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Synthesis and Luminescent Properties of Lanthanide Complexes with a Novel Multipodal Ligand

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Abstract Solid complexes of lanthanide nitrates, picrates and perchlorates with a novel multipodal ligand, 1,2,4, 5-tetramethyl-3,6-bis{*N,N*-bis[((2′-benzylaminoformyl)phenoxyl)ethyl]-aminomethyl}-benzene (**L**) have been synthesized and characterized by elemental analysis, infrared spectra and molar conductivity measurements. At the same time, the luminescent properties of the Eu and Tb complexes in solid state were investigated. Under the excitation of UV light, these complexes exhibited characteristic emission of central metal ions. The lowest triplet state energy level T_1 of this ligand matches better to the lowest resonance energy level of Tb(III) than to Eu(III) ion. The influence of the counter anion on the luminescent intensity was also discussed.

Keywords Multipodal ligand · Lanthanide complexes · Synthesis · Luminescent properties

Introduction

The rational design and synthesis of ligands capable of forming stable and strongly luminescent lanthanide complexes have attracted a great deal of attention due to their potential application as luminescent probes [1]. To achieve strong luminescence, concurrent control of solvation and hydration around the lanthanide ion, and its high coordination number, should be incorporated into the ligand design.

To this end, one promising strategy is encapsulating the lanthanide ion with the ligand, which has a large absorption cross section with suitable excitation energy that can be transferred to a metal excitation state [2, 3]. It is generally accepted that the energy transfer from ligand to Ln(III) ion occurs from the lowest triplet state energy level T_1 of the ligand to the resonance level of Ln(III) [4]. Macrocyclic, macrobicyclic (cryptand) and podand type ligands have been extensively used for these purposes [5–8]. Podand type ligands have drawn much attention in recent years, mainly due to their possessing spheroidal cavities and binding sites that are hard, therefore, stabilizing their complexes and shielding the encapsulated ion from interaction with the surroundings [9]. Ligands containing many of the common donor groups have been synthesized. Among these numerous podands which have demonstrated their potential use in functional supramolecular chemistry [10–12], amide type podands have been attracted more attention in preparing the lanthanide complexes possessing strong luminescent properties. It is expected that the amide type podands, which are flexible in structure and have 'terminal-group effects' [13], will shield the encapsulated lanthanide ion from interaction with the surroundings effectively, and thus to achieve strong luminescent properties. As a part of our systematic studies, a novel multipodal ligand, 1,2,4,5-tetramethyl-3,6-bis{*N,N*-bis[((2′-benzylaminoformyl)phenoxyl)ethyl]amino-methyl}-benzene (**L**, Scheme 1), has been designed and prepared successfully with the goal of expanding the pool of ligand type and studying the coordination and luminescent properties of lanthanide ions with the multipodal ligand, which were not very familiar. The results indicated that counter anion notably affected the luminescence characteristics of europium and terbium ions.

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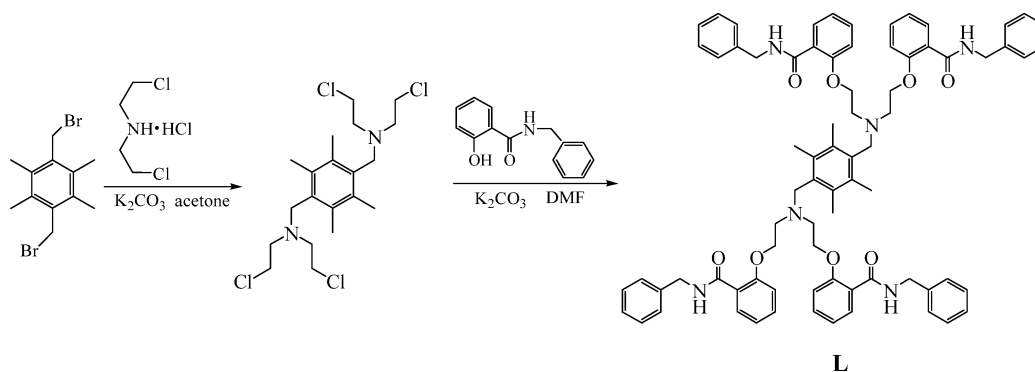
Scheme 1 The synthetic route for the ligand **L**

Experimental section

Materials and physical measurements

N-benzylsalicylamide [14] and β, β'-dichlordiethylamine hydrochloride salt [15] were prepared according to the literature methods, respectively. Other chemicals were obtained from commercial sources and used without further purification. The metal ions were determined by EDTA titration using xylenol orange as an indicator. Carbon, nitrogen and hydrogen analyses were determined using an Elementar Vario EL (see Table 1). Molar conductivity measurements were carried out with a DDSJ-308 type conductivity bridge using 1.0×10^{-3} mol cm^{-3} solutions in acetone at 19 °C. IR spectra were recorded on a Nicolet 360 FT-IR instrument using KBr discs in the 4000–400 cm^{-1} region. ^{1}H NMR spectrum was measured on a Varian Mercury-300B spectrometer in CDCl$_3$ solution with TMS as internal standard. Luminescence and phosphorescence spectra were obtained on a Hitachi F-4500 spectrophotometer at room temperature and 77K.

Synthesis of the ligand L

The synthetic route for the multipodal ligand is shown in Scheme 1. The β, β'-dichlordiethylamine hydrochloride salt (2 mmol) and potassium carbonate (4 mmol) were refluxed in acetone (25 cm^3) for 30 min, and then the 1,4-bis (bromomethyl)-2,3,5,6-tetramethyl-benzene (1 mmol) was added to the solution. The reaction mixture was refluxed for 12 h and the hot solution was filtered off. The collected organic phase was evaporated in vacuum. Then the obtained product was added to a mixture of *N*-benzylsalicylamide (4.0 mmol), potassium carbonate (8 mmol) and DMF (20 cm^3) which was warmed to ca. 90 °C. And the reaction mixture was stirred at 90–95 °C for 8 h. After cooling down, the mixture was poured into water (100 cm^3). The resulted solid was treated with column chromatography on silica gel [petroleum ether : ethyl acetate (2:3)] to get the ligand **L**, yield 68%, m. p. 94–95 °C; Anal. Calcd for C$_{76}$H$_{80}$O$_8$N$_6$: C, 75.72; H, 6.69; N, 6.97; Found: C, 76.02; H, 6.36; N, 7.14%. ^{1}H NMR (CDCl$_3$, 300 MHz): 2.11 (s, 12H), 2.68 (t, 8H), 3.60 (s, 4H), 3.87(t, 8H), 4.56–4.63 (d, 8H), 6.57–7.25 (m, 36H), H (N–H) not detected. IR (KBr pellet, cm^{-1}): 1655 (s, C=O), 1238 (m, Ar-O), 1105 (w, Ar-O).

Synthesis of the lanthanide complexes

An ethyl acetate solution (5 cm^3) of Ln(NO$_3$)$_3$·6H$_2$O (Ln= Eu, Gd, Tb) (0.1 mmol) was added dropwise to a solution of 0.1 mmol ligand **L** in the ethyl acetate (5 cm^3). The mixture was stirred at room temperature for 8 h. And then the precipitated solid complex was filtered, washed with

Table 1 Analytical and molar conductance data of the complexes (calculated values in parentheses)

Complexes	Analysis (%)				Λ_m (cm^2 Ω^{-1} mol^{-1})
	C	H	N	Ln	
[Eu$_3$**L**$_2$(NO$_3$)$_9$]·4H$_2$O	52.56 (52.21)	4.44 (4.84)	8.64 (8.41)	12.88 (13.04)	22.4[a]
[Tb$_3$**L**$_2$(NO$_3$)$_9$]·4H$_2$O	52.03 (51.90)	4.47 (4.81)	8.57 (8.36)	13.67 (13.55)	21.3[a]
[Eu**L**(Pic)$_3$]	55.76 (55.30)	4.28 (4.25)	9.88(10.29)	7.44 (7.32)	22.2[a]
[Tb**L**(Pic)$_3$]	54.66 (55.11)	4.22 (4.23)	9.98(10.26)	7.76 (7.58)	22.4[a]
[Eu$_2$**L**$_3$(ClO$_4$)$_3$](ClO$_4$)$_3$·4H$_2$O	59.36(59.67)	5.45(5.45)	5.20(5.49)	6.62(6.54)	302[b]
[Tb$_2$**L**$_3$(ClO$_4$)$_3$](ClO$_4$)$_3$·4H$_2$O	60.02(59.49)	5.49(5.43)	5.24(5.48)	6.91(6.65)	338[b]

[a] Measured in acetone
[b] Measured in methanol (10^{-3} mol·L^{-1}).

ethyl acetate, dried in vacuo over P_4O_{10} for 48 h and submitted for elemental analysis, yield 70%.

An ethanol solution (5 cm^3) of $Ln(Pic)_3 \cdot 6H_2O$ (Ln=Eu, Gd, Tb) (0.1 mmol) was added dropwise to a solution of 0.1 mmol ligand **L** in 5 cm^3 of ethanol. The mixture was stirred at room temperature for 8 h. And then the precipitated solid complex was filtered, washed with ethanol, dried in vacuo over P_4O_{10} for 48 h and submitted for elemental analysis, yield 75%.

An ethyl acetate solution (5 cm^3) of $Ln(ClO_4)_3 \cdot 9H_2O$ (Ln= Eu, Gd, Tb) (0.1 mmol) was added dropwise to a solution of 0.1 mmol ligand **L** in the chloroform (5 cm^3). The mixture was stirred at room temperature for 8 h. And then the precipitated solid complex was filtered, washed with ethyl acetate and chloroform, dried in vacuo over P_4O_{10} for 48 h and submitted for elemental analysis, yield 60%.

Results and discussion

Analytical data for the newly synthesized complexes, listed in Table 1, indicate that the nitrate complexes conform to a 3:2 metal-to-ligand stoichiometry $Ln_3L_2(NO_3)_9 \cdot 4H_2O$, picrate complexes conform to a 1:1 metal-to-ligand stoichiometry $LnL(Pic)_3$ and perchlorate complexes conform to a 2:3 metal-to-ligand stoichiometry $Ln_2L_3(ClO_4)_6 \cdot 4H_2O$.

All the lanthanide nitrate complexes are soluble in DMF, DMSO, methanol, ethanol, acetone and THF, but slightly soluble in ethyl acetate and chloroform. The molar conductances of the complexes in acetone (see Table 1) indicate that all complexes act as non-eletrolytes [16], implying that all nitrate groups are in coordination sphere. Thus, the formula of the nitrate complexes can be denoted as $[Ln_3L_2(NO_3)_9] \cdot 4H_2O$.

All the lanthanide picrate complexes are soluble in DMF, DMSO, acetone and acetonitrile, but slightly soluble in methanol, ethanol, ethyl acetate and chloroform. The molar conductances of the complexes in acetone (see Table 1) indicate that all complexes act as non-eletrolytes [16], implying that all picrate groups are in coordination sphere. Thus, the formula of the picrate complexes can be denoted as $[LnL(Pic)_3]$.

All the lanthanide perchlorate complexes are soluble in DMF, DMSO, methanol, and acetonitrile, but slightly soluble in ethanol, acetone, ethyl acetate and chloroform. And the molar conductance values of the complexes (see Table 1) indicate the presence of a 1:3 type electrolyte [16]. Thus, the formula of the perchlorate complexes can be denoted as $[Ln_2L_3(ClO_4)_3](ClO_4)_3 \cdot 4H_2O$.

The complexes possessing the similar counter anion have similar IR spectra, of which the characteristic bands have similar shifts, suggesting that they have a similar coordination structure.

The "free" ligand **L** exhibit two absorption bands at 1655 cm^{-1} and 1105 cm^{-1} which are assigned to ν(C=O) and ν(C–O–C), respectively. In the nitrate complexes, the low-energy band remains unchanged, but the high-energy band red shifts to about 1613 cm^{-1} ($\Delta\nu$=40 cm^{-1}) as compared to its counterpart for the "free" ligand, indicating that only the oxygen atom of C=O takes part in coordination to the lanthanide ions. The characteristic frequencies of the coordinating nitrate groups (C_{2v}) appear at *ca.* 1450 and 1480 cm^{-1} (ν_1), 1300 cm^{-1} (ν_4), 1030 cm^{-1} (ν_2) and 815 cm^{-1} (ν_3) cm^{-1} [17], and the difference between two strongest absorptions (ν_1 and ν_4) of the nitrate groups is about 150–180 cm^{-1}, clearly establishing that the NO_3^- groups in the solid complexes coordinate to the lanthanide ion as bidentate ligands [18]. Additionally, no bands at 1380, 820 and 720 cm^{-1} in the spectra of complexes indicates that free nitrate groups (D_{3h}) are absent. In addition, broad bands at *ca.* 3398 cm^{-1} indicate that water molecules are existent in the complexes [18], in agreement with the results of the elemental analysis.

In the picrate complexes, after the formation of the complex, the characteristic frequency of the free ligand ν(C=O) at 1655 cm^{-1} shifts *ca.* 42 cm^{-1} towards lower wave numbers and the ν(C–O–C) absorption band also remains unchanged, indicating that only the oxygen atom of C=O coordinate to the lanthanide ion. The O–H out-of-plane bending vibration of the free HPic at 1151 cm^{-1} disappears, indicating that the H-atom of the OH group is replaced by Ln(III). The vibration ν(C–O) of Pic$^-$ at 1265 cm^{-1} is shifted toward higher frequency by *ca.* 10 cm^{-1} in the complexes. This is due to the following two effects. First, the hydrogen atom of the O–H group is replaced by Ln(III), increasing the π-bond character in the C–O bond. Secondly, coordination of the oxygen atom of **L** to Ln(III) decreases the π-character. The free HPic has ν_{as} (–NO_2) and ν_s(–NO_2) at 1555 and 1342 cm^{-1}, respectively, which split into two bands at *ca.*1575, 1542 cm^{-1} and *ca* 1365, 1330 cm^{-1}, respectively in the complexes. This indicates that some O-atoms in the nitro group of Pic$^-$ take part in coordination.

In the perchlorate complexes, after the formation of the complex, the characteristic frequency of the free ligand ν(C=O) at 1655 cm^{-1} shifts *ca.* 32 cm^{-1} towards lower wave numbers and the ν(C–O–C) absorption band also remains unchanged, indicating that only the oxygen atom of C=O coordinate to the lanthanide ion. In the IR spectra of complexes, the characteristic frequencies of perchlorate ions appear at 1145, 1093, 623 and 489 cm^{-1}. When ClO_4^- is not coordinated, it is T_d symmetry and there are two absorptions. When ClO_4^- is coordinated, it is C_{3v} symmetry and there are five absorptions [19, 20]. In the IR spectra of these complexes, four absorptions can be seen clearly. So ClO_4^- is not all with the T_d symmetry and some should have
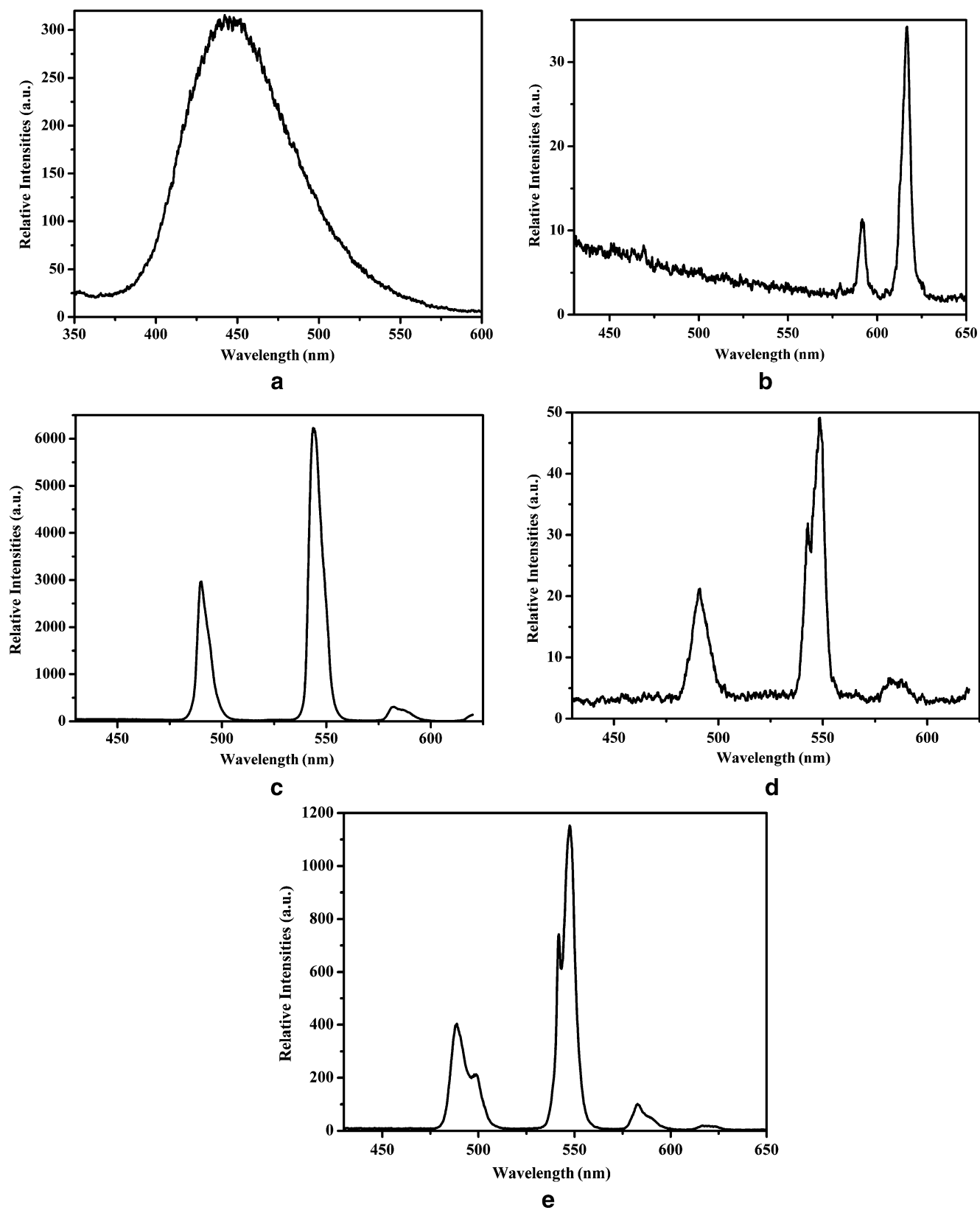
Fig. 1 Emission spectra of **L** (**a**), [Eu$_3$**L**$_2$(NO$_3$)$_9$]·4H$_2$O (**b**), [Tb$_3$**L**$_2$(NO$_3$)$_9$]·4H$_2$O (**c**), [Tb**L**(Pic)$_3$] (**d**) and [Tb$_2$**L**$_3$(ClO$_4$)$_3$](ClO$_4$)$_3$·4H$_2$O (**e**) in solid state

C_{3v} symmetry. And this is in agreement with the results of molar conductances. In addition, broad bands at *ca.* 3395 cm^{-1} indicate that water molecules are existent in the complexes, in agreement with the results of the elemental analysis.

Ligand-based excitations cause the characteristic emission of lanthanide complexes while the ligand fluorescence is completely quenched. This indicates the presence of ligand-to-metal energy transfer [21]. The ability of transfer energy from ligand to metal is important in the design of Ln(III) supramolecular photonic devices [22, 23]. The luminescence spectra of the ligand and its Eu^{3+} and Tb^{3+} complexes in solid state were recorded at room temperature. Among these six complexes, luminescence of the complexes of Eu, Tb nitrates and Tb picrate and Tb perchlorate were observed but not for the Eu picrate and perchlorate complexes. The emission spectra of the ligand and complexes are shown in Fig. 1. and the luminescence data are listed in Table 2.

Excited by the absorption band at 323 nm, the "free" ligand exhibits broad emission bands ($\lambda_{max}=442$ nm) in solid state (Fig. 1a). It is shown in Fig. 1 that the complexes show the characteristic emissions of Eu^{3+} or Tb^{3+}. This indicates that the ligand **L** is a good organic chelator to absorb and transfer energy to lanthanide ions.

In the spectrum of Eu nitrate complex, the relative intensity of $^5D_0 \rightarrow {}^7F_2$ is stronger than that of $^5D_0 \rightarrow {}^7F_1$, showing that the Eu (III) ion is not in a centro-symmetric coordination site [24]. In addition, the Tb complexes show no ligand-based emission bands in *ca.* 450 nm, but this emission bands in the Eu nitrate complex are still visible which means the energy transfer in the Tb complexes are more efficient than that in the Eu complex. Intramolecular
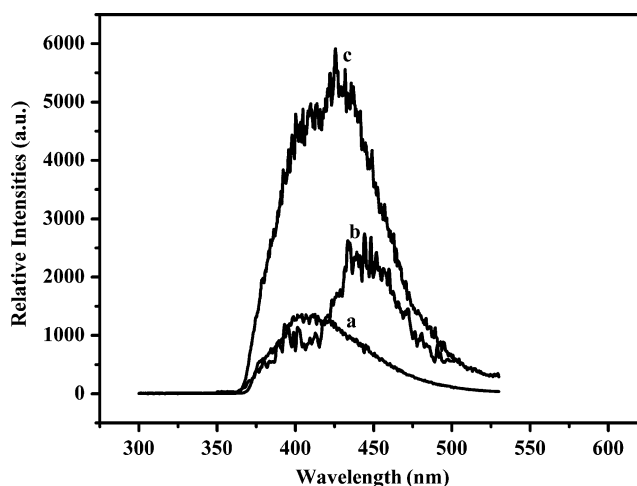

Fig. 2 The phosphorescence spectra of the Gd nitrate (**a**), picrate (**b**) and perchlorate (**c**) complexes

energy transfer from the triplet state of the ligand to the resonance level of the Ln(III) ion is one of the most important processes influencing the luminescence quantum yields of Ln(III) complexes [25]. The energy difference between the triplet state energy level of the ligand and the lowest excited state level of Ln(III) can not be too large or too small. So considering the emission spectra of these four complexes, it can be concluded that the triplet energy of **L** is in an appropriate level to Tb^{3+} in the complex, which makes the energy transition from the ligand to Ln(III) more easily in these three Tb complexes.

In order to acquire the triplet excited state T_1 of the ligand **L**, the phosphorescence spectra of the Gd(III) complexes were measured at 77 K in a methanol-ethanol mixture ($V/V=1:1$). The phosphorescence spectra of the Gd complexes are shown in Fig. 2. The triplet state energy levels T_1 of the ligand **L** in the nitrate, picrate and perchlorate complexes, which were calculated from the shortest-wavelength phosphorescence band [26], are 24,300, 23,148 and 22,523 cm^{-1}, respectively. These energy levels are above the lowest excited resonance level $^5D_0$ (17,286 cm^{-1}) of Eu(III) and the lowest excited resonance level $^5D_4$ (20,545 cm^{-1}) of Tb(III). Thus the energy could be transferred from ligand to the Eu and Tb ions. And this result also indicates that the triplet state energy level T_1 of this ligand **L** matches better to the lowest resonance level of Tb(III) ($\Delta\nu=3755$, 2603 and 1,978 cm^{-1}) than to Eu(III) ($\Delta\nu=7032$, 5862 and 5237 cm^{-1}) ion.

We deduced that the electrostatic factors in the ligand–metal bonding, which may be affected by the different counter anion in these three series complexes, influenced the triplet state energy level of the ligand **L** [26] and made the luminescence intensities of the nitrate complexes highest.

Table 2 Luminescence data for the ligand **L** and the complexes

Compounds	Slit (nm)	λ_{ex} (nm)	λ_{em} (nm)	RLI[a]	Assignment
L	2.5(EX), 1.0 (EM)	323	442	316	
[Eu$_3$L$_2$(NO$_3$)$_9$]·4H$_2$O	2.5(EX), 1.0 (EM)	396	591	12	$^5D_0 \rightarrow {}^7F_1$
			617	34	$^5D_0 \rightarrow {}^7F_2$
[Tb$_3$L$_2$(NO$_3$)$_9$]·4H$_2$O	2.5(EX), 1.0(EM)	320	490	2968	$^5D_4 \rightarrow {}^7F_6$
			544	6225	$^5D_4 \rightarrow {}^7F_5$
			582	307	$^5D_4 \rightarrow {}^7F_4$
[TbL(Pic)$_3$]	2.5(EX), 1.0 (EM)	330	490	21	$^5D_4 \rightarrow {}^7F_6$
			545	49	$^5D_4 \rightarrow {}^7F_5$
			582	8	$^5D_4 \rightarrow {}^7F_4$
[Tb$_2$L$_3$(ClO$_4$)$_3$](ClO$_4$)$_3$·4H$_2$O	2.5(EX), 1.0 (EM)	350	489	213	$^5D_4 \rightarrow {}^7F_6$
			547	1153	$^5D_4 \rightarrow {}^7F_5$
			583	100	$^5D_4 \rightarrow {}^7F_4$

[a] RLI=relative luminescence intensity

Conclusions

In this paper, we report the synthesis, IR spectra and luminescent properties of the solid complexes of lanthanide nitrates, picrates and perchlorate with a novel multipodal ligand, 1,2,4,5-tetramethyl-3,6-bis{N,N-bis[((2′-benzylaminoformyl)phenoxyl)ethyl]aminomethyl}-benzene (L). When the ligand formed the lanthanide complexes, obvious changes in IR spectra were observed. In the complexes, lanthanide ions were coordinated to the C=O oxygen atoms of the ligand L. It is noteworthy that the characterization of these complexes demonstrate 3:2, 1:1 and 2:3 (M:L) type coordination stoichiometries. Thus, the lanthanide ion could be effectively encapsulated and protected by the coordinated ligands. Comparing the luminescence spectra of the three series complexes of europium (III) and terbium (III), we found that this novel multipodal ligand L in Tb complexes is more effective in energy-transfer than in Eu complexes. The Tb complexes show no emission bands from the ligand L in *ca* 450 nm, but the emission bands in the Eu complex are still visible (Fig. 1). The lowest triplet state energy level of the ligand indicates that the triplet state energy level (T_1) of the ligand matches better to the resonance level of Tb^{3+} than Eu^{3+}. Under the same condition, the luminescence intensities of nitrates complexes are strongest. So we may deduce that the counter anion of the complexes is very essential in determining the luminescent properties of the lanthanide complexes by influencing the electrostatic factors in the ligand-metal bonding.

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