

MOLECULAR DESIGN OF LIGHT EMITTING POLYMERS

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Abstract Fluorene-based alternating and statistical copolymers were synthesized by employing reaction methods of Wittig, Heck and Suzuki. The copolymers were classified into three groups with the photoluminescence (PL) emission maxima at 420, 475 and 500 nm, respectively. Statistical copolymers with two chromophores having PL emission maxima at 420 and 475 nm emitted light with the emission maximum at 475 nm on photoexcitation at 365 nm and improved the quantum efficiency by the energy transfer. However, the intramolecular energy transfer was inefficient compared to the intermolecular energy transfer when the two chromophores were apart from each other in the range of the Förster critical distance. Fluorene-pyridinedivinylene alternating copolymer was synthesized by the Wittig reaction and found to have physical, electronic and electrochemical properties of the individual units intact. The double-layered light emitting diode (LED) with the statistical copolymer as an emitting layer and the pyridine-containing copolymer as an electron transporting-hole blocking layer, which were sandwiched between ITO and Al, displayed a quantum efficiency of 0.1%.

Keywords Light emitting polymers

INTRODUCTION

There has been significant progress in light emitting diodes (LEDs) based on light-emissive polymers in recent years and single-color displays of polymer LEDs will soon be commercially available^[1]. A large number of light-emissive polymers have been introduced in the literature^[2]. Fabrication technology of LEDs has been also improved to give a light emission efficiency of 22 L/W and a lifetime of 10,000 h^[3].

LEDs are evaluated by three factors, viz. color, efficiency and stability. Color is the most important element in LEDs. Light with a color of blue, green or red is emitted on radiative decay of a neutral polaron formed in an emissive material^[4]. Fluorophores in polymers for light emission are chemical units of aromatic or heterocyclic structures. These units are photoexcited in the UV-Visible ranges and emit light on returning to the ground state. The centers for light emission by the neutral polaron and by the photoexcitation are mostly the same as each other^[5]. The emission maximum of the photoluminescence (PL) spectrum of a polymer is separated from the absorption maximum of the UV-visible absorption (AB) spectrum by a value of the Stokes' shift^[6]. Unless an emission originates from a secondary source such as excimer or exciplex, the Stokes' shift ranges from 30 to 100 nm. It is, therefore, anticipated that light with a color is emitted from a photoexcited polymer when the electronic absorption spectrum has the absorption maximum in the UV-visible range.

Light emission efficiency of an LED is important in terms of not only the energy supplied to the device but also of the stability of the device since the energy not used for the emission dissipates as thermal energy^[7]. Light emission efficiency is greatly dependent on the device quality but an emissive material with a high quantum yield is a prerequisite for high efficiency. Quantum efficiency of PL emission by poly(para-phenylene vinylene) (PPV) is known to be 80%^[8]. However, theoretical electroluminescence (EL) efficiency is 25% of the PL efficiency

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since excitons generated in an LED have a ratio of singlet to triplet of 1 to 3^[9]. This description, however, has been challenged recently^[11, 10].

Stability of LEDs is the crucial factor for commercialization of the devices at the moment. There are a number of intrinsic and extrinsic factors to shorten the lifetime of LEDs. Since excitons are in the excited state, the excited electrons are able to make new chemical bonds resulting in crosslinking or oxidation. The new chemical groups may act as exciton quenchers^[11]. Quantum efficiency in light emission of an LED has been achieved as high as 10%^[11], which is significant. However, 90% of the energy is dissipated as thermal energy. Emissive polymers are warmed up in an application of a bias potential and have a good chance of degradation. Segmental motion of polymer chains is enhanced on heating and may develop new morphology for excimer forming sites, even if there is no degradation. The extrinsic factors for a short lifetime reside in fabrication of LEDs, which may be reduced greatly by improving the fabrication technology.

The present work attempts to identify the chemical units in fluorene-based light emitting polymers for emitting a specific color in PL and to enhance quantum efficiency in both PL and EL of the polymers by optimizing chemical structures of polymer molecules.

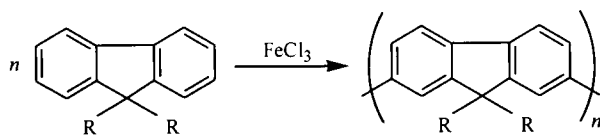
EXPERIMENTAL

There are four different polymerization methods employed to obtain various fluorene-based light emitting polymers. All the reactions are condensation polymerization with different catalysts. The synthesis routes are listed as Schemes 1 through 4. Details of the syntheses are omitted in this article and can be found elsewhere^[12-15]. A Perkin-Elmer DSC-7 was employed to measure the glass transition temperature (T_g) of the polymers.

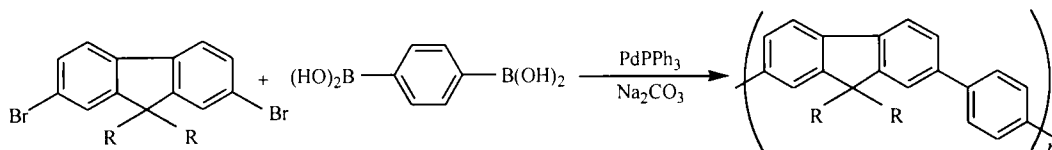
Polymers used in the study are listed in Table 1. The Wittig reaction was also employed for the syntheses of poly(9,9'-di-*n*-hexyl-2,7-fluorenediylvinylene-*alt*-1,3-phenylenevinylene) (PDHFMPV), poly(9,9'-di-*n*-hexyl-2,7-fluorenediylvinylene-*alt*-2,6-pyridinylvinylene) (PDHFPyV) and poly(9,9'-di-*n*-hexyl-2,7-fluorenediylvinylene-*alt*-1,4-(2,5-di-*n*-hexyloxy)phenylenevinylene) (PDHFDHOPPV). The Heck reaction was employed for the synthesis of poly(9,9'-di-*n*-hexyl-2,7-fluorenediylvinylene-*alt*-4,4'-(di-*n*-hexylsilane)-diphenylenevinylene) (PDHFSiPV). Polycondensation reaction was employed for the synthesis of poly(9,9'-di-*n*-hexyl-2,7-fluorenediylvinylene-*alt*-4,4'-{1,1'-(hexamethylene-1,6-diylloxy)}diphenylenevinylene) (PDHFVPHOD). All the polymers can dissolve in organic solvents such as chloroform, chlorobenzene, tetrahydrofuran (THF) and dichloroethane. The pyridine-containing copolymer (PDHFPyV) is soluble in formic acid as well as in other organic solvents.

Specimens for the PL study were spin-cast on glass plates from 2 wt% solution of each copolymer in chlorobenzene. Liquid cells for the PL emission spectra of the solutions were fabricated with two glass plates separated by 75 μm thick spacers. Single-layered LEDs were assembled with 100 nm thick spin-cast copolymers on ITO glass followed by thermal evaporation of aluminum. Multi-layered LEDs were fabricated by sandwiching sequentially spin-cast layers between ITO and Al. The AB spectra were recorded with a HP 8452A Diode Array Spectrophotometer. The copolymers were photoexcited by a xenon lamp, and PL and EL spectra were recorded with an ISS PL-1 Fluorometer. I-V-L characteristics were recorded on a Keithley 236 Source/Measure Unit for the measuring the voltage-current relationship and by a Newport 818-SL photodiode for measuring the voltage-electroluminescence intensity.

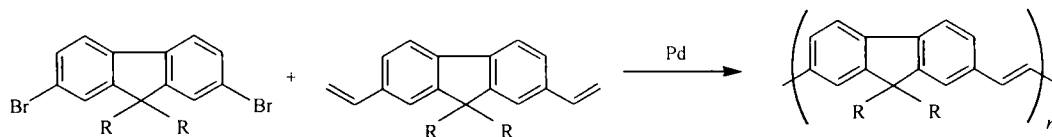
For studies on electrochemical behavior, thin films were prepared on the platinum wire. Cyclic voltammograms (CV) were obtained using a potentiostat (EG&G PAR 273) with a data acquisition module. The concentration of electrolyte, tetrabutylammonium tetrafluoroborate, in acetonitrile in the electrochemical study was 0.1 mol/L to reduce the solution resistance. An internal standard ferrocene/ferrocenium system was employed to calibrate the redox peaks in the CV by adding a small amount of ferrocene to the system. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values were determined from the first oxidation and the reduction potential values with respect to ferrocene with an Ag/AgCl reference electrode.



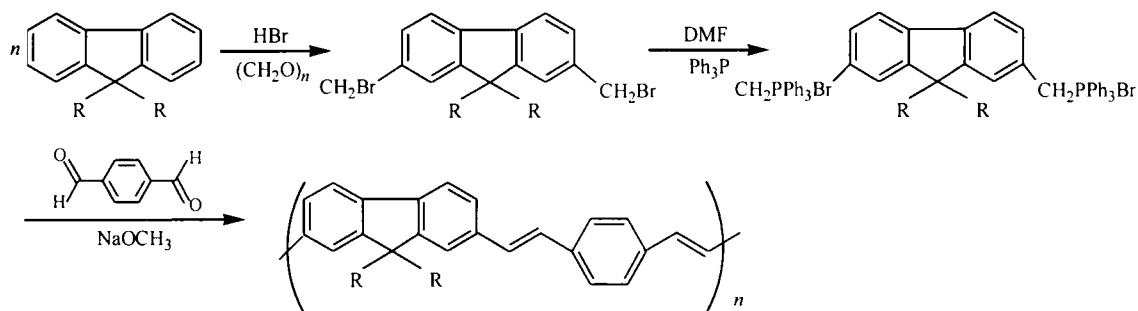
Scheme 1 Synthesis of poly(9,9'-di-*n*-hexyl-2,7-fluorene) (PDHF)



Scheme 2 (Suzuki reaction): synthesis of poly(9,9'-di-*n*-hexyl-2,7-fluorenyl-1,4-phenylene) (PDHFP)



Scheme 3 (Heck reaction): synthesis of poly(9,9'-di-*n*-hexyl-2,7-fluorenylvinylene) (PDHFV)



Scheme 4 (Wittig reaction): synthesis of poly(9,9'-di-*n*-hexyl-2,7-fluorenediyl-vinylene-*alt*-1,4-phenylenevinylene) (PDHFPPV)

A time-correlated single photon counting (TCSPC) system has been described in detail elsewhere^[16]. The main components of the system for the TCSPC study are a femtosecond Ti: sapphire laser as the excitation laser pumped by a BeamLok 2060 CW argon laser from Spectra-Physics, a Jobin-Yvon HR320 monochromator, a microchannel plate photomultiplier tube from Hamamatsu R2809U for collection of the emission intensity, and a data analysis system assembled with the parts supplied by Philips Scientific, Tennelec, and Ortec.

RESULTS AND DISCUSSION

The AB and PL spectra of a PDHF film and the PL spectrum of its solution are shown in Fig. 1. A simple AB spectrum with the absorption maximum at 370 nm indicates a uniform electronic state of the polymer. However, the PL spectrum of the film showed the main peak at 475 nm with two shoulders at 495 and 530 nm, and a second peak at 420 nm. The PL spectrum of the solution with a concentration of 10^{-5} mol/L had a sharp emission peak at 415 nm with weak shoulders at 440 and 475 nm. The main PL peak at 475 nm and the shoulder at 530 nm of the film disappeared upon dilution. It is apparent that the PL peak of the polymer at 420 nm is formed by the radiative singlet exciton decay with the Stokes' shift of 50 nm and the peak at 475 and 530 nm are due to the radiative decay of excimers. The excimers were probably formed intermolecularly between two fluorene units belonging to different molecules. There might be excimers from fully eclipsed excimer sites and from partially

eclipsed ones as deduced from a PVK study^[17]. The peaks at 475 nm and 530 nm are then assigned as the partially and the fully eclipsed excimer emissions, respectively.

The AB and PL spectra of PDHFV, an alternating copolymer of dialkylfluorene and vinylene, are shown in Fig. 2. The AB spectrum looked complex as compared with that of PDHF and the AB maximum was red-shifted to 410 nm. It is apparent that the two units of alkylfluorene and vinylene coupled alternately with each other and formed a new electronic state with a lower energy as compared with that of PDHF. The PL spectrum of the film shows the emission peak at 475 nm with a couple of shoulders at 490 and 535 nm. The PL emission peak of the solution of 10^{-5} mol/L was blue-shifted to 465 nm due to the solvent effect and the intensity of the secondary peaks was not eliminated but reduced, which implied that the shoulders of the PL spectra were vibronic emission. The PDHFV film had far fewer excimer forming sites than PDHF and showed a narrow PL emission spectrum.

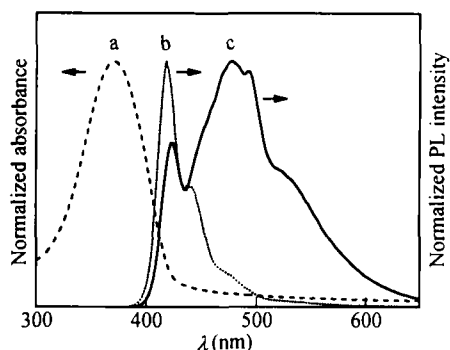


Fig. 1 Absorption and PL emission characteristics of PDHF

a) absorption, b) PL emission of 10^{-5} mol/L solution in chlorobenzene, c) film

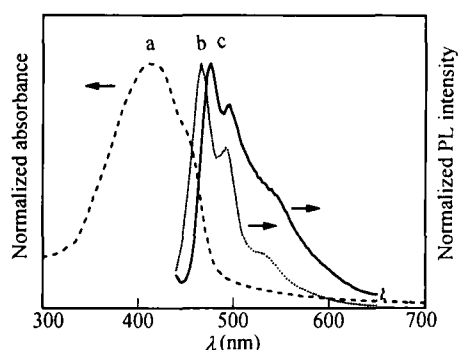


Fig. 2 Absorption and PL emission characteristics of PDHFV

a) absorption, b) PL emission of 10^{-5} mol/L solution in chlorobenzene, c) film

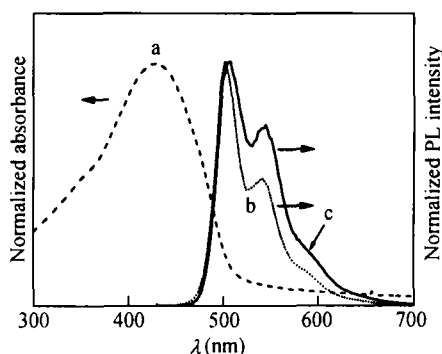


Fig. 3 Absorption and PL emission characteristics of PDHFDHOPV

a) absorption, b) PL emission of 10^{-5} mol/L solution in chlorobenzene, c) film

The AB and PL spectra of PDHFDHOPPV red-shifted further when the vinylene unit in PDHFV was replaced by dihexyloxyparaphenylenedivinylene as shown in Fig. 3. The broad AB spectrum indicates that there are multiple electronic states in the polymer. The narrow PL spectrum of the film with a full width at half maximum (FWHM) of 70 nm suggests that there is energy transfer from excited chromophores with a wider band gap to fluorophores with a narrower one in the film^[18]. It is interesting to note that the PL emission spectrum of the film with the maximum at 500 nm was almost identical with that of the solution and there was only a 5 nm shift of the PL emission peak from the film to the solution. It implies that the PDHFDHOPPV molecules are too bulky to form excimers in the film and the two alkoxy groups on the phenylene unit impart the dilution effect of a solvent to the solid film. The shoulders at 490 and 530 nm are assigned as vibronic decay because they were still

observed for the diluted solution of 10^{-5} mol/L.

A molecular simulation study based on the CERIUS 2 (Molecular Simulation Inc., Version 4.02) revealed the conjugation length and a degree of coplanarity in a single chain of fluorene-based polymers as shown in Fig. 4. PDHF shows the planarity was developed only in the fluorene unit (Fig. 4a). Two adjacent fluorene units were slanted with each other to develop planarity on no more than a single fluorene unit. When a vinylene unit was inserted between the two fluorene units, the planarity was extended by the length of the vinylene unit (Fig. 4b). The ratio of *cis/trans*-vinyl structures (3/6/1) deduced from the IR fitting method^[19] was counted on the simulation. A fluorene-based alternating copolymer with a dihexyloxyphenylene-divinylene unit in PDHFDHOPPV with the *cis/trans*-vinyl structure ratio of 3/6/1 failed to extend the conjugation beyond the adjacent double bond from the fluorene unit on the simulation (Fig. 5c). However, the PL spectrum (Fig. 3b) showed a red shift when dihexyloxy units were attached to the phenylene unit. The alkoxy pendant groups on a phenylene unit tended to give the effect of an elongation in the conjugation length and to improve the planarity.

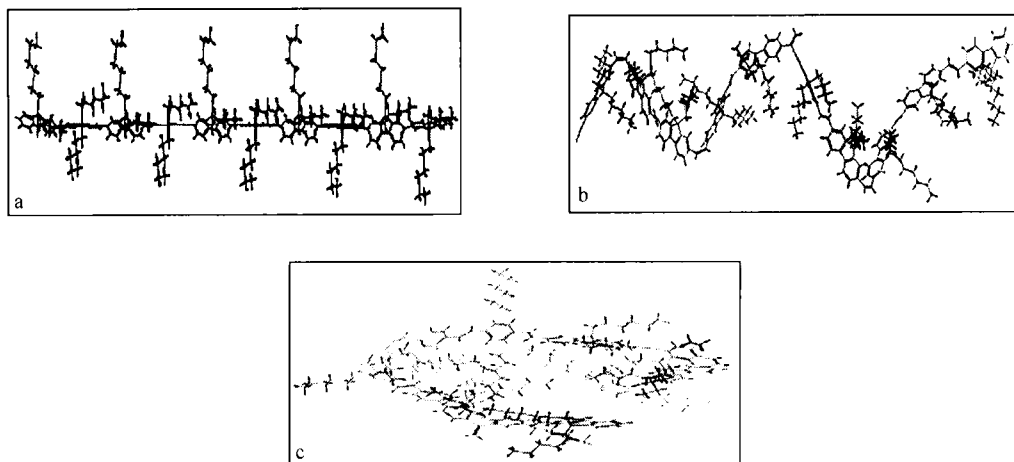


Fig. 4 Optimized chain structures
a) PDHF, b) PDHFV and c) PDHFDHOPV

The fluorene planarity of fluorene-based copolymers was not expanded on attaching a phenylene unit as observed on PDHF (Table 1-4). The polymer of the fluorene and the phenylene units failed to develop coplanarity when coupled with each other but rather the planarity of the fluorene unit was reduced to blue-shift the PL emission maximum by 5 nm. The coplanarity was also not observed for PDHFMPV (Table 1-3), PDHFPyV (Table 1-4), PDHFVPHOD (Table 1-5) and PDHFSiPV (Table 1-6).

It was observed that coplanarity was not formed between the fluorene and the vinyl units in the polymer backbone when the vinyl unit was connected to the other side with a phenylenemetavinylene unit or the conjugation was terminated at the phenyl unit by a sigma bond with an oxygen or a silane element. However, coplanarity between the fluorene and the vinyl units was formed when the phenyl unit was linked with the two vinylene units on the *para*-positions. The phenylene unit on the backbone of PDHFPPV provided no contribution to extending or reducing the coplanarity developed between the fluorene and the vinyl units.

It is concluded that fluorene-based polymers are classified into three groups in terms of emission color as shown in Fig. 5. When coplanarity was confined to each fluorene unit as observed in PDHF, PDHFMPV, PDHFVPHOD, PDHFPyV and PDHFSiPV, the singlet exciton emission spectra showed the emission maximum at ca 420 nm, a violet color. When the planarity extended to a vinylene unit in the chain as observed in PDHFV and PDHFPPV, the radiative exciton decay showed the emission maximum at ca 475 nm, a blue color. The exciton emission maximum red-shifted to 500 nm, a green color, when two hexyloxy groups were attached to the phenylene unit in PDHFPPV as shown in PDHFDHOPPV. Two shoulders of each PL spectra regardless of the polymers were assigned as the vibronic relaxation since the shoulders still stayed with each main peak at the

concentration of the polymer solution of 10^{-5} mol/L which is too dilute to form the excimers.

Table 1. Chemical structures of the light-emissive alternating copolymers and their photophysical characteristics

Serial	Polymer ^a	Chemical Structure [R = $-(CH_2)_3CH_3$]	AB ^b (nm)	PL ^c (nm)	PL ^d (nm)
1	PDHF		370	475	415
2	PDHFP		370	420	410
3	PDHFMPV		380	425	420
4	PDHFPyV		375	440	430
5	PDHFVPHOD		385	445	435
6	PDHFSiPV		380	460	430
7	PDHFV		410	475	465
8	PDHFPPV		410	475	470
9	PDHFDHOPPV		430	500	495

a) full names are given in the text; b) AB maximum of film; c) PL emission maximum of film; d) PL emission maximum of solution (conc. 10^{-5} mol/L)

It was observed that the AB spectrum of PDHFPPV was perfectly superposed on the PL spectrum of PDHFMPV (Fig. 5a and b). It was expected that energy transfer between the two polymers would be carried out when PDHFMPV with a wider bandgap was photoexcited as predicted by the Förster mechanism^[20]. Figure 6 shows that the energy transfer did occur and the PL intensity of PDHFPPV with a narrower band gap was enhanced when blended with PDHFMPV. On photoexcitation of the blend with the blend ratio of 1: 1 at 365 nm, it displayed only the PL spectrum of PDHFPPV with an enhancement of the intensity as compared with that of PDHFPPV photoexcited at the AB maximum of 410 nm. The inset of Fig. 6 revealed that the highest PL intensity of a blend on photoexcitation at 365 nm was obtained when the concentration of PDHFPPV in the blend was 5 wt%. The blend with 1 wt% of PDHFPPV showed a higher PL intensity than that of a simple PDHFPPV film.

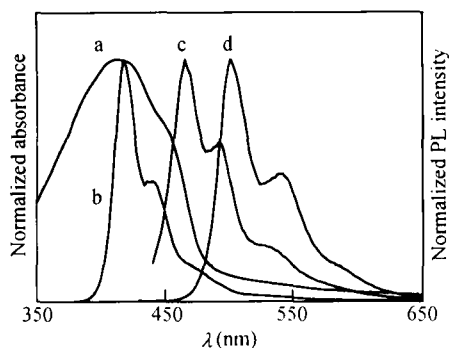


Fig. 5 AB spectrum of PDHFV a), and PL emission spectrum of PDHF b), PDHFV c) and PDHFDHOPV d)

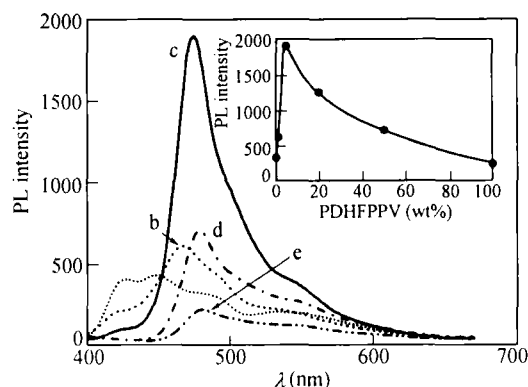


Fig. 6 PL emission spectra of PDHFPPV/PDHFMPV blend films at blend ratios of a) 0/100 [PDHFMPV], b) 1/99, c) 5/95, d) 50/50, (e) 100/0 [PDHFPPV]

The shoulder at 420 nm in the PL spectra of the blend with 1 or 5 wt% of PDHFPPV was observed. There must be a critical concentration ratio between a donor and an acceptor in a blend to accomplish a complete energy transfer. However, it is not necessary to complete the energy transfer for the highest PL intensity since the PL spectrum of the blend with 5 wt% of the donor showed a weak shoulder at 420 nm indicating that less than 100% of energy transfer has taken place. It seems that there is an optimum exciton ratio between the donor and the acceptor for the highest PL efficiency. Below 5 wt% of the acceptor in the blend, the excitons were saturated in the acceptor to be quenched through the exciton annihilation^[21] and at the same time the remaining donor excitons decayed radiatively to show the shoulder at 420 nm in the PL spectrum. Above 5 wt% of the acceptor in the blends, the density of the acceptor excitons was too small to overcome the quenching by the inherent traps in the polymer chain, which was observed in the reduction of the PL intensity for the blends with more than 5 wt% of PDHFPPV.

Homogeneous polymer blends are difficult to obtain because the entropy of mixing is small due to long covalently-bonded polymer chains^[22]. There are also conformational rearrangements in a polymer chain even at room temperature because a polymer has multiple T_g ^[23]. The imperfect blends and the molecular rearrangements at room temperature may exert harmful effects on PL and EL of the blends. Attempts were made to design polymers to enhance homogeneous mixing of two chromophores and to reduce the harmful effect of the molecular rearrangements on the light emission performance. Copolymers containing more than one chromophore may preserve the blend effects on the PL or EL enhancement described previously and eliminate the phase separation possibility. Statistical copolymers [poly(9,9'-dihexylfluorene-2,7-diylvinylene-*m*-phenylenevinylene-*stat-p*-phenylenevinylene) (PDHFMPV)]^[14], consisting of each repeating unit from PDHFMPV and PDHFPPV, exhibited the same trend as the blends of the two polymers as shown in Fig. 7. It is noted that no contribution of the fluorophore from PDHFMPV was observed in the PL spectra of the copolymers on photoexcitation at 365 nm where the AB spectrum of PDHFMPV had the absorption maximum. The structure of the PL spectra were the same for all the blends but the highest PL intensity was obtained for the blend with the donor/acceptor unit ratio of 7/3 as shown in the inset. The statistical copolymers showed T_g of 130°C regardless of the composition ratio.

Figure 8 shows the PL spectra of diluted solutions of the 1:1 statistical copolymers and the blend with the 1:1 ratio between the two polymers at a concentration of 10^{-5} mol/L on photoexcitation at 365 nm. The energy transfer was almost complete for the statistical copolymer (Fig. 8b) while the blend solution showed each PL spectrum of the two polymers (Fig. 8a). A bump at 415 nm was observed for the statistical copolymer solution indicating that the energy transfer was incomplete. Since the bump at 415 nm was not observed for the solution with a concentration of 5×10^{-1} mol/L (not shown) or the solid with 90% of the PDHFMPV repeating unit, the

intramolecular energy transfer was not so efficient as the intermolecular energy transfer in the Förster critical range. The vibronic structure of the PL spectrum of PDHFMPV was more pronounced than that of PDHFPPV indicating that the meta-linkage in PDHFMPV provided a more rigid chain than the para-linkage in PDHFPPV. PDHFPPV in the diluted solution was also excited on photoexcitation at 365 nm to display the PL emission but the PL intensity was lower than that of PDHFMPV.

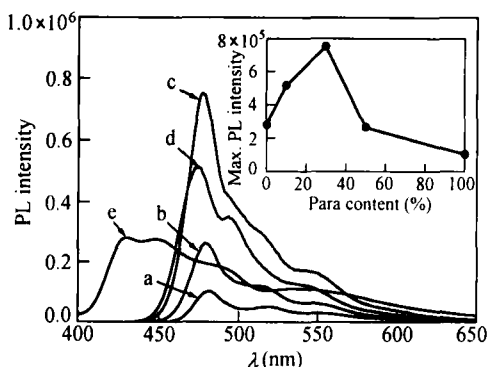


Fig. 7 PL emission spectra of statistical copolymers (PDHFMPV) consisting of repeating units from PDHFMPV and PDHFPPV with ratios of a) 100/0, b) 50/50, c) 70/30, d) 90/10, e) 0/100

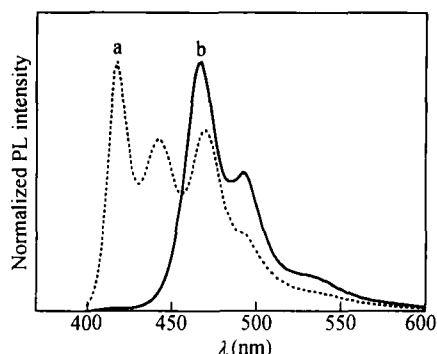


Fig. 8 Comparison of PL emission spectra of solution (10^{-5} mol/L) of a) PDHFMPV/PDHFPPV (50/50) blend and b) statistical copolymer (PDHFMPV) of comparable composition

TCSPC was employed to examine the energy transfer between two chromophores as shown in Fig. 9. The blends of PDHFMPV and PDHFPPV with the blend ratio of 9:1 and 1:1 were made into solutions of 10^{-5} mol/L in chloroform. The statistical copolymers with the same repeating unit ratios were also made into solutions of 10^{-5} mol/L. The solutions were photoexcited at 298 nm for 10 ps and the decay profile of the exciton emission intensity at 420 nm was traced with time. The time-resolved PL intensity profiles of the blend solutions were identical to each other (Fig. 9a) and the lifetime (τ_D) deduced from the profiles were the same as that of the PDHFMPV ($\tau_D = 385$ Ps). The blend ratio gave no effect on the lifetime, which implies that there was no energy transfer between the two chromophores in the diluted solutions.

However, the energy transfer was observed for the statistical copolymer solutions of concentration 10^{-5} mol/L. The decay profiles were different from one another depending on the composition ratio of the repeating units (Fig. 9b). The donor-only solution (S0) showed the same intensity decay profile as those of the diluted blend solutions. When the acceptor unit with 10 wt% in the statistical copolymer (S1) was photoexcited at 398 nm, the decay profile showed a sharp intensity decrease with time ($\tau_A = 86$ Ps). The decrease in the intensity was more pronounced for the copolymer with 50 wt% (S5) of the acceptor unit ($\tau_A = 14$ Ps). It is apparent that the energy transfer from an excited chromophore with a wider band gap to a ground-state chromophore with a narrow band gap is possible but inefficient as compared with the intermolecular energy transfer in the Förster critical range as observed in films of the blends or the statistical copolymers. However, the statistical copolymers still have advantages over the polymer blends because of homogeneous mixing of the two chromophores and no chance of phase separation.

A charge transporting and/or blocking material with a good processibility was designed as PDHFPPyV, which has an alternating copolymer between units of fluorene and divinylbenzopyridine. Polypyridine is known as an electron transporting material with a band gap of 2.85 eV, and HOMO and LUMO levels of -5.67 and -2.82 eV, respectively^[24]. The high HOMO level may favor hole-blocking and the high LUMO level may enhance electron injection into the polymer from a cathode. The pyridine unit is n-dopable and good for electron transporting. As PDHFPPyV can be soluble in both organic solvents and formic acid, it is possible to spin-cast the PDHFPPyV solution in formic acid on a PDHFMPV film spin-cast on ITO glass.

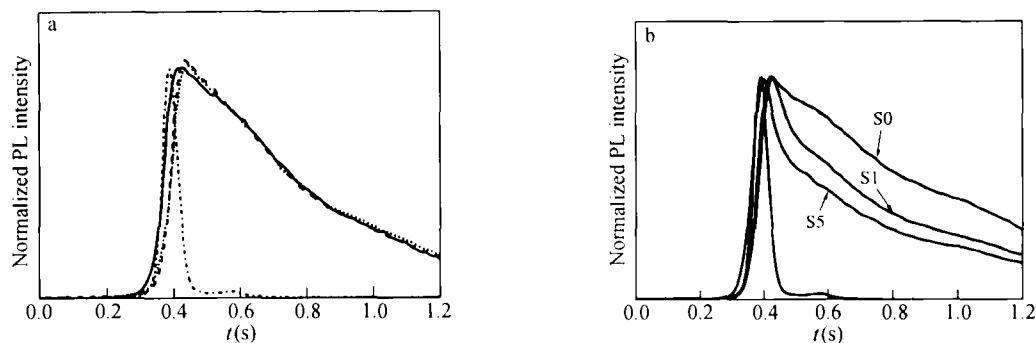


Fig. 9 TCSPC data (10^{-5} mol/L solution)

a) PDHFMPV/PDHFPPV blend (100/0, 90/10, 50/50) and b) statistical copolymer (PDHFMPPV)

Repeating unit ratio(DHFMPV/DHFPPV); S0: 100/0, S1: 90/10, S5: 50/50

Cyclic voltammetry revealed that both the fluorene and pyridine units in the statistical copolymers conserved each electrochemical reactivity intact as shown in Fig. 10. Ferrocene was used as a reference to deduce ionization potential and electron affinity of the polymer (Fig. 10a) and the onset oxidation and reduction potentials of the polymer were 1.07 (Fig. 10b) and -1.78 V (Fig. 10c), respectively. Ferrocene exhibited a reversible oxidation wave in the positive region with a neutral point at 0.2 V. The HOMO and LUMO values of PDHFPPV were deduced as -5.67 and -2.82 eV, respectively, based on the value of ferrocene of -4.8 eV. The oxidation reaction was irreversible in the scanning range. When the electrochemical scan was extended to 1.5 V in the positive region, the oxidation reaction became a two electron process^[25]. The copolymer seemed to have a capacity to lose two electrons independently and the chemical structure was changed on losing electrons at the high potential. The copolymer film coated on the Pt electrode was degraded at the high potential and dissolved in the solution. The reduction current started flowing at -1.5 V probably due to a secondary reaction and the main reaction took place at -1.78 V, accompanied by a color change of the film to yellow from dark brown (Fig. 10c). The onset potential on reduction was the same as that of poly(pyridine-2,5-diyl)^[24], and the reduction of PDHFPPV in the negative potential region was reversible but the reversibility declined with the cycling.

The fluorene-based light emitting polymers in this work except PDHFPPV exhibited only the irreversible oxidation in cyclic voltammetry and no reduction, suggesting that the polymers had hole-transporting characteristics. However, PDHFPPV was reduced as well as oxidized in the neutral state, which implies that it had the capability of both electron and hole transporting. It is important to note that when the fluorene-divinylene and pyridine units were linked alternately by a sigma bond, the two units kept their own electrochemical characteristics intact. It is expected that holes hopped through the fluorene units in the polymer bulk while electrons transported through the pyridine units.

Single-layered LEDs with a thickness of 100 nm fabricated with blends between PVK and S3 (PDHFMPPV with DHFMPV/DHFPPV ratio of 70/30) emitted a blue color with the emission maximum at 475 nm. The quantum efficiency of 0.04% was obtained for the PVK-S3 blend having a ratio of 7:3^[14]. Double-layered LEDs were also fabricated with a layer of the PVK-S3 blend having a ratio of 8:2 as the emitting material and a PDHFPPV layer as the electron transporting material. The EL emission spectra of the single- and double-layered LEDs had the emission maxima at 475 and 470 nm, respectively, as shown in Fig. 11. The FWHM of the double-layered LED was 50 nm while that of the single-layered one was 65 nm. The inset of Fig. 11 revealed that the turn-on potential on light emission was lower for the double-layered LED than that for the single-layered one. The quantum efficiency was improved to 0.1% for the double-layered LED, an increase of 2.5 times of the single-layered one with the efficiency of 0.04%. It is apparent that electrons were injected into PDHFPPV at a lower potential and transported toward the anode on the bias potential. The improvement of the EL quantum efficiency might be obtained due to either balanced charge injection or a substantial distance of exciton-

formation sites from the Al cathode where excitons might be quenched^[26].

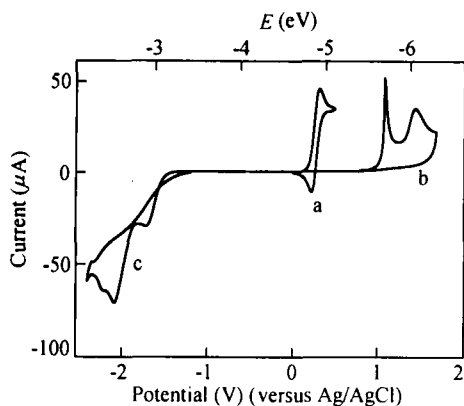


Fig. 10 Cyclic voltammograms of ferrocene a) PDHFPyV in forward sweep b) and in reverse sweep c) with electrolyte (0.1 mol/L TBABF₄) in acetonitrile

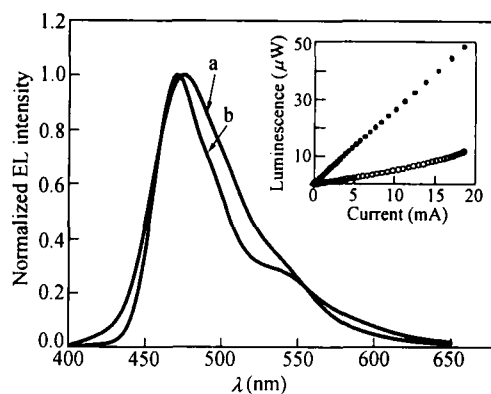


Fig. 11 EL spectra of PDHFMPPV(S3)-PVK (2:8) blend without a) and with b) PDHFPyV layer between the emissive layer and aluminum electrode. The inset shows L-I curves of LED without (○) and with (●) PDHFPyV layer

CONCLUSION

Fluorene-based copolymers are classified into three groups based on the PL emission maxima at 420, 475 and 500 nm, respectively. The steric effect disturbing the planarity beyond the fluorene unit was observed for the fluorene homopolymer, copolymers without conjugation on the main chain and an alternating copolymer with a phenylene or a *meta*-phenylenedivinylene unit. The PL emission maximum shifted from 420 nm to 475 nm for the copolymer with a double bond or a *para*-phenylenedivinylene unit. The emission maximum red-shifted further to 500 nm when the *para*-phenylene unit was attached by dialkoxy groups. Quantum efficiency of PL as well as EL emission was improved by utilizing energy transfer from a wider band gap chromophore to a narrower one in polymer blends or the statistical copolymers. The intramolecular energy transfer was inefficient compared to the intermolecular energy transfer when the two chromophores were in the range of the Förster critical distance. However, the statistical copolymer guaranteed no phase separation and much less conformational rearrangement in the molecules than the polymer blends. An alternating copolymer between fluorene and pyridinedivinylene units preserved the individual physical, electronic and electrochemical characteristics and made sequential spin-casting possible. The highest quantum efficiency of a double-layered LED with the structure of ITO/PVK-S3/PDHFPyV/Al was 0.1%, an enhancement of 2.5 times from that of a single-layered LED with the structure of ITO/PVK-S3/Al.

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