

A terbium (III) complex with triphenylamine-functionalized ligand for organic electroluminescent device

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Received 14 December 2006; received in revised form 13 October 2007; accepted 19 October 2007

Available online 30 October 2007

Abstract

A novel ligand, 4-diphenylamino-benzoic acid (HDPAB), and the corresponding Tb (III) complex, Tb (DPAB)₃ which can be dissolved easily in organic solvents were synthesized and characterized. Organic electroluminescent (EL) device with a structure of indium tin oxide (ITO)/poly(*N*-vinylcarbazole) (PVK): Tb (DPAB)₃ (50 wt%, 80 nm)/1,3,5-tris-(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) (30 nm)/tri(8-hydroxyquinoline)aluminum (AlQ) (20 nm)/LiF (1 nm)/Al (150 nm) in which Tb (DPAB)₃ acted as an emitter were fabricated. The maximum luminance of 230 cd m⁻² at 20 V and the maximum efficiency of 0.62 cd A⁻¹ were obtained due to the introduction of hole-transporting group, representing the best result to date among Tb (III) carboxylate complexes based EL devices. These results indicate that modifications of rare earth complexes are a promising way to improve the properties of EL devices.

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Keywords: Electroluminescence; Terbium complex; Triphenylamine-functionalized

1. Introduction

In the past two decades, considerable research efforts have been devoted to develop organic functional devices, such as organic light-emitting devices (OLEDs) [1], photovoltaic devices [2], field-effect transistors [3], optical pumped lasers [4] and switches [5], having numerous advantages, such as low cost, light weight, compatibility with flexible substrates, over their inorganic counterparts. OLEDs have been intensively studied throughout the world due to potential applications as large-area flat-panel displays [1,6–9]. Therefore, employment of organic small molecules and conjugated polymers as active layers in OLEDs devices has become one of the important subjects recently. Unfortunately, electroluminescent (EL) emission spectra of organic materials usually have a typical full-width at half-maximum (FWHM) of 50–200 nm which is not suited for high performance flat panel displays. Using luminescent lanthanide complexes as emitters in OLEDs is

believed to be a promising solution to this problem [9–11]. Owing to their unique *f–f* transitions, most of the lanthanide ions exhibit sharp emission bands, and there is no limitation, up to 100%, of internal quantum efficiencies for EL devices using these complexes as emitters, because both singlets and triplets are involved in the luminescence process. Device performances based on lanthanide complexes, mainly Eu³⁺- and Tb³⁺-complexes, have been greatly improved [10–14]. However, previous reports are usually focused on β -diketone complexes, which are limited in terms of practical applications by their poor chemical stability and photo stability [10–17]. Lanthanide carboxylates complexes possess good ultraviolet durability and chemical stability. However, little attention has been devoted lanthanide carboxylate complexes due to their poor solubility, volatility and charge carrier transporting properties [18].

To overcome the above-mentioned problems, in this article we designed and synthesized a novel Tb (III) complex with triphenylamine-functionalized ligand. Triphenylamine and its derivatives are widely used as hole-transporting materials [6–8]. The obtained soluble

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complex, Tb (DPAB)₃, combined virtues of sharp green emission of terbium (III) ion and excellent charge carrier transporting ability of triphenylamine group. Efficient pure green EL was observed.

2. Experimental details

2.1. Synthesis

The synthetic routes of the ligand (HDPAB) and the complex [Ln(DPAB)₃] (Ln = Tb, Gd) are presented in Scheme 1.

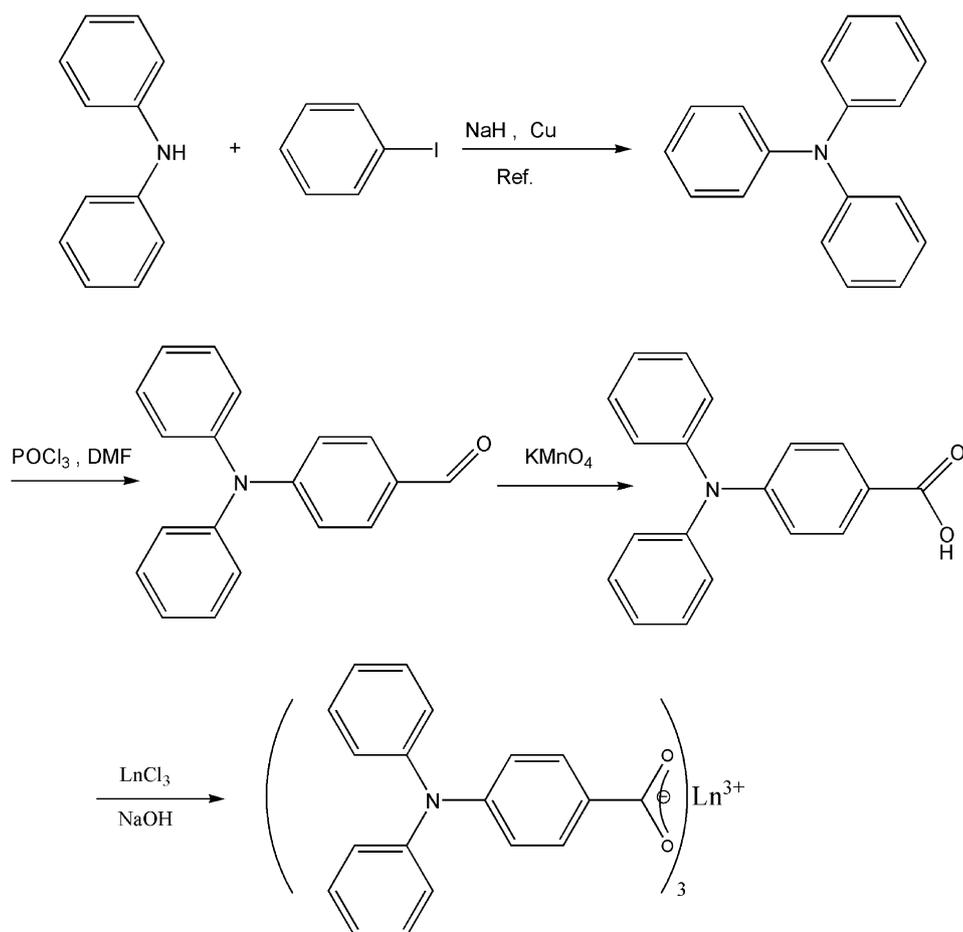
Triphenylamine (**1**). **1** was synthesized by modification of a literature procedure [19,20]. The mixture of diphenylamine (6.76 g, 0.04 mol), iodo-benzene (6.4 g, 0.03 mol), copper powder (2.6 g, 0.04 mol), NaH (2.4 g, 60% NaH, 0.06 mol) and xylene (40 ml) was stirred at 85 °C for 1 h, and additionally stirred at 140 °C for 18 h in a nitrogen atmosphere. After cooling, the mixture was filtered, and washed by water. The solvent was removed at a reduced pressure of 0.02 MPa. The residue was chromatographed through a silica gel column to produce 7.4 g of white powder, yield of 72%. M. p: 126 °C.

4-Diphenylamino-benzaldehyde [21] (**2**). Phosphorus oxychloride (1.9 ml, 0.02 mol) was added dropwise into a

stirred 3.1 ml (0.04 mol) of *N, N*-dimethyl formamide at 0 °C. The mixture was stirred at that temperature for 1 h and then at 20 °C for 1 h. After the addition of 5 g (0.02 mol) of **1** dissolved in dichloroethane, the mixture was stirred at 90 °C for 2 h. After cooling, the mixture was poured into cold water. The resulting mixture was neutralized to pH = 7 with 2 N NaOH aqueous solution and extracted with dichloromethane. The solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column to produce 3.0 g of yellow solid, yield of 58%. ¹H NMR (acetone-d₆, 500 MHz): 10.12 (s, 1H), 7.72 (d, 2H), 7.43–7.37 (t, 4H), 7.24–7.17 (t, 6H), 6.98–6.94 (d, 2H).

4-Diphenylamino-benzoic acid (HDPAB) (**3**). A 2.7 g of **2** was resolved in the mixed solvent of 100 ml acetone and 200 ml water. First 1.1 g of KMnO₄ was added into the mixture and stirred at room temperature for 24 h and then 4.4 g of KMnO₄ was added during this period. At last, the residue was filtered, the solution was acidified to PH = 2 with HCl to produce 2.3 g yellow solid. Yield of 80%. ¹H NMR (acetone-d₆, 500 MHz): 7.74 (d, 2H), 7.46–7.36 (t, 4H), 7.27–7.15 (t, 6H), 6.99–6.95 (d, 2H).

Ln(DPAB)₃. A 0.58 g of **3** was neutralized with 0.02 N NaOH aqueous solution, LnCl₃ aqueous solution was added dropwise into the solution to produce yellow solid,



Scheme 1. Synthetic routes of the ligand (HDPAB) and the complex [Ln(DPAB)₃].

and the crude product was washed in hot water and then dried under vacuum to produce yellow powder. Analysis (% $C_{57}H_{42}N_3O_6Tb$), found (calcd): C, 65.98 (66.86); H, 5.07 (4.13); N, 3.64 (4.10). (% $C_{57}H_{42}N_3O_6Gd$), found (calcd): C, 66.01 (66.97); H, 5.12 (4.14); N, 3.58 (4.25).

2.2. Fabrication of EL devices

The device, ITO/ PVK:Tb (DPAB)₃ (50 wt%, 80 nm)/ TPBI (30 nm)/ AIQ (20 nm)/LiF (1 nm)/Al (150 nm), was constructed on an ITO-coated glass substrate. PVK:Tb (DPAB)₃ layer was formed by spin casting a chloroform solution of hole-transporting PVK containing 50 wt% of Tb (DPAB)₃ (80 nm). TPBI (30 nm) as a hole-blocking and electron-transporting layer, and AIQ (20 nm) as an electron-transporting layer were sequentially grown on the top of the spin-coated PVK layer by thermal evaporation in high vacuum of 2×10^{-4} Pa. Finally, an electron injection layer, LiF (1 nm), was introduced, followed by aluminum cathode (150 nm).

2.3. Instruments and physical characterization

¹H NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer with chemical shifts reported relative to tetramethylsilane. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. Phosphorescence spectrum of Gd (DPAB)₃ in CH₂Cl₂ (10^{-5} mol L⁻¹) at 77 K was observed in a 12-mm square quartz cube in a glass Dewar flask with quartz windows. All the photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. Absorption spectra of organic films on quartz substrates were measured with a Shimadzu UV-3101PC spectrophotometer. All measurements were carried out in air at room temperature if without being specified.

3. Results and discussion

3.1. Syntheses of Ln(DPAB)₃

The ligand, HDPAB, and corresponding Ln (III) complex, Ln (DPAB)₃, were prepared according to literature methods [22], and their structures are shown in Scheme 1. Purity and composition of the complex were confirmed by ¹H NMR and elemental analyses. Introduction of a triphenylamine group into the carboxylate complex improves the solubility of Tb (DPAB)₃ in organic solvent, i.e. chloroform, and the compatibility of the complex with PVK host, enabling Tb (DPAB)₃ homogeneously disperse in PVK film by spin-casting.

3.2. Photophysical properties of Tb (DPAB)₃

The absorption, excitation and emission spectra of complex Tb (DPAB)₃ in CH₂Cl₂ solution (10^{-5} mol L⁻¹) are shown in Fig. 1. The absorption spectrum consists of a

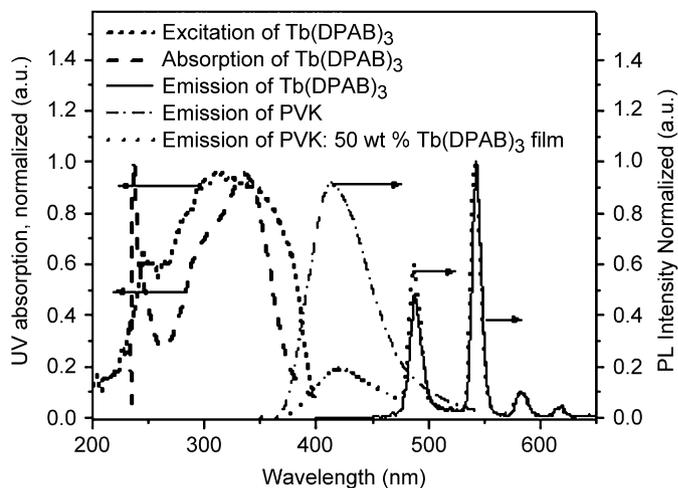


Fig. 1. UV-vis absorption, excitation, and emission spectra of 10^{-5} mol L⁻¹ Tb (DPAB)₃ in CH₂Cl₂, and emission spectra of PVK: 50 wt% Tb (DPAB)₃ and PVK films on quartz substrates.

broad absorption band centered at 330 nm and a shoulder band which is ascribed to intraligand $\pi \rightarrow \pi^*$ transition in DPAB ligand. Excitation of Tb (DPAB)₃ under 240–380 nm UV irradiation leads to strong green PL emission. The main emission peak at 544 nm corresponds to the ⁵D₄ → ⁷F₅ transition of Tb³⁺ ion. The excitation spectrum of Tb (DPAB)₃ monitoring 544 nm peak overlaps well with the absorption band of the DPAB ligand and no emission from DPAB was observed, indicating efficient energy transfer from DPAB to Tb³⁺ ion.

3.3. Triplet energy level of DPAB

Given efficient ligand-to-metal energy transfer, the emission of rare earth complex is generated by the emissive center which is excited by the excitation energy from triplet energy level of ligand to center ion. In order to further understand the mechanism of energy transfer in the complex, a Gd³⁺ complex with DPAB ligand was used to determine the triplet energy level of the ligand [23]. Generally, in a typical PL process of an organic rare earth complex, organic ligand absorb photon energy and then transfer the energy to the rare earth ion, at last, rare earth ion emit light, as shown in Scheme 2. There is usually energy loss when the energy is transferred from organic ligand to rare earth ion; so the energy transferred by organic ligand must be larger than the emitting energy of rare earth ion in order to excite rare earth ion efficiently. However, in a Gd³⁺-complex, Gd³⁺'s emitting energy is so high that energy transferred by organic ligand is usually smaller than Gd³⁺'s emitting energy; thus, the excited Gd³⁺-complex will emit organic ligand's triplet phosphorescence instead of Gd³⁺'s light.

The PL spectrum of Gd (DPAB)₃ at 77 K is shown in Fig. 2 and the emission band that centers at 480 nm is assigned to a 0–0 transition of DPAB. The lowest triplet (T₁) level of DPAB ligand was determined to

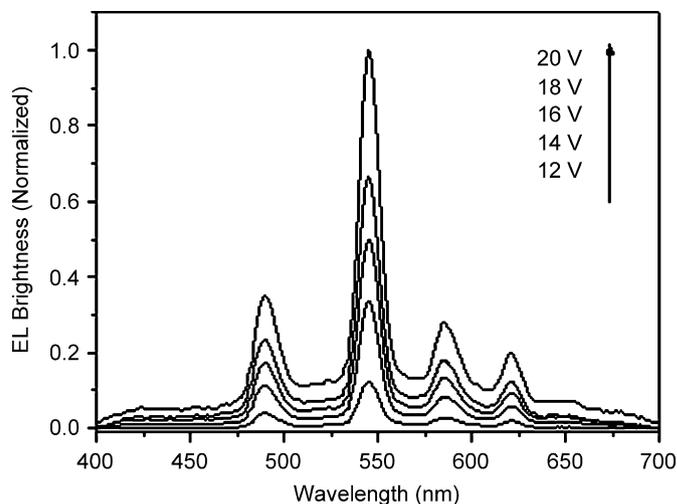
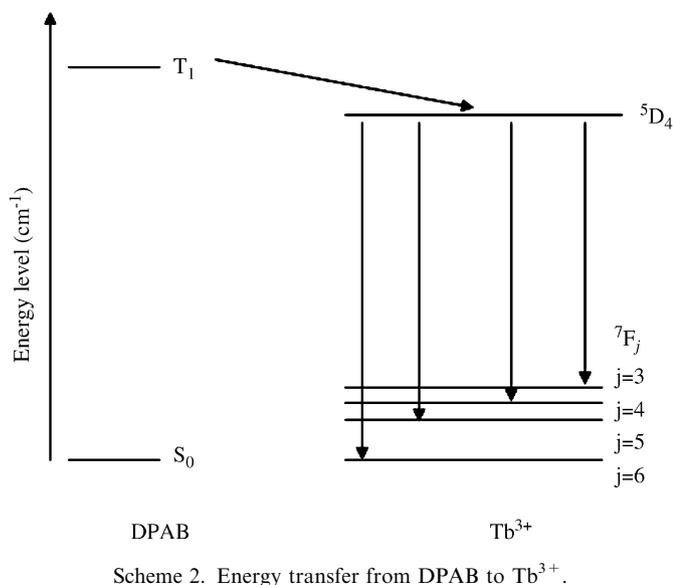


Fig. 3. EL spectra of the device [ITO/PVK: 50 wt% Tb (DPAB)₃ (80 nm)/TPBI (30 nm)/AlQ (20 nm)/LiF (1 nm)/Al (150 nm)] under driving voltage from 12 to 20 V.

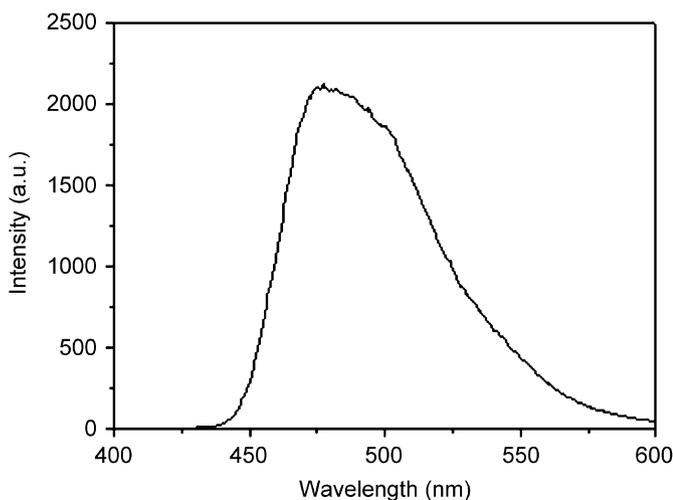


Fig. 2. PL spectrum of Gd (DPAB)₃ in CH₂Cl₂ (10⁻⁵ mol L⁻¹) at 77 K.

be 20833 cm⁻¹. The energy levels of Tb³⁺ are 20 366 cm⁻¹ (⁵D₄→⁷F₆), 18 248 cm⁻¹ (⁵D₄→⁷F₅), 16 950 cm⁻¹ (⁵D₄→⁷F₄), 16 129 cm⁻¹ (⁵D₄→⁷F₃), respectively. According to Sato's luminescence theory [24], there exists an optimal energy difference between T₁ of ligands and metal ion; larger or smaller energy difference will decrease the luminescent efficiency of rare earth complexes. Tb³⁺ can be efficiently sensitized when the energy difference is 2400 ± 300 cm⁻¹. Here, the energy difference between T₁ and the ⁵D₄→⁷F₅ transition is 2585 cm⁻¹, indicating efficient energy transfer from ligand to emissive centers.

3.4. EL properties of Tb (DPAB)₃

The EL spectra of a device, ITO/PVK: 50 wt% Tb (DPAB)₃ (80 nm)/TPBI (30 nm)/AlQ (20 nm)/LiF (1 nm)/Al (150 nm), are shown in Fig. 3. The characteristic

emission of Tb (III), i.e. ⁵D₄→⁷F₆ (491 nm), ⁵D₄→⁷F₅ (548 nm), ⁵D₄→⁷F₄ (590 nm), ⁵D₄→⁷F₃ (620 nm) was observed. The close resemblance of the EL and PL spectra of Tb (DPAB)₃ suggests that EL emission originates from Tb (III) of Tb (DPAB)₃. The EL spectra are independent of driving voltage, indicating that the combination of charge carriers generates excitons within the PVK:Tb (DPAB)₃ layers, and the energy is completely transferred to Tb³⁺. As shown in Fig. 1, there is a poor overlap between absorption of Tb (DPAB)₃ and PL emission of PVK, and emission from PVK is observed from PVK: 50 wt% Tb (DPAB)₃ film. Thus, it can be concluded that energy transfer from PVK to Tb (DPAB)₃ is not the dominant process upon electrical or UV excitation. On the contrary no EL emission from PVK in Tb (DPAB)₃-doped PVK device was observed. The difference between PL and EL spectra of PVK: 50 wt% Tb (DPAB)₃ system indicates serious charge carrier trap on the Tb (DPAB)₃ molecules in PVK film in the EL devices. That is, the injected holes in PVK film are trapped by Tb (DPAB)₃, followed by direct recombination with electrons from TPBI layer. In addition, PVK singlet energies partially transferred to Tb (DPAB)₃ singlet states via a Förster process may be included in the mechanism of the EL process [25].

Fig. 4 shows the current density–brightness–voltage characteristics of the EL device. Green emission was observed under 8 V bias. A maximum brightness of 230 cd m⁻² is achieved at 20 V with the current efficiency of 0.27 cd A⁻¹, while brightness and current efficiency of device using similar terbium (III) carboxylate as an emitter are 150 cd m⁻² and 0.07 cd A⁻¹, respectively [26]. The increase in EL performance suggests that charge transport across the thin-film structure was improved by the triphenylamine group, and confirms that structure design of metal complexes is an effective approach to improve OLED performance.

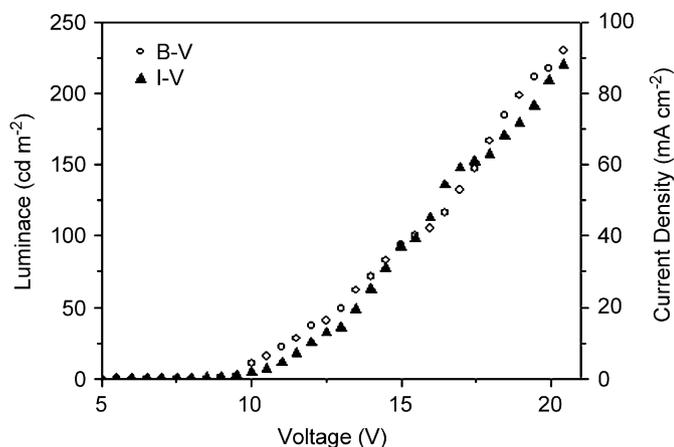


Fig. 4. Current density–brightness–voltage characteristics of the EL device.

4. Conclusions

In summary, we report for the first time the design, synthesis, characterization, EL properties of a novel terbium (III) complex with triphenylamine-functionalized ligand. Even in the device which is not yet optimized, the performances of the new complex are the best among the EL devices based on Tb (III) carboxylate complexes as green emitters. Our results suggest that incorporating triphenylamine moiety into a Tb (III) complex is a feasible strategy to modify the physical properties of the corresponding lanthanide complex.

Acknowledgments

The authors gratefully thank the financial supports of One Hundred Talents Project from Chinese Academy of Sciences, and the National Natural Science Foundations of China (Grant no. 20571071).

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