



The synthesis, structure, magnetic and luminescent properties of a new tetranuclear dysprosium (III) cluster

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ABSTRACT

The synthesis and characterization of $[\text{Dy}_4(\text{dhampH}_3)_4(\text{NO}_3)_2](\text{NO}_3)_2$ (1), a new tetranuclear dysprosium (III) complex, is described. The compound was characterized by its X-ray structure, magnetic properties as well as the luminescent spectra. The compound crystallizes in a $P\bar{1}$ space group with a zig-zag linear form of geometry. The ac magnetic susceptibilities of the molecule indicate that it is a magnetic molecule with a slow magnetization relaxation. The molecule also exhibits an emission spectrum that was confirmed to be ligand based. These results indicate that this molecule has both a slow magnetization relaxation (that could be potentially a SMM) and luminescent properties.

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1. Introduction

The synthesis of new metal clusters is of great interest, because of their wide variety of architectural features [1]. Through different topological arrangements, metal ions can interact with each other differently and thus trigger fascinating physical properties, including luminescence and/or magnetism. Magnetic metal clusters, which have a sluggish magnetization relaxation, are attractive because they are potential candidates for use in memory devices [2]. One extremely successful example are single molecule magnets (SMMs) [3], which have a large molecular spin and zero-field splitting (zfs) and can be utilized quantum computing, spintronics and magnetic refrigeration [4]. Lanthanides, because they have a large number of unpaired electrons and un-quenched $4f$ orbitals, are considered to be excellent building blocks for creating clusters with slow magnetization relaxations. In many cases, chemists have attempted to prepare $3d$ – $4f$ mixed metal clusters by incorporating $3d$ metals such as Cr, Mn, Fe, Co and Ni with lanthanides [5]. However, chemists have also began to focus on pure lanthanide-based clusters as well [6]. A wide variety of $4f$ metals with different molecular geometries have been reported in the literature. Among these, Dy is known to produce more clusters with frequency-dependent ac signals than other lanthanides [6,7]. In particular, in the past year, two linear tetra-nuclear Dy₄

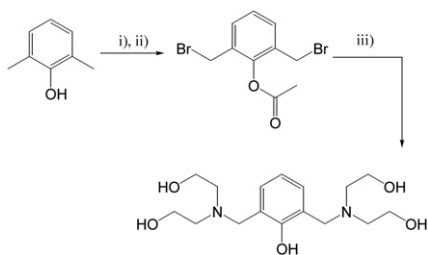
complexes have been developed through association with a novel phenomenon, such as two-step magnetization relaxation [8].

Luminescence has been applied in a wide variety of molecular materials, such as metal–organic frameworks (MOF) [9]. Although not many cases have been reported, magnetic molecules which also have fluorescence properties have attracted interest in recent years [10]. One of the advantages of fluorescent magnetic molecules is that the luminescence provides a means for their detection. This property would facilitate the construction of actual molecular devices. Molecular luminescence is known to be applicable to light-emitting diodes (LED), organic light-emitting diodes (OLED) [11], tunable lasers and for optical storage. A molecule showing both magnetism and luminescence would be quite interesting. However, to the best of our knowledge, a single molecule that has both luminescent and slow magnetization relaxation (SMMs-like) behavior is quite rare. In the present paper, we report on the preparation and characterization of a new linear Dy₄ molecule that simultaneously behaves as an SMM-like and luminescent molecular material [10].

Because the magnetic properties of a metal cluster are strongly dependent on the geometry of the ligand, the choice of an appropriate ligand is important. From literature reports, it is apparent that many phenol-containing ligands have been used in many SMMs studies [12]. Also, amino-alcohol groups have been utilized in the synthesis of a wide variety of metal clusters [13]. Our goal here was to combine these two fragments into a single ligand. To accomplish this, we synthesized a new molecule, 2,6-bis[N,N-di(2-hydroxyethyl)aminomethyl]phenol (dhampH₅). The synthetic strategy for the synthesis is shown in Scheme 1. We then attempted

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Scheme 1. Synthetic strategy used to prepare dhamph₅: (i) AcCl, NEt₃, CH₂Cl₂; (ii) NBS, CHCl₃, IR-irradiation 14 h reflux and (iii) diethanolamine, (NMe₄)₂CO₃, NMe₄HCO₃, MeOH.

to use this ligand to develop a new metal cluster with dysprosium and to examine its magnetic and luminescent properties.

2. Experimental section

2.1. Synthesis

Tetramethylammonium hydrogencarbonate [14] and 2,6-dimethylphenoxy acetate [15] were prepared as described in the literature.

2.1.1. [2,6-Bis(bromomethyl)phenyl ester]

2,6-Dimethylphenoxy acetate (6.60 g, 36.9 mmol) and N-bromosuccinimide (13.13 g, 73.8 mmol) in 130 ml chloroform were refluxed under an atmosphere of nitrogen with continuous irradiation with a 500 W IR lamp. The resulting mixture was washed with 250 ml of an aqueous 1 M NaOH solution three times and once with 30 ml of a saturated brine solution. The organic layer was dried over MgSO₄. After removing the chloroform by evaporation, the resulting solid was dissolved in a 10 ml CH₂Cl₂/13 ml hexanes solution and the solution stored in a refrigerator overnight. Yellow crystals of the product were obtained. Yield: 35%. (¹H NMR in CDCl₃, 300 MHz) δ 7.43(d, 2H, phenyl-**H**), 7.23 (t, 2H, phenyl-**H**), 4.38 (s, 4H, CH₂-Br), 2.46 (s, 3H, CH₃CO); ¹³C (75 MHz) δ 20.8, 27.5, 127.0, 131.2, 131.6, 147.7 and 168.6. HREI-MS: 321.9026. Anal. Calcd. For (C₁₀H₁₀O₂Br₂): C, 37.30; H, 3.14; Found: C, 37.43; H, 3.12%.

2.1.2. [2,6-Bis[N,N-di(2-hydroxyethyl)aminomethyl]phenol]

NMe₄HCO₃ (2.9 g, 21.4 mmol) and (NMe₄)₂OH (1.3 g, 14.3 mmol) were dissolved in 35 ml of methanol and the solution was stirred for 3 h. A solution of diethanolamine (1.5 g, 14.3 mmol) and 3,5-Bis(bromomethyl)phenyl ester (2.3 g, 7.14 mmol) in 35 ml methanol was added to this solution, followed by stirring overnight under a nitrogen atmosphere. After removing the methanol, 60 ml CH₂Cl₂ was added. The organic layer was extracted twice with 20 ml portions of distilled water. The aqueous layer was then washed with diethyl-ether several times and then extracted with CH₂Cl₂. After drying the CH₂Cl₂, the ligand dhamph₅ was obtained in 20% yield. (¹H NMR in CDCl₃, 300 MHz) δ 7.02(d, 2H, phenyl-**H**), 6.75 (t, 1H, phenyl-**H**), 3.82 (s, 4H, PhCH₂N), 3.68 (t, 8H, CH₂OH), 2.73 (t, 8H, NCH₂CH₂); ¹³C (75 MHz) δ 55.8, 57.2, 59.4, 119.0, 124.0, 129.7 and 156.3. HRESI-MS: 329.2056. Anal. Calcd. For (C₁₆H₂₈N₂O₅): C, 58.51; H, 8.59; N, 8.53. Found: C, 58.40; H, 8.56; N, 8.69%.

2.1.3. [Dy₄(dhamph₃)₄(NO₃)₂] · 2(NO₃) · 3CH₃OH · H₂O (1)

The ligand (0.33 g, 1 mmol) was dissolved in 20 ml methanol, and 0.46 ml (4 mmol) triethylamine and Dy(H₂O)₆(NO₃)₃ (0.44 g, 1 mmol) was then added to this solution. The solution was refluxed for 4.5 h under a nitrogen atmosphere. After cooling, the solution was filtered and the filtrate was treated by diethyl-ether

diffusion. Pale yellow crystals suitable for X-ray structure determination were obtained after one week. ATR-IR, ν/cm⁻¹: 3218m, 2851m, 1594w, 1462s, 1383m, 1289s, 1238s, 1089s, 1030m, 979s, 903s, 863w, 757w. Anal. Calcd. For (C₆₄H₁₀₄Dy₄N₁₂O₃₂): C, 34.88; H, 4.77; N, 7.63%. Found: C, 34.57; H, 4.97; N, 7.62%.

2.2. Physical property measurements

NMR spectra of the compound were recorded with a Bruker AV-300 spectrometer. All chemicals were dissolved in CDCl₃. Infrared spectra were recorded on KBr pellets using Perkin Elmer 1600 spectrometer in the 650–4000 cm⁻¹ range. Elemental analysis (C, H, N) and dc magnetic susceptibility data were measured by the National Taiwan University of Instrument Centre College of Science. Part of the ac magnetic susceptibility measurements were performed at the National Chiao Tung University.

2.3. X-ray crystallography

A light yellow crystal of complex **1**, dimension 0.50 × 0.25 × 0.20 mm was selected for X-ray analysis on a Bruker SMART CCD diffractometer using MoKα radiation. The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler at 150 K. The detector was located at a distance of 5.00 cm from the crystal. The crystallographic data were collected over a hemisphere of reciprocal space, by a combination of four sets of exposures. Each set had a different φ angle for the crystal and each exposure of 5 s covered 0.30° in ω. Crystal decay was monitored by repeating the initial 50 frames at the end of the data collection period and analyzing the duplicate reflections. No decay was observed. An empirical absorption was based on the symmetry-equivalent reflections and the data examined using the SADABS [16] program. The structure analysis was completed using the SHELXTL [17] program on PC computer. The compound crystallized in the space group P $\bar{1}$, triclinic, *a* = 16.0192(9) Å, *b* = 18.3060(10) Å, *c* = 18.3287(10) Å, α = 64.826(2)°, β = 65.240(2)°, γ = 74.174(2)°, *V* = 4387.8(4) Å³, *z* = 2, λ = 0.71073 Å, μ(MoKα) = 3.457 mm⁻¹, F(000) = 2312 and *T* = 150(2) K. A total of 47,081 reflections were collected ranging from 1.24° ≤ θ ≤ 25.00°, of which 15,450 unique reflections and 13,534 with *I* ≥ 2σ(*I*) were collected for the analysis. The structure was solved using the Shelxs-97 program and refined using Shelxl-97 program by full-matrix least squares on *F*² values. Hydrogen atoms were fixed at the calculated positions and refined using a riding mode. The final indices were R1 = 0.0399, wR2 = 0.1193 with goodness-of-fit = 1.034. Detailed crystallography data can be found in Table 1.

3. Results and discussion

3.1. Structure description

Complex **1** crystallized in space group P $\bar{1}$. There are two symmetry independent molecules in the unit cell. The structure of complex **1** is depicted in Fig. 1, where the four Dy(III) ions adopt a zig-zag form with Dy–Dy–Dy angles of 116.53° for one molecule and 117.76° for the other. The molecules have centro-symmetry with an inversion center between Dy1 and Dy1A. All of the Dy ions are eight-coordinates with a highly distorted square antiprism geometry. There are two sets of Dy ions, one set located in the middle, numbered Dy1 and Dy1A, that are μ₂-bridged to two alkoxide groups from two dhamph₃²⁻ ligands, and have nitrate ligands bi-dentate coordinated with each of them. The other set of Dy ions are located on both ends of the molecule, numbered Dy2 and Dy2A, which are ligated by two dhamph₃²⁻ ligands, and are μ₂-bridged to Dy1 and Dy1A by a deprotonated phenol group and

Table 1
Crystallographic data for complex **1**.

Complex	1
Formula	C ₆₇ H ₁₁₈ Dy ₄ N ₁₂ O ₃₆
Fw (g mol ⁻¹)	2317.73
T (K)	150(2)
Space group	P1
a (Å)	16.0192(9)
b (Å)	18.3060(10)
c (Å)	18.3287(10)
α (deg.)	64.826(2)
β (deg.)	65.240(2)
γ (deg.)	74.174(2)
Volume (Å ³)	4387.8(4)
Z	2
F(000)	2312
Density (calcd) (mg m ⁻³)	1.754
Absorption coefficient	3.457
Absorption correction	SADABS
Transmission max/min	0.5447/0.2768
Refins, measured	47081
Refins, independent	15450 [R(int)=0.0333]
Data/restraints/parameters	15450/9/1028
Goodness-of-fit on F ²	1.034
R indices [I > 2σ(I)] ^{a,b}	R1=0.0399, wR2=0.1193
R indices (all data) ^{a,b}	R1=0.0466, wR2=0.1292

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^b R(\omega F^2) = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)] \}^{1/2}, \quad \omega = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \quad \text{where } P = [2F_o^2 + \max(F_o, 0)] / 3.$$

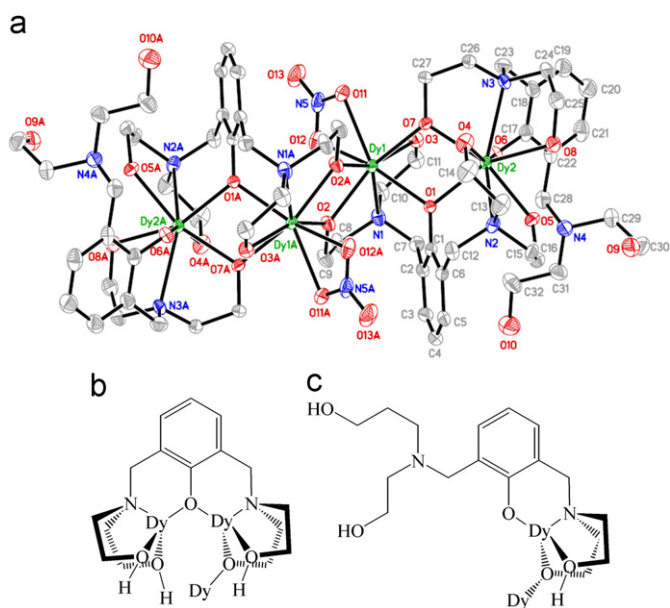


Fig. 1. (a) Molecular structure of the [Dy₄(dhampH₃)₄(NO₃)₂]²⁺ (**1**) cluster. Hydrogen atoms, counter ions and packing solvent molecules are omitted for the sake of clarity. (b) Binding modes of the ligand (dhampH₃)²⁻ in the middle of the complex and (c) binding modes of the ligand (dhampH₃)²⁻ on both ends of the complex.

an alkoxide arm. From the charge of this compound, it seemed reasonable to assume that all ligands take the form dhampH₃²⁻ with all the phenols and μ₂-bridging alcohol groups deprotonated, while all the mono-dentate alcohol groups are not deprotonated. The ligands in the middle coordinate to two Dy(III) ions, and the binding mode is shown in Fig. 1(b). The ligands on both ends of the complex have only one Dy ion in one bis-ethanol-amine structure the other arm is left empty (see Fig. 1(c)). For detailed structure data, please refer to the supplemental information.

3.2. DC magnetic property

Variable temperature dc magnetic susceptibility measurements of complex **1** were performed in a 1000 G magnetic field in temperatures that ranged from 2 to 300 K. Fig. 2 illustrates the $\chi_M T$ vs. T plot. The $\chi_M T$ value was 57.9 cm³ K mol⁻¹ at 300 K, which is quite close to the theoretical value of 56.7 cm³ K mol⁻¹ for the four uncoupled Dy(III) ions (⁶H_{15/2}, $g=4/3$). The $\chi_M T$ values are then slightly decreased to 49.0 cm³ K mol⁻¹ at 30 K and significantly decreased to 40.1 cm³ K mol⁻¹ at 2 K, which can be attributed to the depopulation of excited Stark sublevels [18]. Fig. 3 shows the reduced magnetization data recording under a 10–60,000 G magnetic field. The magnetizations measured at different magnetic field strengths do not superimpose. According to the literature reports, this characteristic is usually attributed to the presence of significant zfs and/or low-lying excited states [19]. The magnetizations reading from 5 T and 6 T are quite close. This can be because the system is approaching to its saturation value. From this fact, as well as the small splitting of magnetization under different magnetic fields, the feature of the non-superimposed reduced magnetization curves seem to more likely be the result of zfs. We also found the maximum value of reduced magnetization is 20.76 β, which is very close to Powell's calculation ($4 \times 5.23 \beta = 20.92 \beta$) for four uncorrelated Dy(III) ions [20].

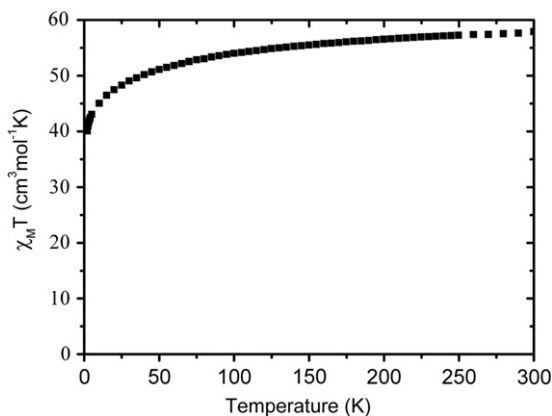


Fig. 2. $\chi_M T$ vs. T plot of complex **1**, collected in a 1000 G magnetic field.

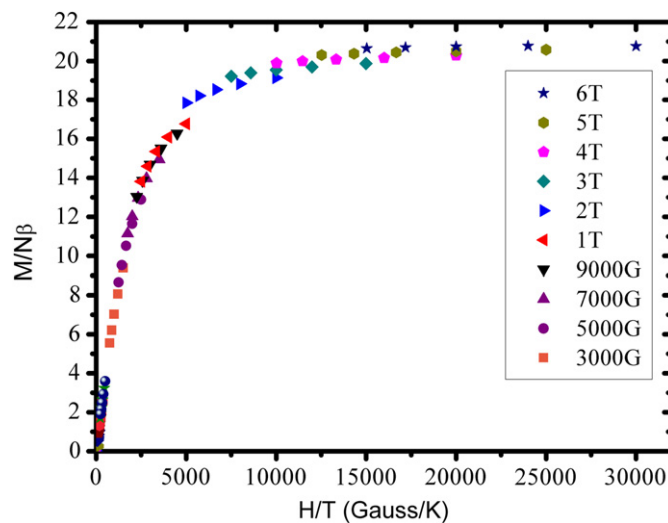


Fig. 3. Reduced magnetization for complex **1** under magnetic fields 10–60,000 G and temperature 2–4 K.

3.3. AC magnetic susceptibility

Alternating current susceptibility data in the temperature range 1.9–10 K were determined by applying a zero dc magnetic field and a 3.5 G ac field with frequencies of 50–1000 Hz. Both in-phase and out-of-phase signals are shown in Fig. 4. The frequency dependent behavior is observed at temperatures below 5 K, which suggests that slow magnetization relaxation processes are involved. To actually locate the position of the peak for the out-of-phase signals, we extended the oscillating frequency to 10,000 Hz. For the further analysis of the Cole–Cole plot, a frequency-scan method was employed in this experiment, i.e. the ac frequency was varied with the temperature held constant. Fig. 5 shows the magnetic susceptibilities vs. the logarithm of the frequency plot for both in-phase and out-of-phase signals. As the temperature is increased, the out-of-phase signals clearly shift to higher frequencies. Again, this frequency-dependent feature indicates that this molecule has slow magnetization relaxation characteristics, suggesting that it could be potentially a SMM. The ac data were thus extracted to estimate the kinetic energy barrier for the magnetization reversal. The inset of Fig. 5 shows an Arrhenius plot, where the solid line represents the least-square fit of the experimental data to the formula $\ln\tau = U_{\text{eff}}/kT + \ln\tau_0$. The calculation from this fit gives the effective energy barrier as $U_{\text{eff}} = 1.5 \text{ cm}^{-1}$. Although it is small, this value for an energy barrier is quite normal for many poly-dysprosium clusters [21]. For further explore the blocking temperature for complex 1, magnetization hysteresis loops and field cooling/zero-field cooling (FC/ZFC) experiments were carried out. (see supporting information Figs. 1S and 2S.) Neither hysteresis (above 1.9 K) nor the splitting of FC/ZFC (above 1.8 K) were detected. This indicates that the blocking temperature is likely far below the temperature that the traditional SQUID can access.

3.4. Cole–Cole plot

To examine the process of magnetization relaxation, ac magnetic susceptibilities were employed to construct a Cole–Cole (or Argand) plot [22]. The results are shown in Fig. 6, in which the solid lines represent the least-square fits of the theoretical curve based on Eqs.

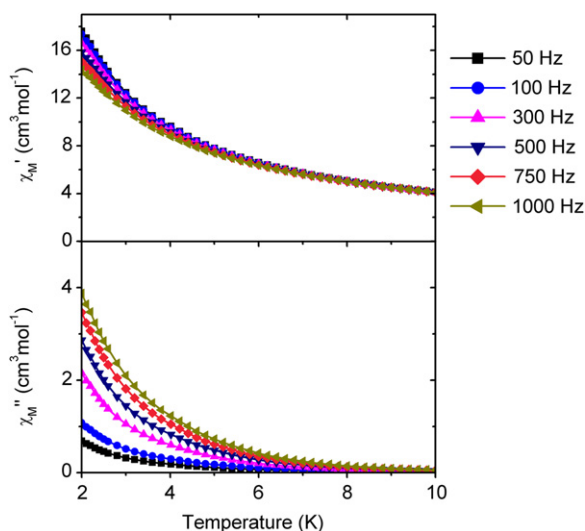


Fig. 4. ac Magnetic susceptibilities of complex 1 in a 3.5 G oscillating field and zero dc field with frequencies held constant and scanning under different temperatures. The in-phase signals are uppermost and the out-of-phase signals are at the bottom.

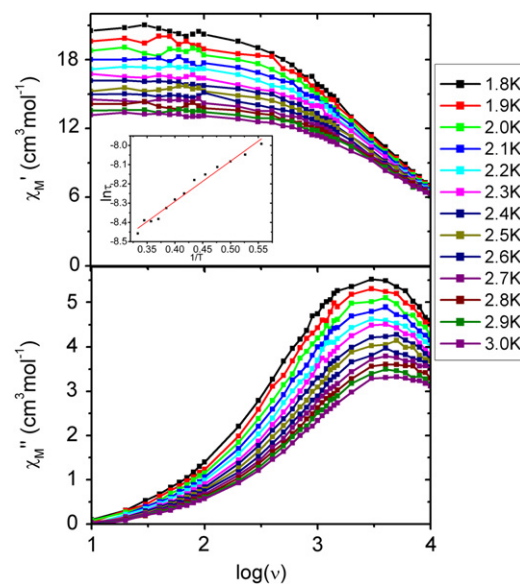


Fig. 5. ac Magnetic susceptibilities of complex 1 in a 3.5 G oscillating field and zero dc field with temperature hold constant and scanning with variable frequencies. The in-phase signals are uppermost and the out-of-phase signals are on the bottom. (inset: the Arrhenius plot of ac measurements. The solid line represents the fit that gives $U_{\text{eff}} = 1.5 \text{ cm}^{-1}$).

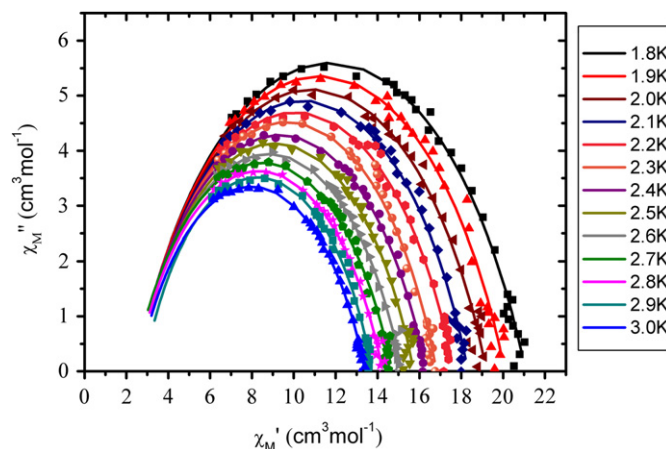


Fig. 6. Cole–Cole plot for complex 1 in the temperature range 1.8–3.0 K. The solid lines are the least-square fit of the data to the distribution of single relaxation processes.

(1) and (2)

$$\chi'(\omega) = \chi_S + \frac{(\chi_T - \chi_S)[1 + (\omega\tau)^{1-\alpha} \sin(1/2)\alpha\pi]}{1 + 2(\omega\tau)^{1-\alpha} \sin(1/2)\alpha\pi + (\omega\tau)^{2(1-\alpha)}} \quad (1)$$

$$\chi''(\omega) = \frac{(\chi_T - \chi_S)[(\omega\tau)^{1-\alpha} \cos(1/2)\alpha\pi]}{1 + 2(\omega\tau)^{1-\alpha} \sin(1/2)\alpha\pi + (\omega\tau)^{2(1-\alpha)}} \quad (2)$$

where χ_T is the isothermal susceptibility, χ_S is the adiabatic susceptibility, and τ is the magnetization relaxation time. The parameter α is an indicator of the distribution of relaxation time, i.e. the larger α values correspond to a wider distribution of the relaxation times. An analysis of the Cole–Cole plots at different temperatures show α parameters ranging from 0.27 to 0.31. Because these values are deviated from zero, the magnetization relaxation seem more likely to involve a distribution of relaxation processes. The ac data were further analyzed by the frequency-dependent shift of the freezing temperatures according to $F = \Delta T_f / (T_f \Delta \log \omega)$, giving

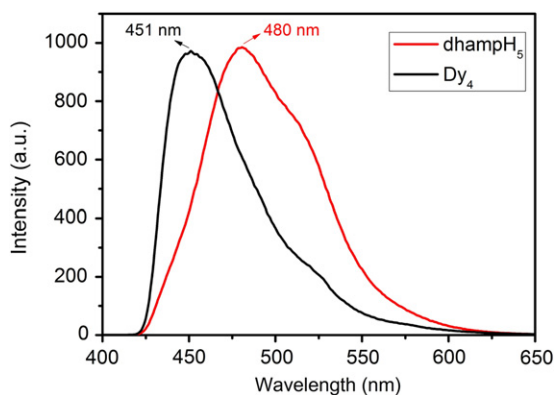


Fig. 7. Emission spectra for complex **1** (black line) in solid state and the ligand (red line) in the liquid state at room temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

an average $F=0.8$ for complex **1**. Although without more data to identify the real nature of the out-of-phase signals, this value rules out the possibility that the out-of-phase peak originates from spin-glass ($0.001 < F < 0.08$) or a ferromagnet ($F < 0.001$) [23].

3.5. Luminescent property

The photo-luminescent properties of complex **1** were further investigated in a spectrum that ranged from 400 to 747 nm after irradiation with a 288 nm UV light. Luminescent readings of a ligand (dhampH₅) were also collected from 400 to 650 nm after excitation at 331 nm. Fig. 7 shows the emission spectra of both the ligand and complex **1**. The main peak of complex **1** appeared at 451 nm with a shoulder at 519 nm. The main peak for the ligand was at 480 nm with a shoulder at 509 nm. It is well known that the luminescent peaks from 4f orbitals of lanthanide ions, which are more like atomic spectra, are usually sharp and narrow. Since the luminescent peak of complex **1** is broad and the emission spectra for complex **1** and the ligand are quite similar, it is evident that the luminescence of complex **1** is mainly ligand based. According to the literature, Dy-centered phosphorescent transitions $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ appear largely in regions around 470 and 570 nm [24]. A detailed search of the spectrum revealed no signals in the vicinity of those values. Hence, these signals could have been quenched or immersed in the ligand peaks.

4. Conclusions

A new tetra-dysprosium cluster incorporating polydentate dhampH₃[−] ligands was synthesized and structurally characterized. Two previous examples of linear tetra-dysprosium complexes have been reported in the literature [8], and both show two out-of-phase peaks in ac susceptibility measurements. Unlike these cases, complex **1** exhibited only one clear out-of-phase signal. The ac data clearly demonstrates that complex **1** actually possesses slow magnetization relaxation properties with an effective energy barrier of 1.5 cm^{-1} , which suggests complex **1** could be potentially a SMM. The Cole–Cole plot reflects the nature of the distribution of the relaxation process with the parameter α in the region of 0.27–0.31. The emission spectra of complex **1** were also collected and examined. The luminescent properties appear to be ligand based, whereas metal-centered transitions were not observed. Therefore, this work provides a rare example of a material that is both luminescent and has slow magnetization relaxation properties (a potential SMM) material. Extensions of this ligand with other lanthanides are currently being investigated.

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Appendix A. Supplementary materials

Supplementary materials associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.10.033.

References

- [1] (a) S. Sculfort, P. Braunstein, *Chem. Soc. Rev.* 40 (2011) 2741; (b) N. Yuan, T. Sheng, C. Tian, S. Hu, R. Fu, Q. Zhu, C. Tan, X. Wu, *Cryst. Eng. Commun.* 13 (2011) 4244.
- [2] (a) R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, *Nature* 365 (1993) 141; (b) R. Sessoli, H.L. Tsai, A.R. Schake, S.Y. Wang, J.B. Vincent, K. Folting, D. Gatteschi, G. Christou, D.N. Hendrickson, *J. Am. Chem. Soc.* 115 (1993) 1804.
- [3] (a) G. Christou, D. Gatteschi, D.N. Hendrickson, R. Sessoli, *M.R.S. Bull.* 25 (2000) 66; (b) D. Gatteschi, R. Sessoli, *Angew. Chem. Int. Ed.* 42 (2003) 268; (c) G. Aromi, E.K. Brechin, *Struct. Bonding* 122 (2006) 1; (d) A.K. Powell, *Nat. Chem.* 2 (2010) 351; (e) G.E. Kostakis, A.M. Ako, A.K. Powell, *Chem. Soc. Rev.* 39 (2010) 2238.
- [4] (a) E. Saitoh, H. Miyajima, T. Yamaoka, T. Tataru, *Nature* 432 (2004) 203; (b) M. Yamanouchi, D. Chiba, F. Matsukura, H. Ohno, *Nature* 428 (2004) 539; (c) M.N. Leuenberger, D. Loss, *Nature* 410 (2001) 789; (d) L. Bogani, W. Wernsdorfer, *Nat. Mater.* 7 (2008) 179; (e) G. Karotsis, S. Kennedy, S.J. Teat, C.M. Beavers, D.A. Fowler, J.J. Morates, M. Evangelisti, S.J. Dalgarno, E.K. Brechin, *J. Am. Chem. Soc.* 132 (2010) 12983; (f) G. Karotsis, M. Evangelisti, S.J. Dalgarno, E.K. Brechin, *Angew. Chem. Int. Ed.* 48 (2009) 9928; (g) M. Manoli, A. Collins, S. Parsons, A. Candini, M. Evangelisti, E.K. Brechin, *J. Am. Chem. Soc.* 130 (2008) 11129.
- [5] (a) M. Orfanoudaki, I. Tamiolakis, M. Siczek, T. Lis, G.S. Armatas, S.A. Pergantis, C.J. Milios, *Dalton Trans.* 40 (2011) 4793; (b) H.L.C. Feltham, R. Clerac, A.K. Powell, S. Brooker, *Inorg. Chem.* 50 (2011) 4232; (c) C. Papatriantafyllopoulou, W. Wernsdorfer, K.A. Abboud, G. Christou, *Inorg. Chem.* 50 (2011) 421; (d) V. Mereacre, D. Prodius, Y. Lan, C. Turta, C.E. Anson, A.K. Powell, *Chem.-Eur. J.* 17 (2011) 123; (e) X.-Q. Zhao, Y. Lan, B. Zhao, P. Cheng, C.E. Anson, A.K. Powell, *Dalton Trans.* 39 (2010) 4911; (f) C.G. Efthymiou, T.C. Stamatos, C. Papatriantafyllopoulou, A.J. Tasiopoulos, W. Wernsdorfer, S.P. Perlepes, G. Christou, *Inorg. Chem.* 49 (2010) 9737; (g) J. Rinck, G. Novitchi, W. Van den Heuvel, L. Ungur, Y. Lan, W. Wernsdorfer, C.E. Anson, L.F. Chibotaru, A.K. Powell, *Angew. Chem., Int. Ed.* 49 (2010) 7583.
- [6] (a) R. Sessoli, A.K. Powell, *Coord. Chem. Rev.* 253 (2009) 2328; (b) D.-P. Li, T.-W. Wang, H.-C. Li, D.-S. Liu, Y.-Z. Li, X.-Z. You, *Chem. Commun.* 46 (2010) 2929; (c) P.-H. Lin, T.J. Burchell, L. Ungur, L.F. Chibotaru, W. Wernsdorfer, M. Murugesu, *Angew. Chem. Int. Ed.* 48 (2009) 9489; (d) G.-J. Chen, C.-Y. Gao, J.-L. Tian, J. Tang, W. Gu, X. Liu, S.-P. Yan, D.-Z. Liao, P. Cheng, *Dalton Trans.* 40 (2011) 5579; (e) I.J. Hewitt, J. Tang, N.T. Madhu, C.E. Anson, Y. Lan, J. Luzon, M. Etienne, R. Sessoli, A.K. Powell, *Angew. Chem. Int. Ed.* 49 (2010) 6352; (f) G. Abbas, Y. Lan, G.E. Kostakis, W. Wernsdorfer, C.E. Anson, A.K. Powell, *Inorg. Chem.* 49 (2010) 8067; (g) C.P. Hauser, D.T. Thielemann, M. Adlung, C. Wickleder, P.W. Roesky, C.K. Weiss, K. Landfester, *Macromol. Chem. Phys.* 212 (2011) 286.
- [7] (a) J. Tang, I. Hewitt, N.T. Madhu, G. Chastanet, W. Wernsdorfer, C.E. Anson, C. Benelli, R. Sessoli, A.K. Powell, *Angew. Chem. Int. Ed.* 45 (2006) 1729; (b) P.H. Lin, T.J. Burchell, R. Clérac, M. Murugesu, *Angew. Chem. Int. Ed.* 47 (2008) 8848; (c) I. Hewitt, Y.H. Lan, C.E. Anson, J. Luzon, R. Sessoli, A.K. Powell, *Chem. Commun.* (2009) 6765; (d) B. Hussain, D. Savard, T.J. Burchell, W. Wernsdorfer, M. Murugesu, *Chem. Commun.* (2009) 1100; (e) S.K. Langley, B. Moubarak, C.M. Forsyth, I.A. Gass, K.S. Murray, *Dalton Trans.* 39 (2010) 1705; (f) R.A. Layfield, J.J.W. McDouall, S.A. Sulway, F. Tuna, D. Collison, R.E.P. Wimpenny, *Chem. Eur. J.* 16 (2010) 4442; (g) G.-F. Xu, Q.-L. Wang, P. Gamez, Y. Ma, R. Clérac, J. Tang, S.-P. Yan, P. Cheng,

- D.-Z. Liao, Chem. Commun. 46 (2010) 1506;
- (h) J. Long, F. Habib, P.-H. Lin, I. Korobkov, G. Enright, L. Ungur, W. Wernsdorfer, L.F. Chibotaru, M. Murugesu, J. Am. Chem. Soc. 133 (2011) 5319;
- (i) J.-B. Peng, Y.-P. Ren, X.-J. Kong, L.-S. Long, R.-B. Huang, L.-S. Zheng, Cryst. Eng. Commun. 13 (2011) 2084.
- [8] (a) Y.-N. Guo, G.-F. Xu, P. Gamez, L. Zhao, S.-Y. Lin, R. Deng, J. Tang, H.-J. Zhang, J. Am. Chem. Soc. 132 (2010) 8538;
- (b) H. Ke, G.-F. Xu, Y.-N. Guo, P. Gamez, C.M. Beavers, S.J. Teat, J. Tang, Chem. Commun. 46 (2010) 6057.
- [9] (a) G.-P. Yang, L. Hou, Y.-Y. Wang, Y.-N. Zhang, Q.-Z. Shi, S.R. Batten, Cryst. Growth Des. 11 (2011) 936;
- (b) G.-P. Yang, Y.-Y. Wang, P. Liu, A.-Y. Fu, Y.-N. Zhang, J.-C. Jin, Q.-Z. Shi, Cryst. Growth Des. 10 (2010) 1443;
- (c) G.-P. Yang, Y.-Y. Wang, W.-H. Zhang, A.-Y. Fu, R.-T. Liu, E.K. Lermontova, Q.-Z. Shi, Cryst. Eng. Commun. 12 (2010) 1509.
- [10] (a) C.C. Beedle, C.J. Stephenson, K.J. Heroux, W. Wernsdorfer, D.N. Hendrickson, Inorg. Chem. 47 (2008) 10798;
- (b) Y. Bi, X.-T. Wang, W. Liao, X. Wang, R. Deng, H. Zang, S. Gao, Inorg. Chem. 48 (2009) 11743.
- [11] (a) M.A. Katkova, M.N. Bochkarev, Dalton Trans. 39 (2010) 6599;
- (b) J.C. Dumke, B. El-Zahab, S. Challa, S. Das, L. Chandler, M. Tolocka, D.J. Hayes, I.M. Warner, Langmuir 26 (2010) 15599;
- (c) Z.-Q. Chen, F. Ding, Z.-Q. Bian, C.-H. Huang, Org. Electron. 11 (2010) 369;
- (d) M.A. Katkova, V.A. Ilichev, A.N. Konev, M.N. Bochkarev, Russ. Chem. Bull. Int. Ed. 57 (2008) 2281;
- (e) R.J. Curry, W.P. Gillin, Appl. Phys. Lett. 75 (1999) 1380.
- [12] (a) J.M. Bradley, A.J. Thomson, R. Inglis, C.J. Milios, E.K. Brechin, S. Piligkos, Dalton Trans. 39 (2010) 9904;
- (b) T.C. Stamatatos, G. Christou, Inorg. Chem. 48 (2009) 3308;
- (c) A. Prescimone, C.J. Milios, J. Sanchez-Benitez, K.V. Kamenev, C. Loose, J. Kortus, S. Moggach, M. Murrie, J.E. Warren, A.R. Lennie, S. Parsons, E.K. Brechin, Dalton Trans. (2009) 4858;
- (d) R. Inglis, S.M. Taylor, L.F. Jones, G.S. Papaefstathiou, S.P. Perlepes, S. Datta, S. Hill, W. Wernsdorfer, E.K. Brechin, Dalton Trans. (2009) 9157;
- (e) C. Lampropoulos, K.A. Abboud, T.C. Stamatatos, G. Christou, Inorg. Chem. 48 (2009) 813;
- (f) A.M. Ako, I.J. Hewitt, V. Mereacre, R. Clérac, W. Wernsdorfer, C.E. Anson, A.K. Powell, Angew. Chem. Int. Ed. 45 (2006) 4926.
- [13] (a) S. Mukherjee, R. Bagai, K.A. Abboud, G. Christou, Inorg. Chem. 50 (2011) 3849;
- (b) T.C. Stamatatos, D. Foguet-Albiol, K.M. Poole, W. Wernsdorfer, K.A. Abboud, T.A. O'Brien, G. Christou, Inorg. Chem. 48 (2009) 9831;
- (c) W.-G. Wang, A.-J. Zhou, W.-X. Zhang, M.-L. Tong, X.-M. Chen, M. Nakano, C.C. Beedle, D.N. Hendrickson, J. Am. Chem. Soc. 129 (2007) 1014;
- (d) D. Foguet-Albiol, T.A. O'Brien, W. Wernsdorfer, B. Moulton, M.J. Zaworotko, K.A. Abboud, G. Christou, Angew. Chem. Int. Ed. 44 (2005) 897.
- [14] K.-H. Tong, K.-Y. Wong, T.H. Chan, Org. Lett. 5 (2003) 3423.
- [15] C. Zondervan, E.v. Beuken, H. Kooijman, A. Spekb, B. Feringa, Tetrahedron Lett. 38 (1997) 3111.
- [16] G.M. Sheldrick, Sadabs: Version 2.03, University of Göttingen, Germany, 2002.
- [17] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.
- [18] M.L. Kahn, R. Ballou, P. Porcher, O. Kahnadagger, J.-P. Sutter, Chem. Eur. J. 8 (2002) 525.
- [19] (a) C.-C. Wu, S. Datta, W. Wernsdorfer, G.-H. Lee, S. Hill, E.-C. Yang, Dalton Trans. 39 (2010) 10160;
- (b) S. Hill, S. Datta, J. Liu, R. Inglis, C.J. Milios, P.L. Feng, J.J. Henderson, E. del Barco, E.K. Brechin, D.N. Hendrickson, Dalton Trans. 39 (2010) 4693.
- [20] J.K. Tang, I. Hewitt, N.T. Madhu, G. Chastanet, W. Wernsdorfer, C.E. Anson, C. Benelli, R. Sessoli, A.K. Powell, Angew. Chem. Int. Ed. 45 (2006) 1729.
- [21] (a) H. Ke, P. Gamez, L. Zhao, G.-F. Xu, S. Xue, J. Tang, Inorg. Chem. 49 (2010) 7549;
- (b) D. Savard, P.-H. Lin, T.J. Burchell, I. Korobkov, W. Wernsdorfer, R. Clérac, M. Murugesu, Inorg. Chem. 48 (2009) 11748;
- (c) Y.-Z. Zheng, Y. Lan, C.E. Anson, A.K. Powell, Inorg. Chem. 47 (2008) 10813;
- (d) Y. Gao, G.-F. Xu, L. Zhao, J. Tang, Z. Liu, Inorg. Chem. 48 (2009) 11495;
- (e) P.-P. Yang, X.-F. Gao, H.-B. Song, S. Zhang, X.-L. Mei, L.-C. Li, D.-Z. Liao, Inorg. Chem. 50 (2011) 720.
- [22] (a) S.M. Aubin, Z. Sun, L. Pardi, J. Krzysteck, K. Folting, L.-J. Brunel, A.L. Rheingold, G. Christou, D.N. Hendrickson, Inorg. Chem. 38 (1999) 5329;
- (b) K.S. Cole, R.H. Cole, J. Chem. Phys. 9 (1941) 341.
- [23] D. Gatteschi, R. Sessoli, J. Villain, Molecular Nanomagnets, Oxford University Press, 2006.
- [24] T.-H. Zhou, F.-Y. Yi, P.-X. Li, J.-G. Mao, Inorg. Chem. 49 (2010) 905.