

Synthesis and Luminescence of a Novel Conjugated Europium Complex with 6-Aniline Carbonyl 2-Pyridine Carboxylic Acid

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A novel organic ligand, 6-aniline carbonyl 2-pyridine carboxylic acid (HAP), and the corresponding europium complex, *tris*(6-aniline carbonyl 2-pyridine carboxylato) europium (III) (Eu-AP) have been designed and synthesized. The results showed that Eu-AP was a conjugated complex, emitting strong red luminescence. The lifetimes of 5D_0 of Eu^{3+} in the complex were examined using time-resolved spectroscopic analysis, and the lifetime value was 0.55 ± 0.01 ms for solid $\text{Eu}(\text{AP})_3$. Thermogravimetric analysis showed that the europium complex had good thermal stability.

KEY WORDS: Europium organic complex; luminescence; lifetime; absorption spectra.

INTRODUCTION

Since a brightly photoluminescent europium complex was firstly reported by Weissman in 1942 [1], great achievement has been gained in research of lanthanide organic complexes. Luminescent lanthanide complexes have been used in medical diagnosis in reality [2–3], and complexes of lanthanide ions with organic ligands have been doped in polymers for optical amplification [4–5]. Presently organic light emitting devices (OLEDs) have been studied extensively for application in new types of flat panel displays driven by low voltage [6–7]. In general, it is difficult to obtain pure emission from conjugated polymers and small organic molecules [8], and narrow electroluminescence bands in red, green colors have been observed with Eu^{3+} , Tb^{3+} organic complexes as emitters [9]. Moreover, the electroluminescence efficiency of rare earth organic complexes is not limited to a theoretical maximum of 25% [10], it could be reached to 100% in theory. Several ternary lanthanide complexes have been applied to fabricate OEL devices (OLEDs), and great

achievements have been gained in improving the brightness and electroluminescence efficiencies of OLEDs with europium(III) and terbium(III) organic complexes as luminescent centers [9].

In general, metal complexes, which have conjugated molecular structure, could form uniform thin film in vacuum vapor deposition and are reasonably stable to heat, which is required for fabrication of OEL devices [11]. In our earlier work a novel organic ligand, 6-[(benzylamino) carbonyl]-2-pyridine carboxylic acid (HBAP), which sensitized europium(III) luminescence as well as terbium(III) luminescence [12]. In this work, a new organic ligand, 6-aniline carbonyl 2-pyridine carboxylic acid (HAP), was designed and synthesized, and the ligand efficiently sensitizes europium(III) luminescence, but does not sensitize terbium(III) luminescence at room temperature. The corresponding europium complex, *tris*(6-aniline carbonyl 2-pyridine carboxylato) europium(III) (Eu-AP), was synthesized and the photo-physical properties for the complex were studied.

EXPERIMENTAL

Preparation of 6-Aniline Carbonyl 2-Pyridine Carboxylic Acid

2,6-Dichlorocarbonyl pyridine (DCP) was prepared by a reaction of 2,6-pyridine dicarboxylic acid

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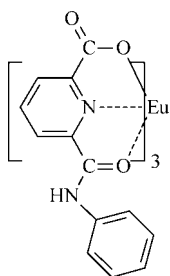
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(H₂DPA) and thionyl chloride [13] with high yield of 95%. Five grams of DCP dissolved in dried benzene was added slowly with 2.28 g of aniline dissolved in dried benzene, stirred for 5 h at room temperature, then refluxed for 6 h, cooled to room temperature and filtrated to remove the yellow precipitate. The benzene solution was concentrated, and hydrolyzed at 40°C for 2 h. The pH value of the solution was adjusted to 9.8, the mixture was filtered and the pH value of the filtrate was adjusted to 3.0, giving a white precipitate. The white precipitate was recrystallized in 95% ethanol: acetone (1:1), giving 3.82 g 6-aniline carbonyl 2-carboxylic acid (HAP) with high yield of 64.4% and melting point 80–83°C.

Preparation of *tris*(6-Aniline Carbonyl 2-Pyridine Carboxylato) Europium (III)

Eu(AP)₃ complex was prepared by adding 3.6 mmol of HAP dissolved in ethanol to an aqueous solution of 1.20 mmol EuCl₃. The pH value of the mixture was adjusted to 6.5 by adding an aqueous solution of sodium hydroxide. The reaction mixture was stirred 6 h at 50°C. After depositing for 24 h, a white precipitate deposited from the solution, then was filtered out and washed with deionized water and 95% ethanol. The precipitate was purified with mixed solution of 95% ethanol and acetone, and dried in vacuum at room temperature for 24 h. Eu(AP)₃ complex was obtained with high yield of 70%. The crystal structure of a similar europium complex, Eu(DPAP)₃·12H₂O (DPAP is 6-(diphenylamino carbonyl)-2-pyridine carboxylic acid), has been obtained [14]. The central Eu³⁺ is wrapped by 3 molecules of the ligand, 2 oxygen and 1 nitrogen atoms from each DPAP ligand coordinated to Eu³⁺, and 12 molecules of H₂O locate around the outside of Eu(DPAP)₃ complex. The structure of the europium complex is proposed as shown in the following sections.



The Tb(AP)₃ and Gd(AP)₃ were prepared as the synthesis method of Eu(AP)₃ with yields of 74 and 72%, respectively.

Apparatuses and Measurements

Elemental analysis were carried out with Elemental 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 USA Varian UNITYINOVA-500 spectrometer (500 MHz). The excitation and emission spectra were measured using a Hitachi F4500 fluorescence spectrophotometer with excitation and emission slits of 2.5 and 5.0 nm for the complex in solid state (compressed powder) and in ethanol solution respectively, and with PMT at 700 V at room temperature. The relative emission intensities were recorded from the highest emission peaks under the optimum excitation wavelengths. Luminescence lifetimes were measured using an EMG 201 MSC quasi-molecular 308 nm laser by monitoring ⁵D₀→⁷F₂ emission line of Eu³⁺ at room temperature. Electronic absorption spectra were recorded on a Varlan UV-Vis spectrophotometer. TG and DSC were carried out up to 700°C in nitrogen atmosphere on a Netzsch STA 409 PG/PC analyzer.

RESULTS AND DISCUSSION

Elemental Analysis and IR Absorption Spectra

The elemental analysis data for C₁₃H₁₀N₂O₃ (HAP) were: found (calculated)/%: C 64.72 (64.46), H 4.16(4.16), and N 11.48 (11.56). IR (KBr)/cm⁻¹: 3271.6, 3430.9 (s, ν_{N-H}), 3133.0, 3056.1 (w, ν_{C-H}), 3600–2500 (m, ν_{COOH}), 2661.0, 2609.8 (w, Fermi resonance), 1730.2, 1700.0 (s, ν_{C=O}), 1672.9 (s, ν_{C=O}, band I), 1538.6 (s, δ_{N-H}, band II), 1598.0, 1495.2 (s, ν_{skeleton}), 1233.2 (s, ν_{C-N}, band III), 744.8, 690.9 (s, δ_{CH}, in plane). ¹H-NMR in CD₃SOCD₃: δ = 13.213 (1H, s), 10.842 (1H, s), 8.403 (1H, d, d, ³J = 7.25 Hz, ⁴J = 1.75 Hz), 8.323 (1H, d, d, ³J = 8.0 Hz, ⁴J = 1.5 Hz), 8.290 (1H, t, ³J = 7.5 Hz), 7.824 (2H, d, t, ³J = 7.5 Hz, ⁴J = 1.5 Hz), 7.430 (2H, t, d, ³J = 6.5 Hz, ⁴J = 2 Hz), 7.183 (1H, t, t, ³J = 7.5 Hz, ⁴J = 1.0 Hz). FAB-MS: *m/z* 243 ([M + H]⁺).

The elemental analysis data for C₃₉H₃₇EuN₆O₁₄ (Eu(AP)₃·5H₂O), were: found (calculated)/%: C 48.43 (48.51), H 3.72 (3.86), N 8.74 (8.70) and Eu 15.92 (15.74).

The infrared absorption spectra for the samples are shown in Fig. 1, and the values of the main absorption bands are given in Table I. Two strong absorption bands for HAP ligand, 3271.1 and 3430.9 cm⁻¹ (ν_{N-H}), largely weakened in the spectrum for the complex, indicating that the N—H stretches were largely weakened in the complex.

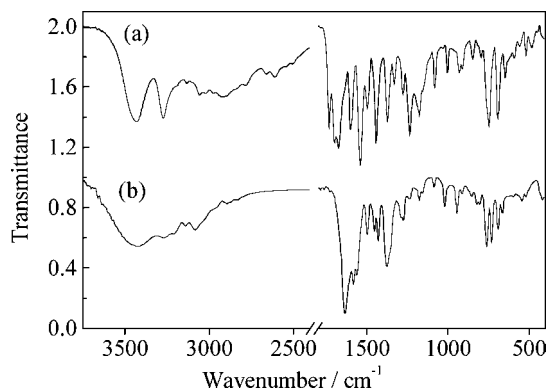


Fig. 1. IR absorption spectra of (a) HAP ligand and (b) $\text{Eu}(\text{AP})_3 \cdot 5\text{H}_2\text{O}$. (Note: The transmittance of (a) was offset 100%).

The absorption bands for $\text{Eu}(\text{AP})_3$ complex based on the C=O stretches, N—H bends and skeleton vibrations of the aromatic rings, 1632.4 cm^{-1} ($\nu_{\text{as,COO}^-}$), 1374.5 ($\nu_{\text{s,COO}^-}$), 1581.3 cm^{-1} ($\nu_{\text{C=O}}$, band I), 1496.0 cm^{-1} ($\delta_{\text{N-H}}$, band II), 1557.0 and 1450.6 cm^{-1} (ν_{skeleton}), shifted to lower wavenumbers compared with those for HAP ligand (Table I) due to weakened strength of C=O, N—H and aromatic ring bonds in the coordination. The absorption bands, located at 1581.1 and 1496.0 cm^{-1} , were obviously weakened in the complex, which was attributed to the rigid structure of the coordinated complex restricting the stretches or bends of C=O and N—H groups.

UV Absorption Spectra

The electronic absorption bands for $\text{Eu}(\text{AP})_3$ were similar to those for HAP ligand, and the maximum absorption bands were located at 283 and 282 nm for the complex and the ligand respectively (Fig. 2). The maximum molar absorption coefficients are shown in Table II.

Luminescence Spectra

The excitation spectra were obtained by scanning the excitation wavelengths with emission wavelength at 614 nm; and the emission spectra were recorded by scanning the emission wavelengths with excitation wavelength at 270 nm and 324 nm for the europium complex in solid

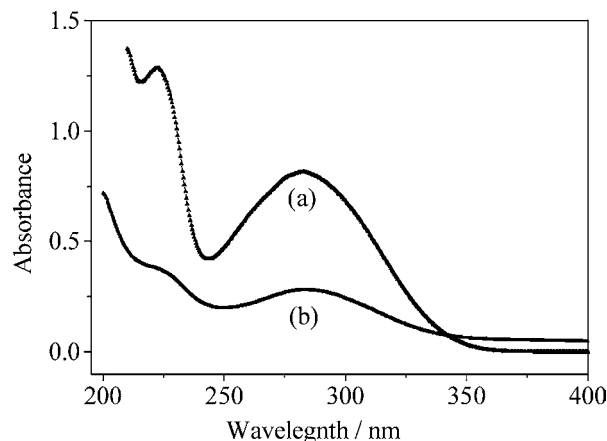
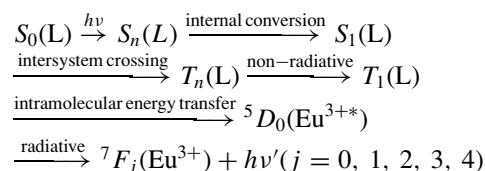


Fig. 2. Electronic absorption spectra of (a) $5.0 \times 10^{-5} \text{ mol/L}$ HAP, and (b) $1.0 \times 10^{-5} \text{ mol/L}$ $\text{Eu}(\text{AP})_3$ ethanol solution.

state and in ethanol dilute solution respectively. The excitation band with a half-peak width of 250–378 nm for the former was broader than that for the latter centered at 324 nm (Fig. 3).

The excitation spectrum for $\text{Eu}(\text{AP})_3$ dilute ethanol solution indicated that most of the excitation energy was mainly absorbed by the ligand, and then transferred to the central Eu^{3+} ion, emitting characteristic luminescence of the latter. The value of the lowest triplet state for HAP ligand was 22360 cm^{-1} , calculated from the maximum emission wavelength of the phosphorescence spectrum for $\text{Gd}(\text{AP})_3$ dimethyl sulfoxide dilute solution determined at 77 K. The triplet state of the ligand, higher by 5093 cm^{-1} than the lowest excited state of Eu^{3+} , 5D_0 , matched the excited states of Eu^{3+} , and therefore the ligand strongly sensitized the luminescence of Eu^{3+} [15]. The dominant luminescence mechanism for the complex could be expressed as:



where $\nu > \nu'$.

Table I. Main Infrared Absorption Bands for HAP and $\text{Eu}(\text{AP})_3$ Complex (cm^{-1})

Sample	$\nu_{\text{N-H}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=O, band I}}$	$\delta_{\text{N-H, band II}}$	ν_{skeleton}
HAP	3430.9 (s)	3133.0 (w)	1744.6 (s)	1672.9 (s)	1538.6 (s)	1598.1 (s)
	3271.6 (s)	3056.0 (w)	1700.0 (s)			1495.2 (m)
$\text{Eu}(\text{AP})_3 \cdot 5\text{H}_2\text{O}$	3264.0 (w)	3144.0 (w)	1632.4 (s)	1581.3 (m)	1496.0 (m)	1557.0 (s)
	3201.7 (w)	3081.9 (w)	1374.5(s)			1450.6 (m)

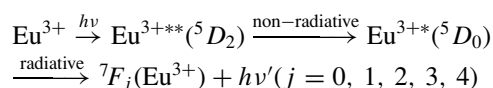
Note. s = strong, m = medium, w = weak.

Table II. Photophysical Properties of Eu(AP)₃ and Tb(AP)₃ Complexes

Sample	UV absorption		Luminescence			Lifetimes τ (ms)
	λ_{\max} (nm)	$\varepsilon \times 10^{-4}$	λ_{ex} (nm)	λ_{em} (nm)	I (a.u.)	
1.0×10^{-5} mol/L Eu(AP) ₃	283	2.8	324	614.8	142	0.46 ± 0.01^a
5.0×10^{-5} mol/L HAP	282	1.6				
Eu(AP) ₃ ·5H ₂ O			270	614.8	1101	0.55 ± 0.01
Tb(AP) ₃ ·4H ₂ O			No emission of Tb ³⁺			

^aThe first decay lifetime is 0.46 ± 0.01 ms, and the second decay lifetime is 2.54 ± 0.05 ms.

An excitation band for solid Eu(AP)₃·5H₂O, 465 nm, disappeared on the excitation spectrum for the complex ethanol solution, which was attributed to the luminescence quenching caused by OH vibrations of the solvent [16–17]. It is interesting that characteristic emissions of Eu³⁺ ion for solid Eu(AP)₃·5H₂O were observed under 465 nm light excitation. 465 nm is one of Eu³⁺ energy levels, ⁵D₂. The fact showed an evidence that there was a direct excitation mechanism of the Eu³⁺ in the solid complex:



The emission spectra for Eu(AP)₃ in solid state and in ethanol solution consisted of two main lines at 590.7/591.6 nm (⁵D₀ → ⁷F₁) and 614.8/614.8 nm (⁵D₀ → ⁷F₂), and the emission at 614 nm was the strongest. Different from Eu³⁺- β -diketonate complexes [18], the 614 nm peak was sharper and stronger, showing higher color purity for the latter.

Lifetimes

The lifetime value for solid Eu(AP)₃ was calculated through the mono-exponential decay method [19], and

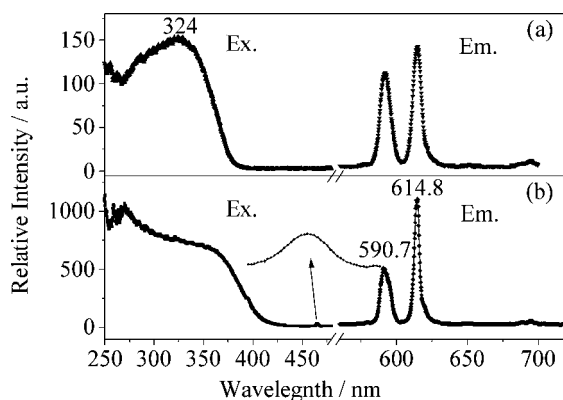


Fig. 3. Excitation and emission spectra of (a) 1.0×10^{-5} mol/L Eu(AP)₃ ethanol solution and (b) solid Eu(AP)₃·5H₂O.

the result was shown in Table II. The lifetime curve for the ethanol solution of the complex was fitted to be very suitable for the bi-exponential decay curve (Fig. 4), and the decay equation was:

$$I = 0.123e^{-(t/0.00046)} + 0.042e^{-(t/0.00254)}$$

Where “*I*” is the relative intensity of luminescence, and “*t*” is the decay time. The result indicated that the decay mechanism of ⁵D₀ excited state of Eu³⁺ for Eu(AP)₃ in ethanol solution might be different from that in solid state.

Thermal Stability

The complex had a little weight loss below 70°C due to water loss (1.5 H₂O), which was absorbed by the sample in air atmosphere (Fig. 5). The second water loss (3.5 H₂O) was observed in region of 100–300°C. The third stage in region of 330–700°C was attributed to elimination and/or decomposition of AP ligand, and the differential scanning calorimetry (DSC) curve indicated that the sample absorbed much thermal energy in the

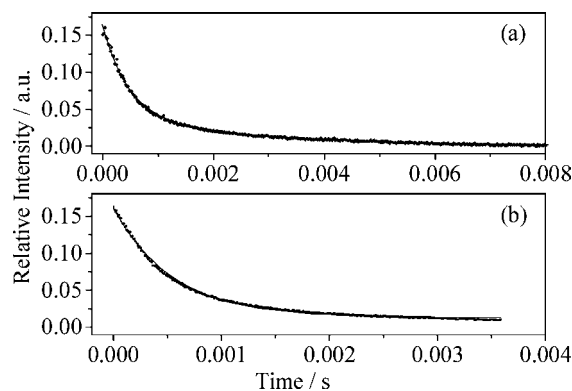


Fig. 4. The decay curves of emission at 614 nm for (a) 1.0×10^{-5} mol/L Eu(AP)₃ ethanol solution and (b) solid Eu(AP)₃·5H₂O. The symbol curves are the experimental lifetime decay curves and the line curves are the bi-exponential and mono-exponential decay curves for the former and the latter, respectively.

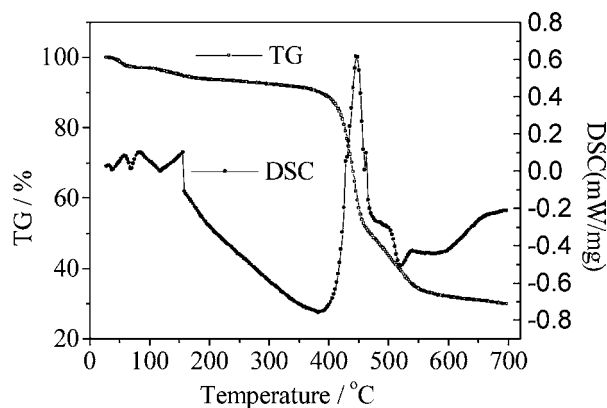


Fig. 5. TG and DSC analysis of solid $\text{Eu}(\text{AP})_3$.

decomposition period. The result showed that $\text{Eu}(\text{AP})_3$ complex has good thermal stability, which was favorable to its potential application in fabrication of an organic electroluminescence device (OEL).

CONCLUSIONS

A novel tridentate organic ligand, 6-aniline carbonyl 2-pyridine carboxylic acid, and the corresponding electro-neutral complex, *tris*(6-aniline carbonyl 2-pyridine carboxylato) europium (III) complex have been synthesized. $\text{Eu}(\text{AP})_3$ emits very strong characteristic emission of Eu^{3+} ions either in solid state or in dilute ethanol solution at room temperature. The europium complex has good thermal stability. The 5D_0 excited state of Eu^{3+} for the complex has long lifetime both in solid state and in ethanol dilute solution. $\text{Eu}(\text{AP})_3$ is a good luminescence material.

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