Excimer Suppression Mechanism in Light Emitting Polymer Blends

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Summary: Alternating copolymer of distyrylenediethylhexyloxyphenylene and phenyltriazine(PPVT) or hydroxyphenyltriazine(PVOT) is synthesized in order to enhance the electron mobility in the light emitting polymers. Photoluminescence(PL) spectrum of PPVT shows excimeric characteristics but PVOT generates excitonic PL emission. A blend of PVOT with polyvinylcarbazole(PVK) enhances the PL intensity of PVOT on photoexcitation of PVK indicating an efficient energy transfer. The excimeric PL emission of PPVT is suppressed on photoexcitation of a blend with PVK at the UV-visible absorption(AB) maximum of PVK, which is an indirect photoexcitation, while the energy transfer from PVK to PPVT is not completed.

Keywords: conjugated polymers; energy transfer; lifetime; light-emitting diodes; photo excitation; photoluminescence

Introduction

A great deal of efforts is put into developing polymer light emitting diodes (PLEDs) since its first discovery.[1] A high volume production of a PLED product has been launched[2] and PLED TV will be introduced in three years[3]. However, there are rooms for improvement of PLEDs in lifetime and power effieciency[4]. Progresses are also made in processing of the devices in terms of ink jet printing[5] and a flexible substrate[6].

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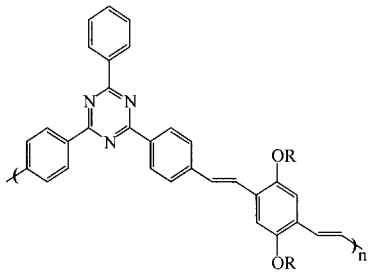
Light emitting polymers consisted of aromatics, heterocyclics or vinyl units in polymer backbones are rigid and the polymer molecules tend to be extended. The flat chromophores in light emitting polymers are stacked easily with each other. It is common to observe that PL spectra of light emitting polymers show the PL emission maximum with vibronic structures and secondary emission. The secondary emission that causes a reduction of color purity is generated by excimers[7] but there is a possibility of excitonic emission of a chromophore of a longer conjugation[8].

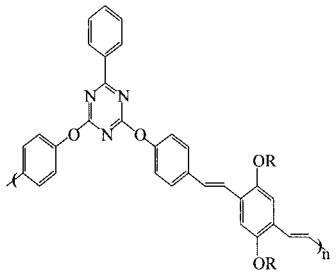
The present work has synthesized polyphenylenevinylene derivatives with an electron transporting unit in the polymer main chain in order to enhance the electron mobility in the polymers. The secondary emission of the polymers is suppressed by indirect photoexcitation of a polymer blend with polyvinylcarbazole (PVK). Energy transfer efficiency between donor and acceptor chromophores in the blend was examined and correlated with the lifetime ratios for the suppression of the secondary PL emission.

Experimental

The alternating copolymers of distyrylenediethylhexyloxyphenylene and phenyltriazine (PPVT) or dihydroxyphenyltriazine (PVOT) are synthesized by employing a Heck reaction. The chemical structures of PPVT and PVOT are shown in Scheme 1.



PPVT



PVOT

Scheme 1. Chemical structures of PPVT and PVOT.

UV-vis absorption spectra were recorded with a HP 8452A diode array spectrophotometer and the PL spectra were recorded with an ISS PL-1 fluorometer. A time-correlated single-photon counting (TCSPC) technique was employed for the time-resolved PL measurements. A detailed description of an instrumental setup for TCSPC is found elsewhere.[9]

Results and Discussion

Cyclovoltammograms of PVOT and PPVT show only the oxidation potential despite of the triazine units in the polymer chains. The triazine unit looses the capability of accepting electrons from the cathode on the reduction cycle, indicating that electrons are supplied to the triazine unit from the phenoxy or styrylenephenylene group of the polymers, respectively. Ultraviolet-visible absorption(AB) and PL spectra of films of PVOT and PPVT, and the solution of PPVT in chloroform are shown in Figures 1 and 2. The AB spectra show the absorption maxima at 380 and 440 nm for PVOT and PPVT, respectively. Inserting an ether linkage between the triazine and distyrylenephenylene units shortens the conjugation length in PVOT.

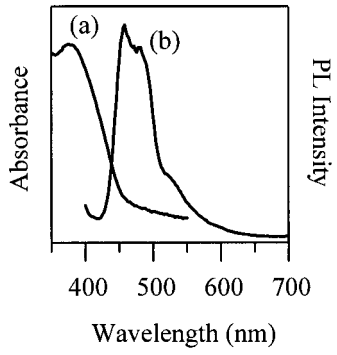


Figure 1. Spectra of AB (a) and PL (b) of a PVOT film on photoexcitation at 375 nm.

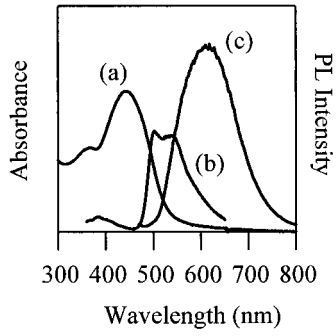


Figure 2. Spectra of AB (a), PL of a solution of 1 x10^{-5} mol/L in chloroform (b) and a film (c) of PVVT on photoexcitation at 440 nm.

The PL spectrum of PVOT on photoexcitation at 375 nm shows the emission maximum at 470 nm with a vibronic shoulder and a weak tail with the peak at 520 nm. No shift in the PL maximum is observed from the solution in chloroform. The PPVT film on photoexcitation at 440 nm shows a structureless PL emission spectrum with the peak maximum at 610 nm. The broad PL spectrum must be a result of radiative excimer emission. The AB maximum of PPVT solution of $1x10^{-5}$ mol/L in chloroform moves little from that of the film. However, the PL spectrum of the solution in chloroform on photoexcitation at 440 nm exhibits the PL maximum at 540 nm with a strong vibronic progression at 505 nm. The PL spectra, then, must be greatly distorted by the self-absorption at around 505 nm due to a small Stokes' shift, which may be the main peak and the peak at 540 nm the vibronic one. Coplanarity seems to be developed between the distyrylenephenylene and the triazine units in PPVT for the longer PL maximum.

A polymer blend of PPVT/PVK(1/9) is prepared in order to dilute PPVT in PVK and to suppress the excimer formation. It is, however, impossible to prevent the phase separation in the polymer blend since the low entropy of mixing prevents homogeneous mixing of the two polymers. It is, then, not surprised to observe that the PL spectrum of the blend film on photoexcitation at 440 nm is the same as that of PPVT photoexcited at the same wavelength, since PPVT forms its own rich domains in the blend film.

When the blend is photoexcited at the AB maximum of PVK of 340 nm, the PL spectrum shows two sets of PL emission; one with the PL maximum at 420 nm and the other at 505 nm as shown in Figure 3. The PL maximum at 420 nm is assigned as the excimer emission peak of PVK. The second spectrum with the PL maximum at 505 nm accompanies a strong shoulder with the peak at 540 nm and has all the characteristics of the PL spectrum of the PPVT solution in chloroform. The intensity of

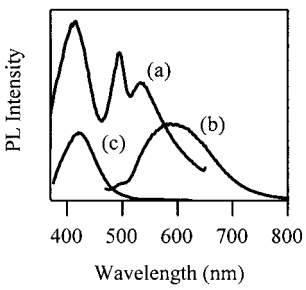


Figure 3. PL spectra of a PPVT / PVK (1/9 by weight) blend film photoexcited at 340 (a) and 440 nm (b), respectively, and PL spectrum of PVK (c).

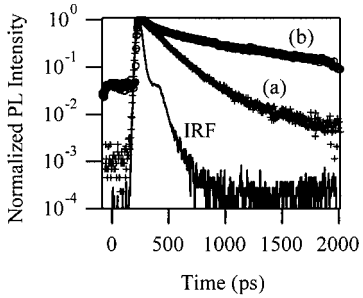


Figure 4. TCSPC data of films of PVK/PVOT (a) and PVK/PPVT (b).

the excimeric emission with the peak at 610nm is greatly reduced.

It is significant to observe that the indirect photoexcitation of PPVT through PVK generates no excimeric emission from the PPVT-rich domains although there is no complete energy transfer from PVK to PPVT. It is apparent that a few of the PVK excimers transfer their energy into PPVT but the excitations in PPVT after the energy transfer fail to form the PPVT excimers. It is suggested that PPVT excimers are formed before the excitations generated on direct photoexcitation of PPVT relax to the critical energy level where the internal conversion takes place for formation of a dimeric structure with an adjacent one. When excitations of PPVT are formed after the energy transfer from PVK, the energy level of the excitations is below that of the intersection of the internal conversion and they fail to generate the dimeric conformation.

Lifetime of the PVK excimer in the blend is determined by employing a TCSPC method. Fig. 4 shows that the PVK excimer in the PVK/ PVOT blend has a shorter lifetime than that of the PVK/PPVT blend on photoexcitation at 340 nm. It is, then, expected that the energy transfer from the excited chromophore of a donor to the fluorophore of an acceptor may be more efficient when the lifetime of the fluorophore in the acceptor is shorter than the excited species of the donor. The indirect photoexcitation of the PVK/ PVOT blend enhances the PL intensity significantly but the PVK/ PPVT blend shows a poor result.

Conclusion

Two copolymers with a phenyltriazine unit, an electron transporting group, attached in a polymer backbone of distyrylenephenylene fail to be reduced electrochemically. PVOT generates no excimeric PL emission on photoexcitation but PPVT does nothing but excimeic PL emission. The polymer blend with PVK generates no excimeric emission of PPVT but the energy transfer is not completed showing both the excimeric emission of PVK and the singlet excitonic emission of PPVT. The degree of energy transfer between PVK and PVOT or PPVT depends on a lifetime ratio of PVK excimers and acceptor fluorophores. A PPVT singlet exciton has a long lifetime and shows a poor energy transfer from PVK.

[1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B.Holmes, *Nature* **1990**, 347,539.
[2] http://www.optics.org/articles/news/8/6/5/1.
[3] http://www.optics.org/articles/news/8/3/30/1.
[4] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Brédas, M. Lögdlund, W.R. Salaneck, *Nature* **1999**, 397, 121.
[5] J. Bharathan, Y. Yang, Appl. Phys. Lett. **1998**, 72, 2660.
[6] G. Gustaffsson, Y. Cao, G.M. Tracy, F. Klavetter, N. Colaneri, A.J. Heeger, *Nature* **1992**, 357, 477.
[7] S.A. Jenekhe, L. Lu, M.M. Alam, *Macromolecules* **2001**, 34, 7315.
[8] C.J. Collison, V. Treemaneekarn, W. Oldham Jr., J.H. Hsu, L.J. Rothberg, *Synth. Met.* **2001**, 119, 515.
[9] M.Y. Lee, D. Kim, *J. Opt. Sci., Korea* **1990**, 1, 52.