Development of Novel Blue Light-emitting Polymers for PLED

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Various kinds of conjugated polymers of arylene vinylene and arylene units have successfully been synthesized. They are suitable for light-emitting materials of PLED. Although some of them showed blue emission, they are not sufficient for practical displays. We have been researching on blue polymers and developed some novel blue polymers.

**Keywords:** conjugated polymer, fluorescence, PLED

1. Introduction

Organic and polymer light-emitting diodes, OLED and PLED, have attracted much attention as an accessible flat panel display device and have shown good progress in the last few years[1,2]. Many polymers for PLED have been reported since 1990[2-8]. Poly(p-phenylene vinylene) (PPV) was the first light-emitting polymer, which have yellowish-green emission[2,3]. After the first report of PPV, its derivatives were studied very well. The first commercial application of PLED using a PPV derivative, electric shaver of Philips, went on market last year. Although all colors were obtainable by using PPV derivatives, it was not easy to obtain blue emission without introducing non-conjugated linkage in main-chain of polymers[3,4]. Poly(p-phenylene) (PPP) and polyfluorene (PF) showed blue emission[5,6]. Many kinds of PF derivatives have been studied and RGB polymers based on PF were reported. Recently some full color PLED were fabricated by using ink-jet process. However, the device performance of the PLED was not sufficient for practical displays. Most serious problem is lack of sufficient blue light-emitting polymers.

We have already reported many kinds of soluble light-emitting polymers based on arylene vinylene units. Their emission colors were at shortest bluish green, not blue.

Light-emitting materials used in OLED and PLED are categorized in Figure 1. Among them, conjugated polymers have suitable characteristics for PLED, such as strong fluorescence, fairly good charge transport, solubility in common organic solvent, easy film formation, etc. Typical structures of light-emitting polymers are shown in Figure 2.

![Category of light-emitting materials](image1)

![Examples of polymer emitters](image2)

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In this paper, we will review and discuss the blue emission of conjugated polymers, and performance of developed blue polymers and PLED using those polymers.

Oxidation: \( \text{Ar} \xrightarrow{\text{Oxidation}} \left( \text{Ar} \right)_{n} \)

Yamamoto: \( X'\text{Ar}X' \xrightarrow{\text{Ni}(0)} \left( \text{Ar} \right)_{n} \)

Suzuki: \( X'\text{Ar}X' + \left( \text{H}_2\text{BArOH}_2 \right) \xrightarrow{\text{Pd}} \left( \text{Ar} \text{Ar} \right)_{n} \)

Figure 3 Synthetic routes of light-emitting polymers.

2. Experimental
2.1. Synthesis of polymers
Polystyrene viylene) were prepared by the method as reported previously[9-12]. Polyarylenes were synthesized by oxidation of arylene, Yamamoto coupling of dihaloarylene or Suzuki coupling of dihaloarylene and arylene diboric acid shown in figure 3. When we use more than two monomers at the same time, monomers were randomly connected each other except for Suzuki coupling. We can easily control molar ratio of repeating units in the copolymer by changing the ratio of monomers.

In order to obtain higher molecular weight of polymers, it was very important to purify monomers.

2.2. Fabrication of PLED
A polymer solution was prepared by dissolving the polymer with toluene. On to a glass substrate carrying an ITO film having a thickness of 150nm formed by a sputtering method was spin-coated poly(ethylene-1,2-dioxy-thiophene) / poly(styrene surfonic acid) (PEDOT) (Baytron P, Bayer) and a polymer solution, successively. Thickness of a PEDOT layer and a light-emitting polymer layer were both about 70nm. Then, in order to form a cathode layer, lithium fluoride of about 4nm, calcium of 20nm and aluminum of 50nm were successively deposited under vacuum (\(<8 \times 10^{-6} \text{Torr})\). The device was encapsulated by glass plate with resin.

2.3. Measurement of absorption and fluorescent spectra, and evaluation of photoluminescent intensity
0.2% chloroform solution of a polymer was spin-coated on a quartz plate to form a thin film of the polymer. An ultraviolet visible absorption spectrum and a fluorescent spectrum of this film were measured by using a UV/Vis spectrophotometer (Hitachi UV3500), a fluorescent spectrophotometer (Hitachi 850), respectively. The relative fluorescent intensity of a polymer was calculated as follows. An area of a fluorescent spectrum plotted against wave-number on the abscissa was divided by the absorption at excited wavelength (e.g. 350nm), to obtain a relative value of the fluorescent intensity.

2.4. Measurement of PLED characteristics
Luminance and current-voltage curves were obtained with a Photo Research PR650 luminance meter, a Keithley 990 digital multimeter and a Takasago GP050-2 DC voltage source which were controlled with a personal computer.

2.5. Evaluation of charge injection and transport
In order to evaluate hole injection, we fabricated a hole-only device, which had gold cathode in place of LiF/Ca/Al. Since it is very hard to inject electrons from cathode in this system, only holes are able to be injected and transferred around lower voltage region. On the other hand, we also fabricated a electron-only device, which had Al anode in place of PEDOT.

Hole mobilities of polymers were measured by time-of-flight (TOF) method. However it was very hard to measure electron mobilities by TOF.

3. Results and Discussion
3.1. Comparison of PLED and OLED
OLED is usually fabricated as a multi-layered device. On the other hand, PLED has typically
single-layered structure, OLED has at least one hetero-interface. Accumulation of charges at the interface will lead to higher combination probability and better charge balance. In PLED, charges injected from electrodes should be recombined during passing through the polymer layer. Therefore injection and transport characteristics of charges must be controlled more precisely in PLED than in OLED.

![Comparison between PLED and OLED](image)

**Figure 5** Difference of Light-emitting mechanism.

3.2. Effect of molecular weight

Figure 6 shows dependence of EL efficiency on molecular weight of a poly(p-phenylene vinylene) derivative. Although PL intensity was almost constant, EL efficiency had a critical point in molecular weight. When the molecular weight of the polymer was larger than it, EL efficiency became constant.

![Dependence of EL efficiency on molecular weight](image)

**Figure 6** Dependence of EL efficiency on molecular weight.

Possible explanations for this phenomena are shown in figure 7. One is that a high molecular weight, which means longer conjugation length in general, a high recombination ratio. Another is a high generation ratio of singlet [13].

![High recombination ratio](image)

<table>
<thead>
<tr>
<th>Mol. weight</th>
<th>Recombination ratio</th>
<th>Mol. weight</th>
<th>Recombination ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>low</td>
<td>low</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>r = σ_e/σ_h</td>
<td>n</td>
<td>σ_e/σ_h</td>
<td>n</td>
</tr>
<tr>
<td>Small molecule</td>
<td>1 / 3</td>
<td>Polymer</td>
<td>1 / 0.7</td>
</tr>
</tbody>
</table>

**Figure 7** Possible explanation for Mw dependence.

3.3. Quenching effect

Ratio of hole and electron mobilities in a polymer layer is a very important factor. When the hole mobility is similar to the electron mobility, recombination must take place in the middle of light-emitting layer. But if the hole mobility is much larger than the electron mobility, generated excitons are quenched by cathode metal and EL efficiency must not be so large. This is shown in figure 8.

EL efficiency is determined by equation below. In PLED, exciton quenching factor may not be zero.

![Schematic model of light-emitting zone and quenching](image)

\[ \eta = \gamma \cdot \eta_{eh} \cdot \phi_{ph} \cdot (1 - \chi_{EL}) \]

- \( \eta \): Electroluminescence efficiency
- \( \gamma \): Balance factor of current
- \( \eta_{eh} \): Generation rate of exciton
- \( \phi_{ph} \): Quantum efficiency of fluorescence
- \( \chi_{EL} \): Exciton quenching factor near cathode
3.5. Hole-only and electron-only devices

Hole-only and electron-only devices as well as an usual bipolar device were fabricated and measured for well-known polymers, that are polyfluorene and fluorene-amine copolymers.

I-V characteristics of these devices are shown in figure 9. The bipolar device of polyfluorene showed larger current densities than the sum of hole-only current and electron-only current. In the case of fluorene-amine copolymer, the bipolar current was similar to the hole-only current. Therefore major carrier is hole.

![I-V characteristics of fluorene polymers](image)

Figure 9 I-V characteristics of fluorene polymers.
(left: polyfluorene right: fluorene-amine copolymer)

3.6. Balance of holes and electrons

Hole mobilities of fluorene-amine copolymers varied a lot depending on the ratio of hole transporting units (amine contents). There was a minimum point around 5mol% shown in figure 10. At the same ratio, EL efficiency had a maximum point in figure 11. This means that hole and electron balance was achieved by reducing the hole mobility.

Holes seemed to be trapped at hole transporting units. Electric field in the light-emitting layer should be changed and distorted shown in figure 12. This will improve an electron injection. Both of the low hole mobility and the trap-assisted electron injection must make the balance better.

![Mobility vs. content of hole transporting units](image)

Figure 10 Mobility vs. content of hole transporting units.

![EL efficiency vs. content of hole transporting units](image)

Figure 11 EL efficiency vs. content of hole transporting units.

3.7. Degradation of the devices

The device of polyfluorene was deteriorated faster than that of fluorene-amine copolymer. Although the device of amine homopolymer was slightly deteriorated, the V-I curve did not change at all shown in figure 13. This means that electron injection or transfer will lead to degradation of the devices.

It is needed to find out stable electron transfer units other than fluorene.

![Schematic model of trap assisted electron injection](image)

Figure 12 Schematic model of trap assisted electron injection.
3.8. PL and EL change during driving

PL and EL intensity decreased gradually during driving the device. As shown in figure 14, EL intensities decreased more than PL intensities did. After driving the devices, PL and EL spectra did not change so much in shape as shown in figure 15.

Therefore degradation at the electrode interface seemed to be more significant than that in the bulk of the light-emitting layer.

3.9. Novel blue light-emitting polymers developed in Sumitomo Chemical

On the basis of the above-mentioned investigation, we have been researching on blue light-emitting polymers, which are not fluorene copolymer. We successfully synthesized novel monomer units suitable for blue light-emitting polymers.

EL spectra of typical polymers are shown in figure 16. EL characteristics are summarized in table 1. EL color and efficiency of our polymers are shown in figure 17.

Figure 13  V-I, V-L characteristics of deteriorated devices.
(left:polyfluorene  middle:fluorene-amine copolymer  right:amine homopolymer)

Figure 14  PL and EL decay of blue emitting polymer.

Figure 15  Spectral change of PL and EL during driving.
(left:EL spectra  right:PL spectra)
Table 1  Device performance of blue polymers.

<table>
<thead>
<tr>
<th>Color</th>
<th>EL peak (nm)</th>
<th>CIE x</th>
<th>CIE y</th>
<th>Vth (V)</th>
<th>EL efficiency (cd/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure blue</td>
<td>440,464</td>
<td>0.15</td>
<td>0.10</td>
<td>3.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Blue</td>
<td>460</td>
<td>0.16</td>
<td>0.20</td>
<td>2.9</td>
<td>2.2</td>
</tr>
<tr>
<td>Greenish blue</td>
<td>492</td>
<td>0.20</td>
<td>0.45</td>
<td>3.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Fig. 16 EL spectra of Sumitomo’s polymers.

4. Conclusion

We successfully synthesized blue light-emitting polymers for PLED. We demonstrated that fluorene units are easily degraded during driving. We already have some candidates, which could replace fluorene units.

We will be able to obtain polymers of all colors suitable for a full color PLED display in the near future.

References