

Available online at www.sciencedirect.com



SPECTROCHIMICA ACTA PART A

Spectrochimica Acta Part A 69 (2008) 654-658

www.elsevier.com/locate/saa

# Preparation, photo- and electro-luminescent properties of a novel complex of Tb (III) with a tripod ligand

Tianzhi Yu<sup>a,\*</sup>, Yuling Zhao<sup>b</sup>, Duowang Fan<sup>a</sup>, Ziruo Hong<sup>c</sup>, Wenming Su<sup>c</sup>

<sup>a</sup> Key Laboratory of Opto-Electronic Technology and Intelligent Control (Lanzhou Jiaotong University), Ministry of Education, Lanzhou 730070, China

<sup>b</sup> School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

<sup>c</sup> Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics,

Chinese Academy of Sciences, Changchun 130033, China

Received 2 March 2007; received in revised form 20 April 2007; accepted 7 May 2007

#### Abstract

A novel Tb(III) complex TbL (L = tris[2-(2-carboxyphenoxy)ethyl]amine,  $H_3L$ ) was synthesized and characterized by means of elemental analyses, IR spectra, thermal analyses, and molar conductivity measurement. The photoluminescent properties of the complex were investigated. In addition, PVK doping Tb(III) complex was fabricated as the emissive layer by spin-coating and its electroluminescent properties were studied, in which the structure of the device was ITO (indium tin oxide)/PVK (polyvinylcarbazole)/PVK: TbL/PBD (2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole)/LiF/Al. It was indicated that pure green and narrow bandwidth emission at 545 nm from photoluminescence of TbL complex film and the organic electroluminescent device is the characteristic emission of Tb(III) ion, and the electroluminescence spectrum of the device was very similar to that of the photoluminescence of TbL complex film. The lowest triplet level of the ligand was calculated from the phosphorescence spectrum of GdL in *N*,*N*-dimethyl formamide (DMF) dilute solution determined at 77 K, and the energy transfer mechanisms in TbL complex were discussed.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Tripod ligand; Photoluminescence; Electroluminescence; Tb(III) complex

# 1. Introduction

The photophysical properties of lanthanide complexes with organic ligands have been extensively studied for their potential applications as luminescent materials and as a probe of chemical and biological molecules [1–3]. It is well-known that the chelating agents commonly used for the sensitization of lanthanide ions luminescence include  $\beta$ -diketones, aromatic carboxylic acids, cryptands, and several other macrocyclic ligands [4–11]. In recent 20 years, lanthanide chelates with organic ligands have been successfully developed as the organic electroluminescent (EL) materials due to their sharp emission bands with colors ranging from blue to red in thin film electroluminescent devices [12–20]. However, the focus of the work has mainly been upon ternary lanthanide complexes with  $\beta$ -diketones, little attention has been paid to the lanthanide complexes with aromatic carboxylic acids [21–24]. Research results indicated

1386-1425/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2007.05.017 that most triplet state energies of aromatic carboxylic acids are more suitable for the resonant energy level of  $Tb^{3+}$  and there may exist an efficient ligand-to-metal energy transfer process (antenna effect) [25,26]. These complexes have not only good luminescence properties, but also possess better photo- and thermal stability compared with that  $\beta$ -diketonates.

In this paper, we report the details of synthesis, characterization, and photo- and electro-luminescent properties of a novel Tb(III) complex with tripodal ligand containing salicylic acid, tris[2-(2-carboxyphenoxy)ethyl]amine (H<sub>3</sub>L).

## 2. Experimental details

#### 2.1. Material and methods

Tris(2-hydroxyethyl)amine was purchased from Alfa Aesar. Salicylic acid was analytical grade reagents from Sichuan Chengdu Chemical Reagent Factory (PR China). Thionyl chloride was freshly distilled prior to use.  $Tb_4O_7$  was converted to its nitrate by treating with concentrated nitric acid. The other solvents were analytical grade reagents. Tris(2-chloroethyl)

<sup>\*</sup> Corresponding author. Tel.: +86 931 4956935; fax: +86 931 4938756. *E-mail address:* ytz823@hotmail.com (T. Yu).

$$HCI \cdot N \left( \checkmark CI \right)_{3} + 3 \left( \bigcirc OH \\ COOH \end{array} \right) (2)HCI HCI \cdot N \left( \checkmark O \bigcirc OH \\ CO_{2}H \\ HI + ICI \\$$

Scheme 1. Synthetic route to tris[2-(2-carboxyphenoxy)ethyl]amine hydrochloride.

amine hydrochloride was prepared according to literature methods [27].

IR spectra (400–4000 cm<sup>-1</sup>) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental analysis instrument. The metal ion concentration of the complex was determined by EDTA titration method, and xylenol orange used as indicator. The molar conductivity of the complex in DMSO solution was measured by using a DDST-308 conductivity instrument made in China. The fluorescent spectra were recorded on a HITACHI F-4500 spectrometer. The thermogravimetry (TG) and differential thermal analysis (DTA) were recorded on a Shimadzu DT-40 thermal analysis instrument. Melting points were measured by using a X-4 microscopic melting point apparatus made in Beijing Taike instrument limited company, and the thermometer was uncorrected.

# 2.2. Synthesis of tris[2-(2-carboxyphenoxy)ethyl]amine hydrochloride (H<sub>3</sub>L·HCl)

 $\label{eq:constraint} \begin{array}{ll} Tris[2-(2-carboxyphenoxy)ethyl]amine & hydrochloride \\ (H_3L\cdot HCl) \mbox{ was synthesized by the synthetic route shown in Scheme 1. \end{array}$ 

Salicylic acid (13.8 g, 0.10 mol) and potassium hydroxide (12.9 g, 0.23 mol) were dissolved in 200 mL of dimethylformamide. After stirring for 1 h at room temperature, tris(2-chloroethyl)amine hydrochloride (7.2 g, 0.03 mol) was added and the reaction mixture was then heated to reflux for 24 h. The solvent was removed from the reaction mixture in vacuo and the residue was stirred with 50 mL of 6N HCl for 1 h at room temperature, then a sticky mass was formed from the solution. The supernatant was decanted and the residue was partitioned between chloroform and water. The chloroform phase was retained, and the aqueous phase was re-extracted two times. The combined chloroform extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. Crystallization occurred upon standing to afford 7.9 g (48.5%) of white needles. m.p. 191-192 °C. Anal. Found C, 59.50(59.40); N, 2.71(2.57); H, 5.51(5.13); C<sub>27</sub>H<sub>28</sub>NO<sub>9</sub>Cl requires C, 59.40; N, 2.57; H, 5.13. FT-IR (KBr) (cm<sup>-1</sup>): 3424 ( $\nu_{-COOH}$ ); 2959 ( $\nu_{C-H}$ , benzene ring); 1699 (v<sub>C=O</sub>); 1603, 1581, 1491 (benzene ring); 1286, 748  $(\delta_{-COO-H})$ ; 1240, 1053 ( $\nu_{Ar-O-C}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz) δ<sub>H</sub> (ppm): 10.3 (3H, S, COOH); 6.9–7.7 (12H, m, –C<sub>6</sub>H<sub>4</sub>); 4.2 (6H, t, NCH<sub>2</sub>-); 3.3 (6H, t, -CH<sub>2</sub>-O-Ar). FAB-MS *m*/*z* (%): 510 (M-Cl)<sup>+</sup>.

### 2.3. Synthesis of Tb(III) complex

The ligand (H<sub>3</sub>L·HCl) (0.2728 g, 0.5 mmol) and terbium nitrate (0.2718 g, 0.6 mmol) were dissolved in 25 mL of abso-

lute methanol, and the pH of the reaction mixture was adjusted to about 6.5 using triethylamine. Then the reaction mixture was stirred for 24 h at room temperature, resulting in a white precipitate. The precipitation was filtered off, washed with ethanol and water. The product was dried under reduced pressure, and purified with recrystallization from methanol. Yield: 75%. m.p. > 250 °C. Anal. Calc. for C<sub>27</sub>H<sub>26</sub>NO<sub>10</sub>Tb [TbL·H<sub>2</sub>O] (%): C, 47.44; H, 3.81; N, 2.05; Tb, 23.28. Found: C, 47.33; H, 4.01; N, 2.21; Tb, 23.48. FT-IR (KBr) (cm<sup>-1</sup>): 3400 ( $\nu_{O-H}$ , H<sub>2</sub>O); 3040 ( $\nu_{C-H}$ ); 1690 ( $\nu_{C=O}$ ); 1603, 1584, 1491 (benzene ring); 1541 ( $\nu_{as}$  (COO<sup>-</sup>)); 1452 ( $\nu_{s}$  (COO<sup>-</sup>)); 1238, 1049 ( $\nu_{Ar-O-C}$ ).

#### 2.4. Preparation of EL devices with the Tb(III) complex

The EL devices with the structure of ITO (indium tin oxide)/PVK (polyvinylcarbazole)/PVK: TbL/PBD (2-(4biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole)/LiF/Al were fabricated to study the electroluminescence of the TbL complex. The emissive layer was formed by spin-casting PVK doped with TbL complex from methanol/chloroform solution. The host transfer layer PBD, LiF and Al were sequentially deposited at a rate of 0.1-0.4 nm/s by thermal evaporation in a vacuum chamber  $(2 \times 10^{-4} \text{ Pa})$ . The emitting area of the EL devices was  $3 \text{ mm} \times 4 \text{ mm}$ . A quartz crystal oscillator placed near the substrate was used to measure the thickness of the thin film. The PL spectra of the Tb(III) complex film on a quartz substrates were studied. The EL spectra were measured with a Hitachi MPF-4 Fluorescence spectrophotometer. The luminance-current-voltage characteristics were measured simultaneously by the EL test system made in Beijing Normal University, PR China. All the performance measurements were carried out under ambient atmosphere without encapsulation.

#### 3. Results and discussion

#### 3.1. IR spectra

Comparing the IR spectra of the free ligand with the complex, the characteristic absorption bands of C=O and C-O bands of the free ligand disappear, while the characteristic absorption peaks of carboxylic group COO<sup>-</sup> appear, which indicate that the oxygen atoms of carboxyl groups of the ligand are coordinated to Tb<sup>3+</sup>. The group C=O stretching vibration of the free ligand is shifted from 1699 to  $1690 \,\mathrm{cm}^{-1}$  upon forming the complex. Besides, it can be observed that the absorption frequencies of Ar-O-C bond of the ligand are shifted from 1240 and 1053 to 1238 and  $1049 \text{ cm}^{-1}$ , respectively. It is shown that the oxygen atoms of C=O and Ar-O-C groups in ligand are coordinated with Tb<sup>3+</sup>. In addition, from the IR spectrum of the complex we can observe a new absorption band at  $415 \,\mathrm{cm}^{-1}$  with weak intensity, which is absent in the spectrum of the free ligand, so it is concluded that the band presumably was ascribed to vibration of the Tb-O bond [28]. The strong asymmetric and symmetric stretching absorptions of carboxylic group COO<sup>-</sup> in the complex appear at 1541 ( $\nu_{as}$ ) and 1452 ( $\nu_{s}$ ) cm<sup>-1</sup>, respectively. The  $\Delta v (\Delta v = v_{as} - v_s)$  of the complex is 89 cm<sup>-1</sup> (<116 cm<sup>-1</sup>, the  $\Delta v$  of Na<sub>3</sub>L), and the result indicates that the carboxylic groups



Fig. 1. TG-DTA of the ligand (a) and the TbL complex (b).

of the ligand coordinate to  $Tb^{3+}$  through bidentate models in the complex. It is noted that there is a broad band at  $3400 \text{ cm}^{-1}$  in IR spectrum of the complex, which is assigned to stretching vibration of the water molecule.

#### 3.2. Thermal property

The ligand and the complex were characterized by the thermogravimetry and differential thermal analysis (TG–DTA), the results of TG and DTA measurements of the ligand and the complex are shown in Fig. 1(a and b). It can be seen from Fig. 1(a) that the DTA curve of the ligand shows an endothermic peak at 192 °C, but without mass loss in the TG curve. It is the melting point of the ligand, which is in agreement with the result obtained by capillary tube method. At 207 °C an endothermic peak was observed in the DTA curve, and corresponds to a sharp weight loss in the TG curve. It should be the sublimation temperature, shown that the ligand undergoes sublimation. By further heating two exothermic peaks at 520 and 593 °C appear in the



Fig. 2. Suggested structure of the Tb(III) complex.

DTA curve, which were accompanied by a weight loss in the TG curve, it shows that the ligand undergoes decomposition.

From Fig. 1(b), at 73 °C an endothermic peak can be observed in the DTA curve, and the weight loss is about 2.5% of the complex in the TG curve, which corresponds to the loss of one molecule of water of the composition TbL·H<sub>2</sub>O, and the result suggests that the water is lattice water. With rising temperature, three exothermic peaks at 171, 352 and 447 °C were observed in the DTA curve, and correspond to sharp weight losses in the TG curve, it shows that the complex undergoes decomposition. The final residue was found to be Tb<sub>4</sub>O<sub>7</sub>. The total loss of weight agrees with the corresponding calculated data.

The results corroborate some of the assumptions made on the basis of infrared spectral and elemental analyses studies. In addition, the molar conductivity of the complex in DMSO solution was  $6.1 \text{ s cm}^2 \text{ mol}^{-1}$ , which indicates that the complex is a non-electrolyte [29]. So the structure proposed for the complex is shown in Fig. 2.

# *3.3. Photo- and electro-luminescent properties of the Tb(III) complex*

Fig. 3 shows the excitation and emission spectra of the Tb(III) complex in thin film. The sample for photoluminescent spectroscopy was made by spin-coating the methanol solution onto clean quartz substrates. From Fig. 3, it is shown that an intense excitation peak was observed at 281 nm. Photoexcitation of the thin film of the complex at 281 nm resulted in photoluminescence (PL) emission characteristic of a terbium ion:  $\lambda = 489$  nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ), 545 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ), 585 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ ), and



Fig. 3. Excitation (---) and emission (--) spectra of the Tb(III) complex in thin film.



Fig. 4. Phosphorescence spectrum of the GdL complex at 77 K.

 $620 \text{ nm} ({}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{3})$ . The most efficient emission originates from the electron transition from  ${}^{5}\text{D}_{4}$  state to  ${}^{7}\text{F}_{5}$  level at 545 nm with a half peak width of less than 10 nm, so the complex exhibits intensive green emission in the thin film.

Molecular phosphorescence can reflect the excited state characteristic of organic molecules and different phosphorescent emission bands correspond to the different ligands, so the excited triplet state energies of the ligand can be determined by their phosphorescence spectra. In general, Gd(III) complex was selected as model complex for the determination of the triplet state energies of the organic ligands due to their high phosphorescence-fluorescence ratio compared with those of the other Ln(III) complex and Gd(III) ion can sensitize the phosphorescence emission of ligands. Fig. 4 shows the phosphorescence spectrum of the GdL complex at nitrogen atmosphere (77 K), and two apparent phosphorescence bands appear at 448 and 510 nm, respectively. The triplet state energy of the ligand based on the first phosphorescence band (448 nm) was found to be  $22,321 \text{ cm}^{-1}$ , which is  $1821 \text{ cm}^{-1}$  above the resonant energy level of  ${}^{5}D_{4}$  of Tb(III) (20,500 cm<sup>-1</sup>). To efficiently sensitize Tb(III) fluorescence, the triplet state of the ligand has to be  $2400 \pm 300 \text{ cm}^{-1}$  above the <sup>5</sup>D<sub>4</sub> of Tb(III) [30]. The triplet energy level of the ligand is slightly lower than the ideal energy level, so it can be predicated that the intramolecular energy transfer from the ligand to Tb(III) occurred in the complex.

The TbL complex cannot be sublimed, so it cannot be used as an emitter in OLEDs by vacuum deposition. To examine the EL properties of the TbL complex in OLED devices, we chose PVK as the host material, and doped the complex into PVK matrix (25 wt%), and then the mixture was deposited to the substrate by spin cast. The electroluminescent device consisted of a layer of spin-casting PVK (30 nm), a layer of the TbL complex doped PVK film (25 wt%, ~45 nm) and a layer of vacuum deposited PBD (30 nm) sandwiched between the ITO anode and the LiF (1 nm)/Al (100 nm) cathode, in which PBD was used as the electron-transporting material. The EL emission was observed at different driving voltages (Fig. 5). The EL spectra had sharp peaks with the maxima at 490, 546, 586 and 620 nm, which correspond closely to the Tb<sup>3+</sup> ion



Fig. 5. EL spectra of OLED device with ITO/PVK (30 nm)/PVK: TbL (25 wt%, 45 nm)/PBD (30 nm)/LiF (1 nm)/Al (100 nm) at different applied voltages.

transitions: 490 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ), 545 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ), 586 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ ), 620 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$ ). It demonstrates that the electroluminescence is also from trivalent Tb<sup>3+</sup> ion of the TbL in the blend emissive layer, no electroluminescence is observed from PVK and PBD. As shown in Fig. 5, the intensity of EL emission increases gradually with increasing the driving voltages, but the emission spectral features do not change.

The EL process based on the multilayer structure device is considered as follows: under forward bias, holes injected from ITO through PVK and electrons injected from Al through PBD migrate and recombinate to form excitons in the PVK doped with TbL film. Then the energy of exciton caused by raditive decay is absorbed by the ligand and finally transferred to Tb<sup>3+</sup> ion of the complex by intersystem crossing from the triplet state of the ligand.

The current–voltage and luminance–voltage relationships of the device are depicted in Fig. 6. The device shows a turn-on voltage of about 10 V. When the forward bias voltage is lower than 10 V, the current increase slowly with increasing the forward bias voltage. When the forward bias voltage is larger than 10 V, the current increases intensively. It is shown that the device has the rectification characteristic. The luminance increases with



Fig. 6. Current-voltage and luminance-voltage characteristics of the device.

increasing the forward bias voltage. The turn-on voltage of the device is observed at 8 V, the maximum brightness is about  $135 \text{ cd m}^{-2}$  at an operating voltage of 19 V.

# 4. Conclusions

A novel terbium carboxylate complex with a tripodal ligand was synthesized and characterized by means of elemental analyses, IR spectra, thermal analyses, and molar conductivity measurement. Preliminary study on electroluminescent property of this complex shows that it is a green emitter for light-emitting device. Further optimization of the EL devices is being carried out.

#### Acknowledgements

This work was supported by 'Qing Lan' talent engineering funds (QL-05-23A) by Lanzhou Jiaotong University. This work was also supported by Program for Changjiang Scholars and Innovative Research Team in University (IRT0629).

## References

- [1] G.L. Denardo, G.R. Mirik, J. Nucl. Med. 37 (1996) 451.
- [2] G.F.H. De Sa, H.A. Nunes, O.L. Malta, J. Chem. Res. (S) (1992) 78.
- [3] F.S. Richardson, J. Chem. Rev. 82 (1982) 541.
- [4] N. Sabbatini, M. Guardigli, J.M. Lehn, Coord. Chem. Rev. 123 (1993) 201.
- [5] Y. Hasegawa, M. Iwamura, K. Murakoshi, Y. Wada, R. Arakawa, T. Yamanaka, N. Nakashima, S. Yanagida, Bull. Chem. Soc. Jpn. 71 (1998) 2573.
- [6] M.H.V. Werts, M.A. Duin, J.W. Hofstraat, J.W. Verhoeven, Chem. Commun. 9 (1999) 799.
- [7] P. Gawryszewska, L. Jerzykiewicz, M. Pietraszkiewicz, J. Legendziewicz, J.P. Riehl, Inorg. Chem. 39 (2000) 5365.

- [8] G.F. De Sá, O.L. Malta, C. De M. Donigá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. Silva Jr., Coord. Chem. Rev. 196 (2000) 165.
- [9] D.Z.V. Bermudez, L.D. Carlos, M.M. Silva, M.J. Smith, J. Chem. Phys. 112 (2000) 3293.
- [10] A. Beeby, L.M. Bushby, D. Maffeo, J.A.G. Williams, J. Chem. Soc., Dalton Trans. (2002) 48.
- [11] S.P. Vila-Nova, G.A.L. Pereira, R.Q. Albuquerque, G. Mathis, H. Bazin, H. Autiero, G.F. de Sá, S. Alves Jr., J. Lumin. 109 (2004) 173.
- [12] J. Kido, K. Nagai, Y. Ohashi, Chem. Lett. 220 (1990) 657.
- [13] J. Kido, H. Hayase, K. Hongawa, K. Nagai, K. Okuyama, Appl. Phys. Lett. 65 (1994) 2124.
- [14] Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, S. Yanagida, Appl. Phys. Lett. 74 (1999) 3245.
- [15] C.J. Liang, D. Zhao, Z.R. Hong, D.X. Zhao, X.Y. Liu, W.L. Li, J.B. Peng, J.Q. Yu, C.S. Lee, S.T. Lee, Appl. Phys. Lett. 76 (2000) 67.
- [16] X.C. Gao, H. Cao, C.H. Huang, B. Li, S. Umitani, Appl. Phys. Lett. 72 (1998) 2217.
- [17] H. Xin, M. Shi, X.M. Zhang, F.Y. Li, Z.Q. Bian, K. Ibrahim, F.Q. Liu, C.H. Huang, Chem. Mater. 15 (2003) 3728.
- [18] J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357.
- [19] P.P. Sun, J.P. Duan, J.J. Lih, C.H. Cheng, Adv. Funct. Mater. 13 (2003) 683.
   [20] F.S. Liang, Q.G. Zhou, Y.X. Cheng, L.X. Wang, D.G. Ma, X.B. Jing, F.S.
- Wang, Chem. Mater. 15 (2003) 1935.
  [21] B. Li, D.G. Ma, H.J. Zhang, X.J. Zhao, J.Z. Ni, Thin Solid Films 325 (1998) 259.
- [22] Q. Lin, C.Y. Shi, Y.J. Liang, Y.X. Zheng, S.B. Wang, H.J. Zhang, Synth. Met. 114 (2000) 373.
- [23] C. Seward, N.-X. Hu, S. Wang, J. Chem. Soc., Dalton Trans. (2001) 134.
- [24] S. Eliseeva, O. Kotova, O. Mirzov, K. Anikin, L. Lepnev, E. Perevedentseva, A. Vitukhnovsky, N. Kuzmina, Synth. Met. 141 (2004) 225.
- [25] B. Yan, H.J. Zhang, S.B. Wang, J.Z. Ni, J. Photochem. Photobiol. A: Chem. 116 (1998) 209.
- [26] B. Yan, H.J. Zhang, J.Z. Ni, Chem. Res. Chin. Univ. 14 (1998) 245.
- [27] J.P. Mason, D.J. Gasch, J. Am. Chem. Soc. 60 (1938) 2816.
- [28] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., John Wiley and Sons, New York, 1986.
- [29] W.J. Greary, Coord. Chem. Rev. 7 (1971) 81.
- [30] S. Sato, M. Wada, Bull. Chem. Soc. Jpn. 43 (1970) 1955.