Solid-State Electronics 69 (2012) 67–71

Contents lists available at SciVerse ScienceDirect

Solid-State Electronics

journal homepage: www.elsevier.com/locate/sse

Red- and white-emitting organic light-emitting diodes based on trimetallic dendritic europium (III) complex: $Eu_3(DBM)_9(TMMB)$

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ARTICLE INFO

Article history:
Received 11 July 2011
Received in revised form 27 October 2011
Accepted 4 December 2011
Available online 16 January 2012

The review of this paper was arranged by Dr. Y. Kuk

Keywords:
Europium complex
Dendritic
Electroluminescence

ABSTRACT

The photoluminescence (PL) and electroluminescence (EL) properties of a trimetallic dendritic europium (III) complex containing three metal cores as branching centers, tris(dibenzoylmethanato) (1,3,5-tris[2-(2′-pyridyl)benzimidazoly]methyl-benzene)-europium (III) ($Eu_3(DBM)_9(TMMB)$), have been investigated and reported. Red and white emissions have been acquired in the four EL devices of device A–D. Characteristic red emission peaking at 613 nm with four shoulder bands due to the $^5D_0 \rightarrow {}^7F_j$ (j = 0–4) transitions of $Eu_3(DBM)_9(TMMB)$ is observed in devices A–C. Device D with a simple non-doping device structure showed a white emission band. Also, the optical and the electrochemical properties of $Eu_3(DBM)_9(TMMB)$ have been characterized to possess a better understanding on the intramolecular energy transfer process. It is concluded that dendritic structure with three DBM ligands as "absorption antennas" facilitates the energy absorption and transportation of the complex.

1. Introduction

Organic dyes and polymers have been widely applied in organic light-emitting diodes (OLEDs), and further in full-color flat panel displays, because of their outstanding emissive characters. Especially, tertiary europium (III) complexes have received extensive attention as red-emitting materials for OLED owing to their sharp pure red monochromic emission and high emission quantum efficiency (up to 100%, theoretically) since the transition is not restricted by the spin inhibition rule [1]. However, the poor carrier-transporting ability, the low extinction coefficient, intense luminescence quenching by matrix vibrations like hydroxyl groups *via* non-radioactive pathways, and the low thermal stability limit their applications in OLED field [2].

Europium (III) complexes have been widely researched. $Eu(DBM)_3$bath has been used to construct the color-tuning organic light-emitting diodes controlled by voltage. Making use of Eu^{3+} featuring a sharp red emission, reversible voltage-controlled continuous color tuning is achieved in the OLEDs by using $Eu[DBM]_3$bath as the strategic starting point close to the red corner of the CIE chromaticity diagram [3]. Eu^{3+} complex is also used to mix with Tb complex to introduce another decay channel for excited Tb ions and accelerates its decay process [4].

Dendritic europium (III) complexes, as a group of third class luminescent materials for OLEDs [5,6], have several interesting properties [7–9], such as promising carrier-transporting, site isolation [10], antenna effect [11], excellent film-forming, thermal and morphological stability [12]. Many successful examples using dendritic Eu(III) complexes as emitters have been reported [10,13–15]. For example, Tian et al. synthesized a few dendritic Eu(III) complexes containing terminal frafted carbazole moieties, $[Eu(MCPD)_3(phen)]$, $[Eu(BCPD)_3(phen)]$ and $[Eu(TCPD)_3(phen)]$. A red emission peaking at 615 nm from $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III) ion has been observed for complexes in solutions or solid films. White light emission with CIE coordinates of (0.333,0.348) has been achieved in $Eu(TCPD)_3(phen)$-based device. The maximum external quantum efficiency is more than 1.1% and the maximum brightness is as high as 229 cd m^{-2} [10]. Two carbazole-based bipolar structural ligands, CPPO and CPO, and their corresponding Eu(III) complexes have been synthesized by Xu et al. [13]. The doping device with a configuration of ITO/NPB/1: CBP/BCP/Alq_3/Mg:Ag shows a maximum brightness of 1271 cd m^{-2} with external quantum efficiency of 3.6%. All devices mentioned above are based on mono-core Eu(III) complexes, and complexes with triple-core have not been investigated to the best of our knowledge.

In this work, a triple-core dendritic [15] europium complex, tris (dibenzoylmethanato) (1,3,5-tris[2-(2′-pyridyl)benzimidazoly]methyl-benzene)-europium (III), or $Eu_3(DBM)_9(TMMB)$, was synthesized

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0038-1101/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.sse.2011.12.005

and used as the luminescent material to construct high efficiency red and white emitting OLEDs.

2. Experimental details

2.1. Preparation and characterization of $Eu_3(DBM)_9(TMMB)$

The molecular structure of $Eu_3(DBM)_9(TMMB)$ is shown in Fig. 1.

Dendritic europium complex $Eu_3(DBM)_9(TMMB)$ was synthesized as reported in Ref. [10] with some minor modifications. A mixture of mesitylene (2.8 ml, 0.02 mol), N-bromosuccinimide (10.62 g, 0.06 mol), and benzoyl peroxide (0.11 g) in CCl_4 (40 ml) was stirred and heated in N_2 at 90 °C for 12 h. After filtration, the filtrate was washed with water and dried with anhydrous Mg_2SO_4. Colorless crystals with needle structure were collected by centrifugation in the CCl_4 solution. The recrystallization with ethanol/hexance (1:1, v/v) solution afforded 6.56 g product (yield, 92%). ^1H NMR (CD_3OD): δ 4.55 (s, 6H), 7.42 (s, 3H). A mixture of 1,3,5-tris(bromomethyl) benzene (0.357 g, 1 mmol), PyBM (0.600 g, 3 mmol), sodium hydroxide (0.12 g, 3 mmol) and DMF (30 ml) was stirred and heated in N_2 at 120 °C for 12 h. The solution was subsequently poured into ice water (100 ml), after extraction with dichloromethane (3 × 30 ml). The organic layer was extracted one more time with water and dried over anhydrous Mg_2SO_4. The solvent was then evaporated, the resulting residue was purified by silica gel column chromatography to give 0.11 g product (yield, 16%). ^1H NMR (500 MHz, $CDCl_3$): δ 5.89 (s, 6H), 6.90 (s, 3H), 7.05–7.08 (t, 3H), 7.14–7.19 (t, 6H), 7.28–7.32 (d, 3H), 7.69–7.73 (t, 3H), 7.83–7.85 (d, 3H), 8.19–8.26 (d, 6H). EI-MS: m/z: 700 (M^+).

A solution of DBM (0.20 g, 0.9 mmol) and TMMB (75 mg, 0.1 mmol) was dissolved in a mixture of hot ethanol/chloroform with stirring. The solution turned yellow immediately after addition of sodium hydroxide (36 mg, 0.9 mmol). $EuCl_3{\cdot}(H_2O)_6$ (36.6 mg, 0.1 mmol) solved in 2 ml ethanol was added dropwise to the solution. The mixture was continued stirring at 60 °C for 1 h. The products (with red color) were collected by filtration and recrystallized with ethanol. About 75% products were recovered after above purification procedure. Elemental analysis for $C_{180}H_{132}N_9O_{18}Eu_3$. Calcd: C, 68.11; H, 4.69; N, 4.20. Found: C, 68.31; H, 4.16; N, 3.97. Fourier-transform IR spectroscopy (KBr pellet): [cm^{-1}] 3058, 3025, 2966, 2928, 1549, 1518, 1458 (C=O, chelated to Eu^{3+}), 618, 508, 413 (O—Eu—O), 3425 (N—H), 1595 (C=N), 1550, 1478 (imidazolering).

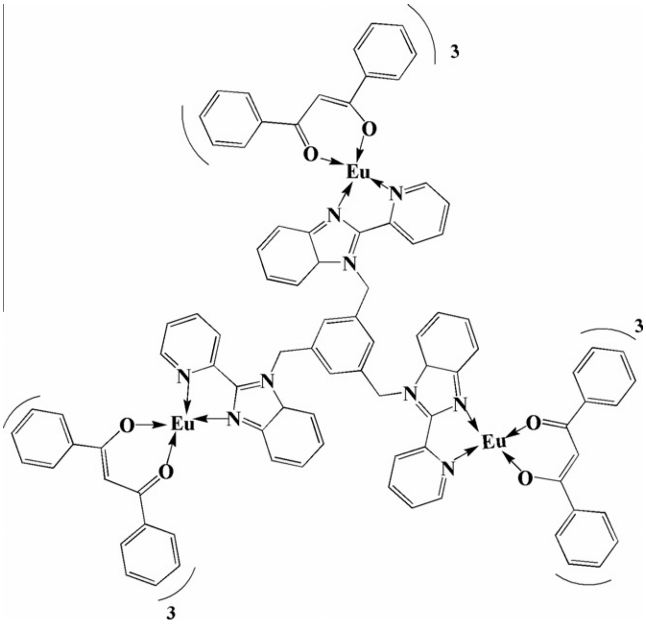

Fig. 1. The chemical structure of $Eu_3(DBM)_9(TMMB)$.

2.2. Fabrication and characterization of the organic electroluminescent device

The other materials, including N,N-bis(naphthylphenyl)-4,4′-biphenyldiamine (NPB), bathocuproine (BCP), 4,4′-bis(carbazole-9-yl)-biphenyl (CBP), and tri(8-hydroxyquinoline)aluminum (Alq_3), were commercially available and applied without further purification.

A pre-patterned indium tin oxide (ITO) coated glass substrate with a sheet resistance of 30 Ω/□ was cleaned by acetone, glass detergent sonication and rinsed with deionized water. After UV ozone treatment, the ITO substrates were loaded in a vacuum chamber. All the organic layers, LiF and Al cathode were sequentially neatly deposited onto the ITO substrates by thermal evaporation at a pressure of 2×10^{-4} Pa. The thickness of depositing film of above materials was monitored by a quartz oscillators and controlled at a rate of 0.2–0.4 nm/s for the organic layers and LiF, and 1.0 nm/s for the Al layer, respectively. The active area of typical device was 10 mm^2. Absorption and PL emission spectra of $Eu_3(DBM)_9(TMMB)$ were measured with a Cary 500 Scan UV–Vis–NIR Spectrophotometer and Cany Eclipse Spectrophotometer, respectively. Electrochemical measurements were performed on a CHI830b electrochemical workstation (CH Instruments, Shanghai Chenhua Instrument Corporation, China) in a conventional three-electrode cell with a platinum-sheet working electrode, a platinum-wire counter electrode, and a silver/silver nitrate (Ag/Ag^+) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature. The measurements on the EL spectra, Commission International de l'Eclairage (CIE) coordinates and the brightness-current–voltage (*B–I–V*) characteristics were carried out with a Spectrascan PR650 photometer and a computer-controlled direct current power supply. All measurements were carried out in ambient air at room temperature without being especially pointed out.

3. Results and discussion

The structure of $Eu_3(DBM)_9(TMMB)$ contains three Eu(III) cores as branching centers, combining three DBM ligands and one phlydentate ligand of TMMB serving as the connector along the branches of a dendritic structure, as shown in Fig. 1. Excellent optical properties of $Eu_3(DBM)_9(TMMB)$ are expected because of its large rigid structure of complex supported by the central TMMB ligand and high absorption efficiency coming from antenna ligand of DBM.

3.1. Optical properties

The absorption spectra of $Eu_3(DBM)_9(TMMB)$, HDBM and TMMB were measured in solid state and shown in Fig. 2. The absorption spectrum of $Eu_3(DBM)_9(TMMB)$ consists of three main absorption peaks at 318, 333 and 345 nm, respectively. TMMB contributes to the absorption at 318 nm. The other two intense absorption bands locate at 333 and 345 nm match the absorption spectrum of HDBM associated with the π–π^* transition of DBM ligand. Therefore, DBM serves as a strongly-absorbing "antenna" for light harvesting in the complex. The singlet state energy level of TMMB is calculated to be 3.54 eV (350 nm) from its absorption edge.

The phosphorescence spectrum of complex $Gd(TMMB)(NO_3)_3$ measured under 77 K is shown in Fig. 3. From the phosphorescence