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# Synthesis, bright luminescence and crystal structure of a novel neutral europium complex

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## Abstract

A novel organic ligand, 6-diphenylamine carbonyl 2-pyridine carboxylic acid, and the corresponding europium complex, tris(6-diphenylamine carbonyl 2-pyridine carboxylato) europium(III) (Eu-DPAP) have been designed and synthesized. The crystal structure and photoluminescence of Eu-DPAP complex have been studied. The results showed that Eu-DPAP is an electroneutral complex that emits very strong red fluorescence. The lifetime of  $^5D_0$  of  $Eu^{3+}$  in the complex solid was examined using time-resolved spectroscopy, and the value for crystalline  $Eu(DPAP)_3 \cdot 12H_2O$  is  $0.69 \pm 0.01$  ms.

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**Keywords:** Crystal structures; Europium organic complexes; Luminescence; Lifetime; Synthesis

## 1. Introduction

Organic electroluminescence (OEL) has been studied extensively for its opportunities of low drive voltage, suitability for integrated circuit and potential application for large plane display [1,2], and green and blue luminescent materials for OEL devices have been basically satisfied for OEL application [3]. To our knowledge, there is an urgent search for stable, strong red luminescent material for application of OEL devices at the present time.

As some lanthanide ions, e.g.  $Eu^{3+}$  and  $Tb^{3+}$ , possess good luminescence characteristics (high color purity) based on the transitions between the 4f energy levels, a series of compounds activated by  $Eu^{3+}$  and  $Tb^{3+}$  have been studied for practical application as

phosphors and laser materials [4,5]. In particular, europium(III) has five narrow emission bands corresponding to the  $^5D_0 \rightarrow ^7F_j$  transitions, where  $j = 0, 1, 2, 3, 4$ . The strongest transition,  $^5D_0 \rightarrow ^7F_2$ , occurs at approximately 613 nm, the narrow intense ‘europium red’ luminescence [6]. Sodium tris(2,6-pyridine dicarboxylato) europium(III) complex has good photoluminescent properties [7,8] and high thermal stability [9], but has not been applied to OEL device because of the following reasons: first, the ionic compound cannot be prepared as a thin film using vacuum vapor deposition; second, the compound is insoluble in non-polar solvents, and cannot be made into a uniform thin film by the spin coating method. Several ternary rare earth complexes have been applied to prepare OEL devices that showed weak visible emission and low electroluminescence efficiency [10–13]. In principle, electroneutral metal complexes may form uniform thin film in vacuum vapor deposition and are reasonably stable to heat, which are required for OEL displays [14]. To search for high efficiently luminescent and electroneutral red

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materials, a novel organic ligand, 6-diphenylamine carbonyl 2-pyridine carboxylic acid (HDPAP), was designed and synthesized. The corresponding europium complex, tris(6-diphenylamine carbonyl 2-pyridine carboxylato) europium(III) (Eu-DPAP), was synthesized, and the structure and luminescence properties for the europium complex have been investigated.

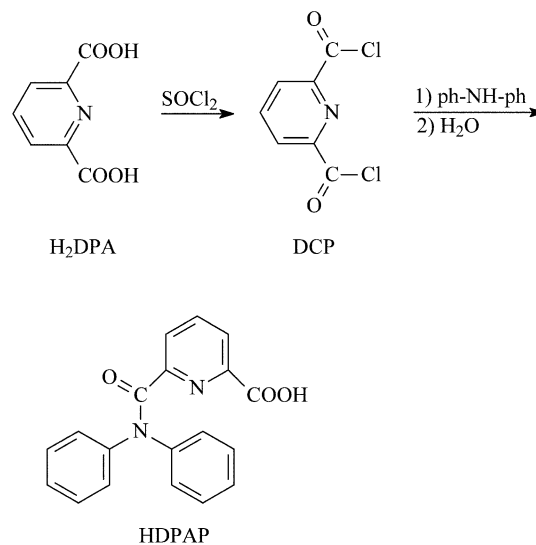
## 2. Experimental

### 2.1. Preparation of 6-diphenylamine carbonyl 2-pyridine carboxylic acid

Seventy-five gram of 2,6-pyridine dicarboxylic acid was added 250 ml of thionyl chloride and was refluxed for 20 h. The reaction mixture was concentrated to remove the excess thionyl chloride in vacuum, then was extracted with 300 ml of dried benzene. The benzene section was concentrated to small volume in vacuum, and a colorless needle crystal precipitated after deposited 24 h. The mixture was filtered, giving 87 g of 2,6-dichlorocarbonyl pyridine (DCP) (yield 95%). Five gram of DCP dissolved in dried benzene was slowly added with 4.14 g of diphenylamine dissolved in dried benzene, stirred for 5 h at 50 °C, cooled to room temperature and filtrated to remove the white precipitate. The benzene solution was concentrated in vacuo and then hydrolyzed at 40 °C for 2 h. The pH value of the solution was adjusted to 9.5 using 2.0 mol l<sup>-1</sup> aqueous NaOH, the mixture was filtered and the pH value of the filtrate was adjusted to 3.0 using 2.0 mol l<sup>-1</sup> HCl, giving a white precipitate. The white precipitate was recrystallized in 95% ethanol: acetone (1:1), giving 2.8 g of HDPAP with yield 35% and m.p. 74–77 °C. The elemental analysis data for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> (HDPAP) are: Found (Calc.) C 71.48 (71.69), H 4.43 (4.43), and N 8.89 (8.80)%. IR (KBr)  $\nu_{\max}$ : 3238.2, 3078.0, 1754.8, 1653.2, 1591.4, 1489.8, 1373.6, 756.5, 695.5 cm<sup>-1</sup>. <sup>1</sup>H NMR in

CD<sub>3</sub>SOCD<sub>3</sub>: 13.084(1H, s), 7.921(1H, t, <sup>3</sup>J = 7.5 Hz), 7.893 (1H, d, d, <sup>3</sup>J = 8.0 Hz, <sup>4</sup>J = 2.0 Hz), 7.768 (d, d, <sup>3</sup>J = 7.25 Hz, <sup>4</sup>J = 1.75 Hz), 7.284 (8H, s), 7.204 (2H, s). FAB-MS: *m/z* 319 ([M + H]<sup>+</sup>).

The synthesis route was expressed as follows:



### 2.2. Preparation of tris(6-diphenylamine carbonyl 2-pyridine carboxylato) europium(III)

The Eu(DPAP)<sub>3</sub>·12H<sub>2</sub>O complex was prepared by adding 12.0 mmol of HDPAP dissolved in ethanol to an aqueous solution containing 4.0 mmol EuCl<sub>3</sub>, which was obtained by reaction of Eu<sub>2</sub>O<sub>3</sub> (99.95%, Zhu-Jiang Smeltery Co.) and HCl (6.0 mol l<sup>-1</sup>). The pH value of the mixture was adjusted to 6–7 by adding an aqueous solution of sodium hydroxide, stirring 12 h at 60 °C. After deposited 72 h, a colorless cubic crystal precipitated from the solution, and was filtered out and washed with de-ionized water and 95% ethanol. A hydrated complex Eu(DPAP)<sub>3</sub>·12H<sub>2</sub>O was obtained. The complex was verified by elemental analysis, IR spectroscopy and X-ray crystal analysis. The elemental analysis results are: Found (Calc. for EuC<sub>57</sub>H<sub>63</sub>N<sub>6</sub>O<sub>21</sub>) C 51.51 (51.86), H 4.51 (4.81), N 6.06 (6.37), Eu 11.63 (11.51)%. IR (KBr)  $\nu_{\max}$ : 3416.4, 3111.0, 3067.0, 1618.7, 1568.2, 1490.2, 1372.5, 757.9, 700.1 cm<sup>-1</sup>.

Single crystal structure determination of the complex. Diffraction intensities for the complex were collected at 21 °C on a Siemens R3m diffractometer using the  $\omega$ -scan technique. Lorentz-polarization and absorption corrections were applied [15]. The structures was solved with direct method and refined with full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs, respectively [16,17]. Anisotropic thermal parameters were applied to all non-hydrogen atoms, and the organic hydrogen atoms were generated geometrically (C–H 0.96 Å); the aqua hydrogen atoms were located

Table 1  
Crystal data for complex Eu(DPAP)<sub>3</sub>·12H<sub>2</sub>O

Formula	C <sub>57</sub> H <sub>63</sub> EuN <sub>6</sub> O <sub>21</sub>
Formula weight	1320.09
Crystal system	cubic
Space group	<i>Pa</i> $\bar{3}$ (No. 205)
<i>a</i> (Å)	23.126(7)
<i>b</i> (Å)	23.126(7)
<i>c</i> (Å)	23.126(7)
<i>V</i> (Å <sup>3</sup> )	12368(6)
<i>Z</i>	8
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.418
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.093
No. unique data	6440
No. data with <i>I</i> $\geq$ 2 $\sigma$ ( <i>I</i> )	3626
<i>R</i> <sub>1</sub> [ <i>I</i> $\geq$ 2 $\sigma$ ( <i>I</i> )]	0.0611
<i>wR</i> <sub>2</sub> (all data)	0.1658

Table 2  
Selected bond lengths (Å) and angles (°) for  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$

Bond lengths			
Eu(1)–O(2)	2.402(5)	Eu(1)–N(1)	2.592(6)
Eu(1)–O(3)	2.466(5)	O(1)–C(1)	1.260(13)
O(2)–C(1)	1.327(13)	O(3)–C(7)	1.261(11)
Bond angles			
O(2)–Eu(1)–O(2b)	80.5(2)	O(3)–Eu(1)–N(1b)	66.8(2)
O(2)–Eu(1)–O(3a)	89.2(2)	O(2)–Eu(1)–N(1)	64.1(2)
O(2)–Eu(1)–O(3)	125.9(2)	O(3)–Eu(1)–N(1)	62.0(2)
O(2)–Eu(1)–O(3b)	149.8(2)	O(2)–Eu(1)–N(1a)	83.2(2)
O(3)–Eu(1)–O(3b)	74.0(2)	O(3)–Eu(1)–N(1a)	126.9(2)
O(2)–Eu(1)–N(1b)	143.0(2)	N(1)–Eu(1)–N(1a)	118.5(1)
C(1)–O(2)–Eu(1)	125.6(7)	C(7)–O(3)–Eu(1)	126.5(6)
C(2)–N(1)–Eu(1)	114.0(7)	C(6)–N(1)–Eu(1)	122.5(7)

Symmetry codes: (a)  $y, z, x$ ; (b)  $z, x, y$ .

from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [18]. Crystal data as well as details of data collection and refinement for the complex are summarised in Table 1. Selected bond distances and bond angles are listed in Table 2. Drawings were produced with SHELXTL [19].

### 2.3. Measurements and apparatus

Elemental analysis for the samples was carried out with an Elementar vario EL elemental analyzer. IR spectra in the region  $4000\text{--}400\text{ cm}^{-1}$  were recorded on a Bruker infrared spectrophotometer using conventional KBr method. FAB-MS spectra were performed on a VG ZAB-HS spectrometer. The  $^1\text{H}$  NMR spectra were recorded on a USA Varian UNITYINOVA-500 spectrometer (500 MHz). The excitation and emission spectra were measured with a Aminco Bowman Series fluorescence spectrophotometer with both excitation and emission slits at 1.0 nm for  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  solid and 4.0 nm for  $1.0 \times 10^{-4}\text{ mol l}^{-1}$   $\text{Eu}(\text{DPAP})_3$  ethanol solution, with same PMT at 700 V at room temperature. Fluorescence lifetimes were measured using an EMG 201 MSC quasi-molecular 308 nm laser by monitoring  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  emission line of  $\text{Eu}^{3+}$  at room temperature. The fluorescence yield was measured with He–Cd 325 nm laser with  $\text{Y}_2\text{O}_3:3\%\text{Eu}^{3+}$  as the standard phosphor. UV spectra were recorded on a Varlan UV–Vis spectrophotometer. Thermogravimetric analysis was carried out up to  $785^\circ\text{C}$  in nitrogen gas atmosphere on a Netzsch TG209 thermogravimetric analyzer.

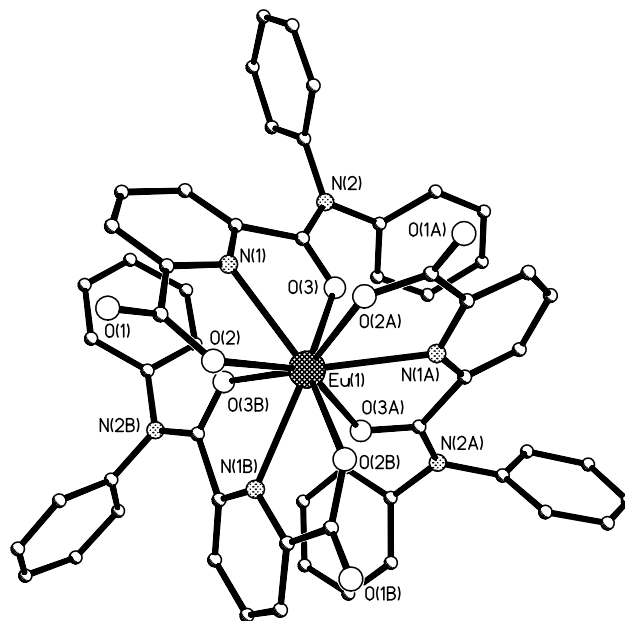


Fig. 1. The crystal structure of  $\text{Eu}(\text{DPAP})_3$ .

## 3. Results and discussion

### 3.1. Crystal structure

The crystal structure consists of the mononuclear  $\text{Eu}(\text{DPAP})_3$  molecules and lattice water molecules. As shown in Fig. 1, the Eu(III) atom is coordinated in a tricapped trigonal prism geometry with three nitrogen atoms [Eu(1)–N(1) 2.592(2) Å] in pyridine ring, three carboxylate oxygen atoms [Eu(1)–O(2) 2.402(5) Å; O(2)–Eu(1)–N(1) 64.1(2)–143.0(2)°] and three carbonyl oxygen atoms [Eu(1)–O(3) 2.466(5) Å, O(3)–Eu(1)–N(or O) 62.0(2)–149.8(2)°] from three different DPAP ligands. It should be noted that the coordinated number of central Eu(III) atom here is nine, reaching its saturated state, therefore, the lattice water molecules are only clathrated among the mononuclear  $\text{Eu}(\text{DPAP})_3$  molecules and form donor hydrogen bonds [O(1w)··O 2.80(1)–3.03(2) Å] with the carboxylate oxygen atoms. The mononuclear  $\text{Eu}(\text{DPAP})_3$  molecules was deduced to have better chemical thermodynamic stability by comparing the stability constants of some europium complexes, in which the metal ion is nine co-ordinate in a pseudo-tricapped trigonal prismatic site [20], with those of the ternary europium- $\beta$ -diketonato-base complexes [21], where the coordination numbers are eight or six. To our knowledge, although the complex of sodium tris(2,6-pyridine dicarboxylato) europate(III) had a good photoluminescence properties [7], it was difficult to form thin film using vacuum vapor deposition method due to the high sublimation temperature of the complex. However, it is reasonable to infer that  $\text{Eu}(\text{DPAP})_3$  complex, as a electroneutral and non-ionic

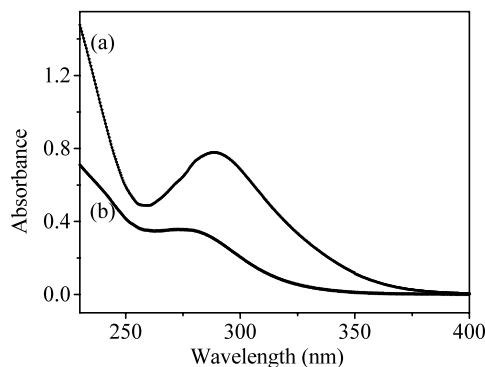


Fig. 2. UV absorption spectra for (a)  $3.2 \times 10^{-5} \text{ mol l}^{-1} \text{ Eu(DPAP)}_3$ , and (b)  $2.5 \times 10^{-5} \text{ mol l}^{-1} \text{ HDPAP}$  ethanol solution.

compound, may be more suitable to form thin film using the vacuum vapor deposition method.

### 3.2. UV absorption spectra

UV absorption spectra for  $2.5 \times 10^{-5} \text{ mol l}^{-1} \text{ HDPAP}$  and  $3.2 \times 10^{-5} \text{ mol l}^{-1} \text{ Eu(DPAP)}_3$  ethanol solution are shown in Fig. 2. The absorption band of  $\text{Eu(DPAP)}_3$  shifted to longer wavelength compared with that of HDPAP ligand (see Table 3), which was attributed to the metal coordination.

### 3.3. Fluorescence spectra

The excitation spectra for the original  $\text{Eu(DPAP)}_3 \cdot 12\text{H}_2\text{O}$  complex and  $1.0 \times 10^{-4} \text{ mol l}^{-1} \text{ Eu(DPAP)}_3$  ethanol solution are shown in Fig. 3, monitored at 614 nm. 300–400 nm wide band and 469 nm narrow band were observed on the excitation spectrum for the original  $\text{Eu(DPAP)}_3 \cdot 12\text{H}_2\text{O}$  complex. Two main excitation bands, centered at 276 and 346 nm, respectively, and two narrow bands located at 396 and 466 nm were observed on the excitation spectrum for  $1.0 \times 10^{-4} \text{ mol l}^{-1} \text{ Eu(DPAP)}_3$  ethanol solution. 360 and 346 nm are the maximum excitation wavelengths for the solid complex and the complex dilute ethanol solution, respectively, and the maximum excitation wavelength for the solid complex shifted 14 nm to longer wavelength compared with that for the complex dilute ethanol solution.

Table 3  
Photophysical properties of  $\text{Eu(DPAP)}_3 \cdot 12\text{H}_2\text{O}$  complex

Sample	UV absorption		Quantum yield (%)	Lifetimes (ms)
	$\lambda_{\text{max}}$ (nm)	$\epsilon^a$		
$3.2 \times 10^{-5} \text{ mol l}^{-1} \text{ Eu(DPAP)}_3$	288	$2.4 \times 10^4$	12 ± 1	0.69 ± 0.01
$2.5 \times 10^{-5} \text{ mol l}^{-1} \text{ HDPAP}$	277	$1.4 \times 10^4$		
$\text{Eu(DPAP)}_3 \cdot 12\text{H}_2\text{O}$				

<sup>a</sup> The unit of  $\epsilon$  is  $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ .

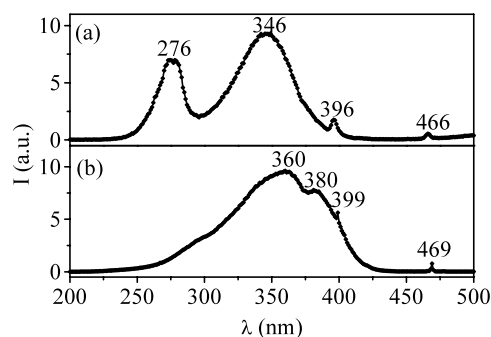
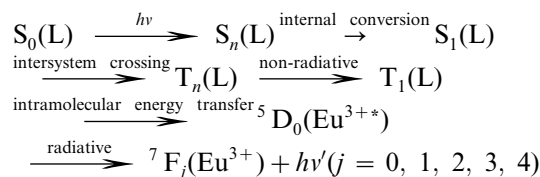


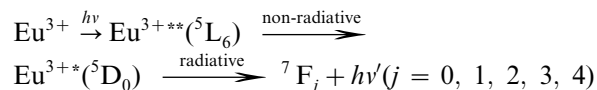
Fig. 3. Excitation spectra for (a)  $1.0 \times 10^{-4} \text{ mol l}^{-1} \text{ Eu(DPAP)}_3$  absolute ethanol solution and (b) solid state of  $\text{Eu(DPAP)}_3 \cdot 12\text{H}_2\text{O}$ .

The excitation spectrum for  $\text{Eu(DPAP)}_3$  dilute solution showed that most of the excitation energy was mainly absorbed by the ligand, and then transferred to the central  $\text{Eu}^{3+}$  ion, emitting the characteristic fluorescence of the latter. The value of the lowest triplet state for HDPAP ligand was  $20477 \text{ cm}^{-1}$ , calculated from the phosphorescence spectrum for  $\text{Gd(DPAP)}_3$  complex dimethyl sulfoxide dilute solution determined at 77 K. The triplet state of the ligand, higher by  $3210 \text{ cm}^{-1}$  than the lowest excited state of  $\text{Eu}^{3+}$ ,  $^5\text{D}_0$ , matched the excited states of  $\text{Eu}^{3+}$ , sensitizing the luminescence of  $\text{Eu}^{3+}$  [22]. The dominant luminescence mechanism for the complex could be expressed as:



where  $\nu > \nu'$ .

It is interesting that the characteristic emissions of  $\text{Eu}^{3+}$  ions for  $\text{Eu(DPAP)}_3$  dilute ethanol solution were observed under 396 and 465 nm light excitation. 396 and 465 nm are  $\text{Eu}^{3+}$  energy levels,  $^5\text{L}_6$ , and  $^5\text{D}_2$ . The facts showed evidences that there was a direct excitation mechanism to  $\text{Eu}^{3+}$  ions in the complex, the mechanism under 396 nm light excitation could be expressed as:



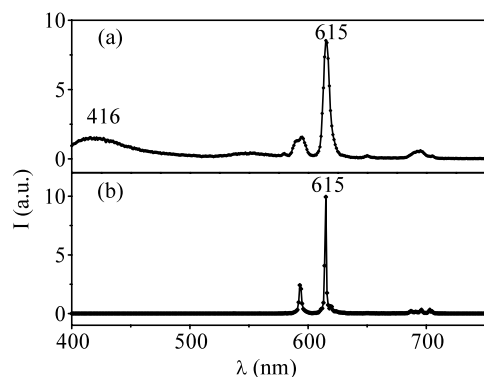


Fig. 4. Emission spectra for (a)  $1.0 \times 10^{-4}$  mol  $l^{-1}$   $\text{Eu}(\text{DPAP})_3$  absolute ethanol solution; (b)  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  solid.

The emission spectra of original  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  complex and  $\text{Eu}(\text{DPAP})_3$  ethanol solution consist of two main lines at 593 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ) and 615 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ) (Fig. 4). The emission at 615 nm was the strongest for both the solid complex and its ethanol solution. 416 nm band was observed on the emission spectrum for  $1.0 \times 10^{-4}$  mol  $l^{-1}$   $\text{Eu}(\text{DPAP})_3$ , due to DPAP ligand fluorescence, which caused the decrease of  $\text{Eu}^{3+}$  fluorescence efficiency for the europium complex dilute ethanol solution.  $\text{Eu}(\text{DPAP})_3$  solid was observed to emit strong characteristic emission of  $\text{Eu}^{3+}$ , but not to emit DPAP ligand fluorescence. Different from  $\text{Eu}^{3+}$ - $\beta$ -diketonate complexes [23], the 615 nm peak for  $\text{Eu}(\text{DPAP})_3$  complex was sharper, showing higher color purity for the latter. The fact indicated  $\text{Eu}(\text{DPAP})_3$  complex was an excellent fluorescent material.

### 3.4. Lifetime and yield

The lifetime of  $^5\text{D}_0$  excited state of  $\text{Eu}^{3+}$  for  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  colorless crystal was measured by time-resolved spectroscopy (Fig. 5). The lifetime value was calculated through the mono-exponential decay method [24], and the result was shown in Table 3. The fluorescence quantum yield of  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  solid was measured by comparison with standard phosphor method [25] as follows:

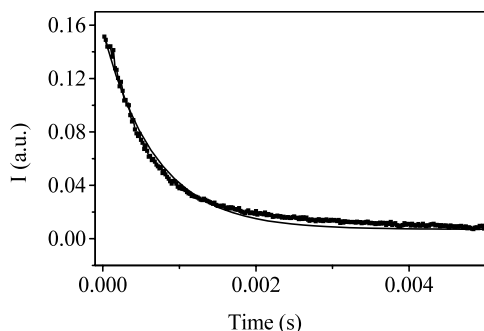


Fig. 5. Time-resolved spectra for  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  solid.

$$q_x = \left( \frac{1 - r_{\text{ST}}}{1 - r_x} \right) \left( \frac{\Delta\Phi_x}{\Delta\Phi_{\text{ST}}} \right) q_{\text{ST}}$$

Where  $r_{\text{ST}}$  and  $r_x$  are the amount of exciting radiation reflected by the standard and by the sample, respectively, and  $q_{\text{ST}}$  is the quantum standard yield of the standard phosphor. The terms of  $\Delta\Phi_x$  and  $\Delta\Phi_{\text{ST}}$  give the integrated photon flux for the sample and the standard phosphor, respectively. The yield of  $\text{Y}_2\text{O}_3:3\%\text{Eu}^{3+}$  is 99%, used as the standard phosphor [25], and the yield value is shown in Table 3.

### 3.5. Thermal stability

The temperature dependence of weight loss of the original  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  is shown in Fig. 6. The initial weight loss of  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  as started about  $20^\circ\text{C}$  was due to water-loss. The second stage in region of  $305\text{--}785^\circ\text{C}$  was attributed to elimination and/or decomposition of DPAP ligand. The results showed that  $\text{Eu}(\text{DPAP})_3$  complex have good thermal stability.

## 4. Conclusions

A novel europium(III) complex, tris(diphenylamine carbonyl 2-pyridine carboxylato) europium(III), has been synthesized. The crystal structure of the europium complex showed that it was an electroneutral molecule, the central  $\text{Eu}^{3+}$  was wrapped by three molecules of the ligand, two oxygen and one nitrogen atoms from each DPAP ligand coordinated to  $\text{Eu}^{3+}$ , and  $12\text{H}_2\text{O}$  located around the outside of  $\text{Eu}(\text{DPAP})_3$  complex. The europium complex emitted very strong and sharp red luminescence. The lifetime of  $^5\text{D}_0$  for excited  $\text{Eu}^{3+}$  in  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$  crystal was  $0.69 \pm 0.01$  ms, and the fluorescence yield of the solid complex was  $12 \pm 1\%$ , showing long lifetime and high luminescence efficiency.  $\text{Eu}(\text{DPAP})_3$  did not decompose below  $305^\circ\text{C}$ , and had very good thermal stability.

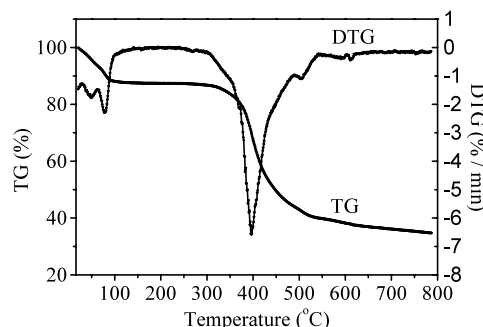


Fig. 6. TG and DTG analysis of  $\text{Eu}(\text{DPAP})_3 \cdot 12\text{H}_2\text{O}$ .



## 5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 173932. Supplementary data are available from the CCDC, 12 Union road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 173932 (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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