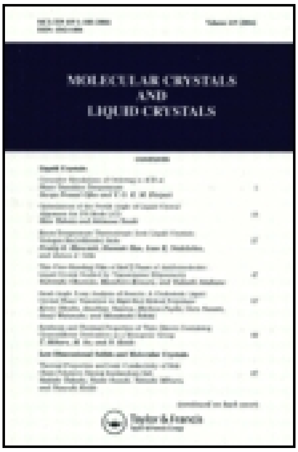

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Fabrication of Water Soluble Conjugated Polymers for WOLED

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*Recently, the novel organic materials for white OLEDs have been researched, but it is not easy to apply polymers to WPLEDs. However, because water soluble conjugated polymers can be spin-coated on organic soluble conjugated polymers, when organic soluble blue and red emission polymers, and water soluble green emission polymer were used as multi-layer device, WPLEDs can be produce by the total color of self emission at multi-layer. Water soluble anionic poly(9,9-bis(4′-sulfonatobutyl)fluorene-*co-alt-*1,4-phenylene) (anion-PF(Na^+)) was synthesized, and we investigated the white color emission by multi-layer of this class of anionic conjugated polyelectrolytes and organic conjugated polymers (MEH-PPV) using the following device structure: ITO/PEDOT:PSS/anion-PF(Na^+)/MEH-PPV/Al, because anionic PFP can get the self-blue emission and green emission by aggregation effect in film condition. Finally, the color of devices made using different device structure of ITO/PEDOT:PSS/MEH-PPV/anion-PF(Na^+)/Al was compared, and this device can get the blue and red emission because the green emission of anionic PFP was absorbed in MEH-PPV.*

Keywords Water soluble conjugated polymers; White emission; OLED.

1. Introduction

Organic light-emitting diodes (OLEDs) have been researched considerably with several advantages over conventional devices such as a low driving voltage, wide viewing angle, thin film structure, and a simpler manufacturing process for the generation of large area and flexible display [1]. Fluorene based polymers, such as polyfluorenes (PFs), have attracted considerable attention caused by the several promising aspects including high photoluminescence (PL) quantum efficiency, good thermal stability and easy functionalization at the 9-position of the fluorene unit [2].

Many approaches have been attempted to realize high performance WPLEDs. One has developed multilayer systems by stacking several layers from three primary color components of red (R), green (G), and blue (B), or simply by using two complementary

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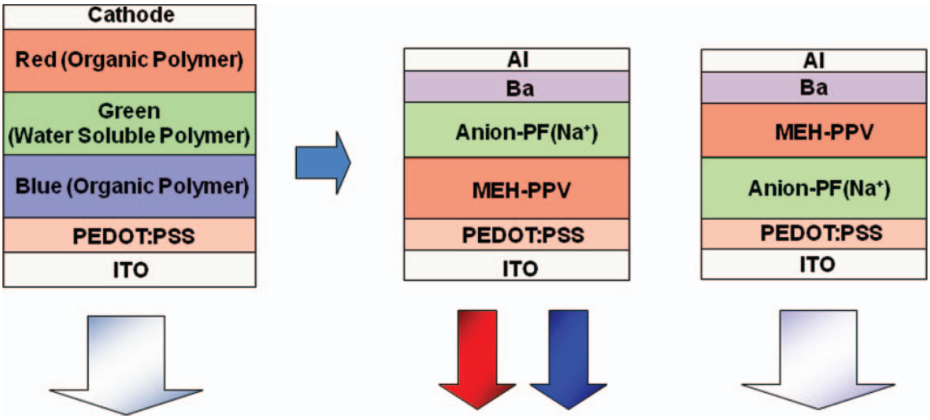


Figure 1. Device structure for the white light emitting diodes.

colors [3–4]. One of the disadvantages of these types of devices is that it is difficult to control the doping level of the long-wavelength light-emitting materials to obtain balanced white-light emission [5]. For the multilayer systems, however, it is difficult to fabricate a well-defined multilayered structure because of the intermixing between the polymer layers. Many researchers showed show a general method to solution-process multilayer PLEDs by using an intermediate liquid buffer between polymer layers [6]. Especially, the water soluble green emission polymer were used as multi-layer device, WPLEDs can be produce by the total color of self emission at multi-layer as shown in Figure 1.

The present investigation deals with the synthesis and characterization of new polymers, water soluble anionic poly(9,9-bis(4′-sulfonatobutyl)fluorene-*co-alt*-1,4-phenylene) (anion-PF(Na^+)) [7–8]. The new polymer was synthesized by Suzuki reaction. To obtain emission with three peaks at blue, green and red emission regions, the bilayer as emitting layer are produced for white light emitting diodes. The electroluminescence properties of the anion-PF(Na^+) were investigated by fabrication of the WPLEDs with the configuration of ITO/PEDOT/MEH-PPV/anion-PF(Na^+)/Ba/Al and ITO/PEDOT/anion-PF(Na^+)/MEH-PPV/Ba/Al.

2. Results and Discussion

Materials. The molecular structure of the anionic conjugated polyelectrolyte, poly(9,9′-bis (4-sulfonatobutyl)fluorene-*co-alt*-1,4-phenylene) (anion-PF(Na^+)), is shown in Fig. 2(a). As synthesized, the polymer contains sodium as the charge compensating countercation.

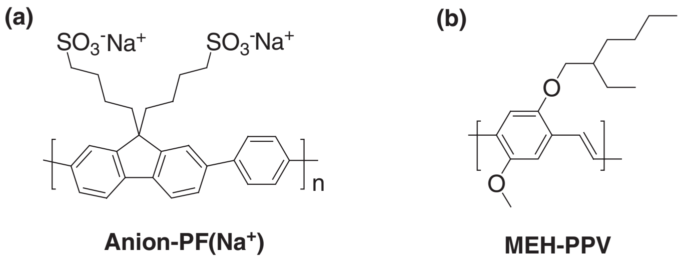


Figure 2. Molecular structure of anion-PF(Na^+) (a) and MEH-PPV (b).

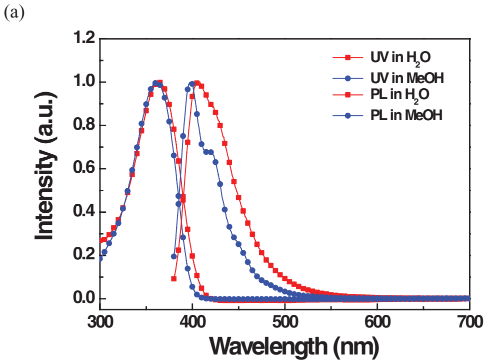
Table 1. Characteristics of the UV-vis absorption and photoluminescence of anion-PF(Na^+)

Polymer	Abs λ_{max} (nm)	PL λ_{max} (nm)	Fwhm[a] of PL
In water	364	408	57
In methanol	361	398	45

[a] Full width at half-maximum of PL spectra.

Ion exchange can be achieved by protonation of the polymer with HCl followed by addition of a suitable base with the cation of interest. The anionic conjugated polyelectrolyte anion-PF(Na^+) is soluble in water, but poorly soluble in alcohols. The molecular structure of poly(1-methoxy-4-(2-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV), [9–10] as red emitting materials is shown in Fig. 2 (b). The alkoxy substituents on the aromatic ring are used to impart solubility to the PPV.

Optical Properties. The absorption and photoluminescence (PL) properties of the synthesized polymer were investigated in water and methanol solution. The absorption and emission data for the anion-PF(Na^+) and MEH-PPV are summarized in Table 1. As shown in Fig. 3 (a), the absorption peaks, corresponding to π-π^* transition of the conjugated backbones, appear at around 360 nm. The PL spectra of anion-PF(Na^+) in water shows the maximum peak at 408 nm. The solutions of the polymers in methanol showed PL emission



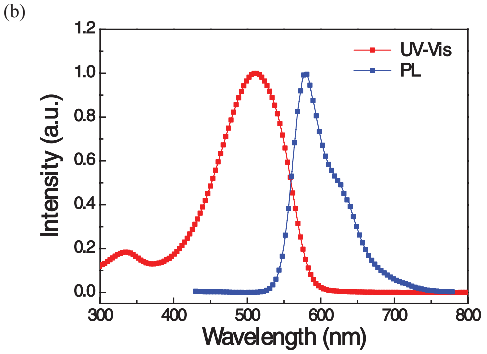


Figure 3. UV-visible absorption spectra of the Anion-PF (Na^+) in water and methanol solution (a) and MEH-PPV in THF solution (b).

peaks with a maximum at 398 nm, and a shoulder at about 420 nm. The full width at half maximum (fwhm) of anion-PF(Na^+) in water was increased caused by the increased π–π^* interaction. As shown in Fig. 3 (b), the absorption peak originating from MEH-PPV appeared at 511 nm in tetrahydrofuran as the solvent. The PL emission spectrum of the MEH-PPV shows maximum peak at about 580 nm, corresponding to red emission region.

Electroluminescence Properties. The investigations of electroluminescence properties of the anion-PF(Na^+) and MEH-PPV were conducted by fabricating the devices with the configuration of ITO/PEDOT (40 nm)/polymer (80 nm)/Ba (10 nm)/Al (100 nm). The electroluminescence (EL) spectra of the devices are shown in Fig. 4. In case of anion-PF(Na^+), the EL spectra of the polymers showed two distinct peaks comprising the maximum at 426 nm, which corresponds to the peak of the fluorine-phenylene backbone, and additional large one at around 502 nm, respectively. The additional peak at around 502 nm corresponded green emission region is increased with increased voltage from 3.5 V to 6.5 V. The emission maximum of the MEH-PPV appears at around 592 nm, which is corresponded red emission region for white light emission.

The investigations of electroluminescence properties of these copolymers were conducted by fabricating the devices with the configuration of ITO/PEDOT/anion-PF(Na^+)/MEH-PPV/Ba/Al and ITO/PEDOT/MEH-PPV/anion-PF(Na^+)/Ba/Al. The electroluminescence (EL) spectra of devices are shown in Fig. 5. The EL spectra of the configuration of ITO/PEDOT/anion-PF(Na^+)/MEH-PPV/Ba/Al showed three peaks at 423, 508 and 592 nm. The two peaks at 423 and 508 nm are provided from anion-PF(Na^+) and the peak at 592 nm is offered from MEH-PPV. In case of the configuration of

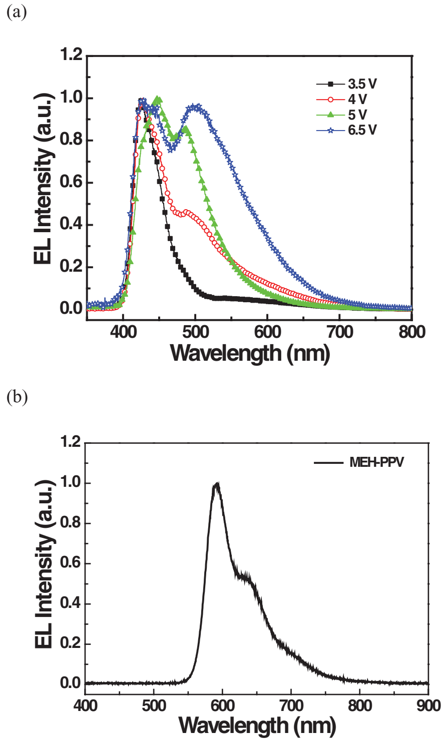


Figure 4. EL spectra of the Anion-PF(Na^+) (a) and MEH-PPV (b) with the configuration of ITO/PEDOT/polymers/Ba:Al.

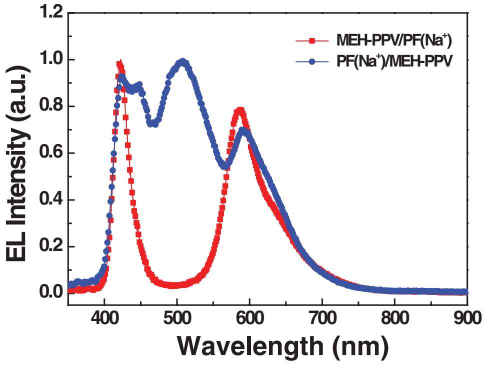


Figure 5. EL spectra of the device with the configuration of ITO/PEDOT/emitting bilayers/Ba:Al.

ITO/PEDOT/MEH-PPV/anion-PF(Na^+)/Ba/Al, the emission maxima of the polymers appear at 422 and 586 nm. The peak at 508 nm, which is additional peak of anion-PF(Na^+), is disappeared caused by corresponding with absorption of MEH-PPV and additional emission of anion-PF(Na^+). The emission color of the device with the configuration of ITO/PEDOT/MEH-PPV/Ba:Al has the CIE coordinates of $x = 0.59$, $y = 0.40$. The CIE coordinates of the device with the configuration of ITO/PEDOT/anion-PF(Na^+)/MEH-PPV/Ba/Al showed (0.29, 0.32) at 20 V, which is close to that of the standard white of NTSC (0.33, 0.33). The device with the configuration of ITO/PEDOT/MEH-PPV/anion-PF(Na^+)/Ba/Al exhibited CIE coordinates of (0.43, 0.31), corresponding to orange yellow emission.

The current-density-voltage (J-V) and luminescence-voltage (L-V) of devices are shown in Fig. 6 and summarized in Table 2. The turn-on voltage of MEH-PPV was about 6.5 V. The turn-on voltages of the devices with configuration of anion-PF(Na^+)/MEH-PPV and MEH-PPV/anion-PF(Na^+) were about 9.5 and 11 V, respectively, which is higher than MEH-PPV. The current density of MEH-PPV is 187.9 mA/cm^2 at 15 V. The current densities of devices of configuration of anion-PF(Na^+)/MEH-PPV and MEH-PPV/anion-PF(Na^+) are 404.6 mA/cm^2 at 26 V and 40.5 mA/cm^2 at 38 V. In case of device with configuration of anion-PF(Na^+)/MEH-PPV, the device has higher current density than

Table 2. Device performance characteristics

Polymers	Turn-on voltage^a (V)	Voltage^b (V)	Current density^b (mA/cm^2)	Luminance^b (cd/m^2)	CIE (x, y)^c
MEH-PPV	6.5	15	187.9	361.6	(0.59, 0.40)
anion-PF(Na^+)/ MEH-PPV	9.5	26	404.6	90.0	(0.29, 0.31)
MEH-PPV/ anion-PF(Na^+)	11	38	40.5	21.9	(0.43, 0.31)

[a] Voltages required to achieve a brightness of 1 cd/m^2.
[b] Measured under the condition of maximum brightness.
[c] Calculated from the EL spectrum.

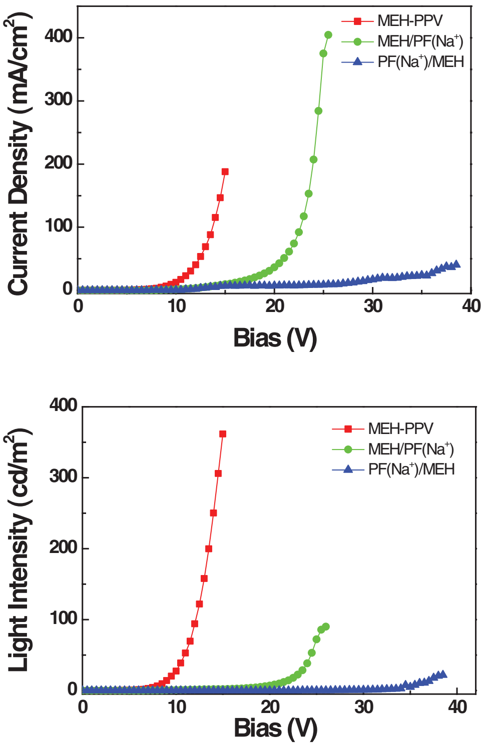


Figure 6. Current density-voltage-luminescence (*J*-*V*-*L*) characteristics.

that of MEH-PPV/anion-PF(Na$^+$). The maximum luminescence (L$_{max}$) of MEH-PPV is 361.6 cd/m^2 at 15 V. The maximum luminescence (L$_{max}$) of anion-PF(Na$^+$)/MEH-PPV and MEH-PPV/anion-PF(Na$^+$) are 90 and 21.9 cd/m^2, respectively. It seems that the barrier for energy transfer is arisen in interface between water soluble anion-PF(Na$^+$) and organic soluble MEH-PPV by spin-casting. Although the devices with configuration of anion-PF(Na$^+$)/MEH-PPV has white emission, the luminescence intensities of devise is low for the PLED device fabrication.

3. Conclusions

We report an achievement of multilayer PLEDs by water soluble conjugated polymer with blue and green emission. The new water soluble anionic conjugated polymer, poly(9,9-bis(4′-sulfonatobutyl)fluorene-*co-alt*-1,4-phenylene) (anion-PF(Na$^+$)), was synthesized by Suzuki reaction. The PL spectra of anion-PF(Na$^+$) in water shows the maximum peak at 408 nm. The solutions of the polymers in methanol showed PL emission peaks with a maximum at 398 nm, and a shoulder at about 420 nm. The EL spectra of the configuration of ITO/PEDOT/anion-PF(Na$^+$)/MEH-PPV/Ba/Al showed three peaks at 423, 508 and 592 nm, which has the luminescence intensities of 90 cd/m^2. The CIE coordinates of the device showed (0.29, 0.32), which is close to that of the standard white of NTSC (0.33, 0.33).

3.1. Experimental Section

EL Device Fabrication and Measurements. For the EL experiment, poly(3,4-ethylene dioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. The solution of the PEDOT:PSS in aqueous isopropyl alcohol was spin-coated on the surface-treated ITO substrate and dried on a hot plate for 30 min at 110 °C. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting chlorobenzene solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in vacuum, and barium (20 nm) and aluminum (100 nm) electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 10^{-7} Torr, yielding active areas of 4 mm^2. For the determination of device characteristics, current density-voltage (J-V) and luminance-voltage (L-V) characteristics of the devices were measured using a Keithley 2400 Source Measure Unit equipped with a calibrated photo-multiplier tube.

Acknowledgements

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