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Suppression of Secondary PL Emission by Indirect Photoexcitation

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Summary: 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

A progress is made to introduce ink jet printing technology in polymer light emitting diodes(PLEDs)[1-2] and a great deal of efforts is also put into applying organic transistors imbedded on a flexible substrate to the devices.[3] It seems apparent that PLEDs have advantages on fabrication and mass production over organic light emitting diodes(OLEDs). It has been announced that a mobile phone equipped with a PLED will be in market this year [4] and larger-screen PLEDs drived by an active matrix system are introduced in 2005.[5] However, device fabricators of PLEDs have a difficulty to receive reliable light emitting polymers and suppliers of blue light emitting polymers are hard to be found, yet.

The latest trend in development of light emitting polymers has shifted to optimizing molecular structures of fluorene-based polymers.[6] Emitting colors of the polymers are tuned by modifying the fluorene unit or by copolymerizing with monomers of specific functions.[7] There are reports of syntheses of fluorene-based light emitting polymers covering the three principle colors.[8] There are also reports of LEDs fabricated with blue light emitting fluorene-

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based polymers with lifetime of 10,000 h.[9] 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 [10] or intrinsic excitonic emission. [11] 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.[12]

Preparation of 2,7-dibromo-9,9'-di(cyclohexylbutyl)fluorene

To a 250 mL two-neck round-bottomed flask containing 2,7-dibromofluorene (3.466 g, 10.7 mmol), 1-bromo-4-cycloethylbutane (5.67 g, 32.0 mmol), 50 mL of toluene, and 0.16g of tetrabutylammonium bromide as a phase-transfer catalyst was added 50 mL of 50-wt% NaOH aqueous solution. This two-phase mixture was refluxed at 100°C with vigorous stirring and nitrogen gas bubbling. TLC monitored the progress of reaction. After 2,7-dibromofluorene, the starting compound, had completely disappeared, the organic layer was washed with aqueous $NaHCO_3$ solution two times to remove excess NaOH and then with water. The organic layer was separated, dried over $MgSO_4$, and concentrated by solvent evaporation. The crude product was washed with warm ethanol several times(yield of 87 %, white crystal). ^1H NMR ($CDCl_3$, 400MHz); 7.5 (q, 2H), 7.4 (q, 4H), 1.9-1.8 (q, 4H), 1.7-1.5 (m, 10H), 1.2-0.9 (m, 16H), 0.8-0.7 (m, 4H), 0.6-0.5 (m, 4H), ^{13}C NMR ($CDCl_3$, 100MHz): 152.6, 139.1, 130.1, 126.2, 121.5, 121.1, 55.7, 40.1, 37.6, 36.9, 33.3, 27.0, 26.7, 26.4, 23.9

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

The homopolymer was synthesized by nickel-mediated polymerization.[13-14] A solution containing 5 mL of anhydrous DMF, bis(1,5-cyclooctadienyl)nickel(0), 2,2'-dipyridyl, and 1,5-cyclooctadiene (the latter three in a molar ratio of 1:1:1 by 2.672 mmol each) was heated at 80 °C for 30 minutes under argon. The monomer (1.35 mmol) dissolved in 5 ml of toluene was added dropwise to the solution. After 3 days of heating at 80 °C, 9-bromoanthracene (0.1 g, 0.39 mmol), the end capper in an excess amount, dissolved in 3 ml of anhydrous toluene was added to the flask. The reaction mixture was further heated at 80 °C for 24 hours. The polymer was precipitated on addition of an equivolume mixture of concentrated HCl, acetone, and methanol. The filtered polymer was extracted with chloroform; K_2CO_3 solution was used instead of distilled water until the aqueous layer became neutralized. The organic layer was separated, dried over $MgSO_4$, concentrated by solvent evaporation, and reprecipitated in methanol. The polymer was further purified by a Soxhlet extraction in methanol/acetone for 2 days. Repeating precipitation of the polymer with methanol did final purification. Filtration and drying under vacuum gave the yield of 0.314g(40 % yield); ^1H NMR ($CDCl_3$, 400MHz): 7.6-7.4 (m, 6H+aromatic protons of end-caps), 1.9-1.8 (d, 4H), 1.7-1.5 (m, 10H), 1.2-0.9 (m, 16H), 0.9-0.7 (m, 8H), ^{13}C NMR ($CDCl_3$, 100MHz): 151.8, 140.5, 140.0, 126.2, 121.5, 119.9, 55.4, 40.3, 37.6, 37.1, 33.4, 27.2, 26.7, 26.4, 24.2.

Instrumentation

^1H and $^{13}CNMR$ 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 Spex Fluorog-3 luminescence spectrometer. PL efficiency values were calculated by comparing to quinine sulfate (ca. $1x10^3$ M) in 0.10 M H_2SO_4 as standard. 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.[15]

Results and Discussion

The number and weight average molecular weights are 45,900 and 118,000 g/mol, respectively, and the polymer dispersion index is 2.6. The glass transition temperature(Tg) and decomposition temperature(Td) are 103 and 423 ^{0}C, respectively. The fluorescence quantum yield of the polymer in chloroform is 0.93.

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.[16] 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.

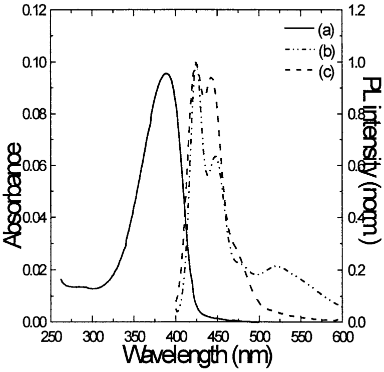

Figure 1. Spectra of UV-Vis absorption(a) and PL emission of film(b) and solution(c) of PDHBF on photoexcitation at 390 nm.

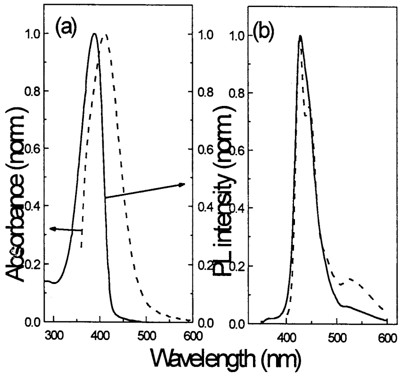

Figure 2-a. UV-Vis absorption spectrum of PDHBF(solid line) and PL emission spectrum of PVK(dashed line) on photoexcitation at 340 nm.

Figure 2-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.

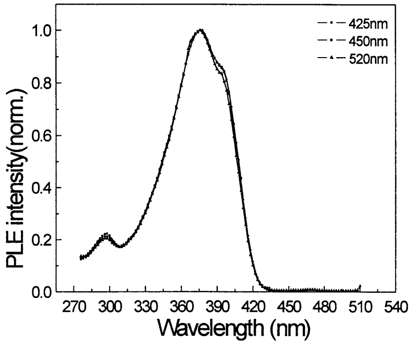

Figure 3. Excitation spectra of PDHBF at three wavelengths of 425, 450 and 520 nm, respectively

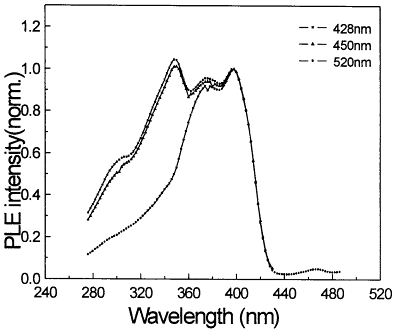

Figure 4. Excitation spectra of a PVK/PDHBF(9/1) blend film at three wavelengths of 425, 450 and 520 nm, respectively.

The excitation spectra of PDHBF fixed at 425 and 520 nm reveal that the photoexcitation of the polymer at around 390 nm generates the highest PL intensities at both 425 and 520 nm as shown in Figure 3. The secondary emission with the maximum at 520 nm might be assigned either as an excimeric radiative decay[10] or as a singlet excitonic emission by an intrinsic structure with a longer conjugation length in the polymer chain.[11] However, the two chromophores for the emission at 425 and 520 nm seems to have a correlation with each other since the normalized PL spectra are fully superposed with each other. It is expected that the population of the overexcited chromophores are present as long as the original chromophores in the polymer are directly photoexcited. The excited chromophores in the S_1 state may derive a change in molecular conformation from the vibrating molecular segments and two sequenced chromophores, one excited and the other at the ground state, may straighten out to form a new chromophore with a longer conjugation. The chromophore decays to the ground state and gives an emission with the PL maximum at 520 nm. The excitation spectra from fixing the two PL emission maxima at 425 and 520 nm display the shallow peak at 295 nm. The peak may indicate the direct excitation of the chromophores to the higher state than S_1. The exciton spectrum at 450 nm, the peak of vibronic feature, fully superposes with those at 425 and 525 nm , which indicates that the three excitation spectra have the same origin.

Figure 4 shows the two different excitation spectra of the polymer blend of PVK and PDHBF with a blending ratio of 9 to 1 on fixing the excitation energy at either 425 and 450 or 520 nm. PDHBF in the blend still generates a strong PL emission with the peak at 520 nm on the direct photoexcitation of PDHBF at 390 nm, the UV-visible absorption maximum of PDHBF and shows no dilution effect on blending. The PL intensity is increased but slightly on the indirect photoexcitation at 340 nm, the UV-visible absorption maximum of PVK. The indirect photoexcitation of PDHBF in the blend reveals that the energy transfer from PVK to PDHBF is not so efficient as observed previously in the different systems.[18] It is, however, demonstrated that the secondary emission with the emission maximum at 520 nm is greatly reduced on the indirect photoexcitation of PDHBF in the blend at 340 nm while the direct photoexcitation of PDHBF in the blend at 390 nm still generates the secondary emission.

It is incorrect to assign the PL emission with the peak at 520 nm as an excimeric one since the direct photoexcitation of PDHBF in the blend at 390 nm generates the emission at 520 nm while the indirect photoexcitation at 340 nm shows no emission at the same wavelength. The chromophores with the same molecular conformation hardly generate different PL emission spectra on photoexcitation at the different wavelength. It is also incorrect, based on the same argument as above, to assign the PL emission at 520 nm as a singlet radiative decay by a chromophore with a longer conjugation. The chromophores photoexcited directly, it is suggested, have energy enough to extend their conjugation length by coupling of the sequenced chromophore in the polymer chain prior to reaching the lowest state of S_1 by loosing the absorbed energy on vibration. The new excitons decay radiatively for the PL emission at 520 nm. However, the transferred energy from PVK to PDHBF is not high enough to form extended chromophores, which results in showing no PL emission at 520 nm. It is significant to notice that the indirect photoexcitation of a chromophore in a polymer blend suppresses a secondary PL emission at a longer wavelength.

Figure 5-a suggests that there are two fluorophores in PVK. The emission maxima of the PL

spectra show a blue shift from 410 to 380 nm on lowering temperature from 300 to 53 K. The PL spectrum with the emission maximum at 380 nm is assigned as the emission of excimers with partially eclipsed carbazole units while that at 410 nm with fully eclipsed ones.[19] The intensity of the PL spectrum of the cold film with the emission maximum at 380 nm is much higher than that with the maximum at 410 nm at room temperature. It shows that the photoexcitation of PVK generates excimers of the partially eclipsed structure more than those of the fully eclipsed one. The excimers in the higher energy state lose little energy by chain vibration at low temperature and decay radiatively to the ground state in their lifetime. However, the excimers in the high energy state either form excimers of the fully exclipsed structure on its way to a lower energy state via vibration at room temperature or decay to the ground state unradiatively.

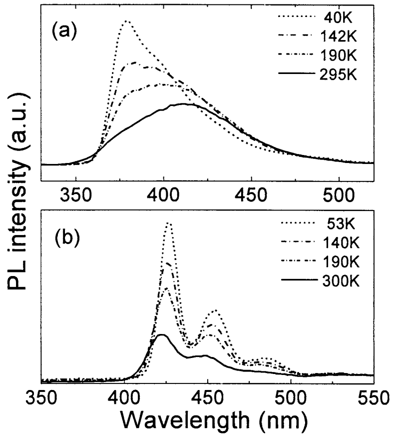

Figure 5. PL emission spectra of PVK(a) and PDHBF(b) photoexcited at 340 and 390 nm, respectively, at various temperature.

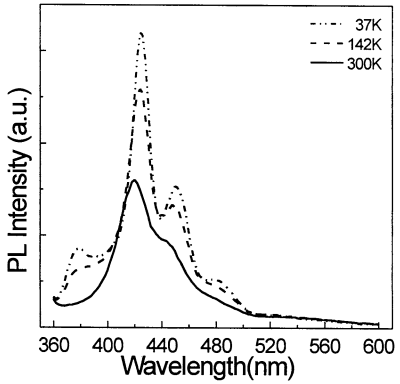

Figure 6. PL spectra of a PVK/PDHBF(9/1) blend film photoexcited at 340 nm at various temperature.

The intensity of PL emission of homopolymer PDHBF is substantially.enhanced at lower temperature as shown in Figure 5-b. It is apparent that vibration of molecular segments in the polymer at the excited state is detrimental to the PL emission. There are a redshift of the emission maximum of PL and a strong vibronic feature on lowering temperature. It implies that the polymer molecules become stiffer at lower temperature and the conjugation length of the chromophres becomes extended. The new peak at 485 nm grows on lowering temperature and is assigned as the second vibronic structure.

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 6. 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 7. The exponential decay curve of PDHBF at 430 nm shows a single component with a lifetime of 190 ps as shown in Table 1. 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.

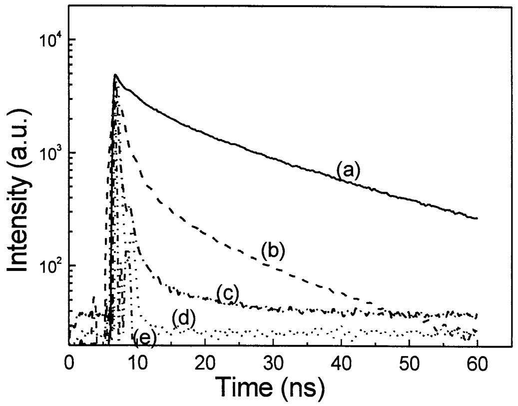

Figure 7. PL intensity profiles of polymer films of PVK(a) and blends of (9/1)(b) and (1/1)(c) at 410 nm on photoexcitation at 280 nm, and of PDHBF(d) at 430 nm on photoexcitation at 280 nm.

Table 1. Fluorescence lifetimes of PVK and PDHBF blend films.
*Lifetimes determined with excitation at 280-283nm on quartz.

System	τ_1 (ns)	% composition	τ_2 (ns)	% composition	τ_3 (ns)	% composition	λ_{max}/nm
PVK	-	-	2.64	52.1	21.31	47.9	410
PVK(9)PDHBF(1)	0.65	83.5	3.42	12.3	18.06	4.2	410
PVK(5)PDHBF(5)	0.10 0.58	88.2 0.6	5.57	11.1	-	-	410
PDHBF	0.19	100.0	-		-	-	430

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.

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