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

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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.

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 Eu^{3+}- and Tb^{3+}-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

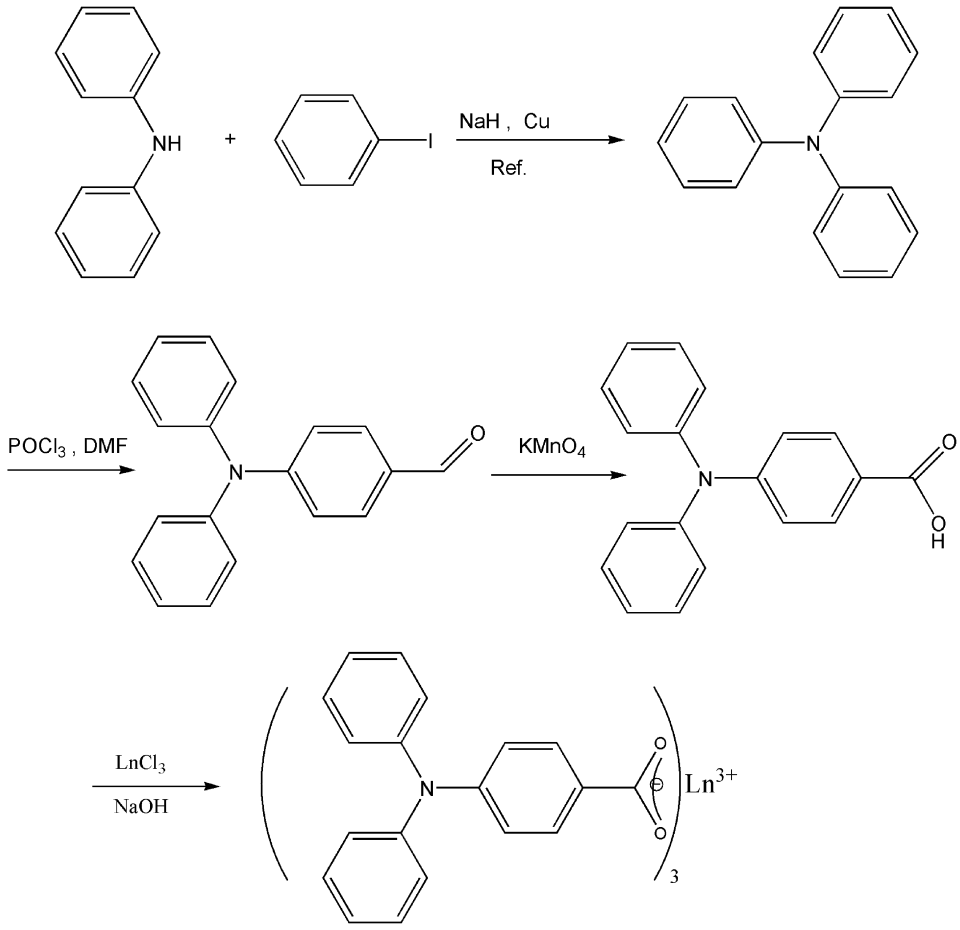
The synthetic routes of the ligand (HDPAB) and the complex $[Ln(DPAB)_3]$ (Ln = Tb, Gd) are presented in Scheme 1.

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%. ^{1}H NMR (acetone-d_6, 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 $KMnO_4$ was added into the mixture and stirred at room temperature for 24 h and then 4.4 g of $KMnO_4$ 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%. ^{1}H NMR (acetone-d_6, 500 MHz): 7.74 (d, 2 H), 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, $LnCl_3$ aqueous solution was added dropwise into the solution to produce yellow solid,



Scheme 1. Synthetic routes of the ligand (HDPAB) and the complex $[Ln(DPAB)_3]$.