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Photophysical properties of novel lanthanide complexes with long chain mono-eicosyl *cis*-butene dicarboxylate

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Abstract

Maleic anhydride was grafted by long chain alcohol 1-eicosanol to a novel sort of corresponding monoester, mono-eicosyl *cis*-butene dicarboxylate. Then the four novel ternary lanthanide (Eu^{3+}, Tb^{3+}, Dy^{3+}, Gd^{3+}) complexes with the as-derived long chain monoester and a second ligand 1,10-phenanthroline were synthesized and characterized by elemental analysis, IR spectra. The photophysical properties of these complexes were studied in detail with ultraviolet absorption spectra, low temperature phosphorescent spectra, fluorescent spectra and luminescent lifetimes, indicating that the intramolecular energy transfer mechanism runs smoothly within these ternary complexes in terms of sensitized functions of 1,10-phenanthroline and strong characteristic green, red or blue emissions of Tb^{3+}, Eu^{3+} or Dy^{3+} have been achieved.
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Keywords: Lanthanide complexes; Long chain maleic monoester; 1,10-Phenanthroline; Energy transfer; Fluorescence

1. Introduction

Recently, lanthanide complexes have received much attention in terms of their interesting photophysical properties, which have potential application in the luminescence probes for chemical or biological macromolecules and the active center for luminescent materials [1–4]. And considerable studies have been focused on the design and assembly of lanthanide complexes with organic ligands such as β-diketone, cryptands, calixarenes, etc. [5–10]. Due to the tendency to form the dimeric or infinite chain polymeric structures, which win an advantage over other ligands in extraction, separation, germicide preparation, catalysis, luminescence and functional material preparation, more researches have concentrated on the lanthanide complexes with aromatic carboxylic acids and heterocyclic ligands, which show higher thermal or luminescent stabilities than β-diketone systems. Yan and Song put more emphasis on the Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+} and Gd^{3+} complexes with 2,2′-bipyridine-*N*,*N*′-dioxide [11,12], 5-bromonicotinic acid [13], 2,6-pyridine dicarboxylic acid and phthalate, [14,15], etc., corresponding coordination behavior and symmetry of central metal ions were investigated especially the outstanding luminescence properties were discussed. In this research, we attempt to select an unsaturated carboxylic acid derivative, maleic anhydride instead of general aromatic carboxylic acid to study its “antenna effect”, excellent emissions of lanthanide ions were obtained because the introduction of the second ligand, i.e. 1,10-phenanthroline which contains a large conjugate π-bond system changes the distribution of π-electronic density in the complexes even leads to the change of bond strength and distances of “RE-ligand”. In addition, owing to the necessity of the Langmuir–Blodgett films, which depend on the film formation and luminescence of the concerned molecules, we have modified the maleic anhydride by 1-eicosanol in order to apply them in integrated and molecular electronics as well as biosensors or biochemical probes.

2. Experimental

Synthesis of maleic monoester by the modification of maleic anhydride: maleic anhydride (0.98 g/10 mmol) was

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reacted with equivalent 1-eicosanol (2.98 g) directly at 110 °C under stirring for 15 h. Then cold hexane was added to precipitate the pale-yellow powder. Recrystallizing twice, gives the sample white powder mono-eicosyl *cis*-butene dicarboxylate. Anal. calcd. for $C_{24}H_{43}O_4$: C 72.91, H 10.87; found: C 72.67; H 11.03.

Synthesis of lanthanide complexes was as follows: the lanthanide oxides (Eu_2O_3, Tb_4O_7, Gd_2O_3, Dy_2O_3) were converted to their nitrates by treatment with concentrated nitric acid. The corresponding lanthanide complexes with this ligand were prepared by homogeneous precipitation. Alcohol solution of lanthanide nitrates was added very slowly to the alcohol solutions of mono-eicosyl *cis*-butene dicarboxylate (MAE). An hour later, 1,10-phenanthroline was introduced to the solutions. Then, white precipitates appeared and were filtered off, washed with ethanol, dried in a vacuum. Four binary lanthanide (Eu, Tb, Dy, Gd) complexes (without 1,10-phenanthroline) and four ternary lanthanide (Eu, Tb, Dy, Gd) complexes were prepared (as shown in Fig. 1). The compositions of the complex systems were confirmed by elemental analysis: binary complexes $Ln(MAE)_3$, Ln = Eu, Tb, Dy, Gd; anal. calcd. for $C_{72}H_{129}EuO_{12}$: C 64.62, H 9.65; found: C 64.77, H 9.55; for $C_{72}H_{129}TbO_{12}$: C 64.29, H 9.60; found: C 64.39, H 9.21; for $C_{72}H_{129}DyO_{12}$: C 64.14, H 9.58; found: C 64.29, H 9.33; for $C_{72}H_{129}GdO_{12}$: C 64.38, H 9.61; found: C 64.43, H 9.42; ternary complexes $Ln(MAE)_3phen$, Ln = Eu, Tb, Dy, Gd. Anal. calcd. for $C_{84}H_{139}EuN_2O_{13}$: C 65.67, H 9.05, N 1.82; found: C 65.77, H 8.55, N 1.68. For $C_{84}H_{139}TbN_2O_{13}$: C 65.37, H 9.01, N 1.82; found: C 65.39, H 8.61, N 1.56. For $C_{84}H_{139}DyN_2O_{13}$: C 65.24, H 9.0, N 1.81; found: C 65.29, H 8.2, N 1.77. For $C_{84}H_{139}GdN_2O_{13}$: C 65.45, H 9.03, N 1.82; found: C 65.43, H 8.96, N 1.78.

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 (5×10^{-5} mol L^{-1} acetone solution) were obtained with an Agilent 8453 spectrophotometer. Low temperature phosphorescence spectrum (5×10^{-5} mol L^{-1} acetone solution) was determined by Perkin-Elmer LS-55 spectrophotometer under 77 K. The fluorescence (excitation and emission) spectra were measured with Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm.

3. Results and discussion

Fig. 2 shows the FT-IR spectra of (A) maleic anhydride, (B) MAE, (C) Tb–MAE–phen and (D) 1,10-phenanthroline. The peak at 1783 cm^{-1} of (A) presents the stretching vibration of C=O and band at 3130 cm^{-1} corresponds to stretching vibration of C–H, which belong to the backbone of maleic anhydride. While in (B), ν_{CH} of the long carbon chains changes to 2918 cm^{-1} and proves that the 1-eicosanol was successfully grafted to maleic anhydride Additionally, the peak at 1739 cm^{-1} substantiates that the absorption of C=O was affected by the long chain group –OR. So far as the ternary complex (C) is concerned, the occurrence of complexation between Tb^{3+} and MAE is evidenced by a new narrow band located at 1384 cm^{-1} appeared to prove that terbium ions may coordinate to two oxygen atoms of the free carboxylic groups. Compared (C) with (D), the twisting bending vibrations of (D) at 854 and 740 cm^{-1}, which correspond to absorption of hydrogen atoms belong to heterocycle of 1,10-phenanthroline have almost disappeared in (C) and the facts firmly prove 1,10-phenanthroline can coordinate to terbium ions effectively. Likewise Eu, Dy systems present similar results.

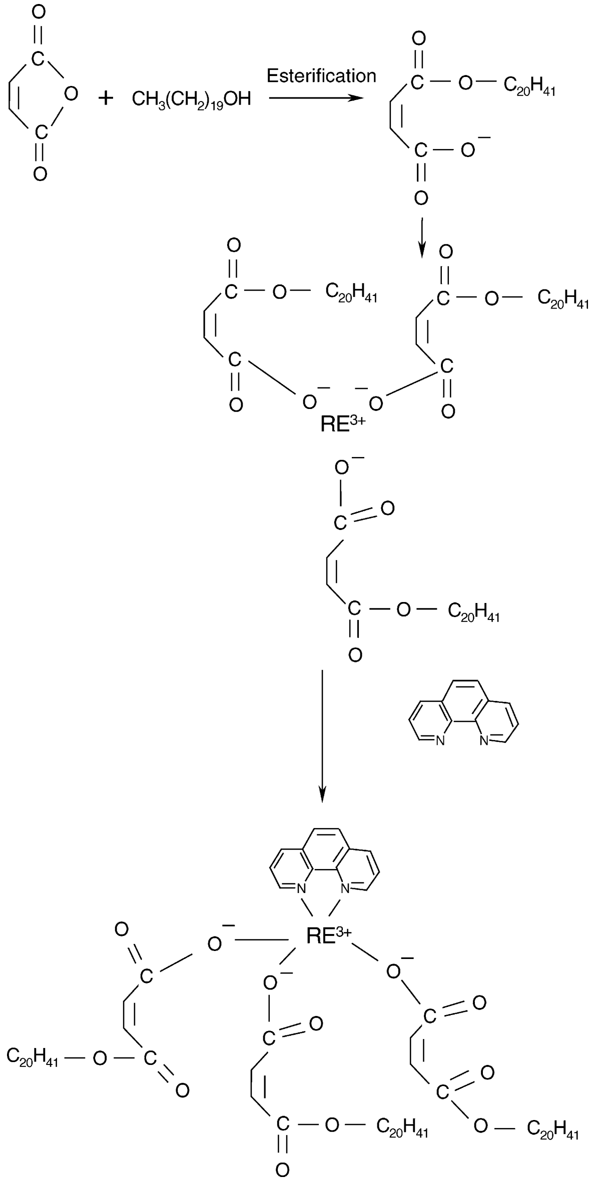

Fig. 1. Preparation scheme of both mono-eicosyl *cis*-butene dicarboxylate and ternary complex of RE–MAE–phen.

Fig. 3 exhibits ultraviolet absorption spectra of (A) maleic anhydride, (B) MAE and (C) Tb–MAE–phen complex. From

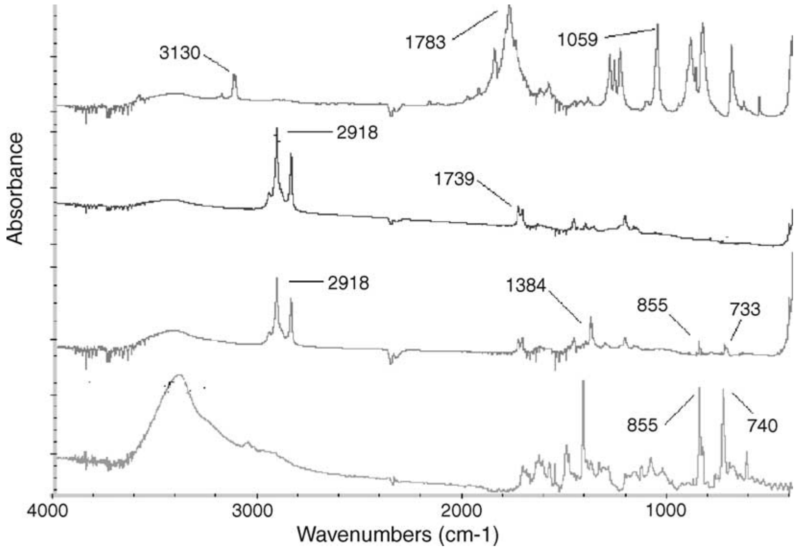

Fig. 2. FT-IR spectra of (A) maleic anhydride (B), MAE (C) Tb–MAE–phen and (D) 1,10-phenanthroline.

the spectra, it is observed that there are nearly no difference between (A) and (B) (243 → 242 nm), because they have the same chromophore C=C and similar π–π^* transitions influenced by conjugating effect of both C=C and C=O groups. As for (C), the obvious band at 266 nm shows characteristic absorption of 1,10-phenanthroline, which can be ascribed as the absorption of phen for free phen appears one absorption peak at 265 nm [15]. The small red-shift of 1 nm is due to the more extensive conjugated system of electronic distribution form because the coordination between lanthanide ions and phen. Therefore, in the ternary complex Tb–MAE–phen, 1,10-phenanthroline plays a major energy donor role and will transfer it to Tb ions.

Figs. 4 and 5 provide further evidences concerning the above predictions, the former gives the ultraviolet absorption

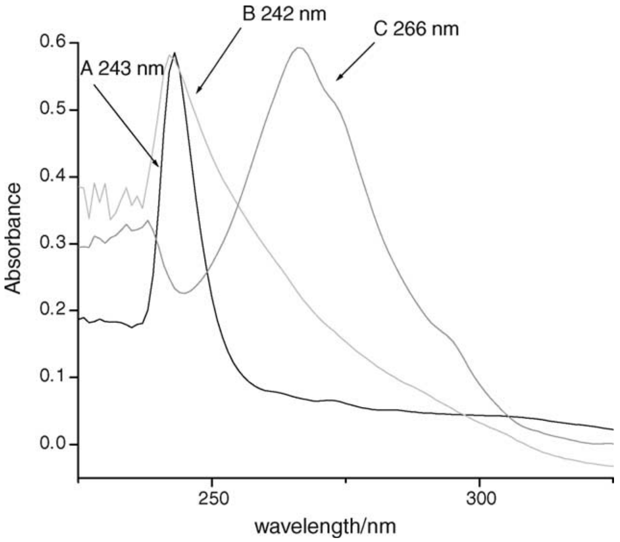

Fig. 3. The ultraviolet absorption spectra of (A) maleic anhydride, (B) MAE and (C) Tb–MAE–phen complex (5×10^{-5} mol L^{-1} acetone solution).

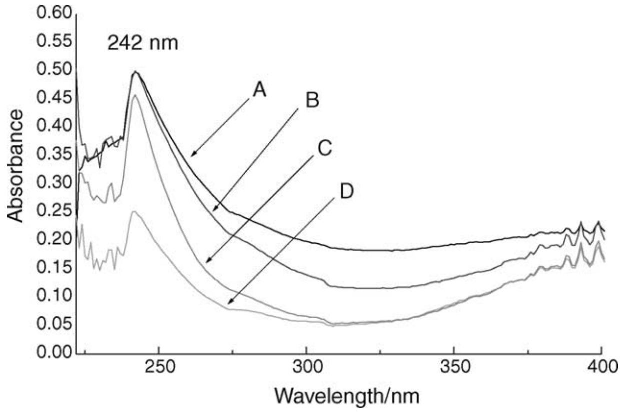

Fig. 4. The ultraviolet absorption spectra of (A) Eu–MAE binary complex, (B) Tb–MAE binary complex, (C) Dy–MAE binary complex and (D) Gd–MAE binary complex (5×10^{-5} mol L^{-1} acetone solution).

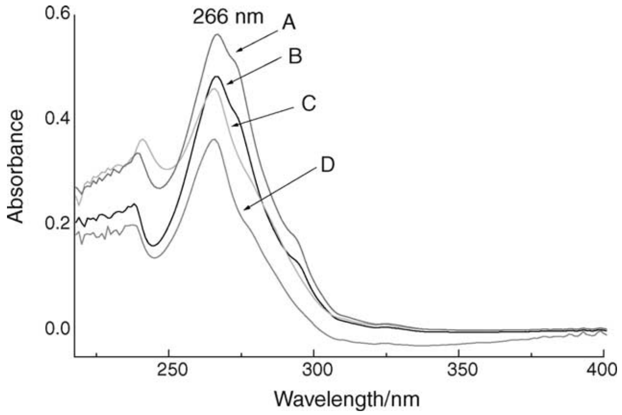

Fig. 5. The ultraviolet absorption spectra of (A) Eu–MAE–phen ternary complex, (B) Tb–MAE–phen ternary complex, (C) Dy–MAE–phen ternary complex and (D) Gd–MAE–phen ternary complex (5×10^{-5} mol L^{-1} acetone solution).

spectra of (A) Eu–MAE binary complex, (B) Tb–MAE binary complex, (C) Dy–MAE binary complex and (D) Gd–MAE binary complex and the latter represents similar ultraviolet absorption spectra with exception that ternary complexes of 1,10-phenanthroline take place of those binary ones. We can safely find in Fig. 4, the four binary complexes exhibit nearly the same peaks (242 nm) indicating that MAE develops a dominating function in binary systems and its π–π^* transition corresponds to the strongest absorption. While in Fig. 5, the major energy donor role of 1,10-phenanthroline was firmly proved by the unanimous absorption bands at 266 nm.

So far as Fig. 6 is concerned, it provides the phosphorescence spectra of (A) Gd–MAE complex, (B) Gd–1,10-phenanthroline complex and (C) Gd–MAE–1,10-phenanthroline ternary complex. We can observe that (B) and (C) are rather similar in terms of the same organic ligand 1,10-phenanthroline responsible for the emissions. According to the energy transfer and intramolecular energy mechanism [16–18], 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 [19]; the second one is just an inverse energy transfer by a thermal deactivation mechanism [20]. Established on this theory, the conclusion can be drawn that energy differences is of opposite influence on the two energy transfer processes and an optimal value can be assumed to exist. The peak at 421 nm of (A) shows MAE's triplet state energy level is approximately 23,753 cm^{-1}, which is higher than 1,10-phenanthroline (453 nm, 22,075 cm^{-1}); therefore, we suppose that energy transfer process will occur from MAE to 1,10-phenanthroline, substantiating that the heterocyclic ligand will become main energy donor and have the possibility to sensitize RE^{3+} ions.

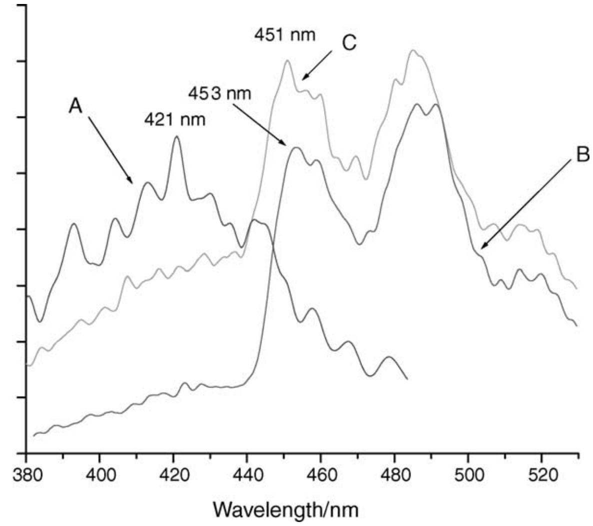

Fig. 6. The phosphorescence spectra of (A) Gd–MAE complex, (B) Gd–1,10-phenanthroline complex and (C) Gd–MAE–1,10-phenanthroline ternary complex (5×10^{-5} mol L^{-1} acetone solution).

The excitation and emission spectra of the resulting complexes are shown in Figs. 7–9. The influence of 1,10-phenanthroline can be illustrated by comparing lanthanide binary complexes with corresponding ternary molecules. As described in Fig. 7 (a: Eu–MAE and b: Eu–MAE–phen), it was observed that the emission of (a) consists of a broad band without any distinctions between $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ions, whereas in ternary complex system, the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions at 590, 614, 650 and 700 nm of Eu^{3+} were obviously obtained and strong red emission ($^5D_0 \rightarrow {}^7F_2$) was dominating. In regard to Fig. 8 (a: Tb–MAE and b: Tb–MAE–phen), there are nearly no characteristic emissions existing in binary complex (a), while (b) gives four assigned transitions from the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions at 490, 544, 587 and 622 nm of terbium ions and a striking green luminescence ($^5D_4 \rightarrow {}^7F_5$) was accomplished. Fig. 9 (a: Dy–MAE and b: Dy–MAE–phen) shows comparison of both binary and ternary complexes of Dy ions. Through the sensitization of 1,10-phenanthroline, $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2) transitions at 481 and 574 nm corresponding to Dy^{3+} were obtained especially the blue emission ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) was relatively strong. Anyway, after the introduction of the second organic ligand, the effective energy transfer took place between the phen–MAE and the chelated RE ions. We

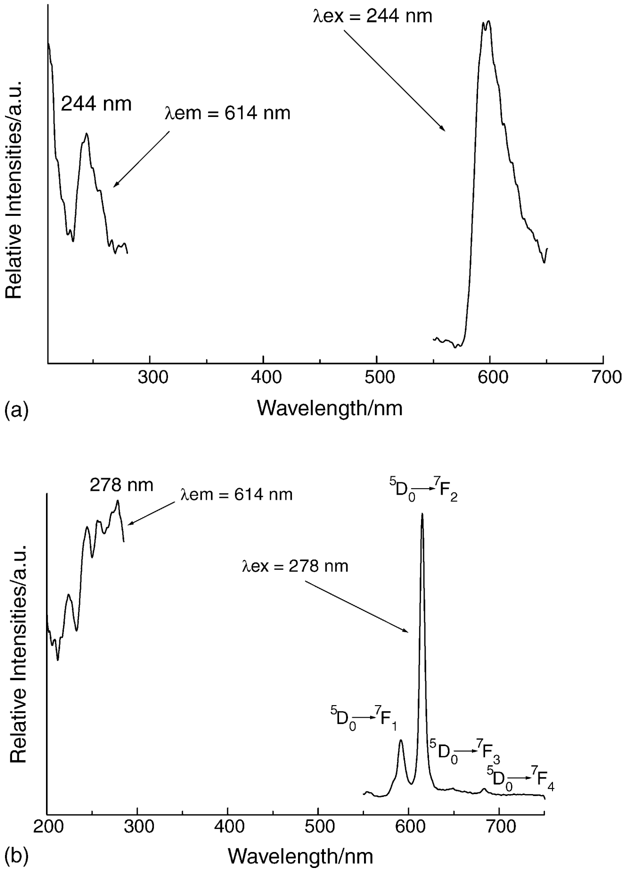

Fig. 7. The excitation and emission spectra of both Eu–MAE (a) and Eu–MAE–phen (b).

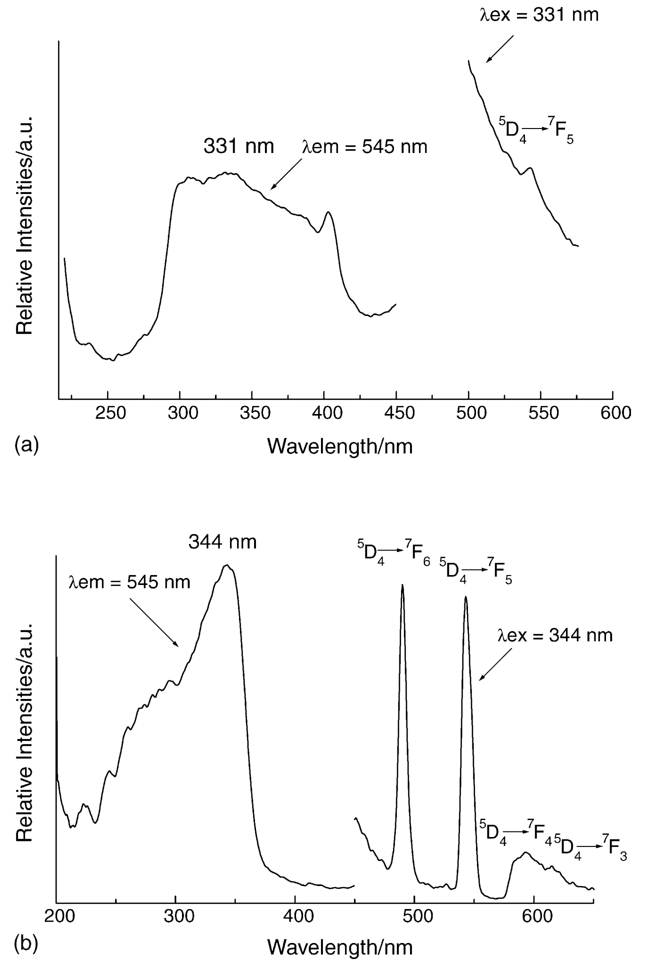

Fig. 8. The excitation and emission spectra of both Tb–MAE (a) and Tb–MAE–phen (b).

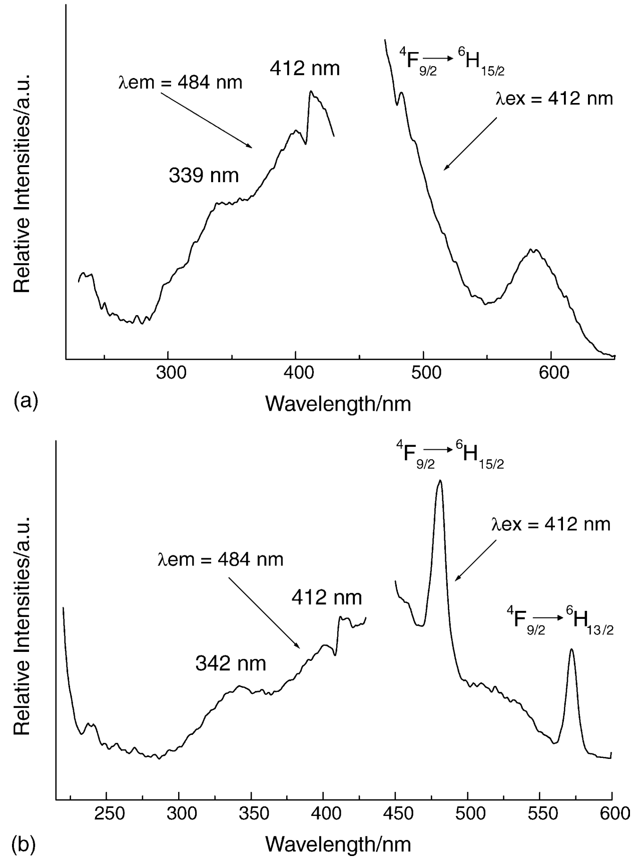

Fig. 9. The excitation and emission spectra of both Dy–MAE (a) and Dy–MAE–phen (b).

further determined the luminescent relative intensities and lifetimes for the ternary complexes and binary complexes of phen, the detailed data have been shown in Table 1. The relative emission intensities of ternary complexes show the similar order to those of corresponding binary ones of phen, indicating that the effective energy transfer and sensitization take place between phen and lanthanide ions in the ternary systems. Especially the luminescent lifetimes of ternary complexes are higher than those of binary one with phen, which suggest that the introduction of long chain monoester in the ternary molecular systems enhances the rigidity and stability of the whole complex and reduces the non-radiative energy loss compared the binary systems of phen.

Table 1
Luminescence relative intensities and lifetimes for ternary lanthanide complexes with mono-eicosyl *cis*-butene dicarboxylate and 1,10-phenanthroline

Ternary complexes	Relative luminescence intensities (a.u.)	Luminescence lifetimes (μs)
Eu–MAE–phen	180	1420
Eu–phen	168	910
Tb–MAE–phen	200	1540
Tb–phen	174	810
Dy–MAE–phen	70	1300
Dy–phen	64	770

4. Conclusions

Eight binary and ternary lanthanide (Eu, Tb, Dy, Gd) complexes with mono-eicosyl *cis*-butene dicarboxylate have been synthesized and characterized. The photophysical properties of them have been studied with ultraviolet spectra, phosphorescence spectra, excitation and emission spectra, and luminescent lifetimes. The energy transfer process initiated from mono-eicosyl *cis*-butene dicarboxylate to 1,10-phenanthroline then to lanthanide ions (Eu^{3+}, Tb^{3+}, Dy^{3+}) has been discussed to predict that the optimum energy transfer exists between the heterocyclic ligand and RE^{3+}. The emission spectra for the three ternary complexes were described in detail and the results indicate that lanthanide complex show the extraordinarily strong luminescence (trichromatism, red, green and blue) especially compared to binary complex molecules with low radiate efficiency. Furthermore, the RE–maleic-20-ester–phen complexes, which were equipped with long carbon chains, will have the potential application to fabricate LB films with trichormatism and higher stability.

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