

Synthesis and Luminescent Properties of Lanthanide Complexes with Structurally Related Novel Multipodal Ligands

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Abstract To explore the relationship between the structure of the ligands and the luminescent properties of the lanthanide complexes, a series of lanthanide nitrate complexes with two novel structurally related multipodal ligands, 1,3-bis{[(2'-(2-picolylaminoformyl))phenoxy]methyl}benzene (**L^I**) and 1,2-bis{[(2'-(2-picolylaminoformyl))phenoxy]methyl}benzene (**L^{II}**), have been synthesized and characterized by elemental analysis, infrared spectra and molar conductivity measurements. At the same time, the luminescent properties of the Eu(III) and Tb(III) nitrate complexes in solid state and the Tb(III) nitrate complexes in solvents were investigated at room temperature. Under the excitation of UV light, these complexes exhibited characteristic emissions of central metal ions. The lowest triplet state energy levels T_1 of these ligands both match better to the lowest resonance energy level of Tb(III) than to Eu(III) ion. The influence of the structure of the ligands on the luminescent intensity of the complexes was also discussed.

Keywords Multipodal ligands · Lanthanide complexes · Synthesis · Luminescent properties

Introduction

Over the past decades, there has been much interesting in design and synthesis of lanthanide complexes due to their

unique photophysical properties (microsecond to millisecond lifetimes, characteristic and narrow emission bands, and large Stokes shifts) [1–7]. Trivalent lanthanide ions are fascinating in luminescence sources for their high color purity and relatively long lifetimes of the excited states arising from transitions within the partially filled 4*f* shell of the Ln(III) ions. Among the luminescent lanthanide complexes, Eu(III) and Tb(III) compounds show strong luminescence in the visible region, making them to be good candidates for fluoroimmunoassays and structural probes [1, 2, 8, 9].

The Laporte-forbidden *f-f* transitions have weak dipole strengths, and the excited states may be easily quenched by high-energy vibrations, particularly O-H oscillators from water molecules both in the inner and outer coordination spheres [10–12]. 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. Taking into account the strong coordination capability of multipodal ligands and the large coordination numbers (commonly 8–10) required for Ln(III) ions, it is therefore not surprising that this type ligands are preferred “antenna” for lanthanides [13–15]. This “antenna effect” involves energy transfer from excited π molecular orbital of conjugated ligands to Ln(III) ions. Furthermore, the complexation with a ligand provides lanthanides with a certain degree of protection from the surrounding water, hence increasing their luminescence quantum yields. Our group has been interested in employing self-assembly strategies for luminescent lanthanide complexes, and has recently used multipodal ligands as sensitizers for lanthanide luminescence. As a part of our systematic studies, two structurally related multipodal ligands, 1,3-bis{[(2'-(2-picolylaminoformyl))phenoxy]methyl}benzene (**L^I**) and 1,2-bis{[(2'-(2-picolylamino-

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Table 1 Analytical and molar conductance data for the complexes 1–6 (calculated values in parentheses)

Complexes	Analysis(%)			$A_m(\text{cm}^2 \cdot \Omega^{-1} \cdot \text{mol}^{-1})$
	C	H	N	
1	44.11(43.81)	3.96(3.68)	10.96(10.52)	86.1
2	43.87(43.56)	3.79(3.66)	10.82(10.46)	86.8
3	44.13(43.48)	3.52(3.65)	10.95(10.44)	92.1
4	44.21(43.81)	3.56(3.68)	10.64(10.52)	85.3
5	44.01(43.56)	3.54(3.66)	10.58(10.46)	90.6
6	43.94(43.48)	3.51(3.65)	10.54(10.44)	86.9

formyl)phenoxy]methyl}benzene (\mathbf{L}^{II}), have been designed and prepared successfully. A series of lanthanide coordination compounds have been obtained, generally formulated as $[\text{LnL}^{\text{I}}(\text{NO}_3)_2](\text{NO}_3) \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}(\mathbf{1})$, $\text{Gd}(\mathbf{2})$, $\text{Tb}(\mathbf{3})$) and $[\text{LnL}^{\text{II}}(\text{NO}_3)_2](\text{NO}_3) \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}(\mathbf{4})$, $\text{Gd}(\mathbf{5})$, $\text{Tb}(\mathbf{6})$). Under the excitation of UV light, Eu and Tb complexes exhibit characteristic emission of corresponding lanthanide ions. The lowest triplet state energy levels of the ligands were calculated from the phosphorescence spectra of the Gd complexes at 77 K. The results indicate that the triplet state energy levels of the ligands both match better to the resonance level of Tb(III) than Eu(III), and the structure of the ligands affects the luminescence characteristics of the complexes.

Experimental section

Materials and methods

o-Xylylene dibromide and *m*-xylylene dibromide were obtained from Alfa Aesar Co. The other commercially available chemicals were of A.R. grade and were used without further purification. Carbon, nitrogen and hydrogen were determined on an Elementar Vario EL (see Table 1). The FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument using KBr discs in the 4,000–400 cm^{-1} region (see Table 2). Conductivity measurements were carried

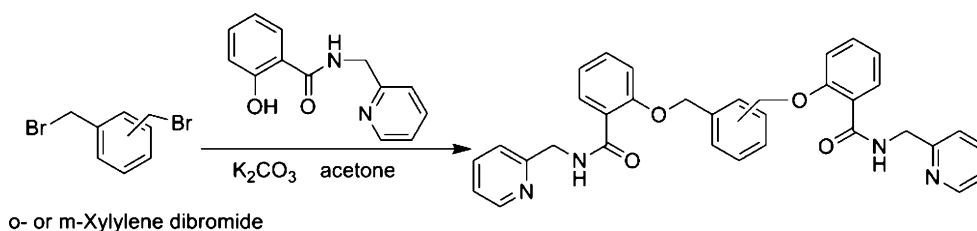
out with a DDSJ-308 type conductivity bridge using $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ solutions in methanol at 25 °C. ^1H NMR spectra were measured on a Varian Mercury-300 M spectrometer in *d*-chloroform solutions, with TMS as internal standard. Luminescence spectra and phosphorescence spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer. The quantum yield of the terbium samples were determined by an absolute method using an integrating sphere (150 mm diameter, BaSO_4 coating) from Edinburgh Instruments FLS920. The lifetime measurements were measured on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with Nd pumped OPOlette laser as the excitation source.

Synthesis of the ligands \mathbf{L}^{I} , \mathbf{L}^{II}

The synthetic route for the ligands (\mathbf{L}^{I} , \mathbf{L}^{II}) is shown in Scheme 1. Picolylsalicylamide was prepared according to the literature methods [16]. Picolylsalicylamide (2 mmol) and potassium carbonate (2 mmol) were refluxed in acetone (25 cm^3) for 30 min, then the *o*-Xylylene dibromide or *m*-xylylene dibromide (1 mmol) was added to the solution. The reaction mixture was refluxed for 12 h. After cooling down, the mixture was filtered and evaporated under reduce pressure to give the crude product, which was purified by column chromatography (petroleum ether / ethyl acetate, 2:1) on silica gel. \mathbf{L}^{I} , yield 89%, m. p. 112–113 °C. Anal. Calcd for

Table 2 The most important IR bands for the ligands (\mathbf{L}^{I} , \mathbf{L}^{II}) and the complexes 1–6 (cm^{-1})

Compounds	$\nu(\text{C}=\text{O})$	$\nu(\text{Ar-O-C})$	$\nu(\text{NO}_3^-)$							
			ν_1	ν_4	ν_2	ν_3	$\nu_{1-\nu_4}$	ν_0	ν_6	ν_5
\mathbf{L}^{I}	1,645	1,116								
1	1,611	1,112	1,489	1,315	1,029	815	174	1,384	843	757
2	1,612	1,112	1,491	1,315	1,029	815	176	1,384	844	757
3	1,613	1,112	1,491	1,315	1,029	815	176	1,384	840	757
\mathbf{L}^{II}	1,642	1,103								
4	1,609	1,109	1,479	1,296	1,031	816	183	1,384	840	757
5	1,609	1,109	1,480	1,297	1,031	816	183	1,384	840	757
6	1,609	1,109	1,479	1,297	1,031	816	182	1,384	840	757



Scheme 1 The synthetic route for the ligands ($L^I = 1,3\text{-bis}\{[(2'\text{-}(2\text{-picolylaminoformyl))\text{phenoxy}]\text{methyl}\}\text{benzene}$, $L^{II} = 1,2\text{-bis}\{[(2'\text{-}(2\text{-picolylaminoformyl))\text{phenoxy}]\text{methyl}\}\text{benzene}$)

$C_{34}H_{30}N_4O_4$: C, 73.16; H, 5.42; N, 10.04; Found: C, 73.59; H, 5.18; N, 9.97%. 1H NMR ($CDCl_3$, 300 MHz): 4.73(d, 4H), 5.17(s, 4H), 6.97(d, 2H), 7.03–7.12(m, 4H), 7.23–7.58(m, 10H), 8.24(dd, 2H), 8.30(d, 2H), 8.85(s, 2H) ppm.

L^{II} , yield 65%, m. p. 129–130 °C. Anal. Calcd for $C_{34}H_{30}N_4O_4$: C, 73.16; H, 5.42; N, 10.04; Found: C, 73.23; H, 5.33; N, 10.00%. 1H NMR ($CDCl_3$, 300 MHz): 4.66(d, 4H), 5.32(s, 4H), 6.93(d, 2H), 6.99–7.09(m, 4H), 7.17(d, 2H), 7.29–7.35(m, 4H), 7.44–7.55(m, 4H), 8.16–8.21(m, 4H), 8.71(s, 2H) ppm.

Preparation of the lanthanide complexes

0.1 mmol lanthanide nitrates was dissolved in 5 cm^3 of ethyl acetate, then the solution of 0.1 mmol ligand in 5 cm^3 of ethyl acetate was added dropwise. The mixture was stirred at room temperature for 6 h. And then the precipitated solid complex was filtered, washed with ethyl acetate, dried in vacuum over P_4O_{10} for 48 h and submitted for elemental analysis, yield 70–85%.

Result and discussion

Analytical data for the complexes, listed in Table 1, indicate that the complexes all conform to a 1:1 metal-to-ligand stoichiometry, $[LnL(NO_3)_3] \cdot 2H_2O$ ($Ln = Eu, Gd, Tb$; $L = L^I, L^{II}$). All complexes are soluble in DMF, DMSO, methanol, ethanol, acetonitrile and acetone, but slightly soluble in THF and ethyl acetate. Conductivity measurements for these complexes in methanol solution indicate that all complexes act as a 1:1 type electrolyte [17], implying that two nitrate groups are in coordination sphere. So the formula of these complexes could be indicated as $[EuL^I(NO_3)_2](NO_3) \cdot 2H_2O$ (1), $[GdL^I(NO_3)_2](NO_3) \cdot 2H_2O$ (2), $[TbL^I(NO_3)_2](NO_3) \cdot 2H_2O$ (3) ($L^I = 1,3\text{-bis}\{[(2'\text{-}(2\text{-picolylaminoformyl))\text{phenoxy}]\text{methyl}\}\text{benzene}$), and $[EuL^{II}(NO_3)_2](NO_3) \cdot 2H_2O$ (4), $[GdL^{II}(NO_3)_2](NO_3) \cdot 2H_2O$ (5) and $[TbL^{II}(NO_3)_2](NO_3) \cdot 2H_2O$ (6) ($L^{II} = 1,2\text{-bis}\{[(2'\text{-}(2\text{-picolylaminoformyl))\text{phenoxy}]\text{methyl}\}\text{benzene}$).

The main infrared bands of the ligands and their complexes are presented in Table 2. The IR spectra of the ligands L^I and L^{II} are shown in Fig. 1. The complexes

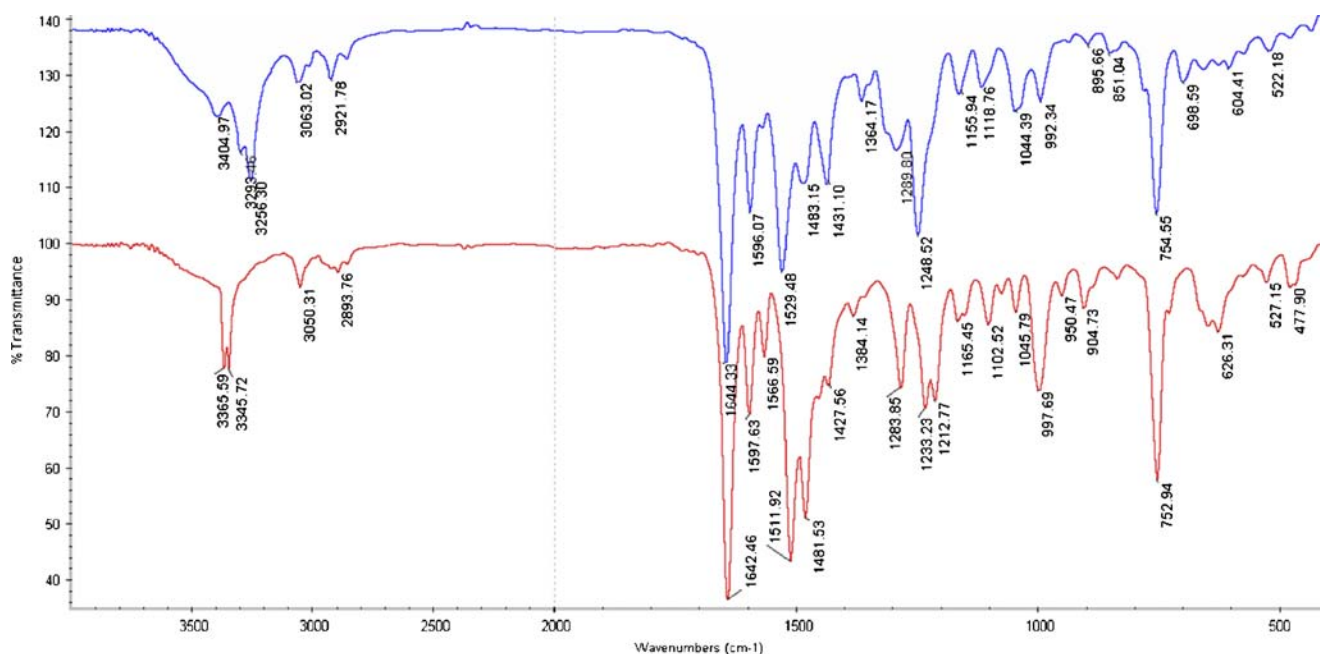


Fig. 1 The IR spectra of the ligands L^I (blue) and L^{II} (red)

possessing the same ligand have the similar IR spectra, of which the characteristic bands have similar shifts, suggesting that they have a similar coordination structure.

The characteristic bands of the $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{O}-\text{C})$ of free ligand **L**^I and **L**^{II} are shown at 1,645 cm^{-1} , 1,116 cm^{-1} , and 1,642 cm^{-1} , 1,103 cm^{-1} respectively. In the IR spectra of the complexes, the low-energy bands remain unchanged, but the high-energy bands of complexes **1–3** red shift to about 1,612 cm^{-1} ($\Delta\nu=33 \text{ cm}^{-1}$) and complexes **4–6** red shift to about 1,609 cm^{-1} ($\Delta\nu=33 \text{ cm}^{-1}$) as compared to the free ligand **L**^I and **L**^{II} respectively, thus indicating that only the oxygen atoms of $\text{C}=\text{O}$ take part in coordination to the lanthanide ions.

The absorption bands of complexes **1–3** assigned to the coordinated nitrate groups (C_{2v}) are observed at about 1,490 cm^{-1} (ν_1), 1,315 cm^{-1} (ν_4), 1,029 cm^{-1} (ν_2) and 815 cm^{-1} (ν_3) [18]. The separation of two strongest frequency bands $|\nu_1-\nu_4|$ lies about 175 cm^{-1} , clearly establishing that the NO_3^- groups in the solid complexes coordinate to the lanthanide ions as bidentate ligands [19]. In addition, three absorptions at 1,384 cm^{-1} , 840 cm^{-1} and 757 cm^{-1} can be seen clearly in the spectra of complexes

1–6, which indicate that free nitrate groups (D_{3h}) are present, in agreement with the results of the conductivity experiments. Furthermore, both elemental analysis and IR data are measured in solid state. In IR spectra, broad bands at about 3,370 cm^{-1} are ascribed to the vibration of the water molecules [19], thus we may deduced that the complexes contain water molecules, which is in agreement with the results of the elemental analysis.

To examine the ability of the ligands to be antenna groups for sensitized luminescence from lanthanides, we measured the luminescent properties of the Eu^{3+} , Tb^{3+} complexes with these two ligands. The luminescence spectra of the two ligands and their complexes in solid state (the excitation and emission slit widths were 1.0 nm) and $[\text{TbL}(\text{NO}_3)_2(\text{NO}_3)\cdot 2\text{H}_2\text{O}]$ ($\text{L} = \text{L}^{\text{I}}, \text{L}^{\text{II}}$) in acetonitrile, acetone, methanol, ethanol and DMF solutions (concentration: $1.0 \times 10^{-3} \text{ mol L}^{-1}$, the excitation and emission slit widths were 2.5 nm) were recorded at room temperature.

Excited by the absorption band at 327 nm and 325 nm, the “free” ligands **L**^I and **L**^{II} exhibit broad emission bands ($\lambda_{\text{max}}=445 \text{ nm}$, $\lambda_{\text{max}} = 447 \text{ nm}$) in solid state respectively. It can be seen from Fig. 2 that these four complexes **1, 3, 4,**

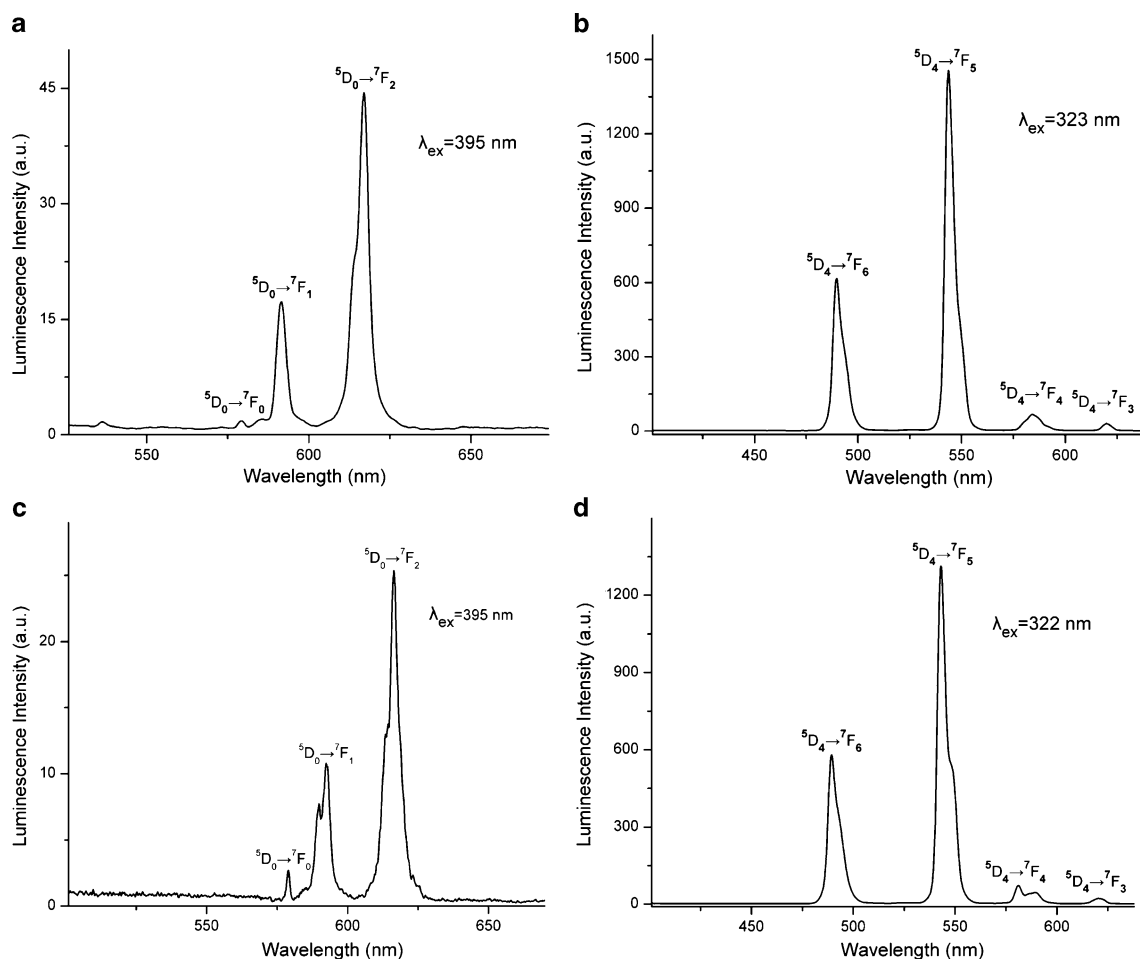


Fig. 2 Emission spectra of the complex **1 a, 3 b, 4 c, 6 d** in solid state

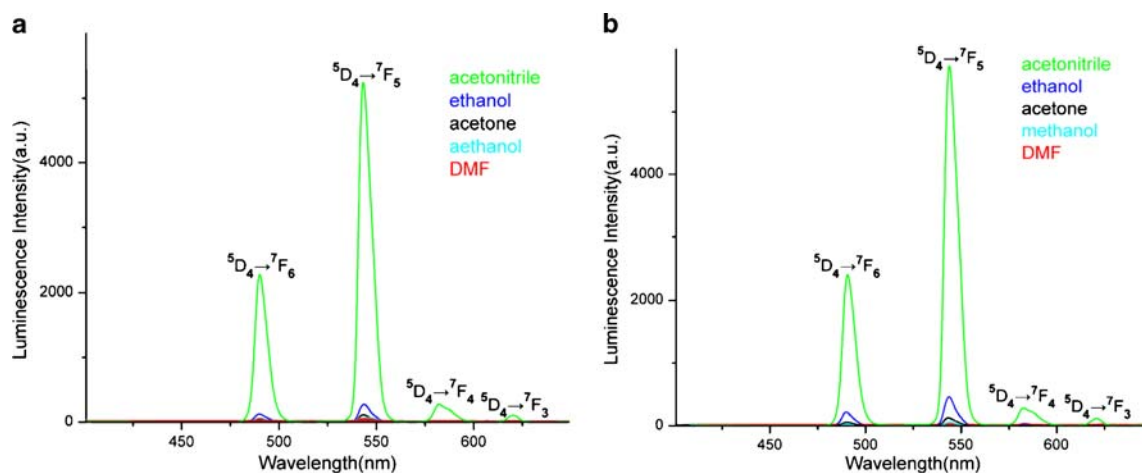


Fig. 3 Emission spectra of the complex **3 a**, **6 b** in different solutions at room temperature

and **6** show the characteristic emissions of Eu^{3+} and Tb^{3+} . This indicates that the two ligands are good organic chelators to absorb and transfer energy to the lanthanide ions. Notably, in the spectra of Eu^{3+} complexes, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is much more intense than the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition, showing that the $\text{Eu}(\text{III})$ ion is not in a centrosymmetric coordination site [20]. Intramolecular energy transfer from the triplet state of the ligand to the resonance level of the $\text{Ln}(\text{III})$ ion is one of the most important processes influencing the luminescence quantum yields of $\text{Ln}(\text{III})$ complexes [21]. The energy difference between the triplet state energy level of the ligand and the lowest excited state level of $\text{Ln}(\text{III})$ cannot be too large or too small. So considering the emission spectra of these four complexes **1**, **3**, **4**, and **6**, it can be concluded that the triplet energy of ligand L^{I} and L^{II} are in an appropriate level to Tb^{3+} in the complexes, which make the energy transition from the ligands to $\text{Ln}(\text{III})$ more easily in these two Tb^{3+} complexes. In order to acquire the triplet excited states T_1 of the ligands, the phosphorescence spectra of the $\text{Gd}(\text{III})$ complexes were measured at 77 K in a methanol-ethanol mixture ($V:V=1:1$). The triplet state energy levels T_1 of the ligands L^{I} and L^{II} in the complexes, which were calculated from the shortest wavelength phosphorescence band [22] of the Gd complexes, are 24,667 and 24,814 cm^{-1} , respectively. These energy levels are above the lowest excited resonance level ${}^5\text{D}_0$ of $\text{Eu}(\text{III})$ (17,286 cm^{-1}) and ${}^5\text{D}_4$ (20,545 cm^{-1}) of $\text{Tb}(\text{III})$. Thus the absorbed energy could be transferred from ligands to the Eu or Tb ions. And this result also indicates that the triplet state energy levels T_1 of the ligands L^{I} and L^{II} match better to the lowest resonance level of $\text{Tb}(\text{III})$ ($\Delta\nu=4,122$, 4,269 cm^{-1}) than to $\text{Eu}(\text{III})$ ($\Delta\nu=7,381$, 7,528 cm^{-1}) ion. The larger energy gap between the ligands triplet and the europium ion excited states led to observation of stronger sensitization of terbium complexes than the europium complexes.

The fluorescence quantum yield Φ of the complex **6** in solid state was found to be $41.1 \pm 0.1\%$ using an integrating sphere, which is two times more than the complex **3** ($15.8 \pm 0.1\%$). The luminescence decay of the complexes **3** and **6** are best described by single exponential processes with significantly longer lifetimes of $\tau=1.215 \pm 0.001$ ms and $\tau=1.372 \pm 0.001$ ms, indicating the presence of one distinct emitting species, respectively. We deduced that the electrostatic factors in the ligand-metal bonding, which may be affected by the different position of the substituents in the ligands, influenced the triplet state energy level of the ligands and made the fluorescence quantum yield of the L^{II} complex higher.

We can also see from Fig. 3 that in the five solvents, the two complexes **3** and **6** have the strongest luminescence in acetonitrile solutions, and the luminescence intensities become weaker from ethanol, acetone, methanol and DMF solution similarly. This is due to the coordinating effects of solvents, namely solvate effect [23]. Together with the raising coordination abilities of acetonitrile, ethanol, acetone, methanol, and DMF for the lanthanide ions, the energy transfer from the triplet excited states of the ligands L^{I} and L^{II} to the emitting level of the Tb^{3+} could not be carried out perfectly because the oscillatory motions of the entering molecules may consume more energy. Otherwise, we deduced that the acetonitrile molecules coordinated to the lanthanide ions can also absorb and transfer the energy to the central ions.

Conclusions

In summary, a series of lanthanide complexes carrying two novel structurally related multipodal ligands, 1,3-bis{[(2'-(2-picolylaminoformyl))phenoxy]methyl}benzene (L^{I}) and 1,2-bis{[(2'-(2-picolylaminoformyl))phenoxy]methyl}benzene (L^{II}) as antenna have been synthesized and

characterized. When the ligands (L^I and L^{II}) 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 ligands. Comparing the luminescence spectra of the europium(III) and terbium(III) complexes, we found that these novel multipodal ligands in Tb complexes are more effective in energy-transfer than in Eu complexes. The lowest triplet state energy levels of the ligands L^I and L^{II} indicate that the triplet state energy levels of the ligands match better to the resonance level of Tb^{3+} than Eu^{3+} . Under the same condition, the complex **6** give longer lifetimes and higher quantum efficiencies than complex **3**. So we may deduce that the position of the substituents of the ligands 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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References

1. Yam VWW, Lo KKW (1998) Recent advances in utilization of transition metal complexes and lanthanides as diagnostic tools. *Coord Chem Rev* 184:157–240
2. Parker D, Dickins RS, Puschnann H, Crossland C, Howard JAK (2002) Being excited by lanthanide coordination complexes: aqua species, chirality, excited-state chemistry, and exchange dynamics. *Chem Rev* 102:1977–2010
3. Faulkner S, Pope SJA (2003) Lanthanide-sensitized lanthanide luminescence: terbium-sensitized ytterbium luminescence in a trinuclear complex. *J Am Chem Soc* 125:10526–10527
4. Xu G, Wang ZM, He Z, Lü Z, Liao CS, Yan CH (2002) Synthesis and structural characterization of nonanuclear lanthanide complexes. *Inorg Chem* 41:6802–6807
5. Rajapakse HE, Reddy DR, Mohandessi S, Butlin NG, Miller LW (2009) Luminescent terbium protein labels for time-resolved microscopy and screening. *Angew Chem Int Ed* 48:4990–4992
6. Montgomery CP, Murray BS, New EJ, Pal R, Parker D (2009) Cell-penetrating metal complex optical probes: targeted and responsive systems based on lanthanide luminescence. *Acc Chem Res* 42:925–937
7. Mooer EG, Samuel APS, Raymond KN (2009) From antenna to assay: lessons learned in lanthanide luminescence. *Acc Chem Res* 42:542–552
8. Montalti M, Prodi L, Zaccaroni N, Charbonnière L, Douce L, Ziessel R (2001) A luminescent anion sensor based on a europium hybrid complex. *J Am Chem Soc* 123:12694–12695
9. Bünzli JCG, Piguet C (2002) Lanthanide-containing molecular and supramolecular polymetallic functional assemblies. *Chem Rev* 102:1897–1928
10. Beeby A, Clarkson IM, Dickins RS, Faulkner S, Parker D, Royle L, de Sousa AS, Williams JAG, Woods MJ (1999) Non-radiative deactivation of the excited states of europium, terbium and ytterbium complexes by proximate energy-matched OH, NH and CH oscillators: an improved luminescence method for establishing solution hydration states. *J Chem Soc Perkin Trans* 23:493–503
11. Maas H, Currao A, Calzaferri G (2002) Encapsulated lanthanides as luminescent materials. *Angew Chem Int Ed* 41:2495–2497
12. Binnemans K (2009) Lanthanide-based luminescent hybrid materials. *Chem Rev*. In press: doi: 10.1021/cr8003983.
13. Renaud F, Piguet C, Bernardinelli G, Bünzli J-CG, Hopfgartner G (1999) Nine-coordinate lanthanide podates with predetermined structural and electronic properties: facial organization of unsymmetrical tridentate binding units by a protonated covalent tripod. *J Am Chem Soc* 121:9326–9342
14. Gade LH (2002) Tripodal amido complexes: molecular “claws” in main group and transition metal chemistry. *Acc Chem Res* 35:575–582
15. Hamann CS, Zelewsky AV, Barbieri A, Barigelletti F, Muller G, Riehl JP, Neels A (2004) Diastereoselective formation of chiral tris-cyclometalated iridium (III) complexes: characterization and photophysical properties. *J Am Chem Soc* 126:9339–9348
16. Michio K (1976) The dual fluorescence nature of some n-monosubstituted salicylamides. *Bull Chem Soc Jpn* 49:2679–2682
17. Geary WJ (1971) The use of conductivity measurements in organic solvents for the characterization of coordination compounds. *Coord Chem Rev* 7:81–122
18. Carnall W, Siegel S, Ferrano J, Tani B, Gebert E (1973) New series of anhydrous double nitrate salts of the lanthanides. Structural and spectral characterization. *Inorg Chem* 12:560–564
19. Nakamoto K (1978) Infrared and raman spectra of inorganic and coordination compounds, 4th edn. Wiley, New York
20. Liu WS, Tan MY, Wang X, Zhang SY (1990) Study on the ternary coordination of compounds of lanthanide elements with 1, 10-phenanthroline-N-oxide and acetylacetonate. *Acta Chim Sin* 48:1090–1095
21. Latva M, Takalo H, Mikkala VM, Marachescu C, Rodriguez-Ubis JC, Kankare J (1997) Correlation between the lowest triplet state energy level of the ligand and lanthanide(III) luminescence quantum yield. *J Lumin* 75:149–169
22. 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. *J Chem Soc Dalton Trans* 9:1334–1347
23. Liu HQ, Cheung TC, Che CM (1996) Cyclometallated platinum (II) complexes as luminescent switches for calf-thymus DNA. *Chem Commun* 9:1039–1040