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ORIGINAL PAPER

Syntheses, Characterization and Fluorescent Properties of Six Novel Lanthanide Complexes with *N*,*N*-diphenyl-2-(quinolin-8-yloxy)acetamide

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Abstract Six novel complexes of lanthanide nitrates (Ln = La, Sm, Eu, Gd, Tb, Dy) with a amide type ligand, *N*-methyl-*N*-phenyl-2-(quinolin-8-yloxy)acetamide (L) have been prepared and characterized by elemental analysis, conductivity measurements, IR and ^{1}H NMR spectra. The fluorescence properties of the complexes and the triplet state energy of the ligand were studied in detail. The result indicates that, the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III). In addition, the fluorescence intensities of the Eu(III) complex in different solutions(tetrahydrofuran, acetone and acetonitrile) are stronger than that in solid state. This is probably due to the solvate effect and the stoichiometry change of ligand with Eu(III) ion in solutions.

Keywords Lanthanide complexes · Aryl amide · Fluorescence properties · Triplet state energy · Complexation constant

Introduction

The Eu(III) and Tb(III) complexes are noted for their fluorescence arising from f–f transitions, which result in emission bands with extremely narrow bandwidth and no theoretical cap on the quantum efficiency. This makes them have potential applications as light-emitting diode (LED), laser materials, optical signal amplification and fluoroimmunoassay [1–4]. However, direct excitation of Eu(III) or Tb(III) ion is not efficient because of its inherently small absorption cross section. To overcome this problem, an organic chromophore, which serves as an antenna or sensitizer, absorbing the excitation light and transferring the energy from its lowest triplet state energy level (*T*) to the resonance level of Eu(III) and Tb(III) ions, is highly desired [5–9].

It is expected that the amide type ligands, which are flexible in structure and have 'terminal-group effects' [10–12], will shield the encapsulated lanthanide ion from interaction with the surroundings effectively, and thus to achieve strong fluorescent properties. Therefore, a amide-based open-chain ligand was selected as 'antenna' in this work. Moreover, the lowest triplet energy level of the ligand (*T*), the fluorescent properties of the complexes and the stoichiometry of ligand with Eu(III) ion in solutions were studied in detail.

Experimental

Materials

The lanthanide(III) nitrates were prepared from their oxide acquired from Yue Long (People's Republic of China). All other chemicals used were of analytical grade. Absolute chloroform and *N*,*N*′-dimethylformamide (DMF) were obtained after being distilled by standard methods.

Physical measurements

The melting point of the ligand was determined on a XT4-100x microscopic melting point apparatus (made in Beijing,

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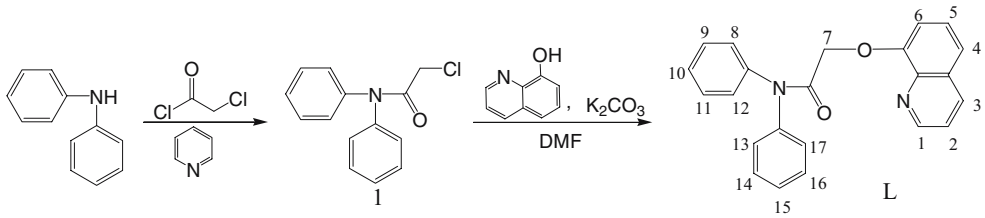

Fig. 1 Synthesis scheme of the ligand

China). Elemental analyses were carried out on an Elemental Vario EL analyzer. The metal contents of the complexes were determined by titration with EDTA. The infrared spectra (IR, ν=4,000–400 cm^{-1}) were determined by the KBr pressed disc method on a Nicolet-170SX FT-IR spectrophotometer. ^1H NMR spectra were recorded on Bruker DRX-200 spectrometer in CD_3COCD_3 solutions. All conductivity measurements were carried out with a DDS-11A conductometer (made in China) bridge using 1.0×10^{-3} mol/l solutions in DMF at 25 °C. The mass spectrum was obtained on a TRACE DSQ GC/MS. The ultraviolet absorption spectra were measured on Shimadzu UV-240 spectrophotometer. Fluorescence emission and excitation spectra were determined on a Hitachi F-4500 FL spectrophotometer. Phosphorescence spectra at 77 K were taken on the same spectrophotometer equipped with phosphorescence measurement apparatus. All the complexes were dried at 100 °C to constant weights before these measurements.

Preparation of **L**

The synthesis scheme is shown in Fig. 1. The compound **1** was prepared according to the literature [13].

8-Hydroxyquinoline (1.5 g, 10.3 mmol) and anhydrous potassium carbonate (1.6 g, 11.6 mmol) were added to DMF(15 ml), then **1** (2.45 g, 10.0 mmol) and a small quantity of KI were added. The reaction mixture was stirred for 5 h at 100–110 °C. After cooling down, 150 ml water was added and stirred for 2 h. The precipitate was collected by filtration and washed with water to get the ligand **L**; yield=88.9 %. m.p. 120–121 °C; MS, m/z=354 $[M]^+$.

The ^1H NMR chemical shifts δ (ppm/TMS) for the protons of L in CD_3COCD_3 are listed in Table 3.

Synthesis of the complexes

The ligand (L) (0.1 mmol) was dissolved in ethyl acetate (2 ml). To this solution was added dropwise a ethyl acetate solution (2 ml) containing $Ln(NO_3)_3{\cdot}nH_2O$ (0.05 mmol). After stirring for 4 h at room temperature, the precipitate was separated from the solution by suction filtration, purified by washing several times with ethyl acetate, and dried for 24 h in a vacuum. The yields were in the range of 50–60 %.

Result and discussion

Analytical data for the complexes, presented in Table 1, conform to $Ln(L)_2(NO_3)_3$. All complexes are white powders, which are soluble in DMF, DMSO, acetone, methanol, acetonitrile and ethanol, slightly soluble in ethyl acetate, while insoluble in water and ether. The molar conductivity values of the complexes in DMF are in the range of 91–115 s cm^2 mol^{-1}, indicating that the complexes are 1:1 electrolytes [14].

IR spectra

On the basis of the similar IR spectra of the complexes (Table 2), it may be assumed that all of them have similar coordination structures. The IR spectrum of the free ligand show strong band at 1,679 cm^{-1}, which are attributable to stretch vibrations of the carbonyl group of amide (ν(C=O)). The peak at 1,618 cm^{-1} to ν(C=N) and the peak at 1,258 cm^{-1} to ν(Ar–O–C). In the IR spectra of their lanthanide(III) complexes, the ν(C=O) and ν(C=N) shift by 13–44 and 19–30 cm^{-1}, respectively; indicating that

Table 1 Analytical and molar conductance data for the complexes

Complexes	C% (calc.)	H% (calc.)	N% (calc.)	Λ_m(s cm^2 mol^{-1})
$La(L)_2(NO_3)_3$	53.54 (53.45)	3.23 (3.51)	9.17 (9.48)	90.5
$Sm(L)_2(NO_3)_3$	52.43 (52.86)	3.34 (3.47)	9.03 (9.38)	115.0
$Eu(L)_2(NO_3)_3$	52.10 (52.78)	3.24 (3.47)	9.04 (9.37)	108.5
$Gd(L)_2(NO_3)_3$	52.14 (52.51)	3.37 (3.45)	8.86 (9.32)	110.3
$Tb(L)_2(NO_3)_3$	51.96 (52.43)	3.22 (3.44)	8.95 (9.30)	106.7
$Dy(L)_2(NO_3)_3$	51.72 (52.25)	3.27 (3.43)	8.91 (9.27)	114.9

Table 2 Major IR data of the free ligand and its complexes (cm^{-1})

Compounds	ν (C=O)	ν (C=N)	ν (Ar–O–C)	ν_0 (NO_3)	ν_1 (NO_3)	ν_4 (NO_3)	ν_1–ν_4 (NO_3)
L	1,679	1,618	1,258				
$La(L)_2(NO_3)_3$	1,666	1,637	1,258	1,384	1,492	1,319	173
$Sm(L)_2(NO_3)_3$	1,642	1,590	1,259	1,384	1,492	1,312	180
$Eu(L)_2(NO_3)_3$	1,638	1,588	1,260	1,384	1,493	1,313	180
$Gd(L)_2(NO_3)_3$	1,640	1,590	1,260	1,384	1,492	1,314	178
$Tb(L)_2(NO_3)_3$	1,636	1,589	1,262	1,384	1,494	1,316	178
$Dy(L)_2(NO_3)_3$	1,635	1,592	1,262	1,384	1,494	1,317	177

carbonyl oxygen atom and quinoline nitrogen atom take part in coordination to the metal ion [15, 16]. However, the slight shift of ν(Ar–O–C) between each complex and the ligand indicates that the etheric oxygen atom does not coordinate with the metal ion. It is possibly due to the fact that the molecules have large sterically hindered effect, which prevents the etheric oxygen atom from coordinating with lanthanide ion.

For all complexes, bands at 1384 cm^{-1} in the spectra of complexes indicate that free nitrate groups (D_{3h}) exist [17]. Additionally, the two intense absorption bands in the spectra associated with the asymmetric stretching appear in the range of 1,312–1,319 cm^{-1} (ν_4) and 1,492–1,494 cm^{-1} (ν_1), clearly establishing that there are some coordinated NO_3^- groups (C_{2v}) in the complexes [18]. The differences between the two bands lie in 173–180 cm^{-1}, suggesting that the coordinated nitrate groups in the complexes are bidentate [19].

^{1}H NMR spectra

The ^{1}H NMR spectra of the free ligand and its La(III) complex were measured in CD_3COCD_3 at room temperature (Table 3). For L, the signals of H_1, H_3, H_6, H_7 and $H_{2,\ 4,\ 5,\ 8–17}$ are at 8.86–8.89, 8.25–8.30, 7.14–7.19, 4.95 and 7.33–7.54 ppm, respectively. Upon coordination, they are shifted by 0.14, 0.17–0.18, 0.03–0.04, 0.27 and 0.16 ppm in the La(III) complex, respectively. Among them, the signal of proton H_6 shifted by only 0.03 ppm, indicating that the etheric oxygen atom has not formed a coordinative bond with La(III) ion. The small shift is probably due to a change in the conformation of the ligand in the complex [20]. Thus, it can be concluded that the oxygen atom of the carbonyl group and quinoline nitrogen atom take part in coordination in the La(III) complex [21, 22]. The result is in accordance with some of the assumptions made on the basis of the IR spectra studies.

Table 3 The ^{1}H NMR data of free ligand and its La(III) complex in CD_3COCD_3 (ppm)

Compounds	H_1	H_3	H_6	H_7	$H_{2,\ 4,\ 5,\ 8–17}$
L	8.86–8.89	8.25–8.30	7.14–7.19	4.95	7.33–7.54
$La(L)_2(NO_3)_3$	9.00–9.03	8.43–8.47	7.18–7.22	5.22	7.33–7.70

According to the data of the elemental analyses, molar conductivity, IR spectra and ^{1}H NMR spectra, composition of the complexes can be inferred: $[Ln(L)_2(NO_3)_2]NO_3$. And the coordination number for the lanthanide ions may be 8. The possible molecular structures of the complexes are shown in Fig. 2.

Fluorescence

The emission spectrum of the Eu(III) complex in solid state is shown in Fig. 3 (solid). The Eu(III) and Sm(III) complexes show the strong red fluorescence in solid state, the spectra data are shown in Table 4. However, the Tb(III) and Dy(III) complexes only exhibit the free ligand band emission, which indicates that the energy would not be transferred efficiently between the ligand triplet level and the resonance levels of the Tb(III) and Dy(III) ions.

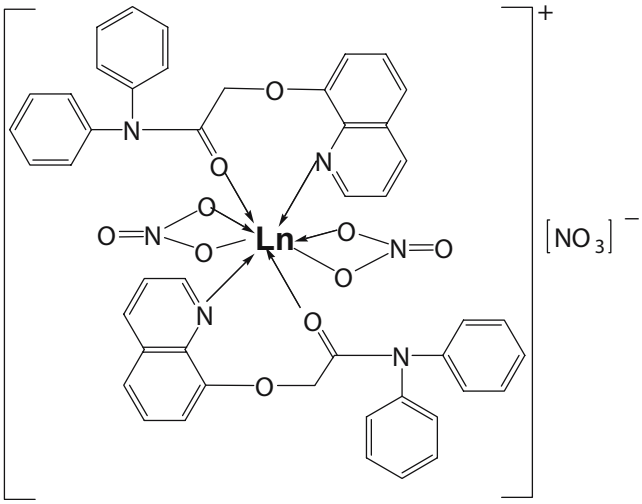

Fig. 2 Possible molecular structure of the complexes

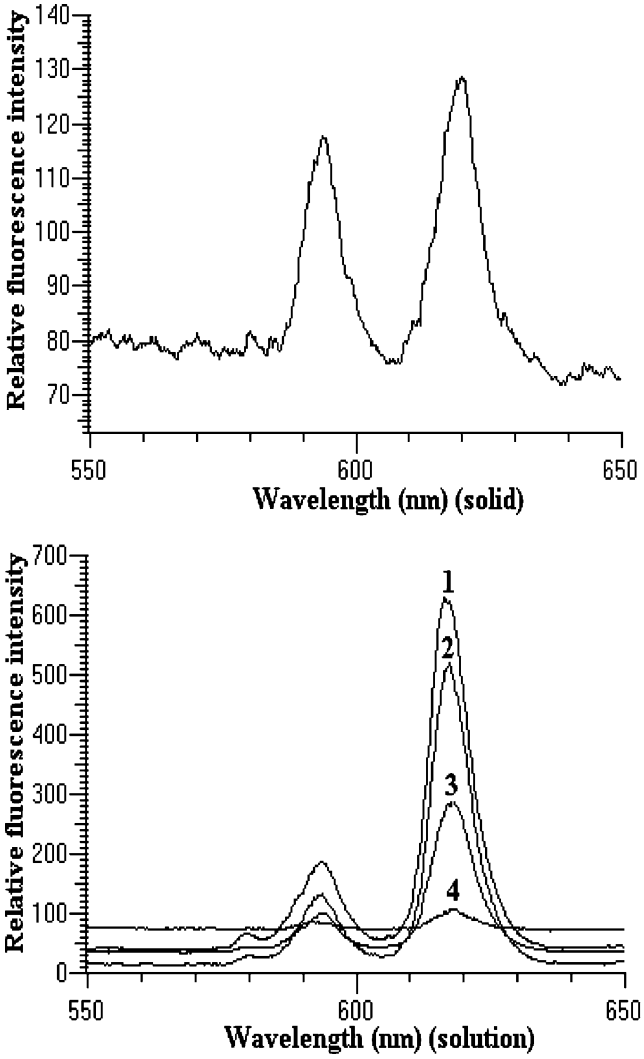

Fig. 3 The fluorescence emission spectrum of the $Eu(L)_2(NO_3)_3$ complex in solid state at room temperature: λ_{Ex}=348 nm (solid). The emission spectra of $EuL(NO_3)_3{\cdot}H_2O$ in different solutions (5×10^{-4} mol/l) at room temperature: *1* tetrahydrofuran, *2* acetone, *3* acetonitrile, *4* ethanol: λ_{Ex}=340 nm (solution). All the emission slit widths were 2.5 nm

The influences of several solvents on the fluorescence intensity of the Eu(III) complex were investigated (Fig. 3 (solution)). It could be seen that in tetrahydrofuran solution the Eu(III) complex has the strongest fluorescence, and then in acetone, acetonitrile and ethanol. This is probably due to the coordinating effects of solvents, namely solvate effect [23]. However, it is interesting that the fluorescence intensities of the Eu(III) complex in tetrahydrofuran, acetone and acetonitrile solutions are stronger than that of powder. This abnormal phenomenon may be owing to the structure difference of the Eu(III) complex between in solution and solid state.

From the emission spectrum data of Eu(III) complex in solid state (Table 4), it can be seen that the intensity of $^5D_0\rightarrow{}^7F_2$ transition is only a little stronger than that of $^5D_0\rightarrow{}^7F_1$ transition, and the value for $\eta_{Eu}={}^5D_0\rightarrow{}^7F_2/{}^5D_0\rightarrow{}^7F_1$ is only 1.1. However, from Table 5, the values for η_{Eu} are 3.34 (tetrahydrofuran), 3.94 (acetone) and 2.86 (acetonitrile). It has been reported that the $^5D_0\rightarrow{}^7F_2$ transition is an electric dipole transition, which can be detected as a relatively strong peak only when Eu(III) does not lie in centrosymmetric ligand field; on the contrary, the $^5D_0\rightarrow{}^7F_1$ transition is a magnetic dipole transition, and its intensity becomes the most intensive only when Eu(III) ion is the centre of ligand field [24]. Consequently, it can be concluded that the structure of the Eu(III) complex changes in the above organic solvents, which leads to the abnormal fluorescence intensity change.

The fluorescence quantum yields for the Eu(III) and Sm (III) complexes were measured using the ratio method, $[Ru(bpy)_3]Cl_2$ in degassed acetonitrile solution as a standard, Φ_s=0.062 [25]. All the complexes were dissolved in tetrahydrofuran (1×10^{-5} mol/l). Each solution was excited at λ_{max} (Table 4) on a Hitachi F-4500 FL spectrophotometer. The Eq. 1 used for determining the quantum yield, Φ_c, of the complexes was [26]:

$$\Phi_c = \frac{F_c\Phi_s A_s}{F_s A_c} \tag{1}$$

where F denotes the integrated area under the emission spectrum; A is the absorbance at the exciting wavelength. A refractive index correction was used: $R_f^2(tetrahydrofuran)/R_f^2(acetonitrile)$ [27]. The values of Φ_c are 0.0151 (Eu(III) complex) and 0.0114 (Sm(III) complex).

Phosphorescence

Phosphorescence spectrum for the methanol–ethanol (1:1) solution (1×10^{-5} mol/l) of the Gd(III) complex with the ligand was measured at 77 K. The lowest triplet-state level

Table 4 Fluorescence spectra data (nm) of Eu(III) and Sm (III) complexes in solid state at room temperature

Compounds	Ex slit	Em slit	λ_{Ex}	λ_{Em}	Emission intensity	Transition
$Eu(L)_2(NO_3)_3$	2.5	2.5	348	580	82	$^5D_0\rightarrow{}^7F_0$
				594	118	$^5D_0\rightarrow{}^7F_1$
				620	130	$^5D_0\rightarrow{}^7F_2$
$Sm(L)_2(NO_3)_3$	2.5	2.5	348	562	87	$^4G_{5/2}\rightarrow{}^6H_{5/2}$
				598	102	$^4G_{5/2}\rightarrow{}^6H_{7/2}$
				644	66	$^4G_{5/2}\rightarrow{}^6H_{9/2}$

Table 5 Fluorescence spectra data (nm) of the Eu(III) complex in different solutions at room temperature

Solvent	Ex slit	Em slit	λ_{Ex}	λ_{Em}	Emission intensity	Transition
Tetrahydrofuran	2.5	2.5	340	579	67	$^5D_0 \rightarrow {}^7F_0$
				594	188	$^5D_0 \rightarrow {}^7F_1$
				616	628	$^5D_0 \rightarrow {}^7F_2$
Acetone	2.5	2.5	340	580	30	$^5D_0 \rightarrow {}^7F_0$
				594	132	$^5D_0 \rightarrow {}^7F_1$
				617	520	$^5D_0 \rightarrow {}^7F_2$
Acetonitrile	2.5	2.5	340	579	45	$^5D_0 \rightarrow {}^7F_0$
				593	101	$^5D_0 \rightarrow {}^7F_1$
				618	289	$^5D_0 \rightarrow {}^7F_2$
Ethanol	2.5	2.5	340	591	87	$^5D_0 \rightarrow {}^7F_1$
				618	106	$^5D_0 \rightarrow {}^7F_2$

Concentration=5×10^{-4} mol/l

energy(T) of the ligand were determined by the shortest wavelength transition in the phosphorescence spectrum to be 21,882 cm^{-1} (457 nm) [28].

Since the triplet state of the ligand is above the resonance level of Eu(III) ion or Tb(III) ion, the energy may be transferred from the excited ligand to metal ion. However, the intramolecular transfer efficiency depends mainly on two energy transfer processes: one is from the lowest triplet level (T) of ligand to the resonance level of Eu(III) ion ($^5D_1$) by resonant exchange interaction, and the other is just an inverse energy transfer by the thermal de-excitation mechanism [29]. Both energy transfer rate constants are dependent on the energy gap (ΔE) between T and ^{5}D (Table 6).

It has been reported that [29, 30], when $\Delta E(T-{}^5D_1)$ for Eu (III) is greater than 4,000 cm^{-1} or $\Delta E(T-{}^5D_4)$ for Tb(III) is less than 1,500 cm^{-1} , the fluorescence quantum yield of the Eu(III) or Tb(III) complexes is approximately zero at room temperature. According to this idea, the strong fluorescence of the Eu(III) complex is due to the optimal $\Delta E(T-{}^5D_1)$, and the Tb(III) complex can not exhibit its characteristic fluorescence should be due to the small $\Delta E(T-{}^5D_4)$.

The stoichiometry of ligand with Eu(III) in solution

Figure 4 shows the changes in the emission spectrum of the ligand L (1×10^{-5} mol/l) in tetrahydrofuran upon addition of

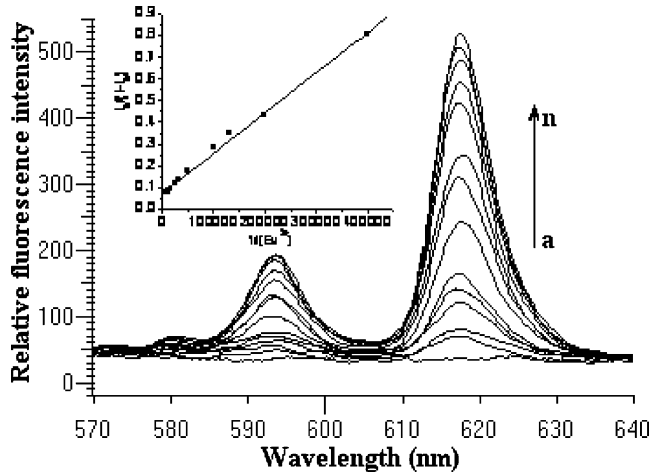

Fig. 4 Fluorescence spectra of ligand (a 1.0×10^{-5} mol/l) with increasing Eu^{3+} concentration in tetrahydrofuran. b 1.0×10^{-6}; c 2.5×10^{-6}; d 5.0×10^{-6}; e 7.5×10^{-6}; f 1.0×10^{-5}; g 2.0×10^{-5}; h 3.0×10^{-5}; i 4.0×10^{-5}; j 6.0×10^{-5}; k 8.0×10^{-5}; l 1.0×10^{-4}; m 1.25×10^{-4}; and n 1.5×10^{-4} mol/l: λ_{Ex}=340 nm. The *inset* shows the plot of $I_0/(I-I_0)$ vs $[Eu^{3+}]^{-1}$

Eu^{3+}.The insert shows the plot of $I_0/(I-I_0)$ versus $[Eu^{3+}]^{-1}$, where I_0 and I represent the emission intensity at 618 nm in the absence and presence of, respectively. The yielded straight line confirms that the complexation of Eu^{3+} into the ligand is in a 1:1 ratio (linearity correlation coefficient R= 0.997) [31]. Using the same method, it can be found that the mole ratios of Eu^{3+} : L are also 1:1 in both acetone (R= 0.984) and acetonitrile (R=0.995). It shows that the structure of the complex in the three solutions is different from that in solid state (Eu^{3+}:L=1:2). The result is consistent with that obtained from the fluorescence spectra measurements. Complexation constants (log Ks), determined from such plots for the Eu^{3+} in different solvents, are 4.60 (tetrahydrofuran), 4.31 (acetone) and 4.34 (acetonitrile), respectively [32]. In addition, the limits of detection (LOD) for Eu^{3+} in tetrahydrofuran, acetone, and acetonitrile were investigated, the value of them are 9.62×10^{-7}, 3.28×10^{-6}, and 1.35×10^{-6} mol/l, respectively.

Conclusions

According to the data and discussion above, it is obvious that the ligand have formed complexes with lanthanide

Table 6 Triplet state energy for the ligand and the data of $\Delta E(T-{}^5D)$

Complexes	0–0 transition (nm)	Triplet state energy level (cm^{-1})	$\Delta E(T-{}^5D_1{}^a)$ (cm^{-1})	$\Delta E(T-{}^5D_4{}^b)$ (cm^{-1})
$Gd(L)_2(NO_3)_3$	457	21882	2862	1382

[a5] D_1=19,020 cm^{-1} [the resonance level of Eu(III) ion] [33]
[b5] D_4=20,500 cm^{-1} [the resonance level of Tb(III) ion] [20]

(III) ions. The Eu(III) and Sm(III) complexes exhibit their strong characteristic fluorescence. And the measurement of the phosphorescence spectrum indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III). In addition, the fluorescence intensity of the Eu(III) complex in solid state is weaker than that in solution. There are two possible reasons: firstly, the change of the molar ratio (Eu^{3+}:L) leads to the change of the intramolecular transfer efficiency from ligand to Eu(III) ion; secondly, the solvents can take part in coordination and transfer energy to the Eu(III) ion. Based on those studies, a series of new aryl amide type ligands could be synthesized to optimize the fluorescence properties of the europium(III).

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References

1. McGehee MD, Bergstedt T, Zhang C, Saab AP, O'Regan MB, Bazan GC, Srdanov VI, Heeger AJ (1999) Narrow bandwidth luminescence from blends with energy transfer from semiconducting conjugated polymers to europium complexes. Adv Mater 11:1349−1354
2. Piguet C, Bunzli JCG, Bernardinelli GB, Hopfgartner G, Williamst AF (1993) Self-assembly and photophysical properties of lanthanide dinuclear triple-helical complexes. J Am Chem Soc 115:8197−8206
3. Elbanowshi M, Makowska B (1996) The lanthanides as luminescent probes in investigations of biochemical systems. J Photochem Photobiol 99:85−92
4. Saha AK, Kross K, Kloszewski ED, Upson DA, Toner JL, Snow RA, Black CDV, Desai VC (1993) Time-Resolved fluorescence of a new europium chelate complex: demonstration of highly sensitive detection of protein and DNA samples. J Am Chem Soc 115:11032−11033
5. de Sa GF, Malta OL, Donega CDM, Simas AM, Longo RL, Santa-Cruz PA, da Silva EF Jr (2000) Spectroscopic properties and design of highly luminescent lanthanide coordination complexes. Coord Chem Rev 196:165–195
6. Bazzicalupi C, Bencini A, Bianchi A, Giorgi C, Masotti A, Valtancoli B, Fusi V, Roque A, Pina F (2000) pH Modulation of the luminescence emission of a new europium cryptate complex. Chem Commun 7:561–562
7. Dawson W, Kropp J, Windsor M (1966) Internal-energy-transfer efficiencies in Eu and Tb chelates using excitation to selected ion levels. J Chem Phys 45:2410–2418
8. Latva M, Takalob H, Mukkala VM, Matachescuc C, Rodriguez-Ubisd JC, Kankarea J (1997) Correlation between the lowest triplet state energy level of the ligand and lanthanide(III) luminescence quantum yield. J Lumin 75:149–169
9. Gutierrez F, Tedeschi C, Maron L, Daudey JP, Poteau R, Azema J, Tisnès P, Picard C (2004) Quantum chemistry-based interpretations on the lowest triplet state of luminescent lanthanides complexes. Part 1. Relation between the triplet state energy of hydroxamate complexes and their luminescence properties. Dalton Transactions 9:1334–1347
10. Yang YS, Cai SH (1984) Studies on response of PVC membrane electrodes of crown compounds to metal cations. Chemical Reagents 6:133–138
11. Ding YZ, Lu JZ, Yang YS, Tan GZ, Xu JZ (1986) Studies on linear polyethers as extractants II. Extraction of light rare earths with glycol-*o*,*o*′-diacetamide with different substitution groups. Chemical Reagents 8:201–204
12. Wang W, Huang Y, Tang N (2007) Synthesis and infrared and fluorescence spectra of rare earth complexes with a novel amide-based ligand. Spectrochim Acta Part A Mol Biomol Spectrosc 66:1058–1062
13. Wu WN, Yuan WB, Tang N, Yang RD, Yan L, Xu ZH (2006) Synthesis, characterizations and luminescent properties of three novel aryl amide type ligands and their lanthanide complexes. Spectrochim Acta Part A Mol Biomol Spectrosc 65:912–918
14. Greary WJ (1971) The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. Coord Chem Rev 7:81–122
15. Jiang YH, Yang RD, Yan L, Hu XL, Yuan WB (2002) Synthesis, Characterization and fluorescent properties of a novel tri-podal compounds containing pyrazolone and of its RE coordinating complexes. J Chin Rare Earth Soc 20:474–477
16. Zhou YP, Yang ZY, Yu HJ, Yang RD (1999) Syntheses, characterization and bacteriostatic activities of 1-phenyl-3-methyl-4-benzoylpyrazolone-5-thiosemicarbazone and its rare earth complexes. Chinese Journal of Applied Chemistry 16:37–41
17. Gou RH, Li G, Liu B, Yang RD, Yan L (2004) Synthesis, characterization and properties of *N*,*N*′- bis(6-methyl-2-pyridine-*N*-oxide)-1,3-propane and europium and terbium complexes. J Rare Earths 22:21–24
18. Carnall WT, Siegel S, Ferrano JR, Tani B, Gebert E (1973) A new series of anhydrous double nitrate salts of the lanthanides structural and spectral characterization. Inorg Chem 12:560–564
19. Zhang YL, Liu WS, Dou W, Qin WW (2004) Synthesis and infrared and fluorescence spectra of new europium and terbium polynuclear complexes with an amide-based 1,10-phenanthroline derivative. Spectrochim Acta Part A Mol Biomol Spectrosc 60:1707–1711
20. Tang KZ, Zhang J, Tang Y, Liu WS, Tan MY, Sun YX (2006) Preparation, crystal structure and luminescent properties of the 3-D netlike supramolecular lanthanide picrate complexes with 2,20-[1,2-phenylenebis(oxy)]bis(*N*-benzylacetamide). Inorg Chim Acta 359:1207–1214
21. Gou BD, Zhu WX (1999) Synthesis and characterization of rare earth complexes with a new podand ligand. Journal of Beijing Normal University 35:242–246
22. Guo ZJ, Tan MY (2003) Synthesis and characterizations of U(VI) and Th(IV) complexes with two open-chain crown ethers with terminal quinolyl groups. Journal of Nuclear and Radiochemistry 25:177–180
23. Liu HQ, Cheung TC, Che CM (1996) Cyclometallated platinum (II) complexes as luminescent switches for calf-thymus DNA. Chem Commun 9:1039−1040
24. Qiang S (1993) Chemistry of rare earths. Henan Technology & Science Press, Zhengzhou, pp 304−314 (in Chinese)
25. Caspar JV, Meyer TJ (1983) Photochemistry of $Ru(bpy)_3^{2+}$ solvent effects. J Am Chem Soc 105:5583−5590
26. Parker CA, Rees WT (1960) Correction of fluorescence spectra and measurement of fluorescence quantum efficiency. Analyst 85:587−600
27. Owens JW, Smith R, Robinson R, Robins M (1998) Photophysical properties of porphyrins, phthalocyanines, and benzochlorins. Inorg Chim Acta 279:226−231

28. Wu SL, Wu YL, Yang YS (1992) Rare earth(iii) complexes with indole-derived acetylacetones II. luminescent intensity for europium(iii) and terbium(iii) complexes. J Alloys Compd 180:399–402
29. Sato S, Wada M (1970) Relations between intramolecular energy transfer efficiencies and triplet state energies in rare β-diketone chelates. Bull Chem Soc Jpn 43:2403–2410
30. Yan B, Zhu HX (2007) Photophysical properties of novel ternary lanthanide complexes with long chain mono-L *cis*-butene dicarboxylate (L = hexadecyl, octadecyl and eicosyl) and 2,2′-bipyridyl (or 1,10-phenanthroline). J Fluoresc 17:331–337
31. Yang QZ, Wu LZH, Zhang H, Chen B, Wu ZX, Zhang LP, Tung CH (2004) A luminescent chemosensor with specific response for Mg^{2+}. Adv Inorg Chem 43:5195–5197
32. Ji HF, Dabestani R, Brown GM, Hettich RL (1999) Spacer length effect on the photoinduced electron transfer fluorescent probe for alkali metal ions. Photochem Photobiol 69:513−516
33. Sayre EV, Freed S (1956) Spectra and quantum states of the europic ion in crystals. II fluroescence and absorption spectra of single crystals of europic ethylsulfate nonahydrate. J Chem Phys 24:1213–1219