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Journal of Luminescence 97 (2002) 55–59

JOURNAL OF
LUMINESCENCE

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Blue organic electroluminescent devices based on a distyrylarylene derivative as emitting layer and a terbium complex as electron-transporting layer

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Received 4 January 2001; received in revised form 22 October 2001; accepted 22 October 2001

Abstract

With a blue distyrylarylene derivative, 4,4'-bis(2,2-di(2-methoxyphenyl)ethenyl)-1,1'-biphenyl (CBS) as emitting material, double-layer and triple-layer electroluminescent (EL) devices were fabricated. For the device using tris(1-phenyl-3-methyl-4-isobutyl-5-pyrazolone)-bis(triphenyl phosphine oxide) terbium ($\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$) as the electron-transporting layer, blue EL emission with a maximum luminance of 253 cd/m^2 was achieved at 19 V. The difference of $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ and tris(8-hydroxyquinolate)aluminum (AlQ) as the electron-transporting materials in these devices were compared and discussed. © 2002 Published by Elsevier Science B.V.

Keywords: Electroluminescence; Rare earth; Photoluminescence; 4,4'-bis(2,2-di(2-methoxyphenyl)ethenyl)-1,1'-biphenyl

1. Introduction

Organic electroluminescent devices (OLED) have attracted much interest from both fundamental and practical viewpoints because of the near at hand commercial probability in flat full-color panel displays [1,2]. In order to obtain high performance, the materials used in OLED must have a high purity. Chemical modification is one

of ways to solve this problem. In this paper, a blue fluorescent material of distyrylarylene derivative, 4,4'-bis(2,2-di(2-methoxyphenyl)ethenyl)-1,1'-biphenyl (CBS), was synthesized and used as an emitting material. Compared with the common blue emitting material, 4,4'-bis(2,2-diphenylethenyl)-1,1'-biphenyl (DPVBi) [3–5], the solubility of CBS is improved by introducing methoxy groups. It is easy to be purified and can satisfy the need of purity for the materials in OLED.

In recent years, rare earth complexes, such as $\text{RE}(\text{III})(\text{acac})_3\text{Phen}$ ($\text{RE} = \text{Y}^{3+}$, La^{3+} or Gd^{3+} , $\text{acac} = \text{acetylacetonate}$, $\text{Phen} = 1,10\text{-phenanthroline}$),

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were reported to be used as the electron-transporting layer (ETL) [6,7]. It is well known that terbium complexes are one kind of green light emitting materials just like AlQ with narrow spectral bandwidth. We found that tris-(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone)-bis(triphenyl phosphine oxide) terbium ($\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$) possesses high electron mobility except its encouraging EL performance [8–10]. Because in either double-layer devices of ITO/ $\text{N,N}'$ -bis(3-methylphenyl)- $\text{N,N}'$ -diphenyl-benzidine (TPD)/ $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2/\text{Al}$ or the triple-layer device of ITO/TPD/ $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2/\text{AlQ}/\text{Al}$, a blue emission from the hole transport layer TPD could be observed at high bias.

Here, we report on the fabrication of double-layer and triple-layer EL devices with an emission from CBS. In order to obtain a strong blue emission, AlQ or $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ was inserted between the aluminum cathode and emitting layer and used as ETL. The hole transporting material was commonly used TPD, whose thickness was kept in constant as 40 nm in all devices.

2. Experimental

CBS was synthesized according to the method mentioned in the literature [11,12]. The chemical structure of CBS was confirmed by ^1H NMR (Bruker AVNCE 500 MHz), mass spectra (America MA1212) and Infrared spectroscopy (Shimadzu IR-408).

Fig. 1 shows the chemical structure of the materials and the configurations of the EL devices. The sheet resistance of the ITO glass is $15\ \Omega/\square$. The cleaning procedures included sonication in detergent solution, pure water, acetone, toluene and ethanol successively. The devices were fabricated by sequential thermal deposition of the organic chemicals and the aluminum below a pressure of 1×10^{-3} Pa in one run. The deposition rates of organic materials and aluminum were 0.2, 1.2 nm/s, respectively. The layer thickness was controlled in vacuum with an IL-1000 quartz crystal monitor. The emitting area of the devices was about $20\ \text{mm}^2$.

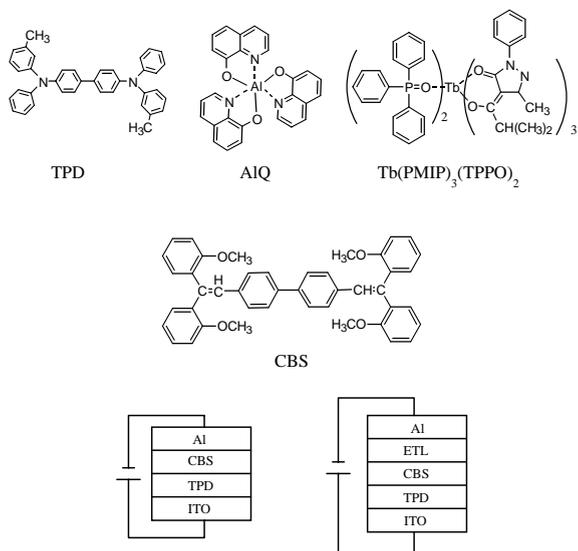


Fig. 1. Chemical structure of the materials studied and the configurations of the EL devices.

PL and EL were measured with a Hitachi F-4500 fluorometer. The brightness was measured with a ST-86LA spot photometer. The energy level of CBS was determined by cyclic voltammetry with a CH Instruments model 600 voltammetric analyzer. All measurements were carried out at room temperature under ambient atmosphere.

3. Results and discussion

Electroluminescence could not be observed in the device of ITO/CBS (40 nm)/AlQ (40 nm)/Al. In the double-layer device of ITO/TPD (40 nm)/CBS (40 nm)/Al, blue emission from CBS was obtained with a maximum luminance of $1.32\ \text{cd}/\text{m}^2$ at 22 V. It is obvious that CBS has poor carrier-transporting property, which results in the low EL efficiency.

In order to obtain higher luminance, AlQ was added as ETL and CBS was used as an emitting layer in the triple-layered device. Fig. 2 shows EL spectra of ITO/TPD (40 nm)/CBS (40 nm)/AlQ (40 nm)/Al. It can be seen that the EL spectrum exhibits three emissions peaking at 505, 456, and 429 nm. Compared with the PL spectra of AlQ and CBS films on quartz substrates, we can conclude

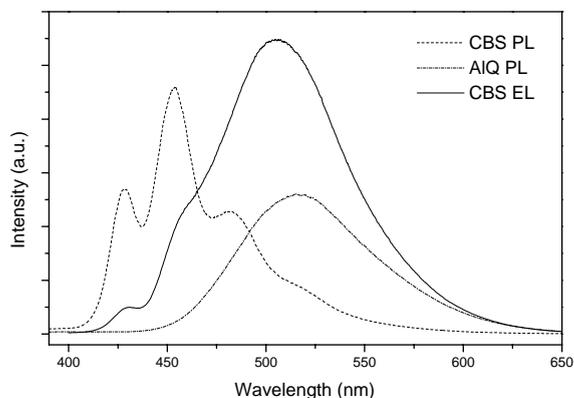


Fig. 2. PL spectra of CBS (dashed line) and AIQ (dashed dot line) films on quartz substrates and the EL spectrum (solid line) of the ITO/TPD(40 nm)/CBS (40 nm)/AIQ (40 nm)/Al device.

that the largest broad band peaking at 505 nm is corresponding to the emission from the AIQ and the other bands are due to the emission from the emitting layer. Regardless of the different thickness ratios of AIQ and CBS, the EL spectra are similar to that in Fig. 2. To the naked eye, the photoemission color of the devices is bluish green. This can be attributed to the emission from the high performance of AIQ with broad band green color except the emission from CBS. Further explanation will be discussed later. Although a maximum luminance of 1480 cd/m² was obtained at 25 V in the device of ITO/TPD (40 nm)/CBS (40 nm)/AIQ (40 nm)/Al, the purpose of blue emission was not achieved.

We changed ETL to Tb(PMIP)₃(TPPO)₂ and fabricated the triple-layered devices. The total thickness of CBS and Tb(PMIP)₃(TPPO)₂ layers was kept constant at 80 nm.

Fig. 3 shows the EL spectra with different thickness ratios of CBS and Tb(PMIP)₃(TPPO)₂. It can be seen that the spectra features are sensitive to the thickness of the emitting and electron-transporting layers. The bright blue emission with a maximum luminance of 253 cd/m² at a current density of 360 mA/cm² at 19 V can be observed in the device of 30 nm CBS and 50 nm Tb(PMIP)₃(TPPO)₂. However, with reduction in the thickness of the emitter layer, three bands peaked at 490, 545, and 590 nm appear and increase, which are characteristic of Tb³⁺ transi-

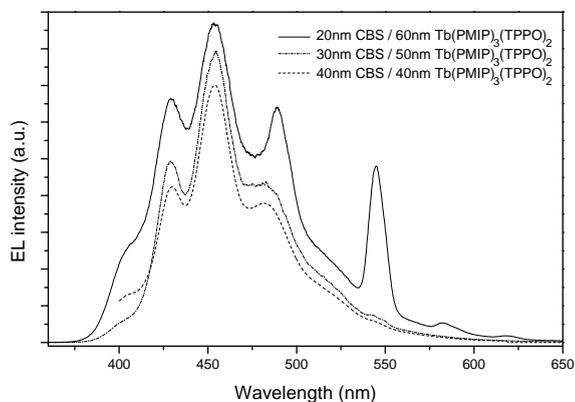


Fig. 3. EL spectra of the triple-layer-type devices with different thickness ratios of CBS and Tb(PMIP)₃(TPPO)₂. The total thickness of CBS and Tb(PMIP)₃(TPPO)₂ was fixed at 80 nm.

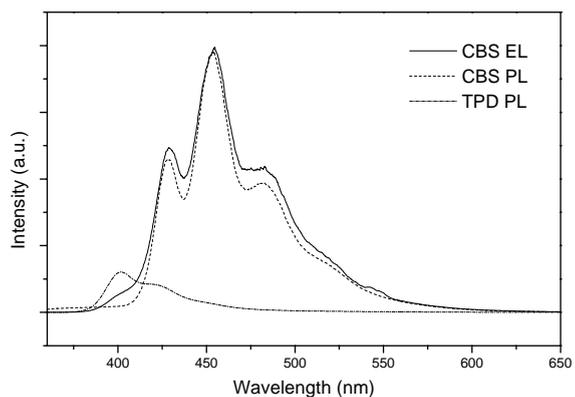


Fig. 4. PL spectra of CBS (dashed line) and TPD (dashed dot line) films on quartz substrates and the EL spectrum (solid line) of the ITO/TPD (40 nm)/CBS (30 nm)/Tb(PMIP)₃(TPPO)₂ (50 nm)/Al device.

tion of ⁵D₄→⁷F₆, ⁵D₄→⁷F₅, ⁵D₄→⁷F₄ respectively. The color of the device turns from blue to greenish blue. This indicates that some part of the recombination zone extends into Tb(PMIP)₃(TPPO)₂ layer to add a green contribution to the emission spectrum.

As shown in Fig. 4, it is not difficult to find that the EL spectrum of the triple-layer device of ITO/TPD (40 nm)/CBS (30 nm)/Tb(PMIP)₃(TPPO)₂ (50 nm)/Al exhibits the emission of TPD except the emission of CBS. It indicates that the recombination zone is from the inside of CBS to

the interface of TPD and CBS. This can be explained by the special electron-transporting property of $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ [9,10].

In order to understand the different roles of AIQ and $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ as the electron-transporting materials, we analyzed the basic transporting and injection mechanisms occurring in OLEDs by the schematic energy diagram for the triple-layer devices of ITO/TPD/CBS/AIQ/Al and ITO/TPD/CBS/ $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ /Al (Fig. 5). The HOMO level of CBS was evaluated from the potential of the first oxidation peak in the voltammogram (1.09 V) while the LUMO level was calculated with reference to the oxidation potential and the band gap of the absorption (340 nm or 3.65 eV). The energy levels of ITO, TPD, $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$, AIQ and Al were cited from Refs. [9,13]. From Fig. 5(a), it can be seen that the HOMO level of CBS is higher than that of TPD, but lower than that of AIQ. So, the hole can inject from TPD into AIQ through CBS. However, because the LUMO level of CBS is lower than that of AIQ and the barrier between them is 0.5 eV, the electron injection is difficult from AIQ to CBS. As a result, the hole and electron recombine mainly in AIQ layer. This is consistent with the experimental results that the EL spectra exhibit the emissions from both the emitting and electron-transporting layers. Fig. 5(b) shows that the EL efficiency is deeply dependent on the electron injection from the cathode to ETL because of 2.41 eV barrier from Al into $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$. However, the

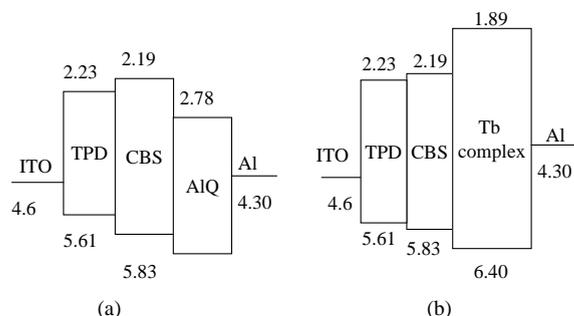


Fig. 5. Schematic energy level (eV) diagram for the triple-layered devices: (a) ITO/TPD/CBS/AIQ/Al device; (b) ITO/TPD/CBS/ $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ /Al device.

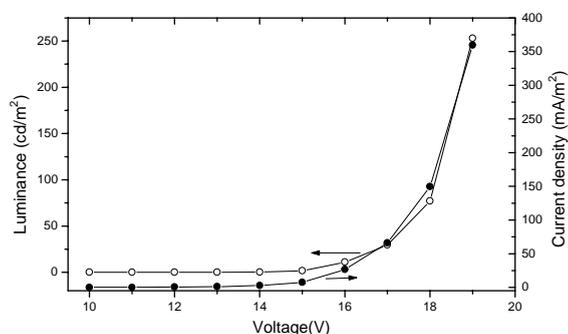


Fig. 6. Luminance-current density-voltage characteristics of the ITO/TPD(40 nm)/CBS (30 nm)/ $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ (50 nm)/Al device.

electron can transport fast from ETL to the emitting layer due to the high mobility of $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$. Because CBS has poor carrier transporting property, the hole and electron combine mainly in CBS layer. A few part of recombination can be in the interface of CBS and TPD. This can be explained by the low LUMO of TPD. So the blue emission was obtained when $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ was used as ETL.

The luminance-current density-voltage characteristics of a triple-layer-type EL device of ITO/TPD(40 nm)/CBS (30 nm)/ $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ (50 nm)/Al (100 nm) is shown in Fig. 6. It can be seen that the luminance increases with increasing injection current as well as bias voltage, because the recombination efficiency increases as the more charge carriers are injected from the electrodes.

4. Conclusion

In order to achieve blue EL emission with a blue material (CBS), $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$, instead of AIQ, was used as ETL. A bright blue emission can be obtained with a maximum luminance of 253 cd/m^2 at 19 V. According to the schematic energy diagram, the transport and injection properties of AIQ and $\text{Tb}(\text{PMIP})_3(\text{TPPO})_2$ were analyzed. Other methods to obtain higher blue luminance of CBS, such as using LiF/Al cathode or reducing the injection barrier from the cathode to ETL, are being processed.

Acknowledgements

The authors thank the State Key Program of Basic Research (G1998061310), National Natural Science Foundation of China (59872001, 20023005) and Doctoral Program Foundation of High Education (99000132) for the financial support.

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