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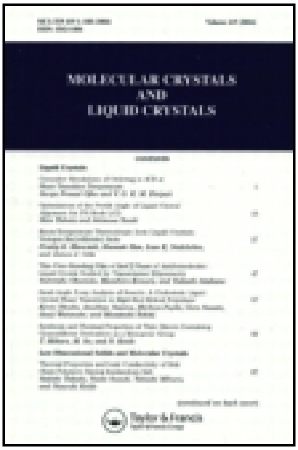

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Light Emitting Properties of Poly(2-Fluoro-1,4-Phenylene Vinylene) as Compared with Poly(1,4-Phenylenevinylene)

H. K. Shim [a], J. I. Lee [a], I. N. Kang [a], S. C. Jeoung [b], D. Kim [b] & T. Zyung [c]

[a] Dept. of Chemistry, KAIST, Taejon, 305-701, Korea
[b] Spectroscopy Lab., KRISS, Taejon, 305-600, Korea
[c] Research Dept., ETRI, Taejon, 305-600, Korea

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LIGHT EMITTING PROPERTIES OF POLY(2-FLUORO-1,4-PHENYLENE VINYLENE) AS COMPARED WITH POLY(1,4-PHENYLENEVINYLENE)

H. K. SHIM, J. I. LEE, I. N. KANG, S. C. JEOUNG[†], D. KIM[†], T. ZYUNG[‡]
Dept. of Chemistry, KAIST, Taejon 305-701, Korea
[†] Spectroscopy Lab., KRISS, Taejon 305-600, Korea
[‡] Research Dept., ETRI, Taejon 305-600, Korea

Abstract Light emitting properties of poly(2-fluoro-1,4-phenylenevinylene) (PFPV) were investigated by using steady-state and time-resolved photoluminescence spectroscopies, EL spectra and current-voltage characteristics. PFPV exhibited a red-shifted structureless emission with higher PL and EL quantum efficiency in comparison with PPV. The time-resolved PL experiments revealed that the shorter wavelength emission is attributable to the free excitons and the longer wavelength emission to the self-trapped excitons. The I-V characteristics of the polymers showed typical diode characteristics and the operating voltages of PPV and PFPV were 6 V and 10 V, respectively. The higher relative EL quantum efficiency of PFPV may be due to the higher PL quantum efficiency and the smaller band offset between the aluminum and the LUMO of the PFPV as compared with that of PPV.

INTRODUCTION

Conjugated polymers brought about many research activities in the past few decades as semiconductors and electroactive materials for possible diverse applications such as batteries, molecular electronic devices, and light-emitting diodes (LEDs), etc.[1,2] Especially, the electroluminescence has emerged as a promising application of polymeric LEDs in semiconducting polymers.[3,4] Poly(1,4-phenylenevinylene) (PPV) and its derivatives are promising new materials for polymeric LEDs because of their good physical, chemical and optical properties compared with other conjugated polymers.[3,4] Substitution on the phenylene ring of the PPV with different types of substituents exhibits a significant change in the electronic structure of the corresponding polymers and affects the electrical properties of the polymer, and thus the color tuning of the electroluminescence is also feasible.[5,6] Recently, substitution of the electron-withdrawing cyano group on the polymer backbone has also accomplished. The HOMO

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and LUMO energy states of cyano substituted polymer are lowered by the cyano group, therefore, the EL efficiency was also enhanced.[7]

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 electron-withdrawing fluorine subsituted PPV, PFPV, is expected to show the reduced mobility of excitons and the lower LUMO and HOMO energy states as compared with PPV. Therefore, the PL and EL quantum efficiency will be highly enhanced.

EXPERIMENTAL

PPV and PFPV were synthesized through water-soluble precursor route reported previously by us[8] and others,[9] and their structures are shown in Figure 1. The viscous precursor polymer solutions were subject to spin-coating on a fused quartz plate and ITO coated glass plate. The desired optical density or thickness was obtained by controlling the spinning rate. The final conjugated polymer films were obtained by thermal elimination under vacuum. The absorption spectra of the polymer films were recorded by a Shimadzu UV-3100S spectrophotometer. Steady-state PL spectra of the films were recorded by photoexcitation with the cw 442 nm line from a He:Cd laser. Fluorescence decay was recorded by the time-correlated single-photon counting method. The light source was a cavity-dumped dye laser synchronously pumped by a mode-locked argon ion laser.

Electroluminescence (EL) spectra were measured by using a dual grating monochromator (Spex 270M) with the photomultiplier tube (Hammamatsu R955) as a detector. 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). All the measurements mentioned above were performed in air and at room temperature.

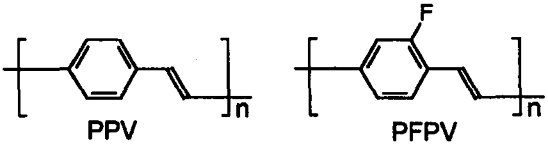

FIGURE 1 Structures of PPV and PFPV.

RESULTS AND DISCUSSION

The room-temperature absorption spectra of PPV and PFPV are shown in Figure 2. The broad absorption bands in 300 ~ 500 nm region are attributable to the π-π^* transitions of polyconjugated systems. The peak maxima of the broad absorption bands were at 415 and 410 nm for PPV and PFPV, respectively. The absorption peak of PFPV exhibited a little blue-shift in comparison with that of PPV, but the absorption edges of PPV and PFPV were nearly identical. 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.

The room-temperature photoluminescence spectra of PPV and PFPV are shown in Figure 2. The photoluminescence spectrum of PPV reveals well-resolved vibronic structures and is very similar to those in the previous reports. However, PFPV exhibits a red-shifted broad and featureless emission. The fluorescence quantum efficiency of PFPV was 1.5 times higher than that of PPV under the same experimental configuration. The room temperature electroluminescence spectra of PPV and PFPV in a device configuration are also shown in Figure 2. The EL emission peaks of PPV and PFPV appeared at around 540 and 560 nm, respectively, which are very similar to the PL spectra because the intermediates of PL and EL (singlet excitons) are identical.

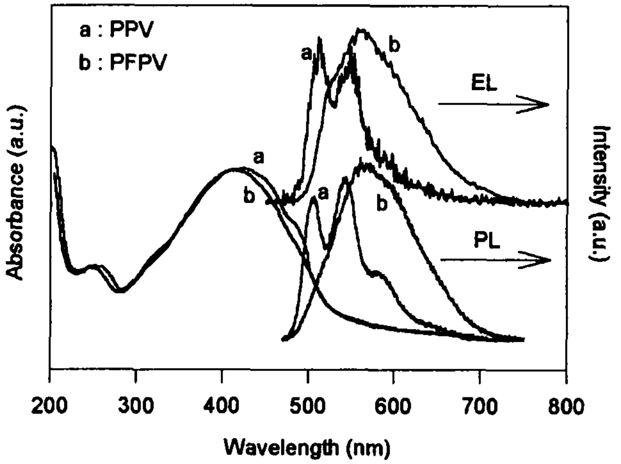

FIGURE 2 Optical absorption, photoluminescence and electroluminescence spectra of PPV and PFPV.

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Time resolved PL measurements were carried out to obtain further information on the relaxation dynamics of photoexcited PFPV. Figure 3 shows the PL decay profiles of PFPV at 13 K and room-temperature observed at 530 nm and 650 nm, respectively. There is a correlation between PL decay profile and emission wavelength, showing that the average PL decay is faster at the high energy side of the PL band than that at the low energy side at 13 K and room temperature. The temporal evolution of PL signals exhibits a fast decay behavior at 530 nm, but that does become slower at 650 nm. If the scattering process with phonon dominates the mean free path in the exciton diffusion,[10] then the diffusion coefficient of free excitons, $D(T)_{free}$, should be proportional to $T^{-1/2}$. Rose et al.[11] reported that the exciton diffusion coefficient of anthracene increases from 0.8 to 10 cm^2/s as the temperature is decreased from 20 to 1.8 K. If the exciton has a high diffusion coefficient to decay via non-radiative diffusion controlled processes such as trapping to quenching sites, exciton-exciton collisional annihilation, etc., then the PL decay profile should reveal a pronounced fast decay component. On the contrary, if diffusion is not so fast, non-radiative diffusion controlled processes will decrease, and the fast decay component becomes the minor process. This suggests that the high-energy band may be due to free excitons whose diffusion coefficient is relatively larger, and thus decay more rapidly through non-radiative diffusion controlled processes. These consideration led us to conclude that the faster decay at 530 nm at lower temperatures is due to diffusion controlled processes of

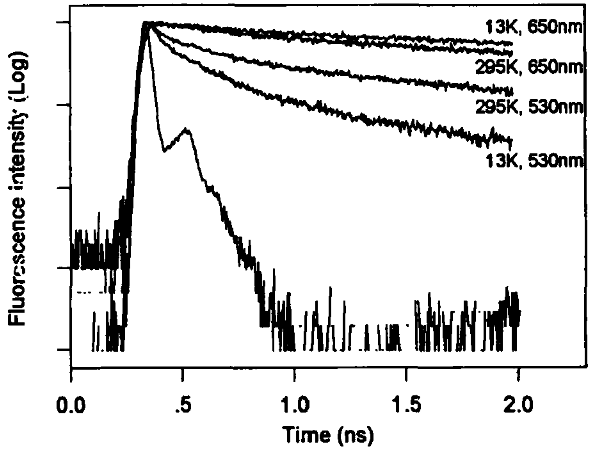

FIGURE 3 PL decay profiles of PFPV at 530 nm and 650 nm at different temperatures.

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free excitons.

Meanwhile, the temperature dependence of PL decay profile at 650 nm is reversed as compared with that at 530 nm; the lowering the temperature slowed down the PL decay processes. From the current investigation, the slower decay of the 650 nm emission band at lower temperatures suggests that this band is attributed to localized exciton states or shallow trap states associated with charge separation between PPV and highly electronegative fluorine atom. Therefore, this donor-acceptor pair recombination process exhibits a longer wavelength emission in PFPV and a longer lifetime as compared to the direct recombination of singlet polaron-excitons in unsubstituted PPV. Furthermore, the rise component may arise from the formation of the trapped excitons. This self-trapped exciton emission results in the red-shifted emission of PFPV as compared PPV.

Current-voltage (I-V) characteristics of PPV and PFPV are shown in Figure 4. The operating electric field strength (voltage/film thickness, V/m) 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. Assuming that the electric field is constant 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 increase 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.

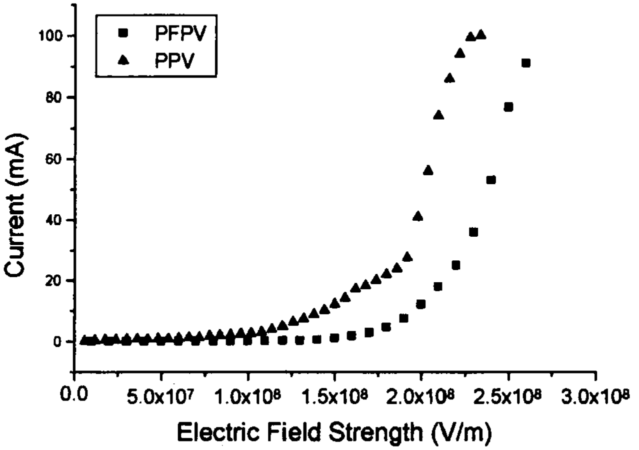

FIGURE 4 Current-voltage (I-V) characteristics of PPV and PFPV.

The negative band offsets of PPV and PFPV were calculated using the positive band offsets and band gap 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. The relative EL efficiency of PFPV was 10 times larger than that of PPV. The enhancement of EL efficiency in PFPV is explained that the electron is easily injected in PFPV. The device quantum efficiency depends inversely on the energy barrier of minor carrier injection. In our experiments, (ITO/polymer/Al), the major carriers are holes and the minor carriers are electrons, so that EL efficiencies of our PPV-based EL devices are dependent on the band offset between the polymers and the cathode(Al). Moreover, the relative PL quantum efficiency of PFPV is higher than that of PPV. Therefore, we could obtain highly improved luminescent polymer by introducing electron-withdrawing fluorine atom on the phenylene ring of PPV.

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REFERENCES

1. W. R. Salaneck, I. Lundstrom, B. Ranby, Conjugated Polymers and Related Materials (Oxpord Univ. Press, Oxford, 1993), pp. 65-169.
2. T. A. Skotheim, Handbook of Conducting Polymers (Dekker, New York, 1986), Vols. 1 and 2.
3. J. H. Burroughes et al., Nature, 347, 539 (1990).
4. D. Braun and A. J. Heeger, Appl. Phys. Lett., 58, 1982 (1991).
5. A. R. Brown et al., Chem. Phys. Lett., 200, 46 (1992).
6. G. Gustafsson et al., Nature, 357, 477 (1992).
7. N. C. Greenham, S. C. Morrati, D. D. C. Bradley, R. H. Freind, A. B. Holmes, Nature, 365, 628 (1993).
8. I.-N. Kang, G. J. Lee, D. Kim, H.-K. Shim, Polymer Bull., 33, 89 (1994).
9. R. A. Wessling, R. G. Zimmerman, U.S. Patent 3,401,152 (1968); U.S. Patent 3,706,667 (1972). Makromol. Chem., Macromol. Symp., 12, 229 (1987).
10. R. C. Powell, Z. G. Soos, Phys. Rev. B, 5, 1547 (1972).
11. T. S. Rose, R. Righini, M. D. Fayer, Chem. Phys. Lett., 106, 13 (1984).