LUMINESCENCE
The Journal of Biological and Chemical Luminescence

Received: 29 June 2009, Revised: 26 January 2010, Accepted: 12 March 2010,

(wileyonlinelibrary.com) DOI 10.1002/bio.1215

Synthesis, characterization and luminescent properties of lanthanide complexes with an unsymmetrical tripodal ligand

Zhen-Zhong Yan,* Guo-Liang Dai, Hua-Ding Liang and Yong-Qiang Lin

ABSTRACT: Solid complexes of lanthanide nitrates with an novel unsymmetrical tripodal ligand, butyl-*N*,*N*-bis[((2′-benzylaminofomyl)phenoxyl)ethyl]-amine (L) have been synthesized and characterized by elemental analysis, infrared spectra and molar conductivity measurements. At the same time, the luminescent properties of the Sm(III), Eu(III), Tb(III) and Dy(III) nitrate complexes in solid state were also investigated. Under the excitation of UV light, these complexes exhibited characteristic emission of central metal ions. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: lanthanide nitrate complexes; unsymmetrical tripodal ligand; luminescent properties

Introduction

There has been much interest in luminescent lanthanide complexes because of their attractive emission properties such as long lifetime, large Stokes shift, and line-like emission (1–4). These complexes can be used as analytical tools ranging from luminescent probes in time-resolved measurements (5–11) to luminescent chemosensors for detection of gases, ions and molecules in solution (12–17). Lanthanide ions are photophysically inert because direct photoexcitation is difficult due to the *f–f* transition (18). For effective excitation of lanthanide ions, an organic chromophore, a so-called 'antenna', is usually attached to lanthanide complexes. In order to obtain strongly luminescent complexes, the chromophoric ligands, which chelate to lanthanide ions, should be able to encapsulate and protect the lanthanide ion from the solvent molecules and to absorb energy and transfer it efficiently to the central metal. More and more chemists are attracted to designing the organized molecular architectures containing trivalent lanthanide ions (Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}), working as efficient light conversion devices (3,19).

Tripodal ligands have drawn much attention in recent years, mainly due to the employment of self-assembly strategies for lanthanide complexes. Zhang and co-workers have used tripodal ligands as sensitizers for lanthanide luminescence (20). Tripodal ligands have the advantages of selective coordinating capacity and hard binding sites, thereby stabilizing their complexes, acquiring novel coordination structure and shielding the encapsulated ion from interaction with the surroundings (21). Most of these ligands are symmetrical with three identical arms while the unsymmetrical tripodal organic ligands are rare (22).

In our research, we designed and prepared a new conformationally flexible unsymmetrical butyl- and (2′-benzylaminoformyl)phenoxyl-containing amide type tripodal ligand butyl-*N*,*N*-bis[(2′-benzylaminofomyl)phenoxyl)ethyl]-amine (**L**) (Scheme 1) and studied the luminescent properties of samarium, europium, terbium and dysprosium complexes with this ligand. Under the excitation of UV light, Sm, Eu, Tb and Dy complexes exhibited characteristic emission of corresponding lanthanide ions. The lowest triplet state energy level of the ligand was calculated from the phosphorescence spectrum of the Gd complex at 77 K. The results indicate that the triplet state energy level of the ligand matches better the resonance level of Tb (III) than other lanthanide ions.

Experimental

Materials

N-benzylsalicylamide (23), *β*,*β*′-dichlordiethylamine hydrochloride salt (24) and lanthanide nitrates (25) were prepared according to the literature methods. Other chemicals were obtained from commercial sources and used without further purification.

Methods

The Ln(III) ion was determined by EDTA titration using xylenol-orange as an indicator. Carbon, nitrogen and hydrogen were determined using an Elementar Vario EL. Conductivity measurements were carried out with a DDS-307 type conductivity bridge using 1.0×10^{-3} mol cm^{-3} solutions at 25°C. The IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets and a Nicolet Nexus 670 FTIR spectrometer. ^1H NMR spectra were measured on a Varian Mercury 200 spectrometer in D-chloroform solutions, with TMS as internal standard. Luminescence and phosphorescence spectra were obtained on a Hitachi F-4500 spectrophotometer.

---

* Correspondence to: Zhen-Zhong Yan, Department of Pharmaceutics and Chemical Engineering, Taizhou University, Linhai 317000, People's Republic of China. E-mail: yanzhzh@tzc.edu.cn

Department of Pharmaceutics and Chemical Engineering, Taizhou University, Linhai 317000, People's Republic of China

Preparation of the Unsymmetrical Tripodal Ligand L

The synthetic route for the unsymmetrical tripodal ligand **L** is shown in Scheme 1. The *β*, *β*′-dichlordiethylamine hydrochloride salt (1 mmol) and potassium carbonate (2 mmol) were refluxed in acetone (25 cm^3) for 30 min, then the 1-bromobutane (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 (2.0 mmol), potassium carbonate (4 mmol) and DMF (20 cm^3), which was warmed to *ca* 95°C. The reaction mixture was stirred at 98–100°C for 8 h. After cooling down, the mixture was poured into water (100 cm^3). The resulting solid was treated with column chromatography on silica gel (petroleum ether : ethyl acetate, 2:1) to get the ligand **L**, yield 70%, m.p. 102–104°C; ^1H NMR ($CDCl_3$, 300 MHz): 0.88–0.94 (t, 3H), 1.64–1.75 (q, 2H), 1.82–1.96 (q, 2H), 2.26–2.38 (q, 2H), 2.60–2.69 (t, 4H), 3.87–3.93 (t, 4H), 4.57–4.61 (d, 4H), 6.67–7.49 (m, 18H), 8.20–8.26 (t, 2H); anal. calcd for $C_{36}H_{41}O_4N_3$: C, 74.58%; H, 7.13%; N, 7.25%. Found: C, 74.42%; H, 7.46%; N, 7.52%.

Preparation of the complexes

An ethyl acetate solution (5 cm^3) of $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Sm, Eu, Gd, Tb, Dy) (0.1 mmol) was added dropwise to a solution of 0.1 mmol ligand **L** in 5 cm^3 of ethyl acetate. The mixture was stirred at room temperature for 8 h. Then the precipitated solid complex was filtered, washed with ethyl acetate, dried *in vacuo* over P_4O_{10} for 48 h and submitted for elemental analysis, yield 65%.

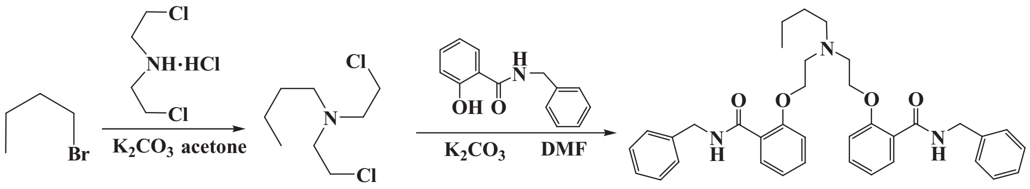
Results and discussion

Properties of the complexes

Analytical data for the newly synthesized complexes, listed in Table 1, indicate that the five nitrate complexes all conform to a 1:1 metal-to-ligand stoichiometry, $[Ln\mathbf{L}(NO_3)_3]{\cdot}H_2O$ (Ln = Sm, Eu, Gd, Tb, Dy). All the complexes are soluble in DMF and DMSO, slightly soluble in methanol, ethanol, acetone and acetonitrile, but sparingly soluble in chloroform, ethyl ether and ethyl acetate. The molar conductances of the complexes in acetone (see Table 1) indicate that all complexes act as noneletrolytes (26), implying that all nitrate groups are in coordination sphere.

IR Spectra

The most important IR peaks of the ligand **L** and the complexes are reported in Table 2. The complexes have similar IR spectra, of which the characteristic bands have similar shifts (see Table 2), suggesting they have a similar coordination structure.



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

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

Complexes	Analysis (%)				Λ_m ($cm^2\ \Omega^{-1}\ mol^{-1}$)
	C	H	N	Ln	
$[Sm\mathbf{L}(NO_3)_3]{\cdot}H_2O$	46.36(46.29)	4.81(4.64)	9.05(9.00)	15.87(16.10)	8.4
$[Eu\mathbf{L}(NO_3)_3]{\cdot}H_2O$	46.02(46.21)	4.78(4.63)	8.92(8.98)	16.44(16.24)	7.8
$[Gd\mathbf{L}(NO_3)_3]{\cdot}H_2O$	45.64(45.95)	4.58(4.61)	9.06(8.93)	16.96(16.71)	7.6
$[Tb\mathbf{L}(NO_3)_3]{\cdot}H_2O$	45.97(45.87)	4.76(4.60)	8.96(8.91)	16.93(16.86)	7.0
$[Dy\mathbf{L}(NO_3)_3]{\cdot}H_2O$	45.72(45.69)	4.76(4.58)	8.68(8.88)	16.98(17.17)	6.8

Table 2. The most important IR spectral data of the ligand **L** and complexes (cm^{-1})

Compounds	ν(C=O)	ν(C–O–C)	$\nu(NO_3^-)$				
			ν_1	ν_4	ν_2	ν_3	$\nu_1-\nu_4$
L	1638	1106					
$[Sm_2\mathbf{L}_3(NO_3)_6]{\cdot}H_2O$	1607	1113	1486	1301	1045	814	185
$[Eu_2\mathbf{L}_3(NO_3)_6]{\cdot}H_2O$	1608	1113	1483	1302	1046	815	181
$[Gd_2\mathbf{L}_3(NO_3)_6]{\cdot}H_2O$	1610	1111	1482	1298	1044	813	184
$[Tb_2\mathbf{L}_3(NO_3)_6]{\cdot}H_2O$	1609	1112	1483	1299	1043	814	184
$[Dy_2\mathbf{L}_3(NO_3)_6]{\cdot}H_2O$	1610	1110	1484	1302	1042	812	182

The IR spectrum of the free ligand **L** shows bands at 1638 and 1106 cm^{-1}, which are attributable to the stretch vibration of the carbonyl group [ν(C=O)] of the amide group and ν(C–O–C), respectively. In the complexes, the low-energy band remains unchanged, but the high-energy band red shifts to about 1610 cm^{-1} ($\Delta\nu = 28$ cm^{-1}) as compared with its counterpart for the 'free' ligand, thus indicating that only the oxygen atom of C=O takes part in coordination to the lanthanide ions.

Table 3. Luminescence data for the ligand and complexes in solid state at room temperature

Compounds	λ_{ex} (nm)	λ_{em} (nm)	RI[a]	Assignment
L	332	466	2218	
[Sm(NO$_3$)$_3$**L**]·H$_2$O	314	561	66	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
		595	82	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
[Eu(NO$_3$)$_3$**L**]·H$_2$O	397	592	140	$^5D_0 \rightarrow {}^7F_1$
		617	368	$^5D_0 \rightarrow {}^7F_2$
[Tb(NO$_3$)$_3$**L**]·H$_2$O	312	490	4355	$^5D_4 \rightarrow {}^7F_6$
		545	8678	$^5D_4 \rightarrow {}^7F_5$
		582	450	$^5D_4 \rightarrow {}^7F_4$
[Dy(NO$_3$)$_3$**L**]·H$_2$O	308	482	289	$^4F_{9/2} \rightarrow {}^6H_{5/2}$
		574	276	$^4F_{9/2} \rightarrow {}^6H1_{3/2}$

[a] RI, relative intensity.

The characteristic frequencies of the coordinating nitrate groups (C$_{2v}$) appear at *ca* 1484 cm^{-1} (ν_1), 1300 cm^{-1} (ν_4), 1045 cm^{-1} (ν_2) and 812 cm^{-1} (ν_3), and the difference between two strongest absorptions (ν_1 and ν_4) of the nitrate groups is about 180 cm^{-1}, clearly establishing that the NO$_3^-$ groups in the solid complexes coordinate to the lanthanide ion as bidentate ligands (27,28). Additionally, the absence bands at 1380, 820 and 720 cm^{-1} in the spectra of complexes indicates that free nitrate groups (D$_{3h}$) are absent, in agreement with the results of the conductivity experiments. In addition, broad bands at *ca* 3400 cm^{-1} indicate that water molecules are existent in the complexes, confirming the elemental results (29).

Luminescent properties of the complexes

Excited by the absorption band at 332 nm, the 'free' unsymmetrical tripodal ligand exhibits broad emission bands ($\lambda_{max} = 466$ nm) in solid state (the excitation and emission slit widths were 1.0 and

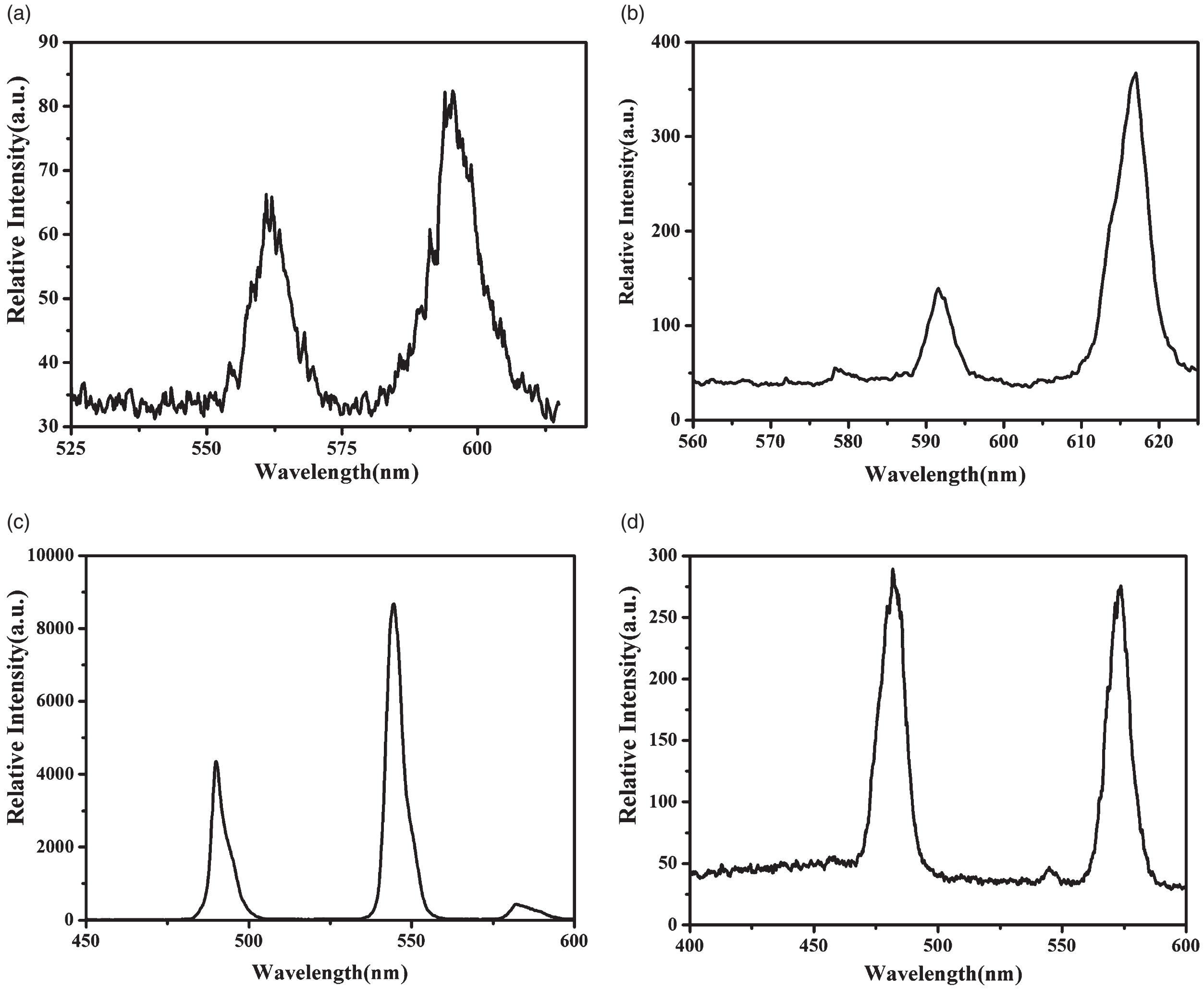


Figure 1. Emission spectra of the complexes [Ln**L**(NO$_3$)$_3$]·H$_2$O in solid state at room temperature: (a) [Sm**L**(NO$_3$)$_3$]·H$_2$O; (b)[Eu**L**(NO$_3$)$_3$]·H$_2$O; (c) [Tb**L**(NO$_3$)$_3$]·H$_2$O; (d) [Dy**L**(NO$_3$)$_3$]·H$_2$O.

2.5 nm, respectively). The luminescence emission spectra of $[Ln\mathbf{L}(NO_3)_3]\cdot H_2O$ (Ln = Sm, Eu, Tb, Dy) in solid state (the excitation and emission slit widths were 1.0 and 2.5 nm, Table 3, Fig. 1a–d) were recorded at room temperature. The efficient energy transfer from ligand to center ions (antenna effect) is one of key factors to achieve lanthanide characteristic luminescence (30,31). It is shown in Fig. 1 that these four complexes all show the characteristic emissions of Sm^{3+}, Eu^{3+}, Tb^{3+} or Dy^{3+}. This indicates that the ligand **L** is a good organic chelator to absorb and transfer energy to lanthanide ions. The ligand has multiple aromatic rings with a semirigid skeleton structure, so it is a strong luminescence substance (32). In the spectrum of Eu complex, the relative intensity of $^5D_0 \rightarrow {}^7F_2$ is more intense than that of $^5D_0 \rightarrow {}^7F_1$; the most intensity ratio value $\eta(^5D_0 \rightarrow {}^7F_2/^5D_0 \rightarrow {}^7F_1)$ is 2.63, showing that the Eu (β) ion does not lie in a centro-symmetric coordination site (33).

A triplet excited state T_1 is localized on one ligand only and is independent of the lanthanide nature (34). In order to acquire the triplet excited state T_1 of the ligand **L**, the phosphorescence spectrum of the Gd(III) complex was measured at 77 K in a methanol–ethanol mixture (v : v, 1:1). The triplet state energy level T_1 of the ligand **L**, which was calculated from the shortest-wavelength phosphorescence band (35), was 23,923 cm^{-1}. This energy level is above the lowest excited resonance level $^4G_{5/2}$ of Sm(III) (17,924 cm^{-1}), $^5D_0$ of Eu(III) (17,286 cm^{-1}), $^5D_4$ of Tb(III) (20,545 cm^{-1}) and $^4F_{9/2}$ of Dy(III) (21,144 cm^{-1}). Thus, the absorbed energy could be transferred from ligand to the Sm, Eu, Tb or Dy ions. We can deduce that the triplet state energy level T_1 of this ligand **L** matches better the lowest resonance level of Tb(III) ($\Delta\nu = 3378\ cm^{-1}$) than Sm(III) ($\Delta\nu = 5999\ cm^{-1}$), Eu(III) ($\Delta\nu = 6637\ cm^{-1}$) and Dy(III) ($\Delta\nu = 2779\ cm^{-1}$) ions, because such large or small $\Delta\nu$ could result in the non-radiative deactivation of the lanthanide emitting state and quench the luminescence of the complexes (36).

Conclusion

According to the data and discussion above, the novel unsymmetrical tripodal ligand butyl-*N*,*N*-bis[(2′-benzylaminofomyl)phenoxyl)ethyl]-amine (**L**) can form stable solid complexes with lanthanide nitrates. 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**. The characterization of these complexes demonstrates 1:1 (M : **L**) type coordination stoichiometries. Thus, the lanthanide ion could be effectively encapsulated and protected by the coordinated ligands. The luminescent properties of the Sm, Eu, Tb and Dy complexes in solid state were investigated. Under UV light excitation, the complexes exhibited characteristic luminescence of samarium, europium, terbium and dysprosium ions. This indicates that the ligand **L** is a good organic chelator to absorb and transfer energy to lanthanide ions. The lowest triplet state energy level of the ligand indicates that the triplet state energy level (T_1) of the ligand matches better the resonance level of Tb(III) than other lanthanide ions.

References

1. Parker D, Dickins RS, Puschmann H, Crossland C, Howard JAK. Being Excited by Lanthanide Coordination Complexes: Aqua Species, Chirality, Excited-State Chemistry, and Exchange Dynamics. Chem Rev 2002;102:1977.
2. Parker D. Excitement in f Block : Structure, Dynamics and Function of Nine-Coordinate Chiral Lanthanide Complexes in Aqueous Media. Chem Soc Rev 2004;33:156.
3. Sabbatini N, Guardigli M, Lehn J-M. Luminescent Lanthanide Complexes as Photochemical Supramolecular Devices. Coord Chem Rev 1993;123:201.
4. Bünzli J-CG, Piguet C. Lanthanide-Containing Molecular and Supramolecular Polymetallic Functional Assemblies. Chem Rev 2002;102:1897.
5. Weibel N, Charbonnière LJ, Guardigli M, Roda A, Ziessel R. Engineering of Highly Luminescent Lanthanide Tags Suitable for Protein Labeling and Time-Resolved Luminescence Imaging. J Am Chem Soc 2004;126:4888.
6. Yuan J, Matsumoto K. A New Tetradentate ß-Diketonate-Europium Chelate That Can Be Covalently Bound to Proteins for Time-Resolved Fluoroimmunoassay. Anal Chem 1998;70:596.
7. Scorilas A, Bjartell A, Lilja H, Moller C, Diamandis EP. Streptavidin-Polyvinylamine Conjugates Labeled with a Europium Chelate: Applications in Immunoassay, Immunohistochemistry, and Microarrays. Clin Chem 2000;46(9):1450.
8. Saha AK, Kross K, Kloszewski ED, Upson DA, Toner JL, Snow RA, Black CDV, Desai VC. Time-resolved Fluorescence of a New Europium-Chelate Complex: Demonstration of Highly Sensitive Detection of Protein and DNA Samples. J Am Chem Soc 1993;115:11032.
9. Christopoulos TK, Diamandis EP. Enzymically Amplified Time-Resolved Fluorescence Immunoassay with Terbium Chelates. Anal Chem 1992;64:342.
10. Parker D. Coord. Luminescent Lanthanide Sensors for pH, pO_2 and Selected Anions. Chem Rev 2000;205:109.
11. Zhao XQ, Zhao B, Wei S, Cheng P. Synthesis, Structures, and Luminescent and Magnetic Properties of Ln-Ag Heterometal-Organic Frameworks. Inorg Chem 2000;48:11048.
12. Gunnlaugsson T, Leonard JP, Sénéchal K, Harte AJ. pH Responsive Eu(III)-Phenanthroline Supramolecular Conjugate: Novel "*Off-On-Off*" Luminescent Signaling in the Physiological pH Range. J Am Chem Soc 2003;125:12062.
13. Gunnlaugsson T, Mac Dónail DA, Parker D. Lanthanide Macrocyclic Quinolyl Conjugates as Luminescent Molecular-Level Devices. J Am Chem Soc 2001;123:12866.
14. Reany O, Gunnlaugsson T, Parker D. Selective Signalling of Zinc Ions by Modulation of Terbium Luminescence. Chem Commun 2000;473.
15. Charbonnière LJ, Ziessel R, Montalti M, Prodi L, Zaccheroni N, Boehme C, Wipff G. Luminescent Lanthanide Complexes of a Bis-bipyridine-phosphine-oxide Ligand as Tools for Anion Detection. J Am Chem Soc 2002;124:7779.
16. Hanaoka K, Kikuchi K, Kojima H, Urano Y, Nagano T. Development of a Zinc Ion-Selective Luminescent Lanthanide Chemosensor for Biological Applications. J Am Chem Soc 2004;126:12470.
17. Gunnlaugsson T, Leonard JP. Responsive Lanthanide Luminescent Cyclen Complexes: from Switching/Sensing to Supramolecular Architectures. Chem Commun 2005;3114.
18. Gschneidner KA, Eyring L. Handbook on the Physics and Chemistry of Rare Earths. Amsterdam: North-Holland, 1979.
19. Piguet C, Bünzli J-CG, Bernardinelli G, Hopfgartner G, Petoud S, Schaad O. Lanthanide Podates with Predetermined Structural and Photophysical Properties: Strongly Luminescent Self-Assembled Heterodinuclear d-f Complexes with a Segmental Ligand Containing Heterocyclic Imines and Carboxamide Binding Units. J Am Chem Soc 1996;118:6681.
20. Zhang J, Tang Y, Tang N, Tan MY, Liu WS, Yu KB. Novel Three-Dimensional Network Generated from The Reaction of $Eu(NO_3)_3$ with an Amide Type Tripodal Ligand. J Chem Soc Dalton Trans 2002;832.
21. Hamann CS, Zelewsky AV, Barbieri A, Barigelletti F, Muller G, Riehl JP, Neels A. Diastereoselective Formation of Chiral Tris-Cyclometalated Iridium (III) Complexes: Characterization and Photophysical Properties. J Am Chem Soc 2004;126:9339.
22. Blackman AG. The Coordination Chemistry of Tripodal Tetraamine Ligands. Polyhedron 2005;24:1.
23. Michio K. The Dual Fluorescence Nature of Some N-Monosubstituted Salicylamides. Bull Chem Soc Jpn 1976;49:2679.
24. Ward K Jr. The Chlorinated Ethylamines: a New Type of Vesicant. J Am Chem Soc 1935;57:914.
25. Nakagawa K, Amita K, Mizuno H, Inoue Y, Hakushi T. Preparation of Some Lanthanoid Picrates and the Behavior of Their Water of Hydration. Bull Chem Soc Jpn 1987;60:2037.

26. Geary WJ. The Use of Conductivity Measurements in Organic Solvents for The Characterisation of Coordination Compounds. Coord Chem Rev 1971;7:81.
27. Tian YC, Liang YQ, Ni JZ. Infrared and Raman Spectra of Rare Earth Picrate Hydrate. J Mol Sci (Int Ed) 1987;5(1):83.
28. Curtis NF, Curtis YM. Some Nitrato-Amine Nickel(II) Compounds with Monodentate and Bidentate Nitrate Ions. Inorg Chem 1964;4:804.
29. Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th edn. New York: Wiley, 1997.
30. Desa GF, Malta OL, De Mello Donega C, Simas AM, Longo RL, Santacruz PA, da Silva EF Jr. Spectroscopic Properties and Design of Highly Luminescent Lanthanide Coordination Complexes. Coord Chem Rev 2000;196:165.
31. Bazzicalupi C, Bencini A, Bianchi A, Ciorgi C, Fusi V, Masotti A, Valtancoli B, Roque A, Pina F. pH Modulation of The Luminescence Emission of a New Europium Cryptate Complex. Chem Commun 2000;7:561.
32. Setyawati IA, Liu S, Rettig SJ, Orvig C. Homotrinuclear Lanthanide (III) Arrays: Assembly of and Conversion from Mononuclear and Dinuclear Units. Inorg Chem 2000;39:496.
33. Zhou DJ, Huang CH, Xu GX. Synthesis, Characterization, Crystal Ctructure and Luminescent Property Studies on a Novel Heteronuclear Lanthanide Lomplex $\{H[EuLa_2(DPA)_5 \cdot 8H_2O] \cdot 8H_2O\}_n$ (H_2DPA = Pyridine-2,6-Dicarboxylic acid). Polyhedron 1994;13:987.
34. Latva M, Takalo H, Mukkala V-M, Marachescu C, Rodriguez-Ubis J-C, Kankare J. Correlation Between The Lowest Triplet State Energy Level of The Ligand and Lanthanide(III) Luminescence Quantum Yield . J Lumin 1997;75:149.
35. Dawson W, Kropp J, Windsor M. Transfer Efficiencies in Eu^{3+} and Tb^{3+} Chelates Using Excitation to Selected Ion Levels. J Chem Phys 1966;45:2410.
36. Gutierrez F, Tedeschi C, Maron L, Daudey J-P, Poteau R, Azema J, Tisnés P, Picard C. 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 2004;1334.