reveal the dynamic magnetic properties. For the temperature-dependent data of 2, there were incipient frequency-dependent χ'' signals under 0 DC field on account of QTM (Fig. S5), but χ'' peaks emerged in 1 500 Oe DC field (Fig.4), displaying the typical SMM behavior. For frequency - dependent signal, χ'' peaks of complex 2 shifted towards the highfrequency district on warming under 1 500 Oe DC field.

The relaxation time (τ) was deduced by the maxima of $\chi''(\nu)$ signals (Fig.4b) and pseudo-linear ln τ vs 1/T plots (Fig.5a), suggesting the existence of Raman, Orbach process and QTM with the following equation: $\tau^{-1}=CT^{n}+\tau_{0}^{-1}\exp[-\Delta/(k_{\rm B}T)]+\tau_{\rm QTM}^{-1}$, giving C=87.3 s⁻¹· K^{-3.93}, n=3.93, $\Delta/k_{\rm B}=21.8(4)$ K, $\tau_{0}=1.0(2)$ µs and $\tau_{\rm QTM}=0.33(6)$ ms for **2**, typical of Ln-based SMMs^[24-30]. Fitting the Cole - Cole plots based on a generalized Debye mode obtained α values varying in a range of 0.297 -



Fig.3 (a) Plot of $\chi_{M}T$ vs T and (b) field dependence of the magnetization at 2 K for complex 2

0.314 for **2** (Fig.5b), hinting at the wide relaxation time distribution.

Employing the MAGELLAN software^[31], the direction of the principal magnetic axes of both Dy(III) ions was investigated (Fig. 6). The magnetic axes on Dy(III) ions are in the same orientation due to the centrosymmetric structure. However, the direction diverges obviously from the shortest bond Dy— O_{hfac} (Dy1—O6 0.231 9(5) nm), with the 68.97° angular difference. To our knowledge, the magnetic relaxation of the Dy(III) - complex could be related to the orientation of the magnetic anisotropy axis. In addition, the combined action of foreseeing ferromagnetic Dy - rad coupling with the diffuse spin orbitals of (*R*)-MePP-Ph-NIT penetrating



The solid lines represent the fitting.





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Fig.5 (a) Arrhenius plot (ln τ vs T^{-1}) and (b) Cole-Cole plots from 2.4 to 3.8 K for complex 2



Fig.6 Magnetic anisotropy axes (blue sticks) of Dy(III) ions in complex 2

the core electron density of 4f orbitals and antiferromagnetic rad - rad interaction through the Dy (III) ion, might be able to cut down QTM in some degree, despite the relatively weak coupling strength^[32-33]. For Ln-complexes, the magnetic relaxation is fantastically sensitive to the coordination symmetry of the Ln^{III} ion^[34]. The Dy^{III} center lies in a D_{2d} symmetry with a relatively low CShM value of 0.112, which is close to ideal D_{2d} geometry. The above geometry may provide a pathway to shut down QTM and improve magnetic anisotropy of the Dy(III) ion. Therefore, the magnetic relaxation may result from the synergy of magnetic couplings and magnetic anisotropy of the Dy(III) ion.

2.3 Luminescence properties

The luminescence of the Eu complex was investigated in a CH_2Cl_2 solution at room temperature. The emission spectrum of complex **1** was achieved by an excitation wavelength (λ_{ex}) of 306 nm, which exhibited five different bands at 579 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{0}$), 594 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$), 614 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$), 650 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{3}$), and 700 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{4}$) (Fig. 7). ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ corresponds to a forbidden transition, hence, its intensity is extremely weak. The magnetically allowed ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is split on account of the crystal field. The signal intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is the most strong in the red range and in charge of the red - orange emission colour. In addition, during the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, the luminescence decay was recorded, which was fitted via a mono-exponential model, $I=I_{0}\exp(-t/\tau)$, with the decay time of 26.6 µs. Related fitting parameters are given in Table S3.



Fig.7 (a) Emission spectrum and (b) luminescence decay of complex 1 at room temperature

3 Conclusions

In summary, two meso 2p-4f complexes with a circle structure have been successfully prepared by the Ln^{III} -mediated self-assembly of chiral nitronyl nitroxide radical ligand. Interestingly, the Dy ring displayed field-induced SMM behavior. Furthermore, the Eu ring exhibited red emission in the visible region. Though only meso 2p - 4f complexes have been obtained, the investigation of molecule - based materials involving chiral nitronyl nitroxide radicals is still rare so far. To construct chiral 2p - 4f complexes, the exploration of other chiral nitronyl nitroxide - Ln functional materials is in progress.

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