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RESEARCH ARTICLE

Emission mechanism in the terbium complex doped PVK system

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Abstract A new kind of rare earth (RE) complex Tb(*o*-MBA)$_3$phen was synthesized and used as an emitting material in electroluminescence. The material was doped into poly(N-vinylcarbazole) (PVK) as the emitting layer, which was made by spin coating. Three kinds of devices were fabricated with the structures: (A) ITO/PVK:Tb(*o*-MBA)$_3$phen/LiF/Al; (B) ITO/PVK:Tb(*o*-MBA)$_3$phen/BCP/AlQ$_3$/LiF/Al; (C) ITO/BCP/PVK:Tb(*o*-MBA)$_3$phen/AlQ$_3$/LiF/Al. Bright green emission could be obtained from device (A) and (C). The photoluminescence (PL) and electroluminescence (EL) mechanisms of this material had been investigated. Since there was an overlap between the PL spectrum of PVK and the excitation spectrum of the terbium complex, there should be a Förster energy transfer process between them. The excitation spectrum of PVK doped Tb(*o*-MBA)$_3$phen system is similar with the excitation spectrum of PVK, yet it is different from that of Tb(*o*-MBA)$_3$phen. So, the emission of Tb(*o*-MBA)$_3$phen should partly come from the excitation of PVK while in the organic light-emitting diode (OLED), based on Tb(*o*-MBA)$_3$phen, the emission mainly comes from the direct recombination of electron and hole. Bright green emission can be obtained from the optimized multi-layer device (C) and the highest EL brightness reached 180 cd/m^2 at the voltage of 17 V.

Keywords terbium complex, organic light-emitting diode (OLED), exciton

1 Introduction

Since Tang et al. reported a stacked electroluminescent cell structure in 1987, which had a luminescent efficiency of 1.5 lm/w and a luminance of 1000 cd/m^2 for green light under an operating voltage lower than 10 V, organic light-emitting diode (OLED) has received much attention because of its potential application for full color flat panel displays [1–3]. OLEDs have many advantages including high efficiency, low driving voltage and fast response time. For full color display, three primary colors, red, green and blue, are desired. Yet obtaining pure colors from conjugated polymers or small organic molecules is difficult because their spectra typically have a full width at half maximum (FWHM) of 50–100 nm. In the 1990s, Kido's team first reported the fabrication of the OLEDs based on rare earth complexes [4–6]. There are advantages in fabricating electroluminescent devices by using rare earth complexes. Theoretically, the upper limit of the inner quantum efficiency can reach 100%, which is four times higher than that of devices that use other fluorescent materials. Rare earth complexes exhibit electroluminescence (EL) with sharp spectral bandwidths which have an FWHM of about 10 nm, and the sharp emission is suitable for flat panel displays. In this report, a terbium complex has been synthesized and applied in the fabrication of OLEDs. The photoluminescence (PL) and EL properties of the two different multiplayer devices both utilizing Tb(*o*-MBA)$_3$phen-dispersed PVK as a light emitting layer were studied. Additionally, the mechanism of the PL was also discussed.

2 Experiment

2.1 Preparation of Tb(*o*-MBA)$_3$phen

A stoichiometric amount of TbCl$_3$·6H$_2$O, *o*-Toluic acid and 1,10-phenanthroline were dissolved separately in 95% C$_2$H$_5$OH. The three solutes have a mol ratio of 1:3:1. The pH of the *o*-Toluic acid solution was adjusted to 6–7 with 1 mol·L^{-1} NaOH solution. The C$_2$H$_5$OH

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solutions of two ligands were mixed, and while this mixture was added, by dropping to the ethanolic $TbCl_3$ solution, a white precipitate formed. Based on the element and single crystal structure analysis, the precipitate has the structure of Tb(*o*-MBA)$_3$phen. The chemical structure of Tb(*o*-MBA)$_3$phen is shown in Fig. 1 [7].

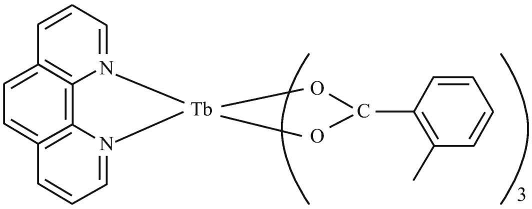

Fig. 1 Molecular structure of Tb(*o*-MBA)$_3$phen

2.2 Preparation of the devices

Three kinds of devices have been fabricated in the experiment.

(A) ITO/PVK:Tb complex (70 nm)/LiF (0.3 nm)/Al (150 nm);

(B) ITO/PVK:Tb(*o*-MBA)$_3$phen (70 nm)/BCP (6 nm)/AlQ_3 (8 nm)/LiF (0.3 nm)/Al (150 nm);

(C) ITO/BCP (6 nm)/PVK:Tb(*o*-MBA)$_3$phen (70 nm)/AlQ_3 (8 nm)/LiF (0.3 nm)/Al (150 nm).

Poly(N-vinylcarbazole) (PVK) was used as host material for the terbium complex in order to get the film-forming capability and conductivity of their mixture. The terbium and PVK were dissolved into chloroform to make a solution with the concentration of 1.5 and 10 mg/mL respectively. Then the mixed solution of PVK and Tb(*o*-MBA)$_3$phen, with the weight ratios of 5:1, 10:1, 15:1 and 20:1, can be formed. To investigate the PL spectra of the thin films of PVK, Tb(*o*-MBA)$_3$phen and their mixture with the different weight ratios can be formed onto the quartz glass by spin-coating.

PVK was used as hole-transporting material, BCP was used as a hole-blocking layer, and tris (8-quinolinolato) aluminum complex (AlQ_3) was used as an electron-transporting material, respectively. The light-emitting film of PVK:Terbium complex was prepared by spin coating their chloroform solution onto ITO glass substrate with a sheet resistance of 20 Ω/square. Then, BCP, AlQ_3, LiF, and Al were deposited onto the emitting layer by conventional thermal evaporation method at a chamber pressure of about 3×10^{-3} Pa. LiF was deposited onto an electron transport layer (ETL) as electron injection material. The thickness of the film made by spin-coating was measured by XP-2 step profiler. The PL and EL spectra were measured by Fluolog-3 fluorescent spectrometer, and the brightness was measured by PR-650 spectrometer. All the measurements were carried out in the air and at room temperature.

3 Results and discussion

The excitation spectra of terbium complex ($\lambda_{em} = 547$ nm), PVK ($\lambda_{em} = 420$ nm), and the mixture of PVK and terbium ($\lambda_{em} = 547$ nm) are shown in Fig. 2. The emission spectrum of PVK ($\lambda_{ex} = 340$ nm) is also shown in Fig. 2.

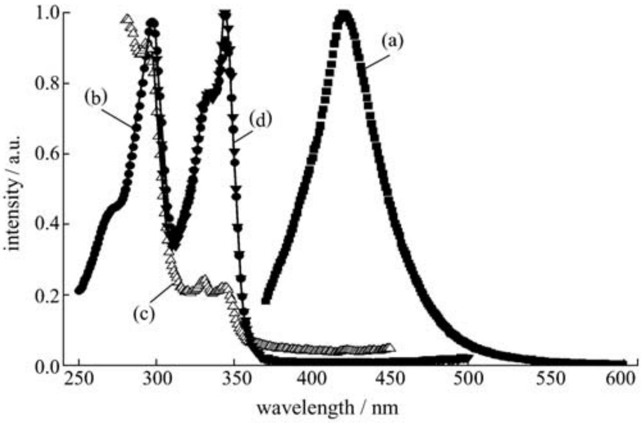

Fig. 2 PL and excitation spectra of these materials: (a) PL spectrum of PVK; (b) excitation spectrum of PVK; (c) terbium complex; (d) doped system

As can be seen from Fig. 2, the excitation spectra of PVK and their mixture (PVK doped with terbium complex) are much alike, and both of them are different from that of the terbium complex. This shows that the emissions of Tb^{3+} ions originate from the excitation of PVK, and there is an overlap with the PVK emission spectrum and the excitation spectrum of the terbium complex. So the Förster energy transfer process from PVK to the terbium complex occurs [8].

The PL spectra of Tb(*o*-MBA)$_3$phen and PVK doped with Tb(*o*-MBA)$_3$phen with different weight ratios in film are shown in Fig. 3(a). As can be seen from Fig. 3(a), the emission peaks at 490, 546, 585 and 620 nm correspond to the transition of $^5D_4 \rightarrow {}^7F_j$ ($j = 6, 5, 4, 3$) of Tb^{3+}, respectively [6]. There is an obvious emission peak at 420 nm, which comes from the PVK emission. And the intensity of PVK emission increases with the increase of the concentration of the terbium complex in the doping system.

Single layer devices have been made with the PVK-doped terbium complex thin film of different weight ratio as the emitting layer.

(A) ITO/PVK:Tb complex (70 nm)/LiF (0.3 nm)/Al (150 nm).

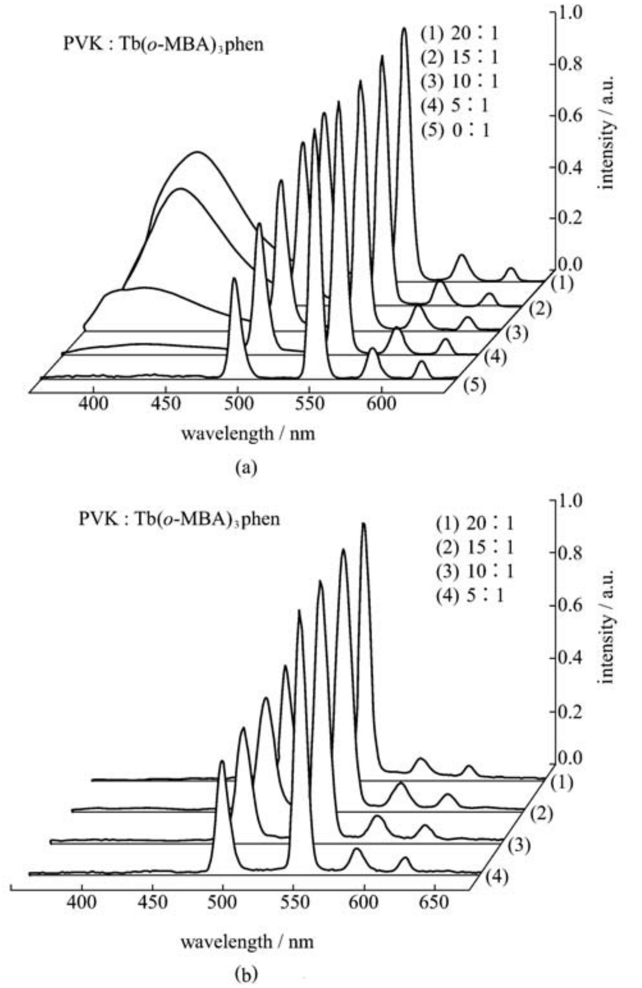

Fig. 3 PL and EL spectra of different doping ratios of terbium complex doped with PVK. (a) PL spectra; (b) EL spectra

EL spectra of this device at 12 V are shown in Fig. 3(b). As can be seen from the figure, only terbium complex emission appears in the EL spectra of the devices. In the EL process, the emission of terbium may come from two different ways, one is Förster energy transfer from PVK to terbium complex [8,9]; and the other is the trapping of the carriers by the terbium complex and the excitons form [10]. At this point, the terbium complex served as a kind of trap and PVK functioned as a hole-transporting material [10–12]. From Fig. 3, it is seen that when the weight ratio of PVK:Tb(o-MBA)$_3$phen is 20:1, the ratio of the emission peak which is PVK at 420 nm and the terbium complex at 547 nm in PL spectrum is 0.42:1, the emission from PVK is very weak in the EL spectrum. As can be drawn from the analysis, the main mechanism is the trapping of the terbium complex in the EL emission.

To further investigate the EL mechanism of the PVK doped Tb(o-MBA)$_3$phen system, multilayer devices have been fabricated.

Device (B): ITO/PVK:Tb(o-MBA)$_3$phen (70 nm)/BCP (6 nm)/AlQ (8 nm)/LiF (0.3 nm)/Al (150 nm);

Device (C): ITO/BCP (6 nm)/PVK:Tb(o-MBA)$_3$phen (70 nm)/AlQ$_3$ (8 nm)/LiF (0.3 nm)/Al (150 nm).

Figure 4(a) shows the EL spectra of the devices with different concentration of the terbium complex doped in PVK layer at 12 V. In the EL spectra of device (B) with a thin BCP layer located between the emitting layer and electron transporting layer, the ratio of PVK intensity divided by the terbium complex intensity at 547 nm is higher than that of device (A) at the same concentration. In device (B), where the terbium complex is used as an electron trap, the trapped electrons can combine with the holes and form excitons. And some electrons may be injected into the LUMO of PVK through the BCP layer, so the excited PVK can be formed and the emission of the terbium complex should partly come from the Förster energy transfer process from PVK.

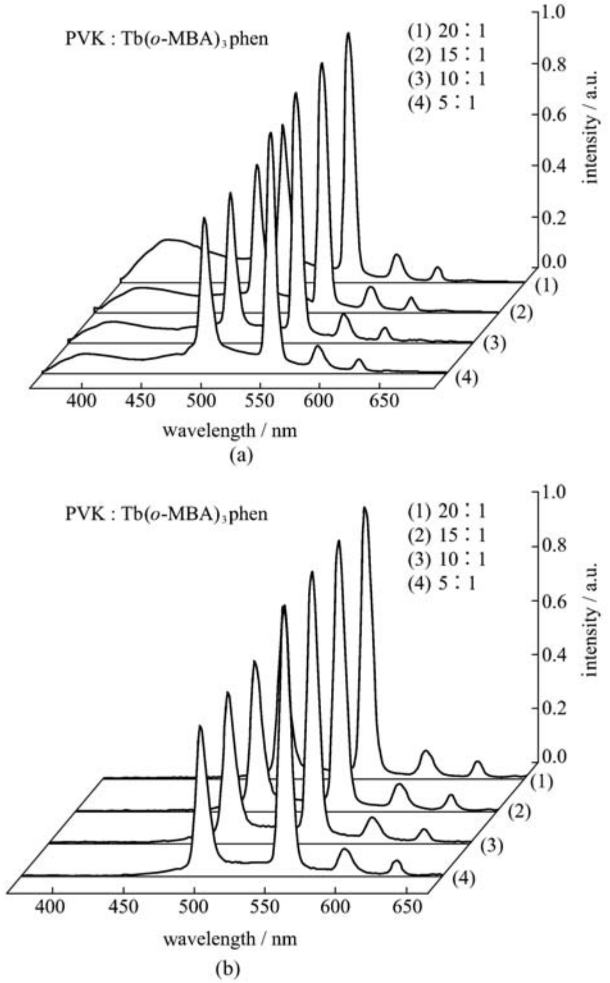

Fig. 4 EL spectra with different doping ratios. (a) EL spectra of device (B); (b) EL spectra of device (C)

Figure 4(b) shows the EL spectra of device (C). In the device (C), the BCP layer was inserted between ITO and the emitting layer. As can be seen from Fig. 4(b), the PVK emission did not appear in the EL spectra of device (C). Because some holes are blocked by the BCP layer, and the concentration of the hole is low in the emitting layer, few excitons can form in PVK molecules. As part of the holes and electrons may be easily trapped by the terbium complex, the emission of the terbium complex is more obvious than the PVK emission in the spectra.

Several devices with the same structure as device (C) have been made. In these devices, the weight ratio of PVK to Tb(*o*-MBA)$_3$phen is 5:1, and the thickness of BCP and AlQ$_3$ is altered. The EL spectra of the optimized device (C) are shown in Fig. 5. The highest brightness of the optimized device (C) reached 180 cd/m^2 at 17 V and the highest EL efficiency is 0.35 cd/A at 11.4 V.

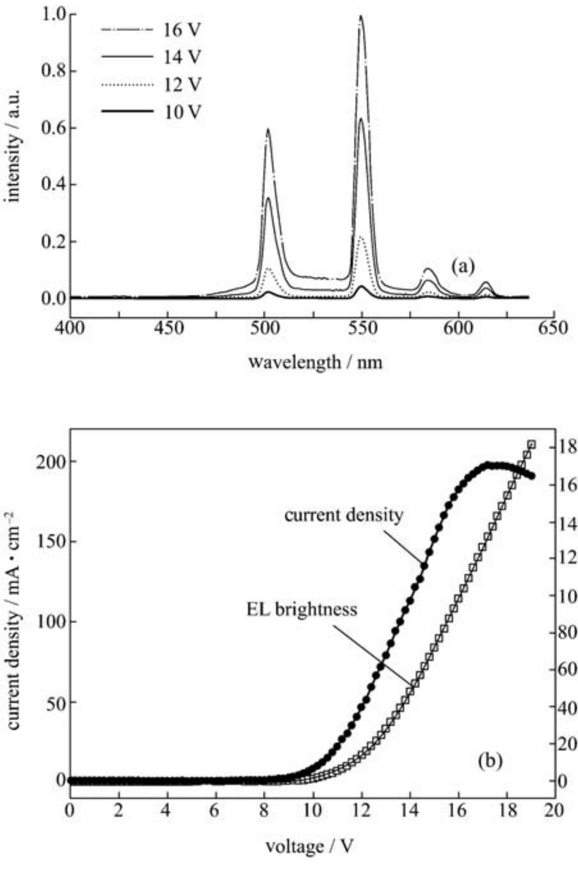

Fig. 5 EL spectra and *I-V-L* characteristics of device (C). (a) EL spectra of device (C) at the weight ratio of 5 : 1; (b) *I-V-L* characteristics of device (C)

4 Conclusions

A new kind of rare earth (RE) complex Tb(*o*-MBA)$_3$phen was synthesized, which was used as an emitting material in electroluminescence. The photoluminescence (PL) and electroluminescence (EL) mechanisms of this material had been investigated. It is found that there was an overlap between the PL spectrum of PVK and the excitation spectrum of the terbium complex, so there should be a Förster energy transfer process between them. The excitation spectrum of the PVK-doped Tb(*o*-MBA)$_3$phen system is similar to the excitation spectrum of PVK, yet it is different from that of Tb(*o*-MBA)$_3$phen. So, the emission of Tb(*o*-MBA)$_3$phen should partly come from the excitation of PVK while in the OLED, based on Tb(*o*-MBA)$_3$phen, the emission mainly comes from the direct recombination of the electron and the hole. The highest EL brightness reached was 180 cd/m^2 at the voltage of 17 V.

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