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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Received February 18, 2009, Accepted August 11, 2009

A novel carbazole functionalized bis-β-diketone type organic ligand, 1,1′-(2,6-bispyridyl)bis-3-(9-ethylcarbazole-3-yl)-1,3-propanedione (H2L) and its corresponding lanthanide complexes Eu2(L)3 and Tb2(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 (H2L) to some extent, in particular, the complex Tb2(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 diagnosis4,5 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 flat panel display.6-8 In particular, Eu(III) and Tb(III) complexes are of special interest because they can emit 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 for emitting materials for OLEDs,16 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-ispyridyl)bis-3-(9-ethylcarbazole-3-yl)-1,3-propanedione (H2L) and its corresponding lanthanide complexes Ln2(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 Ln2(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 formulæ of Eu2(L)3 and Tb2(L)3 respectively.

FT-IR spectra. The characteristic infrared absorption bands of the free ligand (H2L) and its Eu(III) and Tb(III) complexes are given in Table 1. The FT-IR spectrum of the uncoordinated ligand shows at
Table 1. Characteristic FT-IR bands (cm\(^{-1}\)) of the ligand and the complexes.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ν(C−OH) (cm(^{-1}))</th>
<th>ν(C=O) keto (cm(^{-1}))</th>
<th>ν(C=O) enol (cm(^{-1}))</th>
<th>ν(C=N) (cm(^{-1}))</th>
<th>ν(C=C) (cm(^{-1}))</th>
<th>ν(Ln−O) (cm(^{-1}))</th>
<th>ν(Ln−N) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)L</td>
<td>3432, m</td>
<td>1708, m</td>
<td>1593, s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu(_2)(L)(_3)</td>
<td>3422, m</td>
<td>1589, s</td>
<td>1560, s</td>
<td>1518, 1491, s</td>
<td>431, w</td>
<td>526, w</td>
<td></td>
</tr>
<tr>
<td>Tb(_2)(L)(_3)</td>
<td>3416, m</td>
<td>1589, s</td>
<td>1561, s</td>
<td>1518, 1491, s</td>
<td>434, w</td>
<td>525, w</td>
<td></td>
</tr>
</tbody>
</table>

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

3432 cm\(^{-1}\), which can be assigned as ν (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 \(^1\)H 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 cm\(^{-1}\) for ν (C−OH) and 4 cm\(^{-1}\) for enol-isomer ν (C=O). The bands of strong intensity at 1560 cm\(^{-1}\) and 1518 cm\(^{-1}\) can be assigned to ν (C=N) of pyridine ring and ν (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\(_2\)L) 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 π→π* 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 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 π→π* 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-
Carbazole Functionalized Ligand

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

<table>
<thead>
<tr>
<th>Complexes</th>
<th>λex (nm)</th>
<th>λem (nm)</th>
<th>RI</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu2(L)3</td>
<td>281</td>
<td>596</td>
<td>1801</td>
<td>5D0 → 7F1</td>
</tr>
<tr>
<td></td>
<td>618</td>
<td></td>
<td>5616</td>
<td>5D0 → 7F2</td>
</tr>
<tr>
<td>Tb2(L)3</td>
<td>282</td>
<td>495</td>
<td>2930</td>
<td>5D4 → 7F6</td>
</tr>
<tr>
<td></td>
<td>548</td>
<td></td>
<td>6788</td>
<td>5D4 → 7F4</td>
</tr>
<tr>
<td></td>
<td>587</td>
<td></td>
<td>1223</td>
<td>5D0 → 7F4</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td></td>
<td>806</td>
<td>5D4 → 7F4</td>
</tr>
</tbody>
</table>

RI: relative intensity.

Table 2: Photoluminescence data of the complexes in solid state at room temperature. The emission spectra of the complex Eu(L), 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 Tb(L)3 consists of four main lines at approximate 495 nm (5D4 → 7F3), 587 nm (5D4 → 7F5), 596 nm (5D4 → 7F6), and 625 nm (5D0 → 7F4), and we can see that the emission band (5D0 → 7F2) 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 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 xylene 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 JASCO TU-1800PC 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;21 115°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, CH3), 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 9 by adding NaOH, followed by a solution of NaOH (0.10 g, 4.3 mmol) in anhydrous toluene (15 mL), and then a solution of the lanthanide chlorides was added to a solution of the ligand (0.15 g, 0.25 mmol) in ethanol (5.0 mL). The mixture was heated up to 110°C with silicone oil and stirred vigorously until the sodium chloride was removed. Then the mixture was cooled to room temperature, and the mixture was filtered. The crude products were recrystallized from methanol and tetrahydrofuran (1 : 1) to give the yellow crystals of the Eu(III) and Tb(III) complexes (0.37 g, 74%), m.p. 115 ~ 117°C; 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, CH3), 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.
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 48 h 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, 4.28; 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 (H2L) 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 \( \text{Eu}^{III} \) and \( \text{Tb}^{III} \) ions can be sensitized efficiently by the ligand and the \( \text{Tb}^{III} \) 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 (H2L) have a very good luminescent performance that could be used as candidate efficient luminescent materials.

**Acknowledgments.** This project was supported by the China Postdoctoral Science Foundation (NO. 20080431027) and the Postdoctoral Science Foundation of Central South University.

**References**