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Color variable multilayer light emitting devices based on conjugated polymers and oligomers

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Abstract

We report the fabrication and study of color variable multilayer light emitting devices based on pyridine-containing conjugated polymers and para-sexiphenyl (6P) oligomer. Polarity controlled two color devices were fabricated by sandwiching the emitting layer in between emeraldine base and sulfonated forms of polyaniline (SPAN). The emitting layer typically is a blend of two polymers, one of which is a pyridine-based copolymer (PPyVPV). The devices can be operated under either polarity of driving voltage with different colors of light being emitted from different locations. Under forward bias, red light is generated from PPyVPV/SPAN interface. Under reverse bias, light is generated from the bulk of the emitting layer whose color is dependent on the materials used. Voltage controlled multicolor devices were fabricated by combining the pyridine-based polymers with the 6P oligomer. Voltage dependent multicolor emission was observed in both bilayer and trilayer devices. The emission colors of single devices cover a wide range of visible spectra whose CIE color coordinates vary from blue to white to green with increasing voltages.

Keywords: *Light emitting devices, Electroluminescence, Photoluminescence, Poly(phenylene vinylene) and derivatives, Pyridine-containing polymers, Polymer/polymer interfaces.*

1. Introduction

In the past decade, there has been great interest in organic molecular and polymeric electroluminescent devices, particularly conjugated polymer based light-emitting devices (LEDs) [1-5]. To date, a variety of conjugated polymers and/or copolymers have been synthesized whose emission colors cover all the visible spectra. However, for most devices the color of the emitted light is fixed once the device is fabricated. Recently color variable light-emitting devices have attracted much attention. These devices can generate two or more colors of light controlled by device parameters such as driving voltage, current, local temperatures, etc. The most common approach to color variable devices is voltage controlled multicolor LEDs. In this approach, a blend of organic materials, either polymers or molecules or both, often is used as the emitting layer. For example, in the devices using a blend of polythiophene derivatives, different components in the blend emit different colors of light simultaneously with the intensity of each component varying with the applied voltage [6]. Similar voltage dependent EL was observed in the devices using conducting polymer containing fluorescent dye as the emitting layer [7]. While using blends is a good approach to white LEDs, it is often difficult to achieve relatively pure blue emission in such devices due to its difficulty in quenching the low energy component completely at high voltages.

Multilayer approaches are shown to be promising for color variable light emission. In certain multilayer structures that can be operated under both forward and reverse bias, a different color of light can be generated under reverse bias than under forward bias, thus allowing the fabrication of polarity controlled two color devices [8-13]. We have reported a novel interface approach to such polarity controlled two color devices. The device consists of a layer of blend of two active electroluminescent polymers sandwiched between two different redox polymer layers. The redox polymer layers modify the charge injection and transport properties such that the device can be operated under both forward and reverse bias. Also at least one of the redox polymers is capable of modifying the emission properties of the emitting polymers at an interface such that this interface emits different colors of light than the bulk does. In this approach, the colors of light are controlled by selecting the desired emission locations, which in turn are controlled by the polarity of the driving voltage.

In this paper, we show that the concept of using interface control to achieve color variable devices is quite general, it can be applied to a variety of emitting materials. In certain cases, under reverse bias the emission colors are voltage dependent. We also report the fabrication of voltage controlled multicolor light emitting devices combining pyridine-containing conjugated polymers with para-sexiphenyl (6P) oligomer in separate layer

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configurations. The emission colors of single devices cover a wide range of visible spectra including white

2. Experiments

For the polarity controlled two color light emitting devices presented here, a copolymer of poly (pyridyl vinylene) and poly(phenylene vinylene) derivative, PPyVPV is used as the main component of the blend of the emitting materials. A copolymer of polythiophene and polyphenylene derivative, PTP, the derivatives of polyacetylene, poly (diphenyl butyl acetylene) (PDPA-nBu) and poly (hexyl phenyl acetylene) (PhPA), were used as the other component in the blend. Sulfonated polyaniline (SPAN) and the emeraldine base (EB) form of polyaniline were used as the redox materials. The fabrication procedures have been previously reported [10,11]. For the multicolor multilayer devices, PPyVPV, poly (p-pyridine) (PPy) and 6P were used as the active emitting layer, poly (N-vinylcarbazole) (PVK) was used as hole tranporting/electron blocking layer in certain devices. The polymer layers were formed using spin-coating techniques. The solvents used for PPyVPV, PPy and PVK are xylenes, formic acid and tetrahydrofuran, respectively. The 6P layer was formed using the vacuum deposition technique at a rate ~0.1 Å/s. The thickness of the polymer layer and 6P layer is typically 20-50 nm and 40-80 nm, respectively. Figure 1 shows the chemical structures of the materials used for these studies

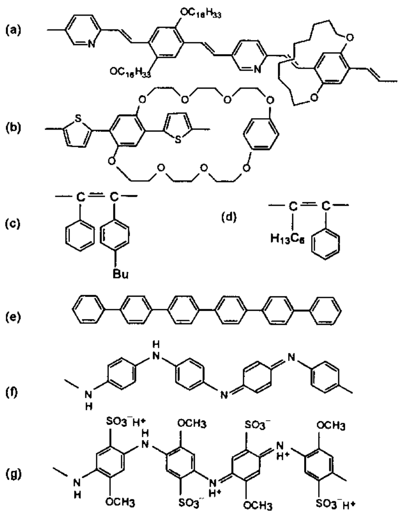

Fig. 1 Repeat units of materials used: (a) poly (pyridyl vinylene phenylene vinylene) (PPyVPV), (b) poly (dithienylene phenylene) (PTP), (c) poly (diphenyl butyl acetylene) (PDPA-nBu), (d) poly (hexyl phenyl acetylene) (PhPA), (e) para-sexiphenyl (6P), (f) emeraldine base (EB), (g) sulfonated polyaniline (SPAN).

Photoluminescence (PL) and electroluminescence (EL) spectra were measured using a PTI fluorometer (model QM-1). The current-voltage (I-V) characteristics were measured simultaneously with EL output while dc voltages were continuously applied by a HP model 6218A DC power supply. The current-voltage data were monitored by two Keithley model 195A multimeters while the EL output was monitored by a calibrated photodiode (UDT UV100). The data were recorded by a computer. Quantum efficiency and brightness were calculated from the I-V-EL data.

3. Results and discussion

The polarity controlled two color light emitting devices using a blend of PPyVPV and PTP as the emitting layer and EB and SPAN as redox layers has been reported earlier [10,11]. The operating mechanism of such devices is as follows: under forward bias, red light is emitted from the new species at the interface between PPyVPV and SPAN as a result of protonation of the pyridyl units inside the PPyVPV by SPAN. Under reverse bias, the emission zone is shifted away from the PPyVPV/SPAN interface with the assistance of hole transporting PTP, resulting in a light-green emission color originated from the bulk of the emitting layer. Note that in such polarity controlled two color devices, the presence of the SPAN layer is critical while the EB is not. Some devices function well without the EB layer.

We have shown that the device structure mentioned above is quite general. It can be applied to other conjugated polymers allowing the choice of colors emitted under reverse bias. In particular, when the PTP is replaced by PDPA-nBu or PhPA, voltage dependent emission colors were observed under reverse bias. Fig. 2 shows the EL spectra of an ITO/PPyVPV:PhPA/SPAN/Al device. The weight ratio of PPyVPV:PhPA is 1:1. Under forward bias, the device emits red light independent of voltage, similar to the PTP devices. Under reverse bias, however, the emission colors change from orange to green as the voltage increases.

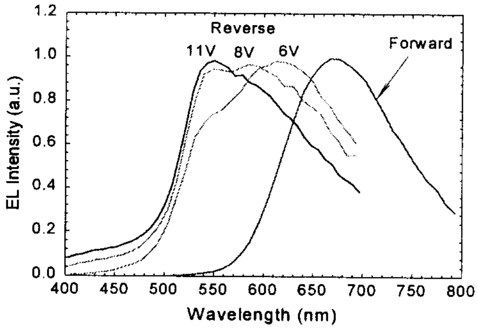

Fig. 2 EL spectra of the ITO/PPyVPV:PhPA/SPAN/Al device under forward and reverse bias conditions.

Here we present another type of multicolor light-emitting devices combining the pyridine-based polymers with the 6P oligomer in separate layer configurations. Voltage dependent multicolor emission was observed in both bilayer and trilayer devices. In the bilayer devices with the configuration of ITO/6P/PPy/Al, blue light is emitted at low voltages. As the driving voltage increases, a component of green light grows, and eventually becomes dominant. When PVK or PPyVPV is introduced in between ITO and 6P, the trilayer device generates light from blue at low voltages to nearly white at high voltages whose color coordinate traverses along a straight line in the CIE chromaticity diagram.

Figure 3(a) shows the PL spectra of the bilayer 6P/PPy structure under different excitation wavelengths. When excited at 350 nm, the PL spectra are similar to those reported for 6P [14]. As the excitation wavelength increases, the contribution from PPy increases, and becomes dominant at excitation wavelength of 420 nm. Figure 3(b) shows the EL spectra of a bilayer device ITO/6P/PPy/Al operated under different applied voltages. Under low voltages, the EL spectra show two peaks at 425 nm and 450 nm, in addition to shoulders at 400 nm and 480 nm. The bilayer EL spectrum can be roughly represented by a superposition of the two individual 6P and PPy EL spectra, suggesting that the light is generated near the interface between 6P and PPy. The EL appears light blue to the eye. As the voltage increases, a peak at 565 nm appears and eventually becomes dominant.

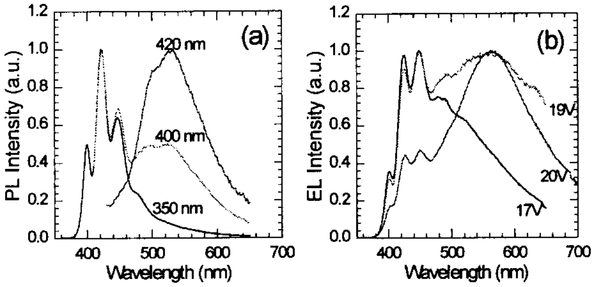

Fig. 3 (a) Normalized PL spectra of 6P/PPy with different excitation wavelengths; (b) Normalized EL spectra of an ITO/6P/PPy/Al device under different applied voltages.

Figure 4(a) and 4(b) shows the PL and EL spectra of a three-layer device ITO/PVK/6P/PPy/Al, respectively. The PL of the three-layer device is similar to those of the two-layer one, except that there is some emission from PVK at 350 nm excitation. At low applied voltages, the EL spectrum is very similar to that of the bilayer device, which is light blue in color. The CIE chromaticity x,y coordinates of the EL spectra at 17 V is calculated to be (0.237,0.224). As voltage increases, the peak at 450 nm grows. At the same time, a new peak at ~ 605 nm appears and grows, which drives the location of the EL spectra in the CIE diagram towards white along a straight line, as shown in Fig. 5(a). At 27 V, the emitted light appears bright white to the eye. The CIE chromaticity x,y coordinates of the spectra at 27 V is calculated to be (0.322,0.315). Below 27 V, the voltage dependent EL spectra are more or less reversible. Above 27 V, the device went through an irreversible change. The features at blue region disappear and the EL spectrum is dominated by a broad peak at 605 nm. The light appears greenish white to the eye and its CIE chromaticity x,y coordinates is calculated to be (0.400,0.411). It is noted that the EL spectra do not change further with applied voltages above 27 V although its brightness increases with increasing applied voltages.

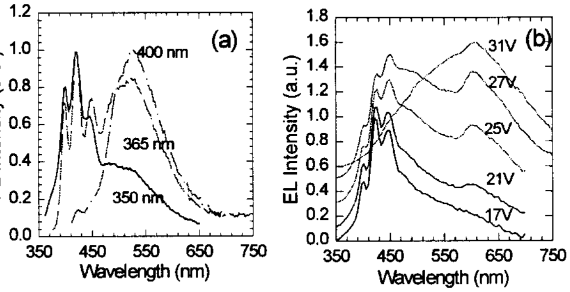

Fig. 4 (a) Normalized PL spectra of PVK/6P/PPy with different excitation wavelengths; (b) Normalized EL spectra of an ITO/PVK/6P/PPy/Al device under different applied voltages. The spectra are offset for clarity.

A modest quantum efficiency and brightness were achieved for the bilayer devices. The incorporation of hole transporting layer PVK in the three-layer device significantly improved the device performance. Figure 5(b) shows the typical current-voltage (I-V) and luminance-voltage characteristics of the three layer devices. The devices have a typical turn on voltage of ~ 15-17 V. After turn on, the light intensity roughly followed the current density. The discrepancy between them is probably due to the spectral change with the applied voltages. The maximum brightness is well above 100 cd/m^2 when the EL spectrum at 27 V is used to calculate the brightness. The external quantum efficiency of greater than 0.1% has been achieved for the initial unoptimized three layer devices.

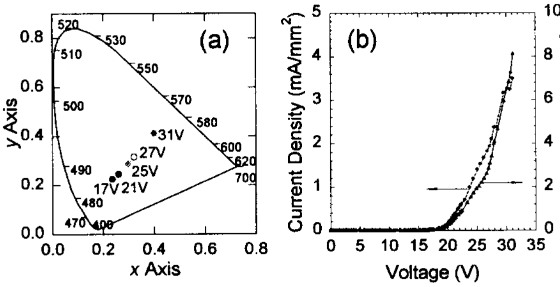

Fig. 5 (a) The CIE color coordinates of the EL spectra of the ITO/PVK/6P/PPy/Al device under different applied voltages. (b) Current-voltage and luminance-voltage characteristics for the ITO/PVK/6P/PPy/Al device.

Figure 6(a) shows EL spectra of a three-layer device ITO/PPyVPV/6P/PPy/Al device under different applied voltages. The EL spectra are dominated by the 6P layer at low applied voltages, appearing blue to the eye. As the voltage increases, a component at ~ 700 nm and a component at ~ 530 nm appear and grow. At 17-21 V, the strength of the blue, green, and red components are almost equal, making the light appearing white to the eye. As the voltage further increases, the green component keeps growing while the blue one is decreasing. The color in the CIE chromaticity diagram of this device is shown in Fig. 6(b).

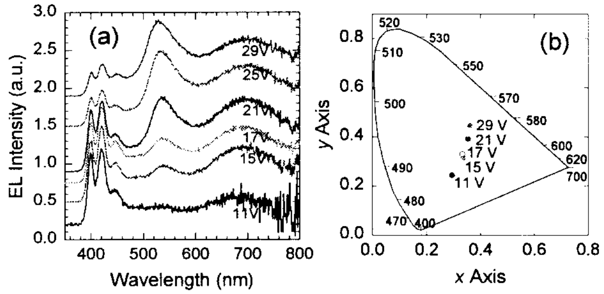

Fig. 6 (a) Normalized EL spectra of an ITO/PPyVPV/6P/PPy/Al device under different applied voltages. The spectra are offset for clarity. (b) The CIE color coordinates of the EL spectra of the ITO/PPyVPV/6P/PPy/Al device under different applied voltages.

The phenomena of voltage dependent EL have been observed most often in blend systems [6,7]. In the blend systems, the change of the EL spectra with applied voltage is usually due to different charge injection threshold of each component. The emission typically starts from low band gap component and gradually shifts to high band gap ones (towards blue) as the applied voltage increases. This mechanism clearly cannot explain the devices presented here. Recently there is one report [15] on voltage controlled color-variable multilayer LEDs in separate layer configurations. In that system, the emitted light composes of a green component from Alq3 and a red component from a perylene bisimide pigment (PBP). For relative thin PBP layer, as the applied voltage increases, the red component decreases while the green one keeps constant. For thick PBP layer, on the other hand, the red component increases with applied voltage. This was explained in terms of electric field-induced quenching of excited states and voltage evolution of the recombination zone in the red emitting material. Field induced quenching is unlikely the mechanism for the devices reported here because the changing component in the EL spectra *grows* with increasing applied voltage. The fact that the new component in the EL spectra does not belong to any of the individual material suggests that the new component comes from the interface instead of bulk. The exact mechanism is under further study. We believe that the voltage dependent emission location change due to different field dependent mobility of the materials may play an important role.

4. Conclusion

In summary, we have presented a number of light-emitting devices based on pyridine-containing conjugated polymers and copolymers and para-sexiphenyl oligomer in various device configurations. We have shown that the earlier reported polarity controlled two color light emitting devices were quite general. It can be applied to other conjugated polymers allowing the choice of colors emitted under reverse bias. In the cases where derivatives of polyacetylene were used as one of the emitting materials in the blend, voltage dependent emission colors were observed under reverse bias. Voltage (magnitude) controlled multicolor devices were fabricated by combining the pyridine-based polymers with the 6P oligomer. Voltage dependent multicolor emission was observed in both bilayer and trilayer devices. The emission color can be tuned from blue to white to green along almost a straight line in the CIE chromaticity diagram.

5. Acknowledgment

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