

Preparation and Luminescent Properties of a Novel Carbazole Functionalized Bis- β -diketone Ligand and Corresponding Eu(III) and Tb(III) Complexes

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A novel carbazole functionalized bis- β -diketone type organic ligand, 1,1'-(2,6-bispyridyl)bis-3-(9-ethylcarbazole-3-yl)-1,3-propanedione (H_2L) and its corresponding lanthanide complexes $Eu_2(L)_3$ and $Tb_2(L)_3$ were successfully prepared. The ligand and complexes were characterized in detail based on FT-IR spectra, 1H NMR and elemental analysis. The observed UV-Vis absorption and photoluminescence properties of the complexes were investigated, it shows that the Eu(III) and Tb(III) ions can be sensitized efficiently by the ligand (H_2L) to some extent, in particular, the complex $Tb_2(L)_3$ exhibits a more excellent luminescence property than the Eu(III) complex. Meanwhile, the introduction of the carbazole moiety can enlarge the π -conjugated system of the ligand and enhance the luminescent intensity of the complexes. The results show that the complexes would be used as excellent luminescent materials.

Key Words: Organic ligand, Carbazole, Bis- β -diketone, Eu(III) and Tb(III) complexes, Luminescent property

Introduction

Since the characteristic line fluorescence of trivalent europium which was sensitized by the organic ligand was first reported by Weissman in 1942,¹ rare earth organic complexes have taken on great significance in academic research and good prospect in applications as diverse as: liquid crystalline materials,² sensors,³ luminescence probes for medical diagnosis^{4,5} and so forth. In recent years, organic light-emitting diodes (OLEDs) have been intensively studied worldwide because of their potential application in the next generation of large full-color flat panel display.⁶⁻⁸ In particular, Eu(III) and Tb(III) complexes are of special interest because they can emit highly monochromatic light and offer 100% quantum efficiency theoretically.^{9,10} However, the quantum efficiency of most these complexes are unfortunately so low that their practical applications are limited seriously, because of the small absorption cross-section of the ions. Therefore, much effort has been devoted to optimize the structure of ligands to make the energy transfer more efficiently and display a more excellent luminescence property.

Pyridine-2,6-dicarboxylic acid and its derivatives are highly useful tridentate ligands, it can form nine-coordinating luminescent complexes with lanthanides, providing high quantum yields of phosphorescence.^{11,12} The complexes of Eu(III) and Tb(III) ions with π -conjugated ligands such as β -diketone have also been researched as emitting materials for OLEDs,¹³ since the reports by Okamoto and his co-workers.¹⁴ Due to its large conjugated structure and special photo-electronic property, carbazole group has been extensively used as a functional substituent or a building block in non-linear optic (NLO) materials,¹⁵ hole transport and light-emissive materials for OLEDs¹⁶ and as a host material for photoluminescence applications.¹⁷

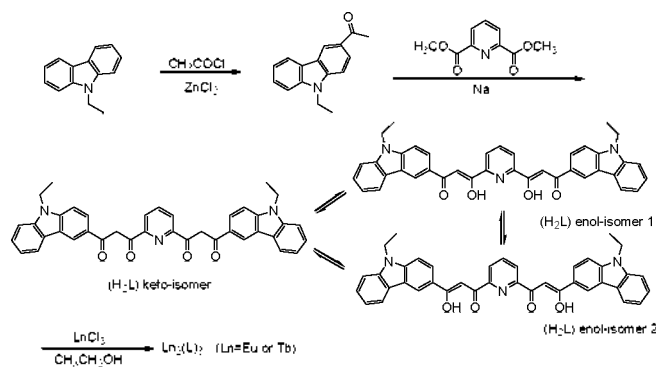
In order to explore novel highly efficient luminescent materials, we designed and synthesized a novel, pyridine containing, carbazole functionalized bis- β -diketone ligand, 1,1'-(2,6-bispyridyl)bis-3-(9-ethylcarbazole-3-yl)-1,3-propanedione (H_2L) and its corresponding lanthanide complexes $Ln_2(L)_3$ ($Ln = Eu$ or Tb) on the basis of earlier work.^{18,19} At the same time, the photoluminescence properties for the lanthanide complexes in solid state at room temperature were investigated, the complexes are sensitive to UV excitation light and emit bright photoluminescence. The synthetic route of the complexes $Ln_2(L)_3$ are expressed in Scheme 1.

Result and Discussion

Compositions of the complexes. The results of elemental analyses of C, H, N and lanthanide ions titration are in good agreement with the theoretical values calculated, indicating that the composition of the complexes conform to formulae of $Eu_2(L)_3$ and $Tb_2(L)_3$ respectively.

FT-IR spectra. The characteristic infrared absorption bands of the free ligand (H_2L) and its Eu(III) and Tb(III) complexes are given in Table 1.

The FT-IR spectrum of the uncoordinated ligand shows at



Scheme 1. Synthetic route of the complexes $Ln_2(L)_3$.

Table 1. Characteristic FT-IR bands (cm^{-1}) of the ligand and the complexes.

Compounds	$\nu(\text{C-OH})$	keto $\nu(\text{C=O})$	enol $\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=C})$	$\nu(\text{Ln-O})$	$\nu(\text{Ln-N})$
H_2L	3432, m	1708, m	1593, s		1492, s		
$\text{Eu}_2(\text{L})_3$	3422, m		1589, s	1560, s	1518, 1491, s	431, w	526, w
$\text{Tb}_2(\text{L})_3$	3416, m		1589, s	1561, s	1518, 1491, s	434, w	525, w

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

3432 cm^{-1} , which can be assigned as $\nu(\text{C-OH})$. The bands at 1708 cm^{-1} and 1593 cm^{-1} are attributed to the stretching vibration of the keto-isomer and enol-isomer carbonyl respectively. The relative peak intensity of the two bands and foregoing ^1H NMR spectra show that the ligand mainly exists in the form of enol-isomer in solid state.

The FT-IR spectra of the two complexes are similar, indicating that they are structurally alike. These bands are shifted downfield by $10 - 16\text{ cm}^{-1}$ for $\nu(\text{C-OH})$ and 4 cm^{-1} for enol-isomer $\nu(\text{C=O})$. The bands of strong intensity at 1560 cm^{-1} and 1518 cm^{-1} can be assigned to $\nu(\text{C=N})$ of pyridine ring and $\nu(\text{C=C})$, respectively. The absorption bands assigned to the coordinated Ln-O and Ln-N are observed at about 431 cm^{-1} and 526 cm^{-1} for the complexes respectively. All the shifts indicate that the lanthanide ions coordinated to the ligand via the nitrogen atom of the pyridine ring and the carbonyl oxygen atoms of the bis- β -diketone unit.

UV-Vis absorption spectra. The UV-Vis absorption spectra of the free ligand (H_2L) and lanthanide complexes were recorded in DMF solution at room temperature as shown in Figure 1.

All of the compounds show similar peak positions. The very strong band appearing below 300 nm can be assigned as intraligand $\pi \rightarrow \pi^*$ transition. Two absorption bands of the complexes at about 346 nm and 405 nm are observed, which shift to longer wavelengths compared with that of the free ligand at 332 nm and 390 nm , due to the coordination of the metal ion to the ligand, and the complexes show relatively stronger and broader absorbance than the ligand at about 400 nm .

Photoluminescence properties. The photoluminescence spectra and data for the complexes in the solid state at room temperature

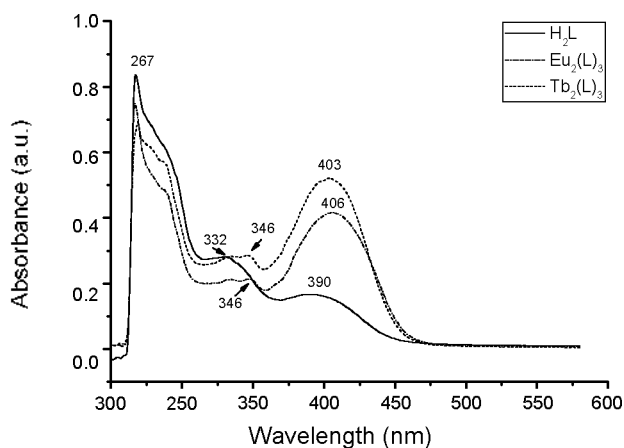


Figure 1. UV-Vis absorption spectra of the ligand and the complexes in DMF ($1 \times 10^{-5}\text{ mol/L}$).

are shown in Figure 2, Figure 3 and Table 2.

The maximum excitation wavelengths of the Eu(III) and Tb(III) complexes can be observed at 281 nm and 282 nm respectively due to the $\pi \rightarrow \pi^*$ transition centered onto the ligand. The solid complexes have characteristics line emission of f-f transition of lanthanide ions when they are excited by UV light. Because there is no trace emission from carbazole group (around 350 nm) in the complexes, an efficient energy transfer can take place from the singlet excited state of carbazole moiety to the singlet excited state of bis- β -diketone unit, and followed by intersystem crossing to the excited triplet state of bis- β -diketone unit, where it is finally trans-

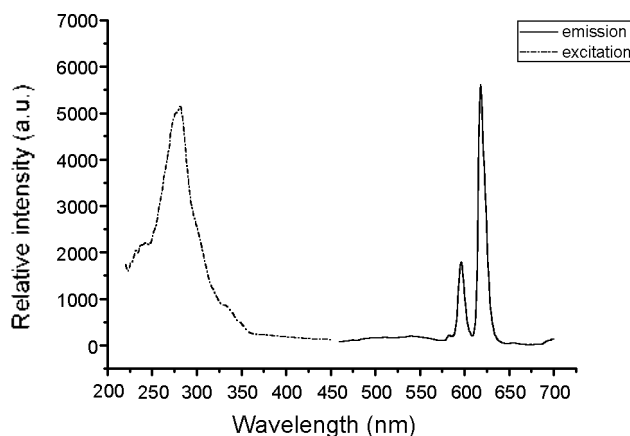


Figure 2. The excitation and emission spectra of the complex $\text{Eu}_2(\text{L})_3$ in solid state. The excitation and emission slit widths were 2.5 nm and the drive voltage of photomultiplier tube was 700 V .

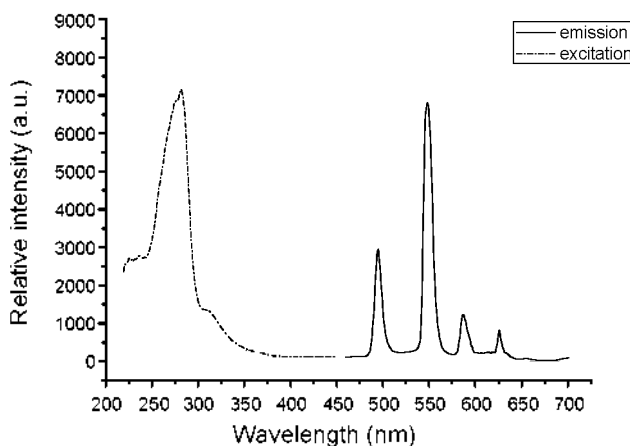


Figure 3. The excitation and emission spectra of the complex $\text{Tb}_2(\text{L})_3$ in solid state. The excitation and emission slit widths were 2.5 nm and the drive voltage of photomultiplier tube was 700 V .

Table 2. Photoluminescence data of the complexes in solid state at room temperature.

Complexes	λ_{ex} (nm)	λ_{em} (nm)	RI ^a	Assignment
Eu ₂ (L) ₃	281	596	1801	⁵ D ₀ → ⁷ F ₁
		618	5616	⁵ D ₀ → ⁷ F ₂
Tb ₂ (L) ₃	282	495	2930	⁵ D ₄ → ⁷ F ₆
		548	6788	⁵ D ₄ → ⁷ F ₅
		587	1223	⁵ D ₄ → ⁷ F ₄
		625	806	⁵ D ₄ → ⁷ F ₃

^aRI: relative intensity.

ferred to the central lanthanide ion, emitting characteristic luminescence of the latter.²⁴

The emission spectra of the complex Eu₂(L)₃ exhibit two sharp characteristic emission peaks at 596 and 618 nm corresponding to the ⁵D₀ → ⁷F₁ (magnetic dipole transition) and ⁵D₀ → ⁷F₂ (induced electric-dipole transition), respectively. The hypersensitive ⁵D₀ → ⁷F₂ transition is the most intense, pointing to a highly polarizable chemical environment around the central ion. The emission spectrum of the complex Tb₂(L)₃ consists of four main lines at approximate 495 nm (⁵D₄ → ⁷F₆), 548 nm (⁵D₄ → ⁷F₅), 587 nm (⁵D₄ → ⁷F₄) and 625 nm (⁵D₄ → ⁷F₃), and we can see that the emission band (⁵D₄ → ⁷F₃) is obviously stronger than the other emission bands.

The emission intensity of the Tb(III) complex at 548 nm is stronger than that of the Eu(III) complex. One factor that can contribute to the observed emission intensity is the energy gap between the triplet energy states of the ligand and the emitting energy states of the lanthanide ions, so it can be inferred that the energy difference between the triplet states of ligand and the emitting energy state of the Tb(III) ion is more favorable for energy transfer than those of the Eu(III) ion. In addition, compared to previous complexes which we designed and synthesized,^{18,19} the introduction of carbazole units can form rigid planar structure, enlarge the π -conjugated system of the ligand (H₂L), exhibit strong light-harvesting potential and produce a strong intense emission from the central Eu(III) and Tb(III) ions *via* sensitization.

Experiments

Materials and measurements. Pyridine-2,6-dicarboxylic acid was obtained from JiuZhou Chemical Co. Ltd. Dimethyl 2,6-pyridinedicarboxylate and 9-ethylcarbazole were synthesized respectively as described in the literatures.^{20,21} The solutions of lanthanide chlorides LnCl₃ were prepared according to the literature method.²² The purity of lanthanide oxide exceeds 99.99%. The solvents CH₂Cl₂ and toluene were dried and redistilled prior to usage. All other reagents used were purchased and used as analytical grade without further purification.

Elemental analysis was carried out by a Perkin-Elmer 2400 elemental analyzer. Content of Eu(III) and Tb(III) were determined by EDTA titration with xylenol orange as an indicator. Melting points were observed on a XR-4 apparatus (thermometer uncorrected). The FT-IR spectra were recorded in the 4000 - 400 cm⁻¹ region by using a Nicolet NEXUS 670 FT-IR spectrophotometer with KBr plates. ¹H NMR spectra were

measured by using a Bruker-400 MHz nuclear magnetic resonance spectrometer with CDCl₃ as solvent and TMS as internal reference. Ultraviolet-visible (UV-Vis) spectra were measured with a Pgeneral TU-1800SPC spectrophotometer. Photoluminescence measurements (excitation and emission spectra) were made on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. The relative emission intensities were recorded from the highest emission peaks under the optimum excitation wavelengths.

Synthesis of 3-acetyl-9-ethylcarbazole. To a solution of 9-ethylcarbazole (4.0 g, 20.5 mmol) in CH₂Cl₂ (30 mL), anhydrous ZnCl₂ (3.4 g, 25.0 mmol) was added quickly and the mixture was stirred at room temperature, meanwhile, a solution of acetyl chloride (1.80 mL, 24.5 mmol) in CH₂Cl₂ (15 mL) was added dropwise. The reaction mixture was incubated and stirred at ambient temperature for about 24 h, and then cooled water (100 mL) was added to the mixture, extracted with CH₂Cl₂ (3 × 20 mL), and dried on anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of ethyl acetate/petroleum ether (1 : 9) as eluent to give the target compound, the crude product was recrystallized from 95% ethanol to give white needles of 3-acetyl-9-ethylcarbazole (3.9 g, 80%), m.p. 114 ~ 116 °C (literature:²³ 115 °C); IR (cm⁻¹): 3042, 2966, 1660, 1622, 1591, 1493, 1436, 1353, 1327, 1245, 1158, 748; ¹H NMR (400 MHz, ppm): δ 8.74 (d, 1H, *J* = 1.2 Hz, PhH), 8.11 ~ 8.16 (m, *J* = 4.0 Hz, *J* = 2.4 Hz, 2H, PhH), 7.26 ~ 7.54 (m, *J* = 4.0 Hz, 4H, PhH), 4.33 ~ 4.39 (q, 2H, *J* = 7.2 Hz, CH₂), 2.73 (s, 3H, OCH₃), 1.42 ~ 1.46 (t, 3H, *J* = 7.2 Hz, CH₃); Anal. Calcd for C₁₆H₁₅NO: C, 80.98; H, 6.37; N, 5.90; Found: C, 81.32; H, 6.39; N, 5.74.

Synthesis of 1,1'-(2,6-bispyridyl)bis-3-(9-ethylcarbazole-3-yl)-1,3-propanedione (H₂L). A suspension of freshly cut sodium (0.10 g, 4.3 mmol) in anhydrous toluene (15 mL) was placed in a three-necked flask. The mixture was heated up to 110 °C with silicone oil and stirred vigorously till the sodium was molten, then dimethyl 2,6-pyridinedicarboxylate (0.38 g, 1.9 mmol) was added, meanwhile, a solution of 3-acetyl-9-ethylcarbazole (1.00 g, 4.2 mmol) in toluene (12 mL) was added dropwise. The reaction mixture was incubated and stirred at 110 °C for about 6 h until the dark brown sodium salt precipitated. The sodium salt was collected by filtration, washed thoroughly with petroleum ether and dried. The dried solid was added to dilute hydrochloric acid and the resulting precipitate was collected by filtration. The crude products were recrystallized from methanol and tetrahydrofuran (1 : 1) to give the brownish yellow of ligand (H₂L) (0.85 g, 74%), m.p. 113 ~ 115; IR (cm⁻¹): 3432, 3051, 2975, 1708, 1593, 1492, 1472, 1448, 1383, 1346, 1233, 796, 749, 545; ¹H NMR (400 MHz, ppm): δ 16.95 (s, 1H, OH), 16.82 (s, 1H, OH), 7.93 ~ 8.95 (m, 3H, PyH), 7.25 ~ 7.52 (m, 16H, PhH, CH), 4.36 ~ 4.39 (q, 4H, *J* = 7.2 Hz, CH₂), 1.27 ~ 1.47 (t, 6H, *J* = 7.2 Hz, CH₃); Anal. Calcd for C₃₉H₃₁N₃O₄: C, 77.34; H, 5.16; N, 6.94; Found: C, 77.50; H, 5.02; N, 6.87.

Synthesis of the Eu(III) and Tb(III) complexes. The Eu(III) and Tb(III) complexes were prepared in the following steps. A solution of LnCl₃ (0.18 mmol) was added to a solution of the ligand (0.15 g, 0.25 mmol) in ethanol (5.0 mL), the pH value

was adjusted to 7.0 by addition of sodium hydroxide solution (0.05 mol/L), then the mixture was stirred for 24 h at 60 °C. The precipitate was separated by suction filtration, purified by washing thoroughly with ethanol and chloroform (1 : 1), and dried in vacuum for 48h to give brownish yellow powders $\text{Ln}_2(\text{L})_3$ (typically about 65% yield). Anal. Calcd for $\text{Eu}_2(\text{L})_3$: C, 66.44; H, 4.15; N, 5.96; Eu, 14.37 Found: C, 66.12; H, 4.01; N, 5.88; Eu, 14.55. Anal. Calcd for $\text{Tb}_2(\text{L})_3$: C, 66.01; H, 4.12; N, 5.92; Tb, 14.93 Found: C, 65.76; H, 4.28; N, 5.79; Eu, 14.88.

Conclusion

To summarize, a novel carbazole functionalized bis- β -diketone-type ligand 1,1'-(2,6-bispyridyl)bis-3-(9-ethylcarbazole-3-yl)-1,3-propanedione (H_2L) and its corresponding complexes $\text{Eu}_2(\text{L})_3$ and $\text{Tb}_2(\text{L})_3$ were successfully synthesized and characterized. Differences in the FT-IR spectra of the free ligand and the lanthanide complexes indicate that coordination of the ligand was occurring at the oxygen atoms of the bis- β -diketone groups and the nitrogen atom of the pyridine ring. The Eu(III) and Tb(III) ions can be sensitized efficiently by the ligand and the Tb(III) complex shows a more excellent luminescence property. Meanwhile, we found that the introduction of the carbazole moiety improve the charge transfer efficiency and enhanced the luminescent intensity of the complexes. The complexes with ligand (H_2L) have a very good luminescent performance that could be used as candidate efficient luminescent materials.

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