Yellow-Light-Emitting Fluorine-Substituted PPV Derivative

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Poly(2-fluoro-1,4-phenylenevinylene) (PFPV) and poly(1,4-phenylenevinylene) (PPV) were synthesized through the water-soluble precursor method. The polymers were characterized by UV−visible spectroscopy, and the light-emitting properties were studied. The absorption maxima of PPV and PFPV are at around 415 and 410 nm, respectively. The electroluminescent (EL) devices were fabricated with ITO and aluminum as positive and negative electrodes, respectively. The EL properties of these polymers were studied by EL spectra, current−voltage characteristics, light intensity−current characteristics, and Fowler−Nordheim plot. The I−V characteristics of the polymers showed typical diode characteristics, and the operating voltages of PPV and PFPV were 6 and 10 V, respectively. The photoluminescent spectra of these polymers were also obtained and similar to the EL spectra. The relative EL quantum efficiency of PFPV was 10 times higher than that of PPV. This result may be due to the smaller band offset between the aluminum and the LUMO of the PFPV as compared with that in PPV.

Introduction

The potential for making large area multicolor display from easily processible polymers has driven much of the recent research in the area of polymeric light-emitting diodes (LEDs).[1−5] The first polymer light-emitting diodes were based on poly(1,4-phenylenevinylene) (PPV), which has attracted the most interest.[6,7] Electroluminescence (EL) in this material is obtained by the recombination of electrons injected at the negative electrode and holes injected at the positive electrode in polymer thin films; the holes and electrons recombine, forming excited carriers (singlet excitons) which decay radiatively.[8,9] The polymer LEDs have many advantages in comparison with inorganic LEDs. One of the important advantages over inorganic LEDs lies in the ability to construct polymer LEDs on flexible substrates permitting the fabrication of displays in variety of unusual shapes.[5] Other advantages include the ability to provide colors which span the visible spectrum by altering the $\pi-\pi^*$ energy gap through the controlled change of molecular structure.[10−12] High quantum efficiency and color tuning can be achieved, so that flat panel display fabrication may be possible. The EL efficiency was greatly enhanced by blending a polyconjugated polymer and a conjugation length confined polymer.[13,14] Substitution of the electron-withdrawing cyano group on the polymer backbone has also accomplished. The HOMO and LUMO energy states of cyano substituted polymer are lowered by the cyano group; therefore, the EL efficiency was also enhanced.[15]

In this article, we describe the synthesis, characterization, and light-emitting characteristics of a yellow-light emitting polymer, poly(2-fluoro-1,4-phenylenevinylene) (PFPV). The electronegativity of fluorine atom is similar with the cyano group. Therefore, we can expect that the fluorine substituted polymers lower the LUMO and HOMO energy states so that the EL efficiency will be highly enhanced.

Experimental Section

Instrumentation. The synthesized compounds were identified by ^{1}H NMR spectra that were collected on a Bruker AM 200 spectrometer. The UV−visible spectra of the PPV and PFPV were performed on Shimadzu UV-3100S. Photoluminescence spectra of the two polymers were obtained by using

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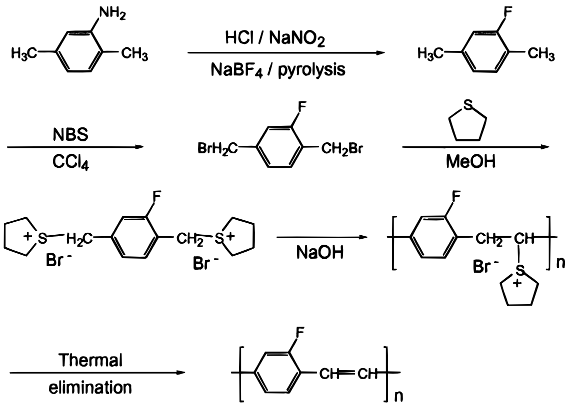
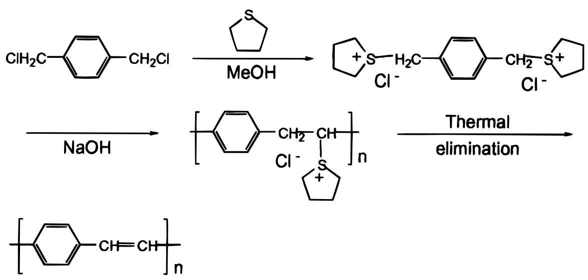
Scheme 1



Scheme 2



a Perkin-Elmer LS-50 luminescence spectrometer. Electroluminescence (EL) spectra were measured by using a dual-grating monochromator (Spex 270M) with the photomultiplier tube (Hamamatsu R955) as a detector. EL spectra were recorded at 3 nm resolution by computer through the photon counter (SR400) averaging the signal from PMT while applying direct current from the current–voltage source (Keithley 238). For the measurement of device properties, current–voltage (*I*–*V*) and light intensity–current (*L*–*I*) characteristics were measured by using the current–voltage source and a optical powermeter (Newport 835). The injected current was measured by the voltage supply while applying forward bias. The emitted light was collected with a silicon photodetector (Newport 818SL) placed in front of the device and recorded by computer. At this time, the solid angle of light detection is very small, therefore, the great loss of the light detection is unavoidable. All the measurements mentioned above were performed in air and at room temperature.

Monomer Synthesis of PFPV. Synthesis and characterization of PFPV were reported by us and other group.[16,17] 2-Fluoro-*p*-xylene (**1**) was prepared by the Schiemann reaction of 2,5-dimethylaniline (colorless liquid); ^{1}H NMR ($CDCl_3$) δ 7.2–6.9 (m, 3H), 2.4 (d, 6H). ^{19}F NMR (CF_3COOH) δ −41.09 (s, aromatic fluorine). By reacting of this product with *N*-bromosuccinimide (NBS) in CCl_4, bisbromomethyl compound **2** was obtained; the product yield was 60%, mp 99–101 °C. ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m, 3H), 4.4 (d, 4H). The sulfonium salt monomer **3** was obtained by reacting bisbromomethyl compound with an excess of tetrahydrothiophene in methanol at 50 °C for 24 h. The reaction mixtures were concentrated and precipitated in cold acetone. The sulfonium salt was purified by recrystallization in acetone and dried under reduced pressure. The 2-fluoro-1,4-phenylenedimethylene bis(tetrahydrothiophenium bromide) **3** was white powder and very hygroscopic; the product yield was 80%. ^{1}H NMR (D_2O) δ 7.3 (m, 3H), 4.4 (d, 4H), 3.3 (m, 8H), 2.3 (m, 8H).

Polymerization of PFPV. PFPV salt monomer **3** was dissolved in deionized water resulting in 1.0 M solution. After the solution was filtered using a 0.45 μm membrane filter to remove the dust and insoluble particles, equimolar 1.0 M NaOH solution was added using membrane filter to reaction solution at 0 °C. The gel-type polyelectrolyte was dissolved with a small amount of methanol solvent. The polymer solution was dialyzed against deionized water for 3 days to remove low molecular weight oligomers and unreacted monomers using a dialysis tube with a molecular cutoff at 12 000. The dialyzed polymer solution was spin coated on the quartz and indium tin oxide (ITO) glass and then thermal elimination at 200 °C for 3 h to give fully conjugated PFPV.

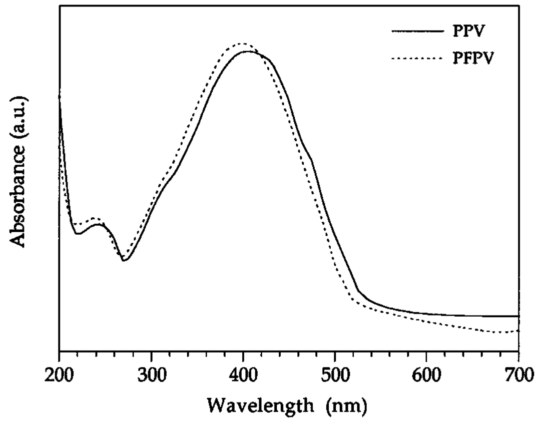


Figure 1. Optical absorption spectra of PPV and PFPV.

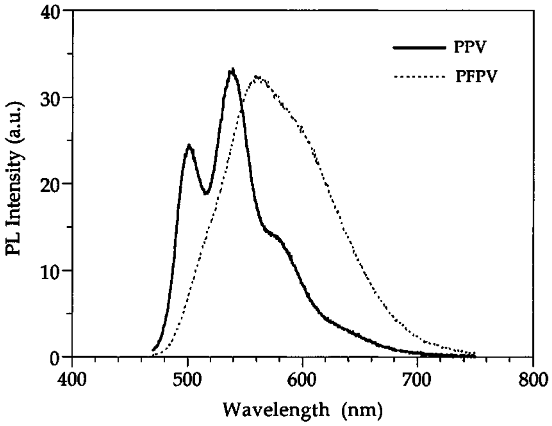


Figure 2. Photoluminescence spectra of PPV and PFPV.

Preparation of PPV. α,α′-Dichloro-*p*-xylene was reacted with an excess of tetrahydrothiophene in methanol solvent. PPV salt monomer was obtained by recrystallization over acetone/methanol (10/1) cosolvents. The polymerization of PPV salt monomer was the same as the case of PFPV. ^{1}H NMR (D_2O) δ 7.4 (s, 4H), 4.4 (s, 4H), 3.3 (m, 8H), 2.1 (m, 8H). Synthetic routes and polymer structures of PPV and PFPV are shown in Schemes 1 and 2.

Results and Discussion

The optical absorption spectra of the PPV and PFPV are shown in Figure 1. The π–π^* transition peak and edge of PPV appeared at 415 and 525 nm, respectively. In the case of PFPV, the π–π^* transition and edge, which were blue-shifted by 5 nm due to the electron-withdrawing fluorine atom in phenylene ring, appeared at 410 and 520 nm, respectively. In this optical absorption spectra, the bandgap energies of two polymers are similar, and the bandgap energies of PPV and PFPV, which were calculated from the absorption band edges, are 2.36 and 2.38 eV, respectively. As the electron-withdrawing fluorine atom is substituted on phenylene rings, the π-electron delocalization of the polymer main chain is diminished because of the electron localization around the fluorine atom.

Figure 2 shows the photoluminescence spectra (PL) of PPV and PFPV obtained at room temperature using an excitation wavelength of 442 nm. The maximum emission peaks of PPV and PFPV appeared at around

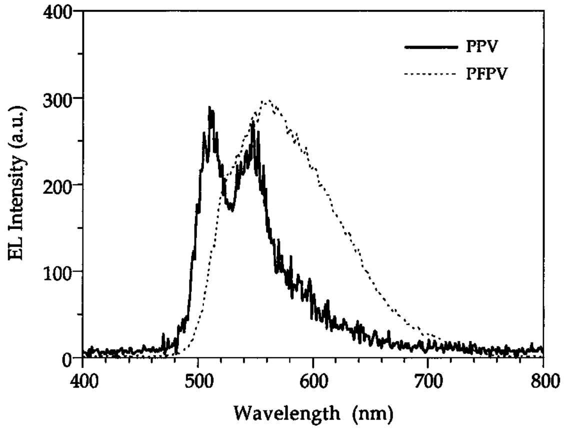


Figure 3. Electroluminescence spectra of PPV and PFPV.

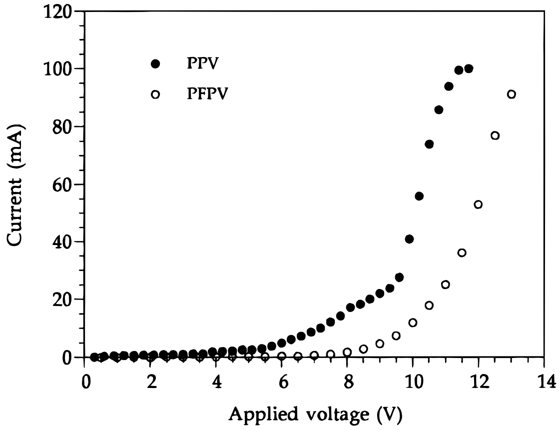


Figure 4. Current—voltage characteristics of PPV and PFPV.

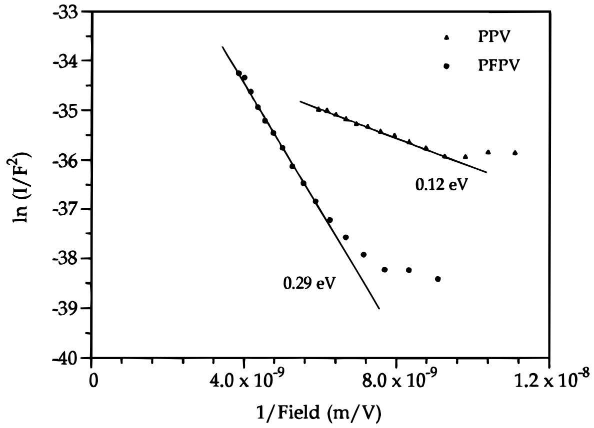


Figure 5. Fowler—Nordheim plots of PPV and PFPV.

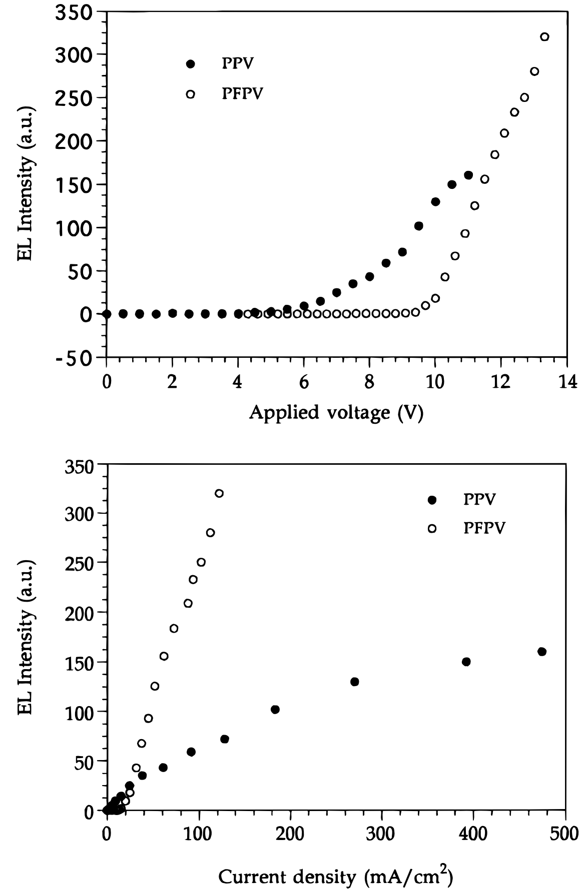


Figure 6. Voltage—EL intensity (a, top) and current density—EL intensity (b, bottom) characteristics of PPV and PFPV.

540 and 560 nm, respectively. Interestingly, the emission of PFPV was more red-shifted, and the PL intensity of PFPV was stronger than that of PPV. These results are not understood; however, we assume that the excitons generated in PFPV may be trapped in shallow trap states associated with charge separation between polymer backbone and highly electronegative fluorine atoms. Therefore, this donor—acceptor pair recombination process exhibits a longer wavelength emission in PFPV.[18]

Room-temperature electroluminescence (EL) spectra of PPV and PFPV in a single layered device are shown in Figure 3. The EL emission peaks of PPV and PFPV appeared at around 540 and 560 nm, respectively, which are very similar with PL spectra because the intermediates of PL and EL (singlet excitons) are the same. The emission of PFPV was also red-shifted (as shown in Figure 3) and the EL intensity of PFPV was much stronger than that of PPV.

Current—voltage (I—V) characteristics of PPV and PFPV are shown in Figure 4. Operating voltage of PFPV is higher than that of PPV, which indicates that band offset between PFPV and a positive electrode (ITO) is higher than that of PPV. The band offset of the hole injections in PFPV could be calculated by using Fowler—Nordhiem plot (Figure 5) and following eqs 1 and 2,[19]

$$I \propto F^2 \exp(-\kappa/F) \tag{1}$$

$$\kappa = 8\pi\sqrt{2m^*}\phi^{3/2}/3qh \tag{2}$$

where I is the current, F is the electric field strength, and κ is a parameter that depends on the barrier shape. If the injected charge is tunneling through a triangular barrier at one of the polymer interfaces, the constant κ in eq 1 is given by eq 2.[20] Here ϕ is the barrier height (band offset), and m^* is the effective mass of the holes in PFPV. Assuming that the electric field is constant

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across the device and that the effective mass equals the free electron mass, the calculated band offsets of PPV and PFPV are 0.12 and 0.29 eV, respectively. The band offset of PFPV is about 2 times larger than that of PPV and thus results in an increase of the operating electric field of PFPV. In these results, we can assume that the electron-withdrawing fluorine atom slightly lowers the HOMO states of PFPV.

Figure 6a,b shows the voltage−EL intensity (*V*−*L*) and current density−EL intensity (*L*−*I*) characteristics, respectively. The feature of the *V*−*L* curve in Figure 6 a exhibits a smiliar behavior compared to the *I*−*V* curve. Light-emitting voltages of PPV and PFPV are 6 and 10 V, respectively, which were smiliar to the operating voltages of PPV and PFPV. The lifetime of the PFPV single-layered EL device (ITO/PFPV/Al) was 500 min at 80 mA/cm^2 current density at air and room-temperature conditions. In Figure 6b, the EL intensity of PFPV is much higher than that of PPV at the same current density, which means that the efficiency of PFPV is higher than that of PPV. The linear dependence of the EL intensity on the current is attributed to linear response of the recombination of the charge carriers injected from the electrodes into the bulk of the polymer films.[21] It is difficult to know accurate external quantum efficiency, defined as photons generated per electrons injected, of the device since the collection of emission light is not perfect. However, we can estimate from the *L*−*I* characteristic curves that the quantum efficiencies of PPV and PFPV are on the order of the 10^{-5} and 10^{-4}%, respectively. The relative EL efficiency of PFPV was about 10 times larger than that of PPV. The enhancement of EL efficiency in PFPV is explained since the electron is easily injected in PFPV. The device quantum efficiency depends inversely on the energy barrier of minor carrier injection.[22] In our experiments (ITO/polymer/Al), the major carriers are holes and the minor carriers are electrons, so that the EL efficiencies of our PPV-based EL devices are dependent on the band offset between the polymers and the cathode (Al). The energy diagrams of the two polymers are shown in Figure 7. The negative band offsets of PPV and PFPV were calculated using the positive band offsets and bandgap energies of the two polymers. The negative band offsets of PPV and PFPV are 1.74 and 1.59 eV, respectively, so that the electron injection is much easier in PFPV. Therefore, the efficiency of PFPV is significantly enhanced as compared with PPV. As a result, we may conclude that the electron-withdrawing fluorine atom in phenylene ring lowers the LUMO and HOMO states of PFPV, and therefore, the relative EL efficiency of PFPV is 10 times increased; on the other hand the operating voltage of PFPV is slightly raised.

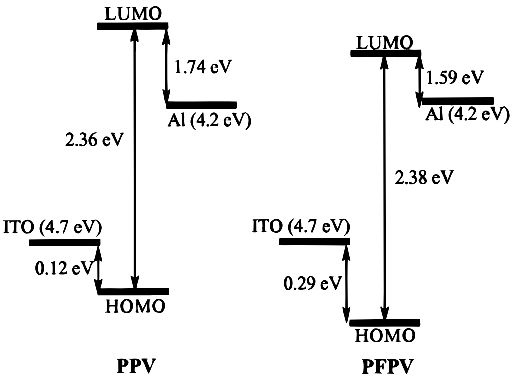

Figure 7. Energy band diagrams of PPV and PFPV.

Conclusion

We synthesized the fluorine-substituted PPV derivative, PFPV, and the PL and EL properties were characterized. The relative EL efficiency of the PFPV is 10 times larger than that of PPV. The enhanced EL efficiency of PFPV is due to the decrease of band offset between polymer and electron injection electrode. In these results we successfully could obtain a high efficient electroluminescent polymer by adopting the electron-withdrawing fluorine atom.

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