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Time-Resolved Photoluminescence Study of Poly(*p*-phenylenevinylene) Derivative Polymers

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We present the steady-state and time-resolved photoluminescence (PL) spectra of poly(*p*-phenylenevinylene)derivatives, which exhibit a marked dependence on the side chains attached to the main chain. The PL spectra of poly(2-carbazolyl-*p*-phenylenevinylene) (PCzPV) and poly[2-[9-(10-phenyl)anthryl]-1,4-phenylenevinylene] (PPAPV) exhibit a vibronic structure with relatively short PL lifetimes. On the other hand, poly[[[2-[9-(10-phenyl)anthryl]-phenoxy]hexoxy]-1,4-phenylenevinylene] (PAHPV) shows the broad and structureless emission with a long tail. In addition, the PL decay time of PAHPV is about 3 times longer than that of PCzPV or PPAPV. Poly[[2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole]-*p*-enylenevinylene] also exhibits the long PL decay time as well as the structureless and red-shifted emission. The difference in the photophysical properties of these polymers is discussed in terms of the electronic nature of the excited states influenced by the pendent groups.

Introduction

Conjugated polymers have drawn much attention because of their feasibilities in tuning electrical and optical properties for application in light-emitting diodes (LEDs) based on these materials.[1−6] One of the most exciting applications is the electroluminescent device based on poly(*p*-phenylenevinylene) (PPV) films.[7−10] Although noticeable improvements have been made in many areas for the application of polymeric LEDs, lots of efforts[11−14] have been continuously made to improve the quantum efficiency of LED devices and to design a molecular structure that can emit light over a very broad spectral range so that the emitted light is white or close to it. If this objective can be achieved, one can produce any color of light by combining the selected wavelengths attainable from the emitted white light. Photoluminescence (PL) and electroluminescence (EL) properties of PPV and its derivatives provide new opportunities for the development of LEDs based on organic polymer films.

As a continuing effort to increase the EL efficiency, a variety of hole- and electron-transporting layers between an anode or cathode electrode and an emitting polymer have been employed.[3,14] With the same analogy, 2-(4-Biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (electron-transporting moiety) and carbazole (hole-transporting moiety) units have been attached to PPV main chains by Chung et al.[15] On the other hand, to attain a wide emission spectral coverage, anthracene moieties have been connected directly {poly[2-[9-(10-phenyl)anthryl]-1,4-phenylenevinylene] (PPAPV)} and with a spacer {poly[[[2-[9-10-phenyl)anthryl]phenoxy]-hexoxy]-1,4-phenylenevinylene] (PAHPV)} to PPV main chains.[16]

PPAPV possesses phenylanthracene moieties directly attached to the phenylene ring in PPV, whereas in PAHPV a 9,10-diphenylanthracene moiety is bound

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(1) Salaneck, W. R.; Lundstrom, I.; Ranby, B. *Conjugated Polymers and Related Materials*; Oxford University Press: Oxford, U.K., 1993; pp 65−169.

(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(3) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* 1995, 1969.

(4) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(5) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(6) **)** Sheats, J. R.; Chang, Y. L.; Roitman, D. B.; Stocking, A. *Acc. Chem. Res.* **1999**, *32*, 193.

(7) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature (London)* **1992**, *256*, 47.

(8) Wong, K. S.; Bradley, D. D. C.; Hayes, W.; Ryan, J. F.; Friend, R. H.; Lindenberger, H.; Roth, S. *J. Phys. C* **1987**, *20*, L187.

(9) Friend, R. H.; Bradley, D. D. C.; Townsend, P. D. *J. Phys. D (Appl. Phys.)* **1987**, *20*, 1367.

(10) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

(11) Parker, I. D.; Pei, Q. *Appl. Phys. Lett.* **1994**, *65*, 1272.

(12) Bradley, D. D. C. *Adv. Mater.* **1992**, *4*, 756.

(13) Zhang, C.; Braun, D.; Heeger, A. J. *J. Appl. Phys.* **1993**, *73*, 5177.

(14) Cacialli, F.; Li, X.-C.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1995**, *75*, 161.

(15) Chung, S.-J.; Kwon, K.-Y.; Lee, S.-W.; Jin, J.-I.; Lee, C.-H.; Lee, C.-E.; Park, Y. *Adv. Mater.* **1998**, *10*, 1112.

(16) Chung, S.-J.; Jin, J.-I.; Kim, K. K. *Adv. Mater.* **1997**, *9*, 551.

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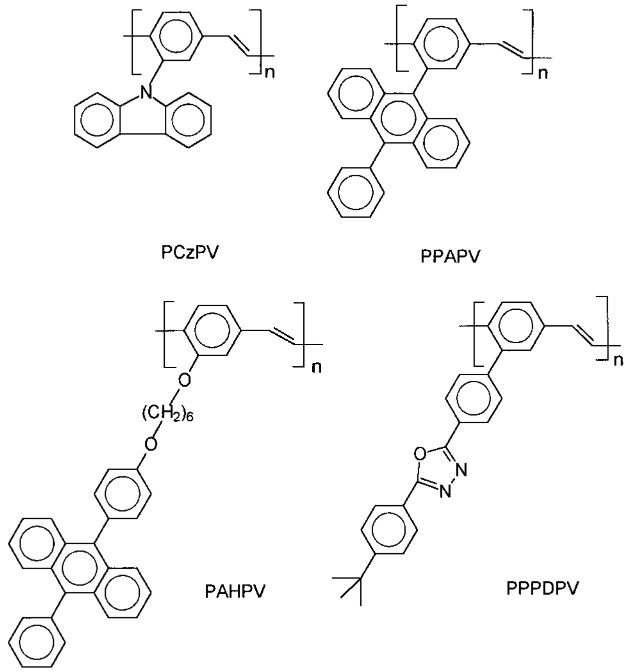
through a hexamethylene spacer to the PPV main chain. It is likely that the excimer formation of a phenyl anthracene unit in PPAPV does not occur easily due to the steric constraint in this polymeric system. On the other hand, the excimer formation in anthracene moieties is plausible in PAHPV because the chain length of the pendent group is relatively long and flexible.

To elucidate the underlying mechanism for the high EL efficiency in poly[[2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole]-*p*-enylenevinylene] (PPPDPV) and for the excimer formation in PAHPV, we have investigated the steady-state and time-resolved PL and the electronic nature of excited states of PPV derivatives to address the issues concerning the side-chain effect on the luminescent properties.

Experimental Section

PPAPV and PAHPV were synthesized through the Wessling−Zimmerman method,[16] and PCzPV and PPPDPV were prepared through the Gilch−Wheelwright method.[15] Thin films of polymers were prepared by spin-coating on fused quartz plates from a 1,1,2,2-tetrachloroethane solution.



The steady-state PL spectra were recorded with an excitation at 325 nm by using a cw He:Cd laser. The steady-state and time-resolved PL spectra were obtained by employing backscattering geometry. Fluorescence lifetimes were measured by a time-correlated single photon counting (TCSPC) method as described in detail previously.[17] A dual-jet picosecond dye laser (Coherent 702) synchronously pumped by a mode-locked argon ion laser (Coherent Innova 200) was employed as an excitation source. The cavity-dumped beam had a ~1 ps pulse width, an average power of ca. 40 mW at 3.8 MHz dumping rate, and a tunability of 560−620 nm when Rhodamine 6G for the gain dye and diethoxydicyanine iodide (DODCI) for the saturable absorber were used. To excite polymer samples, the dye laser pulse was frequency-doubled by a β-BBO (β-barium borate) crystal. All of the standard electronics used for TCSPC were from EG&G Ortec. This method allows a time resolution of about 20 ps after deconvolution.

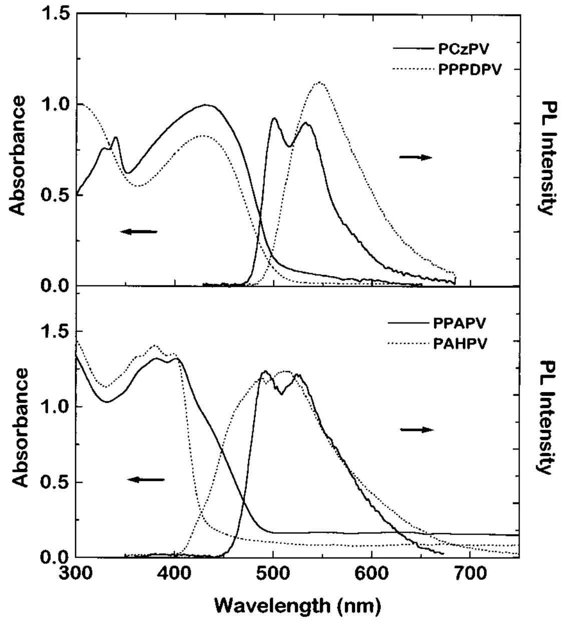


Figure 1. Absorption and PL spectra of PCzPV, PPPDPV, PPAPV, and PAHPV. The PL spectra were recorded with an excitation at 325 nm from a cw He−Cd laser.

Results and Discussion

Figure 1 shows the absorption and PL spectra of various PPV derivatives: poly(2-carbazolyl-*p*-phenylenevinylene) (PCzPV), PPPDPV, PPAPV, and PAHPV. PCzPV and PPPDPV exhibit the absorption bands in the spectral regions of 310−350 and 280−360 nm, which are attributable to carbazole and PBD groups, respectively, in addition to the broad and structureless absorption band centered at around 430 nm due to the PPV main chain. On the other hand, PPAPV and PAHPV exhibit three vibronic absorption peaks in the 325−420 nm region. A weak absorption tail extending to 500 nm is also seen in PPAPV. The three vibronic absorption bands in the shorter wavelength region are caused by anthracene moieties. The featureless absorption tail in the longer wavelength region originates from the polyconjugated main chain. The absorption spectrum of PPAPV is slightly red-shifted as compared with that of PAHPV where the 9,10-diphenylanthracene moiety is far apart from the main chain. This result indicates that PPAPV has a longer π-electronic conjugation length than PAHPV. The weak π-electronic conjugation in PAHPV is ascribed to the spacer between the main chain and the 9,10-diphenylanthracene moiety which is absent in PPAPV.

The PL spectra of PPV derivatives with an excitation at 325 nm under the same experimental conditions were obtained (Figure 1). To investigate the side-chain effect on the PL emission, we recorded the steady-state and time-resolved PL spectra using the excitation wavelength of 300−325 nm to photoexcite the side groups preferentially. The PL spectra of PCzPV and PPAPV are composed of well-resolved vibronic bands, being similar to the spectral features of PPV emission without interference by the pendent group. Thus, it is clear that the direct attachment of the pendent group onto the PPV backbone does not influence the PL characteristics of PPV. In addition, the PL spectra of PCzPV and PPAPV show the exact same features regardless of the

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[17] Kim, Y. H.; Cho, D. W.; Yoon, M.; Kim, D. *J. Phys. Chem.* **1996**, *100*, 15670.

excitation wavelength, indicating that the emissive state is the same even with high-energy excitation. It is likely that the energy-transfer processes may occur from the pendent group to the PPV main chain.

In PPV, a variety of evidences, including the vibronic structure in the emission spectrum, strongly suggest that the luminescence originates from an intrachain singlet exciton.[9] Upon photoexcitaton, the most efficient deactivation mechanism is the formation of intrachain excitation via an energy migration or lattice relaxation process. Thus, little or no emission occurs from the initially excited states. In the case of PPV, the formation rate of interchain excitation from intrachain excitation is slow with respect to the radiative and nonradiative decay processes of intrachain excitation. Consequently, the emission from PPV is mainly induced by the intrachain excitonic species. The PL spectra of PCzPV and PPAPV exhibit the vibronic structure, which is very similar to PPV. Thus, the PL of PCzPV and PPAPV is suggested to arise from the same electronic state as in the case of PPV.

In contrast with PCzPV and PPAPV, the PL spectrum of PPPDPV shows the structureless and red-shifted emission. The EL spectrum also exhibits the similar spectral feature. From a close similarity between the PL and EL spectra, we conclude that the same excited-state species are responsible for the emission in both cases. In PPPDPV, the oxadiazole pendent group is connected to the PPV main chain. Therefore, both the main-chain and pendent groups are to be placed in-plane, which is in favor of π conjugation. We can suggest that the structureless and red-shifted emission is due to either extended π conjugation or another stabilized excited state, e.g., the charge-transfer (CT) state. If the PPPDPV emission arises from the extended π-conjugation state, the absorption spectrum should be shifted to longer wavelength as compared with PCzPV. However, the band edge in the absorption spectrum of PPPDPV is similar to that of PCzPV. From this fact, we can rule out the extended π-conjugation state as a cause of red-shifted emission. Because the oxadiazole unit in PPPDPV has a high electron affinity, the PPV main chain may possess the hole character as compared with the pendent group. Thus, we can suggest that the emission in PPPDPV originates from another stabilized excited state, e.g., the CT state.

The PL spectrum of PAHPV exhibits the broadest emission among all of the PPV derivatives investigated in this work. The enhancement of the emission in the shorter wavelength region is believed to be due to 9,10-diphenylanthracene moieties in addition to the PPV main-chain emission. In addition, it is noteworthy that the PL spectrum of PAHPV exhibits a long tail extending to 700 nm, which arises from the difference in the electronic structure caused by the presence of an oxyalkylene spacer in the main chain of PAHPV. In PAHPV, the 9,10-diphenylanthracence moiety is not expected to be involved in a direct through-bond electronic communication with the PPV main chain because of the oxyalkylene spacer group. This structure results in the emission from the 9,10-diphenylanthracence moieties in the shorter wavelength region. It is well established that anthracene is a representative species for excimer formation. In PPAPV, the excimer formation is unlikely to occur because the pendent group, phenylanthracence, is so bulky that this is to be placed out-of-plane with respect to the PPV main chain. On the other hand, the pendent group in PAHPV is longer than that of PPAPV or PCzPV because of the presence of a spacer group. As a result, the 9,10-diphenylanthracene in PAHPV is less affected by steric hindrance and it has flexibility. Thus, the excimer formation is possible between the 9,10-diphenylanthracence moieties in the same chain or in different chains.[18] The excimer emission is generally characterized by a broad, structureless, and red-shifted emission. The structureless emission and long tail in the longer wavelength region indicate that the excimer state is formed, even though the red-shifted emission is relatively weak.

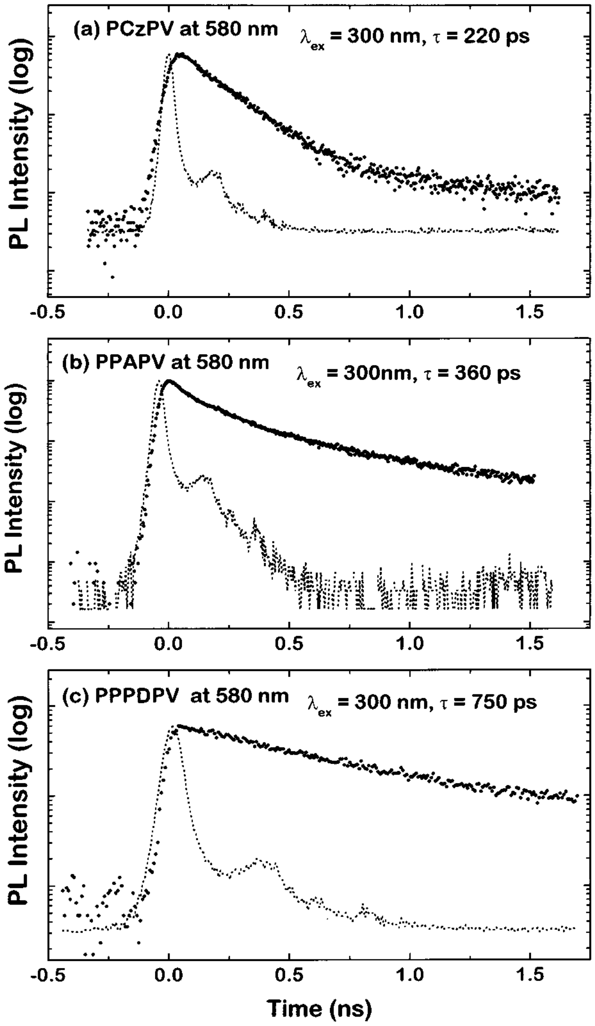

Figure 2. PL decay profiles of PCzPV (a), PPAPV (b), and PPPDPV (c) at 580 nm with an excitation at 300 nm. The dotted line represents the instrument response function of our TCSPC system.

To obtain further information on the nature of the photoexcited state, we measured the PL decay profiles of various PPV derivatives with an excitation at 300 nm. The PL decay profiles were monitored at 580 nm which corresponds to the lower energy emission for PCzPV, PPAPV, and PPPDPV. For PAHPV, the PL decay profiles were monitored at 420, 500, and 580 nm, which correspond to the anthracene moiety, the PPV main

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[18] Matles, S. L.; Farid, S. *Science* **1984**, *226*, 917.

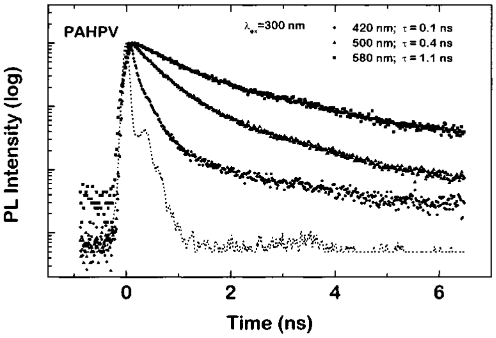

Figure 3. PL decay profiles of PAHPV at 420, 500, and 580 nm with an excitation at 300 nm.

chain, and the extended emission state, respectively. Parts a−c of Figure 2 show the PL decay profiles of PCzPV, PPAPV, and PPPDPV, respectively. The PL lifetimes of PCzPC and PPAPV are determined to be about 220 and 330 ps, respectively, being similar to that of PPV. Because the intrachain excitation is similar in nature to the initially prepared excited state upon photoexcitation, it is a fully allowed transition with a short natural radiative lifetime. It indicates that the emission of PCzPV and PPAPV comes from the initially excited state as in the case of PPV. Therefore, the PL of PCzPV and PPAPV is suggested to arise from intrachain singlet excitons.

On the other hand, the PL lifetime of PPPDPV is increased to 750 ps, which is twice that of PCzPV or PPAPV. In organic molecules, the CT state generally exhibits a long decay time as compared with the initially excited state. As stated above, the PL spectrum of PPPDPV exhibits the structureless and red-shifted emission with increased PL lifetime. Therefore, it is likely that the charge transfer occurs in PPPDPV and the increased PL lifetime is originated from the CT state. These results are consistent with the previous results by Chung et al.[15] in which the EL efficiency of PPPDPV is about 10 times that of PPV and 20 times that of PCzPV. In addition, the EL threshold electric field of PPPDPV is 8.3×10^5 V/cm, which is lower than those of PPV (1.1×10^6 V/cm) and PCzPV (1.7×10^6 V/cm). It was suggested that the charge balance in PPPDPV is maintained because of the PBD units, leading to the enhancement of the EL efficiency.

Figure 3 shows the PL decay profiles of PAHPV monitored at 420, 500, and 580 nm with an excitation at 300 nm, which shows a strong dependence on monitoring wavelengths. In the PL spectrum of PAHPV, the shorter wavelength emission corresponds to phenylanthracence and the main emission band around 500 nm arises from the PPV main chain. Thus, the PL lifetimes of 0.1 and 0.4 ns obtained at 420 and 500 nm, respectively, are due to phenylanthracence and the PPV main chain. The PL lifetime at 500 nm is rather similar to those of PCzPV (0.22 ns) and PPAPV (0.36 ns). On the other hand, the PL lifetime at the long tail emission of PAHPV, which is believed to be due to the excimer state, is about 1.1 ns, being 3 times longer than those of related polymers such as PPV, PCzPV, and PPAPV. Because of the distribution in conjugation lengths in polymers, a rapid energy migration is likely to occur along the chain or between chains upon photoexcitation. As a result, the PL lifetime becomes slightly longer as the probe wavelength is increased. However, the PL lifetime at 580 nm seems to be too long to be explained in terms of the energy migration process. The characteristic feature of the excimer formation along with the structureless and red-shifted emission is the relatively long emission lifetime.[19−21] In this case, it is likely that the PPV excimer contributes to the long tail emission. However, because we did not observe the long decay emission in PCzPV and PPAPV even at 580 nm, we think that the PPV excimer formation in PAHPV becomes hindered because of the bulky 9,10-dipenylanthracence side groups attached to the PPV main chain. Therefore, most of the long tail emission is believed to arise from the excimer formation between 9,10-diphenylanthracene moieties attached to the PPV main chain through a long and flexible hexamethylene spacer. It is well-known that the emission of CN−PPV comes from the interchain excitation and its lifetime is about 0.8 ns. Its natural radiative lifetime is calculated to be longer than 10 ns. Thus, we can suggest that the long tail emission of PAHPV is induced by the excimer state between the 9,10-diphenylanthracence moieties of the pendent group in the same chain or in different chains.

Conclusions

We compared the emission characteristics of various PPV derivatives using the steady-state and time-resolved spectroscopic measurements. Our experimental observations suggest that the excimer formation is feasible in PAHPV. The emission for PCzPV and PPAPV is from the intrachain excitation like PPV. In the case of PPPDPV, a charge -transfer state is formed, which exhibits a red-shifted and structureless emission. Through the combined effect, PAHPV is capable of emitting light over a broad spectral range covering the entire visible region.

Our results demonstrate that the pendent groups affect the chromophoric interaction between the main chain and the pendent group or polymer chains. Thus, the interaction between the main chain and the pendent group should be considered in designing highly fluorescent polymeric materials.

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(19) Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *73*, 744.

(20) Yan, M.; Rothberg, L. J.; Kwock, E. W.; Miller, T. M. *Phys. Rev. Lett.* **1995**, *75*, 1992.

(21) Jakubiak, R.; Collison, C. J.; Wan, W. C.; Rpthberg, L. J. *J. Phys. Chem.* **1999**, *103*, 2394.