Available online at www.sciencedirect.com

ScienceDirect

Spectrochimica Acta Part A 65 (2006) 907–911

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Preparation and photoluminescence of a novel β-diketone ligand containing electro-transporting group and its europium(III) ternary complex

Neng-Jun Xiang [a,b], Louis M. Leung [b], Shu-Kong So [b], Meng-Lian Gong [a,*]

[a] State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

[b] Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Kowloon Tong, Kowloon, Hong Kong, China

Received 27 September 2005; received in revised form 22 January 2006; accepted 23 January 2006

Abstract

A novel β-diketone with an electro-transporting oxadiazole group, 1-(4′-(5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl)biphenyl-4-yl)-4,4,4-trifluorobutane-1,3-dione (MPBDTFA), was prepared with high yield. With this synthesized ligand as the first ligand and 1,10-phenanthroline (Phen) as the secondary ligand, a new europium(III) ternary complex, Eu(MPBDTFA)$_3$Phen, was synthesized. The new β-diketone and its europium(III) ternary complex were characteristized by elemental analysis, thermo-gravimetric analysis, IR and UV–visible spectroscopies. Photoluminescence measurements indicated that the energy absorbed by the organic ligands was efficiently transfered to the central Eu^{3+} ions, and the complex showed intensely and characteristically red emissions due to the $^5D_0 \rightarrow {}^7F_j$ transitions of the central Eu^{3+} ions. With an electro-transporting group in molecule and highly thermal stability, the synthesized Eu(III) ternary complex is expected as a red-emitting candidate material for fabrication of organic light-emitting diodes (OLEDs).

Keywords: Optical material; Europium organic complex; Electro-transporting group; Luminescence

1. Introduction

Europium(III) complex-based electroluminescence (EL) devices were pioneered by Kido et al. [1] in 1991 and recently attracted great interest due to their sharp emission peak with typical bandwidths of 5–10 nm at ~610 nm. This made Eu(III) complexes one of the promising candidates for full color flat-panel displays which require pure red, green and blue emissions. Since subtle changes in the molecular structures of the Eu(III) complexes could dramatically tune the photoluminescence (PL) and electroluminescence (EL) properties, the development of new Eu(III)–β-diketonate mixed ligand complexes for the light-emitting layers of the EL devices is an attract research activity [2–4]. To fabricate an organic electroluminescence device (OLED), the research efforts include designs and synthesis of new β-diketones and neutral second ligands, incorporating electron-transporting and hole-transporting groups into one Eu(III) complex molecule [5–8]. The other way of improving EL performance is to develop multilayer EL devices by using TPBD or Alq$_3$ as electro-transporting layer. However, this is a tedious process and is difficult to select the appropriate thicknesses of different layers to optimize the devices. Therefore, highly efficient and pure red EL devices based on Eu(III) organic complexes are facing a new challenge.

In this work, a novel β-diketone with an electro-transporting group (oxadiazole moiety), 1-(4′-(5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl)biphenyl-4-yl)-4,4,4-trifluorobutane-1,3-dione (MPBDTFA), was designed and synthesized. With this β-diketone as the first ligand and 1,10-phenanthroline (Phen) as the second ligand, a new europium(III) ternary complex, Eu(MPBDTFA)$_3$Phen, was synthesized. The functional moiety oxadiazole and Eu^{3+} ion are expected to respectively retain their own electron-transporting and emission properties. The photoluminescence and thermal stability of the oxadiazole functionalized europium(III) complex were investigated. The photoluminescence of the complex Eu(MPBDTFA)$_3$Phen was compared with that of the complex Eu(TTA)$_3$Phen, where TTA$^-$ is thenoyltrifluoroacetonate.

---

[*] Corresponding author. Tel.: +86 20 84112830; fax: +86 20 84112245.
E-mail address: cesgml@zsu.edu.cn (M.-L. Gong).

1386-1425/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2006.01.030

2. Experimental

2.1. Apparatus and measurements

All the starting materials are analytical reagent grade without further purification. Solvents were freshly distilled and dried by standard methods. Elemental analysis for the synthesized ligand and complex were carried out with an Elementar vario EL elemental analyzer. IR spectra in the region 4000–400 cm^{-1} were recorded on a Bruker infrared spectrophotometer using conventional KBr method. FAB-MS spectra were performed on a VG ZAB-HS spectrometer. ^1H NMR spectra were recorded on a JEOL FT-NMR270 spectrometer. Electronic absorption spectra were recorded on a Varlan UV–vis spectrophotometer. Thermo-gravimetric analysis (TGA) was carried out up to 900 °C in N_2 atmosphere on a Perkin-Elmer TGA6 thermo-gravimetric analyzer. Excitation spectra, emission spectra, fluorescence lifetimes and quantum yield were measured with a Photo Technology International Fluorescence Life time Scanning spectrometer. The relative emission intensity was recorded from the highest emission peak under the optimum excitation wavelength.

2.2. Syntheses of MPBDTFA and its europium(III) ternary complex Eu(MPBDTFA)$_3$Phen

The synthetic routines of MPBDTFA and the europium(III) ternary complex Eu(MPBDTFA)$_3$Phen are shown in Fig. 1.

*2.2.1. Synthesis of 5-p-tolyl-2H-tetrazole (**1**)*

According to the method described in literature [9], 30 g 4-methylbenzonitrile, 200 mL of water, 20 g sodium azide and 20 g zinc chloride were added to a three-necked 500 mL round bottomed flask. The reaction solution was refluxed for 24 h with vigorous stirring. After the mixture was cooled to room temperature, the pH value was adjusted to 1.0 with concentrated HCl, and the solution was stirred for 30 min to form a solid precipitate. The new precipitate was then filtered, washed with 1 mol/L HCl, and dried in a drying oven at 90 °C overnight to give 33.6 g of 5-*p*-tolyl-2H-tetrazole as a white powder, the crude product was recrystallized in ethanol (82% yield). MS(FAB): 161 ($M^+ + 1$).

*2.2.2. Synthesis of 2-(4-biphenyl)-5-(4-methyl-phenyl)-1,3,4-oxadiazole (MPBD, **3**)*

Thirty milliliter thionyl chloride was added to 10 g (50 mmol) 4-biphenylcarboxylic acid and the mixture was refluxed for 24 h. The solution was concentrated to 5 mL under reduced pressure and then dry benzene (20 mL) was added. The benzene was removed also under reduced pressure later. Fifty milliliter dry pyridine was added to the residue and then stirred until dissolved. 5-*p*-tolyl-2H-tetrazole (8.53 g, 52 mmol) in 50 mL dry pyridine was added drop by drop into the mixture, and then refluxed for 2 days. The crude product was concentrated under reduced pressure, then was recrystallized in ethanol, giving 14.2 g product (90% yield). MS (FAB): 313 ($M^+ + 1$).

*2.2.3. Synthesis of 2-[4-(4′-acetylbiphenyl)]-5-(4-methyl-phenyl)-1,3,4-oxadiazole (**4**)*

Acetyl chloride (9 mL, 131.6 mmol) and aluminum chloride (13 g, 98 mmol) were mixed with 100 mL of dry methylene chloride in a 250 mL Schlenk flask. The solution was stirred at room temperature for 10 min, then was droped into a 500 mL Schlenk flask containing 10 g (32 mmol) MPBD and 100 mL methylene chloride equipped with a magnetic stirring bar and a nitrogen

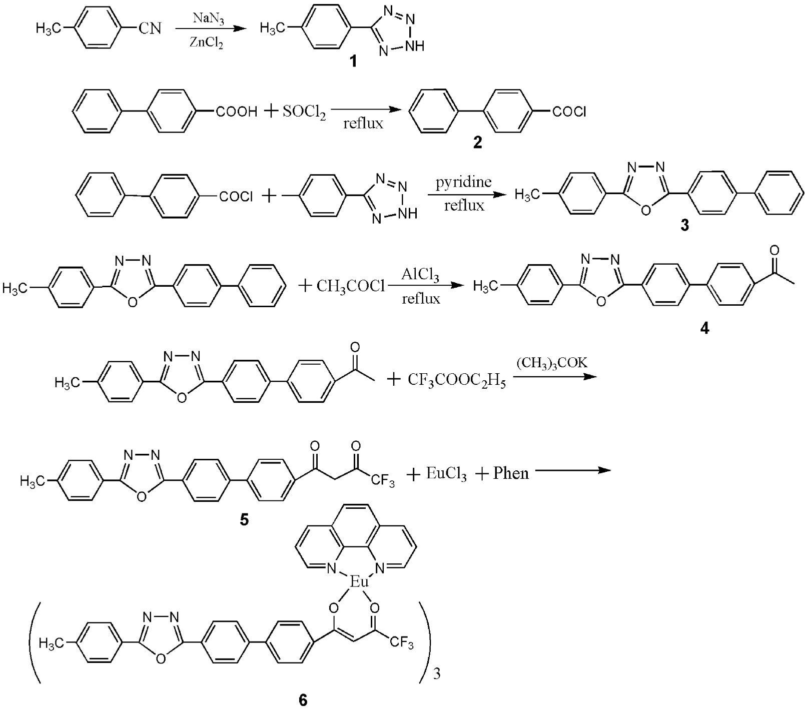

Fig. 1. Synthetic routines of the compounds.

outlet leading to an oil bubbler. The mixture was stirred at ice-water bath for 1 h and refluxed 5 h, then was hydrolyzed by slow addition of 50 mL of water containing 20 mL of concentrated hydrochloric acid. Two layers, aqueous and organic, appeared, then the aqueous layer was extracted with methylene chloride and the combined organic layer was washed with water. The solvent was removed under reduced pressure and the crude product was recrystallized in ethanol, giving 9.8 g product (87% yield). ^{1}H NMR($CDCl_3$): δ (ppm) 8.203–8.234 (d, 2H), 8.016–8.072 (t, 4H), 7.718–7.792 (t, 4H), 7.240–7.349 (d, 2H), 2.647 (s, 3H, –$COCH_3$), 2.439 (s, 3H, Φ–CH_3). MS(FAB): 355 ($M^+ + 1$).

*2.2.4. Synthesis of 1-(4′-(5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl)biphenyl-4-yl)-4,4,4-trifluorobutane-1,3,-dione (MPBDTFA, **5**)*

2-[4-(4′-acetylbiphenyl)]-5-(4-methyl-phenyl)-1,3,4-oxadiazole (5 g, 15 mmol), $CF_3COOC_2H_5$ (7.95 g, 28 mmol), and dry benzene (150 mL) was added into a 250 mL flask. 1.9 g (16.8 mmol) potassium *tert*-butoxide was added to the flask and the reaction mixture was heated at 45 °C for 4 h. After cooling, the reaction solution was poured into a mixture of 150 mL ice-water and 20 mL of concentrated hydrochloric acid. The organic layer was washed twice with water, then the solvent was removed under reduced pressure. The crude product was recrystallized in toluene, giving 5.40 g product (85% yield). The elemental analysis data for MPBDTFA ($C_{25}H_{17}F_3N_2O_3$) were: found (calculated)/%: C 66.53 (66.67), H 3.96 (3.80), and N 6.17 (6.22). ^{1}H NMR($CDCl_3$): δ (ppm) 8.240–8.270 (d, 2H), 8.038–8.088 (t, 4H), 7.786–7.817 (t, 4H), 7.343–7.373 (d, 2H), 6.633 (s, 1H), 2.461 (s, 3H, –CH_3). MS (FAB): 451 ($M^+ + 1$).

*2.2.5. Preparation of the complex, tri (1-(4′-(5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl)biphenyl-4-yl)-4,4,4-trifluorobutane-1,3,-dione)(1,10-phenanthroline)-europium(III) (Eu(MPBDTFA)$_3$Phen, **6**)*

1.6 g (3.6 mmol) MPBDTFA dissolved in 50 mL toluene/ethanol (1:1) was added into an aqueous solution containing 1.2 mmol $EuCl_3$, which was obtained by reaction of Eu_2O_3 (99.5%, Zhu-jiang smeltery Co.) and HCl (6.0 mol/L). The pH value of the mixture was adjusted to 6.0–7.0 by adding an aqueous solution of sodium hydroxide and then 0.22 g 1,10-phenanthroline (Phen, 1.2 mmol) was added into the reaction mixture. The reaction mixture was stirred 24 h at 60 °C. Twelve hour later, a white precipitate deposited from the solution, and was filtered out and washed with deionized water and toluene/ethanol (1:1). Eu(MPBDTFA)$_3$Phen solid complex was obtained and dried in vacuum at 80 °C for 24 h, giving 1.58 g product (85% yield). The elemental analysis data for Eu(MPBDTFA)$_3$Phen ($EuC_{87}H_{56}F_9N_8O_9$) were: found (calculated)/%: C 62.35 (62.23), H 3.56 (3.36), and N 6.52 (6.67).

2.3. Preparation of the complex, tri(thenoyltrifluoroacetonate) (1,10-phenanthroline) europium, Eu(TTA)$_3$Phen

Eu(TTA)$_3$Phen was synthesized according to the same method described in Section 2.2.5. The elemental analysis data for Eu(TTA)$_3$Phen ($EuC_{36}H_{20}F_9N_2O_6S_3$) were: found (calculated)/%: C 43.65 (43.45), H 2.16 (2.04), and N 2.92 (2.81).

3. Results and discussion

3.1. IR absorption spectrum of Eu(MPBDTFA)$_3$Phen

The main IR absorption bands of the europium(III) ternary complex were assigned according to reference [10]. One thousand five hundred and twenty-two per centimeter vibration band is characteristic for MPBDTFA$^-$ ligand coordinated to Eu^{3+} central ion. This shows that the –C=O band in the free ligand was weaken by C–O–Eu and C=O–Eu resonance structure in the complex. New weak absorption bands at 518 and 436 cm^{-1} were ascribed to Eu–N and Eu–O vibrations, respectively. One thousand five hundred and fifty per centimeter was ascribed to the skeleton vibration of the phenanthroline ring. All these evidences indicate that the MPBDTFA$^-$ and Phen ligands coordinated to the central Eu^{3+} ion via the C=O and N–N groups.

3.2. Thermal stability of Eu(MPBDTFA)$_3$Phen

Materials applied in fabrication of OLEDs are required to have high thermal stability (high melting point and high decomposition temperature). Thermo-gravimetric analysis (TGA) showed that the decomposition temperature of the complex is 363.4 °C. Rare earth organic complexes with such high thermal stability are seldom found, which is favourable to fabrication of OLED by vacuum-coating with the Eu^{3+} complex as emitter material.

3.3. UV absorption spectra

The electronic absorption spectra for 1.0×10^{-5} mol/L MPBDTFA, Phen and Eu(MPBDTFA)$_3$Phen in dichloromethane solution were shown in Fig. 2. The absorption band for Eu(MPBDTFA)$_3$Phen complex shifted to longer wavelength and

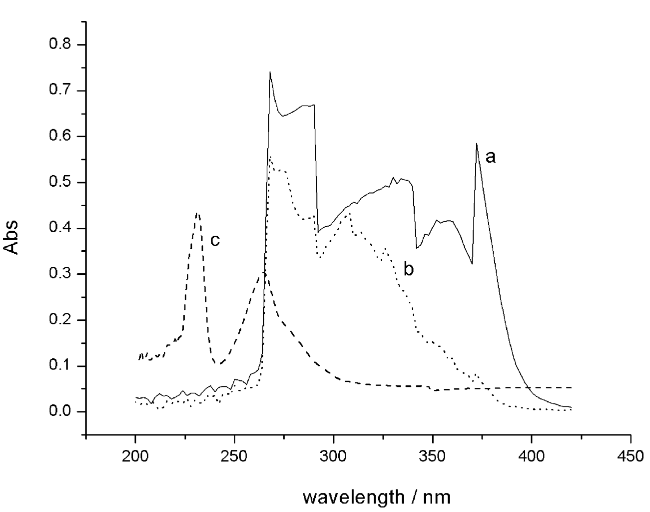

Fig. 2. Absorption spectra of the ligands and the Eu^{3+} complex in dichloromethane (1×10^{-5} mol/L) (a) Eu(MPBDTFA)$_3$Phen; (b) MPBDTFA; (c) Phen.

was broader than that for MPBDTFA and Phen ligands due to the extension of the conjugated system after coordination. Strong and broad absorption bands appear at about 265–380 nm for the complex. Comparison of the three absorption curves showed that both the ligands contribute to the absorption of the complex, and the absorbed energy of the Eu(III) ternary complex mainly originates from the first ligand, MPBDTFA$^-$, and the absorption from the secondary ligand Phen only plays a secondary role. However, existence of the secondary ligand satisfies the high coordination number of 8 of the central Eu^{3+} ion and improves the coordination stability of the complex.

3.4. *The lowest triplet state energy level of the ligand MPBDTFA*

Phosphorescence spectrum for 1×10^{-5} mol/L ethanol: CHCl$_3$ (1:1) solution of the corresponding Gd(III) binary complex with the ligand MPBDTFA was measured at 77 K. The excitation wavelength used to obtain the phosphorescence spectrum was set at the maximum UV-absorption wavelength of the Gd(III) complex ($\lambda_{ex} = 346$ nm). The lowest excited state energy level of Gd^{3+} ion ($^6P_{7/2}$, $\sim$32000 cm^{-1}) is much higher than the T_1 (L) of MPBDTFA ligand, and the energy cannot be transferred to the central gadolinium(III) ion from the ligand. So phosphorescence emission from MPBDTFA ligand was observed for Gd(III)–MPBDTFA binary complex while no Gd^{3+} ion luminescence was found. The lowest triplet state energy of the ligand MPBDTFA was determined by the shortest wavelength transition in the phosphorescence spectrum to be 24277 cm^{-1} (411.9 nm), which is higher by 6977 cm^{-1} than the lowest excited state of Eu^{3+}, $^5D_0$ (17300 cm^{-1}), and is matched with the latter, so in the corresponding europium(III) complex the ligand strongly sensitizes the luminescence of Eu^{3+} [11] (see Section 3.5).

3.5. *Fluorescence spectra and quantum yield*

The excited spectrum (Fig. 3a) monitored at 612 nm for the Eu(MPBDTFA)$_3$Phen powder showed two excitation bands: one is located at 260–320 nm mainly due to phenanthroline (the secondary ligand) absorption, and another centered at 389 nm is very intense and is contributed by the first ligand MPBDTFA since its molecule has of an expanded π-conjugated system (see Fig. 1). Under 389 nm UV light excitation, the emission spectrum for ligand MPBDTFA (Fig. 3c) showed one blue emission band centered at 450 nm while the emission spectrum for the Eu^{3+} complex (Fig. 3b) showed multiple emission bands due to Eu^{3+} $^5D_0 \rightarrow {}^7F_j$ transitions with the strongest peak at 612 nm ($^5D_0 \rightarrow {}^7F_2$). The sharp peak suggests high color purity for Eu(MPBDTFA)$_3$Phen complex. Comparison of the emission of the MPBDTFA ligand (Fig. 3c) with that of the Eu(MPBDTFA)$_3$Phen complex (Fig. 3b) indicated that the ligand emission completely disappeared in the complex, and the energy transfer from the MPBDTFA ligand to the central Eu^{3+} ion was very efficient.

The excited spectrum (Fig. 3d) monitored at 610 nm for the Eu(TTA)$_3$Phen powder showed two excitation bands: one is located at 265–300 nm mainly due to phenanthroline (the secondary ligand) absorption, and another centered at 365 nm is very intense and is contributed by the first ligand TTA$^-$. Under 365 nm light excitation, Eu(TTA)$_3$Phen powder showed multiple emission bands (Fig. 3e) due to Eu^{3+} $^5D_0 \rightarrow {}^7F_j$ transitions with the strongest peak at 610 nm ($^5D_0 \rightarrow {}^7F_2$). Comparison of the emission spectra of the Eu(MPBDTFA)$_3$Phen (Fig. 3b) and the Eu(TTA)$_3$Phen (Fig. 3e) powder showed that the fluorescence intensity for Eu(TTA)$_3$Phen is a little stronger than that of Eu(MPBDTFA)$_3$Phen under the optimum near-UV light excitation. However, existence of an electro-transporting oxadiazole group in Eu(MPBDTFA)$_3$Phen molecule is favourable to fabrication of OLED.

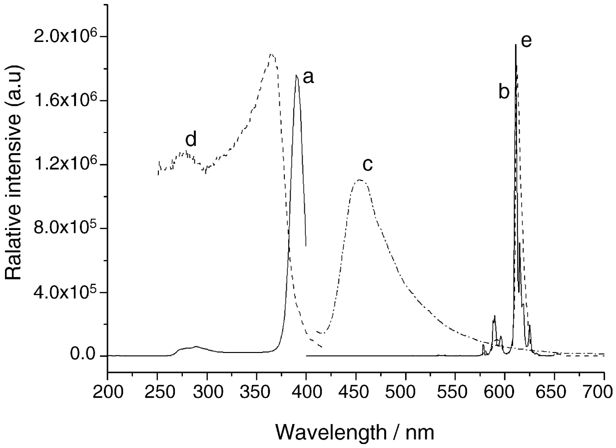

Fig. 3. Excitation (Ex) and emission (Em) spectra. (a) Ex of the complex Eu(MPBDTFA)$_3$Phen ($\lambda_{em} = 612$ nm); (b) Em of the complex Eu(MPBDTFA)$_3$Phen ($\lambda_{ex} = 389$ nm); (c) Em of the MPBDTFA ($\lambda_{ex} = 389$ nm); (d) Ex of the complex Eu(TTA)$_3$Phen ($\lambda_{em} = 610$ nm); (e) Em of the complex Eu(TTA)$_3$Phen ($\lambda_{ex} = 365$ nm).

The photoluminescence mechanism for an Eu^{3+} organic complex can be explained as follows: (1) energy of exciting UV light is absorbed by the ligands; (2) the excited ligands decay rapidly to their lowest triplet state; (3) the energy is transferred from the triplet state of the ligands to the quasi-resonant energy state of the Eu^{3+} ion (the Dexter process); (4) the excited europium ion decays to the ground state via photo emissions in the visible region. The step (3) is crucial in determining the 4f–4f emission quantum yield. The match relationship between the lowest triplet state energy level of the ligand MPBDTFA$^-$ and the lowest excited state level of Eu^{3+}, $^5D_0$ (Section 3.4) is favourable to the energy transfer from the ligand to Eu^{3+}. The overall luminescence quantum yield (φ_{lum}) is in principle determined not only by the luminescence efficiency of europium ion itself (φ_{Eu}), but also by the quantum yields of the intersystem crossing (φ_{ISC}) and the energy transfer steps (φ_{ET}). Thus, get an equation [12], namely

$$\varphi_{lum} = \varphi_{ISC}\varphi_{ET}\varphi_{Eu}$$

The luminescence quantum yield for the Eu^{3+} ternary complexes Eu(MPBDTFA)$_3$Phen and Eu(TTA)$_3$Phen were determined to be $\varphi = 0.14$ and 0.17 with a reference solution of quinine sulfate in 0.5 mol/L sulfuric acid ($\varphi = 0.546$) and were corrected by the refractive index of the solvent at 298 K. The luminescence

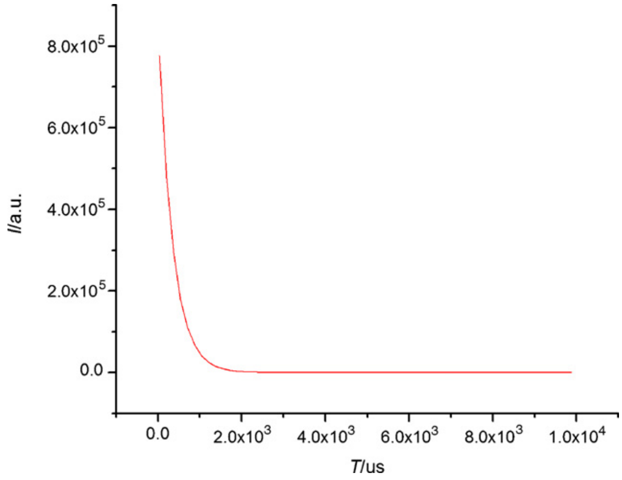

Fig. 4. The decay curve of Eu^{3+} $^5D_0$ excited state for $Eu(MPBDTFA)_3Phen$.

quantum yield is high in rare earth organic complexes, suggesting the synthesized complex is an excellent photoluminescent red-emission material.

3.6. *Excited state lifetime of the Eu^{3+} complex*

The lifetime measurements for the excited state $^5D_0$ of the Eu(III) ion were recorded for the complex $Eu(TPBDTFA)_3Phen$ (Fig. 4). The decay curves for these complexes can be fit with a single exponential [13], consistent also with only one site symmetry for the Eu(III) ion. Fig. 4 shows that the luminescence lifetime of the emitting $^5D_0$ level in the complex. Since the luminescence lifetime of this Eu(III) complex is relatively long (341 μs), the probability of quenching by charge carriers is relatively slow, this is advantageous to luminescence.

4. Conclusions

A novel europium(III) ternary complex, $Eu(MPBDTFA)_3$-Phen, was synthesized. Photoluminescence investigation indicated that the energy absorbed by the organic ligands was efficiently transfered to the central Eu^{3+} ions, and the complex showed intensely and characteristically red emission due to the $^5D_0$–^7F_j transitions of the central Eu^{3+} ions. With an electro-transporting group in molecule and highly thermal stability, the synthesized Eu(III) ternary complex is expected as a red-emitting candidate material for fabrication of organic light-emitting diodes (OLEDs).

Acknowledgements

The authors would like to acknowledge the support from the Scientific and Technical Projects of Guangdong Province (No. B10502) and the Research Grant Council of Hong Kong (grant No. HKBU/22037/02P).

References

[1] Y. Kido, K. Nagai, Y. Okamoto, T. Skothein, Chem. Lett. 235 (1991) 1267.
[2] J. Kido, H. Hayase, K. Hongawa, K. Nagai, K. Okuyama, Appl. Phys. Lett. 65 (1994) 2124.
[3] C. Adachi, M.A. Baldo, S.R. Forrest, J. Appl. Phys. 87 (2000) 8049.
[4] Z.R. Hong, C.J. Liang, R.G. Li, W.L. Li, D. Zhao, D. Fan, D.Y. Wang, B. Chu, F.X. Zang, L.-S. Hong, S.-T. Lee, Adv. Mater. 13 (2001) 1241.
[5] J. Bettenhausen, M. Greczmiel, M. Jandke, P. Strohriegl, Synth. Met. 91 (1997) 223.
[6] M.R. Robinson, M.B. O'Regan, G.C. Bazan, Chem. Commun. 17 (2000) 1645.
[7] P.P. Sun, J.P. Duan, J.J. Li, C.H. Cheng, Adv. Funct. Mater. 13 (2003) 683.
[8] M. Sun, H. Xin, K.Z. Wang, Y.A. Zhang, L.P. Jin, C.H. Huang, Chem. Commun. (6) (2003) 702.
[9] Z.P. Demko, K.B. Sharpless, J. Org. Chem. 66 (2001) 7945.
[10] M. Arivind, K. Sageed, Indian J. Chem. 25A (1986) 589.
[11] Y.S. Yang, M.L. Gong, Y.Y. Li, J. Alloys Compd. 207/208 (1994) 112.
[12] G.F. de Sa, O.L. Malta, C. de Mello Donega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. DaSilva, Coord. Chem. Rev. 196 (2000) 165.
[13] G.Z. Chen, X.Z. Huang, Z.Z. Zheng, J.G. Xu, Z.B. Wang, Fluorescence Analysis Methods, Science Press, Peking, 1990.