

Spectroscopic Study on the Photophysical Properties of Lanthanide Complexes with Long Chain Mono-Docosyl Phthalate

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Ortho phthalic anhydride was modified with long chain alcohol (1-docosanol) to its corresponding monodocosyl phthalate (22-Phth). Subsequently, three novel lanthanide (Eu^{3+} , Tb^{3+} , and Dy^{3+}) complexes with the long chain monodocosyl phthalate were synthesized and characterized by elemental analysis and Infrared spectra. The photophysical properties of these complexes were studied in detail with ultraviolet-visible absorption spectra, low temperature phosphorescence spectra and fluorescent spectra. The triplet state energy of 22-Phth was determined to be around $25,000 \text{ cm}^{-1}$ from the maximum phosphorescent peak at 400 nm, suggesting 22-Phth is suitable for the sensitization of the luminescence of Eu^{3+} , Tb^{3+} , and Dy^{3+} . The fluorescence excitation and emission spectra for these lanthanide complexes of the three ligands take agreement with the above predict from energy match principle.

KEY WORDS: Lanthanide complexes; long chain phthalate monoester; photophysical property; energy transfer; fluorescence.

INTRODUCTION

Lanthanide complexes have potential applications in the luminescent probes or labels for chemical or biological macromolecules [1,2] and the active center for luminescent materials [3,4] and electroluminescent devices [5,6] for their attractive photophysical properties. Various studies have been focused on the design and construction of lanthanide complexes with organic ligands such as aromatic carboxylic acids, β -diketone, cryptands, calixarenes, and heterocyclic ligands, etc. These organic molecules possess strong absorption of ultraviolet light and then occur an effective intramolecular energy transfer process to central lanthanide ions [7–10]. For binary complexes, it was found that most β -diketone derivatives are more suitable for luminescence of Eu^{3+} [11,12] while most aromatic carboxylic acids are more suitable

for the luminescence of Tb^{3+} [13,14]. We also have studied the energy match and intramolecular energy transfer mechanism in ternary lanthanide complexes with aromatic carboxylic acids and 1,10-phenanthroline in details [15,16], indicating that there still exist intramolecular energy transfer mechanism between ligands (i.e., from aromatic carboxylic acids and 1,10-phenanthroline). On the basis of energy match and energy transfer mechanism, it can be realized to predict the luminescent properties of lanthanide complexes. Phthalate or aminobenzoate derivative has been found to exhibit good property of luminescence and film formation [17]. Especially phthalic acid can be modified to obtain its mono ester derivative through esterifying reaction with long chain alcohol, in which the introduction of long chain for the mono ester can be achieved favorable film-formation and expected to fabricate LB films for the potential applications such as integrated and molecular electronics as well as biosensors [18].

In this context, using ortho phthalic anhydride as starting materials, a novel long chain alcohol (1-docosanol)

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was grafted to achieve its monodocosyl phthalate (22-Phth). The corresponding lanthanide (Eu^{3+} , Tb^{3+} , and Dy^{3+}) complexes with this long chain ester were synthesized and characterized. The photophysical properties for this long chain ester and its lanthanide complexes were studied and further expected to have practical application to fabricate the Langmuir–Blodgett films.

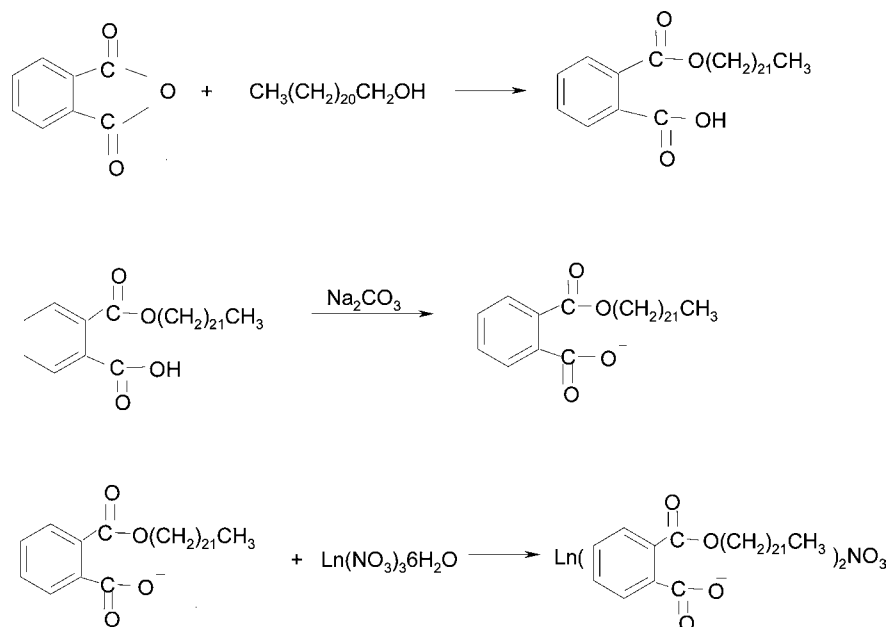
EXPERIMENTAL

Synthesis of Monodocosyl Phthalate by the Modification of *o*-Phthalic Anhydride

Ortho phthalic anhydride (2.96 g/mmol) was mixed with equimolar amount of 1-docosanol (6.53 g) in a flask. Then the solid mixtures were placed in oil bathing at the temperature 110–115°C and refluxed for 15 h. Finally the product was recrystallized with *n*-hexane for three times to afford the final ligands. Scheme 1 gives the reaction process. The composition of the aim product was confirmed by elemental analysis, I.R. and ^1H NMR spectroscopy: Calcd. for $\text{C}_{30}\text{H}_{49}\text{O}_4$ (mp: 78°C): C, 75.95; H, 10.55; Found: C 77.74; H, 10.18. I.R. (KBr) cm^{-1} 2851.89 (ν_{sCH_3}), 2923.24 (ν_{asCH_3}), 1749.19 ($\nu_{\text{C=O}}$), 1074.59 ($\nu_{\text{sc-o-c}}$), 1262.76 ($\nu_{\text{asc-o-c}}$). ^1H NMR δ 7.94 (1H), 7.76 (1H), 7.65 (2H), 4.30 (2H), 3.48 (2H), 2.16 (2H), 1.80 (2H), 1.22 (30H), 0.87 (3H), 11.40 (–COOH).

Synthesis of Lanthanide Complexes with Monodocosyl Phthalate

The lanthanide oxides (Eu_2O_3 , Tb_4O_7 , and Dy_2O_3) were converted to their nitrates by treatment with concentrated nitric acid. Monodocosyl phthalate (0.474 g/1.0 mmol) was dissolved into aqueous solution of Na_2CO_3 (0.1 mol L^{-1}). Then aqueous solution of lanthanide nitrate ($\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, L = Eu, Tb, Dy; 0.33 mmol) was added very slowly to the above mixed solution by stirring acutely, resulting in the white solid products. Continuing to stirring for 1 h, the product was filtered, washed with ethanol and water repeatedly and dried in vacuum. The synthesis reaction process was presented in Scheme 1. The compositions of the complexes were confirmed by elemental analysis: $\text{Ln}(\text{22-Phth})_2\text{NO}_3$, Ln = Eu, Tb, Dy. Anal. Calcd. For $\text{C}_{60}\text{H}_{98}\text{O}_{11}\text{NEu}$: C, 62.07; H, 8.28; N, 1.21; Found: C, 61.59; H, 7.97; N, 1.13. I.R. (KBr) cm^{-1} 2851.89 (ν_{sCH_3}), 2916.76 (ν_{asCH_3}), 1729.37 ($\nu_{\text{C=O}}$), 1405.41 ($\nu_{\text{scoo-}}$), 1606.49 ($\nu_{\text{asc-o-}}$), 1081.08 ($\nu_{\text{sc-o-c}}$), 1262.70 ($\nu_{\text{asc-o-c}}$), 1463.28 ($\nu_{\text{N=O}}$), 1282.16 (ν_{NO_2}). For $\text{C}_{60}\text{H}_{98}\text{O}_{11}\text{NTb}$: C, 61.70; H, 8.40; N, 1.20; Found: C 61.89; H, 8.13; N, 1.12. I.R. (KBr) cm^{-1} 2845.41 (ν_{sCH_3}), 2923.24 (ν_{asCH_3}), 1729.37 ($\nu_{\text{C=O}}$), 1405.41 ($\nu_{\text{scoo-}}$), 1606.49 ($\nu_{\text{asc-o-}}$), 1074.59 ($\nu_{\text{sc-o-c}}$), 1269.29 ($\nu_{\text{asc-o-c}}$), 1463.28 ($\nu_{\text{N=O}}$), 1282.16 (ν_{NO_2}). For $\text{C}_{60}\text{H}_{98}\text{O}_{11}\text{NDy}$: C, 61.51; H, 8.37; N, 1.20; Found: C, 61.90; H, 7.79; N, 1.10. I.R. (KBr) cm^{-1} 2845.41 (ν_{sCH_3}), 2923.24 (ν_{asCH_3}), 1729.37



Scheme 1. Synthesis of long chain ester by modification of ortho phthalic anhydride with 1-docosanol and its lanthanide (Ln = Eu, Tb, Dy) complexes.

($\nu_{C=O}$), 1405.41 (ν_{sCOO^-}), 1606.49 (ν_{asCOO^-}), 1074.59 (ν_{sc-o-c}), 1269.29 ($\nu_{asc-o-c}$), 1463.28 ($\nu_{N=O}$), 1282.16 (ν_{NO_2}).

Physical Measurement

Elemental analyses (C, H, N) were carried out by the Elementar Carlo EL elemental analyzer. Infrared spectroscopy with KBr pellets was performed on a Nicolet Nexus 912 AO446 model spectrophotometer in the 4000–400 cm^{-1} . 1H NMR spectra were recorded in chloroform on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra (10^{-4} mol L^{-1} chloroform solutions) were obtained with an Agilent 8453 spectrophotometer. Low temperature phosphorescence spectrum was determined Perkin-Elmer LS-55 spectrophotometer at 77 K: excitation wavelength = 237 nm, delay time = 0.01 ms, the phosphorescence measurement began 100 microseconds after lamp flash and it continued 200 ms. The fluorescence (excitation and emission) spectra were determined with Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm.

RESULTS AND DISCUSSION

All the infrared spectra of three lanthanide complexes show the similar features. The characteristic absorption

peaks of carboxylate group COO^- appear (1580, 1587, 1580 cm^{-1} for $V_s(COO^-)$ and 1405, 1405, 1405 for $V_a(COO^-)$, respectively) while there do not exist for free ligand of 22-Phth, suggesting that the oxygen atoms of mono 22-Phth carbonyl group are coordinated with Ln^{3+} . Both the free ligand and its complexes show the characteristic absorption bands of carbonyl group (1742 cm^{-1} (s) for 22-Phth and 1723 cm^{-1} for $[Ln(22-Phth)_3]NO_3$) except for the weaker absorption intensity for complexes than that of 22-Phth, which indicates that there still exist one carboxyl group of long chain ester which also take part in the coordination with lanthanide ions. Besides this, NO_3^- also participate the coordination to Ln^{3+} , showing two absorption bands for stretching vibrations of $N=O$ (1472.70 cm^{-1}) and NO_2 (1282.16 cm^{-1}), which suggest that the coordination between Ln^{3+} ions and NO_3^- ions belong to bidentate chelation effect.

Fig. 1 shows selected ultraviolet-visible absorption spectra for the 22-Phth and its lanthanide (Eu^{3+} , Tb^{3+}) complexes (10^{-4} mol L^{-1} chloroform solutions). They all exhibit domain absorption peaks in the ultraviolet region in the range of 200–400 nm, and the maximum absorption peaks are located at around 243 nm (22-Phth), 243 nm (Eu -22-Phth) and 243 nm (Tb -22-Phth), respectively. Besides, there exist one shoulder peak at around 277 nm. Both of the two peaks in these absorption spectra are ascribed to the characteristic absorption peaks of phenyl group in the phthalate groups. Compared to the

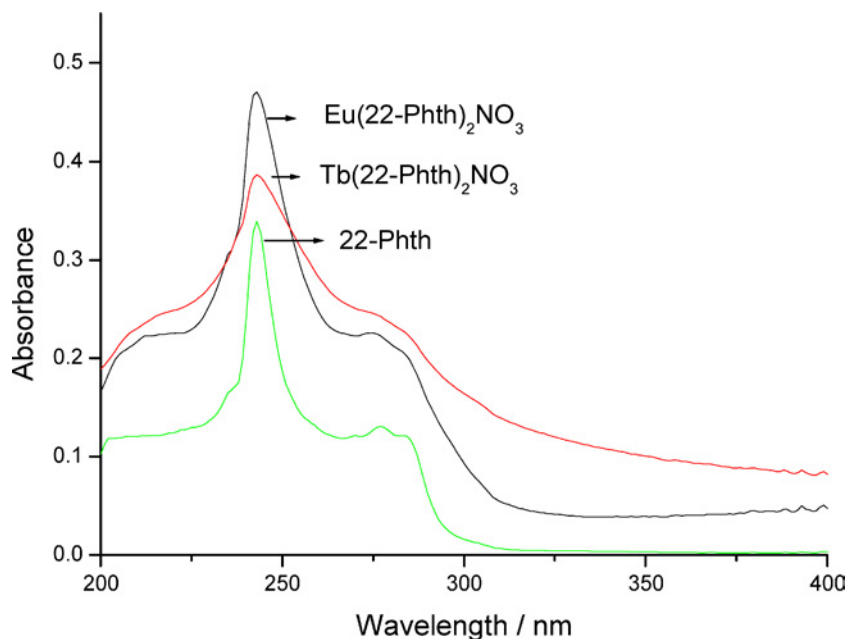


Fig. 1. Ultraviolet-visible absorption spectra of monodocosyl phthalate and its europium and terbium complexes (10^{-4} mol L^{-1} chloroform solution).

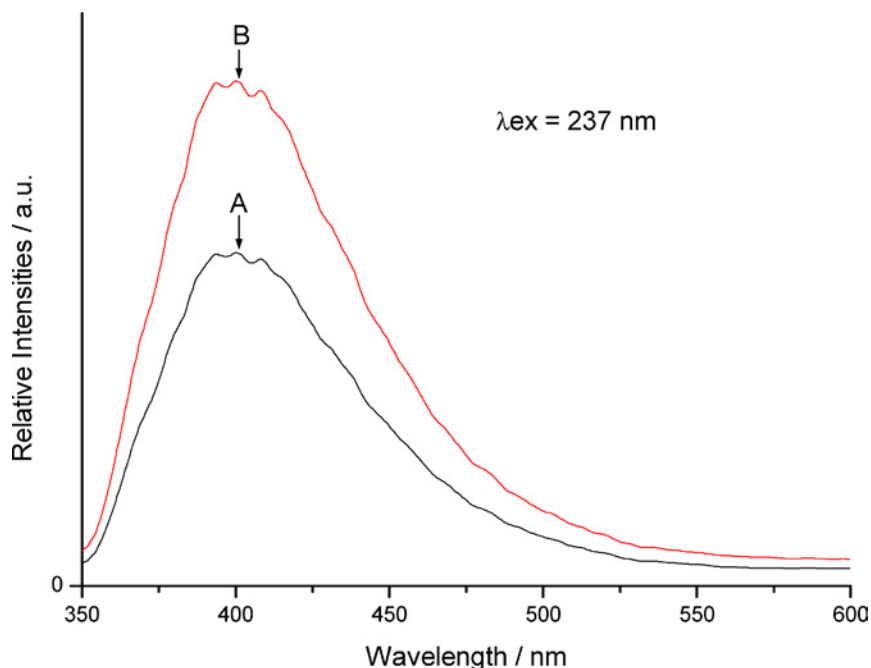


Fig. 2. Low temperature phosphorescent spectra of monodocosyl phthalate (A) and its gadolinium complex (B) at 77 K (10^{-4} mol L $^{-1}$ chloroform solution).

absorption spectra of free ligands, the absorption spectra of both europium and terbium complexes of it show the same maximum absorption peak at 243 nm except for the distinction of band width and intensity, indicating that the coordination between Eu^{3+} and Tb^{3+} and ligands forms more extensive conjugated systems than free ligands. The absorption spectrum for Dy complex shows the similar feature.

We further measured the low temperature phosphorescence spectra of the long chain ligands and the corresponding gadolinium complex were measured owing to its high phosphorescence—fluorescence ratio compared to those of the other Ln^{3+} complexes and Gd^{3+} can sensitize the phosphorescence emission of ligands (as shown in Fig. 2A and B). From the maximum phosphorescent emission band (400 nm) for both of the two spectra, the triplet state energies can be determined as $25,000\text{ cm}^{-1}$. Compared with phosphorescence spectrum of Phth [19], the introduction of long chain group in 22-Phth slightly changed the phosphorescence emission from nm 404 nm of Phth to 400 nm and corresponding triplet state energy changed from $24,750\text{ cm}^{-1}$ of Phth to $25,000\text{ cm}^{-1}$. The energy differences between the triplet state of the ligands (22-Phth) and the resonance energy levels of Eu^{3+} (${}^5\text{D}_0$, $17,265\text{ cm}^{-1}$) (For Eu^{3+} complexes, the general intramolecular energy process was verified to be from triplet state to ${}^5\text{D}_0$ of Eu^{3+} for that the higher energy level ${}^5\text{D}_1$

or ${}^5\text{D}_2$ usually relax to its lower level ${}^5\text{D}_0$. Therefore, the energy gap between triplet state to ${}^5\text{D}_0$ of Eu^{3+} is objective and significant to describe the energy match and intramolecular energy transfer mechanism), Tb^{3+} (${}^5\text{D}_4$, $20,500\text{ cm}^{-1}$) and Dy^{3+} (${}^4\text{F}_{9/2}$, $21,000\text{ cm}^{-1}$) can be calculated as 7235 , 4500 and 4000 cm^{-1} , respectively [19–25]. From these energy differences, it can be seen that the long chain ester can sensitize the three lanthanide ions effectively. According to the intramolecular energy transfer mechanism [19–28], the intramolecular energy transfer efficiency depends chiefly on two energy transfer processes: the first one leads from the triplet level of ligands to the emissive energy level of the Ln^{3+} ion by Dexter's resonant exchange interaction [21]; the second one is just an inverse energy transfer by a thermal deactivation mechanism. Both energy transfer rate constants depend on the energy differences between the triplet level of the ligands and the resonant emissive energy of Ln^{3+} . Intramolecular energy transfer efficiency in lanthanide complexes conforms to Dexter's exchange energy transfer theory [21]:

$$K_{\text{ET}} = (2\pi Z^2/R) \exp(-2rl) \int F_{\text{d}}(E)F_{\text{a}}(E) \text{d}E \quad (1)$$

K_{ET} is the rate constant of energy transfer, r is the intermolecular distance between the energy donor and acceptor atoms, l is the van der Waals radius, the integral represents the overlap between the luminescence

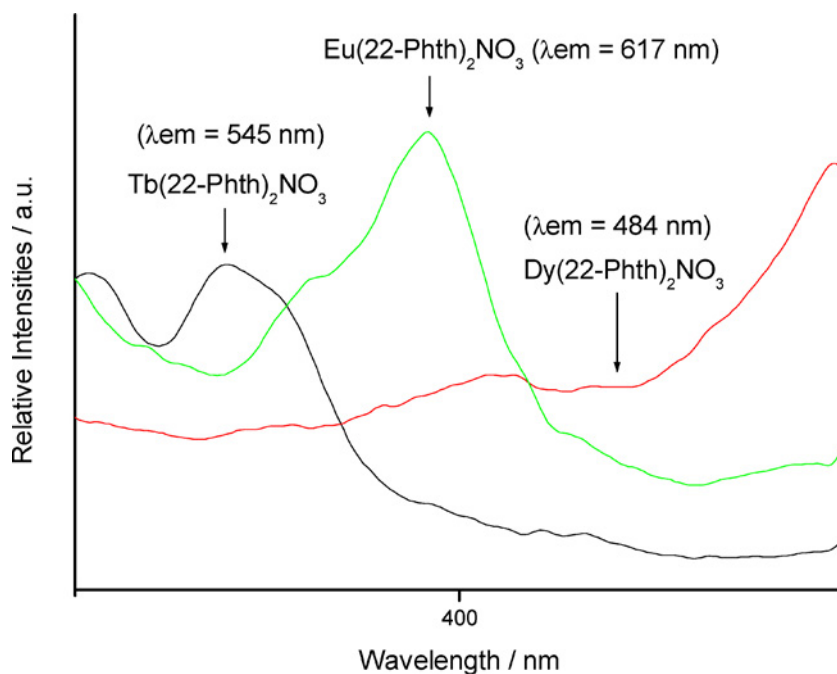


Fig. 3. Excitation spectra of solid lanthanide complexes with monodocosyl phthalate.

spectrum of the ligands and the absorption spectrum of Ln^{3+} ($F_d(E)$): the luminescence spectrum of energy donor (ligand), ($F_a(E)$): absorption spectrum of energy acceptor (Ln^{3+}), and $2\pi Z^2/R$ is a constant relating to the mutual distance between Ln^{3+} and coordinated atom. r and l are both considered to be constant for intramolecular energy transfer processes. From Eq. (1), K_{ET} increases with decreasing energy difference $\Delta E(\text{Tr} - \text{Ln}^{3+})$ between the triplet state energy of ligands and the resonance emission energy of Eu^{3+} and Tb^{3+} . Thus, ligands with a large energy difference can not sensitize rare earth ions effectively. On the other hand, there exists an inverse energy transfer process which affects luminescence intensity by temperature ($k(T)$) [22]: rate constant of inverse energy transfer process (thermal deactivation process), A : preexponential factor):

$$K(T) = A \exp(-\Delta E(\text{Tr} - \text{Ln}^{3+})/RT) \quad (2)$$

It can be seen that the activation energy is approximately equal to $\Delta E(\text{Tr} - \text{Ln}^{3+})$ in the inverse energy transfer process; therefore, a decreasing energy difference increases $k(T)$. Based on this evidence, the conclusion can be drawn that $\Delta E(\text{Tr} - \text{Ln}^{3+})$ is of opposite influence on the two energy transfer processes and an optimal value can be assumed to exist.

The excitation spectra of these lanthanide complexes show that they have no effective absorption in narrow wavelength ultraviolet region of the range 200–300 nm.

The effective energy absorption mainly takes place in the long ultraviolet-visible region of 300–450 nm. Fig. 3 gives the excitation spectra of Eu, Tb and Dy solid complexes of 22-Phth. The excitation bands for Eu complex under the red emission of 613 nm show a broad excitation bands and the maximum excitation peaks are located around 396.5 nm. The excitation bands for Tb complex under the green emission of 544 nm exhibit a broad excitation bands and the maximum excitation peaks are located around 360.5 nm. The excitation bands for Dy complex under the blue emission of 484 nm present a broad excitation bands and the maximum excitation peaks are located around 331 nm. We further measured the corresponding emission spectra by selective excitation with the four different excitation wavelengths, they show the similar emission position except for different luminescent intensities.

Figs. 4–6 show the selected emission spectra of Eu, Tb, and Dy complexes with these three ligands. For europium complex, the emission spectra show two apparent emission peaks under the excitation of 396 nm: 590, 615 nm for Eu-22-Phth, corresponding with the characteristic emissions originated from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions ($J = 1, 2$) of Eu^{3+} ion. Among the luminescent intensities of supersensitive red ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition are the strongest. For Tb complexes, the emission spectra show two apparent emission peaks under the excitation of 370 nm: 490.5, 543 nm for Tb-22-Phth, ascribed to be the characteristic emission ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ ($J = 6, 5$) transition

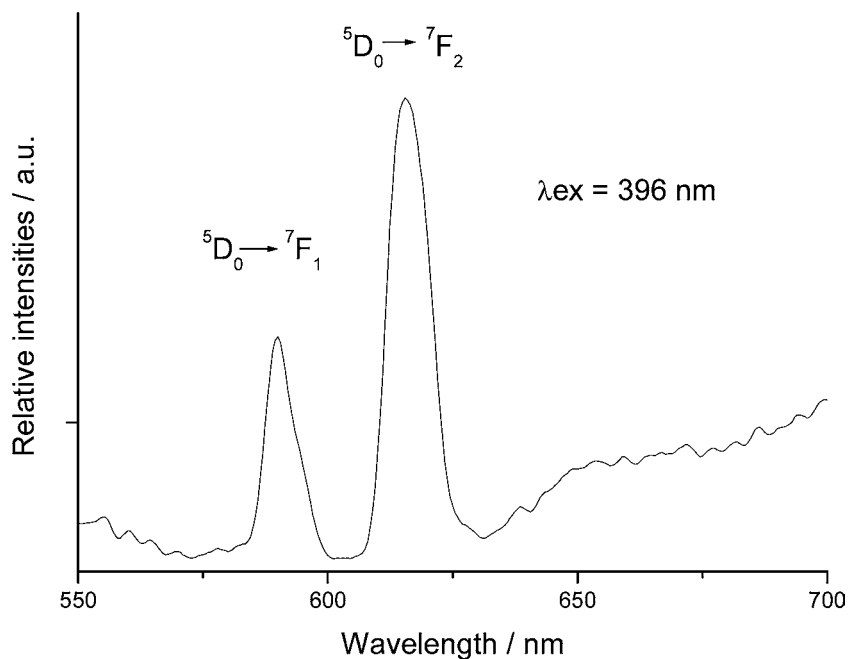


Fig. 4. Emission spectrum of solid Eu complex with monodocosyl phthalate.

of Tb^{3+} ion. Among the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition exhibits the strongest green emission. For Dy complexes, the luminescence spectra of Dy-22-Phth show two apparent emission peaks under the excitation of 400 nm: one is at 482 nm for; the other is at 572 nm, which correspond to the char-

acteristic emission ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_J$ ($J = 15/2, 13/2$) transition of Dy^{3+} ion, respectively. Furthermore, both Figs. 5 and 6 show a high background for terbium and dysprosium complexes, which can be ascribed as the characteristic emission for long chain ester ligands of 22-Phth in the

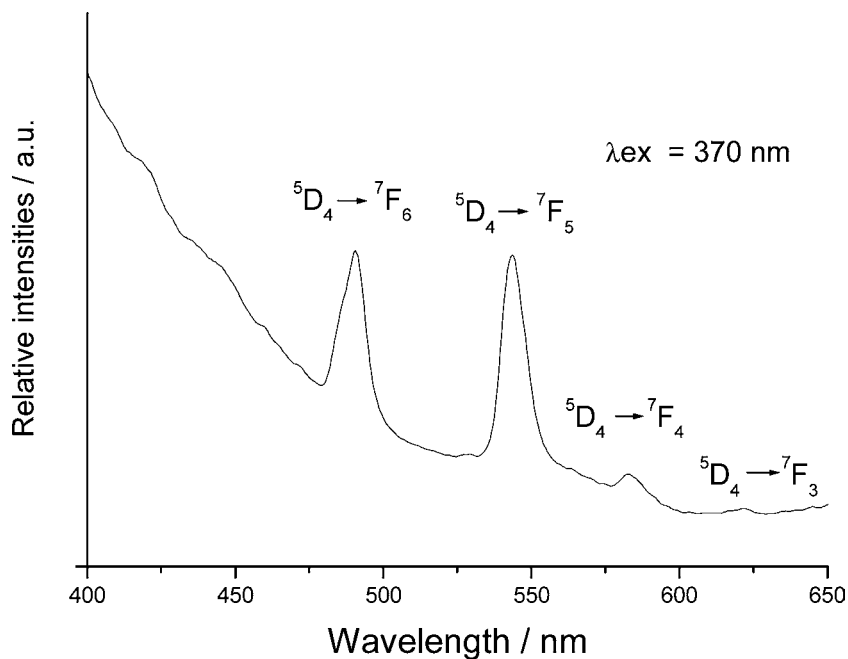


Fig. 5. Emission spectrum of solid Tb complex with monodocosyl phthalate.

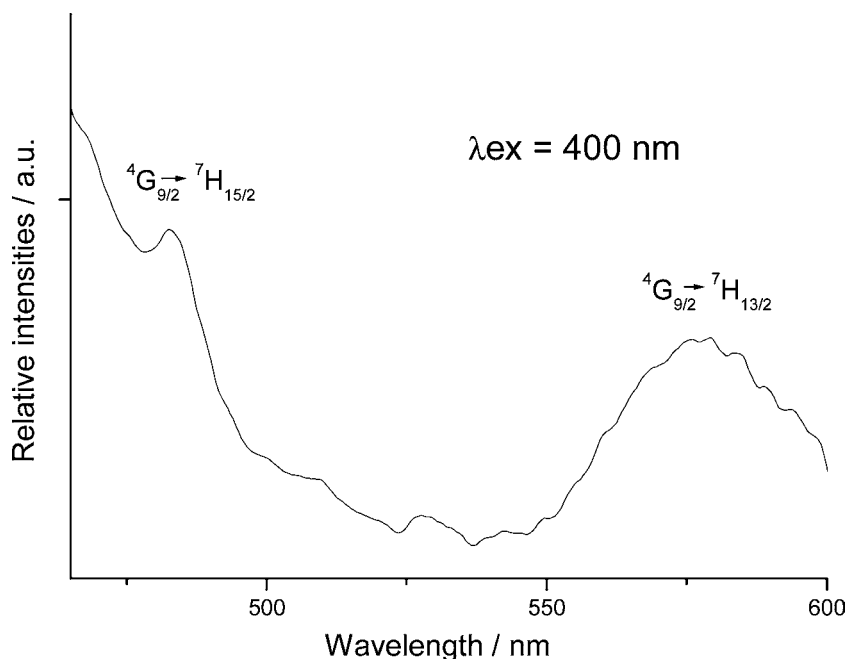


Fig. 6. Emission spectrum of solid Dy complex with monodocosyl phthalate.

complex systems. The appearance of ligands' luminescence suggests that the luminescence of ligands can not be quenched by the coordination to Tb^{3+} and Dy^{3+} ions in their complexes and so the intramolecular energy transfer process from the triplet state energy of 22-Phth ligands to the resonant emissive energy level of Tb^{3+} (or Dy^{3+}) is not effective. While the emission spectrum for europium complexes with 22-Phth does not show this emission band, indicating the effective intramolecular energy transfer process takes place between ligands and Eu^{3+} and entirely quenching of Phth-22's luminescence by Eu^{3+} .

CONCLUSIONS

A novel long chain ester ligand has been synthesized by the modification of ortho phthalic anhydride with docosanol and its complexes with lanthanide ions (Eu^{3+} , Tb^{3+} , Dy^{3+}) have been prepared, whose compositions were confirmed. The photophysical properties of them have been studied with ultraviolet spectra, low temperature phosphorescent spectra, excitation and emission spectra. The triplet state energy of the long chain ligands is determined to be $25,000\text{ cm}^{-1}$ with the maximum phosphorescent emission of 400 nm. The energy match between the long chain ligands and lanthanide ions (Eu^{3+} , Tb^{3+} , Dy^{3+}) has been studied to predict that the energy transfer process exists between the ligand and Ln^{3+} .

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REFERENCES

1. Y. X. Ci, Y. Z. Li, and W. B. Chang (1991). Fluorescence reaction of terbium (III) with nucleic acids in the presence of phenanthroline. *Anal. Chim. Acta* **248**, 589.
2. Y. X. Ci, Y. Z. Li, and X. J. Liu (1995). Selective determination of DNA by its enhancement effect on the fluorescence europium tetracycline complex. *Anal. Chem.* **67**, 1785.
3. B. Yan and J. Y. You (2002). Sol-gel assembly and luminescence of SiO_2 /PEMA hybrid material incorporated with terbium complex. *J. Rare Earths* **20**, 404.
4. B. Yan (2003). Sol-gel preparation and luminescence of silica/polymer hybrid material incorporated with terbium complex. *Mater. Lett.* **57**, 2535.
5. H. Xin, F. Y. Li, M. Shi, Z. Q. Bian, and C. H. Huang (2003). Efficient electroluminescence from a new terbium complex. *J. Am. Chem. Soc.* **125**, 7166.
6. H. Xin, M. Shi, X. M. Zhang, F. Y. Li, Z. Q. Bian, K. Ibrahim, F. Q. Liu, and C. H. Huang (2003). Carrier-transport, photoluminescence, and electroluminescence properties comparison of a series of terbium complexes with different structures. *Chem. Mater.* **15**, 3728.
7. Y. S. Yang, M. L. Gong, Y. Y. Li, H. Y. Lei, and S. L. Wu (1994). Effects of the structure of ligands and their Ln^{3+} complexes on the luminescence of the central Ln^{3+} ions. *J. Alloys Compd.* **207/208**, 112.
8. C. J. Feng, Q. H. Luo, and C. Y. Duan (1998). Synthesis and crystal structural characterization of an unsymmetric neodymium(III) cryptate. *J. Chem. Soc., Dalton Trans.* 1377.
9. T. Gunnlaugsson, A. J. Harte, J. P. Leonard, and M. Nieuwenhuyzen (2002). Delayed lanthanide luminescence sensing of aromatic

- carboxylates using heptadentate triamide Tb(III) cyclen complexes: The recognition of salicylic acid in water. *Chem. Commun.* 2134.
10. B. Yan and Y. S. Song (2004). Spectroscopic study on the photophysical properties of lanthanide complexes with 2,2'-bipyridine-*N,N'*-dioxide. *J. Fluorescence* **14**, 289.
 11. G. A. Crosby, R. E. Whan, and R. M. Alire (1961). Intramolecular energy transfer in rare earth chelates. Role of the triplet state. *J. Chem. Phys.* **34**, 743.
 12. M. L. Bhaumik and L. J. Nugent (1965). Time-resolved spectroscopy of europium chelates. *J. Chem. Phys.* **43**, 1680.
 13. H. J. Zhang, B. Yan, S. B. Wang, and J. Z. Ni (1997). The photophysical properties of binary and ternary complexes of rare earth with conjugated carboxylic acids and 1,10-phenanthroline. *J. Photochem Photobiol. A Chem.* **109**, 223.
 14. B. Yan, H. J. Zhang, S. B. Wang, and J. Z. Ni (1998). Spectroscopic study of luminescence and intramolecular energy transfer of binary and ternary rare earth complexes with aromatic carboxylic acids and 1,10-phenanthroline. *Spectro. Lett.* **31**, 603.
 15. B. Yan, H. J. Zhang, S. B. Wang, and J. Z. Ni (1997). Synthesis, luminescence and intramolecular energy transfer of binary and ternary rare earth complexes with aromatic carboxylic acids and 1,10-phenanthroline. *J. Chin. Chem. Soc.* **44**, 567.
 16. B. Yan, H. J. Zhang, S. B. Wang, and J. Z. Ni (1998). Intramolecular energy transfer mechanism between ligands in ternary complexes with aromatic acids and 1,10-phenanthroline. *J. Photochem. Photobiol. A Chem.* **116**, 209.
 17. H. J. Zhang, B. Li, J. F. Ma, and J. Z. Ni (1997). Luminescent properties of the Langmuir-Blodgett film of terbium (III) stearoylanthranilate. *Thin Solid Films* **310**, 274.
 18. B. Li, H. J. Zhang, J. F. Ma, S. B. Wang, and J. Z. Ni (1996). Study on the luminescent LB films of rare earth complexes with mono-octadecyl phthalate. *Chin. Sci. Bull.* **42**, 825.
 19. S. Sato and M. Wada (1970). Relations between intramolecular energy transfer efficiencies and triplet state energies in rare earth β -diketone chelates. *Bull. Chem. Soc. Japan.* **43**, 2403.
 20. L. J. Nugent, M. L. Bhaumik, S. George, and S. M. Lee (1964). Ligand field spectra of some new laser chelates. *J. Chem. Phys.* **41**, 1305.
 21. D. L. Dexter (1953). A theory of sensitized luminescence in solids. *J. Chem. Phys.* **21**, 836.
 22. C. R. S. Dean and T. M. Shepherd (1975). Evaluation of the intramolecular energy transfer rate constants in crystalline $\text{Eu}(\text{hfaa})_4\text{Bu}^1\text{NH}_3$. *J. Chem. Soc., Faraday Trans. II* **71**, 146.
 23. M. L. Bhaumik and M. A. El-Sayed (1965). Mechanism and rate of the intramolecular energy transfer process in rare-earth chelates. *J. Chem. Phys.* **42**, 787.
 24. J. J. Mikula and R. E. Salomon (1968). Deuterium isotope effects on the luminescence of terbium and europium chelates. *J. Chem. Phys.* **48**, 1077.
 25. A. A. Lamola and G. S. Hammond (1965). Mechanisms of photochemical reactions in solution. XXXIII. intersystem crossing efficiencies. *J. Chem. Phys.* **43**, 2129.
 26. P. K. Gallagher, A. Heller, and E. Wasserman (1964). Two-step energy transfer in solution. *J. Chem. Phys.* **43**, 3921.
 27. B. Yan, H. Shao, H. J. Zhang, S. B. Wang, and J. Z. Ni (1998). The photophysical properties of rare earth complexes with ethyl-4-hydroxy-7-trifluoro-methyl-3-quinolinecarboxylate. *Chin. J. Inorg. Chem.* **14**, 407.
 28. B. Yan, H. J. Zhang, and J. Z. Ni (1998). Luminescence properties and intramolecular energy transfer of rare earth complexes with aromatic carboxylic acids. *Chem. Res. Chin. Univ.* **14**, 245.