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High-efficiency phosphorescent polymer light-emitting devices

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Abstract

In this paper, we describe the performance of polymer light-emitting devices (PLEDs) that are based on phosphorescent polymers involving a carbazole unit and an iridium-complex unit. The PLEDs exhibit red, green or blue emission, depending on the phosphorescent polymer used in the emissive layer. We achieved highly external quantum efficiencies of 5.5%, 9% and 3.5% in respective red, green and blue PLEDs by selecting the electron transport material for the emissive layer and optimizing the content of the iridium-complex unit in the phosphorescent polymer chain. Furthermore, we demonstrated white emission in PLEDs by using blue-phosphorescent and red-phosphorescent polymers. An external quantum efficiency of 4.5% was obtained for this emission.

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1. Introduction

Organic light-emitting devices (OLEDs) and polymer light-emitting devices (PLEDs) have been attracting a great deal of attention for use in flat panel full-color displays [1,2]. Recently, certain Japanese companies developed a 14.7-inch full-color display based on small-molecule OLEDs and a 17-inch full-color display based on PLEDs [3,4]. The 17-inch display, which is the largest PLED screen that has been tested to date, was fabricated with ink-jet printing. These PLEDs are believed to have the potential of being applied, economically, to large-area, fine-pixel displays because polymer film can be prepared by using solution processes such as spin-coating, screen printing, or ink-jet printing [5]. Polymeric materials are also suitable for flexible displays fabricated on plastic film because the materials are themselves mechanically flexible.

The quantum efficiency of PLED light emission is, however, still below 5%, revealing its limitations by the fraction of singlet-excited states [6]. An important breakthrough in emission efficiency was achieved with a phosphorescent small molecule (iridium complex) that emitted light from its triplet states [7]. An external quantum efficiency of nearly 20% (implying a 100% internal quantum efficiency) was achieved in phosphorescent green OLEDs [8,9]. Highly efficient red and blue phosphorescence were also reported in similar iridium-complexes that had a suitable choice of ligands [10,11].

However, these highly efficient phosphorescent OLEDs have complicated structures that consist of hole-transporting, emissive, hole-blocking and electron-transporting layers. Furthermore, they

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require strictly controlled sequential deposition under high-vacuum conditions. Much simpler devices and fabrication methods are needed to manufacture efficient OLEDs.

Previous attempts in this regard have resulted in PLEDs where a hole-transporting polymer was doped with a small phosphorescent molecule, resulting in good efficiencies for green [12,13]. However, the molecularly doped polymer system of these PLEDs might be subject to problematic phase separation resulting in non-uniform emissions and decreased emission intensity.

We recently reported on new emissive polymers where a small amount of phosphorescent units is involved as a side group of a hole-transporting polymer [14]. This is a promising approach toward satisfying the needs for both a higher efficiency and a simpler fabrication process for PLEDs. Kim et al. independently reported a similar approach. However, they obtained a low quantum efficiency of only 0.38% in a green emissive polymer [15]. We succeeded in synthesizing well-controlled phosphorescent polymers with high molecular weight and high purity. PLEDs based on our phosphorescent polymers exhibited higher quantum efficiencies for red, green and blue [13]. The quantum efficiency for green and red, in particular, exceeded 5%.

This paper presents the high performance of optimized PLEDs based on these phosphorescent polymers. The influence on quantum efficiency of using an electron transport material for the emissive layer is shown for the blue PLED. We describe how to optimize phosphorescent unit concentration in three polymers (red, green and blue) to achieve high efficiency. We also describe how we demonstrated white light emission in PLEDs by using both blue-phosphorescent and red-phosphorescent polymers.

2. Experiments

The basic molecular structure of these polymers consists of a phosphorescent monomer unit and a charge transport monomer unit. The structures of red-phosphorescent polymer (RPP), green-phosphorescent polymer (GPP), and blue-phosphorescent polymer (BPP) synthesized in this study are shown in Fig. 1. Iridium (Ir)-complexes, which were reported by the Princeton group, were used for the phosphorescent monomer units [7,10,11]. The Ir-complex unit was connected with a vinyl polymer backbone. The carbazole unit was directly bonded to the backbone as the charge transport unit ; the carbazole is well known to have excellent hole transport ability. The content of the Ir-complex unit in each polymer chain could be easily

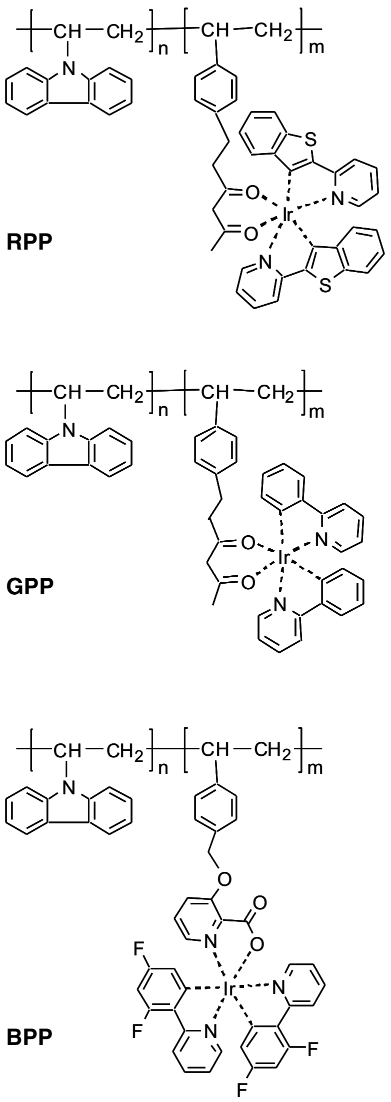

Fig. 1. Synthesized molecular structures of red, green and blue-phosphorescent polymers (RPP, GPP and BPP).

controlled during copolymerization of a vinyl monomer with a carbazole unit and a vinyl monomer with an Ir-complex unit, and it varied within a range of 0.2–1.5 mol%. The molecular weight determined by GPC was around 16 000. These polymers are soluble in common organic solvents and can be formed from solutions into uniform films by spin coating.

We measured transient photoluminescence decay by using a N_2 pulse laser to investigate the light generation mechanism in the emissive layer. The measurements were carried out in dichloroethane solutions of polymers at room temperature. The triplet energy of organic molecules was evaluated from the high-energy peak of phosphorescent spectra recorded at 77 K. The spectra were recorded 100 ms after pulse laser excitation.

The basic structure of the PLEDs consists of an indium-tin-oxide (ITO) anode, a conducting polymer layer, an emissive layer and a metal cathode as shown in Fig. 2. An electron transport material was molecularly doped into the emissive layer to conduct electrons. We used 1,3-bis[(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), a trimer of *N*-arylbenzimidazoles (TPBI), and 3-(4-Biphenyl)-4-phenyl-5-*tert*-butylphenyl-1,2,4-triazole (TAZ), (Fig. 2), as the electron transport material. A conducting polymer layer (PEDOT:PSS, 30 nm) on the ITO anode was used for hole-injection to the emissive layer. First, the conducting polymer layer was spin-coated on the ITO-coated glass substrate. Next, a 85-nm emissive layer consisting of phosphorescent polymer (70 wt%) and an electron transport material (30 wt%) was prepared from toluene solution by spin coating it onto the conducting polymer layer. Finally, we used vacuum deposition under a pressure of 5×10^{-7} Torr to form a bilayer of Ca (10 nm) and Al (150 nm). To achieve white light emission, two phosphorescent polymers (BPP and RPP) were used for the emissive layer. After the cathode was deposited, all PLEDs were encapsulated by using glass plates and UV epoxy resin under a nitrogen atmosphere. External quantum efficiency was calculated from the luminance, current density, and emission spectrum to evaluate their performance, assuming Lambertian emission.

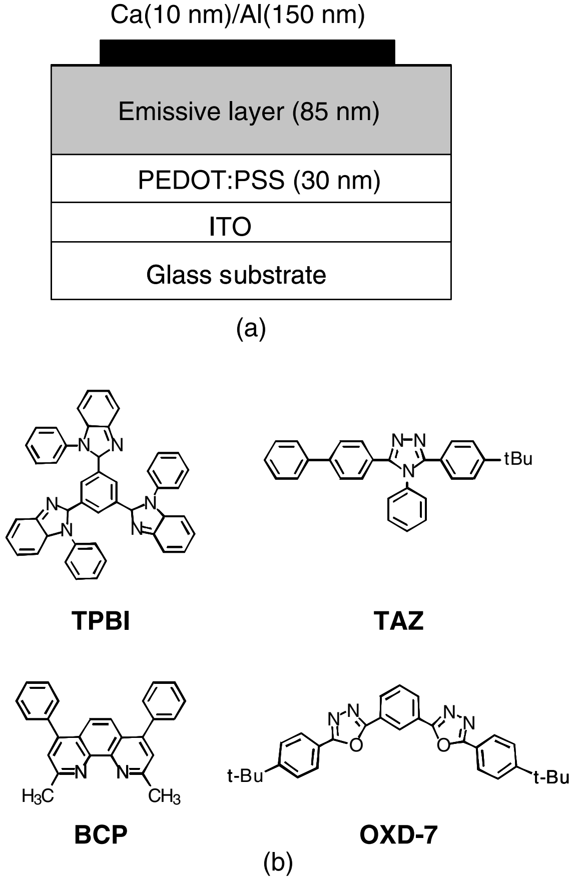

Fig. 2. (a) Basic structure of PLEDs and (b) molecular structures of electron transport materials used for emissive layers.

3. Results and discussion

The three synthesized phosphorescent polymers (RPP, GPP, and BPP) exhibited intense photoluminescence in dichloroethane solutions and even in neat powders. The decay profiles for transient photoluminescence measured in the solutions showed a single exponential decay with a long lifetime as shown in Fig. 3. We estimated the lifetimes of excited states to be 5.4 μs for RPP, 1.2 μs for GPP, and 1.0 μs for BPP. These lifetimes are almost identical with those of the Ir-complexes reported in recent literature [10,16]. These results indicate that the luminescence from phosphorescent polymers resulted from triplet states of the

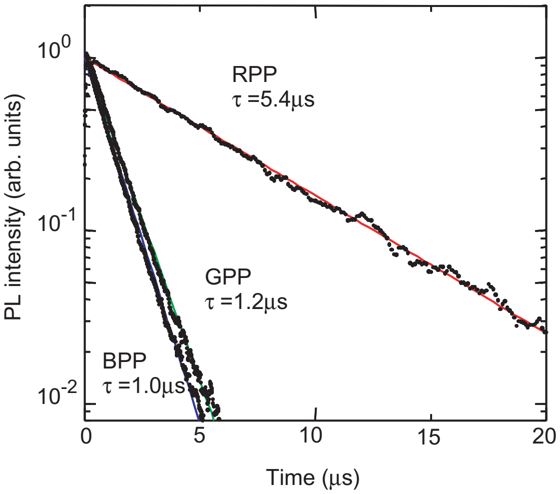

Fig. 3. Transient photoluminescence decays of three polymers observed in dichloroethane solutions after pulsed photoexcitation.

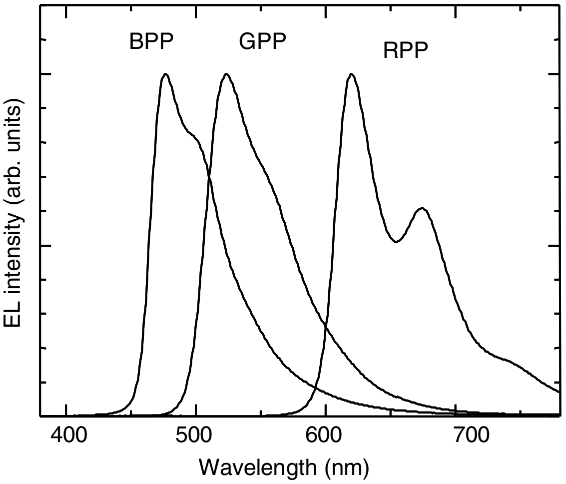

Fig. 4. Electroluminescence spectra of three PLEDs based on phosphorescent polymers (BPP, GPP or RPP).

Ir-complex units and all the energy of singlet states was transferred to triplet states [7]. Similarity of their lifetimes suggests that the photoluminescence quantum yield of these polymers are comparable to those of the Ir-complexes.

Red, green and blue emissions were observed in the PLEDs, depending on the kind of the phosphorescent polymer used for the emissive layer by applying a voltage over 5 V. The turn-on voltage for light emission (1 cd/m^2) was different in each of the three PLEDs though they had the same content of the Ir-complex unit. In order, it was RPP>GPP>BPP. The electroluminescence (EL) spectra for the three PLEDs are shown in Fig. 4. The respective peak wavelengths of blue, green and red emissions were 475, 523 and 620 nm. The color coordinates of the red and green emissions were comparable to those of NTSC. These spectra coincided with the photoluminescence spectrum of each polymer, and this clearly indicated that light emission was generated from the Ir-complex units of the polymers. The possible mechanisms for light generation seem to be energy transfer from the excited carbazole units or the excited electron transport molecules to the Ir-complex units, and the direct recombination of injected holes and electros on the Ir-complex units.

We measured the external quantum efficiencies of the PLEDs with various electron transport materials to investigate the influence of the electron transport material on the device performance. The external quantum efficiencies of green and red devices were not dependent on the electron transport material. However, the blue device exhibited strong dependency on this material. Fig. 5 shows the quantum efficiencies of blue devices obtained with various electron transport materials. The highest quantum efficiency of 3.5% was obtained in the device with OXD-7.

As previously mentioned, energy transfer from the triplet states of the carbazole units and the electron transport molecules to the Ir-complex units is a possible mechanism. Therefore, a high-energy triplet state is preferred for the carbazole units and electron transport molecules. The triplet energy of the carbazole unit was found to be about 3.0 eV, which is significantly higher than that of the blue Ir-complex molecule (FIrpic: ca. 2.71 eV). The triplet energy of the OXD-7 was 2.7 eV, which is comparable to that of the blue Ir-complex molecule. However, the BCP exhibited low triplet energy of 2.6 eV. These results indicate that the high quantum efficiency of the blue device with OXD-7 is related to the high triplet energy of OXD-7. Energy transfer from the blue Ir-complex units to the OXD-7 molecules can be suppressed

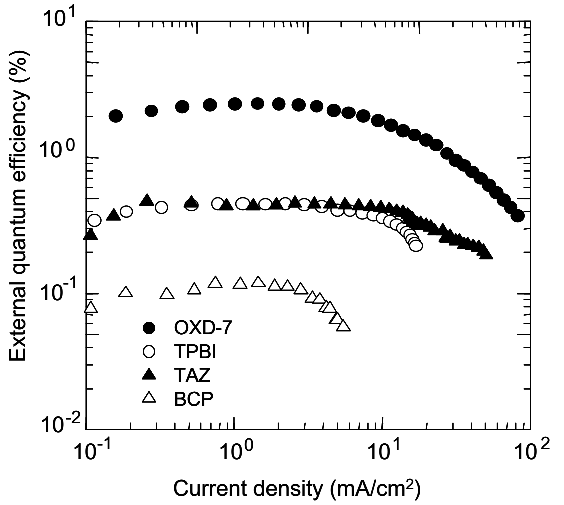

Fig. 5. External quantum efficiencies of blue PLEDs with various electron transport materials (OXD-7, TPBI, TAZ or BCP).

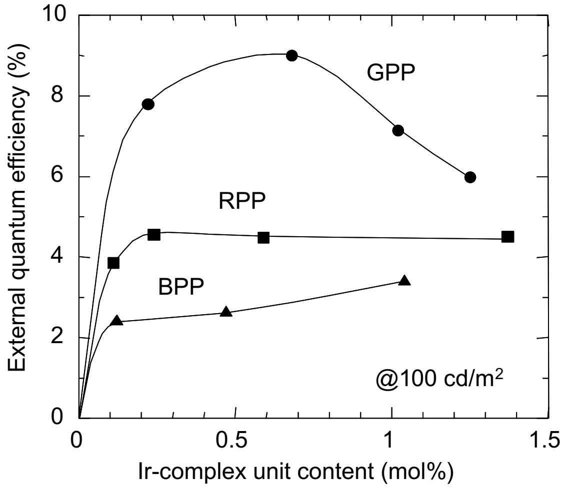

Fig. 6. External quantum efficiency versus Ir-complex unit content in phosphorescent polymer chain for the PLEDs based on RPP, GPP or BPP.

and effectively confined on the blue Ir-complex units.

To achieve higher efficiency, we investigated the optimal content of Ir-complex units in polymer chains. Fig. 6 shows the dependence of external quantum efficiency on the content of each Ir-complex unit. The maximum value of external quantum efficiency was obtained at a content of around 0.2 mol% for RPP, 0.6 mol% for GPP, and more than 1.0 mol% for BPP. The optimal contents for RPP and GPP were much lower than that for Ir-complex molecules in small-molecule OLEDs [7–11]. As our PLEDs have single layer structure, except for the conducting polymer layer, charge transport might be influenced by It-complex units. A widely accepted way of obtaining higher quantum efficiency is balancing the number of injected electrons with that of injected holes. Especially, that the red Ir-complex unit acts as a deeper carrier trap can be inferred from a small energy gap. As previously mentioned, we observed a higher turn-on voltage in the device with RPP than that with GPP and BPP. Similar phenomenon have been reported in a device with a polyfluorene derivative having the same red Ir-complex unit [16]. Carrier trapping leads to carrier imbalance resulting in decreased efficiency.

Fig. 7 shows luminance versus applied voltage and luminance versus current density characteristics for three optimized devices that we fabricated using RPP, GPP and BPP with an optimal Ir-complex unit content. The turn-on voltage for light emission was different in each of the three PLEDs and was in the order of RPP>GPP>BPP, same as was previously mentioned. The maximum luminances were achieved at around 16 V; 700 cd/m^2 for RPP, 7000 cd/m^2 for GPP, and 1000 cd/m^2 for BPP. The luminance was clearly proportional to the current density. The quantum efficiencies for the optimized devices are given in Fig. 8. The respective maximum values were 5.5% in red, 9% in green, and 3.5% in blue devices. Their respective luminance efficiencies were 7.1, 30 and 4.1 cd/A. The efficiencies for red and green were higher than 5%, which are the highest of the reported values for PLEDs [13,17]. These efficiencies decreased with increased current density above 10 mA/m^2, which is attributable to triplet–triplet annihilation [10].

A PLED with a single emissive layer containing both BPP and RPP emitted both blue and red light, resulting in white emission. Fig. 9 shows the EL spectra of a device where the concentration ratios of red Ir-complex unit of RPP to the

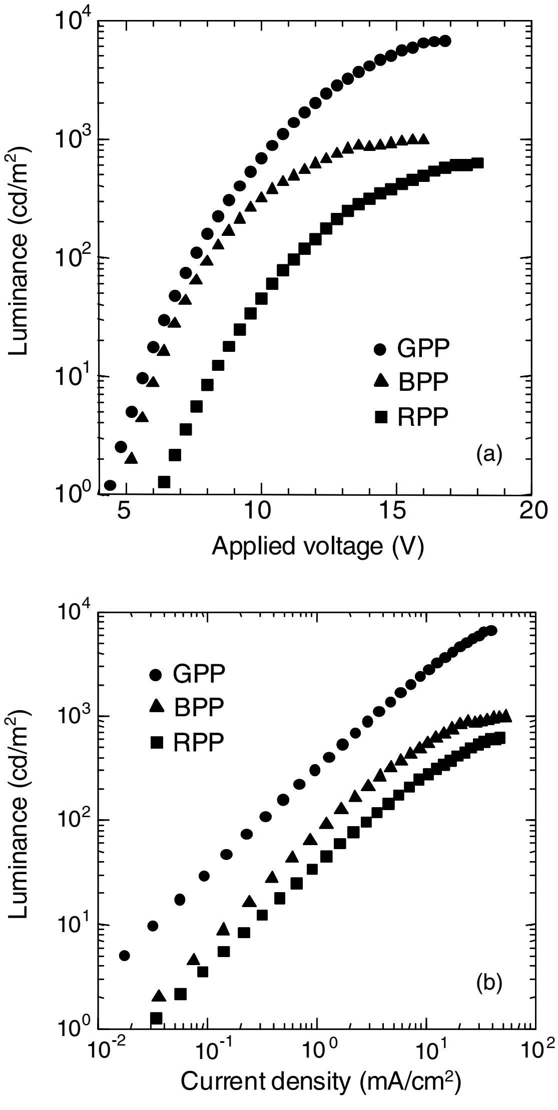

Fig. 7. (a) Luminance versus applied voltage and (b) luminance versus current density for three optimized PLEDs based on RPP, GPP or BPP.

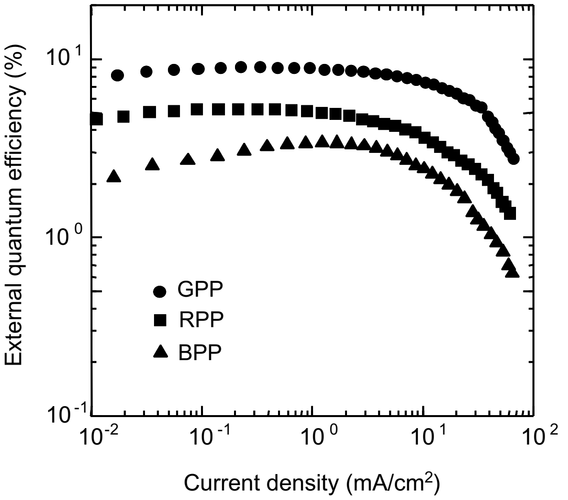

Fig. 8. External quantum efficiency versus current density for three optimized PLEDs based on RPP, GPP or BPP.

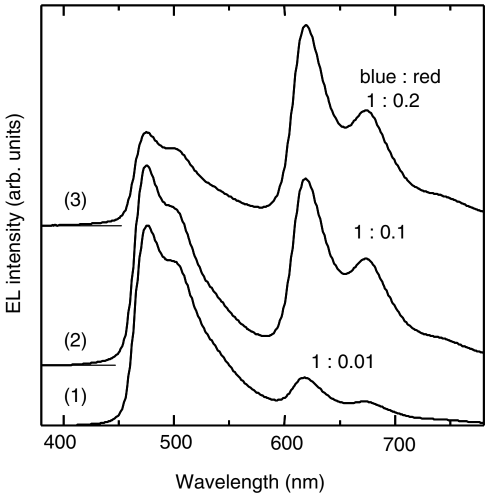

Fig. 9. Electroluminescent spectra of PLEDs employing two phosphorescent polymers (RPP and BPP) for emissive layer; the concentration ratio of red Ir-complex unit of RPP to blue Ir-complex unit of BPP is (1)1:0.01, (2) 1:0.1, and (3)1:0.2.

blue Ir-complex unit of BPP are 1:0.01, 1:0.1, and 1:0.2. Varying the ratio changed the emission color, and a white emission was obtained at the ratio of 1:01. The emission peak at 475 nm is attributable to BPP and that at 620 nm to RPP. The CIE coordinate of white emission was (0.34, 0.36).

The most important aspect affecting white emission is the concentration ratio of the red Ir-complex unit to that of the blue Ir-complex unit in the emissive layer. This is related to energy transfer and light generation in the emissive layer. The external quantum efficiency of white emission was 4.5% [18]. This value is also higher than that of a device based on PVK doped with Ir-complexes [13,18].

4. Summary

This paper presented the performance of PLEDs based on phosphorescent polymers that have a charge transport monomer unit and a phosphorescent monomer unit. Although the device structure is simple, highly efficient red, green and blue emissions were achieved. We achieved high external quantum efficiencies of 5.5%, 9% and 3.5% in respective red, green and blue devices by choosing the electron transport material and optimizing the content of the Ir-complex unit in the polymer chain. Furthermore, we obtained white emission by using blue and red phosphorescent polymers. The emission color was easily controlled by varying the ratio of RPP to BPP.

We are currently attempting further emission efficiency improvements. The ultimate external quantum efficiency might be 20%, which corresponds to an internal efficiency of 100%. As phosphorescent polymers are soluble in organic solvents, printing processes such as screen-printing and ink-jet printing can be used to produce PLEDs.

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