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Spectroscopic study on the photophysical properties of novel lanthanide complexes with long chain mono-L phthalate (L=hexadecyl, octadecyl and eicosyl)

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Abstract

Ortho-phthalic anhydride was modified with long chain alcohol (1-hexadecanol, 1-octadecanol and 1-eicosanol) to their corresponding mono-L phthalate (L=hexadecyl, octadecyl and eicosyl), i.e. monohexadecyl phthalate (16-Phth), monooctadecyl phthalate (18-Phth), and monoeicosyl phthalate (20-Phth), respectively. Nine novel lanthanide (Eu^{3+} , Tb^{3+} and Dy^{3+}) complexes with these three mono-L phthalate ligands were synthesized and characterized by elemental analysis and IR spectra. The photophysical properties of these complexes were studied in detail with various spectroscopes such as ultraviolet–visible absorption spectra, low temperature phosphorescence spectra and fluorescent spectra. The ultraviolet–visible absorption spectra show some band shifts with the different chain-length of phthalate monoester and homologous lanthanide complexes. From the low temperature phosphorescent emission, the triplet state energies for these three ligands were determined to be around 22,650 cm⁻¹ (16-Phth), 23,095 cm⁻¹ (18-Phth) and 22,400 cm⁻¹ (20-Phth), respectively, suggesting they are suitable for the sensitization of the luminescence of Eu^{3+} , Tb^{3+} and Dy^{3+} . The fluorescence excitation and emission spectra for these lanthanides complexes of the three ligands take agreement with the above predict from energy match. © 2004 Elsevier B.V. All rights reserved.

Keywords: Lanthanide complexes; Long chain phthalate monoester; Photophysical property; Energy transfer; Spectroscopy

1. Introduction

Lanthanide complexes have received much attention because of their interesting photophysical properties which 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] or electroluminescent devices [5,6]. Considerable studies have been focused on the design and assembly of lanthanide complexes with organic ligands such as aromatic carboxylic acids, β -diketones, 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+} [11–15] while most aromatic carboxylic acids are more suitable for the luminescence of Tb³⁺ [16–20]. 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 [21,22], indicating there still exist intramolecular energy transfer mechanism between ligands (i.e. from aromatic carboxylic acids and 1,10-phenanthroline). On account of the energy match and energy transfer mechanism, it can be realized to predict the luminescent properties of lanthanide complexes. Phthalate or aminobenzoate derivative have been found to exhibit favorable properties of luminescence and film formation [23,24].

In this context, using *ortho*-phthalic anhydride as staring material, three kinds of long chain alcohol (1-hexadecanol, 1-octadecanol and 1-eicosanol) were grafted to achieve their mono-L phthalates (L=hexadecyl, octadecyl and eicosyl), i.e. monohexadecyl phthalate (16-Phth), monooctadecyl

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Scheme 1. Synthesis of long chain ester by modification of *ortho*-phthalic anhydride with alcohol (n = 15, 17, 19).

phthalate (18-Phth), and monoeicosyl phthalate (20-Phth), respectively. The corresponding lanthanide (Eu^{3+} , Tb^{3+} and Dy^{3+}) complexes with these ligands were synthesized and characterized. The photophysical properties for these long esters and their lanthanide complexes were studied in detail, which can be expected to have practical application to fabricate the Langmuir–Blodgett films.

2. Experimental

2.1. Synthesis of mono-L phthalate by the modification of ortho-phthalic anhydride

The synthesis of mono-L phthalates was adopted as the similar procedure in ref. [25]. Ortho-phthalic anhydride (2.96 g/mmol) was mixed with equimolar amount of long chain alcohols (1-hexadecanol (4.85 g), 1-octadecanol (5.41 g) and 1-eicosanol (5.97 g)) in a flask. Then the solid mixtures were placed in an oil bath at the temperature 110-115 °C and react for 15 h. Finally the samples were recrystallized with n-hexane three times to afford the products (Scheme 1). The compositions of the aim products were confirmed by elemental analysis: Calcd. for $C_{24}H_{37}O_4$ (mp: 65 °C) C, 73.85; H, 9.69; Found: C, 74.21; H, 9.20; H NMR δ 7.97 (1H), 7.75 (1H), 7.60 (2H), 4.33 (2H), 3.49 (2H), 2.24 (26H), 1.18 (3H), 10.50 (–COOH). For C₂₆H₄₁O₄ (mp: 68 °C): C, 74.64; H, 10.05; Found: C, 74.95; H, 9.59; H NMR δ 7.97 (1H), 7.76 (1H), 7.59 (2H), 4.34 (2H), 3.35 (2H), 2.24 (2H), 1.73 (2H), 1.25 (26H), 0.89 (3H), 10.90 (-COOH). For C₂₈H₄₅O₄ (mp: 70 °C): C, 75.34; H, 10.31; Found: C, 75.61; H, 9.58; H NMR δ7.97 (1H), 7.70 (1H), 7.60 (2H), 4.30 (2H),

3.47 (2H), 2.17 (2H), 1.77 (2H), 1.26 (28H), 0.88 (3H), 11.20 (-COOH).

2.2. Synthesis of lanthanide complexes with mono-L 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. Mono-L phthalate (0.390 g for 16-Phth, 0.418 g for 18-Phth and 0.446 g for 20-Phth; 1.0 mmol) was dissolved into the aqueous solution of Na₂CO₃ (0.1 mol L^{-1}). Then aqueous solution of lanthanide nitrate (Ln(NO₃)₃.6H₂O, L = Eu, Tb, Dy; 0.33 mmol) was added very slowly to the above mixed solution with vigorous stirring, resulting in the white solid products (Scheme 2). Continuing to stir for 1 h, the product was filtered, washed with ethanol and water repeatedly and dried in desiccator. The compositions of the complexes were confirmed by elemental analysis: $Ln(L')_2NO_3$, Ln = Eu, Tb, Dy; L' = 16-Phth, 18-Phth, 20-Phth. Anal. Calcd. for $C_{48}H_{74}O_{11}NEu: C, 58.64; H, 7.46; N,$ 1.41; Found: C, 58.26; H, 7.10; N, 1.34. For C₅₂H₈₂O₁₁NEu: C, 59.54; H, 7.82; N, 1.34; Found: C, 59.90; H, 7.29; N, 1.29. For C₅₆H₉₀O₁₁NEu: C, 60.87; H, 8.15; N, 1.27; Found: C, 60.41; H, 7.47; N, 1.31. For C₄₈H₇₄O₁₁NTb: C, 57.66; H, 7.41; N, 1.40; Found: C, 58.16; H, 7.07; N, 1.32. For C₅₂H₈₂O₁₁NTb: C, 59.15; H, 7.77; N, 1.33; Found: C, 58.75; H, 7.36; N, 1.28. For C₅₆H₉₀O₁₁NTb: C, 60.49; H, 8.10; N, 1.26; Found: C, 60.61; H, 7.53; N, 1.27. For C₄₈H₇₄O₁₁NDy: C, 57.46; H, 7.38; N, 1.40; Found: C, 57.21; H, 7.11; N, 1.29. For C₅₂H₈₂O₁₁NDy: C, 58.95; H, 7.75; N, 1.32; Found: C, 59.10; H, 7.41; N, 1.26. For C₅₆H₉₀O₁₁NDy: C, 60.30; H, 8.08; N, 1.26; Found: C, 60.61; H, 7.63; N, 1.23.

2.3. Physical measurements

Elemental analyses (C, H, N) were carried out by the Elementar Cario EL elemental analyzer. Infrared spectroscopy with KBr pellets was performed on a Nicolet Nexus 912 AO446 model spectrophotometer in the 4000–400 cm⁻¹. Ultraviolet absorption spectra were obtained with an Agilent 8453 spectrophotometer. ¹H NMR spectra were recorded in chloroform on a Bruker AVANCE-



Scheme 2. Synthesis of lanthanide complexes with long chain ester (Ln = Eu, Tb, Dy; n = 15, 17, 19).

500 spectrometer with tetramethylsilane (TMS) as internal reference. Low temperature phosphorescence spectrum was determined Perkin-Elmer LS-55 spectrophotometer at 77 K. The fluorescence (excitation and emission) spectra were determined with Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm.

3. Results and discussion

All the IR spectra of these lanthanide complexes show the similar features. For example, in the IR spectra of Ln(16-Phth)₂NO₃ system, the characteristic absorption peaks of carboxylic group COO⁻ appear (1600, 1600, 1587 cm⁻¹ for $v_{as}(COO-)$ and 1405, 1427, 1405 cm⁻¹ for $v_s(COO-)$, respectively) while there does not exist for free 16-Phth ligand, suggesting that the oxygen atoms of mono 16-Phth carbonyl group are coordinated with Ln³⁺. Both the free ligand and its complexes show the characteristic absorption bands of carbonyl group (1743 cm⁻¹ (strong) for 16-Phth and 1723 cm⁻¹ for Ln(16-Phth)₂NO₃) except for the weaker absorption intensity for complexes than that of 16-Phth, which indicates that there still exist one carbonyl group of long chain ester and these carbonyl groups coordinated with Ln ions for the absorption band shift to low frequency. In the IR spectra of Ln(18-Phth)₂NO₃ system, the characteristic absorption peaks of carboxylic group COO⁻ appear (1509, 1503, 1503 cm^{-1} for $v_{as}(COO-)$ and 1386, 1386, 1386 cm⁻¹ for v_s (COO–), respectively) while it is not observed for free 18-Phth ligand, indicating that the oxygen atoms of mono 18-Phth carbonyl group are coordinated with Ln³⁺. Both the free ligand and its complexes show the characteristic absorption bands of carbonyl group (1744 cm⁻¹ (strong) for 18-Phth and 1724 cm^{-1} for Ln(18-Phth)₂NO₃) except for the weaker absorption intensity for complexes than that of 18-Phth, which suggests that there still exist one carboxyl group of long chain ester. In the IR spectra of Ln(20-Phth)₂NO₃ system, the characteristic absorption peaks of carboxylic group COO⁻ appear (1600, 1600, 1606 cm⁻¹ for v_{as} (COO–) and 1405, 1405, 1405 cm⁻¹ for v_s (COO–), respectively) while free 20-Phth

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The IR spectra an	l band assignments	of the lanthanide	complexes
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Fig. 1. Ultraviolet-visible absorption spectra of long chain esters.

ligand does not present, which illuminates that the oxygen atoms of mono 20-Phth carbonyl group are coordinated with Ln^{3+} . Both the free ligand and its complexes show the characteristic absorption bands of carbonyl group (1749 cm⁻¹ (strong) for 20-Phth and 1724 cm⁻¹ (1729 cm⁻¹) for Ln(20-Phth)₂NO₃) except for the lower frequency and weaker absorption intensity for complexes than that of 20-Phth, verifying that there still exist one carboxyl group of long chain ester which also take part in the coordination with Lanthanide ions. Besides this, NO₃⁻ also participate the coordination to Ln^{3+} , showing two absorption bands for stretching vibrations of N=O (1472.70, 1470.28, 1463.28 cm⁻¹) and NO₂ (1301.62, 1288.65, 1282.16 cm⁻¹), which suggest that the coordination between Ln^{3+} ions and NO₃⁻ ions belong to bidentate chelation effect (Table 1).

Fig. 1 shows the ultraviolet–visible absorption spectra for the three long chain esters (16-Phth, 18-Phth and 20-Phth). 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 249 nm (16-Phth), 247 nm (18-Phth) and 243 nm (20-Phth), respectively. Besides, there exist one shoulder peak at around 277 nm for the three long

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Complex	$v_{s}(CH_{3})$	$v_{as}(CH_3)$	v(C=O)	ν _s (COO–)	$v_{as}(COO-)$	ν _s (C–O–C)	$v_{as}(C - O - C)$	ν(N=O)	$\nu(NO_2)$
16-Phth	2845.41	2923.24	1742.70			1074.00	1262.76		
Dy-16-Phth	2858.38	2916.76	1723.24	1405.41	1600.00	1139.46	1269.19	1472.70	1301.62
Eu-16-Phth	2851.89	2923.24	1723.24	1427.66	1600.00	1139.46	1275.68	1472.70	1301.62
Tb-16-Phth	2851.89	2916.76	1723.24	1405.41	1587.03	1139.46	1269.19	1472.70	1301.62
18-Phth	2851.98	2923.24	1743.78			1126.49	1282.16		
Dy-18-Phth	2851.89	2916.76	1723.73	1385.95	1509.19	1055.00	1262.70	1470.28	1288.65
Eu-18-Phth	2845.41	2923.24	1723.73	1385.95	1502.70	1074.00	1262.70	1470.28	1288.65
Tb-18-Phth	2851.89	2910.27	1723.73	1385.95	1502.70	1074.59	1262.70	1470.28	1288.65
20-Phth	2851.89	2923.24	1749.19			1074.59	1249.37		
Dy-20-Phth	2845.41	2916.76	1723.37	1405.41	1600.00	1074.59	1269.19	1463.28	1282.16
Eu-20-Phth	2845.41	2923.24	1729.37	1405.41	1600.00	1132.97	1269.29	1463.28	1282.16
Tb-20-Phth	2851.89	2916.76	1729.37	1405.41	1606.49	1081.08	1262.70	1463.28	1282.16

 Table 2

 The phosphorescence spectra data of aromatic carboxylic acids

Ligands	Triplet state energies (cm ⁻¹)	$\Delta E(\text{Tr-Eu}^{3+})$ (cm ⁻¹)	$\frac{\Delta E(\text{Tr-Tb}^{3+})}{(\text{cm}^{-1})}$	$\Delta E(\text{Tr-Dy}^{3+})$ (cm ⁻¹)
16-Phth	22650	5385	2150	1650
18-Phth	23095	5830	2595	2095
20-Phth	22400	5135	1900	1400

chain ligands (for 18-Phth, it is not apparent). Both of them are ascribed to the characteristic absorption peaks of phenyl cycle with long-chain substituted groups. The little distinction of band position and intensity is due to the different chain length (16-Phth-18-Phth-20-Phth). It also can be observed that the maximum absorption bands exhibit the slightly blue shifts with the increase of chain length, suggesting the increase of substituted alcohol chain has influence on the electron distribution in along the phenyl cycle. Fig. 2(a-c) presents the absorption spectra of Ln-16-Phth, Ln-18-Phth and Ln-20-Phth (Ln = Eu, Tb), respectively. All of them show the similar red shifts compared to the corresponding free ligands: 252 nm for Ln-16-Phth, 250 nm for Ln-18-Phth and 245 nm for Ln-20-Phth, separately, indicating that the coordination effects between Ln³⁺ and ligands form more extensive conjugated systems than free ligands.

We further measured the low temperature phosphorescence spectra of the three long chain ligands at 77 K. From the maximum phosphorescent emission band (441.5 nm for 16-Phth, 433 nm for 18-Phth and 446.5 nm for 20-Phth, respectively), the triplet state energies can be determined as $22,650 \text{ cm}^{-1}$ (16-Phth), $23,095 \text{ cm}^{-1}$ (18-Phth) and $22,400 \,\mathrm{cm}^{-1}$ (20-Phth), separately. The energy differences between the triplet state of thee ligands (16-Phth, 18-Phth and 20-Phth) and the resonance energy levels of Eu^{3+} (⁵D₀, 17,265 cm⁻¹), Tb³⁺ (⁵D₄, 20,500 cm⁻¹) and Dy³⁺ (⁴F_{9/2}, $21,000 \,\mathrm{cm}^{-1}$) can be calculated and the detailed data have been shown in Table 2. From these energy differences, it can be see that all the three long chain esters can sensitize the three lanthanide ions effectively. According to the intramolecular energy mechanism [26-29], 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 [30]; 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 Ln³⁺. Intramolecular energy transfer efficiency in lanthanide complexes conforms to Dexter' exchange energy transfer theory [30]:

$$K_{\rm ET} = \left(\frac{2\pi Z^2}{R}\right) \exp\left(\frac{r}{l}\right) \int F_{\rm d}(E) F_{\rm a}(E) \,\mathrm{d}E \tag{1}$$

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



Fig. 2. Ultraviolet–visible absorption spectra of lanthanide complexes with long chain esters: (a) Ln-16-Phth; (b) Ln-18-Phth; (c) Ln-20-Phth (Ln = Eu, Tb; n = 15, 17, 19).

between the luminescence 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 $2\pi Z^2/R$ the 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 $\Delta E(\text{Tr-Ln}^{3+})$ between the triplet state energy of ligands and the resonance emission energy of Eu³⁺ and Tb³⁺. Thus, ligands with a large energy difference cannot sensitize rare earth ions effectively. On the other hand, there exists an inverse energy transfer process which affects luminescence intensity by temperature (K(T) [31] is the rate constant of inverse energy transfer process (thermal deactivation process), A the preexponential factor):

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

It can be seen that the activation energy is approximately equal to $\Delta E(\text{Tr-Ln}^{3+})$ in the inverse energy transfer process; therefore, a decreasing energy difference increases K(T). Based on this evidence, the conclusion can be drawn that $\Delta E(\text{Tr-Ln}^{3+})$ 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 350-450 nm. Fig. 3(a-c) gives the excitation spectra of Eu, Tb and Dy solid complexes with the three ligands. The excitation bands for Eu complexes under the red emission of 613 nm show broad excitation bands and the maximum excitation peaks are located around 392.5 nm for Eu-16-Phth, 394.5 nm for Eu-18-Phth and 395.5 nm for Eu-20-Phth, respectively. The excitation bands for Tb complexes under the green emission of 544 nm exhibit a broad excitation bands and the maximum excitation peaks are located around 350.5 nm for Tb-16-Phth, 351 nm for Tb-18-Phth and 330.5 nm for Tb-20-Phth, respectively. The excitation bands for Dy complexes under the blue emission of 484 nm present a broad excitation bands and the maximum excitation peaks are located around 331 nm for Dy-16-Phth, 333.5 nm for Dy-18-Phth and 330.5 nm for Dy-20-Phth, respectively. 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 complexes, the emission spectra show two apparent emission peaks under the excitation of 395 nm: 590, 615 nm for Eu-16-Phth, 590, 616 nm for Eu-18-Phth and 590.5, 616 nm for Eu-20-Phth, respectively, corresponding with the characteristic emissions originated from ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{J}$ transitions (J=1, 2) of Eu³⁺ ion. Among the luminescent intensities of

(a) Wavelength/nm Relative intensities / a.u. Tb(20-phth),NO λem = 544 nm Tb(18-phth),NO, λem = 544 nm Tb-(16phth)2NO3 λem = 544 nm 250 300 350 400 450 (b) Wavelength / nm λem = 484 nm Dy(20-Phth),NO, Relative intensities /a.u. Dy(18-Phth) NO Dy(16-Phth) NO 250 350 400 300 (C) Wavelength / nm Fig. 3. Excitation spectra of lanthanide complexes with long chain esters:

Eu(16-Phth),NO,

λem = 613 nm

400

(a) Eu-L; (b) Tb-L; (c) Dy-L (L=16-Phth, 18-Phth, 20-Phth).

supersensitive red ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition are the strongest. For Tb complexes, the emission spectra show two apparent emission peaks under the excitation of 352 nm: 490.5, 543 nm for Tb-16-Phth, 490, 543 nm for Tb-18-Phth and 488, 543.5 nm for Tb-20-Phth, respectively, ascribed to be the characteristic emission {}^{5}D_{4} \rightarrow {}^{7}F_{J} (*J*=6, 5) transition of Tb³⁺ ion.

Relative Intensities/a.u.

350



450

Eu(20-Phth),NO,

Eu(18-Phth),NO,

λem = 613 nm

λem = 617 nm



Fig. 4. Emission spectra of Eu complexes with long chain esters.



Fig. 5. Emission spectra of Tb complexes with long chain esters.



Fig. 6. Emission spectra of Dy complexes with long chain esters.

Among the ${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{5}$ transition exhibits the strongest green emission. For Dy complexes, the luminescence spectra show two apparent emission peaks under the excitation of 356 nm: one is at 482 nm for Dy-16-Phth, 483.5 nm for Dy-18-Phth and 482.5 nm Dy-20-Phth; the other is at 572 nm for Dy-16-Phth, 574.5 nm for Dy-18-Phth and 572.5 nm for Dy-20-Phth, separately, which correspond to the characteristic emission ${}^{4}\text{F}_{9/2} \rightarrow {}^{6}\text{H}_{J}$ (J = 15/2, 13/2) transition of Dy³⁺ ion, respectively.

4. Conclusions

Three long chain ester ligands have been synthesized by the modification of *ortho*-phthalic anhydride with long chain alcohols and their nine complexes with lanthanide ions (Eu³⁺, Tb³⁺, Dy³⁺) have been prepared. 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 three long chain ligands are determined to be $22,650 \text{ cm}^{-1}$ (16-Phth), $23,095 \text{ cm}^{-1}$ (18-Phth) and $22,400 \text{ cm}^{-1}$ (20-Phth), respectively with the phosphorescence spectra. The energy match between the long chain ligands and lanthanide ions (Eu³⁺, Tb³⁺, Dy³⁺) has been studied to predict that the optimum energy transfer exists between the ligand and Ln³⁺.

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