Effects of exciplex on the electroluminescent and photovoltaic properties of organic diodes based on terbium complex

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Received 27 October 2006; received in revised form 30 May 2007; accepted 11 June 2007
Available online 6 August 2007

The review of this paper was arranged by Prof. Y. Arakawa

Abstract

We fabricated two organic diodes, one of which consists of a double layer structure of TPD/Tb(ACA) 3phen and in the other one a mixture layer is inserted between the double layer, i.e., TPD/TPD:Tb(ACA) 3phen (1:1, 30 nm)/Tb(ACA) 3phen, here TPD and Tb(ACA) 3phen are (N,N 0 -diphenyl-N,N 0 -bis(3-methyl-phenyl)-1,1 0 -biphenyl-4,4 0 -diamine) and tris(acetylacetonato)-(mono-phenothroline) terbium, respectively. Both the devices show electroluminescence (EL) properties under forward bias and photovoltaic (PV) effects under illumination of ultraviolet (UV) light. For the device with a mixture layer, the EL performance and PV effects were both significantly improved. A maximum EL brightness of 150 cd/m 2 under bias of 17 V and a maximum efficiency of 1.1 cd/A at 7.5 V were obtained. Moreover, the diode shows a short-circuit current (I sc) of 43 lAc m 2, an open-circuit voltage (V oc) of 1.1 V, a fill factor (FF) of 0.32, and an overall power conversion efficiency (η PV) of 1.0% under illumination of 365 nm UV light with 1.5 mW/cm 2. The improvements of PV- and EL-properties were presumably attributed to the increased intermolecular contacts in the mixture of TPD and Tb-complex. In addition, a shift of EL color from UV-blue to green-yellow was also observed when a mixture layer of TPD with Tb-complex was inserted. The operation mechanisms of the EL- and the PV-processes of the diodes with different structures were further discussed.
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Keywords: Rare earth; Electroluminescence; Exciplex; Mixture; Photovoltaic effect

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable interest due to their potential applications in the development of new optoelectronic components, such as full-color flat panel displays [1]. In recent years, the interfacial exciplex (excited complex) based organic diodes which simultaneously exhibit electroluminescence (EL) properties and photovoltaic (PV) effects have been studied in our group [2–5].

The exciplex emission generally occurs at the interface between a donor-type (D) molecule and an acceptor-type (A) one. Exciplex is a transient charge-transfer (C-T) complex between an electron-donor at the excited state and an
electron-acceptor at the ground state, so its emission should be attributed to a C-T excited state \([D^+A^-]^+\), and the emission wavelength generally corresponds to the energy difference between the highest occupied molecular orbital (HOMO) of a donor and the lowest unoccupied molecular orbital (LUMO) of an accepter [6–10]. The mixture of the donor and the acceptor could greatly increase in the contact of two molecules. Therefore, an insertion of a mixture layer between the donor and the acceptor could significantly affect the exciplex emission in OLEDs, which has been widely investigated [11–15]. However, the relations between the exciplex formation and both the EL- and PV-properties of the diodes with the same structure have not yet been studied in more detail.

There are advantages in fabricating EL devices using rare earth (RE) complexes, e.g., the upper limit of inner quantum efficiency can reach 100% theoretically and the sharp emission bands of RE ions are very suitable for full-color display [1,11]. However, their performance is still unsatisfactory for the practical applications. Recently, the PV effects of the diodes containing the RE complexes as an electron-acceptor have been firstly investigated in our group [2].

In the current work, an emitting trivalent terbium ion \((Tb^{3+})\) complex, tris(acetylacetonato)-(mono-phenothroline) terbium \((Tb(ACA)_3phen)\), was used as the acceptor instead of the inert trivalent yttrium ion \((Y^{3+})\) complex used in our previous study, and \(N,N'-diphenyl-N,N'-bis(3-methyl-phenyl)-1,1'-biphenyl-4,4'-diamine\) (TPD) was used as the donor. The EL- and PV-performances of the diode based on a mixture layer were considerably stronger than those of the double layer diode. The EL luminance under forward bias and PV-performances under illumination of ultraviolet light at 365 nm, such as the open-circuit voltage \((V_{oc})\), the short-circuit current \((I_{sc})\) and the overall power conversion efficiency \((\eta_{PV})\) enhanced by a factor of 2.2, 2.7, and 5.8, respectively.

2. Experimental

The molecular structures of \(Tb(ACA)_3phen\) and TPD and the configurations of the devices are shown in Fig. 1. The Tb-complex was synthesized according to the conventional method [16] and further purified by a recrystallization process. TPD is a commercial product without further purification. All devices were constructed on the pre-cleaned indium-tin oxide (ITO) coated glass substrates with a resistance of 25\(\ \Omega/\text{square}\). The ITO-coated substrates were cleaned by an ultrasonic treatment in solvents followed by an exposure to a UV-ozone ambient. All organic layers were deposited successively by a thermal evaporation in vacuum, respectively.

In order to study the effect of the different structures of diodes on the EL- and PV-performances, two devices with a double layer alone and with an additional inserted mixture layer were fabricated, respectively. The structures are as below.

Device-A: ITO/TPD (40 nm)/\(Tb(ACA)_3phen\) (70 nm)/LiF (1 nm)/Al (150 nm).

Device-B: ITO/TPD (30 nm)/TPD:Tb(ACA)_3phen (1:1, 30 nm)/\(Tb(ACA)_3phen\) (50 nm)/LiF (1 nm)/Al (150 nm).

In addition, to investigate the photoluminescent (PL) properties, a mixture layer film of \(Tb(ACA)_3phen\) and TPD and a double layer film of TPD/\(Tb(ACA)_3phen\) were deposited onto pre-cleaned quartz substrates by thermal evaporation in vacuum, respectively.

The PL spectra and absorption spectra were measured with a Hitachi F-4500 Fluorescence Spectrophotometer and a Shimadzu UV-3101PC Spectrophotometer, respectively. The brightness–current–voltage \((B–I–V)\) characteristics, EL spectra and Commission International de l’Eclairage (CIE) coordinates of the diodes were recorded by a calibrated multifunctional system for EL measurement. Photocurrent response curves were obtained under a 40\(\ \mu\text{W/cm}^2\) Xe lamp. All the measurements were carried out in ambient atmosphere at room temperature.

3. Results and discussion

The EL spectra of Device-A and Device-B are shown in Fig. 2. It can be seen that there is a band at 403 nm with a shoulder at 423 nm which was considered to originate from the TPD [17,18]. Moreover, the sharp peaks at 491, 546, 583 and 618 nm can be respectively assigned to the \(5D_{4}–7F_{j}\) \((j = 6, 5, 4 \text{ and 3})\) transitions of the \(Tb^{3+}\) ions in the Tb-complex [19]. In order to understand the origination
of the broad band at longer wavelength in the EL spectrum, the PL spectra of the mixture layer (TPD:Tb-complex) and the double layer (TPD/Tb-complex) films were respectively determined, as shown in the inset of Fig. 2. Note that the two PL spectra are almost consistent with those of Device-A and Device-B, respectively, both PL based on double layer and EL spectra based on Device-A composed of main blue emission from TPD with a weaker broad band at longer wavelength from 500 to 600 nm, while PL based on the mixture layer and EL spectra based on Device-B composed of a preponderant broad band at longer wavelength overlapped with some lines form Tb$^{3+}$ ions. On the other hand, the absorption spectra of TPD, Tb-complex and (TPD:Tb-complex) (ratio 1:1) films were determined, as shown in Fig. 3. It can be observed that the absorption of the mixture layer is the sum of the absorptions of TPD and Tb-complex, indicating that there is no new absorption feature in the mixture film. The new broad emission band at longer wavelength should originate from the intermolecular exciplex. It should be noted that compared with the PL spectra there is some red shift of the broad band in the EL one, which may be due to the different nature of EL- and PL-mechanisms. We suppose that the exciplex observed under optical excitation behaves a singlet character while the broad band emission peaking at about 565 nm in EL spectrum of Device-B can likely be ascribed to the triplet exciplex under electrical excitation [20].

Device-A with a double layer mainly emits blue-UV light from TPD, weak emission from Tb$^{3+}$ ions and more weak emission from exciplex, differing from our previous result of the double layer device based on TPD and tris(dibenzoylmethanato)-(bathophenanthroline) europium [Eu(DBM)$_3$Bath], in which a dominant red EL emission from the Eu$^{3+}$ ions overlaps with a weaker broad band from the interfacial exciplex. So in our double layer device, the recombination zone is mainly controlled at the side of TPD layer, which was ascribed to the hole-blocking ability of the Tb-complex layer, the blue emissive band of TPD results from $S_1$–$S_0$ transition which is shown at the left side in Fig. 4. The intermolecular contact between TPD and Tb-complex in the double layer device (Device-A) is much less than that in the mixture layer based device (Device-B), so that the smaller exciplex is formed [21].

In addition, in Device-A there are different relative emission intensities from TPD, the exciplex and Tb$^{3+}$ ions compared with other device based on TPD/Tb-complex. It is presumably attributed to the different purities of TPD, such as, TPD with a small quantity of another diamine derivative, $N,N',N''$-tetraphenyl-1,1'-biphenyl-4,4'-diamine (TPB) which is without two methyl’s, because in the double layer device based on TPB/Tb-complex the preponderant blue band from TPB often appears [22].

For Device-B with a mixture layer, the EL process is much complicated. First of all, the mixture layer increases the contact between the two molecules, leading to the decrease in the interfacial barrier of hole-injection because the mixture layer sandwiched between TPD and Tb-complex layers is a homogeneous mixture of TPD:Tb-complex (1:1), so that Tb-complex does not play a role of blocking hole. Therefore, the recombination zone mainly locates at the mixture layer in Device-B. According to the EL emission spectra of Device-B in Fig. 2, the EL processes were supposed as the right side in Fig. 4, that is, under electricity excitation the ACAC ligand was firstly excited into the singlet ($S_1$) and the triplet ($T_1$) simultaneously, and then the
intersystem crossing (IC) process from S\(_1\) to T\(_1\) took place. In succession there are three energy transfer processes, ET(I), ET(II) and ET(III), in sequence would occur, so that the green EL from \(^{5}\text{D}_{4}\) of Tb\(^{3+}\) ion in the complex and the band emission from exciplex (\(E^*\)) resulted from inter-molecules between the donor and the acceptor in the mixture layer were simultaneously observed. The result differed from the Eu-complex device in which the exciplex level was higher than the \(^{5}\text{D}_{0}\) resonant level of Eu\(^{3+}\) ion leading to the elimination of the exciplex emission at a certain TPD-to-Eu-complex ratio because the energy transfer from exciplex level to resonant level (\(^{5}\text{D}_{0}\)) occurs [23]. However, as for the Device-B based on the TPD:Tb-complex mixture layer, the exciplex level \(E^*\) is slightly lower than the \(^{5}\text{D}_{4}\) resonant level of Tb\(^{3+}\) ion so that the exciplex emission cannot be eliminated at any mixing ratio of TPD to Tb-complex.

In addition, the exciplex emission of Device-B is much stronger than that of Device-A due to much more intermolecular exciplex formed in the mixed layer which might be caused by the increase of contact between the donor and acceptor. A maximum EL brightness of 60 cd/m\(^2\) under
13.5 V and a maximum efficiency of 0.085 cd/A at 8.5 V were obtained for Device-A, while for Device-B they are 150 cd/m² under 17 V and 1.1 cd/A at 7.5 V, respectively.

Because there is a competition between EL emissions from TPD, Tb³⁺ and exciplex, the three emissive bands can be applied to design white emission device. For Device-B, as TPD-to-Tb-complex ratio was selected to be 1:3, a white OLED was obtained. The EL spectra is composed of a green-yellow broad band from exciplex overlapping with the sharp peaks from Tb³⁺ ion and a blue band from TPD. A luminance of 120 cd/m², and CIE coordinates of (0.32,0.36) at bias of 10 V were determined, respectively.

PV-properties of Device-A and Device-B were also compared. The photocurrent response curves of Device-A and Device-B have same shape, as shown Fig. 5. Combined with the above normalized absorption spectra (see Fig. 3), it was found that the photocurrent response mainly corresponds to the absorption of TPD, indicating that the photo-generated excitons should be produced in the TPD layer, which is mainly related with the absorption of ITO glass substrate and the relative weak absorption of Tb-complex. Therefore, a UV light of 365 nm at 1.5 mWcm⁻² was selected as the irradiation light to measure the PV-properties. Table 1 lists the $V_{oc}$, $I_{sc}$, FF and $\eta_{pv}$ of Device-A and Device-B. It is evident that the Device-B based on the mixture layer shows superior PV-properties to the Device-A based on the double layer. The $V_{oc}$, $I_{sc}$ and $\eta_{pv}$ of the Device-B are 2.2, 2.7, and 5.8 times of those of Device-A, respectively.

It is obvious that the formation process of the exciplex is similar to the working process of the organic PV device, that is, higher levels of both LUMO and HOMO in the donor than those in the acceptor are generally required [3,24]. Thus it can be speculated that the device with stronger exciplex emission under DC bias would exhibit better PV effect under light illumination. This was verified by our investigation in which the mixture layer based Device-B shows stronger exciplex emission as well as excellent PV effect compared with Device-A. Therefore, the formation of exciplex in the EL diodes is expected to be a criterion in the selection of the PV materials, and the design and fabrication of the PV devices [2–5].

4. Conclusions

The bi-functional performances of organic diodes based on Tb(ACA)₃phen with conversions of light to electricity and electricity to light have been achieved. The effects of the inserted mixture layer on the EL- and PV-properties of diodes were clarified. The mixture layer could lead to an increased exciplex emission and superior PV-properties, due to the increased contact of between the Tb-complex as the acceptor and TPD as the donor. The emission from the exciplex of the device based on the mixture layer can not be eliminated, which was attributed to the lower exciplex level ($E^*$) than the $^5D_4$ resonant level of the Tb³⁺ ions, so that preponderant emission from the exciplex was obviously determined, differing from that of the device based on the TPD-Eu(DBM)₃Bath system. Moreover, white EL device

![Fig. 5. Photocurrent response curve of Device-A and Device-B.](image)

<table>
<thead>
<tr>
<th>Device-A</th>
<th>Device-B</th>
</tr>
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<tbody>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.5</td>
</tr>
<tr>
<td>$I_{sc}$ (µA cm⁻²)</td>
<td>16</td>
</tr>
<tr>
<td>FF</td>
<td>0.30</td>
</tr>
<tr>
<td>$\eta_{pv}$ (%)</td>
<td>0.17</td>
</tr>
</tbody>
</table>
using the mixture layer was obtained and the PV devices are expected to be an UV light-sensor due to its stronger response at 300–400 nm wavelength region.

Acknowledgement

The authors acknowledge the national nature science project of China (Grant No. 90201012) for the support of this research.

References

