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Efficient green light-emitting polymer by balanced injection of electron and hole: new electron accepting perfluorinated substituent

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Abstract

We synthesized a new electron withdrawing group, perfluorinated aryl substituted PPV derivative via Wessling–Zimmerman polymerization in methanol. The synthesized precursor of poly[2-{(2,3,4,5,6-pentafluorobenzene)-2,3,5,6-tetrafluorophenyl}-1,4-phenylenevinylene] (PPFPV) showed good solubility in common organic solvents such as chloroform, methylenechloride, xylene, tetrahydrofuran. The molar mass measured by gel permeation chromatography (GPC) was $M_w = 72,000$. PPFPV showed the PL and EL emission maxima of 520 nm corresponding to green light, because of the strong electron-withdrawing effect of the perfluorinated aryl group. The PPFPV single layer EL device showed 64 times higher EL efficiency than that of PPV with higher turn-on voltage. But, ITO/PPV/PPFPV/Al bilayer EL device showed about 380-fold higher EL efficiency compared with PPV, and its turn-on voltage was lowered to the PPV level. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electroluminescence; Perfluorinated; Poly(1,4-phenylenevinylene) derivative

1. Introduction

A large body of work has accumulated concerning the effects of chemical substitution on emissive efficiency, device longevity, and spectral behavior in conjugated organic compounds that can be used as chromophores in light emitting diodes (LEDs) [1–3]. Some success and good results have been achieved in using both molecular and polymeric materials for such electro-optical uses [4–9]. The electro-optical properties of the conjugated poly(1,4-phenylenevinylene) (PPV) derivatives have been of particular interest [4–9]. Our group has been interested for a considerable time in the effects of ring substituents [10–14], especially those with electron-withdrawing properties [10,11,15,16].

We had reported syntheses and optical studies of halogen substituted PPV, especially fluorine substituted PPV showed very unique results concerning higher electroluminescence (EL) efficiency, but red shifted electroluminescence and photoluminescence (PL) comparing with PPV [11,17–20].We also reported electron capturing properties of the perfluorinated biphenyl group used as the chromophore blocking unit in the conjugated non-conjugated multi block copolymer (CNMBC) system.[21] Direct comparison between the simple propyl group and the perfluorinated aryl group as a non-conjugation part shows clearly the high electron affinity of the perfluorinated aryl group.

In this paper, we report about the PPV derivative (PPFPV), the new electron withdrawing perfluorinated biphenyl substituted directly to the main chain, for the balanced injection of hole and electron, and achieving higher EL efficiency.

Our target is not only getting a green light (510–540 nm) but also improving EL efficiency originated by balanced injection of hole and electron.

2. Experimental

2.1. Reagents

Tetrahydrofuran (THF) was distilled over sodium before use. 2-Bromo-*p*-xylene, magnesium turning, decafluorobiphenyl, *N*-bromosuccinimide, tetrahydrothiophene were purchased from Aldrich.

2.2. Synthesis of the poly(1,4-phenylenevinylene)

The PPV was synthesized via the classical Wessling–Zimmerman method [22,23].

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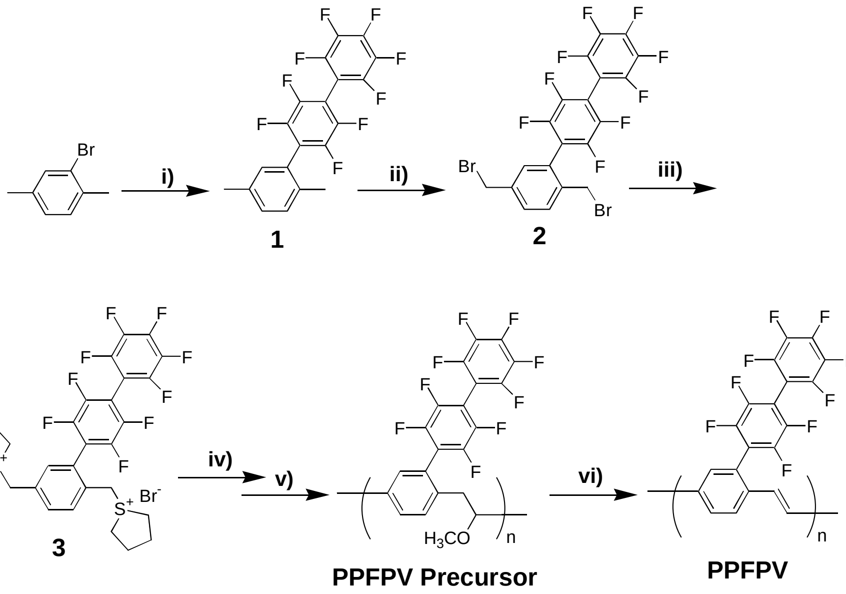


Scheme 1.

2.3. Synthesis of monomer

Scheme 1 shows the synthetic scheme of the monomer and final PPFPV. Reagents and conditions: i) Mg, $C_{12}F_{10}$, Tetrahydrofuran, reflux, 3 h: ii) N-bromosuccinimide (NBS), CCl_4, reflux, 5 h. 40%: iii) tetrahydrothiophene, MeOH, 50°C, 24 h, 75%: iv) NaOH, 0°C: v) MeOH, reflux, 24 h, 55%: vi) 200°C under Vacuum.

2.3.1. 1-[4-(2,5-dimethylphenyl)-2,3,5,6-tetrafluorophenyl]-2,3,4,5,6-pentafluorobenzene (**1**)

2-Bromo-*p*-xylene (30 g, 162 mmol) diluted in anhydrous THF was slowly added to clean magnesium turnings (6.8 g, 279 mmol) after initiation by 5 mol% of 1,2-dibromoethane. When the magnesium was completely consumed, this solution was added to decafluorobiphenyl (102.6 g, 279 mmol) in 80 ml of anhydrous THF. The mixture was refluxed for 3 h, and the reaction was quenched with dilute HCl solution. The THF layer was separated and washed with water several times. The solution was dried with magnesium sulfate, and THF was removed by distillation. After vacuum distillation, 65.7 g of colorless solid was obtained. The product yield was 70%.

M.p. 124.5 ~ 126.0°C. ^{1}H NMR ($CDCl_3$): $\delta = 7.62$ (m, 2H), 7.46 (s, 2H), 2.42 (s, 2H), 2.20 (s, 2H). Elemental analysis: Calc. C 57.16, H 2.16, F 40.68. Found C 57.87, H 2.04.

2.3.2. 1-{4-[2,5-bis(bromomethyl)phenyl]-2,3,5,6-tetrafluorophenyl}-2,3,4,5,6-pentafluorobenzene (**2**)

Compound **2** was prepared by reacting compound **1** (23.5 g, 56 mmol) with *N*-bromosuccinimide (21 g, 118 mmol) in 40 ml of carbon tetrachloride. A small amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 90°C for 5 h under a nitrogen atmosphere. The completion of the reaction was indicated by the appearance of succinimide on the surface of reaction solution. After evaporation of the solvent, yellow solid was obtained. White pure product was obtained by recrystallization in MeOH. The product yield was 40%.

M.p. 118.6 ~ 120.2°C. ^{1}H NMR ($CDCl_3$) $\delta = 7.70$ (m, 2H), 7.56 (s, 2H), 4.50 (s, 2H), 4.36 (s, 2H). Elemental analysis: Calc. C 41.55, H 1.22, Br 27.65, F 29.58. Found C 41.40, H 1.12.

2.3.3. 2-{(2,3,4,5,6-pentafluorobenzene-)-2,3,5,6-tetrafluorophenyl}-1,4-phenylene dimethylene-bis(tetrahydrothiopheniumbromide (**3**)

A total amount of compound **2** (10 g, 17.3 mmol) and excess tetrahydrothiophene were reacted at 50°C for 24 h in 50 ml of methanol. As the reaction proceeded, this suspension was changed to a clear solution. The final salt monomer **3** was obtained by concentration of the reaction solution, precipitation in acetone, filtration and vacuum drying. The product yield was 75%.

M.p. 83.2 ~ 85.2°C. ^{1}H NMR (D_2O): $\delta = 7.69$ (m, 2 H), 7.54 (s, 2 H), 4.48 (s, 2 H), 4.34 (s, 2 H). 3.5-3.05 (m, 8 H), 2.25-2.05 (m, 8 H). Elemental analysis: Calc. C 44.58, H 3.07, Br 21.18, F 22.66, S 8.50. Found C 44.47, H 3.00, S 8.23.

2.4. Polymerization

The precursor polymer of PPFPV was synthesized via the classical Wessling–Zimmerman method. The monomer salt, **3** (1 g, 1.32 mmol) was dissolved in 1.32 ml of methanol and then, the solution was cooled to 0°C. The monomer sulfonium salt solution was polymerized in a

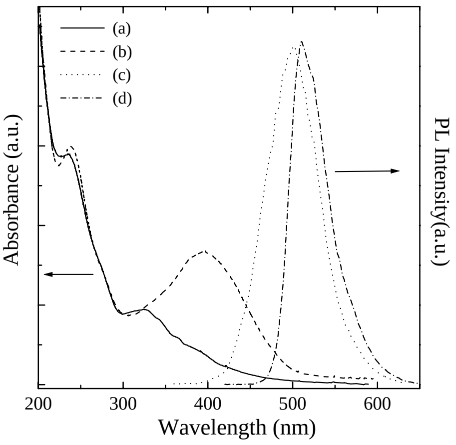


Fig. 1. UV–Vis spectra of (a) precursor and (b) final polymer; PL spectra of (c) precursor and (d) final polymer.

1.0 N NaOH solution at 0°C. A homogeneous and viscous solution was obtained. The polymerization reaction was quenched by neutralization with 0.5 N HCl. After polymerization, solution of the precursor polymer in methanol was refluxed for the replacement of tetrahydrothiophene with methoxy unit. When the solution became clear, methoxy substituted precursor of PPFPV was filtered. The product yield was 55%.

This organic soluble precursor had good solubility in methylene chloride, THF, toluene, etc. The precursor polymer was thermally treated at 200°C for 10 h after spin coating on the ITO substrate.

2.5. Instruments

^{1}H NMR spectra were recorded on a Bruker 200 AM spectrometer. UV–Visible analysis was performed by Shimadzu UV-3100S. Thicknesses of the polymer films were measured by using an Alpha step 200 profilometer. The PL spectrum of the polymer was obtained by using the Perkin–Elmer LS-50 luminescence spectrometer. The EL spectrum was measured by using a dual grating monochrometer (Spex 270M) with the photomultiplier tube (Hamamatsu R955) as a detector. The EL spectrum was recorded at 4 nm resolution by computer through the photon counter (SR400) averaging the signal from PMT while applying direct current from a current/voltage source (Keithley 238). The current/voltage (I–V) and light intensity–current (L–I) characteristic were measured by using the current/voltage source and optical powermeter (Newport 835). The injected current was measured by the voltage supply while applying forward bias and the emitted light was collected with a silicon photodetector (Newport 818SL) placed in front of the device and recorded by computer. All the measurements mentioned above were performed in air at room temperature.

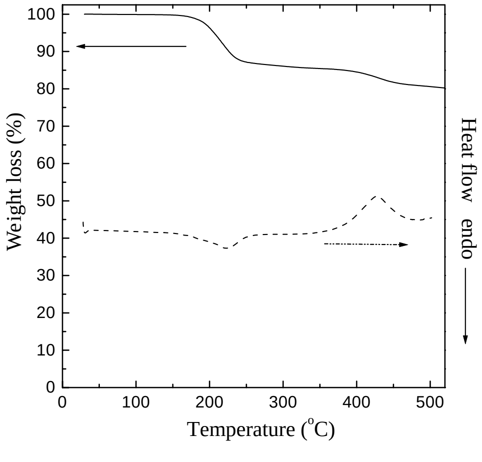


Fig. 2. The TGA (solid line) and DSC (broken line) thermograms of the precursor of PPFPV.

3. Results and discussion

Scheme 1 shows the synthetic procedure of PPFPV via the Wessling–Zimmerman method [22,23]. We used methanol, however, as the solvent for polymerization because the precursor polymer of PPFPV became opaque and insoluble in water caused by hydrophobic properties of the fluorine substituted compound. After polymerization, we obtained the PPFPV precursor, which shows good solubility in common organic solvents such as chloroform, methylenechloride, xylene and THF. The molar mass measured by gel permeation chromatography (GPC) was $\overline{M}_w = 72,000$. THF was employed as an eluent and polystyrene as a standard. The polydispersity index was 1.95.

Fig. 1 shows the UV–Vis absorption and the PL spectra of the PPFPV precursor and final PPFPV after elimination. In the precursor form, some partially eliminated part in the main chain was the origin of a shoulder of 320 nm of absorption spectrum and 500 nm in the emission spectrum. The partial elimination of the PPFPV precursor can be detected using FT-IR, which shows a small peak at 965 cm^{-1}, *trans*-vinylene out of the bending mode. After elimination, absorption and emission maxima were red-shifted to 400 and 520 nm, which correspond to the green light in the visible region.

Fig. 2 shows the thermal elimination process of the PPFPV precursor and the thermal stability of PPFPV. In the differential scanning calorimeter (DSC) thermogram, endotherm of around 200°C shows elimination of methanol, which corresponds to the weight loss at around 200°C in the thermal gravimetric analysis thermogram. The final PPFPV polymer showed excellent thermal stability up to 400°C in nitrogen atmosphere.

The PPFPV precursor solution in methylene chloride was spin coated on the ITO coated glass substrate [HOYA glass ($<100\ \Omega$)]. After thermal elimination, the cathode metal (Al) was vacuum deposited under 10^{-5} Torr. The thicknesses of the PPFPV film and the Al electrode were about

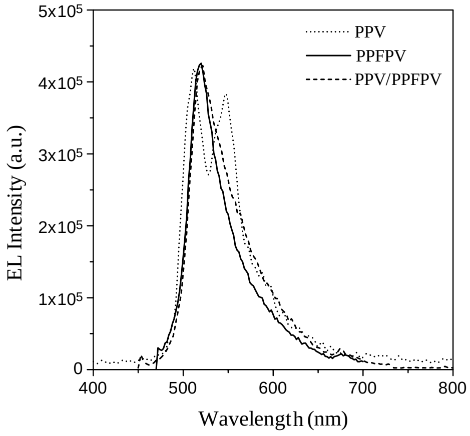


Fig. 3. The EL spectra of PPV, PPFPV single layer and PPV/PPFPV bilayer EL cells.

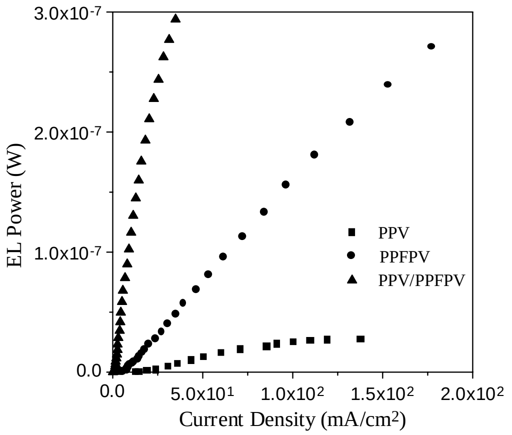


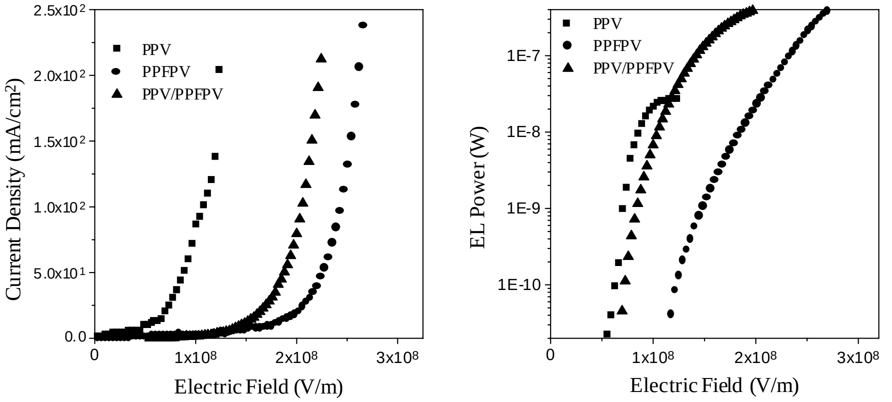
Fig. 5. The EL power vs. current density characteristics of PPV, PPFPV single layer and PPV/PPFPV bilayer EL cells.

120 nm, and we also adopted the PPV thin layer (50 nm) as a hole transporting layer.

Fig. 3 shows the EL spectra of two types of devices (ITO /PPFPV/Al and ITO/PPV/PPFPV/Al) and PPV. In both cases of PPFPV single layer and PPV/PPFPV bilayer, the EL emission maxima were at around 520 nm corresponding to pure green light, and showed a slight difference from the PPV device. From that result, it is supposed that the emitting layer is PPFPV in both cases. In the case of p-type conjugated polymers such as PPV and poly(octylthiophene) (POT), it was reported that the hole is the major carrier and the electron–hole (E–H) collision area is located in the interface between the polymer film and the cathode or nearby [24,25]. If PPFPV has lower LUMO and HOMO than PPV under vacuum level, it is reasonable that the hole can penetrate into the PPV layer and the E–H collision area is moved to the interface between PPV and PPFPV or PPFPV layer.

Current–voltage (*I*–*V*) characteristics of PPV, PPFPV single and PPV/PPFPV double layer are shown in Fig. 4a. The operating electric field strength (voltage/film thickness, V/m) of PPFPV is higher than that of PPV. In the EL intensity-electric field curve (Fig. 4b), PPFPV also showed higher turn-on electric field of 1.2×10^8 V/m, which could be reduced to 7.1×10^7 V/m when PPV was adopted as a hole transport layer (HTL). These results indicate that band offset between PPFPV and a positive electrode (ITO) is larger than that of PPV. (These positive band offsets of PPFPV and PPV could be calculated by using the Fowler–Nordheim plot [26], and the calculated band offsets of PPFPV and PPV are 0.42 and 0.12 eV, respectively). Therefore, the hole (major carrier) mobility should be restricted and thus results in the balanced injection of hole and electron.

In Fig. 5, the EL intensity of PPFPV is much higher than that of PPV at the same current density, because PPFPV had more balanced electron–hole injection caused by the perfluorinated biphenyl substituent acting as an electron withdrawing group. Interestingly, the PPV/PPFPV bilayer device showed similar EL intensity with lowered turn-on electric field than the PPFPV single layer device (Fig 4b). These results are well coincident with the balanced injection



(a) (b)

Fig. 4. EL characteristics of PPV, PPFPV single layer and PPV/PPFPV bilayer EL cells. (a) current density vs. electric field. (b) EL power vs. electric field.

Table 1
Comparison of EL quantum efficiencies and turn-on voltages of single and double layer of PPFPV and PPV

Configuration of EL device (Anode/ELM/Cathode)	Relative EL quantum efficiency	Turn on voltage (electric field (V/m))
ITO/PPV/Al	1	5.0×10^7
ITO/PPFPV/Al	64	1.2×10^8
ITO/PPV/PPFPV/Al	380	7.1×10^7

of hole and electron by the lower negative band offset of PPFPV as expected. (These negative band offsets of PPFPV and PPV were calculated using the positive band offsets and bandgap energies of the two polymers. The negative band offsets of PPFPV and PPV are 1.61 and 1.74 eV, respectively).

The linear dependence of the EL intensity on the current is attributed to the linear response of the recombination of the charge carriers injected from the electrodes into the bulk of polymer films. From Table 1, perfluorinated aryl substituted PPFPV showed about 64 times enhanced EL efficiency compared to PPV, due to the electron transport ability of the electron withdrawing perfluorinated biphenyl unit. Interestingly, the PPV/PPFPV double layered device exhibited much better EL efficiency and lower turn-on voltage than the PPFPV single layered device. The origin of higher EL efficiency of the PPV/PPFPV double layered EL device is thought to balanced charge accumulation effect through the hole transporting PPV layer as well as the prevention of exciton quenching at the vicinity of the cathode as reported elsewhere [5,24].

4. Conculsions

We synthesized poly[2-{(2,3,4,5,6-pentafluorobenzene)-2,3,5,6-tetrafluorophenyl}-1,4-phenylenevinylene] (PPFPV) via the Wessling–Zimmerman method. The PPFPV film shows absorption and emission maxima at 400 and 520 nm, corresponding to green light in the visible region. We could fabricate the highly efficient EL device adopting the powerful electron withdrawing perfluorinated aryl group in EL polymer. Perfluorinated aryl substituted PPFPV exhibited highly enhanced EL efficiency compared to the unsubstituted PPV due to the balanced injection of hole and electron. Especially, the EL cell of the bilayer of PPV and PPFPV revealed about 380-fold higher EL efficiency than that of PPV. From these results, we can expect that perfluorinated aryl is a useful new electron withdrawing group as a substituent of PPV derivatives and other EL polymers.

Acknowledgements

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