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Luminescent single molecule magnets of a series of

β-diketone dysprosium complexes

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Abstract

A series of three luminescent single molecule magnets of *β*-diketone mononuclear dysprosium complexes, namely, $Dy(tfa)_3(H_2O)_2 \cdot Me_2CO$(**1**), $Dy(tfa)_3(bpy)$ (**2**) and $Dy(tfa)_3(phen)$ (**3**) (tfa = trifluoroacetylacetonate, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, $C_3H_6O = Me_2CO$) have been isolated. Single-crystal X-ray analysis shows all the central Dy(III) ions are eight-coordinated adopting the coordination geometries of the distorted dodecahedron, bicapped trigonal prism and square antiprism for complexes **1**−**3**, respectively. Magnetic analyses exhibit slow magnetic relaxation with the barrier heights (U_{eff}/k_B) of 41 K, 33 K and 55 K for complexes **1**−**3**, respectively. Photo-luminescent analysis reveal that complexes **1**−**3** exhibit the typical yellow luminescence of Dy(III) ions. The correlationship between the structure and physical-property has been investigated.

Keywords: *β*-diketone; lanthanide complex; structure; magnetism; luminescence

Introduction

All the time, lanthanide complexes with *β*-diketone have been widely studied for their specific magnetic and luminescent properties. In one hand, single-molecule magnets (SMMs) have got more attention in recent years in virtue of their various potential applications for high-density magnetic

memories, magnetic refrigeration, molecular spintronics and quantum computing devices.[1] Among the lanthanide ions, a large number of Dy-based SMMs have been reported attributed to the large magnetic moment with a Kramers ground state of $^6H_{15/2}$ and a large Ising-type magnetic anisotropy of Dy(III) ion.[2] Notably, the ligand field (LF) is a crucial factor in controlling the magnetic anisotropy of Dy-based SMMs.[3] In another hand, luminescence of β-diketone Dy(III) complexes have been studies although scarce study on both magnetism and luminescence have been documented.[4,5] Since the combination of luminescence and magnetic properties in lanthanide compounds have been applied in drug delivery, therapeutics, optoelectronic and lumino-magnetic applications[6], finding an appropriate ligand controlling the LF to simultaneously promote the anisotropy barriers and improve the luminescent properties for Dy(III) complexes is significant. In our course towards the development of molecular materials based on β-diketones lanthanide complexes, we aimed to design and synthesize such type of bi-functional materials. It is known that the acetyl acetone Dy(III) complexes normally afforded sufficient anisotropic energy barriers as SMMs.[7] However, the characteristic absorption band of Dy(III) ions in β-diketones Dy(III) complexes have been seldom observed[8]. E.g., complex Dy(hfac)$_3$(bpy)[5] (hfac = hexafluoroacetylacetonate) has exhibited the typical characteristic absorption band of Dy(III) ions, with lower anisotropicenergy barriers than those of their analog Dy(acac)$_3$phen[7b] and Dy(acac)$_3$(H$_2$O)$_2$.[7a] Notably, the difference between complexes acac and hfac are strong electron-withdrawing groups (CF$_3$). The replacement of methyl with trifluoromethyl could facilitates intersystem crossing which enhance the lanthanide-centered luminescence[9] and affect the energy barrier of SMMs.[10] Thus, in order to improve the both the luminescence and magnetism of β-diketones Dy(III) complexes, the trifluoroacetylacetonate (tfa) was employed in the study of the structure, magnetism and luminescence. As a result, three luminescent SMMs of tfa Dy(III) complexes **1−3** with different auxiliary ligands have been isolated (Scheme S1). Their crystal structures, magnetism and luminescence have been investigated.

Experimental

Materials and instrumentation

All chemicals except $DyCl_3 \cdot 6H_2O$ was obtained from commercial sources and used without further purification. $DyCl_3 \cdot 6H_2O$ was prepared by the reaction of Dy_2O_3 and hydrochloric acid in aqueous solution. The ligand tfa was obtained by J&K Chemical. FT-IR spectra were run on a PerkinElmer 100 spectrophotometer in the range of $4000-450$ cm^{-1}. UV spectra (in CH_3OH) were performed on a PerkinElmer Lambda 35 spectrometer. Thermal analyses were conducted on a STA-6000 instrument in the temperature range $30-800$ °C with a heating rate of 10 ℃ min^{-1} under atmosphere. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/Max-3B X-ray diffractometer with Cu-Kα radiation, the scanning rate is 4°/s, 2θ ranging from $5-50°$. Excitation and emission spectra were measured with an Edinburgh FLS 920 fluorescence spectrophotometer. The magnetic susceptibility for complexes **1−3** was measured with a Quantum Design SQUID-VSM magnetometer. The diamagnetic corrections were made by using Pascal's constants.

Synthesis of complexes 1−5

Dy(tfa)$_3$(H$_2$O)$_2$·Me$_2$CO (1). NaOH (0.08 g, 2 mmol) and tfa (0.31g, 2 mmol) in methanol was stirred for 15 min. Then, $DyCl_3 \cdot 6H_2O$ (0.245 g, 0.65 mmol) was added to the solution and the mixture was stirred for 24 h at room temperature. Water was then added to this mixture, and the precipitate thus formed. It was filtered, washed with water, and dried in air. Single crystals were obtained in about three weeks by recrystallization from dichloromethane/acetone/hexane. Yield: 533.8 mg (75%). Elemental analysis: (%) calcd for $C_{18}H_{22}DyF_9O_9$ (715.85): C, 30.20; H, 3.10. Found: C, 30.22; H, 3.08. IR (KBr, v/cm^{-1}): 3186 (w), 1620 (s), 1528 (s), 1320 (s), 1273 (s), 1138 (s), 1006 (m), 853 (m), 777 (s). UV−vis (CH_3OH, λ_{max}/nm): 317.

Dy(tfa)$_3$(bpy) (2). Complex **2** was prepared by stirring of a mixture of complex **1** (0.356 g, 0.5 mmol) and 2,2′- bipyridine (0.156 g, 1.0 mmol) in CH_3OH for 24 h at ambient temperature. The raw product was isolated according to the aforementioned method. Single crystals were obtained in about 10 days by recrystallization from dichloromethane/hexane. Yield: 638 mg (82%). Elemental analysis: (%) calcd for $C_{25}H_{24}DyF_9N_2O_6$ (781.95): C, 38.40; H, 3.09; N, 3.58. Found: C, 38.42; H, 3.10; N, 3.57. IR (KBr, v/cm^{-1}): 2935 (w), 1627 (s), 1530 (s), 1360 (m), 1293 (s), 1195 (m), 1132 (s), 1014 (m), 853

(m), 769 (s). UV−vis (CH$_3$OH, λ_{max}/nm): 290, 236.

Dy(tfa)$_3$(phen) (3). Complex **3** was prepared by stirring of a mixture of complex **1** (0.356 g, 0.5 mmol) and 1,10-phenanthroline (0.18 g, 1.0 mmol) in CH$_3$OH for 24 h at ambient temperature. The raw product was isolated according to the aforementioned method. Single crystals were obtained in about 10 days by recrystallization from dichloromethane /hexane. Yield: 698 mg (87%). Elemental analysis: (%) calcd for C$_{27}$H$_{24}$DyF$_9$N$_2$O$_6$ (805.97): C, 42.24; H, 3.00; N, 3.48. Found: C, 42.22; H, 3.01; N, 3.49. IR (KBr, v/cm^{-1}): 2925 (w), 1627 (s), 1522 (s), 1363 (m), 1294 (s), 1223 (m), 1132 (s), 1014 (m), 847 (m), 777 (s). UV−vis (CH$_3$OH, λ_{max}/nm): 291, 231.

X-ray crystallography structures

X-ray single-crystal diffractions of complexes **1**−**3** were performed at 293 K on an Oxford Xcalibur Gemini Ultra diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption corrections on the basis of equivalent reflections were applied. The structures of **1**−**3** were solved by direct methods and refined with a full-matrix least squares technique. All non-hydrogen atoms were refined. All crystal data and refinement parameters for complexes **1**−**3** are summarized in Table 1. The important bond lengths and angles for complexes **1**−**3** are given in Table S1. CCDC No. 1037817, 1037818 and 1037819 for complexes **1**, **2** and **3**, respectively, can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystal data and structure refinement details for complexes **1−3**

Complexes	1	2	3
Empirical formula	$C_{18}H_{22}DyF_9O_9$	$C_{25}H_{24}DyF_9N_2O_6$	$C_{27}H_{24}DyF_9N_2O_6$
Formula weight	715.85	781.95	805.97
Color	Colorless	Colorless	Colorless
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbcn*	$P\bar{1}$	$P2_1/c$
a (Å)	11.124(5)	12.286(5)	16.001(5)
b (Å)	21.760(5)	15.177(5)	18.400(5)
c (Å)	22.119(5)	17.897(5)	22.106(4)
α (deg)	90	93.487(5)	90
β (deg)	90	107.140(5)	114.699(15)
γ (deg)	90	111.979(5)	90
V (Å^3)	5354(3)	2901.5(17)	5913(3)
Z	8	4	4
ρ (g cm^3)	1.766	1.781	1.802
μ (mm^{-1})	2.895	2.674	2.628
F (000)	2760.0	1516.0	3128.0
R_1 ($I > 2\sigma(I)$)	0.0528	0.0832	0.0498
wR_2 ($I > 2\sigma(I)$)	0.1369	0.2177	0.1333
R_1 (all data)	0.0674	0.1035	0.0785
wR_2 (all data)	0.1495	0.2494	0.1609
GOF on F^2	1.040	1.079	1.038

Results and discussion

Descriptions of the structures

Crystal structure analysis suggests that all the complexes are mononuclear. The complex **1** crystallized in the orthorhombic *Pbcn* space group. The central Dy(III) ion is eight-coordinated with six oxygen atoms from three bidentate tfa ligands and two oxygen atoms from two H_2O molecules (Fig. 1a). The Dy−O bond distances range from 2.305 to 2.421 Å. The Dy(tfa)$_3$(H$_2$O)$_2$·Me$_2$CO molecules are stacked by hydrogen bonds with the shortest Dy···Dy distances of 6.12 Å (Fig. S9). Complexes **2** and **3** crystallize in the triclinic space group $P\bar{1}$ and monoclinic space group $P2_1/c$. The central Dy(III) ions are eight-coordinated with six oxygen atoms from three bidentate tfa ligands for complexes **2** and **3**. The Dy−O bond distances range from 1.672 to 2.369 Å for **2** and 2.316 to 2.361Å for **3**. The other two coordination sites of the Dy(III) cation are occupied by two N atoms from the bpy or phen ligands to form the eight coordination environment (Fig. 1b and 1c). Two Dy−N bond distances are 2.578, 2.570 Å and 2.564, 2.569 Å for **2**and**3**, respectively. The shortest Dy···Dy distances between the two molecules are 7.40 Å for **2** and 7.32 Å for **3** (Fig. S10−11). Notably, the Dy(III) ions in complexes

1−3 are of different coordination geometries although they are all eight-coordinated. According to the semiquantitative method of polytopal analysis,[11] the coordination geometries of Dy(III) ions for complexes **1−3**can be defined as a distorted dodecahedron(Fig. 1d), bicapped trigonal prism(Fig. 1e) and square antiprism (Fig. 1f), respectively. Relevant dihedral angles for complexes **1−3** are summarized in Table 2, in which δ_1 and δ_2 represent the planarity of the squares and δ_3 and δ_4 the triangular faces. The δ_1–δ_4 and φ_1–φ_2 values are 32.5, 27.1, 35.2, 27.9° and 10.5, 9.0° for complex **1**, which are relatively close to the angles (29.5, 29.5, 29.5, 29.5° and 0.0, 0.0°) of an ideal dodecahedron, indicative of D_{2d} symmetry. The δ_1–δ_4 and φ_1–φ_2 values are 4.4, 8.2, 48.1, 43.5° and 13.1, 11.8° for complex **2**, which are relatively close to the angles (0.0, 21.8, 48.2, 48.2° and 14.1, 14.1°) of an ideal bicapped trigonal prism, indicative of C_{2V} symmetry. For complex **3**, the δ_1–δ_4 and φ_1–φ_2 values are 6.1, 11.6, 44.2, 45.6° and 22.1, 17.1°, which are close to the angles (0.0, 0.0, 52.4, 52.4° and 24.5, 24.5°) of an ideal square antiprism, indicative of D_{4d} symmetry.
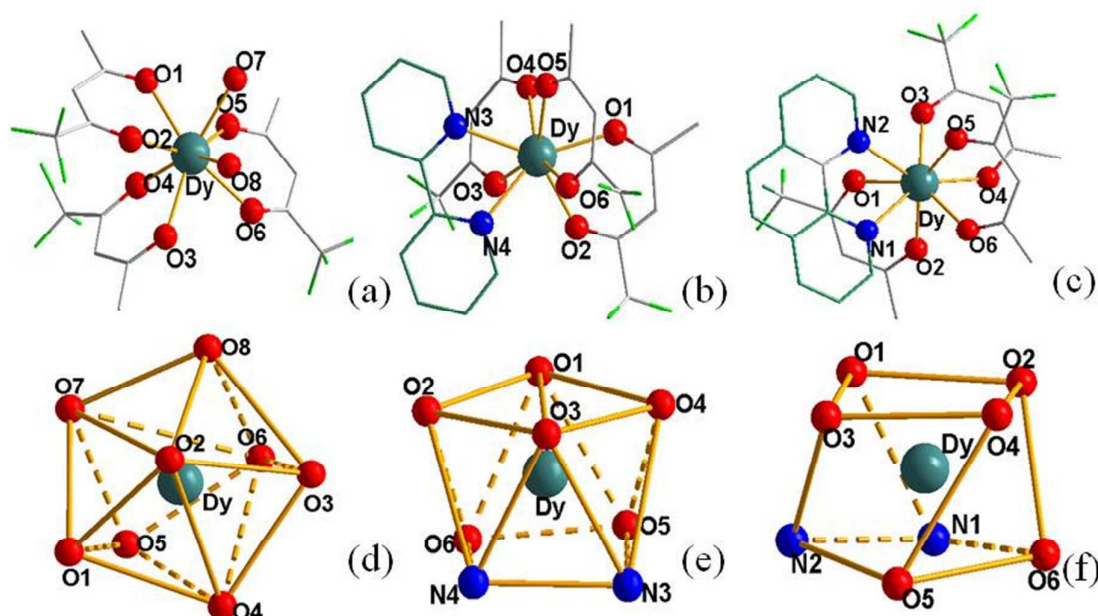

Fig. 1 Molecular structures of complexes **1** (a), **2** (b) and **3** (c) and local coordination geometries of Dy(III) ion for complexes **1** (d), **2** (e) and **3** (f). (Hydrogen atoms are omitted for clarity)

Table 2 δ (deg) and φ (deg) values for complexes **1−3**

Faces	**1**		DD	**2**		TP	**3**		SAP
δ_1	$O_1[O_2O_4]O_3$	32.5	29.5	$O_1[O_2O_4]O_3$	4.4	0.0	$O_2[O_1O_4]O_3$	6.1	0.0
δ_2	$O_5[O_7O_8]O_6$	27.1	29.5	$N_3[N_4O_5]O_6$	8.8	21.8	$N_2[N_1O_5]O_6$	11.6	0.0
δ_3	$O_4[O_3O_5]O_6$	35.2	29.5	$O_5[O_1O_6]O_2$	48.1	48.2	$O_5[O_1O_6]O_2$	44.2	54.2
δ_4	$O_1[O_2O_7]O_8$	27.9	29.5	$N_4[N_3O_3]O_4$	43.5	48.2	$N_2[N_1O_3]O_4$	45.6	54.2
φ_1	$O_8-O_2-O_6-O_1$	10.5	0	$O_6-O_3-O_5-N_4$	13.1	14.1	$O_5-O_2-O_1-N_2$	22.1	24.5
φ_2	$O_5-O_4-O_7-O_3$	9.0	0	$N_3-O_1-O_4-O_2$	11.8	14.1	$N_1-O_3-O_4-O_6$	17.1	24.5

$\delta_1-\delta_4$ A[BC]D are the dihedral angles between the ABC and BCD plane. φ_1 and φ_2 (A−B−C−D) are the dihedral angles between the (AB)CD and AB(CD) plane, where (AB) is the center of A and B.

Magnetic properties

Static magnetic properties

Direct current (dc) magnetic susceptibilities for complexes **1−3** were studied at 1000 Oe over the temperature range 1.8−300 K. At 300 K, the $\chi_m T$ values are 13.99, 14.07 and 13.91 $cm^3 K mol^{-1}$ for **1−3** (Fig. 2), respectively, which are in agreement with the value of 14.17 $cm^3 K mol^{-1}$ for an isolated Dy(III) ion ($^6H_{15/2}$, S = 5/2, L = 5, g = 4/3, C = 14.17 $cm^3 K mol^{-1}$). For complex **1**, the $\chi_m T$ value reduced smoothly along with the temperature reduction in the temperature range of 300−100K (thermal depopulation of the Dy(III) ion Stark sublevels), then further decreases sharply to reach a minimum of 8.38 $cm^3 K mol^{-1}$ at 1.8 K. It is possible due to the antiferromagnetic dipole-dipole interactions between the molecules[12] because the short Dy$\cdots$Dy distances (6.12 Å)for complex **1** which is similar to these previously reported[7a, 13]. For **2** and **3**, the $\chi_m T$ values reduce to 9.55 and 7.66 $cm^3 K mol^{-1}$ at 1.8 K along with the temperature decreases from 300 to 1.8 K. It is attributed to the progressive depopulation of excited Stark sublevels of anisotropic Dy(III) and / or the pure dipole-dipole interactions between the molecules. The magnetization versus dc field data (Fig. 2, inset) from zero dc field to 65 KOe at 1.8 K reveal that the maximum magnetization are 5.14, 5.81 and 5.34 μ_B for complexes **1**, **2** and **3**, respectively. These values are lower than the expected saturation value of 10 μ_B for an isolated Dy(III) ion. It high likely result from the crystal-field effects on the Dy(III) ion that eliminates the degeneracy of the $^6H_{15/2}$ ground[14]. The M-H data measured in different magnetic fields show nonsuperposition (Fig. S12), suggesting the existence of magnetic anisotropy and/or low-lying excited states[15] in complexes **1−3**.
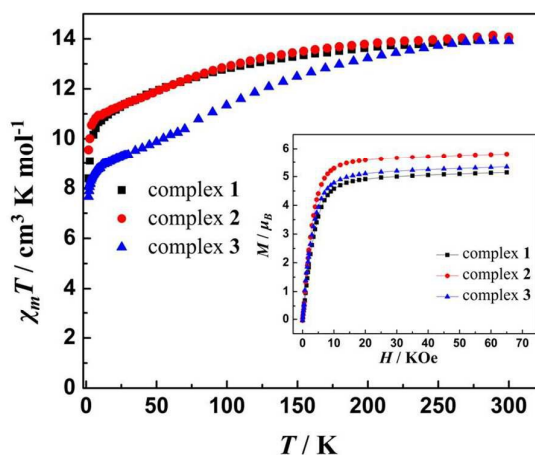
Fig. 2 Temperature dependence of $\chi_m T$ in the range of 1.8−300 K in 1kOe dc field for **1−3**. Inset: The field dependence of magnetization for complexes **1−3** at 1.8 K.

Dynamic magnetic properties

The ac magnetic susceptibilities curves for complexes **1−3** (Fig. 3 and S13) reveal that the ac susceptibilities under zero dc field are temperature and frequency dependent. Further, strong frequency and temperature dependence were found for complexes **1−3** under 0 Oe dc field, suggesting the spin "freezing" by the anisotropy barriers. The χ'' show the maxima in the ranges of 9 K (200 Hz)–13 K (1000 Hz), 7 K (400 Hz)–10 K (1000 Hz) and 11 K (200 Hz)–14K (1000 Hz) for **1**, **2** and **3**, respectively (Fig. S13). Along with the cooling, the χ'' values increase below 6 K, which could be ascribed to the quantum tunneling effects at zero dc field. This behavior is often observed in Dy(III)-based SMMs. To overcome the quantum tunneling effect, the ac susceptibility measurements were further conducted under a static dc field of 2000 Oe (Fig. S14). The magnetic susceptibilities of in-phase (χ') and out-of-phase (χ'') are frequency dependent with the full peaks from 1 to 1000 Hz for complexes **1−3**. It suggests that the quantum tunneling effect can be essentially depressed by external 2000 Oe dc field. Furthermore, the ac magnetic susceptibilities were measure in various external fields at 6K for complexes **1**, **2** and **3** (Fig. 4). Obviously, the peaks of the out-of-phase (χ'') gradually move to the low frequency region with increasing external field and stabilized in the region of 1400−3000 Oe for complex **1** and 1000−3000 Oe for complexes **2** and **3**. Simultaneously,

the susceptible ac magnetic susceptibilities suggest that the relaxation time is significantly increased in the external field range 0-1400 Oe (Fig. S15). It verifies that quantum tunneling is effectively overcome under the external 2000 Oe dc field

The Cole–Cole plots for complexes **1−3** reveal an asymmetrical semi-circular shape (Fig. 5), which can be fitted by the generalized Debye model[16]. The fitted parameters of the Cole-Cole plots at $H_{dc}= 0$ G for complex **1−3** are summarized in Table S1−S3 and Fig. S14. It reveals that the α_{Cole} values are in the range of 0.30−0.05, 0.16−0.04, 0.21−0.04 in the temperature range 2−12 K for complexes **1**, **2** and **3**, respectively. The parameters of the maxima α below 0.30, indicating a single relaxation process with a narrow distribution of relaxation time and further confirming the SMM behavior.[17] On the basis of the frequency dependencies of the ac susceptibility, the magnetization relaxation time in the form of ln(τ) are plotted as a function of 1/T in Fig. 6. Blow 6 K, the magnetization dynamics of complexes **1−3** become as expected temperature independent in a pure quantum regime with magnetization relaxation times (τ). Above 6 K, the relaxation follows a thermally activated mechanism with an energy barriers (U_{eff}/k_B) and a pre-exponential factors (τ_0) could be fitted at 41 K and 3.7×10^{-6} s, 33 K and 5.7×10^{-6} s, 55 K and 2.5×10^{-6} s for **1**, **2** and **3**, respectively, on the basis of the Arrhenius relation [$\tau = \tau_0\exp(U_{eff}/k_BT)$], which are consistent with the expected τ_0 of $10^{-6}−10^{-11}$ for SMMs[18]. The M−H curves of complexes **1−3** (Fig. 6 and Fig. S17) exhibit a hysteresis loop at 1.8 K upon sweep rate of 50 Oe/s within ±4 KOe (Fig. 7, left). Complex **3** exhibits the clearest hysteresis loop and the highest energy barriers (U_{eff}/k_B) among complexes **1−3**, which is the highest blocking temperature among the reported β-diketone mononuclear dysprosium complexes involving tfa and htfc ligands[20-21], Upon decreasing the sweep rate from 400 to 50 Oe/s, the hysteresis loops for complex **3** become slightly narrower (Fig. 7, right), suggesting that complex **3** is field sweep rate dependency which is similar to those previously reported Dy(III) systems[1c,5, 22]. The observed hysteresis loops further prove that complexes **1**, **2** and **3** are typical SMMs.
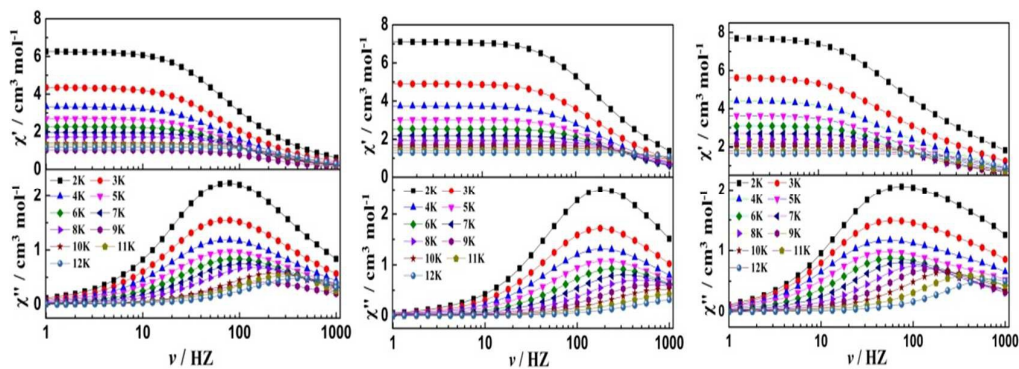
Fig. 3 Frequency dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility of complexes

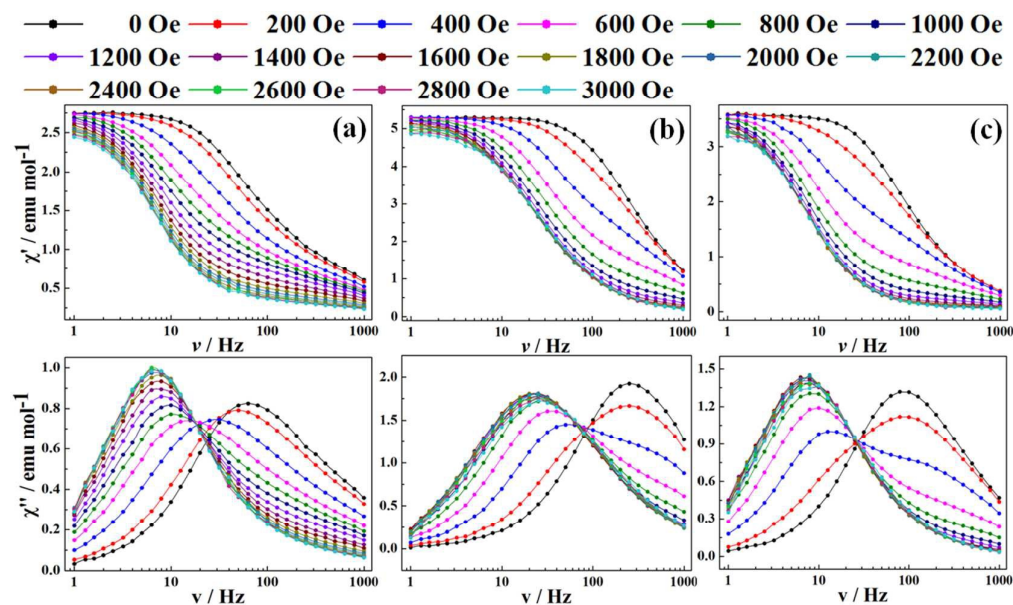**1** (left), **2** (middle) and **3** (right), respectively, under zero dc field.

Fig. 4 Frequency dependence at 6K of the in-phase (χ', top) and the out-of-phase (χ'', bottom) ac

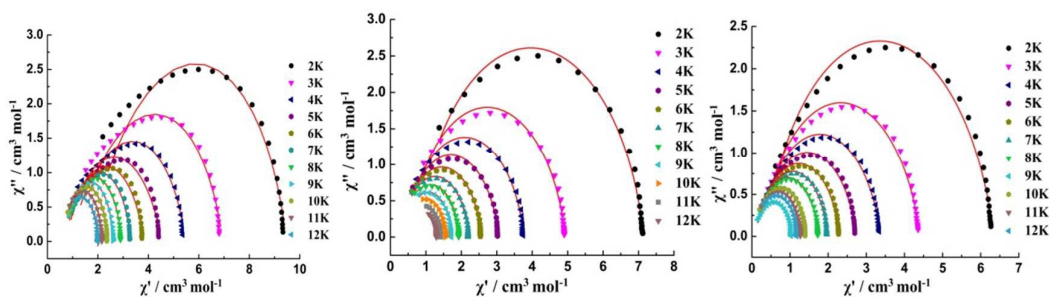susceptibility at varied DC fields for **1** (a)**, 2** (b) and **3** (c).

Fig. 5 The Cole−Cole plots measured in the range of 2−12 K for **1** (left), **2** (middle) and **3** (right), respectively, under zero dc field.
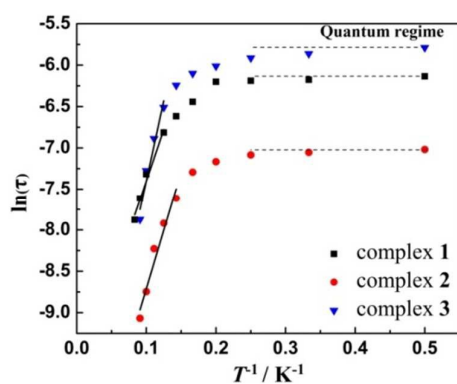

Fig. 6 Temperature dependence of the relaxation time for **1** (squares), **2** (circles) and **3** (triangles) under zero dc field. The solid lines represent linear fits of the Arrhenius law for **1**, **2** and **3**, respectively.
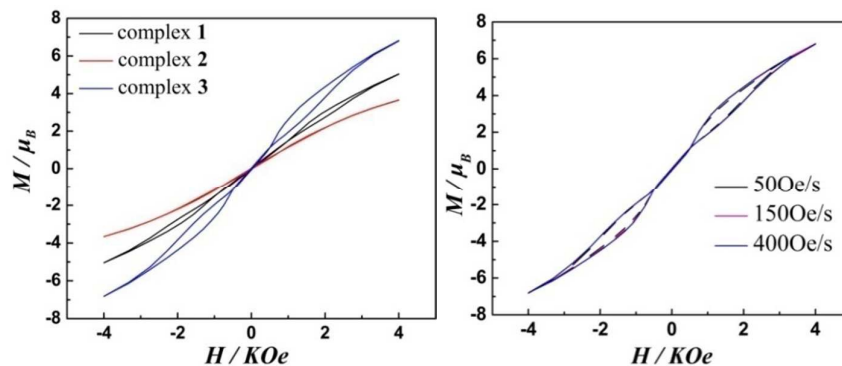

Fig. 7 Hysteresis loop of complexes **1**−**3** with a sweep rate of 50 Oe/s at 1.8 K (left);Hysteresis loop for complex **3** with sweep rate from 50 to 400 Oe/s at 1.8 K (right).

Notably, the barrier height (U_{eff}/k_B) for **3** is higher than those for **1** and **2**, which can be attributed to the ligand field and the symmetry resulting from auxiliary ligand phen in **3**. On the basis of the structural data of δ (deg) and φ (deg) values for complexes **1−3** in Table 2, the coordination geometry of Dy(III) ion in complex **3** is the closest to an ideal square antiprism of D_{4d} symmetry. Therefore, the phen as an auxiliary ligand in **3** increases the degree of longitudinal compression that enhances the SAP ligand field around the Dy(III) ion which enables the lowest doubly degenerate sublevels (formally pertaining to the large J_Z values of± 15/2 for Dy(III) ion in the SAP environment[19]) from the rest of the sub-states to result in a strong uniaxial magnetic anisotropy and a higher thermal barrier. In addition, complex **3** reveals a shorter Dy−N bond (2.564 Å) in comparison to the reported Dy(III) analogue with tfa,[20] which may enhance the ligand field of Dy(III) ion and prompt its magnetism in complex **3**. Nevertheless, the energy barrier for complex **3** is lower than that of the known analogue of [Dy(acac)₃phen][7b]. It should result from the introduction of a CF_3 group replacing the CH_3 group in acac ligand which reduces the local symmetry around the Dy(III) ions in complex **3** due to the asymmetric tfa ligand.

Luminescence

The photo luminescent spectra for complexes **1−3** of both solid state (Fig. 8) and solution (Fig. S18) were conducted at excitation wavelength of 335 nm at room temperature. All emission spectra display characteristic sharp peaks around 20800, 17500, and 15200 cm^{-1} attributed to $^4F_{9/2}\rightarrow$ $^6H_{15/2}$, $^4F_{9/2}\rightarrow$ $^6H_{13/2}$, and $^4F_{9/2}\rightarrow$ $^6H_{11/2}$ transitions, respectively[23]. It indicate that tfa is able to sensitive the characteristic luminescence of Dy(III) ions in complexes **1−3**. The overall emission quantum efficiency of the complexes **1−3** at room temperature were measured based on a formula equation using Eu(tta)₃phen as a reference.

$$\eta_S = \eta_R \frac{A_R I_S n_S^2}{A_S I_R n_R^2}$$

The *A, I* and *n* mean the area of the emission spectrum, the absorbance at the excitation wavelength and the refractive index of solvent, respectively. And η_R is the quantum efficiency of Eu(tta)₃phen in a

10^{-3}mol/L DMF solution[24]. The overall luminescence quantum yield (η_S) and lifetime were calculated to be 0.29, 0.55, 0.68 and 2.50, 2.87, 2.89 μs for complexes **1−3**, respectively (Fig. S19). which are higher than those for corresponding known analogous Dy(III) complexes of Dy(PM)$_3$(TP)$_2$ $(0.035)^{[25]}$ and Dy(hfac)$_3$(bpy) $(0.4)^{[5]}$. It suggests that tfa is more efficacious than hfac in terms of energy absorption and transfer between the central Dy(III) ion. In contrast to complex **1**, complexes **2** and **3** exhibit higher quantum yield and longer lifetime. It is attributed to the substitute of bpy and phen in complexes **2** and **3** that replace the coordination solvent molecules for minimizing the nonradiative deactivation. And the conjugate system of bpy and phen can further enhance the whole molecular π electronic delocalization range. Thus, the ligand can absorb light and transfer excitation energy more effectively to Dy(III) ions that further enhance the luminescence.
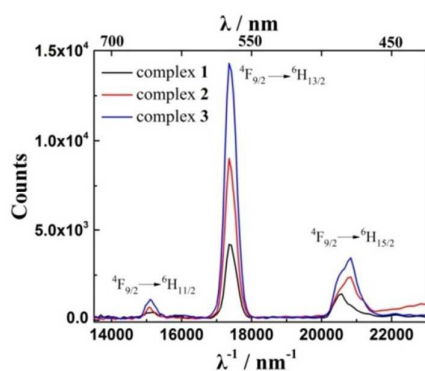

Fig. 8 Emission spectra of complexes **1−3** in the solid state at 298 K (λ_{ex} = 335 nm).

Conclusions

Isolations of a series of tfa dysprosium complexes **1−3** verifies that tfa is able to stabilize Dy(III) ion affording stable tfa mononuclear dysprosium complexes in which Dy(III) ions are eight-coordinated in different coordination geometry. The tfa is able to tune the magnetism and luminescence of Dy(III) ions in complexes **1−3**. The auxiliary ligand can enhance the magnetism of complex **3** by way of the coordination symmetry around the Dy(III) ions and the luminescence of complexes **1−3** *via* the replacement of the coordination solvent molecules. This approach provides an easy route on preparing the luminescent SMMs.

Electronic supplementary information

FT-IR spectra, UV absorption spectra, PXRD, TG-DSC curves, fitted parameters of the Cole-Cole plots, emission spectra in solution and luminescence decay profiles, etc for complexes **1−3** are given in Supporting Information. CCDC No. 1037817−1037819 for complexes **1−3**, can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

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