Optimization of a poly(*p*-phenylene benzobisoxazole)-based light-emitting device with a complex cathode structure*

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In this work, we report the preparation of a series of electroluminescent (EL) devices based on a high-performance polymer, poly(*p*-phenylene benzobisoxazole) (PBO), and their optoelectronic properties, which have been rarely explored. The device structure is optimised using a complex cathode structure of tris-(8-hydoxyquinoline) aluminium (Alq_3)/LiF/Al. By tuning the thickness of the Alq_3 layer, we improve the device efficiency dramatically in an optimized condition. Further analysis reveals that the Alq_3 layer in the complex cathode structure acts as a hole blocker in addition to its electron-injection role. A green light emission with a maximum brightness of 8.7×10^3 cd/m^2 and a moderate current efficiency of 4.8 cd/A is obtained. These values are the highest ever reported for PBO devices. The high operational stability demonstrated by the present device makes it a promising tool for display and lighting applications. A new material is added to the selection of polymers used in this field up to now.

Keywords: electroluminescence, organic semiconductors, light-emitting devices, electronic transport phenomena

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1. Introduction

The most important breakthrough in polymer light emitting devices (PLEDs) was made by a Cambridge-based group in 1990[1] using poly(*p*-phenylene vinylene) (PPV), which was accompanied by the success in processing insoluble and infusible conjugation polymer via a two-step procedure. In the past two decades, tremendous progress has been made, especially in lighting and display applications. The PLEDs have exhibited many advantages over their inorganic rivals in their low-cost fabrication, potential use in flexible devices, high brightness, and efficiency with consequent improvement in energy saving. In this context, the development of new, high-performance polymers is a long-term task.

Poly(*p*-phenylene benzobisoxazole) (PBO) is a conjugated polymer with a backbone containing heterocyclic aromatic moiety (see Scheme 1). Owing to its highly rigid backbone, the PBO has a decomposition temperature higher than 600 °C,[2] and hence is not fusible. It is hardly soluble in organic solvents, except for a few protic acids. PBO's excellent mechanical and optoelectronic properties[3–5] make it a multi-functional material with superior mechanical tenacity, non-linear optical response, and potential optoelectronic properties. In our previous work, a photoluminescence quantum efficiency (η_{PL}) of about 50% was measured, and the photoluminescence quantum efficiency of a solid PBO film was estimated to be about 30% higher than that of PPV.[1,6] So far, only a limited number of studies in the PLED based on PBO have been carried out. The earliest work was done by Osaheni and Jenekhe in 1994.[6] They obtained a blue electroluminescence (EL) from a device with a bilayered structure of PBO and tris(p-tolyl)amine (TTA) due to an exciplex formation. More recently, Wu *et al.*[7] fabricated PLED devices based on PBO oriented film and observed polarized EL. Moreover, a single-layer electroluminescence device with multi-wall carbon nanotubes as dopant was prepared by Huang and Bai,[8] which showed to a certain degree the enhancement of the brightness of the electroluminescence and a decrease in turn-on voltage. However, neither brightness nor efficiency of PBO-based devices can be found in the literature.

In order to understand the performance of PBO-based light emitting devices, the photophysical properties, especially photoluminescence and electroluminescence, have been investigated. In the present work, we focus on the fabrication of the EL device and the improvement of the device performance. Improving film quality and finding suitable injection and charge transport balance schemes are the key issues for obtaining highly efficient PBO-based devices.

With this aim, PBO thin films are fabricated and opti-

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mised, and PBO-based EL devices are fabricated and investigated, with an emphasis on the balance of their charge carrier injection. After device optimization, a moderate efficiency which is the highest ever within PBO-based devices is reported for the first time.

2. Experiments

2.1. Materials

The PBO was prepared in the way as previously reported.[9] The obtained material has an intrinsic viscosity of about 23 dL/g at 30 °C in methanesulfonic acid (MSA). Tris-(8-hydoxyquinoline) aluminum (Alq_3, 99%) was purchased from Sigma-Aldrich, PEDOT:PSS from Bayer Chemicals, LiF (analytical grade) from Beijing Chemical Works, and MSA (99%) from Aladdin Industrial Corporation. Aluminium (Al, 99.9999%) was purchased from the General Research Institute for Nonferrous Metals, China. All materials were used as ex-bottle. Conductive indium–tin–oxide glass (ITO, 10Ω/) was obtained from CSG Holding Co., China.

2.2. Device fabrication and device testing

ITO substrates were washed thoroughly and treated with UV ozone before use, in order to improve the work function. Then, PEDOT:PSS and PBO films were prepared via spin coating. To this aim, PBO was dissolved in MSA of 0.25 wt% for thin film preparation via spin coating with a speed of 3500 r/min. Finally, the films were soaked in ethanol for more than 12 h and dried at 70 °C in a vacuum oven for more than 8 h in order to remove the residual solvent.

Alq_3, LiF, and Al metal electrode layers were evaporated at 1×10^{-4} Pa with a deposition rate of 0.1–0.2 nm/s, which was monitored via a quartz crystal oscillator. Film morphology was observed using a Leica DMR interfacial contrast microscope. The final thickness of films was determined with a surface profiler (Ambios technology, XP-2). The current-voltage-light (*I*–*V*–*L*) characteristics of the devices were measured simultaneously using a self-programmed Keithley 2410 and an optical power meter (Newport 1830-C). Steady state photoluminescent (PL) spectra were measured using a fluorescent spectrophotometer (Hitachi F-4500) at an exciting wavelength of 400 nm, and the EL spectra were obtained by using a charge-coupled device (CCD) spectrometer (ACTON 150). All measurements were carried out in ambient conditions.

3. Results and discussion

3.1. Solution-cast film preparation

PBO is a conjugated polymer with good thermal and oxidative stability. The rigid rod molecular backbone causes the polymer to poorly dissolve in organic solvents. Protonic solvents such as MSA or Lewis acids must be used to prepare a solution. The Lewis acid formulate consisting of 90.5% nitromethane and 9.5% $AlCl_3$ was reported for PBO film preparation in Refs. [5], [6], [8], and [10]. In this work, both MSA and the Lewis acid solution with a PBO concentration of 0.25 wt% were used for film preparation by spin coating. The two series of specimens followed two different after-treatment procedures for over 12 h to remove solvent and were finally dried at 70 °C. Specimen A was prepared using Lewis acid as solvent and was eventually soaked in de-ionized water; specimen B was prepared by using MSA as solvent followed by soaking in ethanol. The film morphologies were compared under optical microscope.

Figure 1 shows the surface morphologies of PBO films. It can be observed that a crystalline texture was found in specimen A, which forms a rough surface on the micron scale. In contrast, the surface of specimen B was rather smooth, which demonstrates a good film quality. It appears that the preparation method and the after-treatment are critical for a good quality film.

The poor film quality of specimen A may be explained by the hydrolyzation of $AlCl_3$ with water when Lewis acid is used as the solvent, which may cause an insoluble aluminium hydroxide to remain in the film. Low-quality film obtained by using the Lewis acid as a solvent could be a reason for the low performances of devices in previous papers.[5,7,8,10]

Since MSA is soluble in ethanol, the after-treatment obviously introduces less impurity in this film, thereby improving the film quality. This preparation procedure can be a more suitable option for device fabrication.

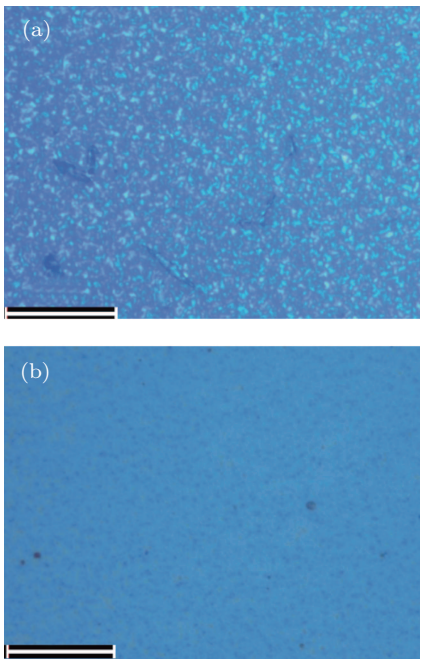


Fig. 1. (color online) Images of the surface morphology of (a) specimen A and (b) specimen B, observed under optical microscope. The scale bar has a length of 20 μm.

3.2. Device optimization by tuning the Alq_3 layer thickness

According to our previous investigations,[5,10] the PBO-based PLED still requires optimization. In order to balance the carrier transport, a complex of "Alq_3/LiF/Al" cathode structure was designed for electron injection. Hence, a series of devices having a multilayered structure was fabricated with the following architecture: ITO/PEDOT:PSS/PBO (80 nm)/Alq_3 (x nm)/LiF (1 nm)/Al (200 nm). PEDOT:PSS was used to modify the anode and Alq_3/LiF/Al as a complex cathode for electron injection (see Fig. 2). In these devices, the thickness of Alq_3 layer was varied from 0 to 25 nm in steps of 5 nm, and the devices were denoted as D0, D1, D2, D3, D4, and D5, respectively.

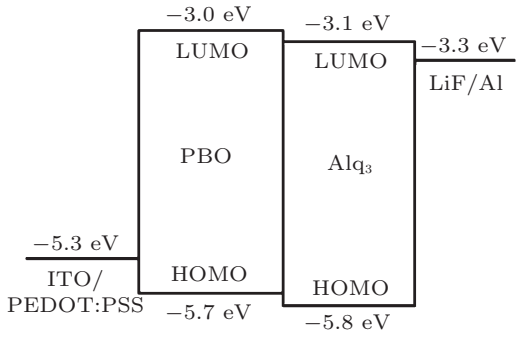


Fig. 2. Energy diagram of PBO-based PLED.

Current–voltage (I–V) characteristics of the prepared PBO-based devices were measured, as shown in Fig. 3(a). It can be seen that the insertion of a very thin layer of Alq_3 in the complex cathode "Alq_3/LiF/Al" causes an abrupt reduction in leaking current at low voltage bias. The change is also related to the thickness of Alq_3 layer: as the thickness of Alq_3 layer increases, the current density of the device decreases monotonically at the same field strength.

From the above devices, a green light emission was observed. The brightness was monitored and plotted against the driving voltages (L–V) in Fig. 3(b) on a single logarithmic scale. It can be observed that when Alq_3 layer thickness was increased from 0 to 15 nm, the light output increased dramatically first, and then fell when comparing at the same voltage bias. However, if the thickness was increased further to 20 and 25 nm, the light output dropped back. The maximum brightness of 8.7×10^3 cd/m^2 is obtained from the device D3 with an Alq_3 layer of 15 nm.

From Fig. 3(b), the threshold voltages ($V_{\rm th}$) of the devices can be easily estimated at a brightness level of 1 cd/m^2. It is found that the V_{th} monotonically falls from 7.6 to 6.1 V as the thickness of Alq_3 layer increases from 0 to 20 nm (see Fig. 3(b) and Table 1).

Although the device brightness is first enhanced and then falls, as the Alq_3 thickness is increased at a given voltage, it can be noted that the device efficiency is continuously improved as the thickness of Alq_3 layer increases. The practical performances of the devices were identified using current efficiencies of the device, as shown in Fig. 3(c). It is interesting to see that the devices were rather stable against the time scale of the measurement. The efficiency fell very slightly and almost leveled off as a function of current density within the time scale of the measurement. The highest efficiency was achieved in the device D4 with an Alq_3 layer of 20 nm. As shown in Table 1, the current efficiency (measured under 20 mA/cm^2) of the device was improved substantially, i.e., from 0.2 cd/A for device D0 to 4.8 cd/A for device D4.

From the above results, it is obvious that the PBO-based device performances have been improved substantially by using a complex cathode "Alq_3/LiF/Al" for electron injection.

The reduction in the leakage current of the devices after the Alq_3 layer was inserted indicates a change in charge transport. Due to a substantial improvement in device performance when adding an electron injection layer, it can be proposed that

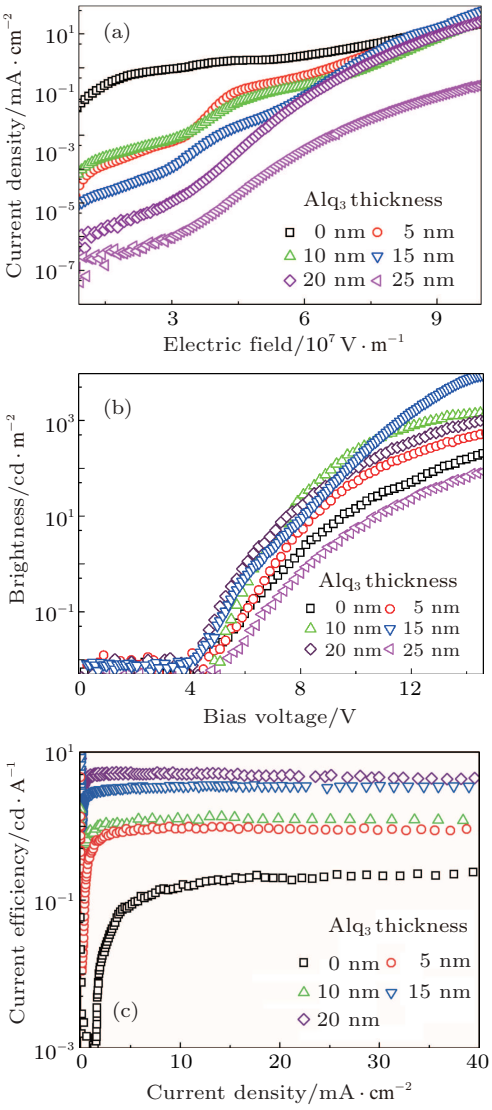


Fig. 3. (color online) Curves of (a) I–V, (b) L–V, and (c) current efficiency versus current density of a series of devices with different thickness values of the Alq_3 layer.

Table 1. EL characteristics of the devices with different thickness values of Alq_3 layer.

Device	D0	D1	D2	D3	D4	D5
Alq_3 thickness/nm	0	5	10	15	20	25
[a] Brightness/cd·m^{-2}	2.0×10^{2}	5.4×10^{2}	1.5×10^{3}	8.7×10^{3}	1.1×10^{3}	8.5×10^{1}
[b] V_{th}/V	7.6	7.1	6.5	6.4	6.1	8.4
[c] η_A/cd · A^{-1}	0.2	0.9	1.3	3.5	4.8	/

[a] Measured under a bias voltage of 14.6 V; [b] measured under a brightness of 1 cd/A; [c] measured under a current density of 20 mA/cm^2.

the PBO layer was predominately hole-transporting, rather than electron-transporting. Furthermore, the hole mobility of PBO was estimated by the space-charge-limited current (SCLC) method to be at a level of 10^{-6} cm^2/Vs, which is much higher than from Alq_3, i.e., 10^{-8} cm^2/Vs, when the bias electric field is relatively low (under room temperature).[11] Therefore, it can be reasonably argued that the Alq_3 layer acts as a hole blocker in these devices. By optimizing the Alq_3 layer thickness, a lot of balanced holes and electron transports were achieved. In addition, this is due to the fact that the lowest unoccupied molecular orbit (LUMO) of Alq_3 (-3.1 eV)[12] is very close to that of PBO (-3.0 eV).[5] With a very small barrier (0.1 eV) at the electron injection junction, an efficient electron injection from the cathode of "Alq_3/LiF/Al" to PBO can be expected.

A well balanced device structure can be identified by its strong enhancement in EL output. The optimized layer thickness of Alq_3 in device D4 is 20 nm or less. At the same time, the threshold voltages also dropped gradually. However, if the thickness of Alq_3 layer was above this value, the device deteriorated, possibly due to an increased bulk resistance. The introduction of a complex cathode structure brought efficient electron injection and balanced the carrier transport via block hole transport, which avoids quenching at the metal/organic interface. As a result, more excitons formed and recombined in the PBO layer far from the Al cathode, so that the enhanced emission was achieved at a smaller threshold voltage.

From the *I*–*V* characteristics of our devices shown in Fig. 3(a), it is also noticeable that the effect of Alq_3 thickness on the current density was weakened (D0-D4) if the electric field was close to a level of 8×10^{7} V·m^{-1}. This may relate to the field-dependent mobility of Alq_3. According to the literature, the mobility μ of Alq_3 is a function of electric field E, following a linear relationship of $\ln\mu \propto E^{1/2}$.[11] In contrast, we found in our experiment that the hole mobility of PBO shows almost no electric field dependence, whose level is around 10^{-6} cm^2/Vs. In Fig. 3(a), the electric field increased from 2×10^{7} to 1×10^{8} V/m, so that the hole mobility μ of Alq_3 could change dramatically from a level of 10^{-9} to 10^{-6} cm^2/Vs or more. This may level to that of PBO's. As a result, the hole-blocking effect of Alq_3 will be weakened gradually as the field increased or even vanished at a high electric field. However, even under a high field strength, the device D5 also showed the lowest current density, which would be considered to be due to the highest bulk resistance, as the Alq_3 layer reached 25 nm.

The most interesting results with these devices can also be found from their current efficiency relations to the driving current density (Fig. 3(c)). It is observed that the efficiency of the device was improved substantially with using the complex cathode and showed almost no reduction against the driving current till the devices broke down. This indicates that the devices are very stable and currently reach a moderate efficiency level compared with the similar PPV devices emitting green light.[13–16]

3.3. Electroluminescence and photoluminescence of PBO film

EL spectra were measured and compared with photoluminescences (PLs) of PBO in solution and in solid films (Fig. 4). The EL spectrum was similar to PL spectrum in solid film, but it was quite different from its solution emission. This is consistent with our previous work with single-layer PBO device.[5] Both EL and PL show a broad and identical single peak around 515–525 nm, while its solution emission is located in a region of shorter wavelength (multiple peaks at 440, 465, and 500 nm), as seen in Fig. 4.

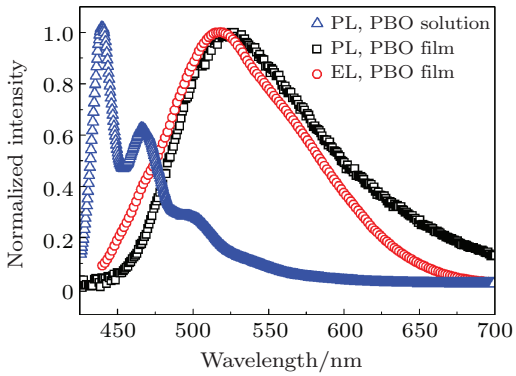


Fig. 4. (color online) EL spectrum and PL spectra of PBO excited at 400 nm.

In order to understand differences between the spectra, time resolved fluorescence spectra of PBO were measured. It was found that the PL from a dilute PBO solution showed a single exponential decay with a unique lifetime factor of 0.5 ns, whereas those from solid films showed double exponential decays with life times around 1.7 and 0.4 ns. This is a strong evidence for a new luminescent mechanism in solid

state. Additionally, the intermolecular distances of such polymers were reported to be $0.33 \sim 0.36$ nm with co-facial chain packing.[17] Such a structure could promote the formation of excimer between polymer chains. It is therefore reasonable to suggest the formation of excimers in the solid state, and hence the light emission, rather than from a stand-alone molecule. This is consistent with what was early proposed by Jenekhe in a similar series of polymers.[18]

4. Conclusions

A series of multilayered PBO based PLED devices is fabricated and optimized followed by film processing optimization and inserting a complex electron injection cathode structure. The device architecture is further optimized against the thickness of the Alq_3 within the complex electrode. This complex structure acts as a hole-blocker in addition to its well known electron injection functionality. Performances of the devices are improved substantially when Alq_3 thickness is in a range of 15–20 nm. A green light emission with a maximum brightness of 8.7×10^3 cd/m^2 and an efficiency of 4.8 cd/A is obtained, which, to the best of our knowledge, is the best performance achieved from a PBO-based device. This result may add PBO into the promising candidates as PLED materials for display or lighting applications.

References

[1] Burroughes J H, Bradley D D C, Brown A R, Marks R N, Mackay K, Friend R H, Burns P L and Holmes A B 1990 *Nature* **347** 539
[2] Wang S, Guo P, Wu P and Han Z 2004 *Macromolecules* **37** 3815
[3] Wolfe J F and Arnold F E 1981 *Macromolecules* **14** 909
[4] Wang S, Wu P and Han Z 2003 *Macromolecules* **36** 4567
[5] Wang J, He Z, Tang R, Mu L, Zhuang Q, Wu P, Han Z, Li X and Jing X 2009 *J. Optoelectron. Laser* **20** 156 (in Chinese)
[6] Osaheni J A and Jenekhe S A 1994 *Macromolecules* **27** 739
[7] Wu C C, Tsay P Y, Cheng H Y and Bai S J 2004 *J. Appl. Phys.* **95** 417
[8] Huang J W and Bai S J 2005 *Nanotechnology* **16** 1406
[9] Wu P, Zhang X and Han Z 1992 *Funct. Polym.* **5** 169 (in Chinese)
[10] Tang R, He Z, Mu L, Wang J, Zhuang Q, Wu P, Han Z, Li X and Jing X 2008 *Chin. J. Lumin.* **29** 950 (in Chinese)
[11] Kepler R G, Beeson P M, Jacobs S J, Anderson R A, Sinclair M B, Valencia V S and Cahill P A 1995 *Appl. Phys. Lett.* **66** 3618
[12] Ishii H, Sugiyama K, Ito E and Seki K 1999 *Adv. Mater.* **11** 605
[13] Wan W C, Antoniadis H, Choong V E, Razafitrimo H, Cao Y, Feld W A and Hsieh B R 1997 *Macromolecules* **30** 6567
[14] Kraft A, Grimsdale A C and Holmes A B 1998 *Angew. Chem. Int. Ed.* **37** 402
[15] Morgado J, Friend R H and Cacialli F 2002 *Appl. Phys. Lett.* **80** 2436
[16] Lee J H, Kee I S, Kang I N, Son J M, Kim K S, Park M J and Hwang D H 2009 *Curr. Appl. Phys.* **9** 861
[17] Osaheni J A and Jenekhe S A 1992 *Chem. Mater.* **4** 1282
[18] Jenekhe S A and Osaheni J A 1994 *Science* **265** 765