PVK 엑시머로부터 Polyfluorene으로의 에너지 전이

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The Energy Transfer from PVK Excimers to Polyfluorene

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Abstract

A blend of a newly synthesized polyfluorene(PDHBF) and polyvinylcarbazole(PVK) exhibits a photoluminescence(PL) emission spectrum of PDHBF without an increase in the PL intensity on photoexcitation at 340 nm, the UV-visible absorption maximum of PVK, despite of a substantial spectrum overlap. However, the indirect photoexcitation of the blend suppresses the secondary emission of the PL with the maximum at 520 nm. The chromophores generating the secondary emission are formed when the chromophores are photoexcited above the critical energy level of an excited state. The chromophores formed by the energy transfer have energy lower than the critical energy and fail to form the excimers. A low temperature PL study of the blend in a cryogenic chamber proves that the energy transfer in the system takes place mainly between the excimers of PVK generated by the partially eclipsed dimeric states of two carbazole units and the fluorophores of PDHBF.

Introduction

The latest trend in development of light emitting polymers has shifted to optimizing molecular structures of fluorene-based polymers.[1] Emitting colors of the polymers are tuned by modifying the fluorene unit or by copolymerizing with monomers of specific functions.[2] There are reports of syntheses of fluorene-based light emitting polymers covering the three principle colors.[3] There are also reports of LEDs fabricated with blue light emitting fluorene-based polymers with lifetime of 10,000 h.[4] The polymers with fluorene units show high efficiencies of power and luminescence. However, the materials are still short in lifetime and its extension is the main huddle to overcome for PLEDs at the moment.

Photoluminescence(PL) emission spectra of polymers generally show a broad secondary emission in addition to the main emission maximum with a vibronic feature. The broad emission is known as either excimeric[5] or intrinsic excitonic emission.[6] Color purity of emitting light, which is important in fabrication of full color LEDs, is reduced by the secondary emission. Most of fluorene-based light emitting polymers shows the secondary emission of a longer wavelength. The present work has tried to understand the mechanism of the secondary emission generated from a polyfluorene with least molecular modification but keeping good solubility and high light emitting efficiency.

Experimental

Synthesis

1-bromo-4-cyclohexylbutane was prepared following the literature procedure.[7]

Polymerization of poly-9,9’-dicyclohexylbutyl-2,7-fluorene (PDHBF)

The homopolymer was synthesized by *2,7-dibromo-9,9'-di(cyclohexylbutyl)fluorene* and nickel-mediated polymerization.[8-9]

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on Brucker Avance 300 and 400 spectrometers, respectively. Molecular weights of the polymers were determined with a Waters GPC-150C calibrated with polystyrene as the standard and THF as the eluent. A Dupont 9900 was used for thermal characterization of the polymer. UV-visible absorption spectra were made on a Jasco V-530. The PL spectra of films spin-coated on quartz plates from the polymer solutions were performed on a ISS PC1 spectroflourometer. 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.[10]

Results and Discussion

PDHBF has a simple electronic structure, indicating that there is a uniform chromophore absorbing the UV-visible light with the absorption maximum at 390 nm as shown in Figure 1-a. The fine resolution of the PL spectrum of a PDHBF film with a shoulder peak at 450 nm as shown in Figure 1-b indicates that the polymer chains are rigid in the solid state.[11] The PL spectrum, however, still shows a rather strong emission at 520 nm on photoexcitation at 390 nm, the UV-visible absorption maximum, despite of the two bulky side chains on position 9 of the fluorene unit where stacking of molecules might be inhibited by the bulky side chains. There is little shift of the PL emission maximum but a strong vibronic feature in the PL spectrum of the solution in chloroform as shown in Figure 1-c. However, the PL emission with the maximum at around 520 nm is shrunk in the polymer solution indicating a reduction of the secondary emission. The small Stokes' shift and the distinctive vibrational structure of the PL spectrum of the solution imply that the polymer chains are reasonably stiff in the solution.

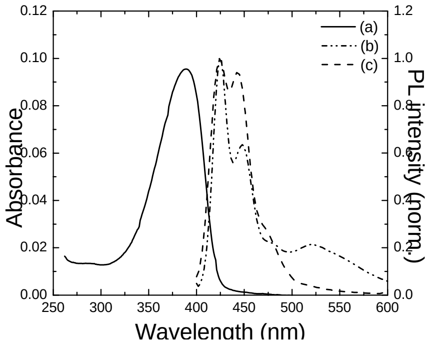

Figure 1. Spectra of UV-Vis absorption(a) and PL emission of film(b) and solution(c) of PDHBF on photoexcitation at 390 nm.

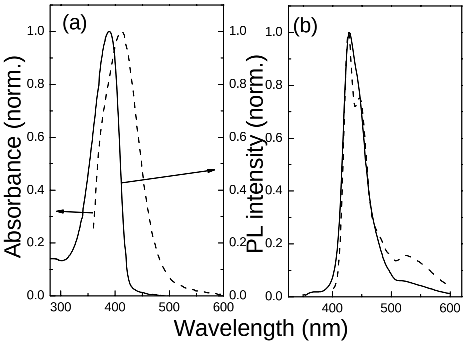

Figure 2. (a) UV-Vis absorption spectrum of PDHBF(solid line) and PL emission spectrum of PVK(dashed line) on photoexcitation at 340 nm. (b) PL spectra of a PVK/PDHBF(9/1) blend film on photoexcitation at 340 nm(solid line) and at 390 nm(dashed line), respectively.

Suppression of the PL emission with the emission maximum at 520 nm is tried by blending PVK and the polymer with a blending ratio of PVK/PDHBF(9/1). The spectrum overlap between the PVK emission and PDHBF absorption is substantial for energy transfer between them as shown in Figurer 2-a. The PL spectrum of a blend film on photoexcitation at 340 nm, the UV-visible absorption maximum of PVK, displays a high intensity of the overall PL emission with the emission maximum at 425 nm as shown in Figure 2-b. However, direct photoexcitation of PDHBF in the blend at 390 nm also generates an intensive PL spectrum. This implies a rather poor result of the indirect photoexcitation of PDHBF in the blend system. It is, nevertheless, important to note that the emission with the peak at 520 nm is substantially reduced. It is also noticed that the PL spectrum of the blend lost the vibronic feature, which suggests that the molecular interaction between the two polymers derives a new environment at the interface.

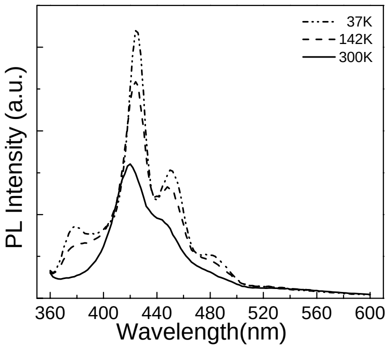

Figure 3. PL spectra of a PVK/PDHBF(9/1) blend film photoexcited at 340 nm at various temperature.

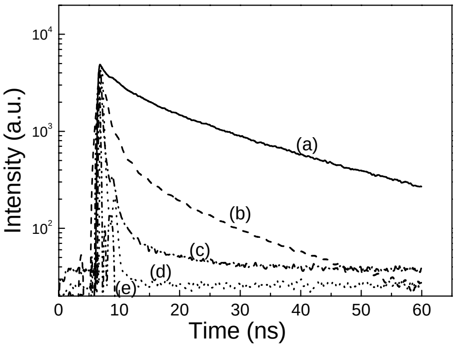

Figure 4. PL intensity profiles of polymer films of PVK(a) and blends of (9/1)(b) and (1/1)(c) at 410 nm on photoexcitation at 280 nm, and of PDHBF(d) at 430 nm on photoexcitation at 280 nm.

The energy transfer from the PVK excimers to the fluorophores of PDHBF is carried out but inefficiently at room temperature and also inefficiently at lower temperature as shown in Figure 3. The shrunk emission peak at 380 nm suggests that the excimers with the partially eclipsed structure failed to complete the energy transfer to PDHBF at lower temperature, which implies that the excimers of the partially eclipsed structure with a long lifetime survive long enough to decay radiatively. It might be expected that a strong emission with the peak maximum at 380 nm would be observed at room temperature if the lifetime of the excimers with the partially eclipsed structure would be short compared to that of the fully eclipsed one.

The time correlated single photon counting(TCSPC) technique is utilized to pursuit the mechanism of charge transfer between two chromophores with different band gaps. The emission intensity both at 410 nm, the PL emission maximum of PVK, and 430 nm, that of PDHBF decrease exponentially as shown in Figure 4. The exponential decay curve of PDHBF at 430 nm shows a single component with a lifetime of 190 ps. The exponential decay curve of PVK at the emission maximum of 410 nm has two components of 2.64 and 21.31 ns. The PVK/PDHBF blend with a ratio of 9/1 shows a faster decay of the PL intensity at 410 nm with three components of the decay lifetime; 650 ps, 3.42 and 18.06 ns. When a blend with a ratio of 1/1 is photoexcited at 340 nm, the PL intensity at 410 nm decreases much faster with two decay components of 100 ps and 5.57 ns than that of the blend of 9/1.

PDHBF has a short lifetime compared to that of PVK, which is a necessary condition for a good acceptor in the blend system. The decay curves of the two blends of PVK/PDHBF with blend ratios of 1/1 and 9/1 are controlled almost single-handedly by PDHBF. However, the blend with a higher concentration of the acceptor with the blend ratio of 1/1 receives the energy faster from the excited chromophores of PVK(lifetime of about 20 ns). There is no component of the lifetime of 20 ns in the exponential decay curve of the 1/1 blend while the exponential curve is still controlled partially by the PVK component of 5.57 ns. All the energy of the PVK chromophore with the lifetime of 20 ns is transferred completely to the acceptor before contributing to the exponential decay of the intensity. When the acceptor concentration in the blend is reduced to 10 %, the energy transfer is incomplete and there is still a different amount of contribution to the exponential decay curve between the two decay components in PVK. It is observed that the component with the longer lifetime loses energy faster to the acceptor than the one with a shorter lifetime.

It suggests that the excimers with the longer lifetime of 21.31 ns are assigned as the partially eclipsed ones and the shorter one of 2.64 ns as the fully eclipsed ones. If the assignment might be made the other way around, there should be two excimer emission maxima at room temperature. Then, it would be correct to predict that excimers of the fully eclipsed structure with a longer lifetime would be saturated on photoexcitation and the excimers of the partially eclipsed ones with shorter lifetime might decay to the ground state before transferring the excess energy to the less populated carbazole units at the circumstance leading to having two emission maxima in the PL spectrum. In reality, the PL spectrum of PVK is rather broad but has a single emission maximum although there are two excimers with different energy. Since the lifetime of the excimers with the fully eclipsed structure is shorter, the excimer formation cycle is short and the density of the excimers with higher energy decreases fast before exhibiting radiative decay at the higher energy.

Conclusion

Two bulky side chains of 4-cyclohexyl-n-butylene attached to position 9 of fluorene units in PDHBF render good solubility in organic solvents but fail to suppress the secondary PL emission with the maximum at around 520 nm on photoexcitation at 390 nm, the UV-visible absorption maximum of the polymer. The emission intensity at 520 nm is greatly reduced only on indirect photoexcitation of PDHBF blended with PVK at 340 nm. It is suggested that the excitons generating the PL emission spectrum with the maximum at 520 nm are formed by coupling of two sequenced fluorophores in the higher state of S_1 by direct photoexcitation at 390 nm while those formed in PDHBF after accepting energy from excited PVK have energy not high enough to extend the polymer chains and result in a radiative decay without the tail at 520 nm in the PL spectrum. However, it is observed that the PVK/PDHBF blend system has a poor energy transfer between the two polymers despite of a reasonable emission/absorption overlap.

References

1. D. Y. Kim. H. N. Cho, C. Y. Kim, *Prog. Polym. Sci*., **25,** 1089 (2000)
2. J. I. Lee, G. Klaerner, M. H. Davey, R. D. Miller, *Syn.Met,.*, **102**, 1087 (1999)
3. I. S. Millard, *Syn.Met.*, **111-112**, 119 (2000)
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*, **397**, 121 (1999)
5. N. T. Harrison, D. R. Baigent, I. D. W. Samuel, R. H. Friend, A. C. Grimsdale, S. C. Moratti, A. B. Holmes, *Phys. Rev. B,* **53,** 15815 (1996)
6. C. J. Collison, V. Treemaneekarn, W. J. Oldham, J. H. Hsu, J. L. Rothberg, *Synth. Met.*, **119**, 515. (2001)
7. C. Xia, R. C. Advincula, *Macromolecules*, **34**, 5854 (2001)
8. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry, 5th ed.***,** Prentice Hall, London (1989)
9. T. Yamamoto, A. Morita, Y. Muyuzaki, T. Maruyama, H. Wakayama, Z.-H. Shou, Y. Nakamura, T. Kanba, S. Sasaki, K. Kubota, *Macromolecules*, **25**, 1214 (1992)
10. M. Y. Lee, D. Kim, *J. Opt. Sci., Korea*, **1**, 52 (1990)
11. M. Belletête, J.-F. Morin, S. Beaupré, M. Ranger, M. Leclerc, G. Durocher, *Macromolecules*, **34**, 2288 (2001)